

# Stability of Matter

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# Contents

<b>1</b>	<b>Introduction and Outline</b>	<b>3</b>
1.1	Purpose . . . . .	3
1.2	An Outlook on the Route to the First Stability Result . . . . .	3
1.3	Physical Motivation . . . . .	4
1.4	Remarks on Notation . . . . .	5
<b>2</b>	<b>Physical Preliminaries</b>	<b>7</b>
2.1	Classical Mechanics and Phase Space . . . . .	7
2.1.1	Newton Mechanics . . . . .	7
2.1.2	Hamilton mechanics . . . . .	8
2.2	A first view of the Coulomb Potential . . . . .	9
2.3	Quantum Mechanics . . . . .	10
2.3.1	The notion of a state . . . . .	10
2.3.2	Formalism of quantum mechanics . . . . .	11
2.3.3	Expectation Values and Sobolev spaces . . . . .	12
<b>3</b>	<b>Electrostatics</b>	<b>14</b>
3.1	Charge Distributions . . . . .	14
3.1.1	Relevant Quantities in Electrostatics . . . . .	14
3.1.2	Basic properties of charge distributions . . . . .	15
3.2	The Atomic Coulomb Potential . . . . .	20
3.3	A note on units . . . . .	21
<b>4</b>	<b>Mathematical Preliminaries</b>	<b>22</b>
4.1	Basic Inequalities and Stability of the First Kind . . . . .	22
4.2	Description of Many-Body Systems . . . . .	24
4.2.1	Spin . . . . .	24
4.2.2	Many-body Wave Functions . . . . .	25
4.2.3	Density Matrices . . . . .	28
4.2.4	Definition of Stability of the Second Kind . . . . .	35
4.3	Key Ideas to prove Stability of the Second Kind . . . . .	37
<b>5</b>	<b>Electrostatic Inequalities</b>	<b>38</b>
5.1	Voronoi cells and the Coulomb tooth . . . . .	38
5.2	Basic Electrostatic Inequality . . . . .	39
5.3	Baxter's Inequality . . . . .	42

<b>6</b>	<b>Lieb-Thirring Inequalities</b>	<b>45</b>
6.1	The Variational Principle: Definition of Negative Eigenvalues . . . . .	45
6.2	The Idea of the Semiclassical Approximation . . . . .	46
6.3	Statement of the LT inequality . . . . .	48
6.4	The Birman-Schwinger Principle . . . . .	50
6.4.1	The Birman-Schwinger Formulation of the Schrödinger Equation . .	50
6.4.2	Proof of the LT inequality . . . . .	52
6.5	A Kinetic Energy Inequality . . . . .	54
<b>7</b>	<b>A First Proof of Non-Relativistic Stability</b>	<b>57</b>
7.1	Monotonicity in the Nuclear Charges . . . . .	57
7.2	Putting it all together . . . . .	58
<b>8</b>	<b>Inequalities for Exchange-Correlation Energies</b>	<b>60</b>
8.1	Exchange and Correlation . . . . .	60
8.2	The Lieb-Oxford Inequality . . . . .	62
8.2.1	Statement . . . . .	62
8.2.2	Onsager's Lemma and Proof of the LO-inequality . . . . .	62
8.3	Alternative Proof of Stability using the LO-inequality . . . . .	67
<b>9</b>	<b>Stability through Thomas-Fermi theory</b>	<b>70</b>
9.1	The TF Functional and the TF Energy . . . . .	70
9.1.1	Definition and Relation to Quantum-Mechanical Energy . . . . .	70
9.2	The TF minimizer . . . . .	73
9.2.1	Basic Properties of the TF Functional and the TF energy . . . . .	73
9.2.2	Existence of TF Minimizer . . . . .	74
9.2.3	The TF equation . . . . .	77
9.3	The No-binding Theorem (or: Teller's Theorem) . . . . .	80
9.4	Scaling of the TF-Energy . . . . .	81
9.4.1	Stability for non-relativistic matter . . . . .	82
<b>10</b>	<b>Conclusions: A comparison of both Approaches to Stability</b>	<b>83</b>

# Chapter 1

## Introduction and Outline

### 1.1 Purpose

This work is a self-contained introduction to the non-relativistic stability of matter problem for Coulomb systems<sup>1</sup>, which makes use of first-principle quantum mechanics and basic functional analysis. Most of the presented material is contained in [16]. The main aims are:

- to develop the mathematical tools required to tackle the stability problem, in particular the relevant inequalities,
- to provide a direct proof of stability for non-relativistic matter, presenting exactly what is necessary for a complete understanding of the non-relativistic case,
- to compare this with the original proof of stability through Thomas-Fermi (TF) theory,
- to develop the physics alongside with the mathematics.

### 1.2 An Outlook on the Route to the First Stability Result

The sections in the beginning of this work introduce basic quantum mechanics and functional analysis needed for our analysis. We now give an outlook on the main path to stability of matter, omitting the general introductory pieces. The following sections are central.

- Section 1.3, for an understanding of the physical background of stability.
- Chapter 3, in which the basic tools for the analysis of electrostatics are provided and the atomic Coulomb potential is defined.
- possibly: Section 4.2.3 for a review of some relevant properties of fermionic density matrices.

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<sup>1</sup>I.e. systems which interact only via the electrostatic force.

- Section 4.3, for a concise presentation of the key concepts of a proof stability.
- Chapter 5, a direct continuation of Chapter 3, where the inequalities required to control the Coulomb potential are shown.
- Chapter 6, which gives another centerpiece of this work, namely a way to control the fermionic ground state energy.
- Chapter 7, where the proof takes place.

### 1.3 Physical Motivation

We begin by showing how the question of stability of matter arises from physical considerations and formulate the two different kinds of stability.

We know that matter is comprised of atoms, which have sizes of the order  $1 \text{ \AA} = 10^{-10}m$ . For every-day matter, the constituents of the atoms are electrons and atomic nuclei. The electrons are elementary particles and are modeled as point-like particles in the physical theories, the nuclei are known to have sizes of order  $1 fm = 10^{-15}m$ . It is a fact of Nature that, on the atomic length scale, the only relevant of the four fundamental forces is the electromagnetic force.<sup>2</sup>

When we compare the length scales above, we notice that for atomic physics the nuclei are essentially point particles and thus atoms are essentially empty. This was initially shown experimentally by E. Rutherford in 1911 [25]. From a classical point of view, it is utterly unclear why the electrons are so far away from the nuclei. If only the electrostatic force is relevant, which is true if there are no external magnetic fields and the electron spin plays no essential role, then the electron should fall (or rather: spiral) into the nucleus within a short time interval and the matter in our world would shrink together indefinitely while releasing an infinite amount of energy.<sup>3</sup> The fact that this does not occur is called the *stability (of matter) of the first kind* and is a direct consequence of the quantum-mechanical description of the atom. The proof of the stability of the hydrogen atom was actually an early validation of quantum mechanics. We will show stability of the first kind for one-particle systems using the basic uncertainty principles given in Section Section 4.1.

However, there is another issue: Physical systems tend to minimize their internal energy. Therefore, bulk matter with a large number of particles  $N \approx 10^{23}$  ordinarily shows the lowest possible energy  $E_0$ . With this notion at hand, we can characterize stability of the first kind for many-body systems by  $E_0 > -\infty$  (i.e. the system cannot release an infinite amount of energy to the environment). Naturally, the lower bound we can assign to  $E_0$  will depend on  $N$ . Is there a property of bulk matter that suggests a certain  $N$ -dependency?

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<sup>2</sup>The weak and the strong force are only relevant on scales comparable to the size of nuclei and the gravitational force is too weak in comparison with the electromagnetic force to have an effect on unscreened (i.e. 'viewed from close-up') charges.

<sup>3</sup>Strictly speaking, there has to exist a mechanism to transfer energy from the atom to the environment. Otherwise, energy is bound to be conserved. This mechanism is given by radiation.

<sup>4</sup>Quantum-mechanically speaking, this is the ground-state energy of the many-body system. We do not occupy ourselves with the existence of an explicit minimizer, namely the ground state. A precise definition of  $E_0$  is given in Section 4.1.

Indeed, it is a fundamental property of systems that some thermodynamic quantities like the volume, the entropy and in particular the internal energy are *extensive* quantities, meaning that they are linear with respect to the particle number. We see that this implies that  $E_0$  should be bounded from below by a *bound linear in  $N$* , i.e. that there exists a  $C > 0$  independent of  $N$  such that

$$E_0 \geq -CN. \quad (1.1)$$

The occurrence of (1.1) will be called the *stability of the second kind*<sup>5</sup>.

The notion of extensivity is closely related to a property called *additivity*, namely that the physics does not change when one divides a system of identical particles into smaller subsystems or, equivalently, if one adds two small systems to receive a large one. Imagine two half-filled glasses of water<sup>6</sup> containing  $N$  particles each. We can always pour these two together into a glass containing  $\tilde{N} = 2N$  particles. Since the electrostatic force is a two-particle interaction the number of terms appearing in a calculation of the energy will be of order  $\mathcal{O}(N^2)$ . So, naively one could think that an optimal lower bound only fulfills  $E_0 \geq -CN^2$ , for some constant  $C > 0$  (constant with respect to  $N$ ). With this assumption, the energy of the large system  $\tilde{E}_0$  will only fulfill  $\tilde{E}_0 \geq -C\tilde{N}^2 = -4CN^2$ . If we assume for the moment that these lower bounds to the ground state energy are sharp, we have a net decrease of internal energy given by  $\tilde{E}_0 - 2E_0 = -2CN^2$ , which leaves the system e.g. as heat.

We have thus created an enormous amount of energy ( $N$  is very large) simply by pouring water together, which is not in accordance with reality. We see that only a linear bound can provide us with the additivity of energy we experience. There must be another mechanism at work, which frees us of the quadratic dependence on the particle number. To summarize, stability of the second kind is a notion which is crucial to our understanding of the material world.

## 1.4 Remarks on Notation

The notation used will be the one in [16], with minor changes when appropriate. Furthermore, we will occasionally use a few other conventions, some of which are widely used in the physics literature:

- Vectors are denoted by boldface letters.
- For  $\mathbf{x} \in \mathbb{R}^3$  and  $R > 0$ , we define  $B_R(\mathbf{x}) := \{\mathbf{y} \in \mathbb{R}^3 \mid |\mathbf{x} - \mathbf{y}| < R\}$ .
- We will put the integration measure right behind the corresponding integral sign, i.e.  $\int dx f(x)$  instead of the usual  $\int f(x) dx$  to make the order of integration more transparent. This will be particularly useful when invoking Fubini's theorem to interchange integrals.
- When dealing with sums of complicated terms which are equal up to exchange of one quantity, we shall use the following notation to save writing (imagine the explicit

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<sup>5</sup>Later on,  $N$  will denote only the total number of electrons, whereas  $M$  will be the total number of nuclei. Then the lower bound should depend on  $(N + M)$ , but the important fact is linearity.

<sup>6</sup>This example is taken from Chapter 8 of [20]

form of  $f$  being a long expression):

$$\int \mu(dx)f(x) + [\mu \leftrightarrow \nu] \quad \text{instead of} \quad \int \mu(dx)f(x) + \int \nu(dx)f(x).$$

So the bracket tells us to copy the preceding term and make the replacement given within.

# Chapter 2

## Physical Preliminaries

This chapter will provide a quick, yet hopefully coherent presentation of the necessary physical framework, particularly of quantum mechanics. A complete introduction to quantum mechanics can be found in many excellent textbooks. Short guides well-suited for mathematicians can be found in Chapter 7 of [28] and Chapter 2 of [16].

### 2.1 Classical Mechanics and Phase Space

#### 2.1.1 Newton Mechanics

Classical mechanics is the physics of massive point particles with position variable given by  $\mathbf{x} = (x_1, x_2, x_3) \in \mathbb{R}^3$  and mass  $m$ .<sup>1</sup> Later on, we will also require our particles to have a certain charge  $q$ . The dynamics are governed by Newton's equation of motion

$$\ddot{\mathbf{x}} = \mathbf{F}(\mathbf{x}, \dot{\mathbf{x}}, t), \quad (2.1)$$

where we have denoted time by  $t$ , the force acting on the particle by  $\mathbf{F}$  and used the dot to indicate a time-derivative. We restrict ourselves to systems, in which the force shows no explicit time-dependence. Since (2.1) is second order in time, we know from the theory of ordinary differential equations that a particular solution is uniquely determined by fixing the two initial values  $\mathbf{x}(t_0) = \mathbf{x}_0$  and  $\dot{\mathbf{x}}(t_0) = \mathbf{v}_0$  at some time  $t_0$ . The time evolution from  $t_0$  into the future (and for that matter, also into the past) is then deterministic.

Instead of considering the velocity, we can also work with the momentum

$$\mathbf{p} := m\dot{\mathbf{x}}. \quad (2.2)$$

As before, the motion of a particle is then completely determined by giving its position and momentum at a certain time  $t_0$ . It can be represented by the motion of a point  $(\mathbf{x}(t), \mathbf{p}(t)) \in \Gamma$ , where  $\Gamma := \mathbb{R}^3 \times \mathbb{R}^3 \cong \mathbb{R}^6$  is called the *phase space*.

The Newtonian framework is a very haptic formulation of mechanics based on particles interacting through collisions<sup>2</sup>. However, it is not well-suited to pass on to quantum theory.

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<sup>1</sup>Actually, most results here do not depend crucially on the dimension and one can often generalise to  $\mathbf{x} \in \mathbb{R}^d$ , for some  $d \in \mathbb{N}$ . We note this here, since the results of Chapter 6 show a strong interplay with the value of  $d$ , which is why we will state the results in full generality there.

<sup>2</sup>[5] calls Newtonian Mechanics „romantic in a way.“

## 2.1.2 Hamilton mechanics

Newton mechanics has an equivalent formulation which, as it stands, lies much closer to quantum mechanics, namely the *Hamiltonian formalism*.<sup>3</sup> In the Hamiltonian formulation, the interesting variables are  $\mathbf{x}$  and its conjugate momentum  $\mathbf{P}$ . They are the arguments of the Hamilton function  $H = H(\mathbf{x}, \mathbf{P})$ , which is defined on the phase space  $\Gamma$ . Given  $H$ , we can define

**Definition 2.1.1** (Hamiltonian vector field).

$$\mathbf{v}_H(\mathbf{x}, \mathbf{P}) := \left( \frac{\partial H}{\partial \mathbf{P}}, -\frac{\partial H}{\partial \mathbf{x}} \right) (\mathbf{x}, \mathbf{P}), \quad \forall (\mathbf{x}, \mathbf{P}) \in \Gamma \quad (2.3)$$

This is the essence of the Hamiltonian formalism, since a vector field defines a set of ODEs. In the case of  $\mathbf{v}_H$  these govern the phase space dynamics and are called *Hamilton's equations*

$$(\dot{\mathbf{x}}, \dot{\mathbf{P}}) = \mathbf{v}_H(\mathbf{x}, \mathbf{P}). \quad (2.4)$$

Note that these are now first order in time, so it is only required to fix one quantity at  $t_0$  as an initial condition. However, this quantity is precisely  $(\mathbf{x}(t_0), \mathbf{P}(t_0)) \in \Gamma$ . The upshot will be, that the same six initial values have to be specified as in the Newton case, i.e. we cannot gain or loose information by changing the formalism.

**Assumption 2.1.2.** We shall make two assumptions to simplify matters. These are very natural in the sense that they are fulfilled by most physically relevant Hamilton functions, in particular for the Coulomb force governing the interaction on the atomic level (see 3).

- (i) All the forces  $\mathbf{F}$  we consider will be conservative, i.e. they are generated by a potential energy  $V$  through

$$\mathbf{F}(\mathbf{x}) = -\nabla V(\mathbf{x}). \quad (2.5)$$

The term conservative refers to the fact that due to the existence of a primitive to  $\mathbf{F}$  all integrals over closed curves will vanish, corresponding to *energy conservation*.

- (ii) The conjugate momentum will just be the physical momentum<sup>4</sup>, i.e.

$$\mathbf{P} = \mathbf{p} = m\dot{\mathbf{x}}. \quad (2.6)$$

This has several implications and simplifies our mechanics substantially. The greatest improvement is that now the Hamilton function will be given explicitly by a kinetic plus a potential term

$$H(\mathbf{x}, \mathbf{p}) = \frac{\mathbf{p}^2}{2m} + V(\mathbf{x}) =: T + V, \quad (2.7)$$

where  $T$  is called the *kinetic energy* and  $V$  the *potential energy*. As a consistency check, we can use Hamilton's equations for (2.7) to immediately reproduce (2.1) and (2.5). Furthermore, we can take the time-derivative of  $H(\mathbf{x}(t), \mathbf{p}(t))$  and see again from (2.4) that

<sup>3</sup>Note that another formalism of classical mechanics is the Lagrangian formulation, which is much more natural when passing to Quantum Field Theory, i.e. relativistic quantum mechanics. This is connected with the fact that the expectation of the Hamiltonian gives the energy for conservative systems, whereas in special relativity the energy is the 0-component of a 4-vector and is therefore not Lorentz-invariant.

<sup>4</sup>The most relevant exception to this appears in the presence of a magnetic field  $\mathbf{B}(\mathbf{x}) = \nabla \times \mathbf{A}(\mathbf{x})$  where the canonical momentum is shifted with the vector potential  $A$ , i.e.  $\mathbf{P} = \mathbf{p} + q\mathbf{A}$ . In particular,  $P$  becomes  $\mathbf{x}$ -dependent.

the value of  $H$  is a constant of mechanical motion. Actually,  $H$  just measures the energy of our system, which is conserved as just argued.

Let us note that all objects we considered can be generalised naturally to the case of  $N$  particles on a phase space given by some  $\Gamma := \mathbb{R}^{3N} \times \mathbb{R}^{3N} \cong \mathbb{R}^{6N}$ . For an illuminating discussion of phase space we refer to Chapter 2 of [5]. We will return to this notion in a moment, when introducing quantum mechanics.

## 2.2 A first view of the Coulomb Potential

Our most important example of a conservative force will be the electrostatic (or Coulomb) force. It will be discussed thoroughly in chapter 3. However, we will introduce it here in the special case of two point particles at positions  $\mathbf{x}_1, \mathbf{x}_2$  carrying charges  $q$  and  $Q$ , respectively. In our language, one of the charges (e.g. the second one) generates a field  $E(\mathbf{x})$  at every  $\mathbf{x} \in \mathbb{R}^3$ , with which the other one interacts through the Coulomb force

$$\mathbf{F}_1 = qE(\mathbf{x}_1). \quad (2.8)$$

This is not very useful, until we give the explicit form of the field  $E(\mathbf{x})$  which is well-known to be

$$E(\mathbf{x}) = \frac{Q}{|\mathbf{x} - \mathbf{x}_2|^2} \frac{\mathbf{x}_1 - \mathbf{x}_2}{|\mathbf{x}_1 - \mathbf{x}_2|}. \quad (2.9)$$

It is generated<sup>5</sup> by the *Coulomb potential* of the point charge  $Q$  at  $\mathbf{x}_2$  given by

$$V_C(\mathbf{x}) := \frac{Q}{|\mathbf{x} - \mathbf{x}_2|}. \quad (2.10)$$

We comment on the fact, that while (2.10) is the definition common in the physics literature, it will suit our purposes better, if we do not include units of charge in its definition. In Section 3.2, we will pull out the  $e$ -dependence<sup>6</sup> from  $V_C$ .

*Note 2.2.1.* Let us collect some properties of (2.9) and (2.10).

- (i) The direction of the Coulomb force is determined by the relative sign of  $q$  and  $Q$ . If their signs are the same, the force is repulsive. Otherwise, it is attractive.
- (ii) The Coulomb potential of a point charge is radially symmetric and falls off as  $\frac{1}{r}$ . This has many useful consequences, as we will see in Chapter 3.
- (iii) We can generally observe that only the derivative of a potential enters the physical laws. Therefore, we retain the freedom of adding an overall constant to  $V_C$  without changing the dynamics. If possible (i.e. if  $V_C$  has a uniform limit at infinity), we will choose this constant in such a way as to make  $V_C$  vanish at infinity.

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<sup>5</sup>In the sense of (2.5). Note, though, that the Coulomb potential differs from the corresponding potential energy by a factor of  $q$ , which originates from (2.8).

<sup>6</sup>This denotes the electron charge given by  $e = 1.6021 \cdot 10^{-19}$  Ampère seconds

## 2.3 Quantum Mechanics

The predictions of classical mechanics break down in two cases: On the velocity scale, in the regime of high speeds, where special relativity governs the laws of motion; and on *atomic length and mass scales*, where quantum mechanics comes in. We are interested in the latter.

### 2.3.1 The notion of a state

Consider the word „quantum“. It refers to a coarse-grained nature of the fundamental objects of study.<sup>7</sup> In mechanics, this is the phase space. Position and momentum can no longer assume exact values. The best we can hope for is to localize them within a box in phase space<sup>8</sup>, the volume of which is given by the third power of *Planck’s constant*

$$h = 6.626 \cdot 10^{-34} \text{ Joule seconds.} \quad (2.11)$$

This is reflected by the famous *Heisenberg uncertainty principle*, which says that

$$\Delta x \Delta p \geq \frac{\hbar^2}{4}, \quad (2.12)$$

where  $\hbar := \frac{h}{2\pi}$  and  $\Delta x, \Delta p$  denote the variance of  $x, p$  respectively.

Note that the variance is a statistical notion. However, we have never assumed any lack of knowledge about our system, which would of course require a treatment with the methods of statistical mechanics and variances would appear. The point is that:

*Even though we can have complete information about the „state“ of our system, this does not give us any right to speak about a definite momentum or position.*

Therefore, what we name „state“<sup>9</sup> of a system must be given differently than in classical mechanics, where knowing  $(\mathbf{x}(t_0), \mathbf{p}(t_0))$  for a fixed  $t_0$  determined our system trajectory in phase space completely. We have to abandon this kind of determinism, which was inherited by our classical system from the global existence and uniqueness theorem for solutions of ODEs — simply because we cannot know  $(\mathbf{x}(t_0), \mathbf{p}(t_0))$ .

The foundation of quantum mechanics is a very interesting and highly important subject. However, it is also incoherent and lengthy. We will not go deeper and finish the discussion with four remarks.

*Remark 2.3.1.* We try to clarify some points made above.

- (i) The statement that we cannot know  $(\mathbf{x}(t_0), \mathbf{p}(t_0))$  is not meant in the sense that our measurement devices are too imprecise to detect them. It is meant in the stronger sense that particles do not have intrinsic properties such as a definite position. However, upon measurement a particle assumes (in the stochastic sense) a definite position value. To distinguish it from randomness appearing due to our incomplete knowledge of the world (‘subjective randomness’), this is sometimes referred to as ‘objective randomness’.

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<sup>7</sup>The appellation originates from Planck’s energy quanta correctly describing the blackbody radiation.

<sup>8</sup>This is the basic principle underlying the LT inequalities in Chapter 6 and is explained in Section 6.2.

<sup>9</sup>This will be made more precise in a moment.

- (ii) Thus, the variance in (2.12) refers to the variance we would get by measuring several systems which are in the same state (an *ensemble*) and doing the statistics.
- (iii) There is determinism in quantum mechanics. Namely, the time evolution of states is given in a definite way, which reflects the fact that we have understood the dynamics of quantum systems (in the sense that we do not lose information by letting an unperturbed system evolve in time, only upon measurement is it that objective randomness occurs).
- (iv) Of course, one can also handle subjective randomness in quantum mechanics. The appropriate tools are density matrices, see Section 4.2.3.

### 2.3.2 Formalism of quantum mechanics

Now that we have addressed the difficulties of interpretation, we take a pragmatic viewpoint: We will postulate the correct formalism and justify this with the simplest argument available to physicists: The predictions of the theory are in accordance with experiment. We comment on the fact that we will not occupy ourselves with an abstract Hilbert space structure, rather we shall define a state through its position representation.

**Definition 2.3.2** (Wave function). All possible information about the (pure) state of a physical system is contained in a function  $\psi \in L^2(\mathbb{R}^3, \mathbb{C})$  satisfying

$$\|\psi\|_2 = \left( \int_{\mathbb{R}^3} d\mathbf{x} |\psi(\mathbf{x})|^2 \right)^{\frac{1}{2}} = 1. \quad (2.13)$$

*Remark 2.3.3.* (i) (2.13) allows us to interpret  $|\psi(\mathbf{x})|^2 =: \varrho(\mathbf{x}) \geq 0$  as a probability density for the position of the particle. This is actually the motivation for the definition and goes back to Born.

- (ii) We observe that the exact knowledge of the wave function requires to specify uncountably many (complex) values, whereas in the classical case it was enough to fix 6 (real) values. In this sense, a quantum state is much richer than a classical state.
- (iii) In fact, any function in  $L^2(\mathbb{R}^3, \mathbb{C})$  can be normalized as in (2.13), so we can consider the whole of  $L^2(\mathbb{R}^3, \mathbb{C})$  as the state space.
- (iv) As a Hilbert space,  $L^2(\mathbb{R}^3, \mathbb{C})$  is equipped with a scalar product given by

$$\langle \psi, \phi \rangle := \int_{\mathbb{R}^3} \overline{\psi(\mathbf{x})} \phi(\mathbf{x}) d\mathbf{x}.$$

Now that we have characterized states, we have to define the dynamics. As it turns out, the time evolution of a state is governed by the *time-dependent Schrödinger's Equation*

$$i\hbar \dot{\psi} = \hat{H}\psi, \quad (2.14)$$

where we obtain the *Hamiltonian*  $\hat{H}$  by the following quantization rules from the classical Hamilton function  $H(\mathbf{x}, \mathbf{p})$  given in (2.7):

$$\mathbf{p} \longrightarrow -i\hbar \nabla, \quad \mathbf{x} \longrightarrow \hat{\mathbf{x}}. \quad (2.15)$$

The multiplication operator  $\hat{\mathbf{x}}$  is defined by its action on wave functions, i.e.  $\hat{\mathbf{x}}\psi := \mathbf{x}\psi$ . We get

$$\hat{H} = -\frac{\hbar^2}{2m}\Delta + V(\hat{\mathbf{x}}) = \hat{T} + \hat{V}. \quad (2.16)$$

We call  $\hat{T}$  and  $\hat{V}$  the kinetic and the potential energy operator, respectively. In the following, we will drop the hat in the notation of operators.

### 2.3.3 Expectation Values and Sobolev spaces

The next step is to actually make predictions for measured values in experiments. From the discussion in Section 2.3.1, we know that we can only make probabilistic statements about these outcomes. A simple quantity we can assign to an experiment involving randomness is the expectation value of the measured object.

But how are measurable quantities represented in our theory? By definition, a measurable quantity is represented by a so-called *observable*, i.e. a self-adjoint operator on  $L^2(\mathbb{R}^3, \mathbb{C})$ .<sup>10</sup> Now we are ready to make the following

**Definition 2.3.4** (Expectation value). Let  $A$  be an observable. Then we define the *expectation value of  $A$  in the state  $\psi$*  by

$$A_\psi := \frac{\langle \psi, A\psi \rangle}{\langle \psi, \psi \rangle}. \quad (2.17)$$

*Remark 2.3.5.* (i) The term in the denominator on the right hand side of (2.17) ensures that we only make predictions for normalized states.

(ii) Note that (2.17) is invariant under the global  $U(1)$  gauge transformation

$$\psi \longrightarrow e^{i\chi}\psi. \quad (2.18)$$

Thus, we can only distinguish between equivalence classes of states. These so-called *rays* are denoted by  $[\psi] = \text{span}(\psi) = \{e^{i\chi\psi} | \chi \in \mathbb{R}\}$ .

(iii) (2.17) explains the motivation behind choosing  $A$  to be self-adjoint: By the spectral theorem,  $A_\psi$  will be a linear combination of eigenvalues of  $A$ . The eigenvalues of self-adjoint operators are real, which implies  $A_\psi \in \mathbb{R}$  as it should be.

By analogy, we can derive from classical mechanics that the associated quantity of the Hamiltonian  $H$  is again the system's energy. We will denote  $H_\psi$  by  $\mathcal{E}(\psi)$ , to emphasize its functional character. As we are interested in lower bounds on the energy,  $H$  will be the only observable of interest to us.

However, we see from (2.16) that  $H$  involves second order derivatives, which certainly do not exist for general  $L^2(\mathbb{R}^3)$ -functions. On the other hand, the space  $C^2(\mathbb{R}^3)$  would be too restrictive for our purposes, since we can make sense of the expectation value of the kinetic energy operator for many more functions. With this goal in mind, we consider a function space lying in between  $L^2$  and  $C^2$  by generalising the notion of a derivative. We shall only require the possibility to formally integrate by parts.<sup>11</sup>

<sup>10</sup>The question of self-adjointness of operators can be highly non-trivial. These kind of problems will be outside of our scope, it should however be noted that there is an issue here.

<sup>11</sup>Note that this implies that the classical derivative, in case it exists (and the function vanishes at infinity), agrees with the newly defined weak one.

**Definition 2.3.6** (Sobolev space). Let  $f \in L^2(\mathbb{R}^3)$ .

(i)  $f$  is said to be *weakly differentiable* iff

$$\exists g \in L^2(\mathbb{R}^3) \quad \forall \phi \in C_c^\infty(\mathbb{R}^3) : \int_{\mathbb{R}^3} d\mathbf{x} f(\mathbf{x}) \nabla \phi(\mathbf{x}) = - \int_{\mathbb{R}^3} d\mathbf{x} \phi(\mathbf{x}) g(\mathbf{x}). \quad (2.19)$$

$g$  is then denoted by  $\nabla f$ .

(ii) We define the *first Sobolev space*<sup>12</sup> by

$$H^1(\mathbb{R}^3) := \{f \in L^2(\mathbb{R}^3) \mid f \text{ is weakly differentiable}\} \quad (2.20)$$

We remark on the fact, that  $H^1(\mathbb{R}^3)$  is also a Hilbert space with norm given by

$$\|f\|_{H^1} := \left( \int_{\mathbb{R}^3} d\mathbf{x} |f(\mathbf{x})|^2 + \int_{\mathbb{R}^3} d\mathbf{x} |\nabla f(\mathbf{x})|^2 \right)^{1/2}. \quad (2.21)$$

From here on, we will mostly restrict ourselves to  $H^1(\mathbb{R}^3) \subset L^2(\mathbb{R}^3)$ . The reason is that for all  $\psi \in H^1(\mathbb{R}^3)$  we can make sense of the expectation of the kinetic energy operator (i.e. the Laplacian) by appropriately redefining the quadratic form

$$\langle \psi, H\psi \rangle := \int_{\mathbb{R}^3} d\mathbf{x} \left( \frac{\hbar^2}{2m} \overline{\nabla \psi(\mathbf{x})} \cdot \nabla \psi(\mathbf{x}) + V(\mathbf{x}) |\psi(\mathbf{x})|^2 \right) = T_\psi + V_\psi. \quad (2.22)$$

For  $C^2(\mathbb{R}^3)$ -functions vanishing at infinity, the former definition follows from integrating by parts. For states  $\psi \notin H^1(\mathbb{R}^3)$ , we define  $T_\psi := \infty$ . In view of (2.22) it makes sense<sup>13</sup> to make the following definition.

**Definition 2.3.7** (Ground state energy). For a fixed  $V$ , we call

$$E_0 := \inf \{ \langle \psi, H\psi \rangle \mid \psi \in H^1(\mathbb{R}^3), V_\psi \text{ is well-defined} \}, \quad (2.23)$$

the *ground state energy* of the system defined by  $V$  (even if the infimum is not attained).

We see that our notion of ground state does not involve the existence of some ground state  $\psi_0$ . Rather, it is a *variational characterization*. This will be generalised in Section 6.1.

*Remark 2.3.8.* We comment on the fact that  $H^1$  can also be defined by use of the Fourier transform  $\mathcal{F}$  on  $L^2(\mathbb{R}^3)$ .<sup>14</sup> It is then the  $\mathcal{F}$ -inverse of a weighted  $L^2$ -space. It is well-known that in Fourier space, (spatial) differentiation becomes multiplication with a monomial of the order of the derivative. This is not needed for our considerations,<sup>15</sup>

So far, we have only considered a single quantum particle. Of course, stability of matter is a notion concerning many-particle systems. We will come back to this in Chapter 4, where we develop the actual mathematical tools needed for many-body quantum mechanics.

<sup>12</sup>For a general treatment of Sobolev spaces, see Chapter 5 in [8]. For an approach using distribution theory, see Chapter 6 of [14]

<sup>13</sup>Recall that  $H_\psi$  gives the expectation value of the system's energy.

<sup>14</sup>We assume basic knowledge of Fourier transformation. An introduction can be found in many textbooks, e.g. chapter 5 of [14].

<sup>15</sup>It would be relevant for relativistic stability. For this we will have to make sense of fractional derivatives (recall that the relativistic energy-momentum relation contains a square root).

# Chapter 3

## Electrostatics

Let us now return to our main example of a conservative potential: the Coulomb potential  $V_C$ . It governs the electrostatic interaction of charge distributions, in particular (as seen in Section 2.2) the interactions between point particles such as nuclei and electrons. Therefore, the potential term in the quantum-mechanical Hamiltonians discussed above will be given by  $V_C$  for most of this work. Before we give the exact form of  $V_C$  for our case, we will develop the basic theory of electrostatics, which has the advantage of being accessible with only a few definitions.

### 3.1 Charge Distributions

#### 3.1.1 Relevant Quantities in Electrostatics

The first question that arises is how to define a notion of charge distributions, which is restrictive enough to allow the computation of the relevant quantities while at the same time allowing for a sufficient variety in the appearance of charges. One solution to this is to consider signed Borel measures on the coordinate space  $\mathbb{R}^3$ .

*Remark 3.1.1.* It is natural here to work with measures, because we will encounter both, continuous and discrete charge distributions. In the mathematical language, the first one corresponds to measures which are absolutely continuous (i.e. have a density  $\varrho(\mathbf{x})$ ) with respect to Lebesgue measure  $d\mathbf{x}$ , while the second one is given by a singular pure-point (i.e. „delta-like“ in the case of point particles) measure with respect to  $d\mathbf{x}$ . The measures are signed because the electric charge has a sign. For a short introduction to measures, see Chapter I.4 of [23].

Before we can define charge distributions precisely, we have to introduce two natural quantities for the analysis of electrostatics. First, we restrict ourselves to non-negative Borel measures, for which we can define the following objects (in the sense that they might be  $+\infty$ , but certainly will not yield an ill-defined expression such as „ $\infty - \infty$ “ due to cancellation problems).

**Definition 3.1.2** (Potential function and Coulomb energy). Let  $\sigma$  be a (non-negative) Borel measure on  $\mathbb{R}^3$

- (i) The *potential function* associated with  $\sigma$  is given by

$$\Phi(\mathbf{x}) := \int_{\mathbb{R}^3} \sigma(d\mathbf{y}) \frac{1}{|\mathbf{x} - \mathbf{y}|}. \quad (3.1)$$

(ii) The *Coulomb energy* of  $\sigma$  is then defined to be

$$D(\sigma, \sigma) := \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \sigma(d\mathbf{x}) \sigma(d\mathbf{y}) \frac{1}{|\mathbf{x} - \mathbf{y}|} \quad (3.2)$$

$$= \frac{1}{2} \int_{\mathbb{R}^3} \sigma(d\mathbf{x}) \Phi(\mathbf{x}), \quad (3.3)$$

where (3.2) holds due to Fubini's theorem ( $\sigma$  is non-negative). The physical interpretation for  $\Phi$  is that it gives the potential energy of a unit test charge subject to the electrostatic field generated by  $\sigma$ . In  $D(\sigma, \sigma)$  the field generated by  $\sigma$  at the point  $\mathbf{x} \in \mathbb{R}^3$  is tested with a charge given by  $\sigma(d\mathbf{x})$  yielding the corresponding potential energy. When we sum up (integrate) over all choices of  $\mathbf{x}$  and  $\mathbf{y}$ , we overcount all self-interactions of the field by a factor of 2 which is remedied by the factor of  $\frac{1}{2}$ . So  $D(\sigma, \sigma)$  gives the total energy stored in the electric field generated by  $\sigma$ . This is why it is called the Coulomb energy.

Now, we are ready to define

**Definition 3.1.3** (Charge distribution). Let  $\mu_+$  and  $\mu_-$  be Borel measures on  $\mathbb{R}^3$  with finite Coulomb energy satisfying

$$\int_{\mathbb{R}^3} \mu_{\pm}(d\mathbf{x}) \frac{1}{1 + |\mathbf{x}|} < \infty. \quad (3.4)$$

In this case we shall call the signed Borel measure given by

$$\mu := \mu_+ - \mu_- \quad (3.5)$$

a *charge distribution*.

*Remark 3.1.4.* Note that we do not require  $\mu_+$  and  $\mu_-$  to have disjoint support, i.e. we are not using the measure-theoretic fact (called the Hahn decomposition), that any signed measure can be written as the difference of two positive measures with disjoint support.

### 3.1.2 Basic properties of charge distributions

Of course, we have defined a charge distribution in such way as to make the objects  $\Phi$  and  $D$  accessible for non-negative Borel measures (in the sense that no cancellation problem can occur). We will show now that this is indeed the case. We begin with a lemma which is the result of a simple integration in polar coordinates.

**Lemma 3.1.5.** *Let  $S^2 \subset \mathbb{R}^3$  denote the unit sphere. We denote by  $d\omega$  the normalized surface measure on  $S^2$ . Then for any  $r > 0$  and  $\mathbf{y} \in \mathbb{R}^3$  we have*

$$\int_{S^2} d\omega \frac{1}{|r\omega - \mathbf{y}|} = \min \left\{ \frac{1}{r}, \frac{1}{|\mathbf{y}|} \right\} \quad (3.6)$$

*Proof.* Without loss of generality, assume  $r > |\mathbf{y}|$ . Find a rotation  $R \in O(\mathbb{R}^3)$  such that  $R\mathbf{y} = |\mathbf{y}|\mathbf{e}_3 = (0, 0, |\mathbf{y}|)$ . Then we can make the change of variables  $\varphi(\omega) := R^{-1}\omega$  followed by a transformation to polar coordinates and an application of the fact that for

any two vectors  $\mathbf{x}, \mathbf{y} \in \mathbb{R}^3$  we know  $|\mathbf{x} - \mathbf{y}| = (|\mathbf{x}|^2 + |\mathbf{y}|^2 - 2\langle \mathbf{x}, \mathbf{y} \rangle)^{1/2}$ . This gives the desired result

$$\begin{aligned} \int_{S^2} d\omega \frac{1}{|r\omega - |\mathbf{y}|\mathbf{e}_3|} &= \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_{-1}^1 d(\cos\theta) \frac{1}{\sqrt{r^2 + |\mathbf{y}|^2 - 2r|\mathbf{y}|\cos\theta}} \\ &= \frac{1}{2r} \int_{-1}^1 d\tau \frac{1}{\sqrt{1 + \frac{|\mathbf{y}|^2}{r^2} - 2\frac{|\mathbf{y}|}{r}\tau}} \\ &= \frac{1}{r} \frac{r}{4|\mathbf{y}|} \int_{(1-\frac{|\mathbf{y}|}{r})^2}^{(1+\frac{|\mathbf{y}|}{r})^2} d\tau \tau^{-\frac{1}{2}} = \frac{1}{r} \frac{r}{2|\mathbf{y}|} \tau^{\frac{1}{2}} \Big|_{(1-\frac{|\mathbf{y}|}{r})^2}^{(1+\frac{|\mathbf{y}|}{r})^2} \\ &= \frac{1}{r}. \end{aligned} \quad \square$$

The following proposition (Thm.9.7 in [14]) comprises two statements of relevance. The first one is that (3.1) makes sense for charge distributions. The second one is a fundamental property of potentials proportional to inverse length<sup>1</sup> and goes back to I. Newton. We shall give further comments after the proof.

**Proposition 3.1.6.** *Let  $\mu$  be a charge distribution with potential function  $\Phi$ . Then*

- (i)  $\Phi \in L^1_{loc}(\mathbb{R}^3)$  (i.e.  $\Phi$  is integrable on every compact subset of  $\mathbb{R}^3$ ). In particular  $\Phi(\mathbf{x})$  is finite for Lebesgue-a.e.  $\mathbf{x} \in \mathbb{R}^3$ .
- (ii) If we assume that  $\mu$  is spherically symmetric with respect to the origin (i.e. rotations around  $(0, 0, 0)$  are measure-preserving), then

$$\Phi(\mathbf{x}) = \frac{1}{|\mathbf{x}|} \int_{|\mathbf{y}| \leq |\mathbf{x}|} \mu(d\mathbf{y}) + \int_{|\mathbf{y}| > |\mathbf{x}|} \mu(d\mathbf{y}) \frac{1}{|\mathbf{y}|}. \quad (3.7)$$

*Proof.* We notice that

$$|\Phi(\mathbf{x})| \leq \int_{\mathbb{R}^3} |\mu(d\mathbf{y})| \frac{1}{|\mathbf{x} - \mathbf{y}|} = \int_{\mathbb{R}^3} (\mu_+(d\mathbf{y}) + \mu_-(d\mathbf{y})) \frac{1}{|\mathbf{x} - \mathbf{y}|}.$$

We can thus restrict our proof to the non-negative measure  $\nu := \mu_+ + \mu_-$ . This allows us to freely use Fubini's Theorem, because  $\frac{1}{|\mathbf{x} - \mathbf{y}|}$  is non-negative as well. Let  $K \subset \mathbb{R}^3$  be compact. We can always find  $R > 0$  such that  $K \subset B_R(0)$ . By monotonicity, it then suffices to consider

$$\begin{aligned} \int_{B_R(0)} d\mathbf{x} \int_{\mathbb{R}^3} \nu(d\mathbf{y}) \frac{1}{|\mathbf{x} - \mathbf{y}|} &= \int_{\mathbb{R}^3} \nu(d\mathbf{y}) \int_{B_R(0)} d\mathbf{x} \frac{1}{|\mathbf{x} - \mathbf{y}|} \\ &= \int_{\mathbb{R}^3} \nu(d\mathbf{y}) \int_0^R dr r^2 \int_{S^2} d\omega \frac{1}{|r\omega - \mathbf{y}|}. \end{aligned}$$

<sup>1</sup>This is also the case for the gravitational potential

By (3.6), the innermost integral gives  $\min\{r^{-1}, |\mathbf{y}|^{-1}\}$ . The  $r$ -integral can then be bounded by  $C_R/(1 + |\mathbf{y}|)$ , with a constant  $C_R > 0$  depending only on  $R$ . This is seen by differentiating cases. For  $|\mathbf{y}| \leq R$ , one can split the integration and drop a negative term in  $|\mathbf{y}|^2$  to get  $C_R = R^2(R+1)/2$ . In the case  $|\mathbf{y}| > R$ , one rewrites  $|\mathbf{y}| = |\mathbf{y}|R(R+1)^{-1} + |\mathbf{y}|(R+1)^{-1}$  and gets  $C_R = R^2(3(1 + R))^{-1}$ . So we can bound the whole expression by

$$C_R \int_{\mathbb{R}^3} \nu(d\mathbf{y}) \frac{1}{1 + |\mathbf{y}|},$$

which is finite because  $\mu_+, \mu_-$  fulfill (3.4).

Now, assume  $\mu$  to be spherically symmetric. For every element of  $\{R \in O(\mathbb{R}^3) \mid R(0) = 0\}$ , the change of variables  $\varphi(\mathbf{y}) := R^{-1}\mathbf{y}$  shows that  $\Phi$  is also spherically symmetric. Therefore we can express  $\Phi$  by its spherical average, invoke Fubini and again use (3.6) to see

$$\begin{aligned} \Phi(\mathbf{x}) &= \frac{1}{4\pi} \int_{\mathbb{R}^3} \mu(d\mathbf{y}) \int_{S^2} d\omega \frac{1}{\|\mathbf{x}\omega - \mathbf{y}\|} \\ &= \frac{1}{4\pi} \int_{\mathbb{R}^3} \mu(d\mathbf{y}) \min \left\{ \frac{1}{|\mathbf{x}|}, \frac{1}{|\mathbf{y}|} \right\}, \end{aligned}$$

which gives the desired result.  $\square$

*Remark 3.1.7.* The following consequence of the second statement is sometimes referred to as *Newton's theorem* or the *screening property* of the Coulomb potential.<sup>2</sup> Consider the case  $\text{supp}(\mu) \subset B_R(0)$  for some  $R > 0$ . Then we see that for all  $\mathbf{x}$  satisfying  $|\mathbf{x}| > R$

$$\Phi(\mathbf{x}) = \frac{Q}{|\mathbf{x}|}, \quad (3.8)$$

where  $Q = \int \mu(d\mathbf{y})$  denotes the total charge. This is just the potential of  $Q\delta(\mathbf{x})$ , i.e. a point carrying charge  $Q$ . If  $\mu$  were the mass density of e.g. the Earth, then the original version of Newton's theorem would state that from above Earth's surface, we cannot distinguish its gravitational attraction from the one of a point particle at its center carrying its entire mass.

We explicitly give an easy consequence which will be our main application of (3.7).

**Corollary 3.1.8** (Point charges have maximal potential). *Let  $\mu$  be a spherically symmetric, positive charge distribution with respect to some  $\mathbf{x}_0 \in \mathbb{R}^3$ . Let  $Q := \int_{\mathbb{R}^3} \mu(d\mathbf{y})$ .*

*Then*

$$\Phi(\mathbf{x}) \leq \frac{Q}{|\mathbf{x} - \mathbf{x}_0|}, \quad \forall \mathbf{x} \in \mathbb{R}^3. \quad (3.9)$$

<sup>2</sup>The term 'screening' was already used in the introduction. It refers to the important fact that a collection of point charges of different sign has a decreased effective charge (and thus interaction strength), when viewed from afar. This can be seen from (3.8) by replacing  $Q$  with some  $Q_{eff}$  satisfying  $|Q_{eff}| < |Q|$ . The term originates from the effect, which occurs when a point charge is placed in a dielectric medium. The alignment of the elementary dipoles of the medium then results in an effective shielding of the point charge from its environment (referring to charges on greater length scales). For more on screening, see [9], p.68.

*Proof.* For  $\mathbf{x}_0 = 0$  this follows immediately from (3.7). The general case follows by translational invariance.  $\square$

Now, we have acquired all necessary results for potentials of charge distributions, particularly of spherically symmetric ones. It is now time to come back to the Coulomb energy defined in (3.2). The following theorem fulfills all wishes about  $D$  as it turns out to not only to be well-defined and finite for charge distributions, it is actually positive definite.<sup>3</sup> Clearly it is also symmetric and bilinear, i.e. a scalar product.

**Theorem 3.1.9** (Positive Semi-Definiteness of the Coulomb Potential). *Let  $\mu$  be a charge distribution. Then*

$$0 \leq D(\mu, \mu) < \infty. \quad (3.10)$$

*Moreover, we have a Cauchy-Schwarz type inequality for  $D$ , i.e. for any two charge distributions  $\mu, \nu$  it holds that*

$$|D(\mu, \nu)|^2 \leq D(\mu, \mu)D(\nu, \nu). \quad (3.11)$$

Before we prove the theorem, we explicitly give the main statement for this version of the proof.

**Lemma 3.1.10.** *Let  $\mathbf{x}, \mathbf{y} \in \mathbb{R}^3$ . There exists a constant  $C > 0$  such that*

$$\frac{1}{|\mathbf{x} - \mathbf{y}|} = C \int_{\mathbb{R}^3} d\mathbf{z} \frac{1}{|\mathbf{x} - \mathbf{z}|^2} \frac{1}{|\mathbf{y} - \mathbf{z}|^2} \quad (3.12)$$

*Proof.* Consider the right hand side of (3.12) as a function  $g(\mathbf{x}, \mathbf{y})$ . The fact that  $g$  is translation and rotation invariant follows directly from the same statement for the Lebesgue measure and appropriate substitutions. Thus,  $g$  depends only on  $|\mathbf{x} - \mathbf{y}|$ . Furthermore, both sides are homogeneous of degree  $-1$  (or more nicely put: both scale as  $1/\text{length}$ ), therefore, they must agree up to a constant factor.  $\square$

*Proof of Theorem 3.1.9.* We wish to use (3.12) with Fubini. For this purpose, we write  $\mu = \mu_+ - \mu_-$ , where  $\mu_{\pm}$  are non-negative by definition. By linearity and symmetry, we can write

$$D(\mu, \mu) = D(\mu_+, \mu_+) + D(\mu_-, \mu_-) - 2D(\mu_+, \mu_-). \quad (3.13)$$

The first two terms on the right hand side are finite, because  $\mu$  is a charge distribution. So, it suffices to consider the third term. Applying (3.12), Fubini's theorem and the

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<sup>3</sup>In the following theorem, we will only show that  $D$  is positive semi-definite, as this is all we need. For the complete version, see Thm. 9.8 in [14].

Cauchy-Schwarz inequality gives

$$\begin{aligned}
D(\mu_+, \mu_-) &= \frac{C}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mu_+(d\mathbf{x}) \mu_-(d\mathbf{y}) \left( \int_{\mathbb{R}^3} d\mathbf{z} \frac{1}{|\mathbf{x} - \mathbf{z}|^2} \frac{1}{|\mathbf{y} - \mathbf{z}|^2} \right) \\
&= \frac{C}{2} \int_{\mathbb{R}^3} d\mathbf{z} \left( \int_{\mathbb{R}^3} \mu_+(d\mathbf{x}) \frac{1}{|\mathbf{x} - \mathbf{z}|^2} \right) \left( \int_{\mathbb{R}^3} \mu_-(d\mathbf{x}) \frac{1}{|\mathbf{x} - \mathbf{z}|^2} \right) \\
&\leq \frac{C}{2} \left( \sqrt{\int_{\mathbb{R}^3} d\mathbf{z} \left( \int_{\mathbb{R}^3} \mu_+(d\mathbf{x}) \frac{1}{|\mathbf{x} - \mathbf{z}|^2} \right) \left( \int_{\mathbb{R}^3} \mu_+(d\mathbf{y}) \frac{1}{|\mathbf{y} - \mathbf{z}|^2} \right)} \cdot [\mu_+ \leftrightarrow \mu_-] \right) \\
&= \frac{1}{2} \left( \sqrt{2D(\mu_+, \mu_+)} \sqrt{2D(\mu_-, \mu_-)} \right),
\end{aligned}$$

which is (3.11) and shows that each term on the right hand side in (3.13) is finite, i.e.  $D(\mu, \mu)$  is well-defined and  $|D(\mu, \mu)| < \infty$ . If we replace  $\mu_+$  and  $\mu_-$  by  $\mu$  in the second line of the above calculation, we can easily see that  $D(\mu, \mu) \geq 0$ .  $\square$

*Remark 3.1.11.* There is a more illuminating fashion to show the result, without use of (3.12). We will not introduce any of the following concepts in this work, but we mention that the same result can be obtained by using the fact that the Coulomb kernel is the Green's function of the Laplacian, namely

$$-\Delta \frac{1}{|\mathbf{x}|} = 4\pi\delta, \quad (3.14)$$

as well as Fourier transform for measures and a representation formula for the regularized resolvent kernel of the Laplacian (also called the Yukawa potential) in Fourier space, namely (6.30). The result is

$$D(\mu_+, \mu_-) = \frac{1}{8\pi} \int_{\mathbb{R}^3} d\mathbf{p} \frac{\overline{\mu_+(\mathbf{p})} \mu_-(\mathbf{p})}{(2\pi p)^2}, \quad (3.15)$$

to which a Cauchy-Schwarz estimate can be readily applied.

Note that  $\delta$  really is a distribution. We will not define precisely what this means (cf. Chapter 6 of [14]), but rather treat  $\delta$  symbolically, i.e. we say that (3.14) holds in the *distributional sense*. Then, it is only meaningful when both sides are integrated with the derivatives applied to appropriate test functions, namely the  $C_c^\infty$ -functions (equipped with a strong notion of convergence). See also the definition of the weak derivative in section 2.3.3.

The main point of the above remark was to introduce (3.14), which will be used in Chapters 5 and 9. For this reason<sup>4</sup>, the elementary proof is given on page 23 of [8] and the shorter version (using distributions and thus treating  $\delta$  not just symbolically) is theorem 6.20 in [14].

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<sup>4</sup>Another reason is that the calculation of the Green's function of the Coulomb kernel essentially solves the problem to determine the potential from a given charge distribution, which is in some sense the main point of electrostatics.

## 3.2 The Atomic Coulomb Potential

Let us now consider a system at the atomic level with arbitrary, but finite particle numbers.

We are given  $N$  electrons and  $M$  nuclei with position vectors  $\underline{\mathbf{x}} = (\mathbf{x}_1, \dots, \mathbf{x}_N) \in \mathbb{R}^{3N}$  and  $\underline{\mathbf{R}} = (\mathbf{R}_1, \dots, \mathbf{R}_M) \in \mathbb{R}^{3M}$ , respectively. The electrons all have the same charge given by  $q_{el} = -e$  and the nuclei have a charge vector  $\underline{q}_{nuc} = e\underline{Z}$  with  $\underline{Z} = (Z_1, \dots, Z_M) \in \mathbb{R}_+^M$  (of course, in nature the nuclear charges would be non-negative multiples of the electron charge  $e = 1.6021 \cdot 10^{-19}$  Ampère seconds, so all  $Z_i \in \mathbb{N}_0$ ). Both, electrons and nuclei, participate in the two-particle interaction given by the electrostatic force, as they are represented by the following self-explanatory charge distributions<sup>5</sup>

$$\begin{aligned}\varrho_k^{nucl}(\mathbf{x}) &:= eZ_k\delta_{\mathbf{R}_k} \\ \varrho^{nucl}(\mathbf{x}) &:= \sum_{k=1}^M \varrho_k^{nucl}(\mathbf{x}) \\ \varrho_i^{el}(\mathbf{x}) &:= -e\delta_{\mathbf{x}_i} \\ \varrho^{el}(\mathbf{x}) &:= \sum_{i=1}^N \varrho_i^{el}(\mathbf{x}).\end{aligned}$$

We then consider the Coulomb energy of the aggregate system, defined as

$$\begin{aligned}V_C(\underline{\mathbf{x}}, \underline{\mathbf{R}}) &:= \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} - \sum_{i=1}^N \sum_{k=1}^M \frac{Z_k}{|\mathbf{x}_i - \mathbf{R}_k|} + \sum_{1 \leq k < l \leq M} \frac{Z_k Z_l}{|\mathbf{R}_k - \mathbf{R}_l|} \\ &=: I(\underline{\mathbf{x}}) + W(\underline{\mathbf{x}}, \underline{\mathbf{R}}) + U(\underline{\mathbf{R}}).\end{aligned}\tag{3.16}$$

We can understand how (3.16) originates from the charge distributions given above, by looking at the formal expression

$$\begin{aligned}e^2 V_C(\underline{\mathbf{x}}, \underline{\mathbf{R}}) &= \left( D(\varrho^{el}, \varrho^{el}) - \sum_{i=1}^N D(\varrho_i^{el}, \varrho_i^{el}) \right) + D(\varrho^{el}, \varrho^{nucl}) \\ &\quad + \left( D(\varrho^{nucl}, \varrho^{nucl}) - \sum_{k=1}^M D(\varrho_k^{nucl}, \varrho_k^{nucl}) \right).\end{aligned}$$

The parentheses suggest to interpret  $V_C$  as the sum of the Coulomb energies of all the possible interactions between our charge distributions — take away the (infinite) self-interactions of all the particles.

*Remark 3.2.1.* (i) Recall that  $e^2 V_C$  gives the potential energy of the system, as discussed in Section 2.2.

(ii) The three terms given in (3.16) represent all possible pairings of the  $N$  electrons and the  $M$  nuclei.  $I$  is the electron-electron repulsion,  $W$  is the electron-nucleus attraction (note the negative sign) and  $U$  is the nucleus-nucleus repulsion.

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<sup>5</sup>Actually, they are the density of a charge distribution with respect to Lebesgue measure  $d\mathbf{x}$ , but we will drop the  $d\mathbf{x}$  in the considerations above.

- (iii) In the real world  $m_{nuc} = 1.6726 \cdot 10^{-27} \text{kg} \gg 9.1094 \cdot 10^{-31} = m_{el}$ , so for our problem the nuclei have an effectively infinite mass. Even if they are dynamic, they will change position so slowly, that the electrons will immediately adapt to the new charge configuration after each infinitesimal movement of the nuclei. This is implemented by treating the nucleus positions  $\mathbf{R}$  as fixed, but arbitrary, parameters and is called the *Born-Oppenheimer approximation*. Only the electrons will be represented by a quantum-mechanical wave function. To prove stability results for all configurations of nuclei, we will have to find  $\mathbf{R}$ -independent bounds.

In the following, we choose  $V = V_C$  in (2.16) and call the resulting  $H_{N,M}$  the *non-relativistic Coulomb (or: atomic) Hamiltonian*.

### 3.3 A note on units

Now that we have introduced all relevant units for our problem, we shall simplify our formulas considerably by working in „natural“ units, i.e. we set

$$\hbar = m_{el} = c = 1, \quad (3.17)$$

where, for the sake of completeness, we have included the *speed of light*  $c = 2.998 \cdot 10^8 \frac{\text{meters}}{\text{second}}$ . In these units, length has units of time or inverse energy or inverse mass. All of this is meant in the sense that we rescale all arguments carrying a dimension appropriately, before we compute quantitative results. A more profound explanation is given in Section 2.1.7 of [16].

We remark that in our units, the electron charge considered above is equal to the square root of the *dimensionless* fine-structure constant given by

$$\alpha := \frac{e^2}{\hbar c} = \frac{1}{137.04}. \quad (3.18)$$

To conclude, we give the form of our Hamiltonian as given in (2.16) in the new convention

$$H_{N,M} = -\frac{1}{2} \sum_{i=1}^N \Delta_i + \sqrt{\alpha} V_C(\mathbf{x}, \mathbf{R}), \quad (3.19)$$

where  $V_C$  is given by (3.16) and  $\Delta_i$  denotes the Laplacian acting only on the  $i$ -particle<sup>6</sup>

This finishes our discussion of electrostatics for the moment. We have in fact already developed the necessary tools to prove the electrostatic inequalities required for the proof of stability. However, we still need to develop the formalism for many-body quantum mechanics in order to calculate the expectation values of our  $V_C$  and to grasp the stability issue through an appropriate definition. Also, we would like to clarify the need for the electrostatic inequalities, before discussing them in Chapter 5.

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<sup>6</sup>This will become more clear in the next Chapter, where we introduce  $N$ -particle spaces as the tensor product of 1-particle spaces. Then the honest notation would be  $\Delta_i = \mathbb{I} \otimes \dots \otimes \Delta \otimes \dots \mathbb{I}$ , where  $\Delta$  stands at the  $i$ -th place and  $\mathbb{I}$  is the identity on the one-particle space.

# Chapter 4

## Mathematical Preliminaries

In this chapter, we will begin by proving stability of the first kind for one-particle systems by using Sobolev's inequality from the theory of partial differential equations. Then, we will introduce the two kinds of statistics quantum particles can follow and subsequently develop the basic tools needed for the analysis of many-body quantum systems, namely density matrices. In the end, we give the precise definition of stability of the second kind.

### 4.1 Basic Inequalities and Stability of the First Kind

Recall the definition of the ground state energy  $E_0$  in (2.23). With this we can directly go on to

**Definition 4.1.1** (Stability of the first kind). Let  $H$  be a one-particle Hamiltonian. We say that the system defined by  $H$  fulfills the *stability of the first kind*, iff

$$E_0 > -\infty \tag{4.1}$$

We begin the discussion of stability of the first kind, by stressing the obvious fact that the classical Hamilton function  $H(\mathbf{x}, \mathbf{p})$  with  $V = Z/|\mathbf{x}|, Z > 0$  is unstable of the first kind (in the sense that it is not bounded from below, as a function). This is due to the fact that — classically — nothing prevents us from making  $\mathbf{x}$  and  $\mathbf{p}$  simultaneously small. Thus, the hydrogenic atom is unstable classically as stated in Chapter 1.3.

We have already seen the mechanism which yields the stability result for one-particle quantum systems. It is the complementary uncertainty in momentum and position that forbids us to repeat the procedure of the classical case. This is reminiscent of Heisenberg's uncertainty principle introduced in (2.12). However, it is only the idea of a general *uncertainty principle* that is useful, i.e. an inequality which prohibits to localize a particle in position space without its kinetic energy (which is non-negative) increasing simultaneously. The reason why (2.12) itself is not terribly useful, is that (in the  $H^1$  sense) one can easily make  $\Delta\mathbf{x}$  arbitrarily large (while leaving  $\Delta\mathbf{p}$  almost unchanged) by adding a small contribution to any state  $\psi$  at a point  $\mathbf{y}$  which is then sent to infinity. We will not give the details, which can be found on page 26 of [16].

Instead, we go on to an uncertainty principle much better suited for our goals. We give the theorem without proof, a slightly stronger version is shown in [14], Thm 8.3.

**Theorem 4.1.2** (Sobolev's inequality for  $H^1$ ). Let  $\psi \in H^1(\mathbb{R}^3)$ . Then we have

$$\|\nabla\psi\|_2^2 \geq S_3\|\psi\|_6^2, \tag{4.2}$$

where  $S_3 := \frac{3}{4}(4\pi^2)^{2/3}$  is the optimal constant.

*Remark 4.1.3.* (i) Note that  $2T_\psi = \|\nabla\psi\|_2^2$ .

(ii) The fact that the  $L^6$ -norm is the natural norm on the right hand side of (4.2) follows immediately from a scaling analysis (i.e. replacing  $\psi$  by  $\psi_\lambda(\mathbf{x}) := \psi(\lambda\mathbf{x})$  on both sides and requiring that the dependence on the parameter  $\lambda$  vanishes).

(iii) The fact that  $S_3$  is optimal can be shown through symmetric decreasing rearrangement inequalities, an elementary exposition can be found in [20].

For the sake of completeness, we also give the well-known

**Theorem 4.1.4** (Hölder's Inequality). *Let  $p \in [1, \infty]$  and  $q$  such that  $\frac{1}{p} + \frac{1}{q} = 1$ . Take  $f \in L^p(\mathbb{R}^3)$  and  $g \in L^q(\mathbb{R}^3)$ . Then*

$$\|fg\| \leq \|f\|_p \|g\|_q. \quad (4.3)$$

With these two inequalities we can continue to prove stability of the first kind for an entire class of one-particle potentials.<sup>1</sup>

**Theorem 4.1.5** (Stability for one-particle potentials). *Let  $V \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ . (This means that there exist  $v \in L^{3/2}(\mathbb{R}^3)$ ,  $w \in L^\infty(\mathbb{R}^3)$  such that  $V(\mathbf{x}) = v(\mathbf{x}) + w(\mathbf{x})$ . Then  $E_0 > -\infty$  and we have the estimate*

$$T_\psi \leq C\mathcal{E}(\psi) + D\|\psi\|_2^2, \quad (4.4)$$

where the constants  $C, D$  depend only on  $V$ .

*Proof.* Without loss of generality, assume  $\|\psi\|_2 = 1$ . Let  $V(\mathbf{x}) = v(\mathbf{x}) + w(\mathbf{x})$  with  $v \in L^{3/2}(\mathbb{R}^3)$ ,  $w \in L^\infty(\mathbb{R}^3)$ . We first prove that we can find  $\lambda \in \mathbb{R}_-^2$  such that  $h(\mathbf{x}) := -[v(\mathbf{x}) - \lambda]_- := -\min\{v(\mathbf{x}) - \lambda, 0\}$  has the property

$$\|h(\mathbf{x})\|_{3/2} \leq \frac{S_3}{4}. \quad (4.5)$$

To show this, assume without loss of generality that  $v \leq 0$ . Then we have that

$$\begin{aligned} \int_{\mathbb{R}^3} d\mathbf{x} (-[v(\mathbf{x}) - \lambda]_-)^{3/2} &= \int_{\{v \leq \lambda\}} d\mathbf{x} \underbrace{(|v(\mathbf{x})| - |\lambda|)^{3/2}}_{\geq 0} \\ &\leq \int_{\{|v|^{3/2} \geq |\lambda|^{3/2}\}} d\mathbf{x} |v(\mathbf{x})|^{3/2}, \end{aligned}$$

where we have used the notation  $\{v \geq \lambda\} := \{\mathbf{x} \mid |v(\mathbf{x})| \geq |\lambda|\}$ . Now, the last line can be made arbitrarily small by picking  $|\lambda|$  large enough, because  $v^{3/2} \in L^1(\mathbb{R}^3)$ . This shows

<sup>1</sup>An overview on the possible results of this type for arbitrary dimensions and in the relativistic case can be found on page 273 of [14].

<sup>2</sup>The reason why all considered objects are negative will become apparent in a moment. It is due to the fact that we will make an estimate of the form  $v - \lambda \geq -[v - \lambda]_-$

(4.5). Next, we use Sobolev's inequality followed by Hölder's inequality and (4.5) to get

$$\begin{aligned} T_\psi &\geq \frac{S_3}{2} \|\psi\|_6^2 = \frac{S_3}{2} \left( \int_{\mathbb{R}^3} d\mathbf{x} \psi(\mathbf{x})^6 |h(\mathbf{x})|^3 |h(\mathbf{x})|^{-3} \right)^{1/3} \\ &\geq \frac{S_3}{2 \|h\|_{\frac{3}{2}}} \underbrace{\langle \psi, |h|\psi \rangle}_{=-h_\psi \geq 0} \\ &\geq (-2)h_\psi. \end{aligned}$$

With this we can conclude, using  $v(\mathbf{x}) - \lambda \geq h(\mathbf{x})$ , that

$$\begin{aligned} \mathcal{E}(\psi) = T_\psi + V_\psi &\geq T_\psi + h_\psi + \lambda + w_\psi \\ &\geq \frac{1}{2}T_\psi + \lambda - \|w\|_\infty \end{aligned}$$

Since  $T_\psi \geq 0$ , this implies  $E_0 \geq \lambda - \|w\|_\infty > -\infty$ . The domination of the kinetic energy follows immediately from the last step.  $\square$

We observe the obvious, but important fact that

$$\frac{1}{|\cdot|} \in L^{\frac{3}{2}}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3). \quad (4.6)$$

So we have shown in particular, that the ground state energy of the hydrogenic atom with quadratic form given by

$$\mathcal{E}(\psi) = T_\psi + \left( \frac{1}{|\cdot|} \right)_\psi = \frac{1}{2} \int_{\mathbb{R}^3} d\mathbf{x} \left( |\nabla\psi(\mathbf{x})|^2 - \frac{Z\alpha}{|\mathbf{x}|} |\psi(\mathbf{x})|^2 \right) \quad (4.7)$$

is stable of the first kind. We remark that this can also be shown directly by calculating a commutator involving a derivative. This is done e.g. in [20] and even yields  $E_0 = -\frac{Z^2}{4}$ .

The above result, as mentioned in the introduction, was a triumph of early quantum mechanics.

## 4.2 Description of Many-Body Systems

We begin by explaining spin, which is not relevant to us in the one particle case, since we neglect the fine-structure and no external magnetic fields are present. Spin will become important when we introduce the symmetry classes of quantum particles.

### 4.2.1 Spin

It is a deep consequence of relativistic quantum field theory,<sup>3</sup> that a particle has further internal degrees of freedom. These correspond to an angular momentum. Its absolute

<sup>3</sup>For electrons, this follows directly from the reducibility of solutions to the Dirac equation, see e.g. [22].

value can be characterised by a dimensionless quantity, which is denoted by  $S$  and is quantized to take on only positive half-integer values, i.e.

$$S \in \{0, \frac{1}{2}, 1, \frac{3}{2}, \dots\}. \quad (4.8)$$

We call the value of  $S$  the *spin* of the particle. A complete set of spin-observables includes the spin component in a fixed direction, which is taken to be the spin in the  $z$  direction  $S_z$ . This component is also quantized and assumes values according to  $S_z \in \{-S, -S + 1, \dots, S\}$ .

This is the usual physical notation. We will denote by  $q = 2S + 1 \in \mathbb{N}$  the number of different spin values, the so-called *spin-degeneracy* of the particle.  $q$  is a characteristic of each particle type, it is  $q = 2$  for electrons. Then  $\sigma$  will play the role of  $S_z$ , i.e.

$$\sigma \in \{1, \dots, q\} \quad (4.9)$$

To each possible  $\sigma$ , there exists one possible eigenstate with exactly this spin value. Therefore, the particle carries a  $q$ -dimensional internal Hilbert space, in addition to its spatial one. As wave functions are complex-valued, so are their coefficients in linear combinations, and we see that we really have to consider

$$\mathcal{H}_1 := L^2(\mathbb{R}^3; \mathbb{C}^q) := L^2(\mathbb{R}^3) \otimes \mathbb{C}^q. \quad (4.10)$$

*Remark 4.2.1.* (i) For an outlook of tensor products of Hilbert spaces, see Section II.4 of [23].

- (ii) A wave function in  $\mathcal{H}_1$  can be thought of as an  $L^2$ -function with values in  $\mathbb{C}^q$ . Therefore, it is often written in vector notation and then called a *spinor*. In case of electrons, spin can then be represented through the famous Pauli matrices, which is particularly useful when considering systems involving a magnetic field.
- (iii) For the purpose of analyzing stability, one can replace  $L^2$  with  $H^1$  in the above definition. As discussed in 2.3.3, this corresponds to a restriction to states with finite kinetic energy.
- (iv) Of course, we will mostly be considering electrons with  $q = 2$ . However, it is not only interesting to follow the  $q$ -dependence (in particular for the LT inequalities discussed in Chapter 6), we will also see in a moment that bosons will correspond to the  $q = N$  case. Therefore, we continue to work with an arbitrary value of  $q$ .

We will not use the spinor notation, but rather write

$$\mathbf{z} = (\mathbf{x}, \sigma) \quad (4.11)$$

which enables us to compactly talk about  $\psi(\mathbf{z}) \in \mathcal{H}_1$ . We remark on the fact that the normalization condition now involves the scalar product on  $\mathbb{C}^q$ .

## 4.2.2 Many-body Wave Functions

### Formalism

The generalization of the concept of a wave function to the many-body case is evident. The main problem is to find an easy notation. We follow the one in [16], though we refrain from generalizations unnecessary for our purposes.

**Definition 4.2.2** (Many-body systems). The  $N$ -particle Hilbert space<sup>4</sup> is given by

$$\mathcal{H}_N := \bigotimes_{i=1}^N \mathcal{H}_1 \cong L^2(\mathbb{R}^{3N}; \mathbb{C}^{q^N}). \quad (4.12)$$

The elements of  $\mathcal{H}_N$  are of the form (abusing the notation for the arguments of  $\psi$ )

$$\psi(\underline{\mathbf{z}}) := \psi(\mathbf{z}_1, \dots, \mathbf{z}_N) = \psi(\mathbf{x}_1, \sigma_1, \dots, \mathbf{x}_N, \sigma_N) \quad (4.13)$$

and are called  $N$ -particle wave functions. For an  $f \in \mathcal{H}_1$ , we write

$$\int d\mathbf{z}_i f(\mathbf{z}_i) := \sum_{\sigma_i=1}^q \int_{\mathbb{R}^3} d\mathbf{x}_i f(\mathbf{x}_i, \sigma_i). \quad (4.14)$$

The normalization condition then becomes

$$\|\psi\|_2^2 := \int d\underline{\mathbf{z}} |\psi(\underline{\mathbf{z}})|^2 = \int \dots \int d\mathbf{z}_1 \dots d\mathbf{z}_N |\psi(\mathbf{z}_1, \dots, \mathbf{z}_N)|^2 = 1. \quad (4.15)$$

*Remark 4.2.3.* (i) The  $\psi \in \mathcal{H}_N$  can be thought of as  $q^N$  functions in  $L^2(\mathbb{R}^3)$ , labelled by the  $\{\sigma_i\}_{i \in \{1, \dots, N\}}$ .

(ii) The interpretation of  $|\psi|^2$  stays probabilistic: It gives the probability to find particle 1 at position  $\mathbf{x}_1$ , carrying spin  $\sigma_1$  and particle 2 at position  $\mathbf{x}_2$ , carrying spin  $\sigma_2$  and so on. Note however, that  $|\psi|^2$  is now a density function of  $2N$  arguments, thus we cannot interpret it as a physical particle density at some point  $\mathbf{x} \in \mathbb{R}^3$ . This is possible, though, by calculating the *marginal distribution* of  $|\psi|^2$  and doing the spin sum. This is done in the following.

**Definition 4.2.4** (One-particle density). We denote

$$\varrho_\psi^i(\mathbf{x}) := \sum_{\sigma_i=1}^q \int \dots \int d\mathbf{z}_1 \dots \widehat{d\mathbf{z}_i} \dots d\mathbf{z}_N |\psi(\mathbf{z}_1, \dots, (\mathbf{x}, \sigma_i), \dots, \mathbf{z}_N)|^2, \quad (4.16)$$

where the hat indicates that the corresponding integration is *not* performed. We note that  $\varrho_\psi^i(\mathbf{x})$  is the probability density to find the  $i$ -th particle at the point  $\mathbf{x}$ . We call

$$\varrho_\psi(\mathbf{x}) := \sum_{i=1}^N \varrho_\psi^i(\mathbf{x}) \quad (4.17)$$

the *one-particle density*<sup>5</sup> associated with  $\psi$ .

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<sup>4</sup>Note that  $\bigotimes_{i=1}^N \mathbb{C}^q \cong \mathbb{C}^{q^N}$ , not to  $\mathbb{C}^{qN}$ .

<sup>5</sup>Clearly  $\int_{\mathbb{R}^3} d\mathbf{x} \varrho_\psi(\mathbf{x}) = N$ , reflecting the fact that the total number of particles is  $N$ .

### Indistinguishability: Bosons and Fermions

There is another peculiar fact about the quantum world, which we have not yet mentioned, namely:

*Quantum particles are fundamentally indistinguishable.*

This means, that we have no means to identify an electron with its position in the argument list of an  $N$ -particle wave function. Consequently, an  $N$ -particle wave function must give the same predictions upon exchange of two argument values, i.e. of two identical particles. As noted in 2.3.3, this implies that

$$\psi(\dots, \mathbf{z}_i, \dots, \mathbf{z}_j, \dots) = e^{i\chi} \psi(\dots, \mathbf{z}_j, \dots, \mathbf{z}_i, \dots), \quad (4.18)$$

for any  $i, j \in \{1, \dots, N\}$ <sup>6</sup>. Let us make a heuristical consideration: When we exchange the  $i$ -th and the  $j$ -th argument of  $\psi$  twice, we regain the original order of arguments. This double exchange thus „should“ not alter the value of  $\psi$  at all — not even up to a phase factor. This leads us to suppose that  $e^{i\chi} \in \{1, -1\}$ . It is a fact of Nature, that this is indeed the case.

**Definition 4.2.5** (Bosons and fermions). The behaviour of the  $N$ -particle wave function under the exchange of two arguments is characteristic of the described particles.<sup>7</sup> Let  $i, j \in \{1, \dots, N\}$ . The wave functions satisfying

$$\psi(\dots, \mathbf{z}_i, \dots, \mathbf{z}_j, \dots) = \psi(\dots, \mathbf{z}_j, \dots, \mathbf{z}_i, \dots), \quad (4.19)$$

are called (*totally*) *symmetric*. The corresponding identical particles are called *bosons*. The ones for which

$$\psi(\dots, \mathbf{z}_i, \dots, \mathbf{z}_j, \dots) = -\psi(\dots, \mathbf{z}_j, \dots, \mathbf{z}_i, \dots) \quad (4.20)$$

holds, are called (*totally*) *antisymmetric* wave functions and their corresponding identical particles are named *fermions*. One can make the obvious generalizations for wave functions in which both types of symmetries appear in the arguments.

*Remark 4.2.6.* (i) Observe that in either case,  $\varrho_\psi$  given in (4.17) is (totally) symmetric in its arguments.

(ii) It is an early consequence of relativistic quantum field theory, that bosons correspond to even spin numbers  $q$ , while fermions correspond to odd ones. This fact is called the *spin-statistics theorem* (see e.g. Section 4 in [27]).

The most important consequence of (4.20) is the famous *Pauli exclusion principle* (short: Pauli principle), which says that no two identical fermions can occupy the same state, in the sense that an antisymmetric wave function which is symmetric in two of its arguments must vanish. As we already remarked, electrons have  $q = 2$ , so they must be fermions by the spin-statistics theorem.<sup>8</sup> Thus, they follow the Pauli principle. Nuclei can be either bosons or fermions, which one is determined by summing the spins of their constituents, i.e. the nucleons.

At this point, it is natural to consider the operators given by

<sup>6</sup>The easy modelling of the particle exchange given here is one of the conveniences of our notation.

<sup>7</sup>In physics, it is called the *statistics* the particle follows.

<sup>8</sup>We also now this directly from experiments.

**Definition 4.2.7.** Let  $\phi \in \mathcal{H}_N$ . We define the *symmetrization* and the *antisymmetrization operator* by their respective action<sup>9</sup> on  $\phi$

$$\mathcal{S}[\phi(\mathbf{z}_1, \dots, \mathbf{z}_N)] := \sum_{\pi \in \mathcal{S}_N} \phi(\mathbf{z}_{\pi(1)}, \dots, \mathbf{z}_{\pi(N)}) \quad (4.21)$$

$$\mathcal{A}[\phi(\mathbf{z}_1, \dots, \mathbf{z}_N)] := \sum_{\pi \in \mathcal{S}_N} \text{sgn}(\pi) \phi(\mathbf{z}_{\pi(1)}, \dots, \mathbf{z}_{\pi(N)}). \quad (4.22)$$

We see that  $\mathcal{S}[\phi]$  is bosonic and  $\mathcal{A}[\phi]$  is fermionic (when appropriately normalized). We denote their respective range by  $R(\mathcal{S}) =: \mathcal{S}_{i=1}^N \mathcal{H}_1 =: \mathcal{H}_N^{(b)}$ , the *symmetric (N-fold) tensor product*; and  $R(\mathcal{A}) =: \bigwedge_{i=1}^N \mathcal{H}_1 =: \mathcal{H}_N^{(f)}$ , the *antisymmetric (N-fold) tensor product* of  $\mathcal{H}_1$ .

Let us pause to consider two examples of physical wave function, which are widely used in chemistry and solid-state physics, namely product wave functions. Fix a set of normalized  $f_i \in \mathcal{H}_1, i = 1, \dots, N$  and define

$$\phi(\mathbf{z}) := \prod_{i=1}^N f_i(\mathbf{z}_i). \quad (4.23)$$

Surely,  $\mathcal{S}[\phi]$  is bosonic. If we take all the  $f_i$  to be the same, then  $\mathcal{S}[\phi] = N! \phi$  and  $\frac{1}{\sqrt{N!}} \phi$  is an easy example of a bosonic  $N$ -particle wave function. Furthermore,

$$\frac{1}{\sqrt{N!}} \mathcal{A}[\phi(\mathbf{z}_1, \dots, \mathbf{z}_N)] = \frac{1}{\sqrt{N!}} \det\{f_i(\mathbf{z}_j)\}_{i,j=1}^N \quad (4.24)$$

is a normalized fermionic  $N$ -particle wave function called a *Slater determinant*. It can be thought of as the closest one can get to a product wave function when considering fermions.<sup>10</sup> There is much more one could add here, but we finish the discussion by mentioning the fact that the Slater determinants form a basis of the space of antisymmetric functions. This is a main motivation for their study.

### 4.2.3 Density Matrices

Before we begin, let us introduce a useful notation from physics.

**Definition 4.2.8** (Dirac bra-ket notation). Let  $\psi, \varphi \in \mathcal{H}_N$ . We define  $|\varphi\rangle\langle\psi|$  to be an operator on  $\mathcal{H}_N$ , which acts on  $\chi \in \mathcal{H}_N$  through

$$|\varphi\rangle\langle\psi|(\chi) := \langle\psi, \chi\rangle \varphi \quad (4.25)$$

#### Physical Motivation of density matrices

When we consider the operator  $|\psi\rangle\langle\psi|$ , we observe that it can be uniquely identified with the entire ray  $[\psi]$ , i.e. it is no longer ambiguous up to a phase factor. Therefore, we might as well consider  $|\psi\rangle\langle\psi|$  as a notion of state.

<sup>9</sup>The  $[\cdot]$  - brackets do *not* signify the ray corresponding to  $\phi$ .

<sup>10</sup>An application of Slater determinants is the procedure referred to as „filling the orbitals“ (of an atom). In that case, the  $f_i$  are orthonormal eigenstates of a one-particle Hamiltonian. The problem about  $\mathcal{A}[\phi]$  is that it does not take into account interactions (it has, after all, product structure). We will come back to this in Section 8.1.

In 2.3.1 we have stressed the fact that the measurement process in quantum mechanics is a manifestation of subjective randomness. On the other hand, we normally do not have access to the precise state of a system. Normally, the best we can hope for is to make a probabilistic model for the possible states our system could be in. However, we cannot construct the whole state as a convex combination of all the possible states, e.g.  $\psi = \frac{1}{2}\psi_1 + \frac{1}{2}\psi_2$ , as this would lead to interference effects between  $\psi_1$  and  $\psi_2$ , which we do not want. On the other hand, when we consider

$$\Gamma := \frac{1}{2}|\psi_1\rangle\langle\psi_1| + \frac{1}{2}|\psi_2\rangle\langle\psi_2|, \quad (4.26)$$

we see that interference is no longer possible and we are dealing with a true *statistical mixture* of the states  $\psi_1, \psi_2$ . This will lead us to call  $\Gamma$  a *density matrix*.<sup>11</sup> With this language, we will call  $|\psi\rangle\langle\psi| =: \Gamma_\psi$  a *pure density matrix*, as it corresponds to a single quantum state.

$\Gamma$  usually describes the whole system we consider, including the environment. Ideally,  $\Gamma$  describes the whole universe. In the atomic case, it describes the simultaneous behaviour of all the  $N$  particles and is still highly complicated. Obviously, we cannot be required to know (or measure) the precise form of  $\Gamma$  — rather, we would like to take its marginal distribution in order to analyse only the small subsystems (i.e. electron pairs<sup>12</sup>) we are interested in. The corresponding operation will be the *partial trace* and the created object will be called a *reduced density matrix*.

## Formalism and Basic Results

Now that the idea has been clarified, we go on to define the corresponding objects. Again, we restrict ourselves only to those needed for further study and avoid unnecessary generalizations. Most of this section will be somewhat informal, as new concepts will closely follow one another.

**Theorem - Definition 4.2.1** (Trace). Let  $\{\phi_n\}_{n \in \mathbb{N}}$  be an orthonormal basis of  $\mathcal{H}_N$  (which is clearly separable) and  $A$  a linear, bounded, self-adjoint and positive<sup>13</sup> operator on  $\mathcal{H}_N$ . Then the *trace of  $A$*  defined by

$$\text{Tr}(A) := \sum_{n=0}^{\infty} \langle \phi_n, A\phi_n \rangle \quad (4.27)$$

is independent of the particular orthonormal basis chosen.

The proof of the statement is trivial, since all terms involved are positive and thus any two infinite sums can be interchanged. It can be found on page 207 of [23].

**Definition 4.2.9** (Density matrix). A linear operator  $\Gamma$  on  $\mathcal{H}_N$  that satisfies

$$\text{Tr}(\Gamma) = 1, \quad (4.28)$$

(in the sense that  $\Gamma$  also fulfills the conditions given above for our definition of the trace, i.e.  $\Gamma$  is positive and self-adjoint) is called an  *$N$ -particle density matrix*. If in addition

$$\Gamma^2 = \Gamma \quad (4.29)$$

then the projection  $\Gamma$  is called a *pure state density matrix*.

<sup>11</sup>Clearly,  $\Gamma$  is really an operator, not a matrix.

<sup>12</sup>Recall that the interaction given by  $V_C$  involves a maximum of two particles at once. We will say more on this later.

<sup>13</sup>This means  $\forall \psi \in \mathcal{H}_N : \langle \psi, A\psi \rangle \geq 0$ .

That  $\Gamma_{pure}$  is a pure state density matrix is equivalent to  $\Gamma_{pure}$  being a rank one operator with exactly one eigenvalue equal to one. Consequently, there exists  $\psi \in \mathcal{H}_N$  (namely the normalized eigenfunction corresponding to eigenvalue one) such that

$$\Gamma_{pure} = \Gamma_\psi := |\psi\rangle\langle\psi|. \quad (4.30)$$

We can see that  $\Gamma$  is a so-called *Hilbert-Schmidt operator*.<sup>14</sup> Since  $\mathcal{H}_N$  is an  $L^2$ -space, this is equivalent with the existence of an  $L^2$ -integral kernel for  $\Gamma$  (which we also denote by  $\Gamma$ ). This means that the density matrix acts on wave functions in the following way

$$(\Gamma\psi)(\mathbf{z}) = \int d\mathbf{z}' \Gamma(\mathbf{z}, \mathbf{z}') \psi(\mathbf{z}'). \quad (4.31)$$

Clearly

$$\Gamma_\psi(\mathbf{z}, \mathbf{z}') = \psi(\mathbf{z}) \overline{\psi(\mathbf{z}')}. \quad (4.32)$$

Even though we shall not treat the spectral theorem explicitly, we now suggest a natural way to think about density matrices in terms of *spectral decomposition*. As it stands, the conditions imposed on a density matrix  $\Gamma$  are sufficient to imply the following eigenfunction expansion in terms of pure state density matrices

$$\Gamma = \sum_{i=1}^{\infty} \lambda_i \Gamma_{\psi_i} = \sum_{i=1}^{\infty} \lambda_i |\psi_i\rangle\langle\psi_i|, \quad (4.33)$$

where the  $\{\psi_i\}_{i \in \mathbb{N}}$  form an orthonormal basis of  $\mathcal{H}_N$ . Also, the family of real  $\{\lambda_i\}_{i \in \mathbb{N}}$  is the set of eigenvalues of  $\Gamma$  and thus satisfies (after appropriate reordering)

$$\lambda_1 \geq \lambda_2 \geq \dots \geq 0, \quad (4.34)$$

$$\sum_{i=1}^{\infty} \lambda_i = \text{Tr}(\Gamma) = 1. \quad (4.35)$$

We gather consequences of (4.33).

- (i) When we step back and review our motivation, we see that  $\Gamma$  is a convex combination of pure states and can thus be interpreted probabilistically.
- (ii) The form of the kernel for general  $\Gamma$  follows from (4.33) and an application of Lebesgue's dominated convergence theorem (using Bessel's inequality)

$$\Gamma(\mathbf{z}, \mathbf{z}') = \sum_{i=1}^{\infty} \lambda_i \psi_i(\mathbf{z}) \psi_i(\mathbf{z}'). \quad (4.36)$$

- (iii) (4.33) gives a way to answer the question of how to get the energy expectation value from a density matrix. We write

$$\mathcal{E}(\Gamma) := \text{Tr}(\Gamma H) := \sum_{i=1}^{\infty} \lambda_i \mathcal{E}(\psi_i), \quad (4.37)$$

---

<sup>14</sup>The notions given here will not be used much in the rest of the work. We give them here quickly and refer to [26] for an overview.  $\Gamma$  is by definition a trace-class operator and therefore also Hilbert-Schmidt.

which is just formal, unless the sum on the right hand side is well-defined. Because of the kinetic term, this certainly requires  $\Gamma$  to satisfy

$$\sum_{i=1}^{\infty} \lambda_i \|\nabla \psi_i\|_2^2 < \infty, \quad (4.38)$$

and such a  $\Gamma$  is called an  $H^1$  *density matrix* (by analogy). We explicitly note the immediate consequence of (4.37) ( $\geq$  is trivial), that

$$E_0 = \inf \{ \mathcal{E}(\Gamma) \mid \Gamma \text{ a density matrix} \}. \quad (4.39)$$

- (iv) (4.33) allows us to speak of a *physical*, i.e. bosonic or fermionic, density matrix  $\Gamma$ , namely when the corresponding  $\{\psi_i\}_{i \in \mathbb{N}}$  follows the respective statistics. Denote by  $\mathcal{D}_N$  the set of all such  $\Gamma$ . In the following, we will always assume  $\Gamma \in \mathcal{D}_N$ .

*Remark 4.2.10.* For considering reduced density matrices, we require to work with the *diagonal part* of the kernel,  $\Gamma(\underline{\mathbf{z}}, \underline{\mathbf{z}})$ . However, the diagonal set  $\{\underline{\mathbf{z}}, \underline{\mathbf{z}}\}$  has Lebesgue measure zero, so the kernel is undefined there, as seen from (4.31). Therefore, we explicitly define  $\Gamma(\underline{\mathbf{z}}, \underline{\mathbf{z}}) := \sum_1^{\infty} \lambda_i |\psi_i(\underline{\mathbf{z}})|^2$ , as in (4.36).<sup>15</sup> This gives the useful formula

$$\text{Tr}(\Gamma) = \int d\underline{\mathbf{z}} \Gamma(\underline{\mathbf{z}}, \underline{\mathbf{z}}). \quad (4.40)$$

### One - Particle Reduced Density Matrices

We restrict ourselves to the simplest non-trivial marginal we can build from a density matrix.

**Definition 4.2.11.** Let  $\Gamma$  be a physical  $N$ -particle density matrix. Then the kernel of its *One - Particle Reduced Density Matrix*  $\gamma^{(1)}$  is

$$\gamma^{(1)}(\mathbf{z}, \mathbf{z}') := N \text{Tr}_{(N-1)} := N \int d\mathbf{z}_2 \dots d\mathbf{z}_N \Gamma(\mathbf{z}, \mathbf{z}_2, \dots; \mathbf{z}', \mathbf{z}_2, \dots, \mathbf{z}_N). \quad (4.41)$$

The corresponding  $\gamma^{(1)}$  then acts on  $\phi \in \mathcal{H}_1$  by

$$(\gamma^{(1)}\phi)(\mathbf{z}) = \int d\mathbf{z}' \gamma^{(1)}(\mathbf{z}, \mathbf{z}') \phi(\mathbf{z}'). \quad (4.42)$$

*Remark 4.2.12.* (i) We say that the variables  $\mathbf{z}_2, \dots, \mathbf{z}_n$  are *integrated out* and the (here only formal) operation  $\text{Tr}_{(N-1)}$  is named taking the *partial trace*. For this definition we needed to define the diagonal part of the kernel.

- (ii) The generalization to a  $k$ -particle reduced density matrix  $\gamma^{(k)}$  for  $k < N$  is obvious, but unneeded in the following. We refer to page 42 of [16] for details. A natural way how to view such  $\gamma^{(k)}$  is in terms of a partial trace  $\text{Tr}_{(N-k)}$ , for a discussion see [21].

- (iii) The prefactor  $N$  implies  $\text{Tr} \gamma^{(1)} = N$  (i.e.  $\gamma^{(1)}$  is not normalized to one). It is a combinatorial factor and stems from the fact that there are  $N$  choices, which variable  $\mathbf{z}$  not to integrate out in (4.41). As  $\Gamma$  is physical, all of these choices give the same result (because each  $\psi_i$  appears quadratically in (4.33)).

<sup>15</sup>For an explicit derivation of this fact using a sophisticated averaging procedure over infinitesimal cubes centered on the diagonal, see [3] and [4].

(iv) Denote

$$\mathcal{D}_N^{(1)} := \{ \delta \in \mathcal{L}(\mathcal{H}_1) \mid \delta \text{ self-adjoint, } \delta \geq 0, \text{Tr}(\delta) = N \}, \quad (4.43)$$

where  $\mathcal{L}(\mathcal{H}_1)$  denotes the set of all bounded linear operators from  $\mathcal{H}_1$  to  $\mathcal{H}_1$ . It is not hard to show that  $\gamma^{(1)} \in \mathcal{D}_N^{(1)}$ . The fact that  $\gamma^{(1)}$  is positive can be seen by using (4.36) and rearranging the integrals appropriately by use of Fubini's theorem (justified by a direct application of the Cauchy-Schwarz inequality).

(v) The diagonal  $\gamma^{(1)}(\mathbf{z}, \mathbf{z})$  is now defined through the diagonal of  $\Gamma$ . On the other hand,  $\gamma^{(1)}$  also has an eigenfunction expansion. One could define the diagonal of the kernel of  $\gamma^{(1)}$  in a similar fashion as before, this would then lead to the question if these two definitions agree. The fact that this is true is shown in [7] by a regularization procedure.

As our coulombic Hamiltonian does not involve a magnetic field, spin is not a quantity of dynamical interest. Therefore it makes sense to simplify matters in the following sense, which can again be understood in terms of a partial trace, this time over the  $\mathbb{C}^q$ -part.

**Definition 4.2.13** (Spin-summed density matrix). We define the kernel

$$\gamma_0^{(1)}(\mathbf{x}, \mathbf{x}') := \sum_{\sigma=1}^q \gamma^{(1)}(\mathbf{x}, \sigma; \mathbf{x}', \sigma) \quad (4.44)$$

and call  $\gamma_0^{(1)}$  the *spin-summed density matrix* corresponding to  $\gamma^{(1)}$ .

Clearly,  $\gamma_0^{(1)}(\mathbf{x}) = \varrho_\psi(\mathbf{x})$ , where  $\varrho_\psi$  was defined in (4.17). We note an obvious consequence of the above definition. It will constitute the main appearance of the parameter  $q$  in all that follows.

**Proposition 4.2.14.** *Let  $\|\gamma^{(1)}\|_\infty$  denote the spectral radius (i.e. the largest eigenvalue) of the density matrix  $\gamma^{(1)}$ . Then*

$$\|\gamma_0^{(1)}\|_\infty \leq q \|\gamma^{(1)}\|_\infty. \quad (4.45)$$

Let  $H = \sum_{i=1}^N h_i$  be a one-particle operator, i.e.  $h_i$  acts only on the  $i$ -th particle (as a fixed  $h$ , which is independent of  $i$ ). This was explained after (3.19). Then, the described particles cannot interact and thus the expectation of  $H$  in any state should not depend on correlations between the particles. The formalism of density matrices provides an illuminating statement of this fact, which will be an important ingredient in our first proof of stability.

**Proposition 4.2.15** (Expectation of one-particle operators). *Let  $\Gamma \in \mathcal{D}_N$  (i.e.  $\Gamma$  is fermionic or bosonic) and  $H = \sum_{i=1}^N h_i$  a one-particle operator with associated quadratic form  $\mathcal{E}$ . Then (under abuse of the Tr-notation)*

$$\mathcal{E}(\Gamma) = \text{Tr}(H\Gamma) = \text{Tr}(h\gamma^{(1)}) \quad (4.46)$$

*If, additionally,  $h$  is independent of spin we get (again abusing the Tr-notation)*

$$\text{Tr}(h\gamma^{(1)}) = \text{Tr}(h\gamma_0^{(1)}). \quad (4.47)$$

*Proof.* When we consider the definition

$$\text{Tr}(H\Gamma) = \sum_{j=1}^{\infty} \lambda_j \int d\mathbf{z} \overline{\psi_j(\mathbf{z})} \sum_{i=1}^N h_i \psi_j(\mathbf{z}),$$

we see that the first statement for the fermionic case follows from the quadratic appearance of  $\psi$  (the bosonic case is trivial) and rearranging. The second statement is obvious.  $\square$

### Admissible One-Particle Density Matrices

Taking the partial trace to get from an  $N$ -particle density matrix  $\Gamma$  to  $\gamma^{(1)} \in \mathcal{D}_N^{(1)}$  is certainly not an injective map. One can ask however, if it is surjective onto  $\mathcal{D}_N^{(1)}$ . We call a  $\gamma \in \mathcal{D}_N^{(1)}$  having a pre-image  $\Gamma$  (i.e.  $\gamma = N\text{Tr}_{(N-1)}\Gamma$ ) *admissible*. The case  $k = 1$  we consider is the only  $k < N$  for which this issue is well-understood. The answer depends heavily on the statistics of  $\gamma$ . In particular, all bosonic  $\gamma \in \mathcal{D}_N^{(1)}$  are admissible.<sup>16</sup> We consider only the fermionic case.

**Theorem 4.2.16** (Admissibility condition for fermionic reduced one-particle density matrices). *Let  $\gamma \in \mathcal{D}_N^{(1)}$ . Then*

$$\exists \Gamma \in \mathcal{D}_N, \Gamma \text{ fermionic} : \gamma = N\text{Tr}_{(N-1)}\Gamma \iff \gamma \leq \mathbb{1}. \quad (4.48)$$

The „ $\Leftarrow$ “ - direction is omitted, it will not be needed in the following. The idea of the proof is to construct  $\Gamma$  as a convex combination of Slater determinants by using a sophisticated re-ordering algorithm for the eigenvalues of  $\gamma$ . The details can be found on page 47 of [16]. The „ $\Rightarrow$ “ uses a tool well-known to physicists, which will be defined in a moment. First, we give an obvious, but very important corollary.

**Corollary 4.2.17.** *For a fermionic  $\psi \in \mathcal{H}_N$  with associated one-particle density matrix  $\gamma^{(1)}$ , it holds that*

$$\|\gamma_0^{(1)}\|_\infty \leq q. \quad (4.49)$$

*Proof.* This follows immediately from theorem 4.2.16 and proposition 4.2.14.  $\square$

**Definition 4.2.18** (Creation and annihilation operators on the fermionic subspace). Let  $\phi \in \mathcal{H}_1 = L^2(\mathbb{R}^3; \mathbb{C}^q)$ . We define the *annihilation operator* associated to  $\phi$

$$\begin{aligned} a_{N,\phi} : \mathcal{H}_N^{(f)} &\longrightarrow \mathcal{H}_{N-1}^{(f)} \\ (a_{N,\phi}\psi)(\mathbf{z}_1, \dots, \mathbf{z}_{N-1}) &:= \sqrt{N} \int d\mathbf{z}_N \psi(\mathbf{z}_1, \dots, \mathbf{z}_N) \overline{\phi(\mathbf{z}_N)}, \end{aligned} \quad (4.50)$$

and the *creation operator* associated to  $\phi$

$$\begin{aligned} a_{N,\phi}^* : \mathcal{H}_{N-1}^{(f)} &\longrightarrow \mathcal{H}_N^{(f)}, \\ (a_{N,\phi}^*\chi)(\mathbf{z}_1, \dots, \mathbf{z}_{N-1}) &:= \frac{1}{\sqrt{N}} \chi(\mathbf{z}_1, \dots, \mathbf{z}_{N-1}) \wedge \phi(\mathbf{z}_N), \end{aligned} \quad (4.51)$$

where we have used the shorthand notation

$$\chi(\mathbf{z}_1, \dots, \mathbf{z}_{N-1}) \wedge \phi(\mathbf{z}_N) := \frac{1}{(N-1)!} \mathcal{A}[\chi(\mathbf{z}_1, \dots, \mathbf{z}_{N-1})\phi(\mathbf{z}_N)] \quad (4.52)$$

We remark on the fact that  $a_{N,\phi}$  and  $a_{N,\phi}^*$  can be easily extended to operators on *Fock space* given by  $\bigoplus_{N=1}^{\infty} \mathcal{H}_N^{(f)}$ . The Fock space is the natural physical space for the analysis of systems with changing particle numbers and it is in fact a Hilbert space. We leave the Fock space aside, and go on to show some basic properties of  $a_{N,\phi}$  and  $a_{N,\phi}^*$ .

<sup>16</sup>In fact, for  $N \geq 2$ , one can check that they are admissible by a pure state density matrix  $\Gamma_\psi$  with  $\psi := \frac{1}{\sqrt{N}} \sum_{i=1}^{\infty} \sqrt{\lambda_i} \prod_{j=1}^N f_i(\mathbf{z}_j)$ , where  $\{(f_i, \lambda_i)\}_{i \in \mathbb{N}}$  are the *orthonormal* eigenfunction-eigenvalue pairs of  $\gamma$ . The case  $N = 1$  is trivial.

**Proposition 4.2.19.** *For any  $\psi \in \mathcal{H}_N, \chi \in \mathcal{H}_{N-1}$  we have (with a slight abuse of the scalar product notation for Hilbert spaces of different particle number):*

$$\langle a_{N,\phi}\psi, a_{N,\phi}\psi \rangle = \langle \phi, N\text{Tr}_{N-1}\Gamma_\psi\phi \rangle, \quad (4.53)$$

$$\langle \chi, a_{N,\phi}\psi \rangle = \langle a_{N,\phi}^*\chi, \psi \rangle, \quad (4.54)$$

$$a_{N+1,\phi}a_{N+1,\phi}^* + a_{N,\phi}^*a_{N,\phi} = \|\phi\|_2^2 \mathbb{1}_N. \quad (4.55)$$

*Remark 4.2.20.* The second equation says that the  $*$  notation is meaningful. The third equation is the most important of the *canonical anti-commutation rules* (ACR) well-known to physicists.

*Proof.* We redefine  $(\mathbf{z}_1, \dots, \mathbf{z}_N) =: (\underline{\mathbf{z}}, \mathbf{z}_N)$  (only for this proof). We begin by noting that we can freely use Fubini's theorem, since all integrals are finite (can be seen from a multiple application of the Cauchy-Schwartz inequality). Thus

$$\begin{aligned} \langle a_{N,\phi}\psi, a_{N,\phi}\psi \rangle &= N \int d\underline{\mathbf{z}} \left( \int d\mathbf{z}_N \psi(\underline{\mathbf{z}}, \mathbf{z}_N) \overline{\phi(\mathbf{z}_N)} \int d\mathbf{z}'_N \psi(\underline{\mathbf{z}}, \mathbf{z}'_N) \overline{\phi(\mathbf{z}'_N)} \right) \\ &= \int d\mathbf{z}_N \int d\mathbf{z}'_N \overline{\phi(\mathbf{z}'_N)} \phi(\mathbf{z}_N) \underbrace{N \int d\underline{\mathbf{z}} \Gamma_\psi(\underline{\mathbf{z}}, \mathbf{z}_N; \underline{\mathbf{z}}, \mathbf{z}'_N)}_{\gamma^{(1)}(\mathbf{z}_N, \mathbf{z}'_N)} \\ &= \langle \phi, N\text{Tr}_{N-1}\Gamma_\psi\phi \rangle. \end{aligned}$$

Next, consider the right hand side of the second property

$$\int d\underline{\mathbf{z}} \int d\mathbf{z}_N \psi(\underline{\mathbf{z}}, \mathbf{z}_N) \frac{1}{\sqrt{N}(N-1)!} \sum_{\pi \in S_N} \phi(\mathbf{z}_{\pi(N)}) \underbrace{\text{sgn}(\pi) \chi(\mathbf{z}_{\pi(1)}, \dots, \mathbf{z}_{\pi(N-1)})}_{=(-1)^{N-\pi(N)} \chi(\mathbf{z}_1, \dots, \widehat{\mathbf{z}_{\pi(N)}}, \dots, \mathbf{z}_N)}. \quad (4.56)$$

since  $\chi$  is antisymmetric. Denote  $N_0 := \pi(N)$ . Then the summands in the  $\pi$ -sum differ only by the value of  $N_0$  and each shows a uniform degeneracy of  $(N-1)!$  (the number of permutations among the sets  $\{1, \dots, N-1\}$  and  $\{1, \dots, \widehat{N_0}, \dots, N\}$ ). By antisymmetry of  $\psi$ , we can rewrite the integrand in (4.56) as

$$\frac{1}{\sqrt{N}} \sum_{N_0=1}^N (-1)^{N-N_0} \psi(\mathbf{z}_1, \dots, \widehat{\mathbf{z}_{N_0}}, \dots, \mathbf{z}_N, \mathbf{z}_{N_0}) (-1)^{N-N_0} \overline{\chi(\mathbf{z}_1, \dots, \widehat{\mathbf{z}_{N_0}}, \dots, \mathbf{z}_N)} \phi(\mathbf{z}_{N_0}).$$

And we see that all  $N$  summands give the same integral when we apply Fubini's theorem. So we get a remaining total factor of  $\sqrt{N}$ , which agrees with the one on the left hand side.

When we apply the left hand side of the ACR to some  $\chi \in \mathcal{H}_N^{(f)}$ , it reads

$$\begin{aligned} &\frac{1}{N!} \int d\mathbf{z}_{N+1} \sum_{\pi \in S_{N+1}} \text{sgn}(\pi) \chi(\mathbf{z}_{\pi(1)}, \dots, \mathbf{z}_{\pi(N)}) \phi(\mathbf{z}_{\pi(N+1)}) \overline{\phi(\mathbf{z}_{N+1})} \\ &+ \frac{1}{(N-1)!} \sum_{\sigma \in S_N} \text{sgn}(\sigma) \phi(\mathbf{z}_{\sigma(N)}) \int d\tilde{\mathbf{z}}_N \chi(\mathbf{z}_{\sigma(1)}, \dots, \mathbf{z}_{\sigma(N-1)}, \tilde{\mathbf{z}}_N) \overline{\phi(\tilde{\mathbf{z}}_N)}. \end{aligned}$$

Consider the first summand. Denote  $M := \pi^{-1}(N+1)$ . We split the sum over  $\pi$  according to the two cases  $M = N+1$  and  $M \neq N+1$ . In the first case, the degeneracy of the  $\pi$ -sum is  $N!$ , since  $\chi$  is already antisymmetric. Thus it yields

$$\langle \phi, \phi \rangle \chi(\mathbf{z}_1, \dots, \mathbf{z}_N),$$

which is all we need. The second case gives

$$\frac{1}{N!} \sum_{M=1}^N \sum_{\pi \in S_{N+1} : \pi(M)=N+1} \phi(\mathbf{z}_{\pi(N+1)}) \int d\mathbf{z}_{N+1} \chi(\mathbf{z}_{\pi(1)}, \dots, \mathbf{z}_{\pi(N)}) \overline{\phi(\mathbf{z}_{N+1})},$$

where we can rewrite

$$\chi(\mathbf{z}_{\pi(1)}, \dots, \mathbf{z}_{\pi(N)}) = -\chi(\mathbf{z}_{\pi(1)}, \dots, \mathbf{z}_{\pi(M-1)}, \mathbf{z}_{\pi(N)}, \mathbf{z}_{\pi(M+1)}, \dots, \mathbf{z}_{\pi(N-1)}, \mathbf{z}_{N+1}).$$

Thus, the  $M$ -sum collapses and gives an additional factor of  $N$  which combines with the  $\frac{1}{N!}$ . The remaining  $\pi$ -sum is the sum over  $S_N$  for appropriately redefined indices and after cancellation the ACR follows.  $\square$

*Proof of Theorem 4.2.16.* Let  $\gamma = N \text{Tr}_{N-1} \Gamma$ . First, we assume the  $\Gamma = \Gamma_\psi$  for some normalized  $\psi \in \mathcal{H}_N^{(f)}$ . To show  $\gamma \leq \mathbb{1}_N$ , we pick a  $\phi \in \mathcal{H}_1$ . By Proposition 4.2.19 we have (again abusing the  $\langle \cdot, \cdot \rangle$ -notation)

$$\begin{aligned} \langle \phi, \gamma \phi \rangle &= \langle \psi, a_{N,\phi}^* a_{N,\phi} \psi \rangle = \langle \phi, \phi \rangle \langle \psi, \psi \rangle - \langle \psi, a_{N+1,\phi} a_{N+1,\phi}^* \psi \rangle \\ &= \langle \phi, \phi \rangle - \langle a_{N+1,\phi}^* \psi, a_{N+1,\phi}^* \psi \rangle \\ &\leq \langle \phi, \phi \rangle. \end{aligned} \quad \square$$

This concludes our treatment of density matrices. With the developed  $N$ -particle formalism we return to the main body of this work.

#### 4.2.4 Definition of Stability of the Second Kind

Recall the non-relativistic atomic Hamiltonian

$$H_{N,M} = -\frac{1}{2} \sum_{i=1}^N \Delta_i + \sqrt{\alpha} V(\underline{\mathbf{x}}, \underline{\mathbf{R}}), \quad (4.57)$$

given in (3.19) with  $V = V_C$ <sup>17</sup> as defined in (3.16)

$$\begin{aligned} V_C(\underline{\mathbf{x}}, \underline{\mathbf{R}}) &= \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} - \sum_{i=1}^N \sum_{k=1}^M \frac{Z_k}{|\mathbf{x}_i - \mathbf{R}_k|} + \sum_{1 \leq k < l \leq M} \frac{Z_k Z_l}{|\mathbf{R}_k - \mathbf{R}_l|} \\ &=: I(\underline{\mathbf{x}}) + W(\underline{\mathbf{x}}, \underline{\mathbf{R}}) + U(\underline{\mathbf{R}}). \end{aligned} \quad (4.58)$$

and  $\alpha \approx \frac{1}{137}$ . We note that this  $H_{N,M}$  is symmetric in the electrons (i.e. in the labels we assign to them), so we can effortlessly make sense of it for antisymmetric  $\psi \in \mathcal{H}_N^{(f)}$ .

**Definition 4.2.21** ( $N$ -particle ground state energy). The *quadratic form*  $\mathcal{E}_{N,M}$  associated to  $H_{N,M}$  is well-defined on

$$\mathbb{D} := H^1(\mathbb{R}^{3N}) \cap \left\{ \psi \in \mathcal{H}_N^{(\#)} \mid W_\psi < \infty \right\}. \quad (4.59)$$

<sup>17</sup>We always work with the explicit Coulomb potential. Everything generalises to potentials  $V \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ , which vanish at infinity.

with  $\# \in \{f, b\}$ . It is given by

$$\mathcal{E}_{N,M}(\psi) := \sum_{i=1}^N T_{\psi,i} + \alpha V_{\psi}, \quad (4.60)$$

where  $T_{\psi,i}$  is the quadratic form defined in (2.22). The *ground state* energy of a certain configuration  $(\underline{\mathbf{R}}, \underline{\mathbf{Z}})$  is defined as

$$E_{N,M}^{(\#)}(\underline{\mathbf{R}}, \underline{\mathbf{Z}}) := \inf \{ \mathcal{E}_N(\psi) \mid \psi \in \mathbb{D}, \|\psi\|_2 = 1 \}, \quad (4.61)$$

and the *absolute ground state energy* is

$$E_{N,M}^{(\#)}(\underline{\mathbf{Z}}) := \inf \left\{ E_{N,M}^{(\#)}(\underline{\mathbf{R}}, \underline{\mathbf{Z}}) \mid \underline{\mathbf{R}} \in \mathbb{R}^{3N} \right\}, \quad (4.62)$$

with  $\# \in \{f, b\}$ .<sup>18</sup>

Note that the nuclear positions  $\underline{\mathbf{R}}$  are indeed treated as parameters, as proposed by the Born-Oppenheimer-Approximation discussed in Section 3.2. The understanding of the absolute ground state energy is that we allow the nuclei to be dynamic — so they will distribute themselves in such a way as to minimize the energy of the whole system. Before we go on to the main definition, we recall the argument given in the introduction, explaining that a linear lower bound to the atomic energy is crucial for the extensivity of matter we experience around us.

**Definition 4.2.22** (Stability of matter). An atomic system<sup>19</sup> satisfies the *stability of the first kind* if for all given distinct values  $\underline{\mathbf{R}}_1, \dots, \underline{\mathbf{R}}_M$ , it holds that

$$E_{N,M}(\underline{\mathbf{R}}, \underline{\mathbf{Z}}) \geq -\infty. \quad (4.63)$$

Furthermore, it satisfies *stability of the second kind* if there exists a real-valued function  $\Xi$  such that

$$E_{N,M}(\underline{\mathbf{Z}}) \geq -\Xi(\max\{Z_1, \dots, Z_M\})(N + M) \quad (4.64)$$

Clearly, stability of the second kind is a stronger notion than stability of the first kind. Actually, we are already in a position to see the latter for our case.

**Proposition 4.2.23** (Stability of the first kind for non-relativistic Coulomb systems). *Let  $H_{N,M}$  be as in (4.57). Then the system defined by  $H_{N,M}$  is stable of the first kind.*

*Proof.* To see this, we do the crudest possible estimate: we simply omit the positive repulsive terms in  $V_C$ , called  $I$  and  $U$  in (3.16). Then, for fixed  $\underline{\mathbf{R}}$  we have to consider

$$-\frac{1}{2} \sum_{i=1}^N \Delta_i - \underbrace{\sum_{i=1}^N \sum_{k=1}^M \frac{Z_k}{|\mathbf{x}_i - \mathbf{R}_k|}}_{=: h_i} = \sum_{i=1}^N \left( -\frac{1}{2} \Delta_i - \sum_{k=1}^M \frac{Z_k}{|\mathbf{x}_i - \mathbf{R}_k|} \right),$$

where  $h_i$  is a one-particle Hamiltonian. For every  $i$ , the sum of the nuclear Coulomb potentials is clearly in  $L^{\frac{3}{2}}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ . So, by Theorem 4.1.5 each  $h_i$  is stable of the first kind. The same then holds for the sum of the  $h_i$ .  $\square$

Physically, it is indeed clear that once we know the stability of the first kind for the hydrogenic atom (i.e. that one electron cannot fall into a single nucleus), then taking finitely many nuclei and electrons (which will even repel each other) will not change that result.

<sup>18</sup>We will drop the  $f$  in the fermionic case from now on.

<sup>19</sup>This definition applies to general atomic systems with some  $\underline{\mathbf{R}}$ -dependence, e.g. to relativistic Hamiltonians.

### 4.3 Key Ideas to prove Stability of the Second Kind

Let us give a roadmap for what follows to improve to stability of the second kind.

- (i) Consider  $V = V_C$  as given in (4.58). The electron-nucleus interaction  $W$  is the only negative term in our Hamiltonian, so any instability can originate only in  $W$ . Since the electrostatic interaction always involves exactly two particles, all terms contained in  $V_C$  (positive and negative) are quadratic in the number of particles. Thus, any naive estimate of the  $\mathcal{O}(NM)$  negative terms is bound to fail. The idea is that *the Coulomb potential will be estimated by a one-particle potential*.
- (ii) The nuclei have to sit at different positions  $\mathbf{R}$ , because of the presence of the repulsive term  $U$ . One could have the feeling that the main problem about  $V_C$  is the Coulomb singularity („Coulomb tooth“) of the particular nucleus the electron will be close to. This is not the case, in fact we have already seen in section 4.1, that by some uncertainty mechanism, the kinetic energy is sufficient to control the Coulomb tooth for one electron. Furthermore, we are dealing with fermions, i.e. *antisymmetric wave functions following the Pauli-principle*. Thus, the uncertainty principle transports to the  $N$ -particle case with appropriate dependence on the spin degeneracy  $q$ . In this spirit, it is not hard to show stability of the second kind for a single hydrogenic atom and  $N$  electrons. We will not do this, rather we will show the more general Lieb-Thirring inequalities in chapter 6, which are equivalent to an uncertainty mechanism, as shown in section 6.5
- (iii) When we return to  $V_C$ , we observe that the more severe problem is that  *$W$  can also be very large a slight distance away from the nuclei, because there might be many of them ( $M$  can be large)*. One somehow has to disentangle the two sources of instability by removing the Coulomb tooth in an appropriate fashion; this will be done in the following chapter 5.

# Chapter 5

## Electrostatic Inequalities

We now return to electrostatics in order to prove the basic inequalities required to control the Coulomb potential away from the nearest nucleus. First, we will treat the exclusion of the Coulomb tooth, then we will prove a basic inequality for general charge distributions. The basic inequality will then be used to prove *Baxter's inequality*, which estimates the Coulomb potential from below with a one-particle potential involving only the Coulomb teeth of each individual electron. For this chapter, we assume that

$$Z_1 = \dots = Z_M =: Z, \quad (5.1)$$

which will not be of importance for the stability issue, as we shall see in section 7.1. In this case, the interaction with a single electron at the point  $\mathbf{x} \in \mathbb{R}^3$  is given by the potential

$$W(\mathbf{x}) = Z \sum_{k=1}^M \frac{1}{|\mathbf{x} - \mathbf{R}_k|}. \quad (5.2)$$

Recall (3.14), which now gives

$$-\Delta W(\mathbf{x}) = 4\pi Z \sum_{k=1}^M \delta(\mathbf{x} - \mathbf{R}_k). \quad (5.3)$$

In particular,  $W$  is harmonic<sup>1</sup> on  $\mathbb{R}^3 \setminus \{\mathbf{R}_1, \dots, \mathbf{R}_M\}$ .

### 5.1 Voronoi cells and the Coulomb tooth

There is only one difficulty about removing the Coulomb tooth, namely that the notion of nearest nuclear singularity depends on an electron's position. From this point of view, it is natural to consider the following cells around each nucleus.

**Definition 5.1.1** (Voronoi cell). Let  $\mathbf{R}_1, \dots, \mathbf{R}_M \in \mathbb{R}^3$  be the distinct nuclear positions. We call

$$\Gamma_j := \{\mathbf{x} \in \mathbb{R}^3 \mid \forall i \neq j : |\mathbf{x} - \mathbf{R}_j| < |\mathbf{x} - \mathbf{R}_i|\} \quad (5.4)$$

the *Voronoi cell* corresponding to the  $j$ -th nucleus.

*Remark 5.1.2.* The Voronoi cells will be the main tool to prove the results of this chapter. We note the following three points.

---

<sup>1</sup>A function  $u$  is called harmonic, if  $\Delta u = 0$ .

- (i) Clearly, each  $\Gamma_j$  is open. Also, it is convex as an intersection of finitely many half-spaces.
- (ii) An instructive picture of two-dimensional Voronoi cells can be found in [16], on page 94.
- (iii)  $\partial\Gamma_j$  may include the point at infinity denoted by  $\{\infty\}$ .

We introduce some other notation, which will be needed for the statement of the first result.

**Theorem - Definition 5.1.1.** (i) We will denote half the *nearest neighbour distance* of the  $j$ -th nucleus by

$$D_j := \text{dist}\{R_j, \partial\Gamma_j\} = \frac{1}{2} \min \{|\mathbf{R}_i - \mathbf{R}_j| \mid i \neq j\}. \quad (5.5)$$

- (ii) We introduce

$$\mathcal{D}(\mathbf{x}) := \min \{|\mathbf{x} - \mathbf{R}_i| \mid 1 \leq i \leq M\}, \quad (5.6)$$

which is continuous everywhere. Its one-sided derivatives exist at each  $\partial\Gamma_i$ , but they do not agree and  $\mathcal{D}(\mathbf{x})$  has a kink.

- (iii) Now, we define the *toothless Coulomb potential*  $\Theta$  by

$$\Theta(\mathbf{x}) := W(\mathbf{x}) - \frac{Z}{\mathcal{D}(\mathbf{x})}. \quad (5.7)$$

Clearly,  $\Theta$  then has the same differentiability properties as  $\mathcal{D}(\mathbf{x})$  (because all the  $Z_k$  are the same) and is harmonic in each Voronoi cell. We also note

$$U(\mathbf{R}) = \frac{Z}{2} \sum_{k=1}^M \Theta(\mathbf{R}_k). \quad (5.8)$$

## 5.2 Basic Electrostatic Inequality

We begin by calculating the charge distribution  $\nu$ , which generates  $\Theta$  in the sense of (3.1). We can reformulate (3.1) by using the notion of a distributional derivative, as discussed briefly after (3.14). This gives

$$-\Delta\Theta = 4\pi\nu, \quad (5.9)$$

which holds in the distributional sense. Since  $\Theta$  is harmonic,  $\nu$  can live only on the boundaries of the Voronoi cells.

**Lemma 5.2.1.** *The charge distribution generating  $\Theta$  is given by the positive<sup>2</sup> surface charge density*

$$\nu(d\mathbf{x}) = -\frac{Z}{2\pi} \hat{\mathbf{n}}_j \cdot \nabla \frac{1}{|\mathbf{x} - \mathbf{R}_j|} \chi_{\left(\bigcup_{j=1}^M \partial\Gamma_j\right) \setminus \{\infty\}} dS(\mathbf{x}), \quad (5.10)$$

where  $\hat{\mathbf{n}}_j$  denotes the unit outward normal of  $\Gamma_j$  and  $dS(\mathbf{x})$  the two-dimensional Lebesgue measure.

---

<sup>2</sup>This follows directly from the convexity of the Voronoi cells.

*Proof.* We pick an  $f \in C_c(\infty)$  and compute (using Green's theorem on each  $\Gamma_j$ , because  $\forall j : \Theta \in C^1(\overline{\partial\Gamma_j})$ )

$$\begin{aligned} \int_{\mathbb{R}^3} d\mathbf{x} \Theta(\mathbf{x}) \Delta f(\mathbf{x}) &= \sum_{j=1}^M \int_{\Gamma_j} d\mathbf{x} \Theta(\mathbf{x}) \Delta f(\mathbf{x}) \\ &= \sum_{j=1}^M \int_{\partial\Gamma_j} dS(\mathbf{x}) \Theta(\mathbf{x}) \hat{\mathbf{n}}_j \cdot \nabla f(\mathbf{x}) - \sum_{j=1}^M \int_{\Gamma_j} d\mathbf{x} \nabla \Theta(\mathbf{x}) \cdot \nabla f(\mathbf{x}) \end{aligned}$$

Consider the first term:  $\Theta$  and  $f$  are continuous everywhere, in particular on the boundary of each Voronoi cell. Furthermore, each boundary integration appears twice (that  $\partial\Gamma_j$  might contain the point at infinity is remedied by the fact that  $f$  is compactly supported), but with a reversed sign due to  $\hat{\mathbf{n}}_j$ . Thus, this term vanishes. For the second term, we again invoke Green's theorem. By harmonicity of  $\Theta$  we can conclude

$$\int_{\mathbb{R}^3} d\mathbf{x} \Theta(\mathbf{x}) \Delta f(\mathbf{x}) = - \sum_{j=1}^M \int_{\partial\Gamma_j} dS(\mathbf{x}) f(\mathbf{x}) \hat{\mathbf{n}}_j \cdot \nabla \Theta(\mathbf{x}).$$

We then use the definition of  $\Theta$ , (5.7), and see that since  $W$  is continuously differentiable everywhere, the integral over  $\nabla W$  vanishes by the same token as above. We get

$$\int_{\mathbb{R}^3} d\mathbf{x} \Theta(\mathbf{x}) \Delta f(\mathbf{x}) = Z \sum_{j=1}^M \int_{\partial\Gamma_j} dS(\mathbf{x}) f(\mathbf{x}) \hat{\mathbf{n}}_j \cdot \nabla \frac{1}{\mathcal{D}(\mathbf{x})}.$$

Now fix  $j, k \in \{1, \dots, M\}, j \neq k$  such that  $\partial\Gamma_j \cap \partial\Gamma_k \neq \emptyset$ . On this intersection,  $1/\mathcal{D}(\mathbf{x})$  shows an upward kink and clearly has one-sided derivatives (a side being either  $\Gamma_j$  or  $\Gamma_k$ , respectively) equal in magnitude but of opposite orientation. This difference in sign is remedied by the fact that  $\hat{\mathbf{n}}_j = -\hat{\mathbf{n}}_k$ . Thus the integral over  $\partial\Gamma_j \cap \partial\Gamma_k$  gives the same value whether it was visited as part of the  $\partial\Gamma_j$ -integral or the  $\partial\Gamma_k$ -integral. The upshot is that

$$\int_{\mathbb{R}^3} d\mathbf{x} \Theta(\mathbf{x}) \Delta f(\mathbf{x}) = 2Z \int_{\mathbb{R}^3} dS(\mathbf{x}) \chi_{\left(\bigcup_{j=1}^M \partial\Gamma_j\right) \setminus \{\infty\}} f(\mathbf{x}) \hat{\mathbf{n}}_j \cdot \nabla \frac{1}{|\mathbf{x} - \mathbf{R}_j|},$$

and from dividing the right hand side by  $4\pi$ , we recognize  $\nu$  as claimed.  $\square$

The following theorem will give a first estimate for the „toothless“ Coulomb energy of any charge distribution  $\mu$ . The lower bound is given by the nearest-neighbour interaction energy of the nuclei and is independent of  $\mu$ .

**Theorem 5.2.2** (Basic electrostatic inequality). *Let  $\mu = \mu_+ - \mu_-$  be a charge distribution and  $\mathbf{R}_1, \dots, \mathbf{R}_M \in \mathbb{R}^3$  distinct points. Then*

$$D(\mu, \mu) - \int_{\mathbb{R}^3} \mu(d\mathbf{x}) \Theta(\mathbf{x}) + \sum_{1 \leq k < l \leq M} \frac{Z^2}{|\mathbf{R}_k - \mathbf{R}_l|} \geq \frac{1}{8} \sum_{j=1}^M \frac{Z^2}{D_j}, \quad (5.11)$$

with  $D_j$  as given in (5.5).

*Proof.* From lemma 5.2.1, we know that

$$\Theta(\mathbf{x}) = \int_{\mathbb{R}^3} \nu(dy) \frac{1}{|\mathbf{x} - \mathbf{y}|},$$

which implies (recall (3.2))

$$\int_{\mathbb{R}^3} \mu(d\mathbf{x}) \Theta(\mathbf{x}) = 2D(\mu, \nu).$$

Therefore, the left hand side can be written as

$$\begin{aligned} & D(\mu - \nu, \mu - \nu) - D(\nu, \nu) + \sum_{1 \leq k < l \leq M} \frac{Z^2}{|\mathbf{R}_k - \mathbf{R}_l|} \\ & \geq -D(\nu, \nu) + \sum_{1 \leq k < l \leq M} \frac{Z^2}{|\mathbf{R}_k - \mathbf{R}_l|}, \end{aligned} \quad (5.12)$$

where we have used the positivity of  $D$  (theorem 3.1.9). Next, we consider

$$D(\nu, \nu) = \frac{1}{2} \int_{\mathbb{R}^3} \nu(d\mathbf{x}) \Theta(\mathbf{x}) = \frac{1}{2} \int_{\mathbb{R}^3} \nu(d\mathbf{x}) W(\mathbf{x}) - \frac{1}{2} \int_{\mathbb{R}^3} \nu(d\mathbf{x}) \frac{Z}{\mathcal{D}(\mathbf{x})}.$$

Since  $W$  is the the potential of the nuclei we can rewrite the first term (using Fubini and (5.8))

$$\begin{aligned} \frac{Z}{2} \int_{\mathbb{R}^3} \nu(d\mathbf{x}) \int_{\mathbb{R}^3} dy \sum_{j=1}^M \delta(\mathbf{y} - \mathbf{R}_j) \frac{1}{|\mathbf{x} - \mathbf{y}|} &= \frac{Z}{2} \int_{\mathbb{R}^3} dy \sum_{j=1}^M \delta(\mathbf{y} - \mathbf{R}_j) \Theta(\mathbf{y}) \\ &= \frac{Z}{2} \sum_{j=1}^M \Theta(\mathbf{R}_j) \\ &= \sum_{1 \leq k < l \leq M} \frac{Z^2}{|\mathbf{R}_k - \mathbf{R}_l|}. \end{aligned}$$

Recall that  $\nabla|\mathbf{x}| = \frac{\mathbf{x}}{|\mathbf{x}|}$ . With this, lemma 5.2.1 and another application of Green's theorem (this time on  $\Gamma_j^c$ ) we get

$$\begin{aligned} \frac{1}{2} \int_{\mathbb{R}^3} \nu(d\mathbf{x}) \frac{Z}{\mathcal{D}(\mathbf{x})} &= - \sum_{j=1}^M \frac{Z^2}{8\pi} \int_{\partial\Gamma_j} dS(\mathbf{x}) \frac{1}{|\mathbf{x} - \mathbf{R}_j|} \hat{\mathbf{n}}_j \cdot \nabla \frac{1}{|\mathbf{x} - \mathbf{R}_j|} \\ &= - \sum_{j=1}^M \frac{Z^2}{16\pi} \int_{\partial\Gamma_j} dS(\mathbf{x}) \hat{\mathbf{n}}_j \cdot \nabla \frac{1}{|\mathbf{x} - \mathbf{R}_j|^2} \\ &= \sum_{j=1}^M \frac{Z^2}{16\pi} \int_{\Gamma_j^c} d\mathbf{x} \Delta \frac{1}{|\mathbf{x} - \mathbf{R}_j|^2}. \end{aligned}$$

We compute

$$\Delta \frac{1}{|\mathbf{x} - \mathbf{R}_j|^2} = \nabla \left( -2 \frac{\mathbf{x} - \mathbf{R}_j}{|\mathbf{x} - \mathbf{R}_j|^4} \right) = \frac{2}{|\mathbf{x} - \mathbf{R}_j|^4}.$$

Coming back to (5.12), we see that what remains is to find a lower bound for

$$\frac{Z^2}{8\pi} \int_{\Gamma_j^c} d\mathbf{x} \frac{1}{|\mathbf{x} - \mathbf{R}_j|^4}.$$

Since a Voronoi cell is an intersection of half-spaces, its complement is the union of complements of half-spaces, which are again half-spaces. Of these, we pick the one separating  $R_j$  from its nearest neighbour; it then has a distance  $D_j$  to  $R_j$ . By performing a euclidean motion we can assume that the chosen half-space is parallel to the  $y$ - $z$ -plane, while leaving the Lebesgue measure invariant. We conclude

$$\begin{aligned} \frac{Z^2}{8\pi} \int_{\Gamma_j^c} d\mathbf{x} \frac{1}{|\mathbf{x} - \mathbf{R}_j|^4} &\geq \frac{Z^2}{8\pi} \int_{\mathbb{R}^3} dz \int_{\mathbb{R}^3} dy \int_{D_j} d\mathbf{x} \frac{1}{(x^2 + y^2 + z^2)^2} \\ &= \frac{Z^2}{4} \int_0^\infty dr \int_{D_j} d\mathbf{x} \frac{r}{(x^2 + r^2)^2} \\ &= \frac{Z^2}{8D_j} \end{aligned} \quad \square$$

### 5.3 Baxter's Inequality

There is an inconvenience about the basic electrostatic inequality 5.2.2 we just proved. To apply it to the Coulomb potential, we have to take  $\mu$  to be the charge distribution of the electrons, which is delta-like and thus has an infinite self-energy  $D(\mu, \mu)$ . This renders theorem 5.2.2 useless for such  $\mu$ . The next theorem frees us of the infinite self-energy terms, by smearing out the electron charges. The justification for the smearing to lower the energy is provided by Newton's theorem and its corollary 3.1.8.

**Theorem 5.3.1** (Baxter's inequality). *Let  $V_C(\underline{\mathbf{x}}, \underline{\mathbf{R}})$  be the Coulomb potential as in (4.58). Then, using the definitions made in 5.1.1, it holds that*

$$V_C(\underline{\mathbf{x}}, \underline{\mathbf{R}}) \geq -(2Z + 1) \sum_{i=1}^N \frac{1}{\mathcal{D}(\mathbf{x}_i)} + \frac{Z^2}{8} \sum_{j=1}^M \frac{1}{D_j}. \quad (5.13)$$

*Remark 5.3.2.* Baxter's inequality has the striking feat of bounding the two-particle Coulomb potential by a one-particle potential involving only the Coulomb tooth, namely  $\frac{1}{\mathcal{D}(\mathbf{x})}$ , which is what we hoped for. The main reason why such an enormous simplification is possible is in fact *Newton's Theorem*, which implies that far away charges cancel each other out („screening“). We observe, that the lower bound to the Coulomb energy is clearly minimal, when the nuclei are infinitely far apart. Thus, there are no molecules in the theory given by our lower bound. This is a first instance of a no-binding result, another one will appear in chapter 9 on the Thomas-Fermi theory.

A peculiarity that appears in Baxter's inequality, is that the weight of the Coulomb tooth has increased to  $2Z + 1$ , instead of being  $Z$  as it should be because nuclei cannot

pile up. One can refine the inequality by smearing out the point charges in a more sophisticated way than in the proof of Baxter's inequality, i.e. depending on how far they are from the singularity. This is done in theorem 5.5 of [16], but is only needed for obtaining the correct sharp bound for the critical value of  $\alpha Z$  up to which *relativistic* stability occurs.

*Proof.* We begin by remarking that the original version by Baxter given in [2] did not have the  $j$ -sum on the right hand side and the proof heavily used potential theory. We smear out the  $i$ -th electron charge to a charge distribution  $\mu_i$  supported on a sphere of radius  $\mathcal{D}(\mathbf{x}_i)/2$  around  $\mathbf{x}_i$ , while keeping the total charge normalized to one, i.e.

$$\begin{aligned}\mu_i(d\mathbf{x}) &:= \frac{1}{\pi \mathcal{D}(\mathbf{x}_i)^2} \delta(|\mathbf{x} - \mathbf{x}_i| - \mathcal{D}(\mathbf{x}_i)/2) d\mathbf{x}, \\ \Phi_i(\mathbf{x}) &:= \int_{\mathbb{R}^3} \mu_i(d\mathbf{y}) \frac{1}{|\mathbf{x} - \mathbf{y}|} \\ \mu(d\mathbf{x}) &:= \sum_{i=1}^N \mu_i(d\mathbf{x}) \\ \Phi(\mathbf{x}) &:= \int_{\mathbb{R}^3} \mu(d\mathbf{y}) \frac{1}{|\mathbf{x} - \mathbf{y}|}.\end{aligned}$$

Let  $i, j \in \{1, \dots, N\}, i \neq j$ . Then we see from (3.1.8) ( $\mu_i$  is positive and spherically symmetric with respect to  $\mathbf{x}_i$ )

$$\begin{aligned}D(\mu_i, \mu_j) &= \int_{\mathbb{R}^3} \mu_i(d\mathbf{x}) \Phi_j(\mathbf{x}) \leq \int_{\mathbb{R}^3} \mu_i(d\mathbf{x}) \frac{1}{|\mathbf{x} - \mathbf{x}_j|} \\ &= \Phi_i(\mathbf{x}_j) \leq \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|}.\end{aligned}$$

Secondly, since

$$\text{dist}\{\text{supp}(\mu_i), \mathbf{R}_1, \dots, \mathbf{R}_M\} = \mathcal{D}(\mathbf{x}_i)/2 > 0,$$

Newton's theorem says that the  $\mu_i$  look to all the nuclei as if they were the electronic point charges at  $\mathbf{x}_i$ . The upshot is that for all  $k \in \{1, \dots, M\}$ , we know

$$\int_{\mathbb{R}^3} \mu_i(d\mathbf{x}) \frac{Z}{|\mathbf{x} - \mathbf{R}_k|} = \frac{Z}{|\mathbf{x}_i - \mathbf{R}_k|}.$$

Thirdly, we can calculate, using (3.6), the exact value of the self-energy (without loss of generality set  $\mathbf{x}_i = 0$ )

$$\begin{aligned}D(\mu_i, \mu_i) &= \frac{1}{2\pi^2 \mathcal{D}(\mathbf{x}_i)^4} \frac{(\mathcal{D}(\mathbf{x}_i)/2)^2}{4\pi} \int_{S^2} d\omega_1 \frac{(\mathcal{D}(\mathbf{x}_i)/2)^2}{4\pi} \underbrace{\int_{S^2} d\omega_2 \frac{1}{\mathcal{D}(\mathbf{x}_i)/2 |\omega_1 - \omega_2|}}_{=\min\{1,1\}=1} \\ &= \frac{1}{\mathcal{D}(\mathbf{x}_i)}.\end{aligned}$$

By virtue of these three comparisons, we can estimate  $V_C$  from below by an expression to which we can apply theorem 5.2.2, i.e.

$$\begin{aligned}
V_C(\mathbf{x}, \mathbf{R}) &= \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} - \sum_{i=1}^N \sum_{k=1}^M \frac{Z}{|\mathbf{x}_i - \mathbf{R}_k|} + \sum_{1 \leq k < l \leq M} \frac{Z^2}{|\mathbf{R}_k - \mathbf{R}_l|} \\
&\geq \sum_{1 \leq i < j \leq N} 2D(\mu_i, \mu_j) - \sum_{k=1}^M \int_{\mathbb{R}^3} \mu(dx) \frac{Z}{|\mathbf{x} - \mathbf{R}_k|} + \sum_{1 \leq k < l \leq M} \frac{Z^2}{|\mathbf{R}_k - \mathbf{R}_l|} \\
&= D(\mu, \mu) - \sum_{i=1}^N \frac{1}{\mathcal{D}(\mathbf{x}_i)} - \int_{\mathbb{R}^3} \mu(d\mathbf{x}) \left( \Phi(\mathbf{x}) - \frac{Z}{\mathcal{D}(\mathbf{x})} \right) + \sum_{1 \leq k < l \leq M} \frac{Z^2}{|\mathbf{R}_k - \mathbf{R}_l|} \\
&\geq - \sum_{i=1}^N \left( \int_{\mathbb{R}^3} \mu_i(dx) \frac{Z}{\mathcal{D}(\mathbf{x})} + \frac{1}{\mathcal{D}(\mathbf{x}_i)} \right) + \frac{Z^2}{8} \sum_{j=1}^M \frac{1}{D_j}. \tag{5.14}
\end{aligned}$$

Finally, observe that for  $\mathbf{x} \in \text{supp}(\mu_i)$  (by definition and triangle inequality)

$$\mathcal{D}(\mathbf{x}) \geq \mathcal{D}(\mathbf{x}_i) - |\mathbf{x}_i - \mathbf{x}| = \mathcal{D}(\mathbf{x}_i)/2,$$

so that the claim follows from (5.14), since  $\mu_i$  is normalized.  $\square$

# Chapter 6

## Lieb-Thirring Inequalities

### 6.1 The Variational Principle: Definition of Negative Eigenvalues

In this section, we will informally sketch some ideas about the variational principle (omitting proofs). The goal is to justify the consideration of the negative eigenvalues of the coulombic Hamiltonian in the forthcoming sections. All of the the results mentioned here can be found in chapter 11 of [14].

Recall the definition of  $E_0$  as the infimum of the quadratic form  $\mathcal{E}(\psi) := T_\psi + V_\psi$  defined on  $\mathbb{D}$ :

$$\mathbb{D} = \{ \psi \in \mathcal{H}(\mathbb{R}^{3N}) \mid \|\psi\|_2 = 1, V_\psi \text{ is well-defined} \} \quad (6.1)$$

$$E_0 = \inf \{ \mathcal{E}(\psi) \mid \psi \in \mathbb{D} \}. \quad (6.2)$$

One hope is to find an explicit minimizer  $\psi_0 \in \mathbb{D}$  such that

$$\mathcal{E}(\psi_0) = E_0 \quad (6.3)$$

In our case, such a  $\psi_0$  always exists. We say that  $\psi_0$  is the *eigenfunction* corresponding to  $E_0$ .<sup>1</sup> The proof is typical for the calculus of variations and follows the usual steps. We give them here, because we will argue in the same fashion when showing the existence of a minimizer for the Thomas-Fermi functional in chapter 9.

- (i) Take a minimizing sequence  $\{\psi_j\}_{j \in \mathbb{N}}$ , i.e.

$$\mathcal{E}(\psi_j) \xrightarrow{j \rightarrow \infty} E_0. \quad (6.4)$$

- (ii) Use some coercivity statement (such as  $T_\psi \leq C\mathcal{E}(\psi) + D\|\psi\|_2^2$ , proved in theorem 4.1.5) to show that  $\{\psi_j\}_{j \in \mathbb{N}}$  is a bounded sequence (with respect to an appropriate norm).
- (iii) Apply the Banach-Alaoglu theorem (bounded sequences have weakly convergent<sup>2</sup> subsequences) to  $\{\psi_j\}_{j \in \mathbb{N}}$ . This can be done because  $H^1$  is a Hilbert space and thus reflexive. Call the subsequence again  $\psi_j$  and the weak limit  $\psi_0$ .

---

<sup>1</sup>See theorem 11.5 in [14]. In fact, there it is also shown that  $\psi_0$  satisfies the time-independent Schrödinger equation  $(-\Delta + V)\psi_0 = E_0\psi_0$  (in the weak sense), hence the name eigenfunction.

<sup>2</sup>I.e.  $\exists \psi_0 : L(\psi_j) \xrightarrow{j \rightarrow \infty} L(\psi_0), \forall L : L$  is a bounded linear functional. Notation:  $\psi_j \xrightarrow{j \rightarrow \infty} \psi_0$

(iv) Show  $\psi_0 \in \mathbb{D}$ .

(v) Show the weak lower semicontinuity of the quadratic form, i.e.

$$\psi_j \xrightarrow{j \rightarrow \infty} \psi_0 \Rightarrow \liminf_{j \rightarrow \infty} \mathcal{E}(\psi_j) \geq \mathcal{E}(\psi_0) \quad (6.5)$$

From this step and  $\psi_0 \in \mathbb{D}$  then follows  $\mathcal{E}(\psi) = E_0$ .

Now, we go on to excited, but still bound states, i.e. to energies  $E_0 < E < 0$ . Again, we aim for a variational characterisation, which is computationally easier to handle. When one thinks in terms of spectral subspaces, it is natural to define the higher eigenvalues by the following recursion.

**Definition 6.1.1** (*k*-th eigenvalue). Let  $H$  be the atomic Hamiltonian with quadratic form given by  $\mathcal{E}(\psi)$ . Let  $E_0$  denote the ground state energy with corresponding eigenfunction  $\psi_0$ . If we have already defined  $E_0 \leq E_1 \leq \dots \leq E_{k-1}$ , with corresponding eigenfunctions  $\psi_0, \dots, \psi_{k-1}$ , then we call

$$E_k := \inf \{ \mathcal{E}(\psi) \mid \psi \in \mathbb{D}, \langle \psi, \psi_i \rangle = 0 \forall i \in \{0, \dots, k-1\} \} \quad (6.6)$$

the *k*-th eigenvalue of  $H$ .

The main result we need is theorem 11.6 in [14]. It says that the recursion given above goes on until one of the  $E_k$  gives 0. Moreover, the sequence  $\{E_k\}_{k < N_0}$  (with  $N_0 \in \mathbb{N} \cup \{\infty\}$ ) can only accumulate at 0. Another important result is that the eigenvalues are independent of the choices of the eigenfunctions and therefore in themselves well-defined. This leads us to the min-max principle (theorem 12.1 in [14]), which says that each individual  $E_k$  can be characterized directly through a variational characterization, i.e.

$$E_k = \min \{ \max \{ \mathcal{E}(\phi) \mid \phi \in \text{span}(\phi_0, \dots, \phi_N) \} \mid \phi_0, \dots, \phi_N \}, \quad (6.7)$$

which is also physically appealing. An immediate consequence of (6.7) is that for given operators  $\tilde{H} \leq H$  (meaning that  $\forall \psi : \tilde{\mathcal{E}}(\psi) \leq \mathcal{E}(\psi)$ ), we have

$$\tilde{E}_k \leq E_k, \quad (6.8)$$

for all negative eigenvalues  $\tilde{E}_k, E_k$  of  $\tilde{H}, H$  respectively.

With this knowledge, we can safely go on to consider *Riesz means* of the negative eigenvalues, i.e. the object

$$\sum_{j \geq 0: E_j \leq 0} |E_j|^\gamma, \quad (6.9)$$

with some parameter  $\gamma \geq 0$ . We will be interested in the case  $\gamma = 1$ .

## 6.2 The Idea of the Semiclassical Approximation

Recall the discussion on the notion of a state in 2.3.1. There it was mentioned that quantum states can be localized in six-dimensional phase space — in the best case — to a box of volume  $h^3$ . The assumption that every quantum state occupies such a volume is called the *semiclassical picture* of quantum mechanics. It is clearly only approximative.

Since we have set  $1 = \hbar := h/(2\pi)$ , this volume now becomes  $1/(2\pi)^3$ . Rephrased in terms of densities, this means that the number of (independent) quantum states per phase space volume is approximately  $1/(2\pi)^3$ . Given a subset  $\Omega \subset \mathbb{R}^6$  of phase space, we can assign to it a number

$$N_e(\Omega) := \frac{1}{(2\pi)^3} |\Omega|, \quad (6.10)$$

where  $|\cdot|$  denotes Lebesgue measure. We can now hope that for sufficiently regular sets (certainly it can be problematic to try to fill sets with very irregular boundaries using boxes of finite volume)  $N_e$  will be close to the number of quantum states that fit into  $\Omega$ . This is in fact true, the precise wording can be found in theorem 12.12 of [14]. The proof uses *coherent states*, which bridge from the quantum to the classical realm.

Also, according to the semiclassical picture, one could hope to replace the expectation of the Hamilton operator  $H = -\Delta + V$  (we drop the  $1/2$  in front of the Laplacian for the moment) in some state  $\psi_{\mathbf{x},\mathbf{p}}$ , which is localised in the box of volume  $1/(2\pi)^3$  around  $(\mathbf{x}, \mathbf{p}) \in \mathbb{R}^6$ , by the value of the classical Hamilton function at  $(\mathbf{x}, \mathbf{p})$ , i.e.

$$p^2 + V(\mathbf{x}) \quad \text{instead of} \quad \langle \psi_{\mathbf{x},\mathbf{p}}, (-\Delta + V)\psi_{\mathbf{x},\mathbf{p}} \rangle.$$

Let us now come back to the Riesz means introduced in the previous section. There, the eigenvalues were restricted to lie below 0, which by the semiclassical picture corresponds to a phase space density given by

$$dE := \frac{1}{(2\pi)^3} \chi_{\{\mathbf{p}^2 + V(\mathbf{x}) \leq 0\}} d\mathbf{x} d\mathbf{p}. \quad (6.11)$$

Furthermore, we can view the  $|E_j|^\gamma$  as objects referring to the expectation of (the absolute value of) the classical Hamilton function to the  $\gamma$ -th power. More precisely, we hope for the approximation

$$\sum_{j \geq 0: E_j \leq 0} |E_j|^\gamma \approx \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} d\mathbf{p} d\mathbf{x} \chi_{\{\mathbf{p}^2 + V(\mathbf{x}) \leq 0\}} |\mathbf{p}^2 + V(\mathbf{x})|^\gamma \quad (6.12)$$

In fact, the  $d\mathbf{p}$ -integral can easily be performed explicitly. Since  $\mathbf{p}^2 \geq 0$ , we can drop the positive part<sup>3</sup> of  $V$ . Using Fubini we get

$$\begin{aligned} & \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3} d\mathbf{x} \int_{\{\mathbf{p} \leq \sqrt{V_-(\mathbf{x})}\}} d\mathbf{p} |V_-(\mathbf{x})|^\gamma \left| \frac{\mathbf{p}^2}{V_-(\mathbf{x})} - 1 \right|^\gamma \\ &= \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3} d\mathbf{x} \int_{\{\mathbf{p} \leq 1\}} d\mathbf{p} |V_-(\mathbf{x})|^{\gamma+3/2} (1 - \mathbf{p}^2)^\gamma \\ &= L_{\gamma,3}^{cl} \int_{\mathbb{R}^3} d\mathbf{x} |V_-(\mathbf{x})|^{\gamma+3/2}, \end{aligned}$$

---

<sup>3</sup>Recall that any function  $V(\mathbf{x}) = V_+(\mathbf{x}) - V_-(\mathbf{x})$ , where  $V_+(\mathbf{x}) := \max\{0, V(\mathbf{x})\}$  and  $V_-(\mathbf{x}) := \max\{0, -V(\mathbf{x})\}$ .

where the *non-relativistic classical Lieb-Thirring constant*  $L_{\gamma,3}^{cl}$  is given by

$$L_{\gamma,3}^{cl} = \frac{1}{(2\pi)^3} \int_{\{|\mathbf{p}|\leq 1\}} d\mathbf{p} (1 - \mathbf{p}^2)^\gamma \quad (6.13)$$

$$= \frac{1}{(2\pi)^2} \int_0^1 dr (1-r)^\gamma r^{1/2} \quad (6.14)$$

$$= \frac{\Gamma(\gamma+1)}{(4\pi)^{3/2} \Gamma(\gamma+1+3/2)}. \quad (6.15)$$

The last equality is an exercise in elementary integration theory. In fact, the integral in the second line is the Beta function  $B(3/2, \gamma+1)$  and it is shown in theorem 8.20 in [24] that for  $x, y > 0$

$$B(x, y) = \int_0^1 dt (1-t)^{y-1} t^{x-1} = \frac{\Gamma(x)\Gamma(y)}{\Gamma(x+y)}. \quad (6.16)$$

Thus, one can directly generalize the above calculation to arbitrary dimensions  $d$  and receive the constant

$$L_{\gamma,d}^{cl} = \frac{\Gamma(\gamma+1)}{(4\pi)^{d/2} \Gamma(\gamma+1+d/2)}. \quad (6.17)$$

We will come back to  $L_{\gamma,d}^{cl}$  in a moment, after we have stated the main result of this chapter.

### 6.3 Statement of the LT inequality

As usual, we only treat the non-relativistic case. Because of its importance, we give this theorem for arbitrary dimension  $d$ .

**Theorem 6.3.1** (Non-relativistic Lieb-Thirring inequality in  $d$  dimensions). *Let  $\gamma \geq 0$ . Let  $V$  be such that  $-\Delta + V$  is stable of the first kind<sup>4</sup> and  $V_- \in L^{d/2}(\mathbb{R}^d)$ . Let  $E_0 \leq E_1 \leq \dots$  denote the non-positive eigenvalues of  $-\Delta + V(\mathbf{x})$ , defined in (6.6) by the variational principle. Let  $\gamma$  also satisfy*

$$\begin{aligned} \gamma &\geq \frac{1}{2} \quad , \text{ for } d = 1, \\ \gamma &> 0 \quad , \text{ for } d = 2, \\ \gamma &\geq 0 \quad , \text{ for } d \geq 3. \end{aligned} \quad (6.18)$$

Then there exists a constant  $L_{\gamma,d} > 0$  such that

$$\sum_{j \geq 0: E_j \leq 0} |E_j|^\gamma \leq L_{\gamma,d} \int_{\mathbb{R}^d} V_-(\mathbf{x})^{\gamma+d/2} \quad (6.19)$$

<sup>4</sup>For  $d \geq 3$ , this just requires  $V \in L^{d/2}(\mathbb{R}^d) + L^\infty(\mathbb{R}^d)$ . For the cases  $d = 2$  and  $d = 1$ , confer page 273 of [14].

holds true.  $L_{\gamma,d} > 0$  can be chosen as

$$L_{\gamma,d} = \frac{\gamma 2^\gamma}{(4\pi)^{d/2}} \frac{(d+\gamma)\Gamma(\gamma/2)^2}{2\Gamma(\gamma+1+d/2)}, \quad \text{for } d > 1, \gamma > 0 \text{ or } d = 1, \gamma \geq 1 \quad (6.20)$$

$$L_{\gamma,d} = \frac{\gamma 2^\gamma}{(4\pi)^{d/2}} \sqrt{\pi}(\gamma^2 - 1/4), \quad \text{for } d = 1, \gamma > 1/2. \quad (6.21)$$

*Remark 6.3.2.* (i) The idea behind the Lieb-Thirring (LT) inequality is that the right hand side counts how much negative energy (represented by a number of energy eigenstates carrying a negative energy) can „fit“ in the negative part of the potential. Note that in our case of a spin-independent Hamiltonian, the possible degeneracy of each energy eigenstate is given by the number of spin states  $q$ .

- (ii) Both sides scale<sup>5</sup> as length<sup>-2 $\gamma$</sup> , so no other choice of exponents would have been possible.
- (iii) There is no exponent outside the integral of the right hand side. Therefore, our bounds on the sums of negative eigenvalues are additive for potentials, which are situated at a distance from one another (e.g. for  $V_1, V_2$  with disjoint support).
- (iv) The reason why the case differentiation in  $d$  occurs, is that in low dimensions one can fit a negative eigenvalue into any arbitrarily small potential  $V_-$ . By scaling, the inequality then fails for  $\gamma$  being too small. A very instructive example for  $d = 1$  is given in [20]. We define

$$f(x) := \frac{1}{\cosh^\alpha(x)}, \quad (6.22)$$

for some  $\alpha > 0$ . Then,  $f$  satisfies the PDE

$$-f''(x) - \alpha(\alpha+1)\frac{1}{\cosh^2(x)}f(x) = -\alpha^2 f(x). \quad (6.23)$$

Assuming the LT inequality with  $V_-(x) = -\alpha(\alpha+1)\frac{1}{\cosh^2(x)} \in L^{\gamma+1/2}$  yields

$$\frac{\alpha^{\gamma-1/2}}{(\alpha+1)^{\gamma+1/2}} \leq L_{\gamma,1} \int_{\mathbb{R}} dx \frac{1}{\cosh^{2\gamma+1}(x)}, \quad (6.24)$$

which is seen to be false for  $\gamma < 1/2$  by letting  $\alpha \rightarrow 0$ .

- (v) The question about the relation between  $L_{\gamma,d}^{cl}$  and  $L_{\gamma,d}$  is intricate. There is a range of results depending heavily on the respective value of  $\gamma$  and  $d$ . A historical overview of the results can be found on page 310 of [14]. Generally, it is known that  $L_{\gamma,d}^{cl}$  is asymptotically correct for large potentials as seen from analyzing the Weyl asymptotics of the eigenvalues. This leads to

$$\Lambda_{\gamma,d} := \frac{L_{\gamma,d}}{L_{\gamma,d}^{cl}} \geq 1. \quad (6.25)$$

Another completely general statement is that the function  $\gamma \mapsto \Lambda_{\gamma,d}$  is monotonically non-increasing for fixed  $d$ , as shown in [1].

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<sup>5</sup>The meaning of this was explained after (4.2).

- (vi) In our case  $\gamma = 1, d = 3$ , it was already conjectured in the original work [19] that  $L_{1,3} = L_{1,3}^{cl}$ . This is also known as the *Lieb-Thirring conjecture*. The best currently known estimate was shown in [10] (2008), namely

$$L_{1,3} \leq \frac{\pi}{\sqrt{3}} L_{1,3}^{cl}. \quad (6.26)$$

## 6.4 The Birman-Schwinger Principle

### 6.4.1 The Birman-Schwinger Formulation of the Schrödinger Equation

Since we are only interested in bounding the negative eigenvalue sums from below, we can use (6.8) to drop the positive part  $V_+$  of the potential and replace  $V$  by  $-V_-$ . As we will see, the proof of theorem 6 uses a rewritten version of the time-independent Schrödinger equation (with Hamiltonian  $H = -\Delta + V_-(\mathbf{x})$ ). The result of this section is the following

**Theorem - Definition 6.4.1** (Birman-Schwinger formulation). Fix  $e > 0$ . There is a one-to-one correspondence between the two sets of eigenfunctions

$$\mathbb{S} := \{ \psi \in L^2(\mathbb{R}^3) \mid (-\Delta + V_-(\mathbf{x}))\psi(\mathbf{x}) = -e\psi(\mathbf{x}) \} \quad (6.27)$$

$$\mathbb{B} := \{ \phi \in H^1(\mathbb{R}^3) \mid \phi = K_e \phi \}, \quad (6.28)$$

where  $K_e$  is a Hilbert-Schmidt<sup>6</sup> operator with kernel given by the *Birman-Schwinger-Kernel* (also called  $K_e$ )

$$K_e(\mathbf{x}, \mathbf{y}) := \sqrt{V_-(\mathbf{x})} G_e(\mathbf{x} - \mathbf{y}) \sqrt{V_-(\mathbf{y})} \quad (6.29)$$

$$G_e(\mathbf{x} - \mathbf{y}) := \frac{1}{-\Delta + e}(\mathbf{x} - \mathbf{y}). \quad (6.30)$$

$G_e$  is called the *Green's function* for the positive operator  $-\Delta + e$ , or the *Yukawa potential*. It is translation invariant and explicitly given in terms of the inverse Fourier transform by

$$G_e(\mathbf{x} - \mathbf{y}) = \int_{\mathbb{R}^3} d\mathbf{k} \frac{1}{|2\pi\mathbf{k}|^2 + e} e^{2\pi i\mathbf{k}(\mathbf{x}-\mathbf{y})}. \quad (6.31)$$

Furthermore, there is also a one-to-one correspondence between all the respective eigenvalues, in the sense that if we denote

$$N_e := \#\{\text{eigenvalues of } H \text{ less than } -e\},$$

$$B_e := \#\{\text{eigenvalues of } K_e \text{ greater than } 1\},$$

then it is true that

$$N_e = B_e. \quad (6.32)$$

*Remark 6.4.1.* The fact that  $K_e$  is an operator on  $L^2(\mathbb{R}^3)$  is non-trivial and will be worked out in the proof.

<sup>6</sup>This notion was defined right after (4.30).

*Proof.* For the proof of the explicit form of the Yukawa potential we refer to theorem 6.23 in [14].

Step 1 We first show the correspondence of the eigenfunctions. Let  $\psi \in \mathbb{S}$ , i.e.  $\psi$  satisfies the Schrödinger equation. We can rewrite  $H\psi = -e\psi$  as

$$\psi(\mathbf{x}) = \frac{1}{-\Delta + e}(V_-(\mathbf{x})\psi(\mathbf{x})).$$

If we define

$$\phi(\mathbf{x}) := \sqrt{V_-(\mathbf{x})}\psi(\mathbf{x}), \quad (6.33)$$

then  $\phi$  is seen to satisfy  $\phi = K_e\phi$ . For the moment,  $\phi$  is just a formal object.

Next, we show that  $K_e$  is an operator from  $L^2(\mathbb{R}^3)$  to  $L^2(\mathbb{R}^3)$ . This can be shown directly by the Hardy-Littlewood-Sobolev inequality, we follow [6], though. We write (notice that  $-\Delta + e \geq 0$  from the Fourier representation, thus its square root exists)

$$K_e = BB^*, \quad \text{where } B := \sqrt{V_-(\mathbf{x})} \frac{1}{\sqrt{-\Delta + e}}.$$

Recall the definition of the  $H^1$ -norm in (2.21). If we now take  $f \in L^2(\mathbb{R}^3)$ , we see (using that the Fourier transform is an isometry from  $H^1$  to a weighted  $L^2$ -space<sup>7</sup>)

$$\begin{aligned} \|Bf\|_{H^1}^2 &= \int_{\mathbb{R}^3} d\mathbf{k} (1 + (2\pi\mathbf{k})^2) \left| \frac{\widehat{f}(\mathbf{k})}{\sqrt{(2\pi\mathbf{k})^2 + e}} \right|^2, \\ &= \int_{\mathbb{R}^3} d\mathbf{k} \underbrace{\frac{1 + (2\pi\mathbf{k})^2}{e + (2\pi\mathbf{k})^2}}_{\leq \max\{1, 1/e\}} |\widehat{f}(\mathbf{k})|^2, \end{aligned}$$

i.e.  $Bf \in H^1(\mathbb{R}^3)$  by the Plancherel formula. This implies that  $K_e = BB^*$  continuously maps  $L^2(\mathbb{R}^3)$  into itself. Thus, for  $\phi$  defined in (6.33) to be an eigenfunction of  $K_e$ , we need to show that  $\phi = \sqrt{V_-(\mathbf{x})}\psi(\mathbf{x}) \in L^2(\mathbb{R}^3)$ . This follows from an application of Hölder's and Sobolev's inequalities to the  $L^{3/2}$ -part  $V_1$  of  $V_-$ , together with the fact that  $\psi \in H^1(\mathbb{R}^3)$ :

$$\begin{aligned} \|\phi\|_2^2 &= \int_{\mathbb{R}^3} d\mathbf{x} V_-(\mathbf{x}) |\psi(\mathbf{x})|^2 \leq \|V_1\|_{3/2} \|\psi\|_6^2 + \|V_2\|_\infty \|\psi\|_2^2 \\ &\leq S_3 \|V_1\|_{3/2} \underbrace{\|\nabla\psi\|_2^2}_{\leq \|\psi\|_{H^1}^2} + \|V_2\|_\infty < \infty. \end{aligned}$$

Clearly  $\psi = 0 \Rightarrow \phi = 0$  and the other direction follows from the fact that the Laplacian has no eigenfunctions in  $H^1(\mathbb{R}^3)$ . So, all that remains to produce the one-to-one correspondence of the eigenfunctions, is to show that given a  $\phi \in \mathbb{B}$  it holds that

$$\psi(\mathbf{x}) := \frac{1}{-\Delta + e}(\sqrt{V_-(\mathbf{x})}\phi(\mathbf{x})) \in L^2(\mathbb{R}^3).$$

<sup>7</sup>Confer theorem 7.9 in [14]

From the considerations in the beginning it will then follow that  $\psi \in \mathbb{S}$ . We notice from the Fourier representation of  $G_e$  that

$$\frac{1}{(-\Delta + e)^2} \leq \frac{1}{e} \frac{1}{(-\Delta + e)},$$

which leads to (using self-adjointness)

$$\|\psi\|^2 = \langle \sqrt{V_-} \phi, (-\Delta + e)^{-2} \sqrt{V_-} \phi \rangle \leq \frac{1}{e} \langle \phi, K_e \phi \rangle = \frac{\|\phi\|_2^2}{e} < \infty.$$

Step 2 To see  $N_e = B_e$  we have to use the fact from operator theory, that a (self-adjoint) Hilbert-Schmidt operator is compact and thus — by the spectral theorem — has a spectral decomposition, in particular there exists a set of eigenvalues  $\{\lambda_j\}$ . Since  $K_e$  is a positive operator, as seen above, the  $\{\lambda_j^e\}$  are non-negative. For a good reason, we wait to show that  $K_e$  is Hilbert-Schmidt until the proof of the Lieb-Thirring inequality (but we assume compactness nevertheless). There are two more important facts about the eigenvalues of  $K_e$ :

- (i)  $K_e$  is a monotonically decreasing operator in  $e$ . This follows from the Fourier representation<sup>8</sup> in (6.30), which implies

$$\tilde{e} \geq e \Rightarrow \frac{1}{-\Delta + \tilde{e}} \leq \frac{1}{-\Delta + e}.$$

It then follows from the Min-Max-principle (see (6.8)), that the eigenvalues of  $K_{\tilde{e}}$  are smaller than those of  $K_e$ . So, the eigenvalues of  $K_e$  go to zero, as  $e \rightarrow \infty$ .

- (ii) The eigenvalues  $\{\lambda_j^e\}$  are continuous in  $e$ . This follows from the fact that that  $K_e$  has a finite spectral radius denoted by  $r_e$ . Thus, for  $0 < e \leq \tilde{e}$  we can estimate as follows (using the fact that the operator inequality<sup>9</sup>  $e(-\Delta) \leq \tilde{e}(-\Delta)$  implies  $\frac{1}{-\Delta + \tilde{e}} \geq \frac{e}{\tilde{e}} \frac{1}{-\Delta + e}$ )

$$0 \leq K_e - K_{\tilde{e}} \leq \frac{\tilde{e} - e}{\tilde{e}} K_e \leq \frac{r_e}{\tilde{e}} |\tilde{e} - e|.$$

With these two facts we can go on to define the *algorithm* rendering the conclusion: Recall that we have fixed  $e > 0$ . We now let the parameter  $\tilde{e}$  increase from  $e$  to  $\infty$ . In this process, all of the eigenvalues of  $K_e$  greater than one (there are  $B_e$  of them) will continuously go to zero. By the intermediate value theorem, they will cross the value one at some  $\tilde{e}_0 \geq e$ . Then, by Step 1,  $-\tilde{e}_0$  will be an eigenvalue of  $H$  below  $-e$  with the same multiplicity as the corresponding eigenvalue 1 of  $K_{\tilde{e}_0}$ . By sending  $\tilde{e} \rightarrow \infty$  we will certainly find all eigenvalues of  $H$  below  $-e$  and thus  $B_e = N_e$  as claimed. A nice pictorial representation of the ongoing process can be found on page 78 of [16].  $\square$

## 6.4.2 Proof of the LT inequality

With the help of the Birman-Schwinger principle, we are now in a position to show the LT inequality. We will only show the case  $\gamma = 1, d = 3$ , so  $V_- \in L^{5/2}(\mathbb{R}^3)$ . For the general proof, the reader is referred to [16] or the original works by Lieb and Thirring: [19], [18].

<sup>8</sup>This can also be seen directly from the resolvent identity.

<sup>9</sup>We remark that this only holds since  $\tilde{e}, e$  are numbers.

*Proof of theorem 6.3.1.*

Step 1 The first step is pedagogical. By naively considering  $N_e$ , we will be led to a divergent integral. For the second step, we will adjust the potential  $V_-$  appropriately and follow the same argumentation for the modified potential as we present now. We start from the left side with  $|E_j| =: e_j$ . Since, in the weak sense

$$\frac{d}{de} N_e = \sum_{j \geq 0: E_j \leq 0} \delta(e - e_j),$$

we can integrate by parts (using  $N_e(-\infty) = 0$ ) to get

$$\sum_{j \geq 0: E_j \leq 0} e_j = \int_0^\infty de N_e. \quad (6.34)$$

By the Birman-Schwinger principle and definition of  $B_e$ , we know

$$N_e = B_e \leq \sum_{j \geq 0: \lambda_j \geq 1} \lambda_j^2 \leq \text{Tr}(K_e)^2,$$

wherein the last expression can be calculated explicitly. By Fubini's theorem, the Cauchy-Schwarz inequality and Plancherel's formula, we get

$$\begin{aligned} \text{Tr}(K_e)^2 &= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} dx dy V_-(\mathbf{x}) V_-(\mathbf{y}) G_e(\mathbf{x} - \mathbf{y})^2 \\ &\leq \int_{\mathbb{R}^3} dy G_e(\mathbf{y})^2 \int_{\mathbb{R}^3} dx V_-(\mathbf{x}) V_-(\mathbf{x} - \mathbf{y}) \\ &\leq \int_{\mathbb{R}^3} dy G_e(\mathbf{y})^2 \int_{\mathbb{R}^3} dx V_-(\mathbf{x})^2 \\ &= \int_{\mathbb{R}^3} dx V_-(\mathbf{x})^2 \int_{\mathbb{R}^3} d\mathbf{k} \frac{1}{(|2\pi\mathbf{k}|^2 + e)^2}. \end{aligned}$$

We make a change of variables in the last term to see that

$$\int_{\mathbb{R}^3} d\mathbf{k} \frac{1}{(|2\pi\mathbf{k}|^2 + e)^2} = e^{-1/2} \int_{\mathbb{R}^3} d\mathbf{k} \frac{1}{(|2\pi\mathbf{k}|^2 + 1)^2} = e^{-1/2} (4\pi)^{-3/2} \frac{\Gamma(1/2)}{\Gamma(2)}.$$

When we put this expression back into (6.34), we obtain the integral over  $e^{-1/2}$  on the positive real axis, which is divergent (even if we would have picked another power of  $\text{Tr} K_e$ , by the way).

Step 2 The way out is to define the new potential

$$W_e(\mathbf{x}) := [V(\mathbf{x}) + e/2]_- \leq V_-(\mathbf{x}),$$

which is clearly in  $L^{5/2}(\mathbb{R}^3)$ , since  $V_-$  is. Let  $N_e(V)$  denote the eigenvalues lower than  $-e$  of the general Hamiltonian  $-\Delta + V$ . Then we can write

$$(-\Delta - V_-)\psi = -\epsilon\psi \Leftrightarrow (-\Delta - V_- + \underbrace{e/2 + \epsilon}_{\leq -e/2})\psi = e/2 \cdot \psi,$$

and notice that  $-W_e \leq -V_- + e/2$  by definition. This leads us to conclude

$$N_e = N_e(-V_-) = N_{e/2}(-V_- + e/2) \leq N_{e/2}(-W_e),$$

which estimates  $N_e$  in the right direction to justify the following crucial step: We now repeat the Birman-Schwinger principle and Step 1 with  $e$  replaced by  $e/2$  and (more importantly)  $-V_-$  replaced by  $W_e$ . We collect all the terms from Step 1, notice that  $W_e(\mathbf{x}) \neq 0$  implies  $e \leq 2V_-(\mathbf{x})$  and get

$$\begin{aligned} \sum_{j \geq 0: E_j \leq 0} |E_j| &= (4\pi)^{-3/2} \frac{\Gamma(1/2)}{\Gamma(2)} \int_0^\infty de \left(\frac{e}{2}\right)^{-1/2} \int_{\mathbb{R}^3} d\mathbf{x} W_e(\mathbf{x}) \\ &\leq \frac{\sqrt{2}}{(4\pi)^{3/2}} \frac{\Gamma(1/2)}{\Gamma(2)} \int_{\mathbb{R}^3} d\mathbf{x} \int_0^{2V_-(\mathbf{x})} de (V_-(\mathbf{x}) - e/2)^2 e^{-1/2}. \end{aligned}$$

After a change of variables, we can apply (6.16) to the  $de$ -integral, i.e.

$$\sqrt{2}V_-(\mathbf{x})^{5/2} \int_0^1 de e^{-1/2} (1-e)^2 = \sqrt{2}V_-(\mathbf{x})^{5/2} \frac{\Gamma(1/2)\Gamma(3)}{\Gamma(7/2)}.$$

Now we can collect all the terms, use the fact that  $\Gamma(3) = 2\Gamma(2)$  and summarize as follows

$$\sum_{j \geq 0: E_j \leq 0} |E_j| \leq \frac{4}{(4\pi)^{3/2}} \frac{\Gamma(1/2)^2}{\Gamma(7/2)} \int_{\mathbb{R}^3} d\mathbf{x} V_-(\mathbf{x})^{5/2},$$

which proves the LT inequality with the right  $L_{1,3}$ -constant. Notice that we have proved along the way that  $\text{Tr}(K_e)^2 < \infty$ , i.e. that  $K_e$  is Hilbert-Schmidt, as promised in the proof of the Birman-Schwinger principle.  $\square$

## 6.5 A Kinetic Energy Inequality

The next theorem is an equivalent formulation of the LT inequality in terms of the kinetic energy and without a particular potential. It will not be needed for the first proof of stability, but for the alternative one in section 8.3 and the one via Thomas-Fermi theory in chapter 9.

Recall the notation  $\|\gamma_0^{(1)}\|_\infty$ , introduced in definition 4.2.13 for the largest eigenvalue of the spin-summed one-particle density matrix. The particle density  $\varrho_\psi$  was defined in (4.17). We refrain from either giving the general version of the theorem or proving its equivalence with 6.3.1 and rather refer to the original source [18] and to chapter 4 of [16] for more on these issues.

**Theorem 6.5.1** (Non-relativistic kinetic energy inequality). *Let  $N \in \mathbb{N}$ . Then, for all  $\psi \in H^1(\mathbb{R}^{3N})$ , it holds that*

$$T_\psi \geq \frac{K}{\|\gamma_0^{(1)}\|_\infty} \int_{\mathbb{R}^3} d\mathbf{x} \varrho_\psi(\mathbf{x})^{5/3}, \quad (6.35)$$

with constant  $K$  given by

$$K = \frac{3}{5} \left( \frac{3}{5L_{1,3}} \right)^{2/3}. \quad (6.36)$$

*Remark 6.5.2.* (i) The constant  $K$  can be shown to satisfy  $K \geq (\frac{3}{\pi^2})^{1/3} K_{cl} \approx 3.065$  with a  $K_{cl} = \frac{3}{5}(6\pi^2)^{2/3}$  emerging from  $L_{1,3}^{cl}$ , which was given in the first section of this chapter.

(ii) Both sides scale as  $\text{length}^{-2}$  and thus the choice of the exponents is the only possible one. To see this, consider the rescaled wave function  $\psi_\lambda(\mathbf{x}) := \lambda^3 \psi(\lambda \mathbf{x})$ .

(iii) The physical content of this theorem is again an uncertainty principle. It provides a lower bound to the kinetic energy, which increases with spatial localization measured by the integral over the particle density. Additionally, upon recalling corollary 4.2.17, we notice that the bound will drop with increasing spin value  $q$ . This can be expected, because a higher spin degeneracy milder the exchange repulsion due to the spatial localization.

*Proof of theorem 6.5.1.*

**Step 1** This step will be mimicked in our first proof of stability of matter. Let  $\psi \in \bar{H}^1(\mathbb{R}^{3N})$  be normalized (without loss of generality). Denote by  $\gamma^{(1)}$  the one-particle density matrix corresponding to  $\psi$  (i.e.  $\gamma^{(1)} = N \text{Tr}_{N-1} \Gamma_\psi$ ). We consider the one-particle Hamiltonian

$$H = T + V,$$

where  $V$  is arbitrary (for the moment), except that  $V$  should not depend on spin and  $V_- \in L^{5/2}(\mathbb{R}^3)$ . Then we can go on to define the  $N$ -particle operator

$$K_N := \sum_{i=1}^N H_i,$$

which has the (very special) property of being a sum of one-particle operators, i.e. it does not describe interactions of any sort. Under abuse of the  $\text{Tr}$ -notation we can write (using proposition 4.2.15)

$$\langle \psi, K_N \psi \rangle = \text{Tr}(H \gamma^{(1)}) = \text{Tr}(H \gamma_0^{(1)}).$$

As a first estimate, we can certainly bound the right hand side by

$$\mathcal{M} := \min \left\{ \text{Tr}(H \gamma_0) \mid \gamma_0 \geq 0, \text{Tr}(\gamma_0) < \infty, \|\gamma_0\|_\infty \leq \|\gamma_0^{(1)}\|_\infty \right\}.$$

The following fact should be clear from the physical point of view. Its proof however requires some tools in spectral theory, which we do not want to introduce. We therefore simply state that  $\mathcal{M}$  is achieved by filling up all the negative energy eigenstates of  $H$  with the maximum degeneracy  $\|\gamma_0^{(1)}\|_\infty$  and leaving all the positive energy eigenstates of  $H$  unoccupied. Mathematically speaking, the optimal choice for a  $\gamma_0$  fulfilling the above conditions is given by the projection onto the negative spectral subspace of  $H$  times the constant  $\|\gamma_0^{(1)}\|_\infty$ .<sup>10</sup> The upshot is that

$$\langle \psi, K_N \psi \rangle \geq \|\gamma_0^{(1)}\|_\infty \sum_{j \geq 0: E_j \leq 0} E_j.$$

This expression is central in our proof. We can go on to relate the left hand side to the density  $\varrho_\psi$  via

$$\langle \psi, K_N \psi \rangle = T_\psi + \int_{\mathbb{R}^3} d\mathbf{x} V(\mathbf{x}) \varrho_\psi(\mathbf{x}),$$

<sup>10</sup>For more on this, confer e.g. section 11 in [7].

and on the right hand side we can deploy the LT inequality (theorem 6.3.1) to get

$$T_\psi + \int_{\mathbb{R}^3} d\mathbf{x} V(\mathbf{x}) \varrho_\psi(\mathbf{x}) \geq -\|\gamma_0^{(1)}\|_\infty L_{1,3} \int_{\mathbb{R}^3} d\mathbf{x} V_-(\mathbf{x})^{5/2}. \quad (6.37)$$

We emphasize that we have used nothing but the fact that  $\psi$  is normalized and the one-particle operator was (up to the necessary conditions for the LT inequality to hold) completely arbitrary.

Step 2 Now, we choose a  $\psi$ -dependent potential, namely

$$V(\mathbf{x}) := -C \varrho_\psi(\mathbf{x})^{2/3}, \quad (6.38)$$

which is in  $L^{5/2}(\mathbb{R}^3)$  whenever  $\varrho_\psi \in L^{5/3}(\mathbb{R}^3)$ . The constant  $C > 0$  will be determined in a moment. From (6.37), it follows that

$$T_\psi \geq C \int_{\mathbb{R}^3} d\mathbf{x} \varrho_\psi^{5/3}(\mathbf{x}) - \|\gamma_0^{(1)}\|_\infty C^{5/2} L_{1,3} \int_{\mathbb{R}^3} d\mathbf{x} \varrho_\psi^{5/3}(\mathbf{x}),$$

and we are done in principle. All that remains is to determine the constant. It is clear that we should maximize<sup>11</sup> the right hand side in  $C$ . We find the optimal value to be  $C = (5/2\|\gamma_0^{(1)}\|_\infty L_{1,3})^{2/3}$ , which gives the correct value of  $K$ .  $\square$

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<sup>11</sup>The method for optimizing is the one from elementary calculus: Setting the  $C$ -derivative equal to zero and solving for  $C$ . For two polynomial terms (as above), one can always determine the right *order* of the optimal  $C$  by setting both terms equal and solving for  $C$ .

# Chapter 7

## A First Proof of Non-Relativistic Stability

In the previous chapters, we followed the route to stability laid out in section 4.3. We have shown in Baxter's inequality that — mainly by the screening property — the Coulomb interaction can be estimated from below by a one-particle potential. We have also proved the LT inequality, which implies that the sum of negative eigenvalues can be controlled by said one-particle potential — times a degeneracy factor. The degeneracy factor can be controlled for fermions thanks to the result that fermionic one-particle density matrices are bounded by the identity. Now that we have assembled all the necessary tools, we are able to prove stability of the second kind for non-relativistic matter governed by the Coulomb interaction.

### 7.1 Monotonicity in the Nuclear Charges

Before we go on to stability, we have to remedy the assumption made in chapter 5, that all the nuclear charges  $Z_1, \dots, Z_K$  are equal to some  $Z$ . In fact, we will show  $Z = \max\{Z_1, \dots, Z_M\}$ . This result will also justify our original definition of *stability of the second kind* in section 4.2.4, which we restate here for the reader's convenience: There exists a real-valued function  $\Xi$  such that

$$E_{N,M}(\underline{Z}) \geq -\Xi(\max\{Z_1, \dots, Z_M\})(N + M), \quad (7.1)$$

where the left hand side was defined by minimizing the quadratic form  $\mathcal{E}$  over all wave functions and nuclear configurations. We go on to show the result of this section.

**Theorem 7.1.1** (Monotonicity in the nuclear charges). *Let  $Z := \max\{Z_1, \dots, Z_M\}$ . Then*

$$E_{N,M}(\underline{Z}, \underline{\mathbf{R}}) \geq \min \left\{ E_{N,K}((Z, \dots, Z), \tilde{\mathbf{R}}_K) \mid \tilde{\mathbf{R}}_K \subset \underline{\mathbf{R}} \right\}, \quad (7.2)$$

where  $\tilde{\mathbf{R}}_K$  is a subset of  $\underline{\mathbf{R}}$  containing  $K \leq M$  elements. Furthermore, the absolute ground state energy is monotonically non-increasing in  $\underline{Z}$ , i.e for  $\underline{Z} \leq \underline{Z}'$  we have that

$$E_{N,M}(\underline{Z}) \geq E_{N,M}(\underline{Z}'). \quad (7.3)$$

*Proof.* The Hamiltonian  $H = -1/2\Delta + \alpha V_C$  is an affine, operator-valued function of each individual  $Z_k$  (i.e for all  $Z_l, l \neq k$  fixed) as can be seen by inspection of (3.16). The

definition of  $E_{N,M}(\underline{Z}, \underline{\mathbf{R}})$  involves taking the infimum over  $\langle \psi, H\psi \rangle$ . For each  $Z_k$ , it is thus the infimum of the uncountably many affine functions

$$Z_k \mapsto \langle \psi, H(Z_k)\psi \rangle,$$

and therefore concave in  $Z_k$ . This implies that it attains its infimum over the interval  $[0, Z]$  either at  $Z_k = 0$  or  $Z_k = 1$ , which proves the first claim.

For the second statement, all that remains to show is that the absolute ground state energy, viewed as a function of  $Z_k$  for a fixed  $k$ , cannot be increasing close to zero. If it were to assume a finite, positive value close to zero, this excitation could be remedied by moving the  $k$ -th nucleus to infinity, thus effectively setting  $Z_k = 0$ , and energy would be set free. The movement to infinity, however, can be achieved by putting an infinitesimal amount of kinetic energy into the nucleus. Then it will move off to infinity since it has effectively infinite mass on our scales. This is a contradiction to the conservation of energy and therefore the (concave) function  $E_{N,M}(Z_k)$  must be monotone non-increasing.  $\square$

## 7.2 Putting it all together

We will now prove the main result of this work. Note that  $N^{1/3}M^{2/3} \leq N + M$ , so the desired linear bound is indeed achieved. The numerical value of this first bound is far from optimal and will be improved using some of the more sophisticated inequalities in chapter 8. The bound obtained for neutral hydrogen (i.e.  $q = 2$ ,  $N = M$  and  $Z = 1$ ) is 7.29 Rydbergs.

**Theorem 7.2.1** (Stability of non-relativistic matter I). *Let  $Z := \max\{Z_1, \dots, Z_M\}$  and  $\psi \in \mathcal{H}_N^{(f)}$  be normalized. Let  $q$  denote the number of spin states of  $\psi$ . Then*

$$\langle \psi, H\psi \rangle \geq -1.073q^{2/3}\alpha^2(2Z + 1)^2M^{2/3}N^{1/3}. \quad (7.4)$$

*Proof.* By theorem 7.1.1, we may assume that all the nuclear charges are equal to  $Z$ . We apply Baxter's inequality (theorem 5.3.1) and drop the positive term on the right hand side to get

$$V_C(\underline{\mathbf{x}}, \underline{\mathbf{R}}) \geq -(2Z + 1) \sum_{i=1}^N \frac{1}{\mathcal{D}(\mathbf{x}_i)}.$$

Now, we have reduced the problem to bounding the ground state energy of the Hamiltonian

$$K_N := \sum_{i=1}^N h_i = \frac{1}{2} \sum_{i=1}^N (-\Delta_i) - (2Z + 1)\alpha \sum_{i=1}^N \frac{1}{\mathcal{D}(\mathbf{x}_i)}.$$

from below. We would like to apply the LT inequality, but we see that  $1/\mathcal{D}(\mathbf{x}) = 1/\min\{|\mathbf{x} - \mathbf{R}_k| | k \in \{1, \dots, M\}\}$  is not in  $L^{5/2}(\mathbb{R}^3)$  as required. But we can rewrite  $1/\mathcal{D}(\mathbf{x})$  using some  $b > 0$  as

$$\left( \frac{1}{\mathcal{D}(\mathbf{x})} - b \right) + b,$$

where the positive part<sup>1</sup> of the first expression will be now seen to lie in  $L^{5/2}(\mathbb{R}^3)$ . The second term just becomes a  $-(2Z+1)\alpha bN$ , i.e. linear in  $N$ . By positivity,

$$\begin{aligned} \left[ \frac{1}{\min \{ |\mathbf{x} - \mathbf{R}_k| \mid k \in \{1, \dots, M\} \}} - b \right]_+^{5/2} &= \max \left\{ \left[ \frac{1}{|\mathbf{x} - \mathbf{R}_k|} - b \right]_+^{5/2} \mid k \in \{1, \dots, M\} \right\} \\ &\leq \sum_{k=1}^M \left[ \frac{1}{|\mathbf{x} - \mathbf{R}_k|} - b \right]_+^{5/2}, \end{aligned}$$

so we can bound (by shifting the integration)

$$\int_{\mathbb{R}^3} d\mathbf{x} \left[ \frac{1}{\mathcal{D}(\mathbf{x})} - b \right]_+^{5/2} \leq M \int_{B_{1/b}(0)} d\mathbf{x} \left( \frac{1}{|\mathbf{x}|} - b \right)_+^{5/2},$$

which is finite. Since we are interested in the exact constant, we calculate its value (using polar coordinates and formula (6.16)) to be

$$\begin{aligned} M \int_{B_{1/b}(0)} d\mathbf{x} \left( \frac{1}{|\mathbf{x}|} - b \right)_+^{5/2} &= \frac{4\pi M}{\sqrt{b}} \int_0^1 dr r^{-1/2} (1-r)^{5/2} = \frac{4\pi M}{\sqrt{b}} \frac{5\Gamma(1/2)^2}{16} \\ &= \frac{5\pi^2 M}{4} b^{-1/2}. \end{aligned}$$

We can thus apply the LT inequality.<sup>2</sup> In fact, we can argue the same way as in step 1 in the proof of theorem 6.5.1, and use corollary 4.2.17 to get

$$\begin{aligned} \langle \psi, H\psi \rangle &\geq \langle \psi, K_N \psi \rangle \\ &\geq -\|\gamma_0^{(1)}\|_\infty L_{1,3} \frac{1}{2} (2\alpha(2Z+1))^{5/2} \int_{\mathbb{R}^3} d\mathbf{x} \left[ \frac{1}{\mathcal{D}(\mathbf{x})} - b \right]_+^{5/2} - \alpha(2Z+1)bN \\ &\geq -qL_{1,3} \frac{5\pi^2 M}{\sqrt{2b}} (\alpha(2Z+1))^{5/2} - \alpha(2Z+1)bN. \end{aligned}$$

We can now optimize this over  $b$ . We skip this elementary calculation and insert the optimal value

$$b = \frac{\alpha(2Z+1)}{2} (L_{1,3}\pi^2 q)^{2/3} M^{2/3} N^{-2/3}$$

directly into the last expression to get

$$\langle \psi, H\psi \rangle \geq -\frac{3}{2} (5\pi^2 L_{1,3})^{2/3} q^{2/3} (\alpha(2Z+1))^2 M^{2/3} N^{1/3}.$$

After inserting all the constants, we see that this yields the claim.  $\square$

<sup>1</sup>The positive part appears because of the minus sign in front of the  $i$ -sum.

<sup>2</sup>Note that the LT inequality was stated without the factor 1/2 in front of the Laplacian.

# Chapter 8

## Inequalities for Exchange-Correlation Energies

Baxter's inequality, as shown in chapter 5, estimated the Coulomb potential  $V_C(\underline{\mathbf{x}}, \underline{\mathbf{R}})$  by smearing out the electronic charges using only the tools of electrostatics. An intermediate step in the proof was to show that  $V_C(\underline{\mathbf{x}}, \underline{\mathbf{R}})$  could be bounded from below by a classical charge distribution coming from the smeared out electron charges. Then, we used it in the proof of stability, where the expectation value  $V_\psi = \langle \psi, V_C \psi \rangle$  could be bounded from below in the same manner, since  $\psi$  was normalized. Clearly, we have ignored all quantum mechanical peculiarities situated within the wave-function  $\psi$ , i.e. two-particle correlations which could have influenced the electron-electron interaction  $I(\underline{\mathbf{x}})$  substantially.

The goal to estimate  $V_\psi$  from below in terms of a classical charge density remains — it is then truly within the realm of electrostatics and can be estimated accordingly. This idea is crucial for the alternative proof of stability via Thomas-Fermi theory in chapter 9. In fact, Thomas-Fermi theory is also the starting point for much more sophisticated density-functional theories which are widely used in computations of quantum chemists (for an introduction, see [11]). In this chapter, we will prove an inequality which controls the intrinsically quantum-mechanical (i.e. the complicated) part of  $V_\psi$  in terms of a one-particle charge density. We will not assume any particular statistics.

### 8.1 Exchange and Correlation

Let us begin with a definition, which is reminiscent of similar ones made in section 4.2. It can be viewed as a partial trace over spin space.

**Definition 8.1.1** ( $N$ -particle density). Let  $\psi \in \mathcal{H}_N$  be normalized with  $q$  spin states. We call

$$\rho_N(\mathbf{x}_1, \dots, \mathbf{x}_N) := \sum_{i=1}^N \sum_{\sigma_i=1}^q \psi(\mathbf{x}_1, \sigma_1, \dots, \mathbf{x}_N, \sigma_N) \quad (8.1)$$

the (normalized)  $N$ -particle density corresponding to  $\psi$ .

*Remark 8.1.2.* Recall the one-particle density  $\varrho_\psi^i$  of the  $i$ -th particle, as defined in definition 4.2.4. It is

$$\varrho_\psi^i(\mathbf{x}) = \int_{\mathbb{R}^{3(N-1)}} d\mathbf{x}_1 \dots \widehat{d\mathbf{x}_i} \dots d\mathbf{x}_N \rho_N(\mathbf{x}_1, \dots, \mathbf{x}_N). \quad (8.2)$$

Now, we assume that all the particles described by  $\rho_N$  carry an individual charge, denoted by  $e_i$  for the  $i$ -th particle. The charges are assumed to have the *same sign*. We will henceforth assume that they are all positive, but the results also hold in the negative case (because the charges always appear as products  $e_i e_j > 0$ ). In particular, all results hold for electrons.

**Definition 8.1.3** (Coulomb self-energy). Given an  $N$ -particle density  $\rho_N$ , we call

$$I_\rho := \sum_{1 \leq i < j \leq N} d\mathbf{x}_1 \dots d\mathbf{x}_N e_i e_j \frac{\rho_N(\mathbf{x}_1, \dots, \mathbf{x}_N)}{|\mathbf{x}_i - \mathbf{x}_j|} \quad (8.3)$$

the *Coulomb self-energy* of the  $N$ -particle system given by  $\rho_N$ .

*Remark 8.1.4.*  $I_\rho$  is a very complicated object. It contains all kinds of correlations between the  $N$  particles, as each particle „sees“ all other ones via the Coulomb interaction. It is practically incalculable and normally treated computationally by self-consistent methods. A special group of correlations is treated linguistically different, namely those arising from the statistics of  $\psi$ , which are inherited by  $\rho_N$ . For obvious reasons, these give rise to the so-called the *exchange energy*  $E_X$ . Any other energy originating in many-particle effects is part of the *correlation energy*  $E_C$ . Taken together, they form the *exchange-correlation energy*, which we will denote by  $E_{XC}$  and define precisely below.<sup>1</sup> It is our goal to find a lower bound on  $E_{XC}$ .

Since all the correlations can be stored in  $E_{XC}$ , what remains of  $I_\rho$  can only depend on the one-particle densities, multiplied by the respective charges. The interaction energy of such distributions is a very accessible object.

**Definition 8.1.5** (Exchange-correlation energy). Let  $\psi \in \mathcal{H}_N$ , with charges  $e_1, \dots, e_N$  given as above. Then we define the *charge density of the  $i$ -th particle* to be

$$Q_i(\mathbf{x}) := e_i \varrho_\psi^i(\mathbf{x}). \quad (8.4)$$

Correspondingly, the *one-particle charge density* is given by

$$Q(\mathbf{x}) := \sum_{i=1}^N Q_i(\mathbf{x}). \quad (8.5)$$

We then define the *exchange-correlation energy* of  $\rho_N$  as

$$E_{XC} := I_\rho - D(Q, Q), \quad (8.6)$$

with  $D(Q, Q)$  being the classical Coulomb energy of  $Q$  as defined in (3.2).

We remark on the fact that  $D(Q, Q)$  is always well-defined, because all the  $e_i$  have the same sign.  $E_{XC}$  may not be well-defined, but one can show (page 112 of [16]) that

$$Q \in L^{4/3}(\mathbb{R}^3) \Rightarrow D(Q, Q) < \infty, \quad (8.7)$$

which implies that  $E_{XC}$  is well-defined. The condition  $Q \in L^{4/3}$  will become clear in a moment, since it is necessary for the following theorem to be non-trivial.

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<sup>1</sup>A classic source of approximative results is Hartree-Fock theory. It approximates the real world by self-consistently choosing Slater determinants as the wave functions of an atomic system. Slater determinants are uncorrelated up to exchange effects, the underlying structure is a product. An explicit calculation of  $E_{XC}$  for a Slater determinant can be found on page 108 of [16].

## 8.2 The Lieb-Oxford Inequality

### 8.2.1 Statement

The main result of this chapter is the following exchange estimate, which we state with the constant 1.68 obtained in [15]. A reasoning on the appearance of the exponent  $4/3$  and an explanation why there is no spin-dependency can be found in section 6.2 of [16].

**Theorem 8.2.1** (Lieb-Oxford inequality). *Let  $\rho_N$  be a normalized  $N$ -particle density and  $e_1, \dots, e_N$  the corresponding charges (having the same sign). Then there exists a  $C \leq 1.68$ , such that*

$$E_{XC} \geq -C \left( \int_{\mathbb{R}^3} d\mathbf{x} \left( \sum_{i=1}^N e_i Q_i(\mathbf{x}) \right)^{4/3} \right)^{1/2} \left( \int_{\mathbb{R}^3} d\mathbf{x} |Q(\mathbf{x})|^{4/3} \right)^{1/2} \quad (8.8)$$

holds. In the special case of  $e_1 = \dots = e_N =: e$ , we have that

$$E_{XC} \geq -C |e|^{2/3} \int_{\mathbb{R}^3} d\mathbf{x} |Q(\mathbf{x})|^{4/3} \quad (8.9)$$

*Remark 8.2.2.* (i) One reason why we do not assume that all charges are equal is that this will not simplify proof.

(ii)  $E_{XC}$  is unbounded from above, even for smooth  $Q$ . An example is easily constructed by assuring the falloff at infinity and counting the order of the relevant Coulomb singularities determining integrability. This leads to e.g.

$$\rho_2(\mathbf{x}_1, \mathbf{x}_2) = C_0 \frac{e^{-\mathbf{x}_1^2 - \mathbf{x}_2^2}}{|\mathbf{x}_1 - \mathbf{x}_2|^2}, \quad (8.10)$$

for which  $I_\rho = \infty$  and  $Q$  is finite.

(iii) We will prove the theorem with constant  $C \leq 3.17$ . The proof of the improved bound relies on a more sophisticated treatment replacing the estimates we make in the third step, using the fundamental theorem of calculus and an adapted charge density  $\mu$ . It can be found in [15].

### 8.2.2 Onsager's Lemma and Proof of the LO-inequality

We begin with the crucial estimate, which bounds  $I(\underline{\mathbf{x}})$  by Coulomb energies of (for the moment arbitrary) charge densities. The Coulomb energies do not depend on diagonal terms, i.e. on any sort of correlation between the particles. Interestingly, the fact that this is possible relies essentially on the positivity of the Coulomb energy (theorem 3.1.9).

**Lemma 8.2.3** (Onsager's lemma). *Let the positive charges  $e_1, \dots, e_N$  be located at the distinct point  $\mathbf{x}_1, \dots, \mathbf{x}_N \in \mathbb{R}^3$ . For each  $i \in \{1, \dots, N\}$ , take  $\mu_{\mathbf{x}_i} \in L^\infty(\mathbb{R}^3)$  to be a non-negative, normalized function, which is spherically symmetric with respect to  $\mathbf{x}_i$ . Let  $\varrho$  be any non-negative function in  $L^1(\mathbb{R}^3)$ . Then it is true that*

$$\sum_{1 \leq i < j \leq N} \frac{e_i e_j}{|\mathbf{x}_i - \mathbf{x}_j|} \geq -D(\varrho, \varrho) + 2 \sum_{i=1}^N e_i D(\varrho, \mu_{\mathbf{x}_i}) - \sum_{i=1}^N e_i^2 D(\mu_{\mathbf{x}_i}, \mu_{\mathbf{x}_i}), \quad (8.11)$$

where we have slightly abused notation by using  $D$  for densities of measures, i.e. functions.

*Proof.* That  $\mu_{\mathbf{x}_i} \in L^\infty(\mathbb{R}^3)$  implies that the last two terms on the right hand side are finite, i.e. the right hand side is well-defined. To see this for  $D(\mu_{\mathbf{x}_i}, \mu_{\mathbf{x}_i})$ , take  $\mathbf{x}_i = 0$  without loss of generality, apply Newton's theorem and use that  $\mu_0$  is normalized and non-negative to get

$$\begin{aligned} D(\mu_0, \mu_0) &= \frac{1}{2} \int_{\mathbb{R}^3} d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{y} \min\left\{\frac{1}{|\mathbf{x}|}, \frac{1}{|\mathbf{y}|}\right\} \mu_0(\mathbf{x}) \mu_0(\mathbf{y}) = \int_{\mathbb{R}^3} d\mathbf{x} \int_{|\mathbf{y}| \leq |\mathbf{x}|} d\mathbf{y} \frac{\mu_0(\mathbf{x}) \mu_0(\mathbf{y})}{|\mathbf{x}|} \\ &\leq \int_{|\mathbf{y}| \leq |\mathbf{x}|} \frac{\mu_0(\mathbf{y})}{|\mathbf{y}|} \leq \|\mu_0\|_\infty \int_{B_{|\mathbf{x}|}(0)} d\mathbf{y} \frac{1}{|\mathbf{y}|} < \infty. \end{aligned}$$

The term  $D(\varrho, \mu_{\mathbf{x}_i})$  is similar. Without loss of generality, we assume  $D(\varrho, \varrho) < \infty$ . By positivity of  $D$ , we know that

$$D\left(\varrho - \sum_{i=1}^N e_i \mu_{\mathbf{x}_i}, \varrho - \sum_{i=1}^N e_i \mu_{\mathbf{x}_i}\right) \geq 0$$

Since  $D$  is bilinear, we can rewrite this as

$$2 \sum_{1 \leq i < j \leq N} e_i e_j D(\mu_{\mathbf{x}_i}, \mu_{\mathbf{x}_j}) \geq -D(\varrho, \varrho) + 2 \sum_{i=1}^N e_i D(\varrho, \mu_{\mathbf{x}_i}) - \sum_{i=1}^N e_i^2 D(\mu_{\mathbf{x}_i}, \mu_{\mathbf{x}_i}),$$

and apply corollary 3.1.8 to the left hand side ( $\mu_{\mathbf{x}_i}$  is spherically symmetric and positive, with total charge equal to one), which gives

$$D(\mu_{\mathbf{x}_i}, \mu_{\mathbf{x}_j}) \leq \frac{1}{2} \int_{\mathbb{R}^3} d\mathbf{x} \mu_{\mathbf{x}_i}(\mathbf{x}) \frac{1}{|\mathbf{x} - \mathbf{x}_j|} = \frac{1}{2} \Phi_i(\mathbf{x}_j) \leq \frac{1}{2} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|}.$$

This proves the claim.  $\square$

*Proof of theorem 8.2.1. Step 1.* We use Onsager's lemma to bound  $E_{XC}$  by two terms, which we will treat separately in steps two and three. The  $\varrho$ , being a non-negative  $L^1$ -function, is sufficiently general for us to choose  $\varrho = Q$ . To create  $I_\rho$  from Onsager's Lemma, we multiply both sides by  $\rho_N(\mathbf{x}_1, \dots, \mathbf{x}_N)$  and integrate. In the terms where we can integrate out all variables but  $\mathbf{x}_i$ , we produce  $Q_i(\mathbf{x}_i)$ . For the other terms we recall that  $\rho_N$  is normalized, so we get

$$I_\rho \geq -D(Q, Q) + 2 \sum_{i=1}^N \int_{\mathbb{R}^3} d\mathbf{x}_i D(Q, \mu_{\mathbf{x}_i}) Q_i(\mathbf{x}_i) - \sum_{i=1}^N \int_{\mathbb{R}^3} d\mathbf{x}_i D(\mu_{\mathbf{x}_i}, \mu_{\mathbf{x}_i}) Q_i(\mathbf{x}_i). \quad (8.12)$$

When we allow ourselves to also use the  $D$ -notation with one argument being a function and the other being a measure, we can rewrite (by Fubini, since all the charges are positive)

$$\begin{aligned} D(Q, Q) &= \sum_{i=1}^N \int_{\mathbb{R}^3} d\mathbf{y} Q_i(\mathbf{y}) \int_{\mathbb{R}^3} d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{z} \frac{Q(\mathbf{x}) \delta_{\mathbf{y}}(\mathbf{z})}{|\mathbf{x} - \mathbf{z}|} \\ &= \sum_{i=1}^N \int_{\mathbb{R}^3} d\mathbf{x}_i Q_i(\mathbf{x}_i) D(Q, \delta_{\mathbf{x}_i}), \end{aligned}$$

where a suggestive integration variable  $\mathbf{x}_i$  has been used. Let us remark that this expression is also physically appealing, as the self-energy of the charge distribution  $Q$  is rewritten as the interaction energy of the  $i$ -th particle, situated at point  $\mathbf{x}_i$  and weighted with  $Q_i(\mathbf{x}_i)$ , with the whole charge distribution  $Q$  — summed up over all points and all particles. Thus, subtracting  $D(Q, Q)$  from both sides of (8.12) yields

$$\begin{aligned} E_{XC} &\geq -2 \sum_{i=1}^N \int_{\mathbb{R}^3} d\mathbf{x}_i D(Q, \delta_{\mathbf{x}_i} - \mu_{\mathbf{x}_i}) Q_i(\mathbf{x}_i) - \sum_{i=1}^N \int_{\mathbb{R}^3} d\mathbf{x}_i D(\mu_{\mathbf{x}_i}, \mu_{\mathbf{x}_i}) Q_i(\mathbf{x}_i) \\ &=: -F_1 - F_2, \end{aligned}$$

where  $F_1$  is positive by corollary 3.1.8 to Newton's theorem and  $F_2$  is obviously positive. In the following, we will thus look for upper bounds on  $F_1$  and  $F_2$ .

For this purpose, we specify  $\mu_{\mathbf{x}_i}$  further. From  $F_1$ , it is suggested that we should pick it to be an *approximate delta function* living on some adjustable length scale. This length scale has to include  $Q(\mathbf{x}_i)$ , since we are looking for a bound in which  $Q^{4/3}$  appears. With this in mind, we fix a bounded, non-negative and normalised  $\mu : \mathbb{R}^3 \rightarrow \mathbb{R}$ , which is spherically symmetric with respect to the origin and has support in the unit ball. Then we define

$$\mu_{\mathbf{x}_i}(\mathbf{y}) := \lambda^3 Q(\mathbf{x}_i)^{1/3} \mu(\lambda Q(\mathbf{x}_i)^{1/3}(\mathbf{x}_i - \mathbf{y})),$$

with some parameter  $\lambda > 0$ . Clearly,  $\mu_{\mathbf{x}_i}$  is non-negative and bounded. By performing the obvious change of variables  $\varphi(\mathbf{y}) := \lambda Q(\mathbf{x}_i)^{1/3}(\mathbf{x}_i - \mathbf{y})$  (i.e. a shift followed by rescaling), one can see that  $\mu_{\mathbf{x}_i}$  is spherically symmetric about  $\mathbf{x}_i$  and supported in the ball of radius

$$\mathcal{R} := \frac{1}{\lambda Q(\mathbf{x}_i)^{1/3}}$$

about  $\mathbf{x}_i$ . This means that small charges are spread out and large ones are concentrated. In particular,  $\mu_{\mathbf{x}_i}$  satisfies the conditions of Onsager's lemma.

Step 2 We first estimate  $F_2$ . One can immediately see that

$$\begin{aligned} D(\mu_{\mathbf{x}_i}, \mu_{\mathbf{x}_i}) &= \lambda^6 Q(\mathbf{x}_i)^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} d\mathbf{x} d\mathbf{y} \frac{1}{|\mathbf{x} - \mathbf{y}|} \mu(\lambda Q(\mathbf{x}_i)^{1/3}(\mathbf{x}_i - \mathbf{x})) \mu(\lambda Q(\mathbf{x}_i)^{1/3}(\mathbf{x}_i - \mathbf{y})) \\ &= \lambda Q(\mathbf{x}_i)^{1/3} D(\mu, \mu), \end{aligned}$$

which gives (using Hölder's inequality with  $p = 4$ )

$$\begin{aligned} F_2 &= \lambda D(\mu, \mu) \int_{\mathbb{R}^3} d\mathbf{x} Q(\mathbf{x})^{1/3} \left( \sum_{i=1}^N e_i Q_i(\mathbf{x}) \right) \\ &\leq \lambda D(\mu, \mu) \left( \int_{\mathbb{R}^3} d\mathbf{x} Q(\mathbf{x})^{4/3} \right)^{1/4} \left( \int_{\mathbb{R}^3} d\mathbf{x} \left( \sum_{i=1}^N e_i Q_i(\mathbf{x}) \right)^{4/3} \right)^{3/4}. \end{aligned}$$

This is of the desired form.

Step 3 We now turn to estimate  $F_1$ . By a direct calculation, we see that

$$\begin{aligned}\phi_i(|\mathbf{x}|) &:= \int_{\mathbb{R}^3} d\mathbf{y} \frac{1}{|\mathbf{x} - \mathbf{y}|} \mu_{\mathbf{x}_i}(\mathbf{y}) = \int_{\mathbb{R}^3} d\mathbf{y} \frac{1}{\left| \frac{\mathbf{y}}{\lambda Q(\mathbf{x}_i)^{1/3}} - (\mathbf{x}_i - \mathbf{x}) \right|} \mu(\mathbf{y}) \\ &= \lambda Q(\mathbf{x}_i)^{1/3} \phi(\lambda Q(\mathbf{x}_i)^{1/3} |\mathbf{x}_i - \mathbf{x}|),\end{aligned}$$

where  $\phi(|\mathbf{x}|) := \Phi(\mathbf{x})$  is the potential corresponding to  $\mu$ . The natural object to consider is the difference of the potentials corresponding to  $\delta_{\mathbf{x}_i}$  and  $\mu_{\mathbf{x}_i}$ . For this reason, we define the function

$$R_\lambda(a, r) := \frac{a}{r} - a\lambda a^{1/3} \phi(\lambda a^{1/3} r),$$

which allows us to rewrite

$$F_1 = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} d\mathbf{x} d\mathbf{y} Q(\mathbf{y}) R_\lambda(Q(\mathbf{x}), |\mathbf{x} - \mathbf{y}|).$$

At this point, we make a *crude estimate* of  $R_\lambda(a, r)$ . The improved constant is achieved by a different estimate, as mentioned above.

As before, corollary 3.1.8 implies that  $\phi(r) \leq r^{-1}$ , i.e. that  $R_\lambda(a, r)$  is non-negative. Also, Newton's Theorem directly implies that  $R_\lambda(a, r)$  vanishes outside the support of  $\mu_{\mathbf{x}_i}$ , i.e. whenever  $|\mathbf{x} - \mathbf{y}| > \mathcal{R}$ . Since  $R_\lambda(a, r)$  is non-negative, we can drop the second term on the inside of the ball  $B_{\mathcal{R}}$ , which gives us

$$F_1 \leq \int_{|\mathbf{x}-\mathbf{y}| \leq (\lambda^{-1} Q(\mathbf{x}))^{-1/3}} d\mathbf{x} d\mathbf{y} \frac{1}{|\mathbf{x} - \mathbf{y}|} Q(\mathbf{x}) Q(\mathbf{y}). \quad (8.13)$$

We now use the so-called *Layer-cake representation* (theorem 1.13 in [14]) for the (non-negative) function  $Q$ . Denote  $\chi_\alpha := \chi_{\{Q \geq \alpha\}}$ , then

$$Q(\mathbf{x}) = \int_0^\infty d\alpha \chi_\alpha(\mathbf{x}).$$

We put this into the right hand side of (8.13) and invoke Fubini's theorem (all objects are non-negative) to write

$$F_1 \leq \int_0^\infty d\alpha \int_0^\infty d\beta \int_{|\mathbf{x}-\mathbf{y}| \leq \lambda^{-1} \alpha^{-1/3}} d\mathbf{x} d\mathbf{y} \frac{1}{|\mathbf{x} - \mathbf{y}|} \chi_\alpha(\mathbf{x}) \chi_\beta(\mathbf{y}). \quad (8.14)$$

We can now split the  $\alpha$  and  $\beta$  integrals into integrals over the two sets  $\{0 \leq \alpha \leq \beta\}$  and  $\{0 \leq \beta \leq \alpha\}$ . When we are in the former set, we can estimate  $\chi_\alpha(\mathbf{x})$  by 1 from above and calculate the innermost integral to be (by Fubini and an elementary calculation)

$$\int_{\mathbb{R}^3} d\mathbf{y} \chi_\beta \int_{|\mathbf{x}| \leq \lambda^{-1} \alpha^{-1/3}} d\mathbf{x} \frac{1}{|\mathbf{x}|} = \frac{2\pi}{\lambda^2 \alpha^{2/3}} \int_{\mathbb{R}^3} d\mathbf{y} \chi_\beta(\mathbf{y}),$$

and where  $0 \leq \beta \leq \alpha$  holds, we drop the  $\chi_\beta$  and argue in the same fashion to get

$$\frac{2\pi}{\lambda^2 \alpha^{2/3}} \int_{\mathbb{R}^3} d\mathbf{x} \chi_\alpha(\mathbf{x}).$$

for the innermost integral. We place these two results back into (8.14) and obtain (by noticing that the second term is just a third of the first term)

$$\begin{aligned}
 F_1 &\leq \frac{2\pi}{\lambda^2 \alpha^{2/3}} \left( \int_0^\infty d\beta \int_0^\beta d\alpha \int_{\mathbb{R}^3} d\mathbf{y} \chi_\beta(\mathbf{y}) \alpha^{-2/3} + \int_0^\infty d\alpha \int_0^\alpha d\beta \int_{\mathbb{R}^3} d\mathbf{x} \chi_\alpha(\mathbf{x}) \alpha^{-2/3} \right) \\
 &= \frac{8\pi}{\lambda^2} \int_0^\infty d\alpha \alpha^{1/3} \int_{\mathbb{R}^3} d\mathbf{x} \chi_\alpha(\mathbf{x}) = \frac{8\pi}{\lambda^2} \int_{\mathbb{R}^3} d\mathbf{x} \int_0^{Q(\mathbf{x})} d\alpha \alpha^{1/3} \\
 &= \frac{6\pi}{\lambda^2} \int_{\mathbb{R}^3} Q(\mathbf{x})^{4/3}.
 \end{aligned}$$

This finishes the third step. We can now use our estimates on  $F_1, F_2$  obtained in the last two steps to bound

$$E_{XC} \geq -\frac{6\pi^2}{\lambda^2} \int_{\mathbb{R}^3} d\mathbf{x} Q(\mathbf{x})^{4/3} - \lambda D(\mu, \mu) \left( \int_{\mathbb{R}^3} d\mathbf{x} Q(\mathbf{x})^{4/3} \right)^{1/4} \left( \int_{\mathbb{R}^3} d\mathbf{x} \left( \sum_{i=1}^N e_i Q_i(\mathbf{x}) \right)^{4/3} \right)^{3/4}.$$

From differentiation, the optimal value of the constant  $\lambda$  is seen to be

$$\lambda_{opt} = \left( \frac{12\pi}{D(\mu, \mu)} \right)^{1/3} \left( \frac{\int_{\mathbb{R}^3} d\mathbf{x} Q(\mathbf{x})^{4/3}}{\int_{\mathbb{R}^3} d\mathbf{x} \left( \sum_{i=1}^N Q_i(\mathbf{x}) \right)^{4/3}} \right)^{1/4},$$

yielding

$$E_{XC} \geq -\frac{3^{4/3}}{2^{1/3}} \pi^{1/3} D(\mu, \mu)^{2/3} \left( \int_{\mathbb{R}^3} d\mathbf{x} Q(\mathbf{x})^{4/3} \right)^{1/2} \left( \int_{\mathbb{R}^3} d\mathbf{x} \left( \sum_{i=1}^N Q_i(\mathbf{x}) \right)^{4/3} \right)^{1/2}.$$

What remains is to optimise this result over all  $\mu$  satisfying the above conditions. In particular, we can apply Newton's theorem and see that

$$D(\mu, \mu) = \int_{B_1(0)} d\mathbf{x} \int_{B_1(0)} d\mathbf{y} \mu(x) \mu(y) \underbrace{\min\left\{ \frac{1}{|\mathbf{x}|}, \frac{1}{|\mathbf{y}|} \right\}}_{\geq 1} \quad (8.15)$$

is clearly minimized by setting the min equal to one, while respecting normalization and spherical symmetry. This gives

$$\mu(\mathbf{x}) = \frac{1}{4\pi} \delta(|\mathbf{x}| - 1),$$

i.e. the charge distributes uniformly over the sphere of radius one. Physically, this corresponds to a spherical conductor carrying some charge. It is then well-known that the energy is minimized when the charge is distributed only on the surface (and it will be uniform by rotational symmetry). Clearly, (8.15) now produces the value 1/2 and the claim follows with a constant given by

$$\frac{3^{4/3} \pi^{1/3}}{2} \approx 3.17. \quad \square$$

### 8.3 Alternative Proof of Stability using the LO-inequality

We are now in a position to prove stability with an improved bound, since the correlation energy is now better understood. The numerical value for the bound on neutral hydrogen (i.e.  $q = 2$ ,  $N = M$  and  $Z = 1$ ) is 7.29 Rydbergs. In the following proof the LT inequality will be replaced by the (equivalent) kinetic energy inequality (theorem 6.5.1). For these reasons, we will estimate the energy from below by a one-particle density functional, which is the same idea as in Thomas-Fermi theory. In fact, we will reproduce a slightly more complicated density functional along the way, namely the Thomas-Fermi-Dirac functional. We note that the bound is again linear due to the fact that  $N^{1/3}M^{2/3} \leq N + M$ .

**Theorem 8.3.1** (Stability of non-relativistic matter II). *Let  $Z = \max\{Z_1, \dots, Z_M\}$ . Let  $\psi \in \mathcal{H}_N^{(f)}$  be normalized with  $q$  spin states. Then*

$$\langle \psi, H\psi \rangle \geq -0.231\alpha^2 Nq^{2/3} \left( 1 + 2.16Z \left( \frac{M}{N} \right)^{1/3} \right)^2. \quad (8.16)$$

*Proof.* To begin with, we assume that  $Z_1 = \dots = Z_M = Z$ , which is sensible because the ground state energy is monotone in the nuclear charges (theorem 7.1.1). We recall the notation

$$\langle \psi, H\psi \rangle = H_\psi = T_\psi + \alpha(I_\psi + W_\psi(\mathbf{R}) + U(\mathbf{R})). \quad (8.17)$$

By the kinetic energy inequality, we can estimate  $T_\psi$  in terms of a particle density functional and use corollary 4.2.17 on the spectral radius of the spin-summed fermionic one-particle density matrix  $\gamma_0^{(1)}$  to get

$$T_\psi = \frac{1}{2} \|\nabla\psi\|_2^2 \geq \frac{K}{2} \underbrace{\frac{1}{\|\gamma_0^{(1)}\|_\infty^{2/3}}}_{\geq q^{-2/3}} \int_{\mathbb{R}^3} d\mathbf{x} \varrho_\psi^{5/3}(\mathbf{x}).$$

Clearly,  $I_\psi = I_\rho$ , since the Coulomb interaction is spin-independent. So, we can apply the LO-inequality (theorem 8.2.1 in the version of equal charges, these are all stored in  $\alpha = e^2$  outside  $V_C$ ) to receive

$$I_\psi \geq D(\varrho_\psi, \varrho_\psi) - 1.68 \int_{\mathbb{R}^3} d\mathbf{x} \varrho_\psi(\mathbf{x})^{4/3}.$$

We notice that the second term can easily be controlled by an  $\epsilon$ -part of the kinetic energy ( $1 > \epsilon > 0$ ). This can be seen from Hölder's and the modified Young's inequality with some  $a > 0$ , i.e.

$$\begin{aligned} \int_{\mathbb{R}^3} d\mathbf{x} \varrho(\mathbf{x})^{5/6} \varrho(\mathbf{x})^{1/2} &\leq \left( \int_{\mathbb{R}^3} d\mathbf{x} \varrho_\psi(\mathbf{x})^{5/3} \right)^{1/2} \underbrace{\left( \int_{\mathbb{R}^3} d\mathbf{x} \varrho_\psi(\mathbf{x}) \right)^{1/2}}_{=\sqrt{N}} \\ &\leq \frac{a}{2} \int_{\mathbb{R}^3} d\mathbf{x} \varrho_\psi(\mathbf{x})^{5/3} + \frac{N}{2a}. \end{aligned}$$

Now, if we just consider the first two terms in (8.17), we get

$$T_\psi + \alpha I_\psi(\mathbf{R}) \geq \left( \frac{K}{2q^{2/3}} - 1.68\alpha \frac{a}{2} \right) \int_{\mathbb{R}^3} d\mathbf{x} \varrho_\psi(\mathbf{x})^{5/3} \frac{N}{2a}.$$

So, by choosing

$$a = q^{-2/3} \frac{K\epsilon}{1.68\alpha},$$

we really have controlled the 4/3-term (up to the linear additive term) with an arbitrarily small amount of kinetic energy. We also note that

$$\begin{aligned} W_\psi(\mathbf{R}) &= \langle \psi, \sum_{i=1}^N \sum_{k=1}^M \frac{Z}{|\mathbf{x}_i - \mathbf{R}_k|} \psi \rangle = \sum_{i=1}^N \sum_{k=1}^M \int_{\mathbb{R}^3} d\mathbf{x}_i \varrho_\psi^i(\mathbf{x}_i) \frac{Z}{|\mathbf{x}_i - \mathbf{R}_k|} \\ &= \sum_{k=1}^M \int_{\mathbb{R}^3} d\mathbf{x} \varrho_\psi(\mathbf{x}) \frac{Z}{|\mathbf{x} - \mathbf{R}_k|} \end{aligned}$$

Putting all of these together, we are provided with the estimate

$$\begin{aligned} H_\psi &\geq (1 - \epsilon) \frac{K}{2q^{2/3}} \int_{\mathbb{R}^3} d\mathbf{x} \varrho_\psi(\mathbf{x})^{5/3} \\ &\quad + \alpha \left( D(\varrho_\psi, \varrho_\psi) - \sum_{k=1}^M \int_{\mathbb{R}^3} d\mathbf{x} \varrho_\psi(\mathbf{x}) \frac{Z}{|\mathbf{x} - \mathbf{R}_k|} + U(\mathbf{R}) - \frac{N}{2a} \right). \end{aligned} \quad (8.18)$$

Since we have used the LO inequality to estimate the correlative parts of the Coulomb energy, Baxter's inequality is no longer of use. However, we can pull the Coulomb tooth of  $W_\psi$  (i.e.  $W(\mathbf{x}) = \Theta(\mathbf{x}) - Z/\mathcal{D}(\mathbf{x})$ ) and then apply the basic electrostatic inequality given in theorem 5.2.2, in which we drop the positive term on the right hand side. This yields

$$D(\varrho_\psi, \varrho_\psi) - \underbrace{\sum_{k=1}^M \int_{\mathbb{R}^3} d\mathbf{x} \varrho_\psi(\mathbf{x}) \frac{Z}{|\mathbf{x} - \mathbf{R}_k|}}_{=\int_{\mathbb{R}^3} d\mathbf{x} W(\mathbf{x}) \varrho_\psi(\mathbf{x})} + U(\mathbf{R}) \geq - \int_{\mathbb{R}^3} d\mathbf{x} \frac{Z}{\mathcal{D}(\mathbf{x})} \varrho_\psi(\mathbf{x}).$$

With this, (8.18) becomes

$$H_\psi \geq (1 - \epsilon) \frac{K}{2q^{2/3}} \int_{\mathbb{R}^3} d\mathbf{x} \varrho_\psi(\mathbf{x})^{5/3} - Z\alpha \int_{\mathbb{R}^3} d\mathbf{x} \frac{1}{\mathcal{D}(\mathbf{x})} \varrho_\psi(\mathbf{x}) - \frac{N}{2a}. \quad (8.19)$$

As in the first proof of stability, we write

$$\frac{1}{\mathcal{D}(\mathbf{x})} = \left( \frac{1}{\mathcal{D}(\mathbf{x})} - b \right) + b,$$

with  $b > 0$ . The contribution of the  $b$  term becomes again  $\alpha Z b N$  and is linear. Next, we sketch the minimization in  $\varrho_\psi$ . We take a  $\varphi \in C_c^\infty(\mathbb{R}^3)$  and  $\delta > 0$ . Then  $t \mapsto \varrho_\psi + t\varphi \chi_{\{\varrho_\psi > \delta\}}$  is still a non-negative function for all  $t \in \{s \in \mathbb{R} \mid |s| < \delta(\max \varphi)^{-1}\}$ . For all such  $t$ , we can

then consider the right hand side of (8.19) as a function  $g(t)$ . This  $g$  attains its minimum at  $t = 0$  for a particular  $\varrho_\psi$ , namely the one for which  $g'(0)$  vanishes, i.e.

$$0 = (1 - \epsilon) \frac{K}{2q^{2/3}} \frac{5}{3} \int_{\mathbb{R}^3} d\mathbf{x} \varphi(\mathbf{x}) \left( \varrho_\psi^{2/3}(\mathbf{x}) \chi_{\{\varrho_\psi > \delta\}} - Z\alpha \left( \frac{1}{\mathcal{D}(\mathbf{x})} - b \right) \chi_{\{\varrho_\psi > \delta\}} \right).$$

Since  $\varphi \in C_c^\infty(\mathbb{R}^3)$  was arbitrary, we can use the fundamental lemma of variational calculus to conclude that the term in the outer parentheses vanishes. This implies  $1/\mathcal{D}(\mathbf{x}) - b \geq \delta'$  (with some  $\delta'$  depending on  $\delta$ ) and so the minimizing  $\rho_\psi$  fulfills

$$\varrho_\psi(\mathbf{x}) = q \left( \frac{6}{5} \frac{Z\alpha}{K(1 - \epsilon)} \frac{1}{\mathcal{D}(\mathbf{x}) - b} \right)^{3/2} \chi_{\{1/\mathcal{D}(\mathbf{x}) - b \geq \delta'\}}.$$

With this and the explicit value of  $a$ , (8.19) becomes

$$H_\psi \geq -\frac{2q}{5} \left( \frac{6}{5K(1 - \epsilon)} \right)^{3/2} (Z\alpha)^{5/2} \int_{\mathbb{R}^3} d\mathbf{x} \left( \frac{1}{\mathcal{D}(\mathbf{x})} - b \right)^{5/2} \chi_{\{\varrho_\psi > \delta'\}}. \quad (8.20)$$

The integral can be bound by that over  $[1/\mathcal{D}(\mathbf{x}) - b]_+^{5/2}$  which also appeared in the first version of the proof. By taking  $\delta' \rightarrow 0$  and the dominated convergence theorem, we obtain the bound

$$\int_{\mathbb{R}^3} d\mathbf{x} \left[ \frac{1}{\mathcal{D}(\mathbf{x})} - b \right]_+ \leq \frac{5\pi^2 M}{4} b^{-1/2}.$$

We can put this back into (8.20) and optimize over the parameters  $b > 0$  and  $1 > \epsilon > 0$ . We omit these elementary calculations and just give the resulting bound, namely

$$H_\psi \geq \frac{2}{K} \alpha^2 N q^{2/3} \left( 0.84 + \sqrt{\frac{9\pi^{4/3}}{10 \cdot 2^{2/3}}} Z \left( \frac{M}{N} \right)^{1/3} \right)^2.$$

We recall that  $K \geq 3.065$ , as remarked after theorem 6.5.1, and see that the numerical values are as claimed.  $\square$

# Chapter 9

## Stability through Thomas-Fermi theory

Thomas-Fermi (TF) theory was one of the first equations designed to approximate Schrödinger's equation. It was developed independently by Thomas and Fermi in 1927.

The TF theory is the classic route to stability and is extensively studied in [17]. It was in fact for the purpose of proving stability, that the Lieb-Thirring inequalities were invented ([19], [18]). TF theory is a rich subject, but we will restrict ourselves to the results we need to prove stability. In particular, we will not discuss the fact that it can be viewed as a realistic physical theory in the  $Z \rightarrow \infty$  limit. A review of rigorous results known about TF theory and similar theories evolving from it can be found in [12].

### 9.1 The TF Functional and the TF Energy

#### 9.1.1 Definition and Relation to Quantum-Mechanical Energy

We shall first give the TF energy functional and then discuss some of its properties. From here on, let

$$V(\mathbf{x}) := \sum_{k=1}^M Z_k \frac{1}{|\mathbf{x} - \mathbf{R}_k|}. \quad (9.1)$$

**Definition 9.1.1** (The TF functional). Given an atomic system with an arbitrary number of electrons and  $M$  nuclei at positions  $\underline{\mathbf{R}}$ , carrying charges  $\underline{Z}$ . For all  $\rho$  in the set

$$\mathcal{C} := \left\{ \rho : \mathbb{R}^3 \rightarrow \mathbb{R} \mid \rho \geq 0, \rho \in L^1(\mathbb{R}^3) \cap L^{5/3}(\mathbb{R}^3) \right\}, \quad (9.2)$$

we define the *Thomas-Fermi (energy) functional* to be

$$\mathcal{E}(\rho) := \mathcal{E}(\underline{Z}, \underline{\mathbf{R}}, \gamma) := \frac{3}{5} \gamma \frac{1}{2q^{2/3}} \int_{\mathbb{R}^3} dx \rho^{5/3}(\mathbf{x}) + \int_{\mathbb{R}^3} dx V(\mathbf{x}) \rho(\mathbf{x}) + D(\rho, \rho) + U(\underline{\mathbf{R}}), \quad (9.3)$$

where  $\gamma := (6\pi^2)^{2/3}$ .

*Remark 9.1.2.* (i) The number of electrons is given by  $\|\rho\|_1$ , which makes sense because  $\rho$  is non-negative.

- (ii) The function  $\rho$  represents a one-particle density associated to some wave function, an object which was denoted by  $\varrho_\psi$  in the previous chapters. This clarifies the appellation of TF theory as a (simple) *density functional theory*, in which the quantum particles are described as a classical gas. It involves no correlation effects between the particles.
- (iii) We remark that the TF theory yields good approximate results for bulk matter, but it is not able to predict any chemical effects, e.g. it cannot see e.g. the oscillations of the binding energy with varying nuclear charge.
- (iv) From the analysis of the LO inequality, we know how all terms but the first one stem from the quantum coulomb interaction. The LT inequality suggests to view the first term as an approximation to the kinetic energy. The original arguments of Thomas and Fermi were based on the semiclassical picture and we will now give a sketch of how the  $\rho^{5/3}$ -term arises from their ideas.<sup>1</sup>

We consider to have  $N$  non-interacting fermions, situated within the spatial volume  $V$ . We assume them to be in the ground state, i.e. to have minimal kinetic energy. Thus, the volume of the particles in momentum space  $V_F$  is given (independently of  $\mathbf{x}$ , since there are no interactions) by the volume inside the „Fermi sphere“ of radius  $R := |\mathbf{p}_F|$ , where  $\mathbf{p}_F$  denotes the maximal momentum, namely

$$V_F = \frac{4\pi}{3}R^3. \quad (9.4)$$

In the semiclassical picture (with  $\hbar = 1$ ), the phase space density is given by

$$\frac{N}{V_F V} = \frac{q}{(2\pi)^3}, \quad (9.5)$$

which can be rewritten (using  $\rho := N/V$ ) as

$$R = \left( \frac{6\pi^2}{q} \right)^{1/3} \rho^{1/3}. \quad (9.6)$$

The kinetic energy at the point  $\mathbf{x}$  is then calculated by averaging the classical kinetic energy over the Fermi sphere, i.e

$$T(\mathbf{x}) = \frac{3}{4\pi R^3} \int_{|\mathbf{p}| \leq R} d\mathbf{p} \mathbf{p}^2 / 2 = \frac{3}{10} R^2 \quad (9.7)$$

and the aggregate kinetic energy is obtained from integrating  $T(\mathbf{x})$  over configuration space, with weight given by the particle density

$$T = \int_{\mathbb{R}^3} d\mathbf{x} T(\mathbf{x}) \rho(\mathbf{x}) = \frac{3}{10} \left( \frac{6\pi^2}{q} \right)^{2/3}. \quad (9.8)$$

This gives the correct value of  $\gamma$ . The factor of  $2^{-1}$  thus arises from the  $1/2$  in front of the Laplacian.

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<sup>1</sup>The true starting point for such a heuristic argument would be to divide space into small boxes and consider the eigenfunctions of the Laplacian on these boxes. These are plane waves with periodic boundary conditions on the wave number  $\mathbf{k}$ . Then one determines the volume of the Fermi sphere of each box and calculates the kinetic energy by approximating the sum over all discrete  $\mathbf{k}$  with an integral (corresponds to making the size of each box small). The result is the same (up to the factor of  $1/2$  which arises here because we considered  $-(1/2)\Delta$  by setting  $m = 1$  in our units.)

- (v) We set  $\alpha = 1$  for notational simplicity. This can also be handled by defining  $\gamma' := \gamma/\alpha$  and  $\mathcal{E}' := \mathcal{E}/\alpha$ . In theorem 9.4.1 on the scaling behaviour, it will be seen that the TF energy depends on  $\gamma'$  through  $\gamma'^{-1}$ , i.e. on  $\alpha^2$  and we can restore the original value for computations.

**Proposition 9.1.3.**  $\mathcal{E}$  is well-defined on  $\mathcal{C}$ .

*Proof.* The kinetic term is clearly finite, since  $\rho \in L^{5/3}$ . For the second term, write  $V = V_1 + V_2$  with  $V_1 \in L^{5/2}$  and  $V_2 \in L^\infty$ , split the integral and use Hölder's inequality with  $p = 5/3$  on the first part to get

$$\int_{\mathbb{R}^3} d\mathbf{x} |\rho(\mathbf{x})V(\mathbf{x})| \leq \|V_1\|_{5/2} \|\rho\|_{5/3} + \|V_2\|_\infty \|\rho\|_1 < \infty. \quad (9.9)$$

The Coulomb kernel can be split in the same way as  $V$  into  $W_1 \in L^{5/2}$  and  $W_2 \in L^\infty$ . One can then use Hölder's inequality with  $p = 1$  on the outer integral and apply Young's inequality on the appearing  $\|\cdot\|_\infty$  norm of convolutions<sup>2</sup> (see theorem 4.2 in [14]) to get

$$\begin{aligned} D(\rho, \rho) &= \|\rho\|_1 \|\rho * W_1 + \rho * W_2\|_\infty \\ &\leq \|\rho\|_1 (\|W_1\|_{5/2} \|\rho\|_{5/3} + \|W_2\|_\infty \|\rho\|_1) < \infty. \quad \square \end{aligned}$$

We have already remarked the similarity of the terms in the TF functional and the lower bounds in the LO and LT inequalities. In fact, in the proof of stability we have already shown that the TF energy functional (for a fixed particle number) indeed bounds the quantum mechanical Hamiltonian from below.<sup>3</sup> We formulate this result as a new theorem, because this clarifies that our task has been reduced to proving stability of the second kind for the TF functional. After each step we take on the Thomas-Fermi side, we will briefly mention how our lower bound improved accordingly.

**Theorem 9.1.4** (TF functional gives lower bound to quantum mechanical energy).

Let  $\psi \in \mathcal{H}_N^{(f)}$  and  $a > 0$ . Then, it holds that

$$\langle \psi, H\psi \rangle \geq \mathcal{E} \left( \underline{Z}, \underline{\mathbf{R}}, 6(\pi^2/2)^{1/3} - 5q^{2/3} \frac{1.68}{3a} \right) (\varrho_\psi) - 1.68 \frac{N}{2a}. \quad (9.10)$$

*Proof.* The proof was carried out when we showed the alternative way to achieve stability (see section 8.3). We will later optimize the parameter  $a > 0$ .  $\square$

It will turn out that the properties of the TF functional depend heavily on the particle number. Thus, we make the dependence on it explicit. We introduce a space on which the particle number is fixed and a space on which it is bounded from above.

**Definition 9.1.5** (Domains with constrained particle numbers, TF energy). Let  $\lambda > 0$ . We denote

$$\begin{aligned} \mathcal{C}_\lambda &:= \left\{ \rho \in \mathcal{C} \mid \int_{\mathbb{R}^3} d\mathbf{x} \rho(\mathbf{x}) \leq \lambda \right\} \\ \mathcal{C}_{\partial\lambda} &:= \left\{ \rho \in \mathcal{C} \mid \int_{\mathbb{R}^3} d\mathbf{x} \rho(\mathbf{x}) = \lambda \right\}. \end{aligned}$$

<sup>2</sup>The *convolution* of  $f, g$  is formally defined by  $(f * g)(\mathbf{x}) := \int_{\mathbb{R}^3} d\mathbf{y} f(\mathbf{x} - \mathbf{y})g(\mathbf{y})$

<sup>3</sup>This actually dictates our particular choice of  $\gamma$ .

Moreover, we call

$$E_{TF} := E_{TF}(\lambda) := E_{TF}(\lambda, \underline{Z}, \underline{\mathbf{R}}, \gamma_0) := \inf \{ \mathcal{E}(\underline{Z}, \underline{\mathbf{R}}, \gamma_0)(\psi) \mid \psi \in \mathcal{C}_\lambda \} \quad (9.11)$$

the *TF ground state energy*.

## 9.2 The TF minimizer

### 9.2.1 Basic Properties of the TF Functional and the TF energy

We hope to find a lower bound to  $E_{TF}$ , in fact we are looking for a minimizer (ground state)  $\rho$  such that  $E_{TF} = \mathcal{E}(\rho)$ . We follow the presentation in [12] and begin by considering the TF functional.

**Proposition 9.2.1** (Convexity of the TF Functional). *The functional  $\rho \mapsto \mathcal{E}(\rho)$  is strictly convex, i.e. for  $\rho_1, \rho_2 \in \mathcal{C}_\lambda$ ,  $\rho_1 \neq \rho_2$  it holds that*

$$\mathcal{E}(t\rho_1 + (1-t)\rho_2) < t\mathcal{E}(\rho_1) + (1-t)\mathcal{E}(\rho_2), \quad (9.12)$$

for all  $0 < t < 1$ .

*Proof.* We note that  $\mathcal{C}_\lambda$  is a convex set, so the left hand side makes sense for  $\rho_1, \rho_2 \in \mathcal{C}_\lambda$ . The kinetic energy term is strictly convex, because the function  $\rho \mapsto \rho^p$  is strictly convex for all  $p > 1$ . The second term is linear in  $\rho$  and therefore convex. The strict convexity of  $D(\rho, \rho)$  follows directly from its symmetry and positivity (theorem 3.1.9):

$$\begin{aligned} & D(t\rho_1 + (1-t)\rho_2, t\rho_1 + (1-t)\rho_2) \\ &= t^2 D(\rho_1, \rho_1) + (1-t)^2 D(\rho_2, \rho_2) + \underbrace{2t(1-t)D(\rho_1, \rho_2)}_{\leq t(1-t)(D(\rho_1, \rho_1) + D(\rho_2, \rho_2))} \\ &\leq tD(\rho_1, \rho_1) + (1-t)D(\rho_2, \rho_2) \quad \square \end{aligned}$$

**Corollary 9.2.2** (Uniqueness of Minimizers). *Suppose  $\rho, \rho'$  were two minimizers of  $\mathcal{E}$  on  $\mathcal{C}_\lambda$ . Then*

$$\rho = \rho', \quad (9.13)$$

in the  $L^1$ -sense.

*Proof.* Suppose  $\rho_1 \neq \rho_2$ . Then, by strict convexity, we have that

$$\mathcal{E}\left(\frac{\rho_1 + \rho_2}{2}\right) < \frac{\mathcal{E}(\rho_1) + \mathcal{E}(\rho_2)}{2} = E_{TF}(\lambda),$$

which is a contradiction.  $\square$

Now, we turn to the TF energy  $E_{TF}$  as a function of the particle number  $\lambda$ . From the physical standpoint, it is clear that if we overload the system with electrons, most of them will move to infinity to minimize the total energy. This idea leads to the following facts about the electronic TF energy.

**Theorem 9.2.3.** (i) *It holds that*

$$\inf \{ \mathcal{E}(\underline{Z}, \underline{\mathbf{R}}, \gamma)(\psi) \mid \psi \in \mathcal{C}_{\partial\lambda} \} = E_{TF}(\lambda). \quad (9.14)$$

which directly implies that  $\lambda \mapsto E_{TF}(\lambda)$  is a monotonically non-increasing function.

(ii)  $E_{TF}(\lambda)$  is a convex function, which is bounded from below.

*Proof.* The first statement corresponds to the fact that unneeded electrons can be deposited at infinity. Since  $C_c^\infty$  is dense in  $L^1 \cap L^{5/3}$ , we may restrict ourselves to  $\rho \in C_c^\infty(\mathbb{R}^3) \cap \mathcal{C}_\lambda$  on the right hand side. Let such a  $\rho$  be given, we claim to find a sequence  $\{\rho_n\}_{n \in \mathbb{N}} \subset \mathcal{C}_{\partial\lambda}$  such that

$$\lim_{n \rightarrow \infty} \mathcal{E}(\rho_n) = \mathcal{E}(\rho),$$

which (due to denseness) implies the „ $\leq$ “ -direction. The other direction is trivial. To any  $n \in \mathbb{N}$ , we can find a point  $\mathbf{x}_n \in \mathbb{R}^3$  such that

$$\text{dist}\{|\mathbf{x}_n|, \text{supp}(\rho)\} > n.$$

We then define

$$\rho_n(\mathbf{x}) := \rho + \delta_n := \rho + (\lambda - \|\rho\|_1) \chi_{B_n(\mathbf{x}_n)} \frac{3}{4\pi n^3} \in \mathcal{C}_{\partial\lambda}$$

and see that

$$\mathcal{E}(\rho_n) - \mathcal{E}(\rho) \xrightarrow{n \rightarrow \infty} 0,$$

since  $\delta_n$  is very flat (for large  $n$ ) and its support is disjoint from  $\text{supp}(\rho)$ , i.e. Newton's theorem applies.

The convexity statement follows directly from the strict convexity of  $\mathcal{E}(\rho)$  in  $\rho$ , by considering two minimizing sequences. The fact that  $E(\lambda)$  is bounded from below uses some electrostatic tools such as Newton's theorem and the pulling of the Coulomb tooth. We refrain from presenting the proof and instead refer to theorem 24 in [20].  $\square$

**Corollary 9.2.4.** For  $\psi \in \mathcal{H}_N^{(f)}$ , we can now write

$$H_\psi \geq E_{TF} \left( N, \underline{Z}, \underline{\mathbf{R}}, 6(\pi^2/2)^{1/3} - 5q^{2/3} \frac{1.68}{3a} \right) (\varrho_\psi) - 1.68 \frac{N}{2a}. \quad (9.15)$$

Since we know that  $E(\lambda)$  is non-increasing and bounded below, it makes sense to define the *critical particle number*  $\lambda_c$  by

$$\lambda_c := \inf \{ \lambda | E(\lambda) = E(\infty) \}, \quad (9.16)$$

which might be plus infinity.

## 9.2.2 Existence of TF Minimizer

From the physical argument above, that in the case of many electrons the energy minimization implies shifting some of them to infinity, it follows that for such high particle numbers  $\lambda$ , no ground state will exist. This is the main reason why we have defined  $E_{TF}$  by minimizing over the set  $\mathcal{C}_\lambda$  and not over  $\mathcal{C}_{\partial\lambda}$ . On  $\mathcal{C}_\lambda$  the TF functional will have a (unique) minimizer. The following theorem is central in TF theory.

**Theorem 9.2.5** (Existence of a minimizer on  $\mathcal{C}_\lambda$ ). *Let  $\lambda > 0$ . Then there exists  $\rho \in \mathcal{C}_\lambda$  such that*

$$\mathcal{E}(\rho) = E_{TF}(\lambda). \quad (9.17)$$

*By corollary 9.2.2,  $\rho$  is then unique.*

*Proof.* We follow the order noted in section 6.1 on the variational principle.

Step 1 First we take a minimizing sequence  $\{\rho_n\}_{n \in \mathbb{N}} \subset \mathcal{C}_\lambda$ , i.e.

$$\mathcal{E}(\rho_n) \xrightarrow{n \rightarrow \infty} E_{TF}(\lambda).$$

Step 2 To see that this sequence is bounded in the  $\|\cdot\|_{5/3}$ -norm, find  $E_0 \in \mathbb{R}$  such that  $\forall n : \mathcal{E}(\rho_n) \leq E_0$ . For any  $\rho \in \mathcal{C}_\lambda$ , we can then drop the positive Coulomb term, use the estimate for the well-definedness (9.9) and the fact that  $\|\rho\|_1 \leq \lambda$  to get

$$\rho \geq \frac{3}{5} \|\rho_n\|_{5/3}^{5/3} - \|V_1\|_{5/2} \|\rho\| - \|V_2\|_\infty \lambda.$$

The facts that we can estimate the left hand side uniformly in  $n$  and that the right hand side diverges to plus infinity as  $\|\rho\|_{5/3} \rightarrow \infty$ , implies the existence of a  $C > 0$  such that

$$\forall n \in \mathbb{N} : \|\rho\|_{5/3} \leq C.$$

Step 3 Since  $L^{5/3}$  is a Hilbert space, it is reflexive and we can therefore apply the Banach-Alaoglu theorem (theorem IV.21 in [23]) to  $\{\rho_n\}_{n \in \mathbb{N}}$ . This provides us with a subsequence (which we also denote by  $\{\rho_n\}_{n \in \mathbb{N}}$ ) that converges weakly to some  $\rho_0 \in L^{5/3}$ . It is well-known that the dual of  $L^{5/3}$  is  $L^{5/2}$  (since  $(5/3)^{-1} + (5/2)^{-1} = 1$ , see e.g. theorem 2.14 in [14]), so we have

$$\forall f \in L^2(\mathbb{R}^3) : \int_{\mathbb{R}^3} d\mathbf{x} \rho_0(\mathbf{x}) f(\mathbf{x}) = \lim_{n \rightarrow \infty} \int_{\mathbb{R}^3} d\mathbf{x} \rho_n(\mathbf{x}) f(\mathbf{x}).$$

The weak limit  $\rho_0$  is the candidate for a minimizer.

Step 4 We check that  $\rho_0 \in \mathcal{C}_\lambda$  and note that  $\rho_0 \in L^{5/3}$  is obvious. To see  $\rho_0 \geq 0$ , pick any non-negative  $\varphi \in C_c^\infty \subset L^{5/2}$  and note that

$$\int_{\mathbb{R}^3} d\mathbf{x} \rho_0(\mathbf{x}) \varphi(\mathbf{x}) = \lim_{n \rightarrow \infty} \int_{\mathbb{R}^3} d\mathbf{x} \rho_n(\mathbf{x}) \varphi(\mathbf{x}) \geq 0.$$

Since  $\varphi \geq 0$  was arbitrary, we can conclude from the fundamental lemma of variational calculus that  $\rho_0 \geq 0$ . Finally, suppose  $\|\rho_0\|_1 > \lambda$ , then there exists a set  $A \subset \mathbb{R}^3$  of finite measure such that  $\|\rho_0 \chi_A\|_1 > \lambda$ . Since  $\chi_A \in L^{5/2}$  we can use weak convergence to see

$$\lambda < \int_{\mathbb{R}^3} d\mathbf{x} \chi_A(\mathbf{x}) \rho_0(\mathbf{x}) = \lim_{n \rightarrow \infty} \int_A \rho_n(\mathbf{x}) \leq \lambda,$$

i.e. a contradiction.

Step 5 The last step is to show lower semicontinuity, i.e. that

$$\mathcal{E}(\rho_0) \leq \liminf_{n \rightarrow \infty} \{\mathcal{E}(\rho_n)\}.$$

We treat each term separately. The first term is lower semicontinuous, because the norm cannot increase along weak limits (see theorem 2.11 in [14]). For the third term, we show that for any  $\rho \in L^{5/3} \cap L^1$  it holds that

$$D(\rho_n, \rho) \rightarrow D(\rho_0, \rho). \tag{9.18}$$

The claim then follows, because  $\rho_0 \in L^{5/3} \cap L^1$  and we can use the Cauchy-Schwarz inequality proved in theorem 3.1.9 to write

$$D(\rho_0, \rho_0) = \lim_{n \rightarrow \infty} D(\rho_n, \rho_0) \leq \liminf_{n \rightarrow \infty} \sqrt{D(\rho_n, \rho_n)} \sqrt{D(\rho_0, \rho_0)}$$

and dividing both sides by  $\sqrt{D(\rho_0, \rho_0)}$ . To see (9.18), one splits the Coulomb potential of  $\rho$  into  $v_1 + v_2$ , with

$$v_1(\mathbf{x}) := \int \frac{d\mathbf{y}}{|\mathbf{x} - \mathbf{y}|} \rho(\mathbf{y})$$

Young's inequality together with the fact that  $\rho \in L^1 \cap L^{5/3}$  directly implies that  $v_1 \in L^1 \cap L^\infty$ . For any  $1 < s < \infty$ , the estimate

$$\|v_1\|_s \leq \|v_1\|_\infty^{s-1} \|v_1\|_1 \quad (9.19)$$

shows that  $v_1 \in L^s$ . Again by Young's inequality and  $\rho \in L^1$ , it follows that  $v_2 \in L^s$ , for all  $s > 3$  and thus

$$\forall 3 < s < \infty : \quad v_1 + v_2 \in L^s(\mathbb{R}^3).$$

We return to consider the sequence  $\{\rho_n\}_{n \in \mathbb{N}}$ . Fix an  $s > 3$ , then its dual index  $s'$  satisfies  $1 < s' < 3/2$ . Since  $\rho_n \geq 0$ , we can estimate

$$\rho_n(\mathbf{x})^{s'} \leq \rho_n(\mathbf{x})^{5/3} + \rho_n(\mathbf{x}),$$

and from integration we have the same statement for the corresponding norms, in which the right hand side is uniformly bounded in  $n$  (by  $C + \lambda$ ). This tells us that the sequence  $\rho_n$  is also uniformly bounded in  $L^{s'}$  and we can apply Banach-Alaoglu to select a subsequence (again denoted by  $\rho_n$ ) that converges weakly in  $L^{s'}$  to  $\rho_0$  (uniqueness of limit follows from fundamental lemma of variational calculus). When we recall that  $v_1, v_2 \in L^s$ , we see that (9.18) holds. The term including  $V$  works through a similar argument as the Coulomb energy. For details, see page 61 of [20].  $\square$

Now that we have access to a minimizer on each set  $\mathcal{C}_\lambda$ , we return to the question when this minimizer is actually in the set  $\mathcal{C}_{\partial\lambda}$ . The intuition formulated above, why no unique ground state can exist for high particle numbers, is shown to be true.

**Theorem 9.2.6** (No minimizer exists for  $\lambda > \lambda_c$ ). *(i) For  $0 \leq \lambda \leq \lambda_c$ , the function  $E_{TF}$  is strictly convex. In particular, the (unique) minimizer  $\rho$  on  $\mathcal{C}_\lambda$  is an element of  $\mathcal{C}_{\partial\lambda_c}$ .*

*(ii) If  $\lambda_c < \infty$ , then for all  $\lambda > \lambda_c$ , the (unique) minimizer on the set  $\mathcal{C}_\lambda$  is also an element of  $\mathcal{C}_{\partial\lambda_c}$ .*

*Proof.* For the first statement, fix  $\lambda \leq \lambda_c$  and denote the unique minimizer on the set  $\mathcal{C}_\lambda$  by  $\rho_\lambda$ . Observe that if

$$\int_{\mathbb{R}^3} d\mathbf{x} \rho_\lambda(\mathbf{x}) = \lambda' < \lambda,$$

then clearly

$$E(\lambda) = E(\lambda').$$

Now, if we take  $0 < a < 1$  and  $\lambda = a\lambda_1 + (1 - a)\lambda_2$  with  $\lambda_1, \lambda_2 \leq \lambda_c$  and  $\lambda_1 \neq \lambda_2$ , then strict convexity follows directly from the above observation and consideration of the trial function

$$\tilde{\rho} := a\rho_1 + (1 - a)\rho_2.$$

For the second statement, take any  $\lambda > \lambda_c$  and assume there was a minimizer  $\rho_\lambda \in \mathcal{C}_{\partial\lambda}$ . Then we can choose the trial function

$$\rho' := \frac{\rho_{\lambda_c} + \rho_\lambda}{2},$$

which satisfies

$$\lambda_c < \|\rho'\|_1 = \frac{\lambda_c + \lambda}{2} < \lambda.$$

Thus, strict convexity (together with the observation from the beginning) implies

$$\mathcal{E}(\rho') < \frac{\mathcal{E}(\rho_{\lambda_c}) + \mathcal{E}(\rho_\lambda)}{2} = E(\lambda_c),$$

which is a contradiction.  $\square$

*Remark 9.2.7.* An illustration of the behaviour of  $\lambda \mapsto E(\lambda)$  can be found on page 606 of [12].

Our next aim is to identify  $\lambda_c$ . As explained before, it is a physical intuition (related to the fact that no doubly charged negative ions occur in Nature), that  $\lambda_c$  should not be much greater than

$$Z_{tot} := \sum_{k=1}^M Z_k. \quad (9.20)$$

This is true and we actually aim for the following, stronger result.

**Theorem 9.2.8** (Neutral case is critical). *It holds that*

$$\lambda_c = Z_{tot}. \quad (9.21)$$

The proof of this result will require some work, since it makes use of the *TF potential*  $\phi$  which originates from the Euler-Lagrange-Equation of the minimization problem. We will find  $\phi$  in the following section and this result will be shown afterwards. We note an immediate consequence of the last two theorems.

**Corollary 9.2.9.** *For  $\psi \in \mathcal{H}_N^{(f)}$ , we can now write*

$$H_\psi \geq E_{TF} \left( Z_{tot}, \underline{Z}, \underline{\mathbf{R}}, 6(\pi^2/2)^{1/3} - 5q^{2/3} \frac{1.68}{3a} \right) (\varrho_\psi) - 1.68 \frac{N}{2a}. \quad (9.22)$$

### 9.2.3 The TF equation

The TF equation is the Euler-Lagrange equation associated to the variational problem of minimizing the TF energy. It is of physical interest, e.g. the introduction of a Lagrange parameter  $\mu$  for fixing the particle number leads to the interpretation of  $\mu$  as the *chemical potential* of the electronic system, since  $\mu$  turns out to be the derivative of the TF energy with respect to  $\lambda$ . This issue — among many others — was extensively studied in [17]. For our purposes, the TF equation just serves as a means to introduce the TF potential

and we will thus occasionally just sketch a technical step. We refer to [17] and to [20] for further details. To save writing, we define

$$\gamma_0 := \gamma \frac{1}{2} q^{2/3}. \quad (9.23)$$

**Theorem 9.2.10** (TF equation). *Assume that  $\lambda \leq \lambda_c$ . Let  $\rho_\lambda$  denote the unique minimizer in the set  $\mathcal{C}_\lambda$ . Then there exists a constant  $\mu \geq 0$  such that the TF-equation*

$$\gamma_0 \rho_\lambda^{2/3} = \left[ -V(\mathbf{x}) - \left( \frac{1}{|\cdot|} * \rho_\lambda \right) (\mathbf{x}) - \mu \right]_+ \quad (9.24)$$

holds true. Furthermore,  $\mu = 0$  for  $\lambda = \lambda_c$ .

*Proof.* The proof is a standard argument in the calculus of variations. We have already seen an example in section 8.3. One has to be aware of the additional necessity to vary  $\rho_\lambda$  only within the set of non-negative functions, however.

Fix  $\lambda \geq 0$ . We know that  $\rho_\lambda \in \mathcal{C}_{\partial\lambda}$ , which is clearly a convex set. Hence it makes sense to define (for some fixed  $\rho \in \mathcal{C}_{\partial\lambda}$  and for all  $0 < t \leq 1$ )

$$F(t) := \mathcal{E}(t\rho + (1-t)\rho_\lambda),$$

which assumes its minimum at  $t = 0$ . This implies that the one side derivative  $F'(0+)$  is non-negative. By a short calculation, one finds that

$$0 \leq F'(0+) = \int_{\mathbb{R}^3} d\mathbf{x} \left( \gamma_0 \rho_\lambda^{2/3}(\mathbf{x}) + V(\mathbf{x}) + \left( \frac{1}{|\cdot|} * \rho_\lambda \right) (\mathbf{x}) \right) (\rho - \rho_\lambda). \quad (9.25)$$

We now make a choice for  $\rho$ . We fix some  $\delta > 0$  and choose  $\epsilon > 0$  small enough, such that

$$\rho = \rho_\lambda + \epsilon f \chi_{\{\rho_\lambda > \delta\}} \geq 0,$$

where  $f$  is some function satisfying

$$\int_{\{\rho_\lambda > \delta\}} d\mathbf{x} f(\mathbf{x}) = 0. \quad (9.26)$$

In particular, we have  $\rho' \geq 0$  and when we put  $\rho'$  into (9.25), we get

$$\int_{\{\rho_\lambda > \delta\}} d\mathbf{x} f(\mathbf{x}) \left( \left( \gamma_0 \rho_\lambda^{2/3}(\mathbf{x}) + V(\mathbf{x}) + \left( \frac{1}{|\cdot|} * \rho_\lambda \right) (\mathbf{x}) \right) \right)$$

and since this holds for any  $f$  satisfying (9.26), the integrand (excluding  $f$ ) must be equal to a constant we call  $-\mu$ , wherever  $\rho_\lambda < \delta$ . So we have

$$\gamma_0 \rho_\lambda^{2/3}(\mathbf{x}) + V(\mathbf{x}) + \left( \frac{1}{|\cdot|} * \rho_\lambda \right) (\mathbf{x}) = -\mu \quad (9.27)$$

on  $\{\rho_\lambda \geq \delta\}$ . Note that the left hand side in (9.27) does not depend on  $\delta$ , which implies that  $\mu$  is independent of  $\delta$  as well and we may take  $\delta \rightarrow \cdot$ . One can now pick

$$\rho_0 := \rho_\lambda + \epsilon f,$$

with  $f \geq 0$  wherever  $\rho_\lambda = 0$  and

$$\int_{\mathbb{R}^3} d\mathbf{x} f(\mathbf{x}) = 0.$$

By putting  $\rho_0$  into (9.25) and using (9.27), one arrives at

$$-V(\mathbf{x}) - \left( \frac{1}{|\cdot|} * \rho_\lambda \right) (\mathbf{x}) - \mu \leq 0,$$

on the set  $\{\rho_\lambda = 0\}$ . When we put the two results back together and let  $\delta \rightarrow 0$ , we get (9.24), namely

$$\gamma_0 \rho_\lambda^{2/3} = \left[ -V(\mathbf{x}) - \left( \frac{1}{|\cdot|} * \rho_\lambda \right) (\mathbf{x}) - \mu \right]_+.$$

The fact that  $\mu = 0$  in the critical case is obvious, because  $\mu$  is really a Lagrange multiplier ensuring that  $\|\rho\|_1 = \lambda$ , which is unnecessary for  $\lambda = \lambda_c$ . The fact that  $\mu \geq 0$  follows from the fact that all the other terms in (9.24) vanish at infinity, so by taking the limit  $|\mathbf{x}| \rightarrow \infty$ , we get

$$[-\mu]_+ = 0,$$

i.e.  $\mu \geq 0$ . □

**Theorem - Definition 9.2.1** (Positivity of the TF potential). For  $\lambda \leq \lambda_c$  and  $\lambda < \infty$ , we define the *TF potential* by

$$\phi(\mathbf{x}) := -V(\mathbf{x}) - \left( \frac{1}{|\cdot|} * \rho_\lambda \right) (\mathbf{x}). \quad (9.28)$$

Moreover,  $\phi$  is non-negative.

*Proof.* By (3.14), where we discussed the Green's function of the Laplacian, we know that

$$\Delta\phi = 4\pi \left( \rho_\lambda(\mathbf{x}) - \sum_{k=1}^M Z_k \delta(\mathbf{x} - \mathbf{R}_k) \right),$$

So, when we are not situated in a nucleus, we can use (9.24) to get

$$\Delta\phi = \gamma_0^{-3/2} [\phi(\mathbf{x}) - \mu]_+. \quad (9.29)$$

We note that  $\phi$  is continuous on  $\mathbb{R}^3 \setminus \{R_1, \dots, R_M\}$ . This follows from splitting the Coulomb kernel, with one summand containing the tooth, and using  $\rho_\lambda \in L^1 \cap L^{5/3}$ , cf. page 65 in [20]. We define the set

$$S := \{\mathbf{x} \in \mathbb{R}^3 \mid \phi(\mathbf{x}) < 0\}.$$

Because  $\phi$  diverges to infinity at the nuclear positions,  $S$  does not contain them. Thus, (9.29) holds and due to the definition of  $S$  and  $\mu \geq 0$ , we know that

$$\Delta\phi = 0$$

on  $S$ , i.e.  $\phi$  is harmonic on  $S$ . Since both terms defining  $\phi$  vanish at infinity,  $\phi$  does so, too. From this we can conclude that

$$\phi = 0 \text{ on } \partial S \cup \{\infty\}.$$

By the maximum principle, the restriction of  $\phi$  to  $S$  attains its minimum on  $\partial S \cup \{\infty\}$ . So  $\phi = 0$  on  $S$ , i.e.  $S = \emptyset$ . □

*Proof of theorem 9.2.8.* There are two cases. First, assume that  $\lambda_c > Z$ . Then, we can find  $Z < \lambda < \lambda_c$ . Since  $\phi \geq 0$ , we can take the spherical average of  $\phi$  over a ball of radius  $r > \max\{\mathbf{R}_1, \dots, \mathbf{R}_m\}$  to and get (using Newton's theorem and dropping a positive term)

$$\begin{aligned} 0 &\leq \frac{1}{4\pi r^2} \int_{S_2} d\boldsymbol{\omega} \phi(r\boldsymbol{\omega}) = \frac{Z}{r} - \int_{\mathbb{R}^3} d\mathbf{y} \min\left\{\frac{1}{r}, \frac{1}{|\mathbf{y}|}\right\} \rho_\lambda(\mathbf{y}) \\ &\leq \frac{Z}{r} - \frac{1}{r} \int_{|\mathbf{y}| \leq r} d\mathbf{y} \rho_\lambda(\mathbf{y}). \end{aligned}$$

This implies

$$\forall r > \max\{\mathbf{R}_1, \dots, \mathbf{R}_m\} : \int_{|\mathbf{y}| \leq r} d\mathbf{y} \rho_\lambda(\mathbf{y}) \leq Z,$$

which is clearly false for  $r \rightarrow \infty$ , since  $\lambda > Z$ .

Now, we assume that  $\lambda_c < Z$ . We take again the spherical average, but now of  $\rho_{\lambda_c}$ . Using Jensen's inequality (theorem 2.2 in [14]), the TF equation with  $\mu = 0$ , we obtain

$$\begin{aligned} \frac{\gamma_0}{4\pi} \left( \int_{S_2} d\boldsymbol{\omega} \rho_{\lambda_c}(r\boldsymbol{\omega}) \right)^{2/3} &\geq \frac{\gamma_0}{4\pi} \int_{S_2} d\boldsymbol{\omega} \rho_{\lambda_c}^{2/3}(r\boldsymbol{\omega}) \\ &= \frac{1}{4\pi r^2} \int_{S_2} d\boldsymbol{\omega} \phi_c(r\boldsymbol{\omega}) \geq \frac{Z}{r} - \frac{1}{r} \int_{\mathbb{R}^3} d\mathbf{y} \rho_{\lambda_c}(\mathbf{y}) = \frac{Z - \lambda_c}{r}. \end{aligned}$$

From here, we see immediately that the spherical average of  $\rho_{\lambda_c}$  is (for large enough  $r$ ) proportional to  $r^{-3/2}$ , i.e. it is not integrable, which is a contradiction to  $\rho_{\lambda_c}$  being accessible.  $\square$

### 9.3 The No-binding Theorem (or: Teller's Theorem)

This section is devoted to one of the main properties of TF theory, namely that *molecules do not exist in TF theory*, i.e. atoms cannot *bind* together. We will refrain from presenting the proof, and refer to the version of Baxter [2] (also discussed in [12]). Before we give the result, we fix notation for grouping the atomic system into two subsets  $A, B$ .

**Definition 9.3.1** (Grouping of nuclei). Let  $\{1, \dots, M\} = A \cup B$ , with  $A \cap B = \emptyset$ . We denote the respective charge distributions of  $A$  and  $B$  by

$$m_\# = \sum_{k \in \#} Z_k \delta(\mathbf{x} - \mathbf{R}_k), \quad \# \in \{A, B\} \quad (9.30)$$

and the corresponding potentials are obtained from

$$V_\#(\mathbf{x}) := - \left( \frac{1}{|\cdot|} * m_\# \right) (\mathbf{x}). \quad (9.31)$$

The TF functional  $\mathcal{E}_\#$  of the system  $\# = A, B$  is the TF functional of the whole system, with  $V$  replaced by  $V_\#$  and  $U(\mathbf{R})$  replaced by the self-interaction of nuclei among the  $\#$ -group. The TF energies are defined correspondingly.

**Theorem 9.3.2** (No-binding theorem). *Let  $\lambda \leq Z = \sum_{k=1}^M$ . Then it holds that*

$$E(\lambda) \geq \inf \{E_A(\lambda_1) + E_B(\lambda_2) \mid \lambda_1 + \lambda_2 = \lambda\}. \quad (9.32)$$

**Corollary 9.3.3.** *For  $\psi \in \mathcal{H}_N^{(f)}$ , we can now write*

$$H_\psi \geq \min \left\{ \sum_{k=1}^M E_{TF} \left( Z_k, Z_k, \mathbf{R}_k, 6(\pi^2/2)^{1/3} - 5q^{2/3} \frac{1.68}{3a} \right) (\varrho_\psi) \right\} - 1.68 \frac{N}{2a}. \quad (9.33)$$

We also note that  $E_{TF}(Z, Z, \mathbf{R}, \gamma) = E_{TF}(Z, Z, 0, \gamma)$ .

*Proof.* The no-binding theorem implies that moving *all nuclei* infinitely far apart lowers the energy. The second statement follows by translational invariance.  $\square$

## 9.4 Scaling of the TF-Energy

We have almost completed our task to prove stability via TF theory. The last step will be to elicit the  $Z$ -dependence of the TF energy of a single atom and will be achieved from scaling  $\mathcal{E}$  appropriately.

**Theorem 9.4.1** (Scaling of single-atom TF energy). *Let  $Z > 0$ . It holds that*

$$E_{TF}(Z, Z, 0, 1) = \frac{Z^{7/3}}{\gamma} E_{TF}(1, 1, 0, 1). \quad (9.34)$$

*Proof.* We note that in the single-atom case  $U(\mathbf{R}) = 0$  and  $V(\mathbf{x}) = Z/|\mathbf{x}|$ . Let  $\rho \in \mathcal{C}_{\partial 1}$  be the unique minimizer with energy  $E_{TF}(1, 1, 0, \gamma)$ . We define the corresponding rescaled density

$$\rho_Z(\mathbf{x}) := Z^2 \rho(Z^{1/3} \mathbf{x}),$$

for which the particle number is given by

$$\int_{\mathbb{R}^3} d\mathbf{x} \rho_Z(\mathbf{x}) = Z \int_{\mathbb{R}^3} d\mathbf{x} \rho(\mathbf{x}) = Z.$$

Moreover, its TF energy can be calculated to be

$$\begin{aligned} \mathcal{E}(Z, 0, \gamma)(\rho_Z) &= \frac{3Z^{10/3}}{5} \gamma_0 \int_{\mathbb{R}^3} d\mathbf{x} \rho^{5/3}(Z^{1/3} \mathbf{x}) + Z^2 \int_{\mathbb{R}^3} d\mathbf{x} \frac{Z}{|\mathbf{x}|} \rho(Z^{1/3} \mathbf{x}) \\ &\quad + \frac{Z^4}{2} \int_{\mathbb{R}^3} d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{y} \frac{1}{|\mathbf{x} - \mathbf{y}|} \frac{Z^{-1}}{|\mathbf{x} - Z^{-1/3} \mathbf{y}|} \rho(Z^{-1/3} \mathbf{x}) \rho(\mathbf{y}) \\ &= Z^{7/3} E_{TF}(1, 0, \gamma)(\rho), \end{aligned}$$

and it is seen that  $\rho_Z \in \mathcal{C}_{\partial Z}$ . The scaling behaviour in  $\gamma$  can be found in [17].  $\square$

### 9.4.1 Stability for non-relativistic matter

Throughout our development of TF theory, we have regularly applied our new results to bound the quantum mechanical ground state energy from further below. This was last done in corollary 9.3.3 of the no-binding theorem. We will now use the above scaling result to the right hand side of that corollary and obtain stability. We note that a numerical analysis shows that

$$E_{TF} = -7.356\alpha^2, \quad (9.35)$$

where we have restored  $\alpha$  as remarked in the beginning of our analysis of TF theory. The resulting bound for neutral hydrogen is now given by 5.60 Rydbergs, which is a slight improvement.

**Theorem 9.4.2** (Stability via TF theory). *Let  $\psi \in \mathcal{H}_N^{(f)}$  with  $q$  spin states. Then it holds that*

$$H_\psi \geq -0.231q^{2/3}\alpha^2 N \left( 1 + 1.77 \sqrt{\frac{1}{N} \sum_{k=1}^M Z_k^{7/3}} \right) \quad (9.36)$$

*Proof.* Recall the result of corollary 9.3.3 for all  $\psi \in \mathcal{H}_N^{(f)}$ :

$$H_\psi \geq \min \left\{ \sum_{k=1}^M E_{TF} \left( Z_k, Z_k, 0, 6(\pi^2/2)^{1/3} - 5q^{2/3} \frac{1.68}{3a} \right) (\varrho_\psi) \right\} - 1.68 \frac{N}{2a} \quad (9.37)$$

The scaling law now implies, that we can estimate the  $k$ -th term in the above sum as follows

$$\begin{aligned} E_{TF} \left( Z_k, Z_k, 0, 6(\pi^2/2)^{1/3} - 5q^{2/3} \frac{1.68}{3a} \right) &= \left( 6(\pi^2/2)^{1/3} - 5q^{2/3} \frac{1.68}{3a} \right)^{-1} Z_k^{7/3} E_{TF}(1, 1, 0, 1) \\ &\geq -7.356 Z_k^{7/3} \alpha^2 \left( 6(\pi^2/2)^{1/3} - 5q^{2/3} \frac{1.68}{3a} \right)^{-1}. \end{aligned}$$

This estimate shows that the first term in (9.37) is at most linear in  $M$ . By optimising over the parameter  $a > 0$ , the numerical values of the claim are obtained.  $\square$

# Chapter 10

## Conclusions: A comparison of the three Approaches to Stability

In this work, we have presented a total of three proofs of stability of non-relativistic matter. The first one uses the essential ideas put forward in section 4.3, namely

- to pull the Coulomb tooth in order to control the potentially large Coulomb energy originating from a large number of nuclei at a certain distance. This is done by use of *electrostatic inequalities*,
- to control the Coulomb tooth by use of an *uncertainty principle* (LT inequality) for a fixed number of non-interacting particles (electrons), which originates in their fermionic character.

This first proof is the quickest way to show stability. The main problem about it is, that it does not account for quantum-mechanical influences on the Coulomb energy. The development of the relevant inequalities, provided us with the possibility of proving stability anew. The second proof uses (among pulling the Coulomb tooth)

- the LO inequality, yielding a lower bound on the *exchange-correlation* effects in terms of the charge density,
- the kinetic energy inequality, i.e. an uncertainty principle, to bound the quantum mechanical kinetic energy by the  $L^{5/3}$ -norm (to the 5/3-power) of the density.

The second proof involves estimating a density functional from below, however it does not make this density functional the main object of analysis. That is the idea behind the third proof, namely estimating the TF energy from below in a linear fashion. Some basic properties of TF theory are used in the proof of stability, namely

- the fact that the critical particle number, from which on the TF energy stays constant, is given by the total nuclear charge,
- the no-binding theorem, which allows to separate the TF energies of all nuclei,
- the elementary scaling property, reflecting the physical behaviour of TF theory on the  $Z^{-1/3}$ -length scale.

When we compare the three results, we notice several differences and similarities. Firstly, all proofs use the LT inequality (or its equivalent formulation, the kinetic energy inequality) to control the fermionic system. The first two proofs are designed exclusively to show stability of matter and nothing else and are therefore comparatively short. The third proof via TF theory develops an entire theory and therefore introduces a variety of objects along the way, which are only needed for the subsequent result. Then, the proof essentially relies on a collection of the previously presented properties of TF theory.

Also, we note that the second and the third proof have in common, that they are both occupied with a one-particle-density approximation to quantum theory. This is a natural possibility to simplify the problem immensely and if the asymptotics are suitable, such a theory can also be used in chemistry for approximative results. This is also reflected in the fact, that the LO inequality is not used in the first proof.

We also remark on the fact that all proofs estimate the quantum mechanical energy from below, by an expression which prohibited binding, in the sense that binding can never minimize the energy. This was stated very explicitly for TF theory, but is clearly also true for the lower bounds on the Coulomb interaction, which is minimized when the Voronoi cells are maximised. Thus, the nuclei tend to stay infinitely far apart in such a theory.

As to numerical results (for the special case of neutral hydrogen), we note that the first proof gives the worst results. The values given by the TF bound are only slightly better than the one provided in the second proof.

As an outlook, we mention the fact that TF theory has already been generalised to give stability results for other potentials, such as the Yukawa potential (introduced by its Fourier representation in (6.31)). This was done in [13]. It is likely that the other route to stability will work also in the Yukawa case.

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