# Stability Of Matter

Version 1.0*

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# Contents

# 1 A few remarks about the History of Quantum Mechanics

The notes below are an extremely abbreviated history of quantum mechanics and are neither complete nor presumably accurate. The point here is to present some of the highlights that shaped our understanding of matter. At the end of the section a few references are given that served as a basis for these notes.

In 1859 Gustav Kirchhoff from Heidelberg, using the Second law of Thermodynamics derives a universal law for the emission-absorbtion ratio of a blackbody. A blackbody is matter in equilibrium with radiation in which the body absorbs heat. It is reasonable to imagine a burning furnace with an opening small enough that not much heat is lost and in which burning material emits heat radiation that is in equilibrium with the walls of the furnace.

Kirchhoff showed that $\rho(T,\nu)$ the energy that comes from the radiation, per unit volume with frequency in the interval $[\nu,\nu+d\nu]$ must be a universal function of temperature and frequency. Hence it does not depend on other, material properties of the blackbody. Thus the challenge was posed to determine that function.

The total energy in a blackbody is

$$E(T) = V\int_0^\infty \rho(T,\nu)d\nu \tag{1}$$

and it was experimentally observed by Josef Stefan in 1879 and derived from Maxwell's equations by Ludwig Boltzmann in 1884 that

$$E(T) = aVT^4\ , \tag{2}$$

where $a$ is a constant.

In 1893 Wilhelm Wien proved, again on the basis of thermodynamics, his displacement law

$$\rho(T,\nu) = \nu^3 f(\nu/T) \tag{3}$$

and thus reduces the problem of finding $\rho$ to finding finding $f$, a function of a single variable. It is interesting to note that $\nu/T$ has the dimension inverse time times inverse temperature. It does not make sense to insert a quantity that carries a dimension into a nonlinear function. $f$ cannot be linear for otherwise the integral (1) would not exist. Using Boltzmann's constant $k$, $kT$ has the dimension of an energy and hence $\nu/kT$ has the dimension inverse time times inverse energy. Thus (3) makes sense if one introduces an additional constant that has the dimensions of time times energy, e.g., $e^2c$ where $e$ is the value of the elementary charge and $c$ the speed of light. (Note that from Coulombs

law the energy of two charges each having charge $e$ and are a distance $r$ apart is $e^2/r$. Hence $e^2c$ has the dimension time times energy.) There is no apparent reason why the elementary charge should enter the considerations at this moment.

It should also be noted that Boltzmann's constant $k$ is related to the gas law

$$pV = RNT \ ,$$

where $p$ is the pressure, $V$ is the volume, $T$ is the temperature and $N$ is the number of molecules per mol and $R$ is the universal gas constant. The relation between $R$ and $k$ is given by

$$R = N_0 k$$

where $N_0$ is Avogadro's number.

Wien in 1896 also proposed that

$$\rho = c_1 \nu^3 e^{-c_2 \nu / T}$$

but it was shown by Lummer and Pringsheim in 1900 that this law fails for small frequencies, oddly enough this is outside what is nowadays called the quantum regime.

Based on this Plank [P1] proposes in October 1900 a new radiation law. Interpreting the the energy density of blackbody radiation he had previously worked out the formula

$$\rho(T, \nu) = \frac{8\pi\nu^2}{c^3} U(T, \nu)$$

where $U(T, \nu)$ is, for given $\nu$ the total equilibrium energy at temperature $T$ of the oscillators. If one knows the entropy $S(U)$ then

$$\frac{1}{T} = \frac{dS}{dU}$$

allows to calculate $U$ as a function of $T$. Choosing

$$\frac{d^2S}{dt^2} = \frac{const.}{U}$$

leads to Wiens law. In [P1], Planck proposed instead

$$\frac{d^2S}{dT^2} = \frac{\alpha}{U(\beta + U)}$$

where $\alpha$ and $\beta$ are constants. Fitting constants he arrived at his new radiation law below. In [P2] he wrote it in the form

$$\rho(\nu, T) = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1} \ . \tag{0}$$

Here $k$, as before, is Boltzmann's constant and $h$ is a new constant of the dimension time times energy. He gave further theoretical reasons for it in December 1900 [P2] where

he 'derived' his radiation law using the statistical method of Boltzmann but with two additional twists. He assumes that the oscillators can have energies in integer multiples of $h\nu$ only and then proceeds in the following way. In how many ways can one distribute $K$ indistinguishable energy packets over $N$ distinguishable oscillators. Think of $K+N-1$ boxes in a row. Marking $N-1$ boxes will subdivide this row into $N$ sub-rows, some of which may be empty. The number of boxes in the $k$-th sub-row counts the number of energy packets of the $k$-th oscillator. In how many ways can we place $N-1$ boxes, obviously in

$$\frac{(N-1+K)!}{K!(N-1)!}$$

ways. Using Boltzmann's statistical method $S_N = k \log W$ yields

$$S_N = k(\log(N-1+K)! - \log K! - \log(N-1)!) \ .$$

With $K = \frac{U}{h\nu}N$ and using Sterling's approximation one obtains for the entropy $S$ per oscillator

$$S = k\left[(1+\frac{U}{h\nu})\log(1+\frac{U}{h\nu}) - \frac{U}{h\nu}\log\frac{U}{h\nu}\right] \ .$$

Using the relation $1/T = dS/dU$ and solving for $U$ as a function of $T$ yields (0). This way of counting the distribution of the energy packets is a precursor of what is now known as Bose Einstein statistics and it is used here by Planck for the sole purpose to arrive at the correct radiation law. An act of desperation as he admitted.

Using the experimental results of Kurlbaum and Lummer and Pringsheim he calculates in [P2] $k$ and hence Avogadro's number and gets

$$N_0 = 6.175 \times 10^{23}$$

The best known value at that time was $6.410^23$ due to O.E. Meyer. Using Faradays constant

$$F = N_0 e$$

he finds for the elementary charge

$$e = 4.6910^{-10} \ \text{electrostaticunits}$$

whereas the known value was somewhere between $1.2910^{-10}$ (F. Richarz) and $6.510^{-10}$ J.J Thompson. In SI units, Planck's value is

$$4.6910^{-10}\frac{1}{3}10^{-9} = 1.563 \times 10^{-19} \ \text{C} \ ,$$

The modern value of the elementary charge $e$ is

$$e = 1.60217653(54) \times 10^{-19} \ \text{C} \ ,$$

and for Avogadro's constant

$$6.0221415(10) \times 10^{23} mol^{-1} \ .$$

For the new constant $h$ which is now named after him, Planck gets the value

$$6.55 \times 10^{-27} \text{ ergsec}$$

which is in SI units

$$6.55 \times 10^{-34} \text{ Js} .$$

The modern value is

$$6.6260693(11) \times 10^{-34} \text{ Js} .$$

The digits in parenthesis are not certain.

It is rather surprising, and belongs into any elementary text book that by staring carefully into a stove one can actually determine the size of atoms. Avogadro's constant allows one to give an estimate of the size of $N_2$ by freezing one mol of nitrogen and then measuring the volume. Although this might not be easy this can be done in principle.

Planck's work did not elicit any great reaction until Einstein took it up again in 1905 in his work on the photoelectric effect. He stated his 'light quantum hypotheses', namely that in thermodynamic respects in the range where Wien's law is valid, light behaves as if it consists of mutually independent energy quanta of magnitude $h\nu$.

With this hypotheses he wrote down his law of the photoelectric effect

$$E = h\nu - \Phi .$$

Here $E$ is the energy of an electron that get kicked out of a metal under the impact of a light quantum or, as we now say, a photon of frequency $\nu$. $\Phi$ is the minimal energy needed to remove the electron from the metal and depends on the type of metal. In particular, the energy of the elctron does not depend on the intensity of the light beam shining on the metal.

That light liberates electrons from metals was discovered by Gustav Hertz in the years 1886-1888, the same years in which he demonstrated electromagnetic waves.

This law in its 'brutal' simplicity was greeted with great skepticism. Here is a quote of Millikan taken from [AP1]: " I spent ten years of my life testing that 1905 equation of Einstein's and contrary to all my expectations, I was compelled in 1915 to assert its unambiguous verification inspite of its unreasonableness, since it seemed to violate everything we knew about the interference of light."

So far some historical markers concerning the 'prehistory' of quantum theory. There were discoveries on other fronts, unrelated to quantum theory at first. In 1899 J.J. Thomson, using cathode rays discovered the electron and gives an estimate of its charge. Previously, 1897, there were a number of people, Emilt Wiechert, Walter Kaufmann and J.J Thomson who gave estimate on the charge to mass ratio of the hypothetical electron. It became clear that the electron was involved in the constitution of atoms, although there was no real proof of it. Planck before 1900 did not believe in atoms after 1900 he did.

Solid evidence for the existence of atoms came in 1911 when Ernest Rutherford proposed his atomic model, after experimenting with scattering of alpha particles on gold foil. The atom consists of an almost point like nucleus with positive charge $Ze|$ and

which carries virtually the whole mass of the atom. This nucleus is surrounded by a cloud of electrons. of charge $-e$ usually $Z$ electrons in order to render the atom charge neutral. He proved this by showing that the observed scattering is consistent with scattering of charged particles of a Coulomb potential. Thus, the force of the interaction between these particles is given by Coulomb's law, i.e., the force $F$ that a charge $Q$ at the position $X$ exerts on the charge $q$ at position $x$ is given by

$$F_{1,2} = qQ\frac{(x-X)}{|x-X|^3} \ ,$$

and the associated potential $V$, defined by $F = -\nabla_x V$ is given by

$$V = qQ\frac{1}{|x-X|} \ .$$

Physicists have toyed with the idea before that matter consists of interacting charged particles, but faced the serious problem that there is no stable equilibrium position for a system of charged particles. This is known in the physics literature as Earnshaw's theorem (Samuel Earnshaw,1805-1888) In modern terms this is known as the maximum principle for harmonic function. A function, harmonic on some domain cannot have a local maximum or local minimum in the domain. Since the Coulomb potential is a harmonic function the only equilibrium positions for the charges are either on top of each other or infinitely separated.

James Jeans in 1915 summarizes the situation as follows:

"There would be a very real difficulty in supposing that the (force) law $1/r^2$ held down to zero values of $r$. For the force between two charges at zero distance would be be infinite; we should have charges of opposite sign continually rushing together and, when once together, no force would be adequate to separate them... . Thus the matter of the universe would tend to shrink into nothing or to diminish indefinitely in size."

The real impetus for the development of quantum mechanics was the accumulation of a vast amount of spectral data. Systematic spectroscopy started with the work of Kirchhoff and Bunsen. By placing various substances into a non-luminous burner and measuring the wavelength of the emitted light they observed the spectral lines of atoms. They found that these lines are fundamental attributes of an element, like its weight. They proposed spectral analysis as a way of finding new elements (they found caesium and shortly thereafter rubidium). Finally they also pointed out that spectral techniques might be used to determine properties of the solar atmosphere and the brighter fixed stars.

Among the vast spectral data the Balmer formula (Johann Jakob Balmer, 1825 -1898, high school teacher in Basel) describing the spectral lines of Hydrogen stands out. The frequencies of the discrete hydrogen spectrum are given by the formula

$$\nu = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \ .$$

where $m, n$ are positive integers.

Interestingly, Bohr who proposed his model of the hydrogen atom in 1913, claims to have learned of the Balmer formula only shortly before finishing his work on the atom. (See [AP2] page 164.) Needless to say that Bohr's model of the atom explained the Balmer series.

Quantum theory took shape essentially within the two years 1925 and 1926. In 1925 Heisenberg discovered (with some help from Born and Jordan) matrix mechanics. To a physically system he associated a Hamiltonian as an infinite matrix whose eigenvalues where the allowed energy values of the system. Based on this theory, in the same year, Wolfgang Pauli found in a purely algebraic fashion the eigenvalues of the Hamiltonian of the hydrogen atom. This had the important consequence that the Balmer formula merged as a consequence from this theory. In the same year, Pauli discovered his 'Esclusion Prinicle', which will be of great importance and we shall talk about it in great detail later.

This development culminated in January 1926 with Erwin Schrödinger's discovery of the equation now named after him. This equation for the first time many body problems which were until that moment completely untractable. The unknown function $\Psi$ is a complex valued function on the configuration space of the system and with Max Born, $|\Psi|^2$ is interpreted as a probability density of finding the system at some point in configuration space.

All the theoretical ingredients are present to study the qualitative and quantitaive properties of matter.

References:

AP1 Abraham Pais, *Subtle is the Lord*, Oxford University Press, Oxford, 1982.

AP2 Abraham Pais, *Inward Bound*, Oxford University Press, Oxford, 1986.

MP1 Max Planck, *Ueber eine Verbesserung der Wien'schen Spektralgleichung*, Verh. Deutsch. Phys. Ges. **2** 202, (1900).

MP2 Max Planck, *Zur Theorie des Gesetzes der Energieverteilung im Normalspektrum* Verh. Deutsch. Phys. Ges. **2** 237, (1900).

JJ James H. Jeans, *The mathematical theory of electricity and magnetism*, Cambridge University Press, Cambridge, 1915.

# 2 Quantum mechanics in a nutshell

The state of a classical particle moving in three space is determined by its position and momentum, i.e., six coordinates. In quantum mechanics the state of a particle is given by a complex valued function $\psi(x)$, the **wave function**. The amount of information, however, is restricted; since Born we interpret $|\psi(x)|^2$ as the probability density of finding a particle at the point $x$. Accordingly we have to require the normalization condition

$$\int_{R^3} |\psi(x)|^2 dx = 1 \ . \tag{1}$$

The kinetic energy for a classical particle is determined by its momentum and is given by

$$\frac{p^2}{2m} \ , \tag{2}$$

where $m$ is the mass of the particle. In quantum mechanics the kinetic energy must be determined by the state $\psi$ and is given by

$$T_\psi = \frac{\hbar^2}{2m} \int_{R^3} |(\nabla\psi)(x)|^2 dx \ . \tag{3}$$

Any external potential $V(x)$, i.e., $-\nabla V(x)$ is the force acting on the particle at the point $x$, has the quantum mechanical analog

$$V_\psi = \int_{R^3} V(x)|\psi(x)|^2 dx. \tag{4}$$

Formula (4) can be interpreted as the expectation value of the potential $V$ with respect to the probability distribution $|\psi(x)|^2 dx$. Likewise the kinetic energy can also be interpreted as an expectation value but that is a bit trickier.

Recall that the Fourier transform is defined by

$$\widehat{\psi}(k) = \int_{R^3} e^{-2\pi i k\cdot x} \psi(x) dx \ ,$$

and its inverse is given by

$$\psi(x) = \int_{R^3} e^{2\pi i k\cdot x} \widehat{\psi}(k) dk \ .$$

Also recall Plancherel's theorem which says that

$$\|\widehat{\psi}\|_2^2 = \|\psi\|_2^2 \ .$$

A simple calculation leads to

$$\int_{R^3} |(\nabla\psi)(x)|^2 dx = 4\pi^2 \int_{R^3} |k|^2 |\widehat{\psi}(k)|^2 dk$$

and hence

$$T_\psi = \frac{\hbar^2}{2m} 4\pi^2 \int_{R^3} |k|^2 |\widehat{\psi}(k)|^2 dk = \frac{h^2}{2m} \int_{R^3} |k|^2 |\widehat{\psi}(k)|^2 dk \ ,$$

since $\hbar = h/2\pi$. Thus $T_\psi$ can be interpreted as the expectation value of the quantity $\frac{h^2}{2m}|k|^2$ with respect to the probability distribution $|\widehat{\psi}(k)|^2$, the probability density for the particle to have momentum $p = hk$. Note our conventions for the Fourier transform differ somewhat from the one usually used.

Classically the total energy of the particle is given by

$$\frac{p^2}{2m} + V(x) \tag{5}$$

and its quantum analog is then

$$E_\psi = T_\psi + V_\psi \ . \tag{6}$$

While the potential $V(x)$ can be fairly general, let us for the moment consider the case where

$$V(x) = -\frac{Ze^2}{|x|}$$

which is the Coulomb potential of an electron of charge $-e$ moving in the field of an infinitely heavy nucleus of charge $Ze$. Note that classically the kinetic energy (5) associated with this force law can have any value between $-\infty$ and $\infty$. I we move the particle towards the origin, the Coulomb potential drowns the potential energy an makes the total energy as large negative as we please.

This is not the case with the quantum mechanical analog given by (6) as we now prove. First let us choose our units. If we replace the wavefunction $\psi(x)$ by $\psi_\lambda(x) = \lambda^{3/2}\psi(\lambda x)$ we see that the normalization is preserved. A simple calculation, changing variables leads to

$$E_{\psi_\lambda} = \lambda^2 \frac{\hbar^2}{2m} \int_{R^3} |(\nabla\psi)(x)|^2 dx - \lambda e^2 \int_{R^3} \frac{1}{|x|} |\psi(x)|^2 dx \ .$$

Pick $\lambda$ so that

$$\lambda^2 \frac{\hbar^2}{2m} = \lambda e^2$$

which leads to

$$\lambda = \frac{2me^2}{\hbar^2}$$

and hence

$$E_{\psi_\lambda} = \frac{2me^4}{\hbar^2} \left[ \int_{R^3} |(\nabla\psi)(x)|^2 dx - \int_{R^3} \frac{1}{|x|} |\psi(x)|^2 dx \right] \ .$$

Note that the constant $\lambda$ has the dimension of an inverse length.

The constant $\frac{2me^2}{\hbar^2}$ can be written as

$$\frac{2mc}{\hbar}\frac{e^2}{\hbar c} = \frac{2mc}{\hbar}\alpha$$

where

$$\alpha = \frac{e^2}{c\hbar} \approx \frac{1}{137.03599911(46)}$$

is a dimensionless number, the **fine structure constant**. In other words the unit of length in which we measure an atom is given by

$$\frac{1}{2}\frac{\hbar}{mc}\frac{1}{\alpha}$$

where

$$\frac{\hbar}{mc} = 386.1592678(26) \times 10^{-15}\ \mathrm{m}$$

is the Compton wavelength divided by $2\pi$. Hence our atomic length scale is

$$2 \times 0.5291772108 \times 10^{-10}\ \mathrm{m},$$

which is twice the Bohr radius. Likewise $\frac{2me^4}{\hbar^2}$ can be written as

$$2mc^2\frac{e^4}{c^2\hbar^2} = 2mc^2\alpha^2$$

The energy

$$2mc^2\alpha^2 = 4\ \mathrm{Ry}$$

where $1\ \mathrm{Ry} = 13.6\ \mathrm{eV}$. $mc^2$ is, of course the rest energy of the electron which is approximately $0.5\ \mathrm{MeV}$. From now on we take as our unit of energy $4\ \mathrm{Ry}$ and our unit of length twice the Bohr radius. In this units the functional $E_\psi$ becomes

$$E_\psi = \int_{R^3} |(\nabla\psi)(x)|^2 dx - Z\int \frac{1}{|x|}|\psi(x)|^2 dx\ .$$

We shall often use the abbreviation

$$\|\nabla\psi\|_2^2 = \int_{R^3} |(\nabla\psi)(x)|^2 dx\ .$$

Recall again the main issue, that in contrast to the classical case, $E_\psi$ cannot be too negative. At the root of this fact is an uncertainty principle. Quite generally, an uncertainty principle says that one cannot localize a state in $x$ space and Fourier space, i.e., $p$ space simultaneously. There is a host of those, the most famous being Heisenberg's uncertainty principle. Here we state another one, namely

**Theorem 1 Theorem 1: Coulomb uncertainty principle** *Let $\psi$ be a square integrable function and assume that its gradient is also square integrable. Then*

$$\int_{R^3} \frac{1}{|x|}|\psi(x)|^2 dx \leq \|\nabla\psi\|_2 \|\psi\|_2 \ , \tag{6}$$

*where equality holds only if $\psi$ is of the form*

$$\text{const. } e^{-c|x|} \ .$$

*where $c > 0$ is a constant.*

**Proof** It is a standard fact of analysis that the smooth compactly supported functions are dense in the set of all function with $\int |\nabla\psi|^2 dx < \infty$. A proof can be found in many text books.

We shall use the abbreviation

$$(f, g) = \int_{R^3} \overline{f(x)} g(x) dx \ .$$

Using integration by parts it follows that

$$2(\psi, \frac{1}{|x|}\psi) = \sum_j (\psi, [\partial_{x_j}, \frac{x_j}{|x|}]\psi) = -\sum_j \left[ (\partial_{x_j}\psi, \frac{x_j}{|x|}\psi) + (\frac{x_j}{|x|}\psi, \partial_{x_j}\psi) \right]$$

$$= -2\Re \sum_j (\partial_{x_j}\psi, \frac{x_j}{|x|}\psi) \lesssim 2|(\partial_{x_j}\psi, \frac{x_j}{|x|}\psi)| \ .$$

Now, using Schwarz' inequality

$$|(\partial_{x_j}\psi, \frac{x_j}{|x|}\psi)| \lesssim \|\partial_{x_j}\psi\|_2 \|\frac{x_j}{|x|}\psi\|_2$$

with equality only if

$$\partial_{x_j}\psi = c_j \frac{x_j}{|x|}\psi \ .$$

Using Schwarz' inequality once more but this time for sums we get

$$\sum_j (\partial_{x_j}\psi, \frac{x_j}{|x|}\psi) \lesssim \|\nabla\psi\|_2 \|\psi\|_2$$

with equality only if

$$\nabla\psi = c\frac{\vec{x}}{|x|}\psi \ . \tag{7}$$

This proves the uncertainty principle (6). Since only the real part is involved the constant $c$ must be real in order to have equality. Further (7) implies that

$$\psi(x) = const. e^{c|x|}$$

and hence $c < 0$ for otherwise $\psi$ would not be square integrable. □

We use now the uncertainty principle to deal with the ground state energy of the hydrogenic atom.

**Theorem 2 Theorem 2: Ground state energy for the hydrogenic atom**
*Consider the minimization problem*

$$E_0 := \inf\{E_\psi : \int_{R^3} |(\nabla\psi)(x)|^2 dx < \infty \, , \int \frac{1}{|x|}|\psi(x)|^2 dx < \infty \, , \int_{R^3} |\psi(x)|^2 dx = 1\} \, .$$

*Then* $E_0 = -Z^2/4$ *and the function*

$$\psi_0(x) = \frac{Z^{3/2}}{\sqrt{8\pi}} e^{-Z|x|/2}$$

*is the unique minimizer, i.e.,*

$$E_{\psi_0} = -Z^2/4 \, .$$

**Remark 3** Note that instead of talking about the constraint $\|\psi\|_2 = 1$ we may instead consider the minimization problem

$$\inf\{E_\psi/\|\psi\|_2 : \int_{R^3} |(\nabla\psi)(x)|^2 dx < \infty \, , \int \frac{1}{|x|}|\psi(x)|^2 dx < \infty \, \} \, ,$$

which leads to the same answer as the one stated in theorem. (Why?)

**Proof** Using the Coulomb uncertainty principle we obtain the lower bound

$$\|\nabla\psi\|^2 - Z\|\nabla\psi\|$$

which is a quadratic function in the 'variable' $\|\nabla\psi\|$ wich has its minimal value precisely at $Z/2$ and its value is $Z^{/}4$. Using what we know about the cases of equality yields the result. □

Some elementary facts about $L^p$-spaces Fix $1 \gtrsim p < \infty$. The set of complex valued functions $f$ on $R^n$ whose $p$-th power is summable, i.e.,

$$\int_{R^n} |f(x)|^p dx < \infty \, ,$$

is denoted by $L^p(R^n)$ and we denote

$$\|f\|_p = (\int_{R^n} |f(x)|^p dx)^{1/p} \, .$$

The integral is the Lebesgue integral. Further we denote by $L^\infty(R^n)$ the space of functions whose essential supremum is finite, i.e., there exists a positive number $K$ so that

$$\{x \in R^n : |f(x)| > K\}$$

has measure zero. The infimum among all such numbers is denoted by

$$\|f\|_\infty \ .$$

The two important inequalities are Hölder's inequality and Minkowsi's inequality. Hölder's says that

$$|\int f(x)g(x)dx| \leq \|f\|_p \|g\|_q$$

provided $1 \lesssim p,q \lesssim \infty$ and $1/p + 1/q = 1$. Minkowski's is essentially the triangle inequality

$$\|f+g\|_p \leq \|f\|_p + \|g\|_p$$

provided $1 \lesssim p \lesssim \infty$. Thus, $L^p(R^n)$ is a normed linear space with norm $\|f\|_p$.

Exercises

1. Prove Hölder's and Minkowski's inequality.

2. Show that for $f \in \cap_{p \gtrsim p_0} L^p(R^n)$

$$\lim_{p\to\infty} \|f\|_p = \|f\|_\infty \ .$$

One of the key points about $L^p$ spaces is that they are examples of **Banach spaces, i.e., complete normed linear spaces**. Concretely this means that for any Cauchy sequence $f_n \in L^p(R^n)$ there exists $f \in L^p(R^n)$ such that $\|f_n - f\| \to 0$ as $n \to \infty$.

Let us finally remark that one can define $L^p$ spaces over any measure space $(\Omega, \Sigma, \mu)$ where $\Omega$ is a set, $\Sigma$ is a sigma algebra and $\mu$ is a measure.

It is clear from the discussion that the space $L^2(R^n)$ plays a special role because it carries an inner product

$$(f,g) := \int_{R^n} \overline{f(x)} g(x) dx \ ,$$

and hence its norm can be expressed as

$$\|f\|_2 = \sqrt{(f,f)} \ .$$

We say that two function $f, g$ are **orthogonal** to each other if $(f,g) = 0$.

Exercises

1. Prove the parallelogram identity

$$\|f-g\|_2^2 + \|f+g\|_2^2 = 2\|f\|_2^2 + 2\|g\|_2^2 \ .$$

2. Prove Schwarz' inequality in the following strong from

$$|(f,g)| \lesssim \|f\|_2 \|g\|_2$$

with equality if and only if $f$ and $g$ are proportional.

3. Why is the notion of completeness usefull?

4. Show Heisenberg's uncertainty principle in $R^n$ which says that

$$n\|\psi\| \lesssim \|\nabla\psi\|_2 \|\vec{x}\psi\|_2 \ ,$$

and deduce from it the ground state energy for the minimization problem

$$H_\psi = \int_{R^3} |(\nabla\psi)(x)|^2 dx + \int |x|^2 |\psi(x)|^2 dx$$

as well as the normalized minimizer.

The Schrödinger equation for the hydrogenic atom It is now a simple exercise to verify that the function $\psi_0$ satisfies the partial differential equation

$$-\Delta\psi_0 - \frac{Z}{|x|}\psi_0 = -\frac{Z^2}{4}\psi_0 \ . \tag{8}$$

Thus the value $E_0 = Z^2/4$ appears as an eigenvalue which is no coincidence since by a perturbing $\psi_0$ by a smooth and compactly supported function $f$ one obtains that

$$F(\varepsilon) := \frac{E_{\psi_0+\varepsilon f}}{\|\psi_0 + \varepsilon f\|_2^2} \gtrsim \frac{E_{\psi_0}}{\|\psi\|_2^2} \ .$$

Since the derivative of $F(\varepsilon)$ at $\varepsilon = 0$ with respect to $\varepsilon$ vansishes we get that

$$\int_{R^3} \overline{(\nabla\psi)(x)} \cdot (\nabla f)(x) dx - Z \int \frac{1}{|x|} \overline{\psi(x)} f(x) = E_{\psi_0} \int \overline{\psi(x)} f(x) dx = 0 \ , \tag{9}$$

for all $f$ smooth and with compact support. Note that from this one cannot conclude that equation (8) holds everywhere on $R^3$ directly. It is, however, possible starting from (9) and in particular not knowing what the explicit solution is, to show that the solution is in fact smooth and decays fast enough so that the equations make sense. This is known as the 'regularity theory' for partial differential equations.

# 3 The Sobolev inequality, a general uncertainty principle

The uses of the Coulomb Uncertainty principle are restricted to problems related to the hydrogenic atom. For more general potentials $V(x)$ the Sobolev inequality serves as a very effective uncertainty principle.

**Theorem 4 Theorem 1: Sobolev's inequality**
*For $n \gtrsim 3$ let $f$ be a function in $C^1(R^n)$ with compact support. Then there exists a constant $C_n$ depending only on the dimension but not on $f$ so that*

$$\|f\|_p \gtrsim S_n \|\nabla f\|_2$$

*where*

$$p = \frac{2n}{n-2} \, ,$$

*which is called the* **Sobolev index**.

**Remark 5** Note that inequality requires $n \gtrsim 3$. It does not make a statement in 2 and 3 dimensions.

**Remark 6** The value of the Sobolev index can be understood as follows. Assuming that the inequality holds, pick any function $f$ and consider its scaled verion $f(\lambda x)$ with $\lambda > 0$ arbitrary. Then, by changing variables

$$\left( \int_{R^n} |f(\lambda x)|^p dx \right)^{1/p} = \lambda^{-n/p} \left( \int_{R^n} |f(x)|^p dx \right)^{1/p}$$

which is

$$\gtrsim C_n \left( \int_{R^n} |\nabla (f(\lambda x))|^2 dx \right)^{1/2} = \lambda^{1-n/2} C_n \left( \int_{R^n} |\nabla (f(x))|^2 dx \right)^{1/2} \, .$$

Thus, the $\lambda$ powers must necessarily be the same, i.e., $n/p = n/2 - 1$.

**Remark 7** The best possible constant in Sobolev's inequality is known and it has the value.

$$\frac{n(n-2)}{4} |S^n|^{2/n}$$

where $|S^n|$ is the surface area of the unit $n$-sphere in $R^{n+1}$, i.e.,

$$|S^n| = \frac{2\pi^{(n+1)/2}}{\Gamma(\frac{n+1}{2})} \, .$$

The functions which yield equality are of the form

$$\frac{\text{const.}}{(\mu^2+|x-a|^2)^{(n-2)/2}} \ .$$

This result is due to Talenti [T] and Aubin[A] and its proof is somewhat more involved. See also [L] and [CL] for other proofs.

Exercise For which values of $p$ is it possible for the inequality

$$\|f\|_p \gtrsim C_{n,q}\|\nabla f\|_q \ , \tag{1}$$

to hold.

ANSWER:

$$p=\frac{qn}{n-q} \ .$$

In particular for $q=1$, $p=n/(n-1)$.

**Proof** We present the standard proof found in the textbooks, which is due to Gagliardo and Nirenberg, and prove the more general inequality (1). In order to present the ideas as clearly as possible we do it in 3-space and leave the general argument as an exercise.

Using the fundamental theorem of calculus

$$f(x,y,z)=\int_{-\infty}^{x}\partial_x f(r,y,z)dr$$

and in particular

$$|f(x,y,z)|\gtrsim\int_{-\infty}^{\infty}|\partial_x f(r,y,z)|dr=:g_1(y,z) \ .$$

Similarly, repeating the same argument in the other variables

$$|f(x,y,z)|^3\gtrsim g_1(y,z)g_2(x,z)g_3(x,y) \ ,$$

and hence

$$\|f\|_{3/2}\gtrsim\left(\int\sqrt{g_1(y,z)}\sqrt{g_2(x,z)}\sqrt{g_3(x,y)}dxdydz\right)^{2/3} \ .$$

Using Schwarz' inequality on the $x$- variable yields the upper bound

$$\left(\int\sqrt{g_1(y,z)}\sqrt{\int g_2(x,z)dx}\sqrt{\int g_3(x,y)dx}dydz\right)^{2/3}$$

Applying Schwarz' inequality once more in the $y$-variable yields

$$\left(\int\sqrt{\int g_1(y,z)dy}\sqrt{\int g_2(x,z)dx}\sqrt{\int g_3(x,y)dxdy}dz\right)^{2/3} \ ,$$

and finally in the $z$-variable

$$\left(\sqrt{\int g_1(y,z)dydz}\sqrt{\int g_2(x,z)dxdz}\sqrt{\int g_3(x,y)dxdy}\right)^{2/3} ,$$

$$= \left(\int g_1(y,z)dydz \int g_2(x,z)dxdz \int g_3(x,y)dxdy\right)^{1/3} ,$$

$$= (\|\partial_x f\|_1 \|\partial_y f\|_1 \|\partial_z f\|_1)^{1/3} ,$$

$$\gtrsim \|\nabla f\|_1 .$$

Thus we have established that

$$\|f\|_{3/2} \leq \|\nabla f\|_1 . \tag{2}$$

To arrive at the general inequality, replace $f$ by $|f|^s$ for a number $s > 0$ to be chosen later and calculate

$$\|f^s\|_{3/2} \leq s\||\nabla f||f|^{s-1}\|_1$$

Using Hölder's inequality on the right side yields the estimate

$$\|f^s\|_{3/2} \leq s\||\nabla f|\|_q \||f|^{s-1}\|_{q'} \tag{3}$$

where $1/q + 1/q' = 1$ or $q' = q/(q-1)$. Now if we choose $s = 2q/(3-q)$ so that

$$3s/2 = (s-1)q/(q-1) = \frac{3q}{3-q} = p ,$$

we get from (3)

$$\|f\|_p^{2p/3} \leq 2q/(3-q)\||\nabla f|\|_q \|f\|_p^{p(q-1)/q}$$

and upon dividing both sides by $\|f\|_p^{p(q-1)/q}$ we obtain

$$\|f\|_p^{2p/3-p(q-1)/q} \leq 2q/(3-q)\||\nabla f|\|_q ,$$

which is our desired inequality. Note, as a check, that

$$p[2/3 - (q-1)/q] = 1 .$$

Exercise By setting up a careful induction argument prove inequality (2) in any dimension. Then preceed to prove (1) for all $1 \gtrsim q < n$,

**Remark 8** The sharp constant in (2) is strongly related to the isoperimetric inequality. This is a substantial subject all by itself and we just touch it with a few remarks. The inequality (2) on $R^n$ in its sharp form reads as

$$\|f\|_{\frac{n}{n-1}} \leq n^{\frac{-(n-1)}{n}} |S^{n-1}|^{-1/n} \|\nabla f\|_1 .$$

In other words, we claim that

$$sup_{f\neq 0}\frac{\|f\|_{\frac{n}{n-1}}}{\|\nabla f\|_1} = n^{\frac{-(n-1)}{n}}|S^{n-1}|^{-1/n} .$$

The constant is precisely the surface area of a ball divided by the $(n-1)/n$-th power of its volume. The constant is not attained by any function whose gradient is integrable but we can get arbitrarily close as the following calculation shows. Define the function $f_\varepsilon(x) = u_\varepsilon(|x|)$ where

$$u_\varepsilon(r) = \begin{cases} 1 & \text{for } r < 1 \\ 0 & \text{for } r > 1+\varepsilon \\ 1+\varepsilon - r & \\ \varepsilon & \text{for } 1 \gtrsim r \gtrsim 1+\varepsilon \end{cases} .$$

We have immediately (please check) that $\lim_{\varepsilon\to 0}\|f_\varepsilon\|_{n/(n-1)} = (|S^{n-1}|/n)^{(n-1)/n}$. Next $\nabla f_\varepsilon = u'_\varepsilon(x/|x|)$ where

$$u'_\varepsilon(r) = \begin{cases} 0 & \text{for } r < 1 \\ 0 & \text{for } r > 1+\varepsilon \\ 1 & \\ \varepsilon & \text{for } 1 \gtrsim r \gtrsim 1+\varepsilon \end{cases} .$$

Hence, using polar coordinates (please check)

$$\|\nabla f_\varepsilon\|_1 = |S^{n-1}|\int_1^{1+\varepsilon}\frac{1}{\varepsilon}r^{n-1}dr = |S^{n-1}|\frac{1}{n}\frac{1}{\varepsilon}\left[(1+\varepsilon)^n - 1\right]^n ,$$

which tends to $|S^{n-1}|$ in the limit as $\varepsilon \to 0$. Hence we get from this example that the sharp constant

$$C_n \gtrsim n^{-(n-1)/n}|S^{n-1}|^{-1/n} .$$

That $C_n \gtrsim n^{-(n-1)/n}|S^{n-1}|^{-1/n}$ is much more difficult to see. One way of getting at it is using the co-area formula. Imagine that $f$ is a nice positive, smooth function, that has no flat spots, i.e., $\nabla f$ vanishes only at isolated points, the critical points. Thus, the level surfaces $\{x : f(x) = \alpha\}$ consist either of critical points or otherwise are $n-1$ dimensional surfaces perpendicular to $\nabla f$ which does not vanish on these surfaces.

For any given funcition $g$ we shall rewrite the integral

$$\int g(x)|(\nabla f)(x)|dx$$

'using $f$ as a variable'. Imagine a point on $\{x : f(x) = \alpha\}$ the level surface of $f$ at height $\alpha$. Pick a small cube of volume '$(\Delta x)^n$' by choosing $n-1$ edges of length $\Delta s_1, \ldots, \Delta s_{n-1}$ tangential and one edge of length $\Delta p$ perpendicular to the surface. The change in $f$ along the perpendicular edge is up to an error of higher order $|\Delta f| = |\nabla f|\Delta p$ and hence

$$(\Delta x)^n = \frac{1}{|\nabla f|}|\Delta f|\Delta s_1 \cdots \Delta s_{n-1} .$$

Note that $\Delta s_1 \cdots \Delta s_{n-1}$ corresponds to the surface area element and hence we can write

$$dx = \frac{1}{|\nabla f|} d\alpha dS$$

and

$$\int g(x)|(\nabla f)(x)|dx = \int_0^\infty d\alpha \int_{\{x:f(x)=\alpha\}} g(x)dS \ , \tag{4}$$

where $d\alpha$ is the change in height of the level surface and $dS$ is the area element on the level surface $\{x : f(x) = \alpha\}$. For a rigorous proof of this formula see [BZ]. Equation (4) is known as the co-area formula. If one replaces the measure $dS$ by the Hausdorff measure then the co-area formula holds in great generality for Sobolev functions, i.e., functions whose weak derivative is $p$-summable for some $p$. In particular we have that

$$\int |(\nabla f)(x)|dx = \int_0^\infty d\alpha \int_{\{x:f(x)=\alpha\}} dS = \int_0^\infty d\alpha |\{x : f(x) = \alpha\}| \ , \tag{5}$$

where $|\{x : f(x) = \alpha\}|$ is the surface area of the level set.

Thus we have now some geometric understanding of the $L^1$ norm of the gradient. Let us emphasize that these considerations are somewhat heuristic but can be made rigorous. They belong properly to geometric measure theory.

Let us try to write the $\int |f(x)|^p dx$ in a similar fashion. Start with

$$|f(x)| = \int_0^{|f(x)|} d\alpha = \int_0^\infty \chi_{\{|f(x)|>\alpha\}}(x) d\alpha \ , \tag{6}$$

where $\chi_A(x)$ is the characteristic function of the set $A$, i.e., it is equals $1$ if $x \in A$ and equals $0$ if $x \notin A$. It is a straightforward computation to see that

$$\int |f(x)|^p dx = p \int_0^\infty \alpha^{p-1} |\{x : |f(x)| > \alpha\}| d\alpha \ , \tag{7}$$

where $|A|$ denotes Lebesgue measure of the set $A$. In essence this is a possible definition of the Lebesgue integral of the function $|f(x)|^p$.

As a consequence we see that the $L^p$ norm of a function is entirely determined by the volume of the regions that are enclosed by the level surfaces $\{x : |f(x)| = \alpha\}$.

From (5) and (7) we can draw an interesting conclusion. The equation (5) says that the $L^1$-norm of $\nabla f$ depends only on the surface area of the level surfaces. Hence it is natural to try to minimize these areas but keeping the volumes fixed. Using the isoperimetric inequality the best arrangement is to deform the level sets $\{x : |f(x)| > \alpha\}$ into balls centered at some common point, say the origin and choosing the radius in such a way that the volume of these balls is the same as $|\{x : |f(x)| > \alpha\}|$. To these rearranged level sets corresponds also a function, which is called $f^*$ the *symmetric decreasing rearrangement* of $f$. This function has the value $\alpha$ on the boundary of the open ball whose volume is $|\{x : |f(x)| > \alpha\}|$.

Returning to our Sobolev inequality (2), but in $R^n$, we see among all functions the spherically symmetric functions deliver the worst constant. Thus, we may assume that all the level sets are rearranged into balls with radius

$$\left[\frac{n}{|S^{n-1}|}\right]^{\frac{1}{n}} |\{x : |f(x)| > \alpha\}|^{1/n}$$

and hence this inequality reads

$$C_n \gtrsim \left[\frac{1}{n-1}\right]^{\frac{n-1}{n}} |S^{n-1}|^{-1/n} \sup_{f\neq 0} \frac{\left[\int_0^\infty \alpha^{1/(n-1)} \lambda(\alpha)^{\frac{n}{n-1}} d\alpha\right]^{\frac{n-1}{n}}}{\int_0^\infty \lambda(\alpha) d\alpha} \tag{8}$$

where $\lambda(\alpha) = |\{x : |f(x)| > \alpha\}|^{\frac{n-1}{n}}$. Two observations about the function $\lambda(\alpha)$: it is a non increasing function and we may assume that $\int_0^\infty \lambda(\alpha) d\alpha = 1$ as well as $\lambda(0) = 1$, since the scaling $\lambda(\alpha) \to C\lambda(D\alpha)$ leaves the ratio in (8) fixed. To maximize

$$\left[\int_0^\infty \alpha^{1/(n-1)} \lambda(\alpha)^{\frac{n}{n-1}} d\alpha\right]^{\frac{n-1}{n}}$$

over all such functions $\lambda(\alpha)$ we proceed as follows. The functional

$$\lambda(\alpha) \mapsto \mathcal{F}(\lambda) = \left[\int_0^\infty \alpha^{1/(n-1)} \lambda(\alpha)^{\frac{n}{n-1}} d\alpha\right]^{\frac{n-1}{n}}$$

is convex. Now restrict the set over which to maximize to consist of non-increasing functions that have the value $1$ at $\alpha = 0$, whose integral equals $1$ and are zero outside the interval $[0, N]$ for some $N$ large. Call this set $T_N$ and note that $T_N$ is a convex set and

$$F(N) = \sup_{\lambda \in T_N} \mathcal{F}(\lambda)$$

is non decreasing as a function of $N$.

Since our functional is convex it attains its maximum on the set $T_N$ at the extreme points which consists of functions that take only zero and $1$ as values. Since the function is non-increasing, has the value $1$ at $\alpha = 0$ and integrates to $1$ it must be

$$\lambda_{opt}(\alpha) = \chi_{[0,1]}(\alpha) \ . \tag{9}$$

which does not depend on the value of $N$ as long as $N > 1$. and hence inserting this into (8) we have that

$$C_n \gtrsim |S^{n-1}|^{-1/n} n^{-(n-1)/n} \ ,$$

which demonstrates our claim.

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# 4 Some remarks about Sobolev spaces

We have been talking about functions that are square integrable and have a square integrable gradient. In this context the standard notion of differentiability of a function is not adequate. The key property of any space of functions in analysis is completeness and while it is possible to construct Banach spaces using the usual definition of the derivative, they are not easy to handle. $L^p$ spaces are fine, since it is easy to identify bounded linear functionals via the Riesz representation theorem.

A notion of derivative that is much better adapted to our purposes is the notion of **weak derivative**.

**Definition 9** *A function $f \in L^2(R^n)$ is in $H^1(R^n)$ if there exist $n$ functions $g_i \in L^2(R^n)$ such that for all $\phi \in C_c^\infty(R^n)$*

$$\int_{R^n} f(x)\frac{\partial \phi}{\partial x_i}(x)dx = -\int_{R^n} g_i(x)\phi(x)dx$$

*for all $i = 1, 2, \ldots n$.*

Of course we should think of the functions $g_i$ as the partials of $f$ and we shall use this notation. However, please remember that $\partial f \partial x_i$ is defined as the function that satisfies the infinite set of equations given by

$$\int_{R^n} f(x)\frac{\partial \phi}{\partial x_i}(x)dx = -\int_{R^n} \frac{\partial f}{\partial x_i}(x)\phi(x)dx$$

Note that the function $\frac{\partial f}{\partial x_i}(x)$ is uniquely defined since the set $C_c^\infty(R^n)$ is dense in $L^2(R^n)$.

We can endow the set $H^1(R^n)$ with the inner product

$$(u, v)_{H^1} := \int_{R^n} \overline{u(x)}v(x)dx + \int_{R^n} \overline{\nabla u(x)}\nabla v(x)dx \ .$$

The wonderful thing about the notion of weak derivative is that $H^1(R^n)$ is a Hilbert space, i.e., it is complete. To see this pick a Cauchy sequence $u_j$. Since $u_j$ is a Cauchy sequence in $L^2$ it converges to an element $u \in L^2(R^n)$. Likewise, the partials $\partial u_j/\partial x_i$ converge to functions $v_i \in L^2(R^n)$. All we have to show that $v_i$ is the weak derivative of $u$. Using Schwarz' inequality we learn that

$$\lim_{j\to\infty} \int_{R^n} u_j(x)\frac{\partial \phi}{\partial x_i}(x)dx = \int_{R^n} u(x)\frac{\partial \phi}{\partial x_i}(x)dx \ ,$$

and

$$\lim_{j\to\infty}\int_{R^n}\frac{\partial u_j}{\partial x_i}(x)\phi(x)dx=\int_{R^n}\frac{\partial u}{\partial x_i}(x)\phi(x)dx\ .$$

Since

$$\int_{R^n}u_j(x)\frac{\partial\phi}{\partial x_i}(x)dx=-\int_{R^n}\frac{\partial u_j}{\partial x_i}(x)\phi(x)dx$$

the same holds for $u$.

A sequence of functions $u_j$ converges to $u$ weakly in $H^1(R^n)$ if for every bounded linear functions $L$, $\lim_{j\to\infty}(u_j)=L(u)$. Using the Riesz representation theorem, an equivalent formulation is that $(u_j,v)_{H^1}\to(u,v)_{H^1}$. One of the really important theorems is

**Theorem 10** *Every bounded sequence in $H^1(R^N)$ has a weakly convergent subsequence, i.e., for every $u_j\in H^1(R^n)$, with $\|u_j\|_{H^1}\lesssim C$ there exists $u\in H^!(R^n)$ and a subsequence $u_{j_k}$ so that $u_{j_k}\to u$ weakly in $H^1(R^n)$.*

All the results about the Sobolev space $H^1(R^n)$ so far have been on an abstract level. Nowhere did we make any specific use of the derivative. This will change dramatically in the next theorem.

**Theorem 11 Rellich-Kondrachev** *Let $u_j$ be a bounded sequence in $H^1(R^n)$ which we can assume to converge weakly to the function $u\in H^1(R^n)$. Then for any measurable set $B$ with finite measure and any $q<p=2n/(n-2)$ we have that*

$$\int_B|u_j(x)-u(x)|^qdx\to 0$$

*as $j\to\infty$.*

**Proof** Quite generally for $f\in H^1(R^n)$ we have that for any $h\in R^n$

$$\int|f(x+h)-f(x)|^2dx\lesssim\|\nabla f\|^2|h|^2\ . \tag{1}$$

A simple way to see this is to use Plancherel's theorem to calculate

$$\int|f(x+h)-f(x)|^2dx=\int|e^{2\pi ip\cdot h}-1|^2|\widehat{f}(p)|^2dp\lesssim 4\pi^2\int|p|^2\widehat{f}(p)|^2dp|h|^2=\|\nabla f\|^2|h|^2\ .,$$

where the inequality

$$|e^{2\pi ip\cdot h}-1|\lesssim 2\pi|p||h|$$

has been used. Further for any smooth function $\phi$ of compact support with $\int\phi(y)dy=1$ and $\int|\phi(y)|y|dy<\infty$ we calculate

$$\|f*\phi-f\|_2\lesssim\int|\phi(y)|y|dy\|\nabla f\|_2\ , \tag{2}$$

where

$$(f * \phi)(x) = \int f(x-y)\phi(y)dy \ .$$

To see this write

$$\|f * \phi - f\|_2 = \left[\int |\int f(x-y)\phi(y)dy - \int f(x)\phi(y)dy|^2 dx\right]^{1/2} \ .$$

Minkowski's inequality allows to pull the $y$ integration outside the $x$ integration to yield the bound

$$\int |\phi(y)| \|f(\cdot - y) - f(\cdot)\|_2$$

which together with (1) proves (2).

Now we consider the sequence $u_j$ and pick $\varepsilon$ arbitrary but fixed. Set

$$\phi_m(y) = m^n \phi(ym)$$

and note that $\int \phi_m = 1$ and

$$\int |\phi_m(y)||y|dy = \frac{1}{m} \int |\phi(y)||y|dy \ .$$

Since $\|\nabla u_j\| \lesssim C$ we have *uniformly in* $j$ that

$$\|u_j * \phi_m - u_j\|_2 \lesssim \frac{1}{m} C \int |\phi(y)|y|dy < \varepsilon \ ,$$

for some fixed $m$ sufficiently large. This follows from (2).

Next since $u_j \to u$ weakly in $H^1(R^n)$ and hence in $L^2(R^n)$ we get that

$$u_j * \phi_m(x) \to u * \phi_m(x)$$

for every $x$. Morover

$$|u_j * \phi_m(x)| \lesssim \|u_j\|_2 \|\phi_m\|_2 \lesssim C'$$

*uniformly in* $j$. Thus we conclude using the dominated convergence theorem that

$$\int_B |u_j * \phi_m(x) - u * \phi_m(x)|^2 dx \to 0 \tag{3}$$

as $j \to \infty$. Hence

$$\|u_j - u\|_{L^2(B)} \lesssim \|u_j - u_j * \phi_m\|_{L^2(B)} + \|u_j * \phi_m - u * \phi_m\|_{L^2(B)} + \|u_j * \phi_m - u\|_{L^2(B)}$$

$$< 2\varepsilon + \|u * \phi_m - u\|_{L^2(B)}$$

and using (30 we conclude that

$$\limsup_{j \to \infty} \|u_j - u\|_{L^2(B)} < 2\varepsilon \ .$$

Since $\varepsilon$ is arbitrary this proves the theorem for $q = 2$ and since $B$ is bounded it holds for all $1 \precsim q \precsim 2$.

For $q < p$ we use Hölders inequality

$$\|u_j - u\|_q \precsim \|u_j - u\|_2^{\theta} \|u_j - u\|_p^{1-\theta}$$

where $\theta = n(1/q - 1/p) > 0$. By Sobolev's inequality

$$\|u_j - u\|_p \precsim S_n(\|\nabla u_j\|_2 + \|\nabla u\|_2) \precsim 2CS_n$$

and the general theorem follows from the case $q = 2$. □

# 5 Higher eigenvalues and eigenfunctions, the Exclusion Priniciple

Consider again the quadratic form $E_\psi$ under the same assumptions as in the previous section, i.e., that $V \in L^{n/2}(R^n) + L^\infty(R^n)$ and $V$ vanish at infinity in measure. The existence of a ground state has been established in the previous section, i.e., we know that there is a function $\psi_0 \in H^1(R^n)$ such that

$$E_{\psi_0} = E_0$$

where

$$E_0 = \inf\{E_\psi : \psi \in H^1(R^n), \|\psi\|_2 = 1\} .$$

Also note that for any $f \in H^1(R^n)$

$$F(\varepsilon) := \frac{E_{\psi_0+\varepsilon f}}{\|\psi_0 + \varepsilon f\|^2} \gtrsim \frac{E_{\psi_0}}{\|\psi_0\|^2} = E_0$$

and hence $F'(0) = 0$ which reads as

$$\int \nabla\psi_0 \cdot \nabla f dx + \int V(x)\psi_0(x)f(x)dx = E_0 \int \psi_0(x)f(x)dx .$$

In the language of partial differential equations one says that $\psi_0$ is a weak solution of the eigenvalue problem

$$-\Delta\psi_0(x) + V(x)\psi_0(x) = E_0\psi_0(x) .$$

Likewise we can find the next higher eigenfunction as follows. Consider the minimization problem

$$E_1 = \inf\{E_\psi : \psi \in H^1(R^n), \|\psi\|_2 = 1, (\psi, \psi_0) = 0\} .$$

As in the previous section we see that a minimizer exists for this problem under the condition that $E_1 < 0$. The only new thing to check is that the for the minimizing sequence, call it $\phi_j$ with $\phi_j \rightharpoonup \psi_1$,

$$\lim_{j\to\infty} (\phi_j, \phi_0) = (\psi_1, \phi_0) = 0$$

which follows immediately from the definition of weak convergence. Consider again a function

$$F(\varepsilon) := \frac{E_{\psi_1+\varepsilon f}}{\|\psi_1 + \varepsilon f\|^2}$$

where $f \in H^1(r^n)$ such that $(f, \psi_0) = 0$. Since $F(\varepsilon) \gtrsim E_1 = F(0)$ we by differentiating that

$$L_1(f) := \int \nabla\psi_1 \cdot \nabla f dx + \int V(x)\psi_1(x)f(x)dx = E_0 \int \psi_1(x)f(x)dx \ ,$$

for all $f \in H^1(R^n)$ with $(f, \psi_0) = 0$. From that it follows that there exists a constant $\mu$ so that $L_1(f) - E_0(\psi_1, f) = \mu(\psi_0, f)$ for *all* $f \in H^1(R^n)$. In particular choosing $f = \psi_0$ we get

$$\int \nabla\psi_1 \cdot \nabla\psi_0 dx + \int V(x)\psi_1(x)\psi_0(x)dx = \mu\|\psi_0\|^2$$

while at the same time

$$\int \nabla\psi_1 \cdot \nabla\psi_0 dx + \int V(x)\psi_1(x)\psi_0(x)dx = E_0(\psi_1, \psi_0) = 0 \ .$$

Hence $\mu = 0$. Therefore, we conclude that

$$\int \nabla\psi_1 \cdot \nabla f dx + \int V(x)\psi_1(x)f(x)dx = E_0 \int \psi_1(x)f(x)dx$$

for *all* $f \in H^1(R^n)$. Hence $\psi_1$ is a weak solution of the eigenvalue equation

$$-\Delta\psi_1(x) + V(x)\psi_1(x) = E_1\psi_1(x) \ .$$

We have, tacitly, assumed that the functions $\psi_0$ and $\psi_1$ are real. Please show that they can be chosen to be real.

In a similar fashion we can now define the other higher eigenvalues and eigenfunctions recursively by minimizing

$$E_k == \inf\{E_\psi : \psi \in H^1(R^n), \|\psi\|_2 = 1, (\psi, \psi_l) = 0, l = 0, 1, \ldots k-1\} \ .$$

As before we find that $L_k(f) = E_k(\psi_k, f)$ for all $f \in H^1(R^n)$ with $(f, \psi_l) = 0, l = 0, 1, \ldots, k-1$. Again from this it follows that $L_k(f) = \sum_{l=0}^{k-1} \mu_k(f, \psi_l)$ for all $f \in H^1(R^n)$ for some numbers $\mu_0, \mu_1, \ldots \mu_{k-1}$. Assuming inductively that $L_l(f) = E_l(\psi_l, f)$ for all $f \in H^1(R^n)$ we get that on the one hand $L_k(\psi_m) = \mu_m\|\psi_m\|_2^2$, while on the other $L_k(\psi_m) = L_m(\psi_k) = E_k(\psi_m, \psi_k) = 0$. Hence $\mu_l = 0, l = 0, \ldots, k-1$.

Continuing this way we get a sequence of negative numbers $E_k$ together with function $\psi_k$. About this sequence we can state the following theorem.

**Theorem 12 Higher eigenvalues and eigenfunctions**

*The sequence $E_k$ is either finite or infinite in which case it can only accumulate at $0$. In particular the eigenvalues can only be finitely degenerate.*

**Proof** Assume that the sequence of eigenvalues $E_k$ is not finite. We may also assume that the eigenfunctions are normalized to one and are orthogonal to each other. We have to show that the sequence $E_k$ converges to zero. Suppose not, i.e., there exists a number $-A$ so that infinitely many eigenvalues are below that number. This means that

$$E_{\psi_k} = E_k\|\psi_k\|^2 < -A\|\psi_k\|^2 \ . \tag{1}$$

and since the energy dominates the kinetic energy we get

$$\|\nabla\psi_k\|^2 \gtrsim 2E_{\psi_k} + \Lambda\|\psi_k\|_2^2 \gtrsim (\Lambda - A) \ .$$

In other words, the sequence $\psi_k$ is a bounded sequence in $H^1(R^n)$. Since the sequence is orthonormal it converges weakly to zero. Pick $A > \varepsilon > 0$ and recall that

$$|\int V(x)|\psi_k(x)|^2dx| \gtrsim |\int_{N>|V|>\varepsilon} V(x)|\psi_k(x)|^2dx| +$$

$$+|\int_{|V|\lesssim N} V(x)|\psi_k(x)|^2dx| + |\int_{|V|\gtrsim\varepsilon} V(x)|\psi_k(x)|^2dx|$$

$$\gtrsim N|\int_{N>|V|>\varepsilon} |\psi_k(x)|^2dx| + \left(\int_{|V|\lesssim N} |V(x)|^{n/2}dx\right)^{2/n} \|\psi_k\|^2_{2n/(n-2)} + \varepsilon\|\psi_k|_2^2 \ .$$

By the Sobolev inequality the second factor in the second term is uniformly bounded. Fix $N$ large enough can make the seond term less than $\varepsilon$ uniformly in $k$. Since $\{x : |V(x)| > \varepsilon\}$ has finite measure we learn from the Rellich Kondrachev Theorem that the first term tends to zero as $k \to \infty$. Hence

$$\limsup_{k\to\infty} |\int V(x)|\psi_k(x)|^2dx| < 2\varepsilon$$

and hence

$$\lim_{k\to\infty} |\int V(x)|\psi_k(x)|^2dx| = 0 \ . \tag{2}$$

But this contradicts equation (1). □

In quantum mechanics, the state of many particles is described a wave function on the configuration space of these particles. More precisely given $N$ particles with coordinates $x_1, \ldots, x_N$ then the wave function

$$\Psi(x_1, \ldots, x_N)$$

is a function in $L^2(R^{3N})$ and its interpretation is that

$$|\Psi(x_1, \ldots, x_N)|^2$$

is the probability density of finding the first particle at $x_1$ the second particle at $x_2$ etc.

It is a fundamental law that wave functions of identical elementary particles come in two flavors.

Fermions The wave function

$$\Psi(x_1, \ldots, x_N)$$

is antisymmetric under exchange of particle labels, i.e.,

$$\Psi(x_{\pi(1)}, \ldots, x_{\pi(N)}) = (-)^\pi\Psi(x_1, \ldots, x_N) \ ,$$

where $\pi$ is any permutation of $N$ objects and $(-)^\pi$ is the signature of the permutation, that is $-1$ for odd permutation and $+1$ for even parmutations.

Bosons The wave function

$$\Psi(x_1, \ldots, x_N)$$

is symmetric under exchange of particle labels, that is

$$\Psi(x_{\pi(1)}, \ldots, x_{\pi(N)}) = \Psi(x_1, \ldots, x_N) \ ,$$

where $\pi$ is any permutation of $N$ objects. If we have $K$ bosons and $N$ fermions then the wave function of the combined system is given by

$$\Psi(R_1, \ldots, R_K, x_1, \ldots, x_N)$$

where the function is symmtric und permutation of the first $K$ labels and antisymmetric under permutations of the other $N$ labels. There is an added complication because of the spin but we neglect this possibility for the moment. As in the one particle case we can now write down an energy for a system of $N$ *non- interacting* particles

$$E_\Psi = T_\Psi + V_\Psi$$

where

$$T_\Psi = \sum_{j=1}^{N} \int_{R^{3N}} |\nabla_{x_j} \Psi(x_1, \ldots, x_N)|^2 dx_1 \cdots dx_N \ ,$$

and

$$V_\Psi = \sum_{j=1}^{N} \int_{R^{3N}} V(x_j) |\Psi(x_1, \ldots, x_N)|^2 dx_1 \cdots dx_N \ .$$

We shall make the same assumption about the potential as in the case of one particle. The problem is now to find

$$E_0(N) = \inf\{E_\Psi : \Psi \in H^1(R^{3N}), \|\Psi\|_{L^2(R^{3N})} = 1\} \ .$$

**Theorem 13 Minimization for non interacting bosons**
*The gound state energy for $N$ noninteracting bosons is given by*

$$E_0(N) = NE_0$$

*and the corresponding minimmizer is given by*

$$\prod_{j=1}^{N} \psi_0(x_j)$$

*where $\psi_0$ is the normalized ground state wave function of the single particle problem.*

**Proof** Clearly by using $\prod_{j=1}^N \psi_0(x_j)$ as a normalized trial function we see right away that $E_0(N) \lesssim NE_0$. To see the converse is a bit more difficult. Define the **one particle density associated with** $\Psi$ by

$$\rho(x) = N \int_{R^{3(N-1)}} |\Psi(x, x_2, \ldots, x_N)|^2 dx_2 \cdots dx_N \ .$$

Note it is immaterial over which variable we integrate since the function $|\Psi(x_1, \ldots, x_N|^2$ is symmetric. this definition holds for bosonic wave functions as well as for fermionic wave functions. For our boson wave function we calculate

$$|\nabla\sqrt{\rho}(x)|^2 = N \left[ \frac{1}{\sqrt{\rho}(x)} \int_{R^{3(N-1)}} \Psi(x, x_2, \ldots, x_N) \nabla_x \Psi(x, x_2, \ldots, x_N) dx_2 \cdots dx_N \right]^2$$

and by Schwarz's inequality we obtain the bound

$$\begin{aligned} |\nabla\sqrt{\rho}(x)|^2 &\lesssim \left[ \frac{1}{\sqrt{\rho}(x)} N\sqrt{\rho(x)} \int |\nabla_x \Psi(x, x_2, \ldots, x_N)|^2 dx_2 \cdots dx_N \right] \\ &= N \int |\nabla_x \Psi(x, x_2, \ldots, x_N)|^2 dx_2 \cdots dx_N \ , \end{aligned}$$

and upon integrating over $x$, using the symmetry of the wave function we get the Hoffmann-Ostenhof inequality

$$\int_{R^3} |\nabla\sqrt{\rho}(x)|^2 dx \lesssim T_\Psi \ .$$

In particular we learn that $\sqrt{\rho} \in H^1(R^3)$. Note that a simple calculation reveals that

$$V_\Psi = \int_{R^3} V(x)\rho(x) dx \ .$$

Thus, we see that

$$E_\Psi \gtrsim \int_{R^3} |\nabla\sqrt{\rho}(x)|^2 dx + \int_{R^3} V(x)\rho(x) dx$$

which we have to minimize over all $\sqrt{\rho} \in H^1(R^3)$ with $\int \rho = N$. Put it differently, we can define $\sqrt{N}\psi(x) = \sqrt{\rho}(x)$ and have to minimize the one particle problem $NE_\psi$ over all $\psi \in H^1(R^3)$ with $\|\psi\| = 1$ which equals $NE_0$. Hence have that $E_0(N) = E_0$ and $\prod_{j=1}^N \psi_0(x_j)$ is a minimizer. If $\Psi_0$ is any other minimizer there must be equality in all the above inequalities. In particular equality in Schwarz's inequality leads to

$$\lambda_j(x)\Psi(x, x_2, \ldots, x_N) = \nabla_j \Psi(x, x_2, \ldots, x_N)$$

for a.e. $x_2, \ldots x_N$. Because of the symmetry of the function under prmutation, $\Psi$ must be a product function of the form $\prod_{j=1}^N \phi(x_j)$ and insering this function into the functional we get that

$$N[T_\phi + V_\phi] = NE_0$$

and hence $\phi$ must be the ground state of the one body problem which, as we have argued somewhere else is unique. □

**Theorem 14 Minimization for non interacting fermions**
*The gound state energy for $N$ noninteracting fermions is given by*

$$E_0(N) = \sum_{j=0, E_j \lesseqgtr 0}^{N-1} E_j \tag{3}$$

*and the corresponding minimmizer is given by a* **slater determinant**

$$\frac{1}{\sqrt{N!}} \det(\psi_i(x_j))$$

*where $\psi_i$ is the normalized eigenfunctions associated with the eigenvalues $E_0, E-1, \ldots, E_{N-1}$ of the single particle problem. If the number of non-positive eigenvalues is strictly less than $N$ there is no minimizer but the energy is just the sum over the available non positive eigenvalues.*

This Theorem is quite a bit trickier. Note that we can write

$$\sum_{i=1}^{N} \int |\nabla_{x_i} \Psi(x_1, \ldots, x_N)|^2 dx_1 \cdots dx_N = N \int |\nabla_{x_1} \Psi(x_1, \ldots, x_N)|^2 dx_1 \cdots dx_N$$

$$= \int \left[\nabla_x \nabla_y \rho\right](x, x) dx \tag{4}$$

where the **one particle density matrix** $\rho$ is given by

$$\rho_\Psi(x, y) = N \int \overline{\Psi(x, \ldots, x_N)} \Psi(y, \ldots, x_N) dx_2 \cdots dx_N \ .$$

Likewise,

$$\sum_{i=1}^{N} \int V(x_i) |\Psi(x_1, \ldots, x_N)|^2 dx_1 \cdots dx_N = N \int V(x_1) |\Psi(x_1, \ldots, x_N)|^2 dx_1 \cdots dx_N$$

$$= \int V(x) \rho_\Psi(x, x) dx \ .$$

Note that

$$\rho_\Psi(y, x) = \overline{\rho_\Psi(x, y)}$$

and hence $\rho(x, y)$ defines a selfadjoint operator. Denote its eigenfunctions by $\phi_j(x)$ which we can choose to be orthonormal, i.e.,

$$(\phi_i, \phi_j) = \delta_{i,j} \ .$$

We denote its eigenvalues by $\lambda_j$. The following Lemma (which I learned from Elliott Lieb) is important.

**Lemma 15** *The operator defined by the kernel $\rho_\Psi(x,y)$ has non-negative eigenvalues and is trace class, in particular*

$$\sum_j \lambda_j = N \ .$$

*Moreover, we have the surprising fact that all the eigenvalues are less than* 1.

**Proof** It is a standard fact that the kernel has an complete set of orthonormal eigenfunctions $\phi_j$, and we can write

$$\rho_\Psi(x,y) = \sum_{j=1}^{\infty} \lambda_j \overline{\phi_j(x)} \phi_j(y) \ .$$

The trace of the associated operator is defined by integrating

$$\int \sum_{j=1}^{\infty} \lambda_j |\phi_j(x)|^2 dx = N \int |\Psi(x_1, \ldots, x_N)|^2 dx_1 \cdots dx_N = N \ .$$

To see that the eigenvalues are less than one we have to use the antisymmetry of $\Psi$. It suffice to show that for any $f \in L^2(R^n)$ we have that

$$\int \overline{f(x)} \rho_\Psi(x,y) f(y) dx dy \gtrsim \|f\|_2^2 \ .$$

Consider now the integral kernel

$$K(x_1, \ldots, x_N, y_1, \ldots, y_N) = \sum_{j=1}^{N} \overline{f(x_j)} f(y_j)$$

It is a sum of rank one projections. To describe the eigenfunctions we complement $f$ to an orthonormal basis and denote it by $f_j$. The eigenfunctions of $K$ are now all products of the form

$$f_{j_1}(x_1) \cdots f_{j_N}(x_N) \ .$$

(Note that we use here the spectral theorem of the operator $K$ which is elementary in this case). The function $\Psi$ can be expanded in terms of products of $f_j$

$$\Psi(x_1, \ldots, x_N) = \sum_{j_1, \ldots, j_N} C(j_1, \ldots, j_N) f_{j_1}(x_1) \ldots f(x_{j_N}) \ .$$

Since $\Psi$ is antisymmetric, the coefficients $C$ are antisymmetric in their variables. This means that $C$ vanishes if any two indices are the same. Moreover, since $\Psi$ is normalized we have that

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

Now we compute for $j_1, \ldots, j_N$ different indices

$$(\prod_k f_{j_k}, K \prod_k f_{j_k}) = \sum_{k=1}^{N} |(f, f_{j_k})|^2$$

and since all the indices are different, at most one term is not zero. Hence

$$(\prod_k f_{j_k}, K \prod_k f_{j_k}) \precsim 1$$

and

$$(\Psi, K\Psi) \precsim \sum_{j_1,\ldots,j_N} |C(j_1, \ldots, j_N)|^2 = 1 \ .$$

But

$$(\Psi, K\Psi) = N(f, \rho_\Psi f) \ ,$$

and this proves the lemma. □

Now we return to (4) and note that

$$\int [\nabla_x \nabla_y \rho]\,(x,x)dx = \sum_{j=1}^{N} \lambda_j \int |\nabla \psi_j(x)|^2 dx$$

and hence

$$E_\Psi = \sum_{j=1}^{N} \lambda_j \left[ \int |\nabla \psi_j(x)|^2 dx + \int V(x) |\phi_j(x)|^2 dx \right]$$

and since the functions are all orthonormal we get that

$$E_0(N) \geq \sum_{j=1}^{N} \lambda_j E_j \ . \tag{5}$$

The $E_j$ are negative and all the $0 \precsim \lambda_j \precsim 1$ and, moreover, $\sum_j \lambda_j = N$. Thus, we have to minimize over all values of $\lambda_j$ satisfying the above two constraints. The solution of that minimization problem is achieved by choosing $\lambda_j = 1, j = 1, \ldots, N$ and $\lambda_j = 0, j > N$. This is nothing but the bathtub principle (see 'Analysis' on p. 28). In this case

$$E_0(N) \geq \sum_{j=1, E_j \precsim 0}^{N} E_j \ .$$

The converse follows from a direct computation using the the slater determinant.

Note that the previous theorem is a precise version of what we mean by filling the energy levels.

Another important result concerning higher eigenfunctions is the min-max principle which we discuss next.

**Theorem 16 Min-Max principle**
*Let $\phi_0, \ldots, \phi_{k-1}$ be any $k$ orthonormal functions in $H^1(R^n)$. Consider the matrix*

$$h_{i,j} = \int \nabla\phi.\nabla\phi_j dx + \int V(x)\phi_i\phi_j \ .$$

*denote by $\lambda_j, j = 0, \ldots, k-1$ the eigenvalues ordered increasingly of the matrix $H = (h_{i,j})$. Then we have that*

$$E_j \gtrsim \lambda_j \ , j = 0, \ldots k-1 \ .$$

**Proof** Denote by $\vec{c}_j$ the eigenvectors of the matrix $H$. Clearly $\chi_0 = \sum_i c_0^i \phi_i$ satisfies $(\chi_0, \chi_0) = 1$ and

$$E_0 \leq \int |\nabla\chi_0|^2 dx + \int V(x)|\chi_0(x)|^2 dx = \lambda_0 \ .$$

Now we proceed by induction and assume that

$$E_j \gtrsim \lambda_j \ , j = 0, \ldots k-2 \ .$$

The space spanned by the linear combinations of $\phi_0, \ldots, \phi_{k-1}$ is $k$-dimensional and hence there exists $\chi = \sum d^i\phi_i$, with $(\chi, \chi) = 1$ such that

$$(\chi, \psi_i) = 0 \ , i = 0, 1, \ldots k-2 \ .$$

Hence, by the definition of $E_{k-1}$ we have that

$$E_{k-1} \gtrsim \int |\nabla\chi|^2 dx + \int V(x)|\chi(x)|^2 dx = (\vec{d}, H\vec{d}) \gtrsim \lambda_{k-1} \ ,$$

since $\lambda_{k-1}$ is the largest eigenvalue. This proves the theroem. □

This theorem allows us to compare eigenvalues of various operators. E.g., assume that $W(x)$ is another potential satisfying the same assumptions as $V$ but with $V(x) \gtrsim W(x)$ for a.e. $x$. Denote by $\mu_j$ the eigenvalues associated with the quadratic form

$$\int |\nabla\psi|^2 dx + \int W(x)|\psi|^2 dx \ .$$

Then

$$\lambda_j \gtrsim \mu_j$$

for all $j$. Note that there maybe fewer eigenvalues for the $W$ problem then for the $V$ problem but in this case $\mu_j = 0$ for $j$ sufficiently large. The proof follows immediately from the min-max priniciple.

# 6 Semiclassical estimates, some heuristics

In the previous section we have learned about higher eigenvalues and how to compute the ground state energy of a number of non-interacting fermions. We have seen that the Sobolev inequality is sufficient to estimate the ground state energy of a single particle. The tool that allows us to estimate the ground state energy of fermionic systems is the Lieb-Thirring inequality, or rather a whole family of Lieb-Thirring inequalities.

The following heuristic principle is, sometimes, a good guide for inventing such kind of inequalities for quantum mechanical systems.

**Theorem 17 Semiclassical picture of quantum states**
*A quantum state occupies a classical phase space volume of size* $\frac{1}{(2\pi)^n}$. *Thus, given a volume* $P$ *in classical phase space of dimension* $2n$ *then the function*

$$\frac{1}{(2\pi)^n}\chi_P(x,p) \tag{1}$$

*serves as a distribution for these states.*

**Remark 18** Note, that one should really consider

$$\frac{1}{h^n}\chi_P \tag{2}$$

as our distribution but since in our units $\hbar = 1$, (2) reduces to (1).

**Remark 19** There are refinements to this principle. True quantum states occupy not just any volume but they have a certain shape in the form of a brick. Hence if we have a set that is very irregular so that very few bricks fit inside this set, the set will carry few quantum states, despite having a large volume.

Consider a the $n$-dimensional Schrödinger problem. We denote the eigenvalues of the quadratic form

$$\int_{R^n}[|\psi'|^2 + V(x)|\psi|^2]dx \ , \ \int |\psi|^2 dx = 1 \tag{3}$$

by $-\lambda_1 < -\lambda_2 \gtrsim -\lambda_3 \cdots$. The classical phase space of our system is $R^{2n}$ and the probability measure for the negative energy quantum states is given by

$$\frac{1}{(2\pi)^n}\chi_{\{p^2+V(x)\gtrsim 0\}}(x,p) \ .$$

To apply the heuristic principle we can ask whether one relate the sum

$$\sum_k (\lambda_k)^\gamma$$

to some expression involving the potential. Here $\gamma$ is any nonnegative constant. If $\gamma = 0$ then we interpret the left side as the *number of negative eigenvalues* of the quadratic form.

According to the heuristic principle it should be

$$\frac{1}{(2\pi)^n} \int_{\{p^2+V(x)\lesssim 0\}} (p^2 + V(x))_-^\gamma dxdp \ .$$

Integrating first over $p$, this expression can be simplified to yield

$$\frac{1}{(2\pi)^n} |S^{n-1}| \int_0^1 (1-s^2)^\gamma s^{n-1} ds \int_{R^n} [V(x)]_-^{\gamma+n/2} dx \ .$$

Here $[V(x)]_-$ denotes the negative part of $V(x)$, i.e., $[V(x)]_- = \min(-V(x), 0)$. Likewise the positive part we denote by $[V(x)]_+$ so that

$$V(x) = [V(x)]_+ - [V(x)]_- \ .$$

The constant in front of the integral involving the potential can be computed in terms of the Gamma function and is given by

$$2^{-n} \pi^{-n/2} \frac{\Gamma(\gamma+1)}{\Gamma(\gamma+n/2+1)} \ . \tag{4}$$

We denote this constant by $L_c(n,\gamma)$, the semiclassical Lieb-Thirring constant.

The interpretation

Thus, a number of questions come up.

1. For which values of $\gamma$ is an inequality of the type

$$\sum \lambda_k^\gamma \lesssim C(n,\gamma) \int_{R^n} [V(x)]_-^{\gamma+n/2} dx \tag{5}$$

   true for some universal constant $C(n,\gamma)$, independent of $V$.

2. Assuming the answer to 1) is yes. Denote the best constant, i.e., the smallest constant for which (2) holds, by $L(n,\gamma)$. Can we calculate $L(n,\gamma)$, or can we estimate it reasonably close?

3. In general $L_c(n,\gamma) \lesssim L(n,\gamma)$ in all dimension and for all values of $\gamma$. This fact is by no means trivial and is related to the Weyl asymptotics for the eigenvalues.

We shall see that this leads to very difficult questions in Analysis and a number of tools have been invented for investigating this questions.

One aspect is that semiclassical estimates are *not always* a good guide. E.g., the inequality

$$\sum_j \lambda_j^\gamma \gtrsim L(\gamma) \int [V(x)]_-^{\gamma+1/2} dx$$

is *false* for all $\gamma < 1/2$ in the one dimensional problem. To see this fix $\alpha > 0$ and consider the function

$$f(x) = \frac{1}{\cosh^\alpha(x)} \ .$$

An elementary calculation shows that

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

Assuming that the Lieb-Thirring inequality holds we must have that

$$\frac{\alpha^{\gamma-1/2}}{(\alpha+1)^{\gamma+1/2}} \gtrsim const. \int \frac{1}{\cosh^{2\gamma+1}(x)} dx \ ,$$

which is obvously falls for $\gamma < 1/2$ as can be readily seen by letting $\alpha$ tend to zero. On the opposite end is the following result due to Lieb and Thirring again in one dimension. Note that the semiclassical constant for $\gamma = 3/2$ in one dimension is $3/16$.

**Theorem 20** *In one dimension the inequality*

$$\sum_j \lambda_j^{3/2} \gtrsim \frac{3}{16} \int [V(x)]_-^2 dx \ .$$

*holds.*

**Proof** We shall establish this result using 'commutation', an idea that goes back to ancient times. We appeal here a bit to functional analysis, e.g., we expect the reader to know a bit about adjoints etc. Also, we shall assume that the potential is nice, i.e., smooth, compact support and everywhere negative. As a result, there are only finitely many negative eigenvalues. It suffices to show the above inequality for such potentials. Denote by $\phi_0(x)$ the ground state of our quadratic form and in this case it is quite easy to see that

$$-\phi_0'' + V(x)\phi_0 = -\lambda_0 \phi_0 \ ,$$

since all the functions involved are smooth. The function $\phi_0$ can be chosen to be non-negative and hence it is strictly positive. Hence it makes sense and hence setting $F_0 = \phi_0'/\phi_0$ we calculate that $F_0$ satisfies a Riccati equation

$$F_0' + F_0^2 = \lambda_0 + V(x) \ . \tag{6}$$

Since $V$ has compact support we see that outside the support of $V$

$$F_0(x) = \begin{cases} \sqrt{\lambda_0} & \text{for } x \text{ large negative} \\ -\sqrt{\lambda_0} & \text{for } x \text{ large positive.} \end{cases} \tag{7}$$

This follows right away from the fact that $\phi_0'' = \lambda_0\phi_0$ outside the support of $V$ and that $\phi_0$ has to decay at infinity. Further,

$$(-d/dx - F_0)(d/dx - F_0) = -d^2/dx^2 + F_0' + F_0^2 = -d^2/dx^2 + V(x) + \lambda_0 \ . \tag{8}$$

Set $A = (d/dx - F_0)$ and $A^* = (-d/dx - F_0)$. Obviously

$$A^*A\phi_0 = 0 \ ,$$

since

$$A\phi_0 = (d/dx - F_0)\phi_0 = 0 \ .$$

In other words, the operator $A^*A$ has zero as a non degenerate eigenvalue. Now we consider the new operator that results by commuting the two differential expressions in (8)

$$AA^* \ .$$

This new operator is strictly positive since

$$(f, AA^*f) = \|A^*f\|^2$$

and it cannot be equal to zero since in that case $A^*f = 0$ or

$$f' = \sqrt{\lambda_0}f$$

for $x$ large which is impossible, since $f$ has to decay at infinity. On the other hand, take any other eigenfunction $\phi_k$ of our problem,i.e.,

$$A^*A\phi_k = (\lambda_0 - \lambda_k)\phi_k$$

where $(\lambda_0 - \lambda_k) \neq 0$. Since

$$AA^*A\phi_k = (\lambda_0 - \lambda_k)A\phi_k$$

we have that

$$AA^*\psi_k = (\lambda_0 - \lambda_k)\psi_k \ .$$

Note that

$$\psi_k = A\phi_k$$

is not identically equals to zero. In other words if $A^*A$ has an eigenvalue $\lambda_0 - \lambda_k$ then $AA^*$ has the same eigenvalue for $k \neq 0$. Next we calculate that

$$AA^* = -d^2/dx^2 - F_0' + F_0^2 = -d^2/dx^2 + F_0' + F_0^2 - 2F_0' = -d^2/dx^2 + V(x) - 2F_0' + \lambda_0 \ .$$

Thus we have a nw Schrödinger problem with another potential

$$V(x) - 2F_0'(x)$$

which is smooth and has compact support, in fact the same as the original potential. The Hamiltonian, i.e., the operator

$$-d^2/dx^2 + V(x) - 2F_0'$$

has *the same eigenvalues as the old one, except for the ground state eigenvalue* $\lambda_0$. Our goal is now to show that

$$\sum_{j=0} \lambda_j^{3/2} - \frac{3}{16} \int [-V(x)]^2 dx \lesssim 0 \; .$$

To see this, write this expression in the form

$$\sum_{j=1} \lambda_j^{3/2} - \frac{3}{16} \left[ \int [-V(x)]^2 dx - \frac{16}{3} \lambda_0^{3/2} \right] \; .$$

Now we claim that

$$\int [-V(x)]^2 dx - \frac{16}{3} \lambda_0^{3/2} = \int [-V(x) + 2F_0']^2 dx$$

or

$$\int [-V(x)]^2 dx - \int [-V(x) + 2F_0']^2 dx = \frac{16}{3} \lambda_0^{3/2} \; .$$

Clearly,

$$\int [-V(x)]^2 dx - \int [-V(x) + 2F_0']^2 dx = \int [4V(x)F_0'(x) - 4F_0'^2] dx$$

and eliminating the potential with the help of (7) yields

$$= \int [4(F_0' + F_0^2 - \lambda_0)F_0' - 4F_0'^2] dx = 4 \int [F_0^2 - \lambda_0] F_0' dx = \frac{16}{3} \lambda_0^{3/2}$$

using the boundary condition (4). Thus

$$\sum_{j=0} \lambda_j^{3/2} - \frac{3}{16} \int [-V(x)]^2 dx = \sum_{j=1} \lambda_j^{3/2} - \frac{3}{16} \int [-V(x) + 2F_0']^2 dx$$

and repeating the arument removes all the eigenvalues leaving a non-positive expression. □

This result has been extended for any power $\gamma \gtrsim 1$ in one dimension by Lieb and Aizenman [AL]. In fact they show that if the for some $n$ and some $\gamma_0$ the Lieb-Thirring inequality holds *with the semiclassical constant* then it holds again *with the semiclassical constant* for all $\gamma \gtrsim \gamma_0$.

Another, relatively recent extension is due to Laptev and Weidl [LW] who proved that the sharp Lieb-Thirring constant for $\gamma \gtrsim 3/2$ *in all dimension* is given by the semiclassical constant. We shall discuss their ideas in more detail later.

Unfortunately, the cases $\gamma \gtrsim 3/2$ is not often used in the applications. The important cases are $\gamma = 1$ (see below) and $\gamma = 1/2$.

Summary The Lieb-Thirring inequality holds in the following cases

1. $n = 1$ and all $\gamma < 1/2$ due to Lieb and Thirring [LT], $n = 1$, $\gamma = 1/2$ due to Weidl [W].

2. $n = 2$ and all $\gamma > 0$ due to Lieb and Thiriing [LT2]

3. $n \gtrsim 3$ and all $\gamma > 0$ due to Lieb and Thirring [LT2]

4. $n \gtrsim 3$, $\gamma = 0$, Cwikel [C], Lieb [L], Rosenbljum [R]

More can be said about the constants but we come to that later

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# 7 The Birman-Schwinger Prinicple

All the proofs of the general inequalities involve in one way or another the Birman-Schwinger principle. To state, we shall from now consider only negative potentials of the form $V(x) = -U(x)$ with $U$ nonnegative. For $E > 0$ introduce the Birman-Schwinger operator

$$K_E = U^{1/2}(-\Delta + E)^{-1}U^{1/2} \ .$$

This operator has an integral kernel given by

$$U^{1/2}(x)(-\Delta + E)^{-1}(x,y)U^{1/2}(y) \ ,$$

where $(-\Delta + E)^{-1}(x,y)$ is the kernel of the Greens functions of the Laplacian. That this operator exists can be seen from the Riesz representation theorem. For every fixed $g \in H^{-1}(R^n)$ there exists a *unique* $u \in H^1(R^n)$ so that

$$\int \nabla u \cdot \nabla f + \lambda \int uf = \int gf$$

holds for all $f \in H^1(R^n)$. Moreover the connection between $u$ and $g$ is linear. Further it is also bounded from $H^{-1}(R^n)$ to $H^1(R^n)$ since

$$\|u\|^2_{H^1(R^n)} \gtrsim \frac{1}{\lambda}(\int |\nabla u|^2 + \lambda \int u^2) = \int gu \gtrsim \|g\|_{H^{-1}(R^n)}\|u\|_{H^1(R^n)} \ .$$

We denote this $u$ by

$$u = (-\Delta + \lambda)^{-1}g \ .$$

This operator has a kernel that can calculated. In one dimension it is given by

$$(-\partial^2 + E)^{-1}(x,y) = \frac{1}{2\sqrt{E}}e^{-\sqrt{E}|x-y|} \ .$$

In three dimension it is given by

$$\frac{1}{4\pi}\frac{e^{-\sqrt{E}|x-y|}}{|x-y|} \ .$$

One can work out the expressions in all the other dimensions. In odd dimensions it is given by elementary function and in even dimension it is given by Bessel functions. It is not difficult to see that for our class of potential, i.e., $U \in L^{n/2} + L^\infty$ with $U$ vanishing

at infinity, the Birman Schwinger operator is a bounded operator on $L^2(R^n)$. Recall that by Sobolev's inequality

$$\int U(x)|\psi(x)|^2 dx \leq \alpha \int |\nabla\psi(x)|^2 dx + \beta\|\psi\|_2^2$$

for constants $\alpha, \beta$. This means that $U^{1/2}$ as a multiplication operator is bounded from $H^1(R^n)$ to $L^2(R^n)$. Now consider

$$B = U^{1/2}(-\Delta + E)^{-1/2}$$

and note that the last factor maps from $L^2(R^n)$ to $H^1(R^n)$ and the first factor maps is back to $L^2(R^n)$ all in a bounded fashion. Thus $B^*$ is also bounded from $L^2(R^n)$ to $L^2(R^n)$ and so is the $BB^*$, the Birman-Schwinger operator. Thus, the Birman-Schwinger operator is a bounded selfadjoint operator on $L^2(R^n)$. Although the discussion did not cover the case of one and two dimensions this properties hold in theses cases too. They are, in fact even easier to prove.

The following summarizes what we need to know about the Birman-Schwinger kernel.

**Theorem 21 Birman-Schwinger principle**

*The number $-\lambda < 0$ is an eigenvalue of the quadratic form (3) if and only of $1$ is an eigenvalue of the Birman-Schwinger operator $K_\lambda(U)$. The eigenvalues of the Birman-Schwinger operator are monotone decreasing functions of $E$.*

**Proof** The monotonicity of the eigenvalues follows from the min-max theorem since for every $f \in L^2(R^n)$

$$(U^{1/2}f, (-\Delta + E)^{-1}U^{1/2}f)$$

is decreasing as a function of $E$.

Next, suppose that $\phi$ is a solution of the Schrödinger equation, i.e.,

$$\int \nabla\phi \cdot \nabla f + \lambda \int \phi f = \int U\phi f$$

for all $f \in H^1(R^n)$. Since $U^{1/2}$ maps $H^1(R^n)$ boundedly to $L^2(R^n)$ we have that $U\phi \in H^{-1}(R^n)$ and hence

$$\phi = (-\Delta + \lambda)^{-1}U\phi\ ,$$

from which we conclude that

$$U^{1/2}\phi = U^{1/2}(-\Delta + \lambda)^{-1}U^{1/2}U^{1/2}\phi$$

which means that $1$ is an eigenvalue of $K_\lambda(U)$ with $U^{1/2}\phi$ as eigenfunction. Conversely if $\psi$ satisfies

$$\psi = U^{1/2}(-\Delta + \lambda)^{-1}U^{1/2}\psi$$

then if we set

$$\phi = (-\Delta + \lambda)^{-1}U^{1/2}\psi$$

we see that $\phi \in H^1(R^n)$. This means that $\phi$ satisfies

$$\int \nabla\phi \cdot \nabla f + \lambda \int \phi f = \int U^{1/2}\psi f$$

for all $f \in H^1(R^n)$. But $U^{1/2}\psi \in H^{-1}(R^n)$ and and moreover from the eigenvalue relation we learn that

$$U^{1/2}\psi = U\phi \ .$$

This proves the claim. □

The first and most important version of the Lieb–Thirring inequality goes back to the paper by Lieb and Thirring 'Bound for the Kinetic Energy of Fermions Which Proves the Stability of Matter' [LT1].

**Theorem 22 Lieb-Thirring bound**
*The negative eigenvalues $-\lambda_j$ of the quadratic form in three dimensions*

$$\int |\nabla\psi|^2 dx + \int V(x)|\psi|^2 dx \ , \ \int |\psi|^2 dx = 1$$

*satisfy the estimate*

$$\sum_j \lambda_j \gtrsim L(3,1) \int [V(x)]_-^{5/2} dx \ ,$$

*where $L(3,1) \gtrsim 4/(15\pi)$.*

**Proof** Using the Birman Schwinger principle we give a bound on the number of bound states less than $-e$. Start with $\lambda$ small, so that some of the eigenvalues of $K_\lambda$ are big. These values decrease as $\lambda$ grows and every time one of them hits the value $1$ the $\lambda$-value or rather its negative is and eigenvalue of the Schrödinger problem. If $\lambda$ arrives at $e$, the number of these crossings equals the number of eigenvalues of $K_e(U)$ that are greater or equals to $1$. In other words the number

$$N_e(U) \ ,$$

the number of eigenvalues of the *Schrödinger problem* that are less than $-e$ , is given by the number of eigenvalues greater or equals $1$ of the Birman-schwinger operator $K_e(U)$.

The quantity $N_e(U)$ can be used to calculate the sum of the eigenvalues since

$$\sum_j \lambda_j = \int_0^\infty N_e(U) de \ .$$

In general

$$\sum_j (\lambda_j)^\gamma = \gamma \int_0^\infty e^{\gamma-1} N_e(U) de \ . \tag{1}$$

To see this, note that

$$(\lambda_j)^\gamma = \int_0^\infty \chi_{\{(\lambda_j)^\gamma > e\}}(e)de$$

Summing over $j$ and noting that

$$\sum_j \chi_{\{(\lambda_j)^\gamma > e\}}(e) = N_e(U)$$

yields (1) by a change of variables.

The most obvious upper bound would be $\mathrm{Tr}K_e(U)$ since we add up all the eigenvalues not just the one greater or equals 1. This, trace is however infinity. Thus the next step would be to consider the Hilbert-Schmidt norm

$$\mathrm{Tr}K_e(U)^2 \ .$$

This is easily calculated to give

$$\int U(x)[(-\Delta + e)^{-1}(x,y)]^2 U(y)dxdy \ .$$

Unfortunately, this is a bit tricky to estimate in terms of $\int U^{5/2}dx$. Following Lieb and Thirring one splits $e$ into two pieces

$$\int \nabla\phi \cdot \nabla f - \int [U - e/2]\phi f = -\lambda + e/2 \int \phi f$$

and replacing $[U - e/2]$ by $[U - e/2]_+$ lowers the eigenvalues, i.e., increases their magnitude. Moreover we have that

$$N_e(U) \gtrsim N_{e/2}([U - e/2]_+) \tag{1}$$

since there are more eigenvalues in the $[U - e/2]_+$ problem that are below $-e/2$ than there are eigenvalues in the $U$ problem that fall below $-e$. Now we trace all the steps for the Birman-Schwinger principle for this tne problem and obtain the upper bound

$$N_{e/2}([U - e/2]_-) \gtrsim \mathrm{Tr}K_e([U - e/2]_-)^2$$

which yields

$$\int [U - e/2]_-(x)[(-\Delta + e)^{-1}(x - y)]^2 [U - e/2]_-(y)dxdy \ .$$

Using Young's inequality* this is bounded above by

$$\|[U - e/2]_-\|_2^2 \int \frac{1}{(4\pi)^2} \frac{e^{-\sqrt{2}\sqrt{e}|x|}}{|x|^2} dx$$

$$= \frac{1}{4\pi} \int_0^\infty e^{-\sqrt{2}\sqrt{e}r} dr \|[U - e/2]_-\|_2^2$$

$$= \frac{1}{4\sqrt{2}\pi\sqrt{e}} \|[U - e/2]_-\|_2^2 \ .$$

Integrating this expression over the positive semi axis leads to

$$\sum_j \lambda_j = \int_0^\infty N_e(U) de \gtrsim \frac{1}{4\sqrt{2}\pi} \int_0^\infty \frac{1}{\sqrt{e}} \int [U - e/2]_-^2(x) dx de \ .$$

Interchanging the two integrals and a bit of scaling leads to

$$\frac{1}{4\sqrt{2}\pi} \int \int_0^\infty \frac{1}{\sqrt{e}} [U - e/2]_-^2(x) de dx \ .$$

$$= \frac{1}{2\pi} \int_0^1 [1 - s^2]^2 ds \int U(x)^{5/2} dx \ ,$$

$$= \frac{4}{15\pi} \int U(x)^{5/2} dx \ .$$

The semi classical constant is given by

$$\frac{1}{30\pi^2} \ .$$

Young's inequality states that

$$\int f(x) g(x - y) h(y) dx dy \gtrsim C_{p,q} \|f\|_p \|g\|_q \|h\|_r$$

with $1/p + 1/q + 1/r = 2$. □

Let us return to Sobolev's inequality, but this time for systems of orthonormal functions. Recall the definition of the one particle density

$$\rho_\Psi(x) = N \int |\Psi|^2(x, x_2, \ldots, x_N) dx_2 \cdots dx_N \ .$$

The following theorem is a classical result of Lieb and Thirring [LT1].

**Theorem 23 Uncertainty priniple for fermions.**
*Let $\Psi$ be any normalized antisymmetric function in $H^1(R3N)$. Then*

$$T_\Psi = \sum_{j=1}^N \int |\nabla_j \Psi|^2(x_1, \ldots, x_N) dx_1 \cdots dx_N \geq \frac{3}{5} (\frac{2}{5})^{2/3} L(3,1)^{-2/3} \int_{R^3} \rho_\Psi^{5/3}(x) dx \ .$$

*We have that*

$$\frac{3}{5} (\frac{2}{5})^{2/3} L(3,1)^{-2/3} < \frac{3^{5/3} \pi^{2/3}}{5 \cdot 2^{2/3}} > 1.68 \ .$$

**Proof** For a given $\Psi$ consider the Schrödinger form

$$T_\Phi + V_\Phi \tag{2}$$

where

$$V(x) = -c\rho_\Psi^{2/3}(x) \ ,$$

and hence

$$V_\Phi = -c\sum_j \int_{R^{3N}} \rho_\Psi^{2/3}(x_j)|\Phi|^2(x_1,\dots,x_N)dx_1\cdots dx_N \ = -c\int_{R^3} \rho_\Psi^{2/3}(x)\rho_\Phi(x)dx. \tag{3}$$

We want to minimize the energy of (2) over all normalized antisymmetric functions $\Phi$ of $n$ variables. Since we are talking about noninteracting fermions we fill the energy levels and find that

$$-\sum_j \lambda_j \le T_\Phi + V_\Phi$$

for all $\Phi \in H^1(R^{3N})$. Further, by the Lieb -Thirring inequality

$$\sum_j \lambda_j \gtrsim L(3,1)\int [V(x)]_-^{5/2}dx = L(3,1)c^{5/2}\int \rho_\Psi^{5/3}(x)dx \ .$$

Hence

$$-L(3,1)c^{5/2}\int \rho_\Psi^{5/3}(x)dx \gtrsim T_\Phi + V_\Phi$$

for all $\Phi \in H^1(R^{3N})$. In particular the inequality holds for $\Phi$ replaced by $\Psi$ and using (3) we get

$$T_\Psi - c\int_{R^3} \rho_\Psi^{5/3}(x)\rho_\Phi(x)dx \gtrsim -L(3,1)c^{5/2}\int \rho_\Psi^{5/3}(x)dx$$

or

$$T_\Psi \gtrsim c\int_{R^3} \rho_\Psi^{5/3}(x)\rho_\Phi(x)dx \gtrsim -L(3,1)c^{5/2}\int \rho_\Psi^{5/3}(x) \ .$$

Maximizing the right side over $c$ yields the result. □

References


- [LT1] Phys. Rev.Lett. **35**, p.687-689, (1975)

# 8 Stability of matter

One of the fundamental attributes of matter is its **extensivity**, that is, its size as well as its energy content is proportional to the number of particles. This is intimately related to the fact that one can combine material systems. While it is an everyday experience that when we pour two separate liters of water together we still have two liters, this is a nontrivial fact from a theoretical point of view. Classical mechanics is unable to explain this most obvious of all the facts. It is indeed curious if one thinks of water as a huge number of molecules, themselves made up of electrons and nuclei interacting with each other via electrostatic forces. If the two liters are poured together the number of molecules that potentially might interact with each other is doubled. This means that the terms in the Coulomb interaction has quadrupled, that is, there are four times as many interaction terms as there were before pouring that stuff together. Indeed the Coulomb energy in each of the separate containers consists of the electron-nuclear attraction ($N \times K$ terms) plus the electron-electron repulsion ($N^2/2$ terms). Thus in total $2 \times N \times K$ attraction terms and $N^2$ repulsion terms. If we pour them together we have $4 \times N \times K$ attraction terms and $2 \times N^2$ repulsion terms. Thus the electrostatic energy is not just additive, it grows with the square of the numbers of particles and not linearly.

Let us assume for the moment that the energy content of matter consisting of $N$ particles is proportional to $-N^2$. The minus sign indicates that we have to spend energy in order to separate the particles. Two separate containers have total energy content of $-2N^2$. Next we pour the two containers together and get a system with $2N$ particles and hence and energy content of $-4N^2$. Thus by pouring the two containers together we have liberated an additional energy $2N^2$ which is enormous since $N$ is a huge number around $10^{26}$ for a liter of water. In such a situation, the ground state of the 'universe' would consist of a huge lump of charged particles sticking together. i.e., a world that looks very different from what we see. To summarize, 'stability of matter' means that the energy content of a lump of matter must be proportional to the number of particles. Thus, there must be a mechanism that beats somehow the quadratic dependence on the number of particles of the Coulomb energy. As we shall see the uncertainty principle for fermions will be that mechanism.

We call a physical quantity extensive if it is proportional to the number of particles involved. While there are other extensive quantities, such as the volume of the system, the free energy, the entropy etc. we shall concentrate on the ground state energy of the system and see later that the extensivity of all the other important quantities follow from this.

We are now ready to define the ground state energy of a quantum system consisting of $K$ nuclei and $N$ electrons. The electrons are **fermions** which will be key in our

investigation while the nuclei maybe fermions as well as bosons. Since their masses are by at least three orders of magnitudes heavier than the one of the electron we shall fix the nuclei at arbitrary positions $R_1, \ldots, R_K$. Let us add that the electrons carry an additional degree of freedom, called the spin. There are electrons with spin up and spin down, i.e., two kinds. It is often convenient to leave the number of spin states as a variable $q$. Thus, when filling up energy levels, we can fill $q$ electrons into the ground state and then $q$ electrons into the first excited and so on. We set

$$\Psi(x_1, \sigma_1; \ldots; x_N, \sigma_N)$$

and the normalization condition is now given by

$$\sum_{\sigma_1,\ldots,\sigma_N=1}^{q} \int |\Psi(x_1, \sigma_1; \ldots; x_N, \sigma_N)|^2 dx_1 \cdots dx_N = 1$$

We shall adopt the notation

$$\int dz = \sum_{\sigma} \int dx \ .$$

The one particle density will be given by

$$\rho_\Psi(x) = \sum_{\sigma_1,\ldots,\sigma_N=1}^{q} \int |\Psi(x, \sigma_1; \ldots; x_N, \sigma_N)|^2 dx_2 \cdots dx_N \ .$$

For such a functions $\Psi$ we have the kinetic energy

$$T_\Psi = \sum_{\sigma_1,\ldots,\sigma_N=1}^{q} \sum_j \int |\nabla_j \Psi(x_1, \sigma_1; \ldots; x_N, \sigma_N)|^2 dx_1 \cdots dx_N$$

and the potential energy

$$V_\Psi = \int V_{\mathrm{C}}(x_1, \ldots, x_N; R_1, \ldots, R_K) |\Psi(x, \sigma_1; \ldots; x_N, \sigma_N)|^2 dz_1 \cdots dz_N \ ,$$

the variable $R_1, dots, R_K$ we keeps fixed. Here

$$V_{\mathrm{C}}(x_1, \ldots, x_N; R_1, \ldots, R_K) = -\sum_{k=1,j=1}^{K,N} \frac{Z_k}{|x_j - R_k|} + \sum_{i<j}^{N} \frac{1}{|x_i - x_j|} + \sum_{k<l} \frac{Z_k Z_l}{|R_k - R_l|}$$

the first term being the attraction between the nuclei and elctrons (the charge number of nucleus $k$ is $Z_k$), the second term is the repulsion between the electrons and the third terms is the repulsion between the nuclei. The latter is jsut a function of the nuclear positions and does not take part in a dynamical fashion but nevertheless it will be an important term.

The ground state energy is defined by

$$E_0(N, K, R_1, \cdots R_K, q) :=$$

$$\inf\{T_\Psi+V_\Psi : \int |\Psi|^2 dz_1\cdots dz_N = 1, \Psi(z_1,\ldots,z_N) \text{ is antisymmetric in the particles labels}\}$$

Now we are ready to define the notion of stability:
We call

$$\inf_{R_1,\ldots,R_K} E_0(N,K,R_1,\cdots R_K,q) > -\infty$$

**stability of the first kind** and

$$\inf_{R_1,\ldots,R_K} E_0(N,K,R_1,\cdots R_K,q) > -C(Z_1,\ldots,Z_K,q)(N+K)$$

**stability of the second kind.**

While stability of the first kind was shown in the early sixties by Kato, stability of the second kind is much more difficult an it was proved by Freeman Dyson and Andrew Lenard around 1968. We shall present another proof due to Lieb and Thirring from the mid seventies which is much more conceptual and yields much better constants. It is one of the classical works that started the industry which we now call Quantum Coulomb systems.

# 9 Thomas-Fermi theory

The main reference for the topics discussed below is [LS]. We follow them with minor modifications. Another very good reference is the review article of [L].

Thomas-Fermi theory is motivated by semiclassical considerations and is given by a **density functional**

$$\mathcal{E}(\rho) = \frac{3}{5}\gamma \int \rho(x)^{5/3} dx + \int V(x)\rho(x)dx + \frac{1}{2}\int \frac{\rho(x)\rho(y)}{|x-y|} dxdy + U(\underline{R}) \ .$$

It was invented independently by Thomas [T] and fermi [F] as a simplified theory for describing atoms and molecules. We interpret $\rho$ as a density of electrons and $\lambda = \int rho(x)dx$ is the total number of electrons which, mathematically, does not have to be an integer. The first term in $\mathcal{E}$ is the kinetic energy, the second describes the attractive interaction of the electrons with the nuclei, which are fixed in space at the positions $\underline{R} = R_1, \ldots, R_K$

$$V(x) = -\sum_k \frac{Z_k}{|x - R_k|} \ .$$

The third term is the classical self energy of a charge distribution $\rho$ and describes the repulsion between the electrons. It is convenient to introduce the notation

$$D(\rho, \mu) = \frac{1}{2}\int \frac{\rho(x)\mu(y)}{|x-y|} dxdy$$

where $\rho$ and $\mu$ are any two chare distributions.

Finally,

$$U(\underline{R}) = \sum_{k<l} \frac{Z_k, Z_l}{|R_k - R_l|}$$

is the repulsive energy of the nuclei. Note that this quantity is just a number since the nuclei are nailed down at the positions $\underline{R}$ but it will be important later.

The ground state energy of $\mathcal{E}$ can be found by minimizing this functional over all densities $\rho$ with $\int \rho(x)dx = \lambda$ given. This theory has been investigated extensively by Lieb and Simon [LS]. They have clarified the relationship between the true quantum mechanical ground state and the Thomas-Fermi ground state. We shall content ourselves with aspects that are related to the problem of 'stability of matter' and leave the other topics aside. In particular we shall address two issues, the *existence of a minimizer* and the *no-binding theorem*.

It is natural to consider the TF-functional on the domain

$$\{\rho \in L^1(R^3) : \rho \in L^{5/3}, \rho(x) \gtrsim 0, \int \rho = \lambda\}$$

because, as we shall see, the functional is bounded below. However, this is not a good idea. Physical reasoning tells us that, most likely, not too many electrons can be bound to a nucleus since the repulsion will at one point dominate the attractive part of the Coulomb energy. Thus, there will not be a ground state for $\lambda$ large. A portion of the electrons will be deposited at infinity and another portion will stick to the nuclei. What that portion might be is a difficult question and can only be answered by solving the variational problem. With this in mind it is more reasonable to consider

$$\mathcal{D}_\lambda = \{\rho \in L^1(R^3) : \rho \in L^{5/3}, \rho(x) \gtrsim 0, \int \rho \gtrsim \lambda\}$$

as our domain on which the TF functional is defined. Our next goal will be to show that the TF functional is bounded below on this domain. In fact we will show that it is bounded below independently of $\lambda$.

**Theorem 24 (Lower bound on the Thomas-Fermi functional)** *The TF-functional is bounded below on $\mathcal{D}_\lambda$ uniformly in $\lambda$. More precisely we have the bound*

$$\mathcal{E}(\rho) \gtrsim -2^{1/3}\frac{3}{2}(\sum Z_k^2)^{1/3}(\sum Z_k)^{5/3} \ .$$

**Proof** Consider the potential associated with a positive charge uniformly distributed over a sphere of radius $R$. The potential is given by

$$\frac{1}{|x|} * \delta$$

where

$$\delta = \frac{1}{4\pi R^2}\delta(|x| - R) \ ,$$

and it is easily calculated to be

$$\min\{\frac{1}{|x|}, \frac{1}{R}\} \ .$$

Consider the potential

$$V_>(x) = -\sum_k Z_k \min\{\frac{1}{|x - R_k|}, \frac{1}{R}\} \ ,$$

which is a potential whose 'Coulomb tooth' has been pulled. It can be written as

$$V_>(x) = \frac{1}{|x|} * \mu$$

where

$$\mu = -\sum_k Z_k \frac{1}{4\pi R^2}\delta(|x - R_k| - R) \ .$$

Further define

$$V_<(x) = V(x) - V_>(x) \ ,$$

which is the 'Coulomb tooth'. First we combine the kinetic energy with the 'Coulomb tooth'

$$\frac{3}{5}\gamma\int\rho^{5/3}(x)dx-\int V_<(x)\rho(x)dx$$

and apply Hölder's inequality to the second term and get the lower bound

$$\frac{3}{5}\gamma\int\rho^{5/3}(x)dx-\|V_<\|_{5/2}\|\rho\|_{5/3}\ .$$

Optimizing over the variable $X=\|\rho\|_{5/3}$ yields

$$-\frac{2}{5}\frac{\int V_<(x)^{5/2}dx}{\gamma^{3/2}}>-\frac{4\pi}{5}(\sum_k Z_k)^{5/2}R^{1/2}\ ,$$

assuming the worst case in which all the nuclei are on top of each other. The rest of the TF-energy can be written as

$$2D(\rho,\mu)+D(\rho,\rho)+U(\underline{R})\ .$$

Note that

$$D(\mu,\mu)=\frac{1}{2}\sum_{k,l}Z_kZ_l\frac{1}{4\pi R^2}\int\min(\frac{1}{|x-R_k|},\frac{1}{R})\delta(|x-R_l|-R)dx$$

$$=\frac{1}{2}\sum_{k\neq l}Z_kZ_l\frac{1}{4\pi R^2}\int\min(\frac{1}{|x-R_k|},\frac{1}{R})\delta(|x-R_l|-R)dx+\frac{\sum_k Z_k^2}{R}$$

$$\gtrsim\sum_{k<l}\frac{Z_kZ_l}{|R_k-R_l|}+\frac{\sum_k Z_k^2}{R}\ .$$

Hence

$$2D(\rho,\mu)+D(\rho,\rho)+U(\underline{R})\gtrsim D(\rho+\mu,\rho+\mu)-\frac{\sum_k Z_k^2}{R}\ .$$

Now the self-energy of any charge distribution is always nonnegative. There are various ways to see that. One of them is to note that

$$\frac{1}{|x-y|}=const.\int\int\frac{1}{|x-z|^2}\frac{1}{|y-z|^2}dz$$

and hence

$$D(\rho+\mu,\rho+\mu)=\int dz|\frac{1}{|z|^2}*(\rho+\mu)|^2\gtrsim 0\ .$$

(Note that there is a subtle point concerning the interchange of integration). Thus

$$\mathcal{E}(\rho)\gtrsim-\frac{4\pi}{5}(\sum_k Z_k)^{5/2}R^{1/2}-\frac{\sum_k Z_k^2}{R}\ .$$

Since this bound holds for all values of $R$ we may maximize the right side over $R$ and obtain

$$\mathcal{E}(\rho) \gtrsim -2^{1/3}\frac{3}{2}(\sum Z_k^2)^{1/3}(\sum Z_k)^{5/3} .$$

Note that the bound, while not particularly good, yields in the case of one nucleus of charge $Z$ a bound of the form $-const.Z^{7/3}$ which, as we shall see, is the right order of magnitude. □

**Remark 25** Note that the only used that $\rho \in L^{5/3}$.

**Theorem 26 (Strict convexity of the TF- functional)** *The domain $\mathcal{D}_\lambda$ is convex and $\mathcal{E}(\rho)$ is a strictly convex functional on this domain*

**Proof** $\rho \to \int \rho^{5/3}(x)dx$ is strictly convex. The potential $\rho \to \int V(x)\rho(x)dx$ is linear and the Coulomb self-energy is also convex. The latter statement can be seen as follows. Since $D(\rho, rho)$ is positive for any charge distribution the Schwarz inequality for Coulomb energies holds

$$|D(\rho,\mu)|^2 \gtrsim D(\rho,\rho)D(\mu,\mu) .$$

From this we get that

$$D(\alpha\rho_1+(1-\alpha)\rho_2, \alpha\rho_1+(1-\alpha)\rho_2) = \alpha^2 D(\rho_1,\rho_1)+(1-\alpha)^2 D(\rho_2,\rho_2)+2\alpha(1-\alpha)D(\rho_1,\rho_2) .$$

But

$$2D(\rho_1,\rho_2) \gtrsim D(\rho_1,\rho_1) + D(\rho_2,\rho_2)$$

which when combined with the previous inequality yields convexity. Our next theorem is the main existence theorem for minimizers. □

**Theorem 27 Existence of minimizer**
*There exists a unique $\rho_0 \in \mathcal{D}_\lambda$ such that*

$$\mathcal{E}(\rho_0) = E(\lambda) := \inf\{\mathcal{E}(\rho) : \rho \in \mathcal{D}_\lambda\}$$

**Proof** Let $\rho_j$ be a minimizing sequence in $\mathcal{D}_\lambda$. We see from the previous Theorem concerning the lower bound, or rather its proof that

$$\int \rho_j(x)^{5/3}dx \gtrsim C$$

for some constant $C$ independent of $j$. Hence there exists $\rho_0$ such that

$$\rho_j \rightharpoonup \rho_0$$

weakly in $L^{5/3}$. By the weak lower semi continuity of the norm

$$\liminf \int \rho_j^{5/3}(x)dx \gtrsim \int \rho_0^{5/3}(x)dx . \tag{1}$$

Further $\rho_0 \in \mathcal{D}_\lambda$, i.e., $\rho_0(x) \gtrsim 0$ and $\int \rho_0(x)dx \gtrsim \lambda$. The first follows from the fact that for any positive function $f \in L^{5/2}$

$$\int \rho_0(x)f(x)dx = \lim_{j\to\infty} \int \rho_j(x)f(x)dx \gtrsim 0 \ ,$$

and for the second we assume the contrary, that $\int_0 \rho_0(x)dx > \lambda$. There exists a set $A$ of finite measure so that

$$\int \rho_0(x)\chi_A(x)dx > \lambda$$

where, as usual, $\chi_A$ is the characteristic function of the set $A$. Since $A$ has finite measure, $\chi_A \in L^{5/3}$ and hence

$$\int \rho_0(x)\chi_A(x)dx = \lim_{j\to\infty} \int \rho_j(x)\chi_A(x)dx \gtrsim \lambda \ .$$

Likewise, $D(\rho_j, \rho_j)$ is also a bounded sequence. Moreover, for any $\rho \in L^{5/3} \cap L^1$ we have that

$$D(\rho_j, \rho) \to D(\rho_0, \rho) \ . \tag{2}$$

To see this we note that

$$\frac{1}{|x|} * \rho(x) = \int_{|x-y|<1} \frac{1}{|x-y|}\rho(y)dy + \int_{|y|\gtrsim 1} \frac{1}{|y|}\rho(x-y)dy = f_1 + f_2 \ .$$

By Young's inequality

$$\|f_1\|_\infty \gtrsim \|\frac{1}{|x|}\chi_{|x|<1}\|_{5/2}\|\rho\|_{5/3} \ .$$

and

$$\|f_1\|_1 \gtrsim \|\frac{1}{|x|}\chi_{|x|<1}\|_1\|\rho\|_1 \ .$$

Further,

$$\|f_2\|_q \gtrsim \|\frac{1}{|x|}\chi_{|x|>1}\|_q\|\rho\|_1$$

for all $q > 3$. Hence $f_1 + f_2 \in L^q$ for all $q > 3$. The dual of this space is $L^{q'}$ with $q' < 3/2$ and since $\rho_j \in L^1 \cap L^{5/3}$ we may assume that $\rho_j \rightharpoonup \rho_0$ weakly in $L^{q'}$ for some $q' < 3/2$. This proves (2). Further

$$D(\rho_0, \rho_0) = \lim_{j\to\infty} D(\rho_j, \rho_0) \gtrsim \liminf D(\rho_j, \rho_j)^{1/2} D(\rho_0, \rho_0)^{1/2}$$

which proves that

$$\liminf D(\rho_j, \rho_j) \gtrsim D(\rho_0, \rho_0) \ . \tag{3}$$

The potential term is weakly continuous. Write it as

$$\int V(x)\rho_j(x)dx = \int V_<(x)\rho_j(x)dx + \int V_>(x)\rho_j(x)dx$$

and note that $V_< \in L^{5/2}$ and $V_> \in L^q$ for all $q > 3$. Since $\rho_j$ converges weakly to $\rho_0$ in $L^{5/3}$ we see that the first term converges to

$$\int V_<(x)\rho_0(x)dx$$

and, moreover, since $\rho_j$ converges weakly to $\rho_0$ in $L^{q'}$ for some $q' < 3/2$ we get that

$$\lim_{j\to\infty} \int V(x)\rho_j(x)dx = \int V(x)\rho_0(x)dx \tag{4}$$

The existence of a minimizer now follows from (1), (3) and (4). The uniqueness follows from the strict convexity of $\mathcal{E}(\rho)$. □

**Theorem 28 Properties of** $E(\lambda)$ *The function* $E(\lambda)$ *is convex, non-increasing and bounded below.*

**Proof** Fix $\lambda_1$ and $\lambda_2$ and denote by $\rho_1$ and $\rho_2$ the corresponding minimizers. Then for any $0 \gtrsim \alpha \gtrsim 1$

$$E(\alpha\lambda_1+(1-\alpha)\lambda_2) \gtrsim \mathcal{E}(\alpha\rho_1+(1-\alpha)\rho_2) \gtrsim \alpha\mathcal{E}(\rho_1)+(1-\alpha)\mathcal{E}(\rho_2) = \alpha E(\lambda_1)+(1-\alpha)E(\lambda_2)\,.$$

Note that there is a strict sign in the second inequality unless $\rho_1 = \rho_2$. Since nothing is known about $\rho_1$ and $\rho_2$ they might be identical. Further, $E(\lambda$ is non increasing since we may always deposit parts of the electrons at infinity without increasing the energy of the others. □

Since $E(\lambda)$ is decreasing and bounded below, It makes sense to define $\lambda_c$ by

$$\lambda_c = \inf\{\lambda; E(\lambda) = E(\infty)\}\,.$$

Note that the value $\lambda_c$ might be infinity.

**Theorem 29** *For* $\lambda \gtrsim \lambda_c$ *there exists a unique minimizer* $\rho_\lambda$ *with the property that*

$$E(\lambda) = \mathcal{E}(\rho_\lambda)$$

*and with*

$$\int \rho_\lambda(x)dx = \lambda\,.$$

*Moreover, on* $[0, \lambda_c]$ *the function* $E(\lambda)$ *is strictly convex and strictly decreasing. If* $\lambda_c < \infty$ *and* $\lambda > \lambda_c$ *there is no minimizer* $\rho_\lambda$ *with* $\int \rho_\lambda(x)dx = \lambda$*. In particular, the unique function* $\rho_c$ *with* $\int \rho_c dx \gtrsim \lambda$ *is the unique minimizer of the energy satisfying* $\int \rho_c dx = \lambda_c$*.*

**Proof** Pick any $\lambda \gtrsim \lambda_c$ and consider the associated minimizer $\rho_\lambda$. If $\int \rho_\lambda(x)dx = \lambda' < \lambda$ then $E(\lambda) = E(\lambda')$ which would mean that $\lambda' \gtrsim \lambda_c \gtrsim \lambda$. The strict convexity of $E(\lambda)$

on the interval $[0, \lambda_c]$ is now obvious. If $\lambda > \lambda_c$ and if there were a minimizer $\rho_\lambda$ with $\int \rho_\lambda(x)dx = \lambda$ then choosing

$$\frac{1}{2}(\rho_{\lambda_c} + \rho_\lambda)$$

as a trial function we get

$$E(\lambda_c) = E(\frac{\lambda + \lambda_c}{2}) < \frac{E(\lambda) + E(\lambda_c)}{2} = E(\lambda_c) \ ,$$

a contradiction. Note that $\rho_\lambda \neq \rho_{\lambda_c}$. This argument also shows that $E(\lambda) = E(\lambda_c)$ for $\lambda \gtrsim \lambda_c$, provided that $\lambda_c$ is finite. The next step is to derive the TF-equation. **Theorem: TF-equation** *Assume that $\lambda \gtrsim \lambda_c$. Then there exists a constant $\mu$ so that the unique minimizer $\rho_\lambda$ satisfies the equation*

$$\gamma \rho_\lambda^{2/3}(x) = \left[ -V(x) - \frac{1}{|x|} * \rho_\lambda - \mu \right]_+ \ .$$

*In general $\mu(\lambda) \gtrsim 0$ but if $\lambda = \lambda_c$ then $\mu = 0$.* Pick any $\rho \gtrsim 0$ and note that $\rho_t = (1-t)\rho_\lambda + t\rho$ satisfies $\int \rho_t(x)dx = \lambda$. Hence

$$F(t) := \mathcal{E}(\rho_t) \gtrsim F(0) = E(\lambda)$$

and

$$0 \gtrsim \lim_{t \to 0, t \gtrsim 0} \frac{F(t) - F(0)}{t} = \int (\gamma \rho_\lambda^{2/3}(x) + V(x) + \frac{1}{|x|} * \rho_\lambda)(\rho - \rho_\lambda)dx \ .$$

For $\delta > 0$ fixed consider the function

$$\rho = \rho_\lambda + \varepsilon f \chi_{\rho_\lambda > \delta}$$

where $f$ is any function that satisfies

$$\int_{\rho_\lambda > \delta} f dx = 0$$

and $\varepsilon$ small enough so that $\rho \gtrsim 0$. With this choice we get

$$\int_{\rho_\lambda > \delta} (\gamma \rho_\lambda^{2/3}(x) + V(x) + \frac{1}{|x|} * \rho_\lambda) f dx = 0$$

for all functions $f$ with

$$\int_{\rho_\lambda > \delta} f dx = 0 \ .$$

Hence there exists a constant $\mu$ so that

$$\gamma \rho_\lambda^{2/3}(x) + V(x) + \frac{1}{|x|} * \rho_\lambda = -\mu \ ,$$

on the set $\{\rho_\lambda > \delta\}$. Next we choose

$$\rho = \rho_\lambda + \varepsilon f$$

with $f \gtrsim 0$ on the set $\{\rho_\lambda = 0\}$ and $\int f dx = 0$. Here $\varepsilon \gtrsim 0$ in order for $\rho \gtrsim 0$. Hence,

$$\int (\gamma \rho_\lambda^{2/3}(x) + V(x) + \frac{1}{|x|} * \rho_\lambda) f dx \gtrsim 0$$

and since on the set $\{\rho_\lambda > 0\}$ (5) is satisfied

$$-\mu \int_{\rho_\lambda > 0} f dx + \int_{\rho_\lambda = 0} (\gamma \rho_\lambda^{2/3}(x) + V(x) + \frac{1}{|x|} * \rho_\lambda) f dx \gtrsim 0 \, .$$

Since $\int f dx = 0$ we conclude that, on the set $\{\rho_\lambda = 0\}$

$$\gamma \rho_\lambda^{2/3}(x) + V(x) + \frac{1}{|x|} * \rho_\lambda + \mu \gtrsim 0 \, .$$

To summarize, on the set $\{\rho_\lambda = 0\}$

$$-V(x) - \frac{1}{|x|} * \rho_\lambda - \mu \gtrsim 0$$

and on the set $\{\rho_\lambda > 0\}$

$$\gamma \rho_\lambda^{2/3}(x) = -V(x) - \frac{1}{|x|} * \rho_\lambda - \mu \, .$$

These two terms can be concatenated into the form

$$\gamma \rho_\lambda^{2/3}(x) = \left[ -V(x) - \frac{1}{|x|} * \rho_\lambda - \mu \right]_+ \, .$$

The case $\lambda = \lambda_c$ does not need any constraint and hence $\mu = 0$. Since both $V$ and $(1/|x|) * \rho_\lambda \to 0$ as $|x| \to \infty$ we get that $\mu \gtrsim 0$ for otherwise $\rho$ would not decay to zero at infinity. □

**Theorem 30** *Fix $\lambda < \infty$ and $\lambda \gtrsim \lambda_c$. Then the potential*

$$\phi(x) = -V(x) - \frac{1}{|x|} * \rho_\lambda(x)$$

*is non-negative.*

**Proof** Poisson's equation says that

$$\Delta \phi = \rho_\lambda$$

and

$$\phi(x) \approx \frac{Z_k}{|x - R_k|} \, , \text{as } x \to R_k \, .$$

Using the TF-equation

$$\Delta\phi = \frac{1}{\gamma^{3/2}}\left[\phi(x) - \mu\right]_+ \tag{5}$$

Since $\rho \in L^1 \cap L^{5/3}$ it follows that $\phi(x)$ is continuous away from the positions of the nuclei. To see this write

$$\frac{1}{|x|} = \frac{1}{|x|}\zeta(x) + \frac{1}{|x|}\overline{\zeta}(x)$$

where $\zeta(x)$ is an infinitely differentiable function with compact support and identically one near the origin and $\overline{\zeta} = 1 - \zeta$ has therefore support away from the origin. The first function is in the dual of $L^{5/3}$ and hence

$$\frac{1}{|x|}\zeta * \rho_\lambda$$

is continuous. Further, since $\rho_\lambda \in L^1$ the function

$$\frac{1}{|x|}\overline{\zeta} * \rho_\lambda$$

is infinitely often differentiable. Next, consider the set

$$A = \{x : \phi(x) < 0\}$$

which is an open set. This set may be empty or non-empty. Since $\mu \gtrsim 0$ it follows from (5) that $\phi$ is harmonic on $A$. This is so, since $\phi$ diverges to infinity at the position of the nuclei. Hence the these positions are not in $A$. Further, as $|x| \to \infty$, $\phi(x) \to 0$. Hence, $\phi$ vanishes on the bundary of $A$. Since $\phi$ is harmonic in $A$, $\phi = 0$ identically in $A$ which means that $A$ is the empty set. □

**Theorem 31** *We have that*

$$\lambda_c = Z := \sum_k Z_k \ .$$

**Proof** Assume that $\lambda_c > Z$ and pick $Z < \lambda < \lambda_c$. Then, since $\phi(x) \gtrsim 0$ we find after taking the average over a spher of radius $r$ sufficiently large that

$$\frac{Z}{r} - \int \min\{\frac{1}{r}, \frac{1}{|y|}\}\rho_\lambda(y)dy \gtrsim 0$$

and in particular

$$\frac{Z}{r} - \frac{1}{r}\int_{|y|<r} \rho_\lambda(y)dy \gtrsim 0 \ ,$$

or

$$Z - \int_{|y|<r} \rho_\lambda(y)dy \gtrsim 0$$

for all $r$ sufficiently large. This means that $Z \gtrsim \lambda$, contradicting our assumption and hence $\lambda_c \gtrsim Z$. Next, assume that $\lambda_c < Z$. Taking again spherical averages we learn, using Jensen's inequality that

$$\gamma \left[\frac{1}{4\pi}\int_{S^2} \rho_c(r\omega)d\omega\right]^{2/3} \gtrsim \gamma \frac{1}{4\pi}\int_{S^2} \rho_c^{2/3}(r\omega)d\omega$$

$$= \frac{Z}{r} - \int \min\{\frac{1}{r}, \frac{1}{|y|}\}\rho_\lambda(y)dy \gtrsim \frac{Z}{r} - \frac{1}{r}\int \rho_\lambda(y)dy \gtrsim \frac{q}{r}$$

for $r$ sufficiently large and some fixed number $q > 0$. Thus,

$$\frac{1}{4\pi}\int_{S^2} \rho_c(r\omega)d\omega \gtrsim (\frac{q}{\gamma r})^{3/2}$$

which is not integrable, not even in $L^{5/3}$. □

*To summarize, the energy $E(\lambda)$ is a monotone decreasing function. It is strictly monotone decreasing for $\lambda \leq Z$ and constant for $\lambda \gtrsim Z$. It is strictly convex for $\lambda \gtrsim Z$. Finally, for every $\lambda \gtrsim Z$ there exists a unique minimizer $\rho_\lambda$ satisfying $\int \rho_\lambda dx = \lambda$. For $\lambda > Z$ there is no minimizer satisfying $\int \rho_\lambda dx = \lambda$. In other words any minimizer with $\int \rho_\lambda dx \gtrsim \lambda$ is given by $\rho_Z$.*

An interesting special case is TF-theory of a single atom.

**Theorem 32 Virial theorem**

*Assume $\lambda \gtrsim Z$. The minimizer satisfies the relations*

$$\gamma \int \rho_\lambda^{5/3}(x)dx + \int V(x)\rho_\lambda(x)dx + 2D(\rho_\lambda, \rho_\lambda) = \mu \int \rho_\lambda(x)dx \ ,$$

*and for a single atom we have the additional relation*

$$2\frac{3}{5}\gamma \int \rho_\lambda^{5/3}(x)dx + \int V(x)\rho_\lambda(x)dx + D(\rho_\lambda, \rho_\lambda) = 0 \ .$$

*In particular we get in the neutral case*

$$\frac{3}{5}\gamma \int \rho_\lambda^{5/3}(x)dx = -E(Z) \ , \ \int V(x)\rho_\lambda(x)dx = \frac{7}{3}E(Z) \ , \ D(\rho_\lambda, \rho_\lambda) = -\frac{1}{3}E(Z) \ .$$

**Proof** The first relation follows by multiplying the TF-equation by $\rho_\lambda$ and integrating. For the other, scale he minimizer $\rho_\lambda(x) \to f_s(x) = s^3\rho_\lambda(sx)$ so that $\int f_s(x)dx = \lambda$. A simple calculation leads to

$$\mathcal{E}(f_s) = s^2\frac{3}{5}\gamma \int \rho_\lambda^{5/3}(x)dx + s\int V(x)\rho_\lambda(x)dx + sD(\rho_\lambda, \rho_\lambda) \ .$$

Since $\mathcal{E}(f_s) \gtrsim E(\lambda)$ differentiating with respect to $s$ at $s = 1$ yields the result. □

**Theorem 33** *In the single atom case, i.e., $V(x) = -Z/|x|$, set $\rho_Z(x) = Z^2\overline{\rho}(Z^{1/3}x)$. Then $\overline{\rho}$ is the minimizer of the problem*

$$e = \inf\{\frac{3}{5}\int \rho^{5/3}(x)dx - \int \frac{1}{|x|}\rho(x)dx + D(\rho,\rho) : \int \rho dx = 1\} \ . \tag{6}$$

*The value of $e = -3.678$ and*

$$E(Z) = -3.678\frac{Z^{7/3}}{\gamma} \ .$$

**Proof** Write $\rho_Z(x) = al^3\overline{\rho}(lx)$ and calculate

$$\mathcal{E}(\rho_Z(x)) = a^{5/3}l^2\frac{3}{5}\gamma\int \overline{\rho}^{5/3}(x)dx - Zal\int \frac{1}{|x|}\overline{\rho}(x)dx + a^2lD(\overline{\rho},\overline{\rho}(lx)) \ .$$

Setting

$$a^{5/3}l^2\gamma = Zal = a^2l$$

yields $a = Z$, $l = Z^{1/3}/\gamma$ and for the energy

$$E(Z) = \frac{Z^{7/3}}{\gamma}e$$

where $e$ is given by (6). The number given in the theorem is a numerical calculation. □

Since $\mathcal{D}_\lambda$ is convex, $t\rho + (1-t)\rho_0 \in \mathcal{D}_\lambda$ for $0 \gtrsim t \gtrsim 1$ and since

$$\mathcal{E}(t\rho + (1-t)\rho_0) \gtrsim \mathcal{E}(\rho_0)$$

differentiating with respect to $t$ at $t = 0$ yields

$$\int \left[\gamma\rho_0^{2/3}(x) + V(x) + \frac{1}{|x|} * \rho_0(x)\right](\rho(x) - \rho_0(x))dx \gtrsim 0$$

for all functions $\rho \in \mathcal{D}_\lambda$.

# 10 The no-binding theorem and stability

The no-binding theorem states, loosely speaking that atoms do not bind in TF-theory. Group the nuclei into two groups, the $A$-group and the $B$-group. Denote

$$m_A = \sum_{k\in A} Z_k\delta(x-R_k)\ ,\ m_B = \sum_{k\in B} Z_k\delta(x-R_k)$$

so that

$$V_A(x) := -\sum_{k\in A}\frac{Z_k}{|x-R_k|} = -\frac{1}{|x|} * m_A\ ,\ V_B(x) := -\sum_{k\in B}\frac{Z_k}{|x-R_k|} = -\frac{1}{|x|} * m_B\ .$$

We are now considering three systems the systems

$$\mathcal{E}_A(\rho) = \frac{3}{5}\gamma\int\rho^{5/3}(x)dx + \int V_A(x)\rho(x) + D(\rho,\rho) + \sum_{k<l\in A}\frac{Z_kZ_l}{|R_k-R_l|}$$

and $\mathcal{E}_B(\rho)$ is defined similarly. The third system is the combined system

$$\mathcal{E}(\rho) = \frac{3}{5}\gamma\int\rho^{5/3}(x)dx + \int V(x)\rho(x) + D(\rho,\rho) + \sum_{k<l}\frac{Z_kZ_l}{|R_k-R_l|}\ .$$

Using the above notation we can write the above energies in the form

$$\mathcal{E}_A(\rho) = \frac{3}{5}\gamma\int\rho^{5/3}(x)dx - 2D(m_A,\rho) + D(\rho,\rho) + \sum_{k<l\in A}\frac{Z_kZ_l}{|R_k-R_l|}$$

and likewise $\mathcal{E}_B$. Denote the corresponding ground state energies by $E_A(\lambda)$, $E_B(\lambda)$ and $E(\lambda)$. The goal is to show that the if we divide up the total electronic charge and distribute them over the subsystems in a suitable fashion and push these systems infinitely far apart, the sum of these energies is less than the energy to start with. More precisely we have

**Theorem 34 (No-binding)** *Assume that $\lambda \le Z = \sum Z_k$. Then*

$$\inf\{E_A(\lambda_1) + E_B(\lambda_2) : \lambda_1+\lambda_2 = \lambda\} \le E(\lambda)\ .$$

This theorem was discovered by Teller. The general proof was given in [LS] and the version we present here is due to Baxter and can also be found in [L].

**Proof** Since $\lambda \gtrsim Z$ we know that we have a minimizer $\rho$ of the total system with $\int \rho(x)dx = \lambda$. The goal is to find $g$ and $h$ both nonnegative such that $g + h = \rho$ and

$$\mathcal{E}_A(g) + \mathcal{E}_B(h) \gtrsim \mathcal{E}(\rho) = E(\lambda) \; .$$

Since $a^{5/3} + b^{5/3} \gtrsim (a+b)^{5/3}$ for nonnegative numbers $a, b$ we have that

$$\int g^{5/3}dx + \int h^{5/3}(x)dx \gtrsim \int \rho^{5/3}dx$$

which goes in the right direction. Thus the proof of the no binding theorem is reduced to comparing Coulomb potentials. For any $g, h$ nonnegative with $g + h = \rho$ the sum of the Coulomb energies of the subsystems is given by

$$-2D(m_A, g) + D(g, g) + \sum_{k<l\in A} \frac{Z_k Z_l}{|R_k - R_l|} - 2D(m_B, h) + D(h, h) \sum_{k<l\in B} \frac{Z_k Z_l}{|R_k - R_l|}$$

which has to be compared with

$$-2D(m_A + m_B, g + h) + D(g + h, g + h) + \sum_{k<l} \frac{Z_k Z_l}{|R_k - R_l|} \; .$$

Thus, we have to find $g$ and $h$ so that

$$0 \gtrsim -2D(m_A, h) - 2D(m_B, g) + 2D(g, h) + \sum_{k\in A \; , l\in B} \frac{Z_k Z_l}{|R_k - R_l|}$$

The last term can be written as

$$2D(m_A, m_B)$$

and hence we have to find $g, h$ nonnegative with $g + h = \rho$ such that

$$2D(g - m_A, h - m_B) \lesssim 0 \; .$$

The following Lemma is a very special case of a Lemma of Baxter.

**Theorem 35 (Lemma, Baxter)** *Assume that $\rho \in L^p \cap L^1$, $p > 3/2$. There exists $g$ with $0 \gtrsim g \gtrsim \rho$ so that*

$$\frac{1}{|x|} * g \gtrsim \frac{1}{|x|} * m_A$$

*everywhere. Moreover,*

$$\frac{1}{|x|} * g = \frac{1}{|x|} * m_A \text{ on } \{x : g < \rho\} \; .$$

With the help of Baxter's lemma we can immediately finish the proof of the no-binding theorem since

$$2D(g - m_A, h - m_B) = \int \left[\frac{1}{|x|} * g - \frac{1}{|x|} * m_A\right] (h - m_B)dx$$

$$= \int_{g<\rho} \left[ \frac{1}{|x|} * g - \frac{1}{|x|} * m_A \right] (h - m_B) dx + \int_{g=\rho} \left[ \frac{1}{|x|} * g - \frac{1}{|x|} * m_A \right] (h - m_B) dx$$

$$= - \int_{h=0} \left[ \frac{1}{|x|} * g - \frac{1}{|x|} * m_A \right] m_B dx \gtrsim 0 \ .$$

**Proof** We follow [L]: Consider the problem of minimizing

$$D(g,g) - \int g \frac{1}{|x|} * m_A$$

subject to the constraint that $0 \lesssim g \lesssim \rho$. Notice that this is a convex minimization problem. Moreover, Since $\rho \in L^p \cap L^1$ we have that

$$\int g \frac{1}{|x|} * m_A = \int \frac{1}{|x|} * g m_A = \sum_{k \in A} \frac{1}{|x|} * g(R_k) \gtrsim \sum_{k \in A} \frac{1}{|x|} * \rho(R_k) < \infty \ .$$

Hence the functional is bounded below. Next we write

$$\frac{1}{|x|} = \frac{1}{|x|} \zeta(x) + \frac{1}{|x|} (1 - \zeta(x))$$

where $\zeta$ is a smooth function of compact supprt, identically equals to $1$ in the vicinity of the origin. In other words we split the Coulomb potential into two pieces, the first is in $L^q$ for all $1 \lesssim q < 3/2$ and the second is in $L^r$ for all $r > 3/2$.

Let $g_j$ be a minimizing sequence. Since $0 \lesssim g_j \lesssim \rho$ this sequence is bounded in $L^p$. Thus there exists a subsequence (again denoted by $g_j$) which converges to some function $g$ weakly in $L^p$. Hence

$$\frac{1}{|x|} \zeta * g_j \to \frac{1}{|x|} \zeta * g$$

pointwise since $\frac{1}{|x|}\zeta$ is in the dual of $L^p$. Since $\rho \in L^1$ we can extract a further subsequence so that $g_j$ converges weakly to $g$ in some $L^s$ space dual to $L^r$. This ensures that

$$\frac{1}{|x|} (1 - \zeta) * g_j \to \frac{1}{|x|} (1 - \zeta) * g$$

and hence

$$\int g_j \frac{1}{|x|} * m_A \to \int g \frac{1}{|x|} * m_A \ .$$

Since $D(g,g)$ is weakly lower semicontinuous we have that

$$\liminf D(g_j, g_j) \gtrsim D(g,g) \ .$$

The fact that $0 \lesssim g \lesssim \rho$ is left as a simple exercise. Thus the minimizer $g$ exists. Note, that since $g \in L^p \cap L^1$ we know that $\frac{1}{|x|} * g$ is a continuous function which vanishes at $\infty$. Using the calculus of variation we learn that

$$\frac{1}{|x|} * g = \frac{1}{|x|} * m_A \text{ on } \{x : 0 < g(x) < \rho(x)\}$$

$$\frac{1}{|x|} * g \gtrsim \frac{1}{|x|} * m_A \text{ on } \{x : g(x) = \rho(x)\}$$

$$\frac{1}{|x|} * g \lesssim \frac{1}{|x|} * m_A \text{ on } \{x : g(x) = 0\}$$

Consider the set

$$P := \{x : \frac{1}{|x|} * g - \frac{1}{|x|} * m_A > 0\}$$

This set is open since $\frac{1}{|x|} * g$ is continous and $P$ does not contain the points $R_k, k \in A$. The function $\frac{1}{|x|} * g$ vanishes on the boundary of $P$ since $\frac{1}{|x|} * g$ tends to zero at infinity. Finally, $P$ it is a subset of $\{x : g(x) = 0\}$. On $P$ we have

$$\Delta[\frac{1}{|x|} * g - \frac{1}{|x|} * m_A] = -g$$

Hence

$$[\frac{1}{|x|} * g - \frac{1}{|x|} * m_A]$$

is harmonic. Since it vanishes on the boundary it must vanish in $P$ and hence $P$ is empty. □

An immediate corollary from the no-binding theorem is the following electrostatic inequality.

**Corrolary 36** *For any nonnegative function $\rho \in L^{5/3}$ and for any positions $R_1, \ldots, R_K$*

$$\frac{3}{5}\gamma \int \rho^{5/3}(x)dx - \sum Z_k \int \frac{1}{|x - R_k|}\rho(x)dx + D(\rho, \rho) + \sum_{k<l} \frac{Z_k Z_l}{|R_k - R_l|} \gtrsim -\frac{3.678}{\gamma} \sum_k Z_k^{7/3}$$

**Proof** We are now ready to apply TF-theory to the problem of stability of matter. There are two terms in the Hamiltonian that are not expressed in terms of the one particle density, the kinetic energy and the Coulomb repulsion among the electrons. The former was dealt with when we considered the Lieb-Thirring inequalities and now we deal with the second problem. Again, we follow Lieb and Thirring [LT]. We consider the previous Corollary but with the positions of the nuclei replaced by the positions of the electrons, in other words we have for any $\rho$ and all positions $x_1, \ldots, x_N$

$$\sum_{i<j} \frac{1}{|x_i - x_j|} \gtrsim -\frac{3}{5}\varepsilon \int \rho^{5/3}(x)dx + \sum_j \int \frac{1}{|x - x_j|}\rho(x)dx - D(\rho, \rho) - \frac{3.678}{\varepsilon}N \ .$$

Here, $\varepsilon > 0$ is an arbitrary parameter. Multipying this inequality with $|\Psi(x_1, \ldots, x_N)|^2$, replacing $\rho$ by $\rho_\Psi$ and integrating over all variables we learn that

$$\sum_{i<j} \int \frac{|\Psi(x_1, \ldots, x_N)|^2}{|x_i - x_j|} dx_1 \cdots dx_N - D(\rho_\Psi, \rho_\Psi)$$

$$\gtrsim -\frac{3}{5}\varepsilon \int \rho_\Psi^{5/3}(x)dx - \frac{3.678}{\varepsilon}N \ . \tag{1}$$

We could optimize over $\varepsilon$ to get the lower bound

$$-2(\frac{3.678\times 3}{5})^{1/2}\sqrt{N}\sqrt{\int \rho_\Psi^{5/3}(x)dx}$$

but we prefer the first version. The difference between the true Coulomb repulsion and the the electrostatic repulsion of the single particle density is called the indirect term.

Using the LT -inequality we know that for any antisymmetric function $\Psi$

$$T_\Psi \gtrsim \frac{3}{5}(\frac{2}{5L})^{2/3}\int \rho_\Psi^{5/3}(x)dx$$

where $L$ is the sharp constant in the inequality that estimates the sum of the negative eigenvalues. Combining this with (1) we learn that the true quantum energy is bounded below by

$$\frac{3}{5}\left[(\frac{2}{5L})^{2/3}-\varepsilon\right]\int \rho_\Psi^{5/3}(x)dx - \sum_k Z_k \int \frac{1}{|x-R_k|}\rho_\Psi(x)dx + D(\rho_\Psi,\rho_\Psi)$$

$$+\sum_{k<l}\frac{Z_kZ_l}{|R_k-R_l|} - \frac{3.678}{\varepsilon}N \ .$$

Using once more the no-binding theorem and the numerical value of the minimum energy of a single atom we get

$$E_0(N,K) \gtrsim -3.678\left[\frac{\sum_k Z_k^{7/3}}{(\frac{2}{5L})^{2/3}-\varepsilon} - \frac{N}{\varepsilon}\right] \ .$$

Optimizing over $\varepsilon$ yields

$$-3.678(\frac{5}{2})^{2/3}L^{2/3}\left[(\sum_k Z_k^{7/3})^{1/2}+\sqrt{N}\right]^2 \ .$$

Using the bound

$$L \gtrsim \frac{4}{15\pi}$$

which was obtained in the chapter on the Birman-Schwinger principle we get the numerical value

$$-1.309\left[(\sum_k Z_k^{7/3})^{1/2}+\sqrt{N}\right]^2 \ .$$

In the case where all the nuclei have the same charge the true QM ground state energy is bounded below by

$$-2.618Z^{7/3}(N+K) \ .$$

in units of four Rydbergs.

So far we have neglected spin. The electron has an additional degree of freedom namely there are electrons with spin 'up' and spin 'down'. Of course the state of an electron can be in any superposition of the two. This leads to consider wave functions

$$\Psi(x_1, \sigma_1; \ldots, , x_N, \sigma_N)$$

which are antisymmetric under exchange of the particle label. We shall assume that the $\sigma$'s take values in the set $\{1, \ldots, q\}$ where $q$ is an integer. The only term in the Hamiltonian that is really sensitive to the spin is the kinetic energy term. Consider the problem of filling up the energy levels of a single particle Hamiltonian with fermions that have $q$ spin degrees of freedom. The first $q$ paricles sit in the ground state, the next $q$ in the first excited etc. If we return to the proof of the fermion uncertainty pprinciple for such kind of wave functions we have to consider filling up the levels of the Hamiltonian

$$-\Delta - c\rho_\Psi^{2/3}(x) \ .$$

Chasing through the proof we get that for any wave function $\Phi$ that has $q$ spin degrees of freedom

$$T_\Phi - c\int \rho_\Psi^{2/3}(x)\rho_\Phi(x)dx \gtrsim -q\sum_{k=1}^{[\frac{N}{q}]}\lambda_k$$

which in turn can be estimated by the LT-inequality and we obtain

$$T_\Phi - c\int \rho_\Psi^{2/3}(x)\rho_\Phi(x)dx \gtrsim -qLc^{5/2}\int \rho_\Psi^{5/3}(x)dx$$

so that

$$T_\Psi \gtrsim \frac{3}{5}(\frac{2}{5qL})^{2/3}\int \rho_\Psi^{5/3}(x)dx \ .$$

Thus we have to augment in all our estimates the LT-constant by a factor of $q$. With this we get the lower bound on the true quantum energy to be

$$-4.156Z^{7/3}(N+K) \ ,$$

which in the case of hydrogen ($Z = 1$) is about 17 Rydbergs per atom. One would expect about 1 Rydberg per atom. □

# 11 Improved constants

In recent years there have been further results concerning optimal constants in the Lieb-Thirring inequality. As it was mantioned before, the most important imequalities concerning stability of matter are the estimates on the sum of the eigenvalues and also on the sum of square roots of the eigenvalues. Without going too much into details we mention here an approach due to Laptev and Weidl [LW] using matrix valued potentials. We consider Schrödinger operators of the form

$$H = -\frac{d^2}{dx^2} \otimes I - U(x)$$

where $U(x)$ is for every $x \in R$ a positive hermitean $n \times n$ matrix and $I$ is he $n \times n$ identity matrix. Recall that an hermitean matrix $A$ is positive if for every vector $x \in C^n$

$$\langle x, Ax \rangle \gtrsim 0$$

where $\langle \cdot, \cdot \rangle$ denotes the inner product on $C^n$. The operator $H$ acts on vectors where each component is a function of the variable $x$. We assume that the potential matrix is nice in the sense that the entries are smooth functions with compact support. This is not really a restriction but avoids technicalities. We consider the operaor $H$ on $L^2(R; C^n)$. Like in the case of a scalar valued potential we consider the eigenvalues and arrange them in increasing order. The lowest eigenvalue is defined by minimizing

$$\int \langle \psi'(x), \psi'(x) \rangle dx - \int \langle \psi(x), U(x)\psi(x) \rangle dx$$

subject to the constraint

$$\int \langle \psi(x), \psi(x) \rangle dx = 1$$

it is easy to see that a minimizer $\psi_0(x)$ exists. The next eigenvalue is found by optimizing orthogonal to $\psi_0$, etc. In this way we get eigenvalues $-\lambda_1 \gtrsim -\lambda_2 \gtrsim \cdots$. The following theorem was proved in [LW] (see also [BL]).

**Theorem 37** *For the operator $H$ we have the inequality*

$$\sum_j \lambda_j^{3/2} \gtrsim \frac{3}{16} \int \mathrm{tr}\,[U(x)^2] dx$$

*Alternatively, the above estimate can be written as*

$$\sum_j \lambda_j^{3/2} \gtrsim \frac{1}{2\pi} \int \mathrm{tr}\,[p^2 \otimes I - U(x)^2]_- dp dx$$

*which displays the semiclassical nature of the bound.*

Following Aizenman and Lieb [AL] we can deduce from this bound a whole series of sharp bounds as follows. Write for $\gamma > 3/2$

$$\lambda^\gamma = \frac{\Gamma(\gamma+1)}{\Gamma(5/2)\Gamma(\gamma-3/2)} \int_0^\infty (\lambda - s)_+^{3/2} s^{\gamma-3/2} \frac{ds}{s} \ .$$

From this we get immediately

**Theorem 38** *For the operator $H$ we have for all $\gamma \gtrsim 3/2$*

$$\sum_j \lambda_j^\gamma \gtrsim \frac{1}{2\sqrt{\pi}} \frac{\Gamma(\gamma+1)}{\Gamma(\gamma+3/2)} \int \mathrm{tr}\,[U(x)^{\gamma+1/2}]dx$$

*or alternatively*

$$\sum_j \lambda_j^\gamma \gtrsim \frac{1}{2\pi} \int \mathrm{tr}\,[p^2 \otimes I - U(x)^2]_-^\gamma dpdx$$

As an application we give a sketch of the proof of the theorem of Laptev and Weidl.

**Theorem 39 (Laptev and Weidl)** *On $L^2(R^n)$ consider the negative eigenvalues $-\lambda_1 < -\lambda_2 \gtrsim \cdots$ of the operator*

$$-\Delta - U(x)$$

*where $U$ is non-negative. Then for all $\gamma \gtrsim 3/2$*

$$\sum_j \lambda_j^\gamma \gtrsim \frac{1}{(2\pi)^n} \int [p^2 - U(x)]_-^\gamma dxdp \ .$$

*This is a semiclassical estimate and best possible.*

**Theorem 40** *Following Laptev and Weidl we use induction on the dimension. We have to estimate*

$$\mathrm{Tr}[-\Delta - U(x)]_-^\gamma = \mathrm{Tr}[-\partial_1^2 - \Delta' - U(x_1, x')]_-^\gamma$$

*where $x' = x_2, \ldots, x_n$. The right side is estimated from above by*

$$\mathrm{Tr}[-\partial_1^2 - [-\Delta' - U(x_1, x')]_-]_-^\gamma \ .$$

*it is not hard to see that*

$$[-\Delta' - U(x_1, x')]_-$$

*is for every $x_1$ a positive, compact operator and hence can by approximated by finite matrices. Applying our theorem, noting that $\gamma \gtrsim 3/2$ we obtain*

$$\mathrm{Tr}[-\Delta - U(x)]_-^\gamma \gtrsim \frac{1}{2\pi} \mathrm{Tr} \int [p_1^2 \otimes I - [-\Delta' - U(x_1, x')]_-]_-^{\gamma+1/2} dp_1 dx_1 \ ,$$

*where the trace is preformed over the remaining variables $x_2 \ldots . x_n$. Since*

$$\frac{1}{2\pi} \mathrm{Tr} \int [p_1^2 \otimes I' - [-\Delta' - U(x_1, x')]_-]_-^{\gamma+1/2} dp_1 dx_1 = const. \int \mathrm{tr}\,[-\Delta' - U(x_1, x')]_-^{\gamma+1/2} dx_1$$

*we can apply the theorem once more since $\gamma + 1/2 > 3/2$ and get that*

$$\int \mathrm{tr}\,[-\Delta' - U(x_1, x')]_-^{\gamma+1/2} dx_1 \lesssim \frac{1}{2\pi} \mathrm{tr} \int [p_2^2 \otimes I'' - [-\Delta'' - U(x_1, x_2, x'')]_-]_- dp_2 dx_2 dx_1$$

*so that*

$$\frac{1}{2\pi} \mathrm{Tr} \int [p_1^2 \otimes I' - [-\Delta' - U(x_1, x')]_-]_-^{\gamma+1/2} dp_1 dx_1$$

$$\lesssim \frac{1}{(2\pi)^2} \mathrm{tr} \int [(p_1^2 + p_2^2) \otimes I'' - [-\Delta'' - U(x_1, x_2, x'')]_-]_- dp_1 dp_2 dx_1 dx_2 \; .$$

*Repating this procedure leads eventually to the desired estimate.*

Another sharp bound is the following, due to Hundertmark, Lieb and Thomas in the scalar case and Hundertmark, Laptev and Weidl in the matrix case

**Theorem 41** *For the operator $H$ we have the inequality*

$$\sum_j \lambda_j^{1/2} \lesssim \frac{1}{2} \int \mathrm{tr}\,[U(x)] dx \; .$$

**Proof** We apply the Birman-Schwinger principle. $-\lambda$ is an eigenvalue if and only if $1$ is an eigenvalue of

$$U(x)^{1/2} \frac{1}{-\partial^2 + \lambda} U(y)^{1/2} \; .$$

The associated kernel is given by

$$U(x)^{1/2} \frac{e^{-\sqrt{\lambda}|x-y|}}{2\sqrt{\lambda}} U(y)^{1/2} = \frac{1}{\sqrt{\lambda}} \mathcal{L}_\lambda \; .$$

Hence whenever the Birman Schwinger kernel has an eigenvalue $1$ the operator $\mathcal{L}_\lambda$ has an eigenvalue $\sqrt{\lambda}$. denote by $e_j(\lambda)$ the eigenvalues of the operator $\mathcal{L}_\lambda$ ordered decreasingly. By what we said above $e_1(\lambda_1) = \sqrt{\lambda_1}, e_2(\lambda_2) = \sqrt{\lambda_2} \ldots$. We shall prove that

$$\sum_{i=1}^k e_i(\lambda)$$

is a decreasing function of $\lambda$ for all $k$. Once this is established we have that

$$\sum_j \sqrt{\lambda_j} = \sum_j e_j(\lambda_j) \lesssim e_1(\lambda_2) + e_2(\lambda_2) + \sum_{j=3} e_j(\lambda_j)$$

$$\lesssim e_1(\lambda_3) + e_2(\lambda_3) + e_3(\lambda_3) + \sum_{j=4} e_j(\lambda_j)$$

etc. so that

$$\sum_j \sqrt{\lambda_j} \lesssim \mathrm{tr}\,\mathcal{L}_{\lambda=0} = \frac{1}{2} \int Tr U(x) dx \; .$$

Note that the first trace is a trace over $L^2 \otimes C^n$ while the second is a trace over $C^n$ only.

To establish the monotonicity we write

$$\mathcal{L}_\lambda = U(x)^{1/2} \frac{\sqrt{\lambda}}{\pi} \int \frac{1}{p^2+\lambda} e^{ip(x-y)} dp dx$$

The kernel

$$G_\varepsilon(p) = \frac{\varepsilon}{\pi} \frac{1}{p^2+\varepsilon^2}$$

is the Poisson kernel and it is easy to check that

$$G_\varepsilon * G_{\varepsilon'} = G_{\varepsilon+\varepsilon'}$$

and by a simple calculation

$$\mathcal{L}_\lambda(x,y) = \int dq e^{iqx} \mathcal{L}_{\lambda-\varepsilon^2}(x,y) e^{-iqy} \frac{\varepsilon}{\pi} \frac{1}{q^2+\varepsilon^2}$$

In other words the operator can be written as an average of the following form

$$\mathcal{L}_\lambda = \int w(q) U_q \mathcal{L}_{\lambda-\varepsilon^2} U_q^*$$

where $U_q$ is unitary and $\int w(q) dq = 1$. Let $P_k$ be the projector onto the space belonging to the $k$ largest eigenvalues. Thus,

$$\sum_{j=1}^k e_j(\lambda) = \operatorname{tr} P_k \mathcal{L}_\lambda P_k = \int w(q) \operatorname{tr} \left[ P_k U_q \mathcal{L}_{\lambda-\varepsilon^2} U_q^* P_k \right]$$

$$= \int w(q) \operatorname{tr} \left[ U_q^* P_k U_q \mathcal{L}_{\lambda-\varepsilon^2} U_q^* P_k U_q \right]$$

by the cyclicity of the trace. The operator $U_q^* P_k U_q$ is again a projection of dimension $k$ and hence by the minimax principle

$$\operatorname{tr} \left[ U_q^* P_k U_q \mathcal{L}_{\lambda-\varepsilon^2} U_q^* P_k U_q \right] \gtrsim \sum_{j=1}^k e_j(\lambda - \varepsilon^2) \, .$$

Therefore

$$\sum_{j=1}^k e_j(\lambda) \gtrsim \sum_{j=1}^k e_j(\lambda - \varepsilon^2)$$

which is what we had to prove. □

We apply now these theorems to prove LT inequalities with good constants. they are not optimal but close.

**Theorem 42** *On $L^2(R^3)$ consider the negative eigenvalues $-\lambda_1 < -\lambda_2 \gtrsim \cdots$ of the operator*

$$-\Delta - U(x)$$

*where $U$ is non-negative. Then*

$$\sum_j \lambda_j^{1/2} \gtrsim \frac{1}{8\pi} \int U(x)^2 dx$$

*and*

$$\sum_j \lambda_j \gtrsim \frac{2}{15\pi^2} \int U(x)^{5/2} dx \ .$$

*which is twice the semiclassical constant.*

**Proof** We proceed as in the previous proof concerning the powers $\gamma \gtrsim 3/2$. We write for $\gamma \gtrsim 1/2$

$$\lambda^\gamma = \frac{\Gamma(\gamma+1)}{\Gamma(3/2)\Gamma(\gamma-1/2)} \int_0^\infty (\lambda-\alpha)_-^{1/2} \alpha^{\gamma-1/2} \frac{d\alpha}{\alpha} \tag{1}$$

Applying the minmax principle to the estimate for matrix valued potentials we get

$$\sum_j (\lambda_j - \alpha)_+^{1/2} \gtrsim \frac{1}{2} \int \mathrm{tr}\,[U(x)-\alpha]_+ dx$$

and inserting this in formula (1) leads to

$$\sum_j \lambda_j^\gamma \gtrsim \frac{1}{\sqrt{\pi}} \frac{\Gamma(\gamma+1)}{\Gamma(\gamma+3/2)} \int \mathrm{Tr}[U(x)]^{\gamma+1/2} dx \tag{2}$$

Using the matrix valued estimate for the $1/2$ powers yields

$$\mathrm{tr}\,[-\Delta - U]_-^{1/2} \gtrsim \frac{1}{2} \int \mathrm{tr}\,[-\Delta' - U(x_1, x')]_- dx_1$$

Using (2) with $\gamma = 1$ yields

$$\mathrm{tr}\,[-\Delta - U]_-^{1/2} \gtrsim \frac{1}{2} \frac{1}{\sqrt{\pi}} \frac{\Gamma(2)}{\Gamma(5/2)} \int dx_1 dx_2 \mathrm{tr}\,[-\partial_3^2 - U(x_1, x_2, x_3)]_-^{3/2} \ .$$

Now we use the sharp estimate for $\gamma = 3/2$ and get

$$\mathrm{tr}\,[-\Delta - U]_-^{1/2} \gtrsim \frac{1}{2} \frac{1}{\sqrt{\pi}} \frac{\Gamma(2)}{\Gamma(5/2)} \frac{3}{16} \int U(x)^2 dx = \frac{1}{8\pi} \int U(x)^2 dx \ .$$

To estimate

$$\mathrm{tr}\,[-\Delta - U]_-$$

we use (1) with $\gamma = 1$ to obtain

$$\mathrm{tr}\,[-\Delta - U]_- \gtrsim \frac{1}{\sqrt{\pi}} \frac{\Gamma(2)}{\Gamma(5/2)} \int dx_1 \mathrm{tr}\,[-\Delta' - U(x_1, x')]_-^{3/2}$$

and applying the sharp esitmate for the powers once for $\gamma = 3/2$ and then for $\gamma = 2$ yields

$$\begin{aligned}\mathrm{tr}\,[-\Delta - U]_- &\gtrsim \frac{1}{\sqrt{\pi}} \frac{\Gamma(2)}{\Gamma(5/2)} \frac{3}{16} \int\int dx_1 dx_2 \mathrm{tr}\,[-\partial_3^2 - U(x_1, x_2, x')]_-^2 \\ &\gtrsim \frac{1}{\sqrt{\pi}} \frac{\Gamma(2)}{\Gamma(5/2)} \frac{3}{16} \frac{8}{15\pi} \int U(x)^{5/2} dx = \frac{2}{15\pi^2} \int U(x)^{5/2} dx\,.\end{aligned}$$

# 12 Relativistic systems

In order to incorporate certain aspects of Einstein's theory of relativity into our treatment of Coulomb systems we replace the non relativistic kinetic energy

$$\frac{p^2}{2m}$$

by

$$\sqrt{c^2p^2 + m^2c^4} - mc^2$$

where $c$ is the speed of light. To pass over to quantum mechanics we have to replace $p$ by

$$\frac{\hbar}{i}\nabla$$

which leads formally to

$$\sqrt{-c^2\hbar^2\Delta + m^2c^4} - mc^2 \ .$$

Thus, e.g, the hydrogen atom is has the Hamiltonian

$$H = \sqrt{-c^2\hbar^2\Delta + m^2c^4} - mc^2 - \frac{Ze^2}{|x|} \ .$$

Before making sense out of these expressions we make some remarks about units. It is natural to choose as our unit of energy $mc^2$ because then our Hamiltonian reduces to

$$H = \sqrt{-\frac{\hbar^2}{m^2c^2}\Delta + 1} - 1 - \frac{Ze^2}{mc^2|x|}$$

Next we note that

$$\frac{\hbar}{mc}$$

has the nunit of length, the Compton wavelength (divided by $2\pi$) and hecne if measure length in these units we get

$$H = \sqrt{-\Delta + 1} - 1 - \frac{Ze^2}{\hbar c|x|} = \sqrt{-\Delta + 1} - 1 - \frac{Z\alpha}{|x|} \tag{1}$$

where $\alpha$ is the dimensionless fine structure constant $\approx 1/137.04$.

The kinetic energy is defined through the Fourier transform

$$(\psi, \sqrt{-\Delta + 1}\psi) = \int \sqrt{4\pi^2|k|^2 + 1}|\widehat{\psi}(k)|^2 dk \ .$$

Note that by definition the Hilbert space $H^{1/2}(R^3)$ consists of all functions with

$$\int \sqrt{4\pi^2|k|^2+1}|\widehat{\psi}(k)|^2 dk < \infty \ .$$

From the definitions we obtain immediately the useful inequalities

$$\sqrt{-\Delta} - 1 \lesssim \sqrt{-\Delta+1} - 1 \lesssim \sqrt{-\Delta} \ . \qquad (I)$$

Notice that the kinetic energy $\sqrt{-\Delta}$ has the same behavior under scaling as the Coulomb energy. As a consequence, the smallest spectral value of Hamiltonian

$$\sqrt{-\Delta} - \frac{Z\alpha}{|x|} \qquad (2)$$

is *either* $-\infty$ *or* $0$. In particular we shall prove the following theorem of Kato, Herbst and Weder. We follow [KPS].

**Theorem 43** *the Hamiltonians (1) and (2) are bounded below if and only if* $Z\alpha \lesssim 2/\pi$.

**Theorem 44** *We have to find an estimate of the type*

$$(\psi, \frac{1}{|x|}\psi) \lesssim C(\psi, \sqrt{-\Delta}\psi)$$

*which can be rewritten as*

$$(\phi, \frac{1}{(-\Delta)^{1/4}}\frac{1}{|x|}\frac{1}{(-\Delta)^{1/4}}\phi) \lesssim C\|\phi\|^2 \ .$$

*In other words we have to find the norm of the operator*

$$\frac{1}{\sqrt{|x|}}\frac{1}{(-\Delta)^{1/4}}$$

*which is the same as the norm of the adjoint*

$$\frac{1}{(-\Delta)^{1/4}}\frac{1}{\sqrt{|x|}} \ .$$

*Using that*

$$(\frac{1}{|k|^a}\widehat{f})\check{}(x) = \frac{c_{n-a}}{c_a}\int \frac{1}{|x-y|^{n-a}} f(y)dy$$

*where*

$$c_a = \pi^{-a/2}\Gamma(a/2)$$

*we have that*

$$\frac{1}{(-\Delta)^{1/2}} f(x) = (\frac{1}{2\pi|k|}\widehat{f})\check{}(x) = \frac{1}{2\pi^2}\int \frac{1}{|x-y|^2} f(y)dy \ .$$

Therefore we have to estimate

$$\frac{1}{2\pi^2}\int \frac{\overline{\phi(x)}\phi(y)}{|x|^{1/2}|x-y|^2|y|^{1/2}}dxdy$$

in terms of $\|\phi\|_2$. Writing the expression as

$$\frac{1}{2\pi^2}\int \frac{\overline{\phi(x)}|x|^{1/2}}{|x-y||y|}\cdot\frac{\phi(y)|y|^{1/2}}{|x||x-y|}dxdy \tag{3}$$

and then using Schwarz's inequality yields the estimate

$$\frac{1}{2\pi^2}\int \frac{|\phi(x)|^2|x|}{|x-y^2||y|^2}dxdy\ .$$

Integrating with respect to $y$ and noting that

$$\int \frac{1}{|x-y^2||y|^2}dy = \pi^3\frac{1}{|x|}$$

we obtain that (3) is bounded above by

$$\frac{\pi}{2}\int |\phi(x)|^2dx\ .$$

Thus, the norm

$$\|\frac{1}{(-\Delta)^{1/4}}\frac{1}{|x|^{1/2}}\| \lesssim \sqrt{\frac{\pi}{2}}$$

To see that it is equal we investigate the cases of equality in our use of Schwarz's inequality. We have equality if

$$\frac{\overline{\phi(x)}|x|^{1/2}}{|x-y||y|} = \text{const.}\frac{\phi(y)|y|^{1/2}}{|x||x-y|}$$

which means that

$$\phi(x) = \text{const.}\frac{1}{|x|^{3/2}}$$

for almost every $x$. Note that this function is not in $L^2(R^3)$ but almost. Consider the sequence of functions

$$\phi_n(x) = \begin{cases} 0 & \text{if } |x| \lesssim \frac{1}{n} \\ \frac{1}{|x|^{3/2}} & \text{if } \frac{1}{n} < |x| < n \\ 0 & \text{if } n \lesssim |x|. \end{cases}$$

Next we calculate

$$\frac{1}{2\pi^2}\int \frac{\phi_n(x)\phi_n(y)}{|x|^{1/2}|x-y|^2|y|^{1/2}}dxdy\frac{1}{2\pi^2}\int \frac{\phi_n(x)}{|x|^{1/2}|x-y|^2|y|^2}dxdy(1+o(1))$$

$$= \frac{\pi}{2} \int_{1/n<|x|<n} |x|^{-3} dx$$

Likewise,

$$\|\phi_n\|^2 = \int_{1/n<|x|<n} |x|^{-3} dx \ .$$

Hence,

$$\frac{1}{2\pi^2} \frac{\int \frac{\phi_n(x)\phi_n(y)}{|x|^{1/2}|x-y|^2|y|^{1/2}} dxdy}{\|\phi_n\|^2} \to \frac{\pi}{2}$$

as $n \to \infty$.

As a consequence, we have stability if and only if

$$Z\alpha \lesssim \frac{2}{\pi} \ .$$

This means that we have stability for all $Z$ values up to about $87$. this is less than $92$ which means that some important physics has been missed. This has largely to do with the fact that the square root operator is the wrong dynamics for an electron. It should really be described by the Dirac equation. The present model, however, is useful for two reasons. Firstly, it will be useful in a variety of circumstances. Secondly, it shows in a simple fashion that in relativistic problems the Coulomb potential cannot be considered as a small perturbation.

**Remark 45** As we have seen, the function that yields the norm is essentially the function $\phi(x) = 1/|x|^{3/2}$. This function is related to the corresponding wave function by $\phi(x) = (-\Delta)^{1/4}\psi$ from which we glean that

$$\psi(x) \approx \frac{1}{|x|} \qquad (Opt)$$

for dimensional reasons.

It is worth pointing out that the above result is the relativistic version of the following uncertainty principle.

**Theorem 46** *For any smooth function with compact support we have that*

$$\int |\nabla f|^2 dx \gtrsim \frac{1}{4} \int \frac{|f(x)|^2}{|x|^2} dx \ .$$

**Proof** Write $f = |x|^{-1/2} g$ with $g(0) = 0$ and compute

$$\int |\nabla f|^2 dx = \int [-\frac{1}{2}|x|^{-3/2} \frac{x}{|x|} g + \frac{1}{|x|^{1/2}} \nabla g]^2 dx$$

$$= \frac{1}{4} \int \frac{1}{|x|^2} |f|^2 dx - 2 \int \frac{1}{2} |x|^{-3/2} \frac{x}{|x|} g \cdot \frac{1}{|x|^{1/2}} \nabla g dx + \int \frac{1}{|x|} |\nabla g|^2 dx \ .$$

The middle term can be written as

$$\frac{1}{2}\int \frac{1}{|x|^2}\frac{x}{|x|}\cdot\nabla g^2 dx = \frac{1}{2}\lim_{\varepsilon\to 0}\int_{|x|>\varepsilon}\frac{1}{|x|^2}\frac{x}{|x|}\cdot\nabla g^2 dx\ .$$

Integrating by parts yields

$$\int_{|x|>\varepsilon}\frac{1}{|x|^2}\frac{x}{|x|}\cdot\nabla g^2 dx = \frac{1}{2}\int_{|x|>\varepsilon}\mathrm{div}(\frac{x}{|x|^3}g^2)dx$$

where we used that $\mathrm{div}\frac{x}{|x|^2} = 0$ away from the origin. Using Gauss theorem we learn that

$$\frac{1}{2}\int_{|x|>\varepsilon}\mathrm{div}(\frac{x}{|x|^3}g^2)dx = -\frac{1}{2}\int_{S^2} g^2(\varepsilon\omega)d\omega$$

which vanishes in the limit as $\varepsilon\to 0$. It is not difficult to see that the constant $1/4$ cannot be improved. □

An alternative proof would be to cast the inequality in the form

$$(g, \frac{1}{\sqrt{-\Delta}}\frac{1}{|x|^2}\frac{1}{\sqrt{-\Delta}}g) \gtrsim 4\|g\|_2^2$$

which amounts to calculating the norm

$$\|\frac{1}{\sqrt{-\Delta}}\frac{1}{|x|}\|\ ,$$

i.e., we have to show

$$(h, \frac{1}{|x|}\frac{1}{-\Delta}\frac{1}{|x|}h) \gtrsim 4\|h\|_2^2\ .$$

The expression on the left is

$$\frac{1}{4\pi}\int\int\frac{\overline{h(x)}h(y)}{|x||x-y||y|}dxdy = \frac{1}{4\pi}\int\int\frac{\overline{h(x)}|x|^{1/4}h(y)|y|1/4}{|x|^{5/4}|x-y||y|^{5/4}}dxdy$$

$$= \frac{1}{4\pi}\int\int\frac{\overline{h(x)}|x|^{1/4}}{|x-y|^{1/2}|y|^{5/4}}\frac{h(y)|y|1/4}{|x|^{5/4}|x-y|^{1/2}}dxdy \gtrsim \frac{1}{4\pi}\int|h(x)|^2|x|^{1/2}\int\frac{1}{|x-y||y|^{5/2}}dydx$$

$$= 4\|h\|_2^2\ ,$$

since

$$\int\frac{1}{|x-y||y|^{5/2}}dy = 16\pi|x|^{-1/2}\ .$$

Returning to the relativistic case, note that we are really talking about two Hamiltonians, (1) and (2). The Hamilonian (2) can only be used to discuss the stability or instability. It does not have any bound states, even in the stable case, because of scaling. The smallest energy is $0$ and the state is infinitely extended. The Hamiltonian (1) has

indeed bound states for any $Z\alpha < 2/\pi$. For small $Z$ the eigenvalues are close to the ones given by the non-relativistic hydrogen atom.

The full model is, like in the non-relativistic case given by

$$H_{\rm mass}(N) = \sum \sqrt{-\Delta_j + 1} - 1 - \alpha V_c \ . \tag{4}$$

Again, if we are only interested in the question of stability it suffices to consider the Hamiltonian

$$H(N) = \sum \sqrt{-\Delta_j} - \alpha V_c \ . \tag{5}$$

As always, we consider this operator on $N$-particle wave functions that are antisymmetric, i.e., satisfy the Pauli exclusion principle. Note that for (5) the question of stability of the first and second kind is one and the same. The system (5) is stable if and only if the Hamiltonian is positive. Note, that once the stability of (5) is established then (4) is also stable. This follows from the inequalities (I) since

$$H_{\rm mass}(N) \gtrsim H(N) - N \gtrsim -N \ .$$

This says that

$$H_{\rm mass}(N) \gtrsim -N \ .$$

In other words in relativity the total energy of the system, i.e., its interaction energy and its rest energy is always positive.

Clearly, it is necessary for stability that $\max_k Z_k\alpha \gtrsim 2/\pi$. From now on we shall *not* assume that $Z_k$ is an integer. $Z_k$ can be, in principle, as small as we like. The following dimensional argument will show that it is not enough to have $Z_k\alpha$ small no matter how small the nuclear charges. It turns out that $\alpha$ itself has to be small for stability to hold. This was first observed by Daubechies and Lieb. [DL] To see this, it suffices to consider one single electron in the field of $K$ nuclei all having charge $Z$. Think of the system as having an overal length scale $L$. The kinetic energy of the electron is of the order

$$\frac{1}{L}$$

. The Coulomb potential has several contributions. There is the attraction of the electron to the nuclei which yields a term of the order

$$-\alpha\frac{KZ}{L}$$

and the nuclear repulsion is of order

$$+\alpha\frac{K^2Z^2}{2L}$$

so that we have in total

$$\frac{1}{L} - \alpha\frac{KZ}{L} + \alpha\frac{K^2Z^2}{2L} = \frac{1}{2L}\left[2 - \alpha + \alpha(KZ-1)^2\right]$$

Thus, no matter how small $Z > 0$ we can always choose $K$ large so that $(KZ-1)^2 < 1$ and, as a consequence if $\alpha > 3$ the expression in $[\cdot]$ is negative and by letting $L \to 0$ we can make the energy as negative as we please. To summarize, for relativistic Coulomb systems a necessary and sufficient condition for stability is that $Z\alpha$ as well as $\alpha$ are sufficiently small. Again, there is no distinction between stability of the first kind and the second kind for relativistic systems.

The challenge is now to prove stability and to do it in such a way that the allowed values for $\alpha$ are sufficiently large as to incorporate the physical case $\alpha \approx 1/137.04$. The first who proved stability was Conlon [C], however the allowed values of $\alpha$ were much to small. This was then improved by De la Llave and Fefferman [LF] using computer assisted proofs. The best results were obtain by Lieb and Yau. [LY] Certain simplifications were obtain by Lieb, Loss and Siedentop.[LLS]. We follow [LY] and [LLS]. It is inconvenient that the $(f, \sqrt{-\Delta}f)$ has to be defined using the Fourier transform. Below is an expression entirely in $x$ space.

**Theorem 47** *For any function $f$ such that $(f, \sqrt{-\Delta}f)$ is finite we have that*

$$(f, \sqrt{-\Delta}f) = \frac{1}{2\pi^2} \int \int \frac{|f(x) - f(y)|^2}{|x-y|^4} dxdy \ .$$

**Proof** Observe that

$$(f, \sqrt{-\Delta}f) = \lim_{t \to 0} \frac{1}{t} \left[ (f,f) - (f, e^{-t\sqrt{-\Delta}} f) \right] \ . \tag{6}$$

This follows by writing the right side of (6) as

$$\frac{1}{t} \left[ (f,f) - (f, e^{-t\sqrt{-\Delta}} f) \right] = \int |\widehat{f}(k)|^2 \frac{1 - e^{-2\pi|k|t}}{t} dk$$

and noting that the right side converges to $(f, \sqrt{-\Delta}f)$. next we calculate the 'relativistic' heat kernel

$$e^{-t\sqrt{-\Delta}}(x,y) \ .$$

As with the heat kernel this can be solved using Fourier transform and to obtain the 'relativistic' heat kernel we have to calculate the inverse Fourier transform of the function

$$e^{-t2\pi|k|} \ .$$

This is easy in one dimension but not entirely trivial in two and higher. In one dimension we have to calculate

$$\int e^{-t2\pi|k|} e^{2\pi i k x} dk = \frac{t}{\pi} \frac{1}{t^2 + x^2} \ . \tag{7}$$

Write the right side as

$$\frac{t}{\pi} \int_0^\infty e^{-(t^2+x^2)s} ds$$

and note that

$$e^{-sx^2} = \sqrt{\frac{\pi}{s}} \int e^{-|2\pi k|^2/4s} e^{2\pi i k x} dk$$

Comparing this with (7) yields

$$e^{-t2\pi|k|} = \frac{1}{\sqrt{\pi}} \int_0^\infty e^{-s-\frac{|2\pi k|^2 t}{4s}} \frac{ds}{\sqrt{s}} \, .$$

In other words, we have that

$$e^{-|a|} = \frac{1}{\sqrt{\pi}} \int_0^\infty e^{-s-\frac{a^2}{4s}} \frac{ds}{\sqrt{s}} \, ,$$

for any real number $a$. Hence we can use this to calculate in arbitrary dimension

$$\begin{aligned} \int e^{-t2\pi|k|} e^{2\pi i k\cdot x} dk &= \frac{1}{\sqrt{\pi}} \int_0^\infty e^{-s} \int e^{-\frac{|2\pi k|^2 t^2}{4s}} e^{2\pi i k\cdot x} \frac{ds}{\sqrt{s}} \\ &= \frac{1}{t^n \pi^{\frac{n+1}{2}}} \int_0^\infty s^{\frac{n+1}{2}} e^{-(1+\frac{|x|^2}{t^2})s} \frac{ds}{s} \\ &= \frac{1}{t^n \pi^{\frac{n+1}{2}}} (1+\frac{|x|^2}{t^2})^{-\frac{n+1}{2}} \int_0^\infty s^{\frac{n+1}{2}} e^{-s} \frac{ds}{s} \\ &= \frac{\Gamma(\frac{n+1}{2})}{\pi^{\frac{n+1}{2}}} \frac{t}{[t^2+|x|^2]^{\frac{n+1}{2}}} \, . \end{aligned}$$

Hence

$$e^{-t\sqrt{-\Delta}}(x,y) = \frac{\Gamma(\frac{n+1}{2})}{\pi^{\frac{n+1}{2}}} \frac{t}{[t^2+|x-y|^2]^{\frac{n+1}{2}}}$$

which is known as the Poisson kernel. As an aside, it is amusing to note that

$$f(t,x) = e^{-t\sqrt{-\Delta}} f(x)$$

is harmonic in $t, x$, since

$$\partial_t^2 f(t,x) = (\sqrt{-\Delta})^2 f(t,x)$$

or

$$[\partial_t^2 + \Delta] f(t,x) = 0 \, .$$

Hence, the name 'Poisson kernel'. Returning to (6) we get that

$$\begin{aligned} (f, \sqrt{-\Delta} f) = \lim_{t\to 0} \frac{1}{2t} [ &\int\int |f(x)|^2 e^{-t\sqrt{-\Delta}}(x,y) dxdy + \int\int |f(y)|^2 e^{-t\sqrt{-\Delta}}(x,y) dxdy \\ &-2 \int\int \Re(\overline{f(x)} f(y)) e^{-t\sqrt{-\Delta}}(x,y) dxdy] \\ = \lim_{t\to 0} \frac{1}{2\pi^2} \int \frac{|f(x)-f(y)|^2}{[t^2+|x-y|^2]^2} dxdy &= \frac{1}{2\pi^2} \int \frac{|f(x)-f(y)|^2}{|x-y|^4} dxdy \, . \end{aligned}$$

**Remark 48** It is fairly straightforward to establish the existence of ground states and higher eigenvalues for the relativistic Schroedinger equation. As before, one needs two ingredients: A Sobolev type inequality:

$$(f, \sqrt{-\Delta} f) \gtrsim S \|f\|_q^2$$

where $q = \frac{2n}{n-1}$ and the Rellich-Kondrachev theorem, i.e., for any sequence $f_j$ , bounded in $H^{1/2}(R^n)$ and any measurable set $A$ of finite measure there exists a subsequence, again denoted by $f_j$ and $f \in H^{1/2}(R^n)$ such that

$$\|f - f_j\|_{L^p(A)} \to 0$$

provided $p < \frac{2n}{n-1}$. All the results for the non relativistic case carry over to the relativistic case for operators of the form

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

where $V$ is a potential which vanishes in measure and can be written as

$$V = v + w$$

$w \in L^\infty(R^n)$, and $v \in L^n(R^n)$.

Analogous to the non relativistic case there is also a LT inequality for the relativistic operator $\sqrt{-\Delta}$. It was proved by Daubechies and we give here an alternative proof based on an inequality due to Birman and Solmyak. (see [LSS])

**Theorem 49 (Birman and Solomyak)** *Let $A$ and $B$ be two selfadjoint positive operators such that $[A-B]_-$ is trace class, i.e., $\mathrm{Tr}[A-B]_-$ exists. Then*

$$\mathrm{Tr}[A-B]_+ \gtrsim \mathrm{Tr}[A^2 - B^2]_+^{1/2} .$$

**Remark 50** It is useful to recall two facts about selfadjoint operators. If $A$ and $B$ are two positive selfadjoint operators and $A \gtrsim B$. Recall that this means that

$$((f, Af) \gtrsim (f, Bf)$$

for all $f$ in the Hilbert space. Then

$$A^\alpha \gtrsim B^\alpha$$

where $0 \gtrsim \alpha \gtrsim 1$. If $A$ is invertible then so is $B$ and

$$B^{-1} \gtrsim A^{-1} .$$

**Proof** Write

$$A^2 = B^2 + C$$

and split $C = C_+ - C_-$. Then the inequality reads

$$\mathrm{Tr}[\sqrt{B^2 + C_+ - C_-} - B]_+ \gtrsim \mathrm{Tr} C_+^{1/2} .$$

Since the square root is matrix monotone we have that

$$\sqrt{B^2 + C_+ - C_-} \gtrsim \sqrt{B^2 + C_+} \, ,$$

and, hence the inequality follows from

$$\mathrm{Tr}[\sqrt{B^2 + C} - B]_+ \gtrsim \mathrm{Tr} C^{1/2}$$

for $B, C \gtrsim 0$. First we assume that $B \gtrsim s$ for some number $s > 0$. Clearly,

$$\begin{aligned} \mathrm{Tr}[\sqrt{B^2 + C} - B]_+ = \mathrm{Tr}[\sqrt{B^2 + C} - BB^{-1}B]_+ &\gtrsim \mathrm{Tr}[\sqrt{B^2 + C} - B[B^2 + C]^{-1/2}B]_+ \\ = \mathrm{Tr}[[B^2 + C]^{-1/4}C[B^2 + C]^{-1/4}]_+ &= \mathrm{Tr}[C^{1/2}[B^2 + C]^{-1/2}C^{1/2}]_+ \\ &\gtrsim \mathrm{Tr} C^{1/2} \, . \end{aligned}$$

The rest follows from a limiting argument. □

The following theorem is due to Daubechies.[D]

**Theorem 51 (Relativistic Lieb-Thirring inequality)** *Let $U(x) \gtrsim 0$ be in $L^4(R^3)$. Then*

$$\mathrm{tr}\,[\sqrt{-\Delta} - U]_- \gtrsim \frac{1}{8\pi} \int U(x)^4 dx \, .$$

**Proof** of the Birman-Solomyak theorem: By the BS inequality

$$\mathrm{tr}\,[\sqrt{-\Delta} - U]_- = \mathrm{tr}\,[U - \sqrt{-\Delta}]_+ \gtrsim \mathrm{tr}\,[-\Delta - U^2]_-^{1/2} \, .$$

Using the LT inequality for the sum of the roots of the eigenvalues

$$\mathrm{tr}\,[-\Delta - U^2]_-^{1/2} \gtrsim \frac{1}{8\pi} \int U(x)^4 dx \, .$$

We have immediately the

**Corrolary 52** *Let $\Psi$ be any antisymmetric wave function of $N$ particles with $q$ spin states. Then*

$$\sum_j (\Psi, \sqrt{-\Delta}_j \Psi) \gtrsim \frac{3}{4}(2\pi)^{1/3} q^{-1/3} \int \rho_\Psi^{4/3}(x) dx \gtrsim 1.3839 \int \rho_\Psi^{4/3}(x) dx \, .$$

**Proof** Consider the quadratic form

$$\sum_j \left[ (\Phi, \sqrt{-\Delta}_j \Phi) - c(\Phi, \rho_\Psi^{1/3} \Phi) \right] \, .$$

where $c$ is some constant. Filling up the energy levels we get that

$$\sum_j \left[ (\Phi, \sqrt{-\Delta}_j \Phi) - c(\Phi, \rho_\Psi^{1/3} \Phi) \right] \gtrsim -q \sum \lambda_j \, .$$

where $-\lambda_j$ are the negative eigenvalues. In other words

$$\sum_j \left[ (\Phi, \sqrt{-\Delta}_j \Phi) - c(\Phi, \rho_\Psi^{1/3} \Phi) \right] \gtrsim -q \mathrm{tr} \, [\sqrt{-\Delta} - c\rho_\Psi^{1/3}]_-$$

which by Daubechies' result is bounded below by

$$-\frac{1}{8\pi} q c^4 \int \rho_\Psi^{4/3}(x) dx \; .$$

Thus picking $\Phi = \Psi$

$$\sum_j (\Psi, \sqrt{-\Delta}_j \Psi) \gtrsim [c - \frac{1}{8\pi} q c^4] \int \rho_\Psi^{4/3}(x) dx \; .$$

Optimizing over $c$ yields the result. □

**Remark 53** The constant in [D] is better and equals $1.63$. we shall use that constant henceforth.

One is tempted to consider a relativistic analog of Thomas Fermi theory, i.e., to consider an energy functional of the form

$$\mathcal{E}(\rho) = \frac{3}{4}\gamma \int \rho^{4/3}(x) dx - \alpha \sum_j Z_j \int \frac{\rho(x)}{|x - R_j|} + \alpha D(\rho, \rho) + \alpha U(\underline{R}) \; .$$

This approach fails for the simple reason that the kinetic energy term is too weak to prevent a collapse. Consider the problem of one nucleus at the origin and note that any function $\rho$ which has compact support and which behaves like $1/|x|^2$ for $x$ small, has a finite kinetic energy and a finite Coulomb repulsion energy. The integral

$$\int \rho(x) \frac{1}{|x|} dx \; ,$$

however diverges. In fact the borderline case for the power of $\rho$ in the kinetic energy is$3/2$. The kinetic energy is of the form

$$\int \rho^p(x) dx \; .$$

If $p > 3/2$ everything is fine and if $p < 3/2$ nothing is fine. As we shall see, the situation

can be saved. This was shown in [LLS]. The idea is instead of considering a TF-like theory we modify and add the term

$$(\sqrt{\rho}, \sqrt{-\Delta}\sqrt{\rho}) \; ,$$

i.e. we consider the energy functional

$$\mathcal{E}(\rho) = \beta(\sqrt{\rho}, \sqrt{-\Delta}\sqrt{\rho}) + \frac{3}{4}\gamma \int \rho^{4/3}(x)dx - \alpha \sum_j Z_j \int \frac{\rho(x)}{|x - R_j|} + \alpha D(\rho, \rho) + \alpha U(\underline{R}) \ .$$

where is $\rho$ subject to the constraint $\int \rho(x)dx < \infty$. Since this additional term is reminiscent of a 'von Weizsäcker correction', we call this function the Thomas-Fermi-von Weizsäcker functional, TFW in short.

Let us introduce a further simplification. With loss of generality we may assume that all the nuclear charges are the same. This can be reasoned as follows. For fixed nuclear positions the energy is in each of the variables $Z_k$ *separately*. Hence, upon minimizing over the wave function the energy is concave in each of the variables $Z_k$ *separately*. Consider for the $Z_k$ variables the interval $[0, Z]$ where $Z\alpha \gtrsim 2/\pi$. Since a concave function has its minimum on the boundary of its domain we get that the energy has a minimum id all the values of $Z_k$ are either $0$ or $Z$. The value $0$ means that the corresponding nucleus has vanished from the picture. Hence, we may assume that our Hamiltonian is of the form (4) but al the nuclear charges are the same.

There are two problems. One is to relate the full problem to the TFW problem and the second is to prove stability for the TFW problem. Recall also that we need a lower bound on the TFW functional that is independent of the number of particles and independent of the position of the nuclei. Hence, since all the terms scale the same way we have to show that $\mathcal{E}(\rho) \gtrsim 0$ for $\alpha$ and $Z_k\alpha$ sufficiently small.

Let us address the first problem. This will involve a number of facts which we now state and prove.

**Theorem 54 ([C)** *, [HO]] Irrespective of the symmetry type of the function $\Psi$ the inequality*

$$\sum_j (\Psi, \sqrt{-\Delta_j}\Psi) \gtrsim (\sqrt{\rho_\Psi}, \sqrt{-\Delta}\sqrt{\rho_\Psi})$$

*aways holds.*

**Proof** Recall that

$$\sum_j (\Psi, \sqrt{-\Delta_j}\Psi) = \lim_{t\to 0} \sum_j [(\Psi, \Psi) - (\Psi, e^{-\sqrt{-\Delta_j}t}\Psi)] \ .$$

Now

$$\sum_j (\Psi, e^{-\sqrt{-\Delta_j}t}\Psi)$$

$$= \sum \int \Psi(x_1, \dots, x_j, \dots, x_N) e^{-\sqrt{-\Delta_j}t}(x_j, y_j) \Psi(x_1, \dots, y_j, \dots, x_N) dx_1 \cdots dx_N dy_j \ .$$

Applying Schwarz's inequality we learn that

$$\sum \int \Psi(x_1, \dots, x_j, \dots, x_N) e^{-\sqrt{-\Delta_j}t}(x_j, y_j) \Psi(x_1, \dots, y_j, \dots, x_N) dx_1 \cdots dx_N dy_j$$

$$\gtrsim N \int dxdy(\int |\Psi(x,x_2,\ldots,x_N)|^2 dx_2\cdots dx_N)^{1/2}$$

$$\times(\int |\Psi(y,x_2,\ldots,x_N)|^2 dx_2\cdots dx_N)^{1/2} e^{-\sqrt{-\Delta}t}(x,y)$$

$$= (\sqrt{\rho_\Psi}, e^{-\sqrt{-\Delta}t}\sqrt{\rho_\Psi}) \; .$$

which by relating this back to the expression in terms of $\sqrt{-\Delta}$ proves the claim. The next theorem will be proved later. It is dues to Lieb and Oxford and is an estimate on the indirect part of the Coulomb repulsion among electrons. We shall prove this estimate later since it is somewhwat involved. □

**Theorem 55** *Let $\Psi$ be any normalied $N$ particle wave function. Then*

$$\sum_{i<j}(\Psi, \frac{1}{|x_i - x_j|}\Psi) - D(\rho_\Psi, \rho_\Psi) \gtrsim -1.68 \int \rho_\Psi^{4/3}(x)dx \; .$$

Corollary 6, Theorem 7 and 8 allows us to find a lower bound in terms of TFW theory. Split the relativistic kinetic energy in (5) into

$$\beta\sqrt{-\Delta_j} + (1-\beta)\sqrt{-\Delta_j}$$

and apply the aforementioned statements. This yields the lower bound

$$(\Psi, H'\Psi) \gtrsim \beta(\sqrt{\rho_\Psi}, \sqrt{-\Delta}\sqrt{\rho_\Psi}) + [(1-\beta)1.63q^{-1/3} - \alpha 1.68]\int \rho_\Psi^{4/3}(x)dx$$

$$-Z\alpha\sum_j \int \frac{\rho_\Psi(x)}{|x-R_j|} + \alpha D(\rho_\Psi,\rho_\Psi) + \alpha Z^2 \sum_{k<l}\frac{1}{|R_k - R_l|} \tag{8}$$

$\beta$ will be chosen later. Thus, our next goal is to study the functional

$$\mathcal{E}(\rho) = \beta(\sqrt{\rho}, \sqrt{-\Delta}\sqrt{\rho}) + [(1-\beta)1.63q^{-1/3} - \alpha 1.68]\int \rho^{4/3}(x)dx$$

$$-Z\alpha\sum_j \int \frac{\rho(x)}{|x-R_j|} + \alpha D(\rho,\rho) + \alpha Z^2 \sum_{k<l}\frac{1}{|R_k - R_l|} \tag{9} \; .$$

# 13 An Estimation Of The Indirect Part Of The Coulomb Energy

## Introduction

A quantum mechanical system of $N$ particles has a state which generally is described by a finite or countably infinite set of wave functions

$$\psi_\beta(x_1, \ldots, x_N) \tag{1}$$

with $\beta = 1, 2, 3, \ldots$ and with the normalization

$$\sum_\beta \int_{\mathbb{R}^{3N}} \left|\psi_\beta(x_1, \ldots, x_N)\right|^2 dx_1 \cdots dx_N = 1. \tag{2}$$

The index $\beta$ describes some "internal quantum numbers" of the particles apart from the spatial coordinates $x_i \in \mathbb{R}^3$. As an example suppose the system is in a pure state and each particle has $q$ spin states available to it. Then the state is described by a function of space and spin

$$\psi(x_1, \sigma_1; \ldots; x_N, \sigma_N) \tag{3}$$

with $\sigma_i \in \{1, \ldots, q\}$ and $i = 1, \ldots, N$. In this case these are $q^N$ functions of $x_1, \ldots, x_N$ indexed by the values of the spin or – more conveniently – by an index $\beta$ which takes values from 1 to $q^N$. Then (2) reads

$$\sum_{\sigma_1 \ldots \sigma_N} \int_{\mathbb{R}^{3N}} |\psi(x_1, \sigma_1; \ldots; x_N, \sigma_N)|^2 dx_1 \ldots dx_N = 1. \tag{4}$$

Another example is provided by an $N$-particle density matrix $\Gamma$ with

$$tr\Gamma = 1. \tag{5}$$

$\Gamma$ can be written as

$$\Gamma = \sum_{\beta=1}^{\infty} \lambda_\beta \Gamma_\beta \tag{6}$$

where the $\Gamma_\beta$'s are projections onto pure states i.e. $(f, \Gamma_\beta f) = |(\psi_\beta, f)|^2$ with $(\psi_\beta, \psi_\beta) = 1$. For more details the reader may consult Sect. 2.6 on density matrices.

For particles with charges $e_i, i = 1, \ldots, N$ the electrostatic energy is defined by

$$I_\psi = \sum_{i<j} e_i e_j \sum_\beta \int\limits_{\mathbb{R}^{3N}} \frac{|\psi_\beta(x_1, \ldots, x_N)|^2}{|x_i - x_j|} dx_1 \ldots dx_N \tag{7}$$

where $e_i$ is the charge of particle $i$; it is not assumed that all the $e_i$'s are the same. As is explained in chapter VI it is desirable to have a lower bound on $I_\psi$ in terms of the single particle *charge density*, which is defined for each $x$ in $\mathbb{R}^3$ by

$$Q(x) = \sum_{i=1}^{N} Q^i_\psi(x) \tag{8}$$

and where the *charge density* of particle $i$ is given by

$$Q^i_\psi(x) = e_i \sum_\beta \int\limits_{\mathbb{R}^{3(N-1)}} |\psi_\beta(x_1, \ldots, x_{i-1}, x, x_{i+1}, \ldots x_N)|^2 dx_1 \ldots d\widehat{x_i} \ldots dx_N. \tag{9}$$

As usual $d\widehat{x_i}$ means that the $x_i$ integration is omitted. Observe that by (2) and the monotone convergence theorem $Q^i(x)$ is a nonnegative function in $L^1(\mathbb{R}^3)$,

$$\int\limits_{\mathbb{R}^3} Q^i_\psi(x) dx = e_i, \tag{10}$$

and hence

$$\int\limits_{\mathbb{R}^3} Q_\psi(x) dx = \sum_{i=1}^{N} e_i. \tag{11}$$

The electrostatic energy associated with the charge density $Q_\psi(x)$ is given by

$$D(Q_\psi, Q_\psi) = \frac{1}{2} \int\limits_{\mathbb{R}^3} \int\limits_{\mathbb{R}^3} \frac{Q_\psi(x) Q_\psi(y)}{|x - y|} dx dy \tag{12}$$

and is called the **direct part of the Coulomb energy**. It is the classical Coulomb energy associated with a "fluid" of charge density $Q_\psi$. Since $Q_\psi(x) \geq 0, D(Q_\psi, Q_\psi)$ is always well defined in the sense that it is either finite or $+\infty$. See Sect. 22.2.

Accordingly, **the indirect part of the Coulomb energy**, denoted by $E_\psi$, is defined by the equation

$$I_\psi = D(Q_\psi, Q_\psi) + E_\psi \tag{13}$$

Thus $E_\psi$ is the difference between the true energy $I_\psi$ and the classical approximation $D(Q_\psi, Q_\psi)$. Sometimes it is called the exchange plus correlation energy. It is the aim of this chapter to give a lower bound on $E_\psi$ in terms of $Q_\psi$. We emphasize that our bound on $E_\psi$ holds for all $\psi$, not only for solutions to Schrödinger's equation.

Examples

The first example comes from Hartree's theory (see Sect. 2.18). Consider $N$ spinless particles (i.e. $q = 1$), each with charge $e$. Assume that they are not correlated i.e.

$$\psi(x_1, \dots, x_N) = f_1(x_1) \dots f_N(x_N), \tag{1}$$

where each $f_i$ is in $L^2(\mathbb{R}^3)$ and normalized. A simple computation yields:

$$Q_\psi(x) = e \sum_{i=1}^{N} |f_i(x)|^2 \tag{2}$$

and

$$I_\psi = D(Q_\psi, Q_\psi) - \sum_{i=1}^{N} D(|f_i|^2, |f_i|^2). \tag{3}$$

Hence $E_\psi$ is the (negative) sum of the self energies of the charge distributions $|f_i(x)|^2$.

Another example is provided by a Hartree-Fock wave function. Again the charges are taken to be equal to $e$. Then $\psi$ is the antisymmetric function of space and spin given by a determinant

$$\psi(x_1, \sigma_1; \dots; x_N, \sigma_N) = (N!)^{-1/2} \det(\phi^i(x_j, \sigma_j)) \tag{4}$$

where the $\phi^i$'s are orthonormal functions in $L^2(\mathbb{R}^3; \mathbb{C}^q)$. In Sect. 2.7 the electrostatic energy of this wave function was computed. The indirect part turns out to be

$$E_\psi = -\frac{1}{2} e^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \gamma^1(z, w) \gamma^1(w, z) |x - y|^{-1} dz dw \tag{5}$$

where

$$\gamma^1(z, w) = \sum_{i=1}^{N} \phi^i(z) \overline{\phi^i(w)} \tag{6}$$

(the notation $z = (x, \sigma)$ and $\int dz = \sum_\sigma \int dx$ is used here). In this context $E_\psi$ is called **the exchange term**. An *approximation* to $E_\psi$ in terms of $Q_\psi$ was computed in [DP] using perturbation theory, i.e. using the eigenfunctions of the kinetic energy operator (i.e. the Laplacian) in a large box $\Lambda$. Choosing the $\phi^i(z)$'s to be

$$\phi_{\alpha,k}(z) = \chi_\alpha(\sigma) \frac{1}{\sqrt{|\Lambda|}} e^{i \vec{k} \cdot \vec{x}}, \tag{7}$$

a dimensional argument immediately shows that for $|\Lambda|$ and $N$ large, and with $\rho = N/|\Lambda|$ fixed

$$E_\psi = -C e^2 q^{-1/3} \rho^{4/3} |\Lambda|. \tag{8}$$

Here $|\Lambda|$ denotes the volume of $\Lambda$. The allowed values of $\vec{k}$ are

$$\vec{k} = \frac{2\pi}{|\Lambda|^{1/3}} \vec{n} \quad \text{with } \vec{n} \in \mathbb{Z}^3_+$$

and $\chi_\alpha(\sigma)$ with $\alpha = 1, \ldots, q$ is an orthonormal basis in $\mathbb{C}^1$. Closer inspection shows that $C = 0.93$.

Formula (8) above suggests that in the general case, i.e., for any antisymmetric function of space and spin, $E_\psi$ given by 14.1(13) should be bounded below by

$$-Ce^{2/3}q^{-1/3}\int\limits_{\mathbb{R}^3} Q_\psi(x)^{4/3}dx \tag{9}$$

for some suitable universal constant $C$. For the case where all the $e_i$'s $= e$, (9) is correct *provided the factor* $q^{-1/3}$ *is omitted*. That the Pauli principle plays no role in the question of bounding $E_\psi$ in terms of $Q_\psi$ *alone* we shall show now. Following [LO] it is easy to find function $\psi_q \in L^2(\mathbb{R}^3; \mathbb{C}^1)^N)$ for $q = 1, 2, 3, \ldots$ each of which is totally antisymmetric and such that all the $\psi_q$'s have the same charge density $Q(x)$, and yet $E_{\psi_q}$ is independent of $q$. Define a function $\theta(z_1, \ldots, z_N)$ with $z_i = (x_i, \sigma_i)$ where $\sigma_i \in \{1, \ldots, q\}, i = 1, \ldots, N$ to be totally antisymmetric and to take only the values $\pm q^{-N}$. Obviously we have

$$\sum_{\sigma_1 \ldots \sigma_N} |\theta(z_1, \ldots, z_N)|^2 = 1 \tag{10}$$

for each $x_1, \ldots, x_N$. Pick any symmetric $\psi(x_1, \ldots, x_N)$ in $L^2(\mathbb{R}^{3N})$ and consider

$$\psi_q(x_1, \sigma_1; \ldots; x_N\sigma_N) = \psi(x_1, \ldots, x_N)\theta(x_1, \sigma_1; \ldots; x_N\sigma_N) \tag{11}$$

which is totally antisymmetric. Since by (10)

$$\sum_{\sigma^1 \ldots \sigma^N} |\psi_q(x_1, \sigma_1; \ldots; x_N, \sigma_N)|^2 = |\psi(x_1, \ldots, x_N)|^2$$

we have $I_\psi = I_{\psi_q}$, and $Q_\psi = Q_{\psi_q}$ for each $q$, and hence $E_\psi = E_{\psi_q}$ independent of $q$.

Thus, the best general estimate we could aim for is

$$E_\psi \geq -C\int\limits_{\mathbb{R}^3} Q_\psi(x)^{4/3}dx \tag{12}$$

with $C$ being a universal constant. One might try to improve the constant in the estimate by *excluding* certain symmetries for wave functions for example totally symmetric(i.e. bosonic) functions. That this is impossible can be seen in a similar fashion as above. Thus the Coulomb repulsion is insensitive to the symmetry properties of a wave function and is therefore not able to see the spin. The reason $q$ entered in (9) was that the kinetic energy operator was taken into account i.e. changing $q$ meant changing the ground state of the kinetic energy operator and hence it meant changing $Q_\psi(x)$. Our point is that when $Q_\psi(x)$ is the *only* available information then (12) is the best one can hope for. This is in contrast to the kinetic energy which is sensitive to the symmetry properties of the spatial part of the wave function. In fact (see chapter XII) a spin dependent bound can be obtained

$$T_\psi \geq Cq^{-2/3}\int\limits_{\mathbb{R}^3} Q_\psi(x)^{5/3}dx \tag{13}$$

The difference i.e. spin dependence of the kinetic energy estimate and spin independence of the exchange estimate can be (somewhat sloppily) rephrased by saying that only an off diagonal operator (like the Laplacian) can "see" the symmetry properties of a wave function and therefore the spin.

## Exchange Estimate Theorem

**Theorem 56 (Exchange Estimate)** *Let $\psi$ be a countable collection of functions $\{\psi_\beta\}_{\beta\in N}$, each $\psi_\beta$ being in $L^2(\mathbb{R}^{3N})$, and assume $\psi$ to be normalized, i.e.,*

$$\sum_\beta \|\psi_\beta\|_2^2 = 1.$$

*Assume also that either $e_i \geq 0$ for all $1 \leq i \leq N$ or else that $e_i \leq 0$ for all $1 \leq i \leq N$. Then the indirect term $E_\psi$ of the Coulomb energy given by 14.1(13) satisfies the estimate*

$$E_\psi \geq -C \left( \int_{\mathbb{R}^3} \left| \sum_{i=1}^N e_i Q_\psi^i(x) \right|^{4/3} dx \right)^{1/2} \left( \int_{\mathbb{R}^3} |Q_\psi(x)|^{4/3} dx \right)^{1/2}, \tag{1}$$

*where $C$ is some constant less than 1.68. Here $Q_\psi(x)$ and $Q_\psi^i(x)$ are given by the expressions 14.1(8) and 14.1(9). In case all the $e_i$ equal a common value $e$ then*

$$E_\psi \geq -C|e|^{2/3} \int_{\mathbb{R}^3} |Q_\psi(x)|^{4/3} dx \tag{2}$$

**Remark 57** This theorem was proved in [LE] and with an improved constant in [LO]. Since the number of particles is fixed one might expect that the sharp constant in (1) is $N$ dependent. This is in fact true. In the case of one particle the constant $C_1$ can in principle be computed exactly. Since $I_\psi = 0$ in this case, $E_\psi = -D(Q_\psi, Q_\psi)$ and we have that

$$C_1 = \sup \left\{ \frac{D(\rho,\rho)}{\int \rho(x)^{4/3} dx} : \rho(x) \geq 0, \int \rho(x) dx = 1 \right\}$$

By 14.3(3) and (4) (see below) $C_1$ is finite. In [TL] and [GBH] the above variational problem was shown to reduce to a Lane-Emden equation of order 3 whose solutions are tabulated. The result is

$$C_1 = 1.092$$

This constant plays a role in the Chandrasekhar mass limit (see Chapter IX). The Lane-Emden equation goes back to Homer Lane in his study of gravitating gas spheres in the year 1869! The existence of a maximizer was shown in [LO], where also a lower bound for $C_2$ is computed:

$$C_2 \geq 1.234 > C_1$$

In general it is not hard to see that

$$C_N \leq C_{N+1}.$$

Again, see [LO] for details. The constant $C$ in (1), which is valid for *all* particle numbers, is the worst possible case, and we note (from the above bound on $C_2$) that the bound 1.68 cannot be improved very much.

**Remark 58** A second remark is of a more technical nature. Since $E_\psi$ is the difference of two positive quantities and since the only assumption on $\psi$ is that it is normalized, the reader might worry that $E_\psi$ is not well defined. Conceivably $I_\psi$ and $D(Q_\psi, Q_\psi)$ could both be infinity and yet $E_\psi$, being the difference of the two, is somehow finite. This does not affect the validity of Theorem 14.3 as the following reasoning shows. We can assume that $\int |Q_\psi(x)|^{4/3} dx < \infty$ for otherwise there is nothing to prove. By the Hardy-Littlewood-Sobolev inequality (see Chapter XVII) we have that

$$D(Q_\psi, Q_\psi) \leq C \|Q_\psi\|_{6/5}^2 \tag{3}$$

and by Hölder's inequality

$$\|Q_\psi\|_{6/5} \leq \left( \int_{\mathbb{R}^3} Q_\psi(x) dx \right)^{1/3} \left( \int_{\mathbb{R}^3} |Q_\psi(x)|^{4/3} dx \right)^{1/2} = \left( \sum_{i=1}^N e_i \right)^{1/3} \left( \int_{\mathbb{R}^3} |Q_\psi(x)|^{4/3} dx \right)^{1/2} \tag{4}$$

Hence, whenever $Q_\psi \in L^{4/3}(\mathbb{R}^3)$ (so that the right side of (1) and (2) is finite) $D(Q_\psi, Q_\psi)$ is also finite and $E_\psi$ is well defined (although it might be $+\infty$, but never $-\infty$). Henceforth we shall consider the case that all $e_i \geq 0$, even though the main application of Theorem 14.3 is to electrons for which $e_i = e < 0$. This is done to avoid writing absolute values everywhere, but it is of no consequence since the only relevant quantities are the products $e_k e_j$ which are always positive.

The first step in the proof is a generalization of a lemma originally due to Onsager [OL].

**Theorem 59 (Smearing Out Charges)** *Let $x^1, \ldots, x^N$ be distinct points in $\mathbb{R}^3$ and, centered at these points, we are given $N$ nonnegative bounded functions $\mu_{x^1}, \ldots, \mu_{x^N}$, each spherical symmetric and such that $\int \mu_{x^i}(x)dx = 1$ for each $i = 1, \ldots, N$. Then for any nonnegative function $\rho$ in $L^1(\mathbb{R}^3)$ there is the inequality*

$$\sum_{i<j} e_i e_j |x_i - x_j|^{-1} \geq -D(\rho, \rho) + 2\sum_{i=1}^{N} e_i D(\rho, \mu_{x^i}) - \sum_{i=1}^{N} e_i^2 D(\mu_{x^i}, \mu_{x^i}) \tag{1}$$

**Proof** The $\mu_{x^i}$'s being bounded guarantees that $D(\rho, \mu_{x^i})$ and $D(\mu_{x^i}, \mu_{x^i})$ are bounded. We can assume that $D(\rho, \rho)$ is not infinite, because then the right side of (1) is $-\infty$ and the lemma is trivial. We know from Sect. 22.2 that $D(\cdot, \cdot)$ is positive definite and hence

$$D\left(\rho - \sum_{i=1}^{N} e_i \mu_{x^i}, \rho - \sum_{i=1}^{N} e_i \mu_{x^i}\right) \geq 0 \tag{2}$$

which implies that

$$\sum_{i \neq j} e_i e_j D(\mu_{x_i}, \mu_{x_j}) \geq -D(\rho, \rho) + 2\sum_{i=1}^{N} e_i D(\rho, \mu_{x_i}) - \sum_{i=1}^{N} e_j^2 D(\mu_{x_i}, \mu_{x_i}). \tag{3}$$

Since $\mu_{x_i}$ and $\mu_{x_j}$ are spherically symmetric around the centers $x_i$ and $x_j$, we know from Sect. 22.8 that

$$D(\mu_{x_i}, \mu_{x_j}) \leq \frac{1}{2} e_i e_j |x_i - x_j|^{-1} \tag{4}$$

which proves (1). ■

**Remark 60** The point of the above lemma is that it estimates a quantity $\left(\sum_{i<j} e_i e_j |x_i - x_j|^{-1}\right)$ in which correlations are important by another one where the correlations of the $x_i$'s are not important. Lemma 14.4 immediately allows us to get a lower bound for $E_\psi$ in terms of the one particle densities $Q_\psi(x)$, resp. $Q^i_\psi(x)$. Multiplying (1) by $|\psi_\beta(x_1, \ldots, x_N)|^2$, integrating and summing over $\beta$ we arrive at

$$I_\psi \geq -D(Q_\psi, Q_\psi) + 2\sum_{i=1}^{N} \int_{\mathbb{R}^3} D(Q_\psi, \mu_{x_i}) Q^i_\psi(x_i) dx_i - \sum_{i=1}^{N} e_i \int_{\mathbb{R}^3} D(\mu_{x_i}, \mu_{x_i}) Q^i_\psi(x_i) dx_i. \tag{5}$$

The normalization $\sum_\beta \int |\psi_\beta(x_1, \ldots, x_N)|^2 dx_1 \ldots dx_N = 1$ has been used as well as the monotone convergence theorem to interchange the $\beta$ summation with the integration.

If we denote by $\delta_{x_i}$ the Dirac measure at the point $x_i$ we can write, in a somewhat formal but correct fashion,

$$\sum_{i=1}^{N} \int_{\mathbb{R}^3} D(Q_\psi, \delta_{x_i}) Q_\psi^i(x_i) dx_i = D(Q_\psi, Q_\psi).$$

Hence, by adding and subtracting we get from (5)

$$E_\psi \geq -F_1 - F_2 \tag{6}$$

where

$$F_1 = 2 \sum_{i=1}^{N} \int_{\mathbb{R}^3} D(Q_\psi, \delta_{x_i} - \mu_{x_i}) Q_\psi^i(x_i) dx_i \tag{13.1}$$

$$F_2 = \sum_{i=1}^{N} e_i \int_{\mathbb{R}^3} D(\mu_{x_i}, \mu_{x_i}) Q_\psi^i(x_i) dx_i \tag{13.2}$$

Observe that $F_1$ is positive and for $\mu_{x_i}$ fixed, quadratic in $Q_\psi^i$.

## Proof Of Exchange Estimate Theorem With Crude Bound

**Proof** In 14.4(6-8) we are still free to choose the functions $\mu_{x_i}$. It is clear that the $\mu_{x_i}$'s have to depend on $Q_\psi$ for otherwise $F_1$ would be quadratic in $Q_\psi$.

Let $\mu : \mathbb{R}^3 \to \mathbb{R}$ be a nonnegative bounded function satisfying

1. $\mu$ is spherically symmetric about the origin.
2. $\int_{\mathbb{R}^3} \mu(y) dy = 1$
3. $\mu(y) = 0$ if $|y| > 1$

We assume, without loss of generality, that all the $e_i$'s are positive. Define $\mu_x(y)$ by the formula

$$\mu_x(y) = \lambda^3 Q_\psi(x) \mu(\lambda Q_\psi(x)^{1/3}(x - y)) \tag{1}$$

where $\lambda$ is a positive number. It is easily seen that the $\mu_{x_i}$'s obtained in this way satisfy the assumptions of Lemma 14.4.

If we denote

$$P_\lambda(\alpha, r) = \alpha r^{-1} - \lambda \alpha^{4/3} \phi(\lambda \alpha^{1/3} r), \tag{2}$$

where $\phi$ is the potential associated with $\mu$, i.e.,

$$\phi(|x|) = \int_{\mathbb{R}^3} \frac{\mu(y)}{|x - y|} dy = \int_{\mathbb{R}^3} \min\left(\frac{1}{|x|}, \frac{1}{|y|}\right) \mu(y) dy, \tag{3}$$

(see Sect. 2.8), then a simple computation shows that

$$F_1 = \int\limits_{\mathbb{R}^3} \int\limits_{\mathbb{R}^3} Q_\psi(y) P_\lambda(Q_\psi(x), |x-y|) dxdy. \tag{4}$$

Since

$$D(\mu_x, \mu_x) = \lambda^6 Q_\psi(x)^2 \int\limits_{\mathbb{R}^3} \int\limits_{\mathbb{R}^3} \frac{\mu(\lambda Q_\psi(x)^{1/3}(x-y))\mu(\lambda Q_\psi(x)^{1/3}(x-z))}{|y-z|} dydz \tag{13.3}$$

$$= \lambda Q_\psi(x)^{1/3} D(\mu, \mu) \tag{13.4}$$

we find that

$$F_2 = \lambda D(\mu, \mu) \int\limits_{\mathbb{R}^3} Q_\psi(x)^{1/3} \left( \sum_{i=1}^{N} e_i Q_\psi^i(x) \right) dx. \tag{5}$$

In case $e_i = e$, all $i = 1, \ldots, N, F_2$ is already of the desired form. We concentrate on $F_1$ and prove first a crude estimate which hopefully clarifies what the choice in (1) of $\mu_x$ accomplishes. Since $\mu$ is nonnegative and $\int \mu(y)dy = 1$, (3) shows that $\phi(r) \leq r^{-1}$ which implies that $P_\lambda(a, r) \geq 0$. Further, since $\mu(y) = 0$ for $|y| > 1$, we find again by (3) that $P_\lambda(a, r) = 0$ if $\lambda a^{1/3} r > 1$. Hence we have the trivial bound

$$P_\lambda(a, r) \leq \begin{cases} ar^{-1} & \text{if } \lambda a^{1/3} \leq 1 \\ 0 & \text{otherwise} \end{cases} \tag{13.5}$$

which implies that

$$F_1 \leq \int\limits_{\lambda Q_\psi(x)^{1/2}|x-y| \leq 1} \frac{Q_\psi(x) Q_\psi(y)}{|x-y|} dxdy. \tag{7}$$

The restriction upon the integration in (7) obviously plays an important role. To make use of it we resort to the following device. Write $Q_\psi(x) = \int\limits_0^\infty d\alpha \chi_\alpha(x)$ where $\chi_\alpha$ is the characteristic function of the set $\{x : Q_\psi(x) \geq \alpha\}$, i.e.

$$\chi_\alpha(x) = \begin{cases} 1 & \text{if } Q_\psi(x) \geq \alpha \\ 0 & \text{otherwise.} \end{cases} \tag{13.6}$$

Using this and Fubini's theorem, (7) becomes

$$\int\limits_0^\infty d\alpha \int\limits_0^\infty d\beta \int\limits_{\lambda Q_\psi(x)^{1/3}|x-y| \leq 1} \frac{\chi_\alpha(x)\chi_\beta(y)}{|x-y|} dxdy \tag{9}$$

$$\leq \int\limits_0^\infty d\alpha \int\limits_0^\infty d\beta \int\limits_{\lambda \alpha^{1/3}|x-y| \leq 1} \frac{\chi_\alpha(x)\chi_\beta(y)}{|x-y|} dxdy \tag{10}$$

Where $\alpha \leq \beta$ we estimate the integrand by

$$\int\limits_{\lambda\alpha^{1/3}|x-y|\leq 1} \frac{\chi_\beta(y)}{|x-y|}dxdy = \int\limits_{\mathbb{R}^3} \chi_\beta(y)dy \int\limits_{|x|\leq(\lambda\alpha^{1/3})^{-1}} |x|^{-1}dx = \int\limits_{\mathbb{R}^3} \chi_\beta(y)\frac{2\pi}{\lambda^2\alpha^{2/3}}dy \quad (11)$$

and where $\alpha \geq \beta$ we estimate the integrand by

$$\int\limits_{\lambda\alpha^{1/3}|x-y|\leq 1} \frac{\chi_\alpha(y)}{|x-y|}dxdy = \int\limits_{\mathbb{R}^3} \chi_\alpha(y)\frac{2\pi}{\lambda^2\alpha^{2/3}}dy.$$

Therefore (10) is bounded above by

$$\frac{2\pi}{\lambda^2}\left\{\int\limits_0^\infty d\beta \int\limits_0^\beta d\alpha \int\limits_{\mathbb{R}^3} \chi_\beta(y)\alpha^{-2/3}dy + \int\limits_0^\infty d\alpha \int\limits_0^\alpha d\beta \int\limits_{\mathbb{R}^3} \chi_\alpha(x)\alpha^{-2/3}dx\right\} = \frac{8\pi}{\lambda^2}\int\limits_0^\infty \alpha^{1/3}d\alpha \int\limits_{\mathbb{R}^3} \chi_\alpha(x)dx \quad (13.7)$$

$$= \frac{6\pi}{\lambda^2}\int\limits_{\mathbb{R}^3} \rho_\psi(x)^{4/3}dx. \quad (13.8)$$

(For the last step see Chapter XVII.) Returning to 14.4(6) and using (5) we have that

$$E_\psi \geq -\left\{\frac{6\pi}{\lambda^2}\int\limits_{\mathbb{R}^3} Q_\psi(x)^{4/3}dx + \lambda D(\mu,\mu)\int\limits_{\mathbb{R}^3} Q_\psi(x)^{1/3}\left(\sum_{i=1}^N e_i Q_\psi^i(x)\right)dx\right\}.$$

Maximizing the right side over $\lambda$ and using Hölders' inequality on the second term yields the bound

$$E_\psi \geq -\frac{3^{4/3}}{2^{1/3}}\pi^{1/3}(D(\mu,\mu))^{2/3}\left(\int\limits_{\mathbb{R}^3} Q_\psi(x)^{4/3}dx\right)^{1/2}\left(\int\limits_{\mathbb{R}^3}\left(\sum_{i=1}^N e_i Q_\psi^i(x)\right)^{4/3}dx\right)^{1/2}. \quad (13)$$

The optimal choice for $\mu$ here is

$$\mu(y) = \frac{1}{4\pi}\delta(|y|-1)$$

which yields

$$E_\psi \geq -\frac{3^{4/3}}{2}\pi^{1/3}\left(\int\limits_{\mathbb{R}^3} Q_\psi(x)^{4/3}dx\right)^{1/2}\left(\int\limits_{\mathbb{R}^3}\left[\sum_{i=1}^N e_i Q_\psi^i(x)\right]^{4/3}dx\right)^{1/2}.$$

Note that $\frac{3^{4/3}}{2}\pi^{1/3} \approx 3.17$. □

**Proof** One can improve the constant by replacing estimate 14.5(6) by a more sophisticated treatment. Since $P_\lambda(a,r)$ is continuously differentiable we have, using the fundamental theorem of calculus, that

$$\int\limits_{\mathbb{R}^3} P_\lambda(Q_\psi(x),|x-y|)dx = \int\limits_{\mathbb{R}^3} dx \int\limits_0^{Q_\psi(x)} \left(\frac{\partial}{\partial\alpha}P_\lambda\right)(\alpha,|x-y|)d\alpha \tag{1}$$

and, again using the definition of $\chi_\alpha$ in 14.5(8), this can be written as

$$\int\limits_{\mathbb{R}^3} dx \int\limits_0^{\infty} \chi_\alpha(x)\left(\frac{\partial}{\partial\alpha}P_\lambda\right)(\alpha,|x-y|)d\alpha. \tag{2}$$

By inspection, using 14.5(3), we see that $\frac{\partial P}{\partial\alpha}(\alpha,r)$ is bounded and hence, by Fubini's theorem, we can write

$$F_1 \equiv \int\limits_{\mathbb{R}^3}\int\limits_{\mathbb{R}^3} \rho_\psi(y)P_\lambda(\rho_\psi(x),|x-y|)dxdy \tag{13.9}$$

$$= \int\limits_0^\infty d\alpha \int\limits_0^\infty d\beta \int\limits_{\mathbb{R}^3}\int\limits_{\mathbb{R}^3} \chi_\alpha(x)\chi_\beta(y)\frac{\partial P_\lambda}{\partial\alpha}(\alpha,|x-y|)dxdy \tag{13.10}$$

An upper bound is obtained by replacing $\frac{\partial P_\lambda}{\partial\alpha}$ by its positive part $\left[\frac{\partial P_\lambda}{\partial\alpha}\right]_+ = \max(\frac{\partial P_\lambda}{\partial\alpha},0)$.

Observe now that $\left[\frac{\partial P_\lambda}{\partial\alpha}\right]_+(\alpha,r)$ plays the role of $r^{-1}\theta(\lambda^{1/3}\alpha r)$ in 14.5(10), where

$$\theta(t) = \begin{cases} 0 & \text{if } t>1 \\ 1 & \text{if } t\le 1. \end{cases}$$

The integral

$$\int\limits_{\mathbb{R}^3} \frac{\theta(\lambda^{1/3}\alpha|x|)}{|x|}dx$$

in 14.5(11) is replaced by

$$\int\limits_{\mathbb{R}^3} \left[\frac{\partial P_\lambda}{\partial\alpha}\right]_+(\alpha,|x|)d^3x. \tag{4}$$

To compute this integral observe that

$$P_\lambda(\alpha,r) = \lambda\alpha^{4/3}G(\lambda\alpha^{1/3}r), \tag{5}$$

where (with $\phi(t)$ given in 14.5(3))

$$G(t) = \frac{1}{t} - \phi(t), \quad \text{for } t > 0. \tag{6}$$

Hence

$$\frac{\partial P_\lambda}{\partial \alpha}(\alpha, r) = \lambda \alpha^{1/3} \left( \frac{\partial P_\lambda}{\partial \alpha} \right) (1, \lambda \alpha^{1/3} r)$$

and therefore (4) becomes

$$(\lambda \alpha^{1/3})^{-2} \int\limits_{\mathbb{R}^3} d^3x \left[ \partial P / \partial \alpha \right]_+ (1, |x|) = (\lambda \alpha^{1/3})^{-2} K(\mu), \tag{7}$$

where $K(\mu)$ depends only on $\mu$. Following through all the steps in 14.5 with the corresponding replacements we end up with the following estimate (see 14.5(13))

$$E_\psi \geq -\frac{3}{2} [6K(\mu) D(\mu, \mu)^2]^{1/3} \left( \int\limits_{\mathbb{R}^3} \left[ \sum_{i=1}^{N} e_i Q_\psi^i(x) \right]^{4/3} dx \right)^{1/2} \left( \int\limits_{\mathbb{R}^3} Q_\psi(x)^{4/3} dx \right)^{1/2}. \tag{8}$$

Before, we chose $\mu$ to be a constant surface charge distribution on the unit sphere which, by making a crude estimate on $K(\mu)$, yielded the constant 3.17. Computing directly from formula (7) yields the constant 1.81.

By choosing $\mu$ more cleverly this constant can be improved. We choose $\mu$ to be a constant, positive, spherically symmetric charge distribution $\mu_0$ with $\int \mu_0(y) dy = 1$, i.e.

$$\mu_0(y) = \begin{cases} (4\pi/3)^{-1} & \text{if } |y| \leq 1 \\ 0 & \text{if } |y| > 1. \end{cases} \tag{13.11}$$

Computing $\phi(r)$ form 14.5(3) we get

$$\phi(r) = \begin{cases} \frac{3}{2}\left(1 - \frac{1}{3} r^2\right) & \text{if } 0 < r \leq 1 \\ \frac{1}{2} & \text{if } r \geq 1 \end{cases} \tag{13.12}$$

and hence

$$P_\lambda(\alpha, r) = \begin{cases} \alpha r^{-1} - \frac{3}{2} \lambda \alpha^{4/3} \left(1 - \frac{1}{3} (\lambda \alpha^{1/3} r)^2\right) & \text{if } 0 \leq r \leq (\lambda \alpha^{1/3})^{-1} \\ 0 & \text{if } r \geq (\lambda \alpha^{1/3})^{-1}. \end{cases} \tag{13.13}$$

Therefore

$$\left[ \frac{\partial P_1}{\partial \alpha} \right] (1, r) = \begin{cases} \frac{1}{r}(1 - r)(1 - r - r^2) & 0 \leq r \leq 1 \\ 0 & 1 \leq r \end{cases} \tag{13.14}$$

This function is nonnegative for $0 \leq r \leq \frac{\sqrt{5}-1}{2}$ and so

$$K(\mu_0) = 4\pi \left( \frac{59}{60} - \frac{5}{12} \sqrt{5} \right) = 0.6489. \tag{13}$$

An elementary calculation shows that

$$D(\mu_0, \mu_0) = \frac{3}{5} \tag{14}$$

and hence

$$C \leq 1.68, \tag{15}$$

which proves theorem 14.3. □

# 14 Localization of the kinetic energy

The next few statements are ingredients wich we shall use to prove the positivity of the TFW theory. We will proceed in an entirely different way than we did in TF theory. The first statement deals with 'pulling the Coulomb tooth'. We understand the situation in the presence of one nucleus the problem comes with many of them. The idea is to localize the kinetic energy and thereby paying a small prize which hopefully does not bother us too much. To elucidate the idea we work out the simpler case for the Laplacian first.

**Theorem 61** *Let $B$ be the unit ball centered at the origin. For any function in $H^1(R^n)$ we have the inequality*

$$\int_B |\nabla f|^2 dx \gtrsim \int_B \left[\frac{1}{4}\frac{1}{|x|^2} - 1 + \frac{1}{4}|x|^2\right] f^2 dx \ .$$

**Proof** Consider first any smooth, radial function $h$ with $h'(1) = 0$. Setting $f = hg$ we calculate

$$\int_B |\nabla f|^2 dx = \int_B [|\nabla g|^2 h^2 + |\nabla h|^2 g^2 + 2gh\nabla g \cdot \nabla h] dx$$

Integration by parts yields

$$2\int_B gh\nabla g \cdot \nabla h dx = \int_B \mathrm{div} \cdot [h\nabla h g^2] dx - \int_B |\nabla h|^2 g^2 dx - \int_B h\Delta h g^2 dx \ .$$

Using Gauss' theorem and the fact that $h'(1) = 0$ we get that

$$\int_B \mathrm{div} \cdot [h\nabla h g^2] dx = 0 \ .$$

Thus,

$$\int_B |\nabla f|^2 dx = \int_B |\nabla g|^2 h^2 dx + \int_B \frac{-\Delta h}{h} f^2 dx \gtrsim \int_B \frac{-\Delta h}{h} f^2 dx \ .$$

Now we choose $h$ carefully, e.g, the choice of Lieb and Yau is

$$h = \frac{1}{|x|^{1/2}} e^{|x|^2/4} \ .$$

Themotivation for this ansatz is that $h$ should be a function that behaves as $\frac{1}{\sqrt{r}}$ as $r \to 0$ because this is the function that is an approximate optimizer for the uncertainty principle in the whole space. The other factor is a matter of trial an error in order to obtain decent constants. Clearly $h'(1) = 0$ and we get

$$\int_B |\nabla f|^2 dx \gtrsim \int_B \left[\frac{1}{4}\frac{1}{|x|^2} - 1 + \frac{1}{4}|x|^2\right] f^2 dx \ .$$

**Theorem 62** *Let $B$ be a ball of radius 1, centered at the origin. Define the local kinetic energy*

$$(f, \sqrt{-\Delta} f)_B = \frac{1}{2\pi^2} \int_B \int_B \frac{|f(x) - f(y)|^2}{|x-y|^4} dxdy \ .$$

*Then*

$$(f, \sqrt{-\Delta} f)_B \gtrsim \int_B |f(x)|^2 \left[ \frac{2}{\pi} \frac{1}{|x|} dx - Y(|x|) \right] dx$$

*where*

$$Y(r) = \frac{2}{\pi(1+r)} + \frac{1+3r^2}{\pi(1+r^2)} \ln(1+r) - \frac{1-r^2}{\pi r(1+r^2)} \ln(1-r) - \frac{4r}{\pi(1+r^2)} \ln r$$

$$\gtrsim 1.56712 \ .$$

*The important point for us is that*

$$4\pi \int Y(r)^4 r^2 dr < 7.6245 \ .$$

**Proof** Although the result looks complicated the proof is quite transparent. First we replace $|x|^{-4}$ by $(|x|^2 + t^2)^{-2}$, i.e. regularizing the kernel. Thus

$$(f, \sqrt{-\Delta} f)_{B,t} = \frac{1}{\pi^2} \int |f(x)|^2 \int_B (|x-y|^2+t^2)^{-2} dy - \frac{1}{\pi^2} \int_B \int_B \overline{f(x)} f(y) (|x-y|^2+t^2)^{-2} dxdy$$

Let $h(x)$ be a positive real valued function which we are going to choose later and write the second term as

$$\int_B \int_B \overline{f(x)} f(y) (|x-y|^2+t^2)^{-2} dxdy = \int_B \int_B \frac{\overline{f(x)} h(y)^{1/2}}{h(x)^{1/2}} \frac{f(y) h(x)^{1/2}}{h(y)^{1/2}} (|x-y|^2+t^2)^{-2} dxdy$$

and use Schwarz's inequality to get the bound

$$\gtrsim \int_B |f(x)|^2 \eta_t(x) dx$$

where

$$\eta_t(x) = h(x)^{-1} \int (|x-y|^2 + t^2)^{-2} h(y) dy \ .$$

Thus we have

$$(f, \sqrt{-\Delta} f)_{B,t} \gtrsim \frac{1}{\pi^2} \int |f(x)|^2 Q_t(x) dx$$

where

$$Q_t(x) = \int_B (|x-y|^2 + t^2)^{-2} (1 - \frac{h(x)}{h(y)}) dy \ .$$

Next we choose $h$ to be

$$h(r) = \frac{1}{r} + r \ .$$

Again, this is motivated by the form of the optimizer of the uncertainty principle for relativistic system in the whole space, i.e., the leading behaviour as $r \to 0$ is $1/r$. Working out the integral over angles leads to

$$\frac{1}{\pi r(1+r^2)} \int_0^1 (s-r)(1-rs)\{[(r-s)^2+t]^{-1} - [(r+s)^2+t]^{-1}\} ds \ .$$

This integral can be computed in the limit as $t \to 0$ and the result is the function $Y(r)$. For details see [LY]. □

We can apply the result of Theorem 2 to the following situation.

**Theorem 63** *Given $K$ disjoint balls $B_k$ centered at the the points $R_k$ and radii $D_k, k = 1, \dots, K$. Then for any function $f$ in $R^3$ we have the bound*

$$(f, \sqrt{-\Delta} f) \gtrsim \sum_{k=1}^K \int_{B_k} |f(x)|^2 \left[ \frac{2}{\pi |x - R_k|} - \frac{1}{D_k} Y(\frac{x-R_k}{D_k}) \right] dx \ .$$

**Proof** Clearly

$$(f, \sqrt{-\Delta} f) \gtrsim \sum_{k=1}^K (f, \sqrt{-\Delta} f)_{B_k}$$

since the balls are disjoint. Set

$$g_k(x) = D_k^{3/2} f(D_k(x + R_k))$$

so that $g$ lives in the unit ball centered at the origin. Next, using Theorem 2 we have

$$(g_k, \sqrt{-\Delta} g_k)_B \gtrsim \int_B |g_k(x)|^2 \left[ \frac{2}{\pi} \frac{1}{|x|} dx - Y(|x|) \right] dx \ .$$

Further, since

$$(g_k, \sqrt{-\Delta} g_k)_B = D_k (f, \sqrt{-\Delta} f)_{B_k}$$

and since

$$\int_B |g_k(x)|^2 \left[ \frac{2}{\pi} \frac{1}{|x|} dx - Y(|x|) \right] dx = \int_{B_k} |f(x)|^2 \left[ \frac{2}{\pi} \frac{D_k}{|x - R_k|} dx - Y(\frac{|x-R_k|}{D_k}) \right] dx$$

we get the result. □

# 15 An electrostatic inequality

The size of the Coulomb potential of a collection of nuclei and electron has two sources. It is singular close to the nuclei and it can be also large because there are many nuclei. To disentangle these two issues one resorts to an electrostatic inequality due to Lieb and Yau. Before we can describe it in detail we need the notion of a Voronoi cell with respect to a collection of nuclei. Define

$$\Gamma_j = \{x \in R^3 : |x - R_j| < |x - R_i|, i \neq j\} \ .$$

Clearly $\Gamma_j$ is open and it easily seen to be convex. Further we define the nearest neighbor distance between among the nuclei by

$$\min_{i \neq j} |R_i - R_j|$$

and set

$$D_j = \frac{\min_{i \neq j} |R_i - R_j|}{2} \ .$$

The Coulomb potential due to all the nuclei that an electrons feels at the point $x$ is

$$W(x) = Z \sum_k \frac{1}{|x - R_k|} \ .$$

Define

$$\delta(x) = \min\{|x - R_i| : 1 \lesssim i \lesssim K\} \ ,$$

and set

$$\Phi(x) = W(x) - \frac{Z}{\delta(x)} \ .$$

Thus, for $x \in \Gamma_j$ the potential $\Phi(x)$ is due to all the nuclei outside of the Voronoi cell $\Gamma_j$.

**Theorem 64** *For any charge distribution $\mu$*

$$D(\mu, \mu) - \int \Phi(x)\mu(dx) + Z^2 \sum_{k<l} \frac{1}{|R_k - R_l|} \gtrsim \frac{Z^2}{8} \sum_j \frac{1}{D_j} \ .$$

**Proof** Note that $\Phi$ is harmonic in each Voronoi cell. It is not harmonic on the whole space since the function $\Phi$ is not differentiable in the boundary of the Voronoi cells. Pick a test function $f$ and calculate

$$\int \Delta f \Phi(x) dx = \sum_j \int_{\Gamma_j} \Delta f \Phi(x) dx = \sum_j \int_{\Gamma_j} \mathrm{div} \cdot (\nabla f \Phi)(x) dx - \sum_j \int_{\Gamma_j} \nabla f \cdot \nabla \Phi(x) dx$$

$$= \sum_j \int_{\partial\Gamma_j} N_j \cdot (\nabla f \Phi)(x) dS - \sum_j \int_{\Gamma_j} \nabla f \cdot \nabla \Phi(x) dx$$

where $N_j$ is the outward normal to the boundar of the Voronoi cell $\Gamma_j$. Since $\Phi$ is continuous the sum of the boundary integrals add up to zero. Further

$$-\sum_j \int_{\Gamma_j} \nabla f \cdot \nabla \Phi(x) dx = -\sum_j \int_{\Gamma_j} \mathrm{div}(f \cdot \nabla \Phi)(x) dx + \sum_j \int_{\Gamma_j} f \Delta \Phi(x) dx$$

$$= -\sum_j \int_{\Gamma_j} \mathrm{div}(f \cdot \nabla \Phi)(x) dx$$

since $\Phi$ is harmonic in $\Gamma_j$.

Hence we have

$$\int \Delta f \Phi(x) dx = -\sum_j \int_{\partial\Gamma_j} (f(x) N_j \cdot \nabla \Phi)(x) dS \ .$$

The boundary $\partial\Gamma_j$ consists of two dimensional planes separating some $\Gamma_i$ form $\Gamma_j$. Note that each boundary segment appears twice, as the boundary of a Voronoi cell and its neighbor. On such a segment the contribution of $W(x)$ drops out since it is differentiable and we are left with

$$\int \Delta f \Phi(x) dx = \sum_j \int_{\partial\Gamma_j} f(x) N_j \cdot \nabla \frac{1}{\delta(x)} dS \ .$$

In other words the charge density that generates the potential $\Phi$ is a measure $\nu$ that is supprted on the boundary of the Voronoi cells. More precisely, for any test function

$$\int \Delta f \Phi(x) dx = -\int f(x) \nu(dx)$$

Since every point on the common boundary of two Voronoi cells $\Gamma_j$ and $\Gamma_k$ has the same distance to the point $R_k$ and $R_j$ we get that the gradients on the common boundary but taken from the interior of $\Gamma_j$ and $\Gamma_k$ are of the same magnitude but of opposite direction. Thus, the density of the measure on the boundary of the Voronoi cell is given by

$$\nu(dx) = -2Z N_j \nabla |x - R_j|^{-1} \ .$$

Hence

$$\Phi(x) = \frac{1}{4\pi} \int \frac{1}{|x-y|} \nu(dy) \ ,$$

and

$$D(\mu,\mu) - \int \Phi(x) \mu(dx) + Z^2 \sum_{k<l} \frac{1}{|R_k - R_l|}$$

$$= D(\mu - \nu, \mu - \nu) - D(\nu,\nu) + Z^2 \sum_{k<l} \frac{1}{|R_k - R_l|}$$

$$\gtrsim -D(\nu,\nu) + Z^2 \sum_{k<l} \frac{1}{|R_k - R_l|}$$

and where we have to calculate $D(\nu,\nu)$.

$$\begin{aligned} D(\nu,\nu) &= \frac{1}{2}\int \Phi(x)\nu(dx) = \frac{1}{2}\int W(x)\nu(dx) - \frac{1}{2}\int \frac{Z}{\delta(x)}\nu(dx) \\ &= \frac{Z}{2}\sum_j \Phi(R_j) - \frac{1}{2}\int \frac{Z}{\delta(x)}\nu(dx) \\ &= \sum_{k<l} \frac{Z^2}{|R_k - R_l|} - \frac{1}{2}\int \frac{Z}{\delta(x)}\nu(dx) \ . \end{aligned}$$

Hence

$$-D(\nu,\nu) + Z^2 \sum_{k<l} \frac{1}{|R_k - R_l|} = \frac{1}{2}\int \frac{Z}{\delta(x)}\nu(dx) \ .$$

The last expression reduces to

$$-\sum_j \frac{Z^2}{8\pi}\int_{\partial\Gamma_j} \frac{1}{|x-R_j|} N_j \cdot \nabla \frac{1}{|x-R_j|} dS \ .$$

note that in this expression we integrate again over each boundary twice once for each Voronoi cell. Straightforward calculation leads to

$$\begin{aligned} &= -\sum_j \frac{Z^2}{16\pi}\int_{\partial\Gamma_j} N_j \cdot \nabla \frac{1}{|x-R_j|^2} \\ &= \sum_j \frac{Z^2}{16\pi}\int_{\Lambda_j} \Delta \frac{1}{|x-R_j|^2} \end{aligned}$$

where $\Lambda_j$ is the complement of $\Gamma_j$. This causes the change in the sign. Since

$$\Delta \frac{1}{|x-R_j|^2} = \frac{2}{|x-R_j|^4} \ ,$$

it remains to calculate the integral

$$\frac{Z^2}{8\pi}\int_{\Lambda_j} \frac{1}{|x-R_j|^4} dx \ .$$

It is an integral over the complement of a convex set and hence this set contains the half space whose boundary plane touches the ball of radius $D_j$ centered at $R_j$. Thus we get a lower bound by just integrating over that half space. By shifting and rotating coordinates we may assume that $R_j = 0$ and hence

$$\frac{Z^2}{8\pi}\int_{\Lambda_j} \frac{1}{|x-R_j|^4} dx \gtrsim \frac{Z^2}{8\pi}\int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dy \int_{D_j}^{\infty} dx \frac{1}{(x^2+y^2+z^2)^2} = \frac{Z^2}{8D_j} \ .$$

This is what we wanted to show. □

# 16 Stability for relativistic systems; putting everything together

In this section we prove the our final result about relativistic stability. Recall that our functional is of the form

$$\mathcal{E}(\rho) = \beta(\sqrt{\rho}, \sqrt{-\Delta}\sqrt{\rho}) + \frac{3}{4}\gamma \int \rho^{4/3}(x)dx$$

$$+\alpha \left[ -Z \sum_k \int \frac{\rho(x)}{|x - R_k|} dx + D(\rho, \rho) + Z^2 \sum_{k<l} \frac{1}{|R_k - R_l|} \right] .$$

We prove

**Theorem 65** *The functional $\mathcal{E}$ is stable if $\beta \gtrsim \pi Z\alpha/2$ and $\gamma \gtrsim 4.8158 Z^{2/3}\alpha$.*

**Proof** Set $\beta = \pi Z\alpha/2$ and'pull the Coulomb tooth' (see section 15) to find that

$$\mathcal{E}(\rho) \gtrsim \frac{3}{4}\gamma \int \rho^{4/3}(x)dx +$$

$$\alpha \left[ -\int \rho(x)U(x)dx + D(\rho, \rho) + Z^2 \sum_{k<l} \frac{1}{|R_k - R_l|} \right] . \tag{1}$$

where

$$U(x) = Z \sum_k \frac{1}{|x - R_k|}(1 - \chi_{B_k}) + \frac{\pi}{2}\chi_{B_k} \frac{1}{D_k} Y(\frac{|x - R_k|}{D_k}) .$$

Recall that

$$\Phi(x) = Z \sum_k \frac{1}{|x - R_k|} - \frac{Z}{\delta(x)}$$

which takes the value

$$Z \sum_{k \neq j} \frac{1}{|x - R_k|}$$

in the Voronoi cell $\Gamma_j$. Now we split $U(x)$ as

$$U(x) = [U(x) - \Phi(x)] + \Phi(x)$$

and the lower bound (1) takes the form

$$\mathcal{E}_1(\rho) + \alpha\mathcal{E}_2(\rho)$$

where

$$\mathcal{E}_1(\rho) = \frac{3}{4}\gamma \int \rho^{4/3}(x)dx - Z\alpha \int \rho(x)[U(x) - \Phi(x)]dx$$

and

$$\mathcal{E}_2(\rho) = D(\rho,\rho) - \int \Phi(x)\rho(x)dx + Z^2 \sum_{k<l} \frac{1}{|R_k - R_l|} \ .$$

The second functional is bounded below by

$$\frac{Z^2}{8} \sum_k \frac{1}{D_k}$$

by the electrostatic inequality in section 16. The first term we bound using Hölder's inequality by

$$\frac{3}{4}\gamma \|\rho\|_{4/3}^{4/3} - Z\alpha \|\rho\|_{4/3} \|U - \Phi\|_4$$

and optimizing over $X = \|\rho\|_{4/3}$ yields

$$-\frac{(Z\alpha)^4}{4\gamma^3} \int [U(x) - \Phi(x)]^4 dx$$

$$= -\frac{(Z\alpha)^4}{4\gamma^3} \sum_k (\frac{\pi}{2})^4 \int_{B_k} D_k^{-4} Y(\frac{|x - R_k|}{D_k})^4 dx + \int_{\Gamma_k - B_k} \frac{1}{|x - R_k|^4} dx \ .$$

Since the Voronoi cell $\Gamma_k$ lies on one side of the mid plane defined by the nearest neighbor nucleus we get an upper bound on the last term by integrating over the outside of the ball $B_k$ and then subtract the integral of the half space whose $z$-coordinate is greater or equals $D_k$. Thus

$$\int_{\Gamma_k - B_k} \frac{1}{|x - R_k|^4} dx \lesssim \frac{4\pi}{D_k} - -\frac{1}{D_k} \int_1^\infty dz \int_0^\infty \frac{2\pi r}{(r^2 + z^2)^2} dr = \frac{3\pi}{D_k} \ .$$

Hence we get that

$$\mathcal{E}_1(\rho) \gtrsim -\frac{(Z\alpha)^4}{4\gamma^3} \left[ (\frac{\pi}{2})^4 4\pi \int_0^1 Y(r)^4 r^2 dr + 3\pi \right] \sum_k \frac{1}{D_k}$$

$$= -\frac{(Z\alpha)^4}{4\gamma^3} \left[ 7.6245 (\frac{\pi}{2})^4 + 3\pi \right] \sum_k \frac{1}{D_k}$$

Adding the bounds yields in total

$$\mathcal{E}(\rho) \gtrsim \left[ -\frac{(Z\alpha)^4}{4\gamma^3} \left[ 7.6245 (\frac{\pi}{2})^4 + 3\pi \right] + \alpha \frac{Z^2}{8} \right] \sum_k \frac{1}{D_k}$$

and the condition on $\gamma$ stated in the theorem yields the result. Next we apply this theorem to the full problem. We recall that

$$\beta = \frac{\pi}{2} Z\alpha$$

and

$$\gamma = \frac{4}{3}\left[1.63q^{-1/3}(1-\frac{\pi}{2}Z\alpha) - 1.68\alpha\right]$$

which yields stability provided that

$$\frac{\pi}{2}Z + 2.2159q^{1/3}Z^{2/3} + 1.0307q^{1/3} \gtrsim \frac{1}{\alpha} \ .$$

To summarize, we have proved the following theorem.

**Theorem 66** *For all antisymmetric, normalized wave functions $\Psi$ associated with particles having $q$ spin states*

$$\sum_{j=1}^{N}(\Psi, \sqrt{-\Delta}\Psi) + \alpha(\Psi, V_c\Psi) \gtrsim 0$$

*provided that*

$$\frac{\pi}{2}Z + 2.2159q^{1/3}Z^{2/3} + 1.0307q^{1/3} \gtrsim \frac{1}{\alpha} \ .$$

This is one of the main theorems in this whole field of research. As an elementary application we use this theorem to prove stability of matter for non-relativistic systems.

**Proof** Note that by Schwarz's inequality

$$(\Psi, \sqrt{-\Delta}\Psi) \gtrsim \|\Psi\|(\Psi, -\Delta\Psi)^{1/2} \ .$$

Hence, since $\Psi$ is normalized

$$N^{1/2}\left[\sum_{j=1}^{N}(\Psi, -\Delta\Psi)\right]^{1/2} \gtrsim \sum_{j=1}^{N}(\Psi, -\Delta\Psi)^{1/2} \gtrsim \sum_{j=1}^{N}(\Psi, \sqrt{-\Delta}\Psi)$$

From this we get that for any $a > 0$

$$\sum_{j=1}^{N}(\Psi, -\Delta\Psi) \gtrsim \frac{2}{a}\sum_{j=1}^{N}(\Psi, \sqrt{-\Delta}\Psi) - N\frac{1}{a^2} \ .$$

Thus,

$$\begin{aligned}\sum_{j=1}^{N}(\Psi, -\Delta\Psi) + (\Psi, V_c\Psi) &\gtrsim \frac{2}{a}\sum_{j=1}^{N}(\Psi, \sqrt{-\Delta}\Psi) + (\Psi, V_c\Psi) - N\frac{1}{a^2} \\ &\gtrsim -\frac{N}{a^2}\end{aligned}$$

provided that $a$ is chosen such that

$$\frac{\pi}{2}Z + 2.2159q^{1/3}Z^{2/3} + 1.0307q^{1/3} \gtrsim \frac{2}{a} \ .$$

For $Z = 1$ and $q = 2$ we choose

$$\frac{2}{a} = 5.6611$$

and the lower bound

$$-8.012N \ .$$

Note that the bound depends only on $N$ and not on $K$. Further, if we go back to the Lieb-Thirring result and take neutral hydrogen, i.e., $Z = 1$ and $N = K$ even the constants are comparable. □

# 17 Magnetic fields

As an application of the results on relativistic systems we treat system with magnetic fields. The plan is the following. First we describe Hamiltonians with magnetic fields, then we discuss an important tool, the Diamagnetic inequality and then we proceed answering the stability question.

Classically, he Hamiltonian of a particle of mass $m$ and charge $e$ moving in a magnetic field $B(x)$ is given by the expression

$$\frac{1}{2m}(p - \frac{e}{c}A(x))^2$$

where $A(x)$ is a vector potential, i.e., is a vector field such that

$$\text{curl } A(x) = B(x) \ .$$

That such a vector field exists follows from one of the homogenous Maxwell equations

$$\text{div } B(x) = 0 \ .$$

Recall the Hamilton equations of motion

$$x' = \nabla_p H(x,p) \ \ p' = -\nabla_x H(x,p) \ .$$

Working this out for the Hamilton function given above yields the eqaution of motion for the particle

$$mx'' = \frac{e}{c}x' \wedge B(x) \ ,$$

which is the Lorentz force law. Here the prime denotes differentiation with respect to time. Note that

$$mx' = p - eA(x)$$

which shows that $p$ is not the physical momentum. It is called the canonical momentum although, as we shall see, there is nothing canonical about it. The step from classical to quantum mechanics proceeds by replacing $p$ by

$$\frac{\hbar}{i}\nabla$$

which leads to the operator

$$\frac{\hbar^2}{2m}(\frac{1}{i}\nabla - \frac{e}{\hbar c}A(x))^2 \ .$$

Since we will be dealing with non-relativistic systems we choose units in which the unit of energy is $2mc^2\alpha^2$, the unit of length $\frac{\hbar}{2mc\alpha}$ and finally we replace $A$ by $\frac{e}{\hbar c}A$. In these units the energy of a hydrogenic atom in a state $\psi$ is given by

$$\int |(\frac{1}{i}\nabla\psi + A(x)\psi(x)|^2 dx - Z\int \frac{1}{|x|}|\psi(x)|^2 dx \ .$$

Note that the electron has negative charge. Moreover, for later purpose the field energy, which in the usual units is given by

$$\frac{1}{8\pi}\int |B(x)|^2 dx$$

is replaced by

$$\frac{1}{8\pi\alpha^2}\int |B(x)|^2 dx \ .$$

To turn this into mathematics we consider the space

$$H^1_A(R^3)$$

which is the collection of all complex valued functions $\psi$ with the property that

$$\nabla\psi(x) + iA(x)\psi \in L^2(R^3)$$

where we interpret $\nabla\psi$ in the weak sense. A reasonable assumption on $A$ is that it is in $L^2_{\rm loc}(R^3)$. In the usual fashion we can equip $H^1_A$ with an inner product

$$(\psi,\phi)_A = \int (\overline{\nabla\psi(x) + iA(x)\psi})(\nabla\phi(x) + iA(x)\phi)dx + \int \overline{\psi(x)}\phi(x)dx \ .$$

It is not hard to see that $H^1_A(R^3)$ is a Hilbert space. It is a bit more difficult to see that the set $C^\infty_c(R^3)$ is dense in this space, but it is true (see [LL] Chapter 7).

One of the important inequalities is the **diamagnetic inequality**

$$\int |\nabla\psi(x) + iA(x)\psi)|^2 dx \gtrsim \int |\nabla|\psi|(x)|^2 dx$$

which formally can be seen by writing

$$\psi(x) = |\psi(x)|e^{iS(x)}$$

and calculating

$$\int |\nabla\psi(x) + iA(x)\psi)|^2 dx = \int (|\nabla|\psi|(x)|^2 + (\nabla S(x) + A(x))^2|\psi(x)|^2 dx$$

the result being evident. It is not difficult to turn this calculation in a formal proof. As a result, we have Sobolev's inequality

$$\int |\nabla\psi(x) + iA(x)\psi)|^2 dx \gtrsim S(\int |\psi(x)|^6 dx)^{1/3}$$

One has to be a bit more careful about the Rellich-Kondrachev theorem. Suppose that $\psi_j$ is a sequence bounded in $H^1_A$. Then by the diamagnetic inequality the absolute value is bounded in $H^1$. Nothing can be said about the phases. Hence we have the statement of the Rellich-Kondrachev for the absolute values only but not for the phases but this is enough to prove the existence of ground states as we did for the case without magnetic fields. Exploring the diamagnetic inequality further one can make some interesting statements about the Green's function. The existence of the resolvent follows by solving The theory of solving the equation

$$(\frac{1}{i}\nabla + A(x))^2\psi + \lambda\psi = g \ . \tag{1}$$

where $\lambda > 0$. Recall that we do this by looking at the weak formulation, i.e., we say that $\psi$ is a weak solution of the equation (1) if

$$\int (\overline{\nabla\psi(x) + iA(x)\psi})(\nabla\phi(x) + iA(x)\phi)dx + \lambda\int \overline{\psi(x)}\phi(x)dx = \int \overline{g}\phi dx$$

for all $\phi \in H^1_A$.

**Theorem 67** *For all $\lambda \gtrsim 0$ there exists an integrable function $G_{A,\lambda}(x,y)$ such that the solution $\psi$ of (1) is given by*

$$\psi(x) = \int G_{A,\lambda}(x,y)g(y)dy \ .$$

*Moroever,*

$$|G_{A,\lambda}(x,y)| \gtrsim \frac{e^{-\sqrt{\lambda}|x-z|}}{4\pi|x-z|} \ .$$

**Proof** Consider the solution $u$ of the problem

$$\int \nabla u \cdot \nabla f dx + \lambda\int uf dx = \int |g|f dx$$

for all $f \in H^1(R^3)$ that are real. We claim that

$$|\psi| \gtrsim u \ . \tag{2}$$

To see this we note that for all $f \in H^1$ positive

$$\int |g|f \gtrsim \Re\int g(x)\frac{\psi}{\sqrt{|\psi|^2+\varepsilon^2}}f(x)dx \ .$$

Since $\psi$ is a weak solution of (1) we get that

$$\Re\int g(x)\frac{\psi}{\sqrt{|\psi|^2+\varepsilon^2}}f(x)dx = \Re\int (\overline{\nabla\psi(x) + iA(x)\psi})(\nabla\phi(x) + iA(x)\phi)dx + \lambda\int \psi\phi dx$$

where we set $\phi = \frac{\psi}{\sqrt{|\psi|^2+\varepsilon^2}} f(x)$. a direct calculation shows that

$$\Re \int (\overline{\nabla\psi(x) + iA(x)\psi})(\nabla\phi(x) + iA(x)\phi)dx \gtrsim \int \nabla\overline{\psi}\nabla(\frac{\psi f}{\sqrt{|\psi|^2+\varepsilon^2}})dx$$

$$\gtrsim \int \nabla|\psi|\nabla(\frac{|\psi| f}{\sqrt{|\psi|^2+\varepsilon^2}})dx$$

which converges to

$$\int \nabla|\psi|\nabla f dx \ .$$

Hence we have that

$$\int \nabla|\psi|\nabla f dx + \lambda \int |\psi| f dx \gtrsim \int \nabla u \cdot \nabla f dx + \lambda \int u f dx$$

which means that

$$\int \nabla(u - |\psi|)\nabla f dx + \lambda \int (u - |\psi|) f dx \gtrsim 0 \ .$$

In other words if we set $h = u - |\psi|)$ we have that

$$-\Delta h + \lambda h \gtrsim 0$$

in the weak sense. We shall deduce from this that $h \gtrsim 0$ a.e. on $R^3$.

Assume first that $h$ is smooth in $H^1$. Then the set $A = \{x : h < 0\}$ is open. Moreover, on this set

$$\Delta h \gtrsim \lambda h < 0$$

which means that the function $h$ has its minimum on the boundary where it is zero. (Remember that $h$ vanishes at infinity.) Hence $A$ is empty. If $h$ is not smooth we convolve it with a smooth function $f_\varepsilon$ of compact support, whose integral equals $1$,

$$h_\varepsilon(x) = f_\varepsilon * h \ ,$$

where

$$f_\varepsilon(x) = \varepsilon^{-3} f(\frac{x}{\varepsilon}) \ .$$

As $\varepsilon$ tends to zero the function $h_\varepsilon$ tends to $h$ a.e. and since $h_\varepsilon \gtrsim 0$ so is $h$ and hence (2) is proved.

Recalling that $g \to \psi$ is linear we we show that the resolvent

$$((\frac{1}{i}\nabla + A(x))^2 + \lambda)^{-1}$$

is a linear operator with an integral kernel. For this we note that for any fixed $x$ by Schwarz's inequality

$$u(x) \gtrsim \| \frac{e^{-\sqrt{\lambda}|x-\cdot|}}{4\pi|x-\cdot|} \|_2 \|g\|_2 \ .$$

Hence

$$|\psi|(x) \lesssim C(x)|g\|_2$$

and by Riesz's theorem there exists a function $G_A(x,y)$ in $L^2(R^3)$ such that

$$\psi(x) = \int G_A(x,y)g(y)dy \ .$$

Next we fix $z \neq x$ and consider the sequence of functions $g_j$ given by

$$g_j(y) = \frac{3}{4\pi}\chi(|z-y|j)j^3$$

where $\chi$ is the characteristic function of the unit ball centered at the origin. Since

$$\limsup_{j\to\infty} |\int G_{A,\lambda}(x,y)g_j(y)dy| \lesssim \frac{e^{-\sqrt{\lambda}|x-z|}}{4\pi|x-z|}$$

it follows from Lebesgue's theorem that

$$|G_{A,\lambda}(x,z)| \lesssim \frac{e^{-\sqrt{\lambda}|x-z|}}{4\pi|x-z|}$$

for a.e. $z$. The case for $\lambda = 0$ follows as a limit. □

The next Theorem follows from Theorem 1 and by inspecting the proof of the Lieb-Thirring inequality. (For details see [AHS], [CSS], [LW] and [HLW]).

**Theorem 68** *Consider the negative eigenvalues $-\lambda_1 \lesssim -\lambda_2 \lesssim \cdots$ of the Schr"odinger operator*

$$(\frac{1}{i}\nabla + A(x))^2 - U(x) \ ,$$

*where $U(x) \gtrsim 0$. Then we have that*

$$\sum_j \lambda_j^{1/2} \gtrsim \frac{1}{8\pi}\int U(x)^2 dx \tag{3}$$

*and*

$$\sum_j \lambda_j \gtrsim \frac{2}{15\pi^2}\int U(x)^{5/2}dx \ . \tag{4}$$

**Proof** We give here the proof of (2) with the 'unimproved constants'. (1) is is a bit more complicated.

Recall that by the Birman Schwinger prinicple

$$N_{e/2}([U-e/2]_+) \lesssim TrK_{A,e/2}([U-e/2]_+)^2$$

(see formula (1) in Section 12), where

$$K_{A,e/2}(x,y) = U^{1/2}(x)G_{A,e/2}(x,y)U^{1/2}(y) \ .$$

Using Theorem 1 we get that

$$TrK_{A,e/2}([U-e/2]_+) \gtrsim TrK_{0,e/2}([U-e/2]_+)^2$$

which leads to the bound

$$\int [U-e/2]_+(x)[(-\Delta+e/2)^{-1}(x-y)]^2[U-e/2]_+(y)dxdy$$

which can be bounded in precisely the same fashion as we did in Section 12. This yields (2). □

As an immediate Corollary we get the stability of matter with magnetic fields.

**Theorem 69** *Consider the Hamiltonian*

$$\sum_{j=1}^{N}(\frac{1}{i}\nabla_j + A(x_j))^2 + V_c$$

*on the space of antisymmetric functions describing particles of* 2 *spin states. Then the ground state energy is bounded below by*

$$-4.156Z^{7/3}(N+K) \ .$$

Gauge invariance: For a given real $C^1$ function $\phi$, consider the transformation

$$A \to A' = A - \nabla\phi$$

and

$$\psi \to \psi' = e^{i\phi}\psi \ .$$

Then a simple calculation shows that

$$(\frac{1}{i}\nabla + A')\psi' = e^{i\phi}(\frac{1}{i}\nabla + A)\psi$$

in particular

$$|(\frac{1}{i}\nabla + A)\psi(x)|^2$$

does not depend on the particular gauge one chooses. Note, that there are no magnetic fields in one dimension there are no non-trivial magnetic fields since

$$(\frac{1}{i}\frac{\partial}{\partial x} + a(x))\psi = e^{-i\int^x a(y)dy}\frac{1}{i}\frac{\partial}{\partial x}e^{i\int^x a(y)dy}\psi$$

in other words, the operator

$$(\frac{1}{i}\frac{\partial}{\partial x} + a(x))$$

is unitarily equivalent to the operator

$$\frac{1}{i}\frac{\partial}{\partial x} .$$

There is another fruitful way of looking at the diamagnetic inequality using the heat equation. In the following presentation there are a number of gaps, e.g., we shall assume the existence of solutions etc.

Recall the heat equation

$$\frac{\partial}{\partial t}\psi = (\nabla + iA(x))^2\psi .$$

which has to be solved with the initial condition $\psi_0$. One can show that there exists a kernel, the heat kernel, $H_{t,A}(x,y)$ such that the solution $\psi_t$ at time $t$ is given by

$$\psi_t(x) = \int H_{t,A}(x,y)\psi_0(y)dy .$$

Symbolically we can also write

$$\psi_t(x) = [e^{(\nabla+iA(x))^2 t}\psi_0](x) .$$

We state now a theorem which we do not prove but instead give some of the ideas invovled. For details see [S].

**Theorem 70** *The heat kernel $H_{t,A}(x,y)$ satisfies the estimate*

$$|H_{t,A}(x,y)| \lesssim H_{t,0}(x,y) = \frac{1}{(4\pi t)^{3/2}} e^{-(x-y)^2/4t} .$$

**Proof (Sketch)** We write formally

$$H_{t,A}(x,y) = e^{-[(p_1+A_1)^2+(p_2+A_2)^2+(p_3+A_3)^2]t}(x,y)$$

and use the Trotter product formula

$$\begin{aligned} e^{-[(p_1+A_1)^2+(p_2+A_2)^2+(p_3+A_3)^2]t} &= \lim_{n\to\infty}\left[e^{-(p_1+A_1)^2 t/n} e^{-(p_2+A_2)^2 t/n} e^{-(p_3+A_3)^2 t/n}\right]^n \\ &= \lim_{n\to\infty} H_{t,A}^n . \end{aligned}$$

The limit is a strong limit. Next we note that

$$e^{-(p_1+A_1)^2 t/n} = e^{-i\int^{x_1} A_1(y,x_2,x_3)dy} e^{-p^2 t/n} e^{i\int^{x_1} A_1(y,x_2,x_3)dy}$$

where the kernel of $e^{-p^2 t/n}$ is given by

$$\frac{1}{(4\pi t/n)^{1/2}} e^{-\frac{(x_1-y_1)^2}{4t/n}} .$$

which is positive. Thus for each fiinite $n$ we have that the kernel $H^n_{t,A}(x,y)$ is an $n$-fold integral over positive functions and phases. Hence, replacing all the phases by $1$ we learn that

$$|H^n_{t,A}(x,y)| \lesssim H^n_{t,0}(x,y) \ .$$

the last expression is simply the kernel associated with the heat kernel without the magnetic field and is given by

$$\frac{1}{(4\pi t)^{3/2}} e^{-(x-y)^2/4t} \ .$$

In particular for any positive function $g$, by taking limits

$$|\int H_{t,A}(x,y)g(y)dy| \lesssim \frac{1}{(4\pi t)^{3/2}} \int e^{-(x-y)^2/4t} g(y)dy \ ,$$

from which the statement follows. □

The idea of a heat kernel can be extended to relativistic systems. One knows how to define the operator

$$\sqrt{(\frac{1}{i}\nabla + A(x))^2} =: |\frac{1}{i}\nabla + A(x)|$$

using the spectral theorem. Note that here something has to proved again, namely that

$$(\frac{1}{i}\nabla + A(x))^2$$

is selfadjoint. Likewise we can consider the associated heat kernel

$$e^{-|\frac{1}{i}\nabla + A(x)|t} \ .$$

Recall that we have proved the formula

$$e^{-|a|} = \frac{1}{\sqrt{\pi}} \int_0^\infty e^{-s - \frac{a^2}{4s}} \frac{ds}{\sqrt{s}} \ ,$$

which we can exploit to write

$$e^{-|\frac{1}{i}\nabla + A(x)|t} = \frac{1}{\sqrt{\pi}} \int_0^\infty e^{-s - \frac{|\frac{1}{i}\nabla + A(x)|^2 t^2}{4s}} \frac{ds}{\sqrt{s}} \ .$$

Using Theorem 4 we see immediately that the diamagnetic inequality also holds for relativistic systems.

**Theorem 71** *For the relativistic heat kernel we have the bound*

$$|e^{-|\frac{1}{i}\nabla + A(x)|t}(x,y)| \lesssim e^{-|\frac{1}{i}\nabla|t}(x,y) = \frac{1}{\pi^2} \frac{t}{[(x-y)^2 + t^2]^2} \ .$$

*Moreover, for any function $\psi$*

$$(\psi, |\frac{1}{i}\nabla + A(x)|\psi) \gtrsim (|\psi|, \sqrt{-\Delta}|\psi|) \ .$$

**Proof** All that is left is to show the last statement. Since

$$(\psi, |\frac{1}{i}\nabla + A(x)|\psi) = \lim_{t\to 0} \frac{1}{t}\left[\|\psi\|_2^2 - (\psi, e^{-|\frac{1}{i}\nabla + A(x)|t}\psi)\right]$$

$$\gtrsim \lim_{t\to 0} \frac{1}{t}\left[\||\psi|\|_2^2 - (|\psi|, e^{-|\frac{1}{i}\nabla|t}|\psi|)\right] = (|\psi|, \sqrt{-\Delta}|\psi|) \ .$$

As a consequence, we see that all the relevant estimates for proving stability for relativistic systems with magnetic fields go through. We have the following theorem.

**Theorem 72** *Let $\Psi$ be any normalized wave function for $N$ particles. Then*

$$\sum_{j=1}^{N} (\Psi, |\frac{1}{i}\nabla_j + A(x_j)|\Psi) \gtrsim (\sqrt{\rho_\Psi}, \sqrt{-\Delta}\sqrt{\rho_\Psi}) \ .$$

*Moreover, if in addition, $\Psi$ is an antisymmetric function for $N$ particels having $q$ spin states we have*

$$\sum_{j=1}^{N} (\Psi, |\frac{1}{i}\nabla_j + A(x_j)|\Psi) \gtrsim 1.64 q^{-1/3} \in \rho_\Psi^{4/3}(x)dx \ .$$

Using Theorem 6 we can follow the proof in Section 17 word by word and get

**Theorem 73** *For any normalized antisymmetric function $\Psi$ of $N$ particles having $q$ spin states*

$$\sum_{j=1}^{N} (\Psi, |\frac{1}{i}\nabla_j + A(x_j)|\Psi) + \alpha(\Psi, V_c\Psi) \gtrsim 0$$

*provided that*

$$\frac{\pi}{2} Z + 2.2159 q^{1/3} Z^{2/3} + 1.0307 q^{1/3} \gtrsim \frac{2}{a} \ .$$

# 18 Magnetic fields and spin

So far the spin of the electron did not have too much influence in our investigations of stability. This situation changes drastically when magnetic fields are included. The operator that describes the motion of an electron in a magnetic field is the **Pauli operator**

$$(\frac{1}{i}\nabla + A(x))^2 \otimes I + \sigma \cdot B(x) \; . \qquad (P)$$

Here $\sigma$ denotes the vector of Pauli matrices $(\sigma_1.\sigma_2, \sigma_3)$ where

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \; , \; \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

and

$$\sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \; .$$

The matrix $I$ is the $2 \times 2$ identity. The wave function of a single electron is given by a 'spinor'

$$\psi(x) = \begin{pmatrix} \psi_1(x) \\ \psi_2(x) \end{pmatrix}$$

where

$$|\psi_1(x)|^2$$

is the probability density of finding the the electron at $x$ with spin up and

$$|\psi_2(x)|^2$$

is the probability density of finding the the electron at $x$ with spin down. These words, 'spin up' and 'spin down' mean the following. Take the spinor

$$\phi_1(x) = \begin{pmatrix} \psi_1(x) \\ 0 \end{pmatrix}$$

and calculate the vector with components

$$\langle \phi_1(x), \sigma.i\phi_1(x) \rangle \; .$$

The vector is given by

$$(0, 0, 1)|\psi_1(x)|^2$$

likewise doing the same thing with

$$\psi_2(x) = \begin{pmatrix} 0 \\ \psi_2(x) \end{pmatrix}$$

one gets the vector

$$(0, 0, -1)|\psi_2(x)|^2 \ .$$

The Pauli matrices have usful commutation relations:

$$\sigma_i^2 = I$$

and

$$\sigma_1\sigma_2 = i\sigma_3 \ ,$$

and further relatation follow by cyclically permuting the indices $1, 2, 3$. Using these relations the Pauli equation can be written in the following compact form

$$(\frac{1}{i}\nabla + A(x))^2 \otimes I + \sigma \cdot B(x) = \left[\sigma \cdot (\frac{1}{i}\nabla + A(x))\right]^2$$

which shows that the Pauli operator is positive. We call

$$\sigma \cdot (\frac{1}{i}\nabla + A(x))$$

the three dimensional Dirac operator. The first system we analyze is hydrogen in a magnetic field. The Hamiltonian is given by

$$\left[\sigma \cdot (\frac{1}{i}\nabla + A(x))\right]^2 - \frac{Z}{|x|} \ . \tag{1}$$

The example where the magnetic field is constant is already interesting. We shall assume that the field points in the $z$ direction, i.e., is given by

$$(0, 0, B) \ ,$$

$B > 0$. Calculating the curl of

$$A(x, y, z) = \frac{B}{2}(-y, x, 0)$$

shows that $A$ is a vector potential for this magnetic field. In this case it is better to write the Hamiltonian in the original form as

$$(\frac{1}{i}\nabla + A(x, y, z))^2 + \sigma_3 B - \frac{Z}{|x|} \ .$$

We are interested in what happens when the magnetic field $B$ gets large. It is not possible to solve for the ground state energy in terms of elementary functions, and hence one has

to resort to trial functions. The trial function will be gleaned from solving the magnetic Hamiltonian first without the Coulomb potential.

The Hamiltonian in this case is given by

$$(\frac{1}{i}\frac{\partial}{\partial x} - \frac{B}{2}y)^2 + (\frac{1}{i}\frac{\partial}{\partial y} + \frac{B}{2}x)^2 - \frac{\partial^2}{\partial z^2} \ . \tag{2}$$

Note that the motion in the $z$ direction is the free motion and completely decouples from the other degrees of freedom. Hence, it suffices to concentrate on the two dimensional problem which we write as

$$B(P^2 + Q^2) \tag{3}$$

where

$$Q = \frac{1}{\sqrt{2}}(\frac{1}{i}\frac{\partial}{\partial y} + x)$$

and

$$P = \frac{1}{\sqrt{2}}(\frac{1}{i}\frac{\partial}{\partial x} - y) \ .$$

One arrives at this form by scaling the wave function

$$\psi(x,y) \to \sqrt{\frac{B}{2}}\psi(\sqrt{\frac{B}{2}}(x,y)) \ .$$

The operators $P$ and $Q$ which are selfadjoint, have the commutation relation

$$PQ - QP = [P,Q] = \frac{1}{i}$$

and we see that the Hamiltonian in an algebraic sense is equivalent to the Harmonic oscillator and hence we get as the eigenvalues of the Hamiltonian (3) the numbers

$$B(2n+1) \ , \ n = 0,1,2,3\ldots \ .$$

The eigen-functions are trickier to find. for this we write

$$B(P^2 + Q^2) = 2BA^*A + B$$

where

$$A = \frac{1}{\sqrt{2}}(P - iQ)$$

and

$$A^* = \frac{1}{\sqrt{2}}(P + iQ) \ .$$

The eigen-functions belonging to the lowest eigenvalue are given by those functions $\psi$ that satisfy

$$A\psi = 0$$

which means that

$$\frac{1}{\sqrt{2}i}(\frac{\partial}{\partial x} - i\frac{\partial}{\partial y} + x - iy)\psi = 0$$

which in complex notation $z = x + iy$ means that

$$(2\frac{\partial}{\partial z} + \overline{z})\psi = 0 \, .$$

This is straightforward to solve and yields

$$\psi = e^{-|z|^2/2}\phi(\overline{z})$$

where $\phi(z)$ is an entire analytic function. Thus, we see that the ground state is in fact infinitely degenerate and we call this space of eigen - functions the **lowest Landau band**.

The eigen-functions of the next higher Landau band can be found by using commutation. If $\psi$ is in the lowest landau band then

$$A^*\psi$$

is not indentically zero and

$$[2BA^*A + B]A^*\psi = 2BA^*[A, A^*]\psi + A^*A^*A\psi + B\psi$$

$$= 3BA^*\psi$$

since $A\psi = 0$ and since $[A, A^*] = 1$. In this way one can ascend and get all the eigen - function of the Hamiltonian (3). In the usual units, the functions in the lowest Landau band of the Hamiltonian (2) are given by

$$e^{-\frac{B(x^2+y^2)}{4}}P(x - iy)$$

where $P$ is any polynomial.

Returning to the Hamiltonian (2) we have to consider the kinetic energy in the $z$ direction which commutes with the other term. This operator can be diagonalized using Fourier transform in the $z$ variable only

$$\widehat{f}(k) = \int e^{-2\pi ikz}f(z)dz \, ,$$

resulting in the Hamiltonian

$$(\frac{1}{i}\frac{\partial}{\partial x} + \frac{B}{2}y)^2 - (\frac{1}{i}\frac{\partial}{\partial y} + \frac{B}{2}x)^2 + (2\pi k)^2 \, . \qquad (2F)$$

Hence we see that the spectrum of the Hamiltonian is given by

$$B(2n + 1) + (2\pi k)^2$$

where $n = 0, 1, \ldots$ and $k \in R$. The spectrum is continuous because of the kinetic energy in the $z$ direction hence there are no square integrable eigenfunctions.
Since the magnetic field is constant in the $z$ direction, the dynamics of the spin is $\sigma_3 B$ which amounts to considering the matrix Hamiltonian

$$\begin{bmatrix} (\frac{1}{i}\nabla + A(x,y,z))^2 + B & 0 \\ 0 & \frac{1}{i}\nabla + A(x,y,z))^2 - B \end{bmatrix} .$$

Although there is not really a ground state we see that the infimum of the spectrum of the Hamilonian (P) for a constant magnetic field is $0$. Note that the spin terms subtracts the kinetic energy. This infimum can be found by considering spinors of the type

$$\sqrt{\frac{B}{2\pi}} e^{-(x^2+y^2)B/4} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \phi(x - iy) f(z) \tag{4}$$

where $f$ is any normalized function of one real variable and $\phi$ is an analytic function obeying the normalization

$$\frac{B}{2\pi} \int e^{-(x^2+y^2)B/2} |\phi(x - iy)|^2 dxdy = 1 .$$

Returning to the hydrogenic Hamiltonian (1) we would like to obtain some estimates on the ground state energy. Using trial functions of the form (4) with $\phi = 1$ we get the expectation value for the energy

$$\int_{-\infty}^{\infty} |f'(z)|^2 dz - Z\frac{B}{2\pi} \int e^{-(x^2+y^2)B/2} \frac{1}{\sqrt{x^2+y^2+z^2}} |f(z)|^2 dxdydz$$

$$= \int_{-\infty}^{\infty} |f'(z)|^2 dz - Z\frac{B}{2} \int e^{-sB/2} \frac{1}{\sqrt{s+z^2}} |f(z)|^2 dsdz$$

where we assume that

$$\int_{-\infty}^{\infty} |f(z)|^2 dz = 1 .$$

Since

$$s \to \frac{1}{\sqrt{s+z^2}}$$

is a convex function we have that

$$Z\frac{B}{2} \int e^{-sB/2} \frac{1}{\sqrt{s+z^2}} ds \gtrsim Z \frac{1}{\sqrt{\frac{2}{B} + z^2}}$$

and hence we have the upper bound

$$\int_{-\infty}^{\infty} |f'(z)|^2 dz - Z \int_{-\infty}^{\infty} \frac{1}{\sqrt{\frac{2}{B} + z^2}} |f(z)|^2 dz$$

$$\gtrsim \int_{-\infty}^{\infty} |f'(z)|^2 dz - Z \int_{-\infty}^{\infty} \frac{1}{\frac{2}{B} + |z|} |f(z)|^2 dz \ .$$

Finally, if we choose the function

$$f(z) = (\frac{1}{2\pi})^{1/4} e^{-z^2/2}$$

we see that the expectation of the energy is a fixed number while the expectation of the potential energy behaves as

$$-\text{const.} \log B$$

as $B \to \infty$.

Thus, there is no diamagnetic inequality and large magnetic fields squeeze the electron into the nucleus because of the interaction of the spin with the magnetic field. It is, however, impossible to produce large magnetic fields without expenditure of energy. Hence we define the stability of matter problem as follows.

**Theorem 74** *Let $E(N, B, Z)$ be the ground state energy of matter interacting with a magnetic field $B(x)$. Consider (in our units) the total energy*

$$E(N, K, B, Z) + \frac{1}{8\pi\alpha^2} \int |B(x)|^2 dx \ .f$$

*We say that the system is stable of the second kind if there exists a constant $C(Z)$ independent of the number of particles $N$ and $K$ and* **independent** *of the magnetic field such that*

$$E(N, K, B, Z) + \frac{1}{8\pi\alpha^2} \int |B(x)|^2 dx \gtrsim -C(Z)(N + K) \ .$$

Let us return to the hydrogen atom and report the bad news.

**Theorem 75** *The hydrogenic atom interacting with a magnetic field is unstable in the sense that if $Z\alpha^2$ is large enough then*

$$\inf\{E(Z, B) + \frac{1}{8\pi\alpha^2} \int |B(x)|^2 dx\} = -\infty \ .$$

**Proof** The proof depends critically on the existence of **zero modes of the three dimensional Dirac operator**. Consider a vector potential $A(x)$ whith

$$\int |\text{curlA}(x)|^2 dx < \infty \ .$$

A spinor $\psi(x)$ is called a zero mode if it is square integrable and if

$$\sigma \cdot (\frac{1}{i}\nabla + A(x))\psi(x) = 0$$

everywhere. Once such a zero mode is given we can scale it

$$\psi \to \psi_\lambda(x) = \lambda^{3/2}\psi(\lambda x)$$

and

$$A(x) \to A_\lambda(x) = \lambda A(\lambda x) \ .$$

Clearly

$$\sigma \cdot (\frac{1}{i}\nabla + A_\lambda(x))\psi_\lambda(x) = 0$$

and hence the expectation value of the hydrogenic Hamiltonian is given by

$$-Z \int \frac{1}{|x|}\langle \psi_\lambda, \psi_\lambda(x)\rangle dx + \frac{1}{8\pi\alpha^2}\int |B_\lambda(x)|^2 dx$$

$$= \lambda \left( -Z \int \frac{1}{|x|}\langle \psi, \psi(x)\rangle dx + \frac{1}{8\pi\alpha^2}\int |B(x)|^2 dx \right) \ .$$

Hence, we see that if $Z\alpha^2$ is too large we get an arbitrarily negative energy by letting $\lambda \to \infty$. □

Thus the main question is, are there any zero modes? Examples are hard to come by although people have discovered infinitely many of them so far. We give an idea how to construct such zero modes. Consider

$$\psi(x) = \frac{1 + i\sigma \cdot x}{(1 + |x|^2)^{3/2}}\phi \tag{5}$$

where $\phi$ is a constant spinor of length 1.

A straightforward calculation leads to

$$\sigma \cdot \frac{\nabla}{i}\psi = \frac{3}{(1 + |x|^2)}\psi \ .$$

Next, we note that every normalized spinor $\eta$ satisfies the eigenvalue equation

$$[\sigma \cdot \langle \eta, \sigma\eta\rangle]\eta = \eta$$

**Proof** (We have the general formula

$$\sigma \cdot a\sigma \cdot b = a \cdot b + i\sigma a \times b \ .$$

Hence

$$[\sigma \cdot \langle \eta, \sigma\eta\rangle]^2 = |\langle \eta, \sigma\eta\rangle|^2 = 1 \ ,$$

Further which means that the eigenvalues of the matrix $[\sigma \cdot \langle \eta, \sigma\eta\rangle]$ are $\pm 1$. Further

$$\langle \eta, [\sigma \cdot \langle \eta, \sigma\eta\rangle]\eta\rangle = 1$$

and hence by the minmax prinicple $\eta$ is the eigenvector with eigenvalue 1.) Hence we know that

$$\sigma \cdot \frac{\langle \psi, \sigma\psi\rangle}{\langle \psi, \psi\rangle}\psi = \psi$$

and if we define

$$A(x) = \frac{3}{1+|x|^2}\frac{\langle\psi, \sigma\psi\rangle}{\langle\psi,\psi\rangle}$$

the spinor $\psi$ is a zeromode.

A straightforward calculation yields

$$A(x) = \frac{3}{(1+|x|^2)^2}((1-|x|^2)w + 2w\cdot xx + 2w\wedge x)\ . \tag{6}$$

A further calculation shows that

$$B(x) = \frac{12}{(1+|x|^2)^3}((1-|x|^2)w + 2w\cdot xx + 2w\wedge x) \tag{7}$$

which is clearly square integrable. □

The field lines form closed Euclidean circles that sit on a family of nested tori and are linked once. In fact the field lines are given by pulling the Hopf-fibration from the three sphere to $R^3$.

The next theorem tells us that for stability to hold, $\alpha$ itself cannot be too large.

**Proof** The energy of an electron in the normalized state $\psi$ and with the vector portential $A(x)$ is given by

$$\|\sigma\cdot(\frac{1}{i}\nabla + A(x))\psi\|^2 - Z\sum_{k=1}^{K}\int\frac{|\psi(x)|^2}{|x-R_k|}dx + Z^2\sum_{k<l}\frac{1}{|R_k-R_l|} + \frac{1}{8\pi\alpha^2}\int|B(x)|^2dx\ .$$

Suppose that$\psi$ is a zero mode for the vector potential $A(x)$ then the energy is given by

$$-Z\sum_{k=1}^{K}\int\frac{|\psi(x)|^2}{|x-R_k|}dx + Z^2\sum_{k<l}\frac{1}{|R_k-R_l|} + \frac{1}{8\pi\alpha^2}\int|B(x)|^2dx\ . \tag{8}$$

Consider the density

$$F(R_1,\ldots,R_K) = \prod_{k=1}^{K}|\psi(R_k)|^2\ .$$

This density is normalized to one

$$\int dR_1\cdots dR_K F(R_1,\ldots,R_K) = 1\ .$$

Next we average the expression (8) with respect to $F$ and get

$$-ZKI + Z^2\frac{K(K-1)}{2}I + \frac{1}{8\pi\alpha^2}J$$

where

$$I = \int dxdy\frac{|\psi(x)|^2|\psi(y)|^2}{|x-y|}$$

and

$$J = \int |B(x)|^2 dx \ .$$

If we scale $A$ and $\psi$ the usual ways we obtain

$$\lambda \left[ -ZKI + Z^2 \frac{K(K-1)}{2} I + \frac{1}{8\pi\alpha^2} J \right] \tag{9}$$

and hence we have to calculate the term in $[\cdot]$. Certainly, instability of (9) is implied by the instability of

$$\lambda \left[ -ZKI + Z^2 \frac{K^2}{2} I + \frac{1}{8\pi\alpha^2} J \right] = \lambda \left[ -\frac{1}{2} I + \frac{1}{2}(1 - ZK)^2 I + \frac{1}{8\pi\alpha^2} J \right] \ .$$

If $Z$ is small of the form $1/L$ where $L$ is an integer, then we can choose $K = L$ and get the expression

$$\lambda \left[ -\frac{1}{2} I + \frac{1}{8\pi\alpha^2} J \right] \ ,$$

and we see that if

$$\alpha > \sqrt{\frac{J}{4\pi I}}$$

then we have instability. Using (5), (6) and (7) we get □

# 19 A short introduction to statistical mechanics

Thermodynamics consists of the application of two principles, the first law which says that heat is energy and hence the law of conservation of energy must apply and the second law of Thermodynamics, which says that there is no machine whose sole purpose is to do work by extracting heat from a reservoir. While it is not our aim to discuss Thermodynamics we treat the ideal gas in some detail.

The ideal gas law says that

$$pV = kNT$$

where $p$ is the pressure, $V$ the volume, $T$ the absolute temperature and $N$ the number of particles (in moles) in the gas. The constant $k$ is Boltzmann's constant. There is another equation which relates the temperature $T$ to the energy contained in the gas

$$U = \gamma kTN$$

where $\gamma$ is a constant that depends on the type of the gas. The first law says

$$dU = dQ - pdV + \mu dN$$

which is a confusing formula. (Here $\mu$ is the chemical potential. The formula suggests that there exists a function $U(Q, V, N))$ so that its gradient is given by $(1, -p, \mu)$. This is not the case! There is, however, the second law which states that there is an integrating factor $1/T$ so that

$$dS = \frac{1}{T} dQ$$

is indeed an exact one form. Thus there exists a function $U(S, V, N)$ so that

$$dU = TdS - pdV \ .$$

In particular

$$\frac{\partial U}{\partial S} = T \ ,$$

$$\frac{\partial U}{\partial V} = -p$$

and

$$\frac{\partial U}{\partial N} = \mu \ .$$

Note the sloppy notation which is at the root of all the confusion in thermodynamics. One does not make the distinction between $U$ as a function of $T$ and $U$ as a function of

$S$. both function are represented by the same symbol. Returning to the ideal case, we note that good variables would be $U, V, N$ and not $S, V, N$. Since $\frac{\partial U}{\partial S} > 0$ we can invert this relation and consider $S(U, V, N)$ and hence

$$\frac{\partial S}{\partial U} = \frac{1}{T}$$

$$\frac{\partial S}{\partial V} = \frac{p}{T}$$

and

$$\frac{\partial S}{\partial N} = -\frac{\mu}{T} .$$

There is the fundamental requirement that the $S$, $U$, $V$ and $N$ all scale the same way as we enlarge the systems. If we have twice as many particles, twice the interal energy and twice the volume then the entropy should be multiplied by two. In other words

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N) .$$

Differentiating the above relation at $\lambda = 1$ gets us

$$S(U, V, N) = \frac{U}{T} + \frac{pV}{T} - \frac{\mu N}{T} .$$

For the ideal gas

$$\frac{1}{T} = \frac{\gamma k N}{U} , \frac{p}{T} = \frac{kN}{V} ,$$

and hence

$$S(U, V, N) = \gamma k N \log U + kN \log V + NC(N)$$

for some unknown function $C(N)$. By scaling

$$\lambda(\gamma k N \log U + kN \log V + NC(N)) = \gamma k \lambda N \log(\lambda U) + k\lambda N \log(\lambda V) + \lambda N C(\lambda N)$$

or

$$C(N) = (\gamma + 1)k \log \lambda + C(\lambda N)$$

Differentiating this at $\lambda = 1$ yields

$$0 = (\gamma + 1)k + C'(N)N$$

and hence

$$C(N) = -(1 + \gamma)k \log N$$

up to some constant. Hence, the entropy for an ideal gas is given by

$$S(U, V, N) = \gamma k N \log U + kN \log V - (1 + \gamma)kN \log N .$$

Gas with a piston

Imagine a a cylinder of length one (in some units) insulated against heat transfer filled with gas. Inside the cylinder is an ideal insulating piston at position $0 < x < 1$. Half of the gas is on the eft of the piston where it has Volume $Ax$, ($A$ is the cross section ) temperature $T$ and half of the gas is on the right of the piston where it has volume $A(1-x)$ and temperature $T$. Thus, the pressure on the left will be larger than on the right. The piston is fixed with a pin. At some moment we pull the pin and let the piston move freely which it does without friction. Eventually it will come to rest and the question is where.

Call the position $y$. The pressures on both sides must be the same, hence

$$\frac{T_L}{y} = \frac{T_R}{(1-y)} \, .$$

Moreover, by the first law the energy must be conserved, i.e.,

$$T_L + T_R = 2T \, .$$

Therefore

$$T_L = 2Ty \, , \; T_R = 2T(1-y) \, .$$

We know from the second law that the entropy must have gone up. Thus the entropy at the end of the process is greater than the entropy of the system before. The total entropy before the process is given by (up to irrelevant constants)

$$2\gamma \log T + \log x + \log(1-x)$$

whereas the entropy after is

$$\gamma \log(2Ty) + \gamma \log(2T(1-y) + \log y + \log(1-y) \, .$$

Hence applying the second law we get the inequality

$$\log(x(1-x)) \gtrsim 2\gamma \log 2 + (1+\gamma) \log(y(1-y))$$

A straightforward calculation leads to the

$$y(1-y) \lesssim \frac{(x(1-x))^{\frac{1}{1+\gamma}}}{4^{\frac{\gamma}{1+\gamma}}} \, .$$

Note that when $x = 1/2$ we get correctly $y = 1/2$.

What this result is saying that the given macroscopic quantities do not suffice the calculate the exact outcome of this experiment. The Second Law, however, yields bounds for the position of the piston. These inequalities are determined entirely by the macroscopic quantities. It might be that shocks and all sorts of nasty things might develop by releasing the piston, but the second law sets absolute bounds on the outcome.

## The statistical theory of entropy

We consider a system of $N$ interacting particles in a box. The system is specified by giving the positions $X = (x_1, \ldots, x_N)$ and the momenta $P = (p_1, \ldots, p_N)$. If we give a probability distribution $\rho(X, P)$ then the Boltzmann entropy is given by

$$S(\rho) = -k \int dX dP \rho(X, P) \log(\rho(X, P)) \ .$$

Assuming that the dynamics of the system is given by the Hamiltonian

$$H(X, P)$$

one might ask what is the state with maximal entropy, given that the system has total energy $U$. In other words, we have to maximize $S(\rho)$ given that

$$\int H(X, P)\rho(X, P)dXdP = U$$

and that

$$\int \rho(X, P)dXdP = 1 \ .$$

To solve this problem we start with the elementary inequality

$$-x \log x \lesssim e^{\alpha} - (\alpha + 1)x$$

which holds for all $x > 0$ and all $\alpha$. There is equality if and only if

$$x = e^{\alpha} \ .$$

Next we have pointwise

$$-k\rho \log \rho \lesssim ke^{-\gamma H+\delta} - k(\gamma H + \delta - 1)\rho$$

where $\gamma$ and $\delta$ are constants. Again, there is equality if and only if

$$\rho = e^{-\gamma H+\delta} \ .$$

We now use the free constants to fix the correct side conditions

$$\int dXdPe^{-\gamma H+\delta} = 1$$

and

$$\int dXdPe^{-\gamma H+\delta}H = U \ .$$

The first says that we choose $\gamma$ such that

$$e^{-\delta} = \int dXdPe^{-\gamma H} \ ,$$

the other means that we have to choose $\gamma$ such that

$$\frac{\int dXdPe^{-\gamma H}H}{\int dXdPe^{-\gamma H}} = U \ . \tag{1}$$

This is an equation for $\gamma$ and we have to show that there is a solution. Differentiate the left side of (1) with respect to $\gamma$ and get

$$-\frac{\int dXdPe^{-\gamma H}H^2}{\int dXdPe^{-\gamma H}} + [\frac{\int dXdPe^{-\gamma H}H}{\int dXdPe^{-\gamma H}}]^2$$

and since the left side of (1) is the expectation value of $H$

$$\langle H\rangle_\rho$$

with respect to the probability distribution

$$\rho = \frac{e^{-\gamma H}}{\int dXdPe^{-\gamma H}}$$

we can write this as

$$-\langle H^2\rangle_\rho + (\langle H\rangle_\rho)^2 = -\langle (H - \langle H\rangle_\rho)^2\rangle_\rho < 0 \ .$$

This means that the left side of (1) is a strictly decreasing function of $\gamma$. Clearly, any allowed value for $U$ must be in the range of $H$. As $\gamma$ tends to $\infty$ the left side of (1) converges to the minimal value of $H$. If we take our system of the form

$$H = \sum_{j=1}^{N} p_j^2 + V(x_1, \ldots, x_N)$$

where the particles are constrained in a box, then we see that as $\gamma \to 0$ the left side of (1) tends to $\infty$. Thus, in this case for any $U$ in the range of $H$ the equation (1) has a unique solution. We call this solution $\beta$. Hence the optimizing $\rho$ is given by

$$\rho_{\text{canon}} = \frac{e^{-\beta H}}{\int dXdPe^{-\beta H}} \ .$$

This is called the **canonical ensemble** and

$$Z = \int dXdPe^{-\beta H}$$

is called the partition function. Further we get

$$S(\rho_{\text{canon}}) = k\beta\langle H\rangle_{\text{canon}} + k\log Z \ . \tag{2}$$

We shall see that this formula has a nice interpretation.

For the case of an ideal gas the Hamiltonian is given by

$$H = \frac{1}{2m}\sum_{j=1}^{N} p_j^2$$

and the particles are confined to a volume $V$. Now

$$\rho_{\text{canon}} = (\frac{\beta}{2m\pi})^{3N/2} e^{-\frac{\beta}{2m}\sum_{j=1}^{N} p_j^2} \prod_{j=1}^{N} \frac{\chi_V(x_j)}{|V|}$$

and

$$Z = (\frac{2m\pi}{\beta})^{3N/2} |V|^N \ .$$

The energy is

$$U = \langle H \rangle_{\text{canon}} = \frac{3}{2} N \frac{1}{\beta} \tag{3}$$

i.e., $\gamma = 3/2$.

and we see that $\beta = \frac{1}{kT}$ is consistent. Further using (2)

$$S(\rho_{\text{canon}}) = \frac{3}{2}Nk + kN[\frac{3}{2}\log(\frac{2m\pi}{\beta}) + \log|V|]$$

and recalling that we have to write $S$ in terms of the variable $U, V, N$ we can eliminate $\beta$ using (3) and get

$$S = \frac{3}{2}kN\log U + kN\log|V| - \frac{3}{2}kN\log N + \frac{3}{2}kN(1 - \log((4m\pi/3)) \ .$$

The last term is just an additive constant and is irrelevant for thermodynamics. All the other terms fit our expectation except the the penultimate term. We have the serious problem that the entropy is not extensive. We should really have

$$-(1 + \frac{3}{2})kN\log N$$

instead of

$$-\frac{3}{2}kN\log N \ .$$

Note that we can get out of this quagmire of replace the partition function by

$$Z = \frac{1}{N!}\int dX dP e^{-\beta H}$$

since this term will yield an addition term of the order of $N\log N$ for the entropy and that would render the entropy extensive. This problem does not show up in quantum statistical mechanics! The way out in the classical case is to undestand that the particles

are indistinguishable. The configuration $(x_1, x_2, x_3, \dot{,} x_N)$ cannot be distinguished from the configuration $(x_2, x_1, x_3, \dot{,} x_N)$. In other words we have to consider the density

$$\rho_{\mathbf{canon}} = \frac{e^{-\beta H}}{\int dX dP e^{-\beta H}} \chi_{\mathcal{S}_N}$$

where $\chi_{\mathcal{S}_N}$ is the characteristic function of a fundamental domain of the permutation group. Such a set is somewhat complicated to describe when the underlying space is $R^3$ but since its contribution to the partition function is $1/N!$ times the whole one. We shall see that the partition function contains in some sense all the information of our thermodynamic system. If the underlying space is one dimensional then a fundamental domain is given by the region

$$x_1 < x_2 < \cdots < x_{N-1} < x_N \ .$$

In this formalism the natural variables are not $U, V, N$ but $T, V, N$. The way out of that is to perform a Legendre transform. One performs this best by starting from the internal energy $U(S, V, N)$. Solve the equation

$$\frac{\partial U}{\partial S} = T$$

to get $S(T, V, N)$. Then consider the **Free Energy** function

$$F(T, V, N) = U(S(T, V, N), V, N) - TS(T, V, N)$$

and note that

$$\frac{\partial F}{\partial T} = -S \ , \ \frac{\partial F}{\partial V} = -p$$

and

$$\frac{\partial F}{\partial N} = \mu \ .$$

Returning to (2) we see that

$$F = -\frac{1}{\beta} \log Z \ ,$$

where

$$Z = \frac{1}{N!} \int dX dP e^{-\beta H} \ .$$

Thus, the log of the partition function yields the free energy.

# 20 Thermodynamic limit of a classical system

We shall consider $N$ classical particles in a volume $V$. The partcles interact with each other through a pair potential $\Phi(x-y)$ which satisfies the following conditions:

- $\Phi$ is bounded and of positive type, i.e., it has a positive Fourier transform.
- $\Phi$ decays faster than $R^{-3}$ as $R \to \infty$, where $R = |x-y|$.

As we have seen the canonical partition function is given by

$$Z = \frac{1}{N!} \int_{V^N} dx_1 \cdots dx_N e^{-\beta \sum_{i<j} \Phi(x_i - x_j)} \ .$$

We ignore here the factor that comes from the kinetic energy of the particles. The free energy per unit volume is then given by

$$f(T,V,N) = -\frac{1}{\beta |V|} \log(Z) \ ,$$

where $|V|$ denotes the volume.

Here we would like to address the question whether the thermodynamic limit exists, i.e, whether $f(T,V,N)$ has a limit as $V, N \to \infty$ in such a way that $N/V \to \rho > 0$, the density. In this case the limiting free energy is a function of the temperature and the the density $f(T,\rho)$.

There are a number of reasons why one wants to consider a thermodynamic limit. While one never considers an infinite systems in practice, it should be large enough so that surface effects are negligible, i.e., one is only interested in bulk properties. Further, one has learned that a phase transition can be qualitatively described only in the thermodynamic limit where it shows up as a lack of analyticity in certain parameters.

Let us return to the assumptions on $\Phi$. The first yields that

$$\sum_{i,j} \Phi(x_i - x_j) = \sum_{i,j} \int dk e^{i2\pi k \cdot (x_i - x_j)} \widehat{\Phi}(k) dk = \int |\sum_j e^{i2\pi k \cdot x_j}|^2 \widehat{\Phi}(k) dk \gtrsim 0$$

and hence

$$\sum_{i<j} \Phi(x_i - x_j) \gtrsim -\frac{N}{2} \Phi(0)$$

which means that the system is stable. This implies immediately that the partition function $Z$ is bounded above by

$$\frac{1}{N!} |V|^N e^{\beta N \Phi(0)}$$

which in turn implies the lower bound

$$f(T,V,N) \gtrsim -\frac{1}{\beta|V|}(-\log(N!) + N\log(|V|) + \beta\frac{N}{2}\Phi(0))$$

$$\gtrsim kT\rho\log(\rho) - \rho\Phi(0)/2 \ .$$

The first term is essentially the free energy of an ideal gas recalling that we have neglected theterm coming from the kinetic energy.

The bound depends only on $\rho$ and $\Phi$ but not on the volume. It tends to zero s $\rho \to 0$, no particles no free energy. It is further remarkable that the $1/N!$ is absolutely necessary to obtain such a result. Without it there would be no expression in terms of the density alone.

To summarize, the stability assumption yields a lower bound that is independent of the volume , it depends only on $\rho$. Thus we need to exhibit a sequence of domains along which the partition function is increasing. We choose these domains to be boxes of sidelength $L$. We shall replace the second assumption on $\Phi$ by a more precise one

• $\Phi$ should satisfy

$$\Phi(x-y) \gtrsim C|x-y|^{-3-\varepsilon} \ ,$$

where $C$ is some constant.

**Proof** Pick a box of side length $L$ and subdivide it into $8$ smaller boxes of side length $L/2$. denote by $Z$ the partition function of the big box containing $N$ particles and by $z$ the partition function of the small box containing $N/8$ particles. We assume that $N$ is divisible by eight. Clearly

$$Z = \frac{1}{N!}\sum_{N_1+\cdots N_8=N}\frac{N!}{N_1!N_2!\cdots N_8!}$$

$$\int dX_1 e^{-\beta\Phi(X_1)}\int dX_2 e^{-\beta\Phi(X_2)}\cdots\int dX_8 e^{-\beta\Phi(X_8)}e^{-\beta\sum_{i\neq j}^{8}\Phi(X_i,X_j)} \ .$$

The first factor is the number of ways one can choose $N_1,\ldots,N_8$ particles out of $N$. Th notation $\Phi(X_1$ denotes the interaction of the particles in the first box with each other and likewise $\Phi(X_2$ denotes the interaction of the particles in the second box with each other etc. and finally the last double sum denotes the interaction of particles in different boxes.

Trivially

$$Z \gtrsim \frac{1}{M!^8}\int dX_1 e^{-\beta\Phi(X_1)}\int dX_2 e^{-\beta\Phi(X_2)}\cdots\int dX_8 e^{-\beta\Phi(X_8)}e^{-\beta\sum_{i<j}^{8}\Phi(X_i,X_j)}$$

where each box contains the same number of particles $M = N/8$ and we have thrown away all other contributions. Next we have to deal with the interaction among the particles in different boxes. There the decay of the interaction is important. Construct a corridor between the boxes of width $\frac{L}{2}^{1-\delta}$ where $\delta > 0$ to be chosen later. Next we restrict the integration of the particles to make sure that they are outside the corridors.

This diminishes the right side once more. Note that the width of the corridor is large but of lower order than $L$. Now we can calculate the contribution of the interaction energy of the particles in different boxes. It is *bounded above* by

$$C(\frac{L}{2})^{-(1-\delta)(3+\varepsilon)}M^2 \ .$$

Choosing

$$\delta = \frac{\varepsilon}{6+2\varepsilon}$$

yields the bound

$$C(\frac{L}{2})^{-3-\varepsilon/2}M^2 = \frac{C}{8^{1+\varepsilon/2}}\rho\frac{N}{L^{\varepsilon/2}} \ .$$

Thus collecting the terms we get that

$$Z \lesssim (z')^8 e^{-\beta 28\frac{C}{8^{1+\varepsilon/2}}\rho\frac{N}{L^{\varepsilon/2}}} \tag{1}$$

where $z'$ denotes the partition function of a small box with the corridors removed. This partition function is again a partition function of a box but with a slightly higher density. reformulating (1) in terms of the free energy per unit volume yields

$$f(T,L^3,N) \lesssim 8f(T,(\frac{L}{2})^3(1-(\frac{L}{2})^{-\delta})^3,\frac{N}{2})\frac{(\frac{L}{2})^3(1-(\frac{L}{2})^{-\delta})^3}{L^3} + 28\frac{C}{8^{1+\varepsilon/2}}\rho\frac{\rho}{L^{\varepsilon/2}} \ . \tag{2}$$

Now we can set up the procedure for taking the limit. Set

$$L_n = \frac{L_{n+1}}{2} - (\frac{L_{n+1}}{2})^{1-\delta}$$

$$N_n = \frac{N_{n+1}}{8}$$

so that both $N_n$ and $L_n$ grow exponentially and

$$\lim_{n\to\infty}\frac{N_n}{L_n^3} = \rho \ .$$

Further define

$$f_n = f(T,L_n^3,N_n)$$

so that

$$f_{n+1} \lesssim c_n f_n + d_n \ . \tag{3}$$

where

$$c_n = 8(\frac{L_n}{L_{n+1}})^3$$

and

$$d_n = \frac{D}{L_{n+1}^{\frac{\varepsilon}{2}}} \ .$$

Write the inequality (3) as an equality

$$f_{n+1} = c_n f_n + d_n - e_n$$

where $e_n \gtrsim 0$. This can be solved explicitely

$$f_{n+1} = c_0 \cdots c_n f_0 + D_{n+1} - E_{n+1}$$

where

$$D_{n+1} = d_0 c_1 \cdots c_n + d_1 c_2 \cdots c_n + \cdots + d_n$$

and

$$E_{n+1} = e_0 c_1 \cdots c_n + e_1 c_2 \cdots c_n + \cdots + e_n \ .$$

Since the $c_i \lesssim 1$ the first term converges as $n \to \infty$. Further $D_{n+1}$ converges since the $d_i$ decay exponentially. Finally $E_{n+1}$ is monotone increasing and bounded since $f_n$ is uniformly bounded below and hence $E_n$ converges as $n \to \infty$. Thus $f_n$ converges too, which was to be proved. □

Thus the thermodynamic limit along a sequence of boxes is established. A further problem is to show that the limit exists along more general sequences than just boxes. They should be nice in the sense that the surface area should grow slower than the volume. The whole procedure is tedious but standard and this will not be carried out here.

# 21 Quantum statistical mechanics

Quantum statistical mechanics is based on the notion of 'density matrix' and the notion of entropy. A density matrix is a positive selfadjoint operator on a Hilbert which is trace class. Any density matrix on $L^2(R^3)$ has a kernel that can be written as

$$\sum_{j=1}^{\infty} \lambda_j \overline{\phi_j}(x)\phi_j(y)$$

where $\lambda_j \gtrsim 0$ and $\sum_j \lambda_j < \infty$.

Density matrices occur under a variety of circumstances. E.g., consider a system of particles whose dynamics is goverend by a Hamiltonian $H$ which has purely discrete spectrum $\mu_j$ with eigenfunctions $\phi_j$. Starting with an initial state $\psi_0$ we get the time evolved state as

$$\psi_t(x) = \sum_j (\phi_j, \psi_0)\phi_j(x)e^{-i\mu_j t} \ .$$

Consider the density matrix

$$\gamma_t = \overline{\psi_t}(x)\psi_t(y) = \sum_{j,k} \overline{(\phi_j, \psi_0)}(\phi_k, \psi_0)\overline{\phi_j}(x)\phi_k(y)e^{i(\mu_j - \mu_k)t} \ .$$

This density matrix contains all the information about the evolution of the system, nothing has been lost. Moreover, if we calculate expectation values of of an observable $A$ which is a selfadjoint operator on the Hilbert space, we get that

$$(\psi_t, A\psi_t) = \mathrm{Tr}(A\gamma_t) \ .$$

Note that expectation values are *linear in the density matrix* but *quadratic in the wave function*.

If we now imagine that we perform lots of observations in time and average them over time we get

$$\lim_{T\to\infty} \frac{1}{T}\int_0^T (\psi_t, A\psi_t)dt = \lim_{T\to\infty} \frac{1}{T}\int_0^T \mathrm{Tr}(A\gamma_t)dt$$

$$= \sum_{j,k} \overline{(\phi_j, \psi_0)}(\phi_k, \psi_0)(\phi_j, A\phi_k) \lim_{T\to\infty} \frac{1}{T}\int_0^T e^{i(\mu_j - \mu_k)t}dt \ .$$

If we further make the *assumption that the eigenvalues are not degenerate* we get that

$$\lim_{T\to\infty} \frac{1}{T}\int_0^T e^{i(\mu_j - \mu_k)t}dt = \delta_{j,k}$$

and hence

$$\lim_{T\to\infty}\frac{1}{T}\int_0^T(\psi_t,A\psi_t)dt=\sum_j|(\phi_j,\psi_0)|^2(\phi_j,A\phi_j)\ . \tag{1}$$

Since we are not interested in the evolution of a particular state but rather would like to describe a thermal ensemble of system, we are invoking again Boltzmann's principle for choosing the numbers

$$D_j=|(\phi_j,\psi_0)|^2\gtrsim 0\ .$$

Note that

$$\sum_j D_j=1\ .$$

We define the entropy of the collection of numbers by $D_j$ by the formula

$$S(D)=-k\sum_j D_j\log D_j\ .$$

Maximizing $S(D)$ under the constraints that $\sum D_j=1$ and that

$$\sum_j D_j\mu_j=U$$

leads to

$$D_j=\frac{e^{-\beta\mu_j}}{\sum_k e^{-\beta\mu_k}}\ .$$

Thus, we can write in an abbreviated way the canonical density matrix as

$$\rho_{\text{canon}}=\frac{e^{-\beta H}}{Z} \tag{2}$$

where

$$Z=\mathrm{Tr}e^{-\beta H} \tag{3}$$

and $\beta$ is the unique solution of the equation

$$\mathrm{Tr}H\rho_{\text{canon}}=U\ . \tag{4}$$

The arguments proceed the same way as in the classical case. This considerations are heuristic and we take equations (2),(3) and (4) as our starting point. We do not require that the eigenvalues are non degenerate. All that is important is that

$$e^{-\beta H}$$

is trace class. As in the classical case the free energy $F$ is given by

$$F=-\frac{1}{\beta}\log Z$$

where $\beta = \frac{1}{kT}$. As an example we calculate the partition function of a noninteracting fermion gas in a box $\Omega$. We consider $N$ fermions with energy

$$H = \sum_{j=1}^{N} p_j^2$$

where $p_j^2$ is the Laplacian with Dirichlet boundary conditions in $\Omega$. The Hilbert space $\mathcal{H}$ consists of functions of space variables and spin variables that take $q$ values. Moreover, the functions ae antisymmetric in the particles lables. Thus, we have to compute

$$\mathrm{Tr}_{\mathcal{H}} e^{-\beta H} \ .$$

There is no closed form solution for that problem in the canonical ensemble but we have the following statement.

**Theorem 76** *The partition function of $N$ fermions each having $q$ spin states is given by*

$$q^N \frac{1}{N!} \int_{\Omega^N} dx_1 \cdots dx_N \det(G_\beta(x_i, x_j))$$

*where $G_\beta(x, y)$ is the heat kernel associated with the Dirichlet Laplacian in the volume $\Omega$. If the particles are Bosons, the determinant is replaced by the permanent.*

**Proof** The main point of the theorem is of course the prefactor $\frac{1}{N!}$ which is in agreement with the classical considerations. Let

$$\Psi(x_1, \sigma_1; \dots; x_N, \sigma_N)$$

by and a normalized function in our Hilbert space. Then

$$(\Psi, e^{-\beta H}\Psi) = \sum_{\sigma_1, \dots, \sigma_N} \int_{\Omega^N} \Psi(x_1, \sigma_1; \dots; x_N, \sigma_N)$$

$$\times \prod_{j=1}^{N} G_\beta(x_j, y_j) \Psi(y_1, \sigma_1; \dots; y_N, \sigma_N) dx_1 \cdots dx_N dy_1 \cdots dy_N \ .$$

In this expression we can replace $\prod_{j=1}^N G_\beta(x_j, y_j)$ by its antisymmetrization over the $y$ variables, i.e.,

$$\frac{1}{N!} \sum_{\pi \in \mathcal{S}_N} (-1)^\pi \prod_{j=1}^{N} G_\beta(x_j, y_{\pi(j)}) \ ,$$

and denote this operator by $B$. Note that this expression is automatically antisymmetric in the $x$ variables. Next, pick an orthonormal basis $\phi_j(x, \sigma)$ in $L^2(R^3; C^q)$ and note that $\Phi_J = \prod_{k=1}^N \phi_{j_k}$ is an orthonormal basis in $\otimes^N L^2(R^3; C^q)$. Since $(\Phi_J, B\Phi_J)$ equals

$$\sum_{\sigma_1, \dots, \sigma_N} \int_{\Omega^N} \Phi(x_1, \sigma_1; \dots) B(x_1, \dots, , y_1, \dots) \Phi(y_1, \sigma_1; \dots) dx_1 \cdots dx_N dy_1 \cdots dy_N \ ,$$

and $B$ is antisymmetric in the $x$ and antisymmetric in the $y$ variables we can replace $\Phi$ by its slater determinant

$$\frac{1}{\sqrt{N!}}\det(\phi_j(x_i))$$

and hence

$$Z = \mathrm{Tr}B$$

which is what we wanted to show. The case for bosons is similar. □

One of the simple tools we shall frequenctly use is the *Peierls Bogolubov inequality*.

**Theorem 77** *Consider two self adjoint operators $A$ and $B$ with discrete spectrum so that*

$$\mathrm{Tr}e^{-A-B} < \infty \, .$$

*Then*

$$\mathrm{Tr}e^{-A-B} \gtrsim \mathrm{Tr}e^{-A}e^{-\langle B\rangle}$$

*where*

$$\langle B\rangle = \frac{\mathrm{Tr}Be^{-A}}{\mathrm{Tr}e^{-A}} \, .$$

**Proof** Let $g_j$ be an orthonormal basis in which $B$ is diagonal and $h_k$ be an orthonormal basis in which $A+B$ is diagonal. Then

$$\mathrm{Tr}e^{-A-B} = \sum_j (g_j, e^{-A-B}g_j) = \sum_{j,k} |(g_j,h_k)|^2 (h_k, e^{-A-B}, h_k) \, .$$

Since for every fixed $j$

$$\sum_k |(g_j,h_k)|^2 = 1$$

and since $x \to e^{-x}$ is convex, we can use Jensen's inequality to get

$$\sum_{j,k} |(g_j,h_k)|^2 (h_k, e^{-A-B}, h_k) \gtrsim \sum_j e^{-\sum_k |(g_j,h_k)|^2 (h_k,(A+B)h_k)}$$

$$= \sum_j e^{-(g_j,(A+B)g_j)} \, .$$

Further

$$\sum_j e^{-(g_j,(A+B)g_j)} = \sum_j e^{-(g_j,Ag_j)-\mu_j} = \mathrm{Tr}e^{-A}\sum_j \frac{e^{-(g_j,Ag_j)}}{\mathrm{Tr}e^{-A}} e^{-\mu_j}$$

where $\mu_j$ are the eigenvalues of $B$. We write this as

$$\mathrm{Tr}e^{-A}\sum_j p_j e^{-\mu_j}$$

with

$$\sum_j p_j = 1 \ .$$

Since $x \to e^{-x}$ is convex, we can use Jensen's inequality

$$\sum_j p_j e^{-(g_j, Bg_j)} \gtrsim e^{-\sum_j p_j \mu_j}$$

but

$$\sum_j p_j \mu_j = \frac{\mathrm{Tr} B e^{-A}}{\mathrm{Tr} e^{-A}}$$

which yields the inequality. □

# 22 The thermodynamic limit for matter

In this section we discuss the result of Lieb and Lebowitz concerning the existence of the free energy for matter consisting of nuclei and electrons. As explained before there will be three steps involved. First, a universal lower bound on the free energy per unit volume that is independent of the volume, second a sequence of volumes going to infinity for which the free energy decreases and finally a proof that the limit is independent for reasonable shapes. We do not discuss the last point.

We consider the Coulomb system given by the Hamiltonian

$$H = \sum_{j1}^{N} p_j^2 + \frac{1}{M} \sum_{k=1}^{K} P_k^2 + V_c \ ,$$

where we have included the kinetic energy of the nuclei. The Hilbert space is then given by

$$\mathcal{H} = \mathcal{H}_{\rm el} \otimes \mathcal{H}_{\rm nucl}$$

where

$$\mathcal{H}_{\rm el} = \wedge^N L^2(\Omega; C^2) \ ,$$

the $N$-fold antisymmetric tensor product. For the Hilbert space of the nuclei we do not make any assumptions since the nuclei may be bosons, fermions or a mixture thereof.

We assume that the particles are all in some volume $\Omega$ and we set Dirichlet boundary conditions for the Laplace operators involved. The partition function is then given by

$$Z = {\rm Tr}_{\mathcal{H}} e^{-\beta H}$$

and the free energy per unit volume is given by

$$f(\beta, V, N, K) = -\frac{1}{|\Omega|\beta} \log Z$$

and we are interested in the the limit as

$$\Omega \to R^3$$

$$N, K \to \infty$$

in such a way that

$$\frac{N}{|\Omega|} \to \rho_{\rm el}$$

and

$$\frac{K}{|\Omega|} \to \rho_{\rm nucl} \ .$$

Step 1: The lower bound

We write

$$H = \frac{1}{2}[\sum_{j1}^{N} p_j^2 + \frac{1}{M}\sum_{k=1}^{K} P_k^2] + \frac{1}{2}[\sum_{j1}^{N} p_j^2 + \frac{1}{M}\sum_{k=1}^{K} P_k^2] + V_c$$

and note that by the result of Dyson-Lenard, resp. Lieb-Thirring there exists a constant $C(Z)$ that is independent of $N, K$ and, of course not on $\Omega$ so that

$$H \gtrsim \frac{1}{2}[\sum_{j1}^{N} p_j^2 + \frac{1}{M}\sum_{k=1}^{K} P_k^2] - C(Z)(N+K) \ .$$

Hence

$$Z \lesssim {\rm Tr}_{\mathcal{H}} e^{-\frac{\beta}{2}[\sum_{j=1}^{N} p_j^2 + \frac{1}{M}\sum_{k=1}^{K} P_k^2]} e^{\beta C(Z)(N+K)} \ .$$
$$= {\rm Tr}_{\mathcal{H}_{\rm el}} e^{-\frac{\beta}{2}\sum_{j=1}^{N} p_j^2} {\rm Tr}_{\mathcal{H}_{\rm nucl}} e^{-\frac{\beta}{2M}\sum_{k=1}^{K} P_k^2} e^{\beta C(Z)(N+K)} \ .$$

From this we see that the free energy per unit volume is bounded below by the sum of the free energies of a noninteracting gas of electrons and nuclei minus

$$C(z)(\rho_{\rm el} + \rho_{\rm nucl}) \ .$$

This is well known to be bounded below by a function that depends only on the temperature and the densities $\rho_{\rm el}$ and $\rho_{\rm nucl}$.

We come now to the second step which amounts to show that along a suitable sequence of volumes the free energy per unit volume is a decreasing sequence. The obvious obstacle here is that the Coulomb potential is of long range and there is no obvious way how to bound this. Clearly, if the system is macroscopically not neutral there is no thermodynamic limit. Hence we shall assume neutrality from now on, i.e., the sum of the nuclear charges is canceled by the sum of the electronic charges.

First we recall Newton's heorem. Imagine two charge distributions, one of them, $\rho(x)$ spherically symmetric and the other one $\mu$ not necessarily spherically symmetric. (Spherically symmetric means that $\rho(x) = \rho(y)$ whenever $|x| = |y|$.

**Theorem 78 (Newton's theorem)** *The interaction energy between the charges $\mu$ and $\rho$, which is given by*

$$\int\int \frac{\rho(x)\mu(y)}{|x-y|} dxdy = \int\int \min(\frac{1}{|x|}, \frac{1}{|y|})\rho(x)\mu(y)dxdy \ .$$

*In particular if $\mu$ is supported inside a ball of radius $R$, $\rho$ supported outside the ball and if*

$$\int \mu(y)dy = 0$$

*then the interaction energy vanishes.*

**Proof** The proof consists of evaluating the integral

$$\int_{S^2} \frac{1}{(|x|^2+|y|^2-2|x|y\cdot w}dw = \min(\frac{1}{|x|},\frac{1}{|y|}) \ .$$

We will encounter the following situation. Given two disjoint balls $B_1$ and $B_2$. In $B_1$ we have $N_1$ electrons and $M_1$ nuclei, so that the system is neutral, i.e,

$$\sum_{j=1}^{M_1} Z_j = N_1 \ .$$

In the other ball we have $N_2$ electrons and $M_2$ nuclei. For the moment it is not necessary to assume neutrality in that ball. The Hamiltonian for the first system we call $H_1$ which includes a Dirichlet condition that confines the particles to the ball $B_1$ and $H_2$ which includes a Dirichlet condition confining all the particles to the ball $B_2$. Further we call $H$ the Hamiltonian that includes all the interactions between the particles, i.e., we have added the Coulomb interactions between the particles in ball $B_1$ and ball $B_2$. Hence

$$H = H_1 + H_2 + W$$

where $W$ is the Coulomb interaction between the particles in ball $B_1$ and $B_2$. The total Hilbert space is the tensor product of the Hilbert spaces of the particles in $B_1$ and $B_2$, i.e.,

$$\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2 \ .$$

Next, consider the partition function

$$\mathrm{Tr} e^{-\beta H} = \int_{{B_1}^{N_1}} dX_1 \int_{{B_1}^{M_1}} dR_1 \int_{{B_2}^{N_2}} dX_2 \int_{{B_2}^{M_2}} dR_2 e^{-\beta[H_1+H_2+W]}(X_1,R_1,X_2,R_2) \ .$$

Here we use the notation $X_1$ for the coordinates of the electrons in the $B_1$, $R_1$ all the coordinates of the nuclei in $B_1$ etc. The function

$$e^{-\beta[H_1+H_2+W]}(X_1,R_1,X_2,R_2)$$

is the heat kernel associated with the operator $H$ evaluated on the diagonal. Our goal is to prove the inequality

$$\mathrm{Tr} e^{-\beta H} \gtrsim \mathrm{Tr} e^{-\beta H_1} \mathrm{Tr} e^{-\beta H_2}$$

where the traces are taken over the respective Hilbert spaces.

Using the Peierls-Bogolubov inequality we get that

$$\mathrm{Tr} e^{-\beta H} \gtrsim \mathrm{Tr} e^{-\beta H_1} \mathrm{Tr} e^{-\beta H_2} e^{-}\beta\langle W\rangle$$

where

$$\langle W\rangle = \frac{\mathrm{Tr} e^{-\beta(H_1+H_2)}W}{\mathrm{Tr} e^{-\beta(H_1+H_2)}}$$

The numerator is given by

$$\int dX_1 \int dR_1 \int dX_2 \int dR_2 e^{-\beta H_1}(X_1, R_1) e^{-\beta H_2}(X_2, R_2) W(X_1, R_1, X_2, R_2)$$

and hence the expectation value is given by

$$\sum_{i,j} \int dx_i dy_j \frac{\rho_1^{\mathrm{el}}(x_i)\rho_2^{\mathrm{el}}(y_j)}{|x_i - y_j|} + Z^2 \sum_{k,l} \int dR_k dS_l \frac{\rho_1^{\mathrm{nuc}}(R_k)\rho_2^{\mathrm{nuc}}(S_l)}{|R_k - S_l|}$$

$$-Z \sum_{i,l} \int dx_i dS_l \frac{\rho_1^{\mathrm{el}}(x_i)\rho_2^{\mathrm{nuc}}(S_l)}{|x_i - S_l|} - Z \sum_{k,j} \int dR_k dy_j \frac{\rho_1^{\mathrm{nuc}}(R_k)\rho_2^{\mathrm{el}}(y_j)}{|R_k - y_j|}$$

where

$$\rho_1(x_i) = \frac{\int \widehat{dx_i} e^{-\beta H_1}(X_1, R_1)}{\int e^{-\beta H_1}(X_1, R_1)}$$

so that

$$\int \rho_1(x_i) dx_i = 1 \, .$$

The same holds for the other densities. Hence

$$\langle W \rangle = \int dx dy \frac{Q_1(x) Q_2(y)}{|x - y|} \tag{1}$$

where

$$Q_1(x) = N_1 \rho_1^{\mathrm{el}}(x) - Z \sum_j \rho^{\mathrm{nuc}}(x)$$

and similarly for $Q_2$. By the neutrality assumption in $B_1$ we have that

$$\int dx Q_1(x) = 0$$

Further, since the Hamiltonian $H_1$ is unchanged under simultaneous rotation of all the variables we get that $Q_1(x)$ is a radial function. Hence by Newton's theorem (1) reduces to

$$\int dx dy Q_1(x) Q_2(y) \min(\frac{1}{|x|}, \frac{1}{|y|}) \, .$$

We have placed the origin into the center of $B_1$. Since the two balls are disjoint and since the origin is in the center of $B_1$ we have that $|x| < |y|$ in the domain of integration. Hence (1) reduces to

$$\int dx Q_1(x) \int dy Q_2(y) \frac{1}{|y|} = 0$$

since $Q_1$ is neutral.

Standard sequence of balls

In the following we give a sequence of balls with particles in them in such a way that the there is charge neutrality in each ball. We fix $\rho_{\rm el}$ and hence, because the system is neutral $Z\rho^{\rm nucl} = \rho^{\rm el}$.

Start with $R_0$ and put

$$N_0 = \frac{4\pi}{3} R_0^3 28 \rho^{\rm el}$$

electrons in this ball and of course $K_0 = N_0/Z$ nuclei. Notice that the density is too big! For $j \gtrsim 1$ define the radii

$$R_j = (28)^j R_0$$

and

$$N_j = (28)^{3j-1} N_0 \, , K_j = N_j/Z$$

so that

$$\frac{N_j}{\frac{4\pi}{3} R_j^3} = \rho^{\rm el} \, .$$

Define the numbers

$$m_j = (27)^{j-1} (28)^{2j} \, .$$

Then by the Cheese Theorem we can pack a ball of radius $R_K$ by $m_K$ balls of radius $R_0$, $m_{K-1}$ balls of radius $R_1$ etc $m_1$ balls of radius $R_{K-1}$ and all these balls are disjoint.

If we consider the partition function $Z_K$ for the Coulomb system in the ball $B_K$ we know from our previous considerations that

$$Z_K \gtrsim \prod_{j=0}^{K-1} Z_j^{m_{K-j}}$$

and hence the free energy $f_K$ per unit volume satisfies the estimate

$$f_K = \frac{-\beta^{-1} \log Z_K}{\frac{4\pi}{3} R_K^3} \gtrsim \sum_{j=0}^{K-1} m_{K-j} \frac{R_j^3}{R_K^3} f_j$$

or

$$f_K \gtrsim \sum_{j=0}^{K-1} (27)^{K-j-1} (28)^{2(K-j)} (28)^{3(j-K)} f_j = \frac{1}{27} \sum_{j=0}^{K-1} \frac{\delta^{K-j}}{27} f_j \, .$$

From this and the stability bound we will derive the existence of the thermodynamic limit.

Define the numbers $e_k \gtrsim 0$ by

$$f_K = \sum_{j=0}^{K-1} \frac{\delta^{K-j}}{27} f_j - e_K \, .$$

This renewal equation can be iterated and one gets soon the clue that the solution is given by

$$f_K = \frac{f_0}{28} - \sum_{j=1}^{K} \frac{e_j}{28} - \delta e_K \tag{2}$$

which can be checked. Note that $f_K$ satisfies the recursion

$$f_K - f_{K-1} = \frac{1}{28} f_{K-1} + e_{K-1} - e_K \ .$$

Since $f_K$ is bounded below we get that

$$\sum_{j=1}^{K} \frac{e_j}{28}$$

is bounded above and hence must converge. In particular this shows that $e_K \to 0$ as $K \to \infty$ and hence

$$f = \lim_{K\to\infty} f_K = \frac{f_0}{28} - \sum_{j=1}^{\infty} e_j \ .$$

# 23 The cheese theorem

First some notation: Let $\Omega$ be some domain in $R^n$. If $h > 0$ then we denote by the *inner rim* of $\Omega$ the set

$$\Omega_h = \{x \in \Omega : \mathrm{dist}(x, \partial\Omega) \lesssim h\}$$

and for $h < 0$ we define the inner rim

$$\Omega_h = \{x \in \Omega^{\mathrm{c}} : \mathrm{dist}(x, \partial\Omega) \lesssim -h\} \ ,$$

where $\Omega^{\mathrm{c}}$ denotes the complement of $\Omega$.

**Lemma 79** *Let $\Omega$ be a domain in $R^n$ and assume that it is covered by a collection of closed cubes of side length $a$ whose interior are disjoint. Denote by $N$ the nuber of cubes that are inside $\Omega$. Denote by $\Delta\Omega$ the set $\Omega$ with all these cubes removed, then*

$$|\Delta\Omega| = |\Omega| - Na^n \lesssim |\Omega_{\sqrt{n}d}| \ .$$

**Proof** Remove all the cubes that are inside $\Omega$. The cubes left over intersect the boundary and hence the interior of these cubes is not farther away than $\sqrt{n}a$ from the boundary. Hence, the union of the intersection of these cubes with $\Omega$ is contained in the inner rim of size $\sqrt{n}a$ from which the above estimate follows.

From this we deduce the bound

$$N \lesssim \frac{1}{a^n}(|\Omega| - |\Omega_{\sqrt{n}a}|) \ . \tag{1}$$

A further elementary lemma concerning the geometry of balls is the following one.

**Lemma 80** *Let $B(r)$ be a ball of radius $r$. Pick $b$ so that*

$$r \gtrsim 2b\sqrt{n} \gtrsim 0 \ .$$

*Then*

$$|B_{2b\sqrt{n}}| \gtrsim |B_{-2b\sqrt{n}}| \gtrsim \gamma_n \omega_n r^{n-1} b$$

*where*

$$\gamma_n = 2\sqrt{n}[2^n - 1]$$

*and $\omega_n$ is the volume of the unit ball in $R^n$.*

**Proof** The first inequality is obvious. We therefore have that

$$\omega_n[r^n - (r - 2b\sqrt{n})^n] \gtrsim \omega_n[(r + 2b\sqrt{n})^n - r^n] = \omega r^n[(1 + \varepsilon)^n - 1]$$

where

$$0 \lesssim \varepsilon = \frac{2b\sqrt{n}}{r} \lesssim 1 \ .$$

Now, by the binomial formula

$$[(1 + \varepsilon)^n - 1] = \varepsilon \sum_{k=1}^{n} \binom{n}{k} \varepsilon^{k-1} \gtrsim \varepsilon \sum_{k=1}^{n} \binom{n}{k} = \varepsilon[2^n - 1] \ .$$

The main goal of this section is the proof of the following theorem of Lieb and Lebowitz.

**Theorem 81 (Cheese theorem)** *Let $p$ be a positive integer and for all $j \gtrsim 1$ define the radii*

$$r_j = \frac{1}{(1 + p)^j}$$

*and the integers*

$$m_j = p^{j-1}(1 + p)^{j(n-1)} \ .$$

*Then, if*

$$1 + p \gtrsim \gamma_n \omega_n + \frac{2^n}{\omega_n}$$

*it is possible to pack*

$$\cup_{j=1}^{\infty} (m_j \text{ balls of radius } r_j)$$

*in the unit $n$-dimensional ball.*

**Proof** Cover the unit ball with closed cubes of size $2r_1$ and put balls of radius $r_1$ into each of the cubes that sit inside the unit ball. Removing these balls wee get a remaining set $\Omega^1$ which we cover by closed cubes of size $2r_2$. Again, we fill those that are inside $\Omega^1$ with balls of radius $r_2$ and so on. Having done this $j$-times we have to show that the remaining uncovered set $\Omega^j$ can be packed with balls of radius $r_{j+1}$. Let is start with $j = 0$, i.e., with the ball itself. We have that

$$|\Omega^1| = \omega_n(1 - m_1 r_1^n) == \omega_n(1 - (1 + p)^{(n-1)}(1 + p)^{-n}) = \omega_n \frac{p}{1 + p} \ .$$

Now, we look at the inner rim

$$\Omega^1_{2\sqrt{n}r_2}$$

which consists of all points that are inside $\Omega^1$ but are not more than a distance $2\sqrt{n}r_2$ away from the boundary of $\Omega^1$. Each of these points is either in the outer rim

$$B^1_{-2\sqrt{n}r_2}$$

of the balls that have been removed or in the inner rim

$$B_{2\sqrt{n}r_2}$$

of the unit ball. Hence

$$|\Omega^1_{2\sqrt{n}r_2}| \gtrsim \gamma_n\omega_n r_2(1+n_1r_1^{n-1}) = 2\gamma_n\omega_n\frac{1}{(1+p)^2}$$

since

$$2\sqrt{n}r_2 < r_1 \ ,$$

because of Lemma 2. Next, we know from Lemma 1 that the number of cubes that have size $r_2$ and that sit inside $\Omega_1$ is not less than

$$\frac{1}{(2r_2)^n}(|\Omega^1| - |\Omega^1_{2\sqrt{n}r_2}|) \gtrsim \frac{1}{2^n}(1+p)^{2n}(\omega_n\frac{p}{1+p} - 2\gamma_n\omega_n\frac{1}{(1+p)^2}) \ .$$

Thus, if it is true that

$$m_2 = p(1+p)^{2(n-1)} \gtrsim \frac{1}{2^n}(1+p)^{2n}(\omega_n\frac{p}{1+p} - 2\gamma_n\omega_n\frac{1}{(1+p)^2})$$

we have completed the first step. But this says that $p$ has to satisfy

$$1 \gtrsim \frac{\omega_n}{2^n}(1+p-\frac{2\gamma_n}{p}) \ .$$

Since $p > 1$ this is implied by

$$1 \gtrsim \frac{\omega_n}{2^n}(1+p-2\gamma_n)$$

which is precisely our condition. Thus we have done the first inductive step.

Suppose that we have arrived at $\Omega^j$ which is what remains of the unit ball after removing the $m_1$ balls of radius $r_1$, the $m_2$ balls of radious $r_2$ etc. and at the end removing the $m_j$ balls of radius $r_j$. Its volume is

$$|\Omega^j| = \omega_n(1 - \sum_{k=1}^{j} m_k r_k^n = \omega_n(\frac{p}{1+p})^j \ .$$

Next we consider the inner rim

$$\Omega^j_{2\sqrt{n}r_{j+1}}$$

which is the collection of all points in $\Omega^j$ that have at most distance $2\sqrt{n}r_{j+1}$ to the boundary of $\Omega^j$. Thus, each of these points is either in the outer rim of some of the balls that have been removed or in the inner rim of the unit ball. Thus by Lemma 2

$$|\Omega^j_{2\sqrt{n}r_{j+1}}| \gtrsim \gamma_n\omega_n r_{j+1}(1+\sum_{k=1}^{j} m_k r_k^{n-1} = \gamma_n\omega_n\frac{(p^j+p-2)}{(p-1)(1+p)^{j+1}} \ .$$

Again, by Lemma 1 we now that we can pack $\Omega^j$ at least

$$\frac{1}{(2r_{j+1})^n}(|\Omega^j| - |\Omega^j_{2\sqrt{n}r_{j+1}}|)$$

cubes of size $2r_{j+1}$. Since

$$(|\Omega^j| - |\Omega^j_{2\sqrt{n}r_{j+1}}|) \gtrsim \omega_n[(\frac{p}{1+p})^j - \gamma_n \frac{(p^j+p-2)}{(p-1)(1+p)^{j+1}}]$$

this amounts to show that

$$m_{j+1} = p^j(1+p)^{(j+1)(n-1)} \gtrsim \frac{\omega_n}{2^n}(1+p)^{(j+1)n}[(\frac{p}{1+p})^j - \gamma_n \frac{(p^j+p-2)}{(p-1)(1+p)^{j+1}}]$$

or

$$1 \gtrsim \frac{\omega_n}{2^n}[(1+p) - \gamma_n \frac{(1+p^{-j}(p-2))}{(p-1)}]$$

which holds if

$$1 \gtrsim \frac{\omega_n}{2^n}[(1+p) - \gamma_n]$$

which is again our condition. Note that we have used that $p > 1$. Thus, we can continue with our packing indefinitely. □

**Corrolary 82** *The packing is asymptotically complete and rapid.*

Since

$$\sum_{j=1}^{N} m_j r_j^n = \sum_{j=1}^{N} p^{j-1}(1+p)^{j(n-1)} \frac{1}{(1+p)^{jn}} = \frac{1}{1+p} \sum_{j=0}^{N-1} (\frac{p}{1+p})^j = 1 - \delta^N$$

where

$$\delta = \frac{p}{1+p} < 1 \, .$$

As $N \to \infty$ this converges to 1.

Further the set that is not covered up and including the $N$-th packing has volume $\delta^N$ and hence the convergence of the packing is exponential.