Nonlinear quantum systems at dissociation: the example of graphene

Jean Cazalis

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Systèmes quantiques non linéaires en dissociation
L'exemple du graphène

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Jean CAZALIS

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Composition du jury :

Clotilde FERMANIAN KAMMERER Professeure, Université Paris Est - Créteil	*Présidente*
Marcello PORTA Professeur, Scuola Internazionale Superiore di Studi Avanzati	*Rapporteur*
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Antoine LEVITT Chargé de recherche, École des Ponts Paristech	*Examinateur*
Mathieu LEWIN Directeur de recherche, Université Paris-Dauphine	*Directeur de thèse*

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	Nicolas Rougerie	directeur de recherche à l'École Normale Supérieure de Lyon	
Examinateurs	Clotilde Fermanian Kammerer	professeure à l'Université Paris Est - Créteil Val de Marne	présidente du jury
	Isabelle Catto	chargée de recherche à l'Université Paris-Dauphine	
	Bernard Helffer	professeur au Nantes Université	
	Antoine Levitt	chargé de recherche à l'École des Ponts ParisTech	
Directeur de thèse	Mathieu Lewin	directeur de recherche à l'Université Paris-Dauphine	

Colophon

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Committee members

Referees	Marcello Porta	Professor at Scuola Internazionale Superiore di Studi Avanzati	
	Nicolas Rougerie	Senior Researcher at École Normale Supérieure de Lyon	
Examiners	Clotilde Fermanian Kammerer	Professor at Université Paris Est - Créteil Val de Marne	Committee President
	Isabelle Catto	Junior Researcher at Université Paris-Dauphine	
	Bernard Helffer	Professor at Nantes Université	
	Antoine Levitt	Junior Researcher at École des Ponts ParisTech	
Supervisor	Mathieu Lewin	Senior Researcher at Université Paris-Dauphine	

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Place du Maréchal De Lattre De Tassigny
75016 Paris
France

☎ +33 1 44 27 42 98
Site http://ceremade.dauphine.fr

À Angèle et Moïse.

A physical law must possess
mathematical beauty.

Paul Dirac

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Systèmes quantiques non linéaires en dissociation
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Résumé

Cette thèse porte sur l'étude mathématique des propriétés électroniques de la matière. Les systèmes, moléculaires ou cristallins, sont décrits à l'aide de modèles non linéaires issus de la mécanique quantique. On considère alors le régime de dissociation, c'est-à-dire lorsque les distances entre les noyaux sont grandes. Dans le Chapitre 1, on étudie le modèle de Hartree diatomique, en dimension deux ou trois, et on quantifie précisément l'effet tunnel entre les deux premiers modes propres. Dans le Chapitre 2, on montre que si une condition de non-dégénérescence est vérifiée alors le modèle de Hartree-Fock réduit du graphène présente des singularités coniques, appelées *points de Dirac*. De plus, on prouve que le niveau de Fermi coïncide avec le niveau d'énergie de ces cônes. Pour cela, on dérive certaines conditions sous lesquelles les relations de dispersion d'un opérateur de Schrödinger périodique sont données, au premier ordre et dans le régime de dissociation, par le modèle de liaison forte correspondant.

Mots clés : opérateurs de Schrödinger périodiques, analyse non linéaire, graphène, Hartree-Fock, points de Dirac

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Nonlinear quantum systems at dissociation
The example of graphene

Abstract

This thesis is devoted to the mathematical study of electronic properties of matter. The systems, both molecular and crystalline, are described by nonlinear models coming from quantum mechanics. Then, we consider the dissociation regime, that is when the distances between the nuclei are large. In Chapter 1, we study the diatomic Hartree model, both in dimension two and three, and we precisely estimate the quantum tunneling between the first two eigenfunctions. In Chapter 2, we show that if a non-degeneracy condition is satisfied then the reduced Hartree-Fock model of graphene presents conical singularities, called *Dirac points*. In addition, we show that the Fermi level coincides with the energy of these cones. In this direction, we derive conditions under which the dispersion relation of periodic Schrödinger operator is given, to leading order and in the dissociation regime, by the corresponding tight-binding model.

Keywords: periodic Schrödinger operators, nonlinear analysis, graphene, Hartree-Fock, Dirac points

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Centre De Recherche en Mathématiques de la Décision, Université Paris-Dauphine
Place du Maréchal De Lattre De Tassigny – 75016 Paris – France

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Chapitre 1

Introduction

Cette thèse est consacrée à l'étude des propriétés électroniques de la matière. On considère des modèles non linéaires, issus de la mécanique quantique et décrivant le comportement de systèmes à plusieurs particules, dans le régime où les noyaux sont éloignés les uns des autres. Une attention particulière est portée sur les systèmes cristallins similaires au graphène, c'est-à-dire présentant les mêmes symétries que celui-ci.

1.1 Cadre général

Dans cette section, on introduit le formalisme mathématique qu'on utilisera pour décrire les systèmes de particules en mécanique quantique. On commence par la description d'un système fini puis on abordera celle d'un système cristallin, infini mais invariant par les translations discrètes d'un réseau.

1.1.1 Modélisation des molécules en mécanique quantique

En premier lieu, on décrit la modélisation d'un système fini en mécanique quantique et dans un second temps, on présente les approximations de type Hartree-Fock, très répandues en chimie computationnelle. Des introductions plus détaillées écrites en français sont exposées dans les livres de Cancés, Le Bris et Maday [CLM06] et de Lewin [Lew22b]. Pour des références en langue anglaise, on renvoie aux livres de Lieb et Seiringer [LS10] et de Gustafson et Sigal [GS20] ou à la revue de Le Bris et Lions [LL05].

Hamiltonien à N particules

On considère $N \in \mathbb{N}^*$ particules non-relativistes, sans spin (pour simplifier l'exposé) et se déplaçant dans l'espace euclidien $\mathbb{R}^d$ où $d \geq 1$. On suppose qu'elles sont soumises à un potentiel extérieur $V : \mathbb{R}^d \to \mathbb{R}$ et que les interactions entre particules ne se font que par paire et à travers un potentiel d'interaction noté $w : \mathbb{R}^d \to \mathbb{R}$. L'espace de Hilbert complexe associé à un tel système quantique est

$$L^2\left(\mathbb{R}^d, \mathbb{C}\right)^{\otimes N} \simeq L^2\left(\mathbb{R}^{dN}, \mathbb{C}\right) .$$

À partir de maintenant, on considérera principalement des fonctions à valeurs complexes et par conséquent, on ne mentionnera pas l'espace d'arrivée dans les notations des espaces fonctionnels, sauf si celui-ci diffère de $\mathbb{C}$. L'état du système est décrit par une fonction d'onde normalisée $\Psi \in L^2\left(\mathbb{R}^{dN}\right)$ avec l'interprétation probabiliste suivante :

— $|\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)|^2$ est la densité de probabilité que pour tout $i \in \{1, \ldots, N\}$ la particule n° i ait pour position $\mathbf{x}_i \in \mathbb{R}^d$;

— $\left|\widehat{\Psi}(\mathbf{k}_1,\dots,\mathbf{k}_N)\right|^2$ est la densité de probabilité que pour tout $i \in \{1,\dots,N\}$ la particule n° i ait pour quantité de mouvement $\mathbf{k}_i \in \mathbb{R}^d$.

On a noté par $\widehat{\Psi}$ la transformée de Fourier [1] de la fonction d'onde Ψ. La dynamique d'un système quantique est régit par l'*équation de Schrödinger* dépendant du temps

$$\begin{cases} i\partial_t \Psi = H_N \Psi \\ \Psi_{t=0} = \Psi_0 \end{cases}, \tag{1.1}$$

où l'opérateur Hamiltonien à N particules est donné par

$$H_N = \sum_{i=1}^{N} \left(-\Delta_{\mathbf{x}_i} + V(\mathbf{x}_i)\right) + \sum_{i<j} w(\mathbf{x}_i - \mathbf{x}_j)\,.$$

Dans cette thèse de doctorat, on ne s'intéressera qu'à l'étude des *états stationnaires* de l'équation (1.1). Ceci amène à l'équation de Schrödinger indépendante du temps

$$H_N \Psi = E \Psi\,, \tag{1.2}$$

qui s'écrit sous la forme d'un problème aux valeurs propres. Pour des potentiels V et w satisfaisant des conditions raisonnables [2], l'opérateur H_N est borné inférieurement, son domaine de forme est l'espace de Sobolev $H^1(\mathbb{R}^{dN})$. L'opérateur H_N est la réalisation auto-adjointe de Friedrichs associée. Le spectre essentiel de H_N est fourni par le célèbre Théorème HVZ : c'est une demi-droite $[\Sigma\,,\infty)$ dont la borne inférieure Σ est égale à l'énergie minimale obtenue lorsqu'on envoie à l'infini certaines particules. Lorsqu'elle existe, la plus petite valeur propre de H_N, appelée *énergie fondamentale*, joue un rôle particulier puisque l'état propre associé, l'*état fondamental*, est celui qui est le plus stable. L'énergie fondamentale E_N de H_N est obtenue par la formulation variationnelle de (1.2) :

$$E_N = \inf\left\{\langle\Psi, H_N\Psi\rangle_{L^2}\;\middle|\;\Psi \in H^1(\mathbb{R}^{dN}) \quad \text{et} \quad \|\Psi\|_{L^2} = 1\right\}\,. \tag{1.3}$$

Ici, nous avons utilisé l'abus de notation $\langle\Psi, H_N\Psi\rangle_{L^2}$ pour désigner la forme quadratique associée.

Indiscernabilité

Dans ce qui suit, on supposera que les particules sont *indiscernables*, c'est-à-dire que, lors d'une expérience, il est impossible de garder la trace du label attribué initialement à chaque particule. Ceci implique que les densités de probabilité $|\Psi|^2$ et $\left|\widehat{\Psi}\right|^2$ sont invariantes par permutation, respectivement, des positions et des quantités de mouvement. De cette contrainte émerge deux types de particules, associés à des statistiques physiques différentes :

— *les bosons* [3] dont la fonction d'onde Ψ est symétrique par permutation des labels

$$\forall\sigma \in \mathfrak{S}_N, \quad \Psi(\mathbf{x}_{\sigma(1)},\dots,\mathbf{x}_{\sigma(N)}) = \Psi(\mathbf{x}_1,\dots,\mathbf{x}_N)\,.$$

— *les fermions* [4] dont la fonction d'onde Ψ est anti-symétrique par permutation des labels

$$\forall\sigma \in \mathfrak{S}_N, \quad \Psi(\mathbf{x}_{\sigma(1)},\dots,\mathbf{x}_{\sigma(N)}) = \varepsilon(\sigma)\Psi(\mathbf{x}_1,\dots,\mathbf{x}_N)\,, \tag{1.4}$$

où $\varepsilon(\sigma)$ désigne la signature de la permutation σ. L'équation (1.4) est appelé *principe de Pauli*.

1. La convention pour la transformée de Fourier est choisie de sorte qu'elle définisse une isométrie de $L^2(\mathbb{R}^{dN})$. Ainsi, si $|\Psi|^2$ définit une densité de probabilité dans l'espace des positions alors $\left|\widehat{\Psi}\right|^2$ définit une densité de probabilité dans l'espace des quantités de mouvement.

2. Par exemple si V et w sont dans $L^p(\mathbb{R}^d,\mathbb{R}) + L^\infty(\mathbb{R}^d,\mathbb{R})$ où $p=1$ si $d=1$, $p>1$ si $d=2$ et $p=\frac{d}{2}$ si $d \geq 3$.

3. Les bosons élémentaires sont : les photons, les gluons, les bosons Z et W et le boson de Higgs (et le graviton, s'il existe).

4. Les fermions élémentaires sont : les électrons, les muons, les tauons, les neutrinos et les quarks. Des exemples importants de fermions composites sont les protons et les neutrons qui sont les constituants des noyaux atomiques.

Puisque le sujet de cette thèse porte uniquement sur l'étude des propriétés électroniques de la matière, nous ne considérons que des particules fermioniques. On se restreint donc à des fonctions d'ondes Ψ vivant dans l'espace de Hilbert (complexe) suivant

$$L_a^2\left(\mathbb{R}^{dN}\right) \coloneqq L^2(\mathbb{R}^d)^{\wedge N} \simeq \left\{\Psi \in L^2\left(\mathbb{R}^{dN}\right) \,\middle|\, \Psi \text{ satisfait (1.4) presque partout}\right\},$$

et le problème de minimisation (1.3) devient

$$E_N = \inf\left\{\langle \Psi, H_N\Psi\rangle_{L^2} \,\middle|\, \Psi \in L_a^2(\mathbb{R}^{dN}) \quad \text{et} \quad \|\Psi\|_{L^2} = 1\right\}. \tag{1.5}$$

Les *déterminants de Slater* sont définis par

$$(\psi_1 \wedge \cdots \wedge \psi_N)(\mathbf{x}_1, \ldots, \mathbf{x}_N) \coloneqq \frac{1}{\sqrt{N!}} \sum_{\sigma \in \mathfrak{S}_N} \varepsilon(\sigma) \prod_{i=1}^N \psi_i(\mathbf{x}_{\sigma(i)}) = \det\left(\psi_i(\mathbf{x}_j)\right)_{1\leq i,j\leq N}, \tag{1.6}$$

où $(\psi_1, \ldots, \psi_N) \in L^2(\mathbb{R}^d)^N$ forme un système orthonormé. Les fonctions ψ_i sont appelées *orbitales*. L'interprétation physique est la suivante : le système est dans l'état $\psi_1 \wedge \cdots \wedge \psi_N$ si pour tout i la particule n° i se trouve dans l'état ψ_i. Le principe de Pauli signifie qu'il ne peut y avoir deux orbitales dans le même état quantique. Les déterminants de Slater engendrent l'espace de Hilbert à N particules fermioniques, c'est-à-dire

$$L_a^2\left(\mathbb{R}^{dN}\right) = \overline{\operatorname{vect}\left\{\psi_{i_1} \wedge \cdots \wedge \psi_{i_N} \mid i_1 < \cdots < i_N\right\}}.$$

Les déterminants de Slater sont les fonctions d'ondes à N corps anti-symétriques les plus simples que l'on puisse imaginer puisque les particules ne sont corrélées qu'à travers le principe de Pauli. Ils sont à la base de l'approximation de Hartree-Fock, exposée plus bas.

Atomes et molécules

On s'intéresse au cas particulier de la modélisation des atomes et molécules. Dans le but d'alléger les notations, on travaillera exclusivement avec les unités physiques suivantes :

$$2 \cdot m_{\text{electron}} = \hbar = \frac{e^2}{4\pi\varepsilon_0} = 1, \tag{1.7}$$

où m_{electron} et e désigne respectivement la masse et la charge d'un électron, $\hbar$ la constante réduite de Planck et ε_0 la permittivité diélectrique du vide.

On se place dans l'approximation de Born-Oppenheimer [BO27]. Cette approximation consiste à supposer que les noyaux des différents atomes constituant la molécule se comportent de manière classique. Puisque la différence d'ordre de grandeur entre la masse des nucléons et celle d'un électron est grande [5], cela revient à supposer que les noyaux sont immobiles.

On se place en dimension $d = 3$ et on se donne N électrons quantiques et M noyaux classiques de charges $(z_1, \ldots, z_M) \in (\mathbb{R}_+^*)^M$ et situés en $(\mathbf{r}_1, \ldots, \mathbf{r}_M) \in (\mathbb{R}^3)^M$. Les potentiels d'interaction sont dérivés de l'interaction coulombienne, c'est-à-dire qu'on a

$$V(\mathbf{x}) = -\sum_{m=1}^M \frac{z_m}{|\mathbf{x} - \mathbf{r}_m|} \quad \text{et} \quad w(\mathbf{x}) = \frac{1}{|\mathbf{x}|}. \tag{1.8}$$

On note $Z = \sum_{m=1}^M z_m$ la charge totale des noyaux. La connaissance de la différence $N - Z$ est un bon indice quant à la stabilité du système (c'est-à-dire à la présence de spectre discret sous le spectre essentiel). En effet, dans le cas des interactions coulombiennes, on a l'alternative suivante (voir [Lew22b] et les références qui y sont citées) :

— (Molécules neutres ou chargées positivement) si $N < Z + 1$ alors il y a une infinité de valeurs propres sous le spectre essentiel ;

5. Leurs masses respectives sont : $m_{\text{proton}} = 1.6726 \cdot 10^{-27}$ kg, $m_{\text{neutron}} = 1.6749 \cdot 10^{-27}$ kg et $m_{\text{electron}} = 9.1094 \cdot 10^{-31}$ kg)

— (Molécules chargées négativement) si $N \geq Z+1$ alors il y a un nombre fini de valeurs propres sous le spectre essentiel ;

— (Instabilité pour N grand) il existe un nombre critique $N_c < 2Z+M$ d'électrons tel que pour tout $N > N_c$ l'opérateur H_N ne possède aucune valeur propre sous le spectre essentiel.

L'estimation du nombre critique N_c n'est pas entièrement satisfaisante puisque, dans la nature, les atomes plusieurs fois ionisés sont rares. On s'attendrait, dans le cas atomique $M = 1$, à avoir $N_c \leq Z+C$ où $C \in \{1,2\}$ est une constante universelle. C'est la *conjecture d'ionisation*. Le lecteur intéressé pourra consulter les revues de Nam sur le sujet [Nam20 ; Nam22] et aux références qui y figurent.

Fléau de la dimension

L'Hamiltonien moléculaire H_N décrit tous les systèmes moléculaires, allant du simple atome d'hydrogène aux plus complexes des macromolécules biologiques comme les protéines ou les acides désoxyribonucléique (ADN). Cependant, très souvent, il n'existe pas de solution analytique [6] au problème de minimisation (1.5). On se voit donc contraint à la résolution numérique d'un problème de minimisation dont la complexité croît exponentiellement [7] avec le nombre de particules N. En pratique, on arrive à calculer avec une précision suffisante l'état fondamental de molécules comprenant moins d'une dizaine d'électrons. Au delà, on doit utiliser des méthodes d'approximation pour réduire la dimension. Les deux plus courantes sont la théorie de la fonctionnelle de densité et les approximations de type Hartree-Fock. Nous ne détaillerons pas cette première et renvoyons le lecteur intéressé à [DG90 ; Rei11] pour des introductions orientées physique et [CLM06 ; LLY19 ; LLS19] orientées mathématiques. La seconde est introduite dans la prochaine sous-section.

Approximation de Hartree-Fock pour les systèmes finis

L'approximation de Hartree-Fock est une méthode d'approximation de l'énergie et de l'état fondamental du problème à N corps, ceux-ci étant fournis par la formulation variationnelle (1.5). La forme de l'énergie est conservée mais l'espace variationnel sur lequel on la minimise est restreint à l'ensemble des déterminants de Slater, définis en (1.6). On obtient le problème de minimisation suivant

$$E_N^{\mathrm{HF}} \coloneqq \inf \left\{ \mathcal{E}^{\mathrm{HF}}(\psi_1, \dots, \psi_N) \,\middle|\, \psi_i \in H^1(\mathbb{R}^d) \quad \text{et} \quad \langle \psi_i, \psi_j \rangle_{L^2} = \delta_{ij}, \quad 1 \leq i,j \leq N \right\}, \tag{HF}$$

où δ_{ij} est la fonction delta de Dirac et où la fonctionnelle d'énergie de Hartree-Fock est donnée par

$$\mathcal{E}^{\mathrm{HF}}(\psi_1, \dots, \psi_N) \coloneqq \langle \psi_1 \wedge \cdots \wedge \psi_N, H_N(\psi_1 \wedge \cdots \wedge \psi_N) \rangle_{L^2} .$$

En faisant cette approximation, on a considérablement réduit la dimension du problème puisqu'on ne cherche plus une fonction d'onde à N corps vivant dans $L^2(\mathbb{R}^{dN})$ mais N orbitales vivant dans $L^2(\mathbb{R}^d)$. Le prix à payer est que la fonctionnelle d'énergie obtenue n'est plus quadratique. Une telle approximation réalise donc un compromis entre la réduction de la dimension et la linéarité du problème initial. Contrairement à la théorie de la fonctionnelle de densité, cette méthode est variationnelle et produit ainsi un majorant de l'énergie du problème à N corps et non pas juste une approximation. La différence $E_N^{\mathrm{HF}} - E_N \geq 0$ est appelée *énergie de corrélation*. L'énergie de Hartree-Fock se réécrit de la façon suivante

$$\begin{aligned}\mathcal{E}^{\mathrm{HF}}(\psi_1, \dots, \psi_N) = \mathrm{Tr}(-\Delta\gamma) + \int_{\mathbb{R}^d} V\rho + \frac{1}{2} \iint_{\mathbb{R}^d \times \mathbb{R}^d} \rho(\mathbf{x}) w(\mathbf{x}-\mathbf{y}) \rho(\mathbf{y}) \,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y} \\ - \frac{1}{2} \iint_{\mathbb{R}^d \times \mathbb{R}^d} |\gamma(\mathbf{x},\mathbf{y})|^2 \, w(\mathbf{x}-\mathbf{y}) \,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y}\,,\end{aligned} \tag{1.9}$$

6. Les modèles intégrables, c'est-à-dire les modèles dont on peut calculer exactement des quantités non-perturbatives, sont rares. On peut citer par exemple les atomes de type hydrogène ou l'oscillateur harmonique, pour lesquels $N = 1$.

7. Si on discrétise l'hypercube $[0\,,a]^{3N} \subset \mathbb{R}^{3N}$ avec 100 points dans chaque direction (ce qui est peu), on obtient un problème de minimisation à 100^{3N} points de discrétisation (ce qui n'est pas peu).

où γ et ρ sont respectivement la *matrice de densité à un corps* et la *densité de particules* associées à l'état $\psi_1 \wedge \cdots \wedge \psi_N$ et où $\mathrm{Tr}(-\Delta\gamma) \coloneqq \mathrm{Tr}(\sqrt{-\Delta}\gamma\sqrt{-\Delta})$. Ici, ces objets prennent la forme suivante

$$\gamma(\mathbf{x},\mathbf{y}) = \sum_{i=1}^{N} \psi_i(\mathbf{x})\overline{\psi_i(\mathbf{y})} \quad \text{et} \quad \rho(\mathbf{x}) = \gamma(\mathbf{x},\mathbf{x}) = \sum_{i=1}^{N} |\psi_i(\mathbf{x})|^2 \ ,$$

où on a défini l'opérateur γ par son noyau. On a les identités suivantes

$$\mathrm{Tr}(-\Delta\gamma) = \sum_{i=1}^{N} \|\nabla\psi_i\|_{L^2}^2 \quad \text{et} \quad \mathrm{Tr}(V\gamma) = \int_{\mathbb{R}^d} V\rho\,.$$

On remarque que γ est la projection orthogonale sur le sous-espace engendré par la famille orthonormale $(\psi_i)_{1\le i\le N}$. De premier terme dans (1.9) s'interprète comme l'*énergie cinétique* du système. Les deux suivants sont respectivement l'*énergie potentielle* et le *terme direct*. Ils correspondent à des énergies d'interaction classiques entre distributions de charges. Le dernier terme, appelé *terme d'échange*, est quant à lui d'origine exclusivement quantique. Il sert notamment à corriger l'erreur que chaque électron interagit avec lui-même dans le terme direct.

Théorie de Hartree-Fock généralisée

Une propriété importante de l'énergie de Hartree-Fock est d'être invariante par l'action du groupe unitaire sur $H^1(\mathbb{R}^d)^N$. Ceci signifie que la variable naturelle de l'énergie est la matrice de densité et non pas la famille des N orbitales. Plus généralement, une matrice de densité fermionique à N corps, notée γ, est un opérateur appartenant à l'espace suivant [8]

$$\mathcal{S}_N = \left\{\gamma \in \mathcal{B}(L^2(\mathbb{R}^d)) \;\middle|\; \gamma = \gamma^*, \quad 0 \le \gamma \le 1 \quad \text{et} \quad \mathrm{Tr}(\gamma) = N\right\} \ ,$$

où $\mathcal{B}(L^2(\mathbb{R}^d))$ désigne l'ensemble des opérateurs linéaires bornés sur $L^2(\mathbb{R}^d)$. La condition $\gamma \le 1$ est l'expression du principe de Pauli et $\mathrm{Tr}(\gamma) = N$ signifie que le nombre de particules du système est égal à N. Les éléments de $\mathcal{S}_N$ sont des mélanges statistiques de projecteurs. En effet, d'après le théorème spectral, on peut écrire, pour tout $\gamma \in \mathcal{S}_N$,

$$\gamma = \sum_{n\in\mathbb{N}} \lambda_n \left|\psi_n\right\rangle \left\langle\psi_n\right| \ ,$$

où $\lambda_n \in [0\,,1]$ pour tout n et où $(\psi_n)_{n\in\mathbb{N}}$ forme une base hilbertienne de $L^2(\mathbb{R}^d)$.

La convexification du problème de minimisation (HF) conduit au modèle de *Hartree-Fock généralisé*

$$E_N^{\mathrm{gHF}} = \inf\left\{\mathcal{E}^{\mathrm{gHF}}(\gamma) \;\middle|\; \gamma \in \mathcal{S}_N \quad \text{et} \quad \mathrm{Tr}(-\Delta\gamma) < \infty\right\} \ , \tag{gHF}$$

où la fonctionnelle d'énergie $\mathcal{E}^{\mathrm{gHF}}(\gamma)$ s'obtient en prolongeant de la formule (1.9) à l'ensemble $\mathcal{S}_N$

$$\mathcal{E}^{\mathrm{gHF}}(\gamma) \coloneqq \mathrm{Tr}\left((-\Delta+V)\gamma\right) + \frac{1}{2}D(\rho_\gamma,\rho_\gamma) - \frac{1}{2}\iint_{\mathbb{R}^d\times\mathbb{R}^d} |\gamma(\mathbf{x},\mathbf{y})|^2\, w(\mathbf{x}-\mathbf{y})\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y}\,. \tag{1.10}$$

Ici, on a noté $\rho_\gamma(\mathbf{x}) \coloneqq \gamma(\mathbf{x},\mathbf{x})$ la densité de γ et

$$D(\rho_\gamma,\rho_\gamma) \coloneqq \iint_{\mathbb{R}^d\times\mathbb{R}^d} \rho(\mathbf{x})w(\mathbf{x}-\mathbf{y})\rho(\mathbf{y})\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y}\,,$$

le terme direct. Dans [Lie81b], Lieb montre que le modèle de Hartree-Fock généralisé est en fait équivalent au modèle de Hartree-Fock : si $-\Delta+V$ est auto-adjoint et si l'interaction entre particule est répulsive $w \ge 0$ alors on a $E_N^{\mathrm{HF}} = E_N^{\mathrm{gHF}}$ et tout minimiseur de (gHF) est en fait un projecteur de rang N.

8. Dans le cas bosonique, on doit enlever la condition $\gamma \le 1$.

Cas atomique

Maintenant, on s'intéresse plus particulièrement à la théorie de Hartree-Fock pour les atomes et molécules [9]. Cela consiste à prendre $d = 3$ et les potentiels d'interaction V et w comme dans (1.8). Dans ce cadre, la question de l'existence de minimiseur pour le modèle de Hartree-Fock (HF) a été largement étudiée dans la littérature, notamment par Lieb et Simon [LS77a] et par Lions [Lio87]. Une approche différente, dans l'espace à N particules, est développée dans [Fri03 ; Lew11] (voir aussi [Lew18] concernant l'existence d'états excités).

— (Conditions d'optimalité [LS77a ; Lio87]) On suppose que $\gamma = \sum_{n=1}^{N} |\psi_n\rangle\langle\psi_n| \in \mathcal{S}_N$ est un minimiseur du problème (gHF). Alors, on note par

$$\mathcal{F}_\gamma := -\Delta - \sum_{m=1}^{M} \frac{z_m}{|\mathbf{x}-\mathbf{r}_m|} + \rho_\gamma * \frac{1}{|\cdot|} - \frac{\gamma(\mathbf{x},\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,, \tag{1.11}$$

l'*opérateur de Fock* (ou opérateur de champ moyen) associé. Par un léger (et courant dans la littérature) abus de notation, on a confondu, dans la définition de $\mathcal{F}_\gamma$, l'opérateur et son noyau en écrivant $\frac{\gamma(\mathbf{x},\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}$. Par la théorie de la perturbation des opérateurs [Kat95 ; RS78], on peut montrer que $\mathcal{F}_\gamma$ est auto-adjoint sur $\mathcal{D}(-\Delta) = H^2(\mathbb{R}^3)$ et que son spectre essentiel est la demi-droite $[0\,,\infty)$. De plus, $\mathcal{F}_\gamma$ admet au moins N valeurs propres (avec multiplicité) négatives. Si $\mathcal{F}_\gamma$ a $N+1$ valeurs propres strictement négatives alors la N-ième est non-dégénérée [10]. Finalement, γ vérifie l'*équation d'Euler-Lagrange* suivante

$$\gamma = \mathbb{1}_{(-\infty,\epsilon_F]}\left(\mathcal{F}_\gamma\right)\,, \tag{1.12}$$

où $\epsilon_F \in \mathbb{R}$, appelé *niveau de Fermi*, joue le rôle d'un potentiel électrochimique et est choisi de sorte que $\mathrm{Tr}(\gamma) = N$. Formulé différemment, γ est le projecteur spectral sur les N plus petites valeurs propres $\lambda_1 \leq \cdots \leq \lambda_N < 0$ de $\mathcal{F}_\gamma$. On obtient les équations de Hartree-Fock

$$\mathcal{F}_\gamma \psi_n = \lambda_n \psi_n, \quad 1 \leq n \leq N\,.$$

— (Condition d'existence de minima [LS77a ; Lio87]) Toutes les suites minimisantes de (HF) sont relativement compactes dès que la condition de liaison forte

$$E_N^{\mathrm{HF}} < E_{N-1}^{\mathrm{HF}}\,, \tag{1.13}$$

est vérifiée [11]. De plus, la condition (1.13) est satisfaite si $Z > N-1$ où on rappelle que $Z = \sum_m z_m$ désigne la charge totale des noyaux.

— (Condition de non-existence de minimum [Sol03]) Il existe m assez grand tel que (gHF) n'admette pas de minimum si $N \geq Z + m$. La conjecture est que $m = 1$ ou 2.

Griesemer et Hantsch ont montré dans [GH12] que, dans le cas d'un atome en couche fermée et si $N \ll Z$, les solutions de Hartree-Fock étaient uniques. Mis à part ceci, la question de l'unicité, et notamment de l'unicité de la densité électronique minimisante, reste largement ouverte. De plus, en raison de l'absence de propriété de convexité de l'énergie de Hartree-Fock, les solutions des équations d'Euler-Lagrange (1.12) ne sont pas nécessairement des minimiseurs de l'énergie.

9. Dans un autre contexte, celui de la physique nucléaire, la théorie de Hartree-Fock a été étudiée par Gogny et Lions dans [GL86]. Le potentiel extérieur V est supposé nul ce qui rend le système invariant par translation. De plus, le potentiel d'interaction w entre particules (ici, les protons et les neutrons) n'est pas coulombien mais plutôt un potentiel à courte portée partiellement attractif.

10. Cette propriété, appelée *principe de aufbau* en chimie, est démontrée par Bach, Lieb, Loss et Solovej dans [Bac+97].

11. Ce genre de résultat, très courant concernant les modèles en chimie quantique, provient de la méthode de concentration-compacité de Lions [Lio84a ; Lio84b ; Lio85a ; Lio85b]. Dans [Lew11] (voir aussi [Fri03]), Lewin montre que cette équivalence est vraie dans la théorie de Hartree-Fock où les potentiels V et w vérifient des conditions très raisonnables : w est pair et V et w s'écrivent sous la forme $\sum_i f_i$ où $f_i \in L^{p_i}(\mathbb{R}^d)$ avec $\max(1, d/2) < p_i < \infty$ ou $p_i = \infty$ mais dans ce cas $f_i \to 0$ à l'infini.

Modèle de Hartree-Fock réduit

Le modèle de Hartree-Fock réduit est une simplification du modèle de Hartree-Fock dans lequel le terme d'échange est négligé. L'énergie s'écrit donc

$$\mathcal{E}^{\mathrm{rHF}}(\gamma) := \mathrm{Tr}\left((-\Delta + V)\gamma\right) + \frac{1}{2} D(\rho_\gamma, \rho_\gamma)\,, \tag{1.14}$$

et le problème de minimisation correspondant est

$$E_N^{\mathrm{rHF}} = \inf\left\{\mathcal{E}^{\mathrm{rHF}}(\gamma) \;\middle|\; \gamma \in \mathcal{S}_N \quad \text{et} \quad \mathrm{Tr}(-\Delta\gamma) < \infty\right\}. \tag{rHF}$$

Ce modèle a été introduit dans le cas atomique par Solovej dans [Sol91]. Pour la définition dans le cas moléculaire, on renvoie à [CLL01 ; CDL08]. La différence principale avec la théorie de Hartree-Fock est que la fonctionnelle d'énergie est maintenant convexe [12] par rapport à γ, ce qui rend l'étude du problème de minimisation (rHF) plus simple à mener. Dans [Sol91], l'auteur montre que, pour des atomes neutres ou positivement chargés, le problème de minimisation (rHF) admet des solutions et qu'il existe une unique densité électronique minimisante. Les solutions vérifient l'équation d'Euler-Lagrange

$$\gamma = \mathbb{1}_{(\infty,\epsilon_F)}\left(-\Delta + V + \rho_\gamma * w\right) + \delta\,,$$

où $0 \leq \delta \leq 1$ et $\mathrm{ran}(\delta) \subset \mathrm{Ker}(-\Delta + V + \rho_\gamma * w - \epsilon_F)$. Il est à noter que les minimiseurs ne sont pas nécessairement des projecteurs. De plus, il n'existe pas de solution pour $N > Z + m$ où m est suffisamment grand et indépendant de Z.

L'approximation de Hartree-Fock réduite est un modèle simplifié mais suffisamment riche pour être vu comme une première étape avant d'aborder la théorie de Hartree-Fock. Lorsque N est grand, le terme d'échange est négligeable à l'ordre principal [Bac92 ; Bac93 ; BPS14]. De plus, du fait de ses propriétés de convexité, sa limite thermodynamique existe [CLL01 ; CDL08] et le modèle limite associé est explicite. Celui-ci sera présenté dans la Section 1.1.2.

Spin

Si le spin des électrons est pris en compte alors l'espace des états admissibles devient [CG17 ; GL19]

$$\tilde{\mathcal{S}}_N = \left\{\gamma \in \mathcal{B}(L^2(\mathbb{R}^d, \mathbb{C}^2)) \;\middle|\; \gamma = \gamma^*, \quad 0 \leq \gamma \leq 1 \quad \text{et} \quad \mathrm{Tr}(\gamma) = N = 2n\right\}.$$

Pour simplifier, on a supposé que le nombre d'électrons est pair. Tout $\gamma \in \tilde{\mathcal{S}}_N$ peut être représenté par une matrice 2×2 de la forme

$$\gamma = \begin{pmatrix} \gamma^{\uparrow\uparrow} & \gamma^{\uparrow\downarrow} \\ \gamma^{\downarrow\uparrow} & \gamma^{\downarrow\downarrow} \end{pmatrix},$$

dont chaque composante est une matrice de densité à un corps. Pour tout $(\sigma, \sigma') \in \{\uparrow, \downarrow\}^2$, on note $\rho^{\sigma\sigma'}(\mathbf{x}) = \gamma^{\sigma\sigma'}(\mathbf{x}, \mathbf{x})$. La densité électronique ρ de γ est donnée par $\rho = \rho^{\uparrow\uparrow} + \rho^{\downarrow\downarrow}$. Lorsqu'il n'y a pas de champ magnétique, le système est paramagnétique, c'est-à-dire que le spin ne joue aucun rôle. Dans ce cas, l'énergie de Hartree-Fock réduit pour $\gamma \in \tilde{\mathcal{S}}_N$ s'écrit

$$\begin{aligned}\tilde{\mathcal{E}}^{\mathrm{rHF}}\begin{pmatrix} \gamma^{\uparrow\uparrow} & \gamma^{\uparrow\downarrow} \\ \gamma^{\downarrow\uparrow} & \gamma^{\downarrow\downarrow} \end{pmatrix} &:= \mathrm{Tr}((-\Delta + V)\gamma) + \frac{1}{2} D(\rho, \rho) \\ &= \mathcal{E}^{\mathrm{rHF}}(\gamma^{\uparrow\uparrow}) + \mathcal{E}^{\mathrm{rHF}}(\gamma^{\downarrow\downarrow}) + D(\rho^{\uparrow\uparrow}, \rho^{\downarrow\downarrow}) = \tilde{\mathcal{E}}^{\mathrm{rHF}}\begin{pmatrix} \frac{\gamma^{\uparrow\uparrow}+\gamma^{\downarrow\downarrow}}{2} & 0 \\ 0 & \frac{\gamma^{\uparrow\uparrow}+\gamma^{\downarrow\downarrow}}{2} \end{pmatrix}.\end{aligned}$$

12. Si l'interaction entre particules w est répulsive : $w \geq 0$ ou $\widehat{w} \geq 0$.

De cette identité, on déduit que les problèmes de minimisation

$$\tilde{E}_N^{\mathrm{rHF}} = \inf\left\{\tilde{\mathcal{E}}^{\mathrm{rHF}}(\gamma) \,\middle|\, \gamma \in \tilde{\mathcal{S}}_N \quad \text{et} \quad \mathrm{Tr}(-\Delta\gamma) < \infty\right\},$$

et

$$E_N^{\mathrm{rHF}} = \frac{1}{2}\inf\left\{\mathcal{E}^{\mathrm{rHF}}(\gamma) + \frac{1}{2}D(\rho_\gamma, \rho_\gamma) \,\middle|\, \gamma \in \mathcal{S}_N \quad \text{et} \quad \mathrm{Tr}(-\Delta\gamma) < \infty\right\}. \tag{1.15}$$

sont équivalents. Lorsque $N = 2$, on dit que le système est *singulet.* Dans ce cas, si les potentiels V et w sont tels que l'opérateur $-\Delta + V + \rho * w$ admette un état fondamental non-dégénéré alors le problème de minimisation (1.15) admet une unique solution qui s'écrit comme un projecteur de rang un. En particulier, on se ramène à un modèle de type Hartree

$$\frac{1}{2}\inf\left\{\int_{\mathbb{R}^d} |\nabla v|^2 + \int_{\mathbb{R}^d} V\,|v|^2 + D(|v|^2, |v|^2) \,\middle|\, v \in H^1(\mathbb{R}^d) \quad \text{et} \quad \int_{\mathbb{R}^d} |v|^2 = 1\right\},$$

où la variable n'est pas une matrice de densité mais une fonction. Ce modèle est contenu dans la théorie de Thomas-Fermi-von Weizsäcker, étudiée par Benguria, Brézis et Lieb dans [BBL81 ; Lie81a].

Ceci achève cette section consacrée à la modélisation des systèmes quantiques finis. Dans la section suivante, on aborde la modélisation des cristaux.

1.1.2 Modélisation des cristaux parfaits en mécanique quantique

Cette section est consacrée à la modélisation des solides cristallins en mécanique quantique. Dans un premier temps, on expose la théorie de Bloch-Floquet, un outil essentiel pour l'étude des opérateurs périodiques. Ces opérateurs sont notamment utilisés pour modéliser la matière à l'état solide [13]. Leur spectre admet une structure de bande dont la géométrie influence grandement les propriétés physico-chimiques de ces matériaux. En particulier, certains, comme le graphène, présentent des singularités coniques, appelées *points de Dirac*, au voisinage desquelles les électrons se comportent comme des fermions de Dirac sans masse, avec une vitesse 300 fois inférieure à la vitesse de la lumière dans le vide. Par la suite, on introduit le modèle de Hartree-Fock réduit pour les cristaux. Ce modèle est obtenu comme la limite thermodynamique [CLL01 ; CDL08 ; HLS09b] de son équivalent pour les systèmes finis, décrit dans la Section 1.1.1. C'est le modèle périodique le plus simple prenant en compte des interactions entre électrons.

La principale référence sur la physique de la matière condensée est le livre de Kittel [Kit04]. Le lecteur intéressé par les propriétés physico-chimiques du graphène pourra consulter les revues [Cas+09 ; Coo+12]. Les références mathématiques sur la théorie de Bloch-Floquet sont le livre de Reed et Simon [RS78] et la revue de Kuchment [Kuc16] (voir aussi les livres de Veliev [Vel19] et de Lewin [Lew22b]).

Réseaux cristallins

Un *cristal parfait* est une collection infinie d'atomes [14] arrangée périodiquement selon un *réseau de Bravais* $\mathscr{L} \subset \mathbb{R}^d$, un groupe discret de la forme

$$\mathscr{L} = \mathbf{u}_1\mathbb{Z} + \cdots + \mathbf{u}_d\mathbb{Z},$$

où $(\mathbf{u}_1, \ldots, \mathbf{u}_d)$ est une base de $\mathbb{R}^d$. Il y a une infinité de choix possibles pour cette base, mais son volume $|\det(\mathbf{u}_1, \ldots, \mathbf{u}_d)|$ est indépendant de ce choix. Une *maille élémentaire* (ou primitive) $\Gamma \subset \mathbb{R}^d$ de $\mathscr{L}$ est une partie de $\mathbb{R}^d$ de volume minimal et qui contient toute l'information du réseau, c'est-à-dire que ses translations par le réseau $\mathscr{L}$ forment un pavage (sans recouvrement) de l'espace

13. Mais pas que ! Il y a les cristaux photoniques aussi [BCM01, Chapter 7].
14. On se place une nouvelle fois dans l'approximation de Born-Oppenheimer en supposant les positions des noyaux atomiques fixées.

tout entier

$$\mathbb{R}^d = \bigsqcup_{\mathbf{u}\in\mathscr{L}} (\Gamma + \mathbf{u}) \ .$$

On voit que l'on peut en fait identifier Γ avec le tore d-dimensionnel $\mathbb{R}^d/\mathscr{L}$. Il y a aussi une infinité de choix possibles de maille élémentaire. La *maille de Wigner-Seitz* est celle dont l'intérieur est la région de l'espace plus proche de l'origine que n'importe quel autre nœud du réseau

$$\mathring{\Gamma} = \left\{ \mathbf{x} \in \mathbb{R}^d \;\middle|\; \forall \mathbf{u} \in \mathscr{L},\ |\mathbf{x}| < |\mathbf{x} - \mathbf{u}| \right\} \ .$$

Le *réseau réciproque* $\mathscr{L}^*$ de $\mathscr{L}$ est aussi un réseau de Bravais et est défini par

$$\mathscr{L}^* = \mathbf{v}_1 + \cdots + \mathbf{v}_d\mathbb{Z} \,,$$

où la base réciproque $(\mathbf{v}_1, \dots, \mathbf{v}_d)$ est déterminée par les relations d'orthogonalité suivantes

$$\forall (i,j) \in \{1, \dots, d\}^2, \quad \mathbf{v}_i \cdot \mathbf{u}_j = 2\pi\delta_{ij} \ .$$

La maille de Wigner-Seitz de $\mathscr{L}^*$, notée Γ^*, est appelée *première zone de Brillouin.*

Un cristal est la superposition de $N \in \mathbb{N}^*$ translations du réseau $\mathscr{L}$. Si on note par $\mathbf{R} = (\mathbf{r}_1, \dots, \mathbf{r}_N) \in \Gamma^N$ l'emplacement des atomes du cristal dans la cellule de Wigner-Seitz alors le réseau cristallin $\mathscr{L}^{\mathbf{R}}$ est donné par

$$\mathscr{L}^{\mathbf{R}} \coloneqq \mathscr{L} + \mathbf{R} = \{\mathbf{u} + \mathbf{r} \mid \mathbf{u} \in \mathscr{L},\ \mathbf{r} \in \mathbf{R}\} \ .$$

Le réseau en nid d'abeilles

Le *graphène*, forme allotropique du carbone, est un matériau bidimensionnel cristallin, formé d'un réseau en nid d'abeilles d'atomes de carbone. C'est un réseau construit comme la superposition de deux réseaux triangulaires, voir Figure 1.1a. Le réseau triangulaire $\mathscr{L}$ est donné par

$$\mathscr{L} = \mathbf{u}_1\mathbb{Z} + \mathbf{u}_2\mathbb{Z} \quad \text{où} \quad \mathbf{u}_1 = \begin{pmatrix} \sqrt{3}/2 \\ 1/2 \end{pmatrix} \quad \text{et} \quad \mathbf{u}_2 = \begin{pmatrix} \sqrt{3}/2 \\ -1/2 \end{pmatrix} , \tag{1.16}$$

et le réseau en nid d'abeilles $\mathscr{L}^H$ par

$$\mathscr{L}^H = (\mathscr{L} + \mathbf{a}) + (\mathscr{L} + \mathbf{b}) \quad \text{où} \quad \mathbf{a} = \frac{1}{2\sqrt{3}} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{et} \quad \mathbf{b} = -\mathbf{a} \,. \tag{1.17}$$

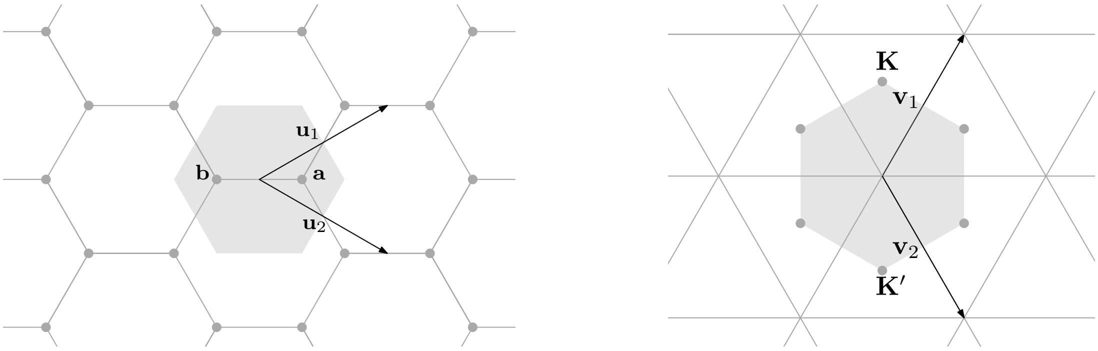
La maille de Wigner-Seitz forme un hexagone régulier. Le réseau réciproque $\mathscr{L}^*$ de $\mathscr{L}*$ est le suivant

$$\mathscr{L}^* = \mathbf{v}_1\mathbb{Z} + \mathbf{v}_2\mathbb{Z} \quad \text{où} \quad \mathbf{v}_1 = \frac{4\pi}{\sqrt{3}} \begin{pmatrix} 1/2 \\ \sqrt{3}/2 \end{pmatrix} \quad \text{et} \quad \mathbf{u}_2 = \frac{4\pi}{\sqrt{3}} \begin{pmatrix} 1/2 \\ -\sqrt{3}/2 \end{pmatrix} .$$

La première zone de Brillouin Γ^* forme aussi un hexagone régulier, voir Figure 1.1b. On note $M_{\mathcal{R}}$ la rotation de $2\pi/3$ par rapport à l'origine. Selon leur orbite par l'action de $M_{\mathcal{R}}$, on distingue deux types de sommets : $\mathbf{K}$ et $\mathbf{K}'$. On utilisera la convention suivante

$$\mathbf{K} = \frac{1}{3}(\mathbf{v}_1 - \mathbf{v}_2) \quad \text{et} \quad \mathbf{K}' = \frac{1}{3}(\mathbf{v}_2 - \mathbf{v}_1) = -\mathbf{K} \,. \tag{1.18}$$

Les sommets de Γ^* seront désignés par la notation générique $\mathbf{K}_\star \in \{\mathbf{K}, \mathbf{K}'\}$. Ils disposent d'une symétrie supplémentaire par rapport aux autres points de Γ^* puisque le réseau réciproque est invariant par rotation de $2\pi/3$ autour des points $\mathbf{K}_\star$. De cette propriété, on s'attend à ce que les relations de dispersion d'une large classe d'opérateurs périodiques invariant par le réseau $\mathscr{L}^H$ présentent des singularités coniques au dessus des points $\mathbf{K}_\star$. Ces singularités sont appelées *points de Dirac* et leur étude constitue la motivation principale de cette thèse. Nous y reviendrons plus largement après avoir introduit la théorie de Bloch-Floquet.



(a) Le réseau en nid d'abeilles $\mathscr{L}^H = (\mathscr{L} + \mathbf{a}) \cup (\mathscr{L} + \mathbf{b})$ est la superposition de deux versions translatées du réseau triangulaire $\mathscr{L} = \mathbf{u}_1\mathbb{Z} + \mathbf{u}_2\mathbb{Z}$. La maille de Wigner-Seitz Γ est colorée en gris et forme un hexagone régulier.

(b) Les vecteurs $\mathbf{v}_1$ et $\mathbf{v}_2$ génèrent le réseau réciproque $\mathscr{L}^*$. La première zone de Brillouin Γ^* est colorée en gris clair. Les sommets $\mathbf{K}$ et $\mathbf{K}'$ sont représentés, les autres étant obtenus par rotation de $2\pi/3$ et $4\pi/3$ autour de l'origine. On observe que le réseau $\mathscr{L}^*$ est invariant par rotation de $2\pi/3$ autour des sommets de Γ^*.

FIGURE 1.1 – Le réseau en nid d'abeilles $\mathscr{L}^H$.

Théorie de Bloch-Floquet

La transformation de Bloch-Floquet [15] permet de décomposer des opérateurs périodiques en intégrale directe [16].

On considère un réseau de Bravais $\mathscr{L} \subset \mathbb{R}^d$, de réseau réciproque $\mathscr{L}^*$. On note Γ une maille élémentaire de $\mathscr{L}$ et Γ^* la première zone de Brillouin. Une *onde de Bloch* de pseudo-moment $\mathbf{k} \in \mathbb{R}^d$ est une fonction appartenant à l'espace

$$L^2_{\mathbf{k}}(\Gamma) \coloneqq \left\{ \varphi \in L^2_{\mathrm{loc}}(\mathbb{R}^d) \;\middle|\; \forall \mathbf{u} \in \mathscr{L},\ \forall \mathbf{x} \in \mathbb{R}^d,\ \varphi(\mathbf{x} + \mathbf{u}) = e^{i\mathbf{k}\cdot\mathbf{u}}\varphi(\mathbf{x}) \quad \text{p.p} \right\} .$$

On note $L^2_{\mathrm{per}}(\Gamma) \coloneqq L^2_0(\Gamma)$ l'ensemble des fonctions $\mathscr{L}$-périodiques. Si φ et ψ sont dans $L^2_{\mathbf{k}}(\Gamma)$ alors $\overline{\varphi}\psi \in L^2_{\mathrm{per}}(\Gamma)$ et on peut munir l'espace $L^2_{\mathbf{k}}(\Gamma)$ du même produit hermitien que $L^2_{\mathrm{per}}(\Gamma)$. Les espaces $L^2_{\mathbf{k}}(\Gamma)$ et $L^2_{\mathrm{per}}(\Gamma)$ sont isométriques par la transformation unitaire suivante

$$\mathcal{U}_{\mathbf{k}} \ : \varphi \in L^2_{\mathbf{k}}(\Gamma) \mapsto \left[\mathbf{x} \mapsto e^{-i\mathbf{x}\cdot\mathbf{k}}\varphi(\mathbf{x})\right] \in L^2_{\mathrm{per}}(\Gamma) . \tag{1.19}$$

Plus généralement, pour tout $s \geq 0$, on définit l'espace de Sobolev d'ordre $s \geq 0$ avec conditions aux bords pseudo-périodiques

$$H^s_{\mathbf{k}}(\Gamma) \coloneqq \left\{ \varphi \in H^s_{\mathrm{loc}}(\mathbb{R}^d) \;\middle|\; \forall \mathbf{u} \in \mathscr{L},\ \forall \mathbf{x} \in \mathbb{R}^d,\ \varphi(\mathbf{x} + \mathbf{u}) = e^{i\mathbf{k}\cdot\mathbf{u}}\varphi(\mathbf{x}) \quad \text{p.p} \right\} .$$

Lorsque $\mathbf{k} = 0$, on écrira $H^s_{\mathrm{per}}(\Gamma)$ au lieu de $H^s_{\mathbf{k}}(\Gamma)$. Pour une fonction φ dans l'espace de Schwartz $\mathcal{S}(\mathbb{R}^d)$, on définit sa *transformée Bloch-Floquet* par

$$\left(\mathcal{U}_{\mathrm{BF}}\varphi\right)(\mathbf{k}, \mathbf{x}) \coloneqq \sum_{\mathbf{u} \in \mathscr{L}} e^{i\mathbf{k}\cdot\mathbf{u}}\varphi(\mathbf{x} - \mathbf{u}), \quad \mathbf{k} \in \mathbb{R}^d, \quad \mathbf{x} \in \mathbb{R}^d .$$

La transformée de Bloch-Floquet vérifie les propriétés de périodicité et pseudo-périodicité suivantes : pour presque tout $(\mathbf{k}, \mathbf{x}) \in \mathbb{R}^d \times \mathbb{R}^d$ et pour tout $\varphi \in \mathcal{S}(\mathbb{R}^d)$, on a

$$\left(\mathcal{U}_{\mathrm{BF}}\varphi\right)(\mathbf{k}, \cdot\,) \in L^2_{\mathbf{k}}(\Gamma) \quad \text{et} \quad \left(\mathcal{U}_{\mathrm{BF}}\varphi\right)(\,\cdot\,, \mathbf{x}) \in L^2_{\mathrm{per}}(\Gamma^*) .$$

Pour alléger les notations, on notera parfois $\varphi_{\mathbf{k}} \coloneqq \left(\mathcal{U}_{\mathrm{BF}}\varphi\right)(\mathbf{k}, \cdot)$. L'espace vectoriel $L^2(\Gamma^*, L^2(\Gamma))$

15. En accord avec le principe d'Arnold "Si une notion porte un nom propre, ce n'est pas celui de son créateur", cette transformation n'a été découverte ni par Bloch ni par Floquet.

16. La théorie des intégrales directes, qui généralisent la notion de somme directe, est par exemple exposée dans [RS78 ; Nie80].

est un espace de Hilbert (séparable) pour le produit hermitien

$$\langle \varphi, \psi \rangle_{L^2(\Gamma^*, L^2(\Gamma))} := \fint_{\Gamma^*} \int_{\Gamma} \overline{\varphi(\mathbf{k}, \mathbf{x})} \psi(\mathbf{k}, \mathbf{x}) \, \mathrm{d}\mathbf{x} \, \mathrm{d}\mathbf{k} \,,$$

où on a noté par $\fint_{\Gamma^*} := \frac{1}{|\Gamma^*|} \int_{\Gamma^*}$ l'intégrale moyennée sur Γ^*. Grâce à l'identité

$$\forall \varphi \in \mathcal{S}(\mathbb{R}^d), \quad \|\mathcal{U}_{\mathrm{BF}}(\varphi)\|_{L^2(\Gamma^*, L^2(\Gamma))} = \|\varphi\|_{L^2(\mathbb{R}^d)} \,,$$

on peut prolonger $\mathcal{U}_{\mathrm{BF}}$ en une isométrie de $L^2(\mathbb{R}^d)$ sur $L^2(\Gamma^*, L^2(\Gamma))$ dont la transformation inverse est définie par la formule

$$\forall \varphi \in \mathcal{S}(\mathbb{R}^d), \quad \varphi(\mathbf{x}) = \fint_{\Gamma^*} \varphi_{\mathbf{k}}(\mathbf{x}) \, \mathrm{d}\mathbf{k} \,.$$

On dit que l'opérateur H agissant sur $L^2(\mathbb{R}^d)$ est *$\mathscr{L}$-invariant* s'il commute avec toutes les translations du réseau $\mathscr{L}$. Si H est un opérateur $\mathscr{L}$-invariant et auto-adjoint alors sont spectre admet une structure de bande. C'est le fameux théorème de Bloch. Pour voir cela, on écrit sa *décomposition de Bloch-Floquet*

$$H \simeq \mathcal{U}_{\mathrm{BF}} H (\mathcal{U}_{\mathrm{BF}})^{-1} = \fint_{\Gamma^*}^{\oplus} H_{\mathbf{k}} \, \mathrm{d}\mathbf{k} \,.$$

Cette décomposition en intégrale directe le long des fibres $L^2_{\mathbf{k}}(\Gamma)$ signifie que si la transformée de Bloch-Floquet de $\varphi \in \mathcal{D}(H)$ est donnée par $(\varphi_{\mathbf{k}})_{\mathbf{k} \in \Gamma^*}$ alors on a les identités

$$(H\varphi)_{\mathbf{k}} = H_{\mathbf{k}} \varphi_{\mathbf{k}} \quad \text{p.p} \quad \text{et} \quad H\varphi = \fint_{\Gamma^*} H_{\mathbf{k}} \varphi_{\mathbf{k}} \, \mathrm{d}\mathbf{k} \,.$$

Si l'opérateur H est un opérateur de Schrödinger de la forme $H = -\Delta + V$ où V est un potentiel $\mathscr{L}$-invariant et tel que H soit auto-adjoint sur le domaine $\mathcal{D}(-\Delta) = H^2(\mathbb{R}^d)$ alors l'opérateur $H_{\mathbf{k}}$ est la restriction de H à la fibre $L^2_{\mathbf{k}}(\Gamma)$. La conjugaison de l'opérateur $H_{\mathbf{k}}$ avec l'opérateur unitaire $\mathcal{U}_{\mathbf{k}}$, défini en (1.19), fournit une décomposition alternative

$$H^{\mathbf{k}} := \mathcal{U}_{\mathbf{k}} H_{\mathbf{k}} \mathcal{U}_{\mathbf{k}}^* = (-i\nabla + \mathbf{k})^2 + V = -\Delta - 2i\mathbf{k} \cdot \nabla + |\mathbf{k}|^2 + V \,.$$

Puisque les opérateurs $H_{\mathbf{k}}$ et $H^{\mathbf{k}}$ sont unitairement équivalents, ils ont les mêmes propriétés spectrales. Cependant, cette seconde représentation a pour avantage que l'espace sur lequel agit $H^{\mathbf{k}}$ ne dépend plus de $\mathbf{k}$ et que la dépendance de l'expression de $H^{\mathbf{k}}$ en $\mathbf{k}$ est explicite et analytique. L'opérateur $H^{\mathbf{k}}$ est auto-adjoint sur $\mathcal{D}(-\Delta^{\mathbf{k}}) = H^2_{\mathrm{per}}$, borné par en dessous et est à résolvante compacte. Ainsi, son spectre est une suite croissante de valeurs propres de multiplicité finie et s'accumulant uniquement à l'infini

$$\sigma(H^{\mathbf{k}}) = \{\lambda_{\mathbf{k}1} \leq \lambda_{\mathbf{k}2} \leq \cdots \leq \lambda_{\mathbf{k}n} \ldots\} \,.$$

La fonction $\mathbf{k} \mapsto \lambda_{\mathbf{k}n}$ est appelée n-ième *fonction de bande* de H. La *relation de dispersion* (ou fibré de Bloch) de H est le sous-ensemble de $\mathbb{R}^{d+1}$ défini par

$$\begin{aligned} &\left\{(\mathbf{k}, \lambda) \in \mathbb{R}^{d+1} \;\middle|\; H_{\mathbf{k}} u = \lambda u \text{ a une solution d'onde de Bloch non triviale } u \in L^2_{\mathbf{k}}(\Gamma)\right\} \\ &= \left\{(\mathbf{k}, \lambda) \in \mathbb{R}^{d+1} \;\middle|\; H^{\mathbf{k}} u = \lambda u \text{ a une solution périodique non triviale } u \in L^2_{\mathrm{per}}(\Gamma)\right\} \,. \end{aligned}$$

Les fonctions de bande et la relation de dispersion sont invariantes par rapport au réseau réciproque $\mathscr{L}^*$. Ainsi, il suffit de considérer leur restriction à la première zone de Brillouin Γ^*. De plus, l'opérateur $H^{\mathbf{k}}$ définit une famille analytique de type (A) au sens de Kato par rapport au paramètre $\mathbf{k}$. Il découle de la théorie des perturbations des opérateurs linéaires que les fonctions de bandes sont continues et analytiques par morceaux. De plus, le spectre de H est purement absolument continu et est donné par l'image des fonctions de bandes

$$\sigma(H) = \bigcup_{\mathbf{k}\in\Gamma^*} \sigma(H^{\mathbf{k}}) = \bigcup_{\mathbf{k}\in\Gamma^*} \sigma(H_{\mathbf{k}}).$$

Le fibré de Bloch donne les niveaux d'énergie accessibles à un électron se déplaçant à travers un cristal. Même si on ignore les interactions entre électrons, le principe de Pauli impose que deux électrons ne peuvent être associés au même couple énergie / pseudo-moment. Le nombre N d'électrons par volume de maille élémentaire doit donc résoudre l'équation

$$N = \sum_{n\geq 1} \fint_{\Gamma^*} \mathbb{1}_{\lambda_{\mathbf{k}n}\leq\epsilon_F}\, \mathrm{d}\mathbf{k},$$

où le terme de droite correspond à la *densité d'états intégrée* et où ϵ_F est le niveau de Fermi. Si ϵ_F est situé dans un trou spectral alors les électrons sont peu susceptibles d'acquérir de l'énergie et le matériaux est un isolant ou un semi-conducteur, selon la taille du trou. Dans le cas contraire, les électrons sont mobiles et le matériaux est un conducteur.

Remarque 1.1. *Dans cette thèse, on considérera aussi des potentiels $\mathscr{L}$-périodiques et singuliers de sorte que $H = -\Delta + V$ ne soit pas auto-adjoint sur $H^2(\mathbb{R}^d)$. Cependant, lorsque V appartient à la classe de Kato [Cyc+87, Definition 1.10], l'opérateur H est borné par en dessous et on peut considérer les extensions de Friedrichs de H et $H_{\mathbf{k}}$. Tout ce qui a été énoncé dans cette sous-section reste valable dans ce cas. On réfère aux articles de [BS99 ; Kna89 ; She01] pour plus de détails dans cette direction.*

Le modèle de liaison forte

Le modèle de liaison forte [17] est une méthode d'approximation des bandes d'énergie qui consiste à approcher la fonction d'onde dans le cristal par une combinaison linéaire d'orbitales atomiques [Kit04 ; Mad78]. Pour les cristaux, cette méthode a été introduite par Slater et Koster dans [SK54]. Elle est connue pour donner une bonne description des électrons de cœur mais par pour ceux de valence.

Décrivons cette méthode pour un cristal dont les noyaux sont situés, pour simplifier, sur les sommets d'un réseau de Bravais $\mathscr{L} \subset \mathbb{R}^d$ et générant un potentiel périodique $V \in L^\infty_{\mathrm{per}}(\Gamma)$. On suppose qu'au voisinage de chaque sommet V peut être approché par un potentiel atomique V^{at}. On considère alors une orbitale atomique ψ^{at} associée à une valeur propre isolée

$$\left(-\Delta + V^{\mathrm{at}}\right)\psi^{\mathrm{at}} = \lambda^{\mathrm{at}}\psi^{\mathrm{at}},$$

et on construit un quasi-mode pour la fonction de bande $\lambda_{\mathbf{k}}$ de l'opérateur $-\Delta + V$ à l'aide de la transformée de Bloch de ψ^{at}

$$\psi_{\mathbf{k}} = \sum_{\mathbf{u}\in\mathscr{L}} e^{i\mathbf{k}\cdot\mathbf{u}}\psi^{\mathrm{at}}(\cdot - \mathbf{u}).$$

Dans cette approximation, on obtient

$$0 \simeq \langle\psi_{\mathbf{k}}, (-\Delta + V - \lambda_{\mathbf{k}})\psi_{\mathbf{k}}\rangle_{L^2(\Gamma)} = \lambda^{\mathrm{at}} - \lambda_{\mathbf{k}} + \sum_{\mathbf{u}\in\mathscr{L}} e^{i\mathbf{k}\cdot\mathbf{u}} \left\langle\psi^{\mathrm{at}}, (V - V^{\mathrm{at}}(\cdot - \mathbf{u}))\psi^{\mathrm{at}}(\cdot - \mathbf{u})\right\rangle_{L^2(\mathbb{R}^2)}.$$

Les orbitales atomiques étant exponentiellement décroissantes, on ne garde que les termes correspondant aux plus proches voisins dans la somme du membre de droite. Si on suppose de plus que les coefficients d'interaction restant sont tous égaux, ceci donne

$$\lambda_{\mathbf{k}} \simeq \lambda^{\mathrm{at}} + \left\langle\psi^{\mathrm{at}}, (V - V^{\mathrm{at}})\psi^{\mathrm{at}}\right\rangle_{L^2(\mathbb{R}^2)} + \gamma\sum_{\mathbf{u}} e^{i\mathbf{k}\cdot\mathbf{u}},$$

où la somme est prise sur l'ensemble des plus proches voisins de l'origine dans $\mathscr{L}$. Si le potentiel atomique V^{at} est bien choisi, on peut alors aussi négliger le second terme. Lorsqu'il y a N sites, on

17. Tight-binding model, en langue de Shakespeare. Ce modèle est aussi connu sous le nom, peut-être plus approprié, de LCAO (linear combination of atomic orbitals).

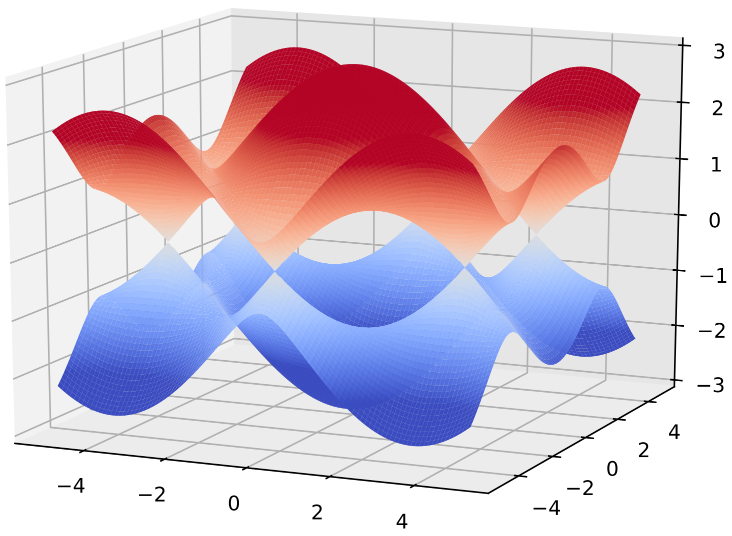


FIGURE 1.2 – Le modèle de Wallace. La relation de dispersion est invariante par rotation de $\pi/3$ autour de l'origine. On observe des points de Dirac à l'intersection entre les deux bandes.

doit considérer une orbitale atomiques distincte pour chaque site et on obtient une approximation pour N bandes. Dans le cas du graphène où le réseau est hexagonal (1.17) en dimension deux, on obtient le *modèle de Wallace* [Wal47]

$$\lambda_{\mathbf{k}}^{\pm} \simeq \lambda^{\mathrm{at}} \pm \left|1 + e^{i\mathbf{k}\cdot\mathbf{u}_1} + e^{i\mathbf{k}\cdot\mathbf{u}_2}\right| , \tag{1.20}$$

où $\mathbf{u}_1$ et $\mathbf{u}_2$ sont donnés en (1.16). La relation de dispersion associée au modèle de Wallace est représentée dans la Figure 1.2. On observe que les deux bandes forment des cônes au dessus des sommets $\mathbf{K}_\star$ de la première zone de Brillouin, voir (1.18). Ce type de singularités apparaissant relativement couramment lorsque deux bandes se rencontrent, on les décrit plus précisément dans la prochaine sous-section.

Graphène et points de Dirac

Alors que le modèle de Wallace a été théorisé en 1947, le graphène n'a été expérimentalement isolé qu'au début des années 2000, par l'équipe de Novoselov et Geim [18] [Nov+04]. Les étonnantes propriétés électroniques, mécaniques et thermiques [Cas+09 ; Coo+12] de ce matériau s'expliquent en partie par la présence de cônes, appelés *points de Dirac*, dans sa relation de dispersion. Cette appellation provient de la similarité avec la relation de dispersion d'un opérateur de Dirac bidimensionnel modélisant des électrons relativistes sans masse [Tha92].

Le modèle de Hubbard du graphène, généralisant le modèle de liaison forte en incluant les interactions, a été étudié par Giuliani, Mastropietro et Porta [GM10 ; GMP12]. Les auteurs montrent que les cônes persistent mais avec une forme renormalisée et que la conductance de Hall ne dépend pas des interactions. Une autre généralisation du modèle de liaison forte par des graphes quantiques a été étudiée par Kuchment et Post dans [KP07] où les auteurs détaillent la structure du spectre et de la relation de dispersion, retrouvant notamment la présence des points de Dirac. Dans [HLS12], Hainzl, Lewin et Sparber étudient l'approximation continue de Hartree-Fock du graphène avec des interactions de Coulomb instantanées, montrant qu'elles perturbent fortement la forme des cônes puisqu'ils deviennent des points singuliers.

18. Par la suite, Novoselov et Geim ont reçu le prix Nobel de physique en 2010 pour leurs travaux sur le graphène.

À partir de 2012, des travaux menés par Fefferman et Weinstein [FW12 ; FLW18] (voir aussi [Gru09 ; BC18]), utilisant le modèle de graphène à un électron libre, mettent en évidence l'universalité des cônes de Dirac. Ils montrent que c'est la structure en nid d'abeilles du graphène qui contraint topologiquement la forme du spectre de l'opérateur, expliquant ainsi l'existence des cônes. On retrouve ainsi des propriétés similaires dans une plus large classe de modèles génériques analogues au graphène [KP07 ; LWZ19]. Dans [FW14], il est montré par Fefferman et Weinstein que la dynamique d'un paquet d'ondes initialement localisé près d'un point de Dirac est gouvernée par une équation de Dirac effective (voir aussi [AS18] pour le cas non linéaire et [XZ19] pour le cas du graphène photonique). Ces mêmes auteurs ont aussi étudié l'existence dans ces modèles d'états de bord qui sont les responsables de la conductivité quantique de Hall observée dans le graphène. Ils sont les premiers à montrer rigoureusement l'existence d'états de bord topologiquement protégés le long de certaines coupures *zigzag* des réseaux hexagonaux [FLW16]. Ces résultats ont par la suite été raffinés par Drouot dans [Dro19a ; Dro19b] puis étendus à tous les bords rationnels dans [DW20] par Drouot et Weinstein.

Énonçons le théorème de Fefferman et Weinstein concernant l'universalité des points de Dirac. On considère le réseau triangulaire $\mathscr{L}$ défini en (1.16). On rappelle que Γ^* désigne la première zone de Brillouin. Une fonction mesurable V est un potentiel en nid d'abeilles s'il existe $\mathbf{x}_0 \in \mathbb{R}^2$ tel que $\widetilde{V} := V(\cdot - \mathbf{x}_0)$ vérifie les conditions suivantes :

(i) $\widetilde{V} \in L^\infty_{\text{per}}(\Gamma)$;

(ii) $\widetilde{V}$ est à valeurs réelles, c'est-à-dire que $\mathcal{C}(\widetilde{V}) := \overline{\widetilde{V}} = \widetilde{V}$;

(iii) $\widetilde{V}$ est pair, c'est-à-dire que $\mathcal{P}(\widetilde{V})(\mathbf{x}) := \widetilde{V}(-\mathbf{x}) = \widetilde{V}(\mathbf{x})$;

(iv) $\widetilde{V}$ est invariant par rotation de $2\pi/3$, c'est-à-dire que $\mathcal{R}(\widetilde{V})(\mathbf{x}) := \widetilde{V}(M^*_{\mathcal{R}}\mathbf{x}) = \widetilde{V}(\mathbf{x})$ où $M_{\mathcal{R}}$ est la matrice de rotation d'angle $2\pi/3$.

Théorème 1.2 (Universalité des points de Dirac [FW12 ; BC18])**.** *Soit V un potentiel en nid d'abeilles. On suppose de plus que*

$$V_{1,1} := \int_\Gamma V(\mathbf{x}) e^{-i(\mathbf{v}_1+\mathbf{v}_2)\cdot\mathbf{x}}\,\mathrm{d}\mathbf{x} \neq 0\,. \tag{1.21}$$

Pour tout $\epsilon \in \mathbb{R}$, on définit l'opérateur

$$H_\epsilon := -\Delta + \epsilon V\,. \tag{1.22}$$

Alors, il existe un ensemble $\mathcal{X} \subset \mathbb{R}$ fermé et au plus dénombrable tel que pour tout $\epsilon \notin \mathcal{X}$ et tout sommet $\mathbf{K}_\star \in \{\mathbf{K}, \mathbf{K}'\}$ de Γ^*, la relation de dispersion de H_ϵ présente un point de Dirac au dessus de $\mathbf{K}_\star$. De plus, il existe $\epsilon_0 > 0$ tel que $\mathcal{X} \cap (-\epsilon_0\,, \epsilon_0) = \{0\}$. Enfin, pour tout $\epsilon \in (-\epsilon_0\,, \epsilon_0) \setminus \{0\}$, un point de Dirac se situe entre les $1^{\text{ère}}$ et 2^{e} bandes (resp. les 2^{e} et 3^{e} bandes) si $\epsilon V_{1,1} > 0$ (resp. si $\epsilon V_{1,1} < 0$).

Ce résultat affirme qu'un potentiel "générique", c'est-à-dire satisfaisant la condition (1.21), et de "presque" n'importe quelle amplitude produit des points de Dirac, pourvu qu'il partage certaines symétries avec le réseau en nid d'abeilles [19] : symétrie par les translations du réseau triangulaire, symétrie $\mathcal{PC}$ (*parity / time reversal* symmetry) et symétrie par rotation de $2\pi/3$.

La preuve du Théorème 1.2 se décompose en deux temps. La plus petite valeur propre de l'opérateur $-\Delta_{\mathbf{K}_\star}$ est triplement dégénérée et, dans la limite des faibles contrastes (c'est-à-dire lorsque $|\epsilon|$ est petit mais non nul), un argument perturbatif montre que si la condition (1.21) est vérifiée alors l'une des trois bifurque tandis que les deux autres doivent rester égales du fait de l'invariance par la symétrie $\mathcal{PC}$. Par la théorie des fonctions invariantes de Hilbert-Weyl [GSS88, Chapitre XII], la relation de dispersion doit former un cône non dégénéré au voisinage de cette paire de valeurs propres. Par la suite, un argument d'analyse complexe prolonge cette conclusion à tout ϵ dans $\mathbb{R}$ excepté pour un ensemble discret.

Le modèle à un électron, considéré par Fefferman et Weinstein dans [FW12], ne prend pas en compte les interactions entre électrons. Une des principales motivations de cette thèse de doctorat

19. Les symétries associées à un potentiel en nid d'abeilles ne sont pas les seules dont on s'attend à ce qu'elles fassent émerger des cônes de Dirac. Voir, par exemple, les revues [WBB14 ; Wan+15] et les références qui y sont citées.

est d'étendre le Théorème 1.2 à des modèles plus réalistes. Dans la sous-section suivante, on présente le modèle de Hartree-Fock réduit périodique. C'est le modèle continu et périodique le plus simple dans lequel les corrélations entre électrons sont non nulles.

Modèle de Hartree-Fock réduit pour les cristaux

Les modèles périodiques en physique de la matière condensée sont généralement obtenus par limite thermodynamique [20], c'est-à-dire lorsqu'on considère un système fini dont le nombre de particules tend vers l'infini. La question de l'existence de la limite thermodynamique d'un système quantique est fortement liée à la stabilité de seconde espèce [LS10 ; HLS09a ; HLS09b], c'est-à-dire à l'extensivité de la matière. Dans le cadre d'un système avec interactions coulombiennes, cette question est rendue difficile par la lente décroissance en $\frac{1}{|\mathbf{x}|}$ du potentiel de Coulomb.

La limite thermodynamique du modèle de Thomas-Fermi a été étudiée par Lieb et Simon dans [Lie81a] et celle du modèle de Thomas-Fermi-von Weizsäcker par Catto, Le Bris et Lions dans [CLL98]. Dans [HLS09a], Hainzl, Lewin et Solovej montrent que l'argument clé pour qu'un système quantique admette une limite thermodynamique est l'estimation de l'écrantage du potentiel d'interaction qui, dans le cadre coulombien, peut être réalisée par l'intermédiaire d'une inégalité due à Graf et Schenker [GS95]. Dans [HLS09b], ces mêmes auteurs montrent que les modèles d'une large classe, incluant celui de Hartree-Fock, admettent une limite thermodynamique. La limite thermodynamique du modèle de Hartree-Fock réduit a, quant à elle, été obtenue par des méthodes plus élémentaires dans l'article de Catto, Le Bris et Lions [CLL01]. Dans [CDL08], Cancès, Deleurence et Lewin raffinent ce résultat en considérant la limite thermodynamique du modèle de supercellule et en étudiant les propriétés des minimiseurs. Gontier et Lahbabi ont montré que les convergences de l'énergie et de l'état fondamental sont exponentielles dans le cas des isolants et des semiconducteurs [GL16] et polynomiales en présence de défauts [GL17]. Dans la suite de cette sous-section, on décrit le modèle limite dans la théorie de Hartree-Fock reduit.

Un opérateur est *localement à trace* si pour toute fonction bornée et à support compact $\chi \in L^\infty_c(\mathbb{R}^d)$ on a $\chi\gamma\chi \in \mathfrak{S}_1(L^2(\mathbb{R}^d))$ [21]. Dans ce cas, on peut définir sa *densité à un corps*, notée ρ_γ, comme étant l'unique fonction de $L^1_{\mathrm{loc}}(\mathbb{R}^d)$ telle que

$$\forall \chi \in L^\infty_c(\mathbb{R}^d), \quad \mathrm{Tr}\,(\chi\gamma\overline{\chi}) = \int_{\mathbb{R}^d} |\chi|^2\,\rho_\gamma\,.$$

On considère un réseau de Bravais $\mathscr{L} \subset \mathbb{R}^d$, on note Γ une maille élémentaire et Γ^* la première zone de Brillouin. Dans la théorie de Hartree-Fock réduit périodique, l'état du système est décrit par un opérateur γ auto-adjoint, localement à trace, tel que $0 \leq \gamma \leq 1$ et invariant par les translations du réseau $\mathscr{L}$. De cette dernière condition, on déduit que $\rho_\gamma \in L^1_{\mathrm{per}}(\Gamma)$ et on définit la trace par unité de maille [22] de γ par

$$\underline{\mathrm{Tr}}_{\mathscr{L}}(\gamma) \coloneqq \mathrm{Tr}(\mathbb{1}_\Gamma\gamma\mathbb{1}_\Gamma) = \|\rho_\gamma\|_{L^1_{\mathrm{per}}(\Gamma)}\,.$$

Cette quantité s'interprète comme le nombre de particules par maille du réseau. Si, de plus, l'opérateur γ admet la décomposition de Bloch-Floquet

$$\gamma = \fint_{\Gamma^*} \gamma_{\mathbf{k}}\,\mathrm{d}\mathbf{k} = \fint_{\Gamma^*} \sum_{n\in\mathbb{N}} \lambda_{\mathbf{k}n}\,|\psi_{\mathbf{k}n}\rangle\,\langle\psi_{\mathbf{k}n}|\,\mathrm{d}\mathbf{k}\,, \tag{1.23}$$

où, pour tout $\mathbf{k} \in \Gamma^*$, la famille $(\psi_{\mathbf{k}n})_{n\in\mathbb{N}}$ forme une base hilbertienne de $L^2_{\mathbf{k}}(\Gamma)$ et $0 \leq \lambda_{\mathbf{k}n} \leq 1$

20. Souvent, les auteurs se placent dans l'approximation de Born-Oppenheimer et présupposent que les noyaux s'arrangent périodiquement selon un réseau cristallin. Cette seconde hypothèse est dénommée *conjecture de la cristallisation*. Bien qu'appuyée par des faits expérimentaux, cette conjecture reste sur un plan théorique largement ouverte. Le lecteur intéressé par cela pourra consulter la revue de Blanc et Lewin [BL15] sur le sujet.

21. On note par $\mathfrak{S}_p(\mathcal{H})$ l'espace de Schatten d'ordre $p \in [1\,,\infty]$ sur un espace de Hilbert $\mathcal{H}$. Sur ce sujet, on pourra consulter le livre de Simon [Sim05].

22. Dans la littérature, le symbole $\underline{\mathrm{Tr}}$ peut parfois désigner la trace par unité de volume, définie par $\underline{\mathrm{Tr}}(\gamma) = \lim\limits_{n\to\infty} \frac{\mathrm{Tr}(\mathbb{1}_{\Omega_n}\gamma\mathbb{1}_{\Omega_n})}{|\Omega_n|}$ où $\Omega_n \to \mathbb{R}^d$ assez rapidement (par exemple, $\Omega_n = n\Omega$ où Ω est un ouvert de $\mathbb{R}^d$), la quantité obtenue ne dépendant pas du réseau $\mathscr{L}$. Dans cette thèse, on considérera un réseau dilaté par un facteur L variable. Dans ce cas de figure, notre convention sera plus commode.

alors, pour presque tout $\mathbf{x} \in \mathbb{R}^d$, on a les identités suivantes

$$\rho_\gamma(\mathbf{x}) = \fint_{\Gamma^*} \rho_{\gamma_\mathbf{k}}(\mathbf{x})\,\mathrm{d}\mathbf{k} = \sum_{n\in\mathbb{N}} \fint_{\Gamma^*} \lambda_{\mathbf{k}n} \left|\psi_{\mathbf{k}n}(\mathbf{x})\right|^2 \mathrm{d}\mathbf{k}\,.$$

L'*énergie cinétique* de γ est définie par la formule

$$\underline{\mathrm{Tr}}_{\mathscr{L}}(-\Delta\gamma) := \underline{\mathrm{Tr}}_{\mathscr{L}}(\sqrt{-\Delta}\gamma\sqrt{-\Delta}) \in [0\,,\infty]\,.$$

Si γ admet la décomposition (1.23) et si, pour presque tout $\mathbf{k}$, on a $\psi_{\mathbf{k}n} \in H^1_\mathbf{k}(\Gamma)$ alors on a l'égalité

$$\underline{\mathrm{Tr}}_{\mathscr{L}}(-\Delta\gamma) = \sum_{n\in\mathbb{N}} \fint_{\Gamma^*} \lambda_{\mathbf{k}n} \left\|\nabla\psi_{\mathbf{k}n}\right\|^2_{L^2_\mathbf{k}(\Gamma)} \mathrm{d}\mathbf{k}\,.$$

Un *état admissible* est un élément de l'ensemble

$$\mathcal{S}_{\mathrm{per}} := \left\{\gamma = \gamma^* \in \mathcal{B}(L^2(\mathbb{R}^d)) \;\middle|\; 0 \leq \gamma \leq 1,\ \forall \mathbf{u} \in \mathscr{L},\ \tau_\mathbf{u}\gamma = \gamma\tau_\mathbf{u} \quad \text{and} \quad \underline{\mathrm{Tr}}_{\mathscr{L}}((1-\Delta)\gamma) < \infty\right\}\,, \tag{1.24}$$

où $\tau_\mathbf{u}$ désigne l'opérateur de translation par $\mathbf{u}$. Cet ensemble est muni de la norme $\|\gamma\|_{\mathcal{S}_{\mathrm{per}}} = \underline{\mathrm{Tr}}_{\mathscr{L}}((1-\Delta)\gamma) = \underline{\mathrm{Tr}}_{\mathscr{L}}(\sqrt{1-\Delta}\gamma\sqrt{1-\Delta})$.

On suppose que les électrons sont soumis à un potentiel $V \in L^p_{\mathrm{per}}(\Gamma)$ généré par le cristal et qu'ils interagissent à travers un potentiel d'interaction $w \in L^q_{\mathrm{per}}(\Gamma)$ où les indices p et q sont suffisamment grands [23]. On supposera de plus que l'interaction est répulsive, c'est-à-dire que les coefficients de Fourier de w sont positifs.

Si ρ est une mesure positive, localement finie et $\mathscr{L}$-invariante alors son *énergie d'interaction propre* est définie par [24]

$$D_{\mathrm{per}}(\rho,\rho) := \iint_{\Gamma\times\Gamma} \rho(\mathbf{x})w(\mathbf{x}-\mathbf{y})\rho(\mathbf{y})\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y} = \sqrt{|\Gamma|} \sum_{\mathbf{v}\in\mathscr{L}^*} \left|\hat{\rho}(\mathbf{v})\right|^2 \hat{w}(\mathbf{v}) \in [0\,,\infty]\,.$$

L'*énergie d'interaction* entre deux mesures ρ et μ localement finies et $\mathscr{L}$-invariantes est définie par

$$D_{\mathrm{per}}(\rho,\mu) := \iint_{\Gamma\times\Gamma} \rho(\mathbf{x})w(\mathbf{x}-\mathbf{y})\rho(\mathbf{y})\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y}\,,$$

dès que $D_{\mathrm{per}}(\rho,\rho) < \infty$ et $D_{\mathrm{per}}(\mu,\mu) < \infty$. Pour tout $N \geq 0$, le modèle de Hartree-Fock réduit périodique consiste à résoudre le problème de minimisation suivant

$$E^{\mathrm{rHF}}_{\mathrm{per}} := \inf\left\{\mathcal{E}^{\mathrm{rHF}}_{\mathrm{per}}(\gamma) \;\middle|\; \gamma \in \mathcal{S}_{\mathrm{per}} \quad \text{et} \quad \underline{\mathrm{Tr}}_{\mathscr{L}}(\gamma) = N\right\}\,, \tag{rHF$_\mathrm{p}$}$$

où la fonctionnelle d'énergie $\gamma \mapsto \mathcal{E}^{\mathrm{rHF}}_{\mathrm{per}}(\gamma)$ est définie pour tout $\gamma \in \mathcal{S}_{\mathrm{per}}$ par

$$\mathcal{E}^{\mathrm{rHF}}_{\mathrm{per}}(\gamma) := \underline{\mathrm{Tr}}_{\mathscr{L}}\left((-\Delta+V)\gamma\right) + \frac{1}{2}D_{\mathrm{per}}(\rho_\gamma,\rho_\gamma)\,.$$

En adaptant les preuves de [CLL01, Theorem 2.1] et [CDL08, Theorem 1] concernant le caractère bien posé du modèle de Hartree-Fock réduit périodique dans le cas d'interactions coulombiennes, on peut montrer que le problème de minimisation (rHF$_\mathrm{p}$) admet un unique minimiseur $\gamma_{\mathrm{per}} \in \mathcal{S}_{\mathrm{per}}$

23. Le choix des indices p et q doit, par exemple, garantir que les applications $\gamma \in \mathcal{S}_{\mathrm{per}} \mapsto \underline{\mathrm{Tr}}_{\mathscr{L}}(V\gamma)$ et $\gamma \in \mathcal{S}_{\mathrm{per}} \mapsto D_{\mathrm{per}}(\rho_\gamma,\rho_\gamma)$ soient continues et que le spectre de l'opérateur de champ moyen soit purement absolument continu. Les indices *naturels* sont $q = \max(1, d/4)$ et $p = \max(1, d/2)$ si $d \neq 2$ et $p > 1$ si $d = 2$. La pure absolue continuité du spectre de l'opérateur de Schrödinger périodique $-\Delta + V$ a été montrée pour $V \in L^{d/2}_{\mathrm{per}}(\Gamma)$ en dimension $d \geq 3$ dans [She01]. En dimension $d = 2$, le résultat optimal est obtenu dans [BS99].

24. On définit les coefficients de Fourier $\hat{\varphi}(\mathbf{v})$ d'une fonction $\varphi \in L^1_{\mathrm{per}}(\Gamma)$ par : $\hat{\varphi}(\mathbf{v}) := |\Gamma|^{-\frac{1}{2}} \int_\Gamma \varphi(\mathbf{x})e^{-i\mathbf{x}\cdot\mathbf{v}}\,\mathrm{d}\mathbf{x}$ pour tout $\mathbf{v} \in \mathscr{L}^*$.

tel que $\underline{\mathrm{Tr}}_{\mathscr{L}}(\gamma) = N$. De plus, $\gamma_{\rm per}$ satisfait l'équation non linéaire suivante

$$\gamma_{\rm per} = \mathbb{1}_{(-\infty,\epsilon_F]}\left(H^{\rm MF}_{\rm per}\right) \quad \text{où} \quad H^{\rm MF}_{\rm per} := -\Delta + V + \rho_{\gamma_{\rm per}} * w\,. \tag{1.25}$$

L'opérateur $H^{\rm MF}_{\rm per}$ est l'opérateur de champ moyen et $\epsilon_F \in \mathbb{R}$ le niveau de Fermi. De plus, pour tout $\epsilon_F \in \mathbb{R}$ tel que (1.25) est vérifié, $\gamma_{\rm per}$ est l'unique minimiseur sur $\mathcal{S}_{\rm per}$ de la fonctionnelle d'énergie

$$\gamma \longmapsto \mathcal{E}^{\rm rHF}_{\rm per}(\gamma) - \epsilon_F \int_\Gamma \rho_\gamma\,.$$

Le minimiseur $\gamma_{\rm per}$ représente la *mer de Fermi* [25], c'est-à-dire l'ensemble de tous les électrons dans le cristal placés de façon périodique en moyenne. Dans plusieurs travaux, les défauts d'un cristal sont décrits comme une perturbation compacte de cette mer de Fermi, par exemple dans [CDL08 ; CL10 ; Lah14 ; Lev20] [26].

Dans le graphène, il est important que l'énergie du niveau de Fermi soit exactement égale au niveau d'intersection des deux cônes. Cette condition est nécessaire pour assurer l'apparition de fermions de Dirac [Cas+09 ; Coo+12] pour les petites excitations de la mer de Fermi.

Il est à noter que pour démontrer le caractère bien posé de ce modèle limite il n'est pas nécessaire de supposer le système neutre [27]. Cependant, cette hypothèse est souvent faite dans le cas moléculaire puisque, sans elle, aucun phénomène d'écrantage ne survient et le passage à la limite thermodynamique est alors impossible.

Dans [CLL01], Catto, Le Bris et Lions ont montré l'existence de minimiseurs d'un modèle limite similaire à ($\mathrm{rHF_p}$) et correspondant à la théorie de Hartree-Fock (où le terme d'échange n'est pas négligé). Les propriétés de ceux-ci ont par la suite été examinées par Ghimenti et Lewin dans [GL08]. Les auteurs montrent qu'ils satisfont une équation non linéaire similaire à (1.25) mais dont l'opérateur de champ moyen peut présenter une valeur propre au niveau de Fermi. Cependant, comme pour les systèmes finis, cette dernière couche électronique doit être ou bien remplie ou bien laissé vide. Aussi, du fait de l'absence de propriété de convexité, on ne sait pas si ce modèle peut être obtenu comme limite thermodynamique du modèle de Hartree-Fock (HF), des brisures de symétrie pouvant avoir lieu, voir [BLS94] (et aussi [Ric18] concernant le modèle de Thomas-Fermi-Dirac-von Weizsäcker).

1.1.3 Problématiques

La motivation principale de ce travail de thèse est d'étendre les conclusions du Théorème 1.2 de Fefferman et Weinstein au modèle de Hartree-Fock réduit périodique (1.14), décrit dans la Section 1.1.2, et correspondant au réseau en nid d'abeilles $\mathscr{L}^H$, décrit dans la Section 1.1.2. Ce modèle, plus réaliste que celui utilisé par Fefferman et Weinstein, prend en compte une infinité d'électrons et une partie des corrélations. Au vu de la discussion qui précède, l'objectif de cette thèse est double :

- Montrer que des cônes de Dirac apparaissent dans la relation de dispersion de l'opérateur de champ moyen $H^{\rm rHF}_{\rm per}$, défini en (1.25) ;
- Montrer que le niveau de Fermi coïncide exactement avec l'énergie des cônes.

On considérera le modèle de Hartree-Fock réduit périodique posé sur le réseau $L\mathscr{L}^H$ où $L > 0$ est un paramètre de longueur, proportionnel à la distance entre les noyaux. Avec nos unités (1.7), le paramètre physique du graphène correspond à $L_{\rm phy} \simeq 5.36$. Cependant, l'étude du modèle à paramètre fixé est difficile. On s'intéressera donc aux régimes limites, c'est-à-dire $L \to 0$ et $L \to \infty$. Il est à noter que, lorsque les potentiels d'interaction sont homogènes de degré -1, un changement d'échelle montre que ces deux régimes sont équivalents respectivement au régime de faible contraste, $|\epsilon| \ll 1$ dans le Théorème 1.2, et au régime semi-classique, $|\epsilon| \to \infty$.

25. En analogie avec la *mer de Dirac*, qui décrit le vide comme une infinité d'électrons remplissant le spectre négatif de l'opérateur de Dirac, voir par exemple le livre de Thaller [Tha92].

26. Pour plus de détails concernant la modélisation mathématique des défauts dans les matériaux (cristallin ou non), on pourra consulter la revue de Cancès et Le Bris [CL13] et les références qui y figurent.

27. Notion dont la définition n'est pas si claire dans le cadre d'interactions quelconques, comme ici.

Lorsque la distance inter-noyaux est petite, c'est-à-dire dans la limite $L \to 0$, la preuve de Fefferman et Weinstein s'adapte à notre modèle (voir le Chapitre 4) : si la condition de non-dégénérescence (1.2) est vérifiée, ce qui est le cas pour des noyaux ponctuels et une large classe de noyaux étalés (*smeared nuclei*), alors l'opérateur de champ moyen $H_{\mathrm{per}}^{\mathrm{rHF}}$ admet des points de Dirac aux sommets de la première zone de Brillouin. Cependant, on peut aussi montrer que les trois premières bandes se superposent et que, par conséquent, le niveau de Fermi n'est **pas donné par l'énergie des cônes**. Ce régime ne présente donc pas de fermions de Dirac et on n'a pas poussé plus loin son étude.

Une importante partie de cette thèse sera donc consacrée au *régime de dissociation* $L \to \infty$, qui consiste à supposer que la distance entre les noyaux tend vers l'infini. Dans cette limite, une certaine classe d'opérateurs de Schrödinger ayant les symétries du graphène a été étudiée par Fefferman, Lee-Thorp et Weinstein dans [FLW18] (voir aussi [Dau93] où Daumer considère des potentiels décroissant polynomialement et estime précisément l'effet tunnel, c'est-à-dire l'épaisseur d'une bande isolée) où les auteurs montrent que la relation de dispersion tend uniformément vers le modèle de Wallace (1.20), décrit dans la Section 1.1.2 et dont les relation de dispersion est représentée sur la Figure 1.2. On cherchera à montrer un résultat analogue pour le modèle de Hartee-Fock réduit, l'intuition derrière étant que les interactions dans ce régime sont négligeables.

On supposera que les électrons se déplacent sur un feuillet et interagissent à travers l'interaction coulombienne tridimensionnelle $\frac{1}{|\mathbf{x}|}$, restreinte à ce feuillet. Cette hypothèse est notamment appuyée par un résultat de Duclos, Šťovíček et Tušek qui ont étudié dans [DŠT10] le modèle de l'atome bidimensionnel avec un potentiel de Coulomb $3d$. Ils ont montré que celui-ci s'obtenait comme la limite du modèle $3d$ où les électrons sont confinés dans une couche dont l'épaisseur tend vers 0.

Dans le Chapitre 2, on s'intéresse à un modèle simple, celui de Hartree-Fock réduit diatomique, et on étudie l'effet tunnel entre les deux premiers modes propres. Ce modèle est équivalent, lorsqu'on suppose que le système est singulet, à un modèle de Hartree diatomique, voir Section 1.1.1. Les résultats de ce chapitre sont présentés dans la Section 1.2. Ils ont servi d'entraînement pour étudier le cas périodique bien plus compliqué.

Dans le Chapitre 3, on étudie une classe d'opérateurs de Schrödinger périodiques dont la dépendance du potentiel selon au facteur d'échelle du réseau peut être non linéaire. On montre que dans la limite de dissociation, le premier ordre est donné par le modèle de liaison forte. On montre aussi que cette classe inclut le modèle de Hartree-Fock réduit périodique et que, pour le réseau hexagonal et lorsqu'une certaine condition de non-dégénérescence est vérifiée, celui-ci converge vers le modèle de Wallace. Cela implique que le niveau de Fermi est donné par l'énergie des cônes pour le modèle du graphène demi-rempli. Les résultats de ce chapitre sont présentés dans la Section 1.3.

Dans le Chapitre 4, on étudie le modèle de Hartree-Fock réduit dans la limite de faible contraste, c'est-à-dire lorsque les distances entre les noyaux sont petites. On adapte la preuve de Fefferman et Weinstein [FW12] pour montrer l'existence de points de Dirac. On montre aussi que le niveau de Fermi ne coïncide pas avec l'énergie des cônes. Les résultats de ce chapitre sont présentés dans la Section 1.4.

1.2 Présentation des résultats du Chapitre 2

Le Chapitre 2, qui porte sur l'étude d'un modèle de Hartree diatomique dans le régime de dissociation, est une version modifiée de l'article [Caz22], qui a été publié dans le journal *Nonlinearity*.

1.2.1 Présentation du modèle diatomique

Dans ce chapitre, on considère le modèle de Hartree-Fock réduit (rHF) pour deux électrons avec spin, de charge -1 et soumis à un potentiel extérieur généré par deux noyaux de charge $+1$ et dont la distance L tend vers l'infini, voir Figure 1.3. On étudie simultanément les cas où les électrons vivent dans $\mathbb{R}^d$ avec $d = 2$ ou 3. Dans les deux situations, on suppose que les interactions entre particules dérivent de l'interaction coulombienne tridimensionnelle $\frac{1}{|\mathbf{x}|}$, restreinte à $\mathbb{R}^2$ lorsque $d = 2$. On supposera aussi que le potentiel généré par chaque noyau contient un terme supplémentaire $V^{\mathrm{pp}} \in L^\infty(\mathbb{R}^d)$ correspondant à un pseudo-potentiel qui modélise le potentiel généré par d'éventuels électrons de cœur et un nombre égal de protons. On détaillera dans la prochaine sous-section les autres hypothèses que l'on fera concernant V^{pp}. Le potentiel extérieur est alors donné par

$$V_L(\mathbf{x}) := -\left(\frac{1}{|\mathbf{x}-\mathbf{x}_L|}+\frac{1}{|\mathbf{x}+\mathbf{x}_L|}\right)+V^{\mathrm{pp}}(\mathbf{x}-\mathbf{x}_L)+V^{\mathrm{pp}}(\mathbf{x}+\mathbf{x}_L)\,,$$

où $\mathbf{x}_L = (\frac{L}{2}, 0)$ si $d = 2$ et $\mathbf{x}_L = (\frac{L}{2}, 0, 0)$ si $d = 3$. La prise en compte du spin et l'absence de champ magnétique rend le système singulet, les électrons de spin haut et bas étant décrits par la même fonction d'onde. Le modèle est alors équivalent à un modèle de Hartree (voir Section 1.1.1) dont la fonctionnelle d'énergie est donnée par

$$\mathcal{E}_L(v) := \int_{\mathbb{R}^d} |\nabla v(\mathbf{x})|^2 \,\mathrm{d}\mathbf{x} + \int_{\mathbb{R}^d} V_L(\mathbf{x})\,|v(\mathbf{x})|^2 \,\mathrm{d}\mathbf{x} + \frac{1}{2}\iint_{\mathbb{R}^d\times\mathbb{R}^d} \frac{|v(\mathbf{x})|^2\,|v(\mathbf{y})|^2}{|\mathbf{x}-\mathbf{y}|}\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y} + \frac{1}{L}\,. \tag{1.26}$$

Le dernier terme correspond à l'énergie d'interaction entre les deux noyaux. L'espace des états

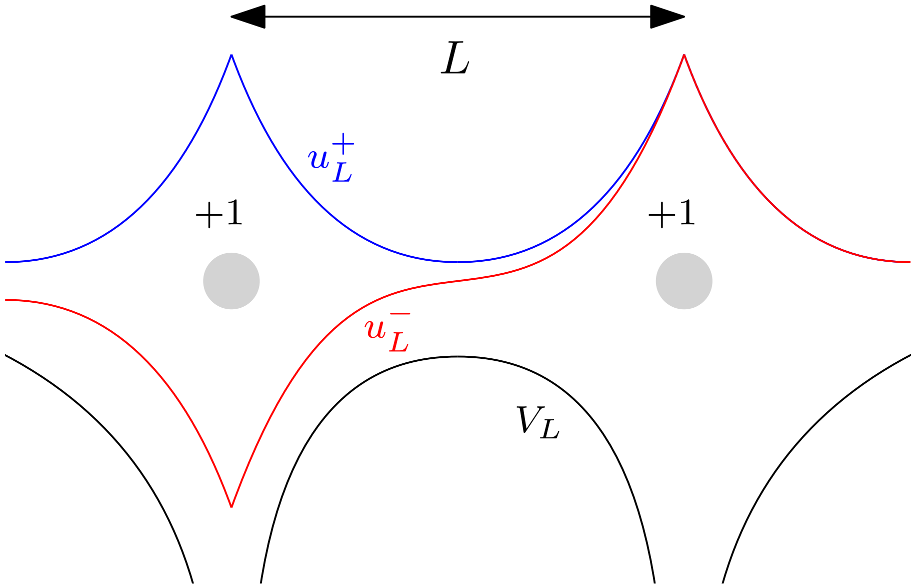


Figure 1.3 – Le double puit de potentiels. Les deux noyaux de charge +1 sont représentés par des disques colorés en gris et le potentiel V_L qu'ils génèrent est représenté par la courbe noire. La première fonction propre u_L^+ (resp. la seconde fonction propre u_L^-) de h_L, représentée par la courbe bleue (resp. la courbe rouge), est approchée par une superposition paire (resp. impaire) de la première fonction propre de l'opérateur mono-atomique h.

admissibles est

$$\mathcal{P} := \left\{ v \in H^1(\mathbb{R}^d) \;\middle|\; \int_{\mathbb{R}^d} |v|^2 = 2 \right\}.$$

La normalisation $\int_{\mathbb{R}^d} |v|^2 = 2$, qui assure la neutralité du système, vient du fait que l'on considère deux électrons. La fonctionnelle $v \mapsto \mathcal{E}_L(v)$ est bornée inférieurement et fortement continue sur $\mathcal{P}$. Elle est de plus faiblement semi-continue inférieurement sur $\left\{ v \in H^1(\mathbb{R}^d) \;\middle|\; \int_{\mathbb{R}^d} |v|^2 \le 2 \right\}$. Dans ce modèle, l'énergie par électron est donnée par le problème de minimisation suivant

$$\boxed{E_L := \frac{1}{2}\inf_{v\in\mathcal{P}} \mathcal{E}_L(v)\,.} \tag{1.27}$$

1.2.2 Modèle mono-atomique

On introduit maintenant un modèle qui jouera le rôle de modèle mono-atomique effectif. C'est le même modèle de Hartree mais dont le potentiel extérieur est généré par un unique noyau. Il est défini par

$$\boxed{I := \inf\left\{\mathcal{E}(v)\;\middle|\; v \in H^1(\mathbb{R}^d) \quad \text{and} \quad \int_{\mathbb{R}^d} |v|^2 = 1\right\},} \tag{1.28}$$

où la fonctionnelle d'énergie est donnée pour tout $v \in H^1(\mathbb{R}^d)$ par

$$\mathcal{E}(v) := \int_{\mathbb{R}^d} |\nabla v(\mathbf{x})|^2 \,\mathrm{d}\mathbf{x} + \int_{\mathbb{R}^d} \left(-\frac{1}{|\mathbf{x}|} + V^{\mathrm{pp}}(\mathbf{x})\right) |v(\mathbf{x})|^2 \,\mathrm{d}\mathbf{x} + \frac{1}{2} \iint_{\mathbb{R}^d \times \mathbb{R}^d} \frac{|v(\mathbf{x})|^2\, |v(\mathbf{y})|^2}{|\mathbf{x}-\mathbf{y}|} \,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y}\,.$$

On suppose que le pseudo-potentiel V^{pp} est radial, lisse et à support compact. De plus, on le choisit de sorte que le problème de minimisation (1.28) admette une unique solution $u \in H^1(\mathbb{R}^d)$ et que l'opérateur de champ moyen associé

$$h := -\Delta - |\cdot|^{-1} + V^{\mathrm{pp}} + |u|^2 * |\cdot|^{-1}\,, \tag{1.29}$$

ait une valeur propre μ strictement négative, son spectre essentiel étant égal à la demi-droite $[0\,,\infty)$. On sait alors que u est strictement positif à un facteur de phase près et est la première fonction propre de h. Puisque celle-ci est non-dégénérée, cela implique que u est radial.

Remarque 1.3. *(i) Un tel pseudo-potentiel V^{pp} existe. Par exemple, $V^{\mathrm{pp}}(\mathbf{x}) = -\lambda \mathbb{1}_{|x|\leq 1} * \chi$ où $\lambda > 1$ est assez grand et $\chi \in \mathcal{C}_c^\infty(\mathbb{R}^d)$ est une fonction de régularisation.*

(ii) L'hypothèse sur l'invariance de V^{pp} par rotation simplifie l'analyse du comportement asymptotique du potentel de champ moyen $-|\cdot|^{-1} + V^{\mathrm{pp}} + |u|^2 * |\cdot|^{-1}$ puisque certains termes[28] du développement multipolaire de $|v|^2 * |\cdot|^{-1}$ s'annulent lorsque la fonction v est radiale.

(iii) Choisir V^{pp} à support compact revient à considérer que l'écrantage est parfait loin des noyaux. Cette hypothèse, non optimale, pourrait être relaxée tant que l'on suppose que V^{pp} décroît suffisamment vite. Les preuves du Chapitre 2 n'en seraient que légèrement modifiées.

(iv) En dimension $d = 3$, on peut prendre $V^{\mathrm{pp}} = 0$, voir [BBL81 ; Lie81a]. En dimension deux, des premières explorations numériques, présentées dans l'Appendice A, suggèrent c'est vrai aussi, mais cela n'a pas été démontré.

1.2.3 Principaux résultats

En adaptant les arguments de [Lie81a, Section VII], on peut montrer que le modèle diatomique (1.27) admet un unique minimiseur $u_L^+ \in \mathcal{P}$. De plus, ce minimiseur est partout strictement positif et satisfait l'équation d'Euler-Lagrange suivante

$$h_L u_L^+ = \left(-\Delta + V_L + |u_L^+|^2 * |\cdot|^{-1}\right) u_L^+ = \mu_L^+ u_L^+\,,$$

où le multiplicateur de Lagrange μ_L^+ est plus petite valeur propre de l'opérateur de champ moyen h_L. L'invariance de l'énergie (1.26) par réflexion selon l'hyperplan $\{\mathbf{x}_1 = 0\}$ implique que u_L^+ est une fonction paire par rapport à cet hyperplan. Lorsque L est grand, une deuxième valeur propre négative μ_L^- existe, la fonction propre associée u_L^- est impaire par rapport à $\{\mathbf{x}_1 = 0\}$ et on peut choisir sa phase de sorte qu'elle soit strictement positive sur le demi-espace $\{\mathbf{x}_1 > 0\}$.

Des modèles diatomiques ont été amplement étudiés dans la littérature, notamment par Harrell [Har80] dans le cas linéaire. Lorsque L est grand, on s'attend à ce que le trou spectral $\mu_L^- - \mu_L^+ > 0$ soit exponentiellement petit, déterminé par l'effet tunnel entre les deux noyaux, et que les fonctions propres associées, u_L^+ et u_L^-, soient données au premier ordre par une superposition respectivement paire et impaire de la première fonction propre d'un opérateur mono-atomique, voir

28. Tous les termes sauf le premier lorsque $d = 3$ et les termes de degré pair lorsque $d = 2$. Voir la formule (1.34) plus bas.

Figure 1.3. Le théorème qui suit contient les principaux résultats obtenus dans le Chapitre 2 qui étendent certaines propriétés du cas linéaire au modèle de Hartree. En particulier, on donne des bornes exponentielles supérieures et inférieures sur le trou spectral, ce qui constitue la principale contribution de ce chapitre.

Théorème 1.4. *Soit $\alpha = 0$ si $d = 3$ et $\alpha > 0$ si $d = 2$. Soit $\epsilon > 0$. Alors, on a*

$$|\mu_L^\pm - \mu| = \begin{cases} O\big(L^{-3+\epsilon}\big) & si\ d = 2\,, \\ O\big(L^{-\infty}\big) & si\ d = 3\,, \end{cases} \tag{1.30}$$

$$\big\|u_L^\pm - (u(\cdot - \mathbf{x}_L) \pm u(\cdot + \mathbf{x}_L))\big\|_{H^{2-\alpha}(\mathbb{R}^d)} = \begin{cases} O\big(L^{-3+\epsilon}\big) & si\ d = 2\,, \\ O\big(L^{-\infty}\big) & si\ d = 3\,. \end{cases} \tag{1.31}$$

Lorsque $d = 2$, les constantes apparaissant dans le O dépendent de α et ϵ. L'énergie E_L satisfait

$$E_L = I + \begin{cases} \big(\frac{3m_1}{4}\big)^2 \frac{1}{L^5} + o\big(\frac{1}{L^5}\big) & si\ d = 2\,, \\ O\big(L^{-\infty}\big) & si\ d = 3\,, \end{cases} \tag{1.32}$$

où $m_1 := \int_{\mathbb{R}^2} |u(\mathbf{x})|^2 |\mathbf{x}|^2 \,\mathrm{d}\mathbf{x}$ est le second moment de $|u|^2$. De plus, il existe une constante $C > 0$ telle que

$$\boxed{\frac{1}{C}\frac{e^{-\sqrt{|\mu|}L}}{L^d} \le \mu_L^- - \mu_L^+ \le Ce^{-\sqrt{|\mu|}L}\,.} \tag{1.33}$$

La notation $O(L^{-\infty})$ signifie un $O\big(L^{-k}\big)$ pour tout $k \in \mathbb{N}$, où la constante peut dépendre de k.

L'effet tunnel entre deux puits distants a d'abord été étudié par Harrell dans le cas linéaire [Har80]. Il est montré que son amplitude est déterminée par la décroissance à l'infini des fonctions propres correspondantes. Dans [Sim84a], Simon montre que, dans la limite semi-classique (équivalente au régime de dissociation pour les potentiels homogènes de degré -1), l'effet tunnel est relié à une certaine métrique riemannienne, la distance d'Agmon. Par la suite, les modèles de puits de potentiel multiples en limite semi-classique ont pleinement été examinés dans un série d'articles par Helffer et Sjöstrand [HS84 ; HS85b ; HS85a ; HS85c ; HS86 ; HS87] ainsi que par leurs collaborateurs [Out84 ; Moh91 ; Dau96].

Alors que la littérature sur le cas linéaire est conséquente, celle concernant le cas non-linéaire semble plus clairsemée. Par des méthodes de point fixe, Daumer a construit des solutions aux équations de Hartree-Fock dans le régime de dissociation [Dau94]. Cependant, les hypothèses y sont restrictives et ne couvrent pas les systèmes coulombiens. En dimension 3, notre modèle a déjà été considéré dans [CL93] par Catto et Lions mais dans un contexte différent. Les auteurs calculent le premier ordre de la différence d'énergie entre le modèle diatomique et les deux modèles mono-atomiques sans interaction. Cependant, le trou spectral n'y est pas étudié. Plus récemment, dans une série d'articles [RS18 ; OR21 ; ORS21], Olgiati, Rougerie et Spehner ont considéré un système de bosons piégés dans un double puit symétrique dans la limite où la distance et la barrière entre les puits sont grandes. L'esprit de l'article [OR21] est proche de ce que l'on a produit dans le Chapitre 2, plusieurs arguments en étant issus.

Dans le Théorème 1.4, les résultats obtenus diffèrent selon la dimension ; les estimées (1.30), (1.31) et (1.32) sont polynomiales lorsque $d = 2$ et super-polynomiales [29] lorsque $d = 3$. Cela provient de la forme que prend l'écrantage du potentiel de Coulomb par le champ moyen des électrons. En effet, en dimension 3, il n'y a aucun terme polynomial d'après le théorème de Newton alors qu'en dimension 2, les termes impairs sont strictement positifs, comme le montre le développement multipolaire

$$\int_{\mathbb{R}^2} \frac{\rho(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,\mathrm{d}\mathbf{y} = \sum_{n=0}^{N-1} \frac{1}{4^{2n}}\binom{2n}{n}^2 \frac{1}{|\mathbf{x}|^{2n+1}}\left(\int_{\mathbb{R}^2} \rho(\mathbf{y})\,|\mathbf{y}|^{2n}\,\mathrm{d}\mathbf{y}\right) + O\left(\frac{1}{|\mathbf{x}|^{2N+1}}\right), \tag{1.34}$$

29. On peut en fait montrer qu'elles sont exponentielles.

vérifié par toute fonction mesurable $\rho \in L^1(\mathbb{R}^2)$, radiale et à décroissance exponentielle. Ce développement est démontré dans l'Appendice Appendix A. du Chapitre 2.

Cependant, dans les deux dimensions, on est capable d'obtenir sur le trou spectral des estimées avec un taux exponentiel *exact*, voir les estimées (1.33). Alors qu'un tel résultat est connu pour le cas linéaire (voir par exemple [Dau96]), cela n'apparaît pas dans la littérature sur le cas non linéaire. Pour les modèles diatomiques, l'effet tunnel est principalement déterminé par le comportement des fonctions propres $u_L^{\pm}$ au voisinage de milieu du segment reliant les deux noyaux, situés ici en $\pm\mathbf{x}_L$, c'est-à-dire dans un voisinage de l'origine. C'est une conséquence de l'invariance du modèle par la réflexion selon l'hyperplan $\{\mathbf{x}_1 = 0\}$ et de la formule de *ground state substitution* (voir [Sim84a])

$$\langle g\psi, (-\Delta + V - \lambda)\, g\psi\rangle_{L^2(\Omega)} = \frac{1}{2}\, \|(\nabla g)\psi\|^2_{L^2(\Omega)}\ ,$$

où ψ (resp. λ) est la première fonction propre (resp. première valeur propre) de l'opérateur $-\Delta+V$ et où g est n'importe quelle fonction $\mathcal{C}^1(\Omega)$ uniformément bornée.

Le décroissance des fonctions propres des opérateurs de Schrödinger a fait l'objet de nombreux travaux dans la littérature, par exemple [HHS85 ; Hof90]. Dans le cas qui nous intéresse, c'est-à-dire celui des opérateurs à une particule dont le potentiel décroît assez vite à l'infini, ce comportement est principalement déterminé par la distance de l'énergie de la fonction propre au spectre essentiel, donné par la demi-droite $[0\,,\infty)$. Concernant la première fonction propre u du modèle mono-atomique (1.28), on obtient les estimées suivantes : il existe $C > 0$ tel que pour tout $\mathbf{x} \in \mathbb{R}^d$, on a

$$\frac{1}{C}\frac{e^{-\sqrt{|\mu|}|\mathbf{x}|}}{1+|\mathbf{x}|^{\frac{d-1}{2}}} \le u(\mathbf{x}) \le C\frac{e^{-\sqrt{|\mu|}|\mathbf{x}|}}{1+|\mathbf{x}|^{\frac{d-1}{2}}} \quad \text{et} \quad |\nabla u(\mathbf{x})| \le C\frac{e^{-\sqrt{|\mu|}|\mathbf{x}|}}{1+|\mathbf{x}|^{\frac{d-1}{2}}}\,. \tag{1.35}$$

Une part importante du Chapitre 2 est dédiée à l'obtention d'estimées analogues à (1.35) pour u_L^+ et u_L^-, dans un voisinage de l'origine et avec le même taux de décroissance exponentielle. Pour cela, il est important de montrer que le taux de convergence des multiplicateurs de Lagrange $\mu_L^{\pm}$ vers μ est au moins polynomial et de degré strictement supérieur à deux. Cela est aisé en dimension 3 puisque le théorème de Newton fournit des taux de convergence super-polynomiaux. L'étude du cas de la dimension 2 requiert une analyse plus fine. Il a notamment fallu déterminer précisément la convergence de l'énergie par électron du modèle diatomique vers celle du modèle mono-atomique (voir (1.32)) ainsi que la convergence des fonctions propres $u_L^{\pm}$ en norme de Sobolev $H^{2-\alpha}(\mathbb{R}^d)$ vers les superpositions paire et impaire des translations de u par $\pm\mathbf{x}_L$ (voir (1.31)). On obtient alors les convergences énoncées en (1.30), suffisantes pour appliquer la formule de ground state substitution.

L'argument clé pour estimer les taux de convergence est la stabilité du modèle de Hartree (1.28) : il existe $C > 0$ tel que pour tout $v \in H^1(\mathbb{R}^d)$ vérifiant $\|v\|_{L^2(\mathbb{R}^d)} = 1$, on a

$$q_h(v) \ge \mu + C \min_{\theta\in[0,2\pi]} \left\|e^{i\theta}v - u\right\|^2_{H^1(\mathbb{R}^d)} \quad \text{et} \quad \mathcal{E}(v) \ge \mathcal{E}(u) + C \min_{\theta\in[0,2\pi]} \left\|e^{i\theta}v - u\right\|^2_{H^1(\mathbb{R}^d)}\ ,$$

où q_h (resp. u) est la forme quadratique associée à (resp. la première fonction propre de) l'opérateur de champ moyen h, défini en (1.29). Ce résultat, dont la démonstration est inspirée de [CFL14, Theorem 5.1], est démontré dans la Section 4.1 du Chapitre 2.

Enfin, il est à noter que, même si on est capable de déterminer les taux de convergence exponentielle exacts dans les estimées (1.33) du trou spectral, notre démonstration ne permet pas de préciser les corrections polynomiales de manière optimale. On pense qu'il est possible d'enlever le L^{-d} de la borne inférieure de (1.33).

1.3 Présentation des résultats du Chapitre 3

Le Chapitre 3 porte sur la recherche de points de Dirac dans une classe de modèles non-linéaires et dans le régime de dissociation.

1.3.1 Introduction

La motivation principale de ce chapitre est de répondre aux deux problématiques soulevées dans la Section 1.1.3, à savoir celle concernant l'existence de points de Dirac dans certains modèles cristallins non linéaires dans le régime de dissociation, et plus particulièrement dans le modèle de Hartree-Fock réduit (rHF) du graphène, et celle concernant la valeur du niveau de Fermi. On rappelle que le modèle rHF a été introduit dans la Section 1.1.2.

Pour répondre à ces questions, on considère un réseau de Bravais $\mathscr{L} \subset \mathbb{R}^2$ et une famille de potentiels $\{V_L\}_{L\geq 1}$ tels que, pour tout L, le potentiel V_L soit périodique selon le réseau dilaté $L\mathscr{L}$. Par la suite, on exhibe des conditions [30] sur cette famille pour que la suite d'opérateurs périodiques $H_L := -\Delta + V_L$ converge vers le modèle de liaison forte lorsque $L \to \infty$ et si une hypothèse de non-dégénérescence est vérifiée. On montre aussi que, dans ce cas et lorsque $\mathscr{L}$ est le réseau en nid d'abeilles (décrit dans la Section 1.1.2), des points de Dirac apparaissent pour L grand entre les deux premières bandes du fibré de Bloch associé à H_L. On montre enfin que le modèle rHF est inclus dans cette classe et que par conséquent, le modèle rHF du graphène demi-rempli est donné dans le régime de dissociation par le modèle de Wallace (voir Section 1.1.2) si l'hypothèse de non-dégénérescence est satisfaite. Dans ce cas, il est immédiat que le niveau de Fermi soit donné par l'énergie des cônes.

Il est à noter que, pour simplifier l'analyse et parce que c'est le cas qui nous intéresse initialement, on ne considèrera que la dimension deux, même si on pense que la majorité des arguments exposés peuvent s'adapter à n'importe quelle dimension $d \geq 1$.

1.3.2 Une classe de potentiels périodiques

Avant d'énoncer les principaux résultats de ce chapitre, on décrit la classe de potentiels en question.

On se donne un réseau de Bravais bidimensionnel $\mathscr{L} \subset \mathbb{R}^2$ ainsi qu'un paramètre d'échelle $L \geq 1$. Pour le confort du lecteur, on rappelle les notations concernant les réseaux introduites dans la Section 1.1.2. La cellule de Wigner-Seitz de $\mathscr{L}$ est notée Γ, le réseau réciproque $\mathscr{L}^*$ et la première zone de Brillouin Γ^*. On considère un cristal avec un nombre quelconque de sites, défini sur le réseau cristallin

$$\mathscr{L}^{\mathbf{R}} := \mathscr{L} + \mathbf{R} = \{\mathbf{u} + \mathbf{r} \mid \mathbf{u} \in \mathscr{L} \quad \text{et} \quad \mathbf{r} \in \mathbf{R}\}\ ,$$

où $\mathbf{R} \subset \Gamma$ est un ensemble fini, de cardinal noté $N = |\mathbf{R}|$ et listant les positions des différents sites dans Γ. Aussi, on ajoute un indice L aux notations lorsqu'on considère le réseau dilaté du facteur L. Par exemple, on écrira $\mathscr{L}_L^{\mathbf{R}} = L\mathscr{L}^{\mathbf{R}}$ et $\Gamma_L = L\Gamma$. Dans tout ce chapitre, on se place dans le régime de dissociation, c'est-à-dire que l'on supposera $L \to \infty$.

On considère une famille $\{V_L\}_{L\geq 1}$ de potentiels à valeurs réelles sur $\mathbb{R}^2$ et on cherche des conditions pour que V_L soit approximativement donné par une superposition périodique exacte de potentiels atomiques, c'est-à-dire

$$V_L \simeq \sum_{\mathbf{r} \in \mathscr{L}^{\mathbf{R}}} V^{\mathrm{at}}(\cdot - L\mathbf{r})\,, \tag{1.36}$$

où V^{at} est un potentiel atomique fixé et lorsque $L \to \infty$. Le cas d'égalité dans (1.36) a été étudié dans un cadre semi-classique par Outassourt pour des potentiels lisses [Out84] et par Mohamed pour des potentiels présentant des singularités coulombiennes [Moh91].

La première hypothèse sur V_L concerne le type de singularités que V_L peut avoir.

Hypothèse 1 (Singularités)**.** *On suppose que*

(i) $V_L \in L^p_{\mathrm{per}}(\Gamma_L)$ *pour un certain* $p \in (1\,,\infty)$ *;*

(ii) $\|V_L\|_{L^\infty_{\mathrm{per}}(\Gamma_L)}$ *tend uniformément vers 0 à une distance d'ordre L des sommets du réseau* $\mathscr{L}_L^{\mathbf{R}}$ *:*

$$\forall \rho > 0, \quad \lim_{L\to\infty} \left\| V_L \mathbb{1}_{\mathrm{d}(\cdot,\mathscr{L}_L^{\mathbf{R}}) \geq L\rho} \right\|_{L^\infty_{\mathrm{per}}(\Gamma_L)} = 0\,.$$

30. Qu'on espère être les plus faibles possibles.

Avec ces hypothèses, on se permet de considérer des potentiels dont les singularités locales sont de la forme $|\mathbf{x}|^{-\alpha}$ où $\alpha < 2$, incluant le potentiel de Coulomb tridimensionnel $\alpha = 1$. L'Hypothèse 1*(ii)* contraint l'emplacement des singularités aux sommets du réseau $\mathscr{L}_L^{\mathbf{R}}$. Enfin, la dépendance en L de V_L peut être non linéaire.

Pour simplifier l'analyse, on va supposer que tous les sommets du réseau $\mathscr{L}^{\mathbf{R}}$ sont équivalents. Plus précisément, si on note par G (resp. par G_L) le groupe de symétrie [31] de $\mathscr{L}^{\mathbf{R}}$ (resp. de $\mathscr{L}_L^{\mathbf{R}}$) alors on fait l'hypothèse que pour chaque paire de sommets de $\mathscr{L}^{\mathbf{R}}$, il existe un élément de G qui envoie l'un sur l'autre.

Hypothèse 2 ($\mathscr{L}^{\mathbf{R}}$ a une seule orbite)**.** *Le réseau $\mathscr{L}^{\mathbf{R}}$ est* sommet-transitif : *le groupe G agit transitivement sur $\mathscr{L}^{\mathbf{R}}$.*

On suppose maintenant que V_L a les mêmes symétries que le réseau $\mathscr{L}_L^{\mathbf{R}}$.

Hypothèse 3 (Symétries de V_L)**.** *Pour tout $L \geq 1$, le potentiel V_L est invariant par l'action du groupe G_L : $\forall g \in G_L$, $g \cdot V_L = V_L$.*

Cette hypothèse est naturelle dans le cadre de la théorie rHF périodique. En effet, la densité minimisante étant unique, celle-ci est donc invariante par l'action du groupe de symétrie du réseau.

Il nous reste maintenant à définir le comportement asymptotique de chaque singularité lorsque L est grand. Pour cela, on se donne un potentiel de référence qui jouera le rôle du potentiel atomique V^{at} dans (1.36).

Hypothèse 4 (Potentiel de référence)**.** *Soit V un potentiel à valeurs réelles tel que*

(i) $V \in L^p(\mathbb{R}^2) + L^\infty(\mathbb{R}^2)$ *où $p \in (1\,,\infty)$ est le nombre introduit dans l'Hypothèse 1(i) ;*

(ii) $V(\mathbf{x}) = O\left(|\mathbf{x}|^{-1-\epsilon}\right)$ *lorsque $|\mathbf{x}| \to \infty$ pour un certain $\epsilon > 0$;*

(iii) L'opérateur de Schrödinger associé

$$H = -\Delta + V\,,$$

admet au moins une valeur propre strictement négative.

Les Hypothèses 4*(i)* et 4*(iii)* impliquent que l'énergie fondamentale μ de H est non-dégénérée et que la phase de l'état propre associé v peut être choisie de sorte que $v > 0$ partout (voir par exemple [Goe77]). De l'Hypothèse 4*(ii)* et de [HHS85, Corollary 2.2], on déduit que v vérifie en plus des estimées exponentielles similaires à (1.35).

On note $d_0 > 0$ (resp. $d_1 > d_0$) la distance entre deux plus proches voisins (resp. seconds plus proches voisins) dans $\mathscr{L}^{\mathbf{R}}$, voir Figure 1.4. On se donne $\delta \in (0\,,1/2)$ et une fonction de coupure $\chi \in \mathcal{C}_c^\infty(\mathbb{R}^2)$ radiale et telle que

$$0 \leq \chi \leq 1, \quad \chi \equiv 1 \quad \text{sur} \quad B\left(0, \frac{1+\delta}{2} d_0\right) \quad \text{et} \quad \operatorname{supp}\chi \subset B\left(0, \left(\frac{1}{2}+\delta\right) d_0\right)\,. \tag{1.37}$$

On note $\chi_{L,\mathbf{r}} \coloneqq \chi(L^{-1} \cdot - \mathbf{r})$. Cette fonction est schématiquement représentée sur la Figure 1.5.

La dernière condition qu'on demande sur V_L est que son comportement au voisinage de chaque sommet de $\mathscr{L}^{\mathbf{R}}$ est asymptotiquement donné par le potentiel de référence V.

Hypothèse 5 (Les puits sont asymptotiquement équivalents à V)**.** *Pour tout $\mathbf{r} \in \mathscr{L}^{\mathbf{R}}$, on a*

$$\lim_{L\to\infty} \|\chi_{L,\mathbf{r}} V_L - V(\cdot - \mathbf{r})\|_{L^p(\mathbb{R}^2)+L^\infty(\mathbb{R}^2)} = 0\,.$$

Ceci conclut la définition de la classe de potentiels $\{V_L\}_{L\geq 1}$. Dans les prochaines sous-sections, on décrit les résultats obtenus dans la Chapitre 3.

31. C'est-à-dire que G est le sous-groupe du groupe $E_2(\mathbb{R})$ des transformations euclidiennes du plan telles que leur action laisse le réseau $\mathscr{L}^{\mathbf{R}}$ invariant. On rappelle que le groupe ponctuel de G_L, c'est-à-dire les transformations linéaires de G_L, est indépendant de L et est donc égal à celui de G.

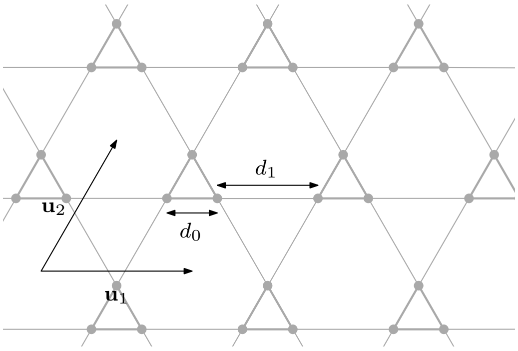


FIGURE 1.4 – $\mathscr{L} = \mathbf{u}_1\mathbb{Z} + \mathbf{u}_2\mathbb{Z}$ est le réseau triangulaire et $N = |\mathbf{R}| = 3$. Les sommets reliés par un trait gris épais (resp. par un trait gris fin) sont des plus proches voisins (resp. des seconds plus proches voisins). La distance d_0 au plus proche voisin et celle d_1 au second plus proche voisin sont affichées.

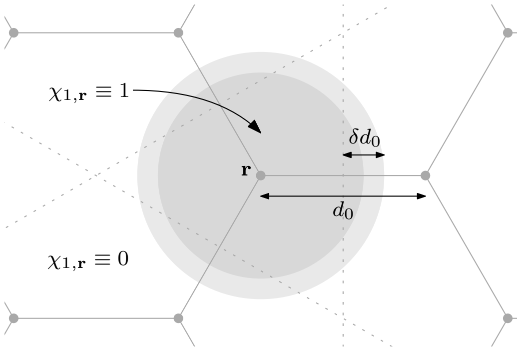


FIGURE 1.5 – Représentation schématique de la fonction de coupure $\chi_{1,\mathbf{r}}$ pour le réseau en nid d'abeilles. Le disque coloré en gris foncé (resp. la couronne colorée en gris clair) correspond à la zone où $\chi_{1,\mathbf{r}} \equiv 1$ (resp. où $\nabla\chi_{1,\mathbf{r}} \neq 0$). Les droites en pointillées sont les médianes entre $\mathbf{r}$ et ses plus proches voisins.

1.3.3 Principaux résultats

On se donne un réseau $\mathscr{L}_L^{\mathbf{R}}$ et une famille de potentiels $\{V_L\}_{L\geq 1}$ vérifiant les Hypothèses 1–5. Pour simplifier l'énoncé des résultats, on va supposer que le graphe $(\mathscr{L}^{\mathbf{R}}, \mathscr{P})$ où $\mathscr{P}$ est l'ensemble des paires de plus proches voisins est arête-transitif, c'est-à-dire que le groupe G agit transitivement sur les arêtes de $\mathscr{L}^{\mathbf{R}}$. Cette hypothèse supplémentaire n'est pas faite dans le Chapitre 3.

Convergence vers le modèle de liaison forte

Dans cette situation, le modèle de liaison forte associée au réseau $\mathscr{L}^{\mathbf{R}}$ est donné par la matrice $B(\mathbf{k})$, définie par

$$\forall \mathbf{k} \in \Gamma^*, \quad \forall (\mathbf{r}, \mathbf{r}') \in \mathbf{R}^2, \quad B(\mathbf{k})_{\mathbf{r},\mathbf{r}'} = \sum_{\substack{\mathbf{u}\in\mathscr{L} \\ (\mathbf{r},\mathbf{u}+\mathbf{r}')\in\mathscr{P}}} e^{i\mathbf{k}\cdot\mathbf{u}}. \tag{1.38}$$

On note par $\lambda_j(A)$ la j^{e} plus petite valeur propre d'un opérateur linéaire A et par $H_L(\mathbf{k})$ l'opérateur de Bloch associé à l'opérateur périodique $H_L = -\Delta + V_L$. Le principal résultat du Chapitre 3 est le

Théorème 1.5 (Convergence vers le modèle de liaison forte)**.** *Pour $\epsilon > 0$ assez petit et $L \geq 1$ assez grand, on a*

$$\boxed{\lambda_j(H_L(\mathbf{k})) = -\mu_L + \theta_L \lambda_j\left(B(L\mathbf{k})\right) + O\left(e^{-(1+\delta-\epsilon)\sqrt{\mu}d_0 L} + e^{-(1-\epsilon)\sqrt{\mu}d_1 L}\right),} \tag{1.39}$$

où la constante dans le O peut être choisie indépendante de $\mathbf{k} \in \Gamma_L^*$, où $-\mu_L < 0$ est la première valeur propre (indépendante de $\mathbf{r}$) de $-\Delta + \chi_{L,\mathbf{r}}V_L$ et où θ_L est un coefficient d'interaction *défini par*

$$\theta_L := \langle v_{L,\mathbf{r}}, V_L\chi_{L,\mathbf{r}}(1-\chi_{L,\mathbf{r}'})v_{L,\mathbf{r}'}\rangle_{L^2(\mathbb{R}^2)}, \tag{1.40}$$

où $v_{L,\mathbf{r}}$ est la première fonction propre de $-\Delta + \chi_{L,\mathbf{r}}V_L$ et où $\{\mathbf{r}, \mathbf{r}'\} \in \mathscr{P}$ est une paire de plus proches voisins[32].

32. Puisqu'on a supposé le graphe $(\mathscr{L}^{\mathbf{R}}, \mathscr{P})$ arête-transitif, la définition de θ_L ne dépend pas du choix de la paire

Les fonctions propres $v_{L,\mathbf{r}}$ vérifient des estimées exponentielles ponctuelles de la forme

$$\forall \mathbf{x} \in \mathbb{R}^2, \quad \frac{1}{C_\epsilon} e^{-(1+\epsilon)\sqrt{\mu}|\mathbf{x}|} \leq v_{L,\mathbf{r}}(\mathbf{x} + L\mathbf{r}) \leq C_\epsilon e^{-(1-\epsilon)\sqrt{\mu}|\mathbf{x}|} ,$$

indépendante de L grâce à l'Hypothèse 5, ainsi que des estimées intégrales similaires et en norme $H^1(\mathbb{R}^2)$. On en déduit que le coefficient d'interaction θ_L est exponentiellement petit

$$|\theta_L| \leq C'_\epsilon e^{-(1-\epsilon)\sqrt{\mu}d_0 L} . \tag{1.41}$$

Ainsi, le Théorème 1.5 nous dit que si l'ordre de θ_L est donné par le membre de droite dans (1.41), c'est-à-dire s'il existe $c > 0$ et $\delta' > 0$ assez petits tels que

$$|\theta_L| \geq c e^{-(1+\delta')\sqrt{\mu}d_0 L} , \tag{1.42}$$

pour L assez grand alors les N premières bandes de Bloch de H_L convergent uniformément vers le modèle de liaison forte lorsque $L \to \infty$. Montrer que la condition de non-dégénérescence (1.42) est vérifiée semble difficile dans un cadre général comme celui qu'on considère ici. Dans [FLW18], les auteurs sont capables de montrer une estimée similaire à (1.42) mais en considérant une superposition périodique exacte de potentiels atomiques dont les supports sont compacts et disjoints deux à deux.

Un outil important utilisé dans la preuve du Théorème 1.5 est la *méthode de Feshbach-Schur* [BFS98b ; GS20]. Cette méthode, aussi appelée complément de Schur ou réduction de Lyapunov-Schmidt dans d'autres contextes, est utilisée pour réduire la dimension d'un problème par la résolution explicite d'une partie. Pour le confort du lecteur [33], on la rappelle succinctement. On considère deux projecteurs orthogonaux, P et $P^\perp$, sur un espace de Hilbert $\mathcal{H}$ tels que $P + P^\perp = 1$. Soit H un opérateur auto-adjoint sur $\mathcal{H}$ que l'on représente sous la forme d'une matrice par blocs

$$H = \begin{pmatrix} A & C^* \\ C & B \end{pmatrix} ,$$

où $A = PHP$, $B = P^\perp H P^\perp$ et $C = P^\perp H P$. On considère $\lambda \in \mathbb{R}$ dans le spectre discret de H et on suppose que $B - \lambda \geq \epsilon P^\perp$ pour un certain $\epsilon > 0$. Alors, le problème aux valeurs propres $H\psi = \lambda\psi$ est équivalent à

$$\left(A - C^*(B-\lambda)^{-1}C - \lambda\right) P\psi = 0 .$$

On a de plus la relation $P^\perp\psi = -(B-\lambda)^{-1}CP\psi$, ce qui permet de retrouver l'autre composante de ψ. On voit que pour obtenir une approximation du spectre de H, il suffit de choisir un projecteur P de sorte que le spectre de A soit "simple" à approcher et que l'opérateur $C^*(B-E)^{-1}C$ soit "petit".

Dans la preuve du Théorème 1.5, on applique cette méthode à l'opérateur de Bloch $H = H_L(\mathbf{k})$ et, suivant les idées de [Out84 ; FLW18], on choisit P comme le projecteur orthogonal sur l'image par la transformée de Bloch-Floquet du sous-espace engendré par les fonctions propres $v_{L,\mathbf{r}}$ des opérateurs effectif $-\Delta + \chi_{L,\mathbf{r}} V_L$, pour $\mathbf{r} \in \mathscr{L}^{\mathbf{R}}$.

Points de Dirac dans le réseau en nid d'abeilles

Notre preuve du Théorème 1.5 ne fournit pas la dépendance explicite du O de (1.39) quant au pseudo-moment $\mathbf{k} \in \Gamma_L^*$. En particulier, si le modèle de liaison forte (1.38) produit des points de Dirac, le Théorème 1.5 ne permet pas de conclure que ceux-ci ne persistent pas dans la relation de dispersion de H_L pour L grand. Le résultat suivant remédie à cela lorsque $\mathscr{L}^{\mathbf{R}}$ est le réseau du graphène (voir Section 1.1.2 et Figure 1.1a).

Théorème 1.6 (Points de Dirac dans le graphène)**.** *On suppose que $\mathscr{L}^{\mathbf{R}} = \mathscr{L}^H$ est le réseau en nid d'abeilles et que la condition de non-dégénérescence* (1.42) *est satisfaite. Alors, pour L assez*

$\{\mathbf{r}, \mathbf{r}'\} \in \mathscr{P}$ de plus proches voisins. Cette hypothèse n'étant pas fait dans le Chapitre 3, on doit introduire autant de coefficients d'interaction que d'orbites de l'action de G sur $\mathscr{P}$.

33. Qui nous tient à cœur ♡.

grand, la relation de dispersion de H_L présente des points de Dirac entre les deux premières bandes de Bloch et au dessus des sommets de la première zone de Brillouin Γ_L^*.

Ce résultat est prouvé en adaptant les arguments de la preuve du Théorème 1.5, sachant que le groupe de symétrie de $\mathscr{L}^H$ est maintenant entièrement explicité. Aussi, les conclusions du Théorème 1.6 devrait perdurer en remplaçant $\mathscr{L}^H$ par n'importe quel réseau dont on s'attend à ce qu'il présente des points de Dirac, voir par exemple les revues [WBB14 ; Wan+15].

1.3.4 Application : le modèle rHF périodique

On considère maintenant le modèle de Hartree-Fock réduit périodique décrit, dans la Section 1.1.2. On se donne un réseau cristallin $\mathscr{L}^{\mathbf{R}}$ vérifiant l'Hypothèse 2.

On suppose que les particules interagissent à travers l'interaction coulombienne tridimensionnelle $\frac{1}{|\mathbf{x}|}$, dont le noyau périodique est donné par

$$W_L = L^{-1}M' + \sum_{\mathbf{u}\in\mathscr{L}} \left(\frac{1}{|\cdot - L\mathbf{u}|} - \frac{1}{|\Gamma_L|}\int_{\Gamma_L} \frac{\mathrm{d}\mathbf{y}}{|\cdot - L\mathbf{u} - \mathbf{y}|} \right),$$

où $M' \in \mathbb{R}$ est une constante choisie de sorte que $W_L \geq 0$. De la même façon que dans le Chapitre 2, on va supposer que le potentiel extérieur est généré par l'interaction des noyaux situés à chaque sommet de $\mathscr{L}_L^{\mathbf{R}}$ plus un terme correctif qu'on interprète comme un pseudo-potentiel décrivant les électrons de cœur. Ainsi, le potentiel extérieur s'écrit

$$V_L \coloneqq \sum_{\mathbf{r}\in\mathbf{R}} \left(-W_L(\cdot - L\mathbf{r}) + \sum_{\mathbf{u}\in\mathscr{L}} V^{\mathrm{pp}}(\cdot - L(\mathbf{u}+\mathbf{r})) \right), \tag{1.43}$$

où V^{pp} satisfait les mêmes conditions [34] que dans le Chapitre 2. On rappelle que le minimiseur γ_L du modèle rHF périodique satisfait l'équation non linéaire suivante

$$\gamma_L = \mathbb{1}_{(-\infty,\epsilon_L]}\left(-\Delta + V_L^{\mathrm{MF}}\right) \quad \text{où} \quad V_L^{\mathrm{MF}} \coloneqq V_L + \rho_L *_L W_L$$

où la convolution se fait sur Γ_L, où $\rho_L(\mathbf{x}) \coloneqq \gamma_L(\mathbf{x},\mathbf{x})$ et où $\epsilon_L \in \mathbb{R}$ est le niveau de Fermi.

La preuve du résultat suivant utilise des arguments classiques de type concentration-compacité, une méthode due à Lions [Lio84a ; Lio84b].

Théorème 1.7. *La famille $\{V_L^{\mathrm{MF}}\}_{L\geq 1}$ de potentiels de champ moyen vérifie les Hypothèses 1–5 où le potentiel de référence est le potentiel de champ moyen V^{MF} associé au modèle de Hartree mono-atomique (1.28) introduit dans le Chapitre 2.*

Comme conséquence des Théorèmes 1.5, 1.6 et 1.7, on obtient le corollaire suivant.

Corollaire 1.8 (Points de Dirac dans le modèle rHF du graphène)**.** *On suppose que la condition de non-dégénérescence (1.42) est vérifiée. Alors le modèle de rHF du graphène demi-rempli présente des points de Dirac. De plus, le niveau de Fermi coïncide exactement avec le niveau d'intersection des cônes.*

Ce corollaire fournit une condition suffisante, la condition (1.42), pour pouvoir répondre par l'affirmative aux deux questions soulevées dans la Section 1.1.3. Cependant, on a déjà mentionné que cette condition est difficile à vérifier théoriquement et, puisque le coefficient est exponentiellement petit, sa détermination par des méthodes numériques ne doit pas être moins ardue.

1.4 Présentation des résultats du Chapitre 4

Dans ce chapitre, on considère les mêmes modèles et problématiques que dans le Chapitre 3 mais dans le régime opposé, c'est-à-dire celui où les distances entre noyaux sont petites. Plus précisément, on considère le modèle de Hartree-Fock réduit (rHF) périodique avec paramètre de

34. De même que dans le Chapitre 2, on n'a pas cherché à optimiser les hypothèses sur V^{pp}.

longueur $L > 0$, introduit dans les Sections 1.1.2 et 1.3.4, et on se propose d'étudier l'apparition éventuelle de points de Dirac dans le régime où $L \to 0$. Pour simplifier, on ne considérera que le cas du réseau en nid d'abeilles $\mathscr{L}^H = (\mathscr{L} + \mathbf{a}) \cup (\mathscr{L} + \mathbf{b})$ où $\mathscr{L}$ est le réseau triangulaire (voir la Section 1.1.2).

Lorsqu'il n'y a pas de pseudo-potentiel, c'est-à-dire lorsque $V^{\mathrm{pp}} = 0$, une remise à l'échelle montre que ce modèle est équivalent à un problème de minimisation formulé sur un réseau de taille fixée

$$F_L = \inf \left\{ \underline{\mathrm{Tr}}_{\mathscr{L}}(-\Delta) + L \left[-\int_\Gamma W^H \rho_\gamma + \frac{q}{2} D_{\mathrm{per}}(\rho_\gamma, \rho_\gamma) \right] \;\middle|\; \gamma \in \mathcal{S}_{\mathrm{per}} \quad \text{et} \quad \underline{\mathrm{Tr}}_{\mathscr{L}}(\gamma) = N/q \right\}, \tag{1.44}$$

où $W^H := W(\cdot - \mathbf{a}) + W(\cdot - \mathbf{b})$. L'unique minimiseur γ_L de (1.44) est solution de l'équation non linéaire suivante

$$\gamma_L = \mathbb{1}_{(-\infty, \epsilon_L]}\left(H_L^{\mathrm{MF}}\right) \quad \text{où} \quad H_L^{\mathrm{MF}} = -\Delta + L(-W^H + \rho_{\gamma_L} * W) =: -\Delta + L V_L^{\mathrm{MF}}.$$

Il est à noté que le potentiel V_L^{MF} satisfait les hypothèses de symétrie (ii)-(iv) d'un potentiel en nid d'abeilles, tel que défini dans la Section 1.1.2. De cette reformulation, on voit que notre configuration est similaire à celle étudiée par Fefferman et Weinstein dans [FW12]. Les auteurs y considèrent l'opérateur $H_L = -\Delta + LV$ où $V \in \mathcal{C}^\infty_{\mathrm{per}}$ est un potentiel en nid d'abeilles et montrent, par un argument perturbatif, que pour tout $L \neq 0$ suffisamment petit l'opérateur H_L admet des cônes de Dirac si une certaine condition de non-dégénérescence est vérifiée (voir le Théorème 1.2). Dans notre situation, deux choses nous empêchent de directement appliquer leur résultat : premièrement, le potentiel V_L^{MF} dépend de L et deuxièmement, il est singulier.

Une part importante de ce chapitre est consacrée à l'adaptation des arguments de Fefferman et Weinstein pour prendre en compte des potentiels tels que V_L^{MF}. On obtient alors le théorème suivant.

Théorème 1.9 (Points de Dirac dans le régime de faible contraste)**.** *Soit $p \in (1, \infty]$. Pour tout $L \in (-1, 1)$, on considère $V_L \in L^p_{\mathrm{per}}(\Gamma)$. On suppose que pour tout $L \in (-1, 1)$, le potentiel V_L vérifie les hypothèses* (ii)-(iv) *de la Section 1.1.2 et que l'application $L \mapsto V_L \in L^p_{\mathrm{per}}$ est continue en 0. Si la condition*

$$\int_\Gamma V_0(\mathbf{x}) e^{-i(\mathbf{v}_1 + \mathbf{v}_2)\cdot \mathbf{x}} \, \mathrm{d}\mathbf{x} \neq 0, \tag{1.45}$$

est satisfaite alors il existe $L_0 > 0$ tel que, pour tout $L \in (-L_0, L_0) \setminus \{0\}$, l'opérateur $-\Delta + LV_L$ admette des points de Dirac.

Pour appliquer ce résultat au modèle rHF précédemment introduit, on voit qu'il suffit de montrer la continuité du potentiel de champ moyen selon L et de vérifier que la condition de non-dégénérescence (1.45) soit satisfaite par V_0^{MF}. C'est bien le cas, comme l'énonce le théorème qui suit.

Théorème 1.10. *L'application $L \in \mathbb{R}_+ \mapsto \rho_{\gamma_L} * W \in L^p_{\mathrm{per}}(\Gamma)$ est continue. De plus, V_0^{MF} satisfait la condition* (1.45) *: $\widehat{V}_0^{\mathrm{MF}}(\mathbf{v}_1 + \mathbf{v}_2) > 0$. Ainsi, pour tout L assez petit, H_L^{MF} admet des points de Dirac.*

Cependant, on montre aussi que, dans ce régime de faible contraste, il ne peut y avoir d'apparition de fermions de Dirac pour le modèle de graphène demi-rempli. En effet, le niveau de Fermi est strictement en dessous de l'énergie des cônes. Plus précisément, on a le résultat suivant.

Théorème 1.11. *On suppose que $q = 2$. Alors, pour tout L assez petit, on a : $\epsilon_L < \lambda_L$, où λ_L désigne le niveau d'énergie des cônes.*

Cette propriété diffère dans le régime de dissociation où les deux niveaux coïncident. Nécessairement, lorsque le paramètre de longueur L évolue du régime $L \ll 1$ vers le régime $L \gg 1$, une ou plusieurs transitions de phase doivent avoir lieu, selon que le niveau de Fermi ou non avec le niveau d'énergie des cônes.

1.5 Conclusions et perspectives

Dans ce travail de thèse, nous avons étudié des modèles non linéaires issus de la modélisation de systèmes quantiques, moléculaires ou cristallins. Nous nous sommes principalement intéressés à des systèmes bidimensionnels dans la limite où les distances entre les différents noyaux sont grandes. Dans ce régime, on a montré certaines propriétés que l'on retrouve dans les modèles linéaires analogues.

Dans le modèle de Hartree diatomique, on a quantifié avec précision l'effet tunnel entre les deux premiers modes propres. Dans un prochain travail, il serait intéressant d'étudier ce même modèle mais avec un plus grand nombre de noyaux. Dans le cas diatomique considéré dans cette thèse, l'analyse est largement simplifiée du fait de l'invariance par réflexion. On peut donc s'attendre à ce que l'étude de systèmes brisant une telle symétrie soit plus délicate.

Concernant le modèle de Hartree-Fock réduit périodique, on a montré que si une condition (raisonnable) de non-dégénérescence est vérifiée alors les surfaces de dispersion sont données, au premier ordre dans le régime de dissociation, par le modèle de liaison forte. Dans le cas particulier du graphène, on montre que celles-ci admettent des points de Dirac au dessus de chaque sommet de la première zone de Brillouin. De plus, le niveau de Fermi coïncide exactement avec l'énergie où les cônes s'intersectent. Cette dernière propriété n'est pas satisfaite lorsque le paramètre d'échelle est petit, bien que des singularités coniques soient également présentent.

On identifie ainsi deux comportements selon que la distance inter-noyaux est grande ou petite et, nécessairement, un ou plusieurs changements de phase surviennent lorsque celle-ci varie. La question naturelle est alors de savoir dans quelle phase se situe le modèle du graphène avec le paramètre physique $L_{\mathrm{phy}} \simeq 5.36$. Notre approche n'étant pas quantitative, elle ne nous permet pas de conclure sur ce point. On pense qu'il serait intéressant de réaliser des simulations numériques comme première étape vers l'exploration de ce régime intermédiaire.

La question de l'estimation du coefficient d'interaction apparaissant dans la condition de non-dégénérescence reste largement ouverte, et notamment dans le cas du modèle de Hartree-Fock réduit. Sur cette question, on a essayé d'adapter la preuve de l'estimation inférieure du trou spectral du modèle diatomique, sans que les résultats ne soient probants. On pense qu'une nouvelle stratégie de preuve est souhaitable. Des explorations numériques pourraient là-aussi nous éclairer.

Enfin, on pense que les conclusions des Théorèmes 1.5 et 1.6 s'appliquent à d'autres modèles non linéaires et périodiques comme ceux de type Thomas-Fermi [CLL98], ceux de type Hartree [CLL02] ou celui de Hartree-Fock [CLL01 ; GL08] où le terme d'échange n'est pas négligé.

Chapter 2

The diatomic Hartree model at dissociation

This chapter is modified version of the article [Caz22] which has been published in the journal *Nonlinearity.* In the previous version, the statement that the mean-field operator defined in [Caz22, Eq. (9)] admits at least one negative eigenvalue when $d = 2$ was not proved. In this chapter, we change the setting by adding a pseudo-potential which ensures that is the case.

Abstract

We study the Hartree model for two electrons with spin, living in the two-dimensional or three-dimensional space with Coulomb interactions and submitted to the potential induced by two nuclei of charge $+1$. In the limit where the nuclei move away from each other, we show that the two lowest eigenfunctions of the mean-field hamiltonian are asymptotically given by an even, respectively odd, superposition of the minimizer associated with the corresponding Hartree one nucleus model. We then give upper and lower bounds on the exponentially small gap between the first two eigenvalues, due to (nonlinear) quantum tunneling.

Contents

1 Introduction and statement of the main theorem

1.1 Diatomic Hartree model

We consider a neutral diatomic system formed of two electrons and two point nuclei of charge $+1$ located at distance L in $\mathbb{R}^d$ where $d \in \{2, 3\}$. We assume the charges interact through the three-dimensional Coulomb potential $\frac{1}{|x|}$. In addition, we assume that the potential indiced by both nucleus contains a corrective term $V^{\text{pp}} \in \mathcal{C}_c^\infty(\mathbb{R}^d)$, interpreted as a pseudo-potential modeling the behavior of the core electrons. For simplicity, we also assume that V^{pp} is radial. Below, we make another assumption on V^{pp}, see (2.11). Our aim is to study the behavior of the electrons in the Hartree approximation in the limit $L \to \infty$. Without loss of generality, we assume that the two nuclei are located at $\pm\mathbf{x}_L$ where $\mathbf{x}_L = (\frac{L}{2}, 0)$ if $d = 2$ and $\mathbf{x}_L = (\frac{L}{2}, 0, 0)$ if $d = 3$. The potential generated by these nuclei is denoted by

$$V_L(x) := -\left(\frac{1}{|x - \mathbf{x}_L|} + \frac{1}{|x + \mathbf{x}_L|}\right) + V^{\text{pp}}(x - \mathbf{x}_L) + V^{\text{pp}}(x + \mathbf{x}_L)\,. \tag{2.1}$$

The nucleus located at $-\mathbf{x}_L$ (resp. $+\mathbf{x}_L$) will be called the *left* (resp. *right*) nucleus. Figure 2.1 below shows a schematic representation of this setting. When $d = 3$ we recover the usual Coulomb potential for two pointlike charges. In dimension $d = 2$, this potential corresponds to the one generated by a system of nuclei confined to a plane.

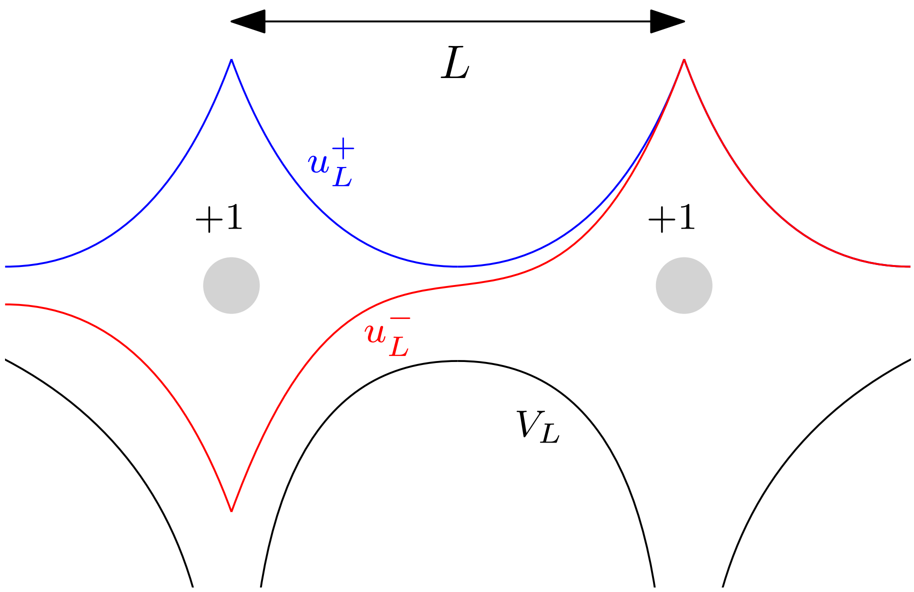


Figure 2.1 – The double well potential. The two nuclei of charge $+1$ are represented by disks colored in gray and the potential V_L by the black curve. The first eigenfunction u_L^+ (resp. the second eigenfunction u_L^-), represented by the blue curve (resp. by the red curve), is approached by an even (resp. odd) superposition of the first eigenfunction of the mono-atomic operator h.

The Hartree energy of the electrons in the state $v \in H^1(\mathbb{R}^d)$ is given by [BBL81; Lie81a]

$$\mathcal{E}_L(v) := \int_{\mathbb{R}^d} |\nabla v(x)|^2 \, \mathrm{d}x + \int_{\mathbb{R}^d} V_L(x)\, |v(x)|^2 \, \mathrm{d}x + \frac{1}{2} \iint_{\mathbb{R}^d \times \mathbb{R}^d} \frac{|v(x)|^2 \, |v(y)|^2}{|x - y|} \, \mathrm{d}x \, \mathrm{d}y + \frac{1}{L}\,. \tag{2.2}$$

We have chosen a system of units such that $\hbar = e = \frac{1}{4\pi\epsilon_0} = 1$ and $m = \frac{1}{2}$ where m and e are respectively the mass and charge of an electron, ϵ_0 is the dielectric permittivity of the vacuum and $\hbar$ is the reduced Planck constant. The first term in (2.2) is the kinetic energy of the two electrons in the state v, the second term its interaction energy with respect to the potential V_L induced by the nuclei at $\pm\mathbf{x}_L$, the third and fourth terms are respectively the self-interaction energy of the charge distribution $|v|^2$ and of the nuclei. The reason we have only one function v as variable is because we look at a singlet state where the anti-symmetry is in the spin. In our setting, the Hartree model consists in minimizing the energy functional $\mathcal{E}_L$ on the set of admissible states

$$\mathcal{P} := \left\{ v \in H^1(\mathbb{R}^d) \;\middle|\; \int_{\mathbb{R}^d} |v|^2 = 2 \right\} .$$

The normalization $\int_{\mathbb{R}^d} |v|^2 = 2$ is because we have two electrons and it ensures the neutrality of the system. It is well known that the functional $v \mapsto \mathcal{E}_L(v)$ is bounded from below and strongly continuous on $\mathcal{P}$ and weakly lower semi-continuous on $\left\{ v \in H^1(\mathbb{R}^d) \;\middle|\; \int_{\mathbb{R}^d} |v|^2 \leq 2 \right\}$ (see [Lie81a, Section VII]). The variational problem corresponding to the Hartree model in consideration reads

$$\boxed{E_L := \frac{1}{2} \inf_{v \in \mathcal{P}} \mathcal{E}_L(v) .} \tag{2.3}$$

The factor $\frac{1}{2}$ is because we compute the energy per electron. It is known (see [Lie81a, Section VII]) that the variational problem (2.3) has a unique positive minimizer u_L^+ which satisfies the Euler-Lagrange equation

$$h_L u_L^+ = \left(-\Delta + V_L + |u_L^+|^2 * |\cdot|^{-1}\right) u_L^+ = \mu_L^+ u_L^+ , \tag{2.4}$$

where μ_L^+ is a Lagrange multiplier and the first eigenvalue of the mean-field hamiltonian h_L. The operator h_L is self-adjoint when defined on the domain $\mathcal{D}(h_L) = H^2(\mathbb{R}^3)$ if $d = 3$ and on

$$\mathcal{D}(h_L) = \left\{ v \in H^1(\mathbb{R}^2) \;\middle|\; (-\Delta + V_L + |u_L^+|^2 * |\cdot|^{-1}) v \in L^2(\mathbb{R}^2) \right\} \tag{2.5}$$

$$= \left\{ v \in H^1(\mathbb{R}^2) \;\middle|\; (-\Delta + V_L) v \in L^2(\mathbb{R}^2) \right\} , \tag{2.6}$$

when $d = 2$. The equality above comes from the fact that $|v|^2 * |\cdot|^{-1}$ belongs to $L^\infty(\mathbb{R}^2)$ whenever $v \in H^1(\mathbb{R}^2)$. By standard arguments [Kat82; RS78], the essential spectrum of h_L is $[0, \infty)$. Below, we will show that, with the additional assumption (2.11) on V^{pp} and L large enough, that μ_L^+ is negative and non-degenerate and, up to a change of phase, we have $u_L^+ > 0$ everywhere on $\mathbb{R}^d$.

Since the nuclei have the same charge and V^{pp} is radial, the model is invariant under reflection with respect to the hyperplane $\{x_1 = 0\}$. To mathematically translate this property, we introduce the reflection operator $\mathcal{R}$, which is the unitary operator defined for all $v \in L^2(\mathbb{R}^d)$ by $\mathcal{R}[v](x) = v(R^* x)$ where

$$R = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \quad \text{if} \quad d = 2 \quad \text{and} \quad R = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \text{if} \quad d = 3 . \tag{2.7}$$

Since $[h_L, \mathcal{R}] = 0$, we can decompose $\mathcal{D}(h_L)$ into an orthogonal sum of two isotypic subspaces, each one carrying irreducible representations of $\mathcal{R}$. As a consequence, we can always choose the eigenfunctions of h_L to be even or odd with respect to the x_1 variable. Since the ground state energy of h_L is non-degenerate, u_L^+ is $\mathcal{R}$-invariant, that is,

$$\mathcal{R}[u_L^+] = u_L^+ .$$

When L is large enough, we will show that h_L admits a second negative eigenvalue $\mu_L^- > \mu_L^+$ and we denote the corresponding eigenstate by u_L^-. We can show that u_L^- is invariant under rotations along the first axis. Up to a change of phase, we can also choose it positive on the half space $\{x_1 > 0\}$ and negative on $\{x_1 < 0\}$.

In the limit where $L \to \infty$, $u_L^\pm$ will split into two bubbles, each of them minimizing the one nucleus Hartree model to leading order, see Figure 2.1. Results of this kind have been shown in the large literature about double well type potentials, see for instance [Har80] in the linear case or [OR21] for a nonlinear model. Our goal will be to prove this in the Coulomb case and determine the behavior of the Lagrange multipliers $\mu_L^\pm$ more precisely.

1.2 Monoatomic Hartree model

Now, we detail the monoatomic Hartree model which will constitute our elementary brick to describe the behavior of $u_L^\pm$ and $\mu_L^\pm$ when L goes to ∞. We introduce the energy functional

$$\mathcal{E}(v) := \int_{\mathbb{R}^d} |\nabla v(x)|^2 \,\mathrm{d}x + \int_{\mathbb{R}^d} \left(-\frac{1}{|x|} + V^{\mathrm{pp}}(x) \right) |v(x)|^2 \,\mathrm{d}x + \frac{1}{2} \iint_{\mathbb{R}^d \times \mathbb{R}^d} \frac{|v(x)|^2 \, |v(y)|^2}{|x-y|} \,\mathrm{d}x \,\mathrm{d}y\,,$$

defined for all $v \in H^1(\mathbb{R}^d)$. The associated minimization problem reads

$$\boxed{I := \inf \left\{ \mathcal{E}(v) \,\middle|\, v \in H^1(\mathbb{R}^d) \quad \text{and} \quad \int_{\mathbb{R}^d} |v|^2 = 1 \right\}.} \tag{2.8}$$

This minimization problem has been extensively studied in the literature, at least in dimension 3 (see for instance [BBL81; Lie81a]). In particular, all the minimizing sequences for (2.8) are precompact in $H^1(\mathbb{R}^d)$ and (2.8) admits a unique minimizer u, up to a phase, which is the unique positive ground state of the self-adjoint operator

$$h := -\Delta + V + |u|^2 * |\cdot|^{-1} \quad \text{where} \quad V := -\frac{1}{|\cdot|} + V^{\mathrm{pp}}\,, \tag{2.9}$$

defined on the domain

$$\mathcal{D}(h) = \left\{ v \in H^1(\mathbb{R}^2) \,\middle|\, (-\Delta - |\cdot|^{-1}) v \in L^2(\mathbb{R}^2) \right\}\,, \tag{2.10}$$

if $d = 2$ and on $H^2(\mathbb{R}^3)$ if $d = 3$. The essential spectrum of h is equal to $[0\,, \infty)$ and we denote by $\mu \leq 0$ its first non-degenerate eigenvalue. Because the energy functional $\mathcal{E}$ is invariant under rotations, u is radial.

Depending on the choice of the pseudo-potential V^{pp}, it may happen that $\mu = 0$. Because having $\mu < 0$ is crucial for our analysis, we make the following assumption

$$\boxed{\text{The pseudo-potential } V^{\mathrm{pp}} \text{ is such that } \mu < 0\,.} \tag{2.11}$$

Remark 2.1 (Assumptions on V^{pp})**.** (i) Such V^{pp} exists. For instance, take $V^{\mathrm{pp}}(x) = -\lambda \mathbb{1}_{|x|\leq 1} * \chi$ with $\lambda \geq 0$ large enough and χ a regularization kernel, see Appendix A. of Chapter 3.

(ii) Assuming $V^{\mathrm{pp}} \in \mathcal{C}_c^\infty(\mathbb{R}^d)$ radial is not necessary but these assumptions make the arguments simpler. Rotation invariance is useful since many terms in the multipole expansion of $|u|^2 * |\cdot|^{-1}$ disappear when u is radial, see Newton's theorem when $d = 3$ and see Lemma 2.41 in the appendix when $d = 2$. Also, we could assume $V \in L^p(\mathbb{R}^d)$ where $p > 1$ if $d = 2$ and $p \geq 3/2$ if $d = 3$ and that V^{pp} decays sufficiently fast without modifying most of the arguments of this chapter.

(iii) When $d = 3$, one can take $V^{\mathrm{pp}} = 0$ [BBL81]. In dimension two, we think it is true but we do not know how to prove it.

1.3 Main result

Now, we can state our main result which provides the leading order when $L \to \infty$ of the ground state u_L^+ and the first excited state u_L^- of the diatomic model (2.3). Those can be expressed as an even or odd superposition of right and left translations of the function u, respectively. Moreover, we give upper and lower exponential bounds on the spectral gap $\mu_L^- - \mu_L^+$ which is our main contribution in this chapter.

Theorem 2.2. *Let $\alpha = 0$ when $d = 3$ and $\alpha > 0$ when $d = 2$. Let $\epsilon > 0$. Then we have*

$$|\mu_L^\pm - \mu| = \begin{cases} O\big(L^{-3+\epsilon}\big) & \text{if } d = 2\,, \\ O(L^{-\infty}) & \text{if } d = 3\,, \end{cases} \tag{2.12}$$

$$\big\|u_L^\pm - (u(\cdot - \mathbf{x}_L) \pm u(\cdot + \mathbf{x}_L))\big\|_{H^{2-\alpha}(\mathbb{R}^d)} = \begin{cases} O\big(L^{-3+\epsilon}\big) & \text{if } d = 2\,, \\ O(L^{-\infty}) & \text{if } d = 3\,. \end{cases} \tag{2.13}$$

When $d = 2$, the constants appearing in the O depend on α and ϵ. The energy E_L satisfies

$$E_L = I + \begin{cases} \big(\frac{3m_1}{4}\big)^2 \frac{1}{L^5} + o\big(\frac{1}{L^5}\big) & \text{if } d = 2\,, \\ O(L^{-\infty}) & \text{if } d = 3\,, \end{cases} \tag{2.14}$$

where the one-electron energy I is defined in (2.8) and $m_1 := \int_{\mathbb{R}^2} |u(x)|^2 |x|^2 \,\mathrm{d}x$ is the second moment of $|u|^2$. Moreover, there exists $C > 0$ such that the following lower and upper exponential bounds on the spectral gap $\mu_L^- - \mu_L^+$ hold

$$\boxed{\frac{1}{C}\frac{e^{-\sqrt{|\mu|}L}}{L^d} \leq \mu_L^- - \mu_L^+ \leq Ce^{-\sqrt{|\mu|}L}\,.} \tag{2.15}$$

In this statement, we have used the notation $O(L^{-\infty})$ to denote a $O\big(L^{-k}\big)$ for all k, where the O may depend on k.

It is well-known that the eigenvalues of a linear Schrödinger operator in a double well tend to group in pairs as the distance between the wells increases [Har80]. The spectral gap between pairs of eigenvalues comes from the tunneling effect between the two wells and its estimation amounts to finding the asymptotics of the corresponding eigenfunctions at infinity, see [Har80; Sim84a]. We refer for instance to [Dau96] where Daumer has precisely quantified the tunneling effect for linear Schrödinger operators with $-\Delta$-compact potentials vanishing at infinity. In dimension 3, this class of potentials contains in particular Coulomb potentials which are physically relevant when one wants to study molecules at dissociation. When the potential is homogeneous of degree -1, the regime where the wells get far apart is equivalent to a semi-classical limit, which has been intensively studied in the 80's. We refer to the series of papers from Helffer and Sjöstrand [HS84; HS85b; HS85a; HS85c; HS86; HS87] and their collaborators [Out84; Moh91; Dau94; Dau96].

To our knowledge, the literature about the tunneling effect emerging from nonlinear models at dissociation seems rather scarce. In [Dau94], using fixed point arguments, Daumer constructed solutions to the Hartree-Fock equations in multiple wells from the ground state of reference monoatomic operators. Nevertheless, the assumptions on the well and interaction potentials are rather restrictive and do not cover Coulomb systems. In [Con83], Conlon studied the Hartree-Fock model where the atomic potentials are assumed to be smooth in the vicinity of the nuclei and with Coulombic behavior at infinity. In the semi-classical regime, the author shows that the exchange energy for the ground state of this system converges toward the Dirac exchange energy of the Thomas-Fermi one-body density. More recently, in a series of papers [RS18; OR21; ORS21], Olgiati, Rougerie and Spehner consider bosonic systems trapped in a symmetric double-well potential in the limit where the distance between the wells increases to infinity and the potential barrier is high. These last works are probably the closest to our and we will use several arguments from [OR21] in this chapter.

In dimension $d = 3$, our model has already been considered by Catto and Lions in [CL93], but in a slightly different context. More specifically, the authors precisely compute the leading order of the energy difference between the diatomic model at dissociation and the two non-interacting monoatomics models. They also give asymptotic estimates on the corresponding ground states but did not considered the spectral gap.

The strategy to prove Theorem 2.2 does not depend on the dimension and combines many arguments already present in the literature. However, many technical issues emerge from the adaptation of these arguments to the nonlinear setting we consider, especially in dimension two.

In dimension three, some are avoided thanks to estimates from [CL93]. More precisely, when $d = 3$, all the estimates are exponentially small when $L \to \infty$ which is a manifestation of Newton's theorem (recall the system is neutral), that is, of the fact that the potential $-|x|^{-1}$ is, up to a constant factor, the Green function of the Laplacian in $\mathbb{R}^3$. That is why we will mainly focus on the more difficult $d = 2$ case and only outline the argument when $d = 3$, giving references whenever it is relevant. When $d = 2$, the multipolar expansion of the potential generated by a radial charge distribution localized in space admits a non zero quadrupole moment (see Lemma 2.41 in Appendix A.). As a consequence, we obtain a polynomial convergence rate for the Lagrange multipliers, the ground state, the first excited state and the energy (see (2.12), (2.13) and (2.14)). The main contribution of this chapter is the estimation (2.15) of the tunneling effect when $d = 2$ in spite of the absence of Newton's theorem. To this end, we use to our advantage the fact that tunneling depends to leading order only on the behavior around the origin of the corresponding eigenfunctions (see Lemma 2.40). We are able to determine the exact exponential decay, but not the polynomial factor. We think one could get rid of the L^{-d} in the left side of (2.15).

1.4 Strategy of proof

We sketch the strategy for the proof of Theorem 2.2. It is convenient to introduce some notation relative to the translated version of the monoatomic model defined in (2.8). We denote by

$$V_L^r := V(\cdot - \mathbf{x}_L)\,, \quad V_L^\ell := V(\cdot + \mathbf{x}_L)\,, \quad u_L^r := u(\cdot - \mathbf{x}_L) \quad \text{and} \quad u_L^\ell := u(\cdot + \mathbf{x}_L)\,, \tag{2.16}$$

the left and right potentials and monoatomic eigenstates. For $\kappa \in \{\ell, r\}$, u_L^κ satisfies the Euler-Lagrange equation

$$\boxed{h_L^\kappa u_L^\kappa := \left(-\Delta + V_L^\kappa + |u_L^\kappa|^2 * |\cdot|^{-1}\right) u_L^\kappa = \mu\, u_L^\kappa\,.} \tag{2.17}$$

First we state regularity properties (see Proposition 2.3, Proposition 2.8 and Remark 2.9) about the eigenfunctions associated with the two mean-field hamiltonians we are interested in. Then, we use the maximum principle (Lemma 2.12 and Lemma 2.13) to establish exponential pointwise and integral bounds on the minimizer u of the monoatomic model (Proposition 2.11). They allow us to estimate interaction terms (Lemma 2.17 and Lemma 2.18) which will appear later on.

Then we show a first convergence result in $H^1(\mathbb{R}^d)-$norm (Proposition 2.19) by inserting the trial function

$$u_{\text{trial}} = \frac{\sqrt{2}(u_L^r + u_L^\ell)}{\left\|u_L^r + u_L^\ell\right\|_{L^2(\mathbb{R}^d)}}\,,$$

into the energy functional $\mathcal{E}_L$ of the diatomic model. The argument uses the precompactness of the minimizing sequence for the monoatomic model. We get the upper bound $E_L \leq \mathcal{E}(u) + o(1)$ from the expansion of the mean-field hamiltonian h (Lemma 2.41). To get the lower bound we localize in the vicinity of the two nuclei. This allows us to show convergence of the Lagrange multiplier (Proposition 2.22)

$$\left|\mu_L^+ - \mu\right| \quad \underset{L\to\infty}{\longrightarrow} \quad 0\,,$$

and convergence in $H^{2-\alpha}(\mathbb{R}^d)-$norm of the eigenfunctions (Proposition 2.24). This finally provides pointwise and integral exponential bounds on u_L^+ (Proposition 2.25).

After that, we will aim at estimating the rates of convergence for both $H^1(\mathbb{R}^d)-$norm errors and for the Lagrange multipliers (Proposition 2.29 and Proposition 2.32). For this purpose, we state a stability result (Proposition 2.26) and we make use of bootstrap-type arguments. We also get similar results for the first excited state u_L^- and its associated Lagrange multiplier μ_L^- (Proposition 2.34). We also show a uniform lower bound on the gap between $\mu_L^\pm$ and the remaining spectrum of h_L (Proposition 2.35).

Then, we give convergence rates in higher Sobolev space (Proposition 2.36). In Proposition 2.37, we give exact pointwise exponential bounds on $u_L^\pm$ at finite but large distance from the nuclei. This allows us to study the spectral gap $\mu_L^- - \mu_L^+$ (Theorem 2.39). By the ground state substitution formula (Lemma 2.40), this spectral gap depends only on the behavior of $u_L^{\pm}$ in the vicinity of the nuclei which is covered by our exponential bound.

1.5 Notations and conventions

We will denote by

$$D(\rho, \mu) := \frac{1}{2} \iint_{\mathbb{R}^d \times \mathbb{R}^d} \frac{\rho(x)\mu(y)}{|x-y|} \, \mathrm{d}x \, \mathrm{d}y \,, \tag{2.18}$$

the d-dimensional *Coulomb interaction energy* between two charge densities ρ and μ whenever it makes sense. This is a non-negative bilinear form [LL01, Theorem 9.8] and, by the Hardy-Littlewood-Sobolev inequality [LL01, Theorem 4.3], it is continuous on $L^{\frac{2d}{2d-1}}(\mathbb{R}^d) \times L^{\frac{2d}{2d-1}}(\mathbb{R}^d)$.

For $R > 0$ and $x \in \mathbb{R}^d$, we denote by $B(x, R)$ the open ball of $\mathbb{R}^d$ centered in x with radius R.

For any $\mathbf{x} \in \mathbb{R}^d$, we introduce the translation operator $\tau_{\mathbf{x}}$ defined for all $v \in L^2(\mathbb{R}^d)$ by

$$\forall x \in \mathbb{R}^d, \ (\tau_{\mathbf{x}} v)(x) = v(x - \mathbf{x}) \,,$$

which is unitary as an operator acting on $L^2(\mathbb{R}^d)$.

In the estimates, the constants can change from line to line. Whenever we consider the exact determination of the constant irrelevant for our purpose, we will drop it, writing $A \lesssim B$ if $A \leq C \cdot B$ for some constant $C > 0$ which is independent from the parameters.

1.6 Organization of the chapter

In Section 2, we show some basic properties of the eigenfunctions of the mean-field hamiltonians h and h_L. In Section 3, we construct quasi-modes for h_L from even or odd superposition of translated versions of u. We also give convergence rates and study the spectral gap $\mu_L^- - \mu_L^+$.

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2 Properties of eigenfunctions

2.1 Regularity away from singularities

In this section, we study the regularity of the eigenfunctions of the mean-field hamiltonians h and h_L. Our first result is that these functions are smooth away from the nuclei. In this section, we assume the existence of the first excited state u_L^- of h_L for L large enough. This will be shown later on (see Proposition 2.32).

Proposition 2.3 (Regularity of eigenfunctions away from the singularities)**.** *Let $d \in \{2, 3\}$. The eigenfunction u belongs to $\mathcal{C}^\infty(\mathbb{R}^d \setminus \{0\})$. The eigenfunctions u_L^+ and u_L^- belong to $\mathcal{C}^\infty(\mathbb{R}^d \setminus \{-\mathbf{x}_L, +\mathbf{x}_L\})$.*

In dimension $d = 3$, this result is fairly standard and it is obtained by bootstrap-type arguments like in [OR21, Lemma 3.2], for instance. In dimension $d = 2$, the analysis is more difficult due to the combination of a singular potential $V \notin L^2_{\mathrm{loc}}(\mathbb{R}^2)$ and the non-local equation

$$\sqrt{-\Delta} \left(| \cdot |^{-1} \right) = 2\pi \delta_0 \,.$$

We start with a technical lemma.

Lemma 2.4. *Let $d \geq 2$. For all $u, v \in H^1(\mathbb{R}^d)$ and all $r \in (d\,,\infty]$, we have*

$$\left\|(uv) * |\cdot|^{-1}\right\|_{L^r(\mathbb{R}^d)} \lesssim \|u\|_{H^1(\mathbb{R}^d)} \|v\|_{H^1(\mathbb{R}^d)} \,. \tag{2.19}$$

Proof. Let $u, v \in H^1(\mathbb{R}^d)$. By Sobolev inequalities, we have the continuous embedding $H^1(\mathbb{R}^d) \subset L^q(\mathbb{R}^d)$ for all $q \in [2\,,\infty)$ if $d = 2$ and for all $q \in [2\,,\frac{2d}{d-2}]$ if $d \geq 3$. Let $r \in (d\,,\infty)$ and denote $p = \frac{dr}{d(r+1)-r} \in (1\,,\frac{d}{d-2})$. Then, by the Hardy-Littlewood-Sobolev inequality and the Cauchy-Schwarz inequality , we have

$$\left\|(uv) * |\cdot|^{-1}\right\|_{L^r(\mathbb{R}^d)} \lesssim \|uv\|_{L^p(\mathbb{R}^d)} \lesssim \|u\|_{L^{2p}(\mathbb{R}^d)} \|v\|_{L^{2p}(\mathbb{R}^d)} \lesssim \|u\|_{H^1(\mathbb{R}^d)} \|v\|_{H^1(\mathbb{R}^d)} \,.$$

This shows inequality (2.19) except for the case $r = \infty$ which cannot be treated this way. To bypass this issue, we write

$$|\cdot|^{-1} = |\cdot|^{-1}\mathbb{1}_{B_1} + |\cdot|^{-1}\mathbb{1}_{B_1^c} \in L^q(\mathbb{R}^d) + L^\infty(\mathbb{R}^d)\,,$$

where $q \in [1\,,d)$ and B_1 denotes the unit ball of $\mathbb{R}^d$. We choose q such that $q' := \frac{q}{q-1} \in (1\,,\frac{d}{d-2})$. Then, we have, using Young's inequality and the Cauchy-Schwarz inequality

$$\begin{aligned}
\left\|(uv) * (|\cdot|^{-1}\mathbb{1}_{B_1}(x))\right\|_{L^\infty(\mathbb{R}^d)} &\lesssim \|uv\|_{L^{q'}(\mathbb{R}^d)} \lesssim \|u\|_{L^{2q'}(\mathbb{R}^d)} \|v\|_{L^{2q'}(\mathbb{R}^d)} \lesssim \|u\|_{H^1(\mathbb{R}^d)} \|v\|_{H^1(\mathbb{R}^d)} \,,\\
\left\|(uv) * (|\cdot|^{-1}\mathbb{1}_{B_1^c}(x))\right\|_{L^\infty(\mathbb{R}^d)} &\lesssim \|uv\|_{L^1(\mathbb{R}^d)} \lesssim \|u\|_{L^2(\mathbb{R}^d)} \|v\|_{L^2(\mathbb{R}^d)} \lesssim \|u\|_{H^1(\mathbb{R}^d)} \|v\|_{H^1(\mathbb{R}^d)} \,.
\end{aligned}$$

This shows inequality (2.19) in the case $r = \infty$. □

Remark 2.5. We cannot have $(uv) * |\cdot|^{-1} \in L^d(\mathbb{R}^d)$ for all $u, v \in H^1(\mathbb{R}^d)$. Indeed, the first order of the large $|x|$ behavior of the convolution $|u|^2 * |\cdot|^{-1}$ is given by $\|u\|^2_{L^2(\mathbb{R}^d)} |x|^{-1}$ which is not in $L^d(\mathbb{R}^d)$ whenever $u \neq 0$.

Lemma 2.6 (Local fractional elliptic regularity)**.** *Let $u \in H^r_{\mathrm{loc}}(\mathbb{R}^2 \setminus \{0\}) \cap L^2(\mathbb{R}^2)$ for some integer $r \geq 1$. Then $|u|^2 * |\cdot|^{-1} \in H^{r-1}_{\mathrm{loc}}(\mathbb{R}^2 \setminus \{0\})$.*

Proof. Let Ω be an open and relatively compact subset of $\mathbb{R}^2 \setminus \{0\}$. Let $\alpha \in \mathbb{N}^2$ such that $|\alpha| \leq r-1$. We will show that $\partial^\alpha(|u|^2 * |\cdot|^{-1}) \in L^2(\Omega)$. Let $\delta > 0$ such that $0 \notin \Omega + B(0,\delta)$. Let $\chi \in \mathcal{C}^\infty_c(\mathbb{R}^2)$ be such that

$$0 \leq \chi \leq 1, \quad \chi \equiv 1 \text{ on } \Omega + B(0,\delta/2) \quad \text{and} \quad \chi \equiv 0 \text{ on } \Omega + B(0,\delta)\,.$$

Let η be such that $\chi^2 + \eta^2 = 1$. We have $\partial^\alpha(|\chi u|^2 * |\cdot|^{-1}) = (\partial^\alpha |\chi u|^2) * |\cdot|^{-1}$ in $\mathcal{D}'(\mathbb{R}^2)$. Moreover, because $u \in H^r_{\mathrm{loc}}(\mathbb{R}^2 \setminus \{0\})$, we see that $\partial^\alpha |\chi u|^2$ is a finite sum of products of two $H^1(\mathbb{R}^2)$ functions. By Lemma 2.4, this implies that $\partial^\alpha(|\chi u|^2 * |\cdot|^{-1}) \in L^\infty(\mathbb{R}^2) \subset L^2(\Omega)$. Because the function $\partial^\alpha |x-y|^{-1}$ is bounded when $x \in \Omega$ and $y \in \operatorname{supp}\eta$, we have $\partial^\alpha(|\eta u|^2 * |\cdot|^{-1}) = |\eta u|^2 * \left(\partial^\alpha |\cdot|^{-1}\right)$ in $\mathcal{D}'(\Omega)$. Finally, because the support of η is localized away from Ω and because $u \in L^2(\mathbb{R}^2)$, we have $|\eta u|^2 * \left(\partial^\alpha |\cdot|^{-1}\right) \in L^\infty(\Omega) \subset L^2(\Omega)$. □

Remark 2.7. The same result holds with the same proof when $\mathbb{R}^2 \setminus \{0\}$ is replaced by any open set of $\mathbb{R}^2$. For instance, we can take $\mathbb{R}^2 \setminus \{\pm \mathbf{x}_L\}$.

Proof of Proposition 2.3. We treat the two-dimensional case for u and only mention the changes for $d = 3$. For $u_L^\pm$, the proof is the same so we do not write it . Let $\Omega \subset \mathbb{R}^2 \setminus \{0\}$ be an open and relatively compact set of $\mathbb{R}^2 \setminus \{0\}$. We denote

$$W(u) = |u|^2 * |\cdot|^{-1} \quad \text{and} \quad \tilde{V}(x) = -|x|^{-1} + V^{\mathrm{pp}}(x) - \mu\,,$$

which are locally essentially bounded in Ω. This is obvious for $\tilde{V}$ and a consequence of Lemma 2.4 for $W(u)$. We recall that u is solution, in the sense of distribution, of the strictly elliptic partial differential equation

$$-\Delta u + W(u)u + \tilde{V}u = 0\,. \tag{2.20}$$

As a consequence, u is also a weak solution in $H^1(\Omega)$ (in the sense of [GT01, Chapter 8]) of the same equation. By [GT01, Theorem 8.8], this implies that $u \in H^2(\Omega)$. Thus, we have $u \in H^2_{\mathrm{loc}}(\mathbb{R}^2 \setminus \{0\})$.

To complete the proof, we use a bootstrap type argument. Assume that $u \in H^r_{\mathrm{loc}}(\mathbb{R}^2 \setminus \{0\})$ for some integer $r \geq 2$. By Lemma 2.6, this implies that $W(u) \in H^{r-1}_{\mathrm{loc}}(\mathbb{R}^2 \setminus \{0\})$. By Theorem 1 of [RS96, Section 4.3], for all open and bounded set $\Omega \subset \mathbb{R}^2 \setminus \{0\}$ with smooth boundary, for all $(f, g) \in H^{s_1}(\Omega) \times H^{s_2}(\Omega)$, we have

$$\|fg\|_{H^s(\Omega)} \lesssim \|f\|_{H^{s_1}(\Omega)} \|g\|_{H^{s_2}(\Omega)} , \tag{2.21}$$

provided that $s_i \geq s \geq 0$ for all $i \in \{1, 2\}$ and $s_1 + s_2 > s + 1$. In particular, $u \in H^r_{\mathrm{loc}}(\mathbb{R}^2 \setminus \{0\})$ and $W(u) \in H^{r-1}_{\mathrm{loc}}(\mathbb{R}^2 \setminus \{0\})$ imply $W(u)u \in H^{r-1}_{\mathrm{loc}}(\mathbb{R}^2 \setminus \{0\})$. Let $\chi \in \mathcal{C}^\infty_c(\mathbb{R}^2)$ be a localization function such that

$$\operatorname{supp}\chi \subset \mathbb{R}^2 \setminus \{0\} \quad \text{and} \quad \chi \equiv 1 \quad \text{on} \quad K ,$$

where $K \subset \mathbb{R}^2 \setminus \{0\}$ is a compact set. Multiplying (2.20) by χ, we find

$$-\Delta(\chi u) = -(\Delta\chi + \chi\tilde{V})u - \chi W(u)u - 2\nabla\chi \cdot \nabla u .$$

The first term on the right hand side belongs to $H^r(\mathbb{R}^2)$ and the last two terms are in $H^{r-1}(\mathbb{R}^2)$. This shows that $\chi u \in H^{r+1}(\mathbb{R}^2)$. As a consequence $u \in H^{r+1}_{\mathrm{loc}}(\mathbb{R}^2 \setminus \{0\})$. By induction, $u \in H^r_{\mathrm{loc}}(\mathbb{R}^2 \setminus \{0\})$ for all $r \geq 0$ and, by the Sobolev embeddings, this shows that $u \in \mathcal{C}^\infty(\mathbb{R}^2 \setminus \{0\})$.

The easier case $d = 3$ is treated similarly, replacing Lemma 2.6 by the usual elliptic regularity for solutions of the Laplace equation $-\Delta u = f$ in $\mathbb{R}^3$. □

2.2 Regularity around singularities

In the sequel, $\mathcal{C}^{\ell,\theta}_0(\mathbb{R}^d)$ denotes the space of $\mathcal{C}^\ell(\mathbb{R}^d)$ functions which vanish at infinity as well as their first ℓ derivatives and such that the derivatives of order ℓ are Hölder continuous with exponent θ. In dimension 3, Sobolev embeddings give that $u \in H^2(\mathbb{R}^3) \subset \mathcal{C}^{0,1/2}_0(\mathbb{R}^3)$. Hence the eigenfunctions $u^\pm_L$ and u are continuous (even Hölder) in the vicinity of the singularities. In dimension 2, because $|\cdot|^{-1} \notin L^2_{\mathrm{loc}}(\mathbb{R}^2)$, the mean-field hamiltonians h and h_L are not self-adjoint on $H^2(\mathbb{R}^2)$ but on the domains $\mathcal{D}(h)$ or $\mathcal{D}(h_L)$ (see (2.10) and (2.5)). In the next proposition, we study the structure of $\mathcal{D}(h)$.

Proposition 2.8 (Regularity around singularities)**.** *Let $\alpha \in (0, 2)$ if $d = 2$ and $\alpha = 0$ if $d = 3$. Let $\epsilon > 0$. Then there exists constants $C(\epsilon)$ and $C(\epsilon, \alpha)$ such that for all $v \in \mathcal{D}(h)$ we have*

$$\|v\|_{H^{2-\alpha}(\mathbb{R}^d)} \leq \begin{cases} \epsilon \|hv\|_{L^2(\mathbb{R}^d)} + C(\epsilon, \alpha) \|v\|_{L^2(\mathbb{R}^d)} & \text{if } d = 2 , \\ (1 + \epsilon) \|hv\|_{L^2(\mathbb{R}^d)} + C(\epsilon) \|v\|_{L^2(\mathbb{R}^d)} & \text{if } d = 3 . \end{cases}$$

In particular, we have $\mathcal{D}(h) \subset H^{2-\alpha}(\mathbb{R}^d)$ with continuous embedding.

Remark 2.9. (i) The conclusions of Proposition 2.8 also hold for h_L but, in that case, the proof needs uniform bounds on $\left\| |u^+_L|^2 * |\cdot|^{-1} \right\|_{L^\infty(\mathbb{R}^d)}$ (see Remark 2.21).

(ii) Sobolev inequalities give the continuous inclusion $H^{2-\alpha}(\mathbb{R}^2) \subset \mathcal{C}^{0,1-\alpha}_0(\mathbb{R}^2)$ for $\alpha < 1$. Hence the eigenfunctions of the mean-field hamiltonians are Hölder with parameter $1 - \alpha$ for any $\alpha \in (0, 1)$ in the vicinity of the nuclei.

(iii) Because $|\cdot|^{-1} \notin L^2_{\mathrm{loc}}(\mathbb{R}^2)$, we cannot have $\mathcal{D}(h) \subset H^2(\mathbb{R}^2)$. Otherwise, for all $v \in \mathcal{D}(h)$, we would have $v/|\cdot| \in L^2(\mathbb{R}^2)$. Similar remarks hold for h^ℓ_L, h^r_L and h_L.

Now, we write the proof of Proposition 2.8. We start with a lemma.

Lemma 2.10. *Let $\alpha \in (0, \frac{1}{2})$. The operator $(-\Delta)^{-\alpha} |x|^{-1} (-\Delta)^{-\frac{1}{2}+\alpha}$ acting on $L^2(\mathbb{R}^2)$ is bounded:*

$$\left\| (-\Delta)^{-\alpha} |x|^{-1} (-\Delta)^{-\frac{1}{2}+\alpha} \right\| \leq C_\alpha , \tag{2.22}$$

for some constant $C_\alpha > 0$.

Proof. By [Sim15, Theorem 6.2.2] (Stein-Weiss inequality) and the remark which follows, the operators $(-\Delta)^{-\beta/2}|x|^{-\beta}$ and $|x|^{-\beta}(-\Delta)^{-\beta/2}$ acting on $L^2(\mathbb{R}^2)$ are bounded for all $\beta \in (0,1)$. It remains to write

$$(-\Delta)^{-\alpha}|x|^{-1}(-\Delta)^{-\frac{1}{2}+\alpha} = (-\Delta)^{-\alpha}|x|^{-2\alpha}|x|^{-1+2\alpha}(-\Delta)^{-\frac{1}{2}+\alpha},$$

to conclude the proof of Lemma 2.10. ☐

Proof of Proposition 2.8. When $d = 3$, Proposition 2.8 is a consequence of the fact that for all $\epsilon > 0$ there exists $C_\epsilon > 0$ such that for all $v \in H^2(\mathbb{R}^3)$ we have (see for instance [RS75, Theorem X.19])

$$\left\| \frac{v}{|\cdot|} \right\|_{L^2(\mathbb{R}^3)} \leq \epsilon \|v\|_{H^2(\mathbb{R}^3)} + C_\epsilon \|v\|_{L^2(\mathbb{R}^3)}.$$

Now, we turn our attention to the two-dimensional case. We write the proof for h in detail and we point out the changes necessary to handle h_L. First, we express the inverse of $-\Delta - |x|^{-1}$ in terms of Neumann series when $\nu > 0$ large enough. We write

$$(-\Delta - |x|^{-1} + \nu) = (-\Delta+\nu)^{1/2}\left(1 - (-\Delta+\nu)^{-1/2}|x|^{-1}(-\Delta+\nu)^{-1/2}\right)(-\Delta+\nu)^{1/2}.$$

Using Lemma 2.10 with the estimates $\left\|\left(\frac{-\Delta}{-\Delta+\nu}\right)^{1/4}\right\| \leq 1$ and $\left\|\left(\frac{1}{-\Delta+\nu}\right)^{1/4}\right\| \leq \nu^{-1/4}$ we obtain

$$\begin{aligned}
&\left\|(-\Delta+\nu)^{-1/2}|x|^{-1}(-\Delta+\nu)^{-1/2}\right\| \\
&= \left\|(-\Delta+\nu)^{-1/4}\left(\frac{-\Delta}{-\Delta+\nu}\right)^{1/4}(-\Delta)^{-1/4}|x|^{-1}(-\Delta)^{-1/4}\left(\frac{-\Delta}{-\Delta+\nu}\right)^{1/4}(-\Delta+\nu)^{-1/4}\right\| \\
&\leq C_{1/4}\nu^{-1/2}.
\end{aligned}$$

If we choose $\nu > C_{1/4}^2$ then the operator $1 - (-\Delta+\nu)^{-1/2}|x|^{-1}(-\Delta+\nu)^{-1/2}$ is invertible and its inverse is given by a Neumann series. Thus we have

$$(-\Delta - |x|^{-1} + \nu)^{-1} = (-\Delta+\nu)^{-1/2}\sum_{n\geq 0}\left[(-\Delta+\nu)^{-1/2}|x|^{-1}(-\Delta+\nu)^{-1/2}\right]^n(-\Delta+\nu)^{-1/2}.$$

Let $\alpha \in (0, \frac{1}{2})$. We have

$$\begin{aligned}
&(-\Delta+1)^{1-\alpha}(-\Delta - |x|^{-1} + \nu)^{-1} \\
&= \left(\frac{-\Delta+1}{-\Delta+\nu}\right)^{1-\alpha}(-\Delta+\nu)^{1/2-\alpha}\sum_{n\geq 0}\left[(-\Delta+\nu)^{-1/2}|x|^{-1}(-\Delta+\nu)^{-1/2}\right]^n(-\Delta+\nu)^{-1/2}.
\end{aligned} \tag{2.23}$$

By functional calculus, we have $\left\|\left((-\Delta+1)(-\Delta+\nu)^{-1}\right)^{1-\alpha}\right\| \leq 1$ if we take $\nu > \max(1, C_{1/4}^2)$. The term of order n in (2.23) is estimated by writing

$$\begin{aligned}
&(-\Delta+\nu)^{1/2-\alpha}\left[(-\Delta+\nu)^{-1/2}|x|^{-1}(-\Delta+\nu)^{-1/2}\right]^n(-\Delta+\nu)^{-1/2} \\
&\qquad = \left[(-\Delta+\nu)^{-\alpha}|x|^{-1}(-\Delta+\nu)^{-1/2+\alpha}(-\Delta+\nu)^{-1/2}\right]^n(-\Delta+\nu)^{-\alpha}.
\end{aligned}$$

Then, using n times Lemma 2.10 and the estimate $\left\|(-\Delta+\nu)^{-\beta}\right\| \leq \nu^{-\beta}$ for any $\beta > 0$, we have

$$\left\|\left[(-\Delta+\nu)^{-\alpha}|x|^{-1}(-\Delta+\nu)^{-1/2+\alpha}(-\Delta+\nu)^{-1/2}\right]^n(-\Delta+\nu)^{-1/2-\alpha}\right\| \leq \nu^{-\alpha}\left(\frac{C_\alpha}{\sqrt{\nu}}\right)^n,$$

where C_α is the constant appearing in Lemma 2.10. Inserting this into (2.23), we obtain

$$\left\|(-\Delta+1)^{1-\alpha}(-\Delta-|x|^{-1}+\nu)^{-1}\right\| \leq 2\nu^{-\alpha}\,,$$

for $\nu > \max(1, C_{1/4}^2, 4C_\alpha^2)$. If in addition we assume $\nu \geq (2/\epsilon)^{1/\alpha}$ then we have

$$\|v\|_{H^{2-2\alpha}(\mathbb{R}^2)} \leq \epsilon\,\|hv\|_{L^2(\mathbb{R}^2)} + \left(\nu + \|V^{\mathrm{pp}}\|_{L^\infty(\mathbb{R}^2)} + \left\||u|^2 * |\cdot|^{-1}\right\|_{L^\infty(\mathbb{R}^2)}\right)\|v\|_{L^2(\mathbb{R}^2)}\,,$$

for all $v \in \mathcal{D}(h)$. We conclude the proof by noticing that $|u|^2 * |\cdot|^{-1} \in L^\infty(\mathbb{R}^2)$ by Lemma 2.4. $\square$

2.3 Exponential decay of u

In this section, we give the precise long-range behavior of the minimizer u of the monoatomic problem (2.8). In particular, u decays exponentially fast at infinity. We will treat both the two and three-dimensional cases. However, in dimension 3, more precise results have already been obtained by Catto and Lions in [CL93, Appendix 2 & 3]. The main result of this section is the following proposition.

Proposition 2.11 (Exponential bounds on u)**.** *Let $d \in \{2,3\}$. There exists a constant $C>0$ such that we have for all $x \in \mathbb{R}^d$ the pointwise exponential estimates*

$$\frac{1}{C}\frac{e^{-|\mu|^{\frac12}|x|}}{1+|x|^{\frac{d-1}{2}}} \leq u(x) \leq C\frac{e^{-|\mu|^{\frac12}|x|}}{1+|x|^{\frac{d-1}{2}}} \quad \text{and} \quad |\nabla u(x)| \leq C\frac{e^{-|\mu|^{\frac12}|x|}}{1+|x|^{\frac{d-1}{2}}}\,, \tag{2.24}$$

and such that for all $R>0$ we have the integral exponential estimate

$$\int_{|x|>R}|u(x)|^2\,\mathrm{d}x + \int_{|x|>R}|\nabla u(x)|^2\,\mathrm{d}x \leq Ce^{-2|\mu|^{\frac12}R}\,. \tag{2.25}$$

In addition, for all $\epsilon \in (0\,,1)$ there exists a constant $C_\epsilon > 0$ such that

$$\|u\|_{H^{2-\alpha}(B(0,R)^c)} \leq Ce^{-(1-\epsilon)\sqrt{|\mu|R}}\,. \tag{2.26}$$

We could also give non optimal exponential bounds on $u_L^\pm$. However, as we do not yet have any information about the eigenvalues of the mean-field hamiltonian h_L, we prefer to postpone this analysis to another section.

The first step will be an easy and non optimal estimate on the decay of u which will allow us to obtain some information about the behavior at infinity of the mean-field potential associated with the monoatomic model (2.8), denoted by

$$V^{\mathrm{MF}} := -|\cdot|^{-1} + V^{\mathrm{pp}} + |u|^2 * |\cdot|^{-1}\,. \tag{2.27}$$

Then, a finer analysis will give the optimal exponential decay rate.

We recall two fundamental comparison lemmas ([Agm85, Corollary 2.8] and [Hof80, Theorem 1.1]) which will be useful in the sequel. We will use the first one for the upper bounds in (2.24) and the second one for the lower bound.

Lemma 2.12 (First comparison lemma [Agm85])**.** *Let $d \in \mathbb{N}$ and $p > d/2$. Let $W \in L^p_{\mathrm{loc}}(\mathbb{R}^d)$ be real-valued and satisfying the condition: there exists $\theta \in (0\,,1)$ and $C>0$ such that*

$$\int_{\mathbb{R}^d} W_-\,|\varphi|^2 \leq \theta\int_{\mathbb{R}^d}|\nabla\varphi|^2 + C\int_{\mathbb{R}^d}|\varphi|^2\,, \quad \forall\varphi \in \mathcal{C}_0^\infty(\mathbb{R}^d)\,,$$

where $W_- \geq 0$ denotes the negative part of W. Let ψ be an eigenfunction of $P = -\Delta + W$ with eigenvalue λ. Let φ be a positive and continuous supersolution of the equation $(P-\lambda)\phi = 0$ in the *region $\{|x| \geq R\}$. Then there exists a constant $C = C(R)$ such that*

$$\forall\, |x| \geq R+1,\ |\psi(x)| \leq C\varphi(x)\,.$$

Lemma 2.13 (Second comparison lemma [Hof80]). *Let $d \in \mathbb{N}$ and $\Omega \subset \mathbb{R}^d$ be an open set. Let W_1 and W_2 two potentials in $L^1_{\mathrm{loc}}(\Omega)$ such that $W_2 \geq W_1 \geq 0$ in Ω. Let ψ and φ such that :*

(i) $\psi, \varphi \in \mathcal{C}^0(\overline{\Omega})$, $\psi, \varphi \geq 0$ a.e in Ω and $\varphi, \psi \to 0$ as $|x| \to \infty$ if Ω is unbounded;

(ii) $\psi \geq \varphi$ on $\partial\Omega$;

(iii) $W_1\psi \geq \Delta\psi$ and $W_2\varphi \leq \Delta\varphi$ in the sense of distribution.

Then, we have $\psi \geq \varphi$ in Ω.

We begin by proving the following *a priori* exponential bound on u.

Lemma 2.14 (*A priori* pointwise exponential bound on u). *Let $d \in \{2,3\}$. Let u be the minimizer of (2.8). Then, for all $\epsilon > 0$ there exists a constant $C_\epsilon > 0$ such that the following pointwise estimate holds*

$$\forall x \in \mathbb{R}^d,\ 0 \leq u(x) \leq C_\epsilon e^{-\sqrt{|\mu|-\epsilon}|x|}\,. \tag{2.28}$$

Proof. Recall that $h = -\Delta - |\cdot|^{-1} + V^{\mathrm{pp}} + |u|^2 * |\cdot|^{-1}$ is the mean-field hamiltonian associated with the minimization problem (2.8) and that $\mu < 0$ is the first eigenvalue of h. Recall also that $V^{\mathrm{pp}} \in L^\infty(\mathbb{R}^d)$ is compactly supported.

Let $\gamma > 0$ and $f(x) = \exp(-\gamma\,|x|)$. We shall prove that f is a supersolution associated with the eigenvalue problem $(h-\mu)u = 0$ in the domain $|x| > R$ for R large enough and γ well-chosen. We have : $\Delta f(x) = f(x)(\gamma^2 - \gamma(d-1)\,|x|^{-1})$. Then, for all $x \notin \operatorname{supp} V^{\mathrm{pp}} \cup \{0\}$, we have

$$(h-\mu)f(x) = f(x)\left(-\gamma^2 + (\gamma(d-1)-1)\,|x|^{-1} + |u|^2 * |\cdot|^{-1} + |\mu|\right) \geq f(x)\left(-\gamma^2 + |\mu| - |x|^{-1}\right).$$

If we choose $\gamma = \sqrt{|\mu| - \epsilon}$ for some $0 < \epsilon < |\mu|$ then f is a supersolution for $h - \mu$ on the domain $|x| > \epsilon^{-1}$. By the first comparison Lemma 2.12, we conclude that for all $|x| > \epsilon^{-1} + 1$, we have the pointwise estimate (2.28). We extend this estimate to $\mathbb{R}^d$ by using the continuity of u on $\mathbb{R}^d$ (see Remark 2.9). ☐

Now, we study the behavior of V^{MF} at infinity. Notice that since u is radial, this is also the case for V^{MF}.

Lemma 2.15 (Long range behavior of V^{MF}). *For any $\epsilon > 0$ there exists $c_\epsilon > 0$ such that for all $|x|$ large enough*

$$-c_\epsilon e^{-\sqrt{|\mu|-\epsilon}|x|} \leq V^{\mathrm{MF}}(x) \leq 0 \quad \text{if} \quad d = 3\,, \tag{2.29}$$

$$V^{\mathrm{MF}}(x) = \frac{m_1}{4\,|x|^3} + \frac{9m_2}{64\,|x|^5} + O\left(\frac{1}{|x|^7}\right) \quad \text{if} \quad d = 2\,, \tag{2.30}$$

where $m_1 = \int_{\mathbb{R}^2} |u(x)|^2\,|x|^2\,\mathrm{d}x$ and $m_2 = \int_{\mathbb{R}^2} |u(x)|^2\,|x|^4\,\mathrm{d}x$.

Proof. In dimension 3, Newton's theorem gives the equality (recall that $\int |u|^2 = 1$)

$$\forall x \in \mathbb{R}^3,\ (|u|^2 * |\cdot|^{-1})(x) = \int_{\mathbb{R}^3} |u(y)|^2\,\frac{1}{\max(|x|\,,|y|)}\,\mathrm{d}y = \frac{1}{|x|} - \int_{|y|\geq|x|}\left(\frac{1}{|x|} - \frac{1}{|y|}\right)|u(y)|^2\,\mathrm{d}y\,.$$

Recalling Lemma 2.14, we get the estimate (2.29).

In the two-dimensional case, Newton's theorem does not apply since $|\cdot|^{-1}$ is not the Green function of the Laplace operator. The multipole expansion of the potential induced by $|u|^2$ produces non-negative odd order terms. In Appendix A., we prove the expansion

$$(|u|^2 * |\cdot|^{-1})(x) = \frac{1}{|x|} + \frac{m_1}{4\,|x|^3} + \frac{9m_2}{64\,|x|^5} + O\left(\frac{1}{|x|^7}\right), \tag{2.31}$$

as $|x| \to \infty$. Expansion (2.30) is a direct consequence of (2.31) and of the definition of V^{MF}. $\square$

Before proving Proposition 2.11, we state a technical lemma whose proof is given in Appendix Appendix B..

Lemma 2.16. *Let $d \in \{2,3\}$. Let $\nu, k > 0$ and $v : \mathbb{R}^d \to \mathbb{R}$ a radial function satisfying the pointwise exponential estimate*

$$\forall x \in \mathbb{R}^d, \quad |v(x)| \leq C \frac{e^{-\nu|x|}}{1+|x|^k},$$

for some constant $C > 0$. Then there exists a constant $C' > 0$ such that for $x \in \mathbb{R}^d$, we have the pointwise estimates

$$|(v * v)(x)| \leq C' \frac{e^{-\nu|x|}}{1+|x|^{k+1-d}} \quad \text{and} \quad \left| \left(v * \frac{v}{|\cdot|} \right)(x) \right| \leq C' \frac{e^{-\nu|x|}}{1+|x|^{k+\frac{3}{2}-d}}. \tag{2.32}$$

The $d = 3$ case of this lemma will not be employed in the proof of Proposition 2.11 but will be of later use, especially when we will compute interaction terms in Lemma 2.17. Now, we are able to prove Proposition 2.11.

Proof of Proposition 2.11. We focus on the two-dimensional case. The argument is inspired by the proof of [GLN21, Lemma 19]. We begin with the proof of the first part of (2.24). By (2.30), we can choose $R > 0$ large enough in order to have for all $|x| \geq R$

$$0 \leq |x|^3 V^{\mathrm{MF}}(x) \leq c,$$

for some constant $c > 0$. We recall that the modified Bessel function K_α of the second kind with parameter $\alpha \in \mathbb{R}$ solves the ordinary differential equation

$$r^2 K_\alpha''(r) + r K_\alpha'(r) - (r^2 + \alpha^2) K_\alpha(r) = 0,$$

and satisfies the asymptotic $K_\alpha(r) \sim \sqrt{\frac{\pi}{2r}} e^{-r}$, see for instance [AS64, Eq. 9.7.2]. This exponential decay is independent of the parameter α. Let $\epsilon \geq 0$. The function $Y_\epsilon(x) := K_\epsilon(|\mu|^{1/2} |x|)$ satisfies the equation

$$\left(-\Delta + \frac{\epsilon}{|x|^2} - \mu \right) Y_\epsilon = 0,$$

in the region $|x| \geq R$. By the first comparison Lemma 2.12, as $V^{\mathrm{MF}} \geq 0$ in the region $|x| \geq R$, we have $u(x) \leq \overline{C} Y_0(x)$ for all $|x| \geq R$ and some constant $\overline{C}$. For the lower bound, we choose $\epsilon > 0$, $R \geq \frac{c_2}{\epsilon}$ and a constant $\underline{C} > 0$ such that $\underline{C} Y_\epsilon(x) \leq u(x)$ for all $|x| = R$. Then we invoke the second comparison Lemma 2.13, remarking that $u(x) \to 0$ as $|x| \to \infty$ by the upper bound, to get $\underline{C} Y_\epsilon(x) \leq u(x)$ for all $|x| \geq R$. To obtain the first bound in (2.24), it remains to use the asymptotics for the modified Bessel functions and to remark that u is positive and continuous on $\mathbb{R}^2$ (see Remark 2.9).

To get the pointwise estimates concerning $|\nabla u|$, we introduce the Yukawa potential $\tilde{Y}$ which solves in the sense of distribution the equation

$$(-\Delta - \mu)\tilde{Y} = \delta_0,$$

where δ_0 denotes the Dirac distribution on 0. Then, the Euler-Lagrange equation satisfied by u is equivalent to

$$u = -(-\Delta - \mu)^{-1} \left(V^{\mathrm{MF}} u \right) = -\tilde{Y} * \left(V^{\mathrm{MF}} u \right).$$

This implies

$$|\nabla u| \leq \left| \nabla \tilde{Y} \right| * \left| V^{\mathrm{MF}} u \right|.$$

By [LL01, Theorem 6.23], we can deduce that $\left| \nabla \tilde{Y} \right|$ is integrable in a neighborhood of the origin and behaves like $\tilde{Y}(x) = O(u(x))$ at infinity. Moreover, by Lemma 2.4 and the fact $u \in H^1(\mathbb{R}^2)$, we have $|u|^2 * |\cdot|^{-1} \in L^\infty(\mathbb{R}^2)$. Hence, we have

$$|\nabla u| \lesssim u * \left(|\cdot|^{-1}u + u\right)$$

Then, the second part of (2.24) follows immediately from Lemma 2.16. The integral exponential decay estimates (2.25) follows from the pointwise ones.

Now, we show (2.26). Let $R > 0$ and $\epsilon \in (0\,, R)$. Let $\chi \in \mathcal{C}^\infty(\mathbb{R}^d)$ a cutoff function such that

$$\begin{gathered}\chi \in W^{1,\infty}(\mathbb{R}^d)\,, \quad 0 \le \chi \le 1\,, \quad \chi \equiv 1 \quad \text{on} \quad \{|x| \ge R\}\,,\\ \operatorname{supp}\chi \subset B(0, R-\epsilon) \quad \text{and} \quad \operatorname{supp}\nabla\chi \subset B(0,R) \setminus B(0, R-\epsilon)\,.\end{gathered}$$

Let $\alpha = 0$ if $d = 3$ and $\alpha \in (0\,, 1)$ if $d = 2$. By Proposition 2.8, we have

$$\begin{aligned}\|u\|_{H^{2-\alpha}(B(0,R)^c)} &\le \|\chi u\|_{H^{2-\alpha}(\mathbb{R}^d)} \le \|h\chi u\|_{L^2(\mathbb{R}^d)} + C\,\|\chi u\|_{L^2(\mathbb{R}^d)}\\ &\le (|\mu| + C)\,\|\chi u\|_{L^2(\mathbb{R}^d)} + \|\chi\|_{W^{1,\infty}(\mathbb{R}^d)}\,\|u\|_{H^1(B(0,R-\epsilon)^c)}\\ &\lesssim \|u\|_{H^1(B(0,R-\epsilon)^c)}\,.\end{aligned}$$

We use estimate (2.25) and choose ϵ small enough in order to show estimate (2.26).

The estimates in dimension 3 are shown as in dimension 2. But in fact in [CL93, Appendix 2] the authors give a more precise statement for (2.24) in the case $d = 3$. Indeed, they show the existence of a constant $a \in \mathbb{R}$ such that

$$u(x)e^{|\mu|^{1/2}|x|}\,|x| \quad \underset{|x|\to\infty}{\longrightarrow} \quad a\,. \qquad \square$$

2.4 Some interaction terms

We recall that $u_L^r = u(\cdot - \mathbf{x}_L)$ and $u_L^\ell = u(\cdot + \mathbf{x}_L)$ where u is the unique positive minimizer of the monoatomic model (2.8) and that u_L^r and u_L^ℓ satisfy the Euler-Lagrange equation (2.17). As in [OR21], we introduce a *tunneling term*

$$\boxed{T_L = \exp\left(-\,|\mu|^{\frac{1}{2}}\,L\right)\,,} \tag{2.33}$$

which is the relevant scale to measure the interaction intensity between u_L^r and u_L^ℓ. In the next proposition, we gather many estimates involving T_L.

Lemma 2.17 (Interaction terms I)**.** *Let $d \in \{2, 3\}$. As $L \to \infty$, we have the estimates*

$$\int_{\mathbb{R}^d} u_L^\ell u_L^r = O\Big(L^{\frac{d-1}{2}}T_L\Big)\,, \quad D(u_L^\ell u_L^r, u_L^\ell u_L^r) = O\big(LT_L^2\big)\,, \quad D(|u_L^\ell|^2, u_L^\ell u_L^r) = O(T_L)\,, \tag{2.34}$$

$$\int_{\mathbb{R}^d} \nabla u_L^\ell \cdot \nabla u_L^r = O\Big(L^{\frac{d-1}{2}}T_L\Big)\,, \quad \big\|u_L^\ell u_L^r\big\|_{L^2(\mathbb{R}^d)} = O(T_L)\,, \quad \int_{\mathbb{R}^d} V_L u_L^\ell u_L^r = O\Big(L^{\frac{d-2}{2}}T_L\Big)\,. \tag{2.35}$$

Proof. We begin with the first estimate of (2.34). We remark that

$$\int_{\mathbb{R}^d} u_L^\ell u_L^r = (u * u)(2\mathbf{x}_L)\,,$$

where $|2\mathbf{x}_L| = L$. Then $\int_{\mathbb{R}^d} u_L^\ell u_L^r = O\Big(L^{\frac{d-1}{2}}T_L\Big)$ is a direct consequence of Lemma 2.16 and of the exponential estimates from Proposition 2.11. The estimates of (2.35) are obtained in the same way. To obtain the second estimate of (2.34), we use the Hardy-Littlewood-Sobolev inequality. The third estimate of (2.34) comes from $D(u_L^\ell u_L^r, u_L^\ell u_L^r) = O\big(LT_L^2\big)$ and the Cauchy-Schwarz inequality for the Coulomb energy [LL01, Theorem 9.8]: $D(v,w) \le \sqrt{D(v,v)}\sqrt{D(w,w)}$. $\square$

All the interaction terms we consider in Lemma 2.17 only depend on the long range behavior of u. These are thus exponentially small, irrespective of the dimension. In the next lemma, we study interaction terms which appear to be exponentially small in dimension 3 but not in dimension 2. We recall that $m_1 = \int_{\mathbb{R}^2} |u(x)|^2 |x|^2 \,\mathrm{d}x$ and $m_2 = \int_{\mathbb{R}^2} |u(x)|^2 |x|^4 \,\mathrm{d}x$.

Lemma 2.18 (Interaction terms II)**.** *We have*

$$\int_{\mathbb{R}^3} V_L^\ell |u_L^r|^2 = \begin{cases} -\left(\dfrac{1}{L} + \dfrac{m_1}{4L^3} + \dfrac{9m_2}{64L^5}\right) + O\left(\dfrac{1}{L^7}\right) & \text{if } d = 2\,, \\ -\dfrac{1}{L} + O\left(\dfrac{T_L^2}{L^2}\right) & \text{if } d = 3\,, \end{cases} \tag{2.36}$$

$$D(|u_L^\ell|^2, |u_L^r|^2) = \begin{cases} \dfrac{1}{2L} + \dfrac{m_1}{4L^3} + \dfrac{9(m_2 + 2m_1^2)}{64L^5} + O\left(\dfrac{1}{L^7}\right) & \text{if } d = 2\,, \\ \dfrac{1}{2L} + O(T_L^2) & \text{if } d = 3\,. \end{cases} \tag{2.37}$$

Proof. We start with the three-dimensional case. By Proposition 2.11, $\int V^{\mathrm{pp}}(\cdot - \mathbf{x}_L)\,|u_L^r|^2 = O(L^{-\infty})$ and, by Newton's theorem, we have

$$\int_{\mathbb{R}^3} V_L^\ell |u_L^r|^2 = -\left(|u|^2 * |\cdot|^{-1}\right)(2\mathbf{x}_L) + O(L^{-\infty}) = -\frac{1}{L} + \int_{|y|\geq L} |u(y)|^2 \left(\frac{1}{L} - \frac{1}{|y|}\right) \mathrm{d}y + O(L^{-\infty})\,.$$

To estimate the last integral, we use the pointwise exponential bound on u from Proposition 2.11 and get

$$\left| \int_{|y|\geq L} |u(y)|^2 \left(\frac{1}{L} - \frac{1}{|y|}\right) \mathrm{d}y \right| \lesssim \frac{e^{-2\sqrt{|\mu|}L}}{2\sqrt{|\mu|}L} - E_1(2\sqrt{|\mu|}L) = O(L^{-2}T_L^2)\,,$$

where $E_1(z) := \int_z^\infty \frac{e^{-t}}{t}\,\mathrm{d}t$ denotes the exponential integral with parameter 1. We get the O by using the asymptotic expansion for E_1, see [AS64, Eq. 5.1.51]

$$E_1(z) = \frac{e^{-z}}{z}\left(\sum_{k=0}^n \frac{(-1)^k k!}{z^k} + O\left(\frac{1}{|z|^{n+1}}\right)\right).$$

This shows (2.36) when $d = 3$. To get (2.37), we use again Newton's theorem

$$D(|u_L^\ell|^2, |u_L^r|^2) = \frac{1}{2}\left(|u|^2 * |u|^2 * |\cdot|^{-1}\right)(2\mathbf{x}_L) = \frac{1}{2}\left(\left(|u|^2 * |\cdot|^{-1}\right)(2\mathbf{x}_L) - \left(|u|^2 * \varphi_u\right)(2\mathbf{x}_L)\right),$$

with $\varphi_u(x) = \int_{|y|\geq|x|} |u(y)|^2 \left(\frac{1}{|x|} - \frac{1}{|y|}\right) \mathrm{d}y$. The same computation as above shows that $\varphi_u(x) = O\Big(|x|^{-2}\, e^{-2\sqrt{|\mu|}\,|x|}\Big)$. It remains to apply Lemma 2.16 to conclude.

In the two-dimensional case, the expansion (2.36) is a consequence of (2.31) and the fact that

$$\int_{\mathbb{R}^2} V_L^\ell |u_L^r|^2 = -\left(|u|^2 * |\cdot|^{-1}\right)(2\mathbf{x}_L) + O(L^{-\infty})\,.$$

Now, we show (2.37). By translation invariance of $D(\cdot,\cdot)$, we have $D(|u_L^\ell|^2, |u_L^r|^2) = D((\tau_L^r)^2 |u|^2, |u|^2)$. If we denote by B_L the ball centered at the origin and with radius $L/4$, we have

$$D(|u_L^\ell|^2, |u_L^r|^2) = D((\tau_L^r)^2(\mathbb{1}_{B_L^c} |u|^2), |u|^2) + D((\tau_L^r)^2(\mathbb{1}_{B_L} |u|^2), |u|^2)\,.$$

The first term is coarsely estimated by the Hardy-Littlewood-Sobolev inequality

$$D((\tau_L^r)^2(\mathbb{1}_{B_L^c} |u|^2), |u|^2) \lesssim \|u\|^2_{L^{8/3}(B_L^c)} = O\left(\frac{1}{L^7}\right).$$

To get the $O(L^{-7})$, we have used the exponential bounds on u (see Proposition 2.11). Now, we turn our attention to the second term. We recall the expansion formula (2.31)

$$\left(|u|^2 * |\cdot|^{-1}\right)(x) = \frac{1}{|x|} + \frac{m_1}{4\,|x|^3} + \frac{9m_2}{64\,|x|^5} + O\left(\frac{1}{|x|^7}\right), \tag{2.38}$$

as $|x|$ goes to ∞. In Appendix A., we also show that for all $a > 0$

$$(\mathbb{1}_{B_L}\,|u|^2 * |\cdot|^{-a})(2\mathbf{x}_L) = \frac{1}{L^a} + \frac{a^2}{4}\frac{m_1}{L^{2+a}} + \left(\frac{a^2}{16} + \frac{a^3}{16} + \frac{a^4}{64}\right)\frac{m_2}{L^{4+a}} + O\left(\frac{1}{L^7}\right). \tag{2.39}$$

Inserting (2.38) into

$$D((\tau_L^r)^2(\mathbb{1}_{B_L}\,|u|^2), |u|^2) = \frac{1}{2}\left(\mathbb{1}_{B_L}\,|u|^2 * \left(|u|^2 * |\cdot|^{-1}\right)\right)(2\mathbf{x}_L),$$

and using (2.39) give (2.37). □

3 Construction of quasi-modes

In this section, we consider a sequence $(L_n)_{n\in\mathbb{N}}$ such that $L_n \to \infty$ as $n \to \infty$. We want to show that to leading order the solution $u_{L_n}^+$ of the minimization problem (2.3) splits into two parts which are given by the monoatomic model minimizer translated by $+\mathbf{x}_{L_n}$ or $-\mathbf{x}_{L_n}$.

For simplicity, we will use the subscript n instead of L_n. For instance, we will write $\mathbf{x}_n$ instead of $\mathbf{x}_{L_n}$. We will use the r (resp. ℓ) superscript for quantities related to the monoatomic model translated by $\mathbf{x}_n$ (resp. $-\mathbf{x}_n$), see (2.16) and (2.17).

Let $d \in \{2,3\}$. It will be handy to define a partition of unity $(\chi^\ell)^2 + (\chi^r)^2 = 1$ such that for all $x \in \mathbb{R}^d$ and $\kappa \in \{\ell, r\}$

$$\chi^\kappa \in \mathcal{C}^\infty(\mathbb{R}^d), \quad 0 \le \chi^\kappa(x) \le 1, \quad \|\nabla\chi^\kappa\|_{L^\infty} < \infty \quad \text{and} \quad \mathcal{R}[\chi^r] = \chi^\ell,$$

where $\mathcal{R}$ is the natural action of the reflection symmetry with respect to the hyperplane $\{x_1 = 0\}$ on $L^2(\mathbb{R}^d)$, see (2.7). Moreover, we assume that there exists $\delta > 0$ such that

$$\operatorname{supp}\chi^\ell \subset \{x_1 \le \delta\} \quad \text{and} \quad \operatorname{supp}\chi^r \subset \{x_1 \ge -\delta\}.$$

Then, we denote the L_n−dependent partition of unity by

$$\chi_n^\ell(x) = \chi^\ell(x/\sqrt{L_n}) \quad \text{and} \quad \chi_n^r(x) = \chi^r(x/\sqrt{L_n}).$$

We have, in particular

$$\operatorname{supp}\chi_n^\ell \subset \{x_1 \le \sqrt{L_n}\delta\}, \quad \operatorname{supp}\nabla\chi_n^\ell \subset \{|x_1| \le \sqrt{L_n}\delta\}, \tag{2.40}$$

$$\|\nabla\chi_n^\ell\|_{L^\infty(\mathbb{R}^d)} = O\left(L_n^{-1/2}\right), \quad \|\Delta\chi_n^\ell\|_{L^\infty(\mathbb{R}^d)} = O\left(L_n^{-1}\right), \tag{2.41}$$

and similar statements for χ_n^r. The cutoff function χ_n^r (resp. χ_n^ℓ) will be useful to localize the right (resp. left) part of u_n^+. The scale $\sqrt{L_n}$ is chosen for convenience, any L_n^β with $\beta < 1$ would do.

Finally, we introduce the left and right translation operators

$$\tau_n^r := \tau_{\mathbf{x}_n} \quad \text{and} \quad \tau_n^\ell := \tau_{-\mathbf{x}_n}. \tag{2.42}$$

3.1 Approximation for u_n^+ in $H^1(\mathbb{R}^d)$

Our first result shows that u_n^+ splits into two symmetric parts which both converge, up to a translation, toward the minimizer u of the one nucleus model (2.8) in $H^1(\mathbb{R}^d)$−norm.

Proposition 2.19 (Strong convergence in $H^1(\mathbb{R}^d)$)**.** *We have the strong convergence*

$$\left\|\chi_n^\ell u_n^+ - u(\cdot + \mathbf{x}_n)\right\|_{H^1(\mathbb{R}^d)} = \left\|\chi_n^r u_n^+ - u(\cdot - \mathbf{x}_n)\right\|_{H^1(\mathbb{R}^d)} \underset{n\to\infty}{\longrightarrow} 0\,. \tag{2.43}$$

Proof. In this proof, we will frequently use the interaction estimates from Lemma 2.17 and Lemma 2.18. We recall that $u_n^r = u(\cdot - \mathbf{x}_n)$ and $u_n^\ell = u(\cdot + \mathbf{x}_n)$. We insert the trial state

$$u_{\text{trial}} = \frac{\sqrt{2}(u_n^r + u_n^\ell)}{\|u_n^r + u_n^\ell\|_{L^2(\mathbb{R}^d)}}$$

into the expression of the energy functional $\mathcal{E}_n$ defined in (2.2) and look for an upper bound involving $\mathcal{E}(u)$. We give a precise estimate of the interaction energy between u_n^ℓ and u_n^r

$$\mathcal{E}_n(u_{\text{trial}}) - 2\mathcal{E}(u)\,,$$

which will also be useful later in the proof of Proposition 2.29. First, using that $\|u_n^\ell\|_{L^2(\mathbb{R}^d)} = \|u_n^r\|_{L^2(\mathbb{R}^d)} = 1$, we have

$$\|u_n^r + u_n^\ell\|_{L^2(\mathbb{R}^d)}^{-2} = \left(2 + 2\left\langle u_n^r, u_n^\ell\right\rangle_{L^2(\mathbb{R}^d)}\right)^{-1} = \frac{1}{2} + O\left(L_n^{\frac{d-1}{2}} T_n\right)\,,$$

where $T_n = T_{L_n} := \exp(-|\mu|^{1/2} L_n)$ is the tunneling term introduced in (2.33). Then, computing the energy, we have

$$\begin{aligned}
\mathcal{E}_n(u_{\text{trial}}) &= \left(1 + O\left(L_n^{\frac{d-1}{2}} T_n\right)\right) \mathcal{E}_n(u_n^\ell + u_n^r)\\
&\leq 2\left(1 + O\left(L_n^{\frac{d-1}{2}} T_n\right)\right)\left(\mathcal{E}(u) + \int_{\mathbb{R}^d} \nabla u_n^r \cdot \nabla u_n^\ell + 2\int_{\mathbb{R}^d} V_n^\ell u_n^\ell u_n^r + 4D(|u_n^\ell|^2, u_n^\ell u_n^r)\right.\\
&\quad \left. + \int_{\mathbb{R}^d} V_n^\ell |u_n^r|^2 + D(|u_n^\ell|^2, |u_n^r|^2) + \frac{1}{2L_n} + 2D(u_n^\ell u_n^r, u_n^\ell u_n^r)\right)\,.
\end{aligned}$$

In this previous estimate, we have used the reflection symmetry and the translation invariance of the integral and, more particularly, the following identities

$$\int_{\mathbb{R}^d} V_n^\ell |u_n^r|^2 = \int_{\mathbb{R}^d} V_n^r |u_n^\ell|^2\,, \quad \int_{\mathbb{R}^d} V_n^\ell u_n^\ell u_n^r = \int_{\mathbb{R}^d} V_n^r u_n^\ell u_n^r\,, \quad D(|u_n^r|^2, u_\ell u_n^r) = D(|u_n^\ell|^2, u_n^\ell u_n^r)\,,$$
$$\mathcal{E}_n^\ell(u_n^\ell) = \mathcal{E}_n^r(u_n^r) = \mathcal{E}(u)\,.$$

Multiplying by u_n^r the Euler-Lagrange equation (2.17) satisfied by u_n^ℓ and integrating, we obtain

$$\int_{\mathbb{R}^d} (\nabla u_n^\ell \cdot \nabla u_n^r + V_n^\ell u_n^\ell u_n^r) + 2D(|u_n^\ell|^2, u_n^\ell u_n^r) = \mu \int_{\mathbb{R}^d} u_n^\ell u_n^r\,.$$

We can thus simplify our estimate into

$$\begin{aligned}
\mathcal{E}_n(u_{\text{trial}}) = 2\left(1 + O\left(L_n^{\frac{d-1}{2}} T_n\right)\right)&\left(\mathcal{E}(u) - \int_{\mathbb{R}^d} \nabla u_n^\ell \cdot \nabla u_n^r + 2\mu\int_{\mathbb{R}^d} u_n^\ell u_n^r + \int_{\mathbb{R}^d} V_n^\ell |u_n^r|^2\right.\\
&\left. + D(|u_n^\ell|^2, |u_n^r|^2) + \frac{1}{2L_n} + 2D(u_n^\ell u_n^r, u_n^\ell u_n^r)\right)\,.
\end{aligned}$$

In the $d = 2$ case, we use the estimates from Lemma 2.17 and the expansions from Lemma 2.18 to get

$$\mathcal{E}_n(u_n^+) \leq \mathcal{E}_n(u_{\text{trial}}) = 2\mathcal{E}(u) + \left(\frac{3m_1}{4}\right)^2 \frac{1}{L_n^5} + O\left(\frac{1}{L_n^7}\right)\,, \tag{2.44}$$

where $m_1 = \int_{\mathbb{R}^2} |u(y)|^2 |y|^2 \, dy$ is the second moment of the probability distribution $|u|^2$. In the $d = 3$ case, we use Lemma 2.18 and find

$$\mathcal{E}_n(u_n^+) \leq \mathcal{E}_n(u_{\text{trial}}) = 2\mathcal{E}(u) + O(L_n T_n) \; . \tag{2.45}$$

In both cases, passing to the limit in (2.44) and (2.45), we get

$$\limsup_{n\to\infty} \mathcal{E}_n(u_n^+) \leq \lim_{n\to\infty} \mathcal{E}_n(u_{\text{trial}}) \leq 2\mathcal{E}(u) = 2I \, . \tag{2.46}$$

Next, we seek a lower bound on the energy of u_n^+. Using the IMS formula [Cyc+87, Theorem 3.2], the positivity of $D(\cdot,\cdot)$ and the reflection symmetry $\mathcal{R}$, we can bound $\mathcal{E}_n(u_n^+)$ from below as follows

$$\begin{aligned}
\mathcal{E}_n(u_n^+) &= \int_{\mathbb{R}^d} |\nabla(\chi_n^\ell u_n^+)|^2 + \int_{\mathbb{R}^d} |\nabla(\chi_n^r u_n^+)|^2 - \int_{\mathbb{R}^d} \left(|\nabla\chi_n^\ell|^2 + |\nabla\chi_n^r|^2\right) |u_n^+|^2 + \frac{1}{L_n} \\
&\quad + \int_{\mathbb{R}^d} V_n(|\chi_n^\ell u_n^+|^2 + |\chi_n^r u_n^+|^2) + D(|u_n^+|^2, |u_n^+|^2) \\
&\geq \mathcal{E}_n^\ell(\chi_n^\ell u_n^+) + \mathcal{E}_n^r(\chi_n^r u_n^+) + 2\left(\int_{\mathbb{R}^d} V_n^\ell |\chi_n^r u_n^+|^2 + D\left(\left|\chi_n^\ell u_n^+\right|^2, \left|\chi_n^r u_n^+\right|^2\right) - \int_{\mathbb{R}^d} |\nabla\chi_n^\ell|^2 |u_n^+|^2\right) \\
&\geq 2\mathcal{E}_n^\ell(\chi_n^\ell u_n^+) + O\big(L_n^{-1}\big) \; .
\end{aligned}$$

The $O\big(L_n^{-1}\big)$ comes from the properties of χ_n^ℓ, see (2.40) and (2.41). Passing to the limit, we find

$$\liminf_{n\to\infty} \mathcal{E}_n(u_n^+) \geq 2 \liminf_{n\to\infty} \mathcal{E}_n^\ell(\chi_n^\ell u_n^+) \, .$$

If we insert this lower bound into (2.46), we deduce

$$\lim_{n\to\infty} \mathcal{E}(\tau_n^r(\chi_n^\ell u_n^+)) = \mathcal{E}(u) = I \, ,$$

where τ_n^r is the right translation operator defined by (2.42). Moreover, by reflection symetry, $\left\|\chi_n^\ell u_n^+\right\|_{L^2(\mathbb{R}^2)} = \|\chi_n^r u_n^+\|_{L^2(\mathbb{R}^2)} = 1$. Thus $\tau_n^r(\chi_n^\ell u_n^+)$ is a minimizing sequence for the minimization problem (2.8). By reflection symmetry, $\tau_n^\ell(\chi_n^r u_n^+)$ is also minimizing sequence for I. By the precompactness of all minimizing sequences (see [Lie81a, Section VII]), we have the strong convergences

$$\tau_n^r(\chi_n^\ell u_n^+) \quad \underset{n\to\infty}{\longrightarrow} \quad u \quad \text{and} \quad \tau_n^\ell(\chi_n^r u_n^+) \quad \underset{n\to\infty}{\longrightarrow} \quad u \quad \text{in} \quad H^1(\mathbb{R}^d) \, ,$$

up to a subsequence. However, since u is unique up to a phase and $u_n^+ > 0$, this statement is true for every sequence $(L'_n)_{n\geq 0}$ such that $L'_n \to \infty$ as $n \to \infty$. Hence, the sequences $\tau_n^r(\chi_n^\ell u_n^+)$ and $\tau_n^\ell(\chi_n^r u_n^+)$ admit only one limit point in $H^1(\mathbb{R}^d)$ and every subsequence admits a converging subsequence in $H^1(\mathbb{R}^d)$ (which converges toward u). This shows (2.43). □

Corollary 2.20 (Uniform bound in $H^1(\mathbb{R}^d)$)**.** *We have*

$$\sup_{n\geq 0} \left\|u_n^+\right\|_{H^1(\mathbb{R}^d)} < \infty \, . \tag{2.47}$$

Proof. Estimate (2.44) from the proof of Proposition 2.19 gives

$$\sup_{n\geq 0} \mathcal{E}_n(u_n^+) < \infty \, .$$

Using the positivity of $D(\cdot,\cdot)$ and the fact that $|\cdot|^{-1}$ is infinitesimally form-bounded with respect to $-\Delta$ (see for instance [RS75, Theorem X.19]), we have $\mathcal{E}_n(v) \geq \epsilon \|\nabla u_n^+\|^2_{L^2(\mathbb{R}^d)} - C_\epsilon$ for all $\epsilon > 0$ and some constant C_ϵ. The uniform bound (2.47) follows immediately. □

Remark 2.21. A consequence of Corollary is the validity of Proposition 2.8 when h is replaced by h_L. Indeed, in the last step of the proof, we need to use the fact that $\sup_{L\geq 1} \left\| |u_L^+|^2 * |\cdot|^{-1} \right\|_{L^\infty(\mathbb{R}^d)} <$

∞ which comes from Lemma 2.4 and Corollary 2.20. Also, in that case there are 2^n terms of order n appearing in (2.23). These are bounded by

$$\left\|(-\Delta+\nu)^{1/2-\alpha}\left[(-\Delta+\nu)^{-1/2}\left(|x-\mathbf{x}_L|^{-1}+|x-\mathbf{x}_L|^{-1}\right)(-\Delta+\nu)^{-1/2}\right]^n(-\Delta+\nu)^{-1/2}\right\|$$
$$\leq \nu^{-\alpha}\left(\frac{2C_\alpha}{\sqrt{\nu}}\right)^n .$$

3.2 Convergence of the Lagrange multiplier

Using Proposition 2.19, we show that the lowest eigenvalue μ_n^+ of the mean-field hamiltonian h_n for the two nuclei model (2.3) converges toward the one associated with the one nucleus model (2.8) as $n \to \infty$.

Proposition 2.22. *We have $\mu_n^+ \to \mu$ as $n \to \infty$.*

Proof. We recall the Euler-Lagrange equation (2.4) which is satisfied by u_n^+

$$\left(-\Delta + V_n + |u_n^+|^2 * |\cdot|^{-1}\right) u_n^+ = \mu_n^+ u_n^+ ,$$

where $\mu_n^+ < 0$. We localize this equation in the sector $\{x_1 \leq \sqrt{L_n}\delta\}$ using the cutoff function χ_n^ℓ

$$\begin{aligned}\left(-\Delta + V_\ell + |\chi_n^\ell u_n^+|^2 * |\cdot|^{-1}\right)\chi_n^\ell u_n^+ &= (-\Delta\chi_n^\ell)u_n^+ - 2\nabla\chi_n^\ell\cdot\nabla u_n^+ - V_n^r\chi_n^\ell u_n^+ \\ &\quad - \left(|\chi_n^r u_n^+|^2 * |\cdot|^{-1}\right)\chi_n^\ell u_n^+ + \mu_n^+\chi_n^\ell u_n^+ .\end{aligned} \tag{2.48}$$

We denote

$$w_n := (-\Delta\chi_n^\ell)u_n^+ - 2\nabla\chi_n^\ell\cdot\nabla u_n^+ - V_n^r\chi_n^\ell u_n^+ .$$

From Corollary 2.20, $\|u_n^+\|_{H^1(\mathbb{R}^d)}$ is uniformly bounded with respect to n. Hence, the terms involving the derivatives of χ_n^ℓ are $O\left(L_n^{-1/2}\right)$ in $L^2(\mathbb{R}^d)-$norm. Moreover, since $\operatorname{supp}\chi_n^\ell \subset \{x_1 \leq \sqrt{L_n}\delta\}$, we have $\left\|V_n^r\chi_n^\ell u_n^+\right\|_{L^2(\mathbb{R}^d)} = O\left(L_n^{-1}\right)$. Hence $\|w_n\|_{L^2(\mathbb{R}^d)} \to 0$ as $n \to \infty$. Now, we multiply (2.48) by $\chi_n^\ell u_n^+$, integrate and translate by $+\mathbf{x}_n$ to get

$$\mathcal{E}(\tau_n^r(\chi_n^\ell u_n^+)) + D\left(\left|\tau_n^r(\chi_n^\ell u_n^+)\right|^2, \left|\tau_n^r(\chi_n^\ell u_n^+)\right|^2\right) = \left\langle w_n, \chi_n^\ell u_n^+\right\rangle_{L^2(\mathbb{R}^d)} + \mu_n^+ . \tag{2.49}$$

We have used the fact that $\int_{\mathbb{R}^d}\left|\tau_n^r(\chi_n^\ell u_n^+)\right|^2 = \int_{\mathbb{R}^d}\left|\chi_n^\ell u_n^+\right|^2 = 1$. By Proposition 2.19, $\tau_n^r(\chi_n^\ell u_n^+) - u$ converges to 0 in $H^1(\mathbb{R}^d)$ as $n \to \infty$. So, by the strong continuity of the energy functional $v \mapsto \mathcal{E}(v)$ and of the Coulomb energy $v \mapsto D(v,v)$ in $H^1(\mathbb{R}^d)-$norm, we can take the limit as $n \to \infty$ in the left term of (2.49)

$$\lim_{n\to\infty}\left(\mathcal{E}(\tau_n^r(\chi_n^\ell u_n^+)) + D\left(\left|\tau_n^r(\chi_n^\ell u_n^+)\right|^2, \left|\tau_n^r(\chi_n^\ell u_n^+)\right|^2\right)\right) = \langle hu, u\rangle_{L^2(\mathbb{R}^d)} = \mu .$$

Then, taking the limit into (2.49) leads to $\lim\limits_{n\to\infty}\mu_n^+ = \mu$. ☐

The next corollary results from Remark 2.21 and Proposition 2.22.

Corollary 2.23 (Uniform bound in $H^{2-\alpha}(\mathbb{R}^d)$)**.** *$u_n^+$ is uniformly bounded in $H^{2-\alpha}(\mathbb{R}^d)$ for $\alpha \in (0,1]$ if $d=2$ and $\alpha = 0$ if $d = 3$. In particular, u_n^+ is uniformly bounded in $L^\infty(\mathbb{R}^d)$.*

3.3 Approximation for u_n^+ in higher Sobolev spaces

The convergence of μ_n^+ toward μ allows us to extend the result stated in Proposition 2.19 by showing that strong convergence also holds in $H^{2-\alpha}(\mathbb{R}^2)$ for any $\alpha > 0$ if $d = 2$ and in $H^2(\mathbb{R}^3)$ if $d = 3$.

Proposition 2.24 (Strong convergence in higher Sobolev spaces)**.** *Let* $0 < \alpha \leq 1$ *if* $d = 2$ *and* $\alpha = 0$ *if* $d = 3$. *We have the strong convergence*

$$\left\|\chi_n^\ell u_n^+ - u(\cdot + \mathbf{x}_n)\right\|_{H^{2-\alpha}(\mathbb{R}^d)} = \left\|\chi_n^r u_n^+ - u(\cdot - \mathbf{x}_n)\right\|_{H^{2-\alpha}(\mathbb{R}^d)} \underset{n\to\infty}{\longrightarrow} 0\,.$$

Proof. In the two-dimensional case, this is a consequence of the interpolation inequality $\|v\|_{H^{2-2\alpha}(\mathbb{R}^d)} \leq \|v\|_{H^1(\mathbb{R}^d)}^{\theta} \|v\|_{H^{2-\alpha}(\mathbb{R}^d)}^{1-\theta}$ (for $\alpha \leq 3/4$ and with $\theta = \frac{\alpha}{3/2-\alpha}$), Proposition 2.22 and Corollary 2.23. However, this argument does not adapt to the three-dimensional case and $\alpha = 0$. So we treat it apart. By reflection symmetry, we have

$$\left\|\chi_n^\ell u_n^+ - u(\cdot + \mathbf{x}_n)\right\|_{H^2(\mathbb{R}^3)} = \left\|\chi_n^r u_n^+ - u(\cdot - \mathbf{x}_n)\right\|_{H^2(\mathbb{R}^3)}\,.$$

We recall that h_n^ℓ and u_n^ℓ are defined by (2.16) and (2.17). In particular, u_n^ℓ solves the Euler-Lagrange equation $h_n^\ell u_n^\ell = \mu u_n^\ell$. As a direct consequence of Proposition 2.8, we have the bound

$$\|v\|_{H^2(\mathbb{R}^3)} \leq \left\|h_n^\ell v\right\|_{L^2(\mathbb{R}^3)} + C\,\|v\|_{L^2(\mathbb{R}^3)}\,,$$

for any $v \in \mathcal{D}(h_n^\ell)$. By Proposition 2.19, we already have $\lim\limits_{n\to\infty} \left\|\chi_n^\ell u_n^+ - u_n^\ell\right\|_{L^2(\mathbb{R}^3)} = 0$. Thus, to prove Proposition 2.24 in the three-dimensional case, it is sufficient to prove that $h_n^\ell(\chi_n^\ell u_n^+ - u_n^\ell)$ converges to 0 in $L^2(\mathbb{R}^3)-$norm as $n \to \infty$. As in the proof of Proposition 2.22, we localize the Euler-Lagrange equation (2.4) using the cutoff function χ_n^ℓ

$$(-\Delta + V_n + |u_n^+|^2 * |\cdot|^{-1})\chi_n^\ell u_n^+ = \mu_n^+ \chi_n^\ell u_n^+ - (\Delta\chi_n^\ell)u_n^+ - 2\nabla\chi_n^\ell \cdot \nabla u_n^+\,.$$

Subtracting the Euler-Lagrange equation $h_n^\ell u_n^\ell = \mu u_n^\ell$ and rearranging the terms, we get

$$\begin{aligned} h_n^\ell(\chi_n^\ell u_n^+ - u_n^\ell) &= \mu_n^+\chi_n^\ell u_n^+ - \mu u_n^\ell - V_n^r \chi_n^\ell u_n^+ - (\Delta\chi_n^\ell)u_n^+ - 2\nabla\chi_n^\ell \cdot \nabla u_n^+ \\ &\quad + \left[(|u_n^\ell|^2 - |\chi_n^\ell u_n^+|^2) * |\cdot|^{-1}\right]\chi_n^\ell u_n^+ - (|\chi_n^r u_n^+|^2 * |\cdot|^{-1})\chi_n^\ell u_n^+\,. \end{aligned} \tag{2.50}$$

By Proposition 2.19 and Proposition 2.32, we have $\lim\limits_{n\to\infty} \left\|\mu_n^+ \chi_n^\ell u_n^+ - \mu u_n^\ell\right\|_{L^2(\mathbb{R}^3)} = 0$. From the definition of χ_n^ℓ, we have the estimates

$$\left\|\Delta\chi_n^\ell\right\|_{L^\infty(\mathbb{R}^3)} = O\big(L_n^{-1}\big)\,, \quad \left\|\nabla\chi_n^\ell\right\|_{L^\infty(\mathbb{R}^3)} = O\Big(L_n^{-1/2}\Big)\,, \quad \left\|V_n^r\chi_n^\ell u_n^+\right\|_{L^2(\mathbb{R}^3)} = O\big(L_n^{-1}\big)\,.$$

The first two come from (2.41) and the last one is a consequence of (2.40). Then, the three last terms of the right side of (2.50) converge to 0. A direct consequence of Lemma 2.4 is the continuity of the multilinear application $(u,v,w) \in H^1(\mathbb{R}^3)^3 \longmapsto \big((uv) * |\cdot|^{-1}\big)\,w \in L^2(\mathbb{R}^3)$. From this previous statement, Proposition 2.19 and the uniform bound (2.47) in $H^1(\mathbb{R}^3)-$norm, we deduce

$$\left\|\left[(|u_n^\ell|^2 - |\chi_n^\ell u_n^+|^2) * |\cdot|^{-1}\right]\chi_n^\ell u_n^+\right\|_{L^2(\mathbb{R}^3)} \underset{n\to\infty}{\longrightarrow} 0\,,$$

and the following identity

$$\lim_{n\to\infty} \left\|(|\chi_n^r u_n^+|^2 * |\cdot|^{-1})\chi_n^\ell u_n^+\right\|_{L^2(\mathbb{R}^3)} = \lim_{n\to\infty} \left\|(|u_n^r|^2 * |\cdot|^{-1})u_n^\ell\right\|_{L^2(\mathbb{R}^3)}\,.$$

The right side of the previous identity is zero. Indeed, we have

$$\left\|(|u_n^r|^2 * |\cdot|^{-1})u_n^\ell\right\|_{L^2(\mathbb{R}^3)} \lesssim \left\|\frac{1}{|x - \mathbf{x}_n| + 1} u_n^\ell\right\|_{L^2(\mathbb{R}^3)} = O\big(L_n^{-1}\big)\,.$$

This concludes the proof of Proposition 2.24. $\square$

3.4 *A priori* exponential decay bounds for u_n^+

We denote by V_n^{MF} the mean-field potential associated with the diatomic model. It is defined by

$$V_n^{\mathrm{MF}} := V_n + |u_n^+|^2 * |\cdot|^{-1}\,, \tag{2.51}$$

where $V_n(x) = -(|x-\mathbf{x}_n|^{-1} + |x+\mathbf{x}_n|^{-1}) + V^{\mathrm{pp}}(x-\mathbf{x}_n) + V^{\mathrm{pp}}(x+\mathbf{x}_n)$ is the diatomic potential.

Proposition 2.25 (Exponential decay bounds on u_n^+). *For all $\epsilon \in (0\,,1)$ and for all n large enough, there exists $C_\epsilon > 0$ such that the following pointwise estimates hold*

$$\frac{1}{C_\epsilon}\left(e^{-(1+\epsilon)|\mu|^{\frac12}|x-\mathbf{x}_n|} + e^{-(1+\epsilon)|\mu|^{\frac12}|x+\mathbf{x}_n|}\right) \le u_n^+(x) \le C_\epsilon\left(e^{-(1-\epsilon)|\mu|^{\frac12}|x-\mathbf{x}_n|} + e^{-(1-\epsilon)|\mu|^{\frac12}|x+\mathbf{x}_n|}\right), \tag{2.52}$$

$$\left|\nabla u_n^+(x)\right| \le C_\epsilon\left(e^{-(1-\epsilon)|\mu|^{\frac12}|x-\mathbf{x}_n|} + e^{-(1-\epsilon)|\mu|^{\frac12}|x+\mathbf{x}_n|}\right), \tag{2.53}$$

for all $x \in \mathbb{R}^d$. Let $\alpha = 0$ if $d = 3$ and $\alpha \in (0\,,1]$ if $d = 2$. There exists $C'_\epsilon > 0$ such that for all $R > 0$, we have

$$\left\|u_n^+\right\|_{H^{2-\alpha}(B(-\mathbf{x}_n,R)^c\cap B(\mathbf{x}_n,R)^c)} \le C'_\epsilon e^{-(1-\epsilon)|\mu|^{\frac12}R}\,. \tag{2.54}$$

Proof. We want to apply the second comparison Lemma 2.13. Let $\epsilon \in (0\,,|\mu|)$. First, using Proposition 2.24 and Lemma 2.4, we can approximate the two nuclei mean-field potential V_n^{MF} by a superposition of translated monoatomic mean-field potentials. For n large enough, we have

$$\left\|V_n^{\mathrm{MF}} - \left(\tau_n^\ell + \tau_n^r\right)V^{\mathrm{MF}}\right\|_{L^\infty(\mathbb{R}^d)} \le \epsilon/8\,.$$

Now, we choose n large enough so that $|\mu_n^+ - \mu| \le \epsilon/8$. We insert these two estimates in the Euler-Lagrange equation (2.4) solved by u_n^+ and we obtain

$$\left(-\Delta + \left(\tau_n^\ell + \tau_n^r\right)V^{\mathrm{MF}} - \mu - \epsilon/2\right)u_n^+ \le 0\,.$$

We have also used that $u_n^+ > 0$. We have just shown that u_n^+ is a positive subsolution for the operator $\tilde h_n := -\Delta + \left(\tau_n^\ell + \tau_n^r\right)V^{\mathrm{MF}} - \mu - \epsilon/2$. Moreover, by Lemma 2.15, there exists $R_\epsilon > 0$ such that $\left|\left(\tau_n^\ell + \tau_n^r\right)V^{\mathrm{MF}}\right| \le \epsilon/2$ on the open set $\Omega_{n,\epsilon} := \{|x \pm \mathbf{x}_n| > R_\epsilon\}$. In particular, we have $\left(\tau_n^\ell + \tau_n^r\right)V^{\mathrm{MF}} - \mu - \epsilon/2 \ge 0$ on $\Omega_{n,\epsilon}$.

We define $f(x) = \exp(-\gamma\,|x-\mathbf{x}_n|) + \exp(-\gamma\,|x+\mathbf{x}_n|)$ for $\gamma < |\mu|^{1/2}$. A computation gives

$$\left(-\Delta + \left(\tau_n^\ell + \tau_n^r\right)V^{\mathrm{MF}} - \mu - \epsilon/2\right)f(x) \ge f(x)\left(-\gamma^2 + |\mu| - \epsilon\right),$$

on $\Omega_{n,\epsilon}$. If we choose $\gamma = \sqrt{|\mu| - \epsilon}$ then f is a supersolution for $\tilde h_n$. Similarly, we can show that f is a supersolution for h_n in the region $\{|x| \ge L_n/2 + R_\epsilon\}$ and the first comparison Lemma 2.12 shows that u_n^+ tends to 0 at infinity for all n. From Proposition 2.24, there exists $C_\epsilon > 0$ (independent from n), such that $u_n^+ \le C_\epsilon f$ on $\mathbb{R}^d \setminus \Omega_{n,\epsilon}$. Now, we can apply the second comparison Lemma 2.13 which shows the upper bound in (2.52). The lower bound can be shown similarly.

The proof of the pointwise estimate on ∇u_n^+ is similar to those of proof of Proposition 2.11, so we will only sketch the arguments. We introduce the Yukawa potential $\tilde Y_n$ defined as the solution in the sense of distribution of the equation

$$(-\Delta - \mu_n^+)\tilde Y_n = \delta_0\,,$$

where δ_0 is the Dirac distribution on 0. Then, we write

$$u_n^+ = -\tilde Y_n * (V_n^{\mathrm{MF}} u_n^+)\,.$$

Using the pointwise estimate (2.52) on u_n^+ and the asymptotic $\left|\nabla\tilde{Y}_n(x)\right| = O\left(e^{-\sqrt{|\mu|-\epsilon}|x|}\right)$ (see [LL01, Theorem 6.23]), this implies

$$\left|\nabla u_n^+\right| \lesssim g * \left[\left(1+\frac{1}{|x-\mathbf{x}_n|}+\frac{1}{|x+\mathbf{x}_n|}\right)\left(\tau_n^\ell g+\tau_n^r g\right)\right],$$

where $g(x)=\exp(-\sqrt{|\mu|-\epsilon}\,|x|)$. Then, it remains to invoke Lemma 2.16 to show (2.53). We can absorb any remaining polynomial terms by slightly modifying the constants. Finally, the integral estimate (2.54) is shown exactly as estimate (2.26) from Proposition 2.11. □

4 Precising the rate of convergence

In the previous section, we have shown the local convergence of u_n^+ to u in some Sobolev spaces. In this section, we show the existence of a first excited state u_n^- for h_n and give several rates of convergence for $u_n^\pm$ and $\mu_n^\pm$.

4.1 Stability of the monoatomic model in $H^1(\mathbb{R}^d)$-norm

Let $d\in\{2,3\}$. The next proposition is a stability result in $H^1(\mathbb{R}^d)-$norm on the monoatomic model which allows us to convert energy estimates into $H^1(\mathbb{R}^d)-$norm estimates. The proof follows the arguments given by Carlen, Frank and Lieb in [CFL14, Theorem 5.1]. In the sequel, we denote by

$$q_h : v\in H^1(\mathbb{R}^d)\longmapsto \int_{\mathbb{R}^d}|\nabla v(x)|^2\,\mathrm{d}x+\int_{\mathbb{R}^d}V^{\mathrm{MF}}(x)\,|v(x)|^2\,\mathrm{d}x\,,$$

the quadratic form associated with the mean-field operator h.

Proposition 2.26 (Stability of the monoatomic model (2.8))**.** *There exists $C>0$ such that for all $v\in H^1(\mathbb{R}^d)$ such that $\|v\|_{L^2(\mathbb{R}^d)}=1$, we have*

$$q_h(v)\geq \mu + C\min_{\theta\in[0,2\pi]}\left\|e^{i\theta}v-u\right\|^2_{H^1(\mathbb{R}^d)} \quad \textit{and}\quad \mathcal{E}(v)\geq\mathcal{E}(u)+C\min_{\theta\in[0,2\pi]}\left\|e^{i\theta}v-u\right\|^2_{H^1(\mathbb{R}^d)}. \tag{2.55}$$

First, we show that, up to a additive constant, the quadratic form associated with h is equivalent to the $H^1(\mathbb{R}^d)-$norm.

Lemma 2.27 (Properties of $v\mapsto q_h(v)$)**.** *For all $\epsilon\in(0,1)$, there exists constants $C_\epsilon, C'_\epsilon>0$ such that for all $v\in H^1(\mathbb{R}^d)$, we have*

$$(1-\epsilon)\,\|v\|^2_{H^1(\mathbb{R}^d)}\leq q_h(v)+C_\epsilon\,\|v\|^2_{L^2(\mathbb{R}^d)}\leq C'_\epsilon\,\|v\|^2_{H^1(\mathbb{R}^d)}. \tag{2.56}$$

Proof. By [LL01, Chap. 11], for any $\epsilon>0$, there exists $C_\epsilon>0$ such that

$$\int_{\mathbb{R}^d}\frac{|v(x)|^2}{|x|}\,\mathrm{d}x\leq\epsilon\,\|\nabla v\|^2_{L^2(\mathbb{R}^d)}+C_\epsilon\,\|v\|^2_{L^2(\mathbb{R}^d)},$$

for all $v\in H^1(\mathbb{R}^d)$. Recall that $|u|^2*|\cdot|^{-1}\in L^\infty(\mathbb{R}^d)$ by Lemma 2.4, then we have

$$0\leq\int_{\mathbb{R}^d}\left(|u|^2*|\cdot|^{-1}\right)|v|^2\leq\left\||u|^2*|\cdot|^{-1}\right\|_{L^\infty(\mathbb{R}^d)}\|v\|^2_{L^2(\mathbb{R}^d)}.$$

Estimate (2.56) follows from these two estimates and the assumption $V^{\mathrm{pp}}\in L^\infty(\mathbb{R}^d)$. □

The next lemma is a local version of Proposition 2.26.

Lemma 2.28. *There exists $\delta, C>0$ such that for all $v\in H^1(\mathbb{R}^d)$ with $\|v\|_{L^2(\mathbb{R}^d)}=1$, we have*

$$\min_{\theta\in[0,2\pi]}\left\|e^{i\theta}v-u\right\|_{L^2(\mathbb{R}^d)}\leq\delta\implies q_h(v)\geq\mu+C\min_{\theta\in[0,2\pi]}\left\|e^{i\theta}v-u\right\|^2_{H^1(\mathbb{R}^d)}.$$

Proof. Let $v \in H^1(\mathbb{R}^d)$ such that $\|v\|_{L^2(\mathbb{R}^d)} = 1$. Let $\theta \in [0\,,2\pi]$ such that

$$\left\|e^{i\theta}v - u\right\|_{L^2(\mathbb{R}^d)} = \min_{\tilde{\theta}\in[0,2\pi]} \left\|e^{i\tilde{\theta}}v - u\right\|_{L^2(\mathbb{R}^d)} .$$

We have $q_h(v) = \mu + q_{h-\mu}(e^{i\theta}v)$. We denote $\tilde{v} = e^{i\theta}v$ and we have $\langle \tilde{v}, u\rangle_{L^2(\mathbb{R}^d)} \in \mathbb{R}_+$. Let $w = \tilde{v} - \langle u, \tilde{v}\rangle_{L^2(\mathbb{R}^d)}\, u$ be the orthogonal projection in $L^2(\mathbb{R}^d)$ of $\tilde{v}$ on the subspace $(\operatorname{span} u)^\perp$. An integration by parts shows $q_{h-\mu}(\tilde{v}) = q_{h-\mu}(w)$. Let $\epsilon \in (0\,,1)$. By Lemma 2.27, there exists a constant $C_\epsilon \geq |\mu|$ such that $q_h + C_\epsilon \geq \epsilon \left\|\cdot\right\|_{H^1(\mathbb{R}^d)}$. By the functional calculus, we also have $q_{h-\mu}(\tilde{v}) \geq G \left\|w\right\|^2_{L^2(\mathbb{R}^d)}$ where $G > 0$ denotes the spectral gap between μ and the remaining spectrum of h. These three previous estimates imply

$$q_{h-\mu}(\tilde{v}) \geq c_\epsilon \left(q_h(w) + C_\epsilon \left\|w\right\|^2_{L^2(\mathbb{R}^d)}\right) \geq c_\epsilon \epsilon \left\|w\right\|^2_{H^1(\mathbb{R}^d)} , \tag{2.57}$$

with $c_\epsilon = \frac{G}{G+\mu+C_\epsilon}$. Moreover, we have

$$\begin{aligned}\left\|w\right\|^2_{H^1(\mathbb{R}^d)} &= \left\|\tilde{v} - u\right\|^2_{H^1(\mathbb{R}^d)} + \left|1 - \langle u, \tilde{v}\rangle_{L^2(\mathbb{R}^d)}\right|^2 \left\|u\right\|^2_{H^1(\mathbb{R}^d)} + 2\Re\left(\langle \tilde{v} - u, \tilde{v}\rangle_{L^2(\mathbb{R}^d)} \langle \tilde{v} - u, u\rangle_{H^1(\mathbb{R}^d)}\right)\\ &\geq \left\|\tilde{v} - u\right\|^2_{H^1(\mathbb{R}^d)} + 2\Re\left(\langle \tilde{v} - u, \tilde{v}\rangle_{L^2(\mathbb{R}^d)} \langle \tilde{v} - u, u\rangle_{H^1(\mathbb{R}^d)}\right) ,\end{aligned}$$

where $\langle\cdot,\cdot\rangle_{H^1(\mathbb{R}^d)}$ denotes the usual scalar product in $H^1(\mathbb{R}^d)$. Using the Cauchy-Schwarz inequality and the identity (recall that $\langle u, \tilde{v}\rangle_{L^2(\mathbb{R}^d)} \in \mathbb{R}_+$)

$$\langle \tilde{v} - u, \tilde{v}\rangle_{L^2(\mathbb{R}^d)} = \frac{1}{2} \langle \tilde{v} - u, \tilde{v} - u\rangle_{L^2(\mathbb{R}^d)} ,$$

we obtain the bound

$$\begin{aligned}\left|2\Re\left(\langle \tilde{v} - u, \tilde{v}\rangle_{L^2(\mathbb{R}^d)} \langle \tilde{v} - u, u\rangle_{H^1(\mathbb{R}^d)}\right)\right| &\leq \left\|u\right\|_{H^1(\mathbb{R}^d)} \left\|\tilde{v} - u\right\|_{H^1(\mathbb{R}^d)} \left\|\tilde{v} - u\right\|^2_{L^2(\mathbb{R}^d)}\\ &\leq \left\|u\right\|_{H^1(\mathbb{R}^d)} \left\|\tilde{v} - u\right\|^2_{H^1(\mathbb{R}^d)} \left\|\tilde{v} - u\right\|_{L^2(\mathbb{R}^d)} .\end{aligned}$$

If $\left\|\tilde{v} - u\right\|_{L^2(\mathbb{R}^d)} \leq (1-\beta) \left\|u\right\|^{-1}_{H^1(\mathbb{R}^d)} =: \delta$ for some $\beta \in (0\,,1)$, we get

$$q_h(v) \geq \mu + c_\epsilon\beta\epsilon \left\|\tilde{v} - u\right\|^2_{H^1(\mathbb{R}^d)} \geq \mu + c_\epsilon\beta\epsilon \min_{\theta\in[0,2\pi]} \left\|e^{i\theta}v - u\right\|^2_{H^1(\mathbb{R}^d)} ,$$

which concludes the proof of Lemma 2.28. ☐

Proof of Proposition 2.26. First, using the positive-definiteness of $D(\cdot,\cdot)$, we find

$$\mathcal{E}(v) = \mathcal{E}(u) + q_h(v) - \mu \left\|v\right\|^2_{L^2(\mathbb{R}^2)} + D(|u|^2 - |v|^2\,, |u|^2 - |v|^2) \geq \mathcal{E}(u) + q_h(v) - \mu \left\|v\right\|^2_{L^2(\mathbb{R}^2)} .$$

Then the right side of (2.55) is a consequence of its left side. To show the left part of (2.55), we argue by contradiction and assume that there exists a sequence $(\delta_n)_{n\in\mathbb{N}}$ of positive numbers and a sequence $(v_n)_{n\in\mathbb{N}}$ of functions in $H^1(\mathbb{R}^d)$ such that

$$\delta_n \underset{n\to\infty}{\longrightarrow} 0\,, \quad \left\|v_n\right\|_{L^2(\mathbb{R}^d)} = 1 \quad \text{and} \quad q_h(v_n) \leq \mu + \delta_n \min_{\theta\in[0,2\pi]} \left\|e^{i\theta}v_n - u\right\|^2_{H^1(\mathbb{R}^d)} .$$

First we show that $\min_{\theta\in[0,2\pi]} \left\|e^{i\theta}v_n - u\right\|^2_{H^1(\mathbb{R}^d)}$ is bounded uniformly in n. For n large enough, we have

$$q_h(v_n) \leq \mu + \frac{1}{2} \min_{\theta\in[0,2\pi]} \left\|e^{i\theta}v_n - u\right\|^2_{H^1(\mathbb{R}^d)} .$$

Moreover, by the Cauchy-Schwarz inequality, we have

$$\begin{aligned}\min_{\theta\in[0,2\pi]} \left\|e^{i\theta}v_n - u\right\|^2_{H^1(\mathbb{R}^d)} &\leq \|u\|^2_{H^1(\mathbb{R}^d)} + \|v_n\|^2_{H^1(\mathbb{R}^d)} + 2\|u\|_{H^1(\mathbb{R}^d)}\|v_n\|_{H^1(\mathbb{R}^d)} \\ &\leq 3\|u\|^2_{H^1(\mathbb{R}^d)} + \frac{3}{2}\|v_n\|^2_{H^1(\mathbb{R}^d)}\,.\end{aligned}$$

By Lemma 2.27, there exists a constant $C' > 0$ such that $\langle v_n, hv_n\rangle_{L^2(\mathbb{R}^d)} \geq \frac{7}{8}\|v_n\|^2_{H^1(\mathbb{R}^d)} - C'$. Then, we have shown that there exists $C'' > 0$ such that $\frac{1}{8}\|v_n\|^2_{H^1(\mathbb{R}^d)} \leq C''$ for all $n \in \mathbb{N}$. As a consequence, we have $\lim\limits_{n\to\infty} q_h(v_n) = \mu$ and, by the functional calculus and the fact μ is non-degenerate, we deduce

$$\min_{\theta\in[0,2\pi]} \left\|e^{i\theta}v_n - u\right\|_{L^2(\mathbb{R}^d)} = 2\left(1 - \left|\langle v_n, u\rangle_{L^2(\mathbb{R}^d)}\right|\right) \underset{n\to\infty}{\longrightarrow} 0\,. \tag{2.58}$$

Let $\epsilon \in (0\,,1)$ and $C_\epsilon \geq |\mu|$ as in Lemma 2.27. An integration by parts shows

$$(1-\epsilon)\min_{\theta\in[0,2\pi]} \left\|e^{i\theta}v_n - u\right\|^2_{H^1(\mathbb{R}^d)} \leq q_{h+C_\epsilon}(v_n) + q_{h+C_\epsilon}(u) - 2(\mu + C_\epsilon)\left|\langle v_n, u\rangle_{L^2(\mathbb{R}^d)}\right|\,.$$

Taking the limit, we obtain

$$\lim_{n\to\infty}\min_{\theta\in[0,2\pi]} \left\|e^{i\theta}v_n - u\right\|^2_{H^1(\mathbb{R}^d)} \leq \frac{2\,(\mu + C_\epsilon)}{1-\epsilon}\lim_{n\to\infty}\left(1 - \left|\langle v_n, u\rangle_{L^2(\mathbb{R}^d)}\right|\right) = 0\,,$$

which is a contradiction by Lemma 2.28. This concludes the proof of Proposition 2.26. □

4.2 Rate of convergence for u_n^+

Proposition 2.29 (Rate of convergence for u_n^+)**.** *For any $\epsilon \in (0\,,3)$, there exists a constant $C_\epsilon > 0$ such that the following estimates hold*

$$\left\||u(\cdot + \mathbf{x}_n)|^2 - |\chi_n^\ell u_n^+|^2\right\|_{L^1(\mathbb{R}^d)} = \left\||u(\cdot - \mathbf{x}_n)|^2 - |\chi_n^r u_n^+|^2\right\|_{L^1(\mathbb{R}^d)} \leq \begin{cases} C_\epsilon L_n^{-3+\epsilon} & \text{if } d = 2\,, \\ O(L_n^{-\infty}) & \text{if } d = 3\,, \end{cases} \tag{2.59}$$

$$\left\|u(\cdot + \mathbf{x}_n) - \chi_n^\ell u_n^+\right\|_{H^1(\mathbb{R}^d)} = \left\|u(\cdot - \mathbf{x}_n) - \chi_n^r u_n^+\right\|_{H^1(\mathbb{R}^d)} \leq \begin{cases} C_\epsilon L_n^{-3+\epsilon} & \text{if } d = 2\,, \\ O(L_n^{-\infty}) & \text{if } d = 3\,. \end{cases} \tag{2.60}$$

Proof. We denote $v_n \coloneqq \tau_n^r \chi_n^\ell u_n^+$ (the right translation operator τ_n^r and the function are defined in the beginning of Section 3). Notice that most of the mass of v_n is localized in the vicinity of the origin. Using the reflection symmetry $\mathcal{R}$, we have $\|v_n\|_{L^2(\mathbb{R}^d)} = 1$. Recall the notation V_n^ℓ, V_n^r, u_n^ℓ and u_n^r defined in (2.16). As in the proof of Proposition 2.19, we look for a lower bound on $\mathcal{E}_n(u_n^+)$ using the IMS formula but without discarding the positive term $D(\left|\chi_n^\ell u_n^+\right|^2, |\chi_n^r u_n^+|^2)$. We find

$$\begin{aligned}\mathcal{E}_n(u_n^+) &= 2\mathcal{E}(v_n) + 2\left(\int_{\mathbb{R}^d} V_n^r \left|\chi_n^\ell u_n^+\right|^2 + D(\left|\chi_n^\ell u_n^+\right|^2, |\chi_n^r u_n^+|^2) + \frac{1}{2L_n} - \int_{\mathbb{R}^d} \left|\nabla\chi_n^\ell\right|^2 |u_n^+|^2\right) \\ &\geq 2\mathcal{E}(u) + 2\left(\int_{\mathbb{R}^d} V_n^r \left|\chi_n^\ell u_n^+\right|^2 + D(\left|\chi_n^\ell u_n^+\right|^2, |\chi_n^r u_n^+|^2) + \frac{1}{2L_n} - \int_{\mathbb{R}^d} \left|\nabla\chi_n^\ell\right|^2 |u_n^+|^2\right) \\ &\quad + C\|v_n - u\|^2_{H^1(\mathbb{R}^d)}\,,\end{aligned}$$

for some constant $C > 0$. To get the lower bound, we have used Proposition 2.26 and the positiveness of v_n and u. As $\operatorname{supp}\nabla\chi_n^\ell \subset \{|x_1| \leq \sqrt{L_n}\delta\}$, by the exponential decay of u_n^+ proved in Proposition 2.25, the term involving $\nabla\chi_n^\ell$ is a $O(L_n^{-\infty})$. Using that V^{pp} is compactly supported, we remark that we can express the potential terms as

$$\int_{\mathbb{R}^d} V_n^r \left|\chi_n^\ell u_n^+\right|^2 = -\left(|v_n|^2 * |\cdot|^{-1}\right)(2\mathbf{x}_n) + O\left(L_n^{-\infty}\right)\,,$$

and

$$D(|\chi_n^\ell u_n^+|^2\,,|\chi_n^r u_n^+|^2) = \frac{1}{2}\left(|v_n|^2 * \mathcal{S}[|v_n|^2] * |\cdot|^{-1}\right)(2\mathbf{x}_n)\,,$$

where the transformation $\mathcal{S}$ is defined by $\mathcal{S}[v](x) = v(-Rx)$ with R the reflection matrix with respect to the first coordinate defined in (2.7). Notice that $-R\mathbf{x}_n = \mathbf{x}_n$ and $\mathcal{S}[u] = u$. Hence, we have obtained the lower bound

$$\mathcal{E}_n(u_n^+) \geq 2\left(\mathcal{E}(u) + \mathcal{Q}_n(v_n)\right) + C\,\|v_n - u\|^2_{H^1(\mathbb{R}^d)} + O\big(L_n^{-\infty}\big)\,,$$

where $\mathcal{Q}_n$ is a quartic function plus a constant defined by

$$\mathcal{Q}_n(v) := \left(\left(\frac{|v|^2 * \mathcal{S}[|v|^2]}{2} - |v|^2\right) * |\cdot|^{-1}\right)(2\mathbf{x}_n) + \frac{1}{2L_n}\,.$$

Let $(R_n)_{n\in\mathbb{N}}$ be an increasing sequence such that $R_n \leq L_n/4$ and $L_n^\gamma = o(R_n)$ for some $\gamma \in (0\,,1)$. In the following, we will choose the constants in the O's independently of the choice of the sequence R_n. Let $\chi \in \mathcal{C}^\infty(\mathbb{R}^d)$ be a cutoff function such that

$$0 \leq \chi \leq 1\,, \quad \chi \equiv 1 \quad \text{on} \quad B(0,1/2) \quad \text{and} \quad \operatorname{supp}\chi \subset B(0,1)\,.$$

Let $\chi_n(x) = \chi(x/R_n)$. We define $v_{n,1} := \chi_n(|v_n|^2 - |u|^2)$ and $v_{n,2} := (1-\chi_n)(|v_n|^2 - |u|^2)$. Hence, we have the decomposition

$$|v_n|^2 = |u|^2 + v_{n,1} + v_{n,2}\,. \tag{2.61}$$

where $\operatorname{supp} v_{n,1} \subset B(0,R_n)$ and $\operatorname{supp} v_{n,2} \subset B(0,\frac{R_n}{2})^c$. In particular, using the fact u and v_n are exponentially decaying away from the origin (see Proposition 2.11 and Proposition 2.25), we have $\|v_{n,2}\|_{W^{2-\alpha,1}(\mathbb{R}^d)} = O(L_n^{-\infty})$ where $\alpha \in (0\,,1)$ if $d=2$ and $\alpha = 0$ if $d=3$. Moreover, from Proposition 2.19 and Corollary 2.23, there exists $\nu \geq 0$ such that $\|v_{n,1}\|_{L^1(\mathbb{R}^d)} = O(L_n^{-\nu})$. We expand $\mathcal{Q}_n(v_n)$ with respect to the decomposition (2.61) and we can show, by means of Sobolev embeddings and Young's inequality, that all the terms involving $v_{n,2}$ are $O(L_n^{-\infty})$. Then, we have

$$\begin{aligned}\mathcal{Q}_n(v_n) = \mathcal{Q}_n(u) &+ \left[\left(|u|^2 * \left(\frac{v_{n,1} + \mathcal{S}[v_{n,1}]}{2}\right) - v_{n,1}\right) * |\cdot|^{-1}\right](2\mathbf{x}_n) &(2.62)\\ &+ \frac{1}{2}\left[v_{n,1} * \mathcal{S}[v_{n,1}] * |\cdot|^{-1}\right](2\mathbf{x}_n) + O\big(L_n^{-\infty}\big)\,. &(2.63)\end{aligned}$$

Assume $d=2$. From the expansion (2.31), we have $(|u|^2 * |\cdot|^{-1})(x) = |x|^{-1} + O\big(|x|^{-3}\big)$ as $|x| \to \infty$. Recall that $v_{n,1}$ is compactly supported in the ball $B(0,R_n) \subset B(0,L_n/4)$. Then, we use

$$\left(\mathcal{S}[v_{n,1}] * |\cdot|^{-1}\right)(2\mathbf{x}_n) = \left(v_{n,1} * |\cdot|^{-1}\right)(2\mathbf{x}_n)\,,$$

to get

$$\left[\left(|u|^2 * \left(\frac{v_{n,1} + \mathcal{S}[v_{n,1}]}{2}\right) - v_{n,1}\right) * |\cdot|^{-1}\right](2\mathbf{x}_n) = O\big(\left(v_{n,1} * |\cdot|^{-3}\right)(2\mathbf{x}_n)\big)\,.$$

As $\operatorname{supp} v_{n,1} \subset B(0,R_n) \subset B(0,L_n/4)$, the quantity $\left(v_{n,1} * |\cdot|^{-3}\right)(2\mathbf{x}_n)$ is well defined (recall that $|2\mathbf{x}_n| = L_n$) and we can estimate it by $O\big(\|v_{n,1}\|_{L^1(\mathbb{R}^2)} L_n^{-3}\big) = O\big(L_n^{-3-\nu}\big)$. If $d=3$, we use Newton's theorem instead of expansion (2.31) and we can estimate by $O(L_n^{-\nu} T_n) = O(L_n^{-\infty})$. For the remaining term of (2.63), we remark that

$$\operatorname{supp}\left(v_{n,1} * \mathcal{S}[v_{n,1}]\right) \subset B(0,2R_n) \subset B(0,L_n/2)\,.$$

Irrespective of the dimension, we have

$$\left|\left[v_{n,1} * \mathcal{S}[v_{n,1}] * |\cdot|^{-1}\right](2\mathbf{x}_n)\right| = O\Big(L_n^{-1}\,\|v_{n,1} * \mathcal{S}[v_{n,1}]\|_{L^1(\mathbb{R}^d)}\Big) = O\big(L_n^{-1-2\nu}\big)\,. \tag{2.64}$$

In the last inequality, we have used Young's inequality. Hence, we end up with

$$\mathcal{E}_n(u_n^+) \geq 2\left(\mathcal{E}(u) + \mathcal{Q}_n(u)\right) + C\,\|v_n - u\|^2_{H^1(\mathbb{R}^d)} + O\Big(L_n^{-2\gamma(\nu)}\Big)\,, \tag{2.65}$$

where

$$\gamma(\nu) := \begin{cases} \min\left(\frac{1}{2}+\nu, \frac{3}{2}+\frac{\nu}{2}\right) & \text{if } d=2\,,\\ \frac{1}{2}+\nu & \text{if } d=3\,. \end{cases}$$

Now, following the proof of Proposition 2.19, we can obtain the upper bound

$$\mathcal{E}_n(u_n^+) \leq 2\left(\mathcal{E}(u) + \mathcal{Q}_n(u)\right) + O\big(L_n^{-\infty}\big)\,. \tag{2.66}$$

From (2.65) and (2.66), we obtain

$$\|v_n - u\|_{H^1(\mathbb{R}^d)} = O\Big(L_n^{-\gamma(\nu)}\Big)\,. \tag{2.67}$$

Recall $\operatorname{supp} v_{n,1} \subset B(0, R_n)$ and $\sup_n \|v_n\|_{L^\infty(\mathbb{R}^d)} < \infty$ (see Proposition 2.24). By the Cauchy-Schwarz inequality, we get

$$\|v_{n,1}\|_{L^1(\mathbb{R}^d)} = O\Big(R_n L_n^{-\gamma(\nu)}\Big)\,.$$

Recall that we can choose R_n of the form $L_n^\gamma/4$ for any $\gamma \in (0\,,1)$ small enough. Then, an induction argument shows that

$$\|v_{n,1}\|_{L^1(\mathbb{R}^d)} = \begin{cases} O\big(L_n^{-3+\epsilon}\big) & \text{if } d=2\,,\\ O\big(L_n^{-\infty}\big) & \text{if } d=3\,, \end{cases}$$

for any $\epsilon > 0$ (notice that 3 is the unique fixed point of the map $\nu \mapsto \gamma(\nu)$ when $d=2$). Recalling estimate (2.67) with $\nu = 3-\epsilon$ if $d=2$ and $\nu = k$ for any $k \in \mathbb{N}$ if $d=3$ and this concludes the proof of Proposition 2.29. □

Remark 2.30. In the three-dimensional case, we are only able to obtain superpolynomial convergence rates but we think they should be exponential.

4.3 Rate of convergence for mean-field potentials

We recall that the mean-field hamiltonians associated with monoatomic and diatomic model are defined by

$$V^{\mathrm{MF}} = -\frac{1}{|\cdot|} + V^{\mathrm{pp}} + |u|^2 * |\cdot|^{-1} \quad \text{and}$$
$$V_n^{\mathrm{MF}} = -\left(\frac{1}{|\cdot - \mathbf{x}_n|} + \frac{1}{|\cdot + \mathbf{x}_n|}\right) + V^{\mathrm{pp}}(\cdot - \mathbf{x}_n) + V^{\mathrm{pp}}(\cdot + \mathbf{x}_n) + |u_n^+|^2 * |\cdot|^{-1}\,.$$

Recall that τ_n^r (resp. τ_n^ℓ) denotes the translation operator by $\mathbf{x}_n$ (resp. $-\mathbf{x}_n$).

Proposition 2.31. *Let w such that for all $x \in \mathbb{R}^d$, we have $|w(x)| \leq c\exp(-\alpha\,|x|)$ where $c, \alpha > 0$. Then, there exists a constant $C(c,\alpha,\epsilon)$ such that we have the estimates*

$$\left|\int_{\mathbb{R}^d} w\left(\tau_n^r V_n^{\mathrm{MF}} - V^{\mathrm{MF}}\right)\right| \leq \begin{cases} C(c,\alpha,\epsilon) L_n^{-3+\epsilon}\Big(\|w\|_{L^1(\mathbb{R}^d)} + \|w\|_{L^2(\mathbb{R}^d)}\Big) + O(L_n^{-\infty}) & \text{if } d=2\,,\\ O(L_n^{-\infty})\Big(1 + \|w\|_{L^1(\mathbb{R}^d)} + \|w\|_{L^2(\mathbb{R}^d)}\Big) & \text{if } d=3\,. \end{cases}$$

for any $\epsilon > 0$. The same estimate holds by replacing τ_n^r with τ_n^ℓ.

Proof. Let $r \in (d\,,\infty)$. As in the proof of Proposition 2.29, we use the notation $v_n = \tau_n^r \chi_n^\ell u_n^+$. Using Lemma 2.4, the facts (see Corollary 2.23 and Proposition 2.8)

$$\sup_n \|v_n\|_{L^\infty(\mathbb{R}^d)} < \infty \quad \text{and} \quad u \in L^\infty(\mathbb{R}^d)\,,$$

and Proposition 2.29, we obtain the following estimate

$$\left\| \left(|v_n|^2 - |u|^2\right) * |\cdot|^{-1} \right\|_{L^r(\mathbb{R}^d)} = \begin{cases} O\big(L_n^{-3+\epsilon}\big) & \text{if } d = 2\,, \\ O\big(L_n^{-\infty}\big) & \text{if } d = 3\,. \end{cases} \tag{2.68}$$

Let $w \in L^1(\mathbb{R}^d) \cap L^2(\mathbb{R}^d)$ such that $|w(x)| \leq c\exp(-\alpha\,|x|)$. Let $r' \in (1\,, \frac{d}{d-1})$ such that $\frac{1}{r} + \frac{1}{r'} = 1$. Then, using Hölder's inequality and the fact that V^{pp} is compactly supported, we have

$$\begin{aligned} \left| \int_{\mathbb{R}^d} w\left(\tau_{\mathbf{x}_n} V_n^{\mathrm{MF}} - V^{\mathrm{MF}}\right) \right| &\leq \left| \int_{\mathbb{R}^d} w\left(|v_n|^2 - |u|^2\right) * |\cdot|^{-1} \right| + \left| \left[w * \left(\mathcal{R}[|v_n|^2] - |u|^2\right) * |\cdot|^{-1} \right] (2\mathbf{x}_n) \right| \\ &\quad + \left| \left[w * \left(|u|^2 * |\cdot|^{-1} - |\cdot|^{-1} \right) \right] (2\mathbf{x}_n) \right| + O\big(L_n^{-\infty}\big) \\ &\leq \|w\|_{L^{r'}(\mathbb{R}^d)} \left\| \left(|v_n|^2 - |u|^2\right) * |\cdot|^{-1} \right\|_{L^r(\mathbb{R}^d)} \\ &\quad + \left| \left[w * \left(|u|^2 * |\cdot|^{-1} - |\cdot|^{-1} \right) \right] (2\mathbf{x}_n) \right| + O\big(L_n^{-\infty}\big)\,. \end{aligned}$$

By (2.68) and Hölder's inequality, the first term is bounded by

$$\|w\|_{L^{r'}(\mathbb{R}^d)} \left\| \left(|v_n|^2 - |u|^2\right) * |\cdot|^{-1} \right\|_{L^r(\mathbb{R}^d)} = \begin{cases} O\big(L_n^{-3+\epsilon}\big) \left(\|w\|_{L^1(\mathbb{R}^d)} + \|w\|_{L^2(\mathbb{R}^d)} \right) & \text{if } d = 2\,, \\ O\big(L_n^{-\infty}\big) \left(\|w\|_{L^1(\mathbb{R}^d)} + \|w\|_{L^2(\mathbb{R}^d)} \right) & \text{if } d = 3\,, \end{cases}$$

where the constants appearing in the O's do not depend on w. It remains to estimate the second term. Assume $d = 2$. From Lemma 2.41, we can write $|u|^2 * |\cdot|^{-1} - |\cdot|^{-1} = O\big(|\cdot|^{-3}\big)$ as $|x| \to \infty$. We use the decomposition $w = w_{n,1} + w_{n,2} + w_{n,3}$ where $w_{n,1} = \mathbb{1}_{B(0,L_n/2)} w$, $w_{n,2} = \mathbb{1}_{B(2\mathbf{x}_n, L_n/2)} w$ and $w_{n,3} = w - w_{n,1} - w_{n,2}$. Because w is exponentially decreasing, we have $\|w_{n,2}\|_{L^\infty(\mathbb{R}^2)} = O(L_n^{-\infty})$ and $\|w_{n,3}\|_{L^1(\mathbb{R}^2)} = O(L_n^{-\infty})$ where the constants only depend on c and α. Then, by Young's inequality, we have

$$\begin{aligned} \left| \left[w * \left(|u|^2 * |\cdot|^{-1} - |\cdot|^{-1} \right) \right] (2\mathbf{x}_n) \right| &\lesssim \left| \left(w_{n,1} * |\cdot|^{-3} \right) (2\mathbf{x}_n) \right| \\ &\quad + \|w_{n,2}\|_{L^\infty(\mathbb{R}^2)} \int_{B(0,L_n/2)} \frac{\mathrm{d}x}{|x|} + \|w_{n,3}\|_{L^1(\mathbb{R}^2)} \\ &\lesssim L_n^{-3} \|w\|_{L^1(\mathbb{R}^2)} + L_n^{-\infty}\,. \end{aligned}$$

When $d = 3$, we replace the estimate $|u|^2 * |\cdot|^{-1} - |\cdot|^{-1} = O\big(|\cdot|^{-3}\big)$ by Newton's theorem and similar arguments show

$$\left| \left[w * \left(|u|^2 * |\cdot|^{-1} - |\cdot|^{-1} \right) \right] (2\mathbf{x}_n) \right| = O\Big(L_n^{-\infty} \left(1 + \|w\|_{L^1(\mathbb{R}^3)} \right) \Big)\,.$$

This concludes the proof of Proposition 2.31. □

4.4 Rate of convergence for the Lagrange multipliers

The next proposition shows that μ_n^- exists for n large enough and gives estimates on the convergence of the Lagrange multipliers $\mu_n^\pm$ toward μ.

Proposition 2.32 (Rate of convergence of Lagrange multipliers)**.** *The diatomic mean-field hamil-*

tonian h_n admits an excited state. Moreover, for any $\epsilon \in (0\,,3)$, there exists $C_\epsilon > 0$ such that

$$|\mu_n^{\pm} - \mu| \leq \begin{cases} C_\epsilon L_n^{-3+\epsilon} & \text{if } d=2\,, \\ O(L_n^{-\infty}) & \text{if } d=3\,, \end{cases} \tag{2.69}$$

for any $\epsilon > 0$.

Proof. Firstly, we estimate $|\mu_n^+ - \mu|$. Using the formulas (recall $\int_{\mathbb{R}^d} |u_n^+|^2 = 2$)

$$\mu = \mathcal{E}(u) + D(|u|^2\,, |u|^2) \quad \text{and} \quad \mu_n^+ = \frac{1}{2}\Big(\mathcal{E}_n(u_n^+) + D(|u_n^+|^2, |u_n^+|^2)\Big)\,,$$

we have

$$\begin{aligned} \left|\mu_n^+ - \mu\right| &= \frac{1}{2}\left|\mathcal{E}_n(u_n^+) - 2\mathcal{E}(u)\right| + \left|D(|v_n|^2\,, |v_n|^2) - D(|u|^2\,, |u|^2)\right| \\ &\quad + \frac{1}{2}\left|D\left(\left|\chi_n^\ell u_n^+\right|^2, \left|\chi_n^r u_n^+\right|^2\right) - \frac{1}{2L_n}\right|\,, \end{aligned} \tag{2.70}$$

where we have denoted $v_n = \tau_{\mathbf{x}_n}\chi_n^\ell u_n^+$. From the proof of Proposition 2.29 and the fact (see Lemma 2.18)

$$\mathcal{Q}_n(u) = \begin{cases} O\big(L_n^{-5}\big) & \text{if } d=2\,, \\ O(L_n^{-\infty}) & \text{if } d=3\,, \end{cases}$$

we have the estimate

$$\left|\mathcal{E}_n(u_n^+) - 2\mathcal{E}(u)\right| = \begin{cases} O\big(L_n^{-5}\big) & \text{if } d=2\,, \\ O(L_n^{-\infty}) & \text{if } d=3\,, \end{cases}$$

for any $\epsilon > 0$. For the second term, we use the Hardy-Littlewood-Sobolev inequality, Hölder's inequality, the uniform estimates (see for instance Proposition 2.8 for u and Corollary 2.23 for u_n^+)

$$\forall r \in [2\,,\infty], \quad \|u\|_{L^r(\mathbb{R}^d)} < \infty \quad \text{and} \quad \sup_n \left\|u_n^+\right\|_{L^r(\mathbb{R}^d)} < \infty\,,$$

and Proposition 2.29 to get

$$\begin{aligned} \left|D(|v_n|^2\,, |v_n|^2) - D(|u|^2\,, |u|^2)\right| &\leq \left\||u|^2 - |v_n|^2\right\|_{L^{\frac{2d}{2d-1}}(\mathbb{R}^d)} \left(\|u\|^2_{L^{\frac{4d}{2d-1}}(\mathbb{R}^d)} + \|v_n\|^2_{L^{\frac{4d}{2d-1}}(\mathbb{R}^d)}\right) \\ &= \begin{cases} O\big(L_n^{-3+\epsilon}\big) & \text{if } d=2\,, \\ O(L_n^{-\infty}) & \text{if } d=3\,. \end{cases} \end{aligned}$$

As in the proof of Proposition 2.29, the last term (2.70) is estimated using the decomposition (2.61) with the additional information that

$$\|v_{n,1}\|_{L^1(\mathbb{R}^d)} + \|v_{n,1}\|_{L^2(\mathbb{R}^d)} = \begin{cases} O\big(L_n^{-3+\epsilon}\big) & \text{if } d=2\,, \\ O(L_n^{-\infty}) & \text{if } d=3\,. \end{cases}$$

After similar arguments as the ones used in the proof of Proposition 2.29, one can show

$$\left|D\left(\left|\chi_n^\ell u_n^+\right|^2, \left|\chi_n^r u_n^+\right|^2\right) - \frac{1}{2L_n}\right| = \begin{cases} O\big(L_n^{-3+\epsilon}\big) & \text{if } d=2\,, \\ O(L_n^{-\infty}) & \text{if } d=3\,. \end{cases}$$

This concludes the proof of the first estimate in (2.69).

Now, we look at μ_n^-. We recall that μ_n^- is defined by

$$\mu_n^- := \min\left\{\langle v, h_n v\rangle_{L^2(\mathbb{R}^d)} \;\middle|\; v \in \mathcal{D}(h_n), \quad \|v\|_{L^2(\mathbb{R}^d)} = 1 \quad \text{and} \quad v \perp u_n^+\right\}\,. \tag{2.71}$$

We also recall that $u_n^r \coloneqq u(\cdot - \mathbf{x}_n)$ and $u_n^\ell \coloneqq u(\cdot + \mathbf{x}_n)$. Let

$$u_{\text{trial}} \coloneqq \frac{(u_n^r - u_n^\ell)}{\|u_n^r - u_n^\ell\|_{L^2(\mathbb{R}^d)}} .$$

Using the reflection symmetry $\mathcal{R}$, we have that $u_{\text{trial}} \perp u_n^+$. Hence u_{trial} is a trial state for the minimization problem (2.71). We have

$$\langle u_{\text{trial}}, h_n u_{\text{trial}} \rangle_{L^2(\mathbb{R}^d)} = 2 \left\| u_n^r - u_n^\ell \right\|_{L^2(\mathbb{R}^d)}^{-2} \left(\langle u_n^\ell, h_n u_n^\ell \rangle_{L^2(\mathbb{R}^d)} - \langle u_n^\ell, h_n u_n^r \rangle_{L^2(\mathbb{R}^d)} \right) .$$

On one hand, remark that by the uniform estimate $\sup_n \left\| |u_n^+|^2 * |\cdot|^{-1} \right\|_{L^\infty(\mathbb{R}^d)} < \infty$ (which is a consequence of Lemma 2.4 and Corollary 2.23) and by Lemma 2.17, we have

$$\langle u_n^\ell, h_n u_n^r \rangle_{L^2(\mathbb{R}^d)} = O\big(L_n^{-\infty}\big) \quad \text{and} \quad \left\| u_n^r - u_n^\ell \right\|_{L^2(\mathbb{R}^d)}^{-2} = \frac{1}{2} \left(1 + O\big(L_n^{-\infty}\big)\right) .$$

On the other hand, we remark that

$$\langle u_n^\ell, h_n u_n^\ell \rangle_{L^2(\mathbb{R}^d)} - \langle u, hu \rangle_{L^2(\mathbb{R}^d)} = \int_{\mathbb{R}^d} |u|^2 \left(\tau_{\mathbf{x}_n} V_n^{\mathrm{MF}} - V^{\mathrm{MF}} \right) .$$

Then, Proposition 2.31 gives us

$$\langle u_n^\ell, h_n u_n^\ell \rangle_{L^2(\mathbb{R}^d)} = \mu + \begin{cases} O\big(L_n^{-3+\epsilon}\big) & \text{if } d = 2 \,, \\ O\big(L_n^{-\infty}\big) & \text{if } d = 3 \,. \end{cases}$$

All in all, we have shown

$$\langle u_{\text{trial}}, h_n u_{\text{trial}} \rangle_{L^2(\mathbb{R}^d)} \leq \mu + \begin{cases} O\big(L_n^{-3+\epsilon}\big) & \text{if } d = 2 \,, \\ O\big(L_n^{-\infty}\big) & \text{if } d = 3 \,, \end{cases}$$

for any $\epsilon > 0$. In particular, h_n admits a second negative eigenvalue for n large enough and for all $\epsilon > 0$, we have

$$\mu_n^- \leq \mu + \begin{cases} O\big(L_n^{-3+\epsilon}\big) & \text{if } d = 2 \,, \\ O\big(L_n^{-\infty}\big) & \text{if } d = 3 \,. \end{cases}$$

We concludes the proof of (2.69) by noticing $\mu_n^- > \mu_n^+$. □

4.5 Approximation for u_n^-

Now, we come to the study of u_n^- which mainly follows the one conducted for u_n^+ (see Proposition 2.29). Recall that u_n^- is the eigenfunction associated with the second lowest eigenvalue μ_n^- of the mean-field hamiltonian (2.4) of the two nuclei model (2.3). We choose the normalization such that $\|u_n^-\|_{L^2(\mathbb{R}^d)}^2 = 2$. Following step by step the proof of [OR21, Lemma 4.2], we see that u_n^- is odd with respect to the line $\{x_1 = 0\}$ that is we have $\mathcal{R}[u_n^-] = -u_n^-$. Moreover, we can choose u_n^- such that $u_n^- > 0$ on the half-plane $\{x_1 > 0\}$ and $u_n^- < 0$ on the half-plane $\{x_1 < 0\}$.

A consequence of Proposition 2.32 is that u_n^- shares similar *a priori* pointwise bounds as u_n^+ (see Proposition 2.25).

Proposition 2.33 (*A priori* exponential decay estimate for u_n^-)**.** *For all $\epsilon \in (0\,,1)$ and for all n large enough, there exists a constant $C_\epsilon > 0$ such that the following pointwise estimate holds*

$$|u_n^-(x)| \leq C_\epsilon \left(e^{-(1-\epsilon)|\mu|^{\frac{1}{2}}|x - \mathbf{x}_n|} + e^{-(1-\epsilon)|\mu|^{\frac{1}{2}}|x + \mathbf{x}_n|} \right) , \tag{2.72}$$

for all $x \in \mathbb{R}^d$.

Proof. We follow the proof of Proposition 2.25, applying Lemma 2.13 to the domain

$$\left\{(x_1,\ldots,x_d)\in\mathbb{R}^d \;\middle|\; x_1>0 \quad\text{and}\quad |x-\mathbf{x}_n|>R\right\}\,,$$

where we have chosen u_n^- positive. Then, we extend the estimate to the left half space by using the reflection symmetry $\mathcal{R}$. □

Proposition 2.34 (Rates of convergence for u_n^-)**.** *For any $\epsilon\in(0\,,3)$, there exists a constant C_ϵ such that the following estimates hold*

$$\left\||u(\cdot+\mathbf{x}_n)|^2-|\chi_n^\ell u_n^-|^2\right\|_{L^1(\mathbb{R}^d)}=\left\||u(\cdot-\mathbf{x}_n)|^2-|\chi_n^\ell u_n^-|^2\right\|_{L^1(\mathbb{R}^d)}\le\begin{cases}C_\epsilon L_n^{-3+\epsilon} & \textit{if } d=2\,,\\ O(L_n^{-\infty}) & \textit{if } d=3\,,\end{cases}\tag{2.73}$$

$$\left\|u(\cdot+\mathbf{x}_n)+\chi_n^\ell u_n^-\right\|_{H^1(\mathbb{R}^d)}=\left\|u(\cdot-\mathbf{x}_n)-\chi_n^r u_n^-\right\|_{H^1(\mathbb{R}^d)}\le\begin{cases}C_\epsilon L_n^{-3+\epsilon} & \textit{if } d=2\,,\\ O(L_n^{-\infty}) & \textit{if } d=3\,.\end{cases}\tag{2.74}$$

Proof. For u_n^- we will carry out the same strategy as for u_n^+ (see proof of Propositions 2.19 and 2.29). The arguments being similar, we will only sketch the proof. Recall that, by the min-max principle, u_n^- is the unique (up to a phase) minimizer of the problem

$$\min\left\{\langle v,h_n v\rangle_{L^2(\mathbb{R}^d)}\;\middle|\; v\in\mathcal{D}(h_n),\quad v\perp u_n^+,\quad \int_{\mathbb{R}^d}|v|^2=2\right\}\,.\tag{2.75}$$

First, we give an *a priori* estimate on u_n^-. We introduce

$$u_{\text{trial}}=\frac{\sqrt{2}(u_n^r-u_n^\ell)}{\|u_n^r-u_n^\ell\|_{L^2(\mathbb{R}^d)}}\,,$$

which is a valid trial state for the minimization problem (2.75) (using the reflection symmetry, one can check that $u_{\text{trial}}\perp u_n^+$). As in the proof of Proposition 2.32, we obtain

$$\frac12\langle u_{\text{trial}},h_n u_{\text{trial}}\rangle_{L^2(\mathbb{R}^d)}\le\mu+\int_{\mathbb{R}^d}|u|^2\left(\tau_{\mathbf{x}_n}V_n^{\text{MF}}-V^{\text{MF}}\right)+O\!\left(L_n^{-\infty}\right)\tag{2.76}$$

$$\le\mu_n^-+\begin{cases}O\!\left(L_n^{-3+\epsilon}\right) & \text{if } d=2\,,\\ O(L_n^{-\infty}) & \text{if } d=3\,,\end{cases}\tag{2.77}$$

for any $\epsilon\in(0\,,3)$. To get the second bound (2.77), we have used Proposition 2.31 and Proposition 2.32. Hence, u_{trial} is a minimizing sequence for the minimization problem (2.75). Proceeding as in the proof of Proposition 2.19 and Proposition 2.24, we can show that

$$\left\|u_n^--u_{\text{trial}}\right\|_{H^{2-\alpha}(\mathbb{R}^d)}\underset{n\to\infty}{\longrightarrow}0\quad\text{and}\quad\sup_n\left\|u_n^-\right\|_{H^{2-\alpha}(\mathbb{R}^d)}<\infty\,,$$

for any $\alpha>0$ if $d=2$ and $\alpha=0$ if $d=3$. We denote $v_n:=\tau_{\mathbf{x}_n}\chi_n^\ell u_n^-$ which, by $\mathcal{R}$ symmetry, satisfies $\|v_n\|_{L^2(\mathbb{R}^d)}=1$. Using the IMS formula and the $\mathcal{R}$ symmetry, we get

$$\begin{aligned}\frac12\langle u_n^-,h_n u_n^-\rangle_{L^2(\mathbb{R}^d)}&=\langle\chi_n^\ell u_n^-,h_n\chi_n^\ell u_n^-\rangle_{L^2(\mathbb{R}^d)}-\int_{\mathbb{R}^d}\left|\nabla\chi_n^\ell\right|^2|u_n^-|^2\\&=\langle v_n,hv_n\rangle_{L^2(\mathbb{R}^d)}+\int_{\mathbb{R}^d}|v_n|^2\left(\tau_{\mathbf{x}_n}V_n^{\text{MF}}-V^{\text{MF}}\right)-\int_{\mathbb{R}^d}\left|\nabla\chi_n^\ell\right|^2|u_n^-|^2\,.\end{aligned}$$

We bound from below the first term using Proposition 2.26 and the the last term is a $O(L_n^{-\infty})$ by Proposition 2.33. Thus, we obtain

$$\frac12\langle u_n^-,h_n u_n^-\rangle_{L^2(\mathbb{R}^d)}\ge\mu+\int_{\mathbb{R}^d}|v_n|^2\left(\tau_{\mathbf{x}_n}V_n^{\text{MF}}-V^{\text{MF}}\right)+C\min_{\theta\in[0,2\pi]}\left\|e^{i\theta}v_n-u\right\|_{H^1(\mathbb{R}^d)}^2+O\!\left(L_n^{-\infty}\right)\,.$$

Recalling (2.76), using Proposition 2.31, the fact that $\sup_{n\in\mathbb{N}}\|v_n\|_{H^1(\mathbb{R}^d)}<\infty$ and the Cauchy-

Schwarz inequality, we get

$$\min_{\theta\in[0,2\pi]} \left\|e^{i\theta}v_n - u\right\|^2_{H^1(\mathbb{R}^d)} \leq \begin{cases} O(L_n^{-3+\epsilon})\left(\|v_n+u\|_{L^1(\mathbb{R}^d)} + \|v_n+u\|_{L^2(\mathbb{R}^d)}\right) + O(L_n^{-\infty}) & \text{if } d=2\,,\\ O(L_n^{-\infty})\left(1+\|v_n+u\|_{L^1(\mathbb{R}^d)} + \|v_n+u\|_{L^2(\mathbb{R}^d)}\right) & \text{if } d=3\,,\end{cases}$$

since $u_n^- < 0$ on $\{x_1<0\}$. Because v_n and u are exponentially decaying, we have $\|v_n+u\|_{L^1(\mathbb{R}^d)} \leq O\Big(L^\epsilon \|v_n+u\|_{L^2(\mathbb{R}^d)}\Big) + O(L_n^{-\infty})$ for any $\epsilon>0$. Hence, we have obtained

$$\min_{\theta\in[0,2\pi]} \left\|e^{i\theta}v_n - u\right\|^2_{H^1(\mathbb{R}^d)} \leq \begin{cases} C_\epsilon L_n^{-3+\epsilon}\|v_n+u\|_{L^2(\mathbb{R}^d)} + O(L_n^{-\infty}) & \text{if } d=2\,,\\ O(L_n^{-\infty})\left(1+\|v_n+u\|_{L^2(\mathbb{R}^d)}\right) & \text{if } d=3\,,\end{cases}$$

for all $\epsilon>0$. Now, the minimization problem

$$\min_{\theta\in[0,2\pi]} \left\|e^{i\theta}v_n - u\right\|^2_{L^2(\mathbb{R}^d)}\,,$$

is solved for $\theta=\pi$. To see this, one can expand $\left\|e^{i\theta}v_n - u\right\|^2_{L^2(\mathbb{R}^d)}$ and notice that $\langle v_n, u\rangle_{L^2(\mathbb{R}^d)} \leq 0$. Thus, we get

$$\|v_n+u\|_{H^1(\mathbb{R}^d)} \leq \begin{cases} C_\epsilon L_n^{-3+\epsilon} & \text{if } d=2\,,\\ O(L_n^{-\infty}) & \text{if } d=3\,.\end{cases}$$

To obtain (2.73), we just have to recall the estimate $\|v_n+u\|_{L^1(\mathbb{R}^d)} \leq O\Big(L_n^\epsilon \|v_n+u\|_{L^2(\mathbb{R}^d)}\Big) + O(L_n^{-\infty})$. This concludes the proof of Proposition 2.34. □

4.6 Lower bound on the second gap

Proposition 2.35 (Lower bound on the second gap)**.** *There exists a constant $C>0$ such that*

$$\mathrm{d}(\mu_n^-, \sigma(h_n)\setminus\{\mu_n^+,\mu_n^-\}) \geq C\,. \tag{2.78}$$

Proof. We denote by $q_{h_n^r}$ (resp. $q_{h_n^r}$, resp. q_{h_n}) the quadratic form associated with h_n^r (resp. h_n^ℓ, resp. h_n) and defined on $H^1(\mathbb{R}^d)$. We consider $v\in H^1(\mathbb{R}^d)$ such that $\|v\|^2_{L^2(\mathbb{R}^2)}=1$, $v\perp u_n^+$ and $v\perp u_n^-$. We denote $G_n \coloneqq \mathrm{d}(\mu_n^-, \sigma(h_n)\setminus\{\mu_n^+,\mu_n^-\}) \geq 0$. Using the IMS formula, Proposition 2.19 and Corollary 2.20, we have

$$\mu + G_n + o(1) = \mu_n^- + G_n \geq q_{h_n}(v) = q_{h_n^\ell}(\chi_n^\ell v) + q_{h_n^r}(\chi_n^r v) + o(1)\,. \tag{2.79}$$

Then, by Proposition 2.26, we have for some $C>0$

$$\begin{aligned} q_{h_n^\ell}(\chi_n^\ell v) &\geq \left\|\chi_n^\ell v\right\|^2_{L^2(\mathbb{R}^d)}(\mu+2C) - 2C\left\|\chi_n^\ell v\right\|_{L^2(\mathbb{R}^d)}\left|\left\langle \chi_n^\ell v, u_n^\ell\right\rangle_{L^2(\mathbb{R}^d)}\right|\\ &\geq \left\|\chi_n^\ell v\right\|^2_{L^2(\mathbb{R}^d)}(\mu+2C) - 2C\left|\left\langle \chi_n^\ell v, u_n^\ell\right\rangle_{L^2(\mathbb{R}^d)}\right|\,.\end{aligned}$$

A similar lower bound also holds for $q_{h_n^r}(\chi_n^r v)$. Inserting these estimates into (2.79), we obtain

$$G_n \geq 2C\left(1 - \left|\left\langle \chi_n^\ell v, u_n^\ell\right\rangle_{L^2(\mathbb{R}^d)}\right| - \left|\left\langle \chi_n^r v, u_n^r\right\rangle_{L^2(\mathbb{R}^d)}\right|\right) + o(1)\,. \tag{2.80}$$

Proposition 2.19 and the orthogonality condition $v\perp u_n^+$ imply

$$0 = \left\langle \chi_n^\ell v, \chi_n^\ell u_n^+\right\rangle_{L^2(\mathbb{R}^d)} + \left\langle \chi_n^r v, \chi_n^r u_n^+\right\rangle_{L^2(\mathbb{R}^d)} = \left\langle \chi_n^\ell v, u_n^\ell\right\rangle_{L^2(\mathbb{R}^d)} + \left\langle \chi_n^r v, u_n^r\right\rangle_{L^2(\mathbb{R}^d)} + o(1)\,. \tag{2.81}$$

In a same manner, using Proposition 2.34, we also have

$$0 = \left\langle v, u_n^-\right\rangle_{L^2(\mathbb{R}^d)} = -\left\langle \chi_n^\ell v, u_n^\ell\right\rangle_{L^2(\mathbb{R}^d)} + \left\langle \chi_n^r v, u_n^r\right\rangle_{L^2(\mathbb{R}^d)} + o(1)\,. \tag{2.82}$$

Suitable linear combinations of (2.81) and (2.82) give

$$\langle \chi_n^r v, u_n^r \rangle_{L^2(\mathbb{R}^d)} = o(1) \quad \text{and} \quad \langle \chi_n^\ell v, u_n^\ell \rangle_{L^2(\mathbb{R}^d)} = o(1)\ .$$

Inserting this into (2.80) shows (2.78). □

4.7 Convergence rates in higher Sobolev spaces

Proposition 2.36 (Convergence rate in higher Sobolev spaces)**.** *Let $\alpha \in (0\,,1)$ if $d=2$ and $\alpha = 0$ if $d=3$. For any $\epsilon \in (0\,,3)$, there exists a constant $C_\epsilon > 0$ such that the following estimates hold*

$$\left\| u_n^\pm - (u(\cdot - \mathbf{x}_n) \pm u(\cdot + \mathbf{x}_n)) \right\|_{H^{2-\alpha}(\mathbb{R}^d)} \le \begin{cases} C_\epsilon L_n^{-3+\epsilon} & \text{if } d=2\,,\\ O(L_n^{-\infty}) & \text{if } d=3\,. \end{cases}$$

Proof. We do the proof for u_n^+, the arguments being similar for u_n^-. Let $\alpha \in (0\,,\frac{1}{2})$. We write

$$\begin{aligned} (-\Delta + |\mu|)^{1-\alpha}\left(u_n^+ - (u_n^r + u_n^\ell)\right) = \frac{1}{(-\Delta+|\mu|)^\alpha}\Big[&(\mu_n^+ - \mu)u_n^+ && (2.83)\\ &+ \left((\tau_n^r + \tau_n^\ell)V^{\mathrm{MF}} - V_n^{\mathrm{MF}}\right)u_n^+ && (2.84)\\ &+ (1+\mathcal{R})\left[(\tau_n^r V^{\mathrm{MF}})(u_n^r - \chi_n^r u_n^+)\right] && (2.85)\\ &+ (1+\mathcal{R})\left[(\tau_n^r V^{\mathrm{MF}})(\chi_n^r - 1)u_n^+\right]\Big]\,. && (2.86) \end{aligned}$$

The right side of (2.83) is bounded in L^2 using Proposition 2.32 and the boundedness of $(-\Delta + |\mu|)^{-\alpha}$. The term (2.84) is bounded using Hölder's inequality, estimate (2.68) from the proof of Proposition 2.31 and Corollary 2.23. To bounds (2.85), we write

$$\begin{aligned} &\left\| \frac{1}{(-\Delta+|\mu|)^\alpha}(\tau_n^r V^{\mathrm{MF}})(u_n^r - \chi_n^r u_n^+) \right\|_{L^2(\mathbb{R}^d)} \\ &\lesssim \left\| \frac{1}{(-\Delta+|\mu|)^\alpha}\left(1 + \frac{1}{|x|}\right)\frac{1}{(-\Delta+|\mu|)^{-\frac{1}{2}+\alpha}} \right\| \left\| u_n^r - \chi_n^r u_n^+ \right\|_{H^{1-2\alpha}(\mathbb{R}^d)}\,, \end{aligned}$$

then we use Lemma 2.10 and Proposition 2.29. Finally, to bound (2.86), we recall that $\mathrm{supp}(1 - \chi_n^r) \subset \{x_1 \le \delta\sqrt{L_n}\}$ for some $\delta > 0$. Then, using Lemma 2.15 and $\sup_n \|u_n^+\|_{L^\infty(\mathbb{R}^d)} < \infty$, we obtain

$$\left\|(\tau_n^r V^{\mathrm{MF}})(\chi_n^r - 1)u_n^+\right\|_{L^2(\mathbb{R}^d)} \le \begin{cases} O(L_n^{-3}) & \text{if } d=2\,,\\ O(L_n^{-\infty}) & \text{if } d=3\,. \end{cases}$$

This ends the proof of Proposition 2.36. □

4.8 Sharper exponential bounds for $u_n^\pm$

Proposition 2.37 (Sharper exponential pointwise bounds for u_n^+)**.** *There exists $C > 0$ such that for n large enough we have for all $x \in \mathbb{R}^d$*

$$u_n^+(x) \ge \frac{1}{C}\left(\frac{e^{-\left(|\mu|+L_n^{-1}\right)^{\frac{1}{2}}|x-\mathbf{x}_n|}}{1+|x-\mathbf{x}_n|^{\frac{d-1}{2}}} + \frac{e^{-\left(|\mu|+L_n^{-1}\right)^{\frac{1}{2}}|x+\mathbf{x}_n|}}{1+|x+\mathbf{x}_n|^{\frac{d-1}{2}}}\right)\,, \tag{2.87}$$

$$u_n^+(x) \le C\left(\frac{e^{-\left(|\mu|-L_n^{-1}\right)^{\frac{1}{2}}|x-\mathbf{x}_n|}}{1+|x-\mathbf{x}_n|^{\frac{d-1}{2}}} + \frac{e^{-\left(|\mu|-L_n^{-1}\right)^{\frac{1}{2}}|x+\mathbf{x}_n|}}{1+|x+\mathbf{x}_n|^{\frac{d-1}{2}}}\right)\,. \tag{2.88}$$

Proof. We write the proof in details in the case $d=2$ and mention the modifications when $d=3$. By Lemma 2.4, Corollary 2.20 and Proposition 2.29, we can write

$$V_n^{\mathrm{MF}} = \left(\tau_n^\ell + \tau_n^r\right)V^{\mathrm{MF}} + O\left(L_n^{-2}\right)\,, \tag{2.89}$$

where the O makes sense in $L^\infty(\mathbb{R}^2)$. By Proposition 2.32, we have

$$\mu_n^+ = \mu + O\big(L_n^{-2}\big)\ . \tag{2.90}$$

By Lemma 2.15, there exists $R > 0$ such that

$$0 \leq V^{\mathrm{MF}}(x) \leq |x|^{-2}\ , \tag{2.91}$$

for all $|x| \geq R$. Let $\Omega = B(-\mathbf{x}_n, R)^c \cup B(\mathbf{x}_n, R)^c$. For $\alpha \geq 0$, we introduce

$$Y_{n,\alpha,\pm} = K_\alpha\left(\big(|\mu| \pm L_n^{-1}\big)^{\frac{1}{2}} |x|\right)\ ,$$

where K_α denotes the modified Bessel function of the second kind with parameter α. The function $Y_{n,\alpha,\pm}$ is positive and satisfies the equation

$$\left(-\Delta + \frac{\alpha}{|x|} - \mu \pm L_n^{-1}\right) Y_{n,\alpha,\pm} = 0\,,$$

in the region $\{|x| \geq R\}$. Fix $A > 0$. Using the following asymptotics [Olv97, pp. 266–267]

$$\forall x > 0, \quad K_\alpha(x) = \sqrt{\frac{\pi}{2x}}e^{-x}\left(1 + R(\alpha, x)\right) \quad \text{where} \quad |R(\alpha,x)| \leq \left|\alpha^2 - 1/4\right| \frac{e^{\frac{|\alpha^2-1/4|}{x}}}{x}\,,$$

we show there exists $C > 0$ such that

$$\frac{1}{C\sqrt{|x|}}e^{-\left(|\mu| \pm L_n^{-1}\right)^{\frac{1}{2}}|x|} \leq Y_{n,\alpha,\pm}(x) \leq \frac{C}{\sqrt{|x|}}e^{-\left(|\mu| \pm L_n^{-1}\right)^{\frac{1}{2}}|x|}\,, \tag{2.92}$$

for n large enough (depending only on A), for all $|x| \geq R$ and for all $\alpha \in [0\,, A]$. In the following, we denote by $Y^{\ell/r}_{n,\alpha,\pm} = \tau_n^{\ell/r} Y_{n,\alpha,\pm}$ the translations of $Y_{n,\alpha,\pm}$ by $\mathbf{x}_n$ or $-\mathbf{x}_n$.

First, we show the upper bound $u_n^+ \leq C\left(Y^r_{n,0,-} + Y^\ell_{n,0,-}\right)$ on $\mathbb{R}^2$ for some constant $C > 0$. By Proposition 2.24, there exists $C > 0$ such that $u_n^+ \leq C\left(Y^r_{n,0,-} + Y^\ell_{n,0,-}\right)$ on Ω^c. Using (2.89), (2.90) and the first inequality in (2.91), we have for n large enough

$$\begin{aligned}
\left(-\Delta + V_n^{\mathrm{MF}} - \mu_n^+\right)\left(Y^r_{n,0,-} + Y^\ell_{n,0,-}\right) &= \left(V_n^{\mathrm{MF}} - \mu_n^+ + \mu + L_n^{-1}\right)\left(Y^r_{n,0,-} + Y^\ell_{n,0,-}\right) \\
&\geq \left((\tau_n^\ell + \tau_n^r)V^{\mathrm{MF}} + L_n^{-1} + O\big(L_n^{-2}\big)\right)\left(Y^r_{n,0,-} + Y^\ell_{n,0,-}\right) \\
&\geq 0\,.
\end{aligned}$$

By the second comparison Lemma 2.13, we deduce

$$u_n^+ \leq C\left(Y^r_{n,0,-} + Y^\ell_{n,0,-}\right) \quad \text{on} \quad \mathbb{R}^2\,. \tag{2.93}$$

Now, we show the lower bound $u_n^+ \geq C^{-1}\left(Y^r_{n,\alpha,+} + Y^\ell_{n,\alpha,+}\right)$ for some $\alpha > 2$. By Proposition 2.24, there exists $C > 0$ such that $u_n^+ \geq C^{-1}\left(Y^r_{n,\alpha,+} + Y^\ell_{n,\alpha,+}\right)$ on Ω^c. Using (2.89), (2.90) and the second inequality in (2.91), we have for n large enough

$$\begin{aligned}
\left(-\Delta + V_n^{\mathrm{MF}} - \mu_n^+\right)\left(Y^r_{n,\alpha,+} + Y^\ell_{n,\alpha,+}\right) &\leq \left(\frac{1}{|x+\mathbf{x}_n|^2} - \frac{\alpha-1}{|x-\mathbf{x}_n|^2}\right)Y^r_{n,\alpha,+} \\
&\quad + \left(\frac{1}{|x-\mathbf{x}_n|^2} - \frac{\alpha-1}{|x+\mathbf{x}_n|^2}\right)Y^\ell_{n,\alpha,+} \\
&\leq\ (1+\mathcal{R})\left[f_n Y^r_{n,\alpha,+}\right]\ ,
\end{aligned}$$

where we have denoted $f_n(x) = \frac{1}{|x+\mathbf{x}_n|^2} - \frac{\beta}{|x-\mathbf{x}_n|^2}$ and $\beta = \alpha - 1 > 1$. An elementary computation shows that $f_n(x) \geq 0$ if and only if $x \in \mathcal{C}_\beta$ where $\mathcal{C}_\beta$ is the disk defined by $\{|x + \gamma_\beta \mathbf{x}_n| \leq s_\beta \frac{L_n}{2}\}$

with $\gamma_\beta = \frac{\beta+1}{\beta-1}$ and $s_\beta = \frac{2\sqrt{\beta}}{\beta-1}$. We also have

$$d_{\min} := \mathrm{d}(\mathbf{x}_n, \mathcal{C}_\beta) = \frac{2\sqrt{\beta}}{\sqrt{\beta}+1}\frac{L_n}{2} \quad \text{and} \quad d_{\max} := \max_{x\notin\mathcal{C}_\beta}|x+\mathbf{x}_n| = \frac{2}{\sqrt{\beta}-1}\frac{L_n}{2}\,.$$

Let $x\in\mathcal{C}_\beta\setminus B(0,R)$. Using the estimates (2.92), we see that

$$\begin{aligned} f_n(x)Y^r_{n,\alpha,+}(x) &\le \frac{C}{R^2\sqrt{d_{\min}}}e^{-\left(|\mu|+L_n^{-1}\right)^{\frac12}d_{\min}}\,,\\ \mathcal{R}[f_nY^r_{n,\alpha,+}](x) &\le -\frac{\beta-1}{|x+\mathbf{x}_n|^2}\frac{C}{\sqrt{d_{\max}}}e^{-\left(|\mu|+L_n^{-1}\right)^{\frac12}d_{\max}}\,. \end{aligned}$$

Comparing the exponents, we see the amplitude of the second term is larger if we choose $\alpha>2$ such that $\frac{2\sqrt{\beta}}{\sqrt{\beta}+1}\ge\frac{2}{\sqrt{\beta}-1}+1$ that is if $\alpha\ge 10+4\sqrt{5}$. As a consequence, for n large enough, we have

$$\left(-\Delta+V_n^{\mathrm{MF}}-\mu_n^+\right)\left(Y^r_{n,\alpha,+}+Y^\ell_{n,\alpha,+}\right)\le 0\,,$$

on Ω and, by the second comparison Lemma 2.13, we have

$$u_n^+\ge C^{-1}\left(Y^r_{n,\alpha,+}+Y^\ell_{n,\alpha,+}\right) \quad \text{on} \quad \mathbb{R}^2\,. \tag{2.94}$$

We obtain the exponential bounds (2.87) and (2.88) for u_n^+ by using (2.93) and (2.94) together with (2.92).

For the case $d=3$, we use modified spherical Bessel functions instead of K_α. The rest of the argument is the same. □

Remark 2.38. In the statement of Proposition 2.37, we can replace L_n^{-1} by $L_n^{-\delta}$ for any $\delta>0$ if $d=2$ and by L_n^{-k} for any $k\in\mathbb{N}$ if $d=3$, the constant C remaining independent from δ or k.

4.9 Estimate on the spectral gap $\mu_L^- - \mu_L^+$

In this section, we estimate the spectral gap $\mu_n^- - \mu_n^+$. From Proposition 2.32, we already know that $|\mu_n^- - \mu_n^+| = O\big(L_n^{-3+\epsilon}\big)$ for any $\epsilon>0$. The next theorem says this gap is in fact exponentially small.

Theorem 2.39 (Spectral gap estimation)**.** *There exists $C>0$ such that we have for n large enough*

$$\boxed{\frac{1}{C}\frac{T_n}{L_n^d}\le \mu_n^- - \mu_n^+\le CT_n\,.} \tag{2.95}$$

As in [Sim84a, Proposition 2.2] or [OR21], we use the ground state substitution formula to improve the convergence rate.

Lemma 2.40 (Ground state substitution formula [Sim84a])**.** *Let $\Omega\subset\mathbb{R}^d$ be an open set. Let $H=-\Delta+V$ be a bounded from below self-adjoint operator on $L^2(\Omega)$. Let ψ (resp. λ) denotes the ground state (resp. ground state energy) associated with H. Let g be any $\mathcal{C}^1(\Omega)$ uniformly bounded function. Then, we have*

$$\langle g\psi,(H-\lambda)\,g\psi\rangle_{L^2(\Omega)}=\frac12\left\|(\nabla g)\psi\right\|^2_{L^2(\Omega)}\,.$$

Proof of Theorem 2.39. Let $\epsilon>0$. We introduce the set

$$\Omega_n := \left\{x\in\mathbb{R}^2 \;\middle|\; |x-\mathbf{x}_n|\le L_n \quad \text{and} \quad |x+\mathbf{x}_n|\le L_n\right\}\,.$$

To get the upper bound in (2.95), we use Lemma 2.40 with a function $g_n \in \mathcal{C}^1(\mathbb{R}^d)$ satisfying

$$\mathcal{R}[g_n] = -g_n \ , \quad -1 \leq g_n \leq 1 \ , \quad \sup_n \|\nabla g_n\|_{L^\infty(\mathbb{R}^d)} < \infty \,,$$
$$g_n \equiv 1 \text{ on } B\left(\mathbf{x}_n, \frac{L_n - \delta}{2}\right) \quad \text{and} \quad g_n \equiv 0 \text{ on } \Omega_n^c \,,$$

for some constant $\delta > 0$. Using the reflection symmetry $\mathcal{R}$, we have $g_n u_n^+ \perp u_n^+$. Hence, $g_n u_n^+$ is a trial state for the minimization problem (2.75) and we have

$$\mu_n^- - \mu_n^+ \leq \frac{\langle g_n u_n^+, (h_n - \mu_n^+)\, g_n u_n^+ \rangle_{L^2(\mathbb{R}^d)}}{\|g_n u_n^+\|^2_{L^2(\mathbb{R}^d)}} = \frac{1}{2}\left(\frac{\|(\nabla g_n) u_n^+\|_{L^2(\mathbb{R}^d)}}{\|g_n u_n^+\|_{L^2(\mathbb{R}^d)}}\right)^2 .$$

Using the exponential bounds for u_n^+ (see for instance Proposition 2.25) and

$$\operatorname{supp} \nabla g_n \subset \Omega_n \setminus \left(B\left(\mathbf{x}_n, \frac{L_n-\delta}{2}\right) \cup B\left(-\mathbf{x}_n, \frac{L_n - \delta}{2}\right)\right) ,$$

one can show that for n large enough $\|g_n u_n^+\|^2_{L^2(\mathbb{R}^d)} \geq 1$. Moreover, using the sharper exponential bounds on u_n^+ from Proposition 2.37, we also have

$$\left\|(\nabla g_n)\, u_n^+\right\|^2_{L^2(\mathbb{R}^d)} \lesssim \int_{\frac{L_n-\delta}{2} \leq |x| \leq 2L_n} \frac{e^{-2(|\mu| - L_n^{-1})^{\frac12} |x|}}{1 + |x|^{d-1}}\,\mathrm{d}x \lesssim e^{-(|\mu| - L_n^{-1})^{\frac12}(L_n - \delta)} \lesssim e^{-|\mu|^{\frac12} L_n} = T_n \,.$$

for some $C_\epsilon > 0$. This gives the upper bound of (2.95).

To get the lower bound in (2.95), we introduce a function $f_n \in \mathcal{C}^1(\mathbb{R}^d)$ satisfying the following conditions

$$\mathcal{R}[f_n] = f_n \ , \quad 0 \leq f_n \leq 1 \ , \quad \sup_n \|\nabla f_n\|_{L^\infty(\mathbb{R}^d)} < \infty \,, \tag{2.96}$$
$$f_n \equiv 1 \text{ on } \Omega_n \quad \text{and} \quad f_n \equiv 0 \text{ on } \left(\Omega_n + B(0,1)\right)^c . \tag{2.97}$$

We notice that by Proposition 2.33 we have

$$\left\|f_n u_n^- - u_n^-\right\|^2_{H^1(\mathbb{R}^d)} \lesssim \int_{\Omega_n^c} \left(\left|\nabla u_n^-\right|^2 + \left|u_n^-\right|^2\right) = O\big(L_n^{-\infty} T_n\big) \ .$$

This implies $\|f_n u_n^-\|^2_{L^2(\mathbb{R}^2)} = 2 + O(L_n^{-\infty} T_n)$. Then, recalling that for all $\epsilon > 0$ there exists $C_\epsilon > 0$ such that $0 \leq h_n - \mu_n^+ \leq -(1+\epsilon)\Delta + C_\epsilon$ in the sense of quadratic forms, we obtain

$$\begin{aligned}
\mu_n^- - \mu_n^+ = \frac{1}{2}\left\langle u_n^-, (h_n - \mu_n^+) u_n^- \right\rangle_{L^2(\mathbb{R}^2)} &= \frac{1}{2}\left\langle f_n u_n^-, (h_n - \mu_n^+) f_n u_n^- \right\rangle_{L^2(\mathbb{R}^d)} + O\Big(\left\|f_n u_n^- - u_n^-\right\|^2_{H^1(\mathbb{R}^d)}\Big) \\
&= \frac{1}{2}\left\langle f_n u_n^-, (h_n - \mu_n^+) f_n u_n^- \right\rangle_{L^2(\mathbb{R}^d)} + O\big(L_n^{-\infty} T_n\big) \ .
\end{aligned}$$

We want to apply Lemma 2.40 with $\widetilde{f}_n = f_n u_n^- / u_n^+$ which is well-defined since $u_n^+ > 0$. First, by Proposition 2.3, we have $\widetilde{f}_n \in \mathcal{C}^1(\mathbb{R}^d \setminus \{\pm \mathbf{x}_n\})$. Using Lemma 2.40, we get

$$\mu_n^- - \mu_n^+ = \frac{1}{2}\left\langle \tilde{f}_n u_n^+, (h_n - \mu_n^+)\tilde{f}_n u_n^+ \right\rangle_{L^2(\mathbb{R}^d)} + O\big(L_n^{-\infty} T_n\big) = \frac{1}{4}\left\|(\nabla \widetilde{f}_n) u_n^+\right\|^2_{L^2(\mathbb{R}^d)} + O\big(L_n^{-\infty} T_n\big) \ .$$

It remains to bound from below the right side. We write the argument only for $d = 2$, the other case being identical. From Proposition 2.37, Young's inequality and triangle inequality, we have

$$\forall x \in \mathbb{R}^d, \quad u_n^+(x) \gtrsim \frac{e^{-\left(|\mu| + L_n^{-1}\right)^{\frac12} \frac{|x - \mathbf{x}_n| + |x + \mathbf{x}_n|}{2}}}{\left(1 + |x - \mathbf{x}_n| + |x + \mathbf{x}_n|\right)^{\frac12}} \,. \tag{2.98}$$

We consider the set $\Gamma_n = \{0 \leq x_1 \leq L_n/2\} \cap \{|x_2| \leq 1\}$ where we have $|x - \mathbf{x}_n| + |x + \mathbf{x}_n| \leq L_n + 1$. Then, from (2.98), we have

$$\left\| (\nabla \widetilde{f}_n) u_n^+ \right\|_{L^2(\mathbb{R}^2)}^2 \geq \int_{\Gamma_n} \left| (\nabla \widetilde{f}_n) u_n^+ \right|^2 \gtrsim \frac{T_n}{L_n} \int_{\Gamma_n} |\nabla \widetilde{f}_n|^2 \gtrsim \frac{T_n}{L_n} \int_{-1}^{1} \mathrm{d}x_2 \int_0^{\frac{L_n}{2}} \mathrm{d}x_1 \left| \partial_{x_1} \widetilde{f}_n(x_1, x_2) \right|^2 .$$

Because $u_n^- \equiv 0$ on $\{x_1 = 0\}$, we have

$$\begin{aligned} \left| \widetilde{f}_n \left(\frac{L_n}{2}, x_2 \right) \right|^2 &= \left| \widetilde{f}_n \left(\frac{L_n}{2}, x_2 \right) - \widetilde{f}_n(0, x_2) \right|^2 = \left| \int_0^{\frac{L_n}{2}} \mathrm{d}x_1 \partial_{x_1} \widetilde{f}_n(x_1, x_2) \right|^2 \\ &\leq \frac{L_n}{2} \int_0^{\frac{L_n}{2}} \mathrm{d}x_1 \left| \partial_{x_1} \widetilde{f}_n(x_1, x_2) \right|^2 . \end{aligned}$$

Moreover, by Proposition 2.36, u_n^+ and u_n^- converge toward u in the vicinity of $\mathbf{x}_n$ in $L^\infty(\mathbb{R}^2)$. We deduce that for all $|x_2| \leq 1$, we have $\widetilde{f}_n \left(\frac{L_n}{2}, x_2 \right) \geq \frac{1}{2}$ for n large enough. Therefore, we have shown

$$\left\| (\nabla \widetilde{f}_n) u_n^+ \right\|_{L^2(\mathbb{R}^2)}^2 \gtrsim \frac{T_n}{L_n^2} ,$$

which is the lower bound in (2.95). □

Appendix A. Two-dimensional multipole expansion

In this section, we give a precise expansion formula for the quasi-coulombic potential created by a exponentially decreasing charge distribution ρ. When the potential is the Green function of the Laplace operator, this question is resolved by the Newton's theorem [New33] and all the orders except the first one disappear. The situation we consider here is more complicated as the potential is not harmonic but derives from the Green function of the non-local operator $\sqrt{-\Delta}$.

Lemma 2.41. *Let $\rho \in L^1(\mathbb{R}^2)$ be exponentially decaying from the origin, that is $|\rho(x)| \leq C \exp(-\alpha |x|)$ for some $C, \alpha > 0$. For $x \in \mathbb{R}^2 \setminus \{0\}$, we denote $\hat{x} = x/|x|$. Then, for any $N \in \mathbb{N}$, we have the expansion formula up to order N*

$$\left(\rho * |\cdot|^{-1} \right)(x) = \sum_{n=0}^{N-1} \frac{1}{|x|^{n+1}} \left(\int_{\mathbb{R}^2} \rho(y) P_n(\widehat{x} \cdot \widehat{y}) \, |y|^n \, \mathrm{d}y \right) + O\left(\frac{1}{|x|^{N+1}} \right) , \tag{2.99}$$

where the O depends on α, C and N and where P_n denotes the Legendre polynomial *of order n. If ρ is radial then*

$$\int_{\mathbb{R}^2} \frac{\rho(y)}{|x-y|} \, \mathrm{d}y = \sum_{n=0}^{N-1} \frac{1}{4^{2n}} \binom{2n}{n}^2 \frac{1}{|x|^{2n+1}} \left(\int_{\mathbb{R}^2} \rho(y) \, |y|^{2n} \, \mathrm{d}y \right) + O\left(\frac{1}{|x|^{2N+1}} \right) , \tag{2.100}$$

where the O depends on α, C and N.

Proof. Let $x, y \in \mathbb{R}^2$ such that $|x| > |y|$. We recall the identity [AS64, Eq. 22.9.3]

$$\frac{1}{|x-y|} = \frac{1}{(|x|^2 - 2x \cdot y + |y|^2)^{1/2}} = \frac{1}{|x|} \sum_{n=0}^{\infty} P_n(\widehat{x} \cdot \widehat{y}) \left(\frac{|y|}{|x|} \right)^n , \tag{2.101}$$

where P_n denotes the Legendre polynomial of order n. Let $R : \mathbb{R}_+ \to \mathbb{R}_+^*$ be a function such that :

$$\exists \gamma \in (0\,,1), \;\; R(r)/r^\gamma \to \infty \,, \quad \forall r \geq 0, \;\; R(r) \leq r/2 \quad \text{and} \quad \lim_{r \to \infty} R(r)/r = 0 \,.$$

Then, we have for all $x \in \mathbb{R}^2 \setminus \{0\}$

$$\left(\rho * |\cdot|^{-1}\right)(x) = \int_{|y|\leq R(|x|)} \frac{\rho(y)}{|x-y|}\,\mathrm{d}y + \int_{|x-y|\leq R(|x|)} \frac{\rho(y)}{|x-y|}\,\mathrm{d}y + \int_{\min(|y|,|x-y|)>R(|x|)} \frac{\rho(y)}{|x-y|}\,\mathrm{d}y\,. \tag{2.102}$$

Using (2.101) and the estimates (see [AS64, Ineq. 22.14.7] for the first one)

$$\forall\, |z|<1\,, |P_n(x)|\leq 1 \quad \text{and} \quad \forall n\in\mathbb{R},\ \forall R\geq 0\,, \int_{|y|\leq R} e^{-\alpha|y|}\,|y|^n\,\mathrm{d}y \leq 2\pi\frac{R^{n+1}}{n+1}\,, \tag{2.103}$$

we can apply Fubini's theorem for the first term in (2.102)

$$\int_{|y|\leq R(|x|)} \frac{\rho(y)}{|x-y|}\,\mathrm{d}y = \frac{1}{|x|}\sum_{n=0}^{\infty}\frac{\widehat{P}_n(x)}{|x|^n} \quad \text{with} \quad \widehat{P}_n(x) = \int_{|y|\leq R(|x|)} \rho(y)P_n(\widehat{x}\cdot\widehat{y})\,|y|^n\,\mathrm{d}y\,.$$

To bound the second term in (2.102), we use the triangle inequality $|y|\geq|x|-|x-y|$ and the properties of the function R. We get

$$\int_{|x-y|\leq R(|x|)} \frac{\rho(y)}{|x-y|}\,\mathrm{d}y \leq 2\pi C e^{-\alpha|x|}\int_0^{R(|x|)} e^{\alpha r}\,\mathrm{d}r \leq \frac{2\pi}{\alpha}e^{-\alpha(|x|-R(|x|))} \leq \frac{2\pi}{\alpha}e^{-\alpha R(|x|)}\,.$$

The last term in (2.102) is easily estimated by $\frac{2\pi C}{\alpha}\left(1+\frac{1}{\alpha R(|x|)}\right)e^{-\alpha R(|x|)}$. Then, we have shown

$$\left(\rho * |\cdot|^{-1}\right)(x) = \sum_{n=0}^{\infty}\frac{\widehat{P}_n(x)}{|x|^{n+1}} + O\Big(e^{-\alpha R(|x|)}\Big)\,, \tag{2.104}$$

where the O depends only on α and C. We truncate this series expansion up to the order N for some $N\in\mathbb{N}$. Then we use the estimate

$$\left|\int_{|y|>R(|x|)} \rho(y)P_n(\widehat{x}\cdot\widehat{y})\,|y|^{n-1}\,\mathrm{d}y\right| \leq 2\pi C\int_{R(|x|)}^{\infty} r^n e^{-\alpha r}\,\mathrm{d}r = \frac{2\pi C n!}{\alpha^{n+1}}e^{-\alpha R(|x|)}\sum_{k\leq n}\frac{(\alpha R(|x|))^k}{k!}\,,$$

to get

$$\sum_{n\leq N-1}\frac{\widehat{P}_n(x)}{|x|^{n+1}} = \sum_{n\leq N-1}\frac{1}{|x|^{n+1}}\left(\int_{\mathbb{R}^2}\rho(y)P_n(\widehat{x}\cdot\widehat{y})\,|y|^n\,\mathrm{d}y\right) + O\left(\left(\frac{R(|x|)}{|x|}\right)^N e^{-\alpha R(|x|)}\right)\,, \tag{2.105}$$

where the O depends only on C, α and N. Recalling estimates from (2.103), we have

$$\begin{aligned}\left|\sum_{n\geq N}\frac{\widehat{P}_n(x)}{|x|^{n+1}}\right| &\leq 2\pi C\sum_{n\geq N}\frac{1}{n+1}\left(\frac{R(|x|)}{|x|}\right)^{n+1} \leq 2\pi C\sqrt{\sum_{n\geq N}\frac{1}{(n+1)^2}}\sqrt{\sum_{n\geq N}\left(\frac{R(|x|)}{|x|}\right)^{2(n+1)}}\\ &= O\left(\frac{1}{\sqrt{N}}\left(\frac{R(|x|)}{|x|}\right)^{N+1}\right)\,,\end{aligned}$$

where the O depend only on C and N. Of course, we have used the Cauchy-Schwarz inequality to get the second line. We insert this previous estimate and (2.105) into (2.104). By choosing $R(|x|)$ small enough compared to $|x|$, we get (2.99) with $O\Big(|x|^{-N-1+\epsilon}\Big)$ as remaining term for some $\epsilon\in(0\,,1)$. To get rid of the ϵ, we write the next order expansion then truncate the expansion to the last order term.

If we assume that ρ is radial, we can explicitly compute the integral $\int_{\mathbb{R}^2}\rho(y)P_n(\widehat{x}\cdot\widehat{y})\,|y|^n\,\mathrm{d}y$ for $n\in\mathbb{N}$. By radial symmetry, we can assume $\widehat{x}=(1,0)$ and switch to polar coordinates. Identity [AS64, Eq. 22.13.6] show that $\int_0^{2\pi}P_{2n}(\cos\theta)\,\mathrm{d}\theta = \frac{2\pi}{4^{2n}}\binom{2n}{n}^2$. Recall that P_{2n+1} involves only odd degree monomials. As a consequence: $\int_0^{2\pi} P_{2n+1}(\cos\theta)\,\mathrm{d}\theta = 0$. Then, we have shown (2.100). $\square$

Remark 2.42. (i) In the case where ρ is radial, the two first orders are given by

$$\int_{\mathbb{R}^2} \frac{\rho(y)}{|x-y|}\,\mathrm{d}y = \frac{1}{|x|}\int_{\mathbb{R}^2}\rho(y)\,\mathrm{d}y + \frac{1}{4\,|x|^3}\int_{\mathbb{R}^2}\rho(y)\,|y|^2\,\mathrm{d}y + \frac{9}{64\,|x|^5}\int_{\mathbb{R}^2}\rho(y)\,|y|^4\,\mathrm{d}y + O\left(\frac{1}{|x|^7}\right).$$

(ii) More generally, with the same assumptions as in Lemma 2.41 and following a similar proof, we can show that for all $a,\delta>0$ and all $N\geq 0$, we have

$$\int_{|y|\leq(1-\delta)|x|}\frac{\rho(y)}{|x-y|^a}\,\mathrm{d}y = \sum_{n=0}^{N-1}\frac{1}{|x|^{n+a}}\left(\int_{\mathbb{R}^2}\rho(y)C_n^{(a/2)}(\widehat{x}\cdot\widehat{y})\,|y|^n\,\mathrm{d}y\right) + O\left(\frac{1}{|x|^{N+a}}\right), \tag{2.106}$$

where the O depends on C, α, N and a. Here, $C_n^{(a/2)}$ denotes the *ultraspherical* (or *Gegenbauer*) polynomials with parameter $a/2$. The cutoff in (2.106) is mandatory only in the case $a\geq 2$. Otherwise, the $\rho*|\cdot|^{-a}$ would not be well-defined. If ρ is radial, then we can explicit the coefficients

$$\int_{|y|\leq(1-\delta)|x|}\frac{\rho(y)}{|x-y|^a}\,\mathrm{d}y = \sum_{n=0}^{N-1}\binom{-a/2}{n}^2\frac{1}{|x|^{2n+a}}\left(\int_{\mathbb{R}^2}\rho(y)\,|y|^{2n}\,\mathrm{d}y\right) + O\left(\frac{1}{|x|^{2N+a}}\right). \tag{2.107}$$

If we assume that ρ has compact support then we can get rid of the cutoff in (2.106) and (2.107).

Appendix B. Proof of Lemma 2.16

The proof of the first part of (2.32) is given in [GLN21, Lemma 21] where the authors give an efficient proof of in the case $k=\frac{d-1}{2}$ and in dimensions $d\geq 1$. Our proof is more computational, not optimal when $k=\frac{d-1}{2}$ and dimension dependent but we are able to handle estimate the second part of (2.32). We recall the following basic convexity/concavity inequalities

$$\forall k\geq 1,\ \forall a\geq 0,\ 1+a^k\leq(1+a)^k\leq 2^{k-1}(1+a^k), \tag{2.108}$$
$$\forall k\in[0\,,1],\ \forall a\geq 0,\ (1+a)^k\leq 1+a^k\leq 2^{1-k}(1+a)^k. \tag{2.109}$$

First, we treat the $d=2$ case. By radial symmetry, we only have to show the first part of (2.32) for $x=(L,0)$ for any $L\geq 0$. Using (2.108) if $k\geq 1$ or (2.109) if $k\in(0\,,1]$ and after an affine change of variables, we obtain

$$|(v*v)(x)|\lesssim\int_{\mathbb{R}^2}\frac{e^{-\nu(|y-\frac{x}{2}|+|y+\frac{x}{2}|)}}{(1+|y-\frac{x}{2}|)^k\,(1+|y+\frac{x}{2}|)^k}\,\mathrm{d}y\lesssim\int_{\mathbb{R}^2}\frac{e^{-\nu(|y-\frac{x}{2}|+|y+\frac{x}{2}|)}}{(1+|y-\frac{x}{2}|+|y+\frac{x}{2}|)^k}\,\mathrm{d}y.$$

We denote by I the second integral. For all $a\geq L/2$, the level set $|y-\frac{x}{2}|+|y+\frac{x}{2}|=2a$ is the ellipse $\mathcal{E}_a$ with linear excentricity $c=L/2$ and semi-major axis a. Recalling the circumference of $\mathcal{E}_a$ is equal to $4aE(\frac{L}{2a})$ where E denoted the complete elliptic integral of second kind, we have

$$I=\int_{L/2}^{\infty}\frac{e^{-2\nu a}}{(1+2a)^k}\left(\int_{\mathcal{E}_a}\mathrm{d}y\right)\mathrm{d}a=\int_{L/2}^{\infty}\frac{4aE(\frac{L}{2a})}{(1+2a)^k}e^{-2\nu a}\,\mathrm{d}a=\int_L^{\infty}\frac{aE(\frac{L}{a})}{(1+a)^k}e^{-\nu a}\,\mathrm{d}a.$$

The map $e\mapsto E(e)$ being bounded on $[0\,,1]$ by $\frac{\pi}{2}$, we deduce

$$I\leq\frac{\pi}{2}\int_L^{\infty}\frac{e^{-\nu a}}{(1+a)^{k-1}}\,\mathrm{d}a.$$

When $k \geq 1$, we bound $(1+a)^{-(k-1)}$ by $(1+L)^{-(k-1)}$. When $0 \leq k < 1$, an integration by parts leads to

$$I \leq \frac{\pi}{2\nu} \frac{e^{-\nu L}}{(1+L)^{k-1}} + \frac{\pi(1-k)}{2\nu} \int_L^\infty \frac{e^{-\nu a}}{(1+a)^k} \,\mathrm{d}a \leq \frac{\pi e^{-\nu L}}{2\nu} \left(\frac{1}{(1+L)^{k-1}} + \frac{1-k}{\nu(1+L)^k} \right) .$$

Using again the convexity/concavity inequalities (2.108) and (2.109) depending on k shows the first part of (2.32).

To prove the second part of (2.32), we use the same strategy which amounts to bound

$$J := \int_{L/2}^\infty \frac{e^{-2\nu a}}{(1+2a)^k} \left(\int_{\mathcal{E}_a} \frac{\mathrm{d}y}{|y + \frac{x}{2}|} \right) \mathrm{d}a \,.$$

First, we estimate $\int_{\mathcal{E}_a} \frac{\mathrm{d}y}{|y+\frac{x}{2}|}$. Let $b = \sqrt{a^2 - c^2}$ (recall that $c = L/2$) be the semi-minor axis of $\mathcal{E}_a$. Then using the standard parametric representation $y(s) = (a\cos(s), b\sin(s))$, we have

$$\begin{aligned} \left| y(s) + \frac{x}{2} \right| &= \sqrt{(c + a\cos(s))^2 + b^2 \sin^2(s)} = a + c\cos(s) \,, \\ |y'(s)| &= \sqrt{a^2 \sin^2(s) + b^2 \cos^2(s)} = \sqrt{a^2 - c^2\cos^2(s)} \,. \end{aligned}$$

This leads to

$$\int_{\mathcal{E}_a} \frac{\mathrm{d}y}{|y + \frac{x}{2}|} = 2 \int_0^\pi \frac{|y'(s)|}{|y(s) + \frac{x}{2}|} \,\mathrm{d}s = 2 \int_0^\pi \sqrt{\frac{a - c\cos(s)}{a + c\cos(s)}} \,\mathrm{d}s \leq 2\pi \sqrt{\frac{a+c}{a-c}} \leq \frac{2\sqrt{2a}\pi}{\sqrt{a-c}} \,.$$

Going back to J, we have

$$J \leq 2\sqrt{2}\pi \int_{L/2}^\infty \frac{\sqrt{a} e^{-2\nu a}}{(1+2a)^k \sqrt{a-c}} \,\mathrm{d}a \leq \frac{\sqrt{2}\pi}{(1+L)^k} \int_L^\infty \frac{\sqrt{a} e^{-\nu a}}{\sqrt{a-L}} \,\mathrm{d}a \,. \tag{2.110}$$

The map $a \mapsto \frac{\sqrt{a}}{\sqrt{a-L}}$ being decreasing on $(L\,,\infty)$, we get

$$\int_{L+1}^\infty \frac{\sqrt{a} e^{-\nu a}}{\sqrt{a-L}} \,\mathrm{d}a \leq \frac{\sqrt{L+1}}{\nu} e^{-\nu(L+1)} \,.$$

Then, by the Hölder's inequality, we get

$$\int_L^{L+1} \frac{\sqrt{a} e^{-\nu a}}{\sqrt{a-L}} \,\mathrm{d}a \leq \sqrt{L+1} \left(\int_0^1 a^{-\frac{p}{2}} \,\mathrm{d}a \right)^{1/p} \left(\int_L^{L+1} e^{-\nu q a} \,\mathrm{d}a \right)^{1/q} ,$$

where we have choosen $p \in (1\,,2)$ and $q \in (2\,,\infty)$ such that $\frac{1}{p} + \frac{1}{q} = 1$. After some computations, we found

$$\int_L^{L+1} \frac{\sqrt{a} e^{-\nu a}}{\sqrt{a-L}} \,\mathrm{d}a \leq \frac{(1 - e^{-\nu q})^{1/q}}{(\nu q)^{1/q} (1 - p/2)^{1/p}} \sqrt{L+1} e^{-\nu L} \,.$$

We could optimize with respect to p and q but it is not necessary. We inject this two previous estimate into (2.110) and we get

$$J \leq \frac{C'}{(1+L)^{k-\frac{1}{2}}} e^{-\nu L} \,,$$

for some constant C'. Then we use the convexity/concavity inequalities (2.108) or (2.109) depending on k to conclude the proof of the second part of (2.32).

Now, we treat the $d = 3$ case. The arguments are similar so we only give a sketch of the proof.

To show left estimate of (2.32), we have to bound the integral

$$I = \int_{\mathbb{R}^2} \frac{e^{-\nu(\left|y-\frac{x}{2}\right|+\left|y+\frac{x}{2}\right|)}}{(1+\left|y-\frac{x}{2}\right|+\left|y+\frac{x}{2}\right|)^k}\,\mathrm{d}y\,.$$

For all $a \geq L/2$, the level set $\left|y-\frac{x}{2}\right|+\left|y+\frac{x}{2}\right| = 2a$ is a prolate spheroid (or ellipsoid of revolution) denotes $\mathcal{E}_{a,2}$. Its parameters are the distance to the poles a, the equatorial semi-axis $b = \sqrt{a^2-c^2}$ where $c = L/2$ and the eccentricity $e = c/a$. The surface of $\mathcal{E}_{a,2}$ is equal to

$$\int_{\mathcal{E}_{a,2}} \mathrm{d}y = 2\pi\left(b^2 + \frac{ba}{e}\arcsin(e)\right)\,.$$

Using the coarse upper bounds $\arcsin(x)/x \leq \pi/2$ and $b \leq a$, we have

$$\int_{\mathcal{E}_{a,2}} \mathrm{d}y \leq 2\pi\left(1+\frac{\pi}{2}\right)a^2\,.$$

We conclude by performing the same computations as in the two-dimensional case.

It remains to show the right estimate of (2.32) when the $d = 3$. For this aim, we need to evaluate the integral $\int_{\mathcal{E}_{a,2}} \frac{\mathrm{d}y}{\left|y+\frac{x}{2}\right|}$. We introduce the parametrization

$$\forall s \in [0\,,2\pi],\ \forall t \in [0\,,\pi],\ \mathbf{x}(s,t) = \begin{pmatrix} a\cos(s)\cos(t) \\ a\cos(s)\sin(t) \\ b\sin(s)\end{pmatrix}\,.$$

Then, we have

$$\left\|\left(\frac{\partial \mathbf{x}}{\partial s}\wedge\frac{\partial \mathbf{x}}{\partial t}\right)(s,t)\right\| = a\left|\cos(s)\right|\sqrt{a^2-c^2\cos^2(s)}\,,$$
$$\left|\mathbf{x}(s,t)+\frac{x}{2}\right| = \sqrt{a^2+c^2\cos^2(s)+2ac\cos(s)\cos(t)}\,.$$

We denote by K the complete elliptic integral of the first kind. Then, we have

$$\int_{\mathcal{E}_{a,2}} \frac{\mathrm{d}y}{\left|y+\frac{x}{2}\right|} = 4a\int_0^{\pi/2}\cos(s)\sqrt{\frac{a-c\cos(s)}{a+c\cos(s)}}\,K\left(\frac{2\sqrt{e\cos(s)}}{1+e\cos(s)}\right)\mathrm{d}s\,.$$

The maps $e \mapsto K\left(\frac{2\sqrt{e}}{1+e}\right)$ being increasing on $[0\,,1]$, we have

$$\int_{\mathcal{E}_{a,2}} \frac{\mathrm{d}y}{\left|y+\frac{x}{2}\right|} \leq 4aK\left(\frac{2\sqrt{e}}{1+e}\right)\int_0^{\pi/2}\sqrt{\frac{a-c\cos(s)}{a+c\cos(s)}}\,\mathrm{d}s \leq \frac{4\pi a\sqrt{2a}}{\sqrt{a-c}}K\left(\frac{2\sqrt{e}}{1+e}\right)\,.$$

Then, using the inequality $K(k) \leq \pi/2 - \ln(\sqrt{1-k^2})$ which is valid for any $k \in (0\,,1)$, we obtain

$$\int_{\mathcal{E}_{a,2}} \frac{\mathrm{d}y}{\left|y+\frac{x}{2}\right|} \leq \frac{4\pi a\sqrt{2a}}{\sqrt{a-c}}\left(\frac{\pi}{2}+\ln\left(1+\frac{2c}{a-c}\right)\right)\,.$$

The remaining computations are similar to the two-dimensional case. We just need to notice that $t \mapsto \frac{1}{\sqrt{t}\ln(t)}$ is integrable in the vicinity of 0.

Chapter 3

Dirac cones for nonlinear periodic Schrödinger operators at dissociation

Abstract

In this chapter, we show that, in the dissociation regime and under a non-degeneracy assumption, the reduced Hartree-Fock theory of graphene presents Dirac points at the vertices of the first Brillouin zone and that the Fermi level is exactly at the coincidence point of the cones. For this purpose, we first consider a general Schrödinger operator $H = -\Delta + V_L$ acting on $L^2(\mathbb{R}^2)$ with a potential V_L which is assumed to be periodic with respect to some lattice with length scale L. Under some assumptions which covers periodic reduced Hartree-Fock theory, we show that, in the limit $L \to \infty$, the low-lying spectral bands of H_L are given to leading order by the tight-binding model. For the hexagonal lattice of graphene, the latter presents singularities at the vertices of the Brillouin zone. In addition, the shape of the Bloch bands is so that the Fermi level is exactly on the cones.

Contents

1 Introduction

In this chapter, we study the spectral properties of a two-dimensional periodic Schrödinger operator $H = -\Delta + V_L$ acting on $L^2(\mathbb{R}^2)$. We assume that the potential V_L comes from a many-sites lattice

$$\mathscr{L}_L^{\mathbf{R}} \coloneqq L\left(\mathscr{L} + \mathbf{R}\right) = \left\{L(\mathbf{u}+\mathbf{r}) \mid \mathbf{u} \in \mathscr{L},\ \mathbf{r} \in \mathbf{R}\right\}\,, \tag{3.1}$$

where $\mathscr{L}_L \coloneqq L\mathscr{L} \subset \mathbb{R}^2$ is a two-dimensional Bravais lattice with length scale $L > 0$ and $\mathbf{R} \subset \mathbb{R}^2$ is a (finite) collection of sublattice shifts. Such a periodic operator exhibits an electronic band structure, described as a Bloch bundle, which gives the range of energies that an electron, moving in the potential V_L, may attain [Kit04; RS78; Kuc16]. The electronic, optical and magnetic properties of crystals depend on the form of these bands. In particular, the dynamics of a wave packet moving in the structure are strongly influenced by the bands geometry at the vicinity of the initial energy-momentum datum [AM76; Teu03].

If $\mathscr{L}^{\mathbf{R}}$ is the honeycomb lattice, which is appropriate for describing graphene, then we expect the Bloch bundle to have conical singularities, called *Dirac points*, at the vertices of the first Brillouin zone Γ^* [WBB14]. This terminology comes from the fact that wave packets whose energy-momentum is initially concentrated near these singularities evolve according to a two dimensional Dirac wave equation, the equation for massless relativistic fermions [FW14; AS18]. The presence of Dirac points in honeycomb structures was first proved for the tight-binding model of graphene by Wallace [Wal47] and is now established for more realistic ones, including continuous models [FW12; BC18; Lee16; FLW18; LWZ19; HLS12]. However, none of these models considers *interacting* electrons. The main motivation for this chapter is to show that Dirac points also appear when interactions between electrons are taken into account through a nonlinear term in the potential V_L.

The simplest model for interacting electrons that one can think of is the *periodic reduced Hartree-Fock (rHF) model*. Hartree-Fock theories are standard approximation methods for atomic models where the electronic wave function is assumed to have the form of a Slater determinant [Har28; LS77a; Lio87]. In the thermodynamic limit, these models converge to periodic nonlinear models [CLL01; CLL02]. The solution satisfies a nonlinear equation, called the mean-field equation [CDL08; GL08]. When the charges interact through the three-dimensional Coulomb potential $\frac{1}{|\mathbf{x}|}$, the mean-field potential V_L^{MF} in the periodic rHF theory for the crystal whose nuclei are located at the vertices of $\mathscr{L}_L^{\mathbf{R}}$ is solution of

$$V_L^{\mathrm{MF}} = \left[\mathbb{1}_{(-\infty,\epsilon_L]}(-\Delta + V_L^{\mathrm{MF}})(\mathbf{x},\mathbf{x}) - \sum_{\mathbf{r}\in\mathscr{L}_L^{\mathbf{R}}} \delta_{\mathbf{r}}\right] * \frac{1}{|\cdot|}\,. \tag{3.2}$$

In this equation, δ is the Dirac delta and $\epsilon_L \in \mathbb{R}$ a Lagrange multiplier called the Fermi level, which can be interpreted as a chemical potential and is used to adjust the number of electron per unit cell, so that the periodic measure in the square bracket of (3.2) is locally neutral. This is necessary for the convolution with $\frac{1}{|\mathbf{x}|}$ to make sense. It seems natural to expect that graphene will exhibit Dirac cones in rHF theory. However, this does not immediately follow from the existing results which only deal with the linear case.

The *dissociation regime* $L \to \infty$, corresponds to taking the nuclei of the crystal are far from each others. The mean-field potential V_L^{MF} then resembles a superposition of mono-atomic potentials:

$$V_L^{\mathrm{MF}} \simeq \sum_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}} V^{\mathrm{MF}}(\cdot - L\mathbf{r})\,, \tag{3.3}$$

for some potential V^{MF} solution of a mono-atomic Hartree model. Schrödinger operators whose potential is given by an exact periodic superposition of potential wells have already been studied in the literature [Sim84b; Out84; Moh91; FLW18]. It is known that, in the semiclassical limit or in the dissociation regime, the width of the bands is exponentially small, determined by quantum tunneling, and that the geometry of the low-lying bands is given by the tight-binding model associated with the crystal. The latter model is often used to efficiently compute band structures in solid-state physics [GBH97]. However, these results does not cover periodic rHF theory.

In addition, it is very important physically to show that ϵ_L is exactly equal to the energy at which the cones touch. In this chapter, we (partially) solve both questions. In Chapter 4, we study the regime $L \to 0$. We can show that the expected cones exist, but that ϵ_L is *not* equal to the expected energy. The general result is therefore *not* true for all values of L. In this chapter, we study the dissociation limit $L \to \infty$, where we can prove the expected result under a reasonable assumption. Our argument is not quantitative and we have unfortunately nothing to say about the finite physical value $L \simeq 5.36$ of graphene [Coo+12].

For this purpose, we consider a general potential V_L and we exhibit conditions under which the low-lying bands in the dispersion relation of $-\Delta+V_L$ can be approached by the corresponding tight-binding model. These conditions include periodic rHF theory with three-dimensional Coulomb interactions. Also, when the lattice has honeycomb symmetries and under a non-degeneracy condition, we prove the presence of Dirac points and we show, as expected, that the Fermi level ϵ_L is equal to the energy level of the cones.

The conditions under which our main result holds seem quite generic and we think that they could be satisfied by more sophisticated periodic nonlinear models, for instance the periodic Hartree-Fock theory where the exchange term is not neglected, see [CLL01; GL08].

Since our main motivation is the study of crystals sharing the symmetries of graphene, we work in $2D$, although many of our arguments hold the same in arbitrary dimension.

Organization of the chapter

In Section 2, we state our main results. Theorem 3.4 is about the convergence to the tight-binding model of the periodic Schrödinger operator $H_L = -\Delta + V_L$ where V_L satisfies some assumptions. Theorem 3.6 states that, under a non-degeneracy condition, the dispersion relation of H_L presents Dirac points when $\mathscr{L}^{\mathbf{R}}$ is the honeycomb lattice. Theorem 3.7 states that the assumptions in Theorem 3.4 cover the periodic rHF theory with three-dimensional Coulomb interactions plus a pseudo-potential term which must satisfy a ionization condition. In Section 3, we show Theorem 3.4 whose proof strongly relies on the Feshbach-Schur method. In Section 4, we show Theorem 3.6. Section 5 is devoted to the proof of Theorem 3.7 which uses the concentration-compactness method. In Appendix A., we show that there exists pseudo-potentials which satisfy the ionization condition. At last, in Appendix B., we show a perturbation theory result for singular potentials.

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2 Statement of the main results

In this section, we state our main results. First, we recall the basic geometric features of two-dimensional many-site lattices. Then, we consider a periodic potential V_L and we add conditions under which the dispersion relation of $-\Delta + V_L$ is given to leading order by the tight-binding model (Theorem 3.4). In Theorem 3.6, we make this statement more precise when $\mathscr{L}^{\mathbf{R}}$ is the honeycomb lattice: under a non-degeneracy condition, the dispersion relation presents Dirac points. Thereafter, we describe the periodic rHF theory with three-dimensional Coulomb interactions and we state in Theorem 3.7 that this model satisfies the conditions mentioned above.

2.1 Lattices

The scalar product of two vectors $\mathbf{u}$ and $\mathbf{v}$ of $\mathbb{R}^2$ is denoted by $\mathbf{u} \cdot \mathbf{v}$ and the associated euclidean norm by $|\mathbf{u}| = \sqrt{\mathbf{u} \cdot \mathbf{u}}$. Let $(\mathbf{u}_1, \mathbf{u}_2)$ be a basis of $\mathbb{R}^2$. We consider the two-dimensional *Bravais* *lattice*

$$\mathscr{L} := \mathbb{Z}\mathbf{u}_1 + \mathbb{Z}\mathbf{u}_2 \subset \mathbb{R}^2 .$$

We denote by Γ its *Wigner-Seitz cell.* This is a choice of primitive cell whose interior consists of the vectors which are closer to the origin than any other vertex of $\mathscr{L}$. The *reciprocal lattice* $\mathscr{L}^*$ of $\mathscr{L}$ is also a Bravais lattice and is defined by

$$\mathscr{L}^* := \mathbb{Z}\mathbf{v}_1 \oplus \mathbb{Z}\mathbf{v}_2 ,$$

where the reciprocal basis is determined by the orthogonality relations $\mathbf{v}_i \cdot \mathbf{u}_j = 2\pi\delta_{ij}$ for all $(i,j) \in \{1,2\}^2$. The Wigner-Seitz cell of the reciprocal lattice $\mathscr{L}^*$, denoted by Γ^*, is called the *first Brillouin zone.*

In the sequel, we consider lattices formed as a superposition of several shifted copies of $\mathscr{L}$. Let $N \in \mathbb{N}$ be the number of vertices per unit cell and $\mathbf{R} = (\mathbf{r}_1, \ldots, \mathbf{r}_N) \in \Gamma^N$ (where $\mathbf{r}_i \neq \mathbf{r}_j$ if $i \neq j$) be their positions in Γ. The lattice associated with $\mathbf{R}$ is

$$\mathscr{L}^{\mathbf{R}} := \mathscr{L} + \mathbf{R} = \{\mathbf{u} + \mathbf{r} \mid \mathbf{u} \in \mathscr{L},\ \mathbf{r} \in \mathbf{R}\} . \tag{3.4}$$

Let $L \geq 1$ be a length parameter. Thereafter, we will use the subscript L to denote the dilation by a factor L. For instance, we write

$$\mathscr{L}_L = L\mathscr{L}, \quad \Gamma_L = L\Gamma, \quad \mathscr{L}_L^* = L^{-1}\mathscr{L}^*, \quad \Gamma_L^* = L^{-1}\Gamma^* \quad \text{and} \quad \mathscr{L}_L^{\mathbf{R}} = L\mathscr{L}^{\mathbf{R}} .$$

Let $\mathbf{k} \in \mathbb{R}^2$ and $p \in [1\,,\infty]$. The space of locally p-integrable functions satisfying pseudo-periodic boundary conditions with quasi-momentum $\mathbf{k}$ is denoted by

$$L^p_{\mathbf{k}}(\Gamma_L) := \left\{\varphi \in L^p_{\mathrm{loc}}(\mathbb{R}^2, \mathbb{C}) \;\middle|\; \forall \mathbf{u} \in \mathscr{L}_L,\ \forall \mathbf{x} \in \mathbb{R}^2,\ \varphi(\mathbf{x}+\mathbf{u}) = e^{i\mathbf{k}\cdot\mathbf{u}}\varphi(\mathbf{x}) \text{ a.e}\right\} .$$

We will also denote by $L^p_{\mathrm{per}}(\Gamma_L) := L^p_0(\Gamma_L)$ the space of locally p-integrable functions which are invariant under the shifts of $\mathscr{L}_L$.

2.2 A class of periodic operators on $\mathscr{L}_L$

We want to study nonlinear models where the effective potential V_L is close but not exactly given by a $\mathscr{L}_L$-periodic superposition of potentials wells, see (3.3). In this section, we describe the class of Schrödinger operators we consider.

Periodic operator

Our first assumption is about the local singularities that V_L may present.

Assumption 1 (Singularities)**.** *We consider a family $\{V_L\}_{L\geq 1}$ of real-valued potentials on $\mathbb{R}^2$ such that*

(i) $V_L \in L^p_{\mathrm{per}}(\Gamma_L)$ for some $p \in (1\,,\infty)$;

(ii) $\|V_L\|_{L^\infty_{\mathrm{per}}(\Gamma_L)}$ goes uniformly to zero at distance L of the vertices of $\mathscr{L}_L^{\mathbf{R}}$ when L goes to infinity:

$$\forall \rho > 0, \quad \lim_{L\to\infty} \left\| V_L \mathbb{1}_{\mathrm{d}(\cdot, \mathscr{L}_L^{\mathbf{R}}) \geq L\rho} \right\|_{L^\infty_{\mathrm{per}}(\Gamma_L)} = 0 .$$

Remark 3.1. (i) Assumption 1 is not very restrictive and the class of admissible potentials V_L is large. By Assumption 1*(i)*, the potential V_L may present local singularities of the form $|\mathbf{x}|^{-\alpha}$ with $\alpha < 2$, including the three-dimensional Coulomb singularity $\alpha = 1$. Their location is constrained by Assumption 1*(ii)* to the vertices of $\mathscr{L}_L^{\mathbf{R}}$, for simplicity. Also, the dependence of V_L on L can be highly nonlinear as long as its L^p-norm does not blow up faster than polynomials (see estimate (3.31) below). Later in Section 2.3, we will consider a nonlinear model, namely the periodic reduced Hartree-Fock model, and show that the corresponding V_L satisfies Assumption 1.

(ii) In the sequel, we are only concerned with the regime where L is large and thus, we do not consider $L \in (0\,,1)$.

In order to simplify the analysis, we assume that $\mathscr{L}_L$ and V_L are invariant under the same symmetry group. If a group G acts on some set X then the action of $g \in G$ on $x \in X$ will be denoted by $g \cdot x$ or $g[x]$. Let $G \subset E_2(\mathbb{R})$ be a subgroup of $E_2(\mathbb{R})$, the *Euclidean group* (or group of isometries) of $\mathbb{R}^2$. The action of G on $\mathbb{R}^2$ is defined by $g \cdot \mathbf{x} := g\mathbf{x}$ and its action on measurable functions by $(g \cdot v)(\mathbf{x}) := v(g^{-1}\mathbf{x})$.

The *symmetry group* of a periodic two-dimensional pattern is the group of euclidean transformations G leaving this pattern invariant. There exists only 17 distinct classes of such groups, called *wallpaper groups* (or plane crystallographic groups) [Arm88; Mar82]. A fundamental domain is a subset which contains exactly one point from each orbits of the action of G. Then, the pattern is uniquely determined by the specification of a fundamental domain and its symmetry group G.

We denote by $G \subset E_2(\mathbb{R})$ the symmetry group of $\mathscr{L}^{\mathbf{R}}$. The following assumption means that any fundamental domain of the lattice $\mathscr{L}^{\mathbf{R}}$ contains exactly one vertex.

Assumption 2 ($\mathscr{L}^{\mathbf{R}}$ has a single orbit)**.** *The lattice $\mathscr{L}^{\mathbf{R}}$ is* vertex-transitive: *the group $G \subset E_2(\mathbb{R})$ acts* transitively *on $\mathscr{L}^{\mathbf{R}}$.*

Remark 3.2. Assumption 2 implies a constraint on the number of sites per primitive cell. An enumeration of possibilities shows that $N \in \{1, 2, 3, 4, 6, 8, 9, 18, 36\}$. Later, we explain how one could relax this assumption (see Remark 3.5).

We denote by G_L the symmetry group of $\mathscr{L}_L^{\mathbf{R}}$ which has the same point group as G. Our next assumption states that V_L has all the same symmetries as $\mathscr{L}_L^{\mathbf{R}}$. In particular, if the potential V_L presents a singularity at one vertex of $\mathscr{L}_L^{\mathbf{R}}$ then the same singularity appears at each vertex, up to an orthogonal transformation.

Assumption 3 (Symmetries of V_L)**.** *For all $L \geq 1$, the potential V_L is invariant under the action of G_L: $\forall g \in G_L$, $g \cdot V_L = V_L$.*

Now, we introduce

$$\boxed{H_L = -\Delta + V_L\,,}$$

the *$\mathscr{L}_L$-periodic operator* on $L^2(\mathbb{R}^2)$ associated with the potential V_L. It is well known that the operator H_L is bounded from below (see for instance [Cyc+87, Section 1.2] or Proposition 3.12). Since we have assumed that $V_L \in L^p_{\mathrm{per}}(\Gamma_L)$ for some $p \in (1\,,\infty)$, we consider the Friedrichs self-adjoint extension of this operator. It admits the decomposition in fibers [RS78, Section XIII.16] (see also [Kna89, Section 2])

$$H_L \simeq \fint_{\Gamma_L^*}^{\oplus} H_L(\mathbf{k})\,\mathrm{d}\mathbf{k}\,.$$

There, for all $\mathbf{k} \in \Gamma_L^*$, the operator $H_L(\mathbf{k}) = -\Delta + V_L$ acts on $L^2_{\mathbf{k}}(\Gamma_L)$ and is self-adjoint on the domain

$$\mathcal{D}(H_L(\mathbf{k})) = \left\{\varphi \in H^1_{\mathbf{k}}(\Gamma_L) \;\middle|\; (-\Delta + V_L)\,\varphi \in L^2_{\mathbf{k}}(\Gamma_L)\right\}\,,$$

where $H^1_{\mathbf{k}}(\Gamma_L) = \left\{\varphi \in L^2_{\mathbf{k}}(\Gamma_L) \;\middle|\; \partial_1\varphi, \partial_2\varphi \in L^2_{\mathbf{k}}(\Gamma_L)\right\}$ denotes the Sobolev space with pseudo-periodic boundary conditions. Moreover, because $H_L(\mathbf{k})$ has a compact resolvent, its spectrum is purely discrete and accumulates at $+\infty$

$$\sigma(H_L(\mathbf{k})) = \{\mu_{1,L}(\mathbf{k}) \leq \mu_{2,L}(\mathbf{k}) \leq \dots\}\,.$$

The maps $\mathbf{k} \mapsto \mu_{n,L}(\mathbf{k})$ for $n \geq 1$ are called *band functions.* They are continuous and piecewise analytic functions of $\mathbf{k}$ (consequence of [BS99, Proposition 2.3] and Hartogs's theorem [Kra01]). The operator H_L has only absolutely continuous spectrum [Kna89; BS99] given by the range of the band functions [RS78, Theorem XIII.85]

$$\sigma(H_L) = \bigcup_{\mathbf{k} \in \Gamma_L^*} \sigma(H_L(\mathbf{k})) = \bigcup_{n \in \mathbb{N}^*} \mu_{n,L}(\Gamma_L^*)\,.$$

The purpose of this article is to study the geometry of the spectral bands of the periodic operator H_L in the *dissociation* regime, that is, when L is large.

Reference operator

So far, the assumptions on the family $\{V_L\}_{L\geq 1}$ do not give any information about the local behavior of V_L when L is large, the dissociation regime we are interested in. We want V_L to be approximately given by a periodic superposition of potential wells. This motivates the introduction of a *reference potential* V which we will assume to be the limit of V_L at each vertex of $\mathscr{L}_L^{\mathbf{R}}$.

Assumption 4 (Reference potential)**.** *Let V be a real-valued potential such that*

(i) $V \in L^p(\mathbb{R}^2) + L^\infty(\mathbb{R}^2)$ where $p \in (1\,,\infty)$ is the number introduced in Assumption 1(i);

(ii) $V(\mathbf{x}) = O\left(|\mathbf{x}|^{-1-\epsilon}\right)$ as $|\mathbf{x}| \to \infty$ for some $\epsilon > 0$;

(iii) The associated mono-atomic Schrödinger operator defined by

$$\boxed{H = -\Delta + V\,,} \tag{3.5}$$

admits at least one negative eigenvalue.

The potential V belongs the Kato class [Cyc+87, Definition 1.10] hence is infinitesimally $(-\Delta)$-form bounded. We always work with the Friedrichs extension of H which defines a self-adjoint operator on the domain

$$\mathcal{D}(H) = \left\{u \in H^1(\mathbb{R}^2) \,\middle|\, (-\Delta + V)u \in L^2(\mathbb{R}^2)\right\}\,.$$

By standard perturbation theory [Kat95; RS78], its essential spectrum is given by $\sigma_{\mathrm{ess}}(H) = [0\,,\infty)$ and the discrete spectrum of H is negative. We denote by

$$\sigma_{\mathrm{d}}(H) = \{-\mu_1 < -\mu_2 \leq -\mu_3 \leq \cdots \leq 0\} \subset (-\infty\,,0]\,,$$

its discrete spectrum. To lighten the notation, we also denote by $-\mu$ the lowest eigenvalue of H, which is non-degenerate [Goe77]. We denote by $g = \mu_1 - \mu_2 > 0$ the *spectral gap* above $-\mu$. We denote by v the normalized eigenfunction associated with $-\mu$. We have

$$Hv = (-\Delta + V)v = -\mu v\,, \tag{3.6}$$

where all the terms make sense in $H^{-1}(\mathbb{R}^2)$.

Remark 3.3. We have not make any explicit assumption about eventual invariance of V under symmetry transformation. We will see below that, as a consequence of Assumption 5, V must have the same symmetries as the lattice $\mathscr{L}^{\mathbf{R}}$, see Section 3.6 for the details. In most applications, one can choose V radial.

Effective mono-atomic operators

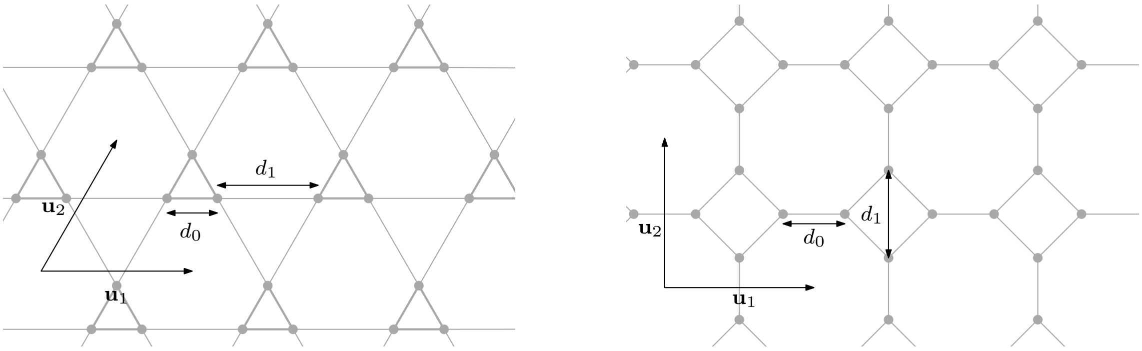
In this section, we introduce effective operators by localizing the periodic potential V_L around a vertex of $\mathscr{L}_L^{\mathbf{R}}$. The eigenfunctions and eigenvalues of these operators will be useful in order to precisely approximate the modes and the dispersion relation of the periodic operator H_L.

We introduce the nearest neighbor distance $d_0 > 0$ of the unscaled lattice $\mathscr{L}^{\mathbf{R}}$ (see Figure 3.1)

$$d_0 := \min\left\{|\mathbf{r} - \mathbf{r}'| \;\middle|\; (\mathbf{r}, \mathbf{r}') \in \left(\mathscr{L}^{\mathbf{R}}\right)^2 \quad \text{and} \quad \mathbf{r} \neq \mathbf{r}'\right\}\,. \tag{3.7}$$

We also denote by $d_1 > d_0$ the second nearest neighbor distance. Let $\delta \in (0\,,1/2)$ and $\chi \in \mathcal{C}_c^\infty(\mathbb{R}^2)$ a localization function such that

$$0 \leq \chi \leq 1, \quad \chi \equiv 1 \quad \text{on} \quad B\left(0, \frac{1+\delta}{2} d_0\right) \quad \text{and} \quad \operatorname{supp}\chi \subset B\left(0, \left(\frac{1}{2} + \delta\right) d_0\right)\,. \tag{3.8}$$



(a) $\mathscr{L} = \mathbf{u}_1\mathbb{Z} + \mathbf{u}_2\mathbb{Z}$ is the triangular lattice, $N = |\mathbf{R}| = 3$ and $m = 1$. Vertices linked by thick gray lines (resp. thin gray lines) are nearest neighbors (resp. second nearest neighbors). The nearest neighbor distance d_0 and the second nearest neighbor distance $d_1 > d_0$ are displayed.

(b) $\mathscr{L} = \mathbf{u}_1\mathbb{Z} + \mathbf{u}_2\mathbb{Z}$ is the square lattice, $N = |\mathbf{R}| = 4$ and $m = 2$. Vertices linked by gray lines are nearest neighbors (none second nearest neighbor link is shown). The nearest neighbor distance d_0 and the second nearest neighbor distance $d_1 > d_0$ are displayed. There are two kinds of edges: octogon-octogon edges and square-octogon edges. Thus $m = 2$.

Figure 3.1 – Examples of lattices $\mathscr{L}^{\mathbf{R}}$ with different parameters.

Notice that we have $\frac{1}{2}d_0 < \left(\frac{1}{2} + \delta\right) d_0 < d_0$. In addition, we also require χ to be *radial* and to satisfy the following technical assumption

$$\sqrt{1-\chi} \in \mathcal{C}^1(\mathbb{R}^2)\,. \tag{3.9}$$

For $L \geq 1$ and $\mathbf{r} \in \mathscr{L}^{\mathbf{R}}$, we introduce the localization functions near the vertex $L\mathbf{r}$

$$\chi_{L,\mathbf{r}}(\mathbf{x}) \coloneqq \chi(L^{-1}\mathbf{x} - \mathbf{r}) \quad \text{and} \quad V_{L,\mathbf{r}} \coloneqq \chi_{L,\mathbf{r}} V_L\,. \tag{3.10}$$

The potential $V_{L,\mathbf{r}}$ belongs to $L^p(\mathbb{R}^2)$ and is compactly supported within the ball $B(L\mathbf{r}, \left(\frac{1}{2} + \delta\right) L d_0)$ which contains one and only one vertex of $\mathscr{L}_L^{\mathbf{R}}$. We recall that the space $L^p(\mathbb{R}^2) + L^\infty(\mathbb{R}^2)$, endowed with

$$\|V\|_{L^p(\mathbb{R}^2)+L^\infty(\mathbb{R}^2)} \coloneqq \inf\left\{\|V_1\|_{L^p(\mathbb{R}^2)} + \|V_2\|_{L^\infty(\mathbb{R}^2)} \;\middle|\; V = V_1 + V_2,\ V_1 \in L^p(\mathbb{R}^2),\ V_2 \in L^\infty(\mathbb{R}^2)\right\}\,,$$

defined a Banach space. Our next assumption is that, up to a translation, $V_{L,\mathbf{r}}$ is asymptotically given by the reference potential V when $L \to \infty$.

Assumption 5 (The wells are asymptotically equivalent to V)**.** *For all $\mathbf{r} \in \mathscr{L}^{\mathbf{R}}$, we have*

$$\lim_{L\to\infty} \|V_{L,\mathbf{r}} - V(\cdot - L\mathbf{r})\|_{L^p(\mathbb{R}^2)+L^\infty(\mathbb{R}^2)} = 0\,.$$

A first consequence of Assumption 5 is that the discrete spectrum of the *effective mono-atomic operator* Schrödinger operator associated with $V_{L,\mathbf{r}}$, defined by

$$\boxed{H_{L,\mathbf{r}} \coloneqq -\Delta + V_{L,\mathbf{r}}\,,} \tag{3.11}$$

is non-empty (see [Kat95, Section XII-3] and also Proposition 3.46 in Appendix B.). In addition, its lowest eigenvalue is non-degenerate. By symmetry arguments, we can show that the operators $\{H_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$ are unitarily equivalent and thus share the same spectrum (see Section 3.6 for the details). We denote by $-\mu_L$ their common lowest eigenvalue and by $v_{L,\mathbf{r}}$ the associated normalized eigenfunction:

$$H_{L,\mathbf{r}} v_{L,\mathbf{r}} = (-\Delta + V_{L,\mathbf{r}}) v_{L,\mathbf{r}} = -\mu_L v_{L,\mathbf{r}}\,, \tag{3.12}$$

where each term makes sense in $H^{-1}(\mathbb{R}^2)$.

Convergence to the tight-binding model

In this section, we state the main result of this article. The first theorem provides expansion to the leading order of the dispersion of $-\Delta + V_L$ when V_L satisfies the assumptions enumerated in the previous section.

We introduce the set of nearest neighbors pairs (see Figure 3.1)

$$\mathscr{P}^{\mathbf{R}} := \left\{ \{\mathbf{r}, \mathbf{r}'\} \in \mathscr{L}^{\mathbf{R}} \times \mathscr{L}^{\mathbf{R}} \;\middle|\; |\mathbf{r} - \mathbf{r}'| = d_0 \right\} . \tag{3.13}$$

The group G acts isometrically on $\mathscr{L}^{\mathbf{R}}$ hence it also defines an action on $\mathscr{P}^{\mathbf{R}}$. When this action is transitive, we say that $\mathscr{P}^{\mathbf{R}}$ is *edge-transitive*. However, this is *not* necessarily the case (see Figure 3.1b for an example of non edge-transitive lattice). Because $\mathscr{P}^{\mathbf{R}}$ is invariant under the shifts of $\mathscr{L}$, this action has finitely many orbits, which are denoted by $\mathcal{O}_1, \dots, \mathcal{O}_m$. For all $k \in \{1, \dots, m\}$, we consider a representative $\mathbf{p}_k = \{\mathbf{r}_k, \mathbf{r}'_k\} \in \mathcal{O}_k$ and we introduce the following interaction coefficient

$$\boxed{\theta_{L,k} := \langle v_{L,\mathbf{r}_k}, V_{L,\mathbf{r}_k}(1 - \chi_{L,\mathbf{r}'_k}) v_{L,\mathbf{r}'_k} \rangle_{L^2(\mathbb{R}^2)} ,} \tag{3.14}$$

where $V_{L,\mathbf{r}}$ and $v_{L,\mathbf{r}}$ are respectively defined in (3.10) and (3.12). Using Assumption 3, we can show that the quantity $\theta_{L,k}$ does not depend on the choice of the pair $\mathbf{p}_k \in \mathcal{O}_k$ (see Section 3.6). In addition, we show in Proposition 3.24 that $\theta_{L,k}$ is exponentially small when L is large: for any $\epsilon > 0$, there exists C_ϵ such that

$$|\theta_{L,k}| \leq C_\epsilon e^{-(1-\epsilon)\sqrt{\mu} d_0 L} .$$

It is expected that in many cases this is essentially optimal, that is, $\theta_{L,k}$ is of order $e^{-\sqrt{\mu} d_0 L}$ up to polynomial factors.

The following theorem is the main result of this chapter.

Theorem 3.4 (Convergence to the tight-binding model)**.** *Let $\delta \in (0, 1/2)$ be the parameter introduced in the definition (3.8) of the cut-off function χ. Under Assumptions 1–5, for all $\epsilon \in (0, \delta)$ and for all $\mathbf{k} \in \Gamma_L^*$, the N first Bloch eigenvalues satisfy*

$$\boxed{\mu_{j,L}(\mathbf{k}) = -\mu_L + \lambda_j \left(\sum_{k=1}^{m} \theta_{L,k} B_k(L\mathbf{k}) \right) + O\Big(e^{-(1+\delta-\epsilon)\sqrt{\mu} d_0 L} + e^{-(1-\epsilon)\sqrt{\mu} d_1 L} \Big) ,} \tag{3.15}$$

for L large enough and where the O is independent from $\mathbf{k}$. Here $d_1 > d_0$ denotes the second nearest neighbor distance in $\mathscr{L}^{\mathbf{R}}$, $\lambda_j(B)$ denotes the j^{th} lowest eigenvalue of a matrix B and $B_k(L\mathbf{k})$ is the $N \times N$ matrix defined by

$$\forall \mathbf{k} \in \Gamma^*, \quad \forall (\mathbf{r}, \mathbf{r}') \in \mathbf{R}^2, \quad B_k(\mathbf{k})_{\mathbf{r},\mathbf{r}'} = \sum_{\substack{\mathbf{u} \in \mathscr{L} \\ (\mathbf{r}, \mathbf{u}+\mathbf{r}') \in \mathcal{O}_k}} e^{i\mathbf{k}\cdot\mathbf{u}} . \tag{3.16}$$

This result says that the lowest part of the spectrum of the periodic operator $H_L = -\Delta + V_L$ is, to leading order, given by the tight-binding model.

Recall that m denotes the number of orbits associated with the action of G on the set of nearest neighbors $\mathscr{P}^{\mathbf{R}}$. When $m = 1$ then the second term in (3.15) is the tight-binding model associated with the crystal $\mathscr{L}^{\mathbf{R}}$. In the case of the honeycomb lattice (which is introduced in Section 4.1), we have $N = 2$ and $m = 1$. The matrix $B_{\mathrm{HC}}(\mathbf{k}) := B_1(\mathbf{k})$ is given by

$$B_{\mathrm{HC}}(\mathbf{k}) = \begin{pmatrix} 0 & 1 + e^{i\mathbf{k}\cdot\mathbf{u}_1} + e^{i\mathbf{k}\cdot\mathbf{u}_2} \\ 1 + e^{-i\mathbf{k}\cdot\mathbf{u}_1} + e^{-i\mathbf{k}\cdot\mathbf{u}_2} & 0 \end{pmatrix} . \tag{3.17}$$

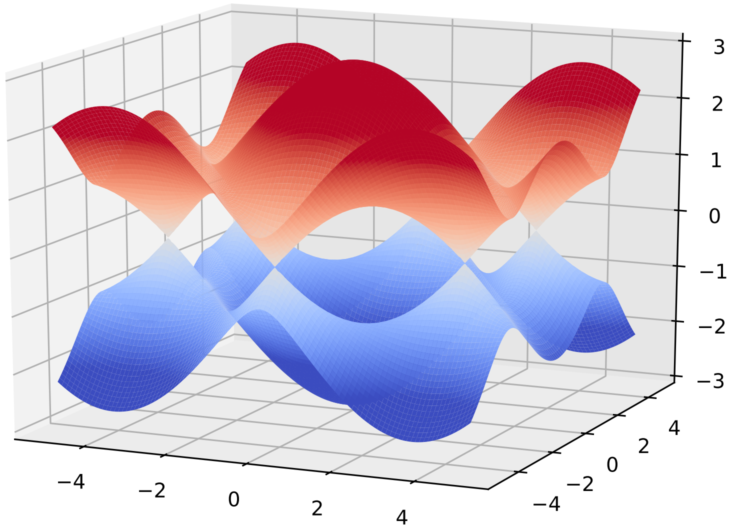


Figure 3.2 – The Wallace model. The dispersion relation is invariant with respect to the rotation by $\pi/3$ about the origin. We observe conical singularities, Dirac points, at the vertices of the Brillouin zone Γ^*.

This is the matrix associated with the tight-binding model of graphene, also known as the *Wallace model* [Wal47]. The dispersion relation, $\mu_{\pm}(\mathbf{k}) = \pm\left|1 + e^{i\mathbf{k}\cdot\mathbf{u}_1} + e^{i\mathbf{k}\cdot\mathbf{u}_2}\right|$, exhibits *Dirac points* at the six vertices of the Brillouin zone, see Figure 3.2. A more precise result is provided later in Theorem 3.6 in this case.

For generic potentials, we expect $\theta_{L,k}$ to be non zero and of order $e^{-\sqrt{\mu}d_0 L}$. If it was indeed the case then the tight binding model defined by the matrices (3.16) would give the leading order of the dispersion relation of H_L.

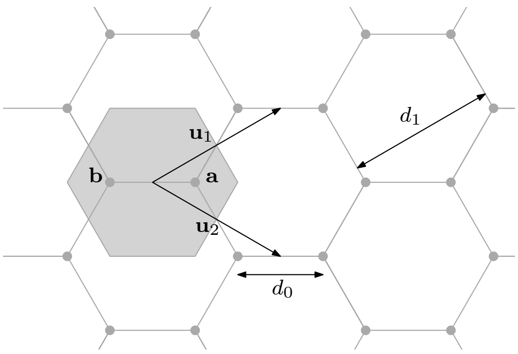
Showing that the interaction coefficients $\theta_{L,k}$ are really of order $e^{-\sqrt{\mu}d_0 L}$ seems challenging in the general setting we consider. In [FW12] (see also [BC18]), Fefferman and Weinstein show that $\theta_{L,k}$ is non zero for all $L > 0$ except in a countable and closed set. This was proved in the case where $V_L = L^{-1}V(L^{-1}\cdot)$ with V a real-valued bounded potential with honeycomb symetries and such that a particular Fourier coefficient does not vanish. In [FLW18], the same authors and Lee-Thorp consider superpositions of localized potential wells centered on the vertices of $\mathscr{L}^H$, that is the case $V_L = L\sum_{\mathbf{r}\in\mathscr{L}^H} V^{\mathrm{at}}(\cdot - \mathbf{r})$ with V^{at} bounded. Under some symmetry, support and spectral assumptions on V, they are able to show that the dispersion relation of $-\Delta + V_L$ converges uniformly toward the Wallace model in the high contrast regime $L \to \infty$. In particular, they show that the interaction coefficient θ_L is non-zero in that regime.

Many results similar to Theorem 3.4 have appeared in the literature. When the potential is homogeneous of degree -1, the regime $L \to \infty$ is equivalent to a semiclassical limit in which multiple wells potentials have been studied. In [Sim84b], Simon shows that, in the semiclassical regime, the width of the ground state band of a Schrödinger operator with smooth and periodic potential is given by the minimum action among all instantons connecting two distinct minima of the external potential. We also refer to the series of papers by Helffer and Sjöstrand [HS84; HS85b; HS85a; HS85c; HS86; HS87] and, in a periodic setting, by their collaborators [Out84; Moh91]. In [Dau96], Daumer considers finitely many wells at dissociation. In general, the results from this literature are more precise (for instance, in [Dau96], the author determines exactly the tunneling coefficient) but the dependence, when it exists, of the potential on the semiclassical parameter is easier to handle than in our setting. Indeed, Assumption 1 allows for potentials with a highly nonlinear dependence in L, which is needed for the study of some nonlinear quantum models at dissociation (see Section 5). In [FLW18], the authors consider superpositions of localized potential wells, centered on the vertices of a regular honeycomb structure in the regime where the depth of the potentials wells is large. For sufficiently deep wells, they show that the two lowest spectral bands, after an appropriate rescaling, converge uniformly to the Wallace model, described in (3.17).

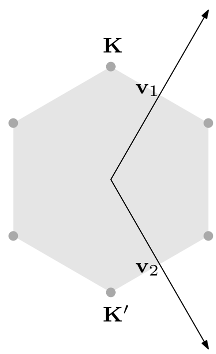
The overall strategy for proving Theorem 3.4 is the following. We first study the projection of H_L on the subspace spanned by the family $\{v_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$ which approximates the spectral subspace associated with the N low-lying bands of H_L. Then we use Feshbach-Schur method to recover the exact spectrum of $H_L(\mathbf{k})$. The Feshbach-Schur method, used to reduce the dimension of perturbative eigenvalue problems, was first developed by Schur in matrix theory [Sch17] and by Feshbach in nuclear physics [Fes58]. It has been reformulated by Bach, Fröhlich and Sigal in [BFS98b; BFS98a]. It was used in the context of periodic operators in [FW12; FLW18].

Remark 3.5. In fact, Assumption 2 is not necessary for the purpose of this work even if it will make the analysis clearer. Without this assumption, the number of vertices in each fundamental domain of $\mathscr{L}^{\mathbf{R}}$ (which is equal to the number of orbits of $\mathscr{L}^{\mathbf{R}}$ under the action of G) is not restricted to one anymore. In this more general situation, a result analogous to Theorem 3.4 would hold if we associate to each orbit a reference potential whose lowest eigenvalue could differ from the one of referential potentials associated with the other orbits. Indeed, in this case, one could decompose H_L into a direct sum of single orbit operators which do not interact to leading order.

The honeycomb lattice case



(a) $\mathscr{L} = \mathbf{u}_1\mathbb{Z} + \mathbf{u}_2\mathbb{Z}$ is the triangular lattice, $N = |\mathbf{R}| = 2$ and $m = 1$. The honeycomb lattice is the superposition of two sifted versions of $\mathscr{L}$: $\mathscr{L}^H = (\mathscr{L}+\mathbf{a})\cup(\mathscr{L}+\mathbf{b})$. The Wigner-Seitz cell Γ is colored in gray. Vertices linked by gray lines are nearest neighbors. The nearest neighbor distance d_0 and the second nearest neighbor distance $d_1 > d_0$ are displayed.



(b) The vectors $\mathbf{v}_1$ and $\mathbf{v}_2$ generate the reciprocal lattice $\mathscr{L}^*$. The first Brillouin zone Γ^* is colored in gray. The vertices $\mathbf{K}$ and $\mathbf{K}'$ of Γ^* are shown, the others are obtained by rotation by $2\pi/3$ and $4\pi/3$ about the origin.

Figure 3.3 – The honeycomb lattice $\mathscr{L}^H$.

In estimate (3.15) of Theorem 3.4, the big O does not explicitly depend on the quasi-momentum $\mathbf{k} \in \Gamma_L^*$. When $\mathscr{L}^{\mathbf{R}} = \mathscr{L}^H$ is the honeycomb lattice, we can make the estimates more precise in the vicinity of the vertices of the first Brillouin zone Γ_L^*. Then, under the additional assumption that the interaction coefficient has the expected order, we show that the dispersion relation has Dirac points at these vertices.

In order to be more explicit, we first briefly recall some features of the honeycomb lattice (this lattice is fully described in Section 4.1). The honeycomb lattice is a two-sites lattice which forms a hexagonal tilling of the plane, see Figure 3.3a. The underlying lattice is the triangular lattice and its first Brillouin zone is a regular hexagon whose vertices are denoted by $\mathbf{K}$ or $\mathbf{K}'$, see Figure 3.3b. As already mentioned, there is only one interaction coefficient (3.14), denoted by θ_L. We also denote by $\mathbf{k} \in \Gamma_L^* \mapsto \mu_{\pm,L}(\mathbf{k})$ the two lowest band functions of H_L. Recall that $\delta \in (0\,,1/2)$ is defined in (3.8) and that d_0 is the nearest neighbor distance, equal to $\frac{1}{\sqrt{3}}$ in this section.

Theorem 3.6 (Dirac points)**.** *Assume that there exists $c > 0$ and $\delta' \in [0\,,\delta)$ small enough such that $|\theta_L| \geq ce^{-(1+\delta')\sqrt{\mu}d_0 L}$. Let $r > 0$ and let $\mathbf{K}_\star \in \{\mathbf{K}, \mathbf{K}'\}$ be a vertex of the first Brillouin zone Γ^*. Then, when $L \to \infty$, we have the expansion*

$$\mu_{\pm,L}\left(\frac{\mathbf{K}_\star + \kappa}{L}\right) = -\mu_L + o(|\theta_L|) \pm \frac{\sqrt{3}}{2}\,|\theta_L|\,|\kappa|\,(1 + E(\kappa))\,(1 + o(1))\,, \tag{3.18}$$

where $|E(\kappa)| \leq C\,|\kappa|$ for all $\kappa \in B(0, r)$ and where the o's do not depend on κ.

For the sake of simplicity, we have only stated Theorem 3.6 in the case of the honeycomb lattice. This case corresponds to graphene, a layer of carbon atoms located at the vertices of the honeycomb lattice [Cas+09]. However, the conclusions of Theorem 3.6 remain valid for any lattice $\mathscr{L}^{\mathbf{R}}$ having the same symmetries as graphene, that is, $\mathcal{PT}$-symmetry (parity / time-reversal symmetry) and rotation by $2\pi/3$ symmetry [BC18]. Lattices with different symmetries are also expected to present Dirac points, see the review [Wan+15].

2.3 Application: the periodic reduced Hartree-Fock model

Now, we illustrate the use of Theorems 3.4 and 3.6 in a nonlinear situation. We consider the two-dimensional periodic reduced Hartree-Fock model with three-dimensional Coulomb interactions. In addition, we assume that the external potential is corrected by a pseudo-potential. This nonlinear model is obtained as the thermodynamic limit of the Hartree-Fock model where the exchange term is neglected [CLL01; CDL08; HLS09b]. It is the simplest model to describe graphene while taking interactions into account.

If we assume that the particles interact through the three-dimensional Coulomb interaction $\frac{1}{|\mathbf{x}|}$ then the $\mathscr{L}_L$-periodic *interaction kernel*, denoted by W_L, is given by

$$W_L = L^{-1}M' + \sum_{\mathbf{u}\in\mathscr{L}}\left(\frac{1}{|\cdot - L\mathbf{u}|} - \frac{1}{|\Gamma_L|}\int_{\Gamma_L}\frac{\mathrm{d}\mathbf{y}}{|\cdot - L\mathbf{u} - \mathbf{y}|}\right),$$

for some constant $M' \in \mathbb{R}$ chosen so that $W_L \geq 0$. The properties of the interaction kernel W_L are given in Section 5.1. Let ρ be a positive and $\mathscr{L}_L$-invariant locally finite measure. Its *self-interaction energy* is defined by

$$D_L(\rho, \rho) \coloneqq \iint_{\Gamma_L\times\Gamma_L}\rho(\mathbf{x})W_L(\mathbf{x}-\mathbf{y})\rho(\mathbf{y})\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y} \in [0\,,\infty]\,.$$

The *interaction energy* of two $\mathscr{L}_L$-periodic charge distributions ρ and μ is defined by

$$D_L(\rho, \mu) \coloneqq \iint_{\Gamma_L\times\Gamma_L}\rho(\mathbf{x})W_L(\mathbf{x}-\mathbf{y})\mu(\mathbf{y})\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y}\,,$$

whenever $D_L(\rho, \rho) < \infty$ and $D_L(\mu, \mu) < \infty$.

We consider the lattice $\mathscr{L}_L^{\mathbf{R}}$ defined in (3.4) where a pointwise nucleus of charge $+1$ is placed at each vertex. Besides the three-dimensional Coulomb interaction $\frac{1}{|\mathbf{x}|}$, we assume that the external potential induced by the lattice has an additional term, localized around each nucleus and which corresponds to a pseudo-potential, that is, an effective potential modeling the behavior of the core electrons which do not explicitly appear in the model [Che11]. Then the potential generated by $\mathscr{L}_L^{\mathbf{R}}$ has the following form

$$-\sum_{\mathbf{r}\in\mathbf{R}}W_L(\cdot - L\mathbf{r}) + \sum_{\mathbf{r}\in\mathbf{R}}\sum_{\mathbf{u}\in\mathscr{L}}V^{\mathrm{pp}}(\cdot - L(\mathbf{u}+\mathbf{r}))\,,$$

where $V^{\mathrm{pp}} \in L^p(\mathbb{R}^2)$ for some $p > 1$. For simplicity, we also choose V^{pp} radial and compactly supported. These two additional assumptions are certainly not optimal and could be relaxed without great effort, see Remark 3.8. We denote

$$W_L^{\mathbf{R}} := \sum_{\mathbf{r}\in\mathbf{R}} W_L(\cdot - L\mathbf{r}) \quad\text{and}\quad V_L^{\mathbf{R}} := \sum_{\mathbf{r}\in\mathbf{R}}\sum_{\mathbf{u}\in\mathscr{L}} V^{\mathrm{pp}}(\cdot - L(\mathbf{u}+\mathbf{r}))\,. \tag{3.19}$$

An *admissible state* is an element of the space

$$\mathcal{S}_{\mathrm{per},L} := \left\{\gamma=\gamma^*\in\mathcal{B}(L^2(\mathbb{R}^2)) \;\middle|\; 0\le\gamma\le 1,\ \forall \mathbf{u}\in\mathscr{L}_L,\ \tau_{\mathbf{u}}\gamma=\gamma\tau_{\mathbf{u}} \quad\text{and}\quad \underline{\mathrm{Tr}}_{\mathscr{L}_L}((1-\Delta)\gamma)<\infty\right\}, \tag{3.20}$$

where $\tau_{\mathbf{u}}$ denotes the translation operator which shifts particles by $\mathbf{u}$ and where the symbol $\underline{\mathrm{Tr}}_{\mathscr{L}_L}$ denotes the trace per cell [CDL08]. In this setting, the periodic *reduced Hartree-Fock model* (rHF) consists in solving the following minimization problem

$$E_L := \inf\left\{\mathcal{E}_L(\gamma) \;\middle|\; \gamma\in\mathcal{S}_{\mathrm{per},L} \quad\text{and}\quad \underline{\mathrm{Tr}}_{\mathscr{L}_L}(\gamma)=N/q\right\}, \tag{3.21}$$

where the periodic rHF energy functional is given by

$$\mathcal{E}_L(\gamma) := \underline{\mathrm{Tr}}_{\mathscr{L}_L}(-\Delta\gamma) + \int_{\Gamma_L}\left(-W_L^{\mathbf{R}}+V_L^{\mathbf{R}}\right)\rho_\gamma + \frac{q}{2}D_L(\rho_\gamma,\rho_\gamma)\,. \tag{3.22}$$

The first term is the kinetic energy per unit cell of the infinitely many (valence) electrons. The second term is the Coulomb interaction with the lattice of nuclei, the third one the correction term, whereas the last term the (mean-field) electronic repulsion. Here the factor q is the number of spin states ($q=2$ for electrons). We restrict ourselves to paramagnetic states, hence q only shows up in the energy. The normalization $\underline{\mathrm{Tr}}_{\mathscr{L}_L}(\gamma)=N/q$ ensures the neutrality of the system. We do not include the energy of the nuclei in the cell Γ_L because it does not play a role in our analysis. An adaptation of [CDL08, Theorem 1] and [CLL01, Theorem 2.1] shows that (3.21) is well-posed in the sense that the minimization problem (3.21) admits a unique minimizer γ_L. We denote by $\rho_L(\mathbf{x}) := \gamma_L(\mathbf{x},\mathbf{x})$ its one-body density. Then γ_L is the unique solution of the mean-field equation

$$\boxed{\gamma_L = \mathbb{1}_{(-\infty,\epsilon_L]}\left(H_L^{\mathrm{MF}}\right) \quad\text{where}\quad H_L^{\mathrm{MF}} := -\Delta - W_L^{\mathbf{R}} + V_L^{\mathbf{R}} + q\rho_L *_L W_L\,.} \tag{3.23}$$

Here, H_L^{MF} is the mean-field hamiltonian and $\epsilon_L\in\mathbb{R}$ is a Lagrange multiplier called the *Fermi level* chosen to ensure that $\underline{\mathrm{Tr}}_{\mathscr{L}_L}(\gamma)=N/q$. The notation $*_L$ stands for convolution on Γ_L. Notice that the mean-field potential

$$V_L^{\mathrm{MF}} := -W_L^{\mathbf{R}} + V_L^{\mathbf{R}} + q\rho_L *_L W_L\,,$$

depends on L in a highly nonlinear way. If the action of G_L on $\mathscr{L}_L$ is free then we can regroup $-W_L^{\mathbf{R}}$ and $q\rho_L *_L W_L$ and write V_L^{MF} as in (3.2) plus the correction $V_L^{\mathbf{R}}$ thanks to the fact that there is no charge and no dipole.

Now, we describe the reference potential occurring in the limit $L\to\infty$. We consider the minimization problem

$$I := \inf\left\{\mathcal{E}(u) \;\middle|\; u\in H^1(\mathbb{R}^2) \quad\text{and}\quad \int_{\mathbb{R}^2}|u|^2=1\right\}, \tag{3.24}$$

with the energy functional

$$\mathcal{E}(u) := \int_{\mathbb{R}^2}|\nabla u|^2 + \int_{\mathbb{R}^2}\left(-\frac{1}{|\mathbf{x}|}+V^{\mathrm{pp}}(\mathbf{x})\right)|u(\mathbf{x})|^2\,\mathrm{d}\mathbf{x} + \frac{1}{2}\iint_{\mathbb{R}^2\times\mathbb{R}^2}\frac{|u(\mathbf{x})|^2\,|u(\mathbf{y})|^2}{|\mathbf{x}-\mathbf{y}|}\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y}\,.$$

Since $V^{\mathrm{pp}}\in L^p(\mathbb{R}^2)$ and is compactly supported, one can show that (3.24) admits a minimizer $v\in H^1(\mathbb{R}^2)$ by following the arguments in [Lie81a, Section VII]. In addition, we assume that V^{pp}

satisfies a *ionization condition* in the sense that the mean-field operator

$$\boxed{H^{\mathrm{MF}} := -\Delta + V^{\mathrm{MF}} \quad \text{where} \quad V^{\mathrm{MF}} := -\frac{1}{|\cdot|} + V^{\mathrm{pp}} + |v|^2 * \frac{1}{|\cdot|}\,.}$$

admits at least one negative eigenvalue $-\mu < 0$. In that case, it is non-degenerate, the minimizer v is unique and it is the eigenfunction associated with $-\mu$. Also, up to a phase factor, v is positive everywhere.

The following theorem states that the mean-field potential V_L^{MF} of the rHF model (3.24) belongs to the class described in Section 2.2.

Theorem 3.7. *If the lattice $\mathscr{L}^{\mathbf{R}}$ satisfies Assumption 2 then Assumptions 1–5 are valid with V^{MF} as reference potential. In particular, the N lowest Bloch eigenvalues of H_L^{MF} satisfy* (3.15)*.*

To our knowledge, nonlinear periodic models as (3.21) in the dissociation or the semiclassical regime have not been addressed very much in the literature. Albanese shows in [Alb88] that the time dependent Hartree equation with a periodic potential consisting of a periodic array of deep wells admits a solution where all single orbital is exponentially decaying if the distance separating the wells is large enough. In a non periodic setting, the Hartree-Fock model (with the exchange term) in the dissociation regime was studied by Daumer in [Dau94]. By fixed-point methods and under assumptions ensuring that spectral tunneling can be neglected, the author constructed solutions to the Hartree-Fock equations which are also minimizers for the Hartree-Fock energy. Recently, in a series of papers [OR21; ORS21; RS18], Olgiati, Rougerie and Spehner consider bosonic systems trapped in a symmetric double-well potential in the limit where the distance between the wells increases to infinity and the potential barrier is high.

Remark 3.8 (Assumptions on V^{pp})**.** (i) There exists pseudo-potentials V^{pp} which satisfy the ionization condition. For instance, one can take $V^{\mathrm{pp}} = -\eta V$ with $V \in L^\infty(\mathbb{R}^2)$ non-negative, non-zero and radial and where $\eta \geq 0$ is large enough. See Appendix A. for a proof.

(ii) To ensure that V_L^{MF} has the same symmetries as $\mathscr{L}^{\mathbf{R}}$ (Assumption 3), it is sufficient for V^{pp} to be invariant with respect to the point group of G. But requiring rotation invariance makes the proofs simpler. Also, the technical assumption that V^{pp} must have compact support could be replaced by an appropriate decay at infinity assumption without modifying most of the arguments in the proof of Theorem 3.7. We think that assuming $V^{\mathrm{pp}}(\mathbf{x}) = O\Big(|\mathbf{x}|^{-2-\epsilon}\Big)$ for some $\epsilon > 0$ should do.

(iii) The assumption that (3.24) admits a minimizer and that the mean-field operator has a negative eigenvalue is crucial for our analysis. Otherwise, Assumption 4 would not be satisfied.

(iv) We think that there is a negative eigenvalue for $V^{\mathrm{pp}} = 0$. This is well known in $3D$ [LS77a; Lie81a] but we have not found it state anywhere in $2D$.

The following corollary is a direct consequence of Theorem 3.6 and Theorem 3.7.

Corollary 3.9 (Dirac points in rHF for the honeycomb lattice)**.** *Assume that $\mathscr{L}^{\mathbf{R}} = \mathscr{L}^H$ is the honeycomb lattice and that $q = 2$. We denote by θ_L the interaction coefficient and we assume there exists $c > 0$ and $\delta' \in [0\,,\delta)$ such that $|\theta_L| \geq c e^{-(1+\delta')\sqrt{\mu} d_0 L}$. Then, the conclusions of Theorem 3.6 hold: the dispersion relation of H_L^{MF} admits Dirac points. In addition, the Fermi level ϵ_L is exactly equal to the energy level of the cones.*

3 Proof of Theorem 3.4

In this section, we consider a Schrödinger operator $H_L = -\Delta + V_L$ which commutes with the shifts of the scaled Bravais lattice $\mathscr{L}_L = L\mathscr{L}$ introduced in Section 2.1. We assume that the potential V_L satisfies Assumptions 1–5. Under these assumptions, we employ the Feshbach-Schur method [BFS98b; GS20] in order to give the first two orders of the low-lying dispersion surfaces of H_L, in the regime where L is large. This strategy has already been used in a similar context in [Out84; FLW18], for instance.

3.1 Strategy of proof

The proof of Theorem 3.4 crucially uses the Feshbach-Schur method . Let us briefly recall it. We consider P and $P^\perp$, two orthogonal projections on a Hilbert space $\mathcal{H}$, such that $P + P^\perp = 1$. Let H be a self-adjoint operator on $\mathcal{H}$. It can be represented as the block matrix

$$H = \begin{pmatrix} A & C^* \\ C & B \end{pmatrix},$$

with $A = PAP$, $B = P^\perp HP^\perp$ and $C = P^\perp HP$. Let $E \in \sigma_{\mathrm{d}}(H)$ and assume that there exists $\epsilon > 0$ such that

$$B - E \geq \epsilon P^\perp . \tag{3.25}$$

Then the eigenvalue problem $H\psi = E\psi$ is equivalent to

$$\big(A - C^*(B-E)^{-1}C - E\big)\, P\psi = 0 .$$

The other component of ψ is recovered thanks to the relation $P^\perp\psi = -(B-E)^{-1}CP\psi$. If the operator $C^*(B-E)^{-1}C$ is bounded then perturbation theory [Kat95] implies that the distance between E and the spectrum of A is estimated by

$$\mathrm{d}(E, \sigma(A)) \leq \left\| C^*(B-E)^{-1}C \right\| \leq \left\| (B-E)^{-1/2} C \right\|^2 . \tag{3.26}$$

We see that, in order to correctly estimate E, the choice of the orthogonal projection P should allow to estimate both $\sigma(A)$ and $\left\|(B-E)^{-1/2}C\right\|$.

In the proof of Theorem 3.4, we apply this method to the Bloch operator $H = H_L(\mathbf{k}) \coloneqq -\Delta + V_L$ which acts on $L^2_{\mathbf{k}}(\Gamma_L)$. We choose the projection $P = P_L(\mathbf{k})$ following ideas in [Out84; Dau96; FLW18]. The projection $P_L(\mathbf{k})$ is chosen as the orthogonal projection on the subspace spanned by the Bloch-Floquet transforms of the functions $v_{L,\mathbf{r}}$, defined in (3.12) as the first eigenfunctions of the operators $H_{L,\mathbf{r}}$. To construct this projector, we first show, in Section 3.8, that the familly $\{v_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$ is almost orthonormal and from it, we form an orthonormal family $\{w_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$ by applying the Gram-Schmidt process. This family shares many properties of (composite) Wannier functions: periodicity, localization (see Proposition 3.21 and Remark 3.22). When applying the Bloch-Floquet transform to each function $w_{L,\mathbf{r}}$, we obtain an orthonormal system of $N = |\mathbf{R}|$ quasi-periodic functions which defines the orthogonal projection $P_L(\mathbf{k})$. The spectrum of $A = P_L(\mathbf{k})H_L(\mathbf{k})P_L(\mathbf{k})$ is computed in Corollary 3.25. The energy inequality (3.25) is shown in Proposition 3.26. Finally, we estimate the right side of (3.26) in Proposition 3.28.

3.2 Notation

We describe some notations we use in the sequel. For two quantities A and B, we write $A \lesssim B$ whenever there exists a constant C independent from any relevant parameters and such that $A \leq CB$. If A_L and B_L are sequences labeled by L and $\alpha > 0$ then the notation $A_L = O\big(B_L^{\alpha-}\big)$ means that for every $\epsilon > 0$ there exists a constant $C_\epsilon > 0$ such that for L large enough (depending on ϵ) we have

$$|A_L| \leq C_\epsilon B_L^{\alpha-\epsilon} .$$

We use the notation $O(L^{-\infty})$ to denote a $O\big(L^{-k}\big)$ for all $k \in \mathbb{N}$, where the O may depend on k.

The open ball centered on $\mathbf{r} \in \mathbb{R}^2$ with radius $R \geq 0$ is denoted by $B(\mathbf{r}, R)$. The distance between two closed sets $A, B \subset \mathbb{R}^d$ is denoted $\mathrm{d}(A, B)$ or $\mathrm{d}(a, B)$ (resp. $\mathrm{d}(A, b)$) when $A = \{a\}$ (resp. $B = \{b\}$) is reduced to a singleton.

3.3 A regularity result

When $V \in L^p(\mathbb{R}^d) + L^\infty(\mathbb{R}^d)$ for some $p \geq \max(\frac{d}{2}, 2)$ if $d \neq 4$ and some $p > 2$ if $d = 4$ then V is infinitesimally $-\Delta$-bounded and that the Schrödinger operator $H = -\Delta + V$ is self-adjoint on $\mathcal{D}(-\Delta) = H^2(\mathbb{R}^d)$ [RS75; Cyc+87]. In dimension two, this is not necessarily the case if $V \in L^p(\mathbb{R}^2) + L^\infty(\mathbb{R}^2)$ with $p \in (1\,, 2)$. However, we can consider the Friedrichs extension of $H = -\Delta + V$ which is self-adjoint on $\mathcal{D}(H) = \left\{u \in H^1(\mathbb{R}^2) \mid (-\Delta + V)u \in L^2(\mathbb{R}^2)\right\}$. The following proposition shows, in that case, that $\mathcal{D}(H) \subset H^p(\mathbb{R}^2)$.

Proposition 3.10. *Let $V \in L^p(\mathbb{R}^2) + L^\infty(\mathbb{R}^2)$ where $p \in (1\,, \infty)$. Let $\alpha = \min(\frac{p}{2}, 1)$. For all $\nu > 0$ large enough, we have*

$$\left\|(-\Delta + \nu)^\alpha(-\Delta + V + \nu)^{-1}(-\Delta + \nu)^{1-\alpha}\right\| \leq 2\,. \tag{3.27}$$

Then there exists $C > 0$ such that for all $u \in L^2(\mathbb{R}^2)$ satisfying $(-\Delta + V)u \in L^2(\mathbb{R}^2)$ we have

$$\|u\|_{H^p(\mathbb{R}^2)} \leq 2\,\|(-\Delta + V)u\|_{L^2(\mathbb{R}^2)} + C\,\|u\|_{L^2(\mathbb{R}^2)}\,, \tag{3.28}$$

where we can choose

$$C \lesssim \max\left[1, \|V\|^{\frac{p}{p-1}}_{L^p(\mathbb{R}^2)+L^\infty(\mathbb{R}^2)}\right]. \tag{3.29}$$

Lemma 3.11. *Let $d \geq 1$ and $p \geq 1$ such that $p > \frac{d}{2}$. Let $\alpha \in [1 - \frac{p}{2}\,, \frac{p}{2}] \cap [0\,, 1]$. There exists a constant $C(d, p)$ such that for all $V \in L^p(\mathbb{R}^d)$ and $\nu > 0$ we have*

$$\left\|(-\Delta + \nu)^{-1+\alpha}V(-\Delta + \nu)^{-\alpha}\right\| \leq C(d, p)\nu^{\frac{d}{2p}-1}\,\|V\|_{L^p(\mathbb{R}^d)}\,. \tag{3.30}$$

Proof. First, we assume $\alpha \in (0\,, 1)$. Using Hölder's inequality for trace ideals [Sim05, Theorem 2.8] and the Kato-Seiler-Simon inequality [Sim05, Theorem 4.1], we have

$$\begin{aligned}\left\|(-\Delta + \nu)^{-1+\alpha}V(-\Delta + \nu)^{-\alpha}\right\| &\leq \left\|(-\Delta + \nu)^{-1+\alpha}\,|V|^{1-\alpha}\right\|_{\mathfrak{S}_{p/(1-\alpha)}}\left\||V|^\alpha\,(-\Delta + \nu)^{-\alpha}\right\|_{\mathfrak{S}_{p/\alpha}}\\ &\leq (2\pi)^{-d/p}\left(\int_{\mathbb{R}^d}\frac{\mathrm{d}\mathbf{k}}{(|\mathbf{k}|^2 + 1)^p}\right)^{1/p}\nu^{\frac{d}{2p}-1}\,\|V\|_{L^p(\mathbb{R}^d)}\,.\end{aligned}$$

Notice that the conditions on p and α ensure that $\frac{p}{1-\alpha} \geq 2$ and $\frac{p}{\alpha} \geq 2$. Using hyperspherical coordinates, we compute

$$\int_{\mathbb{R}^d}\frac{\mathrm{d}\mathbf{k}}{(|\mathbf{k}|^2 + 1)^p} = \left|\mathbb{S}^{d-1}\right|\int_0^\infty\frac{r^{d-1}\,\mathrm{d}r}{(r^2 + 1)^p} = \frac{\left|\mathbb{S}^{d-1}\right|}{2}\int_0^\infty\frac{s^{\frac{d}{2}-1}\,\mathrm{d}s}{(s + 1)^p} = \frac{\left|\mathbb{S}^{d-1}\right|}{2}B\left(\frac{d}{2}, p - \frac{d}{2}\right),$$

where B denotes the Euler beta function. Using the identity $\left|\mathbb{S}^{d-1}\right| = 2\pi^{\frac{d-1}{2}}/\Gamma\left(\frac{d-1}{2}\right)$ where Γ denotes the Euler Gamma function, we have obtained (3.30) with

$$C(d, p) = \left[\frac{B\left(\frac{d}{2}, p - \frac{d}{2}\right)}{2^d\pi^{\frac{d+1}{2}}\Gamma(\frac{d-1}{2})}\right]^{1/p}.$$

If $\alpha \in \{0, 1\}$ then we must have $p \geq 2$ due to our assumptions. Then the proof is the same except we do not use Hölder's inequality. □

Proof of Proposition 3.10. For $V = V_1 + V_2 \in L^p(\mathbb{R}^2) + L^\infty(\mathbb{R}^2)$ with $p \in (1\,, \infty)$, we write

$$-\Delta + V + \nu = (-\Delta + \nu)^{1/2}\left(1 + (-\Delta + \nu)^{-1/2}V(-\Delta + \nu)^{-1/2}\right)(-\Delta + \nu)^{1/2}\,.$$

Using Lemma 3.11 with $\alpha = 1/2$, for all $\nu \geq \max\left[\left(4C(2, p)\,\|V_1\|_{L^p(\mathbb{R}^2)}\right)^{\frac{p}{p-1}}, 4\,\|V_2\|_{L^\infty(\mathbb{R}^2)}\right]$ we have

$$\left\|(-\Delta+\nu)^{-1/2}V(-\Delta+\nu)^{-1/2}\right\| \leq 1/2\,.$$

Hence, the operator $-\Delta+V+\nu$ is invertible and its inverse is given by a Neumann series. We have

$$(-\Delta+V+\nu)^{-1}=(-\Delta+\nu)^{-1/2}\sum_{n\geq 0}(-1)^n\left[(-\Delta+\nu)^{-1/2}V(-\Delta+\nu)^{-1/2}\right]^n(-\Delta+\nu)^{-1/2}\,.$$

We multiply by $(-\Delta+\nu)^{\alpha}$ for $\alpha=\min(\frac{p}{2},1)\in(1/2\,,1]$ and we obtain

$$(-\Delta+\nu)^{\alpha}(-\Delta+V+\nu)^{-1}=\sum_{n\geq 0}(-1)^n\left[(-\Delta+\nu)^{-1+\alpha}V(-\Delta+\nu)^{-\alpha}\right]^n(-\Delta+\nu)^{-1+\alpha}\,.$$

The term of order n is bounded by Lemma 3.11

$$\left\|\left[(-\Delta+\nu)^{-1+\alpha}V(-\Delta+\nu)^{-\alpha}\right]^n\right\| \leq \left(C(2,p)\nu^{\frac{1}{p}-1}\left\|V_1\right\|_{L^p(\mathbb{R}^2)}+\nu^{-1}\left\|V_2\right\|_{L^\infty(\mathbb{R}^2)}\right)^n \leq 2^{-n}\,.$$

Hence, we have obtained estimate (3.27). This also shows that $\mathcal{D}(-\Delta+V)\subset\mathcal{D}((-\Delta+\nu)^{\alpha})=H^{\min(p,2)}(\mathbb{R}^2)$ with the inequality

$$\left\|(-\Delta+\nu)^{\alpha}u\right\|_{L^2(\mathbb{R}^2)} \leq 2\nu^{-1+\alpha}\left\|(-\Delta+V+\nu)u\right\|_{L^2(\mathbb{R}^2)}\,.$$

Thus, we find, for all $u\in\mathcal{D}(-\Delta+V)$ and $\nu\geq 1$,

$$\left\|(-\Delta+1)^{\alpha}u\right\|_{L^2(\mathbb{R}^2)} \leq 2\left\|(-\Delta+V)u\right\|_{L^2(\mathbb{R}^2)}+C(\left\|V_1\right\|_{L^p(\mathbb{R}^2)},\left\|V_2\right\|_{L^\infty(\mathbb{R}^2)})\left\|u\right\|_{L^2(\mathbb{R}^2)}\,,$$

with

$$C(\left\|V_1\right\|_{L^p(\mathbb{R}^2)},\left\|V_2\right\|_{L^\infty(\mathbb{R}^2)})=2\cdot\max\left[1,(4C(2,p)\left\|V_1\right\|_{L^p(\mathbb{R}^2)})^{\frac{p\alpha}{p-1}},4\left\|V_2\right\|^{\alpha}_{L^\infty(\mathbb{R}^2)}\right]\,.$$

Estimate (3.29) is immediate since $\alpha\leq 1$ and $\frac{p}{p-1}\geq 1$. This concludes the proof of Proposition 3.10. □

3.4 Kato's inequalities

In this section, we state Kato type estimates on the periodic potential V_L in both $L^2(\mathbb{R}^2)$ and $L^2_{\mathbf{k}}(\Gamma_L)$ spaces. In addition, we show that the constants appearing in the upper bounds grow polynomially with L.

Before stating our proposition, we notice that Assumption 1 *(ii)* and Assumption 5 implies that the $\left\|V_L\right\|_{L^p_{\mathrm{per}}(\Gamma_L)}$ grows at most polynomially with L:

$$\exists M\in\mathbb{R},\quad \left\|V_L\right\|_{L^p_{\mathrm{per}}(\Gamma_L)}=O\big(L^M\big) \tag{3.31}$$

Proposition 3.12 (Kato's inequalities)**.** *Let $L\geq 1$. For all $\epsilon>0$ there exists $C(\epsilon,L)>0$ such that for all $u\in H^1(\mathbb{R}^2)$, we have*

$$\left\langle u,\left|V_L\right|u\right\rangle_{L^2(\mathbb{R}^2)} \leq \epsilon\left\|\nabla u\right\|^2_{L^2(\mathbb{R}^2)}+C(\epsilon,L)\left\|u\right\|^2_{L^2(\mathbb{R}^2)}\,, \tag{3.32}$$

and such that for all $\mathbf{k}\in\Gamma^*_L$ and for all $u\in H^1_{\mathbf{k}}(\Gamma_L)$, we have

$$\left\langle u,\left|V_L\right|u\right\rangle_{L^2_{\mathbf{k}}(\Gamma_L)} \leq \epsilon\left\|\nabla u\right\|^2_{L^2_{\mathbf{k}}(\Gamma_L)}+C(\epsilon,L)\left\|u\right\|^2_{L^2_{\mathbf{k}}(\Gamma_L)}\,. \tag{3.33}$$

For any $r\in(p\,,\infty)$, we can take $C(\epsilon,L)=O\Big(\epsilon^{-\frac{2r}{p}}L^{M\frac{p+r}{p}}\Big)$ where M is the constant appearing in (3.31).

Proof. We start with the proof of (3.32). Let $A > 0$ and $u \in H^1(\mathbb{R}^2)$. Let $q \in (p, \infty)$ and $q' \in (1, \frac{p}{p-1})$ such that $1/q + 1/q' = 1$. Using the periodicity of V_L and Hölder's inequality, we write

$$\langle u, |V_L|\, u\rangle_{L^2(\mathbb{R}^2)} \leq \left\| V_L \mathbb{1}_{|V_L|\geq A} \right\|_{L^q_{\mathrm{per}}(\Gamma_L)} \left(\sum_{\mathbf{u}\in\mathscr{L}} \|u\|^2_{L^{2q'}(\Gamma_L + L\mathbf{u})} \right) + A \|u\|^2_{L^2(\mathbb{R}^2)} . \tag{3.34}$$

We will show the following inequality

$$\sum_{\mathbf{u}\in\mathscr{L}} \|u\|^2_{L^{2q'}(\Gamma_L + L\mathbf{u})} \lesssim \|u\|^2_{H^1(\mathbb{R}^2)} . \tag{3.35}$$

Let $\eta \in \mathcal{C}^\infty_c(\mathbb{R}^2)$ identically equal to 1 on Γ, with support in 2Γ and such that $0 \leq \eta \leq 1$. Notice that

$$|\{\mathbf{u} \in \mathscr{L} \mid (\Gamma + \mathbf{u}) \cap 2\Gamma \neq \emptyset\}| \leq 9 .$$

We introduce $\eta_{L,\mathbf{u}}(\mathbf{x}) \coloneqq \eta(L^{-1}\mathbf{x} - \mathbf{u})$. Using the Sobolev embedding $H^1(\mathbb{R}^2) \subset L^{2q'}(\mathbb{R}^2)$, we have

$$\begin{aligned}
\sum_{\mathbf{u}\in\mathscr{L}} \|u\|^2_{L^{2q'}(\Gamma_L + L\mathbf{u})} &\leq \sum_{\mathbf{u}\in\mathscr{L}} \|\eta_{L,\mathbf{u}} u\|^2_{L^{2q'}(\mathbb{R}^2)} \lesssim \sum_{\mathbf{u}\in\mathscr{L}} \|\eta_{L,\mathbf{u}} u\|^2_{H^1(\mathbb{R}^2)} \\
&\lesssim \int_{\mathbb{R}^2} \left(\sum_{\mathbf{u}\in\mathscr{L}} |\eta_{L,\mathbf{u}}|^2 + |\nabla \eta_{L,\mathbf{u}}|^2 \right) |u|^2 + \int_{\mathbb{R}^2} \left(\sum_{\mathbf{u}\in\mathscr{L}} |\eta_{L,\mathbf{u}}|^2 \right) |\nabla u|^2 \\
&\lesssim 9 \left(1 + L^{-2} \|\nabla \eta\|^2_{L^\infty(\mathbb{R}^2)} \right) \|u\|^2_{H^1(\mathbb{R}^2)} .
\end{aligned}$$

We insert (3.35) into (3.34) then we can choose A large enough such that (3.32) holds. To show (3.33), we write for $A > 0$ and $u \in H^1_{\mathbf{k}}(\Gamma_L)$

$$\langle u, |V_L|\, u\rangle_{L^2_{\mathbf{k}}(\Gamma_L)} \leq \left\| V_L \mathbb{1}_{|V|\geq A} \right\|_{L^q_{\mathrm{per}}(\Gamma_L)} \|u\|^2_{L^{2q'}_{\mathbf{k}}(\Gamma_L)} + A \|u\|^2_{L^2_{\mathbf{k}}(\Gamma_L)} .$$

We conclude using the Sobolev embedding $H^1_{\mathbf{k}}(\Gamma_L) \subset L^{2q'}_{\mathbf{k}}(\Gamma_L)$ (where the constant of continuity does not depend on L, see for instance [Aub98, Theorem 2.28]) then taking A large enough. For the last statement, we consider $r > p$ such that $\frac{1}{q} = \frac{1}{2}\left(\frac{1}{p} + \frac{1}{r}\right)$. Then, by Hölder's inequality and Tchebychev's inequality, we have

$$\left\| V_L \mathbb{1}_{|V_L|\geq A} \right\|_{L^q_{\mathrm{per}}(\Gamma_L)} \leq \left(\|V_L\|_{L^p_{\mathrm{per}}(\Gamma_L)} \left\| \mathbb{1}_{|V_L|\geq A} \right\|_{L^r_{\mathrm{per}}(\Gamma_L)} \right)^{1/2} \leq \|V_L\|^{\frac{r+p}{2r}}_{L^p_{\mathrm{per}}(\Gamma_L)} A^{-\frac{p}{2r}} \lesssim L^{M\frac{r+p}{2r}} A^{-\frac{p}{2r}} ,$$

where $M \in \mathbb{R}$ is the constant appearing in (3.31). This concludes the proof of Proposition 3.12. $\square$

Remark 3.13. In some cases, the constant $C(\epsilon, L)$ appearing in (3.32) or (3.33) does not depend on L, for instance, if there exists $C > 0$ such that for any $\mathbf{r} \in \mathbf{R}$ we have $|V_L(\mathbf{x} - \mathbf{r})| \leq C |\mathbf{x} - \mathbf{r}|^{-1}$ in some neighborhood of $\mathbf{r}$.

As a consequence of Proposition 3.12, the closure of the operator $(-\Delta+1)^{-1/2} V_L (-\Delta+1)^{-1/2}$ is bounded with norm at most polynomial in L.

Corollary 3.14. *We have*

$$\left\| \frac{1}{\sqrt{-\Delta+1}} V_L \frac{1}{\sqrt{-\Delta+1}} \right\|_{\mathcal{B}(L^2(\mathbb{R}^2))} = O(L^M) \quad \text{and} \quad \left\| \frac{1}{\sqrt{-\Delta+1}} V_L \frac{1}{\sqrt{-\Delta+1}} \right\|_{\mathcal{B}(L^2_{\mathbf{k}}(\Gamma_L))} = O(L^M) , \tag{3.36}$$

where the second O is uniform in $\mathbf{k}$.

Proof. Indeed, we use the estimate $C(L, \epsilon) \lesssim \epsilon^{-\frac{2r}{p}} L^{M\frac{p+r}{p}}$ for some $r > p$ and we take $\epsilon =$

$L^{M\left(1-\frac{r}{p+2r}\right)}$ to obtain

$$\forall \psi \in L^2(\mathbb{R}^2), \quad \left\| \sqrt{|V_L|} \frac{1}{\sqrt{-\Delta+1}} \psi \right\|^2_{L^2(\mathbb{R}^2)} \lesssim L^{M\left(1-\frac{r}{p+2r}\right)} \|\psi\|^2_{L^2(\mathbb{R}^2)} \lesssim L^M \|\psi\|^2_{L^2(\mathbb{R}^2)} .$$

Consequently, the operator $A := \sqrt{|V_L|}\frac{1}{\sqrt{-\Delta+1}}$ is bounded on $L^2(\mathbb{R}^2)$. Let $B := \frac{1}{\sqrt{-\Delta+1}}\sqrt{|V_L|}$ defined on the domain $\mathcal{D}(\sqrt{|V_L|}) = \left\{\psi \in L^2(\mathbb{R}^2) \;\middle|\; \sqrt{|V_L|}\psi \in L^2(\mathbb{R}^2)\right\}$. The operator B is densely defined and closed on $L^2(\mathbb{R}^2)$ (see [Sch12, Example 3.8]). By [Sch12, Proposition 1.7], we have $B^* = A$. This implies that $B^{**} = \overline{B} \in \mathcal{B}(L^2(\mathbb{R}^2))$ and we deduce that the operator

$$B\,\mathrm{sign}(V_L)A = \frac{1}{\sqrt{-\Delta+1}} V_L \frac{1}{\sqrt{-\Delta+1}} ,$$

admits a bounded extension on $L^2(\mathbb{R}^2)$ with norm at most $O\big(L^M\big)$. The proof of the right side of (3.36) is the same. □

3.5 Exponential bounds on v

In the next proposition, we give pointwise and integral exponential bounds on the first eigenfunction v of the self-adjoint operator $H = -\Delta + V$ where the potential V is the reference potential appearing in Assumption 4.

Recall that we can choose the phase of v such that $v > 0$ by [Goe77]. By Proposition 3.10, we also have $v \in H^{\min(p,2)}(\mathbb{R}^2)$. In particular, the Sobolev embeddings imply that $v \in L^\infty(\mathbb{R}^2) \cap \mathcal{C}_0^{0,\min(p-1,1)}(\mathbb{R}^2)$ where $\mathcal{C}_0^{\ell,\theta}(\mathbb{R}^2)$ denotes the spaces of $\mathcal{C}^\ell(\mathbb{R}^2)$ functions which vanish at infinity as well as their first ℓ derivatives and such that the derivatives of order ℓ are Hölder continuous with exponent $\theta \in [0\,,1]$.

Proposition 3.15 (Exponential bounds on v)**.** *There exists a constant $C > 0$ such that*

$$\forall \mathbf{x} \in \mathbb{R}^2, \quad \frac{1}{C}\frac{e^{-\sqrt{\mu}|\mathbf{x}|}}{1+\sqrt{|\mathbf{x}|}} \leq v(\mathbf{x}) \leq C \frac{e^{-\sqrt{\mu}|\mathbf{x}|}}{1+\sqrt{|\mathbf{x}|}} ,$$
$$\forall R \geq 0, \quad \int_{|\mathbf{x}|\geq R} \left(|v(\mathbf{x})|^2 + |\nabla v(\mathbf{x})|^2\right) \mathrm{d}\mathbf{x} \leq C e^{-2\sqrt{\mu}R} .$$

Proof. The result can be found in [HHS85, Corollary 2.2 & Remark 2.2]. For the convenience of the reader, we provide a simple proof under the stronger assumption that $V(\mathbf{x}) = O\Big(|\mathbf{x}|^{-2}\Big)$.

The function v satisfies the equation $(-\Delta + V + \mu)\,v = 0$ in $H^{-1}(\mathbb{R}^2)$. Let $A > 0$ be such that $|V(\mathbf{x})| \leq A/(2\,|\mathbf{x}|^2)$ for all $|\mathbf{x}| \geq 1$ and let $R > 0$ be such that $\mu \geq A/\,|\mathbf{x}|^2$ for all $|\mathbf{x}| \geq R$. Let $\Omega = B(0,R)^c$. We consider a function $Y_\pm$ vanishing at infinity and solution of the equation

$$\left(-\Delta \pm \frac{A}{|\mathbf{x}|^2} + \mu\right) Y_\pm = 0 \quad \text{on} \quad \Omega\,.$$

Up to a multiplicative non zero constant, we have $Y_\pm(\mathbf{x}) = K_{\sqrt{\pm A}}\left(\sqrt{\mu}\,|\mathbf{x}|\right)$ where K_ν denotes the modified Bessel of the second kind with parameter $\nu \in \mathbb{C}$. Following [Olv97, p.266-267], we can show that the function $Y_\pm$ satisfies the following asymptotics

$$Y_\pm(\mathbf{x}) = \sqrt{\frac{\pi}{2\sqrt{\mu}\,|\mathbf{x}|}} e^{-\sqrt{\mu}|\mathbf{x}|} \left(1 + O\left(\frac{1}{|\mathbf{x}|}\right)\right) .$$

Moreover, by the continuity of v, there exists a constant $C > 0$ such that

$$\forall \mathbf{x} \in \partial\Omega, \quad \frac{1}{C} Y_+(\mathbf{x}) \leq v(\mathbf{x}) \leq C Y_-(\mathbf{x})\,.$$

The function v (resp. Y_-) is a supersolution of the operator $-\Delta + A/|\mathbf{x}|^2 + \mu$ (resp. $-\Delta + V + \mu$). We already know that v goes to zero at infinity. Then [Hof80, Theorem 1.1] implies (notice that $V + \mu \geq 0$ and $-A/|\mathbf{x}|^2 + \mu \geq 0$ on Ω)

$$\forall \mathbf{x} \in \Omega, \quad \frac{1}{C} Y_+(\mathbf{x}) \leq v(\mathbf{x}) \leq C Y_-(\mathbf{x}) .$$

We extend these estimates to $\mathbb{R}^2$ using the continuity of v.

The integral bound on v is a direct consequence of the pointwise one. To get the integral bound on ∇v, we multiply $-\Delta v + \mu v = -Vv$ by ηv where $\eta \equiv 1$ on $|\mathbf{x}| \geq R$ and $\eta \equiv 0$ on $|\mathbf{x}| \leq R - \delta$ for $\delta > 0$ small enough and we integrate by parts. $\square$

3.6 Properties of the mono-atomic operators

We recall that the effective potential $V_{L,\mathbf{r}}$ and its associated mono-atomic Schrödinger operator $H_{L,\mathbf{r}} = -\Delta + V_{L,\mathbf{r}}$ are defined in (3.10) and (3.11). In this section, we give spectral properties of this operator. Because they are standard, most statements are given without proof, see [RS75; RS78; Cyc+87].

The function $V_{L,\mathbf{r}}$ belongs to the Kato class and we can consider its Friedrichs extension which defines a self-adjoint operator on the domain

$$\mathcal{D}(H_{L,\mathbf{r}}) = \left\{ u \in H^1(\mathbb{R}^2) \;\middle|\; (-\Delta + V_{L,\mathbf{r}})\, u \in L^2(\mathbb{R}^2) \right\} .$$

The essential spectrum of $H_{L,\mathbf{r}}$ is given by $\sigma_{\mathrm{ess}}(H_{L,\mathbf{r}}) = [0\,,\infty)$. Since H has a negative eigenvalue by Assumption 5, it follows from perturbation theory (see Corollary 3.47 and [RS78, Chapter XII]) that the discrete spectrum of $H_{L,\mathbf{r}}$ is non-empty and the lowest eigenvalue of $H_{L,\mathbf{r}}$ is non-degenerate for L large enough.

Now, we denote by s_L the scaling operator by L defined by $s_L \mathbf{x} = L\mathbf{x}$. Then we can write $\mathscr{L}_L^{\mathbf{R}} = s_L[\mathscr{L}^{\mathbf{R}}]$ and the group $G_L := s_L G s_L^{-1} \subset E_2(\mathbb{R})$. By Assumption 3 and the fact that χ is radial, we have

$$\forall g \in G, \quad \forall \mathbf{r} \in \mathscr{L}^{\mathbf{R}}, \quad (s_L g s_L^{-1}) \cdot V_{L,\mathbf{r}} = V_{L,g\cdot\mathbf{r}} . \tag{3.37}$$

In particular, we notice that the action of G_L on the set $\{V_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$ only operates on the labels $\mathbf{r} \in \mathscr{L}^{\mathbf{R}}$ and, as a consequence of Assumption 2, this action is also transitive. Therefore, the operators $\{H_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$ are unitarily equivalent and share the same spectrum. We denote their common discrete spectrum by

$$\sigma_{\mathrm{d}}(H_{L,\mathbf{r}}) = \{-\mu_{1,L} < -\mu_{2,L} \leq -\mu_{3,L} \leq \cdots \leq 0\} \subset (-\infty\,, 0], \quad \forall \mathbf{r} \in \mathscr{L}^{\mathbf{R}} .$$

To lighten the notations, we will write μ_L instead of $\mu_{1,L}$. We recall that we denote by $v_{L,\mathbf{r}}$ the normalized eigenfunction of $H_{L,\mathbf{r}}$ associated with $-\mu_L$. We can choose the overall phase of $v_{L,\mathbf{r}}$ such that $v_{L,\mathbf{r}} > 0$ and we have $v_{L,\mathbf{r}} \in H^{\min(p,2)}(\mathbb{R}^2) \cap \mathcal{C}_0^{0,\min(p-1,1)}(\mathbb{R}^2)$. Moreover, by the non-degeneracy of $-\mu_L$, the group G_L also acts transitively on the set $\{v_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$ and, as for $V_{L,\mathbf{r}}$, operates only on the labels $\mathbf{r} \in \mathscr{L}^{\mathbf{R}}$

$$\forall g \in G, \quad \forall \mathbf{r} \in \mathscr{L}^{\mathbf{R}}, \quad (s_L g s_L^{-1}) \cdot v_{L,\mathbf{r}} = v_{L,g\cdot\mathbf{r}} . \tag{3.38}$$

In particular, these relations imply that the interaction coefficient $\theta_{L,k}$ defined in (3.14) does not depend on the choice of the pair $\mathbf{p}_k \in \mathcal{O}_k$.

In Corollary 3.47 from the appendix, we show that Assumption 5 implies that the first eigenvalue/eigenfunction pair of $H_{L,\mathbf{r}}$ converges, up to a translation by $L\mathbf{r}$, to the one of H. More precisely, we have

$$\lim_{L\to\infty} \mu_L = \mu \quad \text{and} \quad \forall \mathbf{r} \in \mathscr{L}^{\mathbf{R}}, \quad \lim_{L\to\infty} \|v_{L,\mathbf{r}} - v(\cdot - L\mathbf{r})\|_{H^{\min(p,2)}(\mathbb{R}^2)} = 0 . \tag{3.39}$$

Notice that by the Sobolev embeddings, we have convergence in $L^\infty(\mathbb{R}^2)$

$$\lim_{L\to\infty} \|v_{L,\mathbf{r}} - v(\cdot - L\mathbf{r})\|_{L^\infty(\mathbb{R}^2)} = 0\,. \tag{3.40}$$

Also, the right side of (3.39) implies that v is invariant under the action of the point group of G_L. Also, if we denote by g_L the spectral gap of $H_{L,\mathbf{r}}$ above its lowest eigenvalue $-\mu_L$ then we have $g_L = g + o(1)$.

3.7 Uniform exponential bounds on $v_{L,\mathbf{r}}$

In the next proposition, we give exponential bounds on $v_{L,\mathbf{r}}$. We use Assumption 5 to show they are independent from L.

Proposition 3.16 (Uniform exponential bounds on $v_{L,\mathbf{r}}$)**.** *Let $\epsilon \in (0\,,1)$. There exists $L_\epsilon \geq 1$ and $C_\epsilon > 0$ such that for all $L \geq L_\epsilon$ we have*

$$\begin{aligned} &\forall \mathbf{x}\in\mathbb{R}^2, \quad \forall \mathbf{r}\in\mathscr{L}^{\mathbf{R}}, \quad \frac{1}{C_\epsilon} e^{-(1+\epsilon)\sqrt{\mu}|\mathbf{x}-L\mathbf{r}|} \leq v_{L,\mathbf{r}}(\mathbf{x}) \leq C_\epsilon e^{-(1-\epsilon)\sqrt{\mu}|\mathbf{x}-L\mathbf{r}|}\,,\\ &\forall R>0, \quad \int_{|\mathbf{x}-L\mathbf{r}|\geq R} \left(|v_{L,\mathbf{r}}(\mathbf{x})|^2 + |\nabla v_{L,\mathbf{r}}(\mathbf{x})|^2\right) \mathrm{d}\mathbf{x} \leq C_\epsilon e^{-2(1-\epsilon)\sqrt{\mu}R}\,. \end{aligned} \tag{3.41}$$

Proof. The function v_L satisfies the equation $(-\Delta + V_{L,\mathbf{r}} + \mu_L)\, v_{L,\mathbf{r}} = 0$ in $H^{-1}(\mathbb{R}^2)$ where $V_{L,\mathbf{r}}$ is compactly supported in the ball $B\left(L\mathbf{r}, \left(\frac{1}{2}+\delta\right) L d_0\right)$. Let $\epsilon \in (0\,,\mu)$ and $R_\epsilon > 0$ such that $|V(\mathbf{x})| \leq \epsilon/4$ for all $|\mathbf{x}| \geq R_\epsilon$. Let $\Omega_\epsilon = B(0, R_\epsilon)^c$. We consider $Y_\pm$ the solution of the equation

$$(-\Delta + \mu \pm \epsilon)\, Y_\pm = 0 \quad \text{on} \quad \Omega_\epsilon\,.$$

We have $Y_\pm(\mathbf{x}) = K_0\left((\mu\pm\epsilon)^{\frac{1}{2}}\,|\mathbf{x}|\right)$ where K_0 denotes the modified Bessel of the second kind with parameter 0. Following [Olv97, p.266-267], we can show that the function $Y_\pm$ satisfies the asymptotics

$$Y_\pm(\mathbf{x}) = \sqrt{\frac{\pi}{2(\mu\pm\epsilon)^{\frac{1}{2}}\,|\mathbf{x}|}}\, e^{-(\mu\pm\epsilon)^{\frac{1}{2}}|\mathbf{x}|}\left(1 + O\left(\frac{1}{|\mathbf{x}|}\right)\right)\,.$$

By the continuity of $v_{L,\mathbf{r}}$ and the convergence (3.40) in $L^\infty(\mathbb{R}^2)$, there exists a constant $C_\epsilon > 0$ independent from L and such that

$$\forall \mathbf{x}\in\partial\Omega_\epsilon, \quad \frac{1}{C_\epsilon} Y_+(\mathbf{x}-L\mathbf{r}) \leq v_{L,\mathbf{r}}(\mathbf{x}) \leq C_\epsilon Y_-(\mathbf{x}-L\mathbf{r})\,.$$

Using the right side of (3.39) and Assumption 5, we show that $v_{L,\mathbf{r}}(\cdot + L\mathbf{r})$ (resp. $Y_-(\cdot - L\mathbf{r})$) is a supersolution of the operator $-\Delta+\mu+\epsilon$ (resp. $-\Delta + V_{L,\mathbf{r}} + \mu_L$) for L large enough, depending on ϵ. We already know that $v_{L,\mathbf{r}}$ goes to zero at infinity. Then [Hof80, Theorem 1.1] implies (notice that $V_{L,\mathbf{r}} + \mu_L \geq 0$ on $L\mathbf{r} + \Omega_\epsilon$ for L large enough)

$$\forall \mathbf{x}\in\Omega_\epsilon, \quad \frac{1}{C_\epsilon} Y_+(\mathbf{x}-L\mathbf{r}) \leq v_{L,\mathbf{r}}(\mathbf{x}) \leq C_\epsilon Y_-(\mathbf{x}-L\mathbf{r})\,.$$

We extend these estimates to $\mathbb{R}^2$ using $\|v_{L,\mathbf{r}} - v\|_{L^\infty(\mathbb{R}^2)} = o(1)$ and we absorb the polynomial terms by slightly modifying ϵ. The integral bounds (3.41) are shown as in the proof of Proposition 3.15. □

3.8 Orthonormalization procedure

In this section, we use the Gram-Schmidt process to construct an orthonormal family $\{w_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$ from the almost orthonormal family $\{v_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$.

First, we precise our notation concerning infinite matrices. Let Λ be an infinite countable set. The Hilbert space of square summable and complex valued sequences labeled by Λ is denoted by $\ell^2(\Lambda)$. A bounded operator $A \in \mathcal{B}(\ell^2(\Lambda))$ can be represented by an infinite matrix $(A(\mathbf{u},\mathbf{u}'))_{(\mathbf{u},\mathbf{u}')\in\Lambda\times\Lambda}$ in the orthonormal basis $\{|\mathbf{u}\rangle\}_{\mathbf{u}\in\Lambda}$ where $|\mathbf{u}\rangle = (\delta(\mathbf{u},\mathbf{u}'))_{\mathbf{u}'\in\Lambda}$ with $\delta(\mathbf{u},\mathbf{u}')$ equal 1 if $\mathbf{u}'=\mathbf{u}$ and 0 otherwise. The identity matrix is denoted by I. The operator norm of a bounded operator A will be denoted $\|A\|$. In the sequel, we consider square infinite matrices indexed by $\mathscr{L}^{\mathbf{R}}\times\mathscr{L}^{\mathbf{R}}$. Finally, if a group G acts on Λ then we denote by $g\cdot A$ the action of $g\in G$ on $A\in\mathcal{B}(\ell^2(\Lambda))$ defined by

$$g\cdot A \coloneqq T_g^* A T_g\,, \tag{3.42}$$

where T_g is the permutation matrix $T_g : |\mathbf{u}\rangle \mapsto |g\cdot\mathbf{u}\rangle$.

Now, we discuss the construction of $\{w_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$. In this setting, the tunneling coefficient is given by

$$\boxed{T_L \coloneqq \exp\left(-\sqrt{\mu}L\right)\,.} \tag{3.43}$$

It measures the magnitude of the tunneling effect when $L\to\infty$. We construct the infinite Gram matrix for the family $\{v_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$ as

$$Q_L(\mathbf{r},\mathbf{r}') \coloneqq \langle v_{L,\mathbf{r}}, v_{L,\mathbf{r}'}\rangle_{L^2(\mathbb{R}^2)} > 0, \quad \forall(\mathbf{r},\mathbf{r}')\in\mathscr{L}^{\mathbf{R}}\times\mathscr{L}^{\mathbf{R}}\,.$$

Using the symmetry relations (3.38), the matrix Q_L is G-invariant:

$$\forall g\in G,\quad g\cdot Q_L = Q_L\,. \tag{3.44}$$

In order to estimate the Gram matrix, we first need a technical lemma about convolutions of exponentials.

Lemma 3.17. *Let $\nu>0$. Then, for all $\epsilon\in(0\,,1)$, we have*

$$\forall\mathbf{x}\in\mathbb{R}^2,\quad \frac{1}{\nu^2}\left(1+\nu\,|\mathbf{x}|\right)e^{-\nu|\mathbf{x}|} \le \left(e^{-\nu|\cdot|} * e^{-\nu|\cdot|}\right)(\mathbf{x}) \le \frac{\pi}{2\nu^2}\left(1+\nu\,|\mathbf{x}|\right)e^{-\nu|\mathbf{x}|}\,.$$

Proof. Let $\mathcal{E}_a$ is the ellipse defined by the equation $|\mathbf{y}-\mathbf{x}|+|\mathbf{y}| = 2a$ where $a\ge\frac{|\mathbf{x}|}{2}$ is the semi-major axis. Using the formula $|\mathcal{E}_a| = 4aE(|\mathbf{x}|/2a)$ where E denotes the complete elliptic integral of second kind, we have

$$\left(e^{-\nu|\cdot|} * e^{-\nu|\cdot|}\right)(\mathbf{x}) = \int_{\frac{|\mathbf{x}|}{2}}^{\infty} e^{-2\nu a}\,|\mathcal{E}_a|\,\mathrm{d}a = \int_{|\mathbf{x}|}^{\infty} a e^{-\nu a}E\left(|\mathbf{x}|/a\right)\mathrm{d}a\,.$$

It remains to use the estimates $1\le E(e)\le\frac{\pi}{2}$ valid for all $e\in[0\,,1]$ to conclude the proof of Lemma 3.17. $\square$

The constants appearing in Lemma 3.17 are explicit in ν which is convenient for our setting where we consider $\nu=\sqrt{\mu}L$ with $L\to\infty$.

We recall that $v_{L,\mathbf{r}}$ admits upper and lower pointwise exponential bounds (see Proposition 3.16). Then Lemma 3.17 implies that for all $\epsilon>0$ there exists $C_\epsilon>0$ such that

$$Q_L(0,0)=1 \quad\text{and}\quad \frac{1}{C_\epsilon}T_L^{(1+\epsilon)|\mathbf{r}-\mathbf{r}'|} \le Q_L(\mathbf{r},\mathbf{r}') \le C_\epsilon T_L^{(1-\epsilon)|\mathbf{r}-\mathbf{r}'|}\,. \tag{3.45}$$

The polynomial terms have been absorbed by slightly modifying the ϵ in Proposition 3.16.

We recall that the group G acts on the set of pairs of nearest neighbors

$$\mathscr{P}^{\mathbf{R}} = \left\{(\mathbf{r},\mathbf{r}')\in\mathscr{L}^{\mathbf{R}}\times\mathscr{L}^{\mathbf{R}}\;\middle|\;|\mathbf{r}-\mathbf{r}'| = d_0\right\}\,,$$

introduced in (3.13). The orbits of this action are denoted by $\mathcal{O}_1,\dots,\mathcal{O}_m$. For all $k\in\{1,\dots,m\}$, we consider $\mathbf{p}_k = (\mathbf{r}_k, \mathbf{r}'_k) \in \mathcal{O}_k$ and we introduce the interaction coefficient

$$\zeta_{L,k} \coloneqq \langle v_{L,\mathbf{r}_k}, v_{L,\mathbf{r}'_k} \rangle_{L^2(\mathbb{R}^2)} ,$$

which does not depend on the choice of the representative in $\mathcal{O}_k$. Using the estimate (3.45), we immediately have

$$\frac{1}{C_\epsilon} T_L^{(1+\epsilon)d_0} \leq \zeta_{L,k} \leq C_\epsilon T_L^{(1-\epsilon)d_0} , \tag{3.46}$$

for all $\epsilon > 0$. We also introduce the *adjacency matrix* J_k associated with the orbit $\mathcal{O}_k$, defined as

$$J_k(\mathbf{r}, \mathbf{r}') = \begin{cases} 1 & \text{if } (\mathbf{r}, \mathbf{r}') \in \mathcal{O}_k \, , \\ 0 & \text{otherwise} \, . \end{cases} \tag{3.47}$$

Lemma 3.18. *We have the expansion*

$$\left\| Q_L - I - \sum_{k=1}^m \zeta_{L,k} J_k \right\|_{\ell^2(\mathscr{L}^{\mathbf{R}}) \to \ell^2(\mathscr{L}^{\mathbf{R}})} = O\Big(T_L^{d_1 -}\Big) \, .$$

We recall that the notation $O\Big(T_L^{d_1 -}\Big)$ is defined in Section 3.2.

Proof. To show this expansion, first notice that the matrix element $(\mathbf{r}, \mathbf{r}')$ of $Q_L - I - \sum_{k=1}^m \zeta_{L,k} J_k$ is equal to zero if $\mathbf{r} = \mathbf{r}'$ or $(\mathbf{r}, \mathbf{r}') \in \mathscr{P}^{\mathbf{R}}$. It remains to call on Schur's test [Gra14b, Appendix A.1] and the estimates (3.45). □

Let $K_L \coloneqq Q_L - I$. As a consequence of Lemma 3.18 and (3.46), we have

$$\|K_L\| = O\Big(T_L^{d_0 -}\Big) \, , \tag{3.48}$$

and by the (power series) functional calculus, we can write for L large enough

$$Q_L^{-1} = I - K_L + O\Big(T_L^{2d_0 -}\Big) \quad \text{and} \quad Q_L^{-\frac{1}{2}} = I - \frac{1}{2} K_L + O\Big(T_L^{2d_0 -}\Big) \, . \tag{3.49}$$

The infinite matrices Q_L^{-1} and $Q_L^{-\frac{1}{2}}$ inherit the same periodicity property as Q_L, see (3.44):

$$\forall g \in G, \quad g \cdot Q_L^{-1} = Q_L^{-1} \quad \text{and} \quad g \cdot Q_L^{-\frac{1}{2}} = Q_L^{-\frac{1}{2}} \, . \tag{3.50}$$

The next lemma shows that Q_L^{-1} and $Q_L^{-\frac{1}{2}}$ are well-localized in the sense that their off-diagonal coefficients decays exponentially fast with $|\mathbf{r} - \mathbf{r}'|$.

Lemma 3.19. *Let $\epsilon \in (0, 1)$. There exists $L_\epsilon \geq 1$ such that for $L \geq L_\epsilon$ and for all $(\mathbf{r}, \mathbf{r}') \in (\mathscr{L}^{\mathbf{R}})^2$, we have*

$$\left| Q_L^{-1}(\mathbf{r}, \mathbf{r}') \right| \leq 2 T_L^{(1-\epsilon)|\mathbf{r} - \mathbf{r}'|} \quad \text{and} \quad \left| Q_L^{-\frac{1}{2}}(\mathbf{r}, \mathbf{r}') \right| \leq 2 T_L^{(1-\epsilon)|\mathbf{r} - \mathbf{r}'|} .$$

Remark 3.20. For $\alpha > 0$, the Banach algebra of infinite matrices with exponential off-diagonal decay of rate α is denoted by

$$\mathcal{E}_\alpha(\Lambda) \coloneqq \left\{ A \in \mathcal{B}(\ell^2(\Lambda)) \,\middle|\, \forall \alpha' < \alpha, \quad \exists C_{\alpha'} > 0, \quad \forall \mathbf{u} \neq \mathbf{v} \in \Lambda, \quad |A(\mathbf{u}, \mathbf{v})| \leq C_{\alpha'} e^{-\alpha' |\mathbf{u} - \mathbf{v}|} \right\} ,$$

where $\Lambda \subset \mathbb{R}^2$ is some discrete set without accumulation points. Notice that $Q_L \in \mathcal{E}_{L\sqrt{\mu}}(\mathscr{L}^{\mathbf{R}})$ by the estimates (3.45). If $A \in \mathcal{E}_\alpha(\Lambda)$ is invertible then there exists $0 < \beta < \alpha$ such that $A^{-1} \in \mathcal{E}_\beta(\Lambda)$, see [Jaf90, Proposition 2]. However, because the off-diagonal exponential decay rate of Q_L is L-dependent, this result is not precise enough for our purpose. In the proof of Lemma 3.19, we adapt of the arguments of [Jaf90].

Proof of Lemma 3.19. First, we show the following discrete convolution estimate: there exists $C > 0$ such that for all $\nu > 0$, for all $\epsilon \in (0\,,1)$, for all $L \geq (\epsilon\nu)^{-1}$ and for all $(\mathbf{r}, \mathbf{r}') \in (\mathscr{L}^{\mathbf{R}})^2$ we have

$$\sum_{\mathbf{r}'' \in \mathscr{L}^{\mathbf{R}}} e^{-\nu L\left|\mathbf{r}-\mathbf{r}''\right|} e^{-(1-\epsilon)\nu L\left|\mathbf{r}''-\mathbf{r}'\right|} \leq C e^{-(1-\epsilon)\nu L\left|\mathbf{r}-\mathbf{r}'\right|} . \tag{3.51}$$

Using the triangular inequality $|\mathbf{r}-\mathbf{r}''| + |\mathbf{r}''-\mathbf{r}'| \geq |\mathbf{r}-\mathbf{r}'|$, we have for $L \geq (\epsilon\nu)^{-1}$

$$\begin{aligned}\sum_{\mathbf{r}'' \in \mathscr{L}^{\mathbf{R}}} e^{-\nu L\left|\mathbf{r}-\mathbf{r}''\right|} e^{-(1-\epsilon)\nu L\left|\mathbf{r}''-\mathbf{r}'\right|} &\leq e^{-(1-\epsilon)\nu L\left|\mathbf{r}-\mathbf{r}'\right|} \sum_{\mathbf{r}'' \in \mathscr{L}^{\mathbf{R}}} e^{-\epsilon\nu L\left|\mathbf{r}-\mathbf{r}''\right|} \\ &\leq e^{-(1-\epsilon)\nu L\left|\mathbf{r}-\mathbf{r}'\right|} \sup_{\mathbf{s} \in \mathbf{R}} \sum_{\mathbf{r}'' \in \mathscr{L}^{\mathbf{R}}} e^{-\left|\mathbf{s}-\mathbf{r}''\right|} ,\end{aligned}$$

which shows the estimate (3.51).

Now, let $\epsilon \in (0\,,1)$ and $(\mathbf{r}, \mathbf{r}') \in (\mathscr{L}^{\mathbf{R}})^2$. On one hand, we have $|K_L^n(\mathbf{r}, \mathbf{r}')| \leq \|K_L\|^n$. On the other hand, using (3.45) there exists $C_\epsilon > 0$ such that

$$|K_L^n(\mathbf{r}, \mathbf{r}')| \leq C_\epsilon^n \sum_{\mathbf{r}_1 \in \mathscr{L}^{\mathbf{R}}} \cdots \sum_{\mathbf{r}_{n-1} \in \mathscr{L}^{\mathbf{R}}} T_L^{(1-\epsilon)|\mathbf{r}-\mathbf{r}_1|} \ldots T_L^{(1-\epsilon)\left|\mathbf{r}_{n-1}-\mathbf{r}'\right|}$$

Using (3.51) several times, there exists $C > 0$ such that for L large enough, we have

$$\begin{aligned}|K_L^n(\mathbf{r}, \mathbf{r}')| &\leq C_\epsilon^n \sum_{\mathbf{r}_1 \in \mathscr{L}^{\mathbf{R}}} \cdots \sum_{\mathbf{r}_{n-1} \in \mathscr{L}^{\mathbf{R}}} T_L^{(1-\epsilon)|\mathbf{r}-\mathbf{r}_1|} \ldots T_L^{(1-\epsilon)|\mathbf{r}_{n-2}-\mathbf{r}_{n-1}|} T_L^{(1-\epsilon)^2\left|\mathbf{r}_{n-1}-\mathbf{r}'\right|} \\ &\leq C C_\epsilon^n \sum_{\mathbf{r}_1 \in \mathscr{L}^{\mathbf{R}}} \cdots \sum_{\mathbf{r}_{n-2} \in \mathscr{L}^{\mathbf{R}}} T_L^{(1-\epsilon)|\mathbf{r}-\mathbf{r}_1|} \ldots T_L^{(1-\epsilon)|\mathbf{r}_{n-3}-\mathbf{r}_{n-2}|} T_L^{(1-\epsilon)^2\left|\mathbf{r}_{n-2}-\mathbf{r}'\right|} \\ &\leq (C C_\epsilon)^n T_L^{(1-\epsilon)^2\left|\mathbf{r}-\mathbf{r}'\right|} .\end{aligned}$$

Combining these two estimates, using the norm estimate $\|K_L\| = O\left(T_L^{d_0-}\right)$ and the expansion $Q_L^{-1} = \sum_{n\geq 0} (-1)^n K_L^n$, we have for L large enough

$$\left|Q_L^{-1}(\mathbf{r}, \mathbf{r}')\right| \leq \left(\sum_{n\geq 0} \left[\|K_L\|^\epsilon (C C_\epsilon)^{1-\epsilon}\right]^n\right) T_L^{(1-\epsilon)^3\left|\mathbf{r}-\mathbf{r}'\right|} \leq 2 T_L^{(1-\epsilon)^3\left|\mathbf{r}-\mathbf{r}'\right|} .$$

Replacing ϵ by $1-(1-\epsilon)^{1/3} \in (0\,,1)$, we end up with $\left|Q_L^{-1}(\mathbf{r}, \mathbf{r}')\right| \leq 2 T_L^{(1-\epsilon)\left|\mathbf{r}-\mathbf{r}'\right|}$. For $Q_L^{-\frac{1}{2}}$ the proof is the same except that we have to use the expansion

$$Q_L^{-\frac{1}{2}} = \sum_{n\geq 0} \binom{-1/2}{n} K_L^n \quad \text{where} \quad \binom{-1/2}{n} := (-1)^n \frac{(2n)!}{4^n (n!)^2} \sim_{n\to\infty} \frac{(-1)^n}{\sqrt{\pi n}} ,$$

for L large enough. □

For $\mathbf{r} \in \mathscr{L}^{\mathbf{R}}$, we set

$$\boxed{w_{L,\mathbf{r}} := \sum_{\mathbf{r}' \in \mathscr{L}^{\mathbf{R}}} Q_L^{-\frac{1}{2}}(\mathbf{r}, \mathbf{r}') v_{L,\mathbf{r}'} .} \tag{3.52}$$

We recall that s_L denotes the dilatation operator, defined by $s_L \mathbf{x} = L\mathbf{x}$.

Proposition 3.21 (Properties of $w_{L,\mathbf{r}}$)**.** *The series defining $w_{L,\mathbf{r}}$ converges in $H^{\min(p,2)}(\mathbb{R}^2)$. The family $\{w_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$ forms an orthonormal family of $L^2(\mathbb{R}^2)$, satisfies the same symmetry relations*

(3.38) *as* $\{v_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$

$$\forall g \in G, \quad \forall \mathbf{r} \in \mathscr{L}^{\mathbf{R}}, \quad (s_L g s_L^{-1}) \cdot w_{L,\mathbf{r}} = w_{L,g\cdot\mathbf{r}}\,, \tag{3.53}$$

and the following pointwise exponential bounds: for all $\epsilon \in (0\,,1)$ *there exists* $C_\epsilon > 0$ *such that*

$$\forall \mathbf{r} \in \mathscr{L}^{\mathbf{R}}, \quad \forall \mathbf{x} \in \mathbb{R}^2, \qquad |w_{L,\mathbf{r}}(\mathbf{x})| \leq C_\epsilon e^{-(1-\epsilon)\sqrt{\mu}|\mathbf{x}-L\mathbf{r}|}\,. \tag{3.54}$$

Remark 3.22. The functions $\{w_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$ resemble the *Wannier functions* associated with a periodic operator H [Wan37]. If we consider N spectral bands which are isolated from the remaining spectrum of H then the associated (composite) Wannier functions form an orthonormal basis of the corresponding spectral subspace. This family is generated by the shifts with respect to the underlying lattice of N of its elements (as in (3.53)) and they are exponentially localized if and only if the associated Bloch bundle is analytic which is equivalent to its topological triviality [MP14; Pan07]. The decay rate of the *maximally localized* Wannier functions is conjectured to be equal to the width of the largest analyticity strip for the Bloch bundle, which can be estimated using [RS78, Theorem XII.11] or [Kat95, Remark 2.9 & Remark 2.11].

Proof of Proposition 3.21. By Proposition 3.10 and the fact that $(Q_L^{-\frac{1}{2}}(\mathbf{r},\mathbf{r}'))_{\mathbf{r}'\in\mathscr{L}^{\mathbf{R}}}$ is summable (see Lemma 3.19), we have

$$\begin{aligned}\sum_{\mathbf{r}'\in\mathscr{L}^{\mathbf{R}}} \left|Q_L^{-\frac{1}{2}}(\mathbf{r},\mathbf{r}')\right| \|v_{L,\mathbf{r}'}\|_{H^{\min(p,2)}(\mathbb{R}^2)} &\leq \sum_{\mathbf{r}'\in\mathscr{L}^{\mathbf{R}}} \left|Q_L^{-\frac{1}{2}}(\mathbf{r},\mathbf{r}')\right| \Big(\|H_{L,\mathbf{r}'}v_{L,\mathbf{r}'}\|_{L^2(\mathbb{R}^2)} + C\,\|v_{L,\mathbf{r}'}\|_{L^2(\mathbb{R}^2)}\Big)\\ &\leq (|\mu_L| + C) \sum_{\mathbf{r}'\in\mathscr{L}^{\mathbf{R}}} \left|Q_L^{-\frac{1}{2}}(\mathbf{r},\mathbf{r}')\right| < \infty\,.\end{aligned}$$

Notice that we can take the same constant C for each $\mathbf{r}' \in \mathscr{L}^{\mathbf{R}}$ in Proposition 3.10 since we have $\|V_{L,\mathbf{r}}\|_{L^p(\mathbb{R}^2)+L^\infty(\mathbb{R}^2)} = \|V_{L,\mathbf{r}'}\|_{L^p(\mathbb{R}^2)+L^\infty(\mathbb{R}^2)}$ for all $(\mathbf{r},\mathbf{r}') \in \mathscr{L}^{\mathbf{R}} \times \mathscr{L}^{\mathbf{R}}$, see (3.29). This shows the first assertion of Proposition 3.21.

For the second statement, using that the series defining $w_{L,\mathbf{r}}$ converges in $L^2(\mathbb{R}^2)$ and that $Q_L^{-\frac{1}{2}}$ is self-adjoint, we can write

$$\langle w_{L,\mathbf{r}}, w_{L,\mathbf{r}'}\rangle_{L^2(\mathbb{R}^2)} = \sum_{\mathbf{s},\mathbf{s}'\in\mathscr{L}^{\mathbf{R}}} Q_L^{-\frac{1}{2}}(\mathbf{r},\mathbf{s}) Q^{-\frac{1}{2}}(\mathbf{r}',\mathbf{s}')\,\langle v_{L,\mathbf{s}}, v_{L,\mathbf{s}'}\rangle_{L^2(\mathbb{R}^2)} = (Q_L^{-\frac{1}{2}} Q_L Q_L^{-\frac{1}{2}})(\mathbf{r},\mathbf{r}')\,.$$

The last term being equal to $\delta(\mathbf{r},\mathbf{r}')$, this show the second assertion.

To show (3.53), we use the G-invariance of $Q_L^{-\frac{1}{2}}$ (see the right side of (3.50))

$$\begin{aligned}(s_L g s_L^{-1}) \cdot w_{L,\mathbf{r}} = \sum_{\mathbf{r}'\in\mathscr{L}^{\mathbf{R}}} Q_L^{-\frac{1}{2}}(\mathbf{r},\mathbf{r}')v_{L,g\cdot\mathbf{r}'} &= \sum_{\mathbf{r}'\in\mathscr{L}^{\mathbf{R}}} Q_L^{-\frac{1}{2}}(\mathbf{r},g^{-1}\cdot\mathbf{r}')v_{L,\mathbf{r}'}\\ &= \sum_{\mathbf{r}'\in\mathscr{L}^{\mathbf{R}}} Q_L^{-\frac{1}{2}}(g\cdot\mathbf{r},\mathbf{r}')v_{L,\mathbf{r}'} = w_{L,g\cdot\mathbf{r}}\,.\end{aligned}$$

The exponential bound (3.54) is shown by using Proposition 3.16, Lemma 3.19 and by adapting the proof of the estimate (3.51) to any $\mathbf{r}' = \mathbf{x} \in \mathbb{R}^2$. □

In particular, the family $\{w_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$ is generated by the shifts of the functions $\{w_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathbf{R}}$ with respect to $\mathscr{L}_L$. We introduce the Bloch-Floquet transform of these functions

$$u_{L,\mathbf{r}}(\mathbf{k},\mathbf{x}) := \mathcal{U}_{\mathrm{BF}}(w_{L,\mathbf{r}})(\mathbf{k},\mathbf{x}) = \sum_{\mathbf{u}\in\mathscr{L}} e^{i\mathbf{k}\cdot L\mathbf{u}} w_{L,\mathbf{u}+\mathbf{r}}(\mathbf{x})\,. \tag{3.55}$$

We have the following pseudo-periodicity relations: for all $\mathbf{k} \in \Gamma_L^*$, for all $\mathbf{x} \in \Gamma_L$,

$$u_{L,\mathbf{r}}(\mathbf{k},\cdot) \in L^2_{\mathbf{k}}(\Gamma_L) \quad \text{and} \quad u_{L,\mathbf{r}}(\cdot,\mathbf{x}) \in L^2_{\mathrm{per}}(\Gamma_L^*)\,.$$

Hence, we can extend the definition of $u_{L,\mathbf{r}}$ for any element of $\mathbf{r} \in \mathscr{L}^{\mathbf{R}}$ with

$$\forall \mathbf{k} \in \Gamma_L^*, \quad \forall \mathbf{u} \in \mathscr{L}, \quad \forall \mathbf{r} \in \mathbf{R}, \quad \mathcal{U}_{\mathrm{BF}}(w_{L,\mathbf{u}+\mathbf{r}})(\mathbf{k},\cdot) = e^{-i\mathbf{k}\cdot L\mathbf{u}} u_{L,\mathbf{r}}(\mathbf{k},\cdot)\,. \tag{3.56}$$

Proposition 3.23. *For all $\mathbf{k} \in \Gamma_L^*$ and for all $(\mathbf{r},\mathbf{r}') \in \mathbf{R}^2$, we have the relations*

$$\begin{aligned} \langle u_{L,\mathbf{r}}(\mathbf{k},\cdot), u_{L,\mathbf{r}'}(\mathbf{k},\cdot)\rangle_{L^2(\Gamma_L)} &= \delta_{\mathbf{r}\mathbf{r}'}\,, \\ \langle \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot), \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}'})(\mathbf{k},\cdot)\rangle_{L^2(\Gamma_L)} &= \delta_{\mathbf{r}\mathbf{r}'} + O\left(T_L^{d_0-}\right)\,, \\ \operatorname{span}\{u_{L,\mathbf{r}}(\mathbf{k},\cdot)\}_{\mathbf{r}\in\mathbf{R}} &= \operatorname{span}\{\mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot)\}_{\mathbf{r}\in\mathbf{R}}\,. \end{aligned}$$

Proof. We have

$$\begin{aligned} \langle u_{L,\mathbf{r}}(\mathbf{k},\cdot), u_{L,\mathbf{r}'}(\mathbf{k},\cdot)\rangle_{L^2(\Gamma_L)} &= \sum_{\mathbf{u}\in\mathscr{L}} e^{i\mathbf{k}\cdot L\mathbf{u}} \langle w_{L,\mathbf{r}}, w_{L,\mathbf{u}+\mathbf{r}'}\rangle_{L^2(\mathbb{R}^2)} = \delta_{\mathbf{r}\mathbf{r}'}\,, \\ \langle \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot), \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}'})(\mathbf{k},\cdot)\rangle_{L^2(\Gamma_L)} &= \sum_{\mathbf{u}\in\mathscr{L}} e^{i\mathbf{k}\cdot L\mathbf{u}} \langle v_{L,\mathbf{r}}, v_{L,\mathbf{u}+\mathbf{r}'}\rangle_{L^2(\mathbb{R}^2)} = \delta_{\mathbf{r}\mathbf{r}'} + O\left(T_L^{d_0-}\right)\,. \end{aligned}$$

We have used that $\{w_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$ is an orthonormal family (see Proposition 3.21) in the first line and the estimate (3.45) in the second one. Note that the computation is justified since the sum converges absolutely. Indeed, we have

$$\int_{\Gamma_L} \sum_{\mathbf{u},\mathbf{u}'\in\mathscr{L}} |w_{L,\mathbf{u}+\mathbf{r}} w_{L,\mathbf{u}'+\mathbf{r}'}| = \sum_{\mathbf{u}\in\mathscr{L}} \int_{\mathbb{R}^2} |w_{L,\mathbf{r}} w_{L,\mathbf{u}+\mathbf{r}'}| = \sum_{\mathbf{u}\in\mathscr{L}} (|w_{L,\mathbf{r}}| * |w_{L,\mathbf{r}'}|)(\mathbf{u})\,,$$

and we call on Proposition 3.21 and Lemma 3.17 to show that this sum is finite. Same argument applies to the second sum. The family $\{u_{L,\mathbf{r}}(\mathbf{k},\cdot)\}_{\mathbf{r}\in\mathbf{R}}$ forming an orthonormal system, it spans a subspace of dimension $N = |\mathbf{R}|$. Moreover, we have

$$\begin{aligned} u_{L,\mathbf{r}}(\mathbf{k},\cdot) = \sum_{\mathbf{u}\in\mathscr{L}} e^{i\mathbf{k}\cdot L\mathbf{u}} w_{L,\mathbf{u}+\mathbf{r}} &= \sum_{\mathbf{r}'\in\mathbf{R}} \sum_{\mathbf{u}\in\mathscr{L}} \sum_{\mathbf{u}'\in\mathscr{L}} Q_L^{-\frac{1}{2}}(\mathbf{u}+\mathbf{r},\mathbf{u}'+\mathbf{r}') e^{i\mathbf{k}\cdot L\mathbf{u}} v_{L,\mathbf{u}'+\mathbf{r}'} \\ &= \sum_{\mathbf{r}'\in\mathbf{R}} \sum_{\mathbf{u}\in\mathscr{L}} \sum_{\mathbf{u}'\in\mathscr{L}} Q_L^{-\frac{1}{2}}(\mathbf{u}-\mathbf{u}'+\mathbf{r},\mathbf{r}') e^{i\mathbf{k}\cdot L\mathbf{u}} v_{L,\mathbf{u}'+\mathbf{r}'} \\ &= \sum_{\mathbf{r}'\in\mathbf{R}} \sum_{\mathbf{u}\in\mathscr{L}} \sum_{\mathbf{u}'\in\mathscr{L}} Q_L^{-\frac{1}{2}}(\mathbf{u}+\mathbf{r},\mathbf{r}') e^{i\mathbf{k}\cdot L(\mathbf{u}+\mathbf{u}')} v_{L,\mathbf{u}'+\mathbf{r}'} \\ &= \sum_{\mathbf{r}'\in\mathbf{R}} \left(\sum_{\mathbf{u}\in\mathscr{L}} Q_L^{-\frac{1}{2}}(\mathbf{u}+\mathbf{r},\mathbf{r}') e^{i\mathbf{k}\cdot L\mathbf{u}} \right) \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}'})(\mathbf{k},\cdot)\,. \end{aligned} \tag{3.57}$$

The change of summation indices is justified using the exponential bounds on $v_{L,\mathbf{r}'}$ (Proposition 3.16) and the fact that $Q_L^{-\frac{1}{2}}$ is well-localized (Lemma 3.19). Therefore, we have shown $u_{L,\mathbf{r}}(\mathbf{k},\cdot) \in \operatorname{span}\{\mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}'})(\mathbf{k},\cdot)\}_{\mathbf{r}'\in\mathbf{R}}$. □

3.9 Interaction matrix

We denote by $E_L := \operatorname{span}\{w_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$ the subspace spanned by the family $\{w_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$ and by P_L the orthogonal projector on E_L. In this section, we compute the matrix A_L of $P_L H_L P_{L|E_L}$ in the orthonormal basis $\{w_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$. We recall the definition (3.14) of the interaction coefficient

$$\theta_{L,k} = \langle v_{L,\mathbf{r}_k}, V_{L,\mathbf{r}_k}(1-\chi_{L,\mathbf{r}'_k}) v_{L,\mathbf{r}'_k}\rangle_{L^2(\mathbb{R}^2)}\,,$$

where $\mathbf{c}_k = (\mathbf{r}_k,\mathbf{r}'_k) \in \mathcal{O}_k$. In Section 3.6, we prove that $\theta_{L,k}$ does not depend on the choice of the pair $\mathbf{c}_k \in \mathcal{O}_k$. Also, using the relations (3.53) and Assumption 3, we deduce that A_L has the same symmetries as V_L:

$$\forall g \in G, \quad g\cdot A_L = A_L\,, \tag{3.58}$$

where the action of G on $\mathcal{B}(\ell^2(\mathscr{L}^{\mathbf{R}}))$ is defined in (3.42).

The next proposition provides second order estimates on the coefficients of A_L. We recall that $-\mu_L$ denotes the common first eigenvalue of the mono-atomic operators $H_{L,\mathbf{R}} = -\Delta + V_{L,\mathbf{r}}$, see Section 3.6.

Proposition 3.24. *We have the following expansion*

$$\boxed{A_L = -\mu_L I + \sum_{k=1}^{m} \theta_{L,k} J_k + O\Big(T_L^{(1+\delta)d_0-} + T_L^{d_1-}\Big) \quad \text{and} \quad \forall k \in \{1,\dots,m\}, \quad \theta_{L,k} = O\Big(T_L^{d_0-}\Big)\,,}$$

where J_k, defined in (3.47), is the adjacency matrix associated with the orbit $\mathcal{O}_k$ and where $d_1 > d_0$ denotes the second nearest neighbor distance in $\mathscr{L}^{\mathbf{R}}$.

Proof. For clarity, we decompose the proof into several steps.

First step. We give an explicit expression of the matrix elements of A_L. Let $(\mathbf{r},\mathbf{r}') \in (\mathscr{L}^{\mathbf{R}})^2$. First, notice that the quadratic form associated with H_L is continuous on $H^1(\mathbb{R}^2)$ by Proposition 3.12. Moreover, the series defining $w_{L,\mathbf{r}}$ converges in $H^1(\mathbb{R}^2)$ by Proposition 3.21. Therefore, we have

$$\begin{aligned}
\langle w_{L,\mathbf{r}}, H_L w_{L,\mathbf{r}'}\rangle_{L^2(\mathbb{R}^2)} &= \sum_{\mathbf{s},\mathbf{s}'\in\mathscr{L}^{\mathbf{R}}} Q_L^{-\frac{1}{2}}(\mathbf{r},\mathbf{s}) Q_L^{-\frac{1}{2}}(\mathbf{r}',\mathbf{s}') \langle v_{L,\mathbf{s}}, (-\Delta + V_L) v_{L,\mathbf{s}'}\rangle_{L^2(\mathbb{R}^2)} \\
&= -\mu_L \delta(\mathbf{r},\mathbf{r}') + \sum_{\mathbf{s},\mathbf{s}'\in\mathscr{L}^{\mathbf{R}}} Q_L^{-\frac{1}{2}}(\mathbf{r},\mathbf{s}) Q_L^{-\frac{1}{2}}(\mathbf{r}',\mathbf{s}') \langle v_{L,\mathbf{s}}, V_L(1-\chi_{L,\mathbf{s}'}) v_{L,\mathbf{s}'}\rangle_{L^2(\mathbb{R}^2)} \\
&= -\mu_L \delta(\mathbf{r},\mathbf{r}') + (Q_L^{-\frac{1}{2}} D_L Q_L^{-\frac{1}{2}})(\mathbf{r},\mathbf{r}')\,,
\end{aligned}$$

where D_L is the infinite matrix defined by

$$\forall (\mathbf{r},\mathbf{r}') \in \mathscr{L}^{\mathbf{R}} \times \mathscr{L}^{\mathbf{R}}, \quad D_L(\mathbf{r},\mathbf{r}') = \langle v_{L,\mathbf{r}}, V_L\,(1-\chi_{L,\mathbf{r}'})\, v_{L,\mathbf{r}'}\rangle_{L^2(\mathbb{R}^2)}\,.$$

Using Assumption 3 and the relations (3.38), we have

$$\forall g \in G, \quad g \cdot D_L = D_L\,. \tag{3.59}$$

Second step. Now, we show that D_L is well-localized in the following sense: for all $\epsilon > 0$ there exists $C_\epsilon > 0$ such that for all $(\mathbf{r},\mathbf{r}') \in (\mathscr{L}^{\mathbf{R}})^2$ we have

$$|D_L(\mathbf{r},\mathbf{r}')| \leq \begin{cases} C_\epsilon T_L^{(1-\epsilon)(1+\delta)d_0} & \text{if } \mathbf{r} = \mathbf{r}'\,, \\ C_\epsilon T_L^{(1-\epsilon)|\mathbf{r}-\mathbf{r}'|} & \text{if } \mathbf{r} \neq \mathbf{r}'\,. \end{cases} \tag{3.60}$$

To lighten the notation, we introduce $\rho_{\mathbf{r}\mathbf{r}'} = v_{L,\mathbf{r}}(1-\chi_{L,\mathbf{r}'})v_{L,\mathbf{r}'}$.

If $\mathbf{r} = \mathbf{r}'$ then Proposition 3.12 shows that (recall that we have assumed in (3.9) that $\sqrt{1-\chi_{L,\mathbf{r}}}$ is smooth enough)

$$|D_L(\mathbf{r},\mathbf{r}')| \leq \|\nabla\sqrt{\rho_{\mathbf{r}\mathbf{r}}}\|^2_{L^2(\mathbb{R}^2)} + C(1,L)\, \|\sqrt{\rho_{\mathbf{r}\mathbf{r}}}\|^2_{L^2(\mathbb{R}^2)}\,,$$

where the constant $C(1,L)$ is polynomial in L. We obtain $|D_L(\mathbf{r},\mathbf{r}')| = O\Big(T_L^{(1+\delta)d_0-}\Big)$ with Proposition 3.16.

Now, assume $\mathbf{r} \neq \mathbf{r}'$. Using the periodicity of V_L and Hölder's inequality, we have

$$|D_L(\mathbf{r},\mathbf{r}')| \leq \|V_L\|_{L^p_{\mathrm{per}}} \sum_{\mathbf{u}\in\mathscr{L}} \|\rho_{\mathbf{r}\mathbf{r}'}\|_{L^{p'}(\Gamma_L + L\mathbf{u})}\,,$$

where $p' \in (1\,,\infty)$ is the conjugate exponent of p. Let $\mathcal{B}$ be the ball $B\left(\frac{\mathbf{r}+\mathbf{r}'}{2}, \left(2+\frac{d}{d_0}\right)|\mathbf{r}-\mathbf{r}'|\right)$ where $d_0 > 0$ is defined in (3.7) and where $d := \max_{\mathbf{x}\in\Gamma}|\mathbf{x}|$. We split the sum as follows

$$\sum_{\mathbf{u}\in\mathscr{L}} \|\rho_{\mathbf{r}\mathbf{r}'}\|_{L^{p'}(\Gamma_L+L\mathbf{u})} = \sum_{\mathbf{u}\in\mathscr{L}\cap\mathcal{B}} \|\rho_{\mathbf{r}\mathbf{r}'}\|_{L^{p'}(\Gamma_L+L\mathbf{u})} + \sum_{\mathbf{u}\in\mathscr{L}\cap\mathcal{B}^c} \|\rho_{\mathbf{r}\mathbf{r}'}\|_{L^{p'}(\Gamma_L+L\mathbf{u})} = I_1 + I_2\,.$$

The number of vertices of $\mathscr{L}$ inside the ball $\mathcal{B}$ is estimated by a $O\Big(|\mathbf{r}-\mathbf{r}'|^2\Big)$. Thus, using the concavity inequality $\sum_{i=1}^n |a_i|^\theta \leq n^{1-\theta}\left(\sum_{i=1}^n |a_i|\right)^\theta$ valid for all $\theta\in[0\,,1]$, all $n\in\mathbb{N}$ and all $(a_1,\dots,a_n)\in\mathbb{C}^n$, we can bound I_1 by

$$I_1 \lesssim |\mathbf{r}-\mathbf{r}'|^{2/p} \|\rho_{\mathbf{r}\mathbf{r}'}\|_{L^{p'}(\mathbb{R}^2)}\,.$$

Then, we estimate $\|\rho_{\mathbf{r}\mathbf{r}'}\|_{L^{p'}(\mathbb{R}^2)}$ using Lemma 3.17 and the exponential bounds on $v_{L,\mathbf{r}}$ proved in Proposition 3.16. For all $\epsilon > 0$ there exists $C_\epsilon, C'_\epsilon > 0$ such that

$$I_1 \leq C_\epsilon \frac{|\mathbf{r}-\mathbf{r}'|^{2/p}}{1+(L|\mathbf{r}-\mathbf{r}'|)^{\frac12-\frac{1}{p'}}} T_L^{(1-\epsilon/2)|\mathbf{r}-\mathbf{r}'|} \leq C'_\epsilon T_L^{(1-\epsilon)|\mathbf{r}-\mathbf{r}'|}\,. \tag{3.61}$$

Now, we estimate I_2. First, we notice that $\mathcal{B}^c \subset \mathcal{B}_1^c \cap \mathcal{B}_2^c$ where $\mathcal{B}_1 := B\left(\mathbf{r}, \left(\frac32+\frac{d}{d_0}\right)|\mathbf{r}-\mathbf{r}'|\right)$ and $\mathcal{B}_2 := B\left(\mathbf{r}', \left(\frac32+\frac{d}{d_0}\right)|\mathbf{r}-\mathbf{r}'|\right)$. If $(\mathbf{r},\mathbf{r}')\in\mathscr{L}^{\mathbf{R}}\times\mathscr{L}^{\mathbf{R}}$ are such that $|\mathbf{r}-\mathbf{r}'|\geq d_0$, we have the inclusions

$$\bigcup_{\mathbf{u}\in\mathscr{L}\cap\mathcal{B}_1^c} (\Gamma_L+L\mathbf{u}) \subset L(\mathcal{B}_1^c+\Gamma) \subset LB\left(\mathbf{r}, \left(\frac32+\frac{d}{d_0}\right)|\mathbf{r}-\mathbf{r}'|-d\right)^c \subset LB\left(\mathbf{r}, \frac32|\mathbf{r}-\mathbf{r}'|\right)^c,$$

and similar ones for $\mathcal{B}_2$. Then, using the Cauchy-Schwarz inequality, the Sobolev embedding $H^1(\Gamma_L+L\mathbf{u})\subset L^{2p'}(\Gamma_L+L\mathbf{u})$ (where the embedding constant does not depend on L nor on $\mathbf{u}$, see [Aub98, Theorem 2.28]) and the inclusions stated above, we have

$$\begin{aligned}
I_2 &\leq \sum_{\mathbf{u}\in\mathscr{L}\cap\mathcal{B}_1^c\cap\mathcal{B}_2^c} \|v_{L,\mathbf{r}}\|_{L^{2p'}(\Gamma_L+L\mathbf{u})} \|v_{L,\mathbf{r}'}\|_{L^{2p'}(\Gamma_L+L\mathbf{u})} \\
&\leq \frac12\left(\sum_{\mathbf{u}\in\mathscr{L}\cap\mathcal{B}_1^c} \|v_{L,\mathbf{r}}\|^2_{L^{2p'}(\Gamma_L+L\mathbf{u})} + \sum_{\mathbf{u}\in\mathscr{L}\cap\mathcal{B}_2^c} \|v_{L,\mathbf{r}'}\|^2_{L^{2p'}(\Gamma_L+L\mathbf{u})}\right) \\
&\lesssim \|v_{L,\mathbf{r}}\|^2_{H^1(B(L\mathbf{r},\frac32 L|\mathbf{r}-\mathbf{r}'|)^c)} + \|v_{L,\mathbf{r}'}\|^2_{H^1(B(L\mathbf{r}',\frac32 L|\mathbf{r}-\mathbf{r}'|)^c)}\,.
\end{aligned}$$

Then, using Proposition 3.16, we deduce that for L large enough we have

$$I_2 \lesssim \|v_{L,\mathbf{r}}\|^2_{H^1(B(L\mathbf{r},\frac32 L|\mathbf{r}-\mathbf{r}'|)^c)} \lesssim T_L^{2|\mathbf{r}-\mathbf{r}'|}\,. \tag{3.62}$$

Combining (3.62) with (3.61) shows (3.60).

Third step. Using the symmetry relations (3.59), we can write D_L as

$$D_L = \alpha_L I + \sum_{k=1}^m \beta_{L,k} J_k + R_L\,,$$

for some constants $\alpha_L, \beta_{L,1},\dots,\beta_{L,m}$ such that the diagonal and the nearest neighbor matrix elements of R_L are equal to zero. The operator norm of R_L is estimated thanks to (3.60) and by employing the same method used for the estimation of $\|Q_L - I - \sum_{k=1}^m \zeta_{L,k}J_k\|$ in Section 3.8 : $\|R_L\| = O\Big(T_L^{d_1-}\Big)$ where $d_1 > d_0$ is the second nearest neighbor distance. Now, we estimate the coefficients α_L and $\beta_{L,k}$.

Let $\mathbf{r} \in \mathscr{L}^{\mathbf{R}}$. Using that $\sqrt{1-\chi_{L,\mathbf{r}}} \in \mathcal{C}^1(\mathbb{R}^2)$ (see the assumption (3.9)), we have $\sqrt{1-\chi_{L,\mathbf{r}}}v_{L,\mathbf{r}} \in H^1(\mathbb{R}^2)$. Then, adapting the proof of inequality (3.32) from Proposition 3.12, we can show

$$\alpha_L = \left\langle \sqrt{1-\chi_{L,\mathbf{r}}}v_{L,\mathbf{r}}, V_L\sqrt{1-\chi_{L,\mathbf{r}}}v_{L,\mathbf{r}}\right\rangle_{L^2(\mathbb{R}^2)} \lesssim \|V_L\|_{L^p_{\mathrm{per}}} \left\|\sqrt{1-\chi_{L,\mathbf{r}}}v_{L,\mathbf{r}}\right\|^2_{H^1(\mathbb{R}^2)} .$$

Then, using that $\operatorname{supp}\sqrt{1-\chi_{L,\mathbf{r}}} \subset B\left(L\mathbf{r}, \frac{1+\delta}{2}Ld_0\right)^c$, $\|\nabla\chi_{L,\mathbf{r}}\|_{L^\infty} = O(L^{-1})$ (see Section 2.2 for these two facts), estimate (3.31) and the estimate (3.41) from Proposition 3.16, we show that

$$\alpha_L = O\Big(T_L^{(1+\delta)d_0-}\Big) .$$

Let $(\mathbf{r},\mathbf{r}') \in \mathscr{P}^{\mathbf{R}}$. Using the Cauchy-Schwarz inequality and the previous estimates twice, we obtain

$$\Big|\langle(1-\chi_{L,\mathbf{r}})v_{L,\mathbf{r}}, V_L(1-\chi_{L,\mathbf{r}'})v_{L,\mathbf{r}'}\rangle_{L^2(\mathbb{R}^2)}\Big| = O\Big(T_L^{(1+\delta)d_0-}\Big) .$$

We recall that the nearest neighbor interaction coefficient $\theta_{L,k}$ defined in (3.14) does not depend on the choice of $(\mathbf{r},\mathbf{r}') \in \mathcal{O}_k$. Hence, we have shown

$$\beta_{L,k} = \theta_{L,k} + O\Big(T_L^{(1+\delta)d_0-}\Big) \quad \text{and} \quad D_L = \sum_{k=1}^m \theta_{L,k}J_k + O\Big(T_L^{(1+\delta)d_0-} + T_L^{d_1-}\Big) .$$

Fourth step. From (3.60), we deduce $\beta_{L,k} = O\Big(T_L^{d_0-}\Big)$ which implies $\theta_{L,k} = O\Big(T_L^{d_0-}\Big)$. Then, using (3.49), the norm estimation (3.48) and the first step of the proof, we have

$$A_L = -\mu_L I + Q_L^{-\frac{1}{2}}D_LQ_L^{-\frac{1}{2}} = -\mu_L I + \sum_{k=1}^m \theta_{L,k}J_k + O\Big(T_L^{(1+\delta)d_0-} + T_L^{d_1-}\Big) . \qquad \square$$

This concludes the proof of Proposition 3.24.

We recall that H_L admits the decomposition in fibers $H_L = \fint^{\oplus}_{\Gamma_L^*} H_L(\mathbf{k})\,\mathrm{d}\mathbf{k}$ where $H_L(\mathbf{k}) = -\Delta + V_L$ on the subspace $L^2_{\mathbf{k}}(\Gamma_L)$. We denote by $A_L(\mathbf{k})$ the matrix of $H_L(\mathbf{k})$ restricted to the N-dimensional subspace $E_L(\mathbf{k}) \coloneqq \operatorname{span}\{u_{L,\mathbf{r}}(\mathbf{k},\cdot)\}_{\mathbf{r}\in\mathbf{R}}$.

Corollary 3.25. *We have the expansion*

$$\boxed{A_L(\mathbf{k}) = -\mu_L I + \sum_{k=1}^m \theta_{L,k}B_k(L\mathbf{k}) + O\Big(T_L^{(1+\delta)d_0-} + T_L^{d_1-}\Big) ,}$$

where the O makes sense in $\mathcal{C}^\infty_{\mathrm{per}}(\Gamma_L^*)$, where $d_1 > d_0$ denotes the second nearest neighbor distance in $\mathscr{L}^{\mathbf{R}}$ and where the matrix elements of $B_k(\mathbf{k})$ are given by

$$\forall \mathbf{k} \in \Gamma^*, \quad \forall(\mathbf{r},\mathbf{r}') \in \mathbf{R}^2, \quad B_k(\mathbf{k};\mathbf{r},\mathbf{r}') = \sum_{\substack{\mathbf{u}\in\mathscr{L} \\ (\mathbf{r},\mathbf{u}+\mathbf{r}')\in\mathcal{O}_k}} e^{i\mathbf{k}\cdot\mathbf{u}} .$$

Proof. Let $(\mathbf{r},\mathbf{r}') \in \mathbf{R}^2$. Using that $\mathcal{U}_{\mathrm{BF}}$ defines an isometry from $L^2(\mathbb{R}^2)$ to $L^2(\Gamma_L^*, L^2(\Gamma_L))$ and the relations (3.56), we have

$$\begin{aligned} A_L(\mathbf{r},\mathbf{u}+\mathbf{r}') &= \langle w_{L,\mathbf{r}}, H_L w_{L,\mathbf{u}+\mathbf{r}'}\rangle_{L^2(\mathbb{R}^2)} \\ &= \fint_{\Gamma_L^*} e^{i\mathbf{k}\cdot L\mathbf{u}}\,\langle u_{L,\mathbf{r}}(\mathbf{k},\cdot), H_L(\mathbf{k})u_{L,\mathbf{r}'}(\mathbf{k},\cdot)\rangle_{L^2(\Gamma_L)}\,\mathrm{d}\mathbf{k} = \fint_{\Gamma_L^*} e^{i\mathbf{k}\cdot L\mathbf{u}}A_L(\mathbf{k};\mathbf{r},\mathbf{r}')\,\mathrm{d}\mathbf{k}\,. \end{aligned}$$

By the first step of the proof of Proposition 3.24, the off-diagonal coefficients of A_L are given by $Q_L^{-\frac{1}{2}} D_L Q_L^{-\frac{1}{2}}$. By Lemma 3.19 and the estimates (3.60), the off-diagonal coefficients of D_L and $Q_L^{-\frac{1}{2}}$ are exponentially decaying with the same rate. Using the estimate (3.51), we can show the similar property for $Q_L^{-\frac{1}{2}} D_L Q_L^{-\frac{1}{2}}$, that is, for all $\epsilon \in (0,1)$ there exists $C_\epsilon > 0$ such that

$$\forall (\mathbf{r}, \mathbf{r}') \in (\mathscr{L}^{\mathbf{R}})^2, \quad \left| \left(Q_L^{-\frac{1}{2}} D_L Q_L^{-\frac{1}{2}} \right)(\mathbf{r}, \mathbf{r}') \right| \leq C_\epsilon T_L^{(1-\epsilon)|\mathbf{r}-\mathbf{r}'|}. \tag{3.63}$$

Recalling the relations (3.58), we deduce that $A_L(\mathbf{k}; \mathbf{r}, \mathbf{r}')$ is given by the Fourier series

$$\begin{aligned} A_L(\mathbf{k}; \mathbf{r}, \mathbf{r}') &= \sum_{\mathbf{u} \in \mathscr{L}} e^{i\mathbf{k}\cdot L\mathbf{u}} A_L(\mathbf{r}, \mathbf{u} + \mathbf{r}') \\ &= -\mu_L \delta(\mathbf{r}, \mathbf{r}') + \sum_{k=1}^{m} \theta_{L,k} \left(\sum_{\mathbf{u} \in \mathscr{L}} e^{iL\mathbf{k}\cdot\mathbf{u}} \mathbb{1}_{(\mathbf{r}, \mathbf{u}+\mathbf{r}') \in \mathcal{O}_k} \right) \\ &\quad + \sum_{\mathbf{u} \neq 0} e^{iL\mathbf{k}\cdot\mathbf{u}} (Q_L^{-\frac{1}{2}} D_L Q_L^{-\frac{1}{2}})(\mathbf{r}, \mathbf{u} + \mathbf{r}') \mathbb{1}_{(\mathbf{r}, \mathbf{u}+\mathbf{r}') \notin \mathscr{P}^{\mathbf{R}}}, \end{aligned}$$

where the last term is $O\left(T_L^{d_1 -}\right)$ in $\mathcal{C}^\infty_{\text{per}}(\Gamma_L^*)$ thanks to (3.63). $\square$

3.10 An energy estimate on $E_L^\perp(\mathbf{k})$

For $\mathbf{k} \in \Gamma_L^*$, we recall that the N-dimensional vector space $E_L(\mathbf{k})$ is given by

$$E_L(\mathbf{k}) \coloneqq \operatorname{span}\{u_{L,\mathbf{r}}(\mathbf{k}, \cdot)\}_{\mathbf{r} \in \mathbf{R}} = \operatorname{span}\{\mathcal{U}_{\text{BF}}(v_{L,\mathbf{r}})(\mathbf{k}, \cdot)\}_{\mathbf{r} \in \mathbf{R}}.$$

The equality comes from Proposition 3.23. We denote by $P_L(\mathbf{k})$ the associated orthogonal projection and $P_L^\perp(\mathbf{k}) \coloneqq 1 - P_L(\mathbf{k})$ the orthogonal projection on $E_L^\perp(\mathbf{k}) \coloneqq E_L(\mathbf{k})^\perp$. Our goal is to show that there is an uniform energy gap on $E_L^\perp(\mathbf{k})$ compared with $E_L(\mathbf{k})$.

Proposition 3.26. *Let $\mathbf{k} \in \Gamma_L^*$. We have the energy estimate: for all $u \in H^1_{\mathbf{k}}(\Gamma_L) \cap E_L^\perp(\mathbf{k})$, we have*

$$\langle u, H_L(\mathbf{k}) u \rangle_{L^2(\Gamma_L)} \geq (g_L - \mu_L + o(1)) \|u\|^2_{L^2(\Gamma_L)} = (g - \mu + o(1)) \|u\|^2_{L^2(\Gamma_L)}, \tag{3.64}$$

where $g_L > 0$ and $\mu_L > 0$ (resp. $g > 0$ and $\mu > 0$) denote the first spectral gap and the common lowest eigenvalue of the effective mono-atomic operators $\{H_{L,\mathbf{r}}\}_{\mathbf{r} \in \mathscr{L}^{\mathbf{R}}}$ (resp. reference operator H) introduced in (3.11) (resp. in (3.5)).

Proof. First, we notice that the last equality in (3.64) comes from (3.39). Now, we consider an $\mathscr{L}$-periodic partition of unity $\sum_{\mathbf{r} \in \mathbf{R}} (\eta_{\mathbf{r}})^2 = 1$ with $\eta_{\mathbf{r}} \in W^{1,\infty}_{\text{per}}(\Gamma_L) \cap \mathcal{C}^\infty(\mathbb{R}^2)$ where

$$W^{1,\infty}_{\text{per}}(\Gamma_L) = \left\{ u \in L^\infty_{\text{per}}(\Gamma_L) \;\middle|\; \partial_1 u \in L^\infty_{\text{per}}(\Gamma_L) \quad \text{and} \quad \partial_2 u \in L^\infty_{\text{per}}(\Gamma_L) \right\},$$

and satisfying the following conditions

$$\exists \rho > 0, \quad \forall \mathbf{r} \in \mathbf{R}, \quad \exists \xi_{\mathbf{r}} \in \mathcal{C}^\infty_c(\mathbb{R}^2), \quad \left(\xi_{\mathbf{r}|B(\mathbf{r},\rho)} \equiv 1 \quad \text{and} \quad \eta_{\mathbf{r}} = \sum_{\mathbf{u} \in \mathscr{L}} \xi_{\mathbf{r}}(\cdot - \mathbf{u}) \right).$$

The parameter $\rho > 0$ can be chosen as small as we want. Then, by defining $\eta_{L,\mathbf{r}} \coloneqq \eta_{\mathbf{r}}(L^{-1}\cdot)$ and $\xi_{L,\mathbf{r}} \coloneqq \xi_{\mathbf{r}}(L^{-1}\cdot)$, we obtain a $\mathscr{L}_L$-periodic partition of unity $\sum_{\mathbf{r} \in \mathbf{R}} (\eta_{L,\mathbf{r}})^2 = 1$. Let $u \in H^1_{\mathbf{k}}(\Gamma_L) \cap E_L^\perp(\mathbf{k})$. Using the periodic IMS localization formula, we have

$$\langle u, H_L(\mathbf{k}) u \rangle_{L^2(\Gamma_L)} = \sum_{\mathbf{r} \in \mathbf{R}} \left(\langle \eta_{L,\mathbf{r}} u, H_L(\mathbf{k}) \eta_{L,\mathbf{r}} u \rangle_{L^2(\Gamma_L)} - \left\langle u, |\nabla \eta_{L,\mathbf{r}}|^2 u \right\rangle_{L^2(\Gamma_L)} \right). \tag{3.65}$$

Because $\xi_{\mathbf{r}}$ is compactly supported into a ball $B(\mathbf{r}, R)$ for some constant $R > 0$, we have

$$\langle \eta_{L,\mathbf{r}} u, H_L(\mathbf{k}) \eta_{L,\mathbf{r}} u \rangle_{L^2(\Gamma_L)} = \sum_{|\mathbf{u}| \le 2R} \langle \xi_{L,\mathbf{r}}(\cdot - L\mathbf{u}) u, H_L \xi_{L,\mathbf{r}} u \rangle_{L^2(\mathbb{R}^2)} \,.$$

Inserting this in (3.65), taking the real part and using $\|\nabla \eta_{L,\mathbf{r}}\|_{L^\infty} = O\big(L^{-1}\big)$, we get

$$\begin{aligned}\langle u, H_L(\mathbf{k}) u \rangle_{L^2(\Gamma_L)} = &\sum_{\mathbf{r} \in \mathbf{R}} \langle \xi_{L,\mathbf{r}} u, H_L \xi_{L,\mathbf{r}} u \rangle_{L^2(\mathbb{R}^2)} \\ &+ \sum_{\mathbf{r} \in \mathbf{R}} \sum_{0 < |\mathbf{u}| \le 2R} \Re \Big(\langle \xi_{L,\mathbf{r}}(\cdot - L\mathbf{u}) u, H_L \xi_{L,\mathbf{r}} u \rangle_{L^2(\mathbb{R}^2)} \Big) + O\Big(L^{-2} \|u\|^2_{L^2(\Gamma_L)} \Big) \,.\end{aligned}$$

Recalling the following stability inequality (which results from the functional calculus)

$$\forall v \in H^1(\mathbb{R}^2), \quad \langle v, H_{L,\mathbf{r}} v \rangle_{L^2(\mathbb{R}^2)} \ge (-\mu_L + g_L) \|v\|^2_{L^2(\mathbb{R}^2)} - g_L \left| \langle v, v_{L,\mathbf{r}} \rangle_{L^2(\mathbb{R}^2)} \right|^2 ,$$

we can write

$$\begin{aligned}\langle u, H_L(\mathbf{k}) u \rangle_{L^2(\Gamma_L)} \ge (-\mu_L + g_L) &\sum_{\mathbf{r} \in \mathbf{R}} \|\xi_{L,\mathbf{r}} u\|^2_{L^2(\mathbb{R}^2)} - g_L \sum_{\mathbf{r} \in \mathbf{R}} \left| \langle \xi_{L,\mathbf{r}} u, v_{L,\mathbf{r}} \rangle_{L^2(\mathbb{R}^2)} \right|^2 \\ &+ \sum_{\mathbf{r} \in \mathbf{R}} \langle \xi_{L,\mathbf{r}} u, V_L(1 - \chi_{L,\mathbf{r}}) \xi_{L,\mathbf{r}} u \rangle_{L^2(\mathbb{R}^2)} \\ &+ \sum_{\mathbf{r} \in \mathbf{R}} \sum_{0 < |\mathbf{u}| \le 2R} \Re \Big(\langle \xi_{L,\mathbf{r}}(\cdot - L\mathbf{u}) u, H_L \xi_{L,\mathbf{r}} u \rangle_{L^2(\mathbb{R}^2)} \Big) + o\Big(\|u\|^2_{L^2(\Gamma_L)} \Big) \,.\end{aligned} \tag{3.66}$$

Expanding the identity $\|u\|^2_{L^2(\Gamma_L)} = \sum_{\mathbf{r} \in \mathbf{R}} \|\eta_{L,\mathbf{r}} u\|^2_{L^2(\Gamma_L)}$, we obtain

$$\|u\|^2_{L^2(\Gamma_L)} = \sum_{\mathbf{r} \in \mathbf{R}} \|\xi_{L,\mathbf{r}} u\|^2_{L^2(\mathbb{R}^2)} + \sum_{\mathbf{r} \in \mathbf{R}} \sum_{\mathbf{u} \in \mathscr{L} \setminus \{0\}} \langle \xi_{L,\mathbf{r}}(\cdot - L\mathbf{u}), \xi_{L,\mathbf{r}} u \rangle_{L^2(\mathbb{R}^2)} \ge \sum_{\mathbf{r} \in \mathbf{R}} \|\xi_{L,\mathbf{r}} u\|^2_{L^2(\mathbb{R}^2)} \,.$$

Since $-\mu_L + g_L \le 0$ (recall that $\sigma_{\mathrm{ess}}(H_{L,\mathbf{r}}) = [0\,, \infty)$), we have

$$(-\mu_L + g_L) \sum_{\mathbf{r} \in \mathbf{R}} \|\xi_{L,\mathbf{r}} u\|^2_{L^2(\mathbb{R}^2)} \ge (-\mu_L + g_L) \|u\|^2_{L^2(\Gamma_L)} \,. \tag{3.67}$$

Moreover, using that $E_L(\mathbf{k})$ is spanned by the family $\{\mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k}, \cdot)\}_{\mathbf{r} \in \mathbf{R}}$ (see Proposition 3.23), the Cauchy-Schwarz inequality and Proposition 3.16, we have

$$\begin{aligned}0 &= \langle u, \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k}, \cdot) \rangle_{L^2(\Gamma_L)} \\ &= \langle u, \xi_{L,\mathbf{r}} v_{L,\mathbf{r}} \rangle_{L^2(\Gamma_L)} + \langle u, (1 - \xi_{L,\mathbf{r}}) v_{L,\mathbf{r}} \rangle_{L^2(\Gamma_L)} + \sum_{\mathbf{u} \in \mathscr{L} \setminus \{0\}} \langle u, v_{L,\mathbf{r}} \rangle_{L^2(\Gamma_L + L\mathbf{u})} \\ &= \langle u, \xi_{L,\mathbf{r}} v_{L,\mathbf{r}} \rangle_{L^2(\Gamma_L)} + O\left(\|u\|_{L^2(\Gamma_L)} \left(\|(1 - \xi_{L,\mathbf{r}}) v_{L,\mathbf{r}}\|_{L^2(\Gamma_L)} + \sum_{\mathbf{u} \in \mathscr{L} \setminus \{0\}} \|v_{L,\mathbf{r}}\|_{L^2(\Gamma_L + L\mathbf{u})} \right) \right) \\ &= \langle u, \xi_{L,\mathbf{r}} v_{L,\mathbf{r}} \rangle_{L^2(\Gamma_L)} + o\Big(\|u\|_{L^2(\Gamma_L)} \Big) \,.\end{aligned}$$

Thus, we have shown

$$\langle u, \xi_{L,\mathbf{r}} v_{L,\mathbf{r}} \rangle_{L^2(\Gamma_L)} = o\Big(\|u\|_{L^2(\Gamma_L)} \Big) \,. \tag{3.68}$$

Notice that $\operatorname{supp} \xi_{L,\mathbf{r}} \subset \big[\cup_{\mathbf{r}' \in \mathscr{L}^{\mathbf{R}} \setminus \{\mathbf{r}\}} B(L\mathbf{r}', L\rho) \big]^c \cap B(L\mathbf{r}, LR)$. Then, if we choose ρ small enough in order to have $B(L\mathbf{r}, L\rho) \subset \{\chi_{L,\mathbf{r}} \equiv 1\}$, we have

$$\left|\langle \xi_{L,\mathbf{r}} u, V_L(1-\chi_{L,\mathbf{r}})\xi_{L,\mathbf{r}} u\rangle_{L^2(\mathbb{R}^2)}\right| \leq \int_{\mathbb{R}^2} |V_L|\,|u|^2\,\mathbb{1}_{\operatorname{supp}\xi_{L,\mathbf{r}}\cap\{\chi_{L,\mathbf{r}}\equiv 1\}^c} \lesssim \|V_L \mathbb{1}_{\Lambda_L}\|_{L^\infty_{\mathrm{per}}(\Gamma_L)}\,\|u\|^2_{L^2(\Gamma_L)}\,,$$

where $\Lambda_L = (\cup_{\mathbf{r}'\in\mathscr{L}^{\mathbb{R}}} B(L\mathbf{r}', L\rho))^c$. Assumption 1*(ii)* says that $\|V_L \mathbb{1}_{\Lambda_L}\|_{L^\infty_{\mathrm{per}}(\Gamma_L)} = o(1)$. Thus, we get

$$\langle \xi_{L,\mathbf{r}} u, V_L(1-\chi_{L,\mathbf{r}})\xi_{L,\mathbf{r}} u\rangle_{L^2(\mathbb{R}^2)} = o\Big(\|u\|^2_{L^2(\Gamma_L)}\Big)\,. \tag{3.69}$$

With the same support arguments, we can show that

$$\forall \mathbf{u}\in\mathscr{L}\setminus\{0\},\quad \langle \xi_{L,\mathbf{r}}(\cdot - L\mathbf{u})u, V_L\xi_{L,\mathbf{r}} u\rangle_{L^2(\mathbb{R}^2)} = o\Big(\|u\|^2_{L^2(\Gamma_L)}\Big)\,. \tag{3.70}$$

It remains to treat the kinetic part $\Re\Big(\langle \xi_{L,\mathbf{r}}(\cdot - L\mathbf{u})u, -\Delta\xi_{L,\mathbf{r}} u\rangle_{L^2(\mathbb{R}^2)}\Big)$. We will use the following lemma.

Lemma 3.27. *Let $\xi,\xi' \in \mathcal{C}^\infty_c(\mathbb{R}^2)$ smooth, positive-valued and compactly supported functions. Then, for all $u \in H^1_{\mathrm{loc}}(\mathbb{R}^2,\mathbb{C})$, we have*

$$\Re\Big(\langle \xi u, -\Delta(\xi' u)\rangle_{L^2(\mathbb{R}^2)}\Big) \geq -\frac{1}{2}\int_{\mathbb{R}^2} |u|^2\,(\xi\Delta\xi' + \xi'\Delta\xi)\,.$$

For clarity, we show this lemma after completing the proof of Proposition 3.26. By Lemma 3.27 and the properties of $\xi_{L,\mathbf{r}}$, we can show

$$\forall \mathbf{u}\in\mathscr{L}\setminus\{0\},\quad \langle \xi_{L,\mathbf{r}}(\cdot - L\mathbf{u})u, -\Delta\xi_{L,\mathbf{r}} u\rangle_{L^2(\mathbb{R}^2)} = O\Big(L^{-2}\,\|u\|^2_{L^2(\Gamma_L)}\Big)\,. \tag{3.71}$$

We obtain (3.64) by inserting (3.67), (3.68), (3.69), (3.70) and (3.71) in (3.66) and using that g_L is uniformly bounded for $L \geq 1$ (see (3.39)). □

Proof of Lemma 3.27. Integrating by parts several times, we get

$$\begin{aligned}
\Re\Big(\langle \xi u, -\Delta(\xi' u)\rangle_{L^2(\mathbb{R}^2)}\Big) &= \int \Big(|u|^2\,\nabla\xi\cdot\nabla\xi' + \Re\,(u\nabla\overline{u})\cdot\xi\nabla\xi' + \Re\,(\overline{u}\nabla u)\cdot\xi'\nabla\xi + \xi\xi'\,|\nabla u|^2\Big)\\
&\geq \int |u|^2\,\nabla\xi\cdot\nabla\xi' + \frac{1}{2}\nabla|u|^2\cdot\nabla(\xi\xi')\\
&\geq -\frac{1}{2}\int |u|^2\,(\Delta(\xi\xi') - 2\nabla\xi\cdot\nabla\xi')\\
&\geq -\frac{1}{2}\int_{\mathbb{R}^2} |u|^2\,(\xi\Delta\xi' + \xi'\Delta\xi)\,.
\end{aligned}$$ □

3.11 Estimate of the residual term in the Feshbach-Schur method

In this section, we use the Feshbach-Schur method to express the N lowest eigenvalues of $H_L(\mathbf{k})$ as a perturbation of the spectrum of the $N\times N$ matrix $A_L(\mathbf{k})$.

First, we set notations and facts about order relations for self-adjoint operators (see [Sch12, Chapter 10] for details). Let A and B two lower semibounded self-adjoint operators on a Hilbert space $\mathcal{H}$ with respective form domains $\mathcal{Q}(A)$ and $\mathcal{Q}(B)$. We denote by q_A and q_B their associated closed quadratic form. We write $A \geq B$ (or $B \leq A$) if $\mathcal{Q}(A)\subset\mathcal{Q}(B)$ and $q_A(\psi)\geq q_B(\psi)$ for all $\psi\in\mathcal{Q}(A)$. If A is positive (that is $A\geq 0$) then A admits a unique positive and self-adjoint square root, denoted by $\sqrt{A}$, and we have $\mathcal{Q}(A) = \mathcal{D}(\sqrt{A})$. If A and B are positive then $A\geq B$ if and only if $\mathcal{D}(\sqrt{A})\subset\mathcal{D}(\sqrt{B})$ and $\left\|\sqrt{A}\psi\right\| \geq \left\|\sqrt{B}\psi\right\|$ for all $\psi\in\mathcal{D}(\sqrt{A})$.

As a consequence of Proposition 3.26, we have for L large enough

$$\boxed{P_L^\perp(\mathbf{k})(H_L(\mathbf{k})+\mu_L)P_L^\perp(\mathbf{k}) \geq \frac{g}{2}P_L^\perp(\mathbf{k})\,.} \tag{3.72}$$

We decompose $L^2_{\mathbf{k}}(\Gamma_L) = E_L(\mathbf{k}) \overset{\perp}{\oplus} E_L^\perp(\mathbf{k})$ and we write

$$H_L(\mathbf{k}) = \begin{pmatrix} A_L(\mathbf{k}) & C_L(\mathbf{k})^* \\ C_L(\mathbf{k}) & B_L(\mathbf{k}) \end{pmatrix},$$

with $A_L(\mathbf{k}) = P_L(\mathbf{k})H_L(\mathbf{k})P_L(\mathbf{k})$, $B_L(\mathbf{k}) = P_L^\perp(\mathbf{k})H_L(\mathbf{k})P_L^\perp(\mathbf{k})$ and $C_L(\mathbf{k}) = P_L^\perp(\mathbf{k})H_L(\mathbf{k})P_L(\mathbf{k})$. The Feshbach-Schur method [GS20, Chapter 11] says that for $\lambda \leq -\mu_L + g/3$, we have

$$\boxed{\lambda \in \sigma(H_L(\mathbf{k})) \Longleftrightarrow \lambda \in \sigma\left(A_L(\mathbf{k}) - C_L(\mathbf{k})^*(B_L(\mathbf{k})-\lambda)^{-1}C_L(\mathbf{k})\right)\,.} \tag{3.73}$$

In the right hand side appears an $N\times N$ hermitian matrix. Therefore, (3.73) implies that $H_L(\mathbf{k})$ has exactly N eigenvalues (counted with multiplicity) in the interval $(-\infty\,,-\mu_L+g/3)$. Corollary 3.25 gives the expansion for $A_L(\mathbf{k})$ when $L\to\infty$. The next proposition bounds the residual term $C_L(\mathbf{k})^*(B_L(\mathbf{k})-\lambda)^{-1}C_L(\mathbf{k})$ in operator norm.

Proposition 3.28. *For L large enough, for all $\mathbf{k}\in\Gamma_L^*$ and for all $\lambda\in(-\infty\,,-\mu_L+g/3)$, we have the estimate*

$$\boxed{\left\|C_L(\mathbf{k})^*(B_L(\mathbf{k})-\lambda)^{-1}C_L(\mathbf{k})\right\| = O\left(T_L^{(1+\delta)d_0-}\right)\,,}$$

where the O is independent from $\mathbf{k}$.

The strategy of proof for Proposition 3.28 is the following. First, we notice that

$$\left\|C_L(\mathbf{k})^*(B_L(\mathbf{k})-\lambda)^{-1}C_L(\mathbf{k})\right\| = \left\|(B_L(\mathbf{k})-\lambda)^{-1/2}C_L(\mathbf{k})\right\|^2\,.$$

Now, since $P_L^\perp(\mathbf{k})P_L(\mathbf{k})=0$, we can write

$$C_L(\mathbf{k}) = P_L^\perp(\mathbf{k})\,(H_L(\mathbf{k})+\mu_L)\,P_L(\mathbf{k})\,.$$

Then, a formal computation leads to the identity

$$\frac{1}{\sqrt{B_L(\mathbf{k})-\lambda}}P_L^\perp(\mathbf{k})\,(H_L(\mathbf{k})+\mu_L)\,\mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}}) = \frac{1}{\sqrt{B_L(\mathbf{k})-\lambda}}P_L^\perp(\mathbf{k})V_L\mathcal{U}_{\mathrm{BF}}((1-\chi_{L,\mathbf{r}})v_{L,\mathbf{r}})\,. \tag{3.74}$$

Recall that $(-\Delta+1)^{-1/2}V_L(-\Delta+1)^{-1/2}$ is bounded in operator norm by Corollary 3.14. We take the norm of (3.74) and we approximate $\frac{1}{\sqrt{B_L(\mathbf{k})-\lambda}}P_L^\perp(\mathbf{k})$ by $\frac{1}{\sqrt{-\Delta+1}}$. This amounts to estimate the following quantity

$$\left\|\sqrt{-\Delta+1}V_L\mathcal{U}_{\mathrm{BF}}\left((1-\chi_{L,\mathbf{r}})v_{L,\mathbf{r}}\right)\right\|^2_{L^2(\Gamma_L)}\,.$$

Finally, we use the exponential bounds on $v_{L,\mathbf{r}}$ (see Proposition 3.16) to conclude.

We divide the proof of Proposition 3.28 in several lemmas.

Lemma 3.29. *For L large enough, for all $\mathbf{k}\in\Gamma_L^*$, for all $\lambda\in(-\infty\,,-\mu_L+g/3)$, for all $\varphi\in$*

$H^1_{\mathbf{k}}(\Gamma_L) \cap E_L^\perp(\mathbf{k})$, *we have*

$$\left\| \frac{1}{\sqrt{B_L(\mathbf{k}) - \lambda}} \sqrt{P_L^\perp(\mathbf{k})(-\Delta + 1)P_L^\perp(\mathbf{k})\varphi} \right\|_{L^2(\Gamma_L)} \leq \sqrt{\frac{12}{g} \max\left(1, 2C_L + \frac{g}{3}\right)} \|\varphi\|_{L^2(\Gamma_L)}, \quad (3.75)$$

where $C_L = C(1/2, L)$ *is the constant appearing in the estimate* (3.33) *of Proposition 3.12.*

Proof. As a consequence of the estimate (3.33) of Proposition 3.12, there exists $C_L > 0$ such that

$$\begin{aligned} B_L(\mathbf{k}) - \lambda = P_L^\perp(\mathbf{k})(H_L(\mathbf{k}) - \lambda)P_L^\perp(\mathbf{k}) &\geq P_L^\perp(\mathbf{k}) \left[-\frac{1}{2}\Delta - (C_L + \lambda) \right] P_L^\perp(\mathbf{k}) \\ &\geq P_L^\perp(\mathbf{k}) \left[-\frac{1}{2}\Delta - C_L \right] P_L^\perp(\mathbf{k}) . \end{aligned} \quad (3.76)$$

The second inequality comes from the fact that for L large enough, we have $(-\infty, -\mu_L + g/3) \subset (-\infty, 0)$. By (3.72), we have

$$B_L(\mathbf{k}) - \lambda \geq \frac{g}{6} P_L^\perp(\mathbf{k}), \quad (3.77)$$

for all $\lambda < -\mu_L + g/3$. By taking the convex combination $(1-t) \times (3.76) + t \times (3.77)$ with $t = \frac{g}{2g + 12C_L}$, we obtain

$$B_L(\mathbf{k}) - \lambda \geq \frac{g}{12} \min\left(1, \frac{1}{2C_L + g/3}\right) P_L^\perp(\mathbf{k})(-\Delta + 1)P_L^\perp(\mathbf{k}) .$$

From this previous estimate and [Sch12, Corollary 10.12], we have

$$(B_L(\mathbf{k}) - \lambda)^{-1} \leq \frac{12}{g} \max\left(1, 2C_L + \frac{g}{3}\right) P_L^\perp(\mathbf{k})(-\Delta + 1)^{-1} P_L^\perp(\mathbf{k}) .$$

The estimate (3.75) results from this inequality. □

The following technical lemma is convenient to estimate convolutions when only integral bounds are in our disposal.

Lemma 3.30. *Let* $\varphi, \psi \in L^2(\mathbb{R}^2)$ *such that* $\left\|\varphi \mathbb{1}_{|x| \geq R}\right\|_{L^2(\mathbb{R}^2)} \leq Ce^{-\alpha R}$ *and* $\left\|\psi \mathbb{1}_{|x| \geq R}\right\|_{L^2(\mathbb{R}^2)} \leq Ce^{-\beta R}$ *for some constants* $C, \alpha, \beta \geq 0$ *and for all* $R \geq 0$. *Then, we have*

$$\forall \mathbf{x} \in \mathbb{R}^2, \quad |(\varphi * \psi)(\mathbf{x})| \leq C\left(\|\varphi\|_{L^2(\mathbb{R}^2)} e^{-\frac{\beta}{2}|\mathbf{x}|} + \|\psi\|_{L^2(\mathbb{R}^2)} e^{-\frac{\alpha}{2}|\mathbf{x}|} \right) .$$

Proof. We cannot have $|\mathbf{y}| < |\mathbf{x}|/2$ and $|\mathbf{y} - \mathbf{x}| < |\mathbf{x}|/2$ simultaneously since it would imply $|\mathbf{x}| < |\mathbf{x}|$. Hence, we can write

$$|(\varphi * \psi)(\mathbf{x})| \leq \int_{|\mathbf{x}-\mathbf{y}| \geq \frac{|\mathbf{x}|}{2}} |\varphi(\mathbf{x} - \mathbf{y})| |\psi(\mathbf{y})| \, d\mathbf{y} + \int_{|\mathbf{y}| \geq \frac{|\mathbf{x}|}{2}} |\varphi(\mathbf{x} - \mathbf{y})| |\psi(\mathbf{y})| \, d\mathbf{y} ,$$

and we conclude with the Cauchy-Schwarz inequality. □

We recall Poisson's summation formula (see for instance [Gra14a, Theorem 3.2.8]).

Proposition 3.31 (Poisson's summation formula)**.** *Let* f *be a continuous function on* $\mathbb{R}^2$ *which satisfies for some* $C, \delta > 0$ *and for all* $\mathbf{x} \in \mathbb{R}^2$

$$|f(\mathbf{x})| \leq C(1 + |\mathbf{x}|)^{-2-\delta} \quad \text{and} \quad \sum_{\mathbf{v} \in \mathscr{L}_L^*} \left|\widehat{f}(\mathbf{v})\right| < \infty .$$

Then, for all $\mathbf{x} \in \mathbb{R}^2$ *we have*

$$\frac{2\pi}{|\Gamma_L|} \sum_{\mathbf{v} \in \mathscr{L}_L^*} \widehat{f}(\mathbf{v}) e^{i\mathbf{x}\cdot\mathbf{v}} = \sum_{\mathbf{u} \in \mathscr{L}_L} f(\mathbf{u} + \mathbf{x}) \,.$$

For $\mathbf{v} \in \mathscr{L}_L^*$ and $\mathbf{k} \in \Gamma_L^*$, we denote $e_{\mathbf{v}+\mathbf{k}}(\mathbf{x}) \coloneqq |\Gamma_L|^{-\frac{1}{2}} e^{i\mathbf{x}\cdot(\mathbf{v}+\mathbf{k})} \in L^2_{\mathbf{k}}(\Gamma_L)$. We recall that $e_{\mathbf{v}+\mathbf{k}}$ is a normalized eigenfunction of the Laplace operator $-\Delta$ defined on $L^2_{\mathbf{k}}(\Gamma_L)$ associated with the eigenvalue $|\mathbf{v}+\mathbf{k}|^2$ and that the set $(e_{\mathbf{v}+\mathbf{k}})_{\mathbf{v}\in\mathscr{L}_L^*}$ forms an orthonormal family of $L^2_{\mathbf{k}}(\Gamma_L)$.

Lemma 3.32. *For all* $\mathbf{r} \in \mathbf{R}$*, we have*

$$\sup_{L\geq 1} \sup_{\mathbf{k}\in\Gamma_L^*} \left\| \sqrt{-\Delta+1}\, \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot) \right\|_{L^2(\Gamma_L)} < \infty \,. \tag{3.78}$$

Proof. The parity operator $\mathcal{P}$ is defined by $(\mathcal{P}v)(\mathbf{x}) = v(-\mathbf{x})$. We have

$$\begin{aligned}
\left\| \sqrt{-\Delta+1}\, \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot) \right\|^2_{L^2(\Gamma_L)} &= \sum_{\mathbf{v}\in\mathscr{L}_L^*} \left(|\mathbf{v}+\mathbf{k}|^2+1\right) \left| \langle e_{\mathbf{v}+\mathbf{k}}, \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot)\rangle_{L^2(\Gamma_L)} \right|^2 \\
&= \frac{(2\pi)^2}{|\Gamma_L|} \sum_{\mathbf{v}\in\mathscr{L}_L^*} \left(|\mathbf{v}+\mathbf{k}|^2+1\right) |\mathcal{F}(v_{L,\mathbf{r}})(\mathbf{v}+\mathbf{k})|^2 \\
&= \frac{2\pi}{|\Gamma_L|} \sum_{\mathbf{v}\in\mathscr{L}_L^*} \mathcal{F}\left[\left(\sqrt{-\Delta+1}\mathcal{P}v_{L,\mathbf{r}}\right) * \left(\sqrt{-\Delta+1}v_{L,\mathbf{r}}\right)\right](\mathbf{v}+\mathbf{k}) \\
&= \sum_{\mathbf{u}\in\mathscr{L}_L} e^{-i\mathbf{u}\cdot\mathbf{k}} \left[\left(\sqrt{-\Delta+1}\mathcal{P}v_{L,\mathbf{r}}\right) * \left(\sqrt{-\Delta+1}v_{L,\mathbf{r}}\right)\right](\mathbf{u}) \,.
\end{aligned}$$

The equality $\langle e_{\mathbf{v}+\mathbf{k}}, \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot)\rangle_{L^2(\Gamma_L)} = 2\pi\, |\Gamma_L|^{-1/2} \mathcal{F}(v_{L,\mathbf{r}})(\mathbf{v}+\mathbf{k})$ holds because $v_{L,\mathbf{r}}$ decays exponentially fast by Proposition 3.16. We recall that if $f, g \in L^2(\mathbb{R}^d)$ satisfy $f * g \in L^1(\mathbb{R}^d)$ then we have $\mathcal{F}(f*g) = (2\pi)^{d/2}\widehat{f}\widehat{g}$. By Proposition 3.16 and Lemma 3.30, we have $\left(\sqrt{-\Delta+1}v_{L,\mathbf{r}}\right) * \left(\sqrt{-\Delta+1}v_{L,\mathbf{r}}\right) \in L^1(\mathbb{R}^2)$ which justifies the third equality in the computation above. The last one is justified with Poisson's summation formula (Proposition 3.31) and Lemma 3.30 again. Then, using Lemma 3.30 and the estimate (3.41) from Proposition 3.16, we can bound

$$\left\| \sqrt{-\Delta+1}\, \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot) \right\|^2_{L^2(\Gamma_L)} \lesssim \|v_{L,\mathbf{r}}\|_{H^1(\mathbb{R}^2)} \,.$$

Finally, we show the estimate (3.78) by recalling that $v_{L,\mathbf{r}}$ is uniformly bounded in $H^1(\mathbb{R}^2)$ (see for instance the right side of (3.39)). ☐

Lemma 3.33. *We have*

$$\sup_{L\geq 1} \sup_{\mathbf{k}\in\Gamma_L^*} \left\| \frac{1}{\sqrt{-\Delta+\mu_L}} P_L^\perp(\mathbf{k}) \sqrt{-\Delta+\mu_L} \right\|_{\mathcal{B}(L^2_{\mathbf{k}}(\Gamma_L))} < \infty \,.$$

Proof. Using the identity $P_L^\perp(\mathbf{k}) = \mathrm{id} - P_L(\mathbf{k})$ and $\sup_{L\geq 1}\mu_L < \infty$, it is sufficient to show that $P_L(\mathbf{k})\sqrt{-\Delta+1}$ is bounded uniformly with respect to $L \geq 1$ and $\mathbf{k} \in \Gamma_L^*$. Writing $P_L(\mathbf{k}) = \sum_{\mathbf{r}\in\mathbf{R}} |u_{L,\mathbf{r}}(\mathbf{k},\cdot)\rangle \langle u_{L,\mathbf{r}}(\mathbf{k},\cdot)|$ (see Proposition 3.23), we can show that for all $\varphi \in H^1_{\mathbf{k}}(\Gamma_L)$ we have

$$\left\| P_L(\mathbf{k})\sqrt{-\Delta+1}\varphi \right\|_{L^2(\Gamma_L)} \leq \left(\sum_{\mathbf{r}\in\mathbf{R}} \left\| \sqrt{-\Delta+1} u_{L,\mathbf{r}}(\mathbf{k},\cdot) \right\|_{L^2(\Gamma_L)} \right) \|\varphi\|_{L^2(\Gamma_L)} \,.$$

Then, using identity (3.57), we can bound

$$\sum_{\mathbf{r}\in\mathbf{R}} \left\| \sqrt{-\Delta+1} u_{L,\mathbf{r}}(\mathbf{k},\cdot) \right\|_{L^2(\Gamma_L)} \\ \leq \left(\sup_{\mathbf{r}\in\mathbf{R}} \sum_{\mathbf{u}\in\mathscr{L}^{\mathbf{R}}} \left| G_L^{-\frac{1}{2}}(\mathbf{u},\mathbf{r}) \right| \right) \sum_{\mathbf{r}\in\mathbf{R}} \left\| \sqrt{-\Delta+1}\, \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot) \right\|_{L^2(\Gamma_L)} .$$

We conclude thanks to Lemma 3.19 and Lemma 3.32. □

Lemma 3.34. *For L large enough, we have: for all $\mathbf{r}\in\mathbf{R}$, for all $\mathbf{k}\in\Gamma_L^*$,*

$$\left\| \frac{1}{\sqrt{-\Delta+\mu_L}} (H_L(\mathbf{k})+\mu_L)\mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot) \right\|_{L^2(\Gamma_L)} \\ \lesssim L^M \left\| \sqrt{-\Delta+1}\, \mathcal{U}_{\mathrm{BF}}\left((1-\chi_{L,\mathbf{r}})v_{L,\mathbf{r}}\right)(\mathbf{k},\cdot) \right\|_{L^2(\Gamma_L)} ,$$

where M is the constant appearing in (3.31).

Proof. We have

$$\left\| \frac{1}{\sqrt{-\Delta+\mu_L}} (H_L(\mathbf{k})+\mu_L)\mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot) \right\|^2_{L^2(\Gamma_L)} \\ = \left\| \left(\sqrt{-\Delta+\mu_L} + \frac{1}{\sqrt{-\Delta+\mu_L}} V_L \right) \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot) \right\|^2_{L^2(\Gamma_L)} .$$

The function $\mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot)$ is in $H^1_{\mathbf{k}}(\Gamma_L)$ by Lemma 3.32 and the operator $\frac{1}{\sqrt{-\Delta+1}} V_L \frac{1}{\sqrt{-\Delta+1}}$ is bounded on $L^2_{\mathbf{k}}(\Gamma_L)$ by Corollary 3.14, so all the terms in the previous equality make sense in $L^2_{\mathbf{k}}(\Gamma_L)$. Let $\mathbf{v}\in\mathscr{L}_L^*$. Because $v_{L,\mathbf{r}}$ is exponentially decaying, we have

$$\begin{aligned} \left\langle e_{\mathbf{v}+\mathbf{k}}, \sqrt{-\Delta+\mu_L}\, \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot) \right\rangle_{L^2(\Gamma_L)} &= \sqrt{|\mathbf{v}+\mathbf{k}|^2+\mu_L}\, \langle e_{\mathbf{v}+\mathbf{k}}, \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot)\rangle_{L^2(\Gamma_L)} \\ &= \frac{2\pi}{\sqrt{|\Gamma_L|}} \sqrt{|\mathbf{v}+\mathbf{k}|^2+\mu_L}\mathcal{F}(v_{L,\mathbf{r}})(\mathbf{v}+\mathbf{k}) \\ &= \frac{2\pi}{\sqrt{|\Gamma_L|}} \mathcal{F}\left(\sqrt{-\Delta+\mu_L} v_{L,\mathbf{r}}\right)(\mathbf{v}+\mathbf{k}) \\ &= -\mathcal{F}\left(\frac{1}{\sqrt{-\Delta+\mu_L}} V_{L,\mathbf{r}} v_{L,\mathbf{r}} \right)(\mathbf{v}+\mathbf{k}) . \end{aligned}$$

From the inequality

$$\forall \varphi\in\mathcal{S}(\mathbb{R}^2), \qquad \left\| \frac{1}{\sqrt{-\Delta+\mu_L}} \varphi \right\|_{L^p(\mathbb{R}^2)} \leq \frac{2\pi}{\sqrt{\mu_L}} \|\varphi\|_{L^p(\mathbb{R}^2)} ,$$

we see that the operator $(-\Delta+\mu_L)^{-1/2}$ is a L^p Fourier multiplier. We have $V_{L,\mathbf{r}} v_{L,\mathbf{r}} \in L^p(\mathbb{R}^2)$ since $v_{L,\mathbf{r}} \in L^\infty(\mathbb{R}^2)$. This implies

$$\mathcal{F}\left(\frac{1}{\sqrt{-\Delta+\mu_L}} V_{L,\mathbf{r}} v_{L,\mathbf{r}} \right)(\mathbf{v}+\mathbf{k}) = \frac{1}{\sqrt{|\mathbf{v}+\mathbf{k}|+\mu_L}} \mathcal{F}\left(V_{L,\mathbf{r}} v_{L,\mathbf{r}}\right)(\mathbf{v}+\mathbf{k}) .$$

By [Gra14a, Theorem 4.3.7], the operator $(-\Delta+\mu_L)^{-1/2}$ is also a L^p multiplier on the torus

$\mathbb{R}^2/\mathscr{L}_L$. Then, we have

$$\left\langle e_{\mathbf{v}+\mathbf{k}}, \frac{1}{\sqrt{-\Delta+\mu_L}} V_L \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot)\right\rangle_{L^2(\Gamma_L)} = \frac{1}{\sqrt{|\mathbf{v}+\mathbf{k}|^2+\mu_L}} \langle e_{\mathbf{v}+\mathbf{k}}, V_L \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot)\rangle_{L^2(\Gamma_L)}$$
$$= \frac{2\pi}{\sqrt{|\Gamma_L|}} \frac{1}{\sqrt{|\mathbf{v}+\mathbf{k}|^2+\mu_L}} \mathcal{F}\left(V_L v_{L,\mathbf{r}}\right)(\mathbf{v}+\mathbf{k}).$$

The second equality comes from the fact that $v_{L,\mathbf{r}}$ is exponentially decaying at infinity. Recalling that $\mu_L \to \mu$ as $L \to \infty$ and using the Plancherel theorem, we show

$$\left\| \frac{1}{\sqrt{-\Delta+\mu_L}} \left(H_L(\mathbf{k})+\mu_L\right) \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot)\right\|^2_{L^2(\Gamma_L)}$$
$$\lesssim \frac{(2\pi)^2}{|\Gamma_L|} \sum_{\mathbf{v}\in\mathscr{L}_L^*} \frac{1}{|\mathbf{v}+\mathbf{k}|^2+1} \left|\mathcal{F}\left(V_L(1-\chi_{L,\mathbf{r}})v_{L,\mathbf{r}}\right)(\mathbf{v}+\mathbf{k})\right|^2.$$

Going back up the previous calculations, we have

$$\frac{1}{\sqrt{|\Gamma_L|}} \frac{1}{\sqrt{|\mathbf{v}+\mathbf{k}|^2+1}} \mathcal{F}\left(V_L(1-\chi_{L,\mathbf{r}})v_{L,\mathbf{r}}\right)(\mathbf{v}+\mathbf{k})$$
$$= \left\langle e_{\mathbf{v}+\mathbf{k}}, \frac{1}{\sqrt{-\Delta+1}} V_L \mathcal{U}_{\mathrm{BF}}\left((1-\chi_{L,\mathbf{r}})v_{L,\mathbf{r}}\right)(\mathbf{k},\cdot)\right\rangle_{L^2(\Gamma_L)}.$$

Then, by the Plancherel theorem, we obtain

$$\frac{(2\pi)^2}{|\Gamma_L|} \sum_{\mathbf{v}\in\mathscr{L}_L^*} \frac{1}{|\mathbf{v}+\mathbf{k}|^2+1} \left|\mathcal{F}\left(V_L(1-\chi_{L,\mathbf{r}})v_{L,\mathbf{r}}\right)(\mathbf{v}+\mathbf{k})\right|^2$$
$$= \left\| \frac{1}{\sqrt{-\Delta+1}} V_L \mathcal{U}_{\mathrm{BF}}\left((1-\chi_{L,\mathbf{r}})v_{L,\mathbf{r}}\right)(\mathbf{k},\cdot)\right\|^2_{L^2(\Gamma_L)}$$
$$\lesssim L^{2M} \left\| \sqrt{-\Delta+1}\, \mathcal{U}_{\mathrm{BF}}\left((1-\chi_{L,\mathbf{r}})v_{L,\mathbf{r}}\right)(\mathbf{k},\cdot)\right\|^2_{L^2(\Gamma_L)}.$$

For the last inequality, we have used the boundedness of the operator $(-\Delta+1)^{-1/2}V_L(-\Delta+1)^{-1/2}$ on $L^2_{\mathbf{k}}(\Gamma_L)$, see Corollary 3.14. ☐

Lemma 3.35. *For L large enough we have: for all $\mathbf{r}\in\mathbf{R}$, for all $\mathbf{k}\in\Gamma_L^*$,*

$$\left\| \sqrt{-\Delta+1}\, \mathcal{U}_{\mathrm{BF}}\left((1-\chi_{L,\mathbf{r}})v_{L,\mathbf{r}}\right)(\mathbf{k},\cdot)\right\|^2_{L^2(\Gamma_L)} = O\Big(T_L^{(1+\delta)d_0-}\Big),$$

where the O is independent from $\mathbf{r}$ or $\mathbf{k}$.

Proof. We denote $\psi = (1-\chi_{L,\mathbf{r}})v_{L,\mathbf{r}}$. Following the proof of Lemma 3.32, we get

$$\left\| \sqrt{-\Delta+1}\, (\mathcal{U}_{\mathrm{BF}}\psi)(\mathbf{k},\cdot)\right\|^2_{L^2(\Gamma_L)} = \sum_{\mathbf{u}\in\mathscr{L}_L} e^{-i\mathbf{u}\cdot\mathbf{k}} \left[\left(\sqrt{-\Delta+1}\mathcal{P}\psi\right) * \left(\sqrt{-\Delta+1}\psi\right)\right](\mathbf{u}),$$

where $\mathcal{P}$ is the parity operator. Clearly, ψ and $\mathcal{P}\psi$ satisfy the same integral exponential bound (3.41) from Proposition 3.16 as $v_{L,\mathbf{r}}$. Therefore, by Lemma 3.30, we have for L large enough

$$\left|\left[\left(\sqrt{-\Delta+1}\mathcal{P}\psi\right) * \left(\sqrt{-\Delta+1}\psi\right)\right](\mathbf{u})\right| \lesssim \|\psi\|_{H^1(\mathbb{R}^2)} e^{-\frac{\mu}{4}|\mathbf{u}|}.$$

Also, by Young's inequality, we have

$$\left\| \left[\left(\sqrt{-\Delta+1}\mathcal{P}\psi \right) * \left(\sqrt{-\Delta+1}\psi \right) \right] \right\|_{L^\infty(\mathbb{R}^2)} \leq \|\psi\|^2_{H^1(\mathbb{R}^2)} \,.$$

Hence, for all $\epsilon > 0$ and for all $L \geq 1$, we obtain

$$\left\| \sqrt{-\Delta+1}\,(\mathcal{U}_{\mathrm{BF}}\psi)\,(\mathbf{k},\cdot) \right\|^2_{L^2(\Gamma_L)} \lesssim \|\psi\|^{2-\epsilon}_{H^1(\mathbb{R}^2)} \sum_{\mathbf{u}\in\mathscr{L}} e^{-\frac{\mu\epsilon L|\mathbf{u}|}{4}} \lesssim \|\psi\|^{2-\epsilon}_{H^1(\mathbb{R}^2)} \underbrace{\sum_{\mathbf{u}\in\mathscr{L}} e^{-\frac{\mu\epsilon|\mathbf{u}|}{4}}}_{=C_\epsilon<\infty} \,.$$

We recall that $\{\chi_{L,\mathbf{r}} \equiv 1\} \subset B\left(L\mathbf{r}, \frac{1+\delta}{2}Ld_0\right)$. So, by Proposition 3.16, we have

$$\|\psi\|^2_{H^1(\mathbb{R}^2)} = O\Big(T_L^{(1+\delta)d_0-}\Big) \,.$$

This ends the proof of Lemma 3.35. □

Proof of Proposition 3.28. We notice that

$$\left\| C_L(\mathbf{k})^*(B_L(\mathbf{k})-\lambda)^{-1}C_L(\mathbf{k}) \right\| \leq \left\| (B_L(\mathbf{k})-\lambda)^{-1/2}C_L(\mathbf{k}) \right\|^2 \,.$$

Then, we write

$$(B_L(\mathbf{k})-\lambda)^{-1/2}C_L(\mathbf{k}) = (B_L(\mathbf{k})-\lambda)^{-1/2}P_L^\perp(\mathbf{k})\,(H_L(\mathbf{k})+\mu_L)\,P_L(\mathbf{k})\,.$$

We use successively Lemma 3.29, Lemma 3.33, Lemma 3.34, Lemma 3.35 and the fact that $E_L(\mathbf{k})$ is spanned by the family $\{\mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot)\}_{\mathbf{r}\in\mathbf{R}}$ by Proposition 3.23. The polynomial terms emerging from the norm of $(-\Delta+1)^{-1/2}V_L(-\Delta+1)^{-1/2}$ are absorbed by slightly modifying the ϵ in the definition of $O\Big(T_L^{(1+\delta)d_0-}\Big)$. □

We can conclude this section with the

Proof of Theorem 3.4. Theorem 3.4 is a consequence of Corollary 3.25, statement (3.73) and Proposition 3.28. □

4 Proof of Theorem 3.6

4.1 The triangular and honeycomb lattices

First, we recall some basic geometric features of the triangular and honeycomb lattices, see Figure 3.3. The *triangular lattice* is the Bravais lattice defined as the set of discrete translations

$$\mathscr{L} := \mathbb{Z}\mathbf{u}_1 \oplus \mathbb{Z}\mathbf{u}_2 \quad \text{where} \quad \mathbf{u}_1 = \begin{pmatrix} \sqrt{3}/2 \\ 1/2 \end{pmatrix} \quad \text{and} \quad \mathbf{u}_2 = \begin{pmatrix} \sqrt{3}/2 \\ -1/2 \end{pmatrix} \,.$$

We denote by Γ its Wigner-Seitz cell which is a regular hexagon. The reciprocal lattice $\mathscr{L}^*$ of $\mathscr{L}$ is given by

$$\mathscr{L}^* := \mathbb{Z}\mathbf{v}_1 \oplus \mathbb{Z}\mathbf{v}_2 \quad \text{where} \quad \mathbf{v}_1 = \frac{4\pi}{\sqrt{3}}\begin{pmatrix} 1/2 \\ \sqrt{3}/2 \end{pmatrix} \quad \text{and} \quad \mathbf{v}_2 = \frac{4\pi}{\sqrt{3}}\begin{pmatrix} 1/2 \\ -\sqrt{3}/2 \end{pmatrix} \,.$$

Notice the normalization

$$|\mathbf{u}_i| = 1 \quad \text{and} \quad |\mathbf{v}_i| = \frac{4\pi}{\sqrt{3}} \,.$$

The first Brillouin zone Γ^* is also a regular hexagon. Its vertices are of two types, $\mathbf{K}$ and $\mathbf{K}'$, depending on their orbit under the rotation by $2\pi/3$ about the origin. We use the following conventions

$$\mathbf{K} = \frac{1}{3}(\mathbf{v}_1 - \mathbf{v}_2) \quad \text{and} \quad \mathbf{K}' = \frac{1}{3}(\mathbf{v}_2 - \mathbf{v}_1) = -\mathbf{K}\,.$$

A generic vertex is denoted by $\mathbf{K}_\star \in \{\mathbf{K}, \mathbf{K}'\}$. Notice that for any vertex $\mathbf{K}_\star$, we have $M_{\mathcal{R}}\mathbf{K}_\star \in \mathbf{K}_\star + \mathscr{L}^*$ where $M_{\mathcal{R}}$ is the rotation matrix by $2\pi/3$. The *honeycomb lattice* is defined as

$$\mathscr{L}^H := (\mathscr{L} + \mathbf{a}) \cup (\mathscr{L} + \mathbf{b}) \quad \text{where} \quad \mathbf{a} = \frac{1}{2\sqrt{3}}\begin{pmatrix}1\\0\end{pmatrix} \quad \text{and} \quad \mathbf{b} = -\mathbf{a}\,.$$

The nearest neighbor distance in $\mathscr{L}^H$ is $d_0 = |\mathbf{a} - \mathbf{b}| = 1/\sqrt{3}$ and the second nearest neighbor distance is $d_1 = |\mathbf{u}_i| = 1$. As in the previous sections, for $L \geq 1$, we use the subscript L to denote the objects defined from the dilated lattice $\mathscr{L}_L = L\mathscr{L}$.

The symmetry group G of the honeycomb lattice $\mathscr{L}^H$ belongs to the **p6m** class. In particular, $\mathscr{L}^H$ is invariant with respect to the shifts of the triangular lattice $\mathscr{L}$, under parity symmetry and horizontal reflection symmetry. Also, $\mathscr{L}_H$ is invariant with respect to the rotation by $2\pi/3$ (resp. by $\pi/3$) about $\mathbf{a}$ or $\mathbf{b}$ (resp. about $\mathbf{x}_c$ where $\mathbf{x}_c \in \mathbb{R}^2$ denotes the center of any hexagon).

Notice that because $\mathbf{b} = -\mathbf{a}$, $\mathscr{L}^H$ satisfies Assumption 2; G acts transitively on $\mathscr{L}^H$. In addition, it can be seen that the action of G on the set of nearest neighbors $\mathscr{P}^{\mathbf{R}}$, defined in (3.13), is also transitive. Hence $m = 1$ in this case.

4.2 Existence of Dirac cones

In this section, we consider a potential V_L satisfying Assumptions 1, 3, 4 and 5 with $\mathscr{L}^{\mathbf{R}} = \mathscr{L}^H$, which satisfies Assumption 2. We use the same notations as in Section 3. In particular, we denote by $H_L = -\Delta + V_L$ the periodic Schrödinger operator associated with V_L and by $H_L(\mathbf{k})$ the restriction of H_L along the fiber $L^2_{\mathbf{k}}(\Gamma)$ where $\mathbf{k} \in \Gamma^*_L$. Also the matrix of H_L (resp. $H_L(\mathbf{k})$) in the subspace E_L (resp. $E_L(\mathbf{k})$) spanned by the orthonormal family $\{w_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$ where the functions $w_{L,\mathbf{r}}$ are defined in (3.52) (resp. in the orthonormal family $\{u_{L,\mathbf{r}}(\mathbf{k},\cdot)\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$ where the functions $u_{L,\mathbf{r}}(\mathbf{k},\cdot)$ are defined in (3.55)) are denoted by A_L (resp. $A_L(\mathbf{k})$).

By Theorem 3.4, we know that for L large enough, the spectrum $H_L(\mathbf{k})$ is given to leading order by the Wallace model:

$$\forall \mathbf{k} \in \Gamma^*_L, \quad \mu_{\pm,L}(\mathbf{k}) = -\mu_L \pm |\theta_L|\left|1 + e^{i\mathbf{k}\cdot\mathbf{u}_1} + e^{i\mathbf{k}\cdot\mathbf{u}_2}\right| + O\left(T_L^{\frac{1+\delta}{\sqrt{3}}-} + T_L^{1-}\right),$$

where θ_L is the interaction coefficient defined in (3.14). Assume there exists $c > 0$ and $\delta' \in [0, \delta)$ small enough such that

$$|\theta_L| \geq c T_L^{\frac{1+\delta'}{\sqrt{3}}}\,. \tag{3.79}$$

Let $r > 0$ small enough and $\mathbf{K}_\star \in \{\mathbf{K}, \mathbf{K}'\}$ be a vertex of the first Brillouin zone Γ^*. Then, our goal is to show that, when $L \to \infty$, we have the expansion

$$\mu_{\pm,L}\left(\frac{\mathbf{K}_\star + \kappa}{L}\right) = -\mu_L + o(|\theta_L|) \pm \frac{\sqrt{3}}{2}|\theta_L|\,|\kappa|\,(1 + E(\kappa))\,(1 + o(1))\,, \tag{3.80}$$

where $|E(\kappa)| \leq C\,|\kappa|$ for all $\kappa \in B(0,r)$ and where the o's do not depend on κ. The proof is mainly an adaptation of the arguments used to show Theorem 3.4 but with the additional knowledge that both the symmetry group G and its action on $\mathscr{L}^{\mathbf{R}}$ and $\mathscr{P}^{\mathbf{R}}$ are entirely specified.

We divide the proof in four steps. In the first three, we give the leading order of low-lying eigenvalues of the operator $A_L\left(\frac{\mathbf{K}_\star+\kappa}{L}\right)$ when L is large and $\kappa \in \mathbb{R}^2$ small. Afterwards, we give a more precise expansion around the Dirac point $\mathbf{K}_\star$ of the residual term appearing in the Feshbach-Schur method (see (3.73)).

Throughout the proof, the O's and o's will not depend on the pseudo-momentum $\mathbf{k}$.

First step. For $\mathbf{k} \in \mathbb{R}^2$, we write

$$A_L(\mathbf{k}/L) = \begin{pmatrix} A_L(\mathbf{k}/L; \mathbf{a}, \mathbf{a}) & A_L(\mathbf{k}/L; \mathbf{a}, \mathbf{b}) \\ A_L(\mathbf{k}/L; \mathbf{b}, \mathbf{a}) & A_L(\mathbf{k}/L; \mathbf{b}, \mathbf{b}) \end{pmatrix},$$

where

$$\begin{aligned} A_L(\mathbf{k}/L; \mathbf{a}, \mathbf{a}) &= \overline{A_L(\mathbf{k}/L; \mathbf{a}, \mathbf{a})} = \sum_{\mathbf{u} \in \mathscr{L}} e^{i\mathbf{k}\cdot\mathbf{u}} A_L(\mathbf{a}, \mathbf{a}+\mathbf{u}), \\ A_L(\mathbf{k}/L; \mathbf{b}, \mathbf{b}) &= \overline{A_L(\mathbf{k}/L; \mathbf{b}, \mathbf{b})} = \sum_{\mathbf{u} \in \mathscr{L}} e^{i\mathbf{k}\cdot\mathbf{u}} A_L(\mathbf{b}, \mathbf{b}+\mathbf{u}), \\ A_L(\mathbf{k}/L; \mathbf{a}, \mathbf{b}) &= \overline{A_L(\mathbf{k}/L; \mathbf{b}, \mathbf{a})} = \sum_{\mathbf{u} \in \mathscr{L}} e^{i\mathbf{k}\cdot\mathbf{u}} A_L(\mathbf{a}, \mathbf{b}+\mathbf{u}). \end{aligned}$$

We recall that s_L denotes the scaling operator, defined by $s_L\mathbf{x} = L\mathbf{x}$. Using the fact that the point group of the symmetry group G of $\mathscr{L}^H$ acts on $\mathscr{L}$ (see for instance [Arm88, Theorem 25.2]), we can show the following relations

$$\forall \mathbf{k} \in \Gamma_L^*, \quad \forall \mathbf{r} \in \mathscr{L}^{\mathbf{R}}, \quad \forall g \in G, \quad (s_L g s_L^{-1}) \cdot u_{L,\mathbf{r}}(\mathbf{k}, \cdot) = u_{L, g\cdot\mathbf{r}}(S_g\mathbf{k}, \cdot),$$

where S_g is the linear part of g. Then, we deduce that

$$\forall g \in G, \quad \forall \mathbf{k} \in \Gamma_L^*, \quad g \cdot A_L(\mathbf{k}) := A_L(S_g^{-1}\mathbf{k}), \tag{3.81}$$

where S_g is the linear part of g. Using identity (3.81) with g the parity symmetry $(\mathcal{P}\psi)(\mathbf{x}) = \psi(-\mathbf{x})$, we can show that

$$A_L(\mathbf{k}/L; \mathbf{a}, \mathbf{a}) = \overline{A_L(\mathbf{k}/L; \mathbf{b}, \mathbf{b})} = A_L(\mathbf{k}/L; \mathbf{b}, \mathbf{b}).$$

Second step. Now, we estimate each matrix element of $A_L(\mathbf{k}/L)$, starting with the diagonal terms. We introduce the following equivalence relation on $\mathscr{L}$:

$$\mathbf{u} \sim_1 \mathbf{u}' \iff \exists k \in \{0,1,2\}, \quad \mathbf{u}' = M_{\mathcal{R}}^k \mathbf{u},$$

where we recall that $M_{\mathcal{R}}$ is the rotation matrix by $2\pi/3$ given by

$$M_{\mathcal{R}} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}.$$

Now, using identity (3.58) with g the rotation by $2\pi/3$ about $\mathbf{a}$, we can write

$$\begin{aligned} A_L(\mathbf{k}/L; \mathbf{a}, \mathbf{a}) = \sum_{\mathbf{u} \in \mathscr{L}} & e^{i\mathbf{K}_\star\cdot\mathbf{u}} A_L(\mathbf{a}, \mathbf{a}+\mathbf{u}) \\ & + \sum_{\mathbf{u} \in \mathscr{L}/\sim_1} \left(e^{i\mathbf{k}\cdot\mathbf{u}} + e^{i\mathbf{k}\cdot M_{\mathcal{R}}\mathbf{u}} + e^{i\mathbf{k}\cdot M_{\mathcal{R}}^2\mathbf{u}} - 3e^{i\mathbf{K}_\star\cdot\mathbf{u}} \right) A_L(\mathbf{a}, \mathbf{a}+\mathbf{u}). \end{aligned}$$

Let $\kappa \subset B(0,r)$ for some $r > 0$. Using that $M_{\mathcal{R}}\mathbf{K}_\star \in \mathbf{K}_\star + \mathscr{L}^*$, we have for all $\mathbf{u} \in \mathscr{L}$ and for all $\mathbf{k} = \mathbf{K}_\star + \kappa$

$$\left| e^{i\mathbf{k}\cdot\mathbf{u}} + e^{i\mathbf{k}\cdot M_{\mathcal{R}}\mathbf{u}} + e^{i\mathbf{k}\cdot M_{\mathcal{R}}^2\mathbf{u}} - 3e^{i\mathbf{K}_\star\cdot\mathbf{u}} \right| = \left| e^{i\kappa\cdot\mathbf{u}} + e^{i\kappa\cdot M_{\mathcal{R}}\mathbf{u}} + e^{i\kappa\cdot M_{\mathcal{R}}^2\mathbf{u}} - 3 \right| \lesssim |\kappa|^2 |\mathbf{u}|^2.$$

Then, using the exponential localization of A_L provided in (3.63), the expansion $A_L(\mathbf{a},\mathbf{a}) = -\mu_L + O\left(T_L^{\frac{1+\delta}{\sqrt{3}}-} + T_L^{1-}\right)$ (see Proposition 3.24) and assumption (3.79), we have for L large enough

$$\begin{aligned} A_L\left(\frac{\mathbf{K}_\star + \kappa}{L};\mathbf{a},\mathbf{a}\right) &= \sum_{\mathbf{u}\in\mathscr{L}} e^{i\mathbf{K}_\star\cdot\mathbf{u}} A_L(\mathbf{a},\mathbf{a}+\mathbf{u}) + |\kappa|^2 O\left(\sum_{\mathbf{u}\in\mathscr{L}\setminus\{0\}} |\mathbf{u}|^2 A_L(\mathbf{a},\mathbf{a}+\mathbf{u})\right) \\ &= -\mu_L + (1+|\kappa|^2) O\left(T_L^{\min\left(1,\frac{1+\delta}{\sqrt{3}}\right)-}\right) = -\mu_L + (1+|\kappa|^2) o(|\theta_L|) \,. \end{aligned} \tag{3.82}$$

Third step. Now, we consider the off-diagonal terms. If g denotes the rotation by $2\pi/3$ about $\mathbf{a}$ then, for all $\mathbf{u}\in\mathscr{L}$, we have

$$\begin{aligned} A_L(\mathbf{a},\mathbf{b}+\mathbf{u}) &= A_L(\mathbf{a}, g\cdot(\mathbf{b}+\mathbf{u})) = A_L(\mathbf{a},\mathbf{b}+M_{\mathcal{R}}(\mathbf{u}+\mathbf{u}_1))\,, \\ A_L(\mathbf{a},\mathbf{b}+\mathbf{u}) &= A_L(\mathbf{a}, g^2\cdot(\mathbf{b}+\mathbf{u})) = A_L(\mathbf{a},\mathbf{b}+M_{\mathcal{R}}^2(\mathbf{u}+\mathbf{u}_2))\,. \end{aligned}$$

This leads to the following equivalence relation

$$\mathbf{u}\sim_2\mathbf{u}' \iff \exists k\in\{0,1,2\}, \quad \mathbf{u}' = M_{\mathcal{R}}^k(\mathbf{u}+\mathbf{u}_k)\,, \tag{3.83}$$

where we have used the convention $\mathbf{u}_0 = 0$. We write

$$A_L(\mathbf{k}/L;\mathbf{a},\mathbf{b}) = \sum_{\mathbf{u}\in\mathscr{L}/\sim_2} \left(e^{i\mathbf{k}\cdot\mathbf{u}} + e^{i\mathbf{k}\cdot M_{\mathcal{R}}(\mathbf{u}+\mathbf{u}_1)} + e^{i\mathbf{k}\cdot M_{\mathcal{R}}^2(\mathbf{u}+\mathbf{u}_2)}\right) A_L(\mathbf{a},\mathbf{b}+\mathbf{u})\,.$$

Using again that $M_{\mathcal{R}}\mathbf{K}_\star \in \mathbf{K}_\star + \mathscr{L}^*$, we have for $\mathbf{k} = \mathbf{K}_\star + \kappa$

$$A_L(\mathbf{k}/L;\mathbf{a},\mathbf{b}) = \sum_{\mathbf{u}\in\mathscr{L}/\sim_2} e^{i\mathbf{K}_\star\cdot\mathbf{u}}\left(e^{i\kappa\cdot\mathbf{u}} + e^{i\mathbf{K}_\star\cdot\mathbf{u}_1} e^{i\kappa\cdot M_{\mathcal{R}}(\mathbf{u}+\mathbf{u}_1)} + e^{i\mathbf{K}_\star\cdot\mathbf{u}_2} e^{i\kappa\cdot M_{\mathcal{R}}^2(\mathbf{u}+\mathbf{u}_2)}\right) A_L(\mathbf{a},\mathbf{b}+\mathbf{u})\,. \tag{3.84}$$

From now on, we only consider the case $\mathbf{K}_\star = \mathbf{K}$. The minor changes for the case $\mathbf{K}_\star = \mathbf{K}'$ are left to the reader. Using the identities $e^{i\mathbf{K}\cdot\mathbf{u}_k} = j^k$ where $k\in\{0,1,2\}$ and $j = e^{i\frac{2\pi}{3}}$, we have

$$\begin{aligned} A_L\left(\frac{\mathbf{K}+\kappa}{L};\mathbf{a},\mathbf{b}\right) &= i\kappa\cdot\sum_{\mathbf{u}\in\mathscr{L}/\sim_2} e^{i\mathbf{K}\cdot\mathbf{u}}\left(\mathbf{u} + jM_{\mathcal{R}}(\mathbf{u}+\mathbf{u}_1) + j^2 M_{\mathcal{R}}^2(\mathbf{u}+\mathbf{u}_2)\right) A_L(\mathbf{a},\mathbf{b}+\mathbf{u}) \\ &\quad + |\kappa|^2 O\left(\sum_{\mathbf{u}\in\mathscr{L}/\sim_2} (1+|\mathbf{u}|^2) A_L(\mathbf{a},\mathbf{b}+\mathbf{u})\right)\,. \end{aligned}$$

By assumption (3.79) and Proposition 3.24, we have $A_L(\mathbf{a},\mathbf{b}) = \theta_L(1+o(1))$. Using the exponential localization (3.63) of A_L, the main contributor for both sums when L is large correspond to $\mathbf{u} = 0$. In addition, a computation shows

$$jM_{\mathcal{R}}\mathbf{u}_1 + j^2 M_{\mathcal{R}}^2\mathbf{u}_2 = \frac{\sqrt{3}}{2}\begin{pmatrix}1\\ i\end{pmatrix}\,.$$

Hence, for L large enough, we have

$$A_L\left(\frac{\mathbf{K}+\kappa}{L};\mathbf{a},\mathbf{b}\right) = \frac{\sqrt{3}}{2}\theta_L(\kappa_1 + i\kappa_2 + E(\kappa))(1+o(1))\,, \tag{3.85}$$

where $|E(\kappa)| \le C|\kappa|^2$ for all $\kappa\in B(0,r)$.

Now, the eigenvalues $\lambda_{\pm,L}(\kappa)$ of $A_L\left(\frac{\mathbf{K}+\kappa}{L}\right)$ satisfy the system

$$\mu^2 - 2A_L\left(\frac{\mathbf{K}+\kappa}{L};\mathbf{a},\mathbf{a}\right)\mu + \left|A_L\left(\frac{\mathbf{K}+\kappa}{L};\mathbf{a},\mathbf{b}\right)\right|^2 = 0\,.$$

Using expansions (3.82) and (3.85), we obtain that

$$\lambda_{\pm,L}(\kappa) = -\mu_L + o(|\theta_L|) \pm \frac{\sqrt{3}}{2}\,|\theta_L|\,|\kappa|\,(1+E'(\kappa))\,(1+o(1))\,, \tag{3.86}$$

where $|E'(\kappa)| \le C'\,|\kappa|$ for all $\kappa \in B(0,r)$. In particular, a conical singularity appears at $\kappa = 0$.

Fourth step. Let $\lambda \in (-\infty\,, -\mu_L + g/3)$ where g denotes the first spectral gap of the mono-atomic operators defined in (3.11). Following the proof of Proposition 3.28, it can be seen that for some constant $C > 0$, we have: for all $\mathbf{k} \in \mathbb{R}^2$

$$\begin{aligned}\left\|C_L(\mathbf{k}/L)^*(B_L(\mathbf{k}/L)-\lambda)^{-1}C_L(\mathbf{k}/L)\right\| &= \left\|(B_L(\mathbf{k}/L)-\lambda)^{-1/2}C_L(\mathbf{k}/L)\right\|^2 \\ &\lesssim L^C \sum_{\mathbf{u}\in\mathscr{L}} e^{-i\mathbf{u}\cdot\mathbf{k}}\left[\left(\sqrt{-\Delta+1}\mathcal{P}\psi_{L,\mathbf{r}}\right) * \left(\sqrt{-\Delta+1}\psi_{L,\mathbf{r}}\right)\right](\mathbf{u})\,,\end{aligned}$$

where $\psi_{L,\mathbf{r}} = (1-\chi_{L,\mathbf{r}})v_{L,\mathbf{r}}$ for any $\mathbf{r} \in \{\mathbf{a},\mathbf{b}\}$. Notice that the sum is real by Poisson summation formula, see Proposition 3.31. Assume $\mathbf{r} = \mathbf{a}$ (the case $\mathbf{r} = \mathbf{b}$ is treated similarly). First, notice that $\mathcal{P}\psi_{L,\mathbf{a}} = \psi_{L,\mathbf{b}}$ and that, using the Fourier transform, $\sqrt{-\Delta+1}\psi_{L,\mathbf{a}}$ has the symmetries of $\psi_{L,\mathbf{a}}$. Then, it is not difficult to show that $\left[\left(\sqrt{-\Delta+1}\psi_{L,\mathbf{b}}\right) * \left(\sqrt{-\Delta+1}\psi_{L,\mathbf{a}}\right)\right](\mathbf{u})$ is constant on the equivalence class associated with the equivalence relation $\sim_2$ introduced in (3.83). Then, we combine the arguments used in the proof of (3.85) with those used in the proof of Lemma 3.35 to show: for all $\mathbf{k} = \mathbf{K}_\star + \kappa$ with $\kappa \in B(0,r)$

$$\left\|C_L(\mathbf{k}/L)^*(B_L(\mathbf{k}/L)-\lambda)^{-1}C_L(\mathbf{k}/L)\right\| = (1+|\kappa|+E''(\kappa))O\left(T_L^{\frac{1+\delta}{\sqrt{3}}}\right) = (1+|\kappa|+E''(\kappa))o(|\theta_L|)\,, \tag{3.87}$$

where there exists $C'' > 0$ such that $|E''(\kappa)| \le C''\,|\kappa|^2$ for all $\kappa \in B(0,r)$. Finally, by using the estimate (3.87), the expansion (3.86) and the relation (3.73), we show the expansion (3.80).

5 Proof of Theorem 3.7

In this section, we show that we can apply Theorem 3.4 to the periodic rHF model introduced in Section 2.3. We first recall the main features of this model. For simplicity, we assume $q = 1$. It consists in solving the minimization problem

$$E_L := \inf\left\{\mathcal{E}_L(\gamma)\ \middle|\ \gamma \in \mathcal{S}_{\mathrm{per},L} \quad \text{and} \quad \underline{\mathrm{Tr}}_{\mathscr{L}_L}(\gamma) = N\right\},$$

where $\mathcal{S}_{\mathrm{per},L}$ (resp. $\mathcal{E}_L(\gamma)$) is defined in (3.20) (resp. in (3.22)) and denotes the space of admissible states (resp. the periodic rHF energy of the state γ). For all $L \ge 1$, this model admits a unique minimizer, denoted by γ_L. We also denote by $\rho_L(\mathbf{x}) = \gamma_L(\mathbf{x},\mathbf{x})$ its one-body density. The minimizer γ_L satisfies the self-consistent equation

$$\gamma_L = \mathbb{1}_{(-\infty,\varepsilon_L]}\left(H_L^{\mathrm{MF}}\right) = \mathbb{1}_{(-\infty,\varepsilon_L]}\left(-\Delta + V_L^{\mathrm{MF}}\right)\,.$$

The mean-field potential V_L^{MF} is given by

$$V_L^{\mathrm{MF}} := -W_L^{\mathbf{R}} + V_L^{\mathbf{R}} + \rho_L *_L W_L\,,$$

where W_L is the periodic three-dimensional Coulomb interaction kernel (defined in (3.88) below), where

$$-W_L^{\mathbf{R}} = \sum_{\mathbf{r}\in\mathbf{R}} W_L(\cdot - L\mathbf{r}),$$

is the external potential induced by the nuclei of the lattice and where

$$V_L^{\mathbf{R}} = \sum_{\mathbf{r}\in\mathbf{R}} \sum_{\mathbf{u}\in\mathscr{L}} V^{\mathrm{pp}}(\cdot - L(\mathbf{u}+\mathbf{r})),$$

is a correction term given by an exact $\mathscr{L}^{\mathbf{R}}$-superposition of a radial and compactly supported potential $V^{\mathrm{pp}} \in L^p(\mathbb{R}^2)$ with $p > 1$. The Fermi level $\varepsilon_L \in \mathbb{R}$ is chosen in order to have $\underline{\mathrm{Tr}}_{\mathscr{L}_L}(\gamma_L) = \int_{\Gamma_L} \rho_L = N$. Because Assumption 2 on the symmetry of the lattice does not depend on the model in consideration but only on the underlying lattice $\mathscr{L}^{\mathbf{R}}$, we will assume that

$$\boxed{\mathscr{L}^{\mathbf{R}} \text{ satisfies Assumption 2.}}$$

In this section, we denote by $G \subset E_2(\mathbb{R})$ (resp. G_L) the symmetry group of $\mathscr{L}^{\mathbf{R}}$ (resp. $\mathscr{L}_L^{\mathbf{R}}$).

5.1 Properties of the periodic interaction kernel W_L

The $\mathscr{L}_L$-periodic interaction kernel W_L is defined as the *unique* solution in the sense of tempered distribution of the following system

$$\begin{cases} \sqrt{-\Delta} W_L = 2\pi \left(\displaystyle\sum_{\mathbf{u}\in\mathscr{L}_L} \delta_{\mathbf{u}} - \frac{1}{|\Gamma_L|} \right), \\ W_L \text{ is } \mathscr{L}_L\text{-periodic, } \min\limits_{\mathbb{R}^2} W_L = 0, \end{cases} \tag{3.88}$$

where the operator $\sqrt{-\Delta}$ is defined as the Fourier multiplier

$$\forall T \in \mathcal{D}'(\mathbb{R}^2/\mathscr{L}_L), \quad \forall \mathbf{v} \in \mathscr{L}_L^*, \quad \mathcal{F}(\sqrt{-\Delta}T)(\mathbf{v}) = |\mathbf{v}|\,\mathcal{F}(T)(\mathbf{v}).$$

This choice of kernel is motivated by the fact we consider a model where the charges are confined in two-dimensional space but interact with the three-dimensional Coulomb interaction. The potential W_L is in fact the periodized version of $\frac{1}{|\mathbf{x}|}$. It differs from the well-known three-dimensional periodic Coulomb interaction kernel (see for instance [LS77b, Section XI]) which is the solution of a similar system to (3.88) where the constant 2π is replaced by 4π and the fractional Laplace operator $\sqrt{-\Delta}$ by the Laplace operator $-\Delta$. However, they share the same behavior $|\mathbf{x}|^{-1}$ in the vicinity of the vertices of $\mathscr{L}_L$, as shown in Proposition 3.38.

Remark 3.36. For $g \in L^p(\mathbb{R}^2)$ where $p \in [1,2)$, the solution of the equation $\sqrt{-\Delta} f = 2\pi g$ is given by $f = g * |\cdot|^{-1}$, see for instance [Kwa17]. We recognize the three-dimensional Coulomb potential induced by the charge distribution g, except that it is restricted to a two-dimensional subspace.

The kernel W_L being the unique solution of the system (3.88), we have the relation $W_L = L^{-1} W_1(L^{-1}\cdot)$ for all $L \geq 1$. Since

$$\mathcal{F}\left(\sum_{\mathbf{u}\in\mathscr{L}_L} \delta_{\mathbf{u}} - \frac{1}{|\Gamma_L|} \right)(\mathbf{v}) = \begin{cases} 0 & \text{if } \quad \mathbf{v} = 0, \\ |\Gamma_L|^{-1/2} & \text{otherwise}, \end{cases}$$

we obtain the Fourier expansion of W_L: there exists $M = \fint_\Gamma W_1 > 0$ such that

$$W_L = L^{-1} M + \frac{2\pi}{\sqrt{|\Gamma_L|}} \sum_{\mathbf{v} \in \mathscr{L}_L^* \setminus \{0\}} \frac{e_{\mathbf{v}}}{|\mathbf{v}|}\,, \tag{3.89}$$

where we recall that $e_{\mathbf{v}}(\mathbf{x}) = |\Gamma_L|^{-1/2} e^{i\mathbf{x}\cdot\mathbf{v}}$ and where the limit is taken in the sense of tempered distribution.

Lemma 3.37. *The mean-field potential V_L^{MF} is G_L-invariant, that is,*

$$\boxed{V_L^{\mathrm{MF}} \text{ satisfies Assumption 3.}}$$

Proof. By [Arm88, Theorem 25.2], the point group J (independent from L) of G_L acts on $\mathscr{L}_L$. In particular, the Wigner-Seitz cell Γ_L of $\mathscr{L}_L$ is invariant with respect to J. Then, for all $(\mathbf{u}, \mathbf{v}) \in \mathscr{L}_L \times \mathscr{L}_L^*$ and for all $g \in J$, we have $e^{g\mathbf{v}\cdot u} = e^{i\mathbf{v}\cdot g^{-1}\mathbf{u}} = 1$ which shows that J also acts on $\mathscr{L}_L^*$. Consequently, we can use the Fourier expansion (3.89) to show that the interaction kernel W_L then $W_L^{\mathbf{R}}$ are invariant under the action of G_L. Since V^{pp} is radial, $V_L^{\mathbf{R}}$ is also invariant under the action of G_L. We deduce that the rHF energy $\mathcal{E}_L$ is invariant under the action of G_L. By uniqueness, this is also the case for γ_L and ρ_L, hence also for $\rho_L *_L W_L$. This concludes the proof of Lemma 3.37. ☐

As for the three-dimensional periodic Coulomb interaction kernel, we can describe W_L as a *Madelung potential* that is a $\mathscr{L}_L$-periodic superposition of the potential induced by a neutral charge distribution (see for instance [LS77b, Section XI.3.B]). We introduce the following function

$$f_L(\mathbf{x}) := \frac{1}{|\mathbf{x}|} - \fint_{\Gamma_L} \frac{\mathrm{d}\mathbf{y}}{|\mathbf{x}-\mathbf{y}|} = \left[|\cdot|^{-1} * \left(\delta_0 - \frac{\mathbb{1}_{\Gamma_L}}{|\Gamma_L|} \right) \right](\mathbf{x})\,.$$

In the next proposition, we show that W_L is, up to an additive constant, given by the Madelung potential associated with the function f_L (see also [Lew22a]).

Proposition 3.38 (W_L is a Madelung potential)**.** *There exists $M' \in \mathbb{R}$ such that*

$$W_L = \sum_{\mathbf{u} \in \mathscr{L}_L} f_L(\cdot - \mathbf{u}) + L^{-1} M'\,, \tag{3.90}$$

where the series converges absolutely in $\mathcal{C}^\infty(\mathbb{R}^2 \setminus \mathscr{L}_L)$. In addition, the function W_L is continuous on $\mathbb{R}^2 \setminus \mathscr{L}_L$, the function $W_L - |\cdot|^{-1}$ is bounded on Γ_L and there exists $a \in \mathbb{R}$ and $C > 0$ such that

$$\lim_{|\mathbf{x}| \to 0} \left(W_L(\mathbf{x}) - |\mathbf{x}|^{-1} \right) = L^{-1} a \quad \textit{and} \quad \forall \mathbf{x} \in \Gamma_L, \quad |W_L(\mathbf{x})| \leq C\, |\mathbf{x}|^{-1}\,. \tag{3.91}$$

In order to prove Proposition 3.38, we first collect some properties of f_L in a lemma.

Lemma 3.39 (Properties of f_L)**.** *We have the identity $f_L(\mathbf{x}) = L^{-1} f_1(L^{-1}\mathbf{x})$ and the following asymptotic behaviors*

$$f_1(\mathbf{x}) \sim_{\mathbf{x} \to 0} |\mathbf{x}|^{-1} \quad \textit{and} \quad |f_1(\mathbf{x})| = O\left(|\mathbf{x}|^{-3} \right)\,. \tag{3.92}$$

In addition, we have $f_1 \in \mathcal{C}^\infty(\overline{\Gamma}^c \cup (\mathring{\Gamma} \setminus \{0\}))$ and for all multi-index $\alpha \in \mathbb{N}^2$ and for all $\delta > 0$, it exists a constant $C(\alpha, \delta)$ such that

$$\forall \mathbf{x} \in [\Gamma + B(0,\delta)]^c\,, \quad |\partial^\alpha f_1(\mathbf{x})| \leq C(\alpha, \delta)\, |\mathbf{x}|^{-\max(3, |\alpha|+1)}\,. \tag{3.93}$$

Remark 3.40. In particular, Lemma 3.39 shows that $f_1 \in L^p(\mathbb{R}^2)$ for all $p \in [1\,, 2)$. In addition, we have $\|f_L\|_{L^p(\mathbb{R}^2)} = L^{2/p-1} \|f_1\|_{L^p(\mathbb{R}^2)}$.

Proof of Lemma 3.39. The relation $f_L(\mathbf{x}) = L^{-1} f_1(L^{-1}\mathbf{x})$ comes from a change of variables. The first asymptotic of (3.92) follows from $\mathbb{1}_{\Gamma_L} * |\cdot|^{-1} \in L^\infty(\mathbb{R}^2)$. The second one is a consequence of the fact that $\mathbb{1}_{\Gamma_L}$ has no dipole for the reason that $\Gamma_L = -\Gamma_L$ (see the multipole expansion for two-dimensional charge distributions, for instance [Caz22, Lemma 40]).

We have $f_1 \in \mathcal{C}^\infty(\Gamma^c)$. In addition, we can show that $\left(|\cdot|^{-1} * \mathbb{1}_\Gamma\right) \in \mathcal{C}^\infty(\mathring{\Gamma})$ by adapting the strategy used in the proof of [Caz22, Lemma 5]. Thus we have $f_1 \in \mathcal{C}^\infty(\overline{\Gamma}^c \cup (\mathring{\Gamma} \setminus \{0\}))$.

Now, let $\alpha \in \mathbb{N}^2$. If $|\alpha| = 0$ then the estimate (3.93) is just the right side of (3.92). Now, if $|\alpha| \neq 0$ we have for all $\mathbf{x} \in [\Gamma + B(0,\delta)]^c$

$$
\begin{aligned}
|\partial^\alpha f_1(\mathbf{x})| &\leq C_\alpha \left[|\mathbf{x}|^{-|\alpha|-1} + \left(|\cdot|^{-|\alpha|-1} * \frac{\mathbb{1}_\Gamma}{|\Gamma|} \right)(\mathbf{x}) \right] \\
&\leq C_\alpha \left(|\mathbf{x}|^{-|\alpha|-1} + \mathrm{d}(\mathbf{x}, \partial\Gamma)^{-|\alpha|-1} \right) \leq C(\alpha,\delta)\, |\mathbf{x}|^{-|\alpha|-1} .
\end{aligned}
$$

In the last inequality, we have used the estimate $\mathrm{d}(\mathbf{x},\partial\Gamma) \geq \delta(\delta + \max_{\mathbf{y}\in\partial\Gamma} |\mathbf{y}|)^{-1} |\mathbf{x}|$. When $|\alpha| = 1$, we gain an additional $|\mathbf{x}|^{-1}$ by writing the multipole expansion for $\partial_\alpha |\cdot|^{-1} - (\partial_\alpha |\cdot|^{-1}) * \frac{\mathbb{1}_\Gamma}{|\Gamma|}$ whose first term cancels out. ☐

Proof of Proposition 3.38. First, we compute the Fourier transform of f_L at a vertex $\mathbf{v}$ of $\mathscr{L}_L^*$. In the sense of tempered distributions, we can show that

$$
\mathcal{F}(f_L) = \mathcal{F}\left(|\cdot|^{-1}\right) - 2\pi \mathcal{F}\left(|\cdot|^{-1}\right) \mathcal{F}\left(\frac{\mathbb{1}_{\Gamma_L}}{|\Gamma_L|}\right) .
$$

The following identity is straightforward

$$
\mathcal{F}\left(\frac{\mathbb{1}_{\Gamma_L}}{|\Gamma_L|}\right)(\mathbf{v}) = \begin{cases} \frac{1}{2\pi} & \text{if} \quad \mathbf{v} = 0\,, \\ 0 & \text{if} \quad \mathbf{v} \in \mathscr{L}_L^* \setminus \{0\}\,. \end{cases} \tag{3.94}
$$

The Fourier transform of $|\cdot|^{-1}$ is given by [Gra14a, Theorem 2.4.6] or [LL01, Theorem 5.9]. In order to extract the constant corresponding to our conventions, we reproduce the proof. For $\varphi \in \mathcal{S}(\mathbb{R}^2)$, we have

$$
\left\langle \mathcal{F}\left(|\cdot|^{-1}\right), \varphi \right\rangle = \left\langle |\cdot|^{-1}, \hat{\varphi} \right\rangle = \int_{\mathbb{R}^2} \frac{\hat{\varphi}(\mathbf{k})}{|\mathbf{k}|}\,\mathrm{d}\mathbf{k}\,.
$$

Using the formula

$$
|\mathbf{k}|^{-1} = \int_0^\infty \exp\left[-\pi |\mathbf{k}|^2 \lambda\right] \lambda^{-1/2}\,\mathrm{d}\lambda\,,
$$

we get by Fubini

$$
\begin{aligned}
\left\langle \mathcal{F}\left(|\cdot|^{-1}\right), \varphi \right\rangle &= \int_{\mathbb{R}^2} \int_0^\infty \hat{\varphi}(\mathbf{k}) \exp\left[-\pi |\mathbf{k}|^2 \lambda\right] \lambda^{-1/2}\,\mathrm{d}\lambda\,\mathrm{d}\mathbf{k} \\
&= \int_0^\infty \lambda^{-1/2} \int_{\mathbb{R}^2} \hat{\varphi}(\mathbf{k}) \exp\left[-\pi |\mathbf{k}|^2 \lambda\right] \mathrm{d}\mathbf{k}\,\mathrm{d}\lambda\,.
\end{aligned}
$$

Then, using

$$
\mathcal{F}^{-1}\left(\mathbf{k} \mapsto \exp\left[-\pi |\mathbf{k}|^2 \lambda\right]\right)(\mathbf{x}) = \frac{1}{2\pi\lambda} \exp\left[-\frac{|\mathbf{x}|^2}{4\pi\lambda}\right] ,
$$

we find

$$
\left\langle \mathcal{F}\left(|\cdot|^{-1}\right), \varphi \right\rangle = \frac{1}{2\pi} \int_0^\infty \lambda^{-3/2} \int_{\mathbb{R}^2} \varphi(\mathbf{x}) \exp\left[-\frac{|\mathbf{x}|^2}{4\pi\lambda}\right] \mathrm{d}\mathbf{x}\,\mathrm{d}\lambda\,.
$$

Using Fubini again, we obtain

$$\left\langle \mathcal{F}\left(|\cdot|^{-1}\right), \varphi\right\rangle = \frac{1}{2\pi}\int_{\mathbb{R}^2}\varphi(\mathbf{x})\int_0^\infty \lambda^{-3/2}\exp\left[-\frac{|\mathbf{x}|^2}{4\pi\lambda}\right]\mathrm{d}\lambda\,\mathrm{d}\mathbf{x} = \int_{\mathbb{R}^2}\frac{\varphi(\mathbf{x})}{|\mathbf{x}|}\,\mathrm{d}\mathbf{x} = \left\langle |\cdot|^{-1}, \varphi\right\rangle .$$

This shows the identity $\mathcal{F}(|\cdot|^{-1}) = |\cdot|^{-1}$ which, together with (3.94), implies

$$\mathcal{F}(f_L)(\mathbf{v}) = \begin{cases} M''_L & \text{if} \quad \mathbf{v} = 0\,, \\ |\mathbf{v}|^{-1} & \text{if} \quad \mathbf{v} \in \mathscr{L}_L^* \setminus \{0\}\,, \end{cases}$$

where $M''_L = \frac{1}{2\pi}\int_{\mathbb{R}^2} f_L = LM''$ (which is finite since $f_L \in L^1(\mathbb{R}^2)$ by Lemma 3.39). Now, we set $F_L(\mathbf{x}) = \sum_{\mathbf{u}\in\mathscr{L}_L} f_L(\mathbf{x}-\mathbf{u}) \in L^\infty_{\mathrm{per}}$ which defines a periodic distribution on the torus $\mathbb{R}^2/\mathscr{L}_L$. For all $\varphi \in \mathcal{S}(\mathscr{L}_L^*)$, we have (the following computations are valid since $f_L \in L^1(\mathbb{R}^2)$)

$$\begin{aligned}\left\langle \widehat{F}_L, \varphi\right\rangle = \left\langle F_L, \sum_{\mathbf{v}\in\mathscr{L}_L^*}\varphi_{\mathbf{v}} e_{-\mathbf{v}}\right\rangle &= \sum_{\mathbf{u}\in\mathscr{L}_L}\sum_{\mathbf{v}\in\mathscr{L}_L^*}\varphi_{\mathbf{v}}\int_{\Gamma_L} f_L(\cdot-\mathbf{u})e_{-\mathbf{v}} \\ &= \sum_{\mathbf{v}\in\mathscr{L}_L^*}\varphi_{\mathbf{v}}\int_{\mathbb{R}^2} f_L e_{-\mathbf{v}} = \frac{2\pi}{\sqrt{|\Gamma_L|}}\sum_{\mathbf{v}\in\mathscr{L}_L^*}\varphi_{\mathbf{v}}\hat{f}_L(\mathbf{v})\,.\end{aligned}$$

As a consequence, W_L and F_L share the same Fourier coefficients except for the one corresponding to $\mathbf{v} = 0$. Since $\mathcal{F}$ is a bijection from $\mathcal{D}'(\mathbb{R}^2/\mathscr{L}_L)$ to $\mathcal{S}'(\mathscr{L}_L^*)$, we deduce that the expansion (3.90) holds in $\mathcal{D}'(\mathbb{R}^2/\mathscr{L}_L)$ with $M' = M - 2\pi M''|\Gamma|^{-1}$. Now, we consider the regularity of W_L. We write for $R > 0$

$$\begin{aligned} W_L &= L^{-1}M' + \sum_{|\mathbf{u}|\le R} f_L(\cdot - L\mathbf{u}) + \sum_{|\mathbf{u}|>R} f_L(\cdot - L\mathbf{u}) \\ &= L^{-1}M' + \sum_{|\mathbf{u}|\le R}\frac{1}{|\mathbf{x}-L\mathbf{u}|} - \frac{1}{|\Gamma|}\left(\sum_{|\mathbf{u}|\le R}\mathbb{1}_{\Gamma_L+L\mathbf{u}}\right) * |\cdot|^{-1} + \sum_{|\mathbf{u}|>R} f_L(\cdot - L\mathbf{u})\,,\end{aligned}$$

where the sums are over $\mathscr{L}$. By adapting the proof of [Caz22, Lemma 5], we can show that the third term $\left(\sum_{|\mathbf{u}|\le R}\mathbb{1}_{\Gamma_L+L\mathbf{u}}\right) * |\cdot|^{-1}$ is smooth on $B(0, LR)$. From this and the estimates (3.93), it follows that the series (3.90) converges in $\mathcal{C}^\infty(\mathbb{R}^2\setminus\mathscr{L}_L)$ and that $W_L \in \mathcal{C}^\infty\left(\mathbb{R}^2\setminus\mathscr{L}_L\right)$. In view of Lemma 3.39, the other statements are clear. □

Corollary 3.41. *For all $r \in [1,\infty]$, there exists $C_r > 0$ such that for all $L \ge 1$ and for all $u, v \in H^1_{\mathrm{per}}(\Gamma_L)$, we have*

$$\|(uv) *_L W_L\|_{L^r_{\mathrm{per}}(\Gamma_L)} \le C_r L^{1/r}\|u\|_{H^1_{\mathrm{per}}(\Gamma_L)}\|v\|_{H^1_{\mathrm{per}}(\Gamma_L)}\,. \tag{3.95}$$

Proof. By Young's inequality and Hölder's inequality, we have

$$\|(uv) *_L W_L\|_{L^1_{\mathrm{per}}(\Gamma_L)} \le \|W_L\|_{L^1_{\mathrm{per}}(\Gamma_L)}\|u\|_{L^2_{\mathrm{per}}(\Gamma_L)}\|v\|_{L^2_{\mathrm{per}}(\Gamma_L)}\,.$$

Then, inequality (3.95) for $r = 1$ results from the identity $\|W_L\|_{L^1_{\mathrm{per}}(\Gamma_L)} = L\|W_1\|_{L^1_{\mathrm{per}}(\Gamma)}$ (consequence of the relation $W_L(\mathbf{x}) = L^{-1}W_1(L^{-1}\mathbf{x})$). When $r = \infty$, the proof is similar. We write for $A > 0$

$$\|(uv) *_L W_L\|_{L^\infty_{\mathrm{per}}(\Gamma_L)} \le \left\|(uv) *_L W_L\mathbb{1}_{|W_L|<A}\right\|_{L^\infty_{\mathrm{per}}(\Gamma_L)} + \left\|(uv) *_L W_L\mathbb{1}_{|W_L|\ge A}\right\|_{L^\infty_{\mathrm{per}}(\Gamma_L)}\,.$$

Then, using the inequality $|W_L(\mathbf{x})| \le C|\mathbf{x}|^{-1}$ (see the right side of (3.91)) and Young's inequality, we get, for any $p \in (1\,,2)$ and $p' \in (2\,,\infty)$ such that $p^{-1} + (p')^{-1} = 1$,

$$\|(uv) *_L W_L\|_{L^\infty_{\rm per}(\Gamma_L)} \leq A\,\|uv\|_{L^1_{\rm per}(\Gamma_L)} + C\,\big\||\cdot|^{-1}\big\|_{L^p(B(0,CA^{-1}))}\,\|uv\|_{L^{p'}_{\rm per}(\Gamma_L)}\,.$$

We conclude using Hölder's inequality and the Sobolev embeddings. Finally, we obtain (3.95) for any $r \in [1\,,\infty]$ by interpolation. □

As a direct consequence of Proposition 3.38 and Corollary 3.41, we have

Corollary 3.42. *The mean-field potential $V_L^{\rm MF}$ belongs to $L^p_{\rm per}(\Gamma_L)$ for any $p \in (1\,,2)$, that is*

$$\boxed{V_L^{\rm MF} \textit{ satisfies Assumption 1(i).}}$$

5.2 Reference model

In this section, we describe the mono-atomic Hartree model whose mean-field potential will give the reference potential satisfying Assumption 4 and appearing in Assumption 5. We introduce the energy functional

$$\mathcal{E}(u) \coloneqq \int_{\mathbb{R}^2} |\nabla u(\mathbf{x})|^2\,\mathrm{d}\mathbf{x} + \int_{\mathbb{R}^2}\left(-\frac{1}{|\mathbf{x}|} + V^{\rm pp}(\mathbf{x})\right)|u(\mathbf{x})|^2\,\mathrm{d}\mathbf{x} + \frac{1}{2}\iint_{\mathbb{R}^2\times\mathbb{R}^2} \frac{|u(\mathbf{x})|^2\,|u(\mathbf{y})|^2}{|\mathbf{x}-\mathbf{y}|}\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y}\,,$$

where $V^{\rm pp}$ is radial, compactly supported and belongs to $L^p(\mathbb{R}^2)$ for some $p > 1$. This functional is well-defined and continuous on $H^1(\mathbb{R}^2)$. For $\lambda \geq 0$, we consider the following minimization problem

$$I(\lambda) \coloneqq \inf\left\{\mathcal{E}(u)\;\middle|\; u \in H^1(\mathbb{R}^2) \quad\text{and}\quad \int_{\mathbb{R}^2}|u|^2 = \lambda\right\}\,, \tag{3.96}$$

which has been thoroughly studied in the literature, at least in its three-dimensional version [BBL81; LS77b; Lie81a; Lio81]. In particular, there exists $\lambda_{\max} \geq 1$ such that if $\lambda \leq \lambda_{\max}$ then all the minimizing sequences for (3.96) are precompact in $H^1(\mathbb{R}^2)$ and (3.96) admits a unique minimizer, up to a phase factor. In addition, the following *binding inequality* holds

$$\forall 0 \leq \mu < \lambda \leq \lambda_{\max}, \quad I(\lambda) < I(\mu)\,. \tag{3.97}$$

When $\lambda = 1$, we denote by v the minimizer of (3.96) which is the ground state of the self-adjoint operator

$$H^{\rm MF} \coloneqq -\Delta - |\cdot|^{-1} + V^{\rm pp} + |v|^2 * |\cdot|^{-1}\,,$$

defined on the domain $\mathcal{D}(H^{\rm MF}) = \big\{u \in H^1(\mathbb{R}^2)\;\big|\;(-\Delta - |\cdot|^{-1} + V^{\rm pp})u \in L^2(\mathbb{R}^2)\big\}$. In the following, we denote by

$$V^{\rm MF} \coloneqq -|\cdot|^{-1} + V^{\rm pp} + |v|^2 * |\cdot|^{-1}\,,$$

the mean-field potential which will play the role of reference potential, according to Section 2.2. By Weyl's theorem, the essential spectrum of $H^{\rm MF}$ is given by the half-line $[0\,,\infty)$. We choose $V^{\rm pp}$ such that $H^{\rm MF}$ admits at least one negative eigenvalue (such $V^{\rm pp}$ exists, see Appendix A.) and we denote by $-\mu < 0$ the lowest one. Our assumption that $-\mu < 0$ is equivalent to $\lambda_{\max} > 1$. By [Goe77], it is non degenerate, the phase of v can be chosen such that $v > 0$ everywhere and, since $H^{\rm MF}$ is invariant under rotations, v is radial.

Recall that $V^{\rm pp}$ is compactly supported and belongs to $L^p(\mathbb{R}^2)$ for some $p > 1$. Then, by following [Caz22] and using Proposition 3.10, one can show that:

(i) We have $v \in H^r(\mathbb{R}^2)$ for $r = p$ if $p < 2$ and any $r < 2$ otherwise.

(ii) There exists $C > 0$ such that: for all $\mathbf{x} \in \mathbb{R}^2$,

$$\frac{1}{C}\frac{e^{-\sqrt{\mu}|\mathbf{x}|}}{1+\sqrt{|\mathbf{x}|}} \leq v(\mathbf{x}) \leq C\frac{e^{-\sqrt{\mu}|\mathbf{x}|}}{1+\sqrt{|\mathbf{x}|}} \quad \text{and} \quad |\nabla v(\mathbf{x})| \leq C\frac{e^{-\sqrt{\mu}|\mathbf{x}|}}{1+\sqrt{|\mathbf{x}|}}.$$

(iii) We have $V^{\mathrm{MF}}(\mathbf{x}) \sim m_1/(4|\mathbf{x}|^3)$ with $m_1 = \int_{\mathbb{R}^2} |\mathbf{x}|^2 |v(\mathbf{x})|^2 \,\mathrm{d}\mathbf{x} > 0$ when $|\mathbf{x}| \to \infty$. In particular, we have $V^{\mathrm{MF}} \in L^p(\mathbb{R}^2)$.

(iv) The energy functional $\mathcal{E}$ satisfies the following *stability inequality*: there exists $C > 0$ such that, for all $u \in H^1(\mathbb{R}^2)$ with $\|u\|_{L^2(\mathbb{R}^2)} = 1$, we have

$$\mathcal{E}(u) \geq \mathcal{E}(v) + C \min_{\theta\in[0,2\pi)} \left\|e^{i\theta}u - v\right\|^2_{H^1(\mathbb{R}^2)}. \tag{3.98}$$

Remark 3.43. From this discussion, we see that

$$\boxed{V^{\mathrm{MF}} \text{ satisfies Assumption 4}.}$$

5.3 Convergence of the periodic model to the reference model

In this section, we show that the periodic rHF model (3.21) is given, to leading order, by a periodic superposition of translated versions of the mono-atomic Hartree potential V^{MF}, introduced in the previous section. In this direction, we use the concentration-compactness method [Lio84a; Lio84b]. Our arguments call on the binding inequality (3.97) and the stability inequality (3.98).

Let $\delta \in (0, 1/2)$ and $\chi \in \mathcal{C}_c^\infty(\mathbb{R}^2)$ be a localization function such that

$$0 \leq \chi \leq 1, \quad \chi \equiv 1 \quad \text{on} \quad B(0, \delta d_0/2) \quad \text{and} \quad \operatorname{supp}\chi \subset B(0, \delta d_0), \tag{3.99}$$

where d_0, defined in (3.7), is the nearest neighbor distance of the lattice $\mathscr{L}^{\mathbf{R}}$. Notice that δ is chosen in order to have

$$\operatorname{supp}\chi \subset \frac{1}{2}\Gamma.$$

For $L \geq 1$ and $\mathbf{r} \in \mathscr{L}^{\mathbf{R}}$, we set $\chi_{L,\mathbf{r}}(\mathbf{x}) := \chi(L^{-1}\mathbf{x} - \mathbf{r})$. Notice that the functions $\{\chi_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$ have pairwise disjoint support. We set $\rho_{L,\mathbf{r}} := |\chi_{L,\mathbf{r}}|^2 \rho_L$ for $\mathbf{r} \in \mathscr{L}^{\mathbf{R}}$. Because ρ_L is $\mathscr{L}_L$-invariant by Lemma 3.37, we have

$$\forall \mathbf{u} \in \mathscr{L}, \quad \forall \mathbf{r} \in \mathscr{L}^{\mathbf{R}}, \quad \rho_{L,\mathbf{u}+\mathbf{r}} = \rho_{L,\mathbf{r}}(\cdot - L\mathbf{u}).$$

The following proposition states that the periodic rHF model (3.21) is, in the vicinity of the singularities, well approached by the mono-atomic Hartree model (3.96) with $\lambda = 1$.

Proposition 3.44. *We have*

$$\lim_{L\to\infty} E_L = NI(1) \quad \textit{and} \quad \forall \mathbf{r} \in \mathbf{R}, \quad \lim_{L\to\infty} \left\|\sqrt{\rho_{L,\mathbf{r}}} - v(\cdot - L\mathbf{r})\right\|_{H^1(\mathbb{R}^2)} = 0, \tag{3.100}$$

where we recall that $I(1)$ is defined in (3.96) and v is the associated unique Hartree minimizer. In addition, we have

$$\left\|\rho_L *_L W_L - \sum_{\mathbf{r}\in\mathbf{R}} |v(\cdot - L\mathbf{r})|^2 * |\cdot|^{-1}\right\|_{L^\infty_{\mathrm{per}}(\Gamma_L)} \underset{L\to\infty}{\longrightarrow} 0. \tag{3.101}$$

We temporally admit the conclusions of Proposition 3.44. This allows us to write the

Proof of Theorem 3.7. We have that

$$\boxed{V_L^{\mathrm{MF}} \text{ satisfies Assumption 1\textit{(ii)} and Assumption 5},}$$

with V^{MF} as reference potential. Indeed, the validity of Assumption 1 *(ii)* (resp. Assumption 5 with V^{MF} as reference potential) results from Proposition 3.38 and (3.101) (resp. the left side of (3.91), (3.101) and the fact that V^{pp} is compactly supported). Consequently, Theorem 3.7 holds. □

Proof of Corollary 3.9. We only have to show that the Fermi level ϵ_L is exactly equal to the energy level of the cones. This amounts to show that the two lowest bands of the dispersion relation only overlap at the vertices of the first Brillouin zone.

By Theorem 3.7, we can apply Theorem 3.4 and Theorem 3.6. The first one provides, for all $\kappa \in \Gamma^*$

$$\frac{1}{|\theta_L|}\left(\mu_{+,L}\left(\frac{\kappa}{L}\right) - \mu_{-,L}\left(\frac{\mathbf{K}_\star + \kappa}{L}\right)\right) = 2\left|1 + e^{i\kappa\cdot\mathbf{u}_1} + e^{i\kappa\cdot\mathbf{u}_2}\right| + o(1)\ ,$$

where we recall that the map $\kappa \in \Gamma^* \mapsto \left|1 + e^{i\kappa\cdot\mathbf{u}_1} + e^{i\kappa\cdot\mathbf{u}_2}\right|$ is equal to zero if and only if $\kappa \in \{\mathbf{K}, \mathbf{K}'\}$ is a vertex of Γ^*. The second one gives

$$\frac{1}{|\theta_L|}\left(\mu_{+,L}\left(\frac{\mathbf{K}_\star + \kappa}{L}\right) - \mu_{-,L}\left(\frac{\mathbf{K}_\star + \kappa}{L}\right)\right) = \sqrt{3}\,|\kappa|\,(1 + E(\kappa))(1 + o(1)) \geq |\kappa|\ ,$$

for all $\mathbf{K}_\star \in \{\mathbf{K}, \mathbf{K}'\}$, for all $|\kappa|$ small enough and L large enough. Hence, the two bands only overlap at the vertices of the first Brillouin zone. This concludes the proof of Corollary 3.9. □

Proof of Proposition 3.44. We divide the proof into six steps. First, we show that E_L is bounded from above by NI plus a small correction. For this purpose, we insert a trial state into the periodic rHF energy functional $\mathcal{E}_L$ defined in (3.22). Afterwards, we show, using localization methods, that E_L is bounded from below by $\sum_{\mathbf{r}\in\mathbf{R}} I\left(\|\rho_{L,\mathbf{r}}\|_{L^1(\mathbb{R}^2)}\right)$ plus a small correction. In the third step, we show that $\|\rho_{L,\mathbf{r}}\|_{L^1(\mathbb{R}^2)}$ converges to 1 when $L \to \infty$ using the binding inequality (3.97). Then we prove that the kinetic energy $\underline{\mathrm{Tr}}_{\mathscr{L}_L}(-\Delta\gamma_L)$ is uniformly bounded with respect to $L \geq 1$. In the fifth step, we show the convergence (3.100) thanks to the stability inequality (3.98) and the previous steps. We show the convergence of the potential (3.101) in the sixth and final step.

First step. We claim the upper bound

$$E_L = \mathcal{E}_L(\gamma_L) \leq NI(1) + O\big(L^{-1}\big)\ . \tag{3.102}$$

To show this upper bound, we construct an appropriate trial state for the minimization problem (3.21). For $L \geq 1$ and $\mathbf{r} \in \mathscr{L}^{\mathbf{R}}$, we set

$$v_{L,\mathbf{r}} = \|\chi_{L,\mathbf{r}}v(\cdot - L\mathbf{r})\|^{-1}_{L^2(\mathbb{R}^2)}\,\chi_{L,\mathbf{r}}v(\cdot - L\mathbf{r})\,.$$

Notice that these functions have disjoint supports and that, by construction, the family $\{v_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$ forms an orthonormal system. In addition, in view of the exponential decay of u, we have

$$\forall \mathbf{r} \in \mathscr{L}^{\mathbf{R}},\quad \|v_{L,\mathbf{r}}(\cdot + L\mathbf{r}) - v\|_{H^1(\mathbb{R}^2)} = O\big(L^{-\infty}\big)\ . \tag{3.103}$$

We consider the trial state

$$\gamma_{\mathrm{trial}} = \sum_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}} |v_{L,\mathbf{r}}\rangle\,\langle v_{L,\mathbf{r}}|\ .$$

First, we show that γ_{trial} is indeed an admissible state. Because γ_{trial} is the orthogonal projection on the subspace spanned by the family $\{v_{L,\mathbf{r}}\}_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}}$, we immediately have $0 \leq \gamma_{\mathrm{trial}} \leq 1$ and $\gamma_{\mathrm{trial}} = (\gamma_{\mathrm{trial}})^*$. In addition, since $v_{L,\mathbf{r}}(\cdot - L\mathbf{u}) = v_{L,\mathbf{u}+\mathbf{r}}$ for all $\mathbf{u} \in \mathscr{L}$, γ_{trial} is invariant under the action of $\mathscr{L}_L$. Now, we write the Bloch-Floquet decomposition of γ_{trial}. For $\varphi = \fint_{\Gamma_L^*} \varphi_{\mathbf{k}}\,\mathrm{d}\mathbf{k} \in \mathcal{S}(\mathbb{R}^2)$, we claim that

$$\gamma_{\mathrm{trial}} = \fint^{\oplus}_{\Gamma_L^*} \sum_{\mathbf{r}\in\mathbf{R}} |\mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot)\rangle\,\langle \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot)|\,\mathrm{d}\mathbf{k}\,. \tag{3.104}$$

Indeed, we have

$$
\begin{aligned}
\gamma_{\mathrm{trial}}\varphi &= \sum_{\mathbf{r}\in\mathbf{R}}\sum_{\mathbf{u}\in\mathscr{L}} \langle v_{L,\mathbf{u}+\mathbf{r}},\varphi\rangle_{L^2(\mathbb{R}^2)}\, v_{L,\mathbf{u}+\mathbf{r}} \\
&= \sum_{\mathbf{r}\in\mathbf{R}}\sum_{\mathbf{u}\in\mathscr{L}} \fint_{\Gamma_L^*} \langle \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{u}+\mathbf{r}})(\mathbf{k},\cdot),\varphi_{\mathbf{k}}\rangle_{L^2(\Gamma_L)}\, v_{L,\mathbf{u}+\mathbf{r}}\,\mathrm{d}\mathbf{k} \\
&= \sum_{\mathbf{r}\in\mathbf{R}}\sum_{\mathbf{u}\in\mathscr{L}} \fint_{\Gamma_L^*} \langle \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot),\varphi_{\mathbf{k}}\rangle_{L^2(\Gamma_L)}\, e^{i\mathbf{k}\cdot L\mathbf{u}} v_{L,\mathbf{u}+\mathbf{r}}\,\mathrm{d}\mathbf{k} \\
&= \fint_{\Gamma_L^*} \sum_{\mathbf{r}\in\mathbf{R}} \langle \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot),\varphi_{\mathbf{k}}\rangle_{L^2(\Gamma_L)}\, \mathcal{U}_{\mathrm{BF}}(v_{L,\mathbf{r}})(\mathbf{k},\cdot)\,\mathrm{d}\mathbf{k}\,.
\end{aligned}
$$

From identity (3.104) and the fact that the functions $v_{L,\mathbf{r}}$ have pairwise disjoint support, we can compute the one-body density ρ_{trial} of γ_{trial} and its kinetic energy. We have

$$
\rho_{\mathrm{trial}}(\mathbf{x}) = \sum_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}} |v_{L,\mathbf{r}}(\mathbf{x})|^2 \quad \text{and} \quad \underline{\mathrm{Tr}}_{\mathscr{L}_L}(-\Delta\gamma_{\mathrm{trial}}) = \sum_{\mathbf{r}\in\mathbf{R}} \|\nabla v_{L,\mathbf{r}}\|^2_{L^2(\mathbb{R}^2)}\,.
$$

We deduce that $\gamma_{\mathrm{trial}}\in\mathcal{S}_{\mathrm{per},L}$ and that its periodic rHF energy is given by

$$
\begin{aligned}
\mathcal{E}_L(\gamma_{\mathrm{trial}}) = &\sum_{\mathbf{r}\in\mathbf{R}}\left(\|\nabla v_{L,\mathbf{r}}\|^2_{L^2(\mathbb{R}^2)} + \int_{\Gamma_L}\left(-W_L^{\mathbf{R}}(\mathbf{x})+V_L^{\mathbf{R}}(\mathbf{x})\right)\left(\sum_{\mathbf{u}\in\mathscr{L}}|v_{L,\mathbf{u}+\mathbf{r}}(\mathbf{x})|^2\right)\mathrm{d}\mathbf{x}\right) \\
&+\frac{1}{2}D_L(\rho_{\mathrm{trial}},\rho_{\mathrm{trial}}) \\
= &\sum_{\mathbf{r}\in\mathbf{R}}\left(\|\nabla v_{L,\mathbf{r}}\|^2_{L^2(\mathbb{R}^2)} + \int_{\mathbb{R}^2}\left(-W_L^{\mathbf{R}}(\mathbf{x})+V_L^{\mathbf{R}}(\mathbf{x})\right)|v_{L,\mathbf{r}}(\mathbf{x})|^2\,\mathrm{d}\mathbf{x}\right) \\
&+\frac{1}{2}\sum_{\mathbf{r},\mathbf{r}'\in\mathbf{R}}\iint_{\mathbb{R}^2\times\mathbb{R}^2}|v_{L,\mathbf{r}}(\mathbf{x})|^2\,|v_{L,\mathbf{r}'}(\mathbf{y})|^2\,W_L(\mathbf{x}-\mathbf{y})\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y}\,.
\end{aligned}
$$

Using that $\operatorname{supp} v_{L,\mathbf{r}}\subset\frac{1}{2}\Gamma_L+L\mathbf{r}$, the left side of (3.91) and the fact that $\operatorname{supp}V^{\mathrm{pp}}\subset B(0,R)$ for some fixed $R>0$, we have, for all $\mathbf{r}\in\mathbf{R}$ and L large enough,

$$
\begin{aligned}
\int_{\mathbb{R}^2} W_L(\mathbf{x}-L\mathbf{r})\,|v_{L,\mathbf{r}}(\mathbf{x})|^2\,\mathrm{d}\mathbf{x} &= \int_{\mathbb{R}^2}\frac{|v_{L,\mathbf{r}}(\mathbf{x})|^2}{|\mathbf{x}-L\mathbf{r}|}\,\mathrm{d}\mathbf{x}+O\big(L^{-1}\big)\,, \\
\int_{\mathbb{R}^2} V_L^{\mathbf{R}}(\mathbf{x})\,|v_{L,\mathbf{r}}(\mathbf{x})|^2\,\mathrm{d}\mathbf{x} &= \int_{\mathbb{R}^2} V^{\mathrm{pp}}(\mathbf{x}-L\mathbf{r})\,|v_{L,\mathbf{r}}(\mathbf{x})|^2\,\mathrm{d}\mathbf{x}\,.
\end{aligned}
$$

For $\mathbf{r}\neq\mathbf{r}'$, we use that $\mathrm{d}(\operatorname{supp} v_{L,\mathbf{r}},\mathscr{L}_L+L\mathbf{r}')\geq L(1-\delta)d_0$ and the left side of (3.91) to obtain

$$
\int_{\mathbb{R}^2} W_L(\mathbf{x}-L\mathbf{r}')\,|v_{L,\mathbf{r}}(\mathbf{x})|^2\,\mathrm{d}\mathbf{x} = \sum_{\mathbf{u}\in\mathscr{L}}\int_{\mathbb{R}^2}\frac{|v_{L,\mathbf{r}}(\mathbf{x})|^2}{|\mathbf{x}-L(\mathbf{u}+\mathbf{r}')|}\mathbb{1}_{\mathbf{x}-L(\mathbf{u}+\mathbf{r}')\in\Gamma_L}\,\mathrm{d}\mathbf{x}+O\big(L^{-1}\big)=O\big(L^{-1}\big)\,.
$$

Now, we turn our attention to the direct term. As $\operatorname{supp} v_{L,\mathbf{r}}\subset\frac{1}{2}\Gamma_L+L\mathbf{r}$ implies $\mathbf{x}-\mathbf{y}\in\Gamma_L$ for all $(\mathbf{x},\mathbf{y})\in(\operatorname{supp} v_{L,\mathbf{r}})^2$, we have

$$
\iint_{\mathbb{R}^2\times\mathbb{R}^2}|v_{L,\mathbf{r}}(\mathbf{x})|^2\,|v_{L,\mathbf{r}}(\mathbf{y})|^2\,W_L(\mathbf{x}-\mathbf{y})\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y} = \iint_{\mathbb{R}^2\times\mathbb{R}^2}\frac{|v_{L,\mathbf{r}}(\mathbf{x})|^2\,|v_{L,\mathbf{r}'}(\mathbf{y})|^2}{|\mathbf{x}-\mathbf{y}|}\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y}+O\big(L^{-1}\big)\,,
$$

by the left side of (3.91). For $\mathbf{r}\neq\mathbf{r}'$, we use the left side of (3.91) and the fact that (see (3.99))

$$
\forall\mathbf{u}\in\mathscr{L},\quad \mathrm{d}(\operatorname{supp} v_{L,\mathbf{u}+\mathbf{r}},\operatorname{supp} v_{L,\mathbf{r}'})\geq L(1-2\delta)d_0>0\,,
$$

to obtain

$$
\begin{aligned}
&\iint_{\mathbb{R}^2\times\mathbb{R}^2} |v_{L,\mathbf{r}}(\mathbf{x})|^2 \, |v_{L,\mathbf{r}}(\mathbf{y})|^2 \, W_L(\mathbf{x}-\mathbf{y}) \, \mathrm{d}\mathbf{x} \, \mathrm{d}\mathbf{y} \\
&\qquad = \sum_{\mathbf{u}\in\mathscr{L}} \iint_{\mathbb{R}^2\times\mathbb{R}^2} \frac{|v_{L,\mathbf{r}}(\mathbf{x})|^2 \, |v_{L,\mathbf{r}'}(\mathbf{y})|^2}{|\mathbf{x}-\mathbf{y}-L\mathbf{u}|} \mathbb{1}_{\mathbf{x}-\mathbf{y}-L\mathbf{u}\in\Gamma_L} \, \mathrm{d}\mathbf{x} \, \mathrm{d}\mathbf{y} + O\big(L^{-1}\big) \\
&\qquad = \sum_{\mathbf{u}\in\mathscr{L}} \iint_{\mathbb{R}^2\times\mathbb{R}^2} \frac{|v_{L,\mathbf{u}+\mathbf{r}}(\mathbf{x})|^2 \, |v_{L,\mathbf{r}'}(\mathbf{y})|^2}{|\mathbf{x}-\mathbf{y}|} \mathbb{1}_{\mathbf{x}-\mathbf{y}\in\Gamma_L} \, \mathrm{d}\mathbf{x} \, \mathrm{d}\mathbf{y} + O\big(L^{-1}\big) \\
&\qquad = O\big(L^{-1}\big) \, .
\end{aligned}
$$

Hence, we have shown

$$
\mathcal{E}_L(\gamma_L) \le \sum_{\mathbf{r}\in\mathbf{R}} \mathcal{E}(v_{L,\mathbf{r}}(\cdot + L\mathbf{r})) + O\big(L^{-1}\big) \, .
$$

Finally, from (3.103) and the continuity of the functional $u \in H^1(\mathbb{R}^2) \mapsto \mathcal{E}(u)$, we have that $\mathcal{E}(v_{L,\mathbf{r}}(\cdot + L\mathbf{r})) = \mathcal{E}(v) + O(L^{-\infty})$ for all $\mathbf{r} \in \mathbf{R}$. This concludes the proof of the upper bound (3.102).

Second step. We claim the lower bound

$$
E_L \ge \sum_{\mathbf{r}\in\mathbf{R}} \mathcal{E}\left(\sqrt{\rho_{L,\mathbf{r}}(\cdot + L\mathbf{r})}\right) + O\big(L^{-1}\big) \ge \sum_{\mathbf{r}\in\mathbf{R}} I\left(\|\rho_{L,\mathbf{r}}\|_{L^1(\mathbb{R}^2)}\right) + O\big(L^{-1}\big) \, , \tag{3.105}
$$

where $I(\lambda)$ is defined in (3.96). We consider the $\mathscr{L}_L$-periodic function $\chi_{L,\mathbf{0}}$ defined by

$$
\chi_{L,\mathbf{0}} = \sqrt{1 - \sum_{\mathbf{r}\in\mathscr{L}^{\mathbf{R}}} |\chi_{L,\mathbf{r}}|^2} \, .
$$

We can always choose χ such that $\chi_{L,\mathbf{0}}$ is smooth. Notice that $\|\nabla\chi_{L,\mathbf{0}}\|_{L^\infty_{\mathrm{per}}(\Gamma_L)}$ and $\|\nabla\chi_{L,\mathbf{r}}\|_{L^\infty(\mathbb{R}^2)}$ are $O\big(L^{-1}\big)$. Finally, we set $\rho_{L,\mathbf{0}} = |\chi_{L,\mathbf{0}}|^2 \rho_L$. We recall that we have also defined $\rho_{L,\mathbf{r}} = |\chi_{L,\mathbf{r}}|^2 \rho_L$. This provides a periodic partition of unity

$$
|\chi_{L,\mathbf{0}}|^2 + \sum_{\mathbf{r}\in\mathbf{R}} \sum_{\mathbf{u}\in\mathscr{L}} |\chi_{L,\mathbf{u}+\mathbf{r}}|^2 = 1 \, ,
$$

where the functions $\chi_{L,\mathbf{u}+\mathbf{r}}$ for all $\mathbf{u} \in \mathscr{L}$ and $\mathbf{r} \in \mathbf{R}$ have pairwise disjoint support. We recall the periodic Hoffmann-Ostenhof inequality [CLL01, Eq. (4.42)]

$$
\int_{\Gamma_L} |\nabla\sqrt{\rho_L}|^2 \le \underline{\mathrm{Tr}}_{\mathscr{L}_L}(-\Delta\gamma_L) \, ,
$$

which is a consequence of the convexity of the map $\rho \mapsto \int \left|\nabla\sqrt{\rho}\right|^2$ and the identity $\rho_\gamma = \fint_{\Gamma_L^*} \rho_{\gamma_{\mathbf{k}}} \, \mathrm{d}\mathbf{k}$. By the periodic IMS formula, we can write

$$
\begin{aligned}
\mathcal{E}_L(\gamma_L) &\ge \int_{\Gamma_L} |\nabla\sqrt{\rho_L}|^2 + \int_{\Gamma_L} \left(-W_L^{\mathbf{R}} + V_L^{\mathbf{R}}\right) \rho_L + \frac{1}{2} D_L(\rho_L, \rho_L) \\
&\ge \sum_{\mathbf{r}\in\mathbf{R}} \sum_{\mathbf{u}\in\mathscr{L}} \left(\int_{\Gamma_L} |\nabla\sqrt{\rho_{L,\mathbf{u}+\mathbf{r}}}|^2 - \int_{\Gamma_L} |\nabla\chi_{L,\mathbf{u}+\mathbf{r}}|^2 \rho_L \right) + \int_{\Gamma_L} |\nabla\sqrt{\rho_{L,\mathbf{0}}}|^2 \\
&\qquad\qquad - \int_{\Gamma_L} |\nabla\chi_{L,\mathbf{0}}|^2 \rho_L + \int_{\Gamma_L} \left(-W_L^{\mathbf{R}} + V_L^{\mathbf{R}}\right) \rho_L + \frac{1}{2} D_L(\rho_L, \rho_L) \, .
\end{aligned}
$$

Using that $\operatorname{supp} V^{\mathrm{pp}} \subset B(0,R)$ for a fixed $R>0$ and the $\mathscr{L}_L$-periodicity of W_L and ρ_L, we obtain

$$\begin{aligned}\mathcal{E}_L(\gamma_L) \geq & \sum_{\mathbf{r}\in\mathbf{R}} \left(\int_{\mathbb{R}^2} \left|\nabla\sqrt{\rho_{L,\mathbf{r}}}\right|^2 - \int_{\mathbb{R}^2} \left|\nabla\chi_{L,\mathbf{r}}\right|^2 \rho_L + \int_{\mathbb{R}^2} \left(-W_L^{\mathbf{R}} + V^{\mathrm{pp}}(\cdot - L\mathbf{r})\right)\rho_{L,\mathbf{r}} \right) \\ & + \frac{1}{2}\sum_{\mathbf{r},\mathbf{r}'\in\mathbf{R}} \iint_{\mathbb{R}^2\times\mathbb{R}^2} \rho_{L,\mathbf{r}}(\mathbf{x})\rho_{L,\mathbf{r}'}(\mathbf{y}) W_L(\mathbf{x}-\mathbf{y})\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y} \\ & + \int_{\Gamma_L} \left|\nabla\sqrt{\rho_{L,\mathbf{0}}}\right|^2 + D_L(\rho_L,\rho_{L,\mathbf{0}}) + \frac{1}{2}D_L(\rho_{L,\mathbf{0}},\rho_{L,\mathbf{0}}) - \int_{\Gamma_L} \left|\nabla\chi_{L,\mathbf{0}}\right|^2\rho_L - \int_{\Gamma_L} W_L^{\mathbf{R}}\rho_{L,\mathbf{0}}\,.\end{aligned}$$

The terms where $\nabla\chi_{L,\mathbf{0}}$ or $\nabla\chi_{L,\mathbf{r}}$ appears are $O(L^{-2})$. Because of the non-negativity of W_L, we can bound from below by zero both the terms of the second line corresponding to $\mathbf{r}\neq\mathbf{r}'$ and the three first terms of the third line. Also, using that $\mathrm{d}(\operatorname{supp}\rho_{L,\mathbf{0}}, \mathscr{L}_L^{\mathbf{R}}) \geq L\delta d_0/2$ and the right side of (3.91), we have

$$\int_{\Gamma_L} W_L^{\mathbf{R}}\rho_{L,\mathbf{0}} = \sum_{\mathbf{r}\in\mathbf{R}}\int_{\Gamma_L} W_L(\cdot - L\mathbf{r})\rho_{L,\mathbf{0}} = \sum_{\mathbf{r}\in\mathbf{R}}\int_{\Gamma_L} W_L\rho_{L,\mathbf{0}}(\cdot + L\mathbf{r}) = O(L^{-1})\;.$$

Reproducing the same arguments of the first step, we have, for all $\mathbf{r}\in\mathbf{R}$,

$$\int_{\mathbb{R}^2} W_L^{\mathbf{R}}\rho_{L,\mathbf{r}} = \int_{\mathbb{R}^2} \frac{\rho_{L,\mathbf{r}}(\mathbf{x})}{|\mathbf{x}-L\mathbf{r}|}\,\mathrm{d}\mathbf{x} + O(L^{-1}) \quad \text{and}$$

$$\iint_{\mathbb{R}^2\times\mathbb{R}^2} \rho_{L,\mathbf{r}}(\mathbf{x})\rho_{L,\mathbf{r}}(\mathbf{y})W_L(\mathbf{x}-\mathbf{y})\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y} = \iint_{\mathbb{R}^2\times\mathbb{R}^2} \frac{\rho_{L,\mathbf{r}}(\mathbf{x})\rho_{L,\mathbf{r}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y} + O(L^{-1})\;.$$

From all the previous estimates, we deduce that

$$\mathcal{E}_L(\gamma_L) \geq \sum_{\mathbf{r}\in\mathbf{R}} \mathcal{E}\left(\sqrt{\rho_{L,\mathbf{r}}(\cdot + L\mathbf{r})}\right) + O(L^{-1}) \geq \sum_{\mathbf{r}\in\mathbf{R}} I\left(\|\rho_{L,\mathbf{r}}\|_{L^1(\mathbb{R}^2)}\right) + O(L^{-1})\;.$$

Third step. We claim that

$$\forall \mathbf{r}\in\mathbf{R}, \quad \lim_{L\to\infty} \|\rho_{L,\mathbf{r}}\|_{L^1(\mathbb{R}^2)} = 1\,. \tag{3.106}$$

Since ρ_L is G_L-invariant (see the proof of Lemma 3.37), χ is radial and G_L acts transitively on $\mathscr{L}_L^{\mathbf{R}}$, we obtain that $\|\rho_{L,\mathbf{r}}\|_{L^1(\mathbb{R}^2)}$ is independent of $\mathbf{r}\in\mathbf{R}$. Consequently, since $\|\rho_L\|_{L^1_{\mathrm{per}}(\Gamma_L)} = N$, we must have $\|\rho_{L,\mathbf{r}}\|_{L^1(\mathbb{R}^2)} \leq 1$ for all $\mathbf{r}\in\mathbf{R}$. We combine the upper bound (3.102) and the lower bound (3.105) to get

$$NI(1) \geq NI\left(\|\rho_{L,\mathbf{r}}\|_{L^1(\mathbb{R}^2)}\right) + O(L^{-1})\;,$$

for any $\mathbf{r}\in\mathbf{R}$. Assume there exists a subsequence $L_n\to\infty$ such that $\|\rho_{L_n,\mathbf{r}}\|_{L^1(\mathbb{R}^2)} \to \lambda < 1$ as $n\to\infty$. Then, since $\lambda\mapsto I(\lambda)$ is continuous on $[0\,,1]$, we obtain $I(1)\geq I(\lambda)$. This contradicts the binding inequality (3.97) and we must have (3.106). In particular, $\sqrt{\rho_{L,\mathbf{r}}}$ is a minimizing sequence for $I(1)$.

Fourth step. We claim the uniform bound

$$\sup_{L\geq 1} \underline{\mathrm{Tr}}_{\mathscr{L}_L}(-\Delta\gamma_L) < \infty\,. \tag{3.107}$$

By Proposition 3.38, there exists $C>0$ such that for all $L\geq 1$ we have $\left|W_L^{\mathbf{R}}(\mathbf{x})\right| \leq C\,|\mathbf{x}-\mathbf{r}|^{-1}$ in a neighborhood of any $\mathbf{r}\in\mathbf{R}$. Then, by Proposition 3.12, Remark 3.13 and the periodic Hoffmann-

Ostenhof inequality, we have

$$\left|\int_{\Gamma_L} W_L^{\mathbf{R}}\rho_L\right| \leq \frac{1}{4}\left\|\nabla\sqrt{\rho_L}\right\|^2_{L^2_{\mathrm{per}}(\Gamma_L)} + C'\left\|\rho_L\right\|_{L^1_{\mathrm{per}}(\Gamma_L)} \leq \frac{1}{4}\underline{\mathrm{Tr}}_{\mathscr{L}_L}(-\Delta\gamma_L) + C'N\,,$$

for some constant $C' > 0$ independent of L. We have a similar inequality when $W_L^{\mathbf{R}}$ is replaced by $V_L^{\mathbf{R}}$ since $\left\|V_L^{\mathbf{R}}\right\|_{L^p_{\mathrm{per}}(\Gamma_L)}$ does not depend on L. In addition, because $W_L \geq 0$, the direct energy term $D_L(\rho_L,\rho_L)$ is non-negative. Thus, we have

$$E_L = \mathcal{E}_L(\gamma_L) = \underline{\mathrm{Tr}}_{\mathscr{L}_L}(-\Delta\gamma_L) + \int_{\Gamma_L}\left(-W_L^{\mathbf{R}} + V_L^{\mathbf{R}}\right)\rho_L + \frac{1}{2}D_L(\rho_L,\rho_L) \geq \frac{1}{2}\underline{\mathrm{Tr}}_{\mathscr{L}_L}(-\Delta\gamma_L) - C'N\,.$$

Moreover, by the first step, we also have $\sup_{L\geq 1} E_L < \infty$. The uniform bound (3.107) follows.

Fifth step. We prove the convergences (3.100). From the expression of the energy functional $\mathcal{E}$, we can write for $\mathbf{r}\in\mathbf{R}$

$$\mathcal{E}\left(\sqrt{\rho_{L,\mathbf{r}}(\cdot + L\mathbf{r})}\right) = \left\|\rho_{L,\mathbf{r}}\right\|_{L^1(\mathbb{R}^2)}\left[\mathcal{E}\left(\sqrt{\frac{\rho_{L,\mathbf{r}}(\cdot+L\mathbf{r})}{\left\|\rho_{L,\mathbf{r}}\right\|_{L^1(\mathbb{R}^2)}}}\right)\right.$$
$$\left. + \frac{\left\|\rho_{L,\mathbf{r}}\right\|_{L^1(\mathbb{R}^2)} - 1}{2}\iint_{\mathbb{R}^2\times\mathbb{R}^2}\frac{\rho_{L,\mathbf{r}}(\mathbf{x})\rho_{L,\mathbf{r}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y}\right].$$

By the Hardy-Littlewood-Sobolev inequality and the Sobolev embedding $L^{8/3}(\mathbb{R}^2)\subset H^1(\mathbb{R}^2)$, we have

$$\iint_{\mathbb{R}^2\times\mathbb{R}^2}\frac{\rho_{L,\mathbf{r}}(\mathbf{x})\rho_{L,\mathbf{r}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y} \lesssim \left\|\sqrt{\rho_{L,\mathbf{r}}}\right\|^4_{L^{8/3}(\mathbb{R}^2)} \leq \left\|\sqrt{\rho_{L,\mathbf{r}}}\right\|^4_{H^1(\mathbb{R}^2)}\,.$$

Using that $\operatorname{supp}\rho_{L,\mathbf{r}}\subset\frac{1}{2}\Gamma_L + L\mathbf{r}$ and periodic Hoffmann-Ostenhof's inequality, we deduce

$$\iint_{\mathbb{R}^2\times\mathbb{R}^2}\frac{\rho_{L,\mathbf{r}}(\mathbf{x})\rho_{L,\mathbf{r}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y} \lesssim \left\|\sqrt{\rho_L}\right\|^4_{H^1_{\mathrm{per}}(\Gamma_L)} \lesssim \left|\underline{\mathrm{Tr}}_{\mathscr{L}_L}(-\Delta\gamma_L)\right|^2\,.$$

Recall that $\left\|\rho_{L,\mathbf{r}}\right\|_{L^1(\mathbb{R}^2)} = 1 + o(1)$ from the third step. Using in addition the uniform estimate (3.107) from the fourth step, we obtain

$$\mathcal{E}\left(\sqrt{\rho_{L,\mathbf{r}}(\cdot+L\mathbf{r})}\right) = \left\|\rho_{L,\mathbf{r}}\right\|_{L^1(\mathbb{R}^2)}\mathcal{E}\left(\sqrt{\frac{\rho_{L,\mathbf{r}}(\cdot+L\mathbf{r})}{\left\|\rho_{L,\mathbf{r}}\right\|_{L^1(\mathbb{R}^2)}}}\right) + o(1)\,,$$

which, together with the stability inequality (3.98), leads to

$$\begin{aligned}E_L &\geq \sum_{\mathbf{r}\in\mathbf{R}}\left\|\rho_{L,\mathbf{r}}\right\|_{L^1(\mathbb{R}^2)}\mathcal{E}\left(\sqrt{\frac{\rho_{L,\mathbf{r}}(\cdot+L\mathbf{r})}{\left\|\rho_{L,\mathbf{r}}\right\|_{L^1(\mathbb{R}^2)}}}\right) + o(1)\\
&\geq NI(1) + C\sum_{\mathbf{r}\in\mathbf{R}}\min_{\theta\in[0,2\pi)}\left\|e^{i\theta}\sqrt{\rho_{L,\mathbf{r}}(\cdot+L\mathbf{r})} - \sqrt{\left\|\rho_{L,\mathbf{r}}\right\|_{L^1(\mathbb{R}^2)}}v\right\|^2_{H^1(\mathbb{R}^2)} + o(1)\\
&\geq NI(1) + C\sum_{\mathbf{r}\in\mathbf{R}}\min_{\theta\in[0,2\pi)}\left\|e^{i\theta}\sqrt{\rho_{L,\mathbf{r}}(\cdot+L\mathbf{r})} - v\right\|^2_{H^1(\mathbb{R}^2)} + o(1)\,.\end{aligned}$$

In the last inequality, to extract the $o(1)$ from the norm, we have used, as above, the inequality $\left\|\sqrt{\rho_{L,\mathbf{r}}}\right\|_{H^1(\mathbb{R}^2)} \leq \underline{\mathrm{Tr}}_{\mathscr{L}_L}(-\Delta\gamma_L)$ and the estimate (3.107) from the fourth step. Finally, since $\rho_{L,\mathbf{r}}$

and v are positive functions, the functional

$$\theta \in [0\,,2\pi) \mapsto \left\| e^{i\theta} \sqrt{\rho_{L,\mathbf{r}}(\cdot + L\mathbf{r})} - v \right\|^2_{H^1(\mathbb{R}^2)} \ ,$$

is minimal for $\theta = 0$. Now, recalling the upper bound (3.102), we write

$$NI(1) + O\big(L^{-1}\big) \geq E_L \geq NI(1) + \sum_{\mathbf{r}\in\mathbf{R}} \left\| \sqrt{\rho_{L,\mathbf{r}}(\cdot + L\mathbf{r})} - v \right\|^2_{H^1(\mathbb{R}^2)} + o(1) \ ,$$

which concludes the proof of (3.100).

Sixth step. We show estimate (3.101). Using the periodicity of W_L, we can write

$$\rho_L *_L W_L = \rho_{L,\mathbf{0}} *_L W_L + \sum_{\mathbf{r}\in\mathbf{R}} \left(\sum_{\mathbf{u}\in\mathscr{L}} \rho_{L,\mathbf{u}+\mathbf{r}} \right) *_L W_L = \rho_{L,\mathbf{0}} *_L W_L + \sum_{\mathbf{r}\in\mathbf{R}} \rho_{L,\mathbf{r}} * W_L \,.$$

Let $\mathbf{r} \in \mathbf{R}$ and $\mathbf{x} \in \Gamma_L$. Using the left side of (3.91) and the fact that $\operatorname{supp} \rho_{L,\mathbf{r}} \subset \frac{1}{2}\Gamma_L + L\mathbf{r}$, we have

$$(\rho_{L,\mathbf{r}} * (W_L - |\cdot|^{-1}))(\mathbf{x}) = \sum_{\mathbf{u}\in\mathscr{L}} \int_{\mathbb{R}^2} \frac{\rho_{L,\mathbf{r}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}-L\mathbf{u}|} \mathbb{1}_{\mathbf{x}-\mathbf{y}-L\mathbf{u}\in\Gamma_L} \, \mathrm{d}\mathbf{y} + O\big(L^{-1}\big) = O\big(L^{-1}\big) \ ,$$

where the O is uniform in $\mathbf{x} \in \Gamma_L$. We recall [Caz22, Lemma 3] which is the non-periodic version of Corollary 3.41: for all $r \in (2\,,\infty]$ and for all $(u,w) \in H^1(\mathbb{R}^2)$, we have

$$\left\| (uw) * |\cdot|^{-1} \right\|_{L^r(\mathbb{R}^2)} \lesssim \|u\|_{H^1(\mathbb{R}^2)} \|w\|_{H^1(\mathbb{R}^2)} \ .$$

Using this inequality, we have

$$\begin{aligned} &\left\| \left(\rho_{L,\mathbf{r}} - |v(\cdot - L\mathbf{r})|^2 \right) * |\cdot|^{-1} \right\|_{L^\infty(\mathbb{R}^2)} \\ &\qquad\qquad \lesssim \left(\sup_{L\geq 1} \left\| \sqrt{\rho_{L,\mathbf{r}}} \right\|_{H^1(\mathbb{R}^2)} + \|v\|_{H^1(\mathbb{R}^2)} \right) \left\| \sqrt{\rho_{L,\mathbf{r}}} - v(\cdot - L\mathbf{r}) \right\|_{H^1(\mathbb{R}^2)} \ . \end{aligned}$$

In the fifth step, we have shown that $\sup_{L\geq 1} \left\| \sqrt{\rho_{L,\mathbf{r}}} \right\|_{H^1(\mathbb{R}^2)} < \infty$. Thus, by (3.100), we obtain

$$\rho_L *_L W_L = \rho_{L,\mathbf{0}} *_L W_L + \sum_{\mathbf{r}\in\mathbf{R}} |v(\cdot - L\mathbf{r})|^2 * |\cdot|^{-1} + o(1) \ ,$$

where the o makes sense in $L^\infty(\Gamma_L)$. It remains to show that $\|\rho_{L,\mathbf{0}} *_L W_L\|_{L^\infty_{\mathrm{per}}(\Gamma_L)} = o(1)$ to conclude the proof of Proposition 3.44. By the third step and the normalization $\|\rho_L\|_{L^1_{\mathrm{per}}(\Gamma_L)} = N$, we see that

$$\|\rho_{L,\mathbf{0}}\|_{L^1_{\mathrm{per}}(\Gamma_L)} = o(1) \ . \tag{3.108}$$

In addition, from the identity $\nabla\sqrt{\rho_{L,\mathbf{0}}} = \chi_{L,\mathbf{0}} \nabla\sqrt{\rho_L} + \sqrt{\rho_L}\nabla\chi_{L,\mathbf{0}}$, the fact that $\|\nabla\chi_{L,\mathbf{0}}\|_{L^\infty_{\mathrm{per}}(\Gamma_L)} = O\big(L^{-1}\big)$, the periodic Hoffmann-Ostenhof inequality and the uniform bound (3.107), we have

$$\sup_{L\geq 1} \left\| \sqrt{\rho_{L,\mathbf{0}}} \right\|_{H^1_{\mathrm{per}}(\Gamma_L)} < \infty \,. \tag{3.109}$$

Let $q \in [1\,,\infty)$. From estimates (3.108) and (3.109), the Sobolev embedding $L^{2q}_{\mathrm{per}}(\Gamma_L) \subset H^1_{\mathrm{per}}(\Gamma_L)$ (where the continuity constant does not depend on L, see [Aub98, Theorem 2.28]) and an interpolation argument, we obtain

$$\forall q \in [1\,,\infty), \quad \|\rho_{L,\mathbf{0}}\|_{L^q_{\mathrm{per}}(\Gamma_L)} = o(1)\;. \tag{3.110}$$

From the proof of Corollary 3.41, we see that for any $q \in (2\,,\infty)$ we have

$$\|\rho_{L,\mathbf{0}} *_L W_L\|_{L^\infty_{\mathrm{per}}(\Gamma_L)} \lesssim \|\rho_{L,\mathbf{0}}\|_{L^1_{\mathrm{per}}(\Gamma_L)} + \|\rho_{L,\mathbf{0}}\|_{L^q_{\mathrm{per}}(\Gamma_L)}\;,$$

which is a $o(1)$ by (3.110). This concludes the proof of Proposition 3.44. □

Appendix A. Existence of pseudo-potentials which satisfy the ionization condition

Let $V \in L^\infty(\mathbb{R}^2)$ be a non-zero, *non-negative* almost everywhere, radial and compactly supported function. For all $\eta \in \mathbb{R}$, we consider the Hartree minimization problem

$$I_\eta := \inf\left\{\mathcal{E}_\eta(u)\;\middle|\; u \in H^1(\mathbb{R}^2) \quad \text{and} \quad \int_{\mathbb{R}^2} |u|^2 = 1\right\}, \tag{3.111}$$

where

$$\mathcal{E}_\eta(u) := \int_{\mathbb{R}^2} |\nabla u(\mathbf{x})|^2\,\mathrm{d}\mathbf{x} - \int_{\mathbb{R}^2}\left(\frac{1}{|\mathbf{x}|} + \eta V(\mathbf{x})\right)|u(\mathbf{x})|^2\,\mathrm{d}\mathbf{x} + \frac{1}{2}\iint_{\mathbb{R}^2\times\mathbb{R}^2} \frac{|u(\mathbf{x})|^2\,|u(\mathbf{y})|^2}{|\mathbf{x}-\mathbf{y}|}\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y}\,.$$

We recall that, following the arguments in [Lie81a, Section VII], one can show that the minimization problem (3.111) admits a unique minimizer, denoted by v_η, which is the eigenfunction of the lowest eigenvalue of the mean-field operator

$$H_\eta := -\Delta - \left(|\cdot|^{-1} + \eta V\right) + |v_\eta|^2 * |\cdot|^{-1}\,.$$

Our goal is to show that this eigenvalue is negative.

Proposition 3.45. *For $\eta \geq 0$ large enough, the mean-field operator H_η has at least one negative eigenvalue.*

Proof. Since the function $|\cdot|^{-1}$ belongs to the Kato class, we have the following Kato's inequality [Cyc+87]: there exists $C > 0$ such that, for all $u \in H^1(\mathbb{R}^2)$ with $\|u\|_{L^2(\mathbb{R}^2)} = 1$, we have

$$\int_{\mathbb{R}^2} \frac{|u(\mathbf{x})|^2}{|\mathbf{x}|}\,\mathrm{d}\mathbf{x} \leq \frac{1}{2}\int_{\mathbb{R}^2} |\nabla u(\mathbf{x})|^2\,\mathrm{d}\mathbf{x} + C\,.$$

The map $\eta \mapsto I_\eta$ being non-increasing since $V \geq 0$, we have

$$I_0 \geq I_\eta \geq \frac{1}{2}\int_{\mathbb{R}^2} |\nabla v_\eta(\mathbf{x})|^2\,\mathrm{d}\mathbf{x} - \eta\,\|V\|_{L^\infty(\mathbb{R}^2)} - C\,.$$

Hence, we have shown: $\int_{\mathbb{R}^2} |\nabla v_\eta|^2 \leq I_0 + C + \eta\,\|V\|_{L^\infty(\mathbb{R}^2)}$. From this, the Hardy-Rellich inequality [Yaf99] and the Cauchy-Schwarz inequality, we obtain

$$\left\||v_\eta|^2 * \frac{1}{|\cdot|}\right\|_{L^\infty(\mathbb{R}^2)} \leq C_{\mathrm{HR}}\int_{\mathbb{R}^2} |\mathbf{k}|\,|\hat{v}_\eta(\mathbf{k})|^2\,\mathrm{d}\mathbf{k} \leq C_{\mathrm{HR}}\,\|\nabla v_\eta\|_{L^2(\mathbb{R}^2)} \leq C'(1+\sqrt{\eta})\,,$$

where C_{HR} and C' are some positive constants. We recall that the ground state energy of operator $-\Delta - |\cdot|^{-1}$ acting on $L^2(\mathbb{R}^2)$ is equal to -1 and we denote by $\varphi(\mathbf{x}) = (2\pi)^{-1/2}e^{-|\mathbf{x}|}$ the associated normalized eigenfunction. Then, we have

$$\langle \varphi, H_\eta \varphi\rangle_{L^2(\mathbb{R}^2)} \leq -1 - \eta\int_{\mathbb{R}^2} V\,|\varphi|^2 + C'(1+\sqrt{\eta})\,,$$

which is negative for $\eta \geq 0$ large enough. This concludes the proof of Proposition 3.45. $\square$

Appendix B. Perturbation theory for singular potentials

Let $p \in (1, \infty]$. For all $L \geq 1$, we consider potentials V and $V_L \in L^p(\mathbb{R}^2) + L^\infty(\mathbb{R}^2)$. We denote by $H = -\Delta + V$ and $H_L = -\Delta + V_L$ the associated self-adjoint Schrödinger operators (given by the Friedrichs extension if $p \in (1, 2)$). We recall that the form domain $\mathcal{Q}(H)$ of the quadratic form associated with H is the Sobolev space $H^1(\mathbb{R}^2)$ [Cyc+87]. We also recall that if we endow the vector space $L^p(\mathbb{R}^2) + L^\infty(\mathbb{R}^2)$ with the norm

$$\|V\|_{L^p(\mathbb{R}^2)+L^\infty(\mathbb{R}^2)} := \inf\left\{ \|V_1\|_{L^p(\mathbb{R}^2)} + \|V_2\|_{L^\infty(\mathbb{R}^2)} \,\middle|\, V = V_1 + V_2,\ V_1 \in L^p(\mathbb{R}^2),\ V_2 \in L^\infty(\mathbb{R}^2) \right\},$$

then it defines a Banach space.

Proposition 3.46 (Singular perturbation theory)**.** *Assume that*

$$\lim_{L\to\infty} \|V - V_L\|_{L^p(\mathbb{R}^2)+L^\infty(\mathbb{R}^2)} = 0, \tag{3.112}$$

and that the discrete spectrum of H is non empty. Let $\lambda \in \sigma_{\mathrm{d}}(H)$. Then, for all $\epsilon > 0$ small enough there exists $\mathscr{C} \subset \mathbb{C}$ a contour enclosing λ such that $\mathrm{d}(\mathscr{C}, \sigma_{\mathrm{d}}(H_L)) \geq \epsilon$ for all L large enough. In this case, we denote by

$$P := \frac{-1}{2\pi i} \oint_{\mathscr{C}} \frac{\mathrm{d}z}{H - z} \quad \text{and} \quad P_L := \frac{-1}{2\pi i} \oint_{\mathscr{C}} \frac{\mathrm{d}z}{H_L - z}, \tag{3.113}$$

the spectral projections of H and H_L associated with the interval of real numbers enclosed by $\mathscr{C}$. Then, for all L large enough, the ranks of P_L and P are equal and there exists $C > 0$ such that

$$\left\| (-\Delta + 1)^{\min(\frac{p}{2}, 1)} (P - P_L) \right\| \leq C \|V - V_L\|_{L^p(\mathbb{R}^2)+L^\infty(\mathbb{R}^2)}. \tag{3.114}$$

In the case where λ is non degenerate, we can be more precise.

Corollary 3.47 (Non degenerate case)**.** *Assume (3.112) and that the discrete spectrum of H is non empty. Let $\lambda \in \sigma_{\mathrm{d}}(H)$ be non degenerate. Then, for L large enough, the contour $\mathscr{C}$, given by Proposition 3.46, encloses only one discrete eigenvalue λ_L of H_L and we have*

$$\lim_{L\to\infty} \lambda_L = \lambda.$$

In addition, if we denote by v (resp. v_L) a normalized eigenfunction associated with λ (resp. λ_L) then there exists a constant $C > 0$ such that

$$\min_{\theta\in[0,2\pi]} \left\| e^{i\theta} v - v_L \right\|_{H^{\min(p,2)}(\mathbb{R}^2)} \leq C \|V - V_L\|_{L^p(\mathbb{R}^2)+L^\infty(\mathbb{R}^2)}. \tag{3.115}$$

Proof of Corollary 3.47. Except estimate (3.115), all the statements derive from Proposition 3.46. Since $\lim_{L\to\infty} \|P - P_L\| = 0$, the quantity $\langle v, P_L v\rangle_{L^2(\mathbb{R}^2)}$ is non zero for all L large enough. Hence, we can define

$$v_L = \left[\langle v, P_L v\rangle_{L^2(\mathbb{R}^2)} \right]^{-1/2} P_L v,$$

which is, up to a phase constant, the normalized eigenfunction of H_L associated with λ_L. Then, estimate (3.115) comes from estimate (3.114) and the Taylor expansion

$$\langle v, P_L v\rangle_{L^2(\mathbb{R}^2)} = 1 + \langle v, (P_L - P)v\rangle_{L^2(\mathbb{R}^2)} = 1 + O\Big(\|V - V_L\|_{L^p(\mathbb{R}^2)+L^\infty(\mathbb{R}^2)} \Big),$$

which also results from estimate (3.114). $\square$

Before proving Proposition 3.46, we state a lemma which provides useful commutator estimates.

Lemma 3.48. *Let $\alpha \in [1-\frac{p}{2}, \frac{p}{2}) \cap [0,1)$. Let z in the resolvent set of H. Then, there exists a constant $C > 0$ such that*

$$\left\| \left[\frac{1}{H-z}, (-\Delta+1)^{\alpha} \right] \right\| \leq C\, \mathrm{d}(z, \sigma(H))^{-1}. \tag{3.116}$$

Proof of Lemma 3.48. To lighten the notations, we denote $K = -\Delta + 1$. If $\alpha = 0$ then the result is immediate. Let $\alpha \in (0,1)$. From the identity $\lambda^{\alpha} = \frac{\sin(\alpha\pi)}{\pi} \int_0^{\infty} \frac{\lambda}{\lambda+s} s^{\alpha-1}\, \mathrm{d}s$ satisfied for all $\lambda > 0$ and the spectral theorem, we have the following representation formula:

$$K^{\alpha} = \frac{\sin(\alpha\pi)}{\pi} \int_0^{\infty} \frac{K}{K+s} s^{\alpha-1}\, \mathrm{d}s. \tag{3.117}$$

Using identity (3.117), we can formally compute

$$\left[\frac{1}{H-z}, K^{\alpha} \right] = \frac{\sin(\alpha\pi)}{\pi} \int_0^{\infty} \frac{1}{K+s} \left[\frac{1}{H-z}, \Delta \right] \frac{1}{K+s} s^{\alpha}\, \mathrm{d}s.$$

Now, we show that this integral converges for all $\alpha \in [1-\frac{p}{2}, \beta) \cap (0,1)$ where $\beta := \max(\frac{p}{2}, 1)$. For $\nu > 0$ large enough, we can write, thanks to estimate (3.27) of Lemma 3.10,

$$\begin{aligned} &\left\| \frac{1}{K+s} \Delta \frac{1}{H-z} \frac{1}{K+s} \right\| \\ &\quad = \left\| \frac{1}{(K+s)^{\beta}} \frac{1}{(K+s)^{1-\beta}} \Delta \frac{1}{K^{\beta}} K^{\beta} \frac{1}{H+\nu} \frac{H+\nu}{H-z} \frac{1}{K+s} \right\| \lesssim \frac{1}{(1+s)^{1+\beta}} \frac{1}{\mathrm{d}(z, \sigma(H))}. \end{aligned}$$

Bounding in a similar way $\left\| \frac{1}{K+s} \frac{1}{H-z} \Delta \frac{1}{K+s} \right\|$, we have obtained

$$\sup_{z \in \mathscr{C}} \left\| \left[\frac{1}{H-z}, K^{\alpha} \right] \right\| \lesssim \frac{1}{\mathrm{d}(z, \sigma(H))} \int_0^{\infty} \frac{s^{\alpha}}{(1+s)^{1+\beta}}\, \mathrm{d}s \lesssim \frac{1}{\mathrm{d}(z, \sigma(H))}.$$

This concludes the proof of Lemma 3.48. □

Proof of Proposition 3.46. We denote $W_L := V - V_L$. First, notice that Lemma 3.11 implies the following statement: for all $\alpha \in [1-\frac{p}{2}, \frac{p}{2}] \cap [0,1]$, for all $\nu > 0$, we have

$$\left\| (-\Delta+\nu)^{-1+\alpha} W_L (-\Delta+\nu)^{-\alpha} \right\| \lesssim \nu^{\frac{d}{2p}-1} \left\| W_L \right\|_{L^p(\mathbb{R}^d)+L^{\infty}(\mathbb{R}^2)}. \tag{3.118}$$

We first show that W_L is form relatively bounded with respect to H on $L^2(\mathbb{R}^2)$. Let $p' \in [1,\infty)$ such that $1/p + 1/p' = 1$. For all $\psi \in \mathcal{Q}(H) = H^1(\mathbb{R}^2)$, we have, by the Cauchy-Schwarz inequality,

$$\begin{aligned} \left| \langle \psi, W_L \psi \rangle_{L^2(\mathbb{R}^2)} \right| &\leq \left\| \frac{1}{\sqrt{1-\Delta}} W_L \frac{1}{\sqrt{1-\Delta}} \right\| \left\| \sqrt{1-\Delta}\, \psi \right\|_{L^2(\mathbb{R}^2)}^2 \\ &\lesssim \left\| \frac{1}{\sqrt{1-\Delta}} W_L \frac{1}{\sqrt{1-\Delta}} \right\| \left(\left| \langle \psi, H\psi \rangle_{L^2(\mathbb{R}^2)} \right| + \|\psi\|_{L^2(\mathbb{R}^2)}^2 \right), \end{aligned}$$

Then [Kat95, Theorem VI-3.9], estimate (3.118) and the assumption (3.112) imply that for all $\epsilon > 0$ small enough there exists a contour $\mathscr{C} \subset \mathbb{C}$ enclosing λ such that $\mathrm{d}(\mathscr{C}, \sigma_{\mathrm{d}}(H_L)) \geq \epsilon$ for all L large enough. In particular, the definition (3.113) of the spectral projections makes sense. Using estimates (3.15) and (3.16) of [Kat95, Theorem VI-3.9], one can show that

$$\lim_{L\to\infty} \|P - P_L\| = 0.$$

If we choose L_0 large enough in order to have $\|P - P_L\| < 1/2$ for all $L \geq L_0$. Then, the statement about the rank of P_L follows from [Kat95, Theorem I-6.34] and the adjoining footnote. Using the resolvent formula, we have

$$P - P_L = \frac{-1}{2\pi i}\oint_{\mathscr{C}} \left(\frac{1}{H-z} - \frac{1}{H_L - z}\right) \mathrm{d}z = \frac{1}{2\pi i}\oint_{\mathscr{C}} \frac{1}{H-z} W_L \frac{1}{H_L-z}\,\mathrm{d}z\,.$$

Then, multiplying by $(-\Delta+1)^\alpha$ for $\alpha = \min(\frac{p}{2},1) \in (\frac{1}{2}\,,1]$, we can write

$$(-\Delta+1)^\alpha(P-P_L) = \frac{1}{2\pi i}\oint_{\mathscr{C}} (-\Delta+1)^\alpha \frac{1}{H+\nu}(-\Delta+\nu)^{1-\alpha} \tag{3.119}$$

$$\times\,(-\Delta+\nu)^{-1+\alpha}\frac{H+\nu}{H-z}(-\Delta+1)^{1-\alpha} \tag{3.120}$$

$$\times\,(-\Delta+1)^{-1+\alpha} W_L(-\Delta+1)^{-\alpha} \tag{3.121}$$

$$\times\,(-\Delta+1)^\alpha \frac{1}{H_L+\nu_L}(-\Delta+\nu_L)^{1-\alpha} \tag{3.122}$$

$$\times\,(-\Delta+\nu_L)^{-1+\alpha}\frac{H_L+\nu_L}{H_L-z}\,\mathrm{d}z\,. \tag{3.123}$$

We choose the constants $\nu, \nu_L > 0$ large enough in order to use estimate (3.27) of Proposition 3.10. Thus, we can bound the norm of (3.122) and of the right side of (3.119) as follows

$$\left\|(-\Delta+1)^\alpha \frac{1}{H+\nu}(-\Delta+\nu)^{1-\alpha}\right\| \leq 2 \quad \text{and} \quad \left\|(-\Delta+1)^\alpha \frac{1}{H_L+\nu_L}(-\Delta+\nu_L)^{1-\alpha}\right\| \leq 2\,.$$

Notice that thanks to the proof of Proposition 3.10, we can always choose ν_L bounded by a polynomials in $\|V_L\|_{L^p(\mathbb{R}^2)+L^\infty(\mathbb{R}^2)}$. Then, by assumption (3.112), ν_L is be bounded for all $L \geq L_0$ for some L_0 large enough. In particular, this implies

$$\sup_{L\geq L_0}\sup_{z\in\mathscr{C}}\left\|(-\Delta+\nu_L)^{-1+\alpha}\frac{H_L+\nu_L}{H_L-z}\right\| < \infty\,.$$

The norm of (3.121) is estimated thanks to (3.118)

$$\left\|(-\Delta+1)^{-1+\alpha}W_L(-\Delta+1)^{-\alpha}\right\| \lesssim \|W_L\|_{L^p(\mathbb{R}^2)+L^\infty(\mathbb{R}^2)}\,.$$

Finally, to estimate the norm of (3.120), we write

$$\begin{aligned}\left\|\frac{1}{(-\Delta+\nu)^{1-\alpha}}\frac{H+\nu}{H-z}(-\Delta+1)^{1-\alpha}\right\| &= \left\|\frac{1}{(-\Delta+\nu)^{1-\alpha}}\left(1+\frac{\nu+z}{H-z}\right)(-\Delta+1)^{1-\alpha}\right\| \\ &\lesssim 1 + \left\|\left[\frac{1}{H-z}, (-\Delta+1)^{1-\alpha}\right]\right\|\,,\end{aligned}$$

which is uniformly bounded on $\mathscr{C}$ thanks to Lemma 3.48. Gathering all these previous estimates shows (3.114). This concludes the proof of Proposition 3.46. □

Chapter 4

The weak constrast regime

Abstract

In this chapter, we consider the reduced Hartree-Fock theory of graphene in the weak contrast regime, that is, when the distance between the nuclei is small. We show that the mean-field operator admits Dirac points at the vertices of the first Brillouin zone. However, these Dirac points *do not* separate and the Fermi level *do not* coincide with the energy of the cones, the contrary being expected in real graphene. Consequently, the model behaves differently in this regime compared to the dissociation regime studied in Chapter 3.

Contents

1 Introduction

In this chapter, we consider the reduced Hartree-Fock (rHF) model where the underlying lattice is the honeycomb lattice $\mathscr{L}_L^H = L\mathscr{L}^H$ with length parameter $L > 0$. This model and the honeycomb lattice are respectively introduced in Section 2.3 and Section 4.1.

In Chapter 3, we have mainly considered the dissociation regime, that is when $L \to \infty$. In this chapter, we address the other regime $L \to 0$ in which the following three main features appear:

(i) The dispersion relation presents conical singularities at the vertices of the first Brillouin zone as it does for $L \gg 1$;

(ii) These cones are *not separating* in the sense that the corresponding bands overlap somewhere other than the vertices of the first Brillouin zone;

(iii) The Fermi level is *not* given by the energy of the cones. In particular, the model does not display Dirac fermions, as expected in real graphene.

These results raise the question of what is the critical L for which the Fermi level is correct, and whether this is the case for the physical L of graphene, in the rHF theory.

In the first section, we state a theorem which extend some conclusions of [FW12, Theorem 5.1]. In addition, a continuity argument shows that the cones cannot be separating when L is small. In the second section, we apply this result to the rHF model on $\mathscr{L}_L^H$.

2 Dirac points in the weak contrast regime

First, we briefly recall the definitions of the honeycomb lattice and we refer to Section 4.1 for more details. The triangular lattice $\mathscr{L}$ is defined by

$$\mathscr{L} := \mathbb{Z}\mathbf{u}_1 \oplus \mathbb{Z}\mathbf{u}_2 \quad \text{where} \quad \mathbf{u}_1 = \begin{pmatrix} \sqrt{3}/2 \\ 1/2 \end{pmatrix} \quad \text{and} \quad \mathbf{u}_2 = \begin{pmatrix} \sqrt{3}/2 \\ -1/2 \end{pmatrix}.$$

We denote by Γ its Wigner-Seitz cell, which is a regular hexagon, by $\mathscr{L}^*$ its reciprocal lattice and by Γ^* its first Brillouin zone, which is also a regular hexagon. A generic vertex of Γ is denoted by $\mathbf{K}_\star \in \{\mathbf{K}, \mathbf{K}'\}$. The honeycomb lattice is defined as

$$\mathscr{L}^H := (\mathscr{L} + \mathbf{a}) \cup (\mathscr{L} + \mathbf{b}) \quad \text{where} \quad \mathbf{a} = \frac{1}{2\sqrt{3}} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \mathbf{b} = -\mathbf{a}. \tag{4.1}$$

In this chapter, we mainly consider objects which are invariant with respect to the shifts of $\mathscr{L}$. Hence, whenever there is no confusion on the underlying lattice, we drop the Γ from the function spaces notation, for instance writing L^p_{per} instead of $L^p_{\text{per}}(\Gamma)$.

2.1 Preliminary definitions

We consider a general Schrödinger operator

$$H = -\Delta + V,$$

where $V \in L^p_{\text{per}}$ is $\mathscr{L}$-periodic, locally p-integrable for some $p > 1$ and real-valued. We recall that by the Bloch-Floquet theory [RS78; Kuc16; BS99], we can decompose H in fibers as follows

$$H = \fint_{\Gamma^*}^{\oplus} H(\mathbf{k})\, \mathrm{d}\mathbf{k},$$

where for almost every $\mathbf{k} \in \Gamma^*$, the operator $H(\mathbf{k}) = -\Delta_{\mathbf{k}} + V$ is the restriction of H on the space $L^2_{\mathbf{k}}$ of Bloch functions with quasi-momentum $\mathbf{k}$. The *Bloch variety* or dispersion relation of H is the union of the graph of the band functions

$$B_H := \{(\mathbf{k}, \lambda_n(\mathbf{k})) \mid \mathbf{k} \in \Gamma^* \quad \text{and} \quad n \in \mathbb{N}\},$$

where $\lambda_1(\mathbf{k}) \le \lambda_2(\mathbf{k}) \le \dots$ are the ordered eigenvalues of $H(\mathbf{k})$.

Symmetries. If $\mathcal{S}$ be an unitary or anti-unitary operator on $L^2(\mathbb{R}^2)$ such that $\mathcal{S}\mathcal{D}(H) \subset \mathcal{D}(H)$ then we say that H is $\mathcal{S}$-*invariant* if the commutator $[H, \mathcal{S}]$ vanishes. We say that H is $\mathscr{L}$-invariant if H is $\tau_{\mathbf{u}}$-invariant for all $\mathbf{u} \in \mathscr{L}$, where $\tau_{\mathbf{u}}$ denotes the translation by $\mathbf{u}$ operator. The $\mathscr{L}$-invariance of the operator H implies that the Bloch variety of H is $\mathscr{L}^*$-invariant. If H has other symmetries this may produce additional topological constraints on B_H.

Because we are interested in operators with the symmetries of graphene, we now describe the symmetry group $G \subset E_2(\mathbb{R})$ of the honeycomb lattice $\mathscr{L}^H$ where $E_2(\mathbb{R})$ is Euclidean group of $\mathbb{R}^2$. We recall that G belongs to the **p6m** wallpaper group class [Arm88]. The point group of G is equal to D_6, the dihedral group of order 6, and leaves invariant both the Wigner-Seitz cell and the first Brillouin zone. It is generated by the following transformations

(i) Rotation $\mathcal{R}$ by $2\pi/3$ in the counter-clockwise direction

$$\mathcal{R}\colon \psi \in L^2(\mathbb{R}^2) \longmapsto \left[\mathbf{x} \in \mathbb{R}^2 \longmapsto \psi(M_{\mathcal{R}}^{-1}\mathbf{x})\right] , \tag{4.2}$$

where $M_{\mathcal{R}} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$ is the rotation matrix by $2\pi/3$.

(ii) Inversion $\mathcal{P}$ or *parity inversion*

$$\mathcal{P}\colon \psi \in L^2(\mathbb{R}^2) \longmapsto \left[\mathbf{x} \in \mathbb{R}^2 \longmapsto \psi(-\mathbf{x})\right] .$$

Another transformation plays an important role. This is the complex conjugation $\mathcal{C}$ or *time reversal* symmetry, which is an anti-unitary operator defined by

$$\mathcal{C}\colon \psi \in L^2(\mathbb{R}^2) \longmapsto \left[\mathbf{x} \in \mathbb{R}^2 \longmapsto \overline{\psi(\mathbf{x})}\right] .$$

Honeycomb lattice potentials. In the sequel, we assume that V is a honeycomb lattice potential in the following sense:

Definition 4.1 (Honeycomb lattice potentials)**.** We say that a potential $V \in L^1_{\mathrm{loc}}(\mathbb{R}^2)$ is a *honeycomb lattice potential* if there exists $\mathbf{x}_0 \in \mathbb{R}^2$ such that $\tilde{V} = V(\cdot - \mathbf{x}_0)$ has the following properties:

(i) $\tilde{V}$ is $\mathscr{L}$-invariant, i.e. $\tilde{V}(\cdot - \mathbf{u}) = \tilde{V}$ for all $\mathbf{u} \in \mathscr{L}$;
(ii) $\tilde{V}$ is real-valued, i.e. $\mathcal{C}\tilde{V} = \tilde{V}$;
(iii) $\tilde{V}$ is even or inversion-symmetric, i.e. $\mathcal{P}\tilde{V} = \tilde{V}$;
(iv) $\tilde{V}$ is invariant under rotation by $2\pi/3$, i.e. $\mathcal{R}\tilde{V} = \tilde{V}$.

This definition is almost the same as the one appearing in the work of Fefferman and Weinstein [FW12] (see also [BC18]) except that we allow for more singular potentials.

Example. A honeycomb lattice potential can be constructed as an exact periodic superposition of potential wells. Let m be smooth, radial and rapidly decreasing function which represents an atomic potential. Then, the potentials

$$V_1 = \sum_{\mathbf{u} \in \mathscr{L}} m(\cdot - \mathbf{u}) \quad \text{and} \quad V_2 = \sum_{\mathbf{u} \in \mathscr{L}^H} m(\cdot - \mathbf{u}) ,$$

are honeycomb lattice potentials in the sense of Definition 4.1, with respectively $\mathbf{x}_0 = 0$ and $\mathbf{x}_0 = \mathbf{a}$.

The reference [BC18, Lemma 2.1] details the constraints that each additional symmetries impose on the Bloch variety:

(i) Invariance by parity or time-reversal implies that the dispersion relation is invariant with respect to the inversion $\mathbf{k} \mapsto -\mathbf{k}$;
(ii) Rotational invariance (about any point) implies that the dispersion relation is invariant under both rotation by $2\pi/3$ around the origin $\mathbf{k} \mapsto M_{\mathcal{R}}\mathbf{k}$ and rotation by $2\pi/3$ around any vertex $\mathbf{K}_\star \in \{\mathbf{K}, \mathbf{K}'\}$ of the Brillouin zone $\mathbf{k} \mapsto M_{\mathcal{R}}(\mathbf{k} - \mathbf{K}_\star) + \mathbf{K}_\star$.

From these two facts, we deduce that the dispersion relation of $H = -\Delta + V$ is the same around any vertex $\mathbf{K}_\star \in \{\mathbf{K}, \mathbf{K}'\}$ of the Brillouin zone. Also, the dispersion relation of H presents an additional symmetry (namely, rotation by $2\pi/3$) at the vertices $\mathbf{K}_\star$. The Hilbert–Weyl theory of invariant functions [GSS88, Chapter XII] implies that, in the vicinity of $\mathbf{K}_\star$, the dispersion relation is restricted to be a circular cone (which could be degenerate) plus higher order terms. Consequently, it is convenient to study the restriction of $H(\mathbf{K}_\star)$ to the eigenspaces of the operator $\mathcal{R}$. This motivates the following definitions

$$L^2_{\mathbf{K}_\star,j} \coloneqq \left\{\varphi \in L^2_{\mathbf{K}_\star} \;\middle|\; \mathcal{R}\varphi = \tau^j \varphi\right\}, \quad j \in \{0,1,2\}\,, \tag{4.3}$$

where $\tau = \exp(\frac{2\pi i}{3})$. Since $\mathcal{R}$ is unitary, theses spaces are pairwise orthogonal. We notice that $L^2_{\mathbf{K}_\star,1}$ and $L^2_{\mathbf{K}_\star,2}$ are linked by the anti-unitary operator $\mathcal{PC}$ through the relation

$$L^2_{\mathbf{K}_\star,2} = \mathcal{PC}\left(L^2_{\mathbf{K}_\star,1}\right)\,.$$

Dirac points. We introduce the formal definition of a Dirac point, following [FW12]. We recall that $\lambda_0(\mathbf{k}) \le \lambda_1(\mathbf{k}) \le \dots$ denote the ordered eigenvalues of $H(\mathbf{k})$.

Definition 4.2 (Dirac point)**.** We say that H presents a *Dirac point* at a vertex $\mathbf{K}_\star \in \{\mathbf{K}, \mathbf{K}'\}$ of the first Brillouin zone Γ^* if the following holds: there exists $m \in \mathbb{N}$, a real number $\lambda_\star$ and positive numbers $\nu, \delta > 0$ such that:

(i) $\lambda_\star$ is a degenerate eigenvalue of $H_{\mathbf{K}_\star}$;

(ii) $\dim \operatorname{Ker}(H_{\mathbf{K}_\star} - \lambda_\star) = 2$ and $\operatorname{Ker}(H_{\mathbf{K}_\star} - \lambda_\star) = \operatorname{span}(\Phi_1, \Phi_2)$ where $\Phi_1 \in L^2_{\mathbf{K}_\star,1}$ and $\Phi_2 = \mathcal{PC}(\Phi_1) \in L^2_{\mathbf{K}_\star,2}$;

(iii) There exists Lipschitz functions $\mathbf{k} \mapsto \lambda_\pm(\mathbf{k})$ such that

$$\lambda_m(\mathbf{k}) = \lambda_-(\mathbf{k})\,, \quad \lambda_{m+1}(\mathbf{k}) = \lambda_+(\mathbf{k})\,,$$

and functions $\mathbf{k} \mapsto E_\pm(\mathbf{k})$, defined for $|\mathbf{k} - \mathbf{K}_\star| \le \delta$, such that

$$\lambda_\pm(\mathbf{k}) = \lambda_\star \pm \nu\,|\mathbf{k} - \mathbf{K}_\star|\,(1 + E_\pm(\mathbf{k}))\,,$$

with $|E_\pm(\mathbf{k})| \le C\,|\mathbf{k} - \mathbf{K}_\star|$ for some constant $C > 0$.

Hence, if H presents Dirac points then there exists non-degenerate conical singularities between two successive dispersion bands of its Bloch variety.

Definition 4.3 (Separating Dirac point)**.** Assume that H presents a Dirac point with energy level $\lambda_\star$ between the n^{th} and the $(n+1)^{\text{th}}$ bands. We denote by $\lambda_0(\mathbf{k}) \le \lambda_1(\mathbf{k}) \le \dots$ the discrete spectrum of the Bloch operator $H(\mathbf{k})$ acting on $L^2_{\mathbf{k}}$. We say the Dirac point is *separating* if for all $m \in \{n, n+1\}$

$$\lambda_m(\mathbf{k}) = \lambda_\star \implies \mathbf{k} \text{ is a vertex of the Brillouin zone } \Gamma^*\,.$$

In others words, a Dirac point $(\mathbf{K}_\star, \lambda_\star)$ of H is separating if and only if the dispersion relation of H crosses the plane $\mathbf{k} = \lambda_\star$ only at the vertices of Γ^*. This is the case for graphene at the Fermi level [Coo+12, Section 5.4].

2.2 General result

Let $p \in (1\,,\infty]$. For all $L \in (-1\,,1)$, we consider $V_L \in L^p_{\text{per}}$ and we denote by

$$\boxed{H_L = -\Delta + LV_L\,,} \tag{4.4}$$

the periodic Schrödinger operator associated with the potential LV_L.

Theorem 4.4 (Dirac points in the weak contrast regime)**.** *Assume that, for all $L \in (-1\,,1)$, the potential V_L is a honeycomb lattice potential in the sense of Definition 4.2 and that the map $L \mapsto V_L \in L^p_{\text{per}}$ is continuous at 0. If the condition*

$$c_{1,1} \coloneqq \widehat{V}_0(\mathbf{v}_1 + \mathbf{v}_2) \neq 0\,, \tag{4.5}$$

is satisfied then there exists $L_0 > 0$ such that for all $L \in (-L_0\,, L_0) \setminus \{0\}$ the periodic Schrödinger operator H_L defined in (4.4) admits Dirac points between the first and second bands if $Lc_{1,1} > 0$ and between the second and third bands if $Lc_{1,1} < 0$. In addition, these Dirac points are not *separating.*

The proof of this theorem (except for the statement about non separating Dirac points) is mainly an adaptation of the proof of [FW12, Theorem 5.1] from Fefferman and Weinstein (see also [Gru09; BC18]). There, the authors consider the periodic Schrödinger operator $H_\epsilon = -\Delta + \epsilon V$ where V is a honeycomb lattice potential. They show that H_ϵ admits Dirac point for all $\epsilon \in \mathbb{R}$ except in a countable and closed set. In the weak contrast regime, that is for $|\epsilon|$ small enough, their argument uses the Schur complement and perturbation theory. Then, they employ techniques from complex analysis in order to extend their conclusions beyond a neighborhood of 0.

In Theorem 4.4, there are two main differences in the assumptions compared to [FW12, Theorem 5.1]: first the potential may be more singular and second it may depend on the amplitude L. However, the proof for small L is very similar to [FW12] if we assume that $L \mapsto V_L \in L^p_{\rm per}$ is continuous at 0. Because we lack analyticity, we cannot extend the conclusions to large values of L.

2.3 Application to rHF model

In this section, we consider the periodic rHF model for graphene with length parameter $L > 0$. This model is introduced in Section 2.3.

For simplicity, we assume there is no pseudo-potential, that is $V^{\rm pp} = 0$. Hence, the periodic potential generated by the lattice $\mathscr{L}_L^H$ is given by

$$-W_L^H = -W_L(\cdot - L\mathbf{a}) - W_L(\cdot - L\mathbf{b})\,,$$

where the periodic three-dimensional Coulomb kernel W_L is defined in Section 5.1. The periodic rHF model on $\mathscr{L}_L^H$ consists in solving the minimization problem

$$E_L = \inf\left\{\mathcal{E}_L(\gamma)\;\middle|\;\gamma \in \mathcal{S}_{{\rm per},L} \quad \text{and} \quad \underline{\rm Tr}_{\mathscr{L}_L}(\gamma) = 2/q\right\}, \tag{4.6}$$

where the set of admissible states $\mathcal{S}_{{\rm per},L}$ and the rHF energy functional $\mathcal{E}_L$ are defined in Section 2.3 and where $q \in \mathbb{N}^*$ denotes the number of spin states.

We now rescale everything to work on the fixed lattice $\mathscr{L}^H$. To simplify the notations, we drop the L subscript whenever $L = 1$, writing for instance $D(\rho,\rho)$ instead of $D_1(\rho,\rho)$. We introduce the dilatation by L defined for all $\varphi \in L^1_{\rm loc}(\mathbb{R}^2)$ by

$$\forall \mathbf{x} \in \mathbb{R}^2, \quad d_L\varphi(\mathbf{x}) = L\varphi(L\mathbf{x})\,.$$

The transformation d_L is an isometry of $L^2(\mathbb{R}^2)$ and satisfies the following properties:

(i) We have $d_L^{-1} = d_L^* = d_{1/L}$;

(ii) The map $\gamma \in \mathcal{S}_{\rm per,L} \mapsto d_L\gamma d_L^* \in \mathcal{S}_{\rm per}$ is a bijection;

(iii) For all $\gamma \in \mathcal{S}_{\rm per,L}$ we have $\underline{\rm Tr}_{\mathscr{L}_L}(\gamma) = \underline{\rm Tr}_{\mathscr{L}}(d_L\gamma d_L^*)$;

(iv) If $\gamma \in \mathcal{S}_{\rm per,L}$ admits the decomposition in fibers

$$\gamma = \fint_{\Gamma^*}^{\oplus} \sum_{n\geq 0} |u_n(\mathbf{k},\cdot)\rangle\,\langle u_n(\mathbf{k},\cdot)|\,{\rm d}\mathbf{k}\,,$$

where for (almost) all $\mathbf{k} \in \Gamma_L^*$ the family $\{u_n(\mathbf{k},\cdot)\}_{n\geq 0}$ forms an orthonormal basis of $L^2_{\mathbf{k}}(\Gamma_L)$ then $d_L\gamma d_L^* \in \mathcal{S}_{\rm per}$ admits the decomposition

$$d_L\gamma d_L^* = \fint_{\Gamma_L^*}^{\oplus} \sum_{n\geq 0} |d_L u_n(\mathbf{k}/L,\cdot)\rangle\,\langle d_L u_n(\mathbf{k}/L,\cdot)|\,{\rm d}\mathbf{k}\,.$$

Notice that the family $\{d_L u_n(\mathbf{k}/L,\cdot)\}_{n\geq 0}$ is indeed an orthonormal basis of $L^2_{\mathbf{k}}(\Gamma)$ for all $\mathbf{k} \in \Gamma^*$;

(v) For all $\gamma \in \mathcal{S}_{\rm per}$ we have

$$\mathcal{E}_L(d_L^*\gamma d_L) = L^{-2}\left[\underline{\rm Tr}_{\mathscr{L}}(-\Delta\gamma) + L\left(-\int_\Gamma W^H\rho_\gamma + \frac{q}{2}D(\rho_\gamma,\rho_\gamma)\right)\right] .$$

As a consequence, we can reformulate the minimization problem (4.6) as follows:

$$E_L = L^{-2}F_L \quad \text{where} \quad F_L := \inf\left\{\mathcal{F}_L(\gamma) \mid \gamma \in \mathcal{S}_{\rm per} \quad \text{and} \quad \underline{\rm Tr}_{\mathscr{L}}(\gamma) = 2/q\right\} , \tag{4.7}$$

where the new energy functional $\mathcal{F}_L$ is defined for all $\gamma \in \mathcal{S}_{\rm per}$ by

$$\mathcal{F}_L(\gamma) := \underline{\rm Tr}_{\mathscr{L}}(-\Delta\gamma) + L\left(-\int_\Gamma W^H\rho_\gamma + \frac{q}{2}D(\rho_\gamma,\rho_\gamma)\right) .$$

We thus obtain a small coupling constant L in front of the Coulomb terms, similarly as in the linear case studied in [FW12]. We can adapt the proofs of [CDL08, Theorem 1] and [CLL01, Theorem 2.1] to show that (4.7) is well-posed and admits a unique minimizer $\gamma_L \in \mathcal{S}_{\rm per}$. If we denote by $\rho_L(\mathbf{x}) = \gamma_L(\mathbf{x},\mathbf{x})$ its one-body density then γ_L is the unique solution of the mean-field equation

$$\gamma_L = \mathbb{1}_{(-\infty,\epsilon_L]}(H_L) .$$

where $\epsilon_L \in \mathbb{R}$ is the Fermi level and where the mean-field hamiltonian is given by

$$\boxed{H_L = -\Delta + LV_L^{\rm MF} \quad \text{with} \quad V_L^{\rm MF} := -W^H + q\rho_L *_\Gamma W\,.} \tag{4.8}$$

In the next proposition, we state that $H_L^{\rm MF}$ satisfies the assumptions of Theorem 4.4.

Theorem 4.5 (The rHF model in the weak contrast regime)**.** *The map $L \mapsto \rho_L *_\Gamma W$ is continuous from $\mathbb{R}_+$ to $L^\infty_{\rm per}$. In addition, $V_0^{\rm MF}$ satisfies the non-degeneracy condition (4.5): $\widehat{V}_0^{\rm MF}(\mathbf{v}_1+\mathbf{v}_2) > 0$. Consequently, for all $L > 0$ small enough, $H_L^{\rm MF}$ admits* non separating *Dirac points at the vertices of Γ^* between the first and second bands.*

If we assume that $q = 2$ then, for all L small enough, we have $\epsilon_L < \lambda_L$ where λ_L denotes the energy level of these Dirac points.

Remark 4.6. The conclusions of Theorem 4.5 could be extended to a large class of periodic rHF model with *smeared* nuclei, that is when $W^H = \sum_{\mathbf{u}\in\mathscr{L}}(\delta_{\mathbf{u}+\mathbf{a}} + \delta_{\mathbf{u}+\mathbf{b}}) *_\Gamma W$ is replaced by $\mu_{\rm m} *_\Gamma W$ where

$$\mu_{\rm m} = \sum_{\mathbf{u}\in\mathscr{L}} \left[m(\cdot - (\mathbf{a}+\mathbf{u})) + m(\cdot - (\mathbf{b}+\mathbf{u}))\right] ,$$

for some $m \in \mathcal{C}_c^\infty(\mathbb{R}^2)$ such that $m \geq 0$. If, for instance, we assume that m is invariant under rotation by $\pi/3$ then the mean-field potential $(q\rho_L - \mu_{\rm m}) *_\Gamma W$ is a honeycomb lattice potential. In this setting, the non-degeneracy condition (4.5) is equivalent to (see the fourth step of the proof of Theorem 4.5)

$$\widehat{\mu}_{\rm m}(\mathbf{v}_1+\mathbf{v}_2) = -\frac{\widehat{m}(\mathbf{v}_1+\mathbf{v}_2)}{\sqrt{|\Gamma|}} \neq 0\,,$$

which is generically satisfied.

3 Proof of Theorem 4.4

We start with a result from perturbation theory. We denote by $-\Delta_{\mathbf{k}}$ the free Laplace operator acting on $L^2_{\mathbf{k}}$.

Proposition 4.7 (Singular perturbation theory)**.** *For all $L \in (-1\,,1)$, we consider $V_L \in L^p_{\rm per}$ where $p \in (1\,,\infty]$ and we denote by $H_L = -\Delta + V_L$ the associated periodic Schrödinger operator. Assume that the map $L \in (-1\,,1) \mapsto V_L \in L^p_{\rm per}$ is continuous at 0. Let $\mathbf{k} \in \Gamma^*$ and $\lambda \in \sigma_{\rm d}(H_0(\mathbf{k}))$. Then, there exists $\epsilon, L_0 > 0$ small enough constants and $\mathscr{C} \subset \mathbb{C}$ a contour enclosing λ such that $\mathrm{d}\,(\mathscr{C}, \sigma_{\rm d}(H_L(\mathbf{k}))) \geq \epsilon$ for all $L \leq L_0$. We denote by*

$$P_L(\mathbf{k}) \coloneqq \frac{-1}{2\pi i} \oint_{\mathscr{C}} \frac{\mathrm{d}z}{H_L(\mathbf{k}) - z}\,, \tag{4.9}$$

the spectral projection of $H_L(\mathbf{k})$ associated with the interval of real numbers enclosed by $\mathscr{C}$. Then the rank of $P_L(\mathbf{k})$ is constant on $[-L_0\,, L_0]$ and it exists $C > 0$ such that for all L small enough, we have

$$\left\| (-\Delta_{\mathbf{k}} + 1)^{\max(\frac{p}{2},1)} (P_L(\mathbf{k}) - P_0(\mathbf{k})) \right\| \leq C \left\| V_L - V_0 \right\|_{L^p_{\rm per}} . \tag{4.10}$$

Because the arguments are the same as in the proof of Proposition 3.46, we leave the proof of Proposition 4.7 to the reader (see also [Lew22b, Théorème 5.6]). Also, the conclusions of Proposition 4.7 remain if we replace $L^2_{\mathbf{k}}$ by $L^2_{\mathbf{K}_\star,j}$ for any $j \in \{0,1,2\}$. Now, we write the

Proof of Theorem 4.4. The proof is mainly an adaptation of the proofs of [FW12, Theorem 5.1] and [BC18, Theorem 2.5]. Hence, we do not detail all the arguments.

We divide the proof in six steps. In the five first ones, we show that the dispersion relation admits Dirac points. To this end, we use the Feschbach-Schur method twice. In the sixth step, we show that the cones are not separating. Let $\mathbf{K}_\star \in \{\mathbf{K}, \mathbf{K}'\}$ be any vertex of the first Brillouin zone Γ^*.

First step: We study the low-lying spectrum of $-\Delta_{\mathbf{K}_\star}$. The lowest $L^2_{\mathbf{K}_\star}$-eigenvalue of $-\Delta$ is equal to $|\mathbf{K}_\star|^2$ and is triply degenerate. We recall that $L^2_{\mathbf{K}_\star}$ can be decomposed with respect to the eigenspaces of $\mathcal{R}$, defined in (4.2), as

$$L^2_{\mathbf{K}_\star} = L^2_{\mathbf{K}_\star,0} \overset{\perp}{\oplus} L^2_{\mathbf{K}_\star,1} \overset{\perp}{\oplus} L^2_{\mathbf{K}_\star,2}\,,$$

where the subspaces $L^2_{\mathbf{K}_\star,j}$ are defined in (4.3). If we denote $\Phi(x_1,x_2) \coloneqq \exp\left(\frac{4\pi i}{3} x_2\right)$ then we can choose the three normalized eigenfunctions of $-\Delta_{\mathbf{K}_\star}$ associated to the eigenvalue $|\mathbf{K}_\star|^2$ as

$$\Phi_0^j = \frac{c}{3}\left(\Phi + \tau^j \mathcal{R}(\Phi) + \overline{\tau}^j \mathcal{R}^2(\Phi)\right) \eqqcolon F^j \Phi \in L^2_{\mathbf{K}_\star,j}\,, \quad j \in \{0,1,2\}\,, \tag{4.11}$$

where $c > 0$ is a normalization constant.

Second step: We construct eigenfunctions for H_L. For all L small enough and for all $j \in \{0,1,2\}$, Proposition 4.7 allows us to define P_L^j, the rank one spectral projection on the first $L^2_{\mathbf{K}_\star,j}$-eigenvalue of $H_L(\mathbf{K}_\star)$. The maps $L \mapsto P_L^j$ are continuous at 0 and we can define the normalized eigenfunctions as

$$\Phi_L^j \coloneqq \frac{P_L^j \Phi_0^j}{\sqrt{\left\langle \Phi_0^j, P_L^j \Phi_0^j \right\rangle_{L^2(\Gamma)}}} \in L^2_{\mathbf{K}_\star,j}\,.$$

The associated eigenvalues are given by $\lambda_L^j = \left\langle \Phi_L^j, H_L(\mathbf{K}_\star)\Phi_L^j \right\rangle_{L^2}$. The maps $L \mapsto \Phi_L^j$ and $L \to \lambda_L^j$ are likewise continuous at 0. Since $H_L(\mathbf{K}_\star)$ is $\mathcal{PC}$-invariant, we have the relations

$$\Phi_L^0 = \mathcal{PC}(\Phi_L^0), \quad \Phi_L^2 = \mathcal{PC}(\Phi_L^1) \quad \text{and} \quad \lambda_L^1 = \lambda_L^2\,. \tag{4.12}$$

Third step: We claim that λ_L^0 bifurcates from $\lambda_L^1 = \lambda_L^2$ for non zero and small enough L. Using the estimate (4.10) from Proposition 4.7, one can show the estimates

$$\lambda_L^j = |\mathbf{K}_\star|^2 + L\left(\left\langle \Phi_0^j, V_0\Phi_0^j \right\rangle_{L^2(\Gamma)} + o(1)\right), \quad j \in \{0,1,2\}\,.$$

Since $\tau + \overline{\tau} = -1$, the first order condition for $\lambda_L^0 \neq \lambda_L^1 = \lambda_L^2$ is

$$\left\langle F^0\Phi, V_0F^0\Phi\right\rangle_{L^2(\Gamma)} + \tau\left\langle F^1\Phi, V_0F^1\Phi\right\rangle_{L^2(\Gamma)} + \overline{\tau}\left\langle F^2\Phi, V_0F^2\Phi\right\rangle_{L^2(\Gamma)} \neq 0\,.$$

Now, because the operators F^j and V_0 commute with the rotation by $2\pi/3$ operator $\mathcal{R}$, the condition becomes

$$\left\langle (P^0 + \overline{\tau}P^1 + \tau P^2)\Phi, V_0\Phi\right\rangle_{L^2(\Gamma)} = \langle \mathcal{R}(\Phi), V_0\Phi\rangle_{L^2(\Gamma)} = \left\langle \mathcal{R}^2(\Phi), V_0\mathcal{R}(\Phi)\right\rangle_{L^2(\Gamma)} = \widehat{V}_0(\mathbf{v}_1 + \mathbf{v}_2) \neq 0\,,$$

which is exactly the assumption (4.5). Therefore, we have obtained the expansion

$$\lambda_L^0 = \lambda_L^1 + L(\widehat{V}_0(\mathbf{v}_1 + \mathbf{v}_2) + o(1))\,.$$

Fourth step: We claim that the dispersion is locally conical. To this end, we use the Feshbach-Schur method, introduced in Section 3.1. Because it will be more convenient to work on the same underlying space, we introduce the isometry $\iota_{\mathbf{k}} : \varphi \in L^2_{\mathbf{k}} \mapsto \left[\mathbf{x} \mapsto e^{-i\mathbf{k}\cdot\mathbf{x}}\varphi(\mathbf{x})\right] \in L^2_{\text{per}}$ and we denote $\tilde{H}_L(\mathbf{k}) := \iota_{\mathbf{k}} H_L(\mathbf{k})\iota_{\mathbf{k}}^* = (-i\nabla + \mathbf{k})^2 + LV_L$. We also denote $-\Delta^{\mathbf{k}} := (-i\nabla + \mathbf{k})^2 = \iota_{\mathbf{k}}(-\Delta)\iota_{\mathbf{k}}^*$.

Let Q_L be the orthogonal projection onto the subspace $\operatorname{span}(\Psi_L^0, \Psi_L^1, \Psi_L^2)$ where $\Psi_L^j := \iota_{\mathbf{K}_\star}(\Phi_L^j) \in L^2_{\text{per}}$ and we denote by $Q_L^\perp := 1 - Q_L$ the complementary projection. For $\kappa \in \mathbb{R}^2$ and $\mathbf{k} = \mathbf{K}_\star + \kappa$, we write $\tilde{H}_L(\mathbf{k})$ as the block matrix

$$\tilde{H}_L(\mathbf{k}) = \begin{pmatrix} A_L(\kappa) & C_L(\kappa)^* \\ C_L(\kappa) & B_L(\kappa) \end{pmatrix}\,,$$

where $A_L(\kappa) = Q_L\tilde{H}_L(\mathbf{k})Q_L$, $B_L(\kappa) = Q_L^\perp\tilde{H}_L(\mathbf{k})Q_L^\perp$ and $C_L(\kappa) = Q_L^\perp\tilde{H}_L(\mathbf{k})Q_L$.

By perturbation theory [Kat95], there exists $\delta, \epsilon > 0$ small enough such that

$$\forall E \leq |\mathbf{K}_\star|^2 + \delta,\ \forall L \in [-\delta\,, \delta],\ \forall |\kappa| \leq \delta, \quad B_L(\kappa) - E \geq \epsilon\,.$$

On the other hand, using for instance Proposition 3.12, we have that the estimate $B_L(\kappa) - E \geq -\frac{1}{2}\Delta^{\mathbf{k}} - C$ for some constant $C > 0$ and for all $|L|$ and $|\kappa|$ small enough. Taking a suitable linear combination of these two estimates, we get

$$\forall E \leq |\mathbf{K}_\star|^2 + \delta,\ \forall L \in [-\delta\,, \delta],\ \forall |\kappa| \leq \delta, \quad B_L(\kappa) - E \geq \epsilon' Q_L^\perp(-\Delta^{\mathbf{k}} + 1)Q_L^\perp\,,$$

for some $\epsilon' > 0$. In particular, this implies

$$\forall E \leq |\mathbf{K}_\star|^2 + \delta,\ \forall L \in [-\delta\,, \delta],\ \forall |\kappa| \leq \delta, \quad \left\| Q_L^\perp\sqrt{-\Delta^{\mathbf{k}} + 1}\frac{1}{B_L(\kappa) - E}\sqrt{-\Delta^{\mathbf{k}} + 1}Q_L^\perp \right\| \leq 1/\epsilon'\,.$$

Then, we obtain

$$\begin{aligned}&\left\| C_L(\kappa)^*\frac{1}{B_L(\kappa) - E}C_L(\kappa)\right\| \\ &\qquad \lesssim \left\| Q_L^\perp\sqrt{-\Delta^{\mathbf{k}} + 1}\frac{1}{B_L(\kappa) - E}\sqrt{-\Delta^{\mathbf{k}} + 1}Q_L^\perp\right\| \left\| Q_L^\perp\frac{1}{\sqrt{-\Delta^{\mathbf{k}} + 1}}C_L(\kappa)\right\|^2 \lesssim |\kappa|^2\,.\end{aligned}$$

Then the Feshbach-Schur method implies that, for all L and κ small enough, $\sigma\left(H_L(\mathbf{k})\right) \cap (-\infty\,, |\mathbf{K}_\star|^2 + \delta]$ is equal to the spectrum of $A_L(\kappa)$, up to a $O(|\kappa|^2)$ correction, where the O does not depend on L or κ.

Now, we estimate the spectrum of the 3×3 matrix $A_L(\kappa)$. Using $\tilde{H}_L(\mathbf{K}_\star + \kappa) = \tilde{H}_L(\mathbf{K}_\star) +$

$2\kappa \cdot (-i\nabla + \mathbf{K}_\star) + |\kappa|^2$, we obtain

$$A_L(\kappa) = \begin{pmatrix} \lambda_L^0 & 0 & 0 \\ 0 & \lambda_L^1 & 0 \\ 0 & 0 & \lambda_L^1 \end{pmatrix} + \Lambda(L,\kappa) + |\kappa|^2 I_3 ,$$

where I_3 is the 3×3 identity matrix and $\Lambda(L,\kappa)$ is an interaction matrix, defined by

$$\Lambda(L,\kappa) \coloneqq \left(-2i \left\langle \Phi_L^j, \kappa \cdot \nabla \Phi_L^\ell \right\rangle_{L^2(\Gamma)} \right)_{j,\ell=0,1,2} .$$

Using the relations (4.12) and that $\mathcal{R}\Phi_L^j = \tau^j \Phi_L^j$, we can show the following relations

$$\begin{aligned} \forall j \in \{0,1,2\}, \quad \left\langle \Phi_L^j, \nabla \Phi_L^j \right\rangle_{L^2(\Gamma)} &= M_{\mathcal{R}} \left(\left\langle \Phi_L^j, \nabla \Phi_L^j \right\rangle_{L^2(\Gamma)} \right) , \\ -\overline{\langle \Phi_L^2, \nabla \Phi_L^1 \rangle}_{L^2(\Gamma)} = \langle \Phi_L^1, \nabla \Phi_L^2 \rangle_{L^2(\Gamma)} &= \tau M_{\mathcal{R}} \left(\langle \Phi_L^1, \nabla \Phi_L^2 \rangle_{L^2(\Gamma)} \right) , \\ \langle \Phi_L^1, \nabla \Phi_L^0 \rangle_{L^2(\Gamma)} = \langle \Phi_L^0, \nabla \Phi_L^2 \rangle_{L^2(\Gamma)} &= -\overline{\langle \Phi_L^2, \nabla \Phi_L^0 \rangle}_{L^2(\Gamma)} = -\overline{\langle \Phi_L^0, \nabla \Phi_L^1 \rangle}_{L^2(\Gamma)} , \end{aligned}$$

where $M_{\mathcal{R}}$ is the rotation by $2\pi/3$ matrix. We deduce that $\left\langle \Phi_L^j, \nabla \Phi_L^j \right\rangle_{L^2(\Gamma)} \in \mathrm{Ker}\,(M_{\mathcal{R}} - 1) = \{0\}$ and $\langle \Phi_L^1, \nabla \Phi_L^2 \rangle_{L^2(\Gamma)} \in \mathrm{Ker}\,(\tau M_{\mathcal{R}} - 1) = \mathbb{C} \begin{pmatrix} 1 \\ i \end{pmatrix}$. Hence, we can write

$$\Lambda(L,\kappa) = \begin{pmatrix} 0 & \overline{\boldsymbol{\beta}_L} \cdot \kappa & \boldsymbol{\beta}_L \cdot \kappa \\ \boldsymbol{\beta}_L \cdot \kappa & 0 & \alpha_L(\kappa_1 + i\kappa_2) \\ \overline{\boldsymbol{\beta}_L} \cdot \kappa & \overline{\alpha_L}(\kappa_1 - i\kappa_2) & 0 \end{pmatrix} ,$$

where $\alpha_L \coloneqq -2i \langle \Phi_L^1, \partial_{x_1} \Phi_L^2 \rangle$ and $\boldsymbol{\beta}_L \coloneqq -2i \langle \Phi_L^1, \nabla \Phi_L^0 \rangle$. We use the Feschbach-Schur method again, this time with the orthogonal projection $|\Psi_L^1\rangle \langle \Psi_L^1| + |\Psi_L^2\rangle \langle \Psi_L^2|$. Recall that from the third step, we have $\lambda_L^0 = \lambda_L^1 + L(\widehat{V}_0(\mathbf{v}_1 + \mathbf{v}_2) + o(1))$. Hence, there exists $\delta' > 0$ small enough such that: for all $|\kappa| \le \delta' L$, for all $L \in [-\delta', \delta'] \setminus \{0\}$,

$$\begin{aligned} &E \in \sigma(A_L(\kappa)) \cap [\lambda_L^1 - \delta' L , \lambda_L^1 + \delta' L] \\ &\iff E \in \sigma \left(\begin{pmatrix} \lambda_L^1 & \alpha_L(\kappa_1 + i\kappa_2) \\ \overline{\alpha_L}(\kappa_1 - i\kappa 2) & \lambda_L^1 \end{pmatrix} - \frac{1}{\lambda_L^0 + |\kappa|^2 - \lambda_L^1} D_L(\kappa) D_L(\kappa)^* + |\kappa|^2 I_2 \right) , \end{aligned}$$

where $D_L(\kappa) = \left(\overline{\boldsymbol{\beta}_L} \cdot \kappa, \boldsymbol{\beta}_L \cdot \kappa\right)$. Because $L \mapsto \boldsymbol{\beta}_L$ is continuous at 0, we have the bound $\|D_L(\kappa)\| \le C\,|\kappa|$ where C does not depend on L. Recall that the spectrum in a neighborhood of λ_L^1 is equal to the spectrum of $A_L(\kappa)$ plus a $O(|\kappa|^2)$. Hence, we have shown that for all $L \in [-\delta', \delta'] \setminus \{0\}$ and all $|\kappa| \le \delta' L$, the spectrum of $H_L(\mathbf{K}_\star + \kappa)$ in the interval $[\lambda_L^1 - \delta' L , \lambda_L^1 + \delta' L]$ is given by

$$\lambda_L^{\pm}(\kappa) = \lambda_L^1 \pm |\alpha_L|\,|\kappa| + L^{-1}\,|\kappa|\,E(\kappa) , \tag{4.13}$$

where $\alpha_L = -2i \langle \Phi_L^1, \partial_{x_1} \Phi_L^2 \rangle$ and where there exists $C > 0$ such that $|E(\kappa)| \le C\,|\kappa|$ for all $|\kappa| \le \delta' L$.

Fifth step: We claim that the cones are not degenerate. This amounts to showing that the opening angle α_L is non zero when $L \neq 0$. By continuity of the maps $L \mapsto \Phi_L^1$ and $L \mapsto \Phi_L^2$ at 0, we see that the map $L \mapsto \alpha_L$ is likewise continuous at 0. In the proof of [BC18, Theorem 2.5], the authors compute α_0 explicitly showing it is non zero. Hence, α_L is non zero for all $L \neq 0$ small enough.

Sixth step: We claim that the cones are not separating for L small enough. Let $\mathbf{k} \in \Gamma^*$. We denote by $(\mu_0(\mathbf{k}), \mu_1(\mathbf{k}), \mu_2(\mathbf{k}))$ the three lowest eigenvalues (with multiplicity) of $-\Delta_{\mathbf{k}}$ which are defined by

$$\sigma(-\Delta_{\mathbf{k}}) = \left\{ |\mathbf{k}+\mathbf{v}|^2 \;\middle|\; \mathbf{v} \in \mathscr{L}^* \right\}.$$

Let $\widetilde{\mathcal{R}}$ denotes the rotation by $2\pi/3$ about $\mathbf{K}_\star$, defined by

$$\widetilde{\mathcal{R}}(\mathbf{x}) = M_{\mathcal{R}}(\mathbf{x}+\mathbf{K}_\star) + \mathbf{K}_\star\,,$$

where the matrix $M_{\mathcal{R}}$ is the rotation matrix by $2\pi/3$. We recall that, because $\mathscr{L}^*$ is invariant by $\widetilde{\mathcal{R}}$ (see Figure 4.1a), the lowest eigenvalue of $-\Delta_{\mathbf{K}_\star}$ is triply degenerate. Let $\mathbf{v} \in \mathscr{L}^*$ such that $|\mathbf{K}_\star - \mathbf{v}|$ is minimal. Then, for $\mathbf{k}$ in the vicinity of $\mathbf{K}_\star$, the three lowest eigenvalues $\{\mu_j(\mathbf{k})\}_{j=0,1,2}$ of $-\Delta_{\mathbf{k}}$ are given by

$$\mu_j(\mathbf{k}) = \left|\mathbf{k} - \widetilde{\mathcal{R}}^j(\mathbf{v})\right|^2.$$

Let $\mathbf{v}'$ be the image of $\mathbf{v}$ by the rotation by π about $\mathbf{K}_\star$, see Figure 4.1b. We can explicitly compute $\mu_j(\mathbf{k})$ for $\mathbf{k}$ along the segment with extreme points $\mathbf{v}$ and $\mathbf{v}'$. We denote $\kappa = (\mathbf{v}'-\mathbf{v})/2$ and $\tilde{\mu}_j(x) = \mu_j(\mathbf{K}_\star + \kappa x)$. Then, for $x \in [-1\,,1]$, we have

$$\tilde{\mu}_0(x) = |\kappa|^2 (x+1)^2 \quad \text{and} \quad \tilde{\mu}_1(x) = \tilde{\mu}_2(x) = |\kappa|^2 (x^2 - x + 1)\,.$$

The graphs of these functions are represented in Figure 4.2a. We notice the following inequalities:

$$\forall x \in [-1\,,0), \quad \tilde{\mu}_0(x) < \tilde{\mu}_1(x) = \tilde{\mu}_2(x) \quad \text{and} \quad \forall x \in (0\,,1], \quad \tilde{\mu}_1(x) = \tilde{\mu}_2(x) < \tilde{\mu}_0(x)\,.$$

Now, we consider the ordered eigenvalues $\lambda_{L,0}(x) \le \lambda_{L,1}(x) \le \lambda_{L,2}(x)$ of the Bloch operator $H_L(\mathbf{K}_\star)$ restricted to the segment joining $\mathbf{v}$ and $\mathbf{v}'$. They are continuous functions of (L,x) in a neighborhood of $(0,0)$.

Assume that $\widehat{V}_0(\mathbf{v}_1+\mathbf{v}_2) > 0$ (the case $\widehat{V}_0(\mathbf{v}_1+\mathbf{v}_2) < 0$ is treated similarly). Then, by the first step, $\lambda_{L,2}(0)$ bifurcates from $\lambda_{L,0}(0) = \lambda_{L,1}(0) =: \lambda_\star$ for $L > 0$ (see Figure 4.2b) and the dispersion relation forms a cone, see (4.13). Hence, there exists $\epsilon > 0$ small enough such that for all L small enough and all $x \in (0\,,\epsilon L)$, we have

$$\lambda_{L,0}(x) < \lambda_\star < \lambda_{L,1}(x)\,.$$

However, by continuity, we have: $\lim_{L\to 0} \|\lambda_{L,1}(x) - \mu_1(x)\|_{L^\infty([1/2,1])} = 0$. We deduce that there exists $x > \epsilon L$ such that $\lambda_{L,1}(x) > \lambda_\star$. By the intermediate value theorem, $\lambda_{L,1}(x) = \lambda_\star$ for some $x \neq 0$ which shows that the cone is not separating. $\square$

4 Proof of Theorem 4.5

Before proving Theorem 4.5, we state a lemma which gives *a priori* bounds on the potential terms of the rHF energy. Those are far from optimal, but sufficient for our purposes.

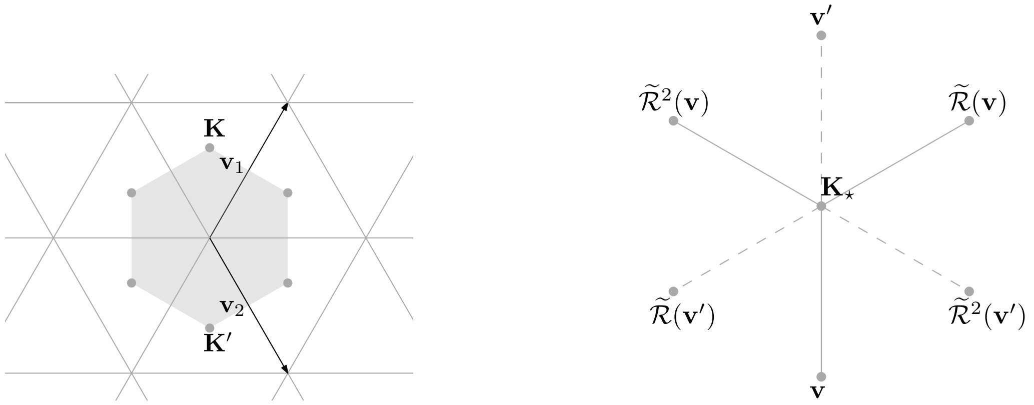
Lemma 4.8. *There exists a constant $C > 0$ such that for all $\gamma \in \mathcal{S}_{\rm per}$ we have*

$$D(\rho_\gamma,\rho_\gamma) \lesssim [\underline{\mathrm{Tr}}_{\mathscr{L}}(-\Delta\gamma)]^2 \tag{4.14}$$

In addition, for all $\theta \in [0\,,1/2)$ there exists $C_\theta > 0$ such that for all $\gamma \in \mathcal{S}_{\rm per}$ we have

$$\left|\int_\Gamma W\rho_\gamma\right| \le C_\theta \left[\underline{\mathrm{Tr}}_{\mathscr{L}}(\gamma)\right]^\theta \left[\underline{\mathrm{Tr}}_{\mathscr{L}}((1-\Delta)\gamma)\right]^{1-\theta}. \tag{4.15}$$

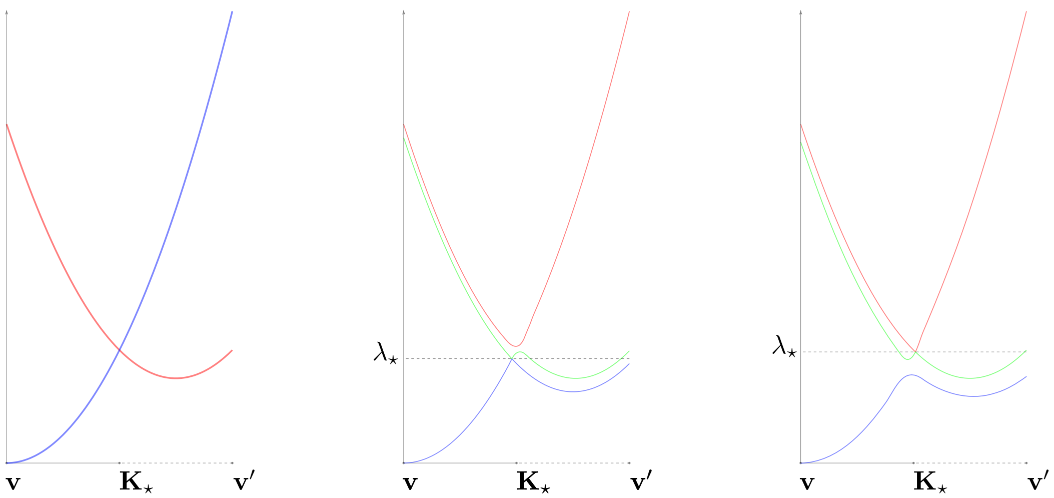
Proof of Lemma 4.8. Using that $W \in L^1_{\rm per}$, the Cauchy-Schwarz inequality and Young's inequality,



(a) The reciprocal lattice $\mathscr{L}^* = \mathbf{v}_1\mathbb{Z} + \mathbf{v}_2\mathbb{Z}$. The first Brillouin zone Γ^* is colored in gray and its vertices are shown. We observe that $\mathscr{L}^*$ is invariant with respect to the rotation $\widetilde{\mathcal{R}}$ by $2\pi/3$ about any vertex of Γ^*.

(b) A vertex $\mathbf{K}_\star$ of Γ^*. Its three nearest vertices in $\mathscr{L}^*$ and their image by the rotation by π about $\mathbf{K}_\star$ shape a regular hexagon.

Figure 4.1 – We compute the dispersion relation on the section above the segment which connects $\mathbf{v}$ and $\mathbf{v}'$.



(a) Low-spectrum of the free Laplacian $-\Delta_{\mathbf{k}}$; $\mu_0(\mathbf{k})$ is drawn in blue, $\mu_1(\mathbf{k})$ and $\mu_2(\mathbf{k})$ are drawn in red.

(b) Case $\widehat{V}_0(\mathbf{v}_1 + \mathbf{v}_2) > 0$.

(c) Case $\widehat{V}_0(\mathbf{v}_1 + \mathbf{v}_2) < 0$.

Figure 4.2 – Dispersion relation slice along the quasi-momenta segment with extreme points $\mathbf{v}$ and $\mathbf{v}'$ of $-\Delta_{\mathbf{k}}$ (Figure 4.2a) and of $-\Delta_{\mathbf{k}} + LV_L$ for L small in both case $\widehat{V}_0(\mathbf{v}_1 + \mathbf{v}_2) > 0$ (Figure 4.2b) and $\widehat{V}_0(\mathbf{v}_1 + \mathbf{v}_2) < 0$ (Figure 4.2c).

we can write

$$D(\rho_\gamma,\rho_\gamma)=\int_\Gamma \rho_\gamma(\rho_\gamma *_\Gamma W)\le \|\rho_\gamma\|_{L^2_{\rm per}}\|\rho_\gamma *_\Gamma W\|_{L^2_{\rm per}}\le \|W\|_{L^1_{\rm per}}\|\rho_\gamma\|^2_{L^2_{\rm per}}\,.$$

To show estimate (4.14), it remains to apply the periodic Lieb-Thirring inequality [Exn+21, Chapter 8]. In sake of clarity, we recall it: there exists a constant $C_{\rm LT}>0$ such that for all $\gamma\in\mathcal{S}_{\rm per}$, we have

$$C_{\rm LT}\int_\Gamma \rho_\gamma^2\le \underline{\rm Tr}_{\mathscr{L}}(-\Delta\gamma)\,.$$

Now, we show estimate (4.15). Let $s\in(1\,,2)$ and $q\in(2\,,\infty)$ its conjugate exposant. Let $r\ge q$ and $\theta\in[0\,,1/2)$ such that:

$$\frac{1}{q}=\theta+\frac{1-\theta}{r}\,.$$

Using the Hölder inequality and Sobolev embedding $L^{2r}_{\rm per}\subset H^1_{\rm per}$, we have

$$\left|\int_\Gamma W\rho_\gamma\right|\le \|W\|_{L^s_{\rm per}}\|\rho_\gamma\|_{L^q_{\rm per}}\le \|W\|_{L^s_{\rm per}}\|\rho_\gamma\|^\theta_{L^1_{\rm per}}\|\rho_\gamma\|^{1-\theta}_{L^r_{\rm per}}\lesssim \|W\|_{L^s_{\rm per}}\left[\underline{\rm Tr}_{\mathscr{L}}(\gamma)\right]^\theta\|\rho_\gamma\|^{2(1-\theta)}_{H^1_{\rm per}}\,.$$

Then, estimate (4.15) stems from the periodic Hoffmann-Ostenhof inequality [CLL01, Eq (4.42)], which we also recall: for all $\gamma\in\mathcal{S}_{\rm per}$, we have

$$\left\|\nabla\sqrt{\rho_\gamma}\right\|_{L^2_{\rm per}}\le \underline{\rm Tr}_{\mathscr{L}}(-\Delta\gamma)\,. \tag{4.16}$$

This concludes the proof of Lemma 4.8. □

Proof of Theorem 4.5. We divide the proof into five steps. In the first three steps, we show that the map $L\mapsto\rho_L *_L W$ is continuous. In the fourth one, we show that $V_0^{\rm MF}$ satisfies the non-degeneracy condition (4.5) of Theorem 4.4. In the last one, we prove that if $q=2$ then the Fermi level is strictly below the energy level of the cones for all L small enough.

Let $L\ge0$ and $(L_n)_{n\in\mathbb{N}}$ be a sequence of non-negative numbers which tends to L as $n\to\infty$. In order to lighten the notations, we denote $\gamma=\gamma_L$, $\rho=\rho_L$, $\gamma_n=\gamma_{L_n}$ and $\rho_n=\rho_{L_n}$.

First step: We claim that $\underline{\rm Tr}_{\mathscr{L}}(-\Delta\gamma_n)$ is uniformly bounded in n. We write

$$F_{L_n}=\mathcal{F}_{L_n}(\gamma_n)\le\mathcal{F}_{L_n}(\gamma)=F_L+(L_n-L)\left(-\int_\Gamma W^H\rho+\frac12 D(\rho,\rho)\right)\,. \tag{4.17}$$

The last term in (4.17) is a $O(|L_n-L|)$. This shows that $(F_{L_n})_{n\in\mathbb{N}}$ is bounded. Then, using Lemma 4.8, the fact that $\underline{\rm Tr}_{\mathscr{L}}(\gamma_n)=2/q$ and the positivity of $D(\cdot,\cdot)$, we can write for $\theta\in(0\,,1/2)$ and some constant $C>0$

$$F_{L_n}\ge\underline{\rm Tr}_{\mathscr{L}}(-\Delta\gamma_n)-C\left[1+\underline{\rm Tr}_{\mathscr{L}}(-\Delta\gamma_n)\right]^{1-\theta}\,.$$

Because F_{L_n} is uniformly bounded in n, this completes the proof of the first step. We have also shown the following subsidiary result:

$$\limsup_{n\to\infty}F_{L_n}\le F_L\,. \tag{4.18}$$

Second step: We claim that $(\gamma_n)_{n\in\mathbb{N}}$ is a minimizing sequence for the minimization problem (4.7). For all $n\in\mathbb{N}$, we have

$$F_L=\mathcal{F}_L(\gamma)\le\mathcal{F}_L(\gamma_n)=F_{L_n}+(L-L_n)\left(-\int_\Gamma W^H\rho_n+\frac12 D(\rho_n,\rho_n)\right)\,.$$

By Lemma 4.8 and the first step, the last term of (4.17) is $O(|L-L_n|)$. Hence, taking the limit inferior, we find

$$F_L \leq \liminf_{n\to\infty} F_{L_n} \,. \tag{4.19}$$

Combining (4.18) and (4.19) gives

$$F_{L_n} \underset{n\to+\infty}{\longrightarrow} F_L \,.$$

Using the estimate $\mathcal{F}_L(\gamma_n) = F_{L_n} + O(|L_n - L|)$ shown earlier, it follows that $(\gamma_n)_{n\in\mathbb{N}}$ is indeed a minimizing sequence for F_L.

Third step: We claim that the map $L \mapsto \rho_L *_\Gamma W$ is continuous from $\mathbb{R}_+$ to $L^\infty_{\rm per}$. From the proof of [CLL01, Theorem 2.1], we see that for any $r \in [1\,,\infty)$ any minimizing sequence $(\tilde\gamma_n)_{n\in\mathbb{N}}$ for F_L admits a subsequence $(\tilde\gamma_{\varphi(n)})_{n\in\mathbb{N}}$ such that $(\rho_{\tilde\gamma_{\varphi(n)}})_{n\in\mathbb{N}}$ converges to ρ in $L^r_{\rm per}$. Hence, by the second step, every subsequence of $(\rho_n)_{n\in\mathbb{N}}$ admits a subsequence which converges to ρ in $L^r_{\rm per}$. By the first step and the periodic Hoffmann-Ostenhof inequality (4.16), the sequence $(\sqrt{\rho_n})_{n\in\mathbb{N}}$ is uniformly bounded in $H^1_{\rm per}$. Let $p \in (4\,,\infty)$. By the Rellich-Kondrakov theorem, it admits at least one subsequence which converges in $L^p_{\rm per}$. Merging these facts, we deduce that the whole sequence $(\rho_n)_{n\in\mathbb{N}}$ converges to ρ in $L^{p/2}_{\rm per}$. To conclude this step, we use Hölder's inequality together with the fact that G belongs to $L^r_{\rm per}$ where $r \in (1\,,2)$ is the conjugate exponent of $p/2$.

Fourth step: We claim that $V_0^{\rm MF}$ satisfies the non-degeneracy condition (4.5). When $L=0$, the rHF energy $\mathcal{F}_L$ is minimized by $\gamma_0 = \mathbb{1}_{(-\infty,\epsilon_0]}(-\Delta)$. The associated one-body density is constant equal to $\frac{2}{q|\Gamma|}$ and the mean-field potential is given by

$$V_0^{\rm MF} = -W^H + \frac{2}{q\,|\Gamma|}\int_\Gamma W = -\mu *_\Gamma W + \text{constant}\,,$$

where $\mu = \sum_{\mathbf{u}\in\mathscr{L}}(\delta_{\mathbf{u}+\mathbf{a}} + \delta_{\mathbf{u}+\mathbf{b}})$ with $\mathbf{a} = -\mathbf{b}$ defined in (4.1). Recall that the Fourier coefficients of W are positive, see Section 5.1. Hence, the condition (4.5) is equivalent to $\widehat{\mu}(\mathbf{v}_1+\mathbf{v}_2) \neq 0$. However, we have

$$\widehat{\mu}(\mathbf{v}_1+\mathbf{v}_2) = \frac{2}{\sqrt{|\Gamma|}}\cos(\mathbf{a}\cdot(\mathbf{v}_1+\mathbf{v}_2)) = \frac{2}{\sqrt{|\Gamma|}}\cos(2\pi/3) = -\frac{1}{\sqrt{|\Gamma|}} < 0\,,$$

which concludes this step.

In particular, we can apply Theorem 4.4 to $H_L^{\rm MF} = -\Delta + LV_L^{\rm MF}$. We denote by λ_L the energy of the cones (which are located between the first and second bands). We recall that ϵ_L denotes the Fermi level.

Fifth step: When $q=2$, we claim that $\epsilon_L < \lambda_L$ for all $L \geq 0$ small enough. We denote by $N(L,\epsilon)$ the *integrated density of states*, defined by

$$N_L(\epsilon) = \sum_{n\geq 0} \fint_{\Gamma^*} \mathbb{1}_{\lambda_{L,n}(\mathbf{k})\leq\epsilon}\,\mathrm{d}\mathbf{k}\,,$$

where $\lambda_{L,0}(\mathbf{k}) \leq \lambda_{L,1}(\mathbf{k}) \leq \dots$ denote the ordered eigenvalues of the operator $H_L^{\rm MF}(\mathbf{k})$ acting on $L^2_{\mathbf{k}}$. We recall that, in our situation, the Fermi level ϵ_L is determined by the implicit equation $N_L(\epsilon_L) = 1$, which admits solutions since the map $\epsilon \mapsto N_L(\epsilon)$ is continuous and non-increasing.

By the third step, we have $\sup_{L\in[0,1]} \left\|V_L^{\rm MF}\right\|_{L^p_{\rm per}} < \infty$. Then, using Proposition 3.12, we deduce that

$$\forall L \in [0\,,1],\ \forall \mathbf{k} \in \Gamma^*,\ -A^{-1}\Delta_{\mathbf{k}} - B \leq H_L(\mathbf{k}) \leq -A\Delta_{\mathbf{k}} + B\,,$$

for some positive constants A and B, independent from $L \in [0\,,1]$ and $\mathbf{k} \in \Gamma^*$. Using the min-max principle, we can show that

$$\forall L \in [0\,,1],\ \forall \mathbf{k} \in \Gamma^*,\ C^{-1}n - D \leq \lambda_{L,n}(\mathbf{k}) \leq Cn + D\,, \tag{4.20}$$

for other positive constants C and D, likewise independent from $L \in [0\,,1]$ and $\mathbf{k} \in \Gamma^*$. The upper bound in (4.20) implies that there exists $\epsilon_{\max} \in \mathbb{R}$ such that

$$\bigcup_{L\in[0,1]} N_L^{-1}([0\,,2]) \subset (-\infty\,, \epsilon_{\max}]\,.$$

Then, the lower bound in (4.20) shows that there exists $N_{\max} \geq 2$ such that

$$\forall L \in [0\,,1],\ \forall \epsilon \leq \epsilon_{\max},\ N_L(\epsilon) = \sum_{n=0}^{N_{\max}} \fint_{\Gamma^*} \mathbb{1}_{\lambda_{L,n}(\mathbf{k})\leq\epsilon}\, \mathrm{d}\mathbf{k}\,.$$

Proposition 4.7 and the third step show that there exists $L_0 > 0$ such that the maps $L \in [0\,, L_0] \mapsto \lambda_{L,n}(\mathbf{k})$ are continuous for almost all $\mathbf{k}$ and for all $n \in \{0, \ldots, N_{\max}\}$. Hence, by the Lebesgue's dominated convergence theorem, we deduce that the map $(L, \epsilon) \in \mathbb{R}_+ \times \mathbb{R} \mapsto N_L(\epsilon)$ is continuous on $[0\,, L_0] \times (-\infty\,, \epsilon_{\max}]$. Since the map $L \mapsto \lambda_L$ is continuous in a neighborhood of 0, the same applies for $L \mapsto N_L(\lambda_L)$. Notice that $\lambda_0 = |\mathbf{K}_\star|^2$. We have

$$N_0(\lambda_0) = N_0(|\mathbf{K}_\star|^2) = 1 + \fint_{\Gamma^*} \mathbb{1}_{\lambda_{0,1}(\mathbf{k})\leq|\mathbf{K}_\star|^2}\, \mathrm{d}\mathbf{k} = \frac{\pi\,|\mathbf{K}_\star|^2}{|\Gamma^*|} = \frac{2\pi}{3\sqrt{3}} \simeq 1.21\text{`} > 1\,.$$

Hence, by monotony of $\epsilon \mapsto N_L(\epsilon)$, we must have $\epsilon_L < \lambda_L$ for all $L \geq 0$ small enough. This concludes the proof of Theorem 4.5. $\square$

Appendix A

Numerical estimation of the ionization threshold

In this appendix, we explain how to estimate by numerical methods the ionization threshold λ_c of the mono-atomic two-dimensional Hartree model when $V^{\mathrm{pp}} = 0$. After recalling the main properties of this model, we present and comment our numerical results. Afterwards, we show that $\lambda_c \le 13/6$. In the last section, we describe the discretization procedure we have implemented.

Contents

1 The two-dimensional Hartree model with three-dimensional Coulomb interactions

For $\lambda \ge 0$, we consider the following minimisation problem

$$I(\lambda) = \inf \left\{ \mathcal{E}(v) \,\middle|\, v \in H^1(\mathbb{R}^2) \quad \text{and} \quad \int_{\mathbb{R}^2} |v|^2 = \lambda \right\}, \tag{A.1}$$

where the energy functional is given, for all $v \in H^1(\mathbb{R}^2)$, by

$$\mathcal{E}(v) = \int_{\mathbb{R}^2} |\nabla v|^2 - \int_{\mathbb{R}^2} \frac{|v(x)|^2}{|x|} \,\mathrm{d}x + \frac{1}{2} \iint_{\mathbb{R}^2 \times \mathbb{R}^2} \frac{|v(x)|^2 \, |v(y)|^2}{|x-y|} \,\mathrm{d}x \,\mathrm{d}y \,. \tag{A.2}$$

We also introduce the relaxed minimization problem

$$I_{\le}(\lambda) = \inf \left\{ \mathcal{E}(v) \,\middle|\, v \in H^1(\mathbb{R}^2) \quad \text{and} \quad \int_{\mathbb{R}^2} |v|^2 \le \lambda \right\}.$$

The problem $I(\lambda)$ shares many properties with the Thomas-Fermi-von Weizsäcker (TFW) theory of atoms, see [BBL81; Lie81a] and also [CLM06, Chapitre 3]. The study of the TFW theory is more delicate because of an additional nonlinear term in the energy functional. Following these references, one can prove the following theorem.

Theorem A.1 (Properties of (A.1))**.** *We have the followings facts: there exists $\lambda_c \in [1\,, 13/6]$ such that map $\lambda \in \mathbb{R}_+ \mapsto I(\lambda)$ is convex and stricly decreasing on $[0\,, \lambda_c]$ and constant for $\lambda \geq \lambda_c$.*

(i) For all $\lambda \in [0\,, \lambda_c]$, we have:

(a) Up to a phase factor, the minimization problem $I(\lambda)$ admits a unique minimizer v_λ, which is radial;

(b) We have $v_\lambda \in \mathcal{D}\left(-\Delta - \frac{1}{|x|}\right)$ [1] and, up to a phase factor, we have $v_\lambda > 0$ everywhere;

(c) v_λ solves the following nonlinear Schrödinger equation

$$\left(-\Delta - \frac{1}{|\cdot|} + |v_\lambda|^2 * \frac{1}{|\cdot|}\right) v_\lambda = \mu_\lambda v_\lambda\,,$$

where $\mu_\lambda \in \mathbb{R}$ is a Lagrange multiplier satisfying

$$\mu_\lambda \begin{cases} < 0 & \text{for } 0 \leq \lambda < \lambda_c\,, \\ = 0 & \text{for } \lambda = \lambda_c\,; \end{cases}$$

(d) v_λ is also the unique minimizer for $I_{\leq}(\lambda)$, up to a phase factor;

(e) All minimizing sequences $\{v_n\}$ for $I(\lambda)$ (or $I_{\leq}(\lambda)$) are precompact in $H^1(\mathbb{R}^2)$;

(f) The map $\lambda \mapsto I(\lambda)$ is continuously differentiable on $[0\,, \lambda_c]$ and we have $\mu_\lambda = (I(\lambda))'(\lambda)$.

(ii) For all $\lambda > \lambda_c$, we have:

(a) There is no minimizer for $I(\lambda)$;

(b) $I_{\leq}(\lambda)$ admits v_{λ_c} as unique minimizer, up to a phase factor;

(c) If $\{v_n\}$ is a minimizing sequence for $I_{\leq}(\lambda)$ (or $I_{\leq}(\lambda)$) such that $v_n \geq 0$ for all n then $v_n \rightharpoonup v_{\lambda_c}$ weakly in $H^1(\mathbb{R}^2)$.

Some consequences of this theorem are summarized in a schematic view in Figure A.1.

In the three-dimensional case, it is proved in the thesis of Benguria [Ben79] that $\lambda_c \leq 2$. Thereafter, this bound has been generalized by Lieb to the N-body case [Lie84]. Recently, the upper bound $\lambda_c \leq 1.5211$ has been proved by Benguria and Tubino in [BT22], following arguments from Nam [Nam12]. In [BL83], Benguria and Lieb show that $\lambda_c \geq 1+\gamma$ for some $\gamma \in (0\,, 1)$ obtained by solving a Hartree equation. In [Bau84], Baumgartner gives the numerical estimation $\gamma \simeq 0.21$. Since it is relevant for our purpose, we show in Section 2 below the upper bound $\lambda_c \leq 13/6$ for the two-dimensional case. To this end, we adapt some of the arguments in [BT22].

Whereas it is also expected that $\lambda_c > 1$ in dimension two, there is no proof available in the literature and the arguments for the dimension three cannot be adapted. Indeed, they rely on Newton's theorem which implies

$$\frac{1}{|\cdot|} - \rho * \frac{1}{|\cdot|} \geq 0\,,$$

for all radial and positive measure ρ such that $\rho(\mathbb{R}^3) = 1$. In dimension two, odd degree terms appear in the multipole expansion of radial distributions. We have implemented a numerical estimation of λ_c by a direct resolution of the Hartree model. Our methods is described in Section 3. Our results for $N = 3000$ discretization points are exposed in Figure A.2. As expected, the energy $\lambda \mapsto I(\lambda)$ is non-increasing and convex while the Lagrange-multiplier curve $\lambda \mapsto \mu_\lambda$ is non-decreasing and converges to 0. The dashed green line corresponds to the energy of the linear problem, that is

$$\inf \left\{ \int_{\mathbb{R}^2} |\nabla v(x)|^2 \,\mathrm{d}x - \int_{\mathbb{R}^2} \frac{|v(x)|^2}{|x|} \,\mathrm{d}x \;\middle|\; v \in H^1(\mathbb{R}^2) \quad \text{and} \quad \int_{\mathbb{R}^2} |v|^2 = 1 \right\} = -1\,.$$

When λ reach 1.358, the energy curves attains a minima then start to slightly increase and the Lagrange multiplier becomes positive, meaning that our algorithm is probably losing accuracy.

1. Some properties of the space $\mathcal{D}\left(-\Delta - \frac{1}{|x|}\right)$ are given in Chapter 2. In particular, for all $\epsilon > 0$, we have $\mathcal{D}\left(-\Delta - \frac{1}{|x|}\right) \subset H^{2-\epsilon}(\mathbb{R}^2)$. See also [DŠT10] where the authors classify all the self-adjoint extensions of two-dimensional Schrödinger operators with hydrogen-like potential.

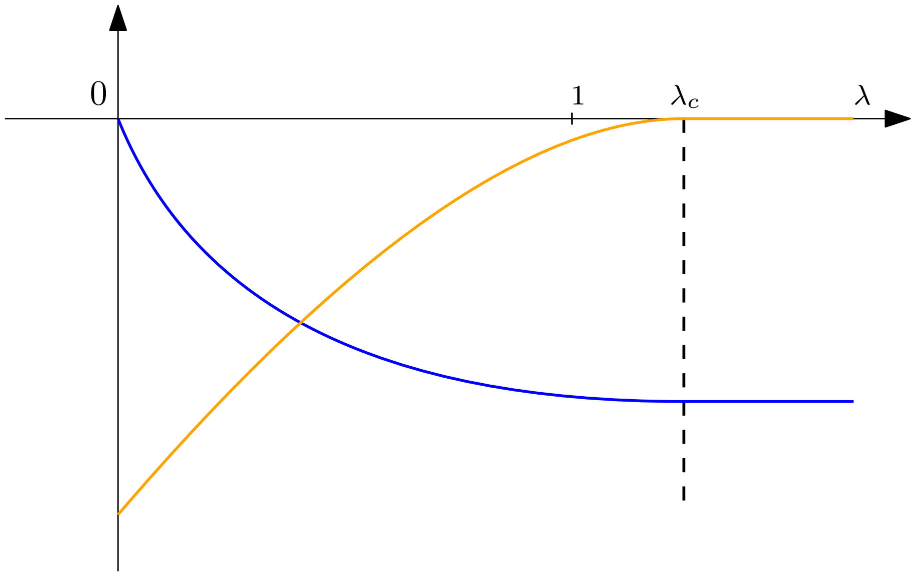


Figure A.1 – Schematic representation of the energy (blue) and the Euler-Lagrange multiplier (orange) as functions of λ.

Even if the results we have obtained support the conjecture $\lambda_c > 1$, they must be taken with care since our discretization is not very tight (only $N = 3000$ points). Note however that $1.358 < 8/3$.

2 Proof of the upper bound $\lambda_c \leq 13/6$

The proof follows the same arguments as in [BT22] where Benguria and Tubino consider the same model but in dimension three.

Let $\lambda < \lambda_c$. We decompose $I(\lambda) = \mathcal{E}(v_\lambda)$ as follows

$$I(\lambda) = K - C + D\,, \tag{A.3}$$

where

$$K := \int_{\mathbb{R}^2} |\nabla v_\lambda(x)|^2 \,\mathrm{d}x\,, \quad C := \int_{\mathbb{R}^2} \frac{|v_\lambda(x)|^2}{|x|}\,\mathrm{d}x \quad \text{and} \quad D := \frac{1}{2}\iint_{\mathbb{R}^2\times\mathbb{R}^2} \frac{|v_\lambda(x)|^2\,|v_\lambda(y)|^2}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y\,. \tag{A.4}$$

First step: We claim that the following relations hold

$$K = -I(\lambda)\,, \quad C = -3I(\lambda) + \mu_\lambda\lambda \quad \text{and} \quad D = -I(\lambda) + \mu_\lambda\lambda\,. \tag{A.5}$$

The Euler-Lagrange equation gives

$$\mu_\lambda\lambda = \left\langle \left(-\Delta - \frac{1}{|x|} + |v_\lambda|^2 * \frac{1}{|\cdot|}\right) v_\lambda, v_\lambda \right\rangle = K - C + 2D\,. \tag{A.6}$$

We get a third non equivalent relation via the Virial theorem. More precisely, for $t \geq 0$, we consider $v_\lambda^t(x) := t v_\lambda(tx)$ and we write the optimality condition $\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{E}(v_\lambda^t)_{|t=1} = 0$. This provides the following relation

$$2K - C + D = 0\,. \tag{A.7}$$

The relations (A.3), (A.6) and (A.7) form a linear system which is invertible. Its resolution furnishes the relations (A.5).

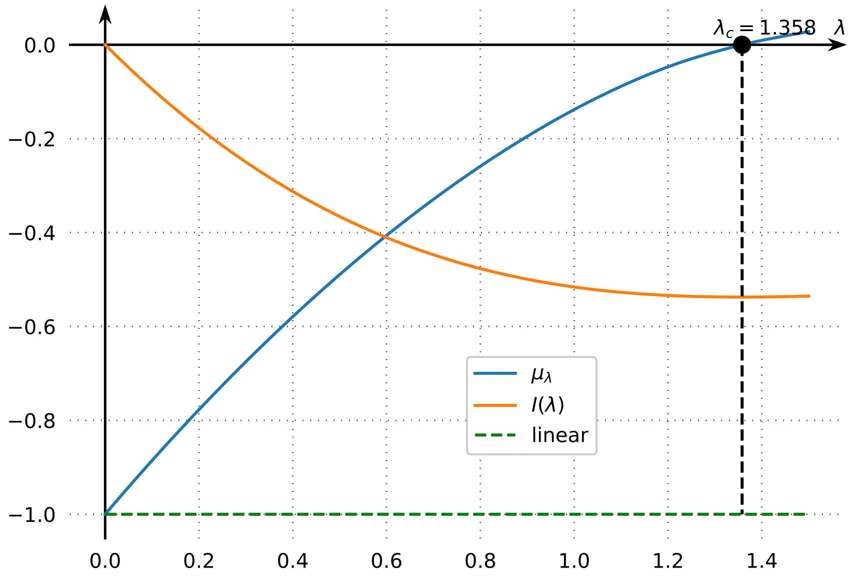


Figure A.2 – Energy and Lagrange multiplier with respect to λ are respectively represented by the blue curve and the orange curve. The black dashed line indicates the value of $\lambda_c \simeq 1,358$ while the green dashed line is the energy of the linear model, without the direct term. Here, the parameters are $a = 15$ and $N = 3000$, see Section 3.

Second step: We claim that for all $v \in H^1(\mathbb{R}^2)$, the following inequality holds

$$\int_{\mathbb{R}^2} \frac{|v(x)|^2}{|x|} \, \mathrm{d}x \leq \|\nabla v\|_{L^2(\mathbb{R}^2)} \|v\|_{L^2(\mathbb{R}^2)} \,. \tag{A.8}$$

For $v \in H^1(\mathbb{R}^2)$, we denote $v^t(x) := tv(tx)$. First, recall that the ground state of $-\Delta - |\cdot|^{-1}$ is -1. Hence, we can write

$$t^2 \int_{\mathbb{R}^2} |\nabla v(x)|^2 \, \mathrm{d}x - t \int_{\mathbb{R}^2} \frac{|v(x)|^2}{|x|} \, \mathrm{d}x = \int_{\mathbb{R}^2} \left|\nabla v^t(x)\right|^2 \mathrm{d}x - \int_{\mathbb{R}^2} \frac{|v^t(x)|^2}{|x|} \, \mathrm{d}x \geq - \int_{\mathbb{R}^2} |v(x)|^2 \, \mathrm{d}x \,. \tag{A.9}$$

Minimizing with respect to t the left side provides (A.8).

Third step: We claim that

$$\frac{1}{2}\lambda^2 - \lambda \leq \frac{1}{4} C \,, \tag{A.10}$$

with C the Coulomb energy in (A.4). To show this, we multiply the Euler-Lagrange equation by $|x| \, v_\lambda(x)$, which defines a $L^2(\mathbb{R}^2)$ function because v_λ is exponentially decaying since $\mu_\lambda < 0$, and we integrate to obtain

$$
\begin{aligned}
0 \geq \mu_\lambda \lambda &= \langle v_\lambda, |x|\,(-\Delta) v_\lambda \rangle_{L^2(\mathbb{R}^2)} - \lambda + \iint_{\mathbb{R}^2\times\mathbb{R}^2} \frac{|x|\,|u(x)|^2\,|u(y)|^2}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y \\
&= \langle v_\lambda, |x|\,(-\Delta) v_\lambda \rangle_{L^2(\mathbb{R}^2)} - \lambda + \frac{1}{2}\iint_{\mathbb{R}^2\times\mathbb{R}^2} \frac{|x|+|y|}{|x-y|}\,|u(x)|^2\,|u(y)|^2\,\mathrm{d}x\,\mathrm{d}y \\
&\geq \langle v_\lambda, |x|\,(-\Delta) v_\lambda \rangle_{L^2(\mathbb{R}^2)} - \lambda + \frac{\lambda^2}{2}\,.
\end{aligned}
\tag{A.11}
$$

Here, by a slight abuse of notation, we have denoted by $\langle v, |x|\,(-\Delta) v\rangle_{L^2(\mathbb{R}^2)}$ the quadratic form of $|x|\,(-\Delta)$ applied to some $v \in H^1(\mathbb{R}^2)$. Several integration by parts show that for all smooth enough and compactly supported radial function $v(x) = f(|x|)$, we have the identity

$$
\langle v, |x|\,(-\Delta) v\rangle_{L^2(\mathbb{R}^2)} = 2\pi \int_0^\infty \left((rf'(r))^2 - \frac{f(r)^2}{2} \right) \mathrm{d}r\,.
$$

For all $\alpha \in \mathbb{R}$, we write

$$
\begin{aligned}
\int_0^\infty (rf'(r))^2\,\mathrm{d}r &= \int_0^\infty (rf'(r) + \alpha f(r))^2\,\mathrm{d}r - 2\alpha \int_0^\infty rf(r)f'(r) - \alpha^2 \int_0^\infty f(r)^2\,\mathrm{d}r \\
&\geq (\alpha - \alpha^2) \int_0^\infty f(r)^2\,\mathrm{d}r\,.
\end{aligned}
$$

Optimizing with respect to α yields the inequality

$$
\langle v, |x|\,(-\Delta) v\rangle_{L^2(\mathbb{R}^2)} \geq -\frac{\pi}{2}\int_0^\infty f(r)^2\,\mathrm{d}r = -\frac{1}{4}\int_{\mathbb{R}^2} \frac{|v(x)|^2}{|x|}\,\mathrm{d}x\,.
$$

Using the same limiting procedure as in [Lie81a, Lemma 7.20], we can replace v by v_λ to get

$$
\langle v_\lambda, |x|\,(-\Delta) v_\lambda\rangle_{L^2(\mathbb{R}^2)} \geq -\frac{1}{4}\int_{\mathbb{R}^2} \frac{|v_\lambda(x)|^2}{|x|}\,\mathrm{d}x\,. \tag{A.12}
$$

Inserting (A.12) in (A.11) gives (A.10).

Fourth step: We claim that $\lambda_c < \infty$. Since $-\Delta - |\cdot|^{-1} \geq -1$, we have $I(\lambda) \geq -\lambda$. Then, by the second relation in (A.5) and the fact $\mu_\lambda \leq 0$, we get

$$
C = -3I(\lambda) + \mu_\lambda \lambda \leq 3\lambda\,.
$$

Inserting this estimate in (A.10) shows that for all $\lambda < \lambda_c$ we have $\frac{1}{2}\lambda^2 - \lambda \leq \frac{3}{4}\lambda$. Hence $\lambda_c \leq 7/2 < \infty$.

Fifth step: We claim that $\lambda_c \leq 8/3$. Since $\lambda_c < \infty$, we can take the limit $\lambda \to \lambda_c$ in the relations (A.5). In particular, for $\lambda = \lambda_c$, we obtain the identity $K = 3C$. Now, from (A.8), we also have $C \leq 2\sqrt{\lambda_c K}$. We deduce that $\sqrt{K} \leq \frac{2}{3}\sqrt{\lambda_c}$ then $C \leq \frac{1}{3}\lambda_c$. Inserting this last estimate in (A.10) (which is satisfied for $\lambda = \lambda_c$ by continuity), we obtain $\lambda_c \leq 13/6$.

3 Discretization procedure

In this section, we explain how we have discretized the minimization problem $I(\lambda)$.

Restriction to radial functions Since the solution is radial, we can reduc the dimension by restricting the minimization. We recall that

$$m \in [0\,,1] \longmapsto K(m) = \int_0^{\frac{\pi}{2}} \frac{\mathrm{d}\theta}{\sqrt{1 - m\sin^2(\theta)}}\,,$$

is the complete elliptic integral of first kind [AS64]. In the next lemma, we use this special function to represent convolutions of the form $|v|^2 * |\cdot|^{-1}$ where v is a radial function which decays fast enough at infinity.

Lemma A.2 (Representation formula for convolution of radial functions)**.** *Let $v(x) = f(|x|)$ be a radial function on $\mathbb{R}^2$ such that $|f(r)| = O\big(r^{-1-\epsilon}\big)$ for some $\epsilon > 0$. Then, we have the representation formula*

$$\boxed{\left(|v|^2 * \frac{1}{|\cdot|}\right)(x) = \frac{1}{|x|}\int_0^\infty |f(s)|^2\, G(|x|\,,s)\,\mathrm{d}s\,,}$$

where the kernel G is symmetric and defined by

$$\forall r \neq s, \quad G(r,s) = \frac{4rs}{r+s} K\left(\frac{4rs}{(r+s)^2}\right)\,.$$

This representation formula is convenient since there exists ready-to-use and efficient methods to compute the integral $K(m)$ in the Python package `scipy.special`.

Proof of Lemma A.2. With the assumptions on v, the convolution $|v|^2 * |\cdot|^{-1}$ is well-defined and a change of variables shows it is also radial. Let $\mathbf{e}_1 = (1, 0)$. For $r > 0$, we write

$$\begin{aligned}\left(|v|^2 * \frac{1}{|\cdot|}\right)(r\mathbf{e}_1) &= \int_{\mathbb{R}^2} \frac{|v(y)|^2}{|r\mathbf{e}_1 - y|}\,\mathrm{d}y = \int_0^\infty s\,|f(s)|^2 \left(\int_{-\pi}^{\pi} \frac{\mathrm{d}\theta}{\sqrt{r^2+s^2+2rs\cos(\theta)}}\right)\mathrm{d}s \\ &= 2\int_0^\infty \frac{s\,|f(s)|^2}{\sqrt{r^2+s^2}}\left(\int_0^\pi \frac{\mathrm{d}\theta}{\sqrt{1+\frac{2rs}{r^2+s^2}\cos(\theta)}}\right)\mathrm{d}s \\ &= 4\int_0^\infty \frac{s\,|f(s)|^2}{r+s} K\left(\frac{4rs}{(r+s)^2}\right)\,.\end{aligned}$$

This concludes the proof of Lemma A.2. ☐

We denote by

$$D(|v|^2\,,|v|^2) = \iint_{\mathbb{R}^2\times\mathbb{R}^2} \frac{|v(x)|^2\,|v(y)|^2}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y\,,$$

the direct term in the Hartree energy functional (A.2). Then, Lemma A.2 implies that, for any radial function $v(x) = f(|x|)$ such that $|f(r)| = O\big(r^{-1-\epsilon}\big)$ for some $\epsilon > 0$, we have

$$\boxed{D\left(|v|^2\,,|v|^2\right) = 2\pi\int_0^\infty\int_0^\infty |f(r)|^2\,|f(s)|^2\,G(r,s)\,\mathrm{d}r\,\mathrm{d}s\,.} \tag{A.13}$$

We denote by $\mathcal{H}^1$ the space

$$\mathcal{H}^1 = \left\{f \in L^2(\mathbb{R}_+)\;\middle|\;\int_0^\infty r\,|f'(r)|^2\,\mathrm{d}r < \infty\right\}\,.$$

Using identity (A.13) and the fact that $\mathcal{C}_c^\infty(\mathbb{R}_+)$ is dense in $\mathcal{H}^1$, one can show that the restrictriction of the minimization problem $I(\lambda)$ to radial functions is equivalent to the following minimization problem

$$\boxed{J(\lambda) = 2\pi \times \inf\left\{\mathcal{F}(f)\;\middle|\; f\in\mathcal{H}^1 \quad \text{and} \quad 2\pi\int_0^\infty r\,|f(r)|^2\,\mathrm{d}r = \lambda\right\},} \tag{A.14}$$

where the energy functional $\mathcal{F}$ reads

$$\mathcal{F}(f) = \int_0^\infty r\,|f'(r)|^2\,\mathrm{d}r - \int_0^\infty |f(r)|^2\,\mathrm{d}r + \frac{1}{2}\int_0^\infty\int_0^\infty |f(r)|^2|f(s)|^2 G(r,s)\,\mathrm{d}r\,\mathrm{d}s\,.$$

Galerkin approximation In order to numerically solve the minimization problem $J(\lambda)$, we use the *Galerkin approximation* [CLM06]. We consider $\mathcal{V}\subset\mathcal{H}^1$ a subspace of finite dimension N and a basis $\{\chi_n\}_{1\le n\le N}$ of $\mathcal{V}$. The Galerkin approximation consists in approaching the problem (A.14) by the minimization problem

$$\inf\left\{\mathcal{F}(f)\;\middle|\; f\in\mathcal{V} \quad \text{and} \quad 2\pi\int_0^\infty r\,|f(r)|^2\,\mathrm{d}r = \lambda\right\}. \tag{A.15}$$

We rewrite each terms with respect to the decomposition $f = \sum_{n=1}^N f_n\chi_n \in \mathcal{V}$. The constraint in (A.15) is equivalent to

$$2\pi\sum_{n,m=1}^N f_n f_m \int_0^\infty r\chi_n(r)\chi_m(r)\,\mathrm{d}r = \lambda\,,$$

and the energy of f is given by

$$\begin{aligned}\mathcal{F}(f) = \sum_{n,m=1}^N f_n f_m &\left(\int_0^\infty r\chi_n'(r)\chi_m'(r)\,\mathrm{d}r - \int_0^\infty \chi_n(r)\chi_m(r)\,\mathrm{d}r\right)\\ &+\frac{1}{2}\sum_{n,m,\ell,k=1}^N f_n f_m f_\ell f_k \int_0^\infty\int_0^\infty \chi_n(r)\chi_m(r)\chi_\ell(s)\chi_k(s)G(r,s)\,\mathrm{d}r\,\mathrm{d}s\,.\end{aligned}$$

We form the $N\times N$ matrices $\mathbf{A}$ and $\mathbf{B}$ as

$$\mathbf{A}_{nm} = \int_0^\infty r\chi_n'(r)\chi_m'(r)\,\mathrm{d}r - \int_0^\infty \chi_n(r)\chi_m(r)\,\mathrm{d}r \quad \text{and} \quad \mathbf{B}_{nm} = \int_0^\infty r\chi_n(r)\chi_m(r)\,\mathrm{d}r\,,$$

and we denote by $(nm\mid \ell k)$ the bielectronic coefficients, defined by

$$(nm\mid\ell k) = \int_0^\infty\int_0^\infty \chi_n(r)\chi_m(r)\chi_\ell(s)\chi_k(s)G(r,s)\,\mathrm{d}r\,\mathrm{d}s\,.$$

We collect all the components of f in the basis $\{\chi_n\}_{1\le n\le N}$ in a vector, denoted by $\mathbf{f} = (f_n)_{1\le n\le N} \in \mathbb{R}^N$. Then, the direct term can be re-express as

$$D(|f|^2, |f|^2) = \mathrm{Tr}\left(\mathbf{J}\left(\mathbf{f}\cdot\mathbf{f}^T\right)\cdot\mathbf{f}\cdot\mathbf{f}^T\right)\,,$$

where $\cdot$ is the matrix multiplication and where the $N\times N$ matrix $\mathbf{J}\left(\mathbf{f}\cdot\mathbf{f}^T\right)$ is defined by

$$\left[\mathbf{J}\left(\mathbf{f}\cdot\mathbf{f}^T\right)\right]_{nm} = \sum_{\ell,k=1}^N f_\ell f_k\,(nm\mid\ell k)\,.$$

Finally, the Galerkin approximation (A.15) is equivalent to the following discretized minimization problem

$$\boxed{\inf_{\mathbf{f}\in\mathbb{R}^N} \left\{\mathbf{F}(\mathbf{f}) \mid 2\pi q_{\mathbf{B}}(\mathbf{f}) = \lambda\right\}\,.}$$

where the $q_{\mathbf{B}}(\mathbf{f}) = \mathrm{Tr}(\mathbf{B}\cdot\mathbf{f}\cdot\mathbf{f}^T)$ and where the discretized energy functional is given by

$$\mathbf{F}(\mathbf{f}) = \mathrm{Tr}\left(\left(\mathbf{A} + \frac{1}{2}\mathbf{J}\left(\mathbf{f}\cdot\mathbf{f}^T\right)\right)\cdot\mathbf{f}\cdot\mathbf{f}^T\right)\,.$$

Choice of the reduced basis and periodization We consider a number $a > 0$, an integer $N \in \mathbb{N}\setminus\{0,1\}$ and the regular grid on the interval $[0\,,a]$ defined as the collection of the points

$$\forall 1 \leq n \leq N, \quad x_n = \epsilon(n-1/2) \quad \text{where} \quad \epsilon = \frac{2a}{N-1}\,.$$

We use the simplest choice of reduced basis, that is, the piecewise constant functions

$$\chi_n(r) = \mathbb{1}_{[x_n-\frac{\epsilon}{2},x_n+\frac{\epsilon}{2}]}(r)\,.$$

We periodize the problem by extending this grid to the interval $[-a\,,0]$ with the relation $\chi_{-n}(r) = \chi_n(-r)$. Hence, our grid contains $2N$ points. The periodization increases the complexity but, while testing the code, it has provided better results. With this choice, the matrix $\mathbf{B}$ is diagonal and its coefficients are given by

$$\mathbf{B}_{nn} = \epsilon x_n\,.$$

To approach the coefficient of $\mathbf{A}$, we use the central finite difference method [2]

$$f'(x_n) \simeq \frac{f(x_{n+1}) - f(x_{n-1})}{2\epsilon}\,.$$

This leads to

$$\mathbf{A} \simeq \mathbf{D}^T\mathbf{B}\mathbf{D} - \epsilon I_N \quad \text{with} \quad \mathbf{D} = \frac{1}{2\epsilon}\begin{pmatrix} 0 & 1 & 0 & \cdots & 0 & -1 \\ -1 & 0 & 1 & \ddots & & 0 \\ 0 & -1 & \ddots & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ 0 & & \ddots & \ddots & \ddots & 1 \\ 1 & 0 & \cdots & 0 & -1 & 0 \end{pmatrix},$$

where I_N is the $2N\times 2N$ identity matrix and where we have implemented the periodic boundary conditions. The bielectronic coefficients mostly vanish. Indeed we have

$$(nm \mid \ell k) = \begin{cases} 0 & \text{if } n \neq m \text{ or } \ell \neq k\,, \\ \mathbf{G}_{n\ell} & \text{if } n = m \text{ and } \ell = k\,, \end{cases}$$

where the diagonal terms of the $2N\times 2N$ matric $\mathbf{G}$ are given by

$$\mathbf{G}_{nn} = \begin{cases} \int_{x_n-\frac{\epsilon}{2}}^{x_n+\frac{\epsilon}{2}}\int_{x_\ell-\frac{\epsilon}{2}}^{x_\ell+\frac{\epsilon}{2}} G(r,s)\,\mathrm{d}r\,\mathrm{d}s & \text{if } n \geq 1\,, \\ \mathbf{G}_{|n||n|} & \text{if } n \leq -1\,, \end{cases}$$

2. In the actual implementations, we use more accurate higher order central finite difference coefficients:

$$f'(x_n) \simeq \frac{-f(x_{n+2}) + 8f(x_{n+1}) - 8f(x_{n-1}) + f(x_{n-2})}{12\epsilon}\,.$$

and where the off-diagonal coefficients of $\mathbf{G}$ are approached by the punctual values of G:

$$\forall n \neq \ell, \quad \mathbf{G}_{n\ell} = \begin{cases} \epsilon^2 G(x_n, x_\ell) & \text{if } n, \ell \geq 1\,, \\ \mathbf{G}_{|n||\ell|} & \text{otherwise}\,. \end{cases}$$

Because $G(r,s)$ has a logarithmic singularity at the diagonal $r = s$, we cannot do the same for the diagonal coefficients. We use the asymptotic $K(m) \simeq -\frac{1}{2}\log(1-m)$ when $m \to 1$ (see [Olv+, Eq. (19.12.1)]) to approach them, which leads to

$$\mathbf{G}_{nn} \simeq \int_{x_n-\frac{\epsilon}{2}}^{x_n+\frac{\epsilon}{2}} \int_{x_n-\frac{\epsilon}{2}}^{x_n+\frac{\epsilon}{2}} \frac{4rs}{r+s} \log\left|\frac{r+s}{r-s}\right| \mathrm{d}r\,\mathrm{d}s\,.$$

The direct term can be rewrote as

$$\mathrm{Tr}\left(\mathbf{J}\left(\mathbf{f}\cdot\mathbf{f}^T\right)\cdot\mathbf{f}\cdot\mathbf{f}^T\right) = \mathrm{Tr}\left(\mathbf{G}\cdot\mathbf{g}\cdot\mathbf{g}^T\right)\,,$$

where $\mathbf{g} \coloneqq \{|f_n|^2\}_{1\leq n\leq N}$. In the same spirit, the convolution $|v|^2 * |\cdot|^{-1}$ is approached by $\widetilde{\mathbf{G}}\cdot\mathbf{g}$ where $\widetilde{\mathbf{G}}$ is the $2N\times 2N$ matrix defined by

$$\widetilde{\mathbf{G}}_{n\ell} = \begin{cases} \epsilon G(x_n, x_\ell) & \text{if } n \neq \ell \text{ and } n, \ell \geq 1\,, \\ \frac{1}{x_n}\int_{x_n-\epsilon/2}^{x_n+\epsilon/2} G(x_n, s)\,\mathrm{d}s & \text{if } n = \ell \geq 1\,, \\ \widetilde{\mathbf{G}}_{|n||\ell|} & \text{otherwise}\,. \end{cases}$$

Algorithm 1 Solve $I(\lambda)$

Initialize with $\mathbf{f}^0$ an ansatz , $\tau > 0$ a tolerance parameter and $\lambda > 0$;
while $\left\|\mathbf{f}^k - \mathbf{f}^{k-1}\right\| \geq \tau$ **do**
  Compute the convolution $\widetilde{\mathbf{G}}\cdot\mathbf{g}^k$ where $\mathbf{g^k} \coloneqq \{\left|f_n^k\right|^2\}_{1\leq n\leq N}$;
  $\mathbf{H}^k \leftarrow \mathbf{A} + \mathtt{diag}(\widetilde{\mathbf{G}}\cdot\mathbf{g}^k)$;
  $(\tilde{\mathbf{f}}^{k+1}, \mu^k) \leftarrow$ eigenvector/eigenvalue solution of the generalized eigenvalue problem

$$\inf_{\mathbf{f}\in\mathbb{R}^N} \left\{\left\langle \mathbf{f}, \mathbf{H}^k\mathbf{f}\right\rangle \;\middle|\; 2\pi q_{\mathbf{B}}(\mathbf{f}) = \lambda\right\}\,;$$

  $\mathbf{f}^{k+1} \leftarrow$ solution of the minimization problem

$$\inf_{t\in[0,1]} \mathcal{F}\left(\frac{(1-t)\mathbf{f}^k + t\tilde{\mathbf{f}}^{k+1}}{\sqrt{2\pi q_{\mathbf{B}}\left((1-t)\mathbf{f}^k + t\tilde{\mathbf{f}}^{k+1}\right)}}\right)\,.$$

end while

$\mu^k \leftarrow \inf_{\mathbf{f}\in\mathbb{R}^N}\left\{\left\langle \mathbf{f}, \mathbf{H}^k\mathbf{f}\right\rangle \;\middle|\; 2\pi q_{\mathbf{B}}(\mathbf{f}) = \lambda\right\}$;

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Systèmes quantiques non linéaires en dissociation
L'exemple du graphène

Résumé

Cette thèse porte sur l'étude mathématique des propriétés électroniques de la matière. Les systèmes, moléculaires ou cristallins, sont décrits à l'aide de modèles non linéaires issus de la mécanique quantique. On considère alors le régime de dissociation, c'est-à-dire lorsque les distances entre les noyaux sont grandes. Dans le Chapitre 1, on étudie le modèle de Hartree diatomique, en dimension deux ou trois, et on quantifie précisément l'effet tunnel entre les deux premiers modes propres. Dans le Chapitre 2, on montre que si une condition de non-dégénérescence est vérifiée alors le modèle de Hartree-Fock réduit du graphène présente des singularités coniques, appelées *points de Dirac*. De plus, on prouve que le niveau de Fermi coïncide avec le niveau d'énergie de ces cônes. Pour cela, on dérive certaines conditions sous lesquelles les relations de dispersion d'un opérateur de Schrödinger périodique sont données, au premier ordre et dans le régime de dissociation, par le modèle de liaison forte correspondant.

Mots clés : opérateurs de Schrödinger périodiques, analyse non linéaire, graphène, Hartree-Fock, points de Dirac

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Nonlinear quantum systems at dissociation
The example of graphene

Abstract

This thesis is devoted to the mathematical study of electronic properties of matter. The systems, both molecular and crystalline, are described by nonlinear models coming from quantum mechanics. Then, we consider the dissociation regime, that is when the distances between the nuclei are large. In Chapter 1, we study the diatomic Hartree model, both in dimension two and three, and we precisely estimate the quantum tunneling between the first two eigenfunctions. In Chapter 2, we show that if a non-degeneracy condition is satisfied then the reduced Hartree-Fock model of graphene presents conical singularities, called *Dirac points*. In addition, we show that the Fermi level coincides with the energy of these cones. In this direction, we derive conditions under which the dispersion relation of periodic Schrödinger operator is given, to leading order and in the dissociation regime, by the corresponding tight-binding model.

Keywords: periodic Schrödinger operators, nonlinear analysis, graphene, Hartree-Fock, Dirac points

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Centre De Recherche en Mathématiques de la Décision, Université Paris-Dauphine
Place du Maréchal De Lattre De Tassigny – 75016 Paris – France

RÉSUMÉ

Cette thèse porte sur l'étude mathématique des propriétés électroniques de la matière. Les systèmes, moléculaires ou cristallins, sont décrits à l'aide de modèles non linéaires issus de la mécanique quantique. On considère alors le régime de dissociation, c'est-à-dire lorsque les distances entre les noyaux sont grandes. Dans le Chapitre 1, on étudie le modèle de Hartree diatomique, en dimension deux ou trois, et on quantifie précisément l'effet tunnel entre les deux premiers modes propres. Dans le Chapitre 2, on montre que si une condition de non-dégénérescence est vérifiée alors le modèle de Hartree-Fock réduit du graphène présente des singularités coniques, appelées *points de Dirac*. De plus, on montre que le niveau de Fermi coïncide avec le niveau d'énergie de ces cônes. Pour cela, on dérive certaines conditions sous lesquelles les relations de dispersion d'un opérateur de Schrödinger périodique sont données, au premier ordre et dans le régime de dissociation, par le modèle de liaison forte correspondant.

MOTS CLÉS

Opérateurs de Schrödinger périodiques, analyse non linéaire, graphène, Hartree-Fock, points de Dirac

ABSTRACT

This thesis is devoted to the mathematical study of electronic properties of matter. The systems, both molecular and crystalline, are described by nonlinear models coming from quantum mechanics. Then, we consider the dissociation regime, that is when the distances between the nuclei are large. In Chapter 1, we study the diatomic Hartree model, both in dimension two and three, and we precisely estimate the quantum tunneling between the first two eigenfunctions. In Chapter 2, we show that if a non-degeneracy condition is satisfied then the reduced Hartree-Fock model of graphene presents conical singularities, called *Dirac points*. In addition, we show that the Fermi level coincides with the energy of these cones. In this direction, we derive conditions under which the dispersion relation of periodic Schrödinger operator is given, to leading order and in the dissociation regime, by the corresponding tight-binding model.

KEYWORDS

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