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Calculus of variations in quantum mechanics

Stéphane Capet

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Contents

To Xavier And Natalia

Acknowledgements

This thesis grew out of the desire to understand (from a rigorous mathematical standpoint as well as physically) various aspects of the quantum mechanical models used in physics, quantum chemistry... I am very pleased to have participated to the intellectual effort. During the duration of my PhD I have learned a lot about mathematics but also about myself. This has been a rich experience which I will continue to benefit from for many years to come. However this experience would have not been possible without many actors.

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Declaration

I declare that this thesis is entirely my own work, except where otherwise stated. I confirm that this thesis has not been submitted for a degree at another university.

Abstract

We marginally improve the bound of Lieb on the stability of ions i.e. we show that $N_c < 2Z + 1 - f(Z)$ with $f(Z) > 0$ explicitly given. Then, we study the existence of a ground state for a classical model derived from the N-body Hamiltonian operator. We establish amongst other things that the N-body Coulomb potential does not favour shell formation. We also expose some properties related to the screening effect and conjecture, using numerical data, that the negative ionization charge is unbounded as the nuclear charge grows to infinity. In joint work with my supervisor, we study the ground state of the model just described as N tends to infinity. We show that our model Gamma-converges toward a Gamma-limit. We derive from it an angular equidistribution law, a radial condensation law, and the asymptotic neutrality of the crossover point from attainment and non-attainment. Finally we prove the existence of a minimizer for hydrogen Kohn-Sham functional if $N \leq Z$. More generally we show existence of a minimizer for the Kohn-Sham functional in the case $N \leq Z$ without taking into account the orthogonality condition between orbitals.

Chapter 1

Introduction

In the present work we inspect quantum mechanical models using methods from the calculus of variations.

Definition 1 *A model: A simple description of a system used for explaining, calculating...For example a quantum mechanical model for a molecule.*

Definition 2 *Quantum mechanics: A mathematical model of light and matter based on the idea that energy exists in units which cannot be divided.*

More specifically we will be interested in the non-relativistic time independent Schrödinger equation in the Born Oppenheimer approximation (denoted (SE)) and the Kohn-Sham density functional (denoted (KS)). For more details see introduction on (SE) in 2.1 and 2.2 and see for (KS) 5.1, 5.2. These two models describe the motion of the electrons around nuclei and are both only partially understood while of real importance in science. Roughly speaking chapters $2, 3, 4$ are devoted to the study of (SE) while chapter 5 is devoted to the study of (KS). We give now an overview of the content of this thesis.

1.1 Stability versus instability in quantum mechanics (SE): chapters 2, 3, 4

These three chapters deal with (SE) for atoms only. However chapters 3 and 4 can be adapted to the molecular setting (see [FC06]) while the second chapter cannot easily be generalized to the molecular setting. We recall that (SE) allows to compute the stationary states of the electrons. Indeed in theory these states are given by the so called wave functions $\psi : (\mathbb{R}^3 \times \mathbb{Z})^N \to \mathbb{C}$ which satisfy certain conditions (see also 2.1 and 2.2), namely anti-symmetry and normalization, as well as solve the partial differential equation (SE):

$$-\frac{1}{2}\sum_{i=1}^{N}\Delta_i\psi(x) + V(x)\psi(x) + W(x)\psi(x) = E\psi(x)$$

where

$$V(x) = \sum_{i=1}^{N}\sum_{l=1}^{M} -\frac{Z_l}{|r_i - R_l|},$$
$$W(x) = \sum_{1\leq i<j\leq N} \frac{1}{|r_i - r_j|},$$

where $E \in \mathbb{R}$ is the eigenvalue, Δ_i is the usual Laplacian for the spatial coordinate i and where the R_i are the positions of the nuclei. The smaller E is the less exited the state is. The partial differential equation can be written as $H_{N,Z}\psi = E\psi$ with $H_{N,Z}$ called the Hamiltonian of the system, here the molecule (the dependence on M the number of nuclei could be explicitly given by writing $H_{N,Z,M}$). It is well known (Ritz-variational principle) that Ψ is a ground state (i.e. the less exited state, i.e. the state in which the electrons have the less energy) if and only if

$$\langle H_{N,Z}\Psi, \Psi\rangle = \inf_{\psi\in A_N} \langle H_{N,Z}\psi, \psi\rangle$$

where

$$A_N := \left\{\psi \in H^1(\mathbb{R}^{3N};\mathbb{C}) \mid \|\psi\|_{L^2} = 1 \text{ and } \psi \text{ is antisymmetric}\right\}.$$

For a detailed introduction to the mathematical theory of quantum mechanics see for example [GS03].

We recall the known results on existence of a ground state for (SE). The first result is about the existence of ground state for atoms and molecules:

Theorem 1 *(Zhislin [Zh60])*
If the total nuclear charge Z satisfies $Z > N-1$ then there exists a ground state.

For a short proof see for example [Fr03].

The second result is about the so called stability of matter. It shows that the theory of quantum mechanics is coherent with statistical mechanics and thermodynamics, fact which was a priori not obvious. Indeed these later theories (for large systems) are grounded on the premise that the average energy per particle is bounded. However if one estimates each term of the Coulomb potential (nuclei-nuclei repulsion term, nuclei-electron attraction term and electron-electron repulsion term: see for example [FC06]) one sees that the potential energy scales like $M^{\frac{5}{3}}$ while an estimate on the kinetic energy shows that it scales like M. Hence for the energy of the system to scale like M it implies spectacular cancellation between the potential energy terms. The following result shows exactly that.

Theorem 2 *(Dyson-Lenard [DL67])*

$$\langle H_{N,Z}\psi, \psi\rangle \geq -C(M+N)$$

where C is a constant and where M is the number of nuclei in the molecule.

A proof can be found in [Lie76] or for a short proof see [FC06].

We introduce

$$N_c(Z) := \max\{N \in \mathbb{N} \mid \text{ there exists a ground state of } H_{N,Z}\}.$$

The third result on the atomic and molecular ions is

Theorem 3 *(Lieb)*
For any $Z > 0$ we have $N_c < 2Z + M$ where again M is the number of nuclei in the molecule.

A proof can be found in [Lie84].

The last result is a result on approximate neutrality of large-Z ions (see [LSST88]):

Theorem 4 *(Lieb-Sigal-Simon-Thirring)*

$$\lim_{Z\to\infty} \frac{N_c}{Z} = 1.$$

The first result on stability given (Zhislin) is somewhat very different from the other results. Many other models in quantum mechanics like Hartree-Fock [LS77] for example enjoy similar result on stability for $N < Z + 1$. In fact we prove in chapter 5 the existence of a minimizer for the Kohn-Sham functional using the classical argument for this 'regime' i.e. if $N \leq Z$ the electrons do not completely cancel the long range forces of the Coulomb potential. On the other hand the other results are conceptually much more complicated. One cannot rely on some "favourable electrostatic phenomenon". Behind the proofs of these results lies the poorly understood screening effect, i.e. the tendency of the electrons to surround nuclei in order to annihilate their electrostatic influence (see for example [At98] for a chemist's description of screening also called shielding). We devote chapter 3 and 4 to the study of this effect. However in chapter 2 we follow our intuitive understanding of the screening effect and attempt "naively", via geometric methods adapted to a variational setting (see [Fr03]), to obtain a gain on the bound $N_c < 2Z + 1$ for atoms ($M = 1$). It leads to a slight sharpening of the bound on the maximum negative ionization of atoms. We believe it also makes clear that the information crucially needed on the ground state in order to make progress in the grey area $Z + 1 \leq N < 2Z + 1$ will be hard to derive directly. An alternative way would be to understand first the screening effect via the study of its creator: the N-body Coulomb potential. And this is exactly what we do in chapter 3. We study a classical model derived from (SE) retaining exactly the electron-electron interaction term of the N-body Coulomb potential while truncating the electron-nucleus interaction term with a hard core around zero. As far as we know such a model has never been studied even though it offers some resemblance to what is referred to in the literature as Thomson's problem (see 3.2).

More precisely we study the problem:

Minimize

$$V_{N,Z}(x_1, \ldots, x_N) := -\sum_{i=1}^{N} \frac{Z}{|x_i|} + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|} \qquad (Z > 0,\ N \in \mathbb{N})$$

over the set

$$\mathcal{A}_N := \{(x_1, .., x_N) \in \mathbb{R}^{3N} \,\big|\, |x_i| \geq 1 \text{ for all } i\}.$$

It describes a system of N[1] particles in $\mathbb{R}^3$ of charge -1 ('electrons') which Coulomb-repel each other and are Coulomb-attracted to a particle at the origin of charge $+Z$[2] ('atomic nucleus').

The model was chosen 'simple' enough so as to define a meaningful problem and complicated enough so as to keep its essential screening feature and as a consequence opening the possibility of a future return to the quantum setting (SE). Despite difficulties related to the high dimension of our problem and to the curvature of the sphere we show that some general properties of minimizers can be derived. More precisely we show that results of stability (related to existence of a ground sate) analogous to the ones known for (SE) hold. Next we establish that the Coulomb potential does not favour shell formation even though there is experimental evidence of shell formation, as well as computational evidence, for the quantum setting [BB53]. Indeed in order to screen the nuclei the electrons seem 'to localize themselves'. Since some are closer on average to the nucleus than others we say that they favour shell formation. To have a good picture in mind one can think of the orbitals of the hydrogen atoms. For more on spatial distribution of the electrons see for example [Fu95]. We highlight some properties related to the screening effect, we show the neutrality of large atoms (using a result from chapter 4) and we conjecture, using the numerical data available, the surprising fact that the negative ionization charge is unbounded as the nuclear charge tends

[1] N will always denote the number of electrons.

[2] Z will in this thesis always denote the nuclear charge.

to infinity. Due in part to the difficulty of analyzing the ground states of our model in greater depth, and motivated by some heuristic arguments (see Remark 2 p40) we quickly move on to the study of our model for large N. This is the topic of the chapter 4 (joint work) where we use Gamma convergence, a powerful variational method, to extract from our model some information in the limit when (N, Z) tends to infinity. Amongst other things, we display asymptotically exact screening effect of the N-body Coulomb potential and recover an explicit result proved in [LSST88]. We also obtain a strengthening of a result found in [Lan72].

1.2 Existence of minimizer for Kohn-Sham: Chapter 5

Density functional theory or in short DFT is an alternative option to the Schrödinger equation (See for example [Fu95]). By minimizing the Kohn-Sham functional (see below) over the correct set one obtains the density distribution of the electrons. In fact (KS) can be viewed as both an approximation and in various instances, an empirical improvement of Hartree-Fock: The kinetic and the electron-nuclei interaction terms are retained while the electron-electron interaction term is replaced.

Despite the fact that this model is extensively used in quantum chemistry and that it presents a number of difficulties which are of mathematical interest no proof of existence of minimizers has been published.

We give explicitly first the functional and the variational problem associated and then give our result of existence.

We define

$$\xi_N^{KS}((\psi_1, ..., \psi_N)) = T[\psi] + V_{ne}[\psi] + J[\psi, \psi] + E_{xc}[\psi]$$

where, using $V = \mathbb{R}^3 \times \mathbb{Z}_2$,

$$T[\psi] = \sum_{i=1}^{N} \frac{1}{2} \int_V |\nabla \psi_i|^2 dx$$

$$V_{ne}[\psi] = \sum_{i=1}^{N} \int_V v_{ne}(x) |\psi_i|^2 dx$$

$$J[\psi, \phi] = \frac{1}{2} \int_V \int_V \frac{\sum_{i=1}^{N} |\psi_i(x)|^2 \sum_{j=1}^{N} |\phi_j(y)|^2}{|x-y|} dx dy$$

$$E_{xc}[\psi] = -C_{xc} \int_V (\sum_{i=1}^{N} |\psi_i(x)|^2)^p dx$$

and where $v_{ne}(x) = \sum_{i=1}^{M} \frac{-Z_i}{|x-l_i|}$ with l_i being the position of the ith nucleus. The density is the minimizer of ξ_N^{KS} over the set

$$A_\alpha^{\sim} = \left\{ (\psi_1, .., \psi_N) \mid \psi_i \in H^1(V; \mathbb{C}) \quad \forall i \text{ and } \int \psi_i (\psi_j)^* dx = \alpha_i \delta_{i,j} \right\}$$

where $\alpha = (\alpha_1, .., \alpha_N)$ for some $0 \leq \alpha_1, ., \alpha_N \leq 1$.

We prove the following result using methods from [Lio84a], [Lio84b], [Lio87], [Fr97] and [Fr03] as well as additional ideas.

Theorem 5 *If* $\sum_{i=1}^{N} \alpha_i \leq Z$ *there exists a minimizer to the problem* $\inf_{\psi \in A_\alpha} \xi_N^{KS}(\psi)$ *where*

$$A_\alpha = \left\{ (\psi_1, .., \psi_N) \mid \psi_i \in H^1(V; \mathbb{C}) \quad \forall i \textit{ and } \int |\psi_i|^2 dx = \alpha_i \right\}$$

(with α *as in defined above) and every minimizing sequence stays in a compact set of* $H^1(V)^N$.

As a trivial corollary one gets the proof of existence of a minimizer for the hydrogen Kohn-Sham.

Remark: The Kohn-Sham functional minimized over A_α instead of $A_\alpha^\sim$ can be viewed as "bosonic Kohn-Sham" (since bosons do not have the anti-symmetry requirement which translates into the orthogonality condition between the orbitals).

Our proof is based on some localization arguments of the bound part and scattering part of any minimizing sequence, on the analysis of the problem at infinity and on the exponential decay of the bound part. Even though our techniques do not extend in a straightforward manner to the Kohn-Sham orbitals for atoms and molecules we believe that it could be achieved as the orthogonality condition does not seem to bring more than sheer technicalities. More precisely it is difficult to keep track of the orthogonality condition between the orbitals as we perform local surgery (the orthogonality requirement is a global property which is not preserved under localization). But while our proof shall be adaptable to accommodate orthogonality it can certainly not be extended to treat the case of negative ions: In this setting ($N \geq Z + 1$) one cannot use Newton's theorem anymore and our proof uses it not just once but twice! Physically, one would in fact expect non-existence at least when N is substantially larger than Z. Finally we note that we have given no uniqueness results with or without orthogonality (the lack of proofs of uniqueness is widespread in quantum mechanics (see [LeB06])). For the Kohn-Sham functional this can be mathematically associated to a lack of convexity.

Chapter 2

Quantum instability

2.1 The Raleigh-Ritz variational principle in quantum mechanics

In this section we review briefly some basics of quantum mechanics and fix the notation to be used in this chapter. In the theory of quantum mechanics (non-relativistic time independent Schrödinger equation) the behaviour of electrons in the presence of a nucleus is captured by a wave function which has certain properties (described below) including being a solution of the eigenvalue problem $H\Psi = E\Psi$ where H is the Hamiltonian operator.

More precisely for an atom with N electrons and nuclear charge Z

$$H_{N,Z} := -\frac{1}{2}\sum_{i=1}^{N}\Delta_i + \overbrace{\sum_{i=1}^{N} -\frac{Z}{|r_i|} + \sum_{1\leq i<j\leq N} \frac{1}{|r_i - r_j|}}^{V_N}$$

is the Hamiltonian of the system. It is remarkable that this system can be understood (considering the nucleus fixed) by the sole knowledge of the wave functions $\Psi : (\mathbb{R} \times \mathbb{Z}_2)^N \to \mathbb{C}$ satisfying the following

- (Normalized to 1)

  $\|\psi\|_{L^2((\mathbb{R}^3\times\mathbb{Z}_2)^N)} = 1$

- (Anti-symmetric)

  $\Psi(r_1, s_1, ..r_j, s_j, ..r_i, s_i, .., r_N, s_N) = -\Psi(r_1, s_1, ..r_i, s_i, ..r_j, s_j, .., r_N, s_N)$ for all $i \neq j$.

- (eigenvector with eigenvalue $E^{\Psi}_{N,Z}$)

  $H_{N,Z}\Psi = E^{\Psi}_{N,Z}\Psi.$

Remark 1: $|\Psi(x_1, .., x_N)|^2 dx_1..dx_N$ can be physically understood as the probability density of finding the electron i in the state $x_i = (r_i, s_i)$ (r_i is the spatial position in $\mathbb{R}^3$ and s_i the spin).

Remark 2: From now on we omit the spin but everything that we do in this chapter can be done with it.

Definition 1 *If a lowest eigenvalue exists the eigenfunction corresponding to this eigenvalue is called a ground state.*

Remark: The ground state is the most stable state that the system can be in.

In practice we use the Ritz-variational principle which states that Ψ is a ground state if and only if

$$\langle H_{N,Z}\Psi, \Psi\rangle = \inf_{\psi\in A_N} \langle H_{N,Z}\psi, \psi\rangle$$

where

$$A_N := \left\{\psi \in H^1(\mathbb{R}^{3N}; \mathbb{C}) \mid \|\psi\|_{L^2} = 1 \text{ and } \psi \text{ is antisymmetric}\right\}.$$

In any case (i.e whether the infimum is reached or not) we write $E^0_{N,Z} := \inf_{\psi \in A_N} \langle H_{N,Z}\psi, \psi\rangle$. The space $H^1(\mathbb{R}^{3N};\mathbb{C})$, the Sobolev space (Hilbert space), consists of the $L^2(\mathbb{R}^{3N};\mathbb{C})$ functions whose first weak derivatives are also in L^2, endowed with the inner product

$$\langle \psi, \phi\rangle_{H^1} = \langle \psi, \phi\rangle_{L^2} + \langle \nabla\psi, \nabla\phi\rangle_{L^2}$$

where

$$\langle \psi, \phi\rangle_{L^2} = \int_{\mathbb{R}^{3N}} \psi(x_1, .., x_N) \cdot \psi(x_1, .., x_N)^* dx_1..dx_N.$$

The quadratic form $\langle H_{N,Z}\psi, \psi\rangle$ on $H^1(\mathbb{R}^{3N};\mathbb{C}) \times H^1(\mathbb{R}^{3N};\mathbb{C})$ is defined by

$$\langle H_{N,Z}\psi, \psi\rangle := \frac{1}{2}\int_{\mathbb{R}^{3N}} |\nabla\psi|^2 dx_1..dx_N + \sum_{i=1}^{N}\int_{\mathbb{R}^{3N}} \frac{-Z}{|x_i|}|\psi|^2 dx_1..dx_N$$
$$+ \sum_{1\le i<j\le N}\int_{\mathbb{R}^{3N}} \frac{1}{|x_i - x_j|}|\psi|^2 dx_1..dx_N.$$

It is well known (see for example [Fr03]) that we have

$$E^0_{N,Z} = \inf_{\psi\in A_N}\langle H_{N,Z}\psi, \psi\rangle < \inf_{\psi\in A_{N-1}}\langle H_{N-1,Z}\psi, \psi\rangle = E^0_{N-1,Z}$$

for $N \le Z$ and hence we have existence of a ground state. In fact

Definition 2 *If $E^0_{N,Z} < E^0_{N-1,Z}$ we say that the ground state is a bound state.*

Remark: Physically it means that it is energetically favourable to keep all the electrons, hence the terminology.

2.2 Stability of negative ions

In this chapter we look at the problem of existence/non-existence of negative ions for the non-relativistic time independent Schrödinger equation in the Born-Oppenheimer approximation (SE) for which we have introduced its associated variational principle (see 2.1). By existence of ions, physically one means that the electrons are not scattered to infinity but stay within a 'reasonable' distance from the nucleus. In the mathematical context of (SE) it means existence of a ground state (as already explained). It is widely believed, in view of the observations made by physicists and chemists, that the number of extra electrons that can be bound to a neutral atom is one or two at most. This is surprising as it means that the atomic number plays no role: one would intuitively expect the number of electrons that can be bound by the nucleus to grow with the nuclear charge. To prove such a conjecture, if at all true for the (SE) model, is still an open problem (except in the hydrogen case). In the 80s a special emphasis was set by many authors (see [Lie84b], [LSST88], [FS90], [SS90]) on establishing the existence/non existence of (large Z or not) negative ions. We refer to [Lie84a] for a nice summary of what was known in 1984 and for the proof of non existence of ions for $N \geq 2Z + 1$. As far as we know there has been no progress on this issue since even though the results known are far from sharp. Indeed as already mentioned hydrogen is the only settled case: H^+, H, H^- (see [Lie84a]) are stable while H^{--}, H^{---} and others are unstable. In the oxygen case for example it is known that O^{17-} is unstable but nothing is known about the stability/instability of O^{16-}. Part of the reason why this is so comes from the lack of information on the localization of the mass of the purported ground state (i.e. a supposedly existing ground state) and on the associated landscape of the potential (in the area of mass localization). Such information is very hard to obtain but crucially needed in order to make progress. We have tried to use some simple techniques from the calculus of variation on a purported ground state but without much success. For example we supposed the wave function had a maximum away from the singularities of the Coulomb potential. Then we tried to generate a contradiction by lowering the energy with an outer variation (or inner variation). The deformation used was required to be the null function (we reached differential inequalities of the type given in Gronwall's lemma). In the vein of what should be required in order to make some headway we present in the conclusion an easy lemma providing some information on the localization of minimum/maximum of the N-body ground state (the proof uses a special feature of the Coulomb potential namely the dilation property).

In what follows we show that it is possible to extract some information on the wave function and on the potential so as to make some incremental progress (using Lieb's proof) on the bound for N_c.

We are going to extend by an ϵ amount the much celebrated bound of Lieb [Lie84b] on the maximum negative ionization of atoms. We will treat the case for atoms without including the spin. However incorporating the spin, as already mentioned, merely generates trivial changes.

Remark 1: Our method cannot be easily extended to the molecular case as the proof for it in [Lie84b] is different.

Remark 2: Our result does not improve Lieb's result in the case where Z is an integer. Nevertheless it has been pointed out in [Lie84b] that the case where Z is a positive real number may be relevant in physics: due to some dielectric effect particles in semiconductors can have non-integer effective charges.

Remark 3: We will only establish a lower bound of the gain that can be made. However it will be apparent to the reader that the difference between upper bound and lower bound is not of real importance.

Remark 4: Most models used in physics and quantum chemistry have been shown to possess a minimizer (corresponding to the stability) $Z + 1 > N$ or $Z \geq N$ but the case $Z + 1 \leq N$ has proven much more difficult to tackle. An example of gain can be found for example in [LeB93b] where the author shows the existence of a $Z < N_c$ such that for $0 < N < N_c$ (where $N = \int \rho dx$) the Thomas-Fermis-Dirac-von Weizsäcker variational problem admits a minimizer and its associated Lagrange multiplier is positive.

2.3 Brief summary of Lieb's proof and its non-optimal estimate

Our work reuses the proof of [Lie84b] for atoms (it can also be found in [CFKS87] page 50). For the convenience of the reader (and for the sake of completeness) we recall it briefly in the atomic case without spin.

2.3.1 Sketch of the proof

Let suppose that $\phi \in \mathcal{A}_N$ is a ground state of $H_{N,Z}$ i.e. $H_{N,Z}\phi = E^0_{N,Z}\phi$ where we suppose that $E^0_{N,Z} \leq E^0_{N-1,Z}$. We compute

$$0 = \int |x_1|\phi^*(H_{N,Z} - E^0_{N,Z})\phi dx_1..dx_N$$

$$= \int |x_1|\phi^*(H_{N-1,Z} - E^0_{N,Z} - \frac{1}{2}\Delta_{x_1} - \frac{Z}{|x_1|} + \sum_{i=2}^{N} \frac{1}{|x_1 - x_i|})\phi dx_1..dx_N$$

$$= \int |x_1| dx_1 \int \phi^*_{x_1}(x_2,..,x_N)(H_{N-1,Z} - E^0_{N,Z})\phi_{x_1}(x_2,..,x_N)dx_2..dx_N$$

$$+ \int |x_1| dx_1 \int \phi^*_{x_1}(x_2,..,x_N)(-\frac{1}{2}\Delta_{x_1}\phi_{x_1})dx_2..dx_N$$

$$+ \int (-Z + \sum_{i=2}^{N} \frac{|x_1|}{|x_1 - x_i|})|\phi|^2 dx_1..dx_N.$$

We first note that the first term and the last term are both real and therefore the second term is also real. Further the first term can be bounded from below by $(E^0_{N-1,Z} - E^0_{N,Z}) \int |x_1||\phi|^2 dx_1..dx_N \geq 0$ (≥ 0 by assumption). Less trivial is the fact that the second term can be shown to be non negative (see [Lie84b]). This implies that the last term, i.e. the term of interest, must be non positive. Since the choice of x_1 was arbitrary we can carry out the same computation with x_i and summing over the i's we get:

$$0 \geq \int \left(-NZ + \sum_{1 \leq i < j \leq N} \frac{|x_i| + |x_j|}{|x_i - x_j|} \right) |\phi|^2 dX.$$

With Cauchy-Schwarz inequality we obtain that $\frac{|x_i|+|x_j|}{|x_i - x_j|} > 1$ almost everywhere. This gives $2Z + 1 > N$ as we set out to show.

2.3.2 The lose bolt

Lieb's proof is 'sharp' up to the last step where some coarse approximation is required in order to deal with the fact that no information is known about the purported ground state used under the integral. The strict inequality is crude as can already be seen for the sum of two terms when 3 electrons are involved. Our strategy to improve the bound $2Z + 1 > N_c$ will be as follows: In the region where one expects 'most' of the mass of the ground state to lie, the bound $\sum_{1\le i<j\le N} \frac{|x_i|+|x_j|}{|x_i-x_j|} > \frac{N(N-1)}{2}$ is expected to be far from sharp. We first construct a region where a lower bound holds and then prove that a minimum amount of mass of the ground state lies in that region using geometric methods ([En77],[Sim77], [Sig82]) applied in a variational setting as in [Fr03].

2.4 The result and the main ingredients to its proof

We recall that we use N_c to represent the maximum number of electrons that can be bound by a nucleus of charge Z or more formally written

$$N_c(Z) = \max\{N \in \mathbb{N} \mid \text{ there exits a minimizer of } \langle H_{N,Z}\psi, \psi\rangle\}.$$

Theorem 1 *Suppose that $Z \ge 4$. Then we have*

$$N_c < 2Z + 1 - \frac{3}{4}\frac{\beta(Z)}{2Z+1}$$

where

$$\beta(Z) = \inf_{B_4} \sum_{1\le i<j\le 4} \frac{|x_i| + |x_j|}{|x_i - x_j|}$$

with

$$B_4 := \left\{(x_1, .., x_4) \in (\mathbb{R}^3)^4 \mid 0 \le |x_1| \le R, \tau \le |x_i| \le R \text{ for } i = 2, 3, 4\right\}$$

$$R := \max\left\{4 \cdot 2^{2Z+2}(2Z+1), \frac{4Z^2}{D_Z}\right\}$$

$$\tau := \frac{1}{8Z^3}$$

and

$$D_Z := E^0_{Z,Z} - E^0_{3,Z} < 0.$$

As discussed earlier, the proof of the theorem will be based on two main ingredients: Selecting a region of the configuration space where some better estimate for the sum can be obtained and deriving some estimate for the mass of the wave function in the chosen region so that a concrete gain can be made. It turns out that a good region to look at is a region where at most one electron is in a small neighbourhood of zero and at least 4 electrons are in a radius R of zero. The outline of the proof is as follows. We will split the configuration space into three parts namely $A_{R,\tau}$, $B_{R,\tau}$, A_R^C where R and τ will be chosen later as functions of Z only. Then we will show that on $B_{R,\tau}$ we can make a gain (strictly positive) from the summation under the integral: In other words we show the existence of $\beta = \beta(R,\tau) > 0$ such that $\sum_{i<j} \frac{|x_i|+|x_j|}{|x_i-x_j|} \geq \frac{N(N-1)}{2} + \beta$ on $B_{R,\tau}$. Then we will obtain some lower bound for the mass of the wave function on $B_{R,\tau}$ or more precisely we will show the existence of $\theta = \theta(R,\tau) > 0$ such that for any ground state of $H_{N,Z}$ we must have

$$\int_{B_{R,\tau}} |\psi|^2 dx \geq \theta(R,\tau).$$

Supposing the existence of β and θ defined above gives us the following

$$\int_{\mathbb{R}^{3N}} \sum_{1\leq i<j\leq N} \frac{|x_i|+|x_j|}{|x_i-x_j|} |\psi(X)|^2 dX =$$

$$\begin{aligned}
&\int_{A_{R,\tau}\cup A_R^C} \sum_{1\leq i<j\leq N} \frac{|x_i|+|x_j|}{|x_i-x_j|} |\psi(X)|^2 dX + \int_{B_{R,\tau}} \sum_{1\leq i<j\leq N} \frac{|x_i|+|x_j|}{|x_i-x_j|} |\psi(X)|^2 dX \\
&> \frac{N(N-1)}{2} \int_{A_{R,\tau}\cup A_R^C} |\psi(X)|^2 dX + \left(\frac{N(N-1)}{2} + \beta\right) \int_{B_{R,\tau}} |\psi(X)|^2 dX \\
&> \frac{N(N-1)}{2} \int_{\mathbb{R}^{3N}} |\psi(X)|^2 dX + \beta\theta = \frac{N(N-1)}{2} + \beta\theta.
\end{aligned}$$

So we now reproduce the end of the proof from Lieb's paper:

$$0 \geq \int_{\mathbb{R}^{3N}} (-NZ) + \sum_{1\leq i<j\leq N} \frac{|x_i| + |x_j|}{|x_i - x_j|} |\psi(X)|^2 dX > -NZ + \frac{N(N-1)}{2} + \beta\theta.$$

But this exactly says that in order to have stability the above strict inequality must be satisfied and this means that we need $N^2 - N(2Z+1) + 2\beta\theta < 0$. Solving this quadratic equation in N gives that $N < 2Z + 1 - \frac{3}{2}\frac{\beta\theta}{2Z+1}$. Conversely there is no stability if $N \geq 2Z + 1 - \frac{3}{2}\frac{\beta\theta}{2Z+1}$. The theorem is proved when one sets $\varepsilon := \frac{3}{2}\frac{\beta\theta}{2Z+1}$. To prove Theorem 1 It is therefore enough to show the existence of β, $\theta = \frac{1}{2}$ and $B_{R,\tau}$ for τ and R given only in function of Z.

2.5 The proof

2.5.1 The fragmentation of the configuration space

We split first $\mathbb{R}^{3N}$ into two parts namely $\mathbb{R}^{3N} = A_R \uplus A_R^c$ where

$$A_R = \left\{(x_1, .., x_N) \in \mathbb{R}^{3N} \mid \exists C \subseteq \{1, .., N\} \text{ with } |C| \geq 4 \text{ and } |x_i| \leq R \quad \forall i \in C\right\}.$$

A_R is the part of the configuration space where at least 4 electrons are within a radius R of the nucleus and A_R^c is its complement i.e. the part of the configuration space where at most 3 electrons are within a radius R of the nucleus. Now for reasons which will become clearer later on A_R is still too big for our purposes and we therefore introduce the following:

$$B_{R,\tau} := \{(x_1, .., x_N) \in A_R \mid |x_i| \geq \tau \text{ for all } i \text{ except at most one }\}$$

and we call $A_{R,\tau}$ the complement of $B_{R,\tau}$ in A_R i.e.

$$A_{R,\tau} := A_R \setminus B_{R,\tau}.$$

So $\mathbb{R}^{3N} = A_R^c \uplus A_{R,\tau} \uplus B_{R,\tau}$.

2.5.2 The existence of β

Proposition 2 *Let $N \geq 4$. Then*

$$S := \inf_{(x_1,..,x_N)\in B_{R,\tau}} \sum_{1\leq i<j\leq N} \frac{|x_i| + |x_j|}{|x_i - x_j|}$$

is attained and in particular is greater than $\frac{N(N-1)}{2} + \beta$ where $\beta > 0$.

Proof:

Let $f_N(x) := \sum_{1\leq i<j\leq N} \frac{|x_i|+|x_j|}{|x_i-x_j|}$ with $x \in B_{R,\tau}$. The function f_N has some singularities at places where at least two electrons have the same coordinates. We remove these singularities by noticing that the infimum is clearly not realized when two electrons (or more) are nearby. Indeed suppose that $x \in B_{R,\tau}$ is such that $|x_1 - x_2| < \gamma$ then

$$f_N(x) \geq \frac{\tau}{\gamma} >> \frac{N(N-1)}{2} \quad \text{if} \quad \gamma < \frac{\tau}{N^3}.$$

It is then clear that such a part of the configuration space is not relevant when looking for the infimum of f_N over the set $B_{R,\tau}$. We therefore can look for the infimum on $B = B_{R,\tau} \cap L^c$ where

$$L := \left\{(x_1, ..., x_N) \in \mathbb{R}^{3N} \setminus |x_i - x_j| < \gamma \text{ for some } i \neq j\right\}$$

and where γ is chosen as above. L is obviously open since the maps $G_{i,j}$: $\mathbb{R}^{3N} \to \mathbb{R}$ defined by $G_{i,j}(x_1, .., x_N) = |x_i - x_j| - \delta$ with $1 \leq i < j \leq N$ are continuous on $\mathbb{R}^{3N}$ (therefore $G_{i,j}^{-1}((-\infty, 0))$ is open and so is $L = \cup_{i<j} G_{i,j}^{-1}((-\infty, 0)$ by countable union of open sets. Hence L^c is closed and

we can conclude that $B = B_{R,\tau} \cap L^c$ is closed (since $B_{R,\tau}$ is also closed). We then have

$$S = \inf_{(x_1,..,x_N)\in B_{R,\tau}} \sum_{1\leq i<j\leq N} \frac{|x_i|+|x_j|}{|x_i - x_j|} = \inf_{(x_1,..,x_N)\in B} \sum_{1\leq i<j\leq N} \frac{|x_i|+|x_j|}{|x_i - x_j|}$$

$$\geq \inf_{B_4} \overbrace{\sum_{1\leq i<j\leq 4} \frac{|x_i|+|x_j|}{|x_i - x_j|}}^{g_4} + \frac{N(N-1)}{2} - 6$$

where we have defined

$$B_4 := B \cap \left\{(x_1,..,x_N) \in \mathbb{R}^{3N} \setminus 0 \leq |x_1| \leq R, \tau \leq |x_i| \leq R \text{ for } i = 2,3,4\right\}.$$

Now it is clear that g_4 attains its infimum on B_4. Further if

$$\sum_{1\leq i<j\leq 4} \frac{|x_i|+|x_j|}{|x_i - x_j|} = 6 \text{ with } (x_1,x_2,x_3,x_4) \in B_4$$

then we must have $|x_i - x_j| = |x_i| + |x_j|$ for all $i \neq j$. But this in turn implies that $x_1 = 0, x_2 = -x_3, x_2 = -x_4, x_3 = -x_4$ which has no solution unless $x_i = 0$ for $i = 1,2,3,4$. And this is not possible since B_4 forces $|x_2| \geq \tau, |x_3| \geq \tau, |x_4| \geq \tau$. Therefore we deduce the existence of $\beta > 0$ such that $S \geq \frac{N(N-1)}{2} + \beta$ as we set out to show. □

2.5.3 The bound on the mass of the wave function in the region $B_{R,\tau}$

Introduction of the localization tool: the cut-off functions

In order to obtain the necessary bound we will use geometric localization methods which were first introduced in [En77], [Sim77], [Sig82] and adapted to a variational setting in [Fr03]. We will split the configuration space into 2^N

disjoint subsets (which we are indicating using the 2^N subsets of the power set I_N of the set $\{1, 2..., N\}$) by introducing the smooth cut-off functions $\tilde{\rho}_1$ and $\tilde{\rho}_2$ from $\mathbb{R}^3$ with values in $[0, 1]$ defined as follows:

$$\tilde{\rho}_1(x) = \begin{cases} 1 & \text{if } 0 \leq |x| \leq \frac{1}{2} \\ 0 & \text{if } 1 \leq |x| \end{cases}$$

$$\tilde{\rho}_2(x) = \begin{cases} 0 & \text{if } 0 \leq |x| \leq \frac{1}{2} \\ 1 & \text{if } 1 \leq |x| \end{cases}$$

with the property that $(\tilde{\rho}_1(x))^2 + (\tilde{\rho}_2(x))^2 = 1$, $|(\tilde{\rho}_1)'| \leq 2$ and that $|(\tilde{\rho}_2)'| \leq 2$. For a concrete example of such functions (see chapter 5.8.1).

So let C denote any subset of $\{1, .., N\}$ and let us define

$$\tilde{\rho}_C(x_1, ..x_N) := \prod_{i \in C} \tilde{\rho}_1(x_i) \prod_{j \notin C} \tilde{\rho}_2(x_j)$$

where $j \notin C$ is to be understood as $j \in \{1, .., N\} \setminus C$. We also define

$$(\tilde{\rho}_b)^2 := \sum_{|C| \geq 4} (\tilde{\rho}_C)^2 \text{ and } (\tilde{\rho}_s)^2 := \sum_{|C| < 4} (\tilde{\rho}_C)^2.$$

Note that we have used the letter s and b to emphasize the link between bound state (and scattering state) and our configuration split. The advantage of working with these cut-off functions can be felt through the following properties:

$$(\tilde{\rho}_b)^2 + (\tilde{\rho}_s)^2 = 1 \text{ and } A_1^c \subset Supp(\tilde{\rho}_s).$$

The second property is obvious since $\chi_{A_1^c} = \tilde{\rho}_s$ on A_1^c while the first property can easily be deduced from $\sum_{C \in I_N} (\tilde{\rho}_C)^2 = 1$. That this formula is true can be shown by induction. The first step for $I_2 = \{1, 2\}$ follows from the definition of the cut-off functions and some trivial rearrangements. We suppose that it is true up to $N-1$ and show that it still holds for N. We have

$$\sum_{C\in I_N}(\tilde\rho_C)^2 = \sum_{C\in I_N}\left(\prod_{i\in C}(\tilde\rho_1)^2(x_i)\prod_{j\notin C}\tilde\rho_2)^2(x_j)\right)$$

$$= \sum_{C\in I_{N-1}}\left(\prod_{i\in C}(\tilde\rho_1)^2(x_i)\prod_{j\notin C}(\tilde\rho_2)^2(x_j)\right)\overbrace{\left((\tilde\rho_1)^2(x_N)+(\tilde\rho_2)^2(x_N)\right)}^{=1}$$

where the last equality holds since for fixed C either $N\in C$ or $N\notin C$ and therefore either

$$\left(\prod_{i\in C}(\tilde\rho_1)^2(x_i)\prod_{j\notin C}(\tilde\rho_2)^2(x_j)\right) = \left(\prod_{i\in C, i\neq N}(\tilde\rho_1)^2(x_i)\prod_{j\notin C}(\tilde\rho_2)^2(x_j)\right)\left((\tilde\rho_1)^2(x_N)\right)$$

or

$$= \left(\prod_{i\in C}(\tilde\rho_1)^2(x_i)\prod_{j\notin C, j\neq N}(\tilde\rho_2)^2(x_j)\right)\left((\tilde\rho_2)^2(x_N)\right).$$

But for each $V\subset\{1,...,N\}$ with say $N\in V$ there exist a $\tilde V$ such that $N\uplus\tilde V = V$ and hence the factorization is possible.

Upper bound on the mass in the region A_R^c

Let us define

$$\chi_{A_R^c}(x) = \begin{cases} 1 & \text{if } x\in A_R^c \\ 0 & \text{if } x\notin A_R^c \end{cases}$$

Lemma 3 *(N-electrons and 3-electrons ground states are very different)*

Let ψ be the ground state of $H_{N,Z}$ i.e. $H_{N,Z}\psi = E^0_{N,Z}\psi$ for $Z,N\geq 4$. Then

$$\|\psi\chi_{A_R^c}\|^2_{L^2} \leq \frac{2^{2Z+2}(2Z+1)}{R^2|D_Z| - 2(N-3)ZR} \quad \textit{for } R > \frac{(2N-3)Z}{|D_Z|}.$$

An almost immediate corollary is the following:

Corollary 4 *Let the assumptions of Lemma* 3 *hold. Then*

$$\|\psi\chi_{A_R}\|_{L^2}^2 \geq \frac{3}{4}$$

with $R = \max\left\{4\cdot 2^{2Z+2}(2Z+1), \frac{4Z^2}{|D_Z|}\right\}$.

In fact it is easy to get rid of the dependence on N of R by using Lieb's theorem which provides an upper bound for N. Indeed we know that $N \leq 2Z+1$.

Proof: We will need the cut-off functions to be acting far enough away from zero and for that purpose we re-scale $\tilde{\rho}_C$ using $R > 0$:

$$\rho_C(x_1, ..., x_N) := \tilde{\rho}_C(\frac{x_1}{R}, .., \frac{x_N}{R}).$$

We still have the following properties

$$\rho_b^2 + \rho_s^2 = 1, \qquad \text{Supp}(\rho_s) \supset A_R^c \text{ together with } \chi_{A_R^c} = \rho_s \text{ on } A_R^c.$$

Furthermore

$$|\nabla\rho_b|^2 + \sum_{|C|\leq 3} |\nabla\rho_C|^2 \leq \frac{M}{R^2}\sum_{i=1}^{N}\chi_{B_R(0)\setminus B_{\frac{R}{2}}(0)}(|x_i|)$$

where

$$M := \max\left\{|\nabla\tilde{\rho_b}|^2 + \sum_{|C|\leq 3}|\nabla\tilde{\rho_C}|^2\right\} \leq 4\cdot 2^{2Z+1}.$$

Now for all $\psi \in L^2(\mathbb{R}^{3N})$

$$\int_{A_R^c} |\psi|^2 dx \leq \int_{\mathbb{R}^{3N}} |\rho_s\psi|^2 dx.$$

So all we need is an upper bound on the last term in the case where the above ψ is a ground state. This can be derived as follows. Suppose that

$$\xi(\psi) := \langle H_{N,Z}\psi, \psi\rangle = E_{N,Z}^0.$$

Using the properties of ρ_s and ρ_b we obtain $|\psi|^2 = \sum_{|C|\leq 3} \rho_C^2|\psi|^2 + \rho_b^2|\psi|^2$, $\nabla(\rho_b^2 + \sum_{|C|\leq 3}\rho_C^2) = 0$ and

$$|\nabla\psi|^2 = |\nabla\rho_b\psi|^2 + \sum_{|C|\leq 3} |\nabla\rho_C\psi|^2 - (|\nabla\rho_b|^2 + \sum_{|C|\leq 3} |\nabla\rho_C|^2)|\psi|^2.$$

Consequently since ψ is the ground state we have

$$E^0_{N,Z} = \xi(\psi) = \xi(\rho_b\psi) + \sum_{|C|\leq 3} \xi(\rho_C\psi) - \frac{1}{2}\int(|\nabla\rho_b|^2 + \sum_{|C|\leq 3}|\nabla\rho_C|^2)|\psi|^2 dx. \qquad (\star)$$

Note that the last term on the right hand side is the error term due to the localization. Obviously

$$\xi(\rho_b\psi) \geq E^0_{N,Z}\|\rho_b\psi\|^2$$

by definition of $E^0_{N,Z}$. Furthermore

$$\xi(\rho_C\psi) = \frac{1}{2}\int_{x_j\backslash j\notin C}\int_{x_j\backslash j\in C} \sum_{i\in C}|\nabla_{x_i}\rho_C\psi|^2 + \sum_{x_i\notin C}|\nabla_{x_i}\rho_C\psi|^2 dx_C dx_{\not C}$$

$$-\int_{x_j\backslash j\notin C}\int_{x_j\backslash j\in C}\sum_{i\in C}\frac{Z}{|x_i|}|\rho_C\psi|^2 + \sum_{j\notin C}\frac{Z}{|x_j|}|\rho_C\psi|^2 dx_C dx_{\not C}$$

$$+\int_{x_j\backslash j\notin C}\int_{x_j\backslash j\in C}\sum_{l,k\in C}\frac{|\rho_C\psi|^2}{|x_l - x_k|} + \sum_{(l,k)\notin(C,C)}\frac{|\rho_C\psi|^2}{|x_l - x_k|} dx_C dx_{\not C}$$

$$= \int_{x_j\backslash j\notin C}\int_{x_j\backslash j\in C}\left(\frac{1}{2}\sum_{i\in C}|\nabla_{x_i}\rho_C\psi|^2 - \frac{Z}{|x_i|}|\rho_C\psi|^2\right) + \sum_{l<k\in(C,C)}\frac{|\rho_C\psi|^2}{|x_l - x_k|} dx_C dx_{\not C}$$

$$+ \int_{x_j\backslash j\notin C}\int_{x_j\backslash j\in C}\left(\frac{1}{2}\sum_{i\notin C}|\nabla_{x_i}\rho_C\psi|^2 - \frac{Z}{|x_i|}|\rho_C\psi|^2\right) + \sum_{l<k\notin(C,C)}\frac{|\rho_C\psi|^2}{|x_l - x_k|} dx_C dx_{\not C}.$$

Using that $|C| \leq 3$ and that $\rho_C\psi$ is antisymmetric with respect to $(x_{i_1}, x_{i_2}, x_{i_{|C|}})$ where $i_1, i_2, i_{|C|} \in C$ we have

$$\int_{x_j\backslash j\in C}\sum_{i\in C}\left(\frac{1}{2}|\nabla_{x_i}\rho_C\psi|^2 - \frac{Z}{|x_i|}|\rho_C\psi|^2\right) + \sum_{l<k\in(C,C)}\frac{|\rho_C\psi|^2}{|x_l - x_k|} dx_C$$

$$\geq E^0_{3,Z} \int_{x_j \backslash j \in C} |\rho_C \psi|^2 dx_C.$$

Hence

$$\xi(\rho_C\psi) \geq \int_{x_j \backslash j \notin C} E^0_{3,Z} \int_{x_j \backslash j \in C} |\rho_C \psi|^2 dx_C dx_{\not C}$$

$$+ \int_{x_j \backslash j \notin C} \int_{x_j \backslash j \in C} \sum_{j \notin C} \underbrace{(-\frac{Z}{|x_j|})}_{\geq \frac{-2Z}{R} \text{ on supp } (\rho_C \psi)} |\rho_C \psi|^2 dx_C dx_{\not C}$$

$$\geq \left(E^0_{3,Z} - \frac{2(N-3)Z}{R} \right) \|\rho_C \psi\|^2 \qquad \text{since } |C| \leq 3.$$

Finally since

$$\frac{1}{2} \int (|\nabla \rho_b|^2 + \sum_{|C| \leq 3} |\nabla \rho_C|^2) |\psi|^2 dx \leq \frac{2^{2Z+2}(2Z+1)}{R^2},$$

substituting these estimates in $(\star)$ one obtains

$$E^0_{N,Z} \geq E^0_{N,Z} \|\rho_b \psi\|^2 + (E^0_{3,Z} - \frac{2(N-3)Z}{R}) \|\rho_s \psi\|^2 - \frac{2^{2Z+2}(2Z+1)}{R^2}.$$

But since $E^0_{N,Z} = E^0_{N,Z}(\|\rho_b \psi\|^2 + \|\rho_s \psi\|^2)$ we get

$$E^0_{N,Z} \|\rho_s \psi\|^2 \geq (E^0_{3,Z} - \frac{2(N-3)Z}{R}) \|\rho_s \psi\|^2 - \frac{2^{2Z+2}(2Z+1)}{R^2}.$$

Rearranging provides

$$(E^0_{3,Z} - E^0_{N,Z} - \frac{2(N-3)Z}{R}) \|\rho_s \psi\|^2 \leq \frac{2^{2Z+2}(2Z+1)}{R^2}.$$

We can consider w.l.o.g that $N > Z$ and hence $E^0_{3,Z} - E^0_{N,Z} \geq |D_Z| = E^0_{3,Z} - E^0_{Z,Z}$ which implies that

$$(E^0_{3,Z} - E^0_{Z,Z} - \frac{2(N-3)Z}{R}) \|\rho_s \psi\|^2 \leq \frac{2^{2Z+2}(2Z+1)}{R^2}.$$

As we have $0 > E^0_{3,Z} > E^0_{Z,Z}$ (since $Z \geq 4$) the left hand side is strictly positive as long as $R > \frac{2(N-3)Z}{E^0_{3,Z} - E^0_{Z,Z}}$ and consequently

$$\|\rho_s \psi\|^2 \leq \frac{2^{2Z+2}(2Z+1)}{R} \frac{1}{(E^0_{3,Z} - E^0_{N,Z})R - 2(N-3)Z}$$

as we set out to show.

□

We now prove Corollary 4

Proof: We first show that if $R > \frac{2(2Z)Z}{E_{3,Z}-E_{Z,Z}}$ then $\frac{1}{(E^0_{3,Z}-E^0_{N,Z})R-2(N-3)Z} \leq 1$. Indeed $(E^0_{3,Z}-E^0_{N,Z})R-2(N-3)Z \geq 1$ implies that $|D_Z|R \geq 1+2(N-3)Z$. So we need $|D_Z|R \geq 1+2(2Z-2)Z$ which means $R \geq \frac{1+2(2Z-2)Z}{|D_Z|}$. However $\frac{2(2Z)Z}{|D_Z|} > \frac{1+2(2Z-2)Z}{|D_Z|}$ hence the claim. Now $\|\psi\chi_{A^c_R}\|^2_{L^2} + \|\psi\chi_{A_R}\|_{L^2} = 1$ so $\|\psi\chi_{A_R}\|^2_{L^2} \geq 1 - \|\rho_s\psi\|^2$. We want to choose R so that $\|\rho_s\psi\|^2 \leq \frac{1}{4}$. This implies that $R \geq 4 \cdot 2^{2Z+2}$. We take $R = \max\left\{4 \cdot 2^{2Z+2}(2Z+1), \frac{2(2Z)Z}{|D_Z|}\right\}$ □

Upper bound on the mass of the ground state on $A_{R,\tau}$

Lemma 5 *(The probability of having two or more electrons in a radius τ of the nucleus tends to zero as τ tends to zero)*

Let ψ be the ground state as in Lemma 3. Then

$$\int_{A_{R,\tau}} |\psi|^2 dx \leq \gamma \text{ whenever } \tau < \frac{\gamma}{(N+1)Z^2}.$$

Proof:

For any $\phi \in H^1(\mathbb{R}^{3N})$ we have

$$\begin{aligned}
T[\phi] + V_{ne}[\phi] &:= \sum_{i=1}^{N}\Big(\int \frac{1}{2}|\nabla_{x_i}\phi|^2 - \frac{Z}{|x_i|}|\phi|^2\Big)dx_1..dx_N \\
&= \sum_{i=1}^{N}\int_{x_{i'}}\Big(\int_{x_i}\frac{1}{2}|\nabla_{x_i}\phi|^2 - \frac{Z}{|x_i|}|\phi|^2 dx_i\Big)dx_{i'} \\
&\geq \sum_{i=1}^{N}\int_{x_{i'}}\int_{x_i}(E^0_{1,Z}|\phi|^2 dx_i)dx_{i'} = -\frac{1}{2}NZ^2
\end{aligned}$$

where $x_{i'} = (x_1, .., x_{i-1}, x_{i+1}, .., x_N)$. Further

$$V_{ee}[\phi] = \sum_{1\leq i<j\leq N}\int \frac{1}{|x_i - x_j|}|\phi|^2 dx \geq \frac{1}{2\tau}\int_{A_{R,\tau}} |\phi|^2 dx.$$

Let us choose a fixed $\gamma > 0$ and suppose that for the ground state ψ we have

$$\int_{A_{R,\tau}} |\psi|^2 dx \geq \gamma \int |\psi|^2 dx = \gamma$$

that is to say that the probability of having at least two electrons in a radius τ of the nucleus is uniformly bounded from below. This implies some condition on τ. Indeed

$$E^0_{N,Z} \geq \frac{\gamma}{2\tau} - \frac{1}{2} N Z^2$$

but $E^0_{N,Z} \leq E^0_{1,Z} = -\frac{1}{2}Z^2$. So it shows that

$$\frac{\gamma}{2\tau} \leq \frac{1}{2}(N-1)Z^2 \quad \text{if} \quad \frac{\gamma}{(N-1)Z^2} \leq \tau$$

which in turn implies that

$$\int_{A_{R,\tau}} |\psi|^2 dx < \gamma \quad \text{if} \quad \tau < \frac{\gamma}{(N-1)Z^2}$$

hence Lemma 5 holds.

□

Corollary 6 *Let ψ be as in Lemma 3. Then we have*

$$\int_{A_{R,\tau}} |\psi|^2 dx < \frac{1}{4} \quad \textit{if} \quad \tau < \frac{1}{4Z^3}.$$

Remark: We have found a condition on τ only depending on Z as required. The proof is the direct consequence of Lemma 5. Note that we have given the bound on τ in function of Z using Lieb's theorem one more time.

With Corollary 4 and 6 we obtained the desired estimate namely

$$\theta = \int_{B_{R,\tau}} |\psi|^2 \geq \frac{1}{2} \text{ for } \quad \tau < \frac{1}{4Z^3} \text{ and } R > R_0$$

if ψ is the ground state of $H_{N,Z}$ and this finishes the proof of Theorem 1.

2.6 The ε gain

What is the gain? As explained in the introduction there is no gain on the physical cases since $2Z+1$ will always be an integer for Z integer (recall that N is also an integer). Now if Z is taken in $[4, +\infty)$ we claim that there exists at least infinitely (countably) many Z for which our ε gain gives a better result. Indeed we have the following (writing $g(Z) = \frac{3}{4}\beta(Z)$ and $h(Z) = 2Z+1$):

$$\text{For } N \geq 2Z + 1 - \frac{g(Z)}{h(Z)} \text{ there is no ground state}$$

with

$$g(Z_1) > g(Z_2) \text{ for } Z_1 < Z_2, \qquad \lim_{Z\to\infty} g(Z) = 0$$

and

$$h(Z_1) < h(Z_2) \text{ for } Z_1 < Z_2, \qquad \lim_{Z\to\infty} h(Z) = \infty.$$

So to make a difference we need Z to satisfy the equation $2Z+1-\frac{g(Z)}{h(Z)} = K$ where K is an integer (remember that $N \in \mathbb{N}$). We only need to note that

$$f : [4, \infty) \to [9, \infty) \text{ where } \qquad f(Z) = 2Z + 1 - \frac{g(Z)}{h(Z)}$$

is a strictly increasing function and therefore by a basic theorem of analysis one obtains the existence of an inverse function $F^{-1} : [8, \infty) \supset \{9, 10, 11, ..\} \to [4, \infty)$. Hence we know that for each $K \in \{9, 10, ..\}$ there exist a $Z = Z_K$ for which our result predicts instability when the earlier bound $K < 2Z_K + 1$ fails to deliver it.

2.7 Conclusion

2.7.1 A difficult problem

It has proven difficult to find a quantitative expression for ϵ. The reason, as explained already, is the lack of information on the position of the electrons. In our case we were able to extract some information from the purported ground state using that intuitively if there is a gap between the energy $E^0_{N,Z}$ and $E^0_{3,3}$ it should then not be possible to construct an N-body ground state out of the 3-electrons ground state i.e. the mass has to be spread in a very different way. However in order to obtain bounds one is forced to make some 'unpleasant' approximation (which could certainly be improved but the overall bound would only be marginally better unless more information was known). With more qualitative or quantitative knowledge on the wave function one could hope for some sharper result. However it appears that except for regularity theory (decay rate, smoothness away from singularity [Ka51], [Ka57], [HOS94], [OC73]) there is very little which is rigorously known about the ground state. We conclude with an easy lemma which highlights the influence of the N-body potential on the eigen-states.

2.7.2 Example of qualitative result about the many electrons ground state

Lemma 7 *($V_N < E_\psi$ where the probability density has a maximum)*

Let Ψ be a real (or purely imaginary) eigen-state of the N-body Hamiltonian operator $H_{N,Z}$ i.e.

$$H_{N,Z}\Psi = E_\Psi\Psi.$$

Suppose that $x_0 \in \mathbb{R}^{3N}$ is neither a singular point nor a vanishing point of the Coulomb potential V_N and that Ψ has a local maximum/local minimum and is strictly positive/negative at the point x_0 respectively. Then

$$V_N(x_0) < E_\Psi.$$

Proof:

We treat the case where Ψ has a maximum at x_0 and is positive there. The other case can be treated in a similar fashion. Let Ψ be the solution of (SE) with eigenvalue E_Ψ. It is well known fact that Ψ is smooth away from singular points of the potential (see for example [HOS94]). Let x_0 satisfy the conditions of the lemma. Then one has the stationary Schrödinger equation pointwise i.e.

$$-\frac{1}{2}\Delta\Psi(x_0) + V_N(x_0)\Psi(x_0) = E_\Psi\Psi(x_0)$$

or in the form

$$-\frac{1}{2}\text{tr}(D^2\Psi(x_0)) = -\frac{1}{2}\Delta\Psi(x_0) = (E_\Psi - V(x_0))\Psi(x_0). \qquad (\dagger)$$

$D^2\Psi(x_0)$ is a real symmetric matrix so it is diagonalizable with eigenvalues $\lambda_i \in \mathbb{R}$ and associated eigenvectors v_i where $i = 1,..,3N$. Further since Ψ has a maximum at x_0 $D^2\Psi(x_0) \leq 0$ and hence the eigenvalues are all non positive since

$$\lambda_i = \langle D^2\Psi(x_0)v_i, v_i\rangle \leq 0 \qquad \forall i = 1,..,3N.$$

In fact it can be shown that the at least one eigenvalue is strictly negative. Indeed suppose that all the eigenvalues are equal to zero or equivalently that $D^2\Psi(x_0) = 0$. Because Ψ is smooth around x_0 one can differentiate (SE) in a direction $\overrightarrow{e}$ say i.e.

$$\overrightarrow{e}.\nabla_x\left(-\frac{1}{2}\triangle\Psi(x)+(-E_\Psi+V(x))\Psi(x)\right)|_{x_0}=0.$$

This gives the following equation

$$(-\frac{1}{2}\overrightarrow{e}.\nabla_x(\triangle\Psi(x)))|_{x_0}+(\overrightarrow{e}.\nabla V_N)(x_0)+(V_N(x_0)-E_\Psi)(\overrightarrow{e}\cdot\nabla\Psi)(x_0)=0.$$

But $\nabla\Psi(x_0)=0$. So the above gives

$$(-\frac{1}{2}\overrightarrow{e}.\nabla_x(\triangle\Psi(x)))|_{x_0}+\overrightarrow{e}.\nabla V_N(x_0)=0.$$

Choose suitably $\overrightarrow{e}$ so that $(\overrightarrow{e}.\nabla V_N)(x_0)\neq 0$. Such a choice of $\overrightarrow{e}$ is always possible since the potential is strictly decreasing under dilation at any point x such that $V_N(x)\neq 0$. Therefore one obtains that some elements of $D^3\Psi(x_0)$ are different from zero. But if $D^3\Psi(x_0)\neq 0$ it cannot be negative since if $D^3\Psi(x_0)(x,y,z)\leq 0$ then $D^3\Psi(x_0)(-x,-y,-z)\geq 0$. This implies that Ψ does not have a local max at x_0 which leads to a contradiction. Hence $D^2\Psi(x_0)\neq 0$. Using (†) we obtain

$$(E_\Psi-V_N(x_0))\Psi(x_0)=-\frac{1}{2}\sum_{i=1}^{3N}\lambda_i>0$$

which gives

$$E_\Psi>V_N(x_0).$$

□

Remark 1: When Ψ solves (SE) and is purely imaginary we observe that in fact $i\Psi$ is a real solution of (SE) with the same eigenvalue.

Remark 2: The ground state can always taken to be real.

Remark 3: When Ψ has a local minimum/maximum and is strictly positive/negative at the point x_0 with $V_N(x_0) \neq 0$ we obtain in the same way as above that $V_N(x_0) > E_\Psi$.

Remark 4: It makes sense to expect a minimum or maximum to exist since we know that the ground state tend to zero as $|x| \to 0$. However it is believed that the maximum lies on a singularity.

Remark 5: This lemma can be physically understood as follows: E_ψ is the expected value for the energy of the system. The most likely configuration must have lower energy.

Chapter 3

Minimum energy configuration of charged particles in the potential of an atomic nucleus

3.1 Formulation of the variational many body problem

We study the following problem:

Minimize

$$V_{N,Z}(x_1, .., x_N) := -\sum_{i=1}^{N} \frac{Z}{|x_i|} + \sum_{1 \le i < j \le N} \frac{1}{|x_i - x_j|} \qquad (Z > 0,\ N \in \mathbb{N}) \quad (3.1)$$

over the set

$$\mathcal{A}_N := \{(x_1, .., x_N) \in \mathbb{R}^{3N} \,\big|\, |x_i| \ge 1 \text{ for all } i\}. \qquad (3.2)$$

As explained in chapter 1 it describes a system of N particles in $\mathbb{R}^3$ of charge

-1 ('electrons') which Coulomb-repel each other and are Coulomb-attracted to a particle at the origin of charge $+Z$ ('atomic nucleus').

The hard core assumption in (3.2) may be viewed as a crude "uncertainty principle". More precisely excluding the possibility for the electrons to be too close to the nucleus can be compared to the phenomenon in quantum mechanics, the uncertainty principle, which prevents the electrons from falling into the nucleus. The model (3.1), (3.2) arises from the full quantum mechanical Hamiltonian of an atom,

$$H_{N,Z} = -\frac{1}{2}\Delta + V_{N,Z} = \sum_{i=1}^{N}\Big(-\frac{1}{2}\Delta_{x_i} - \frac{Z}{|x_i|}\Big) + \sum_{1\le i<j\le N} \frac{1}{|x_i - x_j|},$$

by retaining electron interaction exactly, but – crudely – replacing the one-body operator $-\frac{1}{2}\Delta_{x_i} - Z/|x_i|$ by the effective potential $v(x_i) := -Z/|x_i|$ for $|x_i| \ge 1$, $+\infty$ otherwise.

The physics of the model (3.1), (3.2) is independent of the choice of hard core radius. A different choice just corresponds to an overall scale factor of length and energy, independent of the x_i, Z, and N.

Note also that we trivially have $-NZ < \inf_{\mathcal{A}_N} V_{N,Z} < 0$.

Definition 3 *Let $E_{N,Z} = \inf_{x\in\mathcal{A}_N} V_{N,Z}(x)$. An atom made of $N+1$ electrons and with nuclear charge Z is said to be a bound state or classically stable if and only if $E_{N+1,Z} < E_{N,Z}$.*

Remark 1: We will call an atom classically unstable when it is not classically stable.

Remark 2: Trivially $E_{N+1,Z} \le E_{N,Z}$ for all $N \in \mathbb{N}$, $Z > 0$.

Remark 3: This definition is exactly the classical equivalent of the bound state in quantum mechanics (see section 2.1): it implies attainment of the infimum (but attainment is obviously not enough for stability).

3.2 Thomson's problem and our model

At the beginning of the 20th century Thomson proposed a model for the atom (see [Tho04]): The "Plum pudding". It is made of a uniformly charged ball (the pudding) and of classical charges "the plums" (equally charged) which are to be placed inside the sphere. The problem is to determine where. From this model, viewed by Thomson himself as extremely difficult to solve (even for small N), came the following simpler problem: minimize the interaction between N electrons constrained on a sphere of radius 1 say. Only for "easy" cases ($N = 1, 2, 3, 4, 6, 12$) have minimum energy configurations been shown rigorously so far: see [DLT02]. In the 80s this area benefited from a resurgence of interest after the discovery that carbon-60 molecules are stable. Nevertheless most of the results up to today are asymptotic i.e. for N large, or related to numerical simulations and efficient algorithms to find minimizers numerically. We refer to some interesting papers [CKT87], [RSZ94], [SK97], [KS98], [DLT02] for more. The difficulty in pinpointing the minimal energy configuration is not just explained by the dimension of the problem but also related to the curvature of the sphere which creates defects in the arrangements of the minimizers. The problem of N electrons interacting via the Coulomb potential on a neutrally charged disc was raised in 1985 and it was found that for N large enough some electrons would lie inside the disc. The analogous problem with a ball was then considered and it was shown, perhaps surprisingly, that the electrons would lie on the surface ([La72], [GTK87]).

Even though the model we introduce has some similarities with the above our motivation is quite different. Indeed our model originated from the desire to understand stability versus instability of negative ions in the quantum setting. Recall that the existence/non-existence of ground states for negative ions with the Schrödinger equation (see [Lie84a], [Lie84b]) is still an open problem. Amongst other things the understanding of the screening effect is thought to be the key to proving the stability/instability of negative ions. Yet no thorough study of its creator has been undertaken. With some elementary analysis we uncover some features of the N-body Coulomb potential. Looking at the crossover between stability and instability provides some partial understanding of the shielding of the nuclear charge. Using a result of chapter 4 we also derive the neutrality of large atoms.

We believe that our classical instability implies quantum instability (recall that in [LSST88] the authors introduced some stronger form of instability to prove the asymptotic neutrality of large negative ions) even though we have so far no result in that direction.

3.3 The results

We begin with the startling

Theorem 8 *a) (Attainment for neutral atoms and singly-negative ions) For $N \leq Z+1$ there exists a minimizer of $V_{N,Z}$ on $\mathcal{A}_N$.*

b) (Absorption principle) Every minimizer $(x_1, .., x_N)$ of $V_{N,Z}$ on $\mathcal{A}_N$ satisfies $|x_i| = 1$ for all i.

Regarding a) we note that a corresponding attainment result is known for the analogous quantum problem, except that it requires the slightly stronger assumption $N < Z + 1$, or equivalently $N \leq Z$ in the physical situation $Z \in \mathbb{N}$. (Zhislin's theorem [Zh60], see [Fr03] for a short proof.)

As regards b), no result of this sort is known for the quantum problem. It shows no shell formation (see explanation of shell in 1.1) or more precisely that the electrons are arranging themselves in one shell. It would be very interesting to investigate whether some fingerprint of the result survives in quantum mechanics, despite the fact that the quantum kinetic term is known to favour formation of 'shells' of the electrons with staggered mean distance from the nucleus (indeed when one considers (SE) without the electron-electron interaction it reduces to Hartree-Fock theory whose minimizers are known to display the shell formation feature). Also, we emphasize that the result in b) is false in certain circonstances, e.g. for classical Coulomb particles in the analogous *two*-dimensional region, in which ground states would extend into the radial direction; but it would become true if the Coulomb interaction were replaced by the Green's function of the *two*-dimensional Laplacian. The result in b) will also allow us to compute the minimum energy with the data already available from the work done on Thomson's problem ([MDH96]) and hence to conjecture that the ionization charge is unbounded. Our second result may be familiar to the reader:

Theorem 9 *For $N \geq 1$ the following two assertions are equivalent:*

- *Every minimizing sequences of $V_{N+1,Z}$ stay in a compact set of* $(\mathbb{R} \setminus B_1)^{3N+1}$
- $E_{N+1,Z} < E_{N,Z}$

This theorem is well known for (SE), see for example [Fr03] for a proof. It provides a convienient way to show that one can extract a converging subsequence from every minimizing sequence. Physically it is a natural equivalence: If it is energetically favourable for the electrons to remain within a reasonable distance from the nucleus then no mass of the minimizing sequence will be lost and hence it will stay in a compact subset. This is the classical version of the sub-additivity condition introduced in [lio84a]. In chapter 5 we use yet another equally physically meaningful requirement: the scattering charge. We have as a simple consequence the following result:

Corollary 10 *If* $E_{N+1,Z} < E_{N,Z}$ *then* $\inf_{x \in A_{N+1}} V_{N+1,Z}(x)$ *is attained.*

The classical result that is analogous to Lieb's result on quantum instability (if $N \geq 2Z + 1$ then $E_{N,Z} = E_{N-1,Z}$) is trivial to show in our setting and can in fact be sharpened further using electron grouping (by three for example).

We also have the following related result whose proof hinges on Corollary 15 of chapter 4. Let

$$N_*(Z) := \sup\{N \in \mathbb{N} \mid E_{N,Z} < E_{N-1,Z}\}.$$

Then

Theorem 11 *(Asymptotic neutrality of large ions)*

$$\frac{N_*(Z)}{Z} \longrightarrow 1 \text{ as } Z \to \infty.$$

Remark 1: This is not quite a satisfactory result, since we would have wished to obtain more than merely the term of higher order. Our second conjecture partially addresses this issue.

Remark 2: In fact this result can be anticipated using the following heuristic argument. We first note that $E_{N,Z} \leq -NZ + \frac{N(N-1)}{2}$. We conjecture that $E_{N,Z} \sim -NZ + \frac{N(N-1)}{2} = E^{asy}_{N,Z}$ as N tends to infinity. Differentiating formally gives

$$\frac{dE^{asy}_{N,Z}}{dN} > 0 \Leftrightarrow N > Z.$$

We therefore expect to have attainment (for large N) only when N is of the same order as Z.

Remark 3: We will wait until chapter 4 for the proof as we will need Gamma-convergence. Note that the 'heavy machinery' needed to gather this sort of information highlights in our view the difficulties hidden behind a deceptively simple model.

Using the numerical results we have 2 main conjectures:

Conjecture 1 *The energy is convex in N i.e.* $\frac{E_{N-1,Z}-E_{N+1,Z}}{2} \geq E_{N,Z}$.

Remark 1: The convexity can be understood physically as the decrease of the ionization energy (the more electrons there are the easier it is to pull one away).

Remark 2: The convexity implies that N_* is such that for $N(Z) \leq N_*(Z)$ we have stability and for $N(Z) > N_*(Z)$ we have instability.

Remark 3: If the electrons were taken to be confined either on the circle (as opposed to the sphere) or at infinity the minimizer can be found explicitly for (N, Z) fixed. Although not easy to do so from this knowledge one can prove the conjecture 1 for this constraint problem. It is mainly the lack of information on the minimal configurations which prevents us from doing the same in our case.

Conjecture 2 $\lim_{Z\to\infty} N_*(Z) - Z = +\infty$.

What we observe is a true discreteness effect. It raises the following question related to the stability of ions: Is the phase space volume big enough to accommodate a quantum state as one adds the Laplacian back in? On spatial segmentation of an atom see [Fu95] page 36. It has been conjectured in [Sim00] (ionization conjecture) for the quantum case that $\lim_Z N_*(Z) - Z = K < +\infty$. Our data on the N-body Coulomb potential do not substantiate this claim. We mention a related result, the ionization conjecture for Hartree-Fock theory which was recently proved by Solovej (see [So03]).

Theorem 12 *(Universal Bound on the maximal ionization charge)*

There exists a universal constant $Q > 0$ such that for all positive integers N and Z satisfying $N \geq Z + Q$ there are no minimizers to the Hartree-Fock functional of the atom with N electrons and nuclear charge Z.

3.4 Proofs

3.4.1 Proof of Theorem 8

We start with b). The proof uses the harmonicity property (as previously noticed by [La72], [GKT87]) of $x \mapsto \frac{1}{|x-y|}$ away from the point $x = y$.

Suppose that $(x_1, .., x_N)$ is a minimizer of $V_{N,Z}$ over $\mathcal{A}_N$. Let

$$I := \{i \in \{1, .., N\} \,||x_i| > 1\}.$$

If $|I| = \emptyset$ then there is nothing to prove. So suppose $|I| = k \geq 1$ and w.l.o.g we take the last k particles to be away from S^2. Choose $\delta > 0$ so that we have for all $i = 1, ..N$ and for all $z \in (\mathbb{R}^3 \backslash B_1(0)) \cap B_\delta(x_i)$ that $\frac{1}{|x_i - z|} > NZ$. Then consider the function

$$V_{N,Z}(z) := -NZ + \sum_{i=1}^{N-1} \frac{1}{|x_i - z|} \text{ on } B_R(0) \backslash (B_1(0) \bigcup_{i=1}^{N-1} B_\delta(x_i))$$

where R is chosen such that $R \geq 2 \max_{i=1,..N} |x_i|$. Since $V_{N,Z}$ is harmonic on its domain and non constant it must attain its infimum on its boundary. By the choice of δ and R it can only be located on S_2 and so $|x_N| = 1$. We repeat the procedure for $i = N-1, .., N - |I|$ and hence $|x_i| = 1$ for all i as claimed.

We now prove part a).

Since we wish to show that stability is implied by $N \leq Z + 1$ with $N \in \mathbb{N}$ we may suppose w.l.o.g that $Z > \frac{1}{2}$. Note that for any $Z > \frac{1}{2}$ fixed we have that $E_{1,Z} > E_{2,Z}$. Hence to prove b) we only have to show that if we have $E_{k-1,Z} > E_{k,Z}$ for some $k \in \mathbb{N}, k \leq Z$ then $E_{k,Z} > E_{k+1,Z}$. Suppose $E_{k,Z}$ attained for some $k \leq Z$. We have the existence of $(X_1, .., X_k)$ such that $V_{k,Z}(X_1, .., X_k) = E_{k,Z}$ with $|X_i| = 1$ for all $i = 1, ..k$. We show the existence of $X_{k+1} \in \mathbb{R}^3 \backslash B_1$ such that $V_{k+1,Z}(X_1, .., X_k, X_{k+1}) < E_{k,Z}$. Suppose $X \in S_R^2$ where $S_R^2 := \{x \in \mathbb{R}^3 \setminus |x| = R\}$ with any $1 + \epsilon > R > 1$ (and $\epsilon > 0$ chosen small enough). We compute

$$\frac{1}{|S_R^2|} \int_{S_R^2} V_{k,Z}(X_1, .., X_k) + (-\frac{Z}{|X|} + \sum_{i=1}^{k} \frac{1}{|X - X_i|}) dX = V_{k,Z}(X_1, .., X_k) + (\frac{k - Z}{R}).$$

It is now clear that if $k \leq Z$ there exists a $X_{k+1} \in S_R^2$ such that

$$V_{k+1,Z}(X_1, .., X_k, X_{k+1}) < E_{k,Z}.$$

□

Remark 1: It is remarkable that for any minimizing sequence say $(X_1^n,..,X_N^n)$ of $V_{N,Z}$ there exist a subsequence called again $(X_1^n,..,X_N^n)$ such that for all $i=1,..N$ we have either $\lim_{n\to\infty}|X_i^n|=1$ or $\lim_{n\to\infty}|X_i^n|=\infty$.

Remark 2: Unfortunately the attainment does not automatically guarantee classical stability.

3.4.2 Proof of Theorem 9

The proof is straightforward: First we show that if all minimizing sequences are compact then $E_{N+1,Z}<E_{N,Z}$. Suppose not, i.e. that we have $E_{N+1,Z}=E_{N,Z}$. Let x^n be a minimizing sequence of $V_{N,Z}$. We construct a minimizing sequence for $V_{N+1,Z}$ out of x^n by adding one coordinate $y_{N+1}^n=(\max_{i=1,..,N}\{|x_i^n|\}+2^n)e_1$, e_1 being any unit vector of $\mathbb{R}^3$. $y^n:=(x_1^n,..,x_N^n,y_{N+1}^n)$ is a non compact minimizing sequence of $V_{N+1,Z}$ since $\frac{1}{|x_i^n-y_{N+1}^n|}\to_n 0$ for all $i=1,..,N$, hence the contradiction.

If $E_{N+1,Z}<E_{N,Z}$ it is trivial since if there exists a non compact minimizing sequence we can assume, after taking a subsequence if necessary, that at least one coordinate converges to infinity say x_{N+1}^n. Hence when n is large enough we have (after taking a subsequence if necessary) either that $\frac{-Z}{|x_{N+1}^n|}+\sum_{i=1}^N\frac{1}{|x_i^n-x_{N+1}^n|}\geq 0$ or that $\frac{-Z}{|x_{N+1}^n|}+\sum_{i=1}^N\frac{1}{|x_i^n-x_{N+1}^n|}\to 0$ which implies that $E_{N+1,Z}=E_{N,Z}$. This is obviously a contradiction.

□

3.4.3 Proof of Corollary 10

The proof is a trivial consequence of Theorem 9. Indeed take a minimizing sequence $(x_n)_{n\in\mathbb{N}}$ of $V_{N+1,Z}$. By Theorem 9 it stays in a compact set of

$(\mathbb{R}^3 \setminus B_1)^{N+1}$. It is then easy to show that we can obtain a convergent minimizing subsequence. To finish the proof one only need to see that the subsequence and its limit remain in a set where $V_{N+1,Z}$ is continuous. □

3.4.4 About the conjectures

The minimizers on the sphere

We recall briefly for the convenience of the reader what the minimizers of $I_N(x_1, .., x_N) := \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|}$ look like for specific values of N. We refer to [DLT02], [AWRTSDW97], [AP05] for general N-configurations.

For $N = 2$ the two electrons sit opposite each other, for $N = 3$ three electrons form a equilateral triangle at the equator, for $N = 4$ four electrons form a tetrahedron, for $N = 5$ three electrons form an equilateral triangle at the equator and the remaining two sit at the north and south pole (this has not been proved rigorously). For $N = 8$ the eight electrons do not form a cube as one might first expect but a cube which is twisted and slightly crunched. Numerical plots of minimizers (see for example [AP05] or [SK97]) show an approximate crystallization phenomenon for large N. The optimizers exhibit crystalline order in large patches, interrupted by defects whose presence and density is believed to be intimately connected to the curvature of the sphere. Highly symmetrical arrangements are not always preferred as N grows: The introduction of dislocation defects in the lattice can lower the energy.

Stability versus instability

Taking advantage of the extensive numerical data on the minimizers of I_N we provide a table of the stability/instability of atoms for our model $V_{N,Z}$.

The values of the energy I_N are obtained from [MDH96]. The table is given for N, Z integers. One could also deduce the threshold in Z for N fixed but we want to focus on the convexity in N and the cut-off N_*.

We write in the table $E_{N,Z}$ if it is stable and $\times$ if it is not. Since we find that any energy on the left of an $E_{N,Z}$ is stable and any energy on the right of an $\times$ is unstable we will omit part of the results for convenience. The tables suggest convexity of $E_{N,Z}$ (conjecture 1) and conjecture 2.

Remark: We write the neutral $E_{N,N}$ in bold characters for improved readability.

$\boldsymbol{E_{1,1}}$	$E_{2,1}$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$
$E_{1,2}$	$\boldsymbol{E_{2,2}}$	$E_{3,2}$	$E_{4,2}$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$
$E_{1,3}$	$E_{2,3}$	$\boldsymbol{E_{3,3}}$	$E_{4,3}$	$E_{5,3}$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$
$E_{1,4}$	$E_{2,4}$	$E_{3,4}$	$\boldsymbol{E_{4,4}}$	$E_{5,4}$	$E_{6,4}$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$
$E_{1,5}$	$E_{2,5}$	$E_{3,4}$	$E_{4,5}$	$\boldsymbol{E_{5,5}}$	$E_{6,5}$	$E_{7,5}$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$
$E_{1,6}$	$E_{2,6}$	$E_{3,6}$	$E_{4,6}$	$E_{5,6}$	$\boldsymbol{E_{6,6}}$	$E_{7,6}$	$E_{8,6}$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$
$E_{1,7}$	$E_{2,7}$	$E_{3,7}$	$E_{4,7}$	$E_{5,7}$	$E_{6,7}$	$\boldsymbol{E_{7,7}}$	$E_{8,7}$	$E_{9,7}$	$E_{10,7}$	$\times$	$\times$	$\times$	$\times$	$\times$
$E_{1,8}$	$E_{2,8}$	$E_{3,8}$	$E_{4,8}$	$E_{5,8}$	$E_{6,8}$	$E_{7,8}$	$\boldsymbol{E_{8,8}}$	$E_{9,8}$	$E_{10,8}$	$E_{11,8}$	$\times$	$\times$	$\times$	$\times$
$E_{1,9}$	$E_{2,9}$	$E_{3,9}$	$E_{4,9}$	$E_{5,9}$	$E_{6,9}$	$E_{7,9}$	$E_{8,9}$	$\boldsymbol{E_{9,9}}$	$E_{10,9}$	$E_{11,9}$	$E_{12,9}$	$\times$	$\times$	$\times$
$E_{1,10}$	$E_{2,10}$	$E_{3,10}$	$E_{4,10}$	$E_{5,10}$	$E_{6,10}$	$E_{7,10}$	$E_{8,10}$	$E_{9,10}$	$\boldsymbol{E_{10,10}}$	$E_{11,10}$	$E_{12,10}$	$E_{13,10}$	$\times$	$\times$
$E_{1,11}$	$E_{2,11}$	$E_{3,11}$	$E_{4,11}$	$E_{5,11}$	$E_{6,11}$	$E_{7,11}$	$E_{8,11}$	$E_{9,11}$	$E_{10,11}$	$\boldsymbol{E_{11,11}}$	$E_{12,11}$	$E_{13,11}$	$E_{14,11}$	$\times$

$\boldsymbol{E_{12,12}}$	$E_{13,12}$	$E_{14,12}$	$E_{15,12}$	×	×	×	×	×	×	×	×	×	×
$E_{12,13}$	$\boldsymbol{E_{13,13}}$	$E_{14,13}$	$E_{15,13}$	$E_{16,13}$	×	×	×	×	×	×	×	×	×
$E_{12,14}$	$E_{13,14}$	$\boldsymbol{E_{14,14}}$	$E_{15,14}$	$E_{16,14}$	$E_{17,14}$	×	×	×	×	×	×	×	×
$E_{12,15}$	$E_{13,15}$	$E_{14,15}$	$\boldsymbol{E_{15,15}}$	$E_{16,15}$	$E_{17,15}$	$E_{18,15}$	×	×	×	×	×	×	×
$E_{12,16}$	$E_{13,16}$	$E_{14,16}$	$E_{15,16}$	$\boldsymbol{E_{16,16}}$	$E_{17,16}$	$E_{18,16}$	$E_{19,16}$	$E_{20,16}$	×	×	×	×	×
$E_{12,17}$	$E_{13,17}$	$E_{14,17}$	$E_{15,17}$	$E_{16,17}$	$\boldsymbol{E_{17,17}}$	$E_{18,17}$	$E_{19,17}$	$E_{20,17}$	$E_{21,17}$	×	×	×	×
$E_{12,18}$	$E_{13,18}$	$E_{14,18}$	$E_{15,18}$	$E_{16,18}$	$E_{17,18}$	$\boldsymbol{E_{18,18}}$	$E_{19,18}$	$E_{20,18}$	$E_{21,18}$	$E_{22,18}$	×	×	×
$E_{12,19}$	$E_{13,19}$	$E_{14,19}$	$E_{15,19}$	$E_{16,19}$	$E_{17,19}$	$E_{18,19}$	$\boldsymbol{E_{19,19}}$	$E_{20,19}$	$E_{21,19}$	$E_{22,19}$	$E_{23,19}$	×	×
$E_{12,20}$	$E_{13,20}$	$E_{14,20}$	$E_{15,20}$	$E_{16,20}$	$E_{17,20}$	$E_{18,20}$	$E_{19,20}$	$\boldsymbol{E_{20,20}}$	$E_{21,20}$	$E_{22,20}$	$E_{23,20}$	$E_{24,20}$	×

$\boldsymbol{E_{21,21}}$	$E_{22,21}$	$E_{23,21}$	$E_{24,21}$	$E_{25,21}$	×	×	×	×	×	×	×	×	×
$E_{21,22}$	$\boldsymbol{E_{22,22}}$	$E_{23,22}$	$E_{24,22}$	$E_{25,22}$	$E_{26,22}$	×	×	×	×	×	×	×	×
$E_{21,23}$	$E_{22,23}$	$\boldsymbol{E_{23,23}}$	$E_{24,23}$	$E_{25,23}$	$E_{26,23}$	$E_{27,23}$	×	×	×	×	×	×	×
$E_{21,24}$	$E_{22,24}$	$E_{23,24}$	$\boldsymbol{E_{24,24}}$	$E_{25,241}$	$E_{26,24}$	$E_{27,24}$	$E_{28,24}$	×	×	×	×	×	×
$E_{21,25}$	$E_{22,25}$	$E_{23,25}$	$E_{24,25}$	$\boldsymbol{E_{25,25}}$	$E_{26,25}$	$E_{27,25}$	$E_{28,25}$	$E_{29,25}$	$E_{30,25}$	×	×	×	×
$E_{21,26}$	$E_{22,26}$	$E_{23,26}$	$E_{24,26}$	$E_{25,26}$	$\boldsymbol{E_{26,26}}$	$E_{27,26}$	$E_{28,26}$	$E_{29,26}$	$E_{30,26}$	$E_{31,26}$	×	×	×
$E_{21,27}$	$E_{22,27}$	$E_{23,27}$	$E_{24,27}$	$E_{25,27}$	$E_{26,27}$	$\boldsymbol{E_{27,27}}$	$E_{28,27}$	$E_{29,27}$	$E_{30,27}$	$E_{31,27}$	$E_{32,27}$	×	×
$E_{21,28}$	$E_{22,28}$	$E_{23,28}$	$E_{24,28}$	$E_{25,28}$	$E_{26,28}$	$E_{27,28}$	$\boldsymbol{E_{28,28}}$	$E_{29,28}$	$E_{30,28}$	$E_{31,28}$	$E_{32,28}$	$E_{33,28}$	×

$\boldsymbol{E_{29,29}}$	$E_{30,29}$	$E_{31,29}$	$E_{32,29}$	$E_{33,29}$	$E_{34,29}$	×	×	×	×	×	×	×	×
$E_{29,30}$	$\boldsymbol{E_{30,30}}$	$E_{31,30}$	$E_{32,30}$	$E_{33,30}$	$E_{34,30}$	$E_{35,30}$	×	×	×	×	×	×	×
$E_{29,31}$	$E_{30,31}$	$\boldsymbol{E_{31,31}}$	$E_{32,31}$	$E_{33,31}$	$E_{34,31}$	$E_{35,31}$	$E_{36,31}$	×	×	×	×	×	×
$E_{29,32}$	$E_{30,32}$	$E_{31,32}$	$\boldsymbol{E_{32,32}}$	$E_{33,32}$	$E_{34,32}$	$E_{35,32}$	$E_{36,32}$	$E_{37,32}$	×	×	×	×	×
$E_{29,33}$	$E_{30,33}$	$E_{31,33}$	$E_{32,33}$	$\boldsymbol{E_{33,33}}$	$E_{34,33}$	$E_{35,33}$	$E_{36,33}$	$E_{37,33}$	$E_{38,33}$	×	×	×	×
$E_{29,34}$	$E_{30,34}$	$E_{31,34}$	$E_{32,34}$	$E_{33,34}$	$\boldsymbol{E_{34,34}}$	$E_{35,34}$	$E_{36,34}$	$E_{37,34}$	$E_{38,34}$	$E_{39,34}$	×	×	×
$E_{29,35}$	$E_{30,35}$	$E_{31,35}$	$E_{32,35}$	$E_{33,35}$	$E_{34,35}$	$\boldsymbol{E_{35,35}}$	$E_{36,35}$	$E_{37,35}$	$E_{38,35}$	$E_{39,35}$	$E_{40,35}$	×	×
$E_{29,36}$	$E_{30,36}$	$E_{31,36}$	$E_{32,36}$	$E_{33,36}$	$E_{34,36}$	$E_{35,36}$	$\boldsymbol{E_{36,36}}$	$E_{37,36}$	$E_{38,36}$	$E_{39,36}$	$E_{40,36}$	$E_{41,36}$	×

$\boldsymbol{E_{37,37}}$	$E_{38,37}$	$E_{39,37}$	$E_{40,37}$	$E_{41,37}$	$E_{42,37}$	×	×	×	×	×	×	×	×
$E_{37,38}$	$\boldsymbol{E_{38,38}}$	$E_{39,38}$	$E_{40,38}$	$E_{41,38}$	$E_{42,38}$	$E_{43,38}$	$E_{44,38}$	×	×	×	×	×	×
$E_{37,39}$	$E_{38,39}$	$\boldsymbol{E_{39,39}}$	$E_{40,39}$	$E_{41,39}$	$E_{42,39}$	$E_{43,39}$	$E_{44,39}$	×	×	×	×	×	×
$E_{37,40}$	$E_{38,40}$	$E_{39,40}$	$\boldsymbol{E_{40,40}}$	$E_{41,40}$	$E_{42,40}$	$E_{43,40}$	$E_{44,40}$	$E_{45,40}$	$E_{46,40}$	×	×	×	×
$E_{37,41}$	$E_{38,41}$	$E_{39,41}$	$E_{40,41}$	$\boldsymbol{E_{41,41}}$	$E_{42,41}$	$E_{43,41}$	$E_{44,41}$	$E_{45,41}$	$E_{46,41}$	$E_{47,41}$	×	×	×
$E_{37,42}$	$E_{38,42}$	$E_{39,42}$	$E_{40,42}$	$E_{41,42}$	$\boldsymbol{E_{42,42}}$	$E_{43,42}$	$E_{44,42}$	$E_{45,42}$	$E_{46,42}$	$E_{47,42}$	$E_{48,42}$	×	×
$E_{37,43}$	$E_{38,43}$	$E_{39,43}$	$E_{40,43}$	$E_{41,43}$	$E_{42,43}$	$\boldsymbol{E_{43,43}}$	$E_{44,43}$	$E_{45,43}$	$E_{46,43}$	$E_{47,43}$	$E_{48,43}$	$E_{49,43}$	×

$\boldsymbol{E_{53,53}}$	$E_{54,53}$	$E_{55,53}$	$E_{56,53}$	$E_{57,53}$	$E_{58,53}$	$E_{59,53}$	×	×	×	×	×	×	×
$E_{53,54}$	$\boldsymbol{E_{54,54}}$	$E_{55,54}$	$E_{56,54}$	$E_{57,54}$	$E_{58,54}$	$E_{59,54}$	$E_{60,54}$	$E_{61,54}$	×	×	×	×	×
$E_{53,55}$	$E_{54,55}$	$\boldsymbol{E_{55,55}}$	$E_{56,55}$	$E_{57,55}$	$E_{58,55}$	$E_{59,55}$	$E_{60,55}$	$E_{61,55}$	$E_{62,55}$	×	×	×	×

$\boldsymbol{E_{73,73}}$	$E_{74,73}$	$E_{75,73}$	$E_{76,73}$	$E_{77,73}$	$E_{78,73}$	$E_{79,73}$	$E_{80,73}$	×	×	×	×	×
$E_{73,74}$	$\boldsymbol{E_{74,74}}$	$E_{75,74}$	$E_{76,74}$	$E_{77,74}$	$E_{78,74}$	$E_{79,74}$	$E_{80,74}$	$E_{81,74}$	$E_{82,74}$	×	×	×
$E_{73,75}$	$E_{74,75}$	$\boldsymbol{E_{75,75}}$	$E_{76,75}$	$E_{77,75}$	$E_{78,75}$	$E_{79,75}$	$E_{80,75}$	$E_{81,75}$	$E_{82,75}$	$E_{83,75}$	×	×

$E_{97,96}$	$E_{98,96}$	$E_{99,96}$	$E_{100,96}$	$E_{101,96}$	$E_{102,96}$	$E_{103,96}$	$E_{104,96}$	$\times$	$\times$	$\times$	$\times$
$E_{97,97}$	$E_{98,97}$	$E_{99,97}$	$E_{100,97}$	$E_{101,97}$	$E_{102,97}$	$E_{103,97}$	$E_{104,97}$	$E_{105,97}$	$E_{106,97}$	$\times$	$\times$
$E_{97,98}$	$E_{98,98}$	$E_{99,98}$	$E_{100,98}$	$E_{101,98}$	$E_{102,98}$	$E_{103,98}$	$E_{104,98}$	$E_{105,98}$	$E_{106,98}$	$E_{107,98}$	$\times$

$E_{125,121}$	$E_{126,121}$	$E_{127,121}$	$E_{128,121}$	$E_{129,121}$	$E_{130,121}$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$
$E_{125,122}$	$E_{126,121}$	$E_{127,122}$	$E_{128,122}$	$E_{129,122}$	$E_{130,122}$	$E_{131,122}$	$E_{132,122}$	$\times$	$\times$	$\times$	$\times$
$E_{125,123}$	$E_{126,123}$	$E_{127,123}$	$E_{128,123}$	$E_{129,123}$	$E_{130,123}$	$E_{131,123}$	$E_{132,123}$	$\times$	$\times$	$\times$	$\times$
$E_{125,124}$	$E_{126,124}$	$E_{127,124}$	$E_{128,124}$	$E_{129,124}$	$E_{130,124}$	$E_{131,124}$	$E_{132,124}$	$E_{133,124}$	$E_{134,124}$	$\times$	$\times$

$E_{154,150}$	$E_{155,150}$	$E_{156,150}$	$E_{157,150}$	$E_{158,150}$	$E_{159,150}$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$
$E_{154,151}$	$E_{155,151}$	$E_{156,151}$	$E_{157,151}$	$E_{158,151}$	$E_{159,151}$	$E_{160,151}$	$E_{161,151}$	$E_{162,151}$	$\times$	$\times$	$\times$
$E_{154,152}$	$E_{155,152}$	$E_{156,152}$	$E_{157,152}$	$E_{158,152}$	$E_{159,152}$	$E_{160,152}$	$E_{161,152}$	$E_{162,152}$	$E_{163,152}$	$\times$	$\times$

$E_{185,179}$	$E_{186,179}$	$E_{187,179}$	$E_{188,179}$	$E_{189,179}$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$
$E_{185,180}$	$E_{186,180}$	$E_{187,180}$	$E_{188,180}$	$E_{189,180}$	$E_{190,180}$	$E_{191,180}$	$E_{192,180}$	$\times$	$\times$	$\times$	$\times$
$E_{185,181}$	$E_{186,181}$	$E_{187,181}$	$E_{188,181}$	$E_{189,181}$	$E_{190,181}$	$E_{191,181}$	$E_{192,181}$	$\Delta\times$	$\times$	$\times$	$\times$
$E_{185,182}$	$E_{186,182}$	$E_{187,182}$	$E_{188,182}$	$E_{189,182}$	$E_{190,182}$	$E_{191,182}$	$E_{192,182}$	$E_{193,182}$	$E_{194,182}$	$\times$	$\times$

Note that the number of stable states (after neutrality) is almost always increasing with (N, Z) up to one increment occationally (see for example the last table). This suggest the following conjecture: We can almost be sure that if $E_{N,Z}$ is stable then $E_{N+1,Z+1}$ is stable. This can be understood physically as follows: First define for $T_n(E_{N,Z}) = N - Z$ the net charge and $T_r(E_{N,Z}) = \frac{N}{Z}$ the ratio charge. Now suppose E_{N_1,Z_1} is stable. Then for every $E_{N,Z}$ such that $T_n(E_{N,Z}) = T_n(E_{N_1,Z_1})$ and $T_r(E_{N,Z}) \leq T_r(E_{N_1,Z_1})$ we can (almost) conclude that it is stable.

Remark: The 'almost' (see last table before last line Δ) could be due to the lack of precision in the numerical data.

3.5 Conclusion

Quantitatively our difficulties turned out to be the same as the ones encountered in Thomson's problem. We refer to papers that we have already quoted on the subject to understand in more detail the challenges faced by the lack of information on the exact or approximate minimizers due to a large extent to the curvature of the sphere. However our simple analysis revealed some special features of the Coulomb potential, in particular it sheds some light on the behaviour of the electrons (shielding): Theorem 8 will be extremely useful in the next chapter. Finally we want to emphasize that the $V_{N,Z}$ can be generalized to the molecular case and the results given in this chapter still hold up to some trivial modifications (see [FC06]).

Chapter 4

Minimum energy configurations of classical charges in the potential of an atomic nucleus: Large N asymptotics

4.1 The family of variational problems (revisited)

In the case of Thomson's problem, as already noticed by Landkof [La72] (see also [KS98]), despite the complexity (see 3.4.4), for large N the ground state energy and the ground state itself becomes extremely simple. In particular the particles become equidistributed over the sphere. In what follows we will in fact recover this result. We will study the large-N asymptotics of the already known[1] (see chapter 3) variational many-particle problem. By reformulating our variational problem (see below) we will be able to carry out an asymptotic inspection of the screening effect.

Starting point is the observation that the particle energy $V_{N,Z}$ can be reinterpreted in a natural way as an energy functional on the space $\mathcal{M}_+(\mathbb{R}^3 \backslash B_1)$ of nonnegative Radon measures on $\mathbb{R}^3 \backslash B_1$ (where $B_1 = \{x \in \mathbb{R}^3 \,|\, |x| < 1\}$). Define

$$I^{(N,Z)}(\mu) := -\int_{\mathbb{R}^3 \backslash B_1} \frac{1}{|x|} d\mu(x) + \frac{1}{2} \int\int_{(\mathbb{R}^3 \backslash B_1)^2 \backslash \mathrm{diag}} \frac{1}{|x-y|} d\mu(x)\, d\mu(y)$$

if $\mu = \frac{1}{Z}\sum_{i=1}^{N} \delta_{x_i}$ for some distinct $x_1, .., x_N \in \mathbb{R}^3 \backslash B_1$, and set $I^{(N,Z)}(\mu) := +\infty$ otherwise. Then for μ as in the first alternative, we have the identity

$$I^{(N,Z)}(\mu) = \frac{1}{Z^2} V_{N,Z}(x_1, ..., x_N). \tag{4.1}$$

Here and below diag denotes the diagonal $\{(x,x) \,|\, x \in \mathbb{R}^3 \backslash B_1\}$. Before presenting the results of this chapter we need the reader to be familiar with Gamma-convergence.

We recall the basics in the next section but if the reader is already acquainted with the tool, he or she may move on directly to section 4.3.

4.2 Introduction to Gamma-convergence

The Gamma-convergence is a tool which aims at describing the asymptotic behaviour of families of variational problems and their associated minimizers/maximizers. It was introduced by De Giorgi in the 70s and has since

[1] Since chapter 4 is really the follow up of chapter 3 we will use the notations of chapter 3

been extensively used first mainly in the calculus of variations and then later in many other fields of mathematics. Indeed by its own nature Gamma-convergence is a very adaptable tool. It can be seen as a natural extension of the direct method in the calculus of variations for families of variational problems. We will now explain 'heuristically' how to tackle a general problem with Gamma-convergence. We will then give a simple example to illustrate the general theory in order to facilitate the comprehension of our work by the reader who may not be familiar with these techniques. In fact the aforementioned example is close in spirit to the work presented in this chapter. We refer the interested reader to [DM88], [Br02] (the latter is an excellent graduate textbook for beginners to Gamma-convergence from which we were strongly inspired to write the introduction).

4.2.1 The general theory of Gamma-convergence

The concrete benefit that one derives from Gamma-convergence is usually to go from an initial family of problems to a new problem which is simplified in some sense (for example it might not depend on a small parameter anymore). One then solves it and derives some information on the asymptotic behaviour of minimizing sequences amongst other things.

Definition of Gamma-convergence for families of functionals depending on a parameter (many parameters only makes the notation heavier)

Let $I^{(j)} : X \to \mathbb{R} \cup \{\infty\}$ be a sequence of functionals on a topological space X. We say that I_j Gamma-converges to $I : X \to \mathbb{R} \cup \{\infty\}$ if for all $\mu \in X$

we have:

(i) (Ansatz-free lower bound) For every sequence $\mu_j \in X$ converging to μ we have $I(\mu) \leq \liminf_{j\to\infty} I^{(j)}(\mu_j)$.

(ii) (Attainment of lower bound) There exists a sequence $\mu_j \in X$ converging to μ such that $I(\mu) = \lim_{j\to\infty} I^{(j)}(\mu_j)$.

We would like to emphasize that in most family of problems the domain on which each one of the functional is defined varies. The trick is to include these changes of domain in the definition of the functionals. This can be achieved by defining the functionals to take the value $+\infty$ on the complement of their domain in the newly chosen space, namely the union of all spaces. Care has to be taken in order to make the space big enough to include the limits of minimizing sequences (see below). Note also that we have assumed the limit functional to be known. It may very well be that it has to be found. Some optimization over a set of potential candidates might be necessary. Since in our case we start with the right limit functional we do not enter into the details of such problems.

The need for compactness

We want to consider minimizing sequences (as in the direct method). Precisely what we mean by a minimizing sequence is a sequence $(x_j)_{j\in\mathbb{N}} \in (X)^{\mathbb{N}}$ such that

$$\lim_j \left(F_j(x_j) - \inf\{F_j(y) \mid y \in X\}\right) = 0.$$

We will need to ensure that every minimizing sequence has at least a convergent subsequence. The right choice of space X as explained above is an important first step. Then comes the choice of the topology on X which needs to be coarse enough to allow the convergence of our minimizing sequences (or at least subsequences). In our problem the natural choice will be the weak star topology on the set of positive, finite, radon measures for which we have the well known compactness theorem for bounded sequences. From the existence of a convergent subsequence one may want to extend to convergence of the entire sequence. This can often be achieved by an ad hoc argument. In our case we will use the uniqueness of the minimizer for the limit problem. Note that the Ansatz free lower bound has more chances to be satisfied if the topology has fewer convergent sequences whereas to insure compactness of all minimizing sequences the topology has to have as many convergent sequences as possible: one has to strike a balance between these two competing requirements.

How to deduce existence, convergence of minimum values and convergence of minimizers

When one has found the right setting (the limit functional, the right topology) one is in a position to prove the Gamma convergence. There is no general way to do this: it depends on the problem at hand. Let us suppose that we have the Gamma-convergence. We shall now explain how to extract some information from it. Take a minimization sequence $(x_j)_{j\in\mathbb{N}}$. And suppose for the sake of simplicity that thanks to some compactness property we can assume that this sequence converges to say $x \in X$. Using the definition of minimizing sequence we have the following

$$\limsup \inf \{I_j(y) \mid y \in X\} = \limsup_j I_j(x_j) \leq \limsup I_j(u_j)$$

which holds for all sequences $(u_j)_j$ in X. Further since we have (i) and (ii) (Gamma convergence) we have:

$$\begin{aligned}\limsup_j I_j(x_j) &\leq \inf \{I(u) \mid u \in X\} \leq I(x) \\ &\leq \liminf_j I_j(x_j) = \liminf_j \inf \{I_j(u) \mid u \in X\}.\end{aligned}$$

The existence of what is called recovery sequences justifies the first inequality above.

We easily infer from the above the following:

- Existence of a minimizer to the limit problem
- Sequences of the minimum values of the sequence of functionals converge to the minimum value of the limit problem
- Minimizing sequences converge toward a minimizer of the limit problem.

4.2.2 Simple example (similar to an example given in [Br02])

We consider the sequence of functionals $f_j : [-1, 1] \to \mathbb{R}$

$$f_j(x) = \cos(jx) + x^2.$$

We are looking for minimizers of the f_j. For j fixed the minimizers satisfy $\sin(xj) = \frac{2x}{j}$. This equation is not so easy to solve explicitly. We use Gamma-convergence.

Let $f : [-1,1] \to \mathbb{R}$ be defined as $f(x) = x^2 - 1$. We show that we have $f = \Gamma\text{-}\lim f_j$. Hence we will have amongst other things that $x_j^{min} \to x^{min}$ where $(x_j^{min})_j$ and x^{min} are the sequence of minimizers of the $(f_j)_j$ and (unique) minimizer of f respectively.

We first show the ansatz-free lower bound.

$$\cos(jx) \geq -1 \quad \Rightarrow f_j(x) \geq x^2 - 1 \qquad \forall x \in [-1,1].$$

Hence for any $x \in [-1,1]$ and any sequence $(x_j)_{j\in\mathbb{N}}$ in $[-1,1]$ such that $x_j \to x$ we have

$$f_j(x_j) \geq x_j^2 - 1$$

and consequently

$$\liminf_{j\to\infty} f_j(x_j) \geq x^2 - 1.$$

We have now only to show that there exists for every $x \in [-1,1]$ a recovery sequence called $(x_j)_{j\in\mathbb{N}}$ such that $\lim f_j(x_j) = x^2 - 1$. Fix $x \in [-1,1]$. We construct such a sequence: Take x_j :=nearest point to x in $\frac{\pi(2\mathbb{Z}+1)}{j}$. Then it is easy to see that $x_j \to x$ and that

$$f_j(x_j) = x_j^2 - 1 \to x^2 - 1.$$

We have now some information on the sequence of minimizers (which obviously exists). Indeed we have that the sequence of minimizers converges toward 0, the unique minimizer of f.

Remark: As in our case (see later in proof of Gamma-convergence) the entire sequence converges since the minimizer of the limit problem is unique.

4.3 The results

We first give the following result:

Theorem 13 *(Equidistribution) Let $\Omega \subset S^2$ be measurable such that area $(\partial\Omega) = 0$. For $N = Z \to \infty$, and any minimizers $(x_1^{(N)}, .., x_N^{(N)})$ of $V_{N,Z}$,*

$$\frac{\sharp\{x_i^{(N)} \,|\, x_i^{(N)} \in \Omega\}}{N} \longrightarrow \frac{area\,(\Omega)}{area\,(S^2)},$$

and

$$\frac{V_{N,Z}(x_1^{(N)}, .., x_N^{(N)})}{N^2} \longrightarrow -\frac{1}{2}.$$

Here area$(\Omega) = \int_\Omega dA$, with dA denoting the usual area element (= two-dimensional Hausdorff measure $H^2|_{S^2}$) on the sphere $S^2 = \{x \in \mathbb{R}^3 \,|\, |x| = 1\}$.

The above equidistribution law is a corollary of the following more general result, which in addition uncovers interesting behaviour of excess charges moving off to infinity in case of negative ions $N > Z$.

To include this case we consider, instead of $N = Z \to \infty$, the more general limit

$$N \to \infty, \quad Z \to \infty, \quad \frac{N}{Z} \to \lambda, \tag{4.2}$$

where $\lambda \in (0, \infty)$ is a filling factor. Positive ions correspond to $\lambda < 1$, neutral atoms to $\lambda = 1$, and negative ions to $\lambda > 1$.

For negative ions, the minimum of $V_{N,Z}$ on $\mathcal{A}_N$ is typically not attained (see below) and so one needs to relax the restriction to exact minimizers in Theorem 13. Instead one considers more general low-energy states, in the sense of

energy difference from infimum $<<$ total energy,

as made precise by the following

Definition 4 *A sequence $\{(x_1^{(N)},..,x_N^{(N)})\}$ is called a sequence of approximate minimizers of $\frac{V_{N,Z}}{Z^2}$ in the limit (4.2) if*

$$\frac{V_{N,Z}(x_1^{(N)},..,x_N^{(N)}) - E_{N,Z}}{Z^2} \longrightarrow 0 \tag{4.3}$$

where we recall that $E_{N,Z} = \inf_{x\in\mathcal{A}_N} V_{N,Z}$ (see page 35).

Theorem 14 *(Equidistribution and escape to infinity)*
For any sequence $\{(x_1^{(N)},..,x_N^{(N)})\}$ of approximate minimizers of $V_{N,Z}$, in the limit (4.2) the associated measures

$$\mu^{(N,Z)} := \frac{1}{Z}\sum_{i=1}^{N} \delta_{x_i^{(N)}} \tag{4.4}$$

satisfy

$$\mu^{(N,Z)} \rightharpoonup^* c(\lambda)\frac{H^2|_{S^2}}{4\pi} \tag{4.5}$$

and

$$\frac{V_{N,Z}(x_1^{(N)},..,x_N^{(N)})}{Z^2} \longrightarrow -c(\lambda) + \frac{1}{2}c(\lambda)^2, \tag{4.6}$$

where $c(\lambda) = \min\{\lambda, 1\}$.

Here and below the halfarrow $\rightharpoonup^*$ denotes weak* convergence in the space $\mathcal{M}(\mathbb{R}^3\backslash B_1)$ of Radon measures on $\mathbb{R}^3\backslash B_1$, where $B_1 = \{x \in \mathbb{R}^3 \,|\, |x| < 1\}$.[2]

Note that for negative ions ($\lambda > 1$) the weak* limit has less mass than the approximating measures (namely 1 instead of λ). Physically this means that only $Z + o(Z)$ particles stay bound and $N - (Z + o(Z))$ particles move off to infinity. More precisely we recover the following result which is implicit

[2] Recall that for any closed subset $\Omega \subseteq \mathbb{R}^d$, $\mathcal{M}(\Omega)$ is the dual of the space $C_0(\Omega) = \{f : \Omega \to \mathbb{R} \,|\, f \text{ continuous}, f(x) \to 0 \text{ for } |x| \to \infty\}$, and that a sequence of Radon measures μ_ν is said to converge weak* to μ, notation: $\mu_\nu \rightharpoonup^* \mu$, if $\int_\Omega f\, d\mu_\nu \to \int_\Omega f\, d\mu$ for all $f \in C_0(\Omega)$.

in the work of Lieb, Sigal, Simon and Thirring [LSST88] on non-attainment for quantum mechanical atoms.[3]

Let us define $N^*(Z) = \sup\{N \in \mathbb{N} \mid \inf_{\mathcal{A}_N} V_{N,Z} \text{ attained}\}$ (although related to the $N_*(Z)$ defined p39 this is not the same quantity). Then we have

Corollary 15 *(Asymptotic neutrality of large ions)*

$$\frac{N^*(Z)}{Z} \longrightarrow 1 \text{ as } Z \to \infty.$$

See Section 4.6 for the easy argument how the corollary follows from Theorem 14.

We establish Theorem 14 by passage to a continuum limit, in the mathematically rigorous sense of Gamma-convergence.

We then show:

Theorem 16 *In the limit (4.2), the sequence of functionals $I^{(N,Z)}$ Gamma-converges (with respect to weak* convergence of Radon measures) to the functional $I : \mathcal{M}_+(\mathbb{R}^3 \backslash B_1) \to \mathbb{R} \cup \{+\infty\}$ defined by*

$$I(\mu) := -\int_{\mathbb{R}^3 \backslash B_1} \frac{1}{|x|} d\mu(x) + \frac{1}{2} \int\int_{(\mathbb{R}^3 \backslash B_1)^2} \frac{1}{|x-y|} d\mu(x)\, d\mu(y) \tag{4.7}$$

if $\int d\mu \leq \lambda$, and $I(\mu) = +\infty$ otherwise.

Note that the restriction to discrete measures has disappeared, and in the domain of integration of the second term the diagonal is now included.

[3] These authors do not study classical non-attainment, nor formulate the classical model (3.1), (3.2). Instead they investigate the occurrence of a stronger classical instability which they show to be sufficient for quantum instability.

It is now an easy matter to show that I is uniquely minimized by the measure appearing on the right hand side of (4.5); see Proposition 17 in Section 4.4. Standard arguments in Gamma-convergence then imply the equidistribution results in Theorems 13 and 14; see Section 4.5. In particular, the mass of the minimizing measure (i.e. physically the amount of electronic charge that can be bound by the nucleus) is $\min\{1, \lambda\}$.

It is essential for the behaviour of the limit functional I that the diagonal is included in the domain of integration. If it were still removed, the functional would promote clustering rather than condensation on the sphere, and the minimizers would be given by $\lambda\delta_x$ for $x \in S^2$.

Finally we remark that no statement analogous to Theorem 16 is known in the quantum case. It is conceivable that the correct Gamma-limit will then be given by Thomas-Fermi theory. But to our knowledge the value of the Thomas-Fermi functional has only been justified at its own minimizer [LS77b], and its mathematical status on non-minimizing states is unknown. Physically this means that our classical limit functional, unlike the Thomas-Fermi functional, is known not only to capture correctly the ground state energy, but also the energy change when the ground state is deformed.

4.4 Analysis of the limit theory

We postpone the rigorous justification of the limit theory from the particle system (see Theorem 16) to Section 4.7 below. Here we analyse the limit theory, and in the next section we will deduce the equidistribution and escape-to-infinity results of Theorems 13 and 14.

The fundamental advantage of the limit theory over the particle system is that it can be minimized explicitly. Related work on minimizing problems with loss of constraint can be found in [Ba88].

Proposition 17 *a) The unique minimizer of*

$$I(\mu) = -\int_{\mathbb{R}^3\backslash B_1} \frac{1}{|x|} d\mu(x) + \frac{1}{2}\int\int_{(\mathbb{R}^3\backslash B_1)^2} \frac{1}{|x-y|} d\mu(x) d\mu(y)$$

on

$$\mathcal{M}_{[0,\lambda]} = \{\mu \in \mathcal{M}(\mathbb{R}^3\backslash B_1) \,|\, \mu \geq 0, \int d\mu \leq \lambda\} \tag{4.8}$$

is given by

$$\mu = \min\{\lambda,\, 1\}\frac{H^2|_{S^2}}{4\pi}. \tag{4.9}$$

b) Let $\mathcal{M}_\lambda := \{\mu \in \mathcal{M}(\mathbb{R}^3\backslash B_1) \,|\, \mu \geq 0, \int d\mu = \lambda\}$. If $\lambda \leq 1$, then the unique minimizer of I on $\mathcal{M}_\lambda$ is given by (4.9). If $\lambda > 1$, then the infimum of I on $\mathcal{M}_\lambda$ is not attained, and any minimizing sequence converges weak but not strongly to (4.9).*

Note that I is well-defined on $\{\mu \in \mathcal{M}(\mathbb{R}^3\backslash B_1) \,|\, \mu \geq 0\}$ (the space of nonnegative Radon measures of finite mass on $\mathbb{R}^3\backslash B_1$) as an element of $\mathbb{R} \cup \{+\infty\}$, because the negative term $-\int_{\mathbb{R}^3\backslash B_1} |x|^{-1} d\mu(x)$ is always finite, due to the boundedness of the integrand on the domain of integration. That there exists a minimizer to the Gamma-limit on $\mathcal{M}_{[0,\lambda]}$ can easily be seen. Indeed we have the following

Lemma 18 *I is (sequentially) weak* lower semicontinuous on $\mathcal{C}(\mathbb{R}^3\backslash\Omega)$, i.e. if μ, $\mu_j \in \mathcal{C}(\mathbb{R}^3\backslash\Omega)$ with $\mu_j \rightharpoonup^* \mu$, then $I(\mu) \leq \liminf_{j\to\infty} I(\mu_j)$.*

Proof: This follows, e.g. from Theorem 16 and the general fact that Gamma-limits are lower semicontinuous (see [Br02, Proposition 1.28]). However since the proof of the Ansatz-free lower bound also relies on this lemma we give it here. We use a simple truncation argument which replaces the discontinuous integrand $1/|x-y|$ in I by a continuous function. Let

$$f^{\alpha}(x,y) := \begin{cases} \frac{1}{|x-y|} & \text{if } |x-y| \geq \alpha \\ \frac{1}{\alpha} & \text{if } |x-y| \leq \alpha, \end{cases} \tag{4.10}$$

and let I_α be the functional obtained by replacing the integrand $1/|x-y|$ in the second term of I by $f^\alpha(x,y)$. Then $\liminf_{j\to\infty} I(\mu_j) \geq \liminf_{j\to\infty} I_\alpha(\mu_j) \geq I_\alpha(\mu)$, due to the trivial inequality $1/|x-y| \geq f_\alpha(x,y)$ and the convergences $\mu_j \rightharpoonup^* \mu$ and $\mu_j \otimes \mu_j \rightharpoonup^* \mu \otimes \mu$. To finish the proof it suffices to show that $\lim_{\alpha\to 0} I_\alpha(\mu) = I(\mu)$. If $(\mu\otimes\mu)(\text{diag}) > 0$ then this is true because both sides are equal to $+\infty$; if $(\mu\otimes\mu)(\text{diag}) = 0$ then this follows by monotone convergence, because $f_\alpha(x,y)$ is monotonically increasing in α and tends to $1/|x-y|$ for all $(x,y) \neq \text{diag}$, and hence for $(\mu\otimes\mu)$-a.e. (x,y).

□

Existence of a minimizer is immediate from Lemma 18: any minimizing sequence $\mu^{(j)}$ is bounded in $\mathcal{M}(\mathbb{R}^3 \backslash B_1)$, since $\int d\mu^{(j)} \leq \lambda$; thus there exists a weak* convergent subsequence, by the Banach-Alaoglu theorem; its limit must be a minimizer, by Lemma 18. Uniqueness follows from Lemma 20.

Proof of Proposition 17:

Step 1: basic functional analysis for the Coulomb self-energy functional

$$J(\mu) := \frac{1}{2} \int\int_{\mathbb{R}^6} \frac{1}{|x-y|} d\mu(x) d\mu(y) \tag{4.11}$$

on Radon measures. Let $\mathcal{M}_+(\mathbb{R}^3)$ denote the set of nonnegative Radon measures of finite mass on $\mathbb{R}^3$, and let denote by $\mathcal{C}(\mathbb{R}^3)$ the set of nonnegative Radon measures on $\mathbb{R}^3$ of finite mass for which $J(\mu)$ is finite. Define an extension of J to measures with both negative and positive part, as follows: if $\mu = \mu_1 - \mu_2$ with $\mu_1, \mu_2 \in \mathcal{C}(\mathbb{R}^3)$, set

$$
\begin{aligned}
J(\mu_1 - \mu_2) \;:=\; & \frac{1}{2}\int\int_{\mathbb{R}^6} \frac{1}{|x-y|} d\mu_1(x) d\mu_1(y) - \int\int_{\mathbb{R}^6} \frac{1}{|x-y|} d\mu_1(x) d\mu_2(y) \\
+ & \int\frac{1}{2}\int_{\mathbb{R}^6} \frac{1}{|x-y|} d\mu_2(x) d\mu_2(y).
\end{aligned}
$$

Since the first and last term are finite by assumption, and the integrand in the middle term is nonnegative, this is well defined as an element of $\mathbb{R} \cup \{-\infty\}$. The key property of J needed in the proof of Proposition 17 is

Lemma 19 $J(\mu_1 - \mu_2) \geq 0$ *for any* $\mu_1, \mu_2 \in \mathcal{C}(\mathbb{R}^3)$*, with equality if and only if* $\mu_1 = \mu_2$.

This result is trivial for smooth, rapidly decaying measures, as well as for nonnegative measures. That it should continue to hold for rough measures without a sign is well known "folklore" in part of the potential theoretic literature (see e.g. [La72]). Our proof relies on an approximation lemma which concerns the behaviour of the Coulomb energy under mollification of measures, and on a generalization of an identity of Mattila [Ma95].

The lemma readily yields

Lemma 20 I *is strictly convex on* $\mathcal{C}(\mathbb{R}^3 \backslash \Omega) = \{\mu \in \mathcal{M}(\mathbb{R}^3 \backslash \Omega) \,|\, \mu \geq 0, J(\mu) < \infty\}$.

Proof: Because the first term of I is linear and the second term is quadratic, we have

$$
\frac{I(\mu_1) + I(\mu_2)}{2} - I\Big(\frac{\mu_1 + \mu_2}{2}\Big) = \frac{1}{4} J(\mu_1 - \mu_2)
$$

for any μ_1, μ_2 in the above set. The assertion now follows from Lemma 19.

□

We now prove Lemma 19. We need two technical lemmas to do so. Denote by $C_0(\mathbb{R}^3)$ the function space $\{u : \mathbb{R}^3 \to \mathbb{R} \,|\, u \text{ continuous}, u(x) \to 0 \text{ as } |x| \to \infty\}$.

Lemma 21 *Let $\phi \in C_0(\mathbb{R}^3)$ be nonnegative, radially symmetric, and satisfy $\int_{\mathbb{R}^3} \phi = 1$. Let $\mu_1, \mu_2 \in \mathcal{C}(\mathbb{R}^3)$, let $\mu = \mu_1 - \mu_2$, and for $\varepsilon > 0$ let μ^ε denote the mollified measure*

$$\mu^\varepsilon(x) = (\phi_\varepsilon * \mu)(x) = \int_{\mathbb{R}^3} \phi_\varepsilon(x - x')d\mu(x'), \tag{4.12}$$

where $\phi_\varepsilon(z) = \varepsilon^{-3}\phi(\varepsilon^{-1}z)$. Then $J(\mu) = \lim_{\varepsilon\to 0} J(\mu^\varepsilon)$.

Proof: It suffices to consider the middle term in the definition of J, i.e. to show

$$\int\int_{\mathbb{R}^6} \frac{1}{|x-y|} d\mu_1(x)d\mu_2(y) = \lim_{\varepsilon\to 0} \int\int_{\mathbb{R}^6} \frac{1}{|x-y|} d\mu_1^\varepsilon(x)d\mu_2^\varepsilon(y) \tag{4.13}$$

(for the other terms, set $\mu_1 = \mu_2$). By Fubini's theorem,

$$\int\int_{\mathbb{R}^6} \frac{1}{|x-y|} d\mu_1^\varepsilon(x)d\mu_2^\varepsilon(y) = \int\int_{\mathbb{R}^6}\int\int_{\mathbb{R}^6} \frac{\phi_\varepsilon(x-x')\phi_\varepsilon(y-y')}{|x-y|} dx\, dy d\mu_1\, d\mu_2. \tag{4.14}$$

Clearly the term in brackets converges pointwise to $1/|x'-y'|$ as $\varepsilon \to 0$. Moreover setting $z = x - x'$ and using the radial symmetry of ϕ_ε together with Newton's theorem that the electrostatic potential exerted by a spherical charge distribution onto a point inside it is constant, while that exerted onto a point outside it is the same as that exerted by the same amount of charge placed at the centre,

$$\begin{aligned}\int_{\mathbb{R}^3} \frac{\phi_\varepsilon(x-x')}{|x-y|} dx &= \int_{\mathbb{R}^3} \frac{\phi_\varepsilon(z)}{|z-(y-x')|} dz = \int_{\mathbb{R}^3} \min\{\frac{1}{|z|}, \frac{1}{|y-x'|}\}\phi_\varepsilon(z)dz \\ &\le \frac{1}{|y-x'|}\int_{\mathbb{R}^3} \phi_\varepsilon(z)dz = \frac{1}{|y-x'|}. \end{aligned} \tag{4.15}$$

Multiplying by $\phi_\varepsilon(y-y')$, integrating over y and applying (4.15) again yields

$$\int\int_{\mathbb{R}^6} \frac{\phi_\varepsilon(x-x')\phi_\varepsilon(y-y')}{|x-y|} dx\, dy \leq \int_{\mathbb{R}^3} \frac{1}{|y-x'|}\phi_\varepsilon(y-y')dy \leq \frac{1}{|x'-y'|}.$$

Hence we can apply the dominated convergence theorem to the right hand side of (4.14), deducing that it converges to the left hand side of (4.13). This establishes the lemma. □

Next, we derive an expression for the Coulomb energy in terms of the Fourier transform, defined for any nonnegative Radon measure of finite mass, $\mu \in \mathcal{M}_+(\mathbb{R}^3)$, by

$$\widehat{\mu}(k) := \int_{\mathbb{R}^3} e^{-ik\cdot x} d\mu(x).$$

Note that for any such measure, its Fourier transform is a bounded continuous function.

Lemma 22 *Let μ_1, $\mu_2 \in \mathcal{C}(\mathbb{R}^3)$. Then*

$$J(\mu_1 - \mu_2) = \frac{1}{2}\frac{1}{(2\pi)^3}\int_{\mathbb{R}^3} \frac{4\pi}{|k|^2}|\widehat{\mu_1} - \widehat{\mu_2}|^2 dk. \tag{4.16}$$

Proof: We approximate μ_1, μ_2 by smoother measures, as follows. For $\varepsilon > 0$, let $\phi_\varepsilon(x) := (2\pi\varepsilon)^{-3/2}e^{-|x|^2/(2\varepsilon)}$. Given any $\mu \in \mathcal{C}(\mathbb{R}^3)$, denote the associated mollified measure (4.12) by μ_ε. Then $\mu_\varepsilon \in L^1(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3)$, because

$$\int \phi_\varepsilon * \mu = \Big(\int \phi_\varepsilon\Big)\cdot\Big(\int d\mu\Big) = \int d\mu < \infty$$

and $\sup(\phi_\varepsilon * \mu) \leq (\sup \phi_\varepsilon) \cdot \int d\mu < \infty$. In particular $\mu_\varepsilon \in L^2(\mathbb{R}^3)$, and so its Fourier transform $\widehat{\mu_\varepsilon}$ is well-defined as an element of $L^2(\mathbb{R}^3)$. By standard Fourier calculus and the fact that $f(x) = 1/|x|$ has Fourier transform $4\pi/|k|^2$,

$$\widehat{\mu_\varepsilon} = \widehat{\phi_\varepsilon} \cdot \hat{\mu},$$

$$J(\mu_1^\varepsilon - \mu_2^\varepsilon) = \frac{1}{2}\frac{1}{(2\pi)^3}\int_{\mathbb{R}^3} \frac{4\pi}{|k|^2}|\widehat{\phi_\varepsilon}(k)|^2|\widehat{\mu_1}(k) - \widehat{\mu_2}(k)|^2 dk. \tag{4.17}$$

As $\varepsilon \to 0$, because $\widehat{\phi_\varepsilon}(k) = e^{-\varepsilon|k|^2/2}$ we have that $|\widehat{\phi_\varepsilon}(k)|^2$ tends monotonically to 1, and hence by monotone convergence the right hand side of (4.17) tends to the right hand side of (4.16). On the other hand, by Lemma 21 the left hand side of (4.17) tends to the left hand side of (4.16). This establishes the lemma. □

Lemma 23 *Let μ_1, $\mu_2 \in \mathcal{C}(\mathbb{R}^3)$. Then $J(\mu_1 - \mu_2) \geq 0$, with equality if and only if $\mu_1 = \mu_2$.*

Proof Nonnegativity is clear from (4.16). Moreover the right hand side of (4.16) is strictly positive unless $\hat{\mu}_1 = \hat{\mu}_2$ Lebesgue-almost everywhere. But by continuity of the $\hat{\mu}_i$, this means $\hat{\mu_1} = \hat{\mu_2}$, and hence $\mu_1 = \mu_2$. The proof is complete. □

The symmetrization argument and expression of the energy functional in term of the radial measure

Given $\mu \in \mathcal{C}(\mathbb{R}^3)$, let

$$\bar{\mu} = \frac{1}{\mathrm{vol}(SO(3))} \int_{SO(3)} \mu_R d\mathcal{H}(R),$$

where $\mathcal{H}$ is the Haar measure on $SO(3)$ and μ_R is the rotated measure $\mu_R(\Omega) = \mu(R^{-1}\Omega)$ ($R \in SO(3)$, Ω measurable). By the strict convexity of I and Jensen's inequality,

$$I(\bar{\mu}) \leq I(\mu), \text{ with equality if and only if } \mu = \bar{\mu}. \tag{4.18}$$

Hence it suffices to show that among radially symmetric measures in $\mathcal{M}_{[0,\lambda]}$, the unique minimizer of I is given by (4.9).

For such μ, we can rewrite I in terms of the radial measure

$$\nu(r) := \mu(S_r), \quad S_r = \{x \in \mathbb{R}^3 \,|\, |x| = r\},$$

as follows. (Note that a radially symmetric $\mu \in \mathcal{M}_{[0,\lambda]}$ is equivalent to $\nu \in \mathcal{M}^{radial}_{[0,\lambda]} = \{\nu \in \mathcal{M}([1,\infty)) \,|\, \nu \geq 0, \int d\nu \leq \lambda\}$, and $\mu \in \mathcal{M}_\lambda$ is equivalent to $\nu \in \mathcal{M}^{radial}_\lambda = \{\nu \in \mathcal{M}([1,\infty)) \,|\, \nu \geq 0, \int d\nu = \lambda\}$.) We use the fact that the electrostatic potential exerted by a radial charge distribution onto a point outside it is the same as that exerted by the same amount of total charge located at the origin (Newton's theorem),

$$\int_{\{y \,|\, |y| \leq |x|\}} \frac{d\mu(y)}{|x-y|} = \Big(\int_{[1,|x|]} d\nu(|y|)\Big) \cdot \frac{1}{|x|},$$

and that the electrostatic potential exerted by a radial charge distribution onto a point inside it is constant,

$$\int_{\{y \,|\, |y| > |x|\}} \frac{d\mu(y)}{|x-y|} = \int_{(|x|,\infty)} \frac{1}{|y|} d\nu(|y|).$$

Consequently

$$\int_{\mathbb{R}^3 \backslash B_1} \frac{d\mu(y)}{|x-y|} = \int_{[1,\infty)} \min\{\frac{1}{|x|}, \frac{1}{|y|}\} d\nu(|y|)$$

and

$$I(\mu) = -\int_{[1,\infty)} \frac{1}{r} d\nu(r) + \frac{1}{2} \int\int_{[1,\infty)^2} \min\{\frac{1}{r}, \frac{1}{r'}\} d\nu(r) d\nu(r') =: \tilde{I}(\nu). \quad (4.19)$$

Hence to complete the proof of Proposition 17 a), it suffices to show that

$$\nu(r) = \min\{\lambda, 1\}\delta_1 \quad (4.20)$$

is a minimizer of $\tilde{I}$ on $\mathcal{M}^{radial}_{[0,\lambda]}$; uniqueness then follows from strict convexity.

The behaviour of $\tilde{I}$ on discrete measures

Let $\nu = \sum_{\alpha=1}^{K} c_\alpha \delta_{r_\alpha}$, $c_\alpha \geq 0$, $\sum_{\alpha=1}^{K} c_\alpha \leq \lambda$, $r_1 < r_2 < ... < r_K$. For such ν

$$\begin{aligned}\tilde{I}(\nu) &= -\sum_{\alpha=1}^{K} \frac{c_\alpha}{r_\alpha} + \frac{1}{2}\sum_{\alpha=1}^{K} \frac{c_\alpha^2}{r_\alpha} + \sum_{\alpha<\beta} \frac{c_\alpha c_\beta}{r_\beta} \\ &= \frac{(c_1/2-1)c_1}{r_1} + \frac{(c_1+c_2/2-1)c_2}{r_2} + ... + \frac{(c_1+...+c_{K-1}+c_K/2-1)c_K}{r_K}.\end{aligned}$$

But any function $f(r) = \alpha/r$, $\alpha \in \mathbb{R}$ attains its minimum on $[1, R]$ on the boundary. Hence the above expression, as a function of $(r_1, ..., r_K) \in [1, R]^K$, always attains a minimum when all $r_i \in \{1, R\}$, that is to say when ν is of the form $\nu = C_1\delta_1 + C_2\delta_R$.

In this case, $\tilde{I}(\nu) = (C_1/2 - 1)C_1 + (C_1 + C_2/2 - 1)C_2/R$, which is minimized as a function of $C_1, C_2 \geq 0$, $C_1 + C_2 \leq \lambda$ if and only if $C_1 = \min\{\lambda, 1\}$, $C_2 = 0$.

It follows that (4.20) is a minimizer of $\tilde{I}$ among discrete measures.

Finally, discrete measures are weak* dense in $\mathcal{M}^{radial}_{[0,\lambda]}$ (see for example [Ba90]) and $\tilde{I}$ is weak* continuous, due to the fact that the integrands $1/r$ and $\min\{1/r, 1/r'\}$ are continuous and tend to zero as r respectively (r, r') tend to infinity; hence (4.20) is also a minimizer on the full space $\mathcal{M}^{radial}_{[0,\lambda]}$. This completes the proof of a).

To establish b), note that by (4.18) and (4.19) it suffices to show that the infimum of $\tilde{I}$ on $\mathcal{M}^{radial}_{\lambda}$ is not attained and that every minimizing sequence converges weak* but not strongly to (4.20). But this follows analogously to the last part of the proof of a), by observing that among measures of form $\nu = C_1\delta_1 + C_2\delta_R$, $C_1, C_2 \geq 0$, $C_1 + C_2 = \lambda$, $\tilde{I}$ is minimized if and only if $C_1 = \min\{\lambda, 1\}$, $C_2 = \lambda - \min\{\lambda, 1\}$. This completes the proof of Proposition 17. □

4.5 Equidistribution revisited and escape to infinity

Here we show how the explicit solution of the limit theory derived above, combined with the abstract Gamma-convergence result of Theorem 13, allows us to infer the equidistribution and escape-to-infinity results for the particle system stated in Theorem 13 and 14.

The main point is that in the topology in which the Gamma-convergence occurs, the sequence of (associated measures of) approximate minimizers of the particle energy $V_{N,Z}$ is compact. The rest of the argument is as explained in the introduction.

Proof of Theorem 14: First, note that by (4.1) and Theorem 16,

$$\frac{\inf V_{N,Z}}{Z^2} = \inf I^{(N,Z)} \to \inf I \tag{4.21}$$

as $N \to \infty$, $Z \to \infty$, $N/Z \to \lambda$.

Now let $(x_1^{(N,Z)}, ..., x_N^{(N,Z)})$ be a sequence of approximate minimizers of $V_{N,Z}$. It follows from definition (4.3) and (4.21) that

$$I^{(N,Z)}(x_1^{(N,Z)}, ..., x_N^{(N,Z)}) \to \inf I. \tag{4.22}$$

In addition the associated sequence of measures $\mu^{(N,Z)}$ defined in (4.4) is bounded in $\mathcal{M}(\mathbb{R}^3 \backslash B_1)$ (because $\mu^{(N,Z)} \geq 0$ and $\int_{\mathbb{R}^3 \backslash B_1} d\mu^{(N,Z)} = N/Z$ is bounded), and hence weak* compact, by the Banach-Alaoglu theorem.

By the lower bound property (i) contained in the Gamma-convergence result of Theorem 16, for every weak* convergent subsequence $\mu^{(N_j,Z_j)}$ the limit $\bar{\mu}$ satisfies $I(\bar{\mu}) \leq \liminf I^{(N_j,Z_j)}(\mu^{(N_j,Z_j)})$. But by (4.22) and Proposition 17, $\bar{\mu}$ must equal the unique minimizer (4.9) of I.

Finally, since every subsequence of $\mu^{(N,Z)}$ converges to (4.9), so must the whole sequence.

This establishes the theorem. □

Proof of Theorem 13: This is a straightforward consequence of Theorem 14. Specializing to $N = Z$ (whence $\lambda = c(\lambda) = 1$) and using the fact that the measures $\mu^{(N,Z)}$ are supported on the sphere S^2 (by Theorem 8, we infer that $\mu^{(N,Z)} \rightharpoonup^* \frac{1}{4\pi} H^2|_{S^2} =: \mu$ in $\mathcal{M}(S^2)$. We now use the well known fact that if a sequence of Radon measures $\mu^{(j)}$ on any compact d-dimensional manifold X converges weak* to μ, then for all Borel sets $\Omega \subseteq X$ with $\mu(\partial\Omega) = 0$, $\mu^{(j)}(\Omega) \to \mu(\Omega)$. Consequently for $\Omega \subseteq S^2$

$$\frac{\sharp\{x_i^{(N)} \mid x_i^{(N)} \in \Omega\}}{N} = \int_{S^2} \chi_\Omega(x) d\mu^{(N,Z)}(x) \to \int_{S^2} \chi_\Omega(x) d\mu(x) = \frac{area(\Omega)}{area(S^2)}.$$

This proves Theorem 13. □

4.6 Proof of asymptotic neutrality of large ions

4.6.1 Proof of Corollary 15

Here we give the easy argument why Corollary 15 follows from Theorem 14.

Recall that $N^*(Z)$ denotes the maximal integer N such that the infimum of $V_{N,Z}$ on $\mathcal{A}_N$ is attained. The essentially trivial attainment result in Theorem 8 a) implies that $N^*(Z) \geq Z + 1$; hence it is clear that $\liminf_{Z\to\infty} \frac{N^*(Z)}{Z} \geq 1$. The nontrivial assertion in the corollary is that

$$\limsup_{Z\to\infty} \frac{N^*(Z)}{Z} \leq 1. \tag{4.23}$$

But this is an easy consequence of Theorem 14, as follows. Denote the value of the lim sup in (4.23) by λ_*, and consider any subsequence realizing it, i.e. $N^*(Z_j)/Z_j \to \lambda_*$ as $j \to \infty$. Let $(x_1^{(N^*(Z_j))}, ..., x_{N^*(Z_j)}^{(N^*(Z_j))})$ be a minimizer of $V_{N^*(Z_j),Z_j}$.

On the one hand, by Theorem 14, the associated measure satisfies $\mu^{(N^*(Z_j))} \rightharpoonup^* \mu$ with $\mu = \min\{\lambda_*, 1\}\frac{1}{4\pi}H^2|_{S^2}$; in particular $\int_{S^2} d\mu = \min\{\lambda_*, 1\}$.

On the other hand, by the absorption principle (Theorem 8 b))

$$\int_{S^2} d\mu^{(N^*(Z_j))} = N^*(Z_j)/Z_j$$

for all j, and hence, by weak* convergence of $\mu^{(N^*(Z_j))}|_{S^2}$ in $\mathcal{M}(S^2)$, $\int_{S^2} d\mu = \lambda_*$.

Consequently $\min\{\lambda_*, 1\} = \lambda_*$, or equivalently $\lambda_* \leq 1$, as was to be shown. □

We are now in the position to prove the result announced in chapter 3.

4.6.2 Proof of Theorem 11

It is a trivial corollary of Corollary 15. We have that $N_* \geq Z + 1$. So $\liminf \frac{N_*}{Z} \geq 1$. Now by definition we have that $N_* \leq N^*$. Hence it follows $\limsup \frac{N_*}{Z} \leq \limsup \frac{N^*}{Z} = 1$ as claimed. □

4.7 The continuum theory as the rigorous Gamma-limit of the many-particle Coulomb system

Here we show that the continuum theory (4.7) arises in a mathematically rigorous way (namely as a Gamma-limit) from the many-particle Coulomb system, i.e. we prove Theorem 16.

We identify our setting with the definition of Gamma convergence given in 4.1.1: $X = \mathcal{M}_{[0,\lambda]}$ (see (4.8)), the space of nonnegative Radon measures on $\mathbb{R}^3 \backslash B_1$ of mass $\leq \lambda$, endowed with the weak* topology, and $I^{(j)} = I^{(N_j, Z_j)}$, where $N_j \in \mathbb{N}$, $Z_j > 0$, $N_j/Z_j \to \lambda$ $(j \to \infty)$. In order to establish Theorem 16 we need to verify (i) and (ii).

4.7.1 Proof of the lower bound (i)

Suppose that $\mu_j \rightharpoonup^* \mu$. We may assume without loss of generality that $I^{(j)}(\mu_j) < \infty$ for all j (because if $J := \{j \in \mathbb{N} \,|\, I^{(j)}(\mu_j) < \infty\}$ is finite the assertion is trivial and if it is infinite then $\liminf_{j\to\infty} I^{(j)}(\mu_j) = \liminf_{j\in J, j\to\infty} I^{(j)}(\mu_j)$). By passing to a subsequence we may in addition assume that $I^{(j)}(\mu_j) \to \liminf_{j\to\infty} I^{(j)}(\mu_j)$.

We use the truncated f^α and the corresponding truncated energy functional I_α introduced in the proof of Lemma 18.

We compute

$$\begin{aligned}
I^{(k)}(\mu_k) &= -\int_{\mathbb{R}^3\setminus B_1} \frac{1}{|x|} d\mu_k(x) + \frac{1}{2}\int\int_{(\mathbb{R}^3\setminus B_1)^2\setminus\text{diag}} \frac{1}{|x-y|} d\mu_k(x) d\mu_k(y) \\
&\geq -\int_{\mathbb{R}^3\setminus B_1} \frac{1}{|x|} d\mu_k(x) + \frac{1}{2}\int\int_{(\mathbb{R}^3\setminus B_1)^2\setminus\text{diag}} f^\alpha(x,y) d\mu_k(x) d\mu_k(y) \\
&= I_\alpha(\mu_k) - \frac{N_k}{2Z_k^2\alpha}.
\end{aligned}$$

Using the fact that the last term on the right hand side tends to zero by (4.2) and that if $\mu_k \rightharpoonup^* \mu$ in $\mathcal{M}(\mathbb{R}^3\setminus B_1)$ then $\mu_k \otimes \mu_k \rightharpoonup^* \mu \otimes \mu$ in $\mathcal{M}((\mathbb{R}^3\setminus B_1)^2)$, letting k tend to infinity gives

$$\lim_k I^{(k)}(\mu_k) \geq \lim_k I_\alpha(\mu_k) = I_\alpha(\mu). \tag{4.24}$$

To finish the proof it suffices to show that $\lim_{\alpha\to 0} I_\alpha(\mu) = I(\mu)$. But this was shown in Lemma 18. □

4.7.2 Proof of the upper bound (ii)

Fix a sequence $N_\nu \to \infty$, $Z_\nu \to \infty$, $N_\nu/Z_\nu \to \lambda \in (0,\infty)$. Given $\mu \in \mathcal{M}_+(\mathbb{R}^3\setminus B_1)$, we need to construct a sequence $\mu_\nu \in \mathcal{M}_+(\mathbb{R}^3\setminus B_1)$ (or, in Gamma-convergence terminology, a "recovery sequence") such that $\mu_\nu \rightharpoonup^* \mu$ and $\limsup_{\nu\to\infty} I^{(N_\nu,Z_\nu)}(\mu_\nu) \leq I(\mu)$.

This is achieved by a careful multiscale construction, by introducing a mesoscale h with particle spacing << mesoscale << support of μ (see Step 2) and approximating μ in each mesoscale region by a uniform lattice of Dirac masses, but with region-dependent lattice constant (see Step 4). The latter is governed by the amount of mass to be accommodated in the region (see Step 3).

The fundamental difficulty to be overcome is that one expects the energy to be highly sensitive to the precise placement of the particles; but the structure of approximate or exact minimizers of the many-body Coulomb interaction is completely unknown mathematically. We are not aware of any attempt to prove minimizers are crystalline, or approximately crystalline, nor even to establish the optimal lattice structure – neither for Coulomb interactions nor for any other realistic interaction law in three dimensions.

Remarkably, the long range nature of the Coulomb force, usually considered a complicating rather than a simplifying feature, works in our favour. It implies that the energy is dominated by long range contributions, and so at short range a rough knowledge of bondlengths (to within a factor) turns out to be sufficient, as long as knowledge of the long range distances, governed by the "packing density", is precise. The key point in the proof is the implementation of these ideas in Step 5.

Step 1 *Reduction to compactly supported measures of finite energy and mass* λ

If $I(\mu) = \infty$ existence of a recovery sequence is trivial: for instance the sequence $\mu_\nu \equiv \mu$ will do. So we may assume that $I(\mu) < \infty$.

By a standard approximation argument, we may also assume that μ is compactly supported.

A little less trivially, we claim that it is enough to establish existence of a recovery sequence for measures with $\int d\mu = \lambda$. This is because if $\int d\mu > \lambda$, then $I(\mu) = \infty$ and we are back in the case dealt with above, whereas if $\int d\mu < \lambda$ we can always "place unwanted mass at infinity". More precisely, if $\int d\mu = \bar{\lambda} < \lambda$, we choose $\bar{N}_\nu \in \mathbb{N}$, $\bar{N}_\nu < N_\nu$, such that $\tilde{N}_\nu/Z_\nu \to \tilde{\lambda}$, apply existence of a recovery sequence $\tilde{\mu}_\nu$ for μ with respect to the functionals $I^{(\tilde{N}_\nu, Z_\nu)}$, and set $\mu_\nu = \tilde{\mu}_\nu + \sum_{k=1}^{N_\nu - \tilde{N}_\nu}(1/Z_\nu)\delta_{x_\nu^k}$ with $\min_k |x_\nu^k| \to \infty$, $\min_{k \neq \ell} |x_\nu^k - x_\nu^\ell| \to \infty$. It follows that $\mu_\nu - \tilde{\mu}_\nu \rightharpoonup^* 0$ and $I^{(N_\nu, Z_\nu)}(\mu_\nu) - I^{(\tilde{N}_\nu, Z_\nu)}(\tilde{\mu}_\nu) \to 0$.

Step 2 *Discretization of* $\mathbb{R}^3\backslash B_1$ *into mesh of size* h

From now on we fix a measure $\mu \in \mathcal{M}_+(\mathbb{R}^3\backslash B_1)$ which is compactly supported and has finite energy. Because the boundary of $\mathbb{R}^3\backslash B_1$ is curved, it is technically convenient to instead discretize $\mathbb{R}^3\backslash Q_1$, where Q_R denotes the cube centred at the origin of sidelength R, $\{x \in \mathbb{R}^3 \mid \max_\alpha |x \cdot e_\alpha| < R/2\}$, where e_1, e_2, e_3 are the standard basis vectors of $\mathbb{R}^3$. We then use a bi-Lipschitz bijection $f : \mathbb{R}^3\backslash B_1 \to \mathbb{R}^3\backslash Q_1$, and let L_0 denote the Lipschitz constant of f, i.e. $L_0^{-1}|x - y| \leq |f(x) - f(y)| \leq L_0|x - y|$ for all x and y.

The next task is to partition $\operatorname{supp}\mu$ into inverse images under f of finitely many unit cubes. Choose $R \in \mathbb{N}$, odd, so that $f^{-1}(Q_R\backslash Q_1)$ contains $\operatorname{supp}\mu$. Decompose $Q_R\backslash Q_1$ into $R^3 - 1 =: N_0$ cubes of sidelength 1. Now given any $n \in \mathbb{N}$ (to be chosen later, depending on N and Z) we obtain a mesh of size $h := 1/n$ by dividing each cube of sidelength 1 into n^3 smaller cubes of sidelength $1/n$. This way we obtain a disjoint family of cubes $\{Q^{(i)}\}_{i=1}^{N_0 h^{-3}}$ of sidelength h whose union is $Q_R\backslash Q_1$. Hence their images $\tilde{Q}^{(i)} := f^{-1}(Q^{(i)})$ form a disjoint family of regions whose union contains $\operatorname{supp}\mu$ and which satisfy the diameter estimate

$$\operatorname{diam}\tilde{Q}^{(i)} \leq L_0 \operatorname{diam} Q^{(i)} = \sqrt{3} \cdot L_0 \cdot h. \tag{4.25}$$

Step 3 *Choice of number of Dirac masses in each region and mass error analysis*

For given μ, N, Z, we need to approximate $\mu|_{\tilde{Q}^{(i)}}$ by a measure of form

$$\mu^{(N,Z)}\Big|_{\tilde{Q}^{(i)}} = \frac{1}{Z}\sum_{k=1}^{L_i}\delta_{\tilde{x}_i^{(k)}}, \quad L_i \in \mathbb{N}\cup\{0\}, \ \sum_i L_i = N, \tag{4.26}$$

because otherwise $I^{(N,Z)}(\mu^{(N,Z)})$ is infinite. In particular, the allowed mass has to be an integer multiple of $1/Z$, enforcing a mass error. Here we deal with the latter, postponing the choice of positions $\tilde{x}_i^{(k)}$ to the next step.

It will be convenient to introduce a trivial amplitude factor

$$\phi(N,Z) := \frac{N}{Z}\cdot\lambda^{-1} \tag{4.27}$$

and approximate the measure $\phi\cdot\mu$, because $\int d(\phi\mu) = N/Z = \int d\mu^{(N,Z)}$ (note $\phi(N,Z)\to 1$ in the limit (4.2)).

Choose $\ell_i \in \mathbb{N}\cup\{0\}$ such that ℓ_i/Z is a good approximation to the mass of $\phi\mu$ in $Q^{(i)}$, i.e.

$$\frac{\ell_i}{Z} \le \phi\mu(Q^{(i)}) \le \frac{\ell_i+1}{Z}. \tag{4.28}$$

This that implies $\sum_i \ell_i/Z \le N/Z \le \sum_{i\,|\,\mu(Q^{(i)})>0}(\ell_i+1)/Z$. Hence $(\sum_i \ell_i) + r = N$ for some integer r less or equal to the number of indices i with $\mu(Q^{(i)}) > 0$. It follows that if for r such indices we set $L_i := \ell_i + 1$, and let $L_i := \ell_i$ otherwise, we have $\sum_i L_i = N$, $L_i = 0$ when $\phi\mu(Q^{(i)}) = 0$, and, by (4.28),

$$\frac{L_i - 1}{Z} \le \phi\mu(\tilde{Q}^{(i)}) \le \frac{L_i+1}{Z}. \tag{4.29}$$

Hence if $\mu^{(N,Z)}|_{\tilde{Q}^{(i)}}$ is given by (4.26), regardless of the choice of positions $\tilde{x}_i^{(k)}$ we have

$$\Big|\int_{\tilde{Q}^{(i)}} A\, d(\phi\mu) - \int_{\tilde{Q}^{(i)}} A\, d\mu^{(N,Z)}\Big| \le \frac{|A|}{Z} \quad \text{for all } A\in\mathbb{R}. \tag{4.30}$$

Let c_i denote the centre of the cube $Q^{(i)}$, and set $\tilde{c}_i := f^{-1}(c_i)$. Then by (4.30), if $g \in C(\mathbb{R}^3\backslash B_1)$ and δ is its modulus of continuity on the lengthscale of the mesh,

$$\delta := \sup_{|x-y|\le \max_i \operatorname{diam} \tilde{Q}^{(i)}} \Big| g(x) - g(y) \Big|,$$

then

$$\begin{aligned}
&\Big| \int_{\mathbb{R}^3\setminus B_1} g d\phi\mu - \int_{\mathbb{R}^3\setminus B_1} g\, d\mu^{(N,Z)} \Big| = \\
&\Big| \sum_i \int_{\tilde{Q}^{(i)}} \Big((g(x) - g(\tilde{c}_i)\Big) d(\phi\mu)(x) \;+\; g(\tilde{c}_i)\Big(d(\phi\mu)(x) - d\mu^{(N,Z)}(x) \Big) \;+ \\
&\quad \int_{\tilde{Q}^{(i)}} \Big(g(\tilde{c}_i) - g(x) \Big) d\mu^{(N,Z)}(x) \Big) \Big| \\
&\le \delta \int d(\phi\mu) \;+\; \sum_i \frac{\sup |g|}{Z} \;+\; \delta \int d\mu^{(N,Z)} \\
&= \;2\delta \frac{N}{Z} + \sup |g| \frac{N_0}{h^3 Z} \qquad (4.31)
\end{aligned}$$

where the factor $N_0/h^3 = N_0 n^3$ in the last term is the number of cells $\tilde{Q}^{(i)}$.

If $N \to \infty$, $Z \to \infty$, $h = h(N, Z)$, it follows that the right hand side tends to zero for all $g \in C_0(\mathbb{R}^3\setminus B_1)$ *provided* the meshsize h satisfies

$$h \to 0 \quad (\text{"small mesh"}) \qquad (4.32)$$

(whence, due to (4.25), $\delta \to 0$),

$$\frac{Z^{-1/3}}{h} \to 0 \quad (\text{"particle spacing smaller than mesh"}) \qquad (4.33)$$

(whence the second term in (4.31) tends to zero).

To understand the meaning of (4.33), it is instructive to consider the case when μ is the uniform measure on some region of finite diameter, and when $\mu^{(N,Z)}$ is positioned on a periodic lattice in this region. Because $\mu^{(N,Z)}$ has N Dirac masses, the lattice spacing must be $\sim N^{-1/3} \sim Z^{-1/3}$ and hence $Z^{-1/3}/h \sim$ (particle spacing)/meshsize.

To summarize: provided h is chosen so as to satisfy (4.32) and (4.33), which is always possible (e.g. take $h = Z^{-1/6}$), $\mu^{(N,Z)} - \phi(N,Z)\mu \rightharpoonup^* 0$, and hence, thanks to $\phi(N,Z) \to 1$, $\mu^{(N,Z)} \rightharpoonup^* \mu$.

Step 4 *Choice of positions of Dirac masses*

The Dirac masses in each $\tilde{Q}^{(i)}$ will be positioned by placing a lattice of spacing $\sim L_i^{-1/3}$ in $Q^{(i)}$, then pulling it back via f onto $\tilde{Q}^{(i)}$. Let $\lceil (L_i)^{1/3} \rceil$ denote the smallest integer $\geq (L_i)^{1/3}$. If $L_i = 0$ then $\lceil (L_i)^{1/3} \rceil = 0$. If $L_i \geq 1$ then $(L_i)^{1/3} \leq \lceil (L_i)^{1/3} \rceil \leq 2(L_i)^{1/3}$. Now for each $Q^{(i)}$, we choose $\{x_i^{(1)}, ..., x_i^{(L_i)}\}$ as a subset of the cubic lattice

$$c_i + \frac{h}{2\lceil (L_i)^{1/3} \rceil}\mathbb{Z}^3 \tag{4.34}$$

intersected with a cube inside $Q^{(i)}$ of half the sidelength,

$$\{x \in \mathbb{R}^3 \mid \max_\alpha |(x - c_i) \cdot e_\alpha| \leq \frac{h}{4}\};$$

we then set $\bar{x}_i^{(k)} := f^{-1}(x_i^{(k)})$.

The reason for placing the $x_i^{(k)}$ safely away from the boundary of $Q^{(i)}$ will become apparent later (see the proof of Lemma 25).

Step 5 *Analysis of energy error*

With the above choice of the $\bar{x}_i^{(k)}$, and with $h = h_\nu$ chosen to satisfy (4.32) and (4.33), we claim that

$$\lim_{\nu \to \infty} I^{(N_\nu, Z_\nu)}(\mu^{(N_\nu, Z_\nu)}) = I(\mu). \tag{4.35}$$

By the weak* convergence of $\mu^{(N_\nu, Z_\nu)}$ to μ, we can immediately pass to the limit in the electron-nuclei interaction since $\frac{1}{|x|} \in C_0(\mathbb{R}^3 \backslash B_1)$:

$$-\int_{\mathbb{R}^3 \backslash B_1} \frac{1}{|x|} d\mu^{(N_\nu, Z_\nu)}(x) \quad \longrightarrow \quad -\int_{\mathbb{R}^3 \backslash B_1} \frac{1}{|x|} d\mu(x).$$

As for the electron-electron interaction, we decompose

$$
\begin{aligned}
&\frac{1}{2}\int\int_{(\mathbb{R}^3\backslash B_1)^2\backslash\mathrm{diag}} \frac{1}{|x-y|} d\mu^{(N_\nu,Z_\nu)}(x)d\mu^{(N_\nu,Z_\nu)}(y) \\
&-\frac{1}{2}\int\int_{(\mathbb{R}^3\backslash B_1)^2} \frac{1}{|x-y|} d\mu(x)d\mu(y) \\
= &\frac{1}{2}\int\int_{(\mathbb{R}^3\backslash B_1)^2} f_\alpha\Big(d\mu^{(N_\nu,Z_\nu)}\otimes d\mu^{(N_\nu,Z_\nu)} - d\mu\otimes d\mu\Big) \quad - \quad \frac{1}{2\alpha}\frac{N_\nu}{(Z_\nu)^2} \\
&+\frac{1}{2}\int\int_{(\mathbb{R}^3\backslash B_1)^2\backslash\mathrm{diag}} \Big(\frac{1}{|x-y|} - f_\alpha\Big) d\mu^{(N_\nu,Z_\nu)}\otimes d\mu^{(N_\nu,Z_\nu)} \\
&-\frac{1}{2}\int\int_{(\mathbb{R}^3\backslash B_1)^2} \Big(\frac{1}{|x-y|} - f_\alpha\Big) d\mu\otimes d\mu.
\end{aligned}
$$

Because the measures $\mu^{(N_\nu,Z_\nu)}$ are supported in $f^{-1}(Q_R)$, and $f_\alpha \in C(f^{-1}(Q_R)\times f^{-1}(Q_R))$, it follows from the weak* convergence of $\mu^{(N_\nu,Z_\nu)}$ that the first term tends to zero as $\nu \to \infty$. The second and fourth term are ≤ 0, and the integrand in the third term is bounded from above by $\frac{1}{|x-y|}\chi_{\{|x-y|<\alpha\}}$. It follows that, abbreviating $\Omega := (\mathbb{R}^3\backslash B_1)^2\backslash\mathrm{diag}$,

$$
\begin{aligned}
&\leq \limsup_{\nu\to\infty}\Big(I^{(N_\nu,Z_\nu)}(\mu^{(N_\nu,Z_\nu)}) - I(\mu)\Big) \\
&\qquad \leq \limsup_{\nu\to\infty}\frac{1}{2}\int\int_{\Omega\cap\{|x-y|<\alpha\}} \frac{1}{|x-y|} d\mu^{(N_\nu,Z_\nu)}\otimes d\mu^{(N_\nu,Z_\nu)} \qquad (4.36)
\end{aligned}
$$

for all $\alpha > 0$.

The idea now is to control the right hand side, uniformly with respect to N_ν and Z_ν, by a corresponding integral with the discrete measure replaced by the original measure μ.

It is useful to decompose the domain of integration into the cartesian products $\tilde{Q}^{(i)} \times \tilde{Q}^{(j)}$, and deal separately with inter-cell and intra-cell interactions. We claim that only pairs of cells with centre distance $|c_i - c_j| \leq L_0\alpha + \sqrt{3}h_\nu$ contribute. Indeed, if $|x-y| < \alpha$, $x \in \tilde{Q}^{(i)}$, $y \in \tilde{Q}^{(j)}$, then $|f(x) - f(y)| < L_0\alpha$, $f(x) \in Q^{(i)}$, $f(y) \in Q^{(j)}$, and the above claim follows because $|c_i - f(x)|$ and $|c_j - f(y)|$ are $\leq \sqrt{3}h_\nu/2$.

Hence when ν is sufficiently large, because $h_\nu \to 0$ we infer $|c_i - c_j| \leq 2L_0\alpha$, and consequently

$$\int\int_{\Omega\cap\{|x-y|<\alpha\}} \frac{1}{|x-y|} d\mu^{(N_\nu,Z_\nu)} \otimes d\mu^{(N_\nu,Z_\nu)}$$
$$\leq \sum_{\{(i,j)\,|\,|c_i-c_j|\leq 2L_0\alpha\}} \int\int_{q^{i,j}} \frac{1}{|x-y|} d\mu^{(N_\nu,Z_\nu)} \otimes d\mu^{(N_\nu,Z_\nu)}. \quad (4.37)$$

where $q^{i,j} := \bar{Q}^{(i)} \times \bar{Q}^{(j)} \backslash \text{diag}$

Lemma 24 *(Intra-cell interactions)*

$$\int\int_{q^{i,i}} \frac{1}{|x-y|} d\mu^{(N,Z)}(x) d\mu^{(N,Z)}(y) \leq C_1 \Big(\frac{\frac{N}{Z}}{\lambda}\Big)^2 \int\int_{\bar{Q}^{(i)}\times\bar{Q}^{(i)}} \frac{1}{|x-y|} d\mu(x) d\mu(y)$$

where $C_1 = (128\,\pi)^2 L_0^2 C_0/\sqrt{3}$, L_0 *is the Lipschitz constant from Step 1, and* C_0 *is the universal constant from* (4.38) *below.*

Proof: We estimate the left hand side from above by converting it into a standard lattice sum, and estimate the right hand side from below via the seemingly crude uniform estimate on the integrand $1/|x-y| \geq 1/\text{diam}\,\bar{Q}^{(i)}$.

The left hand side equals $\frac{1}{Z^2}\sum_{k\neq \ell} \frac{1}{|\bar{x}_i^{(k)} - \bar{x}_i^{(\ell)}|} \leq \frac{L_0}{Z^2}\sum_{k\neq\ell} \frac{1}{|x_i^{(k)} - x_i^{(\ell)}|}$.

If $L_i = 1$, i.e. the cube $Q^{(i)}$ contains only one point, this term is zero, so we may assume that$L_i \geq 2$. This will be important later.

Since $\{x_i^{(1)}, ..., x_i^{(L_i)}\}$ is a subset of the lattice (4.34), and $|x_i^{(k)} - c_i| \leq \sqrt{3}h/4 \leq h/2$, the left hand side in the lemma is bounded from above by

$$\frac{L_0}{Z^2} \sum_{x\neq y\in \frac{h}{2\lceil (L_i)^{1/3}\rceil}\mathbb{Z}^3,\ |x|,|y|\leq h/2} \frac{1}{|x-y|}$$
$$\leq \frac{L_0}{Z^2} \sum_{x\neq y\in \frac{h}{4(L_i)^{1/3}}\mathbb{Z}^3,\ |x|,|y|\leq h/2} \frac{1}{|x-y|}$$
$$= \frac{4L_0(L_i)^{1/3}}{Z^2 h} \sum_{x\neq y\in\mathbb{Z}^3,\ |x|,|y|\leq 2(L_i)^{1/3}} \frac{1}{|x-y|}.$$

We now use the following elementary estimate:

$$\sum_{x \neq y \in \mathbb{Z}^3, |x|,|y| \leq A} \frac{1}{|x-y|} \leq C_0 \int\int_{|x|,|y|\leq A} \frac{1}{|x-y|} dx\, dy \tag{4.38}$$

for some $C_0 > 0$ and all $A \geq 1$. It follows, letting $z := x - y$, that the left hand side in the lemma is bounded from above by

$$\frac{4C_0L_0(L_i)^{1/3}}{Z^2h}\Big(\int_{|x|\leq 2(L_i)^{1/3}} dx\Big)\Big(\int_{|z|\leq 4(L_i)^{1/3}} \frac{1}{|z|}dz\Big) = \frac{(64\,\pi)^2C_0L_0}{3}\frac{L_i^2}{Z^2h}. \tag{4.39}$$

On the other hand, we have

$$\int\int_{\bar{Q}^{(i)}\times\bar{Q}^{(i)}} \frac{1}{|x-y|} d\mu \otimes d\mu \geq \frac{1}{\operatorname{diam} \bar{Q}^{(i)}}\Big(\int_{\bar{Q}^{(i)}} d\mu\Big)^2.$$

Now we use the fact that (4.29) (with ϕ as in (4.27)), together with the fact that $(L_i - 1)/Z \geq L_i/(2Z)$ when $L_i \geq 2$, implies the mass estimate

$$\int_{\bar{Q}^{(i)}} d\mu = \frac{1}{\phi}\int_{\bar{Q}^{(i)}} d(\phi\mu) \geq \frac{1}{\phi}\frac{L_i}{2Z} \text{ when} L_i \geq 2. \tag{4.40}$$

From (4.40) and (4.25) we infer

$$\int\int_{\bar{Q}^{(i)}\times\bar{Q}^{(i)}} \frac{1}{|x-y|} d\mu(x)d\mu(y) \geq \frac{1}{4\sqrt{3}L_0\phi^2}\frac{L_i^2}{Z^2h}.$$

Combining this with (4.39) yields the assertion of the lemma.

□

Lemma 25 *(Inter-cell interactions) Let $i \neq j$. If L_i(=number of Dirac masses of $\mu^{(N,Z)}|_{\bar{Q}^{(i)}}$) and L_j(=number of Dirac masses of $\mu^{(N,Z)}|_{\bar{Q}^{(j)}}$) are both ≥ 2, then*

$$\int\int_{q^{i,j}} \frac{1}{|x-y|} d\mu^{(N,Z)}(x)d\mu^{(N,Z)}(y) \leq C_2\Big(\frac{\frac{N}{Z}}{\lambda}\Big)^2 \int\int_{\bar{Q}^{(i)}\times\bar{Q}^{(j)}} \frac{1}{|x-y|} d\mu(x)d\mu(y)$$

where $C_2 = 4L_0^2\frac{1+\sqrt{3}}{1-\frac{\sqrt{3}}{2}}$ and L_0 is the Lipschitz constant from Step 1.

Proof: At this point a previously unused aspect of our construction of $\mu^{(N,Z)}$ becomes important, namely that the distance of the support of $\mu^{(N,Z)}|_{\tilde{Q}^{(i)}}$ is of the same order as the diameter of $\tilde{Q}^{(i)}$. More precisely: For any k, ℓ,

$$|\tilde{x}_i^{(k)} - \tilde{x}_j^{(\ell)}| \geq \frac{1}{L_0}|x_i^{(k)} - x_j^{(\ell)}| \geq \frac{1}{L_0}\Big(|c_i - c_j| - 2\frac{\sqrt{3}h}{4}\Big) \geq \frac{1}{L_0}\Big(1 - \frac{\sqrt{3}}{2}\Big)|c_i - c_j|, \tag{4.41}$$

the last inequality being due to $|c_i - c_j| \geq h$.

On the other hand,

$$\max_{x \in \tilde{Q}^{(i)},\, y \in \tilde{Q}^{(j)}} |x - y| \leq L_0\Big(|c_i - c_j| + 2\frac{\sqrt{3}h}{2}\Big) \leq L_0(1 + \sqrt{3})|c_i - c_j|, \tag{4.42}$$

the last inequality again being due to $|c_i - c_j| \geq h$.

Combining these estimates yields

$$\begin{aligned} &\max_{x \in \operatorname{supp} \mu|_{\tilde{Q}^{(i)}},\, y \in \operatorname{supp} \mu|_{\tilde{Q}^{(j)}}} |x - y| \\ &\leq L_0^2 \frac{1 + \sqrt{3}}{1 - \frac{\sqrt{3}}{2}} \min_{x \in \operatorname{supp} \mu^{(N,Z)}|_{\tilde{Q}^{(i)}},\, y \in \operatorname{supp} \mu^{(N,Z)}|_{\tilde{Q}^{(j)}}} |x - y|. \end{aligned} \tag{4.43}$$

But the mass of $\mu^{(N,Z)} \otimes \mu^{(N,Z)}$ on $\tilde{Q}^{(i)} \times \tilde{Q}^{(j)}$ is controlled by that of $\mu \otimes \mu$, more precisely: due to $L_i \geq 2$, $L_j \geq 2$ we infer from (4.40) that

$$\int\!\!\int_{\tilde{Q}^{(i)} \times \tilde{Q}^{(j)}} d\mu^{(N,Z)} \otimes d\mu^{(N,Z)} \leq 4\phi^2 \int\!\!\int_{\tilde{Q}^{(i)} \times \tilde{Q}^{(j)}} d\mu \otimes d\mu. \tag{4.44}$$

Combining (4.43) and (4.44) establishes the lemma.

□

It remains to analyze the case when $\min\{L_i, L_j\} \leq 1$. In this case we cannot bound the mass of $\mu^{(N,Z)}$ in $\tilde{Q}^{(i)}$ from above by a universal multiple of the mass of μ in $\tilde{Q}^{(i)}$, because the latter can be arbitrarily small. Instead we estimate using (4.41)

$$\int\!\!\int_{\tilde{Q}^{(i)} \times \tilde{Q}^{(j)}} \frac{1}{|x - y|} d\mu^{(N,Z)} \otimes d\mu^{(N,Z)} \leq \frac{L_0}{1 - \frac{\sqrt{3}}{2}} \frac{1}{|c_i - c_j|} \frac{1}{Z}\Big(\frac{L_i}{Z} + \frac{L_j}{Z}\Big)$$

and hence by summation over the set

$$S := \{(i,j)\, i \neq j |\ \min\{L_i, L_j\} \leq 1, |c_i - c_j| \leq 2L_0\alpha\}$$

$$\begin{aligned}
&\sum_{(i,j)\in S,\, i\neq j} \int\int_{\tilde{Q}^{(i)}\times\tilde{Q}^{(j)}} \frac{1}{|x-y|} d\mu^{(N,Z)} \otimes d\mu^{(N,Z)} \\
&\leq \frac{2L_0}{1-\frac{\sqrt{3}}{2}} \frac{\sum_i L_i}{Z^2} \sum_{0\neq c\in h\mathbb{Z}^3,\, |c|\leq 4L_0\alpha} \frac{1}{|c|} \\
&= \frac{2L_0}{1-\frac{\sqrt{3}}{2}} \frac{N}{Z^2 h} \sum_{0\neq c\in \mathbb{Z}^3,\, |c|\leq 4L_0\alpha/h} \frac{1}{|c|},
\end{aligned} \tag{4.45}$$

the factor 2 being due to the two terms L_i/Z and L_j/Z in the previous estimate.

We now use the elementary estimate

$$\sum_{0\neq x\in\mathbb{Z}^3,\, |x|\leq A} \frac{1}{|x|} \leq \tilde{C}_0 \int_{|x|\leq A} \frac{1}{|x|} dx \text{ for some } \tilde{C}_0 > 0 \text{ and all } A \geq 1. \tag{4.46}$$

Consequently the right hand side in (4.45) is bounded from above by

$$\frac{2\tilde{C}_0 L_0}{1-\frac{\sqrt{3}}{2}} \frac{N}{Z^2 h} \int_{|x|\leq \frac{4L_0\alpha}{h}} \frac{1}{|x|} dx = \frac{64\tilde{C}_0 L_0^3 \alpha^2}{1-\frac{\sqrt{3}}{2}} \frac{N}{Z^2 h^3}.$$

Thus we have established:

Lemma 26 *(Inter-cell interactions at low mass)*

$$\sum_{i\neq j\,|\,|c_i - c_j|\leq 2L_0\alpha, \min\{L_i,L_j\}\leq 1} \int\int_{\tilde{Q}^{(i)}\times\tilde{Q}^{(j)}} \frac{1}{|x-y|} d\mu^{(N,Z)} \otimes d\mu^{(N,Z)} \leq C_2 \cdot \frac{N}{Z} \cdot \frac{1}{Zh^3},$$

where $C_2 = 64(1-\frac{\sqrt{3}}{2})^{-1}\tilde{C}_0 L_0^3\alpha^2$, L_0 is the Lipschitz constant from Step 1, and $\tilde{C}_0$ is the universal constant from (4.46).

But note that in the limit $N = N_\nu \to \infty$, $Z = Z_\nu \to \infty$, $h = h_\nu$, due to condition (4.33) on the choice of h ("many particles per cell"), $\frac{1}{Zh^3} \to 0$.

Hence by combining (4.38), (4.39), and Lemmas 24, 25, 26, and using the fact that by (4.25) $\cup_{i,j\,|\,|c_i-c_j|\le 2L_0\alpha}\tilde{Q}^{(i)}\times\tilde{Q}^{(j)} \subseteq \{|x-y|\le 2L_0\alpha+2L_0\sqrt{3}h\} \subseteq \{|x-y|\le 4L_0\alpha\}$ for all sufficiently small h, we obtain the following estimate:

Proposition 27

$$\limsup_{\nu\to\infty}\Big(I^{(N_\nu,Z_\nu)}(\mu^{(N_\nu,Z_\nu)})-I(\mu)\Big)$$
$$\le \max\{(128\,\pi)^2 L_0^2 C_0/\sqrt{3},\ 4\frac{1+\sqrt{3}}{1-\frac{\sqrt{3}}{2}}L_0^2\}\int\int_{|x-y|\le 4L_0\alpha}\frac{1}{|x-y|}d\mu(x)d\mu(y).$$

Note in particular that the mesoscale h no longer appears in the above result.

Finally, because the function $g(x,y)=\frac{1}{|x-y|}$ satisfies $g\in L^1((\mathbb{R}^3\backslash B_1)^2;d\mu\otimes d\mu)$, it follows, e.g. from the Fubini-type formula

$$\int g\,d\tilde{\mu}=\int_0^\infty \tilde{\mu}(\{(x,y)\,|\,g(x,y)\ge t\})dt$$

valid for nonnegative integrands $g\in L^1(d\tilde{\mu})$ and general Radon measures $\tilde{\mu}$, that $\int_{\{(x,y)\,|\,g(x,y)>\frac{1}{\alpha}\}}g\,d\mu\otimes d\mu\to 0$ as $\alpha\to 0$. Hence the integral on the right hand side of the Proposition tends to zero as $\alpha\to 0$.

This establishes (4.35), and completes the proof that the constructed multiscale lattice measures $\mu^{(N_\nu,Z_\nu)}$ constitute a recovery sequence. □

The proof of Theorem 16 is now complete.

Chapter 5

Density functional theory: Kohn-Sham

5.1 Density Functional theory

We have investigated in chapter 2 the existence of solutions of the "exact" non relativistic Schrödinger equation (SE). Part of the difficulty encountered when dealing with (SE) came from the set of possible trial functions: There are many of them (every anti-symmetric function in H^1 with L^2-norm equal to 1) and their domain of definition grows with N ($\mathbb{R}^{3N}$ without spin). In 1964 Hohenberg and Kohn [HK64] showed that the properties of the ground state of molecules are completely determined by the sole knowledge of a density function depending only on three variables. This information gave rise to the density functional theory or in short DFT. However there was a problem: the proof did not give the energy functional to minimize in order to obtain the density associated to the system. Not long after (1965) Kohn and Sham [KS65] found a sufficiently accurate approximate functional together with an explicit set over which to minimize. Their original approximation to the unknown abstract exchange-correlation term E_{xc} is described in the next section. In fact this model had already been used by Slater (1951) but was at the time only perceived as an approximation of Hatree-Fock: one just simplifies the electron-electron interaction. Associated to this density functional is a system of N nonlinear PDEs in $\mathbb{R}^3$ (one linear PDE in $\mathbb{R}^{3N}$ versus a system of N nonlinear PDE's in $\mathbb{R}^3$). This is the trade-off from "exact" non-relativistic Schrödinger to the density functional. The only results on the subject of which we are aware of are in the unpublished thesis [LeB93]. The problem of the existence of a minimizer for Kohn-Sham is of mathematical interest. Indeed similar models have been shown to have a minimizer [Lio87] but the Kohn-Sham model presents a number of difficulties: It is not weakly lower semi-continuous, not convex, highly nonlinear, defined on vector valued functions (whose components are called orbitals) with its orbitals orthogonal with respect to each other, and in addition there is a non trivial problem at infinity. Further, from a practical point of view the compactness of all minimizing sequence is of relevance in the field of quantum chemistry and solid state physics where the Kohn-Sham model is used extensively in numerical simulations. Roughly speaking in a numerical context compactness guarantees convergence of solutions obtained in finite basis sets as the basis set approaches completeness.

5.2 Introduction to the Kohn-Sham problem: Notations, definitions and results

We first introduce some basics of the Kohn-Sham model.

$$\xi_N^{KS}((\psi_1, ..., \psi_N)) = T[\psi] + V_{ne}[\psi] + J[\psi, \psi] + E_{xc}[\psi]$$

where, using $V = \mathbb{R}^3 \times \mathbb{Z}_2$,

$$T[\psi] = \sum_{i=1}^{N} \frac{1}{2} \int_V |\nabla \psi_i|^2 dx$$

$$V_{ne}[\psi] = \sum_{i=1}^{N} \int_V v_{ne}(x) |\psi_i|^2 dx$$

$$J[\psi, \phi] = \frac{1}{2} \int_V \int_V \frac{\sum_{i=1}^N |\psi_i(x)|^2 \sum_{j=1}^N |\psi_j(y)|^2}{|x-y|} dxdy$$

$$E_{xc}[\psi] = -C_{xc} \int_V (\sum_{i=1}^{N} |\psi_i(x)|^2)^p dx$$

where the functions $\psi_i : \mathbb{R}^3 \times \mathbb{Z}_2 \to \mathbb{C}$ are called the Kohn-Sham orbitals and where $v_{ne}(x) = \sum_{i=1}^{M} \frac{-Z_i}{|x-l_i|}$ with l_i being the position of the ith nucleus and where C_{xc} is a positive constant. Further we define the minimizing sets associated to ξ_N^{KS}:

$$A_\alpha = \left\{ (\psi_1, .., \psi_N) \mid \psi_i \in H^1(V; \mathbb{C}) \quad \forall i \text{ and } \int_V |\psi_i|^2 dx = \alpha_i \right\}$$

and

$$A_\alpha^{\sim} = \left\{ (\psi_1, .., \psi_N) \mid \psi_i \in H^1(V; \mathbb{C}) \quad \forall i \text{ and } \int_V \psi_i (\psi_j)^* dx = \alpha_i \delta_{i,j} \right\}$$

where $\alpha = (\alpha_1, .., \alpha_N)$ for some $0 \le \alpha_1, ., \alpha_N \le 1$. We also will need to define a functional called the Kohn-Sham functional at infinity. It is in brief the translation invariant term from the Kohn-Sham functional. Indeed due to the possible lack of compactness of minimizing sequences some fragments might be escaping to infinity and these fragments need to minimize a slightly different problem, namely

$$\xi_N^{KS\infty}((\psi_1, ..., \psi_N)) = \sum_{i=1}^{N} \frac{1}{2} \int_V |\nabla \psi_i|^2$$

$$+\frac{1}{2} \int_V \int_V \frac{\sum_{i=1}^N |\psi_i(x)|^2 \sum_{j=1}^N |\psi_j(y)|^2}{|x-y|} dxdy - C_{xc} \int_V (\sum_{i=1}^N |\psi_i(x)|^2)^p dx.$$

We define $E_\alpha^{KS} = \inf_{\psi A_\alpha} \xi_N^{KS}(\psi)$ with convention that if we use the model with only one orbital

$$E_{\alpha_i}^{KS} = \inf \left\{ \xi_1^{KS}(\psi) \mid \psi \in H^1(V, \mathbb{C}) \text{ and } \int |\psi|^2 dx = \alpha_i \right\}.$$

We define similarly $E_\alpha^{KS\infty} = \inf_{\psi A_\alpha} \xi_1^{KS\infty}(\psi)$ with convention that

$$E_{\alpha_i}^{KS\infty} = \inf \left\{ \xi_1^{KS\infty}(\psi) \mid \psi \in H^1(V, \mathbb{C}) \text{ and } \int |\psi|^2 dx = \alpha_i \right\}.$$

We remark that the functional is only well defined for certain values of p. We recall the Sobolev inequality for any function $\psi \in H^1(V)$: $\|\psi\|_{L^6} \leq C_s \|\nabla\psi\|_{L^2}$. Further using the Hölder interpolation inequalities we obtain that $\psi \in H^1(V)$ implies $\psi \in L^q$ for $q \in [2, 6]$. Also the Kohn-Sham problem defined with the Coulomb potential $\frac{1}{|.|}$ (in the term V_{ne} and J) can be generalized to potentials which belong to the Kato space denoted by $L^{\frac{3}{2}}(\mathbb{R}^3) + (L^\infty(\mathbb{R}^3))_\epsilon$ and defined by

$$\left\{ v : \mathbb{R}^3 \to \mathbb{R} \mid \forall \epsilon > 0 \quad v = v_1 + v_2 \text{ for some } v_1 \in L^{\frac{3}{2}}(\mathbb{R}^3), \|v_2\|_{L^\infty(\mathbb{R}^3)} \leq \epsilon \right\}.$$

That the Kato space contains the Coulomb potential can be seen using the decomposition

$$v_1(r) = \begin{cases} -\frac{Z}{|r|} \text{ for } |r| \leq \beta \\ 0 \text{ otherwise.} \end{cases}$$

$$v_2(r) = \begin{cases} -\frac{Z}{|r|} \text{ for } |r| > \beta \\ 0 \text{ otherwise.} \end{cases}$$

where the parameter $\beta > 0$ can be adjusted so as to make the $L^{\frac{3}{2}}-$norm arbitrarily small (or the L^∞ but not both at the same time). We will make good use of this property. More precisely we have

$$\|v_1\|_{\frac{3}{2}} = \left(\frac{8\pi}{3}\right)^{\frac{2}{3}} Z\beta \text{ and } \|v_2\|_\infty = \max_{|r|\geq\beta} \frac{Z}{|r|} = \frac{Z}{\beta}.$$

Even though some of the results (for example Lemma 30 and Lemma 34) can easily be extended to hold for this class of potential we will assume in what follows that v_{ne} is the Coulomb potential for molecules, since the final stage of our argument rely on this form of the potential. Finally we note that the E_{xc} can be generalized: We have taken $e_{xc} := \rho^p$ but we could have take any e_{xc} such that $e_{xc}(\rho) \leq C(\rho + \rho^3)$. However we will only treat the case where $e_{cx}(\rho) = \rho^p$ with p in the range $[1, \frac{5}{3})$ (unless otherwise stated) since it already includes $\rho^{\frac{4}{3}}$ (i.e. the term used in practice).

We prove the following:

Theorem 28 *(Bosonic Kohn-Sham)*

If $\sum_{i=1}^N \alpha_i \leq Z$ *then there exists a minimizer to the problem* $\inf_{\psi\in A_\alpha} \xi_N^{KS}(\psi)$ *and furthermore every minimizing sequence stays in a compact set of* $H^1(V)^N$.

Corollary 29 *(Existence of a minimizer for hydrogen Kohn-Sham)*

If $\sum_{i=1}^N \alpha_i \leq Z$ *then* $E_{\alpha_1}^{KS} = \inf_{\psi\in A_{\alpha_1}} \xi_1^{KS}(\psi)$ *is attained on* A_{α_1} *and furthermore every minimizing sequence stays in a compact set of* $H^1(V)$.

Remark: The last statement has some importance in practice since one wants to know that from any minimizing sequence one chooses one can extract a convergent subsequence which converges to the minimizer.

5.3 Introduction to the variational methods needed

In this chapter we will use the so called concentration compactness principle ([Lio84]) which is very effective to prove the existence of minimizers for certain type of functionals defined on spaces of functions in unbounded domains (namely a subset of $H^1(V)$ for our purpose). This method ,which will be described below, is well suited to deal with cases where the only problem is a possible lack of compactness of the minimizing sequences due to some mass escaping to infinity. In other words the method is suitable if the usual requirement (for these sort of problems in unbounded domains) like weakly lower semi-continuity (or continuity) is fulfilled because it usually provides explicitly a potential candidate as minimizer. In this setting one does not know whether the candidate really belongs to the set on which one minimizes. In the case of Hartree-Fock [LS77] the authors managed to by-pass the difficulty. However the proof is not easily generalized to other problems. P. L. Lions in [Lio84a], [Lio84b], [Lio87] following some work of [LS77] generalized the machinery available to tackle the possible loss of compactness. We briefly review the method and refer to [Lio84a], [Lio84b], [Lio87], [LeLio05] for a more detailed introduction. We suppose $E : A_1 \subset H^1 \to \mathbb{R}$ to be a functional on a subset A_1 of H^1. More precisely we assume that if $\psi \in A_1$ then $\|\psi\|_{L^2} = 1$. We want to know whether the infimum over the set A_1 is attained, i.e. whether there exists some $\varphi \in A_1$ such that $\inf_{\psi\in A_1} E(\psi) = E(\varphi)$. Now by the usual techniques, the direct methods of the calculus of variation (see for example [Da04], [FL07], [LL97], [Ev98]), we suppose that we have obtained a candidate-minimizer φ but that we only have the information $\int |\varphi|^2 dx \leq 1$ (and we crucially need to have equality). The idea on how to obtain the missing information in order to conclude is simple in essence but far reaching in practice. We know that if there has been some mass which has disappeared it must have "leaked" to infinity (indeed we have our minimizing sequence which satisfies $\|\psi_n\| = 1$ for all n). So one introduces two families of problems: The first family is identical to our original problem except that we are now looking at the minimizer over the set with mass α fixed satisfying $0 \leq \alpha < 1$ and the second family almost equal to the first family but with the terms depending on x having been removed (by dependence on x we mean that the problem may not be translation invariant: $E(\phi(x)) \neq E(\phi(x-a))$ for an arbitrary ϕ). The second family is introduced in order to deal with the mass at infinity. Even if part of the minimizer is going to infinity it is easy to show that it minimizes one functional member of the second family of problems. Obviously if the first family has no dependence on x then the second family is identical to the first: The only difference may be on the constraint. Denoting in an obvious way the infimum of the different members of the two families by I_α and I_β^∞ respectively, if some mass leaks to infinity then $I_1 = I_\alpha + I_{1-\alpha}^\infty$. So the idea is clear: show that $I_1 < I_\alpha + I_{1-\alpha}^\infty$ for any $\alpha \in [0, 1)$ and the loss of mass will be prevented. This sub-additivity condition has been used extensively to prove the existence of minimizer for numerous functionals with success see [Lio87] and more recently [Fr03]. In this chapter the key fact to show $I_1 < I_\alpha + I_{1-\alpha}^\infty$ is the construction of a trial function based on the weak limits of each fragment. The knowledge of the decay rate at infinity of the bound part is of great importance as it allows one to estimate precisely the interaction between the different parts of the trial function. This decay can be obtained using the Euler-Lagrange equations associated to the variational principle ([Lie81] for example) as long as the Lagrange multiplier is known to be of the right sign (see for example [Th94] page 229).

5.4 Outline of our proof of existence

First we will establish some useful properties of the Kohn-Sham functional such as the fact that minimizing sequences are bounded in H^1 or that continuity on H^1. This means that if one can show the compactness of any minimizing sequence in the topology in which the functional has been identified to be continuous (here H^1) the problem will be solved. Indeed the minimum will be attained (by compactness and then continuity) and the constraint $\|\varphi_n\| = 1$ for all n leads to $\|\varphi\| = 1$ i.e. the minimizer belongs to the minimizing set. Thus the key ingredient is the compactness of the minimizing sequences which can in turn be shown equivalent to the nullity of the scattering charge [Fr97], [Fr03] (this means that in our problem one has lack of compactness if and only if some mass of the minimizing sequence is escaping to infinity). Now comes one of the cornerstones of the proof of existence: It can be shown that at least some part of the mass escaping to infinity must remain clustered (in brief no complete vanishing or spreading at infinity). This is very important to know since we then will only have to practise a careful surgery (some smooth cut-off functions are used as in chapter 3) and perform a gluing in order to show that there is a better arrangement of the sequence which lowers the energy and therefore contradicts the escape of a lump to infinity if $N \leq Z$. The decay rate of the bound part of the minimizing sequence (i.e. the part which does not escape to infinity) will be crucially needed.

5.5 General properties of ξ_N^{KS}

Lemma 30 *(continuity of ξ_N^{KS})*

Let $p \in [1,3]$. Then for any bounded set A in $H^1(V)^N$

$$|\xi_N^{KS}(\varphi)-\xi_N^{KS}(\psi)| \leq C\sum_{i=1}^{N}(\|\varphi_i-\psi_i\|_{L^2(V)}+\|\nabla\varphi_i-\nabla\psi_i\|_{L^2(V)}+\|\psi_i-\varphi_i\|_{L^2(V)}^{\frac{1}{p}})$$

where

$\varphi = (\varphi_1, .., \varphi_N) \in A, \psi = (\psi_1, .., \psi_N) \in A$ *and C only depending on A and p.*

Proof:

We start with the terms coming from the kinetic energy: In particular we look at one coordinate at a time, i.e.

$$\sum_{s_i \in Z^2}\left|\int(|\nabla\varphi_i(.,s_i)|^2 - |\nabla\psi(.,s_i)|^2)dx\right| \text{ for } \varphi, \psi \in A.$$

Since the spin brings no extra difficulty for this term we omit it.

$$\left|\int(|\nabla\varphi_i(.,s_i)|^2 - |\nabla\psi(.,s_i)|^2)dx\right| \leq \left|Re\left(\int(\nabla\varphi_i + \nabla\psi_i)((\nabla\varphi_i)^* - (\nabla\psi_i)^*)dx\right)\right|$$

$$\leq_{C.S} \|\nabla\varphi_i + \nabla\psi_i\|_{L^2}\|\nabla\psi_i - \nabla\varphi_i\|_{L^2}$$

$$\leq K\|\nabla\psi_i - \nabla\varphi_i\|_{L^2} \text{ where } K \text{ is a constant depending on } A.$$

We now deal with the nuclei-electrons interaction terms of the type (again omitting the spin)

$$\left|\int\frac{|\varphi_i(x)|^2 - |\psi_i(x)|^2}{|x-a|}dx\right| = \left|Re(\langle\varphi_i + \psi_i, \frac{1}{|x-a|}(\varphi_i - \psi_i)\rangle_{L^2})\right|$$

$$= |Re(\langle(\varphi_i + \psi_i), v_1(\varphi_i - \psi_i)\rangle_{L^2}) + (\langle\varphi_i + \psi_i, v_2(\varphi_i - \psi_i)\rangle_{L^2})|$$

$$\leq C_s^2 \|v_1\|_{L^{\frac{3}{2}}} \|\nabla\varphi_i + \nabla\psi_i\|_{L^2} \|\nabla\varphi_i - \nabla\psi_i\|_{L^2} + \|v_2\|_{L^\infty} \|\varphi_i + \psi_i\|_{L^2} \|\varphi_i - \psi_i\|_{L^2}$$

$$\text{where } v_1 + v_2 = \frac{1}{|x-a|}, \quad v_1 \in L^{\frac{3}{2}}, \quad v_2 \in L_\infty.$$

The second term in the last inequality above comes from Cauchy-Schwarz while the first term comes from the Sobolev inequality

$$\|\varphi_i\|_{L^6} \leq C_s \|\nabla\varphi_i\|_{L^2} \quad \forall \varphi_i \in H^1(\mathbb{R}^3)$$

and Hölder's inequality namely

$$\left| \int v_1(x)(\varphi_i(x) + \psi_i(x))(\varphi_i(x) - \psi_i(x))^* dx \right| \leq \|v_1\|_{L^{\frac{3}{2}}} \|\varphi_i + \psi_i\|_{L^6} \|\varphi_i - \psi_i\|_{L^6}.$$

We now establish a similar result for the electron-electron interactions for which we keep the spin since it is not as obvious as above. We want to evaluate

$$\left| \int\int \frac{\rho_\psi(x)\rho_\psi(y)}{|x-y|} dxdy - \int\int \frac{\rho_\varphi(x)\rho_\varphi(y)}{|x-y|} dxdy \right| =$$

$$\left| \int\int \frac{\sum_{I,J,l,k} |\psi_I(x,s_l)|^2 |\psi_J(y,s_k)|^2}{|x-y|} dxdy - \int\int \frac{\sum_{I,J,l,k} |\varphi_I(x,s_l)|^2 |\varphi_J(y,s_k)|^2}{|x-y|} dxdy \right|.$$

We look at terms involving

$$|\psi_i(x,s_l)|^2 |\psi_j(y,s_k)|^2 - |\varphi_i(x,s_l)|^2 |\varphi_j(y,s_k)|^2$$

for $k, l \in 1, 2, \quad i, j \in \{1, .., N\}$. When $k = l$ and $i \neq j$ (case where $i = j$ is easily derived from below)

$$(|\psi_i(x,s_k)|^2 + |\varphi_i(x,s_k)|^2)(|\psi_j(y,s_k)|^2 - |\varphi_j(y,s_k)|^2) =$$

$$-|\psi_i(x,s_k)|^2|\varphi_j(y,s_k)|^2 \overbrace{+|\varphi_i(x,s_k)|^2|\psi_j(y,s_k)|^2}^{\star\star}$$

$$+|\psi_i(x,s_k)|^2|\psi_j(y,s_k)|^2-|\varphi_i(x,s_k)|^2|\varphi_j(y,s_k)|^2.$$

Now note that we also have the term (coming from the sum over I and J)

$$|\psi_j(x,s_l)|^2|\psi_i(y,s_k)|^2 - |\varphi_j(x,s_l)|^2|\varphi_i(y,s_k)|^2$$

which we can be factorized as above (when $k=l$) giving

$$(|\psi_j(x,s_k)|^2+|\varphi_j(x,s_k)|^2)(|\psi_i(y,s_k)|^2-|\varphi_i(y,s_k)|^2) =$$

$$\overbrace{-|\psi_j(x,s_k)|^2|\varphi_i(y,s_k)|^2}^{\star}+|\varphi_j(x,s_k)|^2|\psi_i(y,s_k)|^2$$

$$+|\psi_j(x,s_k)|^2|\psi_i(y,s_k)|^2-|\varphi_j(x,s_k)|^2|\varphi_i(y,s_k)|^2.$$

Note now that

$$\int\int \frac{(\star)+(\star\star)}{|x-y|}dxdy = 0$$

after a trivial change of variable in one term. In the same way the second extra term cancels leaving us only 2 terms almost identical in nature to deal with. We only treat the first one

$$\int(|\psi_i(x,s_k)|^2+|\varphi_i(x,s_k)|^2)\int\frac{(|\psi_j(y,s_k)|^2-|\varphi_j(y,s_k)|^2)}{|x-y|}dydx$$

$$\leq \left(\|\varphi_i(.,s_k)\|^2+\|\psi_i(.,s_k)\|^2\right)\times$$

$$\Big(C_s^2\|v_1\|_{L^{\frac{3}{2}}}\|\nabla\varphi_j(.,s_k)+\nabla\psi_j(.,s_k)\|_{L^2}\|\nabla\varphi_j(.,s_k)-\nabla\psi_j(.,s_k)\|_{L^2}$$

$$+\|v_2\|_{L^\infty}\|\varphi_j(.,s_k)+\psi_j(.,s_k)\|_{L^2}\|\varphi_j(.,s_k)-\psi_j(.,s_k)\|_{L^2})$$

$$\leq C(\|\varphi_j(.s_k)-\psi_j(.,s_k)\|+\|\nabla\varphi_j(.,s_k)-\nabla\psi_j(.,s_k)\|).$$

The aim now is to show that in fact when $k\neq l$ we can factorize in order to make terms like the above appear and that the extra terms (due to the forced factorization) cancel. Suppose now that $k \neq l$ we have the following terms

$$\begin{aligned}
&(1) \qquad |\psi_i(x,s_l)|^2|\psi_j(y,s_k)|^2 - |\varphi_i(x,s_l)|^2|\varphi_j(y,s_k)|^2 +\\
&(2) \qquad |\psi_i(x,s_k)|^2|\psi_j(y,s_l)|^2 - |\varphi_i(x,s_k)|^2|\varphi_j(y,s_l)|^2 +\\
&(3) \qquad |\psi_j(x,s_l)|^2|\psi_i(y,s_k)|^2 - |\varphi_j(x,s_l)|^2|\varphi_i(y,s_k)|^2 +\\
&(4) \qquad |\psi_j(x,s_k)|^2|\psi_i(y,s_l)|^2 - |\varphi_j(x,s_k)|^2|\varphi_i(y,s_l)|^2 \quad .
\end{aligned}$$

But we have, for example,

$$(1) = (|\psi_i(x,s_l)|^2 + |\varphi_i(x,s_l)|^2)(|\psi_j(y,s_k)|^2 - |\varphi_j(y,s_k)|^2) -$$

$$|\varphi_i(x,s_l)|^2|\psi_j(y,s_k)|^2 + \underbrace{|\psi_i(x,s_l)|^2|\varphi_j(y,s_k)|^2}_{\bullet}$$

and

$$(4) = (|\psi_j(x,s_k)|^2 + |\varphi_j(x,s_k)|^2)(|\psi_i(y,s_l)|^2 - |\varphi_i(y,s_l)|^2) -$$

$$\underbrace{|\psi_i(y,s_l)|^2|\varphi_j(x,s_k)|^2}_{\bullet\bullet} + |\varphi_i(y,s_l)|^2|\psi_j(x,s_k)|^2.$$

As seen before $\bullet$ and $\bullet\bullet$ cancel with each other when integrating and operating a change of variable($x \leftrightarrow y$). The same happens for the other two extra terms from (1) and (4) (and similarly for (2) and (3)). This shows that

$$\left| \int\int \frac{\rho_\psi(x)\rho_\psi(y) - \rho_\varphi(x)\rho_\varphi(y)}{|x-y|} dxdy \right| \leq$$

$$C\Big(\sum_{i,l} \|\psi_i(.,s_l) - \varphi_i(.,s_l)\| + \|\nabla\psi_i(.,s_l) - \nabla\varphi_i(.,s_l)\|\Big)$$

as claimed. The only term left to treat is the exchange energy term E_{xc}. We do not have to worry about the spin since there is no extra difficulty including it. We first show that

$$\left| \int (\rho_\psi(x))^p dx - \int (\rho_\varphi(x))^p dx \right| \leq C\left(\int (|\rho_\psi(x) - \rho_\varphi(x)|)^p dx \right)^{\frac{1}{p}}.$$

For $p \geq 1$ $|x^p - y^p| \leq C_p|x-y||x^{p-1}+y^{p-1}|$ which gives

$$\left|\int (\rho_\psi(x))^p - (\rho_\varphi(x))^p dx\right| \leq C_p \int |\rho_\psi(x)-\rho_\varphi(x)||(\rho_\psi(x))^{(p-1)}+(\rho_\varphi(x))^{(p-1)}|dx$$

$$\leq \left(\int |\rho_\psi(x) - \rho_\varphi(x)|^p dx\right)^{\frac{1}{p}} \left(\left(\int (\rho_\psi(x))^{(p-1)q}dx\right)^{\frac{1}{q}} + \left(\int (\rho_\varphi(x))^{(p-1)q}dx\right)^{\frac{1}{q}}\right).$$

In the last line we have used Hölder's inequality with $\frac{1}{p}+\frac{1}{q}=1$ $((p-1)q=p)$.

Since

$$|\rho_\psi - \rho_\varphi|^p \leq K((|\rho_\psi - \rho_\varphi|) + (|\rho_\psi - \rho_\varphi|)^3) \text{ for } p \in [1,3]$$

we deduce that

$$\left(\int (|\rho_\psi - \rho_\varphi|^p)\right)^{\frac{1}{p}} \leq K\left(\int |\rho_\psi - \rho_\varphi|dx + \int |\rho_\psi - \rho_\varphi|^3 dx\right)^{\frac{1}{p}}.$$

Then we see that

$$\int |\rho_\psi - \rho_\varphi|dx \leq \sum_{i=1}^N \int ||\psi_i(x)|^2 - |\varphi_i(x)|^2|dx$$

$$\leq \sum_{i=1}^N \left(\int (||\psi_i(x)| - |\varphi_i(x)||)^2 dx\right)^{\frac{1}{2}} \left(\int (||\psi_i(x)| + |\varphi_i(x)||)^2 dx\right)^{\frac{1}{2}}$$

$$\leq C\sum_i |||\psi_i| - |\varphi_i||| \leq C\sum_i ||\psi_i - \varphi_i||$$

and that

$$\int |\rho_\psi - \rho_\varphi|^3 dx \leq C \sum_{i,j,k=1}^N \Bigg($$

$$\int ||\psi_i(x)| - |\varphi_i(x)||(|\psi_i(x)| + |\varphi_i(x)|)(|\psi_j(x)|^2 + |\varphi_j(x)|^2)(|\psi_k(x)|^2 + |\varphi_k(x)|^2)dx\Bigg).$$

Using the general Hölder inequality with the first term to the power 2 and using that $\varphi_i, \psi_i \in L^r$ for $r \in [2,6]$ by combination of the Sobolev inequality, and interpolation inequality for L^q-norms we obtain

$$\int |\rho_\psi - \rho_\varphi|^3 dx \leq C\sum_i |||\psi_i| - |\varphi_i||| \leq C\sum_i ||\psi_i - \varphi_i||.$$

This finishes the proof of Lemma 30.

□

Lemma 31

Let $p \in [1, \frac{5}{3})$. Given $\epsilon > 0$ there exists $C_\epsilon > 0$ such that for all $\psi \in (H^1(V))^N$ with $\|\psi\|^2 \leq K$

$$\xi_N^{KS}(\psi) \geq (1 - \epsilon(K^{\frac{2}{3}} + K))T[\psi] - C_\epsilon(1 + K)\|\psi\|^2.$$

Corollary 32 $\inf_{A_\alpha} \xi_N^{KS} > -\infty$ *and minimizing sequences of the Kohn-Sham functional are bounded in $(H^1(V))^N$.*

We start proving Corollary 32.

Proof: ϵ can be chosen small enough to make the coefficient in front of the kinetic term positive. If the minimizing sequence is unbounded in H^1 we must have $\|\nabla\psi\| \to \infty$ and then we would have $E_\alpha^{KS} = +\infty$, which is absurd. Furthermore $\xi_N^{KS}(\psi) \geq -C_\epsilon(1 + K)K^2$.

□ **Proof of Lemma 31:**

The following proof of this lemma can be found in [Fr97]:

$$|V_{ne}[\psi]| \leq \sum_{i=1}^{N}(\|v_1\|_{L^{\frac{3}{2}}}\|\psi_i\|_{L^6}^2 + \|v_2\|_{L^\infty}\|\psi_i\|_{L^2}^2) \leq 2C_s\|v_1\|_{L^{\frac{3}{2}}}T[\psi] + \|v_2\|_{L^\infty}\|\psi\|_{L^2}^2$$

$$|J[\rho_\psi]| \leq C_s\|w_1\|_{L^{\frac{3}{2}}}T[\psi]\|\rho_\psi\|_{L^1} + \frac{1}{2}\|w_2\|_{L^\infty}\|\rho_\psi\|_{L^1}^2.$$

For the exchange correlation functional: because of the requirements on p given ϵ there exist c_ϵ such that $|\rho^p| \leq \epsilon\rho^{\frac{5}{3}} + C_\epsilon\rho$ for all $\rho \geq 0$ and hence using Hölder and Sobolev inequalities as well as convexity inequality for gradients (see for example Analysis [LL97] page 177)

$$\|\rho_\psi\|_{L^{\frac{5}{3}}}^{\frac{5}{3}} \leq \|\rho_\psi\|_{L^1}^{\frac{2}{3}}\|\rho_\psi\|_{L^3} \leq C_s\|\rho_\psi\|_{L^1}^{\frac{2}{3}}\|\nabla(\sqrt{\rho_\psi})\|^2 \leq 2C_s\|\rho_\psi\|_{L^1}^{\frac{2}{3}}T[\psi].$$

Choosing v_1 and w_1 such that $\|v_1\|_{L^{\frac{3}{2}}}, \|w_2\|_{L^{\frac{3}{2}}} < \epsilon$ we obtain the desired result. $\square$

5.6 One body-density and compactness

Our next result (and its proof) is taken from [Fr97] or [Fr03]. It establishes the equivalence between compactness of a minimizing sequence and nullity of its scattering charge (defined in the lemma).

Lemma 33 *Let ψ^n be a minimizing sequence of ξ_N^{KS} over the set A_α. Then the two following statements are equivalent*

- $(\psi^n)_{n\in\mathbb{N}}$ *stays in a compact subset of* $(H^1(V))^N$
- $\lim_{R\to\infty}\limsup_{n\to\infty}\int_{\mathbb{R}^3\setminus B_R(0)}\rho_{\psi^n}(r)dr = 0.$

Remark: It is not so obvious to recover convergence in a stronger norm from the convergence in the weaker norm. The fact that the sequence is a minimizing sequence is essential. This lemma will be useful when dealing with the bound part and the scattering part of a supposedly non-compact minimizing sequence.

Proof:

Suppose that (ψ^n) remains in a compact set of $(H^1(V))^N$. Then we have (if necessary by taking a subsequence) strong convergence in $(L^2(V))^N$. This gives the strong convergence of ρ_{ψ^n} in $L^1(V)$ which gives that the scattering charge is null since L^1 functions are almost everywhere equal to zero at infinity.

In the argument below we do not include the spin but the proof can be easily adapted to accommodate it. Suppose that we have

$$\lim_{R\to\infty} \limsup_{n\to\infty} \int_{\mathbb{R}^3\setminus B_R(0)} \rho_{\psi^n}(r)dr = 0.$$

We first show that $(\psi^n)_{n\in\mathbb{N}}$ is relatively compact in $(L^2(\mathbb{R}^3))^N$. Choose $\epsilon > 0$. Then there exists a $R_0 > 0$, $n_0 \in \mathbb{N}$ so that

$$(\star) \quad \int_{\mathbb{R}^3\setminus B_R(0)} \rho_{\psi^n}(r)dr < \epsilon \text{ for all } n \geq n_0.$$

Using the Rellich-Kondrackov theorem we can extract from any subsequence of ψ^n a subsequence say ψ^n so that $\psi^n \to \psi$ in $(L^2(B_R(0)))^N$ for all $R > 0$. Further by compactness of the unit ball in $(H^1(\mathbb{R}^3))^N$ in the weak topology (and the fact that ψ^n is bounded in $(H^1(\mathbb{R}^3))^N$) we have also $\psi^n \rightharpoonup \psi$ in $(H^1(\mathbb{R}^3))^N$. With the above estimate we can easily evaluate the norm of ψ i.e.

$$\begin{aligned}
\|\psi\| = \int_{\mathbb{R}^3} |\psi|^2 dx \geq \int_{B_R(0)} |\psi|^2 dx \\
= \lim_{n\to\infty} \int_{B_R(0)} |\psi^n|^2 dx \\
= \lim_{n\to\infty} \left(\int_{\mathbb{R}^3} |\psi^n|^2 dx - \int_{\mathbb{R}^3\setminus B_R(0)} |\psi^n|^2 dx \right) \\
\geq 1 - \epsilon \text{ using } (\star).
\end{aligned}$$

Since ϵ is arbitrary we deduce that $\|\psi\| \geq 1$. However we still have the weak convergence in L^2 which gives that $\|\psi\| \leq \liminf \|\psi^n\| = 1$. Hence $\|\psi\| = 1$. We use now a classical lemma (see [LL97] p 57 for example or see [Bre05]) which tells us that if $\psi^n \rightharpoonup \psi$ and $\|\psi\| = \lim \|\psi^n\|$ then $\psi^n \to \psi$ strongly. Hence $\psi^n \to \psi$ in $(L^2(\mathbb{R}^3))^N$. The convergence of $\nabla\psi^n$ toward $\nabla\psi$

in $(L^2(\mathbb{R}^3))^N$ will be established in an indirect way. We know that $\|\psi^n\|_{H^1} \leq C$. We can find v_1, v_2, w_1, w_2 such that $v_{ne} = v_1 + v_2$ and $v_{ee} = w_1 + w_2$ (where $v_{ee} := \frac{1}{|x-y|}$) with $\|v_1\|_{L^{\frac{3}{2}}}, \|w_1\|_{L^{\frac{3}{2}}} < \varepsilon$ and $v_2, w_2 \in L^\infty$. Since $\psi^n \to \psi$ in L^2 then

$$\lim_n \int v_2 |\psi^n|^2 dx = \int v_2 |\psi|^2 dx.$$

Furthermore

$$\left| \int v_1 |\psi^n|^2 dx \right|, \left| \int v_1 |\psi|^2 dx \right| \leq \varepsilon C_s C^2.$$

This provides

$$\left| \int v_{ne} \left(|\psi^n|^2 - |\psi|^2 \right) dx \right| \leq 3 C_s C^2 \varepsilon$$

for n large enough. Next we claim that

$$J[\psi^n, \psi^n] \to J[\psi, \psi]$$

i.e. that

$$\int\int v_{ee} \rho_{\psi^n}(x) \rho_{\psi^n}(y) dx dy \to \int\int v_{ee} \rho_\psi(x) \rho_\psi(y) dx dy.$$

We note that $\psi^n \to_{(L^2(\mathbb{R}^3))^N} \psi \Rightarrow \rho_{\psi^n} \to_{L^1(\mathbb{R}^3)} \rho_\psi$ which implies that

$$\int\int \rho_{\psi^n}(x) \rho_{\psi^n}(y) dx dy \to \int\int \rho_\psi(x) \rho_\psi(y) dx dy.$$

As for the term V_{ne} we have that

$$\left| \int\int w_1 \rho_{\psi^n} \rho_{\psi^n} dx dy \right|, \left| \int\int w_1 \rho_\psi \rho_\psi dx dy \right| \leq \epsilon N C^2 C_s.$$

Furthermore

$$\left| \int\int w_2 (\rho\rho - \rho_{\psi^n} \rho_{\psi^n}) dx dy \right| \leq \|w_2\|_\infty \left| \int\int (\rho\rho - \rho_{\psi^n} \rho_{\psi^n}) dx dy \right| \to_n 0$$

which finishes to prove the claim.

We show that $E_{xc}[\psi^n] \to E_{xc}[\psi]$. We have

$$\psi^n \to_{(L^2(\mathbb{R}^3))^N} \psi \Rightarrow \sqrt{\rho_{\psi^n}} \to_{L^2(\mathbb{R}^3)} \sqrt{\rho_\psi} \text{ and } \psi^n \subset (H^1(\mathbb{R}^3))^N \Rightarrow \sqrt{\rho_{\psi^n}} \subset H^1(\mathbb{R}^3)$$

with $\|\sqrt{\rho_{\psi^n}}\|_{H^1(\mathbb{R}^3)} \leq C$ and $\rho_{\psi^n}, \rho_\psi \in L^p$ for $p \in [1,3]$ and $\rho_{\psi^n} \to \rho_\psi$ in L^1. By the Rellich-Kondrakov theorem we obtain, after taking a subsequence if necessary, that

$$\sqrt{\rho_{\psi^n}} \to_{L^p(B_R(0))} \sqrt{\rho_\psi} \quad \forall R \geq 0 \quad \forall p \in [2,6)$$

or equivalently

$$\rho_{\psi^n} \longrightarrow_{L^p(B_R(0))} \rho_\psi \quad \forall R \geq 0 \quad \forall p \in [1,3).$$

Hence

$$\int |\rho_{\psi^n} - \rho_\psi|^p dx = \int_{B_R(0)} |\rho_{\psi^n} - \rho_\psi|^p dx + \int_{\mathbb{R}^3 \setminus B_R(0)} |\rho_{\psi^n} - \rho_\psi|^p dx < \epsilon$$

if $R > R_0(\epsilon)$ and $n > n_0(\epsilon)$ or in other words $\rho_{\psi^n} \to_{L^p(\mathbb{R}^3)} \rho_\psi$ for all $p \in [1,3)$ which finishes the proof of the claim.

We have shown so far that

$$V_{ne}[\psi^n] + J[\psi^n, \psi^n] + E_{xc}[\psi^n] \to V_{ne}[\psi] + J[\psi, \psi] + E_{xc}[\psi]$$

which leaves us with the kinetic term only. By the weak lower semi continuity of the L^2-norm and the weak convergence of $\nabla\psi^n$ toward $\nabla\psi$ in L^2 we have $T[\psi] \leq \liminf_n T[\psi^n]$. Therefore combined with the result above we readily obtain

$$\xi_N^{KS}(\psi) \leq \liminf_n \xi_N^{KS}(\psi^n) = \inf\left\{\xi_N^{KS}(\phi) \mid \phi \in A_\alpha\right\} = E_\alpha^{KS}.$$

By the convergence in L^2 of ψ^n and weak convergence in H^1 we have that $\psi \in H^1$ and $\langle \psi_i, \psi_j \rangle = \alpha_i \delta_{ij}$ which makes ψ an element of A_α and therefore with hindsight $\xi_N^{KS}(\psi) \geq E_\alpha^{KS}$. Hence $T[\psi^n] \to T[\psi]$ which together with $\nabla\psi^n \rightharpoonup_{L^2} \nabla\psi$ implies strong convergence in L^2 of the gradient sequence and at last convergence in H^1 as claimed. □

5.6.1 The problem at infinity: The unphysical behaviour of the scattering state

This section is intimately related to the preceding one. Indeed we have shown the equivalence between compactness and nullity of the scattering charge and we are now about to show the striking clustering of the scattering charge (if there is one). In a way it is completely unphysical since one would expect the density of the scattering charge to flatten at infinity since there is no nucleus there to keep it together. We adapt a result from [Fr97].

Lemma 34 *(Behaviour of the scattering states)*

$$E_\alpha^{KS\infty} \in (-\infty, 0) \text{ for } p \in [1, \frac{3}{2})$$

Further for any minimizing sequence ψ^n and for any $p \in (1, \frac{3}{2})$ we have

$$\liminf_{n\to\infty} \sup_{a\in\mathbb{R}^3} \int_{B_1(a)} \rho_{\psi^n}(x)dx \geq \delta > 0.$$

Proof: For $p = 1$ this is trivial since $E_{xc} = -C_{xc}\mu$ which is independent of the ψ. We can w.l.o.g. assume that $p > 1$.

We claim first that

$$E_\alpha^{KS\infty} \leq \sum_{i=1}^{N} E_{\alpha_i}^{KS\infty}$$

where we recall that $\alpha = (\alpha_1, ..., \alpha_N), 0 \leq \alpha_i \leq 1 \quad \forall i = 1, ..N$. Then we will show that

$$E_{\alpha_i}^{KS\infty} < 0 \text{ if } \alpha_i > 0$$

and the first statement of the lemma will be proved. We start by choosing $\varepsilon > 0$. Then we take N orbitals $(\psi_1, ., \psi_N)$ such that $\psi_i \in A_{\alpha_i} \cap C_0^\infty(V)$ and $\xi_1^{KS\infty}(\psi_i) \leq E_{\alpha_i}^{KS\infty} + \frac{\varepsilon}{N}$ for $i = 1, ..N$. We also construct N sequences $(a_i^n)_n$ with $a_i^n \in \mathbb{R}^3$ and $|a_i^n - a_j^n| \to_{n\to\infty} \infty$. We define $\phi_i^n(x) = \psi_i(x - a_i^n)$. If n is large enough we obtain

$$\xi_N^{KS\infty}(\phi_1^n, .., \phi_N^n) = \sum_{i=1}^{N} E_{\alpha_i}^{KS\infty} + \varepsilon + \sum_{i<j} \int \frac{|\phi_i^n(x)|^2 |\phi_j^n(y)|^2}{|x-y|} dx.$$

Using the fact that by construction the distance between the support of the orbitals is going to infinity we see that the last term tend to zero as n tends to infinity. Since ε was arbitrary the claim is proved.

Now we prove the second claim. We begin by looking at different energy terms under dilation. Let $\phi \in C_0^\infty(V)$ such that $\int |\phi|^2 dx = \mu > 0$. To ϕ we associate $\phi_\lambda(x) = \lambda^{-\frac{3}{2}} \phi(\frac{r}{\lambda}, s)$ which has the same L^2 norm. We obtain after a trivial change of variables that

$$T[\phi_\lambda] = \frac{1}{\lambda^2} T[\phi], \qquad J[\phi_\lambda, \phi_\lambda] = \frac{1}{\lambda} J[\phi, \phi], \qquad E_{xc}[\phi_\lambda] = \frac{1}{\lambda^{3(p-1)}} E_{xc}[\phi].$$

Now if $3(p-1) < 1$ i.e. $p < \frac{4}{3}$ we can see that the exchange energy term dominates both other terms as λ tends to zero. It may give the impression that $\frac{4}{3}$ is a border line case. It is not. We also see that if $3(p-1) < 2$ (i.e. if $p < \frac{5}{3}$) and if λ tends to zero the exchange term dominates the kinetic energy and therefore we have

$$\inf_{\psi \in A_\mu} \{T[\psi] + E_{xc}[\psi]\} < 0.$$

Introduce the following sets $A_{\mu\lambda} := \left\{\psi \in H^1(V) \setminus \|\psi\|_{L^2}^2 = \lambda\mu\right\}$ where $\lambda > 0$ and introduce a different scaling, namely $\phi_\lambda(r, s) = \lambda^{(\frac{1+3\beta}{2})} \phi(\lambda^\beta r, s)$ where $\phi \in A_\mu$ and where $\beta \geq 0$ (so that $\|\phi_\lambda\|^2 = \lambda\mu$). Under this scaling we obtain

$$T[\phi_\lambda] = \lambda^{1+2\beta} T[\phi], \qquad J[\phi_\lambda, \phi_\lambda] = \alpha^{2+\beta} J[\phi, \phi] \qquad E_{xc}[\phi_\lambda] = \lambda^{3\beta(p-1)+p} E_{xc}[\phi].$$

If we choose $\beta = \frac{p-1}{5-3p}$ then T and E_{xc} scale in the same way and with this value of β

$$\inf_{\psi \in A_{\lambda\mu}} \xi_1^{KS\infty}(\psi) \leq \lambda^{1+2\beta} \inf_{\psi \in A_{1\mu}} \left\{ T[\psi] + E_{xc}[\psi] + \lambda^{1-\beta} J[\psi, \psi] \right\}.$$

We notice now that J becomes lower order as λ tends to zero if $0 < 1 - \beta = \frac{6-4p}{5-3p}$, i.e. if and only if $p < \frac{3}{2}$. For these p it then follows from the dilation argument above (when $p < \frac{5}{3}$ the exchange term dominates the kinetic energy term) together with $\lambda_0(p) > 0$ chosen sufficiently small that $\inf_{\psi \in A_{\lambda\mu}} \xi_1^{KS\infty}(\psi) < 0$ for all $\lambda \in (0, \lambda_0)$. Now chose $M \in \mathbb{N}$ such that $\frac{1}{M} < \lambda_0 \mu$ and let $\phi \in A_{\mu\frac{1}{M}} \cap C_0^\infty(V)$ with $\xi_1^{KS\infty}(\phi) < 0$ and construct again a sequence a_i^n for $i = 1, ...M$ (as in the first part of the proof) so that $\varphi^n(r,s) = \sum_{i=1}^M \phi(r - a_i^n, s)$ belongs to A_μ for each n and $\xi_1^{KS\infty}(\varphi^n)$ tends to $M\xi_1^{KS\infty}(\phi) < 0$. This proves the second claim and therefore the first statement of Lemma 34. Knowing that the energy is negative is exactly the sort of information that one needs in order to show that in fact the scattering states are not vanishing (at least not completely). Intuitively this comes from the fact that if vanishing occurs the best that one can reach is having energy zero. Nonetheless the case where $p = 1$ shows that one needs to be careful. To prove non vanishing of the entire scattering mass we invoke first the following

Lemma 35 *([Lio84b]) Suppose $u^n, \nabla u^n$ are bounded sequences in $L^2(\mathbb{R}^N, \mathbb{C}^K)$ and $\sup_{a \in \mathbb{R}^3} \int_{B_1(a)} |u^n(x)|^2 dx \to 0$. Then $u^n \to 0$ in $L^q(\mathbb{R}^N)$ for all $q \in (2, 2*)$ where $2* = \frac{2N}{N-2}$.*

We apply this lemma to the minimizing sequences of $\xi_N^{KS\infty}$ which can be viewed as elements $L^2(\mathbb{R}^3; \mathbb{C}^N))$ (including the spin). By Corollary 32 we have that for any minimizing sequence ψ^n there exist a $C > 0$ such that $\|\psi^n\| \leq C, \limsup_{n\to\infty} \|\nabla\psi^n\| \leq C$. So if we assume that $\limsup_{a\in\mathbb{R}^3} \int_{B_1(a)} |\psi^n(x)|^2 dx = 0$ then

$$\liminf_{n\to\infty} \int_{\mathbb{R}^3} |\psi^n(x)|^{2p} dx = \liminf_{n\to\infty} \int_{\mathbb{R}^3} (\rho_{\psi^n}(x))^p dx \geq \frac{1}{C_{xc}} |E_\alpha^{KS\infty}| > 0$$

where the strict positivity comes from the first part of Lemma 34. But this contradicts Lemma 35. Hence there exist a $\delta > 0$ such that

$$\sup_{a\in\mathbb{R}^3} \int_{B_1(a)} \rho_{\psi^n}(x) dx \geq \delta > 0$$

for some $\delta = \delta(C, |E_\alpha^{KS\infty}|)$.

□

Remark 1: Note that the proof of Lemma 34 did not involve in any way the value of the C_{xc}.

Remark 2: The trial function used in the proof actually shows that ξ_N^{KS} is not weakly lower semi-continuous. Indeed the trial function tends weakly to zero giving an energy of zero but $\liminf \xi_N^{KS}(\psi^n) < 0$.

5.7 Alteration of minimizing sequences via decomposition of the one body density matrix

Now we will establish Lemma 36 which is an adaptation of the geometric localization (similar to chapter 2) of the one body density in [Fr03] to our setting. The aim is to produce out of any given minimizing sequence a new minimizing sequence with the same scattering charge but with some extra properties which will be extremely useful later.

Lemma 36 *Let ψ^n be a minimizing sequence of ξ_N^{KS} on A_α ($\alpha = (\alpha_1, .., \alpha_N)$) with scattering charge*

$$\lim_{R\to\infty} \limsup_{n\to\infty} \int_{|r|\geq R} \rho_{\psi^n}(r)dr = \mu - \theta$$

where $\mu := \sum_{i=1}^N \alpha_i$. Then there exists another sequence $\varphi^n \in A_\alpha, R_1^n, R_2^n \geq 0, y^n \in \mathbb{R}^3$ for each n with the following properties:

- *φ^n is also a minimizing sequence of ξ_N^{KS} on A_α*
- $\|\psi^n - \varphi^n\|_{H^1} \to 0$
- $\varphi^n = \varphi_1^n + \varphi_2^n + \varphi_3^n$
- $\int |\varphi_{1,i}^n|^2 dx = \beta_i, \quad \|\varphi_1^n\|^2 = \sum_{i=1}^N \beta_i = \theta,$

$$Supp(\rho_{\varphi_1^n}) \subset B_{R_1^n}(0) \text{ with } \quad R_1^n \to \infty$$

- $\int |\varphi_{2,i}^n|^2 dx = \gamma_i$ *with* $\quad \|\varphi_2^n\|^2 = \sum_{i=1}^N \gamma_i = \lambda$ *and*

$$Supp(\rho_{\varphi_2^n}) \subset B_{R_2^n}(y^n) \cap (\mathbb{R}^3 \backslash B_{2R_1^n}(0)) \text{ with } \quad |y^n| \geq 2R_1^n, \quad R_2^n \to \infty$$

- $\|\varphi_{3,i}^n\|^2 = \alpha_i - \beta_i - \gamma_i \quad \forall i = 1, .., N$ *with* $\|\varphi_3^n\|^2 = \mu - \theta - \lambda$ *and*

$$Supp(\rho_{\varphi_3^n}) \subset \mathbb{R}^3 \setminus (B_{2R_1^n}(0) \cup B_{2R_2^n}(y^n))$$

- $\varphi_1^n \to^{H^1} \varphi_1$ *where φ_1 minimizes ξ_N^{KS} on A_β*
- $\varphi_2^n(. + y_n) \to^{H^1} \varphi_2$ *where φ_2 minimizes $\xi_N^{KS\infty}$ on A_γ*
- $\lim_{n\to\infty} \xi_N^{KS}(\varphi^n) = E_\beta^{KS} + E_\gamma^{KS\infty} + E_{\alpha-\beta-\gamma}^{KS\infty}$.

Proof:

Since the vector case and the spin bring no extra difficulties we prove the case where we have only one orbital without spin. So we consider $\psi^n : \mathbb{R}^3 \to \mathbb{C}$ with $\|\psi^n\|^2 = \alpha$ for all n. We assume that the scattering charge of ψ^n is $\alpha - \beta$. Let $\rho_{\psi^n}(r) = |\psi^n(r)|^2$ be the one body density and let $\rho_{\nabla\psi^n}(r) = |\nabla\psi^n(r)|^2$ be the one body kinetic density. We then consider the two concentration functions introduced first by Levy [Lev54]

$$Q_1^n(R) = \int_{|r|<R} \rho_{\psi^n}(r)dr \text{ and } Q_2(R) = \int_{|r|<R} \rho_{\nabla\psi^n}(r)dr.$$

We know (see [Lio84a] or [Fr03]) that $(Q_1^n)_n$ and $(Q_2^n)_n$ are bounded in $BV(0,R)$ (the space of functions in L^1 with bounded variation (see for example [Zi99])) and that $BV(0,R)$ is compactly embedded in $L^1(0,R)$ (for all $R>0$) we obtain some subsequences of Q_1^n and Q_2^n (called again Q_1^n and Q_2^n) such that Q_1^n, Q_2^n tend respectively to Q_1, Q_2 almost everywhere for all $R \in (0,\infty)$. Note that Q_1 and Q_2 are monotone non decreasing in R and bounded (as limits of bounded non decreasing functions). In particular $0 \le Q_1^n \le \alpha$. However Q_1, Q_2 need not be continuous. By the above the following limits are well defined: $q_1 := \lim_{R\to\infty} Q_1(R)$ and $q_2 := \lim_{R\to\infty} Q_2(R)$. By hypothesis $q_1 = \beta$. Fix $\epsilon > 0$ and let $i = 1,2$. There exists a R_0 such that for all $R \ge R_0, Q_i(2R+1) < q_i + \frac{\epsilon}{2}, Q_i(R-1) > q_i - \frac{\epsilon}{2}$. Without loss of generality we can assume that $R-1$ and $2R+1$ are points of convergence of Q_i^n and therefore there exists a ϑ_0 such that for all $n \ge \vartheta_0 = \vartheta_0(R,\epsilon)$ we have $Q_i^n(2R+1) < q_i + \frac{\epsilon}{2}, Q_i^n(R-1) > q_i - \frac{\epsilon}{2}$. Then we obtain

$$\int_{R-1\le|r|\le 2R+1} \rho_{\psi^n}(r)dr = Q_1^n(2R+1) - Q_1^n(R-1) < \epsilon$$

and

$$\int_{R-1\leq|r|\leq 2R+1} \rho_{\nabla\psi^n}(r)dr = Q_2^n(2R+1) - Q_2^n(R-1) < \epsilon.$$

We use a continuous cut-off $\chi : [0, +\infty) \to [0, 1]$ which is equal to 1 outside $[R-1, 2R+1]$, 0 on $[R, 2R]$ and has gradient $-1, +1$ on $(R-1, R), (2R, 2R+1)$ respectively. Then

$$\int |\psi^n(r) - \chi(|r|)\psi^n(r)|^2 dr \leq \int_{R-1\leq|r|\leq 2R+1} |\psi^n(r)|^2 dr < \epsilon$$

$$\int |\nabla\psi^n(r) - \nabla(\chi(|r|)\psi^n(r))|^2 dr \leq 2\int_{R-1\leq|r|\leq 2R+1} (|\psi^n(r)|^2 + |\nabla\psi^n(r)|^2)dr < 4\epsilon.$$

The last line holds since

$$|\nabla\psi^n(r) - \nabla(\chi(|r|)\psi^n(r))|^2 = (1-\chi(|r|))^2|\nabla\psi^n(r)|^2 + |\psi^n(r)|^2|\nabla(1-\chi(|r|))|^2 +$$

$$2Re(\langle\nabla\psi^n(x), \nabla(1-\chi(|r|))\rangle\psi^n(x)(1-\chi(|r|)))$$

and

$$|\langle\nabla(1-\chi(|r|)), \nabla\psi^n(r)\rangle|\,|\psi^n||1-\chi| \leq_{C.S} |\nabla(1-\chi(|r|))||\nabla\psi^n(r)||\psi^n(r)||1-\chi(|r|)|$$

$$\leq \frac{1}{2}\left(|\nabla\psi^n(r)|^2|1-\chi(|r|)|^2 + |\nabla(1-\chi(|r|))|^2|\psi^n(r)|^2\right).$$

Choosing a sequence of ϵ^ν, a corresponding sequence of radii R^ν and R_0^ν such that $R^\nu \geq R_0^\nu$, $R^\nu \to \infty$ and a subsequence ψ^{n_ν} with $n_\nu \geq n_{\nu_0} = n_{\nu_0}(R^\nu, \epsilon^\nu)$ we obtain a sequence $\chi^\nu(|r|)\psi^{n_\nu}(r)$ such that $\|\psi^{n_\nu} - \chi^\nu\psi^{n_\nu}\|_{H^1} < 5\epsilon^\nu$. Note that the following holds:

$$\int_{|r|\geq R^\nu} \rho_{\chi^\nu\psi^{n_\nu}}(r)dr \to \alpha - \beta$$

and

$$|\xi_1^{KS}(\psi^{n_\nu}) - \xi_1^{KS}(\chi^\nu\psi^{n_\nu})| \to 0.$$

It remains only to deal with the fact that the norm of $\chi^{\nu}\psi^{n_\nu}$ is not α. We may write $\chi^{\nu}\psi^{n_\nu}$ as $\varphi_1^{\nu} + \varphi_2^{\nu}$ where $\varphi_1^{\nu} := \chi^{\nu}(|.|)\psi^{n_\nu}\chi_{[0,R]}(|.|), \varphi_2^{\nu} := \chi^{\nu}(|.|)\psi^{n_\nu}\chi_{[2R,\infty)}(|.|)$. We have

$$\|\varphi_1^{\nu}\|^2 \to_{\nu\to\infty} \beta, \quad \|\varphi_2^{\nu}\|^2 \to_{\nu\to\infty} \alpha - \beta.$$

Since

$$\frac{\beta}{\|\varphi_1^{\nu}\|^2} \to 1, \quad \frac{\alpha-\beta}{\|\varphi_2^{\nu}\|^2} \to 1$$

then

$$\|\Phi_1^{\nu} + \Phi_2^{\nu} - \varphi_1^{\nu} - \varphi_2^{\nu}\|_{H^1} \to_{\nu\to\infty} 0$$

where

$$\Phi_1^{\nu} := \sqrt{\frac{\beta}{\|\varphi_1^{\nu}\|^2}}\varphi_1^{\nu}, \qquad \Phi_2^{\nu} := \sqrt{\frac{\alpha-\beta}{\|\varphi_2^{\nu}\|^2}}\varphi_2^{\nu}.$$

We claim now that Φ_1^{ν} (respectively Φ_2^{ν}) is minimizer of ξ_1^{KS} over A_β (respectively $\xi_1^{KS\infty}$ over $A_{\alpha-\beta}$). Indeed if it were not we could easily obtain a contradiction using a truncated version (compactly supported approximation) of an "almost" minimizer. By Lemma 34 on scattering states we know that $\liminf_{\nu\to\infty}\sup_{y\in\mathbb{R}^3}\int_{B_1(y)}\rho_{\Phi_2^{\nu}}(r)dr \geq \delta > 0$. So this means that there exists a subsequence Φ_2^{ν} say and a sequence $(y_\nu)_{\nu\in\mathbb{N}} \in (\mathbb{R}^3)^{\mathbb{N}}$ with $|y_\nu| \geq 2R_1^{\nu}$ such that

$$\int_{B_1(y^{\nu})}\rho_{\Phi_2^{\nu}}(r)dr \geq \delta > 0.$$

We want now to look at the weak limit of the scattering state i.e. we want to separate from Φ_2^{ν} the bound part from the scattering part. We proceed as follows: We consider $\Phi^{\nu} := \Phi_2^{\nu}(. + y_\nu)$ which is still a minimizing sequence of $\xi_1^{KS\infty}$ over $A_{\alpha-\beta}$ with $supp(\rho_{\Phi^{\nu}}) \subset \mathbb{R}^3 \setminus B_{2R_1^{\nu}}(-y_\nu)$. We apply the same procedure used in the first part of the proof to obtain $\Psi_2^{\nu} + \Phi_3^{\nu}$ a minimizing sequence of $\xi_1^{KS\infty}$ over $A_{\alpha-\beta}$ with the following properties:

$$\|\Psi_2^\nu\|^2 = \gamma > 0, \quad supp(\rho_{\Psi_2^\nu}) \subset B_{R_2^\nu}(0) \setminus B_{2R_1^\nu}(-y_\nu), \qquad \xi_1^{KS}(\Psi_2^\nu) \to_\nu E_\gamma^\infty$$

$$\|\Phi_3^\nu\|^2 = \alpha-\beta-\gamma, supp(\rho_{\Phi_3^\nu}) \subset \mathbb{R}^3 \setminus (B_{2R_2^\nu}(0) \cup B_{2R_1^\nu}(-y_\nu)), \xi_1^{KS}(\Phi_3^\nu) \to_\nu E_{\alpha-\beta-\gamma}^\infty$$

with $R_2^\nu \to \infty$ and

$$E_\beta + E_\gamma^\infty + E_{\alpha-\beta-\gamma}^\infty = \lim_{\nu\to\infty} \xi_1^{KS}(\psi^\nu).$$

We now use $\Phi_2^\nu := \Psi_2^\nu(. - y_\nu), \Psi_3^\nu := \Phi_3(. - y_\nu)$ to construct a sequence $\Phi_1^\nu + \Phi_2^\nu + \Psi_3^\nu$ that has the required properties. So the only thing left to prove is the existence of φ_1 and φ_2. But now it is enough to see that by construction Φ_1^ν has no scattering charge and therefore this yields the existence of a limit φ_1 (because the minimizing sequence is compact in H^1 (by Lemma 33)). The case of φ_2 is identical.

□

First, we note that the proof where $\psi^n = (\psi_1^n, .., \psi_N^n)$ is essentially the same. Second, we see that the above lemma cannot be easily extended to the case where we keep the orthogonality condition between the orbitals. The minimizing problems arising from the separation of the bound and scattering parts are not of the same type anymore: For the constraint we have now a Gram matrix.

5.8 The Variation leading to the contradiction

In the rest of this thesis we will use the notation of Lemma 34 and 36. We first describe what will be done in this section. With the two weak limits φ_1, φ_2 and φ_3^n and φ^n (the sequence constructed by the Lemma 36 above) we are going to construct a new sequence which will be shown to give a lower energy than the starting minimizing sequence (ψ^n) hence giving the desired contradiction. φ^n will be used as a "template", that is to say that we will consider $\varphi^n - \varphi_1^n - \varphi_2^n = \varphi_3^n$ and use the two empty spaces (one of which is escaping to infinity) of this sequence to accommodate some pieces of functions properly chosen. The "hole" (in the configuration space) going to infinity will be used to add the mass missing by just choosing an arbitrary function with compact support (scaled to give the sequence the right mass) and dilated (dilation coefficient will depend on n) so as to give very little contribution in term of energy. Note that this gap might also prove very useful when dealing with the constraint of orthogonality for the orbitals. Indeed the fact that the function can be chosen arbitrary should leave some freedom to help to construct a sequence which has the orthogonality property. We detail the construction for the convenience of the reader. φ_1 will be truncated (using the exponential decay which will be proved below) and φ_2 will have a "small hole" dug into it (far away enough so as to accommodate the truncation of φ_1 without generating too much spurious kinetic energy) and it will also be truncated at a distance which will be chosen large enough as to only involve contribution of lower order. Then as mentioned above we will use a subsequence of φ_3^n (from Lemma 36) and use R_1^n and y_n. φ_4^n, centred at y_n, will be created in order to balance out the mass missing and will be squashed (by dilation) as it escapes to infinity.

5.8.1 Step 1: Construction of the pieces for the new minimizing sequence

We first introduce the following cut-off:

$$\chi_1(x) = \begin{cases} 1 & \text{if } 0 \leq x \leq 2R_1 - 1 \\ 1 - (x - 2R_1 + 1)^2 & \text{if } x \in (2R_1 - 1, 2R_1) \\ 0 & \text{if } x \geq 2R_1 \end{cases}$$

$$\chi_2(x) = \begin{cases} 0 & \text{if } 0 \leq x \leq 2R_1 - 1 \\ (x - 2R_1 + 1)\sqrt{2 - (x - 2R_1 + 1)^2} & \text{if } x \in (2R_1 - 1, 2R_1) \\ 1 & \text{if } x \geq 2R_1 \end{cases}$$

where $\chi_1^2(x) + \chi_2^2(x) = 1$ and

$$\zeta_1^{R_1}(x) = \begin{cases} 1 & \text{if } 0 \leq x \leq R_1 - 1 \\ 1 - (x - R_1 + 1)^2 & \text{if } x \in (R_1 - 1, R_1) \\ 0 & \text{if } x \geq R_1 \end{cases}$$

$$\zeta_2^{R_1}(x) = \begin{cases} 0 & \text{if } 0 \leq x \leq R_1 - 1 \\ (x - R_1 + 1)\sqrt{2 - (x - R_1 + 1)^2} & \text{if } x \in (R_1 - 1, R_1) \\ 1 & \text{if } x \geq R_1 \end{cases}$$

where $(\zeta_1^{R_1})^2(x) + (\zeta_2^{R_1})^2(x) = 1$. Furthermore after a trivial computation we see that $|(\zeta_i^{R_1})'|, |\chi_i'| \leq 2$ for $i = 1, 2$.

We now introduce the different pieces which will make up our new minimizing sequence. We start with φ_1. We will assume its exponential decay at infinity and prove it in section 5.9. We will need a few new variables called say $R_1 > 0, R_2 > 0$. These parameters will be fixed at a later stage but we always assume that they are large enough or small enough as to leave the different fragments with disjoint support in most cases. We take n large enough so that R_1^n (defined in Lemma 36) is large enough for what we have in mind. Let

$$\varphi_1^{R_1} = \varphi_1 \zeta_1^{R_1}(|.|) \quad \text{with } \mathrm{supp}(\rho_{\varphi_1^{R_1}}) \subset B_{R_1}(0).$$

We can now evaluate $\xi_N^{KS}(\varphi_1^{R_1})$. We show that

$$|\xi_N^{KS}(\varphi_1^{R_1}) - \xi_N^{KS}(\varphi_1))| \leq C\exp(-\nu(R_1 - 1)) \text{ for } R_1 \text{ large enough and some } \nu > 0.$$

Using the special properties of the cut-off i.e. that

$$T[\varphi_1] = T[\varphi_1^{R_1}] + T[\varphi_1 \zeta_2^{R_1}] - \frac{1}{2}\int_{|r| \geq R_1 - 1} (|\nabla \zeta_1^{R_1}|^2 + |\nabla \zeta_2^{R_1}|^2)|\varphi_1|^2 dx$$

we obtain that

$$T[\varphi_1^{R_1}] \leq T[\varphi_1] + C\exp(-\nu(R_1 - 1)).$$

We now look at

$$|V_{ne}[\varphi_1^{R_1}] - V_{ne}[\varphi_1]| \leq V_{ne}[\varphi_1 \zeta_2^{R_1}] \leq C\exp(\nu(R_1 - 1))$$

if $R_1 > \max\{|l_1|, .., |l_M|\}$ the l_i's being the location of the nuclei. It is obvious that

$$J[\varphi_1^{R_1}, \varphi_1^{R_1}] \leq J[\varphi_1, \varphi_1]$$

so the only term left to evaluate is the exchange term. We have shown (proof of Lemma 30) that

$$|E_{xc}[\varphi_1] - E_{xc}[\varphi_1^{R_1}]| \leq CE_{xc}[\varphi_1 \zeta_2^{R_1}] \leq C\exp(-\nu(R_1 - 1)).$$

Adding all these estimates together gives that

$$\xi_N^{KS}(\varphi_1^{R_1}) \leq \xi_N^{KS}(\varphi_1) + C\exp(-\nu(R_1 - 1)).$$

Now we deal with the second part of the minimizing sequence i.e. we construct $\varphi_2^R := \varphi_2 \zeta_1^R(|.|)$. We note that $\varphi_2^R \to \varphi_2$ in H^1 (using that $\int |\varphi_2(x)|^2 \chi_{[R,\infty)}(x)dx \to 0$ as $R \to \infty$). Hence using the continuity property we have the existence of $R_0 > 0$ such that for all $R > R_0 = R_0(R_1, R_2, k)$

$$|\xi_N^{KS\infty}(\varphi_2) - \xi_N^{KS\infty}(\varphi_2^R)| \leq \frac{\omega}{(R_1 + R_2)^k}$$

for some $k > 2$ to be chosen later.

We have so far

$$\xi_N^{KS}(\varphi_1^{R_1}) + \xi_N^{KS\infty}(\varphi_2^{R_2}) \leq E_\beta + E_\gamma^\infty + C\exp(-\nu(R_1 - 1)) + \frac{\omega}{(R_1 + R_2)^k}.$$

We now create a "hole" in φ_2^R at a distance $|a| \in [R_2 + 3R_1, R_2 + 2R_1]$ from its centre: a will be used as a variation parameter (for the spherical averaging). We will also use a rotational averaging. We introduce $T_{\theta\vartheta\phi}$ (where $\theta \in [0, 2\pi], \vartheta \in [0, 2\pi], \phi \in [0, \pi]$) which represents the rotation of center 0 and uniquely defined by the three given angles. We define

$$\Upsilon^R(x) := \varphi_{2,a,\theta\vartheta\phi}^R(x) = \varphi_2^R(T_{\theta\vartheta\phi}x + a)\chi_2(|x|).$$

We note that supp $\varphi_1^{R_1} \cap \operatorname{supp}(\Upsilon^R) = \emptyset$. Choose $\varphi \subset C_c^\infty(B_1(0))$ with $||\varphi|| = 1$. Then define

$$\varphi_4^n(x) = \begin{pmatrix} \sqrt{||\varphi_{1,1}||^2 + ||\varphi_{2,1}||^2 - ||\varphi_{1,1}^{R_1}||^2 - ||\Upsilon_1^R||^2} \\ \vdots \\ \sqrt{||\varphi_{1,N}||^2 + ||\varphi_{2,N}||^2 - ||\varphi_{1,N}^{R_1}||^2 - ||\Upsilon_N^R||^2} \end{pmatrix} \lambda_n^{-\frac{3}{2}} \varphi(\frac{x - y^n}{\lambda_n})$$

with $\lambda_n < R_2^n$ and $\lambda_n \to_{n\to\infty} \infty$. We can easily see that

$$\xi_N^{KS}(\varphi_4^n) \to 0 \text{ as } n \to \infty \text{ because of the nature of the dilation.}$$

We now have our complete trial minimizing sequence namely

$$\Psi^n := \varphi_1^{R_1} + \Upsilon^R + \varphi_3^n + \varphi_4^n \quad \text{with } \|\Psi_i^n\|^2 = \alpha_i \quad \forall i = 1,..,N.$$

5.8.2 Step 2: Spherical averaging

The only terms which depend on a and θ, ϑ, ϕ are the terms involving Υ (only one cross term will be relevant since the others will tend to zero with n).

The argument is based on a similar variation used in [Fr03]. We want to evaluate the following quantity

$$\frac{1}{4\pi^3}\int_{\theta,\vartheta,\phi}\int_{a\in B_{R_2+3R_1}(0)\setminus B_{R_2+2R_1}(0)} \xi_N^{KS}(\underbrace{\varphi_1^{R_1} + \Upsilon^R + \varphi_3^n + \varphi_4^n}_{\Psi_n})da\, d\theta\, d\vartheta\, d\phi$$

where the integrals over a are to be read as averaging i.e. $\int_{a\in B} := \frac{1}{Vol(B)}\int_{a\in B}$.

We will show

$$\frac{1}{4\pi^3}\int_{\theta\vartheta\phi}\int_a (\xi_N^{KS}(\Psi_n))dad\theta d\vartheta d\phi \leq E_\beta + E_\gamma^\infty + \xi_N^{KS\infty}(\varphi_3^n) + \xi_N^{KS}(\varphi_4^n) + C\exp(-\nu R_1) +$$

$$\frac{\omega}{(R_1+R_2)^k} + \frac{(\eta(R_2)+\Pi(R_2))|B_{2R_1}|}{|B_{R_2+3R_1}\setminus B_{R_2+2R_1}|} + \Xi(n) + \text{Gain}$$

where η, Π, Ξ and Gain will enable us to obtain

$$\frac{1}{4\pi^3}\int_{\theta\vartheta\phi}\int_a (\xi_N^{KS}(\Psi_n))da\, d\theta\, d\vartheta\, d\phi < E_\beta + E_\gamma^\infty + E_{\alpha-\beta-\gamma}^\infty.$$

By choosing R_1^n, R, and R_2^n properly we have

$$dist(supp(\varphi_1^{R^1}), supp(\varphi_3^n)) \longrightarrow_{n\to\infty} \infty$$

$$dist(supp(\Upsilon^R), supp(\varphi_3^n)) \longrightarrow_{n\to\infty} \infty$$

$$dist(supp(\varphi_1^{R^1}), supp(\varphi_4^n)) \longrightarrow_{n\to\infty} \infty$$

$$dist(supp(\Upsilon^R), supp(\varphi_4^n)) \longrightarrow_{n\to\infty} \infty$$

$$dist(supp(\varphi_3^n), supp(\varphi_4^n)) \longrightarrow_{n\to\infty} \infty.$$

Hence we deduce that

$$J[\varphi_3^n, \varphi_1^{R^1}] \longrightarrow_{n\to\infty} 0, \qquad J[\varphi_3^n, \Upsilon^R] \longrightarrow_{n\to\infty} 0$$

$$J[\varphi_3^n, \varphi_4^n] \longrightarrow_{n\to\infty} 0$$

and

$$J[\varphi_1^{R^1}, \varphi_4^n] \longrightarrow_{n\to\infty} 0 \qquad J[\Upsilon^R, \varphi_4^n] \longrightarrow_{n\to\infty} 0.$$

We have also trivially that $J[\Upsilon^R, \Upsilon^R] \leq J[\varphi_2^R, \varphi_2^R]$. Hence we only need to look carefully at the terms

$$T[\Upsilon^R], V_{ne}[\Upsilon^R], J[\varphi_1^{R^1}, \Upsilon^R], E_{xc}[\Upsilon^R]$$

under the integral since it is easy to obtain

$$\frac{1}{4\pi^3}\int_{\theta\vartheta\phi}\int_a \xi^{KS}(\Psi_n)da\,d\theta\,d\vartheta\,d\phi \leq \xi_N^{KS}((\varphi_1))+\xi_N^{KS\infty}(\varphi_3^n))+\Xi(n)+J[\varphi_2^R,\varphi_2^R]+$$

$$\frac{1}{4\pi^3}\int_{\theta\vartheta\phi}\int_a T[\Upsilon^R]+E_{xc}[\Upsilon^R]+2J[\varphi_1^{R^1},\Upsilon^R]+V_{ne}[\Upsilon^R]da\,d\theta\,d\vartheta\,d\phi+C\exp(-\nu(R_1-1))$$

where $\Xi(n) \to_{n\to\infty} 0$.

We start with

$$\int_{\theta\vartheta\phi}\int_a 2T[\Upsilon^R]da\,d\theta\,d\vartheta\,d\phi = \int_{\theta\vartheta\phi}\int_a\int |\nabla(\varphi_2^R(T_{\theta\vartheta\phi}x)\chi_2(|x-a|))|^2dx\,da\,d\theta\,d\vartheta\,d\phi$$

$$\leq \int_{\theta\vartheta\phi}\int_a\int |\nabla\varphi_2^R(T_{\theta\vartheta\phi}x)|^2dx\,da\,d\theta\,d\vartheta\,d\phi$$

$$+\int_{\theta\vartheta\phi}\int_a\int (|\nabla\chi_1(|x-a|)|^2+|\nabla\chi_2(|x-a|)|^2)|\varphi_2^R(T_{\theta\vartheta\phi}x)|^2dx\,da\,d\theta\,d\vartheta\,d\phi$$

$$\leq 8\pi^3 T[\varphi_2^R] + 8\int_{\theta\vartheta\phi}\int_a\int \chi_{B_{2R_1}(a)}(x)\chi_{(R_2,\infty)}(|x|)|\varphi_2^R(T_{\theta\vartheta\phi}x)|^2 dx\, da\, d\theta\, d\vartheta\, d\phi$$

$$\leq 8\pi^3 T[\varphi_2^R] + 8\frac{|B_{2R_1}|}{|B_{R_2+3R_1}\setminus B_{R_2+2R_1}|}\int_{\theta\vartheta\phi}\int \chi_{(R_2,\infty)}(|x|)|\varphi_2^R(T_{\theta\vartheta\phi}x)|^2 dx\, d\theta\, d\vartheta\, d\phi$$

$$= 8\pi^3 T[\varphi_2^R] + 8\frac{|B_{2R_1}|}{|B_{R_2+3R_1}\setminus B_{R_2+2R_1}|}4\pi^3 \underbrace{\int \chi_{(R_2,\infty)}(|x|)|\varphi_2^R(x)|^2 dx}_{\eta(R_2)}.$$

We therefore have

$$\frac{1}{4\pi^3}\int_{\theta\vartheta\phi}\int_a T[\Upsilon^R]da\, d\theta\, d\vartheta\, d\phi \leq T[\varphi_2^R] + 4\frac{|B_{2R_1}|}{|B_{R_2+3R_1}\setminus B_{R_2+2R_1}|}\eta(R_2)$$

with $\eta(R_2)\to 0$ as $R_2\to\infty$. Now we look at

$$\left|\int_{\theta\vartheta\phi}\int_a E_{xc}[\Upsilon^R] - E_{xc}[\varphi_2^R]da\, d\theta\, d\vartheta\, d\phi\right| =$$

$$\left|\int_{\theta\vartheta\phi}\int_a\int |\varphi_2^R(T_{\theta\vartheta\phi}x)\chi_2(|x-a|)|^{2p}dx da d\theta d\vartheta d\phi - \int_{\theta\vartheta\phi}\int_a\int |\varphi_2^R(T_{\theta\vartheta\phi}x)|^{2p}dx da d\theta d\vartheta d\phi\right|$$

$$\leq C(p,\varphi_2)\int_{\theta\vartheta\phi}\int_a\int |\varphi_2^R(T_{\theta\vartheta\phi}x)\chi_1(|x-a|)|^{2p}dx\, da\, d\theta\, d\vartheta\, d\phi$$

using a similar computation as the one used in the proof of Lemma 30.

$$\leq 4C\frac{|B_{2R_1}|}{|B_{R_2+3R_1}\setminus B_{R_2+2R_1}|}4\pi^3 \underbrace{\int \chi_{(R_2,\infty)}(|x|)|\varphi_2^R(x)|^{2p}dx}_{\Pi(R_2)}.$$

where $\Pi(R_2)\to 0$ as $R_2\to\infty$. Hence we have found that

$$\frac{1}{4\pi^3}\int_{\theta\vartheta\phi}\int_a\int (\rho_{\Upsilon^R(x)})^p dx\, da\, d\theta\, d\vartheta\, d\phi \leq E_{xc}[\varphi_2^R] + 4C\Pi(R_2)\frac{|B_{2R_1}|}{|B_{R_2+3R_1}\setminus B_{R_2+2R_1}|}.$$

The only thing left to do is to evaluate the terms which are going to produce the contradiction namely

$$\frac{1}{4\pi^3}\int_{\theta\vartheta\phi}\int_{a\in B_{R_2+3R_1}(0)\setminus B_{R_2+2R_1}(0)}\left(V_{ne}[\Upsilon^R] + 2J[\Upsilon^R,\varphi_1^{R^1}]\right)da\, d\theta\, d\vartheta\, d\phi.$$

But before we proceed we need to introduce some notations which will be needed. First we recall to the reader Newton's theorem

$$\frac{1}{|S_t|}\int_{S_t}\frac{1}{|r-y|}dH^2(r)=\frac{1}{\max\{|y|,t\}}$$

where $S_t=\{r\in\mathbb{R}^3\setminus|r|=t\}$ and $dH^2(r)=r^2 sin\theta d\theta d\omega$ is the Hausdorff measure on S_t. We also introduce the Radon measure $\mu=\sum_{i=1}^M Z_i\delta_{l_i}$ (i.e. $\int_{\mathbb{R}^3}d\mu=\sum_{i=1}^M Z_i=Z$) and the cut-off functions $\zeta_1^{R_2}(|.+a|),\zeta_2^{R_2}(|.+a|)$ such that

$$|\Upsilon^R(x)|^2=\underbrace{|\Upsilon^R(x)|^2(\zeta_1^{R_2}(|T_{\theta\vartheta\phi}x+a|))^2}_{\Upsilon_1}+\overbrace{|\Upsilon^R(x)|^2(\zeta_1^{R_2}(|T_{\theta\vartheta\phi}x+a|))^2}^{\Upsilon_2}$$

holds for every x and every a,θ,ϑ,ϕ. We define the functions

$$f_1(|x|):=\frac{1}{4\pi^3}\int_{\theta\vartheta\phi}\int_{a\in B_{R_2+3R_1}(0)\setminus B_{R_2+2R_1}(0)}\rho_{\Upsilon_1}(x)da\,d\theta\,d\vartheta\,d\phi$$

where $supp(f_1)\subset[R_1,2R_2+3R_1]$ and

$$f_2(|x|):=\frac{1}{4\pi^3}\int_{\theta\vartheta\phi}\int_{a\in B_{R_2+3R_1}(0)\setminus B_{R_2+2R_1}(0)}\rho_{\Upsilon_2}(x)da\,d\theta\,d\vartheta\,d\phi.$$

where $supp(f_2)\subset[R_1,R+R_2+3R_1]$ (recall $\Upsilon^R(x)=\varphi_2^R(T_{\theta\vartheta\phi}x+a)\chi_2(|x|)$). That $f_1(x)=f_1(|x|)$ can be seen as follows:

$$\frac{1}{4\pi^3}\int_{\theta\vartheta\phi}\int_{a\in B_{R_2+3R_1}(0)\setminus B_{R_2+2R_1}(0)}\rho_{\Upsilon_1}(x)da\,d\theta\,d\vartheta\,d\phi=$$

$$\frac{1}{4\pi^3}\int_{\theta\vartheta\phi}\int_{z\in B_{R_2+3R_1}(T_{\theta\vartheta\phi}x)\setminus B_{R_2+2R_1}(T_{\theta\vartheta\phi}x)}|\varphi_2^R(z)\chi_2(|x|)\zeta_1^{R_2}(|z|)|^2dz\,d\theta\,d\vartheta\,d\phi$$

which is clearly a function only depending on $|x|$ (this is in fact the reason why such a variation over all possible rotation was necessary). We also note that

$$\int f_1(|x|)dx=\int_{R_1}^{2R_2+3R_1}f_1(t)|S_t|dt\geq\delta>0$$

and

$$\int f_2(|x|)dx = \int_{R_1}^{R+R_2+3R_1} f_2(t)|S_t|dt \geq 0.$$

We now proceed to evaluate

$$\frac{1}{4\pi^3}\int_{\theta\vartheta\phi}\int_a 2J[\varphi_1^{R^1},\Upsilon^R] + V_{ne}[\Upsilon^R]da\, d\theta\, d\vartheta\, d\phi$$

$$= \frac{1}{4\pi^3}\int_{\theta\vartheta\phi}\int_a\int_x\int_y \frac{1}{|x-y|}(\rho_{\varphi_1^{R_1}}(y)dy - d\mu(y))\rho_\Upsilon(x)dx\, da\, d\theta\, d\vartheta\, d\phi$$

$$= \frac{1}{4\pi^3}\int_{\theta\vartheta\phi}\int_a\int_x\int_y \frac{1}{|x-y|}(\rho_{\varphi_1^{R_1}}(y)dy - d\mu(y))(\rho_{\Upsilon_1}(x)+\rho_{\Upsilon_2}(x))dx\, da\, d\theta\, d\vartheta\, d\phi.$$

We deal with the term producing the gain namely

$$\frac{1}{4\pi^3}\int_{\theta\vartheta\phi}\int_a\int_x\int_y \frac{1}{|x-y|}(\rho_{\varphi_1^{R_1}}(y)dy - d\mu(y))\rho_{\Upsilon_1}(x)dx\, da\, d\theta\, d\vartheta\, d\phi$$

$$= \int_x\int_y \frac{1}{|x-y|}(\rho_{\varphi_1^{R_1}}dy - d\mu(y))f_1(|x|)dx$$

$$= \int_{R_1}^{2R_2+3R_1} f_1(t)|S_t|\int_y \frac{1}{|S_t|}\int_{z\in S_t}\frac{1}{|z-y|}dH^2(z)(\rho_{\varphi_1^{R_1}}dy - d\mu(y))dt$$

$$= \int_{R_1}^{2R_2+3R_1} f_1(t)|S_t|\int_y \frac{1}{\max\{t,|y|\}}(\rho_{\varphi_1^{R_1}}dy - d\mu(y))dt$$

$$\leq \int_{R_1}^{2R_2+3R_1} f_1(t)|S_t|\frac{(\theta-Z)}{t}dt \leq \frac{1}{2R_2+3R_1}(\theta-Z)\delta.$$

Here we chose $R_1 > \max(l_1, .., l_M)$ in order to apply Newton's theorem and we used that $\frac{1}{\max\{t,|y|\}} \leq \frac{1}{t}$ and that $\int_y \rho_{\varphi_1^{R_1}}dy - d\mu(y) \leq (\theta - Z)$. Now the second term involving Υ_2 can de dealt with in the same way but we obtain no gain since we do not know how much mass is involved i.e. we just know that it is non-positive which in any case adds nothing. We also note that $|B_{2R_1}| = 8|B_1|R_1^3$ and that

$$|B_{R_2+3R_1}\setminus B_{R_2+2R_1}| = |B_1|((R_2+3R_1)^3 - (R_2+2R_1)^3) \geq 3(R_2+3R_1)^2R_1.$$

We now put everything together to obtain:

$$\frac{1}{4\pi^3}\int_{\theta\vartheta\phi}\int_a \xi_N^{KS}(\Psi_n)da d\theta d\vartheta d\phi \leq \xi_N^{KS}(\varphi_1) + \xi_N^{KS\infty}(\varphi_2) + \xi_N^{KS\infty}(\varphi_3^n) + \Xi(n) +$$

$$\frac{\delta(\theta - Z)}{2R_2 + 3R_1} + C\frac{R_1^2}{(R_2 + R_1)^2}(\Pi(R_2) + \eta(R_2)) + C\exp(-\nu(R_1 - 1)) + \frac{w}{(R_1 + R_2)^k}$$

Now take $R_2 > R_1^{\frac{1}{3}}$ with R_1, R large enough, then n large enough and we obtain the claim. Indeed since the leading term is $\frac{\delta(\theta-Z)}{2R_2+3R_1}$, $\theta < Z$ implies that the contribution is negative. Further if $N < Z$ then $\theta < Z$ and therefore the sequence is compact by the above. If $N = Z$ then either $\theta < N = Z$ or $\theta = N = Z$ in which case the scattering charge is zero and therefore the minimizing sequence is compact providing the existence of the minimizer.

5.9 Exponential decay of the bound part φ_1

The first step of the existence proof was achieved assuming the exponential decay of the weak limit φ_1. So we need, in order to finish the proof, to show that we have such a decay. The first step will be to prove the negativity of the Lagrange multipliers and then to derive some regularity properties for the minimizers. It will then be possible to obtain the decay rate of the density using the usual weak maximum principle. We would like to emphasize that since our method does not involve the decay rate of the second fragment (φ_2) our proof does not require us to adapt the Ekeland [Ek79]-Borwein-Preiss [BP87] variational principle to our setting (as in [Lio87] or [Lew04]). The trade-off works in our favour: a slightly more complicated variational method (in 5.8) against a very much simplified derivation of the crucial exponential decay (one needs to work hard in order to show the Lagrange multipliers of the first fragment are the same as the ones of the second fragment).

5.9.1 Derivation of the Euler-Lagrange equations

In all this section we will not take the spin into account as it adds no extra difficulties but merely heavier notations. We now establish the Euler-Lagrange equations associated to our minimization problem. We will do so for the vector case without the orthogonality condition. However we remark that in Kohn-Sham for atoms and molecules we would obtain the same Euler equations up to a unitary transformation (hence making this part suited for $A_\alpha^\sim$). Suppose that $(\psi_1, ..., \psi_N))$ is a minimizer of ξ_N^{KS} over A_α. Choose $\chi \in H^1$ such that $\int \psi_1 \chi^* dx = 0$ and $\int |\chi|^2 dx = \alpha_1$. Then for $|t| < \frac{1}{2}$

$$\psi_t(x) := (\psi_1(t, x), \psi_2(x), .., \psi_N(x)) \in A_\alpha^\sim$$

where $\psi_{1,t}(x) = \sqrt{1-t^2}\psi_1 + t\chi$. We show that $g(t) := \xi_N^{KS}(\psi(t))$ is C^1 and since it has a minimum for $t = 0$ we will have that $\frac{d}{dt}g(t)\mid_{t=0} = 0$.

It is clear that the only non trivial term comes from $E_{xc}[\psi(t)]$. We set $h(x,t) := \left(\sum_{i=2}^N |\psi_i(x)|^2 + |\sqrt{1-t^2}\psi_1 + t\chi|^2\right)^p$. We have that

$$\frac{d}{dt}h(t) = 2p$$

$$Re\left((\frac{-t}{\sqrt{1-t^2}}\psi_1 + \chi)(\sqrt{1-t^2}\psi_1 + t\chi)\right)\left(\sum_{i=2}^N |\psi_i(x)|^2 + |\sqrt{1-t^2}\psi_1 + t\chi|^2\right)^{p-1}$$

where

$$|Re\left((\frac{-t}{\sqrt{1-t^2}}\psi_1 + \chi)(\sqrt{1-t^2}\psi_1 + t\chi)\right)| \le (|\psi_1| + |\chi|)^2 \le 2(|\psi_1|^2 + |\chi|^2).$$

We note also that the right hand side is an L^r function for $r \in [1,3]$. Using Hölder's inequality with $q = \frac{p}{p-1}$ (hence $\frac{1}{p} + \frac{1}{q} = 1$) we have that

$$\int \left|\frac{d}{dt}h(t)\right| \le 2p \int ((|\psi_1|^2 + |\chi|^2)) \left(\sum_{i=2}^N |\psi_i(x)|^2 + |\sqrt{1-t^2}\psi_1 + t\chi|^2\right)^{p-1} dx$$

$$\leq C\left(\int\left(\sum_{i=2}^{N}|\psi_i(x)|^2+|\sqrt{1-t^2}\psi_1+t\chi|^2\right)^p dx\right)^{\frac{p}{p-1}}\left(\int|\chi|^{2p}dx+\int|\psi|^{2p}dx\right)^{\frac{1}{p}}$$

$$\leq C(\rho,\chi) \qquad \forall|t|<\frac{1}{2}.$$

Note that we have used the fact that $p\in[1,\frac{3}{2})$. The theorem of derivation under an integral allows us to conclude that g is differentiable on $(\frac{-1}{2},\frac{1}{2})$. We show that in fact g is twice differentiable. Again the only term for which it is not clear is the exchange term E_{xc}.

$$\frac{d^2}{dt^2}h(t)=4p(p-1)(\star)+2p(\bullet)$$

where

$$(\star)=\left(\sum_{i=2}^{N}|\psi_i(x)|^2+|\sqrt{1-t^2}\psi_1+t\chi|^2\right)^{p-2}\times$$
$$\left(Re\left((\frac{-t}{\sqrt{1-t^2}}\psi_1+\chi)(\sqrt{1-t^2}\psi_1+t\chi)\right)\right)^2$$

and

$$(\bullet)=\left(\sum_{i=2}^{N}|\psi_i(x)|^2+|\sqrt{1-t^2}\psi_1+t\chi|^2\right)^{p-1}\left(\left|\frac{-t}{\sqrt{1-t^2}}\psi_1+\chi\right|^2+\right.$$
$$\left.Re\left((\frac{-1}{\sqrt{1-t^2}}+\frac{t^2}{(\sqrt{1-t^2})^3})\psi_1(\sqrt{1-t^2}\psi_1+t\chi)\right)\right).$$

the second term can be easily estimated in the same way as for the first derivative. We only deal with the first term. Using that $(Re(Z))^2\leq|Z|^2$ we have

$$\star\leq\frac{\left|\frac{-t}{\sqrt{1-t^2}}\psi_1+\chi\right|^2\left|\sqrt{1-t^2}\psi_1+t\chi\right|^2}{\left(\sum_{i=2}^{N}|\psi_i(x)|^2+|\sqrt{1-t^2}\psi_1+t\chi|^2\right)^{2-p}}$$
$$\leq\frac{\left|\frac{-t}{\sqrt{1-t^2}}\psi_1+\chi\right|^2\left|\sqrt{1-t^2}\psi_1+t\chi\right|^2}{|\sqrt{1-t^2}\psi_1+t\chi|^{4-2p}}$$

$$
\begin{aligned}
&\leq \frac{\left|\frac{-t}{\sqrt{1-t^2}}\psi_1 + \chi\right|^2}{|\sqrt{1-t^2}\psi_1 + t\chi|^{2-2p}} \\
&\leq 2\frac{|\psi_1|^2}{|\psi_1|^{2-2p}} + 2\frac{|\chi|^2}{|\chi|^{2-2p}} \\
&= |\psi_1|^{2p} + |\chi|^{2p}.
\end{aligned}
$$

Again the theorem of derivation under an integral gives us that g is twice differentiable. Next we derive the Euler-Lagrange equations associated to our variational problem.

$$
\frac{d}{dt}\xi_N^{KS} = \frac{d}{dt}\Bigg(\overbrace{\frac{1}{2}\int|\sqrt{1-t^2}\nabla\psi_1 + t\nabla\chi|^2 dx}^{(1)} + \overbrace{\int V(x)|\sqrt{1-t^2}\psi_1 + t\chi|^2 dx}^{(2)}
$$

$$
+\overbrace{2\frac{1}{2}\int\int\frac{\left(\sum_{i=2}^N|\psi_i(y)|^2\right)|\sqrt{1-t^2}\psi_1(x) + t\chi(x)|^2 dx}{|x-y|}dxdy}^{(3)}
$$

$$
+\overbrace{\frac{1}{2}\int\int\frac{|\sqrt{1-t^2}\psi_1(x) + t\chi(x)|^2|\sqrt{1-t^2}\psi_1(y) + t\chi(y)|^2}{|x-y|}dxdy}^{(4)}
$$

$$
\underbrace{-C_{xc}\int\left(|\sqrt{1-t^2}\psi_1(x) + t\chi(x)|2 + \sum_{i=2}^N|\psi_i(x)|^2\right)^p dx}_{(5)}\Bigg).
$$

We find that

$$
\begin{aligned}
\frac{d}{dt}(1)\bigg|_{t=0} &= Re\left(\int\langle\nabla\psi_1, \nabla\chi\rangle dx\right) \\
\frac{d}{dt}(2)\bigg|_{t=0} &= 2Re\left(\int\psi_1(x)\chi^*(x)V(x)dx\right)
\end{aligned}
$$

$$\frac{d}{dt}(3)\bigg|_{t=0} = 2Re\left(\int\int \frac{\psi_1(x)\chi^*(x)\left(\sum_{i=2}^N |\psi_i(y)|^2\right)}{|x-y|}dxdy\right)$$

$$\frac{d}{dt}(4)\bigg|_{t=0} = 2Re\left(\int\int \frac{\psi_1(x)\chi^*(x)|\psi_1(y)|^2}{|x-y|}dxdy\right)$$

$$\frac{d}{dt}(5)\bigg|_{t=0} = 2Re\left(\int \psi_1(x)\chi^*(x)\left(\sum_{i=1}^N |\psi_1(x)|^2\right)^{p-1} dx\right).$$

Now using $i\psi_1$ instead of ψ_1 ($(i\psi_1, \psi_2, .., \psi_N)$ is still a minimizer) we obtain exactly the same thing as above but with the imaginary part instead of the real part Re. Adding everything together yields for any χ orthogonal to ψ_1

$$\int\left(\frac{-1}{2}\Delta + V(x) + \int\frac{\sum_{i=1}^N |\psi_i(y)|^2}{|x-y|}dy - pC_{xc}\left(\sum_{i=1}^N |\psi_i(x)|^2\right)^{p-1}\right)\psi_1(x)\chi^*(x)dx = 0$$

where the Laplacian is taken in the sense of the distributions. We deduce that we must have

$$\left(\frac{-1}{2}\Delta + V(x) + \int\frac{\rho(y)}{|x-y|}dy - pC_{xc}(\rho(x))^{p-1}\right)\psi_1(x) = \lambda_1\psi_1(x)$$

where $\lambda_1 \in \mathbb{R}$ is some fixed constant (that the λ_i's are real can be seen by applying the above to $\psi^*(t)$ instead of $\psi(t)$). The variation with ψ_1 was completely general and we could very well have chosen ψ_i for $i = 2, ..., N$ thus giving the general

$$\left(\frac{-1}{2}\Delta + V(x) + \left(\int\frac{\rho(y)}{|x-y|}dy\right) - pC_{xc}\rho(x)^{p-1} - \lambda_i\right)\psi_i(x) = 0 \quad \forall i = 1, .., N$$

where $(\lambda_i)_{i=1}^N \in (\mathbb{R})^N$ and $\rho(x) = \sum_{j=1}^N |\psi_j(y)|^2$.

We now want to derive the second variation condition. We obtain after a tedious but trivial computation

$$\frac{d^2}{dt^2}T[\psi(t)]\bigg|_{t=0} = \int |\nabla\chi_i|^2 - |\nabla\psi_i|^2 dx$$

$$\frac{d^2}{dt^2}V_{ne}[\psi(t)]\bigg|_{t=0} = 2\int (|\chi_i|^2 - |\psi_i|^2)V(x)dx$$

$$\frac{d^2}{dt^2}J[\psi(t),\psi_i(t)]\bigg|_{t=0} = 4\int\int \frac{1}{|x-y|} Re\left(\chi_i(y)(\psi_i(y))^*\right) Re\left(\chi_i(x)(\psi_i(x))^*\right) dxdy$$
$$+2\int\int \frac{1}{|x-y|}\rho(y)\left(|\chi_i(x)|^2 - |\psi_i(x)|^2\right) dx$$

$$\frac{d^2}{dt^2}E_{xc}[\psi(t)]\bigg|_{t=0} = -2pC_{xc}\int |\chi_i(x)|^2(\rho_n(x))^{p-1}dx$$
$$+2pC_{xc}\int (|\psi_i(x)|^2)\rho^{p-1}dx$$
$$-4p(p-1)C_{xc}\int (Re(\chi_i(x)(\psi_i^n(x))^*))^2 \left(\sum_{i=1}^{N} |\psi_i(x)|^2\right)^{p-2} dx.$$

We note now that all the terms involving only the ψ_i (i.e. no χ_i) yield

$$2\lambda_i \int |\psi_i|^2 dx = 2\lambda_i \int |\chi_i|^2 dx.$$

Replacing and simplifying gives

$$\int |\nabla\chi_i|^2 dx + 2\int |\chi_i|^2 V(x)dx - \lambda_i \int |\chi_i|^2 dx$$

$$+4\int\int \frac{1}{|x-y|} Re\left(\chi_i(y)(\psi_i(y))^*\right) Re\left(\chi_i(x)(\psi_i(x))^*\right) dxdy$$

$$+2\int\int \frac{1}{|x-y|}\rho(y)|\chi_i(x)|^2 dxdy - 2pC_{xc}\int (|\psi_i(x)|^2)\rho^{p-1}dx$$
$$-4p(p-1)C_{xc}\int (Re(\chi_i(x)(\psi_i(x))^*))^2 \left(|\psi_i(x)|^2\right)^{p-2} dx \geq 0.$$

We see that the last two terms are negative. This yields

$$\int |\nabla\chi_i|^2 dx + \int |\chi_i|^2 V(x) dx - \lambda_i \int |\chi_i|^2 dx + \int\int \frac{1}{|x-y|}\rho(y)|\chi_i(x)|^2 dxdy$$
$$+2\int\int \frac{1}{|x-y|} Re\left(\chi_i(y)(\psi_i(y))^*\right) Re\left(\chi_i(x)(\psi_i(x))^*\right) dxdy \geq 0.$$

5.9.2 The sign of the Lagrange multipliers

The operator

$$A := -\Delta + V(x) + \rho * \frac{1}{|x|} + 2R$$

where

$$\langle R\phi, \phi\rangle := \int\int \frac{1}{|x-y|} Re\left(\phi(y)(\psi_i(y))^*\right) Re\left(\phi(x)(\psi_i(x))^*\right) dxdy$$

has been already investigated in [lio84a]. The only constraint associated to the operator is $\int \chi_i \psi_i^* dx = 0$. The operator A has infinitely many strictly negative eigenvalues if we have $\int \sum_{i=1}^N |\psi_i|^2 dx < Z$. Indeed we have the following:

Lemma 37 *([Lie84],[Lio87]) Suppose that $\int \sum_{i=1}^N |\psi_i|^2 dx < Z$. Then for each $k \geq 1$ there exists $\epsilon_k > 0$ such that A has infinitely many strictly negative eigenvalues below $-\epsilon_k$.*

Proof [Lio87]:

We find for each integer k a subspace of dimension k denoted by F_k such that

$$\min\left\{\langle A\phi, \phi\rangle \setminus \phi \in F_k, \int |\phi|^2 = 1\right\} < 0.$$

In order to find such a F_k we take a k dimensional subspace made of k smooth spherically symmetric functions with compact support say in $\{1 \leq |x| \leq 2\}$.

We call them ϕ_i with $i = 1, .., k$. We now dilate them all by the same factor σ. We show that by taking σ large enough we obtain F_k. Take w.l.o.g ψ_1 and let $\phi_\sigma(x) := \sigma^{\frac{-3}{2}}\phi_1(\frac{x}{\sigma})$. We first compute

$$\langle (A-2R)\phi_\sigma, \phi_\sigma\rangle = \frac{1}{\sigma^2}\int |\nabla\phi_1|^2 dx + \frac{1}{\sigma}\int V_\sigma(x)|\phi_1|^2 dx + \frac{1}{\sigma}\int (\rho_\sigma * \frac{1}{|x|})|\phi_1|^2 dx$$

where $V_\sigma(x) := \sum_{i=1}^{M} \frac{-Z_i}{|x-\frac{L_i}{\sigma}|}$ and where $\rho_\sigma(x) = \sigma^3\sum_{i=1}^{N}|\psi_i(\sigma x)|^2$. We now see that on one hand $V_\sigma(x)$ has a term of order $\frac{1}{|x|}$ (when σ is large) namely $\sum_{i=1}^{N} Z_i$ and higher order involve some $\frac{1}{\sigma}$. On the other hand we have

$$\begin{aligned}
\int\int \rho_\sigma(x)\frac{1}{|x-y|}|\phi_1(y)|^2 dxdy &= \int\int |\phi_1(y)|^2\frac{1}{|x-y|}\rho_\sigma(x)dydx \\
&= \int \rho_\sigma(x)\int_0^{+\infty} |\phi_1(re)|^2 r^2 4\pi\frac{1}{4r^2\pi}\int_{S_r}\frac{1}{|x-y|}d^2H drdx \\
&= \int \rho_\sigma(x)\int_0^{+\infty} |\phi_1(re)|^2 r^2 4\pi\frac{1}{\max(|x|,r)}drdx \\
&\leq \int\int \rho_\sigma(x)\frac{1}{|y|}dx|\phi_1(y)|^2 dy \\
&\leq \int \frac{1}{|y|}|\phi_1(y)|^2 dy\int \rho_\sigma(x)dx.
\end{aligned}$$

Hence to prove the lemma we only have to show that

$$\langle R\phi_\sigma, \phi_\sigma\rangle = \frac{1}{\sigma}B_\sigma \text{ where } B_\sigma \to_{\sigma\to\infty} 0.$$

Indeed

$$|\langle R\phi_\sigma, \phi_\sigma\rangle| = \left|\frac{1}{\sigma}\int\int Re(\psi_{\frac{1}{\sigma}}(y)\phi_1^*(y))\frac{1}{|x-y|}Re(\psi_{\frac{1}{\sigma}}(x)\phi_1^*(x))dxdy\right|$$

$$\leq C\int\int |\psi_{\frac{1}{\sigma}}(x)|\frac{1}{|x-y|}|\psi_{\frac{1}{\sigma}}(y)|1_{\{2\geq|x|\geq 1\}}(x)1_{\{2\geq|y|\geq 1\}}(y)dxdy.$$

We now use the Hardy-Littlewood-Sobolev inequality (sometimes referred to as the weak Young inequality). See for example [LL97] p106 for a proof.

Theorem 38 *(HLS) Let $p, r > 1$ and $0 < \lambda < n$ with $\frac{\lambda}{n} + \frac{1}{p} + \frac{1}{r} = 2$. Let $f \in L^p(\mathbb{R}^n)$ and $h \in L^r(\mathbb{R}^n)$. Then there exists a constant $C_{n,p,r}$ independent of f and h such that*

$$\left|\int_{\mathbb{R}^n}\int_{\mathbb{R}^n} f(x)|x-y|^{-\lambda}h(y)dxdy\right| \leq C_{n,p,r}\|f\|_p\|h\|_r.$$

We have $\lambda = 1$ and we take $r = p = \frac{6}{5}$ (which is possible since $f(x) := |\psi_{\frac{1}{\sigma}}(x)|1_{\{2\geq|x|\geq1\}}(x)$ and similarly for h). Hence

$$\begin{aligned}
|\langle R\phi_\sigma, \phi_\sigma\rangle| &\leq C_{1,\frac{5}{6},\frac{5}{6}}\left(\int_{\{2\geq|x|\geq1\}} |\psi_{\frac{1}{\sigma}}(x)|^{\frac{6}{5}}dx\right)^{\frac{5}{3}} \\
&= C_{1,\frac{5}{6},\frac{5}{6}}\left(\sigma^{\frac{-6}{5}}\int_{\{2\sigma\geq|x|\geq\sigma\}} |\psi(x)|^{\frac{6}{5}}dx\right)^{\frac{5}{3}} \\
&\leq C\int_{\{2\sigma\geq|x|\geq\sigma\}} |\psi(x)|^2dx.
\end{aligned}$$

Since $\psi \in L^2$ this last quantity goes to zero as σ goes to infinity finishing the proof.

□

We obtain a contradiction unless $\lambda_i < 0$ (in the case where $\alpha_i \neq 0$). This information will give us the decay. In the case where $\sum_{i=1}^N \alpha_i = N$ then the minimizing sequence is in fact compact in H^1 and therefore the problem of existence is solved. So what we have is that if $\sum_{i=1}^N \alpha_i < N$ and $Z \geq N$ the above gives the strict negativity of each λ_i's. If $\alpha_i = 0$ for some i the decay rate is not needed so without loss of generality we could assume $0 < \alpha_i \leq 1$ for all $i = 1, .., N$.

5.9.3 The decay rate

We have the following equation for each orbital:

$$\frac{-1}{2}\Delta\phi_i(x) + V(x)\phi_i(x) + (\rho * \frac{1}{|.|})(x)\phi_i + C_p\rho(x)^{p-1}\phi_i(x) + |\lambda_i|\phi_i = 0$$

where $p \in (1, \frac{3}{2})$ or equivalently $p - 1 \in (0, \frac{1}{2})$ and $\rho \in L^1 \cap L^3, \phi_i \in H^1$.

The density is continuous and it decays to zero as $|x| \to \infty$

Lemma 39

$$\|D^2 \phi_i\|_{L^2} < \infty$$

and consequently all ϕ_i's and therefore also ρ are continuous and $\rho^{p-1} \to 0$ as $|x| \to \infty$.

Proof: We have

$$\|\Delta\phi_i\|_{L^2} = \|V\phi_i + (\rho * \frac{1}{|\cdot|})\phi_i - C_p \rho^{p-1}\phi_i - \lambda_i \phi_i\|_{L^2}$$

$$\leq \|V\phi_i\|_{L^2} + \|(\rho * \frac{1}{|\cdot|})\|_{L^2} + C_p\|\rho^{p-1}\phi_i\|_{L^2} + \lambda_i\|\phi_i\|_{L^2}.$$

We show that in fact the right hand side is bounded. First by Hardy's inequality

$$\int |V\phi_i|^2 dx \leq 4C(N)Z \int |\nabla\phi_i|^2 dx.$$

Secondly

$$\left|\int \rho(y)\frac{1}{|r-y|}dy\right| \leq \int \chi_{|r-y|\leq 1}\frac{1}{|r-y|}\rho(y)dy + \int \chi_{|r-y|\geq 1}\frac{1}{|r-y|}\rho(y)dy$$

$$\leq \|\rho\|_{L^3}\|\chi_{\{|r-y|\leq 1\}}(\cdot)\frac{1}{|r-y|}\|_{L^{\frac{3}{2}}} + \|\rho\|_{L^1}\|\chi_{\{|r-y|\geq 1\}}(\cdot)\frac{1}{|r-y|}\|_{L^\infty}.$$

Hence $\rho * \frac{1}{|\cdot|} \in L^\infty$ which implies that

$$\|(\rho * \frac{1}{|\cdot|})\phi_i\|_{L^2} \leq \|\phi_i\|_{L^2}\|\rho * \frac{1}{|\cdot|}\|_{L^\infty} < \infty.$$

Thirdly we want to show that for every $p \in (1, \frac{3}{2})$ we have $\|\rho^{p-1}\phi_i\|_2 < \infty$. We note that by using Hölder's inequality we get

$$\|\rho^{p-1}\phi_i\|_2^2 \leq \|\rho^{2p-2}\|_{q'}\|\phi_i^2\|_q \text{ with } \frac{1}{q} + \frac{1}{q'} = 1.$$

Since $\phi_i \in H^1$ we have $\|\phi_i^2\|_q < \infty$ for all $q \in [1,3]$. So we only need to check that for any p in our range there exists a q' such that $\|\rho^{2p-2}\|_{q'} < \infty$ and such that $q \in [1,3]$. Put differently

$$\int \rho^{(2p-2)q'}(x)dx < \infty \Leftrightarrow (2p-2)q' \in [1,3]$$

$$\Leftrightarrow (2p-2) \in [1-\frac{1}{q}, 3(1-\frac{1}{q})]$$

$$\Leftrightarrow p \in [\frac{3}{2}-\frac{1}{2q}, \frac{5}{2}-\frac{3}{2q}].$$

We note now that if $q=3$ then the above is always finite for $p \in [\frac{4}{3}, \frac{3}{2})$. If we have a $p \in (1, \frac{4}{3})$ it is enough to see that $\frac{3}{2}-\frac{1}{2q} < \frac{5}{2}-\frac{3}{2q}$ if $q > 1$ and that $G(q) := \frac{3}{2}-\frac{1}{2q}$ takes any value in $(1, \frac{4}{3})$ when $q \in (1,3)$. This finishes to prove that $D^2\phi_i \in L^2$. Hence we have $\phi_i \in W^{k,p}|_{k=2}^{p=2}$ and therefore by the Sobolev embedding theorem we have $\phi_i \in C^{0,\alpha} \cap L^\infty$ because $kp > 3$ (see for example [LL97] p213). In fact we have even more: we have for all $X_0 \in \mathbb{R}^3$ and all $R > 0$

$$\|\phi_i\|_{C^{0,\alpha}(B_R(X_0))} \leq C_R \|\phi_i\|_{W^{2,2}(B_R(X_0))}$$

where the constant C_R depends only on R (this is in fact a fine point). This allows us to obtain the desired decay rate of the orbitals (and hence of the density) since

$$\|\phi_i\|^2_{W^{2,2}(B_R(X_0))} \leq \int_{B_R(X_0)} |\phi_i|^2 + |\nabla\phi_i|^2 + |D^2\phi_i|^2 dx$$

$$\leq \int_{|x|\geq r-R} |\phi_i|^2 + |\nabla u|^2 + |D^2\phi_i|^2 dx \quad \text{for all } |X_0| \geq r$$

$$\to 0 \text{ when } r \to \infty.$$

□

The min/max principle

We are now in a position to finish the proof. With the above we have that Δu is in fact continuous for all $x \in \mathbb{R}^3 \setminus B_l$ where $l \geq \max_{i=1,..,M} |l_i|$. Indeed since ρ is continuous, decays to zero at infinity and since the Coulomb potential is in the Kato space we have that $(\rho * \frac{1}{|\cdot|})(x)$ is continuous. Furthermore as we have seen

$$\left(\frac{-1}{2}\Delta + V(x) + \int \frac{\rho(y)}{|x-y|}dy - pC_{xc}\rho(x)^{p-1} - \lambda_i\right)\phi_i(x) = 0 \quad \forall i = 1,..,N,$$

then $D^2\phi_i$ is continuous on $\mathbb{R}^3 \setminus B_l$. Hence the ϕ_i's are twice continuously differentiable on $\mathbb{R}^3 \setminus B_l$. We can now say that the following holds for $i = 1,..,N$:

$$\left(\frac{-1}{2}\Delta - \frac{2NZ}{|x|} + (|\lambda_i| - \kappa)\right)\phi_i(x) \leq 0$$

if $|x|$ is large enough and where $0 < \kappa << |\lambda_i|$. The term V has been exchanged for $\frac{2NZ}{|x|}$ using a trivial expansion as $|x|$ can be chosen large enough.

We are now precisely in the same setting as the one given in [Th94] page 229. We only need to use the weak maximum principle using the comparison function $C\frac{\exp(-\nu|x|)}{|x|}$ (where $\nu > 0$ and C are constant properly chosen) which solves $(-\Delta + \nu)\phi = 0$ (see Evans [Ev98] page 327 for example). This finishes the proof of the decay rate as well as the proof of Theorem 28.

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