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THÈSE DE DOCTORAT

DE L'UNIVERSITÉ PSL

Préparée à Université Paris-Dauphine

**Contributions mathématiques à
la théorie des fonctionnelles de la densité**

Soutenue par

Louis GARRIGUE

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Dauphine**

Spécialité

Mathématiques

Composition du jury :

Xavier BLANC Professeur des universités, Université Paris-Diderot	<i>Rapporteur</i>
Robert SEIRINGER Professeur des universités, IST Austria	<i>Rapporteur</i>
Éric CANCÈS Professeur, Cermics, École des Ponts ParisTech	<i>Examineur, président du jury</i>
Virginie EHLACHER Chargée de recherche, Cermics, École des Ponts ParisTech	<i>Examineur</i>
Vladimir GEORGESCU Professeur émérite, Université de Cergy-Pontoise	<i>Examineur</i>
Julien TOULOUSE Maître de conférences, Université de la Sorbonne	<i>Examineur</i>
Mathieu LEWIN Directeur de recherche CNRS, Université Paris-Dauphine	<i>Directeur de thèse</i>

Abstract in English: Density functional theory (DFT) is the most efficient method to model matter at the microscopic scale. Its range of applicability is very wide, covering atoms, molecules, solids, fluids. Despite its tremendous success in physics and quantum chemistry, few mathematical works were devoted to its rigorous foundations. The goal of this PhD thesis is to address the main ones. We analyze mathematical aspects about the Hohenberg-Kohn theorem, about the potential-to-density map, and about the Kohn-Sham inversion procedure.

Résumé en français : La théorie de la fonctionnelle de la densité est la méthode la plus efficace pour modéliser la matière quantique à l'échelle microscopique. Son champ d'applications est très large, il couvre les atomes, molécules, solides, fluides. Malgré son éclatant succès en physique et chimie quantique, peu de travaux mathématiques ont porté sur ses fondations. L'objectif de cette thèse a été d'étudier les principales questions liées aux fondements de la théorie. Nous avons traité certaines questions mathématiques autour du théorème de Hohenberg-Kohn, analysé les propriétés de l'application des potentiels vers les densités des états fondamentaux, et avons enfin étudié le problème inverse de Kohn-Sham.

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Chapitre 0

Introduction

0.1 Présentation de la DFT

La Théorie de la fonctionnelle de la densité, Density Functional Theory (DFT) en anglais, est une approche de la mécanique quantique décrivant N particules qui se donne pour but d'exprimer toutes les quantités physiques en fonction de la densité à un corps, autant que faire se peut. En physique, les méthodes effectives à un corps sont très courantes car elles permettent de remplacer des problèmes complexes en problèmes plus simples presque indépendants du nombre de variables. C'est par exemple le cas de l'approximation de "champ moyen" [20, 39]. Ils sont extensivement utilisés car très efficaces pratiquement, et présents dans des disciplines très variées, comme la mécanique statistique classique, la mécanique quantique, la dynamique des trous noirs, etc [4, 12, 18, 21]. La DFT est aujourd'hui la méthode la plus efficace pour simuler la matière au niveau microscopique. Elle s'applique à des situations très diverses : atomes, molécules, solides, noyaux atomiques, fluides classiques et quantiques. Des introductions à la DFT sont présentées d'un point de vue physique dans [8, 9], et dans [5, 33] d'un point de vue mathématique. Les documents [25, 27] présentent également certaines propriétés mathématiques de la DFT.

Dans cette section nous introduisons le contexte physico-mathématique puis présentons les principaux paradigmes qui fondent la DFT.

0.1.1 Contexte physique

Nous considérerons la DFT du point de vue de la physique atomique, bien qu'elle s'applique également à la physique nucléaire et aux plasmas, entre autres. Les particules en jeu sont donc les noyaux atomiques et les électrons. Par ailleurs, nous nous plaçons dans l'approximation non-relativiste. Les protons et neutrons étant de l'ordre de 10^3 fois plus lourds que les électrons, l'approximation de Born-Oppenheimer justifie un traitement classique des noyaux, et constitue une approximation très précise. Nous considérerons

l'espace Euclidien \mathbb{R}^d de dimension $d \geq 1$, appelé espace libre, ou bien des systèmes confinés dans un domaine borné avec conditions de Dirichlet. Nous nous plaçons dans le système d'unités suivant

$$2m_e = \hbar = \frac{e^2}{4\pi\epsilon_0} = 1,$$

où m_e est la masse de l'électron, $-e$ est la charge électrique de l'électron, \hbar est la constante de Planck et enfin ϵ_0 est la constante de Coulomb. Notons $w \in L^1_{\text{loc}}(\mathbb{R}^d, \mathbb{R})$ l'interaction entre les électrons, qui est bien sûr $|\cdot|^{-1}$, mais que nous prenons sous forme générale pour les résultats présentés. Considérons un exposant réel p qui sera choisi en fonction de la situation. En réponse à un champ électrique extérieur classique, découlant du potentiel $v \in (L^p + L^\infty)(\mathbb{R}^d, \mathbb{R})$, les N électrons du système sont pilotés par le Hamiltonien

$$H^N(v) := - \sum_{i=1}^N \Delta_i + \sum_{1 \leq i < j \leq N} w(x_i - x_j) + \sum_{i=1}^N v(x_i).$$

Dans notre cadre atomique et moléculaire, le potentiel Coulombien créé par les noyaux est de la forme

$$v(x) = - \sum_{i=1}^M \frac{Z_i}{|x - R_i|},$$

où $M \in \mathbb{N}$ est le nombre de noyaux, les $Z_i \in \mathbb{N}$ sont leurs charges, et enfin $R_i \in \mathbb{R}^d$ sont leurs positions. Nous n'incluons pas l'énergie d'interaction entre noyaux $\sum_{1 \leq i < j \leq M} Z_i Z_j / |R_i - R_j|$, puisque sous l'approximation de Born-Oppenheimer celle-ci est une constante indépendante de la configuration électronique. En DFT standard, seul l'état électronique fondamental est pris en compte, puisque la différence d'énergie typique entre le fondamental et le premier état excité est de l'ordre de l'électron-volt, alors que l'énergie thermique d'une salle à 20°C est de l'ordre de $2,5 \cdot 10^{-2} eV$. La distribution de Boltzmann exponentielle montre que le fondamental domine largement l'occupation des états.

Un axiome de la théorie des champs quantiques établit que toutes les particules proviennent de l'excitation d'une toile de fond universelle, et sont donc indiscernables. L'indiscernabilité est le fait que la quantité observable $|\Psi|^2$ doit être invariante sous changement des indices des particules. Les seules représentations algébriques sont les représentations fermioniques et bosoniques. Il s'avère que les particules élémentaires de matière, comprenant les électrons, respectent la première possibilité. Nos états sont donc antisymétriques, c'est-à-dire que pour toute permutation σ de $\{1, \dots, N\}$, on doit travailler avec la contrainte

$$\Psi(x_{\sigma(1)}, \dots, x_{\sigma(N)}) = \epsilon(\sigma) \Psi(x_1, \dots, x_N),$$

où $\epsilon(\sigma)$ est la signature de la permutation. L'état des N particules de matière est donc représenté par une fonction d'onde

$$\Psi \in L_a^2 \left((\mathbb{R}^d)^N \right) := \bigwedge_{i=1}^N L^2 \left(\mathbb{R}^d, \mathbb{C}^q \right),$$

où $q \geq 1$ est le spin, égal à 2 pour les électrons. Cependant, nous considéreront la plupart du temps $q = 1$, c'est-à-dire des systèmes sans spin, car ceci affecte peu les résultats présentés, tout en alourdissant les notations. Rappelons que les degrés de liberté de spin apparaissent lors de la recherche de représentations de l'algèbre de Lorenz, implémentant le principe de relativité.

Les observables $|\Psi|^2$ sont des densités volumiques de probabilité de présence des électrons, la normalisation est donc $\int |\Psi|^2 = 1$. L'énergie d'un état $\Psi \in L_a^2(\mathbb{R}^{dN})$ plongé dans le potentiel extérieur v est alors $\langle \Psi, H^N(v)\Psi \rangle$. L'état fondamental est donné par le problème de minimisation

$$E^N(v) := \inf_{\substack{\Psi \in L_a^2(\mathbb{R}^{dN}) \\ \int |\Psi|^2 = 1}} \langle \Psi, H^N(v)\Psi \rangle, \quad (1)$$

compris au sens des formes quadratiques. Le minimum est l'énergie fondamentale, et les minimiseurs, s'ils existent, sont les états fondamentaux, atteints lorsque le système est à l'équilibre. Lorsque $N \gtrsim 10$, ce problème de minimisation est absolument hors de portée des ordinateurs classiques actuels, et le restera certainement encore au moins quelques dizaines d'années d'après les spécialistes.

Définissons des quantités réduites de ces fonctions d'onde [31]. Considérons la matrice densité à un corps, dont le noyau intégral est défini par

$$\gamma_\Psi(x, y) := N \int_{\mathbb{R}^{d(N-1)}} \Psi(x, x_2, \dots, x_N) \overline{\Psi(y, x_2, \dots, x_N)} dx_2 \cdots dx_N, \quad (2)$$

et est vue comme un opérateur sur $L^2(\mathbb{R}^{dN})$. Des calculs utilisant la symétrie de $|\Psi|^2$ montrent que l'énergie cinétique peut s'exprimer seulement avec elle, c'est-à-dire

$$\left\langle \Psi, \left(\sum_{i=1}^N -\Delta_i \right) \Psi \right\rangle = \text{Tr} (-\Delta \gamma_\Psi).$$

L'énergie d'interaction s'exprime uniquement via la densité de paire

$$\rho_\Psi^{(2)}(x, y) := \frac{N(N-1)}{2} \int_{\mathbb{R}^{d(N-2)}} |\Psi|^2(x, y, x_3, \dots, x_N) dx_3 \cdots dx_N, \quad (3)$$

par la relation

$$\left\langle \Psi, \left(\sum_{1 \leq i < j \leq N} w(x_i - x_j) \right) \Psi \right\rangle = \int_{\mathbb{R}^{2d}} w(x - y) \rho_\Psi^{(2)}(x, y) dx dy. \quad (4)$$

Enfin, l'énergie de couplage entre les électrons et le potentiel électrique extérieur peut s'écrire en fonction de la densité à un corps, ou densité

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

par la relation

$$\left\langle \Psi, \left(\sum_{i=1}^N v(x_i) \right) \Psi \right\rangle = \int_{\mathbb{R}^d} v \rho_{\Psi}. \quad (5)$$

La relation (5) est fondamentale en DFT, elle montre qu'un système est couplé à un potentiel extérieur seulement par la densité ρ_{Ψ} . En revanche, la matrice densité à un corps et la densité de paire contiennent strictement plus d'information que la densité, puisque

$$\rho_{\Psi}(x) = \frac{2}{N-1} \int_{\mathbb{R}^d} \rho_{\Psi}^{(2)}(x, y)_{\mathbb{R}^d} dy = \gamma_{\Psi}(x, x).$$

Les énergies internes, cinétique et d'interaction, ne peuvent pas d'exprimer avec la densité à un corps seulement.

0.1.2 Le modèle de Thomas-Fermi

L'approche en densité prend ses racines dans les débuts du développement de la mécanique quantique, quand Llewellyn Thomas et Enrico Fermi présentent indépendamment en 1927 [10, 36] une approximation de l'énergie d'un système électronique, décrivant l'état fondamental, uniquement par la densité. Leur fonctionnelle d'énergie est

$$\mathcal{E}_v^{\text{TF}}(\rho) = c_{\text{TF}} \int_{\mathbb{R}^3} \rho^{\frac{5}{3}} + \frac{1}{2} \int_{\mathbb{R}^6} \frac{\rho(x)\rho(y)}{|x-y|} dx dy + \int_{\mathbb{R}^3} v \rho,$$

pour $w = |\cdot|^{-1}$. La minimisation de cette fonctionnelle sur l'ensemble des fonctions $\rho \in (L^1 \cap L^3)(\mathbb{R}^3)$ mène à une énergie fondamentale proche de l'exact dans certaines situations, par exemple pour les atomes lourds [32]. L'énergie de couplage avec le potentiel extérieur, $\int v \rho$, reste exacte, le terme $c_{\text{TF}} \int \rho^{\frac{5}{3}}$ est une approximation de l'énergie cinétique fermionique, et le terme $\frac{1}{2} \int \frac{\rho(x)\rho(y)}{|x-y|} dx dy$, appelé terme direct, approche l'énergie d'interaction. Cette fonctionnelle a par la suite été améliorée, Dirac ajoutant en 1928 le terme $-c_{\text{D}} \int \rho^{4/3}$ constituant l'ordre suivant du terme d'interaction [7]. Par l'inégalité de Lieb-Oxford [30], c'est une borne inférieure à l'énergie Coulombienne totale dont on retranche l'énergie directe, cette différence étant aussi appelée énergie indirecte. Puis von Weizsäcker a ajouté en 1935 [37]

le terme d'ordre suivant du terme d'énergie cinétique, $c_{vW} \int |\nabla \sqrt{\rho}|^2$, c'est également une borne inférieure [3]. La fonctionnelle résultante est donc

$$\begin{aligned} \mathcal{E}_v^{\text{TFDW}}(\rho) = c_{\text{TF}} \int_{\mathbb{R}^3} \rho^{\frac{5}{3}} + c_{vW} \int_{\mathbb{R}^3} |\nabla \sqrt{\rho}|^2 \\ + \frac{1}{2} \int_{\mathbb{R}^6} \frac{\rho(x)\rho(y)}{|x-y|} dx dy - c_{\text{D}} \int_{\mathbb{R}^3} \rho^{\frac{4}{3}} + \int_{\mathbb{R}^3} v\rho. \end{aligned}$$

Des propriétés mathématiques de cette fonctionnelle sont contenues dans [28]. Ces approximations permettent de prévoir certains effets physiques, mais leur précision reste trop faible pour être utilisées à des fins de modélisation quantitative dans les applications modernes.

0.1.3 Hohenberg-Kohn

Bien plus tard, en 1964, Hohenberg et Kohn montrent par un court raisonnement mathématique que deux potentiels différents ne peuvent avoir des densités à un corps identiques [16]. Autrement dit, l'application qui va des potentiels électriques v vers les densités ρ_Ψ du fondamental Ψ est injective. Cette application est donc bijective sur son image, et la connaissance de la densité du fondamental implique la connaissance du potentiel. Or, la connaissance du potentiel permet de théoriquement tout connaître du système. Donc la connaissance de la densité du fondamental permet de tout déduire du système et il n'y a théoriquement pas besoin de calculer la fonction d'onde totale Ψ du fondamental. Ceci peut se résumer par le schéma

$$\rho \longrightarrow v_\rho \longrightarrow \Psi(v_\rho)$$

Physiquement, ce résultat est assez surprenant. Il fonde la DFT et justifie sa pratique, car alors toute grandeur observable du système s'exprime de manière unique par des fonctionnelles de la densité ρ . Par exemple, les énergies cinétiques et d'interaction doivent pouvoir s'exprimer en fonction de la densité du fondamental, c'est ce principe qui avait déjà été appliqué par Thomas et Fermi sans cette justification théorique.

0.1.4 Levy-Lieb

Discutons maintenant d'une approche variationnelle des idées de Hohenberg et Kohn, formulée par Levy et Lieb dans [22, 27]. Une densité $\rho \in L^1(\mathbb{R}^d, \mathbb{R})$ est dite représentable s'il existe un état fermionique $\Psi \in H_a^1(\mathbb{R}^{dN}, \mathbb{C})$ normalisé par $\int |\Psi|^2 = 1$ et tel que $\rho_\Psi = \rho$. Dans [27], Lieb a montré qu'une densité donnée ρ est représentable si et seulement si

$$\rho \in L^1(\mathbb{R}^d, \mathbb{R}_+), \quad \sqrt{\rho} \in H^1(\mathbb{R}^d), \quad \int_{\mathbb{R}^d} \rho = N.$$

Connaissant la densité du fondamental du système à l'équilibre, l'énergie fondamentale peut être exprimée de manière exacte par la fonctionnelle de Levy-Lieb [22, 27]

$$F^N(\rho) := \inf_{\substack{\Psi \in L^2_a(\mathbb{R}^{dN}) \\ \rho_\Psi = \rho}} \langle \Psi, H^N(0)\Psi \rangle.$$

C'est la fonctionnelle intermédiaire lorsqu'on scinde le problème de minimisation initial (1) en deux étapes :

$$\begin{aligned} E^N(v) &= \inf_{\substack{\Psi \in L^2_a(\mathbb{R}^{dN}) \\ \int |\Psi|^2 = 1}} \langle \Psi, H^N(v)\Psi \rangle \\ &= \inf_{\substack{\rho \in L^1(\mathbb{R}^d, \mathbb{R}_+) \\ \int \rho = N \\ \sqrt{\rho} \in H^1(\mathbb{R}^d)}} \inf_{\substack{\Psi \in L^2_a(\mathbb{R}^{dN}) \\ \rho_\Psi = \rho}} \langle \Psi, H^N(v)\Psi \rangle \\ &= \inf_{\substack{\rho \in L^1(\mathbb{R}^d, \mathbb{R}_+) \\ \int \rho = N \\ \sqrt{\rho} \in H^1(\mathbb{R}^d)}} \left(\int_{\mathbb{R}^d} v\rho + \inf_{\substack{\Psi \in L^2_a(\mathbb{R}^{dN}) \\ \rho_\Psi = \rho}} \langle \Psi, H^N(0)\Psi \rangle \right) \\ &= \inf_{\substack{\rho \in L^1(\mathbb{R}^d, \mathbb{R}_+) \\ \int \rho = N \\ \sqrt{\rho} \in H^1(\mathbb{R}^d)}} \left(\int_{\mathbb{R}^d} v\rho + F^N(\rho) \right). \end{aligned}$$

Ceci montre que $E^N(v)$ peut s'exprimer comme un problème variationnel basé uniquement sur la densité ρ . La fonctionnelle $F^N(\rho)$ est universelle au sens où elle ne dépend pas du potentiel externe. Ainsi, si elle pouvait être calculée à bas coût numérique, cela donnerait accès à la résolution du problème de Schrödinger à N corps, et de très nombreux problèmes de physique trouveraient leur solution numérique. Par ailleurs, l'énergie d'échange-corrélation est définie comme étant

$$E_{xc}^N(\rho) = F^N(\rho) - \frac{1}{2} \int_{\mathbb{R}^{2d}} \rho(x)\rho(y)w(x-y)dx dy - T^N(\rho),$$

où

$$T^N(\rho) := \inf_{\substack{\Psi \in H^1_a(\mathbb{R}^{dN}) \\ \int |\Psi|^2 = 1 \\ \rho_\Psi = \rho}} \int |\nabla \Psi|^2.$$

Elle représente l'erreur qu'on commet lorsqu'on approche la fonctionnelle de Levy-Lieb par l'énergie directe et la fonctionnelle de Levy-Lieb avec $w = 0$. Comme cette dernière fonctionnelle ayant $w = 0$ est moins coûteuse numériquement, approximer $F^N(\rho)$ est équivalent à approximer $E_{xc}^N(\rho)$.

0.1.5 Approximations des fonctionnelles de la densité

Ainsi théoriquement justifiée par le théorème de Hohenberg-Kohn et la formulation variationnelle de Levy-Lieb, la recherche d'approximations de fonctionnelles de la densité a été et est toujours un problème très important en physique et en chimie quantique, tout particulièrement celle qui donne l'énergie du fondamental. La fonctionnelle de Thomas-Fermi revient à écrire

$$F^N(\rho) \simeq c_{\text{TF}} \int_{\mathbb{R}^3} \rho^{\frac{5}{3}} + \frac{1}{2} \int_{\mathbb{R}^6} \rho(x)\rho(y)w(x-y)dx dy,$$

ou encore $T^N(\rho) \simeq c_{\text{TF}} \int_{\mathbb{R}^3} \rho^{\frac{5}{3}}$ et $E_{\text{xc}}^N(\rho) \simeq 0$. Cette fonctionnelle a servi de base pour améliorer leur précision, et capturer plus d'effets physiques [34]. Les approximations les plus crues sont celles de type LDA (local density approximation), qui s'expriment par des intégrales explicites de ρ , c'est-à-dire par un choix de fonction f_{LDA} et en estimant

$$E_{\text{xc}}^N(\rho) \simeq \int_{\mathbb{R}^d} f_{\text{LDA}}(\rho(x))dx.$$

Elles sont exactes dans certains régimes [24]. Les raffinements suivants sont les GGA (generalized gradient approximation) qui utilisent le gradient $|\nabla\sqrt{\rho}|$ apparaissant par exemple dans le terme de von Weizsäcker. On considère alors une fonction $f_{\text{GGA}} \in L^1_{\text{loc}}(\mathbb{R}^2, \mathbb{R})$ et l'estimation

$$E_{\text{xc}}^N(\rho) \simeq \int_{\mathbb{R}^d} f_{\text{GGA}}(\rho(x), |\nabla\sqrt{\rho}|(x))dx.$$

Précision chimique

RPA et au-delà	↑	$\rho, \nabla\sqrt{\rho} , \tau, \varphi_{\text{ks},i}, E_i$
Hybrides		$\rho, \nabla\sqrt{\rho} , \tau, \varphi_{\text{ks},i}$
Meta GGAs		$\rho, \nabla\sqrt{\rho} , \tau$
GGAs		$\rho, \nabla\sqrt{\rho} $
LDA		ρ

Champ moyen

FIGURE 1 : Échelle de Jacob des approximations en DFT

On peut continuer à complexifier les approximations de $F^N(\rho)$, en incluant la densité cinétique

$$\tau(x) := \int_{\mathbb{R}^{d(N-1)}} |\nabla\Psi|^2 dx_2 \cdots dx_N,$$

ce qui fait sortir du domaine de la DFT puisque τ ne peut pas être déduit de ρ , mais reste cependant dans le même esprit. On peut encore inclure les orbitales électroniques $\varphi_{\text{KS},i}$ du système de Kohn-Sham que nous présenterons dans la section suivante, ceci est appelé RPA (random phase approximation), et encore bien d'autres grandeurs. L'objectif est d'atteindre puis dépasser la précision chimique $2 \cdot 10^{-2} eV$, définie comme étant la précision atteignable expérimentalement, et qui permet de faire des prédictions suffisamment fiables pour les applications en chimie quantique.

La complexification à outrance des fonctionnelles engendre fréquemment une forte spécialisation aux situations particulières. La qualité de l'approximation s'accroît pour une application donnée, pendant que son universalité diminue. Des compromis sont donc effectués pour atteindre un bon équilibre entre polyvalence et précision.

0.1.6 Kohn-Sham

L'idée de Kohn et Sham [21] de 1965, intimement liée à celles présentées précédemment, est, étant donné un potentiel v , de remplacer le système exact par un autre dont le Hamiltonien ne contient pas d'interaction. On essaie de faire cela en modifiant le potentiel v , qui devient alors ce qu'on appelle le potentiel de Kohn-Sham v_{KS} . Le nouveau système est décrit par un problème sans interaction ($w = 0$),

$$H_{w=0}^N(v_{\text{KS}}) := - \sum_{i=1}^N \Delta_i + \sum_{i=1}^N v_{\text{KS}}(x_i).$$

La contrainte cible est que la densité du fondamental du système équivalent doit être égale à la densité du fondamental du système initial,

$$\rho_{w=0}(v) = \rho(v_{\text{KS}}).$$

L'intérêt de cette procédure est que le nouveau système peut être résolu numériquement puisqu'il n'y a plus d'interaction. Il suffit de calculer les N premiers états de l'opérateur à un corps

$$-\Delta + v_{\text{KS}},$$

notés $\varphi_i \in H^1(\mathbb{R}^d, \mathbb{C})$ et appelés orbitales de Kohn-Sham, d'énergies

$$E_i = \int_{\mathbb{R}^d} (|\nabla \varphi_i|^2 + v_{\text{KS}} |\varphi_i|^2)$$

croissantes. Elles forment une famille orthonormée dans $L^2(\mathbb{R}^d)$ et sont relativement facilement accessibles numériquement. L'état fondamental à N corps est alors simplement

$$\Psi = \bigwedge_{i=1}^N \varphi_i,$$

la densité à un corps s'exprime par

$$\rho_{w=0}(v_{\text{KS}}) = \sum_{i=1}^N |\varphi_i|^2,$$

et l'énergie fondamentale est $E_{w=0}^N(v_{\text{KS}}) = \sum_{i=1}^N E_i$. Toutes les autres grandeurs physiques d'intérêt sont également accessibles.

Nous pouvons alors définir le potentiel d'échange-corrélation

$$v_{\text{XC}} := v_{\text{KS}} - v - \rho(v) * w,$$

qui est fréquemment présent dans la littérature sur la DFT. Cette définition dit implicitement qu'au premier ordre, le potentiel de Kohn-Sham est $v + \rho(v) * w$, où $\rho(v) * w$ est le potentiel semi-classique de Hartree correspondant à l'approximation de champ moyen.

A priori, il n'est pas clair que le remplacement du système exact par ce système équivalent doit mener à une bonne approximation. Cependant, il est constaté pratiquement que c'est une technique très efficace compte tenu de son bas coût numérique.

0.1.7 Gaz uniforme d'électrons et jellium

Dans la fonctionnelle de Levy-Lieb, fixons la densité électronique à une certaine valeur constante à l'intérieur d'une boîte, dont on peut augmenter le volume à densité fixée en ajoutant des électrons. On y laisse libre la densité à proximité des bords afin de respecter les conditions de Dirichlet, le minimiseur correspondant est le gaz uniforme d'électrons. Les effets de bord sont négligeables quand la boîte est grande, et on prend la limite de volume infini. C'est le modèle qui est à la base de l'approximation LDA, laquelle peut être vue comme une série de gaz uniformes locaux approximant une certaine densité par des fonctions en escalier. Il a récemment été étudié mathématiquement dans [24, 26].

Le jellium [13] peut en quelque sorte être vu comme le modèle dual du gaz uniforme d'électrons. Ce dernier considère des électrons confinés dans une boîte plongée dans un potentiel électrique constant qui permet de compenser la charge électrique des électrons. On prend alors la limite de volume infini en ajoutant des électrons et en gardant la densité de charge moyenne totale fixe, pour s'affranchir des effets de bord. Il a été étudié mathématiquement dans [14, 29] jusqu'à l'ordre de Dirac et plus récemment à l'ordre suivant dans [1, 2, 15] par bosonisation.

Ces deux modèles sont deux importants paradigmes situés à la base de la DFT.

0.1.8 Perspectives futures

La DFT a été augmentée et hybridisée avec de nombreuses méthodes. La DMFT (dynamical mean field theory) utilise le même type d'idées pour construire un système équivalent reproduisant les grandeurs internes avec précision. La littérature spécialisée comporte beaucoup d'études mélangeant les principes de la DFT avec d'autres, à chaque fois dans le but d'augmenter la précision sur une classe de systèmes.

La résolution numérique du problème de Schrödinger exact devrait rester encore hors de portée dans le futur proche, car les processeurs quantiques comportent toujours de fortes limites. Cependant, nous pouvons noter l'essor de méthodes hybrides qui découpent les problèmes exacts en sous-problèmes, sur lesquels on peut dès aujourd'hui utiliser les performances des ordinateurs quantiques de manière avantageuse. Ainsi des algorithmes quantiques et classiques sont associés. Le développement inexorable des ordinateurs et des algorithmes quantiques rendra-t-il la DFT caduque d'ici quelques dizaines d'années? Même si c'est le cas, son approche théorique restera très riche.

0.2 Résultats obtenus dans la thèse

Nous résumons ici l'ensemble des résultats obtenus dans la thèse.

Partie I. Le théorème de Hohenberg-Kohn

Le théorème de Hohenberg-Kohn se situe à la base de la DFT. Cependant, certaines questions mathématiques le concernant restaient en suspens. Cette première partie comprend deux chapitres sur ce résultat fondamental.

Chapitre 1. Continuation unique

Le théorème de Hohenberg-Kohn peut s'exprimer sous la forme suivante.

Théorème 0.2.1 (Hohenberg-Kohn). *Soit $w \in (L^p + L^\infty)(\mathbb{R}^d, \mathbb{R})$ une fonction d'interaction. Soit $v, u \in (L^p + L^\infty)(\mathbb{R}^d, \mathbb{R})$ des potentiels tels que $H^N(v)$ et $H^N(u)$ vérifient la continuation unique forte et admettent des états fondamentaux Ψ_v et Ψ_u . Si $\rho_{\Psi_v} = \rho_{\Psi_u}$, alors il existe une constante $c \in \mathbb{R}$ telle que $v = u + c$.*

Nous allons maintenant discuter des exposants p pour lesquels ce théorème est valable. Notons

$$V := \sum_{1 \leq i < j \leq N} w(x_i - x_j) + \sum_{i=1}^N v(x_i) \quad (6)$$

le potentiel total. Dans [27], Lieb a montré que ce résultat reposait sur une propriété de continuation unique forte, à savoir qu'il faut montrer que lorsqu'une fonction d'onde $\Psi \in H^1(\mathbb{R}^{dN})$ vérifie l'équation de Schrödinger

$$-\Delta\Psi + V\Psi = 0,$$

alors

$$\left| \left\{ x \in \mathbb{R}^d \mid \Psi(x) = 0 \right\} \right| = 0. \quad (7)$$

Les résultats d'unicité proviennent très souvent de propriétés de continuation unique. Nous auront besoin de la définition suivante, une fonction f s'annule à tout ordre en $x_0 \in \mathbb{R}^d$ si pour tout $n \in \mathbb{N}$, il existe $c_n \geq 0$ telle que

$$\int_{|x-x_0| \leq \epsilon} |f(x)|^2 dx \leq c_n \epsilon^n$$

lorsque $\epsilon \rightarrow 0^+$. Il s'avère que la propriété (7) implique qu'il existe un point sur lequel la fonction Ψ s'annule à tout ordre [19]. La continuation unique forte consiste à montrer que lorsqu'une fonction f vérifie une équation différentielle du second ordre et qu'elle s'annule à tout ordre en un point, alors elle est presque partout nulle. C'est donc cette propriété que nous avons besoin de montrer. Avant les résultats de cette thèse, ce théorème était prouvé pour des valeurs de p qui dépendaient du nombre N d'électrons. En effet, en appliquant les travaux de Jerison et Kenig [19], nous constatons que le plus petit exposant qu'il est possible de prendre pour que le théorème soit vrai est $p = dN/2$. Or, quand N est grand, cela revient essentiellement à prendre des potentiels bornés.

Le résultat de continuation unique forte que nous avons prouvé est essentiellement le suivant.

Théorème 0.2.2 (Continuation unique forte). *Soient $p > \max(2d/3, 2)$ et $w, v \in L^p_{\text{loc}}(\mathbb{R}^d, \mathbb{R})$, et V comme dans (6). Si une fonction $\Psi \in H^2(\mathbb{R}^n, \mathbb{R})$ vérifie $-\Delta\Psi + V\Psi = 0$ et s'annule à tout ordre en un point, alors $\Psi = 0$ presque partout.*

Une extension en présence de potentiels magnétiques est fournie. L'application de ce résultat permet donc d'utiliser $p > \max(2d/3, 2)$ dans le Théorème 0.2.1, ce qui couvre les potentiels Coulombiens de la physique électronique. Ce travail est présenté au Chapitre 1 et publié dans [11].

Chapitre 2. Extensions du théorème de Hohenberg-Kohn

Dans ce chapitre, nous étudierons certaines des extensions possibles du théorème de Hohenberg-Kohn classique à d'autres modèles. Le Théorème 0.2.1 fournit l'unicité dans le cas le plus simple où l'espace des paramètres

est celui des potentiels électriques v . Cependant, beaucoup de résultats similaires existent ou ont été examinés dans la littérature physique, dans des configurations différentes. La question centrale est : quelle est la grandeur interne minimale qu'il suffit de connaître pour tout connaître sur le système ? Les preuves sont les mêmes que pour le théorème de Hohenberg-Kohn standard, les seuls résultats supplémentaires nécessaires sont des lemmes montrant que différents paramètres extérieurs ne peuvent pas mener aux mêmes densités réduites, lesquels lemmes étaient la plupart du temps absents de la littérature physique. Ces travaux sont présentés au Chapitre 2.

Considérons un système similaire aux précédents, mais supposons par exemple que nous ne connaissons pas l'interaction. Définissons

$$H^N(v, w) := - \sum_{i=1}^N \Delta_i + \sum_{1 \leq i < j \leq N} w(x_i - x_j) + \sum_{i=1}^N v(x_i).$$

Comme les états ne se couplent avec l'interaction que par la densité de paires définie en (3), car

$$\left\langle \Psi, \left(\sum_{1 \leq i < j \leq N} w(x_i - x_j) \right) \Psi \right\rangle = \int w(x - y) \rho_{\Psi}^{(2)}(x, y) dx dy, \quad (8)$$

il est alors naturel de penser que l'application $(v, w) \mapsto \rho^{(2)}$ associant la densité de paires du fondamental, est injective. Ce résultat, présent dans [35] pour la première fois, trouve une preuve rigoureuse grâce au Théorème 0.2.2 et à un lemme indépendant, le Lemme 2.2.3, qui montre que deux potentiels différents ne peuvent donner le même fondamental.

Considérons maintenant des champs magnétiques, des systèmes avec spin $q = 2$, et ajoutons au Hamiltonien le terme d'interaction Zeeman

$$H^N(v, B) := - \sum_{i=1}^N \Delta_i + \sum_{1 \leq i < j \leq N} w(x_i - x_j) + \sum_{i=1}^N v(x_i) + \sum_{i=1}^N B(x_i) \cdot \sigma_i,$$

où les matrices σ sont les matrices de Pauli. Définissons des densités à deux corps en spin

$$\rho_{\Psi}^{\alpha\beta}(x) := N \sum_{(s_2, \dots, s_N) \in \{\uparrow, \downarrow\}^{N-1}} \int_{\mathbb{R}^{d(N-1)}} \Psi(\alpha, x; s_2, x_2; \dots) \bar{\Psi}(\beta, x; s_2, x_2; \dots) \times dx_2 \cdots dx_N.$$

Un état se couple au champ magnétique extérieur seulement via la magnétisation

$$m := \begin{pmatrix} \rho^{\uparrow\downarrow} + \rho^{\downarrow\uparrow} \\ -i(\rho^{\uparrow\downarrow} - \rho^{\downarrow\uparrow}) \\ \rho^{\uparrow\uparrow} - \rho^{\downarrow\downarrow} \end{pmatrix},$$

puisque

$$\left\langle \Psi, \sum_{i=1}^N (\sigma_i \cdot B(x_i)) \Psi \right\rangle = \int_{\mathbb{R}^3} B \cdot m_\Psi.$$

Dans [6], Capelle et Vignale ont montré que l'application associant aux potentiels externes les densités à un corps $(v, B) \mapsto (\rho, m)$ n'est pas injective. Cependant, lorsque deux champs électromagnétiques ont les mêmes densités à un corps, nous avons pu prouver au Théorème 2.3.1 qu'il existait alors une relation très contraignante entre les champs initiaux, qui prend la forme

$$|B_1 - B_2| \chi = \frac{E_1 - E_2}{N} + v_2 - v_1.$$

où χ est une fonction mesurable prenant ses valeurs dans l'ensemble discret

$$\left\{ -1, -1 + \frac{2}{N}, -1 + \frac{4}{N}, \dots, 1 - \frac{2}{N}, 1 \right\}.$$

Par la suite, nous avons considéré les Hamiltoniens comportant des potentiels non locaux

$$H^N(G) := - \sum_{i=1}^N \Delta_i + \sum_{1 \leq i < j \leq N} w(x_i - x_j) + \sum_{i=1}^N G_i,$$

où G est un opérateur de $L^2(\mathbb{R}^d)$ infiniment borné par le Laplacien afin de garder les bonnes propriétés d'auto-adjonction. Le système se couple alors au potentiel non local uniquement via la matrice densité à un corps γ déjà définie en (2), puisque

$$\left\langle \Psi, \left(\sum_{i=1}^N G_i \right) \Psi \right\rangle = \text{Tr } G\gamma.$$

Ceci amène à supposer que l'application $G \mapsto \gamma$ est injective, néanmoins nous avons trouvé une grande classe de contre-exemples.

Enfin, nous avons considéré en Section 2.4.1 des systèmes à température positive, en laissant les températures potentiellement différentes entre systèmes qu'on compare. Dans ce cadre, toutes les propriétés d'injectivité sont alors vraies, même celles qui étaient fausses à température nulle. Par ailleurs, nous avons montré que la connaissance de l'entropie du système implique la connaissance de la température, complétant la dualité entre les paramètres externes et internes.

Partie II. Propriétés de l'application $v \mapsto \rho$

Sachant que l'application $v \mapsto \rho$ est injective, d'autres questions naturelles se posent alors, les résultats étant présentés au Chapitre 4. Tout

d'abord, quitte à être multivaluée, elle est naturellement définie sur l'espace des potentiels liants, c'est-à-dire tels que $H^N(v)$ possède une valeur propre sous son spectre essentiel. Afin d'appréhender un peu mieux la topologie de cet espace, nous montrerons qu'il est connexe par arcs. Puis nous voudrions savoir si le problème direct de la DFT est bien posé, c'est-à-dire si elle est régulière \mathcal{C}^∞ . Nous montrerons au Chapitre 4 que c'est le cas sur l'ensemble des potentiels non dégénérés, c'est-à-dire ceux qui sont tels que $H^N(v)$ a son espace propre fondamental de dimension un. Sur les potentiels dégénérés, l'application $v \mapsto \rho$ contient des singularités, que nous étudierons également en cherchant comment ces états propres dégénérés se transforment sous une perturbation. Enfin, nous étudierons la "taille" topologique de l'image de l'application, pour savoir si elle est dense dans l'espace des fonctions positives d'intégrale N , ou encore si elle est d'intérieur vide.

Chapitre 3. L'espace des potentiels liants est connexe par arcs

Considérons les exposants

$$\begin{cases} p = 1 & d = 1 \\ p > 1 & d = 2 \\ p = d/2 & d \geq 3. \end{cases} \quad (9)$$

Nous choisissons une interaction $w \in (L^p + L^\infty)(\mathbb{R}^d)$, et des potentiels $v \in (L^p + L^\infty)(\mathbb{R}^d)$. Définissons l'ensemble des potentiels électriques capables de lier de manière stable un système de N particules, de manière non dégénérée,

$$\mathcal{V}^N := \left\{ v \in (L^p + L^\infty)(\mathbb{R}^d) \mid E^N(v) < \Sigma^N(v), \quad (10) \right.$$

$$\left. \dim \text{Ker} (H^N(v) - E^N(v)) = 1 \right\}, \quad (11)$$

où $E^N(v) := \min \sigma(H^N(v))$ est l'énergie fondamentale et nous désignons par $\Sigma^N(v) := \min \sigma_{\text{ess}}(H^N(v))$ le bas du spectre essentiel. Définissons également le surensemble des potentiels liants pouvant être dégénérés,

$$\mathcal{V}_\partial^N := \left\{ v \in (L^p + L^\infty)(\mathbb{R}^d) \mid E^N(v) < \Sigma^N(v) \right\}.$$

Cet ensemble est difficile à appréhender, néanmoins nous sommes parvenus à montrer une de ses propriétés topologiques, à savoir qu'il est connexe par arcs.

Theorème 0.2.3 (Connexité par arcs de l'ensemble des potentiels liants). *Considérons p comme dans (9), avec $w \in L^p + L^\infty$, tel que $w \geq 0$. Alors $\bigcap_{n=1}^N \mathcal{V}_\partial^n$ est connexe par arcs.*

L'hypothèse sur l'interaction sert à appliquer le théorème HVZ [17, 38, 40] sous la forme [23, Theorem 3.1].

Le résultat montre que tout potentiel peut être déformé en un simple puits, tout en restant liant. Cependant, la première valeur propre peut dégénérer le long du chemin. Nous voudrions montrer qu'on peut passer de n'importe quelle configuration à n'importe quelle autre sans dégénérescence et sans qu'une particule ne s'échappe. On peut appeler cette propriété *l'équivalence adiabatique des potentiels*. Malheureusement, ce résultat repose sur la connexité par arcs de l'ensemble \mathcal{V}_∂^N des potentiels liants non dégénérés, que nous n'avons pas réussi à prouver. Une question naturelle est de se demander si on peut "lever les dégénérescences" en modifiant un peu le potentiel. Ceci sera étudié au Chapitre 5. Notre résultat pourrait inciter de futures études, pour savoir si l'ensemble \mathcal{V}_∂^N résultant contient une, plusieurs, ou une infinité de composantes connexes.

Par ailleurs, il permet de montrer une propriété sur l'ensemble des densités v -représentables.

Corollary 0.2.1. *L'ensemble des densités v -représentables*

$$\left\{ \rho_\Psi \in L^1(\mathbb{R}^d, \mathbb{R}_+) \mid \Psi \text{ est le fondamental de } H^N(v) \text{ pour un } v \in \cap_{i=1}^N \mathcal{V}_\partial^n \right\}$$

est connexe par arcs.

Chapitre 4. Compacité de $v \mapsto \rho(v)$

Considérons un ouvert $\Omega \subset \mathbb{R}^d$, ayant un bord Lipschitz. L'étude du problème direct de la DFT $v \mapsto \rho(v)$ nous a amené à montrer les propriétés de régularité de cette application. Essentiellement, elle est lisse sur \mathcal{V}^N et de différentielle compacte. Cette application va des potentiels électriques liants non dégénérés vers les densités des fondamentaux,

$$\begin{aligned} \rho : \mathcal{V}^N &\longrightarrow W^{1,1}(\Omega, \mathbb{R}_+) \cap \{ \int_\Omega \cdot = N \} \\ v &\longmapsto \rho(v) := \rho_{\Psi(v)}. \end{aligned}$$

Theorème 0.2.4 (Régularité de $v \mapsto \rho(v)$). *Soit p comme dans (9), et $w \in L^p + L^\infty$ avec $w \geq 0$.*

- (i - Régularité). *L'application ρ est C^∞ . Elle est injective quand $p > \max(2d/3, 2)$, à constante près.*

- (ii - Compacité de la différentielle). *Sa différentielle, évaluée en un $v \in \mathcal{V}^N$, est donnée par*

$$\begin{aligned} (d_v \rho) u &= -2N \int_{\mathbb{R}^{d(N-1)}} dx_2 \cdots dx_N \\ &\overline{\Psi(v)} (H^N(v) - E^N(v))_{\perp}^{-1} (1 - |\Psi(v)\rangle \langle \Psi(v)|) \left(\sum_{i=1}^N u(x_i) \right) \Psi(v). \end{aligned}$$

Pour tout $v \in \mathcal{V}^N$, $d_v \rho$ est compacte de $L^p + L^\infty$ dans $W^{1,1}$, non surjective, et elle vérifie

$$\|(d_v \rho) u\|_{W^{1,1}}^2 \leq c_v \|u\|_{L^p + L^\infty} \int |u| \rho(v).$$

La différentielle $d_v \rho$ est injective quand $p > \max(2d/3, 2)$.

• (iii - Continuité faible-forte locale). Soit p comme dans (9), avec $p > d/2$ quand $d \geq 3$, et $w \in L^p + L^\infty$, $w \geq 0$ et nous remplaçons $L^p + L^\infty$ par $L^p + L^\infty_\epsilon$ dans la définition (10) de \mathcal{V}^N . Soit $\Lambda \subset \Omega$ un ouvert borné de Ω . Considérons que $v \in \mathcal{V}^N$, $v_n \rightharpoonup v$ faiblement, et $v_n \mathbf{1}_{\Omega \setminus \Lambda} \rightarrow v \mathbf{1}_{\Omega \setminus \Lambda}$ fortement dans $L^p + L^\infty$. Alors $E^N(v_n) \rightarrow E^N(v)$, pour n assez grand $v_n \in \mathcal{V}^N$, et enfin $\sqrt{\rho(v_n)} \rightarrow \sqrt{\rho(v)}$ fortement dans $H^1(\Omega)$.

En corollaire, nous pouvons montrer que l'énergie d'un système est différentiable, et cette différentielle est donc une application linéaire, c'est le théorème de Hellman-Feynman.

Corollaire 0.2.2 (Hellmann-Feynman). Soit p comme dans (9). L'énergie $v \mapsto E^N(v)$ est Lipschitz, concave, faiblement sur semi-continue sur $(L^p + L^\infty)(\mathbb{R}^d)$, C^∞ sur \mathcal{V}^N et pour tout $v \in \mathcal{V}^N$ et tout $u \in (L^p + L^\infty)(\mathbb{R}^d)$, on a

$$(d_v E^N) u = \int_{\Omega} u \rho(v)$$

Si $p > \max(2d/3, 2)$, $v \mapsto E^N(v)$ est strictement concave et strictement croissante sur \mathcal{V}^N_∂ .

D'autres conséquences du Théorème 0.2.4 sont que le problème inverse au problème linéarisé de $v \mapsto \rho(v)$ est mal posé car $d_v \rho$ est compacte, et nous avons également le résultat suivant.

Corollaire 0.2.3 (L'ensemble des densités v -représentables est "petit"). Soit p comme dans (9), avec $p > d/2$ lorsque $d \geq 3$. Quand le système est confiné dans un ensemble ouvert borné $\Omega \subset \mathbb{R}^d$, alors ρ est compacte et $\rho(\mathcal{V}^N)$ est une union dénombrable de compacts. Par conséquent cette image est d'intérieur vide dans $W^{1,1} \cap \{\int \cdot = N\}$ et ρ^{-1} est discontinue.

A priori, même si $\rho(\mathcal{V}^N)$ est topologiquement petit, il est toujours possible qu'il soit dense dans l'espace des fonctions positives. Nous apporterons une réponse numérique à cette question au Chapitre 7.

Chapitre 5. Perturbation des systèmes dégénérés

Nous avons vu précédemment que l'application $v \mapsto \rho$ intervenant dans le problème direct de la DFT est lisse sur l'ensemble des potentiels non dégénérés. Cependant, à l'approche des potentiels dégénérés, la situation se

complexifie fortement et les objets ne sont plus lisses. Afin de compléter la description, nous avons aussi commencé à analyser certaines questions naturelles qui sont survenues.

Tout d'abord, nous nous sommes demandé s'il existait des perturbations qui brisent la dégénérescence. Ensuite, comme l'application qui semble la plus lisse est l'énergie $v \mapsto E^N(v)$, nous voudrions savoir si elle est différentiable en ces potentiels dégénérés. Le théorème suivant montre que ce n'est pas le cas lorsqu'il n'y a pas d'interaction.

Proposition 0.2.4. *Soit p comme dans (9) et $w \in L^p + L^\infty$.*

(i - Brisure de symétrie générique.) *Supposons que*

$$\dim \text{Ker} (H^N(v) - E^N(v)) = 2,$$

et choisissons deux vecteurs $\psi, \varphi \in \text{Ker} (H^N(v) - E^N(v))$ avec $\psi \perp \varphi$. La dégénérescence n'est brisée dans aucune direction au premier ordre si et seulement si

$$\rho_\psi = \rho_\varphi \quad \text{et} \quad \int_{\mathbb{R}^{d(N-1)}} \psi \varphi dx_2 \cdots dx_N = 0. \quad (12)$$

(ii - L'énergie n'est pas différentiable quand $w = 0$.) *Soit $v \in \mathcal{V}_\partial^N \setminus \mathcal{V}^N$ un potentiel dégénéré, et $w = 0$. Alors E^N n'est pas différentiable en v , en particulier on a ${}^+\delta_v E^N(u) < {}^-\delta_v E^N(u)$ selon au moins une direction $u \in L^p + L^\infty$.*

Nous pensons que la brisure de symétrie se fait génériquement au premier ordre, et quelle que soit la dimension de l'espace propre, puisque la condition (12) est vraisemblablement rarement respectée. Nous conjecturons que l'énergie E^N n'est pas non plus différentiable dans le cas d'une interaction $w \in L^p + L^\infty$ générale.

Partie III. Le problème de Kohn-Sham

Nous pouvons considérer que le problème de Kohn-Sham est le problème inverse de la détermination $v \mapsto \rho(v)$ lorsqu'il n'y a pas d'interaction. Étant donnée une densité $\rho \geq 0$, telle que $\sqrt{\rho} \in H^1(\mathbb{R}^d)$ et $\int \rho = N$, peut-on trouver un potentiel v tel que $\rho(v)$, la densité du fondamental de $H_{w=0}^N(v)$, est égale à ρ ?

Chapitre 6. Régularisation du problème dual

Considérons un système vivant dans le domaine $\Omega \subset \mathbb{R}^d$, dont les bords sont lisses, et choisissons les conditions de Dirichlet au bord. Lieb a exprimé dans [27] le problème dual de la fonctionnelle de Levy-Lieb. Considérons une densité ρ et la fonctionnelle

$$G_\rho(V) := E^N(V) - \int_\Omega V \rho,$$

définie sur $(L^p + L^\infty)(\Omega, \mathbb{R})$ avec $p > \max(2d/3, 2)$, et invariante sous la transformation $V \rightarrow V + c$ pour les constantes $c \in \mathbb{R}$. Définissons la fonctionnelle de Lieb

$$F_{\text{mix}}^N(\rho) := \inf_{\substack{\Gamma \in \mathcal{B}(L^2(\wedge^N \Omega)) \\ \Gamma^* = \Gamma \geq 0 \\ \text{Tr } \Gamma = 1 \\ \rho_\Gamma = \rho}} \text{Tr } H^N(0)\Gamma,$$

qui vérifie $F_{\text{mix}}^N(\rho) \leq F^N(\rho)$. Nous disposons alors de la formulation duale [27]

$$\sup_{V \in (L^p + L^\infty)(\Omega, \mathbb{R})} G_\rho(V) = F_{\text{mix}}^N(\rho).$$

Nous dirons que ce problème est bien posé s'il existe un potentiel atteignant ce maximum. Il n'est pas évident de déterminer un bon espace fonctionnel pour les potentiels. Par exemple pour les normes L^p quand $p > 1$, le problème paraît même mal posé. Exhibons par exemple ρ continue à l'origine et un potentiel positif $V \in (L^1 \cap L^p)(\Omega)$ à support compact. Considérons la suite $V_n(x) := n^d V(nx)$, nous avons alors $\|V_n\|_{L^p}^p = n^{d(p-1)} \int V^p \rightarrow +\infty$ car $p > 1$ mais $E^N(V_n) = 0$ car $v_n \geq 0$, et $\int V_n \rho \rightarrow \rho(0) \int V$ est borné. On constate donc que la fonctionnelle G_ρ n'est pas coercive dans les normes L^p . Or, cette coercivité serait la propriété idéale pour montrer que le problème est bien posé. L'objectif principal de cette étude a donc été de modifier légèrement le modèle afin d'aboutir à une fonctionnelle coercive. Remarquons que le potentiel V doit être égal à $+\infty$ sur les ouverts où ρ s'annule, par continuation unique.

Nous allons essentiellement discrétiser l'espace des potentiels. Pour cela, considérons un sous-ensemble $I \subset \mathbb{N}$ et une suite de fonctions de poids $\alpha = (\alpha_i)_{i \in I}$, où $\alpha_i \in L^\infty(\Omega, \mathbb{R}_+)$, formant une partition de l'unité pour Ω , c'est-à-dire

$$\mathbf{1}_\Omega \sum_{i \in I} \alpha_i = \mathbf{1}_\Omega.$$

Nous nous restreignons ensuite aux potentiels de la forme

$$V = \sum_{i \in I} v_i \alpha_i,$$

où $v = (v_i)_{i \in I} \in \ell^\infty(I, \mathbb{R})$. L'espace des densités est alors remplacé par les valeurs de densités intégrées, ce sont les éléments

$$r = (r_i)_{i \in I} \in \ell^1(I, \mathbb{R}_+) \cap \left\{ \sum_{i \in I} r_i = N \right\}.$$

Les fonctionnelles de Levy-Lieb et Lieb régularisées sont alors

$$F^{N,\alpha}(r) := \inf_{\substack{\Psi \in H_a^1(\Omega^N) \\ \int \rho_\Psi = N \\ \int \alpha_i \rho_\Psi = r_i \quad \forall i \in I}} \langle \Psi, H^N(0) \Psi \rangle, \quad F_{\text{mix}}^{N,\alpha}(r) := \inf_{\substack{\Gamma \in \mathcal{S}_{\text{mix}}^N(\Omega) \\ \int \rho_\Gamma = N \\ \int \alpha_i \rho_\Gamma = r_i \quad \forall i \in I}} \text{Tr } H^N(0) \Gamma,$$

où les états mixtes sont les éléments de

$$\mathcal{S}_{\text{mix}}^N(\Omega) := \mathfrak{S}_1(L^2(\wedge^N \Omega)) \cap \{\Gamma = \Gamma^* \geq 0, \text{Tr}(-\Delta)\Gamma < +\infty\},$$

normalisés à $\text{Tr } \Gamma = 1$. La fonctionnelle G_ρ devient

$$G_{r,\alpha} : \begin{array}{ll} \ell^\infty(I, \mathbb{R}) & \longrightarrow \mathbb{R} \\ v = (v_i)_{i \in I} & \longmapsto E^N(\sum_{i \in I} v_i \alpha_i) - \sum_{i \in I} v_i r_i. \end{array}$$

Nous avons montré en Théorème 6.1.2 que les fonctionnelles de Levy-Lieb et Lieb convergent vers les fonctionnelles exactes lorsque le maillage induit par les poids α s'affine jusqu'à représenter le continu. Mais notre résultat principal est que la fonctionnelle $G_{r,\alpha}$ est maintenant coercive, ce qui permet d'en déduire l'existence d'un potentiel de Kohn-Sham.

Théorème 0.2.5 (Caractère bien posé du problème dual). *Soit une interaction positive $w \in (L^p + L^\infty)(\mathbb{R}^d, \mathbb{R}_+)$, où p est comme dans (9).*

• (Coercivité) *Soit α une partition de l'unité pour Ω , où $\alpha_i \in L^\infty(\mathbb{R}^d, \mathbb{R}_+)$, telle qu'il existe $R > 0$ tel que pour tout $i \in I$,*

$$(\text{supp } \alpha_i) \setminus \cup_{j \neq i, j \in I} \text{supp } \alpha_j$$

contient une boule de rayon R . Soit $r \in \ell^1(I, \mathbb{R}_+)$ tel que $\sum_{i \in I} r_i = N$ et $r_i > 0$ pour tout $i \in I$. Pour tout $v \in \ell_r^1(I, \mathbb{R})$ tel que $E^N(\sum v_i \alpha_i) = 0$, on a

$$G_{r,\alpha}(v) \leq - \min \left(1, \frac{\sum_{v_i \geq c_\Omega} r_i}{\sum_{v_i < c_\Omega} r_i} \right) \|v - c_\Omega\|_{\ell_r^1} + \min_{\substack{\Psi \in \wedge^N H_0^1(B_R) \\ \int |\Psi|^2 = 1}} \langle \Psi, H^N(0) \Psi \rangle.$$

En particulier quand I est fini, alors $G_{r,\alpha}$ est coercive dans $\ell_r^1(I, \mathbb{R}) = \ell^1(I, \mathbb{R})$.

• (Existence d'un optimiseur) *Soit I fini, et nous prenons les hypothèses précédentes. Il existe un unique potentiel $v \in \ell^1(I, \mathbb{R})$ (au choix de jauge près) maximisant $G_{r,\alpha}$. Il y a donc un état fondamental mixte à N particules $\Gamma_v \in \mathcal{S}_{\text{mix}}^N(\Omega)$ de $H^N(\sum_{i \in I} v_i \alpha_i)$ tel que pour tout $i \in I$, $\int \rho_{\Gamma_v} \alpha_i = r_i$, et tel que*

$$\sup_{u \in \ell_r^1(I, \mathbb{R})} G_{r,\alpha}(u) = G_{r,\alpha}(v) = \mathcal{E}_0(\Gamma_v) = F_{\text{mix}}^{N,\alpha}(r).$$

Les corollaires de ce théorème sont qu'on peut approcher n'importe quelle densité $\rho \in L^1(\mathbb{R}^d, \mathbb{R}_+)$ telle que $\int \rho = N$ et $\sqrt{\rho} \in H^1(\mathbb{R}^d)$ par des densités v -représentables dans le modèle des états mixtes. Il suffit de prendre une suite de fonctions de poids de plus en plus aptes à épouser la forme de ρ . Ceci est vrai dans l'espace total, et donne donc une procédure théorique pour représenter ces densités.

Enfin, nous avons conjecturé que les minimiseurs états purs Ψ de $F^{N,\alpha}(r)$ sont tels que $\left| \left\{ X \in \mathbb{R}^{dN} \mid \Psi(X) = 0 \right\} \right| = 0$. Nous avons montré que ceci impliquerait que ces minimiseurs vérifient une équation de Schrödinger pour un potentiel dual, et que ce potentiel dual aurait donc un état excité dont la densité vérifie $\int \rho \alpha_i = r_i$ pour tout $i \in I$. C'est un résultat de v -représentabilité par des densités d'états excités, dans le cas des états purs.

Chapitre 7. Étude numérique des densités atteignables

Notre dernier travail consiste en une analyse numérique du caractère représentable des densités. Pour ce faire, nous choisissons une densité ρ cible, pour laquelle nous souhaiterions trouver un potentiel de Kohn-Sham, c'est-à-dire un potentiel v tel que $\rho_{w=0}(v) = \rho$. Dans le cas des états mixtes, d'après [27, (4.5)] nous avons

$$\sup_{v \in (L^p + L^\infty)(\Omega)} G_\rho(v) = \inf_{\substack{\Gamma \in \mathcal{S}_{\text{mix}}^N(\Omega) \\ \rho_\Gamma = \rho}} \text{Tr } H^N(0) \Gamma, \quad (13)$$

où

$$G_\rho(v) := E^N(v) - \int_\Omega v \rho.$$

Maximiser la fonctionnelle concave G_ρ mènerait donc au potentiel de Kohn-Sham "mixte", qui par le théorème de Hohenberg-Kohn en configurations mixtes est égal au potentiel de Kohn-Sham à état pur s'il existe. Cependant, dans le cas des états purs, la relation (13) n'est plus vraie mais nous pouvons tout de même maximiser G_ρ . Au cas où $H_{w=0}^N(v)$ est non dégénéré, le théorème de Hellman-Feynman donne

$$(d_v G_\rho) u = \int_\Omega u(\rho(v) - \rho)$$

pour tout potentiel u . L'algorithme que nous appliquons démarre du potentiel exact à un corps

$$v_0 := \frac{\Delta \sqrt{\rho}}{\sqrt{\rho}},$$

et suit une montée de gradient

$$v_{n+1} = v_n + \lambda(\rho(v_n) - \rho).$$

Nous considérons que l'algorithme a convergé si

$$\|\rho(v_n) - \rho\|_{L^1} / N \leq 10^{-3}.$$

Dans les cas où il ne converge pas, $\|\rho(v_n) - \rho\|_{L^1} / N$ oscille entre plusieurs valeurs et $\min_{n \in \mathbb{N}} \|\rho(v_n) - \rho\|_{L^1} / N$ est typiquement entre N et 10^{-2} . Nous nous sommes restreints au cas $w = 0$ d'intérêt dans l'approche de Kohn-Sham. Le cas w Coulombien (ou autre) serait également intéressant à analyser d'un point de vue théorique, il pourrait mener à des conclusions différentes du cas $w = 0$, mais il est très coûteux en opérations numériques. Nous avons également appliqué l'algorithme précédent dans des configurations d'états excités, dans ce cas nous renvoyons au Chapitre 7 pour les détails.

Voici les principales observations que nous avons été amenés à faire.

- En dimension $d = 1$, toute densité à N corps est génériquement v -représentable, que ce soit par des fondamentaux ou des états excités. L'algorithme converge rapidement vers un unique potentiel.
- En dimension $d = 2$, nous n'appliquons l'algorithme que pour le fondamental. Lorsqu'on choisit un potentiel v et que nous lançons l'algorithme sur $\rho(v)$, il retrouve bien v , ce qui légitime son utilisation. Nous constatons que notre algorithme oscille et donc diverge dans le cas où v est radial. Plus généralement, pour un choix générique de fonction positive d'intégrale N , l'algorithme a le même comportement divergeant. Il ne converge donc que dans les cas très spécifiques où la densité provient d'un potentiel initialement choisi.

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Part I

**The Hohenberg-Kohn
theorem**

Chapter 1

Unique continuation and application to the Hohenberg-Kohn theorem

This chapter contains the results published in the two papers [11, 12].

A statement by Hohenberg and Kohn [16] lies at the heart of DFT. It proves that, at equilibrium, the density contains all the information of the system. Later, Lieb [30] showed that the rigorous proof of the Hohenberg-Kohn theorem relies on a strong unique continuation property (UCP). In this chapter we prove the strong unique continuation property for many-body Pauli operators with external potentials, interaction potentials and magnetic fields in $L^p_{\text{loc}}(\mathbb{R}^d)$, and with magnetic potentials in $L^q_{\text{loc}}(\mathbb{R}^d)$, where $p > \max(2d/3, 2)$ and $q > 2d$. For this purpose, we prove a singular Carleman estimate involving fractional Laplacian operators. Consequently, we obtain Tellgren's the Hohenberg-Kohn theorem for the Maxwell-Schrödinger model.

1.1 Introduction

Unique continuation is an important and versatile tool in analysis. In particular, it is used to prove uniqueness of Cauchy problems, see [46] for a review of some results. Unique continuation mainly relies on Carleman inequalities, first developed by Carleman [4], later improved by Hörmander [17] and Koch and Tataru [22]. It implies that, under general assumptions, a function verifying a second order partial differential equation and vanishing “strongly” at one point vanishes everywhere. A famous result of this kind is due to Jerison and Kenig [19], who dealt with eigenfunctions of Schrödinger's operator $-\Delta + V(x)$ where $V \in L^{n/2}_{\text{loc}}(\mathbb{R}^n)$.

Nevertheless, most of the existing results fail to apply to situations that are relevant in many-body quantum physics, because their assumptions on potentials, which are generally L^p conditions, depend on the number of

particles N . For instance if we want to use the result of Jerison and Kenig, we need the electric potential to belong to $L^{dN/2}(\mathbb{R}^d)$, which is very restrictive when N is large. The only two adapted works, having N -independent assumptions on the potentials, are the ones of Georgescu [13] and Schechter-Simon [44]. But they hold only in a weak version, where it is assumed that the function vanishes in an open set. We also mention [28, 57, 58] on this subject, and finally [21] which goal is reached in this work.

In this document, we replace L^p conditions on potentials by relative boundedness with respect to the Laplacian, which is a classical assumption used in the analysis of Schrödinger operators. Our proof relies on a Carleman inequality involving fractional Laplacians, which we prove using well-known techniques developed by Hörmander in [18], further used by Koch and Tataru in [22], and by Rüländ in [43]. This inequality pairs very naturally with Sobolev multipliers assumptions on the external potentials, which are independent of the number of particles. One of the difficulties with strong UCP results is that they need to use Carleman inequalities with singular weights. They are more delicate to show than for regular weights, because Gårding's inequality cannot be applied. We refer to [29] for more details on Carleman estimates with regular weights.

In this chapter, we provide the first strong UCP for many-body operators in L^p spaces and deduce the first complete proof of the Hohenberg-Kohn theorem in these spaces. Our proof mainly uses the method of Georgescu [13]. We also use ideas from Figueiredo-Gossez [6] to pass from the vanishing of Ψ on a set of positive measure to the vanishing to infinite order at one point. The dimension of space being d , we can deal with external and interaction potentials as well as magnetic fields in $L_{\text{loc}}^p(\mathbb{R}^d)$ and magnetic potentials in $L_{\text{loc}}^q(\mathbb{R}^d)$, where

$$\begin{cases} p > \max\left(\frac{2d}{3}, 2\right), \\ q > 2d. \end{cases}$$

Our assumptions are independent of the number of particles N and can treat the singular potentials involved in physics like the Coulomb one. Following Simon in [45, Section C.9] and in light of [19, 22, 54], we conjecture that the same results hold for $p = d/2$ if $d \geq 3$, $p > 1$ if $d = 2$ and $p = 1$ if $d = 1$, and $q = 2p$ for any dimension d . We tried to adapt the approach of [22] to the N -body setting, but did not manage to do so. We hope our work will stimulate further results in this direction.

We also prove the strong UCP for the Pauli operator, which can be seen as an operator-valued matrix and thus belongs to the category of UCP results for systems of equations. Our result implies the Hohenberg-Kohn theorem in presence of a fixed magnetic field.

In order to take into account photons in a DFT context, Ruggenthaler and coworkers [41, 42] considered the Pauli-Fierz operator together with a

corresponding model where light and electrons are quantized, stating an adapted Hohenberg-Kohn theorem and calling the resulting theory QEDFT. Maxwell-Schrödinger theory is a variation of this hybrid model, in which photons are treated semi-classically through an internal self-generated magnetic potential a . Tellgren studied this model in [47] within DFT and baptized the resulting framework Maxwell DFT. In a model describing external magnetic fields but not internal ones [50, 51], a generalization of the Hohenberg-Kohn theorem does not hold, counterexamples were provided in [2]. In DFT, an important problem has been to find a model bringing back this property [8, 25, 26, 34–36, 48, 49, 52, 56]. The models containing internal magnetic potentials do so, as explained in [41, 47] and in this work, and our strong UCP result enables us to rigorously prove the Hohenberg-Kohn theorem in the Maxwell-Schrödinger model. Thus in this setting the one-body density ρ and internal current $j + \text{curl } m + \rho a$ of the ground state contain all the information of the system, that is the knowledge of the external classical electromagnetic field.

1.2 Main results

Because it is of independent interest, we start by explaining the Carleman estimate which is the main tool of our approach.

1.2.1 Carleman estimates for singular weights

We denote by B_R the ball of radius R centered at the origin in \mathbb{R}^n , for $n \geq 1$. The first step in our study consists in a Carleman inequality obtained by standard techniques.

Theorem 1.2.1 (Carleman inequality). *Let $0 < \alpha \leq 1/2$, and let us define $\phi(x) := -\ln|x| + (-\ln|x|)^{-\alpha}$ for $|x| \leq 1/2$. In dimension n , there exist constants c_n and $\tau_n \geq 1$ such that for any $\tau \geq \tau_n$ and any $u \in C_c^\infty(B_{1/2} \setminus \{0\}, \mathbb{C})$, we have*

$$\begin{aligned} \tau^3 \int_{B_{1/2}} \frac{|e^{(\tau+2)\phi} u|^2}{(\ln|x|^{-1})^{2+\alpha}} + \tau \int_{B_{1/2}} \frac{|e^{(\tau+1)\phi} \nabla u|^2}{(\ln|x|^{-1})^{2+\alpha}} + \tau \int_{B_{1/2}} \frac{|\nabla(e^{(\tau+1)\phi} u)|^2}{(\ln|x|^{-1})^{2+\alpha}} \\ + \tau^{-1} \int_{B_{1/2}} \frac{|\Delta(e^{\tau\phi} u)|^2}{(\ln|x|^{-1})^{2+\alpha}} \leq \frac{c_n}{\alpha} \int_{B_{1/2}} |e^{\tau\phi} \Delta u|^2. \end{aligned} \quad (1.1)$$

Those are variants of known Carleman inequalities. The proof, given in Section 1.3, follows from a rather standard reasoning. With ϕ a smooth pseudo-convex function, the classical Carleman estimate for *regular* weights

is

$$\tau^3 \left\| e^{(\tau+2)\phi} u \right\|_{L^2}^2 + \tau \left\| e^{(\tau+1)\phi} \nabla u \right\|_{L^2}^2 + \tau^{-1} \left\| \Delta \left(e^{\tau\phi} u \right) \right\|_{L^2}^2 \leq c_n \left\| e^{\tau\phi} \Delta u \right\|_{L^2}^2, \quad (1.2)$$

for τ large enough, see [29, 46] for more detail. In [39], Regbaoui showed the estimate

$$\tau^2 \left\| |x|^{-(\tau+2)} u \right\|_{L^2}^2 + \left\| |x|^{-(\tau+1)} \nabla u \right\|_{L^2}^2 \leq c_n \left\| |x|^{-\tau} \Delta u \right\|_{L^2}^2, \quad (1.3)$$

where $\phi = \ln |x|^{-1}$. This holds for $\tau \in \mathbb{N} + \frac{1}{2}$ which is a set preventing some quantity to intersect the spectrum of the Laplace-Beltrami operator on the sphere. The estimate (1.3) is not good enough for us due to the slower increase of the coefficients in τ . In [46], Tataru also presents a Carleman estimate with singular weights,

$$\tau^3 \left\| e^{(\tau+1)\phi} u \right\|_{L^2}^2 + \tau \left\| e^{\tau\phi} \nabla u \right\|_{L^2}^2 \leq c_n \left\| e^{\tau\phi} \Delta u \right\|_{L^2}^2, \quad (1.4)$$

with

$$e^{\phi(x)} = (|x| + \lambda |x|^2)^{-1}, \quad (1.5)$$

where λ has to be negative for ϕ to be strictly convex, and where u needs to be supported near the origin. Here the behavior in τ is optimal but the estimate on Δu was not considered in [46]. Another Carleman estimate with singular weights was proved in [43]. It is similar to (1.4) and the weight function is

$$\phi(x) = -\ln |x| + \frac{1}{10} \left((\ln |x|) \arctan \ln |x| - \frac{1}{2} \ln \left(1 + (\ln |x|)^2 \right) \right),$$

for which $\phi(x) \sim -(1 + \pi/20) \ln |x|$ when $|x| \rightarrow 0^+$.

In our application to many-body Schrödinger operators, we needed a Carleman inequality having the best possible powers of τ outside the integrals, with a weight such that $\phi(x) \sim -\ln |x|$ when $|x| \rightarrow 0^+$, for e^ϕ to be close enough to $|\cdot|^{-1}$, and with the same powers of e^ϕ as in the classical estimate (1.2). Our inequality (1.1) fulfills those requirements. The function ϕ in Theorem 1.2.1 respects

$$\frac{1}{|x|} \leq e^{\phi(x)} \leq \frac{e}{|x|}.$$

We obtain the same powers of τ as the classical estimate, and the singularity of the weight is the same as in the regular case, up to some logarithms.

Defining $\varphi(x) := (-\ln|x|)^{-\alpha}$, the inequality (1.1) can be rewritten as

$$\begin{aligned} & \tau^3 \int_{B_{1/2}} \varphi^{2(2+\alpha)} \left| \frac{e^{(\tau+2)\varphi} u}{|x|^{\tau+2}} \right|^2 + \tau \int_{B_{1/2}} \varphi^{2(2+\alpha)} \left| \frac{e^{(\tau+1)\varphi} \nabla u}{|x|^{\tau+1}} \right|^2 \\ & + \tau \int_{B_{1/2}} \varphi^{2(2+\alpha)} \left| \nabla \left(\frac{e^{(\tau+1)\varphi} u}{|x|^{\tau+1}} \right) \right|^2 + \tau^{-1} \int_{B_{1/2}} \varphi^{2(2+\alpha)} \left| \Delta \left(\frac{e^{\tau\varphi} u}{|x|^\tau} \right) \right|^2 \\ & \leq \frac{c_n}{\alpha} \int_{B_{1/2}} \left| \frac{e^{\tau\varphi} \Delta u}{|x|^\tau} \right|^2. \end{aligned}$$

We transform now the inequality (1.1) in a form tailored to be used in a very natural way for many-body operators.

Corollary 1.2.2 (Fractional Carleman inequality). *In dimension n , for any $\delta \in]0, 1]$ there exist constants κ_n and $\tau_0 \geq 1$ such that for any $s \in [0, 1]$, $s' \in [0, \frac{1}{2}]$, any $\tau \geq \tau_0$ and any $u \in C_c^\infty(B_1 \setminus \{0\}, \mathbb{C})$, we have*

$$\begin{aligned} & \tau^{3-4s} \left\| (-\Delta)^{(1-\delta)s} \left(e^{\tau\phi} u \right) \right\|_{L^2(\mathbb{R}^n)}^2 + \tau^{1-4s'} \sum_{i=1}^n \left\| (-\Delta)^{(1-\delta)s'} \left(e^{\tau\phi} \partial_i u \right) \right\|_{L^2(\mathbb{R}^n)}^2 \\ & \leq \frac{\kappa_n}{\delta^{5/2}} \left\| e^{\tau\phi} \Delta u \right\|_{L^2(B_1)}^2. \quad (1.6) \end{aligned}$$

The constant κ_n depends only on the dimension n . The proofs of Theorem 1.2.1 and Corollary 1.2.2 are provided later in Section 1.3.

1.2.2 Unique continuation properties

We are going to state a strong unique continuation property (UCP) result for Schrödinger operators involving gradients, in which potentials are Sobolev multipliers. This type of assumption pairs very naturally with the Carleman inequality involving fractional Laplacians (1.6), as we can see from the proof. At the same time, those assumptions will allow us to prove a corresponding result for the many-body Pauli operator.

Theorem 1.2.3 (Strong UCP for systems with gradients). *Let $\delta > 0$ (small), let $\tilde{V} := (V_{\alpha,\beta})_{1 \leq \alpha, \beta \leq m}$ be a $m \times m$ matrix of potentials in $L_{\text{loc}}^2(\mathbb{R}^n, \mathbb{C})$ and let $\tilde{A} := (A_\alpha)_{1 \leq \alpha \leq m}$ be a list of vector potentials in $L_{\text{loc}}^2(\mathbb{R}^n, \mathbb{R}^n)$, such that for every $R > 0$, there exists $c_R \geq 0$ such that*

$$\begin{cases} \mathbf{1}_{B_R} |V_{\alpha,\beta}|^2 & \leq \epsilon_{n,m,\delta} (-\Delta)^{\frac{3}{2}-\delta} + c_R, \\ \mathbf{1}_{B_R} |A_\alpha|^2 & \leq \epsilon_{n,m,\delta} (-\Delta)^{\frac{1}{2}-\delta} + c_R, \\ |\langle u, -i \mathbf{1}_{B_R} A_\alpha \cdot \nabla u \rangle| & \leq \epsilon_{n,m} \langle u, ((-\Delta) + c_R) u \rangle, \quad \forall u \in C_c^\infty(\mathbb{R}^n), \end{cases} \quad (1.7)$$

in \mathbb{R}^n in the sense of quadratic forms, where $\epsilon_{n,m,\delta}$ and $\epsilon_{n,m}$ are small constants depending only on their indices. Let $\Psi \in H_{\text{loc}}^2(\mathbb{R}^n, \mathbb{C}^m)$ be a weak solution of the $m \times m$ system

$$\left(-\mathbf{1}_{m \times m} \Delta_{\mathbb{R}^n} + i\tilde{A} \cdot \nabla_{\mathbb{R}^n} + \tilde{V}\right) \Psi = 0, \quad (1.8)$$

where $\tilde{A} \cdot \nabla_{\mathbb{R}^n}$ is the $m \times m$ operator-valued matrix $\text{diag}(A_\alpha \cdot \nabla_{\mathbb{R}^n})_{1 \leq \alpha \leq m}$. If Ψ vanishes on a set of positive measure or if it vanishes to infinite order at a point, then $\Psi = 0$.

In all this document, when we write $L \leq J$ for two symmetric operators L and J , we mean it in the sense of forms. We recall that Ψ vanishes to infinite order at $x_0 \in \mathbb{R}^n$ when for all $k \geq 1$, there is a c_k such that

$$\int_{|x-x_0|<\epsilon} |\Psi|^2 dx < c_k \epsilon^k, \quad (1.9)$$

for every $\epsilon < 1$.

Let A be a magnetic potential and B a magnetic field. Physically in dimension 3, A and B are linked by $B = \text{curl } A$, but we will consider arbitrary dimensions and artificially remove the link between A and B . We consider the N -particle Pauli Hamiltonian

$$H^N(v, A, B) := \sum_{\ell=1}^N \left((-i\nabla_\ell + A(x_\ell))^2 + \sigma_\ell \cdot B(x_\ell) + v(x_\ell) \right) + \sum_{1 \leq t < \ell \leq N} w(x_t - x_\ell), \quad (1.10)$$

where σ_ℓ are generalizations of Pauli matrices. They are d square matrices of size $2^{\lfloor (d-1)/2 \rfloor} \times 2^{\lfloor (d-1)/2 \rfloor}$ used to form the $(d+1)$ -dimensional chiral representation of the Clifford algebra, which structures Lorentz-invariant spinor fields [7, Appendix E]. As an operator-valued matrix, the only non-diagonal member is the Stern-Gerlach term $\sum_{\ell=1}^N \sigma_\ell \cdot B(x_\ell)$, responsible for the Zeeman effect. We refer to [5, Chapter XII and Complement A_{XII}] for a discussion on this Hamiltonian. The previous theorem implies the strong UCP for this operator, which is our main result.

Corollary 1.2.4 (Strong UCP for the many-body Pauli operator). *Let $\delta > 0$ and assume that the potentials satisfy*

$$\left(|v|^2 + |w|^2 + |B|^2 + |\text{div } A|^2\right) \mathbf{1}_{B_R} \leq \epsilon_{d,N} (-\Delta)^{\frac{3}{2}-\delta} + c_R \quad \text{in } \mathbb{R}^d, \quad (1.11)$$

$$|A|^2 \mathbf{1}_{B_R} \leq \epsilon_{d,N} (-\Delta)^{\frac{1}{2}-\delta} + c_R \quad \text{in } \mathbb{R}^d, \quad (1.12)$$

for all $R > 0$, where $\epsilon_{d,N}$ is a small constant depending only on d and N . For instance $A \in L^q_{\text{loc}}(\mathbb{R}^d, \mathbb{R}^d)$ and $|B|, \text{div } A, v, w \in L^p_{\text{loc}}(\mathbb{R}^d, \mathbb{R})$ where

$$\begin{cases} p > \max\left(\frac{2d}{3}, 2\right), \\ q > 2d. \end{cases} \quad (1.13)$$

Let $\Psi \in H^2_{\text{loc}}(\mathbb{R}^{dN})$ be a solution to $H^N(v, A, B)\Psi = 0$. If Ψ vanishes on a set of positive measure or if it vanishes to infinite order at a point, then $\Psi = 0$.

In particular, this result can be applied to the magnetic Schrödinger operator $H^N(v, A, 0)$. In the Appendix we recall how assumptions of this Corollary 1.2.4 imply assumption of Theorem 1.4.2 on the gradient term.

1.2.3 Hohenberg-Kohn theorems in presence of magnetic fields

We give here two applications of our strong UCP result in Density Functional Theory. The first one is the classical Hohenberg-Kohn theorem in presence of a fixed magnetic field.

Fixed magnetic fields

In presence of one spin internal degree of freedom, the one-particle density and the paramagnetic current of a wave function Ψ are respectively defined by

$$\begin{aligned} \rho_{\Psi}(x) &:= \sum_{(s_k)_{1 \leq k \leq N} \in \{\uparrow, \downarrow\}^N} \sum_{i=1}^N \int_{\mathbb{R}^{d(N-1)}} |\Psi^{s_k}|^2 dx_1 \cdots dx_{i-1} dx_{i+1} \cdots dx_N, \\ j_{\Psi}(x) &:= \text{Im} \sum_{(s_k)_{1 \leq k \leq N} \in \{\uparrow, \downarrow\}^N} \sum_{i=1}^N \int_{\mathbb{R}^{d(N-1)}} \overline{\Psi^{s_k}} \nabla_i \Psi^{s_k} dx_1 \cdots dx_{i-1} dx_{i+1} \cdots dx_N. \end{aligned}$$

Theorem 1.2.5 (Hohenberg-Kohn with a fixed magnetic field). *Let $A \in (L^q + L^\infty)(\mathbb{R}^d, \mathbb{R}^d)$, $B \in (L^p + L^\infty)(\mathbb{R}^d, \mathbb{R}^d)$ and $w, v_1, v_2 \in (L^p + L^\infty)(\mathbb{R}^d, \mathbb{R})$, with p and q as in (1.13). If there are two normalized eigenfunctions Ψ_1 and Ψ_2 of $H^N(v_1, A, B)$ and $H^N(v_2, A, B)$, corresponding to the first eigenvalues, and such that $\rho_{\Psi_1} = \rho_{\Psi_2}$, then there exists a constant c such that $v_1 = v_2 + c$.*

We do not present the proof because it can be reproduced from the one of Theorem 1.2.7.

Ill-posedness of the Hohenberg-Kohn theorem for Spin-Current DFT

We recall the definition of Pauli matrices in dimension 3,

$$\sigma^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma^y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

they act on one-particle two-component wavefunctions $\phi = (\phi^\uparrow \ \phi^\downarrow)^T$, where $\phi^\uparrow, \phi^\downarrow \in L^2(\mathbb{R}^d, \mathbb{C})$ and $\int |\phi|^2 = 1$. We denote by $L_a^2(\mathbb{R}^{dN})$ the space of antisymmetric functions of N variables in \mathbb{R}^d . The state of a system is described by wavefunctions $\Psi \in L_a^2(\mathbb{R}^{dN}, \mathbb{C}^{2^N})$. We introduce the one-body densities

$$\rho_\Psi^{\alpha\beta}(x) := \sum_{s \in \{\uparrow, \downarrow\}^{N-1}} \sum_{i=1}^N \int_{\mathbb{R}^{d(N-1)}} \Psi^{\alpha,s}(x, Y) \overline{\Psi^{\beta,s}(x, Y)} dY,$$

where $\alpha, \beta \in \{\uparrow, \downarrow\}$. We remark that $\rho_\Psi^{\uparrow\downarrow} = \overline{\rho_\Psi^{\downarrow\uparrow}} =: \xi_\Psi$. We define the density $\rho_\Psi := \rho_\Psi^{\uparrow\uparrow} + \rho_\Psi^{\downarrow\downarrow}$ and the locally gauge invariant magnetization

$$m_\Psi := \begin{pmatrix} \rho_\Psi^{\uparrow\downarrow} + \rho_\Psi^{\downarrow\uparrow} \\ -i(\rho_\Psi^{\uparrow\downarrow} - \rho_\Psi^{\downarrow\uparrow}) \\ \rho_\Psi^{\uparrow\uparrow} - \rho_\Psi^{\downarrow\downarrow} \end{pmatrix} = \begin{pmatrix} 2 \operatorname{Re} \xi_\Psi \\ 2 \operatorname{Im} \xi_\Psi \\ \rho_\Psi^{\uparrow\uparrow} - \rho_\Psi^{\downarrow\downarrow} \end{pmatrix}.$$

The energy of a quantum wavefunction is coupled to the magnetic field only through the density ρ_Ψ and through the magnetization current $j_\Psi + \operatorname{curl} m_\Psi$. Indeed, using either bosonic or fermionic statistics,

$$\begin{aligned} & \left\langle \Psi, \sum_{\ell=1}^N (\sigma_\ell \cdot (-i\nabla_\ell + A(x_\ell)))^2 \Psi \right\rangle \\ &= \int |\nabla \Psi|^2 + \int A^2 \rho_\Psi + \int A \cdot (2j_\Psi + \operatorname{curl} m_\Psi). \end{aligned}$$

Previously, the fields A and B were independent. We now assume the physical relation $B = \operatorname{curl} A$, take the Coulomb gauge $\operatorname{div} A = 0$ and consider the physical Hamiltonian $H^N(v, A) := H^N(v, A, \operatorname{curl} A)$.

A natural question is whether the model with Pauli operator and varying magnetic fields has a corresponding Hohenberg-Kohn theorem, i.e. we ask whether $(\rho_{\Psi_1}, 2j_{\Psi_1} + \operatorname{curl} m_{\Psi_1}) = (\rho_{\Psi_2}, 2j_{\Psi_2} + \operatorname{curl} m_{\Psi_2})$ (or even $(\rho_{\Psi_1}, j_{\Psi_1}, m_{\Psi_1}) = (\rho_{\Psi_2}, j_{\Psi_2}, m_{\Psi_2})$) implies $A_1 = A_2$ and $v_1 = v_2 + c$. This turns out to be wrong, due to counterexamples found by Capelle and Vignale in [2].

Many authors studied this ill-posedness issue [2, 8, 25, 26, 34–36, 48, 49, 52, 56], also from the point of view of Spin DFT, in which current effects

are neglected [3, 10, 23, 24, 36, 37, 40, 53], and from the point of view of Current DFT, in which spin effects are neglected [8, 26, 27, 34, 35, 49, 52]. In particular, see Laestadius and Benedicks in [26, Theorem 2] for a counterexample in Current DFT.

Nevertheless, one could try to find a similar result using the physical total current, that is the one which can be measured in experiments, $j_t := j + \text{curl } m + \rho A$ and respects $\text{div } j_t = 0$. As explained in [35, 49], for one particle and for Current DFT where $j_t := j + \rho A$, the relation $\text{curl}(j_t/\rho) = \text{curl } A$ shows that the knowledge of j_t and ρ gives the knowledge of A and v by the Hohenberg-Kohn theorem. The case of $N \geq 2$ particles is still open.

Hohenberg-Kohn for the Maxwell-Schrödinger model

We keep the dimension $d = 3$. In order to get a model taking into account current effects but having a Hohenberg-Kohn theorem, and as a second application of our strong UCP result, we follow Tellgren [47] and investigate the Maxwell-Schrödinger theory. This is a hybrid model of quantum mechanics where electrons are treated quantum mechanically and light is treated classically, and provides an approximation of non-relativistic QED [9, 14]. It was studied through a DFT approach in [47] and the resulting framework was called Maxwell DFT. We define

$$\mathcal{A}(\mathbb{R}^d, \mathbb{R}^d) := \left\{ A \in H^1(\mathbb{R}^d, \mathbb{R}^d) \mid \text{div } A = 0 \text{ weakly in } H^1(\mathbb{R}^d) \right\},$$

the set of divergence-free magnetic potentials, i.e. potentials in the Coulomb gauge. A state of matter and light is given by a pair $(\Psi, a) \in L_a^2(\mathbb{R}^{dN}, \mathbb{C}^{2^N}) \times \mathcal{A}$, where Ψ describes electrons and where a is an internal magnetic potential describing the photon cloud around the electrons.

We denote by $H_0^N := H^N(0, 0)$ the kinetic and interaction parts of the Schrödinger operator. The energy functional takes into account the energy of Ψ coupled to the total magnetic field, and the kinetic energy of the internal magnetic field. We denote by α the fine structure constant and define $\epsilon := (8\pi\alpha^2)^{-1}$. The Maxwell-Schrödinger energy functional is

$$\begin{aligned} \mathcal{E}_{v,A}(\Psi, a) &:= \left\langle \Psi, H^N(v, a + A)\Psi \right\rangle + \epsilon \int |\text{curl } a|^2 \\ &= \left\langle \Psi, H_0^N \Psi \right\rangle + \int (v + |a + A|^2) \rho_\Psi \\ &\quad + \int (a + A) \cdot (2j_\Psi + \text{curl } m_\Psi) + \epsilon \int |\text{curl } a|^2, \end{aligned}$$

for bosons or fermions. We denote by

$$E := \inf_{\substack{\Psi \in (H^1 \cap L_a^2)(\mathbb{R}^{dN}, \mathbb{C}) \\ \int |\Psi|^2 = 1 \\ a \in (L_{\text{loc}}^q \cap \mathcal{A})(\mathbb{R}^d, \mathbb{C}^d)}} \mathcal{E}_{v,A}(\Psi, a),$$

the ground state energy. This functional was studied in [9, 32, 33] when $A = 0$, where the authors found that in the case of a Coulomb potential generated by only one atom having a large number of protons, this minimum was $-\infty$. In [32, Theorem 1], they also prove that for Coulomb potentials induced by molecules, if the total number of protons in the molecule is lower than 1050, independently of the positions of the nucleus, then the functional is bounded below. This justifies the applicability of the next theorem to physical systems. When one removes the Zeeman term $\sum_{\ell=1}^N \sigma_\ell \cdot B(x_\ell)$ and considers the corresponding functional, then this issue disappears and the functional is always bounded from below for $v, w \in (L^{d/2} + L^\infty)(\mathbb{R}^d)$ and $A \in (L^d + L^\infty)(\mathbb{R}^d)$, by the diamagnetic inequality.

The corresponding Euler-Lagrange equations are the Schrödinger equation together with a Maxwell equation. Using $\text{curl}^* = \text{curl}$ and $\text{curl curl} = \nabla \text{div} - \Delta$ we can show that if it exists, the ground state (Ψ, a) respects

$$\begin{cases} \sum_{\ell=1}^N \left(-\Delta_\ell - 2i(a + A) \cdot \nabla_\ell + v + |a + A|^2 + \sigma_\ell \cdot (\text{curl}(a + A))_\ell \right) \Psi = E\Psi, \\ j_\Psi + \text{curl } m_\Psi + \rho_\Psi(a + A) - \epsilon \Delta a = 0, \end{cases}$$

where we did not write all the x_j arguments in the first equation for simplicity of notation. The internal current of a state (Ψ, a) is defined by

$$j_{(\Psi, a)} := j_\Psi + \text{curl } m_\Psi + \rho_\Psi a.$$

We remark that if we did not fix the gauge $\text{div } A = 0$, $j_{(\Psi, a)}$ would be locally gauge invariant. We make an other preliminary remark on the density of solutions of Schrödinger's equation.

Remark 1.2.6. *Let Ψ be a solution of $H^N(v, A, B)\Psi = 0$, under the assumptions of Corollary 1.2.4. Then its density vanishes almost nowhere,*

$$\left| \left\{ x \in \mathbb{R}^d \mid \rho_\Psi(x) = 0 \right\} \right| = 0.$$

Indeed, if ρ_Ψ vanishes on a set $S \subset \mathbb{R}^d$ of positive measure, then

$$N \int_{S \times \mathbb{R}^{d(N-1)}} |\Psi|^2 = \int_S \rho_\Psi = 0$$

so Ψ vanishes on $S \times \mathbb{R}^{d(N-1)}$ which has infinite volume. But by the strong UCP theorem for Pauli operators, Corollary 1.2.4, Ψ does not vanish on sets of positive measure. This holds in any spin number, in particular this holds when there is no spin. We are now ready to prove the Hohenberg-Kohn theorem for this model.

Theorem 1.2.7 (Hohenberg-Kohn for Maxwell DFT). *Let $p > 2$ and $q > 6$ and let $w, v_1, v_2 \in (L^p + L^\infty)(\mathbb{R}^3, \mathbb{R})$, $A_1, A_2 \in (L_{\text{loc}}^q \cap \mathcal{A})(\mathbb{R}^3, \mathbb{R}^3)$ be potentials*

such that \mathcal{E}_{v_1, A_1} and \mathcal{E}_{v_2, A_2} are bounded from below and admit lowest energy states (Ψ_1, a_1) and (Ψ_2, a_2) . If $\rho_{\Psi_1} = \rho_{\Psi_2}$ and $j_{(\Psi_1, a_1)} = j_{(\Psi_2, a_2)}$, then $A_1 = A_2$ and there is a constant c such that $v_1 = v_2 + c$.

This result shows that in the Maxwell-Schrödinger framework, the knowledge of the ground state density ρ and internal current $j + \text{curl } m + \rho a$ gives the knowledge of v and A . Said differently, at equilibrium, ρ and $j + \text{curl } m + \rho a$ contain the information of v and A . This is a rigorous justification of Tellgren's Hohenberg-Kohn theorem [47].

Proof. Let us denote by $\rho := \rho_{\Psi_1} = \rho_{\Psi_2}$ the common densities, by $j' := j_{(\Psi_1, a_1)} = j_{(\Psi_2, a_2)}$ the common internal currents, and by $E_i := \mathcal{E}_{v_i, A_i}(\Psi_i, a_i)$ for $i \in \{1, 2\}$ the ground state energies. By the standard proof of the Hohenberg-Kohn theorem [11, 16], we can prove that $\mathcal{E}_{v_1, A_1}(\Psi_2, a_2) = E_1$. So (Ψ_2, A_2) respects the Euler-Lagrange equations for \mathcal{E}_{v_1, a_1} , that is

$$\begin{cases} \sum_{\ell=1}^N \left(-\Delta_{\ell} - 2i(a_2 + A_1) \cdot \nabla_{\ell} + v_1 + |a_2 + A_1|^2 \right) \Psi_2 \\ \quad + \sum_{\ell=1}^N \sigma_{\ell} \cdot (\text{curl}(a_2 + A_1))_{\ell} \Psi_2 = E_1 \Psi_2, \\ j' + \rho A_1 - \epsilon \Delta a_2 = 0. \end{cases}$$

We take the difference of those equations with the Euler-Lagrange equations verified by (Ψ_2, a_2) for \mathcal{E}_{v_2, A_2} and get

$$\begin{cases} E_2 - E_1 + \sum_{\ell=1}^N \left(-2i(A_1 - A_2) \cdot \nabla_{\ell} + \sigma_{\ell} \cdot (\text{curl}(A_1 - A_2))_{\ell} \right) \Psi_2 \\ \quad + \sum_{\ell=1}^N (v_1 - v_2 + |a_2 + A_1|^2 - |a_2 + A_2|^2)(x_{\ell}) \Psi_2 = 0, \\ \rho(A_1 - A_2) = 0. \end{cases} \quad (1.14)$$

By the unique continuation result of Corollary 1.2.4, and by Remark 1.2.6, ρ does not vanish on sets of positive measure, therefore the second equation in (1.14) yields $A_1 = A_2$. Using it in the first equation of (1.14), we get

$$\left(E_2 - E_1 + \sum_{\ell=1}^N (v_1 - v_2)(x_{\ell}) \right) \Psi_2 = 0$$

so, by the same argument as in [11], we conclude that $v_1 = v_2 + (E_1 - E_2)/N$. \square

One could still want to search for a Hohenberg-Kohn theorem in the standard Schrödinger model but involving the knowledge of j_t instead of the knowledge of j . This is an open problem. Our result easily extends to the same model but without spin effects, that is when we take for the one-body kinetic operator $(-i\nabla + A)^2$ instead of $(\sigma \cdot (-i\nabla + A))^2$. Then the internal current is $j + \rho a$ and the above results hold.

1.3 Proofs of Carleman inequalities

1.3.1 Proof of Theorem 1.2.1

We use standard arguments which can for instance be read in [22, 43]. We denote by $r := |x|$ the radial coordinate. In dimension n , the Laplace operator in spherical coordinates is $\Delta = \partial_{rr} + \frac{n-1}{r}\partial_r + \frac{1}{r^2}\Delta_S$, where Δ_S is the Laplace-Beltrami operator on the $(n-1)$ -dimensional sphere. Using log-spherical coordinates $t := \ln r$, we have

$$|x|^2 \Delta = \partial_{tt} + (n-2)\partial_t + \Delta_S.$$

We take the function $\phi(x) = -\ln|x| + (-\ln|x|)^{-\alpha}$ as in the statement of the Theorem, and define $\varphi(t) := \phi(e^t)$. More explicitly,

$$\begin{aligned} \varphi(t) &= -t + \frac{1}{(-t)^\alpha}, & \varphi'(t) &= -1 + \frac{\alpha}{(-t)^{\alpha+1}}, & \varphi''(t) &= \frac{\alpha(\alpha+1)}{(-t)^{\alpha+2}}, \\ \varphi'''(t) &= \frac{\alpha(\alpha+1)(\alpha+2)}{(-t)^{\alpha+3}}, & \varphi''''(t) &= \frac{\alpha(\alpha+1)(\alpha+2)(\alpha+3)}{(-t)^{\alpha+4}}, \end{aligned}$$

so $-1 < \varphi' < -1/8$ and $\varphi'', \varphi''', \varphi'''' > 0$ on $] -\infty, -\ln 2]$. Conjugating the previous operator $|x|^2 \Delta$ with $e^{\tau\phi}$ yields

$$P := e^{\tau\phi} |x|^2 \Delta e^{-\tau\phi} = \partial_{tt} + (-2\tau\varphi' + n - 2) \partial_t + \tau^2 \varphi'^2 - \tau(n-2)\varphi' + \Delta_S,$$

and decomposing the result in symmetric and antisymmetric parts, we have $P = S + A$, where

$$\begin{aligned} S &:= \partial_{tt} + \tau^2 \varphi'^2 - \tau(n-2)\varphi' + \tau\varphi'' + \Delta_S, \\ A &:= (-2\tau\varphi' + n - 2) \partial_t - \tau\varphi'''. \end{aligned}$$

We implicitly take the $L^2(\mathbb{R}^n)$ norm. We want to manipulate $Pv^2 = Sv^2 + Av^2 + \langle v, [S, A]v \rangle$ for a function $v \in C_c^\infty(] -\infty, -\ln 2] \times \mathbb{S}^{n-1}, \mathbb{C})$. We compute

$$\begin{aligned} [S, A] &= -4\tau\varphi''\partial_{tt} - 2\tau\varphi'''\partial_t \\ &\quad - (-2\tau\varphi' + n - 2) \left(2\tau^2\varphi'\varphi'' - \tau(n-2)\varphi'' + \tau\varphi'''' \right) - \tau\varphi'''''. \end{aligned}$$

We have $2 \operatorname{Re} \langle Sv, Av \rangle = \langle v, [S, A]v \rangle$ so this term is real and integrating by parts yields

$$\begin{aligned} \langle v, [S, A]v \rangle &= 4\tau^3 \int \varphi'^2 \varphi'' |v|^2 + 2\tau^2 \int \varphi' (\varphi''' - n\varphi'') |v|^2 \\ &+ 4\tau \int \varphi'' |\partial_t v|^2 + \tau(n-2)^2 \int \varphi'' |v|^2 - 2\tau \int \varphi'''' |v|^2 - \tau(n-2) \int \varphi'''' |v|^2. \end{aligned}$$

Thus for τ large enough,

$$4\tau^3 \int \varphi'^2 \varphi'' |v|^2 + 4\tau \int \varphi'' |\partial_t v|^2 \leq \langle v, [S, A]v \rangle \leq Pv^2. \quad (1.15)$$

With $|\langle \varphi'' v, Sv \rangle| \leq \varphi'' v Sv \leq \tau^{-\frac{3}{2}} Pv^2/2$, we compute the radial part of the gradient

$$\begin{aligned} \int \varphi'' |\nabla_S v|^2 &= \langle \varphi'' v, (-\Delta_S)v \rangle \\ &= \langle \varphi'' v, (-S + \partial_{tt} + \tau^2 \varphi'^2 - \tau(n-2)\varphi' + \tau\varphi'')v \rangle \\ &= \tau^2 \int \varphi'^2 \varphi'' |v|^2 - \tau(n-2) \int \varphi' \varphi'' |v|^2 + \tau \int \varphi'' |v|^2 \\ &\quad + \frac{1}{2} \int \varphi'''' |v|^2 - \langle \varphi'' v, Sv \rangle - \int \varphi'' |\partial_t v|^2 \\ &\leq \tau^2 \int \varphi'^2 \varphi'' |v|^2 - \langle \varphi'' v, Sv \rangle \leq \frac{1}{2\tau} Pv^2, \end{aligned}$$

for τ large enough. Now, using the inequality (1.15) again, we find

$$\tau^3 \int \varphi'^2 \varphi'' |v|^2 + \tau \int \varphi'' (|\partial_t v|^2 + |\nabla_S v|^2) \leq Pv^2. \quad (1.16)$$

Working back in cartesian coordinates, we have

$$|\partial_t v|^2 + |\nabla_S v|^2 = |x|^2 |\nabla v|^2.$$

We can now apply the previous well-known techniques to form the inequality (1.1), which is fitted with our application. Defining $u := e^{\tau\phi}v$ and using

$$1 \leq |x|e^\phi \leq e, \quad (1.17)$$

inequality (1.16) implies

$$\tau^3 \int \frac{|e^{(\tau+2)\phi}u|^2}{(-\ln|x|)^{2+\alpha}} + \tau \int \frac{|x|^2 |\nabla(e^{(\tau+2)\phi}u)|^2}{(-\ln|x|)^{2+\alpha}} \leq \frac{2^6 e^4}{\alpha} \int |e^{\tau\phi} \Delta u|^2.$$

Using also

$$1 \leq |x| |\nabla\phi| \leq e^{(\ln 2)^{-1/2}} \leq 4, \quad (1.18)$$

in $B_{1/2}$, we have

$$\begin{aligned}
\left| e^{(\tau+1)\phi} \nabla u \right|^2 &= \left| e^{-\phi} \left(e^{(\tau+2)\phi} \nabla u \right) \right|^2 \\
&= \left| e^{-\phi} \nabla \left(e^{(\tau+2)\phi} u \right) - (\tau+2) e^{-\phi} (\nabla \phi) e^{(\tau+2)\phi} u \right|^2 \\
&\leq 2e^{-2\phi} \left| \nabla \left(e^{(\tau+2)\phi} u \right) \right|^2 + 2(\tau+2)^2 e^{-2\phi} |\nabla \phi|^2 \left| e^{(\tau+2)\phi} u \right|^2 \\
&\leq 2|x|^2 \left| \nabla \left(e^{(\tau+2)\phi} u \right) \right|^2 + 2^5 (\tau+2)^2 \left| e^{(\tau+2)\phi} u \right|^2,
\end{aligned}$$

and similarly

$$\begin{aligned}
\left| \nabla \left(e^{(\tau+1)\phi} u \right) \right|^2 &= \left| (\tau+1) (\nabla \phi) e^{(\tau+1)\phi} u + e^{(\tau+1)\phi} \nabla u \right|^2 \\
&\leq 2^5 (\tau+1)^2 \left| e^{(\tau+2)\phi} u \right|^2 + 2 \left| e^{(\tau+1)\phi} \nabla u \right|^2.
\end{aligned}$$

Eventually, we obtain

$$\begin{aligned}
\tau^3 \int \frac{\left| e^{(\tau+2)\phi} u \right|^2}{(-\ln|x|)^{2+\alpha}} + \tau \int \frac{\left| e^{(\tau+1)\phi} \nabla u \right|^2}{(-\ln|x|)^{2+\alpha}} + \tau \int \frac{\left| \nabla \left(e^{(\tau+1)\phi} u \right) \right|^2}{(-\ln|x|)^{2+\alpha}} \\
\leq \frac{2^{14} e^4}{\alpha} \int \left| e^{\tau\phi} \Delta u \right|^2.
\end{aligned}$$

These are the first terms in (1.1). We now turn to the estimates on the second derivative. Since $|x|^2 \Delta \phi = (n-2)\varphi'(\ln|x|) + \varphi''(\ln|x|)$ we have

$$|x|^2 |\Delta \phi| \leq |n-2| + \frac{3}{4(\ln 2)^{3/2}} \leq n+4. \quad (1.19)$$

Since

$$\nabla e^{\tau\phi} = \tau e^{\tau\phi} \nabla \phi, \quad \Delta e^{\tau\phi} = \tau e^{\tau\phi} (\Delta \phi + \tau |\nabla \phi|^2), \quad (1.20)$$

then we find

$$\tau^{-1} \int \frac{\left| \Delta \left(e^{\tau\phi} u \right) \right|^2}{(-\ln|x|)^{2+\alpha}} \leq \frac{2^{25} e^4 (n+4)^2}{\alpha} \int \left| e^{\tau\phi} \Delta u \right|^2.$$

The constant c_n in (1.1) can be taken to be $2^{25} e^4 (n+4)^2$, for instance. \square

1.3.2 Proof of Corollary 1.2.2

We denote by c a constant which only depends on the dimension n . We fix $\alpha = 1/2$. For any $a \in]0, 1[$, we have

$$e^{-2a\phi} \leq \frac{c}{a^{\frac{5}{2}} (-\ln|x|)^{\frac{5}{2}}},$$

on $B_{1/2}$. So the inequality (1.1) taken from Theorem 1.2.1 implies

$$\begin{aligned}
& \tau^3 e^{(\tau+2-a)\phi} u^2 + \tau e^{(\tau+1-a)\phi} \nabla u^2 \\
& \leq c \tau^3 a^{-\frac{5}{2}} \frac{e^{(\tau+2)\phi} u^2}{(-\ln|x|)^{\frac{5}{4}}} + c \tau a^{-\frac{5}{2}} \frac{e^{(\tau+1)\phi} \nabla u^2}{(-\ln|x|)^{\frac{5}{4}}} \\
& \leq c a^{-\frac{5}{2}} e^{\tau\phi} \Delta u^2.
\end{aligned} \tag{1.21}$$

We now compute

$$\begin{aligned}
& |x|^a \left| \Delta \left(e^{\tau\phi} u \right) \right| \\
& = |x|^a \left| u \Delta e^{\tau\phi} + 2 \nabla u \cdot \nabla e^{\tau\phi} + e^{\tau\phi} \Delta u \right| \\
& = |x|^a \left| \tau e^{\tau\phi} u \Delta \phi + \tau^2 |\nabla \phi|^2 e^{\tau\phi} u + 2 \tau \nabla \phi \cdot e^{\tau\phi} \nabla u + e^{\tau\phi} \Delta u \right| \\
& \leq \tau^2 e^{\tau\phi} |u| \left(|x|^a |\Delta \phi| + |x|^a |\nabla \phi|^2 \right) + 2 \tau e^{\tau\phi} |\nabla u| |x|^a |\nabla \phi| \\
& \quad + e^{\tau\phi} |\Delta u| |x|^a.
\end{aligned}$$

Since we work in $B_{1/2}$, we have $|x|^a \leq 1$. Using (1.18) yields $|x|^a |\nabla \phi|^2 \leq 16 |x|^{a-2}$ and $|x|^a |\nabla \phi| \leq 4 |x|^{a-1}$, and (1.19) yields $|x|^a |\Delta \phi| \leq (n+4) |x|^{a-2}$, so we get

$$\begin{aligned}
& |x|^a \left| \Delta \left(e^{\tau\phi} u \right) \right| \\
& \leq (n+20) \tau^2 |x|^{a-2} e^{\tau\phi} |u| + 8 \tau |x|^{a-1} e^{\tau\phi} |\nabla u| + e^{\tau\phi} |\Delta u| \\
& \leq (n+20) e^{a-2} \tau^2 e^{(\tau+2-a)\phi} |u| + 8 e^{a-1} \tau e^{(\tau+1-a)\phi} |\nabla u| + e^{\tau\phi} |\Delta u| \\
& \leq c \left(\tau^2 e^{(\tau+2-a)\phi} |u| + \tau e^{(\tau+1-a)\phi} |\nabla u| + e^{\tau\phi} |\Delta u| \right),
\end{aligned} \tag{1.22}$$

where in the second inequality we applied (1.17). We will also use the fractional Hardy inequality,

$$\left\| (-\Delta)^{-\delta} |x|^{-2\delta} \right\|_{L^2(\mathbb{R}^n) \rightarrow L^2(\mathbb{R}^n)} = 4^{-\delta} \left(\frac{\Gamma\left(\frac{n-2\delta}{4}\right)}{\Gamma\left(\frac{n+2\delta}{4}\right)} \right)^2 \leq 1, \tag{1.23}$$

which holds for any $\delta \in [0, n/2[$. Its sharp constant was found in [1, 15, 55]. Choosing $a = \delta/2 \in [0, n/4]$, we are ready to deduce that

$$\begin{aligned}
& (-\Delta)^{1-\frac{a}{2}} \left(e^{\tau\phi} u \right) \\
& = (-\Delta)^{-\frac{a}{2}} |x|^{-a} |x|^a (-\Delta) \left(e^{\tau\phi} u \right) \\
& \leq |x|^a (-\Delta) \left(e^{\tau\phi} u \right) \\
& \leq c \left(\tau^2 e^{(\tau+2-a)\phi} u + \tau e^{(\tau+1-a)\phi} \nabla u + e^{\tau\phi} \Delta u \right) \\
& \leq c a^{-\frac{5}{4}} \tau^{\frac{1}{2}} e^{\tau\phi} \Delta u,
\end{aligned}$$

where, in the inequalities, we respectively used (1.23), (1.22) and (1.21). Applying Hölder's inequality together with

$$e^{\tau\phi}u \leq ca^{-\frac{5}{4}}\tau^{-\frac{3}{2}}e^{\tau\phi}\Delta u,$$

as implied by (1.1), yields the first part of our claim (1.6). We remark that this is also true for $a \in [n/4, 1[$.

Now we show the second part of the inequality. We begin by expanding

$$\begin{aligned} & |x|^a \left| \partial_i \left(e^{\tau\phi} \partial_j u \right) \right| \\ &= |x|^a \left| \partial_{ij} \left(e^{\tau\phi} u \right) - \tau (\partial_{ij}\phi) e^{\tau\phi} u - \tau^2 (\partial_j\phi) (\partial_i\phi) e^{\tau\phi} u - \tau (\partial_j\phi) e^{\tau\phi} \partial_i u \right| \\ &\leq c\tau^2 e^{(\tau+2-a)\phi} |u| + c\tau e^{(\tau+1-a)\phi} |\partial_i u| + \left| \partial_{ij} \left(e^{\tau\phi} u \right) \right|. \end{aligned}$$

Therefore by (1.23),

$$\begin{aligned} & (-\Delta)^{\frac{1}{2}-\frac{a}{2}} \left(e^{\tau\phi} \partial_j u \right) \\ &= (-\Delta)^{-\frac{a}{2}} \nabla \left(e^{\tau\phi} \partial_j u \right) \\ &\leq |x|^a \nabla \left(e^{\tau\phi} \partial_j u \right) \\ &\leq c \left(\tau^2 e^{(\tau+2-a)\phi} u + \tau e^{(\tau+1-a)\phi} \nabla u + \partial_{ij} \left(e^{(\tau-a)\phi} u \right) \right) \\ &\leq c \left(\tau^2 e^{(\tau+2-a)\phi} u + \tau e^{(\tau+1-a)\phi} \nabla u + \Delta \left(e^{(\tau-a)\phi} u \right) \right) \\ &\leq ca^{-\frac{5}{4}}\tau^{\frac{1}{2}}e^{\tau\phi}\Delta u, \end{aligned}$$

where we used $2|k_i k_j| \leq k_i^2 + k_j^2$. Applying Hölder's inequality together with

$$e^{\tau\phi} \partial_j u \leq ca^{-\frac{5}{4}}\tau^{-\frac{3}{2}}e^{\tau\phi} \Delta u,$$

we obtain the second part of the sought-after inequality (1.6). \square

1.4 Proof of the strong unique continuation property

We present here the proof of Theorem 1.4.2.

Step 1. Vanishing on a set of positive measure implies vanishing to infinite order at one point.

To prove that Ψ vanishes to infinite order at a point, we extend a property showed by Figueiredo and Gossez in [6], to magnetic fields.

Proposition 1.4.1 (Figueiredo-Gossez with magnetic term).

Let $V \in L^1_{\text{loc}}(\mathbb{R}^n, \mathbb{C})$ and $A \in L^1_{\text{loc}}(\mathbb{R}^n, \mathbb{R}^n)$ such that for every $R > 0$, there exist a, a' and $c > 0$ such that $a + a' < 1$ and

$$\begin{aligned} -\mathbf{1}_{B_R} \operatorname{Re} V &\leq a(-\Delta) + c, \\ \langle u, -i\mathbf{1}_{B_R} A \cdot \nabla u \rangle &\leq \langle u, (a'(-\Delta) + c)u \rangle, \quad \forall u \in C_c^\infty(\mathbb{R}^n). \end{aligned}$$

Let $\Psi \in H^1_{\text{loc}}(\mathbb{R}^n)$ satisfying $-\Delta\Psi + iA \cdot \nabla\Psi + V\Psi = 0$ weakly. If Ψ vanishes on a set of positive measure, then Ψ has a zero of infinite order.

Proof. We take $\delta \in (0, 1/2]$ and define a smooth real positive localisation function η with support in $B_{2\delta}$, equal to 1 in B_δ , and such that $|\nabla\eta| \leq c/\delta$ and $|\Delta\eta| \leq c/\delta^2$. And integration by parts and the use of $2 \operatorname{Re} \bar{\Psi} \nabla \Psi = \nabla |\Psi|^2$ yields

$$\begin{aligned} \operatorname{Re} \int \eta^2 \bar{\Psi} \Delta \Psi &= - \int |\eta \nabla \Psi|^2 - \int \nabla(\eta^2) \operatorname{Re} \bar{\Psi} \nabla \Psi \\ &= - \int |\eta \nabla \Psi|^2 + \frac{1}{2} \int |\Psi|^2 \Delta(\eta^2). \end{aligned}$$

Hence, multiplying Schrödinger's equation by $\eta^2 \bar{\Psi}$, taking the real parts, integrating by parts and rearranging the obtained equation yields

$$\begin{aligned} \int |\eta \nabla \Psi|^2 &= - \operatorname{Re} \int \eta^2 \bar{\Psi} iA \cdot \nabla \Psi - \operatorname{Re} \int V |\eta \Psi|^2 + \frac{1}{2} \int |\Psi|^2 \Delta \eta^2 \\ &= - \int \eta \bar{\Psi} iA \cdot \nabla(\eta \Psi) - \int (\operatorname{Re} V) |\eta \Psi|^2 + \frac{1}{2} \int |\Psi|^2 \Delta \eta^2 \\ &\leq (a + a') \int |\nabla(\eta \Psi)|^2 + 2c \int |\eta \Psi|^2 + \frac{1}{2} \int |\Psi|^2 \Delta \eta^2 \\ &= (a + a') \int |\eta \nabla \Psi|^2 + (a + a') \int |\Psi \nabla \eta|^2 + \frac{1 - a - a'}{2} \int |\Psi|^2 \Delta \eta^2 \\ &\quad + 2c \int |\eta \Psi|^2, \end{aligned} \tag{1.24}$$

where we used the assumptions on the potentials. We move the first term of the right-hand-side to the left, which yields

$$\int |\eta \nabla \Psi|^2 \leq c \int |\Psi|^2 (\eta^2 + |\nabla \eta|^2 + |\Delta \eta^2|) \leq \frac{c}{\delta^2} \int_{B_{2\delta}} |\Psi|^2, \tag{1.25}$$

where we used that $\operatorname{supp} \eta \subset B_{2\delta}$. Then we have

$$\int_{B_\delta} |\nabla \Psi|^2 = \int_{B_\delta} |\eta \nabla \Psi|^2 \leq \int |\eta \nabla \Psi|^2 \leq \frac{c}{\delta^2} \int_{B_{2\delta}} |\Psi|^2,$$

where c is independent of δ , and where we used that $\eta = 1$ in B_δ . This estimate is the same statement as [6, Lemma 1]. The end of the proof is thus exactly the proof of [6, Proposition 3]. This consists in applying Hölder's

and Sobolev's inequalities, so $\int_{B_\delta} |\Psi|^2$ is controlled by $\int_{B_{2\delta}} |\Psi|^2$ times a factor which is proved to be small by using Lebesgue's density theorem. Iterating this estimate yields (1.9), that is the definition of Ψ vanishes to infinite order at the origin. \square

The last proof extends to Pauli operators, which Zeeman part can be put in a matrix potential.

Proposition 1.4.2 (Figueiredo-Gossez for Pauli systems).

Let $\tilde{V} := (V_{\alpha,\beta})_{1 \leq \alpha,\beta \leq m}$ be a $m \times m$ matrix of potentials in $L^2_{\text{loc}}(\mathbb{R}^n, \mathbb{C})$ and let $\tilde{A} := (A_\alpha)_{1 \leq \alpha \leq m}$ be a list of vector potentials in $L^2_{\text{loc}}(\mathbb{R}^n, \mathbb{R}^n)$, such that for every $R > 0$, there exists $c_R \geq 0$ such that

$$\begin{aligned} -\mathbf{1}_{B_R} \operatorname{Re} V_{\alpha,\beta} &\leq \epsilon_{n,m}(-\Delta) + c_R, \\ \langle u, -i\mathbf{1}_{B_R} A_\alpha \cdot \nabla u \rangle &\leq \langle u, (\epsilon_{n,m}(-\Delta) + c_R) u \rangle, \quad \forall u \in C_c^\infty(\mathbb{R}^n), \end{aligned}$$

where $\epsilon_{n,m}$ is a small constant depending only on the dimensions n and m . Let $\Psi \in H^2_{\text{loc}}(\mathbb{R}^n, \mathbb{C}^m)$ be a weak solution of the $m \times m$ system (1.8), that is

$$\left(-\mathbf{1}_{m \times m} \Delta_{\mathbb{R}^n} + i\tilde{A} \cdot \nabla_{\mathbb{R}^n} + \tilde{V} \right) \Psi = 0.$$

If Ψ vanishes on a set of positive measure, then Ψ has a zero of infinite order.

Without loss of generality, we can thus assume that Ψ vanishes to infinite order at the origin.

Step 2. $\nabla \Psi$ and $\Delta \Psi$ vanish to infinite order as well.

First we remark that if $\Psi \in L^2(\mathbb{R}^n)$, then vanishing to infinite order at the origin is equivalent to $\int_{B_1} |x|^{-\tau} |\Psi|^2 dx$ being finite for every $\tau \geq 0$. Indeed, if Ψ vanishes to infinite order at the origin, that is $\int_{B_\epsilon} |\Psi|^2 \leq c_k \epsilon^k$, then we get, after integrating over ϵ ,

$$\begin{aligned} c_k &\geq \int_0^1 \frac{\int_{B_\epsilon} |\Psi|^2}{\epsilon^k} d\epsilon = \int_{B_1} \int_0^1 |\Psi(x)|^2 \frac{\mathbf{1}_{|x| \leq \epsilon}}{\epsilon^k} d\epsilon dx \\ &= \frac{1}{k-1} \int_{B_1} |\Psi(x)|^2 \left(\frac{1}{|x|^{k-1}} - 1 \right) dx. \end{aligned}$$

Conversely, if $\int_{|x| \leq 1} |x|^{-\tau} |\Psi|^2$ is finite for every $\tau \geq 0$, then

$$\epsilon^{-k} \int_{B_\epsilon} |\Psi|^2 \leq \int_{B_\epsilon} |x|^{-k} |\Psi(x)|^2 dx \leq \int_{B_1} |x|^{-k} |\Psi(x)|^2 dx.$$

The finiteness of these integrals will play an important role later.

Lemma 1.4.3 (Finiteness of weighted norms).

i) If $\Psi \in H_{\text{loc}}^{1+\epsilon}(\mathbb{R}^n)$ with $\epsilon > 0$ and if Ψ vanishes to infinite order at the origin, then $\nabla\Psi$ as well.

ii) Let $V \in L_{\text{loc}}^2(\mathbb{R}^n, \mathbb{C})$ and $A \in L_{\text{loc}}^2(\mathbb{R}^n, \mathbb{R}^n)$ be such that

$$\begin{aligned} -\mathbf{1}_{B_1} \operatorname{Re} V &\leq a(-\Delta) + c, \\ \langle u, -i\mathbf{1}_{B_1} A \cdot \nabla u \rangle &\leq \langle u, (a'(-\Delta) + c') u \rangle, \quad \forall u \in C_c^\infty(\mathbb{R}^n), \end{aligned}$$

for some a, a' such that $a + a' < 1$ and $c, c' \geq 0$. Let $\Psi \in H_{\text{loc}}^1(\mathbb{R}^n)$ satisfying $-\Delta\Psi + iA \cdot \nabla\Psi + V\Psi = 0$ weakly. If Ψ vanishes to infinite order at the origin, then $\nabla\Psi$ as well.

iii) Let $V \in L_{\text{loc}}^2(\mathbb{R}^n, \mathbb{C})$ and $A \in L_{\text{loc}}^2(\mathbb{R}^n, \mathbb{C}^n)$ be such that

$$|V|^2 \mathbf{1}_{B_1} \leq a(-\Delta)^2 + c, \quad |A|^2 \mathbf{1}_{B_1} \leq \epsilon(-\Delta) + c_\epsilon,$$

for some $a < 1$, $c \geq 0$, for all $\epsilon > 0$ and some $c_\epsilon \geq 0$ depending on ϵ . Let $\Psi \in H_{\text{loc}}^2(\mathbb{R}^n)$ satisfying $-\Delta\Psi + iA \cdot \nabla\Psi + V\Psi = 0$. If Ψ vanishes to infinite order at the origin, then $\nabla\Psi$ and $\Delta\Psi$ as well.

This lemma also extends to Pauli operators.

Proof. *i)* Take $\delta \in]0, 1/4[$, and choose a smooth real positive localization function η equal to 1 in $B_\delta \subset \mathbb{R}^n$, supported in $B_{2\delta}$, and such that $0 \leq \eta \leq 1$, $|\nabla\eta| \leq c/\delta$, and $|\Delta\eta| \leq c/\delta^2$. For any $k \in \mathbb{N}$, $k \geq 0$, there exists $c_k \geq 0$ such that

$$\begin{aligned} \int_{B_\delta} |\nabla\Psi|^2 &= \int_{B_\delta} |\nabla(\eta\Psi)|^2 \leq \int |\nabla(\eta\Psi)|^2 \leq c \left\| (-\Delta)^{\frac{1+\epsilon}{2}}(\eta\Psi) \right\|_{L^2}^{\frac{1}{1+\epsilon}} \|\eta\Psi\|_{L^2}^{\frac{\epsilon}{1+\epsilon}} \\ &\leq \frac{c \|\Psi\|_{H^{1+\epsilon}(B_{2\delta})}^{\frac{1}{1+\epsilon}}}{\delta^2} \left(\int_{B_{2\delta}} |\Psi|^2 \right)^{\frac{\epsilon}{1+\epsilon}} \leq \frac{c}{\delta^2} (c_k (2\delta)^k)^{\frac{\epsilon}{1+\epsilon}} = c'_k \delta^{\frac{k\epsilon}{1+\epsilon} - 2}, \end{aligned}$$

where we applied the Gagliardo-Nirenberg inequality in the second inequality, we used $\Psi \in H_{\text{loc}}^{1+\epsilon}(\mathbb{R}^n)$ in the following one, and we used the definition of Ψ vanishing to infinite order at the origin (1.9) in the last inequality. We notice that our estimate is the definition of $\nabla\Psi$ vanishing to infinite order at the origin.

ii) Let η be the same function as in *i)*, and consider the inequality (1.24) again, in which we used Schrödinger's equation of Ψ , we obtained (1.25), and we will use it once more. Since $\eta = 1$ in B_δ , we have

$$\int_{B_\delta} |\nabla\Psi|^2 = \int_{B_\delta} |\eta\nabla\Psi|^2 \leq \int |\eta\nabla\Psi|^2 \leq \frac{c}{\delta^2} \int_{B_{2\delta}} |\Psi|^2 \leq \frac{c}{\delta^2} (c_k (2\delta)^k) = c'_k \delta^k,$$

where we used the definition of Ψ vanishing to infinite order, and this proves that $\nabla\Psi$ vanishes to infinite order as well.

iii) We take the same function η as in i), adding the constraint $|\partial_{ij}\eta| < c/r^2$ for any $i, j \in \{1, \dots, n\}$, and we take $\delta \in]0, 1/4[$. We know that for any $\xi, \theta \in \mathbb{R}$ and any $\alpha \in]0, +\infty[$, we have

$$(\xi + \theta)^2 \leq (1 + \alpha)\xi^2 + (1 + \alpha^{-1})\theta^2.$$

So using the assumption on V , we have

$$\begin{aligned} & \int |V\eta\Psi|^2 \\ & \leq a \int |\Delta(\eta\Psi)|^2 + c \int |\eta\Psi|^2 \\ & = a \int |\eta\Delta\Psi + 2\nabla\eta \cdot \nabla\Psi + \Psi\Delta\eta|^2 + c \int |\eta\Psi|^2 \\ & \leq a(1 + \alpha) \int |\eta\Delta\Psi|^2 + \left(1 + \frac{1}{\alpha}\right) \int |2\nabla\eta \cdot \nabla\Psi + \Psi\Delta\eta|^2 + c \int |\eta\Psi|^2 \\ & \leq a(1 + \alpha) \int |\eta\Delta\Psi|^2 + 2\left(1 + \frac{1}{\alpha}\right) \int |\Psi\Delta\eta|^2 \\ & \quad + 4\left(1 + \frac{1}{\alpha}\right) \int |\nabla\Psi \cdot \nabla\eta|^2 + c \int |\eta\Psi|^2, \end{aligned}$$

for any $\alpha > 0$. As for the gradient term, we have

$$\begin{aligned} \int |\eta A \cdot \nabla\Psi|^2 & \leq \int |A|^2 |\eta\nabla\Psi|^2 \\ & \leq \epsilon \int |\nabla|\eta\nabla\Psi||^2 + c_\epsilon \int |\eta\nabla\Psi|^2 \\ & = \epsilon \int |\eta\nabla|\nabla\Psi| + |\nabla\Psi|\nabla\eta|^2 + c_\epsilon \int |\eta\nabla\Psi|^2 \\ & \leq 2\epsilon \int \eta^2 |\nabla|\nabla\Psi||^2 + 2\epsilon \int |\nabla\eta|^2 |\nabla\Psi|^2 + c_\epsilon \int |\eta\nabla\Psi|^2. \end{aligned}$$

We denote by $\nabla^2\Psi = (\partial_{ij}\Psi)_{1 \leq i, j \leq n}$ the Hessian of Ψ , its square being $|\nabla^2\Psi|^2 = \sum_{1 \leq i, j \leq n} |\partial_{ij}\Psi|^2$. Now by convexity of the map $f \mapsto |\nabla\sqrt{f}|^2$ and then the diamagnetic inequality, we have

$$|\nabla|\nabla\Psi||^2 = \left| \nabla \sqrt{\sum_{i=1}^n |\partial_i\Psi|^2} \right|^2 \leq \sum_{i=1}^n |\nabla|\partial_i\Psi||^2 \leq \sum_{i=1}^n |\nabla\partial_i\Psi|^2 = |\nabla^2\Psi|^2.$$

Also,

$$\begin{aligned} \int |\nabla^2(\eta\Psi)|^2 & = \sum_{1 \leq i, j \leq n} \int |k_i k_j \widehat{\eta\Psi}|^2 \\ & \leq \frac{1}{2} \sum_{1 \leq i, j \leq n} \int (|k_i|^2 + |k_j|^2) |\widehat{\eta\Psi}|^2 = n \int |\Delta(\eta\Psi)|^2, \end{aligned}$$

therefore, denoting by \otimes the tensor product on $n \times n$ matrices, and making use of previous inequalities, we obtain

$$\begin{aligned}
\int |\eta \nabla^2 \Psi|^2 &= \int |\nabla^2(\eta \Psi) - \Psi \nabla^2 \eta - \nabla \eta \otimes \nabla \Psi - \nabla \Psi \otimes \nabla \eta|^2 \\
&\leq 4 \int |\nabla^2(\eta \Psi)|^2 + 4 \int |\Psi \nabla^2 \eta|^2 + 8 \int |\nabla \eta \otimes \nabla \Psi|^2 \\
&\leq 4n \int |\Delta(\eta \Psi)|^2 + 4 \int |\Psi \nabla^2 \eta|^2 + 4n^2 \int |\nabla \eta|^2 |\nabla \Psi|^2 \\
&\leq 4n \int |\eta \Delta \Psi|^2 + 4n \int |\Psi \Delta \eta|^2 + 4 \int |\Psi \nabla^2 \eta|^2 \\
&\quad + 4n(n+2) \int |\nabla \eta|^2 |\nabla \Psi|^2.
\end{aligned}$$

We use Schrödinger's equation pointwise and gather our previous inequalities. We get, for any $\alpha, \beta > 0$,

$$\begin{aligned}
\int |\eta \Delta \Psi|^2 &= \int |\eta V \Psi + i\eta A \cdot \nabla \Psi|^2 \\
&\leq (1+\beta) \int |V \eta \Psi|^2 + \left(1 + \frac{1}{\beta}\right) \int |\eta A \cdot \nabla \Psi|^2 \\
&\leq \left(a(1+\beta)(1+\alpha) + 8\epsilon n \left(1 + \frac{1}{\beta}\right)\right) \int |\eta \Delta \Psi|^2 \\
&\quad + \left(2 \left(1 + \frac{1}{\alpha}\right) (1+\beta) + 8\epsilon n \left(1 + \frac{1}{\beta}\right)\right) \int |\Psi \Delta \eta|^2 \\
&\quad + \left(4 \left(1 + \frac{1}{\alpha}\right) (1+\beta) + 2\epsilon(4n(n+2) + 1) \left(1 + \frac{1}{\beta}\right)\right) \int |\nabla \eta|^2 |\nabla \Psi|^2 \\
&\quad + (1+\beta)c \int |\eta \Psi|^2 + c_\epsilon \left(1 + \frac{1}{\beta}\right) \int |\eta \nabla \Psi|^2 + 8\epsilon \left(1 + \frac{1}{\beta}\right) \int |\Psi \nabla^2 \eta|^2.
\end{aligned}$$

We take α, β and ϵ such that $a(1+\beta)(1+\alpha) + 8\epsilon n(1+\beta^{-1}) < 1$. This allows us to move the term $\int |\eta \Delta \Psi|^2$ to the left and obtain

$$\int_{B_\delta} |\Delta \Psi|^2 \leq \int |\eta \Delta \Psi|^2 \leq \frac{c}{\delta^4} \int_{B_{2\delta}} (|\Psi|^2 + |\nabla \Psi|^2) \leq \frac{c}{\delta^4} (c_k (2\delta)^k) = c'_k \delta^{k-4}.$$

This proves that $\Delta \Psi$ vanishes to infinite order at the origin, by the definition (1.9). \square

Step 3. Proof that $\Psi = 0$.

We consider some number $\tau \geq 0$ (large), and we call c any constant which does not depend on τ . We take a smooth localisation function η , equal to 1 in $B_{1/2} \subset \mathbb{R}^n$, supported in B_1 , and such that $0 \leq \eta \leq 1$. We take the same weight function ϕ as in Theorem 1.2.1. Thanks to Step 3, all

the expressions we write are finite. We define $\kappa_{\delta,n} := \kappa_n \delta^{-3}$. We start by controlling the gradient term by using the assumption on \tilde{A} ,

$$\begin{aligned} \left\| e^{\tau\phi} \tilde{A} \cdot \nabla (\eta\Psi) \right\|_{L^2(B_1)}^2 &= \sum_{\alpha=1}^m \left\| e^{\tau\phi} \sum_{i=1}^n A_{\alpha}^i \partial_i (\eta\Psi_{\alpha}) \right\|_{L^2(B_1)}^2 \\ &\leq n \sum_{\substack{1 \leq \alpha \leq m \\ 1 \leq i \leq n}} \left\| e^{\tau\phi} A_{\alpha}^i \partial_i (\eta\Psi_{\alpha}) \right\|_{L^2(B_1)}^2 \\ &\leq nm\epsilon_{n,m,\delta} \sum_{\substack{1 \leq \alpha \leq m \\ 1 \leq i \leq n}} \left\| (-\Delta)^{\frac{1}{4}-\delta} \left(e^{\tau\phi} \partial_i (\eta\Psi_{\alpha}) \right) \right\|_{L^2(B_1)}^2 \\ &\quad + nmc \sum_{\substack{1 \leq \alpha \leq m \\ 1 \leq i \leq n}} \left\| e^{\tau\phi} \partial_i (\eta\Psi_{\alpha}) \right\|_{L^2(B_1)}^2. \end{aligned}$$

We now use the fractional Carleman inequality (1.2.2) with $s' = 1/4$ and $s' = 0$, this yields

$$\begin{aligned} \left\| e^{\tau\phi} \tilde{A} \cdot \nabla (\eta\Psi) \right\|_{L^2(B_1)}^2 &\leq \kappa_n nm^2 \left(\epsilon_{n,m,\delta} (\delta/4)^{-\frac{5}{2}} + \tau^{-1}c \right) \sum_{\alpha=1}^m \left\| e^{\tau\phi} \Delta (\eta\Psi_{\alpha}) \right\|_{L^2(B_1)}^2 \\ &= \kappa_n nm^2 \left(\epsilon_{n,m,\delta} (\delta/4)^{-\frac{5}{2}} + \tau^{-1}c \right) \left\| e^{\tau\phi} \Delta (\eta\Psi) \right\|_{L^2(B_1)}^2. \end{aligned}$$

Similarly, for the multiplication potential \tilde{V} , we begin by using the assumption (1.7) and we get

$$\begin{aligned} \left\| e^{\tau\phi} \eta \tilde{V} \Psi \right\|_{L^2(B_1)}^2 &= \sum_{\alpha=1}^m \left\| e^{\tau\phi} \eta \sum_{\beta=1}^m V_{\alpha\beta} \Psi_{\beta} \right\|_{L^2(B_1)}^2 \\ &\leq m \sum_{1 \leq \alpha, \beta \leq m} \left\| e^{\tau\phi} \eta V_{\alpha\beta} \Psi_{\beta} \right\|_{L^2(B_1)}^2 \\ &\leq m \sum_{\beta=1}^m \left(\epsilon_{n,m,\delta} \left\| (-\Delta)^{\frac{3}{4}-\delta} \left(e^{\tau\phi} \eta \Psi_{\beta} \right) \right\|_{L^2(B_1)}^2 + c \left\| e^{\tau\phi} \eta \Psi_{\beta} \right\|_{L^2(B_1)}^2 \right). \end{aligned}$$

We proceed by using our fractional Carleman inequality of Corollary 1.2.2, yielding

$$\begin{aligned} \left\| e^{\tau\phi} \eta \tilde{V} \Psi \right\|_{L^2(B_1)}^2 &\leq \kappa_n m \left(\epsilon_{n,m,\delta} (3\delta/4)^{-\frac{5}{2}} + \tau^{-3}c \right) \sum_{\beta=1}^m \left\| e^{\tau\phi} \Delta (\eta\Psi_{\beta}) \right\|_{L^2(B_1)}^2 \\ &= \kappa_n m \left(\epsilon_{n,m,\delta} (3\delta/4)^{-\frac{5}{2}} + \tau^{-3}c \right) \left\| e^{\tau\phi} \Delta (\eta\Psi) \right\|_{L^2(B_1)}^2. \end{aligned}$$

We can now estimate

$$\begin{aligned}
\left\| e^{\tau\phi} \eta \Delta \Psi \right\|_{L^2(B_1)}^2 &= \sum_{\alpha=1}^m \left\| e^{\tau\phi} \eta \Delta \Psi_\alpha \right\|_{L^2(B_1)}^2 \\
&\leq 2 \left\| e^{\tau\phi} \eta \tilde{A} \cdot \nabla \Psi \right\|_{L^2(B_1)}^2 + 2 \left\| e^{\tau\phi} \eta \tilde{V} \Psi \right\|_{L^2(B_1)}^2 \\
&= 2 \left\| e^{\tau\phi} \tilde{A} \cdot (\nabla(\eta \Psi) - \Psi \nabla \eta) \right\|_{L^2(B_1)}^2 + 2 \left\| e^{\tau\phi} \eta \tilde{V} \Psi \right\|_{L^2(B_1)}^2 \\
&\leq 4 \left\| e^{\tau\phi} \tilde{A} \cdot \nabla(\eta \Psi) \right\|_{L^2(B_1)}^2 + 4 \left\| e^{\tau\phi} \Psi \tilde{A} \cdot \nabla \eta \right\|_{L^2(B_1)}^2 \\
&\quad + 2 \left\| e^{\tau\phi} \eta \tilde{V} \Psi \right\|_{L^2(B_1)}^2 \\
&\leq 6\kappa_n n m^2 \left(\epsilon_{n,m,\delta} (\delta/4)^{-\frac{5}{2}} + \tau^{-1} c \right) \left\| e^{\tau\phi} \Delta(\eta \Psi) \right\|_{L^2(B_1)}^2 \\
&\quad + 4 \left\| e^{\tau\phi} \Psi \tilde{A} \cdot \nabla \eta \right\|_{L^2(B_1)}^2 \\
&= c_{\epsilon,\delta,\tau}^2 \left\| e^{\tau\phi} \Delta(\eta \Psi) \right\|_{L^2(B_1)}^2 + 4 \left\| e^{\tau\phi} \Psi \tilde{A} \cdot \nabla \eta \right\|_{L^2(B_1)}^2,
\end{aligned}$$

where

$$c_{\epsilon,\delta,\tau}^2 := 6\kappa_n n m^2 \left(\epsilon_{n,m,\delta} \left(\frac{4}{\delta} \right)^{\frac{5}{2}} + \frac{c}{\tau} \right).$$

Eventually, the last inequality yields

$$\begin{aligned}
&\left\| e^{\tau\phi} \Delta(\eta \Psi) \right\|_{L^2(B_1)} \\
&\leq \left\| e^{\tau\phi} \eta \Delta \Psi \right\|_{L^2(B_1)} + 2 \left\| e^{\tau\phi} \nabla \eta \cdot \nabla \Psi \right\|_{L^2(B_1)} + \left\| e^{\tau\phi} \Psi \Delta \eta \right\|_{L^2(B_1)} \\
&\leq c_{\epsilon,\delta,\tau} \left\| e^{\tau\phi} \Delta(\eta \Psi) \right\|_{L^2(B_1)} + 2 \left\| e^{\tau\phi} \Psi \tilde{A} \cdot \nabla \eta \right\|_{L^2(B_1)} \\
&\quad + 2 \left\| e^{\tau\phi} \nabla \eta \cdot \nabla \Psi \right\|_{L^2(B_1)} + \left\| e^{\tau\phi} \Psi \Delta \eta \right\|_{L^2(B_1)}.
\end{aligned}$$

Now we recall that $\nabla \eta$ and $\Delta \eta$ are supported in $B_1 \setminus B_{1/2}$ and that they are bounded by a constant independent of τ, ϵ, δ , hence

$$\begin{aligned}
&\left\| e^{\tau\phi} \Delta(\eta \Psi) \right\|_{L^2(B_1)} \\
&\leq c_{\epsilon,\delta,\tau} \left\| e^{\tau\phi} \Delta(\eta \Psi) \right\|_{L^2(B_1)} + c \left\| e^{\tau\phi} \Psi \tilde{A} \right\|_{L^2(B_1 \setminus B_{1/2})} \quad (1.26)
\end{aligned}$$

$$\begin{aligned}
&\quad + c \left\| e^{\tau\phi} \nabla \Psi \right\|_{L^2(B_1 \setminus B_{1/2})} + c \left\| e^{\tau\phi} \Psi \right\|_{L^2(B_1 \setminus B_{1/2})} \\
&\leq c_{\epsilon,\delta,\tau} \left\| e^{\tau\phi} \Delta(\eta \Psi) \right\|_{L^2(B_1)} + c e^{\tau\phi(\frac{1}{2})} \left\| \Psi \tilde{A} \right\|_{L^2(B_1 \setminus B_{1/2})} \quad (1.27)
\end{aligned}$$

$$\begin{aligned}
&\quad + c e^{\tau\phi(\frac{1}{2})} \left\| \nabla \Psi \right\|_{L^2(B_1 \setminus B_{1/2})} + c e^{\tau\phi(\frac{1}{2})} \left\| \Psi \right\|_{L^2(B_1 \setminus B_{1/2})} \\
&\leq c_{\epsilon,\delta,\tau} \left\| e^{\tau\phi} \Delta(\eta \Psi) \right\|_{L^2(B_1)} + c e^{\tau\phi(\frac{1}{2})}, \quad (1.28)
\end{aligned}$$

where c does not depend on δ , τ or ϵ , and where we used that ϕ is decreasing. We recall that δ is fixed, and can be taken as small as we want. The constant $\epsilon_{n,m,\delta}$ needs to be small enough so that $6\kappa_n n m^2 (4/\delta)^{5/2} \epsilon_{n,m,\delta} < 1$. Then τ needs to be large enough so that $c_{\epsilon,\delta,\tau} < 1$. Then we move the first term of the right hand side of (1.26) to the left and get

$$\left\| e^{\tau\phi} \Delta (\eta\Psi) \right\|_{L^2(B_1)} \leq c e^{\tau\phi(\frac{1}{2})}. \quad (1.29)$$

Finally, using our Carleman inequality once more, and because ϕ is decreasing, we find

$$\begin{aligned} \|\Psi\|_{L^2(B_{1/2})} &\leq \left\| e^{\tau(\phi(\cdot)-\phi(\frac{1}{2}))} \Psi \right\|_{L^2(B_{1/2})} \\ &= \left\| e^{\tau(\phi(\cdot)-\phi(\frac{1}{2}))} \eta\Psi \right\|_{L^2(B_{1/2})} \\ &\leq \left\| e^{\tau(\phi(\cdot)-\phi(\frac{1}{2}))} \eta\Psi \right\|_{L^2(B_1)} \\ &\leq c\sqrt{\kappa_n} \tau^{-\frac{3}{2}} \left\| e^{\tau(\phi(\cdot)-\phi(\frac{1}{2}))} \Delta (\eta\Psi) \right\|_{L^2(B_1)} \\ &\leq c\tau^{-\frac{3}{2}}, \end{aligned}$$

where we used (1.29) is the last step. Letting $\tau \rightarrow +\infty$ proves that $\Psi = 0$ in $B_{1/2}$. We can propagate this information by a well known argument, see for instance the proof of [38, Theorem XIII.63]. This concludes the proof of Theorem 1.4.2. \square

1.5 Proof of Corollary 1.2.4

We give a proof without magnetic potentials for simplicity, and provide a lemma at the end enabling to extend it. We take $n = dN$. Let $R > 0$ and $\Psi \in H^{3/2}(\mathbb{R}^{dN})$. We apply the inequality (1.11) to the function $x_i \mapsto \Psi(\dots, x_i, \dots)$ and then integrate over $x_1, \dots, x_{i-1}, x_{i+1}, \dots, x_N$ to get

$$\int_{B_R} |v(x_i)|^2 |\Psi|^2 \leq \epsilon_{\delta,d,N} \int_{\mathbb{R}^{dN}} |(-\Delta_{x_i})^{\frac{3}{4}-\delta} \Psi|^2 + c_R \int_{\mathbb{R}^{dN}} |\Psi|^2.$$

For $j \neq i$, applying (1.11) with a radius $2R$, we have similarly

$$\int_{B_R} |w(x_i - x_j)|^2 |\Psi|^2 \leq \epsilon_{\delta,d,N} \int_{\mathbb{R}^{dN}} |(-\Delta_{x_i})^{\frac{3}{4}-\delta} \Psi|^2 + c_R \int_{\mathbb{R}^{dN}} |\Psi|^2.$$

We consider the many-body potential

$$V(x_1, \dots, x_N) := \sum_{i=1}^N v(x_i) + \sum_{1 \leq i < j \leq N} w(x_i - x_j), \quad (1.30)$$

for which

$$\begin{aligned}
|V|^2 \mathbf{1}_{B_R} &= \mathbf{1}_{B_R} \left| \sum_{i=1}^N v(x_i) + \sum_{1 \leq i < j \leq N} w(x_i - x_j) \right|^2 \\
&\leq \frac{N(N+1)}{2} \left(\sum_{i=1}^N \mathbf{1}_{B_R} |v(x_i)|^2 + \sum_{1 \leq i < j \leq N} \mathbf{1}_{B_R} |w(x_i - x_j)|^2 \right) \\
&\leq \frac{N(N+1)^2}{4} \left(\epsilon_{\delta, d, N} \sum_{i=1}^N (-\Delta_{x_i})^{\frac{3}{2}-2\delta} + N c_R \right) \\
&\leq \frac{N(N+1)^2}{4} \left(\epsilon_{\delta, d, N} (-\Delta)^{\frac{3}{2}-2\delta} + N c_R \right),
\end{aligned}$$

where in the last inequality we have used that

$$\sum_{i=1}^N |k_i|^{3-4\delta} \leq \left(\sum_{i=1}^N |k_i|^2 \right)^{\frac{3}{2}-2\delta}.$$

Thus we can take

$$\epsilon_{\delta, d, N} = \frac{4\epsilon_{\delta, d, N}}{N(N+1)^2} = \frac{1}{N(N+1)^2 \kappa_{4\delta/3, dN}^2},$$

and we obtain the result by applying Theorem 1.4.2.

To finish, we prove that the assumption that $v, w \in L_{\text{loc}}^p(\mathbb{R}^d)$ with $p > \max(2d/3, 2)$ implies (1.11). This is very classical [20, 31]. First let $s \in (0, d/2)$, let $v \in L_{\text{loc}}^{\frac{d}{2s}}(\mathbb{R}^d)$, $R > 0$ and $u \in H^s(\mathbb{R}^d)$ supported in $B_R \subset \mathbb{R}^d$. We have $v = v \mathbf{1}_{|v|>M} + v \mathbf{1}_{|v|<M}$, so

$$\begin{aligned}
\int_{\mathbb{R}^d} |v| |u|^2 &\leq \int_{\mathbb{R}^d} |v \mathbf{1}_{\{|v|>M\} \cap B_R}| |u|^2 + M \int_{\mathbb{R}^d} |u|^2 \\
&\leq \|v \mathbf{1}_{|v|>M}\|_{L^{\frac{d}{2s}}(B_R)} \|u\|_{L^{\frac{2d}{d-2s}}}^2 + M u^2 \\
&\leq c_{d,s} \|v \mathbf{1}_{|v|>M}\|_{L^{\frac{d}{2s}}(B_R)} (-\Delta)^{\frac{s}{2}} u^2 + M u^2,
\end{aligned}$$

where, in the last line, we have used the Sobolev inequality. By dominated convergence, $\|v \mathbf{1}_{|v|>M}\|_{L^{\frac{d}{2s}}(B_R)}$ tends to 0 when $M \rightarrow +\infty$. We can do a similar treatment for w . Therefore, this proves that for $s \in (0, d/2)$ and $q \geq 1$, if $v, w \in L_{\text{loc}}^{\frac{qd}{2s}}(\mathbb{R}^d)$, then for any $R > 0$ and any $\epsilon > 0$, there is $c_{\epsilon, R}$ such that

$$|v|^q \mathbf{1}_{B_R} + |w|^q \mathbf{1}_{B_R} \leq \epsilon (-\Delta)^s + c_{\epsilon, R} \quad \text{in } \mathbb{R}^d.$$

For the case $d \in \{1, 2\}$, we need $v, w \in L_{\text{loc}}^2(\mathbb{R}^d)$ because we use $|V|^2$. We have the Sobolev embedding $H^{3/2}(\mathbb{R}^d) \hookrightarrow L^\infty(\mathbb{R}^d)$, and the argument is the same. The potential term can be handled by using the following Lemma.

Lemma 1.5.1. *Let $A \in L^d_{\text{loc}}(\mathbb{R}^d, \mathbb{R}^d)$, then for any $\epsilon > 0$ and any $r \geq 0$, there exists $c_{\epsilon, r} \geq 0$ such that*

$$|\langle u, -i\mathbf{1}_{B_r} A \cdot \nabla u \rangle| \leq \langle u, (\epsilon(-\Delta) + c_{\epsilon, r}) u \rangle \quad \forall u \in \mathcal{C}_c^\infty(\mathbb{R}^d). \quad (1.31)$$

Moreover, for any $\epsilon > 0$ and any $R \geq 0$, there exists $c_{\epsilon, R} \geq 0$ such that

$$\left| \left\langle u, -i\mathbf{1}_{B_R} \sum_{\ell=1}^N A(x_\ell) \cdot \nabla_\ell u \right\rangle \right| \leq \langle u, (\epsilon(-\Delta) + c_{\epsilon, R}) u \rangle, \quad \forall u \in \mathcal{C}_c^\infty(\mathbb{R}^{dN}).$$

Proof. Let $d \geq 3$ and $r > 1$. Take $M > 0$ and let us decompose $A = A\mathbf{1}_{|A| \geq M} + A\mathbf{1}_{|A| < M}$. For any $u \in \mathcal{C}_c^\infty(\mathbb{R}^d)$, we have

$$\begin{aligned} |\langle u, -i\mathbf{1}_{B_r} A \cdot \nabla u \rangle| &\leq \int |A\mathbf{1}_{B_r}| |u \nabla u| \\ &\leq \int_{\{|A| > M\} \cap B_r} |A| |u \nabla u| + M \int |u \nabla u| \\ &\leq \left\| A\mathbf{1}_{|A| > M} \right\|_{L^d(B_r)} \|u \nabla u\|_{L^{\frac{d}{d-1}}} + M^{-1} \int |\nabla u|^2 + M^3 \int |u|^2 \\ &\leq \left\| A\mathbf{1}_{|A| > M} \right\|_{L^d(B_r)} \|u\|_{L^{\frac{2d}{d-2}}} \|\nabla u\|_{L^2} + M^{-1} \int |\nabla u|^2 + M^3 \int |u|^2 \\ &\leq \left(c \left\| A\mathbf{1}_{|A| > M} \right\|_{L^d(B_r)} + M^{-1} \right) \|\nabla u\|_{L^2}^2 + M^3 \int |u|^2, \end{aligned}$$

where we used Hölder's and Sobolev's inequalities, and where the coefficients are independent of u . By dominated convergence, $\left\| A\mathbf{1}_{|A| > M} \right\|_{L^d} \rightarrow 0$ when $M \rightarrow +\infty$, so this proves (1.31). For the N -body case, we use the previous result on each N components and sum. For $d \in \{1, 2\}$, we have the subcritical Sobolev injections and the argument is the same. \square

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Chapter 2

New Hohenberg-Kohn theorems

This chapter is identical to the paper [19].

We prove Hohenberg-Kohn theorems for several models of quantum mechanics. First, we show that the pair correlation function of any ground state contains the information of the interactions and of the external potentials. Then, in the presence of the Zeeman interaction, a strong constraint on external fields is derived for systems having the same ground state densities and magnetizations. Moreover, we provide a counterexample in a setting involving non-local potentials. Next, we prove that the density and the entropy of a ground state contain the information of both the imposed external potential and temperature. Eventually, we conclude that at positive temperature, Hohenberg-Kohn theorems generically hold, in particular they hold in the classical case.

2.1 Introduction

The ground state of a many-body quantum system at equilibrium is a quantity involving a large number of variables, and one cannot measure it directly. Therefore, it is natural to ask which simple and measurable quantity is sufficient to know to get all the information of a system. Then one can work only with this relevant reduced information as in Density Functional Theory, which is one of the most successful methods in quantum physics and chemistry to simulate matter at the microscopic scale [8, 30, 32, 33]. A famous result of Hohenberg and Kohn [30] from 1964 shows that, at equilibrium, the ground state density of a system of quantum electrons contains all the information of the external electric potential. This implies that any physical quantity is a functional of this density and justifies Density Functional Theory. Then, many articles were devoted to extend this initial work to other configurations, because those conceptual results provide fundamental

insights on the structure of quantum mechanical models. The main goal is to establish a bijective matching between an external imposed field, and a ground state internal reduced density.

In chronological order but not exhaustively, Mermin extended the theorem to fixed positive temperature [46] (Thermal DFT), Barth and Hedin looked at Hamiltonians having a Zeeman term [72] (Spin DFT), Gilbert considered non-local potentials [23] (Matrix DFT), Vignale and Rasolt treated Pauli Hamiltonians without the Zeeman term [71] (Current DFT), and Siedentop, Müller and Ziesche considered pair potentials [66, 75] (Pair DFT). In those works, the authors conjectured corresponding Hohenberg-Kohn theorems, that is some reduced ground state densities contain the information of external potentials applied to the systems. Nevertheless, the provided proofs turn out to be incomplete and first counterexamples were found by Capelle and Vignale in models dealing with magnetic fields [9, 10] (Spin DFT, Spin-Current DFT and Superconducting DFT at zero temperature), invalidating such general Hohenberg-Kohn properties. In two recent articles [20, 21] grouped in Chapter 1, we proved a unique continuation property necessary in the final step of the rigorous proof of the original Hohenberg-Kohn theorem. But our work does not cover much of the systems mentioned above.

In this chapter we further analyze Hohenberg-Kohn theorems for interactions, spin, non-local potentials and temperature, and complete the proofs present in the literature when possible. First, we comment on the original Hohenberg-Kohn property. In Theorem 2.2.5, we show a Hohenberg-Kohn theorem for interactions, indicating that pair correlations of any ground state are sufficient to deduce the interactions between particles, in general settings containing several types of particles. Next in Theorem 2.3.1, we prove a partial Hohenberg-Kohn type result for Spin DFT, that is, a strong constraint on external fields when ground state one-body densities are equal, and we provide a counterexample to the Hohenberg-Kohn theorem in Matrix DFT. Then, we give a rigorous proof of the Hohenberg-Kohn theorem in Thermal DFT in Theorem 2.4.1, extending the existing statements by showing that the ground state entropy and the one-body density contain the information of both the temperature and the external electric potential. Eventually, we show that at positive temperatures, Hohenberg-Kohn theorems “generically” hold, in particular in the classical case.

2.2 Standard setting and interactions

The original Hohenberg-Kohn theorem initiated many works, like [21, 30, 38, 48, 55] for instance. In this section we present weaker assumptions under which it holds. Most of them can be applied to other Hohenberg-Kohn theorems presented in sections below. We denote by d the dimension of the

one-body space \mathbb{R}^d , and by N the number of particles. Let us consider the interacting Hamiltonian

$$H^N(v) := \sum_{i=1}^N -\Delta_i + \sum_{i=1}^N v(x_i) + \sum_{1 \leq i < j \leq N} w(x_i - x_j), \quad (2.1)$$

where v and w are respectively the external and interacting potentials. Let $q \in \mathbb{N}$ be the spin number. The one-body density of a wavefunction $\Psi \in L^2(\mathbb{R}^{dN}, \mathbb{C}^{q^N})$, simply called the density hereafter, is defined by

$$\rho_\Psi(x) := \sum_{s \in \{1, \dots, q\}^N} \sum_{i=1}^N \int_{\mathbb{R}^{d(N-1)}} |\Psi^s|^2(x_1, \dots, x_{i-1}, x, x_{i+1}, \dots, x_N) \times dx_1 \cdots dx_{i-1} dx_{i+1} \cdots dx_N.$$

The set of square-integrable N -particle antisymmetric wavefunctions will be denoted by $L_a^2(\mathbb{R}^{dN}) := \bigwedge_{i=1}^N L^2(\mathbb{R}^d)$. In the paper we will write E_i , $i \in \{1, 2\}$ for ground state energies of the corresponding models we are treating. For instance here, $E_i := \langle \Psi_i, H(v_i) \Psi_i \rangle$.

2.2.1 Standard Hohenberg-Kohn

The usual assumption in the Hohenberg-Kohn theorem is the equality of ground state densities, $\rho_{\Psi_1} = \rho_{\Psi_2}$ almost everywhere, where Ψ_1 and Ψ_2 are ground states produced by two electric potentials v_1 and v_2 . In the case of Coulomb systems of molecules, this can be replaced by $\rho_{\Psi_1} = \rho_{\Psi_2}$ in a ball, by real analyticity [15, 16, 31, 48]. Nevertheless, we remark that in the general case, the proof only requires the following constraint (2.2), which we present together with the proof of the Hohenberg-Kohn theorem [20, 21, 30, 39, 55], for completeness. We will denote by $f_+ = \max(f, 0)$ and $f_- = \max(-f, 0)$ the positive and negative parts of a function $f = f_+ - f_-$. Let Ω be a connected open set, we work on Ω^N with any boundary condition for the Laplacian. We call $\mathcal{Q}(\sum_{i=1}^N -\Delta_i)$ the corresponding form domain. For $v \in L_{\text{loc}}^{d/2}(\mathbb{R}^d)$ such that $v_- \in (L^{d/2} + L^\infty)(\mathbb{R}^d)$, we also denote by $H^N(v)$ the Friedrich extension of the operator in (2.1), whose form domain is

$$\mathcal{Q}(H^N(v)) = \left\{ \Psi \in \mathcal{Q} \left(\sum_{i=1}^N -\Delta_i \right) \mid \int_{\mathbb{R}^d} v_+ \rho_\Psi < +\infty \right\}.$$

Theorem 2.2.1 (Hohenberg-Kohn theorem). *Let $\Omega \subset \mathbb{R}^d$ be an open and connected set, and choose any boundary condition. Let $p > \max(2d/3, 2)$, let $v_1, v_2 \in L_{\text{loc}}^p(\Omega)$ having $(v_1)_-, (v_2)_- \in (L^p + L^\infty)(\Omega)$, and $w \in (L^p + L^\infty)(\mathbb{R}^d)$ such that $H^N(v_1)$ and $H^N(v_2)$ have at least one ground state each, we respectively denote by Ψ_1 and Ψ_2 one of the ground states of $H^N(v_1)$ and $H^N(v_2)$, and we assume that $\int (v_1)_+ \rho_{\Psi_2}$ and $\int (v_2)_+ \rho_{\Psi_1}$ are finite. If*

$$\int_{\Omega} (v_1 - v_2)(\rho_{\Psi_1} - \rho_{\Psi_2}) = 0, \quad (2.2)$$

then $v_1 = v_2 + (E_1 - E_2)/N$.

Proof. From the conditions imposed on the potentials, $\Psi_2 \in \mathcal{Q}(H^N(v_1))$ and $\Psi_1 \in \mathcal{Q}(H^N(v_2))$. Using the definition of the ground state energy, we have

$$E_1 \leq \langle \Psi_2, H^N(v_1)\Psi_2 \rangle = E_2 + \int (v_1 - v_2)\rho_{\Psi_2},$$

which can be written

$$E_1 - E_2 \leq \int (v_1 - v_2)\rho_{\Psi_2}. \quad (2.3)$$

Exchanging labels 1 and 2, we also have

$$E_2 - E_1 \leq \int (v_2 - v_1)\rho_{\Psi_1}. \quad (2.4)$$

Now using the hypothesis (2.2), we get

$$E_1 - E_2 = \int (v_1 - v_2)\rho_{\Psi_1} = \int (v_1 - v_2)\rho_{\Psi_2},$$

and thus $\langle \Psi_2, H^N(v_1)\Psi_2 \rangle = E_1$. Consequently, Ψ_2 respects Schrödinger's equation for $H^N(v_1)$, that is $H^N(v_1)\Psi_2 = E_1\Psi_2$. Taking the difference with Schrödinger's equation verified by Ψ_2 for $H^N(v_2)$, we have

$$\left(E_2 - E_1 + \sum_{i=1}^N (v_1 - v_2)(x_i) \right) \Psi_2 = 0.$$

Since Schrödinger's equation is verified by Ψ_2 , it does not vanish on sets of positive measure by unique continuation by [20, 21] (or see Chapter 1), which is a local property, and we get

$$E_2 - E_1 + \sum_{i=1}^N (v_1 - v_2)(x_i) = 0, \quad (2.5)$$

a.e. in Ω^N . Integrating this equation on $(x_i)_{2 \leq i \leq N} \in A^{N-1}$ where $A \subset \Omega$ is bounded, we obtain that there is a constant c such that $v_1 = v_2 + c$ almost everywhere on Ω . Eventually, $c = (E_1 - E_2)/N$ by using (2.5) once again. \square

This proof relies on a unique continuation result [20, 21] (Chapter 1), itself based on a Carleman inequality, and its use yields the condition $p > \max(2d/3, 2)$. In the quantum case, the Laplace operator forces minimizers to be spread in the whole space by unique continuation, which is linked to the Heisenberg principle. Note that, on the contrary, in the classical case

minimizers of the energy at zero temperature have a very small support (they concentrate on the minimizers of the energy), and therefore they provide almost no information on the potential.

The hypothesis (2.2) is a much weaker assumption than $\rho_{\Psi_1} = \rho_{\Psi_2}$. Indeed it replaces an infinite set of equations by only one. Moreover, it is global, and it better exhibits the duality between electric potentials and ground state densities. This reduces to $\rho_{\Psi_1} = \rho_{\Psi_2}$ when one wants it to be independent of external potentials.

2.2.2 Remark on the original proof

The original proof of Hohenberg and Kohn is by contradiction, it assumes the non-degeneracy of the systems and uses strict inequalities in (2.3) and (2.4). The authors precised that two different potentials could not lead to the same ground state, and Lieb [38] remarked that this fact relies on a unique continuation property, later proved in [20, 21] (Chapter 1). The proof using non-strict inequalities, first appearing in [55], is more general because it avoids to assume non-degeneracy of systems. Moreover, it is direct (proofs by contradiction are avoided when possible) and does not involve any additional argument compared to the original proof.

In the literature, there are many articles presenting Hohenberg-Kohn results but in which authors do not show that two different operators cannot produce the same ground states. This leads to incomplete proofs at best, but to false statements at worse. For instance the Hohenberg-Kohn theorems for interactions [66], and at positive temperature in the canonical case, hold by using Lemmas 2.2.3 and 2.4.2, but in the case of non-local potentials, a counterexample can be found as presented in section 2.3.2. The proof of a Hohenberg-Kohn result always follows the same scheme, and the only extra properties to show concern this step. They usually consist in a lemma, as Lemmas 2.2.3, 2.2.6, 2.4.2, 2.4.5, see also the proof of Theorem 2.3.1. Providing those results for some of the main Hohenberg-Kohn statements is one of the goals of this work.

2.2.3 A semi-metric on the space of binding potentials

In the following, we take $\Omega = \mathbb{R}^d$ for simplicity, and we show that the quantity involved in (2.2) has special properties. We define the equivalence relation \sim on the space L^1_{loc} of functions and write $v \sim u$ if there is some constant c such that $v = u + c$. We define the space of potentials

$$\mathcal{V}^N := \left\{ v \in L^p_{\text{loc}}(\mathbb{R}^d) \mid v_- \in (L^p + L^\infty)(\mathbb{R}^d), \right. \\ \left. H^N(v) \text{ has a non-degenerate fermionic ground state} \right\} / \sim,$$

where we identified potentials modulo constants, and where $p > \max(2d/3, 2)$. We define the map

$$\rho: \begin{array}{ccc} \mathcal{V}^N & \longrightarrow & (L^1 \cap L^q)(\mathbb{R}^d) \\ v & \longmapsto & \rho(v), \end{array}$$

which associates the unique ground state density to any potential $v \in \mathcal{V}^N$, and where $q := d/(d-2)$ if $d \geq 3$, q can take any value in $[1, +\infty[$ if $d = 2$, and $q = +\infty$ if $d = 1$. The Hohenberg-Kohn theorem implies the injectivity of ρ , therefore it is bijective on its image. This is the reason why it is commonly said that, at equilibrium, the ground state density contains the information of the external classical electric field. Now we define the function

$$\mathfrak{d}(v, u) := - \int_{\mathbb{R}^d} (v - u)(\rho(v) - \rho(u))$$

if $\int u_+ \rho(v)$ and $\int v_+ \rho(u)$ are finite, and $\mathfrak{d}(v, u) := +\infty$ otherwise. We remark that $\mathfrak{d}(v, u) \geq 0$ for any $v, u \in \mathcal{V}^N$, using the inequalities (2.3) and (2.4) presented in the proof of the Hohenberg-Kohn theorem, and we remark that $\mathfrak{d}(v, u) = 0$ if and only if $v \sim u$. Thus \mathfrak{d} is a semi-metric. For example, $\mathfrak{d}(v, u)$ is finite when applied to $v(x) = x^2$ and $u(x) = -Z_N |x|^{-1}$ (for Z_N large enough so that $u \in \mathcal{V}^N$), because of the exponential decay of ground states when the potentials grow polynomially and in presence of a gap between the ground energy and the essential spectrum [1, 29, 67]. Those are examples of standard physical potentials, but their $L^p + L^\infty$ distance is infinite. Therefore \mathfrak{d} seems to be a natural “physical distance”, because it enables to compare very different, but still physical, potentials.

In Theorem 2.2.1 and in the definition of \mathfrak{d} , we can avoid the assumptions $\int (v_1)_+ \rho_{\Psi_2}$ and $\int (v_2)_+ \rho_{\Psi_1}$ to be finite, replacing them by the assumptions that $(v_1)_+$ and $(v_2)_+$ are at most polynomially increasing when $|x| \rightarrow +\infty$. Then by the exponential decay of ground states, $\int (v_1)_+ \rho_{\Psi_2}$ and $\int (v_2)_+ \rho_{\Psi_1}$ are automatically finite if $E_i < \min \sigma_{\text{ess}}(H^N(v_i))$.

2.2.4 Hohenberg-Kohn for interactions

We consider N particles in \mathbb{R}^d , submitted to a two-body multiplication operator W , accounting both for interactions and external potentials. The corresponding N -body Hamiltonian takes the form

$$H^N(W) = \sum_{i=1}^N -\Delta_i + \sum_{1 \leq i < j \leq N} W(x_i, x_j), \quad (2.6)$$

acting on $L^2(\mathbb{R}^{dN})$. We will also use

$$H^N(v, w) = \sum_{i=1}^N -\Delta_i + \sum_{i=1}^N v(x_i) + \sum_{1 \leq i < j \leq N} w(x_i - x_j), \quad (2.7)$$

on $L^2(\mathbb{R}^{dN})$, which corresponds to $W(x, y) = \frac{1}{N-1}(v(x) + v(y)) + w(x - y)$. The two-body reduced density of a state Ψ , or *pair density*, is defined by

$$\rho_{\Psi}^{(2)}(x, y) := \frac{N(N-1)}{2} \int_{\mathbb{R}^{d(N-2)}} |\Psi|^2(x, y, x_3, \dots, x_N) dx_3 \cdots dx_N.$$

We can deduce the density from $\rho_{\Psi}^{(2)}$ by taking its marginal

$$\rho_{\Psi}(x) = \frac{2}{N-1} \int_{\mathbb{R}^d} \rho_{\Psi}^{(2)}(x, y) dy.$$

The energy of a state is coupled to the two-body potential W only via $\rho_{\Psi}^{(2)}$, because

$$\left\langle \Psi, \sum_{1 \leq i < j \leq N} W(x_i, x_j) \Psi \right\rangle = \int_{\mathbb{R}^{2d}} W \rho_{\Psi}^{(2)}.$$

The next Hohenberg-Kohn theorem establishes a duality between W and $\rho^{(2)}$, and between (v, w) and $\rho^{(2)}$. A similar statement is present in [66], but with an incomplete proof, which needs Lemma 2.2.3 *ii*) (see the remark in section 2.2.2). The knowledge of $\rho^{(2)}$ is sufficient to determine W alone or the pair (v, w) , hence the ground state pair correlations $\rho^{(2)}$ contain all the information of the system.

Theorem 2.2.2 (Hohenberg-Kohn for interactions).

i) Let $q > \max(4d/3, 2)$, and let $W_1, W_2 \in (L^q + L^\infty)(\mathbb{R}^{2d})$ be even two-body potentials such that $H^N(W_1)$ and $H^N(W_2)$ have ground states Ψ_1 and Ψ_2 . If

$$\int_{\mathbb{R}^{2d}} (W_1 - W_2)(\rho_{\Psi_1}^{(2)} - \rho_{\Psi_2}^{(2)}) = 0,$$

then

$$W_1 = W_2 + \frac{2(E_1 - E_2)}{N(N-1)}.$$

ii) Let $p > \max(2d/3, 2)$ and let the potentials $v_1, v_2, w_1, w_2 \in (L^p + L^\infty)(\mathbb{R}^d)$, w_1, w_2 even, be such that $H^N(v_1, w_1)$ and $H^N(v_2, w_2)$ have ground states Ψ_1 and Ψ_2 . If

$$\int_{\mathbb{R}^d} (v_1 - v_2)(\rho_{\Psi_1} - \rho_{\Psi_2}) + \int_{\mathbb{R}^{2d}} (w_1 - w_2)(x - y)(\rho_{\Psi_1}^{(2)} - \rho_{\Psi_2}^{(2)})(x, y) dx dy = 0,$$

then there exists a constant $c \in \mathbb{R}$ such that

$$\begin{cases} w_1 = w_2 + c, \\ v_1 = v_2 + \frac{E_1 - E_2}{N} - \frac{c(N-1)}{2}. \end{cases}$$

We stated the theorem in the whole space \mathbb{R}^d for the sake of simplicity, but as Theorem 2.2.1, it holds for any open connected domain $\Omega \subset \mathbb{R}^d$, with any boundary condition. More precisely, knowing $\rho^{(2)}$ on Ω^2 enables to know v on Ω and w on $\{x - y \mid x, y \in \Omega\}$.

Pair DFT (or 2RDFT for two-body reduced density functional theory) was founded in [66, 74, 75], and further explored in [2–4, 11, 18, 24, 28, 37, 49–51] among other works. In particular, Mazziotti [41–45] studied it extensively. This framework gives to the ground state two-body reduced density the central role. Theorem 2.2.2 shows that this theory is well-posed.

Proof. *i)* By the standard proof of the Hohenberg-Kohn theorem recalled above, we have $\langle \Psi_2, H^N(W_1)\Psi_2 \rangle = E_1$, so Ψ_2 is a ground state for $H^N(W_1)$, and $H^N(W_1)\Psi_2 = E_1\Psi_2$. Taking the difference with $H^N(W_2)\Psi_2 = E_2\Psi_2$ yields

$$\left(E_1 - E_2 + \sum_{1 \leq i < j \leq N}^N (W_1 - W_2)(x_i, x_j) \right) \Psi_2 = 0.$$

We use the Theorem 1.4.2, in which we need an assumption of the type $|W| \leq \epsilon(-\Delta)^{\frac{3}{2}-\delta} + c$ in \mathbb{R}^{2d} . We can apply Corollary 1.2.4 without w , replacing v by W , and d by $d' = 2d$, hence the number $2d'/3 = 4d/3$. The normalized function Ψ_2 thus cannot vanish on a set of positive measure and we have

$$E_1 - E_2 + \sum_{1 \leq i < j \leq N}^N (W_1 - W_2)(x_i, x_j) = 0$$

a.e. in \mathbb{R}^{dN} . We conclude by the following lemma, which also enables to prove *ii)*. \square

Lemma 2.2.3.

i) Let $W \in L^1_{\text{loc}}(\mathbb{R}^{2d})$ be even and such that

$$\sum_{1 \leq i < j \leq N} W(x_i, x_j) = 0, \quad (2.8)$$

a.e. in \mathbb{R}^{dN} . Then $W = 0$ a.e. in \mathbb{R}^{2d} .

ii) If $v, w \in L^1_{\text{loc}}(\mathbb{R}^d)$, with w even, and if

$$\sum_{i=1}^N v(x_i) + \sum_{1 \leq i < j \leq N} w(x_i - x_j) = 0, \quad (2.9)$$

a.e. in \mathbb{R}^{dN} , then v and w are a.e. constant and verify

$$v + \frac{N-1}{2}w = 0.$$

Proof of Lemma 2.2.3. i) We consider $\varphi \in \mathcal{C}_c^\infty(\mathbb{R}^d)$ such that $\int \varphi \neq 0$ and integrate (2.8) against $\varphi^{\otimes N}$, which yields

$$\int W \varphi^{\otimes 2} = 0.$$

We use it with $\varphi = \chi + \epsilon \eta$, $\chi, \eta \in \mathcal{C}_c^\infty(\mathbb{R}^d)$, $\int \chi \neq 0$ and ϵ small, and viewing the result as a polynomial in ϵ , the coefficient in ϵ has to vanish, therefore

$$\int W(\chi \otimes \eta) = 0. \quad (2.10)$$

Let $f \in \mathcal{C}_c^\infty(\mathbb{R}^d, \mathbb{R}_+)$ be a regularizing function such that $\int f = 1$. For $x_0 \in \mathbb{R}^d$ and $\epsilon > 0$, we denote by $f_{x_0}^\epsilon(x) := \epsilon^{-d} f((x - x_0)/\epsilon)$ the translated and scaled function, and write $f^\epsilon := f_0^\epsilon$. We apply (2.10) to $\chi = f_{x_0}^\epsilon$ and $\eta = f_{y_0}^\epsilon$ for any $x_0, y_0 \in \mathbb{R}^d$, to obtain

$$0 = (W * (f^\epsilon \otimes f^\epsilon))(x_0, y_0).$$

We let $\epsilon \rightarrow 0$, so $W * (f^\epsilon \otimes f^\epsilon) \rightarrow W$ a.e. in \mathbb{R}^{2d} , and we get $W = 0$.

ii) We apply *i)* to $W(x, y) = (N - 1)^{-1} (v(x) + v(y)) + w(x - y)$, yielding

$$v(x) + v(y) + (N - 1)w(x - y) = 0 \quad (2.11)$$

a.e. in \mathbb{R}^{2d} . This can be rewritten

$$v(x + y) + v(y) = -(N - 1)w(x) = -(N - 1)w(-x) = v(-x + y) + v(y),$$

and we have thus $v(x + y) = v(y - x)$. This implies $v(y) = v(y - 2x)$ for a.e. $(x, y) \in \mathbb{R}^{2d}$, hence v is constant and w as well. \square

A first consequence is that in a Kohn-Sham configuration, pair densities are different.

Corollary 2.2.4 (Pair densities in the Kohn-Sham setting). *Let potentials $v_1, v_2, w \in (L^p + L^\infty)(\mathbb{R}^d)$, with $p > \max(2d/3, 2)$, where w is even and not constant, such that $H^N(v_1, w)$ and $H^N(v_2, 0)$ have ground states Ψ_1 and Ψ_2 . Then $\rho_{\Psi_1}^{(2)} \neq \rho_{\Psi_2}^{(2)}$.*

The proof can be done by contraposition, applying Theorem 2.2.2 *ii)*. We note that we did not need to assume that $\rho_{\Psi_1} = \rho_{\Psi_2}$, as in the Kohn-Sham setting. This corollary is to compare with a similar result in Matrix DFT, claiming that it is not possible to reproduce the ground state one-body density matrix of an interacting system by a non-interacting system driven by a different electric potential. Indeed, for interacting Coulomb systems, Friesecke proved that the ground state one-body density matrix has infinite rank [17, Theorem 2.1], whereas it is a finite rank projector for non-interacting systems.

When several types of particles are present, we can use the same principle. This illustrates the robustness of Hohenberg-Kohn results for interactions. For instance let us consider a mixture of two types of particles, $N \in \mathbb{N} \setminus \{0\}$ of the first type and $M \in \mathbb{N} \setminus \{0\}$ of the second, either fermions or bosons, represented by a wavefunction $\Psi \in L^2\left((\mathbb{R}^d)^N \times (\mathbb{R}^d)^M, \mathbb{C}\right)$ (anti)symmetric in the first N variables and (anti)symmetric in the last M variables. The interactions between the particles of the first (resp. second) group are mediated by a function w_a (resp. w_b), and the interactions between the two types are mediated by a third one w_{ab} . An external potential v_a (resp. v_b) acts on the first (resp. second) type of particles. The difference in masses is implemented in a constant $\alpha \neq 0$. The Hamiltonian is

$$\begin{aligned} H(v_a, v_b, w_a, w_b, w_{ab}) &:= \sum_{i=1}^N (-\Delta_i + v_a(x_i)) + \sum_{k=N+1}^{N+M} (-\alpha \Delta_k + v_b(x_k)) \\ &+ \sum_{1 \leq i < j \leq N} w_a(x_i - x_j) + \sum_{N+1 \leq k < l \leq N+M} w_b(x_k - x_l) + \sum_{\substack{1 \leq i \leq N \\ N+1 \leq k \leq N+M}} w_{ab}(x_i - x_k). \end{aligned}$$

We define the pair function of the first type

$$\rho_{a,\Psi}^{(2)}(x, y) := \binom{N}{2} \int_{\mathbb{R}^{d(N+M-2)}} |\Psi|^2(x, y, x_3, \dots) dx_3 \dots dx_{N+M},$$

the one of the second type

$$\begin{aligned} \rho_{b,\Psi}^{(2)}(x, y) &:= \binom{M}{2} \int_{\mathbb{R}^{d(N+M-2)}} |\Psi|^2(x_1, \dots, x_N, x, y, x_{N+3}, \dots) \\ &\quad \times dx_1 \dots dx_N dx_{N+3} \dots dx_{N+M}, \end{aligned}$$

and the pair function between the two types

$$\begin{aligned} \rho_{ab,\Psi}^{(2)}(x, y) &:= NM \int_{\mathbb{R}^{d(N+M-2)}} |\Psi|^2(x, x_2, \dots, x_N, y, x_{N+2}, \dots) \\ &\quad \times dx_2 \dots dx_N dx_{N+2} \dots dx_{N+M}. \end{aligned}$$

Using the symmetries, the energy is thus

$$\begin{aligned} \langle \Psi, H(v_a, v_b, w_a, w_b, w_{ab}) \Psi \rangle &= \sum_{i=1}^N \int_{\mathbb{R}^d} |\nabla_i \Psi|^2 + \alpha \sum_{k=N+1}^{N+M} \int_{\mathbb{R}^d} |\nabla_k \Psi|^2 \\ &+ \frac{2}{N-1} \int_{\mathbb{R}^d} \rho_{a,\Psi}^{(2)}(x, x) v_a(x) dx + \frac{2}{M-1} \int_{\mathbb{R}^d} \rho_{b,\Psi}^{(2)}(x, x) v_b(x) dx \\ &+ \int_{\mathbb{R}^{2d}} \rho_{a,\Psi}^{(2)}(x, y) w_a(x-y) dx dy + \int_{\mathbb{R}^{2d}} \rho_{b,\Psi}^{(2)}(x, y) w_b(x-y) dx dy \\ &\quad + \int_{\mathbb{R}^{2d}} \rho_{ab,\Psi}^{(2)}(x, y) w_{ab}(x-y) dx dy. \end{aligned}$$

Theorem 2.2.5 (Hohenberg-Kohn for different particles). *Let $p > \max(2d/3, 2)$ and let the potentials $v_{\eta,i}, w_{\eta,i}, w_{ab,i} \in (L^p + L^\infty)(\mathbb{R}^d)$ for $\eta \in \{a, b\}$ and $i \in \{1, 2\}$, with $w_{\eta,i}, w_{ab,i}$ even, such that $H(v_{a,i}, v_{a,i}, w_{a,i}, w_{b,i}, w_{ab,i})$ have ground states Ψ_i . If*

$$\rho_{a,\Psi_1}^{(2)} = \rho_{a,\Psi_2}^{(2)}, \quad \rho_{b,\Psi_1}^{(2)} = \rho_{b,\Psi_2}^{(2)}, \quad \rho_{ab,\Psi_1}^{(2)} = \rho_{ab,\Psi_2}^{(2)},$$

then $v_{\eta,1} - v_{\eta,2}$, $w_{\eta,1} - w_{\eta,2}$, and $w_{ab,1} - w_{ab,2}$ are constant, for $\eta \in \{a, b\}$, and satisfy

$$\begin{aligned} \frac{N(N-1)}{2}(w_{a,1} - w_{a,2}) + \frac{M(M-1)}{2}(w_{b,1} - w_{b,2}) + NM(w_{ab,1} - w_{ab,2}) \\ + N(v_{a,1} - v_{a,2}) + M(v_{b,1} - v_{b,2}) = E_1 - E_2. \end{aligned}$$

A slightly modified unique continuation property is necessary for the proof, which takes into account the presence of α . Also, the proof follows the same steps as for the standard Hohenberg-Kohn theorem, and requires the following lemma.

Lemma 2.2.6. *If $v_a, v_b, w_a, w_b, w_{ab} \in L^1_{\text{loc}}(\mathbb{R}^d)$, with w_a, w_b and w_{ab} even, and if*

$$\begin{aligned} \sum_{i=1}^N v_a(x_i) + \sum_{k=N+1}^{N+M} v_b(x_k) + \sum_{1 \leq i < j \leq N} w_a(x_i - x_j) \\ + \sum_{N+1 \leq k < l \leq N+M} w_b(x_k - x_l) + \sum_{\substack{1 \leq i \leq N \\ N+1 \leq k \leq N+M}} w_{ab}(x_i - x_k) = 0, \end{aligned} \quad (2.12)$$

a.e. in \mathbb{R}^{dN} , then v_a, v_b, w_a, w_b and w_{ab} are a.e. constant and verify

$$Nv_a + Mv_b + \frac{N(N-1)}{2}w_a + \frac{M(M-1)}{2}w_b + NMw_{ab} = 0.$$

Proof. We start by taking $\varphi \in C_c^\infty(\mathbb{R}^d)$ such that $\int \varphi = 1$, we multiply (2.12) by $\prod_{k=N+1}^{N+M} \varphi(x_k)$ and we integrate over $(x_k)_{N+1 \leq k \leq N+M} \in (\mathbb{R}^d)^M$, which yields

$$\sum_{i=1}^N (v_a(x_i) + Mw_{ab} * \varphi) + \sum_{1 \leq i < j \leq N} w_a(x_i - x_j) = c,$$

where c is a constant. Applying Lemma 2.2.3, *ii*), we know that w_a is constant, and by symmetry, w_b as well. We thus want to show that if

$$\sum_{i=1}^N v_a(x_i) + \sum_{k=N+1}^{N+M} v_b(x_k) + \sum_{\substack{1 \leq i \leq N \\ N+1 \leq k \leq N+M}} w_{ab}(x_i - x_k) = 0,$$

then v_a, v_b and w_{ab} are constant. With similar notations as in the proof of Lemma 2.2.3 *i*), and choosing f even, we take any $x, y \in \mathbb{R}^d$ and multiply the equation by

$$f_x^\epsilon(x_1) \dots f_x^\epsilon(x_N) f_y^\epsilon(x_{N+1}) \dots f_y^\epsilon(x_{N+M}),$$

and then integrate over all coordinates, giving

$$Nv_a * f^\epsilon(x) + Mv_b * f^\epsilon(y) + NM(w_{ab} * f^\epsilon * f^\epsilon)(x - y) = 0.$$

Letting $\epsilon \rightarrow 0$ yields

$$Nv_a(x) + Mv_b(y) + NMw_{ab}(x - y) = 0, \quad (2.13)$$

for a.e. $(x, y) \in \mathbb{R}^d$. Using the fact that w_{ab} is even, we have

$$\begin{aligned} Nv_a(x) + Mv_b(y) &= -NMw_{ab}(x - y) = -NMw_{ab}(y - x) \\ &= Nv_a(y) + Mv_b(x), \end{aligned}$$

hence

$$(Nv_a - Mv_b)(x) = (Nv_a - Mv_b)(y)$$

a.e. so $Nv_a - Mv_b = c$ is constant. Equation (2.13) can then be rewritten

$$v_b(x) + v_b(y) + Nw_{ab}(x - y) + c/M = 0,$$

which is similar to (2.11). With the same argument as in the proof of Lemma 2.2.3 *ii*), we can prove that v_b, v_a and w_{ab} are constant. \square

Many quantum models are replaced by approximate effective ones in which interactions are changed, because they are easier to study and are exact in some limits. Theorem 2.2.5 shows that they cannot have the same ground state pair correlations, hence it provides a limit to their predictive power.

By measuring pair functions of bound ground states, one can thus exhaustively reconstruct the interactions between particles in non relativistic quantum settings, using an inverse procedure. In particular, this could be applied to the phonon-mediated effective interactions between electrons in a superconducting medium.

2.3 Absence of Hohenberg-Kohn in Spin and Matrix DFT

We have seen that for the standard model, a Hohenberg-Kohn theorem holds. However, for other models, this is not necessarily the case. In Spin DFT, it is well-known that it does not hold [10], however we will show a partial Hohenberg-Kohn result in this model. We also give a counterexample to a Hohenberg-Kohn theorem in Matrix DFT.

2.3.1 Partial Hohenberg-Kohn in Spin DFT

Spin DFT was founded by von Barth and Hedin in [72]. It is a version of Density Functional Theory based on a variant of the Pauli Hamiltonian, in which the coupling between the current and the magnetic field is neglected. The only magnetic feature taken into account is the Zeeman interaction. It is a very active field of research in quantum physics and chemistry [14, 26, 34, 52–54, 58–60, 72]. This framework enables to study the relations between the ground state magnetization and the electromagnetic field.

We consider the Hamiltonian of Spin DFT

$$H^N(v, B) = \sum_{i=1}^N (-\Delta_i + \sigma_i \cdot B(x_i) + v(x_i)) + \sum_{1 \leq i < j \leq N} w(x_i - x_j),$$

where \cdot is the scalar product of \mathbb{R}^d . We fix the dimension $d = 3$ and recall the definition of the Pauli matrices

$$\sigma^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma^y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

acting on one-particle two-components wavefunctions $\phi = (\phi^\uparrow, \phi^\downarrow)^T$, where $\phi^\uparrow, \phi^\downarrow \in L^2(\mathbb{R}^d, \mathbb{C})$ and $\int_{\mathbb{R}^d} |\phi|^2 = 1$. In this case, $\sigma_i \cdot B(x_i) = B_x(x_i)\sigma_i^x + B_y(x_i)\sigma_i^y + B_z(x_i)\sigma_i^z$. The state of the system is described by antisymmetric and normalized wavefunctions $\Psi \in L_a^2((\mathbb{R}^d \times \{\uparrow, \downarrow\})^N)$. We introduce their one-body densities

$$\rho_\Psi^{\alpha\beta}(x) := \sum_{(s_2, \dots, s_N) \in \{\uparrow, \downarrow\}^{N-1}} \sum_{i=1}^N \int_{\mathbb{R}^{d(N-1)}} \Psi(\alpha, x; s_2, x_2; \dots) \bar{\Psi}(\beta, x; s_2, x_2; \dots) \times dx_2 \cdots dx_N,$$

where $\alpha, \beta \in \{\uparrow, \downarrow\}$, but for the sake of simplicity we will not always write the subscript Ψ . We remark that $\rho^{\uparrow\downarrow} = \overline{\rho^{\downarrow\uparrow}} =: \xi$. We define the density $\rho := \rho^\uparrow + \rho^\downarrow$ and the magnetization

$$m := \begin{pmatrix} \rho^{\uparrow\downarrow} + \rho^{\downarrow\uparrow} \\ -i(\rho^{\uparrow\downarrow} - \rho^{\downarrow\uparrow}) \\ \rho^{\uparrow\uparrow} - \rho^{\downarrow\downarrow} \end{pmatrix} = \begin{pmatrix} 2 \operatorname{Re} \xi \\ 2 \operatorname{Im} \xi \\ \rho^{\uparrow\uparrow} - \rho^{\downarrow\downarrow} \end{pmatrix}. \quad (2.14)$$

The quantum wavefunction is coupled to the external magnetic field only via the magnetization. Indeed, using fermionic statistics, we have

$$\left\langle \Psi, \sum_{i=1}^N (\sigma_i \cdot B(x_i)) \Psi \right\rangle = \int_{\mathbb{R}^3} B \cdot m_\Psi.$$

It is well-known that there is no complete Hohenberg-Kohn theorem in this model, due to a counterexample of Capelle and Vignale [10] recalled below (see also [14]). More explicitly, if the ground state densities and magnetizations of two systems are equal, this does not imply that the external potentials and magnetic fields are equal. However, in the following theorem, we show that those assumptions imply a strong constraint on the external fields imposed on the system. This specifies the relation between (v, B) and (ρ, m) .

Theorem 2.3.1 (Partial Hohenberg-Kohn for Spin DFT). *Let $p > 2$, let $w, v_1, v_2 \in (L^p + L^\infty)(\mathbb{R}^3, \mathbb{R})$ be potentials and $B_1, B_2 \in (L^p + L^\infty)(\mathbb{R}^3, \mathbb{R}^3)$ be magnetic fields. We assume that $H^N(v_1, B_1)$ and $H^N(v_2, B_2)$ have ground states, which we denote by Ψ_1 and Ψ_2 . If*

$$\int_{\mathbb{R}^3} (v_1 - v_2)(\rho_{\Psi_1} - \rho_{\Psi_2}) + \int_{\mathbb{R}^3} (B_1 - B_2) \cdot (m_{\Psi_1} - m_{\Psi_2}) = 0, \quad (2.15)$$

then

$$|B_1 - B_2| \chi = \frac{E_1 - E_2}{N} + v_2 - v_1, \quad (2.16)$$

where χ is a measurable function taking its values in the discrete and finite set $\{-1, -1 + \frac{2}{N}, -1 + \frac{4}{N}, \dots, 1 - \frac{2}{N}, 1\}$.

In particular, the condition (2.15) is satisfied when $(\rho_{\Psi_1}, m_{\Psi_1}) = (\rho_{\Psi_2}, m_{\Psi_2})$. We remark that on connected subsets where v_1, v_2, B_1, B_2 are continuous and where $B_1 \neq B_2$ everywhere, χ is continuous hence constant. Also, when N is odd, χ can never vanish, thus if we have $v_1 - E_1/N = v_2 - E_2/N$ and $m_{\Psi_1} = m_{\Psi_2}$, we can deduce that $B_1 = B_2$. At fixed v , if we formally define a function $f_{\text{HK}}(B) := (m_\Psi, E)$ associating to a magnetic field the ground state magnetization and energy, Theorem 2.3.1 implies that f_{HK} is injective, so it is bijective on its image. This shows that knowing m_Ψ and E enables to know B . Consequently, for a fixed v and N odd, all physical quantities are functionals of the ground state pair (m, E) .

To build a counterexample, Capelle and Vignale [10] start from a system which ground state is an eigenvalue of the z momentum operator $\sum_{i=1}^N \sigma_i^z$, and where the ground energy of $H^N(v_1, 0)$ is isolated from the rest of the spectrum. For instance one can choose to start from $B_1 = 0$, with a binding v_1 . Then they perturb this initial system by adding $B_2 = be_z$ where $b \in \mathbb{R}$ is so small that there is no energy levels crossing, and they keep the electric potential $v_2 = v_1$ unchanged. In this case, our equation (2.16) becomes $Nb\chi = E_1 - E_2$, where χ is as in the statement of the theorem.

Proof. Following the same steps as in the proof of the standard Hohenberg-Kohn theorem, we can show that $\langle \Psi_2, H^N(v_1, B_1)\Psi_2 \rangle = E_1$. Thus Ψ_2

respects Schrödinger's equation of the first operator $H^N(v_1, B_1)\Psi_2 = E_1\Psi_2$. Taking the difference with $H^N(v_2, B_2)\Psi_2 = E_2\Psi_2$ yields

$$\left(\sum_{i=1}^N (\mathbb{1}_{2^N \times 2^N} v(x_i) + B(x_i) \cdot \sigma_i) \right) \Psi_2 = 0,$$

where $v := v_1 - v_2 + (E_2 - E_1)/N$ and $B := B_1 - B_2$. By strong unique continuation for the Pauli operator [21] (see Chapter 1), Ψ_2 does not vanish on sets of positive measure, thus we get

$$0 \in \sigma \left(\sum_{i=1}^N (\mathbb{1}_{2^N \times 2^N} v(x_i) + B(x_i) \cdot \sigma_i) \right) \quad (2.17)$$

a.e. in \mathbb{R}^{dN} . We work in a cube $C := [0, a]^d$ for a fixed $a \in \mathbb{R}_+$. The function $x \mapsto v(x) + B(x) \cdot \sigma_i$ is continuous on a set L_n such that $|C \setminus L_n| \leq 1/n$, by Lusin's theorem. Hence, $\sum_{i=1}^N v(x_i) + B(x_i) \cdot \sigma_i$ is continuous on $(L_n)^N$. We take the limit $n \rightarrow +\infty$ and use that the map giving the eigenvalues of a matrix is continuous, to infer that

$$0 \in \sigma \left(Nv(x) + B(x) \cdot \sum_{i=1}^N \sigma_i \right)$$

for a.e. $x \in C$. We extend this conclusion a.e. in $x \in \mathbb{R}^3$ by letting $a \rightarrow +\infty$. Eventually, one deduces that for a.e. $x \in \mathbb{R}^3$, at least one of the eigenvalues of $Nv(x) + B(x) \cdot \sum_{i=1}^N \sigma_i$ vanishes. Those eigenvalues are

$$\{Nv(x) + j |B(x)|\}_{j \in \{-N, -N+2, \dots, N-2, N\}},$$

by next Lemma 2.3.2, for which we give a proof in the appendix.

Lemma 2.3.2 (Local diagonalization of the Zeeman interaction).

For $B \in L_{\text{loc}}^1(\mathbb{R}^3, \mathbb{R}^3)$, $\sum_{i=1}^N B(x_i) \cdot \sigma_i$ is diagonalizable in the spin variables, with eigenvalues

$$\left\{ \sum_{i=1}^N (-1)^{s_i} |B(x_i)| \right\}_{(s_i)_{1 \leq i \leq N} \in \{0,1\}^N},$$

a.e. in \mathbb{R}^{dN} .

Hence, for each $x \in \mathbb{R}^3$ such that $B(x) \neq 0$, and such that $v(x)$ and $B(x)$ are finite, there is a real number $\chi(x) \in \{-1, -1 + 2/N, \dots, 1 - 2/N, 1\}$ respecting $v(x) + \chi(x) |B(x)| = 0$. On the set

$$\{x \in \mathbb{R}^3 \mid B(x) \neq 0, |v(x)| + |B(x)| < +\infty\},$$

χ is measurable, and on the complementary space we choose $\chi(x) = 1$ for instance. The function χ is thus measurable. \square

2.3.2 Counterexample in Matrix DFT

Founded by Gilbert [23], Reduced Density Matrix Functional Theory (RDMFT), hereafter called Matrix DFT, is extensively used in quantum chemistry [5, 6, 13, 32, 36, 40, 47, 64, 65, 70, 73]. This method is similar to standard DFT but the central internal quantity is now the one-particle reduced density matrix (1RDM) which is defined by

$$\gamma_{\Gamma}(x, y) := N \int_{\mathbb{R}^{d(N-1)}} \Gamma(x, x_2, \dots, x_N; y, x_2, \dots, x_N) dx_2 \cdots dx_N$$

for mixed states Γ , and reduces to

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

in the case of pure states $\Gamma = |\Psi\rangle\langle\Psi|$. The kinetic energy part of the exchange-correlation functional is not approximated, since the kinetic energy is an exact functional of the 1RDM. The drawback is that it is computationally more expensive than standard DFT, because 1RDM kernels have two space arguments instead of one. The external non-local potentials at stake in this framework are one-body operators of

$$\mathcal{G} := \left\{ G = G^* \mid \mathcal{D}(|G|^{\frac{1}{2}}) \subset H^1(\mathbb{R}^d), \forall \epsilon > 0 \exists c_{\epsilon} \geq 0 \mid G| \leq -\epsilon \Delta + c_{\epsilon} \right\}.$$

The multiplication by $v \in (L^{d/2} + L^{\infty})(\mathbb{R}^d)$, or a gradient magnetic operator $-2iA \cdot \nabla$ where $A \in (L^d + L^{\infty})(\mathbb{R}^d)$, belong to this class. One obtains the full Pauli Hamiltonian when $G = -2iA \cdot \nabla + A^2 + \sigma \cdot \text{curl } A$. Also, we can choose it to act by multiplication on the momentum space $(\widehat{G\Psi})(k) = g(k)\widehat{\Psi}(k)$ with $|g| \leq \epsilon k^2 + c_{\epsilon}$ for any $\epsilon > 0$. An operator $G \in \mathcal{G}$ acts on many-body functions by the second quantized $G^{(N)} \in \mathcal{L}(L^2(\mathbb{R}^{dN}))$ of G on the N -particle sector

$$G^{(N)} = \sum_{i=1}^N G_i, \quad (2.18)$$

where each G_i is a copy of G acting on the i^{th} body, that is $G_i := \mathbb{1} \otimes \cdots \otimes G \otimes \cdots \otimes \mathbb{1}$. For instance, when G has a kernel,

$$\left(G^{(N)} \Psi \right) (x_1, \dots, x_N) = \sum_{i=1}^N \int_{\mathbb{R}^d} G(x_i, y) \Psi(x_1, \dots, x_{i-1}, y, x_{i+1}, \dots, x_N) dy.$$

The Hamiltonian in this formalism is

$$H^N(G) = \sum_{i=1}^N -\Delta_i + \sum_{i=1}^N G_i + \sum_{1 \leq i < j \leq N} w(x_i - x_j), \quad (2.19)$$

and the operators in \mathcal{G} are such that all $H^N(G)$ have the same form domain $H^1(\mathbb{R}^d)$. A state is coupled to the external non-local potential only via its

one-body density matrix, and the interaction energy of Ψ with G is equal to $\text{Tr } G\gamma_\Psi$.

In his pioneering work, Gilbert [23] wrote that the proof of Hohenberg and Kohn cannot be extended to $G \mapsto \gamma$, but he remarked that the injectivity $\Psi \mapsto \gamma_\Psi$ holds, when Ψ is taken in the set of ground states of $H^N(G)$'s, and where G 's are chosen in \mathcal{G} and produce non-degenerate ground states. Here we provide a counter-example showing that the map $G \mapsto \gamma$ is not injective. This implies that in its most general formulation, Matrix DFT is ill-posed because it does not respect uniqueness.

Let $G_1 \in \mathcal{G}$ be such that $H(G_1)$ has a unique ground state Ψ_1 isolated from the rest of the spectrum. We assume that

$$\exists \phi \in H^1(\mathbb{R}^d), \int |\phi|^2 = 1 \text{ such that } \left(\phi \wedge L_a^2(\mathbb{R}^{d(N-1)}) \right) \perp \Psi_1. \quad (2.20)$$

The assumption (2.20) is equivalent to the existence of an orthonormal basis $\{\phi_i\}_{i \in \mathbb{N}}$ such that ϕ_1 never appears in the decomposition of Ψ_1 on the basis built from $\{\phi_i\}_{i \in \mathbb{N}}$. We take $G_2 = G_1 + \epsilon |\phi\rangle \langle \phi|$. We have $|\phi\rangle \langle \phi| \in \mathcal{G}$ and

$$H^N(G_2)\Psi_1 = H^N(G_1)\Psi_1 + \epsilon \left(\sum_{i=1}^N |\phi\rangle \langle \phi|_i \right) \Psi_1 = E_1 \Psi_1.$$

We also have $H^N(G_1) \leq H^N(G_2)$ in the sense of forms, therefore by the min-max principle, $E_1 \leq E_2$ and Ψ_1 is a ground state of $H^N(G_2)$. Hence we have two Hamiltonians having different non-local potentials but the same ground state. We get counterexamples if we can find w and G_1 such that (2.20) holds. This is the case when $w = 0$ because then, Ψ_1 is a Slater determinant. We have thus here a class of counterexamples to the Hohenberg-Kohn property $G \mapsto \gamma$. This argument also works for the corresponding theory considering mixed states, because when $w = 0$, the ground state is still a Slater determinant. We note that in [17, Theorem 2.1], Friesecke proved that for interacting Coulomb systems and denoting by Ψ the ground state, $\text{rank } \gamma_\Psi = +\infty$, but it is not proved that $\text{Im } \gamma_\Psi$ spans the full space, in which case the condition (2.20) would be wrong for Coulomb interactions. This uniqueness property for non-local potentials when $w = |\cdot|^{-1}$ is thus an open problem, one could also try to determine it in the simpler Hartree-Fock model for instance.

2.4 Recovering Hohenberg-Kohn in Thermal DFT

In this section we show that Hohenberg-Kohn theorems which do not hold at zero temperature are true when $T > 0$. Founded by Mermin [46], Thermal DFT is the Density Functional Theory framework dealing with a fixed positive temperature. This formalism was used in several works [5, 7, 12, 56, 57, 63, 68], in particular to model warm dense matter [25], and

nuclear matter. We provide here a new formalism of Thermal DFT enabling to work with systems having possibly different temperatures.

The set of N -particle canonical states is

$$\mathcal{S}_{\text{can}}^N := \left\{ \Gamma \in \mathcal{L}(L_a^2(\mathbb{R}^{dN})) \mid 0 \leq \Gamma = \Gamma^*, \text{Tr } \Gamma = 1 \right\},$$

and the set of grand canonical states is

$$\mathcal{S}_{\text{gc}} := \left\{ \Gamma \in \mathcal{L}\left(\mathbb{C} \oplus_{N=1}^{+\infty} L_a^2(\mathbb{R}^{dN})\right) \mid 0 \leq \Gamma = \Gamma^*, \text{Tr } \Gamma = 1 \right\}.$$

The entropy is denoted by $S_\Gamma := -\text{Tr } \Gamma \ln \Gamma$. We denote the particle number operator by \mathcal{N} , the average number of particles of a state Γ is $\text{Tr } \mathcal{N} \Gamma$. We define the k -particle matrix densities

$$\Gamma^{(k)} := \sum_{k \geq n} \binom{k}{n} \text{Tr}_{k+1 \rightarrow n} \Gamma,$$

and the density

$$\rho_\Gamma(x) := \Gamma^{(1)}(x, x).$$

In the grand canonical case, for states $\Gamma = G_0 \oplus G_1 \oplus \dots$ where $G_n \geq 0$, we define the partial densities $\rho_n(x) := n (\text{Tr}_{2 \rightarrow n} G_n)(x, x)$, and thus $\rho_\Gamma(x) = \sum_{n \geq 1} \rho_n(x)$. Also, the number of particles is the total mass of the density $\int \rho_\Gamma = \text{Tr } \mathcal{N} \Gamma$. We define the second quantized operators $\mathbb{K} := \oplus_{n=1}^{+\infty} \sum_{i=1}^n -\Delta_i$, $\mathbb{V} := \oplus_{n=1}^{+\infty} \sum_{i=1}^n v(x_i)$, $\mathbb{W} := \oplus_{n \geq 2} \sum_{1 \leq i < j \leq n} w(x_i - x_j)$, and

$$\mathbb{H}(v) := \mathbb{K} + \mathbb{V} + \mathbb{W}.$$

The wavefunction is coupled to the external potential only via its density, $\text{Tr } \mathbb{V} \Gamma = \int v \rho_\Gamma$. We denote by $H^N(v)$ the usual N -body Hamiltonian (2.1). The free energy of canonical states is

$$\begin{aligned} \mathcal{E}_{v,T}^N(\Gamma_N) &:= \text{Tr } H^N(v) \Gamma_N - T S_{\Gamma_N} \\ &= \text{Tr } H^N(0) \Gamma_N + \int v \rho_{\Gamma_N} - T S_{\Gamma_N}. \end{aligned}$$

The free energy of grand canonical states is

$$\begin{aligned} \mathcal{E}_{v,T}(\Gamma) &:= \text{Tr } \mathbb{H}(v) \Gamma - T S_\Gamma \\ &= \text{Tr } \mathbb{H}(0) \Gamma + \int v \rho_\Gamma - T S_\Gamma. \end{aligned}$$

We can add a chemical potential in the manner $\mathcal{E}_{v,T,\mu}(\Gamma) := \mathcal{E}_{v,T}(\Gamma) - \mu \text{Tr } \mathcal{N} \Gamma$ but $\mathcal{E}_{v,T,\mu} = \mathcal{E}_{v-\mu,T}$ so without loss of generality, we can set $\mu = 0$ (or change

$v \rightarrow v - \mu$ everywhere), and work with $\mathcal{E}_{v,T}$. By Gibbs' variational principle, when

$$\mathrm{Tr} e^{-\mathbb{H}(v)/T}, \mathrm{Tr} e^{-H^N(v)/T} < +\infty,$$

those functionals have a unique minimizer, called the Gibbs state. It is $\Gamma = Z^{-1}e^{-\mathbb{H}(v)/T}$ in the grand canonical ensemble, and $\Gamma_N = Z^{-1}e^{-H^N(v)/T}$ in the canonical one, where $Z := \mathrm{Tr} e^{-\mathbb{H}(v)/T}$ (resp. $Z := \mathrm{Tr} e^{-H^N(v)/T}$) is the partition function.

2.4.1 A Hohenberg-Kohn theorem for $(v, T) \mapsto (\rho, S)$

We can now show a complete Hohenberg-Kohn theorem for Thermal DFT, extending Mermin's statement [46] to systems having different temperatures, and to the canonical case. We define the exponent

$$\begin{cases} p = d/2 & \text{for } d \geq 3, \\ p > 1 & \text{for } d = 2, \\ p = 1 & \text{for } d = 1. \end{cases} \quad (2.21)$$

Theorem 2.4.1 (Hohenberg-Kohn at positive temperatures). *Let $T_1, T_2 > 0$, and p as in (2.21). Let $v_1, v_2 \in L^p_{\mathrm{loc}}(\mathbb{R}^d)$, $w, (v_1)_-, (v_2)_- \in (L^p + L^\infty)(\mathbb{R}^d)$ be potentials such that $\mathrm{Tr} e^{-\mathbb{H}(v_j)/T_j} < +\infty$ for $j \in \{1, 2\}$. We denote by Γ_1, Γ_2 the grand canonical Gibbs states corresponding respectively to \mathcal{E}_{v_1, T_1} and \mathcal{E}_{v_2, T_2} , and we assume that $\int (v_1)_+ \rho_{\Gamma_2}$ and $\int (v_2)_+ \rho_{\Gamma_1}$ are finite. If*

$$-(T_1 - T_2)(S_{\Gamma_1} - S_{\Gamma_2}) + \int_{\mathbb{R}^d} (v_1 - v_2)(\rho_{\Gamma_1} - \rho_{\Gamma_2}) = 0,$$

then $T_1 = T_2$, $v_1 = v_2$, $Z_1 = Z_2$ and $\Gamma_1 = \Gamma_2$. In the canonical setting, with similar assumptions we deduce that $T_1 = T_2$, $v_1 = v_2 + T_1 \ln \frac{Z_2}{Z_1}$ and $\Gamma_1 = \Gamma_2$.

This result shows a duality between the internal equilibrium state quantities (ρ, S) and the external imposed quantities (v, T) . The equilibrium state density and entropy of a quantum system contains the information of (v, T) . In particular, all physical quantities are functionals of the ground state pair (ρ, S) . Nevertheless, we are not aware of any functional of the ground state energy defined in terms of (ρ, S) , approximating the exact one.

Proof. By the standard proof of the Hohenberg-Kohn theorem, we show that $\mathcal{E}_{v_1, T_1}(\Gamma_2) = E_1$ using that Γ_2 belongs to the quadratic form domain of $\mathbb{H}(v_1)$. Gibbs minimizers are unique, this can be proved by using Klein's inequality [61, (5.3)] or Pinsker, so $\Gamma_1 = \Gamma_2$, that is

$$Z_1^{-1} e^{-(\mathbb{T}+\mathbb{W}+\mathbb{V}_1)/T_1} = Z_2^{-1} e^{-(\mathbb{T}+\mathbb{W}+\mathbb{V}_2)/T_2},$$

on the antisymmetric Fock space. Restricting to the zero-body sector yields $Z_1 = Z_2$, so we can rewrite

$$e^{-\frac{1}{T_1}(\mathbb{T}+\mathbb{W}+\mathbb{V}_1)} = e^{-\frac{\alpha}{T_1}(\mathbb{T}+\mathbb{W}+\mathbb{V}_2)},$$

with $\alpha := T_1/T_2$. By injectivity of the exponential map for operators, we obtain

$$\mathbb{T} + \mathbb{W} + \mathbb{V}_1 = \alpha (\mathbb{T} + \mathbb{W} + \mathbb{V}_2),$$

on the antisymmetric Fock space. Restricting to the one-body sector gives

$$-\Delta + v_1 = \alpha (-\Delta + v_2),$$

and

$$(\alpha - 1)\Delta = \alpha v_2 - v_1.$$

In $H_{\text{loc}}^1(\mathbb{R}^d)$, the left-hand side is translation invariant, thus so is the right hand side, and we deduce that $\alpha = 1$, and then $v_1 = v_2$.

If we consider the canonical setting instead of the grand canonical one, we only have a constraint on the antisymmetric N -body sector but the proof is the same. Indeed, the same reasoning leads to

$$\begin{aligned} & \sum_{i=1}^N (-\Delta_i + v_1(x_i)) + \sum_{1 \leq i < j \leq N} w(x_i - x_j) \\ &= \alpha \left(\sum_{i=1}^N (-\Delta_i + v_2(x_i)) + \sum_{1 \leq i < j \leq N} w(x_i - x_j) - NT_2 \ln \frac{Z_1}{Z_2} \right) \end{aligned} \quad (2.22)$$

in $L_a^2(\mathbb{R}^{dN})$. We conclude by using the following lemma. \square

Lemma 2.4.2. *Let $A, B \in L_{\text{loc}}^1(\mathbb{R}^3, \mathbb{R}^3)$, $v, w \in L_{\text{loc}}^1(\mathbb{R}^3)$, with w even, and $\alpha \in \mathbb{R}$ be such that*

$$\begin{aligned} \mathbb{1}_{2 \times 2} \left(\sum_{j=1}^N (\alpha(-\Delta_j) - 2iA(x_j) \cdot \nabla_j + v(x_j)) + \sum_{1 \leq j < k \leq N} w(x_j - x_k) \right) \\ + \sum_{j=1}^N \sigma_j \cdot B(x_j) = 0, \end{aligned}$$

as an operator of $L_a^2(\mathbb{R}^{dN})$ (or of the bosonic counterpart). Then $\alpha = 0$, $A = 0$, $B = 0$, v and w are constant and verify $v + w(N-1)/2 = 0$.

Proof. We only provide a proof in the fermionic case, since the bosonic one follows from similar arguments. We choose a basis of the spin variable $(s_1, \dots, s_N)_{s_i \in \{\uparrow, \downarrow\}}$ in which the first element is $|\uparrow, \dots, \uparrow\rangle$ and the second one is $|\uparrow, \dots, \uparrow, \downarrow\rangle$. We consider a purely spatial antisymmetric function $\psi \in L_a^2(\mathbb{R}^{dN})$ and form the fermionic function $\Psi := \psi \otimes \sum_{s_i \in \{\uparrow, \downarrow\}} |s_1, \dots, s_N\rangle$, symmetric in spin and antisymmetric in space. We apply (2.22), seen as

a matrix in the previous spin basis, to our function, and we subtract the second component of the resulting vector from the first one, which yields

$$(B_z - iB_y)(x_N)\psi(x_1, \dots, x_N) = 0,$$

a.e. in \mathbb{R}^{dN} . Since this holds for any antisymmetric ψ , we deduce that $B_z = iB_y$, and since B is real, then $B_z = B_y = 0$. A similar argument leads to $B_x = 0$. We thus have

$$\sum_{j=1}^N (\alpha(-\Delta_j) - 2iA(x_j) \cdot \nabla_j + v(x_j)) + \sum_{1 \leq j < k \leq N} w(x_j - x_k) = 0 \quad (2.23)$$

on $L_a^2(\mathbb{R}^{dN})$. We choose a smooth localizing function χ with support in the ball $B_r \subset \mathbb{R}^d$ for some $r \in \mathbb{R}_+$, we take centers $y_1, \dots, y_N \in \mathbb{R}^3$ separated by distances larger than r , we form the orbitals $\phi_i(x) := (\chi e^{-a|\cdot|})(x - y_i)$ and the N -body wavefunction $\Phi := \wedge_{i=1}^N \phi_i$. We apply (2.23) to it, yielding

$$V\Phi + \sum_{i=1}^N \phi_1 \wedge \dots \wedge (-\alpha\Delta - 2iA \cdot \nabla) \phi_i \wedge \dots \wedge \phi_N = 0, \quad (2.24)$$

where $V := \sum_{j=1}^N v(x_j) + \sum_{1 \leq j < k \leq N} w(x_j - x_k)$. We compute

$$\begin{aligned} (-\alpha\Delta - 2iA \cdot \nabla) (\chi(x)e^{-a|x|}) &= \frac{e^{-a|x|}}{|x|} (-a^2\alpha|x|\chi \\ &\quad + 2a(\alpha(\chi + x \cdot \nabla\chi) + i\chi A \cdot x) - \alpha|x|\Delta\chi - 2i|x|A \cdot \nabla\chi). \end{aligned}$$

Finally we evaluate (2.24) in the neighborhood of one of the y_i 's, and as a polynomial in a , the resulting equation implies $\alpha = 0$, and then $A = 0$ a.e. in an open region, which can be extended to the whole space \mathbb{R}^d by moving the y_i 's. Hence we can also deduce that $V = 0$ a.e. in \mathbb{R}^{dN} , and we conclude by using Lemma 2.2.3. \square

We could have stated the theorem with the assumption $T_1, T_2 \in \mathbb{R}_+$. In this case, we should also assume that $v_1, v_2, w \in L_{\text{loc}}^q(\mathbb{R}^d)$ with $q > \max(2d/3, 2)$ in order to use the standard Hohenberg-Kohn theorem in the case $T_1 = T_2 = 0$. Indeed, if $T_1 = 0$ and $T_2 > 0$, the minimizer Γ_1 of the first functional is pure, but it minimizes \mathcal{E}_{v_2, T_2} and is in its variational minimization set. Consequently it is equal to the Gibbs state Γ_2 which is not pure. There is a contradiction and therefore this configuration is impossible, T_1 and T_2 are either both equal to zero, or both strictly positive. We emphasize the fact that when temperatures are strictly positive, the proof does not involve any unique continuation argument, and is thus much simpler than at zero temperature.

We showed that the knowledge of the ground state pair (ρ, S) contains the information of (v, T) . We conjecture now that the knowledge of ρ alone does not contain the information of (v, T) , i.e. that the map $(v, T) \mapsto \rho$, giving the density of the Gibbs state for the pair (v, T) , is not injective.

2.4.2 Lifting ill-posedness at positive temperature

We are going to see now that increasing the temperature generically removes the ill-posedness of Hohenberg-Kohn theorems. We begin to analyze Current DFT, for which there are counterexamples to a Hohenberg-Kohn theorem [9, 35]. We define the paramagnetic current of a wavefunction Ψ by

$$j_\Psi(x) := \text{Im} \sum_{(s_k)_{1 \leq k \leq N} \in \{\uparrow, \downarrow\}^N} \sum_{i=1}^N \int_{\mathbb{R}^{d(N-1)}} \overline{\Psi^{s_k}} \nabla_i \Psi^{s_k} dx_1 \cdots dx_{i-1} dx_{i+1} \cdots dx_N,$$

and its total current by $j_t := j + \rho A + \text{curl } m$, where the magnetization of a state is defined in (2.14). The Hamiltonian that we consider is the many-body Pauli operator

$$H^N(v, A, w) := \sum_{j=1}^N \left((\sigma_j \cdot (-i\nabla_j + A(x_j)))^2 + v(x_j) \right) + \sum_{1 \leq i < j \leq N} w(x_i - x_j),$$

which is $\mathbb{H}(v, A, w) := \bigoplus_{n=1}^{+\infty} \sum_{j=1}^n (\sigma_j \cdot (-i\nabla_j + A(x_j)))^2 + \mathbb{V} + \mathbb{W}$ in the grand canonical setting. In the case of canonical and grand canonical states, we can also define a current and a magnetization j_Γ, m_Γ by the decomposition of Γ into pure states. We choose the Coulomb gauge, and using fermionic statistics and the grand canonical ensemble, the kinetic energy of a state can be expressed by

$$\begin{aligned} \text{Tr} \left(\sum_{j=1}^N (\sigma_j \cdot (-i\nabla_j + A(x_j)))^2 \right) \Gamma \\ = \text{Tr}(-\Delta)\Gamma + \int A^2 \rho_\Gamma + \int A \cdot (2j_\Gamma + \text{curl } m_\Gamma). \end{aligned}$$

Theorem 2.4.3 (Hohenberg-Kohn for interacting Pauli systems at $T > 0$). *Let $T_1, T_2 > 0$, let $v_1, v_2 \in L_{\text{loc}}^{3/2}(\mathbb{R}^3)$, let $A_1, A_2 \in (L^3 + L^\infty)(\mathbb{R}^3)$, $(v_1)_-, (v_2)_-, w_1, w_2, |\text{curl } A_1|, |\text{curl } A_2| \in (L^{3/2} + L^\infty)(\mathbb{R}^3)$ be potentials such that w_1 and w_2 are even and such that the two grand canonical partition functions $\text{Tr} e^{-\mathbb{H}(v_j, A_j, w_j)/T_j}$ are finite. We denote by Γ_1, Γ_2 the grand canonical Gibbs states corresponding to the free energies in the Pauli model with temperature, and we assume that all the quantities involved in (2.25) are finite. If*

$$\begin{aligned} - (T_1 - T_2)(S_{\Gamma_1} - S_{\Gamma_2}) + \int_{\mathbb{R}^d} (v_1 - A_1^2 - v_2 + A_2^2)(\rho_{\Gamma_1} - \rho_{\Gamma_2}) \\ + \int_{\mathbb{R}^d} (A_1 - A_2) \cdot (2j_{t, \Gamma_1} - \text{curl } m_{\Gamma_1} - 2j_{t, \Gamma_2} + \text{curl } m_{\Gamma_2}) \\ + \int_{\mathbb{R}^{2d}} (w_1 - w_2)(x - y)(\rho_{\Gamma_1}^{(2)} - \rho_{\Gamma_2}^{(2)})(x, y) dx dy = 0, \quad (2.25) \end{aligned}$$

then there exists $c \in \mathbb{R}$ such that $T_1 = T_2$, $A_1 = A_2$, $w_1 = w_2 + c$, $v_1 = v_2 - c(N-1)/2$, $Z_1 = Z_2$ and $\Gamma_1 = \Gamma_2$. In the canonical setting, we deduce that $T_1 = T_2$, $A_1 = A_2$, $w_1 = w_2 + c$, $v_1 = v_2 + T_1 \ln \frac{Z_2}{Z_1} - c(N-1)/2$, and $\Gamma_1 = \Gamma_2$.

The proof follows the one of Theorem 2.4.1 and uses Lemma 2.4.2. The assumption (2.25) is fulfilled when

$$(\rho_{\Gamma_1}, j_{t,\Gamma_1}, m_{\Gamma_1}, S_{\Gamma_1}) = (\rho_{\Gamma_2}, j_{t,\Gamma_2}, m_{\Gamma_2}, S_{\Gamma_2})$$

for instance. This remedies to the ill-posedness of the problem at zero temperature. Following ideas of Ruggenthaler and Tellgren [21, 62, 69] (see also Chapter 1), another way to do so is by adding internal magnetic degrees of freedom.

The last theorem (without spin) holds for classical canonical and grand canonical systems, and the proof is the same. A similar statement with different interactions is present in Henderson [27]. In the classical canonical case, states are symmetric probability measures $\mu \in \mathcal{P}_s(\mathbb{R}^{dN} \times \mathbb{R}^{dN})$ on the phase space, and the current is

$$j_\mu(x) := N \int_{\mathbb{R}^{d(N-1)} \times \mathbb{R}^{dN}} p_1 \mu(x, p_1, x_2, p_2, x_3, p_3, \dots) dx_2 \dots dx_N dp_1 \dots dp_N.$$

Other internal variables can be defined similarly, and the assumption

$$\begin{aligned} & - (T_1 - T_2)(S_{\mu_1} - S_{\mu_2}) + \int_{\mathbb{R}^d} (v_1 + A_1^2 - v_2 - A_2^2) (\rho_{\mu_1} - \rho_{\mu_2}) \\ & \quad + 2 \int_{\mathbb{R}^d} (A_1 - A_2) \cdot (j_{\mu_1} - j_{\mu_2}) \\ & \quad + \int_{\mathbb{R}^d \times \mathbb{R}^d} (w_1 - w_2) (x - y) (\rho_{\mu_1}^{(2)} - \rho_{\mu_2}^{(2)})(x, y) dx dy = 0, \end{aligned}$$

has the same consequences as in the quantum counterpart. In particular, it is ensured that $(\rho^{(2)}, j, S)$ contains all the information of a classical system at equilibrium. Without magnetic fields and at fixed temperatures, $\rho^{(2)}$ alone contains all the information. It is nevertheless important that temperatures are strictly positive in the classical case, whereas they can vanish in the quantum case.

A similar version of the next theorem at fixed temperature in the grand canonical case was presented in [5]. It shows that at positive temperature, Matrix DFT is well-posed.

Theorem 2.4.4 (Hohenberg-Kohn for non-local potentials at $T > 0$). *Let $T_1, T_2 > 0$, let p be as in (2.21), let $v \in L_{\text{loc}}^p(\mathbb{R}^d)$ with $v_- \in (L^p + L^\infty)(\mathbb{R}^d)$ be a trapping potential, let $G_1, G_2 \in \mathcal{G}$ be such that $G_j \geq \epsilon \Delta - c_\epsilon$ for any $\epsilon > 0$, and such that $\text{Tr} e^{-(\mathbb{H}(v) + \oplus_{n=0}^{+\infty} \sum_{i=1}^n (G_j)_i) / T_j}$ are finite. We denote by*

Γ_1, Γ_2 the grand canonical Gibbs states corresponding to the free energies with temperature in this model, and we assume that $\int G_1 \gamma_{\Gamma_2}$ and $\int G_2 \gamma_{\Gamma_1}$ are finite. If

$$-(T_1 - T_2)(S_{\Gamma_1} - S_{\Gamma_2}) + \text{Tr}(G_1 - G_2)(\gamma_{\Gamma_1} - \gamma_{\Gamma_2}) = 0, \quad (2.26)$$

then $T_1 = T_2$, $G_1 = G_2$, $Z_1 = Z_2$ and $\Gamma_1 = \Gamma_2$. In the canonical setting, we deduce that $T_1 = T_2$, $G_1 = G_2 + T_1 \ln \frac{Z_2}{Z_1}$ and $\Gamma_1 = \Gamma_2$.

The proof follows the one of Theorem 2.4.1 and uses the following lemma.

Lemma 2.4.5. *Let G be a self-adjoint operator for which $G \geq \epsilon \Delta - c_\epsilon$ in the sense of forms in $L^2(B)$ for some ball $B \subset \mathbb{R}^d$, for any $\epsilon > 0$ and some $c_\epsilon \geq 0$. If*

$$\sum_{i=1}^N (-\alpha \Delta_i + G_i) = 0 \quad (2.27)$$

in $L^2_a(B^N)$ (or in the bosonic counterpart) for some $\alpha \in \mathbb{R}$, then $\alpha = 0$ and $G = 0$ on B .

Proof. We treat the fermionic case, since the bosonic one follows from similar arguments. Let $(\phi_i)_{i \in \mathbb{N}}$ be an orthonormal basis of $L^2(B)$. We apply (2.27) to $\wedge_{i=1}^N \phi_i$ and take the scalar product with this same vector, which gives

$$\sum_{i=1}^N \langle \phi_i, (-\alpha \Delta + G) \phi_i \rangle = 0. \quad (2.28)$$

The same procedure applied to $\wedge_{i=2}^{N+1} \phi_i$ yields $\sum_{i=2}^{N+1} \langle \phi_i, (-\alpha \Delta + G) \phi_i \rangle = 0$ and taking the difference between those equations, we get

$$\langle \phi_1, (-\alpha \Delta + G) \phi_1 \rangle = \langle \phi_{N+1}, (-\alpha \Delta + G) \phi_{N+1} \rangle.$$

Similarly, we have $\langle \phi_i, (-\alpha \Delta + G) \phi_i \rangle = \langle \phi_j, (-\alpha \Delta + G) \phi_j \rangle$ for any $i, j \in \mathbb{N}$, and using (2.28) again, we conclude that $\langle \phi_i, (-\alpha \Delta + G) \phi_i \rangle = 0$ for any $i \in \mathbb{N}$. By polarization, we deduce that $-\alpha \Delta + G = 0$ and we reduced the problem to the 1-particle case. With $\epsilon = \alpha/2$, we have $G = \alpha \Delta \geq \frac{\alpha}{2} - c_{\alpha/2}$, and thus $\frac{\alpha}{2}(-\Delta) \leq c_{\alpha/2}$, which implies $\alpha = 0$ and $G = 0$. \square

We refer to [22] for a review about Matrix DFT at positive temperature.

Appendix

Proof of Lemma 2.3.2

We consider the canonical spin basis $(|p_1, \dots, p_N\rangle)_{p_i \in \{\uparrow, \downarrow\}}$, which we are going to rotate. We define $B_\perp := B_x + iB_y$ and assume that $B_\perp(x_i) \neq 0$

for all $i \in \{1, \dots, N\}$, otherwise the corresponding one-particle operators are already diagonal. For one particle and $B \in \mathbb{R}^3$, we define the rotated orthonormal spin basis

$$|\rightarrow\rangle := \frac{(B_z + |B|)|\uparrow\rangle + B_\perp|\downarrow\rangle}{\sqrt{(B_z + |B|)^2 + |B_\perp|^2}}, \quad |\leftarrow\rangle := \frac{(B_z - |B|)|\uparrow\rangle + B_\perp|\downarrow\rangle}{\sqrt{(B_z - |B|)^2 + |B_\perp|^2}}.$$

The operator $B \cdot \sigma$ is then diagonal on this one-particle basis, $\sigma \cdot B |\rightarrow\rangle = |B| |\rightarrow\rangle$, $\sigma \cdot B |\leftarrow\rangle = -|B| |\leftarrow\rangle$. Now we work at a fixed (x_1, \dots, x_N) such that all $B(x_i)$ are finite. We define $B_{\rightarrow\uparrow} := B_z + |B|$, $B_{\rightarrow\downarrow} := B_\perp =: B_{\leftarrow\downarrow}$, $B_{\leftarrow\uparrow} := B_z - |B|$, and for N bodies we define similar rotations, that is for $(s_i)_{1 \leq i \leq N} \in \{\rightarrow, \leftarrow\}^N$, where $(-1)^\rightarrow := 1$ and $(-1)^\leftarrow := -1$,

$$|s_1, \dots, s_N\rangle := \frac{\sum_{(p_i)_{1 \leq i \leq N} \in \{\uparrow, \downarrow\}^N} \prod_{i=1}^N B_{s_i p_i}(x_i) |p_1, \dots, p_N\rangle}{\prod_{j=1}^N \sqrt{(B_z(x_j) + (-1)^{s_j} |B(x_j)|)^2 + |B_\perp(x_j)|^2}},$$

which is built from N consecutive one-body rotations. We finally compute

$$\left(\sum_{i=1}^N B(x_i) \cdot \sigma_i \right) |s_1, \dots, s_N\rangle = \left(\sum_{i=1}^N (-1)^{s_i} |B(x_i)| \right) |s_1, \dots, s_N\rangle. \quad \square$$

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Part II

Properties of the potential-to-density map

Our goal is to study the potential-to-density map. We first have to remark that its starting space is the set of binding potentials. In Chapter 3, we prove that this set is path-connected.

Then, in Chapter 4, we look at the subset of potentials for which the ground state is non-degenerate. We prove that on this set $v \mapsto \rho(v)$ is smooth and locally compact. We also show that its differential is compact. This allows us to deduce that the Kohn-Sham problem is ill-posed on a bounded set Ω , when restricted to the non-degenerate case.

Finally, we complete the picture by providing in Chapter 5 some aspects of linear degenerate perturbation theory. We show that the potential-to-ground state density map is singular on degenerate potentials.

Chapter 3

Path-connectedness

3.1 Statement

Let us recall [10] that

$$(L^p + L^\infty_\epsilon)(\mathbb{R}^d, \mathbb{R}) := \left\{ f \in (L^p + L^\infty)(\mathbb{R}^d, \mathbb{R}) \mid \forall \epsilon > 0, \exists g_\epsilon, h_\epsilon, f = g_\epsilon + h_\epsilon, \|h_\epsilon\|_{L^\infty} \leq \epsilon, g_\epsilon \in L^p \right\}.$$

We consider an open connected set $\Omega \subset \mathbb{R}^d$ with smooth boundary, in which the systems live. We consider an external potential $v \in (L^p + L^\infty)(\mathbb{R}^d, \mathbb{R})$, which does not have to be negligible at infinity, and an even positive interaction potential $w \in (L^p + L^\infty_\epsilon)(\mathbb{R}^d, \mathbb{R}_+)$. The exponent p can be taken to be $p > \max\left(\frac{2d}{3}, 2\right)$ in case we need to apply unique continuation for the many-body Schrödinger's operator [2], or it can be taken to be

$$\begin{cases} p = 1 & d = 1 \\ p > 1 & d = 2 \\ p = d/2 & d \geq 3, \end{cases} \quad (3.1)$$

otherwise. In any case, our space includes Coulomb-like singularities involved in the physical situation. We consider the N -particle Schrödinger operator

$$H^N(v) := \sum_{i=1}^N -\Delta_i + \sum_{1 \leq i < j \leq N} w(x_i - x_j) + \sum_{i=1}^N v(x_i), \quad (3.2)$$

acting on the space of antisymmetric spinless wavefunctions $L^2_a((\mathbb{R}^d)^N) := \wedge^N L^2(\mathbb{R}^d)$. Its Friedrichs extension has the quadratic form domain $H^1(\mathbb{R}^{dN})$. We denote by $\mathcal{E}_v(\Psi) := \langle \Psi, H^N(v)\Psi \rangle$ the energy functional, by $T(\Psi) := \int |\nabla \Psi|^2$ the kinetic energy and by

$$W(\Psi) := \frac{N(N-1)}{2} \int_{\mathbb{R}^{dN}} w(x_1 - x_2) |\Psi|^2(x_1, \dots, x_N) dx_1 \cdots dx_N$$

the interaction energy of a state Ψ . We denote by

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

the one-body density of a state and by

$$E^N(v) := \inf_{\substack{\Psi \in L^2_a(\mathbb{R}^{dN}) \\ \int |\Psi|^2 = 1}} \langle \Psi, H^N(v) \Psi \rangle$$

the ground energy of a potential v . We also denote by $\Sigma^N(v) := \inf \sigma_{\text{ess}}(H^N(v))$ the bottom of the essential spectrum of $H^N(v)$. Since we work under the condition that $0 \leq v \in L^p + L^\infty$, the HVZ theorem [4, 8, 14, 15] says that $E^{N-1}(v) = \Sigma^N(v)$ whenever $v \in L^p + L^\infty$.

Definitions

We now introduce the space of non-degenerate binding potentials

$$\mathcal{V}^N := \left\{ v \in (L^p + L^\infty)(\mathbb{R}^d) \mid E^N(v) < \Sigma^N(v), \right. \\ \left. \dim \text{Ker} \left(H^N(v) - E^N(v) \right) = 1 \right\},$$

the subspace of (possibly degenerate) binding potentials

$$\mathcal{V}_\partial^N := \left\{ v \in (L^p + L^\infty)(\mathbb{R}^d) \mid E^N(v) < \Sigma^N(v) \right\},$$

and the most general set of metastable binding potentials ¹

$$\mathcal{V}_{\text{meta}}^N := \left\{ v \in (L^p + L^\infty)(\mathbb{R}^d) \mid \dim \text{Ker} \left(H^N(v) - E^N(v) \right) \geq 1 \right\}$$

all endowed with the norm of $L^p + L^\infty$, recalled below in (3.3). They satisfy $\mathcal{V}^N \subset \mathcal{V}_\partial^N \subset \mathcal{V}_{\text{meta}}^N \subset L^p + L^\infty$, and we will not consider $\mathcal{V}_{\text{meta}}^N$ in this document.

Geometry

By perturbation theory [6, 10] (see also (iii) in Lemma 4.2.1 in Chapter 4), \mathcal{V}^N and \mathcal{V}_∂^N are open in $\mathcal{V} := L^p + L^\infty$. The manifold structure is then canonical and locally flat. The injections $\mathcal{V}^N \hookrightarrow \mathcal{V}$ and $\mathcal{V}_\partial^N \hookrightarrow \mathcal{V}$ make them smooth closed embedded manifolds of \mathcal{V} , and $T_v \mathcal{V}^N = \mathcal{V}$. We now show that the set of trapping electric potentials is path-connected.

¹Elements of $\mathcal{V}_{\text{meta}}^N \setminus \mathcal{V}_\partial^N$ have $E^N(v) = \Sigma^N(v)$, here is an example. Take $N = 1$, $d \geq 5$, $\Psi(x) = c(1 + x^2)^{1-\frac{d}{2}}$ where c normalizes Ψ . We have $-\Delta \Psi + v \Psi = 0$ with $v(x) = -d(d-2)(1+x^2)^{-2} \in L^{d/2} \cap L^\infty$. We know that Ψ is the ground state since it is strictly positive everywhere. Hence $E^N(v) = \Sigma^N(v) = 0$.

Theorem 3.1.1 (Path-connectedness of the space of binding potentials). *Take p as in (3.1), and take $w \in L^p + L^\infty_\epsilon$ with $w \geq 0$. Then $\cap_{n=1}^N \mathcal{V}_\partial^n$ is path-connected.*

Remark 3.1.2. *For instance we can connect all the elements to a well $-c_{d,N} \mathbb{1}_{B_1}$, where the constant $c_{d,N} > 0$ is chosen large enough so that $-c_{d,N} \mathbb{1}_{B_1}$ belongs to $\cap_{n=1}^N \mathcal{V}_\partial^n$. The assumption on w is present because we use the HVZ theorem. We conjecture that $\mathcal{V}_\partial^{N+1} \subset \mathcal{V}_\partial^N$ for any $N \geq 1$ and any interaction $w \geq 0$, which would imply $\cap_{n=1}^N \mathcal{V}_\partial^n = \mathcal{V}_\partial^N$.*

Remark 3.1.3. *If in the definition of \mathcal{V}_∂^N , we replace $L^p + L^\infty$ by $L^p + L^\infty_\epsilon$, then $\cap_{n=1}^N \mathcal{V}_\partial^n$ is path-connected as well, as can be seen from our proof below.*

Remark 3.1.4. *As proved in [9, Thm 3.11, Thm 3.12, Thm 3.13] the set of binding potentials $\mathcal{V}_\partial^N \cap L^p$ is dense in L^p . We can see it by approaching $v \in L^p$ with a sequence $v_n = v - \sum_{i=1}^N L_n \mathbb{1}_{B_{r_n}(y_i^n)}$ where L_n and r_n are chosen such that $v_n \in \mathcal{V}_\partial^N$, $0 \leq L_n \rightarrow 0$, $r_n \rightarrow +\infty$, $y_i^n \in \mathbb{R}^d$, $|y_i^n| \rightarrow +\infty$, $|y_i^n - y_j^n| \rightarrow +\infty$. This result also holds in $L^p + L^\infty_\epsilon$ by density of L^p in this space.*

Remark 3.1.5. *Theorem 3.1.1 raises the question of path-connectedness of \mathcal{V}^N . Adiabatic processes are deformations of the potential when the initial system is in its ground state, slowly enough so that the system remains in the ground state thanks to the adiabatic theorem [5, 13]. The time scale of change in v needs to be small with respect to the energy difference between the first two levels, hence a necessary and sufficient condition for this process to be possible is to remain in \mathcal{V}^N during the deformation, without crossing the degenerate potentials $\mathcal{V}_\partial^N \setminus \mathcal{V}^N$, otherwise excited states can be populated. By analogy with other areas of quantum physics we say that two potentials $v, u \in \mathcal{V}^N$ are adiabatically equivalent if they are path-connected in \mathcal{V}^N . This defines equivalence classes in \mathcal{V}^N and it would be interesting to know whether this is only one class. We remark that in classical mechanics this is the case. Graphically, degenerate potentials $\mathcal{V}_\partial^N \setminus \mathcal{V}^N$ constitute a “web” in the space of binding potentials.*

Remark 3.1.6. *We could also define an “excited” adiabatic equivalence, that is when we transform the potentials infinitely slowly, the occupied states can populate the excited levels, but they have to remain bound. More precisely, for $k \in \mathbb{N}$, we define the set of potentials $v \in L^p + L^\infty$ such that $E^{N,(k)}(v) < \Sigma^N(v)$, where $E^{N,(k)}(v)$ is the energy of the k^{th} excited level. By a slight adaptation of the proof of Theorem 3.1.1, this set is path-connected.*

We will explain in the proof that to any path connecting two given binding potentials, there is a corresponding piecewise real analytic path $t \mapsto \Psi(t)$ of ground states connecting two initial ground states. Hence there also exists a corresponding path of densities $t \mapsto \rho(t)$.

Corollary 3.1.7. *The set of v -representable densities*

$$\left\{ \rho_\Psi \in L^1(\mathbb{R}^d, \mathbb{R}_+) \mid \Psi \text{ is the ground state of } H^N(v) \text{ for some } v \in \cap_{n=1}^N \mathcal{V}_\partial^n \right\}$$

is path-connected.

3.2 Proof of Theorem 3.1.1

We recall that the natural norm of $L^p + L^\infty$ is

$$\|v\|_{L^p+L^\infty} = \min_{\substack{f \in L^p, g \in L^\infty \\ f+g=v}} (\|f\|_{L^p} + \|g\|_{L^\infty}). \quad (3.3)$$

The set $L^p + L^\infty$ is a closed subspace, it is the closure of L^p in $L^p + L^\infty$.

We now prepare for the proof of Theorem 3.1.1. The following lemma will allow us to modify potentials while remaining bound.

Lemma 3.2.1. *If $v \in \mathcal{V}_\partial^N$, $0 \leq u \in L^p + L^\infty$ and*

$$\inf_{\substack{\Psi \in \text{Ker}(H^N(v) - E^N(v)) \\ \int |\Psi|^2 = 1}} \int u \rho_\Psi < \Sigma^N(v) - E^N(v), \quad (3.4)$$

then $E^N(v + u) < \Sigma^N(v + u)$.

Proof. By the min-max theorem, $\Sigma^N(v) \leq \Sigma^N(v + u)$. Let Ψ_v be one ground state minimizing the left hand side of (3.4), which is a minimization problem in a compact set since $\dim \text{Ker}(H^N(v) - E^N(v)) < +\infty$. We compute

$$E^N(v + u) \leq \mathcal{E}_{v+u}(\Psi_v) = E^N(v) + \int u \rho_{\Psi_v} < \Sigma^N(v) \leq \Sigma^N(v + u),$$

and consequently $v + u \in \mathcal{V}_\partial^N$. \square

Proof of Theorem 3.1.1. We split the proof into several steps. Consider a binding potential $v \in \cap_{n=1}^N \mathcal{V}_\partial^n$. We will deform it continuously into a hole of type $-c\mathbb{1}_B$, such that it remains in $\cap_{n=1}^N \mathcal{V}_\partial^n$ during the deformation.

Step 1: connection to a negative bounded potential with compact support.

We decompose $v = v_p + v_\infty$ where $v_p \in L^p$ and $v_\infty \in L^\infty$. We start by transforming v_p to $v_p \mathbb{1}_{|v_p| \leq M}$, and when M is large enough, this operation changes infinitesimally $E^n(v)$ and $\Sigma^n(v)$ by classical perturbation theorems [6, 10], so $\Sigma^n - E^n$ remains strictly positive during the modification. More precisely, we can take

$$v(t) := (1-t)v + t \left(v_p \mathbb{1}_{|v_p| \leq M} + v_\infty \right) = v_\infty + v_p \mathbb{1}_{|v_p| \leq M} + (1-t)v_p \mathbb{1}_{|v_p| > M}$$

which links v to $v_1 := v_p \mathbb{1}_{|v_p| \leq M} + v_\infty \in L^\infty$ by a line on which $v(t) \in \cap_{n=1}^N \mathcal{V}_\partial^n$ for all $t \in [0, 1]$.

Let us denote by $\Psi_{v_1}^n$ a ground state of v_1 , for all $n \in \{1, \dots, N\}$. We take some $L \geq \|v_1\|_{L^\infty}$, and consider the path of positive potentials $u(t) = t(L - v_1) \mathbb{1}_{\mathbb{R}^d \setminus B_r} \geq 0$ for $t \in [0, 1]$. We know that $\Psi_{v_1}^n$ decays exponentially at infinity [1, 12], so we can choose $r = r(L, v_1, w, N)$ large enough such that

$$\sup_{t \in [0, 1]} \int u(t) \rho_{\Psi_{v_1}^n} \leq (L + \|v_1\|_{L^\infty}) \int_{\mathbb{R}^d \setminus B_r} \rho_{\Psi_{v_1}^n} < \Sigma^n(v_1) - E^n(v_1),$$

for any $n \in \{1, \dots, N\}$. Hence by Lemma 3.2.1, $v_1 + u(t) \in \cap_{n=1}^N \mathcal{V}_\partial^n$ for any $t \in [0, 1]$, and we redefine

$$v_2 := v_1 + u(1) = L \mathbb{1}_{\mathbb{R}^d \setminus B_r} + v_1 \mathbb{1}_{B_r},$$

for the following. We then use that $\Sigma^n(v_2) - E^n(v_2)$ is invariant under the gauge transformation $v_2 \rightarrow v_2 + c$ so we move the potential by adding $-tL$, $t \in [0, 1]$. We “filled v_2 up to the roof” and obtain

$$v_3 := v_2 - L = (v_1 - L) \mathbb{1}_{B_r} \leq 0.$$

We have thus linked our potential to a negative potential with compact support.

Step 2: build the wall. Next we raise some big wall again, further away. We want to apply Lemma 3.2.1 to $u(t) = t\ell \mathbb{1}_{\mathbb{R}^d \setminus B_R}$. We choose $R \geq \max(r, \text{diam supp } v_3)$ and $\ell \geq 1$ so that

$$\ell \int_{\mathbb{R}^d \setminus B_R} \rho_{\Psi_{v_3}^n} \leq \Sigma^n(v_3) - E^n(v_3) \quad (3.5)$$

where $\Psi_{v_3}^n$ is one of the ground states of v_3 . We know that there exist $\alpha, \beta > 0$ such that $\int_{\mathbb{R}^d \setminus B_R} \rho_{\Psi_{v_3}^n} \leq \alpha e^{-\beta R}$ [1, 3, 12], hence we link ℓ and R by taking

$$R = c(1 + \ln \ell), \quad (3.6)$$

with c large enough so that (3.5) holds. By Lemma 3.2.1 we deduce that $t\ell \mathbb{1}_{\mathbb{R}^d \setminus B_R} + v_3 \in \cap_{n=1}^N \mathcal{V}_\partial^n$ for any $t \in [0, 1]$. In particular, $\ell \mathbb{1}_{\mathbb{R}^d \setminus B_R} + v_3 \in \cap_{n=1}^N \mathcal{V}_\partial^n$. Shifting this last potential by the constant $-t\ell$ for $t \in [0, 1]$, we also have

$$\ell(1 - t) \mathbb{1}_{\mathbb{R}^d \setminus B_R} + (v_3 - t\ell) \mathbb{1}_{B_R} \in \cap_{n=1}^N \mathcal{V}_\partial^n.$$

In particular, $(v_3 - \ell) \mathbb{1}_{B_R} \in \cap_{n=1}^N \mathcal{V}_\partial^n$. We can hence choose ℓ as large as we want, and $R(\ell)$ will also be large.

Step 3: seal the hole. Next we define $V_{\ell,R} := (v_3 - \ell) \mathbf{1}_{B_R}$, for any $\ell \geq 1$ and $R = R(\ell)$ linked by (3.6). By the HVZ theorem [4, 14, 15] used in the form of [8, Theorem 3.1], we have $\Sigma^n(V_{\ell,R}) = E^{n-1}(V_{\ell,R})$ for any $n \geq 1$, $\ell \geq 0$ (with the convention $E^0 := 0$). We will misuse notations for $\Psi^n(V_{\ell,R})$ and $\Psi^n(v_3)$ because they can be degenerate, but by [11, Theorem 1.4.4, Corollary 1.4.5] and by working with $\ell \geq \ell_0$ with ℓ_0 large enough, we can take branches of associated ground states.

Take $a > 0$ fixed and let us denote by $(\varphi_i)_{1 \leq i \leq N}$, $\varphi_i \in H^1(B_a, \mathbb{C})$ an orthonormal family of functions. For $R \geq a$ and for any $n \in \{1, \dots, N\}$ we have

$$-\ell n \leq E^n(-\ell \mathbf{1}_{B_R}) \leq \mathcal{E}_0(\wedge_{i=1}^n \varphi_i) - \ell n,$$

and we deduce that $E^n(-\ell \mathbf{1}_{B_R}) = -\ell n + O(1)$ when $\ell \rightarrow +\infty$. Since $\|v_3\|_{L^\infty} \leq M$ by the first step, then

$$\begin{aligned} E^n(V_{\ell,R}) - \Sigma^n(V_{\ell,R}) &= E^n(V_{\ell,R}) - E^{n-1}(V_{\ell,R}) \\ &\leq E^n(-\ell \mathbf{1}_{B_R}) - E^{n-1}(-(\ell + \|v_3\|_{L^\infty}) \mathbf{1}_{B_R}) \\ &\leq \mathcal{E}_0(\wedge_{i=1}^n \varphi_i) - \ell n + (\ell + \|v_3\|_{L^\infty})(n-1) \\ &\leq -\ell + c_{M,w,N}, \end{aligned}$$

where $c_{M,w,N}$ does not depend on ℓ or on R . We thus showed that

$$\max_{n \in \{1, \dots, N\}} (E^n(V_{\ell,R}) - \Sigma^n(V_{\ell,R})) \rightarrow -\infty$$

when $\ell \rightarrow +\infty$. We take ℓ large enough so that

$$\int v_3 \rho_{\Psi^n(V_{\ell,R})} \leq MN < \ell - c_{M,w,N} < \Sigma^n(V_{\ell,R}) - E^n(V_{\ell,R}), \quad (3.7)$$

for any $n \in \{1, \dots, N\}$.

Then again applying Lemma 3.2.1 to $u(t) = -tv_3 \geq 0$, and using (3.7), we have $V_{\ell,R} - tv_3 \in \cap_{n=1}^N \mathcal{V}_\partial^n$ for any $t \in [0, 1]$. In particular, $V_{\ell,R} - v_3 = -\ell \mathbf{1}_{B_R} \in \cap_{n=1}^N \mathcal{V}_\partial^n$.

Step 4: connect any two potentials. We showed how to connect an initial binding potential v with one well $-\ell \mathbf{1}_{B_R}$. To connect v with an other binding potential u , we can just connect both of them to a same well $-\ell' \mathbf{1}_{B_{R'}}$, by taking ℓ' and R' adapted for the two. \square

Proof of Corollary 3.1.7. We show here how to find a continuous path of ground states which links any initial and final ground states corresponding to the path of potentials in the previous proof. We follow an argument used in the proof of [7, Theorem 4]. We take a ground state Ψ_0 of the initial potential $v = v(0)$ and a ground state Ψ_1 of the final potential well

$-c\mathbf{1}_{B_R} = v(1)$. We consider the previous path of potentials $t \in [0, 1] \mapsto v(t)$, which is piecewise linear.

Let us denote by $(\varphi_i(t))_{i \in D(t)}$ an orthonormal basis of $\text{Ker}(H^N(v) - E^N(v))$. By analytic perturbation theory [10, Theorem XII.13], at each point, we can choose this family to be analytic on the left and on the right, with possibly different limits. There is only a finite number of jumps. Indeed, the essential spectrum is strictly separated from $E^N(v(t))$, uniformly in $t \in [0, 1]$, thus only a finite number of eigenfunctions are involved. So if the left and right limits are different an infinite number of times, this is because two eigenfunctions $\phi_j(t)$ and $\phi_\ell(t)$ cross an infinite number of times at the ground state energy level. Since they are analytic, their energies must be equal and hence their energies *a posteriori* do not cross.

By the above argument, we have $k \in \mathbb{N}$ and $t_0, \dots, t_k \in [0, 1]$ such that $(\varphi_i(t))_{i \in D(t)}$ is piecewise analytic on $[t_i, t_{i+1}]$. On $]t_i, t_{i+1}[$, we choose a ground eigenfunction path $\Psi(t) \in \text{Ran}(\varphi_i(t))_{i \in D(t)}$. When there is a crossing of eigenvalues at $t_i \in [0, 1]$, by analyticity of the eigenfunctions, there are definite limits $(\varphi_i(t_i^-))_{i \in D(t_i^-)}$ and $(\varphi_i(t_i^+))_{i \in D(t_i^+)}$ on the left and on the right of t_i . Let us denote by $\Psi(t_0^-)$ and $\Psi(t_0^+)$ the ground state limits on the left and on the right. At the interface, the ground eigenspace of $v(t_0)$ is $\text{Ran}(\varphi_i(t_i^-))_{i \in D(t_i^-)} + \text{Ran}(\varphi_i(t_i^+))_{i \in D(t_i^+)}$. The set of normalized ground eigenstates is the unit sphere of this vector space, and we can add a path of ground eigenfunctions staying on this sphere to connect $\Psi(t_i^-)$ and $\Psi(t_i^+)$. \square

We conjecture that $\mathcal{V}^{N+1} \subset \mathcal{V}^N$. This is striking that such an intuitive fact is not direct to show. We also remark that the convexity of $N \mapsto E^N(v)$ would imply it. A counterexample to the convexity of $N \mapsto E^N(v)$ is given in a remark after [9, Theorem 4.1] when the interaction w is a soft core. But in this case $\mathcal{V}_\delta^{N+1} \subset \mathcal{V}_\delta^N$ still holds, so we conjecture that $\mathcal{V}^{N+1} \subset \mathcal{V}^N$ holds for any interaction $w \geq 0$.

It also seems natural that if $w = |\cdot|^{-1}$, $v, u \in \mathcal{V}$, $v \leq u$ and $u \in \mathcal{V}^N$, then $v \in \mathcal{V}^N$. We hence conjecture that $v \mapsto E^{N+1}(v) - E^N(v)$ is increasing on $\mathcal{V}^N \cap \mathcal{V}^{N+1}$ for the Coulomb interaction.

Chapter 4

Smoothness of $v \mapsto \rho(v)$, compact differential

In this chapter, we show that on the set of non-degenerate potentials, the potential-to-ground state density map is smooth, locally weak-strong continuous and has a compact differential. The first section presents the results and the following ones contain the proofs. We recall that the set of non-degenerate potentials is

$$\mathcal{V}^N := \left\{ v \in \mathcal{V} \mid E^N(v) < \Sigma^N(v), \dim \text{Ker} \left(H^N(v) - E^N(v) \right) = 1 \right\}, \quad (4.1)$$

where $\mathcal{V} = L^p + L^\infty$ or $\mathcal{V} = L^p + L^\infty_\epsilon$ depending on the situation.

4.1 Statements

The main purpose of this chapter is to investigate properties of the map $v \mapsto \rho(v)$. The interaction and potentials are in the space $L^p + L^\infty$, where we will consider exponents

$$\begin{cases} p = 1 & \text{for } d = 1 \\ p > 1 & \text{for } d = 2 \\ p = d/2 & \text{for } d \geq 3, \end{cases} \quad (4.2)$$

if we work in the sense of quadratic forms, or $p > \max(2d/3, 2)$ when we need to use the unique continuation property (see Chapter 1 and [8]). We take a bounded or unbounded domain $\Omega \subset \mathbb{R}^d$ with Lipschitz boundary. We define the potential-to-ground state density map

$$\rho : \begin{array}{ll} \mathcal{V}^N & \longrightarrow W^{1,1}(\Omega, \mathbb{R}_+) \cap \{f \cdot = N\} \\ v & \longmapsto \rho(v) := \rho_{\Psi(v)}, \end{array}$$

where $\Psi(v)$ is the unique ground state of $H^N(v)$ (up to a phase factor). The space $W^{k,1}(\Omega) \cap \{\int_\Omega \cdot = N\}$ is a closed embedded submanifold of $W^{k,1}(\Omega)$,

hence it is a smooth manifold. The main property of $v \mapsto \rho(v)$, lying at the heart of DFT, is its injectivity, this is the Hohenberg-Kohn theorem proved in Chapter 1 and in [8, 15, 21], when $p > \max(2d/3, 2)$. The next result provides some other properties.

Theorem 4.1.1 (Properties of ρ). *Take $\mathcal{V} = L^p + L^\infty$ with p as in (4.2), and $w \in L^p + L^\infty$.*

• (i - Smoothness). *The map ρ is C^∞ from \mathcal{V}^N to $W^{1,1} \cap \{\int \cdot = N\}$. It is injective when $p > \max(2d/3, 2)$.*

• (ii - Compactness of the differential). *Its differential, evaluated at some $v \in \mathcal{V}^N$, is given by*

$$(\mathrm{d}_v \rho) u = -2N \int_{\mathbb{R}^{d(N-1)}} \mathrm{d}x_2 \cdots \mathrm{d}x_N \\ \overline{\Psi(v)} (H^N(v) - E^N(v))_{\perp}^{-1} (1 - |\Psi(v)\rangle \langle \Psi(v)|) \left(\sum_{i=1}^N u(x_i) \right) \Psi(v).$$

For all $v \in \mathcal{V}^N$, $\mathrm{d}_v \rho$ is compact from $L^p + L^\infty$ to $W^{1,1}$, not surjective, and moreover,

$$\|(\mathrm{d}_v \rho) u\|_{W^{1,1}}^2 \leq c_v \|u\|_{L^p + L^\infty} \int |u| \rho(v).$$

The differential $\mathrm{d}_v \rho$ is injective when $p > \max(2d/3, 2)$.

• (iii - Local weak-strong continuity). *Let p be as in (4.2), with $p > d/2$ when $d \geq 3$, $w \in L^p + L^\infty$, $w \geq 0$ and $\mathcal{V} = L^p + L^\infty$ in the definition (4.1) of \mathcal{V}^N . Let $\Lambda \subset \Omega$ be a bounded open subset of Ω . Consider that $v \in \mathcal{V}^N$, $v_n \rightharpoonup v$ weakly and $v_n \mathbf{1}_{\Omega \setminus \Lambda} \rightarrow v \mathbf{1}_{\Omega \setminus \Lambda}$ strongly in $L^p + L^\infty$. Then $E^N(v_n) \rightarrow E^N(v)$, $v_n \in \mathcal{V}^N$ for n large enough, and $\sqrt{\rho(v_n)} \rightarrow \sqrt{\rho(v)}$ strongly in $H^1(\Omega)$.*

The regularity properties of ρ enable us to deduce a Hellmann-Feynman formula [5] in its full generality.

Corollary 4.1.2 (Hellmann-Feynman). *Let p be as in (4.2), and choose $\mathcal{V} = L^p + L^\infty$. The energy $v \mapsto E^N(v)$ is Lipschitz continuous, concave and weakly upper semi-continuous on $L^p + L^\infty$, C^∞ on \mathcal{V}^N . For any $v \in \mathcal{V}^N$, $u \in L^p + L^\infty$, its differential is*

$$(\mathrm{d}_v E) u = \int_{\Omega} u \rho(v).$$

When $p > \max(2d/3, 2)$, $v \mapsto E^N(v)$ is strictly concave and strictly increasing on \mathcal{V}_{∂}^N .

The previous expression can be formally written $(d_v E)^* = \rho(v)$, where $*$ denotes the dual representation at stake in Riesz' theorem, and this corresponds to the notation $\frac{\delta E}{\delta u(x)}|_v$ used in the physics literature.

Since $v \mapsto \Psi(v)$ is locally weak-strong continuous similarly to (iii) in Theorem 4.1.1, then for Ω bounded Ψ^{-1} is discontinuous as we will see in Corollary 4.1.4. But we can still prove a weak inverse continuity property.

Proposition 4.1.3 (Weak inverse continuity of Ψ). *Let $p > \max(2d/3, 2)$. Let $v_n \in \mathcal{V}^N$ be a sequence of potentials such that $v_n - E^N(v_n)/N$ is bounded in $L^p + L^\infty$, and such that $\Psi(v_n) \rightarrow \Psi(v)$ strongly in $H^2(\mathbb{R}^{dN})$, for some $v \in \mathcal{V}^N$. Then $\int_\Omega (v_n - v)^2 \rho_{\Psi(v)}$ and $v_n \rightarrow v$ a.e. in Ω , up to a constant and a subsequence.*

Consequences for the Kohn-Sham problem

In 1965, Kohn and Sham postulated the existence of effective one-body potentials which would remove the electronic interaction while keeping the same ground state density [17], by adding a one-body potential. The resulting non-interacting problem $\sum_{i=1}^N -\Delta_i + v_{\text{ks}}(x_i)$ is then much easier to handle than $H^N(v)$ since it has no interaction. By the Hohenberg-Kohn theorem, the inverse map ρ^{-1} exists on its range. Let us denote by $\rho_{w=0}$ the map ρ for which $w = 0$, then $\rho_{w=0}(\mathcal{V}_{\partial, w=0}^N)$ is the set of non-interacting v -representable densities. Considering elements

$$v \in \rho^{-1} \left(\rho(\mathcal{V}^N) \cap \rho_{w=0}(\mathcal{V}_{w=0}^N) \right) = \mathcal{V}^N \cap \rho^{-1} \circ \rho_{w=0} \left(\mathcal{V}_{w=0}^N \right),$$

(which set is possibly empty), the Kohn-Sham potential is defined as

$$v_{\text{ks}}(v) := \rho_{w=0}^{-1} \circ \rho(v).$$

In other words we have $\rho(v) = \rho_{w=0}(v_{\text{ks}}(v))$. Knowing $\rho(\mathcal{V}^N) \cap \rho_{w=0}(\mathcal{V}_{w=0}^N)$, as raised by Lieb in [21, Question 8], is thus an important open problem. The direct problem ρ is well-posed in the standard sense [3, 9, 10] by injectivity and regularity, and the Kohn-Sham problem is its corresponding inverse problem.

The linearization of this inverse problem is ill-posed because ρ has a compact differential by Theorem 4.1.1, which indicates the problematic nature of the existence of Kohn-Sham potentials. In bounded domains, the Kohn-Sham problem is ill-posed in the sense of Hadamard [13, Definition p8], because ρ^{-1} is discontinuous.

Corollary 4.1.4 (The set of v -representable densities is very small). *Let p be as in (4.2), with $p > d/2$ when $d \geq 3$. When the system lives in a bounded open connected set $\Omega \subset \mathbb{R}^d$, then $v \mapsto \rho(v)$ is compact, its inverse ρ^{-1} is discontinuous, and $\rho(\mathcal{V}^N)$ is a countable union of compact sets. In particular, $\rho(\mathcal{V}^N)$ has empty interior in $W^{1,1} \cap \{f \cdot = N\}$.*

By Corollary 4.1.4, $\rho_{w=0}(\mathcal{V}_{w=0}^N) \cap \rho(\mathcal{V}^N)$ is included in a countable union of compact sets, hence it is meagre in the sense of Baire. The Kohn-Sham potential thus seems to be defined on a sparse set, possibly empty, under our conditions on p . The situation cannot be much better when Ω is unbounded.

The challenge raised by the Kohn-Sham problem is to find relevant approximations of this effective potential. Such one-body effective potentials methods are very common, successful and versatile in many areas of physics. The mean-field approximation consists in removing the interaction operator and replacing v by $v + w * \rho(v)$, the rest of the expansion is called the exchange-correlation potential

$$v_{\text{xc}}(v) := v_{\text{ks}}(v) - v - w * \rho(v). \quad (4.3)$$

If it exists, the Kohn-Sham potential is unique by the Hohenberg-Kohn theorem, when $p > \max(2, 2d/3)$. The self-consistent field (SCF) equations are two equivalent fixed-point relations fulfilled by (resp.) potentials in $\mathcal{V}_{w=0}^N$ and densities in $\rho_{w=0}(\mathcal{V}_{w=0}^N)$,

$$v = \rho_{w=0}^{-1}(x \mapsto \mathbb{1}_{-\Delta+v < \epsilon_{\text{F}}}(x, x)), \quad \chi = x \mapsto \mathbb{1}_{-\Delta+\rho_{w=0}^{-1}(\chi) < \epsilon_{\text{F}}}(x, x),$$

where the Fermi level $\epsilon_{\text{F}} \in \mathbb{R}$ is such that only the first N orbitals are taken.

The rest of the chapter is devoted to the proofs of Theorem 4.1.1, Proposition 4.1.3 and Corollaries 4.1.2 and 4.1.4.

4.2 Proofs: basic inequalities on potentials

We recall here in Lemma 4.2.1 several well-known facts about potentials. In this chapter, the $L^2(\mathbb{R}^n) \rightarrow L^2(\mathbb{R}^n)$ operator norm will be denoted by $\|\cdot\|$. For simplicity, we will also use the notations

$$\sum_i v_i := \sum_{i=1}^N v(x_i), \quad \sum_{ij} w_{ij} := \sum_{1 \leq i < j \leq N} w(x_i - x_j).$$

Lemma 4.2.1. *Take $v, w \in (L^p + L^\infty)(\mathbb{R}^d)$.*

(i) *Taking p as in (4.2), we have*

$$\begin{aligned} & \left\| (-\Delta_{\mathbb{R}^{dN}} + 1)^{-\frac{1}{2}} (\sum_i v_i) (-\Delta_{\mathbb{R}^{dN}} + 1)^{-\frac{1}{2}} \right\| \\ & \leq N \left\| (-\Delta_{\mathbb{R}^d} + 1)^{-\frac{1}{2}} v (-\Delta_{\mathbb{R}^d} + 1)^{-\frac{1}{2}} \right\| \\ & \leq c_{d,p} N \|v\|_{L^p + L^\infty}. \end{aligned} \quad (4.4)$$

(ii) *Let $\mathcal{C} \subset \mathbb{C}$, be a contour in the complex plane which is such that $\text{dist}(z, \sigma(H^N(v))) \geq \eta > 0$ uniformly in $z \in \mathcal{C}$. Let p be as in (4.2), then the operators*

$$(-\Delta + 1)^{-\frac{1}{2}} (H^N - z) (-\Delta + 1)^{-\frac{1}{2}}, \quad (-\Delta + 1)^{\frac{1}{2}} (H^N - z)^{-1} (-\Delta + 1)^{\frac{1}{2}}$$

are uniformly bounded in $z \in \mathcal{C}$.

(iii) Let $v \in \mathcal{V}^N$, and p as in (4.2). For $u \in L^p + L^\infty$ such that $\|u\|_{L^p + L^\infty}$ is small enough, we have $v + u \in \mathcal{V}^N$.

Proof.

(i) • If p is as in (4.2), we have

$$\begin{aligned} & \left\| (-\Delta_{\mathbb{R}^{dN}} + 1)^{-\frac{1}{2}} (\sum_i v_i) (-\Delta_{\mathbb{R}^{dN}} + 1)^{-\frac{1}{2}} \right\| \\ & \leq \sum_{i=1}^N \left\| (-\Delta_{\mathbb{R}^{dN}} + 1)^{-\frac{1}{2}} v_i (-\Delta_{\mathbb{R}^{dN}} + 1)^{-\frac{1}{2}} \right\| \\ & \leq N \left\| (-\Delta_{\mathbb{R}^d} + 1)^{-\frac{1}{2}} v (-\Delta_{\mathbb{R}^d} + 1)^{-\frac{1}{2}} \right\|, \end{aligned}$$

where we used that $\left\| (-\Delta_i)^{\frac{1}{2}} (-\Delta_{\mathbb{R}^{dN}} + 1)^{-\frac{1}{2}} \right\| = 1$.

• Let us write $v = v_p + v_\infty$. We have

$$\begin{aligned} & \left\| (-\Delta + 1)^{-\frac{1}{2}} v (-\Delta + 1)^{-\frac{1}{2}} \right\| \\ & \leq \left\| (-\Delta + 1)^{-\frac{1}{2}} v_p (-\Delta + 1)^{-\frac{1}{2}} \right\| + \left\| (-\Delta + 1)^{-\frac{1}{2}} v_\infty (-\Delta + 1)^{-\frac{1}{2}} \right\| \\ & \leq \left\| (-\Delta + 1)^{-\frac{1}{2}} v_p (-\Delta + 1)^{-\frac{1}{2}} \right\| + \|v_\infty\|_{L^\infty} \\ & \leq \left\| \sqrt{|v_p|} (-\Delta + 1)^{-\frac{1}{2}} \right\|^2 + \|v_\infty\|_{L^\infty}. \end{aligned} \tag{4.5}$$

In the last inequality, we used that

$$(-\Delta + 1)^{-\frac{1}{2}} v_p (-\Delta + 1)^{-\frac{1}{2}} = (-\Delta + 1)^{-\frac{1}{2}} \sqrt{|v_p|} \operatorname{sgn}(v_p) \sqrt{|v_p|} (-\Delta + 1)^{-\frac{1}{2}},$$

where $\operatorname{sgn}(v)$ is equal to 1 if $v > 0$, -1 if $v < 0$ and 0 if $v = 0$, it verifies $\|\operatorname{sgn}(v)\| \leq 1$, hence

$$\left\| (-\Delta + 1)^{-\frac{1}{2}} v_p (-\Delta + 1)^{-\frac{1}{2}} \right\| \leq \left\| \sqrt{|v_p|} (-\Delta + 1)^{-\frac{1}{2}} \right\|^2.$$

As for the first term in (4.5), for $d \geq 3$, with $p = d/2$ we have

$$\left\| \sqrt{|v_p|} (-\Delta + 1)^{-\frac{1}{2}} \right\| \leq \left\| \sqrt{|v_p|} (-\Delta)^{-\frac{1}{2}} \right\| \leq c_d \left\| \sqrt{|v_p|} \right\|_{L^{2p}} = c_d \sqrt{\|v_p\|_{L^p}},$$

where we used the Hardy-Littlewood-Sobolev inequality [22, Theorem 4.3] in the last inequality. For $d \in \{1, 2\}$, we can use the Kato-Seiler-Simon inequality [29, Theorem 4.1] to get

$$\begin{aligned} \left\| \sqrt{|v_p|} (-\Delta + 1)^{-\frac{1}{2}} \right\| & \leq \left\| \sqrt{|v_p|} (-\Delta + 1)^{-\frac{1}{2}} \right\|_{\mathfrak{S}_{2p}} \\ & \leq (2\pi)^{-d/(2p)} \left\| \sqrt{|v_p|} \right\|_{L^{2p}} \left\| (|x|^2 + 1)^{-\frac{1}{2}} \right\|_{L^{2p}} \\ & \leq c_{d,p} \sqrt{\|v_p\|_{L^p}}. \end{aligned}$$

(ii) Take $c \geq 0$ and let us define $A := \sum_i v_i + \sum_{ij} w_{ij}$. We remark that

$$H + c = (-\Delta + c)^{\frac{1}{2}} \left(1 + (-\Delta + c)^{-\frac{1}{2}} A (-\Delta + c)^{-\frac{1}{2}} \right) (-\Delta + c)^{\frac{1}{2}},$$

hence we only need to show that $\left\| (-\Delta + c)^{-\frac{1}{2}} A (-\Delta + c)^{-\frac{1}{2}} \right\| < 1$. For instance we will show that

$$\left\| (-\Delta_{\mathbb{R}^d} + c)^{-\frac{1}{2}} v (-\Delta_{\mathbb{R}^d} + c)^{-\frac{1}{2}} \right\| \leq \left\| \sqrt{|v|} (-\Delta_{\mathbb{R}^d} + c)^{-\frac{1}{2}} \right\|^2$$

is as small as we want. For any $\epsilon > 0$, there exists $c_\epsilon \geq 0$ such that $|v| \leq \epsilon(-\Delta) + c_\epsilon$ in the sense of forms, hence for all $u \in \mathcal{C}^\infty$, we have

$$\begin{aligned} \left\| \sqrt{|v|} (-\Delta + c)^{-\frac{1}{2}} u \right\|_{L^2}^2 &\leq \epsilon \left\| (-\Delta)^{\frac{1}{2}} (-\Delta + c)^{-\frac{1}{2}} u \right\|_{L^2}^2 + c_\epsilon \left\| (-\Delta + c)^{-\frac{1}{2}} u \right\|_{L^2}^2 \\ &\leq \left(\epsilon + \frac{c_\epsilon}{c} \right) \|u\|_{L^2}^2. \end{aligned}$$

We can first choose ϵ small and then choose c large so that $\left\| \sqrt{|v|} (-\Delta + c)^{-\frac{1}{2}} \right\|$ is arbitrarily small.

(iii) The statement follows from the resolvent formula

$$\begin{aligned} (z - H^N(v + u))^{-1} - (z - H^N(v))^{-1} \\ = (z - H^N(v + u))^{-1} (\sum_i u_i) (z - H^N(v))^{-1}, \end{aligned}$$

and Cauchy's formula

$$\mathbf{1}_{\{E^N(v)\}} = \frac{1}{2i\pi} \oint_{\mathcal{C}} \frac{dz}{z - H^N(v)},$$

see for instance [20, 27]. □

4.3 Proofs: the wavefunction-to-projector map

In this section we present several basic facts about the space of orthogonal projectors $\left\{ |\Psi\rangle \langle \Psi| \mid \Psi \in H^1(\Omega^N), \|\Psi\|_{L^2}^2 = 1 \right\}$.

4.3.1 Main properties

Quantum pure states are rays of projective Hilbert spaces [31, Section 2.1]. By nature, the map $v \mapsto |\Psi(v)\rangle \langle \Psi(v)|$ has no information on the phase of the ground states, so we will need to adapt the projective approach to regular pure states. We denote by

$$\mathbb{S} := \left\{ \Psi \in L_a^2(\mathbb{R}^{dN}) \mid \|\Psi\|_{L^2} = 1 \right\}, \quad H_p^k := \frac{H^k \cap \mathbb{S}}{S^1},$$

respectively the unit sphere of the set of antisymmetric wavefunctions $L_a^2(\mathbb{R}^{dN})$, and the Sobolev spaces corresponding to physical wavefunction, where S^1 is the unit circle of dimension one representing the phase of a pure state. We denote by $[\cdot]$ the canonical projection of H^k onto H_p^k . The indice “p” can either stand for “physical” or “projective”. On this space, the natural metric is

$$\mathbb{D}_k(\Psi, \Phi) := \inf_{\substack{\psi, \phi \in H^k \cap \mathbb{S} \\ [\psi] = \Psi, [\phi] = \Phi}} \|\phi - \psi\|_{H^k} = \mathbb{D}\left(\left(-\Delta + 1\right)^{\frac{k}{2}}\Psi, \left(-\Delta + 1\right)^{\frac{k}{2}}\Phi\right),$$

where

$$\mathbb{D}(\Psi, \Phi)^2 := \mathbb{D}_0(\Psi, \Phi)^2 = \|\Psi\|_{L^2}^2 + \|\varphi\|_{L^2}^2 - 2|\langle \varphi, \psi \rangle|.$$

In the case $k = 0$, the main properties of these objects are well-known [24], and we adapt them for $k \geq 1$. The next proposition shows that H_p^k is a smooth manifold, on which one can use differential geometry.

Proposition 4.3.1. *The space H_p^k is a completely metrizable (via \mathbb{D}_k) smooth manifold modelled on a Hilbert space isomorphic to each of the Hilbert spaces $\{\psi\}^\perp \cap H^k$ where $\psi \in H^k$. Moreover, for any $\Psi \in H_p^k$, $T_\Psi H_p^k \simeq \{\psi\}^\perp \cap H^k$ locally, where $[\psi] = \Psi$.*

The space of regular rank-one projectors

We define the k^{th} Sobolev space of operators $\mathfrak{S}_{\infty, k}$ as being the linear subspace of $\mathcal{B}(L^2(\mathbb{R}^{dN}))$ which norm

$$\|A\|_{\mathfrak{S}_{\infty, k}} := \left\| \left(-\Delta + 1\right)^{\frac{k}{2}} A \left(-\Delta + 1\right)^{\frac{k}{2}} \right\|$$

is finite, it is a Banach space. We then define the state-to-projector map

$$\mathcal{P} : \begin{array}{ll} H_p^k & \longrightarrow \mathfrak{S}_{\infty, k} \cap \{\text{Tr} \cdot = 1\} \cap \{\|\cdot\| = 1\} \\ \Psi & \longmapsto |\Psi\rangle \langle \Psi|, \end{array}$$

and can show that it is very regular.

Proposition 4.3.2 (\mathcal{P} is an embedding). *\mathcal{P} is a smooth embedding, \mathcal{P}^{-1} is globally Hölder and \mathcal{C}^∞ .*

For the definition of an embedding, see [33, p559]. As a corollary of the previous results, the space $\text{Im } \mathcal{P}$ is smooth.

Corollary 4.3.3. *$\text{Im } \mathcal{P}$ is a submanifold of $\mathfrak{S}_{\infty, k} \cap \{\text{Tr} \cdot = 1\} \cap \{\|\cdot\| = 1\}$, $T_{\mathcal{P}(\Psi)} \text{Im } \mathcal{P} = \text{Im } d_\Psi \mathcal{P}$, and all the topologies $(\mathfrak{S}_{p, k})_{p \in [1, +\infty]}$ on $\mathfrak{S}_{\infty, k}$ are equivalent.*

4.3.2 Proofs of Propositions 4.3.1 and 4.3.2

In the literature, the case H_p^0 is studied in [24]. Its natural inner product is the projective inner product

$$([\psi], [\varphi]) := \frac{|\langle \psi, \varphi \rangle|}{\|\psi\|_{L^2} \|\varphi\|_{L^2}}.$$

The space H_p^k is in bijection with $\mathbb{P}H^k$, but we will not directly endow it with the same structure as in general projective Hilbert spaces theory. Indeed, in this case the metric would be

$$(\Psi, \Phi) \mapsto \inf_{\substack{[\psi]=\Psi, [\phi]=\Phi \\ \|\psi\|_{H^k}=\|\phi\|_{H^k}=1}} \|\psi - \phi\|_{H^k}$$

but it is not the one we want to work with. The relevant one is \mathbb{D}_k . On $H^\ell \times H^\ell$, we have $\mathbb{D}_k \leq \mathbb{D}_\ell$ for $k \leq \ell$. A property of \mathbb{D} is that

$$\left| \|\Psi\|_{L^2}^2 - \|\Phi\|_{L^2}^2 \right| \leq \mathbb{D}(\Psi, \Phi)^2. \quad (4.6)$$

We have

$$\begin{aligned} \mathbb{D}_k([\psi], [\varphi]) &= \inf_{\theta \in [0, 2\pi[} \left\| (-\Delta + 1)^{\frac{k}{2}} (\varphi - e^{i\theta} \psi) \right\|_{L^2} \\ &= \sqrt{\|\psi\|_{H^k}^2 + \|\varphi\|_{H^k}^2 - 2 \left| \left\langle (-\Delta + 1)^{\frac{k}{2}} \psi, (-\Delta + 1)^{\frac{k}{2}} \varphi \right\rangle \right|} \\ &= \mathbb{D} \left(\left[(-\Delta + 1)^{\frac{k}{2}} \psi \right], \left[(-\Delta + 1)^{\frac{k}{2}} \varphi \right] \right). \end{aligned}$$

First we prove Proposition 4.3.1.

Proof of Proposition 4.3.1.

• Let us denote by π the canonical projection from $H^k \cap \mathbb{S}$ onto H_p^k . For each unit vector $\varphi \in H^k \cap \mathbb{S}$ we define the open sets $U_\varphi := \pi(H^k \setminus \{\varphi\}^\perp) \subset H_p^k$. The charts $h_\varphi : U_\varphi \rightarrow \{\varphi\}^\perp$ are defined by

$$h_\varphi(\pi(\psi)) := \frac{(1 - P_\varphi)\psi}{\langle \varphi, \psi \rangle} = \frac{\psi}{\langle \varphi, \psi \rangle} - \varphi$$

for any $\psi \in H^k \setminus \{\varphi\}^\perp$, where $(U_\varphi)_{\varphi \in H^k \cap \mathbb{S}}$ covers H_p^k . Those charts are \mathcal{C}^∞ , we can verify that they are also injective and that their inverses are the maps $\{\varphi\}^\perp \rightarrow U_\varphi, \psi \mapsto \pi(\psi + \varphi)$, which are also \mathcal{C}^∞ , hence h_φ are smooth diffeomorphisms. For $\varphi, \psi \in H^k \cap \mathbb{S}$, the transition maps

$$h_\varphi \circ h_\psi^{-1} : \begin{array}{ccc} h_\psi(U_\varphi \cap U_\psi) & \longrightarrow & h_\varphi(U_\varphi \cap U_\psi) \\ \phi & \longmapsto & \frac{(1 - P_\varphi)(\varphi + \psi)}{\langle \varphi + \psi, \phi \rangle} \end{array}$$

are \mathcal{C}^∞ by composition. More precisely, the proofs follow from [24].

• \mathbb{D}_k is positive and symmetric. Assume that for $\Psi, \Phi \in H_p^k$, $\mathbb{D}_k(\Psi, \Phi) = 0$. Then for given $\psi, \phi \in H^k \cap \mathbb{S}$ such that $[\psi] = \Psi$ and $[\phi] = \Phi$, there exists a sequence $\theta_n \in [0, 2\pi[$ such that

$$\left\| \psi - e^{i\theta_n} \phi \right\|_{H^k} \xrightarrow{n \rightarrow +\infty} 0.$$

Up to a subsequence, $\theta_n \xrightarrow{n \rightarrow +\infty} \theta \in [0, 2\pi[$, then $\left\| \psi - e^{i\theta} \phi \right\|_{H^k}$ and $\Psi = \Phi$.

Now for Ψ, Φ, Ξ and $\xi \in H_p^k$ such that $[\xi] = \Xi$, we have

$$\begin{aligned} \mathbb{D}_k(\Phi, \Psi) &= \inf_{\substack{\psi, \phi \in H^k \cap \mathbb{S} \\ [\psi] = \Psi, [\phi] = \Phi}} \|\phi - \psi\|_{H^k} \leq \inf_{\substack{\psi, \phi \in H^k \cap \mathbb{S} \\ [\psi] = \Psi, [\phi] = \Phi}} (\|\phi - \xi\|_{H^k} + \|\xi - \psi\|_{H^k}) \\ &= \inf_{\substack{\phi \in H^k \cap \mathbb{S} \\ [\phi] = \Phi}} \|\phi - \xi\|_{H^k} + \inf_{\substack{\psi \in H^k \cap \mathbb{S} \\ [\psi] = \Psi}} \|\xi - \psi\|_{H^k} = \mathbb{D}_k(\Phi, \Xi) + \mathbb{D}_k(\Xi, \Psi), \end{aligned}$$

and we can conclude that \mathbb{D}_k is a metric. \square

Next, our goal is to relate vectors in H_p^k with their corresponding rank-one projectors. For $k = 0$ [24], \mathcal{P} is bi-Lipschitz, with constants

$$2^{-\frac{1}{2}} \mathbb{D}(\Psi, \Phi) \leq \|P_\Psi - P_\Phi\| \leq \mathbb{D}(\Psi, \Phi). \quad (4.7)$$

For our application we will need to work at $k = 1$. We first make some preliminary computations.

Lemma 4.3.4.

- (i) For any $\chi, \phi \in L^2$, $\|\phi\| \langle \chi | \rangle = \|\phi\|_{L^2} \|\chi\|_{L^2}$.
- (ii) If moreover $\chi \perp \phi$, then $\|\chi\| \langle \phi | \rangle + \|\phi\| \langle \chi | \rangle = \|\chi\|_{L^2} \|\phi\|_{L^2}$.

Proof. (i) We have

$$\begin{aligned} \|\phi\| \langle \chi | \rangle &= \sup_{\xi \in L^2 \cap \mathbb{S}} \|\phi\| \langle \chi | \xi \rangle_{L^2} = \|\phi\|_{L^2} \sup_{\xi \in L^2 \cap \mathbb{S}} |\langle \chi, \xi \rangle| \\ &= \|\phi\|_{L^2} \left| \left\langle \chi, \frac{\chi}{\|\chi\|_{L^2}} \right\rangle \right| = \|\chi\|_{L^2} \|\phi\|_{L^2}. \end{aligned}$$

(ii) We can compute the norm by using the equality

$$(\|\chi\| \langle \phi | \rangle + \|\phi\| \langle \chi | \rangle)^2 = \|\chi\|_{L^2}^2 \|\phi\| \langle \phi | \rangle + \|\phi\|_{L^2}^2 \|\chi\| \langle \chi | \rangle,$$

and the fact that $\phi \perp \chi$. \square

Now we establish our main estimates, relating the metric \mathbb{D}_k with the $\mathfrak{S}_{\infty, k}$ norm on rank one projectors.

Lemma 4.3.5. *For any $\psi, \varphi \in L^2$, we have*

$$\begin{aligned} (\operatorname{Tr} |P_\varphi - P_\psi|)^2 &= \left(\|\psi\|_{L^2}^2 + \|\varphi\|_{L^2}^2 \right)^2 - 4 |\langle \psi, \varphi \rangle|^2 \\ &= \mathbb{D}([\psi], [\varphi])^4 + 4 |\langle \psi, \varphi \rangle| \mathbb{D}([\psi], [\varphi])^2, \end{aligned} \quad (4.8)$$

and

$$\|P_\psi - P_\varphi\| = \frac{1}{2} \operatorname{Tr} |P_\psi - P_\varphi| + \frac{1}{2} \left| \|\psi\|_{L^2}^2 - \|\varphi\|_{L^2}^2 \right|.$$

Proof. The operator $P_\psi - P_\varphi$ has its eigenvalues of the form $\chi = \alpha\psi + \beta\varphi$ for some $\alpha, \beta \in \mathbb{C}$. Hence the system $(P_\psi - P_\varphi)\chi = \lambda\chi$ can be written

$$\begin{cases} \alpha \|\psi\|_{L^2}^2 + \beta \bar{z} - \lambda\alpha = 0 \\ \alpha z + \beta \|\varphi\|_{L^2}^2 + \lambda\beta = 0, \end{cases}$$

where $z := \langle \varphi, \psi \rangle$. We assume that $\psi \neq \varphi$ (in $(L^2 \cap \mathbb{S})/S^1$), $z \neq 0$, $\alpha \neq 0$ and $\beta \neq 0$, because the same conclusions will hold in those cases. Expressing α using the second equation, replacing it in the first one, multiplying by z and dividing by β , we obtain

$$\lambda^2 + \lambda \left(\|\varphi\|_{L^2}^2 - \|\psi\|_{L^2}^2 \right) + |z|^2 - \|\psi\|_{L^2}^2 \|\varphi\|_{L^2}^2 = 0.$$

The eigenvalues are thus $\lambda_\pm = \frac{1}{2} \left(\|\psi\|_{L^2}^2 - \|\varphi\|_{L^2}^2 \right) \pm \sqrt{\Delta}$ where

$$\Delta := \left(\|\psi\|_{L^2}^2 + \|\varphi\|_{L^2}^2 \right)^2 - 4|z|^2.$$

Since $\left| \|\psi\|_{L^2}^2 - \|\varphi\|_{L^2}^2 \right| \leq \sqrt{\Delta}$, we have

$$\begin{cases} \|P_\psi - P_\varphi\| = \max(|\lambda_-|, |\lambda_+|) = \frac{1}{2} \left| \|\psi\|_{L^2}^2 - \|\varphi\|_{L^2}^2 \right| + \frac{1}{2} \sqrt{\Delta}, \\ \operatorname{Tr} |P_\psi - P_\varphi| = |\lambda_-| + |\lambda_+| = \sqrt{\Delta}. \end{cases} \quad (4.9)$$

This implies the conclusion of the lemma. \square

This lemma shows that

$$\frac{1}{2} \operatorname{Tr} |P_\psi - P_\varphi| \leq \|P_\psi - P_\varphi\| \leq \operatorname{Tr} |P_\psi - P_\varphi| \quad (4.10)$$

and proves that the $\mathfrak{S}_{p,k}$ norms are all equivalent, for all $p \in [1, +\infty]$, on the space $\{P_\Psi \mid \Psi \in H^k\}$. This also implies

$$\mathbb{D}([\psi], [\varphi])^4 \leq (\operatorname{Tr} |P_\varphi - P_\Psi|)^2 \leq (1 + \epsilon) \mathbb{D}([\psi], [\varphi])^4 + \frac{4 |\langle \psi, \varphi \rangle|^2}{\epsilon}$$

for any $\epsilon > 0$. Finally, for any $c > 1$, and any $\psi, \varphi \in H_p^k$,

$$\frac{1}{2}\mathbb{D}_k(\Psi, \Phi)^2 \leq \|P_\Psi - P_\Phi\|_{\mathfrak{S}_{\infty,k}} \leq (1 + \epsilon)\mathbb{D}_k(\Psi, \Phi)^2 + \frac{2}{\sqrt{c^2 - 1}} \|\Psi\|_{H^k} \|\Phi\|_{H^k}. \quad (4.11)$$

We now consider the state-to-projector map \mathcal{P} . We cannot directly work on $\mathfrak{S}_{\infty,k} \cap \{\|\cdot\| = 1\}$ because this is not a manifold since $\|\cdot\|$ is not differentiable, and we cannot choose $\mathfrak{S}_{\infty,k} \cap \{\text{Tr} \cdot = 1\}$ either because we cannot prove it to be a manifold by applying the preimage theorem [33, Theorem 73.C] since the trace norm is not controlled by the operator norm. Proposition 4.3.2 states that $\text{Im } \mathcal{P}$ has a convenient geometric structure on which we can use differential geometry without complications.

Proof of Proposition 4.3.2.

• *Regularity.* First, \mathcal{P} is injective. The map $\psi \mapsto |\psi\rangle\langle\psi|$ from $H^1 \cap \mathbb{S}$ to $\mathfrak{S}_{\infty,1}$ is \mathcal{C}^∞ . Since H_p^1 is the quotient of $H^1 \cap \mathbb{S}$ by the action of the proper and compact group S^1 , then \mathcal{P} is also \mathcal{C}^∞ . The tangent space of $H^k \cap \mathbb{S}$ at some point $\psi \in H^k \cap \mathbb{S}$ is

$$\text{T}_\psi(H^k \cap \mathbb{S}) = H^k \cap \text{T}_\psi\mathbb{S} = \left\{ \phi \in H^k \mid \text{Re} \langle \psi, \phi \rangle = 0 \right\},$$

and the tangent space of H_p^k at some $\psi \in H_p^k$ is

$$\begin{aligned} \text{T}_{\pi(\psi)}H_p^k &\simeq \left(\text{T}_\psi(H^k \cap \mathbb{S}) \right) / \left(\text{T}_\psi(S^1 \cdot \psi) \right) \simeq \left\{ \phi \in H^k \mid \langle \psi, \phi \rangle = 0 \right\} \\ &= H^k \cap \{\psi\}^\perp. \end{aligned} \quad (4.12)$$

Finally, the differential of \mathcal{P} , defined on each chart $U_{[\psi]}$, is given by

$$\begin{aligned} \text{d}\mathcal{P} : \quad U_{[\psi]} \subset H_p^k &\longrightarrow \mathcal{B}\left(H_p^k \cap \{\psi\}^\perp, \mathfrak{S}_{\infty,k}\right) \\ [\psi] &\longmapsto (\varphi \mapsto |\varphi\rangle\langle\psi| + |\psi\rangle\langle\varphi|). \end{aligned}$$

We can show that it is injective.

• *Splitting.* To show that \mathcal{P} is an immersion, it remains to show that for any $\psi \in H^k \cap \mathbb{S}$, $\text{Im } \text{d}_{[\psi]}\mathcal{P}$ splits $\mathfrak{S}_{\infty,k}$ (see [32, p766]), i.e. that there is a projection from $\mathfrak{S}_{\infty,k}$ onto $\text{Im } \text{d}_{[\psi]}\mathcal{P}$, where

$$\text{Im } \text{d}_{[\psi]}\mathcal{P} \simeq \left\{ |\varphi\rangle\langle\psi| + |\psi\rangle\langle\varphi| \mid \varphi \in H^k \cap \{\psi\}^\perp \right\} \subset \mathfrak{S}_{\infty,k}.$$

First, $\text{Im } \text{d}_{[\psi]}\mathcal{P}$ is closed. We define the linear operator

$$\begin{aligned} \gamma_\psi : \quad \mathfrak{S}_{\infty,k} &\longrightarrow \text{Im } \text{d}_{[\psi]}\mathcal{P} \\ G &\longmapsto P_{\{\psi\}^\perp} G P_\psi + P_\psi G P_{\{\psi\}^\perp}. \end{aligned}$$

We decompose $H^k = \text{Span } \psi \oplus \{\psi\}^\perp$, where the projections on each parts are continuous in $H^k \rightarrow H^k$. We can represent an element $G \in \mathfrak{S}_{\infty,k}$ as

$$G = \alpha |\psi\rangle \langle \psi| + |\varphi\rangle \langle \psi| + |\Psi\rangle \langle \varphi| + M$$

where $\alpha \in \mathbb{R}$, $\varphi \in H^k \cap \{\psi\}^\perp$ and $M \in \mathfrak{S}_{\infty,k}(\{\psi\}^\perp)$. This is the division

$$\mathfrak{S}_{\infty,k} = \text{Im } \gamma \oplus \text{Im}(1 - \gamma),$$

where \oplus means that $\text{Im } \gamma \cap \text{Im}(1 - \gamma) = \{0\}$. We compute $\gamma G = |\varphi\rangle \langle \psi| + |\psi\rangle \langle \varphi|$, thus $\gamma^2 = \gamma$.

• *Im γ and $\text{Im}(1 - \gamma)$ are closed in $\mathfrak{S}_{\infty,k}$* For $\varphi \in H^k \cap \{\psi\}^\perp$, we define $G_\varphi := |\psi\rangle \langle \varphi| + |\varphi\rangle \langle \psi| \in \text{Im } \gamma$. Let $\varphi_n \in H^k \cap \{\psi\}^\perp$ be a sequence such that $G_{\varphi_n} \xrightarrow{\mathfrak{S}_{\infty,k}} G$ for some $G \in \mathfrak{S}_{\infty,k}$. We define $\varphi := G\psi$. We have $\varphi - \varphi_n = (G - G_{\varphi_n})\psi$ and then $\|\varphi - \varphi_n\|_{H^k} \leq \|G - G_{\varphi_n}\|_{\mathfrak{S}_{\infty,k}} \|\psi\|_{H^{-k}}$ and $\varphi_n \xrightarrow{H^k} \varphi$. We have $G - G_{\varphi_n} = G_{\varphi - \varphi_n}$ so $\|G_\varphi - G_{\varphi_n}\|_{\mathfrak{S}_{\infty,k}} \leq 2 \|\psi\|_{H^k} \|\varphi - \varphi_n\|_{H^k}$ and $G_{\varphi_n} \xrightarrow{\mathfrak{S}_{\infty,k}} G_\varphi$, so $G = G_\varphi$. We conclude that $\text{Im } \gamma$ is closed in $\mathfrak{S}_{\infty,k}$.

For $\alpha \in \mathbb{R}$ and $M \in \mathfrak{S}_{\infty,k}(\{\psi\}^\perp)$, we define $G_{\alpha,M} := \alpha P_\psi + M \in \text{Im}(1 - \gamma)$. Let $(\alpha_n, M_n) \in \mathbb{R} \times \mathfrak{S}_{\infty,k}(\{\psi\}^\perp)$ such that $G_{(\alpha_n, M_n)} \xrightarrow{\mathfrak{S}_{\infty,k}} G$ for some $G \in \mathfrak{S}_{\infty,k}$. We define $\alpha := \langle \psi, G\psi \rangle$ and $M := G - \alpha P_\psi$. We have

$$\begin{aligned} \alpha - \alpha_n &= \langle \psi, (G - G_{(\alpha_n, M_n)})\psi \rangle \\ &= \left\langle (-\Delta + 1)^{-\frac{k}{2}} \psi, (-\Delta + 1)^{\frac{k}{2}} (G - G_{(\alpha_n, M_n)}) (-\Delta + 1)^{\frac{k}{2}} (-\Delta + 1)^{-\frac{k}{2}} \psi \right\rangle \end{aligned}$$

so $|\alpha - \alpha_n| \leq \|\psi\|_{H^{-k}}^2 \|G - G_{(\alpha_n, M_n)}\|_{\mathfrak{S}_{\infty,k}}$ and $\alpha_n \rightarrow \alpha$. Moreover, $M_n - M = G_n - G + (\alpha_n - \alpha)P_\psi$ so $\|M_n - M\|_{\mathfrak{S}_{\infty,k}} \leq \|G_{(\alpha_n, M_n)} - G\|_{\mathfrak{S}_{\infty,k}} + |\alpha_n - \alpha| \|\psi\|_{H^k}^2$ and $M_n \xrightarrow{\mathfrak{S}_{\infty,k}} M$. Eventually,

$$\|G_{(\alpha_n, M_n)} - G_{(\alpha, M)}\|_{\mathfrak{S}_{\infty,k}} \leq \|M_n - M\|_{\mathfrak{S}_{\infty,k}} + |\alpha_n - \alpha| \|\psi\|_{H^k}^2,$$

and $G_{(\alpha_n, M_n)} \xrightarrow{\mathfrak{S}_{\infty,k}} G_{(\alpha, M)}$ so $G = G_{(\alpha, M)} \in \text{Im}(1 - \gamma)$. We conclude that $\text{Im}(1 - \gamma)$ is closed.

• *γ is continuous.* Let $\mathcal{G}_\gamma := \{(G, \gamma G) \mid G \in \mathfrak{S}_{\infty,k}\}$ be the graph of γ . Let $(G_n)_{n \in \mathbb{N}} \in \mathfrak{S}_{\infty,k}^{\mathbb{N}}$ be a sequence such that $G_n \xrightarrow{\mathfrak{S}_{\infty,k}} G$ and $\gamma G_n \xrightarrow{\mathfrak{S}_{\infty,k}} F$ for some $G, F \in \mathfrak{S}_{\infty,k}$. $\text{Im } \gamma$ is closed so $F \in \text{Im } \gamma$ and $\gamma F = F$. Also, $G_n - \gamma G_n = (1 - \gamma)G_n \xrightarrow{\mathfrak{S}_{\infty,k}} G - F$, but since $\text{Im}(1 - \gamma)$ is closed, then $G - F \in \text{Im}(1 - \gamma)$ so $0 = \gamma(G - F) = \gamma G - F$ and $\gamma G = F$. This proves that \mathcal{G}_γ is closed in $\mathfrak{S}_{\infty,k}$, and thus by the closed graph theorem, γ is continuous.

• *Conclusion.* γ is thus a projector and $\text{Im } d_{[\psi]}\mathcal{P}$ splits $\mathfrak{S}_{\infty,k}$. We conclude that \mathcal{P} is an embedding.

• \mathcal{P}^{-1} is \mathcal{C}^∞ . We know that \mathcal{P} is a \mathcal{C}^1 -embedding, thus at any point Ψ and working in local charts, $d_\Psi\mathcal{P}$ is invertible and its image splits, so we can apply the inverse function theorem. We refer to [33, Theorem 73.E] and [18, Section I.5]. All the degrees of regularity of \mathcal{P} are passed on its inverse [18, Proposition 5.3]. \square

The proof of Corollary 4.3.3 consists in applying [33, Theorem 73.E], and the fact that the topologies are equivalent by (4.10). Since \mathcal{P} and \mathcal{P}^{-1} are \mathcal{C}^1 , then $d_{\mathcal{P}(\Psi)}\mathcal{P}^{-1} = (d_\Psi\mathcal{P})^{-1}$ by the chain rule. Also, \mathcal{P} is bi-Lipschitz for $k = 0$ by (4.7).

4.4 Proofs: the wavefunction-to-density map $\tilde{\rho}$

In this section, we provide a basic property on the map $\Psi \mapsto \rho_\Psi$ from $H_{\mathbb{P}}^1(\mathbb{R}^{dN})$ to $H^1(\mathbb{R}^d)$. We define the map from a wavefunction to its one-body density,

$$\tilde{\rho}: H_{\mathbb{P}}^k \longrightarrow W^{k,1}(\mathbb{R}^d) \cap \{f \cdot = N\}$$

by $\tilde{\rho}(\mathbb{C}\psi) := \rho_\psi$, and we also use the notation $\rho_\Psi := \tilde{\rho}(\Psi)$. Its differential has to be defined in local charts, by

$$\begin{aligned} d\tilde{\rho}: H_{\mathbb{P}}^k &\longrightarrow \mathcal{B}\left(H^k \cap \{\psi\}^\perp, W^{k,1} \cap \{f \cdot = 0\}\right) \\ [\psi] &\longmapsto d_{[\psi]}\tilde{\rho} = 2N \operatorname{Re} \int_{\mathbb{R}^{d(N-1)}} \bar{\psi} \cdot, \end{aligned}$$

which depends on the point of H^k at which we look, contrarily to $\tilde{\rho}$. The choice of ψ is the choice of a relative phase in the corresponding chart. This section consists in proving that it is smooth as claimed in the next lemma.

Lemma 4.4.1 (Smoothness of $\tilde{\rho}$). *For any $k \in \mathbb{N}$, $\tilde{\rho}$ is \mathcal{C}^∞ . For any $\Psi, \Phi \in H_{\mathbb{P}}^k$, we have*

$$\|\rho_\Psi - \rho_\Phi\|_{W^{k,1}} \leq c_{k,d} (\|\Psi\|_{H_{\mathbb{P}}^k} + \|\Phi\|_{H_{\mathbb{P}}^k}) \mathbb{D}_k(\Psi, \Phi), \quad (4.13)$$

where $c_{k,d}$ is a constant depending only on k and d . The map $\tilde{\rho}$ is nowhere injective and not proper.

The map $\varphi \mapsto \int \psi\varphi$, from L^2 to L^2 for instance, is compact. For this reason we believe that $d_\Psi\tilde{\rho}$ is a source of compactness in $d_v\rho = d_{\Psi(v)}\tilde{\rho} \circ d_v\Psi$, which is itself a source of ill-posedness in the inverse Kohn-Sham problem.

Proof of Lemma 4.4.1.

• *Not proper.* We take $\rho \in \mathcal{C}^\infty(\Omega, \mathbb{R}_+)$ such that $\int \rho = N$ and show that $\tilde{\rho}^{-1}(\{\rho\})$ is not compact. Indeed, considering the Harriman-Lieb representation Ψ_k of ρ , having an orbital with $(k, 0, 0)$ momentum [12] [21, proof of Theorem 1.2], it verifies $\rho_{\Psi_k} = \rho$ but $\|\Psi_k\|_{H^1} \rightarrow +\infty$.

• *Continuity.* Let $Y := \{(x_2, \dots, x_N) \in \Omega^{N-1}\}$. We have

$$\begin{aligned} |\rho_\psi - \rho_\varphi| &= \left| \int_Y (|\psi|^2 - |\varphi|^2) dY \right| \leq \int_Y \left| |\psi|^2 - |\varphi|^2 \right| dY \\ &\leq \int_Y (|\psi| + |\varphi|) (|\psi| + |\varphi|) dY, \end{aligned}$$

thus by integrating in the last variable we obtain

$$\int |\rho_\psi - \rho_\varphi| \leq \|\psi - \varphi\|_{L^2} \sqrt{\int (|\psi| + |\varphi|)^2} \leq 2 \|\psi - \varphi\|_{L^2}.$$

We conclude that

$$\|\sqrt{\rho_\psi} - \sqrt{\rho_\varphi}\|_{L^2}^2 \leq \|\rho_\psi - \rho_\varphi\|_{L^1} \leq 2 \|\psi - \varphi\|_{L^2}, \quad (4.14)$$

As for the derivatives,

$$\nabla(\rho_\psi - \rho_\varphi) = 2 \operatorname{Re} \int_Y \bar{\psi} \nabla(\psi - \varphi) + 2 \operatorname{Re} \int_Y \overline{\psi - \varphi} \nabla \varphi,$$

so

$$\begin{aligned} \|\nabla(\rho_\psi - \rho_\varphi)\|_{L^1} &\leq 2 \|\nabla(\psi - \varphi)\|_{L^2} + 2 \|\nabla \varphi\|_{L^2} \|\psi - \varphi\|_{L^2} \\ &\leq 2(1 + \|\nabla \varphi\|_{L^2}) \left\| (-\Delta + 1)^{\frac{1}{2}} (\psi - \varphi) \right\|_{L^2}. \end{aligned}$$

For the double derivatives, we can show that

$$\begin{aligned} \|\Delta(\rho_\psi - \rho_\varphi)\|_{L^1} &\leq 2(\|\nabla \psi\|_{L^2} + \|\nabla \varphi\|_{L^2}) \|\nabla(\psi - \varphi)\|_{L^2} \\ &\quad + 2\|\psi - \varphi\|_{L^2} \|\Delta \psi\|_{L^2} + 2\|\varphi\|_{L^2} \|\Delta(\psi - \varphi)\|_{L^2}, \end{aligned}$$

and more generally for any $k \in \mathbb{N}$, there is a constant $c_{k,d}$, depending only on k and on the dimension, such that

$$\begin{aligned} \|\rho_\psi - \rho_\varphi\|_{W^{k,1}} &\leq c_{k,d} \sum_{i=1}^k (\|\psi\|_{H^{k-i}} + \|\varphi\|_{H^{k-i}}) \|\psi - \varphi\|_{H^i} \\ &\leq c_{k,d} (\|\psi\|_{H^k} + \|\varphi\|_{H^k}) \|\psi - \varphi\|_{H^k}. \end{aligned}$$

In the right term involving both ψ and φ , we can change the global phase to estimate by the \mathbb{D}_k metric, this leads to (4.13).

• *Differentiability.* We see H_p^k as a smooth manifold, with charts c_ψ for $\psi \in H^k$ as considered in the proof of Proposition 4.3.1. The description of $\tilde{\rho}$ is then done in those charts. We denote by $\bar{\rho}$ the map $H^k \rightarrow W^{k,1}$, $\psi \mapsto \rho_\psi$. For $\varphi \in H^k$ close to $\psi \in H^k \cap \mathbb{S}$, we can represent $\tilde{\rho}$ by $\tilde{\rho}(\varphi) = \bar{\rho} \circ c_\psi^{-1}(\varphi) = \bar{\rho}(\pi(\psi + \varphi)) = \rho_{\psi+\varphi}$, hence $\tilde{\rho}$ is smooth. We have

$$\rho_{\psi+\varphi} - \rho_\psi - 2N \operatorname{Re} \int_Y \bar{\psi} \varphi = \int_Y |\varphi|^2,$$

with $\left\| \int_Y \bar{\psi} \varphi \right\|_{W^{k,1}} \leq c \|\psi\|_{H^k} \|\varphi\|_{H^k}$, therefore $2N \operatorname{Re} \int_Y \bar{\psi} \cdot$ is bounded. Eventually,

$$\left\| \int_Y |\varphi|^2 \right\|_{W^{k,1}} \leq c_{d,k} \|\varphi\|_{L^2} \|\varphi\|_{H^k}.$$

Hence $\bar{\rho}$ has differential $d_\psi \bar{\rho} = 2N \operatorname{Re} \int_Y \bar{\psi} \cdot$, which is a representative of $d_{[\psi]} \tilde{\rho}$ in the chart (U_ψ, c_ψ) . \square

The conclusions of this section hold for other potential-to-ground state density maps, for instance for the current map $\Psi \mapsto j_\Psi$ etc.

4.5 Proofs: maps from potentials to ground state quantities

In this section, we prove the corresponding results for the map $v \mapsto |\Psi(v)\rangle \langle \Psi(v)|$, and then transport them to the map $v \mapsto \rho(v)$.

4.5.1 The restriction

For any operator A of $L^2(\Omega)$, we define $\tilde{A}_\perp := (1 - P_\Psi)A|_{\{\Psi\}^\perp}$ as an operator of $\{\Psi\}^\perp$, and $A_\perp := A(1 - P_\Psi)$ as an operator of L^2 . We need to work in $\{\Psi\}^\perp$ because it corresponds to the tangent space of \mathbb{S} at Ψ . We split $L^2 = \operatorname{Span} \Psi \oplus \{\Psi\}^\perp$. Let us write H and E instead of $H^N(v)$ and $E^N(v)$, P is the orthogonal projection on $\operatorname{Ker}(H - E)$ and $P_\perp := 1 - P$.

Proposition 4.5.1 (Properties of H_\perp). *Let p be as in (4.2), and let $v \in \mathcal{V}^N$, $H := H^N(v)$, $E := E^N(v)$ and $\lambda \in \mathbb{R}$.*

- (i) *As an operator on $\{\Psi\}^\perp$, \tilde{H}_\perp is self-adjoint on $D(H^N(v)) \cap \{\Psi\}^\perp$. On $\{\Psi\}^\perp$, $(\widetilde{H - \lambda})_\perp^{-1/2} = (H - \lambda)^{-1/2}$ for $\lambda \notin \sigma(H)$. Moreover $\sigma(\tilde{H}_\perp) = \sigma(H) \setminus \{E\}$ and $\sigma_{\text{ess}}(\tilde{H}_\perp) = \sigma_{\text{ess}}(H)$.*

- (ii) *The operator $(-\Delta + 1)^{\frac{1}{2}}(H - E)_\perp^{-1} P_\perp (-\Delta + 1)^{\frac{1}{2}}$ is bounded.*

Proof. The first part (i) is well-known and follows from the spectral calculus [20, 26]. Since H and $(H - E)_\perp^{-1}$ commute, we have for $\lambda > 0$,

$$\begin{aligned} & \left\| (-\Delta + 1)^{\frac{1}{2}} (H - E)_\perp^{-1} (-\Delta + 1)^{\frac{1}{2}} \right\| \\ &= \left\| (-\Delta + 1)^{\frac{1}{2}} \frac{H - E + \lambda}{(H - E + \lambda)^{\frac{1}{2}}} (H - E)_\perp^{-1} (H - E + \lambda)^{-\frac{1}{2}} (-\Delta + 1)^{\frac{1}{2}} \right\| \\ &\leq \left\| (-\Delta + 1)^{\frac{1}{2}} (H - E + \lambda)^{-\frac{1}{2}} \right\|^2 \left\| (H - E + \lambda)(H - E)_\perp^{-1} \right\| \\ &= \left\| (-\Delta + 1)^{\frac{1}{2}} (H - E + \lambda)^{-\frac{1}{2}} \right\|^2 \left\| \lambda(H - E)_\perp^{-1} + P_\perp \right\| \\ &\leq \left(\lambda \text{d}(E, \sigma(H) \setminus \{E\})^{-1} + 1 \right) \left\| (-\Delta + 1)^{\frac{1}{2}} (H - E + \lambda)^{-\frac{1}{2}} \right\|^2. \end{aligned}$$

By decomposing

$$\begin{aligned} & (-\Delta + 1)^{\frac{1}{2}} (H - E + \lambda)^{-1} (-\Delta + 1)^{\frac{1}{2}} \\ &= \left((H - E + \lambda)^{-\frac{1}{2}} (-\Delta + 1)^{\frac{1}{2}} \right)^* \left((H - E + \lambda)^{-\frac{1}{2}} (-\Delta + 1)^{\frac{1}{2}} \right), \end{aligned}$$

we obtain

$$\left\| (-\Delta + 1)^{\frac{1}{2}} (H - E + \lambda)^{-\frac{1}{2}} \right\|^2 = \left\| (-\Delta + 1)^{\frac{1}{2}} (H - E + \lambda)^{-1} (-\Delta + 1)^{\frac{1}{2}} \right\|,$$

which is finite by Lemma 4.2.1. \square

4.5.2 The potential-to-density matrix map \mathcal{P}

We define the map

$$\mathcal{P} : \begin{array}{ll} \mathcal{V}^N & \longrightarrow \text{Im } \mathcal{P} \\ v & \longmapsto P_{\Psi(v)} = |\Psi(v)\rangle \langle \Psi(v)| \end{array}$$

giving the ground state density matrix. Its differential is

$$\text{d}\mathcal{P} : \begin{array}{ll} \mathcal{V}^N & \longrightarrow \mathcal{B}(\mathcal{V}, \mathfrak{S}_{1,1}) \\ v & \longmapsto (u \mapsto (\text{d}_v \mathcal{P}) u) \end{array}$$

and we recall that, if $\psi(v)$ is a representative of $\Psi(v)$, then

$$\begin{aligned} (\text{d}_v \mathcal{P}) u &\in \left(\text{d}_{\Psi(v)} \mathcal{P} \right) \left(\text{T}_{\Psi(v)} H_{\mathbb{P}}^k \right) \\ &= \left\{ |\psi(v)\rangle \langle \phi| + |\phi\rangle \langle \psi(v)| \mid \phi \in H^k \cap \{\psi(v)\}^\perp \right\}. \end{aligned} \tag{4.15}$$

The differential of \mathcal{P} takes its values in the tangent space of $\text{Im } \mathcal{P}$, corresponding to the tangent space of $H_{\mathbb{P}}^k$. On this last space, the relevant operator acting on tangent vectors is $H^N(v)_\perp$.

We define the contour $\mathcal{C} := \left\{ z \in \mathbb{C} \mid |z - E^N(v)| = \eta(v) \right\}$ where $\eta(v) := \text{dist}(E^N(v), \sigma(H^N(v)) \setminus \{E^N(v)\})/2$.

Theorem 4.5.2 (Properties of \mathcal{P}). *Let p be as in (4.2) and $\mathcal{V} = L^p + L^\infty$. The potential-to-ground state density matrix map \mathcal{P} is C^∞ . At some point $v \in \mathcal{V}^N$, its differential is*

$$(\mathrm{d}_v \mathcal{P})u = \frac{1}{2\pi i} \oint_{\mathcal{C}} dz (z - H^N(v))^{-1} (\sum_i u_i) (z - H^N(v))^{-1} \quad (4.16)$$

$$= (E^N(v) - H^N(v))_{\perp}^{-1} (\sum_i u_i) \mathcal{P}(v) + \mathcal{P}(v) (\sum_i u_i) (E^N(v) - H^N(v))_{\perp}^{-1}. \quad (4.17)$$

Also, for any $v \in \mathcal{V}^N$, $\mathrm{Tr}((\mathrm{d}_v \mathcal{P})u) = 0$ for any $u \in L^p + L^\infty$. The differential $\mathrm{d}_v \mathcal{P}$ is compact from $L^p + L^\infty$ to $\mathfrak{S}_{\infty,1}$ and not surjective. If $p > \max(2d/3, 2)$, then \mathcal{P} and $\mathrm{d}_v \mathcal{P}$ are injective.

Proof.

• *Continuity.* Let $v, u \in \mathcal{V}^N$ be such that $\|v - u\|_{L^p + L^\infty} \leq \epsilon$ with ϵ so small that $|E^N(v) - E^N(u)| < \eta(v)/8 < \eta(u)$. For all $z \in \mathbb{C}$ such that $|z - E^N(v)| = \eta(v)/2$, we have thus $\mathrm{dist}(z, \sigma(H^N(u))) \geq \eta(v)/8$. We use the resolvent formula and integrate over a contour \mathcal{C} located around $E^N(v)$ and $E^N(u)$, we have

$$\begin{aligned} \mathcal{P}(v) - \mathcal{P}(u) &= \int_{\mathcal{C}} (-\Delta + 1)^{-\frac{1}{2}} C(z) (-\Delta + 1)^{-\frac{1}{2}} (\sum_i (v - u)_i) (-\Delta + 1)^{-\frac{1}{2}} \\ &\quad \times D(z) (-\Delta + 1)^{-\frac{1}{2}}, \end{aligned}$$

where

$$\begin{aligned} C(z) &:= (-\Delta + 1)^{\frac{1}{2}} (z - H^N(v))^{-1} (-\Delta + 1)^{\frac{1}{2}} \\ D(z) &:= (-\Delta + 1)^{\frac{1}{2}} (z - H^N(u))^{-1} (-\Delta + 1)^{\frac{1}{2}} \end{aligned}$$

are bounded uniformly in z , as justified by Lemma 4.2.1. We estimate

$$\begin{aligned} \|\mathcal{P}(v) - \mathcal{P}(u)\|_{\mathfrak{S}_{\infty,1}} &\leq c \left\| (-\Delta + 1)^{-\frac{1}{2}} (\sum_i (v - u)_i) (-\Delta + 1)^{-\frac{1}{2}} \right\| \\ &\leq cN \left\| (-\Delta_{\mathbb{R}^d} + 1)^{-\frac{1}{2}} (v - u) (-\Delta_{\mathbb{R}^d} + 1)^{-\frac{1}{2}} \right\| \\ &\leq cN \|v - u\|_{L^p + L^\infty}, \end{aligned}$$

where we used Lemma 4.2.1. Finally, we saw in Corollary 4.3.3 that on $\mathrm{Im} \mathcal{P}$, the norms $\mathfrak{S}_{\infty,1}$ and $\mathfrak{S}_{1,1}$ are equivalent.

• *Differentiability.* Let $v \in \mathcal{V}^N$ and $u \in L^p + L^\infty$ be small enough so

that $v + u \in \mathcal{V}^N$. By the resolvent formula, we have

$$\begin{aligned} \mathcal{P}(v + u) - \mathcal{P}(v) - \frac{1}{2\pi i} \oint_{\mathcal{C}} (z - H^N(v))^{-1} (\sum_i u_i) (z - H^N(v))^{-1} \\ = \frac{1}{2\pi i} \oint_{\mathcal{C}} (z - H^N(v + u))^{-1} \left[(\sum_i u_i) (z - H^N(v))^{-1} \right]^2 \\ = \frac{1}{2\pi i} \oint_{\mathcal{C}} (-\Delta + 1)^{-\frac{1}{2}} G(z) (-\Delta + 1)^{-\frac{1}{2}} (\sum_i u_i) (-\Delta + 1)^{-\frac{1}{2}} C(z) \\ \quad \times (-\Delta + 1)^{-\frac{1}{2}} (\sum_i u_i) (-\Delta + 1)^{-\frac{1}{2}} C(z) (-\Delta + 1)^{-\frac{1}{2}}, \end{aligned}$$

where the operator $G(z) := (-\Delta + 1)^{\frac{1}{2}} (z - H^N(v + u))^{-1} (-\Delta + 1)^{\frac{1}{2}}$ is uniformly bounded in z . Therefore

$$\begin{aligned} \left\| \mathcal{P}(v + u) - \mathcal{P}(v) - \frac{1}{2\pi i} \oint_{\mathcal{C}} (z - H^N(v))^{-1} (\sum_i u_i) (z - H^N(v))^{-1} \right\|_{\mathfrak{S}_{\infty,1}} \\ \leq c \|u\|_{L^p + L^\infty}^2, \end{aligned}$$

where c is independent of u . Hence $d_v \mathcal{P}$ exists and is given by the first equality in (4.16).

• *Formula (4.16).* We denote by Λ the domain delimited by \mathcal{C} . First, because the only singularity inside Λ is on $z = E^N(v)$, we have by the spectral theorem

$$\oint (z - H^N(v))^{-1} \mathcal{P}(v) (\sum_i u_i) (z - H^N(v))^{-1} \mathcal{P}(v) = 0.$$

Moreover, since Λ and $\sigma(\widetilde{H^N(v)}_{\perp})$ are disjoint, we have by the spectral theorem

$$\begin{aligned} \frac{1}{2\pi i} \oint_{\mathcal{C}} (z - H^N(v))^{-1} (1 - \mathcal{P}(v)) (\sum_i u_i) (z - H^N(v))^{-1} \mathcal{P}(v) \\ = \frac{1}{2\pi i} \oint_{\mathcal{C}} (z - H^N(v))_{\perp}^{-1} (\sum_i u_i) (z - H^N(v))^{-1} \mathcal{P}(v) \\ = \frac{1}{2\pi i} (E^N(v) - H^N(v))_{\perp}^{-1} (\sum_i u_i) \left(\oint_{\mathcal{C}} (z - H^N(v))^{-1} \right) \mathcal{P}(v) \\ = (E^N(v) - H^N(v))_{\perp}^{-1} (\sum_i u_i) \mathcal{P}(v)^2 \\ = (E^N(v) - H^N(v))_{\perp}^{-1} (\sum_i u_i) \mathcal{P}(v). \end{aligned}$$

Similarly,

$$\begin{aligned} \frac{1}{2\pi i} \oint_{\mathcal{C}} (z - H^N(v))^{-1} \mathcal{P}(v) (\sum_i u_i) (z - H^N(v))^{-1} \\ = \frac{1}{2\pi i} \left(\oint_{\mathcal{C}} (z - H^N(v))^{-1} \right) \mathcal{P}(v) (\sum_i u_i) (E^N(v) - H^N(v))_{\perp}^{-1} \\ = \mathcal{P}(v) (\sum_i u_i) (E^N(v) - H^N(v))_{\perp}^{-1}. \end{aligned}$$

• *Regularity of the differential.* The following expressions are well-known [16]. Let $v, h \in \mathcal{V}^N$ be potentials, close enough so that we can find a common relevant integration contour \mathcal{C} , and $u \in L^p + L^\infty$ an element of the tangent spaces. We have

$$\begin{aligned} & (d_v \mathcal{P} - d_h \mathcal{P}) u \\ &= \frac{1}{2\pi i} \oint_{\mathcal{C}} \left((z - H^N(v))^{-1} (\sum_i u_i) (z - H^N(v))^{-1} \sum_i (v - h)_i (z - H^N(h))^{-1} \right. \\ & \quad \left. + (z - H^N(v))^{-1} (\sum_i (v - h)_i) (z - H^N(h))^{-1} (\sum_i u_i) (z - H^N(h))^{-1} \right) \end{aligned}$$

therefore $\|(d_v \mathcal{P} - d_h \mathcal{P}) u\|_{\mathfrak{S}_{\infty,1}} \leq c \|v - h\|_{L^p + L^\infty} \|u\|_{L^p + L^\infty}$ and

$$\|d_v \mathcal{P} - d_h \mathcal{P}\|_{L^p + L^\infty \rightarrow \mathfrak{S}_{\infty,1}} \leq c \|v - h\|_{L^p + L^\infty},$$

and thus $v \mapsto d_v \mathcal{P}$ is locally Lipschitz.

By similar methods, we can show that \mathcal{P} is infinitely differentiable and that for any $m \in \mathbb{N}$, the m^{th} derivative is given by

$$(d_v^m \mathcal{P})(v_1, \dots, v_m) = \frac{1}{2\pi i} \oint_{\mathcal{C}} (z - H^N(v))^{-1} \prod_{\ell=1}^m (\sum_i (v_\ell)_i) (z - H^N(v))^{-1},$$

with $\|(d_v^m \mathcal{P})(v_1, \dots, v_m)\|_{\mathfrak{S}_{\infty,1}} \leq c \prod_{\ell=1}^m \|v_\ell\|_{L^p + L^\infty}$.

• $\text{Tr}(d_v \mathcal{P})u = 0$. This is because the differential takes its values in the tangent space of the image space, but we verify it analytically here. Take $v \in \mathcal{V}^N$ and $u \in L^p + L^\infty$. We have

$$\begin{aligned} & \left\langle \Psi(v), (E^N(v) - H^N(v))_{\perp}^{-1} (\sum_i u_i) \mathcal{P}(v) \Psi(v) \right\rangle \\ &= \left\langle \Psi(v), (1 - \mathcal{P}(v)) (E^N(v) - H^N(v))_{\perp}^{-1} (\sum_i u_i) \Psi(v) \right\rangle \\ &= \left\langle (1 - \mathcal{P}(v)) \Psi(v), (E^N(v) - H^N(v))_{\perp}^{-1} (\sum_i u_i) \Psi(v) \right\rangle = 0. \end{aligned}$$

• *Injectivity of the differential.* Let $v \in \mathcal{V}^N$ and $u \in L^p + L^\infty$ be such that $(d_v \mathcal{P})u = 0$. We consider the representation (4.16) and let $H^N(v) - E^N(v)$ act on the left, this yields $(1 - \mathcal{P}(v))(\sum_i u_i) \mathcal{P}(v) = 0$, that is $(\sum_i u_i) \Psi(v) = \Psi(v) \int u \rho(v)$. By unique continuation (see Chapter 1 and [7, 8]), the nodal set of $\Psi(v)$ has zero measure, hence $\sum_i u_i = \int u \rho(v)$ and by integrating on $[0, 1]^{d(N-1)}$ we can conclude that u is constant.

• *Compactness of the differential.* Let us first show a lemma. We recall that a sequence of operators L_n of $L^2(\mathbb{R}^n)$, such that $\|L_n\| \leq c$, converges strongly to 0 if $\|L_n f\|_{L^2} \rightarrow 0$ for any $f \in L^2(\mathbb{R}^n)$, and converges weakly to 0 if $\langle g, L_n f \rangle \rightarrow 0$ for any $f, g \in L^2(\mathbb{R}^n)$.

Lemma 4.5.3.

(i) Let L_n be a sequence of operators such that $\|L_n\| \leq c$, $L_n \rightharpoonup 0$ weakly, and let A and B be two compact operators, then $\|AL_nB\| \rightarrow 0$.

(ii) Let $L_n := (-\Delta + 1)^{-\frac{1}{2}} u_n (-\Delta + 1)^{-\frac{1}{2}}$ with $u_n \rightharpoonup 0$ in $L^p + L^\infty$ and p as in (4.2). Then $\|L_n\| \leq c$ and $L_n \rightarrow 0$ strongly.

(iii) Let L_n be a sequence of operators of $L^2(\mathbb{R}^n)$ such that $\|L_n\| \leq c$ and $L_n \rightarrow 0$ strongly, and let $A \in \mathfrak{S}_1(\mathbb{R}^n)$ be a self-adjoint trace-class operator. Then $\text{Tr}(L_nAL_n) \rightarrow 0$.

Proof. (i) The set of finite rank operators is dense in the set of compact operators so by an “ $\epsilon/2$ ” argument, we can assume that A and B have finite rank. So let us write them $A = \sum_{i=1}^m |f_i\rangle \langle g_i|$ and $B = \sum_{i=1}^m |h_i\rangle \langle u_i|$. We have

$$\|AL_nB\| = \left\| \sum_{1 \leq i, j \leq m} \langle g_i, L_n h_i \rangle |f_i\rangle \langle u_i| \right\| \leq \sum_{1 \leq i, j \leq m} |\langle g_i, L_n h_i \rangle| \|f_i\|_{L^2} \|u_i\|_{L^2},$$

and we conclude by letting $n \rightarrow +\infty$, where $\langle g_i, L_n h_i \rangle \rightarrow 0$.

(ii) As we showed in Lemma 4.2.1, $\|L_n\| \leq c \|u_n\|_{L^p + L^\infty}$, with c independent of n , hence $\|L_n\|$ is bounded. By density of $C_c^\infty(\mathbb{R}^d)$ in $L^2(\mathbb{R}^d)$, we hence only need to show that $\|L_n f\| \rightarrow 0$ for any $f \in C_c^\infty(\mathbb{R}^d)$. So let $f \in C_c^\infty(\mathbb{R}^d)$, and take a function χ of \mathbb{R}_+ , equal to 1 on $[0, 1]$, vanishing on $[2, +\infty)$ and smooth and decreasing on $[1, 2]$, and define the localization function $\chi_r(x) := \chi(|x|/r)$ on \mathbb{R}^d . We take r large enough so that $\text{supp } f \subset B_r$. We have

$$\|L_n \chi_r^2 f\|_{L^2} = \|L_n \chi_r^2 (-\Delta + 1)^{-\frac{1}{2}} (-\Delta + 1)^{\frac{1}{2}} f\|_{L^2}$$

and since $(-\Delta + 1)^{\frac{1}{2}} f \in L^2(\mathbb{R}^d)$, we only need to show that $L_n \chi_r^2 (-\Delta + 1)^{-\frac{1}{2}}$ converges strongly to 0. We will in fact prove that

$$\lim_{r \rightarrow +\infty} \lim_{n \rightarrow +\infty} \|L_n \chi_r^2 (-\Delta + 1)^{-\frac{1}{2}}\| = 0.$$

Let us consider the decomposition

$$\begin{aligned} & L_n \chi_r^2 (-\Delta + 1)^{-\frac{1}{2}} \\ &= (-\Delta + 1)^{-\frac{1}{2}} u_n (-\Delta + 1)^{-\frac{1}{2}} \chi_r \left[\chi_r, (-\Delta + 1)^{-\frac{1}{2}} \right] \\ & \quad + (-\Delta + 1)^{-\frac{1}{2}} u_n \left[(-\Delta + 1)^{-\frac{1}{2}}, \chi_r \right] (-\Delta + 1)^{-\frac{1}{2}} \chi_r \\ & \quad + \left[(-\Delta + 1)^{-\frac{1}{2}}, \chi_r \right] u_n (-\Delta + 1)^{-1} \chi_r \\ & \quad + \chi_r (-\Delta + 1)^{-\frac{1}{2}} u_n (-\Delta + 1)^{-1} \chi_r. \end{aligned}$$

We also have

$$\left[(-\Delta + 1)^{-\frac{1}{2}}, \chi_r\right] = -(-\Delta + 1)^{-\frac{1}{2}} \left[(-\Delta + 1)^{\frac{1}{2}}, \chi_r\right] (-\Delta + 1)^{-\frac{1}{2}},$$

For r large enough, we have $\left\| \left[(-\Delta + 1)^{\frac{1}{2}}, \chi_r\right] \right\| \leq c/r$ for some constant c independent of r [11, Lemma 1], hence

$$\left\| L_n \chi_r^2 (-\Delta + 1)^{-\frac{1}{2}} - \chi_r (-\Delta + 1)^{-\frac{1}{2}} u_n (-\Delta + 1)^{-1} \chi_r \right\| \leq c/r, \quad (4.18)$$

where c is independent of n and r . Now we decompose

$$\begin{aligned} & \chi_r (-\Delta + 1)^{-\frac{1}{2}} u_n (-\Delta + 1)^{-1} \chi_r \\ &= \chi_r (-\Delta + 1)^{-\frac{\epsilon}{2}} (-\Delta + 1)^{-\frac{1-\epsilon}{2}} |u_n|^{\frac{1-\epsilon}{2}} \\ & \quad \times \operatorname{sgn}(u_n) |u_n|^{\frac{1+\epsilon}{2}} (-\Delta + 1)^{-\frac{1+\epsilon}{2}} (-\Delta + 1)^{-\frac{1-\epsilon}{2}} \chi_r. \end{aligned}$$

For $d \geq 3$, $p > d/2$, and for ϵ small enough we can still use the HLS inequality to prove that

$$\left\| |u_p|^{\frac{1+\epsilon}{2}} (-\Delta)^{-\frac{1+\epsilon}{2}} \right\| \leq c_d \|u_p\|_{L^p}^{\frac{1+\epsilon}{2}}.$$

For $d = 2$, we can still use the Kato-Seiler-Simon inequality, where we have to take $0 < \epsilon < \min(p - 1, 1)$, so $2p/(1 \pm \epsilon) > 2$ and

$$\begin{aligned} \left\| |u_p|^{\frac{1+\epsilon}{2}} (-\Delta + 1)^{-\frac{1+\epsilon}{2}} \right\| &\leq (2\pi)^{-\frac{d(1+\epsilon)}{p}} \left\| |u_p|^{\frac{1+\epsilon}{2}} \right\|_{L^{\frac{2p}{1+\epsilon}}} \left\| (|x|^2 + 1)^{-\frac{1+\epsilon}{2}} \right\|_{L^{\frac{2p}{1+\epsilon}}} \\ &= c_{d,p,\epsilon} \left\| (|x|^2 + 1)^{-1} \right\|_{L^p}^{\frac{1+\epsilon}{2}} \|u_p\|_{L^p}^{\frac{1+\epsilon}{2}}. \end{aligned}$$

For $d = 1$, $p = 1$ we also use the same argument. Hence

$$(-\Delta + 1)^{-\frac{1-\epsilon}{2}} u_n (-\Delta + 1)^{-\frac{1+\epsilon}{2}} \quad (4.19)$$

is bounded uniformly in n . Let us take $h, g \in C^\infty(\mathbb{R}^d)$. We have

$$\begin{aligned} & \left\langle h, (-\Delta + 1)^{-\frac{1-\epsilon}{2}} u_n (-\Delta + 1)^{-\frac{1+\epsilon}{2}} g \right\rangle \\ &= \int u_n \left((-\Delta + 1)^{-\frac{1-\epsilon}{2}} h \right) \left((-\Delta + 1)^{-\frac{1+\epsilon}{2}} g \right), \end{aligned}$$

and by regularity of h and g , $(-\Delta + 1)^{-\frac{1-\epsilon}{2}} h, (-\Delta + 1)^{-\frac{1+\epsilon}{2}} g \in H^1(\mathbb{R}^d)$ so the above expression converges to 0 when $n \rightarrow +\infty$. By density of $C^\infty(\mathbb{R}^d)$ in $L^2(\mathbb{R}^d)$, this shows that (4.19) converges weakly to 0 when $n \rightarrow +\infty$. Finally, since $\chi_r (-\Delta + 1)^{-\frac{\epsilon}{2}}$ and $(-\Delta + 1)^{-\frac{1-\epsilon}{2}} \chi_r$ are compact, then $\chi_r (-\Delta + 1)^{-\frac{1}{2}} u_n (-\Delta + 1)^{-1} \chi_r \rightarrow 0$ strongly by applying Lemma 4.5.3 (i). Considering (4.18) again, by choosing r large and then n large, we can make

$\|L_n \chi_r^2 (-\Delta + 1)^{-\frac{1}{2}}\|$ arbitrarily small.

(iii) We consider the representation $A = \sum_{i=1}^{\infty} \lambda_i |f_i\rangle \langle f_i|$ where $(f_i)_i$ is an orthonormal family of $L^2(\mathbb{R}^d)$ and $\sum_{i=1}^{\infty} |\lambda_i| < +\infty$. Take $m \in \mathbb{N}$, we have

$$|\mathrm{Tr}(L_n A L_n)| = \left| \sum_{i=1}^{\infty} \lambda_i \|L_n f_i\|_{L^2}^2 \right| \leq \sum_{i=1}^m |\lambda_i| \|L_n f_i\|_{L^2}^2 + c \sum_{i \geq m+1} |\lambda_i|.$$

Let $\epsilon > 0$. By choosing m large enough, we can have $c \sum_{i \geq m+1} |\lambda_i| \leq \epsilon/2$ and then, since $\|L_n f_i\|_{L^2} \rightarrow 0$, we can also choose n large enough so that $\sum_{i=1}^m |\lambda_i| \|L_n f_i\|_{L^2}^2 \leq \epsilon/2$. \square

We denote by Ψ a representative of $\Psi(v)$. Let $u_n \in L^p + L^\infty$ be such that $u_n \rightarrow 0$ in $L^p + L^\infty$. We have

$$\begin{aligned} & \left\| (H^N(v) - E^N(v))_{\perp}^{-1} (\sum_i (u_n)_i) |\Psi\rangle \langle \Psi| \right\|_{\mathfrak{S}_{\infty,1}} \\ &= \|\Psi\|_{H^1} \left\| (H^N(v) - E^N(v))_{\perp}^{-1} (\sum_i (u_n)_i) \Psi \right\|_{H^1}. \end{aligned}$$

We want to show that the following quantity converges to zero,

$$\begin{aligned} & \left\| (H^N(v) - E^N(v))_{\perp}^{-1} (\sum_i (u_n)_i) \Psi \right\|_{H^1} \\ & \leq \left\| (-\Delta + 1)^{\frac{1}{2}} (H^N(v) - E^N(v))_{\perp}^{-1} (-\Delta + 1)^{\frac{1}{2}} \right\| \\ & \quad \times \left\| (-\Delta + 1)^{-\frac{1}{2}} (\sum_i (u_n)_i) \Psi \right\|_{L^2} \\ & \leq c_v \sum_{i=1}^N \left\| (-\Delta + 1)^{-\frac{1}{2}} u_n(x_i) \Psi \right\|_{L^2} \\ & \leq c_v \sum_{i=1}^N \left\| (-\Delta_i + 1)^{-\frac{1}{2}} u_n(x_i) \Psi \right\|_{L^2}. \end{aligned}$$

We define $L_n := (-\Delta + 1)^{-\frac{1}{2}} u_n (-\Delta + 1)^{-\frac{1}{2}}$ and notice that

$$\left\| (-\Delta_i + 1)^{-\frac{1}{2}} u_n(x_i) \Psi \right\|_{L^2}^2 = \frac{1}{N} \mathrm{Tr}_{\mathbb{R}^d} \left(L_n (-\Delta + 1)^{\frac{1}{2}} \gamma_{\Psi} (-\Delta + 1)^{\frac{1}{2}} L_n \right),$$

where γ_{Ψ} is the one-particle density matrix and $(-\Delta + 1)^{\frac{1}{2}} \gamma_{\Psi} (-\Delta + 1)^{\frac{1}{2}} \in \mathfrak{S}_1$. By Lemma 4.5.3 (ii), the operator L_n converges strongly to 0 as an operator of $L^2(\mathbb{R}^d)$. Finally we apply Lemma 4.5.3 (iii) to deduce that

$$\left\| (-\Delta_i + 1)^{-\frac{1}{2}} u_n(x_i) \Psi \right\|_{L^2}^2 \rightarrow 0.$$

By the open mapping theorem, an operator cannot be compact and surjective, hence $d_v \mathcal{P}$ is not surjective. \square

4.5.3 The potential-to-ground state map Ψ

We define the map

$$\Psi : \begin{array}{ccc} \mathcal{V}^N & \longrightarrow & H_p^1(\Omega) \\ v & \longrightarrow & \Psi(v), \end{array}$$

as being the composition $\Psi := \mathcal{P}^{-1} \circ \mathcal{P}$.

Theorem 4.5.4 (Regularity and local weak-strong continuity). *We take p as in (4.2), $\mathcal{V} = L^p + L^\infty$ and $w \in L^p + L^\infty$.*

(i – Smoothness). *The map Ψ is C^∞ from \mathcal{V}^N to H_p^1 . It is injective if $p > \max(2d/3, 2)$.*

(ii – Compactness of the differential). *For $v \in \mathcal{V}^N$, $d_v \Psi : L^p + L^\infty \rightarrow \{\Psi(v)\}^\perp \cap H^1$ equals*

$$(d_v \Psi) u = -(H^N(v) - E^N(v))_{\perp}^{-1} (\sum_{i=1}^N u(x_i)) \Psi(v), \quad (4.20)$$

where $(H^N(v) - E^N(v))_{\perp}^{-1}$ is the inverse of the restriction of $H^N(v) - E^N(v)$ to $\{\Psi(v)\}^\perp$ on this space, and 0 on $\mathbb{C}\Psi(v)$. Moreover, $\int \Psi (d_v \Psi) u = 0$, for all $v \in \mathcal{V}^N$, $d_v \Psi$ is compact, not surjective, and we have

$$\|(d_v \Psi) u\|_{H^1}^2 \leq c_v \|u\|_{L^p + L^\infty} \int_{\Omega} |u| \rho(v).$$

If $p > \max(2d/3, 2)$, then at some $v \in \mathcal{V}^N$, $d_v \Psi$ is injective.

(iii – Local weak-strong continuity). *Let p be as in (4.2), with $p > d/2$ when $d \geq 3$, $w \in L^p + L^\infty$, $w \geq 0$ and $\mathcal{V} = L^p + L^\infty$ in the definition (4.1) of \mathcal{V}^N . Let $\Lambda \subset \Omega$ be a bounded open subset of Ω . Consider that $v \in \mathcal{V}^N$, $v_n \rightharpoonup v$ weakly and $v_n \mathbf{1}_{\Omega \setminus \Lambda} \rightarrow v \mathbf{1}_{\Omega \setminus \Lambda}$ strongly in $L^p + L^\infty$. Then $E^N(v_n) \rightarrow E^N(v)$, $v_n \in \mathcal{V}^N$ for n large enough, and $\Psi(v_n) \rightarrow \Psi(v)$ in H_p^1 .*

(iv – Compactness for Ω bounded). *Let p be as in (4.2), with $p > d/2$ when $d \geq 3$. When Ω is bounded, $v \mapsto \Psi(v)$ is compact, and Ψ^{-1} is discontinuous.*

If $\Omega = \mathbb{R}^d$, Ψ is not weak-strong continuous because of simple counterexamples. For instance by taking a sequence $v_n(x) = u(x - n)$ where $u \in \mathcal{V}^N$, and $v \in \mathcal{V}^N$, $\Psi(v_n + v)$ does not necessarily converge to $\Psi(v)$. When Ω is bounded, weak-strong continuity implies compactness. Such input-output maps involving second order differential equations are generically locally compact [13]. In particular, Theorem 4.5.4 (iii) implies that quantum particles are insensitive to highly oscillating local electric fields.

Proof of Theorem 4.5.4.

• The properties (i) and (ii) are deduced from the composition $\Psi = \mathcal{P}^{-1} \circ \mathcal{P}$ and from Theorem 4.5.2. We only have to prove the expression (4.20). We remark that

$$\begin{aligned} (d_v \mathcal{P}) u &= \left| \left(E^N(v) - H^N(v) \right)_\perp^{-1} (\sum_i u_i \Psi(v)) \right\rangle \langle \Psi(v) | \\ &\quad + |\Psi(v)\rangle \langle \Psi(v) (\sum_i u_i) (E^N(v) - H^N(v))_\perp^{-1} | \\ &= (d_{\Psi(v)} \mathcal{P}) \left(\left(E^N(v) - H^N(v) \right)_\perp^{-1} (\sum_i u_i \Psi(v)) \right). \end{aligned}$$

Now since \mathcal{P}^{-1} is \mathcal{C}^1 , we have

$$\begin{aligned} (d_v \Psi) u &= d_v \left(\mathcal{P}^{-1} \circ \mathcal{P} \right) u = \left(d_{\Psi(v)} \mathcal{P} \right)^{-1} \circ (d_v \mathcal{P}) u \\ &= \left(E^N(v) - H^N(v) \right)_\perp^{-1} (\sum_i u_i \Psi(v)). \end{aligned}$$

We have

$$\begin{aligned} \|(d_v \Psi) u\|_{H^1} &\leq \left\| (-\Delta + 1)^{-\frac{1}{2}} \left(E^N(v) - H^N(v) \right)_\perp^{-1} (-\Delta + 1)^{-\frac{1}{2}} \right\|_{L^2} \\ &\quad \times \left\| (-\Delta + 1)^{\frac{1}{2}} \sqrt{\sum_i |u_i|} \right\|_{L^2} \left\| \sqrt{\sum_i |u_i|} \Psi(v) \right\|_{L^2} \\ &\leq c_v \left(\|u\|_{L^p + L^\infty} \int |u| \rho(v) \right)^{\frac{1}{2}}. \end{aligned}$$

• (iii) Let $v_n \in L^p + L^\infty_\epsilon$ be a sequence which converges to 0 weakly. Let Ψ_n be an approximate minimizer of $E^N(v + v_n)$, that is

$$\mathcal{E}_{v+v_n}(\Psi_n) \leq E^N(v + v_n) + \frac{1}{n},$$

and $\rho_n := \rho_{\Psi_n}$.

• If $d \geq 3$ and $p > d/2$, then we know that

$$|v_n| \leq c_{d,s} \|v_n\|_{(L^p + L^\infty)(\Omega)} \left((-\Delta)^{1-s} + 1 \right)$$

for some $s > 0$ depending on p . But $\|v_n\|_{(L^p + L^\infty)(\Omega)}$ is bounded in n , and for any $\epsilon > 0$, we have $(-\Delta)^{1-s} \leq (1-s)\epsilon(-\Delta) + s\epsilon^{-1+1/s}$. We thus proved that for any $\epsilon > 0$ there is some $c_\epsilon \in \mathbb{R}$ independent of n such that $|v_n| \leq \epsilon(-\Delta) + c_\epsilon$ in the sense of forms in Ω . In dimensions $d \in \{1, 2\}$, the same holds under our assumptions on p .

• Next we prove that $\int v_n \rho_n \rightarrow 0$. First, take some wavefunction function $\Phi \in \wedge^N H^1(\Omega)$, we have

$$E^N(v + v_n) \leq \mathcal{E}_v(\Phi) + \int v_n \rho_\Phi \leq \mathcal{E}_v(\Phi) + c_{d,N} \|v_n\|_{L^p + L^\infty} \|\sqrt{\rho_\Phi}\|_{H^1},$$

and since $\|v_n\|_{L^p+L^\infty}$ is bounded, then $E^N(v+v_n)$ as well. By the statements above, for any $\epsilon > 0$, we have

$$(1 - \epsilon) \int |\nabla \Psi|^2 - c_\epsilon \leq \mathcal{E}_{v_n+v}(\Psi) \leq c_{d,N,v}$$

uniformly in Ψ and in n , for some $c_\epsilon \geq 0$. Hence Ψ_n is bounded in $H^1(\Omega)$ and $\Psi_n \rightharpoonup \Psi_\infty$ weakly in $H^1(\Omega)$ for some $\Psi_\infty \in H^1(\Omega)$ and up to a subsequence. We have $\int |\nabla \sqrt{\rho_n}|^2 \leq \int |\nabla \Psi_n|^2$ so $\sqrt{\rho_n}$ is bounded in $H^1(\Omega)$, hence there is some $\chi \geq 0$ in $H^1(\Omega)$ such that $\sqrt{\rho_n} \rightharpoonup \chi$ weakly in $H^1(\Omega)$ hence strongly in $L^2(\Omega)$ locally. We define $\rho_\infty := \chi^2$. Let $\epsilon > 0$, and let us decompose $\int v_n \rho_n$ into

$$\begin{aligned} \left| \int_\Omega v_n \rho_n \right| &\leq \left| \int_{B_r \cap \Omega} v_n (\rho_n - \rho_\infty) \right| + \left| \int_{B_r \cap \Omega} v_n \rho_\infty \right| + \left| \int_{\Omega \setminus B_r} v_n \rho_n \right| \\ &\leq \left| \int_{B_r \cap \Omega} v_n (\sqrt{\rho_n} - \sqrt{\rho_\infty}) (\sqrt{\rho_n} + \sqrt{\rho_\infty}) \right| + \left| \int_{B_r \cap \Omega} v_n \rho_\infty \right| \\ &\quad + \|v_n\|_{(L^p+L^\infty)(\Omega \setminus B_r)} \sup_{n \in \mathbb{N}} \|\sqrt{\rho_n}\|_{H^1}. \end{aligned} \quad (4.21)$$

Also, the sequence $\|v_n\|_{L^p+L^\infty}$ is bounded. We take r large enough so that $\Lambda \subset B_r$, and recall that $v_n \mathbf{1}_{\Omega \setminus B_r} \rightarrow 0$ strongly. Then we take n large enough so that the last term in (4.21) is smaller than ϵ , which is possible since $v_n \mathbf{1}_{\Omega \setminus \Lambda} \rightarrow 0$. We also take n large enough so that the second term in (4.21) is smaller than ϵ . As for the first term, we will need that for any functions f, g, h in the appropriate spaces,

$$\left| \int fgh \right| \leq \|f\|_{L^{p+\delta}} \|g\|_{L^{\frac{2d}{d-2}-\eta(\delta)}} \|h\|_{L^{\frac{2d}{d-2}}} \leq \|f\|_{L^{p+\delta}} \|g\|_{W^{1-\lambda, \frac{2d}{d-2\lambda}-\xi(\delta,\lambda)}} \|h\|_{H^1}.$$

where $\eta(\delta) = \frac{16\delta}{(d-2)(d-2+2\delta(1+2/d))}$, $\xi(\delta, \lambda) = \frac{\eta(\delta)(d-2)}{(d-2\lambda)(1+\frac{1-\lambda}{d}(\frac{2d}{d-2}-\eta(\delta)))}$, this holds for any $\delta \geq 0$ and any $\lambda \in]0, 1[$ small enough, and we used the Hölder and Gagliardo-Nirenberg inequalities. We apply it to our decomposition, where $\sqrt{\rho_n} \rightarrow \sqrt{\rho_\infty}$ strongly in $W^{1-\lambda, \frac{2d}{d-2\lambda}-\xi(\delta,\lambda)}(B_r \cap \Omega)$ by the theorem of Rellich-Kondrachov, where $\lambda > 0$ and $\delta > 0$ are close to zero. This term is smaller than ϵ for n large enough, and we conclude that $\int v_n \rho_n \rightarrow 0$ for the considered subsequence.

• Since $w \geq 0$, then E is weakly upper semi-continuous, and we have $\limsup E^N(v+v_n) \leq E^N(v)$. Moreover, let $\Gamma_\infty = G_0 \oplus \dots \oplus G_N$ with $\text{Tr} \Gamma_\infty = 1$ being a geometric limit defined in [19, Definition 2.1], up to a further subsequence, of $|\Psi_n\rangle \langle \Psi_n|$ in the sector of the Fock space with number of particles less than N . This last space is compact as shown in [19, Lemma 2.2]. Since

$$E^N(v+v_n) \leq \mathcal{E}_{v+v_n}(\Psi_n) = \mathcal{E}_v(\Psi_n) + \int v_n \rho_n \leq E^N(v+v_n) + \frac{1}{n},$$

then by weak semi-continuity of \mathcal{E}_v under geometric convergence [19, Lemma 2.4], we have

$$\begin{aligned} \liminf E^N(v + v_n) &\geq \mathcal{E}_v(\Gamma_\infty) = \sum_{m=0}^N \text{Tr } H^m(v) G_m \geq \sum_{m=0}^N E^m(v) \text{Tr } G_m \\ &\geq E^N(v). \end{aligned} \quad (4.22)$$

We used the HVZ theorem to deduce that $E^M(v)$ is decreasing in M in the last inequality. We thus have $E^N(v + v_n) \rightarrow E^N(v) = \mathcal{E}_v(\Gamma_\infty)$. We did not use the assumption $v \in \mathcal{V}^N$ yet, so repeating the same argument, we can also deduce that $E^n(v + v_n) \rightarrow E^n(v)$ for any $n \in \{1, \dots, N\}$.

Since $E^{N-1}(v + v_n) \rightarrow E^{N-1}(v)$, then

$$\Sigma^N(v + v_n) = E^{N-1}(v + v_n) \rightarrow E^{N-1}(v) = \Sigma^N(v) > E^N(v),$$

where we also used that $v \in \mathcal{V}^N$ and $E^{N-1}(v) = \Sigma^N(v)$ by the HVZ theorem. Hence for n large enough, we have $E^N(v + v_n) < \Sigma^N(v + v_n)$ and $v + v_n \in \mathcal{V}^N$.

Since $v \in \mathcal{V}^N$ and by the HVZ theorem, we have $E^N(v) < E^{N-1}(v)$ so since $E^n(v)$ strictly decreases in n , we have $E^N(v) < E^m(v)$ for any $m \in \{0, \dots, N-1\}$. By considering (4.22) again, we have $\sum_{m=0}^N E^m(v) \text{Tr } G_m = E^N(v)$ and can deduce that $\text{Tr } G_N = 1$. This yields $|\Psi_n\rangle \langle \Psi_n|$ converges geometrically to Γ_∞ , with $\text{Im } \Gamma_\infty \subset \text{Ker}(H^N(v) - E^N(v)) = \mathbb{C}\Psi(v)$. By [19, Lemma 2.1], we deduce that $|\Psi_n\rangle \langle \Psi_n| \rightarrow |\Psi(v)\rangle \langle \Psi(v)|$ in $\mathfrak{S}_{1,0}$, and since

$$\| |\Psi_n\rangle \langle \Psi_n| \|_{\mathfrak{S}_{1,0}} = \text{Tr } \| |\Psi_n\rangle \langle \Psi_n| \| = \text{Tr } |\Psi_n\rangle \langle \Psi_n| = 1 = \| |\Psi(v)\rangle \langle \Psi(v)| \|_{\mathfrak{S}_{1,0}},$$

then $|\Psi_n\rangle \langle \Psi_n| \rightarrow |\Psi(v)\rangle \langle \Psi(v)|$ in $\mathfrak{S}_{1,0}$, so $\Psi_n \rightarrow \Psi(v)$ in $L^2_{\mathbb{P}}$ up to a subsequence. A posteriori this also holds for the full sequence by uniqueness of the limit $\Psi(v)$. Moreover, Ψ_n converges to $\psi(v)$ weakly in H^1 and strongly in L^2 , where $\psi(v)$ is a representative in L^2 of $\Psi(v)$. Since the norm associated to \mathcal{E}_v is equivalent to the H^1 one, then $\Psi_n \rightarrow \psi(v)$ strongly in H^1 . By continuity of the map $\Psi \mapsto \rho$, we also have $\rho_\infty = \rho_{\Psi_\infty}$.

• (iv) When Ω is bounded, Lemma 4.5.6 implies that $v \mapsto \Psi(v)$ and its differential are compact, and Ψ^{-1} is discontinuous. \square

We turn to the proof of Proposition 4.1.3.

Proof of Proposition 4.1.3 (iii) and (iv). Here we will write Ψ for a representative of $\Psi(v)$ and Ψ_n for a representative of $\Psi(v_n)$, and define $V_n := v_n - E^N(v_n)/N$ and $V := v - E^N(v)/N$. We have Schrödinger's equations

$$(\sum_i (V_n)_i) \Psi_n = (\Delta - \sum_{ij} w_{ij}) \Psi_n, \quad (\sum_i V_i) \Psi = (\Delta - \sum_{ij} w_{ij}) \Psi.$$

Since $p > \max(2d/3, 2)$, then w and V_n are infinitesimally bounded by $(-\Delta)$ in the sense of operators with uniform constants, and therefore

$$\begin{aligned} \|\sum_i (V_n - V)_i \Psi\|_{L^2} &= \left\| (-\Delta + \sum_{ij} w_{ij} + \sum_i (V_n)_i)(\Psi_n - \Psi) \right\| \\ &\leq c_{d,N} \left(c_{w,d} + \|V_n\|_{L^p + L^\infty} \right) \|\Psi_n - \Psi\|_{H^2}. \end{aligned}$$

Since V_n is bounded in $L^p + L^\infty$, then $\|\sum_i (V_n - V)_i \Psi\|_{L^2} \rightarrow 0$. We also deduce that $\sum_i (V_n - V)_i \Psi \rightarrow 0$ a.e. in Ω^N up to a subsequence. By unique continuation [8], the nodal set

$$S := \{x \in \Omega^N \mid \Psi(x) = 0\}$$

has zero measure in Ω^N and we deduce that

$$\sum_{i=1}^N v_n(x_i) \xrightarrow{n \rightarrow +\infty} \sum_{i=1}^N v(x_i),$$

a.e. in Ω^N , up to a constant and to a subsequence. We can deduce that $v_n \rightarrow v$ a.e. up to a subsequence by using Lemma 4.5.5 provided at the end of this proof. Since $v_n - v$ is bounded, then $v_n \rightharpoonup v$ weakly in $L^p + L^\infty$. We have

$$\begin{aligned} \|\sum_i (V_n - V)_i \Psi\|_{L^2} &= \int_{\Omega} (v_n - v)^2 \rho_{\Psi} + 2 \int_{\Omega^2} (v_n - v)(x)(v_n - v)(y) \rho_{\Psi}^{(2)}(x, y) dx dy, \end{aligned}$$

where $\rho_{\Psi}^{(2)}(x, y) := N(N-1)/2 \int |\Psi|^2(x, y, x_3, \dots, x_N) dx_3 \cdots dx_N$ is the pair density of Ψ . Since $v_n \rightharpoonup v$ weakly, then

$$\int_{\Omega^2} (v_n - v)(x)(v_n - v)(y) \rho_{\Psi}^{(2)}(x, y) dx dy \rightarrow 0$$

and we conclude that $\int_{\Omega} (v_n - v)^2 \rho_{\Psi} \rightarrow 0$. \square

Lemma 4.5.5. *Let $v_n \in L^1_{\text{loc}}(\mathbb{R}^d)$. Then $v_n \xrightarrow{n \rightarrow +\infty} 0$ a.e. in \mathbb{R}^d if and only if $\sum_i v_n(x_i) \xrightarrow{n \rightarrow +\infty} 0$ a.e. in \mathbb{R}^{dN} .*

Proof. Let $S \subset \mathbb{R}^d$ be the set of x 's such that $v_n(x) \xrightarrow{n \rightarrow +\infty} 0$. Then for $(x_1, \dots, x_N) \in S^N$, we have $\sum_i v_n(x_i) \xrightarrow{n \rightarrow +\infty} 0$, and S^N has full measure in \mathbb{R}^{dN} .

For the converse statement, we define

$$L := \left\{ x \in \mathbb{R}^d \mid v_n(x) + \sum_{i=1}^{N-1} v_n(x_i) \xrightarrow{n \rightarrow +\infty} 0 \text{ a.e. in } (x_1, \dots, x_{N-1}) \in \mathbb{R}^{d(N-1)} \right\},$$

and for any $x \in L$ we define

$$L_x := \left\{ (x_1, \dots, x_{N-1}) \in \mathbb{R}^{d(N-1)} \mid v_n(x) + \sum_{i=1}^{N-1} v_n(x_i) \xrightarrow{n \rightarrow +\infty} 0 \right\}.$$

By the theorem of Fubini, L has full measure in \mathbb{R}^d and L_x has full measure in $\mathbb{R}^{d(N-1)}$. We also define

$$L' := \left\{ (x_1, \dots, x_{N-1}) \in \mathbb{R}^{d(N-1)} \mid v_n(y) + \sum_{i=1}^{N-1} v_n(x_i) \xrightarrow{n \rightarrow +\infty} 0 \text{ a.e. } y \in \mathbb{R}^d \right\}.$$

and for $(x_1, \dots, x_{N-1}) \in L'$,

$$L'_{(x_1, \dots, x_{N-1})} := \left\{ y \in \mathbb{R}^d \mid v_n(y) + \sum_{i=1}^{N-1} v_n(x_i) \xrightarrow{n \rightarrow +\infty} 0 \right\}.$$

L' has full measure in $\mathbb{R}^{d(N-1)}$ and $L_{(x_1, \dots, x_{N-1})}$ has full measure in \mathbb{R}^d . Now let $y_1, \dots, y_{N-1} \in L$ such that $(y_1, \dots, y_{N-1}) \in L'$, and let $y'_1, \dots, y'_{N-1} \in L'_{(y_1, \dots, y_{N-1})} \cap L$. We have

$$v_n(y'_i) \underset{n \rightarrow +\infty}{\sim} - \sum_{k=1}^{N-1} v_n(y_k)$$

for any $i \in \{1, \dots, N-1\}$, therefore

$$\sum_{k=1}^{N-1} v_n(y'_k) \underset{n \rightarrow +\infty}{\sim} -(N-1) \sum_{k=1}^{N-1} v_n(y_k).$$

Now let $z \in L'_{(y_1, \dots, y_{N-1})} \cap L'_{(y'_1, \dots, y'_{N-1})}$, we have

$$v_n(z) \underset{n \rightarrow +\infty}{\sim} - \sum_{k=1}^{N-1} v_n(y_k) \quad \text{and} \quad v_n(z) \underset{n \rightarrow +\infty}{\sim} - \sum_{k=1}^{N-1} v_n(y'_k),$$

and therefore

$$\frac{1}{N-1} v_n(z) \underset{n \rightarrow +\infty}{\sim} \sum_{k=1}^{N-1} v_n(y_k),$$

and finally we obtain $v_n(z) \xrightarrow{n \rightarrow +\infty} 0$. Since $L'_{(y_1, \dots, y_{N-1})} \cap L'_{(y'_1, \dots, y'_{N-1})}$ has full measure in \mathbb{R}^d , then $v_n(z) \xrightarrow{n \rightarrow +\infty} 0$ a.e. in $z \in \mathbb{R}^d$. \square

4.5.4 The potential-to-density map ρ : proof of Theorem 4.1.1

Proof of Theorem 4.1.1.

(i) We can decompose $\rho = \tilde{\rho} \circ \Psi$ and those two maps are smooth so the composition is so as well.

(ii) • The differential is injective because if $(d_v \rho)u = 0$, then

$$(1 - \mathcal{P}(v)) (\sum_i u_i) \Psi(v) = 0,$$

so $(\sum_i u_i) \Psi(v) = \alpha \Psi(v)$ for some constant $\alpha \in \mathbb{R}$. By unique continuation [8], we deduce that $\sum_i u_i = \alpha$ and then u is constant.

• The operator $d_v \rho$ cannot be simultaneously compact, surjective and continuous, by the open mapping theorem. The formula for the differential follows from (4.20) and Lemma 4.4.1. The bounds follow from Theorem 4.5.4, and by the smoothness of $\tilde{\rho}$ implying that $\|d_\Psi \tilde{\rho}\|_{W^{k,1} \rightarrow H^k}$ is bounded for any $k \in \mathbb{N}$. Let us denote by $E_1^N(v)$ the first excited eigenvalue if it exists, or $\Sigma^N(v)$ otherwise. An expression for the quadratic form $d_v \rho$ is

$$\begin{aligned} & - \langle u, (d_v \rho)u \rangle \\ &= 2 \left\langle (\sum_i u_i) \Psi(v), (H^N(v) - E^N(v))_{\perp}^{-1} (\sum_i u_i) \Psi(v) \right\rangle \\ &= 2 \left\langle (1 - \mathcal{P}(v)) (\sum_i u_i) \Psi(v), (H^N(v) - E^N(v))_{\perp}^{-1} (\sum_i u_i) \Psi(v) \right\rangle \\ &= 2 \left\| (H^N(v) - E^N(v))_{\perp}^{-\frac{1}{2}} (\sum_i u_i) \Psi(v) \right\|^2. \end{aligned}$$

We remark that for any $u \in L^p + L^\infty$, we have $\langle u, (d_v \rho)u \rangle < 0$. The inequality $\int (v-u)(\rho(v)-\rho(u)) < 0$ for any potentials v, u such that $v-u \neq 0$, presented in [6, Section 2.3], implies $\langle u, (d_v \rho)u \rangle < 0$ for any potential which is not constant, hence $d_v \rho < 0$ in the sense of forms. \square

The fact that $\text{Im } d_v \rho$ is probably dense in $W^{1,1}$ could suggest to prove a local surjectivity result using [1, Theorem 2.5.9] or [25]. Unfortunately, the compactness of $d_v \rho$ prevents us from doing so.

Proof of Corollary 4.1.4. In this particular case, $\mathcal{V}^N = L^p + L^\infty = L^p$. By Theorem 4.5.4 and Theorem 4.1.1, ρ is weak-strong continuous. We conclude by applying Lemma 4.5.6 (iii). \square

4.5.5 The potential-to-ground energy map

Finally, the regularity of $v \mapsto \rho(v)$ can be transported to $v \mapsto E^N(v)$.

Proof of Corollary 4.1.2.

• The energy is weakly upper-semicontinuous by the same proof as for the weak lower-semicontinuity of the Lieb functional [21, Theorem 3.6]. It is Lipschitz continuous and concave by [21, Theorem 3.1].

- We can decompose $E^N(v) = \langle \Psi(v), H^N(0)\Psi(v) \rangle + \int v\rho(v)$, where $v \mapsto \int v\rho(v)$ is \mathcal{C}^∞ because $v \mapsto \rho(v)$ is so, and $(\varphi, \phi) \mapsto \langle \varphi, H^N(0)\phi \rangle$ is bilinear so $v \mapsto \langle \Psi(v), H^N(0)\Psi(v) \rangle$ and $v \mapsto E^N(v)$ are \mathcal{C}^∞ .

- As for the differential, we start by following similar arguments as in [23, Theorem II.16]. By definition of the minima, we have

$$E^N(v+u) - E^N(v) \leq \mathcal{E}_{v+u}(\Psi(v)) - \mathcal{E}_v(\Psi(v)) = \int u\rho(v),$$

$$\int u\rho(v+u) = \mathcal{E}_{v+u}(\Psi(v+u)) - \mathcal{E}_v(\Psi(v+u)) \leq E^N(v+u) - E^N(v),$$

hence

$$\int u(\rho(v+u) - \rho(v)) \leq E^N(v+u) - E^N(v) - \int u\rho(v) \leq 0.$$

By the Gagliardo-Nirenberg inequality, if $q \in [1, d/(d-1)]$ (with $d/(d-1) := +\infty$ if $d = 1$), then for any $f \in W^{1,1}(\mathbb{R}^d)$,

$$\|f\|_{L^q} \leq c \|\nabla f\|_{L^1}^{d(1-\frac{1}{q})} \|f\|_{L^1}^{1-d(1-\frac{1}{q})}.$$

Take $q := p/(p-1) \in [1, d/(d-1)]$. By continuity of ρ proved in Theorem 4.1.1, we have

$$\begin{aligned} \left| E^N(v+u) - E^N(v) - \int u\rho(v) \right| &\leq \left| \int u(\rho(v+u) - \rho(v)) \right| \\ &\leq c \|u\|_{L^p+L^\infty} \|\rho(v+u) - \rho(v)\|_{L^1 \cap L^q} \\ &\leq c \|u\|_{L^p+L^\infty} (\|\rho(v+u) - \rho(v)\|_{L^1} + \|\rho(v+u) - \rho(v)\|_{L^q}) \\ &\leq c \|u\|_{L^p+L^\infty}^{1+\min(1, d(1-\frac{1}{q}))}, \end{aligned}$$

and $q > 1$ so $1 + \min(1, d(1 - \frac{1}{q})) > 1$ and this proves the existence of the differential.

- We show that $E^N(v)$ is strictly decreasing on \mathcal{V}_∂^N . Take $u \in \mathcal{V}_\partial^N$, $v \in \mathcal{V}$ with $v \leq u$, and $v < u$ on a set of positive measure. By unique continuation [8, Remark 1.6], the nodal set of $\rho(u)$ has zero volume, hence $|\{v\rho(u) < u\rho(u)\}| > 0$ and

$$E^N(v) \leq \mathcal{E}_0(\Psi(u)) + \int v\rho(u) < \mathcal{E}_0(\Psi(u)) + \int u\rho(u) = E^N(u).$$

- Eventually, we prove by contradiction that E^N is strictly concave on \mathcal{V}_∂^N . Let $v, u \in \mathcal{V}_\partial^N$, we start from the point u and look at the (half line) direction $v - u$. By using the concavity of E^N and formula (5.9), we have

$$E^N(v) - E^N(u) \leq \left({}^+\delta_u E^N \right) (v - u) = \inf_{\substack{\Psi \in \text{Ker}(H^N(u) - E^N(u)) \\ \int |\Psi|^2 = 1}} \int \rho_\Psi(v - u).$$

The minimizing set in the right hand side of the previous inequality is compact, let us denote by $\Psi_{u,v}$ one of the minimizers. This yields

$$E^N(v) - E^N(u) \leq \mathcal{E}_v(\Psi_{u,v}) - \mathcal{E}_u(\Psi_{u,v}) = \mathcal{E}_v(\Psi_{u,v}) - E^N(u).$$

Let us assume that we have equality above, then $E^N(v) = \mathcal{E}_v(\Psi_{u,v})$. The following is the same argument as the second part of the Hohenberg-Kohn theorem [15], as presented in [6, Proof of Theorem 2.1] for instance. We know that $\Psi_{u,v}$ is a ground state for $H^N(v)$, hence it respects its Schrödinger's equation $H^N(v)\Psi_{u,v} = E^N(v)\Psi_{u,v}$. Subtracting with $\Psi_{u,v}$'s own Schrödinger's equation, we obtain $(E^N(u) - E^N(v) + \sum_i(v - u)_i)\Psi_{u,v} = 0$, and by strong unique continuation [7, 8], that $v = u + (E^N(v) - E^N(u))/N$. \square

4.5.6 Appendix: weak-strong continuity and compactness

We recall here relations between weak-strong continuity and compactness.

Following [14, Definition 7.6], we say that a map is compact if it maps bounded sets into relatively compact sets. The link between ill-posedness of a problem and its linearization can be involved, see for instance [28] and [4, Appendix]. We start by considering standard results, and adapt them to the case when the image space is an embedded submanifold.

Lemma 4.5.6. *Let X and Y be Banach spaces, $U \subset X$ an open set, $M \hookrightarrow Y$ a closed embedded submanifold of Y , and a map $f : U \rightarrow M$.*

- (i) *If f is compact, continuous and differentiable on U , then $d_x f$ is compact for any $x \in U$.*
- (ii) *If $U = X$ is the dual of a Banach space, and if f is weak-strong continuous, then f is compact.*
- (iii) *If f is compact and M is infinite-dimensional, then $f(X)$ is a countable union of compact sets, and $f(X)$ has empty interior.*
- (iv) *If f is compact and X is infinite-dimensional, then f^{-1} is discontinuous.*

Proof. The only difference in the proof, with respect to the standard $M = Y$ case, is (i).

(i) In the case $M = Y$, this is proved in [14]. We apply it to $\iota_{M \rightarrow Y} \circ f : U \rightarrow Y$ and get that $d_x(\iota_{M \rightarrow Y} \circ f)(X \cap \{\|\cdot\| \leq 1\}) = \iota_{T_{f(x)}M \rightarrow Y} \circ (d_x f)(X \cap \{\|\cdot\| \leq 1\})$ is compact. A map is proper if preimages of relatively compact open sets are relatively compact open sets [30, Definition 16.26]. One can prove that for a Banach space F and a closed subset $E \subset F$, the inclusion map $E \hookrightarrow F$ is proper. Since $\iota_{T_{f(x)}M \rightarrow Y}$ is proper,

then $(d_x f)(X \cap \{\|\cdot\| \leq 1\})$ is relatively compact. We remark that we only used that $M \hookrightarrow Y$ is an embedded submanifold of Y , we did not use the closed condition.

(ii) Let $G \subset B_0(r) \subset X$ be a bounded set and $x_n \in G$ a sequence. By Banach-Alaoglu's theorem, $x_n \rightharpoonup x$ for some $x \in B_0(r)$ and up to a subsequence. By weak-strong continuity of f , $f(x_n) \rightarrow f(x)$ strongly.

(iii) We define the sets $X_r := X \cap \{x \in X \mid \|x\|_X \leq r\}$, for $r \geq 0$. Since f is compact, then the $\overline{f(X_r)}$'s are compact and thus have empty interiors by Riesz's theorem [2, Theorem 6.5], which applies in our case because M is locally a normed vector space. We have

$$f(X) = \cup_{r \in \mathbb{N}} f(X_r) \subset \cup_{r \in \mathbb{N}} \overline{f(X_r)}.$$

Finally, by Baire's theorem [2, Theorem 2.1] $f(X)$ has empty interior. We recall that a closed subset of a compact space is compact.

(iv) Let $B \subset X$ be a ball, $f(B)$ is relatively compact. Assuming that f^{-1} is continuous, $f^{-1}(f(B)) \supset B$, is also relatively compact, and hence B as well. But this is a contradiction with [2, Theorem 6.5]. The inverse f^{-1} is thus discontinuous. \square

Here is a summary of the relations between compactness and weak-strong continuity for a map and its differential.

$$\begin{array}{ccc} f \text{ compact} & \implies & d_x f \text{ compact } \forall x \\ \text{if } U = X \text{ is a dual } \uparrow & & \downarrow \uparrow \text{if } X \text{ reflexive} \\ f \text{ locally weak-strong } \mathcal{C} & & d_x f \text{ weak-strong } \mathcal{C} \forall x \end{array}$$

We also remark that $d_x f$ weak-strong continuous for any $x \in U$ does not imply that f is weak-strong continuous, a simple counterexample is $L^2(\mathbb{R}^n) \ni x \mapsto \|x\|_{L^2}^2$, and this is also the case for ρ . Lemma 4.5.6 enables us to justify Corollary 4.1.4 on the discontinuity of ρ .

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Chapter 5

Perturbations of degenerate systems

In the previous chapter we studied the set of non-degenerate potentials. Here we look at the situation where the first (or any other) eigenvalue is degenerate, but still isolated from the rest of the spectrum. A very natural question is to ask whether the degeneracy can be lifted by perturbing a little bit the external potential v and, if it is so, to which order in the perturbation this happens. The effect of a small perturbation can in principle be computed exactly to any order, but the formulas are not easy to handle in the case of an external potential. We explain here the situation for the first order and prove, in particular, that in a non interacting system ($w = 0$), most perturbations will lift a two-fold degenerate ground state. The important question of whether this holds for higher degeneracies or for $w \neq 0$ will, unfortunately, be left open.

Perturbation theory started with the work of Rayleigh on the propagation of sound, which inspired Schrödinger [15, 16] to apply it to quantum mechanics in its beginning, initially used for the Stark and Zeeman effects. Perturbation theory for systems at equilibrium is one of the main approaches in quantum mechanics. It is versatile and has been extensively studied and applied in many situations. Its mathematical framework was initiated by Kato, among others, and is presented in [10, 13, 19] for instance. See also the reviews [5, 11].

By perturbing the initial Hamiltonian having a degenerate level, one usually wants to know whether the degeneracy will be broken, and compute the eigenenergies and eigenstates shifts. This has been extensively studied when the symmetry group breaks into a subgroup, providing important concepts in theoretical physics in general. One can refer to [14, Chapter 5.2] for a first presentation. The analysis of degenerate perturbation produces quite involved structures in general cases [1, 2, 4, 6, 17], see also [9, Section 5], [13, p28] and [3, 7] for mathematical aspects, as well as [12, 20] for reviews.

In [4], Hirschfelder studied the most general case where the perturbation is analytic, that is of the form $\sum_{i=1}^{+\infty} \lambda^i h_i$, and he provided a full solution of the Rayleigh-Schrödinger series.

We present those relations and recall the mechanism of solving the problem in Section 5.1.1. Then in Section 5.1.2, we apply these results to many-body systems and link them to questions arising from the general DFT framework.

5.1 Results

5.1.1 Known results

We work here in a general case where we consider a separable complex Hilbert space \mathcal{H} carrying states, its scalar product is denoted by $\langle \cdot, \cdot \rangle$. We consider a general perturbation operator, which can be chosen to be an electric or magnetic potential, a non-local one, an operator acting on spin, an interaction etc.

In a neighborhood of $\lambda = 0$, we study a Hamiltonian in the form

$$H(\lambda) := \sum_{n=0}^{\infty} \lambda^n h^{(n)},$$

where $H(0) = h^{(0)} = H$ is our initial operator. In particular, we study the level E , and define $D := \dim \text{Ker}(H - E)$. Our starting point is [18, Theorem 1.4.4, Corollary 1.4.5], stating that close to $\lambda = 0$, the singularities arising from degeneracies are removable. In the given reference this is stated for $\mathcal{H} = L^2(\mathbb{R}^d)$ but this applies for any separable Hilbert space. It justifies the existence of D maps $E_i : \mathbb{R} \rightarrow \mathbb{R}$, $\phi_i : \mathbb{R} \rightarrow \mathcal{H}$, $i \in \{1, \dots, D\}$, analytic in a neighborhood of 0, E_i being the eigenvalues of $H(\lambda)$ such that $E_i(0) = E$, and their associated orthonormal eigenfunctions ϕ_i . By analyticity, E_i and ϕ_i can be expressed in the so-called Rayleigh-Schrödinger series

$$E_i(\lambda) = \sum_{n=0}^{+\infty} \lambda^n E_i^{(n)}, \quad \phi_i(\lambda) = \sum_{n=0}^{+\infty} \lambda^n \phi_i^{(n)}, \quad (5.1)$$

valid in a neighborhood of 0 and solving Schrödinger's equation

$$H(\lambda)\phi_i(\lambda) = E_i(\lambda)\phi_i(\lambda). \quad (5.2)$$

We sort the energies by increasing order in the sense that $E_i(\lambda) \leq E_{i+1}(\lambda)$ asymptotically for $\lambda \rightarrow 0^+$. There can be several possible definitions of E_i and ϕ_i with those constraints, but this will not affect the results presented here. The coefficients are the derivatives $E_i^{(n)} = (n!)^{-1} (d^n E_i / d\lambda^n)(0)$ and

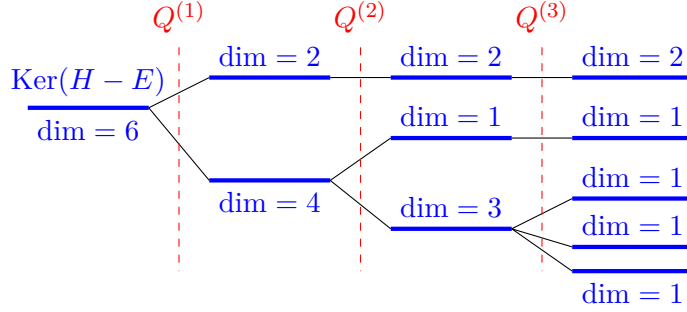


Figure 5.1: Example of successive breakings of degeneracies, at different orders. Illustrates (5.3).

$\phi_i^{(n)} = (n!)^{-1} (d^n \phi_i / d\lambda^n)(0)$. By defining $H^{(n)} := h^{(n)} - E_i^{(n)}$, equation (5.2) can be rewritten as

$$\sum_{k=0}^n H^{(k)} \phi_i^{(n-k)} = 0,$$

for any $n \geq 0$.

We need to do a “tree diagonalization” to find all the quantities we want. Even if its rigorous description can seem technical, it is quite intuitive. The picture is that some central operators $Q_{n-2}^{(n)}$ are successively diagonalized, each time by reducing our attention to some eigenspaces $\text{Im } P_i^{(n)}$. This defines a series of eigenvalues and eigenprojections, where the eigenvalues correspond to the Rayleigh-Schrödinger series $E_i^{(n)}$, and the ranks of the eigenprojections $\text{dim Im } P_i^{(n)}$ decrease. Thus there exists $M \in \mathbb{N}$ such that for any $n \geq M$, the dimensions of the spaces $\text{Im } P_i^{(n)}$ remain constant, at this point all removable degeneracies are removed. If $\text{dim Im } P_i^{(M)} = 1$ for any $i \in \{1, \dots, D\}$, the degeneracy is completely broken at order M and the natural orthonormal basis of $\text{Ker}(H - E)$ is $(\phi_i^{(0)})_{1 \leq i \leq D}$, where the $\phi_i^{(0)}$ are extracted from the projections $P_i^{(M)}$. Otherwise, some degeneracies remain but we still obtain the projections on both broken and unbroken eigenspaces. To illustrate our presentation, we display in Figure 5.1 a graphical representation of a situation corresponding to the example

$$\begin{aligned} E_1(\lambda) &= E - 2\lambda + 3\lambda^2 - 5\lambda^3 + O(\lambda^4), & E_2(\lambda) &= E - 2\lambda + 3\lambda^2 - 4\lambda^3 + O(\lambda^4) \\ E_3(\lambda) &= E - 2\lambda + 3\lambda^2 + \lambda^3 + O(\lambda^4), & E_4(\lambda) &= E - 2\lambda + 4\lambda^2 - \lambda^3 + O(\lambda^4) \\ E_5(\lambda), E_6(\lambda) &= E + 3\lambda - \lambda^2 + \lambda^3 + O(\lambda^4). \end{aligned} \tag{5.3}$$

Here a 6-fold degenerate system is split into smaller degeneracies, depending on the order in λ .

Computing the zero order eigenbasis and the energies shifts

We now explain how to find the Rayleigh-Schrödinger series, from the work of Hirschfelder [4]. Let P be the orthogonal projection of \mathcal{H} onto the degenerate eigenspace $\text{Ker}(H - E)$. For any $n \in \mathbb{N}$, we define the eigenprojections

$$P_i^{(n)} := \sum_{\substack{1 \leq j \leq D \\ E_j^{(\ell)} = E_i^{(\ell)} \forall \ell \in \{1, \dots, n\}}} |\phi_j^{(0)}\rangle \langle \phi_j^{(0)}|,$$

corresponding to the eigenspaces at order n in λ , the complementary projections

$$\tilde{P}_i^{(n)} := \sum_{\substack{1 \leq j \leq D \\ E_j^{(\ell)} = E_i^{(\ell)} \forall \ell \in \{1, \dots, n-1\} \\ E_j^{(n)} \neq E_i^{(n)}}} |\phi_j^{(0)}\rangle \langle \phi_j^{(0)}|.$$

and the resolvents $R_0 := -(H - E)_\perp^{-1} P_\perp$, and for $n \geq 1$,

$$R_n := \sum_{\substack{1 \leq j \leq D \\ E_j^{(\ell)} = E_i^{(\ell)} \forall \ell \in \{1, \dots, n-1\} \\ E_j^{(n)} \neq E_i^{(n)}}} \frac{|\phi_j^{(0)}\rangle \langle \phi_j^{(0)}|}{E_j^{(n)} - E_i^{(n)}}.$$

Let us define the operators $\Gamma_{-1}^{(n)} := H_i^{(n)}$ for $n \geq 0$, and for $n \geq 0$, $p \geq 0$, we define the operators $\Gamma_p^{(n)}$ by the recursive formula

$$\Gamma_p^{(n)} = \Gamma_{p-1}^{(n)} + \sum_{k=p+1}^{n-1} \Gamma_{p-1}^{(k)} R_p \Gamma_p^{(n-k+p)}. \quad (5.4)$$

Let us choose one state label i . Then it is shown in [4] that for any $n \geq 1$, and for any state $\phi_j^{(0)} \in \text{Im } P_i^{(n-1)}$, we have

$$\boxed{P_i^{(n-1)} \Gamma_{n-2}^{(n)} P_i^{(n-1)} \phi_i^{(0)} = 0.} \quad (5.5)$$

Moreover, the operator $M_n := \Gamma_{n-2}^{(n)} + E_i^{(n)}$ contains only terms $E_i^{(\ell)}$ with $\ell \leq n-1$, hence the diagonalization (5.5) gives the energy shifts $E_j^{(n)} = \langle \phi_j^{(0)}, M_n \phi_j^{(0)} \rangle$ of the states $\phi_j^{(0)} \in \text{Im } P_i^{(n-1)}$, which are the eigenvalues, and it gives the eigenprojections $P_j^{(n)}$. It also constrains the basis states

which have to respect $\phi_j^{(0)} \in \text{Im } P_j^{(n)}$. This is the tree diagonalization. We can also explicit the operator

$$\tilde{P}_i^{(n)} \Gamma_{n-2}^{(n)} \tilde{P}_i^{(n)} = \sum_{\substack{j \in \{1, \dots, D\} \\ E_j^{(\ell)} = E_i^{(\ell)} \forall \ell \leq n}} (E_i^{(n)} - E_j^{(n)}) |\phi_j^{(0)}\rangle \langle \phi_j^{(0)}|.$$

Remark that we can compute $\phi_i^{(0)}$ and $E_i^{(n)}$ independently from $\phi_i^{(n)}$. Those formulas enable to compute the $\phi_i^{(0)}$'s, up to $U(D_i^{(M)})$ rotations in case some degeneracies are never broken, that is, in case $D_i^{(M)} \geq 2$ for some i 's.

Gauge

We normalize the states $\phi_i^{(0)}$ to 1 by convention. Let us show that we can choose the Rayleigh-Schrödinger series (5.1) such that

$$\phi_i^{(n)} \perp \phi_i^{(0)}, \quad \forall n \geq 1, \quad \forall i \in \{1, \dots, D\}. \quad (5.6)$$

Decomposing the states series onto $\mathbb{C}\phi_i^{(0)}$ and its orthogonal space, we have

$$\phi_i(\lambda) = \left(1 + \sum_{j=1}^{+\infty} \lambda^j \langle \phi_i^{(0)}, \phi_i^{(j)} \rangle \right) \phi_i^{(0)} + \sum_{i=1}^{+\infty} \lambda^i P_{\phi_i^{(0)}}^\perp \phi_i^{(i)}.$$

Dividing by $1 + \sum_{j=1}^{+\infty} \lambda^j \langle \phi_i^{(0)}, \phi_i^{(j)} \rangle$, we obtain a new series which still respects Schrödinger's equation, and respects (5.6). We remark that we cannot freely normalize $\|\phi_i(\lambda)\| = 1$ and at the same time fix (5.6). For instance if we also have $\|\phi_i^{(0)}\| = 1$, then the first order equation in λ of $\|\phi_i(\lambda)\| = 1$ is $2 \text{Re} \langle \phi_i^{(2)}, \phi_i^{(0)} \rangle + \|\phi_i^{(1)}\|^2 = \|\phi_i^{(1)}\|^2 = 0$, so $\phi_i^{(1)} = 0$. We see that this normalization modifies the Rayleigh-Schrödinger series. For this reason, in this document we will not consider that our vectors are normalized, but we will consider that they respect (5.6). Only the $\phi_i^{(0)}$'s are normalized to one.

Computing the states shifts

Most authors usually assume that there exists an operator, called the wave operator by analogy with scattering theory, such that $\phi_i^{(n)} = W_i^{(n)} \phi_i^{(0)}$. It can be written in the form

$$\phi_i^{(n)} = \left(R_0 J^{(n)} + \sum_{j \geq 1} R_j B_n^{(j+n)} \right) \phi_i^{(0)}, \quad (5.7)$$

where the operators $B_n^{(j+n)}$ are defined by $B_1^{(n)} = \Gamma_{n-2}^{(n)}$, for $k \geq 1$ and $n \geq 1$,

$$B_{k+1}^{(n)} = B_k^{(n)} + \Gamma_{n-k-2}^{(n-k)} \sum_{\ell \geq n-k} R_\ell B_k^{(\ell+k)},$$

and for $n \geq 1$,

$$J^{(n)} = \Gamma_0^{(n)} + \sum_{k=1}^{n-1} \Gamma_0^{(k)} \sum_{\ell \geq 1} R_\ell B_{n-k}^{(\ell+n-k)}. \quad (5.8)$$

We recall that $R_\ell = 0$ for any $\ell \geq M_i$, where M_i is the order at which ϕ_i becomes non-degenerate.

5.1.2 Applications to $H^N(v)$

We want to study the map $v \mapsto \rho(v)$ on the singular potentials $\mathcal{V}_\partial^N \setminus \mathcal{V}^N$, to complete our general picture. So we now relate the results presented in Section 5.1.1 with the framework of the rest of this document. We need to define a slightly weaker definition of Gateaux derivation, because the ground state of $H + \lambda G$ in a neighborhood of 0^+ is in general different from the one at 0^- . Take X a manifold locally modelled on a real vector space Y . We say that a function $f : X \rightarrow \mathbb{R}$ is half Gateaux differentiable at $x \in X$ if for any direction $y \in Y$,

$$\lim_{0 \leq t \rightarrow 0^+} (f(x + ty) - f(x)) / t =: \left({}^+ \delta_x f \right) (y)$$

exists, i.e. f has a right derivative in every direction. Higher half Gateau derivatives $({}^+ \delta_x^n f) (y)$ are defined similarly.

Theorem 5.1.1 (Degenerate Hellman-Feynman). *Let p be as in (4.2), $\mathcal{V} = L^p + L^\infty$, and $w \in L^p + L^\infty$. The energy E^N is infinitely half Gateaux differentiable on the singular points $\mathcal{V}_\partial^N \setminus \mathcal{V}^N$, with*

$$\begin{aligned} {}^+ \delta_v E^N(u) &= \min \sigma(\mathcal{P}(v)(\sum_i u_i) \mathcal{P}(v)) = \min_{\substack{\Psi \in \text{Ker}(H^N(v) - E^N(v)) \\ \int |\Psi|^2 = 1}} \int \rho_\Psi u \quad (5.9) \\ -\delta_v E^N(u) &= -\left({}^+ \delta_v E^N \right) (-u) = \max_{\substack{\Psi \in \text{Ker}(H^N(v) - E^N(v)) \\ \int |\Psi|^2 = 1}} \int \rho_\Psi u. \end{aligned}$$

If ${}^+ \delta_v E^N(u) < -\delta_v E^N(u)$, then the perturbation of $H^N(v)$ by u makes decrease the degeneracy by at least one. If moreover $\dim \text{Ker}(H^N(v) - E^N(v)) = 2$ and if Ψ_1, Ψ_2 is an orthonormal basis, we have

$$\begin{aligned} &{}^\pm \delta_v E^N(u) \\ &= \frac{1}{2} \int u (\rho_{\Psi_1} + \rho_{\Psi_2}) \mp \frac{1}{2} \sqrt{\left(\int u (\rho_{\Psi_1} - \rho_{\Psi_2}) \right)^2 + 4 |\langle \Psi_1, (\sum_i u_i) \Psi_2 \rangle|^2}. \end{aligned} \quad (5.10)$$

In the case where $\dim \text{Ker} (H^N(v) - E^N(v)) \geq 3$, the same optimization problem as for (5.10) leads to more complicated formulas.

Note that for the first order, we could deduce (5.9) by using that concave functions have subdifferentials, but in Theorem 5.1.1 we can also deduce formulas for all orders.

Given some degenerate potential $v \in \mathcal{V}_\delta^N \setminus \mathcal{V}^N$, we want now to know whether there is a direction in which one can break the degeneracy. At first order and for $D = 2$, there is a simple criterion. We also want to know whether E^N is differentiable at those degenerate potentials.

Corollary 5.1.2. *Let p be as in (4.2), $\mathcal{V} = L^p + L^\infty$ and $w \in L^p + L^\infty$.*

(i - Generic breaking.) *Let $D = 2$, take two unit vectors $\psi, \varphi \in \text{Ker} (H^N(v) - E^N(v))$ with $\psi \perp \varphi$. The degeneracy is broken in no direction at first order if and only if $\rho_\psi = \rho_\varphi$ and $\int_{\mathbb{R}^{d(N-1)}} \psi \varphi dx_2 \cdots dx_N = 0$.*

(ii - The energy is not differentiable.) *Let $v \in \mathcal{V}_\delta^N \setminus \mathcal{V}^N$ be a degenerate potential, and $w = 0$. Then E^N is not differentiable at v , in particular ${}^+\delta_v E^N(u) < -\delta_v E^N(u)$ for at least one direction $u \in L^p + L^\infty$.*

We think that almost all directions break the ground degeneracies at some order since \mathcal{V}^N is dense in \mathcal{V}_δ^N . We conjecture that at those degenerate potentials, E^N is not differentiable either in the interacting case, that is, there is a direction in which the left and right derivatives are different.

5.2 Proofs of Theorem 5.1.1 and Corollary 5.1.2

Proof of Theorem 5.1.1. We prove (5.10). In this case we minimize over the Bloch sphere projective space $P \text{Span} (\Psi_1, \Psi_2)$, we have

$$\left({}^+\delta_v E^N \right) (u) = \min_{a, b \in \mathbb{C}} \int_{|a\Psi_1 + b\Psi_2|^2 = 1} u \rho_{a\Psi_1 + b\Psi_2},$$

and the constraint on a, b reduces to $|a|^2 + |b|^2 = 1$. We can take the parametrization $a = (\cos t) e^{i\eta}$, $b = (\sin t) e^{i(\eta + \theta)}$ and Ψ_1, Ψ_2 are real. We define $A := \frac{1}{2} \int u (\rho_{\Psi_1} - \rho_{\Psi_2})$, $B := \langle \Psi_1, (\sum_i u_i) \Psi_2 \rangle$, and have

$$\begin{aligned} & \left({}^+\delta_v E^N \right) (u) \\ &= \min_{t, \theta \in [0, 2\pi]} (\cos t)^2 \int u \rho_{\Psi_1} + (\sin t)^2 \int u \rho_{\Psi_2} + \langle \Psi_1, (\sum_i u_i) \Psi_2 \rangle \cos \theta \sin(2t) \\ &= \frac{1}{2} \int u (\rho_{\Psi_1} + \rho_{\Psi_2}) + \min_{t, \theta \in [0, 2\pi]} A \cos t + B \cos \theta \sin t. \end{aligned}$$

Optimizing over t yields the optimal value $t^* \in \pi\mathbb{N} + \arctan(B(\cos \theta)/A)$ and using the classical formula for $\cos \arctan$ and $\sin \arctan$, we get

$$A \cos t^* + B \cos \theta \sin t^* = \pm \frac{A^2 + B^2(\cos \theta)^2}{A\sqrt{1 + (B(\cos \theta)/A)^2}} = \pm \sqrt{A^2 + (\cos \theta)^2 B^2}.$$

Finally optimizing over θ gives (5.10). We could also have computed the eigenvalues from

$$\mathcal{P}(v)(\sum_i u_i)\mathcal{P}(v) = \begin{pmatrix} \int u\rho_{\Psi_1} & \int \Psi_1\Psi_2(\sum_i u_i) \\ \int \Psi_1\Psi_2(\sum_i u_i) & \int u\rho_{\Psi_2} \end{pmatrix},$$

but this would not have given us the rotation enabling to compute the eigenvectors from the initial vectors. \square

Proof of Corollary 5.1.2.

- (i) is a corollary of equation (5.10).
- (ii) When $w = 0$, then $E^N(v) = \sum_{i=1}^N \lambda_i$ where λ_i is the i^{th} eigenvalue of $-\Delta + v$. So $H^N(v)$ is degenerate if and only if $\lambda_N = \lambda_{N+1}$. Let $(\varphi_i)_{1 \leq i \leq D}$ be an orthogonal basis of $\text{Ker}(-\Delta + v - \lambda_N)$, and $(\Psi_i)_{1 \leq i \leq N-k}$ be an orthogonal basis of $\text{Im } \mathbb{1}_{-\Delta+v < \lambda_N}$, where $1 \leq k \leq D-1$ is the number of particles in the degenerate Fermi level. We form two orthonormal minimizers $\Psi_1 := \phi_1 \wedge \cdots \wedge \phi_{N-k} \wedge_{m=1}^k \varphi_m$ and $\Psi_2 := \phi_1 \wedge \cdots \wedge \phi_{N-k} \wedge \varphi_{k+1} \wedge_{m=1}^{k-1} \varphi_m$. We assume that $\delta_v E^N$ is differentiable, hence degeneracy is broken in no direction at first order, then applying (i) to Ψ_1, Ψ_2 yields $\varphi_k \varphi_{k+1} = 0$, contradicting $|\{\varphi_k = 0\}| = 0$ implied by unique continuation [8]. \square

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Part III

The Kohn-Sham problem

Chapter 6

Regularization of the problem

In 1965, Kohn and Sham postulated the existence of effective one-body potentials which would replace the electronic interaction while keeping the same ground state density, and stated its relation with the exchange-correlation functionals [15]. This led to the development of very successful approximations and techniques enabling to predict properties of microscopic systems in quantum chemistry and physics. The existence of such a potential producing a prescribed ground state density is called the v -representability problem. Despite its importance, there are only a few works addressing the mathematical aspects of this theory, although several numerical studies were carried over. In [20] Lieb proved that any density can be *approximately* represented by a ground mixed state in some external potential v . In classical Density Functional Theory (DFT) at positive temperature, the v -representability problem was solved by Chayes, Chayes and Lieb in [5]. In this work, the authors use a variational approach to prove that given a density, there exists an electric potential whose Gibbs' state has the targeted one-body density. Then, Chayes, Chayes and Ruskai proved in [6] that for quantum lattice systems, any density is v -representable in the mixed states setting, both at zero and positive temperature.

In [25], Wu and Yang numerically apply the dual variational principle which leads to an evaluation of the Kohn-Sham potential. This inverse procedure has also received significant attention recently in [4, 11, 13, 14, 16, 22–24] for the standard problem and in [1] for nuclear DFT. However, this method has never been shown to be mathematically legitimate. In particular, the exact Kohn-Sham potential of some density ρ maximizes $V \mapsto E^N(V) - \int V\rho$ in $(L^p + L^\infty)(\mathbb{R}^d, \mathbb{R})$, where p is as in (6.1) and where $E^N(V)$ is the N -particle ground state energy, but this functional is not coercive in this space as we will see in Section 6.1.2.

Hence, to practically compute the Kohn-Sham potential, we need to reg-

ularize the problem. In our approach, we restrict our attention to potentials of the form $\sum_i v_i \alpha_i$ where the α_i are fixed weight functions and $v_i \in \mathbb{R}$ are the only parameters. This is a discretization of the space of potentials in the spirit of the finite element method, for instance. The corresponding functional is then coercive and hence the dual problem is well-posed. Said differently, the discretization amounts to integrating the problematic short-distance degrees of freedom, and implements an ultra-violet cut-off. Correspondingly, we define pseudo-discrete regularized Levy-Lieb and Lieb functionals by relaxing the condition $\rho_\Psi = \rho$ to $\int \rho_\Psi \alpha_i = \int \rho \alpha_i$ for any i . A similar approach was applied to optimal transport in [2], where the numerical efficiency seems promising.

In this chapter, we first present our main results, and then provide their proofs.

6.1 Main results

Let $d \in \mathbb{N}$ and let $\Omega \subset \mathbb{R}^d$ be a (bounded or unbounded) open set with Lipschitz boundary, representing the space in which our quantum system lives. We do not consider spin degrees of freedom but our results can be extended in this way without complications. We define

$$p = 1 \text{ if } d = 1, \quad p > 1 \text{ if } d = 2, \quad p = d/2 \text{ if } d \geq 3. \quad (6.1)$$

In all this chapter, we consider an even non-negative interaction potential $w \in (L^p + L^\infty)(\mathbb{R}^d, \mathbb{R}_+)$. We take external electric potentials $V \in (L^p + L^\infty)(\Omega, \mathbb{R})$, and consider the self-adjoint N -particle Schrödinger operator

$$H^N(V) := \sum_{i=1}^N -\Delta_i + \sum_{1 \leq i < j \leq N} w(x_i - x_j) + \sum_{i=1}^N V(x_i), \quad (6.2)$$

acting on the antisymmetric N -particle space $L_a^2(\Omega^N) := \wedge^N L^2(\Omega)$ with Dirichlet boundary conditions. We denote by

$$E^N(V) := \inf_{\substack{\Psi \in L_a^2(\Omega^N) \\ \int |\Psi|^2 = 1}} \langle \Psi, H^N(V) \Psi \rangle > -\infty$$

the ground state energy, and by $\mathcal{E}_V(\Psi) := \langle \Psi, H^N(V) \Psi \rangle$ the corresponding energy functional. The one-body density of a state $\Psi \in L_a^2(\Omega^N)$ is defined as

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

A mixed state is an element of

$$\mathcal{S}_{\text{mix}}^N(\Omega) := \mathfrak{S}_1(L^2(\wedge^N \Omega)) \cap \{\Gamma = \Gamma^* \geq 0, \text{Tr}(-\Delta)\Gamma < +\infty\},$$

and having $\text{Tr } \Gamma = 1$, where $\mathfrak{S}_1(L^2(\wedge^N \Omega))$ is the space of trace-class operators of $L^2(\wedge^N \Omega)$. The one-body density of such a mixed state Γ is

$$\rho_\Gamma(x) := N \int_{\Omega^{N-1}} \Gamma(x, x_2, \dots, x_N; x, x_2, \dots, x_N) dx_2 \cdots dx_N,$$

where we denote by $\Gamma(x_1, \dots, x_N; y_1, \dots, y_N)$ the integral kernel of the operator Γ .

In this section we state our results. Their proofs are provided in the following section.

6.1.1 Pseudo-discrete regularizations of Levy-Lieb and Lieb

The exact Levy-Lieb (or pure) and Lieb (or mixed) functionals [17, 19, 20], are

$$F^N(\rho) := \inf_{\substack{\Psi \in H_a^1(\Omega^N) \\ \rho_\Psi = \rho}} \langle \Psi, H^N(0) \Psi \rangle, \quad F_{\text{mix}}^N(\rho) := \inf_{\substack{\Gamma \in \mathcal{S}_{\text{mix}}^N(\Omega) \\ \rho_\Gamma = \rho}} \text{Tr } H^N(0) \Gamma.$$

We now relax the density constraint. Let us consider a subset $I \subset \mathbb{N}$ and a set $\alpha = (\alpha_i)_{i \in I}$ of weight functions forming a partition of unity for Ω , that is $\sum_{i \in I} \alpha_i = \mathbf{1}_\Omega$, where $\alpha_i \in L^\infty(\Omega, \mathbb{R}_+)$. For $r \in \ell^1(I, \mathbb{R}_+) \cap \{\sum_{i \in I} r_i = N\}$, we introduce the regularized Levy-Lieb and Lieb functionals

$$F^{N,\alpha}(r) := \inf_{\substack{\Psi \in H_a^1(\Omega^N) \\ \int \alpha_i \rho_\Psi = r_i \quad \forall i \in I}} \langle \Psi, H^N(0) \Psi \rangle, \quad F_{\text{mix}}^{N,\alpha}(r) := \inf_{\substack{\Gamma \in \mathcal{S}_{\text{mix}}^N(\Omega) \\ \int \alpha_i \rho_\Gamma = r_i \quad \forall i \in I}} \text{Tr } (H^N(0) \Gamma),$$

and we define them to be $+\infty$ when the minimizing sets are empty. We know that $F_{\text{mix}}^{N,\alpha}$ is convex. Consider now the assumption

$$\lim_{R \rightarrow +\infty} \sum_{\substack{i \in I \\ \text{supp } \alpha_i^n \cap B_R^c \neq \emptyset}} r_i = 0. \quad (6.3)$$

Theorem 6.1.1 (Existence of minimizers). *Take $w \geq 0$ and $r \in \ell^1(I, \mathbb{R}_+)$ such that $\sum_{i \in I} r_i = N$, and $\alpha = (\alpha_i)_{i \in I}$ a partition of unity for Ω . Under the tightness condition (6.3), $F^{N,\alpha}(r)$ and $F_{\text{mix}}^{N,\alpha}(r)$ have at least one minimizer when they are finite.*

For a given $\rho \in L^1(\Omega, \mathbb{R}_+)$, we define

$$r_\rho := \left(\int \alpha_i \rho \right)_{i \in I} \in \ell^1(I, \mathbb{R}_+).$$

This sequence contains the partial information on the density ρ which we are going to retain. Since the minimizing set of $F^{N,\alpha}(\rho)$ is included in the

one of $F^{N,\alpha}(r_\rho)$, for any $\rho \geq 0$ with $\sqrt{\rho} \in H^1(\Omega)$ and α as defined above we have

$$F^{N,\alpha}(r_\rho) \leq F^N(\rho) \quad \text{and} \quad F_{\text{mix}}^{N,\alpha}(r_\rho) \leq F_{\text{mix}}^N(\rho).$$

In particular, $F^{N,\alpha}(r_\rho)$ and $F_{\text{mix}}^{N,\alpha}(r_\rho)$ are finite.

Our approximate Levy-Lieb and Lieb functionals converge to the exact ones when the integrated weights tend to carry all the information of the density.

Theorem 6.1.2 (Convergence to the exact model). *Take $0 \leq w \in L^p + L^\infty$ with p as in (6.1). Let Ω be a connected open set. Consider a density $\rho \in L^1(\Omega, \mathbb{R}_+)$ such that $\sqrt{\rho} \in H_0^1(\Omega)$ and $\int \rho = N$. We assume that $\alpha_n = (\alpha_i^n)_{i \in I_n}$, where $\alpha_i^n \in L^\infty(\Omega)$, is a sequence of weights forming a partition of unity for Ω , and such that for any $f \in C_c^\infty(\Omega)$, we have*

$$\inf_{g_n \in \text{Span}\{\alpha_i^n, i \in I_n\}} \|f - g_n\|_{(L^p + L^\infty)(\Omega)} \longrightarrow 0 \quad (6.4)$$

when $n \rightarrow +\infty$. We also assume that

$$\lim_{r \rightarrow +\infty} \sup_{n \in \mathbb{N}} \sum_{\substack{i \in I \\ \text{supp } \alpha_i^n \cap B_r^c \neq \emptyset}} \int \rho \alpha_i^n = 0. \quad (6.5)$$

Then

$$\lim_{n \rightarrow +\infty} F^{N,\alpha_n}(r_\rho) = F^N(\rho), \quad \lim_{n \rightarrow +\infty} F_{\text{mix}}^{N,\alpha_n}(r_\rho) = F_{\text{mix}}^N(\rho).$$

Let Ψ_n be a sequence of approximate minimizers for $F^{N,\alpha_n}(r_\rho)$, that is, such that $\mathcal{E}_0(\Psi_n) \leq F^{N,\alpha_n}(r_\rho) + \epsilon_n$ where $\epsilon_n \rightarrow 0$ when $n \rightarrow +\infty$ and $\int \alpha_i \rho \Psi_n = \int \alpha_i \rho$ for any $i \in I$. Then $\Psi_n \rightarrow \Psi_{\text{exact}}$ strongly in $H^1(\Omega^N)$ up to a subsequence, where Ψ_{exact} is a minimizer of $F^N(\rho)$. If Γ_n is a sequence of approximate minimizers for $F_{\text{mix}}^{N,\alpha_n}(r_\rho)$, then $\Gamma_n \rightarrow \Gamma_{\text{exact}}$ strongly in the kinetic energy space $\mathfrak{S}_{1,1}$ up to a subsequence, where Γ_{exact} is a minimizer of $F_{\text{mix}}^N(\rho)$.

The space $\mathfrak{S}_{1,1}$ is the set of operators A of $L^2(\mathbb{R}^{dN})$ endowed with the norm $\|A\|_{\mathfrak{S}_{1,1}} = \text{Tr} \left| (-\Delta + 1)^{\frac{1}{2}} A (-\Delta + 1)^{\frac{1}{2}} \right|$.

Our assumption (6.5) is used to control the decay at infinity. If all the α_i^n have a compact support of diameter bounded by δ independent of i and n , then

$$\sum_{\substack{i \in I \\ \text{supp } \alpha_i^n \cap B_r^c \neq \emptyset}} \int \rho \alpha_i^n \leq \int_{|x| \geq r - \delta} \rho \xrightarrow{r \rightarrow +\infty} 0$$

and (6.5) is satisfied.

If $\alpha_i^n = \mathbb{1}_{\Omega_i^n}$ is a sequence of partitions of $\Omega = \cup_{i \in \mathbb{N}} \Omega_i^n$ where Ω_i^n are convex, and $\sup_{i \in \mathbb{N}} \text{diam } \Omega_i^n \rightarrow 0$ when $n \rightarrow +\infty$, then the assumption (6.4) is verified by Lemma 6.2.1 below. Assumption (6.5) is verified as well. Again by Lemma 6.2.1, in this case we have an explicit bound on the convergence of densities

$$\|\rho - \rho_{\Psi_n}\|_{(L^1 \cap L^q)(\Omega)} \leq c_d \left(\|\sqrt{\rho}\|_{H^1} + \sup_{n \in \mathbb{N}} \|\sqrt{\rho_{\Psi_n}}\|_{H^1} \right) \sup_{i \in \mathbb{N}} \text{diam } \Omega_i^n,$$

where c_d only depends on d , and q is as in (6.9). Note that $\|\sqrt{\rho_{\Psi}}\|_{H^1}$ and $\|\sqrt{\rho_{\Psi_n}}\|_{H^1}$ are controlled by $F^N(\rho)$ due to the Hoffmann-Ostenhof inequality.

A typical choice for the α_i^n is given by the partition of unity finite element method [3, 21],

6.1.2 The dual problem

Correspondingly to the previous approach, we change the exact model by discretizing the space of potentials. We consider a sequence of weights $\alpha = (\alpha_i)_{i \in I}$, take $r \in \ell^1(I, \mathbb{R}_+)$. The dual problem is the maximization of

$$G_{r,\alpha}(v) := E^N \left(\sum_{i \in I} v_i \alpha_i \right) - \sum_{i \in I} v_i r_i,$$

over the space $\ell^\infty(I, \mathbb{R})$ of potential coefficients $v = (v_i)_{i \in I}$. We have

$$E^N \left(\sum_{i \in I} v_i \alpha_i \right) = \inf_{\substack{r \in \ell^1(I, \mathbb{R}_+) \\ \sum_{i \in I} r_i = N}} \left(F_{\text{mix}}^{N,\alpha}(r) + \sum_{i \in I} v_i r_i \right), \quad \sup_{v \in \ell^\infty(I, \mathbb{R})} G_{r,\alpha}(v) = F_{\text{mix}}^{N,\alpha}(r),$$

as in the exact models, and by the same proofs as [20, Theorem 4.3]. Again by the same proof as for the lower semi-continuity of the exact Lieb functional [20, Theorem 3.6], $G_{r,\alpha}$ is weakly upper semi-continuous in the $\ell^\infty(I, \mathbb{R})$ topology. Moreover, if $H^N(\sum_{i \in I} v_i \alpha_i)$ has a ground state Ψ_v , then

$$G_{r,\alpha}(v) = \mathcal{E}_0(\Psi_v) + \sum_{i \in I} v_i \left(-r_i + \int \rho_{\Psi_v} \alpha_i \right).$$

Gauge invariance

The gauge we are dealing with is the choice of a reference for energies, that is the transformation $V \rightarrow V + c$ for a constant $c \in \mathbb{R}$. The exact dual functional $V \mapsto E^N(V) - \int V \rho$ is gauge invariant, and since we want our approximate functional to be so as well, we are naturally led to take

$$\sum_{i \in I} \alpha_i = 1 \text{ on } \Omega, \quad \sum_{i \in I} r_i = N. \quad (6.6)$$

The last condition is of course fulfilled for $r = r_\rho$, which is the interesting situation.

Remark 6.1.3. *Let us explain why the previous conditions (6.6) are necessary to ensure gauge invariance. Let $v \in \ell^\infty(I, \mathbb{R})$ be such that $H^N(\sum_{i \in I} v_i \alpha_i)$ has a ground state, which we denote by Ψ_v . Take $c \in \mathbb{R}$, we have*

$$E^N \left(\sum_{i \in I} (v_i + c) \alpha_i \right) \leq \mathcal{E}_{\sum_{i \in I} (v_i + c) \alpha_i}(\Psi_v) = E^N \left(\sum_{i \in I} v_i \alpha_i \right) + c \int \sum_{i \in I} \alpha_i \rho_{\Psi_v},$$

and hence

$$G_{r, \alpha}(v + c) \leq G_{r, \alpha}(v) + c \left(- \sum_{i \in I} r_i + \int_{\Omega} \left(\sum_{i \in I} \alpha_i \right) \rho_{\Psi_v} \right).$$

To have a gauge invariant theory, we want to have

$$\int_{\Omega} \left(N^{-1} \sum_{i \in I} r_i - \sum_{i \in I} \alpha_i \right) \rho_{\Psi_v} = 0,$$

otherwise $G_{r, \alpha}(v + c) \rightarrow -\infty$ for $c \rightarrow +\infty$ or $c \rightarrow -\infty$. This requirement should not depend on v , hence we need $\sum_{i \in I} r_i = N \sum_{i \in I} \alpha_i$ a.e on Ω . We are thus naturally led to assume (6.6).

Uniqueness

A Hohenberg-Kohn theorem adapted to our situation shows that the map $v \mapsto r_{\rho_{\Psi_v}}$, where Ψ_v is a ground state of $H^N(\sum v_i \alpha_i)$, is essentially injective. Hence if $G_{r, \alpha}$ has a maximum, it is unique.

Theorem 6.1.4 (Hohenberg-Kohn). *Let $\Omega \subset \mathbb{R}^d$ be an open and connected set, with Dirichlet any boundary conditions. Let $p > \max(2d/3, 2)$, and take an interaction $w \in (L^p + L^\infty)(\mathbb{R}^d)$. Let $v, u \in \ell^\infty(I, \mathbb{R})$ and $\alpha = (\alpha_i)_{i \in I}$ where $\alpha_i \in L^\infty(\Omega, \mathbb{R}_+)$, be such that $H^N(\sum_{i \in I} v_i \alpha_i)$ and $H^N(\sum_{i \in I} u_i \alpha_i)$ have at least one ground state each, which we respectively denote by Ψ_v and Ψ_u . If $\int \alpha_i \rho_{\Psi_v} = \int \alpha_i \rho_{\Psi_u}$ for any $i \in I$, then $v = u + c$ for some constant $c \in \mathbb{R}$.*

The proof follows from the standard Hohenberg-Kohn theorem [9, 12] in the form of [10, Theorem 2.1] and Theorem 2.2.1 in Chapter 2.

Coercivity

Let $\rho \in L^1(\mathbb{R}^d, \mathbb{R}_+)$ be a target density which we want to represent by a potential. In the exact model, the dual problem boils down to maximize $V \mapsto E^N(V) - \int V \rho$ over $(L^p + L^\infty)(\Omega, \mathbb{R})$. First of all, as a consequence of [20, Theorem 3.8], one needs to assume that $\sqrt{\rho} \in H^1(\mathbb{R}^d)$, otherwise the above

functional is not bounded from above. Moreover, even if $\sqrt{\rho} \in H^1(\mathbb{R}^d)$, this functional is not coercive for $d \geq 2$, not even locally in $(L^p + L^\infty)(\Omega, \mathbb{R})$. For instance take $p > 1$, take ρ continuous at the origin, and take a positive potential $V \in (L^1 \cap L^p)(\mathbb{R}^d)$ with compact support. Consider the sequence $V_n(x) := n^d V(nx)$. Then $\|V_n\|_{L^p}^p = n^{d(p-1)} \int V^p \rightarrow +\infty$ because $p > 1$ but $E^N(V_n) = 0$ because $V_n \geq 0$, and $\int V_n \rho \rightarrow \rho(0) \int V$ is bounded. We remark that this last counterexample does not hold when $d = 1$, because then $p = 1$. The main goal of this section is to recover coercivity for the discretized dual problem, in order to make it well-posed.

If there is some $i \in I$ such that $r_i = 0$, denoting by e_i the i^{th} degree of freedom of the potentials, when $c \rightarrow +\infty$ we expect that $G_{r,\alpha}(v + ce_i) \rightarrow E_D^N(\sum_{j \neq i} v_j \alpha_j)$, where $E_D^N(\sum_{j \neq i} v_j \alpha_j)$ is finite and is the ground energy of the system living in $\Omega \setminus \text{supp } \alpha_i$ with Dirichlet boundary conditions. Hence $G_{r,\alpha}$ is not coercive in this case. This shows that

$$r_i > 0 \quad \forall i \in I$$

is a necessary condition for $G_{r,\alpha}$ to be coercive.

We define

$$c_\Omega := -\frac{E^N(0)}{N} \leq 0,$$

where $E^N(0)$ is the energy of N interacting particles without external potential. It respects $E^N(c_\Omega \mathbb{1}_\Omega) = 0$ and it is non-positive because $w \geq 0$. It vanishes when $\Omega = \mathbb{R}^d$ for instance. We can choose the gauge we want, so we will take potentials v such that $E^N(\sum_{i \in I} v_i \alpha_i) = 0$ for convenience. Our variational space of potentials can thus be

$$\left\{ v \in \ell_r^1(I, \mathbb{R}) \mid E^N\left(\sum v_i \alpha_i\right) = 0 \right\},$$

where $\|v\|_{\ell_r^1} := \sum_{i \in I} |v_i| r_i$.

Now we can state our main result for the discretized model.

Theorem 6.1.5 (Well-posedness of the dual problem). *Take a non-negative interaction $w \in (L^p + L^\infty)(\mathbb{R}^d, \mathbb{R}_+)$ where p is as in (6.1).*

• (Coercivity) *Let α be a partition of unity of Ω , with $\alpha_i \in L^\infty(\mathbb{R}^d, \mathbb{R}_+)$, such that we have $R > 0$ for which*

$$(\text{supp } \alpha_i) \setminus \cup_{j \in I, j \neq i} \text{supp } \alpha_j$$

contains a ball of radius R , uniformly in $i \in I$. Let $r \in \ell^1(I, \mathbb{R}_+)$ be such that $\sum_{i \in I} r_i = N$ and $r_i > 0$ for all $i \in I$. For any $v \in \ell_r^1(I, \mathbb{R})$ such that $E^N(\sum_{i \in I} v_i \alpha_i) = 0$, we have

$$G_{r,\alpha}(v) \leq -\min\left(1, \frac{\sum_{v_i \geq c_\Omega} r_i}{\sum_{v_i < c_\Omega} r_i}\right) \|v - c_\Omega\|_{\ell_r^1} + \min_{\substack{\Psi \in \wedge^N H_0^1(B_R) \\ \int |\Psi|^2 = 1}} \langle \Psi, H^N(0)\Psi \rangle. \quad (6.7)$$

In particular when I is finite, $G_{r,\alpha}$ is coercive in $\ell_r^1(I, \mathbb{R}) = \ell^1(I, \mathbb{R})$.

• (Existence of an optimizer) Let I be finite, and make the previous assumptions. There exists a unique $v \in \ell^1(I, \mathbb{R})$ (up to the gauge choice) maximizing $G_{r,\alpha}$. If moreover Ω is bounded, there is an N -particle ground mixed state $\Gamma_v \in \mathcal{S}_{\text{mix}}^N(\Omega)$ of $H^N(\sum_{i \in I} v_i \alpha_i)$ such that for all $i \in I$, $\int \rho_{\Gamma_v} \alpha_i = r_i$, and such that

$$\sup_{u \in \ell_r^1(I, \mathbb{R})} G_{r,\alpha}(u) = G_{r,\alpha}(v) = \mathcal{E}_0(\Gamma_v) = F_{\text{mix}}^{N,\alpha}(r). \quad (6.8)$$

In (6.7), we use the convention that $\min\left(1, \frac{\sum_{v_i \geq c_\Omega} r_i}{\sum_{v_i < c_\Omega} r_i}\right) = 1$ when $v \geq c_\Omega$.

Here are some remarks.

(i) If the ground eigenspace is non-degenerate, that is, if

$$\dim \text{Ker}\left(H^N\left(\sum v_i \alpha_i\right) - E^N\left(\sum v_i \alpha_i\right)\right) = 1,$$

then Γ_v is a pure state, and (6.8) is also equal to the discretized Levy-Lieb functional $F^{N,\alpha}(r)$.

(ii) The weight functions α_i can have overlapping supports, but our assumption essentially says that the inside part is not too small. In the case I infinite, it is not clear whether the bound (6.7) implies that $G_{r,\alpha}$ is coercive. However, when I is finite, we have $\sum_{v_i < c_\Omega} r_i \leq N$ and $\sum_{v_i \geq c_\Omega} r_i \geq \min r$ so (6.7) yields

$$G_{r,\alpha}(v) \leq -\frac{\min r}{N} \|v\|_{\ell^1} + c$$

for any $v \in \ell_r^1(I, \mathbb{R}) = \ell^1(I, \mathbb{R})$, where $c = c_\Omega \min r / N + \mathcal{E}_0(\Phi)$ is independent of v , and $\min r > 0$ thus $G_{r,\alpha}$ is coercive in the ℓ_r^1 norm. Here Φ is a minimizer for the interacting Dirichlet problem on B_R .

(iii) Our bound (6.7) does not pass to the continuous model because then $R \rightarrow 0$ and

$$\min_{\substack{\Psi \in \wedge^N H_0^1(B_R) \\ \int |\Psi|^2 = 1}} \langle \Psi, H^N(0)\Psi \rangle \xrightarrow{R \rightarrow 0} +\infty.$$

(iv) In the statement, Γ is a ground mixed state of $H^N(\sum v_i \alpha_i)$ in the sense that $\text{Ran } \Gamma \subset \text{Ker}\left(H^N(\sum v_i \alpha_i) - E^N(\sum v_i \alpha_i)\right)$.

(v) The pair (v, Γ_v) is a saddle point of the Lagrangian

$$\mathcal{L}(v, \Gamma) = \mathcal{E}_0(\Gamma) + \sum_{i \in I} v_i \left(-r_i + \int \rho_\Gamma \alpha_i\right)$$

and v is a Lagrange multiplier.

(vi) If $v \in \ell^\infty(I, \mathbb{R})$ is such that $H^N(\sum v_i \alpha_i)$ has a non-degenerate ground state $\Psi(v)$, then $G_{r, \alpha}$ is \mathcal{C}^∞ at this point, with

$$\frac{dG_{r, \alpha}}{dv_i}(v) = -r_i + \int \rho_{\Psi(v)} \alpha_i.$$

(vii) In the exact model, the existence of a maximizing potential has not been shown, even when Ω is bounded. We recall that the existence was proved for the quantum theory on a \mathbb{Z}^d lattice [6], and in the exact classical case with positive temperature [5].

6.1.3 Building Kohn-Sham potentials

The problem of v -representability is, given a density $\rho \in L^1(\Omega, \mathbb{R}_+)$ with $\int \rho = N$, $\sqrt{\rho} \in H^1$, and $|\{\rho = 0\} \cap \Omega| = 0$, to find a potential v having a ground state Ψ_v respecting $\rho_{\Psi_v} = \rho$. We will call it the inverse potential. When $w = 0$, it is the Kohn-Sham potential [15].

The mixed states case

In the mixed states setting (at zero temperature) and using the Bishop-Phelps theorem, Lieb showed in [20, Theorem 3.10, Theorem 3.11, Theorem 3.14], that any such ρ can be approached to any precision in $L^1 \cap L^{d/(d-2)}$ by a v -representable ground state density. We can state a similar result using our variational approach.

Corollary 6.1.6 (Constructive approximate v -representability in the mixed states setting). *Let $\Omega \subset \mathbb{R}^d$ be a possibly unbounded open set with Lipschitz boundary. Let $\rho \in L^1(\Omega, \mathbb{R}_+)$ be such that $\sqrt{\rho} \in H_0^1(\Omega)$ and $|\{\rho = 0\} \cap \Omega| = 0$. There exists a sequence $v_n \in L^\infty(\Omega, \mathbb{R})$ with compact support such that $H^N(v_n)$ has a mixed ground state Γ_{v_n} with $\Gamma_{v_n} \rightarrow \Gamma_\infty$ strongly in $\mathfrak{S}_{1,1}$ up to a subsequence, where Γ_∞ is a minimizer of $F_{\text{mix}}^N(\rho)$. Moreover, $\sqrt{\rho_{\Gamma_{v_n}}} \rightarrow \sqrt{\rho}$ strongly $H^1(\Omega)$, $\mathcal{E}_0(\Gamma_{v_n}) \leq F_{\text{mix}}^N(\rho)$, and $\mathcal{E}_0(\Gamma_{v_n}) \rightarrow F_{\text{mix}}^N(\rho)$.*

Although the existence part of Theorem 6.1.5 holds only for bounded open sets Ω , Corollary 6.1.6 holds when Ω is unbounded. The proof uses Theorem 6.1.5 on a sequence of growing bounded sets Ω_n with well chosen weight functions α_i^n . We conjecture that if there exists a potential which exactly produces ρ , this sequence v_n converges to this exact inverse potential, in a suitable sense.

The pure states case

For any density ρ , $F_{\text{mix}}^N(\rho) < F^N(\rho)$ implies that ρ is not v -representable with pure ground states. This is also closely related to the degeneracy of the ground eigenspace. To continue, we make a conjecture.

Conjecture 6.1.7 (Continuity of the Levy-Lieb and Lieb functionals). *Take densities $\rho, \rho_n \in L^1(\mathbb{R}^d, \mathbb{R}_+)$ such that $\sqrt{\rho}, \sqrt{\rho_n} \in H^1(\mathbb{R}^d)$. If $\sqrt{\rho_n} \rightarrow \sqrt{\rho}$ in $H^1(\mathbb{R}^d)$, then $F^N(\rho_n) \rightarrow F^N(\rho)$ and $F_{\text{mix}}^N(\rho_n) \rightarrow F_{\text{mix}}^N(\rho)$.*

Conjecture 6.1.7 would imply that the set of pure-state v -representable densities is not dense in $L^1(\mathbb{R}^d, \mathbb{R}_+)$ when $d \geq 2$. Indeed, consider a density ρ such that $F_{\text{mix}}^N(\rho) < F^N(\rho)$, the existence of such densities is presented in [20, Theorem 3.4 (ii)] for $d = 3$ but similar examples hold for any $d \geq 2$. Then by Conjecture 6.1.7 there exists $R > 0$ such that $F_{\text{mix}}^N(\chi) < F^N(\chi)$ for any positive $\sqrt{\chi} \in \mathbb{B}_R(\sqrt{\rho})$, where the ball $\mathbb{B}_R(\sqrt{\rho})$ is in the $H^1(\mathbb{R}^d, \mathbb{R})$. Hence $\mathbb{B}_R(\sqrt{\rho})$ is an open (in the set of non-negative square functions) set of densities which are not pure-state v -representable.

However, with a different method which is not variational, it might still be possible to represent those densities, with excited states. As presented in [8] for instance, the Kohn-Sham potential can be seen as a Lagrange multiplier corresponding to the Euler-Lagrange equation of the Levy-Lieb functional. We give here a result for the discretized problem which only works for $N = 1$.

Theorem 6.1.8 (Pure excited v -representability, $N = 1$). *Take $N = 1$, let $\Omega \subset \mathbb{R}^d$ be a bounded open domain with Lipschitz boundary, consider a finite partition of unity $(\alpha_i)_{i \in I}$ for Ω , and $r \in \ell^1(I, \mathbb{R}_+)$, $\sum_{i \in I} r_i = 1$ and such that $r_i > 0$ for any $i \in I$. There exist $v \in \ell^\infty(I, \mathbb{R})$ and a pure one-particle ground or excited state $\Psi_r \in H_a^1(\Omega)$ of $-\Delta + \sum_{i \in I} v_i \alpha_i$ such that for all $i \in I$, $\int \rho_{\Psi_r} \alpha_i = r_i$.*

The state representing r is a ground state if and only if $F_{\text{mix}}^{N, \alpha}(r) = F^{N, \alpha}(r)$. Applying the last result for an increasing sequence of α 's, we get the corresponding approximate representability, as we obtained Corollary 6.1.6. For $N = 1$ the limit potential must be $\Delta\sqrt{\rho}/\sqrt{\rho}$ and the state must be the ground state. We conjecture that Theorem 6.1.8 holds for any N . A sufficient property to prove it, is that minimizers Ψ of our approximate Levy-Lieb functionals have $|\{\Psi = 0\}| = 0$.

Conjecture 6.1.9. *Any minimizer Ψ of $F^{N, \alpha}(r)$ satisfies*

$$|\{x \in \mathbb{R}^{dN} \mid \Psi(x) = 0\}| = 0.$$

This conjecture is related to a unique continuation property. In the Hohenberg-Kohn theorem, one considers minimizers of the energy \mathcal{E}_v , respecting Schrödinger's equation, and this implies $|\{\Psi = 0\}| = 0$ by unique continuation [10]. Here, this is a converse property in the sense that we consider minimizers of $F^{N, \alpha}(r)$, and the property $|\{\Psi = 0\}| = 0$ of minimizers, that we want to show, would imply that they respect Schrödinger's equation (see the proof of Theorem 6.1.8).

We remark that Conjecture 6.1.9 also implies that for any $r \in \ell^1(I, \mathbb{R}_+)$, $\kappa^{-1}(r)$ is a manifold, because $d_\Psi \kappa$ is then surjective and one can apply the preimage theorem [27, Theorem 73.C p556]. Since $d_\Psi \kappa$ is closed, this mathematical framework can be applied to define the so-called adiabatic connection of DFT, because one can apply the implicit functions theorem and let w decrease while the inverse potential v increases, keeping the density fixed.

6.2 Proofs

6.2.1 Proofs of Theorems 6.1.1 and 6.1.2

We start by proving the existence of minimizers.

Proof of Theorem 6.1.1. Let us denote by Ψ_n a minimizing sequence for $F^{N,\alpha}(r)$. Since $w \geq 0$, then

$$\int |\nabla \sqrt{\rho_{\Psi_n}}|^2 \leq \int |\nabla \Psi_n|^2 \leq \mathcal{E}_0(\Psi_n) \rightarrow F^{N,\alpha}(r),$$

by the Hoffman-Ostenhof inequality, and Ψ_n is bounded in $H^1(\Omega^N)$ and there exists $\Psi_\infty \in \wedge^N H^1(\Omega)$ such that $\Psi_n \rightharpoonup \Psi_\infty$ in $H^1(\Omega^N)$ and $\sqrt{\rho_{\Psi_n}} \rightharpoonup \sqrt{\rho_\infty}$ in $H^1(\Omega)$. At this step, ρ_∞ and Ψ_∞ are not related. By summing all the constraints on the density and using that $\mathbf{1}_\Omega \sum_{i \in I} \alpha_i = \mathbf{1}_\Omega$, we have $\int \rho_{\Psi_n} = N$. We estimate

$$\int_{B_r^c \cap \Omega} \rho_{\Psi_n} \leq \int \rho_{\Psi_n} \sum_{\text{supp } \alpha_i \cap B_r^c \neq \emptyset} \alpha_i = \sum_{\text{supp } \alpha_i \cap B_r^c \neq \emptyset} r_i,$$

and using the assumption (6.3) yields $\sup_n \int_{B_r^c \cap \Omega} \rho_{\Psi_n} \rightarrow 0$ when $r \rightarrow +\infty$. This implies that $\sqrt{\rho_{\Psi_n}}$ converges strongly in $L^2(\Omega)$ and weakly in $H^1(\Omega)$, up to extraction of a subsequence. The tightness of ρ_{Ψ_n} also implies that $\Psi_n \rightarrow \Psi_\infty$ strongly in $L^2(\Omega^N)$, that the limit of ρ_{Ψ_n} is ρ_{Ψ_∞} , and eventually that $\int \rho_{\Psi_\infty} \alpha_i = r_i$. By lower semi-continuity of the energy functional since $w \geq 0$, $\mathcal{E}_0(\Psi_\infty) \leq F^{N,\alpha}(r)$, hence Ψ_∞ is a minimizer. By equivalence of the quadratic form \mathcal{E}_0 with the one of H^1 , $\Psi \rightarrow \Psi_\infty$ strongly in $H^1(\Omega)$.

In the mixed state case, let us denote by Γ_n a minimizing sequence. We use the compactness of the Fock space of particle number less than N , $\mathcal{S}(\mathcal{F}^{\leq N})$ for the geometric convergence [18, Lemma 2.2], we thus have $\Gamma_n \rightarrow_g \Gamma_\infty$ for some $\Gamma_\infty \in \mathcal{S}(\mathcal{F}^{\leq N})$. As before, the tightness of ρ_{Γ_n} implies $\Gamma_n \rightarrow \Gamma_\infty$ strongly in trace-class by [18, Lemma 2.3], hence Γ_∞ is an N -particle density matrix. \square

One does not need the weight functions α_i to have the diameters of their supports converging to zero to get that our regularized functionals

converge to the exact one. Nevertheless, when this is the case, we can deduce bounds on the rate of convergence of the densities of minimizers to the target density. More precisely, the following result quantifies the distance between two densities satisfying $\int \rho \alpha_i = \int \chi \alpha_i$ for all $i \in I$. We consider exponents

$$q \in [1, +\infty) \text{ if } d = 1, \quad q \in [1, 2) \text{ if } d = 2 \quad \text{and} \quad q = d/(d-1) \text{ if } d \geq 3. \quad (6.9)$$

Lemma 6.2.1 (Bounds on approximate densities). *Let q be as in (6.9). Let Ω be an open set, $\alpha_i = \beta_i^{k_i}$ where $k_i \in \mathbb{R}_+$ and β_i are non-negative concave functions on $\text{supp } \alpha_i$, with $\sup_{i \in \mathbb{N}} \text{diam supp } \alpha_i < +\infty$, $\mathbf{1}_\Omega \sum_{i=1}^{+\infty} \alpha_i = \mathbf{1}_\Omega$. Let $\rho, \chi \in L^1(\Omega, \mathbb{R}_+)$ such that $\sqrt{\rho}, \sqrt{\chi} \in H_0^1(\Omega)$. If $\int \rho \alpha_i = \int \chi \alpha_i$ for any $i \in I$, then*

$$\|\rho - \chi\|_{(L^1 \cap L^q)(\Omega)} \leq c_d (\|\sqrt{\rho}\|_{H^1} + \|\sqrt{\chi}\|_{H^1}) \sup_{i \in \mathbb{N}} \text{diam supp } \alpha_i,$$

where c_d only depends on d .

Proof of Lemma 6.2.1. Take $p \geq 1$. We use the weighted Poincaré-Wirtinger inequality from [7, Theorem 1.1] with $c_{f,i} := (\int \alpha_i)^{-1} \int f \alpha_i$. We obtain

$$\int |f - c_{f,i}|^p \alpha_i \leq c_p (\text{diam supp } \alpha_i)^p \int |\nabla f|^p \alpha_i,$$

for $f \in \{\rho, \chi\}$. Thus, since $c_{\rho,i} = c_{\chi,i}$ by assumption,

$$\begin{aligned} \int |\rho - \chi|^p \alpha_i &= \int |\rho - c_{\rho,i} - (\chi - c_{\rho,i})|^p \alpha_i \\ &\leq c_p \left(\int |\rho - c_{\rho,i}|^p \alpha_i + \int |\chi - c_{\rho,i}|^p \alpha_i \right) \\ &\leq c_p \left(\sup_{i \in \mathbb{N}} \text{diam supp } \alpha_i \right)^p \int (|\nabla \rho|^p + |\nabla \chi|^p) \alpha_i. \end{aligned}$$

Summing over i and raising to the power $1/p$ yields

$$\|\rho - \chi\|_{L^p} \leq c_p \left(\sup_{i \in \mathbb{N}} \text{diam supp } \alpha_i \right) (\|\nabla \rho\|_{L^p} + \|\nabla \chi\|_{L^p}). \quad (6.10)$$

We take $p = q$, so by writing $\nabla f = 2\sqrt{f}\nabla\sqrt{f}$ and by the Sobolev inequality, we have

$$\|\nabla f\|_{L^p} \leq 2 \|\nabla \sqrt{f}\|_{L^2} \|\sqrt{f}\|_{L^{\frac{2p}{2-p}}} \leq c_d \|\nabla \sqrt{f}\|_{L^2}^2.$$

Applying (6.10) concludes the proof. \square

We prove now the convergence of our regularized functionals to the exact ones.

Proof of Theorem 6.1.2. Let us denote by Ψ_n a sequence of approximate minimizers for $F^{N,\alpha_n}(r_\rho)$. Since $w \geq 0$, then

$$\int |\nabla \sqrt{\rho_{\Psi_n}}|^2 \leq \int |\nabla \Psi_n|^2 \leq \mathcal{E}_0(\Psi_n) \leq F^{N,\alpha_n}(r_\rho) + \epsilon_n \leq F^N(\rho) + \epsilon_n,$$

where $\epsilon_n \rightarrow 0$. Hence $(\Psi_n)_{n \in \mathbb{N}}$ is bounded in $H^1(\Omega^N)$ and there exists $\Psi_\infty \in \wedge^N H^1(\Omega)$ such that $\Psi_n \rightharpoonup \Psi_\infty$ weakly in $H^1(\Omega^N)$. By summing all the constraints on the density and using that $\mathbf{1}_\Omega \sum_{i \in I} \alpha_i = \mathbf{1}_\Omega$, we have $\int \rho_{\Psi_n} = N$. We estimate

$$\int_{B_r^c \cap \Omega} \rho_{\Psi_n} \leq \int \rho_{\Psi_n} \sum_{\text{supp } \alpha_i^n \cap B_r^c \neq \emptyset} \alpha_i^n = \int \rho \sum_{\text{supp } \alpha_i^n \cap B_r^c \neq \emptyset} \alpha_i^n,$$

and using the assumption (6.5) yields $\sup_n \int_{B_r^c \cap \Omega} \rho_{\Psi_n} \rightarrow 0$ when $r \rightarrow +\infty$. This implies that $\sqrt{\rho_{\Psi_n}}$ converges strongly in $L^2(\Omega)$ and weakly in $H^1(\Omega)$, up to extraction of a subsequence. The tightness of ρ_{Ψ_n} also implies that $\Psi_n \rightarrow \Psi_\infty$ strongly in $L^2(\Omega^N)$ and that the limit of ρ_{Ψ_n} is ρ_{Ψ_∞} .

Let $f \in \mathcal{C}_c^\infty(\Omega)$, by assumption (6.4), there exists a sequence of functions $f_n \in \text{Span} \{\alpha_i^n, i \in I_n\}$ such that $\|f - f_n\|_{L^p + L^\infty} \rightarrow 0$ when $n \rightarrow +\infty$. We also have $\int f_n \rho_{\Psi_n} = \int f_n \rho$ because $f_n \in \text{Span} \{\alpha_i^n, i \in I_n\}$. By using

$$\begin{aligned} \left| \int f(\rho_{\Psi_n} - \rho) \right| &= \left| \int (f - f_n)(\rho_{\Psi_n} - \rho) \right| \\ &\leq c_d \left(\|\sqrt{\rho}\|_{H^1} + \sup_{n \in \mathbb{N}} \|\sqrt{\rho_{\Psi_n}}\|_{H^1} \right) \|f - f_n\|_{L^p + L^\infty}, \end{aligned}$$

we deduce that $\int f \rho_{\Psi_n} \rightarrow \int f \rho$. This is a convergence of ρ_{Ψ_n} to ρ in the sense of distributions and by uniqueness of the limit, we have then $\rho = \rho_{\Psi_\infty}$.

We deduce that Ψ_∞ belongs to the minimizing set of $F^N(\rho)$, consequently $F^N(\rho) \leq \mathcal{E}_0(\Psi_\infty)$. By also using lower semi-continuity of the energy functional since $w \geq 0$, we have

$$F^N(\rho) \leq \mathcal{E}_0(\Psi_\infty) \leq \liminf \mathcal{E}_0(\Psi_n) \leq F^N(\rho).$$

We have thus equality and we conclude that Ψ_∞ is a minimizer of $F^N(\rho)$. Let us consider the quadratic form $q(\Psi) := \langle \Psi, H^N(0)\Psi \rangle$. The convergence on the Levy-Lieb functionals $F^{N,\alpha_n}(r_\rho) \rightarrow F^N(\rho)$ gives $q(\Psi_n) \rightarrow q(\Psi_\infty)$, and since $w \geq 0$ is $(-\Delta)$ -bounded as a quadratic form, the associated norm of q is equivalent to the H^1 norm, and hence $\Psi_n \rightarrow \Psi_\infty$ in H^1 .

In the mixed states case, we follow a similar adaptation as for proving Theorem 6.1.1. As in the pure states case, the norm of \mathcal{E}_0 is equivalent to the norm of $\mathfrak{S}_{1,1}$, hence $\Gamma_n \rightarrow \Gamma_\infty$ strongly in $\mathfrak{S}_{1,1}$. \square

6.2.2 The dual problem: proof of Theorem 6.1.5

In this section, we prove Theorem 6.1.5 on the coercivity of the dual functional $G_{r,\alpha}$. In the proofs we will use the notation

$$E_{\text{dis}}^N(v) := E^N\left(\sum_{i \in I} v_i \alpha_i\right), \quad V(v) := \sum_{i \in I} v_i \alpha_i.$$

We recall that $c_\Omega := -E^N(0)/N$ is the constant such that the energy $E^N(\sum_{i \in I} c_\Omega \alpha_i) = E^N(c_\Omega) = 0$ vanishes. We present a fact about the sign of the potential.

Lemma 6.2.2. *Let $v \in \ell^\infty(I, \mathbb{R})$ be such that $E_{\text{dis}}^N(v) = 0$ and $v \neq c_\Omega$. If $H^N(V(v))$ has a minimizer, then there exists $k \in I$ such that $v_k < c_\Omega$. If Ω is bounded, then there exists $\ell, j \in I$ such that $v_j < c_\Omega < v_\ell$.*

Proof of Lemma 6.2.2.

- Let Ψ be a ground state of $H^N(V(v))$. We have

$$\begin{aligned} 0 &= E_{\text{dis}}^N(v) = \mathcal{E}_{V(v)}(\Psi) = \mathcal{E}_{c_\Omega}(\Psi) + \int (V(v) - c_\Omega) \rho_\Psi \\ &\geq E^N(c_\Omega) + \int (V(v) - c_\Omega) \rho_\Psi = \sum_{i \in I} (v_i - c_\Omega) \int \rho_\Psi \alpha_i. \end{aligned}$$

Thus

$$\sum_{v_i > c_\Omega} |v_i - c_\Omega| \int \rho_{\Psi_v} \alpha_i \leq \sum_{v_i < c_\Omega} |v_i - c_\Omega| \int \rho_{\Psi_v} \alpha_i. \quad (6.11)$$

If $v \geq c_\Omega$, then the right hand side of (6.11) vanishes and $v = c_\Omega$ because $|\{\rho_{\Psi_v} = 0\}| = 0$ and therefore $\int \rho_{\Psi_v} \alpha_i > 0$ by unique continuation [10, Remark 1.6].

- If Ω is bounded, then $E^N(0)$ has a minimizer Ψ and

$$\begin{aligned} 0 &= E_{\text{dis}}^N(v) \leq \mathcal{E}_{V(v)}(\Psi) = \mathcal{E}_{c_\Omega}(\Psi) + \int (V(v) - c_\Omega) \rho_\Psi \\ &= \sum_{i \in I} (v_i - c_\Omega) \int \rho_\Psi \alpha_i, \end{aligned}$$

then we obtain the inequality opposite to (6.11),

$$\sum_{v_i < c_\Omega} |v_i - c_\Omega| \int \rho_\Psi \alpha_i \leq \sum_{v_i > c_\Omega} |v_i - c_\Omega| \int \rho_\Psi \alpha_i, \quad (6.12)$$

for this particular state. If $v \leq c_\Omega$, then the right hand side of (6.12) vanishes, but this is not possible since the left hand side has to be strictly positive, hence there is $\ell \in I$ such that $v_\ell > c_\Omega$.

By unique continuation [10, Remark 1.6], $\int \rho_u \alpha_i > 0$ for any $i \in I$ and any ground state density ρ_u of $u \in L^\infty(I, \mathbb{R})$. Hence $u \mapsto E_{\text{dis}}^N(u)$ is strictly increasing. By taking a potential $v \in \ell^\infty(\Omega, \mathbb{R})$ such that $E_{\text{dis}}^N(v) = 0$ and $v_\ell > c_\Omega$ for some $\ell \in I$, if we suppose that $v \geq c_\Omega$, then $0 = E_{\text{dis}}^N(c_\Omega) < E_{\text{dis}}^N(v)$, which is a contradiction. We conclude that there is also $j \in I$ such that $v_j < c_\Omega$. \square

We are now ready to prove the coercivity for the dual functional.

Proof of Theorem 6.1.5.

• We first prove (6.7). We assumed that there are points $y_i \in \mathbb{R}^d$ such that for any $i \in I$,

$$B_R(y_i) \subset (\text{supp } \alpha_i) \setminus \cup_{j \in I, j \neq i} \text{supp } \alpha_j.$$

We write $X = (x_1, \dots, x_N)$ and $Y_i = (y_i, \dots, y_i)$. Let $\Phi \in \wedge^N H_0^1(B_R)$ be a minimizer of

$$\min_{\substack{\Psi \in \wedge^N H_0^1(B_R) \\ \int |\Psi|^2 = 1}} \langle \Psi, H^N(0)\Psi \rangle.$$

We take some non-empty $Q \subset I$ and form

$$\Psi_Q := \frac{1}{\sqrt{\sum_{i \in Q} r_i}} \sum_{i \in Q} \sqrt{r_i} \Phi(X - Y_i).$$

This satisfies $\int_{\mathbb{R}^{dN}} |\Psi_Q|^2 = 1$, $T(\Psi_Q) = T(\Phi)$, $W(\Psi_Q) = W(\Phi)$ and

$$\rho_{\Psi_Q}(x) = \left(\sum_{i \in Q} r_i \right)^{-1} \sum_{i \in Q} r_i \rho_\Phi(x - y_i).$$

For any $i \in I$, the only non-vanishing element of α in $B_R(y_i)$ is α_i , so $\alpha_i = 1$ on $B_R(y_i)$. We deduce that

$$\begin{aligned} G_{r, \alpha}(v) &\leq \mathcal{E}_v(\Psi_Q) - \sum_{i \in I} v_i r_i \\ &= \mathcal{E}_0(\Phi) + \frac{N - \sum_{i \in Q} r_i}{\sum_{i \in Q} r_i} \sum_{i \in Q} v_i r_i - \sum_{i \in I \setminus Q} v_i r_i \\ &= \mathcal{E}_0(\Phi) + \frac{\sum_{i \in I \setminus Q} r_i}{\sum_{i \in Q} r_i} \sum_{i \in Q} v_i r_i - \sum_{i \in I \setminus Q} v_i r_i. \end{aligned}$$

Since G is gauge invariant, for any $\mu \in \mathbb{R}$ and any non-empty $Q \subset I$, we have

$$G_{r, \alpha}(v) = G_{r, \alpha}(v - \mu) \leq \mathcal{E}_0(\Phi) + \frac{\sum_{i \in I \setminus Q} r_i}{\sum_{i \in Q} r_i} \sum_{i \in Q} (v_i - \mu) r_i - \sum_{i \in I \setminus Q} (v_i - \mu) r_i. \quad (6.13)$$

We define the two sets $I_v^\pm := \{i \in I \mid \pm v_i > c_\Omega\}$. In the case $I_v^- \neq \emptyset$, we take $Q = I_v^-$ and $\mu = c_\Omega$ yielding

$$\begin{aligned} G_{r,\alpha}(v) - \mathcal{E}_0(\Phi) &\leq \frac{\sum_{v_i \geq c_\Omega} r_i}{\sum_{v_i < c_\Omega} r_i} \sum_{v_i < c_\Omega} (v_i - c_\Omega) r_i - \sum_{v_i \geq c_\Omega} (v_i - c_\Omega) r_i \\ &\leq \min \left(1, \frac{\sum_{v_i \geq c_\Omega} r_i}{\sum_{v_i < c_\Omega} r_i} \right) \left(\sum_{v_i < c_\Omega} (v_i - c_\Omega) r_i - \sum_{v_i \geq c_\Omega} (v_i - c_\Omega) r_i \right) \\ &\leq -\frac{\sum_{v_i \geq c_\Omega} r_i}{N} \|v - c_\Omega\|_{\ell_r^1}. \end{aligned} \quad (6.14)$$

In the case $v = c_\Omega$, we have $G_{r,\alpha}(v) = -c_\Omega N = E^N(0) \leq \mathcal{E}_0(\Phi)$ hence the bound also holds.

If $v \geq c_\Omega$, then $\inf v = c_\Omega$ otherwise $0 = E_{\text{dis}}^N(v) \geq E_{\text{dis}}^N(\inf v) > E_{\text{dis}}^N c_\Omega = 0$. We take a sequence $(v_{\varphi(n)})_{n \in \mathbb{N}}$ where $\varphi(n) \in I$ is such that $v_{\varphi(n)} \rightarrow c_\Omega$ when $n \rightarrow +\infty$. If I is finite, then there is $\ell \in I$ such that $v_\ell = 0$ and we take $\varphi(n) = \ell$ for any $n \in \mathbb{N}$. We choose $Q = \{\varphi(n)\}$ with only one element, and then

$$\begin{aligned} G_{r,\alpha}(v) &\leq \mathcal{E}_v(\Psi_Q) - \sum_{i \in I} v_i r_i \leq \mathcal{E}_0(\Phi) + v_{\varphi(n)} \int \rho_{\Psi_Q} \alpha_{\varphi(n)} - \sum_{i \in I} v_i r_i \\ &\leq -\|v\|_{\ell_r^1} + N v_{\varphi(n)} + \mathcal{E}_0(\Phi). \end{aligned}$$

By gauge invariance, we also have

$$G_{r,\alpha}(v) = G_{r,\alpha}(v - c_\Omega) \leq -\|v - c_\Omega\|_{\ell_r^1} + N (v_{\varphi(n)} - c_\Omega) + \mathcal{E}_0(\Phi),$$

and taking the limit $n \rightarrow +\infty$ yields

$$G_{r,\alpha}(v) \leq -\|v - c_\Omega\|_{\ell_r^1} + \mathcal{E}_0(\Phi).$$

• Let v^n be a maximizing sequence. By coercivity, $\sum_{i \in I} |v_i^n| r_i$ is bounded hence $|v_i^n| \leq c/r_i$ uniformly in i, n . There exists $(v_i^\infty)_{i \in I} \in \ell^\infty(I, \mathbb{R})$ such that $v_i^n \rightarrow v_i^\infty$ for all $i \in I$, up to a subsequence and finally $v^\infty \in \ell_r^1(I, \mathbb{R})$ by Fatou's lemma. By weak upper-semicontinuity of $G_{r,\alpha}$, we have

$$\sup_{\ell^\infty(I, \mathbb{R})} G_{r,\alpha} = \limsup G_{r,\alpha}(v^n) \leq G_{r,\alpha}(v^\infty),$$

hence v^∞ maximizes $G_{r,\alpha}$. The maximizing potential is unique by concavity of the functional.

Now assume that Ω is bounded. Let Γ_r be the minimizer of $F_{\text{mix}}^{N,\alpha}(r)$, which exists by Theorem 6.1.1. Since $\int \rho_{\Gamma_r} \alpha_i = r_i$, then

$$\begin{aligned} \mathcal{E}_{V(v^\infty)}(\Gamma_r) &= \text{Tr } H^N(V(v^\infty)) \Gamma_r = \text{Tr } H^N(0) \Gamma_r + \sum_{i \in I} v_i^\infty r_i \\ &= G_{r,\alpha}(v^\infty) + \sum_{i \in I} v_i^\infty r_i = E_{\text{dis}}^N(v^\infty). \end{aligned}$$

By diagonalizing $\Gamma_r =: \sum_{\ell \in \mathbb{N}} \lambda_\ell |\varphi_\ell\rangle \langle \varphi_\ell|$, where $\sum_{\ell \in \mathbb{N}} \lambda_\ell = 1$, and since $\mathcal{E}_0(\Gamma)$ is linear in Γ , we have

$$\sum_{\ell \in \mathbb{N}} \lambda_\ell \mathcal{E}_{V(v^\infty)}(\varphi_\ell) = E_{\text{dis}}^N(v^\infty).$$

But $\mathcal{E}_{V(v^\infty)}(\varphi_\ell) \geq E_{\text{dis}}^N(v^\infty)$ and thus $\mathcal{E}_{V(v^\infty)}(\varphi_\ell) = E_{\text{dis}}^N(v^\infty)$ for any $\ell \in \mathbb{N}$, and finally

$$\varphi_\ell \in \text{Ker} \left(H^N(V(v^\infty)) - E_{\text{dis}}^N(v^\infty) \right).$$

□

Remark 6.2.3. When $\Omega = \mathbb{R}^d$, the situation is different. Assume also $E_{\text{dis}}^N(v) = 0$. We apply (6.13) with $Q = \{v_i < \epsilon\}$ for some $\epsilon > 0$, which is not empty since $\inf v = 0$. This yields

$$G_{r,\alpha}(v) - \mathcal{E}_0(\Phi) \leq - \min \left(1, \frac{\sum_{v_i \geq \epsilon} r_i}{\sum_{v_i < \epsilon} r_i} \right) \|v - \epsilon\|_{\ell_r^1, \alpha}$$

and we conclude by letting $\epsilon \rightarrow 0$,

$$G_{r,\alpha}(v) - \mathcal{E}_0(\Phi) \leq - \min \left(1, \frac{\sum_{v_i > 0} r_i}{\sum_{v_i \leq 0} r_i} \right) \|v\|_{\ell_r^1} \leq - \min \left(1, \frac{\sum_{v_i > 0} r_i}{N} \right) \|v\|_{\ell_r^1}.$$

The problem is that we are not able to find a strictly positive lower bound for $\sum_{v_i > 0} r_i$, which would provide coercivity.

Remark 6.2.4. A natural norm on potentials is the gauge invariant quotient norm

$$\|v\|_{\ell_r^1 / \sim} = \inf_{\mu \in \mathbb{R}} \|v - \mu\|_{\ell_r^1},$$

where $v \sim u$ when $v - u$ is constant. If in (6.13) we take $Q = \{i \in I \mid v_i = \inf v\}$, $\mu = \inf v$ we obtain

$$G_{r,\alpha}(v) - \mathcal{E}_0(\Phi) \leq - \sum_{v_i > \inf v} (v_i - \inf v) r_i = - \|v - \inf v\|_{\ell_r^1} \leq - \|v\|_{\ell_r^1 / \sim}.$$

Hence $G_{r,\alpha}$ is coercive in the ℓ_r^1 / \sim norm, but this is not a convenient norm because by definition we do not control the constant.

6.2.3 Building Kohn-Sham potentials: proofs of Corollary 6.1.6 and Theorem 6.1.8

In this section, we show how Theorem 6.1.5 yields approximate v -representability when Ω is unbounded.

The mixed states case

Proof of Corollary 6.1.6. Consider copies of the cube $C^n := [-1/n, 1/n]^d$, centered on the grid points of $(\mathbb{Z}/n)^d$. Take Ω_n to be the union of all those cubes $(C_i^n)_{i \in I_n}$ which are included in $\Omega \cap B_n$, where B_r is the ball of radius n . They form an increasing sequence $\Omega_n \subset \Omega_{n+1}$. We choose $\alpha_i^n := \mathbf{1}_{C_i^n}$. We apply Theorem 6.1.5 to $r^{(n)} := c_n r \rho \mathbf{1}_{\Omega_n}$ with $c_n := N / \int_{\Omega_n} \rho$. The condition $|\{\rho = 0\}| = 0$ ensures that $r_i^{(n)} > 0$ for any $i \in I_n$, $n \in \mathbb{N}$. We denote by $v^n \in \ell^\infty(I, \mathbb{R})$ the maximizer of $G_{r^{(n)}, \alpha_n}$, and by Γ_n a minimizer of $F^{N, \alpha_n}(r^{(n)})$. We have $\int \rho_{\Gamma_n} \alpha_i^n = c_n \int \rho \alpha_i^n$ and finally apply Theorem 6.1.2.

Each Γ_n lives in $\mathcal{S}_{\text{mix}}^N(\Omega_n)$ and each $H^N(\sum v_i^n \alpha_i^n)$ is an operator of $L_a^2(\Omega_n^N)$, but by “digging pits” close to where the density is localized, we can create a potential $V_n = -\lambda_n \mathbf{1}_{\Omega_n} + \sum_i v_i^n \alpha_i^n$ with λ_n large enough so that we keep the same properties for systems living in \mathbb{R}^d . \square

The pure states case

Proof of Theorem 6.1.8. We assume $N \geq 1$ and only restrict to $N = 1$ at the end of the argument. We define the map

$$\begin{aligned} \kappa : H_a^1(\Omega^N) \cap \left\{ \int |\Psi|^2 = 1 \right\} &\longrightarrow (\mathbb{R}_+)^{|I|} \\ \Psi &\longmapsto \left(\int \rho_\Psi \alpha_i \right)_{i \in I}. \end{aligned}$$

It is \mathcal{C}^∞ and since I is finite, $\text{Ran } d_\Psi \kappa$ is closed for any $\Psi \in L_a^2(\Omega^N)$ because the image lives in a finite-dimensional space. Now $d_\Psi G$ has closed range for any $\Psi \in \wedge^N H^1(\Omega)$ because its target space is finite-dimensional. We compute, for any $\varphi \in H_a^1(\Omega^N)$ and any $v \in \mathbb{R}^{|I|}$,

$$\begin{aligned} \sum_{i \in I} v_i ((d_\Psi \kappa) \varphi)_i &= 2N \operatorname{Re} \sum_{i \in I} v_i \int_{\Omega^N} (\Psi \bar{\varphi})(x_1, \dots, x_N) \alpha_i(x_1) dx_1 \cdots dx_N \\ &= 2 \operatorname{Re} \int_{\Omega^N} \sum_{j=1}^N \left(\sum_{i \in I} v_i \alpha_i \right) (x_j) (\Psi \bar{\varphi})(x_1, \dots, x_N) dx_1 \cdots dx_N \\ &= 2 \operatorname{Re} \langle \varphi, (\sum_i V(v)_i) \Psi \rangle \end{aligned}$$

Furthermore, $h : \Psi \mapsto \langle \Psi, H^N(0) \Psi \rangle$ is \mathcal{C}^∞ with differential

$$(d_\Psi h) \varphi = 2 \operatorname{Re} \langle \varphi, H^N(0) \Psi \rangle.$$

Let $\Psi \in H_a^1(\Omega^N)$ with unit norm be a minimizer of $F^{N, \alpha}(r)$, then $\int \rho_\Psi \alpha_i = r_i$ for any $i \in I$. We apply [26, Prop 43.19 p291], ensuring the existence of Lagrange multipliers $(v_i)_{i \in I} \in (\ell^1(I, \mathbb{R}))^* = \ell^\infty(I, \mathbb{R})$ such that $H^N(V(v)) \Psi = 0$ weakly, or such that $(\sum_i V(v)_i) \Psi = 0$ weakly and $v \neq 0$.

We prove by contradiction that the second case is impossible, so let us assume that $(\sum_i V(v)_i) \Psi = 0$. This is where we need $N = 1$, which implies

$V(v)\Psi = 0$ and $0 = v_i \int \rho_\Psi \alpha_i = v_i r_i$, but since $r_i > 0$, we conclude that $v_i = 0$, which is a contradiction. If Conjecture 6.1.9 holds, then $(\sum_i V(v)_i)\Psi = 0$ implies $(\sum_i V(v)_i) = 0$ a.e and $v = 0$, and this avoids the second case for all N .

We hence know that

$$H^N(V(v))\Psi = 0 \tag{6.15}$$

with $V(v) \in L^p(\Omega)$, p as in (6.1), so Ψ is in the domain of $H^N(V(v))$ and consequently is an eigenvalue. Since Ω is bounded, Ψ is in the discrete spectrum. \square

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Chapter 7

Numerical investigation of the attainability set

In this chapter, we numerically analyze the dual problem and try to compute the Kohn-Sham potential. This can also be seen as an inverse problem. We conclude that for $d = 1$, given a density, we can always find a potential which ground (or excited) state density is equal to our initial target density. In dimensions $d = 2$ and $d = 3$, the state of our analysis does not enable to make such conclusions, but we think that further work will bring an answer.

For practical reasons, we do not use the framework of Chapter 6. Instead we discretize the space on a finite grid $(\mathbb{Z} \cap [-L, L])^d$, this corresponds to the model studied in [5]. In this case and for $d = 1$ for instance, the laplacian and the potential multiplication are respectively the matrices

$$-\Delta = \begin{pmatrix} 2 & -1 & 0 & \dots \\ -1 & 2 & -1 & \\ 0 & -1 & 2 & \\ \vdots & & & \ddots \end{pmatrix}, \quad v = \begin{pmatrix} v(x_1) & 0 & \dots \\ 0 & v(x_2) & \\ \vdots & & \ddots \end{pmatrix}.$$

We implemented the algorithm in Python. We consider the operators in a plane waves basis, and compute the Fourier series of functions with the fast Fourier transform methods of Numpy.

We consider the operator

$$H_{w=0}^N(v) := \sum_{i=1}^N (-\Delta_i + v(x_i)).$$

Given some density ρ belonging to the set

$$\left\{ \rho \in L^1(\mathbb{R}^d) \mid \rho \geq 0, \int \rho = N, \sqrt{\rho} \in H^1(\mathbb{R}^d) \right\}, \quad (7.1)$$

called the target density, our goal is to find a potential v such that $H_{w=0}^N(v)$ has at least one k^{th} excited state $\Psi^{(k)}(v)$ and such that for some $\Psi^{(k)}(v) \in \text{Ker}(H_{w=0}^N(v) - E^{(k),N}(v))$,

$$\boxed{\rho_{\Psi^{(k)}(v)} = \rho.}$$

We would also like to know whether the set of v -representable densities

$$\left\{ \rho_{\Psi^{(k)}(v)} \mid v \in (L^p + L^\infty)(\mathbb{R}^d), \Psi^{(k)}(v) \in \text{Ker}(H_{w=0}^N(v) - E^{(k),N}(v)) \right\} \quad (7.2)$$

is dense in the set of densities (7.1). We recall that for $k = 0$, when the searched potential v exists, it is unique by the Hohenberg-Kohn theorem [6, 7], as seen in Chapter 1. No similar result seems to be known for $k \geq 1$.

More explicitly, since $w = 0$, we are led to study the one-body operator $-\Delta + v$, its eigenvectors are denoted by φ_v^i , having energies $E_v^i = \int |\nabla \varphi_v^i|^2 + \int v |\varphi_v^i|^2$. The N -body excited states are $\Psi^{(k)} = \wedge_{i \in S_k} \varphi_v^i$, where $S_k \subset \mathbb{N}^{\geq 0}$ is one of the corresponding sets of fundamental and excited states labels and depends on v , in particular $S_0 = \{0, \dots, N-1\}$. The sets S_k can take several configurations for some given k in which case the N -body level k is degenerate. The density is

$$\rho_{\Psi^{(k)}(v)} = \sum_{i \in S_k} |\varphi_v^i|^2,$$

and the energy is $E^{(k),N}(v) = \sum_{i \in S_k} E_v^i$. Hence given some positive density ρ with $\int \rho = N$, we search v such that $\sum_{i \in S_k} |\varphi_v^i|^2 = \rho$.

In [11, (3.17)], Lieb introduces the density functional $F_{\text{mix}}^N(\rho)$ in the form of the maximization of the map $v \mapsto E^N(v) - \int v \rho$, which is the dual problem of the Levy-Lieb functional. For quantum lattices [5], for classical systems at positive temperature [4] and for the exact discretized model in a bounded domain (see Chapter 6), the corresponding dual problem is well-posed, that is, this functional has a unique maximizer. This is the Kohn-Sham potential of the prescribed density. This shows that for $k = 0$, the numerical maximization of $v \mapsto E^N(v) - \int v \rho$ is expected to provide the potential v such that $\rho(v) = \rho$.

We investigate the cases $d = 1$ and $d = 2$, and we conjecture that the cases $d \geq 3$ are similar to the case $d = 2$. Each of our tests were made on several dozens of input functions, which were randomly chosen.

7.1 Algorithm for ground and excited states

In the case of mixed states, according to [11, (4.5)], we have

$$\sup_{v \in L^p + L^\infty} G_\rho(v) = \inf_{\substack{\Gamma \in \mathcal{S}_{\text{mix}}^N \\ \rho_\Gamma = \rho}} \text{Tr} H^N(0) \Gamma. \quad (7.3)$$

Hence, maximizing

$$G_\rho(v) := E^N(v) - \int v\rho$$

would lead to the “mixed” Kohn-Sham potential. In the pure states case, (7.3) does not hold anymore but we can still try to maximize G_ρ . We extend the original problem by considering the maps

$$G_\rho^{(k),N}(v) := E^{(k),N}(v) - \int v\rho = - \int v\rho + \sum_{i \in S_k} \int \left(|\nabla \varphi_v^i|^2 + v |\varphi_v^i|^2 \right)$$

for $k \in \mathbb{N}^{\geq 0}$, where excited energies $E^{(k),N}(v)$ are defined by the usual min-max formula [12, Section 12.1], the ground energy being $E^N = E^{(0),N}$. In the case where the k^{th} level of $H_{w=0}^N(v)$ is non-degenerate, the Hellman-Feynman theorem yields

$$\left(d_v G_\rho^{(k),N} \right) u = \int u (\rho_{\Psi^{(k)}(v)} - \rho),$$

for any potential u . We apply a gradient ascent algorithm on $G_\rho^{(k),N}$ to maximize it, expecting that the maximizing potential would have its k^{th} excited state density equal to ρ , as it is the case for $k = 0$ [5]. That is, we start from the exact one-body potential

$$v_0 := \frac{\Delta \sqrt{\rho}}{\sqrt{\rho}},$$

and compute iteratively

$$v_{n+1} = v_n + \lambda (\rho_{\Psi^{(k)}(v_n)} - \rho),$$

for some $\Psi^{(k)}(v_n)$ chosen arbitrarily in $\text{Ker}(H_{w=0}^N(v) - E^{(k),N}(v))$. The global constant in potentials has no importance during the scheme, we only fix it in the graphs, such that $\int v = 0$, for readability purposes. As expected, for $N = 1$ and $k = 0$, the potential $v_0 = \Delta \sqrt{\rho} / \sqrt{\rho}$ has a density very close to the target density ρ . Moreover, we found that $\lambda = 1$, kept fixed during the procedure, is a good speed-convergence trade-off. Note that in [15], the authors use $v^{n+1} = \rho_{\Psi^{(k)}(v_n)} v^n / \rho$, and in [9] they use $v^{n+1} = v^n + \lambda (\rho_{\Psi^{(k)}(v_n)} - \rho) / \rho$.

We consider that the algorithm converged when

$$\left\| \rho_{\Psi^{(k)}(v_n)} - \rho \right\|_{L^1} / N \leq 10^{-3}.$$

If it does not converge, $\left\| \rho_{\Psi^{(k)}(v_n)} - \rho \right\|_{L^1} / N$ oscillates between higher values, and $\min_{n \in \mathbb{N}} \left\| \rho_{\Psi^{(k)}(v_n)} - \rho \right\|_{L^1} / N$ is typically between N and 10^{-2} .

7.2 Justification of the algorithm

We want to provide evidence that the outputs of the algorithm are legitimate. To this purpose, we take potentials v and their target densities $\rho_{\Psi^{(k)}(v)}$ and we launch the algorithm on this density, as it is the case in Figure 7.2.

For $d = 1, k = 0$ and for any $N \geq 1$, the output potential of the algorithm is close to the initial v . For $d = 1, k \geq 1$ and $N \geq 1$, the output potential is also close to the initial v , modulo some oscillations as in Figure 7.2, but the output density converges to the targeted one. For $d = 2, k = 0$ and any $N \geq 1$, the output potential is also close to v . However, for $d = 2, N \geq 1$ and $k \geq 1$, the algorithm is not able to converge, neither in density, nor in potential. So we cannot test our technique in these cases hence for $d = 2$ we only consider $k = 0$.

7.3 Preliminary remarks

In the simulations, we noted that the densities can be very close while the potentials are not. This is a usual property for locally weak-strong continuous maps. Highly oscillating parameters do not change much the final quantities, see Theorem 4.1.1 in Chapter 4.

In the ground state case, starting from $v_0 = 0$ only slightly affects the convergence, whereas in the excited state case, the algorithm converges significantly quicker when we start from $v_0 = \Delta\sqrt{\rho}/\sqrt{\rho}$ compared to $v_0 = 0$. Remark that in practice we need to impose a cut-off on v_0 , because it diverges in the areas where $\sqrt{\rho}$ is close to zero.

The presence of nodes is problematic, and excited orbitals have more nodes. In those areas where an orbital is close to zero, and from the point of view of the algorithm, the transmission of information between potentials and orbital densities is blocked, this is certainly the reason of the presence of oscillations in the excited state case. Also, if we split the density into two separated parts of non-integer integrals, the algorithm does not converge. The area situated between the two separated pieces, where the density is close to zero, raises the divergence issue. Indeed, one electron has then to split by tunnelling effect, which has a very short range. Our target densities hence have to hold in only one piece. We illustrate this fact in Figure 7.1, for $d = 1$, where the target density is split in two separated gaussians. In the first case, the two gaussians are equal, each of integral 1.5, hence one of the electrons has to be split into two parts for the target density to be represented, and we can see that the algorithm diverges. In the second case, the left gaussian has integral 2 and the second has integral 1, and the density can be represented, and the problem boils down to two independent representability problems.

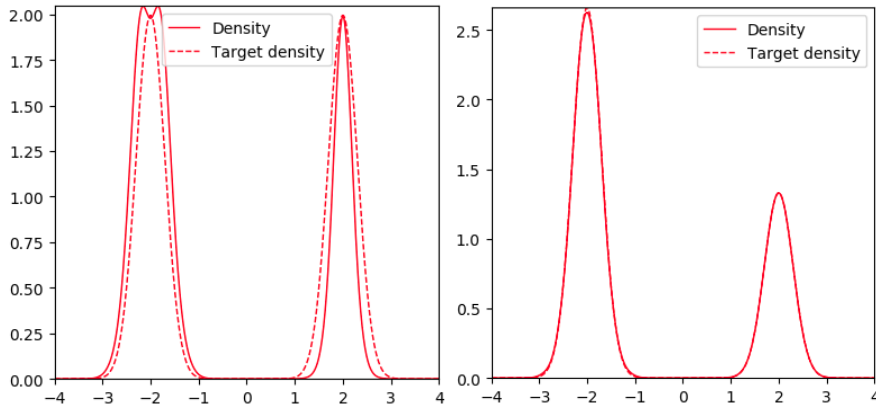


Figure 7.1: Plot of target and algorithm densities for $d = 1$, $N = 3$. In the first case, the left and right Gaussians have integral 1.5 whereas in the second case, the first has integral 2 and the second one has integral 1. We see that when the different Gaussians have integer masses, the density can be represented but when they have fractional masses, the density cannot be represented.

7.4 Dimension 1

Let us start from some target potential v and its target density $\rho_{\Psi^{(k)}(v)}$. After a few iterations, we show in Figure 7.2 an example of what one can obtain, in the ground state setting $k = 0$ and for the second excited state $k = 2$, with the same target potential.

For any $N \geq 1$ and any $k \geq 0$, the algorithm always converges to a potential v such that $\rho_{\Psi^{(k)}(v)}$. This provides evidence to the fact that the set of k^{th} excited state v -representable densities (7.2) is dense in the set of normalized positive functions (7.1) for $d = 1$.

To illustrate the response of the algorithm to different kinds of input densities, we give examples of Kohn-Sham potentials in Figure 7.3. It is surprising that the algorithm, using a dual formulation, finds the inverse potential in the excited state configuration, while the primal problem does not admit a formulation for excited states. The fact that the map $v \mapsto \rho_{\Psi^{(k)}(v)}$ seems injective could motivate the development of functionals in terms of excited densities, for $d = 1$.

7.4.1 Levy-Lieb, degeneracies and convergence

We restrict to the ground state case. The convergence of the algorithm has a very close relationship with degeneracies of the ground eigenspace. In the proof of [11, Theorem 3.4], Lieb identified a class of densities ρ such that

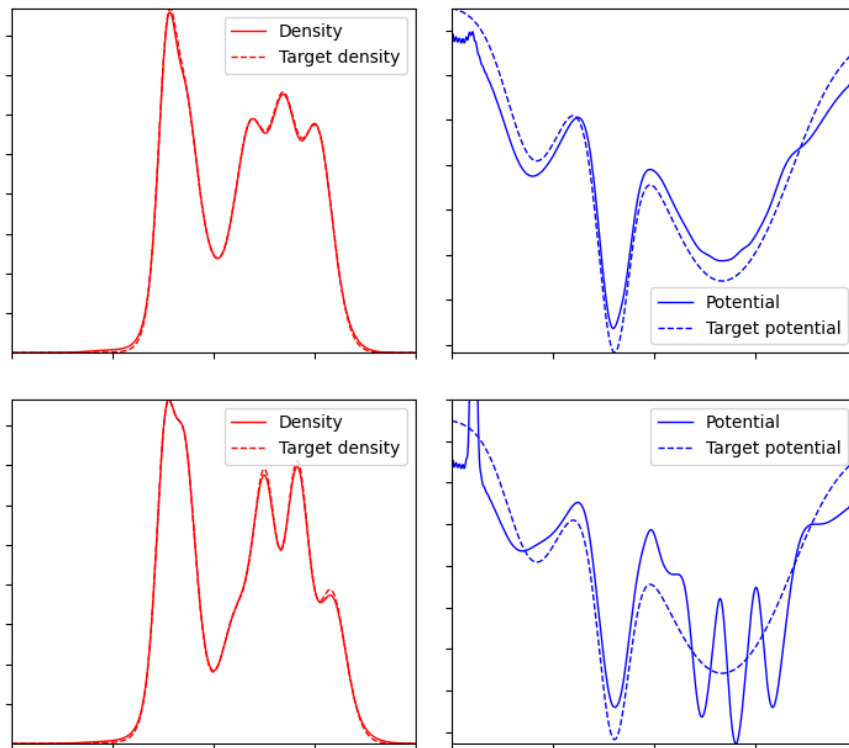


Figure 7.2: Plot for $d = 1$, $N = 5$, in the ground state setting $k = 0$ on the first line and for the second excited state $k = 2$ on the second line. We start from a target potential v and launch the algorithm on $\rho_{\Psi^{(k)}(v)}$.

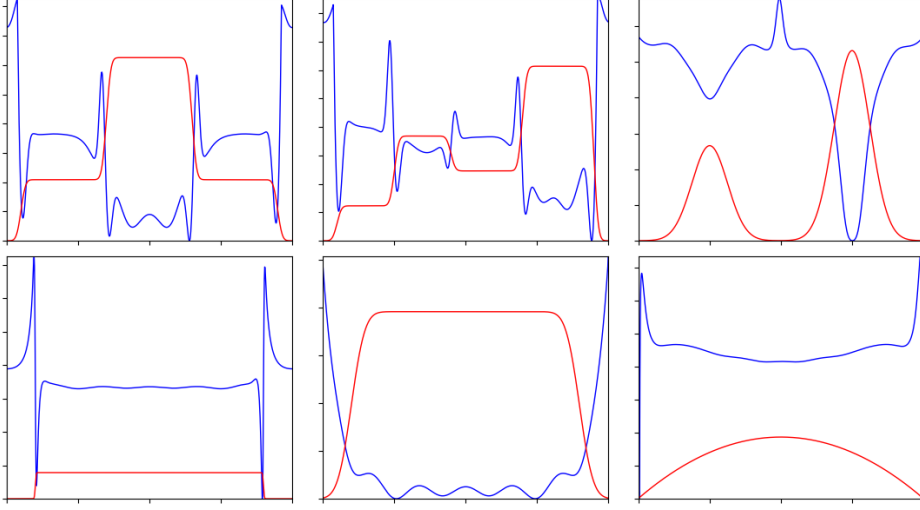


Figure 7.3: Target densities in red and their Kohn-Sham potential (in different units) in blue, for $d = 1$, $N = 5$, for the ground state setting and starting from several initial target densities.

$F_{\text{mix}}^N(\rho) < F^N(\rho)$. He used radial symmetry and degeneracies of spherical orbitals in dimension 3, which can also be used in dimension $d \geq 3$ but not in dimension 1. Moreover, relying also on [11, Theorem 3.10], we think that a density ρ is v -representable with ground states if and only if $F_{\text{mix}}^N(\rho) = F^N(\rho)$.

We think that our algorithm converges if and only if $F_{\text{mix}}^N(\rho) = F^N(\rho)$, and that this is also equivalent to the fact that the ground eigenspace of $H_{w=0}^N(v_{\text{ks}}(\rho))$ is non-degenerate, where $v_{\text{ks}}(\rho)$ is the Kohn-Sham potential of the mixed state case.

To prepare the discussion, we recall a well-known result specific to the dimension one.

Proposition 7.4.1 (Non-degeneracy theorem). *For $d = 1$ and $N = 1$, for $v \in (L^1 + L^\infty)(\mathbb{R})$, every eigenstate of $H^N(v)$ is non-degenerate.*

We recall its proof for the convenience of the reader.

Proof. Let $\Psi_1, \Psi_2 \in H^1(\mathbb{R}, \mathbb{R})$ be such that $H^N(v)\Psi_i = E\Psi_i$ for $i \in \{1, 2\}$, with $E \in \mathbb{R}$. Then by multiplying the first equation by Ψ_2 and the second by Ψ_1 and subtracting, we can work on the Wronskian and get $0 = \Psi_1\Psi_2'' - \Psi_2\Psi_1'' = (\Psi_1\Psi_2' - \Psi_2\Psi_1')'$. Hence $\Psi_1\Psi_2' - \Psi_2\Psi_1' = c$ for some constant $c \in \mathbb{R}$, but since $\Psi_1, \Psi_2 \in H^1$, then $c = 0$. We have then $\Psi_1'/\Psi_1 = \Psi_2'/\Psi_2$ on $\{x \in \mathbb{R} \mid \Psi_1 \neq 0, \Psi_2 \neq 0\}$, which has full measure by unique continuation [6]. Finally $\Psi_1 = a\Psi_2$ with $a = \pm 1$. \square

This result could justify the fact that the case $d = 1$ is very different from the case $d \geq 2$ that we will study. Even for $N \geq 2$ and $k \geq 0$, the eigenspaces of $H_{w=0}^N(v)$ might be “generically” non-degenerate in a sense that should be precised, and this would justify that densities are always v -representable as seen in simulations. For a general $N \geq 1$ and $w = 0$, ground states can be degenerate, this happens when several combinations of the N first orbitals have the same energy, but this must be a quite “rare” situation. Hence for $d = 1$, we conjecture that densities are generically representable, with any excited state, and $F_{\text{mix}}^N(\rho) = F^N(\rho)$ for any regular density ρ . This would legitimate the inversion of ρ for one-dimensional systems, as done in [8, 10, 13] for instance.

7.5 Dimension 2

7.5.1 Experiments

For $d = 2$, we restrict to $k = 0$ because the algorithm did not manage to reconstruct potentials from excited densities. We noted that the convergence of the algorithm depends on the target density ρ . In Figure 7.4, we present the case $N = 2$ and a gaussian target $\rho(x) = (2\pi\sigma)^{-1}e^{-x^2/(2\sigma^2)}$. In this case, the algorithm oscillates between two rotated configurations. In Figure 7.4, the picture on the left is the target density, and the two others are the final two configurations which persist indefinitely. The curve shows $\|\rho_{\Psi^{(0)}(v_n)} - \rho\|_{L^1} / 2$ against the iteration n , we see that it converges to some threshold above 0.6.

We tested the algorithm on hundreds of different densities, chosen to be sums of gaussians having random parameters. Even for densities which present less symmetries, the algorithm hardly attains precisions lower than 10^{-2} , whereas on densities $\rho_{\Psi^{(k)}(v)}$ coming from potentials, they always reach 10^{-3} .

7.5.2 Levy-Lieb, degeneracies and convergence

We launched the algorithm on many densities, chosen randomly, and most of the time it did not converge. We now give a quantification of the relation between symmetry, degeneracy and convergence. We consider a family of densities

$$\rho_\alpha(x) := c_\alpha \left(e^{-\|x-x_0\|_2^2/(2\sigma^2)} + \alpha e^{-\|x+x_0\|_2^2/(2\sigma^2)} \right), \quad (7.4)$$

where c_α is such that $\int \rho_\alpha = N$, and $x_0 = \begin{pmatrix} \sigma/5 \\ 0 \end{pmatrix}$. We then compute

$$\inf_{n \in \mathbb{N}} \|\rho^{(0)}(v_n) - \rho_\alpha\|_{L^1} / N$$

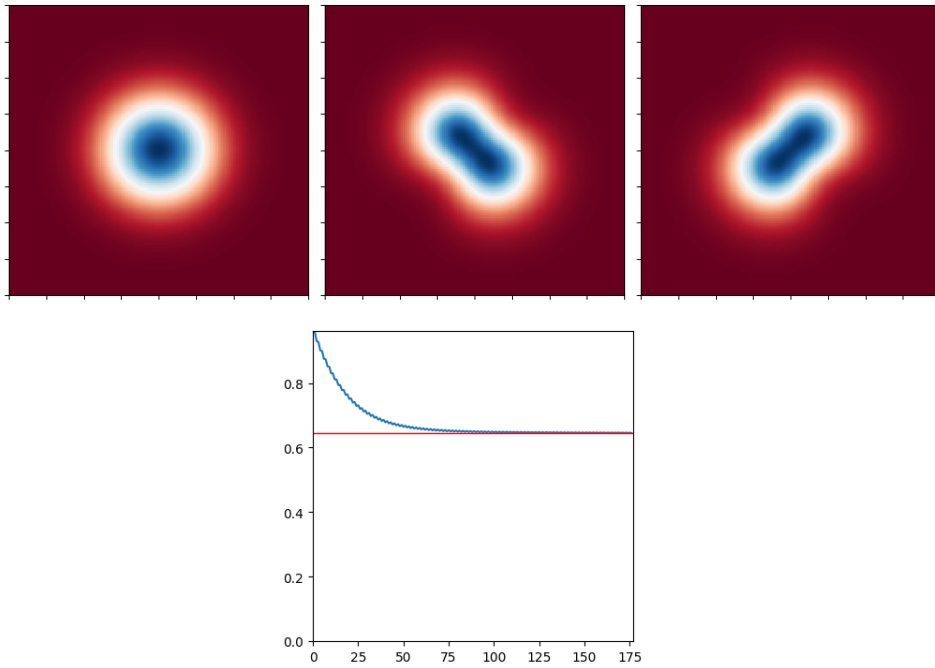


Figure 7.4: Gaussian target density for $d = N = 2$, $\sigma = 1$, the two ground state density configurations of potentials maximizing $G_\rho^{(0);2}$, and $\left\| \rho_{\Psi^{(0)}(v_n)} - (2\pi\sigma)^{-1} e^{-x^2/(2\sigma^2)} \right\|_{L^1} / 2$ against n .

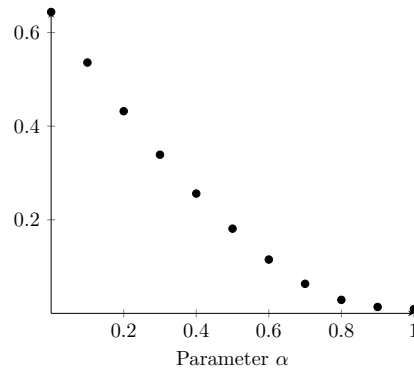


Figure 7.5: Plot of $\inf_{n \in \mathbb{N}} \|\rho_{\Psi^{(0)}(v_n)} - \rho_\alpha\|_{L^1} / N$ against α for $d = N = 2$, $\sigma = 1$, when we progressively break the radial symmetry of a gaussian target density.

for several values of α between 0 and 1, and plot the results on Figure 7.5. This progressive breaking of the radial symmetry shows that densities are closer to be v -representability when they are less symmetric. We also conjecture that $F^N(\rho) - F_{\text{mix}}^N(\rho)$ decreases when symmetry is broken.

The oscillations we see in Figure 7.4 look like oscillations of the Roothaan algorithm used in the Hartree-Fock case [14]. This oscillating behaviour is circumvented by passing to the mixed states case, as done in the Optimal Damping Algorithm [1–3].

Finally, we show here that the radial symmetry can also enable the system to converge. Indeed, for values of N such that the Fermi level is full, then the density of the system is also radial. Hence this boils down to one dimension, in which case the algorithm always converge. In Figure 7.6, we provide the minimal distances for different values of N , where the target density is one Gaussian with the same parameter σ as in (7.4). We see that for the values of N such that the external electronic shell is closed in dimension 2, the algorithm is convergent, otherwise it diverges.

7.6 Improvements

In $d = 1$ and for $k \geq 1$, at each iteration of the potential, one can convolve it with a gaussian, to avoid oscillations of the searched potential. This is a standard technique in inverse problems. We will also improve the algorithm to make it converge in all cases to the Kohn-Sham potential for mixed states. A final step can then check whether a pure state representing the described density exists, from the knowledge of this mixed states Kohn-Sham potential.

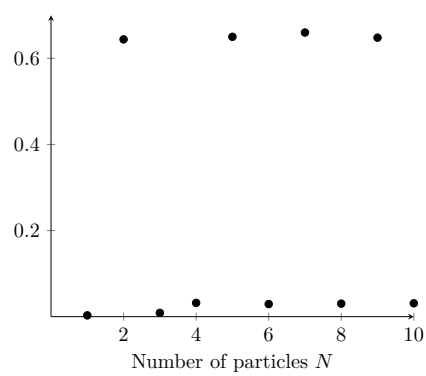


Figure 7.6: Gaussian target density, plot of $\inf_{n \in \mathbb{N}} \left\| \rho_{\Psi^{(0)}(v_n)} - (2\pi\sigma)^{-1} e^{-x^2/(2\sigma^2)} \right\|_{L^1} / N$ against N for $d = 2$. We see that the algorithm converges if and only if the external electronic shells are closed.

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RÉSUMÉ

La théorie de la fonctionnelle de la densité est la méthode la plus efficace pour modéliser la matière quantique à l'échelle microscopique. Son champ d'applications est très large, il couvre les atomes, molécules, solides, fluides. Malgré son éclatant succès en physique et chimie quantique, peu de travaux mathématiques ont porté sur ses fondations. L'objectif de cette thèse a été d'étudier les principales questions liées aux fondements de la théorie. Nous avons traité certaines questions mathématiques autour du théorème de Hohenberg-Kohn, analysé les propriétés de l'application des potentiels vers les densités des états fondamentaux, et avons enfin étudié le problème inverse de Kohn-Sham.

MOTS CLÉS

Physique mathématique, mécanique quantique à N corps, théorie de la fonctionnelle de la densité, théorie spectrale, analyse fonctionnelle.

ABSTRACT

Density functional theory (DFT) is the most efficient method to model matter at the microscopic scale. Its range of applicability is very wide, covering atoms, molecules, solids, fluids. Despite its tremendous success in physics and quantum chemistry, few mathematical works were devoted to its rigorous foundations. The goal of this PhD thesis is to address the main ones. We analyze mathematical aspects about the Hohenberg-Kohn theorem, about the potential-to-density map, and about the Kohn-Sham inversion procedure.

KEYWORDS

Mathematical physics, N -body quantum mechanics, density functional theory, spectral analysis, spectral theory, functional analysis.