The Stability of Matter in Non-Relativistic Quantum Mechanics

Lecture notes for part one of the Advanced Mathematical Physics course at the University of Copenhagen

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Foreword

These lecture notes were written for the first half of the "Advanced Mathematical Physics" course at the University of Copenhagen. They summarise a self-contained proof of stability of matter of the second kind of a non-relativistic quantum mechanical many-body system. The notes do not claim to contain any original results as the material is only a collection of excerpts from [5, 6, 9, 11, 12, 15, 18]. The design of the notes was inspired by the work of Edward Tufte on information design.

1. Classical Mechanics

We begin by revisiting classical mechanics.

This introduction is taken from [12, pp. 9-14].

1.1. Newton's laws of motion

Imagine a particle of *mass* m in $\mathbb{R}^3$. It is fully described by its *position*

$$x = (x_1, x_2, x_3) \in \mathbb{R}^3$$

and its *velocity*

$$v = \frac{\mathrm{d}x}{\mathrm{d}t} = \dot{x} \in \mathbb{R}^3$$

at any time t. Instead of the velocity, we may equivalently consider the *momentum* of the particle which is defined as[1]

$$p = m\dot{x} = mv\,.$$

If a force F acts on the particle, Newton's law of motion says that the particle's *acceleration* satisfies

$$m\frac{\mathrm{d}^2x}{\mathrm{d}t^2} = m\ddot{x} = F(x, \dot{x}, t) \tag{1}$$

which yields a system of differential equations. If we know the position $x(t_0)$ and velocity $\dot{x}(t_0)$ at some time t_0, then we we can determine $x(t)$ and $\dot{x}(t)$ for all times t. A visualisation can be found in Figure 1.

We can also consider several particles $x_1, \dots, x_N \in \mathbb{R}^3$. Then Newton's law says that

$$m_i\ddot{x}_i = F_i$$

where F_i is the sum of all forces action on the i-th particle. A visualisation can be found in Figure 2.

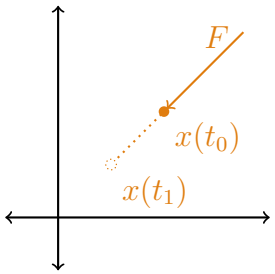

Figure 1: A force acts on a particle.

[1] In this course we will not consider magnetic fields. The corresponding results in this setting can be found in [12].

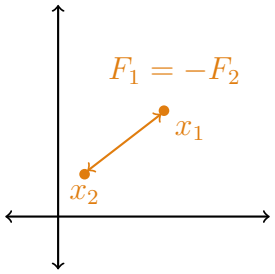

Figure 2: Two particles interact.

Example 1. Consider two charged particles. The force between them is the *Coulomb force*

$$F_1 = Q_1 Q_2 \frac{x_1 - x_2}{|x_1 - x_2|^3} = -F_2$$

where Q_1, Q_2 are the charges.[2] We can define the *potential energy function* as

$$V(x_1, x_2) = \frac{Q_1 Q_2}{|x_1 - x_2|}$$

such that

$$F_1 = -\nabla_{x_1} V\,, \qquad F_2 = -\nabla_{x_2} V\,.$$

The potential is negative, if the particles attract each other (Q_1, Q_2 have different signs) and positive if they repel each other (Q_1, Q_2 have the same sign). A visualisation can be found in Figure 3.

[2] The charge of a particle is the physical property that causes it to experience a force when placed in an electromagnetic field.

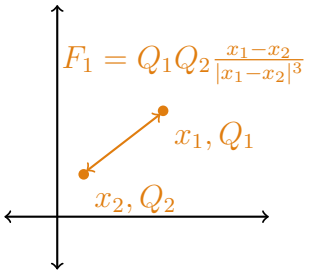

Figure 3: Two charged particles interact.

1.2. Hamiltonians

Consider again one particle. Assume that a force F acts on the particle and $F = -\nabla V$ for some potential V. We call

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

the *Hamiltonian function*. The function $T(p) = p^2/(2m)$ is called the *kinetic energy*. Hamilton's equations say that

$$\dot{x} = \frac{\partial H}{\partial p}\,, \qquad \dot{p} = -\frac{\partial H}{\partial x}$$

and indeed a quick computation yields (1) from Hamilton's equations. We call $p^2/(2m)$ the *kinetic energy* and V the *potential energy*. Note that along each trajectory the function $H(x(t), p(t))$ is constant. We call this constant the *energy* E

$$E = H(x(t), p(t))\,.$$

Example 2. If we consider the hydrogenic atom, we can think of one electron at position x surrounding one nucleus at position $R = 0$. The charge of the electron is $-e$ and the nucleus has the charge of one proton e. The force between the electron and nucleus is given by

$$F = -e^2 \frac{x}{|x|^3}$$

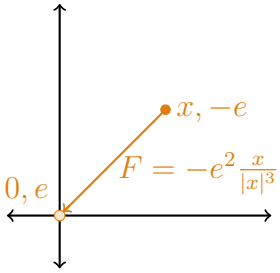

Figure 4: Hydrogen.

with potential energy function

$$V = -e^2 \frac{1}{|x|} .$$

The force between electron and nucleus at zero distance would be infinite and thus we expect the two particles to rush together and once they are together, no force would be large enough to separate them. So why does the point-like electron not fall into the (nearly) point-like nucleus? Even if we assume that the nucleus is not point-like, we know from experiments that the equilibrium distance of electron and nucleus is much larger (10^{-8}cm) than the nuclear diameter (10^{-13}cm).[3]

We can also formulate this problem using the corresponding Hamiltonian

$$H(x,p) = \frac{p^2}{2m} - \frac{e^2}{|x|} .$$

In principle, all energies in $[-\infty, \infty]$ are possible, in particular

$$\inf_{x,p\in\mathbb{R}^3} H(x,p) = -\infty .$$

However, we know from experiments that the smallest energy of the hydrogenic atom is finite.

Even though experiments and our own observations tell us that the hydrogenic atom is stable, we cannot conclude this form the arguments above.

[3] In this model, we have not prescribed any initial conditions. One may argue that the electron moves around the nucleus in an orbit, similar to the earth's movement around the sun. However, such a particle would continuously accelerate and thus emit energy through radiation, eventually falling into the nucleus.

2. One-Body Quantum Mechanics

We now provide a quick introduction to the theory of Quantum Mechanics and prove that the hydrogen atom is stable in this theory.[4]

In Quantum Mechanics a (spinless) particle in $\mathbb{R}^3$ is described by a *wave function* $\psi(x,t)$ which is, for fixed time t, an element of the Hilbert space $\mathcal{H} = L^2(\mathbb{R}^3)$ with unit norm $\|\psi\|_2 = 1$, i.e.

$$\int_{\mathbb{R}^3} |\psi(x)|^2 \, \mathrm{d}x = 1 .$$

[4] Taken from [12, pp. 14–30]

Definition 3. $L^2(\mathbb{R}^3)$ is the space of all (measurable) functions $f : \mathbb{R}^3 \to \mathbb{C}$ such that

$$\int_{\mathbb{R}^3} |f(x)|^2 \, \mathrm{d}x < \infty .$$

It is a Hilbert space equipped with the inner product

$$\langle f, g\rangle_2 = \int_{\mathbb{R}^3} \overline{f(x)} g(x) \, \mathrm{d}x$$

and corresponding norm

$$\|f\|_2 \coloneqq \sqrt{\int_{\mathbb{R}^3} |f(x)|^2 \,\mathrm{d}x}\,.$$

We interpret $\rho_\psi(x,t) \coloneqq |\psi(x,t)|^2$ as a probability density for the particle. We need infinitely many numbers (a whole function) to describe the particle. In this course, we will not consider the dynamic behaviour of ψ, i.e. we are only interested in the particle at a fixed time t_0. We will thus omit the variable t from now on.

2.1. The energy functional and one-body Hamiltonians

The classical energy $E = H(x,p)$ is replaced by an energy functional

$$\mathcal{E}(\psi) = T_\psi + V_\psi$$

with the *expectation value of the kinetic energy*, or *kinetic energy*, given by

$$T_\psi = \frac{\hbar^2}{2m} \int_{\mathbb{R}^3} |(\nabla\psi)(x)|^2 \,\mathrm{d}x\,.$$

Here ∇ denotes the gradient of a function and is defined as

$$(\nabla\psi)(x) = \begin{pmatrix} \frac{\partial\psi}{\partial x_1}(x) \\ \frac{\partial\psi}{\partial x_2}(x) \\ \frac{\partial\psi}{\partial x_3}(x) \end{pmatrix} : \mathbb{R}^3 \to \mathbb{C}^3\,, \qquad x = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} \in \mathbb{R}^3$$

such that

$$T_\psi = \frac{\hbar^2}{2m} \int_{\mathbb{R}^3} \left|\frac{\partial\psi}{\partial x_1}(x)\right|^2 + \left|\frac{\partial\psi}{\partial x_2}(x)\right|^2 + \left|\frac{\partial\psi}{\partial x_3}(x)\right|^2 \,\mathrm{d}x\,.$$

The *expectation value of the potential energy*, or *potential energy*, is given by

$$V_\psi = \int_{\mathbb{R}^3} V(x)|\psi(x)|^2 \,\mathrm{d}x\,.$$

In the remainder of this course we will set the reduced Planck constant[5] $\hbar$ to be 1 and will further assume that $m = 1/2$, such that from now on $h/(2m) = 1$. This can be done by choosing the units appropriately.[6] Comparing to classical mechanics, we notice that the classical momentum p has been replaced by an operator $-\mathrm{i}\nabla$. Similarly, the position x has been replaced by the multiplication operator $(X\psi)(x) = x\psi(x)$.

Associated to the kinetic energy is an operator H_0, the free *Hamiltonian* (or more specifically the *free Schrödinger operator*)

$$H_0 = -\Delta = -\frac{\partial^2}{\partial x_1^2} - \frac{\partial^2}{\partial x_2^2} - \frac{\partial^2}{\partial x_3^2}$$

[5] Planck's constant $h = 2\pi\hbar$ was first recognised by Planck in 1900. It has the dimension of energy multiplied with time and is (in standard units) approximately $\hbar \approx 6.626 \cdot 10^{-34}\,\mathrm{J}\cdot\mathrm{s}$

[6] See [12, Section 2.1.7].

such that for 'nice' functions ψ (e.g. $\psi \in \mathcal{C}_0^\infty(\mathbb{R}^3)$)

$$T_\psi = \langle \psi, H_0 \psi \rangle_2 \ .$$

Similarly, associated with the potential energy is the multiplication operator V such that[7]

$$V_\psi = \langle \psi, V\psi \rangle_2 \ .$$

In total, we have the Hamiltonian $H = H_0 + V$ (or more specifically the *Schrödinger operator*) defined on sufficiently regular functions ψ as

$$(H\psi)(x) = -(\Delta\psi)(x) + V(x)\psi(x)$$

and (for 'nice' functions ψ)

$$\mathcal{E}(\psi) = \langle \psi, H\psi \rangle_2 \ .$$

In order to rigorously define the Hamiltonian H, we need to understand the notion of unbounded operators. However, since we are only interested in the energy functional $\mathcal{E}$, we will define all the relevant quantities (ground states, excited states, eigenfucntions) via quadratic forms thus completely avoiding the need to talk about operator domains and self-adjointness.

[7] This is a slight abuse of notation. We use the same symbol V for the real valued function $V : \mathbb{R}^3 \to \mathbb{R}$ as well as for the multiplication operator $V : \mathrm{dom}(V) \subset L^2(\mathbb{R}^3) \to L^2(\mathbb{R}^3)$.

2.2. Proof of stability of the first kind

Leaving regularity considerations aside for the moment, we want to know whether the energy of the system can be made arbitrarily small. We have seen that this is possible in classical mechanics, however we still have to determine whether

$$E_0 = \inf_\psi \left\{ \mathcal{E}(\psi) : \int_{\mathbb{R}^3} |\psi(x)|^2 \, \mathrm{d}x = 1 \right\}$$

is finite. If this is the case, then we say the system is *stable of the first kind*.

We see that the energy functional makes sense for all wave functions $\psi \in L^2(\mathbb{R}^3)$ which are also in the Sobolev space $H^1(\mathbb{R}^3)$.

Definition 4. 1. A function $f \in L^2(\mathbb{R}^3)$ is *weakly differentiable*[8], if there exists a function $g \in L^2(\mathbb{R}^3)$ such that for all $\phi \in \mathcal{C}_0^\infty(\mathbb{R}^3)$

$$\int_{\mathbb{R}^3} \overline{(\nabla\phi)(x)} f(x) \, \mathrm{d}x = -\int_{\mathbb{R}^3} \overline{\phi(x)} g(x) \, \mathrm{d}x \, .$$

and we then define $\nabla f := g$.

[8] If you are not familiar with this terminology, you could try to prove as an exercise that a continuously differentiable function is weakly differentiable and that the two derivatives coincide.

2. The *first Sobolev space* $H^1(\mathbb{R}^3)$ is the space of all functions $f \in L^2(\mathbb{R}^3)$ that are weakly differentiable. It is a Hilbert space with inner product

$$\langle f, g\rangle_{H^1} = \int_{\mathbb{R}^3} \overline{f(x)} g(x)\,\mathrm{d}x + \int_{\mathbb{R}^3} \overline{(\nabla f)(x)}(\nabla g)(x)\,\mathrm{d}x$$

and corresponding norm

$$\|f\|_{H^1} = \sqrt{\int_{\mathbb{R}^3} |f(x)|^2\,\mathrm{d}x + \int_{\mathbb{R}^3} |(\nabla f)(x)|^2\,\mathrm{d}x}\,.$$

Remark 5. $H^1(\mathbb{R}^3)$ is the space of functions in $L^2(\mathbb{R}^3)$ that have distributional derivatives that are also in $L^2(\mathbb{R}^3)$

Clearly $H^1(\mathbb{R}^3)$ is a subspace of $L^2(\mathbb{R}^3)$. Even though in the remainder of this course we will mostly work with wave functions $\psi \in H^1(\mathbb{R}^3)$, it is important to remember that the physically relevant normalisation of a wave function is $\|\psi\|_2 = 1$.

We now define, more precisely, the *ground state energy* of a single quantum mechanical particle under the influence of a potential V as

$$E_0 = \inf_{\psi} \left\{ \mathcal{E}(\psi) : \int_{\mathbb{R}^3} |\psi(x)|^2\,\mathrm{d}x = 1, \psi \in H^1(\mathbb{R}^3), V_\psi \text{ is well defined} \right\}$$

and investigate whether this eneregy is finite.

Theorem 6 (Stability of the first kind of one-body quantum systems)**.** *Let $d \geq 3$. If the potential V satisfies*

$$V \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$$

then E_0 is finite and for all $\psi \in H^1(\mathbb{R}^d)$

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

with constants C, D that only depend on V (not on ψ).

In the proof we will use two important inequalities of mathematical analysis. One of them is the well-known Hölder inequality. Recall that for $1 \leq p < \infty$ the *Lebesgue space* $L^p(\mathbb{R}^3)$ is a Banach space defined as

$$L^p(\mathbb{R}^3) = \left\{ f : \mathbb{R}^3 \to \mathbb{C} \text{ measurable} : \int_{\mathbb{R}^3} |f(x)|^p\,\mathrm{d}x < \infty \right\}$$

with norm

$$\|f\|_p = \left(\int_{\mathbb{R}^3} |f(x)|^p\,\mathrm{d}x \right)^{1/p}.$$

For $p = \infty$ the space $L^\infty(\mathbb{R}^3)$ is a Banach space defined as

$$L^\infty(\mathbb{R}^3) = \left\{ f : \mathbb{R}^3 \to \mathbb{C} \text{ measurable} : \exists K > 0 \text{ such that } |f(x)| \leq K \text{ a.e.} \right\}$$

with norm

$$\|f\|_\infty = \inf \{K : |f(x)| \leq K \text{ a.e.}\} .$$

Theorem 7 (Hölder's inequality[9]). *Let $p \in [1, \infty]$ and $q \in [1, \infty]$ such that $1/p + 1/q = 1$. Then for any $f \in L^p(\mathbb{R}^3)$ and $g \in L^q(\mathbb{R}^3)$*

$$\|fg\|_1 \leq \|f\|_p \|g\|_q .$$

[9] This result is well-known and will be applied many times throughout this course. A proof can for example be found in [11, Theorem 2.3].

The other inequality that we need to prove Theorem 6 is a Sobolev inequality, which allows us to bound the kinetic energy from below by a certain L^p norm of the wave function.

Theorem 8 (Sobolev's inequality[10]). *There is a constant S_3 such that for any $\psi \in H^1(\mathbb{R}^3)$*

$$\|\nabla\psi\|_2^2 \geq S_3 \|\psi\|_6^2 .$$

[10] A proof can be found in [11, Theorem 8.3]

We will later prove a generalisation of this inequality to the many-body case in Theorem 35.

Proof of Theorem 6[11]. Let $\|\psi\|_2 = 1$ and $V(x) = v(x) + w(x)$ with $v \in L^{3/2}(\mathbb{R}^3)$, $w \in L^\infty(\mathbb{R}^3)$. We first claim[12] that there is a constant $\lambda < 0$ such that $h(x) := \min(v(x) - \lambda, 0) \leq 0$ satisfies $\|h\|_{3/2} \leq \frac{1}{2} S_3$. We may assume that $v \leq 0$ and thus

$$\begin{aligned} \int_{\mathbb{R}^3} |h(x)|^{3/2} \, \mathrm{d}x = \int_{\mathbb{R}^3} (-\min(v(x) - \lambda, 0))^{3/2} \, \mathrm{d}x &= \int_{v \leq \lambda} (|v(x)| - |\lambda|)^{3/2} \, \mathrm{d}x \\ &\leq \int_{|v|^{3/2} \geq |\lambda|^{3/2}} |v(x)|^{3/2} \, \mathrm{d}x . \end{aligned}$$

The term on the right can be made arbitrarily small by choosing $|\lambda|$ large since by assumption $v \in L^{3/2}(\mathbb{R}^3)$.

Using Sobolev's inequality in Theorem 8 and then Hölder's inequality in the form $\langle \psi, |h|\psi \rangle_2 \leq \|h\|_{3/2} \||\psi|^2\|_3$, we obtain[13]

$$T_\psi \geq S_3 \|\psi\|_6^2 = S_3 \left\| |\psi^2| \right\|_3 \geq \frac{S_3}{\|h\|_{3/2}} \langle \psi, |h|\psi \rangle_2 \geq -2h_\psi$$

where we used that $-h_\psi = -\langle \psi, h\psi \rangle_2 = \langle \psi, |h|\psi \rangle_2 \geq 0$. Since by definition

$$(v - \lambda)_\psi \geq h_\psi$$

[11] Taken from [12, pp. 27-29] as well as [9, Theorem 4.1.5]. The main proof idea is to bound the potential energy from below in terms of the kinetic energy. The w part can easily be bounded from below and the Sobolev inequality has the correct form to bound the v part. To understand the role of h I suggest you try to do apply the arguments in the proof directly to v. You will see that we then only obtain the result for sufficiently small $\|v\|_{3/2}$. The introduction of h allows us to move some of the mass of v into a constant potential.

[12] While the proof seems technical, the main idea can be seen by considering a simple picture

[13] Here we use that $\||\psi|^r\|_p = \|\psi\|_{pr}^r$.

we can conclude that

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

Recalling that $T_\psi \geq 0$ we get that $E_0 \geq \lambda - \|w\|_\infty > -\infty$ and the claimed bound. □

[14] Exercise.

Remark 9. If $V \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ we can show[14] that V_ψ is well-defined for all $\psi \in H^1(\mathbb{R}^3)$.

Sobolev's inequality played an essential role in the proof. It allowed us to conclude that the kinetic energy cannot become arbitrarily small without some norm of ψ becoming very small too. Any inequality in which the kinetic energy T_ψ dominates some kind of integral of ψ (but not involving $\nabla\psi$) is called an *uncertainty principle*. In the many-body case, we will see that a similar bound is necessary. The most famous uncertainty principle is the *Heisenberg uncertainty principle*, which says that

$$\left(\int_{\mathbb{R}^3} |(\nabla\psi)(x)|^2 \,\mathrm{d}x\right)\left(\int_{\mathbb{R}^3} x^2|\psi(x)|^2 \,\mathrm{d}x\right) \geq \frac{9}{4}$$

or equivalently

$$T_\psi \geq \frac{9}{8}\left(\int_{\mathbb{R}^3} x^2|\psi(x)|^2 \,\mathrm{d}x\right)^{-1}.$$

[15] See [12, p. 26].

It is, however, not useful in the investigation of stability of matter.[15] A proof of the inequality can be found in the appendix.

Example 10 (The hydrogenic atom)**.** Consider the hydrogenic atom with one electron surrounding a nucleus fixed[16] at $R = 0 \in \mathbb{R}^3$. The quantum mechanical energy is then given by (ignoring multiplicative constants)

$$\mathcal{E}(\psi) = \int_{\mathbb{R}^3} \left(|(\nabla\psi)(x)|^2 - \frac{1}{|x|}|\psi(x)|^2\right) \mathrm{d}x \,.$$

[16] Here we treat the nucleus classically. Once we understand many-body quantum mechanics we will see that proving stability in this model is a stronger result (albeit mathematically easier) than if the nucleus was also treated quantum mechanically.

Since $1/|x| \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$, the hydrogenic atom is stable (of the first kind). In fact, we can even compute the minimiser ψ_0 to be

$$\psi_0(x) = \exp(-|x|/2)$$

with $E_0 = -1/4$.

In the remainder of this section, we will analyse the one-body operator H through its quadratic form $\mathcal{E}$. This will be necessary to solve the stability question in the many-body case. We will in particular see that there are excited energy levels above the ground state energy.

2.3. A brief digression for students familiar with spectral theory

Students who have not taken a course on operator theory may ignore this subsection.

For students who are familiar with self-adjoint extensions of symmetric operators, we note that under the assumptions of Theorem 6, the operator

$$H = -\Delta + V(x)$$

is bounded from below by E_0 on $\mathcal{C}_0^\infty(\mathbb{R}^3)$, i.e. $\langle \psi, H\psi \rangle_2 \geq E_0 \|\psi\|_2^2$ for all $\psi \in \mathcal{C}_0^\infty(\mathbb{R}^3)$. Since the operator is also symmetric, we can consider its self-adjoint Friedrichs extension (let us denote it by H for simplicity). We can then prove the following.

Theorem 11. *Let $V \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ and assume that it vanishes at infinity, i.e. for all $a > 0$*

$$|\{x \in \mathbb{R}^3 : |V(x)| > a\}| < \infty .$$

Then the Freidrichs extension H has countably many eigenvalues $E_0 \leq E_1 \leq \ldots 0$ below zero and essential spectrum $[0, \infty)$.

Knowing this, we could immediately proceed to Subsection 2.5 and discuss Lieb–Thirring inequalities.

Following the textbook [12] though, we will avoid talking about self-adjoint operators in this course. Instead in the next subsection we will simply define the eigenvalues E_k by a variational principle and show that eigenfunctions exist. We think of H as an operator acting in the distributional sense on $H^1(\mathbb{R}^3)$.

2.4. The eigenvalues of one-body Hamiltonians

This subsection is taken from [11, pp. 275–279].

Let $\mathcal{E}(\psi) = T_\psi + V_\psi$ and the corresponding Hamiltonian $H = -\Delta + V$ be defined as in the previous subsection. We think of H simply as an operator acting in the distributional sense on $H^1(\mathbb{R}^3)$. We first prove that the ground state energy is attained.

Theorem 12. *Let $V \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ and assume that it vanishes at infinity, i.e. for all $a > 0$*

Here $|S|$ denotes the Lebesgue measure of a set $S \subset \mathbb{R}^3$.

$$|\{x \in \mathbb{R}^3 : |V(x)| > a\}| < \infty .$$

Then, if $E_0 < 0$, there is a unique function $\psi_0 \in H^1(\mathbb{R}^3)$ such that

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

and for any such ψ_0 in a distributional sense

$$H\psi_0 = E_0\psi_0 .$$

Proof [17]. We will only prove existence, not uniqueness. The proof applies a strategy that has proved itself to be very useful in several problems in variational calculus.[18]

We consider a minimising sequence $\psi^j \in H^1(\mathbb{R}^3)$ with $\mathcal{E}(\psi^j) \to E_0$ as $j \to \infty$ and $\|\psi^j\|_2 = 1$. Note that there is a constant $C > 0$ independent of j such that

$$\left\|\psi^j\right\|_{H^1}^2 = \int_{\mathbb{R}^3} (|\psi^j(x)|^2 + |(\nabla\psi^j)(x)|^2)\,\mathrm{d}x = 1 + T_{\psi^j} \leq C$$

by the one-body stability in Theorem 6. By the Banach-Alaoglu theorem, we can find a function $\psi_0 \in H^1(\mathbb{R}^3)$ such that $\psi^j \rightharpoonup \psi_0$ (weak convergence), i.e.

$$\left\langle \phi, \psi^j \right\rangle_{H^1} \to \langle \phi, \psi_0 \rangle_{H^1}$$

for all $\phi \in H^1(\mathbb{R}^3)$. Assume for the moment that we know that

$$\|\psi_0\|_2 \leq \liminf_{j\to\infty} \left\|\psi^j\right\|_2 = 1 \qquad \mathcal{E}(\psi_0) \leq \liminf_{j\to\infty} \mathcal{E}(\psi^j) = E_0\,. \tag{2}$$

We say that the norm and the energy functional are *lower semicontinuous*. Under these assumptions we have

$$0 > E_0 \geq \mathcal{E}(\psi_0) \geq E_0 \|\psi_0\|_2^2 \geq E_0$$

which implies that $\|\psi_0\|_2 = 1$ and $\mathcal{E}(\psi_0) = E_0$. The assumed lower semicontinuity (2) will be proved later.

To prove that ψ_0 satisfies the Schrödinger equation, we take $f \in \mathcal{C}_0^\infty(\mathbb{R}^3)$ and set $\psi^\varepsilon := \psi_0 + \varepsilon f$ for $\varepsilon \in \mathbb{R}$. Then the ratio

$$\mathcal{R}(\varepsilon) = \frac{\mathcal{E}(\psi^\varepsilon)}{\langle \psi^\varepsilon, \psi^\varepsilon \rangle_2}$$

is the ratio of two second degree polynomials in ε and hence differentiable for sufficiently small ε. Its minimum E_0 occurs at $\varepsilon = 0$ and thus $\mathrm{d}\mathcal{R}(\varepsilon)/\,\mathrm{d}\varepsilon = 0$ which yields

$$\frac{\mathrm{d}\mathcal{E}(\psi^\varepsilon)}{\mathrm{d}\varepsilon}\Big|_{\varepsilon=0} = E_0 \frac{\mathrm{d}\,\langle \psi^\varepsilon, \psi^\varepsilon \rangle_2}{\mathrm{d}\varepsilon}\Big|_{\varepsilon=0}.$$

As a consequence

$$\langle Hf, \psi_0 \rangle_2 = E_0 \langle f, \psi_0 \rangle_2$$

which by the definition of distributional derivatives yields the result. □

It remains to prove (2). The first inequality is a very general result that holds for all L^p norms.[19] Before we prove this, we note that H^1 weak convergence implies L^2 weak convergence.[20]

[17] Taken from [11, Theorem 11.5]

[18] This is called the *direct method* and consits of four steps:

1. Take a minimising sequence $\mathcal{E}(\psi^j) \to E_0$.
2. Show that ψ^j has a subsequence that converges to a ψ_0 with respect to a topology.
3. Show that ψ_0 is in the domain of $\mathcal{E}$.
4. Show that $\mathcal{E}$ is lower semicontinuous with respect to this topology.

[19] See [11, Theorem 2.11].

[20] Exercise.

Theorem 13. *If $\psi^j \rightharpoonup \psi_0$ weakly in $L^2(\mathbb{R}^3)$ then*

$$\|\psi_0\|_2 \leq \liminf_{j\to\infty} \left\|\psi^j\right\|_2 .$$

Proof. The statement then follows from the Cauchy–Schwarz inequality

$$\|\psi_0\|_2^2 = \langle \psi_0, \psi_0\rangle_2 = \lim_{j\to\infty} \left\langle \psi_0, \psi^j\right\rangle_2 \leq \|\psi_0\|_2 \liminf_{j\to\infty} \left\|\psi^j\right\|_2 .$$

□

The lower semicontinuity of the energy functional can be proved by showing that $\psi \mapsto T_\psi$ is lower semicontinuous and that $\psi \mapsto V_\psi$ is continuous (with respect to the weak topology on $H^1(\mathbb{R}^3)$).

Theorem 14. *Let $V \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ and assume that it vanishes at infinity, i.e. for all $a > 0$*

$$|\left\{x \in \mathbb{R}^3 : |V(x)| > a\right\}| < \infty .$$

Then, if $\psi^j \rightharpoonup \psi_0$ weakly in $H^1(\mathbb{R}^3)$, it holds that

$$V_{\psi_j} \to V_{\psi_0} .$$

Proof [21]. By an application of the uniform boundedness principle $\|\psi^j\|_{H^1}$ is uniformly bounded.[22] We then define

$$V^\delta(x) = \begin{cases} V(x), & \text{if } |V(x)| \leq 1/\delta \\ 0, & \text{if } |V(x)| > 1/\delta \end{cases}$$

and note that by dominated convergence (for small enough δ the L^∞ part of V cancels out)

$$\int_{\mathbb{R}^3} |V(x) - V^\delta(x)|^{3/2}\,\mathrm{d}x \to 0$$

as $\delta \to 0$. Since $\|\psi^j\|_{H^1} \leq t$, Sobolev's inequality in Theorem 8 implies that

$$\begin{aligned}\int_{\mathbb{R}^3} (V(x) - V^\delta(x))|\psi^j(x)|^2\,\mathrm{d}x &\leq \left\|V - V^\delta\right\|_{3/2} \left\|\psi^j\right\|_6^2 \\ &\leq \frac{1}{S_3} \left\|V - V^\delta\right\|_{3/2} \left\|\psi^j\right\|_{H^1}^2 \leq C_\delta\end{aligned}$$

with some C_δ independent of j. By an application of the triangle inequality, we see that it is sufficient to prove that

$$V^\delta_{\psi^j} \to V^\delta_{\psi_0}$$

[21] Taken from [11, Theorem 11.4].

[22] You may not immediately recognise this as the uniform boundedness principle taught in a basic functional analysis course. To understand it, identify the dual of a Hilbert space with itself.

for any $\delta > 0$. Difficulties arise from the fact that V^δ vanishes only in a weak sense at infinity. For any $\varepsilon > 0$ we define the set

$$A_\varepsilon = \left\{x \in \mathbb{R}^3 : |V^\delta(x)| \geq \varepsilon\right\} .$$

[23] This is the only point in the proof where we need the additional assumption that V vanishes at infinity.

By assumption[23] $|A_\varepsilon| < \infty$ and we decompose

$$V^\delta_{\psi^j} = \int_{A_\varepsilon} V^\delta(x)|\psi^j(x)|^2\,\mathrm{d}x + \int_{\mathbb{R}^3\setminus A_\varepsilon} V^\delta(x)|\psi^j(x)|^2\,\mathrm{d}x\,.$$

and

$$V^\delta_{\psi_0} = \int_{A_\varepsilon} V^\delta(x)|\psi_0(x)|^2\,\mathrm{d}x + \int_{\mathbb{R}^3\setminus A_\varepsilon} V^\delta(x)|\psi_0(x)|^2\,\mathrm{d}x\,.$$

The second terms can be bounded by (using lower semiconitnuity of the L^2 norm)

$$\int_{A_\varepsilon} V^\delta(x)|\psi^j(x)|^2\,\mathrm{d}x \leq \varepsilon \left\|\psi^j\right\|_2^2 = \varepsilon$$
$$\int_{A_\varepsilon} V^\delta(x)|\psi_0(x)|^2\,\mathrm{d}x \leq \varepsilon \left\|\psi_0\right\|_2^2 \leq \varepsilon$$

and thus we only need to show that for fixed δ, ε (here we need that C_δ does not depend on j)

$$\int_{A_\varepsilon} V^\delta(x)|\psi^j(x)|^2\,\mathrm{d}x \to \int_{A_\varepsilon} V^\delta(x)|\psi_0(x)|^2\,\mathrm{d}x\,.$$

[24] See e.g. [11, Theorem 8.6].

Since weak H^1 convergence implies strong L^p convergence ($2 \leq p < 6$) on any set of finite measure[24] we have that ψ^j converges strongly to ψ_0 in L^r for any $2 < r \leq 6$. By means of the inequality

$$||\psi^j|^2 - |\psi_0|^2| \leq |\psi^j - \psi_0||\psi^j + \psi_0|$$

we can prove that $\left\||\psi^j|^2 - |\psi_0|^2\right\|_{r/2} \to 0$. By construction $V^\delta \in L^\infty(\mathbb{R}^3)$ and thus $V^\delta \in L^s(A_\varepsilon)$ for any $1 \leq s \leq \infty$. The statement now follows from taking $1/2 + 2/r = 1$ and applying Hölder's inequality

$$\left|\int_{A_\varepsilon} |V^\delta(x)|(|\psi^j(x)|^2 - |\psi_0(x)|^2)\,\mathrm{d}x\right| \leq \left\|V^\delta\right\|_s \left\||\psi^j|^2 - |\psi_0|^2\right\|_{r/2} .$$

□

It remains to prove the lower semicontinuity of the kinetic energy.

Theorem 15. *If $\psi^j \rightharpoonup \psi_0$ weakly in $H^1(\mathbb{R}^3)$ then $\nabla\psi^j \rightharpoonup \nabla\psi_0$ weakly in $L^2(\mathbb{R}^3)$ and thus*

$$T_{\psi_0} \leq \liminf_{j\to\infty} T_{\psi^j} .$$

Proof. Again we use the Cauchy–Schwarz inequality

$$\begin{aligned} T_{\psi_0} &= \int_{\mathbb{R}^3} |(\nabla\psi_0)(x)|^2 \,\mathrm{d}x = \lim_{j\to\infty} \int_{\mathbb{R}^3} \overline{(\nabla\psi_0)(x)}(\nabla\psi^j)(x)\,\mathrm{d}x \\ &\leq \|\nabla\psi_0\|_2 \liminf_{j\to\infty} \left\|\nabla\psi^j\right\|_2 . \end{aligned}$$

□

Similarly to the definition of E_0, we can also define numbers E_k. We will call them *eigenvalues*, a name that will become clearer soon. Under the assumptions on V as above, the first eigenvalue is defined as

$$E_1 = \inf\left\{\mathcal{E}(\psi) : \|\psi\|_2 = 1, \psi \in H_1(\mathbb{R}^3), \langle\psi,\psi_0\rangle_2 = 0\right\} \geq E_0 .$$

If the infinum is attained at ψ_1, then we call ψ the *first excited state* or the *eigenfunction* for E_1. Assuming that we have defined $\psi_0,\ldots,\psi_{k-1}$ in a similar fashion,we define the $(k+1)$-th eigenvalue recursively as

$$E_k \coloneqq \inf\left\{\mathcal{E}(\psi) \colon \|\psi\|_2 = 1, \psi \in H^1(\mathbb{R}^3), \langle\psi,\psi_j\rangle_2 = 0, j = 0,\ldots,k-1\right\} \geq E_{k-1}$$

and if the infinum is attained at ψ_k, we call ψ_k an eigenfunction for E_k.

Theorem 16. *Let $V \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ and assume that it vanishes at infinity, i.e. for all $a > 0$*

$$|\left\{x \in \mathbb{R}^3 : |V(x)| > a\right\}| < \infty .$$

If $E_k < 0$ then $\psi_k \in H^1(\mathbb{R}^3)$ exists and in a distributional sense

$$H\psi_k = E_k\psi_k .$$

Each number $E_k < 0$ can only occur finitely many times in the list of eigenvalues.

Conversely, any $\psi \in H^1(\mathbb{R}^3)$ that satisfies $H\psi = E\psi$ for some $E < 0$ is a linear combination of eigenfunctions to the eigenvalue E.

Proof [25]. The proof of the existence of the eigenfunction ψ_k is similar to the existence of a ground state in Theorem 12.

To prove that ψ_k solves the eigenequation in a distributional sense, we can show, again similar to Theorem 12, that

$$D(f) = \langle\psi_k, (H - E_k)f\rangle_2 = 0$$

for all $f \in \mathcal{C}_0^\infty(\mathbb{R}^3)$ with $\langle f,\psi_i\rangle_2 = 0, i = 0,\ldots,k-1$. We can conclude[26] that there exist $c_0,\ldots,c_{k-1}$ such that

$$D = \sum_{i=0}^{k-1} c_i\psi_i .$$

[25] Taken from [11, Theorem 11.6].

[26] This is a consequence of the fact that the ψ_i span the vector space of all distributions that vanish on the intersection of all the individual kernels $\ker\psi_i$, see [11, Theorem 6.14].

Multiplying this equation by ψ_j ($j \leq k-1$) and using partial integration we obtain

$$\int_{\mathbb{R}^n} \overline{(\nabla\psi_j)(x)} \cdot (\nabla\psi_k)(x)\,\mathrm{d}x + \int_{\mathbb{R}^n} V(x)\overline{\psi_j(x)}\psi_k(x)\,\mathrm{d}x = c_j\,.$$

Similarly, we multiply the complex conjugate of $H\psi_j = E_j\psi_j$ by ψ_k and use partial integration to obtain

$$\int_{\mathbb{R}^n} \overline{(\nabla\psi_j)(x)} \cdot (\nabla\psi_k)(x)\,\mathrm{d}x + \int_{\mathbb{R}^n} V(x)\overline{\psi_j(x)}\psi_k(x)\,\mathrm{d}x = 0\,.$$

While these computations were strictly formal, we can make them rigorous by an approximation argument.[27] We conclude that $c_j = 0$, which proves the result.

[27] Exercise.

To show that each E_k has only finite multiplicity, we argue by contradiction. Assuming that $E_k = E_{k+1} = E_{k+2} = \ldots$, the above implies that there exists an orthonormal sequence $\psi_k, \psi_{k+1}, \ldots$ satisfying the eigenequation $H\psi = E_k\psi$ in a distributional sense. From the one-body stability result of Theorem 6 we know $T_{\psi_j} \leq C$ for some $C > 0$ and thus $\psi_j \rightharpoonup \psi_0$ weakly in $H^1(\mathbb{R}^3)$. By the orthogonality ψ_j must converge weakly to zero in $L^2(\mathbb{R}^3)$ and thus also in $H^1(\mathbb{R}^3)$. Then by the continuity of the potential energy in Theorem 14 necessarily $V_{\psi_j} \to 0$ and thus we get the contradiction

$$E_k = \lim_{j\to\infty} (T_{\psi_j} + V_{\psi_j}) \geq 0\,.$$

The last statement can be proved using partial integration similar to the arguments above.[28] □

[28] Exercise.

Remark 17. Using the same method as in the last step of the proof, it is possible to show that the eigenvalues E_k cannot accumulate at any point that is strictly smaller than zero.[29] The situation typically looks as visualised in Figure 5.

[29] Exercise.

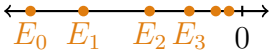

Figure 5: The typical discrete spectrum.

In the definition of E_k, the preceding eigenfunctions $\psi_0, \ldots, \psi_{k-1}$ play an important role. As it turns out, each E_k can also be characterised directly through a variational principle, which does not need explicit knowledge of $\psi_0, \ldots, \psi_{k-1}$.

Theorem 18 (Min-Max principle)**.** *Let $V \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ and assume that it vanishes at infinity, i.e. for all $a > 0$*

$$|\{x \in \mathbb{R}^3 : |V(x)| > a\}| < \infty\,.$$

Then the eigenvalues are also given by

$$E_k = \max_{\phi_0,\ldots,\phi_{k-1}} \min\{\mathcal{E}(\phi_k) : \phi_k \perp \phi_0, \ldots, \phi_{k-1}\}$$

and

$$E_k = \min_{\phi_0,\dots,\phi_k} \max\{\mathcal{E}(\phi) : \phi \in \operatorname{span}(\phi_0,\dots,\phi_{k-1})\}$$

where the maximum (minimum, respectively) extends over all collections of k ($k+1$, respectively) orthonormal functions $\phi_j \in L^2(\mathbb{R}^3)$ which are also in $H^1(\mathbb{R}^3)$.

Proof [30]. To prove the first identity, let

$$\gamma_k \coloneqq \max_{\phi_0,\dots,\phi_{k-1}} \min\{\mathcal{E}(\psi) : \phi_k \perp \phi_0,\dots,\phi_{k-1}\} .$$

Choosing $\phi_0,\dots,\phi_{k-1}$ to be the eigenfunctions $\psi_0,\dots,\psi_{k-1}$, we immediately get that $\gamma_k \geq E_k$. Conversely, for any choice of $\phi_0,\dots,\phi_{k-1}$ there is[31] always a linear combination $f = \sum_{j=0}^{k} c_j\psi_j$ such that f is normalised and orthogonal onto $\phi_0,\dots,\phi_{k-1}$. Then

$$\mathcal{E}(f) = \sum_{j=1}^{k} |c_j|^2 E_j \leq E_k \sum_{j=1}^{k} |c_j|^2 = E_k$$

and consequently

$$\min\{\mathcal{E}(\psi) : \phi_k \perp \phi_0,\dots,\phi_{k-1}\} \leq E_k$$

which implies $\gamma_k \leq E_k$.

To prove the second identity, let

$$\gamma_k \coloneqq \min_{\phi_0,\dots,\phi_k} \max\{\mathcal{E}(\phi) : \phi \in \operatorname{span}(\phi_0,\dots,\phi_k)\} .$$

Choosing $\phi_0,\dots,\phi_k$ to be the eigenfunctions $\psi_0,\dots,\psi_k$, we immediately get that $\gamma_k \leq E_k$. Conversely, for any orthogonal $\phi_0\dots,\phi_k$, there is[32] always a linear combination $f = \sum_{j=0}^{k} c_j\phi_j$ such that f is normalised and orthogonal onto $\psi_0,\dots,\psi_{k-1}$. Then by definition of the eigenvalues $\mathcal{E}(f) \geq E_k$ and hence $\gamma_k \geq E_k$.

□

Remark 19. It is sufficient[33] to assume that $V_- = -\min(V,0) \in L^2(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ vanishes at infinity without any assumptions on $V_+ = V - V_-$. We then need to consider only those ϕ_j in the minimum/maximum, for which V_{ϕ_j} is well-defined.

An immediate consequence of this theorem is the monotonicity of all the excited states. Let V^A, V^B be two potentials satisfying the assumptions of the Min-Max principle. Let $\mathcal{E}^A, \mathcal{E}^B$ be the corresponding energy functionals and

[30] Taken from [11, Theorem 12.1].

[31] The sum extends over $k+1$ linearly independent functions.

[32] The sum extends over $k+1$ linearly independent functions.

[33] See [11, Theorem 12.1].

$E_0^A, \dots, E_0^B, \dots$ the eigenvalues. If $V^A(x) \leq V^B(x)$ for all $x \in \mathbb{R}^3$ then for all $\psi \in H^1(\mathbb{R}^3)$

$$\mathcal{E}^A(\psi) \leq \mathcal{E}^B(\psi)\,.$$

By the Min-Max principle we now see that this does not only imply

$$E_0^A \leq E_0^B$$

but more generally that

$$E_k^A \leq E_k^B$$

for all $k \geq 0$.

2.5. Lieb–Thirring inequalities

This section is taken from [12, Chapter 4].

In this subsection we investigate how fast E_k converges to zero as $k \to \infty$. In particular we will prove that under decay assumptions on the potential, the eigenvalues form a convergent series. This will be important for the many-body considerations later, once we know that specific non-interacting particles fill up the energy levels $E_1, E_2, \dots$. The total energy is then precisely a sum of the form $E_1 + E_2 + \dots$ and we will need bounds for this quantity.

On $L^2(\mathbb{R}^3)$ we consider the Schrödinger operator

$$H = -\Delta + V(x)\,.$$

Throughout this section, we assume that the potential Vsatisfies the assumptions of the previous subsection. Let $E_0 \leq E_1 \leq E_2 \leq \dots$ be the eigenvalues of H smaller than zero, defined as in the previous subsection. We denote by V_- the negative part of the potential, i.e.

$$V_-(x) = \frac{|V(x)| - V(x)}{2} = -\min(V(x), 0) \geq 0\,.$$

Theorem 20 (Lieb–Thirring inequality[34]). *Let $\gamma \geq 0$ and assume that $V_- \in L^{\gamma+3/2}(\mathbb{R}^3)$. Then there exists a constant $L_{\gamma,3}$ independent of V such that the negative eigenvalues E_j of $-\Delta + V$ satisfy*

$$\sum_{j \geq 0} |E_j|^\gamma \leq L_{\gamma,3} \int_{\mathbb{R}^3} V_-(x)^{\gamma+3/2}\,\mathrm{d}x\,.$$

More generally, in any dimension $d \geq 1$ if $V_- \in L^{\gamma+d/2}(\mathbb{R}^d)$ if one of the following holds

$$\begin{aligned} d = 1\,, &\qquad \gamma \geq \frac{1}{2}\,, &&\qquad V \in L^1(\mathbb{R}^1) + L^\infty(\mathbb{R}^1)\,,\\ d = 2\,, &\qquad \gamma > 0\,, &&\qquad V \in L^{1+\varepsilon}(\mathbb{R}^2) + L^\infty(\mathbb{R}^2)\,,\\ d \geq 3\,, &\qquad \gamma \geq 0\,, &&\qquad V \in L^{d/2}(\mathbb{R}^d) + L^\infty(\mathbb{R}^d)\,, \end{aligned}$$

[34] This result was first proved by Lieb and Thirring [13]. The critical case $d \geq 3, \gamma = 0$ was independently proved in [3, 10, 17] and is thus also called CLR bound. The remaining case $d = 1, \gamma = 1/2$ was proved by Weidl [21].

then there exists a constant $L_{\gamma,d}$ independent of V such that the negative eigenvalues E_j of $-\Delta + V$ satisfy

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

The left-hand side can also be written as $\operatorname{tr}(-\Delta+V)_-^\gamma$. The interesting case for the stability of matter is $\gamma = 1, d = 3$. Before we prove the Lieb–Thirring inequality for $\gamma = 1, d = 3$, we will give a heuristic argument that allows us to better understand the origins of such a bound.

2.5.1. Semiclassical approximation

According to the semiclassical approach, which dates back to the early days of Quantum Mechanics, each volume $(2\pi)^3$ in 6-dimensional phase space can support one quantum state.[35] We can hope to compute the number of negative eigenvalues by

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

and similarly

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

[35] To motivate this, consider a Gaussian wavefunction $\psi(x) = C\mathrm{e}^{-x^2/d}$ and use the Heisenberg uncertainty principle to compute how much volume this state takes up at least in phase space.

We can calculate that

$$\begin{aligned}
\iint_{p^2+V(x)\leq 0} |p^2+V(x)|^\gamma\,\mathrm{d}p\,\mathrm{d}x &= \int_{\mathbb{R}^3}\int_{|p|\leq\sqrt{V_-(x)}} (V_-(x)-p^2)^\gamma\,\mathrm{d}p\,\mathrm{d}x \\
&= \int_{\mathbb{R}^3} V_-(x)^\gamma \int_{|p|\leq\sqrt{V_-(x)}} |1-(p/\sqrt{V_-(x)})^2|^\gamma\,\mathrm{d}p\,\mathrm{d}x \\
&= \int_{\mathbb{R}^3} V_-(x)^{\gamma+3/2} \int_{|q|\leq 1} (1-|q|^2)^\gamma\,\mathrm{d}q\,\mathrm{d}x
\end{aligned}$$

As a consequence we can hope that the approximation

$$\sum_{j\geq 0} |E_j|^\gamma \approx L_\gamma \int_{\mathbb{R}^3} V_-(x)^{\gamma+3/2}\,\mathrm{d}x$$

holds, where

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

is the so-called *semiclassical Lieb–Thirring constant*. Of course, we could apply this approximation in any dimension d and we would end up with

$$L_{\gamma,d}^{cl} = \frac{1}{(2\pi)^d}\int_{\{p\in\mathbb{R}^d:\,|p|\leq 1\}}(1-p^2)^\gamma\,\mathrm{d}p$$

Remark 21. Although these approximations are not mathematically rigorous, the Lieb–Thirring inequality says that (up to a multiplicative constant) the term $\sum_{j\geq 0}|E_j|^\gamma$ can be bounded by $\int_{\mathbb{R}^d} V_-^{\gamma+d/2}$ if γ satisfies the required bounds. The best choice of $L_{\gamma,d}$ is however, not always exactly the semi-classical constant $L^{cl}_{\gamma,d}$. For example, in one dimension $d = 1$ it is known that

$$L_{1/2,1} = 2L^{cl}_{1/2,1} = 1/2\,.$$

[36] See e.g. [11, Theorem 12.12]

However, an asymptotic result by Weyl[36] says that the approximation above is true in the limit of large potentials. To be more precise, if $E_j(\lambda)$ are the negative eigenvalues of $-\Delta + \lambda V$ then

$$\lim_{\lambda\to\infty} \frac{\sum_{j\geq 0}|E_j(\lambda)|^\gamma}{\lambda^{\gamma+d/2}} = L^{cl}_{\gamma,d}\int_{\mathbb{R}^3} V_-(x)^{\gamma+d/2}\,\mathrm{d}x$$

for all $\gamma \geq 0$. This implies that necessarily $L_{\gamma,d} \geq L^{cl}_{\gamma,d}$.

2.5.2. The Birman–Schwinger principle

We can assume that $V = -V_-$, for otherwise we simply replace V by $-V_-$, which only decreases the eigenvalues as we have seen at the end of the last subsection. We will now express the Schrödinger equation in a different way by means of an operator K_e.

Let $-e$ be a negative eigenvalue of $H = -\Delta + V_-$ with eigenfunction ψ. If we define

$$\phi(x) := \sqrt{V_-(x)}\psi(x)$$

then

$$(-\Delta + e)\psi = \sqrt{V_-}\phi\,.$$

We need the following result from spectral theory.

Lemma 22. *Let $e > 0$. For any $f \in L^2(\mathbb{R}^3)$ the unique solution $g \in H^2(\mathbb{R}^3)$ to the partial differential equation*

$$(-\Delta + e)g = f$$

is given by

$$(-\Delta + e)^{-1}f := \int_{\mathbb{R}^3} G_e(x-y)f(y)\,\mathrm{d}y$$

where G_e is the Green's function (also known as Yukawa potential)

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

Proof. For a complete proof including existence and uniqueness of the solution, we refer to [11, Theorem 6.23 and Section 9.11]. We will only derive the Green's function formally. We recall that the Fourier transform

$$\widehat{f}(k) = [\mathcal{F}f](k) = \int_{\mathbb{R}^3} \mathrm{e}^{-2\pi \mathrm{i} k\cdot x} f(x)\,\mathrm{d}x$$

can be extended to a unitary operator on $L^2(\mathbb{R}^3)$. Applying $\mathcal{F}$ to the partial differential equation and writing the solution as $g = \mathcal{F}^{-1}h$ and we get from the well-known properties of the Fourier transform

$$\mathcal{F}[f] = \mathcal{F}[(-\Delta + e)\mathcal{F}^{-1}h] = (|2\pi k|^2 + e)h$$

and consequently $h = \mathcal{F}[f]/(|2\pi k|^2 + e)$. Applying the inverse Fourier transform we obtain the claimed result

$$\begin{aligned} g(x) = \mathcal{F}^{-1}[[\mathcal{F}f]/(|2\pi k|^2 + e)](x) &= (f * \mathcal{F}[1/(|2\pi k|^2 + e)])(x) \\ &= \int_{\mathbb{R}^3} G_e(x-y) f(y)\,\mathrm{d}y\,. \end{aligned}$$

□

Remark 23. For students who are familiar with spectral theory, the statement above is a consequence of the fact that the operator $-\Delta : H^2(\mathbb{R}^3) \to L^2(\mathbb{R}^3)$ is a self-adjoint, positive operator. In particular $(-\Delta + e)$ is invertible for any $e > 0$. The operator is furthermore unitarily equivalent to the multiplication operator $|2\pi k|^2$.

Continuing the above calculation, we see that

$$\phi = \sqrt{V_-}(-\Delta + e)^{-1}\sqrt{V_-}\phi\,.$$

which can be written by introducing the operator $K_e \coloneqq \sqrt{V_-}(-\Delta + e)^{-1}\sqrt{V_-}$ as

$$K_e\phi = \phi\,.$$

Note that K_e is an integral operator, i.e.

$$(K_e\phi)(x) = \int_{\mathbb{R}^3} K_e(x,y)\phi(y)\,\mathrm{d}y$$

with kernel given by

$$K_e(x,y) = \sqrt{V_-(x)}G_e(x-y)\sqrt{V_-(y)}\,,$$

which is called the *Birman–Schwinger kernel*. We now investigate this operator and show that there is a one-to-one correspondence between K_e having an eigenvalue 1 and H having an eigenvalue $-e$.

[37] This principle was first proved by Birman [2] and Schwinger [19].

Theorem 24 (Birman–Schwinger principle[37]). *For K_e defined as above, the following holds:*

1. *K_e is a bounded operator on $L^2(\mathbb{R}^3)$.*
2. *There is a one-to-one correspondence between the two sets of eigenfunctions*
$$\{\psi \in H^1(\mathbb{R}^3) : H\psi = -e\psi\}$$
$$\{\phi \in L^2(\mathbb{R}^3) : K_e\phi = \phi\}$$
via $\phi = \sqrt{V_-}\psi$ and $\psi = (-\Delta + e)^{-1}\sqrt{V_-}\phi$.
3. *There is a one-to one correspondence between the eigenvalues, in the sense that $N_e = B_e$ for*
$$N_e := \#\{\textit{Eigenvalues of } H \textit{ less than or equal to } -e\},$$
$$B_e := \#\{\textit{Eigenvalues of } K_e \textit{ greater than or equal to } 1\}.$$
This is the Birman–Schwinger principle.

[38] Taken from [12, Section 4.3.], as well as [5, pp. 7–9] and [9, pp. 50–52].

[39] Exercise. For the statement and proof of the inequality see [11, Theorem 4.3].

[40] See [5, p. 8].

Proof [38]. We omit the proof of (1). The statement can be proved using the Hardy–Littlewood–Sobolev inequality[39] or with the help of the Plancherel formula[40].

To show that $\phi = \sqrt{V_-}\psi \in L^2(\mathbb{R}^3)$ if $\psi \in H^1(\mathbb{R}^3)$ is an eigenfunction of H with eigenvalue $-e$, we recall that $V = V_1 + V_2$ with $V_1 \in L^{3/2}(\mathbb{R}^3)$ and $V_2 \in L^\infty(\mathbb{R}^3)$. An application of Hölder's inequality and Sobolev's inequality of Theorem 8 yields

$$\int_{\mathbb{R}^3} |\sqrt{V_-(x)}\psi(x)|^2\,\mathrm{d}x = \int_{\mathbb{R}^3} V_-(x)|\psi(x)|^2\,\mathrm{d}x \leq \|V_1\|_{3/2}\,\|\psi\|_6^2 + \|V_2\|_\infty\,\|\psi\|_2^2$$
$$\leq S_3^{-1}\,\|V_1\|_{3/2}\,\|\nabla\psi\|_2^2 + \|V_2\|_\infty < \infty\,.$$

Thus $\phi \in L^2(\mathbb{R}^3)$ and we have already seen that $K_e\phi = \phi$.

Conversely, let ϕ be an eigenfunction of K_e with eigenvalue 1 and define[41]

$$\psi = (-\Delta + e)^{-1}\sqrt{V_-}\phi\,.$$

[41] It seems more obvious to define $\psi = \phi/\sqrt{V_-}$. However, we then have to argue what happens at the points where V_- vanishes.

Then

$$(-\Delta + e)\psi = \sqrt{V_-}\phi = \sqrt{V_-}K_e\phi = V_-(-\Delta + e)^{-1}\sqrt{V_-}\phi = V_-\psi$$

and it only remains to prove that $\psi \in L^2(\mathbb{R}^3)$. With the operator inequality

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

which can be seen from the Fourier representation, we obtain

$$\|\psi\|_2^2 = \left\langle \sqrt{V_-}\phi, (-\Delta + e)^{-2}\sqrt{V_-}\phi \right\rangle_2 \leq e^{-1} \left\langle \sqrt{V_-}\phi, (-\Delta + e)^{-1}\sqrt{V_-}\phi \right\rangle_2$$
$$= e^{-1} \langle \phi, K_e \phi \rangle_2 = e^{-1} \|\phi\|_2^2 < \infty .$$

To prove that $N_e = B_e$, we need three more facts, which we will give here without a proof.[42]

[42] For some details see [12, p. 77].

1. The operator K_e has only non-negative eigenvalues $\lambda_1(e) \geq \lambda_2(e) \geq \cdots \geq 0$. In, fact K_e is a positive, compact operator.

2. K_e is decreasing in e, i.e. for $e \leq e'$ and all $\phi \in L^2(\mathbb{R}^3)$
$$\langle \phi, K_e \phi \rangle_2 \geq \langle \phi, K_{e'} \phi \rangle_2 .$$
and by the Min-Max principle $\lambda_j(e) \geq \lambda_j(e')$. Furthermore $K_e \to 0$ as $e \to \infty$.

3. The eigenvalues $\lambda_j(e)$ depend continuously on $e > 0$.

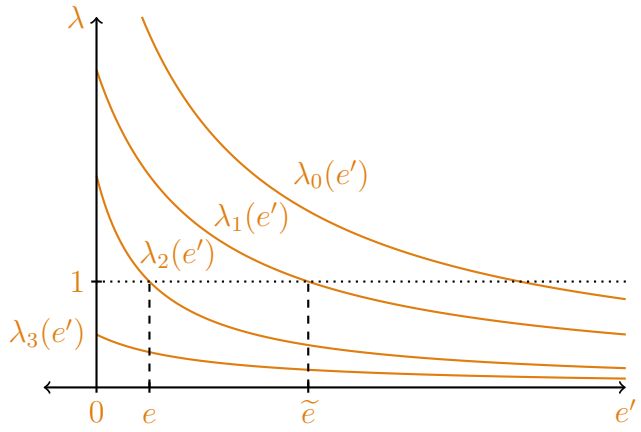

Figure 6: The Birman–Schwinger principle.

Equipped with these results, we now fix $e > 0$ and let e' increase from e to ∞. At the start $e' = e$ and $K_{e'}$ has B_e many eigenvalues that are greater than 1. As e' increases from e to ∞, these eigenvalues will continuously go to zero. By the intermediate value theorem an eigenvalue $\lambda_j(e')$ will eventually become 1, say at $e' = \widetilde{e}$. Record that number. Then $-\widetilde{e}$ is an eigenvalue of H that lies below $-e$ and that has the same multiplicity as the eigenvalue 1 of $K_{\widetilde{e}}$. As $e' \to \infty$ the operator $K_{e'} \to 0$ and thus eventually all the eigenvalues $\lambda_j(e')$ will be below 1. Thus the number B_e of eigenvalues of K_e above 1 is the same as the number of $\widetilde{e}$ that we find in the process above. This number is precisely the number of times a $\lambda_j(e')$ crosses the 'barrier' 1, which is N_e. Thus $B_e = N_e$. A visual representation of this proof can be found in Figure 6, adapted from [12, Figure 4.1 p. 78].

□

2.5.3. The proof of the Lieb–Thirring inequality

We only consider the (for our considerations) relevant case $\gamma = 1$. The general proof can be found in [12, pp. 77–78]. For pedagogic reasons, we will first present a wrong proof (an integral will diverge) and then correct it (by introducing an additional parameter that guarantees convergence of the aforementioned integral).[43]

[43] Taken from [12, pp. 77–78]. The main idea of the proof is that we can compute traces of K_e since we know its kernel explicitly. We thus aim to bound the left-hand side of the Lieb–Thirring inequality by some trace of K_e using the Birman–Schwinger principle.

To use Theorem 24, we rewrite $e_j := |E_j|$ and note that

$$\sum_{j\geq 0} |E_j| = \sum_{j\geq 0} e_j = \int_0^\infty N_e \,\mathrm{d}e\,. \tag{3}$$

By the Birman–Schwinger principle (with λ_j denoting the eigenvalues of K_e)

$$N_e = B_e \leq \sum_{\lambda_j \geq 1} \lambda_j(e)^2 \leq \operatorname{tr}\bigl(K_e^2\bigr)$$

and we now bound the right-hand side. The trace of the integral operator K_e^2 is[44]

[44] Exercise.

$$\operatorname{tr}\bigl(K_e^2\bigr) = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} V_-(x) G_e(x-y)^2 V_-(y)\,\mathrm{d}y\,\mathrm{d}x\,.$$

Using the Cauchy–Schwarz inequality we bound

$$\begin{aligned}\operatorname{tr}\bigl(K_e^2\bigr) &= \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} V_-(x) G_e(x-y) G_e(x-y) V_-(y)\,\mathrm{d}y\,\mathrm{d}x \\ &\leq \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} V_-(x)^2 G_e(x-y)^2\,\mathrm{d}x\,\mathrm{d}y = \int_{\mathbb{R}^3} V_-(x)^2\,\mathrm{d}x \int_{\mathbb{R}^3} G_e(y)^2\,\mathrm{d}y\end{aligned}$$

and using Plancherel's formula we rewrite the second integral as an integral in Fourier space to get

$$\operatorname{tr}\bigl(K_e^2\bigr) \leq \int_{\mathbb{R}^3} V_-(x)^2\,\mathrm{d}x \int_{\mathbb{R}^3} \frac{1}{(|2\pi k|^2 + e)^2}\,\mathrm{d}k\,.$$

The last integral can be computed explicitly, as it is of the form $Ce^{-1/2}$ by scaling, or more precisely

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

If we insert this bound back into (3), we obtain an integral of $e^{-1/2}$ over the half-axis $(0,\infty)$, which unfortunately diverges.

To remedy the situation, we consider the new potential

$$W_e(x) := (V(x) + e/2)_- = \max(-V(x) - e/2, 0) \leq V_-(x)\,.$$

Note that $W_e \in L^{5/2}(\mathbb{R}^3)$. We now compare the number $N_e = N_e(-V_-)$ of eigenvalues of $-\Delta - V_-$ to those of $-\Delta - W_e$, denoted by $N_e(-W_e)$. By the Min-Max principle and $W_e \geq V_- - e/2$

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

Repeating the same calculation as before with e replaced by $e/2$ and V_- by W_e, we obtain

$$\begin{aligned}\sum_{j\geq 0} |E_j| \leq \int_0^\infty \mathrm{d}N_e(-W_e) &\leq C \int_0^\infty (e/2)^{-1/2} \int_{\mathbb{R}^3} W_e(x)^2 \,\mathrm{d}x\,\mathrm{d}e \\ &= C \int_0^\infty (e/2)^{-1/2} \int_{\mathbb{R}^3} (V(x) + e/2)_-^2 \,\mathrm{d}x\,\mathrm{d}e \\ &= C \int_0^\infty (e/2)^{-1/2} \int_{\mathbb{R}^3} (V_-(x) - e/2)_+^2 \,\mathrm{d}x\,\mathrm{d}e \\ &= C \int_{\mathbb{R}^3} \int_0^{2V_-(x)} (e/2)^{-1/2} (V_-(x) - e/2)^2 \,\mathrm{d}x\,\mathrm{d}e\,.\end{aligned}$$

The inner integral can be computed just like the integral in the semiclassical motivation and we obtain the desired bound

$$\sum_{j\geq 0} |E_j| = \int_0^\infty \mathrm{d}N_e \leq C \left(\sqrt{2} \int_0^1 e^{-1/2}(1-e)^2 \,\mathrm{d}e\right) \int_{\mathbb{R}^3} V_-(x)^{5/2} \,\mathrm{d}x\,.$$

3. Many-body Quantum Mechanics

This introduction is based on [12, Chapter 3].

In the preceding section, we only considered one quantum mechanical particle. To define atoms other than hydrogen, we need to introduce many-body Quantum Mechanics.

A wave function for N spinless particles is any function $\psi \in L^2(\mathbb{R}^{3N})$ with unit norm $\|\psi\| = 1$, i.e.

$$\int_{\mathbb{R}^3} |\psi(x_1, \ldots, x_N)|^2 \,\mathrm{d}x_1 \ldots \,\mathrm{d}x_N = 1\,.$$

Again, we interpret $|\psi(x_1, \ldots, x_N)|^2$ as the probability that the first particle is at x_1 the second at x_2 and so on. An important function, is the *one-particle density* ρ_ψ which is defined for $x \in \mathbb{R}^3$ as

$$\rho_\psi(x) = \sum_{i=1}^N \int_{\mathbb{R}^{3(N-1)}} |\psi(x_1, \ldots, x_{i-1}, x, x_{i+1}, \ldots, x_N)|^2 \,\mathrm{d}x_1 \ldots \,\mathrm{d}x_{i-1}\,\mathrm{d}x_{i+1} \ldots \,\mathrm{d}x_N\,.$$

Note that $\int_{\mathbb{R}^3} \rho_\psi \,\mathrm{d}x = N$.

In the one-particle case, all wave functions were admissible. In the many-particle case, it is a postulate of quantum mechanics that for a given particle

species the wave function must have characteristic symmetries. In particular, the wave functions of identical particles satisfies

$$|\psi(x_1, \dots, x_i \dots, x_j, \dots, x_N)|^2 = |\psi(x_1, \dots, x_j \dots, x_i, \dots, x_N)|^2 .$$

In nature[45], theses particles fall into two categories, bosons and fermions.

[45] In two dimensional systems, there are also quasiparticles that do not fall into these two categories but are so-called *anyons*.

3.1. Bosons and fermions

Definition 25. *Bosons* are given by wave functions that are totally symmetric, i.e.

$$\psi(x_1, \dots, x_i, \dots, x_j, \dots, x_N) = \psi(x_1, \dots, x_j \dots, x_i, \dots, x_N)$$

for all $i \neq j$.

Fermions are given by wave functions that are totally antisymmetric, i.e.

$$\psi(x_1, \dots, x_i, \dots, x_j, \dots, x_N) = -\psi(x_1, \dots, x_j \dots, x_i, \dots, x_N)$$

for all $i \neq j$.

In both cases, the one-body density ρ_ψ can be written as

$$\rho_\psi(x) = N \int_{\mathbb{R}^{3(N-1)}} |\psi(x, x_2, \dots, x_N)|^2 \, \mathrm{d}x_2 \dots \, \mathrm{d}x_N .$$

The antisymmetry property can be rephrased as the *Pauli exclusion principle*. While nuclei can be either bosons or fermions, electrons are fermions, a fact that will be crucial to prove stability of matter of the second kind. An example of bosons are photons.

Example 26. Let $\varphi \in L^2(\mathbb{R}^3)$ be a one particle wave function. Then the function

$$\psi(x_1, x_2) = \varphi(x_1)\varphi(x_2)$$

is a bosonic two particle wave function. More generally

$$\psi(x_1, \dots, x_N) = \varphi(x_1) \dots \varphi(x_N)$$

is a bosonic N particle wave function.

Example 27. Let $\varphi_1, \varphi_2 \in L^2(\mathbb{R}^3)$ be one particle wave functions which are orthogonal $\langle \varphi_1, \varphi_2 \rangle_2 = 0$. Then the function

$$\psi(x_1, x_2) = \frac{1}{\sqrt{2}}(\varphi(x_1)\varphi(x_2) - \varphi(x_1)\varphi(x_2))$$

is a fermionic two particle wave function. More generally let $\varphi_1, \dots, \varphi_N \in L^2(\mathbb{R}^3)$ be one particle wave functions with $\langle \varphi_i, \varphi_j \rangle_2 = 0$ for $i \neq j$. Then

$$\psi(x_1, \dots, x_N) = \frac{1}{\sqrt{N!}} \det(\varphi_i(x_j))_{i,j=1}^N$$

is a fermionic N particle wave function[46]. A wave function of this form is called a *determinantal wave function*.

[46] Exercise.

3.2. The energy functional and many-body Hamiltonians

If $V(x_1, \ldots, x_N) : \mathbb{R}^{3N} \to \mathbb{R}$ is potential function and ψ a many-body wave function, then the potential energy is defined as

$$V_\psi = \int_{\mathbb{R}^{3N}} V(x_1, \ldots, x_N) |\psi(x_1, \ldots, x_N)|^2 \, \mathrm{d}x_1 \ldots \mathrm{d}x_N \, .$$

The kinetic energy is defined to be

$$T_\psi = \sum_{i=1}^{N} T_\psi^{(i)}$$

where

$$T_\psi^{(i)} = \int_{\mathbb{R}^{3N}} |(\nabla_{x_i} \psi)(x_1, \ldots, x_N)|^2 \, \mathrm{d}x_1 \ldots \mathrm{d}x_N$$

and the energy functional is $\mathcal{E}(\psi) = T_\psi + V_\psi$. For 'nice' (e.g. $\mathcal{C}_0^\infty(\mathbb{R}^{3N})$) functions we can write the energy as

$$\mathcal{E}(\psi) = \langle \psi, H\psi \rangle_2$$

with the many-body Hamiltonian (or more specifically the *Schrödinger operator*) given by

$$H = -\sum_{i=1}^{N} \Delta_i + V(x_1, \ldots, x_N) \, .$$

3.3. Stability of the second kind of molecules

Assume we have N electrons and M static nuclei, interacting with each other via the Coulomb force. The electrons have charge $-e$ and are at positions $x_1, \ldots, x_n$. The nuclei have charges $eZ_1, \ldots, eZ_M$ and are located at fixed locations $R_1, \ldots, R_M \in \mathbb{R}^3$. The potential energy function is given by (we will again for simlicity set e to be 1)

$$\begin{aligned} &V_C(x_1, \ldots, x_N, R_1, \ldots, R_N) \\ &= -\sum_{i=1}^{N} \sum_{j=1}^{M} \frac{Z_j}{|x_i - R_j|} + \sum_{1 \le i < j \le N} \frac{1}{|x_i - x_j|} + \sum_{1 \le i < j \le M} \frac{Z_i Z_j}{|R_i - R_j|} \end{aligned}$$

and we can define the potential energy as

$$(V_C)_\psi = \int_{\mathbb{R}^{3N}} V_C(x_1, \ldots, x_N) |\psi(x_1, \ldots, x_N)|^2 \, \mathrm{d}x_1 \ldots \mathrm{d}x_N = \langle \psi, V_C \psi \rangle_2 \, .$$

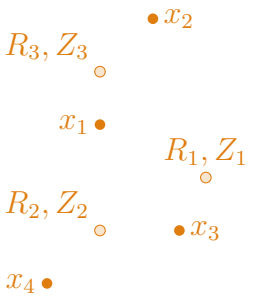

Figure 7: The classical picture.

In contrast to the one-body case, we will not consider general potential V in our investigation of stability but restrict our investigations to V_C. The corresponding classical picture can be found in Figure 7.

Assuming again that $\hbar^2/(2m_i) = 1$ the energy functional is

$$\mathcal{E}_N(\psi) = \sum_{i=1}^{N} T_\psi^i + (V_C)_\psi = \langle \psi, H_{N,M}\psi \rangle_2$$

where the corresponding Hamiltonian (or more specifically the *Schrödinger operator*) is given by

$$H_{N,M} = -\sum_{i=1}^{N} \Delta_i + V_C(x_1, \dots, x_N, R_1, \dots, R_M)\,.$$

We have ignored several constants which our calculations should include in order to be physically relevant. It is an easy exercise to keep track of them but for the sake of brevity and clarity of the proofs, we will only mention how the results change at the very end.

Similar to the one-particle case, we define *stability of the first kind* as the statement that the ground state energy $E_N(Z_1, \dots, R_1, \dots)$ is finite, where

$$E_N(Z_1, \dots, R_1, \dots) = \inf\left\{\mathcal{E}(\psi) : \psi \, \|\psi\|_2 = 1, \psi \in H_1(\mathbb{R}^{3N})\right\}\,.$$

It will be important to consider the bosonic and fermionic separately, i.e.

$$E_N^b(Z_1, \dots, R_1, \dots) = \inf\left\{\mathcal{E}(\psi) : \psi \text{ is bosonic, } \|\psi\|_2 = 1, \psi \in H_1(\mathbb{R}^{3N})\right\}\,,$$
$$E_N^f(Z_1, \dots, R_1, \dots) = \inf\left\{\mathcal{E}(\psi) : \psi \text{ is fermionic, } \|\psi\|_2 = 1, \psi \in H_1(\mathbb{R}^{3N})\right\}\,.$$

Note that for fixed $R_1, \dots, R_M$, the nucleus-nucleus interaction only adds a constant to the ground state energy.

Theorem 28 (Stability of the first kind of quantum mechanical molecules)**.** *The Hamiltonian $H_{N,M}$ of a molecule is stable of the first kind,*

$$E(Z_1, \dots, R_1, \dots) > -\infty\,.$$

In particular $E^b(Z_1, \dots, R_1, \dots), E^f(Z_1, \dots, R_1, \dots) > -\infty$.

Proof. We can omit all the positive interactions, i.e. the repulsive electron-electron and nucleus-nucleus interactions. We are left with

$$\sum_{i=1}^{N} T_\psi^i - \sum_{i=1}^{N}\sum_{j=1}^{M} \frac{Z_j}{|x_i - R_j|}\,.$$

We consider one particle at a time, i.e. let $x_2, \dots, x_N$ be fixed. Then the fucntion $x \mapsto \psi(x, x_2, \dots, x_N)$ is a one-body wave function. By Theorem 6 we know that the energy

$$\mathcal{E}^1(\psi) = \int_{\mathbb{R}^3} |(\nabla\psi)(x, x_2, \dots, x_N)|^2 \,\mathrm{d}x - \int_{\mathbb{R}^3} \sum_{j=1}^{M} \frac{Z_j}{|x - R_j|} |\psi(x, x_2, \dots, x_N)|^2 \,\mathrm{d}x \,.$$

is bounded from below, that is $\mathcal{E}^1(\psi) \geq E_0^1 \int_{\mathbb{R}^3} |\psi(x, x_2, \dots, x_N)|^2 \,\mathrm{d}x$. Integrating over the remaining variables and repeating this argument for all particles we can conclude that the many-body system is stable. Note that we have not imposed any symmetry assumptions on the wave functions. □

The *fermionic absolute ground state energy* is defined as

$$E^f_{N,M}(Z_1, \dots, Z_M) = \inf \left\{ E^f_N(Z_1, \dots, R_1, \dots) : R_1, \dots, R_M \in \mathbb{R}^3 \right\}$$

and does not depend on $R_1, \dots, R_M$. We call the system *stable of the second kind* if

$$E^f_{N,M}(Z_1, \dots, Z_M) \geq C(Z)(N + M)$$

with a number $C(Z)$ that only depends on $Z \coloneqq \max(Z_1, \dots, Z_N)$. The importance of the lower bound is its linearity in the number of particles. It implies that the energy and volume occupied by $2n$ atoms are twice that of n atoms. Our intuition tells us that this is the case. Were the energy to grow by a larger power of the number of particles, one could extract a huge amount of energy simply by pouring one half-filled glass of water into another.

We will see that stability of the second kind only holds for fermions. The main result of the first part of the "Advanced Mathematical Physics" course will be the following.

Theorem 29 (Stability of the second kind of many-body fermionic quantum systems[47]). *Let $Z \coloneqq \max(Z_1, \dots, Z_M)$. Then*

$$E^f_{N,M}(Z_1, \dots, Z_M) \geq C(Z)(N + M)$$

with a number $C(Z)$ that only depends on Z.

[47] A result of this form was first proved by Dyson and Lenard [4]. We will follow the arguments of a simpler proof that was given in [14]. Since then several other proofs have been established, an overview can be found in [12, Section 8.6].

To prove this theorem, we will need good lower bounds on the kinetic energy (an uncertainty principle) and on the potential energy. The former will be a consequence of the Lieb–Thirring inequality. For the latter we will have to develop some more mathematical tools.

As a first observation, we prove that is suffices to consider the case $Z_1 = \dots = Z_M = Z$, which will help us to simplify the notation.

Proposition 30. *If $Z_j \leq Z$ for $j = 1, \dots, M$ then*

$$E_N(Z_1, \dots, Z_M, R_1, \dots, R_M) \geq \min_{j=1,\dots,M} \min_{\substack{i_1,\dots,i_j \in \{1,\dots,M\} \\ i_\ell \neq i_k}} E_N(Z, \dots, Z, R_{i_1}, \dots, R_{i_j}) \,.$$

The proposition says that for fixed $R_1, \dots, R_M$ a lower bound is obtained by replacing each Z_j by either 0 or Z and taking the minimum over all such choices.

[48] Taken from [12, Proposition 3.1].

Proof [48]. For any fixed $j \in \{1, \dots, M\}$ and fixed wave function ψ the function

$$Z_j \mapsto \mathcal{E}_N(\psi)$$

is an affine function and in particular concave. As a consequence

$$Z_j \mapsto \inf_\psi \mathcal{E}_N(\psi)$$

is also concave. Thus, leaving the other $Z_k, k \neq j$ fixed, the minimum of the energies $E_N(Z_1, \dots, Z_M, R_1, \dots, R_M)$ over $Z_j \in [0, Z]$ is attained at either $Z_j = 0$ or $Z_j = Z$. Applying this argument to all the nuclear charges separately proves the proposition. □

In the remainder, we can thus assume without loss of generality that $Z_1 = \cdots = Z_M = Z$.

3.4. Non-interacting bosons and fermions

To get a better understanding of the important differences between bosons and fermions, we first consider non-interacting particles. The potential is then of the form

$$V(x_1, \dots, x_N) = \sum_{i=1}^N v(x_i)$$

where v is a one-body potential. The energy functional is

$$\mathcal{E}(\psi) = \sum_{i=1}^N \int_{\mathbb{R}^{3N}} \left(|(\nabla_{x_i} \psi)(x_1, \dots, x_N)|^2 + v(x_i) |\psi(x_1, \dots, x_N)|^2 \right) \mathrm{d}x_1 \dots \mathrm{d}x_N$$

and we are interested in the ground state energies

$$E_N^b = \inf \left\{ \mathcal{E}(\psi) : \|\psi\|_2 = 1, \psi \in H^1(\mathbb{R}^{3N}), \psi \text{ bosonic} \right\},$$
$$E_N^f = \inf \left\{ \mathcal{E}(\psi) : \|\psi\|_2 = 1, \psi \in H^1(\mathbb{R}^{3N}), \psi \text{ fermionic} \right\}.$$

The results and proofs of this section are based on the material in [6, pp. Chapter 5 and Chapter 12] as well as [15, pp. 34–38].

Let v satisfy the assumptions of Subsection 2.4 and let $e_0 \leq e_1 \leq \cdots < 0$ denote the negative eigenvalues of the one-body Hamiltonian $-\Delta + v$.

Theorem 31. *The ground state energy of N non-interacting bosons is*

$$E_N^b = Ne_0$$

Proof [49]. By Theorem 12 there exists a unique eigenfunction φ such that $(-\Delta + v)\varphi = e_0\varphi$ in the distributional sense. We can construct the bosonic N-body wave function

$$\psi(x_1, \dots, x_N) = \prod_{i=1}^{N} \varphi(x_i)$$

which clearly satisfies

$$\mathcal{E}(\psi) = NE_0\,.$$

[49] Taken from [5, Theorem 5.1].

Conversely[50], we start with a many-body wave function $\psi \in L^2(\mathbb{R}^{3N})$ and aim to prove that $\mathcal{E}(\psi) \geq Ne_0$. To this end we consider the one-body density

$$\rho_\psi(x) = N \int_{\mathbb{R}^{3(N-1)}} |\psi(x, x_2, \dots, x_N)|^2 \,\mathrm{d}x_2 \dots \,\mathrm{d}x_N\,.$$

We aim to compare $\mathcal{E}(\psi)$ to the one-body energy of $\sqrt{\rho_\psi/N} \in L^2(\mathbb{R}^3)$. For the potential energy we get

$$\begin{aligned} V_\psi = \sum_{i=1}^{N} \int_{\mathbb{R}^{3N}} v(x_i)|\psi(x_1, \dots, x_N)|^2 \,\mathrm{d}x_1 \dots \,\mathrm{d}x_N &= \int_{\mathbb{R}^3} v(x)\rho_\psi(x)\,\mathrm{d}x \\ &= N \int_{\mathbb{R}^3} v(x) \left|\sqrt{\rho_\psi(x)/N}\right|^2 \mathrm{d}x\,. \end{aligned}$$

To compare the kinetic energies we compute that (*c.c.* denotes the complex conjugate of the preceding term)

$$\begin{aligned} &\left|(\nabla\sqrt{\rho_\psi})(x)\right|^2 = \frac{|(\nabla\rho_\psi)(x)|^2}{4\rho_\psi(x)} \\ &= \frac{N^2}{4\rho_\psi(x)} \left| \int_{\mathbb{R}^{3(N-1)}} \left(\overline{\psi(x, x_2, \dots, x_N)} \nabla_x \psi(x, x_2, \dots, x_N) + c.c.\right) \mathrm{d}x_2 \dots \,\mathrm{d}x_N \right|^2 . \end{aligned}$$

To make this computation completely rigorous we should in fact consider $\sqrt{\rho_\psi + \varepsilon}$ to make sure that we do not divide by zero and later let $\varepsilon \to 0$.[51] Using the Cauchy–Schwarz inequality we obtain

[50] The idea is to turn the many-body wave function into a one body wave function. A sensible choice is $\sqrt{\rho_\psi/N}$ and we then prove $\mathcal{E}(\psi) \geq N\mathcal{E}(\sqrt{\rho_\psi/N})$.

[51] Exercise.

$$\begin{aligned} &\left|(\nabla\sqrt{\rho_\psi})(x)\right|^2 \\ &\leq \frac{N^2}{\rho_\psi(x)} \left| \int_{\mathbb{R}^{3(N-1)}} |\psi(x, x_2, \dots, x_N)| |\nabla_x \psi(x, x_2, \dots, x_N)| \,\mathrm{d}x_2 \dots \,\mathrm{d}x_N \right|^2 \\ &\leq \frac{N^2}{\rho_\psi(x)} \int_{\mathbb{R}^{3(N-1)}} |\psi(x, x_2, \dots)|^2 \,\mathrm{d}x_2 \dots \,\mathrm{d}x_N \int_{\mathbb{R}^{3(N-1)}} |\nabla_x \psi(x, x_2, \dots)|^2 \,\mathrm{d}x_2 \dots \,\mathrm{d}x_N \\ &= N \int_{\mathbb{R}^{3(N-1)}} |\nabla_x \psi(x, x_2, \dots)|^2 \,\mathrm{d}x_2 \dots \,\mathrm{d}x_N\,. \end{aligned}$$

Integrating this inequality and using the symmetry of ψ yields

$$T_\psi \geq \int_{\mathbb{R}^3} \left|(\nabla\sqrt{\rho_\psi})(x)\right|^2 \mathrm{d}x = N \int_{\mathbb{R}^3} \left|(\nabla\sqrt{\rho_\psi/N})(x)\right|^2 \mathrm{d}x$$

and together with the potential energy computed above we arrive at

$$\begin{aligned}\mathcal{E}(\psi) &\geq \int_{\mathbb{R}^3} \left(\left|(\nabla\sqrt{\rho_\psi})(x)\right|^2 + v(x)\rho_\psi(x)\right) \mathrm{d}x \\ &= N \int_{\mathbb{R}^3} \left(\left|(\nabla\sqrt{\rho_\psi/N})(x)\right|^2 + v(x)\left|\sqrt{\rho_\psi(x)/N}\right|^2\right) \mathrm{d}x\,.\end{aligned}$$

The function $\varphi(x) = \sqrt{\rho_\psi(x)/N}$ is a one-body wave function and consequently

$$\int_{\mathbb{R}^3} (|(\nabla\varphi)(x)|^2 + v(x)|\varphi(x)|^2)\,\mathrm{d}x \geq e_0$$

which implies the desired

$$\mathcal{E}(\psi) \geq N e_0\,.$$

□

[52] Exercise.

This result is perhaps not surprising. One can show[52] that the bosonic ground state is energy is also achieved without any symmetry assumptions on the many-body wave function ψ. In that sense, the non-interacting bosons really 'do not see' each other.

We will now consider the fermionic case. Even though the fermionic particles do not interact via a potential, the antisymmetry condition forces them to be in different states. For simplicity we will assume that the one-body Hamiltonian $-\Delta + v$ has at least N negative eigenvalues $e_0 \leq e_1 \leq \cdots \leq e_{N-1} < 0$.

Theorem 32. *If the one-body Hamiltonian has at least N negative eigenvalues $e_0 \leq \cdots \leq e_{N-1} < 0$ then the ground state energy of N non-interacting fermions is*

$$E_N^f = e_0 + \cdots + e_{N-1} = \sum_{j=0}^{N-1} e_j$$

In order to prove this theorem, it is not sufficient to consider the one particle density ρ_ψ. Instead we will consider the *one-particle density matrix* γ_ψ defined as

$$\gamma_\psi(x,y) = N \int_{\mathbb{R}^{3(N-1)}} \psi(x,x_2,\ldots,x_N)\overline{\psi(y,x_2,\ldots,x_N)}\,\mathrm{d}x_2 \ldots \mathrm{d}x_N\,.$$

Note that $\rho_\psi(x) = \gamma_\psi(x,x)$. This γ_ψ defines a self-adjoint operator that maps $L^2(\mathbb{R}^3)$ into itself via

$$(\gamma_\psi\varphi)(x) \coloneqq \int_{\mathbb{R}^3} \gamma_\psi(x,y)\varphi(y)\,\mathrm{d}y\,.$$

Lemma 33. *As an operator* $0 \leq \gamma_\psi \leq 1$*, i.e.*

$$0 \leq \langle \varphi, \gamma_\psi \varphi \rangle_2 \leq \langle \varphi, \varphi \rangle_2 \,.$$

and $\sigma(\gamma_\psi) = \{\lambda_j : j \in \mathbb{N}\}$ *with* $0 \leq \lambda_j \leq 1$ *and*

$$\sum_{j=1}^{N} \lambda_j = N \,.$$

In particular, γ_ψ *can be written in terms of its eigenfunctions* θ_j *as*

$$\gamma(x,y) = \sum_{j \geq 1} \lambda_j \theta_j(x) \overline{\theta_j(y)} \,.$$

To get a better understanding of this lemma, I suggest you compute the one-body density matrix of a determinantal wave function and of a bosonic product function.

Proof [53]. It is straightforward to show that $\gamma \geq 0$. To prove $\gamma \leq 1$ we need to use the antisymmetry of ψ. We will show that for any normalised φ we have $\langle \varphi, \gamma\varphi \rangle_2 \leq 1$. We can complement φ to an orthonormal basis of $L^2(\mathbb{R}^3)$. Let those functions be $g_0, g_1 \ldots$ with $g_0 = \varphi$. We can expand $\psi \in L^2(\mathbb{R}^{3N})$ in this basis as

$$\psi(x_1, \ldots, x_N) = \sum_{j_1, \ldots, j_N \geq 0} C(j_1, \ldots, j_N) g_{j_1}(x_1) \ldots g_{j_N}(x_N) \,.$$

Since $\|\psi\|_2 = 1$ we must have

$$\sum_{j_1, \ldots, j_N \geq 0} |C(j_1, \ldots, j_N)|^2 = 1 \,.$$

Furthermore, since ψ is antisymmetric, we have that $(k \neq \ell)$

$$C(j_1, \ldots, j_k, \ldots, j_\ell, \ldots, j_N) = -C(j_1, \ldots, j_\ell, \ldots, j_k, \ldots, j_N)$$

which implies that the coefficient C vanishes if any two indices are the same, i.e. $C(j_1, \ldots, j_N) = 0$ unless $j_1, \ldots, j_N$ are all different.[54] Now let K be the operator on $L^2(\mathbb{R}^{3N})$ which acts as

$$\begin{aligned}(Kf)(x_1, \ldots, x_N) &= \sum_{j=1}^{N} g_0(x_j) \int_{\mathbb{R}^3} \overline{g_0(y_j)} f(x_1, \ldots, y_j, \ldots, x_N) \, \mathrm{d}y_j \\ &= \sum_{j=1}^{N} \varphi(x_j) \int_{\mathbb{R}^3} \overline{\varphi(y_j)} f(x_1, \ldots, y_j, \ldots, x_N) \, \mathrm{d}y_j\end{aligned}$$

[53] Taken from [15, Lemma 15].

[54] Here we us that ψ is fermionic.

the operator is constructed in such a way that the products $g_{j_1}(x_1)\dots g_{j_N}(x_N)$ are precisely all the eigenfunctions of K. A simple calculation yields

$$\begin{aligned}
&\langle\psi, K\psi\rangle_2 \\
&= \sum_{j=1}^{N} \int_{\mathbb{R}^{3N}} \int_{\mathbb{R}^3} \overline{\psi(x_1,\dots,x_j,\dots)}\varphi(x_j)\overline{\varphi(y_j)}\psi(x_1,\dots,y_j,\dots)\,\mathrm{d}y_j\,\mathrm{d}x_1\dots\,\mathrm{d}x_N \\
&= N\int_{\mathbb{R}^3}\varphi(x)\int_{\mathbb{R}^3}\overline{\varphi(y)}\left(\int_{\mathbb{R}^{3(N-1)}}\overline{\psi(x,x_2,\dots)}\psi(y,x_2\dots)\,\mathrm{d}x_2\dots\,\mathrm{d}x_N\right)\mathrm{d}y\,\mathrm{d}x \\
&= \langle\varphi,\gamma\varphi\rangle_2\ .
\end{aligned}$$

On the other hand for $j_1,\dots,j_N$ all different

$$\langle g_{j_1}\dots g_{j_N}, K g_{j_1}\dots g_{j_N}\rangle_2 = \sum_{k=1}^{N} |\langle g_0, g_{j_k}\rangle_2|^2 \le 1$$

since at most one term can be non-zero in the sum. As a consequence

$$\langle\psi, K\psi\rangle_2 \le \sum_{j_1,\dots,j_N\ge 0} |C(j_1,\dots,j_N)|^2 = 1$$

which together with the above yields $\langle\varphi,\gamma\varphi\rangle_2 \le 1$.

The rest follows from the fact that γ is trace-class with

$$\mathrm{tr}\gamma = \int_{\mathbb{R}^3}\gamma(x,x)\,\mathrm{d}x = N\,.$$

□

[55] Taken from [5, Theorem 12.1] and [15, Theorem 14].

[56] Exercise.

Proof of Theorem 32 [55]. If $\varphi_0,\dots,\varphi_{N-1}$ are the eigenfunctions of the one-body Hamiltonian, we can compute[56] that the determinantal wave function $\psi(x) = \det(\varphi_i(x_j))_{i,j}$ satisfies

$$\mathcal{E}(\psi) = \sum_{i=0}^{N-1} e_i\,.$$

Conversely, we aim to express the energy $\mathcal{E}(\psi)$ in terms of γ_ψ. For the potential energy we note that

$$V_\psi = \sum_{i=1}^{N}\int_{\mathbb{R}^{3N}} v(x_i)|\psi(x_1,\dots,x_N)|^2\,\mathrm{d}x_1\dots\,\mathrm{d}x_N = \int_{\mathbb{R}^3} v(x)\gamma_\psi(x,x)\,\mathrm{d}x\,.$$

and for the kinetic energy we compute that

$$T_\psi = N\int_{\mathbb{R}^{3N}} |(\nabla_{x_1}\psi)(x_1,\dots,x_N)|^2\,\mathrm{d}x_1\dots\,\mathrm{d}x_n = \int_{\mathbb{R}^3}(\nabla_x\nabla_y\gamma)(x,x)\,\mathrm{d}x$$

Using that

$$\gamma_\psi(x,y) = \sum_{j\geq 1} \lambda_j \overline{\theta_j(x)}\theta_j(y)$$

we can conclude that

$$\mathcal{E}(\psi) = \sum_{j\geq 1} \lambda_j \left(\int_{\mathbb{R}^3} |(\nabla\theta_j)(x)|^2 \,\mathrm{d}x + \int_{\mathbb{R}^3} v(x)|\theta_j(x)|^2 \,\mathrm{d}x \right).$$

Since the functions θ_j are orthogonal onto each other, it is intuitively clear that the above term is larger than $\sum_{j\geq 1} \lambda_j e_{j-1}$. Since $0 \leq \lambda_j \leq N$ and $\sum_{j\geq 1} \lambda_j = N$ we can argue that a lower bound is achieved for $\lambda_1 = \cdots = \lambda_N = 1$ and $\lambda_j = 0$ for $j > N$. This gives the desired

$$\mathcal{E}(\psi) \geq \sum_{i=0}^{N-1} e_i \,.$$

To prove this rigorously[57], we may write

$$\theta_j = \sum_{\ell\geq 0} c_{j\ell}\varphi_\ell + q_j$$

where φ_ℓ are the eigenfunctions of the one-body Hamiltonian and q_j is in the orthogonal complement of their span. The identity above immediately yields that $q \in H^1(\mathbb{R}^3)$. By Pythagoras' theorem

$$\|\theta_j\|_2^2 = \|q_j\|_2^2 + \sum_{\ell\geq 0} |c_{j\ell}|^2 = 1$$

and consequently

$$\sum_{\ell\geq 0} |c_{j\ell}|^2 \leq 1 \,.$$

By the Min-Max principle of Theorem 18 we know that for q_j necessarily

$$\mathcal{E}(q_j) = \int_{\mathbb{R}^3} |(\nabla q_j)(x)|^2 \,\mathrm{d}x + \int_{\mathbb{R}^3} v(x)|q_j(x)|^2 \,\mathrm{d}x \geq 0 \,.$$

Similarly as in the proof of Theorem 16 we can conclude (by approximation with smooth functions) that

$$\int_{\mathbb{R}^3} \left(\overline{(\nabla\varphi_\ell)(x)} \cdot (\nabla\varphi_k)(x) + v(x)\overline{\varphi_\ell(x)}\varphi_k(x) \right) \mathrm{d}x = e_k\delta_{k=\ell}$$

as well as

$$\int_{\mathbb{R}^3} \left(\overline{(\nabla\varphi_\ell)(x)} \cdot (\nabla q_j)(x) + v(x)\overline{\varphi_\ell(x)}q_j(x) \right) \mathrm{d}x = 0 \,.$$

[57] The main idea is to expand the θ_j into the eigenfuntcions φ_ℓ and an orthogonal remainder term. The variational problem can then be reduced to a variational problem for the coefficients in this expansion, which can be solved explicitly.

As a consequence

$$\mathcal{E}(\theta_j) = \int_{\mathbb{R}^3} |(\nabla\theta_j)(x)|^2 \,\mathrm{d}x + \int_{\mathbb{R}^3} v(x)|\theta_j(x)|^2 \,\mathrm{d}x \geq \sum_{\ell\geq 0} |c_{j\ell}|^2 e_\ell$$

and thus we can bound

$$\mathcal{E}(\psi) \geq \sum_{j\geq 1} \lambda_j \sum_{\ell\geq 0} |c_{j\ell}|^2 e_\ell = \sum_{\ell\geq 0} \mu_\ell e_\ell$$

with the new coefficient

$$\mu_\ell = \sum_{j\geq 1} \lambda_j |c_{j\ell}|^2 \,.$$

Here we use that we deal with fermions.

Since $0 \leq \lambda_j \leq 1$ we observe that

$$\mu_\ell \leq \sum_{j\geq 1} |c_{j\ell}|^2 = \sum_{j\geq 1} |\left\langle f_\ell, \theta_j \right\rangle_2|^2 \leq \|f_\ell\|_2^2 \leq 1$$

and since $\sum_{j\geq 1} \lambda_j = N$ furthermore

$$\sum_{\ell\geq 0} \mu_\ell = \sum_{j\geq 1} \lambda_j \sum_{\ell\geq 0} |c_{j\ell}|^2 \leq \sum_{j\geq 1} \lambda_j = N \,.$$

We obtain that

$$\mathcal{E}(\psi) \geq \inf\left\{ \sum_{\ell\geq 0} \mu_\ell e_\ell \,:\, 0 \leq \mu_\ell \leq 1, \sum_{\ell\geq 0} \mu_\ell \leq N \right\}.$$

Since $e_0 \leq e_1 \leq \cdots \leq 0$ we get the smallest value if we select $\mu_0 = \mu_2 = \cdots = \mu_{N-1} = 1$, and zero for the remaining μ_ℓ. This proves the desired

$$\mathcal{E}(\psi) \geq \sum_{j=0}^{N-1} e_j \,.$$

□

Remark 34. If there are fewer than N negative eigenvalues, the ground state energy of the non-interacting fermions is given by $E_N = \sum_{e_j<0} e_j$ and there exists no minimiser $\psi \in H^1(\mathbb{R}^{3N})$ such that $\mathcal{E}(\psi) = E_N$.[58]

[58] See [5, Theorem 12.1].

In the literature the property proved in the theorem is often referred to as fermions 'filling up the energy levels'.

3.5. Kinetic energy inequalities

We will now show that the Lieb–Thirring inequality is equivalent to an uncertainty principle. Recall that for bosonic or fermionic wave functions $\psi \in L^2(\mathbb{R}^{3N})$ the one-body density is given by

$$\rho_\psi(x) = N \int_{\mathbb{R}^{3(N-1)}} |\psi(x, x_2, \dots, x_N)|^2 \, \mathrm{d}x_2 \dots \mathrm{d}x_N \,.$$

Theorem 35 (Kinetic energy inequality for fermions)**.** *There is a constant K independent of N such that*

$$T_\psi \geq K \int_{\mathbb{R}^3} \rho_\psi(x)^{5/3} \, \mathrm{d}x$$

for all fermionic $\psi \in H^1(\mathbb{R}^{3N})$.

Remark 36. Consider the case $N = 1$. By Hölder's inequality

$$\left\|\psi^2\right\|_{5/3}^{5/3} \leq \left\|\psi^2\right\|_3 \left\|\psi^2\right\|_1$$

and thus by the Sobolev inequality in Theorem 8 and the fact that $\|\psi\|_2 = 1$

$$T_\psi \geq S_3 \left\|\psi^2\right\|_3 \geq S_3 \left\|\psi^2\right\|_{5/3}^{5/3} \left\|\psi^2\right\|_1^{-1} = S_3 \int_{\mathbb{R}^3} \rho_\psi(x)^{5/3} \, \mathrm{d}x \,.$$

Let now $N \geq 1$. If $\psi \in H^1(\mathbb{R}^{3N})$ is a bosonic (or fermionic) wave function, then $T_\psi \geq N T_{\sqrt{\rho_\psi/N}}$ as established in the proof of Theorem 31 and thus

$$T_\psi \geq S_3 N^{-2/3} \int_{\mathbb{R}^3} \rho_\psi(x)^{5/3} \, \mathrm{d}x \,.$$

This bound is weaker than the bound in Theorem 35 by a factor of $N^{-2/3}$. For bosons this constant cannot be improved. The kinetic energy inequality can be seen as a generalisation of (a suitably weakened) Theorem 8.

Proof of Theorem 35[59]. Recall that for any fermionic N-body wave function and non-interacting potential $V(x_1, \dots, x_N) = \sum_{i=1}^N v(x_i)$ it holds that

$$\mathcal{E}(\psi) \geq \sum_{j=0}^{N-1} e_j = -\sum_{j=0}^{N-1} |e_j|$$

where $e_0 \leq e_1 \leq \dots \leq 0$ are the eigenvalues of the one-body Schrödinger operator $-\Delta + v(x)$. By the Lieb–Thirring inequality in Theorem 20 for $\gamma = 1$ we also know that there is a constant $L_{1,3}$ such that

$$\sum_{j \geq 0} |e_j| \leq L_{1,3} \int_{\mathbb{R}^3} v_-(x)^{5/2} \, \mathrm{d}x \,.$$

[59] Taken from [12, Corollary 4.1]. The main idea is to consider non-interacting fermions with one-body potential v. From the previous subsection together with the Lieb–Thirring inequality we know good lower bounds on the energy and thus also on the kinetic energy. It remains to choose v such that the remaining terms have the desired form.

We can thus bound

$$\begin{aligned} T_\psi &= \mathcal{E}(\psi) - V_\psi \\ &= \mathcal{E}(\psi) - \int_{\mathbb{R}^3} v(x)\rho_\psi(x)\,\mathrm{d}x \geq -\int_{\mathbb{R}^3} v_-(x)^{5/2}\,\mathrm{d}x - \int_{\mathbb{R}^3} v(x)\rho_\psi(x)\,\mathrm{d}x\,. \end{aligned}$$

This holds for any potential, in particular we can choose[60]

$$v(x) = -c\rho_\psi(x)^{2/3}$$

with $c > 0$ still to be determined. Then

$$T_\psi \geq (c - L_{1,3}c^{5/2}) \int_{\mathbb{R}^3} \rho_\psi(x)^{5/3}\,\mathrm{d}x$$

and the constant on the right is positive, if c is sufficiently small. It remains to optimise over c (note that the constant is positive if c is small).

□

[60] In fact we could take the supremum over all suitable v of the right-hand side in the inequality. The right-hand side then takes the form of a Legendre transformation. The best choice for v is exactly the one given here.

Remark 37. The proof of the kinetic energy inequality relied on the Lieb–Thirring inequality. In fact, the converse is also true. As showed in [12, pp. 74–75] the Lieb–Thirring inequality can be proved using Theorem 35.

In our proof of stability of matter of the second kind we will use the Lieb–Thirring inequality in the form of Theorem 20. However, proofs using the kinetic energy inequality of Theorem 35 exist too.

3.6. Electrostatic inequalities

This subsection is taken from [12, Chapter 5] with some simplifications as in [18].

In the previous subsections, we considered bounds on the kinetic energy. In addition, we will now establish a lower bound in the Coulomb interaction. The only negative contributions are the electron-nucleus interactions. Naïve estimates will yield lower bounds of order NM. The difficulty is not so much that an electron can be close to a nucleus. We have already seen in the one-body case how to deal with this. The difficulty is more that one electron can be close to several nuclei. We will replace the potential by a appropriate one-body potentials. The results in this subsection do not make use of quantum mechanics.

Theorem 38 (Baxter's Electrostatic Inequality[61])**.** *For any $x_i \in \mathbb{R}^3$ and $R_j \in \mathbb{R}^3$ it holds that*

$$V_C(x_1 \ldots, x_N, R_1, \ldots, R_M) \geq -(2Z+1)\sum_{i=1}^{N} \frac{1}{\mathfrak{D}(x_i)}$$

where $\mathfrak{D}(x) = \min_{j=1,\ldots,M} |x - R_j|$.

[61] This is the statement that Baxter [1] proved originally. In [12, Theorem 5.4] a stronger result is proved, featuring an additional positive term on the right-hand side.

In Figure 8 the function $\mathfrak{D}$ is visualised. The important feature of Baxter's electrostatic inequality is that the two-body Coulomb potential can be bounded by a one-body potential involving only the interaction with the closest nucleus. Effectively, each electron sees only its nearest nucleus. To prove Baxter's electrostatic inequality, we need Newton's theorem.

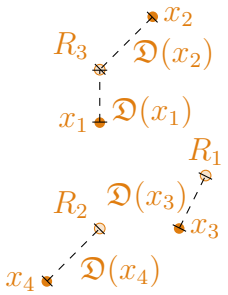

Figure 8: The nearest nuclei.

Definition 39. Let μ be a non-negative Borel measure on $\mathbb{R}^3$. The *potential function* Φ associated with μ is defined as

$$\Phi(x) = \int_{\mathbb{R}^3} \frac{1}{|x-y|}\mu(\mathrm{d}y) \in [0, +\infty]\,.$$

The *Coulomb energy* of μ is defined as

$$D(\mu,\mu) = \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{1}{|x-y|}\mu(\mathrm{d}x)\mu(\mathrm{d}y) \in [0, +\infty]\,.$$

We think of μ as some *charge distribution*. The total charge is given by $Q = \mu(\mathbb{R}^3)$. In many cases μ is of the form $\mu(\mathrm{d}x) = \rho(x)\,\mathrm{d}x$, for an integrable function $\rho \in L^1(\mathbb{R}^3)$. With a slight abuse of notation, we write $D(\rho,\rho)$ in this case. In order to compute potential functions, the following result is extremely helpful.

Theorem 40 (Newton's theorem[62])**.** *Let μ be a non-negative Borel measure on $\mathbb{R}^3$ that is rotationally symmetric with respect to the origin, i.e. $\mu(\mathcal{R}A) = \mu(A)$ for all rotations $\mathcal{R}$ around the origin and for all Borel sets A. Then*

$$\Phi(x) = \int_{\mathbb{R}^3} \frac{1}{|x-y|}\mu(\mathrm{d}y) = \frac{1}{|x|}\int_{|y|\le|x|}\mu(\mathrm{d}y) + \int_{|y|>|x|}\frac{1}{|y|}\mu(\mathrm{d}y)\,.$$

Proof [63]. Since Φ is rotationally symmetric with respect to the origin, the same holds for Φ, i.e. $\Phi(x) = \Phi(|x|)$. Thus we can write $\Phi(x)$ as its spherical average

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

where we used Fubini's theorem (all terms involved are non-negative). To compute the inner integral we can again use rotational invariance to assume that $y = (0,0,1)$. A simple calculation yields

$$\begin{aligned}\frac{1}{4\pi}\int_{\mathbb{S}^2}\frac{1}{||x|\omega - y|}\mu(\mathrm{d}y)\,\mathrm{d}\omega &= \frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi}\frac{1}{\sqrt{|x|^2+|y|^2-2|x||y|\cos\theta}}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi \\ &= \frac{1}{2}\int_{-1}^{1}\frac{1}{\sqrt{|x|^2+|y|^2-2|x||y|s}}\,\mathrm{d}s \\ &= \min\left(\frac{1}{|x|},\frac{1}{|y|}\right)\end{aligned}$$

which yields the desired result. □

[62] A result of this form was proved in Newton's famous 'Principia' in Theorem XXXI. In the first English translation [16], it is phrased as: "*... I say that a corpuscle placed without the spherical superficies is attracted towards the centre of the sphere with a force reciprocally proportional to the square of its distance from that centre*".

[63] Taken from [12, Theorem 5.2].

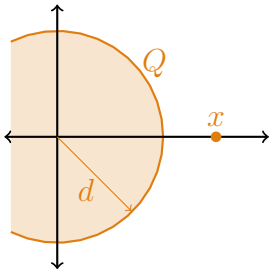

Figure 9: The charge μ.

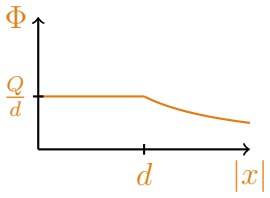

Figure 10: The potential Φ of μ.

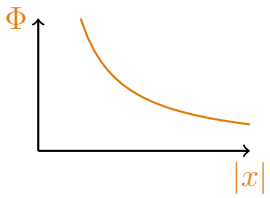

Figure 11: The potential Φ of a point charge.

By translational invariance, the result can immediately be generalised to rotational symmetry around a point $x_0 \in \mathbb{R}^3$.

Example 41. Let $\mu(y) = \frac{Q}{4\pi\lambda^2}\delta(|y| - d)$ be the uniform charge distribution of total charge Q supported on a sphere of radius d. Then for any $|x| > d$

$$\int_{\mathbb{R}^3} \frac{1}{|x-y|}\mu(\mathrm{d}y) = \frac{1}{|x|}\int_{|y|\le|x|} \mu(\mathrm{d}y) = \frac{Q}{|x|}\,.$$

i.e. from outside of the sphere the charge looks just like a point charge Q located at the origin of the sphere. If $|x| < d$ then

$$\Phi(x) = \int_{|y|>|x|} \frac{1}{|y|}\mu(\mathrm{d}y) = \frac{Q}{d}\,.$$

The result is visualised in Figures 9, 10 and 11.

Another important application of Newton's theorem is the following result, which says that point charges have maximal potential.

Corollary 42. *Let μ be a non-negative Borel measure that is rotationally symmetric with respect to x_0 and let $Q = \mu(\mathbb{R}^3)$. Then for all $x \in \mathbb{R}^3$*

$$\Phi(x) = \int_{\mathbb{R}^3} \frac{1}{|x-y|}\mu(\mathrm{d}y) \le \frac{Q}{|x-x_0|}\,.$$

Proof. This is an immediate consequence of Newton's theorem. □

The last two results dealt with the potential function Φ. We also need a fact about the Coulomb energy $D(\mu,\mu)$. Note that in the following lemma μ is not assumed to be non-negative. In order to guarantee that the Coulomb energy is still well defined[64], we may assume that μ is of the form $\mu_1 - \mu_2$ for some non-negative Borel measures with finite Coulomb energies $D(\mu_j,\mu_j) < \infty$. As we will see later, this is precisely the situation we are interested in.

[64] To be more precise, we also need the additional assumption $\int(1+|x|)^{-1}(\mu_1+\mu_2)(\mathrm{d}x) < \infty$, see [12, pp. 89–90].

Lemma 43. *For $\mu = \mu_1 - \mu_2$ as above it holds that $0 \le D(\mu,\mu) < \infty$.*

Proof. We first note that

$$\frac{1}{|x-y|} = \frac{1}{\pi^3}\int_{\mathbb{R}^3} \frac{1}{|x-z|^2}\frac{1}{|y-z|^2}\,\mathrm{d}z\,.$$

The fact that the two sides are proportional to each other follows from the observation that both are functions of $|x-y|$ and both are homogenous of degree -1, i.e. $f(\lambda|x-y|) = \lambda^{-1}f(|x-y|)$. The factor $1/\pi^3$ can then be computed at any conveniently chosen $x, y \in \mathbb{R}^3$. Using this formula, we see that

$$D(\mu,\mu) = \frac{1}{2\pi^3}\int_{\mathbb{R}^3}\left(\int_{\mathbb{R}^3}\frac{1}{|x-z|^2}\mu(\mathrm{d}x)\right)^2 \mathrm{d}z \ge 0$$

Since $D(\mu_j,\mu_j) < \infty$ for $j = 1, 2$, it is straightforward to show[65] that $D(\mu,\mu) < \infty$. □

[65] Exercise.

With these tools in hand, we can now estimate the potential energy of an electron, taking into account all the other electrons and all the nuclei, except for the one that is nearest. To this end we consider the Coulomb potential Φ_C with respect to all but the nearest nucleus, i.e.

$$\Phi_C(x) = \sum_{j=1}^{M} \frac{Z}{|x - R_j|} - \frac{Z}{\mathfrak{D}(x)} \,. \tag{4}$$

The function is continuous. The following result is a weaker version of [12, Theorem 5.3], omitting a positive term on the right-hand side, which suffices for our purposes. We will later choose μ to be the smeared out charge density of all the electrons.

Theorem 44 (Basic electrostatic inequality)**.** *For Φ_C defined in (4) and any non-negative Borel measure μ on $\mathbb{R}^3$ it holds that*

$$D(\mu,\mu) - \int_{\mathbb{R}^3} \Phi_C(x)\mu(\mathrm{d}x) + \sum_{1\leq i<j\leq M} \frac{Z^2}{|R_i - R_j|} \geq 0$$

or equivalently,

$$D(\mu,\mu) - \sum_{j=1}^{M} \int_{\mathbb{R}^3} \frac{Z}{|x - R_j|}\mu(\mathrm{d}x) + \sum_{1\leq i<j\leq M} \frac{Z^2}{|R_i - R_j|} \geq - \int_{\mathbb{R}^3} \frac{Z}{\mathfrak{D}(x)}\mu(\mathrm{d}x) \,.$$

Proof [66]. We aim to write Φ_C, as foreshadowed by the notation, as a potential function

$$\Phi_C(x) = \int_{\mathbb{R}^3} \frac{1}{|x - y|}\nu(\mathrm{d}x)$$

with some positive Borel measure ν. The existence of such a measure is proved in [12, Theorem 5.3] by an explicit construction. The proof relies on the fact that $\Delta\Phi = 0$ everywhere except for on the surfaces (see Figure 12)

$$\left\{x \in \mathbb{R}^3 : \, |x - R_j| = |x - R_k| \text{ for some } j \neq k\right\}$$

and ν is then supported on these sets with

$$-\Delta\Phi_C(x) = 4\pi\nu(\mathrm{d}x) \,.$$

We then have that

$$\int_{\mathbb{R}^3} \Phi_C(x)\mu(\mathrm{d}x) = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{1}{|x - y|}\nu(\mathrm{d}x)\mu(\mathrm{d}x) = 2D(\mu,\nu) \,.$$

[66] Taken from [18].

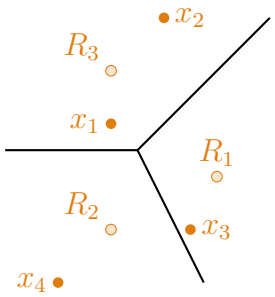

Figure 12: The surfaces.

Since $D(\mu-\nu,\mu-\nu)\geq 0$ by Lemma 43, we obtain

$$\begin{aligned} D(\mu,\mu)-\int_{\mathbb{R}^3}\Phi_C(x)\mu(\mathrm{d}x) &= D(\mu,\mu)-2D(\mu,\nu) \\ &= D(\mu-\nu,\mu-\nu)-D(\nu,\nu)\geq -D(\nu,\nu)\,. \end{aligned} \tag{5}$$

To compute the term on the right-hand side, we note that

$$D(\nu,\nu)=\frac{1}{2}\int_{\mathbb{R}^3}\Phi_C(x)\nu(\mathrm{d}x)=\frac{1}{2}\sum_{j=1}^{M}\int_{\mathbb{R}^3}\frac{Z}{|x-R_j|}\nu(\mathrm{d}x)-\frac{1}{2}\int_{\mathbb{R}^3}\frac{Z}{\mathfrak{D}(x)}\nu(\mathrm{d}x)\,.$$

The second term is negative and can thus be discarded for a lower bound on $-D(\nu,\nu)$. The first term is

$$\begin{aligned} \frac{1}{2}\sum_{j=1}^{M}\int_{\mathbb{R}^3}\frac{Z}{|x-R_j|}\nu(\mathrm{d}x) &= \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\sum_{j=1}^{M}\delta(y-R_j)\frac{Z}{|x-y|}\,\mathrm{d}y\nu(\mathrm{d}x) \\ &= \frac{Z}{2}\int_{\mathbb{R}^3}\sum_{j=1}^{M}\delta(y-R_j)\Phi_C(y)\,\mathrm{d}y \\ &= \frac{Z}{2}\sum_{j=1}^{M}\Phi_C(R_j)=\sum_{1\leq i<j\leq M}\frac{Z^2}{|R_j-R_k|}\,. \end{aligned}$$

Inserting this back into (5) yields the desired result. □

We can now prove Baxter's electrostatic inequality. If we chose μ in the last theorem to be precisely the charge distribution of all the electrons, i.e. a sum of delta potentials at the locations x_i,

$$\mu(\mathrm{d}x)=\sum_{i=1}^{N}\mu_i(\mathrm{d}x)=\sum_{i=1}^{N}\delta(|x-x_i|)$$

the second term in the basic electrostatic inequality would yield the electron-nucleus interactions. Unfortunately, $D(\mu,\mu)$ would the be infinite. We will smear out the charges over appropriately chosen spheres. Newton's theorem will allow us to obtain a lower bound on the energy in this way.

Proof of Theorem 38. For simplicity, denote $d_i=\mathfrak{D}(x_i)$. Let $\mu_i(\mathrm{d}x)$ be the normalised uniform measure supported on a sphere of radius $d_i/2$ and centred at x_i, i.e.

$$\mu_i(\mathrm{d}x)=\frac{1}{d_i^2\pi}\delta(|x-x_i|-d_i/2)$$

as depicted in Figure 13. We further define $\mu=\sum_{i=1}^{N}\mu_i$. We now replace the point charges by the smeared out spherical charges μ_i. The electrostatic

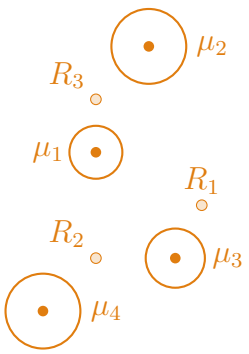

Figure 13: The measures μ_i.

interaction between the electrons is reduced because the interaction energy between two spheres is less than or equal to that between two points, as proved in Corollary 42 with the help of Newton's theorem

$$\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{1}{|x-y|}\mu_i(\mathrm{d}x)\mu_j(\mathrm{d}y) \leq \int_{\mathbb{R}^3}\frac{1}{|x-x_i|}\mu_j(\mathrm{d}x) \leq \frac{1}{|x_j-x_i|}\,.$$

Furthermore, again by Newton's theorem, the interaction between the smeared out electrons and the nuclei is not changed since $d_i/2 < |x_i - R_j|$ for any j, see Example 41

$$\int_{\mathbb{R}^3}\frac{Z}{|x-R_j|}\mu_i(\mathrm{d}x) = \frac{Z}{|x_i-R_j|}\,.$$

As a consequence we obtain the lower bound

$$\begin{aligned}
&\sum_{1\leq i<j\leq N}\frac{1}{|x_i-x_j|} - \sum_{i=1}^{N}\sum_{j=1}^{M}\frac{Z}{|x_i-R_j|}\\
&\geq \sum_{1\leq i<j\leq N}\int_{\mathbb{R}^6}\frac{1}{|x-y|}\mu_i(\mathrm{d}x)\mu_j(\mathrm{d}y) - \sum_{j=1}^{M}\sum_{i=1}^{N}\int_{\mathbb{R}^3}\frac{Z}{|x-R_j|}\mu_i(\mathrm{d}x)\\
&= D(\mu,\mu) - \sum_{j=1}^{M}\int_{\mathbb{R}^3}\frac{Z}{|x-R_j|}\mu(\mathrm{d}x) - \sum_{i=1}^{N}\frac{1}{d_i}\,.
\end{aligned}$$

In the last equality we used that[67] $D(\mu_i,\mu_i) = 1/d_i$.

[67] Exercise.

Applying Theorem 44 yields

$$\begin{aligned}
&V_C(x_1,\dots,x_N,R_1,\dots,R_M)\\
&= \sum_{1\leq i<j\leq N}\frac{1}{|x_i-x_j|} - \sum_{i=1}^{N}\sum_{j=1}^{M}\frac{Z}{|x_i-R_j|} + \sum_{1\leq i<j\leq M}\frac{Z^2}{|R_i-R_j|}\\
&\geq -\sum_{i=1}^{N}\left(\int_{\mathbb{R}^3}\frac{Z}{\mathfrak{D}(x)}\mu_i(\mathrm{d}x) + \frac{1}{d_i}\right).
\end{aligned}$$

To finish the proof we have to show that

$$\int_{\mathbb{R}^3}\frac{1}{\mathfrak{D}(x)}\mu_i(\mathrm{d}x) \leq \frac{2}{d_i}$$

which is the case if we can show that $\mathfrak{D}(x) = \min_{j=1,\dots,M}|x-R_j| \geq d_i/2$ for any x in the support of μ_i (i.e. if $|x-x_i| = d_i/2$). This is a consequence of the fact

$$|x-R_j| \geq |x_i-R_j| - |x_i-x| \geq d_i - \frac{d_i}{2} = \frac{d_i}{2}$$

for any such x (see Figure 14). □

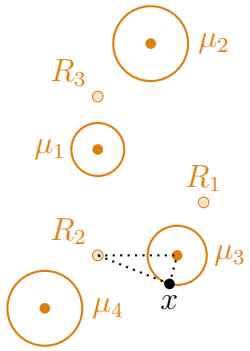

Figure 14: $\mathfrak{D}(x)$ on the support of μ_i.

3.7. Proof of stability of the second kind

To prove Theorem 29, we only need to collect the results from the previous subsections.[68] We already know from Proposition 30 that we can assume that all the nuclei charges are equal to Z. Let $R_1, \dots, R_M$ be fixed. By Baxter's electrostatic inequality in Theorem 38 the energy for a fixed fermionic wavefunction can be bounded from below

$$\begin{aligned}\mathcal{E}(\psi) &= T_\psi + (V_C)_\psi \\ &\geq T_\psi - (2Z+1)\sum_{i=1}^{N}\int_{\mathbb{R}^{3N}} \frac{1}{\mathfrak{D}(x_i)}|\psi(x_1,\dots,x_N)|^2\,\mathrm{d}x_1\dots\,\mathrm{d}x_N\,.\end{aligned}$$

The right-hand side is now just the a sum of non-interacting one-body terms. Since ψ is fermionic, Theorem 32 allows us to conclude that right-hand side is bounded by the sum of the N lowest eigenvalues of the one-body Hamiltonian $-\Delta - (2Z+1)/\mathfrak{D}(x)$. We would like to apply the Lieb–Thirring inequality directly, but unfortunately $1/\mathfrak{D}(x) \notin L^{5/2}(\mathbb{R}^3)$. To circumvent this problem we rewrite the inequality above as

$$\begin{aligned}&\mathcal{E}(\psi) \\ &\geq T_\psi - (2Z+1)\sum_{i=1}^{N}\int_{\mathbb{R}^{3N}}\left(\frac{1}{\mathfrak{D}(x_i)} - b\right)|\psi(x_1,\dots,x_N)|^2\,\mathrm{d}x_1\dots\,\mathrm{d}x_N - b(2Z+1)N\end{aligned}$$

for a still to be defined $b > 0$. Theorem 32 together with the Min-Max principle of Theorem 18 allows us to conclude that the energy on the right-hand side is bounded by the sum of the N lowest eigenvalues $e_0, \dots, e_{N-1}$ of the one-body Hamiltonian $-\Delta - (2Z+1)(b - 1/\mathfrak{D}(x))_-$, i.e.

$$\mathcal{E}(\psi) \geq -b(2Z+1)N - \sum_{j=0}^{N-1} e_j\,.$$

Applying the Lieb–Thirring inequality of Theorem 20 we get

$$\mathcal{E}(\psi) \geq -b(2Z+1)N - L_{1,3}(2Z+1)^{5/2}\int_{\mathbb{R}^3}\left(b - \frac{1}{\mathfrak{D}(x)}\right)_-^{5/2}\mathrm{d}x\,.$$

To compute the integral, we note that

$$\begin{aligned}\left(b - \frac{1}{\mathfrak{D}(x)}\right)_-^{5/2} = \left(b - \frac{1}{\min_{j=1,\dots,M}|x-R_j|}\right)_-^{5/2} &\leq \max_{j=1,\dots,M}\left(b - \frac{1}{|x-R_j|}\right)_-^{5/2} \\ &\leq \sum_{j=1}^{M}\left(b - \frac{1}{|x-R_j|}\right)_-^{5/2}.\end{aligned}$$

Which allows us to conclude that[69]

[68] The computations are taken from [9, pp. 58-59] and [18].

[69] While this bound looks too rough at first glance, we cannot hope for a bound that is better than linear in M. The integrand is singular at M different points $R_1, \dots, R_M$.

$$\int_{\mathbb{R}^3} \left(b - \frac{1}{\mathfrak{D}(x)}\right)_-^{5/2} \mathrm{d}x \leq M \int_{\mathbb{R}^3} \left(b - \frac{1}{|x|}\right)_-^{5/2} \mathrm{d}x = M \frac{5\pi^2}{4\sqrt{b}} .$$

Inserting this back into the energy bound we obtain

$$\mathcal{E}(\psi) \geq -b(2Z+1)N - L_{1,3}(2Z+1)^{5/2} M \frac{5\pi^2}{4\sqrt{b}} .$$

This bound is already of the desired form. It remains to optimise this bound with respect to $b > 0$ which is given by

$$b = \frac{2Z+1}{4} (L_{1,3}\pi^2)^{2/3} M^{2/3} N^{-2/3}$$

and we arrive at the lower bound

$$\mathcal{E}(\psi) \geq -\frac{3}{4} (5\pi^2 L_{1,3})^{2/3} (2Z+1)^2 M^{2/3} N^{1/3} .$$

Since this bound holds for all fermionic wave functions ψ and all choices of $R_1, \ldots, R_M$ we have proved that

$$E^f_{N,M} \geq -\frac{3}{4} (5\pi^2 L_{1,3})^{2/3} (2Z+1)^2 M^{2/3} N^{1/3}$$

and using $N^{1/3} M^{2/3} \leq N + M$ we obtain the desired result

$$E^f_{N,M} \geq C(Z)(N+M) .$$

3.8. Concluding remarks

There are some nuances, that we have not included for the sake of brevity. The corresponding results can be found in [12].

- We have not included the spin of each electron.

  Each electron can have two spin states. We label these internal spins with $\sigma = 1, 2$. The wave function is then

  $$\psi(x_1, \sigma_1, \ldots, x_N, \sigma_N)$$

  and for any choice of the σ_i, it is an element of $H^1(\mathbb{R}^{3N})$. Alternatively, we may think of ψ as an $H^1(\mathbb{R}^{3N})$ function with values in $\mathbb{C}^Q$ where $Q = 2^N$. The correct normalisation condition is that

  $$\sum_{\sigma_1=1}^{2} \cdots \sum_{\sigma_N=1}^{2} \int_{\mathbb{R}^{3N}} |\psi(x_1, \sigma_1, \ldots, x_N, \sigma_N)|^2 \, \mathrm{d}x_1 \ldots \mathrm{d}x_N = 1 .$$

It is convenient to write $z_j = (x_j, \sigma_j)$. Fermionic wave functions have to be totally antisymmetric ($i \neq j$)

$$\psi(z_1, \dots, z_i, \dots, z_j, \dots, z_N) = -\psi(z_1, \dots, z_j, \dots, z_i, \dots, z_N)\,.$$

Introducing spin changes some parts of the proof of stability of the second kind but, roughly speaking, only adds a multiplicative factor of (some power of) 2. For example, the ground state energy of non-interacting fermionic particles increases, as two particles can be in the state corresponding to e_0.

- We have not included any physical constants.

  Taking into account all the relevant physical constants $(\hbar, m, e)$, we obtain a lower bound

  $$E^f_{N,M} \geq -1.0732^{2/3}[(2Z+1)\alpha]^2 M^{2/3} N^{1/3}$$

  where $\alpha = e^2/(\hbar c) \approx 1/137$. For hydrogen ($Z = 1$, $M = N = 1$) this yields 30.52 Rydbergs.

- We have not included the nuclei in the wave function.

  We considered the nuclei to be static. If both the positive and the negative particles are dynamic, the wave functions are functions in $x_1, \dots, x_N$ and $R_1, \dots, R_N$, i.e. $\psi \in L^2(\mathbb{R}^{3N+3M})$

  $$\psi = \psi(x_1, \dots, x_N, R_1, \dots, R_N)\,.$$

  The wave function satisfies symmetry requirements separately for permutations of the x_i (fermionic) and the R_i (bosonic or fermionic). Note that the energy we investigated, $E^f_{N,M}$, is a lower bound for the energy where the nuclei are treated dynamically. The kinetic energy of the nuclei was not needed to prove stability.

- We have not included relativity theory.

  The relativistic one-body Hamiltonian can be defined as

  $$H = \sqrt{-\Delta + 1} - 1 + V(x)$$

  and the kinetic energy can be most easily expressed in Fourier space

  $$T_\psi = \int_{\mathbb{R}^3} (\sqrt{(2\pi k)^2 + 1} - 1)|\widehat{\psi}(k)|^2 \,\mathrm{d}k\,.$$

  The definitions of the many-body energy functional and the many-body Hamiltonian are the analogous. Simply mimicking the proof of non-relativistic stability of matter does not yield stability. The proof requires an additional bound on the kinetic energy, see [12, Lemma 8.4]. Stability of the second kind is then proved under certain conditions on Z in [12, Theorem 8.1]. In particular, stability holds for $Z < 58.5$. This bound was improved only recently to $Z < 87.2$ [7].

A. The Heisenberg Uncertainty Principle

The Heisenberg uncertainty principle is most often in the literature stated as

$$\sigma_X \sigma_P \geq \frac{\hbar}{2}$$

and was proved by Heisenberg in 1927 [8]. Here σ_A denotes the standard deviation

$$\sigma_A = \sqrt{\langle \psi, A^2\psi\rangle - \langle \psi, A\psi\rangle^2}$$

for an self-adjoint operator A in a state ψ. On $L^2(\mathbb{R}^d)$ the momentum operator X and the position operator P are defined by

$$(X\psi)(x) = x\psi(x)\,, \qquad (P\psi)(x) = -\mathrm{i}\hbar\nabla = -\mathrm{i}\hbar\left(\frac{\partial\psi}{\partial x_1}, \ldots, \frac{\partial\psi}{\partial x_d}\right)^{\mathrm{T}}.$$

The standard proof found in many textbooks only covers the case $d = 1$, it uses the following result.[70].

[70] Taken from [20, Theorem 8.2]

Theorem 45. *Let A, B be two symmetric operators. Then for any $\psi \in D(AB) \cap D(BA)$ we have that*

$$\sigma_A^2 \sigma_B^2 \geq \frac{1}{4}\left|\langle \psi, [A,B]\psi\rangle\right|^2$$

and in particular

$$\sigma_A \sigma_B \geq \frac{1}{2}\left|\,\langle \psi, [A,B]\psi\rangle\,\right|$$

with the anti commutator $[A,B] = AB - BA$.

Proof. Let $\widehat{A} = A - \langle\psi, A\psi\rangle\,\mathbb{I}$ and $\widehat{B} = B - \langle\psi, B\psi\rangle\,\mathbb{I}$ such that $\sigma_A = \left\|\widehat{A}\psi\right\|$ and $\sigma_B = \left\|\widehat{B}\psi\right\|$ and $[A,B] = [\widehat{A},\widehat{B}]$. By Cauchy–Schwarz

$$\left|\left\langle \widehat{A}\psi, \widehat{B}\psi\right\rangle\right|^2 \leq \sigma_A\sigma_B\,.$$

Observe that with the commutator $\{\widehat{A},\widehat{B}\} = \widehat{A}\widehat{B} + \widehat{B}\widehat{A}$

$$\widehat{A}\widehat{B} = \frac{1}{2}[\widehat{A},\widehat{B}] + \frac{1}{2}\{\widehat{A},\widehat{B}\} = \frac{1}{2}[A,B] + \frac{1}{2}\{\widehat{A},\widehat{B}\}$$

and thus

$$\left|\left\langle \widehat{A}\psi, \widehat{B}\psi\right\rangle\right|^2 = \left|\left\langle \psi, \widehat{A}\widehat{B}\psi\right\rangle\right|^2 = \left|\left\langle \psi, \frac{1}{2}[A,B]\psi + \frac{1}{2}\{\widehat{A},\widehat{B}\}\psi\right\rangle\right|^2.$$

Note that $\mathrm{i}[\widehat{A},\widehat{B}]$ and $\{\widehat{A},\widehat{B}\}$ are both symmetric. We can conclude that

$$\left|\left\langle \widehat{A}\psi,\widehat{B}\psi\right\rangle\right|^2=\frac{1}{4}\left|\langle\psi,[A,B]\psi\rangle\right|^2+\frac{1}{4}\left|\left\langle\psi,\{\widehat{A},\widehat{B}\}\psi\right\rangle\right|^2.$$

which proves that

$$\sigma_A^2\sigma_B^2\geq\frac{1}{4}\left|\langle\psi,[A,B]\psi\rangle\right|^2\,.$$

□

Now assume $d=1$, then $[P,X]=-\mathrm{i}\hbar$ and thus

$$\sigma_X^2\sigma_P^2\geq\frac{\hbar^2}{4}\,,\qquad\sigma_X\sigma_P\geq\frac{\hbar}{2}\,.$$

In higher dimensions we can use that $\nabla\cdot x-x\cdot\nabla=d\mathbb{I}$ to obtain

$$\sigma_X^2\sigma_P^2\geq\frac{\hbar^2d^2}{4}\,,\qquad\sigma_X\sigma_P\geq\frac{\hbar d}{2}\,.$$

Writing the first equation out, we get

$$\frac{\hbar^2d^2}{4}\leq\left(\langle\psi,X^2\psi\rangle-\langle\psi,X\psi\rangle^2\right)\left(\langle\psi,P^2\psi\rangle-\langle\psi,P\psi\rangle^2\right)\leq\langle\psi,X^2\psi\rangle\,\langle\psi,P^2\psi\rangle$$

which is the inequality that was introduced as Heisenberg's uncertainty principle in Subsection 2.1.

As shown in the exercises, we can also use the properties of the Fourier transform to prove that for all for all $\psi\in\mathcal{S}(\mathbb{R})$

$$\|x\psi\|_2\left\|2\pi k\widehat{\psi}\right\|_2\geq\frac{1}{2}\|\psi\|_2^2\,.$$

For fixed $x_0,k_0\in\mathbb{R}$ and $\psi\in\mathcal{S}(\mathbb{R})$ we can consider

$$\varphi(x)=\mathrm{e}^{-2\pi\mathrm{i}xk_0}\psi(x+x_0)\,,\qquad\widehat{\varphi}(k)=\mathrm{e}^{2\pi\mathrm{i}x_0k}\widehat{\psi}(k+k_0)\,.$$

We observe that

$$\begin{aligned}\|\varphi\|_2^2&=\int_{\mathbb{R}}|\psi(x+x_0)|^2\,\mathrm{d}x=\|\psi\|_2^2\,,\\ \|x\varphi\|_2^2&=\int_{\mathbb{R}}|x\psi(x+x_0)|^2\,\mathrm{d}x=\|(x-x_0)\psi\|_2^2\,,\\ \|2\pi k\widehat{\varphi}\|_2^2&=\int_{\mathbb{R}}|2\pi k\widehat{\psi}(k+k_0)|^2\,\mathrm{d}x=\left\|2\pi(k-k_0)\widehat{\psi}\right\|_2^2\,,\end{aligned}$$

and applying the inequality above to φ yields that

$$\|(x-x_0)\psi\|_2\left\|2\pi(k-k_0)\widehat{\psi}\right\|_2\geq\frac{1}{2}\|\psi\|_2^2\,.$$

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