Université de Cergy-Pontoise

Étude mathématique de modèles quantiques et classiques pour les matériaux aléatoires à l'échelle atomique

Thèse de doctorat en Mathématiques

présentée par

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Étude mathématique de modèles quantiques et classiques pour les matériaux aléatoires à l'échelle atomique.

Résumé: Les contributions de cette thèse portent sur deux sujets.

La première partie est dédiée à l'étude de modèles de champ moyen pour la structure électronique de matériaux avec des défauts. Dans le chapitre 2, nous introduisons et étudions le modèle de Hartree-Fock réduit (rHF) pour des cristaux désordonnés. Nous prouvons l'existence d'un état fondamental et établissons, pour les interactions de Yukawa (à courte portée), certaines propriétés de cet état. Dans le chapitre 3, nous considérons des matériaux avec des défauts étendus. Dans le cas des interactions de Yukawa, nous prouvons l'existence d'un état fondamental, solution de l'équation auto-cohérente. Nous étudions également le cas de cristaux avec une faible concentration de défauts aléatoires. Dans le chapitre 4, nous présentons des résultats de simulations numériques de systèmes aléatoires en dimension un.

Dans la deuxième partie, nous étudions des modèles Monte-Carlo cinétique multi-échelles en temps. Nous prouvons, pour les trois modèles présentés au chapitre 6, que les variables lentes convergent, dans la limite de la grande séparation des échelles de temps, vers une dynamique effective. Nos résultats sont illustrés par des simulations numériques.

Mots-clés: opérateurs de Schrödinger aléatoires, cristaux désordonnés, modèle de Hartree-Fock réduit, limite thermodynamique, modèle de type Monte-Carlo cinétique, dynamique effective, problèmes multi-échelles en temps, processus de Poisson.

Mathematical study of quantum and classical models for random materials in the atomic scale.

Abstract: The contributions of this thesis concern two topics.

The first part is dedicated to the study of mean-field models for the electronic structure of materials with defects. In Chapter 2, we introduce and study the reduced Hartree-Fock (rHF) model for disordered crystals. We prove the existence of a ground state and establish, for (short-range) Yukawa interactions, some properties of this ground state. In Chapter 3, we consider crystals with extended defects. Assuming Yukawa interactions, we prove the existence of an electronic ground state, solution of the self-consistent field equation. We also investigate the case of crystals with low concentration of random defects. In Chapter 4, we present some numerical results obtained from the simulation of one-dimensional random systems.

In the second part, we consider multiscale-in-time kinetic Monte Carlo models. We prove, for the three models presented in Chapter 6, that in the limit of large time-scale separation, the slow variables converge to an effective dynamics. Our results are illustrated by numerical simulations.

Key words: random Schrödinger operators, disordered crystals, electronic structure, reduced Hartree-Fock theory, thermodynamic limit, kinetic Monte-carlo type models, effective dynamics, multiscale-in-time problems, Poisson process.

Publications and Preprints

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Contents

Introduction (Fr)

Cette thèse comporte deux parties. La première partie concerne l'étude de modèles de champ moyen pour la structure électronique de matériaux avec des défauts. Nous y étudions le modèle de Hartree-Fock réduit pour des cristaux avec des défauts locaux, étendus et stochastiques. Dans la deuxième partie, nous étudions la dérivation de modèles effectifs de systèmes multi-échelles en temps dans le cadre du modèle Monte-Carlo cinétique.

Nous décrivons ci-après les résultats obtenus dans les divers chapitres de la thèse.

Chapitre 1: Introduction et résumé des résultats de la partie I

Dans le premier chapitre, nous présentons le contexte scientifique des chapitres 2 et 3 et résumons les résultats principaux de ces chapitres. Dans la section 1.2, nous présentons trois modèles pour décrire les systèmes moléculaires finis en chimie quantique. Nous commençons par le modèle de Schrödinger à N-corps, qui est le modèle de référence pour les systèmes finis non relativistes. Les sections 1.2.2 et 1.2.3 sont dédiées à la présentation de deux types d'approximation du modèle de Schrödinger à N-corps, à savoir les modèles de type Hartree-Fock et les modèles de la Théorie de la Fonctionnelle de la Densité (DFT). Ensuite, nous expliquons dans la section 1.3 comment les modèles pour des systèmes infinis sont dérivés à partir des modèles pour les systèmes finis. Dans la section 1.3, nous nous concentrons sur la description des cristaux parfaits et des cristaux avec des défauts déterministes dans le cadre du modèle Hartree-Fock réduit (rHF). Nous présentons dans la section 1.5 deux modèles pour les systèmes stochastiques: le modèle linéaire et le modèle rHF. Dans la section 1.5.3, nous nous intéressons à un cas particulier de systèmes stochastiques, qui est celui des cristaux avec une faible concentration de défauts aléatoires. Finalement, nous présentons quelques résultats numériques de la simulation de systèmes stochastiques en dimension un.

Chapitre 2: Modèles de champ moyen pour les cristaux désordonnés

Dans le chapitre 2, nous détaillons et développons la théorie introduite dans un article [29], écrit avec Éric Cancès et Mathieu Lewin, qui a été publié dans le *Journal de mathématiques pures et appliquées*. Nous y construisons un cadre fonctionnel pour les modèles de structure électronique de champ moyen de type Hartree-Fock ou Kohn-Sham pour des systèmes quantiques

désordonnés. Dans un premier temps, nous établissons quelques propriétés importantes des matrices densité à un corps fermioniques stochastiques, sous une hypothèse de stationnarité vis-à-vis de l'action ergodique d'un groupe de translations. En particulier, nous démontrons des inégalités de Hoffmann-Ostenhof et de Lieb-Thirring pour les matrices densité ergodiques, ainsi que des propriétés de compacité faible de l'ensemble de ces matrices densité. Nous discutons également la question de la représentabilité des densités à un corps associées. Dans un deuxième temps, nous étudions le problème de la résolution de l'équation de Poisson pour une distribution de charge stationnaire donnée, en définissant l'énergie de Coulomb comme la limite de l'énergie de Yukawa lorsque le paramètre de Yukawa tend vers zéro. Enfin, nous utilisons ces outils pour étudier un modèle de champ moyen particulier (le modèle rHF) pour un cristal désordonné dans lequel les noyaux sont modélisés par des particules classiques dont les positions et les charges sont aléatoires. Nous démontrons l'existence d'un minimiseur de l'énergie par unité de volume et l'unicité de la densité de l'état fondamental. Pour des interactions de Yukawa (à courte portée), nous prouvons en outre que la matrice densité de l'état fondamental vérifie une équation non linéaire, et que le modèle proposé est bien la limite thermodynamique du modèle de supercellule.

Chapitre 3: Le modèle de Hartree-Fock réduit pour des cristaux avec des défauts non-locaux interagissant avec un potentiel à courte portée

Dans le chapitre 3, nous détaillons les résultats contenus dans un article [92] qui a été accepté pour publication dans les *Annales Henri Poincaré*. Nous y considérons des matériaux avec des défauts dans le cadre du modèle rHF. Les noyaux sont modélisés par des particules classiques disposées autour d'une configuration périodique de référence. Nous supposons que cette perturbation est petite en amplitude, mais elle n'a pas besoin d'être localisée dans une certaine région de l'espace ou d'avoir une quelconque invariance spatiale. En supposant que toutes les particules intéragissent à travers le potentiel de Yukawa, nous prouvons l'existence d'un état fondamental électronique, solution de l'équation rHF non linéaire. Ensuite, en étudiant les propriétés de décroissance de cette solution pour des défauts locaux, nous traitons le cas de cristaux avec une faible concentration de défauts aléatoires. Nous prouvons que la densité d'états de l'opérateur de champ moyen associé à de tels cristaux admet un développement limité par rapport au paramètre de Bernoulli p qui détermine la concentration des défauts. Une étape importante dans notre analyse est l'étude de la réponse diélectrique d'un cristal à une perturbation de charge effective.

Chapitre 4: Simulation numérique de cristaux aléatoires

Dans le chapitre 4, nous présentons les résultats de simulations numériques de systèmes stochastiques en dimension un dans le cadre du modèle linéaire et du modèle rHF. Ces simulations ont pour but d'illustrer quelques résultats théoriques discutés dans les chapitres précédents d'une part, et d'essayer de comprendre des phénomènes qui n'ont pas encore été étudié théoriquement, d'autre part. Nous simulons des alliages aléatoires résultants de la combinaison de deux cristaux parfaits. Nous supposons qu'à chaque site $k \in \mathbb{Z}$, il y a une probabilité p de voir le premier type de cristaux et une probabilité $1-p$ de voir le deuxième type de cristaux, et ce, indépendamment de ce qui se passe dans les autres sites. Les méthodes numériques que nous utilisons sont la méthode de supercellule avec une discrétisation en ondes planes, l'Optimal Damping Algorithm (ODA) et la méthode de Monte-Carlo. Une fois l'état fondamental du système obtenu, nous pouvons calculer les quantités d'intérêt pour notre étude. Nous nous intéressons dans un premier temps à la convergence de l'énergie par unité de volume et de la densité d'états dans la limite thermodynamique, à savoir, quand la taille du domaine de simulation devient très grande. Ensuite, nous étudions les propriétés de localisation de l'Hamiltonien. Comme le spectre de l'Hamiltonien restreint à une boite de taille finie est purement discret, nous caractérisons ses propriétés de localisation en regardant combien les vecteurs propres associés sont localisés. Pour cela, nous utilisons un critère basé sur la variance de ces vecteurs propres. Enfin, nous simulons des cristaux avec une faible concentration de défauts aléatoires et étudions le comportement de la densité d'états en fonction du paramètre de Bernoulli p, dans la limite $p \to 0$.

Dans la deuxième partie de la thèse, nous étudions des système multi-échelles en temps dans le cadre du modèle Monte-Carlo cinétique.

Chapitre 5: Introduction et résumé des résultats de la partie II

Dans ce chapitre, nous présentons le contexte scientifique du travail détaillé dans le chapitre 6 et nous résumons les principaux résultats qui y sont obtenus. Nous commençons par présenter trois classes de modèles communément utilisés en dynamique moléculaire (MD). Il s'agit de la dynamique Hamiltonienne, la dynamique de Langevin et les modèles de Monte-Carlo cinétique (kMC). Nous nous concentrons ensuite sur les systèmes multi-échelles en temps dans le cadre des modèles kMC et discutons la problématique de trouver une dynamique effective pour des observables macroscopiques. Un résumé de nos travaux est aussi inclus dans ce chapitre.

Chapitre 6: Dynamique effective pour des modèles de Monte-Carlo cinétique avec des échelles de temps rapides et lentes

Les résultats de ce chapitre ont fait l'objet d'un article [93] qui a été soumis pour publication. Nous considérons trois systèmes multi-échelles en temps dans le cadre du modèle kMC, où certaines variables évoluent à une échelle de temps rapide, alors que d'autres variables évoluent à une échelle de temps lente. Dans les deux premiers modèles, nous considérons une particule qui évolue dans un potentiel en dimension un qui a des petites et des hautes barrières d'énergie. Ces dernières, divisent l'espace d'états en régions métastables (macro-états). Dans la limite où le rapport entre les hautes et les petites barrières tend vers l'infini, nous identifions une dynamique effective qui porte uniquement sur ces macro-états et prouvons la convergence du processus vers un modèle kMC. Le troisième modèle que nous considérons consiste en un système de deux particules. L'état de chaque particule évolue à une échelle de temps rapide en conservant sa propre énergie. De plus, les particules peuvent échanger de l'énergie à une échelle de temps lente. Nous considérons la variable macroscopique "énergie de la première particule" et prouvons, dans la limite d'une grande séparation des échelles de temps, que sa dynamique converge vers une dynamique effective portant sur les énergies admissibles. Pour tous les modèles, nous illustrons nos résultats théoriques par des simulations numériques.

Part I

Modeling of the electronic structure of crystals

Chapter 1

Introduction and summary of results

Contents

1.1 Introduction

The first part of this thesis concerns the mathematical modeling of materials with defects at the atomic scale.

The mathematical modeling and the numerical simulation of materials with defects is a prominent topic in solid state physics and materials science [85, 149]. The presence of defects in materials induces many interesting properties that are crucial in applications such as doped semi-conductors, aging materials and thin films.

In addition to industrial applications, the modeling of materials raises interesting mathematical and numerical questions. Mathematicians have increasingly studied condensed matter problems and fruitful collaborations between mathematicians and physicists gave answers to complex questions.

The present work follows on from this context. Our results are theoretical, but some of them are motivated by numerical simulation considerations. The mathematical fields involved in this work are variational calculus, spectral theory, probability theory, PDEs and numerical methods.

We describe matter at the atomic scale in the framework of quantum mechanics. Unlike classical molecular dynamics (see Chapter 5) where the atoms are considered as point particles with no internal structure, this theory describes the elementary components of matter such as the nuclei and the electrons. We do not recall here the founding principles of quantum mechanics and refer the reader to [63] for a very good introduction.

We are mainly interested in the description of the electronic ground state of the systems we study, which is the state of the electrons that minimizes the energy. Computing the electronic ground state is a key step in the calculation of the chemical and physical properties of materials.

In the first chapter, we present the scientific context of our work detailed in Chapters 2 and 3, and we summarize the main results of these chapters. It is organized as follow. In Section 1.2 we present three models for finite molecular systems. We start with the N-body Schrödinger model in Section 1.2.1, which is the reference model to describe non-relativistic finite quantum systems. Sections 1.2.2 and 1.2.3 are devoted to two types of approximation of the N-body Schrödinger model, namely, the Hartree-Fock type models and Density Functional Theory (DFT) models. We then explain how to derive models for infinite systems in Section 1.3. In Section 1.4, we concentrate on describing perfect crystals and crystals with deterministic defects in the reduced Hartree-Fock model. We present in Section 1.5 two models for stochastic systems: the random linear model and the reduced Hartree-Fock model. In Section 1.5.3, we study a particular case of stochastic systems, which is crystals with a low concentration of random defects. Finally, we present some numerical results concerning the simulation of one-dimensional stochastic systems.

1.2 Mathematical models for finite systems

We present in this section three categories of models used to describe finite molecular systems. The reader can also find a mathematical description of these models in [32].

We start by defining the N-body Schrödinger model. It is the reference model in non-relativistic quantum chemistry, from which are derived the approximate models of Hartree-Fock type and Density Functional Theory

presented in Sections 1.2.2 and 1.2.3.

1.2.1 The N-body Schrödinger model

In quantum chemistry, the N-body Schrödinger model is the fundamental model describing finite systems of electrons and nuclei in molecules containing no heavy atoms. It is an *ab initio* model, that is, it does not depend on any empirical parameters and only depends on universal physical constants.

To simplify notation, we adopt the system of atomic units in which

$$\hbar = 1, \quad m_e = 1, \quad e = 1, \quad 4\pi\varepsilon_0 = 1,$$

where $\hbar$ is the reduced Planck constant, m_e the mass of the electron, e the elementary charge, and ε_0 the dielectric permittivity of the vacuum. Also, we work with spinless electrons. As the spin plays no role in our study, our arguments can be straightforwardly extended to models with spin.

As usual in quantum chemistry, we adopt the Born-Oppenheimer approximation [16], which consists in considering that nuclei are classical particles and that only electrons are quantum particles. This approximation relies on the fact that nuclei are much heavier than electrons; their dynamics can thus be decoupled [86].

We consider a system composed of

- M classical nuclei at positions $R = (R_1, \dots R_M)$ and of charges $z = (z_1, \dots z_M)$, described by a positive Radon measure μ,
- N electrons described by a wavefunction $\Psi \in L^2(\mathbb{R}^{3N})$.

Here, the space dimension is equal to $d = 3$ corresponding to the physical space. Most of the results below are also valid in dimensions $d = 1$ and $d = 2$.

The nuclear density is assumed to be of the form

$$\mu = \sum_{k=1}^{M} z_k \chi_k, \tag{1.1}$$

where $\int \chi_k = 1$. For point-like nuclei, we have $\chi_k = \delta_{R_k}$, while for smeared nuclei, $\chi_k \in C_c^\infty(\mathbb{R}^3)$.

In quantum mechanics, $|\Psi(x_1, \cdots, x_N)|^2$ is interpreted as the probability density to find the particles $1, \cdots, N$ at the positions $x_1, \cdots, x_N$ respectively. The wavefunction Ψ thus needs to be normalized: $\|\Psi\|_{L^2(\mathbb{R}^{3N})} = 1$. Also, the particles are assumed to be indistinguishable. Therefore, permuting two indexes x_i and x_j should not change the probability, that is, for any $1 \leq i < j \leq N$, Ψ should satisfy

$$|\Psi(\cdots, x_i, \cdots, x_j, \cdots)| = |\Psi(\cdots, x_j, \cdots, x_i, \cdots)|. \tag{1.2}$$

In fact, it can be proved that in quantum mechanics, the wavefunction of a system of N identical particles is either symmetric

$$\Psi(\cdots, x_i, \cdots, x_j, \cdots) = \Psi(\cdots, x_j, \cdots, x_i, \cdots)$$

or antisymmetric

$$\Psi(\cdots, x_i, \cdots, x_j, \cdots) = -\Psi(\cdots, x_j, \cdots, x_i, \cdots)$$

with respect to the permutation of the $\mathbb{R}^3$-variables x_i. This condition classifies the particles into two categories: *bosons*, such as photons, which have symmetric wavefunctions, and *fermions*, such as electrons, which have antisymmetric wavefunctions. The antisymmetry of the wavefunction implies that if $x_i = x_j$ for $i \neq j$, then $\Psi(x_1, \cdots, x_N) = 0$, which corresponds to the fact that two electrons cannot be in the same state. This is called the *Pauli exclusion principle*. In the following, we consider wavefunctions Ψ which are normalized functions in $L^2_{\mathrm{a}}(\mathbb{R}^{3N})$, the space of antisymmetric square integrable functions.

In the Born-Oppenheimer approximation, the total energy of the system at the state Ψ is then given by

$$\mathcal{E}_N(\mu, \Psi) = \langle \Psi, H_{\mu,N}\Psi \rangle_{L^2(\mathbb{R}^{3N})}, \tag{1.3}$$

where the Hamiltonian $H_{\mu,N}$ reads

$$H_{\mu,N} = \sum_{i=1}^{N} -\frac{1}{2}\Delta_{x_i} + \sum_{i=1}^{N} V_\mu(x_i) + \sum_{1\leq i<j\leq N} \frac{1}{|x_i - x_j|} + U(\mu). \tag{1.4}$$

The first term of the Hamiltonian represents the kinetic energy of the electrons, where we have denoted by Δ_{x_i} the Laplace operator acting only on the x_i variable. The second term accounts for the electrostatic interaction energy between the electrons and the nuclei. The potential created by the nuclei V_μ is the unique solution of Poisson's equation

$$-\Delta V_\mu = 4\pi(-\mu) \tag{1.5}$$

that vanishes at infinity. It is given by

$$V_\mu(x) = -\mu * \frac{1}{|x|}.$$

The third term of (1.4) accounts for the electrostatic interaction energy between the electrons. Finally, $U(\mu)$ is the electrostatic interaction between the nuclei. When the nuclei are assumed to be point-like particles, then

$$U(\mu) = \sum_{1\leq j<k\leq M} \frac{z_j z_k}{|R_j - R_k|}.$$

When μ is given by (1.1), with smooth enough functions χ_k, then

$$U(\mu) = \sum_{1\leq j<k\leq M} z_j z_k \int_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\chi_j(x)\chi_k(y)}{|x-y|}\,dx\,dy.$$

Here, we have assumed that all the particles interact through the Coulomb potential $1/|x|$. The operator $H_{\mu,N}$ is a self-adjoint operator on $L^2_{\rm a}(\mathbb{R}^{3N})$ with domain $H^2_{\rm a}(\mathbb{R}^{3N})$ and form domain $H^1_{\rm a}(\mathbb{R}^{3N})$, where the subscript "a" indicates that we only consider antisymmetric functions.

The ground state energy of the system is given by

$$I_N(\mu) = \inf\left\{\mathcal{E}_N(\mu,\Psi),\ \Psi\in H^1_{\rm a}(\mathbb{R}^{3N}),\ \|\Psi\|_{L^2(\mathbb{R}^{3N})}=1\right\}. \tag{1.6}$$

One of the most important problems in electronic structure calculations is to find the electronic ground state Ψ_0, that is, the minimizer of $I_N(\mu)$. This state greatly influences the physical and chemical properties of the system as, according to Hamilton principle, it is the "most stable" state of the electrons. One can also find Ψ_0 by solving the stationary Schrödinger equation

$$H_{\mu,N}\Psi_0 = \lambda_0\Psi_0, \tag{1.7}$$

where λ_0 is the smallest eigenvalue of the operator $H_{\mu,N}$. As Ψ_0 is normalized, then the ground state energy is given by

$$I_N(\mu) = \mathcal{E}_N(\mu,\Psi_0) = \lambda_0.$$

The excited states are the solutions of the stationary Schrödinger equation

$$H_{\mu,N}\Psi = \lambda\Psi,$$

for higher energies $\lambda > \lambda_0$.

When (1.6) admits a minimizer, we say that the electrons are *bound* to the nuclei and Ψ_0 is called a *bound state*. It has been proved by Zhislin [157] that if $N < Z+1$, then the system admits a ground state. It is an interesting open problem, known as the *ionization conjecture*, to determine the maximum number of electrons $N_c(Z)$ that a molecule of total nuclear charge Z can actually bound. It has been proved by Lieb [108] that the system has no bound states if $N \geq 2Z+1$, thus $N_c(Z) \leq 2Z+1$. This bound has been improved by Nam [120] who proved that $N_c(Z) < 1.22Z + 3Z^{\frac{1}{3}}$. We also mention the result of Lenzmann and Lewin [98] for systems with only one atom which states that $H_{\mu,N}$ has no eigenvalues, even embedded in the essential spectrum, if $N \geq 4Z+1$.

The wavefunction Ψ contains in principle all the information about the system. But computing Ψ numerically is a challenging task. Indeed, a direct numerical approach to solve (1.7) demands to discretize the space $\mathbb{R}^{3N}$, N being the number of electrons in the system. When N is more than a few

units, this discretization problem is out of reach of the current computational and algorithmic capacities because of its high dimensionality. Also, we are interested in studying large systems where $N, M \to +\infty$. Deriving models for such systems from the N-body Schrödinger model is a very difficult task as we will explain in Section 1.3. One of the difficulties is that the wavefunction Ψ lives in the function space $L^2_{\rm a}(\mathbb{R}^{3N})$, which depends on N, the number of electrons.

For these reasons, the N-body model is often approximated by nonlinear mean-field models, where the variable that describes the electronic state is a "simpler" mathematical object compared to the wavefunction. To introduce these models, let us define the *electronic density* ρ_Ψ associated with a wavefunction Ψ

$$\rho_\Psi(x) = N \int_{\mathbb{R}^{3(N-1)}} |\Psi(x, x_2, \cdots, x_N)|^2 \, dx_2 \cdots dx_N.$$

It satisfies

$$\rho_\Psi \in L^1(\mathbb{R}^3), \quad \rho_\Psi \geq 0 \quad \text{and} \quad \int_{\mathbb{R}^{3N}} \rho_\Psi = N.$$

We also define the *one-body density matrix* γ_Ψ which is the linear operator on $L^2(\mathbb{R}^3)$ whose kernel is given by

$$\gamma_\Psi(x, y) = N \int_{\mathbb{R}^{3(N-1)}} \Psi(x, x_2, \cdots, x_N) \overline{\Psi(y, x_2, \cdots, x_N)} \, dx_2 \cdots dx_N,$$

in the sense that for any $\varphi \in L^2(\mathbb{R}^3)$,

$$(\gamma_\Psi \varphi)(x) = \int_{\mathbb{R}^3} \gamma_\Psi(x, y) \varphi(y) \, dy.$$

The two main approximations of the N-body model are:

- wavefunction methods, where the energy functional of the system is unchanged, but the minimization problem (1.6) is considered on a smaller set of wavefunctions. A famous model in this class is the Hartree-Fock model, where the electrons are described by a Slater determinant. The energy can then be expressed only in terms of the one-body density matrix γ_Ψ (see Section 1.2.2). For these methods, the ground state energy is always greater than or equal to the N-body ground state energy.

- Density Functional Theory, where the electrons are described by the electronic density ρ_Ψ only. The information contained in the electronic density is less precise than the one contained in the wavefunction, but it is sufficient to calculate certain properties of the system.

1.2.2 Hartree-Fock type models

The Hartree-Fock model

The Hartree-Fock (HF) model is the first step of all wavefunction methods. In these methods, the energy $\mathcal{E}^{\rm el}_{\mu,N}$ is minimized on a particular class of wavefunctions.

In the Hartree-Fock model, we restrict the minimization set in (1.6) to the set of Slater determinants, which are functions of the form

$$\Phi(x_1,\cdots,x_N) = (\varphi_1 \wedge \cdots \wedge \varphi_N)(x_1,\cdots,x_N) = \frac{1}{\sqrt{N!}}\det(\varphi_i(x_j)),$$

where the functions $\varphi_i \in H^1(\mathbb{R}^3)$ satisfy $\langle \varphi_i, \varphi_j \rangle_{L^2(\mathbb{R}^3)} = \delta_{ij}$. It is easy to check that Φ is a normalized function of $L^2_{\rm a}(\mathbb{R}^{3N})$. In this case, the electronic density and the one-body density matrix read

$$\rho_\Phi = \sum_{i=1}^N |\varphi_i|^2$$

and

$$\gamma_\Phi = \sum_{i=1}^N |\varphi_i\rangle\langle\varphi_i|\,.$$

The notation $|u\rangle\langle v|$ denotes the operator defined for any $\varphi \in L^2(\mathbb{R}^3)$ by $|u\rangle\langle v|\,\varphi = \langle v, \varphi\rangle_{L^2(\mathbb{R}^3)} u$. This form of wavefunctions mathematically originates from the fact $L^2_{\rm a}(\mathbb{R}^{3N}) = \wedge_{i=1}^N L^2(\mathbb{R}^3)$, where the latter is the vector space generated by Slater determinants. This means that any function in $L^2_{\rm a}(\mathbb{R}^{3N})$ can be approximated to any precision by a finite linear combination of Slater determinants. Models where the wavefunction is approximated by a finite linear combination of Slater determinants are called *multiconfiguration* methods. These methods are more precise than the Hartree-Fock model, but are more complicated to study theoretically and to solve numerically. We refer to [94, 53, 142, 103, 23] for an introduction to these methods. From a physical point of view, the Slater determinant can be interpreted as the state of N "uncorrelated" electrons, each electron i living in the orbital φ_i.

Calculating the N-body energy for the state Φ gives the Hartree-Fock energy

$$\begin{aligned}\mathcal{E}_{\mu,N}(\mu,\Phi) = \mathcal{E}^{\rm HF}_{\mu,N}(\varphi_1,\cdots,\varphi_N) := \frac{1}{2}\sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla\varphi_i|^2 + \int_{\mathbb{R}^3} V_\mu \rho_\Phi \\ + \frac{1}{2}\int_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho_\Phi(x)\rho_\Phi(y)}{|x-y|}\,dx\,dy - \frac{1}{2}\int_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\gamma_\Phi(x,y)}{|x-y|}\,dx\,dy + U(\mu).\end{aligned} \tag{1.8}$$

The first term of (1.8) represents the kinetic energy of the electrons. The second term stands for the electrostatic interaction between the electrons

and the nuclei. The third term, called the *Hartree* or *direct* term, accounts for the classical electrostatic interaction energy between the electrons. The next to the last term is called the *exchange* term. It is a purely quantum term as it results from the antisymmetry of the wavefunction.

Finding the electronic ground state within the HF model boils down to solving the minimization problem

$$\inf \left\{ \mathcal{E}^{\mathrm{HF}}_{\mu,N}(\varphi_1, \cdots, \varphi_N),\ \varphi_i \in H^1(\mathbb{R}^3),\ \langle \varphi_i, \varphi_j \rangle_{L^2(\mathbb{R}^3)} = \delta_{ij}\ \forall 1 \leq i,j \leq N \right\}. \tag{1.9}$$

As we have restricted the minimization set of the N-body minimization problem, the ground state energy given by the Hartree-Fock theory is always greater or equal to the ground state energy given by the N-body model. The difference between these two energies is called the *correlation* energy. The terminology comes from the fact that the Slater determinants do not include correlation between electrons, apart from the one originating from the Pauli exclusion principle.

The model we obtain is still an *ab initio* model. It has the advantage of being less costly to solve numerically compared with the N-body problem, as we now need to discretize N times the space $\mathbb{R}^3$ instead of discretizing $\mathbb{R}^{3N}$. But the HF functional is non-quadratic and non-convex in the orbitals φ_i, which makes the theoretical analysis of the Hartree-Fock model complicated.

The existence of a minimizer of the Hartree-Fock energy has been proved for neutral or positively charged systems $N < Z + 1$ in [113]. The proof of Lieb [108] can be adapted to show that the HF functional has no minimizers if $N \geq 2Z + 1$ and it has been proved in [147] that there exists a constant C such that there are no minimizers if $N \geq Z + C$. The question of the uniqueness of the minimizer in its full generality is still an open problem. The uniqueness in the case of closed shell atoms is partially treated in [62].

When the Hartree-Fock energy admits a minimizer $\Phi = \varphi_1 \wedge \cdots \wedge \varphi_N$, then, up to a change of $(\varphi_1, \cdots, \varphi_N)$ using an orthogonal transformation which does not change the energy, the φ_i's satisfy

$$\begin{cases} H^{\mathrm{HF}}_{\Phi} \varphi_i = \lambda_i \varphi_i \\ H^{\mathrm{HF}}_{\Phi} = -\dfrac{1}{2}\Delta + V - K_{\gamma_\Phi} \quad , \forall 1 \leq i \leq N, \\ -\Delta V = 4\pi \left(\rho_\Phi - \mu \right) \end{cases} \tag{1.10}$$

where the operator K_γ is defined for an integral operator γ by

$$\left(K_\gamma \varphi \right)(x) = \int_{\mathbb{R}^3} \frac{\gamma(x,y)}{|x-y|} \varphi(y)\, dy.$$

The operator H^{HF}_{Φ}, called the *Fock operator*, is the mean-field Hamiltonian of the system. Each electron is described by the Hamiltonian H^{HF}_{Φ} that includes the mean-field created by all the other electrons. The Lagrange multipliers

$\lambda_1 \leq \cdots \leq \lambda_N$ are the smallest eigenvalues, counting multiplicities, of the operator $H_\Phi^{\rm HF}$. An important result known as *no unfilled shell property* due to Bach, Lieb, Loss and Solovej [7] states that there is a gap between the occupied energies and the rest of the spectrum $\lambda_N < \lambda_{N+1}$. These two properties are specific to the HF theory and are important in the numerical resolution of the HF problem [31, 100].

Density matrix formalism

To describe infinite systems later on, it is more convenient to reformulate the HF problem in terms of the one-body density matrix [6, 105]. In this formalism, the electrons are described by the orthogonal projector γ_Φ of rank N and (1.10) can be recast as

$$\begin{cases} \gamma = 1(H_\gamma^{\rm HF} \leq \varepsilon_F) \\ H_\gamma^{\rm HF} = -\dfrac{1}{2}\Delta + V - K_\gamma \\ -\Delta V = 4\pi\left(\rho_\gamma - \mu\right), \end{cases}$$

where formally $\rho_\gamma(x) = \gamma(x,x)$ and the Fermi level ε_F is any real number in the gap $[\lambda_N, \lambda_{N+1})$. For a self-adjoint operator A and an interval $I \subset \mathbb{R}$, we use the notation $1(A \in I)$ to refer to the operator $f(A)$, where $f : x \mapsto 1_I(x)$, defined by the functional calculus. The HF energy then reads

$$\begin{aligned} \mathcal{E}_\mu^{\rm HF}(\gamma) = \frac{1}{2}{\rm Tr}\,\left(-\Delta\gamma\right) + \int_{\mathbb{R}^3} V_\mu \rho_\gamma + \frac{1}{2}\int_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|}\,dx\,dy \\ - \frac{1}{2}\int_{\mathbb{R}^3\times\mathbb{R}^3} \frac{|\gamma(x,y)|^2}{|x-y|}\,dx\,dy + U(\mu). \end{aligned} \tag{1.11}$$

and is minimized on the set of rank N projectors

$$\mathcal{P}_N = \left\{\gamma^* = \gamma,\ \gamma^2 = \gamma, {\rm Tr}\,(\gamma) = N,\ {\rm Tr}\,\left(-\Delta\gamma\right) < \infty\right\}.$$

Minimizing the energy $\mathcal{E}_\mu^{\rm HF}$ on $\mathcal{P}_N$ turns out to be equivalent [105] to minimizing $\mathcal{E}_\mu^{\rm HF}$ on $\mathcal{K}_N$, the convex hull of $\mathcal{P}_N$

$$\mathcal{K}_N = \left\{\gamma^* = \gamma,\ 0 \leq \gamma \leq 1, {\rm Tr}\,(\gamma) = N,\ {\rm Tr}\,\left(-\Delta\gamma\right) < \infty\right\}.$$

This property is very useful in mathematical analysis as well as for numerical methods. The properties of the one-body density matrices of $\mathcal{K}_N$ can be found in the Appendix 2.B.

The reduced Hartree-Fock model

The reduced Hartree-Fock (rHF) model, also called the *Hartree* model in the physics literature, is obtained from the HF model by neglecting the exchange term in (1.11). In certain regimes, the exchange term is a lower order term compared to the other terms [111]. The rHF problem reads

$$I_N^{\rm rHF}(\mu) = \inf\left\{\mathcal{E}_\mu^{\rm rHF}(\gamma),\ \gamma \in \mathcal{K}_N\right\}, \tag{1.12}$$

where

$$\mathcal{E}_\mu^{\mathrm{rHF}}(\gamma) = \frac{1}{2}\mathrm{Tr}\ (-\Delta\gamma) + \int_{\mathbb{R}^3} V_\mu \rho_\gamma + \frac{1}{2}\int_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|}\,dx\,dy + U(\mu).$$

The rHF energy functional is more amenable to mathematical analysis as it is a convex functional of the density matrix γ. Similarly to the HF case, the rHF problem (1.12) has been proved in [146] to admit a ground state when $N < Z+1$ and not to have a ground state when $N \geq 2Z+M-1$. When the rHF functional has a minimizer, then, thanks to the strict convexity of $\rho \mapsto \int_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\,dx\,dy$ and the convexity of the set $\mathcal{K}_N$, these minimizers share the same density, and they are solutions of the rHF equation:

$$\begin{cases} \gamma = 1(H_\gamma^{\mathrm{rHF}} < \varepsilon_F) + \delta \\ H_\gamma^{\mathrm{rHF}} = -\dfrac{1}{2}\Delta + V \\ -\Delta V = 4\pi\left(\rho_\gamma - \mu\right), \end{cases} \tag{1.13}$$

where δ is a self-adjoint operator satisfying $0 \leq \delta \leq 1(H_\gamma^{\mathrm{rHF}} = \varepsilon_F)$. The operator δ is non zero if the last shell is only partially filled.

In the sequel we concentrate on the rHF model as it is a simple enough model to allow a rigorous mathematical analysis, while still being rich enough to describe interesting physical phenomena.

Finally, we note that the density matrix γ describing the electrons in the HF and rHF models belongs to $\mathcal{B}(L^2(\mathbb{R}^3))$, the space of bounded linear operators on $L^2(\mathbb{R}^3)$, independently of the number of electrons in the system, unlike the N-body model as we explained earlier. This is an interesting feature for the derivation of models for infinite systems.

1.2.3 Density Functional Theory

Presentation of Density Functional Theory

The idea behind Density Functional Theory (DFT) is that the ground state energy $I_N(\mu)$ defined in (1.6) can be found by solving a problem depending only on the electronic density ρ. The evident computational gain is that the new problem is posed on the low dimension space $\mathbb{R}^3$ compared to $\mathbb{R}^{3N}$. The first theoretical justification of this approach goes back to Hohnenberg and Kohn [74]. Kohn was awarded the Nobel prize in chemistry in 1998 for the significant contribution of the DFT in the understanding of the electronic structure of materials. We present here an approach that has been developed by Levy and Lieb [101, 107]. It relies on writing $I_N(\mu)$ as

$$\begin{aligned} I_N(\mu) &= \inf\left\{\int_{\mathbb{R}^3} V_\mu\rho_\Psi + \langle\Psi, H_{0,N}\Psi\rangle,\ \Psi \in H^1_{\mathrm{a}}(\mathbb{R}^{3N}),\ \|\Psi\| = 1\right\} + U(\mu) \\ &= \inf_{\rho\in\mathcal{C}_N}\left\{\int_{\mathbb{R}^3} V_\mu\rho + F_{\mathrm{LL}}(\rho)\right\} + U(\mu) \end{aligned} \tag{1.14}$$

where

$$\mathcal{C}_N = \left\{ \rho,\ \exists \Psi \in H^1_{\mathrm{a}}(\mathbb{R}^{3N}),\ \|\Psi\|_{L^2(\mathbb{R}^{3N})} = 1,\ \rho_\Psi = \rho \right\}$$

and

$$F_{\mathrm{LL}}(\rho) = \inf \left\{ \langle \Psi, H_{0,N}\Psi \rangle,\ \Psi \in H^1_{\mathrm{a}}(\mathbb{R}^{3N}),\ \|\Psi\|_{L^2(\mathbb{R}^{3N})} = 1,\ \rho_\Psi = \rho \right\}.$$

Identifying the set of admissible densities $\mathcal{C}_N$ is known as an *N-representability* problem. It has been proved by Lieb in [107] that

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

The *Levy-Lieb* functional F_{LL} is a universal functional that does not depend on the particular molecular system at hand. Unfortunately, we cannot use (1.14) to calculate the ground state energy $I_N(\mu)$ as there is no explicit formula of the Levy-Lieb functional F_{LL}. However, a great effort and a large literature are devoted to find good approximations of F_{LL}. We present below two important examples of such approximations.

Thomas-Fermi like models

The Thomas-Fermi (TF) and the Thomas-Fermi-von Weizsäcker (TFW) models are orbital-free DFT models, that is, the functional F_{LL} is approximated by an explicit functional of ρ and its derivatives. These functionals are given by

$$F^{\mathrm{TF}}(\rho) = C_{\mathrm{TF}} \int_{\mathbb{R}^3} \rho^{5/3} + \frac{1}{2} \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\, dx\, dy \tag{1.15}$$

and

$$F^{\mathrm{TFW}}(\rho) = C_{\mathrm{W}} \int_{\mathbb{R}^3} |\nabla \sqrt{\rho}|^2 + C_{\mathrm{TF}} \int_{\mathbb{R}^3} \rho^{5/3} + \frac{1}{2} \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\, dx\, dy.$$

In both models, the electrostatic interaction between the electrons is approximated by the Hartree term

$$\frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\, dx\, dy.$$

As to the approximation of the kinetic energy, it relies on the expression of the kinetic energy of a non-interacting homogeneous electron gas, whose kinetic energy per unit volume is $C_{\mathrm{TF}}\rho_0^{5/3}$, where ρ_0 is its uniform density. Note that we have the lower bound given by the Lieb-Thirring inequality [115, 116]

$$K \int_{\mathbb{R}^3} \rho_\Psi^{5/3} \leq \|\nabla \Psi\|^2_{L^2(\mathbb{R}^{3N})}. \tag{1.16}$$

Solving the minimization problem with the energy (1.15) gives singular densities as no derivative of ρ is involved. Von Weizsäcker brought in a correction to this approximation, by adding the term $\int_{\mathbb{R}^3} |\nabla\sqrt{\rho_\Psi}|^2$ which is also controlled by the kinetic energy of the N-body wavefunction thanks to the Hoffman-Ostenhoff inequality [73]

$$\int_{\mathbb{R}^3} |\nabla\sqrt{\rho_\Psi}|^2 \leq \|\nabla\Psi\|^2_{L^2(\mathbb{R}^{3N})}\,. \tag{1.17}$$

There is no clear choice of the constant $C_{\rm W}$. Von Weizsäcker has proposed $C_{\rm W} = 1$ based on (1.17), but other values have been proposed to suit particular regimes (see e.g. [106, 41]). The TF and TFW models are not very much used in electronic structure calculations, but their mathematical analysis raises many interesting questions that are also relevant for more complicated models.

Kohn-Sham models
Similarly to the HF model, Kohn Sham (KS) models describe the electrons through N orbitals $(\varphi_1, \cdots, \varphi_N)$. In these models, the kinetic energy and the potential energy are respectively approximated by

$$\frac{1}{2}\sum_{i=1}^{N} \|\nabla\varphi_i\|^2_{L^2(\mathbb{R}^3)} \quad \text{and} \quad \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\,dx\,dy.$$

An exchange-correlation term $E_{\rm xc}(\rho)$ is added to correct these approximations. A huge number of functionals have been proposed in the literature for $E_{\rm xc}(\rho)$ [44]. The most widely used in condensed matter physics are obtained from the *Local Density Approximation* (LDA) [90, 129] or the *Generalized Gradient Approximation* GGA [10, 127, 128, 41].

1.3 Infinite quantum systems

In the sequel, we are interested in the macroscopic properties of materials. For this reason, we need to consider bulk matter where M and N are very large ($M \simeq 10^{23}$ in $1\,\mathrm{cm}^3$ of material). Mathematically, we consider the limit $M, N \to +\infty$.

An important mathematical question when considering large quantum systems is the *stability of matter*, that is, does the matter collapse or explode when $M, N \to \infty$? Loosely speaking, a well known fact to physicists is that the energy is an extensive quantity, in the sense that the energy of a homogeneous system composed of $2M$ atoms is asymptotically twice the energy of a system composed of M atoms. The question of the *thermodynamic limit* concerns the mathematical proof of this fact in the context of quantum mechanics. A first step for answering this question is to prove the lower bound

$$I_{N_L}(\mu_L) \geq -CN_L \tag{1.18}$$

which is known as the *stability of the second kind*. Here, the energy $I_N(\mu)$ has been defined in (1.6), $\mu_L = \mu 1_{\Gamma_L}$, where Γ_L is a box of side size L, μ is the nuclear density, and N_L is the number of electrons in the box Γ_L. Several types of conditions can be imposed on the boundary of the box Γ_L and the charge constraint N_L. For example, one can assume Dirichlet boundary conditions and the neutrality of the system $N_L = \int_{\Gamma_L} \mu$. The bound (1.18) has been proved in the context of the Schrödinger model [115, 112, 66, 67] under the assumption that the charges of the nuclei are bounded $z_i \leq C$. The next important question is the existence of the thermodynamic limit, that is, the proof of the behavior

$$I_{N_L}(\mu_L) \underset{L\to\infty}{\sim} eN_L, \tag{1.19}$$

where e is to be interpreted as the energy per unit volume. When e exists, it is also interesting to be able to calculate it and to identify the limiting state. The first results of this form for Coulomb interacting systems are due to Lieb and Lebowitz in [109]. In the latter work, nuclei are considered as quantum particles and rotational invariance plays a crucial role. For quantum systems in which the nuclei are classical particles, the thermodynamic limit was proved for perfect crystals by Fefferman [47] (a recent proof has been proposed in [67]). But in all these cases no information about the limiting energy, the convergence of the ground state or its properties is known.

For some of the mean-field models presented in Sections 1.2.2 and 1.2.3, it was possible to identify the limiting state and to study its properties. For TF and TFW models, this was done in [114, 35, 13]. The main ingredient of the proof for these models is the strict convexity of the energy functional, thus the uniqueness of the minimizing density.

Similar results are obtained for the rHF model. We will detail these results in Section 1.4.

In the framework of the HF and KS models, it is possible to guess what the limiting model is for perfect crystals, thanks to the periodic structure. But the rigorous proof of the thermodynamic limit toward this limiting models is still an open question.

Once the existence of the thermodynamic limit is proved, an interesting question is to study the next term in the expansion (1.19). A typical case of interest is local perturbations of infinite systems. In this case, the energy per unit volume of the system with and without the perturbation converges to the same quantity e, but clearly, the states of the electrons do not. For a defect ν, the next order in the expansion (1.19) is the defect energy I^ν:

$$I_{N_L}(\mu_L + \nu) - I_{N_L}(\mu_L) \underset{L\to\infty}{=} I^\nu + o(1). \tag{1.20}$$

The existence of I^ν in the N-body model is still an open problem even for short-range interactions. For the TFW and the rHF model, I^ν has been

proved to exist and a variational model allowing its calculation has been proposed respectively in [26, 24]. We also mention the work of Lieb and Simon [114] who have treated local defects in the homogeneous electron gas in the TF framework. We will detail the rHF case in Section 1.4.2.

The main difficulty of these problems is the long range character of the Coulomb interaction. To understand this difficulty, let us consider the potential created by point-like nuclei of charge $z_i = 1$ located at the sites of $\mathbb{Z}^3 \cap \Gamma_L$:

$$V_L(x) = \left(\sum_{k \in \mathbb{Z}^3 \cap \Gamma_L} \delta_k \right) * \frac{1}{|x|} = \sum_{k \in \mathbb{Z}^3 \cap \Gamma_L} \frac{1}{|x-k|}.$$

This series is not convergent as L goes to infinity, which means that the potential goes to infinity everywhere in $\mathbb{R}^3$. To ensure the stability of matter, this suggests that each electron does not see the bare nuclei, but sees the nuclei screened by the neighboring electrons. For this reason, it is necessary when studying infinite systems to prove that this screening actually happens and that each electron only sees the dipole or the multipole that the nuclei and their neighboring electrons form. The potential then decays faster and the series become convergent.

In the following, we also consider models with short-range Yukawa interaction of parameter $m > 0$, that is, the potential V created by a charge density ρ is the solution of the regularized Poisson equation

$$-\Delta V + m^2 V = 4\pi\rho. \tag{1.21}$$

The Coulomb interaction is then the limit when m goes to 0 of the Yukawa interaction. Taking the Fourier transform of (1.21), we have that

$$V = \rho * Y_m,$$

where the Yukawa kernel Y_m is the inverse Fourier transform of $K \mapsto 4\pi(m^2 + |K|^2)^{-1}$. It is given in dimension $d = 3$ by

$$Y_m(x) = \frac{e^{-m|x|}}{|x|}.$$

The proof of the existence of the thermodynamic limit with Yukawa interaction is simpler than the Coulomb case. For perfect crystals, it follows from the work of Fisher and Ruelle [49].

1.4 The reduced Hartree-Fock model for crystals

In ideal crystals, also called *perfect crystals*, the nuclei are arranged according to a discrete periodic lattice. While there are crystals in nature that are close to this description, many of them contain defects, either local such as

vacancies, interstitial atoms and impurities, or extended such as dislocations and grain boundaries.

In the following we present the rHF model used to describe each of these three cases.

1.4.1 Perfect crystals

In perfect crystals, the nuclei and electrons are arranged according to a discrete periodic lattice $\mathcal{R}$ of $\mathbb{R}^3$, in the sense that both the nuclear density μ and the electronic density are $\mathcal{R}$-periodic functions (see Figure 1.1). For simplicity, we take $\mathcal{R} = \mathbb{Z}^3$ in the following. The rHF model for perfect crystals

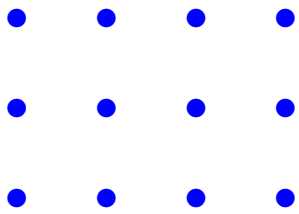

Figure 1.1: Perfect crystal: periodic arrangement of atoms.

has been rigorously derived from the rHF model for finite molecular systems (see Section 1.2.2) by means of thermodynamic limit procedure in [36, 24] in the case of Coulomb interaction. In [36], Dirichlet boundary conditions at infinity are imposed, while in [24], the authors use the supercell model, that is, they impose periodic boundary conditions. The same results for Yukawa interaction can be obtained with similar arguments.

In the limiting model, we suppose that the nuclei are described by a $\mathbb{Z}^3$-periodic function $\mu_{\rm per}$. The electrons are described by a one-body density matrix γ, which is now an infinite rank operator as there are infinitely many electrons in the system. The admissible density matrices are the $\mathbb{Z}^3$-periodic density matrices with finite number of electrons and kinetic energy per unit volume:

$$\mathcal{K}_{\rm per} = \left\{\gamma^* = \gamma,\ 0 \leq \gamma \leq 1,\ U_k\gamma = \gamma U_k\ \forall k \in \mathbb{Z}^3,\ \underline{\rm Tr}\ ((-\Delta + 1)\,\gamma) < \infty\right\}.$$

Here, U_k denotes the translation operator of vector k:

$$U_k\varphi(x) = \varphi(x + k), \quad \forall \varphi \in L^2(\mathbb{R}^3), \tag{1.22}$$

and $\underline{\rm Tr}\,(\cdot)$ is the trace per unit volume, which is defined for $\mathbb{Z}^3$-periodic locally

trace class operators A by

$$\underline{\mathrm{Tr}}\,(A) := \lim_{L\to\infty} \frac{\mathrm{Tr}\,(1_{\Gamma_L} A 1_{\Gamma_L})}{L^3} = \mathrm{Tr}\,(1_\Gamma A 1_\Gamma)\,. \tag{1.23}$$

where $\Gamma_L = [-L/2, L/2)^3$ and $\Gamma = [-1/2, 1/2)^3$ is the unit cell. We refer the reader to Appendix 2.B for the definition and properties of locally trace class operators. For a density matrix γ, the trace per unit volume $\underline{\mathrm{Tr}}\,(\gamma)$ represents the number of electrons per unit volume, and

$$-\frac{1}{2}\underline{\mathrm{Tr}}\,(\Delta\gamma) = \frac{1}{2}\sum_{j=1}^{3} \underline{\mathrm{Tr}}\,(P_j \gamma P_j)\,,$$

$P_j = -i\partial_{x_j}$ being the momentum operator in the direction j, is the kinetic energy per unit volume. The rHF energy associated with $\gamma \in \mathcal{K}_{\mathrm{per}}$ is then given by

$$\mathcal{E}^{\mathrm{rHF}}_{\mathrm{per},m}(\mu_{\mathrm{per}}, \gamma) = \frac{1}{2}\underline{\mathrm{Tr}}\,(-\Delta\gamma) + \frac{1}{2}\underline{D}_m\left(\rho_\gamma - \mu_{\mathrm{per}}, \rho_\gamma - \mu_{\mathrm{per}}\right), \tag{1.24}$$

where $\underline{D}_m(\cdot,\cdot)$ is the interaction energy per unit volume. It is defined for any $\mathbb{Z}^3$-periodic charge densities f and g by

$$\underline{D}_m(f,g) = \sum_{K\in(2\pi\mathbb{Z})^3} 4\pi \frac{\overline{c_K(f)} c_K(g)}{|K|^2 + m^2}, \tag{1.25}$$

where $c_K(f)$ is the K^{th} Fourier coefficient of f. When $m = 0$, we see that for the Coulomb interaction energy $\underline{D}_m\left(\rho_\gamma - \mu_{\mathrm{per}}, \rho_\gamma - \mu_{\mathrm{per}}\right)$ to be finite, the system needs to be neutral: $\int_\Gamma \rho_\gamma = \int_\Gamma \mu_{\mathrm{per}}$. In this case, we remove the term $K = 0$ in the sum (1.25). While this condition is not necessary for Yukawa interacting systems, we impose it for consistency. The minimization problem then reads

$$\inf\left\{\mathcal{E}^{\mathrm{rHF}}_{\mathrm{per},m}(\mu_{\mathrm{per}}, \gamma),\ \gamma \in \mathcal{K}_{\mathrm{per}},\ \underline{\mathrm{Tr}}\,(\gamma) = \int_\Gamma \mu_{\mathrm{per}}\right\}. \tag{1.26}$$

Note that in (1.24), we have included, for convenience, the self-interaction of each nuclei with itself, which was not included in (1.3). This term is a constant with respect to the electronic minimization problem and it plays no role in the sequel.

It has been proved in [36, 24] that (1.26) admits a unique minimizer which is a solution to the periodic rHF equation

$$\begin{cases} \gamma_0 = 1\left(H_{\mathrm{per}} \le \varepsilon_F\right) \\ H_{\mathrm{per}} = -\dfrac{1}{2}\Delta + V_{\mathrm{per}} \\ -\Delta V_{\mathrm{per}} + m^2 V_{\mathrm{per}} = 4\pi\left(\rho_{\gamma_0} - \mu_{\mathrm{per}}\right), \end{cases} \tag{1.27}$$

where ε_F is the Lagrange multiplier corresponding to the charge constraint and $m \geq 0$ is the Yukawa parameter. The proofs in [36, 24] are based on the formulation of the problem within the Bloch-Floquet theory. We refer the reader to [133] for a presentation of this theory.

The periodic Schrödinger operator H_{per} is the mean-field Hamiltonian of the system. The spectral properties of such operators are easy to study thanks to the Bloch-Floquet transform [133]. In particular, their spectrum is known to be absolutely continuous and composed of, possibly overlapping, bands, that is,

$$\sigma\left(H_{\text{per}}\right) = \cup_{n\in\mathbb{N}}\left[a_n, b_n\right].$$

From a physical point of view, the band structure is important to describe the electrical properties of the crystal. In particular, if ε_F lays in a spectral gap, then the crystal is an insulator or a semi-conductor. Otherwise, the crystal is a conductor (see Figure 1.2).

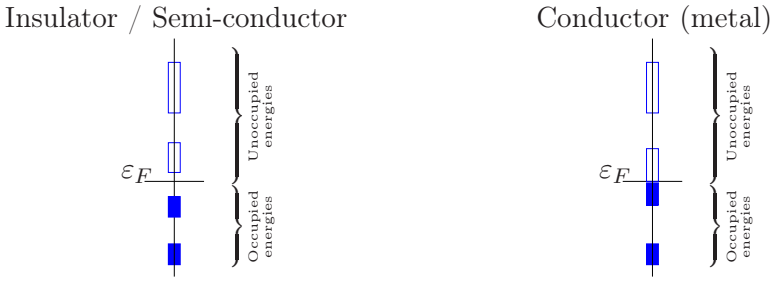

Figure 1.2: Insulating and conducting materials

Most of our results below hold only for insulators (or semi-conductors). We therefore make the assumption that

$$H_{\text{per}} \text{ has a spectral gap around } \varepsilon_F. \tag{1.28}$$

As we said before, the thermodynamic limit is not yet proved for the HF model. However, a model similar to (1.26) has been proposed, and proved to be well posed by Catto, Le Bris and Lions in [36]. In [59], the authors prove that the minimizers of this HF functional are solutions of a self-consistent field equation similar to (1.27) and satisfy the no unfilled shell property.

1.4.2 Crystals with local defects

A local defect in a crystal corresponds to perturbing the periodic nuclear density locally (see Figure 1.3). For example, when the nucleus in the site $k \in \mathbb{Z}^3$ and of charge z is displaced to $k' \in \mathbb{R}^3$ or replaced by another nucleus of charge z', then the defect is

$$\nu = z(\chi_{k'} - \chi_k) \quad \text{or} \quad \nu = (z' - z)\chi_k.$$

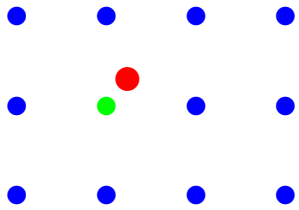

Figure 1.3: Local perturbation of a perfect crystal.

Mathematically, local defects are modeled by a perturbation ν of the nuclear distribution, with ν going to 0 at infinity. In the following we typically consider that the defect ν is in $L^1(\mathbb{R}^3) \cap L^2(\mathbb{R}^3)$. The total nuclear distribution is then

$$\mu = \mu_{\rm per} + \nu.$$

In our study, the nuclear distribution $\mu_{\rm per}$ is such that the background perfect crystal is an insulator. To describe the electronic structure of the perturbed system, a variational model in the rHF framework has been introduced and studied by Cancès, Deleurence and Lewin in [24]. The defect is considered as a quasi-particle embedded in the background crystal, following ideas of [65] in the study of quantum electrodynamics (QED) models. The defect energy I^ν (see (1.20)) is then given as the minimum of the defect energy functional $\mathcal{F}^\nu_{\gamma_0}(\gamma)$ which is the difference between the energy of the system where the electrons are in the test state γ and the energy of the system where the electrons are in the state γ_0, the ground state of the background perfect crystal. These two energies are infinite, but their difference can be given a rigorous meaning in terms of the difference $Q = \gamma - \gamma_0$, when the latter is in a suitable functional space. To do so, let us rather consider the free energy $\mathcal{E}^{\rm rHF}_\mu(\gamma) - \varepsilon_F {\rm Tr}\,(\gamma)$ and define

$$\begin{aligned}\mathcal{F}^\nu_{\gamma_0}(Q) &= \text{“}\left(\mathcal{E}^{\rm rHF}_{\mu_{\rm per}+\nu}(\gamma_0+Q) - \varepsilon_F {\rm Tr}\,(\gamma_0+Q)\right) - \left(\mathcal{E}^{\rm rHF}_{\mu_{\rm per}+\nu}(\gamma_0) - \varepsilon_F {\rm Tr}\,(\gamma_0)\right)\text{”} \\ &:= {\rm Tr}\,((H_{\rm per} - \varepsilon_F)Q) + D_m(\rho_Q, \nu) + \frac{1}{2} D_m(\rho_Q, \rho_Q). \end{aligned} \tag{1.29}$$

The right hand side of the first line of (1.29) has *a priori* no mathematical meaning since both quantities are infinite, but the right hand side of the second line is well-defined if Q is finite rank and smooth enough for instance. The interaction energy is defined for any charge densities f, g by

$$D_m(f,g) = 4\pi \int_{\mathbb{R}^3} \frac{\overline{\widehat{f}(K)}\widehat{g}(K)}{|K|^2 + m^2}\, dK, \tag{1.30}$$

where $\widehat{f}(K) = (2\pi)^{-\frac{d}{2}} \int_{\mathbb{R}^3} f(x)\, e^{-iK\cdot x} dx$ is the Fourier transform of f. When $m = 0$, then D_0 is finite for functions in the Coulomb space

$$\mathcal{C}_0(\mathbb{R}^3) = \left\{ f \in \mathcal{S}'(\mathbb{R}^3),\ D_0(f,f) < \infty \right\}.$$

When $m > 0$, then D_m is finite for functions in $H^{-1}(\mathbb{R}^3)$.

The "defect state" Q should be so that γ is an admissible density matrix (self-adjointness $\gamma^* = \gamma$ and Pauli principle $0 \leq \gamma \leq 1$) and has finite defect energy. The set of admissible defect states is given by

$$\begin{aligned} \mathcal{K} = \Big\{ Q^* = Q,\ -\gamma_0 \leq Q \leq 1 - \gamma_0,\ (-\Delta+1)^{\frac{1}{2}} Q \in \mathfrak{S}_2(L^2(\mathbb{R}^3)), \\ (-\Delta+1)^{\frac{1}{2}} Q^{\pm\pm} (-\Delta+1)^{\frac{1}{2}} \in \mathfrak{S}_1(L^2(\mathbb{R}^3)) \Big\}, \end{aligned} \tag{1.31}$$

where $A^{++} = (1-\gamma_0)A(1-\gamma_0)$ and $A^{--} = \gamma_0 A \gamma_0$. Here $\mathfrak{S}_1$ denotes the space of trace class operators and $\mathfrak{S}_2$ the space of Hilbert-Schmidt operators. Note that one can associate to any Q in $\mathcal{K}$ a density ρ_Q which is not necessarily integrable, but is in $\mathcal{C}_0(\mathbb{R}^3) \cap L^2(\mathbb{R}^3)$ (see [24, Proposition 1]), therefore, its energy is always finite.

It has been proved in [24] that the minimization problem

$$I^\nu = \inf \left\{ \mathcal{F}^\nu_{\gamma_0}(Q),\ Q \in \mathcal{K} \right\}$$

admits a minimizer Q_ν and that all the minimizers share the same density ρ_ν. It has also been proved that the ground state energy I^ν is the thermodynamic limit of the supercell model. The ground states of the perturbed crystal are then given by

$$\gamma = \gamma_0 + Q_\nu.$$

These ground states are the solutions of the self-consistent field equation

$$\begin{cases} \gamma = 1\,(H \leq \varepsilon_F) + \delta \\ H = -\dfrac{1}{2}\Delta + V \\ -\Delta V + m^2 V = 4\pi(\rho_\gamma - \mu_{\mathrm{per}} - \nu), \end{cases} \tag{1.32}$$

where $0 \leq \delta \leq 1\,(H = \varepsilon_F)$. The potential V can be written $V = V_{\mathrm{per}} + V_\nu$ where $V_\nu = (\rho_\nu - \nu) * Y_m$ is in $L^6(\mathbb{R}^3)$. Therefore V_ν is a compact perturbation of the periodic Hamiltonian H_{per}. It follows that the spectrum of the mean-field Hamiltonian H is composed of the spectrum of H_{per} and possibly isolated eigenvalues of finite multiplicity, which can accumulate at the edges of the bands (see Figure 1.4). If $D_m(\nu,\nu)$ is small enough, then ε_F is not an eigenvalue of H and $\delta = 0$. This implies that the system admits a unique ground state.

Under this assumption, the properties of this unique ground state have been investigated in [33] with the Coulomb interaction. In particular, it is

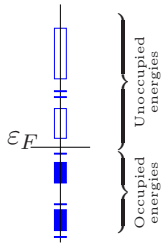

Figure 1.4: The spectrum of the mean field operator H in presence of a local defect.

proved that if the material is anisotropic and $\int_{\mathbb{R}^3} \nu \neq 0$, then the density ρ_ν is not integrable at infinity. This behavior is due to the oscillations created by the Coulomb potential.

One contribution of this thesis is the study of the decay properties of the density ρ_ν and the potential V_ν in the case of Yukawa interaction. Thanks to the short-range character of the Yukawa interaction, these quantities are proved to decay, when ν is compactly supported and small enough, faster that any polynomial far from the support of ν. Denoting by $L^2_c(\mathbb{R}^3)$ the space of square integrable functions with compact support and by $L^2_{\text{unif}}(\mathbb{R}^3)$ the Banach space of uniformly square integrable functions $L^2_{\text{unif}}(\mathbb{R}^3) = \left\{ f \in L^2(\mathbb{R}^3),\ \sup_{k\in\mathbb{Z}^3} \|f\|_{L^2(\Gamma+k)} < \infty \right\}$, we have the following result.

Theorem 1.4.1 (Decay rate of the mean-field potential and density)**.** *[92, Th 2.3, Rem. 2.4] [Th. 3.2.3, Th. 3.A.1 Chapter 3] Assume that the background crystal is an insulator and that $m > 0$. Then, for any $\nu \in L^2_c(\mathbb{R}^3)$ such that $\|\nu\|_{L^2_{\text{unif}}}$ and $\|\nu\|_{H^{-1}}$ are small enough, we have for $R \geq 2$*

$$\|V_\nu\|_{H^2(\mathbb{R}^3\setminus C_R(\nu))} + \|\rho_\nu\|_{L^2(\mathbb{R}^3\setminus C_R(\nu))} \leq Ce^{-C'(\log R)^2} \|\nu\|_{L^2(\mathbb{R}^3)},$$

where $C_R(\nu) = \left\{x \in \mathbb{R}^3,\ \mathrm{d}\left(x, \mathrm{supp}(\nu)\right) < R\right\}$.

We also prove that the potential generated by two defects that are far enough from one another is close to the sum of the potentials generated by each defect alone:

Theorem 1.4.2. *[92, Prop. 2.6] [Prop. 3.2.6 Chapter 3] Assume that the background crystal is an insulator and that $m > 0$. Then for any $\beta \geq 2$ and any $\nu_1, \nu_2 \in L^2_c(\mathbb{R}^3)$ such that $\|\nu_1\|_{L^2_{\text{unif}}}$ and $\|\nu_2\|_{L^2_{\text{unif}}}$ are small enough, we have*

$$\|V_{\nu_1+\nu_2} - V_{\nu_2}\|_{H^2_{\text{unif}}(C_{R/(4^\beta)}(\nu_2))} + \|\rho_{\nu_1+\nu_2} - \rho_{\nu_2}\|_{L^2_{\text{unif}}(C_{R/(4^\beta)}(\nu_2))} \leq \frac{C}{R^\beta}\left(\|\nu_1\|_{L^2_{\text{unif}}} + \|\nu_2\|_{L^2_{\text{unif}}}\right),$$

where $R = \mathrm{d}(\mathrm{supp}(\nu_1), \mathrm{supp}(\nu_2)) > 0$.

These decay estimates are a necessary input in the study of more complicated systems, such as crystals with rare random defects presented in Section 1.5.3 below.

1.4.3 Crystals with extended defects

In this section, we discuss the case of extended defects, such as dislocations or doping in semi-conductors. The effects of such perturbations on the physical and mechanical properties of the material are more important than those induced by a local defect. For example, we have seen that the spectrum of the mean-field Hamiltonian of a locally perturbed crystal has the same band structure as the background crystal, with possibly some discrete eigenvalues in the gaps. For extended defects, this picture changes, as we can observe the narrowing or widening of the bands or even the disappearance of a spectral gap.

One contribution of this thesis is the study of extended defects in the rHF framework for systems interacting through Yukawa potential. The results presented below are contained in [92] and are detailed in Chapter 3.

We consider a perfect crystal characterized by a periodic nuclear density $\mu_{\mathrm{per}} \in L^2_{\mathrm{unif}}(\mathbb{R}^3)$ such that the gap assumption (1.28) holds. This crystal is perturbed by a nuclear distribution $\nu \in L^2_{\mathrm{unif}}(\mathbb{R}^3)$. The total nuclear distribution is then (see Figure 1.5)

$$\mu_{\mathrm{nuc}} = \mu_{\mathrm{per}} + \nu.$$

We assume that the perturbed nuclear distribution is close to the one of

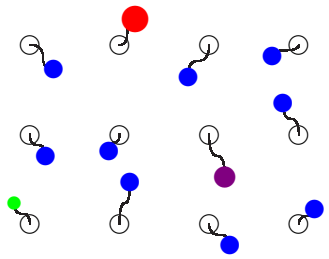

Figure 1.5: Extended perturbation of a perfect crystal

the host perfect crystal *locally* (the L^2_{unif}-norm of ν is small enough), but the perturbation need not be localized in a specific region of space and it also need not have any spatial invariance. This assumption ensures that the perturbed crystal is still an insulator.

It is difficult to adopt here a variational approach similar to the one of local defects, since the energy difference between the perturbed crystal and

the host crystal can be infinite. We proceed slightly differently. We start by solving the rHF equation and we compare the energy of suitable test states γ to the energy of these solutions. The convexity of the rHF energy is thus important.

In the following theorem, we prove that the rHF equation admits a solution γ. Moreover, this solution is unique in a neighborhood of γ_0.

Theorem 1.4.3 (Existence of a ground state)**.** *[92, Th. 2.1] [Th. 3.2.1 Chapter 3] Let $m > 0$. Then, for any $\nu \in L^2_{\rm unif}(\mathbb{R}^3)$ such that $\|\nu\|_{L^2_{\rm unif}}$ is small enough, there is a unique solution γ to the self-consistent equation*

$$\begin{cases} \gamma = 1\left(H \leq \varepsilon_F\right) \\ H = -\dfrac{1}{2}\Delta + V \\ -\Delta V + m^2 V = 4\pi(\rho_\gamma - \nu - \mu_{\rm per}) \end{cases}$$

satisfying

$$\|\rho_\gamma - \rho_{\gamma_0}\|_{L^2_{\rm unif}} \leq C\,\|\nu\|_{L^2_{\rm unif}}\,.$$

The proof of Theorem 1.4.3 consists in formulating the problem in terms of the density ρ_γ and using a fixed point technique, in the spirit of [64].

A solution γ_ν constructed in Theorem 1.4.3 is a good candidate for being the ground state of the electrons in the field of the nuclei arranged according to $\mu_{\rm per} + \nu$. Following the quasi-particle ideas explained in Section 1.4.2, we define the free energy difference

$$\begin{aligned} \mathcal{F}^\nu_{\gamma_\nu}(\gamma - \gamma_\nu) &= \text{“}\left(\mathcal{E}^{\rm rHF}_{\mu_{\rm per}+\nu}(\gamma) - \varepsilon_F {\rm Tr}\,(\gamma)\right) - \left(\mathcal{E}^{\rm rHF}_{\mu_{\rm per}+\nu}(\gamma_\nu) - \varepsilon_F {\rm Tr}\,(\gamma_\nu)\right)\text{”} \\ &:= {\rm Tr}\left(\left(H - \varepsilon_F\right)(\gamma - \gamma_\nu)\right) + D_m\left(\rho_\gamma - \rho_{\gamma_\nu}, \nu\right) \\ &\quad + \frac{1}{2} D_m\left(\rho_\gamma - \rho_{\gamma_\nu}, \rho_\gamma - \rho_{\gamma_\nu}\right), \end{aligned} \tag{1.33}$$

where D_m has been defined in (1.30). Similarly to the case of local defects, the right hand side of the first line of (1.33) has *a priori* no mathematical meaning, but the right hand side of the second line is well-defined for states γ such that $\gamma - \gamma_\nu$ is finite rank and smooth enough, for instance. One can extend its definition to states in a set similar to $\mathcal{K}$ in (1.31). The minimum of the energy $\mathcal{F}^\nu_{\gamma_\nu}$ is attained for $\gamma = \gamma_\nu = 1\left(H \leq \varepsilon_F\right)$. Moreover, as H has a gap around ε_F, $\mathcal{F}^\nu_{\gamma_\nu}$ is strictly convex and γ_ν is its unique minimizer.

If $\nu \in L^1(\mathbb{R}^3) \cap L^2(\mathbb{R}^3)$ is such that $\|\nu\|_{L^2_{\rm unif}}$ is small enough, then the solution constructed in Theorem 1.4.3 coincides with the ground state of the perturbed crystal given by the theory of local defects presented in Section 1.4.2.

We also prove a thermodynamic limit, namely, the ground state of the system with the perturbation ν confined to a box Γ_L of side size L converges, when the size of the box goes to infinity, to the ground state of the system with the perturbation ν.

Theorem 1.4.4 (Thermodynamic limit)**.** *[92, Th. 2.2][Th. 3.2.2 Chapter 3] Let $m > 0$. Then, for any $\nu \in L^2_{\mathrm{unif}}(\mathbb{R}^3)$ such that $\|\nu\|_{L^2_{\mathrm{unif}}}$ is small enough, the sequence $(\gamma_{\nu 1_{\Gamma_L}})_{L\in\mathbb{N}\setminus\{0\}}$ converges to γ_ν as $L \to \infty$.*

Thanks to the short-range character of the Yukawa interaction, the mean-field density $\rho_\nu = \rho_{\gamma_\nu} - \rho_{\gamma_0}$ and potential $V_\nu = V - V_{\mathrm{per}}$ are local in the sense that their values on a compact set depend mainly on the nuclear distribution in a neighborhood of this compact set.

Proposition 1.4.5 (The mean-field potential and density depend locally on ν)**.** *[92, Prop. 2.5] [Prop. 3.2.5 Chapter 3] Let $m > 0$. Then, for any $\beta \geq 2$ and any $\nu \in L^2_{\mathrm{unif}}(\mathbb{R}^3)$ such that $\|\nu\|_{L^2_{\mathrm{unif}}}$ is small enough and any $L \geq 1$, we have*

$$\|V_\nu - V_{\nu_L}\|_{H^2_{\mathrm{unif}}(B(0,L/4^\beta))} + \|\rho_\nu - \rho_{\nu_L}\|_{L^2_{\mathrm{unif}}(B(0,L/4^\beta))} \leq \frac{C}{L^\beta}\|\nu\|_{L^2_{\mathrm{unif}}},$$

where $\nu_L = \nu 1_{\Gamma_L}$.

Our results presented in this section concern small perturbations of perfect crystals interacting through short-range Yukawa potential. It would be interesting to remove the condition on the "size" of the perturbation and to treat the long-range Coulomb interaction. These are future research projects.

1.5 Stochastic systems

In the type of materials we have considered in Section 1.4, the nuclear distribution is close to a reference periodic distribution. Disordered materials such as unordered alloys and amorphous solids and liquids are more or less far from this picture. They are mathematically modeled by *random distributions* of nuclei.

There are two main classes of models to describe the electronic structure of such stochastic systems: random linear models where the electrons are assumed to be non-interacting particles, and nonlinear models where interactions are taken into account. In the former, the study of the properties of the Hamiltonian of the system and its spectrum could be achieved. In the latter, the proof of the thermodynamic limit for stochastic systems starting from finite molecular models was obtained, and, in certain cases, the characterization of the infinite limiting electronic structure was possible.

The contribution of this thesis falls into the second category. It follows on from [14, 15, 153]. In the framework of the N-body model, Veniaminov [153] has considered stochastic systems with short-range interactions and Blanc and Lewin [15] have considered stochastic systems interacting through Coulomb forces. They both show the existence of the thermodynamic limit of the energy. In [14], Blanc, Le Bris and Lions introduce and study Thomas-Fermi type models for stochastic systems and show that they

are indeed the thermodynamic limits of the corresponding finite size systems. Unfortunately, these models are not able to reproduce important physical properties of stochastic quantum crystals, like the Anderson localization under weak disorder. In collaboration with Cancès and Lewin, we introduce and study the rHF model for stochastic systems in [29]. We show that this model is well posed and prove that, in the case of Yukawa interaction, it is the thermodynamic limit of the rHF supercell model. We present the main results of this study in Section 1.5.2; the details are provided in Chapter 2. In Section 1.5.3, we concentrate on a case of physical interest: crystals with a low concentration of random defects. Throughout Sections 1.5.1- 1.5.3, we illustrate our presentation with numerical simulations that we performed on simple one-dimensional systems in a supercell (a representative finite volume). The context of these simulations is explained in Section 1.5.4 (see also Chapter 4).

1.5.1 The random linear model

In the random linear model, the electrons are supposed to be non-interacting particles, apart from the interaction originating from the Pauli principle. The electronic properties of the system are encoded in the one-body Hamiltonian

$$H(\omega) = -\frac{1}{2}\Delta + V(\omega, x),$$

where $V(\omega, x)$ is a given effective potential. Such an operator is called a *Random Schrödinger Operator* (RSO). RSOs were introduced by Anderson when studying the transport properties of disordered media. He claimed, based on physical arguments, that if the disorder is strong enough, then the electrons get trapped in a localized region of space implying the absence of conductivity. This phenomenon is known as *Anderson localization*. This discovery owed him the 1977 Nobel prize in physics [4, 5]. Since then, the study of RSOs is a very active research field [72, 80, 34, 148, 125].

In the following, we present some properties of RSOs.

Random Schrödinger operators

We consider here the continuous setting, where $H(\omega)$ is an operator on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$. We refer the reader to [81] for an introduction to discrete Schrödinger operators acting on $\ell^2(\mathbb{Z}^3)$. As we have said before, $H(\omega)$ represents the Hamiltonian associated to an electron evolving in the effective random potential $V(\omega, x)$. A typical example of disordered medium considered in this theory is alloys described by the *Bernoulli-Anderson* model for which

$$V(\omega, x) = \sum_{k \in \mathbb{Z}^3} q_k(\omega)\eta(x - k), \tag{1.34}$$

where the (q_k) are independent and identically distributed (i.i.d.) random

variables taking values z_1 or z_2 depending on the type of atom in the site k, and the *single site potential* η is in $C_c^\infty(\mathbb{R}^3)$ for example.

Studying the operator $H(\omega)$ for every ω in the probability space Ω boils down to the deterministic setting presented in the previous sections. Here, we rather consider the whole family $(H(\omega))_{\omega\in\Omega}$ and seek to identify almost sure properties of this family. For this reason, we need to impose a certain spatial invariance on the probabilistic laws of the variables $V(\omega,\cdot)$. In the Bernoulli-Anderson model (1.34), this spatial invariance is ensured by the i.i.d. character of the nuclear charges (q_k). In general, the assumption RSOs are asked to satisfy is *ergodicity*[1]. To precise the notion of ergodicity, we consider a probability space $(\Omega,\mathcal{F},\mathbb{P})$ and a group action τ of $\mathbb{Z}^3$ on Ω which is measure preserving ($\mathbb{P}(\tau_k(A))=\mathbb{P}(A)$ for any $A\in\mathcal{F}$) and ergodic ($\tau_k(A)=A$ for all $k\in\mathbb{Z}^3$ implies $\mathbb{P}(A)\in\{0,1\}$). An important consequence of the ergodicity of τ is the ergodic theorem [151], which states that if $X\in L^p(\Omega)$, with $1\leq p<\infty$, then,

$$\lim_{n\to\infty}\frac{1}{(2n+1)^3}\sum_{k\in\mathbb{Z}^3\cap\left[-\frac{n}{2},\frac{n}{2}\right]}X(\tau_k(\omega))=\mathbb{E}(X), \tag{1.35}$$

almost surely and in $L^p(\Omega)$. An *ergodic operator* A of domain $\mathcal{D}$ is a measurable family of operators $(A(\omega))_{\omega\in\Omega}$ such that a.s. $\mathcal{D}\subset D(A(\omega))$ and that for any $k\in\mathbb{Z}^3$, $\mathcal{D}\subset U_k(\mathcal{D})$ and

$$A(\tau_k(\omega))=U_kA(\omega)U_k^*,\quad \text{a.s.},$$

where we recall that U_k is the translation operator defined in (1.22). As the Laplacian commutes with the translations of the lattice, then a random Schrödinger operator is ergodic if and only if the potential V is *stationary* in the sense

$$V(\tau_k(\omega),x)=V(\omega,x+k),\quad \forall k\in\mathbb{Z}^3,\ \text{a.s. and a.e.} \tag{1.36}$$

If V is stationary and satisfies

$$\mathbb{E}\left(\left(\int_\Gamma|V|^p\right)^{r/p}\right)<\infty, \tag{1.37}$$

for $p>2$ and $r>3p/(2p-4)$, then $H(\omega)$ is a.s. essentially self-adjoint on $C_c^\infty(\mathbb{R}^3)$ [34].

The spectrum of RSOs

One of the fundamental theorems for ergodic operators, due to Pastur [125], states that for any self-adjoint ergodic operator A, there exists a closed set $\Sigma\subset\mathbb{R}$ and a set $\Omega_1\in\mathcal{F}$ with $\mathbb{P}(\Omega_1)=1$, such that

$$\sigma(A(\omega))=\Sigma,$$

[1] We, however, mention the recent work [118] where a particular case of non-ergodic random Schrödinger operators is studied.

for all $\omega \in \Omega_1$ (see Figure 1.6). The set Σ is called the *almost sure spectrum* of A. Respective statements hold true for $\sigma_{ac}(A(\omega))$, $\sigma_{sc}(A(\omega))$ and $\sigma_{pp}(A(\omega))$ [82, 91].

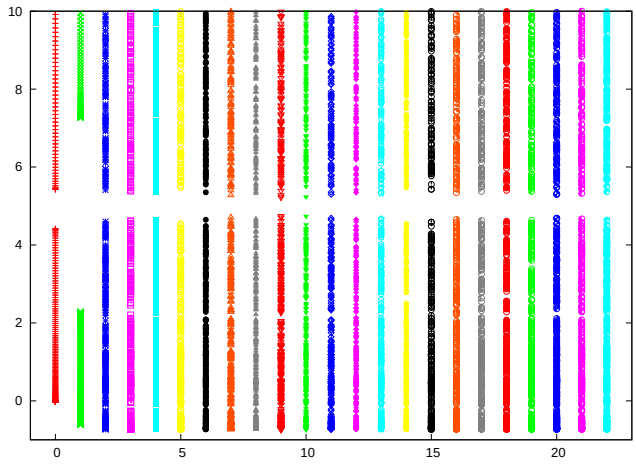

Figure 1.6: Columns 0 and 1 respectively correspond to the spectra of the Hamiltonians $H_{\mathrm{per},1}$ and $H_{\mathrm{per},2}$ of two perfect crystals. The other columns correspond to the spectra of the Hamiltonians $H(\omega)$ for 21 realizations ω of alloys of these two perfect crystals in representative finite volumes of size $L = 240$.

A very important question in the study of the spectrum of RSOs is *localization*. From a physical point of view, this means the identification of energy regimes where there is an absence of diffusion of the electrons in the disordered material. Mathematically, there are three definitions of localization: spectral localization, which is the existence of pure point spectrum, Anderson localization, which is the existence of pure point spectrum with exponentially decaying eigenfunctions (see Figure 1.7) and dynamical localization, which corresponds to the non spreading of localized wave packets under the time evolution e^{-itH}. In dimension $d = 1$ and under reasonable assumptions, it was proven that the almost sure spectrum of $H(\omega)$ is pure point with exponentially decaying eigenfunctions [61, 34]. In dimension $d \geq 2$ the situation is more delicate. The breakthrough technique is the Multi-Scale Analysis (MSA) introduced by Fröhlich and Spencer [55]. Various variants of MSA have then been used to prove the existence of localization regimes for a large class of models (see e.g. [56, 58]). For the Bernoulli-Anderson model (1.34) for example, localization has been proved in all dimensions [58]. We do not detail this topic here and refer the reader to the monographs [72, 80, 34, 148, 125].

Density of states

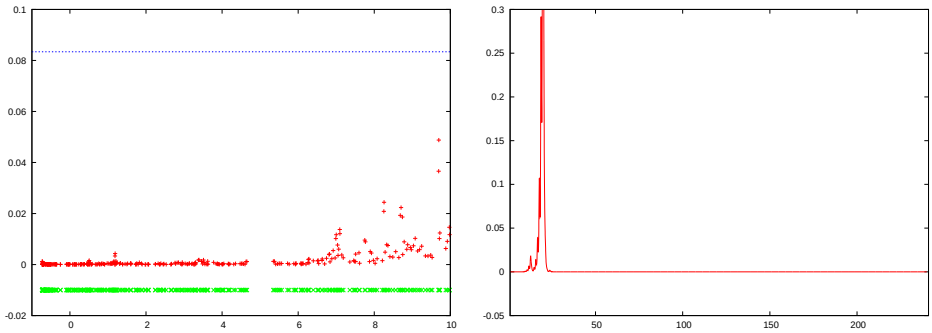

Figure 1.7: Left: the spectrum of $H(\omega)$ is represented in green. The y-axis represents the values of the variance v that quantifies the "spreading" of the eigenfunctions. Each red dot represents the variance v of the eigenfunction corresponding to the eigenvalue in the same vertical line. The blue line indicates the maximal value of v. Right: The eigenfunction corresponding to the first eigenvalue.

As we said before, in the random linear theory, the electrostatic interaction between the electrons is neglected and the electrons interact only through the Pauli exclusion principal, in the sense that two electrons cannot be in the same quantum state. Therefore, the state of the electrons which minimizes the energy, is when the electrons fill in the energy levels from the bottom of the spectrum of $H(\omega)$ up to the Fermi level ε_F. Using a thermodynamic limit procedure and the ergodic theorem (see (1.35)), one can prove that the state of the electrons in the infinite random media is given by the one-body density matrix

$$\gamma(\omega) = 1(H(\omega) \leq \varepsilon_F).$$

The average number of electrons and the ground state energy per unit volume (see Figure 1.8) are then respectively given by

$$\underline{\mathrm{Tr}}\,(\gamma) = \mathbb{E}\left(\int_\Gamma \rho_\gamma\right)$$

and

$$\underline{\mathrm{Tr}}\,(H\gamma) = -\frac{1}{2}\underline{\mathrm{Tr}}\,(\Delta\gamma) + \mathbb{E}\left(\int_\Gamma V\rho_\gamma\right). \tag{1.38}$$

It is easily obtained using the ergodic theorem that for an ergodic operator A, the average trace per unit volume $\underline{\mathrm{Tr}}\,(A)$ defined in (1.23) is actually equal to $\underline{\mathrm{Tr}}\,(A) = \mathbb{E}\,(\mathrm{Tr}\,(1_\Gamma A 1_\Gamma))$. We recall that ε_F is the Lagrange multiplier corresponding to the constraint on the average number of electrons per unit volume. Note that both the average number of electrons and the ground state energy per unit volume are given by the average trace per unit volume of two particular functions of the Hamiltonian $H(\omega)$, namely $x \mapsto 1(x \leq 0)$ and $x \mapsto -x_-$. The trace per unit volume of a general (sufficiently smooth and

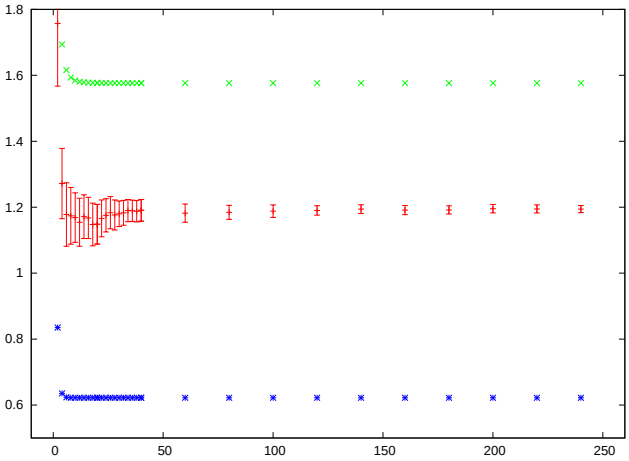

Figure 1.8: The convergence of the average energy per unit volume in the thermodynamic limit for the linear model. The error bars correspond to 95% confidence intervals computed with $N_{\mathrm{MC}} = 21$ realizations.

decaying) function φ of the Hamiltonian $H(\omega)$ actually depends on the function of $E \mapsto \underline{\mathrm{Tr}}\ (1(H \leq E))$ only. Indeed, using that $\varphi(x) = \int_{-\infty}^{x} \varphi'(E)\, dE$ and denoting the spectral projection of H by $P_\lambda(\omega) = 1(H(\omega) \leq \lambda)$, a formal calculation gives

$$\begin{aligned}\underline{\mathrm{Tr}}\ (\varphi(H)) &= \underline{\mathrm{Tr}} \left(\int_{\mathbb{R}} \int_{-\infty}^{\lambda} \varphi'(E)\, dE\, dP_\lambda \right) = \underline{\mathrm{Tr}} \left(\int_{\mathbb{R}} \int_{E}^{+\infty} dP_\lambda \varphi'(E)\, dE \right) \\ &= \underline{\mathrm{Tr}} \left(\int_{\mathbb{R}} (1 - P_E) \varphi'(E)\, dE \right) = \int_{\mathbb{R}} \underline{\mathrm{Tr}}\ (P_E)' \, \varphi(E)\, dE,\end{aligned}$$

where we have used an integration by parts in the last step. The function $N : E \mapsto \underline{\mathrm{Tr}}\ (1(H \leq E))$ is called the *Integrated Density Of State* (IDOS) of $H(\omega)$. As N is non-decreasing, its derivative n is a positive measure called the *Density Of States* (DOS) of $H(\omega)$. Loosely speaking, the density of states $n(I)$ measures the number of electrons per unit volume that can be put in the energy interval I. The IDOS of $H(\omega)$ has been proved to be the thermodynamic limit of the IDOS N_L of the Hamiltonian $H_L(\omega) = -\frac{1}{2}\Delta_L + V(\omega, x)$ of the system confined to the box Γ_L of side size L with Dirichlet, Neumann or periodic boundary conditions. The spectrum of $H_L(\omega)$ is given by a bounded below sequence of real numbers $(\lambda_{L,n})_{n \in \mathbb{N}}$ going to infinity as $n \to \infty$. In this case, N_L is the counting function

$$N_L(E) = \frac{1}{|\Gamma_L|} \#\left\{\lambda_{L,n},\ \lambda_{L,n} \leq E\right\} = \frac{1}{|\Gamma_L|} \mathrm{Tr}\ (1_{H_L \leq E}) = \frac{1}{|\Gamma_L|} \int_{\Gamma_L} \rho 1_{H_L \leq E}.$$

We mention here the main two methods for proving this thermodynamic limit. The proof of Pastur [124] is based on the Laplace transform of the

IDOS and the Feynman-Kac representation of the Schrödinger semi-group e^{-tH}. The latter method is called Neumann-Dirichlet bracketing, which relies on the fact that $\Delta_L^N \leq \Delta_L^D$ in the sense of quadratic forms, where Δ_L^N and Δ_L^D are the realizations of the Laplacian on Γ_L with Neumann and Dirichlet boundary conditions respectively, and sub- and superadditive versions of the ergodic theorem. Klopp has proposed in [89] a proof where periodic boundary conditions are imposed.

The DOS characterizes the almost sure spectrum of $H(\omega)$. Indeed, the latter coincides with the support of n, or equivalently, the points of growth of the IDOS, and the energies E such that $n(\{E\}) \neq 0$ correspond to the almost sure eigenvalues of $H(\omega)$.

The study of the properties of the DOS and the IDOS is an interesting mathematical question. It is also an important input in the study of the localization properties of the Hamiltonian. On the one hand, various results of continuity and differentiability of the IDOS have been proved for several types of models. We also mention the recent work of Bourgain and Klein [20] proving the log-Hölder continuity of the IDOS as soon as the potential V is bounded. On the other hand, the asymptotic behavior of the IDOS at the bottom of the spectrum and at the band edges, called *Lifshitz tails*, has been thoroughly studied. For a recent review on these subjects, see [84].

1.5.2 The random reduced Hartree-Fock model

For a proper physical description of the electronic structure of random materials, the electrostatic interactions between the electrons need to be taken into account. In [29] (see also [28] and Chapter 2 of this thesis), we are interested in the definition of a mean-field model for electrons in random materials. We first set up the necessary functional setting for the study of a large class of mean-field models of HF or KS types. We then concentrate on the simple case of the rHF model.

We consider here "ergodic" materials, in the same sense as in the random linear model presented in Section 1.5.1. The nuclear distribution μ satisfies the stationary condition:

$$\mu(\tau_k(\omega), x) = \mu(\omega, x + k), \quad \forall k \in \mathbb{Z}^3, \text{ a.s. and a.e..}$$

The state of the electrons is described by an ergodic one-body density matrix, that is, an ergodic self-adjoint operator $\gamma(\omega) : L^2(\mathbb{R}^3) \to L^2(\mathbb{R}^3)$ satisfying the Pauli principle: $0 \leq \gamma(\omega) \leq 1$ almost surely. In particular, the kernel of γ is stationary in the sense $\gamma(\tau_k(\omega), x, y) = \gamma(\omega, x + k, y + k)$. As in the linear model, the average trace per unit volume $\underline{\mathrm{Tr}}\,(\gamma)$ is interpreted as the average number of electrons per unit volume and

$$-\frac{1}{2}\underline{\mathrm{Tr}}\,(\Delta\gamma) := \frac{1}{2}\sum_{j=1}^{3}\underline{\mathrm{Tr}}\,(P_j\gamma P_j)\,,$$

represents the average kinetic energy per unit volume of γ, P_j being the momentum operator in the direction j. The set of admissible density matrices in the ergodic setting is then the set of ergodic density matrices having finite average number of particles and kinetic energy per unit volume:

$$\underline{\mathcal{K}} = \{\gamma \text{ ergodic}, \ \gamma^* = \gamma, \ 0 \leq \gamma \leq 1 \text{ a.s.}, \ \underline{\mathrm{Tr}} \ ((1-\Delta)\gamma) < \infty\} \, .$$

The set $\underline{\mathcal{K}}$ is a weak-$*$ closed convex subset of $L^\infty(\Omega, \mathcal{B})$, the set of uniformly bounded random operators. We have proved that admissible density matrices $\gamma \in \underline{\mathcal{K}}$ satisfy inequalities similar to the Hoffmann-Ostenhof [73] and Lieb-Thirring inequalities [115, 116] for finite systems (see (1.16) and (1.17)). These inequalities are very important estimates and will be very useful in the sequel.

Theorem 1.5.1 (Hoffmann-Ostenhof and Lieb-Thirring inequalities for ergodic operators)**.** *[29, Prop. 2.6, Prop. 2.8] [Prop. 2.2.9, Prop 2.2.11 Chapter 2] There exists $K > 0$ such that for any $\gamma \in \underline{\mathcal{K}}$, we have*

$$\mathbb{E}\left(\int_\Gamma |\nabla \sqrt{\rho_\gamma}|^2\right) \leq \underline{\mathrm{Tr}} \ (-\Delta\gamma)$$

and

$$K \, \mathbb{E}\left(\int_\Gamma \rho_\gamma^{5/3}\right) \leq \underline{\mathrm{Tr}} \ (-\Delta\gamma) \, .$$

Unlike the random linear model, in mean-field models, the effective potential V the electrons are subjected to is an output of the problem. In the rHF model, it is given by solving the (regularized) Poisson equation

$$-\Delta V + m^2 V = 4\pi f, \tag{1.39}$$

where f is the total charge density and Δ is the Laplace operator with respect to the x variable. In the models we consider here, the total charge density is the stationary function $f = \rho_\gamma - \mu$, where γ is the ground state density matrix of the system. For the Yukawa interaction ($m > 0$), (1.39) admits a unique solution

$$V(\omega, x) = \int_{\mathbb{R}^3} Y_m(x-y) f(\omega, y) \, dy.$$

For the Coulomb interaction ($m = 0$), the situation is more complicated. For a start, we have seen that in the periodic setting, a necessary and sufficient condition for (1.39) to have a periodic solution is the neutrality condition $\int_\Gamma f = 0$. In the stationary setting, the condition $\mathbb{E}(\int_\Gamma f) = 0$ is necessary but, in general, not sufficient to find a stationary solution V. In Section 2.3.1, Chapter 2, we show that a necessary and sufficient condition for (1.39) to have a stationary solution V satisfying $\mathbb{E}(\int_\Gamma V^2) < \infty$ is that f is in the range of the "stationary Laplacian" which is a particular self-adjoint extension of

the Laplace operator with respect to the space variable x on $L^2(\Omega \times Q)$ with "stationary boundary conditions".

To circumvent this difficulty, we adopt a variational approach and define the Coulomb interaction energy as the limit of the Yukawa interaction energy, when the Yukawa parameter m goes to 0. For $m > 0$, the average Yukawa interaction energy per unit volume for a stationary charge density f is given by

$$\begin{aligned}\underline{D}_m(f,f) :&= \mathbb{E}\left(\int_\Gamma V(x)f(x)\,dx\right)\\ &= \mathbb{E}\left(\int_\Gamma\int_{\mathbb{R}^3} f(x)Y_m(x-y)f(y)\,dx\,dy\right)\\ &= \mathbb{E}\left(\int_\Gamma |W_m * f(y)|^2\,dy\right),\end{aligned}$$

where W_m is the inverse Fourier transform of $\sqrt{4\pi}(m^2+|K|^2)^{-1/2}$. It is finite for any f in the space of locally integrable stationary functions with *locally finite Yukawa energy*:

$$\mathcal{D}_Y := \left\{f \text{ stationary},\ f \in L^1(\Omega, L^1_{\mathrm{loc}}(\mathbb{R}^3)),\ W_m * f \in L^2(\Omega, L^2_{\mathrm{loc}}(\mathbb{R}^3))\right\}.$$

Note that the space $\mathcal{D}_Y$ does not depend on the parameter m. By the decay properties of W_m, one can show that the stationary functions in $L^2(\Omega, L^{6/5}_{\mathrm{loc}}(\mathbb{R}^3))$ are in $\mathcal{D}_Y$.

As $m \mapsto \underline{D}_m(f,f)$ is a non-increasing function, it is therefore natural to define, for any f in

$$\mathcal{D}_C = \left\{f \in \mathcal{D}_Y \mid \lim_{m\to 0} \underline{D}_m(f,f) < \infty\right\},$$

the average Coulomb interaction energy per unit volume to be

$$\underline{D}_0(f,f) := \lim_{m\to 0} \underline{D}_m(f,\,f).$$

The space $\mathcal{D}_C$ is called the space of locally integrable stationary functions with *locally finite Coulomb energy*. We retrieve the neutrality condition we mentioned before, as if $\mathbb{E}(\int_\Gamma f) \neq 0$, then $f \notin \mathcal{D}_C$. The space $\mathcal{D}_C$ contains, in particular, the stationary functions in $L^2(\Omega, L^{6/5}_{\mathrm{loc}}(\mathbb{R}^3))$ whose charge and dipolar momentum per unit cell are almost surely equal to zero [29, Prop. 3.3] [Prop. 2.3.4 Chapter 2].

In mean-field models, the energy is the sum of the kinetic energy, the (Coulomb or Yukawa) interaction energy and possibly other quantum terms such as exchange and/or correlation corrections. We concentrate on the rHF model, where these corrections are neglected. The average energy per unit volume then reads

$$\underline{\mathcal{E}}^{\mathrm{rHF}}_m(\mu,\gamma) = \frac{1}{2}\,\underline{\mathrm{Tr}}\,(-\Delta\gamma) + \frac{1}{2}\underline{D}_m(\rho_\gamma - \mu, \rho_\gamma - \mu). \tag{1.40}$$

The ground state energy with Coulomb interaction is given by

$$\underline{I}_0^{\mathrm{rHF}}(\mu) = \inf\left\{\underline{\mathcal{E}}_0^{\mathrm{rHF}}(\mu,\gamma),\ \gamma \in \underline{\mathcal{K}},\ \rho_\gamma - \mu \in \mathcal{D}_C\right\}.$$

For the Yukawa interaction ($m > 0$), it is given by

$$\underline{I}_m^{\mathrm{rHF}}(\mu) = \inf\left\{\underline{\mathcal{E}}_m^{\mathrm{rHF}}(\mu,\gamma),\ \gamma \in \underline{\mathcal{K}},\ \rho_\gamma - \mu \in \mathcal{D}_Y,\ \underline{\mathrm{Tr}}\,(\gamma) = \mathbb{E}\left(\int_\Gamma \mu\right)\right\}. \tag{1.41}$$

Note that, as in the periodic setting, the charge neutrality condition $\underline{\mathrm{Tr}}\,(\gamma) = \mathbb{E}\left(\int_\Gamma \mu\right)$ is not necessary in the Yukawa case, but we impose it for consistency. In the following theorem we prove that the system admits a ground state as soon as the minimization set is non empty. This is indeed the case for the Yukawa case whenever $\mu \in \mathcal{D}_Y$. For the Coulomb case we give in [29, Lemma 4.1] sufficient conditions for the minimization set not to be empty.

Theorem 1.5.2 (Existence of ergodic ground states)**.** *[29, Th. 4.2]/[Th. 2.4.2 Chapter 2] If $\{\gamma \in \underline{\mathcal{K}},\ \rho_\gamma - \mu \in \mathcal{D}_C\}$ is non empty, then $\underline{I}_0^{\mathrm{rHF}}(\mu)$ admits minimizers and all the minimizers share the same density.*

If $\left\{\gamma \in \underline{\mathcal{K}},\ \rho_\gamma - \mu \in \mathcal{D}_Y,\ \underline{\mathrm{Tr}}\,(\gamma) = \mathbb{E}\left(\int_\Gamma \mu\right)\right\}$ is non empty, then, for any $m > 0$, $\underline{I}_m^{\mathrm{rHF}}(\mu)$ admits minimizers and all the minimizers share the same density.

The main ingredient of the proof of Theorem 1.5.2 is the weak-$*$ compactness of the set $\underline{\mathcal{K}}$ and the strict convexity of the functional $\underline{\mathcal{E}}_m^{\mathrm{rHF}}(\mu,\gamma)$ with respect to the electronic density ρ_γ.

For (short-range) Yukawa interactions, we prove in addition that the rHF ground state density matrix satisfies a self-consistent equation similar to (1.13), and that the model is the thermodynamic limit of the supercell model.

Theorem 1.5.3 (Properties of the Yukawa ground state)**.** *[29, Lemma 4.4, Prop. 4.5, Cor. 4.6, Th. 5.2] / [Lemma 2.4.4, Prop. 2.4.5, Cor. 2.4.6, Th. 2.5.2 Chapter 2] / Let $m > 0$, $\mu \in \mathcal{D}_Y$ and γ be a minimizer of* (1.41)*. Under reasonable integrability assumptions on μ, we have the following results:*

1. From Yukawa to Coulomb*: we have*

$$\underline{I}_m^{\mathrm{rHF}}(\mu) \underset{m\to 0}{\longrightarrow} \underline{I}_0^{\mathrm{rHF}}(\mu).$$

2. Mean-field Hamiltonian*: the random Schrödinger operator*

$$H = -\frac{1}{2}\Delta + V \tag{1.42}$$

where $V = Y_m * (\rho_\gamma - \mu)$, is ergodic and almost surely essentially self-adjoint on $C_c^\infty(\mathbb{R}^3)$.

3. Self-consistent field equation*: There exists ε_F such that any minimizer γ of* (1.41) *is of the form*

$$\gamma = 1(H < \varepsilon_F) + \delta,$$

where δ is an ergodic self-adjoint operator satisfying $0 \leq \delta \leq 1(H = \varepsilon_F)$.

4. Uniqueness of the minimizer*: if $\mu \in L^\infty(\Omega \times \mathbb{R}^3)$ then $\rho_\gamma, V \in L^\infty(\Omega \times \mathbb{R}^3)$, $\delta = 0$ and*

$$\gamma = 1(H \leq \varepsilon_F)$$

is the unique minimizer of (1.41).

5. Thermodynamic limit*: we have*

$$\underline{I}_m^{\mathrm{rHF}}(\mu) - \varepsilon_F \mathbb{E}\left(\int_\Gamma \mu\right) = \lim_{L\to\infty} \frac{I_{m,\varepsilon_F}^{\mathrm{rHF}}(\mu_L)}{L^3},$$

where $I_{m,\varepsilon_F}^{\mathrm{rHF}}(\mu_L)$ is the ground state energy of the system confined to a box of size L with periodic boundary conditions, and with the constraint that the chemical potential of the electrons is equal to ε_F. (See Figure 1.9)

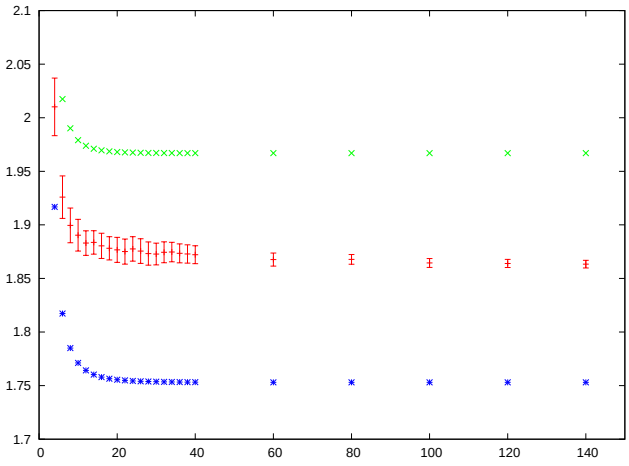

Figure 1.9: The convergence of the average energy per unit volume in the thermodynamic limit for the rHF model. The error bars correspond to 95% confidence intervals computed with $N_{\mathrm{MC}} = 21$ realizations.

The first assertion essentially follows from our definition of the Coulomb energy $\underline{D}_0$ as the limit of $\underline{D}_m$ as $m \to 0$ and the weak-$*$ compactness of the set $\underline{\mathcal{K}}$. The second assertion is a consequence of the integrability properties

of μ, thus those of ρ_γ and V, and of the self-adjointness criterion for random Schrödinger operators (see (1.37) and the remark below). In view of the third assertion, we see that studying the spectral properties of the mean-field Hamiltonian H with the techniques presented in Section 1.5.1 would allow to understand the localization and transport properties of the interacting stochastic systems (see Figure 1.10). These questions have not been addressed in the present work. Using the result of Bourgain and Klein [20] mentioned before about the log-Hölder continuity of the IDOS of the RSOs with bounded potentials, we prove that the minimizer of our problem is unique as soon as the nuclear density is uniformly bounded (Assertion *4* of Theorem 1.5.3).

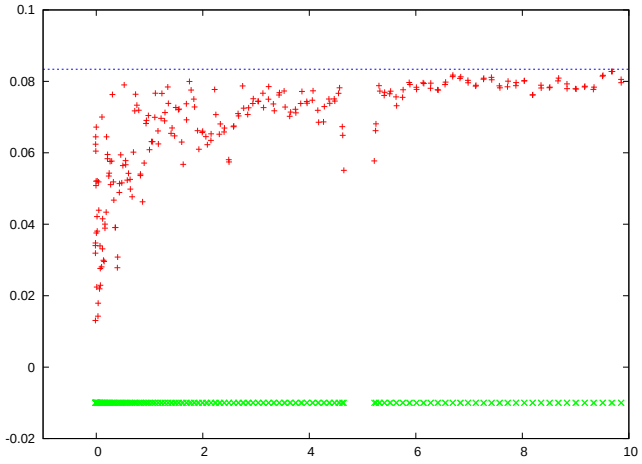

Figure 1.10: The spectrum of the mean-field Hamiltonian $H(\omega)$ is represented in green. The y-axis represents the values of the variance v that quantify the "spreading" of the eigenfunctions. Each red dot represents the variance v of the eigenfunction corresponding to the eigenvalue in the same vertical line. The blue line indicates the maximal value of v.

To extend these results to the Coulomb case, we would need to prove some screening effects and rigorously define the Coulomb potential in appropriate functional spaces.

1.5.3 Crystals with low concentration of random defects

We are interested in this section in materials with a low concentration of defects. A typical example of such materials are doped semi-conductors. For example, in standard applications, $1\,\mathrm{cm}^3$ of silicon, containing approximately 10^{22} silicon atoms, is doped with 10^{13} to 10^{18} atoms of phosphorus or boron. If we model this (infinite) material by the Bernoulli-Anderson model, then

the total nuclear density is given by

$$\mu(\omega, x) = \sum_{k\in\mathbb{Z}^3} \chi_{\text{silicon}}(\omega, x-k) + \sum_{k\in\mathbb{Z}^3} q_k(\omega)(\chi_{\text{dopant}} - \chi_{\text{silicon}})(x-k),$$

where q_k are i.i.d. Bernoulli variables of parameter $10^{-9} \leq p \leq 10^{-4}$, that is $\mathbb{P}(q_k = 1) = p$ and $\mathbb{P}(q_k = 0) = 1 - p$.

To compute the macroscopic properties of random materials, one needs to compute expectancies of random variables. For example, for the average energy per unit volume, one can use (1.38) or (1.40). But calculating the expectation, with a Monte-Carlo method for example, is very costly as one needs to evaluate the quantity of interest for a large number of realizations.

In random materials with low concentrations of defects, one can hope that the computation of the macroscopic quantities can be less costly, given the fact that these materials are perturbations of the host perfect crystal.

In the context of the random linear model presented in Section 1.5.1, this problem has been studied by Kirsch and Hempel [70] and by Klopp [87, 88]. In the rHF presented in Section 1.5.2, this problem is addressed in [92] and the results are reported on in Chapter 3.

We also mention that similar models have been studied in the context of stochastic homogenization [1, 2, 3, 119].

Our quantity of interest in the following will be the density of states n, as it allows for the calculation of macroscopic quantities. We recall that for any sufficiently decaying and smooth function φ on $\mathbb{R}$

$$\underline{\text{Tr}}\ (\varphi(H)) = \int_{\mathbb{R}} \varphi(x)\, dn(x).$$

We also recall that the *spectral shift function* $\xi(A_1, A_2)$ for the pair of operators A_1 and A_2 (see [156]), when it exists, is the unique tempered distribution in $\mathcal{S}'(\mathbb{R})$ satisfying, for any $\varphi \in \mathcal{S}(\mathbb{R})$,

$$\text{Tr}\ (\varphi(A_1) - \varphi(A_2)) = \langle \xi(A_1, A_2), \varphi' \rangle_{\mathcal{S}'(\mathbb{R}),\mathcal{S}(\mathbb{R})} = -\langle \xi(A_1, A_2)', \varphi \rangle_{\mathcal{S}'(\mathbb{R}),\mathcal{S}(\mathbb{R})}.$$

In [87], Klopp considers a random Schrödinger operator

$$H_p = -\frac{1}{2}\Delta + V_0 + V_p$$

where V_0 is a periodic potential representing the host crystal and V_p is the potential created by the random defects. The latter is of the form

$$V_p(\omega, x) = \sum_{k\in\mathbb{Z}^3} q_k(\omega)\eta(x-k)$$

where q_k are i.i.d. Bernoulli variables of parameter p and the single site potential η is an exponentially decaying function. For $K \subset \mathbb{Z}^3$, let H_K be

the Hamiltonian of the system with defects in the sites of K:

$$H_K = -\frac{1}{2}\Delta + V_0 + \sum_{k\in K} \eta(x-k).$$

Then the density of states n_p of H_p admits an asymptotic expansion in powers of p to any order, that is, for any $J \in \mathbb{N}\setminus\{0\}$,

$$n_p = n_0 + \sum_{j=1}^{J} \vartheta_j p^j + O(p^{J+1}), \tag{1.43}$$

where n_0 is the density of states of the unperturbed Hamiltonian $H_0 = -\frac{1}{2}\Delta + V_0$ and for any $j \in \mathbb{N}\setminus\{0\}$, the tempered distribution ϑ_j is given by

$$\vartheta_j = -\frac{1}{j} \sum_{\substack{K\subset\mathbb{Z}^3,\\ |K|=j,\, 0\in K}} \sum_{K'\subset K} (-1)^{|K\setminus K'|} \xi(H_{K'}, H_0)'.$$

In particular, the first order term $\vartheta_1 = -\xi(H_{\{0\}}, H_0)'$ is a function of the spectral shift function between the unperturbed Hamiltonian and the Hamiltonian of the system with only one defect. The notation $O(p^{J+1})$ means that there exists a semi-norm $|\cdot|_J$ in $\mathcal{S}(\mathbb{R})$ such that for any $\varphi \in \mathcal{S}(\mathbb{R})$

$$\left|\langle O(p^{J+1}), \varphi\rangle_{\mathcal{S}',\mathcal{S}}\right| \le C_J \left|\varphi\right|_J.$$

We extend this result to the rHF framework with the short-range Yukawa interaction in [92] and in Chapter 3. The proof of our result (Theorem 1.5.4 below) follows essentially the proof of [87, Theorem 1.1]. The main difference is that we deal here with self-consistent potentials, while in [87] the single site potential is an input of the problem and is assumed to be exponentially decaying. The short-range character is needed in our analysis for the potential created by each defect to decay fast enough. We assume that the nuclear charge distribution is given by

$$\mu_p(\omega, x) = \mu_{\rm per}(\omega, x) + \sum_{k\in\mathbb{Z}^3} q_k(\omega)\chi(x-k),$$

where, as in the linear case, the q_k are i.i.d. Bernoulli variables of parameter p and $\chi \in L^2_c(\mathbb{R}^3)$ is such that $\mathrm{supp}(\chi) \subset \Gamma$. Treating nonlinear potentials is done at the price of assuming that the host crystal, characterized by $\mu_{\rm per}$, is an insulator and that the defect χ is small enough in the L^2-norm, so that the conclusions of Theorems 1.4.1 and 1.4.2 hold true. We introduce the rHF mean-field Hamiltonian $\widetilde{H}_p$ corresponding to the system with the nuclear distribution μ_p defined by the stochastic rHF theory of the previous section (see (1.42)) and for $K \subset \mathbb{Z}^3$, we introduce the rHF mean-field Hamiltonian $\widetilde{H}_K$ corresponding to the nuclear charge

$$\mu_K = \mu_{\rm per} + \sum_{k\in K} \chi(\cdot - k)$$

defined by the rHF theory of local defects of Section 1.4.2 (see (1.32)). We then have the following theorem:

Theorem 1.5.4 (Density of states expansion)**.** *[92, Th. 2.7] [Th. 3.2.7 Chap. 3] For any $\chi \in L^2_c(\mathbb{R}^3)$ such that* $\mathrm{supp}(\chi) \subset \Gamma$ *and $\|\chi\|_{L^2}$ is small enough, the density of states $\widetilde{n}_p$ of $\widetilde{H}_p$ admits an asymptotic expansion in powers of p to the order 2, that is,*

$$\widetilde{n}_p = \widetilde{n}_0 + \widetilde{\vartheta}_1 p + \widetilde{\vartheta}_2 p^2 + O(p^3), \tag{1.44}$$

where $\widetilde{n}_0$ is the density of states of the unperturbed Hamiltonian $\widetilde{H}_0$ and for $j \in \{1, 2\}$, the tempered distribution $\widetilde{\vartheta}_j$ is given by

$$\widetilde{\vartheta}_j = -\frac{1}{j} \sum_{\substack{K \subset \mathbb{Z}^3, \\ |K|=j,\, 0 \in K}} \sum_{K' \subset K} (-1)^{|K \setminus K'|} \xi(\widetilde{H}_{K'}, \widetilde{H}_0)'.$$

The extension of this theorem to higher orders $J \geq 3$ should follow the same lines and techniques as the ones used to prove (1.44). A challenging task however, which is still an open problem, is to prove a similar result assuming Coulomb interactions.

From the computational point of view, (1.43) and (1.44) show that when p is small, then one can accurately approximate the average of any macroscopic quantity using only a (relatively) small number of electronic structure calculations. For example, if we restrict to the first order, then one only needs to do two calculations, one for the perfect crystal and one for the crystal with a single defect, to obtain an accuracy of order p^2 (see Figure 1.11).

1.5.4 Numerical simulation

In this section, we present a summary of the numerical simulation carried out in this thesis and detailed in Chapter 4. We have simulated 1-dimensional stochastic systems within the random linear model (presented in Section 1.5.1) and the random rHF model with the Yukawa interaction (presented in Section 1.5.2). The purpose of these simulations is twofold: first we illustrate some of the theoretical results discussed in the previous sections. Second we try to understand phenomena that are not covered by the theoretical study. The numerical methods we use are the supercell method (finite representative volume with periodic boundary conditions) with planewave discretization, Optimal Damping Algorithm (ODA), and Monte-Carlo method.

We simulate random alloys resulting from the combination of two perfect crystals. We suppose that at each site $k \in \mathbb{Z}$, there is a probability p to see the first kind of crystals and a probability $1 - p$ to see the second type of

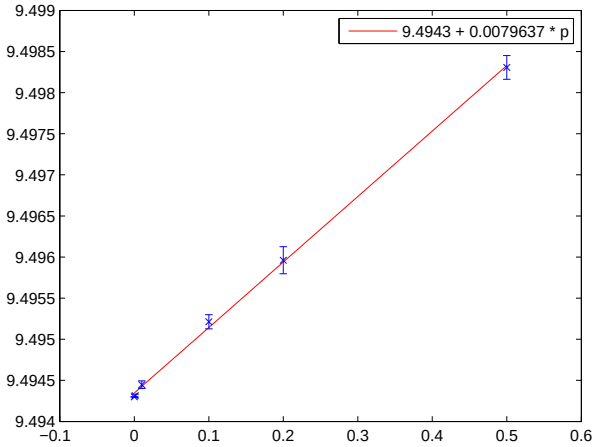

Figure 1.11: The average of the $L^1((-\infty, E_{\text{cut}}])$-norm of the IDOS N_p as a function of p in the rHF model.

crystals, independently of what is happening in the other sites. This means that in the linear model, the mean-field potential is of the form

$$V(\omega, x) = \sum_{k\in\mathbb{Z}} q_k(\omega)V_1(x-k) + (1-q_k(\omega))V_2(x-k), \tag{1.45}$$

and that in the rHF model, the nuclear density is of the form

$$\mu(\omega, x) = \sum_{k\in\mathbb{Z}} q_k(\omega)\mu_1(x-k) + (1-q_k(\omega))\mu_2(x-k),$$

where (q_k) are i.i.d. Bernoulli random variables of parameter p, and V_i (respectively μ_i), for $i \in \{1,2\}$, is the single site potential (respectively nuclear density) corresponding to the crystal i. We suppose that V_i and μ_i, for $i \in \{1,2\}$, are supported in the unit cell $\Gamma = [0,1)$. In our simulations, we take V_i and μ_i, for $i \in \{0,1\}$, to be defined on Γ by

$$V_1(x) = \sin(4\pi x) - \sin(2\pi x), \quad V_2(x) = 5\sin(2\pi x),$$

$$\mu_1(x) = \frac{1}{\sqrt{0,02\pi}} \exp\left(-\frac{\left(x-\frac{1}{2}\right)^2}{0,02}\right) \quad \text{and} \quad \mu_2(x) = 1-\cos(2\pi x).$$

A typical $V(\omega, x)$ and $\mu(\omega, x)$ are represented in Figures 1.12 and 1.13.

In both cases, the Hamiltonian of the system is of the form

$$H(\omega) = -\frac{1}{2}\frac{d^2}{dx^2} + V(\omega, x),$$

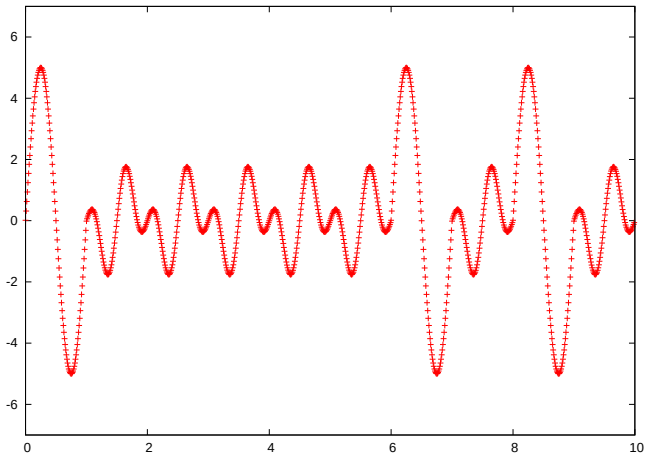

Figure 1.12: A realization of the potential V.

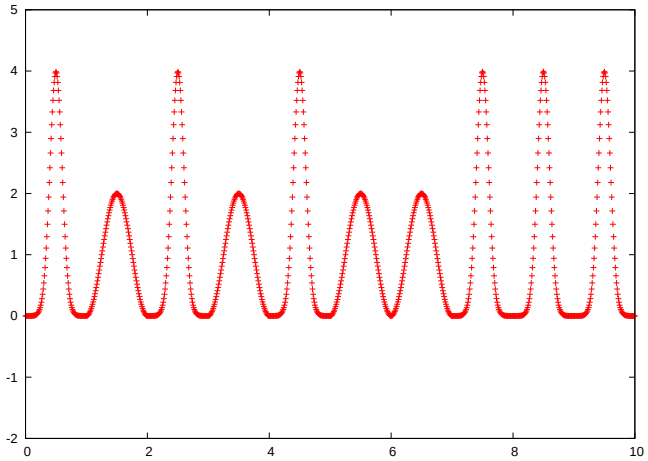

Figure 1.13: A realization of the nuclear density μ.

where the potential V is a stationary function. For each realization ω in the probability space Ω, we simulate the system using the supercell model, which consists in restricting the system to the box $\Gamma_L = [0, L)$, where $L \in \mathbb{N} \setminus \{0\}$, with periodic boundary conditions. The corresponding Hamiltonian is then

$$H_L = -\frac{1}{2}\frac{d^2}{dx^2} + V_L,$$

where V_L is the $L\mathbb{Z}$-periodic potential which is equal to $V(\omega, \cdot)$ on Γ_L. For a number of electrons per unit volume N_e, the ground state of the system is

given by

$$\gamma_L = \sum_{n=1}^{N_e L} |u_{L,n}\rangle\langle u_{L,n}|\,, \tag{1.46}$$

where $(u_{L,n})_{1\leq n\leq N_e L}$ is an orthonormal family of eigenvectors corresponding to the smallest eigenvalues $\lambda_{L,1} \leq \cdots \leq \lambda_{L,N_e L}$ of H_L.

To compute the eigenmodes of H_L, we discretize the space $H^1_{\mathrm{per}}(\mathbb{R})$ using a planewave basis. The resulting linear system is solved using the C++ linear algebra library LAPACK.

In the rHF framework with Yukawa interaction, the potential V_L is given self-consistently by

$$V_L = Y_m * (\rho_{\gamma_L} - \mu_L), \tag{1.47}$$

where μ_L is the $L\mathbb{Z}$-periodic function which is equal to the nuclear distribution $\mu(\omega, \cdot)$ on Γ_L. We use the ODA to solve the self-consistent equation (4.7)-(4.8).

Once we obtain the ground state of the system, we are able to calculate quantities of interest to our study.

We first monitor the convergence of the energy per unit volume and the density of states in the thermodynamic limit, that is, when $L \to \infty$. For the linear model, these convergences have been proved in [89, Th. 5.1]. For the rHF model, the convergence of the energy per unit volume is given by theorem 1.5.3.

We next study the localization properties of the Hamiltonian. As the spectrum of H_L is always discrete, we characterize it by observing "how much" the corresponding eigenfunctions are localized. We use a variance-based criterion. In the linear model, there is localization at all energies when there is disorder ($p \in (0,1)$) and absence of localization in perfect crystals ($p \in \{0,1\}$). In the rHF model, we are not aware of any theoretical results on the localization properties of the mean-field Hamiltonian. Our numerical results do not allow us to conclude whether there is localization or not.

Finally, we simulate crystals with low concentration of random defects and study the behavior of the integrated density of states as a function of the Bernoulli parameter p in the limit $p \to 0$.

The numerical results of our simulations are presented in Chapter 4.

Chapter 2

Mean-field models for disordered crystals

In this chapter, we detail and develop the theory exposed in an article [29], written with Éric Cancès and Mathieu Lewin, which appeared in *Journal de mathématiques pures et appliquées*. We set up a functional setting for mean-field electronic structure models of Hartree-Fock or Kohn-Sham types for disordered quantum systems. In the first part, we establish important properties of stochastic fermionic one-body density matrices, assuming that they are stationary under the ergodic action of a translation group. In particular, we prove the Hoffmann-Ostenhof and the Lieb-Thirring inequalities for ergodic density matrices, and deduce some weak compactness properties of the set of such matrices. We also discuss the representability problem for the associated one-particle density. In the second part, we investigate the problem of solving Poisson's equation for a given stationary charge distribution, using the Yukawa potential to appropriately define the Coulomb self-interaction in the limit when the Yukawa parameter goes to zero. Finally, in the last part of the chapter, we use these tools to study a specific mean-field model (reduced Hartree-Fock, rHF) for a disordered crystal where the nuclei are classical particles whose positions and charges are random. We prove the existence of a minimizer of the energy per unit volume and the uniqueness of the ground state density. For (short-range) Yukawa interactions, we prove in addition that the rHF ground state density matrix satisfies a self-consistent equation, and that our model is the thermodynamic limit of the supercell model.

Contents

2.1 Introduction

The modeling and simulation of the electronic structure of crystals is one of the main challenges in solid state physics and materials science. Indeed, a crystal contains an extremely large number (in fact an infinite number in mathematical models) of quantum particles interacting through long-range

Coulomb forces. This complicates dramatically the mathematical analysis of such systems.

Finite size molecular systems containing no heavy atoms can be accurately described by the N-body Schrödinger equation, or its relativistic corrections. Because of its very high complexity, this equation is often approximated by nonlinear models which are more amenable to numerical simulations. On the other hand, no such reference model is available for infinite molecular systems such as crystals. For this reason, in solid state physics and materials science, the electronic structure of crystals is often described by *linear empirical models* on the one hand, and *mean-field models* of Hartree-Fock or Kohn-Sham types on the other hand.

In linear empirical models, the electrons in the crystal are seen as non-interacting particles in an effective potential V_{eff}, so that their behavior is completely characterized by the effective Hamiltonian

$$H = -\frac{1}{2}\Delta + V_{\text{eff}},$$

a self-adjoint operator on $L^2(\mathbb{R}^d)$. Here d is the space dimension which is $d = 3$ for usual crystals. The cases $d = 1$ and $d = 2$ are also of interest since linear polymers and crystalline surfaces behave, in some respects, as one- and two-dimensional systems, respectively. Throughout this study, we adopt the system of atomic units in which $\hbar = 1$, $m_e = 1$, $e = 1$ and $4\pi\varepsilon_0 = 1$, where $\hbar$ is the reduced Planck constant, m_e the mass of the electron, e the elementary charge, and ε_0 the dielectric permittivity of the vacuum. For the sake of simplicity, we work with spinless electrons, but our arguments can be straightforwardly extended to models with spin.

When the system under study is a perfect crystal, the effective potential V_{eff} is an $\mathcal{R}$-periodic function V_{per}, where $\mathcal{R}$ is a discrete lattice of $\mathbb{R}^d$, and the effective Hamiltonian is then a periodic Schrödinger operator on $L^2(\mathbb{R}^d)$, $H = H_{\text{per}} = -\frac{1}{2}\Delta + V_{\text{per}}$. The spectral properties of such operators are well-known [133]. Under some appropriate integrability conditions on V_{per}, it follows from Bloch theory that the spectrum of H_{per} is purely absolutely continuous and composed of a countable number of (possibly overlapping) bands.

It is possible to describe *local defects* in such effective linear models. Displacing or changing the charge of a finite number of nuclei corresponds to adding a potential W to V_{per}. Because such perturbations are local, the potential W decays at infinity and therefore the effective Hamiltonian $H_{\text{defect}} = -\frac{1}{2}\Delta + V_{\text{per}} + W$ has the same essential spectrum as the unperturbed Hamiltonian H_{per}. On the other hand, H_{defect} may possess discrete eigenvalues below its essential spectrum, or lying in spectral gaps. They correspond to bound states of electrons in the presence of the local defects.

Doped semiconductors and alloys are examples of disordered crystals, which are perturbed in a non-local fashion. Such systems can be adequately

modeled by random Schrödinger operators [34, 148]. One famous example is the continuous Anderson model

$$H_\omega = -\frac{1}{2}\Delta + V_\omega \quad \text{with} \quad V_\omega(x) = \sum_{k\in\mathcal{R}} q_k(\omega)\,\chi(x-k),$$

where, typically, $\chi \in C_c^\infty(\mathbb{R}^d)$ and the q_k's are i.i.d. random variables. Here, only the charges are changed but it is possible to also account for stochastic displacements of the atoms. The study of the spectral properties of ergodic Schrödinger operators is a very active research topic (see e.g. [72] and the references therein).

In linear empirical models, the interactions between electrons are neglected (apart from the implicit interaction originating from the Pauli principle preventing two electrons from being in the same quantum state). Taking these interactions into account is however a necessity for a proper physical description of these systems. One main difficulty is then that the Coulomb interaction is long-range and screening becomes extremely important to explain the macroscopic stability of such systems. Understanding screening effects in a precise manner is a difficult mathematical question.

As already mentioned above, there is no well-defined N-body Schrödinger equation for crystals. The only available way to rigorously derive models for interacting electrons in crystals is to use a thermodynamic limit procedure. The idea is to confine the system to a box, with suitable boundary conditions, and to study the limit when the size of the box grows to infinity. For stochastic many-body systems based on Schrödinger's equation, it is sometimes possible to show that the limit exists. In [153], Veniaminov has first considered a many-body quantum system with short range interactions. Shortly after, the existence of the limit for a crystal made of quantum electrons and stochastic nuclei interacting through Coulomb forces was shown in [15], by Blanc and Lewin. In these two works dealing with the true many-body Schrödinger equation, the value of the thermodynamic limit is not known. For Thomas-Fermi and Thomas-Fermi-von Weizsäcker theories, Blanc, Le Bris and Lions were able to identify the thermodynamic limit and to study its properties [14]. Unfortunately, these models are not able to reproduce important physical properties of stochastic quantum crystals, like the Anderson localization under weak disorder.

The purpose of the present work is to initiate the study of *mean-field* models for an infinite interacting disordered quantum crystal. These models are not as precise as the many-body Schrödinger equation, but they are still much richer than Thomas-Fermi type theories. In particular, they seem adequate for the description of Anderson localization in infinite interacting systems.

More specifically, we consider a random nuclear charge $\mu(\omega, x) \geq 0$. For simplicity we do not consider point-like charges, and we assume that

$\mu(\omega,\cdot) \in L^1_{\rm loc}(\mathbb{R}^d)$ almost surely. Also we are interested in describing random perturbations which have some space invariance, and we make the assumption that they are the same in average when the system is translated by any vector of the underlying periodic lattice $\mathcal{R}$. We assume that the group $\mathcal{R}$ acts on the probability space in an ergodic fashion and we always make the assumption that μ is *stationary*, which means $\mu(\tau_k(\omega),x) = \mu(\omega,x+k)$, where $\tau = (\tau_k)_{k\in\mathcal{R}}$ is the ergodic group action on the probability space. A typical example is given by a lattice $\mathcal{R}$ with one nucleus per unit cell, whose charge and position are perturbed by i.i.d. random variables,

$$\mu(\omega,x) = \sum_{k\in\mathcal{R}} q_k(\omega)\,\chi\big(x-k-\eta_k(\omega)\big).$$

The state of the electrons in the crystal is modelled by a *one-particle density matrix* [112], that is, a random family of operators $\gamma(\omega) : L^2(\mathbb{R}^d) \to L^2(\mathbb{R}^d)$ such that $0 \le \gamma(\omega) \le 1$ almost surely. It is also assumed that γ is stationary in the sense that its kernel satisfies $\gamma(\tau_k(\omega),x,y) = \gamma(\omega,x+k,y+k)$ for all $k \in \mathcal{R}$. These concepts will be explained later in Section 2.2.1.

In mean-field models, the energy of the system is a functional of the nuclear charge μ and of the electronic density matrix γ. In the random setting, it is the sum of the kinetic energy per unit volume (a function of γ), of the potential energy per unit volume (a function of γ and μ) and, possibly, of other quantum correction terms such as exchange and/or correlation contributions. In order to rigorously define and study the properties of models of this type, we need to introduce some tools of functional analysis, which is the purpose of Sections 2.2 and 2.3. We believe that these tools will be useful for future studies of interacting random quantum systems.

In Section 2.2, we start by defining the average number of particles and the kinetic energy per unit volume for ergodic density matrices and we show useful inequalities. In particular we derive Hoffmann-Ostenhof [73] and Lieb-Thirring inequalities [115, 116] for ergodic density matrices, which are very important estimates that we will use several times throughout this study. Loosely speaking, they can respectively be stated as follows:

$$\text{Average kinetic energy per unit vol. of } \gamma \;\ge\; \mathbb{E}\left(\int_Q |\nabla\sqrt{\rho_\gamma}|^2\right)$$

and

$$\text{Average kinetic energy per unit vol. of } \gamma \;\ge\; K\,\mathbb{E}\left(\int_Q \rho_\gamma^{\frac{d+2}{d}}\right),$$

where Q is the unit cell, ρ_γ is the electronic density associated with the state γ and K is a constant independent of γ.

In Section 2.3, we discuss Poisson's equation

$$-\Delta V = 4\pi\rho \tag{2.1}$$

for stationary functions $\rho(\omega, x)$, where Δ is the Laplace operator with respect to the x-variable, and we explain that the situation is much more complicated than in the periodic case. In particular, the neutrality condition $\mathbb{E}(\int_Q \rho) = 0$ on the charge density appearing on the right side of (2.1) is necessary but in general not sufficient to find a stationary solution V. When $\mathbb{E}(\int_Q \rho^2) < \infty$ and $\mathbb{E}(\int_Q \rho) = 0$, it is possible to give a necessary and sufficient condition for the existence of a stationary solution V to (2.1) such that $\mathbb{E}(\int_Q V^2) < \infty$. In words, ρ should be in the range of the "stationary Laplacian" which is a particular self-adjoint extension of $-\Delta$ on $L^2(\Omega \times Q)$ with "stationary boundary conditions". See Section 2.3.1 for details.

Understanding Poisson's equation (2.1) for general stochastic charge densities ρ is an important and interesting problem in itself. In order to define the associated Coulomb energy per unit volume, we adopt here a simple strategy and take the limit $m \to 0$ of the Yukawa energy. This means that we consider the regularized equation

$$-\Delta V_m + m^2 V_m = 4\pi\rho$$

and we define the Coulomb energy as the limit of $\mathbb{E}\left(\int_Q V_m \rho\right)$ when $m \to 0$. We then give in Section 2.3 several properties of this energy.

In Section 2.4, we use the mathematical framework introduced in the previous sections to study the simplest mean-field theory for electrons, namely, the so-called *reduced Hartree-Fock* (rHF) model. It is obtained from the generalized Hartree-Fock model [113, 8] by removing the exchange term [146]. Alternatively, it can be seen as an extended Kohn-Sham model [41] with no exchange-correlation. In the random setting considered here, the corresponding energy is the sum of the kinetic energy per unit volume of γ and of the potential energy per unit volume of γ and μ.

We prove the existence of a minimizer γ of this energy and the uniqueness of the ground state density ρ_γ. In the Yukawa case $m > 0$, we also show that the minimizers solve a self-consistent equation of the form

$$\begin{cases} \gamma = 1_{(-\infty,\varepsilon_{\mathrm{F}})}(H_m) + \delta, \\ H_m = -\frac{1}{2}\Delta + V_m, \\ -\Delta V_m + m^2 V_m = 4\pi\big(\rho_\gamma - \mu\big), \end{cases}$$

where ε_{F} is the Fermi level, and $\mathrm{Ran}(\delta) \subset 1_{\{\varepsilon_{\mathrm{F}}\}}(H_m)$. Under the additional assumption that $\mu \in L^\infty(\Omega \times \mathbb{R}^d)$, the operator δ is a.s. equal to zero, and the ground state density matrix is unique.

The mean-field operator H_m is a random Schrödinger operator describing the collective behavior of the electrons in the system. Studying its spectral properties would allow to understand localization and transport properties

in the interacting stochastic crystal. These are interesting and important questions which we hope to address in the near future.

In Section 2.5, we finally prove that, in the Yukawa case, our model is actually the thermodynamic limit of the supercell reduced Hartree-Fock theory (the system is confined to a box with periodic boundary conditions). This justifies our theory with Yukawa interactions. For Coulomb forces, our proof does not apply because of some missing screening estimates. We make more comments about this later in Section 2.5.

Let us end this introduction by mentioning that our theory is rather general and it actually works for any reasonable interaction potential which decays fast enough at infinity. We concentrate on the Yukawa interaction because of the limit $m \to 0$ which corresponds to the more physical Coulomb case and which we study as well here. Note that we consider here the action of a discrete group on Ω because we have in mind the case of a randomly perturbed crystal. Our approach can also be applied to the case when the group acting on Ω is $\mathbb{R}^d$ (amorphous material), using the formalism of [123].

2.2 Electronic states in disordered crystals

In mean-field models (such as Hartree-Fock or Kohn-Sham), the state of the electrons is described by a self-adjoint operator γ acting on $L^2(\mathbb{R}^d)$, satisfying $0 \leq \gamma \leq 1$ in the sense of quadratic forms, and such that $\mathrm{Tr}\,(\gamma)$ is the total number of electrons in the system [112]. In (infinite) crystals, we always have $\mathrm{Tr}\,(\gamma) = +\infty$. Such an operator γ is called a *(one-particle) density matrix*. The purpose of this section is to collect the main properties of electronic states in a class of *random* media, satisfying an appropriate invariance property called *stationarity*. Some of these properties are classical, while others seem to be completely new. We recall in Appendix 2.B some properties of finite density matrices.

2.2.1 Basic definitions and properties

Throughout this chapter, d will denote the space dimension. We will later focus on the cases where $d \in \{1, 2, 3\}$, but we keep d arbitrary in this section. We restrict ourselves to the cubic lattice group $\mathcal{R} = \mathbb{Z}^d$ to simplify the notation; general discrete subgroups $\mathcal{R}$ can be tackled similarly without any additional difficulty. We consider a probability space $(\Omega, \mathcal{F}, \mathbb{P})$ and an ergodic group action τ of $\mathbb{Z}^d$ on Ω. We recall that τ is called ergodic if it is measure preserving and if for any $A \in \mathcal{F}$ satisfying $\tau_k(A) = A$ for all $k \in \mathbb{Z}^d$, it holds that $\mathbb{P}(A) \in \{0, 1\}$.

Example 2.2.1 (i.i.d. charges)**.** *A typical probability space we have in mind is the one arising from a random distribution of particles of charges q_1 and q_2*

on the sites of the lattice $\mathbb{Z}^d$ with probabilities p_1 and $1-p_1$. The probability space is then given by $\Omega = \{q_1, q_2\}^{\mathbb{Z}^d}$ and $\mathbb{P} = p^{\otimes \mathbb{Z}^d}$ where $p = p_1\delta_{q_1} + (1-p_1)\delta_{q_2}$. In this case, the group action is $\tau_k(\omega) = \omega_{\cdot+k}$. See Appendix 2.A for details about probability spaces and ergodic group actions.

The ergodic theorem [151, Theorem 6.1, Theorem 6.4], which will be extensively used in the sequel, can be stated as follows:

Theorem 2.2.2 (Ergodic theorem)**.** *If τ is an ergodic group action of $\mathbb{Z}^d$ on Ω and $X \in L^p(\Omega)$, with $1 \leq p < \infty$, then,*

$$\lim_{n\to\infty} \frac{1}{(2n+1)^d} \sum_{k\in\mathbb{Z}^d\cap\left[-\frac{n}{2},\frac{n}{2}\right]} X(\tau_k(\omega)) = \mathbb{E}(X),$$

almost surely and in $L^p(\Omega)$.

We recall the following consequence of the ergodicity of the group action, that we will use later.

Theorem 2.2.3. *[125, Theorem 1.10] Let τ be a group action of $\mathbb{Z}^d$ on Ω. Then τ is ergodic if and only if any random variable (r.v.) which is invariant under τ, that is, $X \circ \tau_k = X$ for any $k \in \mathbb{Z}^d$, is constant almost surely.*

Proof. Assume that τ is ergodic and let X be a r.v. invariant under τ. For $t \in \mathbb{R}$, let $A_t = \{\omega : X(\omega) \leq t\}$. We easily check that $\tau_k(A_t) = A_t$ for any $k \in \mathbb{Z}^d$, therefore $\mathbb{P}(A_t) \in \{0, 1\}$. As $t \mapsto \mathbb{P}(A_t)$ is a non-decreasing function going to 0 as $t \to -\infty$ and going to 1 as $t \to +\infty$, then it is a step function, stepping at a certain value t_0. Thus

$$\mathbb{P}(X \neq t_0) = \lim_{t\to t_0^-} \mathbb{P}(A_t) + \lim_{t\to t_0^+} \mathbb{P}(\Omega \setminus A_t) = 0 + 1 - 1 = 0$$

and

$$X = t_0 \quad \text{a.s.}$$

Conversely, suppose that any τ-invariant r.v. is constant almost surely and let $A \in \mathcal{F}$ such that $\tau_k(A) = A$ for any $k \in \mathbb{Z}^d$. The r.v. $X = 1_A$ is clearly invariant under τ. Therefore, it is a constant equal to 0 or 1. Thus, $\mathbb{P}(X = 1) = \mathbb{P}(A) \in \{0, 1\}$. □

A measurable function $f : \Omega \times \mathbb{R}^d \to \mathbb{C}$ is called *stationary* if

$$\forall k \in \mathbb{Z}^d,\ f(\tau_k(\omega), x) = f(\omega, k + x),\ \text{a.s. and a.e.}$$

Note that if the probability set Ω is finite, then the stationary functions on $\Omega \times \mathbb{R}^d$ coincide with the $n\mathbb{Z}^d$-periodic functions on $\mathbb{R}^d$, n being the cardinal of Ω. We also have the following result, which is a direct consequence of Theorem 2.2.3.

Proposition 2.2.4 (Characterization of ergodicity)**.** *Let τ be a group action of $\mathbb{Z}^d$ on Ω. Then τ is ergodic if and only if the stationary functions that are constant with respect to x a.e. are constant with respect to ω a.s.*

Proof. Assume that τ is ergodic and let f be a stationary function constant with respect to x a.e. Then, for any $\omega \in \Omega$, there exists a constant $X(\omega)$ and a Borel set $B(\omega) \subset \mathbb{R}^d$ satisfying $m(\mathbb{R}^d \backslash B(\omega)) = 0$ such that $f(\omega, x) = X(\omega)$ for any $x \in B(\omega)$; m being the Lebesgue measure. For $k \in \mathbb{Z}^d$ and $\omega \in \Omega$, it is easy to see that there exists $x \in B(\tau_k(\omega))$ such that $x + k \in B(\omega)$. Therefore, as f is stationary, we have a.s.

$$X(\tau_k(\omega)) = f(\tau_k(\omega), x) = f(\omega, x + k) = X(\omega).$$

It follows that X is invariant under τ, thus constant a.s. by Theorem 2.2.3. We deduce that f is constant with respect to ω a.s.

Conversely, assume that the stationary functions that are constant with respect to x a.e. are constant with respect to ω a.s. Let X be a r.v. invariant under τ and $f(\omega, x) := X(\omega)$ a.s. and a.e. It is clear that f is stationary. Using the assumption, we conclude that X is constant a.s. and that τ is ergodic by Theorem 2.2.3. □

We will make use of the families of stationary function spaces

$$L^p_s\left(L^q\right) = \left\{ f \in L^p\left(\Omega, L^q_{\mathrm{loc}}\left(\mathbb{R}^d\right)\right) \mid f \text{ is stationary} \right\},$$

and

$$H^m_s = \left\{ f \in L^2\left(\Omega, H^m_{\mathrm{loc}}\left(\mathbb{R}^d\right)\right) \mid f \text{ is stationary} \right\},$$

and resort, for convenience, to the shorthand notation $L^p_s = L^p_s\left(L^p\right)$. Endowed with the norms

$$\|f\|_{L^p_s(L^q)} = \mathbb{E}\left(\|f\|^p_{L^q(Q)}\right)^{\frac{1}{p}},$$

and the scalar products

$$\langle f, g\rangle_{L^2_s} = \mathbb{E}\left(\langle f, g\rangle_{L^2(Q)}\right), \qquad \langle f, g\rangle_{H^m_s} = \mathbb{E}\left(\langle f, g\rangle_{H^m(Q)}\right),$$

where

$$Q := \left[-\frac{1}{2}, \frac{1}{2}\right)^d$$

denotes the semi-open unit cube, the spaces $L^p_s\left(L^q\right)$ are Banach spaces and the spaces L^2_s and H^m_s are Hilbert spaces.

Starting from the usual Sobolev embedding theorems, it is easy to show embeddings of the form $H^m_s \hookrightarrow L^2_s(L^p)$. For example, in dimension $d = 3$, it holds that $H^1(Q) \hookrightarrow L^6(Q)$. Denoting by C_* the Sobolev constant such that

$$\forall f \in H^1(Q),\ \|f\|_{L^6(Q)} \leq C_* \|f\|_{H^1(Q)},$$

we have for $f \in H^1_s$,

$$\|f(\omega,\cdot)\|_{L^6(Q)} \leq C_* \|f(\omega,\cdot)\|_{H^1(Q)}, \text{ a.s,}$$

hence

$$\mathbb{E}\left(\|f\|^2_{L^6(Q)}\right) \leq C_*^2 \mathbb{E}\left(\|f\|^2_{H^1(Q)}\right),$$

that is,

$$\|f\|_{L^2_s(L^6)} \leq C_* \|f\|_{H^1_s}.$$

We denote by $\mathcal{H} = L^2\left(\mathbb{R}^d\right)$ the space of complex valued, square integrable functions, equipped with its usual scalar product $\langle \cdot, \cdot \rangle$. We also denote by

- $\mathcal{B}$ the space of the bounded linear operators on $\mathcal{H}$, endowed with the operator norm $\|\cdot\|$;
- $\mathcal{S}$ the space of the bounded self-adjoint operators on $\mathcal{H}$;
- $\mathfrak{S}_p$ the p^{th} Schatten class on $\mathcal{H}$. Recall that $\mathfrak{S}_1$ is the space of the trace class operators on $\mathcal{H}$ and $\mathfrak{S}_2$ the space of the Hilbert-Schmidt operators on $\mathcal{H}$.

Let $\mathcal{D}$ be a dense linear subspace of $\mathcal{H}$. A *random operator* with domain $\mathcal{D}$ is a map A from Ω into the set of the linear operators on $\mathcal{H}$ such that $\mathcal{D} \subset D(A(\omega))$ a.s. and such that the map $\omega \mapsto \langle A(\omega)x, y\rangle$ is measurable for all $x \in \mathcal{D}$ and $y \in \mathcal{H}$.

Of importance to us will be the *uniformly bounded random operators* A which are such that $\sup \operatorname{ess}_{\omega\in\Omega} \|A(\omega)\| < \infty$. The Banach space of such operators is denoted by $L^\infty(\Omega, \mathcal{B})$. This is a W^*-algebra which is known to be the dual of $L^1(\Omega, \mathfrak{S}_1)$ (see, e.g., [138, Corollary 3.2.2]). We will often use the corresponding weak-$*$ topology on $L^\infty(\Omega, \mathcal{B})$ for which $A_n \rightharpoonup_* A$ means

$$\mathbb{E}\left(\operatorname{Tr}\left(A_n B\right)\right) \to \mathbb{E}\left(\operatorname{Tr}\left(AB\right)\right)$$

for all $B \in L^1(\Omega, \mathfrak{S}_1)$. Since $L^1(\Omega, \mathfrak{S}_1)$ is separable, any bounded sequence (A_n) in $L^\infty(\Omega, \mathcal{B})$ has a subsequence (A_{n_k}) which converges weakly-$*$ to some $A \in L^\infty(\Omega, \mathcal{B})$. Similarly, we know that the dual of $L^p(\Omega, \mathfrak{S}_q)$ is nothing else but $L^{p'}(\Omega, \mathfrak{S}_{q'})$ where $1 = 1/p + 1/p' = 1/q + 1/q'$ and $1 \leq p, q < \infty$.

Let $(U_k)_{k\in\mathbb{Z}^d}$ be the group of unitary operators on $\mathcal{H}$ defined by

$$U_k f(x) = f(x+k), \text{ a.e., } \forall f \in \mathcal{H}, \ \forall k \in \mathbb{Z}^d.$$

A random operator A (not necessarily uniformly bounded) is called *ergodic* or *stationary* if for any $k \in \mathbb{Z}^d$, $\mathcal{D} \subset U_k(\mathcal{D})$ and the following equality holds

$$A(\tau_k(\omega)) = U_k A(\omega) U_k^*, \text{ a.s.}$$

One of the fundamental theorems for ergodic operators [148, Theorem 1.2.5 p.13] states that for any self-adjoint ergodic operator A, there exists a closed set $\Sigma \subset \mathbb{R}$ and a set $\Omega_1 \in \mathcal{F}$ with $\mathbb{P}(\Omega_1) = 1$, such that $\sigma(A(\omega)) = \Sigma$, for all $\omega \in \Omega_1$. The set Σ is called the almost sure spectrum of A.

We finally denote by $\underline{\mathcal{S}}$ the space of the ergodic operators on $\mathcal{H}$ that are almost surely bounded and self-adjoint.

2.2.2 Ergodic locally trace class operators

In this section, we recall the definitions of the trace per unit volume, the density and the kernel of an ergodic locally trace class operator (see e.g. [17, 40]). For $1 \leq p \leq \infty$, we denote by $L^p_c\left(\mathbb{R}^d\right)$ the space of the compactly supported L^p functions on $\mathbb{R}^d$.

Definition 2.2.5 (Locally trace-class operators)**.** *A random operator A is called* locally trace class *if $\chi A \chi \in L^1(\Omega, \mathfrak{S}_1)$ for all $\chi \in L^\infty_c(\mathbb{R}^d)$, that is,*

$$\forall \chi \in L^\infty_c(\mathbb{R}^d), \quad \mathbb{E}\Big(\mathrm{Tr}\,\left(\left|\chi A(\cdot)\chi\right|\right)\Big) < \infty.$$

We recall in Appendix 2.B.4 some properties of locally trace class operators that we will use in the sequel.

We now focus on the particular case of ergodic operators, and denote by $\underline{\mathfrak{S}_1}$ the space of the ergodic, locally trace class operators. The following characterization of the positive operators of $\underline{\mathfrak{S}_1}$ will be useful.

Proposition 2.2.6 (Characterization of ergodic locally trace-class operators)**.** *Let A be a positive, almost surely bounded, ergodic operator. Then A is locally trace class if and only if $\mathbb{E}(\mathrm{Tr}\,(1_Q A(\cdot)1_Q)) < \infty$.*

Proof. If A is locally trace class, then by definition $\mathbb{E}(\mathrm{Tr}\,(1_Q A(\cdot)1_Q)) < \infty$. Conversely, assume that $\mathbb{E}(\mathrm{Tr}\,(1_Q A(\cdot)1_Q)) < \infty$ and let B be a compact set of $\mathbb{R}^d$. As $A(\omega) \geq 0$ a.s., then a.s.

$$\mathrm{Tr}\,(1_B A(\omega)1_B) \leq \mathrm{Tr}\,\left(\sum_{k\in I} 1_{Q+k} A(\omega) \sum_{j\in I} 1_{Q+l}\right),$$

where $I = \left\{k \in \mathbb{Z}^d,\ Q + k \cap B \neq \emptyset\right\}$. Therefore

$$\begin{aligned}
\mathrm{Tr}\,(1_B A(\omega)1_B) &\leq \sum_{k,j\in I} \mathrm{Tr}\,(1_{Q+k} A(\omega) 1_{Q+j}) \\
&= \sum_{j\in I} \mathrm{Tr}\,(1_{Q+j} A(\omega) 1_{Q+j}) \\
&= \sum_{j\in I} \mathrm{Tr}\,\left(U_j^* 1_Q U_j A(\omega) U_j^* 1_Q U_j\right) \\
&= \sum_{j\in I} \mathrm{Tr}\,(1_Q A(\tau_j(\omega)) 1_Q)\,.
\end{aligned}$$

It follows that

$$\begin{aligned}\mathbb{E}\left(\mathrm{Tr}\ (1_B A(\omega)1_B)\right) &\leq \sum_{j\in I}\mathbb{E}\left(\mathrm{Tr}\ (1_Q A(\tau_j(\omega))1_Q)\right)\\ &= |I|\,\mathbb{E}\left(\mathrm{Tr}\ (1_Q A(\omega)1_Q)\right) < \infty.\end{aligned}$$

As $\left\{1_B,\ B \text{ a compact set of } \mathbb{R}^d\right\}$ is dense in $L^\infty_c(\mathbb{R}^d)$, we deduce that $A \in \underline{\mathfrak{S}}_1$, which concludes the proof of the proposition. □

The trace per unit volume of an operator $A \in \underline{\mathfrak{S}}_1$ is defined as

$$\boxed{\underline{\mathrm{Tr}}\ (A) = \mathbb{E}\big(\mathrm{Tr}\ (1_Q A(\cdot)\, 1_Q)\big).} \tag{2.2}$$

The following summarizes the main properties of locally trace-class ergodic operators.

Proposition 2.2.7 (Kernel and density)**.** *Let $A \in \underline{\mathfrak{S}}_1$. Then, there exists a unique function $A(\cdot,\cdot,\cdot) \in L^1(\Omega, L^2_{\mathrm{loc}}(\mathbb{R}^d \times \mathbb{R}^d))$, called the* kernel *of A, and a unique function $\rho_A \in L^1_s$, called the* density *of A, such that*

$$\forall \varphi \in L^2_c(\mathbb{R}^d),\ (A(\omega)\varphi)(x) = \int_{\mathbb{R}^d} A(\omega, x, y)\varphi(y)\,dy \quad a.s.\ and\ a.e.$$

and

$$\forall \chi \in L^\infty_c(\mathbb{R}^d),\ \mathrm{Tr}\,(\chi A(\omega)\chi) = \int_{\mathbb{R}^d} \chi^2(x)\rho_A(\omega, x)\,dx \quad a.s. \tag{2.3}$$

The kernel $A(\cdot,\cdot,\cdot)$ is stationary in the following sense

$$A(\tau_k(\omega), x, y) = A(\omega, x+k, y+k),\ \forall k \in \mathbb{Z}^d \quad a.e.\ and\ a.s. \tag{2.4}$$

Moreover, if $A \geq 0$, then $\rho_A \geq 0$.

Note that it follows from (2.2) and (2.3) that

$$\underline{\mathrm{Tr}}\ (A) = \mathbb{E}\left(\int_Q \rho_A\right).$$

Proof of Proposition 2.2.7. As the operator $A(\omega)$ is locally trace class a.s., there exists a unique function $A_\omega(x,y) \in L^2_{\mathrm{loc}}(\mathbb{R}^d \times \mathbb{R}^d)$ and a unique function $\rho_\omega(x)$ satisfying

$$\forall \varphi \in L^2_c(\mathbb{R}^d),\ (A(\omega)\varphi)(x) = \int_{\mathbb{R}^d} A_\omega(x, y)\varphi(y)\,dy \quad \text{a.e.} \tag{2.5}$$

and

$$\forall \chi \in L^\infty_c(\mathbb{R}^d),\ \mathrm{Tr}\,(\chi A(\omega)\chi) = \int_{\mathbb{R}^d} \chi^2(x)\rho_\omega(x)\,dx \quad \text{a.s.} \tag{2.6}$$

We set $A(\omega,x,y) := A_\omega(x,y)$ and $\rho_A(\omega,x) = \rho_\omega(x)$. For a compact set $B \subset \mathbb{R}^d$, we deduce from (2.5) that a.s.

$$\|A(\omega,\cdot,\cdot)\|_{L^2(B\times B)} = \|1_B A(\omega) 1_B\|_{\mathfrak{S}_2} \leq C\|1_B A(\omega)1_B\|_{\mathfrak{S}_1}.$$

Therefore, since $A \in \underline{\mathfrak{S}}_1$,

$$\mathbb{E}\left(\|A(\omega,\cdot,\cdot)\|_{L^2(B\times B)}\right) \;\leq\; C\mathbb{E}\left(\|1_B A(\omega)1_B\|_{\mathfrak{S}_1}\right) < \infty,$$

which proves that $A(\omega,x,y) \in L^1(\Omega, L^2_{\mathrm{loc}}(\mathbb{R}^d \times \mathbb{R}^d))$. By (2.6), we have a.s.

$$\int_B |\rho_A(\omega,x)|\, dx = \int_{\mathbb{R}^d} \left|\rho_{A(\omega)1_B}(x)\right| dx \leq \mathrm{Tr}\,\left(|1_B A(\omega)1_B|\right).$$

Therefore, since $A \in \underline{\mathfrak{S}}_1$,

$$\mathbb{E}\left(\int_B |\rho_A(\omega,x)|\, dx\right) \leq \mathbb{E}\left(\mathrm{Tr}\,\left(|1_B A(\omega)1_B|\right)\right) < \infty,$$

which proves that $\rho_A(\omega,x) \in L^1_{\mathrm{loc}}(\mathbb{R}^d)$. Let us now prove the stationarity of the kernel and the density of A. Let $k \in \mathbb{Z}^d$. For $\varphi,\psi \in L^2_c(\mathbb{R}^d)$, we have a.s.

$$\begin{aligned}
\int_{\mathbb{R}^d} A(\tau_k(\omega),x,y)\varphi(y)\psi(x)\,dy\,dx &= \langle\overline{\psi}, A(\tau_k(\omega))\varphi\rangle \\
&= \langle\overline{\psi}, U_k A(\omega) U_k^*\varphi\rangle \\
&= \langle U_k^*\overline{\psi}, A(\omega)U_k^*\varphi\rangle \\
&= \int_{\mathbb{R}^d} A(\omega,x,y)\varphi(y-k)\psi(x-k)\,dy\,dx \\
&= \int_{\mathbb{R}^d} A(\omega,x+k,y+k)\varphi(y)\psi(x)\,dy\,dx,
\end{aligned}$$

which proves that $A(\omega,x,y)$ satisfies (2.4) by the uniqueness of the kernel. Finally, for $\chi \in L^\infty_c(\mathbb{R}^d)$, we have a.s.,

$$\begin{aligned}
\int_{\mathbb{R}^d} \rho_A(\tau_k(\omega),x)\chi(x)^2\,dx &= \mathrm{Tr}\,\left(\chi A(\tau_k(\omega))\chi\right) \\
&= \mathrm{Tr}\,\left(\chi U_k A(\omega) U_k^*\chi\right) \\
&= \mathrm{Tr}\,\left(U_k\chi(\cdot-k)A(\omega)\chi(\cdot-k)U_k^*\right) \\
&= \mathrm{Tr}\,\left(\chi(\cdot-k)A(\omega)\chi(\cdot-k)\right) \\
&= \int_{\mathbb{R}^d} \rho_{A(\omega)}(x)\chi^2(x-k)\,dx \\
&= \int_{\mathbb{R}^d} \rho_{A(\omega)}(x+k)\chi^2(x)\,dx.
\end{aligned}$$

By linearity and the uniqueness of the density, we conclude that $\rho_A \in L^1_s$. □

The following cyclicity property is proved in [40], based on arguments in [39]. We give here a detailed proof.

Lemma 2.2.8 (The cyclicity of the trace per unit volume)**.** *If B is an ergodic operator in $L^\infty(\Omega, \mathcal{B})$ and A an operator in $\underline{\mathfrak{S}}_1 \cap L^\infty(\Omega, \mathcal{B})$, then BA and AB are in $\underline{\mathfrak{S}}_1 \cap L^\infty(\Omega, \mathcal{B})$ and*

$$\underline{\mathrm{Tr}}\,(BA) = \underline{\mathrm{Tr}}\,(AB)\,. \tag{2.7}$$

Proof. We consider the Von Neumann algebra $\mathcal{A} = \{A \in L^\infty(\Omega, \mathcal{B}),\ A \text{ ergodic}\}$ and its positive part $\mathcal{A}^+ = \{A \in \mathcal{A} \mid A \geq 0\}$. Let $A \in \mathcal{A}$ such that $A1_B \in \mathfrak{S}_2$ for any compact set $B \subset \mathbb{R}^d$. Then $A^*A \in \underline{\mathfrak{S}}_1$ and by Fubini's theorem, we have

$$\begin{aligned}\underline{\mathrm{Tr}}\,(A^*A) &= \mathbb{E}\left(\mathrm{Tr}\,\left(1_Q A^* \sum_{k\in\mathbb{Z}^d} 1_{Q+k} A 1_Q\right)\right)\\ &= \sum_{k\in\mathbb{Z}^d} \mathbb{E}\left(\mathrm{Tr}\,\left(1_Q A^* 1_{Q+k} A 1_Q\right)\right).\end{aligned}$$

By the cyclicity property of the trace, we have

$$\begin{aligned}\underline{\mathrm{Tr}}\,(A^*A) &= \sum_{k\in\mathbb{Z}^d} \mathbb{E}\left(\mathrm{Tr}\,\left(1_{Q+k} A 1_Q A^* 1_{Q+k}\right)\right)\\ &= \sum_{k\in\mathbb{Z}^d} \mathbb{E}\left(\mathrm{Tr}\,\left(U_k^* 1_Q U_k A U_k^* U_k 1_Q U_k^* U_k A^* U_k^* 1_Q U_k\right)\right)\\ &= \sum_{k\in\mathbb{Z}^d} \mathbb{E}\left(\mathrm{Tr}\,\left(1_Q A(\tau_k(\cdot)) 1_{Q-k} A^*(\tau_k(\cdot)) 1_Q\right)\right)\\ &= \sum_{k\in\mathbb{Z}^d} \mathbb{E}\left(\mathrm{Tr}\,\left(1_Q A 1_{Q-k} A^* 1_Q\right)\right)\\ &= \mathbb{E}\left(\mathrm{Tr}\,\left(1_Q A A^* 1_Q\right)\right)\\ &= \underline{\mathrm{Tr}}\,(AA^*)\,,\end{aligned}$$

where we have used that τ is measure preserving. By [39, Corollary 1, p.83], the function $\underline{\mathrm{Tr}}\,(\cdot)$ is a trace on $\mathcal{A}^+$ (see [39, Definition 1, p.81]). Therefore, by [39, Proposition 1, p.82], $\underline{\mathrm{Tr}}\,(\cdot)$ can be extended to a linear form on the ideal $\mathcal{M} = L^\infty(\Omega, \mathcal{B}) \cap \underline{\mathfrak{S}}_1$ which satisfies $\underline{\mathrm{Tr}}\,(BA) = \underline{\mathrm{Tr}}\,(AB)$ for any $A \in \mathcal{M}$ and any $B \in \mathcal{A}$. □

2.2.3 Ergodic operators with locally finite kinetic energy

Ergodic density matrices for fermions are operators $\gamma \in \underline{\mathfrak{S}}_1 \cap \underline{\mathcal{S}}$ such that $0 \leq \gamma \leq 1$ a.s. By the ergodic theorem, the trace per unit volume can be interpreted from a physical viewpoint as the average number of particles per unit volume. In this section, we define and study in a similar fashion the average kinetic energy per unit volume.

2.2.3.1 Definition

For $1 \leq j \leq d$, as usual, we denote by $P_j = -i\partial_{x_j}$ the momentum operator in the j^{th} direction, which is self-adjoint with $D(P_j) = \{\varphi \in \mathcal{H} \mid \partial_{x_j}\varphi \in \mathcal{H}\}$. As P_j commutes with the translations, we see that for all $A \in \underline{\mathfrak{S}}_1$, the operator P_jAP_j is ergodic. The operator P_jAP_j is well defined and bounded on $D(P_j)$, with values in $D(P_j)'$, where $D(P_j)'$ is the topological dual space of $D(P_j)$. We say that the kinetic energy of A is locally finite if $P_jAP_j \in \underline{\mathfrak{S}}_1$ for all $1 \leq j \leq d$, and we then call

$$\boxed{\underline{\mathrm{Tr}}\,(-\Delta A) := \sum_{j=1}^{d} \underline{\mathrm{Tr}}\,(P_jAP_j)}$$

the average kinetic energy per unit volume of A. We denote by $\underline{\mathfrak{S}}_{1,1}$ the subspace of $\underline{\mathfrak{S}}_1$ composed of the ergodic locally trace class operators with locally finite kinetic energy.

2.2.3.2 Hoffmann-Ostenhof and Lieb-Thirring inequalities for ergodic operators

For finite systems ($\gamma \in \mathfrak{S}_1 \cap \mathcal{S}$, $0 \leq \gamma \leq 1$ and $\mathrm{Tr}\,(-\Delta\gamma) < \infty$), the Hoffmann-Ostenhof [73, 112] and Lieb-Thirring [115, 116, 112] inequalities provide useful properties of the map $\gamma \mapsto \rho_\gamma$. In this section, we state and prove an equivalent of these inequalities for ergodic density matrices with locally finite kinetic energy.

Proposition 2.2.9 (Hoffmann-Ostenhof inequality for ergodic operators)**.** *Let A be a positive operator in $\underline{\mathfrak{S}}_{1,1} \cap \underline{\mathcal{S}}$. Then*

$$\sqrt{\rho_A} \in H^1_s \quad \textit{and} \quad \mathbb{E}\left(\int_Q |\nabla\sqrt{\rho_A}|^2\right) \leq \underline{\mathrm{Tr}}\,(-\Delta A).$$

Proof. It follows from Proposition 2.2.7 that $\sqrt{\rho_A} \in L^2_s$. Let B be a compact set of $\mathbb{R}^d$ and $\eta \in C^\infty_c(\mathbb{R}^d)$ such that $\eta \equiv 1$ on B and $0 \leq \eta \leq 1$. By the uniqueness of the density, we easily see that $\rho_{\eta A\eta} = \rho_A$ on B. Besides, the operator $\eta A(\omega)\eta$ has finite kinetic energy a.s. Indeed, for any $1 \leq j \leq d$, we have $[Pj, \eta] = -i\partial_{x_j}\eta \in C^\infty_c(\mathbb{R}^d)$ and

$$\begin{aligned}
\mathbb{E}\left(\mathrm{Tr}\,\left(P_j\eta A\eta P_j\right)\right) &= \mathbb{E}\left(\mathrm{Tr}\,\left(\eta P_jAP_j\eta\right)\right) + 2Re\left(\mathbb{E}\left(\mathrm{Tr}\,\left((-i\partial_{x_j}\eta)AP_j\eta\right)\right)\right) \\
&\quad - \mathbb{E}\left(\mathrm{Tr}\,\left(\left(-i\partial_{x_j}\eta\right)A\left(-i\partial_{x_j}\eta\right)\right)\right) \\
&\leq 2\mathbb{E}\left(\mathrm{Tr}\,\left(\partial_{x_j}\eta A\partial_{x_j}\eta\right)\right) + 2\mathbb{E}\left(\mathrm{Tr}\,\left(\eta P_jAP_j\eta\right)\right) \\
&\leq C\left(\underline{\mathrm{Tr}}\,(A) + \underline{\mathrm{Tr}}\,(-\Delta A)\right).
\end{aligned}$$

Therefore, the Hoffmann-Ostenhof inequality applied to the operator $\eta A \eta$ gives

$$\left|\nabla\sqrt{\rho_{A(\omega)}}\right| = |\nabla\sqrt{\rho_{\eta A(\omega)\eta}}| \leq \sqrt{\sum_{n\in\mathbb{N}} \lambda_n(\omega)|\nabla\varphi_n(\omega)|^2} \quad \text{a.s. and a.e. on } B,$$

where $(\varphi_n(\omega))_{n\in\mathbb{N}}$ is an orthonormal basis of eigenvectors of the compact self-adjoint operator $\eta A(\omega)\eta$ and $(\lambda_n(\omega))_{n\in\mathbb{N}}$ the associated eigenvalues. As

$$\int_B \sum_{n\in\mathbb{N}} \lambda_n(\omega)|\nabla\varphi_n(\omega)|^2 = \sum_{j=1}^{d} \mathrm{Tr}\ \left(1_B P_j \eta A\left(\omega\right)\eta P_j 1_B\right) \text{ a.s.}$$

and as for all $1 \leq j \leq d$, $1_B\left[P_j, \eta\right] = -i1_B\partial_{x_j}\eta = 0$, we deduce that

$$\int_B |\nabla\sqrt{\rho_{A(\omega)}}|^2 \leq \sum_{j=1}^{d} \mathrm{Tr}\ \left(1_B \eta P_j A\left(\omega\right) P_j \eta 1_B\right) = \sum_{j=1}^{d} \mathrm{Tr}\ \left(1_B P_j A\left(\omega\right) P_j 1_B\right).$$

Therefore

$$\mathbb{E}\left(\int_B |\nabla\sqrt{\rho_A}|^2\right) \leq \sum_{j=1}^{d} \mathbb{E}\left(\mathrm{Tr}\ \left(1_B P_j A P_j 1_B\right)\right).$$

As A has locally finite kinetic energy, we conclude that $\sqrt{\rho_A} \in H^1_s$. For $B = Q$, we obtain the stated inequality. □

The following corollary is an obvious consequence of Proposition 2.2.9 and of the Sobolev embeddings.

Corollary 2.2.10. *Let A be a positive operator in $\underline{\mathfrak{S}}_{1,1} \cap \underline{\mathcal{S}}$. Then, $\rho_A \in L^1_s\left(L^p\right)$, for $p = +\infty$ if $d = 1$, $p \in [1, +\infty)$ if $d = 2$ and $1 \leq p \leq \frac{d}{d-2}$ if $d \geq 3$.*

The following is now the ergodic equivalent of the Lieb-Thirring inequality [115, 116, 112].

Proposition 2.2.11 (Lieb-Thirring inequality for ergodic operators)**.** *There exists a constant $K(d) > 0$, depending only on the space dimension $d \geq 1$, such that for all $\gamma \in \underline{\mathfrak{S}}_{1,1} \cap \underline{\mathcal{S}}$ with $0 \leq \gamma(\omega) \leq 1$ a.s.,*

$$\rho_\gamma \in L^{\frac{d+2}{d}}_s \quad \text{and} \quad K(d)\,\mathbb{E}\left(\int_Q \rho_\gamma^{\frac{d+2}{d}}\right) \leq \underline{\mathrm{Tr}}\left(-\Delta\gamma\right). \tag{2.8}$$

Proof. To prove (2.8), we apply the Lieb-Thirring inequality in a box of side-length L, and then let L go to infinity. The constant $K(d)$ can be chosen equal to the optimal Lieb-Thirring constant in the whole space. Let $\Gamma_L = [-L/2, L/2)^d$ and let $(\chi_L)_{L\in\mathbb{N}^*}$ be a sequence of localizing functions in

$C_c^\infty\left(\mathbb{R}^d\right)$, such that $0 \leq \chi_L \leq 1$, $\chi_L \equiv 1$ on Γ_{L-1}, $\chi_L \equiv 0$ outside of Γ_L, and $|\nabla \chi_L(x)| \leq C$. We first apply the Lieb-Thirring inequality to $\chi_L \gamma(\omega) \chi_L$ and obtain

$$K(d) \int_{\Gamma_{L-1}} \rho_\gamma(\omega, x)^{\frac{d+2}{d}}\, dx \leq \mathrm{Tr}\, \left(-\Delta \chi_L \gamma(\omega) \chi_L\right) \quad \text{a.s.}$$

Next, using the stationarity of ρ_γ and the equality $[P_j, \chi_L] = -i\partial_{x_j}\chi_L$, we get for any $\varepsilon > 0$

$$\begin{aligned} K(d)\, \mathbb{E}\left(\int_Q \rho_\gamma^{\frac{d+2}{d}}\right) \leq \frac{(1+\varepsilon)}{(L-1)^d} \sum_{j=1}^d \mathbb{E}\left(\mathrm{Tr}\, \left(\chi_L P_j \gamma P_j \chi_L\right)\right) \\ + \frac{1+1/\varepsilon}{(L-1)^d} \sum_{j=1}^d \mathbb{E}\left(\mathrm{Tr}\, \left(\left(\partial_{x_j}\chi_L\right) \gamma \left(\partial_{x_j}\chi_L\right)\right)\right). \quad (2.9) \end{aligned}$$

For each $1 \leq j \leq d$, as P_j commutes with translations, we have a.s.,

$$\begin{aligned} \mathrm{Tr}\, \left(\chi_L P_j \gamma(\omega) P_j \chi_L\right) &\leq \sum_{k \in \mathbb{Z}^d,\, Q+k \subset \Gamma_L} \mathrm{Tr}\, \left(1_{Q+k} P_j \gamma(\omega) P_j 1_{Q+k}\right) \\ &= \sum_{k \in \mathbb{Z}^d,\, Q+k \subset \Gamma_L} \mathrm{Tr}\, \left(U_k^* 1_Q U_k P_j \gamma(\omega) P_j U_k^* 1_Q U_k\right) \\ &= \sum_{k \in \mathbb{Z}^d,\, Q+k \subset \Gamma_L} \mathrm{Tr}\, \left(1_Q P_j \gamma(\tau_k(\omega)) P_j 1_Q\right). \end{aligned}$$

It follows from the measure preserving character of τ that

$$\begin{aligned} \sum_{j=1}^d \mathbb{E}\left(\mathrm{Tr}\, \left(\chi_L P_j \gamma P_j \chi_L\right)\right) &\leq \sum_{k \in \Gamma_L \cap \mathbb{Z}^d} \mathbb{E}\left(\mathrm{Tr}\, \left(1_Q P_j \gamma(\omega) P_j 1_Q\right)\right) \\ &= L^d \underline{\mathrm{Tr}}\, \left(-\Delta\gamma\right). \quad (2.10) \end{aligned}$$

Besides,

$$\mathrm{Tr}\, \left((\partial_{x_j}\chi_L)\gamma(\partial_{x_j}\chi_L)\right) = \int_{\Gamma_L \setminus \Gamma_{L-1}} \rho_\gamma(\omega, \cdot)(\partial_{x_j}\chi_L)^2 \leq C \int_{\Gamma_L \setminus \Gamma_{L-1}} \rho_\gamma(\omega, \cdot),$$

where we have used that $\nabla\chi_L$ is uniformly bounded. Using again the stationarity of ρ_γ, we obtain

$$\sum_{j=1}^d \mathbb{E}\left(\mathrm{Tr}\, \left(\partial_{x_j}\chi_L\right) \gamma \left(\partial_{x_j}\chi_L\right)\right) \leq C L^{d-1} \underline{\mathrm{Tr}}\, (\gamma). \quad (2.11)$$

Combining (2.9), (2.10) and (2.11), letting L go to infinity then letting ε go to 0, we end up with the claimed inequality. □

2.2.3.3 A compactness result

In this section we investigate the weak compactness properties of the set of fermionic density matrices with finite average number of particles and kinetic energy per unit volume

$$\mathcal{K} := \left\{ \gamma \in \underline{\mathfrak{S}}_{1,1} \cap \underline{\mathcal{S}},\ 0 \leq \gamma \leq 1 \text{ a.s.} \right\}.$$

This set is a weakly-$*$ closed convex subset of $L^\infty(\Omega, \mathcal{B})$. The following result will be very useful.

Proposition 2.2.12 (Weak compactness of ergodic density matrices)**.** *Let (γ_n) be any bounded sequence in $\mathcal{K}$. Then there exists $\gamma \in \mathcal{K}$ and a subsequence (γ_{n_k}) such that*

1. $\gamma_{n_k} \underset{k\to\infty}{\rightharpoonup}_* \gamma$ *in* $L^\infty(\Omega, \mathcal{B})$,
2. $\lim\limits_{k\to\infty} \underline{\mathrm{Tr}}\,(\gamma_{n_k}) = \underline{\mathrm{Tr}}\,(\gamma)$,
3. $\rho_{\gamma_{n_k}} \underset{k\to\infty}{\rightharpoonup} \rho_\gamma$ *weakly in* $L_s^{\frac{d+2}{d}}$,
4. $\underline{\mathrm{Tr}}\,(-\Delta\gamma) \leq \liminf\limits_{n\to\infty} \underline{\mathrm{Tr}}\,(-\Delta\gamma_{n_k})$.

Note that, in average, there is never any loss of particles when passing to weak limits: $\underline{\mathrm{Tr}}\,(\gamma_n)$ tends to $\underline{\mathrm{Tr}}\,(\gamma)$ as $n \to \infty$. On the other hand, even if we have $\rho_{\gamma_n} \rightharpoonup \rho_\gamma$ weakly and $\mathbb{E}(\int_Q \rho_{\gamma_n}) \to \mathbb{E}(\int_Q \rho_\gamma)$, in general we do not have almost sure convergence and we do not expect strong convergence in L_s^p for $1 \leq p \leq 1 + 2/d$.

Example 2.2.13 (Weak versus strong convergence for ρ_{γ_n})**.** *Consider a smooth function φ with compact support in the ball $B(0, 1/2)$ such that $\|\varphi\|_{L^2} = 1$, and the operator*

$$\gamma_n = \sum_{k\in\mathbb{Z}^d} \frac{1 + \sin(2\pi n\omega_k)}{2} \left|\varphi(\cdot + k)\right\rangle\left\langle\varphi(\cdot + k)\right|,$$

where $(\omega_k)_{k\in\mathbb{Z}^d}$ are i.i.d. variables, uniformly distributed on $[0, 1]$. Then we have $\gamma_n \in \underline{\mathfrak{S}}_{1,1}$, $0 \leq \gamma_n \leq 1$,

$$\gamma_n \rightharpoonup_* \gamma = \frac{1}{2} \sum_{k\in\mathbb{Z}^d} \left|\varphi(\cdot + k)\right\rangle\left\langle\varphi(\cdot + k)\right| \quad \text{in } L^\infty(\Omega, \mathcal{B})$$

and

$$\rho_{\gamma_n} = \sum_{k\in\mathbb{Z}^d} \frac{1 + \sin(2\pi n\omega_k)}{2} \left|\varphi(\cdot + k)\right|^2 \rightharpoonup \rho_\gamma = \frac{1}{2} \sum_{k\in\mathbb{Z}^d} \left|\varphi(\cdot + k)\right|^2$$

weakly in L^p_s *for* $1 < p < \infty$. *We also have*

$$\mathbb{E}\left(\int_Q \rho_{\gamma_n}\right) = \mathbb{E}\left(\int_Q \rho_{\gamma}\right), \qquad \forall n \in \mathbb{N}.$$

However, since $\sin(2\pi n\omega_k) \rightharpoonup 0$ *weakly but not strongly in* $L^p([0,1])$, *we do not have any strong convergence for* ρ_{γ_n}.

Proof of Proposition 2.2.12. Consider a sequence (γ_n) as in the statement. As detailed in Section 2.2.1 after Theorem 2.2.2, $L^\infty(\Omega, \mathcal{B})$ is for us the W^*-algebra which is the dual of the separable Banach space $L^1(\Omega, \mathfrak{S}_1)$, see [138, Corollary 3.2.2]. Since (γ_n) is bounded in $L^\infty(\Omega, \mathcal{B})$, there exists $\gamma \in L^\infty(\Omega, \mathcal{B})$ such that γ_n converges to γ weakly-$*$ in $L^\infty(\Omega, \mathcal{B})$, up to extraction of a subsequence (denoted the same for simplicity). Recall that $\gamma_n \rightharpoonup_* \gamma$ means

$$\lim_{n\to\infty} \mathbb{E}\left(\mathrm{Tr}\left(A\gamma_n\right)\right) = \mathbb{E}\left(\mathrm{Tr}\left(A\gamma\right)\right)$$

for all $A \in L^1(\Omega, \mathfrak{S}_1)$. Using for instance $A = Y\,|f\rangle\langle g|$ for some fixed $f, g \in \mathcal{H} = L^2(\mathbb{R}^d)$ and some fixed $Y \in L^1(\Omega)$, we find in particular that

$$\forall f, g \in \mathcal{H},\ \forall Y \in L^1(\Omega), \quad \mathbb{E}\left(Y\langle g, \gamma f\rangle\right) = \lim_{n\to\infty} \mathbb{E}\left(Y\langle g, \gamma_n f\rangle\right). \tag{2.12}$$

Hence, $\langle g, \gamma_n f\rangle$ converges to $\langle g, \gamma f\rangle$ weakly$-*$ in $L^\infty(\Omega)$. Using this, it is easy to verify that γ is ergodic and satisfies $\gamma^* = \gamma$, $0 \le \gamma \le 1$ a.s.

Let now $(f_k)_{k\ge1}$ be an orthonormal basis of $L^2(Q)$ where we recall that Q is the unit cell. Using that $\mathbb{E}\left(\langle f_k, \gamma_n f_k\rangle\right) \to \mathbb{E}\left(\langle f_k, \gamma f_k\rangle\right)$ for each $k \ge 1$ as $n \to \infty$, and Fatou's lemma in $\ell^1(\mathbb{N})$, we obtain

$$\begin{aligned}\mathbb{E}\left(\mathrm{Tr}\left(1_Q\gamma 1_Q\right)\right) = \sum_{k\ge1} \mathbb{E}\left(\langle f_k, \gamma f_k\rangle\right) &\le \liminf_{n\to\infty} \mathbb{E}\left(\sum_{k\ge1} \langle f_k, \gamma_n f_k\rangle\right) \\ &= \liminf_{n\to\infty} \mathbb{E}\left(\mathrm{Tr}\left(1_Q\gamma_n 1_Q\right)\right). \end{aligned} \tag{2.13}$$

By Proposition 2.2.6, we conclude that $\gamma \in \underline{\mathfrak{S}}_1$. The same argument can be employed to show that $\gamma \in \underline{\mathfrak{S}}_{1,1}$, assuming this time that each f_k is in $H^1_0(Q)$. Then we have for each k

$$\lim_{n\to\infty} \mathbb{E}\left(\langle f_k, P_j\gamma_n P_j f_k\rangle\right) = \lim_{n\to\infty} \mathbb{E}\left(\langle (P_j f_k), \gamma_n (P_j f_k)\rangle\right) = \mathbb{E}\left(\langle (P_j f_k), \gamma (P_j f_k)\rangle\right),$$

by (2.12) and with $P_j = -i\partial_{x_j}$. By Fatou's Lemma in $\ell^1(\mathbb{N})$ we see that

$$\underline{\mathrm{Tr}}\left(-\Delta\gamma\right) = \sum_{j=1}^{d}\sum_{i} \mathbb{E}\left(\langle (P_j f_k), \gamma (P_j f_k)\rangle\right) \le \liminf_{n\to\infty} \underline{\mathrm{Tr}}\left(-\Delta\gamma_n\right). \tag{2.14}$$

Let us now prove that $\underline{\mathrm{Tr}}\,(\gamma_n)$ indeed converges to $\underline{\mathrm{Tr}}\,(\gamma)$. We consider a smooth function χ in $C_c^\infty(\mathbb{R}^d)$. The sequence (γ_n) being bounded in $\underline{\mathfrak{S}}_{1,1}$, there exists a constant $C \in \mathbb{R}_+$ such that for all $n \in \mathbb{N}$ and $1 \leq j \leq d$,

$$\mathbb{E}\left(\mathrm{Tr}\,\left(\chi\gamma_n\chi\right)\right) + \mathbb{E}\left(\mathrm{Tr}\left(\chi P_j\gamma_n P_j\chi\right)\right) + \mathbb{E}\left(\mathrm{Tr}\,\left(\partial_{x_j}\chi\right)\gamma_n\left(\partial_{x_j}\chi\right)\right) \leq C.$$

Using again the relation $[P_j, \chi] = -i\partial_{x_j}\chi$, we obtain

$$\mathbb{E}\left(\mathrm{Tr}\,\left(P_j\chi\gamma_n\chi P_j\right)\right) \leq 4C.$$

We next use that for a non-negative self-adjoint trace class operator A with finite kinetic energy, we have

$$\mathrm{Tr}\,\left((1-\Delta)^{\frac{1}{2}}A\,(1-\Delta)^{\frac{1}{2}}\right) = \mathrm{Tr}\,\left(A\right) + \mathrm{Tr}\,\left(-\Delta A\right).$$

Indeed, writing $A = \sum_{n\in\mathbb{N}}\lambda_n|\varphi_n\rangle\langle\varphi_n|$, where $(\lambda_n)_{n\in\mathbb{N}}$ is a summable sequence of positive real numbers, and $(\varphi_n)_{n\in\mathbb{N}}$ an orthonormal family of $L^2\left(\mathbb{R}^d\right)$ consisting of functions of $H^1(\mathbb{R}^d)$ (see Proposition 2.B.5), then

$$\begin{aligned}
\mathrm{Tr}\,\left((1-\Delta)^{\frac{1}{2}}A\,(1-\Delta)^{\frac{1}{2}}\right) &= \sum_{n\in\mathbb{N}}\lambda_n\sum_{i\in\mathbb{N}}\left|\langle\varphi_n, (1-\Delta)^{\frac{1}{2}}\varphi_i\rangle\right|^2 \\
&= \sum_{n\in\mathbb{N}}\lambda_n\left\|(1-\Delta)^{\frac{1}{2}}\varphi_n\right\|^2_{L^2(\mathbb{R}^d)} \\
&= \sum_{n\in\mathbb{N}}\lambda_n\frac{1}{(2\pi)^d}\int_{\mathbb{R}^d}(1+|p|^2)\,|\widehat{\varphi_n}\,(p)|^2\,dp \\
&= \sum_{n\in\mathbb{N}}\lambda_n\frac{1}{(2\pi)^d}\int_{\mathbb{R}^d}|\widehat{\varphi_n}|^2 \\
&\quad + \sum_{n\in\mathbb{N}}\lambda_n\frac{1}{(2\pi)^d}\int_{\mathbb{R}^d}|p|^2\,|\widehat{\varphi_n}\,(p)|^2\,dp \\
&= \sum_{n\in\mathbb{N}}\lambda_n + \sum_{n\in\mathbb{N}}\lambda_n\,\|\nabla\varphi_n\|^2_{L^2(\mathbb{R}^d)^d} \\
&= \mathrm{Tr}\,(A) + \mathrm{Tr}\,(-\Delta A).
\end{aligned}$$

Hence,

$$\begin{aligned}
\mathbb{E}\left(\mathrm{Tr}\,\left((1-\Delta)^{\frac{1}{2}}\chi\gamma_n\chi\,(1-\Delta)^{\frac{1}{2}}\right)\right) &= \mathbb{E}\left(\mathrm{Tr}\,\left(\chi\gamma_n\chi\right)\right) + \mathbb{E}\left(\mathrm{Tr}\,\left(-\Delta(\chi\gamma_n\chi)\right)\right) \\
&= \mathbb{E}\left(\mathrm{Tr}\,\left(\chi\gamma_n\chi\right)\right) + \sum_{j=1}^{d}\mathbb{E}\left(\mathrm{Tr}\,\left(P_j\chi\gamma_n\chi P_j\right)\right) \\
&\leq (1+4d)C.
\end{aligned}$$

This proves that $(1-\Delta)^{1/2}\,\chi\gamma_n\chi\,(1-\Delta)^{1/2}$ is bounded in $L^1(\Omega, \mathfrak{S}_1)$ or, equivalently, that $(1-\Delta)^{1/2}\,\chi\sqrt{\gamma_n}$ is bounded in $L^2(\Omega, \mathfrak{S}_2)$. From this we

infer that

$$(1-\Delta)^{\frac{1}{2}}\,\chi\gamma_n\chi = \left\{(1-\Delta)^{\frac{1}{2}}\,\chi\gamma_n\chi\,(1-\Delta)^{\frac{1}{2}}\right\}(1-\Delta)^{-\frac{1}{2}}$$

is bounded in $L^1(\Omega,\mathfrak{S}_1)$, since $(1-\Delta)^{-1/2}$ is a bounded operator. Similarly, we can write

$$(1-\Delta)^{\frac{1}{2}}\,\chi\gamma_n\chi = \left\{(1-\Delta)^{\frac{1}{2}}\,\chi\sqrt{\gamma_n}\right\}\sqrt{\gamma_n}\chi,$$

which is now bounded in $L^2(\Omega,\mathfrak{S}_2)$, since $\left\|\sqrt{\gamma_n}\chi\right\| \leq C$ due to the assumption that $0 \leq \gamma_n \leq 1$. We conclude that $(1-\Delta)^{1/2}\,\chi\gamma_n\chi$ is bounded in $L^1(\Omega,\mathfrak{S}_1)\cap L^2(\Omega,\mathfrak{S}_2)$, hence in $L^p(\Omega,\mathfrak{S}_p)$ for all $1\leq p\leq 2$, by interpolation. In particular,

$$(1-\Delta)^{\frac{1}{2}}\,\chi\gamma_n\chi \rightharpoonup (1-\Delta)^{\frac{1}{2}}\,\chi\gamma\chi \quad \text{weakly in } L^p(\Omega,\mathfrak{S}_p) \text{ for all } 1<p\leq 2. \tag{2.15}$$

That the limit can only be $(1-\Delta)^{1/2}\,\chi\gamma\chi$ follows for instance from (2.12) with functions $f,g\in H^1(\mathbb{R}^d)$.

We consider now a fixed function $Y\in L^\infty(\Omega)$ and write

$$\mathbb{E}\left(Y\mathrm{Tr}\left(\chi\gamma_n\chi\right)\right) = \mathbb{E}\left(Y\mathrm{Tr}\left(\left(1-\Delta\right)^{1/2}\chi\gamma_n\chi 1_B\left(1-\Delta\right)^{-1/2}\right)\right),$$

where B is a large enough ball containing the support of χ. By the Kato-Seiler-Simon inequality [145, Theorem 4.1],

$$\forall p\geq 2, \qquad \left\|f(x)g(-i\nabla)\right\|_{\mathfrak{S}_p} \leq (2\pi)^{-d/p}\left\|f\right\|_{L^p(\mathbb{R}^d)}\left\|g\right\|_{L^p(\mathbb{R}^d)},$$

we have

$$\left\|1_B\left(1-\Delta\right)^{-1/2}\right\|_{\mathfrak{S}_{1+d}} \leq (2\pi)^{-d/p}|B|^{\frac{1}{1+d}}\left(\int_{\mathbb{R}^d}\frac{dp}{(1+|p|^2)^{\frac{1+d}{2}}}\right)^{\frac{1}{1+d}},$$

hence $1_B\left(1-\Delta\right)^{-1/2}\in\mathfrak{S}_{1+d}$. Thus $Y1_B\left(1-\Delta\right)^{-1/2}\in L^\infty(\Omega,\mathfrak{S}_{1+d})\subset L^{1+d}(\Omega,\mathfrak{S}_{1+d})$. Since $1<1+1/d\leq 2$ we obtain by the weak convergence (2.15) in $L^{1+1/d}(\Omega,\mathfrak{S}_{1+1/d}) = L^{1+d}(\Omega,\mathfrak{S}_{1+d})'$,

$$\lim_{n\to\infty}\mathbb{E}\left(Y\mathrm{Tr}\left(\chi\gamma_n\chi\right)\right) = \mathbb{E}\left(Y\mathrm{Tr}\left(\left(1-\Delta\right)^{1/2}\chi\gamma\chi 1_B\left(1-\Delta\right)^{-1/2}\right)\right) = \mathbb{E}\left(Y\mathrm{Tr}\left(\chi\gamma\chi\right)\right).$$

We can reformulate this into

$$\lim_{n\to\infty}\mathbb{E}\left(Y\int_{\mathbb{R}^d}\chi^2\rho_{\gamma_n}\right) = \mathbb{E}\left(Y\int_{\mathbb{R}^d}\chi^2\rho_{\gamma}\right), \tag{2.16}$$

for all $Y\in L^\infty(\Omega)$ and all $\chi\in C_c^\infty(\mathbb{R}^d)$.

As $\underline{\mathrm{Tr}}\,(-\Delta\gamma_n)$ is bounded, we infer from the Lieb-Thirring inequality for ergodic operators (Proposition 2.2.11) that (ρ_{γ_n}) is bounded in $L_s^{1+2/d}$. We can therefore extract a subsequence which weakly converges in $L_s^{1+2/d}$ to some $\rho \in L_s^{1+2/d}$. Since the space spanned by the functions of the form $Y\chi^2$ with $Y \in L^\infty(Q)$ and $\chi \in C_c^\infty(Q)$ is dense in $L^{1+d/2}(\Omega \times Q)$, we deduce from (2.16) that $\rho_\gamma = \rho$. Now, using that $1_Q \in L^{1+d/2}(\Omega \times Q)$, we finally obtain the claimed convergence

$$\lim_{n\to\infty} \underline{\mathrm{Tr}}\,(\gamma_n) = \lim_{n\to\infty} \mathbb{E}\left(\int_Q \rho_{\gamma_n}\right) = \mathbb{E}\left(\int_Q \rho_\gamma\right) = \underline{\mathrm{Tr}}\,(\gamma)\,.$$

This concludes the proof of the proposition. □

2.2.3.4 Spectral projections of ergodic Schrödinger operators

The following result provides a control of the average number of particles and kinetic energy per unit volume of the spectral projections of an ergodic Schrödinger operator, in terms of the negative component $V_- = \max(-V, 0)$ of the external potential. We will use it later in Section 2.4.4 to prove that the ground state density matrix of the reduced Hartree-Fock model with Yukawa potential is solution to a self-consistent equation.

Proposition 2.2.14 (Spectral projections are in $\underline{\mathfrak{S}}_{1,1}$)**.** *Let $V \in L_s^2$ be such that the operator $H = -\Delta + V$ is essentially self-adjoint on $C_c^\infty(\mathbb{R}^d)$ and $V_- \in L_s^{1+d/2}$. Denote by $P_\lambda = 1_{(-\infty,\lambda)}(H)$ the spectral projection of H corresponding to filling all the energy levels below λ. Then, $P_\lambda \in \underline{\mathfrak{S}}_{1,1}$ for any $\lambda \in \mathbb{R}$ and there is a constant $C > 0$ (depending only on $d \geq 1$) such that*

$$\underline{\mathrm{Tr}}\,(P_\lambda) \leq C\left(\mathbb{E}\left(\int_Q (V-\lambda)_-^{\frac{d+2}{2}}\right)\right)^{\frac{d}{d+2}}, \tag{2.17}$$

and

$$\underline{\mathrm{Tr}}\,(-\Delta P_\lambda) \leq C\,\mathbb{E}\left(\int_Q (V-\lambda)_-^{\frac{d+2}{2}}\right).$$

The estimate (2.17) on $\underline{\mathrm{Tr}}\,(P_\lambda)$ is probably not optimal but it is sufficient for our purposes.

Proof. Let us first prove that $P_\lambda \in \underline{\mathfrak{S}}_{1,1}$ under the assumption that $V_- \in L^\infty\left(\Omega \times \mathbb{R}^d\right)$. The general case will then follow from an approximation argument. By the Feynman-Kac formula [143, Theorem 6.2 p.51], we have for all $t > 0$

$$\rho_{e^{-t(-\Delta+V)}} \leq \frac{e^{t\|V_-\|_{L^\infty(\mathbb{R}^d)}}}{(4\pi t)^{d/2}} \quad \text{a.s.}$$

Then, using the inequality $1_{(-\infty,\lambda]}(x) \leq e^{-t(x-\lambda)}$, we have

$$\rho_{P_\lambda} \leq \rho_{e^{-t(-\Delta+V-\lambda)}} \leq \frac{e^{t\|(V-\lambda)_-\|_{L^\infty(\mathbb{R}^d)}}}{(4\pi t)^{d/2}} \text{ a.s.} \tag{2.18}$$

By the assumption that V is uniformly bounded from below, we deduce that $\rho_{P_\lambda} \in L^\infty\left(\Omega \times \mathbb{R}^d\right)$. Likewise, using the inequality $x1_{(-\infty,\lambda]}(x) \leq \lambda 1_{\lambda\geq 0} e^{-t(x-\lambda)}$, we obtain that

$$\rho_{HP_\lambda} \leq \lambda 1_{\lambda\geq 0}\rho_{e^{-t(-\Delta+V-\lambda)}} \leq \lambda 1_{\lambda\geq 0}\frac{e^{t\|(V-\lambda)_-\|_{L^\infty(\mathbb{R}^d)}}}{(4\pi t)^{d/2}} \text{ a.s.}$$

Therefore

$$\rho_{-\Delta P_\lambda} \leq \lambda 1_{\lambda\geq 0}\frac{e^{t\|(V-\lambda)_-\|_{L^\infty(\mathbb{R}^d)}}}{(4\pi t)^{d/2}} - V\rho_{P_\lambda} \text{ a.s.} \tag{2.19}$$

Since $\rho_{P_\lambda} \in L^\infty\left(\Omega \times \mathbb{R}^d\right)$, then the RHS of (2.19) is in L^1_s and $-\Delta P_\lambda \in \underline{\mathfrak{S}}_1$. Hence $P_\lambda \in \underline{\mathfrak{S}}_{1,1}$.

Now that we know that $P_\lambda \in \underline{\mathfrak{S}}_{1,1}$, we can derive bounds which only depend on $\|(V-\lambda)_-\|_{L^{1+d/2}_s}$. We start by noting that by the Lieb-Thirring inequality (2.8) for ergodic operators, we have

$$\begin{aligned} 0 \leq \underline{\mathrm{Tr}}\left((-\Delta+V-\lambda)_-\right) &= -\underline{\mathrm{Tr}}\left((-\Delta+V-\lambda)P_\lambda\right) \\ &\leq -C\|\rho_{P_\lambda}\|^{\frac{d+2}{d}}_{L_s^{\frac{d+2}{d}}} + \left\|(V-\lambda)_-\right\|_{L_s^{\frac{d+2}{2}}}\|\rho_{P_\lambda}\|_{L_s^{\frac{d+2}{d}}}. \end{aligned}$$

Therefore

$$\|\rho_{P_\lambda}\|_{L_s^{\frac{d+2}{d}}} \leq C\left\|(V-\lambda)_-\right\|^{\frac{d}{2}}_{L_s^{\frac{d+2}{2}}} \tag{2.20}$$

and

$$\underline{\mathrm{Tr}}\left(P_\lambda\right) = \|\rho_{P_\lambda}\|_{L^1_s} \leq C\|\rho_{P_\lambda}\|_{L_s^{\frac{d+2}{d}}} \leq C\left\|(V-\lambda)_-\right\|^{\frac{d}{2}}_{L_s^{\frac{d+2}{2}}}. \tag{2.21}$$

As $0 \leq -\underline{\mathrm{Tr}}\left((-\Delta+V-\lambda)P_\lambda\right)$, then using (2.20), we obtain

$$\begin{aligned} \underline{\mathrm{Tr}}\left(-\Delta P_\lambda\right) \leq -\underline{\mathrm{Tr}}\left((V-\lambda)P_\lambda\right) &\leq C\left\|(V-\lambda)_-\right\|_{L_s^{\frac{d+2}{2}}}\|\rho_{P_\lambda}\|_{L_s^{\frac{d+2}{d}}} \\ &\leq C\left\|(V-\lambda)_-\right\|^{\frac{d+2}{2}}_{L_s^{\frac{d+2}{2}}}. \end{aligned} \tag{2.22}$$

This concludes the proof in the case of bounded below potentials. In the general case we consider the sequences of cutoff potentials $V_n = \max\{V, -n\}$ and corresponding operators $H_n = -\Delta + V_n$ and show that for any bounded

continuous function f, the operator $f(H_n)$ converges to $f(H)$ weakly-$*$ in $L^\infty(\Omega,\mathcal{B})$. Indeed, since $C_c^\infty\left(\mathbb{R}^d\right)$ is a common core for all the operators H_n a.s. and since, for each $\varphi \in C_c^\infty\left(\mathbb{R}^d\right)$, we have that $H_n\varphi$ converges to $H\varphi$ in $L^2\left(\mathbb{R}^d\right)$ a.s., we conclude that H_n converges to H in the strong resolvent sense a.s. (see [34, Proposition I.1.8, p.8]). Therefore $f(H_n)$ converges to $f(H)$ in the strong operator topology a.s. (see [131, Theorem VIII.20, p.286]). Finally, as f is bounded, then for any $\varphi,\psi \in L^2(\mathbb{R}^d)$, we have $|\langle\varphi, f(H_n)\psi\rangle| \leq C\,\|\varphi\|\,\|\psi\|$ a.s. We deduce by the dominated convergence theorem that for any $u \in L^\infty(\Omega)$, $\mathbb{E}\left(u\langle\varphi, f(H_n)\psi\rangle\right)$ converges to $\mathbb{E}\left(u\langle\varphi, f(H_n)\psi\rangle\right)$, which implies the weak-$*$ convergence of $f(H_n)$ to $f(H)$.

Let now $\lambda \in \mathbb{R}$, $\varepsilon > 0$ and f_ε be a continuous function satisfying

$$1_{(-\infty,\lambda]} \leq f_\varepsilon \leq 1_{(-\infty,\lambda+\varepsilon)}.$$

Using Fatou's Lemma and the weak-$*$ convergence of $f_\varepsilon(H_n)$ to $f_\varepsilon(H)$, we deduce in the same way as in (2.13) and (2.14) that $f_\varepsilon(H) \in \underline{\mathfrak{S}}_{1,1}$ and

$$\underline{\mathrm{Tr}}\,\left(f_\varepsilon(H)\right) \leq \liminf_{n\to\infty} \underline{\mathrm{Tr}}\,\left(f_\varepsilon(H_n)\right)$$

and

$$\underline{\mathrm{Tr}}\,\left(-\Delta f_\varepsilon(H)\right) \leq \liminf_{n\to\infty} \underline{\mathrm{Tr}}\,\left(-\Delta f_\varepsilon(H_n)\right).$$

Besides, for any $n \in \mathbb{N}$ and $1 \leq j \leq d$, we have

$$P_\lambda \leq f_\varepsilon(H), \quad f_\varepsilon(H_n) \leq 1_{H_n\leq\lambda+\varepsilon},$$

$$P_jP_\lambda P_j \leq P_jf_\varepsilon(H)P_j \quad \text{and} \quad P_jf_\varepsilon(H_n)P_j \leq P_j1_{H_n\leq\lambda+\varepsilon}P_j.$$

Therefore,

$$\underline{\mathrm{Tr}}\,\left(P_\lambda\right) \leq \liminf_{n\to\infty} \underline{\mathrm{Tr}}\,\left(1_{H_n\leq\lambda+\varepsilon}\right)$$

and

$$\underline{\mathrm{Tr}}\,\left(-\Delta P_\lambda\right) \leq \liminf_{n\to\infty} \underline{\mathrm{Tr}}\,\left(-\Delta 1_{H_n\leq\lambda+\varepsilon}\right).$$

Finally, as for any $n \in \mathbb{N}$, the potential V_n is uniformly bounded below, then we can use (2.21) and (2.22) for the operators H_n. We get

$$\begin{aligned}\underline{\mathrm{Tr}}\,\left(P_\lambda\right) \leq \liminf_{n\to\infty} \underline{\mathrm{Tr}}\,\left(1_{H_n\leq\lambda+\varepsilon}\right) &\leq C\left\|\left(V_n-\lambda-\varepsilon\right)_-\right\|^{\frac{d}{2}}_{L_s^{\frac{d+2}{2}}}\\ &\leq C\left\|\left(V-\lambda-\varepsilon\right)_-\right\|^{\frac{d}{2}}_{L_s^{\frac{d+2}{2}}}. \qquad (2.23)\end{aligned}$$

Similarly, for the kinetic energy term, we obtain

$$\underline{\mathrm{Tr}}\,\left(-\Delta P_\lambda\right) \leq \liminf_{n\to\infty} \underline{\mathrm{Tr}}\,\left(-\Delta 1_{H_n\leq\lambda+\varepsilon}\right) \leq C\left\|\left(V-\lambda-\varepsilon\right)_-\right\|^{\frac{d+2}{2}}_{L_s^{\frac{d+2}{2}}}. \qquad (2.24)$$

Letting ε go to zero in (2.23) and (2.24), we conclude the proof of the proposition. □

We can now use the previous theorem to deduce a useful variational characterization of the spectral projection P_λ among all ergodic fermionic density matrices $\gamma \in \mathcal{K}$ having a locally finite kinetic energy.

Proposition 2.2.15 (Variational characterization of spectral projections)**.** *Assume that V is as in Proposition 2.2.14 and denote again $P_\lambda := 1_{(-\infty,\lambda)}(H)$ with $H = -\Delta + V$. For every $\lambda \in \mathbb{R}$, the minimization problem*

$$\inf_{\gamma \in \mathcal{K}} \left\{ \underline{\mathrm{Tr}}\,(-\Delta\gamma) + \mathbb{E}\left(\int_Q V\,\rho_\gamma \right) - \lambda\,\underline{\mathrm{Tr}}\,(\gamma) \right\} \tag{2.25}$$

admits as unique minimizers the operators of the form $\gamma = P_\lambda + \delta$ where $0 \leq \delta \leq 1_{\{\lambda\}}(H)$.

Note that $\mathbb{E}(\int_Q V\,\rho_\gamma)$ is well defined in $(-\infty, +\infty]$ since $V_- \in L^{1+d/2}_s$ by assumption, whereas $\rho_\gamma \in L^{1+2/d}_s$ by the Lieb-Thirring inequality (2.8).

Proof. When γ is smooth enough ($-\Delta\gamma \in \underline{\mathfrak{S}}_1$ for example) and $V \in L^\infty_s$, we can write

$$\begin{aligned} &\underline{\mathrm{Tr}}\,(-\Delta(\gamma - P_\lambda)) + \mathbb{E}\left(\int_Q V\,(\rho_\gamma - \rho_{P_\lambda}) \right) - \lambda \underline{\mathrm{Tr}}\,(\gamma - P_\lambda) \\ &\qquad = \underline{\mathrm{Tr}}\,((-\Delta + V - \lambda)(\gamma - P_\lambda)) \geq \underline{\mathrm{Tr}}\,\left(|-\Delta + V - \lambda|(\gamma - P_\lambda)^2 \right). \end{aligned}$$

In the last estimate we have used the cyclicity property (2.7) and the fact that

$$P_\lambda^\perp(\gamma - P_\lambda)P_\lambda^\perp - P_\lambda(\gamma - P_\lambda)P_\lambda \geq (\gamma - P_\lambda)^2,$$

which turns out to be equivalent to $0 \leq \gamma \leq 1$. Here, we use the notation $P^\perp = 1 - P$, for any orthogonal projector P. A simple approximation argument now shows that the inequality

$$\begin{aligned} \underline{\mathrm{Tr}}\,(-\Delta\gamma) + \mathbb{E}\left(\int_Q V\,\rho_\gamma \right) - \lambda \underline{\mathrm{Tr}}\,(\gamma) \geq \underline{\mathrm{Tr}}\,(-\Delta P_\lambda) + \mathbb{E}\left(\int_Q V\,\rho_{P_\lambda} \right) - \lambda \underline{\mathrm{Tr}}\,(P_\lambda) \\ + \underline{\mathrm{Tr}}\,\left(|H - \lambda|^{1/2}(\gamma - P_\lambda)^2 |H - \lambda|^{1/2} \right) \end{aligned}$$

is actually valid under the weaker assumptions of the proposition. It is then clear that P_λ minimizes (2.25) and that the other minimizers must satisfy $|H - \lambda|^{1/2}(\gamma - P_\lambda) = 0$, which is the same as saying that the range of $\gamma - P_\lambda$ is included in the kernel of $H - \lambda$. □

2.2.3.5 A representability criterion

In the ergodic case, we know that a density ρ must satisfy $\rho \geq 0$, $\sqrt{\rho} \in H^1_s$ and $\rho \in L^{1+2/d}_s$, by the Lieb-Thirring inequality (2.8). Clearly a stationary

function ρ such that $\rho \geq 0$ and $\sqrt{\rho} \in H^1_s$ is not necessarily the density of an ergodic density matrix with finite kinetic energy, since in general

$$\left\{\rho \geq 0 \mid \sqrt{\rho} \in H^1_s\right\} \not\subset L_s^{\frac{d+2}{d}}.$$

It is an interesting open problem to determine the exact representability conditions in the ergodic case. Theorem 2.2.16 below gives sufficient conditions for ρ to be representable. These conditions are also necessary for $d = 1$.

Theorem 2.2.16 (A sufficient condition for representability)**.** *We assume that $d \geq 1$. Let ρ be a function satisfying*

$$\rho \geq 0,\ \rho \in L^3_s \text{ and } \sqrt{\rho} \in H^1_s.$$

Then, there exists a self-adjoint operator γ in $\underline{\mathfrak{S}}_{1,1} \cap \underline{\mathcal{S}}$, satisfying $0 \leq \gamma \leq 1$ and $\rho_\gamma = \rho$ a.s.

The proof of Theorem 2.2.16 follows the ideas of Lieb [107].

Proof. We start with the case $d = 1$. We consider two functions $\varphi_0, \varphi_1 \in C^\infty_c(\mathbb{R})$ satisfying

- $\varphi_0 \geq 0$, $\varphi_1 \geq 0$,
- $\mathrm{supp}(\varphi_0) \subset \left[-\frac{1}{2}, \frac{1}{2}\right]$ and $\mathrm{supp}(\varphi_1) \subset [0, 1]$,
- $\sum_{k\in\mathbb{Z}} \varphi_k = 2$ where $\varphi_{2k}(\cdot) = \varphi_0(\cdot - k)$ and $\varphi_{2k+1}(\cdot) = \varphi_1(\cdot - k)$.

Such two functions can be constructed by considering a function $\varphi_0 \in C^\infty_c(\mathbb{R}^d)$, with support in $\left[-\frac{1}{2}, \frac{1}{2}\right]$ such that $\varphi_0 \equiv 2$ on $\left[-\frac{1}{4}, \frac{1}{4}\right]$ and $0 \leq \varphi_0 \leq 2$, and define the function φ_1 as follow

$$\begin{cases} \varphi_1(x) = 2 - \varphi_0(x) & , \quad x \in [0, \frac{1}{2}] \\ \varphi_1(x) = 2 - \varphi_0(x-1) & , \quad x \in [\frac{1}{2}, 1] \end{cases}$$

(see Figure 2.1).

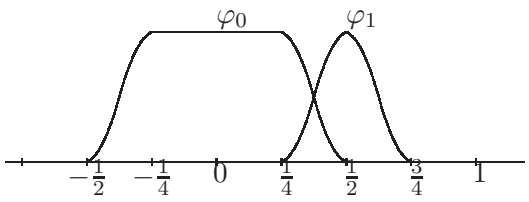

Figure 2.1: Example of functions φ_0 and φ_1 used in the proof of of Theorem 2.2.16.

We denote by

$$\rho_k(\omega, x) := \rho(\omega, x)\varphi_k(x),$$

and observe that $\rho = \sum_{k\in\mathbb{Z}} \rho_k/2$. Let

$$N_k(\omega) = \int_{\mathbb{R}^d} \rho_k(\omega, x)\, dx.$$

For each $k \in \mathbb{Z}$, we set $\varphi_{j,k}(\omega, x) = 0$ for all $j \in \mathbb{Z}$ if $N_k(\omega) = 0$, and

$$\varphi_{j,k}(\omega, x) = \frac{\sqrt{\rho_k(\omega, x)}}{\sqrt{N_k(\omega)}} \exp\left(\frac{2i\pi j}{N_k(\omega)} \int_{-\infty}^{x} \rho_k(\omega, t)\, dt\right)$$

otherwise. If $N_k(\omega) \neq 0$, then the family of functions $(\varphi_{j,k}(\omega, \cdot))_{j\in\mathbb{Z}^d}$ is an orthonormal family of $L^2(\mathbb{R})$ and for each $j \in \mathbb{Z}$, $\varphi_{j,k}(\omega, \cdot) \in H^1(\mathbb{R})$. Indeed, let $j \neq j' \in \mathbb{Z}$. We have

$$\begin{aligned}\int_{\mathbb{R}} |\varphi_{j,k}(\omega, x)|^2\, dx &= \int_{\mathbb{R}} \frac{\rho_k(\omega, x)}{N_k(\omega)}\, dx \\ &= 1\end{aligned}$$

and

$$\begin{aligned}\int_{\mathbb{R}} \overline{\varphi_{j,k}}(\omega, x)\varphi_{j',k}(\omega, x)\, dx &= \int_{\mathbb{R}} \frac{\rho_k(\omega, x)}{N_k(\omega)} \exp\left(\frac{2i\pi(j'-j)}{N_k(\omega)} \int_{-\infty}^{x} \rho_k(\omega, t)\, dt\right) \\ &= \frac{1}{2i\pi(j'-j)} \left[\exp\left(\frac{2i\pi(j'-j)}{N_k(\omega)} \int_{-\infty}^{x} \rho_k(\omega, t)\, dt\right)\right]_{-\infty}^{+\infty} \\ &= \frac{1}{2i\pi(j'-j)} \left(\exp\left(\frac{2i\pi(j'-j)}{N_k(\omega)} N_k(\omega)\right) - 1\right) = 0.\end{aligned}$$

Moreover,

$$\begin{aligned}\nabla\varphi_{j,k}(\omega, x) = &\left(\frac{\nabla\sqrt{\rho_k(\omega, x)}}{\sqrt{N_k(\omega)}} + \frac{\sqrt{\rho_k(\omega, x)}}{\sqrt{N_k(\omega)}} \frac{2i\pi j}{N_k(\omega)} \rho_k(\omega, x)\right) \\ &\times \exp\left(\frac{2i\pi j}{N_k(\omega)} \int_{-\infty}^{x} \rho_k(\omega, t)\, dt\right).\end{aligned}$$

As $\rho_k(\omega, \cdot)$ has a compact support, then by the assumptions that $\sqrt{\rho} \in H^1_s$ and $\rho \in L^3_s$, we have $\sqrt{\rho_k}(\omega, \cdot) \in H^1(\mathbb{R})$ and $\rho_k(\omega, x) \in L^3(\mathbb{R})$ almost surely and

$$\|\nabla\varphi_{j,k}(\omega, x)\|_{L^2(\mathbb{R})} \leq \frac{1}{\sqrt{N_k(\omega)}} \left\|\sqrt{\rho_k(\omega, x)}\right\|_{H^1(\mathbb{R})} + \frac{2\pi j}{N_k(\omega)^{\frac{3}{2}}} \|\rho_k\|^{\frac{3}{2}}_{L^3(\mathbb{R})}.$$

For $k \in \mathbb{Z}$, we introduce the density matrix

$$\gamma_k = \sum_{j=1}^{\infty} n_{j,k} \left|\varphi_{j,k}\right\rangle\left\langle \varphi_{j,k}\right|,$$

where $n_{j,k}(\omega) = 1_{1\leq j\leq N_k(\omega)} + (N_k(\omega) - [N_k(\omega)])1_{j=[N_k(\omega)]+1}$. Almost surely, $\gamma_k(\omega)$ is in $\{\gamma \in \mathfrak{S}_1 \cap \mathcal{S} \mid 0 \leq \gamma \leq 1,\ \mathrm{Tr}\ (-\Delta\gamma) < \infty\}$ and $\rho_{\gamma_k}(\omega,\cdot) = \rho_k(\omega,\cdot)$. Indeed, it is easy to check that γ_k is self adjoint and $0 \leq \gamma_k \leq 1$ a.s. The density of γ_k is given by

$$\rho_{\gamma_k} = \sum_{j\in\mathbb{Z}} n_{j,k} \left|\varphi_{j,k}\right|^2 = \sum_{j\in\mathbb{Z}} n_{j,k} \frac{\rho_k}{N_k} 1_{N_k\neq 0} = \rho_k.$$

Thus

$$\mathrm{Tr}\ (\gamma_k) = \int_{\mathbb{R}^d} \rho_k = N_k.$$

It follows that

$$\mathbb{E}\left(\mathrm{Tr}\ (\gamma_k)\right) = \mathbb{E}\left(\int_{\mathbb{R}} \rho_k\right) \leq \left\|\rho\right\|_{L^1_s}. \tag{2.26}$$

Similarly for the kinetic energy, we have

$$\begin{aligned}
&\mathrm{Tr}\ (-\Delta\gamma_k) \\
&\quad = \sum_{j\in\mathbb{Z}} n_{j,k} \left\|\nabla\varphi_{j,k}\right\|^2_{L^2(\mathbb{R})} \\
&\quad \leq N_k \frac{1}{N_k} \left\|\sqrt{\rho_k}\right\|^2_{H^1(\mathbb{R})} 1_{N_k\neq 0} + 2\sum_{j\in\mathbb{Z}} n_{j,k} \frac{4\pi^2 j^2}{N_k^3} \left\|\rho_k\right\|^3_{L^3(\mathbb{R})} 1_{N_k\neq 0} \\
&\quad = 2\left\|\sqrt{\rho_k}\right\|^2_{H^1(\mathbb{R})} + 8\pi^2 \frac{\sum_{j=1}^{[N_k]} j^2 + (N_k - [N_k])([N_k]+1)^2}{N_k^3} \left\|\rho_k\right\|^3_{L^3(\mathbb{R})} 1_{N_k\neq 0} \\
&\quad \leq 2\left\|\sqrt{\rho_k}\right\|^2_{H^1(\mathbb{R})} + C\left\|\rho_k\right\|^3_{L^3(\mathbb{R})}.
\end{aligned}$$

Therefore

$$\begin{aligned}
\mathbb{E}\left(\mathrm{Tr}\ (-\Delta\gamma_k)\right) &\leq 2\mathbb{E}\left(\left\|\sqrt{\rho_k(\omega,x)}\right\|^2_{H^1(\mathbb{R})}\right) + C\mathbb{E}\left(\left\|\rho_k\right\|^3_{L^3(\mathbb{R})}\right) \\
&\leq C\left(\left\|\sqrt{\rho}\right\|^2_{H^1_s} + \left\|\rho\right\|^3_{L^3_s}\right).
\end{aligned} \tag{2.27}$$

Since the supports of the kernels of γ_k and γ_{k+2l} are disjoints for all $k, l \in \mathbb{Z}$, and since the operators γ_k are uniformly bounded, the operators $\gamma_e = \sum_{k\in\mathbb{Z}} \gamma_{2k}$ and $\gamma_o = \sum_{k\in\mathbb{Z}} \gamma_{2k+1}$ are well defined as operators on $L^2(\mathbb{R})$, self-adjoint and satisfy $0 \leq \gamma_o, \gamma_e \leq 1$ a.s. Moreover, they are ergodic operators. Indeed, as ρ is stationary, we have for all $R, k \in \mathbb{Z}$, a.s. $\omega \in \Omega$ and a.e. $x \in \mathbb{R}$

$$\begin{aligned}
\rho_{2k}\left(\tau_R(\omega), x\right) &= \rho(\tau_R(\omega), x)\varphi_{2k}(x) \\
&= \rho(\tau_R(\omega), x)\varphi_0(x-k) \\
&= \rho(\omega, x+R)\varphi_0(x+R-(R+k)) \\
&= \rho_{2(R+k)}(\omega, R+x).
\end{aligned}$$

Therefore, for all $j \in \mathbb{N}$,

$$\varphi_{j,2k}\left(\tau_R(\omega), x\right) = \varphi_{j,2(k+R)}(\omega, x+R),$$

and

$$n_{j,2k}(\tau_R(\omega)) = n_{j,2(k+R)}(\omega).$$

It follows that

$$\begin{aligned}
\gamma_e(\tau_R(\omega)) &= \sum_{k\in\mathbb{Z}}\sum_{j\in\mathbb{N}} n_{j,2k}\left(\tau_R\left(\omega\right)\right) \left|\varphi_{j,k}(\tau_R(\omega),\cdot)\right\rangle\left\langle\varphi_{j,k}(\tau_R(\omega),\cdot)\right| \\
&= \sum_{k\in\mathbb{Z}}\sum_{j\in\mathbb{N}} n_{j,2(k+R)}\left(\omega\right) \left|U_R\varphi_{j,2(R+k)}(\omega,\cdot)\right\rangle\left\langle U_R\varphi_{j,2(R+k)}(\omega,\cdot)\right| \\
&= \sum_{k\in\mathbb{Z}}\sum_{j\in\mathbb{N}} U_R n_{j,2(k+R)}\left(\omega\right) \left|\varphi_{j,2(R+k)}(\omega,\cdot)\right\rangle\left\langle\varphi_{j,2(R+k)}(\omega,\cdot)\right| U_R^* \\
&= U_R\gamma_e(\omega)U_R^*,
\end{aligned}$$

which proves that γ_e is ergodic. We proceed similarly for γ_o. By (2.26) and (2.27), we deduce that γ_o and γ_e are locally trace class and have locally finite kinetic energy. It follows that γ_o and γ_e are in the set $\mathcal{K} = \left\{\gamma \in \underline{\mathfrak{S}}_{1,1} \cap \underline{\mathcal{S}},\ 0 \le \gamma \le 1 \text{ a.s.}\right\}$. By the convexity of $\mathcal{K}$, so is $\gamma = \frac{\gamma_e+\gamma_o}{2}$. It is finally easily checked that $\rho_\gamma = \rho$.

We now turn to the case $d = 2$. In the same spirit as for $d = 1$, we cover the space with a finite number of periodic patterns, in such a way that the elements of each pattern do not intersect (see Figure 2.2). For example, let

$$A_0 = \left[-\frac{5}{12}, \frac{5}{12}\right)^2,\ B_0 = \left[\frac{1}{3}, \frac{2}{3}\right)\times\left[-\frac{1}{4}, \frac{1}{4}\right)\cup\left[-\frac{1}{4}, \frac{1}{4}\right)\times\left[\frac{1}{3}, \frac{2}{3}\right),\ C_0 = \left[\frac{1}{6}, \frac{5}{6}\right)^2.$$

The $\mathbb{Z}^2$-translations of these sets $I_k = I_0+k$, $I \in \{A, B, C\}$, satisfy $I_k \cap I_j = \emptyset$ for $k \neq j$ and $\cup_{k\in\mathbb{Z}^2} A_k \cup B_k \cup C_k = \mathbb{R}^2$. Next, we consider three sequences of regular functions $(\varphi_k^I)_{k\in\mathbb{Z}^d}$, $I \in \{A, B, C\}$, such that

$$\varphi_k^I \ge 0, \quad \mathrm{supp}(\varphi_k^I) \subset I_k, \quad \text{and } \sum_{k\in\mathbb{Z}^2} \varphi_k^A + \varphi_k^B + \varphi_k^C = 3.$$

Repeating the argument detailed above in the one-dimensional case, we define γ_I, for $I \in \{A, B, C\}$, and $\gamma = \sum_{I\in\{A,B,C\}} \gamma_I/3$ and we check that $\rho_\gamma = \rho$ and that γ satisfies the desired conditions. We proceed similarly for $d \ge 3$. □

2.3 Yukawa and Coulomb interaction

This section is devoted to the definition of the potential energy per unit volume of a stationary charge distribution f. In our setting, f will be $\rho_\gamma - \mu$,

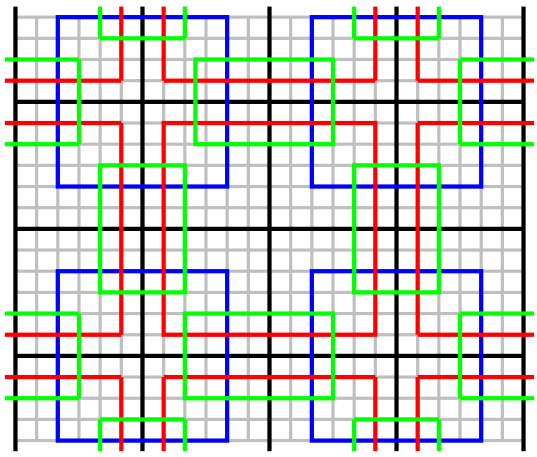

Figure 2.2: Covering in dimension $d = 2$ used in the proof of Theorem 2.2.16.

where μ is the nuclear charge distribution and ρ_γ is the density associated with an electronic state γ. We will consider two types of interactions, namely the (long-range) Coulomb and the (short-range) Yukawa interactions.

In dimension $d \geq 1$, the Coulomb self-interaction of a charge density f is given by

$$D(f,f) = \int_{\mathbb{R}^d} V(x)\, f(x)\, dx,$$

where V is the Coulomb potential induced by f itself, which is solution to Poisson's equation

$$-\Delta V = |S^{d-1}|\, f. \tag{2.28}$$

Here $|S^{d-1}|$ is the Lebesgue measure of the unit sphere S^{d-1} ($|S^0| = 2$, $|S^1| = 2\pi$, $|S^2| = 4\pi$). For later purposes, it is convenient to regularize this equation by adding a small mass m as follows :

$$(-\Delta + m^2)V = |S^{d-1}|\, f. \tag{2.29}$$

Whenever $m = 0$ or $m > 0$, we have the following formulas for the Coulomb ($m = 0$) and Yukawa ($m > 0$) self-energies:

$$D_m(f,f) = \left|S^{d-1}\right| \int_{\mathbb{R}^d} \frac{\left|\widehat{f}\,(K)\right|^2}{|K|^2 + m^2}\, dK = \left|S^{d-1}\right| \left\| \left(-\Delta + m^2\right)^{-\frac{1}{2}} f \right\|_{L^2}^2 \tag{2.30}$$

$$= \int_{\mathbb{R}^d} \int_{\mathbb{R}^d} Y_m(x-y) f(x)\, f(y)\, dx\, dy \tag{2.31}$$

$$= \int_{\mathbb{R}^d} \left| \int_{\mathbb{R}^d} W_m(x-y) f(y)\, dy \right|^2 dx. \tag{2.32}$$

Here $\widehat{f}$ is the Fourier transform[1] of f. Of course we need appropriate decay and integrability assumptions on f to make the previous formulas meaningful. The Yukawa and Coulomb kernels are given by

$$Y_m(x) = \begin{cases} m^{-1}e^{-m|x|} \\ K_0(m|x|) \\ |x|^{-1}e^{-m|x|} \end{cases} \quad \text{and} \quad Y_0(x) = \begin{cases} -|x| & \text{if } d=1, \\ -\log(|x|) & \text{if } d=2, \\ |x|^{-1} & \text{if } d=3, \end{cases}$$

with $K_0(r) = \int_0^\infty e^{-r\cosh t}\,dt$ the modified Bessel function of the second type [110]. The Coulomb potential is nothing but the limit of the Yukawa potential when the parameter m goes to 0. Similarly, the function W_m is defined by its Fourier transform

$$\widehat{W_m}(K) = \frac{\sqrt{|S^{d-1}|}(2\pi)^{-d/2}}{\sqrt{m^2+|K|^2}}.$$

Using the integral representation $x^{-1/2} = 2\pi^{-1}\int_0^\infty (x+s^2)^{-1}ds$, we see that

$$W_m(x) = \frac{2}{\pi\sqrt{|S^{d-1}|}}\int_0^\infty Y_{\sqrt{s^2+m^2}}(x)\,ds. \tag{2.33}$$

This can be used to compute W_m in some cases, or to simply deduce that, when $m>0$, W_m is positive, decays exponentially at infinity, and behaves at zero like $|x|^{-2}$ in dimension $d=3$, like $|x|^{-1}$ when $d=2$ and like $\log|x|$ for $d=1$.

Our goal in this section is to define the Yukawa and Coulomb energies per unit volume for a stationary charge distribution f. Formally, this is just

$$\mathbb{E}\left(\int_Q V f\right)$$

where V solves (2.28) for $m=0$ or (2.29) for $m>0$. We are implicitly using here the fact that the potential V is stationary when f has this property. Unfortunately, giving a meaning to Poisson's equation (2.28) in the stochastic setting in not an easy task. Already when f is periodic, we know that this equation can only have a solution when $\int_Q f = 0$. Here the situation is even worse, as we explain below. To simplify matters, we first introduce the Yukawa energy per unit volume $D_m(f,f)$ for $m>0$ and then we define the Coulomb energy as the limit of $D_m(f,f)$ as $m\to 0$, when it exists. Thus we start by giving a clear meaning to the three possible formulas (2.30), (2.31) and (2.32) in the Yukawa case $m>0$. In the next section we introduce the *stationary Laplacian* $-\Delta_s$ which allows to write a formula similar to (2.30).

[1] We use the convention $\widehat{f}(K) = (2\pi)^{-\frac{d}{2}}\int_{\mathbb{R}^d} f(x)\,e^{-iK\cdot x}dx$.

2.3.1 The stationary Laplacian

In this section we define an operator which we call the *stationary Laplacian*, which is nothing but the usual Laplacian in the x variable acting on $L^2(\Omega \times Q)$, with stationary boundary conditions at the boundary of Q. Surprisingly, this operator does not seem to have been considered before.

Let A_0 be the operator on L^2_s defined by

$$\begin{cases} D(A_0) = L^2_s \cap L^2(\Omega, C^2(\mathbb{R}^d)), \\ A_0 f(\omega, x) = -\Delta f(\omega, x) \text{ a.s. and a.e., } \forall f \in D(A_0), \end{cases}$$

where $\Delta = \sum_{j=1}^d \partial^2_{x_j}$ refers to the usual Laplace operator on $C^2(\mathbb{R}^d)$ with respect to the x variable. For $f, g \in D(A_0)$, we have

$$\begin{aligned} \langle g, A_0 f \rangle_{L^2_s} &= \mathbb{E}\left(- \int_Q \overline{g(\cdot,x)} \Delta f(\cdot,x)\, dx \right) \\ &= \mathbb{E}\left(\int_Q \overline{\nabla_x g(\cdot,x)} \cdot \nabla_x f(\cdot,x)\, dx \right) - \mathbb{E}\left(\int_{\partial Q} \overline{g(\cdot,x)} \nabla_x f(\cdot,x) \cdot n\, dx \right), \end{aligned} \tag{2.34}$$

∂Q is the boundary of the cube Q and n is the exterior normal vector. We denote by $F_i^{\pm} = \left\{ x \in \partial Q \mid x_i = \pm \frac{1}{2} \right\}$. Then,

$$\mathbb{E}\left(\int_{\partial Q} \overline{g(\cdot,x)} \nabla_x f(\cdot,x) \cdot n\, dx \right) = \sum_{i=1}^d \mathbb{E}\left(\int_{F_i^+ \cup F_i^-} \overline{g(\cdot,x)} \nabla_x f(\cdot,x) \cdot n\, dx \right).$$

Denoting by e_i the unit vector in the direction i, for $1 \le i \le d$, we have

$$\begin{aligned} \mathbb{E}\left(\int_{F_i^+} \overline{g(\cdot,x)} \nabla_x f(\cdot,x) \cdot n\, dx \right) &= \mathbb{E}\left(\int_{F_i^-} \overline{g(\cdot, x+e_i)} \nabla_x f(\cdot, x+e_i) \cdot e_i\, dx \right) \\ &= \mathbb{E}\left(\int_{F_i^-} \overline{g(\tau_{e_i}(\cdot), x)} \nabla_x f(\tau_{e_i}(\cdot), x) \cdot e_i\, dx \right) \\ &= -\mathbb{E}\left(\int_{F_i^-} \overline{g(\cdot,x)} \nabla_x f(\cdot,x) \cdot (-e_i)\, dx \right) \\ &= -\mathbb{E}\left(\int_{F_i^-} \overline{g(\cdot,x)} \nabla_x f(\cdot,x) \cdot n\, dx \right), \end{aligned}$$

where we have used that f and g are stationary and that τ is measure preserving. Thus the second term of the right hand side of (2.34) vanishes and we conclude that

$$\langle g, A_0 f \rangle_{L^2_s} = \mathbb{E}\left(\int_Q \nabla_x \overline{g(\cdot,x)} \cdot \nabla_x f(\cdot,x)\, dx \right). \tag{2.35}$$

Thus, A_0 is a symmetric, non-negative operator on L^2_s with dense domain $D(A_0)$. We denote by $-\Delta_s$ its Friedrichs extension [148, theorem 4.1.5, p.115], and call the operator Δ_s the *stationary Laplacian*. The following proposition gives the form domain and the domain of the operator $-\Delta_s$.

Proposition 2.3.1 (Domain and form domain of $-\Delta_s$)**.** *It holds that*

$$\mathcal{Q}(-\Delta_s) = \overline{D(A_0)} = H^1_s \quad \textit{and} \quad D(-\Delta_s) = H^2_s.$$

Proof. We recall that the Friedrichs extension of A_0 is the unique self-adjoint operator A satisfying

$$D(A_0) \subset D(A) \subset \overline{D(A_0)},$$

where

$$\overline{D(A_0)} = \Big\{ f \in L^2_s,\ \exists (f_n) \in D(A_0) \text{ s.t. } f_n \longrightarrow_{n\to\infty} f \text{ in } L^2_s \text{ and } \langle f_p - f_q, A_0(f_p - f_q)\rangle_{L^2_s} \longrightarrow_{p,q\to\infty} 0 \Big\}.$$

The form domain of A is $\overline{D(A_0)}$ and its domain is given by

$$D(A) = \left\{ f \in \overline{D(A_0)},\ \exists g \in L^2_s \text{ s.t. } \forall h \in \overline{D(A_0)},\ q(f,h) = \langle g, h\rangle_{L^2_s} \right\},$$

where $q(f,f) = \lim_{n\to\infty} \langle f_n, A_0 f_n\rangle_{L^2_s}$ and (f_n) is a sequence given by the definition of $\overline{D(A_0)}$.

By (2.35), we have for any $f \in D(A_0)$

$$\langle f, A_0 f\rangle_{L^2_s} = \mathbb{E}\left(\int_Q |\nabla f|^2 \right) = \|\nabla f\|^2_{(L^2_s)^d}.$$

Therefore,

$$\mathcal{Q}(-\Delta_s) = \overline{D(A_0)} = \Big\{ f \in L^2_s,\ \exists (f_n) \in D(A_0) \text{ s.t. } f_n \longrightarrow_{n\to\infty} f \text{ in } L^2_s \text{ and } (\nabla f_n) \text{ is a Cauchy sequence in } (L^2_s)^d \Big\}.$$

It follows that for $f \in \overline{D(A_0)}$, there exists (f_n), a Cauchy sequence in H^1_s converging to f in L^2_s. Thus $f \in H^1_s$ and (f_n) converges to f in H^1_s.

Conversely, convolving $f \in H^1_s$ with a smooth approximation of the identity, one can construct a sequence $f_n \in D(A_0)$ such that (f_n) converges to f in H^1_s. This concludes the proof of $\mathcal{Q}(-\Delta_s) = \overline{D(A_0)} = H^1_s$.

We turn to the domain of $-\Delta_s$. It is easy to see that

$$D(-\Delta_s) = \left\{ f \in H^1_s,\ \exists g \in L^2_s \text{ s.t. } \forall h \in H^1_s,\ \langle \nabla f, \nabla h\rangle_{(L^2_s)^d} = \langle g, h\rangle_{L^2_s} \right\}.$$

For $f \in H^2_s$, $g = -\Delta f$ satisfies the condition of the definition. Conversely, for $f \in D(-\Delta_s)$, by the density of H^1_s in L^2_s, we deduce that $-\Delta f$, defined in the sense of distributions, is equal to g given by the definition. Therefore $-\Delta f \in L^2_s$ and $f \in H^2_s$, which concludes the proof of the Proposition.

□

When Ω is finite, the spectrum of $-\Delta_s$ is purely discrete. Indeed, we can identify H^2_s with the $n\mathbb{Z}^d$-periodic functions in $H^2_{\mathrm{loc}}(\mathbb{R}^d)$ and identify $-\Delta_s$ with $-\Delta$ with $n\mathbb{Z}^d$-periodic boundary conditions, where $n = \mathrm{card}(\Omega)$. The spectrum of the later operator is an infinite sequence of discrete eigenvalues converging to $+\infty$. We prove in Appendix 2.C.1 that if the probability space is defined as in Example 2.2.1, then $\sigma(-\Delta_s) = [0, +\infty)$.

Thanks to the ergodicity of the group action, one can prove that $\ker(-\Delta_s) = \mathrm{span}\{1\}$. Indeed, for $f \in \ker(-\Delta_s)$, (2.35) gives

$$\langle f, -\Delta_s f\rangle_{L^2_s} = \|\nabla f\|^2_{L^2_s} = 0.$$

Therefore, for a.s. $\omega \in \Omega$, we have $\nabla f(\omega, \cdot) = 0$, thus $f(\omega, \cdot) = c(\omega)$. As f is stationary, then by Proposition 2.2.4, f is a constant.

In contrast to the periodic case, there is (in general) no gap in the spectrum of $-\Delta_s$ above 0. In other words, there is no Poincaré-Wirtinger type inequality in H^1_s. This can be seen, for instance, by considering the sequence of functions $\Phi_n(\omega, x) = n^{-d/2}\Phi\left(\omega, n^{-1}x\right)$, where $\Phi(\omega, x) = \sum_{k\in\mathbb{Z}^d} Y(\tau_k(\omega))\chi(x-k)$ with $Y \in L^2(\Omega)$ and $\chi \in C^\infty_c\left(\mathbb{R}^d\right)$ with support in the unit cube Q and such that $\int_Q \chi(x)\,dx = 0$. These functions are such that $\|\Phi_n\|_{L^2_s} = \|Y\|_{L^2(\Omega)}\|\chi\|_{L^2(Q)}$ and $\mathbb{E}(\int_Q \Phi_n) = 0$ for any $n \in \mathbb{N}$, and $\|\nabla\Phi_n\|_{(L^2_s)^d} \to 0$ as $n \to \infty$.

That there is no Poincaré-Wirtinger inequality means that solving Poisson's equation (2.28) in the stochastic (ergodic) setting is complicated. Contrarily to the periodic case, it is *not* sufficient to ask that $f \in \ker(-\Delta_s)^\perp$, that is $\mathbb{E}(\int_Q f) = 0$. If we are given $f \in L^2_s$, then we see that there exists $V \in L^2_s$ such that $-\Delta_s V = |S^{d-1}|f$ if and only if f belongs to the range of $-\Delta_s$. In the next section we consider the simpler Yukawa equation (2.29).

2.3.2 The Yukawa interaction

Let $m > 0$. If $f \in L^2_s$, we can define by analogy with (2.30)

$$D_m(f, f) = \left|S^{d-1}\right| \left\|\left(-\Delta_s + m^2\right)^{-\frac{1}{2}} f\right\|^2_{L^2_s}. \tag{2.36}$$

The operator $\left(-\Delta_s + m^2\right)^{-\frac{1}{2}}$ being bounded, D_m is well-defined on L^2_s. To set up our mean-field model for disordered crystals, we however need to extend the quadratic form D_m to a larger class of functions. Formal manipulations show that for a stationary function f

$$\begin{aligned} D_m(f, f) &= \mathbb{E}\left(\int_Q \int_{\mathbb{R}^d} Y_m(x-y)\, f(\cdot, x)\, f(\cdot, y)\, dx\, dy\right) \\ &= \mathbb{E}\left(\int_Q \left|\int_{\mathbb{R}^d} W_m(x-y) f(\cdot, y)\, dy\right|^2 dx\right). \end{aligned} \tag{2.37}$$

The second formula is more suitable for a proper definition of D_m. We claim that the function $(W_m * f)(\omega, x) := \int_{\mathbb{R}^d} f(\omega, y) W_m(x-y)\, dy$ is well-defined for all $f \in L^1_s$, and is in L^1_s. This follows from the following elementary result.

Lemma 2.3.2 (Convolution of stationary functions)**.** *Let $f \in L^t_s(L^q)$ and $W \in L^p_{\mathrm{loc}}(\mathbb{R}^d)$ such that*

$$\sum_{k\in\mathbb{Z}^d} \|W\|_{L^p(Q+k)} < \infty,$$

for some $1 \le p, q, t \le \infty$. Then the function

$$(W * f)(\omega, x) := \int_{\mathbb{R}^d} f(\omega, y) W(x-y)\, dy \tag{2.38}$$

belongs to $L^t_s(L^r)$ with $1 + 1/r = 1/p + 1/q$, and

$$\|W * f\|_{L^t_s(L^r)} \le C \|f\|_{L^t_s(L^q)} \left(\sum_{k\in\mathbb{Z}^d} \|W\|_{L^p(Q+k)} \right) \tag{2.39}$$

for a constant C depending only on the dimension d. If $1 < p, q, r < \infty$, we can replace $\|W\|_{L^p(Q+k)}$ by the weak norm $\|W 1_{Q+k}\|_{L^p_w}$ in (2.39).

Proof. In order to prove the convergence of the integral in (2.38), we write

$$\begin{aligned}\int_{\mathbb{R}^d} |f(\omega, y)|\, |W(x-y)|\, dy &= \sum_{k\in\mathbb{Z}^d} \int_{Q+k} |f(\omega, y)|\, |W(x-y)|\, dy \\ &= \sum_{k\in\mathbb{Z}^d} \int_{Q} |f(\tau_k(\omega), y)|\, |W(x-y-k)|\, dy,\end{aligned}$$

where we have used the stationarity of f. By the standard Young inequality we have for a.e. $x \in Q$ and a.s.

$$\left\| \int_Q |f(\tau_k(\omega), y)|\, |W(x-y-k)|\, dy \right\|_{L^r(Q)} \le \|W(\cdot - k)\|_{L^p(2Q)} \|f(\tau_k(\omega), \cdot)\|_{L^q(Q)}$$

and therefore

$$\left\| \int_Q |f(\tau_k(\omega), y)|\, |W(x-y-k)|\, dy \right\|_{L^t_s(L^r)} \le \|W(\cdot - k)\|_{L^p(2Q)} \|f\|_{L^t_s(L^q)}.$$

The rest follows. The estimate with the weak norm $\|W 1_{Q+k}\|_{L^p_w}$ follows from the generalized Young inequality [132]. □

Since $W_m \in L^1(\mathbb{R}^d)$ and exponentially decaying when $m > 0$, Lemma 2.3.2 shows that $W_m * f \in L^1_s$ when $f \in L^1_s$. Now we can define

$$\boxed{D_m(f,f) := \mathbb{E}\left(\int_Q |W_m * f|^2\right)}$$

for any f in the space

$$\boxed{\mathcal{D}_Y := \left\{f \in L^1_s \mid W_m * f \in L^2_s\right\}}$$

which we call the space of locally integrable stationary functions with *locally finite Yukawa energy*. It is easy to see that the space $\mathcal{D}_Y$ in fact does *not* depend on $m > 0$. It is a subspace of L^1_s , with associated norm $\|f\|_{L^1_s} + D_1(f,f)^{1/2}$, and a Banach space for this norm.

Using Lemma 2.3.2, (2.33) and the known properties of W_m, we deduce the following result.

Corollary 2.3.3 (Some functions of $\mathcal{D}_Y$)**.** *We have, in dimension d,*

$$L^1_s \supset \mathcal{D}_Y \supset \begin{cases} L^2_s(L^1) & \text{if } d = 1, \\ L^2_s(L^q),\ \forall q > 1 & \text{if } d = 2, \\ L^2_s(L^{6/5}) & \text{if } d = 3. \end{cases}$$

When $f \in L^2_s$ we have that both $Y_m * f$ and $W_m * f$ belong to L^2_s, since Y_m and W_m are in $L^1(\mathbb{R}^d)$ and exponentially decaying when $m > 0$. Thus we always have $f \in \mathcal{D}_Y$ and it is then an exercise to show that all the formulas for $D_m(f,f)$ in (2.36) and (2.37) make sense and coincide. Indeed, we have

$$Y_m * f = |S^{d-1}| \left(-\Delta_s + m^2\right)^{-1} f \quad \text{and} \quad W_m * f = \sqrt{|S^{d-1}|}\, \left(-\Delta_s + m^2\right)^{-1/2} f. \tag{2.40}$$

2.3.3 The Coulomb interaction

As mentioned previously, the Coulomb potential can be seen as the limit of the Yukawa potential when the parameter $m > 0$ goes to zero. More precisely, as $0 \leq (-\Delta_s + m^2)^{-1/2} \leq (-\Delta_s + m'^2)^{-1/2}$ for all $m \geq m' > 0$, the function $m \mapsto D_m(f,f)$ is non-increasing on $(0, +\infty)$, for any $f \in \mathcal{D}_Y$. It would therefore be natural to define the average Coulomb energy per unit volume as the limit of $D_m(f,f)$ when $m \to 0$, but we will proceed slightly differently.

To simplify some later arguments, we define the Coulomb energy per unit volume by compensating the charge by a jellium background. This means we introduce for a stationary charge distribution $f \in \mathcal{D}_Y$

$$\boxed{D_0(f,f) := \lim_{m \to 0} D_m\left(f - \mathbb{E}\left(\int_Q f\right),\ f - \mathbb{E}\left(\int_Q f\right)\right),}$$

together with the associated space

$$\boxed{\mathcal{D}_C = \left\{ f \in \mathcal{D}_Y \mid \lim_{m\to 0} D_m \left(f - \mathbb{E}\left(\int_Q f\right),\, f - \mathbb{E}\left(\int_Q f\right)\right) < \infty \right\},}$$

of the locally integrable stationary charge distributions f with *locally finite Coulomb energy* (when compensated by a jellium background). We again emphasize that $\mathcal{D}_C \subset L^1_s$ by construction.

When $f \in L^2_s$, the limit is finite if and only if $f - \mathbb{E}(\int_Q f)$ belongs to the quadratic form domain of $(-\Delta_s)^{-1}$, and we have by the functional calculus

$$\begin{aligned} D_0(f,f) &= \lim_{m\to 0} D_m \left(f - \mathbb{E}\left(\int_Q f\right),\, f - \mathbb{E}\left(\int_Q f\right)\right) \\ &= \left|S^{d-1}\right| \left\| (-\Delta_s)^{-\frac{1}{2}} \left(f - \mathbb{E}\left(\int_Q f\right)\right)\right\|^2_{L^2_s}. \end{aligned}$$

For f only in $\mathcal{D}_C$, the family $(-\Delta_s + m^2)^{-1/2}(f - \mathbb{E}(\int_Q f))$ is Cauchy in L^2_s when m goes to zero and we still denote its limit by $(-\Delta_s)^{-1/2}(f - \mathbb{E}(\int_Q f))$.

The following result means, in particular, that in the physically relevant case $d = 3$, a stationary function $f \in L^2_s(L^{6/5})$ whose charge and dipole moment in the unit cell Q vanish a.s., has a finite average Coulomb energy per unit volume.

Proposition 2.3.4 (Some functions in $\mathcal{D}_C$)**.** *Let $d \le 3$ and f be a function of $L^2_s(L^q)$, with $q = 1$ if $d = 1$, $q > 1$ if $d = 2$ and $q = \frac{6}{5}$ if $d = 3$, such that*

$$q(\omega) = \int_Q f(\omega, x)\, dx = 0 \quad \text{and} \quad p(\omega) = \int_Q x f(\omega, x)\, dx = 0 \quad \text{a.s.} \tag{2.41}$$

Then, $f \in \mathcal{D}_C$.

Proof. For the sake of brevity, we only detail the proof for $d = 3$. Let f be a function of $L^2_s\left(L^{\frac{6}{5}}\right)$ satisfying (2.41). As $\mathbb{E}(\int_Q f) = 0$, we have for all $m > 0$,

$$\begin{aligned} D_m \left(f - \mathbb{E}\left(\int_Q f\right),\, f - \mathbb{E}\left(\int_Q f\right)\right) &= \mathbb{E}\left(\int_Q \int_{\mathbb{R}^d} \frac{e^{-m|x-y|}}{|x-y|} f(\cdot, y) f(\cdot, x)\, dy\, dx \right) \\ &\le C \|f\|^2_{L^2_s(L^{\frac{6}{5}})} + \mathbb{E}\left(\sum_{k\in\mathbb{Z}^3,\, |k|\ge 3} A_{m,k} \right), \end{aligned}$$

where

$$A_{m,k}(\omega) = \int_{Q\times Q} \frac{e^{-m|k+y-x|}}{|k+y-x|} f(\tau_k(\omega), y)\, f(\omega, x)\, dy\, dx.$$

Noticing that for all $m > 0$, $(x, y) \in Q \times Q$, and $k \in \mathbb{Z}^d$ such that $|k| \geq 3$,

$$\left| e^{-m|k+y-x|} - e^{-m|k|} + me^{-m|k|}(|k+y-x| - |k|) \right| \leq m^2 e^{-m|k|/2},$$

and using the fact that $q(\omega) = 0$ a.s. we obtain that

$$A_{m,k}(\omega) = (1 + m|k|)e^{-m|k|} B_{m,k}(\omega) + C_{m,k}(\omega) \text{ a.s.},$$

with

$$B_{m,k}(\omega) = \int_{Q\times Q} \frac{f(\tau_k(\omega), y) f(\omega, x)}{|k+y-x|} \, dy \, dx$$

and

$$|C_{m,k}(\omega)| \leq 2m^2 |k|^{-1} e^{-m|k|/2} \|f(\tau_k(\omega), \cdot)\|_{L^1(Q)} \|f(\omega, \cdot)\|_{L^1(Q)}.$$

Denoting by

$$F(k, h) = \frac{1}{|k+h|} - \left(\frac{1}{|k|} - \frac{e_k \cdot h}{|k|^2} + \frac{3(e_k \cdot h)^2 - |h|^2}{2|k|^3} \right),$$

where $e_k = k/|k|$, and by $M(\omega) = \int_Q f(\omega, x) \left(3x \cdot x^\perp - |x|^2\right) dx$, we have

$$\begin{aligned}
B_{m,k}(\omega) = &\int_{Q\times Q} \frac{f(\tau_k(\omega), y) f(\omega, x)}{|k|} \, dx \, dy \\
&- \int_{Q\times Q} \frac{f(\tau_k(\omega), y) f(\omega, x) \, e_k \cdot (y-x)}{|k|^2} \, dx \, dy \\
&+ \int_{Q\times Q} \frac{f(\tau_k(\omega), y) f(\omega, x) \left[3(e_k \cdot (y-x))^2 - |y-x|^2\right]}{2|k|^3} \, dx \, dy \\
&+ \int_{Q\times Q} f(\tau_k(\omega), y) f(\omega, x) F(k, y-x) \, dx \, dy \\
= &\frac{q(\omega) q(\tau_k(\omega))}{|k|} - \left[\frac{q(\omega) p(\tau_k(\omega)) - q(\tau_k(\omega)) p(\omega)}{|k|^2} \right] \cdot e_k \\
&+ \left[\frac{p(\omega) \cdot p(\tau_k(\omega)) - 3p \cdot e_k p(\tau_k(\omega)) \cdot e_k}{|k|^3} \right] \\
&+ \left[\frac{q(\tau_k(\omega)) e_k^\perp M(\omega) e_k + q(\omega) e_k^\perp M(\tau_k(\omega)) e_k}{2|k|^3} \right] \\
&+ \int_{Q\times Q} f(\tau_k(\omega), y) f(\omega, x) F(k, y-x) \, dx \, dy.
\end{aligned}$$

It then follows from (2.41) that

$$B_{m,k}(\omega) = \int_{Q\times Q} f(\tau_k(\omega), y) f(\omega, x) F(k, x-y) \, dx \, dy \text{ a.s.}$$

Thanks to the multipole expansion formula (see e.g. [102, Lemma 9]), there exists a constant C such that for all $k \in \mathbb{R}^3 \setminus \{0\}$ and $h \in \mathbb{R}^3$ with $k+h \neq 0$, $|F(k,h)| \leq \frac{C|h|^3}{|k|^3|k+h|}$. Therefore,

$$|B_{m,k}(\omega)| \leq C|k|^{-4} \left\|f\left(\omega,\cdot\right)\right\|_{L^1(Q)} \left\|f\left(\tau_k\left(\omega\right),\cdot\right)\right\|_{L^1(Q)} \quad \text{a.s.}$$

Consequently,

$$\mathbb{E}\left(\sum_{k\in\mathbb{Z}^3,\,|k|\geq 3} A_{m,k}\right) \leq C\|f\|^2_{L^2_s(L^1)} \left(\sum_{k\in\mathbb{Z}^3\setminus\{0\}} \frac{1}{|k|^4} + \sum_{k\in\mathbb{Z}^3\setminus\{0\}} m^2 \frac{e^{-m|k|/2}}{|k|}\right),$$

from which we infer that

$$D_m\left(f - \mathbb{E}\left(\int_Q f\right),\, f - \mathbb{E}\left(\int_Q f\right)\right) \leq C\|f\|^2_{L^2_s(L^{\frac{6}{5}})} \left(1 + \sum_{k\in\mathbb{Z}^3\setminus\{0\}} m^2 \frac{e^{-m|k|/2}}{|k|}\right),$$

for a constant C independent of f. As

$$\lim_{m\to 0^+} \sum_{k\in\mathbb{Z}^3\setminus\{0\}} m^2 \frac{e^{-m|k|/2}}{|k|} = \int_{\mathbb{R}^3} \frac{e^{-|x|/2}}{|x|}\,dx < \infty,$$

we finally obtain that $f \in \mathcal{D}_C$. □

The proof of Proposition 2.3.4 can be adapted to show that $D_0(f,f)$ is the limit of the supercell Coulomb energy per unit volume (see Section 2.5 and [24]), for any fixed f satisfying the neutrality assumptions (2.41). It is an open problem to prove the same for the functions $f \in \mathcal{D}_C$ which do not satisfy (2.41).

2.3.4 Dual characterization

The purpose of this section is to provide a useful characterization of the Yukawa and Coulomb spaces $\mathcal{D}_Y$ and $\mathcal{D}_C$ by duality. Let us introduce the spaces of test functions

$$E_Y = \text{span}\left\{\Phi_{\chi,Y} \text{ with } Y \in L^\infty(\Omega),\ \chi \in \mathcal{S}\left(\mathbb{R}^d\right)\right\},$$

and

$$E_C = \text{span}\left\{\Phi_{\chi,Y} \text{ with } Y \in L^\infty(\Omega),\ \chi \in \mathcal{S}_0\left(\mathbb{R}^d\right)\right\},$$

where $\mathcal{S}\left(\mathbb{R}^d\right)$ is the Schwartz space, $\mathcal{S}_0\left(\mathbb{R}^d\right) = \left\{\chi \in \mathcal{S}(\mathbb{R}^d) \mid \widehat{\chi} \in C_c^\infty(\mathbb{R}^d \setminus \{0\})\right\}$, and

$$\Phi_{\chi,Y}(\omega,x) = \sum_{k\in\mathbb{Z}^d} Y(\tau_k(\omega))\chi(x-k), \text{ a.s. and a.e.}$$

The following says that E_Y (resp. E_C) are dense in L^p_s (resp. in $L^p_s \cap \ker(-\Delta_s)^\perp$).

Lemma 2.3.5 (Density of E_Y and E_C)**.** *For any $1 \leq p < \infty$, the set E_Y is dense in L^p_s and the set E_C is dense in $\widetilde{L}^p_s = \left\{ f \in L^p_s \mid \mathbb{E}\left(\int_Q f\right) = 0 \right\}$.*

Proof. We prove that E_C is dense in $\widetilde{L}^p_s$; the proof of the density of E_Y in L^p_s is similar, even simpler. We first note that $(\widetilde{L}^p_s)'$ can be identified with $\widetilde{L}^{p'}_s$, where $p' = (1-p^{-1})^{-1}$ is the conjugate exponent of p. Indeed, as $(L^p_s)' = L^{p'}_s$ then any φ in $\widetilde{L}^{p'}_s$ defines a continuous form on $\widetilde{L}^p_s$. Conversely, any Φ in $(\widetilde{L}^p_s)'$ is also in $(L^p_s)' = L^{p'}_s$. Therefore there exists $\varphi \in L^{p'}_s$ such that for any $f \in \widetilde{L}^p_s$, we have $\langle \Phi, f \rangle_{(\widetilde{L}^p_s)', \widetilde{L}^p_s} = \mathbb{E}\left(\int_Q \varphi f\right)$. Taking $\widetilde{\varphi} = \varphi - \mathbb{E}\left(\int_Q \varphi\right)$, then $\widetilde{\varphi}$ is in $\widetilde{L}^{p'}_s$ and for any $f \in \widetilde{L}^p_s$,

$$\langle \Phi, f \rangle_{(\widetilde{L}^p_s)', \widetilde{L}^p_s} = \mathbb{E}\left(\int_Q \varphi f\right) = \mathbb{E}\left(\int_Q \widetilde{\varphi} f\right) + \mathbb{E}\left(\int_Q \varphi\right) \mathbb{E}\left(\int_Q f\right) = \mathbb{E}\left(\int_Q \widetilde{\varphi} f\right),$$

which ends the proof of the identification. Let now $\varphi \in (\widetilde{L}^p_s)' = \widetilde{L}^{p'}_s$ be such that

$$\forall Y \in L^\infty(\Omega),\ \forall \chi \in \mathcal{S}_0(\mathbb{R}^d), \quad \mathbb{E}\left(\int_Q \varphi\, \Phi_{\chi,Y}\right) = 0. \tag{2.42}$$

For $Y \in L^\infty(\Omega)$, we denote by $f_Y(x) = \mathbb{E}\left(Y(\cdot)\varphi(\cdot, x)\right)$. The function f_Y is in $L^{p'}_{\mathrm{unif}}(\mathbb{R}^d)$, hence it is a tempered distribution: $f_Y \in \mathcal{S}'(\mathbb{R}^d)$. In view of (2.42), we have for all $\chi \in \mathcal{S}_0(\mathbb{R}^d)$,

$$\langle \mathcal{F}^{-1}(f_Y), \widehat{\chi} \rangle_{\mathcal{S}'(\mathbb{R}^d), \mathcal{S}(\mathbb{R}^d)} = 0.$$

Therefore $\mathcal{F}^{-1}(f_Y)$ is supported in $\{0\}$, which implies that

$$\mathcal{F}^{-1}(f_Y) = \sum_{|\alpha| \leq N} c_\alpha \partial^\alpha \delta_0,$$

with $N \in \mathbb{N}$ and $c_\alpha \in \mathbb{C}$. It follows that

$$f_Y(x) = \sum_{|\alpha| \leq N} \widetilde{c}_\alpha x^\alpha,$$

with $\widetilde{c}_\alpha \in \mathbb{C}$. As f_Y is in $L^{p'}_{\mathrm{unif}}(\mathbb{R}^d)$, all the coefficients $\widetilde{c}_\alpha$ are equal to zero, except possibly $\widetilde{c}_0$, and f_Y is a constant. We next notice that $Y \mapsto f_Y$ is a continuous linear form on $L^p(\Omega)$, therefore there exists $Z \in L^{p'}(\Omega)$ such that for all $Y \in L^\infty(\Omega)$, we have $\mathbb{E}(YZ) = f_Y$. It follows that for all $x \in \mathbb{R}^d$, $\varphi(\omega, x) = Z(\omega)$ a.s. We know by Proposition 2.2.4 that any stationary function independent of x is a.s. and a.e. constant. As $\mathbb{E}(\int_Q \varphi(\omega, x)) = 0$, we conclude that $\varphi = 0$, which proves that E_C is dense in $\widetilde{L}^p_s$ in view of the characterization of density of [137, Theorem 5.19, p.107]. □

We now verify that

$$\forall \Phi_{\chi,Y} \in E_Y, \quad (-\Delta_s + 1)^{-\frac{1}{2}} \Phi_{\chi,Y} = \Phi_{(-\Delta+1)^{-1/2}\chi,Y} \tag{2.43}$$

and, similarly, that

$$\forall \Phi_{\chi,Y} \in E_C, \quad (-\Delta_s)^{-\frac{1}{2}} \Phi_{\chi,Y} = \Phi_{(-\Delta)^{-1/2}\chi,Y}. \tag{2.44}$$

Let $Y \in L^\infty(\Omega)$ and $\chi \in \mathcal{S}(\mathbb{R}^d)$. Then

$$(-\Delta+1)^{-1/2}\chi = \mathcal{F}^{-1}\left(K \mapsto \frac{1}{(2\pi)^{\frac{d}{2}}} \frac{\widehat{\chi}(K)}{\sqrt{1+|K|^2}}\right) = \frac{1}{\sqrt{|S^{d-1}|}} W_1 * \chi \in \mathcal{S}(\mathbb{R}^d).$$

Therefore $\Phi_{(-\Delta+1)^{-1/2}\chi,Y}$ is in E_Y and

$$\begin{aligned}
\Phi_{(-\Delta+1)^{-1/2}\chi,Y}(x) &= \frac{1}{\sqrt{|S^{d-1}|}} \sum_{k\in\mathbb{Z}^d} Y(\tau_k(\omega)) \int_{\mathbb{R}^d} W_1(x-k-y)\chi(y)\,dy \\
&= \frac{1}{\sqrt{|S^{d-1}|}} \sum_{k\in\mathbb{Z}^d} Y(\tau_k(\omega)) \int_{\mathbb{R}^d} W_1(x-y)\chi(y-k)\,dy \\
&= \frac{1}{\sqrt{|S^{d-1}|}} (W_1 * \Phi_{\chi,Y})(x) = (-\Delta_s + 1)^{-\frac{1}{2}} \Phi_{\chi,Y},
\end{aligned}$$

where the last inequality follows from (2.40).

Similarly, for $\chi \in \mathcal{S}_0(\mathbb{R}^d)$, we have that $\widehat{\chi}$ vanishes in a neighborhood of 0 and

$$(-\Delta+1)^{-1/2}\chi = \mathcal{F}^{-1}\left(K \mapsto \frac{1}{(2\pi)^{\frac{d}{2}}} \frac{\widehat{\chi}(K)}{|K|}\right) \in \mathcal{S}_0(\mathbb{R}^d).$$

Therefore $\Phi_{(-\Delta)^{-1/2}\chi,Y}$ is in E_C. To prove (2.44), we need to show that

$$\left(-\Delta_s + m^2\right)^{-\frac{1}{2}} \Phi_{\chi,Y} \underset{m\to 0}{\longrightarrow} \Phi_{(-\Delta)^{-1/2}\chi,Y} \quad \text{in } L^2_s,$$

which, in view of (2.43), comes down to showing that

$$\Phi_{\eta_m,Y} \to 0 \quad \text{in } L^2_s,$$

where

$$\begin{aligned}
\widehat{\eta}_m(K) &= \frac{\widehat{\chi}(K)}{\sqrt{|K|^2+m^2}} - \frac{\widehat{\chi}(K)}{|K|} \\
&= m^2 \widehat{\chi}(K) \frac{1}{|K|\sqrt{|K|^2+m^2}\left(\sqrt{|K|^2+m^2}+|K|\right)}.
\end{aligned}$$

We have

$$\|\Phi_{\eta_m,Y}\|_{L^2_s} \leq \|Y\|_{L^\infty} \sum_{k\in\mathbb{Z}^d} \|\eta_m\|_{L^2(Q+k)}$$

and, for $k \in \mathbb{Z}^d$,

$$\begin{aligned}
\|\eta_m\|_{L^2(Q+k)} &= \left\| \frac{1}{2+|x|^{d+1}} \left(2+|x|^{d+1}\right) \eta_m \right\|_{L^2(Q+k)} \\
&= \left\| \frac{1}{2+|x|^{d+1}} \right\|_{L^\infty(Q+k)} \left\| \left(2+|x|^{d+1}\right) \eta_m \right\|_{L^\infty(Q+k)} \\
&\leq C \frac{1}{1+|k|^{d+1}} \left\| \left(2 + \sum_{j=1}^d |x_j|^{d+1} \right) \eta_m \right\|_{L^\infty(Q+k)} \\
&\leq C \frac{1}{1+|k|^{d+1}} \sup_{|\alpha|\leq d+1} \|x^\alpha \eta_m\|_{L^\infty(\mathbb{R}^d)} .
\end{aligned}$$

It follows that

$$\begin{aligned}
\|\Phi_{\eta_m,Y}\|_{L^2_s} &\leq C \|Y\|_{L^\infty(\Omega)} \sup_{|\alpha|\leq d+1} \|x^\alpha \eta_m\|_{L^\infty(\mathbb{R}^d)} \\
&\leq C \|Y\|_{L^\infty(\Omega)} \sup_{|\alpha|\leq d+1} \|\partial^\alpha \widehat{\eta}_m\|_{L^1(\mathbb{R}^d)} .
\end{aligned}$$

It is easy to see that for any $\alpha \in \mathbb{N}^d$, $\|\partial^\alpha \widehat{\eta}_m\|_{L^1(\mathbb{R}^d)}$ tends to 0 as m goes to 0, which concludes the proof of (2.44).

A straightforward consequence of Lemma 2.3.5 and (2.43)-(2.44) is the following

Corollary 2.3.6 (Dual characterization of $\mathcal{D}_Y$ and $\mathcal{D}_C$)**.** *Let $f \in L^1_s$.*

(i) If $(-\Delta_s+1)^{-1/2} f$, seen as a linear form on E_Y, is continuous on $(E_Y, \|\cdot\|_{L^2_s})$, then $f \in \mathcal{D}_Y$ and $D_m(f,f) = |S^{d-1}| \|(-\Delta_s+m^2)^{-1/2} f\|^2_{E_Y^*}$.

(ii) If $\mathbb{E}(\int_Q f) = 0$ and $(-\Delta_s)^{-1/2} f$, seen as a linear form on E_C, is continuous on $(E_C, \|\cdot\|_{L^2_s})$, then $f \in \mathcal{D}_C$ and $D_0(f,f) = |S^{d-1}| \|(-\Delta_s)^{-1/2} f\|^2_{E_C^*}$.

2.4 Stationary reduced Hartree-Fock model

We now define and study, using the tools introduced in the previous sections, a reduced Hartree-Fock (rHF) model for crystals with nuclear charges randomly distributed following a stationary function $\mu \geq 0$. We typically think of μ being of the form

$$\mu(\omega, x) = \sum_{k\in\mathbb{Z}^d} q_k(\omega) \chi(x - k - \eta_k(\omega))$$

with $\int \chi = 1$ and which describes a lattice of nuclei whose charges and positions are perturbed in an i.i.d. ergodic fashion. However in this work we do not want to restrict ourselves to μ's of this very specific form and for us μ is any non-negative stationary function in L^1_s. Our only restriction in this work is that we do not allow point-like charges.

In Section 2.4.1, we define the minimization sets and the rHF energy functionals associated with the Yukawa interaction of parameter $m > 0$ on the one hand, and with the Coulomb interaction on the other hand. In Section 2.4.2 we prove the existence of a ground state density matrix γ, and the uniqueness of the associated ground state density ρ_γ. We then show in Section 2.4.3 that the m-Yukawa rHF model converges to the Coulomb rHF model when the parameter m goes to 0. Finally, we prove in Section 2.4.4 that, in the Yukawa setting, any rHF ground state satisfies a self-consistent equation.

In Section 2.5, we will prove that, still in the Yukawa setting, the rHF model for disordered crystals we have introduced is in fact the thermodynamic limit of the supercell model.

2.4.1 Presentation of the model

As in the usual rHF model for perfect crystals [24], the rHF model we propose consists in minimizing, on the set of admissible density matrices, an energy functional composed of two terms: the kinetic energy per unit volume and the average Coulomb (or Yukawa) energy per unit volume. This leads us to introduce the family of energy functionals

$$\boxed{\mathcal{E}_{\mu,m}(\gamma) = \frac{1}{2}\underline{\mathrm{Tr}}\,(-\Delta\gamma) + \frac{1}{2}D_m(\rho_\gamma - \mu, \rho_\gamma - \mu)} \tag{2.45}$$

with $m = 0$ for Coulomb and $m > 0$ for Yukawa. The sets of admissible density matrices are defined by

$$\mathcal{K}_{\mu,Y} = \left\{\gamma \in \underline{\mathfrak{S}}_{1,1} \cap \underline{\mathcal{S}},\ 0 \le \gamma \le 1 \text{ a.s.},\ \underline{\mathrm{Tr}}\,(\gamma) = \mathbb{E}\left(\int_Q \mu\right),\ \rho_\gamma - \mu \in \mathcal{D}_Y\right\} \tag{2.46}$$

in the Yukawa setting, and by

$$\mathcal{K}_{\mu,C} = \left\{\gamma \in \underline{\mathfrak{S}}_{1,1} \cap \underline{\mathcal{S}},\ 0 \le \gamma \le 1 \text{ a.s.},\ \underline{\mathrm{Tr}}\,(\gamma) = \mathbb{E}\left(\int_Q \mu\right),\ \rho_\gamma - \mu \in \mathcal{D}_C\right\}$$

in the Coulomb setting. The constraint $\underline{\mathrm{Tr}}\,(\gamma) = \mathbb{E}(\int_Q \mu)$ (neutrality condition) must be added in the latter setting since the average Coulomb energy per unit volume of a non globally neutral stationary charge distribution is infinite (recall that in our definition of D_0, we have added a jellium background to enforce the neutrality condition). We also impose this constraint

in the Yukawa setting for consistency. In our model it is not essential that $\mu \geq 0$ but we keep this constraint for obvious physical reasons.

The following lemma gives sufficient conditions on $\mu \geq 0$ for the sets $\mathcal{K}_{\mu,Y}$ and $\mathcal{K}_{\mu,C}$ to be non empty.

Lemma 2.4.1 (Conditions for $\mathcal{K}_{\mu,Y}$ and $\mathcal{K}_{\mu,C}$ to be non empty)**.** *If $\mu \in \mathcal{D}_Y$, then $\mathcal{K}_{\mu,Y}$ is non empty. If $\mu \geq 0$ satisfies the following conditions*

(i) $\mu \in L^3_s(L^1)$,

(ii) there exists $\varepsilon > 0$ such that $|p(\omega)| \leq q(\omega)\left(\frac{1}{2} - \varepsilon\right)$ a.s., where $q(\omega) = \int_Q \mu(\omega, x)\, dx$ and $p(\omega) = \int_Q x\mu(\omega, x)\, dx$,

then $\mathcal{K}_{\mu,C}$ is non empty.

Loosely speaking, the interpretation of the condition $|p(\omega)| \leq q(\omega)\left(\frac{1}{2} - \varepsilon\right)$ is that the nuclei do not touch the boundary of Q too often.

Proof. Let $\mu \in \mathcal{D}_Y$ and $\rho := \mathbb{E}(\int_Q \mu)$ a.s. and a.e. It is clear that there exists a self-adjoint operator $\gamma \in \underline{\mathfrak{S}}_{1,1}$ such that $0 \leq \gamma \leq 1$ a.s. and $\rho_\gamma = \rho$. We can take for instance a free electron gas with constant density ρ, that is,

$$\gamma = 1_{(-\infty,\varepsilon]}(-\Delta), \qquad \text{with} \quad \varepsilon = \left(\frac{d(2\pi)^d}{|S^{d-1}|}\right)^{2/d} \rho^{2/d}.$$

This state is obviously ergodic since it is fully translation-invariant. Moreover it satisfies

$$\underline{\mathrm{Tr}}\,(-\Delta\gamma) = \frac{d}{d+2}\left(\frac{d(2\pi)^d}{|S^{d-1}|}\right)^{2/d} \rho^{1+2/d}.$$

Besides, $\rho - \mu \in \mathcal{D}_Y$ and therefore $\gamma \in \mathcal{K}_{\mu,Y}$.

Suppose now that μ satisfies conditions (i) and (ii) of the statement. Let ρ be the stationary function defined on Q by

$$\rho(\omega, x) = \begin{cases} 0 & \text{if } q(\omega) = 0 \\ \frac{q(\omega)}{d(\omega)^d}\, \chi\left(\frac{x - \frac{p(\omega)}{q(\omega)}}{d(\omega)}\right)^2 & \text{otherwise.} \end{cases}$$

Here $d(\omega) = \mathrm{dist}(p(\omega)/q(\omega), \partial Q)$ and χ is any non-negative radial function of $C^\infty_c(\mathbb{R}^d)$ with support in $B(0, 1/2)$, such that $\int_Q \chi^2 = 1$. We check that $\rho \in L^2_s(L^q) \cap L^3_s$, where q satisfy the conditions in Proposition 2.3.4, and $\sqrt{\rho} \in H^1_s$. Therefore, by the representability Theorem 2.2.16, there exists a self-adjoint operator $\gamma \in \underline{\mathfrak{S}}_{1,1}$ such that $0 \leq \gamma \leq 1$ a.s. and $\rho_\gamma = \rho$. Moreover, $\int_Q (\rho(\omega, x) - \mu(\omega, x))\, dx = 0$ and $\int_Q x\,(\rho(\omega, x) - \mu(\omega, x))\, dx = 0$. It follows from Proposition 2.3.4 that $\rho - \mu \in \mathcal{D}_C$, and therefore that $\gamma \in \mathcal{K}_{\mu,C}$. □

2.4.2 Existence of a ground state

Now that we have properly defined the rHF energy, it is natural to look for ground states, that is, minimizers of $\mathcal{E}_{\mu,m}$ on $\mathcal{K}_{\mu,Y/C}$. The ground state energy of a disordered crystal is defined by

$$\boxed{I_{\mu,m} = \inf\left\{\mathcal{E}_{\mu,m}(\gamma),\ \gamma \in \mathcal{K}_{\mu,Y}\right\}} \tag{2.47}$$

with $m > 0$, in the Yukawa case, and by

$$\boxed{I_{\mu,0} = \inf\left\{\mathcal{E}_{\mu,0}(\gamma),\ \gamma \in \mathcal{K}_{\mu,C}\right\}} \tag{2.48}$$

in the Coulomb case.

Theorem 2.4.2 (Existence of ergodic ground states)**.** *Let $0 \leq \mu \in L^1_s$. If $\mathcal{K}_{\mu,Y}$ (resp. $\mathcal{K}_{\mu,C}$) is non empty, then (2.47) (resp. (2.48)) has a minimizer and all the minimizers share the same density.*

The proof of Theorem 2.4.2 is based on the weak-compactness of $\mathcal{K}_{\mu,Y/C}$ (Proposition 2.2.12), and on the characterization of the spaces $\mathcal{D}_{C/Y}$ by duality (Corollary 2.3.6). We recall that in Lemma 2.4.1 above, we have given natural conditions which guarantee that $\mathcal{K}_{\mu,Y/C}$ is non empty.

Proof. Let $m \geq 0$ and let (γ_n) be a minimizing sequence for $I_{\mu,m}$. As the functional $\mathcal{E}_{\mu,m}$ is the sum of two non-negative terms, these two terms must be uniformly bounded. Since $\underline{\mathrm{Tr}}\,(-\Delta\gamma_n)$ and $\underline{\mathrm{Tr}}\,(\gamma_n) = \mathbb{E}(\int_Q \mu)$ are bounded, we can apply Proposition 2.2.12 and extract a subsequence (denoted the same for simplicity), such that $\gamma_n \rightharpoonup_* \gamma$, with all the convergence properties of the statement of Proposition 2.2.12. In particular, we have

$$\underline{\mathrm{Tr}}\,(-\Delta\gamma) \leq \liminf_{n\to\infty} \underline{\mathrm{Tr}}\,(-\Delta\gamma_n) \quad \text{and} \quad \underline{\mathrm{Tr}}\,(\gamma) = \mathbb{E}\left(\int_Q \mu\right).$$

Similarly, we know that $z_n := W_m * (\rho_{\gamma_n} - \mu) = (-\Delta_s + m^2)^{-1/2}(\rho_{\gamma_n} - \mu)$ is a bounded sequence in L^2_s. Thus we can extract another subsequence such that $z_n \rightharpoonup z$ weakly in L^2_s.

Passing to weak limits using that $\rho_{\gamma_n} \rightharpoonup \rho_\gamma$ in $L^{1+2/d}_s$, it is readily checked that for any $\Phi \in E_{C/Y}$

$$\begin{aligned}
\lim_{n\to\infty} \langle z_n, \Phi\rangle_{L^2_s} &= \lim_{n\to\infty} \left\langle \rho_{\gamma_n} - \mu, \left(-\Delta_s + m^2\right)^{-\frac{1}{2}} \Phi \right\rangle_{E^*_{C/Y}, E_{C/Y}} \\
&= \left\langle \rho_\gamma - \mu, \left(-\Delta_s + m^2\right)^{-\frac{1}{2}} \Phi \right\rangle_{E^*_{C/Y}, E_{C/Y}} \\
&= \left\langle \left(-\Delta_s + m^2\right)^{-\frac{1}{2}} (\rho_\gamma - \mu), \Phi \right\rangle_{E^*_{C/Y}, E_{C/Y}}.
\end{aligned}$$

Hence

$$\langle z, \Phi \rangle_{L^2_s} = \left\langle \left(-\Delta_s + m^2\right)^{-\frac{1}{2}} (\rho_\gamma - \mu), \Phi \right\rangle_{E^*_{C/Y}, E_{C/Y}}.$$

Therefore, using the lower semi-continuity of the L^2_s-norm, we obtain

$$\left\| \left(-\Delta_s + m^2\right)^{-\frac{1}{2}} (\rho_\gamma - \mu) \right\|_{E^*_{C/Y}} = \|z\|_{L^2_s} \leq \liminf_{n\to\infty} \left\| \left(-\Delta_s + m^2\right)^{-\frac{1}{2}} (\rho_{\gamma_n} - \mu) \right\|_{L^2_s}.$$

We deduce from Corollary 2.3.6 that $\rho_\gamma - \mu \in \mathcal{D}_{C/Y}$ and that

$$\mathcal{E}_{\mu,m}(\gamma) \leq \liminf_{n\to\infty} \mathcal{E}_{\mu,m}(\gamma_n) = I_{\mu,m}.$$

Thus, γ is a minimizer of (2.47) (resp. (2.48)).

Let us now prove the uniqueness of the minimizing density ρ_γ. Assume that γ_1 and γ_2 are two minimizers of (2.47) (resp. (2.48)). A simple calculation shows that

$$\begin{aligned} \mathcal{E}_{\mu,m}\left(\frac{\gamma_1+\gamma_2}{2}\right) &= \frac{1}{2}\mathcal{E}_{\mu,m}(\gamma_1) + \frac{1}{2}\mathcal{E}_{\mu,m}(\gamma_2) - \frac{1}{4} D_m(\rho_{\gamma_1} - \rho_{\gamma_2}, \rho_{\gamma_1} - \rho_{\gamma_2}) \\ &= I_{\mu,m} - \frac{1}{4} D_m(\rho_{\gamma_1} - \rho_{\gamma_2}, \rho_{\gamma_1} - \rho_{\gamma_2}). \end{aligned}$$

As $I_{\mu,m}$ is the infimum of $\mathcal{E}_{\mu,m}$ and as $(\gamma_1+\gamma_2)/2$ belongs to the minimization set $\mathcal{K}_{\mu,C/Y}$, we deduce that $\|(-\Delta_s+m^2)^{-\frac{1}{2}}(\rho_{\gamma_1} - \rho_{\gamma_2})\|_{L^2_s} = 0$. Thus $(-\Delta_s + m^2)^{-\frac{1}{2}}(\rho_{\gamma_1} - \rho_{\gamma_2}) = 0$. For all $\Phi \in E_C$, $(-\Delta_s + m^2)^{1/2}\Phi \in E_C$ and

$$\left\langle \left(-\Delta_s + m^2\right)^{-\frac{1}{2}} (\rho_{\gamma_1} - \rho_{\gamma_2}), (-\Delta_s + m^2)^{\frac{1}{2}}\Phi \right\rangle_{L^2_s} = 0.$$

Hence, $\mathbb{E}(\int_Q (\rho_{\gamma_1} - \rho_{\gamma_2})\Phi) = 0$ for all $\Phi \in E_C$. As E_C is dense in $L^{1+d/2}_s \cap \{1\}^\perp$ (see Lemma 2.3.5) and as, in addition, $\mathbb{E}(\int_Q (\rho_{\gamma_1} - \rho_{\gamma_2})) = 0$ by the charge constraint, we conclude that $\rho_{\gamma_1} = \rho_{\gamma_2}$. □

2.4.3 From Yukawa to Coulomb

In this section, we prove that the ground state energy of the Yukawa problem converges to the ground state energy of the Coulomb problem as the parameter m goes to 0. The result essentially follows from our definition of the Coulomb energy D_0 as the limit of D_m when $m \to 0$.

Theorem 2.4.3 (Convergence of Yukawa to Coulomb)**.** *Let $0 \leq \mu \in L^1_s$ be such that $\mathcal{K}_{\mu,C} \neq \emptyset$. The function $m \mapsto I_{\mu,m}$ is decreasing and continuous on $[0, +\infty)$. In particular, we have*

$$\lim_{m\to 0^+} I_{\mu,m} = I_{\mu,0}.$$

Moreover, if for each $m > 0$, γ_m is a minimizer of (2.47), then the family $(\gamma_m)_{m>0}$ converges, up to extraction, to some minimizer γ_0 of (2.48), in the same fashion as in Proposition 2.2.12.

Proof. That $m \mapsto I_{\mu,m}$ is decreasing and continuous on $(0,+\infty)$ is easy to check (the strict monotonicity follows from the existence of minimizers). For $f \in \mathcal{D}_C$ such that $\mathbb{E}(\int_Q f) = 0$, we have $D_m(f,f) \leq D_0(f,f)$ for all $m \geq 0$. It follows that

$$\forall \gamma \in \mathcal{K}_{\mu,C},\ \forall m > 0, \qquad \mathcal{E}_{\mu,m}(\gamma) \leq \mathcal{E}_{\mu,0}(\gamma) < \infty,$$

and therefore that

$$I_{\mu,m} \leq I_{\mu,0}. \tag{2.49}$$

This proves that $\lim_{m\to 0^+} I_{\mu,m} \leq I_{\mu,0}$.

For $m > 0$, we denote by γ_m a minimizer of (2.47). We deduce from (2.49) that there exists a positive constant C such that, for all $m > 0$, $\underline{\mathrm{Tr}}\,(-\Delta\gamma_m) \leq C$ and $\left\|(-\Delta_s + m^2)^{-1/2}(\rho_{\gamma_m} - \mu)\right\|_{L^2_s} \leq C$. Reasoning as in the proof of Theorem 2.4.2, we can extract a subsequence $(\gamma_{m_k})_{k\in\mathbb{N}}$ with $m_k \searrow 0$, such that there exists $\gamma \in \mathcal{K}$ with

$$\underline{\mathrm{Tr}}\,(\gamma) = \|\mu\|_{L^1_s}, \qquad \underline{\mathrm{Tr}}\,(-\Delta\gamma) \leq \liminf_{k\to\infty} \underline{\mathrm{Tr}}\,(-\Delta\gamma_{m_k}),$$

and

$$\left\|(-\Delta_s)^{-\frac{1}{2}}(\rho_\gamma - \mu)\right\|_{L^2_s} \leq \liminf_{k\to\infty} \left\|(-\Delta_s + m_k^2)^{-\frac{1}{2}}\left(\rho_{\gamma_{m_k}} - \mu\right)\right\|_{L^2_s}.$$

This proves that $\gamma \in \mathcal{K}_{\mu,C}$ and that

$$I_{\mu,0} \leq \mathcal{E}_{\mu,0}(\gamma) \leq \liminf_{k\to\infty} \mathcal{E}_{\mu,m_k}(\gamma_{m_k}) = \lim_{m\to 0} I_{\mu,m} \leq I_{\mu,0},$$

which concludes the proof of the theorem. □

2.4.4 Self-consistent field equation

In this section, we define the mean-field Hamiltonian $H = -\frac{1}{2}\Delta + V$ associated with the ground state for $m > 0$ (Yukawa interaction), and we prove that any ground state of (2.47) satisfies a self-consistent field equation. The same holds formally in the Coulomb case but, unfortunately, we are not able to give a rigorous meaning to the Coulomb potential V. For this reason we consider a fixed parameter $m > 0$ in the rest of the section.

We introduce the stationary mean-field potential V defined by

$$V(\omega,x) = \int_{\mathbb{R}^d} Y_m(x-y)\,(\rho_m - \mu)\,(\omega,y)\,dy, \tag{2.50}$$

where ρ_m is the common density of the minimizers of (2.47). The following says that, under the appropriate assumptions on μ, V is a well-defined stationary function such that the associated random Schrödinger operator $H = -\frac{1}{2}\Delta + V$ is also well defined.

Lemma 2.4.4 (Mean-field random Schrödinger operator)**.** *Let $d \in \{1,2,3\}$, $m > 0$ and $0 \leq \mu \in L^{1+2/d}_s \cap \mathcal{D}_Y$. Let ρ_m be the (unique) ground state electronic density for the Yukawa minimization problem* (2.47)*, obtained in Theorem 2.4.2, and V the associated mean-field potential defined in* (2.50)*. Then we have*

$$V \in \begin{cases} L^3_s(L^\infty) & \text{for } d = 1, \\ L^2_s(L^\infty) & \text{for } d = 2, \\ L^{5/3}_s(L^\infty) \cap L^2_s(L^6) & \text{for } d = 3, \end{cases} \tag{2.51}$$

and the random Schrödinger operator $H := -\frac{1}{2}\Delta + V$ is almost surely essentially self-adjoint on $C^\infty_c(\mathbb{R}^d)$. In dimension $d = 3$, if $\mu \in L^{5/2}_s\left(L^1\right)$, then we also have

$$V_- \in L^{5/2}_s. \tag{2.52}$$

Let us emphasize that H is a uniquely defined operator since ρ_m is itself unique. Note that under the sole assumption that $\mu \in L^{1+2/d}_s$ in dimensions $d = 1, 2$ we have $\mu \in \mathcal{D}_Y$ by Corollary 2.3.3. In dimension $d = 3$, the additional hypothesis $\mu \in L^{5/2}_s(L^1)$ ensures that $\mu \in \mathcal{D}_Y$, by Corollary 2.3.3 and the fact that $L^{5/2}_s\left(L^1\right) \cap L^{5/3}_s \subset L^2_s\left(L^{6/5}\right)$.

Proof. As we know that $\rho_m \in L^{1+2/d}_s$, (4.1) and (2.52) follow from Lemma 2.3.2 and the fact that $V = c\, W_m * (W_m * (\rho_m - \mu))$ with $W_m * (\rho_m - \mu) \in L^2_s$ since $\rho_m - \mu \in \mathcal{D}_Y$. We know from [34, Proposition V.3.2, p.258] that $-\frac{1}{2}\Delta + V$ is essentially self-adjoint on $C^\infty_c(\mathbb{R}^d)$ when $V \in L^r_s(L^p)$ for some $p > 2$ and $r > dp/(2(p-2))$. In our case we can apply this with $(p, r) = (3, 3)$ for $d = 1$, $(p, r) = (5, 2)$ for $d = 2$ and $(p, r) = (21, 5/3)$ for $d = 3$. □

The following now gives the self-consistent equation satisfied by a minimizer γ_m.

Proposition 2.4.5 (Self-consistent equation)**.** *Let $d \in \{1,2,3\}$, $m > 0$ and $0 \leq \mu \in L^{1+2/d}_s$. Suppose also that $\mu \in L^{5/2}_s\left(L^1\right)$ if $d = 3$. Then there exists $\varepsilon_{\mathrm{F}} \in \mathbb{R}$, called the* Fermi level*, such that any minimizer γ_m of the Yukawa minimization problem* (2.47) *is of the form*

$$\gamma_m = 1_{(-\infty, \varepsilon_{\mathrm{F}})}(H) + \delta,$$

for some ergodic self-adjoint operator δ satisfying $0 \leq \delta \leq 1_{\{\varepsilon_{\mathrm{F}}\}}(H)$.

Since H is uniquely defined, we deduce that two different minimizers need to have different operators δ's at the Fermi level ε_{F}. In particular, when ε_{F} is not an eigenvalue of H, we deduce that $\gamma_m = 1_{(-\infty, \varepsilon_{\mathrm{F}})}(H)$ is the unique minimizer of (2.47). We will see in Corollary 2.4.6 below that this is indeed the case under the assumption that $\mu \in L^\infty(\Omega \times \mathbb{R}^d)$.

Proof. As $\mu \in \mathcal{D}_Y$, (2.47) has a minimizer γ by Theorem 2.4.2. The Euler inequality associated with the convex optimization problem (2.47) then reads:

$$\forall \gamma' \in \mathcal{K}_{\mu,Y}, \qquad \frac{1}{2}\underline{\mathrm{Tr}}\left(-\Delta(\gamma'-\gamma)\right) + D_m(\rho_{\gamma'}-\rho_\gamma, \rho_\gamma - \mu) \geq 0.$$

For $q \in \mathbb{R}_+$, we set

$$E(q) = \inf_{\substack{\gamma' \in \mathcal{K} \\ \underline{\mathrm{Tr}}(\gamma')=q \\ \rho_{\gamma'} \in \mathcal{D}_Y}} \left(\frac{1}{2}\underline{\mathrm{Tr}}\left(-\Delta(\gamma'-\gamma)\right) + D_m(\rho_{\gamma'}-\rho_\gamma, \rho_\gamma - \mu)\right).$$

It is easily checked that the function E is convex on $\mathbb{R}_+$, hence left and right differentiable everywhere. Also, for any

$$\varepsilon_{\mathrm{F}} \in \left[E'\left(\mathbb{E}\left(\int_Q \mu\right) - 0\right), E'\left(\mathbb{E}\left(\int_Q \mu\right) + 0\right)\right],$$

where $E'(\mathbb{E}(\int_Q \mu) - 0)$ and $E'(\mathbb{E}(\int_Q \mu) + 0)$ respectively denote the left limit and the right limit of the non-decreasing function E' at $\mathbb{E}(\int_Q \mu)$, we have

$$\begin{aligned} &\frac{1}{2}\underline{\mathrm{Tr}}\left(-\Delta(\gamma'-\gamma)\right) + D_m(\rho_{\gamma'}-\rho_\gamma, \rho_\gamma - \mu) - \varepsilon_{\mathrm{F}}\underline{\mathrm{Tr}}\,(\gamma'-\gamma) \\ &\qquad = E\left(\underline{\mathrm{Tr}}\,(\gamma')\right) - E\left(\mathbb{E}\left(\int_Q \mu\right)\right) - \varepsilon_F\left(\underline{\mathrm{Tr}}\,(\gamma') - \mathbb{E}\left(\int_Q \mu\right)\right) \geq 0 \end{aligned} \tag{2.53}$$

for any ergodic operator $\gamma' \in \mathcal{K}$ such that $\rho_{\gamma'} \in \mathcal{D}_Y$. As $\rho_\gamma \in \mathcal{D}_Y$, $V_\mu = Y_m * \mu \in L^{1+d/2}_s$, and $\rho_{\gamma'} \in L^{1+2/d}_s$ for any $\gamma' \in \mathcal{K}$, the above inequality actually holds for any $\gamma' \in \mathcal{K}$. In addition,

$$D_m(\rho_{\gamma'}-\rho_\gamma, \rho_\gamma - \mu) = \mathbb{E}\left(\int_Q V(\rho_{\gamma'}-\rho_\gamma)\right)$$

in $\mathbb{R}_+ \cup \{+\infty\}$. Taking now $\gamma' = 1_{(-\infty,\varepsilon_{\mathrm{F}})}(H)$, which belongs to $\mathcal{K}$ by Proposition 2.2.14, and using Proposition 2.2.15, leads to

$$\begin{aligned} 0 \leq \frac{1}{2}\underline{\mathrm{Tr}}\left(-\Delta(\gamma'-\gamma)\right) + D_m(\rho_{\gamma'}-\rho_\gamma, \rho_\gamma - \mu) - \varepsilon_{\mathrm{F}}\underline{\mathrm{Tr}}\,(\gamma'-\gamma) \\ \leq -\underline{\mathrm{Tr}}\left(|H-\varepsilon_{\mathrm{F}}|^{1/2}(\gamma'-\gamma)^2|H-\varepsilon_{\mathrm{F}}|^{1/2}\right) \leq 0. \end{aligned}$$

Hence, $\gamma = \gamma' + \delta$ with δ as in the statement. □

The following result deals with the special case of $\mu \in L^\infty\left(\Omega \times \mathbb{R}^d\right)$, for which we can prove uniqueness of γ_m.

Corollary 2.4.6 (Uniqueness of the minimizer)**.** *If $\mu \in L^\infty\left(\Omega \times \mathbb{R}^d\right)$, then, for each $m > 0$, the density ρ_m is in $L^\infty\left(\Omega \times \mathbb{R}^d\right)$, and*

$$\gamma_m = 1_{(-\infty,\varepsilon_{\rm F})}(H)$$

is the unique minimizer for (2.47)*.*

Proof. That $\rho_m \in L^\infty\left(\Omega \times \mathbb{R}^d\right)$ is a consequence of Proposition 2.4.5 and of the Feynman-Kac formula (2.18). This implies that $V \in L^\infty\left(\Omega \times \mathbb{R}^d\right)$. In this case the density of states of H is known to be continuous [20], which shows that $\varepsilon_{\rm F}$ is (almost surely) not an eigenvalue [125]. Therefore $\delta \equiv 0$ and γ_m is unique. □

2.5 Thermodynamic limit in the Yukawa case

The purpose of this section is to provide a mathematical justification of the Yukawa model (2.47) by means of a thermodynamic limit. So far, we did not manage to extend the results below to the Coulomb case.

Let us quickly recall that the thermodynamic limit problem consists in studying the behavior of the energy per unit volume (as well as, possibly, the ground state itself and some other properties like the mean-field potential, etc) when the system is confined to a box with chosen boundary conditions and when the size of the box is increased towards infinity.

For a perfect (unperturbed) crystal, the existence of the limit in the many-body case goes back to Fefferman [47], after the fundamental work of Lieb and Lebowitz [109]. A new proof of this recently appeared in [67]. However, for the many-body Schrödinger equation, the value of the limiting energy per unit volume is unknown. For effective theories (Thomas-Fermi or Hartree-Fock for instance), it is often possible to identify the limit and to prove the convergence of ground states. In [114], Lieb and Simon prove that, for the Thomas-Fermi model, the energy per unit volume and the ground state density of a perfect crystal are obtained by solving a certain periodic Thomas-Fermi model on the unit cell of the crystal. The same conclusion has been reached by Catto, Le Bris and Lions for the Thomas-Fermi-von Weizsäcker model [35], and for the reduced Hartree-Fock (rHF) model [36] we focus on in the present work.

In the stochastic case, Veniaminov has initiated in [153] the study of the thermodynamic limit of random quantum systems, but with short range interactions. The case of a random Coulomb crystal was recently tackled by Blanc and Lewin in [15]. Blanc, Le Bris and Lions had already considered the stochastic Thomas-Fermi and Thomas-Fermi-von Weizsäcker models in [14], for which they could also identify the limit.

Here we follow [24] and we consider the so-called *supercell model*. We put the system in a box $\Gamma_L = [-L/2, L/2)^d$ of side $L \in \mathbb{N} \setminus \{0\}$, with

periodic boundary conditions. When $m > 0$, we show that the ground states converge, when L goes to infinity, to a ground state of problem (2.47) (up to extraction and in a sense that will be made precise later).

Let $m > 0$ be fixed for the rest of the section. We introduce the Hilbert space

$$L^2_{\rm per}(\Gamma_L) = \left\{ \varphi \in L^2_{\rm loc}\left(\mathbb{R}^d\right) \mid \varphi \ (L\mathbb{Z})^d\text{-periodic} \right\}.$$

The Fourier coefficients of a function $f \in L^2_{\rm per}(\Gamma_L)$ are defined by

$$c^L_K(f) = \frac{1}{L^{\frac{d}{2}}} \int_{\Gamma_L} f(x)\, e^{-iK\cdot x}\, dx, \qquad \forall K \in \left(\frac{2\pi}{L}\mathbb{Z}\right)^d.$$

We denote by $-\Delta_L$ and $P_{j,L}$, $1 \le j \le d$, the self-adjoint operators on $L^2_{\rm per}(\Gamma_L)$ defined by

$$c^L_K(-\Delta_L f) = |K|^2 c^L_K(f), \quad \text{and} \quad c^L_K(P_{j,L} f) = k_j c^L_K(f), \quad \forall K \in \left(\frac{2\pi}{L}\mathbb{Z}\right)^d.$$

For $k \in \mathbb{Z}^d$, we denote as before by U_k the translation operators on $L^2_{\rm loc}\left(\mathbb{R}^d\right)$ defined by $U_k f(x) = f(x+k)$. For any $f, g \in L^2_{\rm per}(\Gamma_L)$, we set

$$\begin{aligned} D_{m,L}(f,g) &= \left|S^{d-1}\right| \left\langle \left(-\Delta_L + m^2\right)^{-\frac{1}{2}} f, \left(-\Delta_L + m^2\right)^{-\frac{1}{2}} g \right\rangle_{L^2_{\rm per}(\Gamma_L)} \\ &= \sum_{K \in \left(\frac{2\pi}{L}\mathbb{Z}\right)^d} \frac{\left|S^{d-1}\right|}{|K|^2 + m^2} \overline{c^L_K(f)} c^L_K(g) = \int_{\Gamma_L} \int_{\mathbb{R}^d} Y_m(x-y) f(x) g(y)\, dx\, dy. \end{aligned}$$

Denoting by $\mathfrak{S}_{1,L}$ (resp. $\mathcal{S}_L$) the space of the trace class (resp. bounded self-adjoint) operators on $L^2_{\rm per}(\Gamma_L)$. The set of admissible electronic states for the supercell model is then

$$\mathcal{K}_L = \left\{ \gamma_L \in \mathfrak{S}_{1,L} \cap \mathcal{S}_L,\ 0 \le \gamma_L \le 1,\ \mathrm{Tr}_{L^2_{\rm per}(\Gamma_L)}(-\Delta_L \gamma_L) < \infty \right\}.$$

For any $\omega \in \Omega$, we denote by $\mu_L(\omega, \cdot)$ the $(L\mathbb{Z})^d$-periodic nuclear distribution which is equal to $\mu(\omega, \cdot)$ on Γ_L, and by $\mathcal{E}^L_{\mu,m}$ the (ω-dependent) energy functional defined on $\mathcal{K}_L$ by

$$\mathcal{E}^L_{\mu,m}(\omega, \gamma_L) = \frac{1}{2}\mathrm{Tr}_{L^2_{\rm per}(\Gamma_L)}(-\Delta_L \gamma_L) + \frac{1}{2} D_{m,L}\big(\rho_{\gamma_L} - \mu_L(\omega,\cdot),\, \rho_{\gamma_L} - \mu_L(\omega,\cdot)\big).$$

Let $\varepsilon_{\rm F}$ be as in Proposition 2.4.5. For any $\omega \in \Omega$, the ground state energy of the system in the box of size L with Fermi level $\varepsilon_{\rm F}$ is given by

$$\boxed{I^L_{\mu,m,\varepsilon_{\rm F}}(\omega) = \inf\left\{ \mathcal{E}^L_{\mu,m}(\omega, \gamma_L) - \varepsilon_{\rm F}\mathrm{Tr}_{L^2_{\rm per}(\Gamma_L)}(\gamma_L),\ \gamma_L \in \mathcal{K}_L \right\}.} \tag{2.54}$$

Proposition 2.5.1 (Existence of ground states for the supercell model)**.** *Let $\mu \in L^2_s$. For each $L \in \mathbb{N}\backslash\{0\}$,* (2.54) *has a minimizer, and all the minimizers of* (2.54) *share the same density.*

Proof. The proof follows the same lines as the proof of [36, Theorem 2.1], replacing the periodic Coulomb kernel by the periodic Yukawa kernel $Y_{m,L}(x) = \sum_{k\in(L\mathbb{Z})^d} Y_m(x-k)$. □

On the other hand, the ground state energy of the full space ergodic problem with Fermi level ε_{F} is defined by

$$I_{\mu,m,\varepsilon_{\mathrm{F}}} = \inf\left\{\mathcal{E}_{\mu,m}(\gamma) - \varepsilon_{\mathrm{F}}\underline{\mathrm{Tr}}\,(\gamma)\,,\ \gamma \in \mathcal{K}_Y\right\}, \tag{2.55}$$

where $\mathcal{E}_{\mu,m}$ is given by (2.45), and

$$\mathcal{K}_Y := \left\{\gamma \in \underline{\mathfrak{S}}_{1,1} \cap \underline{\mathcal{S}},\ 0 \le \gamma \le 1 \text{ a.s.},\ \rho_\gamma - \mu \in \mathcal{D}_Y\right\}$$

(the neutrality constraint has been removed compared to $\mathcal{K}_{\mu,Y}$ defined before in (2.46)). It is a classical result of convex optimization that (2.47) and (2.55) have the same minimizers (see (2.53)).

Theorem 2.5.2 (Thermodynamic limit for $m > 0$)**.** *Let $\mu \in L^2_s$. We have*

$$\lim_{L\to\infty} \frac{I^L_{\mu,m,\varepsilon_{\mathrm{F}}}(\omega)}{L^d} = I_{\mu,m,\varepsilon_{\mathrm{F}}} \quad \text{in } L^1(\Omega)\,. \tag{2.56}$$

Our proof also gives the convergence of minimizers for (2.54) towards those of (2.55), in a rather weak sense. More precisely, the operators γ'_L defined by (2.68) and (2.67) weakly-$*$ converge to a minimizer γ for (2.55), up to extraction of a subsequence. See Remark 2.5.8.

To prove Theorem 2.5.2, we first establish preliminary estimates in Proposition 2.5.3. Then, we prove a lower bound in expectation in Proposition 2.5.4, and an almost sure upper bound in Proposition 2.5.6. We then conclude the proof of Theorem 2.5.2 using Lemma 2.5.7.

In order to adapt our proof to the Coulomb case, we would need some estimates on the Coulomb potential V_L in the box Γ_L. It is reasonable to believe that screening effects will make (V_L) bounded in, say, $L^1(\Omega, L^1_{\mathrm{unif}}(\mathbb{R}^d))$. For a very general arrangement of the nuclei, bounds of this type are known in Thomas-Fermi theory (see [14, Theorem 7], which is taken from Brezis' paper [21]) and in Thomas-Fermi-von Weizsäcker theory [35, Theorem 6.10], but they have not yet been established in reduced Hartree-Fock theory. Proving such bounds is of considerable interest, but it is beyond the scope of this study.

Proposition 2.5.3 (Upper bounds)**.** *Let $\mu \in L^2_s$ and let $\gamma_L(\omega)$ be a minimizer of $I^L_{\mu,m,\varepsilon_{\mathrm{F}}}(\omega)$. Then, there exists $C > 0$ and a sequence of integrable*

random variables (Z_L) *converging to some* $Z \in L^1(\Omega)$ *a.s. and in* $L^1(\Omega)$*, such that*

$$I^L_{\mu,m,\varepsilon_{\rm F}}(\omega) + D_{m,L}\left(\rho_{\gamma_L}(\omega,\cdot), \rho_{\gamma_L}(\omega,\cdot)\right) \leq C\, L^d Z_L(\omega) \ \text{ a.s.}, \tag{2.57}$$

$$\mathbb{E}\left(\mathrm{Tr}_{L^2_{\rm per}(\Gamma_L)}(1-\Delta_L)\gamma_L\right) + \mathbb{E}\Big(D_{m,L}\left(\rho_{\gamma_L}-\mu_L, \rho_{\gamma_L}-\mu_L\right)\Big) \leq C\, L^d \tag{2.58}$$

for all $L \in \mathbb{N}\setminus\{0\}$.

Proof. Taking $\gamma'_L = 0$ as a trial state in the minimization problem (2.54), we obtain that, almost surely,

$$\frac{I^L_{\mu,m,\varepsilon_{\rm F}}(\omega)}{L^d} \leq \frac{1}{2L^d} D_{m,L}\left(\mu_L(\omega,\cdot), \mu_L(\omega,\cdot)\right) \leq \frac{1}{2m^2} Z_L(\omega), \tag{2.59}$$

where $Z_L = L^{-d}\int_{\Gamma_L}\mu^2$ converges to $\mathbb{E}(\int_Q \mu^2)$, a.s. and in $L^1(\Omega)$, by the ergodic theorem. Besides, for any $\alpha \in \mathbb{R}$ and any $\gamma'_L \in \mathcal{K}_L$, we have

$$\mathrm{Tr}_{L^2_{\rm per}(\Gamma_L)}\left((-\Delta_L-\alpha)\gamma'_L\right) \geq -\mathrm{Tr}_{L^2_{\rm per}(\Gamma_L)}\Big(\big(-\Delta_L-\alpha\big)_-\Big).$$

The trace of $\big(-\Delta_L-\alpha\big)_-$ is given by

$$\mathrm{Tr}_{L^2_{\rm per}(\Gamma_L)}\Big(\big(-\Delta_L-\alpha\big)_-\Big) = \sum_{k\in\frac{2\pi}{L}\mathbb{Z}^d} 1_{|k|^2-\alpha\leq 0}\left(\alpha-|k|^2\right).$$

The Riemann sum $L^{-d}\sum_{k\in\frac{2\pi}{L}\mathbb{Z}^d} 1_{|k|^2-\alpha\leq 0}(\alpha-|k|^2)$ converges to

$$\int_{\mathbb{R}^d} 1_{|k|^2-\alpha\leq 0}\left(\alpha-|k|^2\right)dk = -C\alpha^{\frac{d+2}{2}},$$

where the constant $C \geq 0$ depends only on the dimension d. Therefore, the sequence $L^{-d}\mathrm{Tr}\left((-\Delta_L-\alpha)_-\right)$ is bounded and

$$\mathrm{Tr}_{L^2_{\rm per}(\Gamma_L)}\left((-\Delta_L-\alpha)\gamma'_L\right) \geq -CL^d, \tag{2.60}$$

where C depends, in general, on α and d, but not on γ'_L. The bounds (2.57) and (2.58) follow from (2.59) and (2.60). Indeed, by (2.59), we have

$$\mathrm{Tr}_{L^2_{\rm per}(\Gamma_L)}\left((-\Delta-\varepsilon_F)\gamma_L\right) + D_{m,L}\left(\rho_{\gamma_L},\rho_{\gamma_L}\right) \leq CL^d Z_L. \tag{2.61}$$

As $D_{m,L}\left(\rho_{\gamma_L},\rho_{\gamma_L}\right)$ is non-negative, we deduce that

$$\mathrm{Tr}_{L^2_{\rm per}(\Gamma_L)}\left((-\Delta-\varepsilon_F)\gamma_L\right) \leq CL^d Z_L \tag{2.62}$$

and, using (2.60),

$$D_{m,L}\left(\rho_{\gamma_L},\rho_{\gamma_L}\right) \leq CL^d Z_L,$$

which concludes the proof of (2.57). Next, taking the expectancy of (2.61) and using that $\mathbb{E}(Z_L) = \|\mu\|^2_{L^2_s}$ is independent of L, we obtain

$$\mathbb{E}\left(\mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma_L)}\left((-\Delta - \varepsilon_F)\gamma_L\right)\right) + \mathbb{E}\left(D_{m,L}\left(\rho_{\gamma_L}, \rho_{\gamma_L}\right)\right) \leq CL^d.$$

Thus

$$\begin{aligned}\mathbb{E}\left(\mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma_L)}\left((1-\Delta)\gamma_L\right)\right) + \mathbb{E}\left(D_{m,L}\left(\rho_{\gamma_L}, \rho_{\gamma_L}\right)\right) \\ \leq CL^d + (1+\varepsilon_F)\mathbb{E}\left(\mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma_L)}\left(\gamma_L\right)\right).\end{aligned} \tag{2.63}$$

Using now (2.60) with $\gamma'_L = \gamma_L$ and $\alpha = -1 - 2\varepsilon$, we get

$$\begin{aligned}(1+\varepsilon_F)\mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma_L)}\left(\gamma_L\right) &\leq \mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma_L)}\left((-\Delta_L - \varepsilon_F)\gamma_L\right) + CL^d \\ &\leq CL^d Z_L + CL^d,\end{aligned} \tag{2.64}$$

where we have used (2.62). Taking the expectancy of (2.64) and combining it with (2.63), we conclude the proof of (2.58). □

Proposition 2.5.4 (Lower bound in average)**.** *Let $\mu \in L^2_s$. Then*

$$\liminf_{L\to+\infty} \frac{\mathbb{E}\left(I^L_{\mu,m,\varepsilon_{\mathrm{F}}}(\cdot)\right)}{L^d} \geq I_{\mu,m,\varepsilon_{\mathrm{F}}}. \tag{2.65}$$

The following definition introduced in [14] will be used repeatedly in the proof of Proposition 2.5.4.

Definition 2.5.5 (The tilde-transform)**.** *For a function $g : \Omega \times \mathbb{R}^d \to \mathbb{C}$ and $L \in \mathbb{N}$, we call the* tilde-transform *$\tilde{g}$ of g the following function*

$$\tilde{g}\left(\omega, x\right) = \frac{1}{L^d} \sum_{k \in \Gamma_L \cap \mathbb{Z}^d} g\left(\tau_{-k}\left(\omega\right), x + k\right) \ \textit{a.s. and a.e.} \tag{2.66}$$

We can now write the

Proof of Proposition 2.5.4. Let $\gamma_L(\omega)$ be a minimizer of (2.54) and set

$$\tilde{\gamma}_L(\omega) = \frac{1}{L^d} \sum_{k \in \Gamma_L \cap \mathbb{Z}^d} U_k \gamma_L(\tau_{-k}(\omega)) U_k^*. \tag{2.67}$$

Notice that $\rho_{\tilde{\gamma}_L} = \widetilde{\rho}_{\gamma_L}$ where the latter is the tilde-transform defined in (2.66). For any $L \in \mathbb{N} \setminus \{0\}$, we define the operator

$$\begin{array}{rccc}\gamma'_L : & L^2\left(\mathbb{R}^d\right) & \to & L^2\left(\mathbb{R}^d\right) \\ & \varphi & \mapsto & 1_{\Gamma_L}\tilde{\gamma}_L\varphi_L,\end{array} \tag{2.68}$$

where φ_L is the $(L\mathbb{Z})^d$-periodic function equal to φ on Γ_L. It is easily checked that γ'_L is self-adjoint and that $0 \leq \gamma'_L \leq 1$. Thus, the family (γ'_L) is bounded in $L^\infty(\Omega, \mathcal{B})$. Up to extraction of a subsequence, there exists an operator $\gamma \in L^\infty(\Omega, \mathcal{B})$ such that γ'_L converges weakly-$*$ to γ. Moreover, γ is self-adjoint and $0 \leq \gamma \leq 1$ a.s. Besides, $\gamma'_L(\omega, x, y) = \tilde{\gamma}_L(\omega, x, y)$ a.s. and a.e. on $\Omega \times \Gamma_L \times \Gamma_L$. In the following, we will show that $\gamma \in \mathcal{K}_Y$ and that

$$\mathcal{E}_{\mu,m}(\gamma) - \varepsilon_{\mathrm{F}} \underline{\mathrm{Tr}}\,(\gamma) \leq \liminf_{L\to\infty} \frac{\mathbb{E}\left(I^L_{\mu,m,\varepsilon_{\mathrm{F}}}(\cdot)\right)}{L^d}, \tag{2.69}$$

leading to (2.65).

Step 1 *The operator γ is ergodic.* By density argument, like in the proof of Proposition 2.2.12, it is sufficient to show that for all $u \in L^1(\Omega)$, $\varphi, \psi \in C_c^\infty(\mathbb{R}^d)$ and $R \in \mathbb{Z}^d$,

$$\mathbb{E}\Big(u\big\langle \left(\gamma(\tau_R(\omega)) - U_R\gamma(\omega)U_R^*\right)\varphi, \psi\big\rangle_{L^2}\Big) = 0. \tag{2.70}$$

Let u, φ, ψ and R as above and $L \in \mathbb{N}$. We have

$$\begin{aligned}
&\tilde{\gamma}_L(\tau_R(\omega)) - U_R\tilde{\gamma}_L(\omega)U_R^* \\
&\quad= \frac{1}{L^d}\left(\sum_{k\in\Gamma_L\cap\mathbb{Z}^d} U_k\gamma_L(\tau_{-k+R}(\omega))U_k^* - \sum_{k\in\Gamma_L\cap\mathbb{Z}^d} U_{k+R}\gamma_L(\tau_{-k}(\omega))U_{k+R}^*\right) \\
&\quad= \frac{1}{L^d}\left(\sum_{k\in\Gamma_L\cap\mathbb{Z}^d} U_k\gamma_L(\tau_{-k+R}(\omega))U_k^* - \sum_{k\in(\Gamma_L+R)\cap\mathbb{Z}^d} U_k\gamma_L(\tau_{-k+R}(\omega))U_k^*\right) \\
&\quad= \frac{1}{L^d}\sum_{k\in(\Gamma_L\Delta(\Gamma_L+R))\cap\mathbb{Z}^d} U_k\gamma_L(\tau_{-k+R}(\omega))U_k^*,
\end{aligned}$$

where $A\Delta B := (A \setminus B) \cup (B \setminus A)$. Hence, for L sufficiently large, we have

$$\begin{aligned}
\left|\mathbb{E}\left(u\langle\left(\gamma'_L(\tau_R\cdot) - U_R\gamma'_LU_R^*\right)\varphi, \psi\rangle_{L^2}\right)\right| &= \left|\mathbb{E}\left(u\langle(\tilde{\gamma}_L(\tau_R\cdot) - U_R\tilde{\gamma}_LU_R^*)\,\varphi_L, \psi_L\rangle_{L^2(\Gamma_L)}\right)\right| \\
&\leq \frac{|\Gamma_L\Delta(\Gamma_L+R)|}{L^d}\,\|u\|_{L^1(\Omega)}\,\|\varphi\|_{L^2}\,\|\psi\|_{L^2}.
\end{aligned}$$

The left side converges to $\mathbb{E}\left(u\langle(\gamma\circ\tau_R - U_R\gamma U_R^*)\,\varphi, \psi\rangle_{L^2}\right)$, and the right side decays as L^{-1}. Thus, (2.70) is proved.

Step 2 *We have*

$$\underline{\mathrm{Tr}}\,(\gamma) = \lim_{L\to\infty} \frac{\mathbb{E}\left(\mathrm{Tr}_{\,L^2_{\mathrm{per}}(\Gamma_L)}\,(\gamma_L)\right)}{L^d}. \tag{2.71}$$

Thanks to the estimate (2.58), for any $\chi \in W_c^{1,\infty}(\mathbb{R}^d)$, there exists a constant C such that for all $L \in \mathbb{N} \setminus \{0\}$, we have

$$|\mathbb{E}\left(\mathrm{Tr}\left(\chi\tilde{\gamma}_L\chi\right)\right)| + \sum_{j=1}^{d} |\mathbb{E}\left(\mathrm{Tr}\left(\chi P_j\tilde{\gamma}_L P_j\chi\right)\right)| \leq C, \tag{2.72}$$

Indeed, let $I \subset \mathbb{Z}^d$, with $|I| < \infty$, such that $\mathrm{supp}(\chi) \subset B_I = \cup_{i\in I} 1_{Q+i}$. We have

$$\begin{aligned}
\mathbb{E}\left(\mathrm{Tr}\ \left(\chi\widetilde{\gamma}_L\chi\right)\right) &= \mathbb{E}\left(\int_{B_I} \chi^2 \rho_{\widetilde{\gamma}_L}\right) \\
&\leq \|\chi\|^2_{L^\infty\left(\mathbb{R}^d\right)} \mathbb{E}\left(\int_{B_I} \rho_{\widetilde{\gamma}_L}\right) \\
&= \frac{1}{L^d}\|\chi\|^2_{L^\infty\left(\mathbb{R}^d\right)} \sum_{i\in I} \sum_{k\in\Gamma_L\cap\mathbb{Z}^d} \mathbb{E}\left(\int_{Q+i+k} \rho_{\gamma_L}\right) \\
&= \frac{1}{L^d}\|\chi\|^2_{L^\infty\left(\mathbb{R}^d\right)} \sum_{i\in I} \mathbb{E}\left(\int_{\Gamma_L+i} \rho_{\gamma_L}\right) \\
&= \frac{1}{L^d}\|\chi\|^2_{L^\infty\left(\mathbb{R}^d\right)} |I|\, \mathbb{E}\left(\int_{\Gamma_L} \rho_{\gamma_L}\right) \\
&= \frac{1}{L^d}\|\chi\|^2_{L^\infty\left(\mathbb{R}^d\right)} |I|\, \mathbb{E}\left(\mathrm{Tr}_{\,L^2_{\mathrm{per}}(\Gamma_L)}(\gamma_L)\right).
\end{aligned} \tag{2.73}$$

Similarly, for $1 \leq j \leq d$

$$\begin{aligned}
\mathbb{E}\left(\mathrm{Tr}\ \left(\chi P_{j,L}\widetilde{\gamma}_L P_{j,L}\chi\right)\right) &\leq \frac{1}{L^d}\|\chi\|^2_{L^\infty\left(\mathbb{R}^d\right)} |I|\, \mathbb{E}\left(\int_{\Gamma_L} \rho_{P_{j,L}\gamma_L P_{j,L}}\right) \\
&= \frac{1}{L^d}\|\chi\|^2_{L^\infty\left(\mathbb{R}^d\right)} |I|\, \mathbb{E}\left(\mathrm{Tr}_{\,L^2_{per}(\Gamma_L)}\left(-\Delta_L\gamma_L\right)\right).
\end{aligned} \tag{2.74}$$

The right hand sides of (2.73) and (2.74) are both bounded in view of (2.58), which proves (2.72).

Following the proof of Proposition 2.2.12, we can show that

$$\mathbb{E}\left(u\,\mathrm{Tr}\ \left(\chi\gamma\chi\right)\right) = \lim_{L\to\infty} \mathbb{E}\left(u\int_{\mathbb{R}^d} \rho_{\gamma'_L}\chi^2\right) \tag{2.75}$$

for all $u \in L^\infty(\Omega)$ and all $\chi \in L^\infty_c(\mathbb{R}^d)$. Choosing $u = 1$ and $\chi = 1_Q$, we get

$$\underline{\mathrm{Tr}}\left(\gamma\right) = \lim_{L\to\infty} \mathbb{E}\left(\int_Q \rho_{\gamma'_L}\right).$$

Finally, we remark that

$$\mathbb{E}\left(\int_Q \rho_{\gamma_L'}\right) = \mathbb{E}\left(\int_Q \tilde{\rho}_{\gamma_L}\right) = \frac{1}{L^d}\mathbb{E}\left(\int_Q \sum_{k\in\Gamma_L\cap\mathbb{Z}^d} \rho_{\gamma_L}(\cdot, x+k)\,dx\right)$$
$$= \frac{1}{L^d}\mathbb{E}\left(\int_{\Gamma_L} \rho_{\gamma_L}\right) = \frac{1}{L^d}\mathbb{E}\left(\mathrm{Tr}_{\,L^2_{\mathrm{per}}(\Gamma_L)}\left(\gamma_L\right)\right),$$

which concludes the proof of (2.71).

Step 3 *The sequence $(\rho_{\tilde{\gamma}_L})$ converges weakly to ρ_γ in $L^{1+2/d}(\Omega, L^{1+2/d}_{\mathrm{loc}}(\mathbb{R}^d))$.* By (2.75), we obtain

$$\lim_{L\to\infty} \mathbb{E}\left(u\int_{\mathbb{R}^d} \rho_{\tilde{\gamma}_L}(\omega,x)\chi(x)^2\,dx\right) = \mathbb{E}\left(u\int_{\mathbb{R}^d} \rho_{\gamma}(\omega,x)\chi(x)^2\,dx\right),$$

for all $u \in L^\infty(\Omega)$ and all $\chi \in C_c^\infty\left(\mathbb{R}^d\right)$. To proceed as in the proof of Proposition 2.2.12, we only need to show that $(\rho_{\tilde{\gamma}_L})$ is bounded in $L^{1+2/d}\left(\Omega, L^{1+2/d}\left(B_I\right)\right)$, independently of L, for any $B_I = \cup_{k\in I}(Q+k)$, with $I \subset \mathbb{Z}^d$ such that $|I| < \infty$. This bound now follows from the convexity of the function $x \mapsto x^{1+2/d}$, the Lieb-Thirring inequality in a box [50] and the estimate (2.58)

$$\mathbb{E}\left(\int_{B_I} |\rho_{\tilde{\gamma}_L}|^{\frac{d+2}{d}}\right) \le \sum_{k\in I}\frac{1}{L^d}\mathbb{E}\left(\int_{\Gamma_L+k} |\rho_{\gamma_L}|^{\frac{d+2}{d}}\right) \tag{2.76}$$
$$\le C\,|I|\left(\frac{\mathbb{E}\left(\mathrm{Tr}_{\,L^2_{\mathrm{per}}}\left(-\Delta_L\gamma_L\right)\right)}{L^d} + \frac{\mathbb{E}\left(\mathrm{Tr}_{\,L^2_{\mathrm{per}}}\left(\gamma_L\right)\right)}{L^d}\right) \le C.$$

Step 4 *We have*

$$\underline{\mathrm{Tr}}\,(-\Delta\gamma) \le \liminf_{L\to\infty} \frac{\mathbb{E}\left(\mathrm{Tr}_{\,L^2_{\mathrm{per}}}(-\Delta_L\gamma_L)\right)}{L^d}.$$

As γ_L' converges weakly-$*$ in $L^\infty\left(\Omega,\mathcal{B}\right)$ to γ, we can argue like in the proof of Proposition 2.2.12. Indeed, Let $(\varphi_n)_{n\in\mathbb{N}}$ be an orthonormal basis of $L^2(Q)$ consisting of functions of $H^1_0(Q)$. We denote by $\varphi_{n,L}$ the $L\mathbb{Z}^d$-periodic function defined on Γ_L by

$$\begin{cases} \varphi_{n,L}\left(x\right) = \varphi_n\left(x\right), & \text{if } x \in Q, \\ \varphi_{n,L}\left(x\right) = 0, & \text{if } x \in \Gamma_L \setminus Q. \end{cases}$$

Note that $(U_k\varphi_{n,L})_{k\in\Gamma_L\cap\mathbb{Z}^d,\,n\in\mathbb{N}}$ is an orthonormal basis of $L^2_{\rm per}(\Gamma)$. By the weak-$*$ convergence in $L^\infty(\Omega,\mathcal{B})$, we have for any $n\in\mathbb{N}$ and $1\le j\le d$

$$\begin{aligned}\mathbb{E}\left(\langle P_j\gamma P_j\varphi_n,\varphi_n\rangle\right) &= \mathbb{E}\left(\gamma\left(-i\partial_{x_j}\varphi_n\right),-i\partial_{x_j}\varphi_n\rangle\right)\\ &= \lim_{L\to\infty}\mathbb{E}\left(\gamma_L'\left(-i\partial_{x_j}\varphi_n\right),-i\partial_{x_j}\varphi_n\rangle\right)\\ &= \lim_{L\to\infty}\mathbb{E}\left(\tilde\gamma_L\left(-i\partial_{x_j}\varphi_{n,L}\right),-i\partial_{x_j}\varphi_{n,L}\rangle\right)\\ &= \lim_{L\to\infty}\mathbb{E}\left(P_{j,L}\tilde\gamma_L P_{j,L}\varphi_{n,L},\varphi_{n,L}\rangle\right).\end{aligned}$$

For any $n\in\mathbb{N}$, $L\in\mathbb{N}^*$ and $1\le j\le d$, the terms $\mathbb{E}\left(P_{j,L}\tilde\gamma_L P_{j,L}\varphi_{n,L},\varphi_{n,L}\rangle\right)$ are non negative. Therefore, by Fatou lemma in $\ell^1(\mathbb{N})$, we have

$$\underline{\rm Tr}\,\left(P_j\gamma P_j\right)\le\liminf_{L\to\infty}\sum_{n\in\mathbb{N}}\mathbb{E}\left(P_{j,L}\tilde\gamma_L P_{j,L}\varphi_{n,L},\varphi_{n,L}\rangle\right).$$

Thus

$$\begin{aligned}\underline{\rm Tr}\,(-\Delta\gamma) &\le \liminf_{L\to\infty}\sum_{j=1}^d\sum_{n\in\mathbb{N}}\mathbb{E}\left(\langle P_{j,L}\tilde\gamma_L P_{j,L}\varphi_{n,L},\varphi_{n,L}\rangle_{L^2(Q)}\right)\\ &\le \liminf_{L\to\infty}\sum_{j=1}^d\sum_{n\in\mathbb{N}}\frac{1}{L^d}\sum_{k\in\Gamma_L\cap\mathbb{Z}^d}\mathbb{E}\left(\langle P_{j,L}\gamma_L P_{j,L}U_k^*\varphi_{n,L},U_k^*\varphi_{n,L}\rangle_{L^2(Q)}\right)\\ &\le \liminf_{L\to\infty}\frac{1}{L^d}\sum_{j=1}^d\mathbb{E}\left({\rm Tr}_{\,L^2_{per}(\Gamma_L)}\left(P_{j,L}\gamma_L P_{j,L}\right)\right)\\ &\le \liminf_{L\to\infty}\frac{1}{L^d}\mathbb{E}\left({\rm Tr}_{\,L^2_{per}(\Gamma_L)}(-\Delta_L\gamma_L)\right),\end{aligned}$$

where we have used that the operators $P_{j,L}$ commute with the translations U_k and that the semi-group τ preserves the probability measure.

Step 5 *We have*

$$D_m(\rho_\gamma-\mu,\rho_\gamma-\mu)\le\liminf_{L\to\infty}\frac{\mathbb{E}\Big(D_{m,L}(\rho_{\gamma_L}-\mu_L,\rho_{\gamma_L}-\mu_L)\Big)}{L^d}. \tag{2.77}$$

We denote by $f_L=\rho_{\gamma_L}-\mu_L$ and $f=\rho_\gamma-\mu$. It follows from a simple convexity argument that for all $k\in\mathbb{Z}^d$,

$$\begin{aligned}&\mathbb{E}\left(\left\|\left(-\Delta_L+m^2\right)^{-\frac12}\tilde f_L\right\|^2_{L^2(Q+k)}\right)\\ &\qquad=\frac{1}{L^d}\sum_{R\in\Gamma_L\cap\mathbb{Z}^d}\left\|\left(-\Delta_L+m^2\right)^{-\frac12}f_L(\tau_R(\cdot),\cdot+R)\right\|^2_{L^2(\Omega\times(Q+k))}\\ &\qquad\le\frac{1}{L^d}\mathbb{E}\left(\int_{\Gamma_L}\left|\left(-\Delta_L+m^2\right)^{-\frac12}f_L\right|^2\right).\end{aligned}$$

As

$$\int_{\Gamma_L} \left|\left(-\Delta_L + m^2\right)^{-\frac{1}{2}} f_L\right|^2 = \left|S^{d-1}\right|^{-1} D_{m,L}\left(f_L, f_L\right),$$

we obtain by (2.58) that for all $k \in \mathbb{Z}^d$,

$$\left\|\left(-\Delta_L + m^2\right)^{-\frac{1}{2}} \tilde{f}_L\right\|^2_{L^2(\Omega\times(Q+k))} \leq \frac{\left|S^{d-1}\right|^{-1}}{L^d} \mathbb{E}\left(D_{m,L}\left(f_L, f_L\right)\right) \leq C.$$

Therefore, there exists a function $z \in L^2(\Omega, L^2_{\text{unif}}(\mathbb{R}^d))$ such that, up to extraction, $(-\Delta_L + m^2)^{-1/2}\tilde{f}_L$ converges weakly-$*$ to z in $L^2(\Omega, L^2_{\text{unif}}(\mathbb{R}^d))$. By the weak lower semi-continuity of the L^2-norm, we have

$$\mathbb{E}\left(\int_Q z^2\right) \leq \liminf_{L\to\infty} \mathbb{E}\left(\left\|\left(-\Delta_L + m^2\right)^{-\frac{1}{2}} \tilde{f}_L\right\|^2_{L^2(Q)}\right) \leq \liminf_{L\to\infty} \frac{\mathbb{E}\left(D_{m,L}(f_L, f_L)\right)}{\left|S^{d-1}\right| L^d}.$$

We are going to show that $z = (-\Delta_s + m^2)^{-1/2}(\rho_\gamma - \mu)$, which will conclude the proof. To do so, by density, we just need to check that for any $u \in L^{1+d/2}(\Omega)$ and $\chi \in \mathcal{C}_c^\infty\left(\mathbb{R}^d\right)$,

$$\lim_{L\to\infty} \mathbb{E}\left(u \int_{\mathbb{R}^d} \chi\left(-\Delta_L + m^2\right)^{-\frac{1}{2}} \tilde{f}_L\right) = \mathbb{E}\left(u \int_{\mathbb{R}^d} \left(\left(-\Delta + m^2\right)^{-\frac{1}{2}} \chi\right) f\right). \tag{2.78}$$

Let u and χ be such functions. Reasoning as in Step 1, we notice that the tilde-transform $\tilde{\mu}_L$ converges weakly to μ in $L^{1+2/d}(\Omega, L^{1+2/d}_{\text{loc}}(\mathbb{R}^d))$. Then, we proceed in two steps. First, we show that

$$\int_{\mathbb{R}^d} \chi\left(-\Delta_L + m^2\right)^{-\frac{1}{2}} \tilde{f}_L = \int_{\mathbb{R}^d} \eta \tilde{f}_L,$$

where $\eta = (-\Delta + m^2)^{-1/2}\chi$. Recall that, for any $h \in \mathcal{S}(\mathbb{R}^d)$, the function defined by $h_L(x) = \sum_{k\in(L\mathbb{Z})^d} h(x-k)$ is in $L^2_{\text{per}}(\Gamma_L)$ with $c_K^L(h_L) =$

$(2\pi/L)^{d/2}\widehat{h}\,(K)$. For L sufficiently large, we therefore have

$$\begin{aligned}
\int_{\mathbb{R}^d} \chi\left(-\Delta_L + m^2\right)^{-\frac{1}{2}} \tilde{f}_L &= \int_{\Gamma_L} \chi\left(-\Delta_L + m^2\right)^{-\frac{1}{2}} \tilde{f}_L \\
&= \sum_{k \in \frac{2\pi}{L}\mathbb{Z}^d} \overline{c_k^L\left(\chi_L\right)} c_k^L \left(\left(-\Delta_L + m^2\right)^{-\frac{1}{2}} \tilde{f}_L\right) \\
&= \left(\frac{2\pi}{L}\right)^{\frac{d}{2}} \sum_{K \in \frac{2\pi}{L}\mathbb{Z}^d} \frac{\overline{\widehat{\chi}\,(K)} c_K^L\left(\tilde{f}_L\right)}{\sqrt{|K|^2 + m^2}} \\
&= \left(\frac{2\pi}{L}\right)^{\frac{d}{2}} \sum_{K \in \frac{2\pi}{L}\mathbb{Z}^d} \overline{\widehat{\eta}\,(K)} c_K^L\left(\tilde{f}_L\right) \\
&= \sum_{K \in \frac{2\pi}{L}\mathbb{Z}^d} \overline{c_K^L\left(\eta_L\right)} c_K^L\left(\tilde{f}_L\right) \\
&= \int_{\Gamma_L} \left(\sum_{k \in (L\mathbb{Z})^d} \eta\left(x - k\right)\right) \tilde{f}_L\left(x\right)\, dx \\
&= \int_{\mathbb{R}^d} \eta \tilde{f}_L.
\end{aligned}$$

Next, using the fact that $\eta \in \mathcal{S}\left(\mathbb{R}^d\right)$, the weak convergence of $\tilde{f}_L$ to f in $L^{1+2/d}(\Omega, L^{1+2/d}_{\mathrm{loc}}(\mathbb{R}^d))$, and the bound (2.76), we prove that

$$\mathbb{E}\left(u \int_{\mathbb{R}^d} \eta \tilde{f}_L\right) \underset{L \to \infty}{\longrightarrow} \mathbb{E}\left(u \int_{\mathbb{R}^d} \eta f\right), \tag{2.79}$$

which concludes the proof of (2.78), hence of (2.77). For this purpose, let $\varepsilon > 0$. As $\eta \in \mathcal{S}(\mathbb{R}^d)$, then the series $\sum_{k \in \mathbb{Z}^d} \|\eta\|_{L^p(Q+k)}$ is convergent for any $1 \leq p \leq +\infty$. Therefore, there exists $R_0 > 0$ such that

$$\sum_{\substack{k \in \mathbb{Z}^d \\ |k| > R_0 - 1}} \|\eta\|_{L^{d/2+1}(Q+k)} \leq \frac{\varepsilon}{3C},$$

where $C = \|u\|_{L^{d/2+1}(\Omega)} \sup_{R \in \mathbb{Z}^d,\, L \in \mathbb{N}\setminus 0} \left\|\tilde{f}_L\right\|_{L^{2/d+1}(\Omega \times (Q+R))}$. By the weak convergence of $\tilde{f}_L$ to f in $L^{2/d+1}(\Omega, L^{2/d+1}_{\mathrm{loc}}(\mathbb{R}^d))$, there exists $L_1 \geq L_0$ such that $\forall L \geq L_1$

$$\left|\mathbb{E}\left(u \int_{B(0,R_0)} \eta \tilde{f}_L\right) - \mathbb{E}\left(u \int_{B(0,R_0)} \eta f\right)\right| \leq \frac{\varepsilon}{3}. \tag{2.80}$$

By Hölder inequality, we have

$$\begin{aligned}\left|\mathbb{E}\left(u\int_{\mathbb{R}^d\setminus B(0,R_0)}\eta\tilde{f}_L\right)\right| &\leq \sum_{\substack{k\in\mathbb{Z}^d\\ |k|>R_0-1}}\left|\mathbb{E}\left(u\int_{Q+k}\eta\tilde{f}_L\right)\right| \\ &\leq \sum_{\substack{k\in\mathbb{Z}^d\\ |k|>R_0-1}}\|u\|_{L^{d/2+1}(\Omega)}\|\eta\|_{L^{d/2+1}(Q+k)}\left\|\tilde{f}_L\right\|_{L^{2/d+1}(\Omega\times(Q+k))} \\ &\leq \frac{\varepsilon}{3}. \end{aligned} \tag{2.81}$$

As the latter inequality holds for f as well (by the weak lower semi-continuity of the norm), we also have

$$\left|\mathbb{E}\left(u\int_{\mathbb{R}^d\setminus B(0,R_0)}\eta f\right)\right| \leq \frac{\varepsilon}{3}. \tag{2.82}$$

From (2.80), (2.81) and (2.82), we conclude that for any $L \geq L_1$

$$\left|\mathbb{E}\left(u\int_{\mathbb{R}^d}\eta\tilde{f}_L\right)-\mathbb{E}\left(u\int_{\mathbb{R}^d}\eta f\right)\right| \leq \varepsilon,$$

which concludes the proof of (2.79). □

Proposition 2.5.6 (Almost sure upper bound)**.** *Let $\mu \in L^2_s$. Then,*

$$\limsup_{L\to\infty}\frac{I^L_{\mu,m,\varepsilon_{\mathrm{F}}}(\omega)}{L^d} \leq I_{\mu,m,\varepsilon_{\mathrm{F}}},\ \textit{a.s.} \tag{2.83}$$

Proof. We first prove (2.83) assuming that $\mu \in L^\infty\left(\Omega\times\mathbb{R}^d\right)$; we then deduce the general case by an $\varepsilon/2$ argument using (2.57) and (2.60). Let γ be a minimizer of (2.55). By the ergodic theorem, there exists $\Omega'_\mu \subset \Omega$, with $\mathbb{P}\left(\Omega'_\mu\right)=1$, such that on Ω'_μ

$$\lim_{L\to\infty}\frac{1}{L^d}\int_{\Gamma_L}\rho_\gamma = \mathbb{E}\left(\int_Q\rho_\gamma\right),\quad \lim_{L\to\infty}\frac{1}{L^d}\int_{\Gamma_L}\rho_{P_j\gamma P_j} = \mathbb{E}\left(\int_Q\rho_{P_j\gamma P_j}\right), \tag{2.84}$$

for any $1\leq j\leq d$, and

$$\lim_{L\to\infty}\frac{\left\|\left(-\Delta_s+m^2\right)^{-\frac{1}{2}}(\rho_\gamma-\mu)\right\|^2_{L^2(\Gamma_L)}}{L^d} = \left\|\left(-\Delta_s+m^2\right)^{-\frac{1}{2}}(\rho_\gamma-\mu)\right\|^2_{L^2_s}. \tag{2.85}$$

Let $\omega_0\in\Omega'_\mu$ be fixed for the rest of the proof. Let $0\leq\chi_L\leq 1$ be a sequence of localization functions of $C^\infty_c\left(\mathbb{R}^d\right)$, which equals 1 on Γ_{L-1}, has its support in Γ_L, and satisfies $|\nabla\chi_L|\leq C$. For $L\in\mathbb{N}\setminus\{0\}$, we introduce the operators

$\gamma_L^0 : L^2\left(\mathbb{R}^d\right) \to L^2\left(\mathbb{R}^d\right)$ and $\gamma_L : L^2_{\rm per}\left(\Gamma_L\right) \to L^2_{\rm per}\left(\Gamma_L\right)$, whose kernels are given by

$$\gamma_L^0\left(x,y\right) = \chi_L\left(x\right)\gamma\left(\omega_0,x,y\right)\chi_L\left(y\right) \text{ and } \gamma_L\left(x,y\right) = \sum_{j,k\in(L\mathbb{Z})^d} \gamma_L^0\left(x+j,y+k\right).$$

We first check that the charge per unit volume of γ_L converges to the one of γ. We have

$$\begin{aligned}\frac{1}{L^d}\int_{\Gamma_L}\rho_{\gamma_L} &= \frac{1}{L^d}\int_{\Gamma_L}\rho_\gamma\chi_L^2 \\ &= \frac{1}{L^d}\int_{\Gamma_L}\rho_\gamma + \frac{1}{L^d}\int_{\Gamma_L}\rho_\gamma\left(\chi_L^2-1\right). \end{aligned} \tag{2.86}$$

We recall that as $\mu \in L^\infty(\Omega\times\mathbb{R}^d)$, then $\rho_\gamma \in L^\infty(\Omega\times\mathbb{R}^d)$ by Corollary 2.4.6. It follows that the second term of the RHS of (2.86) goes to 0 since

$$\begin{aligned}\left|\frac{1}{L^d}\int_{\Gamma_L}\rho_\gamma\left(\chi_L^2-1\right)\right| &\leq \frac{1}{L^d}\int_{\Gamma_L\setminus\Gamma_{L-1}}\rho_\gamma \\ &\leq C\frac{L^{d-1}}{L^d}\left\|\rho_\gamma\right\|_{L^\infty(\Omega\times\mathbb{R}^d)} \underset{L\to\infty}{\longrightarrow} 0.\end{aligned}$$

Therefore, using (2.84), we conclude that

$$\lim_{L\to\infty}\frac{1}{L^d}\int_{\Gamma_L}\rho_{\gamma_L} = \lim_{L\to\infty}\frac{1}{L^d}\int_{\Gamma_L}\rho_\gamma = \mathbb{E}\left(\int_Q\rho_\gamma\right). \tag{2.87}$$

Next, we check that the kinetic energy per unit volume converges as well. It holds that

$$\begin{aligned}\mathrm{Tr}_{\,L^2_{\rm per}(\Gamma_L)}\left(-\Delta_L\gamma_L\right) &= \mathrm{Tr}\,\left(-\Delta\gamma_L^0\right) \\ &= \sum_{j=1}^d \mathrm{Tr}\,\left(P_j\chi_L\gamma(\omega_0)\chi_L P_j\right) \\ &= \sum_{j=1}^d \left(I_{j,1}^L + 2I_{j,2}^L + I_{j,3}^L\right),\end{aligned}$$

where $I_{j,1}^L$, $I_{j,2}^L$ and $I_{j,3}^L$ are given by

$$I_{j,1}^L = \mathrm{Tr}\,\left(\chi_L P_j\gamma(\omega_0)P_j\chi_L\right), \quad I_{j,2}^L = -\mathrm{Im}\left(\mathrm{Tr}\,\left(\chi_L P_j\gamma(\omega_0)(\partial_{x_j}\chi_L)\right)\right),$$

and

$$I_{j,3}^L = \mathrm{Tr}\,\left((\partial_{x_j}\chi_L)\gamma(\omega_0)(\partial_{x_j}\chi_L)\right).$$

We first show that the term $L^{-d}I_{j,1}^L$ converges to $\underline{\mathrm{Tr}}\,(P_j\gamma P_j)$. Indeed,

$$\begin{aligned}\frac{1}{L^d}\left(I_{j,1}^L - \mathrm{Tr}\,\left(1_{\Gamma_L}P_j\gamma(\omega_0)P_j1_\Gamma\right)\right) &= -\frac{1}{L^d}\mathrm{Tr}\,\left(1_{\Gamma_L}\sqrt{1-\chi_L^2}P_j\gamma(\omega_0)P_j\sqrt{1-\chi_L^2}1_\Gamma\right)\\ &= -\frac{1}{L^d}\int_{\Gamma_L\setminus\Gamma_{L-1}}\left(1-\chi_L^2\right)\rho_{P_j\gamma(\omega_0)P_j},\end{aligned}$$

we conclude as before using (2.84). We now prove that the term $L^{-d}I_{j,3}^L$ vanishes at infinity. We have

$$\begin{aligned}\frac{1}{L^d}I_{j,3}^L &= \frac{1}{L^d}\int_{\Gamma_L\setminus\Gamma_{L-1}}\left(\partial_{x_j}\chi_L\right)^2\rho_{\gamma(\omega_0)}\\ &\leq \frac{1}{L^d}\left\|\rho_{\gamma(\omega_0)}\right\|_{L^\infty\left(\mathbb{R}^d\right)}\left\|\partial_{x_j}\chi_L\right\|_{L^\infty\left(\mathbb{R}^d\right)}^2 CL^{d-1}\underset{L\to\infty}{\longrightarrow}0.\end{aligned}$$

Finally, we have

$$\left|\frac{1}{L^d}I_{j,2}^L\right| \;\leq\; \frac{1}{L^d}\left(I_{j,1}^L\right)^{\frac{1}{2}}\left(I_{j,3}^L\right)^{\frac{1}{2}}\underset{L\to\infty}{\longrightarrow}0$$

since $L^{-d}I_{j,1}$ is convergent, thus bounded. Therefore, we have proved that

$$\lim_{L\to\infty}\frac{1}{L^d}\mathrm{Tr}_{\,L^2_{\mathrm{per}}(\Gamma_L)}\left(-\Delta_L\gamma_L\right) = \underline{\mathrm{Tr}}\,\left(-\Delta\gamma\right). \tag{2.88}$$

We now turn to the convergence of the potential energy, that is,

$$\lim_{L\to\infty}\frac{1}{L^d}D_{m,L}\left(g_L,g_L\right) = D_m\left(f,f\right), \tag{2.89}$$

where $f=\rho_\gamma-\mu$ and $g_L=\rho_{\gamma_L}-\mu_L(\omega_0,\cdot)$. We introduce the auxiliary function f_L, defined as the $L\mathbb{Z}^d$-periodic function equal to $f(\omega_0,\cdot)$ on Γ_L. We first prove that

$$\lim_{L\to\infty}\frac{1}{L^d}\left(D_{m,L}\left(g_L,g_L\right)-D_{m,L}\left(f_L,f_L\right)\right)=0. \tag{2.90}$$

Indeed, rewriting g_L as $g_L=\chi_{L,\mathrm{per}}^2f_L+\left(\chi_{L,\mathrm{per}}^2-1\right)\mu_L$, with the definition $\chi_{L,\mathrm{per}}=\sum_{k\in(L\mathbb{Z})^d}\chi_L\left(\cdot+k\right)$, we have

$$\begin{aligned}\left\|\left(-\Delta_L+m^2\right)^{-\frac{1}{2}}\left(g_L-f_L\right)\right\|_{L^2(\Gamma_L)}^2 &\leq m^{-2}\left\|g_L-f_L\right\|_{L^2(\Gamma_L)}^2\\ &\leq m^{-2}\left\|\left(\chi_{L,\mathrm{per}}^2-1\right)\left(f_L-\mu_L\right)\right\|_{L^2(\Gamma_L)}^2\\ &\leq Cm^{-2}\left\|f_L-\mu_L\right\|_{L^\infty}^2L^{d-1}\\ &\leq C\left(\left\|\mu\right\|_{L^\infty}+\left\|\rho_\gamma\right\|_{L^\infty}\right)^2L^{d-1},\end{aligned}$$

which proves (2.90). Then, we prove that

$$\lim_{L\to\infty} \frac{D_{m,L}\left(f_L, f_L\right)}{L^d} = D_m\left(f, f\right). \tag{2.91}$$

Below, we detail the proof of (2.91) which corrects a slight error in [29]. In view of (2.85), it is sufficient to show that

$$\alpha_L = \frac{\left|S^{d-1}\right|}{L^d}\left(\left\|\left(-\Delta_L + m^2\right)^{-\frac{1}{2}} f_L\right\|^2_{L^2(\Gamma_L)} - \left\|\left(\left(-\Delta_s + m^2\right)^{-\frac{1}{2}} f\right)(\omega_0, \cdot)\right\|^2_{L^2(\Gamma_L)}\right)$$

tends to zero. We have

$$\begin{aligned}\alpha_L &= \frac{1}{L^d}\int_{\Gamma_L} (W_m * f_L)^2(x)\, dx - \frac{1}{L^d}\int_{\Gamma_L} (W_m * f)^2(\omega_0, x)\, dx \\ &= \frac{1}{L^d}\int_{\Gamma_L} dx\, h_L(x) \int_{\mathbb{R}^d\setminus\Gamma_L} dy\, W_m(x-y)\left(f_L(y) - f(\omega_0, y)\right),\end{aligned}$$

where $h_L = W_m * f_L + (W_m * f)(\omega_0, \cdot)$ is in $L^\infty(\mathbb{R}^d)$ and satisfies $\|h_L\|_{L^\infty(\mathbb{R}^d)} \leq C\left\|f_L + f\right\|_{L^\infty(\Omega\times\mathbb{R}^d)} \leq C\left\|f\right\|_{L^\infty(\Omega\times\mathbb{R}^d)}$. We split α_L into two parts, namely

$$\alpha_{L,\text{out}} = \frac{1}{L^d}\int_{\Gamma_L} dx\, h_L\left(x\right) \int_{\mathbb{R}^d\setminus\Gamma_{L+\sqrt{L}}} dy\, W_m\left(x-y\right)\left(f_L\left(y\right) - f\left(\omega_0, y\right)\right)$$

and

$$\alpha_{L,\text{in}} = \frac{1}{L^d}\int_{\Gamma_L} dx\, h_L\left(x\right) \int_{\Gamma_{L+\sqrt{L}}\setminus\Gamma_L} dy\, W_m\left(x-y\right)\left(f_L\left(y\right) - f\left(\omega_0, y\right)\right).$$

For the first term, it holds that

$$\begin{aligned}\left|\alpha_{L,\text{out}}\right| &\leq \frac{1}{L^d}\int_{\Gamma_L} dx\ \left|h_L\left(x\right)\right| \left(2\left\|f\right\|_{L^\infty\left(\Omega\times\mathbb{R}^d\right)} \int_{|z|\geq C\sqrt{L}} dz W_m\left(z\right)\right) \\ &\leq C\left\|f\right\|^2_{L^\infty\left(\Omega\times\mathbb{R}^d\right)} \int_{|z|\geq C\sqrt{L}} dz W_m\left(z\right) \underset{L\to\infty}{\longrightarrow} 0,\end{aligned}$$

where we have used that W_m is integrable over $\mathbb{R}^d$. We turn to the second term

$$\begin{aligned}\left|\alpha_{L,\text{in}}\right| &\leq \frac{C}{L^d}\left\|f\right\|^2_{L^\infty\left(\Omega\times\mathbb{R}^d\right)} \int_{\Gamma_{L+\sqrt{L}}\setminus\Gamma_L} dy\ \left(\int_{\Gamma_L} dx\, W_m\left(x-y\right)\right) \\ &\leq C\left\|f\right\|^2_{L^\infty\left(\mathbb{R}^d\right)} \left\|W_m\right\|_{L^1\left(\mathbb{R}^d\right)} \frac{L^{d-1}\sqrt{L}}{L^d} \underset{L\to\infty}{\longrightarrow} 0,\end{aligned}$$

which concludes the proof of (2.91), thus proving (2.89). In view (2.88) and (2.89), we conclude that

$$\lim_{L\to\infty} \frac{1}{L^d}\mathcal{E}^L_{\mu,m}\left(\omega_0, \gamma_L\right) = \mathcal{E}_{\mu,m}\left(\gamma\right) = I_{\mu,m}.$$

Therefore, using (2.87),

$$\limsup_{L\to\infty} \frac{I^L_{\mu,m,\varepsilon_{\rm F}}(\omega_0)}{L^d} \leq I_{\mu,m,\varepsilon_{\rm F}},$$

which concludes the proof of (2.83) for $\mu \in L^\infty(\Omega \times \mathbb{R}^d)$. For the general case, we consider $\mu_n = \min\{n, \mu\}$, and denote by $I = I_{\mu,m,\varepsilon_F}$, $I_n = I_{\mu_n,m,\varepsilon_F}$, $I_L(\omega) = I^L_{\mu,m,\varepsilon_F}(\omega)$, $I_{L,n}(\omega) = I^L_{\mu,m_n,\varepsilon_F}(\omega)$ and by γ_n, γ, $\gamma_{L,n}$ γ_L minimizers of I_n, I, $I_{L,n}$ and I_L respectively. Using a test state $\gamma' = 0$, we have, similarly as in the proof of (2.57),

$$D_{m,L}(\rho_{\gamma_{L,n}}, \rho_{\gamma_{L,n}}) \leq \frac{1}{m^2}\int_{\Gamma_L} \mu_n^2 \leq \frac{1}{m^2}\int_{\Gamma_L} \mu^2.$$

and

$$D_m(\rho_{\gamma_L}, \rho_{\gamma_L}) \leq \frac{1}{m^2}\|\mu\|^2_{L^2_s}. \tag{2.92}$$

Next, using γ as test state in the problem I_n, we obtain a.s.

$$\begin{aligned}
I_n &\leq I + D_m(\rho_\gamma - \mu_n, \rho_\gamma - \mu_n) - D_m(\rho_\gamma - \mu, \rho_\gamma - \mu)\\
&\leq I + 2D_m(\rho_\gamma, \mu - \mu_n) + D_m(\mu_n, \mu_n) - D_m(\mu, \mu)\\
&\leq I + \left(2D_m(\rho_\gamma, \rho_\gamma)^{\frac{1}{2}} + D_m(\mu, \mu)^{\frac{1}{2}} + D_m(\mu_n, \mu_n)^{\frac{1}{2}}\right) D_m(\mu - \mu_n, \mu - \mu_n)^{\frac{1}{2}}\\
&\leq I + \frac{4}{m^2}\|\mu\|_{L^2_s}\|\mu - \mu_n\|_{L^2_s}
\end{aligned} \tag{2.93}$$

where we have used (2.92). Similarly, we have a.s.

$$\begin{aligned}
I_L &\leq I_{L,n} + \left(2D_{m,L}\left(\rho_{\gamma_{L,n}}, \rho_{\gamma_{L,n}}\right)^{\frac{1}{2}} + D_{m,L}(\mu_L + \mu_{L,n}, \mu_L + \mu_{L,n})^{\frac{1}{2}}\right)\\
&\quad \times D_{m,L}(\mu_L - \mu_{L,n}, \mu_L - \mu_{L,n})^{\frac{1}{2}}\\
&\leq I_{L,n} + \frac{4}{m^2}\|\mu\|_{L^2(\Gamma_L)}\|\mu - \mu_n\|_{L^2(\Gamma_L)}.
\end{aligned} \tag{2.94}$$

Let $\varepsilon > 0$ and let $N \in \mathbb{N}$ such that $\|\mu - \mu_N\|_{L^2_s} \leq m^2\varepsilon/(12(\|\mu\|_{L^2_s} + 1))$. We now consider Ω'', the set of probability 1 such that for any $\omega \in \Omega''$

$$\lim_{L\to\infty} \frac{1}{L^d}\|\mu(\omega,\cdot) - \mu_N(\omega,\cdot)\|^2_{L^2(\Gamma_L)} = \|\mu - \mu_N\|^2_{L^2_s}$$

and

$$\lim_{L\to\infty} \frac{1}{L^d}\|\mu(\omega,\cdot)\|^2_{L^2(\Gamma_L)} = \|\mu\|^2_{L^2_s}.$$

Let $\omega_0 \in \Omega'_{\mu_N} \cap \Omega''$. There thus exists L_0 such that for any $L \geq L_0$, it holds

$$\left|\frac{1}{L^d}\|\mu(\omega_0,\cdot) - \mu_N(\omega_0,\cdot)\|^2_{L^2(\Gamma_L)} - \|\mu - \mu_N\|^2_{L^2_s}\right| \leq \frac{m^4\varepsilon^2}{(12(\|\mu\|_{L^2_s} + 1))^2}$$

and

$$\left| \frac{1}{L^d} \|\mu(\omega_0, \cdot)\|^2_{L^2(\Gamma_L)} - \|\mu\|^2_{L^2_s} \right| \leq 1.$$

For $L \geq L_0$, we have by (2.94)

$$\begin{aligned}
\frac{I_L(\omega_0)}{L^d} &\leq \frac{I_{L,N}(\omega_0)}{L^d} + \frac{4}{m^2} \frac{\|\mu(\omega_0, \cdot)\|_{L^2(\Gamma_L)}}{L^{\frac{d}{2}}} \frac{\|\mu(\omega_0, \cdot) - \mu_N(\omega_0, \cdot)\|_{L^2(\Gamma_L)}}{L^{\frac{d}{2}}} \\
&\leq \frac{I_{L,N}(\omega_0)}{L^d} + \frac{4}{m^2}(\|\mu\|_{L^2_s} + 1) \left(\|\mu - \mu_N\|_{L^2_s} + \frac{m^2 \varepsilon}{12(\|\mu\|_{L^2_s} + 1)} \right) \\
&\leq \frac{I_{L,N}(\omega_0)}{L^d} + \frac{4}{m^2}(\|\mu\|_{L^2_s} + 1) \frac{m^2 \varepsilon}{6(\|\mu\|_{L^2_s} + 1)} \\
&\leq \frac{I_{L,N}(\omega_0)}{L^d} + \frac{2\varepsilon}{3}.
\end{aligned}$$

Therefore

$$\limsup_{L \to \infty} \frac{I_L(\omega_0)}{L^d} \leq \limsup_{L \to \infty} \frac{I_{L,N}(\omega_0)}{L^d} + \frac{2\varepsilon}{3}.$$

As $\mu_N \in L^\infty(\Omega \times \mathbb{R}^d)$, we have already proved that $\limsup_{L \to \infty} L^{-d} I_{L,N}(\omega_0) \leq I_N$. Thus

$$\limsup_{L \to \infty} \frac{I_L(\omega_0)}{L^d} \leq I_N + \frac{2\varepsilon}{3} \leq I + \varepsilon, \tag{2.95}$$

where the last inequality follows from (2.93). As (2.95) is valid for any $\varepsilon > 0$ and any ω_0 in the set $\Omega'_{\mu_N} \cap \Omega''$ of probability 1, this concludes the proof of the Proposition. □

We complete the proof of Theorem 2.5.2 using Lemma 2.5.7 below applied to $X_L(\omega) = L^{-d} I^L_{\mu, m, \varepsilon_F}(\omega)$ and the bound (2.57).

Lemma 2.5.7. *Let $(X_n)_{n \in \mathbb{N}}$ be a sequence of random variables in $L^1(\Omega)$ and $X \in L^1(\Omega)$. We assume that there exists a sequence of random variables $(Z_n)_{n \in \mathbb{N}}$ converging in $L^1(\Omega)$ to $Z \in L^1(\Omega)$ such that*

- $\liminf_{n \to \infty} \mathbb{E}(X_n) \geq \mathbb{E}(X)$
- $\limsup_{n \to \infty} X_n \leq X$ *a.s.*
- $X_n \leq Z_n$ *a.s.*

Then, $X_n \to X$ strongly in $L^1(\Omega)$ as $n \to \infty$.

Proof. Replacing X_n by $X_n - X$, we can assume without loss of generality that $X = 0$. We then write $X_n = (X_n)_+ - (X_n)_-$. We first notice that $(X_n)_+ \to 0$ a.s. By the dominated convergence theorem with "moving bound" (see e.g. [110, Theorem 1.8]), we conclude that $(X_n)_+ \to 0$ in $L^1(\Omega)$. By the liminf condition, we have $\limsup_{n \to \infty} \mathbb{E}((X_n)_-) \leq 0$. As $(X_n)_- \geq 0$, we conclude that $(X_n)_- \to 0$ in $L^1(\Omega)$. Finally, $\mathbb{E}(|X_n|) = \mathbb{E}((X_n)_+) + \mathbb{E}((X_n)_-)$ tends to 0. □

Remark 2.5.8 (Convergence of γ'_L)**.** *We deduce from* (2.69) *and* (2.56) *that the weak-∗ limit* γ *of* γ'_L *satisfies* $\mathcal{E}_{\mu,m}(\gamma) - \varepsilon_{\mathrm{F}}\underline{\mathrm{Tr}}(\gamma) = I_{\mu,m,\varepsilon_{\mathrm{F}}}$ *and is therefore a minimizer of* $I_{\mu,m,\varepsilon_{\mathrm{F}}}$*.*

2.A Ergodic group actions

In this section, we recall the definition of an ergodic group action and give some examples of probability spaces and ergodic group actions on these probability spaces.

We recall that a probability space is a triplet $(\Omega, \mathcal{F}, \mathbb{P})$, where Ω is an arbitrary non empty set, $\mathcal{F} \subset \mathcal{P}(\Omega)$ is a σ-algebra of Ω and $\mathbb{P}$ a positive measure on $\mathcal{F}$ such that $\mathbb{P}(\Omega) = 1$. A random variable (r.v. in short) on Ω is a measurable function on Ω that takes finite values on a subset of Ω of measure 1.

Let $(\Omega, \mathcal{F}, \mathbb{P})$ be a probability space and G a group. A *group action* of G on $(\Omega, \mathcal{F})$ is a family of transformations $\tau = \{\tau_k : \Omega \to \Omega,\ k \in G\}$ satisfying

- $\tau_k \circ \tau_{k'} = \tau_{k+k'}\ \forall k, k' \in G$,
- $\tau_0 = Id$,
- the map τ_k is measurable for all $k \in G$.

Note that for every $k \in G$, the function $\omega \mapsto \tau_k(\omega)$ is a bijective map from Ω to Ω, with inverse τ_{-k}. We now define ergodic group actions.

Definition 2.A.1 (Ergodic group actions)**.** *Let* $\tau = (\tau_k)_{k\in G}$ *be a group action of* G *on* Ω*.*

- τ *is called measure preserving if for all* $A \in \mathcal{F}$ *and for all* $k \in G$*, we have* $\mathbb{P}(\tau_k(A)) = \mathbb{P}(A)$*.*
- τ *is called ergodic if it is measure preserving and if* $\tau_k(A) = A$ *for all* $k \in G$ *implies that* $\mathbb{P}(A) \in \{0, 1\}$*.*

In the next sections, we give some examples of probability spaces and ergodic group actions on these probability spaces.

2.A.1 Finite or countable sets of events

We consider in this section the case where Ω is finite or countable.

Proposition 2.A.2. *Let* $\Omega = \{\omega_1, \omega_2, \cdots, \omega_n\}$ *be a finite set,* $\mathcal{F}$ *be the set of subsets of* Ω*, and* $\mathbb{P}$ *be a measure on* Ω *such that for any* $\omega \in \Omega$, $\mathbb{P}(\{\omega\}) > 0$*. Let* τ *be a group action of* $\mathbb{Z}$ *on* Ω*. Then,*

(i) if τ *is ergodic, then* τ *is cyclic, that is, for any* ω *in* Ω *we have*

$$\{\tau_k(\omega),\ k \in \mathbb{Z}\} = \{\tau_k(\omega),\ 0 \le k \le n-1\} = \Omega,$$

(ii) if τ is ergodic, then the measure $\mathbb{P}$ is necessarily uniform, that is, $\mathbb{P}(\omega) = \frac{1}{n}$ for all $\omega \in \Omega$.

Proof. We start with Assertion *(i)*. Assume that for a given $\omega \in \Omega$, we have

$$\{\tau_k(\omega),\ k \in \mathbb{Z}\} \neq \{\tau_k(\omega),\ 0 \leq k \leq n-1\}.$$

Then there exist $0 \leq k < k' \leq n-1$ such that $\tau_k(\omega) = \tau_{k'}(\omega)$. Thus $\tau_{(k'-k)i}(\omega) = \omega$ for any $i \in \mathbb{Z}$. Let $m \in \mathbb{Z}$. We can write $m-k = m'+(k'-k)i$, where $i \in \mathbb{Z}$ and $0 \leq m' < k'-k$. It follows that $\tau_m(\omega) = \tau_{m'+k}(\omega) \in \{\tau_k(\omega),\ 0 \leq k \leq n-1\}$, which contradicts the assumption. Thus, the first part of the equality holds true.

Assume now that for a given $\omega \in \Omega$ there exists $\omega' \in \Omega$ such that $\omega' \notin \{\tau_k(\omega),\ k \in \mathbb{Z}\}$, then

$$0 < \mathbb{P}\left(\{\omega\}\right) \leq \mathbb{P}\left(\{\tau_k(\omega),\ k \in \mathbb{Z}\}\right) \leq 1 - \mathbb{P}\left(\left\{\omega'\right\}\right) < 1. \tag{2.96}$$

As $\{\tau_k(\omega),\ k \in \mathbb{Z}\}$ is invariant under τ, then (2.96) contradicts the ergodicity assumption.

We turn to the proof of Assertion *(ii)*. From Assertion *(i)*, we deduce that for any $\omega, \omega' \in \Omega$ there exists $k \in \mathbb{Z}$ such that $\tau_k(\omega) = \omega'$. If in addition τ is measure preserving, then

$$\mathbb{P}\left(\left\{\omega'\right\}\right) = \mathbb{P}\left(\{\tau_k\left(\omega\right)\}\right) = \mathbb{P}\left(\{\omega\}\right).$$

□

We turn now to the case of infinite countable probability set Ω.

Proposition 2.A.3. *Let $\Omega = (\omega_i)_{i\in\mathbb{N}}$ be a countable infinite set, $\mathcal{F}$ the set of the subsets of Ω and $\mathbb{P}$ a measure on $(\Omega, \mathcal{F})$ such that for any $\omega \in \Omega$, $\mathbb{P}(\{\omega\}) > 0$. Let τ be a measure preserving group action of $\mathbb{Z}$ on Ω. Then the cycles of τ are finite, that is, for any ω in Ω the set $\{\tau_k(\omega),\ k \in \mathbb{Z}\}$ is finite.*

Proof. Suppose that there exists $\omega \in \Omega$ such that $A(\omega) = \{\tau_k(\omega),\ k \in \mathbb{Z}\}$ is infinite; we denote its elements by $(a_k)_{k\in\mathbb{N}}$. They satisfy $a_k \neq a_{k'}$ and $\mathbb{P}(\{a_k\}) = \mathbb{P}(\{\omega\})$ for all $k, k' \in \mathbb{Z}$. Also,

$$\begin{aligned} 1 \geq \mathbb{P}(\{\tau_k(\omega), k \in \mathbb{Z}\}) &= \sum_{k\in\mathbb{N}} \mathbb{P}(\{a_k\}) \\ &= \sum_{k\in\mathbb{N}} \mathbb{P}(\{\omega\}) = \infty. \end{aligned}$$

This contradiction concludes the proof. □

Corollary 2.A.4. *If Ω is a countable infinite set, then there exists no ergodic group action of $\mathbb{Z}$ on Ω.*

The case of Ω being uncountable is more delicate. Here are two significant examples.

2.A.2 Independent and identically distributed variables on $\mathbb{Z}^d$

Let $d \in \mathbb{N}^*$ be the space dimension. We define a probability space by

- $\Omega = \{-1, 1\}^{\mathbb{Z}^d}$,
- $\mathcal{F} = \sigma(Y_i, i \in \mathbb{Z}^d)$, where $Y_i(\omega) = \omega_i$ is a sequence of real valued random variables,
- $\mathbb{P} = p^{\otimes \mathbb{Z}^d}$ where $p = p_1\delta_1 + (1 - p_1)\delta_{-1}$ and $0 < p_1 < 1$.

The variables Y_i are independent and identically distributed (i.i.d.). Here, we consider the group action of $G = \mathbb{Z}^d$ on Ω defined by $\tau_k(\omega) = \omega_{\cdot+k}$. It is called *the shift on* $\mathbb{Z}^d$.

Remark 2.A.5.
- *This probability space models a crystal with one particle at each site of the lattice $\mathbb{Z}^d$. The charges of the particles take their values in $\{-1, 1\}$ and are independently and identically distributed following the measure p.*
- *The results of this section are still valid if we replace $\{-1, 1\}$ in the definition of the probability space by an arbitrary set $\mathcal{O}$ with p a measure on $\mathcal{O}$.*

Proposition 2.A.6. *The shift on $\mathbb{Z}^d$ is measure preserving.*

Proof. By a monotone-class argument (see e.g. [78, Theorem 1.1]), we only need to show that τ preserves the measure of the sets of the form $C = \{\omega \in \Omega \mid \omega_i = x\}$, where $x \in \{-1, 1\}$ and $i \in \mathbb{Z}^d$. Let C be such a set. Then, we have $\mathbb{P}(C) = p(\{x\})$ by the definition of the measure $\mathbb{P}$. Therefore

$$\forall k \in \mathbb{Z}^d, \quad \mathbb{P}(\tau_k(C)) = \mathbb{P}(\{\omega \in \Omega \mid \omega_{i+k} = x\}) = p(\{x\}) = \mathbb{P}(C).$$

□

Proposition 2.A.7. *The shift on $\mathbb{Z}^d$ is ergodic.*

Proof (inspired by the proof of [68, Proposition 5.2]). For a set $A \in \mathcal{F}$, and a subset $I \subset \mathbb{Z}^d$ we define

$$\pi_I A = \{y \in \Omega \mid \exists x \in A \text{ with } x_k = y_k,\ \forall k \in I\}.$$

We notice that $\cap_{n\in\mathbb{N}} \pi_{[-n,n]^d} A = A$, thus $\lim_{n\to+\infty} \mathbb{P}\left(\pi_{[-n,n]^d} A\right) = \mathbb{P}(A)$. We denote by $\sigma^+ = \sigma(Y_k,\ k_i \geq 1,\ 1 \leq i \leq d)$ and $\sigma^- = \sigma(Y_k,\ k_i \leq -1,\ 1 \leq i \leq d)$. As the sequence (Y_i) is i.i.d, then σ^+ and σ^- are independent. Recall that two σ-algebras $\mathcal{F}$ and $\mathcal{G}$ are independent if for all A in $\mathcal{F}$ and $B \in \mathcal{G}$, we have $\mathbb{P}(A \cap B) = \mathbb{P}(A)\mathbb{P}(B)$.

We introduce the sets

$$A_n = \pi_{[1,2n+1]^d} A, \quad A_\infty = \cap_{n\in\mathbb{N}} A_n \in \sigma^+, \quad A_n^- = \pi_{[-2n-1,-1]^d} A$$

and

$$A_\infty^- = \cap_{n\in\mathbb{N}} A_n^- \in \sigma^-.$$

We suppose that $\tau_k(A) = A$ for all $k \in \mathbb{Z}^d$. We will show that $A = A_\infty$ and $A = A_\infty^-$ a.s. We denote by $u_n = (n+1, \cdots, n+1)^T$. A simple calculation, using the invariance of A under τ, shows that

$$\pi_{[-n,n]^d} A = \tau_{-u_n} \left(\pi_{[1,2n+1]^d} \tau_{u_n} (A) \right).$$

Hence,

$$\mathbb{P}\left(\pi_{[-n,n]^d} A\right) = \mathbb{P}\left(\pi_{[1,2n+1]^d} A\right) = \mathbb{P}(A_n).$$

Therefore $\lim_{n\to+\infty} \mathbb{P}(A_n) = \mathbb{P}(A)$. It follows that

$$1_{A_\infty} - 1_A \geq 0 \text{ and } \mathbb{E}(1_{A_\infty} - 1_A) = 0,$$

therefore $1_{A_\infty} = 1_A$ a.s. Similarly, we show that $1_{A_\infty^-} = 1_A$ a.s. Finally,

$$\mathbb{P}(A) = \mathbb{P}(A_\infty \cap A_\infty^-) = \mathbb{P}(A_\infty)\mathbb{P}(A_\infty^-) = \mathbb{P}(A)^2,$$

where we have used that A_∞ and A_∞^- are independent. We conclude that $\mathbb{P}(A) \in \{0, 1\}$. □

2.A.3 The a-periodic case

In this section, we consider the probability space defined by

- $\Omega = [0, 1)$,
- $\mathcal{F}$ is the Borel algebra of $[0, 1)$,
- $\mathbb{P}$ is the Lebesgue measure.

We consider the group $G = \mathbb{Z}$, and the group action defined by

$$\tau_k(\omega) = \omega + ak - [\omega + ak] = \mathrm{mod}(\omega + ak, 1) \quad \forall k \in \mathbb{Z},$$

for a given $a \in \mathbb{R}$. τ is called *the a-periodic shift on* $[0, 1)$.

Proposition 2.A.8. *The a-periodic shift is measure preserving.*

Proof. Let $A \in \mathcal{F}$ and let $f : \mathbb{R} \to \mathbb{R}$ be the 1-periodic function that equals to 1_A on $[0, 1)$. Then $\mathbb{P}(A) = \int_x^{x+1} f(t)dt$, for all $x \in \mathbb{R}$, and

$$\mathbb{P}(\tau(A)) = \int_0^1 f(t + a)dt = \int_a^{a+1} f(t)dt = \mathbb{P}(A).$$

□

Proposition 2.A.9. *If a is rational, then τ is not ergodic.*

Proof. Let $a = \frac{p}{q}$ with $p \in \mathbb{N}$ and $q \in \mathbb{N} \setminus \{0\}$, and $A = \cup_{i=1}^{q} [\frac{i-1}{q}, \frac{2i-1}{2q})$. We can easily show that $\mathbb{P}(A) = \frac{1}{2}$ and that for all $k \in \mathbb{Z}$, $\tau_k(A) = A$. □

Proposition 2.A.10. *If a is irrational, then τ is ergodic.*

Proof. Let $A \in \mathcal{F}$ and f be the same function as in the proof on Proposition 2.A.9. The Fourier expansions of f and $f(a + \cdot)$ read

$$f(x) = \sum_{n \in \mathbb{Z}} c_n e^{2i\pi x n}$$

and

$$f(x + a) = \sum_{n \in \mathbb{Z}} c_n e^{2i\pi a n} e^{2i\pi x n}.$$

If $\tau_1(A) = A$, then $f(x + a) = f(x)$, for all $x \in [0, 1)$. Therefore

$$\forall n \in \mathbb{N}, \quad c_n = c_n e^{2i\pi a n}, \tag{2.97}$$

by identification of the Fourier coefficients. As a is irrational, (2.97) leads to $c_n = 0$ for all $n \neq 0$. Thus f is constant, equal to 0 or 1, which concludes the proof. □

2.B Some properties of density matrices

In this section we recall some properties of density matrices for finite systems. These are self-adjoint operators γ satisfying the Pauli principle $0 \leq \gamma \leq 1$. Moreover, they have finite number of particles $\mathrm{Tr}\,(\gamma) < \infty$ and finite kinetic energy $\mathrm{Tr}\,(-\Delta\gamma) < \infty$. We recall these notions and some properties of the density matrices for finite systems in Sections 2.B.1 and 2.B.2. In Section 2.B.3, we recall a representability theorem identifying the set of electronic densities that arise from finite density matrices. Finally, we recall in Section 2.B.4 some properties of locally finite density matrices.

2.B.1 The trace class property

A bounded operator A is said to be *trace class* if for one (hence all) orthonormal basis $(\varphi_n)_{n \in \mathbb{N}}$,

$$\sum_{n \in \mathbb{N}} \langle \varphi_n, |A| \varphi_n \rangle < \infty.$$

Its *trace* is then given by

$$\mathrm{Tr}\,(A) = \sum_{n \in \mathbb{N}} \langle \varphi_n, A \varphi_n \rangle.$$

Equipped with the norm $\|A\|_{\mathfrak{S}_1} = \mathrm{Tr}\,(|A|)$, the set of trace class operators $\mathfrak{S}_1$ is a Banach space.

A bounded operator A is said to be *Hilbert-Schmidt* if $\mathrm{Tr}\,(A^*A) < \infty$. Equipped with the scalar product $\langle A, B\rangle_{\mathfrak{S}_2} = \mathrm{Tr}\,(A^*B)$, the set of Hilbert-Schmidt operators $\mathfrak{S}_2$ is a Hilbert space.

The following Propositions recall the definitions of the kernel associated with a Hilbert-Schmidt operator and density associated with a trace class operator.

Proposition 2.B.1 (The kernel)**.** *Let $A \in \mathfrak{S}_2$. Then there exists a unique function $A \in L^2(\mathbb{R}^d \times \mathbb{R}^d)$ such that*

$$\forall \varphi \in L^2(\mathbb{R}^d), \quad A\varphi(x) = \int_{\mathbb{R}^d} A(x,y)\varphi(y)\,dy.$$

Moreover $\|A\|_{\mathfrak{S}_2} = \|A\|_{L^2(\mathbb{R}^d\times\mathbb{R}^d)}$. $A(.,.)$ is called the kernel of A.

Proposition 2.B.2 (The density)**.** *Let A be a trace class operator. Then there exists a unique function $\rho_A \in L^1(\mathbb{R}^d)$ such that*

$$\forall W \in L^\infty_c(\mathbb{R}^d), \quad \mathrm{Tr}\,(AW) = \int_{\mathbb{R}^d} \rho_A(x)W(x)\,dx.$$

If $A \geq 0$, then $\rho_A \geq 0$. ρ_A is called the density of A.

Moreover the map $A: \begin{array}{ccc} \mathfrak{S}_1 & \longrightarrow & L^1(\mathbb{R}^d) \\ A & \mapsto & \rho_A \end{array}$ *is linear and continuous, and*

$$\|\rho_A\|_{L^1(\mathbb{R}^d)} \leq \|A\|_{\mathfrak{S}_1}.$$

2.B.2 Operators with finite kinetic energy

We recall that $\widehat{f}$ denotes the Fourier transform f, that is,

$$\widehat{f}\,(k) = \frac{1}{(2\pi)^{d/2}} \int_{\mathbb{R}^d} f\,(x)\,e^{-ik\cdot x}\,dx.$$

For $1 \leq j \leq d$, the momentum operator P_j in the direction j defined by

$$\begin{cases} D(P_j) = \left\{\varphi \in L^2(\mathbb{R}^d),\ \dfrac{\partial\varphi}{\partial x_j} \in L^2(\mathbb{R}^d)\right\} \\ P_j\varphi = -i\dfrac{\partial\varphi}{\partial x_j},\ \forall\varphi \in D(P_j) \end{cases}$$

is self-adjoint. Indeed, for $\varphi, \psi \in D(P_j)$, we have $\widehat{P_j\varphi}\,(p) = p_i\widehat{\varphi}\,(p)$ and

$$\langle P_j\varphi, \psi\rangle = \langle p_j\widehat{\varphi}, \widehat{\psi}\rangle = \langle \widehat{\varphi}, p_j\widehat{\psi}\rangle = \langle \varphi, P_j\psi\rangle.$$

Therefore P_j is symmetric. Besides, for $\varphi \in L^2(\mathbb{R}^d)$, the function $\widehat{\psi_\pm}(p) = \frac{\widehat{\varphi}(p)}{p_j \pm i}$ satisfies

$$\int_{\mathbb{R}^d} (1+p_j^2) \left|\widehat{\psi_\pm}(p)\right|^2 dp = \int_{\mathbb{R}^d} |\widehat{\varphi}(p)|^2 < \infty.$$

Thus $\psi_\pm = \mathcal{F}^{-1}(\widehat{\psi_\pm})$ is in $D(P_j)$ and $(P_j \pm i)\psi_\pm = \varphi$, which shows that $\mathrm{Ran}(P_j \pm i) = L^2(\mathbb{R}^d)$. Therefore, P_j is self-adjoint.

We can now define operators with finite kinetic energy.

Definition 2.B.3 (Operators with finite kinetic energy)**.** *Let A be a trace class operator. We say that A has a finite kinetic energy if for all $1 \leq j \leq d$, $P_jAP_j \in \mathfrak{S}_1$. In other words, if we denote by $D(P_j)'$ the set of the continuous linear forms on $D(P_j)$, then A has finite kinetic energy if the operator $P_jAP_j : D(P_j) \longrightarrow D(P_j)'$ satisfies*

- *$P_jAP_j\,(D(P_j)) \subset L^2(\mathbb{R}^d)$, that is, for all $\varphi \in D(P_j)$, there exists $f \in L^2(\mathbb{R}^d)$ such that for all $\psi \in D(P_j)$, $\langle P_j\psi, AP_j\varphi\rangle_{L^2(\mathbb{R}^d)} = \langle \psi, f\rangle_{L^2(\mathbb{R}^d)}$,*
- *the operator*

$$\begin{array}{rccc} P_jAP_j: & D(P_j) & \longrightarrow & L^2(\mathbb{R}^d) \\ & \varphi & \mapsto & f \end{array}$$

  can be uniquely extended to a bounded operator on $L^2(\mathbb{R}^d)$,
- *the so defined extension of the operator P_jAP_j is trace class.*

We denote by $\mathrm{Tr}\,(-\Delta A) := \sum_{j=1}^d \mathrm{Tr}\,(P_jAP_j)$ and by $\mathfrak{S}_{1,1}$ the subspace of $\mathfrak{S}_1$, consisting of the trace class operators on $L^2\left(\mathbb{R}^d\right)$ with finite kinetic energy.

Remark 2.B.4. *If $A \geq 0$ and $A \in \mathfrak{S}_1$, then $\sum_{j=1}^d \mathrm{Tr}\,(P_jAP_j)$ always makes sense in $[0, +\infty]$ as*

$$\sum_{j=1}^d \mathrm{Tr}\,(P_jAP_j) = \sum_{n\in\mathbb{N}} \langle \nabla\varphi_n, A\nabla\varphi_n\rangle_{L^2(\mathbb{R}^d)^d},$$

where $(\varphi_n)_{n\in\mathbb{N}}$ is an orthonormal basis of $L^2(\mathbb{R}^d)$ consisting of functions in $H^1(\mathbb{R}^d)$. This quantity is finite if and only if A has a finite kinetic energy as will be shown in the Proposition 2.B.5.

Proposition 2.B.5 (Characterization of the operators with finite kinetic energy)**.** *Let $A \in \mathfrak{S}_1$ be a positive (hence self-adjoint) operator which we write $A = \sum_{n\in\mathbb{N}} \lambda_n |\varphi_n\rangle\langle\varphi_n|$, where $(\lambda_n)_{n\in\mathbb{N}}$ is a summable sequence of non negative real numbers and $(\varphi_n)_{n\in\mathbb{N}}$ an orthonormal basis of $L^2(\mathbb{R}^d)$. Then, A is in $\mathfrak{S}_{1,1}$ if and only if the following conditions are satisfied*

(i) $\forall n \in \mathbb{N},\ \varphi_n \in H^1(\mathbb{R}^d)$,

(ii) $\sum_{n\in\mathbb{N}} \lambda_n \|\nabla\varphi_n\|^2_{L^2(\mathbb{R}^d)} < \infty$.

Moreover, for $1 \le j \le d$, *it holds that* $\rho_{P_jAP_j} = \sum_{n\in\mathbb{N}} \lambda_n \left|\frac{\partial\varphi_n}{\partial x_j}\right|^2$ *and* $\mathrm{Tr}\,(-\Delta A) = \sum_{n\in\mathbb{N}} \lambda_n \|\nabla\varphi_n\|^2_{L^2(\mathbb{R}^d)}$.

Proof. First, assume that $A = \sum_{n\in\mathbb{N}} \lambda_n |\varphi_n\rangle\langle\varphi_n|$ satisfies conditions *(i)* and *(ii)*. Let $1 \le j \le d$ and $\varphi, \psi \in D(P_j)$. Then, we have

$$\begin{aligned}\langle P_jAP_j, \psi\varphi\rangle_{D(P_j)',D(P_j)} &= \sum_{n\in\mathbb{N}} \lambda_n \langle P_j\varphi, \varphi_n\rangle_{L^2(\mathbb{R}^d)} \langle\varphi_n, P_j\psi\rangle_{L^2(\mathbb{R}^d)} \\ &= \sum_{n\in\mathbb{N}} \lambda_n \langle\varphi, P_j\varphi_n\rangle_{L^2(\mathbb{R}^d)} \langle P_j\varphi_n, \psi\rangle_{L^2(\mathbb{R}^d)}.\end{aligned}$$

Therefore

$$\begin{aligned}\left|\langle P_jAP_j\varphi, \psi\rangle_{D(P_j)',D(P_j)}\right| &\le \sum_{n\in\mathbb{N}} \lambda_n \|P_j\varphi_n\|^2_{L^2(\mathbb{R}^d)} \|\varphi\|_{L^2(\mathbb{R}^d)} \|\psi\|_{L^2(\mathbb{R}^d)} \\ &\le \sum_{n\in\mathbb{N}} \lambda_n \|\nabla\varphi_n\|^2_{L^2(\mathbb{R}^d)} \|\varphi\|_{L^2(\mathbb{R}^d)} \|\psi\|_{L^2(\mathbb{R}^d)} < \infty.\end{aligned}$$

It follows that $P_jAP_j\varphi \in L^2(\mathbb{R}^d)$ and P_jAP_j defines a bounded operator on $L^2(\mathbb{R}^d)$. Let $(\psi_n)_{n\in\mathbb{N}}$ be an orthonormal basis of $L^2(\mathbb{R}^d)$. Then

$$\begin{aligned}\sum_{i\in\mathbb{N}} \langle\psi_i, P_jAP_j\psi_i\rangle_{L^2(\mathbb{R}^d)} &= \sum_{i\in\mathbb{N}}\sum_{n\in\mathbb{N}} \lambda_n \left|\langle P_j\varphi_n, \psi_i\rangle_{L^2(\mathbb{R}^d)}\right|^2 \\ &= \sum_{n\in\mathbb{N}} \lambda_n \sum_{i\in\mathbb{N}} \left|\langle P_j\varphi_n, \psi_i\rangle_{L^2(\mathbb{R}^d)}\right|^2 \\ &= \sum_{n\in\mathbb{N}} \lambda_n \|P_j\varphi_n\|^2_{L^2(\mathbb{R}^d)} \\ &\le \sum_{n\in\mathbb{N}} \lambda_n \|\nabla\varphi_n\|^2_{L^2(\mathbb{R}^d)} < \infty.\end{aligned}$$

Conversely, let $A = \sum_{n\in\mathbb{N}} \lambda_n |\varphi_n\rangle\langle\varphi_n| \in \mathfrak{S}_{1,1}$, and let $(\psi_n)_{n\in\mathbb{N}}$ be an orthonormal basis of $L^2(\mathbb{R}^d)$. Then

$$\sum_{n\in\mathbb{N}} \lambda_n \|\nabla\varphi_n\|^2_{L^2(\mathbb{R}^d)} = \sum_{j=1}^{d}\sum_{i\in\mathbb{N}} \langle\psi_i, P_jAP_j\psi_i\rangle_{L^2(\mathbb{R}^d)} < \infty,$$

which proves that conditions *(i)* and *(ii)* are satisfied. □

We now state the Hoffmann-Ostenhof [73] and Llieb-Thirring [115, 116] inequalities for finite systems.

Proposition 2.B.6 (Hoffmann-Ostenhof inequality for finite systems)**.** *Let A be a positive trace class operator with finite kinetic energy. Then $\sqrt{\rho_A} \in H^1(\mathbb{R}^d)$ and*

$$\|\nabla\sqrt{\rho_A}\|^2_{L^2(\mathbb{R}^d)} \leq \mathrm{Tr}\,(-\Delta A).$$

Proposition 2.B.7 (Lieb-Thirring inequality for finite systems)**.** *There exists a constant K such that for all $A \in \mathfrak{S}_{1,1}$ satisfying $0 \leq A \leq 1$,*

$$K\int_{\mathbb{R}^d} \rho_A^{1+2/d} \leq \mathrm{Tr}\,(-\Delta A)\,.$$

2.B.3 A representability result for finite systems

The aim of representability criteria is to identify sets of densities ρ that arise from admissible density matrices. For finite systems, if $\gamma \in \mathfrak{S}_1 \cap \mathcal{S}$, $0 \leq \gamma \leq 1$, and $\mathrm{Tr}\,(-\Delta\gamma) < \infty$, then $\rho_\gamma \geq 0$ and $\sqrt{\rho_\gamma} \in H^1\left(\mathbb{R}^d\right)$ by the Hoffmann-Ostenhof inequality. Lieb's representability theorem [107, Theorem 1.2] shows that these conditions are in fact sufficient for a function ρ to be representable. We recall here this theorem.

Theorem 2.B.8 (Representability for finite systems)**.** *Let $N \in \mathbb{R}_+$ and ρ be a non-negative function of $L^1_c(\mathbb{R}^d)$ satisfying*

$$\sqrt{\rho} \in H^1(\mathbb{R}^d) \quad \text{and} \quad \int_{\mathbb{R}^d} \rho = N.$$

Then there exists a self-adjoint operator $\gamma \in \mathfrak{S}_{1,1}$, satisfying $0 \leq \gamma \leq 1$ and $\rho_\gamma = \rho$.

2.B.4 Locally trace class operators

In this section, we recall some properties of locally trace class operators. We restrict ourselves to bounded operators to avoid technical difficulties arising from the domains of the operators. Such difficulties can be overcome by adding appropriate conditions on the domain.

Definition 2.B.9 (Locally trace class operators)**.** *Let A be a bounded operator on $L^2(\mathbb{R}^d)$. A is said to be locally trace class if for all functions $\chi \in L^\infty_c(\mathbb{R}^d)$, the operator $\chi A\chi$ is trace class.*

Similarly, we define locally Hilbert-Schmidt operators.

Definition 2.B.10 (Locally Hilbert-Schmidt)**.** *Let A be a bounded operator on $L^2(\mathbb{R}^d)$. A is said to be locally Hilbert-Schmidt if A^*A is locally trace class, that is, $A\chi$ is Hilbert-Schmidt for all functions $\chi \in L^\infty_c(\mathbb{R}^d)$.*

We now define the kernel and the density associated with a locally trace class operator.

Proposition 2.B.11 (The kernel of locally trace class and Hilbert-Schmidt operators)**.** *Let A be a bounded operator which is either locally trace class or locally Hilbert-Schmidt. Then there exists a unique $A \in L^2_{\mathrm{loc}}(\mathbb{R}^d \times \mathbb{R}^d)$ such that*

$$\forall \varphi \in L^2_c(\mathbb{R}^d), \quad A\varphi(x) = \int_{\mathbb{R}^d} A(x,y)\varphi(y)\, dy$$

and for any compact set $B \subset \mathbb{R}^d$,

$$\|A\|_{B\times B} = \|1_B A 1_B\|_{\mathfrak{S}_2}\,.$$

$A(.,.)$ is called the kernel of A.

Proof. In both cases $\chi A \chi \in \mathfrak{S}_2$ for any $\chi \in L^\infty_c(\mathbb{R}^d)$. Let B_1 and B_2 be two compact sets of $\mathbb{R}^d$, and A_i the kernel of $1_{B_i} A 1_{B_i}$, $i \in \{1,2\}$. We first prove that if $B_1 \subset B_2$, then $A_2 = A_1$ on $B_1 \times B_1$. Indeed, for $\varphi, \psi \in L^2(\mathbb{R}^d)$ with supports in B_1, we have

$$\begin{aligned}
\int_{\mathbb{R}^d} A_2(x,y)\varphi(y)\psi(x)\, dy\, dx &= \langle \overline{\psi}, 1_{B_2} A 1_{B_2}\varphi\rangle_{L^2(\mathbb{R}^d)} \\
&= \langle 1_{B_1}\overline{\psi}, 1_{B_2} A 1_{B_2} 1_{B_1}\varphi\rangle_{L^2(\mathbb{R}^d)} \\
&= \langle \overline{\psi}, 1_{B_1} 1_{B_2} A 1_{B_2} 1_{B_1}\varphi\rangle_{L^2(\mathbb{R}^d)} \\
&= \langle \overline{\psi}, 1_{B_1} A 1_{B_1}\varphi\rangle_{L^2(\mathbb{R}^d)} \\
&= \int_{\mathbb{R}^d} A_1(x,y)\varphi(y)\psi(x)\, dy\, dx.
\end{aligned}$$

We are now able to define $A(\cdot,\cdot)$ to be equal to A_B on $B \times B$ for all compact sets B. $A(\cdot,\cdot)$ is then clearly in $L^2_{\mathrm{loc}}\left(\mathbb{R}^d\right)$ and for $\varphi \in L^2(\mathbb{R}^d)$ with compact support, we have

$$A\varphi(x) = \int_{\mathbb{R}^d} A(x,y)\varphi(y)\, dy \quad \text{a.e.}$$

□

Proposition 2.B.12 (The density of locally trace class operators)**.** *Let A be a bounded and locally trace class operator. Then there exists a unique $\rho_A \in L^1_{\mathrm{loc}}(\mathbb{R}^d)$ such that for all functions $\chi \in L^\infty_c(\mathbb{R}^d)$, we have*

$$\mathrm{Tr}\,(\chi A \chi) = \int_{\mathbb{R}^d} \chi^2(x)\rho_A(x)\, dx.$$

Moreover, if $A \geq 0$ then $\rho_A \geq 0$. ρ_A is called the density of A.

Proof. Let B_1 and B_2 be two compact sets of $\mathbb{R}^d$. We denote by ρ_{A,B_i} the density corresponding to $1_{B_i}A1_{B_i}$, $i \in \{1,2\}$. We first prove that if $B_1 \subset B_2$, then $\rho_{A,B_2} = \rho_{A,B_1}$ on B_1. Let $B \subset B_1$. We have

$$\begin{aligned}\int_{\mathbb{R}^d} \rho_{A,B_2} 1_B &= \mathrm{Tr}\,(1_{B_2}A1_{B_2}1_B)\\ &= \mathrm{Tr}\,(1_B 1_{B_2}A1_{B_2}1_B)\\ &= \mathrm{Tr}\,(1_B 1_{B_1}A1_{B_1}1_B)\\ &= \int_{\mathbb{R}^d} \rho_{A,B_1} 1_B,\end{aligned}$$

where we have used the cyclicity property of the trace [131, Theorem VI.25 p.212]. We are now able to define ρ_A to be equal to $\rho_{A,B}$ on B for all compact sets B. ρ_A is then clearly in $L^1_{\mathrm{loc}}(\mathbb{R}^d)$ and for $\chi \in L^\infty_c(\mathbb{R}^d)$, we have, denoting by $B = \mathrm{supp}(\chi)$,

$$\begin{aligned}\mathrm{Tr}\ (\chi A\chi) = \mathrm{Tr}\ (\chi 1_B A 1_B \chi) &= \mathrm{Tr}\,(1_B A 1_B \chi^2)\\ = \int_B \rho_{A,B}\chi^2 &= \int_{\mathbb{R}^d} \rho_A \chi^2.\end{aligned}$$

□

Finally, we define the operators with locally finite kinetic energy.

Definition 2.B.13 (Operators with locally finite kinetic energy)**.** *Let A be a locally trace class operator. We say that A has a locally finite kinetic energy if for all $1 \le j \le d$, we have*

$$\forall \chi \in L^\infty_c(\mathbb{R}^d),\ \ \chi P_j A P_j \chi \in \mathfrak{S}_1.$$

2.C Some elements about the spectrum of $-\Delta_s$

We have seen in Section 2.3.1 that if the probability space Ω is finite, then the spectrum of $-\Delta_s$ is a sequence of discrete eigenvalues going to infinity. We also recall that if Ω is countable and infinite, then there is no ergodic group action τ of $\mathbb{Z}^d$ on Ω. The case of infinite non countable probability spaces is more intricate. In this section, we study the spectrum of $-\Delta_s$ in two particular cases of such probability spaces, namely, the probability spaces presented in Sections 2.A.2 and 2.A.3. In both cases, we show that $\sigma(-\Delta_s) = [0, +\infty)$.

Before going on with the proofs, let us recall that by Weyl's Theorem [148, Proposition 4.1.10. p. 121], the spectrum of a self-adjoint operator A on a Hilbert space $\mathcal{H}$ is characterized as follow

$$\lambda \in \sigma(A) \quad \Longleftrightarrow \quad \exists (f_n)_{n\in\mathbb{N}} \in D(A)\ s.t. \begin{cases} \|f_n\| = 1,\ \forall n \in \mathbb{N}, \\ \|(A-\lambda)f_n\| \longrightarrow_{n\to\infty} 0 \end{cases}$$

and

$$\lambda \in \sigma_{ess}(A) \quad \Longleftrightarrow \quad \exists (g_n)_{n\in\mathbb{N}} \in D(A) \; s.t. \begin{cases} g_n \rightharpoonup 0 \text{ weakly in } \mathcal{H}, \\ \|g_n\| = 1, \; \forall n \in \mathbb{N}, \\ \|(A-\lambda)g_n\| \longrightarrow_{n\to\infty} 0. \end{cases}$$

The sequence (f_n) is called a *Weyl sequence* and (g_n) is called a *singular Weyl sequence*.

2.C.1 The i.i.d case

We consider in this section the settings of Section 2.A.2. We have the following result.

Proposition 2.C.1. *The spectrum of $-\Delta_s$ is given by*

$$\sigma(-\Delta_s) = \sigma_{ess}(-\Delta_s) = [0, +\infty).$$

Proof. For the sake of simplicity, we take $p_1 = \frac{1}{2}$, so that the variables $(Y_i)_{i\in\mathbb{Z}^d}$ are centered at 0. For $\chi \in L^2(\mathbb{R}^d)$, we introduce

$$\Phi_{\chi,Y}(\omega, x) = \sum_{i\in\mathbb{Z}^d} Y_i(\omega)\chi(x-i).$$

For $k \in \mathbb{Z}^d$, we have

$$\begin{aligned} \Phi_{\chi,Y}(\tau_k(\omega), x) &= \sum_{i\in\mathbb{Z}^d} Y_i(\tau_k(\omega))\chi(x-i) \\ &= \sum_{i\in\mathbb{Z}^d} Y_{i+k}(\omega)\chi(x-i) \\ &= \sum_{i\in\mathbb{Z}^d} Y_i(\omega)\chi(x-i+k) \\ &= \Phi_{\chi,Y}(\omega, x+k). \end{aligned}$$

Thus the function $\Phi_{\chi,Y}$ is stationary. Moreover, it is in L^2_s and $\|f\|_{L^2_s} = \|\chi\|_{L^2(\mathbb{R}^d)}$. Indeed,

$$\begin{aligned} \|\Phi_{\chi,Y}\|^2_{L^2_s} &= \mathbb{E}\left(\int_Q \left| \sum_{i\in\mathbb{Z}^d} Y_i(\omega)\,\chi(x-i) \right|^2 dx \right) \\ &= \sum_{i\in\mathbb{Z}^d} \mathbb{E}\left(Y_i^2\right) \int_Q \chi(x-i)^2\, dx \\ &= \sum_{i\in\mathbb{Z}^d} \int_Q \chi(x-i)^2\, dx \\ &= \int_{\mathbb{R}^d} \chi(x)^2\, dx = \|\chi\|^2_{L^2(\mathbb{R}^d)}. \end{aligned} \tag{2.98}$$

In the above equalities, we have used the fact that $\mathbb{E}(Y_iY_j) = \delta_{ij}$, which follows from the independence of the variables Y_i and from their common first and second moments: $\mathbb{E}(Y_i) = 0$ and $\mathbb{E}(Y_i^2) = 1$. If $\chi \in H^2(\mathbb{R}^d)$ then $f \in H^2_s$, $\Delta_s f = \sum_{i\in\mathbb{Z}^d} Y_i(\omega)\Delta\chi(x-i)$ and

$$\|-\Delta_s f\|_{L^2_s} = \|-\Delta\chi\|_{L^2(\mathbb{R}^d)}. \tag{2.99}$$

Let now $\lambda \in [0,+\infty)$. We know that $\sigma_{ess}(-\Delta) = [0,+\infty)$. By Weyl's theorem there exists a normalized sequence $(\chi_n)_{n\in\mathbb{N}}$ in $H^2(\mathbb{R}^d)$ such that

$$\|(-\Delta-\lambda)\chi_n\|_{L^2(\mathbb{R}^d)} \underset{n\to\infty}{\longrightarrow} 0.$$

Using (2.98) and (2.99), we obtain that $(\Phi_{\chi_n,Y})$ is a normalized sequence in L^2_s and

$$\|(-\Delta_s-\lambda)\Phi_{\chi_n,Y}\|_{L^2_s} \underset{n\to\infty}{\longrightarrow} 0.$$

Therefore, $(\Phi_{\chi_n,Y})$ is a Weyl sequence for $-\Delta_s$ corresponding to the singular value λ; thus $\lambda \in \sigma(-\Delta_s)$. As $-\Delta_s \geq 0$ in the sense of quadratic forms, we deduce that $\sigma(-\Delta_s) = [0,+\infty)$. □

Proposition 2.C.2. *The spectrum of $-\Delta_s$ contains an infinite sequence of eigenvalues.*

Proof. Let $(\chi_n)_{n\in\mathbb{N}}$ and $(\lambda_n)_{n\in\mathbb{N}}$ be an orthonormal basis of eigenfunctions of $-\Delta_{\text{per}}$ and their corresponding eigenvalues, where $-\Delta_{\text{per}}$ denotes the Laplacian on $L^2_{\text{per}}(Q)$. We introduce the stationary functions $f_n := \chi_n$ a.s. It is easily checked that $f_n \in H^2_s$ and that $-\Delta_s f_n = \lambda_n f_n$. □

2.C.2 The a-periodic case, a irrational

We consider in this section the settings of Section 2.A.3 with an irrational parameter a. We have the following

Proposition 2.C.3. *The spectrum of $-\Delta_s$ is given by*

$$\sigma(-\Delta_s) = \sigma_{ess}(-\Delta_s) = [0,+\infty).$$

Proof. Let us show that

$$\{4\pi^2|j+ak|^2,\ j,k\in\mathbb{Z}\} \subset \sigma_p(-\Delta_s). \tag{2.100}$$

For $k,j \in \mathbb{Z}^2$, the function

$$f_{k,j}(\omega,x) = e^{2i\pi k(ax+\omega)+2i\pi jx}.$$

is stationary. Indeed, for $R \in \mathbb{Z}$ we have a.s. and a.e.

$$\begin{aligned} f_{k,j}(\tau_R(\omega), x) &= e^{2i\pi k(ax+(\omega+aR-[\omega+aR]))+2i\pi jx} \\ &= e^{2i\pi k(ax+\omega+aR)} e^{-2i\pi k[\omega+aR]} e^{2i\pi jx} e^{2i\pi jR} \\ &= e^{2i\pi k(a(x+R)+\omega)} e^{2i\pi j(x+R)} \\ &= f_{k,j}(\omega, x+R). \end{aligned}$$

Moreover $f_{k,j}$ is in H^2_s and

$$-\Delta_s f_{k,j} = 4\pi^2 |j+ak|^2 f_{k,j},$$

which proves (2.100). It is then a classical and elementary result that $\{4\pi^2|j+ak|^2,\ j,k \in \mathbb{Z}\}$ is dense in $[0,+\infty)$. □

Chapter 3

The reduced Hartree-Fock model for short-range quantum crystals with nonlocal defects

We detail in this chapter the results contained in an article [92] which has been accepted for publication in *Annales Henri Poincaré*. We consider quantum crystals with defects in the reduced Hartree-Fock framework. The nuclei are supposed to be classical particles arranged around a reference periodic configuration. The perturbation is assumed to be small in amplitude, but need not be localized in a specific region of space or have any spatial invariance. Assuming Yukawa interactions, we prove the existence of an electronic ground state, solution of the self-consistent field equation. Next, by studying precisely the decay properties of this solution for local defects, we are able to expand the density of states of the nonlinear Hamiltonian of a system with a random perturbation of Anderson-Bernoulli type, in the limit of low concentration of defects. One important step in the proof of our results is the analysis of the dielectric response of the crystal to an effective charge perturbation.

Contents

3.1 Introduction

In solid state physics and materials science, the presence of defects in materials induces many interesting properties, such as Anderson localization [4, 5] and leads to many applications such as doped semi-conductors [149]. The mathematical modeling and the numerical simulation of the electronic structure of these materials is a challenging task, as we are in the presence of infinitely many interacting particles.

The purpose of this chapter is to construct the state of the quantum electrons of a mean-field crystal, in which the nuclei are classical particles arranged around a reference periodic configuration. We work with the assumption that the nuclear distribution is close to a chosen periodic arrangement *locally*, but the perturbation need not be localized in a specific region of space and it also need not have any spatial invariance. To our knowledge, this is the first result of this kind for Hartree-Fock type models for quantum crystals, with short-range interactions. By studying precisely the behavior of our solution, we are then able to expand the density of states of the Hamiltonian of the system in the presence of a random perturbation of Anderson-Bernoulli type, in the limit of low concentration of defects, that is when the Bernoulli parameter p tends to zero. The state of the random crystal and the mean-field Hamiltonian were recently constructed in [29]. Our small-p expansion is the nonlinear equivalent of a previous result by Klopp [87] in the linear case.

The mean-field model we consider in this study is the reduced Hartree-Fock model [146], also called the Hartree model in the physics literature. It is obtained from the generalized Hartree-Fock model [113] by removing the exchange term. As the Coulomb interaction is long-range, it is a difficult mathematical question to describe infinite systems interacting through the Coulomb potential. In the following, we assume that all the particles interact through Yukawa potential of parameter $m > 0$. In fact, we can assume any reasonable short-range potential, but we concentrate on the Yukawa interaction in dimension $d \in \{1, 2, 3\}$ for simplicity. We consider systems

composed of infinitely many classical nuclei distributed over the whole space and infinitely many electrons.

We start by recalling the definition of the reduced Hartree-Fock (rHF) model for a finite system composed of a set of nuclei having a density of charge $\nu_{\rm nuc}$ and N electrons. The electrons are described by the N-body wave-function (called a Slater determinant)

$$\psi(x_1, \cdots, x_N) = \frac{1}{\sqrt{N!}} \det(\varphi_j(x_i)),$$

where the functions $\varphi_i \in L^2(\mathbb{R}^d)$ satisfy $\langle \varphi_i, \varphi_j \rangle = \delta_{ij}$. The rHF equations then read

$$\begin{cases} H\varphi_i = \lambda_i \varphi_i \\ H = -\dfrac{1}{2}\Delta + V \qquad\qquad \forall\, 1 \le i \le N, \\ -\Delta V + m^2 V = \left|S^{d-1}\right| (\rho_\psi - \nu_{\rm nuc}) \end{cases} \tag{3.1}$$

where $\rho_\psi(x) = \sum_{i=1}^N |\varphi_i(x)|^2$ and $\lambda_1, \cdots, \lambda_N$ are the smallest N eigenvalues of the operator H, assuming that $\lambda_N < \lambda_{N+1}$. Here, $\left|S^{d-1}\right|$ is the Lebesgue measure of the unit sphere S^{d-1} ($|S^0| = 2$, $|S^1| = 2\pi$, $|S^2| = 4\pi$). The existence of a solution of (3.1) is due to Lieb and Simon [114]. See [130] for the finite temperature case.

In order to describe infinite systems, it is more convenient to reformulate the rHF problem in terms of the *one-particle density matrix* formalism [112]. In this formalism, the state of the electrons is described by the orthogonal projector $\gamma = \sum_{i=1}^N |\varphi_i\rangle\langle\varphi_i|$ of rank N and the equations (3.1) can be recast as

$$\begin{cases} \gamma = 1\,(H \le \varepsilon_F) \\ H = -\dfrac{1}{2}\Delta + V \\ -\Delta V + m^2 V = \left|S^{d-1}\right| (\rho_\gamma - \nu_{\rm nuc})\,, \end{cases} \tag{3.2}$$

where formally $\rho_\gamma(x) = \gamma(x,x)$ and the Fermi level ε_F is any real number in the gap $[\lambda_N, \lambda_{N+1})$.

For infinite systems, the rHF equation is still given by (3.2), but γ is now an infinite rank operator as there are infinitely many electrons in the system. The operator γ needs to be locally trace class for the electronic density ρ_γ to be well-defined in $L^1_{\rm loc}(\mathbb{R}^d)$.

The rHF equation (3.2) was solved for periodic nuclear densities

$$\nu_{\rm nuc} = \nu_{\rm per} = \sum_{k \in \mathcal{R}} \eta(\cdot - k)$$

by Catto, Le Bris and Lions in [36], and periodic nuclear densities with local perturbations

$$\nu_{\rm nuc} = \sum_{k \in \mathcal{R}} \eta(\cdot - k) + \nu$$

were studied by Cancès, Deleurence and Lewin in [24]. We have denoted by $\mathcal{R}$ the underlying discrete periodic lattice. The corresponding Hamiltonians are denoted by $H_{\rm per}$ and H_ν. See [121] for the finite temperature case. Stochastic distributions,

$$\nu_{\rm nuc}(\omega,\cdot)=\sum_{k\in\mathcal{R}}\eta(\cdot-k)+\sum_{k\in\mathcal{R}}q_k(\omega)\chi(\cdot-k)$$

for instance, were treated in [29].

Our present work follows on from [24, 33, 29]. We are going to solve the equation (3.2) in the particular case where

$$\nu_{\rm nuc}=\nu_{\rm per}+\nu, \tag{3.3}$$

where $\nu_{\rm per}$ is a periodic nuclear distribution so that the corresponding background crystal is an insulator (the mean-field Hamiltonian $H_{\rm per}$ has a gap around ε_F), and $\nu\in L^2_{\rm unif}\left(\mathbb{R}^d\right)$ is a small enough arbitrary perturbation of the background crystal. The perturbation ν needs to be small in amplitude locally, but must not be local or have any spatial invariance.

The rHF model is an approximation of the N-body Schrödinger model, for which there is no well-defined formulation for infinite systems so far. The only available result is the existence of the thermodynamic limit of the energy: the energy per unit volume of the system confined to a box, with suitable boundary conditions, converges when the size of the box grows to infinity. The first theorem of this form for Coulomb interacting systems is due to Lieb and Lebowitz in [109]. In the latter work, nuclei are considered as quantum particle and rotational invariance plays a crucial role. For quantum systems in which the nuclei are classical particles, the thermodynamic limit was proved for perfect crystals by Fefferman [47] (a recent proof has been proposed in [67]) and for stationary stochastic systems by Blanc and Lewin [15]. Similar results for Yukawa interacting systems are simpler than for the Coulomb case and follow from the work of Ruelle and Fisher [49] for perfect crystals and Veniaminov [153] for stationary stochastic systems. Unfortunately, very little is known about the limiting quantum state in both cases.

For (orbital-free) Thomas-Fermi like theories, the periodic model was studied in [114, 35], the case of crystals with local defects was studied in [26] and stochastic systems were investigated in [14]. To the best of our knowledge, the only works dealing with systems with arbitrary distributed nuclei are [35, 13] for Thomas-Fermi type models.

As mentioned before, our work is the first one to consider this kind of systems in the framework of Hartree-Fock type models. Our results concern small perturbations of perfect crystals interacting through short-range Yukawa potential. Extending these results to more general geometries and

for the long-range Coulomb interaction are important questions that we hope to address in the future.

After having found solutions of (3.2) for any (small enough) $\nu \in L^2_{\mathrm{unif}}(\mathbb{R}^d)$, we study the properties of this solution for local perturbations ν. This enables us to investigate small random perturbations of perfect crystals. Precisely, we consider nuclear distributions

$$\nu_{\mathrm{nuc}}(\omega, x) = \nu_{\mathrm{per}}(x) + \sum_{k \in \mathcal{R}} q_k(\omega)\chi(x-k),$$

where $(q_k)_{k\in\mathcal{R}}$ are i.i.d. Bernoulli variables of parameter p and χ is a compactly supported function which is small enough in $L^2(\mathbb{R}^d)$. We are interested in the properties of the system in the limit of low concentration of defects, that is when the parameter p goes to zero. We prove that the density of states of the mean-field Hamiltonian $H_p = -\frac{1}{2}\Delta + V_p$, which describes the collective behavior of the electrons, admits an expansion of the form

$$n_p = n_0 + \sum_{j=1}^{J} \mu_j p^j + O(p^{J+1}). \tag{3.4}$$

Here, n_0 is the density of states of the unperturbed Hamiltonian $H_{\mathrm{per}} = -\frac{1}{2}\Delta + V_{\mathrm{per}}$ and μ_1 is a function of the spectral shift function for the pair of operators H_{per} and H_χ, the latter being the mean-field Hamiltonian of the system with only one local defect constructed in [24]. We give in Theorem 3.2.7 a precise meaning of $O(p^{J+1})$.

In [87], Klopp considers the empirical linear Anderson-Bernoulli model

$$H = -\frac{1}{2}\Delta + V_0 + V \quad \text{with} \quad V(\omega, x) = \sum_{k\in\mathcal{R}} q_k(\omega)\eta(x-k),$$

where V_0 is a linear periodic potential and η an exponentially decaying potential. He proves that the density of states of the Hamiltonian H admits an asymptotic expansion similar to (3.4). The case where $V(\omega, x)$ is distributed following a Poisson law instead of Bernoulli is dealt with in [88]. Our proof of (3.4) follows the same lines as the one of Klopp. The main difficulty here is to understand the decay properties of the mean-field potential V solution of the self-consistent equations (3.2). For this reason, we dedicate an important part of this chapter to the study of these decay properties. In Theorem 3.2.3 below, we show that for a compactly supported perturbation ν, the difference $V - V_{\mathrm{per}}$ decays faster than any polynomial far from the support of the perturbation ν. Moreover, we show that the potential generated by two defects that are far enough is close to the sum of the potentials generated by each defect alone.

The chapter is organized as follow. In Section 3.2, we present the main results of the chapter. We start by recalling the reduced Hartree-Fock model

for perfect crystals and perfect crystals with local defects in Section 3.2.1. In Section 3.2.2, we state the existence of solutions to the self-consistent equations (3.2) for $\nu_{\rm nuc}$ given by (3.3). We also explain that our solution is in some sense the minimizer of the energy of the system. We also prove a thermodynamic limit, namely, the ground state of the system with the perturbation ν confined to a box converges, when the size of the box goes to infinity, to the ground state of the system with the perturbation ν. In Section 3.2.3, we prove decay estimates for the mean-field density and potential. In Section 3.2.4, we present the expansion of the density of states of the mean-field Hamiltonian. The proofs of all these results are provided in Sections 3.4, 3.5, 3.6 and 3.7. In Section 3.3, we study the dielectric response of a perfect crystal to a variation of the effective charge distribution, which plays a key role in this study.

3.2 Statement of the main results

3.2.1 The rHF model for crystals with and without local defects

In defect-free materials, the nuclei and electrons are arranged according to a discrete periodic lattice $\mathcal{R}$ of $\mathbb{R}^d$, in the sense that both the nuclear density $\nu_{\rm nuc} = \nu_{\rm per}$ and the electronic density are $\mathcal{R}$-periodic functions. For simplicity, we take $\mathcal{R} = \mathbb{Z}^d$ in the following. The reduced Hartree-Fock model for perfect crystals has been rigorously derived from the reduced Hartree-Fock model for finite molecular systems by means of thermodynamic limit procedure in [36, 24] in the case of Coulomb interaction. The same results for Yukawa interaction are obtained with similar arguments. The self-consistent equation (3.2) then reads

$$\begin{cases} \gamma_0 = 1\left(H_{\rm per} \leq \varepsilon_F\right) \\ H_{\rm per} = -\dfrac{1}{2}\Delta + V_{\rm per} \\ -\Delta V_{\rm per} + m^2 V_{\rm per} = \left|S^{d-1}\right|\left(\rho_{\gamma_0} - \nu_{\rm per}\right). \end{cases} \tag{3.5}$$

It has been proved in [36, 24] that (3.5) admits a unique solution which is the unique minimizer of the periodic rHF energy functional.

Most of our results below hold only for insulators (or semi-conductors). We therefore make the assumption that

$$H_{\rm per} \text{ has a spectral gap around } \varepsilon_F. \tag{3.6}$$

The rHF model for crystals with local defects was introduced and studied in [24]. A solution of the rHF equation (3.2) is constructed using a variational method. One advantage of this method is that there is no need to

assume that the perturbation ν is small in amplitude. The idea is to find a minimizer of the infinite energy of the system by minimizing the energy difference between the perturbed state and the perfect crystal. The ground state density matrix can thus be decomposed as

$$\gamma = \gamma_0 + Q_\nu, \tag{3.7}$$

where Q_ν is a minimizer of the energy functional

$$\mathcal{E}^\nu(Q) = \mathrm{Tr}_{\,\gamma_0}\left((H_{\mathrm{per}} - \varepsilon_F)Q\right) + D_m(\rho_Q, \nu) + \frac{1}{2}D_m(\rho_Q, \rho_Q) \tag{3.8}$$

on the convex set

$$\begin{aligned}\mathcal{K} = \Big\{ Q^* = Q,\ -\gamma_0 \leq Q \leq 1-\gamma_0,\ (-\Delta+1)^{\frac{1}{2}}\, Q \in \mathfrak{S}_2(L^2(\mathbb{R}^d)),\\ (-\Delta+1)^{\frac{1}{2}}\, Q^{++}\, (-\Delta+1)^{\frac{1}{2}} \in \mathfrak{S}_1(L^2(\mathbb{R}^d))\Big\},\end{aligned} \tag{3.9}$$

where $Q^{++} = (1-\gamma_0)Q(1-\gamma_0)$, $Q^{--} = \gamma_0 Q \gamma_0$ and $\mathrm{Tr}_{\,\gamma_0}(A) = \mathrm{Tr}\,(A^{++} + A^{--})$. We use the notation $\mathfrak{S}_p$ to denote the p^{th} Schatten class. In particular $\mathfrak{S}_2$ is the set of Hilbert-Schmidt operators. The second term of (3.8) accounts for the interaction energy and is defined for any charge densities $f, g \in H^{-1}(\mathbb{R}^d)$ by

$$D_m(f,g) = \left|S^{d-1}\right| \int_{\mathbb{R}^d} \frac{\overline{\widehat{f}(p)}\widehat{g}(p)}{|p|^2 + m^2} dp = \int_{\mathbb{R}^d}\int_{\mathbb{R}^d} f(x) Y_m(x-y) g(y)\, dx\, dy,$$

where $\widehat{f}(p) = (2\pi)^{-\frac{d}{2}} \int_{\mathbb{R}^d} f(x)\, e^{-ip\cdot x} dx$ is the Fourier transform of f. The Yukawa kernel Y_m, the inverse Fourier transform of $\left|S^{d-1}\right| (|p|^2 + m^2)^{-1}$, is given by

$$Y_m(x) = \begin{cases} m^{-1} e^{-m|x|} & \text{if } d = 1, \\ K_0(m|x|) & \text{if } d = 2, \\ |x|^{-1} e^{-m|x|} & \text{if } d = 3, \end{cases}$$

where $K_0(r) = \int_0^\infty e^{-r\cosh t}\, dt$ is the modified Bessel function of the second type [110]. It has been proved in [24] that the energy functional (3.8) is convex and that all its minimizers share the same density ρ_γ. These minimizers are of the form

$$\begin{cases} \gamma = 1(H \leq \varepsilon_F) + \delta \\ H = -\dfrac{1}{2}\Delta + V \\ -\Delta V + m^2 V = \left|S^{d-1}\right| (\rho_\gamma - \nu_{\mathrm{per}} - \nu), \end{cases} \tag{3.10}$$

where $0 \leq \delta \leq 1(H = \varepsilon_F)$. If ν is small enough in the H^{-1}-norm, then $\delta = 0$.

One of the purposes of this study is to find decay estimates of the potential V solution of (3.10) that are necessary in the study of the Anderson-Bernoulli random perturbations of crystals.

3.2.2 Existence of ground states

In this section, we state our results concerning the electronic state of a perturbed crystal. The host crystal is characterized by a periodic nuclear density $\nu_{\rm per} \in L^2_{\rm unif}(\mathbb{R}^d)$ such that the gap assumption (3.6) holds. The perturbation is given by a distribution $\nu \in L^2_{\rm unif}(\mathbb{R}^d)$. The total nuclear distribution is then

$$\nu_{\rm nuc} = \nu_{\rm per} + \nu.$$

In Theorem 3.2.1 below, we show that if ν is small enough in the $L^2_{\rm unif}$-norm, then the rHF equation (3.2) admits a solution γ. This solution is unique in a neighborhood of γ_0. The proof consists in formulating the problem in terms of the density ρ_γ and using a fixed point technique, in the spirit of [64].

Theorem 3.2.1 (Existence of a ground state)**.** *There exist $\alpha_c > 0$ and $C \geq 0$ such that for any $\nu \in L^2_{\rm unif}(\mathbb{R}^d)$ satisfying $\|\nu\|_{L^2_{\rm unif}} \leq \alpha_c$, there is a unique solution $\gamma \in \mathfrak{S}_{1,\rm loc}(L^2(\mathbb{R}^d))$ to the self-consistent equation*

$$\begin{cases} \gamma = 1\,(H \leq \varepsilon_F) \\ H = -\dfrac{1}{2}\Delta + V \\ -\Delta V + m^2 V = \left|S^{d-1}\right|(\rho_\gamma - \nu - \nu_{\rm per}) \end{cases} \tag{3.11}$$

satisfying

$$\|\rho_\gamma - \rho_{\gamma_0}\|_{L^2_{\rm unif}} \leq C\,\|\nu\|_{L^2_{\rm unif}}\,. \tag{3.12}$$

We denote this solution by γ_ν, the response electronic density by $\rho_\nu = \rho_{\gamma_\nu} - \rho_{\gamma_0}$ and the defect mean-field potential by $V_\nu = V - V_{\rm per}$.

For a local defect $\nu \in L^2(\mathbb{R}^d) \cap L^1(\mathbb{R}^d)$ such that $\|\nu\|_{L^2_{\rm unif}} \leq \alpha_c$, equation (3.11) admits a unique solution which coincides with the ground state γ solution of (3.7)-(3.9) constructed in [24]. Indeed, the solution γ_ν given in Theorem 3.2.1 is a solution of the defect problem (3.10). Moreover, in the proof of Theorem 3.2.1, we prove that H has a gap around ε_F, thus necessarily $\delta = 0$ in (3.10). As all the solutions of (3.10) share the same density, (3.10) (thus (3.11)) admits a unique solution.

The ground state constructed in Theorem 3.2.1 is in fact the unique minimizer of the "infinite" rHF energy functional. Indeed, following ideas of [65], we can define the relative energy of the system with nuclear distribution $\nu_{\rm nuc}$ by subtracting the "infinite" energy of γ_ν from the "infinite" energy of a test state γ:

$$\mathcal{E}^{\rm rel}_\nu(\gamma) := {\rm Tr}_{\,\gamma_\nu}\left((H - \varepsilon_F)(\gamma - \gamma_\nu)\right) + \frac{1}{2} D_m\left(\rho_\gamma - \rho_{\gamma_\nu}, \rho_\gamma - \rho_{\gamma_\nu}\right).$$

This energy is well-defined for states γ such that $\gamma - \gamma_\nu$ is finite rank and smooth enough for instance, but one can extend it to states in a set similar

to $\mathcal{K}$ in (3.9). The minimum of the energy $\mathcal{E}_\nu^{\mathrm{rel}}$ is attained for $\gamma = \gamma_\nu = 1\,(H \leq \varepsilon_F)$. Moreover, as H has a gap around ε_F, $\mathcal{E}_\nu^{\mathrm{rel}}$ is strictly convex and γ_ν is its unique minimizer.

In the following theorem, we show that if we confine the defect ν to a box of finite size, then the ground state of the system defined by the theory of local defects presented in Section 3.2.1 converges, when the size of the box goes to infinity, to the ground state of the system with the defect ν defined in Theorem 3.2.1. We denote by $\Gamma_L = [-L/2, L/2)^d$.

Theorem 3.2.2 (Thermodynamic limit)**.** *There exists $\alpha_c > 0$ such that for any $\nu \in L^2_{\mathrm{unif}}(\mathbb{R}^d)$ satisfying $\|\nu\|_{L^2_{\mathrm{unif}}} \leq \alpha_c$, the sequence $(\gamma_{\nu 1_{\Gamma_L}})_{L\in\mathbb{N}\setminus\{0\}}$ converges in $\mathfrak{S}_{1,loc}(L^2(\mathbb{R}^d))$ to γ_ν as $L \to \infty$.*

3.2.3 Decay estimates

In this section, we prove some decay estimates of the mean-field potential V_ν and the mean-field density ρ_ν, which will be particularly important to understand the system in the presence of rare perturbations in the next section.

Theorem 3.2.3 below is crucial in the proof of Theorem 3.2.7. Indeed, we will need uniform decay estimates for compactly supported defects, with growing supports and uniform local norms.

Theorem 3.2.3 (Decay rate of the mean-field potential and density)**.** *There exists $\alpha_c, C' > 0$ and $C \geq 0$ such that for any $\nu \in L^2_c(\mathbb{R}^d)$ satisfying $\|\nu\|_{L^2_{\mathrm{unif}}} \leq \alpha_c$, we have for $R \geq 2$*

$$\|V_\nu\|_{H^2_{\mathrm{unif}}(\mathbb{R}^d\setminus C_R(\nu))} + \|\rho_\nu\|_{L^2_{\mathrm{unif}}(\mathbb{R}^d\setminus C_R(\nu))} \leq Ce^{-C'(\log R)^2}\|\nu\|_{L^2_{\mathrm{unif}}(\mathbb{R}^d)}, \tag{3.13}$$

where $C_R(\nu) = \left\{x \in \mathbb{R}^d,\ \mathrm{d}\,(x, \mathrm{supp}(\nu)) < R\right\}$.

Remark 3.2.4. *Using the same techniques as in the proof of Theorem 3.2.3, we can prove (see 3.A.1) that there exist $\alpha, \alpha_c, C' > 0$ and $C \geq 0$ such that for any $\nu \in L^2_c(\mathbb{R}^d)$ satisfying $\|\nu\|_{L^2_{\mathrm{unif}}} \leq \alpha_c$ and $\|\nu\|_{H^{-1}} \leq \alpha$, we have for $R \geq 2$*

$$\|V_\nu\|_{H^2(\mathbb{R}^d\setminus C_R(\nu))} + \|\rho_\nu\|_{L^2(\mathbb{R}^d\setminus C_R(\nu))} \leq Ce^{-C'(\log R)^2}\|\nu\|_{L^2(\mathbb{R}^d)}. \tag{3.14}$$

Estimate (3.14) *gives a decay rate of the solution of the rHF equation for crystals with local defects, far from the support of the defect. In particular, it shows that $\rho_\nu \in L^1(\mathbb{R}^d)$. This decay is due to the short-range character of the Yukawa interaction. In the Coulomb case, it has been proved in [33] that for anisotropic materials, $\rho_\nu \notin L^1(\mathbb{R}^d)$.*

The decay rate of V_ν and ρ_ν proved in Theorem 3.2.3 is faster than the decay of any polynomial, but is not exponential, which we think should be the optimal rate.

Proposition 3.2.5 below is an important intermediary result in the proof of Theorem 3.2.2. It says that the mean-field density ρ_ν and potential V_ν on a compact set depend mainly on the nuclear distribution in a neighborhood of this compact set.

Proposition 3.2.5 (The mean-field potential and density depend locally on ν)**.** *There exists $\alpha_c > 0$ such that for any $\beta \geq 2$ there exists $C \geq 0$ such that for any $\nu \in L^2_{\mathrm{unif}}(\mathbb{R}^d)$ satisfying $\|\nu\|_{L^2_{\mathrm{unif}}} \leq \alpha_c$ and any $L \geq 1$ we have*

$$\|V_\nu - V_{\nu_L}\|_{H^2_{\mathrm{unif}}(B(0,L/4^\beta))} + \|\rho_\nu - \rho_{\nu_L}\|_{L^2_{\mathrm{unif}}(B(0,L/4^\beta))} \leq \frac{C}{L^\beta} \|\nu\|_{L^2_{\mathrm{unif}}},$$

where $\nu_L = \nu 1_{\Gamma_L}$.

In the same way, we obtain the following result which will be very useful in the proof of Theorem 3.2.7. We prove that the potential generated by two defects that are far enough is close to the sum of the potentials generated by each defect alone in the sense of

Proposition 3.2.6. *There exists $\alpha_c > 0$ such that for any $\beta \geq 2$, there exists $C \geq 0$ such that for any $\nu_1, \nu_2 \in L^2_c(\mathbb{R}^d)$ satisfying $\|\nu_1\|_{L^2_{\mathrm{unif}}}, \|\nu_2\|_{L^2_{\mathrm{unif}}} \leq \alpha_c$ and $R = \mathrm{d}(\mathrm{supp}(\nu_1), \mathrm{supp}(\nu_2)) > 0$, we have*

$$\|V_{\nu_1+\nu_2} - V_{\nu_2}\|_{H^2_{\mathrm{unif}}(C_{R/4^\beta}(\nu_2))} + \|\rho_{\nu_1+\nu_2} - \rho_{\nu_2}\|_{L^2_{\mathrm{unif}}(C_{R/4^\beta}(\nu_2))} \leq \frac{C}{R^\beta} \left(\|\nu_1\|_{L^2_{\mathrm{unif}}} + \|\nu_2\|_{L^2_{\mathrm{unif}}} \right).$$

Proof. The proof is the same as the one of Proposition 3.2.5 with $\nu = \nu_1 + \nu_2$ and $L = 2R$. □

3.2.4 Asymptotic expansion of the density of states

In this section, we use our previous results to study a particular case of random materials. In the so-called statistically homogeneous materials, the particles are randomly distributed over the space with a certain spatial invariance. More precisely, the nuclear distribution (thus the electronic density) is stationary in the sense

$$\nu_{\mathrm{nuc}}(\tau_k(\omega), x) = \nu_{\mathrm{nuc}}(\omega, x + k),$$

where $(\tau_k)_{k\in\mathbb{Z}^d}$ is an ergodic group action of $\mathbb{Z}^d$ on the probability set Ω (see Figure 3.1). One famous example of such distributions is the Anderson model

$$\nu_{\mathrm{nuc}}(\omega, x) = \sum_{k\in\mathbb{Z}^d} q_k(\omega)\, \chi(x - k),$$

where, typically, $\chi \in C^\infty_c(\mathbb{R}^3)$ and the q_k's are i.i.d. random variables. The reduced Hartree-Fock model for statistically homogeneous materials was

Figure 3.1: Example of a stationary nuclear distribution

introduced in [29]. The state of the electrons is described by a random self-adjoint operator $(\gamma(\omega))_{\omega\in\Omega}$ acting on $L^2(\mathbb{R}^d)$ such that $0 \leq \gamma(\omega) \leq 1$ almost surely. The rHF equation is then

$$\begin{cases} \gamma(\omega) = 1\left(H(\omega) \leq \varepsilon_F\right) + \delta(\omega) \\ H(\omega) = -\dfrac{1}{2}\Delta + V(\omega,\cdot) & \text{almost surely,} \\ -\Delta V(\omega,\cdot) + m^2 V(\omega,\cdot) = \left|S^{d-1}\right|\left(\rho_{\gamma(\omega)} - \nu_{\mathrm{nuc}}(\omega,\cdot)\right) \end{cases} \tag{3.15}$$

where $0 \leq \delta(\omega) \leq 1_{\{\varepsilon_F\}}(H(\omega))$ almost surely. The solutions of (3.15) turn out to be the minimizers of the energy functional

$$\underline{\mathcal{E}}_{\nu_{\mathrm{nuc}}}(\gamma) = \underline{\mathrm{Tr}}\left(\left(-\frac{1}{2}\Delta - \varepsilon_F\right)\gamma\right) + \underline{D}_m(\rho_\gamma - \nu_{\mathrm{nuc}}, \rho_\gamma - \nu_{\mathrm{nuc}}),$$

where $\underline{\mathrm{Tr}}\ (A) = \mathbb{E}\left(\mathrm{Tr}\ (1_\Gamma A 1_\Gamma)\right)$ and

$$\underline{D}_m(f,g) = \mathbb{E}\left(\int_{\mathbb{R}^d}\int_\Gamma f(x)Y_m(x-y)g(y)\,dx\,dy\right).$$

Here, $\Gamma = [-1/2, 1/2)^d$ denotes the semi-open unit cube. Thanks to the convexity of $\underline{\mathcal{E}}_{\nu_{\mathrm{nuc}}}$, it has been proved in [29] that the minimizers of $\underline{\mathcal{E}}_{\nu_{\mathrm{nuc}}}$ share the same density. Therefore, the Hamiltonian H solution of (3.15) is uniquely defined.

In this study, we are interested in the particular case of random perturbation of perfect crystals

$$\nu_{\mathrm{nuc}}(\omega, x) = \nu_{\mathrm{per}}(x) + \nu_p(\omega, x)$$

in the limit of low concentration of defects. We restrict our study to Anderson-Bernoulli type perturbations, that is, we suppose that at each site of $\mathbb{Z}^d$,

there is a probability p to see a local defect χ, independently of what is happening in the other sites. More precisely, we consider the probability space $\Omega = \{0,1\}^{\mathbb{Z}^d}$ endowed with the measure $\mathbb{P} = (p\delta_1 + (1-p)\delta_0)^{\otimes \mathbb{Z}^d}$ and the ergodic group action $\tau_k(\omega) = \omega_{\cdot + k}$. The defect distribution we consider is then given by

$$\nu_p(\omega, x) = \sum_{k \in \mathbb{Z}^d} q_k(\omega) \chi(x - k)$$

where q_k is the k^{th} coordinates of ω and $\chi \in L^2(\mathbb{R}^d)$ with $\mathrm{supp}(\chi) \subset \Gamma$. The q_k's are i.i.d. Bernoulli variables of parameter p. If $\|\chi\|_{L^2} \leq \alpha_c$, then $\delta(\omega) = 0$ almost surely and (3.15) admits a unique solution. For almost every ω, this solution coincides with the solution of (3.11) constructed in Theorem 3.2.1. For convenience, we will from now on use the notation

$$H_0 = H_{\text{per}} - \varepsilon_F,$$

where we recall that ε_F is the Fermi level. We introduce the mean-field Hamiltonian corresponding to the system with the defect ν_p

$$H_p = H_0 + V_{\nu_p} \quad \text{with} \quad V_{\nu_p}(\omega, x) = Y_m * \left(\rho_{\nu_p} - \nu_p\right).$$

As V_p is stationary with respect to the ergodic group $(\tau_k)_{k \in \mathbb{Z}^d}$ and uniformly bounded in $\Omega \times \mathbb{R}^d$, then by [125, Theorem 5.20], there exists a deterministic positive measure $n_p(dx)$, the density of states of H_p, such that for any φ in the Schwartz space $\mathcal{S}(\mathbb{R})$

$$\int_{\mathbb{R}} \varphi(x) n_p(dx) = \underline{\mathrm{Tr}}\ (\varphi(H_p)).$$

For $K \subset \mathbb{Z}^d$, we define the self-consistent operator corresponding to the system with the defects in K

$$H_K = H_0 + V_K,$$

where

$$V_K = Y_m * (\rho_K - \nu_K), \qquad \nu_K = \sum_{k \in K} \chi(\cdot - k) \quad \text{and} \quad \rho_K = \rho_{\nu_K}.$$

If $|K| < \infty$, we denote by $\xi_K(x)$ the spectral shift function [156] for the pair of operators H_K and H_0. It is the tempered distribution in $\mathcal{S}'(\mathbb{R})$ satisfying, for any $\varphi \in \mathcal{S}(\mathbb{R})$,

$$\mathrm{Tr}\ (\varphi(H_K) - \varphi(H_0)) = \int_{\mathbb{R}} \xi_K(x) \varphi'(x)\, dx = -\int_{\mathbb{R}} \xi_K'(x) \varphi(x)\, dx.$$

In Theorem 3.2.7 below, we give the asymptotic expansion of the density of states n_p in terms of powers of the Bernoulli parameter p.

Theorem 3.2.7. *For $\chi \in L^2(\mathbb{R}^d)$ such that $\mathrm{supp}(\chi) \subset \Gamma$ and $K \subset \mathbb{Z}^d$ such that $|K| < \infty$, we define the tempered distribution μ_K by*

$$\mu_K(x) = -\frac{1}{|K|} \sum_{K' \subset K} (-1)^{|K \setminus K'|} \xi'_{K'}(x).$$

There exists $\alpha_c > 0$ such that if $\|\chi\|_{L^2} \leq \alpha_c$, then

(i) for $j \in \{1, 2\}$, $\mu_j = \sum_{\substack{K \subset \mathbb{Z}^d, \\ |K|=j,\, 0 \in K}} \mu_K$ is a well-defined convergent series in $\mathcal{S}'(\mathbb{R})$.

(ii) for $J \leq 2$, there exists $C_J \geq 0$, independent of χ such that for any $\varphi \in \mathcal{S}(\mathbb{R})$,

$$\left| \langle n_p, \varphi \rangle - \langle n_0, \varphi \rangle - \sum_{j=1}^{J} \langle \mu_j, \varphi \rangle \right| \leq C_J \|\chi\|_{L^2} \sup_{\substack{\alpha \leq (J+3)(d+1) \\ \beta \leq J+4+(J+2)d}} \mathcal{N}_{\alpha,\beta}(\varphi)\, p^{J+1},$$

where n_0 is the density of states of the unperturbed Hamiltonian H_0 and $\mathcal{N}_{\alpha,\beta}(\varphi) = \sup_{x \in \mathbb{R}} \left| x^\alpha \frac{\partial^\beta \varphi}{\partial x^\beta} \right|$.

In Theorem 3.2.7, we only present the expansion of the density of states until the second order $J = 2$. The proof of the expansion up to any order $J \in \mathbb{N}$ should follow the same lines and techniques used here.

A result similar to Theorem 3.2.7 was obtained in [87] in the linear case. Materials with low concentration of defects were studied by Le Bris, Anantharaman and Mourrat [3, 2, 1, 119] in the framework of stochastic homogenization.

The proof of Theorem 3.2.7 follows essentially the proof of [87, Theorem 1.1]. It uses the decay of the potential related to each local defect. In [87, Theorem 1.1], the linear potential is assumed to decay exponentially. In our nonlinear model, the decay estimates established in Section 3.2.3 play a crucial role in the proof.

The rest of the chapter is devoted to the proofs of the results presented in this section. In the next section, we study the dielectric response of the crystal to an effective charge perturbation. The results of Section 3.3 will be used in later sections.

3.3 Dielectric response for Yukawa interaction

In this section, we study the dielectric response of the electronic ground state of a crystal to a small effective charge perturbation $f \in L^2_{\mathrm{unif}}(\mathbb{R}^d)$. This means more precisely that we expand the formula

$$Q_f = 1\left(H_0 + f * Y_m \leq 0\right) - 1\left(H_0 \leq 0\right)$$

in powers of f (for f small enough) and state important properties of the first order term. The higher order term will be dealt with later in Lemma 3.4.1. For Coulomb interactions and local perturbation $f \in L^2(\mathbb{R}^d) \cap \mathcal{C}_0(\mathbb{R}^d)$, where $\mathcal{C}_0(\mathbb{R}^d)$ is the Coulomb space, this study has been carried out in [33] in dimension $d = 3$.

The results of this section can be used in the linear model or the mean-field framework. In the reduced Hartree-Fock model we consider in this study, the effective charge perturbation is $f = \rho_\nu - \nu$, where ρ_ν is the electronic density of the response of the crystal to the nuclear perturbation ν defined in Theorem 3.2.1. Expanding (formally) Q_f in powers of f and using the resolvent formula leads to considering the following operator

$$Q_{1,f} = \frac{1}{2i\pi} \oint_{\mathcal{C}} \frac{1}{z - H_0} f * Y_m \frac{1}{z - H_0} dz,$$

where $\mathcal{C}$ is a smooth curve in the complex plane enclosing the whole spectrum of H_0 below 0 (see Figure 3.2). By the residue Theorem, the operator $Q_{1,f}$

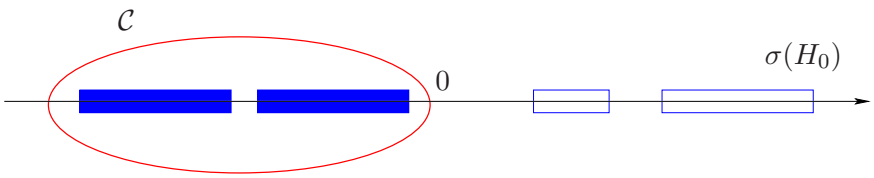

Figure 3.2: Graphical representation of a contour $\mathcal{C} \subset \mathbb{C}$ enclosing $\sigma(H_0) \cap (-\infty, 0]$.

does not depend on the particular curve $\mathcal{C}$ chosen as above. We recall that $V_{\rm per}$ is $-\Delta$ bounded with relative bound 0. Thus H_0 is bounded below by the Rellich-Kato theorem [132, Theorem X.12]. Theorem 3.3.1 below studies the properties of the dielectric response operator $\mathcal{L} : f \to \rho_{Q_{1,f}}$ and the operator $(1 + \mathcal{L})^{-1}$, which will play an important role in the resolution of the self-consistent equation (3.11). In particular, it gives the functional spaces on which $\mathcal{L}$ and $(1 + \mathcal{L})^{-1}$ are well-defined for both local and extended charge densities. It also says that $(1 + \mathcal{L})^{-1}$ is local in the sense that its off-diagonal components decay faster than any polynomial. We consider $H^{-1}(\mathbb{R}^d)$, endowed with the scalar product

$$\langle f, g \rangle_{H^{-1}} = \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} \frac{\overline{\widehat{f}(p)} \widehat{g}(p)}{|p|^2 + m^2} dp.$$

Theorem 3.3.1 (Properties of the dielectric response)**.** *We have*

(i) The operator

$$\begin{array}{rccc} \mathcal{L}: & H^{-1}(\mathbb{R}^d) & \to & H^{-1}(\mathbb{R}^d) \\ & f & \mapsto & -\rho_{Q_{1,f}}, \end{array}$$

is well-defined, bounded, non-negative and self-adjoint. Hence $1+\mathcal{L}$ *is invertible and bicontinuous.*

(ii) The operator $\mathcal{L}$ *is bounded from* $H^{-1}(\mathbb{R}^d)$ *to* $L^2(\mathbb{R}^d)$ *and* $1/(1+\mathcal{L})$ *is a well-defined, bounded operator from* $L^2(\mathbb{R}^d)$ *into itself.*

(iii) The operator

$$\begin{array}{rccc} \mathcal{L}: & L^2_{\mathrm{unif}}(\mathbb{R}^d) & \to & L^2_{\mathrm{unif}}(\mathbb{R}^d) \\ & f & \mapsto & -\rho_{Q_{1,f}}, \end{array}$$

is well-defined and bounded. The operator $1+\mathcal{L}$ *is invertible on* $L^2_{\mathrm{unif}}(\mathbb{R}^d)$ *and its inverse is bounded.*

(iv) There exist $C \geq 0$ *and* $C' > 0$ *such that for any* $j, k \in \mathbb{Z}^d$ *such that* $|k-j| \geq 1$*, we have*

$$\left\| 1_{\Gamma+j} \frac{1}{1+\mathcal{L}} 1_{\Gamma+k} \right\|_{\mathcal{B}} \leq C e^{-C'(\log|k-j|)^2}. \tag{3.16}$$

Proof. The proof consists in the following 6 steps. In the whole chapter $C \geq 0$ and $C' > 0$ are constants whose values might change from one line to the next.

Step 1 *Proof of (i).* The proof is similar to the one of [33, Proposition 2], with the Yukawa kernel Y_m, instead of the Coulomb kernel. In the Yukawa case, $H^{-1}(\mathbb{R}^d)$ plays the role of the Coulomb space. The proof of [33, Proposition 2] can easily be adapted to our case. We skip the details for the sake of brevity.

Step 2 *Proof of (ii).* Let $f \in H^{-1}(\mathbb{R}^d)$. Then $Y_m * f \in L^2(\mathbb{R}^d)$ and

$$\|Y_m * f\|_{L^2}^2 = \left|S^{d-1}\right|^2 \int_{\mathbb{R}^d} \frac{\left|\widehat{f}(p)\right|^2}{\left(|p|^2+m^2\right)^2} dp \leq C \int_{\mathbb{R}^d} \frac{\left|\widehat{f}(p)\right|^2}{|p|^2+m^2} dp = C \|f\|_{H^{-1}}^2 . \tag{3.17}$$

Therefore, by [33, Proposition 1], $Q_{1,f} \in \mathcal{K}$, where $\mathcal{K}$ has been defined in (3.9), and $\mathcal{L}f = -\rho_{Q_{1,f}} \in L^2(\mathbb{R}^d)$. Arguing by duality, we have for any $W \in L^2(\mathbb{R}^d)$,

$$\mathrm{Tr}\,(Q_{1,f}W) = \int_{\mathbb{R}^d} \rho_{Q_{1,f}} W. \tag{3.18}$$

Besides, by the Kato-Seiler-Simon inequality [145, Theorem 4.1] for $d \leq 3$

$$\forall p \geq 2, \quad \|f(-i\nabla)g(x)\|_{\mathfrak{S}_2} \leq (2\pi)^{-\frac{d}{p}} \|f\|_{L^p} \|g\|_{L^p} \tag{3.19}$$

and the fact that

$$(z-H_0)^{-1}(1-\Delta) \text{ is uniformly bounded on the contour } \mathcal{C}, \tag{3.20}$$

we have

$$\frac{1}{z-H_0}Y_m * f\frac{1}{z-H_0}W \in \mathfrak{S}_2(L^2(\mathbb{R}^d))$$

and

$$|\mathrm{Tr}\,(Q_{1,f}W)| = \left|\frac{1}{2i\pi}\oint_{\mathcal{C}} \mathrm{Tr}\,\left(\frac{1}{z-H_0}Y_m * f\frac{1}{z-H_0}W\right)\,dz\right| \leq C\,\|Y_m * f\|_{L^2}\,\|W\|_{L^2}\,. \tag{3.21}$$

The bound (3.20) follows from the following lemma.

Lemma 3.3.2. *Let $W \in L^2_{\mathrm{unif}}(\mathbb{R}^d)$. Then there exists $C \geq 0$, depending only on the L^2_{unif}-norm of W, such that for any $z \in \mathbb{C}\setminus\sigma(-\Delta+W)$, we have*

$$\left\|(-\Delta+1)(-\Delta+W-z)^{-1}\right\|_{\mathcal{B}} \leq C\frac{1+|z|}{\mathrm{d}(z,\sigma(-\Delta+W))}.$$

In particular, if Λ is a compact set of $\mathbb{C}\setminus\sigma(-\Delta+W)$, then $(-\Delta+1)(-\Delta+W-z)^{-1}$ is uniformly bounded on Λ.

Proof. The proof of Lemma 3.3.2 follows the proof of [24, Lemma 3]. For $c>0$, we have

$$(-\Delta+W-z+c)(-\Delta+c)^{-1} = 1+(W-z)(-\Delta+c)^{-1}.$$

As W is $-\Delta$-bounded with relative bound 0 [133, Theorem XIII.96], then for any $a>0$ there exists $b>0$, depending only on $\|W\|_{L^2_{\mathrm{unif}}}$ such that for any $\varphi \in L^2(\mathbb{R}^d)$

$$\begin{aligned}\left\|(W-z)(-\Delta+c)^{-1}\varphi\right\|_{L^2(\mathbb{R}^d)} &\leq a\left\|-\Delta(-\Delta+c)^{-1}\varphi\right\|_{L^2(\mathbb{R}^d)} \\ &\quad + (b+|z|)\left\|(-\Delta+c)^{-1}\varphi\right\|_{L^2(\mathbb{R}^d)} \\ &\leq \left(a+\frac{b+|z|}{c}\right)\|\varphi\|_{L^2(\mathbb{R}^d)}\,.\end{aligned}$$

Choosing $a=\frac{1}{4}$ and $c=\max\{1,4(b+|z|)\}$, we obtain

$$\left\|(-\Delta+c)(-\Delta+W-z+c)^{-1}\right\|_{\mathcal{B}} \leq 2.$$

Finally, as

$$\left\|\frac{-\Delta+1}{-\Delta+c}\right\|_{\mathcal{B}} \leq \frac{1}{c} \leq 1 \quad \text{and} \quad \left\|\frac{-\Delta+W-z+c}{-\Delta+W-z}\right\|_{\mathcal{B}} \leq 1+\frac{c}{\mathrm{d}(z,\sigma(-\Delta+W))} \leq C\frac{1+|z|}{\mathrm{d}(z,\sigma(-\Delta+W))},$$

then the operator

$$(-\Delta+1)\,(-\Delta+W-z)^{-1} = \frac{-\Delta+1}{-\Delta+c}\,(-\Delta+c)\,(-\Delta+W-z+c)^{-1} \times \frac{-\Delta+W-z+c}{-\Delta+W-z}$$

satisfies

$$\left\|(-\Delta+1)\,(-\Delta+W-z)^{-1}\right\|_{\mathcal{B}} \leq C\frac{1+|z|}{\mathrm{d}(z,\sigma(-\Delta+W))}.$$

□

In view of (3.17), (3.18) and (3.21), it follows that

$$\left|\int_{\mathbb{R}^d}(\mathcal{L}f)W\right| \leq C\,\|f\|_{H^{-1}}\,\|W\|_{L^2}\,.$$

We deduce that

$$\|\mathcal{L}f\|_{L^2} \leq C\,\|f\|_{H^{-1}}\,.$$

We now prove that $(1+\mathcal{L})^{-1}$ is bounded on $L^2(\mathbb{R}^d)$. Let $g \in L^2(\mathbb{R}^d)$ and $f \in H^{-1}(\mathbb{R}^d)$ such that $(1+\mathcal{L})f = g$. Then, $f = g - \mathcal{L}f \in L^2(\mathbb{R}^d)$. As $1/(1+\mathcal{L})$ is bounded from $H^{-1}(\mathbb{R}^d)$ into itself, we have

$$\|f\|_{H^{-1}} \leq C\,\|g\|_{H^{-1}} \leq C\,\|g\|_{L^2}\,.$$

Therefore, as $\mathcal{L}$ is continuous from $H^{-1}(\mathbb{R}^d)$ to $L^2(\mathbb{R}^d)$,

$$\|f\|_{L^2} = \|g-\mathcal{L}f\|_{L^2} \leq \|g\|_{L^2} + \|\mathcal{L}f\|_{L^2} \leq \|g\|_{L^2} + C\,\|f\|_{H^{-1}} \leq C\,\|g\|_{L^2}\,,$$

which concludes the proof of *(ii)*.

Step 3 *Proof of the first part of (iii):* $\mathcal{L}$ *is well-defined and bounded on* $L^2_{\mathrm{unif}}(\mathbb{R}^d)$. First, we consider a bounded operator $A \in \mathcal{B}(L^2(\mathbb{R}^d))$ and prove that $(z-H_0)^{-1}A(z-H_0)^{-1}$ is locally trace class. For $\chi \in L^\infty_c(\mathbb{R}^d)$ and $z \in \mathcal{C}$, we have by (3.20) and the Kato-Simon-Seiler inequality (3.19) that $\chi(z-H_0)^{-1}A(z-H_0)^{-1}\chi$ is trace class and that there exists $C \geq 0$ independent of $z \in \mathcal{C}$ such that

$$\begin{aligned}\left|\mathrm{Tr}\,\left(\chi\frac{1}{z-H_0}A\frac{1}{z-H_0}\chi\right)\right| &\leq \left\|\chi\frac{1}{z-H_0}A\frac{1}{z-H_0}\chi\right\|_{\mathfrak{S}_1}\\ &\leq \left\|\chi\frac{1}{z-H_0}\right\|_{\mathfrak{S}_2}\|A\|_{\mathcal{B}}\left\|\frac{1}{z-H_0}\chi\right\|_{\mathfrak{S}_2}\\ &\leq C\,\|A\|_{\mathcal{B}}\,\|\chi\|^2_{L^2}\,.\end{aligned}$$

It follows that the operator $(z-H_0)^{-1}A(z-H_0)^{-1}$ is locally trace class and that its density ρ_z is in $L^1_{\rm loc}(\mathbb{R}^d)$. We now show that ρ_z is in fact in $L^2_{\rm unif}(\mathbb{R}^d)$. Let $k\in\mathbb{Z}^d$ and u be a non-negative function in $L^\infty(\Gamma+k)$. It holds, taking $\chi=\sqrt{u}$, that

$$\left|\int_{\mathbb{R}^d}\rho_z u\right| = \left|\int_{\mathbb{R}^d}\rho_z\chi^2\right| = \left|\mathrm{Tr}\,\left(\chi\frac{1}{z-H_0}A\frac{1}{z-H_0}\chi\right)\right| \leq C\,\|A\|_{\mathcal{B}}\,\|u\|_{L^1}\,. \tag{3.22}$$

By linearity, we deduce that $\rho_z\in L^\infty(\mathbb{R}^d)$ and

$$\|\rho_z\|_{L^2_{\rm unif}} \leq \|\rho_z\|_{L^\infty} \leq C\,\|A\|_{\mathcal{B}}\,.$$

As all these estimates are uniform on the compact set $\mathcal{C}$, the operator $(2i\pi)^{-1}\oint_{\mathcal{C}}(z-H_0)^{-1}\,A\,(z-H_0)^{-1}\,dz$ is locally trace class and its density ρ is in $L^2_{\rm unif}(\mathbb{R}^d)$ and satisfies

$$\|\rho\|_{L^2_{\rm unif}} \leq C\,\|A\|_{\mathcal{B}}\,. \tag{3.23}$$

We now consider the case when $A=Y_m*f$ is a potential generated by a charge density $f\in L^2_{\rm unif}(\mathbb{R}^d)$. The following Lemma gives the functional space Y_m*f belongs to when $f\in L^2_{\rm unif}(\mathbb{R}^d)$.

Lemma 3.3.3. *Let $f\in L^q_{\rm unif}(\mathbb{R}^d)$ and $Y\in L^p_{\rm loc}(\mathbb{R}^d)$ such that*

$$\sum_{k\in\mathbb{Z}^d}\|Y\|_{L^p(\Gamma+k)}<\infty, \tag{3.24}$$

for some $1\leq p,q\leq\infty$. Then, the function $Y*f$ is in $L^r_{\rm unif}(\mathbb{R}^d)$ with $1+1/r=1/p+1/q$ and there exists $C\geq 0$ independent of f such that

$$\|Y*f\|_{L^r_{\rm unif}} \leq C\,\|f\|_{L^q_{\rm unif}}\,.$$

The proof of Lemma 3.3.3 is exactly the same than the one of [29, Lemma 3.1], we omit it here. As Y_m satisfies (3.24) for $p=2$, we have

$$Y_m*f\in L^\infty(\mathbb{R}^d) \quad\text{and}\quad \|Y_m*f\|_{L^\infty}\leq C\,\|f\|_{L^2_{\rm unif}}\,. \tag{3.25}$$

Therefore, by (3.23)

$$\left\|\rho_{Q_{1,f}}\right\|_{L^2_{\rm unif}} \leq C\,\|Y_m*f\|_{L^\infty}\leq C\,\|f\|_{L^2_{\rm unif}}\,,$$

which proves that $\mathcal{L}$ is well-defined and bounded from $L^2_{\rm unif}(\mathbb{R}^d)$ into itself. This concludes Step 3.

In the rest of the proof, we use a localization technique. We will thus need Lemmas 3.3.4 and 3.3.5 below. Lemma 3.3.4 gives an estimate on

the commutator between the dielectric response operator $\mathcal{L}$ and a localizing function in both $L^2(\mathbb{R}^d)$ and $L^2_{\text{unif}}(\mathbb{R}^d)$. Lemma 3.3.5 gives a decay rate of a real sequence satisfying a recursion relation that will be satisfied by the localized sequence. The proofs of Lemmas 3.3.4 and 3.3.5 are postponed until the end of the proof of the proposition.

Lemma 3.3.4. *Let χ be a smooth function in $C_c^\infty(\mathbb{R}^d)$ such that $0 \le \chi \le 1$, $\chi \equiv 1$ on $B(0,1)$ and $\chi \equiv 0$ outside $B(0,2)$. For any set $I \subset \mathbb{Z}^d$ and $R \ge 1$ we denote by $B_{I,R} = \cup_{k\in I}(B(0,R)+k)$ and by $\chi_{I,R}(x) = \chi(\mathrm{d}(x,I)/R)$. The family of functions $(\chi_{I,R})_{R\ge 1}$ satisfy $0 \le \chi_{I,R} \le 1$, $\chi_{I,R} \equiv 1$ on $B_{I,R}$, $\chi_{I,R} \equiv 0$ outside $B_{I,2R}$ and*

$$R\,|\nabla\chi_{I,R}(x)| + R^2\,|\Delta\chi_{I,R}(x)| \le C \quad a.e., \tag{3.26}$$

where C is independent of the set I. We denote by $\eta_{I,R} = 1 - \chi_{I,R}$. Then, there exist $C \ge 0$ and $C' > 0$ such that for any $I \subset \mathbb{Z}^d$ and any $f \in L^2(\mathbb{R}^d)$, we have[1]

$$\begin{aligned}
&\|\eta_{I,R}Y_m * f - Y_m * (\eta_{I,R}f)\|_{H^2} + \|[\eta_{I,R},\mathcal{L}]\,f\|_{L^2} \\
&\qquad \le \frac{C}{R}\left(e^{-C'R}\left\|1_{(\mathbb{R}^d\setminus B_{I,3R})\cap B_{I,R/2}}f\right\|_{H^{-1}} + \left\|1_{B_{I,3R}\setminus B_{I,R/2}}f\right\|_{H^{-1}}\right) \\
&\qquad \le \frac{C}{R}\left(e^{-C'R}\,\|f\|_{L^2} + \left\|1_{B_{I,3R}\setminus B_{I,R/2}}f\right\|_{L^2}\right),
\end{aligned} \tag{3.27}$$

and for any $f \in L^2_{\text{unif}}(\mathbb{R}^d)$

$$\begin{aligned}
&\|\eta_{I,R}Y_m * f - Y_m * (\eta_{I,R}f)\|_{H^2_{\text{unif}}} + \|[\eta_{I,R},\mathcal{L}]\,f\|_{L^2_{\text{unif}}} \\
&\qquad \le \frac{C}{R}\left(e^{-C'R}\,\|f\|_{L^2_{\text{unif}}} + \left\|1_{B_{I,3R}\setminus B_{I,R/2}}f\right\|_{L^2_{\text{unif}}}\right).
\end{aligned} \tag{3.28}$$

Lemma 3.3.5. *Let $(x_R)_{R\ge 0}$ be a non-increasing family of real numbers such that for any $R > 0$,*

$$x_R \le \frac{C}{R}e^{-C'R}x_0 + \frac{C}{R}x_{R/a} \tag{3.29}$$

for given $C \ge 0$ and $C', a > 0$. Then, there exist $C \ge 0$ and $C' > 0$ such that for any $R \ge 2$

$$x_R \le Ce^{-C'(\log R)^2}x_0. \tag{3.30}$$

Consequently, for any $\beta \ge 0$ there exists $C \ge 0$ such that for any $R \ge 1$

$$x_R \le \frac{C}{R^\beta}x_0. \tag{3.31}$$

We now proceed with the proof of Theorem 3.3.1. We first prove *(iv)*, then we prove that $1 + \mathcal{L}$ is invertible on $L^2_{\text{unif}}(\mathbb{R}^d)$.

[1] In the whole chapter, we use the convention $f * gh = hf * g = h(f * g)$, that is, the convolution of functions is higher-precedence than the multiplication.

Step 4 *Proof of (iv).* We explain how to use Lemmas 3.3.4 and 3.3.5 to prove (3.16). Let $k \in \mathbb{Z}^d$ and for $R \geq 1$, let $\eta_R = \eta_{\{k\},R}$ and $B_R = B_{\{k\},R}$ as defined in Lemma 3.3.4. Let $g \in L^2(\mathbb{R}^d)$ and denote by $f = (1+\mathcal{L})^{-1} 1_{\Gamma+k} g$. For $R \geq 1$, we have

$$\eta_R (f + \mathcal{L}f) = \eta_R 1_{\Gamma+k} g = 0.$$

Therefore

$$(1+\mathcal{L})\,\eta_R f = \eta_R f + \mathcal{L}\eta_R f = \mathcal{L}\eta_R f - \eta_R \mathcal{L} f = [\mathcal{L}, \eta_R]\, f.$$

Since $1/(1+\mathcal{L})$ is bounded on $L^2(\mathbb{R}^d)$, it follows that

$$\begin{aligned} \|\eta_R f\|_{L^2} = \left\| \frac{1}{1+\mathcal{L}} [\mathcal{L}, \eta_R]\, f \right\|_{L^2} &\leq C \left\| [\mathcal{L}, \eta_R]\, f \right\|_{L^2} \\ &\leq \frac{C}{R} e^{-C'R} \|f\|_{L^2} + \frac{C}{R} \left\| 1_{B_{3R} \setminus B_{R/2}} f \right\|_{L^2}, \end{aligned} \tag{3.32}$$

where we have used Lemma 3.3.4 in the last step. Denoting by $x_R = \left\| 1_{\mathbb{R}^d \setminus B_{2R}} f \right\|_{L^2}$, the estimate (3.32) leads to

$$x_R \leq \frac{C}{R} e^{-C'R} x_0 + \frac{C}{R} x_{R/4}.$$

Therefore, Lemma 3.3.5 gives that there exist $C \geq 0$ and $C' > 0$ such that for any $R \geq 2$

$$\begin{aligned} \|\eta_R f\|_{L^2} \leq x_{R/2} \leq C e^{-C'(\log R)^2} x_0 &= C e^{-C'(\log R)^2} \|f\|_{L^2} \\ &\leq C e^{-C'(\log R)^2} \|g\|_{L^2(\Gamma+k)}, \end{aligned}$$

where the last inequality follows from the fact that $(1+\mathcal{L})^{-1}$ is bounded on $L^2(\mathbb{R}^d)$. Finally, as $1_{\Gamma+j} \leq \eta_{|k-j|/1-1/2}$, then

$$\left\| 1_{\Gamma+j} \frac{1}{1+\mathcal{L}} 1_{\Gamma+k} g \right\|_{L^2} \leq C e^{-C'(\log|k-j|)^2} \|g\|_{L^2(\Gamma+k)} \leq C e^{-C'(\log|k-j|)^2} \|g\|_{L^2}.$$

Step 5 *Proof that $1+\mathcal{L}$ is surjective on $L^2_{\mathrm{unif}}(\mathbb{R}^d)$.* Let $g \in L^2_{\mathrm{unif}}(\mathbb{R}^d)$ and consider $g_L = g 1_{\Gamma_L}$ for $L \in 2\mathbb{N}+1$. As $1+\mathcal{L}$ is invertible on $L^2(\mathbb{R}^d)$, there exists $f_L \in L^2(\mathbb{R}^d)$ such that

$$(1+\mathcal{L}) f_L = g_L \tag{3.33}$$

and

$$\begin{aligned} \|f_L\|_{L^2_{\mathrm{unif}}} &= \sup_{j \in \mathbb{Z}^d} \left\| 1_{\Gamma+j} \frac{1}{1+\mathcal{L}} \sum_{k \in \mathbb{Z}^d \cap \Gamma_L} 1_{\Gamma+k} g \right\|_{L^2} \\ &\leq \sup_{j \in \mathbb{Z}^d} \sum_{k \in \mathbb{Z}^d \cap \Gamma_L} \left\| 1_{\Gamma+j} \frac{1}{1+\mathcal{L}} 1_{\Gamma+k} g \right\|_{L^2}. \end{aligned}$$

Using (3.16), we obtain

$$\|f_L\|_{L^2_{\rm unif}} \leq \sup_{j\in\mathbb{Z}^d} C \sum_{k\in\mathbb{Z}^d\setminus\{j\}} e^{-C'(\log|j-k|)^2} \|g\|_{L^2(\Gamma+k)} + C\|g\|_{L^2_{\rm unif}} \leq C\|g\|_{L^2_{\rm unif}}$$

for a constant C independent of L. The space $L^2_{\rm unif}(\mathbb{R}^d)$ is known to be the dual of $\ell^1(L^2) = \left\{ f \in L^2_{\rm loc}(\mathbb{R}^d),\ \sum_{k\in\mathbb{Z}^d} \|f\|_{L^2(\Gamma+k)} < \infty \right\}$, which is a separable Banach space. Therefore, since the sequence $(f_L)_{L\geq 1}$ is bounded in $L^2_{\rm unif}(\mathbb{R}^d)$, there exists a subsequence of $(f_L)_{L\geq 1}$ (denoted the same for simplicity) and $f \in L^2_{\rm unif}(\mathbb{R}^d)$ such that $f_L \rightharpoonup_* f$ in $L^2_{\rm unif}(\mathbb{R}^d)$ and

$$\|f\|_{L^2_{\rm unif}} \leq \liminf_{k\to\infty} \|f_L\|_{L^2_{\rm unif}} \leq C\|g\|_{L^2_{\rm unif}}\,. \tag{3.34}$$

We now want to pass to the limit in the sense of distributions in (3.33). Since $C^\infty_c(\mathbb{R}^d)$ is dense in $\ell^1(L^2)$, the sequence (f_L) converges to f in $\mathcal{D}'(\mathbb{R}^d)$. Next, we need to show that for any $\varphi \in \mathcal{D}(\mathbb{R}^d)$,

$$\int_{\mathbb{R}^d} (\mathcal{L}(f_L - f))\,\varphi \underset{L\to\infty}{\longrightarrow} 0. \tag{3.35}$$

We denote by $\rho_{z,L}$ the density associated with the operator $(z-H_0)^{-1} Y_m * (f-f_L)(z-H_0)^{-1}$. Then

$$\int_{\mathbb{R}^d} (\mathcal{L}(f_L - f))\,\varphi = \frac{1}{2i\pi} \oint_{\mathcal{C}} \int_{\mathbb{R}^d} \rho_{z,L}\varphi\, dz$$

and, as φ has compact support, we have by (3.22) and (3.25)

$$\begin{aligned}\left| \int_{\mathbb{R}^d} \rho_{z,L}\varphi \right| &\leq C\|Y_m * (f-f_L)\|_{L^\infty} \|\varphi\|_{L^1} \leq C\|f-f_L\|_{L^2_{\rm unif}} \|\varphi\|_{L^1} \\ &\leq C\|g\|_{L^2_{\rm unif}} \|\varphi\|_{L^1}\,,\end{aligned}$$

where the constant $C \geq 0$ is independent of L and $z \in \mathcal{C}$. By the dominated convergence theorem, it is therefore sufficient, for proving (3.35), to show that for any $z \in \mathcal{C}$

$$\int_{\mathbb{R}^d} \rho_{z,L}\varphi \underset{L\to\infty}{\longrightarrow} 0. \tag{3.36}$$

For $R \geq 1$, we define $\rho_{z,L,{\rm out},R}$ and $\rho_{z,L,{\rm in},R}$ to be the densities associated with the operators

$$\frac{1}{z-H_0} 1_{\mathbb{R}^d\setminus B(0,R)} Y_m * (f-f_L) \frac{1}{z-H_0} \quad \text{and} \quad \frac{1}{z-H_0} 1_{B(0,R)} Y_m * (f-f_L) \frac{1}{z-H_0}$$

respectively. Therefore $\rho_{z,L} = \rho_{z,L,{\rm out,R}} + \rho_{z,L,{\rm in},R}$. Let $\varepsilon > 0$. In the following, we will choose R large enough such that $\int \rho_{z,L,{\rm out},R}\varphi$ is small for any L. Then, using the weak-$*$ convergence of f_L to f we show that

$\int \rho_{z,L,\mathrm{in},R}\varphi$ is small for L large enough. Reasoning similarly than in the proof of (3.22), we find

$$\left|\int_{\mathbb{R}^d} \rho_{z,L,\mathrm{out},R}\varphi\right| \leq C \left\|f - f_L\right\|_{L^2_{\mathrm{unif}}} \tag{3.37}$$
$$\times \left(\left\|1_{\mathbb{R}^d\setminus B(0,R)}\frac{1}{z-H_0}\sqrt{\varphi_+}\right\|^2_{\mathfrak{S}_2} + \left\|1_{\mathbb{R}^d\setminus B(0,R)}\frac{1}{z-H_0}\sqrt{\varphi_-}\right\|^2_{\mathfrak{S}_2}\right)$$

Now, we need the following lemma, a modified version of [87, Prop. 4.1].

Lemma 3.3.6. *Let $W \in L^2_{\mathrm{unif}}(\mathbb{R}^d)$ and $H = -\Delta + W$. There exists $C \geq 0$ and $C' > 0$, depending only on $\|W\|_{L^2_{\mathrm{unif}}}$, such that for any $\chi \in L^2(\mathbb{R}^d)$ and $\eta \in L^\infty(\mathbb{R}^d)$ satisfying $R = \mathrm{d}\left(supp(\chi), supp(\eta)\right) \geq 1$, and any $z \in \mathbb{C}\setminus\sigma(H)$, we have*

$$\left\|\chi\left(z-H\right)^{-1}\eta\right\|_{\mathfrak{S}_2} \leq Cc_1(z)e^{-C'c_2(z)R}\left\|\eta\right\|_{L^\infty}\left\|\chi\right\|_{L^2},$$

where $c_1(z) = \mathrm{d}(z,\sigma(H))^{-1}$, $c_2(z) = \mathrm{d}(z,\sigma(H))/(|z|+1)$. In particular, if Λ is a compact set of $\mathbb{C}\setminus\sigma(H)$, then

$$\left\|\chi\left(z-H\right)^{-1}\eta\right\|_{\mathfrak{S}_2} \leq Ce^{-C'R}\left\|\eta\right\|_{L^\infty}\left\|\chi\right\|_{L^2},$$

where C and C' do not depend on z but depend, in general, on Λ.

Proof of Lemma 3.3.6. We have

$$\left\|\chi\left(z-H\right)^{-1}\eta\right\|^2_{\mathfrak{S}_2} = \int_{\mathbb{R}^d\times\mathbb{R}^d} \left|\chi(x)G_z(x,y)\eta(y)\right|^2 dx\,dy,$$

where $G_z(x,y)$ in the kernel of $(z-H)^{-1}$. By [144, Theorem B.7.2] and [57, Corollary 1] we have for $|x-y| \geq 1$

$$|G_z(x,y)| \leq Cc_1(z)e^{-C'c_2(z)|x-y|},$$

where $C \geq 0$ and $C' > 0$ depend only on $\|W\|_{L^2_{\mathrm{unif}}}$. Therefore

$$\begin{aligned}\left\|\chi\left(z-H\right)^{-1}\eta\right\|^2_{\mathfrak{S}_2} &\leq Cc_1(z)^2\left\|\eta\right\|^2_{L^\infty}\left\|\chi\right\|^2_{L^2}\sup_{x\in\mathrm{supp}(\chi)}\int_{\mathbb{R}^d} 1_{\mathrm{supp}(\eta)}(y)e^{-2C'c_2(z)|x-y|}\,dy\\ &\leq Cc_1(z)^2\left\|\eta\right\|^2_{L^\infty}\left\|\chi\right\|^2_{L^2}e^{-C'c_2(z)R}.\end{aligned}$$

□

Going back to (3.37), we deduce using Lemma 3.3.6, that for R large enough

$$\left\|1_{\mathbb{R}^d\setminus B(0,R)}\frac{1}{z-H_0}\sqrt{\varphi_\pm}\right\|_{\mathfrak{S}_2} \leq C\left\|\sqrt{\varphi_\pm}\right\|_{L^2}e^{-C'R},$$

As $\|f - f_L\|_{L^2_{\text{unif}}} \leq C \|g\|_{L^2_{\text{unif}}}$, we obtain

$$\left| \int_{\mathbb{R}^d} \rho_{z,L,\text{out},R\varphi} \right| \leq C \|g\|_{L^2_{\text{unif}}} \|\varphi\|^2_{L^1} e^{-C'R}. \tag{3.38}$$

We can thus choose R such that (3.38) is smaller than $\varepsilon/2$. Besides, we have

$$\begin{aligned} \int_{\mathbb{R}^d} \rho_{z,L,\text{in},R\varphi} &= \text{Tr} \left(1_{B(0,R)} Y_m * (f - f_L) \frac{1}{z - H_0} \varphi \frac{1}{z - H_0} \right) \\ &= \int_{\mathbb{R}^d} 1_{B(0,R)} Y_m * (f_L - f)\rho, \end{aligned}$$

where ρ is the density associated with the trace class operator $(z - H_0)^{-1} \varphi (z - H_0)^{-1}$. For $R' > 0$, we have

$$\begin{aligned} \left| \int_{\mathbb{R}^d} 1_{B(0,R)} Y_m * (f_L - f)\rho \right| &= \left| \int_{B(0,R)} \int_{\mathbb{R}^d} Y_m(x - y) (f - f_L)(y) \, dy \rho(x) \, dx \right| \\ &\leq \left| \int_{B(0,R)} \int_{B(0,R')} Y_m(x - y) (f - f_L)(y) \, dy \rho(x) \, dx \right| \\ &+ \left\| \int_{\mathbb{R}^d \setminus B(0,R')} Y_m(\cdot - y) (f - f_L)(y) \, dy \right\|_{L^\infty(B(0,R))} \|\rho\|_{L^1}. \end{aligned} \tag{3.39}$$

As Y_m is exponentially decaying, we can choose R' such that the second term of the RHS of (3.39) is smaller that $\varepsilon/4$. As to the first term, by the weak-$*$ convergence of f_L to f in $L^2_{\text{unif}}(\mathbb{R}^d)$, we have that

$$h_L(x) = \int_{B(0,R')} Y_m(x - y) (f - f_L)(y) \, dy \underset{L \to \infty}{\longrightarrow} 0,$$

for any $x \in B(0, R)$. Besides, we have for a.e. $x \in B(0, R)$

$$|h_L(x)| \leq \|h_L\|_{L^\infty} \leq C \|f - f_L\|_{L^2_{\text{unif}}} \leq C \|g\|_{L^2_{\text{unif}}}$$

(see (3.25)). By the dominated convergence theorem, it follows that one can choose L large enough such that the first term of the RHS of (3.39) is smaller that $\varepsilon/4$. This concludes the proof of (3.36), thus the proof of (3.35). We are now able to pass to the limit in (3.33), which concludes the proof of the surjectivity of $1 + \mathcal{L}$ on $L^2_{\text{unif}}(\mathbb{R}^d)$. In view of (3.34), we have shown that there exists $C \geq 0$ such that for any $g \in L^2_{\text{unif}}(\mathbb{R}^d)$, there exists $f \in L^2_{\text{unif}}(\mathbb{R}^d)$ such that

$$(1 + \mathcal{L})f = g \quad \text{and} \quad \|f\|_{L^2_{\text{unif}}} \leq C \|g\|_{L^2_{\text{unif}}}. \tag{3.40}$$

Step 6 *Proof that* $1+\mathcal{L}$ *is injective on* $L^2_{\text{unif}}(\mathbb{R}^d)$. Let $f \in L^2_{\text{unif}}(\mathbb{R}^d)$ be such that $(1+\mathcal{L})f = 0$. For $R \geq 1$, let $\chi_R = \chi_{\{0\},R}$ as in Lemma 3.3.4. Then,

$$\chi_R f + \chi_R \mathcal{L}(f) = 0,$$

and thus

$$(1+\mathcal{L})(\chi_R f) = \mathcal{L}\chi_R f - \chi_R \mathcal{L}(f) = [\mathcal{L}, \chi_R] f.$$

As $g := [\mathcal{L}, \chi_R] f \in L^2(\mathbb{R}^d)$, then the solution $\varphi = \chi_R f$ of $(1+\mathcal{L})\varphi = g$ is unique and satisfies $\|\varphi\|_{L^2_{\text{unif}}} \leq C \|g\|_{L^2_{\text{unif}}}$ by (3.40). Therefore

$$\|\chi_R f\|_{L^2_{\text{unif}}} \leq C \|[\mathcal{L}, \chi_R] f\|_{L^2_{\text{unif}}}.$$

Using Lemma 3.3.4, we have

$$\|\chi_R f\|_{L^2_{\text{unif}}} \leq C \|[\mathcal{L}, \chi_R] f\|_{L^2_{\text{unif}}} = C \|[\mathcal{L}, \eta_R] f\|_{L^2_{\text{unif}}} \leq \frac{C}{R} \|f\|_{L^2_{\text{unif}}}. \quad (3.41)$$

As $\|\chi_R f\|_{L^2_{\text{unif}}}$ is a non-decreasing function of R converging to $\|f\|_{L^2_{\text{unif}}}$ when $R \to +\infty$ and the RHS of (3.41) goes to 0 when $R \to +\infty$, then $\|f\|_{L^2_{\text{unif}}} = 0$ and $f = 0$; which proves that $1+\mathcal{L}$ is injective. The boundedness of $1/(1+\mathcal{L})$ then follows from (3.40). This concludes the proof of Theorem 3.3.1. □

In order to complete the proof of Theorem 3.3.1, we need to prove Lemmas 3.3.4 and 3.3.5.

Proof of Lemma 3.3.4. For simplicity, we use the shorthand notation $\chi_R = \chi_{I,R}$, $\eta_R = \eta_{I,R}$ and $B_R = B_{I,R}$.

Step 1 *Proof of* (3.27). We have

$$\begin{aligned}\eta_R f * Y_m - Y_m * (\eta_R f) &= \eta_R \left(-\Delta + m^2\right)^{-1} f - \left(-\Delta + m^2\right)^{-1} \eta_R f \\ &= \left[\eta_R, \left(-\Delta + m^2\right)^{-1}\right] f.\end{aligned}$$

We now use that $\left[B, (z-A)^{-1}\right] = (z-A)^{-1}[B, A](z-A)^{-1}$ and the fact that $[\eta_R, \Delta] = -(\Delta\eta_R + 2\nabla\eta_R \cdot \nabla)$. We thus obtain

$$\begin{aligned}\eta_R f * Y_m - Y_m * (\eta_R f) &= \left(-\Delta + m^2\right)^{-1} [\eta_R, \Delta] \left(-\Delta + m^2\right)^{-1} f \\ &= -\left(-\Delta + m^2\right)^{-1} \left((\Delta\eta_R) + 2(\nabla\eta_R) \cdot \nabla\right) \left(-\Delta + m^2\right)^{-1} f.\end{aligned} \quad (3.42)$$

As $\nabla\eta_R = -\nabla\chi_R$ and $\Delta\eta_R = -\Delta\chi_R$ are supported in $B_{2R}\setminus B_R$, then, by (3.26),

$$\begin{aligned}\|\eta_R f * Y_m - Y_m * (\eta_R f)\|_{H_2} \leq \frac{C}{R^2}\left\|1_{B_{2R}\setminus B_R}\left(-\Delta+m^2\right)^{-1} f\right\|_{L^2} \\ + \frac{C}{R}\left\|1_{B_{2R}\setminus B_R}\nabla\left(-\Delta+m^2\right)^{-1} f\right\|_{\left(L^2(\mathbb{R}^d)\right)^d}.\end{aligned} \tag{3.43}$$

To bound the first term of the RHS of (3.43), we write

$$\begin{aligned}\left(-\Delta+m^2\right)^{-1} f(x) &= \int_{\mathbb{R}^d} Y_m(x-y)f(y)\,dy \\ &= \int_{\mathbb{R}^d} Y_m(x-y)f(y)1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}}(y)\,dy \\ &\quad + \int_{\mathbb{R}^d} Y_m(x-y)f(y)1_{B_{3R}\setminus B_{R/2}}(y)\,dy\end{aligned} \tag{3.44}$$

Thanks to the exponential decay of Y_m and the fact that for any $x\in B_{2R}\setminus B_R$ and $y\in(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}$, $|x-y|\geq R/2$, we get

$$\begin{aligned}&\left\|1_{B_{2R}\setminus B_R}\left(-\Delta+m^2\right)^{-1} f 1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}}\right\|_{L^2} \\ &\qquad \leq Ce^{-\frac{mR}{4}}\left\|Y_{\frac{m}{2}} * (f1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}})\right\|_{L^2} \leq Ce^{-\frac{mR}{4}}\left\|f1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}}\right\|_{H^{-2}}.\end{aligned}$$

Controlling in the same way the second term of the RHS of (3.44), we deduce

$$\begin{aligned}\left\|1_{B_{2R}\setminus B_R}\left(-\Delta+m^2\right)^{-1} f\right\|_{L^2} &\leq Ce^{-\frac{mR}{4}}\left\|1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}} f\right\|_{H^{-2}} \\ &\quad + C\left\|1_{B_{3R}\setminus B_{R/2}} f\right\|_{H^{-2}}.\end{aligned}$$

We proceed similarly for the second term of the RHS of (3.43) using that $W_m = \nabla Y_m$, the inverse Fourier transform of $i\left|S^{d-1}\right|\frac{p}{|p|^2+m^2}$, is exponentially decaying and satisfies $\|W_m * g\|_{L^2}\leq\|g\|_{H^{-1}}$ for any $g\in H^{-1}$. We get

$$\|\eta_R f * Y_m - Y_m * (\eta_R f)\|_{H_2} \leq \frac{C}{R}e^{-\frac{mR}{4}}\left\|1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}} f\right\|_{H^{-1}} + \frac{C}{R}\left\|1_{B_{3R}\setminus B_{R/2}} f\right\|_{H^{-1}}. \tag{3.45}$$

We turn now to estimating $\|[\eta_R,\mathcal{L}]\,f\|_{L^2}$. We know that $[\eta_R,\mathcal{L}]\,f$ is the density associated with the operator

$$\begin{aligned}&-\eta_R Q_{1,f} + Q_{1,\eta_R f} \\ &\quad = \frac{1}{2i\pi}\int_{\mathcal{C}}\left(\frac{1}{z-H_0}Y_m * (\eta_R f)\frac{1}{z-H_0} - \eta_R\frac{1}{z-H_0}Y_m * f\frac{1}{z-H_0}\right)dz \\ &\quad = \frac{1}{2i\pi}\int_{\mathcal{C}}\frac{1}{z-H_0}\left(Y * (\eta_R f) - \eta_R Y_m * f\right)\frac{1}{z-H_0}\,dz \\ &\qquad - \frac{1}{2i\pi}\int_{\mathcal{C}}\left[\eta_R,\frac{1}{z-H_0}\right]Y_m * f\frac{1}{z-H_0}\,dz.\end{aligned} \tag{3.46}$$

We denote by r_1 and r_2 the densities associated with the first and second terms of the RHS of (3.46) respectively. For any $W \in L^2(\mathbb{R}^d)$, we have

$$\begin{aligned}\left|\int_{\mathbb{R}^d} r_1 W\right| &= \left|\frac{1}{2i\pi}\int_{\mathcal{C}} \mathrm{Tr}\left(\frac{1}{z-H_0}\left(Y_m*(\eta_R f)-\eta_R Y_m * f\right)\frac{1}{z-H_0}W\right)dz\right| \\ &\leq C\left\|Y_m*(\eta_R f)-\eta_R Y_m * f\right\|_{L^2}\|W\|_{L^2}, \end{aligned} \tag{3.47}$$

where we have used (3.19) and (3.20). Therefore, in view of (3.45),

$$\begin{aligned}\|r_1\|_{L^2} &\leq C\left\|Y_m*(\eta_R f)-\eta_R Y_m * f\right\|_{L^2} \\ &\leq \frac{C}{R}e^{-\frac{mR}{4}}\left\|1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}}f\right\|_{H^{-1}} + \frac{C}{R}\left\|1_{B_{3R}\setminus B_{R/2}}f\right\|_{H^{-1}}. \end{aligned} \tag{3.48}$$

It remains to estimate r_2. For any $A \in \mathfrak{S}_2(L^2(\mathbb{R}^d))$ and $W \in L^2(\mathbb{R}^d)$, the density ρ associated with the operator $(-\Delta+1)^{-1/2}A(-\Delta+1)^{-1/2}$ satisfies

$$\begin{aligned}\left|\int_{\mathbb{R}^d}\rho W\right| &\leq \left\|\sqrt{|W|}\right\|_{L^4}\left\|\left(|p|^2+1\right)^{-\frac{1}{2}}\right\|_{L^4}\|A\|_{\mathfrak{S}_2}\left\|\left(|p|^2+1\right)^{-\frac{1}{2}}\right\|_{L^4}\left\|\sqrt{|W|}\right\|_{L^4} \\ &\leq C\|W\|_{L^2}\|A\|_{\mathfrak{S}_2}. \end{aligned}$$

Therefore

$$\|\rho\|_{L^2} \leq C\|A\|_{\mathfrak{S}_2}. \tag{3.49}$$

Applying (3.49) for $A = (-\Delta+1)^{1/2}\left[\eta_R,(z-H_0)^{-1}\right]Y_m * f(z-H_0)^{-1}(-\Delta+1)^{1/2}$, we obtain

$$\|r_2\|_{L^2} \leq C\oint_{\mathcal{C}}\left\|(-\Delta+1)^{-\frac{1}{2}}\left[\eta_R,\Delta\right]\frac{1}{z-H_0}Y_m*f\,(-\Delta+1)^{-\frac{1}{2}}\right\|_{\mathfrak{S}_2}dz, \tag{3.50}$$

where we have used that $C_1(1-\Delta) \leq |z-H_0| \leq C_2(1-\Delta)$, whose proof is similar to the the one of Lemma 3.3.2. As the commutator $[\eta_R,\Delta]$ has its support in $B_{2R}\setminus B_R$, we consider separately $f1_{B_{3R}\setminus B_{R/2}}$ and $f1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}}$. Using the same techniques as above, we obtain

$$\begin{aligned}&\left\|(-\Delta+1)^{-\frac{1}{2}}\left[\eta_R,\Delta\right]\frac{1}{z-H_0}Y_m*\left(1_{B_{3R}\setminus B_{R/2}}f\right)(-\Delta+1)^{-\frac{1}{2}}\right\|_{\mathfrak{S}_2} \\ &\qquad\leq C\left\|(-\Delta+1)^{-\frac{1}{2}}\left[\eta_R,\Delta\right]\right\|_{\mathcal{B}}\left\|\frac{1}{z-H_0}Y_m*\left(1_{B_{3R}\setminus B_{R/2}}f\right)\right\|_{\mathfrak{S}_2} \\ &\qquad\leq C\left(\|\nabla\eta_R\|_{L^\infty}+\|\Delta\eta_R\|_{L^\infty}\right)\left\|Y_m*\left(1_{B_{3R}\setminus B_{R/2}}f\right)\right\|_{L^2} \\ &\qquad\leq \frac{C}{R}\left\|1_{B_{3R}\setminus B_{R/2}}f\right\|_{H^{-2}}. \end{aligned} \tag{3.51}$$

Far from the support of $[\eta_R, \Delta]$, we have

$$\begin{aligned}\left\|(-\Delta+1)^{-\frac{1}{2}}\,[\eta_R,\Delta]\,\frac{1}{z-H_0}Y_m * \left(1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}}f\right)(-\Delta+1)^{-\frac{1}{2}}\right\|_{\mathfrak{S}_2}\\ \leq C\left\|(-\Delta+1)^{-\frac{1}{2}}\,(\Delta\eta_R - 2\nabla\cdot\nabla\eta_R)\right\|_{\mathcal{B}}\\ \sum_{k\in\mathbb{Z}^d}\left\|1_{B_{2R}\setminus B_R}\frac{1}{z-H_0}1_{\Gamma+k}\right\|_{\mathfrak{S}_2}\\ \times\left\|1_{\Gamma+k}Y_m * \left(1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}}f\right)(-\Delta+1)^{-\frac{1}{2}}\right\|_{\mathcal{B}}. \quad (3.52)\end{aligned}$$

In dimension $d\leq 3$, $H^1(\mathbb{R}^d)\hookrightarrow L^4(\mathbb{R}^d)$. Therefore

$$\begin{aligned}\left\|1_{\Gamma+k}Y_m * \left(1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}}f\right)(-\Delta+1)^{-\frac{1}{2}}\right\|_{\mathcal{B}}\\ \leq C\left\|1_{\Gamma+k}Y_m * \left(1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}}f\right)(-\Delta+1)^{-\frac{1}{2}}\right\|_{\mathfrak{S}_4}\\ \leq C\left\|1_{\Gamma+k}Y_m * \left(1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}}f\right)\right\|_{L^4}\\ \leq C\left\|Y_m * \left(1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}}f\right)\right\|_{H^1(\Gamma+k)}. \quad (3.53)\end{aligned}$$

Using the exponential decay of Y_m, we obtain

$$\left\|Y_m * \left(1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}}f\right)\right\|_{H^1(\Gamma+k)} \leq Ce^{-\frac{m}{2}\mathrm{d}(k,(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2})}\left\|1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}}f\right\|_{H^{-1}}. \quad (3.54)$$

In particular, for $k\in\mathbb{Z}^d\cap\left(B_{5R/2}\setminus B_{3R/4}\right)$ (the pink part in Figure 3.3 below), the distance between k and $(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}$ (the blue part in Figure 3.3) is greater than or equal to $R/4$ and

Figure 3.3: Schematic representation of $\mathbb{R}_+$ used in the proof of Lemma 3.3.4.

$$\begin{aligned}\left\|Y_m * \left(1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}}f\right)\right\|_{H^1(\Gamma+k)} \leq Ce^{-\frac{mR}{16}}e^{-\frac{m}{4}\mathrm{d}(k,(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2})}\\ \times\left\|1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}}f\right\|_{H^{-1}}. \quad (3.55)\end{aligned}$$

Besides, using Lemma 3.3.6 with $\eta = 1_{B_{2R}\setminus B_R}$ and $\chi = 1_{\Gamma+k}$, we obtain

$$\left\|1_{B_{2R}\setminus B_R}\frac{1}{z-H_0}1_{\Gamma+k}\right\|_{\mathfrak{S}_2} \leq Ce^{-C'\mathrm{d}(k,B_{2R}\setminus B_R)}.$$

In particular for $k \in \mathbb{Z}^d \setminus \left(B_{5R/2} \setminus B_{3R/4}\right)$, we have $\mathrm{d}(k, B_{2R} \setminus B_R) \geq \frac{R}{4}$ (see Figure 3.3) and

$$\left\| 1_{B_{2R}\setminus B_R} \frac{1}{z - H_0} 1_{\Gamma+k} \right\|_{\mathfrak{S}_2} \leq C e^{-\frac{C'}{2}\frac{R}{4}} e^{-\frac{C'}{2}\mathrm{d}(k, B_{2R}\setminus B_R)}. \tag{3.56}$$

Combining (3.52), (3.53), (3.54), (3.55) and (3.56), we obtain

$$\begin{aligned}
&\left\| (-\Delta+1)^{-\frac{1}{2}} \left[\eta_R, \Delta\right] \frac{1}{z - H_0} Y_m * \left(1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}} f\right) (-\Delta+1)^{-\frac{1}{2}} \right\|_{\mathfrak{S}_2} \\
&\qquad \leq \frac{C}{R} e^{-C'R} \sum_{k\in\mathbb{Z}^d} e^{-C'|k|} \left\| 1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}} f \right\|_{H^{-1}} \\
&\qquad \leq \frac{C}{R} e^{-C'R} \left\| 1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}} f \right\|_{H^{-1}}.
\end{aligned} \tag{3.57}$$

This completes our estimate on r_2. Indeed, in view of (3.50), (3.51) and (3.57), we deduce that

$$\|r_2\|_{L^2} \leq \frac{C}{R} e^{-C'R} \left\| 1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}} f \right\|_{H^{-1}} + \frac{C}{R} \left\| 1_{B_{3R}\setminus B_{R/2}} f \right\|_{H^{-1}},$$

which concludes the proof of (3.27).

Step 2 *Proof of* (3.28). The proof of (3.28) for functions in L^2_{unif} is similar to the one of (3.27) for L^2 functions. We sketch here the main steps of the proof, and only highlighting the differences. Let $f \in L^2_{\mathrm{unif}}(\mathbb{R}^d)$. Using (3.42), we have

$$\begin{aligned}
\eta_R Y_m * f - Y_m * (\eta_R f) &= \sum_{k\in\mathbb{Z}^d} \eta_R Y_m * (1_{\Gamma+k} f) - Y_m * (\eta_R 1_{\Gamma+k} f) \\
&= \sum_{k\in\mathbb{Z}^d} (-\Delta+m^2)^{-1} \left((\Delta\eta_R) + 2(\nabla\eta_R)\cdot\nabla\right) (-\Delta+m^2)^{-1} 1_{\Gamma+k} f \\
&= Y_m * \left(\Delta\eta_R Y_m * f + 2\nabla\eta_R \cdot \nabla Y_m * f\right).
\end{aligned}$$

Therefore

$$\begin{aligned}
\|\eta_R Y_m * f - Y * (\eta_R f)\|_{H^2_{\mathrm{unif}}} &\leq C \left\| (-\Delta+m^2) \left(\eta_R Y_m * f - Y_m * (\eta_R f)\right) \right\|_{L^2_{\mathrm{unif}}} \\
&\leq C \left\| \Delta\eta_R Y_m * f + 2\nabla\eta_R \cdot \nabla Y_m * f \right\|_{L^2_{\mathrm{unif}}} \\
&\leq \frac{C}{R^2} \left\| 1_{B_{2R}\setminus B_R} Y_m * f \right\|_{L^2_{\mathrm{unif}}} + \frac{C}{R} \left\| 1_{B_{2R}\setminus B_R} \nabla Y_m * f \right\|_{L^2_{\mathrm{unif}}}.
\end{aligned} \tag{3.58}$$

To bound the first term of the RHS of (3.58), we use the exponential decay of Y_m, the fact that $Y_m \in \ell^1(L^1)$ and Lemma 3.3.3. We get

$$\begin{aligned}
\left\|1_{B_{2R}\setminus B_R} Y_m * f\right\|_{L^2_{\mathrm{unif}}} &\leq \left\|1_{B_{2R}\setminus B_R} Y_m * \left(f 1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}}\right)\right\|_{L^2_{\mathrm{unif}}} \\
&\quad + \left\|1_{B_{2R}\setminus B_R} Y_m * \left(f 1_{y\in B_{3R}\setminus B_{R/2}}\right)\right\|_{L^2_{\mathrm{unif}}} \\
&\leq e^{-\frac{mR}{4}} \left\|Y_{\frac{m}{2}} * \left(f 1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}}\right)\right\|_{L^2_{\mathrm{unif}}} + \left\|Y_m * \left(f 1_{B_{3R}\setminus B_{R/2}}\right)\right\|_{L^2_{\mathrm{unif}}} \\
&\leq C\left(e^{-\frac{mR}{4}} \|f\|_{L^2_{\mathrm{unif}}} + \left\|1_{B_{3R}\setminus B_{R/2}} f\right\|_{L^2_{\mathrm{unif}}}\right).
\end{aligned}$$

As ∇Y_m is also exponentially decaying and is in $\ell^1(L^1)$, we proceed similarly for the second term of the RHS of (3.58). Finally we obtain the stated inequality

$$\|\eta_R Y_m * f - Y_m * (\eta_R f)\|_{H^2_{\mathrm{unif}}} \leq \frac{C}{R}\left(e^{-C'R} \|f\|_{L^2_{\mathrm{unif}}} + \left\|1_{B_{3R}\setminus B_{R/2}} f\right\|_{L^2_{\mathrm{unif}}}\right). \tag{3.59}$$

We turn to estimating $\|[\eta_R, \mathcal{L}]\, f\|_{L^2_{\mathrm{unif}}}$. By (3.46), we have that

$$[\eta_R, \mathcal{L}]\, f = r_1 + r_{21} + r_{22}$$

where r_1, r_{21} and r_{22} are the densities associated with the operators

$$\frac{1}{2i\pi}\oint_{\mathcal{C}} \frac{1}{z - H_0}\left(Y_m * (\eta_R f) - \eta_R Y_m * f\right)\frac{1}{z - H_0} dz,$$

$$\frac{1}{2i\pi}\oint_{\mathcal{C}} \left[\eta_R, \frac{1}{z - H_0}\right] Y_m * \left(1_{B_{3R}\setminus B_{R/2}} f\right)\frac{1}{z - H_0} dz,$$

and

$$\frac{1}{2i\pi}\oint_{\mathcal{C}} \left[\eta_R, \frac{1}{z - H_0}\right] Y_m * \left(f 1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}}\right)\frac{1}{z - H_0} dz,$$

which are now locally trace class operators. By (3.23) and using that, in dimension $d \leq 3$, $H^2_{\mathrm{unif}}(\mathbb{R}^d) \hookrightarrow L^\infty(\mathbb{R}^d)$, we find

$$\begin{aligned}
\|r_1\|_{L^2_{\mathrm{unif}}} &\leq C\,\|Y_m * (\eta_R f) - \eta_R Y_m * f\|_{L^\infty} \leq C\,\|Y_m * (\eta_R f) - \eta_R Y_m * f\|_{H^2_{\mathrm{unif}}} \\
&\leq \frac{C}{R}\left(e^{-C'R} \|f\|_{L^2_{\mathrm{unif}}} + \left\|1_{B_{3R}\setminus B_{R/2}} f\right\|_{L^2_{\mathrm{unif}}}\right),
\end{aligned}$$

where we have used (3.59) in the last step. Similarly for r_{21}, since $\|\Delta\eta_R\|_{L^\infty} + \|\nabla\eta_R\|_{L^\infty} \leq C/R$, we have

$$\begin{aligned}
\|r_{21}\|_{L^2_{\text{unif}}} &\leq \left\| [\eta_R, \Delta] \frac{1}{z - H_0} Y_m * (1_{B_{3R}\setminus B_{R/2}} f) \right\|_{\mathcal{B}} \\
&\leq \left\| ((\Delta\eta_R) + 2(\nabla\eta_R)\cdot\nabla) \frac{1}{z - H_0} \right\|_{\mathcal{B}} \left\| Y_m * \left(1_{B_{3R}\setminus B_{R/2}} f \right) \right\|_{L^\infty} \\
&\leq \frac{C}{R} \left\| 1_{B_{3R}\setminus B_{R/2}} f \right\|_{L^2_{\text{unif}}} . \qquad (3.60)
\end{aligned}$$

As to r_{22}, it is actually in $L^2(\mathbb{R}^d)$ and

$$\begin{aligned}
\|r_{22}\|_{L^2_{\text{unif}}} \leq \|r_{22}\|_{L^2} &\leq \left\| (-\Delta + 1)^{-\frac{1}{2}} [\eta_R, \Delta] \frac{1}{z - H_0} Y_m * (1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{R/2}} f) \right\|_{\mathfrak{S}_2} \\
&\leq \frac{C}{R} \left(e^{-C'R} \|f\|_{L^2_{\text{unif}}} + \left\| 1_{B_{3R}\setminus B_{R/2}} f \right\|_{L^2_{\text{unif}}} \right) . \qquad (3.61)
\end{aligned}$$

The proof of (3.61) is exactly the same than the proof of (3.57), except that in (3.54), we use the inequality $\|Y_m * f\|_{L^\infty} \leq C \|f\|_{L^2_{\text{unif}}}$ instead of the inequality $\|Y_m * f\|_{H^1} \leq C \|f\|_{H^{-1}}$. This concludes the proof of the lemma. □

We pass now to the proof of Lemma 3.3.5.

Proof of Lemma 3.3.5. To prove (3.30), we denote by $y_n = x_{\alpha^n}$ and $b_n = C\alpha^{-n} e^{-C'\alpha^n}$ for $n \in \mathbb{N}$ and $\alpha \geq \alpha_0 = \max\{a, 2\}$. By the assumption (3.29), (x_R) is non-increasing. Thus $x_{\alpha^n/a} \leq x_{\alpha^{n-1}} = y_{n-1}$, and we have

$$y_n \leq b_n x_0 + \frac{C}{\alpha^n} x_{\alpha^n/a} \leq b_n x_0 + \frac{C}{\alpha^n} y_{n-1}.$$

We first study the sequence z_n defined by the induction relation

$$z_n = \frac{C}{\alpha^n} z_{n-1}, \quad z_0 > 0.$$

We have

$$z_n = \frac{C}{\alpha^n} \frac{C}{\alpha^{n-1}} \cdots \frac{C}{\alpha} z_0 = \frac{C^n}{\alpha^{n(n+1)/2}} z_0.$$

We then show that $y_n \leq C z_n$. Indeed, we have

$$y_n \leq b_n x_0 + \frac{z_n}{z_{n-1}} y_{n-1}.$$

Thus

$$\frac{y_n}{z_n} \leq \frac{b_n}{z_n} x_0 + \frac{y_{n-1}}{z_{n-1}} \leq \sum_{i=1}^{n} \frac{b_i}{z_i} x_0 + \frac{y_0}{z_0}.$$

As the series of general term

$$\frac{b_n}{z_n} = \frac{C\alpha^{-n}e^{-C'\alpha^n}}{C^n\alpha^{-\frac{n(n+1)}{2}}} \sim e^{-C'\alpha^n+\frac{n^2}{2}\log\alpha+C''n}$$

is convergent, then

$$y_n \leq Cz_n\left(x_0+y_0\right) \leq Cz_nx_0,$$

where the constant C is continuous as a function of the parameter α. We now go back to x_R and deduce that for any $n \in \mathbb{N}\setminus 0$ and $R=\alpha^n$, we have

$$x_R \leq Ce^{-C'\frac{\log(R)^2}{\log(\alpha)}+C''\frac{\log(R)}{\log(\alpha)}}x_0 \leq Ce^{-C'\frac{\log(R)^2}{\log(\alpha)}}x_0. \tag{3.62}$$

As (3.62) holds true for any $\alpha \in \left[\alpha_0,\alpha_0^2\right]$, we deduce that there exists $C \geq 0$ independent of α, but depending in general on a, such that for any $R \geq 2$,

$$x_R \leq Ce^{-C'\log(R)^2}x_0,$$

which concludes the proof of the lemma.

□

3.4 Proof of Theorem 3.2.1 (Existence of ground states)

Let us now establish the existence of a ground state for the perturbed crystal in the rHF framework. The proof of Theorem 3.2.1 is a consequence of our results on the operator $\mathcal{L}$ stated in the last section, and of the properties of the higher-order term in the expansion of Q_f for a charge distribution $f \in L^2_{\mathrm{unif}}\left(\mathbb{R}^d\right)$.

To solve the self-consistent equation (3.11), we first formulate the system in terms of the response electronic density $\rho=\rho_\gamma-\rho_{\gamma_0}$ as follow

$$\begin{cases} \rho = \rho_Q \\ Q = 1_{H_0+V_\nu\leq 0}-1_{H_0\leq 0} \\ -\Delta V_\nu + m^2V_\nu = \left|S^{d-1}\right|(\rho-\nu). \end{cases} \tag{3.63}$$

Indeed, if ρ is solution of (3.63), then $\gamma = 1\left(H_0+Y_m*(\rho-\rho_{\gamma_0}-\nu)\leq 0\right)$ solves (3.11). For a charge density $f \in L^2_{\mathrm{unif}}\left(\mathbb{R}^d\right)$, we expand

$$Q_f = 1\left(H_0+Y_m*f\leq 0\right)-1\left(H_0\leq 0\right)$$

as powers of f when f is small. For this purpose, we assume that

$$\mathrm{d}(\mathcal{C},\sigma(H_0)) \geq g,$$

where $g = \mathrm{d}(0, \sigma(H_0))$ and $\mathcal{C}$ is now a smooth curve in the complex plane enclosing the whole spectrum of H_0 below 0 and crossing the real line at 0 and at some point $c < \inf \sigma(H_0) - g$ (see Figure 3.2). Let us recall that for $V \in L^\infty(\mathbb{R}^d)$, $\sigma(H_0 + V) \subset \sigma(H_0) + [-\|V\|_{L^\infty}, \|V\|_{L^\infty}]$. Therefore if $\|V\|_{L^\infty} < g$, then $H_0 + V$ has a gap around 0 and $\sigma(H) \subset [\inf \sigma(H_0) - g, +\infty)$. For such a V, we have using Cauchy's residue formula,

$$Q = 1(H_0 + V \leq 0) - 1(H_0 \leq 0) = \frac{1}{2i\pi} \oint_{\mathcal{C}} \frac{1}{z - H_0 - V} dz - \frac{1}{2i\pi} \oint_{\mathcal{C}} \frac{1}{z - H_0} dz.$$

By the resolvent formula, we obtain

$$\begin{aligned} Q &= \frac{1}{2i\pi} \oint_{\mathcal{C}} \frac{1}{z - H_0} V \frac{1}{z - H_0 - V} dz \\ &= \frac{1}{2i\pi} \oint_{\mathcal{C}} \frac{1}{z - H_0} V \frac{1}{z - H_0} dz + \frac{1}{2i\pi} \oint_{\mathcal{C}} \left(\frac{1}{z - H_0} V \right)^2 \frac{1}{z - H_0 - V} dz. \end{aligned}$$

Therefore for $f \in L^2_{\mathrm{unif}}(\mathbb{R}^d)$ such that $\|f * Y_m\|_{L^\infty} < g$,

$$Q_f = Q_{1,f} + \widetilde{Q}_{2,f}, \tag{3.64}$$

where $Q_{1,f}$ has been defined and studied in Section 3.3 and $\widetilde{Q}_{2,f}$ is defined by

$$\widetilde{Q}_{2,f} = \frac{1}{2i\pi} \oint_{\mathcal{C}} \left(\frac{1}{z - H_0} Y_m * f \right)^2 \frac{1}{z - H_0 - Y_m * f} \, dz.$$

We give some properties of the second order term $\widetilde{Q}_{2,f}$ in Lemma 3.4.1 below. Using the decomposition (3.64), equation (3.63) becomes

$$\rho = \rho_{Q_{1,\rho-\nu}} + \rho_{\widetilde{Q}_{2,\rho-\nu}} = -\mathcal{L}(\rho - \nu) + \rho_{\widetilde{Q}_{2,\rho-\nu}}. \tag{3.65}$$

Following ideas of [64], we recast (3.65) as

$$\rho = \frac{\mathcal{L}}{1 + \mathcal{L}} \nu + \frac{1}{1 + \mathcal{L}} \rho_{\widetilde{Q}_2(\rho-\nu)}. \tag{3.66}$$

In Proposition 3.4.2 below, we show that for ν small enough, the operator $\mathcal{G}_\nu : \rho \mapsto \mathcal{L}(1 + \mathcal{L})^{-1} \nu + (1 + \mathcal{L})^{-1} \rho_{\widetilde{Q}_2(\rho-\nu)}$ admits a fixed point, which is controlled in the L^2_{unif} norm by the nuclear perturbation ν. This will conclude the proof of Theorem 3.2.1.

Lemma 3.4.1 (Properties of the second order term)**.** *There exists $\delta_c > 0$ and $C \geq 0$ such that for any $f \in L^2_{\mathrm{unif}}(\mathbb{R}^d)$ satisfying $\|f\|_{L^2_{\mathrm{unif}}} \leq \delta_c$, the operator $\widetilde{Q}_{2,f}$ is trace class, the density $\rho_{\widetilde{Q}_{2,f}}$ is in $L^2_{\mathrm{unif}}(\mathbb{R}^d)$ and*

$$\left\| \rho_{\widetilde{Q}_{2,f}} \right\|_{L^2_{\mathrm{unif}}} \leq C \|f\|^2_{L^2_{\mathrm{unif}}}.$$

Proof. Since $\|Y_m * f\|_{L^\infty} \leq C_0 \|f\|_{L^2_{\text{unif}}}$ (see (3.25)), we can choose $\delta_c = g/2C_0$, where, we recall that $g = \mathrm{d}(0, \sigma(H_0))$. In this case, $(z - H - Y_m * f)^{-1}(-\Delta + 1)$ and its inverse are uniformly bounded w.r.t $z \in \mathcal{C}$ (see Lemma 3.3.2). Using the exact same procedure as in the proof of (3.23), we obtain that $\widetilde{Q}_{2,f}$ is trace class, $\rho_{\widetilde{Q}_{2,f}} \in L^2_{\text{unif}}(\mathbb{R}^d)$ and

$$\left\|\rho_{\widetilde{Q}_{2,f}}\right\|_{L^2_{\text{unif}}} \leq C \left\| \oint_{\mathcal{C}} Y_m * f \frac{1}{z - H_0} Y_m * f \, dz \right\|_{\mathcal{B}} \leq C \|Y_m * f\|^2_{L^\infty} \leq C \|f\|^2_{L^2_{\text{unif}}},$$

which concludes the proof of the lemma. □

Proposition 3.4.2. *There exists $\alpha_c, \varepsilon > 0$ such that if $\|\nu\|_{L^2_{\text{unif}}} \leq \alpha_c$, then*

$$\begin{array}{rccc} \mathcal{G}_\nu : & B_{L^2_{\text{unif}}}(\varepsilon) & \to & B_{L^2_{\text{unif}}}(\varepsilon) \\ & \rho & \mapsto & \frac{\mathcal{L}}{1+\mathcal{L}}\nu + \frac{1}{1+\mathcal{L}}\rho_{\widetilde{Q}_{2,\rho-\nu}} \end{array}$$

is well-defined and contracting on $B_{L^2_{\text{unif}}}(\varepsilon) = \left\{ f \in L^2_{\text{unif}}(\mathbb{R}^d),\ \|f\|_{L^2_{\text{unif}}} \leq \varepsilon \right\}$. Thus, it admits a unique fixed point ρ in the ball $B_{L^2_{\text{unif}}}(\varepsilon)$. Moreover ρ satisfies

$$\|\rho\|_{L^2_{\text{unif}}} \leq C \|\nu\|_{L^2_{\text{unif}}}, \tag{3.67}$$

for a constant C independent of ν.

Proof. We want to use Lemma 3.4.1 to show that $\mathcal{G}$ is well-defined on a small ball of $L^2_{\text{unif}}(\mathbb{R}^d)$. Here, the charge distribution is $f = \rho - \nu$. We thus need to choose α_c and ε such that $\|\rho - \nu\|_{L^2_{\text{unif}}} \leq \|\rho\|_{L^2_{\text{unif}}} + \|\nu\|_{L^2_{\text{unif}}} \leq \varepsilon + \alpha_c \leq \delta_c$, where δ_c is given by Lemma 3.4.1. Let $A > 0$, $0 < \varepsilon \leq \delta_c/(1 + A)$ and $\alpha_c = A\varepsilon$. Let ν and ρ such that $\|\nu\|_{L^2_{\text{unif}}} \leq \alpha_c$ and $\|\rho\|_{L^2_{\text{unif}}} \leq \varepsilon$. By Lemma 3.4.1 and the fact that $\mathcal{L}$ and $1/(1 + \mathcal{L})$ are bounded on $L^2_{\text{unif}}(\mathbb{R}^d)$ (see Theorem 3.3.1), we have

$$\begin{aligned} \|\mathcal{G}_\nu(\rho)\|_{L^2_{\text{unif}}} &\leq \left\| \frac{\mathcal{L}}{1+\mathcal{L}} \right\|_{\mathcal{B}(L^2_{\text{unif}})} \|\nu\|_{L^2_{\text{unif}}} + \left\| \frac{1}{1+\mathcal{L}} \right\|_{\mathcal{B}(L^2_{\text{unif}})} \left\|\rho_{\widetilde{Q}_{2,\rho-\nu}}\right\|_{L^2_{\text{unif}}} \\ &\leq C_1 \|\nu\|_{L^2_{\text{unif}}} + C_2 \|\rho - \nu\|^2_{L^2_{\text{unif}}} \leq \left(C_1 A + C_2 (1 + A)^2 \varepsilon\right) \varepsilon. \end{aligned} \tag{3.68}$$

We choose $A < 1/C_1$ such that for $\varepsilon \leq (1 - AC_1)/(C_2(1 + A)^2)$, we have

$$\|\mathcal{G}_\nu(\rho)\|_{L^2_{\text{unif}}} \leq \varepsilon.$$

To show that $\mathcal{G}_\nu$ is contracting on $B_{L^2_{\text{unif}}}(\varepsilon)$ for ε small enough, we use the explicit expression of $\widetilde{Q}_{2,\rho-\nu}$. Let $\rho, \rho' \in B_{L^2_{\text{unif}}}(\varepsilon)$ and denote by $H = H_0 +$

$Y_m*(\rho-\nu)$ and $H' = H_0+Y_m*(\rho'-\nu)$. The function $(1+\mathcal{L})\left(\mathcal{G}_\nu(\rho) - \mathcal{G}_\nu(\rho')\right)$ is the density associated with the operator

$$\frac{1}{2i\pi}\oint_{\mathcal{C}}\left(\frac{1}{z-H_0}Y_m*(\rho-\nu)\right)^2\frac{1}{z-H} - \left(\frac{1}{z-H_0}Y_m*(\rho'-\nu)\right)^2\frac{1}{z-H'}\,dz.$$

A straightforward calculation shows that this operator can be written as

$$\begin{aligned}\frac{1}{2i\pi}\oint_{\mathcal{C}}&\left(\frac{1}{z-H_0}Y_m*(\rho-\nu)\right)^2\frac{1}{z-H}Y_m*(\rho-\rho')\frac{1}{z-H'}\\ &+\frac{1}{z-H_0}Y_m*(\rho-\nu)\frac{1}{z-H_0}Y_m*(\rho-\rho')\frac{1}{z-H'}\\ &+\frac{1}{z-H_0}Y_m*(\rho-\rho')\frac{1}{z-H_0}Y_m*(\rho'-\nu)\frac{1}{z-H'}dz. \quad (3.69)\end{aligned}$$

Using the same techniques as before, we deduce that

$$\begin{aligned}\left\|\mathcal{G}_\nu(\rho)-\mathcal{G}_\nu(\rho')\right\|_{L^2_{\mathrm{unif}}} &\leq C\left(\|\rho-\nu\|^2_{L^2_{\mathrm{unif}}}+\|\rho-\nu\|_{L^2_{\mathrm{unif}}}+\left\|\rho'-\nu\right\|_{L^2_{\mathrm{unif}}}\right)\\ &\quad\times\left\|\rho-\rho'\right\|_{L^2_{\mathrm{unif}}}\\ &\leq C_3\left(\|\rho\|_{L^2_{\mathrm{unif}}}+\left\|\rho'\right\|_{L^2_{\mathrm{unif}}}+\|\nu\|_{L^2_{\mathrm{unif}}}\right)\left\|\rho-\rho'\right\|_{L^2_{\mathrm{unif}}}\\ &\leq C_3\,(2+A)\,\varepsilon\left\|\rho-\rho'\right\|_{L^2_{\mathrm{unif}}}.\end{aligned}$$

Taking, in addition, $\varepsilon < 1/(C_3(2+A))$, we have that $\mathcal{G}_\nu$ is contracting on $B_{L^2_{\mathrm{unif}}}(\varepsilon)$. Let ρ be the unique fixed point of $\mathcal{G}_\nu$ in $B_{L^2_{\mathrm{unif}}}(\varepsilon)$. It remains to prove (3.67). By (3.68), we have

$$\|\rho\|_{L^2_{\mathrm{unif}}} = \|\mathcal{G}_\nu(\rho)\|_{L^2_{\mathrm{unif}}} \leq C_1\|\nu\|_{L^2_{\mathrm{unif}}} + C_2(1+A)\varepsilon\left(\|\rho\|_{L^2_{\mathrm{unif}}}+\|\nu\|_{L^2_{\mathrm{unif}}}\right).$$

Therefore

$$(1-C_2(1+A)\varepsilon)\,\|\rho\|_{L^2_{\mathrm{unif}}} \leq (C_1+C_2(1+A)\varepsilon)\,\|\nu\|_{L^2_{\mathrm{unif}}}.$$

Using that $\varepsilon \leq (1-AC_1)\,/\left(C_2(1+A)^2\right)$, we have $1-C_2(1+A)\varepsilon > 0$ and we deduce that

$$\|\rho\|_{L^2_{\mathrm{unif}}} \leq \frac{C_1+C_2(1+A)\varepsilon}{1-C_2(1+A)\varepsilon}\,\|\nu\|_{L^2_{\mathrm{unif}}} \leq \frac{1}{A}\,\|\nu\|_{L^2_{\mathrm{unif}}},$$

which concludes the proof of the proposition. □

3.5 Proofs of Theorem 3.2.3 and Proposition 3.2.5 (Decay estimates)

We present in this section the proofs of Theorem 3.2.3 and Proposition 3.2.5. They consist in decay estimates of the mean-field potential V_ν and the mean-field density ρ_ν. These estimates are used later on in the proofs of Theorems 3.2.2 and 3.2.7.

3.5.1 Proof of Theorem 3.2.3

Proof of Theorem 3.2.3. Assume that $\|\nu\|_{L^2_{\text{unif}}} \leq \alpha_c$, where α_c is given in Theorem 3.2.1. We use the notation ρ to denote the mean-field density $\rho_\nu = \rho_{\gamma_\nu - \gamma_0}$, the solution of (3.66), and denote by $V = V_\nu = Y_m * (\rho - \nu)$. Recall the decomposition (3.65) of ρ in a linear term and a higher order term

$$\rho = -\mathcal{L}(\rho - \nu) + \rho_{\widetilde{Q}_{2,\rho-\nu}}.$$

Using localizing functions, we will show that ρ decays far from the support of ν. To do so, let us introduce the set $I = \left\{k \in \mathbb{Z}^d,\ \text{supp}(\nu) \cap B(0,1) + k \neq \emptyset\right\}$ and for $R \geq 1$, the set $B_R = B_{I,R} = \cup_{k\in I}(B(0,R) + k)$ and the the function $\chi_R = \chi_{I,R}$ defined in Lemma 3.3.4. They satisfy $0 \leq \chi_R \leq 1$, $\chi_R \equiv 1$ on B_R, $\chi_R \equiv 0$ outside B_{2R} and $R|\nabla\chi_R(x)| + R^2|\Delta\chi_R(x)| \leq C$ for a constant $C \geq 0$ independent of the set I (thus independent of ν). We denote by $\eta_R = 1 - \chi_R$. We thus have

$$\eta_R\rho = -\eta_R\mathcal{L}(\rho - \nu) + \eta_R\rho_{\widetilde{Q}_{2,\rho-\nu}} = -\mathcal{L}\eta_R(\rho - \nu) + [\mathcal{L}, \eta_R](\rho - \nu) + \eta_R\rho_{\widetilde{Q}_{2,\rho-\nu}}.$$

As for $R \geq 1$, $\eta_R\nu = 0$, it follows

$$\eta_R\rho = \frac{1}{(1+\mathcal{L})}[\mathcal{L}, \eta_R](\rho - \nu) + \frac{1}{(1+\mathcal{L})}\eta_R\rho_{\widetilde{Q}_{2,\rho-\nu}}. \tag{3.70}$$

We will successively bound each term of the RHS of (3.70). For the first term, we have by Lemma 3.3.4 for $R \geq 2$,

$$\begin{aligned}\|[\mathcal{L}, \eta_R](\rho - \nu)\|_{L^2_{\text{unif}}} &\leq \frac{C}{R}\left(e^{-C'R}\|\rho - \nu\|_{L^2_{\text{unif}}} + \left\|1_{B_{3R}\setminus B_{R/2}}(\rho - \nu)\right\|_{L^2_{\text{unif}}}\right)\\ &\leq \frac{C}{R}\left(e^{-C'R}\|\nu\|_{L^2_{\text{unif}}} + \left\|1_{B_{3R}\setminus B_{R/2}}\rho\right\|_{L^2_{\text{unif}}}\right),\end{aligned}$$

where we have used that $1_{B_{3R}\setminus B_{R/2}}\nu = 0$ for $R \geq 2$ and that ρ is controlled by ν in the L^2_{unif} norm. As that $1/(1+\mathcal{L})$ is bounded on $L^2_{\text{unif}}(\mathbb{R}^d)$, we obtain

$$\left\|\frac{1}{(1+\mathcal{L})}[\mathcal{L}, \eta_R](\rho - \nu)\right\|_{L^2_{\text{unif}}} \leq \frac{C}{R}e^{-C'R}\|\nu\|_{L^2_{\text{unif}}} + \frac{C}{R}\left\|1_{B_{3R}\setminus B_{R/2}}\rho\right\|_{L^2_{\text{unif}}}. \tag{3.71}$$

As to the second term of the RHS of (3.70), since $1_{\mathbb{R}^d\setminus B_R}\eta_R = \eta_R$, we have

$$\begin{aligned}
\eta_R\widetilde{Q}_{2,\rho-\nu} &= \frac{1}{2i\pi}\oint_{\mathcal{C}} \eta_R \frac{1}{z-H_0}V\frac{1}{z-H_0}V\frac{1}{z-H}dz \\
&= \frac{1}{2i\pi}\oint_{\mathcal{C}} \frac{1}{z-H_0}\eta_R V\frac{1}{z-H_0}V\frac{1}{z-H} \\
&\quad + \left[\eta_R, \frac{1}{z-H_0}\right]V\frac{1}{z-H_0}V\frac{1}{z-H}dz \\
&= \frac{1}{2i\pi}\oint_{\mathcal{C}} \frac{1}{z-H_0}1_{\mathbb{R}^d\setminus B_R}V\frac{1}{z-H_0}\eta_R V\frac{1}{z-H}dz \\
&\quad + \frac{1}{2i\pi}\oint_{\mathcal{C}} \frac{1}{z-H_0}1_{\mathbb{R}^d\setminus B_R}V\left[\eta_R, \frac{1}{z-H_0}\right]V\frac{1}{z-H}dz \\
&\quad + \frac{1}{2i\pi}\oint_{\mathcal{C}} \left[\eta_R, \frac{1}{z-H_0}\right]V\frac{1}{z-H_0}V\frac{1}{z-H}dz, \qquad (3.72)
\end{aligned}$$

where $H = H_0 + V$ and $\mathcal{C}$ is as in the previous section. We recall that by the assumption $\|\nu\|_{L^2_{\mathrm{unif}}} \leq \alpha_c$, the operator H has a gap around 0, thus the operator $(z-H)^{-1}(-\Delta+1)$ and its inverse are uniformly bounded on $\mathcal{C}$ and all the estimates obtained in the previous sections hold when we replace H_0 by H. We denote by r_3, r_4 and r_5 the densities associated with the three operators of the RHS of (3.72) respectively. Using an inequality similar to (3.23), involving H instead of H_0 in the resolvent in the right, we have

$$\|r_3\|_{L^2_{\mathrm{unif}}} \leq C\int_{\mathcal{C}}\left\|1_{\mathbb{R}^d\setminus B_R}V\frac{1}{z-H_0}V\eta_R\right\|_{\mathcal{B}}dz \leq C\left\|V1_{\mathbb{R}^d\setminus B_R}\right\|_{L^\infty}\|V\eta_R\|_{L^\infty}.$$

By (3.28) in Lemma 3.3.4, and using that $\|Y_m * f\|_{H^2_{\mathrm{unif}}} = \|f\|_{L^2_{\mathrm{unif}}}$, we have that for $R \geq 2$

$$\begin{aligned}
\|\eta_R V\|_{H^2_{\mathrm{unif}}} &\leq \|Y_m * (\eta_R(\rho-\nu))\|_{L^2_{\mathrm{unif}}} \\
&\quad + \frac{C}{R}\left(e^{-C'R}\|\nu\|_{L^2_{\mathrm{unif}}} + \left\|1_{B_{3R}\setminus B_{R/2}}\rho\right\|_{L^2_{\mathrm{unif}}}\right). \qquad (3.73)
\end{aligned}$$

Therefore

$$\begin{aligned}
\|r_3\|_{L^2_{\mathrm{unif}}} &\leq \left\|1_{\mathbb{R}^d\setminus B_R}V\right\|_{L^\infty}\Big(C\|Y_m * (\eta_R\rho)\|_{H^2_{\mathrm{unif}}} + \frac{C}{R}e^{-C'R}\|\nu\|_{L^2_{\mathrm{unif}}} \\
&\qquad + \frac{C}{R}\left\|1_{B_{3R}\setminus B_{R/2}}\rho\right\|_{L^2_{\mathrm{unif}}}\Big) \\
&\leq C\left\|1_{\mathbb{R}^d\setminus B_R}V\right\|_{L^\infty}\Big(C\|\eta_R\rho\|_{L^2_{\mathrm{unif}}} + \frac{C}{R}e^{-C'R}\|\nu\|_{L^2_{\mathrm{unif}}} \\
&\qquad + \frac{C}{R}\left\|1_{B_{3R}\setminus B_{R/2}}\rho\right\|_{L^2_{\mathrm{unif}}}\Big).
\end{aligned}$$

To bound r_4 and r_5, we recall that we have shown in the proof of (3.28) (see (3.60) and (3.61)) that for any $f \in L^2_{\text{unif}}(\mathbb{R}^d)$

$$\begin{aligned}\left\|(-\Delta+1)^{-\frac{1}{2}}\left[\eta_R,\Delta\right]\frac{1}{z-H_0}Y_m * \left(1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{2R}}f\right)\right\|_{\mathfrak{S}_2} \\ + \left\|\left[\eta_R,\Delta\right]\frac{1}{z-H_0}Y_m * \left(1_{B_{3R}\setminus B_{2R}}f\right)\right\|_{\mathcal{B}} \\ \leq \frac{C}{R}\left(e^{-C'R}\left\|f\right\|_{L^2_{\text{unif}}} + \left\|1_{B_{3R}\setminus B_{R/2}}f\right\|_{L^2_{\text{unif}}}\right).\end{aligned}$$

Therefore, using again the equality $\left[\eta_R,(z-H_0)^{-1}\right] = -(z-H_0)^{-1}\left[\eta_R,\Delta\right](z-H_0)^{-1}$, and an inequality similar to (3.23), we obtain that for any $R \geq 2$,

$$\begin{aligned}\left\|r_4\right\|_{L^2_{\text{unif}}} &\leq C\oint_{\mathcal{C}}\left\|1_{\mathbb{R}^d\setminus B_R}V\right\|_{L^\infty}\left\|\frac{1}{z-H_0}\left[\eta_R,\Delta\right]\frac{1}{z-H_0}V\right\|_{\mathcal{B}}dz \\ &\leq \frac{C}{R}\left\|1_{\mathbb{R}^d\setminus B_R}V\right\|_{L^\infty}\left(e^{-C'R}\left\|\nu\right\|_{L^2_{\text{unif}}} + \left\|1_{B_{3R}\setminus B_{R/2}}\rho\right\|_{L^2_{\text{unif}}}\right).\end{aligned} \tag{3.74}$$

The last term of the RHS of (3.72) can be written $Q_{\text{in}} + Q_{\text{out}}$, where

$$Q_{\text{in}} = \frac{1}{2i\pi}\oint_{\mathcal{C}}\left[\eta_R,\frac{1}{z-H_0}\right]Y_m * \left(1_{B_{3R}\setminus B_{2R}}\left(\rho-\nu\right)\right)\frac{1}{z-H_0}V\frac{1}{z-H}dz.$$

In the same way we obtained (3.74), we get

$$\begin{aligned}\left\|\rho_{Q_{\text{in}}}\right\|_{L^2_{\text{unif}}} &\leq C\oint_{\mathcal{C}}\left\|\left[\eta_R,\Delta\right]\frac{1}{z-H_0}Y_m * \left(1_{B_{3R}\setminus B_{2R}}\left(\rho-\nu\right)\right)\right\|_{\mathcal{B}}\left\|\frac{1}{z-H_0}V\right\|_{\mathcal{B}}dz \\ &\leq \frac{C}{R}\left\|V\right\|_{L^\infty}\left(e^{-C'R}\left\|\nu\right\|_{L^2_{\text{unif}}} + \left\|1_{B_{3R}\setminus B_{R/2}}\rho\right\|_{L^2_{\text{unif}}}\right).\end{aligned}$$

To estimate $\rho_{Q_{\text{out}}}$, we recall that by (3.49), we have that for any $A \in \mathfrak{S}_2(L^2(\mathbb{R}^d))$

$$\left\|\rho_{(-\Delta+1)^{-\frac{1}{2}}A(-\Delta+1)^{-\frac{1}{2}}}\right\|_{L^2} \leq C\left\|A\right\|_{\mathfrak{S}_2}.$$

Therefore

$$\begin{aligned}\left\|\rho_{Q_{\text{out}}}\right\|_{L^2_{\text{unif}}} &\leq C\oint_{\mathcal{C}}\left\|(-\Delta+1)^{-\frac{1}{2}}\left[\eta_R,\Delta\right]\frac{1}{z-H_0}Y_m * \left(1_{(\mathbb{R}^d\setminus B_{3R})\cup B_{2R}}\left(\rho-\nu\right)\right)\right\|_{\mathfrak{S}_2} \\ &\quad\times\left\|\frac{1}{z-H_0}V(1-\Delta)^{-\frac{1}{2}}\right\|_{\mathcal{B}}dz \\ &\leq \frac{C}{R}\left\|V\right\|_{L^\infty}\left(e^{-C'R}\left\|\nu\right\|_{L^2_{\text{unif}}} + \left\|1_{B_{3R}\setminus B_{R/2}}\rho\right\|_{L^2_{\text{unif}}}\right).\end{aligned}$$

Now that we have found estimates on r_3, r_4 and $r_5 = \rho_{Q_{\text{in}}} + \rho_{Q_{\text{out}}}$, we use that

$$\left\| 1_{\mathbb{R}^d \setminus B_R} V \right\|_{L^\infty} \leq \|V\|_{L^\infty} \leq C \|\rho - \nu\|_{L^2_{\text{unif}}} \leq C \|\nu\|_{L^2_{\text{unif}}} \leq C\alpha_c,$$

to estimate $\eta_R \rho_{\widetilde{Q}_{2,\rho-\nu}}$ as follow

$$\left\| \eta_R \rho_{\widetilde{Q}_{2,\rho-\nu}} \right\|_{L^2_{\text{unif}}} \leq C\alpha_c \|\eta_R \rho\|_{L^2_{\text{unif}}} + \frac{C}{R} e^{-C'R} \|\nu\|_{L^2_{\text{unif}}} + \frac{C}{R} \left\| 1_{B_{3R} \setminus B_{R/2}} \rho \right\|_{L^2_{\text{unif}}}. \tag{3.75}$$

Using once more that $1/(1+\mathcal{L})$ is bounded on $L^2_{\text{unif}}(\mathbb{R}^d)$, we deduce the following bound on the second term of the RHS of (3.70)

$$\begin{aligned} \left\| \frac{1}{1+\mathcal{L}} \eta_R \rho_{\widetilde{Q}_{2,\rho-\nu}} \right\|_{L^2_{\text{unif}}} &\leq C_0 \alpha_c \|\eta_R \rho\|_{L^2_{\text{unif}}} + \frac{C}{R} e^{-C'R} \|\nu\|_{L^2_{\text{unif}}} \\ &\quad + \frac{C}{R} \left\| 1_{B_{3R} \setminus B_{R/2}} \rho \right\|_{L^2_{\text{unif}}}. \end{aligned} \tag{3.76}$$

Gathering (3.70), (3.71) and (3.76), we obtain

$$\|\eta_R \rho\|_{L^2_{\text{unif}}} \leq C_0 \alpha_c \|\eta_R \rho\|_{L^2_{\text{unif}}} + \frac{C}{R} e^{-C'R} \|\nu\|_{L^2_{\text{unif}}} + \frac{C}{R} \left\| 1_{B_{3R} \setminus B_{R/2}} \rho \right\|_{L^2_{\text{unif}}}.$$

We choose $\alpha_c' \leq \min\{1/(2C_0), \alpha_c\}$, where C_0 is defined in (3.76), and assume that $\|\nu\|_{L^2_{\text{unif}}} \leq \alpha_c'$. It follows

$$\|\eta_R \rho\|_{L^2_{\text{unif}}} \leq \frac{C}{R} e^{-C'R} \|\nu\|_{L^2_{\text{unif}}} + \frac{C}{R} \left\| 1_{B_{3R} \setminus B_{R/2}} \rho \right\|_{L^2_{\text{unif}}}.$$

We have a similar inequality for V. Indeed, by (3.73), we have

$$\begin{aligned} \|\eta_R V\|_{H^2_{\text{unif}}} &\leq \|Y_m * (\eta_R (\rho - \nu))\|_{H^2_{\text{unif}}} + \frac{C}{R} e^{-C'R} \|\rho - \nu\|_{L^2_{\text{unif}}} \\ &\quad + \frac{C}{R} \left\| 1_{B_{3R} \setminus B_{R/2}} (\rho - \nu) \right\|_{L^2_{\text{unif}}} \\ &\leq \|\eta_R \rho\|_{L^2_{\text{unif}}} + \frac{C}{R} e^{-C'R} \|\nu\|_{L^2_{\text{unif}}} + \frac{C}{R} \left\| 1_{B_{3R} \setminus B_{R/2}} \rho \right\|_{L^2_{\text{unif}}} \\ &\leq \frac{C}{R} e^{-C'R} \|\nu\|_{L^2_{\text{unif}}} + \frac{C}{R} \left\| 1_{B_{3R} \setminus B_{R/2}} \rho \right\|_{L^2_{\text{unif}}}. \end{aligned} \tag{3.77}$$

Using Lemma 3.3.5 with x_R to $\left\| 1_{\mathbb{R}^d \setminus B_R} \rho \right\|_{L^2_{\text{unif}}}$, we obtain

$$\|\eta_R \rho\|_{L^2_{\text{unif}}} \leq C e^{-C'(\log R)^2} \|\nu\|_{L^2_{\text{unif}}}. \tag{3.78}$$

Inserting (3.78) in (3.77), we get

$$\|\eta_R V\|_{H^2_{\mathrm{unif}}} \leq Ce^{-C'(\log R)^2} \|\nu\|_{L^2_{\mathrm{unif}}} .$$

Finally, noticing that $1_{\mathbb{R}^d \setminus C_R(\nu)} \leq \eta_{R/2}$, we conclude the proof of (3.13). □

We now turn to the

3.5.2 Proof of Proposition 3.2.5

Proof of Proposition 3.2.5. Assume that $\|\nu\|_{L^2_{\mathrm{unif}}} \leq \alpha_c$, where α_c is given in Theorem 3.2.1. As ρ_ν and ρ_{ν_L} are fixed points of the functionals $\mathcal{G}_\nu$ and $\mathcal{G}_{\nu_L}$ respectively, then

$$\rho_\nu - \rho_{\nu_L} = \frac{\mathcal{L}}{1+\mathcal{L}}(\nu - \nu_L) + \frac{1}{1+\mathcal{L}}\rho_{\widetilde{Q_2}(\rho_\nu - \nu) - \widetilde{Q_2}(\rho_{\nu_L} - \nu_L)}.$$

For $R \geq 1$, let $\chi_R = \chi_{\{0\},R}$ and $B_R = B_{\{0\},R}$ as defined in Lemma 3.3.4. Since $1_{B_R} \leq \chi_R$, then

$$\begin{aligned}\|1_{B_R}(\rho_\nu - \rho_{\nu_L})\|_{L^2_{\mathrm{unif}}} &\leq \|\chi_R(\rho_\nu - \rho_{\nu_L})\|_{L^2_{\mathrm{unif}}} \\ &\leq \left\| \chi_R \frac{1}{1+\mathcal{L}} \left(\mathcal{L}(\nu - \nu_L) + \rho_{\widetilde{Q_2}(\rho_\nu - \nu) - \widetilde{Q_2}(\rho_{\nu_L} - \nu_L)} \right) \right\|_{L^2_{\mathrm{unif}}} .\end{aligned}$$

Besides, there exists $C \geq 0$ such that for any $f \in L^2_{\mathrm{unif}}(\mathbb{R}^d)$ and any $R \geq 1$,

$$\left\| \left[\chi_R, \frac{1}{1+\mathcal{L}} \right] f \right\|_{L^2_{\mathrm{unif}}} \leq \frac{C}{R} \left(e^{-C'R} \|f\|_{L^2_{\mathrm{unif}}} + \left\| 1_{B_{3R}} \frac{1}{1+\mathcal{L}} f \right\|_{L^2_{\mathrm{unif}}} \right). \tag{3.79}$$

Indeed, using that $1/(1+\mathcal{L})$ is bounded on $L^2_{\mathrm{unif}}(\mathbb{R}^d)$ and estimate (3.28) in Lemma 3.3.4 (notice that $\mathcal{L}\chi_R - \chi_R\mathcal{L} = \eta_R\mathcal{L} - \mathcal{L}\eta_R$), we obtain

$$\begin{aligned}\left\| \left[\chi_R, \frac{1}{1+\mathcal{L}} \right] f \right\|_{L^2_{\mathrm{unif}}} &= \left\| \frac{1}{1+\mathcal{L}} [\mathcal{L}, \chi_R] \frac{1}{1+\mathcal{L}} f \right\|_{L^2_{\mathrm{unif}}} \\ &\leq C \left\| [\mathcal{L}, \chi_R] \frac{1}{1+\mathcal{L}} f \right\|_{L^2_{\mathrm{unif}}} \\ &\leq \frac{C}{R} \left(e^{-C'R} \left\| \frac{1}{1+\mathcal{L}} f \right\|_{L^2_{\mathrm{unif}}} + \left\| 1_{B_{3R} \setminus B_{R/2}} \frac{1}{1+\mathcal{L}} f \right\|_{L^2_{\mathrm{unif}}} \right) \\ &\leq \frac{C}{R} \left(e^{-C'R} \|f\|_{L^2_{\mathrm{unif}}} + \left\| 1_{B_{3R} \setminus B_{R/2}} \frac{1}{1+\mathcal{L}} f \right\|_{L^2_{\mathrm{unif}}} \right).\end{aligned}$$

Using (3.79) for $f = \mathcal{L}(\nu - \nu_L) + \rho_{\widetilde{Q_2}(\rho_\nu - \nu) - \widetilde{Q_2}(\rho_{\nu_L} - \nu_L)}$, we have

$$\begin{aligned}\|\chi_R(\rho_\nu - \rho_{\nu_L})\|_{L^2_{\text{unif}}} \leq & \left\| \frac{1}{1+\mathcal{L}} \chi_R \mathcal{L}(\nu - \nu_L) \right\|_{L^2_{\text{unif}}} \\ & + \left\| \frac{1}{1+\mathcal{L}} \chi_R \rho_{\widetilde{Q_2}(\rho_\nu - \nu) - \widetilde{Q_2}(\rho_{\nu_L} - \nu_L)} \right\|_{L^2_{\text{unif}}} \\ & + \frac{C}{R} e^{-C'R} \|\nu\|_{L^2_{\text{unif}}} + \frac{C}{R} \|1_{B_{3R}}(\rho_\nu - \rho_{\nu_L})\|_{L^2_{\text{unif}}} . \end{aligned} \tag{3.80}$$

We first bound the first term of the RHS of (3.80). Using (3.28) in Lemma 3.3.4 and that for $R \leq L/4$ it holds that $\chi_R(\nu - \nu_L) = 0$, we have for $R \leq L/4$

$$\begin{aligned}\left\| \frac{1}{1+\mathcal{L}} \chi_R \mathcal{L}(\nu - \nu_L) \right\|_{L^2_{\text{unif}}} & \leq C \|\chi_R \mathcal{L}(\nu - \nu_L)\|_{L^2_{\text{unif}}} \\ & \leq C \|\chi_R(\nu - \nu_L)\|_{L^2_{\text{unif}}} + \frac{C}{R} e^{-C'R} \|\nu\|_{L^2_{\text{unif}}} + \frac{C}{R} \|1_{B_{3R}}(\nu - \nu_L)\|_{L^2_{\text{unif}}} \\ & \leq \frac{C}{R} e^{-C'R} \|\nu\|_{L^2_{\text{unif}}} + \frac{C}{R} \|1_{B_{3R}}(\nu - \nu_L)\|_{L^2_{\text{unif}}} . \end{aligned} \tag{3.81}$$

To estimate the second term of the RHS of (3.80), we denote by $H_\infty = H_0 + Y_m * (\rho_\nu - \nu)$, $H_L = H_0 + Y_m * (\rho_{\nu_L} - \nu_L)$ and $f_L = \rho_\nu - \rho_{\nu_L} - \nu + \nu_L$. A straightforward calculation shows that

$$\widetilde{Q_2}(\rho_\nu - \nu) - \widetilde{Q_2}(\rho_{\nu_L} - \nu_L) = R_1(f_L) + R_2(f_L) + R_3(f_L), \tag{3.82}$$

where

$$R_1(f) = \frac{1}{2i\pi} \oint_{\mathcal{C}} \frac{1}{z - H_0} Y_m * f \frac{1}{z - H_0} Y_m * (\rho_\nu - \nu) \frac{1}{z - H_\infty} dz$$

$$R_2(f) = \oint_{\mathcal{C}} \frac{1}{z - H_0} Y_m * (\rho_{\nu_L} - \nu_L) \frac{1}{z - H_0} Y_m * f \frac{1}{z - H_\infty} dz$$

and

$$R_3(f) = \frac{1}{z - H_0} Y_m * (\rho_{\nu_L} - \nu_L) \frac{1}{z - H_0} Y_m * (\rho_{\nu_L} - \nu_L) \frac{1}{z - H_\infty} Y_m * f \frac{1}{z - H_L} dz.$$

We bound the densities of the three operators of the RHS of (3.82) separately. We detail the proof for $\rho_{R_1(f_L)}$; the other terms are treated in the same way.

For $R \geq 1$, we have

$$\begin{aligned}
&\chi_R \frac{1}{z-H_0} Y_m * f_L \frac{1}{z-H_0} Y_m * (\rho_\nu - \nu) \frac{1}{z-H_\infty} \\
&\quad = \frac{1}{z-H_0} \chi_R Y_m * f_L \frac{1}{z-H_0} Y_m * (\rho_\nu - \nu) \frac{1}{z-H_\infty} \\
&\qquad + \left[\chi_R, \frac{1}{z-H_0} \right] Y_m * f_L \frac{1}{z-H_0} Y_m * (\rho_\nu - \nu) \frac{1}{z-H_\infty} \\
&\quad = \frac{1}{z-H_0} Y_m * (\chi_R f_L) \frac{1}{z-H_0} Y_m * (\rho_\nu - \nu) \frac{1}{z-H_\infty} \\
&\qquad + \frac{1}{z-H_0} \left(\chi_R Y_m * f_L - Y_m * (\chi_R f_L) \right) \frac{1}{z-H_0} Y_m * (\rho_\nu - \nu) \frac{1}{z-H_\infty} \\
&\qquad + \left[\chi_R, \frac{1}{z-H_0} \right] Y_m * f_L \frac{1}{z-H_0} Y_m * (\rho_\nu - \nu) \frac{1}{z-H_\infty}.
\end{aligned}$$

Therefore, using (3.28) and reasoning as in the proof of (3.75), we find for $R \leq L/4$,

$$\begin{aligned}
\left\| \chi_R \rho_{R_1(f_L)} \right\|_{L^2_{\mathrm{unif}}} &\leq C \left\| \chi_R f_L \right\|_{L^2_{\mathrm{unif}}} \left\| \rho_\nu - \nu \right\|_{L^2_{\mathrm{unif}}} \\
&\quad + \left\| \chi_R Y_m * f_L - Y_m * (\chi_R f_L) \right\|_{L^2_{\mathrm{unif}}} \left\| \rho_\nu - \nu \right\|_{L^2_{\mathrm{unif}}} \\
&\quad + \frac{C}{R} \left(e^{-C'R} \left\| f_L \right\|_{L^2_{\mathrm{unif}}} + \left\| 1_{B_{3R}} f_L \right\|_{L^2_{\mathrm{unif}}} \right) \left\| \rho_\nu - \nu \right\|_{L^2_{\mathrm{unif}}} \\
&\leq C \left\| \nu \right\|_{L^2_{\mathrm{unif}}} \left(\left\| \chi_R (\rho_\nu - \rho_{\nu_L}) \right\|_{L^2_{\mathrm{unif}}} + \frac{C}{R} e^{-C'R} \left\| \nu \right\|_{L^2_{\mathrm{unif}}} + \frac{C}{R} \left\| 1_{B_{3R}} f_L \right\|_{L^2_{\mathrm{unif}}} \right).
\end{aligned}$$

Similarly, we obtain

$$\begin{aligned}
\left\| \chi_R \rho_{R_2(f_L)} \right\|_{L^2_{\mathrm{unif}}} &\leq C \left\| \nu \right\|_{L^2_{\mathrm{unif}}} \\
&\quad \times \left(\left\| \chi_R (\rho_\nu - \rho_{\nu_L}) \right\|_{L^2_{\mathrm{unif}}} + \frac{C}{R} e^{-C'R} \left\| \nu \right\|_{L^2_{\mathrm{unif}}} + \frac{C}{R} \left\| 1_{B_{3R}} f_L \right\|_{L^2_{\mathrm{unif}}} \right)
\end{aligned}$$

and

$$\begin{aligned}
\left\| \chi_R \rho_{R_3(f_L)} \right\|_{L^2_{\mathrm{unif}}} &\leq C \left\| \nu \right\|^2_{L^2_{\mathrm{unif}}} \\
&\quad \times \left(\left\| \chi_R (\rho_\nu - \rho_{\nu_L}) \right\|_{L^2_{\mathrm{unif}}} + \frac{C}{R} e^{-C'R} \left\| \nu \right\|_{L^2_{\mathrm{unif}}} + \frac{C}{R} \left\| 1_{B_{3R}} f_L \right\|_{L^2_{\mathrm{unif}}} \right).
\end{aligned}$$

It follows that the second term of the RHS of (3.80) is bounded by

$$\begin{aligned}
\left\| \frac{1}{1+\mathcal{L}} \chi_R \rho_{\widetilde{Q}_2(\rho_\nu - \nu) - \widetilde{Q}_2(\rho_{\nu_L} - \nu_L)} \right\|_{L^2_{\mathrm{unif}}} &\leq C_0 \left(\left\| \nu \right\|_{L^2_{\mathrm{unif}}} + \left\| \nu \right\|^2_{L^2_{\mathrm{unif}}} \right) \\
&\quad \times \left(\left\| \chi_R (\rho_\nu - \rho_{\nu_L}) \right\|_{L^2_{\mathrm{unif}}} + \frac{C}{R} e^{-C'R} \left\| \nu \right\|_{L^2_{\mathrm{unif}}} + \frac{C}{R} \left\| 1_{B_{3R}} f_L \right\|_{L^2_{\mathrm{unif}}} \right).
\end{aligned}$$

We choose $\alpha_c' \leq \alpha_c$ such that $C_0(\alpha_c' + \alpha_c'^2) \leq 1/2$. Thus, if $\|\nu\|_{L^2_{\text{unif}}} \leq \alpha_c'$ then

$$\left\| \frac{1}{1+\mathcal{L}} \chi_R \rho_{\widetilde{Q_2}(\rho_\nu - \nu) - \widetilde{Q_2}(\rho_{\nu_L} - \nu_L)} \right\|_{L^2_{\text{unif}}} \leq \frac{1}{2} \|\chi_R(\rho_\nu - \rho_{\nu_L})\|_{L^2_{\text{unif}}} + \frac{C}{R} \left(e^{-C'R} \|\nu\|_{L^2_{\text{unif}}} + \|1_{B_{3R}} f_L\|_{L^2_{\text{unif}}} \right). \tag{3.83}$$

In this case, combining (3.80), (3.81) and (3.83), we obtain for $R \leq L/4$

$$\begin{aligned} \|1_{B_R}(\rho_\nu - \rho_{\nu_L})\|_{L^2_{\text{unif}}} &\leq \|\chi_R(\rho_\nu - \rho_{\nu_L})\|_{L^2_{\text{unif}}} \\ &\leq \frac{C}{R} \left(e^{-C'R} \|\nu\|_{L^2_{\text{unif}}} + \|1_{B_{3R}}(\rho_\nu - \rho_{\nu_L})\|_{L^2_{\text{unif}}} + \|1_{B_{3R}}(\nu - \nu_L)\|_{L^2_{\text{unif}}} \right). \end{aligned}$$

Using a recursion argument, we easily see that for any $\beta \geq 1$, there exists $C \geq 0$ such that

$$\begin{aligned} \|\rho_\nu - \rho_{\nu_L}\|_{L^2_{\text{unif}}(B_{L/4^\beta})} &\leq \frac{C}{L^\beta} e^{-C'L} \|\nu\|_{L^2_{\text{unif}}} + \frac{C}{L^\beta} \|1_{B_L}(\rho_\nu - \rho_{\nu_L})\|_{L^2_{\text{unif}}} \\ &\quad + \frac{C}{L^\beta} \|1_{B_L}(\nu - \nu_L)\|_{L^2_{\text{unif}}} \leq \frac{C}{L^\beta} \|\nu\|_{L^2_{\text{unif}}}. \end{aligned}$$

To conclude the proof of the proposition, it remains to prove the bound on the potential. Using (3.28) and denoting by $f_L = \rho_\nu - \rho_{\nu_L} - \nu + \nu_L$, we have

$$\begin{aligned} \|V_\nu - V_{\nu_L}\|_{H^2_{\text{unif}}(B_{L/4^\beta})} &\leq \left\| \chi_{L/4^\beta} Y_m * f_L \right\|_{H^2_{\text{unif}}} \\ &\leq \left\| Y_m * \left(\chi_{L/4^\beta}(\rho_\nu - \rho_{\nu_L}) \right) \right\|_{H^2_{\text{unif}}} \\ &\quad + \frac{C}{L} \left(e^{-C'L} \|\nu\|_{L^2_{\text{unif}}} + \left\| 1_{B_{3L/4^\beta}} f_L \right\|_{L^2_{\text{unif}}} \right) \\ &\leq C \left\| \chi_{L/4^\beta}(\rho_\nu - \rho_{\nu_L}) \right\|_{L^2_{\text{unif}}} + \frac{C}{L} \left(e^{-C'L} \|\nu\|_{L^2_{\text{unif}}} + \left\| 1_{B_{3L/4^\beta}} f_L \right\|_{L^2_{\text{unif}}} \right) \\ &\leq \frac{C}{L^\beta} \|\nu\|_{L^2_{\text{unif}}} + \frac{C}{L} \left(e^{-C'L} \|\nu\|_{L^2_{\text{unif}}} + \frac{C}{L^{\beta-1}} \|\nu\|_{L^2_{\text{unif}}} \right) \\ &\leq \frac{C}{L^\beta} \|\nu\|_{L^2_{\text{unif}}}. \end{aligned}$$

□

3.6 Proof of Theorem 3.2.2 (Thermodynamic limit)

Proof of Theorem 3.2.2. Assume that $\|\nu\|_{L^2_{\text{unif}}} \leq \alpha_c$, where α_c is given by Proposition 3.2.5. By Cauchy's formula, we have

$$\gamma_\nu - \gamma_{\nu_L} = \frac{1}{2i\pi} \int_{\mathcal{C}} \frac{1}{z - H_0 - V_\nu} - \frac{1}{z - H_0 - V_{\nu_L}} dz,$$

where the curve $\mathcal{C}$ is as in Section 3.4. We write the resolvent difference as

$$\frac{1}{z-H_0-V_\nu}-\frac{1}{z-H_0-V_{\nu_L}}=\frac{1}{z-H_0-V_\nu}Y_m*f_L\frac{1}{z-H_0-V_{\nu_L}},$$

where $f_L=\rho_\nu-\nu-\rho_{\nu_L}+\nu_L$. For a compact set $B\subset\mathbb{R}^d$, we have

$$\mathrm{Tr}\left|1_B\frac{1}{z-H_0-V_\nu}Y_m*f_L\frac{1}{z-H_0-V_{\nu_L}}1_B\right|\leq C\left\|1_B\frac{1}{z-H_0-V_\nu}Y_m*f_L\right\|_{\mathfrak{S}_2}.$$

For L large enough, we have $B\subset B(0,L/8)$ and, by Proposition 3.2.5,

$$\begin{aligned}\left\|1_B\frac{1}{z-H_0-V_\nu}1_{B(0,L/4)}Y_m*f_L\right\|_{\mathfrak{S}_2}&\leq\left\|1_B\frac{1}{z-H_0-V_\nu}\right\|_{\mathfrak{S}_2}\left\|1_{B(0,L/4)}Y_m*f_L\right\|_{L^\infty}\\&\leq\frac{C}{L}\left\|\nu\right\|_{L^2_{\mathrm{unif}}}.\end{aligned}$$

Besides, as $\mathrm{d}(B,\mathbb{R}^d\setminus B_{L/4})\geq L/8$, we have using Lemma 3.3.6,

$$\begin{aligned}\left\|1_B\frac{1}{z-H_0-V_\nu}1_{\mathbb{R}^d\setminus B(0,L/4)}Y_m*f_L\right\|_{\mathfrak{S}_2}&\leq Ce^{-C'L}\left\|1_{\mathbb{R}^d\setminus B(0,L/4)}Y_m*f_L\right\|_{L^\infty}\\&\leq\frac{C}{L}\left\|\nu\right\|_{L^2_{\mathrm{unif}}}.\end{aligned}$$

As $\mathcal{C}$ is a compact set and all the estimates are uniform on $\mathcal{C}$, we conclude that

$$\left\|1_B\left(\gamma_\nu-\gamma_{\nu_L}\right)1_B\right\|_{\mathfrak{S}_1}\leq\frac{C}{L}\left\|\nu\right\|_{L^2_{\mathrm{unif}}}\underset{L\to\infty}{\longrightarrow}0.$$

□

3.7 Proof of Theorem 3.2.7 (Expansion of the density of states)

The proof of Theorem 3.2.7 follows essentially the proof of [87, Theorem 1.1]. The main difference is the proof of Proposition 3.7.1 below, which deals with self-consistent potentials, while [87, Proposition 2.1] deals with linear potentials. Treating nonlinear potentials is done at the price of assuming that the defect χ is small in the L^2_{unif}-norm, so that the potential decays fast enough. For the sake of self-containment, we mention here the main steps of the proof.

Proof of Theorem 3.2.7 . Following [87], we first express the density of states of the random operator $H_p(\omega)$ in terms of the resolvent $(z-H_p)^{-1}$ for $z\in\mathbb{C}$. We next find an asymptotic expansion of $\underline{\mathrm{Tr}}\left((z-H_p)^{-1}\right)$ using a thermodynamic limit procedure.

We recall the Helffer-Sjostrand formula [69, 38]. For a self-adjoint operator A and $\varphi \in \mathcal{S}(\mathbb{R})$, we have

$$\varphi(A) = -\frac{1}{\pi}\int_{\mathbb{C}} \frac{\partial \widetilde{\varphi}}{\partial \overline{z}}(z)\frac{1}{z-A}\,dx\,dy,$$

where $\widetilde{\varphi} : \mathbb{C} \to \mathbb{C}$ is an appropriate complex extension of φ such that

(i) $\widetilde{\varphi} = \varphi$ on $\mathbb{R}$,

(ii) $\mathrm{supp}(\widetilde{\varphi}) \subset \{z \in \mathbb{C},\ |\mathrm{Im(z)}| < 1\}$,

(iii) $\widetilde{\varphi} \in \mathcal{S}(\{z \in \mathbb{C},\ |\mathrm{Im(z)}| < 1\})$,

(iv) for any $n \in \mathbb{N}$ and $\alpha, \beta \geq 0$, one has

$$\sup_{|y|<1} \mathcal{N}_{\alpha,\beta}\left(x \mapsto \left(|y|^{-n}\,\frac{\partial \widetilde{\varphi}}{\partial \overline{z}}(x+iy)\right)\right) \leq C_{n,\alpha,\beta} \sup_{\substack{\beta' \leq n+\beta+2 \\ \alpha' \leq \alpha}} \mathcal{N}_{\alpha',\beta'}(\varphi), \tag{3.84}$$

where $\mathcal{N}_{\alpha,\beta}(\varphi) = \sup_{x\in\mathbb{R}} \left|x^{\alpha}\frac{\partial^{\beta}\varphi}{\partial x^{\beta}}\right|$.

Hence, for $\varphi \in \mathcal{S}(\mathbb{R})$,

$$\begin{aligned}\langle n_p - n_0, \varphi\rangle &= \int_{\mathbb{R}} \varphi(x) n_p(dx) - \int_{\mathbb{R}} \varphi(x) n_0(dx) = \mathrm{Tr}\ (\varphi(H_p) - \varphi(H_0)) \\ &= -\frac{1}{\pi}\underline{\mathrm{Tr}}\left(\int_{\mathbb{C}} \frac{\partial \widetilde{\varphi}}{\partial \overline{z}}(z)\left(\frac{1}{z-H_p} - \frac{1}{z-H_0}\right)\,dx\,dy\right).\end{aligned}$$

Besides, denoting by $V_p = V_{\nu_p}$, we have

$$\frac{1}{z-H_p} - \frac{1}{z-H_0} = \frac{1}{z-H_0} V_p \frac{1}{z-H_p}$$

Therefore, using the Kato-Seiler-Simon inequality (3.19) and Lemma 3.3.2, we obtain

$$\begin{aligned}\left|\underline{\mathrm{Tr}}\left(\frac{1}{z-H_p} - \frac{1}{z-H_0}\right)\right| &\leq \left\|1_\Gamma\,(-\Delta+1)^{-1}\right\|_{\mathfrak{S}_2} \left\|(-\Delta+1)\,\frac{1}{z-H_0}\right\|_{\mathcal{B}} \|V_p\|_{L^\infty} \\ &\quad \times \left\|\frac{1}{z-H_p}\,(-\Delta+1)\right\|_{\mathcal{B}} \left\|(-\Delta+1)^{-1}\,1_\Gamma\right\|_{\mathfrak{S}_2} \\ &\leq C\left(\frac{1+|z|}{|\mathrm{Im}(z)|}\right)^2 \|V_p\|_{L^\infty}.\end{aligned}$$

By Fubini's theorem, we get

$$\langle n_p - n_0, \varphi\rangle = -\frac{1}{\pi}\int_{\mathbb{C}} \frac{\partial \widetilde{\varphi}}{\partial \overline{z}}(z)\underline{\mathrm{Tr}}\left(\frac{1}{z-H_p} - \frac{1}{z-H_0}\right)\,dx\,dy. \tag{3.85}$$

In the following, we find the asymptotic expansion of
$\underline{\mathrm{Tr}}\left((z-H_p)^{-1}-(z-H_0)^{-1}\right)$ as $p\to 0$ for $z\in\{\mathbb{C}\setminus\mathbb{R},\ |\mathrm{Im}(z)|\leq 1\}$. To use a thermodynamic limit procedure, we consider, for each realization $\omega\in\Omega$ and each box size $L\in 2\mathbb{N}+1$, the system with defects only in the box Γ_L, that is, we consider the defect distribution $\nu_{K_L(\omega)}(x)$, with $K_L(\omega)=\left\{k\in\mathbb{Z}^d\cap\Gamma_L,\ q_k(\omega)=1\right\}$. For $K\subset\mathbb{Z}^d$, we recall the notation
$\nu_K=\sum_{k\in K}\chi(\cdot-k)$, $V_K=V_{\nu_K}=Y_m*(\rho_{\nu_K}-\nu_K)$ and $H_K=H_0+V_K$.
By the proof of Theorem 3.2.2, we have, almost surely,

$$\mathrm{Tr}\left(1_\Gamma\left(\frac{1}{z-H_p(\omega)}-\frac{1}{z-H_{K_L(\omega)}}\right)1_\Gamma\right)\underset{L\to\infty}{\longrightarrow}0.$$

Besides, from (3.12) and (3.25), it follows

$$\begin{aligned}&\left|\mathrm{Tr}\left(1_\Gamma\left(\frac{1}{z-H_p(\omega)}-\frac{1}{z-H_{K_L(\omega)}}\right)1_\Gamma\right)\right|\\&\qquad\leq C\left(\frac{1+|z|}{|\mathrm{Im}|\,(z)}\right)^2\|V_p(\omega,\cdot)-V_{K_L}(\omega,\cdot)\|_{L^\infty}\leq C\left(\frac{1+|z|}{|\mathrm{Im}(z)|}\right)^2\|\chi\|_{L^2},\end{aligned}$$

The dominated converge theorem thus gives

$$\mathbb{E}\left(\mathrm{Tr}\left(1_\Gamma\left(\frac{1}{z-H_p}-\frac{1}{z-H_{K_L}}\right)1_\Gamma\right)\right)\underset{L\to\infty}{\longrightarrow}0,$$

and

$$\underline{\mathrm{Tr}}\left(\frac{1}{z-H_p}-\frac{1}{z-H_0}\right)=\lim_{L\to\infty}\mathbb{E}\left(\mathrm{Tr}\left(1_\Gamma\left(\frac{1}{z-H_{K_L}}-\frac{1}{z-H_0}\right)1_\Gamma\right)\right).\tag{3.86}$$

Let $L\in 2\mathbb{N}+1$ and $N=L^d$. As the random variable $\mathrm{Tr}\,(1_\Gamma((z-H_{K_L})^{-1}-(z-H_0)^{-1})1_\Gamma)$ depends only on the N independent Bernoulli random variables $(q_k)_{k\in\mathbb{Z}^d\cap\Gamma_L}$, we have

$$\begin{aligned}&\mathbb{E}\left(\mathrm{Tr}\left(1_\Gamma\left(\frac{1}{z-H_{K_L}}-\frac{1}{z-H_0}\right)1_\Gamma\right)\right)\\&\qquad=\sum_{K\subset\mathbb{Z}^d\cap\Gamma_L}\mathbb{P}(K_L(\omega)=K)\mathrm{Tr}\left(1_\Gamma\left(\frac{1}{z-H_K}-\frac{1}{z-H_0}\right)1_\Gamma\right)\\&\qquad=\sum_{K\subset\mathbb{Z}^d\cap\Gamma_L}p^{|K|}(1-p)^{N-|K|}\mathrm{Tr}\left(1_\Gamma\left(\frac{1}{z-H_K}-\frac{1}{z-H_0}\right)1_\Gamma\right)\\&\qquad=\sum_{n=0}^{N}p^n(1-p)^{N-n}\sum_{\substack{K\subset\mathbb{Z}^d\cap\Gamma_L\\|K|=n}}\mathrm{Tr}\left(1_\Gamma\left(\frac{1}{z-H_K}-\frac{1}{z-H_0}\right)1_\Gamma\right).\end{aligned}$$

Expanding the term $(1-p)^{N-n}$ as powers of p and rearranging the sums, we obtain

$$\begin{aligned}
&\mathbb{E}\left(\mathrm{Tr}\,\left(1_\Gamma\left(\frac{1}{z-H_{K_L}}-\frac{1}{z-H_0}\right)1_\Gamma\right)\right)\\
&\quad=\sum_{n=0}^{N}p^n\sum_{j=0}^{N-n}(-p)^j\binom{N-n}{j}\sum_{\substack{K\subset\mathbb{Z}^d\cap\Gamma_L\\|K|=n}}\mathrm{Tr}\,\left(1_\Gamma\left(\frac{1}{z-H_K}-\frac{1}{z-H_0}\right)1_\Gamma\right)\\
&\quad=\sum_{n=0}^{N}p^n\sum_{j=n}^{N}(-p)^{j-n}\binom{N-n}{j-n}\sum_{\substack{K\subset\mathbb{Z}^d\cap\Gamma_L\\|K|=n}}\mathrm{Tr}\,\left(1_\Gamma\left(\frac{1}{z-H_K}-\frac{1}{z-H_0}\right)1_\Gamma\right)\\
&\quad=\sum_{j=0}^{N}p^j\sum_{n=0}^{j}(-1)^{j-n}\binom{N-n}{j-n}\sum_{\substack{K\subset\mathbb{Z}^d\cap\Gamma_L\\|K|=n}}\mathrm{Tr}\,\left(1_\Gamma\left(\frac{1}{z-H_K}-\frac{1}{z-H_0}\right)1_\Gamma\right)\\
&\quad=\sum_{j=0}^{J}a_{j,L}p^j+R_{J,L}(z,p),
\end{aligned}\tag{3.87}$$

where we have denoted the j^{th} order term by

$$\begin{aligned}
a_{j,L}(z)&=\sum_{n=0}^{j}\binom{N-n}{j-n}\sum_{\substack{K\subset\mathbb{Z}^d\cap\Gamma_L\\|K|=n}}(-1)^{j-n}\mathrm{Tr}\,\left(1_\Gamma\left(\frac{1}{z-H_K}-\frac{1}{z-H_0}\right)1_\Gamma\right)\\
&=\sum_{\substack{K\subset\mathbb{Z}^d\cap\Gamma_L\\|K|=j}}\sum_{K'\subset K}(-1)^{|K\setminus K'|}\mathrm{Tr}\,\left(1_\Gamma\left(\frac{1}{z-H_{K'}}-\frac{1}{z-H_0}\right)1_\Gamma\right)
\end{aligned}$$

and the remainder of the series by

$$\begin{aligned}
R_{J,L}(z,p)=&\sum_{n=0}^{N}p^n(1-p)^{N-n}\sum_{\substack{K\subset\mathbb{Z}^d\cap\Gamma_L\\|K|=n}}\mathrm{Tr}\,\left(1_\Gamma\left(\frac{1}{z-H_K}-\frac{1}{z-H_0}\right)1_\Gamma\right)\\
&-\sum_{j=0}^{J}a_{j,L}p^j.
\end{aligned}$$

The result will now follow from the next proposition, whose proof is postponed until the end of the proof of the theorem.

Proposition 3.7.1 (Estimates on $a_{j,L}$ and $R_{J,L}$)**.** *There exists $\alpha_c>0$ such that*

• *for $j\le 2$, there exists $C\ge 0$ such that for any $\chi\in L^2(\mathbb{R}^d)$ satisfying*

$\mathrm{supp}(\chi) \subset \Gamma$ *and* $\|\chi\|_{L^2} \leq \alpha_c$ *and any* $z \in \mathbb{C} \setminus \mathbb{R}$,

$$\sum_{\substack{K \subset \mathbb{Z}^d \\ |K|=j}} \left| \sum_{K' \subset K} (-1)^{|K \setminus K'|} \mathrm{Tr} \left(1_\Gamma \left(\frac{1}{z - H_{K'}} - \frac{1}{z - H_0} \right) 1_\Gamma \right) \right| \leq C \|\chi\|_{L^2} \left(\frac{1 + |z|}{|\mathrm{Im(z)}|} \right)^{j+1+jd}. \quad (3.88)$$

• *for* $J \leq 2$, *there exists* $C \geq 0$ *such that for any* $\chi \in L^2(\mathbb{R}^d)$ *satisfying* $\mathrm{supp}(\chi) \subset \Gamma$ *and* $\|\chi\|_{L^2} \leq \alpha_c$, $z \in \mathbb{C} \setminus \mathbb{R}$, $p \in [0,1]$ *and* $L \in 2\mathbb{N} + 1$

$$|R_{J,L}(z,p)| \leq C \|\chi\|_{L^2} p^{J+1} \left(\frac{1 + |z|}{|\mathrm{Im(z)}|} \right)^{(J+2)(d+1)}. \quad (3.89)$$

We deduce from Proposition 3.7.1 that for any $j \leq 2$, and $z \in \mathbb{C} \setminus \mathbb{R}$, $a_{j,L}(z)$ converges as $L \to \infty$ to

$$a_j(z) = \sum_{\substack{K \subset \mathbb{Z}^d \\ |K|=j}} \sum_{K' \subset K} (-1)^{|K \setminus K'|} \mathrm{Tr} \left(1_\Gamma \left(\frac{1}{z - H_{K'}} - \frac{1}{z - H_0} \right) 1_\Gamma \right), \quad (3.90)$$

and that for any $J \leq 2$ and $p \in [0,1]$, $R_{J,L}(z,p)$ converges, up to extraction, as $L \to \infty$ to $R_J(z,p)$, which satisfies

$$|R_J(z,p)| \leq C \|\chi\|_{L^2} p^{J+1} \left(\frac{1 + |z|}{|\mathrm{Im(z)}|} \right)^{(J+2)(d+1)}.$$

Passing to the limit as $L \to \infty$ for this subsequence in (3.87) and in view of (3.86), we obtain

$$\underline{\mathrm{Tr}} \left(\frac{1}{z - H_p} - \frac{1}{z - H_0} \right) = \sum_{j=1}^{J} a_j(z) p^j + p^{J+1} R_J(z,p).$$

Going back to (3.85), we thus have

$$\langle n_p - n_0, \varphi \rangle = \sum_{i=1}^{J} -\frac{1}{\pi} \int_{\mathbb{C}} \frac{\partial \widetilde{\varphi}}{\partial \overline{z}}(z) a_j(z)\, dx\, dy\, p^j - \frac{1}{\pi} \int_{\mathbb{C}} \frac{\partial \widetilde{\varphi}}{\partial \overline{z}}(z) R_J(z,p)\, dx\, dy\, p^{J+1}.$$

We now show that the terms of the expansion are of the form claimed in the

theorem. Indeed,

$$\begin{aligned}
a_j(z) &= \frac{1}{j} \sum_{\substack{K\subset\mathbb{Z}^d \\ |K|=j,\ 0\in K}} \sum_{k\in\mathbb{Z}^d} \sum_{K'\subset K+k} (-1)^{|K\setminus K'|} \operatorname{Tr}\left(1_\Gamma \left(\frac{1}{z-H_{K'}} - \frac{1}{z-H_0}\right) 1_\Gamma\right) \\
&= \frac{1}{j} \sum_{\substack{K\subset\mathbb{Z}^d \\ |K|=j,\ 0\in K}} \sum_{k\in\mathbb{Z}^d} \sum_{K'\subset K} (-1)^{|K\setminus K'|} \operatorname{Tr}\left(1_\Gamma \left(\frac{1}{z-H_{K'+k}} - \frac{1}{z-H_0}\right) 1_\Gamma\right) \\
&= \frac{1}{j} \sum_{\substack{K\subset\mathbb{Z}^d \\ |K|=j,\ 0\in K}} \sum_{k\in\mathbb{Z}^d} \sum_{K'\subset K} (-1)^{|K\setminus K'|} \operatorname{Tr}\left(1_{\Gamma+k} \left(\frac{1}{z-H_{K'}} - \frac{1}{z-H_0}\right) 1_{\Gamma+k}\right) \\
&= \frac{1}{j} \sum_{\substack{K\subset\mathbb{Z}^d \\ |K|=j,\ 0\in K}} \sum_{K'\subset K} (-1)^{|K\setminus K'|} \operatorname{Tr}\left(\frac{1}{z-H_{K'}} - \frac{1}{z-H_0}\right).
\end{aligned}$$

Therefore, by the dominated convergence theorem for series, we obtain

$$\begin{aligned}
-\frac{1}{\pi}\int_{\mathbb{C}} \frac{\partial\widetilde{\varphi}}{\partial\overline{z}}(z) a_j(z)\, dx\, dy &= \frac{1}{j} \sum_{\substack{K\subset\mathbb{Z}^d \\ |K|=j,\ 0\in K}} \sum_{K'\subset K} (-1)^{|K\setminus K'|} \operatorname{Tr}\left(\varphi(H_{K'}) - \varphi(H_0)\right) \\
&= -\frac{1}{j} \sum_{\substack{K\subset\mathbb{Z}^d \\ |K|=j,\ 0\in K}} \sum_{K'\subset K} (-1)^{|K\setminus K'|} \int_{\mathbb{R}} \varphi(x)\xi'_{K'}(x)\, dx \\
&= \langle \mu_j, \varphi\rangle.
\end{aligned}$$

Moreover, using (3.84), (3.88) and (3.90), we see that μ_j the distribution defined by

$$\varphi \mapsto \langle \mu_j, \varphi\rangle = -\frac{1}{\pi}\int_{\mathbb{C}} \frac{\partial\widetilde{\varphi}}{\partial\overline{z}}(z) a_j(z)\, dx\, dy$$

is a distribution of order at most $j+3+jd$. Finally,
$\varphi \mapsto -\frac{1}{\pi}\int_{\mathbb{C}} \frac{\partial\widetilde{\varphi}}{\partial\overline{z}}(z) R_J(z,p)\, dx\, dy$ defines a distribution of order at most $J+4+(J+2)d$ and satisfies

$$\left|\frac{1}{\pi}\int_{\mathbb{C}} \frac{\partial\widetilde{\varphi}}{\partial\overline{z}}(z) R_J(z,p)\, dx\, dy\right| \leq C_J \sup_{\substack{\beta\leq J+4+(J+2)d \\ \alpha\leq (J+3)(d+1)}} \|\chi\|_{L^2}\, \mathcal{N}_{\alpha,\beta}(\varphi).$$

This concludes the proof of Theorem 3.2.7. □

To complete the proof of Theorem 3.2.7, we need to prove Proposition 3.7.1. We first state and prove Lemma 3.7.2 which will be useful in the proof of Proposition 3.7.1.

Lemma 3.7.2. *Let $H = -\Delta + W$, with $W \in L^2_{\mathrm{unif}}(\mathbb{R}^d)$. Then, for any $\beta \in \mathbb{N}$ and any Borel set $B \subset \mathbb{R}^d$, there exist $C \geq 0$ and $C' > 0$ such that for any $z \in \mathbb{C}\setminus\mathbb{R}$ and any $\nu, \nu' \in L^2_c(\mathbb{R}^d)$ satisfying $\|\nu\|_{L^2_{\mathrm{unif}}}, \|\nu'\|_{L^2_{\mathrm{unif}}} \leq \alpha_c$, $R =$*

$\mathrm{d}(\mathrm{supp}(\nu),0) \geq 1$, $R' = \mathrm{d}(\mathrm{supp}(\nu'),0) \geq 1$, $D = \mathrm{d}(\mathrm{supp}(\nu),\mathrm{supp}(\nu')) \geq 1$, *we have*

$$\left\| 1_\Gamma \frac{1}{z-H} V_\nu \right\|_{\mathfrak{S}_2} \leq C \frac{1+|z|}{|\mathrm{Im}(z)|} \left(e^{-C'(\log R)^2} + e^{-C' c_2(z) R} \right) \|\nu\|_{L^2_{\mathrm{unif}}} , \quad (3.91)$$

$$\left\| V_{\nu 1_B} \frac{1}{z-H} \left(V_{\nu+\nu'} - V_\nu \right) \right\|_{\mathcal{B}} \leq \frac{C}{|\mathrm{Im}(z)|} \left(\frac{1}{D^\beta} + e^{-C' c_2(z) D} \right) \|\nu\|_{L^2_{\mathrm{unif}}} \times \left(\|\nu\|_{L^2_{\mathrm{unif}}} + \left\|\nu'\right\|_{L^2_{\mathrm{unif}}} \right), \quad (3.92)$$

$$\left\| 1_\Gamma \frac{1}{z-H} \left(V_{\nu+\nu'} - V_\nu \right) \right\|_{\mathfrak{S}_2} \leq C \frac{1+|z|}{|\mathrm{Im}(z)|} \left(\|\nu\|_{L^2_{\mathrm{unif}}} + \left\|\nu'\right\|_{L^2_{\mathrm{unif}}} \right) \times \left[\frac{1}{D^\beta} + e^{-C' c_2(z) D} + e^{-C' (\log R')^2} + e^{-C' c_2(z) R'} \right] \quad (3.93)$$

and

$$\left\| 1_\Gamma \frac{1}{z-H} \left(V_{\nu+\nu'} - V_\nu - V_{\nu'} \right) \right\|_{\mathfrak{S}_2} \leq C \frac{1+|z|}{|\mathrm{Im}(z)|} \left(\|\nu\|_{L^2_{\mathrm{unif}}} + \left\|\nu'\right\|_{L^2_{\mathrm{unif}}} \right) \times \left(\frac{1}{D^\beta} \left(e^{-C' \left(\log \widetilde{R}\right)^2} + e^{-C' c_2(z) \widetilde{R}} \right) \right), \quad (3.94)$$

where $\widetilde{R} = \min\{R, R'\}$, $c_2(z) = \mathrm{d}(z, \sigma(H))/(1+|z|)$ *and where the constants* C *and* C' *depend on* W *only through its* L^2_{unif} *-norm.*

Proof. Inequalities (3.91) - (3.94) follow from Lemmas 3.3.2 and 3.3.6, Theorem 3.2.3 and Proposition 3.2.6. Indeed, in order to prove (3.91), we first look at V_ν far from Γ. Using Lemma 3.3.6, we have

$$\begin{aligned} \left\| 1_\Gamma \frac{1}{z-H} 1_{\mathbb{R}^d \setminus B(0,\frac{R}{4})} V_\nu \right\|_{\mathfrak{S}_2} &\leq \frac{C}{|\mathrm{Im}(z)|} e^{-C' c_2(z) R} \|V_\nu\|_{L^\infty} \\ &\leq \frac{C}{|\mathrm{Im}(z)|} e^{-C' c_2(z) R} \|\nu\|_{L^2_{\mathrm{unif}}} . \end{aligned}$$

Near Γ, V_ν decays as R gets large by Theorem 3.2.3. As $\mathrm{d}(B(0,\frac{R}{4}), \mathrm{supp}(\nu)) \geq R/2$, then, by (3.13), we have

$$\left\| 1_{B(0,\frac{R}{4})} V_\nu \right\|_{L^\infty} \leq C \left\| 1_{B(0,\frac{R}{4})} V_\nu \right\|_{H^2_{\mathrm{unif}}} \leq C e^{-C' (\log R)^2} \|\nu\|_{L^2_{\mathrm{unif}}} ,$$

where we have used that in dimension $d \leq 3$, $H^2_{\mathrm{unif}}(\mathbb{R}^d) \hookrightarrow L^\infty(\mathbb{R}^d)$. We next use Lemma 3.3.2 and the Kato-Seiler-Simon inequality (3.19) to obtain

$$\begin{aligned}\left\| 1_\Gamma \frac{1}{z-H} 1_{B(0,\frac{R}{4})} V_\nu \right\|_{\mathfrak{S}_2} &\leq \left\| 1_\Gamma \frac{1}{-\Delta+1} \right\|_{\mathfrak{S}_2} \left\| (-\Delta+1)\frac{1}{z-H} \right\|_{\mathcal{B}} \left\| 1_{B(0,\frac{R}{4})} V_\nu \right\|_{L^\infty} \\ &\leq C \frac{1+|z|}{|\mathrm{Im}(z)|} e^{-C'(\log R)^2} \|\nu\|_{L^2_{\mathrm{unif}}} ,\end{aligned}$$

which concludes the proof of (3.91). We turn to the proof of (3.92). Let $\beta \geq 0$ and $a = 4^\beta$. By Proposition 3.2.6, we have that near ν, $V_{\nu+\nu'} - V_\nu$ is small:

$$\left\| 1_{C_{2D/a}(\nu)} (V_{\nu+\nu'} - V_\nu) \right\|_{L^\infty} \leq \frac{C}{D^\beta} \left(\|\nu\|_{L^2_{\mathrm{unif}}} + \|\nu'\|_{L^2_{\mathrm{unif}}} \right), \tag{3.95}$$

where, we recall $C_R(\nu) = \left\{ x \in \mathbb{R}^d,\ \mathrm{d}(x, \mathrm{supp}(\nu)) \leq R \right\}$. Therefore

$$\begin{aligned}&\left\| V_{\nu 1_B} \frac{1}{z-H} 1_{C_{2D/a}(\nu)} (V_{\nu+\nu'} - V_\nu) \right\|_{\mathcal{B}} \\ &\qquad \leq \|V_{\nu 1_B}\|_{L^\infty} \left\| \frac{1}{z-H} \right\|_{\mathcal{B}} \frac{C}{D^\beta} \left(\|\nu\|_{L^2_{\mathrm{unif}}} + \|\nu'\|_{L^2_{\mathrm{unif}}} \right) \\ &\qquad \leq \frac{C}{|\mathrm{Im}(z)|} \frac{1}{D^\beta} \|\nu\|_{L^2_{\mathrm{unif}}} \left(\|\nu\|_{L^2_{\mathrm{unif}}} + \|\nu'\|_{L^2_{\mathrm{unif}}} \right).\end{aligned}$$

Besides, by the decay of $V_{\nu 1_B}$ far from k proved in Theorem 3.2.3, we have

$$\left\| V_{\nu 1_B} 1_{\mathbb{R}^d \setminus C_{D/a}(\nu)} \right\|_{L^\infty} \leq \frac{C}{D^\beta} \|\nu\|_{L^2_{\mathrm{unif}}} .$$

Therefore

$$\begin{aligned}\left\| V_{\nu 1_B} 1_{\mathbb{R}^d \setminus C_{D/a}(\nu)} \frac{1}{z-H} 1_{\mathbb{R}^d \setminus C_{2D/a}(\nu)} (V_{\nu+\nu'} - V_\nu) \right\|_{\mathcal{B}} &\leq \frac{C}{|\mathrm{Im}(z)|} \frac{1}{D^\beta} \\ &\times \|\nu\|_{L^2_{\mathrm{unif}}} \left(\|\nu\|_{L^2_{\mathrm{unif}}} + \|\nu'\|_{L^2_{\mathrm{unif}}} \right).\end{aligned}$$

Using Lemma 3.3.6 for the remaining term, we obtain

$$\begin{aligned}\left\| V_{\nu 1_B} 1_{C_{D/a}(\nu)} \frac{1}{z-H} 1_{\mathbb{R}^d \setminus C_{2D/a}(\nu)} (V_{\nu+\nu'} - V_\nu) \right\|_{\mathcal{B}} &\leq \frac{C}{|\mathrm{Im}(z)|} e^{-C' c_2(z) D} \\ &\times \|\nu\|_{L^2_{\mathrm{unif}}} \left(\|\nu\|_{L^2_{\mathrm{unif}}} + \|\nu'\|_{L^2_{\mathrm{unif}}} \right),\end{aligned}$$

which concludes the proof of (3.92).

We now prove (3.93). Let $\beta \geq 0$ and $a = 4^\beta$. If $\Gamma \subset C_{D/a}(\nu)$, then similarly to the proof of (3.92), we show that

$$\left\| 1_\Gamma \frac{1}{z-H} (V_{\nu+\nu'} - V_\nu) \right\|_{\mathfrak{S}_2} \leq \frac{1+|z|}{|\mathrm{Im}(z)|} \left(\frac{1}{D^\beta} + e^{-C' c_2(z) D} \right) \left(\|\nu\|_{L^2_{\mathrm{unif}}} + \|\nu'\|_{L^2_{\mathrm{unif}}} \right).$$

Otherwise, we use (3.91) to obtain

$$\left\| 1_\Gamma \frac{1}{z-H} \left(V_{\nu+\nu'} - V_\nu \right) \right\|_{\mathfrak{S}_2} \leq C \frac{1+|z|}{|\mathrm{Im}(z)|} \left(e^{-C' \left(\log \widetilde{R} \right)^2} + e^{-C' c_2(z) \widetilde{R}} \right) \|\nu\|_{L^2_{\mathrm{unif}}} ,$$

In the latter case $R \geq D/a$ and $R' \leq (1+a)R$. Thus $\widetilde{R} \geq CR'$, which concludes the proof of (3.93).

Finally, by (3.91), we have

$$\begin{aligned} \left\| 1_\Gamma \frac{1}{z-H} \left(V_{\nu+\nu'} - V_\nu - V_{\nu'} \right) \right\|_{\mathfrak{S}_2} &\leq \frac{1+|z|}{|\mathrm{Im}(z)|} \left(e^{-C' \left(\log(\widetilde{R}) \right)^2} + e^{-C' c_2(z) \widetilde{R}} \right) \\ &\quad \times \frac{C}{\widetilde{R}^\beta} \left(\|\nu\|_{L^2_{\mathrm{unif}}} + \left\| \nu' \right\|_{L^2_{\mathrm{unif}}} \right) . \end{aligned} \tag{3.96}$$

By Theorem 3.2.3, we have

$$\left\| 1_{C_{D/a}(\nu)} V_{\nu'} \right\|_{L^\infty} \leq \frac{C}{D^\beta} \left\| \nu' \right\|_{L^2_{\mathrm{unif}}} .$$

In view of (3.95), we obtain

$$\left\| 1_{C_{D/a}(\nu)} \left(V_{\nu+\nu'} - V_\nu - V_{\nu'} \right) \right\|_{L^\infty} \leq \frac{C}{D^\beta} \left(\|\nu\|_{L^2_{\mathrm{unif}}} + \left\| \nu' \right\|_{L^2_{\mathrm{unif}}} \right) .$$

Similarly, we obtain,

$$\left\| 1_{C_{D/a}(\nu')} \left(V_{\nu+\nu'} - V_\nu - V_{\nu'} \right) \right\|_{L^\infty} \leq \frac{C}{D^\beta} \left(\|\nu\|_{L^2_{\mathrm{unif}}} + \left\| \nu' \right\|_{L^2_{\mathrm{unif}}} \right) .$$

Finally, using Theorem 3.2.3 to control $V_{\nu+\nu'} - V_\nu - V_{\nu'}$ outside of the two balls $C_{D/a}(\nu)$ and $C_{D/a}(\nu')$, we conclude that

$$\left\| V_{\nu+\nu'} - V_\nu - V_{\nu'} \right\|_{L^\infty} \leq \frac{C}{D^\beta} \left(\|\nu\|_{L^2_{\mathrm{unif}}} + \left\| \nu' \right\|_{L^2_{\mathrm{unif}}} \right) . \tag{3.97}$$

Therefore

$$\left\| 1_\Gamma \frac{1}{z-H} \left(V_{\nu+\nu'} - V_\nu - V_{\nu'} \right) \right\|_{\mathfrak{S}_2} \leq \frac{1+|z|}{|\mathrm{Im}(z)|} \frac{C}{D^\beta} \left(\|\nu\|_{L^2_{\mathrm{unif}}} + \left\| \nu' \right\|_{L^2_{\mathrm{unif}}} \right) . \tag{3.98}$$

By (3.96) and (3.98), we find

$$\begin{aligned} \left\| 1_\Gamma \frac{1}{z-H} \left(V_{\nu+\nu'} - V_\nu - V_{\nu'} \right) \right\|_{\mathfrak{S}_2} &\leq \frac{1+|z|}{|\mathrm{Im}(z)|} \frac{C}{D^{\beta/2}} \left(e^{-\frac{C'}{2} \left(\log(\widetilde{R}) \right)^2} + e^{-\frac{C'}{2} c_2(z) \widetilde{R}} \right) \\ &\quad \times \left(\|\nu\|_{L^2_{\mathrm{unif}}} + \left\| \nu' \right\|_{L^2_{\mathrm{unif}}} \right) , \end{aligned}$$

which concludes the proof of (3.94). □

We now prove Proposition 3.7.1.

Proof of Proposition 3.7.1. Let α_c be the minimum of the constants α_c defined in Theorems 3.2.1 and 3.2.3 and Propositions 3.2.5 and 3.2.6. We assume that $\|\chi\|_{L^2} \leq \alpha_c$. Throughout the proof, β will denote an integer greater than $d+1$ whose value might change from one line to another and $C \geq 0$ and $C' > 0$ constants that depend, in general, on β. For $z \in \mathbb{C} \setminus \mathbb{R}$, we denote by $R_0(z) = (z - H_0)^{-1}$ and for any $K \subset \mathbb{Z}^d$, we set $R_K(z) = (z - H_K)^{-1}$. We omit the dependence on z when there is no ambiguity. We also omit the $\|\chi\|_{L^2}$ in our estimates. Let $L \in 2\mathbb{N}+1$ and denote by $N = L^d$.

For $j = 1$ and $K = \{k\}$, with $k \in \mathbb{Z}^d$, we have

$$\begin{aligned}\left|\mathrm{Tr}\,\left(1_\Gamma\left(R_{\{k\}} - R_0\right)1_\Gamma\right)\right| &= \left|\mathrm{Tr}\,\left(1_\Gamma R_0 V_{\{k\}} R_{\{k\}} 1_\Gamma\right)\right| \\ &\leq \left\|1_\Gamma R_0 V_{\{k\}}\right\|_{\mathfrak{S}_2} \left\|R_{\{k\}} 1_\Gamma\right\|_{\mathfrak{S}_2}.\end{aligned}$$

Therefore, using (3.91) in Lemma 3.7.2, we get

$$\left|\mathrm{Tr}\,\left(1_\Gamma R_{\{k\}} V_{\{k\}} R_0 1_\Gamma\right)\right| \leq C\left(\frac{1+|z|}{|\mathrm{Im}(z)|}\right)^2 \left(e^{-\frac{C'}{2}(\log|k|)^2} + e^{-\frac{C'}{2}c_2(z)|k|}\right).$$

Since the series $\sum_{k\in\mathbb{Z}^d} e^{-\lambda|k|}$, with $\lambda > 0$, is equivalent to $\int_{\mathbb{R}^d} e^{-\lambda|x|}dx = 1/\lambda^d$, and for $z \in \{z \in \mathbb{C},\ |\mathrm{Im}(z)| \leq 1\}$, it holds $1/c_2(z) \leq (1+|z|)/|\mathrm{Im}(z)|$ and $1 \leq (1+|z|)/|\mathrm{Im}(z)|$, we deduce that the series $\sum_{k\in\mathbb{Z}^d}\left|\mathrm{Tr}\,\left(1_\Gamma R_{\{k\}} V_{\{k\}} R_0 1_\Gamma\right)\right|$ is convergent and its sum satisfies

$$\sum_{k\in\mathbb{Z}^d}\left|\mathrm{Tr}\,\left(1_\Gamma R_{\{k\}} V_{\{k\}} R_0 1_\Gamma\right)\right| \leq C\left(\frac{1+|z|}{|\mathrm{Im}(z)|}\right)^{2+d}.$$

For $j = 2$ and $K = \{k, k'\}$, with $k, k' \in \mathbb{Z}^d$, a straightforward calculation gives

$$\begin{aligned}&\sum_{K'\subset K}(-1)^{|K\setminus K'|}\mathrm{Tr}\,\left(1_\Gamma\left(R_{K'} - R_0\right)1_\Gamma\right) \\ &\qquad = \mathrm{Tr}\,\left(1_\Gamma R_0(V_{\{k,k'\}} - V_{\{k\}} - V_{\{k'\}})R_{\{k,k'\}}1_\Gamma\right) \\ &\qquad + \mathrm{Tr}\,\left(1_\Gamma R_0 V_{\{k\}} R_{\{k\}}\left(V_{\{k,k'\}} - V_{\{k\}}\right)R_{\{k,k'\}}1_\Gamma\right) \\ &\qquad + \mathrm{Tr}\,\left(1_\Gamma R_0 V_{\{k'\}} R_{\{k'\}}\left(V_{\{k,k'\}} - V_{\{k'\}}\right)R_{\{k,k'\}}1_\Gamma\right). \qquad (3.99)\end{aligned}$$

Using the inequality (3.94), the first term of the RHS of (3.99) can be estimated by

$$\begin{aligned}&\left\|1_\Gamma R_0(V_{\{k,k'\}} - V_{\{k\}} - V_{\{k'\}})\right\|_{\mathfrak{S}_2}\left\|R_{\{k,k'\}}1_\Gamma\right\|_{\mathfrak{S}_2} \\ &\quad \leq \left(\frac{1+|z|}{|\mathrm{Im}(z)|}\right)^2\left(\frac{C}{|k-k'|^\beta}\left(e^{-C'(\log\min\{|k|,|k'|\})^2} + e^{-C'c_2(z)\min\{|k|,|k'|\}}\right)\right).\end{aligned}$$

As to bound the second term of the RHS of (3.99), it is bounded by

$$\left\|1_\Gamma R_0 V_{\{k\}}\right\|_{\mathfrak{S}_2} \left\|R_{\{k\}}\left(V_{\{k,k'\}} - V_{\{k\}}\right)\right\|_{\mathcal{B}} \left\|R_{\{k,k'\}} 1_\Gamma\right\|_{\mathfrak{S}_2} \leq C\left(\frac{1+|z|}{|\mathrm{Im}(z)|}\right)^3 \left(e^{-C'(\log|k|)^2} + e^{-C'c_2(z)|k|}\right).$$

using (3.91), and by

$$\|1_\Gamma R_0\|_{\mathfrak{S}_2} \left\|V_{\{k\}} R_{\{k\}}\left(V_{\{k,k'\}} - V_{\{k\}}\right)\right\|_{\mathcal{B}} \left\|R_{\{k,k'\}} 1_\Gamma\right\|_{\mathfrak{S}_2} \leq C\left(\frac{1+|z|}{|\mathrm{Im}(z)|}\right)^3 \left(\frac{1}{|k-k'|^\beta} + e^{-C'c_2(z)|k-k'|}\right).$$

using (3.92). Therefore

$$\left|\mathrm{Tr}\,\left(1_\Gamma R_0 V_{\{k\}} R_{\{k\}}\left(V_{\{k,k'\}} - V_{\{k\}}\right) R_{\{k,k'\}} 1_\Gamma\right)\right| \leq C\left(\frac{1+|z|}{|\mathrm{Im}(z)|}\right)^3 \times \left(e^{-C'(\log|k|)^2} + e^{-C'c_2(z)|k|}\right)^{\frac{1}{2}} \left(\frac{1}{|k-k'|^\beta} + e^{-C'c_2(z)|k-k'|}\right)^{\frac{1}{2}}.$$

We have the same bound for the third term of the RHS of (3.99). Therefore, the series $\sum_{\substack{K\subset\mathbb{Z}^d \\ |K|=2}} \left|\sum_{K'\subset K}(-1)^{|K\setminus K'|}\mathrm{Tr}\,\left(1_\Gamma\left(R_{K'} - R_0\right)1_\Gamma\right)\right|$ is convergent and its sum satisfies

$$\sum_{\substack{K\subset\mathbb{Z}^d \\ |K|=2}} \left|\sum_{K'\subset K}(-1)^{|K\setminus K'|}\mathrm{Tr}\,\left(1_\Gamma\left(R_{K'} - R_0\right)1_\Gamma\right)\right| \leq C\left(\frac{|z|+1}{|\mathrm{Im}(z)|}\right)^{3+2d}.$$

We turn to the proof of the estimate on the remainder (3.89). Let $J \leq 2$ and $p \in [0,1]$. We first write $R_{J,L}(z,p)$ in the form of the expectancy of a binomial variable. Indeed, we have

$$R_{J,L}(z,p) = \sum_{n=0}^{N} p^n (1-p)^{N-n} \sum_{\substack{K\subset\mathbb{Z}^d\cap\Gamma \\ |K|=n}} f_{L,K} - \sum_{j=1}^{J} a_{j,L}(z) p^j,$$

where $f_{L,K} = \mathrm{Tr}\,(1_\Gamma\,(R_K - R_0)\,1_\Gamma)$. Rearranging all the terms, we obtain

$$\begin{aligned}
&\sum_{j=1}^{J} a_{j,L}(z)p^j \\
&\quad= \sum_{j=1}^{J} p^j \sum_{n=0}^{N-j} p^n(1-p)^{N-j-n}\binom{N-j}{n} \sum_{\substack{K\subset\mathbb{Z}^d\cap\Gamma_L\\|K|=j}} \sum_{K'\subset K} (-1)^{|K\setminus K'|} f_{L,K'} \\
&\quad= \sum_{j=1}^{J}\sum_{n=j}^{N} p^n(1-p)^{N-n}\binom{N-j}{n-j} \sum_{\substack{K\subset\mathbb{Z}^d\cap\Gamma_L\\|K|=j}} \sum_{K'\subset K} (-1)^{|K\setminus K'|} f_{L,K'} \\
&\quad= \sum_{n=0}^{N} p^n(1-p)^{N-n} \sum_{j=1}^{\inf\{J,n\}} \binom{N-j}{n-j} \sum_{\substack{K\subset\mathbb{Z}^d\cap\Gamma_L\\|K|=j}} \sum_{K'\subset K} (-1)^{|K\setminus K'|} f_{L,K'} \\
&\quad= \sum_{n=0}^{N} p^n(1-p)^{N-n} \sum_{\substack{K\subset\mathbb{Z}^d\cap\Gamma_L\\|K|=n}} \sum_{\substack{K'\subset K\\|K'|\le J}} \sum_{K''\subset K'} (-1)^{|K'\setminus K''|} f_{L,K''}.
\end{aligned}$$

It follows that

$$R_{J,L}(z,p) = \sum_{n=0}^{N} p^n(1-p)^{N-n} \sum_{\substack{K\subset\mathbb{Z}^d\cap\Gamma\\|K|=n}} D_{J,K}(z),$$

where

$$D_{J,K} = f_{L,K} - \sum_{\substack{K'\subset K\\|K'|\le J}} \sum_{K''\subset K'} (-1)^{K'\setminus K''} f_{L,K''}.$$

We next notice that for $K \subset \mathbb{Z}^d$ such that $j = |K| \leq J$, $D_{J,K} = 0$. Indeed

$$\begin{aligned}
\sum_{\substack{K' \subset K \\ |K'| \leq J}} \sum_{K'' \subset K'} (-1)^{K' \setminus K''} f_{L,K''} &= \sum_{K' \subset K} \sum_{K'' \subset K'} (-1)^{|K' \setminus K''|} f_{K''} \\
&= \sum_{i=1}^{j} \sum_{n=1}^{i} (-1)^{i-n} \sum_{\substack{K' \subset K \\ |K'|=i}} \sum_{\substack{K'' \subset K' \\ |K''|=n}} f_{K''} \\
&= \sum_{i=1}^{j} \sum_{n=1}^{i} (-1)^{i-n} \binom{j-n}{j-i} \sum_{\substack{K'' \subset K \\ |K''|=n}} f_{K''} \\
&= \sum_{n=1}^{j} \sum_{i=n}^{j} (-1)^{i-n} \binom{j-n}{j-i} \sum_{\substack{K'' \subset K \\ |K''|=n}} f_{K''} \\
&= \sum_{n=1}^{j} \sum_{i=0}^{j-n} (-1)^{i} \binom{j-n}{j-n-i} \sum_{\substack{K'' \subset K \\ |K''|=n}} f_{K''} \\
&= \sum_{n=1}^{j} \delta_{j-n=0} \sum_{\substack{K'' \subset K \\ |K''|=n}} f_{K''} \\
&= f_K.
\end{aligned}$$

We thus have

$$\begin{aligned}
R_{J,L}(z,p) &= p^{J+1} \sum_{n=0}^{N-J-1} p^n (1-p)^{N-J-1} \binom{N-J-1}{n} \binom{N-J-1}{n}^{-1} \\
&\quad \times \Big(\sum_{\substack{K \subset \mathbb{Z}^d \cap \Gamma_L \\ |K|=n+J+1}} D_{J,K}(z) \Big) \\
&= p^{J+1} \mathbb{E} \left(g_{J,L} \left(Y_L + J + 1, z \right) \right),
\end{aligned}$$

where Y_L is a random variable of binomial distribution of parameters p and $N - J - 1$ and $g_{J,L}(\cdot, z) : \{J+1, \cdots, N\} \to \mathbb{R}$ is defined by

$$g_{J,L}(n,z) = \binom{N-J-1}{n-J-1}^{-1} \sum_{\substack{K \subset \mathbb{Z}^d \cap \Gamma_L \\ |K|=n}} D_{J,K}(z).$$

In order to prove (3.89), it is therefore sufficient to show that there exists $C \geq 0$ such that for any $L \in 2\mathbb{N}+1$ and $J+1 \leq n \leq N$,

$$|g_{J,L}(n,z)| \leq C \left(\frac{1+|z|}{|\mathrm{Im}(z)|} \right)^{J+2+(J+2)d}.$$

It is sufficient to prove the above inequality for $J = 2$. Let $J+1 \leq n \leq N$ and consider a configuration $K \subset \mathbb{Z}^d \cap \Gamma_L$ such that $|K| = n$. A straightforward calculation shows that

$$g_{J,L}(n,z) = \binom{N-J-1}{n-J-1}^{-1} \sum_{\substack{K \subset \mathbb{Z}^d \cap \Gamma_L \\ |K| = n+J+1}} \mathrm{Tr}\, \left(1_\Gamma R_0 \left(P_{1,K} - P_{2,K}\right) R_K 1_\Gamma\right)$$

where

$$P_{1,K} = V_K - \sum_{k \in K} V_{\{k\}} - \sum_{\substack{k,k' \in K \\ k \neq k'}} \left(V_{\{k,k'\}} - V_{\{k\}} - V_{\{k'\}}\right)$$

and

$$P_{2,K} = \sum_{k \in K} V_{\{k\}} R_k \left(V_K - V_{\{k\}}\right) + \sum_{\{k,k'\} \subset K} \Big(V_{\{k,k'\}} R_{\{k,k'\}} \left(V_K - V_{\{k,k'\}}\right) - V_{\{k\}} R_{\{k\}} \left(V_K - V_{\{k\}}\right) - V_{\{k'\}} R_{\{k'\}} \left(V_K - V_{\{k'\}}\right) \Big).$$

Besides

$$P_{1,K} = \sum_{r \in \mathbb{Z}^d} 1_{\Gamma+r} P_{1,K}.$$

For each $r \in \mathbb{Z}^d$, we split $1_{\Gamma+r} P_{1,K}$ into two r-dependent quantities: a part involving the defect in $k_0 = \arg\inf_{k \in K} |k - r|$ and the rest. We denote by

$$A_{K,k_0} = V_K - V_{\{k_0\}} - \sum_{k \in K \setminus \{k_0\}} \left(V_{\{k,k_0\}} - V_{\{k_0\}}\right)$$

and

$$B_{K,k_0} = \sum_{\{k,k'\} \subset K \setminus \{k_0\}} \left(V_{\{k,k'\}} - V_{\{k\}} - V_{\{k'\}}\right).$$

Then

$$P_{1,K} = \sum_{r \in \mathbb{Z}^d} 1_{\Gamma+r} A_{K,k_0} - \sum_{r \in \mathbb{Z}^d} 1_{\Gamma+r} B_{K,k_0}.$$

We have thus split $g_{J,L}(n,z)$ into three parts

$$\begin{aligned} g_{J,L}(n,z) = {} & \binom{N-J-1}{n-J-1}^{-1} \sum_{\substack{K \subset \mathbb{Z}^d \cap \Gamma_L \\ |K| = n}} \mathrm{Tr}\, \left(1_\Gamma R_0 \sum_{r \in \mathbb{Z}^d} 1_{\Gamma+r} A_{K,k_0} R_K 1_\Gamma\right) \\ & - \binom{N-J-1}{n-J-1}^{-1} \sum_{\substack{K \subset \mathbb{Z}^d \cap \Gamma_L \\ |K| = n}} \mathrm{Tr}\, \left(\sum_{r \in \mathbb{Z}^d} 1_{\Gamma+r} B_{K,k_0} R_K 1_\Gamma\right) \\ & + \binom{N-J-1}{n-J-1}^{-1} \sum_{\substack{K \subset \mathbb{Z}^d \cap \Gamma_L \\ |K| = n}} \mathrm{Tr}\, \left(P_{2,K} R_K 1_\Gamma\right) \end{aligned} \tag{3.100}$$

that we will bound successively. We start by the first term. Let $r \in \mathbb{Z}^d$ and denote by $k_1 = \arg\inf_{k \in K \setminus \{k_0\}} \mathrm{d}\left(k, \{r, k_0\}\right)$. We introduce

$$\ell_0(K, r) = |r - k_0|\,, \quad \ell_1(K, r) = \mathrm{d}\left(K \setminus \{k_0\}\,, \{r, k_0\}\right)$$

and

$$\ell_2(K, r) = \mathrm{d}\left(K \setminus \{k_0, k_1\}\,, \{r, k_0, k_1\}\right).$$

When there is no ambiguity, we omit to note the dependence of these quantities on K and r. By Theorem 3.2.3, we first have

$$\left\|1_{\Gamma+r}\left(V_K - V_{\{k_0\}}\right)\right\|_{L^\infty} \leq \left\|1_{\Gamma+r} V_K\right\|_{L^\infty} + \left\|1_{\Gamma+r} V_{\{k_0\}}\right\|_{L^\infty} \leq \frac{C}{(\ell_0+1)^\beta}. \tag{3.101}$$

We now want to control $\left\|1_{\Gamma+r}\left(V_K - V_{\{k_0\}}\right)\right\|_{L^\infty}$ by $1/(\ell_1+1)^\beta$. If $\ell_0 < \ell_1/4^\beta$ (see Figure 3.4), then by Proposition 3.2.6, we have

$$\left\|1_{\Gamma+r}\left(V_K - V_{\{k_0\}}\right)\right\|_{L^\infty} \leq \frac{C}{(\ell_1+1)^\beta}. \tag{3.102}$$

If $\ell_0 \geq \ell_1/4^\beta$, then (3.101) gives

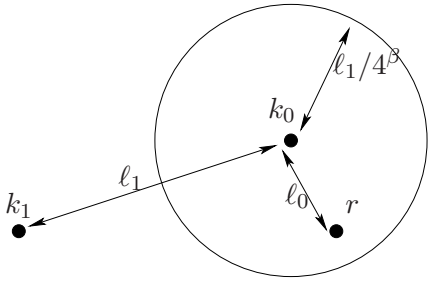

Figure 3.4: A configuration of r, k_0 and k_1 where $\ell_0 \leq \ell_1/4^\beta$ used in the proof of Lemma 3.7.2.

$$\left\|1_{\Gamma+r}\left(V_K - V_{\{k_0\}}\right)\right\|_{L^\infty} \leq \frac{C}{(\ell_0+1)^\beta} \leq \frac{C}{(\ell_1+1)^\beta}. \tag{3.103}$$

Therefore, by (3.101), (3.102) and (3.103),

$$\begin{aligned}\left\|1_{\Gamma+r}\left(V_K - V_{\{k_0\}}\right)\right\|_{L^\infty} &= \left\|1_{\Gamma+r}\left(V_K - V_{\{k_0\}}\right)\right\|_{L^\infty}^{\frac{1}{2}} \times \left\|1_{\Gamma+r}\left(V_K - V_{\{k_0\}}\right)\right\|_{L^\infty}^{\frac{1}{2}} \\ &\leq \frac{C}{(\ell_0+1)^{\frac{\beta}{2}}\,(\ell_1+1)^{\frac{\beta}{2}}}\end{aligned} \tag{3.104}$$

We proceed similarly for the remaining term of A_{K,k_0}. First, as (3.104) holds for any $\beta \geq 0$ and any $K \ni k_0$, then we have for any $k \in K \setminus \{k_0\}$

$$\left\|1_{\Gamma+r}\left(V_{\{k_0,k\}} - V_{\{k_0\}}\right)\right\|_{L^\infty} \leq \frac{C}{(\ell_1+1)^\beta(\ell_0+1)^\beta}. \tag{3.105}$$

Next, if $\ell_0 < |k-k_0|/4^\beta$, then by Proposition 3.2.6, we have

$$\left\|1_{\Gamma+r}\left(V_{\{k_0,k\}}-V_{\{k_0\}}\right)\right\|_{L^\infty} \leq \frac{C}{|k_0-k|^\beta}.$$

Otherwise, by (3.105)

$$\left\|1_{\Gamma+r}\left(V_{\{k_0,k\}}-V_{\{k_0\}}\right)\right\|_{L^\infty} \leq \frac{C}{(\ell_0+1)^\beta} \leq \frac{C}{(|k-k_0|+1)^\beta}.$$

Therefore, reasoning as in (3.104), we have for β large enough

$$\begin{aligned}\left\|\sum_{k\in K\setminus\{k_0\}} 1_{\Gamma+r}\left(V_{\{k_0,k\}}-V_{\{k_0\}}\right)\right\|_{L^\infty} &\leq \sum_{k\in K\setminus\{k_0\}}\left(\left\|1_{\Gamma+r}\left(V_{\{k_0,k\}}-V_{\{k_0\}}\right)\right\|_{L^\infty}^{\frac{1}{2}}\right)^2\\ &\leq \frac{C}{(\ell_1+1)^{\frac{\beta}{2}}(\ell_0+1)^{\frac{\beta}{2}}}\sum_{k\in K\setminus\{k_0\}}\frac{1}{|k_0-k|^{\frac{\beta}{2}}}\\ &\leq \frac{C}{(\ell_1+1)^{\frac{\beta}{2}}(\ell_0+1)^{\frac{\beta}{2}}}. \qquad (3.106)\end{aligned}$$

As (3.106) and (3.104) holds for any $\beta \geq 0$, then by the definition of A_{K,k_0}, we obtain

$$|1_{\Gamma+r}A_{K,k_0}| \leq \frac{C}{(\ell_1+1)^\beta(\ell_0+1)^\beta}. \qquad (3.107)$$

To control A_{K,k_0} by $1/\ell_2^\beta$, we rearrange the terms of A_{K,k_0} as follows

$$A_{K,k_0} = V_K - V_{\{k_0,k_1\}} - \sum_{K\setminus\{k_0,k_1\}}\left(V_{\{k,k_0\}}-V_{\{k_0\}}\right).$$

By Proposition 3.2.6, we thus have

$$|1_{\Gamma+r}A_{K,k_0}| \leq \frac{C}{\ell_2^\beta} + \sum_{k\in K\setminus\{k_0,k_1\}}\frac{C}{|k-k_0|^\beta} \leq \frac{C}{\ell_2^\beta}. \qquad (3.108)$$

As (3.107) and (3.108) hold for any β, then reasoning as in the proof of (3.104) we have

$$\begin{aligned}\mathrm{Tr}\left(|1_\Gamma R_0 1_{\Gamma+r}A_{K,k_0}R_K 1_\Gamma|\right) &\leq \|1_\Gamma R_0 1_{\Gamma+r}\|_{\mathfrak{S}_2}\|1_{\Gamma+r}A_{K,k_0}\|_{L^\infty}\|R_K 1_\Gamma\|_{\mathfrak{S}_2}\\ &\leq C\frac{e^{-C'c_2(z)|r|}}{|\mathrm{Im}(z)|}\frac{1}{(\ell_0+1)^\beta(\ell_1+1)^\beta\ell_2^\beta}\frac{1+|z|}{|\mathrm{Im}(z)|}.\end{aligned}$$

Therefore $\sum_{r\in\mathbb{Z}^d}\mathrm{Tr}\left(|1_\Gamma R_0 1_{\Gamma+r}A_{K,k_0}R_K 1_\Gamma|\right)$ is a convergent series. By Fubini's Theorem, we thus have

$$\begin{aligned}&\sum_{\substack{K\subset\mathbb{Z}^d\cap\Gamma_L\\|K|=n}}\mathrm{Tr}\left(1_\Gamma R_0\Big(\sum_{r\in\mathbb{Z}^d}1_{\Gamma+r}A_{K,k_0}\Big)R_K 1_\Gamma\right)\\ &\qquad = \sum_{r\in\mathbb{Z}^d}\sum_{\substack{K\subset\mathbb{Z}^d\cap\Gamma_L\\|K|=n}}\mathrm{Tr}\left(1_\Gamma R_0 1_{\Gamma+r}A_{K,k_0}R_K 1_\Gamma\right).\end{aligned}$$

To perform the sum over the configurations $K \in \big\{K \subset \mathbb{Z}^d \cap \Gamma_L,\ |K| = n\big\}$, we classify these configurations depending on the value of $\ell_i(r, K)$, $i \in \{0, 1, 2\}$:

$$\begin{aligned}
&\left| \sum_{\substack{K \subset \mathbb{Z}^d \cap \Gamma_L \\ |K| = n}} \mathrm{Tr}\left(1_\Gamma R_0 \Big(\sum_{r \in \mathbb{Z}^d} 1_{\Gamma + r} A_{K,k_0} \Big) R_K 1_\Gamma\right) \right| \\
&\quad \leq \sum_{r \in \mathbb{Z}^d} \sum_{L_0, L_1, L_2 = 0}^{\sqrt{d}L} \sum_{\substack{K \subset \mathbb{Z}^d \cap \Gamma_L,\ |K| = n \\ L_i \leq \ell_i(K,r) < L_i + 1}} C e^{-C' c_2(z)|r|} \left(\frac{1 + |z|}{|\mathrm{Im}(z)|} \right)^2 \frac{1}{\Pi_{i=0}^2 (L_i + 1)^\beta}. \\
&\quad \leq \sum_{r \in \mathbb{Z}^d} \sum_{L_0, L_1, L_2 = 0}^{\sqrt{d}L} C e^{-C' c_2(z)|r|} \left(\frac{1 + |z|}{|\mathrm{Im}(z)|} \right)^2 \frac{N_{L,n,r}(L_0, L_1, L_2)}{\Pi_{i=0}^2 (L_i + 1)^\beta},
\end{aligned}$$

where $N_{L,n,r}(L_0, L_1, L_2)$ is the number of configurations $K \subset \mathbb{Z}^d \cap \Gamma_L$ such that $|K| = n$ and $L_i \leq \ell_i(K, r) < L_i + 1$ for $i \in \{0, 1, 2\}$. This number can be estimated by the asymptotic value $C\binom{N-3}{n-3} \prod_{i=0}^2 L_i^{d-1}$ when $N \to \infty$. Therefore, taking β large enough, we obtain that the first term of the RHS of (3.100) is bounded by

$$\sum_{r \in \mathbb{Z}^d} \sum_{L_0, L_1, L_2 = 1}^{L} C e^{-C' c_2(z)|r|} \left(\frac{1 + |z|}{|\mathrm{Im}(z)|} \right)^2 \frac{1}{\Pi_{i=0}^2 (L_i + 1)^\beta} \leq C \left(\frac{1 + |z|}{|\mathrm{Im}(z)|} \right)^{2+d}.$$

We turn now to the second term of the RHS of (3.100). Let $r \in \mathbb{Z}^d$. With the same techniques used to bound $1_{\Gamma+r} A_{K,k_0}$, we now bound $1_{\Gamma+r} B_{K,k_0}$. Indeed, for any $k, k' \neq k_0$, we have by Theorem 3.2.3 and the same techniques used in the proof of Lemma 3.7.2

$$\begin{aligned}
\left\| 1_{\Gamma+r} \left(V_{\{k,k'\}} - V_{\{k\}} - V_{\{k'\}} \right) \right\|_{L^\infty} &\leq \frac{C}{(\mathrm{d}\,(r, \{k, k'\}) + 1)^\beta \, |k - k'|^\beta} \\
&\leq \frac{C}{(\ell_0(K, r) + 1)^\beta \mathrm{d}\,(r, \{k, k'\})^\beta \, |k - k'|^\beta}.
\end{aligned}$$

It follows that

$$\begin{aligned}
\mathrm{Tr}\ (|1_\Gamma R_0 1_{\Gamma+r} B_{K,k_0} R_K 1_\Gamma|) \leq C &\left(\frac{1 + |z|}{|\mathrm{Im}(z)|} \right)^2 \\
&\times \sum_{\{k,k'\} \subset K \setminus \{k_0\}} \frac{e^{-C' c_2(z)|r|}}{(\ell_0(K, r) + 1)^\beta \mathrm{d}\,(r, \{k, k'\})^\beta \, |k - k'|^\beta}
\end{aligned}$$

and

$$\begin{aligned}
&\left| \sum_{\substack{K\subset\mathbb{Z}^d\cap\Gamma_L\\ |K|=n}} \mathrm{Tr}\,\left(1_\Gamma R_0\left(\sum_{r\in\mathbb{Z}^d} 1_{\Gamma+r}B_{K,k_0}\right)R_K 1_\Gamma\right)\right| \\
&\quad\le C\left(\frac{1+|z|}{|\mathrm{Im}(z)|}\right)^2 \sum_{r\in\mathbb{Z}^d}\sum_{\substack{K\subset\Gamma_L\\ |K|=n}}\sum_{\{k,k'\}\subset K\setminus\{k_0\}} \\
&\qquad\qquad \frac{e^{-C'c_2(z)|r|}}{(\ell_0(K,r)+1)^\beta \mathrm{d}\,(r,\{k,k'\})^\beta\,|k-k'|^\beta} \\
&\quad\le C\left(\frac{1+|z|}{|\mathrm{Im}(z)|}\right)^2 \sum_{r\in\mathbb{Z}^d}\sum_{L_0=0}^{\sqrt{d}L}\sum_{\substack{\{k,k'\}\subset\mathbb{Z}^d\\ |k-r|\le|k'-r|}}\sum_{K\in S_{L,n,r}(L_0,k,k')} \\
&\qquad\qquad \frac{e^{-C'c_2(z)|r|}}{(L_0+1)^\beta(|r-k|+1)^\beta\,|k-k'|^\beta} \\
&\quad\le C\left(\frac{1+|z|}{|\mathrm{Im}(z)|}\right)^2 \sum_{r\in\mathbb{Z}^d}\sum_{L_0=0}^{\sqrt{d}L}\sum_{\substack{\{k,k'\}\subset\mathbb{Z}^d\\ |k-r|\le|k'-r|}} \frac{e^{-C'c_2(z)|r|}N_{L,n,r}(L_0,k,k')}{(L_0+1)^\beta(|r-k|+1)^\beta\,|k-k'|^\beta},
\end{aligned} \tag{3.109}$$

where $N_{L,n,r}(L_0,k,k')$ is the number of configurations in

$$S_{L,n,r}(L_0,k,k') = \Big\{K\subset\mathbb{Z}^d\cap\Gamma_L,\ |K|=n,\ L_0\le\ell_0(K,r)<L_0+1,\\ k,k'\in K\setminus\{k_0(K,r)\}\Big\}.$$

$N_{L,n,r}(L_0,k,k')$ can be estimated by $C\binom{N-3}{n-3}L_0^{d-1}$. Taking β large enough, we thus obtain that the second term of the RHS of (3.100) is bounded by

$$\left|\binom{N-3}{n-3}^{-1}\sum_{\substack{K\subset\mathbb{Z}^d\cap\Gamma_L\\ |K|=n}}\mathrm{Tr}\left(1_\Gamma R_0\Big(\sum_{r\in\mathbb{Z}^d}1_{\Gamma+r}B_{K,k_0}\Big)R_K 1_\Gamma\right)\right| \le C\left(\frac{1+|z|}{|\mathrm{Im}(z)|}\right)^{2+d}. \tag{3.110}$$

We are now left with estimating the last term of (3.100). A straightforward

calculation shows that

$$P_{2,K} = \sum_{k\in K} V_{\{k\}} R_{\{k\}} \left(V_K - V_{\{k\}} - \sum_{k'\in K\setminus\{k\}} \left(V_{\{k,k'\}} - V_{\{k\}}\right)\right) + \sum_{\{k,k'\}\subset K} \left(V_{\{k,k'\}} - V_{\{k\}} - V_{\{k'\}}\right) R_{\{k,k'\}} \left(V_K - V_{\{k,k'\}}\right) + \sum_{\substack{k,k'\in K\\ k\neq k'}} V_{\{k\}} R_{\{k\}} \left(V_{\{k,k'\}} - V_{\{k\}}\right) R_{\{k,k'\}} \left(V_K - V_{\{k,k'\}}\right). \quad (3.111)$$

Using the same techniques as before, we show that

$$\sum_{\substack{K\subset\Gamma_L\\ |K|=n}} |\mathrm{Tr}\ (1_\Gamma R_0 P_{2,K} R_K 1_\Gamma)| \leq C\binom{N-3}{n-3} \left(\frac{1+|z|}{|\mathrm{Im}(z)|}\right)^{4+4d}, \quad (3.112)$$

which concludes the proof of (3.89). Indeed, for example for the first term of the RHS of (3.111), we have for any $k \in K$

$$\left|\mathrm{Tr}\ \left(1_\Gamma R_0 V_{\{k\}} R_{\{k\}} \left(V_K - V_{\{k\}} - \sum_{k'\in K\setminus\{k\}} \left(V_{\{k,k'\}} - V_{\{k\}}\right)\right) R_K 1_\Gamma\right)\right| \leq \left\|1_\Gamma R_0 V_{\{k\}}\right\|_{\mathfrak{S}_2} \left\|R_{\{k\}}\right\|_{\mathcal{B}} \left\| \left(V_K - V_{\{k\}} - \sum_{k'\in K\setminus\{k\}} \left(V_{\{k,k'\}} - V_{\{k\}}\right)\right) R_K 1_\Gamma \right\|_{\mathfrak{S}_2}. \quad (3.113)$$

Using (3.91), we have

$$\left\|1_\Gamma R_0 V_{\{k\}}\right\|_{\mathfrak{S}_2} \leq C\frac{1+|z|}{|\mathrm{Im}(z)|}\left(e^{-C'(\log|k|)^2} + e^{-C'c_2(z)|k|}\right)$$

and

$$\left\|R_{\{k\}}\right\|_{\mathcal{B}} \leq \frac{1}{|\mathrm{Im}(z)|}.$$

For the last term of (3.113), we have by (3.93)

$$\left\| \left(V_K - V_{\{k\}} - \sum_{k'\in K\setminus\{k\}} \left(V_{\{k,k'\}} - V_{\{k\}}\right)\right) R_K 1_\Gamma \right\|_{\mathfrak{S}_2} \leq C\frac{1+|z|}{|\mathrm{Im}(z)|} \times \left(1 + \sum_{k'\in K\setminus\{k\}} \frac{1}{|k-k'|^\beta} + e^{-C'c_2(z)|k-k'|} + \frac{1}{|k'|^\beta} + e^{-C'c_2(z)|k'|}\right) \leq C\left(\frac{1+|z|}{|\mathrm{Im}(z)|}\right)^{1+d}.$$

It follows that

$$\left|\mathrm{Tr}\,\left(1_\Gamma R_0 V_{\{k\}} R_{\{k\}} \left(V_K - V_{\{k\}} - \sum_{k'\in K\setminus\{k\}} \left(V_{\{k,k'\}} - V_{\{k\}}\right)\right) R_K 1_\Gamma\right)\right|$$
$$\leq C\left(\frac{1+|z|}{|\mathrm{Im}(z)|}\right)^{3+d}\left(e^{-C'(\log|k|)^2} + e^{-C'c_2(z)|k|}\right). \tag{3.114}$$

Besides, by (3.92), we have

$$\left|\mathrm{Tr}\,\left(1_\Gamma R_0 V_{\{k\}} R_{\{k\}} \left(V_K - V_{\{k\}} - \sum_{k'\in K\setminus\{k\}} \left(V_{\{k,k'\}} - V_{\{k\}}\right)\right) R_K 1_\Gamma\right)\right|$$
$$\leq \|1_\Gamma R_0\|_{\mathfrak{S}_2}\left\|V_{\{k\}} R_{\{k\}} \left(V_K - V_{\{k\}} - \sum_{k'\in K\setminus\{k\}} \left(V_{\{k,k'\}} - V_{\{k\}}\right)\right)\right\|_{\mathcal{B}} \|R_K 1_\Gamma\|_{\mathfrak{S}_2}$$
$$\leq C\left(\frac{1+|z|}{|\mathrm{Im}(z)|}\right)^3\left(\frac{1}{\ell_0(K\setminus\{k\},k)^\beta} + e^{-C'c_2(z)\ell_0(K\setminus\{k\},k)}\right.$$
$$\left. + \sum_{k'\in K\setminus\{k\}} \frac{1}{|k-k'|^\beta} + e^{-C'c_2(z)|k-k'|}\right)$$
$$\leq C\left(\frac{1+|z|}{|\mathrm{Im}(z)|}\right)^{3+d}\left(\frac{1}{\ell_0(K\setminus\{k\},k)^\beta} + e^{-C'c_2(z)\ell_0(K\setminus\{k\},k)}\right). \tag{3.115}$$

Finally, we introduce $k_0 = k_0(K\setminus\{k\},k)$ and write

$$V_K - V_{\{k\}} - \sum_{k'\in K\setminus\{k\}} \left(V_{\{k,k'\}} - V_{\{k\}}\right) = V_K - V_{\{k,k_0\}} - \sum_{k'\in K\setminus\{k,k_0\}} \left(V_{\{k,k'\}} - V_{\{k\}}\right).$$

Using (3.92), we obtain

$$\left|\mathrm{Tr}\,\left(1_\Gamma R_0 V_{\{k\}} R_{\{k\}} \left(V_K - V_{\{k\}} - \sum_{k'\in K\setminus\{k\}} \left(V_{\{k,k'\}} - V_{\{k\}}\right)\right) R_K 1_\Gamma\right)\right|$$
$$\leq \|1_\Gamma R_0\|_{\mathfrak{S}_2}\left\|V_{\{k\}} R_{\{k\}} \left(V_K - V_{\{k,k_0\}} - \sum_{k'\in K\setminus\{k,k_0\}} \left(V_{\{k,k'\}} - V_{\{k\}}\right)\right)\right\|_{\mathcal{B}} \|R_K 1_\Gamma\|_{\mathfrak{S}_2}$$
$$\leq C\left(\frac{1+|z|}{|\mathrm{Im}(z)|}\right)^3\left(\frac{1}{\ell_1(K\setminus\{k\},k)^\beta} + e^{-C'c_2(z)\ell_1(K\setminus\{k\},k)}\right.$$
$$\left. + \sum_{k'\in K\setminus\{k,k_0\}} \frac{1}{|k-k'|^\beta} + e^{-C'c_2(z)|k-k'|}\right)$$
$$\leq C\left(\frac{1+|z|}{|\mathrm{Im}(z)|}\right)^{3+d}\left(\frac{1}{\ell_1(K\setminus\{k\},k)^\beta} + e^{-C'c_2(z)\ell_1(K\setminus\{k\},k)}\right). \tag{3.116}$$

Therefore, reasoning as in the proof of (3.106), we find

$$\left|\mathrm{Tr}\,\left(1_\Gamma R_0 V_{\{k\}} R_{\{k\}}\left(V_K - V_{\{k\}} - \sum_{k'\in K\setminus\{k\}}\left(V_{\{k,k'\}} - V_{\{k\}}\right)\right) R_K 1_\Gamma\right)\right| \\ \leq C\left(\frac{1+|z|}{|\mathrm{Im}(z)|}\right)^{3+d} f(|k|)^{\frac{1}{3}} f(\ell_0(K\setminus\{k\},k))^{\frac{1}{3}} f(\ell_1(K\setminus\{k\},k))^{\frac{1}{3}},$$

where $f(R) = 1/R^\beta + e^{-C'c_2(z)R}$ is the function appearing in the RHS of (3.114), (3.115) and (3.116). Proceeding in the same way than in the proof of (3.109) and (3.110), we obtain

$$\left|\binom{N-3}{n-3}^{-1} \sum_{\substack{K\subset\mathbb{Z}^d\cap\Gamma_L \\ |K|=n}} \mathrm{Tr}\,\left(1_\Gamma R_0 P_{2,1,K} R_K 1_\Gamma\right)\right| \leq \left(\frac{1+|z|}{|\mathrm{Im}(z)|}\right)^{3+4d},$$

where we have denoted the first term of the RHS of (3.111) by $P_{1,2,K}$ We proceed similarly for the other terms of the RHS of (3.111) to obtain (3.112). This concludes the proof of the proposition.

□

3.A Decay estimates in the whole space

In this section, we give a decay estimates in the whole space of the solution of the rHF equation for crystals with local defects, far from the support of the defect. In particular, we show that $\rho_\nu \in L^1(\mathbb{R}^d)$. This decay is due to the short-range character of the Yukawa interaction, as in the Coulomb case, it has been proved in [33] that for anisotropic materials, $\rho_\nu \notin L^1(\mathbb{R}^d)$.

Theorem 3.A.1. *There exist $\alpha, \alpha_c, C' > 0$ and $C \geq 0$ such that for any $\nu \in L^2_c(\mathbb{R}^d)$ satisfying $\|\nu\|_{L^2_{\mathrm{unif}}} \leq \alpha_c$ and $\|\nu\|_{H^{-1}} \leq \alpha$, we have for $R \geq 2$*

$$\|V_\nu\|_{H^2(\mathbb{R}^d\setminus C_R(\nu))} + \|\rho_\nu\|_{L^2(\mathbb{R}^d\setminus C_R(\nu))} \leq Ce^{-C'(\log R)^2}\|\nu\|_{L^2(\mathbb{R}^d)}. \quad (3.117)$$

We recall that by [24, Prop. 1, Cor. 2], that in this case the density ρ_ν satisfies

$$\|\rho_\nu - \rho_{\gamma_0}\|_{L^2} \leq C\left\|(-\Delta+1)^{\frac{1}{2}}(\gamma_\nu - \gamma_0)\right\|_{\mathfrak{S}_2} \leq C\left(\|\nu\|_{H^{-1}} + \|\nu\|^2_{H^{-1}}\right). \quad (3.118)$$

Proof of (3.117). We use the notation ρ to denote the mean-field density $\rho_\nu = \rho_{\gamma_\nu-\gamma_0}$, the solution of (3.66), and denote by $V = V_\nu = Y_m * (\rho - \nu)$. Recall the decomposition (3.65) of ρ in a linear term and a higher order term

$$\rho = -\mathcal{L}(\rho-\nu) + \rho_{\widetilde{Q}_{2,\rho-\nu}}. \quad (3.119)$$

Using localizing functions, we will show that each of the terms of the RHS of (3.119) decays far from the support of ν. To do so, let us introduce the set $I = \left\{k \in \mathbb{Z}^d,\ \mathrm{supp}(\nu) \cap B(0,1) + k \neq \emptyset\right\}$ and for $R \geq 1$, the set $B_R = B_{I,R} = \cup_{k\in I}\left(B(0,R)+k\right)$ and the the function $\chi_R = \chi_{I,R}$ defined in Lemma 3.3.4. They satisfy $0 \leq \chi_R \leq 1$, $\chi_R \equiv 1$ on B_R, $\chi_R \equiv 0$ outside B_{2R} and $R\left|\nabla\chi_R(x)\right| + R^2\left|\Delta\chi_R(x)\right| \leq C$ for a constant $C \geq 0$ independent of the set I (thus independent of ν). We denote by $\eta_R = 1 - \chi_R$. We thus have

$$\begin{aligned}\eta_R\rho &= -\eta_R\mathcal{L}(\rho-\nu) + \eta_R\rho_{\widetilde{Q}_{2,\rho-\nu}}\\ &= -\mathcal{L}\eta_R(\rho-\nu) + \left[\mathcal{L},\eta_R\right](\rho-\nu) + \eta_R\rho_{\widetilde{Q}_{2,\rho-\nu}}.\end{aligned}$$

As for $R \geq 1$, $\eta_R\nu = 0$, it follows

$$\eta_R\rho = \frac{1}{(1+\mathcal{L})}\left[\mathcal{L},\eta_R\right](\rho-\nu) + \frac{1}{(1+\mathcal{L})}\eta_R\rho_{\widetilde{Q}_{2,\rho-\nu}}. \tag{3.120}$$

We will bound successively each term of the RHS of (3.120). For the first term, we have by Lemma 3.3.4 for $R \geq 2$,

$$\begin{aligned}\left\|\left[\mathcal{L},\eta_R\right](\rho-\nu)\right\|_{L^2} &\leq \frac{C}{R}\left(e^{-C'R}\left\|\rho-\nu\right\|_{L^2} + \left\|1_{B_{3R}\setminus B_{R/2}}(\rho-\nu)\right\|_{L^2}\right)\\ &\leq \frac{C}{R}\left(e^{-C'R}\left\|\nu\right\|_{L^2} + \left\|1_{B_{3R}\setminus B_{R/2}}\rho\right\|_{L^2}\right),\end{aligned}$$

where we have used that $1_{B_{3R}\setminus B_{R/2}}\nu = 0$ for $R \geq 2$, that ρ is controlled by ν in the L^2 norm (see (3.118)) and that $\left\|\nu\right\|_{H^{-1}} \leq C\left\|\nu\right\|_{L^2} \leq C\alpha$. As $1/(1+\mathcal{L})$ is bounded on $L^2(\mathbb{R}^d)$, we obtain

$$\left\|\frac{1}{(1+\mathcal{L})}\left[\mathcal{L},\eta_R\right](\rho-\nu)\right\|_{L^2} \leq \frac{C}{R}\left(e^{-C'R}\left\|\nu\right\|_{L^2} + \left\|1_{B_{3R}\setminus B_{R/2}}\rho\right\|_{L^2}\right). \tag{3.121}$$

As to the second term of the RHS of (3.120), since $1_{\mathbb{R}^d\setminus B_R}\eta_R = \eta_R$, we have

$$\begin{aligned}\eta_R\widetilde{Q}_{2,\rho-\nu} &= \frac{1}{2i\pi}\oint_{\mathcal{C}}\eta_R\frac{1}{z-H_0}V\frac{1}{z-H_0}V\frac{1}{z-H}dz\\ &= \frac{1}{2i\pi}\oint_{\mathcal{C}}\frac{1}{z-H_0}\eta_R V\frac{1}{z-H_0}V\frac{1}{z-H}\\ &\quad + \left[\eta_R,\frac{1}{z-H_0}\right]V\frac{1}{z-H_0}V\frac{1}{z-H}dz\\ &= \frac{1}{2i\pi}\oint_{\mathcal{C}}\frac{1}{z-H_0}1_{\mathbb{R}^d\setminus B_R}V\frac{1}{z-H_0}\eta_R V\frac{1}{z-H}dz\\ &+ \frac{1}{2i\pi}\oint_{\mathcal{C}}\frac{1}{z-H_0}1_{\mathbb{R}^d\setminus B_R}V\left[\eta_R,\frac{1}{z-H_0}\right]V\frac{1}{z-H}dz\\ &+ \frac{1}{2i\pi}\oint_{\mathcal{C}}\left[\eta_R,\frac{1}{z-H_0}\right]V\frac{1}{z-H_0}V\frac{1}{z-H}dz,\end{aligned} \tag{3.122}$$

where $H = H_0 + V$ and $\mathcal{C}$ is as in the previous section. We recall that by the assumption $\|\nu\|_{L^2_{\text{unif}}} \leq \alpha_c$, the operator H has a gap around 0, thus the operator $(z-H)^{-1}(-\Delta+1)$ and its inverse are uniformly bounded on $\mathcal{C}$ and all the estimates obtained in the previous sections hold when we replace H_0 by H. We denote by r_3, r_4 and r_5 the densities associated with the three operators of the RHS of (3.122) respectively. With the same duality argument as we have used before, we have

$$\|r_3\|_{L^2} \leq C \left\| 1_{\mathbb{R}^d \setminus B_R} V \right\|_{L^2} \|V \eta_R\|_{H^2} .$$

By (3.27) in Lemma 3.3.4, we have that

$$\begin{aligned} \|\eta_R V\|_{H^2} \leq & \|Y_m * (\eta_R (\rho - \nu))\|_{H^2} \\ & + \frac{C}{R} e^{-C'R} \|\rho - \nu\|_{L^2} + \frac{C}{R} \left\| 1_{B_{3R} \setminus B_{R/2}} (\rho - \nu) \right\|_{L^2} . \end{aligned} \tag{3.123}$$

Therefore, for $R \geq 2$, $\eta_R \nu = 0$ and

$$\begin{aligned} \|r_3\|_{L^2} \leq & \left\| 1_{\mathbb{R}^d \setminus B_R} V \right\|_{L^2} \left(C \|Y_m * (\eta_R \rho)\|_{H^2} + \frac{C}{R} e^{-C'R} \|\nu\|_{L^2} \right. \\ & \left. + \frac{C}{R} \left\| 1_{B_{3R} \setminus B_{R/2}} \rho \right\|_{L^2} \right) \\ \leq & \left\| 1_{\mathbb{R}^d \setminus B_R} V \right\|_{L^2} \left(C_1 \|\eta_R \rho\|_{L^2} + \frac{C}{R} e^{-C'R} \|\nu\|_{L^2} + \frac{C}{R} \left\| 1_{B_{3R} \setminus B_{R/2}} \rho \right\|_{L^2} \right) . \end{aligned}$$

To bound r_4 and r_5, we recall that we have shown in (3.49), (3.51) and (3.57) in the proof of Lemma 3.3.4 that for any $A \in \mathfrak{S}_2(L^2(\mathbb{R}^d))$ and any $f \in L^2(\mathbb{R}^d)$

$$\left\| \rho_{(-\Delta+1)^{-\frac{1}{2}} A (-\Delta+1)^{-\frac{1}{2}}} \right\|_{L^2} \leq C \|A\|_{\mathfrak{S}_2}$$

and

$$\begin{aligned} \left\| (-\Delta+1)^{-\frac{1}{2}} [\eta_R, \Delta] \frac{1}{z - H_0} Y_m * f (-\Delta+1)^{-\frac{1}{2}} \right\|_{\mathfrak{S}_2} \leq & \frac{C}{R} e^{-C'R} \|f\|_{L^2} \\ & + \frac{C}{R} \left\| 1_{B_{3R} \setminus B_{R/2}} f \right\|_{L^2} . \end{aligned}$$

Therefore, using again the equality
$\left[\eta_R, (z-H_0)^{-1}\right] = -(z-H_0)^{-1} [\eta_R, \Delta] (z-H_0)^{-1}$, we obtain that for any $R \geq 2$,

$$\begin{aligned} \|r_4\|_{L^2} \leq & C \oint_{\mathcal{C}} \left\| (-\Delta+1)^{-\frac{1}{2}} 1_{\mathbb{R}^d \setminus B_R} V (-\Delta+1)^{-\frac{1}{2}} \right\|_{\mathfrak{S}_2} \\ & \times \left\| (-\Delta+1)^{-\frac{1}{2}} [\eta_R, \Delta] \frac{1}{z - H_0} V (-\Delta+1)^{-\frac{1}{2}} \right\|_{\mathfrak{S}_2} dz \\ \leq & \left\| 1_{\mathbb{R}^d \setminus B_R} V \right\|_{L^2} \left(\frac{C}{R} e^{-C'R} \|\nu\|_{L^2} + \frac{C}{R} \left\| 1_{B_{3R} \setminus B_{R/2}} \rho \right\|_{L^2} \right) \end{aligned}$$

and, similarly,

$$\|r_5\|_{L^2} \leq C \|V\|_{L^2} \left(\frac{C}{R} e^{-C'R} \|\nu\|_{L^2} + \frac{C}{R} \left\| 1_{B_{3R} \setminus B_{R/2}} \rho \right\|_{L^2} \right).$$

Using that

$$\begin{aligned} \left\| 1_{\mathbb{R}^d \setminus B_R} V \right\|_{L^2} \leq \|V\|_{L^2} \leq C \|\rho - \nu\|_{H^{-1}} &\leq C_0 \|\nu\|_{H^{-1}} \left(1 + \|\nu\|_{H^{-1}}\right) \\ &\leq C_0 \alpha \left(1 + \alpha\right), \end{aligned}$$

we obtain,

$$\begin{aligned} \left\| \eta_R \rho_{\widetilde{Q}_{2,\rho-\nu}} \right\|_{L^2} \leq C_1 \left\| 1_{\mathbb{R}^d \setminus B_R} V \right\|_{L^2} \|\eta_R \rho\|_{L^2} + \frac{C}{R} e^{-C'R} \|\nu\|_{L^2} \\ + \frac{C}{R} \left\| 1_{B_{3R} \setminus B_{R/2}} \rho \right\|_{L^2}. \end{aligned}$$

Using once more that $1/(1+\mathcal{L})$ is bounded on $L^2(\mathbb{R}^d)$, we deduce the following bound on the second term of the RHS of (3.120)

$$\begin{aligned} \left\| \frac{1}{1+\mathcal{L}} \eta_R \rho_{\widetilde{Q}_{2,\rho-\nu}} \right\|_{L^2} \leq C_1 \left\| 1_{\mathbb{R}^d \setminus B_R} V \right\|_{L^2} \|\eta_R \rho\|_{L^2} + \frac{C}{R} e^{-C'R} \|\nu\|_{L^2} \\ + \frac{C}{R} \left\| 1_{B_{3R} \setminus B_{R/2}} \rho \right\|_{L^2}. \end{aligned} \tag{3.124}$$

Gathering (3.120), (3.121) and (3.124), we obtain

$$\|\eta_R \rho\|_{L^2} \leq C_1 \left\| 1_{\mathbb{R}^d \setminus B_R} V \right\|_{L^2} \|\eta_R \rho\|_{L^2} + \frac{C}{R} e^{-C'R} \|\nu\|_{L^2} + \frac{C}{R} \left\| 1_{B_{3R} \setminus B_{R/2}} \rho \right\|_{L^2}.$$

Let α be small enough so that $C_1 C_0 \alpha(1+\alpha) \leq 1/2$. Thus $C_1 \left\| 1_{\mathbb{R}^d \setminus B_R} V \right\|_{L^2} \leq 1/2$ for any $R \geq 2$ and

$$\|\eta_R \rho\|_{L^2} \leq \frac{C}{R} e^{-C'R} \|\nu\|_{L^2} + \frac{C}{R} \left\| 1_{B_{3R} \setminus B_{R/2}} \rho \right\|_{L^2}.$$

We have a similar inequality for V. Indeed, by (3.123), we have

$$\begin{aligned} \|\eta_R V\|_{H^2} &\leq \|Y_m * (\eta_R (\rho - \nu))\|_{H^2} + \frac{C}{R} e^{-C'R} \|\rho - \nu\|_{L^2} \\ &\quad + \frac{C}{R} \left\| 1_{B_{3R} \setminus B_{R/2}} (\rho - \nu) \right\|_{L^2} \\ &\leq \|\eta_R (\rho - \nu)\|_{L^2} + \frac{C}{R} e^{-C'R} \|\nu\|_{L^2} + \frac{C}{R} \left\| 1_{B_{3R} \setminus B_{R/2}} \rho \right\|_{L^2} \\ &\leq \frac{C}{R} e^{-C'R} \|\nu\|_{L^2} + \frac{C}{R} \left\| 1_{B_{3R} \setminus B_{R/2}} \rho \right\|_{L^2}. \end{aligned} \tag{3.125}$$

Using Lemma 3.3.5 with x_R to $\left\|1_{\mathbb{R}^d\setminus B_R}\rho\right\|_{L^2}$ and $\left\|1_{\mathbb{R}^d\setminus B_R}V\right\|_{H^2}$, we obtain

$$\|\eta_R\rho\|_{L^2} \leq Ce^{-C'(\log R)^2}\|\nu\|_{L^2(\mathbb{R}^d)}\,. \tag{3.126}$$

Inserting (3.126) into (3.125), we get

$$\|\eta_R V\|_{H^2} \leq Ce^{-C'(\log R)^2}\|\nu\|_{L^2(\mathbb{R}^d)}\,.$$

Finally, noticing that $1_{\mathbb{R}^d\setminus C_R(\nu)} \leq \eta_{R/2}$, we conclude the proof of (3.117). □

Chapter 4

Numerical simulation of stochastic crystals

We present in this chapter the numerical results obtained from the simulation of one-dimensional stochastic systems.

Contents

4.1 Introduction

The numerical simulation of materials is a useful tool in the understanding of their properties.

In this study, we are interested in computing the electronic ground state and ground state properties in the Born-Oppenheimer approximation [16] of disordered materials. We concentrate on the random linear model and the random reduced Hartree-Fock (rHF) model presented in Sections 1.5.1 and 1.5.2.

In linear empirical models and mean-field models, a system with N_e electrons is described by the one-body Hamiltonian

$$H = -\frac{1}{2}\Delta + V.$$

In the linear setting, the effective potential V is prescribed by the model, while it is obtained by solving a self-consistent equation in the mean-field theory. In the rHF model with Yukawa interaction Y_m, the mean-field potential V depends on the ground state density matrix γ of the system as follows

$$V = Y_m * (\rho_\gamma - \mu), \tag{4.1}$$

where formally $\rho_\gamma(x) = \gamma(x, x)$, μ is the nuclear density and Y_m is the inverse Fourier transform of $K \mapsto 4\pi(1 + |K|^2)^{-1}$. Under suitable assumptions on V and μ, the operator H is self-adjoint and bounded below on $L^2(\mathbb{R}^d)$ with domain $H^2(\mathbb{R}^d)$, $d \in \{1, 2, 3\}$ being the space dimension. In both cases, the ground state density matrix of the system is given by

$$\gamma = \sum_{i=1}^{N_e} |\varphi_i\rangle\langle\varphi_i| , \tag{4.2}$$

where $(\varphi_i)_{1\leq i\leq N_e}$ are the eigenfunctions corresponding to the smallest N_e eigenvalues $\lambda_1 \leq \cdots \leq \lambda_{N_e}$, counting multiplicities, of the operator H. Here we have assumed that $\lambda_{N_e} < \lambda_{N_e+1}$. In the linear model, approximating the ground state of the system boils down to computing the eigenmodes of the Hamiltonian H. For the rHF model, one needs, in addition, to solve the self-consistent equation (4.1)-(4.2).

To approximate the eigenmodes of H, a Galerkin method is often used. It consists in finding the eigenmodes of H_N, the restriction of H to an N-dimensional subspace X_N of $H^1(\mathbb{R}^d)$. The choice of the subspace X_N is crucial for the quality of the results. The most commonly used bases in quantum chemistry consist of Atomic Orbitals [32].

The "natural" algorithm to solve (4.1)-(4.2) is to use a fixed point procedure, that is, to start with an initial state γ^0, to calculate V^0 using (4.1) and to calculate recursively γ^k and V^k as follows

$$\gamma^k = 1\left(-\frac{1}{2}\Delta + V^{k-1} \leq \lambda_{N_e}^{k-1}\right) \tag{4.3}$$

and

$$V^k = Y_m * (\rho_{\gamma^k} - \mu),$$

where $\lambda_{N_e}^{k-1}$ is the ${N_e}^{\text{th}}$ eigenvalue of $-\frac{1}{2}\Delta + V^{k-1}$. In practice, (4.3) is solved using a Galerkin method, as for the linear model. This algorithm, called the *Roothaan* algorithm [136], gives good results in certain situations such as closed shells atoms, but, in many other situations, this algorithm does not converge. We refer to the recent work [100] on the convergence of the Roothaan algorithm.

An alternative approach, called *Relaxed Constrained Algorithms*, consists in finding γ as a minimizer of

$$\inf\left\{\mathcal{E}_\mu^{\mathrm{rHF}}(\gamma),\ \gamma\in\mathcal{K}_{N_e}\right\},\quad \mathcal{K}_{N_e}=\{\gamma^*=\gamma,\ 0\le\gamma\le 1,\ \mathrm{Tr}\ (\gamma)=N_e\} \tag{4.4}$$

rather than a minimizer of

$$\inf\left\{\mathcal{E}_\mu^{\mathrm{rHF}}(\gamma),\ \gamma\in\mathcal{P}_{N_e}\right\},\quad \mathcal{P}_{N_e}=\left\{\gamma^*=\gamma,\ \gamma^2=\gamma,\ \mathrm{Tr}\ (\gamma)=N_e\right\}, \tag{4.5}$$

where we recall that $\mathcal{E}_\mu^{\mathrm{rHF}}(\gamma)$ is the rHF energy functional defined by

$$\mathcal{E}_\mu^{\mathrm{rHF}}(\gamma)=\frac{1}{2}\mathrm{Tr}\ (-\Delta\gamma) + \frac{1}{2}\int_{\mathbb{R}^d\times\mathbb{R}^d}(\rho_\gamma(x)-\mu(x))\,Y_m(x-y)\,(\rho_\gamma(y)-\mu(y))\,dx\,dy.$$

Problems (4.4) and (4.5) are known to have the same minimizer γ given by (4.2) under the gap condition $\lambda_{N_e}<\lambda_{N_e+1}$. The simplest of such algorithms is the *Optimal Damping Algorithm* (ODA) introduced in [30]. Each iteration of ODA consists of two steps: find a descent direction (this step turns out to be exactly equivalent to a Roothaan iteration) which gives a projector $\widetilde{\gamma}^{k+1}\in\mathcal{P}_{N_e}$, and do a line search to find γ^{k+1}, the minimizer of $\mathcal{E}_\mu^{\mathrm{rHF}}(\gamma)$ on the segment $[\gamma^k,\widetilde{\gamma}^{k+1}]$. The cost of one iteration of ODA is the same as that of one iteration of the Roothaan algorithm since the optimization step can be done analytically at a negligible cost (see Section 4.3). The ODA has been proved to converge to a local minimum when used for the Hartree-Fock model and has showed in practice very nice convergence properties [31].

For perfect crystals, the Hamiltonian of the system is of the form

$$H_{\mathrm{per}}=-\frac{1}{2}\Delta+V_{\mathrm{per}}$$

where V_{per} is an $\mathcal{R}$-periodic function, with $\mathcal{R}$ the underlying periodic lattice. In the following we take $\mathcal{R}=\mathbb{Z}^d$ for simplicity and denote by $\Gamma=[0,1)^d$ the unit cell. As in the molecular case, the potential V_{per} is prescribed in the linear model and obtained by a self-consistent equation in the rHF model. The self-consistent equation can be solved using the ODA for example. To compute the eigenmodes of H_{per}, Bloch theory [133] is often used. It consists in decomposing H_{per} as the direct sum

$$H_{\mathrm{per}}=\int_{\Gamma^*}^{\oplus}H_q\,dq,$$

where $\Gamma^*=[0,2\pi)^d$ is the reciprocal unit cell, called the *Brillouin* zone, and $H_q=-\frac{1}{2}\left(\nabla+iq\right)^2+V_{\mathrm{per}}$ is a bounded below self-adjoint operator on $L^2(\Gamma)$

with periodic boundary conditions, which has a compact resolvent. The spectrum of H_q is thus purely discrete and can be easily computed using a planewave (Fourier) discretization of $L^2(\Gamma)$.

For crystals with local defects, the Hamiltonian of the system is of the form

$$H = -\frac{1}{2}\Delta + V_{\text{per}} + W, \tag{4.6}$$

where V_{per} is a $\mathbb{Z}^d$-periodic function corresponding to the mean-field potential of the host crystal and W is a perturbation going to zero at infinity. Under reasonable integrability assumptions on V_{per} and W, W is H_{per}-compact, so that H has the same essential spectrum as H_{per}. But H may have discrete eigenvalues below the essential spectrum or in the spectral gaps (see Figure 4.1).

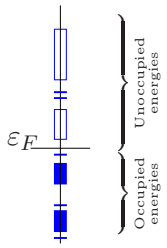

Figure 4.1: The spectrum of the mean field operator H in presence of a local defect.

The eigenvalues of H that are below the essential spectrum can be easily obtained by standard variational methods in view of Rayleigh-Ritz theorem. On the other hand, the computation of the eigenvalues that are in spectral gaps is more delicate. Indeed, a Galerkin approximation for instance can lead to the phenomenon of *spectral pollution* [99, 19, 104], that is, some sequence (λ_N) of eigenvalues of (H_N) may converge to a real number that does not belong to the spectrum of H.

The state-of-the-art method to compute the spectrum of operators of the form (4.6) is the *supercell* method. It consists in considering a large box Γ_L, containing the defect, with periodic boundary conditions. In a recent article [27], Cancès, Ehrlacher and Maday prove that using the supercell method with a planewave discretization gives no spectral pollution. This follows previous results in [104, 18]. The drawbacks of this method is that it cannot model a charged defect with Coulomb interaction (one always needs to add a jellium background to compensate charged defects) and induces spurious interactions between the defect and its periodic images. Several numerical methods have been proposed in the physics literature to improve the performance rate of the supercell method when used with charged defects.

We mention the work of Freysoldt, Neugebauer and van de Walle [51, 52] for recent developments.

To solve the rHF model with local defects, one may use the ODA together with the supercell model. An alternative approach has been proposed in [25], based on the rHF theory for local defects introduced in [24]. This approach consists in treating the defect as a quasi-particle embedded in the host crystal and to discretize the difference $\gamma - \gamma_0$ using localized Wannier functions of the perfect crystal.

In this thesis, we have simulated one-dimensional stochastic systems within the random linear model and the random rHF model with the Yukawa interaction. We have used the methods mentioned above, namely, the supercell method with planewave discretization, ODA, and Monte-Carlo method. The purpose of these simulations is, on the one hand, to illustrate some of the theoretical results discussed in Sections 1.5.1-1.5.3 and, on the other hand, to try to understand some points that have been left open in the theoretical investigation.

We simulate random alloys resulting from the combination of two perfect crystals. Specifically, we suppose that at each site $k \in \mathbb{Z}$, there is a probability p to see the first kind of crystal and a probability $1-p$ to see the second type of crystal, independently of what is happening in the other sites (see Figure 4.2). The Hamiltonian of the system is of the form

Figure 4.2: Example of an alloy in 1 dimension.

$$H(\omega) = -\frac{1}{2}\frac{d^2}{dx^2} + V(\omega, x),$$

where the potential V is a stationary function (see Chapter 2).

For each realization ω in the probability space Ω, we simulate the system using the supercell model, which consists in restricting $H(\omega)$ to the box $\Gamma_L = [0, L)$, where $L \in \mathbb{N} \setminus \{0\}$, and imposing periodic boundary conditions. The corresponding Hamiltonian is then

$$H_L = -\frac{1}{2}\frac{d^2}{dx^2} + V_L,$$

where V_L is the $L\mathbb{Z}$-periodic potential which is equal to $V(\omega, \cdot)$ on Γ_L. For a number of electrons N_e per unit volume, the ground state of the system is given by

$$\gamma_L = \sum_{n=1}^{N_e L} |u_{L,n}\rangle\langle u_{L,n}|\,, \tag{4.7}$$

where $(u_{L,n})_{1\leq n\leq N_e L}$ is an orthonormal family of eigenvectors corresponding to the smallest eigenvalues $\lambda_{L,1} \leq \cdots \leq \lambda_{L,N_e L}$ of H_L. To compute the eigenmodes of H_L, we discretize the space $H^1(\Gamma_L)$ using a planewave basis, which is well adapted to the periodic setting. We explain this discretization in Section 4.2 below. In the rHF framework with Yukawa interaction, the potential V_L is given by

$$V_L = Y_m * (\rho_{\gamma_L} - \mu_L), \tag{4.8}$$

where μ_L is the $L\mathbb{Z}$-periodic function which is equal to the nuclear distribution $\mu(\omega, \cdot)$ on Γ_L and $Y_m(x) = e^{-m|x|}/m$. We use the ODA to solve the self-consistent equation (4.7)-(4.8). This is explained in Section 4.3.

Once we obtain the eigenmodes of the Hamiltonian, we can calculate quantities of interest to our study. We are first interested in the convergence of the energy per unit volume and the integrated density of states in the thermodynamic limit, that is, when $L \to \infty$. For the linear model, these convergences have been proved in [89, Th. 5.1]. For the rHF model, the convergence of the energy per unit volume has been proved in [29, Th. 5.2] [Th. 2.5.2 Chapter 2]. See Section 4.4.3 for the numerical results.

We next study the localization properties of the Hamiltonian. As the spectrum of H_L is always discrete, we characterize it by observing "how much" the corresponding eigenfunctions are localized. We use a variance-based criterion that will be explained in Section 4.4.4. As predicted by the theory, we observe that, in the linear model, there is localization at all energies when there is disorder ($p \in (0, 1)$) and absence of localization in perfect crystals ($p \in \{0, 1\}$). In the rHF model, we are not aware of any theoretical results on the localization properties of the mean-field Hamiltonian. Our results (see Section 4.4.4) do not allow us to conclude whether there is localization or not.

Finally, in Section 4.4.5, we simulate crystals with a low concentration of random defects and study the behavior of the integrated density of states as a function of the Bernoulli parameter p, in the limit $p \to 0$.

4.2 Solving the supercell model

In this section, we explain how we compute the eigenmodes of the Hamiltonian $H_L = -\frac{1}{2}\frac{d^2}{dx^2} + V_L$, for a given $L\mathbb{Z}$-periodic potential V_L. We suppose that V_L is given by its Fourier coefficients $c_K^L(V_L)$ for $K \in \frac{2\pi}{L}\mathbb{Z}$.

For $N \in \mathbb{N} \setminus \{0\}$, we introduce the discretization space

$$X_N = \operatorname{span}\{f_j,\ 0 \leq j \leq NL\}$$

where

$$f_j(x) = \frac{1}{\sqrt{L}} e^{2i\pi(j - \frac{NL}{2})\frac{x}{L}}.$$

The restriction $H_{L,N}$ of H_L to X_N is given, for any $0 \leq j,k \leq NL$, by the matrix

$$(H_{L,N})_{j,k} = \langle f_j, H_L f_k \rangle_{L^2(\Gamma_L)} = \frac{1}{2}\langle f_j', f_k' \rangle_{L^2(\Gamma_L)} + \langle f_j, V_L f_k \rangle_{L^2(\Gamma_L)}.$$

An easy calculation shows that

$$\begin{aligned}\frac{1}{2}\langle f_j', f_k' \rangle_{L^2(\Gamma_L)} &= \frac{1}{2}\frac{4\pi^2}{L^2}\left(k - \frac{NL}{2}\right)^2 \langle f_j, f_k \rangle_{L^2(\Gamma_L)} \\ &= \frac{2\pi^2}{L^2}\left(k - \frac{NL}{2}\right)^2 \delta_{j=k}.\end{aligned}$$

Besides,

$$\langle f_j, V_L f_k \rangle_{L^2(\Gamma_L)} = \frac{1}{L}\int_0^L V(x) e^{-2i\pi(j-k)x} = \frac{1}{\sqrt{L}} c^L_{j-k}(V_L).$$

We denote by $\lambda_{N,1} \leq \cdots \leq \lambda_{N,NL+1}$ the eigenvalues of the $(NL+1) \times (NL+1)$ matrix $H_{L,N}$ and by $(u_{N,n}(\cdot))_{1 \leq n \leq NL+1}$ the corresponding eigenvectors.

The eigenvalues of $H_{L,N}$ are known to converge, as $N \to \infty$, to those of H_L and the eigenvectors of H_L are the limits of

$$v_{N,n}(x) = \sum_{j=1}^{NL+1} u_{N,n}(j) f_j(x).$$

Therefore, the kernel of γ_L is approximated by

$$\begin{aligned}\gamma_{L,N}(x,y) &= \sum_{n=1}^{N_e L} v_{N,n}(x)\overline{v_{N,n}(y)} \\ &= \sum_{n=1}^{N_e L}\left(\sum_{j=1}^{NL+1} u_{N,n}(j) f_j(x)\right)\left(\overline{\sum_{k=1}^{NL+1} u_{N,n}(k) f_k(y)}\right) \\ &= \frac{1}{L}\sum_{n=1}^{N_e L}\sum_{j,k=1}^{NL+1} u_{N,n}(j)\overline{u_{N,n}(k)} e^{2i\pi\left(j-\frac{NL}{2}\right)\frac{x}{L}} e^{-2i\pi\left(k-\frac{NL}{2}\right)\frac{y}{L}}\end{aligned}$$

and the density associated with γ_L is approximated by

$$\begin{aligned}\rho_{L,N}(x) &= \sum_{n=1}^{N_eL}\left|\sum_{j=1}^{NL+1} u_{N,n}(j)f_j(x)\right|^2 \\ &= \frac{1}{L}\sum_{n=1}^{N_eL}\left|\sum_{j=1}^{NL+1} u_{N,n}(j)e^{2i\pi\left(j-\frac{NL}{2}\right)\frac{x}{L}}\right|^2 \\ &= \frac{1}{L}\sum_{n=1}^{N_eL}\sum_{j,j'=1}^{NL+1} u_{N,n}(j)\overline{u_{N,n}(j')}e^{2i\pi(j-j')\frac{x}{L}} \\ &= \frac{1}{\sqrt{L}}\sum_{K=-NL}^{NL} c_{N,K}^L(\rho)e^{-2i\pi K\frac{x}{L}},\end{aligned}$$

where

$$c_{N,K}^L(\rho) = \frac{1}{\sqrt{L}}\sum_{n=1}^{N_eL}\sum_{j,j'=1}^{NL+1}\delta_{j'-j=K}u_{N,n}(j)\overline{u_{N,n}(j')}. \tag{4.9}$$

The coefficients $c_{N,K}^L(\rho)$ will be used as an approximation of the Fourier coefficients of the electronic density ρ.

4.3 Optimal Damping Algorithm

We explain in this section how to use the ODA to find an approximation of the ground state of the rHF supercell model. Given an $L\mathbb{Z}$-periodic nuclear density μ, we recall that the rHF supercell energy functional is

$$\mathcal{E}_{\mu,L}^{\mathrm{rHF}}(\gamma) = \frac{1}{2}\mathrm{Tr}_L\left(-\Delta_L\gamma\right) + \frac{1}{2}D_{m,L}(\rho_\gamma-\mu,\rho_\gamma-\mu),$$

where Tr_L is the trace in $L^2(\Gamma_L)$ with periodic boundary conditions, Δ_L is the $L\mathbb{Z}$-periodic Laplacian on Γ_L, and $D_{m,L}$ is defined for any $L\mathbb{Z}$-periodic functions f and g by

$$D_{m,L}(f,g) = a_p\sum_{K\in\frac{2\pi}{L}\mathbb{Z}}\frac{\overline{c_K^L(f)}c_K^L(g)}{m^2+|K|^2}.$$

Here, a_p is a multiplication parameter chosen so that the kinetic and potential energy terms are of the same order of magnitude. We want to find a minimizer of $\mathcal{E}_{\mu,L}^{\mathrm{rHF}}$ on

$$\mathcal{K}_{L,N_e} = \left\{\gamma\in\mathcal{S}(L^2_{\mathrm{per}}(\Gamma_L)),\ 0\le\gamma\le 1,\ \mathrm{Tr}_L\left(\gamma\right)=N_eL\right\},$$

where $\mathcal{S}(\mathcal{H})$ is the set of self-adjoint operators on the Hilbert space $\mathcal{H}$.

The ODA is an iterative algorithm, each iteration consisting of two steps. Given the approximation $\gamma^k \in \mathcal{K}_{L,N_e}$ at the iteration k, the iteration $k+1$ is composed of

(i) **the calculation of a descent direction**: find $\widetilde{\gamma}^{k+1}$, a minimizer of

$$\left\{ \frac{d}{dt}\mathcal{E}^{\mathrm{rHF}}_{\mu,L}\left((1-t)\,\gamma^k + t\widetilde{\gamma}\right)\big|_{t=0},\ \widetilde{\gamma} \in \mathcal{P}_{L,N_e} \right\},$$

where

$$\mathcal{P}_{L,N_e} = \left\{ \gamma \in \mathcal{S}(L^2_{\mathrm{per}}(\Gamma_L)),\ \gamma^2 = \gamma,\ \mathrm{Tr}_L\left(\gamma\right) = N_e L \right\}.$$

Note that $\mathcal{K}_{L,N_e}$ is the convex hull of $\mathcal{P}_{L,N_e}$;

(ii) **a line search**: find $\gamma^{k+1} \in \mathcal{K}_{L,N_e}$, the minimizer of $\mathcal{E}^{\mathrm{rHF}}_{\mu,L}(\gamma)$ on the segment $\left[\gamma^k, \widetilde{\gamma}^{k+1}\right]$.

To perform the first step, we calculate, for $k \in \mathbb{N}$,

$$\begin{aligned}\frac{d}{dt}\mathcal{E}^{\mathrm{rHF}}_{\mu,L}\left((1-t)\,\gamma^k + t\widetilde{\gamma}\right) = \frac{1}{2}\mathrm{Tr}_L\left(-\Delta\left(\widetilde{\gamma}-\gamma^k\right)\right)\\ + D_{m,L}\left(\rho_{\widetilde{\gamma}}-\rho_{\gamma^k}, (1-t)\,\rho_{\gamma^k} + t\rho_{\widetilde{\gamma}} - \mu\right).\end{aligned}$$

It follows that

$$\begin{aligned}\frac{d}{dt}\mathcal{E}^{\mathrm{rHF}}_{\mu,L}\left((1-t)\,\gamma^k + t\widetilde{\gamma}\right)\big|_{t=0} &= \frac{1}{2}\mathrm{Tr}_L\left(-\Delta\left(\widetilde{\gamma}-\gamma^k\right)\right)\\ &\quad + D_{m,L}\left(\rho_{\widetilde{\gamma}}-\rho_{\gamma^k}, \rho_{\gamma^k}-\mu\right)\\ &= \mathrm{Tr}_L\left(H_{\gamma^k}\left(\widetilde{\gamma}-\gamma^k\right)\right),\end{aligned}$$

where $H_\gamma = -\frac{1}{2}\Delta + Y_m * (\rho_\gamma - \mu)$ is the mean-field Hamiltonian corresponding to the density matrix γ. Therefore

$$\widetilde{\gamma}^{k+1} = \sum_{n=1}^{N_e L} |u_n^k\rangle\langle u_n^k|,$$

where $(u_n^k)_{1\le n\le N_e L}$ are the eigenvectors corresponding to $\lambda_1^k \le \cdots \le \lambda_{N_e L}^k$, the smallest $N_e L$ eigenvalues of H_{γ^k}. To compute the eigenmodes of H_{γ^k}, we use the planewave discretization presented in Section 4.2.

To find γ^{k+1}, we introduce the function

$$\begin{aligned}f^k(t) &= \mathcal{E}^{\mathrm{rHF}}_{\mu,L}\left((1-t)\,\gamma^k + t\widetilde{\gamma}^{k+1}\right)\\ &= \frac{1}{2}\mathrm{Tr}_L\left(-\Delta\gamma^k\right) + t\frac{1}{2}\mathrm{Tr}_L\left(-\Delta\left(\widetilde{\gamma}^{k+1}-\gamma^k\right)\right) + \frac{1}{2}D_{m,L}\left(\rho_{\gamma^k}-\mu, \rho_{\gamma^k}-\mu\right)\\ &\quad + tD_{m,L}\left(\widetilde{\gamma}^{k+1}-\rho_{\gamma^k}, \rho_{\gamma^k}-\mu\right) + t^2\frac{1}{2}D_{m,L}\left(\widetilde{\gamma}^{k+1}-\rho_{\gamma^k}, \widetilde{\gamma}^{k+1}-\rho_{\gamma^k}\right)\\ &= \mathcal{E}^{\mathrm{rHF}}_{\mu,L}(\gamma^k) + b^k t + a^k t^2,\end{aligned}$$

where

$$a^k = \frac{1}{2} D_{m,L}\left(\rho_{\widetilde{\gamma}^{k+1}} - \rho_{\gamma^k}, \rho_{\widetilde{\gamma}^{k+1}} - \rho_{\gamma^k}\right)$$

and

$$\begin{aligned} b^k &= \frac{1}{2}\mathrm{Tr}_L\left(-\Delta\left(\widetilde{\gamma}^{k+1} - \gamma^k\right)\right) + D_{m,L}\left(\rho_{\widetilde{\gamma}^{k+1}} - \rho_{\gamma^k}, \rho_{\gamma^k} - \mu\right) \\ &= \mathrm{Tr}_L\left(H_{\gamma^k}\left(\widetilde{\gamma}^{k+1} - \gamma^k\right)\right) \\ &= \sum_{n=1}^{N_e L} \lambda_n^k - \left(\frac{1}{2}\mathrm{Tr}_L\left(-\Delta\gamma^k\right) + D_{m,L}(\rho_{\gamma^k} - \mu, \rho_{\gamma^k})\right). \end{aligned}$$

Minimizing f^k, we obtain that

$$\inf_{0\le t\le 1} f^k(t) = f^k(t_0)$$

where

$$t_0 = \begin{cases} 0 & \text{if} \quad -\frac{b^k}{2a^k} \le 0 \\ -\frac{b^k}{2a^k} & \text{if} \quad 0 \le -\frac{b^k}{2a^k} \le 1 \\ 1 & \text{if} \quad 1 \le -\frac{b^k}{2a^k}. \end{cases}$$

Note that $t_0 = 0$ can only occur at convergence. We then take

$$\gamma^{k+1} = (1 - t_0)\,\gamma^k + t_0\widetilde{\gamma}^{k+1}.$$

4.4 Numerical results

In this section, we present the model used in our numerical simulation and give some numerical results.

4.4.1 Settings

We simulate random alloys resulting from the combination of two perfect crystals. For the linear model, we choose the mean-field potential of the form

$$V(\omega, x) = \sum_{k\in\mathbb{Z}} q_k(\omega)V_1(x-k) + (1 - q_k(\omega))V_2(x-k), \tag{4.10}$$

and for the rHF model, we choose the nuclear density of the form

$$\mu(\omega, x) = \sum_{k\in\mathbb{Z}} q_k(\omega)\mu_1(x-k) + (1 - q_k(\omega))\mu_2(x-k),$$

where (q_k) are i.i.d. Bernoulli random variables of parameter p, and V_i (respectively μ_i) is the single site potential (respectively nuclear density) corresponding to the crystal i. We suppose that V_i and μ_i are supported in

the unit cell $\Gamma = [0, 1)$. In our simulations, we take them to be defined on Γ by

$$V_1(x) = \sin(4\pi x) - \sin(2\pi x), \quad V_2(x) = 5\sin(2\pi x),$$

$$\mu_1(x) = \frac{1}{\sqrt{0,02\pi}} \exp\left(-\frac{\left(x - \frac{1}{2}\right)^2}{0,02}\right) \quad \text{and} \quad \mu_2(x) = 1 - \cos(2\pi x)$$

(see Figures 4.3 and 4.5). A typical $V(\omega, x)$ and $\mu(\omega, x)$ are represented in Figures 4.4 and 4.6.

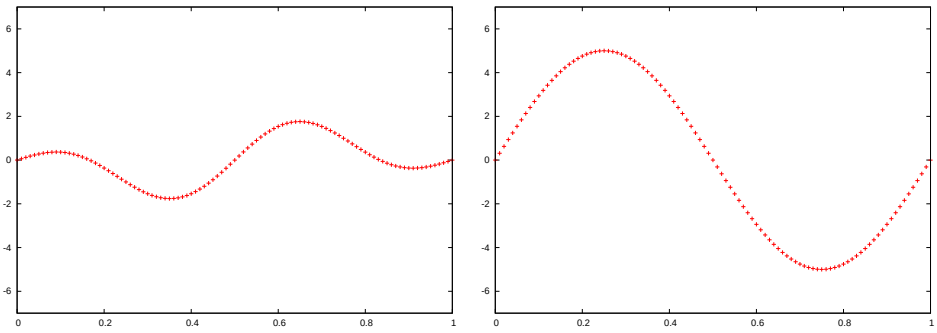

Figure 4.3: The potentials V_1 and V_2 used in the simulation.

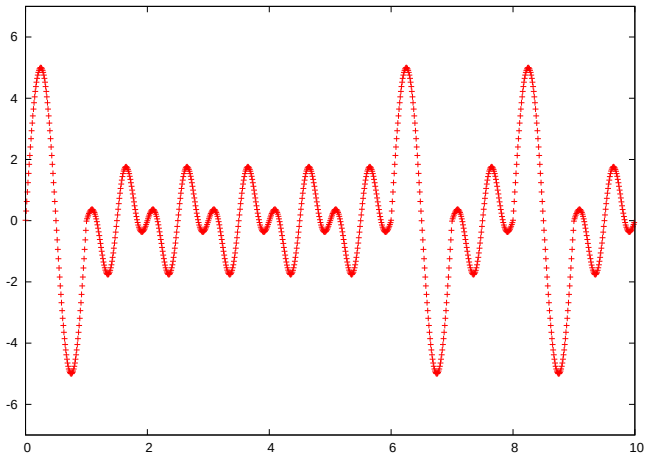

Figure 4.4: A realization of the potential V.

For a supercell size $L \in \mathbb{N} \setminus \{0\}$, the Fourier coefficients of $V_L(\omega, x)$ are

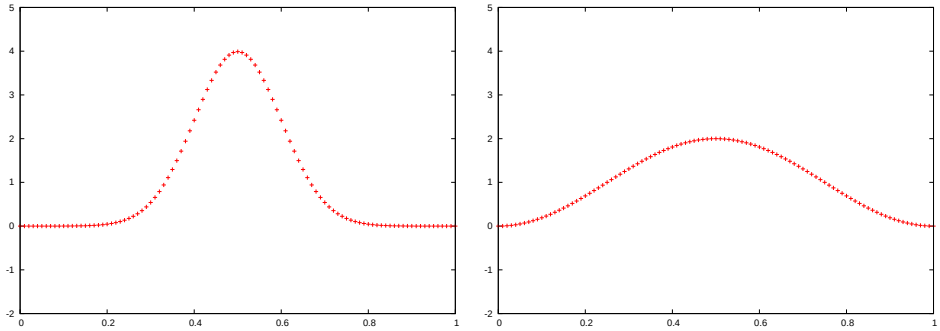

Figure 4.5: The nuclear densities μ_1 and μ_2 used in the simulation.

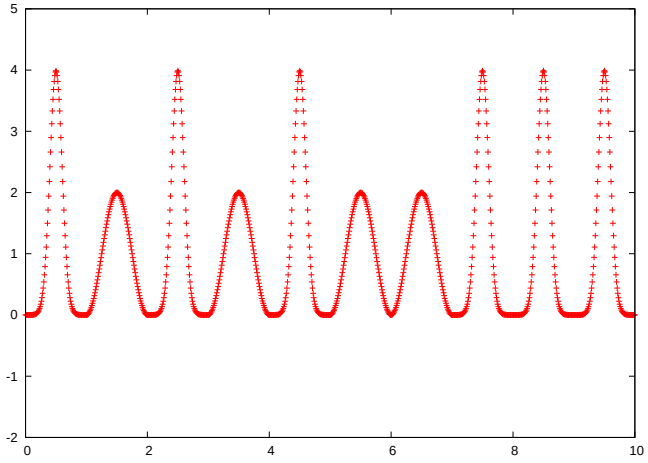

Figure 4.6: A realization of the nuclear density μ.

calculated using the formula

$$\begin{aligned} c_K^L(V_L) &= \frac{1}{\sqrt{L}} \sum_{\ell=0}^{L-1} \int_{\ell}^{\ell+1} V_L(\omega, x) e^{-2i\pi K \frac{x}{L}} \\ &= \frac{1}{\sqrt{L}} \sum_{\ell=0}^{L-1} e^{-2i\pi K \frac{\ell}{L}} \int_0^1 V_L(\omega, x+\ell) e^{-2i\pi K \frac{x}{L}}\, dx \\ &= \frac{1}{\sqrt{L}} \sum_{\ell=0}^{L-1} e^{-2i\pi K \frac{\ell}{L}} \Big(q_\ell(\omega) \int_0^1 V_1(x) e^{-2i\pi K \frac{x}{L}}\, dx \\ &\qquad + (1 - q_k(\omega)) \int_0^1 V_2(x) e^{-2i\pi K \frac{x}{L}}\, dx \Big). \end{aligned}$$

The coefficients $\int_0^1 V_i(x) e^{-2i\pi K \frac{x}{L}}\, dx$ are pre-calculated analytically. The same procedure is used to calculate the Fourier coefficients of μ_L.

In our code, unless otherwise stated, we take the Bernoulli parameter $p = 0.5$, the discretization parameter $N = 30$, the Yukawa parameter $m = 1$, and the number of electrons per unit volume $N_e = 1$. Here, we impose the neutrality condition $N_e = \int_\Gamma \mu(\omega, x)$ almost surely, for consistency with the Coulomb case (see Chapter 2 for a discussion about the necessity of the neutrality condition for Coulomb interactions). To compute expectations, we use a Monte-Carlo method with N_{MC} realizations.

Our code has been written in C++. The eigenmodes of the matrix $H_{L,N}$ are computed using the linear algebra library LAPACK.

In the following sections, we give some numerical results of our simulations.

4.4.2 The spectrum

We are first interested in the spectrum of $H(\omega)$. As the operator H is ergodic, the spectrum of $H(\omega)$ is deterministic [125]. The following proposition says that, in the linear case, the almost sure spectrum of $H(\omega)$ is the limit of the spectrum of the operator $H_L(\omega)$ as L goes to infinity.

Lemma 4.4.1 (Thermodynamic limit for the spectrum)**.** *Let V be of the form* (4.10) *with V_1 and V_2 in $L^\infty(\Gamma)$. Then, a.s.,*

$$\Sigma = \overline{\cup_{L\in 2\mathbb{N}+1}\sigma(H_L(\omega))},$$

where Σ is the almost sure spectrum of the ergodic operator $H(\omega)$.

Proof. For any $\omega \in \Omega$, [148, Proposition 1.4.3] gives

$$\sigma(H(\omega)) \subset \overline{\cup_{L\in 2\mathbb{N}+1}\sigma(H_L(\omega))}. \tag{4.11}$$

In particular, if we denote by $\Omega_1 = \{\omega,\ \sigma(H(\omega)) = \Sigma\}$, then for any $\omega \in \Omega_1$,

$$\Sigma \subset \overline{\cup_{L\in 2\mathbb{N}+1}\sigma(H_L(\omega))}.$$

As $\mathbb{P}(\Omega_1) = 1$, then

$$\Sigma \subset \overline{\cup_{L\in 2\mathbb{N}+1}\sigma(H_L(\omega))}$$

almost surely. Let us show the inverse inclusion. Let $L \in 2\mathbb{N}+1$ and $\omega \in \Omega$. By Bloch theory, it is easy to see that

$$\sigma(H_L(\omega)) \subset \sigma(A_L), \tag{4.12}$$

where

$$A_L = -\frac{1}{2}\Delta + V_L,$$

with V_L the $L\mathbb{Z}$-periodic function equal to $V(\omega,\cdot)$ on Γ_L, is an operator on $L^2(\mathbb{R}^d)$. Let $\lambda \in \sigma(A_L)$ and let us show that $\lambda \in \Sigma$. By [148, Lemma 1.4.4], there exist L^2-normalized functions $(f_n)_{n\in\mathbb{N}}$ in $C_c^\infty(\mathbb{R}^d)$ such that

$$\sup_{\substack{g\in C_c^\infty(\mathbb{R}^d)\\ \|g\|_{H^1(\mathbb{R}^d)}=1}} \langle (A_L-\lambda)f_n, g\rangle_{L^2(\mathbb{R}^d)} \underset{n\to\infty}{\longrightarrow} 0.$$

As A_L is a periodic operator, then one can choose f_n and $L_n \in L\mathbb{N}$ such that $\mathrm{supp}(f_n) \subset \Gamma_{L_n}$. Let

$$\Omega_n(\omega) = \left\{ \omega' \in \Omega,\ \exists x \in L\mathbb{Z}^d :\ V(\omega',\cdot) = V_L \text{ on } \Gamma_{L_n} + x \right\},$$

and

$$\Omega_2 = \cap_{n\in\mathbb{N}} \Omega_n(\omega).$$

As the variables $(q_k)_{k\in\mathbb{Z}^d}$ are independent, then for any $n \in \mathbb{N}$ we have that $\mathbb{P}(\Omega_n(\omega)) = 1$, thus $\mathbb{P}(\Omega_2) = 1$. Let $\omega_1 \in \Omega_2 \cap \Omega_1$ and $x_n \in L\mathbb{Z}^d$ such that $V(\omega_1,\cdot) = V_L$ on $\Gamma_{L_n} + x_n$. We have

$$\begin{aligned}
&\sup_{\substack{g\in C_c^\infty(\mathbb{R}^d)\\ \|g\|_{H^1(\mathbb{R}^d)}=1}} \langle (H(\omega_1)-\lambda)f_n(\cdot - x_n), g\rangle_{L^2(\mathbb{R}^d)} \\
&\qquad = \sup_{\substack{g\in C_c^\infty(\mathbb{R}^d)\\ \|g\|_{H^1(\mathbb{R}^d)}=1}} \langle (A_L-\lambda)f_n(\cdot - x_n), g\rangle_{L^2(\mathbb{R}^d)} \\
&\qquad = \sup_{\substack{g\in C_c^\infty(\mathbb{R}^d)\\ \|g\|_{H^1(\mathbb{R}^d)}=1}} \langle (A_L-\lambda)f_n, g(\cdot + x_n)\rangle_{L^2(\mathbb{R}^d)} \\
&\qquad = \sup_{\substack{g\in C_c^\infty(\mathbb{R}^d)\\ \|g\|_{H^1(\mathbb{R}^d)}=1}} \langle (A_L-\lambda)f_n, g\rangle_{L^2(\mathbb{R}^d)} \quad \underset{n\to\infty}{\longrightarrow} 0.
\end{aligned}$$

Therefore, by [148, Lemma 1.4.4], we have that $\lambda \in \sigma(H(\omega_1)) = \Sigma$, thus $\sigma(H_L(\omega)) \subset \Sigma$ for any $L \in 2\mathbb{N}+1$ by (4.12). As Σ is a closed set, we conclude that for any $\omega \in \Omega$,

$$\overline{\cup_{L\in 2\mathbb{N}+1} \sigma(H_L(\omega))} \subset \Sigma.$$

□

We represent in Figure 4.7 the spectrum of $H_{L,N}(\omega)$ in the linear model, with $L = 240$. The first two columns give the spectra of the pure crystals ($p = 0$ and $p = 1$). For numerical efficiency, these spectra are calculated using Bloch theory. Indeed, for the same accuracy, one needs to solve a system of size $NL \times NL$ in the supercell method, while in Bloch theory, one needs to solve L times a system of size $N \times N$. The other columns represent the spectrum of $H_{L,N}(\omega)$ for $N_{\mathrm{MC}} = 21$ realizations ω obtained with $p = 0.5$.

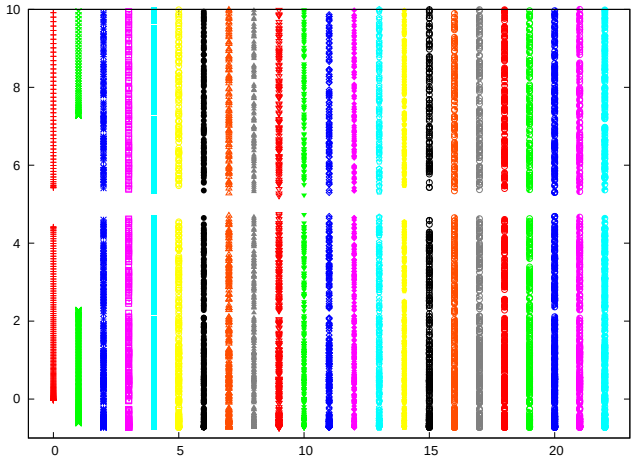

Figure 4.7: The spectrum of $H_{N,L}(\omega)$ in the linear model, with $L = 240$. Columns 0 and 1 correspond resp. to $p = 0$ and $p = 1$. The other columns correspond to 21 realizations ω obtained with $p = 0.5$.

For the rHF model, we have the inclusion (4.11) by [148, Proposition 1.4.3]. The proof of the inverse inclusion should follow the same steps as the proof of Lemma 4.4.1, as we have assumed (short-range) Yukawa interactions. Figure 4.8 gives the spectra of $H_{L,N}(\omega)$ in the rHF case for $L = 160$. Similarly to the linear case, the first two columns give the spectra of the pure crystals ($p = 0$ and $p = 1$). The difference in the maximum supercell size used in our simulations ($L = 240$ in the linear model and $L = 160$ in the rHF model) is due to the difference of the calculation time needed for each model. Indeed, for each iteration of the rHF calculation, we need to solve a system of the same size as that of the total calculation in the linear case. Thus, the calculation time in the rHF model is N_{it} times the one of the linear model, N_{it} being the number of iterations needed for the ODA algorithm to converge.

In both cases, we can observe the asymptotic non-random character of the spectrum of the Hamiltonian. In the linear case, we see that the disordered material have spectrum in the common spectral gap of the pure crystals, while this phenomenon does not appear in the rHF system we have studied.

4.4.3 Thermodynamic limit

In this section, we are interested in the convergence of the ground state energy per unit volume and of the integrated density of states in the thermodynamic limit. For the linear model, these convergences have been proved in [89, Th. 5.1]. For the rHF model, the convergence of the energy per unit volume has been proved in [29, Th. 5.2] [Th. 2.5.2 Chapter 2].

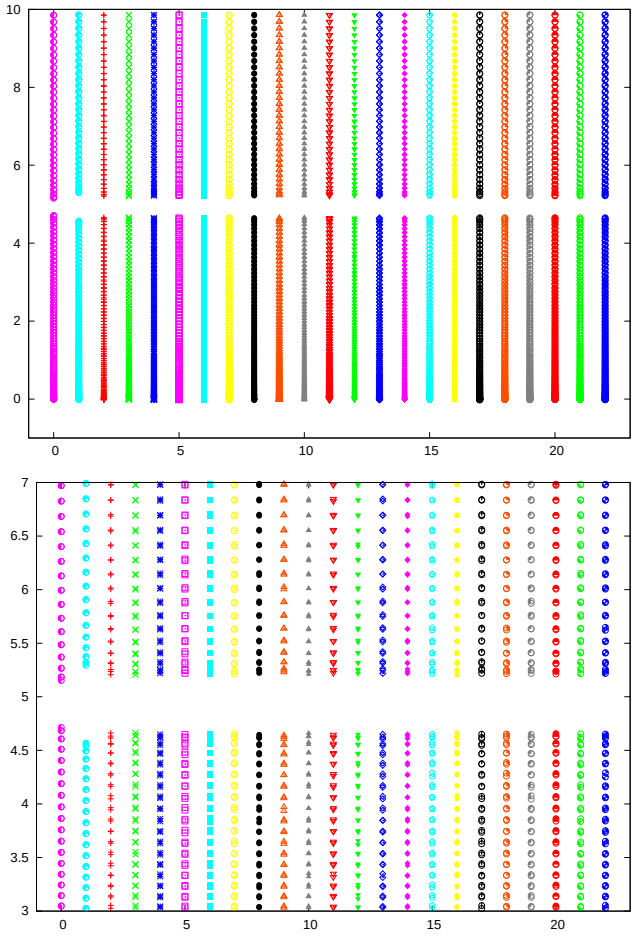

Figure 4.8: Top: the spectrum of $H_{N,L}(\omega)$ in the rHF model, with $L = 160$. Columns 0 and 1 correspond resp. to $p = 0$ and $p = 1$. The other columns correspond to 21 realizations ω obtained with $p = 0.5$. Down: zooming around the spectral gap.

In the linear case, the ground state energy of the system in the supercell is

$$I_L = \mathrm{Tr}_L \left(H_L \gamma_L \right).$$

The energy per unit volume $L^{-1} I_L$ converges, as $L \to \infty$, to

$$I = \underline{\mathrm{Tr}} \left(H \gamma \right), \tag{4.13}$$

where

$$\gamma = 1(H \leq \varepsilon_F)$$

is the ground state of the system and ε_F is the Lagrange multiplier corresponding to the charge constraint $\underline{\mathrm{Tr}}\,(\gamma) = N_e$. The average trace per unit volume $\underline{\mathrm{Tr}}\,(A)$ is defined for any ergodic trace class operator by $\underline{\mathrm{Tr}}\,(A) = \mathbb{E}\left(\mathrm{Tr}\,(1_\Gamma A 1_\Gamma)\right)$ (see Chapter 2 for details). The energy I_L is approximated by

$$I_{L,N} = \mathrm{Tr}\left(H_{L,N}\gamma_{L,N}\right) = \sum_{n=1}^{N_e L} \lambda_{N,n},$$

where we recall that $\lambda_{N,1} \leq \cdots \leq \lambda_{N,NL+1}$ are the eigenvalues of the matrix $H_{L,N}$.

In the rHF model, the energy of the system in the supercell is

$$I_L = \frac{1}{2}\mathrm{Tr}_L\left(-\Delta_L\gamma_L\right) + \frac{1}{2}D_{m,L}(\rho_{\gamma_L} - \mu_L, \rho_{\gamma_L} - \mu_L).$$

The energy per unit volume $L^{-1}I_L$ converges, as $L \to \infty$, to

$$I = \frac{1}{2}\underline{\mathrm{Tr}}\,\left(-\Delta\gamma\right) + \frac{1}{2}\underline{D}_m(\rho_\gamma - \mu, \rho_{\gamma_L} - \mu), \tag{4.14}$$

where $\underline{D}_m$ is defined, for any stationary functions f and g by

$$\underline{D}_m(f,g) = \frac{a_p}{2}\mathbb{E}\left(\int_{\mathbb{R}}\int_\Gamma f(x)Y_m(x-y)g(y)\,dx\,dy\right).$$

The kinetic energy is approximated by

$$\begin{aligned}
\frac{1}{2}\mathrm{Tr}_L\left(-\Delta_L\gamma_{L,N}\right) &= \frac{1}{2}\sum_{n=1}^{N_eL}\int_{\Gamma_L}\left|v'_{N,n}(x)\right|^2\,dx \\
&= \frac{1}{2}\sum_{n=1}^{N_eL}\int_{\Gamma_L}\left|\sum_{j=1}^{NL+1} u_{N,n}(j)f'_j(x)\right|^2\,dx \\
&= \frac{1}{2}\sum_{n=1}^{N_eL}\int_{\Gamma_L}\left|\sum_{j=1}^{NL+1}\left(\frac{2i\pi}{L}\left(j-\frac{NL}{2}\right)\right)u_{N,n}(j)f_j(x)\right|^2\,dx \\
&= \frac{1}{2}\sum_{n=1}^{N_eL}\sum_{j=1}^{NL+1}\frac{4\pi^2}{L^2}\left(j-\frac{NL}{2}\right)^2\left|u_{N,n}(j)\right|^2\,dx.
\end{aligned}$$

As to the interaction energy, it is approximated by

$$\frac{1}{2}D_{m,L}(\rho_{\gamma_{L,N}} - \mu_L, \rho_{\gamma_{L,N}} - \mu_L) = \frac{a_p}{2}\sum_{K=-NL}^{NL}\frac{\left|c^L_{N,K}(\rho) - c^L_K(\mu_L)\right|^2}{m^2 + |K|^2},$$

where the coefficients $c^L_{N,K}(\rho)$ have been defined in (4.9). In our code, we take $a_p = 10$.

In Figures 4.9 and 4.10, we see that the discretized energy per unit volume $L^{-1}I_{L,N}$ converges as $L \to \infty$ for both models a.s. and in average. We have used $N_{\mathrm{MC}} = 21$ Monte-Carlo realizations. The limiting value can be respectively be taken as an approximation of (4.13) and (4.14).

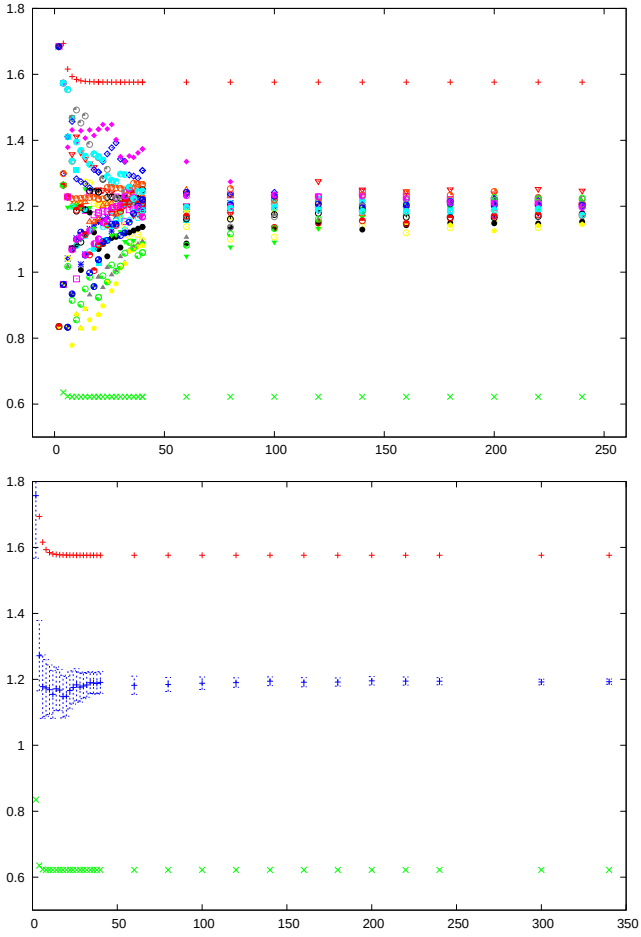

Figure 4.9: The convergence of the energy per unit volume $\frac{I_{L,N}}{L}$ in the linear model a.s. (top) and in average (down). The red and green lines correspond to the perfect crystals.

As far as we know, there are no theoretical results on the convergence rate of these quantities. We have evaluated the asymptotic convergence rate

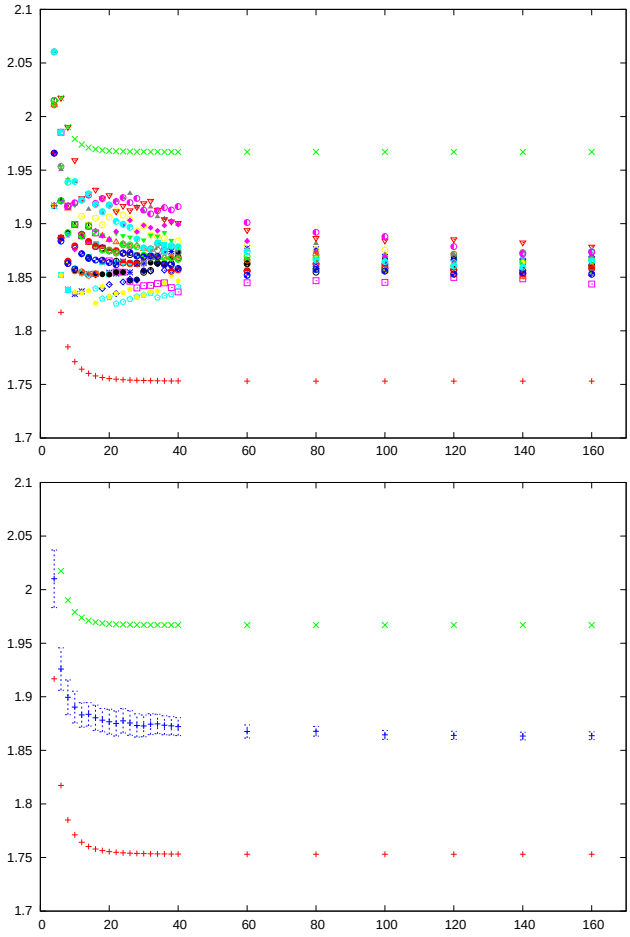

Figure 4.10: The convergence of the energy per unit volume $\frac{I_{L,N}}{L}$ in the rHF model a.s. (top) and in average (down). The red and green lines correspond to the perfect crystals.

for the average energy per unit volume

$$\alpha_L = \frac{\ln\left(\left|\frac{\mathbb{E}(I_{L,N})}{L} - I\right|\right)}{\ln(L)}$$

in our examples. The results are shown in Figure 4.11. The observed convergence rate is then $\alpha = -1$ in both cases. This confirms the intuition that the supercell energy per unit volume behaves as

$$I = \frac{I_L}{L} + O\left(\frac{1}{L}\right).$$

The Integrated Density Of States (IDOS) of the Hamiltonian H and the

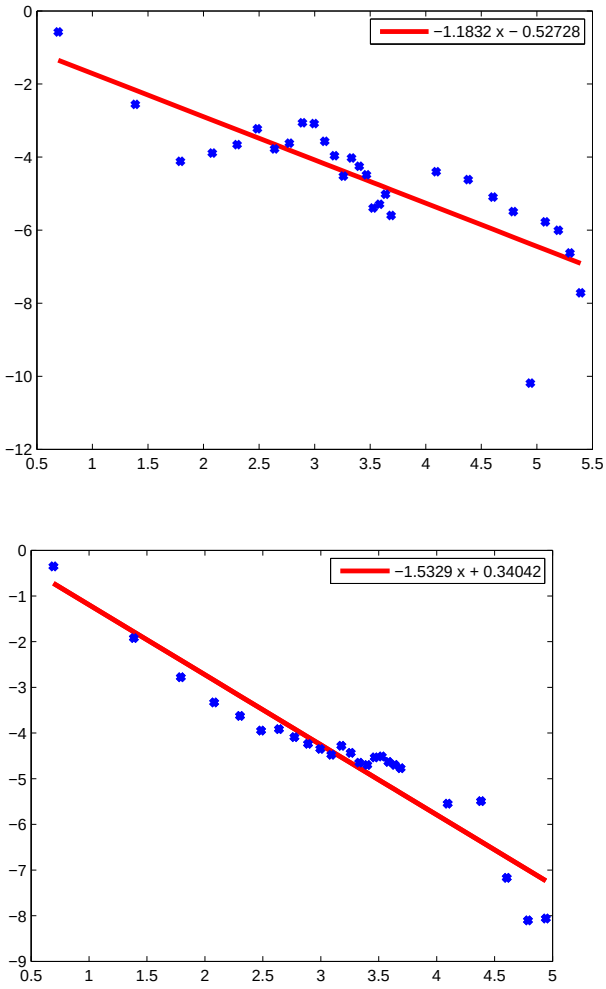

Figure 4.11: Representation of $\ln\left(\left|\frac{\mathbb{E}(I_{L,N})}{L} - I\right|\right)$ as a function of $\ln(L)$ in the linear model (top) and the rHF model (down).

IDOS of the supercell Hamiltonian H_L are respectively given by

$$\mathcal{N} : E \mapsto \underline{\mathrm{Tr}}\left(1(H \leq E)\right).$$

and

$$\mathcal{N}_L : E \mapsto \frac{1}{L}\mathrm{Tr_L}\left(1(H_L \leq E)\right).$$

In the linear model, $\mathcal{N}_L$ converges weakly to $\mathcal{N}$. In the rHF model, the convergence of the IDOS in the thermodynamic limit has not been proved,

but we believe that the proof should follow from the proof of [29, Th. 5.2] [Th. 2.5.2 Chapter 2].

The discretized IDOS is a step function given by

$$\mathcal{N}_{N,L} : E \mapsto \frac{1}{L} \sum_{n=1}^{NL+1} 1_{\lambda_{N,n} \leq E}$$

(see Figure 4.12).

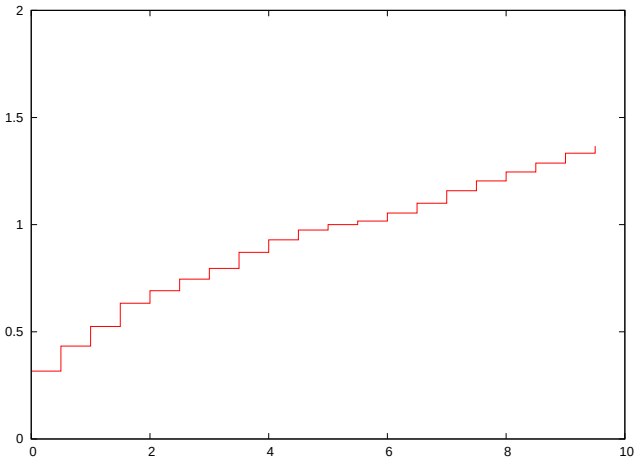

Figure 4.12: The IDOS of $H_{L,N}(\omega)$ for the linear model with $L = 240$ and for a realization ω obtained with $p = 0.5$.

To illustrate the convergence of the IDOS per unit volume, we look at the L^1 norm of $\mathcal{N}_{L,N}$ on an interval I. In our code, we take $I = (-\infty, E_{\text{cut}}]$, with $E_{\text{cut}} = 10$. In this case,

$$\|\mathcal{N}_{L,N}\|_{L^1((-\infty,E_{\text{cut}}])} = \frac{1}{L} \sum_{n=1}^{NL+1} 1(\lambda_{N,n} \in I)(E_{\text{cut}} - \lambda_{N,n}). \tag{4.15}$$

In Figure 4.13 we see that $\|\mathcal{N}_{L,N}\|_{L^1((-\infty,E_{\text{cut}}])}$ indeed converges as $L \to \infty$ in average. We also obtain a.s. convergence.

4.4.4 Localization properties

Anderson localization (see Section 1.5.1) is the presence in the almost sure spectrum of $H(\omega)$ of pure point spectrum with exponentially decaying eigenfunctions. When V is given by (4.10), it has been proved (see e.g. [58]) that $H = -\frac{1}{2}\Delta + V$ is localized at all energies when there is disorder ($p \in (0, 1)$) and that there is no localization in perfect crystals ($p \in \{0, 1\}$) [152]. In the

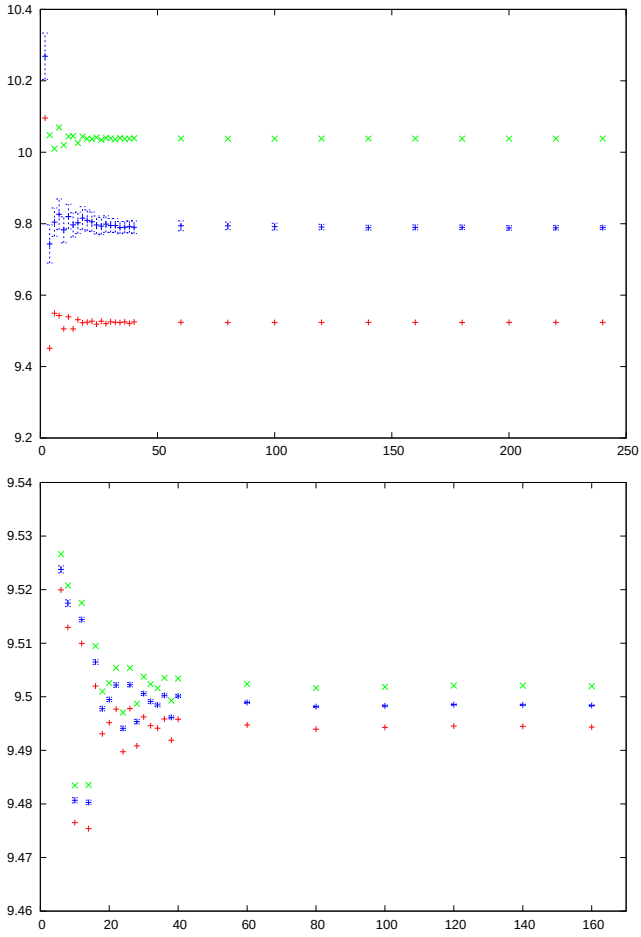

Figure 4.13: The convergence of the average of $\mathcal{N}_{L,N}$ in $L^1((-\infty, E_{\rm cut}])$ in the linear model (top) and the rHF model (down). The red and green lines correspond to the perfect crystals.

rHF model, we are not aware of any results on the localization properties of the mean-field Hamiltonian.

We numerically investigate the localization properties of the Hamiltonian in our two models. The spectrum of the supercell Hamiltonian H_L is always discrete. We thus characterize the eigenvalues by looking at the localization or the spreading of the corresponding eigenfunctions. Precisely, for f in

$$A = \left\{ f \ L-\text{periodic Radon measure}, \ f \geq 0, \ \int_0^L f = 1 \right\},$$

we consider the variance

$$v_L(f) = \frac{1}{L^2} \inf_{0 \leq \ell \leq L} \int_\ell^{\ell+L} x^2 f(x)\, dx - \left(\int_\ell^{\ell+L} x f(x)\, dx \right)^2.$$

The functional v_L is bounded and non-negative. Its minimal and maximal value are given by the following lemma.

Lemma 4.4.2. *The minimal value of v_L on A is 0, reached for $f(x) = \sum_{k\in\mathbb{Z}} \delta_{a+kL}(x)$, for any $a \in \mathbb{R}$, and its maximal value on A is $\frac{1}{12}$ attained for $f(x) = \frac{1}{L}$.*

Proof. It is easy to see that $v_L\left(\sum_{k\in\mathbb{Z}} \delta_{a+kL}(x)\right) = 0$. Since v_L in non negative, then 0 is its minimum. Besides, as $f \mapsto \int_\ell^{\ell+L} x^2 f(x)\,dx - \left(\int_\ell^{\ell+L} x f(x)\,dx\right)^2$ is a concave functional for any ℓ, then v_L is a concave functional. It follows that

$$v_L\left(x \mapsto \frac{1}{L}\int_0^L U_r f(x)\,dr\right) \geq \frac{1}{L}\int_0^L v_L(U_r f)\,dr,$$

where U_r is the translation operator. Finally, noticing that $v_L(U_r f) = v_L(f)$ for any $r \in \mathbb{R}$, and that if $f \in A$ then $x \mapsto L^{-1}\int_0^L U_r f(x)\,dr = 1/L$, we obtain for any $f \in A$

$$\frac{1}{12} = v_L\left(\frac{1}{L}\right) \geq \frac{1}{L}\int_0^L v_L(f)\,dr = v_L(f),$$

which concludes the proof of the lemma. □

The lower $v_L(f)$, the more localized the function f. To measure the localization of an eigenfunction $v_{N,n}$ we look at the variance of the normalized function $f = |v_{N,n}|^2 \in A$. The results obtained for our two models are presented in Figures 4.14 and 4.16. For the linear model, as predicted by the theory, we see that for $p = 0.5$ there is localization at all energies. When $p \in \{0, 1\}$, we see that there is no localization. Typical eigenfunctions are represented in Figure 4.15.

In the rHF case, the variances associated with the eigenvalues of the spectrum of $H_{L,N}$ in the rHF model are higher than that of the linear case (see Figure 4.16). These variances approach the maximal value of the variance v_L in some regions of the spectrum. We have represented in Figure 4.17 the eigenfunctions corresponding resp. to the first and the last eigenfunctions represented in Figure 4.16. It is not clear whether there is localization or not.

4.4.5 Low concentration of random defects

We concentrate in this section on the case of a crystal with a low concentration of random defects, that is, when the Bernoulli parameter p goes to zero. In the linear model, we know [83] that the almost sure spectrum of $H(\omega)$ does not depend on p. However, when p is small, this phenomenon is

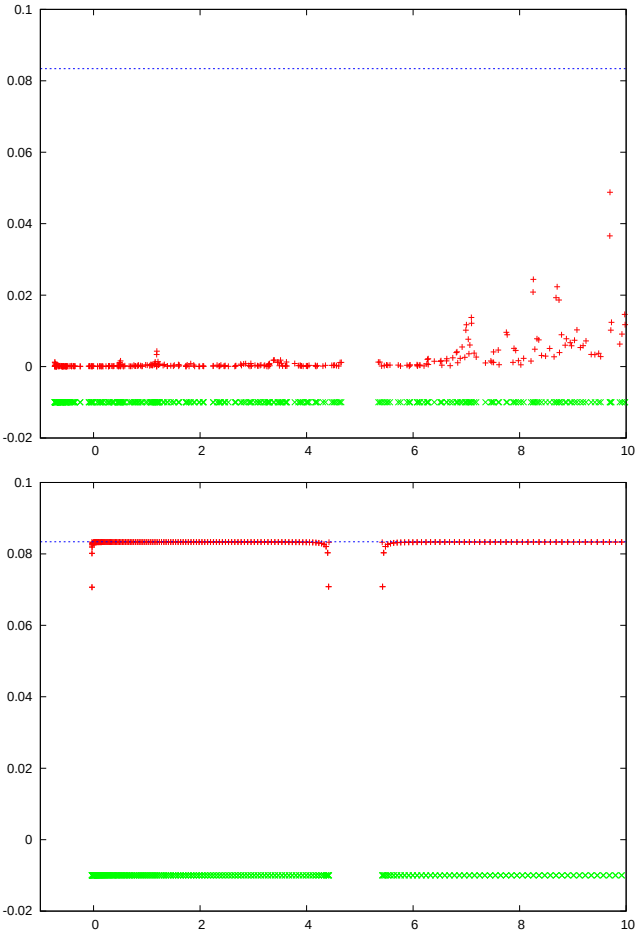

Figure 4.14: In green: the spectrum of the Hamiltonian $H_{L,N}$ for the linear model and with $L = 240$. In red: the variance v_L associated with each eigenvalue. In blue: the maximum value $\frac{1}{12}$ of the variance. Top: a random realization ω obtained with $p = 0.5$. Down: a perfect crystal ($p = 0$).

difficult to capture numerically, as, at a fixed supercell size L, the Hamiltonian is determined by the L random variables $(q_k)_{1\leq k\leq L}$. When p is small, the probability that all q_k, $1 \leq k \leq L$, are equal to zero is high, and in this case the spectrum of $H(\omega)$ is the same as that of the perfect crystal. The IDOS is a more precise description of the spectrum as it quantifies precisely how many "states" per unit volume can be in a certain energy interval. The IDOS has been proved to admit an expansion in powers of p of the form

$$\mathcal{N}_p = \mathcal{N}_0 + \vartheta p + O(p^2),$$

where $\mathcal{N}_0$ is IDOS of the perfect crystal and ϑ is a function of the spectral shift function between the unperturbed Hamiltonian and the Hamiltonian of

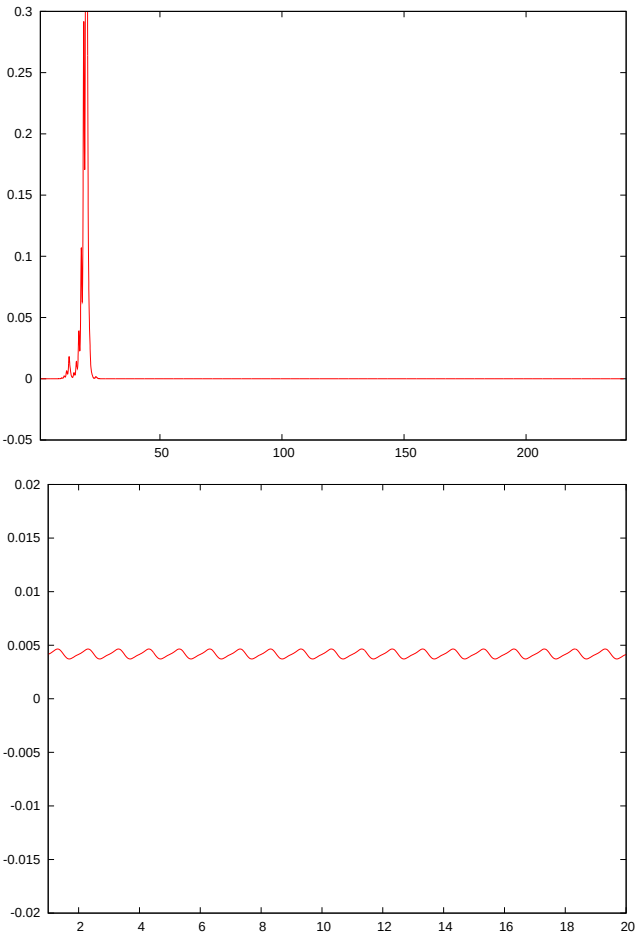

Figure 4.15: The eigenfunctions associated with the eigenvalue $\lambda_{N,1}$ for the linear model and with $L = 240$. Top: a random realization ω obtained with $p = 0.5$ ($\lambda_{N,1} = -0.0174$). Down: the perfect crystal corresponding to $p = 0$ ($\lambda_{N,1} = -0,03$).

the system with a single defect. This result has been proved for the linear model in [87] and for the rHF model in [92] (see also Chapter 3 of this thesis).

In Figures 4.18 and 4.19 we represent the L^1 norm of the IDOS (see (4.15)) as a function of p. We see that for both models, the L^1 norm of the IDOS is almost a line. The error bars are relatively big as we only use $N_{\mathrm{MC}} = 15$ realizations of our system.

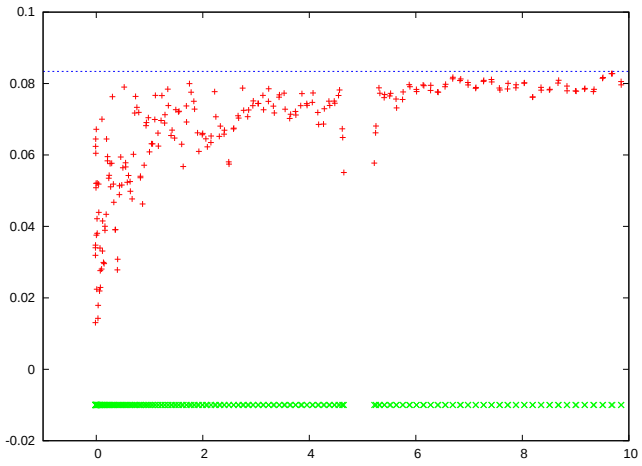

Figure 4.16: In green: the spectrum of the Hamiltonian $H_{L,N}$ for the rHF model and with $L = 160$, for a random realization ω obtained with $p = 0.5$. In red: the variance v_L associated with each eigenvalue. In blue: the maximum value $\frac{1}{12}$ of the variance.

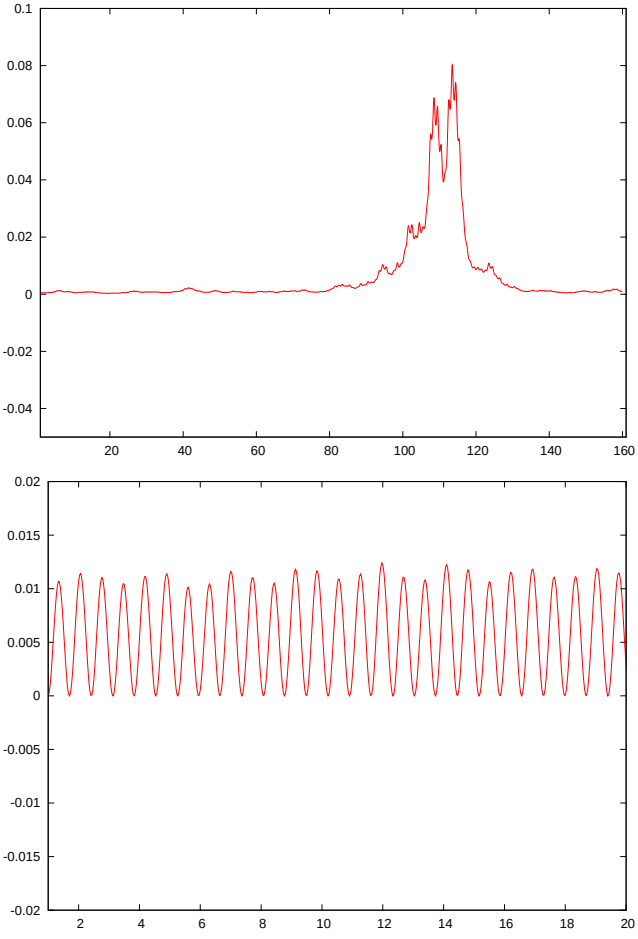

Figure 4.17: The eigenfunctions associated with resp. the eigenvalues $\lambda_{N,1} = -0.0174$ (top) and $\lambda_{N,227} = 9.85$ (down) for the rHF model and with $L = 160$ for a given realization ω obtained with $p = 0.5$.

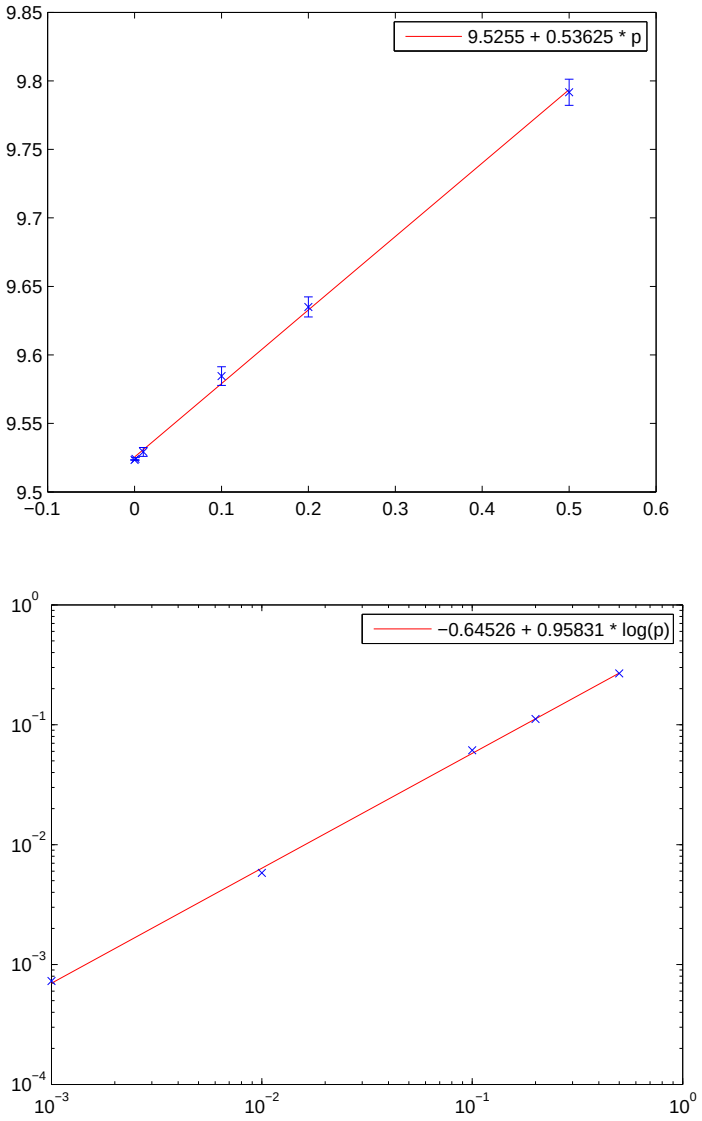

Figure 4.18: Top: the average of the L^1 norm of the IDOS as a function of p for the linear model. Down: the average of the L^1 norm of the IDOS as a function of p for the linear model in the logarithmic scaling.

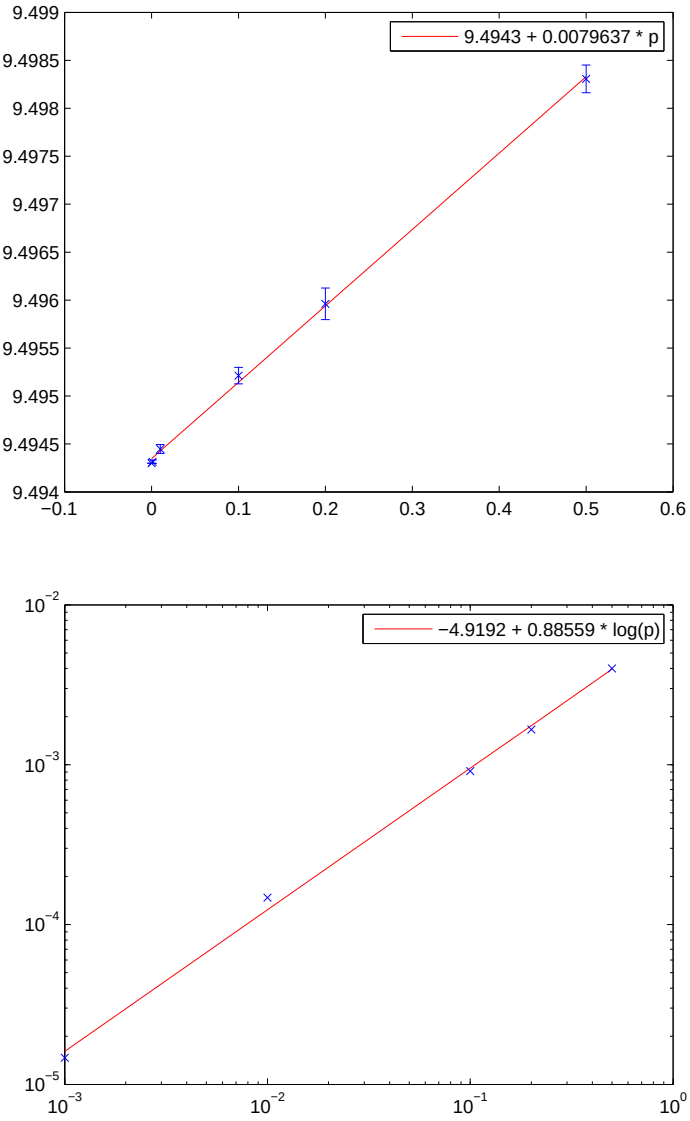

Figure 4.19: Top: the average of the L^1 norm of the IDOS as a function of p for rHF model. Down: the average of the L^1 norm of the IDOS as a function of p for the rHF model in the logarithmic scaling.

Part II

Coarse-graining of kinetic Monte-Carlo models

Chapter 5

Introduction and summary of results

In this chapter, we present three classes of models that are commonly used in molecular dynamics and discuss the "low barrier" problem in kMC models. A summary of the results obtained in Chapter 6 is included in this chapter.

Contents

5.1 Introduction

The second part of this thesis is concerned with the study of multiscale-in-time systems, in the context of Molecular Dynamics (MD).

The main two objectives of MD are the calculation of macroscopic quantities of physical systems containing a large number of atoms starting from their microscopic structures on the one hand; and the numerical simulation of non-equilibrium systems, on the other hand. Our work fits into the second category. Similarly to the first part of the thesis, our results are theoretical but they are motivated by numerical simulation considerations. The mathematical fields involved are mainly probability theory and numerical methods.

In this chapter, we present the scientific context of the work detailed in Chapter 6 and the main results we have obtained. In Section 5.2, we present three classes of models that are commonly used in MD, namely, the Hamiltonian dynamics, the Langevin dynamics, and kinetic Monte-Carlo

models. Then, in Section 5.3, we focus on kMC models, present multiscale-in-time systems and discuss the issue of finding effective dynamics to compute macroscopic quantities. A summary of our results is also included in this section.

5.2 Models in molecular dynamics

In this section, we describe the matter at the atomic scale in the framework of classical statistical mechanics, where atoms are considered as point particles. Hamiltonian dynamics is the fundamental system of equations governing the motion of classical particles. Langevin and overdamped Langevin dynamics are perturbations of the Hamiltonian dynamics which take into account the effect of the environment. They are also commonly used in MD, both to simulate the evolution of systems which are not isolated (e.g. in contact with thermostats) and as a numerical tool to sample equilibrium measures (e.g. the Boltzmann-Gibbs measure). Due to the metastable character of these dynamics, they can be coarse-grained into discrete space dynamics. An example of such discrete dynamics are the kinetic Monte-Carlo models presented in Section 5.2.3.

5.2.1 Hamiltonian dynamics

In classical mechanics, a system of N particles (atoms for instance), of masses $m_1, \cdots, m_N$, is described by a configuration $(Q, P) \in (\mathbb{R}^3)^N \times (\mathbb{R}^3)^N$, where $Q = (q_1, \cdots, q_N)$ and $P = (p_1, \cdots, p_N)$ are respectively the positions and the momenta of the particles. The interactions between the particles are modeled by the potential energy $V(Q)$ and the total energy of the system is given by

$$\mathcal{E}(Q, P) = \frac{1}{2} P^T M^{-1} P + V(Q), \tag{5.1}$$

where $M = \mathrm{diag}(m_1, \cdots, m_N)$ is the mass matrix. In *ab-initio* molecular dynamics, the potential $V(Q)$ is given by $I_{N_e}(\mu)$ defined in (1.6), with $\mu = \sum_{i=1}^N \delta_{q_i}$ and N_e the number of electrons in the system. To simulate such systems, one needs to solve, at each time step (thus for each new configuration of the atoms) an electronic structure problem (see Section 1.2 and Chapter 4). This approach is numerically very costly and cannot be used for systems with more than a few hundreds of atoms. In practice, $V(Q)$ is approximated by an empirical potential. The latter is obtained by assuming an *a priori* parametric form and fitting the parameters with experimental data or *ab-initio* molecular simulations of small systems. In both cases, a closed form of $V(Q)$ as a function of Q is used. A simple form of potentials

is the pair interaction potential, for which V is of the form

$$V(q_1, \cdots, q_N) = \sum_{1 \le i < j \le N} \mathcal{V}(|q_i - q_j|).$$

A typical example of potentials $\mathcal{V}$ is the Lennard-Jones potential

$$\mathcal{V}(r) = 4\varepsilon \left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right),$$

where ε is the depth of the potential well and $2^{1/6}\sigma$ is the distance at which the potential is minimal. The Lennard-Jones potential is particularly accurate for noble gas atoms. See e.g. [139] for other forms of potentials.

When the system is isolated, the dynamics of the particles is given by Newton's law of motion, or equivalently by the *Hamiltonian dynamics* associated with the Hamiltonian function (5.1). It is the system of the $6N$ coupled ODEs:

$$\begin{cases} dQ(t) = \nabla_P \mathcal{E}(Q,P)dt = M^{-1}P(t)dt \\ dP(t) = -\nabla_Q \mathcal{E}(Q,P)dt = -\nabla V(Q(t))dt. \end{cases} \tag{5.2}$$

Under regularity conditions on the potential V, (5.2) admits a unique solution. In practice, (5.2) is discretized using symplectic numerical methods, which have the characteristic feature of (almost) conserving the total energy of the system over a long simulation time. An example of such algorithms is the Störmer-Verlet scheme [154] which reads

$$\begin{cases} P_{n+1/2} = P_n - \nabla V(Q_n)\Delta t/2 \\ Q_{n+1} = Q_n + \Delta t M^{-1} P_{n+1/2} \\ P_{n+1} = P_{n+1/2} - \nabla V(Q_{n+1})\Delta t/2, \end{cases}$$

where Δt is the time step.

5.2.2 Langevin dynamics

In Section 5.2.1, we have supposed that the system we study was isolated. However the external environment, such as air or solvent frictions, or the fluctuations due to the coupling with a thermostat often affect the dynamics of the system. Langevin dynamics is a perturbation of the Hamiltonian dynamics that models molecular systems at constant temperature T, and it takes into account two types of external effects: random fluctuations of Brownian [22] type, and viscous effects through a friction force term proportional to the velocity of the particle. Note that this dynamics can be derived as the limit dynamics of an atom immersed in a heat bath of infinitely many

light particles (see [42, 43]). The dynamics is then given by the following system of stochastic differential equations:

$$\begin{cases} dQ(t) = M^{-1}P(t)dt \\ dP(t) = -\nabla V(Q(t))dt - \gamma M^{-1}P(t) + \sqrt{2\gamma\beta^{-1}}dW_t, \end{cases} \tag{5.3}$$

where γ is the friction coefficient, $\beta = 1/(k_B T)$, k_B being the Boltzmann constant, and (W_t) is a Brownian motion. Under regularity and integrability conditions on the potential V, (5.3) admits a unique solution $Y_t = (Q(t), P(t))$ which is a continuous Markov process. The infinitesimal generator associated with (Y_t) is given, for any smooth enough function $\varphi : (\mathbb{R}^3)^N \times (\mathbb{R}^3)^N \to \mathbb{R}$, by

$$\begin{aligned}(L\varphi)(q,p) = M^{-1}p \cdot \nabla_q \varphi(q,p) - \big(\gamma M^{-1}p + \nabla V(q)\big) \cdot \nabla_p \varphi(q,p) \\ + \gamma\beta^{-1}\Delta_p \varphi(q,p).\end{aligned}$$

In practice, (5.3) is often discretized using the Brünger-Brooks-Karplus (BBK) algorithm, which is a generalization of the Störmer-Verlet algorithm to the stochastic setting.

Overdamped Langevin dynamics

The overdamped Langevin dynamics is obtained from the Langevin dynamics by setting $\gamma = 1$ and taking the limit $M \to 0$. It reads

$$dQ(t) = -\nabla V(Q(t))dt + \sqrt{2\beta^{-1}}dW_t, \tag{5.4}$$

where the sole position variable Q appears. The same conditions on V as in the Langevin case ensure the existence and the uniqueness of a Markov process solution of (5.4). Its generator is given, for any sufficiently smooth function $\varphi : (\mathbb{R}^3)^N \to \mathbb{R}$, by

$$(L\varphi)(q) = -\nabla V(q) \cdot \nabla \varphi(q) + \beta^{-1}\Delta\varphi(q).$$

As we have explained above, Langevin and overdamped Langevin dynamics can be derived from the Hamiltonian dynamics and model the dynamics of a physical system. In this case, the parameters γ and M and the potential V are given by the physical properties of the system. These dynamics can also be seen as a numerical tool for sampling measures. Indeed, in statistical mechanics, a macroscopic quantity is defined as the average $\langle A \rangle$ of the corresponding microscopic quantity $A(q,p)$. This average is taken with respect to a probability measure μ on the phase space $(\mathbb{R}^3)^N \times (\mathbb{R}^3)^N$, which depends on the statistical ensemble at hand. For example, if the canonical ensemble is considered (the number N of particles, the temperature T and the volume are fixed), the measure μ is given by the *Gibbs measure*:

$$d\mu(q,p) = Z^{-1} \exp\left(-\beta \mathcal{E}(q,p)\right) \, dq \, dp, \tag{5.5}$$

where Z is a normalization factor. We thus wish to compute the ensemble average

$$\langle A \rangle = \int_{(\mathbb{R}^3)^N \times (\mathbb{R}^3)^N} A(q,p) d\mu(q,p), \tag{5.6}$$

that provides macroscopic information on a system (e.g. the pressure) on the basis of a microscopic model (encoded in the energy $\mathcal{E}$ that appears in (5.5)). However, the integral (5.6) is an integral in high dimension. Standard quadrature rules can therefore not be used to evaluate it. One method to compute (5.6) is to consider a process $(q(t), p(t))$ which is ergodic with respect to the measure μ, that is, a process that satisfies for any μ-integrable observable A,

$$\int_{(\mathbb{R}^3)^N \times (\mathbb{R}^3)^N} A(q,p) d\mu(q,p) = \lim_{t \to \infty} \frac{1}{t} \int_0^t A(q(s), p(s))\, ds. \tag{5.7}$$

The average $\langle A \rangle$ is then approximated by the one-dimensional integral over time of the right hand side of (5.7), instead of the high dimensional integral (5.6). Overdamped Langevin dynamics gives a process $Q(t)$ which is ergodic with respect to the position part of the Gibbs measure, and can thus be used to compute (5.7) for observables A that are independent of p. For observables that depend on q and p, one can use Langevin dynamics with any $\gamma > 0$. In this case, the parameter γ is chosen to ensure numerical efficiency rather than physical accuracy.

Metastability

Langevin and overdamped Langevin dynamics are generically metastable. This means that a system following these dynamics will spend a long time in a metastable region of the phase space, then will quickly move to another metastable region. These low energy regions (high probability) are separated by high energy barriers (low probability). We present in Figure 5.1 a typical trajectory of such systems. In practice, a direct time integration of (5.3) and (5.4) requires very short time steps due to stability requirements. Consequently, in view of the limited computational capacities, the physical time simulated does not exceed few microseconds for moderate size molecular systems. Because of the metastable character of the dynamics, this duration is far from being enough to observe many interesting physical and chemical phenomena such as the diffusion and the clustering of point defects in crystals for instance. A simplification of these models consists in coarse-graining the phase space into a discrete set of states which represent the metastable positions of the system. On the typical example of Figure 5.1, the state of the system would be described by a scalar variable equal to -1 if the system is in the left well and equal to 1 if the system is in the right one. Examples of such models are kinetic Monte-Carlo models that we present in the following section. Adopting this approach allows one to simulate typical systems over much longer times scales than with MD.

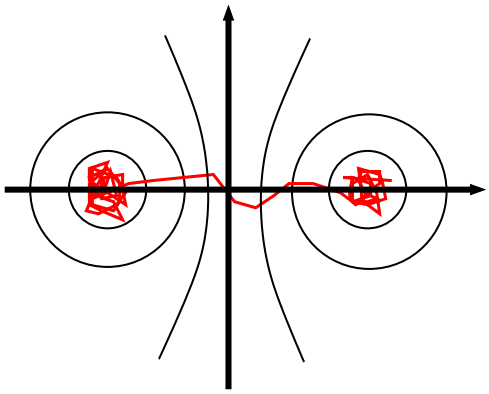

Figure 5.1: A typical trajectory of a molecular system.

5.2.3 Kinetic Monte-Carlo models

In kinetic Monte-Carlo (kMC) models, the state of the system is valued in a discrete set E, whose elements represent the metastable regions of the original dynamics. The key assumption in kMC models is that the system stays so long in a metastable region (compared to the duration of the transition to another metastable region) that it forgets where it came from. The resulting dynamics is then a continuous in time, discrete in space, Markov process (Y_t), also called a *jump process* [45]. This assumption is well justified for low temperature dynamics as the difference between the time spent in a metastable state and the transition time is large, but its validity is questionable at high temperatures when this difference gets smaller.

Jump processes are determined by transition rates $\left(q_{y,y'}\right)_{y\neq y'}$. When the system is in a state y, then

- it stays there for a time S, which is a random variable distributed according to an exponential law of parameter

$$q_y := \sum_{y'\in E,\, y'\neq y} q_{y,y'},$$

  that is, $\mathbb{P}\left(S \leq t\right) = 1 - \exp\left(-q_y t\right)$.

- At this time S, it jumps to another state. The probability that it jumps to the state $y' \neq y$ is given by $\frac{q_{y,y'}}{q_y}$.

The transition rates $\left(q_{y,y'}\right)_{y\neq y'}$ mainly depend on the shape of the potential V. They are considered as an input in kMC models and are often obtained by Transition State Theory [46] from the underlying MD model. If the transition rates are well approximated, the kMC model is accurate in the sense that the trajectories given by this theory have the same probability law as the trajectories of the original Langevin or overdamped Langevin dynamics [155].

In practice, the number of metastable states is so large that the cost of the *a priori* determination of all the possible states of the system and the corresponding transition rates is prohibitive. On-the-fly kMC models [71], where the possible states and the transition rates are calculated in a neighborhood of the current state as the simulation proceeds, are often used to overcome this issue. Otherwise, in certain regimes, it is possible to represent the dynamics on a smaller state space, depending on the quantities of interest. In some situations, the derivation of such dynamics can be rigorously proved, but in general, this derivation is only formal. In the latter case, a parametric form of the reduced dynamics is assumed and the parameters are obtained by comparison with the complete dynamics simulation. We present in the following section a particular regime where the derivation of a reduced dynamics is possible.

5.3 Multi-scale in time systems in kMC models

We consider in this section situations where many time scales are present in the kMC model. It is indeed common for statistical systems to evolve in an energy landscape with high and low barriers (see Figure 5.2). Therefore, the state variables can be decomposed into slow and fast variables. On a typical trajectory, the values of the fast variables change many times before a significant evolution of the slowly varying variables is observed. Therefore, a direct discretization is numerically very costly. This problem is known as the *low barrier problem* [155]. To overcome this difficulty in practice, many approaches have been proposed by applied physicists and chemists [37, 48, 117, 122]. We mention the approach consisting in raising the low barriers so that the transition between metastable states occur more often. When used for sampling purposes, the so obtained time averages must be appropriately "debiased" to converge towards the canonical average of the observables under consideration. Another approach consists in gathering states separated by low barriers into “super-states”, so that all barriers between these super-states are of the same order of magnitude.

In [93] (see also Chapter 6 of this thesis), we follow the latter idea and consider simple models for which we are able to rigorously *prove* the pathwise convergence of the reference dynamics to an effective dynamics. As expected, the asymptotic dynamics that we identify coincides with the one that is used in practice in the works mentioned above. This effective dynamics is a kMC model where the transition rates are given as weighted averages of the original dynamics rates, with weights given by the invariant measure of the fast variables. The intuition behind this result, is that, for large time-scale separation between the slow and fast dynamics, the fast dynamics is so fast that it reaches a local equilibrium where the configurations are distributed according to the invariant measure.

In the framework of Langevin and overdamped Langevin dynamics, the construction and the analysis of effective dynamics has been undertaken in several works, see e.g. [96, 97]. In these works, a macroscopic quantity of interest ξ is considered. Using the large time-scale separation between the slowly varying variable $Z_t = \xi(Y_t)$ and the fast varying microscopic variables, an effective dynamics on (Z_t) is rigorously derived.

The difficulty of the questions addressed in [96, 97, 93] comes from the fact that the slow observable is not a Markov process and keeps in memory information about the fast variables. In order to obtain an effective dynamics on the slow variable only, the fast variables need to be filtered out. This memory effect is negligible in the large time-scale separation regime.

To fix ideas, we now present one of the three models treated in [93] (see also Chapter 6). We consider a particle moving in a potential energy surface presenting two macro-states separated by a high energy barrier. Inside each macro-state, there are finitely many micro-states separated by relatively low energy barriers (see Figure 5.2). The ratio ε between the low energy barriers and the large energy barriers encodes the difference of time scales between the (fast) dynamics within a macro-state, where low energy barriers have to be overcome, and the global (slow) dynamics, where large energy barriers have to be overcome.

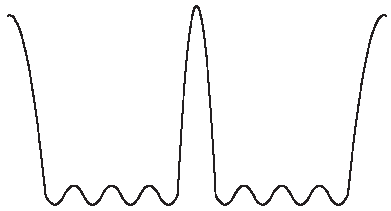

Figure 5.2: Example of a potential energy surface with two macro-states of energy wells.

The dynamics of the system is then given by the jump process $\overline{Y}_t^\varepsilon = (\overline{X}_t^\varepsilon, \overline{Z}_t^\varepsilon)$, where the variables $\overline{X}_t^\varepsilon$ and $\overline{Z}_t^\varepsilon$ respectively indicate in which micro and macro states the system is located. $\overline{X}_t^\varepsilon$ is valued in $\{x_1, \cdots, x_m\}$, m being the number of micro-states in each macro-state and $\overline{Z}_t^\varepsilon$ is valued in $\{0, 1\}$. The intensity matrix of the process $(\overline{Y}_t^\varepsilon)$ is of the form

$$\begin{pmatrix} Q_0 & \varepsilon C_{0,1} \\ \varepsilon C_{1,0} & Q_1 \end{pmatrix}. \tag{5.8}$$

The rates contained in Q_0 and Q_1 correspond to the transition rates between micro states of the same macro-state (internal dynamics), while the rates in $C_{0,1}$ and $C_{1,0}$ determine the transition rates between states belonging to different macro states.

We have studied the long time behavior of a simple function of the slow variable $\overline{Z}_t^\varepsilon$ which is the macro-state in which the particle is located. Other functions can be treated in a similar way. Under the assumption that the internal dynamics within a macro-state is irreducible (thus admitting a unique invariant measure), we prove that, in the limit of asymptotically large time scale separation, namely when ε goes to zero, the dynamics of the slow variable converges to a jump process over the two macro-states. The transition rates of this limiting process are, in some sense, the weighted averages of the transition rates of the reference model.

Theorem 5.3.1. *[93, Th. 2.3][Th. 6.2.3 Chapter 6] Under the irreducibility assumption on the internal dynamics, the rescaled-in-time process $Z_t^\varepsilon = \overline{Z}_{t/\varepsilon}^\varepsilon$ converges, as ε goes to 0, to a process (Z_t) which is a Poisson process of intensity matrix*

$$\begin{pmatrix} 0 & \lambda_0 \\ \lambda_1 & 0 \end{pmatrix}, \tag{5.9}$$

where, for $z \in \{0,1\}$, the transition rate λ_z is given by

$$\sum_x \pi_z(x) \sum_{x'} C_{z,1-z}(x,x')$$

and π_z is the invariant measure of the internal dynamics z.

Note that we obtain a convergence on the path of the system (weak convergence of the corresponding probability measure) and not only on the state of the system for any given time. The proof is essentially based on tightness criteria for probability measures on càd-làg (right continuous with left limits) functions and on both the existence and the uniqueness results of the martingale problem, in particular to identify the asymptotic dynamics.

We have also carried out numerical simulations illustrating our theoretical conclusions.

For example, for the model presented above, we simulate a system with m micro-states in each macro-state and for which the transitions are only possible from one well to its two nearest neighbors. In addition, we apply periodic boundary conditions. The matrices Q_0, Q_1, $C_{0,1}$ and $C_{1,0}$ of the intensity matrix (5.8) read

$$Q_0 = Q_1 = Q \quad \text{and} \quad C_{0,1} = C_{1,0} = C$$

with

$$Q = \begin{pmatrix} 0 & 1 & & & \\ 1 & 0 & 1 & & \\ \ddots & \ddots & \ddots & & \\ & & 1 & 0 & 1 \\ & & & 1 & 0 \end{pmatrix}, \quad C = \begin{pmatrix} 0 & \cdots & & 0 & 1 \\ 0 & \cdots & & & 0 \\ \vdots & & & & \vdots \\ 1 & 0 & \cdots & & 0 \end{pmatrix}.$$

The limiting intensity matrix (5.9) is

$$\begin{pmatrix} 0 & \lambda \\ \lambda & 0 \end{pmatrix},$$

with $\lambda = 2/m$. We monitor the probability distribution of the first exit time S_0^ε of Z_t^ε from a macro-state, and check that this distribution indeed converges to the asymptotic distribution given by Theorem 5.3.1, which is an exponential distribution of parameter λ. On Figure 5.3, we show the convergence of the empirical expectation of S_0^ε to the asymptotic value. We have used $N_{\mathrm{MC}} = 10^4$ Monte-Carlo realizations of the process to compute 95% confidence intervals. We indeed observe the expected convergence when $\varepsilon \to 0$. On Figure 5.4, we show the histogram of S_0^ε in the case $m = 20$ for

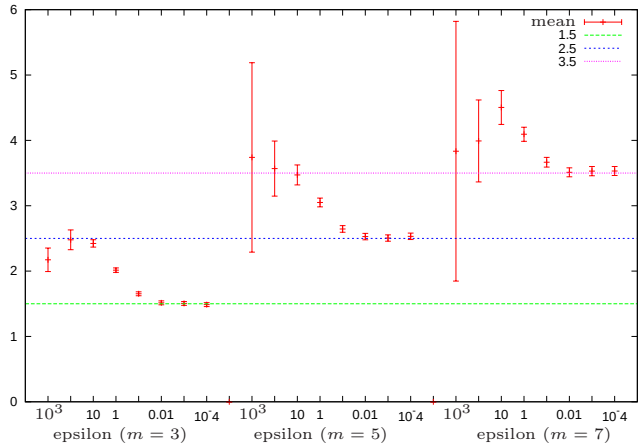

Figure 5.3: Empirical expectation of S_0^ε as a function of ε, for $m = 3$ (left), $m = 5$ (middle) and $m = 7$ (right). The asymptotic values (when $\varepsilon \to 0$) are also represented (solid lines).

two values of ε. We again observe a good qualitative agreement with the limit distribution for small enough ε.

We refer to Chapter 6 for details.

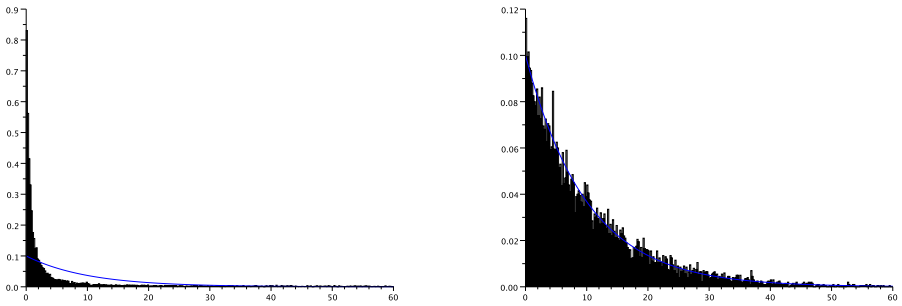

Figure 5.4: Distribution of S_0^ε, the first exit time from a macro-state ($m = 20$). Left: large $\varepsilon = 1$. Right: small $\varepsilon = 10^{-3}$.

Chapter 6

Effective dynamics for a kinetic Monte-Carlo model with slow and fast time scales

The results of this chapter were the object of an article [93], which has been submitted for publication. We consider several multiscale-in-time kinetic Monte Carlo models, in which some variables evolve on a fast time scale, while the others evolve on a slow time scale. In the first two models we consider a particle evolving in a one-dimensional potential energy landscape which has some small and some large barriers, the latter dividing the state space into metastable regions. In the limit of infinitely large barriers, we identify the effective dynamics between these macro-states, and prove the convergence of the process towards a kinetic Monte Carlo model. We next consider a third model, which consists of a system of two particles. The state of each particle evolves on a fast time-scale while conserving their respective energy. In addition, the particles can exchange energy on a slow time scale. Considering the energy of the first particle, we identify its effective dynamics in the limit of asymptotically small ratio between the characteristic times of the fast and the slow dynamics. For all models, our results are illustrated by representative numerical simulations.

Contents

6.1 Introduction

Langevin dynamics is commonly used in computational statistical physics to model the evolution of atomistic systems at finite temperature. The state of the system evolves according to a stochastic differential equation, and is thus modelled as a real vector valued Markov process. Generically, the state space of such atomistic systems can be decomposed into several metastable regions, separated by high energy barriers. It is therefore natural to introduce kinetic Monte-Carlo models as a simplification of the continuous-in-space reference model, where the state space is coarse-grained into discrete states that each corresponds to a metastable region of the continuous model. We refer e.g. to [95] for a formalization of this idea. The resulting dynamics is a time continuous Markov chain, also called jump process.

In this work, we consider such a jump process, with the particularity that two different time scales are present in the system. On a typical trajectory, many jumps of the fast degrees of freedom occur before a significant evolution of the slowly varying variables is observed. Therefore, a direct discretization is numerically very costly. The aim of this work is to find an effective dynamics for the slow variables (which turns out to be again a kinetic Monte Carlo model) while filtering out the fast variables. This effective dynamics is derived in the regime of large time scale separation between the slow and the fast variables.

The problem considered here is well-known in the applied physics and chemistry communities, where it is called the low barrier problem [155]. According to [134], "the low-barrier problem prevails as one of the long-standing challenges to kMC simulations". Several practical approaches have been proposed to address this issue (see e.g. [37, 48, 117, 122]), which include either raising the low barriers (so that the fast processes become slower, and *all* processes end up sharing the same characteristic time scale), or gathering states

separated by low barriers into so-called "super-states", so that all barriers between these super-states are of the same order of magnitude.

In this work, we follow the second track mentioned above. We consider simple models for which we are able to rigorously *prove* the convergence of the reference dynamics to an effective dynamics. As expected, this asymptotic dynamics that we identify coincides with the one that is used in practice in the works mentioned above.

We will successively perform this derivation for three different models.

First, in Section 6.2, we consider a particle subjected to a potential energy presenting two macro-states separated by a high energy barrier. Inside each macro-state, there are finitely many micro-states separated by relatively low energy barriers (see Fig. 6.1). The ratio between the low energy barriers and the large energy barriers is characterized by a parameter ε that we will take asymptotically small. This ratio encodes the difference of time scales between the dynamics within a macro-state (only low energy barriers have to be overcome, and the dynamics is therefore fast), and the global dynamics (for which large energy barriers have to be overcome, making this dynamics slow). See Section 6.2.1 for a complete description of the model.

We are interested in the long time behavior of functions of the slow variables. We consider in this study the simplest case of such function, that is, the macro-state in which the particle is located. At the price of additional technicalities, our approach carries over to more general functions of the slow variables.

Under an irreducibility assumption on the dynamics within the macro-states, we prove that, in the limit of asymptotically large time scale separation (namely when ε goes to zero), the dynamics of the slow variable converges to a jump process over the two macro-states. The transition rates of this limiting process are, in some sense, the weighted averages of the transition rates of the reference model. We underline that our convergence is a convergence on the *path* of the system, and not only on the state of the system at any given time. Our main result, Theorem 6.2.3, is presented in Section 6.2.1 and proved in Section 6.2.2.

In Section 6.2.3, we present detailed numerical results illustrating our theoretical conclusions. In particular, we monitor the probability distribution of the first waiting time in a macro-state, and check that this distribution indeed converges to the asymptotic distribution.

In Section 6.3, we turn to our second model, which is a generalization of the model considered in Section 6.2 where the potential energy presents *infinitely many* macro-states instead of two. To simplify the problem, we assume that the internal dynamics within each macro-state are identical (see Section 6.3.1 for a detailed presentation of the model). In this case, the effective dynamics is a time continuous random walk with Poissonian

waiting times, as stated in our main result of that Section, Theorem 6.3.1. We provide some representative numerical results in Section 6.3.2.

We finally turn in Section 6.4 to our third model, which is different in spirit from the models studied in Sections 6.2 and 6.3. One interest of this last section is to show that the arguments employed to analyze the first two models can be used to study a model different in nature. The system at hand in Section 6.4 contains two particles, each one being described by k spin-like variables. The system evolves either due to the internal evolution of each particle (which occurs on a fast time-scale), or due to the interaction between the two particles (which occurs on a slow time-scale). In the first case, the energy of each particle is preserved while in the second, there is an exchange of energy between the two particles. Note that the total energy of the system is preserved in both cases. Our quantity of interest is the energy of the first particle, which is indeed a slow observable (see Section 6.4.1 for a complete description of the model). We show that the dynamics of the first particle energy converges to a jump process on the (finite) set of admissible energies, this set being determined by the initial energy (see Section 6.4.2, Theorem 6.4.1, for our main result). We collect in Section 6.4.3 some numerical illustrations.

The difficulty of the question we address stems from the fact that the slow observable is not a Markov process: this is a closure problem. A typical tool in this context is the Mori-Zwanzig projection formalism, which is described in details in [60]. This leads to approximating the slow observable by a process which has some memory in time. In our work, we assume that a time-scale separation is present in the system. Memory effects may then be neglected, and the slow observables be approximated by a Markov process. As often the case in such settings, an essential ingredient of our proof is an averaging principle (see [126] for a comprehensive review of that principle in various contexts). We refer to [54, 140, 141] for related works in the framework of discrete time Markov chains in a discrete state space.

As pointed out above, kinetic Monte Carlo models are somewhat obtained as a coarse-grained approximation of real valued Markov processes, such as the Langevin equation (or its overdamped limit). In that framework, the construction and the analysis of effective dynamics has been undertaken in several works, see e.g. [96, 97] and the comprehensive bibliography contained therein.

Throughout this chapter, we use several well-known results that we recall in Appendix 6.A below.

6.2 A particle in a potential energy landscape with two macro-states

In this section we study the dynamics of a particle in a potential energy with two macro-states (see Fig. 6.1). The state of the particle is represented by a macroscopic variable (the index of the macro-state), which can take here only two values, and a microscopic variable (the index of the micro-state within the macro-state). We are concerned with the long time behaviour of the macroscopic variable. In Section 6.2.1, we present the model and state our convergence result (Theorem 6.2.3), the proof of which is given in Section 6.2.2. Numerical results illustrating our theoretical conclusions are gathered in Section 6.2.3.

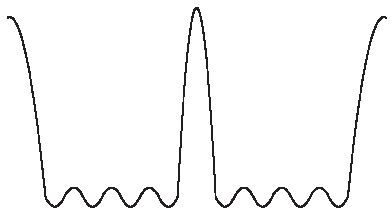

Figure 6.1: Example of a potential energy with two macro-states of energy wells.

6.2.1 Presentation of the model and main result

We now formalize the model described above. We introduce a parameter ε which represents the ratio between the characteristic time of the internal dynamic inside a given macro-state (fast time scale) and the characteristic time of evolution of the macro-state, namely the characteristic time the system spends in a given macro-state before going to the other one. For simplicity, we assume that both macro-states contain the same number of micro-states. The macro-states are labelled by 0 and 1, whereas the micro-states are labelled as 1, 2, ..., m. We set $M = \{1, 2, \dots, m\}$.

The state of the particle is modelled by a time continuous Markov chain $\overline{Y_t^\varepsilon} = \left(\overline{X_t^\varepsilon}, \overline{Z_t^\varepsilon}\right)$, which takes its values in the space $E = M \times \{0, 1\}$. The first coordinate of $\overline{Y_t^\varepsilon}$ represents the micro-state of the particle inside a given macro-state, and thus takes its value in M. The second coordinate determines in which macro-state the particle is located at time t: $\overline{Z_t^\varepsilon} = 0$ or 1.

We denote by $\overline{Q}^\varepsilon$ the transition matrix of the process $\overline{Y_t^\varepsilon}$. Let Q_0 and Q_1 be two $m \times m$ matrices that determine the internal dynamic within each macro-state and let $C_{0,1}$ and $C_{1,0}$ be two $m \times m$ matrices that determine the coupling between micro-states that belong to different macro-states. The

transition rates of $\overline{Y_t^\varepsilon}$ are given by

$$\begin{aligned}\overline{Q}^\varepsilon\left((x,z),\left(x',z\right)\right) &= Q_z\left(x,x'\right), \quad z=0 \text{ or } 1,\ x\neq x',\\ \overline{Q}^\varepsilon\left((x,z),\left(x',z'\right)\right) &= \varepsilon C_{z,1-z}\left(x,x'\right) \quad \text{for } z\neq z'.\end{aligned}$$

Thus, $\overline{Q}^\varepsilon$ is of the form

$$\overline{Q}^\varepsilon = \begin{pmatrix} Q_0 & \varepsilon C_{0,1} \\ \varepsilon C_{1,0} & Q_1 \end{pmatrix}.$$

Remark 6.2.1. *As always for Markov jump processes, the diagonal entries of the transition matrix are irrelevant. Our convention is to take them equal to zero.*

The process $\overline{Y_t^\varepsilon}$ is a jump process. It means that, when it is in a state (x,z), then

- it stays there for a time S, which is a random variable distributed according to an exponential distribution of parameter

$$\overline{q}^\varepsilon(x,z) := \sum_{\substack{(x',z')\in E\\(x',z')\neq(x,z)}} \overline{Q}^\varepsilon\left((x,z),\left(x',z'\right)\right),$$

  that is $\mathbb{P}(S\leq t) = 1-\exp\left(-\overline{q}^\varepsilon(x,z)\,t\right)$.

- At this time S, it jumps to another state. The probability that it jumps to the state $(x',z')\neq(x,z)$ is given by

$$\frac{\overline{Q}^\varepsilon\left((x,z),(x',z')\right)}{\overline{q}^\varepsilon(x,z)}.$$

Note that the paths of a jump process are by convention right continuous, with left limits (they are thus càd-làg functions).

We are interested in the behaviour of a macroscopic observable, that is a function of the slow variable $\overline{Z}_t^\varepsilon$. The dynamic inside a given macro-state, i.e. when the variable z does not change, has a characteristic time of the order of $O(1)$ (i.e. independent of ε), whereas the characteristic time for the particle to go from one macro-state to the other is of the order of $O\left(\varepsilon^{-1}\right)$. We therefore consider henceforth the rescaled-in-time process $\left(\overline{Z}^\varepsilon_{t/\varepsilon}\right)_t$. We introduce the process $Y_t^\varepsilon := \overline{Y}^\varepsilon_{t/\varepsilon}$, which is a jump process of intensity matrix Q^ε given by

$$Q^\varepsilon = \begin{pmatrix} \varepsilon^{-1}Q_0 & C_{0,1} \\ C_{1,0} & \varepsilon^{-1}Q_1 \end{pmatrix}. \tag{6.1}$$

We assume that

$$\text{the matrices } Q_0 \text{ and } Q_1 \text{ are irreducible,} \tag{6.2}$$

therefore admitting unique invariant measures denoted by π_0 and π_1, respectively.

Remark 6.2.2. *Due to our convention on the transition matrix (see Remark 6.2.1), the invariant measure π of a transition matrix $Q = \{q_{i,j}\}_{1\leq i,j\leq m}$ satisfies $\pi^T Q = \pi^T \Delta$, where Δ is a diagonal matrix with $\Delta_i = \sum_{j=1}^m q_{i,j}$.*

Definitions and notations We denote by $D_{\mathbb{R}}[0,\infty)$ the set of càd-làg functions defined on $[0,\infty)$ and valued in $\mathbb{R}$, and by $C_{\mathbb{R}}[0,\infty)$ the set of continuous functions defined on $[0,\infty)$ and valued in $\mathbb{R}$. Endowed with the Skorohod metric (see e.g. [45, p. 116–118]), $D_{\mathbb{R}}[0,\infty)$ is a complete separable space.

A family of probability measures $\mathcal{P}_n$ on $D_{\mathbb{R}}[0,\infty)$ is said to *weakly* converge to a probability measure $\mathcal{P}$ on $D_{\mathbb{R}}[0,\infty)$ if, for any bounded continuous function Φ on $D_{\mathbb{R}}[0,\infty)$,

$$\lim_{n\to\infty} \int \Phi \, d\mathcal{P}_n = \int \Phi \, d\mathcal{P}.$$

A family of random variables X_n valued in $D_{\mathbb{R}}[0,\infty)$ is said to converge *in distribution* to $X \in D_{\mathbb{R}}[0,\infty)$ if the distribution of X_n weakly converges to the distribution of X. Throughout this study, we use the symbol $\Rightarrow$ to denote that convergence.

Main result We are now in position to present the main result of this section. For $z \in \{0,1\}$, we define

$$\overline{C}_{z,1-z}(x) = \sum_{x'\in M} C_{z,1-z}\left(x,x'\right)$$

and

$$\lambda_z = \sum_{x\in M} \overline{C}_{z,1-z}(x)\,\pi_z(x) = \sum_{x\in M} \pi_z(x) \sum_{x'\in M} C_{z,1-z}\left(x,x'\right). \tag{6.3}$$

Theorem 6.2.3. *Let $Y_t^\varepsilon = (X_t^\varepsilon, Z_t^\varepsilon)$ be the jump process of intensity matrix* (6.1) *and starting from an initial condition $Y_0 = (X_0, Z_0)$ independent of ε. We make the assumption* (6.2)*. We denote by $\mathcal{P}^\varepsilon$ the distribution of the process (Z_t^ε) and by $\mathcal{P}$ the distribution of the jump process of initial condition Z_0 and of intensity matrix*

$$\begin{pmatrix} 0 & \lambda_0 \\ \lambda_1 & 0 \end{pmatrix}, \tag{6.4}$$

where λ_0 and λ_1 are defined by (6.3)*. Then, we have $\mathcal{P}^\varepsilon \Rightarrow \mathcal{P}$ as ε goes to* 0*.*

Note that, in (6.4), we have used the convention detailed in Remark 6.2.1.

The above result confirms the intuition according to which, when ε goes to zero, the internal dynamic within each macro-state is speeded up, thus

attaining a local equilibrium where configurations are distributed according to the invariant measures π_0 and π_1 within the macro-states. In the limit when ε goes to 0, the transition from one macro state z to the other one, $1-z$, occurs with the frequency λ_z, which is a weighted average (over the micro-states x, with weights given by the invariant measure π_z) of the frequencies $\overline{C}_{z,1-z}(x)$. In turn, these frequencies are the transition frequencies from the micro-state x of the macro-state z to the other macro-state.

As already emphasized in the introduction, we point out that the above theorem states a convergence result on the *path* $(Z_t^\varepsilon)_{t\geq 0}$, and not only of the random variable Z_t^ε at any time t.

6.2.2 Proofs

To simplify the notation, we first consider the case when both macro-states are similar: in that case, $Q_0 = Q_1 = Q$ and $C_{0,1} = C_{1,0} = C$. The proof of Theorem 6.2.3 is performed in Section 6.2.2.2, and uses some intermediate results shown in Section 6.2.2.1. We briefly mention in Section 6.2.2.3 how to adapt the proof to handle the general case.

The following computation will be very useful in what follows. Recall that the generator of the process Y_t^ε is given by

$$L^\varepsilon \varphi(x,z) = \sum_{x'\in M} \varepsilon^{-1} Q\left(x,x'\right)\left(\varphi\left(x',z\right)-\varphi\left(x,z\right)\right) + \sum_{x'\in M} C\left(x,x'\right)\left(\varphi\left(x',1-z\right)-\varphi\left(x,z\right)\right).$$

We refer the reader to the textbook [45, Section 4.2] for more details on semi-groups and generators associated to jump processes.

Taking $\varphi(x,z) = 1_{z=1}(x,z)$ in the above relation, we obtain

$$L^\varepsilon 1_{z=1}(x,z) = -\sum_{x'\in M} C\left(x,x'\right) 1_{z=1}(x,z) + \sum_{x'\in M} C\left(x,x'\right) 1_{z=0}(x,z),$$

and thus, taking $(x,z) = Y_t^\varepsilon = (X_t^\varepsilon, Z_t^\varepsilon)$, we have

$$L^\varepsilon 1_{z=1}(Y_t^\varepsilon) = \sum_{x'\in M} C\left(X_t^\varepsilon,x'\right)(1-2Z_t^\varepsilon) = \overline{C}\left(X_t^\varepsilon\right)(1-2Z_t^\varepsilon)$$

where $\overline{C}(x) = \sum_{x'\in M} C(x,x')$. We now define the process $(M_t^\varepsilon)_{t\geq 0}$ by

$$\begin{aligned} M_t^\varepsilon &= 1_{z=1}(Y_t^\varepsilon) - 1_{z=1}(Y_0^\varepsilon) - \int_0^t L^\varepsilon 1_{z=1}\left(Y_s^\varepsilon\right) ds \\ &= Z_t^\varepsilon - Z_0 - \int_0^t \sum_{x'\in M} C\left(X_s^\varepsilon,x'\right)(1-2Z_s^\varepsilon)\, ds. \end{aligned} \tag{6.5}$$

Using Proposition 6.A.1, we see that M_t^ε is a martingale with respect to the filtration $\mathcal{F}_t^\varepsilon = \sigma\left(Y_s^\varepsilon, s \leq t\right)$, and that its quadratic variation is given by

$$\begin{aligned}
\langle M^\varepsilon \rangle_t &= \int_0^t \left(L^\varepsilon 1_{z=1}\left(Y_s^\varepsilon\right) - 2\, 1_{z=1}\left(Y_s^\varepsilon\right)\, L^\varepsilon 1_{z=1}\left(Y_s^\varepsilon\right)\right) ds \\
&= \int_0^t \overline{C}\left(X_s^\varepsilon\right)\left(1 - 2Z_s^\varepsilon\right) - 2Z_s^\varepsilon\, \overline{C}\left(X_s^\varepsilon\right)\, \left(1 - 2Z_s^\varepsilon\right) ds \\
&= \int_0^t \overline{C}\left(X_s^\varepsilon\right)\, \left(1 - 2Z_s^\varepsilon\right)^2 ds \\
&= \int_0^t \overline{C}\left(X_s^\varepsilon\right) ds \\
&= \int_0^t g\left(X_s^\varepsilon\right) ds + \lambda t, \qquad (6.6)
\end{aligned}$$

where $\lambda = \lambda_0 = \lambda_1$ (see (6.3)) and

$$g\left(x\right) = \overline{C}\left(x\right) - \lambda = \sum_{x' \in M} C\left(x, x'\right) - \lambda. \qquad (6.7)$$

We have used in the above computation the fact that $\left(1 - 2Z_s^\varepsilon\right)^2 = 1$, a direct consequence of the fact that $Z_s^\varepsilon = 0$ or 1.

In what follows, we will use the fact that

$$Z_t^\varepsilon = Z_0 + \int_0^t f\left(Y_s^\varepsilon\right) ds + \int_0^t \lambda\left(1 - 2Z_s^\varepsilon\right)\, ds + M_t^\varepsilon \qquad (6.8)$$

with

$$f\left(x, z\right) = \left(\sum_{x' \in M} C\left(x, x'\right) - \lambda\right)\, \left(1 - 2z\right), \qquad (6.9)$$

which is a straightforward reformulation of (6.5).

6.2.2.1 Some intermediate results

The following results are useful in the proof of Theorem 6.2.3.

Lemma 6.2.4. *Let $F = \{0, 1\}$, Z_0 be a random variable valued in F, $\lambda_0, \lambda_1 \geq 0$, and $(Z_t)_{t \geq 0}$ be a stochastic process on F. If the process*

$$M_t = Z_t - Z_0 - \int_0^t \left(\lambda_0 - \left(\lambda_0 + \lambda_1\right) Z_s\right) ds$$

is a martingale with respect to the natural filtration of $(Z_t)_{t \geq 0}$, then $(Z_t)_{t \geq 0}$ is a Markov jump process of initial condition Z_0 and of intensity matrix given by

$$R = \begin{pmatrix} 0 & \lambda_0 \\ \lambda_1 & 0 \end{pmatrix}. \qquad (6.10)$$

Proof. We use the uniqueness result of the martingale problem associated to the Markov jump process with intensity matrix R introduced by D.W. Stroock and S.R.S. Varadhan (see e.g. [78, Theorem 21.11]). We recall a simple version of that result in Lemma 6.A.2 below. In view of that result, we only need to check that, for any bounded function $\varphi : F \mapsto \mathbb{R}$, the process

$$M_t^\varphi = \varphi(Z_t) - \varphi(Z_0) - \int_0^t L\varphi(Z_s)\, ds$$

is a martingale, where L is the generator of the jump process associated to the intensity matrix (6.10), which reads

$$L\varphi(z) = \sum_{z' \in F} R(z, z') \left(\varphi(z') - \varphi(z)\right).$$

We note that

$$L\varphi(z=0) = \lambda_0 \left(\varphi(1) - \varphi(0)\right), \quad L\varphi(z=1) = \lambda_1 \left(\varphi(0) - \varphi(1)\right).$$

Since $F = \{0, 1\}$, any bounded function $\varphi : F \mapsto \mathbb{R}$ is of the form

$$\forall z \in F, \quad \varphi(z) = a\delta_{0z} + b\delta_{1z} = a + (b-a)\,\delta_{1z},$$

for some a and b, where δ_{1z} is the Kronecker symbol. The application $\varphi \mapsto M_t^\varphi$ is obviously linear, and it vanishes for constant functions. Therefore, to show that M_t^φ is a martingale for any bounded function $\varphi : F \mapsto \mathbb{R}$, it is sufficient to show that $M_t^{\delta_{1z}}$ is a martingale. On F, we see that $\delta_{1z} = \mathrm{Id}$. We thus have

$$\begin{aligned} M_t^{\delta_{1z}} &= M_t^{\mathrm{Id}} \\ &= Z_t - Z_0 - \int_0^t L\mathrm{Id}\,(Z_s)\, ds \\ &= Z_t - Z_0 - \int_0^t \left(\lambda_0 - (\lambda_0 + \lambda_1)\, Z_s\right) ds. \end{aligned}$$

Using the assumption of the Lemma, we have that $M_t^{\delta_{1z}}$ is a martingale. This concludes the proof. □

Lemma 6.2.5. *Let $g : \mathbb{R} \to \mathbb{R}$ be a Lipschitz function. Then, the function Φ defined by*

$$\begin{aligned} \Phi : D_{\mathbb{R}}[0,\infty) &\to C_{\mathbb{R}}[0,\infty) \subset D_{\mathbb{R}}[0,\infty) \\ x &\mapsto \left(\int_0^t g(x(s))\, ds\right)_t \end{aligned}$$

is continuous.

Proof. Let $(x_n)_{n\in\mathbb{N}}$ be a sequence in $D_{\mathbb{R}}[0,\infty)$ and x in $D_{\mathbb{R}}[0,\infty)$ such that $(x_n)_{n\in\mathbb{N}}$ converges to x in $D_{\mathbb{R}}[0,\infty)$ for the Skorohod topology. We show that $(\Phi(x_n))_{n\in\mathbb{N}}$ converges to $\Phi(x)$ in the Skorohod topology.

We first observe that, for any $y \in D_{\mathbb{R}}[0,\infty)$, the function $\Phi(y)$ is continuous. Since the limit function $\Phi(x)$ is continuous, the convergence of $(\Phi(x_n))_{n\in\mathbb{N}}$ to $\Phi(x)$ in the Skorohod topology is equivalent to the convergence of $(\Phi(x_n))_{n\in\mathbb{N}}$ to $\Phi(x)$ according to the norm $\|\cdot\|_{C^0([0,T])}$, on any compact time interval $[0,T]$ (see e.g. [12, p. 124]).

We now proceed and show that, for any $T > 0$, $\|\Phi(x_n) - \Phi(x)\|_{C^0([0,T])}$ goes to zero as n goes to ∞. Using the characterization of the convergence of $(x_n)_{n\in\mathbb{N}}$ to x given in Proposition 6.A.4, we know that there exists a sequence of strictly increasing, continuous maps λ_n defined on $[0,\infty)$ satisfying (6.45) and (6.46) below. We then have, for any $t \in [0,T]$,

$$\begin{aligned}|\Phi(x_n)(t) - \Phi(x)(t)| &= \left|\int_0^t (g(x_n(s)) - g(x(s)))\,ds\right| \\ &\leq \int_0^t |g(x_n(s)) - g(x(\lambda_n(s)))|\,ds + \int_0^t |g(x(\lambda_n(s))) - g(x(s))|\,ds.\end{aligned} \tag{6.11}$$

The first term of the right-hand side of (6.11) tends to 0 as n goes to ∞ uniformly on $[0,T]$. Indeed,

$$\begin{aligned}\sup_{t\in[0,T]} \int_0^t |g(x_n(s)) - g(x(\lambda_n(s)))|\,ds &\leq T \sup_{s\in[0,T]} |g(x_n(s)) - g(x(\lambda_n(s)))| \\ &\leq T\,C_g \sup_{s\in[0,T]} |x_n(s) - x(\lambda_n(s))|,\end{aligned}$$

where C_g is the Lipschitz constant of g. Using (6.46), we deduce that

$$\lim_{n\to\infty} \sup_{t\in[0,T]} \int_0^t |g(x_n(s)) - g(x(\lambda_n(s)))|\,ds = 0. \tag{6.12}$$

We now turn to the second term of the right-hand side of (6.11). Take $\alpha > 0$. Using [11, Lemma 1 p. 110], we know that there exists a subdivision

$$0 = t_0 < t_1 < \cdots < t_r = T$$

of $[0,T]$ such that, for any i,

$$\sup\{|x(s) - x(t)|,\ t_i \leq s \leq t \leq t_{i+1}\} \leq \alpha.$$

This result is based on the fact that (i) a continuous function on a compact set is also uniformly continuous on this set, and (ii) for any $\beta > 0$, a càdlàg function on a compact set has a finite number of jumps larger than the threshold β.

Using this subdivision of $[0,T]$, we bound the second term of the right-hand side of (6.11) by

$$\int_0^t |g(x(\lambda_n(s))) - g(x(s))|\,ds \leq \sum_{i=0}^{r-1} \int_{t_i}^{t_{i+1}} |g(x(\lambda_n(s))) - g(x(s))|\,ds$$
$$\leq \sum_{i=0}^{r-1} C_g \int_{t_i}^{t_{i+1}} |x(\lambda_n(s)) - x(s)|\,ds. \quad (6.13)$$

Let us introduce $\delta > 0$ such that for any $0 \leq i \leq r-1$, we have $2\delta < t_{i+1} - t_i$. As there is a finite number of points t_i, such a $\delta > 0$ exists. Using the property (6.45) of λ_n, we know that there exists N such that, for any $n > N$, we have $\sup_{s\in[0,T]} |\lambda_n(s) - s| \leq \delta$. We therefore deduce that, for any $n > N$,

$$\sum_{i=0}^{r-1} \int_{t_i}^{t_{i+1}} |x(\lambda_n(s)) - x(s)|ds$$
$$\leq \sum_{i=0}^{r-1} \int_{t_i+\delta}^{t_{i+1}-\delta} |x(\lambda_n(s)) - x(s)|ds + 4r\delta \sup_{t\in[0,T+\delta]} |x(t)|$$
$$\leq \sum_{i=0}^{r-1} (t_{i+1} - t_i - 2\delta)\,\alpha + 4r\delta \sup_{t\in[0,T+\delta]} |x(t)|$$
$$\leq T\alpha + 4r\delta \sup_{t\in[0,T+\delta]} |x(t)|. \quad (6.14)$$

Inserting (6.14) in (6.13), we deduce that the second term of the right-hand side of (6.11) is bounded by

$$\int_0^t |g(x(\lambda_n(s))) - g(x(s))|\,ds \leq C_g T\alpha + 4C_g r\delta \sup_{t\in[0,T+\delta]} |x(t)|.$$

As α and δ are arbitrary small, and r only depends on α, we conclude that the second term of the right-hand side of (6.11) converges to 0 uniformly in t on $[0,T]$.

Collecting this result with the limit (6.12) on the first term and (6.11), we deduce that

$$\lim_{n\to\infty} \sup_{t\in[0,T]} |\Phi(x_n)(t) - \Phi(x)(t)| = 0.$$

This concludes the proof of Lemma 6.2.5. □

Remark 6.2.6. *If the function g is not continuous, then Φ is not continuous. Consider indeed a sequence $(x_n)_{n\in\mathbb{N}}$ of real numbers that converges from above to x, a discontinuity point of g. Denoting $\Phi(x_n)$ the image by Φ of the constant function equal to x_n, we see that, for any t,*

$$\Phi(x_n)(t) - \Phi(x)(t) \longrightarrow t(g(x+) - g(x)) \neq 0.$$

We conclude these intermediate results with the following proposition, that will be useful to study the limit when $\varepsilon \to 0$ of the second term in the right-hand side of (6.8).

Proposition 6.2.7. *Let f be given by* (6.9)*. Under the hypothesis of Theorem 6.2.3, we have, for any $t \geq 0$,*

$$\mathbb{E}\left[\left(\int_0^t f\left(Y_s^\varepsilon\right) ds\right)^2\right] \longrightarrow 0 \quad as\ \varepsilon \to 0. \tag{6.15}$$

Proof. Since E is a finite set, we identify functions $\varphi : E \to \mathbb{R}$ with the vectors $\left((\varphi(x,0))_{x\in M}, (\varphi(x,1))_{x\in M}\right) \in \mathbb{R}^{2m}$ throughout the proof. We likewise identify operators with matrices.

Let $\overline{L}^0$ be the generator corresponding to the intensity matrix $\overline{Q}^0$:

$$\overline{L}^0 u\left(x,z\right) = \sum_{x'\in M} Q\left(x,x'\right)\left(u\left(x',z\right) - u\left(x,z\right)\right).$$

First, we claim that

$$\text{there exists a function } u : E \mapsto \mathbb{R} \text{ such that } \overline{L}^0 u = f. \tag{6.16}$$

Indeed, as Q is irreducible, the only vectors $\mu \in \mathbb{R}^{2m}$ such that $\mu^T \overline{L}^0 = 0$ are the vectors of the form $\mu_{\alpha,\beta} = (\alpha\pi, \beta\pi)$ for any $\alpha, \beta \in \mathbb{R}$ (this is a simple consequence of the Perron-Frobenius theorem). Using (6.9) and (6.3), we compute

$$\begin{aligned}
\mu_{\alpha,\beta}^T f &= \sum_{x\in M} \alpha\pi\left(x\right) f\left(x,0\right) + \sum_{x\in M} \beta\pi\left(x\right) f\left(x,1\right) \\
&= \left(\alpha-\beta\right)\left(\sum_{x\in M} \pi\left(x\right) \sum_{x'\in M} C\left(x,x'\right) - \lambda\right) \\
&= 0.
\end{aligned} \tag{6.17}$$

We thus see that $f \in \left(\mathrm{Ker}\left(\overline{L}^0\right)^*\right)^\perp = \mathrm{Im}\left(\overline{L}^0\right)$, from which we deduce the claim (6.16).

Second, using (6.16), we write that

$$\begin{aligned}
\int_0^t f\left(Y_s^\varepsilon\right) ds &= \int_0^t \overline{L}^0 u\left(Y_s^\varepsilon\right) ds \\
&= \varepsilon \int_0^t L^\varepsilon u\left(Y_s^\varepsilon\right) - \varepsilon \int_0^t L^C u\left(Y_s^\varepsilon\right) ds
\end{aligned} \tag{6.18}$$

where we have used the decomposition

$$\varepsilon L^\varepsilon u = \overline{L}^0 u + \varepsilon L^C u$$

with

$$L^C u(x,z) = \sum_{x' \in M} C\left(x,x'\right)\left(u\left(x',1-z\right) - u\left(x,z\right)\right).$$

We successively bound the two terms of the right-hand side of (6.18). Introduce $N_t^u = u\left(Y_t^\varepsilon\right) - u\left(Y_0^\varepsilon\right) - \displaystyle\int_0^t L^\varepsilon u\left(Y_s^\varepsilon\right) ds$. In view of Proposition 6.A.1, we know that N_t^u is a martingale of quadratic variation given by

$$\langle N^u \rangle_t = \int_0^t \left(L^\varepsilon u^2\left(Y_s^\varepsilon\right) - 2u\left(Y_s^\varepsilon\right)\, L^\varepsilon u\left(Y_s^\varepsilon\right)\right) ds.$$

For any $v : E \to \mathbb{R}$, we have

$$\|L^\varepsilon v\|_\infty \leq 2m\|v\|_\infty \left(\varepsilon^{-1}\|Q\|_\infty + \|C\|_\infty\right).$$

Therefore,

$$\begin{aligned}
\mathbb{E}\left[\left(N_t^u\right)^2\right] &= \mathbb{E}\left(\langle N^u\rangle_t\right) \\
&\leq 2mt\left[\|u^2\|_\infty\left(\varepsilon^{-1}\|Q\|_\infty + \|C\|_\infty\right) + 2\|u\|_\infty^2\left(\varepsilon^{-1}\|Q\|_\infty + \|C\|_\infty\right)\right] \\
&\leq A + \varepsilon^{-1}B,
\end{aligned}$$

where A and B are positive constants independent of ε. It follows that the first term of the right hand side of (6.18) satisfies

$$\begin{aligned}
\mathbb{E}\left[\left(\varepsilon\int_0^t L^\varepsilon u\left(Y_s^\varepsilon\right)\right)^2\right] &= \mathbb{E}\left[\left(\varepsilon\left(N_t^u - u\left(Y_t^\varepsilon\right) + u\left(Y_0^\varepsilon\right)\right)\right)^2\right] \\
&\leq 2\varepsilon^2\left(\mathbb{E}\left[\left(N_t^u\right)^2\right] + 4\|u^2\|_\infty\right) \\
&\leq 2\varepsilon^2\left(A' + \varepsilon^{-1}B\right). \qquad (6.19)
\end{aligned}$$

For the second term of the right hand side of (6.18), we directly obtain

$$\mathbb{E}\left[\left(\varepsilon\int_0^t L^C u\left(Y_s^\varepsilon\right)\right)^2\right] \leq \varepsilon^2 t^2\left(4m\|C\|_\infty^2\|u\|_\infty^2\right). \qquad (6.20)$$

Collecting (6.18), (6.19) and (6.20), we obtain the desired result (6.15). This concludes the proof of Proposition 6.2.7. □

6.2.2.2 Proof of Theorem 6.2.3 (symmetric case)

All the convergences in this proof are taken when ε goes to 0. We will omit to recall it. The proof consists of four steps.

Step 1: the family of probability measures $\left(\mathcal{P}^\varepsilon\right)_{\varepsilon>0}$ is relatively compact

We use the tightness criterion of Theorem 6.A.5, and check that its conditions (6.47) and (6.48) are satisfied.

As the variables Z_t^ε take only two values, 0 and 1, the condition (6.47) is trivially satisfied with the choices $K = 1$ and $n_0 = 1$.

Let us now show that the condition (6.48) is satisfied. Let $N \in \mathbb{N}$, $\alpha > 0$, $\theta > 0$ and $\varepsilon > 0$. Let S and T be two $\mathcal{F}^\varepsilon$-stopping times such that $S \leq T \leq S + \theta \leq N$. Recall that a random variable $T : \left(\Omega, (\mathcal{F}_t)_{t\geq 0}\right) \to \mathbb{R}^+ \cup \{\infty\}$ is a stopping time if, for any $t \geq 0$, the set $\{T \leq t\}$ is $\mathcal{F}_t$-measurable. Using (6.5), we have

$$|Z_T^\varepsilon - Z_S^\varepsilon| \leq \left| \int_S^T \sum_{y\in M} C\left(X_s^\varepsilon, y\right)\left(1 - 2Z_s^\varepsilon\right) ds \right| + \left|M_T^\varepsilon - M_S^\varepsilon\right|. \tag{6.21}$$

The first term of the right-hand side of (6.21) is bounded as follows:

$$\left| \int_S^T \sum_{y\in M} C\left(X_s^\varepsilon, y\right)\left(1 - 2Z_s^\varepsilon\right) ds \right| \leq |T - S|\, m\|C\|_\infty \leq \theta m \|C\|_\infty. \tag{6.22}$$

To bound the second term of the right-hand side of (6.21), we use the Tchebytchev inequality:

$$\mathbb{P}\left(\left|M_T^\varepsilon - M_S^\varepsilon\right| \geq \alpha\right) \leq \frac{\mathbb{E}\left|M_T^\varepsilon - M_S^\varepsilon\right|^2}{\alpha^2}. \tag{6.23}$$

We denote by $\widetilde{M}_t^\varepsilon = M_{t+S}^\varepsilon - M_S^\varepsilon$ and $\widetilde{\mathcal{F}}_t^\varepsilon = \mathcal{F}_{t+S}^\varepsilon$. As S is a bounded stopping time, we infer from the optional stopping theorem (see e.g. [135, Theorem 3.2]) that $\widetilde{M}^\varepsilon$ is a $\widetilde{\mathcal{F}}^\varepsilon$-martingale, of quadratic variation

$$\langle \widetilde{M}^\varepsilon \rangle_t = \langle M^\varepsilon \rangle_{S+t} - \langle M^\varepsilon \rangle_S.$$

In particular, we have

$$\langle \widetilde{M}^\varepsilon \rangle_{T-S} = \langle M^\varepsilon \rangle_T - \langle M^\varepsilon \rangle_S.$$

It follows that

$$\begin{aligned}
\mathbb{E}\left[\left|M_T^\varepsilon - M_S^\varepsilon\right|^2\right] &= \mathbb{E}\left[\left|\widetilde{M}_{T-S}^\varepsilon\right|^2\right] \\
&= \mathbb{E}\left[\langle \widetilde{M}^\varepsilon \rangle_{T-S}\right] \\
&= \mathbb{E}\left[\langle M^\varepsilon \rangle_T - \langle M^\varepsilon \rangle_S\right] \\
&= \mathbb{E}\left[\int_S^T g\left(X_s^\varepsilon\right) ds + \lambda\left(T - S\right)\right] \\
&\leq \theta\left(\|g\|_\infty + \lambda\right), \qquad (6.24)
\end{aligned}$$

where we have used (6.6) and where g is defined by (6.7). We then infer from (6.23) that

$$\mathbb{P}\left(|M_T^\varepsilon - M_S^\varepsilon| \geq \alpha\right) \leq \frac{\theta\left(\|g\|_\infty + \lambda\right)}{\alpha^2}. \tag{6.25}$$

We deduce from (6.21), (6.22) and (6.25) that the condition (6.48) of Theorem 6.A.5 below is satisfied.

Assumptions (6.47) and (6.48) being satisfied, we can apply Theorem 6.A.5, which implies that the family of probability measures $(\mathcal{P}^\varepsilon)_\varepsilon$ is tight. In view of Prohorov's theorem (see e.g. [45, Theorem 2.2]), this implies that the family $(\mathcal{P}^\varepsilon)_{\varepsilon>0}$ is relatively compact.

There thus exists a sub-family of $(\mathcal{P}^\varepsilon)_\varepsilon$, that we denote $\left(\mathcal{P}^{\varepsilon'}\right)_{\varepsilon'}$, which is convergent. Otherwise stated, there exists a process Z such that $Z^{\varepsilon'} \Rightarrow Z$.

Step 2: there exists a martingale M_t and a sub-family $M_t^{\varepsilon'}$ such that $M_t^{\varepsilon'} \Rightarrow M_t$

In view of [77, Theorem VI.4.13], a sufficient criterion for (M^ε) to be relatively compact is that $(\langle M^\varepsilon \rangle)$ is C-tight. Let us check this criterion. We have shown above (see (6.6)) that

$$\langle M^\varepsilon \rangle_t = \int_0^t g\left(X_s^\varepsilon\right) ds + \lambda t,$$

where g is defined by (6.7). Therefore, the family of paths $\left(\langle M^\varepsilon \rangle\right)_{\varepsilon>0}$ is uniformly Lipschitz, and hence C-tight (see [77, Definition VI.3.25 and Proposition VI.3.26]). We can thus consider a sub-family of $(M_t^\varepsilon)_{t\geq 0}$, that we denote $\left(M_t^{\varepsilon'}\right)_{t\geq 0}$, which weakly converges to a process M. Using [77, Proposition IX.1.1], we know that the process $(M_t)_{t\geq 0}$ is a martingale with respect to its natural filtration.

Step 3: equation satisfied by Z

We have shown at the end of Step 1 that there exists a process Z and a sub-family $Z^{\varepsilon'}$ such that $Z^{\varepsilon'} \Rightarrow Z$. We now identify a stochastic differential equation satisfied by $(Z_t)_{t\geq 0}$.

Recall first that $(Z_t^\varepsilon)_{t\geq 0}$ satisfies (6.8), namely

$$Z_t^\varepsilon = Z_0 + \int_0^t f\left(Y_s^\varepsilon\right) ds + \int_0^t \lambda\left(1 - 2Z_s^\varepsilon\right) ds + M_t^\varepsilon. \tag{6.26}$$

Passing to the limit $\varepsilon' \to 0$, let us show that $(Z_t)_{t\geq 0}$ satisfies

$$Z_t = Z_0 + \int_0^t \lambda\left(1 - 2Z_s\right) ds + M_t. \tag{6.27}$$

We first consider $B_t^\varepsilon = \displaystyle\int_0^t f\left(Y_s^\varepsilon\right) ds$. With the same techniques as above, we can show that $\left(B_t^\varepsilon\right)$ is a relatively compact family. There thus exists (B_t) and a sub-family $\left(B_t^{\varepsilon'}\right)$ such that $B^{\varepsilon'} \Rightarrow B$. We infer from Proposition 6.2.7 that, for all $t \geq 0$, B_t^ε converges to 0 in $L^2(\Omega)$, hence $\mathbb{E}\left[B_t^2\right] = 0$ for all $t \geq 0$. It follows that the family $\left(B_t^{\varepsilon'}\right)$ converges to 0 in distribution.

We next turn to $J_t^\varepsilon = \displaystyle\int_0^t \lambda\left(1 - 2Z_s^\varepsilon\right) ds$. Introduce $J_t = \displaystyle\int_0^t \lambda\left(1 - 2Z_s\right) ds$. The function $g : z \mapsto \lambda\left(1 - 2z\right)$ is Lipschitz on $\mathbb{R}$, thus, using Lemma 6.2.5, we know that the function

$$\begin{array}{rccc} \Phi : D_{\mathbb{R}}\left[0,\infty\right) & \longrightarrow & D_{\mathbb{R}}\left[0,\infty\right) \\ z & \mapsto & \left(\displaystyle\int_0^t \lambda\left(1 - 2z\left(s\right)\right) ds\right)_t \end{array}$$

is continuous. The convergence $Z^{\varepsilon'} \Rightarrow Z$ therefore implies that

$$J^{\varepsilon'} = \Phi(Z^{\varepsilon'}) \Rightarrow \Phi(Z) = J.$$

We have thus obtained that all the terms in (6.26) weakly converge. It remains to show that we can add up the weak limits. To do so, we show with the same techniques as before that the family $(B^\varepsilon, J^\varepsilon, M^\varepsilon)$ is relatively compact, and that the limit of any sub-family has as marginal distributions those of B, J and M. We conclude that $B^{\varepsilon'} + J^{\varepsilon'} + M^{\varepsilon'} \Rightarrow B + J + M$. Passing to the limit $\varepsilon' \to 0$ in (6.26), we then indeed obtain (6.27).

Step 4: conclusion

We infer from (6.27) (where, we recall, M_t is a martingale) and Lemma 6.2.4 (with $\lambda_0 = \lambda_1 = \lambda$) that $(Z_t)_{t\geq 0}$ is a Markov jump process of initial condition Z_0 and of intensity matrix given

$$\begin{pmatrix} 0 & \lambda \\ \lambda & 0 \end{pmatrix}.$$

The process Z is thus uniquely defined.

It follows that all convergent sub-families $Z^{\varepsilon'}$ have the same limit Z. The whole sequence Z^ε therefore converges to this common limit Z. This concludes the proof of Theorem 6.2.3 in the symmetric case.

6.2.2.3 Non-symmetric case

In this Section, we briefly sketch the proof in the non-symmetric case, that is when $Q_0 \neq Q_1$ or $C_{0,1} \neq C_{1,0}$ in (6.1). The structure of the proof is similar to that in the symmetric case.

First, the generator associated to the process (Y_t^ε) reads

$$L^\varepsilon \varphi(x,z) = \sum_{x' \in M} \varepsilon^{-1} Q_z(x,x') \left(\varphi(x',z) - \varphi(x,z)\right) + \sum_{x' \in M} C_{z,1-z}(x,x') \left(\varphi(x',1-z) - \varphi(x,z)\right).$$

Choosing the function $\varphi(x,z) = z$, we see that

$$L^\varepsilon \varphi(x,z) = \sum_{x' \in M} C_{z,1-z}(x,x')(1-2z) = f(x,z) + h(z),$$

where we have introduced (recall (6.3))

$$f(x,z) = \left(\sum_{x' \in M} C_{z,1-z}(x,x') - \lambda_z \right)(1-2z)$$

and

$$h(z) = (1-2z)\lambda_z = (1-2z) \sum_{x,x' \in M} C_{z,1-z}(x,x')\pi_z(x).$$

Using again Proposition 6.A.1, we see that the process

$$M_t^\varepsilon = \varphi(Y_t^\varepsilon) - \varphi(Y_0^\varepsilon) - \int_0^t L^\varepsilon \varphi(Y_s^\varepsilon)\, ds \tag{6.28}$$

is a martingale. Using the above notation, the equation (6.28) can be recast as

$$Z_t^\varepsilon = Z_0 + \int_0^t f(Y_s^\varepsilon)\, ds + \int_0^t h(Z_s^\varepsilon)\, ds + M_t^\varepsilon. \tag{6.29}$$

To pass to the limit $\varepsilon \to 0$ in the above equation, we follow the same lines as in the proof detailed in Sections 6.2.2.1 and 6.2.2.2.

Consider the second term of the right-hand side of (6.29). As in the proof of Proposition 6.2.7, we can show that $\mu^T f = 0$ for any $\mu \in \mathbb{R}^{2m}$ such that $\mu^T \overline{L}^0 = 0$, which are vectors of the form $(\alpha\pi_0, \beta\pi_1)$ for any α and β in $\mathbb{R}$. This implies that $\displaystyle\int_0^t f(Y_s^\varepsilon)\, ds$ converges to 0 in $L^2(\Omega)$ for any $t \geq 0$.

We turn now to the third term of the right-hand side of (6.29). Let $\widetilde{h}$ be the affine function defined on $\mathbb{R}$ by $\widetilde{h}(0) = h(0)$ and $\widetilde{h}(1) = h(1)$. The function $\widetilde{h}$ is obviously Lipschitz on $\mathbb{R}$, hence, using Lemma 6.2.5, we know that the function

$$\begin{aligned} \Phi : D_{\mathbb{R}}[0,\infty) &\to D_{\mathbb{R}}[0,\infty) \\ z &\mapsto \left(\int_0^t \widetilde{h}(z(s))\, ds \right)_t \end{aligned}$$

is continuous. Since $\int_0^t h\left(Z_s^\varepsilon\right) ds = \int_0^t \widetilde{h}\left(Z_s^\varepsilon\right) ds$, this allows to pass to the limit in that term.

As in Section 6.2.2.2 (Step 3 of the proof), we can thus pass to the limit $\varepsilon \to 0$ in (6.29), and show that Z^ε converges in distribution to a process Z, that satisfies

$$\begin{aligned} Z_t &= Z_0 + \int_0^t h(Z_s) ds + M_t \\ &= Z_0 + \int_0^t \left[\lambda_0 - Z_s\left(\lambda_0 + \lambda_1\right)\right] ds + M_t, \end{aligned}$$

where M is a martingale. We then infer from Lemma 6.2.4 that $(Z_t)_{t\geq 0}$ is a jump process on $\{0,1\}$, of initial condition Z_0 and of intensity matrix

$$\begin{pmatrix} 0 & \lambda_0 \\ \lambda_1 & 0 \end{pmatrix},$$

as claimed in Theorem 6.2.3.

6.2.3 Numerical illustration

We have implemented the model presented in Section 6.2.1. As shown on Fig. 6.1, the energy wells can be gathered in two macro-states (each of them containing m micro-states) separated by a high potential energy barrier. The transitions are only possible from one well to its two nearest neighbours. In addition, we apply periodic boundary conditions. The matrices Q_0, Q_1, $C_{0,1}$ and $C_{1,0}$ of the intensity matrix (6.1) read

$$Q_0 = Q_1 = Q \quad \text{and} \quad C_{0,1} = C_{1,0} = C$$

with

$$Q = \begin{pmatrix} 0 & q & & & \\ q & 0 & q & & \\ \ddots & \ddots & \ddots & & \\ & & q & 0 & q \\ & & & q & 0 \end{pmatrix}, \quad C = \begin{pmatrix} 0 & \cdots & & 0 & c \\ 0 & \cdots & & & 0 \\ \vdots & & & & \vdots \\ c & 0 & \cdots & & 0 \end{pmatrix}.$$

We work with $q = c = 1$.

We are interested in the distribution of the first exit time S_0^ε from a macro-state. From Theorem 6.2.3, we know that, in the limit ε going to 0, S_0^ε follows an exponential distribution of parameter $\lambda = 2c/m$ (independently of what the initial condition of the system is). In order to quantify

the convergence of the distribution of S_0^ε to the predicted distribution, we consider the L^1 norm of the difference of the densities:

$$\mathrm{err}_{L^1} = \int_0^\infty |f - f^\varepsilon| \approx \frac{1}{n} \sum_{i=1}^{n} |f\,(i\Delta x) - f_i^\varepsilon|, \tag{6.30}$$

where $f\,(x) = \lambda e^{-\lambda x}$ is the limit distribution and f^ε is the distribution of S_0^ε. This latter distribution is calculated on the bounded interval $[0, s]$ with $s = n\Delta x$ on a grid of size Δx: $f_i^\varepsilon \approx \dfrac{1}{\Delta x} \displaystyle\sum_{x \in [i\Delta x, (i+1)\Delta x]} f^\varepsilon(x)$ for any $i \in [1, n]$. In the sequel, we work with $\Delta x = 0.05$ and $s = n\Delta x = 5$.

Remark 6.2.8. *Other criteria can also be considered to characterize the convergence of the probability distribution f^ε towards f. One example is the discrepancy, which is the difference (in L^∞ norm) of the cumulative distribution functions:*

$$D = \sup_{A \geq 0} \left| \int_0^A f - \int_0^A f^\varepsilon \right|. \tag{6.31}$$

We have used this criterion e.g. on Fig. 6.5 below.

We first consider how results depend on ε. We work with a fixed initial condition, namely $Y_0 = (0, 0)$. At the initial time, the particle is in the first macro-state, and in the micro-state which is the closest to the energy barrier between the two macro-states (see Fig. 6.1).

On Figs. 6.2 and 6.3, we show the convergence of the empirical expectation and variance of S_0^ε to the asymptotic value (we have considered 10^4 independent and identically distributed realizations of the process to compute 95 % confidence intervals). We indeed observe convergence of both quantities to their asymptotic limits when $\varepsilon \to 0$.

On Fig. 6.4, we show the histogram of S_0^ε in the case $m = 20$ for two values of ε. We again observe a good qualitative agreement with the limit distribution for small enough ε. This can be quantified by looking precisely at the convergence of the distribution of S_0^ε to the asymptotic distribution when ε goes to 0, for different values of m (see Fig. 6.5). The left part of that figure seems to show that the convergence slows down when the number m of micro-states within a macro-state increases.

We next monitor how the distribution of S_0^ε behaves when we vary the initial condition. For this test, we work with $m = 5$. Figures 6.6 and 6.7 show the empirical expectation and variance for different initial positions and for different values of ε. We notice that, for an initial condition which is at the middle of the macro-state, the convergence with respect to ε is slower than for the initial conditions which are at the boundaries of a macro-state.

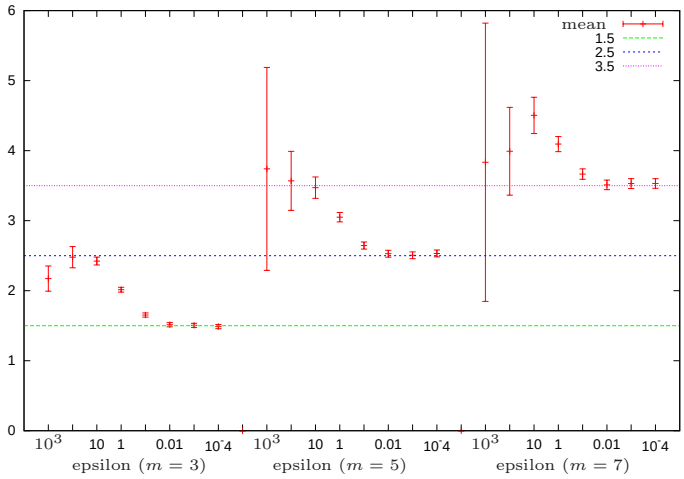

Figure 6.2: Empirical expectation of S_0^ε as a function of ε, for $m = 3$ (left), $m = 5$ (middle) and $m = 7$ (right). The asymptotic values (when $\varepsilon \to 0$) are also represented (solid lines).

This difference is due to the diffusion phenomenon which occurs inside each macro-state as a result of the transition to the nearest neighbors.

To better understand the behavior of the system for large values of m, we have simulated our model with $m = 20$. We show on Figs. 6.8 and 6.9 the empirical expectation and variance of S_0^ε for two different initial conditions, one on the boundary ($Y_0 = (0, 0)$) and the other in the middle of the macro-state ($Y_0 = (10, 1)$). On Fig. 6.10, we show the convergence of the distribution of S_0^ε to its limit for these two initial conditions.

We clearly see that the convergence is slower and the error margins are larger (for the same number of Monte-Carlo realizations) than when we chose smaller values of m (compare for example Fig. 6.8 with Fig. 6.2 or Fig. 6.10 with Fig. 6.5). The system indeed takes more time in a given macro-state before reaching its boundary and possibly jumping.

To conclude this numerical illustration, we have monitored the distribution of S_1^ε, the exit time from the second macro state, and compared it with that of S_0^ε, the exit time from the first macro-state. We observe (results not shown) that S_1^ε has the same asymptotic behaviour as S_0^ε, a fact which is in agreement with the theoretical predictions.

Remark 6.2.9. *The parameters of the numerical simulations reported here have been chosen so that the limit dynamics (at $\varepsilon = 0$) is an inaccurate approximation of the reference dynamics when ε is large (say $\varepsilon \geq 1$).*

There are actually cases when the limit dynamics is an accurate approximation of the reference dynamics, even if ε is not small. For example,

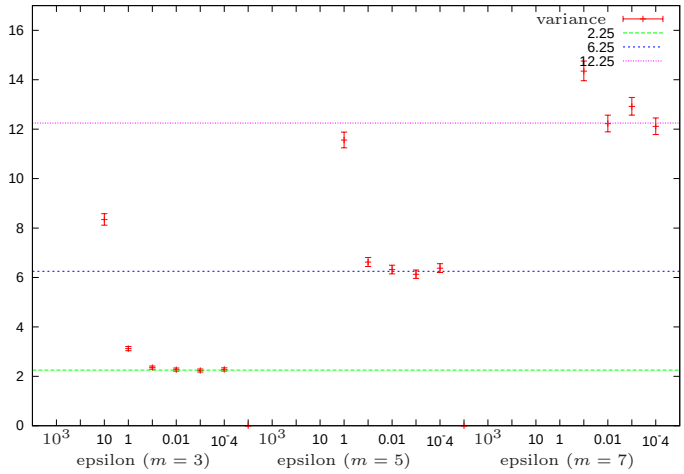

Figure 6.3: Empirical variance of S_0^ε as a function of ε, for $m = 3$ (left), $m = 5$ (middle) and $m = 7$ (right). The asymptotic values (when $\varepsilon \to 0$) are also represented (solid lines).

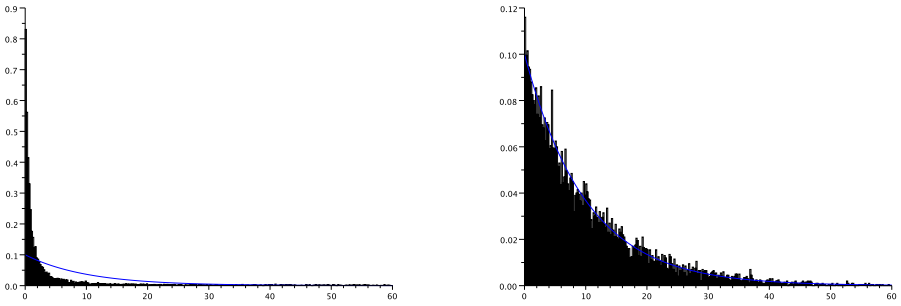

Figure 6.4: Distribution of S_0^ε, the first exit time from a macro-state ($m = 20$). Left: large $\varepsilon = 1$. Right: small $\varepsilon = 10^{-3}$.

consider the case where, for a given macro-state (say $Z = 0$), the transitions from each micro-state of this macro-state to any micro-state of the other macro-state ($Z = 1$) share the same frequency. In the case of the symmetric model considered in Section 6.2.2, the homogeneity condition means that

$$\sum_{x' \in M} C\left(x, x'\right) = \textit{Cte independent of } x.$$

In this case, the macroscopic dynamic is decoupled from the microscopic variable, as can be seen from (6.5)*, and of course does not depend on ε.*

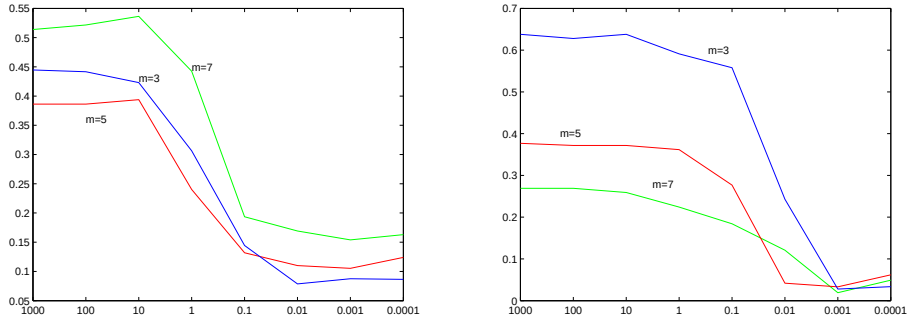

Figure 6.5: L^1 error (6.30) (left) and discrepancy (6.31) (right) on the distribution of S_0^ε as a function of ε.

6.3 A particle in a potential energy landscape with infinitely many macro-states

In Section 6.2, we have studied the dynamics of a particle in a potential energy with two macro-states. We now turn to the system composed of a particle in a potential energy with infinitely many macro-states. We establish a convergence result on the dynamics of a slow quantity of interest in Section 6.3.1, before turning to numerical illustrations in Section 6.3.2.

6.3.1 Presentation of the model and main result

As mentioned above, we consider here the dynamics of a particle in a potential energy with infinitely many macro-states. As in Section 6.2.1, the state of the particle is described by $\overline{Y_t^\varepsilon} = \left(\overline{X_t^\varepsilon}, \overline{Z_t^\varepsilon}\right)$, which takes its values in $M \times \mathbb{Z}$, where again $\overline{X_t^\varepsilon} \in M = \{1, \ldots, m\}$ is the label of the micro-state in which the particle is. The variable $\overline{Z_t^\varepsilon}$ is the label of the macro-state in which the particle is at time t, and it now takes any value of $\mathbb{Z}$.

For simplicity, we assume that the dynamics within each macro-state is similar. We also restrict the transitions from one macro-state to its two neighbors. The transition from z to $z+1$ may have different properties than the transition from z to $z-1$ (thus creating a macroscopic drift in the dynamics). We also assume that the system is macroscopically homogeneous, in the sense that properties are translation invariant with respect to z. Under these assumptions, a typical transition intensity for the process $\left(\overline{Y_t^\varepsilon}\right)_t$ is given by

$$\begin{array}{rcl} \forall z \in \mathbb{Z}, \quad \overline{Q}^\varepsilon\left((x,z),(x',z)\right) & = & Q\left(x,x'\right), \\ \forall z \in \mathbb{Z}, \quad \overline{Q}^\varepsilon\left((x,z),(x',z+1)\right) & = & \varepsilon C_r\left(x,x'\right), \\ \forall z \in \mathbb{Z}, \quad \overline{Q}^\varepsilon\left((x,z),(x',z-1)\right) & = & \varepsilon C_l\left(x,x'\right), \\ \forall z \in \mathbb{Z}, \quad \overline{Q}^\varepsilon\left((x,z),(x',z')\right) & = & 0 \text{ if } z' \neq z,\, z+1 \text{ or } z-1. \end{array} \tag{6.32}$$

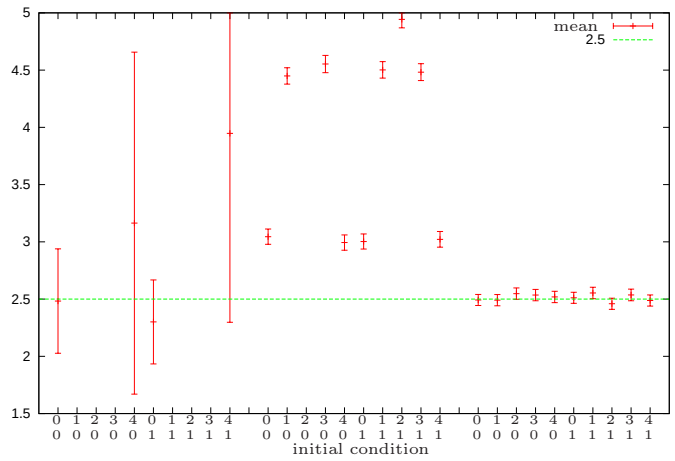

Figure 6.6: Empirical expectation of S_0^ε for different initial conditions and for $\varepsilon = 10^3$ (left), $\varepsilon = 1$ (center) and $\varepsilon = 10^{-3}$ (right). Initial conditions are shown on the x-axis in the format $\begin{pmatrix} X_0 \\ Z_0 \end{pmatrix} \in \begin{pmatrix} M \\ \{0,1\} \end{pmatrix}$, with $M = \{0,1,2,3,4\}$.

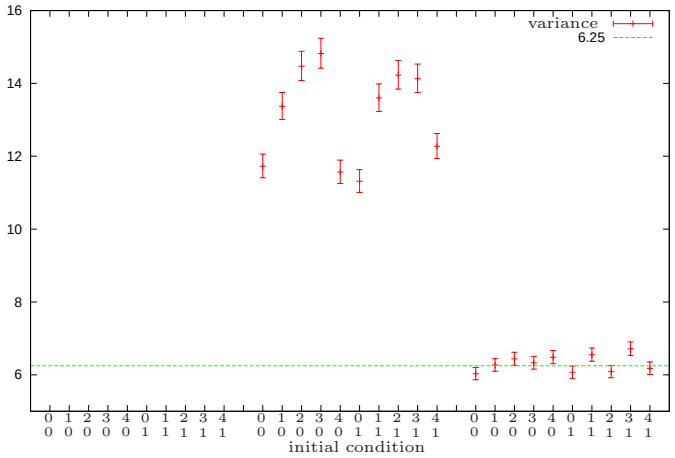

Figure 6.7: Empirical variance of S_0^ε for different initial conditions and different values of ε, with the same convention as on Fig. 6.6 (results for $\varepsilon = 10^3$ do not fit in the chosen y-range).

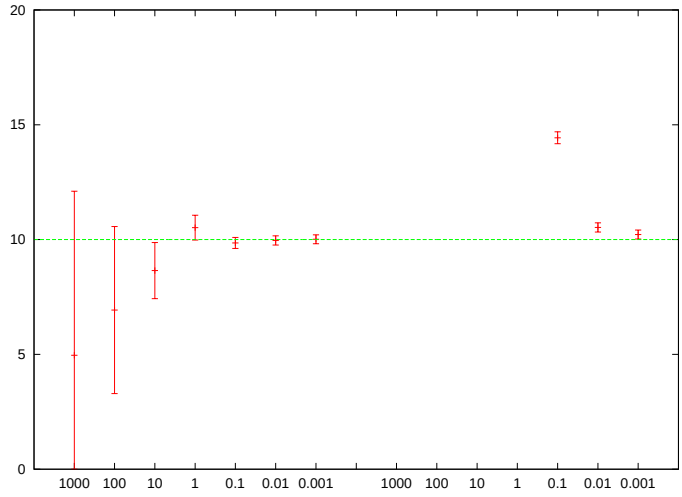

Figure 6.8: Empirical expectation of S_0^ε for $m = 20$, as a function of ε, for two different initial conditions: $Y_0 = (0, 0)$ (left) and $Y_0 = (10, 1)$ (right).

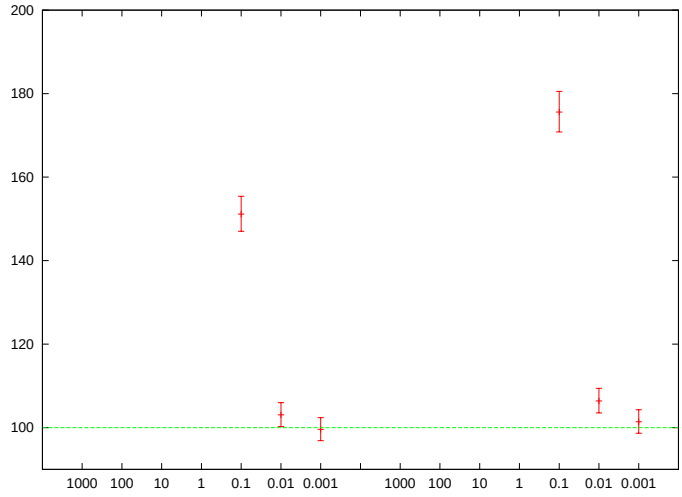

Figure 6.9: Empirical variance of S_0^ε for $m = 20$, as a function of ε, for two different initial conditions: $Y_0 = (0, 0)$ (left) and $Y_0 = (10, 1)$ (right).

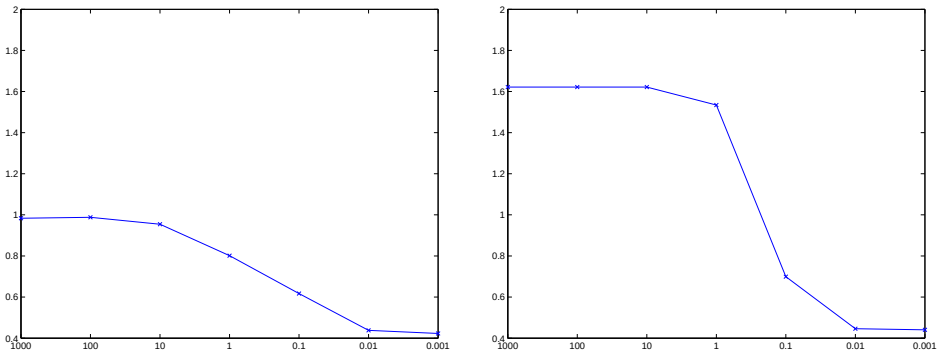

Figure 6.10: L^1 error (6.30) on the distribution of S_0^ε for $m = 20$. Left: initial condition $Y_0 = (0, 0)$. Right: initial condition $Y_0 = (10, 1)$.

We again assume that the matrix Q is irreducible (see (6.2)) and introduce its unique invariant measure π. The average of the jump frequency according to the invariant measure reads

$$\lambda_l = \sum_{x,x' \in M} C_l\left(x, x'\right) \pi\left(x\right), \quad \lambda_r = \sum_{x,x' \in M} C_r\left(x, x'\right) \pi\left(x\right). \tag{6.33}$$

We introduce the generator L defined by: for any bounded function φ on $\mathbb{Z}$,

$$L\varphi(z) = \lambda_l \varphi(z-1) + \lambda_r \varphi(z+1) - \left(\lambda_r + \lambda_l\right) \varphi(z), \tag{6.34}$$

which is the generator of a jump process $(Z_t)_{t \geq 0}$ on $\mathbb{Z}$, with jumps at times defined by a Poisson process of parameter $\lambda_l + \lambda_r$. When the process jumps, it jumps to the right (resp. to the left) with probability $\dfrac{\lambda_r}{\lambda_r + \lambda_l}$ (resp. $\dfrac{\lambda_l}{\lambda_r + \lambda_l}$).

The main result of this section is the following:

Theorem 6.3.1. *Assume that the matrix Q is irreducible. Consider the rescaled-in-time process $Y_t^\varepsilon = (X_t^\varepsilon, Z_t^\varepsilon) = \overline{Y}_{t/\varepsilon}^\varepsilon$ with initial condition $Y_0 = (X_0, Z_0)$ independent of ε. We denote by $\mathcal{P}^\varepsilon$ the distribution of the process $(Z_t^\varepsilon)_t$ and by $\mathcal{P}$ the distribution of the process starting from the initial condition Z_0 and having as generator the operator L defined by* (6.34)*. Then*

$$\mathcal{P}^\varepsilon \Rightarrow \mathcal{P} \text{ as } \varepsilon \text{ goes to } 0.$$

The proof of this result follows the same steps as that of Theorem 6.2.3, up to the fact that the process Z^ε is no longer bounded. To circumvent this difficulty, we need to work with an *arbitrary* bounded function of Z^ε, in contrast to the proof of Theorem 6.2.3, where it is sufficient to directly work with Z^ε.

We briefly sketch the proof of Theorem 6.3.1. The generator L^ε of Y_t^ε reads, for a bounded function φ,

$$\begin{aligned} L^\varepsilon \varphi(x,z) = &\sum_{x' \in M} \varepsilon^{-1} Q\left(x,x'\right)\left(\varphi\left(x',z\right)-\varphi\left(x,z\right)\right) \\ &+ \sum_{x' \in M} C_l\left(x,x'\right)\left(\varphi\left(x',z-1\right)-\varphi\left(x,z\right)\right) \\ &+ \sum_{x' \in M} C_r\left(x,x'\right)\left(\varphi\left(x',z+1\right)-\varphi\left(x,z\right)\right). \end{aligned}$$

For a function $\varphi(x,z) = F(z)$ which only depends on the macroscopic variable (where F is a bounded function on $\mathbb{Z}$), we have

$$\begin{aligned} \left(L^\varepsilon F\right)(x,z) = &\sum_{x' \in M} C_l\left(x,x'\right)\left(F\left(z-1\right)-F\left(z\right)\right) \\ &+ \sum_{x' \in M} C_r\left(x,x'\right)\left(F\left(z+1\right)-F\left(z\right)\right). \end{aligned}$$

Using Proposition 6.A.1, we know that the process

$$M_t^\varepsilon = F\left(Z_t^\varepsilon\right) - F\left(Z_0\right) - \int_0^t \left(L^\varepsilon F\right)\left(X_s^\varepsilon, Z_s^\varepsilon\right) ds \tag{6.35}$$

is a $\mathcal{F}_t^\varepsilon$-martingale. We now introduce

$$\begin{aligned} G(F)(x,z) = &\left(F\left(z-1\right)-F\left(z\right)\right) \sum_{x' \in M} \left(C_l\left(x,x'\right)-\lambda_l\right) \\ &+ \left(F\left(z+1\right)-F\left(z\right)\right) \sum_{x' \in M} \left(C_r\left(x,x'\right)-\lambda_r\right), \end{aligned} \tag{6.36}$$

so that

$$\left(L^\varepsilon F\right)(x,z) = G(F)(x,z) + LF(z)$$

where L is defined by (6.34). We then recast (6.35) as

$$F\left(Z_t^\varepsilon\right) = F\left(Z_0\right) + \int_0^t G\left(F\right)\left(Y_s^\varepsilon\right) ds + \int_0^t LF\left(Z_s^\varepsilon\right) ds + M_t^\varepsilon. \tag{6.37}$$

We are now left with passing to the limit $\varepsilon \to 0$ in (6.37).

Consider first the second term of the right-hand side of (6.37). We have the following result (compare with Proposition 6.2.7):

Proposition 6.3.2. *For any bounded function F defined on $\mathbb{Z}$ and any $t \geq 0$, under the assumptions of Theorem 6.3.1, we have*

$$\mathbb{E}\left[\left(\int_0^t G\left(F\right)\left(Y_s^\varepsilon\right) ds\right)^2\right] \longrightarrow 0 \quad \text{as } \varepsilon \to 0,$$

where $G(F)$ is defined by (6.36).

Proof. The proof follows the same steps as that of Proposition 6.2.7. Fix $z \in \mathbb{Z}$ and consider the function $x \in M \mapsto G_z(x) = G(F)(x,z)$, that we identify with a vector in $\mathbb{R}^m$, denoted G_z. Using (6.33), we observe that $\pi^T G_z = 0$. We then deduce that, for any $y \in \mathbb{R}^m$ such that $y^T(Q-\Delta) = 0$ (where Δ has been defined in Remark 6.2.2), we have $y^T G_z = 0$. Thus $G_z \in (\mathrm{Ker}(Q-\Delta)^*)^\perp = \mathrm{Im}(Q-\Delta)$ and that there exists $u_z \in \mathbb{R}^m$ such that $(Q-\Delta)\,u_z = G_z$. Introducing the function $u(x,z) = u_z(x)$, we easily check that $\overline{L}^0 u = G(F)$. The rest of the proof is identical to that of Proposition 6.2.7. □

For the other terms of (6.37), the proof follows exactly the same steps as in the proof of Theorem 6.2.3. We hence obtain that the weak limit Z of (Z^ε) satisfies that, for every bounded function F on $\mathbb{Z}$, there exists a martingale M^F such that

$$F(Z_t) = F(Z_0) + \int_0^t LF(Z_s)\,ds + M_t^F. \tag{6.38}$$

Using Lemma 6.A.2, we conclude that Z is a jump process of generator L defined by (6.34).

Remark 6.3.3. *We refer to Appendix 6.B for the study of the limit process introduced in Theorem 6.3.1, after a rescaling both* in time and space*. We show there that it converges to a Brownian motion (up to a multiplicative constant).*

6.3.2 Numerical illustration

We have simulated the model described in Section 6.3.1, with the choices

$$Q = \begin{pmatrix} 0 & q & & & \\ q & 0 & q & & \\ \ddots & \ddots & \ddots & & \\ & & q & 0 & q \\ & & & q & 0 \end{pmatrix},$$

$$C_l = \begin{pmatrix} 0 & \cdots & & 0 & c_l \\ 0 & \cdots & & & 0 \\ \vdots & & & & \vdots \\ 0 & 0 & \cdots & & 0 \end{pmatrix} \quad \text{and} \quad C_r = \begin{pmatrix} 0 & \cdots & & 0 & 0 \\ 0 & \cdots & & & 0 \\ \vdots & & & & \vdots \\ c_r & 0 & \cdots & & 0 \end{pmatrix}$$

with $q = 1$, $c_r = 2$, $c_l = 1$, $m = 5$ and the initial condition $Y_0 = (0,0)$ (similar results are obtained for other initial conditions). The parameters λ_r and λ_l of the macroscopic evolution are

$$\lambda_l = \frac{c_l}{m} = \frac{1}{5} \quad \text{and} \quad \lambda_r = \frac{c_r}{m} = \frac{2}{5}.$$

We first monitor the convergence of the distribution of S_0^ε, the exit time from the first well. On Fig. 6.11, we show its empirical expectation and variance. We see that they converge to their asymptotic values as ε goes to zero. This convergence is confirmed by the histogram representation (on Fig. 6.12), where we see a good agreement between the discrete curve and the asymptotic curve for sufficiently small values of ε. Likewise, the L^1 error, also shown on Fig. 6.12, indeed converges to zero.

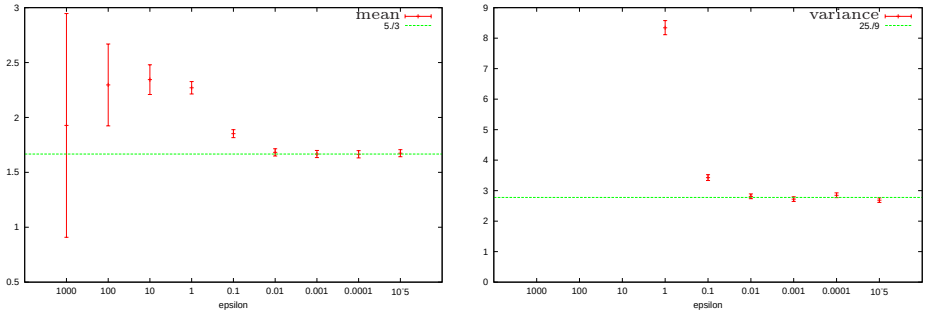

Figure 6.11: Empirical expectation (left) and variance (right) of S_0^ε as a function of ε.

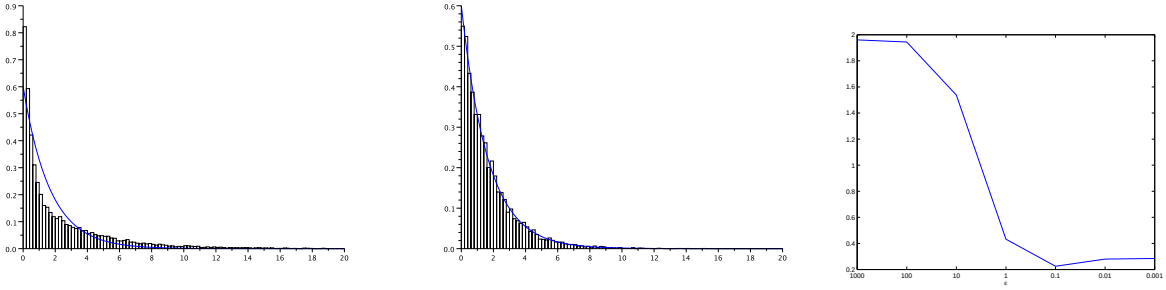

Figure 6.12: Left and Center: Distribution of S_0^ε, the first exit time from a macro-state (Left: large $\varepsilon = 1$. Center: small $\varepsilon = 10^{-3}$). Right: L^1 error (6.30) on the distribution of S_0^ε, as a function of ε.

We next study the distribution of the amplitude of the first jump of the macroscopic variable Z^ε, that is the distribution of the random variable

$$\Delta Z^\varepsilon := Z^\varepsilon_{S_0^\varepsilon} - Z_0.$$

On Fig. 6.13, we show the empirical expectation and variance of ΔZ^ε, which are observed to converge to their asymptotic values. Note that the limiting

process Z, the generator of which is the operator (6.34), drifts to the right, since $\lambda_r > \lambda_l$. We compute that

$$\mathbb{E}(\Delta Z) = \mathbb{P}(\Delta Z = 1) \times 1 + \mathbb{P}(\Delta Z = -1) \times (-1) = \frac{2/5}{3/5} - \frac{1/5}{3/5} = \frac{1}{3},$$

and we indeed see on Fig. 6.13 that $\lim_{\varepsilon \to 0} \mathbb{E}(\Delta Z^\varepsilon) = \mathbb{E}(\Delta Z)$. On Fig. 6.14, we show the empirical distribution of ΔZ^ε for a small ε, and we observe that

$$\mathbb{P}(\Delta Z^\varepsilon = 1) \approx \mathbb{P}(\Delta Z = 1) = \frac{2}{3}, \quad \mathbb{P}(\Delta Z^\varepsilon = -1) \approx \mathbb{P}(\Delta Z = -1) = \frac{1}{3}.$$

We also check on Fig. 6.14 that the L^1 error between the distribution of ΔZ^ε and that of ΔZ goes to 0 as ε goes to zero.

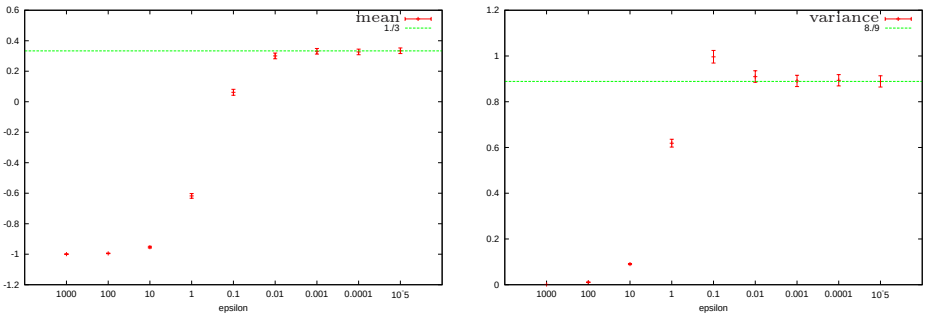

Figure 6.13: Empirical expectation (left) and variance (right) of ΔZ^ε as a function of ε.

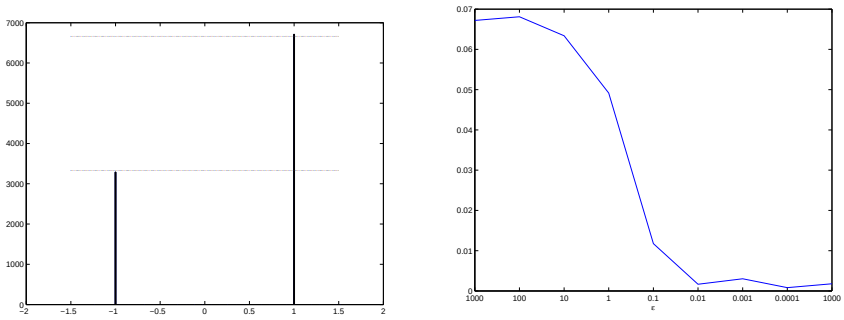

Figure 6.14: Left: Empirical estimation of the probabilities $\mathbb{P}(\Delta Z^\varepsilon = -1)$ and $\mathbb{P}(\Delta Z^\varepsilon = 1)$ for $\varepsilon = 10^{-5}$. Right: L^1 error (6.30) on the distribution of ΔZ^ε as a function of ε.

6.4 Exchange of energy in a system of two particles

In this final section, we consider a more elaborate model. This model is composed of two particles. The state of the first (resp. second) particle is described by the vector X (resp. Z) with k components. An energy functional $\mathcal{E}$ is associated to each particle. The system evolves either due to the internal evolution within a particle, or due to the interaction between the two particles. In the first case, the energy of each particle is preserved. In the second case, the internal energy of each particle varies, but the total energy of the system, $\mathcal{E}(X) + \mathcal{E}(Z)$, is preserved. Interactions between the particles occur on a much slower time scale than the internal evolution of each particle. One must hence wait for a long time before observing any change in each particle energy.

The model is presented in details in Section 6.4.1. In Section 6.4.2, we establish a convergence result on the time evolution of the energy of the first particle, which is our macroscopic variable of interest. We only give there a sketch of the proof as it follows the same arguments as before.

One of the interesting features of this model is that the macroscopic variable of interest is *not* one cartesian coordinate of the system. We show that the arguments used in Sections 6.2 and 6.3 carry over to this more general case.

6.4.1 Presentation of the model

We consider a model with two particles. Each particle contains k spin-like variables, that can take the value 0 (spin down) or 1 (spin up). At time t, the state of the system is given by $\overline{Y}_t^\varepsilon = \left(\overline{X}_t^\varepsilon, \overline{Z}_t^\varepsilon\right) \in M \times M$, where $M = \{0,1\}^k$ is the space for the k spins of each particle. For each particle, we are given an energy functional $\mathcal{E}(x) = \mathcal{E}(x_1, \ldots, x_k)$ (with $x_j \in \{0,1\}$, $1 \leq j \leq k$) that depends on the state of the k spins of the particle. One choice is to set $\mathcal{E}(x) = x_1 + \cdots + x_k$, which would correspond (up to a multiplicative factor) to the energy of k spins in a uniform magnetic field.

The intensity matrix of the process $\overline{Y}^\varepsilon$ is built as follows:

- the internal dynamic of each particle is governed by an intensity matrix Q that conserves its energy, i.e. $Q(x,x') = 0$ if $\mathcal{E}(x) \neq \mathcal{E}(x')$. We define the global internal dynamic intensity matrix $\overline{Q}^0$ by

$$\begin{aligned}
\overline{Q}^0\left((x,z),(x',z)\right) &= Q\left(x,x'\right) \quad \text{if } x \neq x', \\
\overline{Q}^0\left((x,z),(x,z')\right) &= Q\left(z,z'\right) \quad \text{if } z \neq z', \\
\overline{Q}^0\left((x,z),(x',z')\right) &= 0 \quad \text{if } x \neq x' \text{ and } z \neq z'.
\end{aligned}$$

- the coupling between the two particles is described by a matrix C. This coupling introduces an exchange of energy between the two particles,

while keeping the total energy constant. We assume that C is such that

$C\left((x,z),\left(x',z'\right)\right)=0$ if $\mathcal{E}(x)+\mathcal{E}(z)\neq\mathcal{E}(x')+\mathcal{E}(z')$ or if $\mathcal{E}(x)=\mathcal{E}(x')$.

- the transition intensities of the process Y^{ε} are given by

$$\overline{Q}^{\varepsilon}=\overline{Q}^{0}+\varepsilon C.$$

We make the following assumption:

$$\begin{array}{c}\text{the matrix } Q \text{ is such that, for every admissible energy level } e,\\ \text{the state class of energy } e \text{ is irreducible}\\ \text{and thus admits a unique invariant probability measure } \overline{\pi}^{e}.\end{array}\tag{6.39}$$

We denote by π^{e} the probability measure on M defined by $\pi^{e}(x)=\overline{\pi}^{e}(x)$ if $\mathcal{E}(x)=e$ and $\pi^{e}(x)=0$ otherwise. Any normalized linear combination of the measures π^{e} (with non-negative coefficients) is thus an invariant probability measure of Q. We consider the state classes of $M\times M$ such that the energy of each particle stays constant. These classes are irreducible and admit a unique invariant probability measure $\pi^{e}\otimes\pi^{e'}$. The invariant probability measures of $\overline{Q}^{0}$ are of the form $(Z')^{-1}\sum_{e,e'}Z(e,e')\,\pi^{e}\otimes\pi^{e'}$, where $Z(e,e')\geq 0$ are some coefficients and where Z' is a normalization constant.

6.4.2 Main result

As pointed out above, our quantity of interest is $\mathcal{E}\left(\overline{X}_{t}^{\varepsilon}\right)$, the energy of the first particle. In view of the chosen scaling in $\overline{Q}^{\varepsilon}$, the characteristic time scale of evolution of this energy is of the order of ε^{-1}. We thus need to rescale in time the evolution, and therefore introduce $Y_{t}^{\varepsilon}=(X_{t}^{\varepsilon},Z_{t}^{\varepsilon}):=\overline{Y}_{t/\varepsilon}^{\varepsilon}$ and $\mathcal{E}_{t}^{\varepsilon}=\mathcal{E}\left(\overline{X}_{t/\varepsilon}^{\varepsilon}\right)$.

We now identify the limit of the process $\mathcal{E}_{t}^{\varepsilon}$, and state the main convergence result of that section, namely Theorem 6.4.1 below. Let L^{ε} be the generator of $(Y_{t}^{\varepsilon})_{t\geq 0}$, which is a jump process of intensity matrix $Q^{\varepsilon}=\varepsilon^{-1}\overline{Q}^{\varepsilon}$. We have

$$L^{\varepsilon}\varphi(x,z)=\sum_{x',z'\in M}Q^{\varepsilon}\left((x,z),\left(x',z'\right)\right)\;\left[\varphi\left(x',z'\right)-\varphi(x,z)\right].$$

For a function $\varphi(x,z)=F(x)$ that only depends on the state of the first particle, we have

$$\begin{aligned}\left(L^{\varepsilon}F\right)(x,z) &= \sum_{x',z'\in M}Q^{\varepsilon}\left((x,z),\left(x',z'\right)\right)\;\left[F\left(x'\right)-F(x)\right]\\ &= \varepsilon^{-1}\sum_{x'\in M}Q\left(x,x'\right)\;\left[F\left(x'\right)-F(x)\right]\\ &\quad+\sum_{x',z'\in M}C\left((x,z),\left(x',z'\right)\right)\left[F\left(x'\right)-F(x)\right].\end{aligned}$$

Now choosing $F = \mathcal{E}$, we obtain

$$l(x,z) := (L^{\varepsilon}\mathcal{E})(x,z) = \sum_{x',z' \in M} C\left((x,z),(x',z')\right)\ \left[\mathcal{E}\left(x'\right) - \mathcal{E}(x)\right]$$

since $Q(x,x') = 0$ if $\mathcal{E}(x') \neq \mathcal{E}(x)$. We suppose that, at the initial time, the energy of each particle is independent of ε: $\mathcal{E}(X_0^{\varepsilon}) = E_x$ and $\mathcal{E}(Z_0^{\varepsilon}) = E_z$, where E_x and E_z are independent of ε. The total initial energy is denoted $E = E_x + E_z$.

Using Proposition 6.A.1, we see that there exists a martingale M_t^{ε} such that

$$\mathcal{E}_t^{\varepsilon} = E_x + \int_0^t l(X_s^{\varepsilon}, Z_s^{\varepsilon})\, ds + M_t^{\varepsilon}. \tag{6.40}$$

As in Section 6.2.2, we can show that there exists a process $\mathcal{E}$ such that $\mathcal{E}^{\varepsilon}$ converges to $\mathcal{E}$, up to extraction. We now identify the distribution of the process $\mathcal{E}$ and show that it is independent of the chosen sub-sequence (thereby proving that all the sequence $\mathcal{E}^{\varepsilon}$ converges to $\mathcal{E}$, and not only a subsequence).

We introduce the average of the drift in (6.40) with respect to an invariant measure of $\overline{Q}^0$:

$$\begin{aligned}
\widetilde{l}(e_1,e_2) &= \sum_{\substack{x \text{ s.t. } \mathcal{E}(x)=e_1 \\ z \text{ s.t. } \mathcal{E}(z)=e_2}} l(x,z)\pi^{e_1}(x)\pi^{e_2}(z) \\
&= \sum_{\substack{x \text{ s.t. } \mathcal{E}(x)=e_1 \\ z \text{ s.t. } \mathcal{E}(z)=e_2}} \pi^{e_1}(x)\pi^{e_2}(z) \sum_{x',z' \in M} C\left((x,z),(x',z')\right)\ \left[\mathcal{E}\left(x'\right) - \mathcal{E}(x)\right] \\
&= \sum_{\substack{x \text{ s.t. } \mathcal{E}(x)=e_1 \\ z \text{ s.t. } \mathcal{E}(z)=e_2}} \pi^{e_1}(x)\pi^{e_2}(z) \sum_{\substack{x',z' \text{ s.t.} \\ \mathcal{E}(x')+\mathcal{E}(z')=e_1+e_2}} C\left((x,z),(x',z')\right)\ \left[\mathcal{E}\left(x'\right) - e_1\right].
\end{aligned}$$

We further define

$$f(x,z) = l(x,z) - \widetilde{l}\left(\mathcal{E}(x),\mathcal{E}(z)\right)$$

and

$$g(e) = \widetilde{l}\,(e, E-e)\,, \tag{6.41}$$

and recast (6.40) as

$$\mathcal{E}_t^{\varepsilon} = E_x + \int_0^t f(X_s^{\varepsilon}, Z_s^{\varepsilon})\, ds + \int_0^t g\left(\mathcal{E}_s^{\varepsilon}\right) ds + M_t^{\varepsilon}. \tag{6.42}$$

We now want to pass to the limit $\varepsilon \to 0$ in (6.42).

Consider the second term in the right-hand side of(6.42). By construction, f is the difference between the function l and its average $\widetilde{l}$. The average

of f is thus expected to vanish. This is indeed the case: for any two energies e_1 and e_2, we compute

$$\begin{aligned}
(\pi^{e_1} \otimes \pi^{e_2})^T f &= \sum_{\substack{x \text{ s.t. } \mathcal{E}(x)=e_1 \\ z \text{ s.t. } \mathcal{E}(z)=e_2}} \pi^{e_1}(x)\pi^{e_2}(z) f(x,z) \\
&= \sum_{\substack{x \text{ s.t. } \mathcal{E}(x)=e_1 \\ z \text{ s.t. } \mathcal{E}(z)=e_2}} \pi^{e_1}(x)\pi^{e_2}(z) l(x,z) - \sum_{\substack{x \text{ s.t. } \mathcal{E}(x)=e_1 \\ z \text{ s.t. } \mathcal{E}(z)=e_2}} \pi^{e_1}(x)\pi^{e_2}(z) \widetilde{l}(e_1,e_2) \\
&= \sum_{\substack{x \text{ s.t. } \mathcal{E}(x)=e_1 \\ z \text{ s.t. } \mathcal{E}(z)=e_2}} \pi^{e_1}(x)\pi^{e_2}(z) l(x,z) - \widetilde{l}(e_1,e_2) \\
&= 0.
\end{aligned}$$

Therefore, for any μ such that $\mu^T \overline{L}^0 = 0$, we have $\mu^T f = 0$. Following the arguments of Proposition 6.2.7, we deduce that, for any t, the random variable $\displaystyle\int_0^t f\left(X_s^\varepsilon, Z_s^\varepsilon\right) ds$ converges to 0 in $L^2(\Omega)$, and that the random process also weakly converges to 0.

We now turn to the third term of the right-hand side of (6.42), and claim that (up to the extraction of a sub-sequence)

$$\int_0^t g\left(\mathcal{E}_s^\varepsilon\right) ds \;\Rightarrow\; \int_0^t g\left(\mathcal{E}_s\right) ds, \tag{6.43}$$

where $\mathcal{E}_s$ is such that $\mathcal{E}_s^\varepsilon \;\Rightarrow\; \mathcal{E}_s$. The function g is defined on the set $\mathcal{E}(M)$ of the admissible energies, which is a finite set (we recall that $M = \{0,1\}^k$). We denote by $\widetilde{g}$ the P1 interpolation of g on $\mathbb{R}$, which is a piecewise linear function defined on $\mathbb{R}$ and that coincides with g on $\mathcal{E}(M)$. The function $\widetilde{g}$ being Lipschitz on $\mathbb{R}$, we infer from Lemma 6.2.5 that the function $\Phi : x \mapsto \left(\displaystyle\int_0^t \widetilde{g}\left(x_s\right) ds\right)_t$ is continuous. Therefore, the convergence $\mathcal{E}_s^\varepsilon \;\Rightarrow\; \mathcal{E}_s$ implies that

$$\left(\int_0^t g\left(\mathcal{E}_s^\varepsilon\right)\right) = \left(\int_0^t \widetilde{g}\left(\mathcal{E}_s^\varepsilon\right)\right) \text{ converges to } \left(\int_0^t \widetilde{g}\left(\mathcal{E}_s\right)\right) = \left(\int_0^t g\left(\mathcal{E}_s\right)\right).$$

We thus have proved (6.43).

We next turn to the last term in the right-hand side of (6.42). As in the previous sections, we can show that M^ε weakly converges (up to extraction) to some martingale M.

We can now pass to the limit $\varepsilon \to 0$ in (6.42), and obtain that the limit process $\mathcal{E}$ satisfies

$$\mathcal{E}_t = E_x + \int_0^t g\left(\mathcal{E}_s\right) ds + M_t. \tag{6.44}$$

It is now easy to recast the above equation in a more useful form. In view of (6.41), we indeed note that

$$g(e) = \sum_{e'} \underbrace{\sum_{\substack{x \text{ s.t. } \mathcal{E}(x)=e \\ z \text{ s.t. } \mathcal{E}(z)=E-e}} \sum_{\substack{x' \text{ s.t. } \mathcal{E}(x')=e' \\ z' \text{ s.t. } \mathcal{E}(z')=E-e'}} \pi^e(x)\pi^{E-e}(z)\; C\left((x,z),\left(x',z'\right)\right)}_{B_E(e,e')} (e'-e).$$

Therefore, the equation (6.44) reads

$$\mathcal{E}_t = E_x + \int_0^t \sum_{e'} B_E\left(\mathcal{E}_s, e'\right)\; \left(e' - \mathcal{E}_s\right) ds + M_t,$$

where, we recall, E is the total energy of the system, which is preserved along the dynamics.

We conclude this formal approach by pointing out that the above equation actually does not allow to identify the law of the process $(\mathcal{E}_t)_t$. In the proof of Theorem 6.2.3 (see Section 6.2.2), we performed that step of the proof by using Lemma 6.2.4, which is not possible in our context here. To identify the law of the process $(\mathcal{E}_t)_t$, we resort to Lemma 6.A.2. Consider a bounded function φ on $\mathcal{E}(M)$, and the martingale

$$M_t^{\varphi,\varepsilon} := \varphi\left(\mathcal{E}_t^\varepsilon\right) - \varphi\left(E_x\right) - \int_0^t \sum_{e'} B_E\left(\mathcal{E}_s^\varepsilon, e'\right)\left(\varphi\left(e'\right) - \varphi\left(\mathcal{E}_s^\varepsilon\right)\right) ds.$$

Following the same steps as above, we show that each term converges when ε goes to zero. In particular, $M_t^{\varphi,\varepsilon}$ converges to a martingale M^φ that satisfies

$$M_t^\varphi = \varphi\left(\mathcal{E}_t\right) - \varphi\left(E_x\right) - \int_0^t \sum_{e'} B_E\left(\mathcal{E}_s, e'\right)\left(\varphi\left(e'\right) - \varphi\left(\mathcal{E}_s\right)\right) ds.$$

Lemma 6.A.2 then implies that $\mathcal{E}$ is a jump process of intensity matrix $B = B_E(e,e')$.

We thus have the following result:

Theorem 6.4.1. *We denote by $\mathcal{P}^\varepsilon$ the distribution of the process $(\mathcal{E}^\varepsilon)$, where we assumed that the initial condition (E_x, E_z) is independent of ε. We denote by $\mathcal{P}$ the distribution of the jump process of initial condition E_x and of intensity matrix $B = B_E(e,e')$, with $E = E_x + E_z$. Under the assumptions on the matrices Q and C described in Section 6.4.1, we have*

$$\mathcal{P}^\varepsilon \Rightarrow \mathcal{P} \text{ as } \varepsilon \to 0.$$

6.4.3 Numerical illustration

We have numerically simulated the system described above, when each particle has two spins, i.e. $k = 2$. In this case, $\mathrm{Card}(M) = 4$, and the admissible states for each particle are labelled as 1: $\downarrow\downarrow$, 2: $\uparrow\downarrow$, 3: $\downarrow\uparrow$ and 4: $\uparrow\uparrow$. The energy of each particle is the sum of the energies of its two spins, which are equal to 0 (spin down, $\downarrow$) or 1 (spin up, $\uparrow$). The matrix Q that governs the internal dynamic of each particle is of the form

$$Q = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -q_1 & q_1 & 0 \\ 0 & q_2 & -q_2 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}.$$

This matrix preserves the energy of the particle as it only allows transitions between states of the same energy (namely, $\uparrow\downarrow$ and $\downarrow\uparrow$). We work with $q_1 = 10$ and $q_2 = 1$.

There are five possible initial energies for the complete system:

- $E = 0$ (both particles are initially in the state 1: $\downarrow\downarrow$). The system then does not evolve, as only one state corresponds to that total energy. The case when $E = 4$ is similar.
- $E = 1$: initially, one particle is in the state 1: $\downarrow\downarrow$, while the other particle is in the state 2: $\uparrow\downarrow$ or 3: $\downarrow\uparrow$. We consider this case below. Note that the case when $E = 3$ is similar.
- $E = 2$: without loss of generality, we may assume that the initial state of each particle is 2: $\uparrow\downarrow$.

In what follows, we only consider the case $E = 1$. We have checked that results obtained in the case $E = 2$ lead to the same qualitative conclusions.

As mentioned above, we assume that the initial state of the first particle is 2: $\uparrow\downarrow$ (corresponding to the energy $E_x = 1$), and that the initial state of the second particle is 1: $\downarrow\downarrow$ (corresponding to the energy $E_z = 0$).

The matrix C (which encodes how the two particles interact) is chosen of the form

$$\begin{aligned} C\left((2,z),\left(x',z'\right)\right) &= c_1 \text{ if } \mathcal{E}(x)+\mathcal{E}(z)=\mathcal{E}\left(x'\right)+\mathcal{E}\left(z'\right) \text{ and } \mathcal{E}(x)\neq\mathcal{E}\left(x'\right), \\ C\left((x,z),\left(x',z'\right)\right) &= c_2 \text{ if } x\neq 2 \text{ and } \mathcal{E}(x)+\mathcal{E}(z)=\mathcal{E}\left(x'\right)+\mathcal{E}\left(z'\right) \text{ and } \mathcal{E}(x)\neq\mathcal{E}\left(x'\right), \\ C\left((x,z),\left(x',z'\right)\right) &= 0 \text{ otherwise.} \end{aligned}$$

We work with $c_1 = 1$ and $c_2 = 0.2$.

We monitor the distribution of S_0^ε, the first waiting time before an exchange of energy between the two particles occurs. Figures 6.15 and 6.16 show the convergence of the distribution of S_0^ε to the asymptotic distribution, which is an exponential distribution of parameter $B(1,0) = 6/11$.

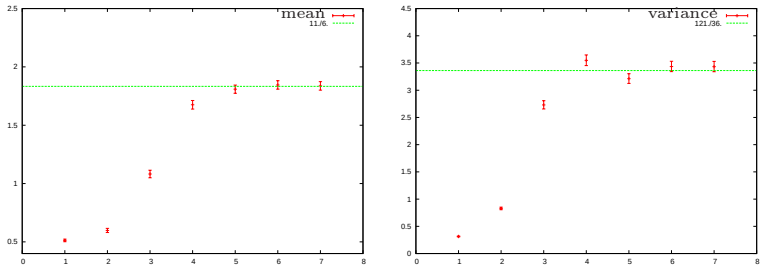

Figure 6.15: Empirical expectation (left) and variance (right) of S_0^ε as a function of ε.

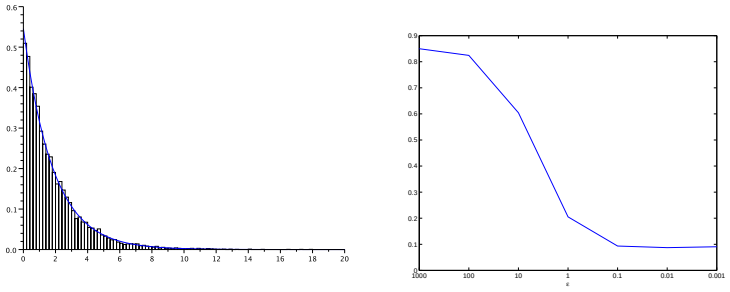

Figure 6.16: Left: Distribution of the first waiting time S_0^ε before the energy of the first particle changes ($\varepsilon = 10^{-3}$); Right: L^1 error (6.30) between the distribution of S_0^ε and its limit distribution.

6.A Some useful results

For convenience, we recall in this Appendix some classical results of probability theory that are needed in this study.

Martingales Several results on martingales are useful in this work. The first one is an existence and uniqueness result for the martingale problem introduced by D.W. Stroock and S.R.S. Varadhan (see e.g. [9] and [150]):

Proposition 6.A.1 (Lemma 5.1 of Appendix 1 of [79])**.** *Let $(X_t)_{t\geq 0}$ be a Markov process and let $(\mathcal{F}_t)_{t\geq 0}$ be its natural filtration. For any bounded function F, we introduce*

$$M_t^F = F(X_t) - F(X_0) - \int_0^t LF(X_s)\, ds$$

and

$$N_t^F = \left(M_t^F\right)^2 - \int_0^t \left(LF^2(X_s) - 2F(X_s)\, LF(X_s)\right) ds,$$

where L is the generator of the Markov process (X_t). Then M^F and N^F are $\mathcal{F}_t$-martingales. In particular, the quadratic variation of M^F reads

$$\langle M^F \rangle_t = \int_0^t \left(LF^2(X_s) - 2F(X_s) LF(X_s) \right) ds.$$

We recall that for a continuous local martingale M, the process $\langle M \rangle$ is defined to be the unique right-continuous and increasing predictable process starting at zero such that $M^2 - \langle M \rangle$ is a local martingale.

The next result is of paramount importance to prove that a process is a jump process, and to identify its generator. We state here this result as a simplified version of [78, Theorem 21.11].

Lemma 6.A.2 (Uniqueness result for the martingale problem)**.** *Let F be a countable space, Z_t a stochastic process valued in F and L an operator on bounded functions $\varphi : F \to \mathbb{R}$ defined by*

$$L\varphi(x) = \sum_{x' \in F} L_{x,x'} \left(\varphi(x') - \varphi(x) \right),$$

where $L_{x,x'} \geq 0$ for any $x, x' \in F$ and $\sup_{x,x' \in F} L_{x,x'} < \infty$. If for any bounded function $\varphi : F \to \mathbb{R}$, the process

$$M_t^\varphi := \varphi(Z_t) - \varphi(Z_0) - \int_0^t L\varphi(Z_s)\, ds$$

is a martingale w.r.t. the natural filtration of $(Z_t)_{t \geq 0}$, then $(Z_t)_{t \geq 0}$ is the jump process of initial condition Z_0 and of generator L.

Finally, Doob's maximal inequality for martingales (see e.g. [76, Proposition 2.4.1]) gives an upper bound on the probability that a martingale exceeds a certain value over a given interval of time.

Proposition 6.A.3 (Doob's maximal inequality)**.** *Let $(X_t)_{t \geq 0}$ be a martingale. Then, for any t and $a > 0$, we have*

$$\mathbb{P}\left(\sup_{s \in [0,t]} |X_s| > a \right) \leq \frac{\mathbb{E}(|X_t|)}{a}.$$

Convergence of probability measures We now turn to classical results concerning the convergence of probability measures in $D_{\mathbb{R}}[0, \infty)$, which is the space of functions that are right continuous with left limits (the so-called càd-làg functions), defined on $[0, \infty)$ and valued in $\mathbb{R}$. Proposition 6.A.4 gives an equivalent definition of the Skorohod metric on $D_{\mathbb{R}}[0, \infty)$ (see [45, p. 116-118] for the original definition of the Skorohod metric, that we actually do not use in this work). Theorem 6.A.5 and 6.A.6 state convergence criteria for probability measures on $D_{\mathbb{R}}[0, \infty)$. Finally, Theorem 6.A.7 is a standard application of the weak-convergence theory in $D_{\mathbb{R}}[0, \infty)$.

Proposition 6.A.4 (Proposition 5.3, Chap. 3 of [45]). *Let $(x_n)_{n\geq 0}$ be a sequence in $D_{\mathbb{R}}[0,\infty)$ and $x \in D_{\mathbb{R}}[0,\infty)$. The following assertions are equivalent:*

- $\lim_{n\to\infty} x_n = x$ *in the space $D_{\mathbb{R}}[0,\infty)$ endowed with the Skorohod metric.*
- *For any $T > 0$, there exists a sequence of strictly increasing, continuous maps $(\lambda_n)_{n\geq 0}$ defined on $[0,\infty)$ and valued in $[0,\infty)$ such that*

$$\lim_{n\to\infty} \sup_{0\leq t\leq T} |\lambda_n(t) - t| = 0 \tag{6.45}$$

and

$$\lim_{n\to\infty} \sup_{0\leq t\leq T} |x_n(t) - x(\lambda_n(t))| = 0. \tag{6.46}$$

Theorem 6.A.5 (Aldous' criterion, Theorem VI.4.5 of [77]). *Let $(X^n)_{n\geq 1}$ be a sequence of càd-làg processes, with distributions $\mathcal{P}^n$. Suppose that*

- *for any $N \in \mathbb{N}$ and $\varepsilon > 0$, there exists $n_0 \in \mathbb{N}$, $n_0 > 0$, and $K \in \mathbb{R}^+$ such that, for any $n \geq n_0$,*

$$\mathcal{P}^n\left(\sup_{t\leq N} |X_t^n| > K\right) \leq \varepsilon. \tag{6.47}$$

- *for any $N \in \mathbb{N}$ and $\alpha > 0$, we have*

$$\lim_{\theta\to 0} \limsup_n \sup_{S,T\in\mathfrak{T}_N^n,\, S\leq T\leq S+\theta} \mathcal{P}^n(|X_T^n - X_S^n| \geq \alpha) = 0, \tag{6.48}$$

where $\mathfrak{T}_N^n$ is the set of all $\mathcal{F}^n$ stopping times that are bounded by N.

Then the sequence $(X^n)_{n\in\mathbb{N}}$ is tight.

Theorem 6.A.6 (Theorem 15.5 of [11]). *Let $(\mathcal{P}^n)_{n\geq 1}$ be a sequence of probability measures on $D_{\mathbb{R}}[0,T]$. Suppose that*

- *for any $\eta > 0$, there exists τ such that*

$$\forall n \geq 1, \quad \mathcal{P}^n(\{x \in D_{\mathbb{R}}[0,T],\ |x(0)| > \tau\}) \leq \eta. \tag{6.49}$$

- *for any $\varepsilon > 0$ and $\eta > 0$, there exists $0 < \delta$ and $n_0 \in \mathbb{N}$, $n_0 > 0$, such that*

$$\forall n \geq n_0, \quad \mathcal{P}^n\left(\left\{x \in D_{\mathbb{R}}[0,T],\ \sup_{|t-s|\leq\delta} |x(t) - x(s)| \geq \varepsilon\right\}\right) \leq \eta. \tag{6.50}$$

Then the sequence $(\mathcal{P}^n)_{n\geq 1}$ is tight.

Theorem 6.A.7 (Donsker's theorem, Theorem 14.1 of [11]). *Consider a sequence $(x_n)_{n\in\mathbb{N}}$ of independent and identically distributed random variables, with mean 0 and variance σ^2. Introduce*

$$X_t^n(\omega) = \frac{1}{\sigma\sqrt{n}}\, S_{[nt]}(\omega),$$

where, for any $n \in \mathbb{N}$, $S_n = \sum_{i=1}^n x_i$. Then $X^n \Rightarrow B$, where B is the Brownian motion.

6.B Convergence in a diffusive rescaling

In Section 6.3.1, we have shown that the macroscopic variable Z_t^ε converges, when $\varepsilon \to 0$, to a process Z_t, the generator of which is the operator L defined by (6.34). We now study the limit of this process Z_t, after an appropriate rescaling in time and space. As the problem is translation invariant, we can assume that $Z_0 = 0$ without loss of generality.

We assume from now on that the initial process is symmetric. In (6.32), we thus take $C_r = C_l = C$, so (6.33) now reads

$$\lambda = \lambda_r = \lambda_l = \sum_{x,x'\in M} C\left(x, x'\right)\pi\left(x\right), \tag{6.51}$$

and the operator L is defined (see (6.34)) by

$$\forall \varphi \in \mathcal{C}_b\left(\mathbb{Z}\right), \quad L\varphi\left(z\right) = \lambda\left(\varphi\left(z+1\right) + \varphi\left(z-1\right) - 2\varphi\left(z\right)\right). \tag{6.52}$$

The main result of this section is the following:

Theorem 6.B.1. *Let Z be the process associated to the generator (6.52). Let B be a Brownian motion. Then*

$$\delta Z_{t\delta^{-2}} \Rightarrow \sqrt{2\lambda}\, B_t \text{ as } \delta \to 0$$

in $D_{\mathbb{R}}[0,T]$ for any $T > 0$.

The two following results will be useful to prove Theorem 6.B.1.

Lemma 6.B.2. *Let Z be a jump process with initial measure δ_0 and intensity matrix Q given by $Q_{i,i+1} = \lambda_1$, $Q_{i,i-1} = \lambda_2$ and $Q_{i,j} = 0$ otherwise, for some λ_1 and λ_2. Then Z has the same distribution as $N^1 - N^2$, where N^1 and N^2 are two independent Poisson processes of intensities λ_1 and λ_2 respectively.*

Proof. Let N^1 and N^2 be two independent Poisson processes of intensities λ_1 and λ_2 respectively. We introduce $Z' = N^1 - N^2$, and we show in what follows that Z' and Z have the same distribution.

The process Z' is a jump process, of initial measure δ_0. Let $\{S_i\}_{i\geq 0}$ denote the durations between two consecutive jumps of Z', and let $A_i =$

$Z'_{(\sum_{k=0}^{i-1} S_k)^+}$ denote the jump chain. The random variable S_0 can be written $S_0 = \inf\left(S_0^1, S_0^2\right)$, where S_0^1 and S_0^2 are the first jump times of the processes N^1 and N^2. As S_0^1 and S_0^2 are distributed according to an exponential distribution of parameters λ_1 and λ_2, the random variable S_0 is distributed according to an exponential distribution of parameter $\lambda_1 + \lambda_2$. Besides,

$$\mathbb{P}\left(A_1 = A_0 + 1\right) = \mathbb{P}\left(S_0 = S_0^1\right) = \frac{\lambda_1}{\lambda_1 + \lambda_2}$$

and

$$\mathbb{P}\left(A_1 = A_0 - 1\right) = \mathbb{P}\left(S_0 = S_0^2\right) = \frac{\lambda_2}{\lambda_1 + \lambda_2}.$$

Using a recursive argument and strong Markov property, we show that for any $i \in \mathbb{N} \setminus \{0\}$, S_i and $A_i - A_{i-1}$ have the same laws as S_0 and $A_1 - A_0$ and are mutually independent. We hence obtain that the distribution of $(Z'_t)_{t\geq 0}$ is the same as that of $(Z_t)_{t\geq 0}$. This concludes the proof. □

Proposition 6.B.3. *Let Z be a jump process of intensity matrix Q given by $Q_{i,i+1} = \lambda_1$, $Q_{i,i-1} = \lambda_2$ and $Q_{i,j} = 0$ otherwise, for some λ_1 and λ_2. Then the increments of Z are stationary and independent.*

Proof. In view of Lemma 6.B.2, we know that the process Z has the same distribution as $N^1 - N^2$, where N^1 and N^2 are two independent Poisson processes of intensities λ_1 and λ_2. We next use the fact that the increments of a Poisson process are stationary and independent (see e.g. [75, Chapter 3]) to conclude. □

We present in the following two proofs of Theorem 6.B.1. The first one is short, and mostly based on Donsker's theorem [11] (recalled in Theorem 6.A.7 below). The second one is a detailed proof using elementary arguments.

Proof of Theorem 6.B.1 based on Donsker's theorem. Let $(\xi_k)_{k\in\mathbb{N}}$ be a sequence of i.i.d. variables following the same distribution as Z_1. By construction,

$$\mathbb{E}\left(\xi_i\right) = 0 \quad \text{and} \quad \mathbb{E}\left(\xi_i^2\right) = 2\lambda.$$

In view of Propostion 6.B.3, the increments of Z are independent and stationary. Hence, at any time $n \in \mathbb{N} \setminus \{0\}$

$$Z_n = \sum_{i=1}^{n} Z_i - Z_{i-1}$$

has the same distribution as $\xi_1 + \xi_2 + \ldots + \xi_n$. Using Donsker's theorem, we have

$$\frac{1}{\sqrt{2\lambda}}\ \delta\ Z_{[t\delta^{-2}]} \Rightarrow B_t \text{ as } \delta \to 0,$$

where B is a Brownian motion. Hence,

$$\delta Z_{[t\delta^{-2}]} \Rightarrow \sqrt{2\lambda}\ B_t \text{ as } \delta \to 0. \tag{6.53}$$

In addition, we see that, for any t, the random variable $\delta Z_{t\delta^{-2}} - \delta Z_{[t\delta^{-2}]}$ converges to 0 when $\delta \to 0$. By independence of the increments, all the finite-dimensional distributions converge to zero. Using a criterion of tightness, it is easy to show that the family $\left(\delta Z_{t\delta^{-2}} - \delta Z_{[t\delta^{-2}]}\right)_\delta$ is relatively compact, and thus that the process $\delta Z_{t\delta^{-2}} - \delta Z_{[t\delta^{-2}]}$ converges to zero. It then follows from (6.53) that

$$\delta Z_{t\delta^{-2}} \Rightarrow \sqrt{2\lambda}\ B \text{ as } \delta \to 0.$$

□

Remark 6.B.4. *Recall that the process Z is defined as the weak limit of Z^ε as $\varepsilon \to 0$ (see Section 6.3.1). In Theorem 6.B.1, we have studied the limit of $(\delta Z_{\delta^{-2}t})_t$ as δ goes to 0. An interesting question, that we leave open in this work, is to study the limit of the process $\left(\varepsilon Z^\varepsilon_{t\varepsilon^{-2}}\right)_t$ as ε goes to 0.*

The rest of this section is devoted to proving Theorem 6.B.1 only using elementary arguments.

Direct proof of Theorem 6.B.1. We set $V^\delta_t = \delta Z_{t\delta^{-2}}$, and prove the convergence of the process V^δ_t to $\sqrt{2\lambda}\ B_t$ using the convergence criteria presented in [11, Theorem 15.1]. Therefore, we need to show that

(i) the finite dimensional distributions of V^δ_t converge to those of $\sqrt{2\lambda}B_t$,

(ii) the family $\left(V^\delta_t\right)_\delta$ is relatively compact.

Before proving the above assertions, we establish an equation satisfied by V^δ_t. Let F be a bounded function on $\mathbb{Z}$ and let δ be a positive real number. We set $F^\delta(x) = F(\delta x)$. Writing (6.38) for the bounded function F^δ, we see that

$$F\left(\delta Z_t\right) = F\left(\delta Z_0\right) + \int_0^t LF^\delta\left(Z_s\right) ds + M^\delta_t,$$

where, for each δ, M^δ_t is a martingale. Writing the above equation at time $t\delta^{-2}$, we see that

$$F\left(\delta Z_{t\delta^{-2}}\right) = F\left(\delta Z_0\right) + \int_0^{t\delta^{-2}} LF^\delta\left(Z_s\right) ds + M^\delta_{t\delta^{-2}},$$

which we recast as

$$F\left(V^\delta_t\right) = F\left(V^\delta_0\right) + \int_0^t L^\delta F\left(V^\delta_s\right) ds + N^\delta_t \tag{6.54}$$

where

$$N_t^\delta := M_{t\delta^{-2}}^\delta$$

and where the operator L^δ is defined on bounded functions $\varphi : \delta\mathbb{Z} \to \mathbb{R}$ by

$$L^\delta \varphi(z) := \frac{\lambda}{\delta^2}\left(\varphi(z+\delta) + \varphi(z-\delta) - 2\varphi(z)\right). \tag{6.55}$$

The quadratic variation of the martingale (N_t^δ) is given by

$$\langle N^\delta \rangle_t = \int_0^{t\delta^{-2}} \left(L\left(F^\delta\right)^2\left(Z_s^\delta\right) - 2F^\delta\left(Z_s^\delta\right) LF^\delta\left(Z_s^\delta\right)\right) ds. \tag{6.56}$$

We are now in position to prove the above two assertions.

Step 1: convergence of the finite dimensional distributions

The characteristic function of V_t^δ at a given time t is defined by

$$\forall u \in \mathbb{R}, \quad \varphi_t^\delta(u) = \mathbb{E}\left(\exp\left(iuV_t^\delta\right)\right).$$

For any $u \in \mathbb{R}$, we write (6.54) for the bounded function $F(x) = \exp(iux)$:

$$\exp\left(iuV_t^\delta\right) = \exp\left(iuV_0^\delta\right) + \int_0^t \left(L^\delta \exp^{iu\cdot}\right)\left(V_s^\delta\right) ds + N_t^\delta.$$

Taking expectations, we obtain the ordinary differential equation

$$\varphi_t^\delta(u) = \varphi_0^\delta(u) + \int_0^t \frac{\lambda}{\delta^2}\left(e^{iu\delta} + e^{-iu\delta} - 2\right)\varphi_s^\delta(u)\, ds,$$

the solution of which is

$$\varphi_t^\delta(u) = \varphi_0^\delta(u) \exp\left[\frac{\lambda}{\delta^2}\left(e^{iu\delta} + e^{-iu\delta} - 2\right)t\right]. \tag{6.57}$$

We now pass to the limit $\delta \to 0$. We see that

$$\lim_{\delta\to 0} \frac{\lambda}{\delta^2}\left[e^{iu\delta} + e^{-iu\delta} - 2\right] = -u^2\lambda,$$

and that, using the dominated convergence theorem,

$$\varphi_0^\delta(u) = \mathbb{E}\left(e^{iu\delta Z_0}\right) = \int e^{iu\delta z} p_{Z_0}(z)\, dz \underset{\delta\to 0}{\longrightarrow} 1.$$

Passing to the limit $\delta \to 0$ in (6.57), we obtain that, for any t,

$$\forall u \in \mathbb{R}, \quad \varphi_t^\delta(u) \underset{\delta\to 0}{\longrightarrow} \exp(-u^2\lambda t) = \mathbb{E}\left(\exp\left(iu\sqrt{2\lambda}\, B_t\right)\right).$$

It then follows from the Lévy continuity theorem, relating the convergence in distribution of random variables with the pointwise convergence of their

characteristic functions, that, for any t, the random variable V_t^δ converges in distribution to $\sqrt{2\lambda}\, B_t$.

By the stationarity and the independence of the increments of Z (see Proposition 6.B.3), we deduce from the above convergence that, in distribution,

$$\left(V_s^\delta, V_t^\delta - V_s^\delta\right) \longrightarrow \sqrt{2\lambda}\, (B_s, B_t - B_s) \quad \text{for any } t \geq s.$$

Hence,

$$\left(V_t^\delta, V_s^\delta\right) \longrightarrow \sqrt{2\lambda}\, (B_t, B_s) \quad \text{for any } t \geq s.$$

Using the same arguments, we prove that the distribution of any finite-dimensional vector $\left(V_{t_1}^\delta, V_{t_2}^\delta, \cdots, V_{t_n}^\delta\right)$ converges to the distribution of the vector $\sqrt{2\lambda}\, (B_{t_1}, B_{t_2}, \cdots, B_{t_n})$. This concludes the proof of the first assertion and of Step 1.

Step 2: the family $\left(V_t^\delta\right)_\delta$ is relatively compact

We recall that, in view of Prohorov's theorem (see e.g. [45, Theorem 2.2]), we only have to show that the family $\left(V_t^\delta\right)_\delta$ is tight. To do so, we use the criterion of [11, Theorem 15.5], recalled in Theorem 6.A.6. Let us check its assumptions (6.49) and (6.50).

The condition (6.49) is trivially satisfied: we set $Z_0 = 0$, hence $V_0^\delta = 0$ for any δ.

The condition (6.50) is more technical to prove. It is equivalent to showing that, for any $\eta > 0$ and $\nu > 0$, there exist $\alpha > 0$ and $\delta_0 > 0$ such that, for all $t \in [0, T]$,

$$\forall \delta \leq \delta_0, \quad \mathbb{P}\left(\omega : \sup_{t' \in [t, \max(T, t+\alpha)]} \left|V_t^\delta(\omega) - V_{t'}^\delta(\omega)\right| \geq \nu\right) \leq \eta. \tag{6.58}$$

Let $t > 0$. Using (6.54) where F is a bounded function of class C^2 with bounded derivatives up to second order, we have

$$F\left(V_t^\delta\right) - F\left(V_{t'}^\delta\right) = \int_{t'}^t L^\delta F\left(V_s^\delta\right)\, ds + N_t^\delta - N_{t'}^\delta. \tag{6.59}$$

In what follows, we successively bound the two terms of the right-hand side of (6.59).

To bound from above the second term, we use (6.56) and (6.52), from which we see that

$$\langle N^\delta \rangle_t - \langle N^\delta \rangle_{t'} = \int_{t'\delta^{-2}}^{t\delta^{-2}} \left[F\left(\delta Z_s^\delta + \delta\right) - F\left(\delta Z_s^\delta\right)\right]^2 + \left[F\left(\delta Z_s^\delta - \delta\right) - F\left(\delta Z_s^\delta\right)\right]^2 ds,$$

thus

$$\begin{aligned}\left|\langle N^\delta\rangle_t - \langle N^\delta\rangle_{t'}\right| &\leq 2|t-t'|\delta^{-2}\sup_z\left[F\left(\delta z+\delta\right)-F\left(\delta z\right)\right]^2\\ &\leq 2\,|t-t'|\,\|F'\|_\infty^2. \end{aligned} \tag{6.60}$$

We now infer from the optional stopping theorem that $\widetilde{N}_u := N^\delta_{u+t} - N^\delta_t$ is a martingale with respect to the filtration $\left(\widetilde{\mathcal{F}}^\delta_u, u\geq 0\right) = \left(\mathcal{F}^\delta_{u+t}, u\geq 0\right)$. By the uniqueness of the quadratic variation, a simple calculation shows that

$$\langle\widetilde{N}_u\rangle = \langle N^\delta\rangle_{u+t} - \langle N^\delta\rangle_t.$$

We therefore deduce from (6.60) that

$$\begin{aligned}\mathbb{E}\left[\left(N^\delta_{t'}-N^\delta_t\right)^2\right] &= \mathbb{E}\left[\left(\widetilde{N}_{t'-t}\right)^2\right] = \mathbb{E}\left(\langle\widetilde{N}_{t'-t}\rangle\right)\\ &= \mathbb{E}\left(\langle N^\delta\rangle_{t'} - \langle N^\delta\rangle_t\right) \leq 2\,|t-t'|\,\|F'\|_\infty^2.\end{aligned}$$

Successively using Doob's maximal inequality (see Proposition 6.A.3) for the martingale $\widetilde{N}$, the Cauchy-Schwartz inequality and the above estimate, we obtain

$$\begin{aligned}\mathbb{P}\left(\sup_{t'\in[t,t+\alpha]}\left|N^\delta_t - N^\delta_{t'}\right|\geq\frac{\nu}{2}\right) &\leq \frac{\mathbb{E}\left|N^\delta_{t+\alpha}-N^\delta_t\right|}{\nu/2}\\ &\leq \frac{\sqrt{\mathbb{E}\left[\left(N^\delta_{t+\alpha}-N^\delta_t\right)^2\right]}}{\nu/2}\\ &\leq \frac{\sqrt{2\,\alpha\,\|F'\|_\infty^2}}{\nu/2}.\end{aligned}$$

Choosing α_1 such that $\dfrac{\sqrt{2\,\alpha_1\,\|F'\|_\infty^2}}{\nu/2}\leq\eta$, we deduce that, for any $\alpha\leq\alpha_1$, we have

$$\mathbb{P}\left(\sup_{t'\in[t,t+\alpha]}\left|N^\delta_t - N^\delta_{t'}\right|\geq\frac{\nu}{2}\right)\leq\eta. \tag{6.61}$$

We now turn to the first term of the right-hand side of (6.59). Using the definition (6.55) of L^δ, we see that

$$\forall z,\quad \left|L^\delta F\left(z\right)\right|\leq\lambda\|F''\|_\infty.$$

It follows that the first term of the right-hand side of (6.59) is bounded by

$$\left|\int_{t'}^t L^\delta F\left(V^\delta_s\right)ds\right|\leq\lambda\left\|F''\right\|_\infty\left|t-t'\right|.$$

Choosing α_2 such that $\lambda\|F''\|_\infty \alpha_2 \leq \nu/2$, we obtain for any $\alpha \leq \alpha_2$ that

$$\sup_{t' \in [t,t+\alpha]} \left| \int_{t'}^{t} L^\delta F\left(V_s^\delta\right) ds \right| \leq \nu/2. \tag{6.62}$$

We deduce from (6.59), (6.61) and (6.62) that there exists $\alpha = \min(\alpha_1, \alpha_2)$, depending only on ν, η, $\|F'\|_\infty$ and $\|F''\|_\infty$, such that, for all $\delta \leq \delta_0 = 1$,

$$\mathbb{P}\left(\omega : \sup_{t' \in [t,t+\alpha]} \left| F\left(V_t^\delta(\omega)\right) - F\left(V_{t'}^\delta(\omega)\right) \right| \geq \nu \right) \leq \eta. \tag{6.63}$$

Recall that our aim is to prove (6.58), that is the above bound for $F(z) = z$. Recall also that (6.63) has been proved for functions F that are regular enough and *bounded*. In the sequel, we introduce a sequence of bounded functions $(F_n)_n$ that approach the identity and for which we can define a uniform α.

For any $n \in \mathbb{N}$, we define F_n (see Fig. 6.17) by

$$\left\{ \begin{array}{rcll} F_n(x) & = & -n - 1/2 & , \quad x \leq -n-1 \\ F_n(x) & = & x + (x+n)^2/2 & , \quad x \in [-n-1, -n] \\ F_n(x) & = & x & , \quad x \in [-n, n] \\ F_n(x) & = & x - (x-n)^2/2 & , \quad x \in [n, n+1] \\ F_n(x) & = & n + 1/2 & , \quad x \geq n+1. \end{array} \right. \tag{6.64}$$

By construction, the norms $\|F_n'\|_\infty$ and $\|F_n''\|_\infty$ are independent of n. Since the parameter α in (6.63) only depends on $\|F'\|_\infty$ and $\|F''\|_\infty$ (besides ν and η), we deduce from (6.63) that, for all $\delta \leq \delta_0 = 1$, all $n \in \mathbb{N}$ and all $t \in [0, T]$,

$$\mathbb{P}\left(\Omega_n(t)\right) \leq \eta, \tag{6.65}$$

where, for any t,

$$\Omega_n(t) = \left\{ \omega : \sup_{t' \in [t,t+\alpha]} \left| F_n\left(V_t^\delta(\omega)\right) - F_n\left(V_{t'}^\delta(\omega)\right) \right| \geq \nu \right\}. \tag{6.66}$$

We now wish to pass to the limit $n \to \infty$ in (6.65). We first claim that the functions $(F_n)_{n \in \mathbb{N}}$ satisfy

$$\forall n \in \mathbb{N},\ \forall x, y \in \mathbb{R},\ |F_{n+1}(x) - F_{n+1}(y)| \geq |F_n(x) - F_n(y)|. \tag{6.67}$$

As the functions F_n are increasing, it is sufficient to show that the function $G_n(x) = F_{n+1}(x) - F_n(x)$ is increasing to obtain (6.67). A direct computation of G_n shows that this function is indeed increasing. We thus obtain (6.67).

Second, we observe that

$$\forall n \in \mathbb{N}, \quad \Omega_n(t) \subset \Omega_{n+1}(t), \tag{6.68}$$

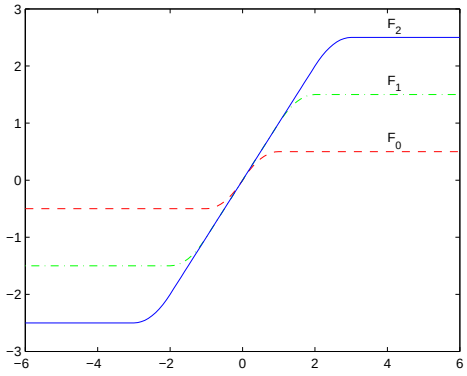

Figure 6.17: The functions F_n defined by (6.64).

where, we recall that the set $\Omega_n(t)$ is defined by (6.66). Indeed, let $\omega \in \Omega_n(t)$ and let $t' \in [t, t+\alpha]$ be such that $\left|F_n\left(V_t^\delta(\omega)\right) - F_n\left(V_{t'}^\delta(\omega)\right)\right| \geq \nu$. Then, we deduce from (6.67) that

$$\left|F_{n+1}\left(V_t^\delta(\omega)\right) - F_{n+1}\left(V_{t'}^\delta(\omega)\right)\right| \geq \left|F_n\left(V_t^\delta(\omega)\right) - F_n\left(V_{t'}^\delta(\omega)\right)\right| \geq \nu,$$

hence $\omega \in \Omega_{n+1}(t)$. We thus have shown (6.68).

Third, we introduce

$$\Omega'(t) = \left\{\omega : \sup_{t' \in [t,t+\alpha]} \left|V_t^\delta(\omega) - V_{t'}^\delta(\omega)\right| \geq \nu\right\}$$

and compute $\mathbb{P}(\Omega'(t))$. Let $\omega \in \Omega'(t)$. As any cad-lag function is bounded on any compact set (see e.g. [11, Lemma 1 p. 110], and also the proof of Lemma 6.2.5), there exists an integer N such that, for all $t' \in [t, t+\alpha]$, we have $\left|V_{t'}^\delta(\omega)\right| \leq N$. It follows that

$$\sup_{t' \in [t,t+\alpha]} \left|V_t^\delta(\omega) - V_{t'}^\delta(\omega)\right| = \sup_{t' \in [t,t+\alpha]} \left|F_N\left(V_t^\delta(\omega)\right) - F_N\left(V_{t'}^\delta(\omega)\right)\right|,$$

hence $\omega \in \Omega_N(t) \subset \bigcup_{n \in \mathbb{N}} \Omega_n(t)$. We have therefore shown that

$$\Omega'(t) \subset \bigcup_{n \in \mathbb{N}} \Omega_n(t).$$

Hence, using (6.68) and (6.65), we obtain

$$\mathbb{P}\left(\Omega'(t)\right) \leq \mathbb{P}\left(\bigcup_{n \in \mathbb{N}} \Omega_n(t)\right) = \lim_n \mathbb{P}\left(\Omega_n(t)\right) \leq \eta$$

for all $t \in [0,1]$. We have thus obtained (6.58). This concludes the proof of the Step 2.

Conclusion: We have checked in the above two steps that the two assertions mentioned at the begininng of the proof are satisfied. We are hence in position to make use of [11, Theorem 15.1], which shows the convergence of the process $V_t^\delta = \delta Z_{t\delta^{-2}}$ to $\sqrt{2\lambda}\ B_t$. This concludes the proof of Theorem 6.B.1. □

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