LOWER BOUNDS FOR THE GROUND STATE ENERGY OF ATOMS

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Abstract

The ground state energy of an atom is defined to be lowest possible value of the energy Hamiltonian.

This work describes an algorithm to obtain lower bounds for the ground state energy of atoms, together with its implementation.

The results are within a few precent of the upper bounds given by Hartree–Fock's method.

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If anyone finds anything worthwhile in this work, it is certainly due to some of the above.

Contents

Computer Programs

Chapter 1: The History

Quantum Mechanics was introduced with the goal of understanding the atom. probably its first success was to compute accurately the ground state energy of Hydrogen. However, it was realized very early that to do the same for the other atoms was no easy task.

The formulation of the problem is as follows:
The operator

$$H_Z = \sum_{i=1}^{Z} \left(-\tfrac{1}{2}\Delta_{x_i} - \frac{Z}{|x_i|} \right) + \tfrac{1}{2} \sum_{i \neq j} \frac{1}{|x_i - x_j|}$$

is called the Hamiltonian for the atom of charge Z; it acts on functions ψ which are in $L^2\left(\mathbf{R}^{3Z}\right)$ with some antisymmetry condition. The energy, $E(Z)$, corresponds to the infimum of its spectrum. The term $-\Delta_i$ represents the kinetic energy of each atom, the term $-Z/|x_i|$ represents the attraction each electron feels towards the nucleus, and the term $\frac{1}{2}\sum_{i\neq j}\frac{1}{|x_i - x_j|}$, which is the one that makes this a non–trivial problem, is the repulsion between electrons. The nuclear kinetic energy is not included in the formulation of the problem; this is a reasonable approximation, since the nucleus is very heavy.

Some qualitative properties associated with the atomic Hamiltonian, such as essential self–adjointness (i.e. physical significance), qualitative properties of the spectrum, regularity results for the bound states (i.e. eigenfunctions), etc. we

soon established. See [K1], [K2] and [K3], for example.

At the same time, a more computational motivation lead others to tackle the problem of computing atomic energies.

The first important result in this direction was the creation of Thomas-Fermi (TF) theory. They attempted to understand atoms using a different atomic model in which the object of study was not the wave function, but the electric density; this simplifies the problem in the sense that the nuclear charge does not enter as the dimension of the problem, but rather as a parameter in a one-dimensional problem.
The main results according to this theory are:

1. $E_{TF}(Z) = C_{TF} \cdot Z^{7/3}$
2. Most of the electrons are at distance $Z^{-1/3}$ from the nucleus.
3. The outermost electron (chemistry) is at a distance of the order of 1.
4. Atoms are neutral.
5. Molecules do not exist.

It was clear empirically that Thomas-Fermi energy was quite accurate for large atoms (although not entirely satisfactory) and not so good for small ones, and with the exception of item 5, the other properties look obvious in nature. But a rigorous analysis had to wait until 1977, when it was proved that atoms behave as Thomas-Fermi theory predicts in the limit $Z \to \infty$ (see [Li] and [LS]).
Other people also considered the problem of atomic energies for large Z (in the limit as $Z \to \infty$). Scott predicted a correction for Thomas-Fermi energy that recently has been proved correct (see [Hu] and [SW]), and other atomic models due to Dirac, von Weizsäcker and others were created, in an attempt to capture certain aspects of the real problem neglected by TF theory.

Also, with the creation of computers, other purely computational techniques were

introduced. A specially accurate method to compute upper bounds to atomic energies was developed by Hartree, Fock, Slater and others (although the first Hartree papers were done by hand computation!). Their method consists in finding the ground–state energy for the same Hamiltonian restricted to a smaller class of functions (this gives upper bounds), namely the antisymmetric product of one–electron functions. This method leads to a collection of ODE's that can be solved numerically. It is believed that the results obtained by this method are very good for all values of Z. The present work will actually give a bound for the error in their approximation.

Another method to compute both upper and lower bounds was introduced by A. Weinstein and his collaborators, the so–called method of "Intermediate Hamiltonians". It is basically a regularity result in which a particular orthogonal family of functions is constructed and it is proved that the ground–state eigenfunction has Fourier coefficients that decrease very fast with respect to this orthogonal family; this allows to reduce the problem to a finite dimensional one, with a good control on the error. This method works well for small atoms and molecules. In particular, very good upper and lower bounds are known for the energy of Helium. See [We].

Up to this point, an open problem is to produce good methods to compute lower bounds to atomic energies for atoms. An important result was obtained Hertel, Lieb and Thirring in [HLT]. In this work, we will present another approach to this problem that improves their bounds.

There is one common feature in all these theories to approximate atomic energies: they are basically reductions to one–electron problems, which are much easier in general than many electron problems, even if you loose linearity or other nice features along the way. In Chapter 7 we introduce a method which is essentially many–electron analysis.

It is interesting to point out that good bounds for atomic energies are important not only quantitatively, but also because certain qualitative aspects of ordinary matter, such as binding and no-binding theorems, stability of matter, neutrality of atoms, etc., depend critically on whether the energy of atoms is within a certain range or not. See [Fe], [FS1] and [FS2] and [SSS] for examples of such results.

In particular, it was shown in [Fe] that nuclei and electrons arrange themselves into atoms and molecules provided that the ground state energy of atoms is within a factor 2 —roughly speaking— of the constant in the inequality of the stability of matter (see [DL], [LT] and [Ll]). We also refer to [Fe] for a detailed description of some of these results.

Chapter 2: The Problem

Consider the Hamiltonian for an atom of charge Z with Z electrons:

$$H_Z = \sum_{i=1}^{Z} \left(-\tfrac{1}{2}\Delta_{x_i} - \frac{Z}{|x_i|} \right) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|x_i - x_j|}$$

acting on functions

$$\psi \in \mathcal{H} = \wedge_{i=1}^{Z} \left(L^2(\mathbf{R}^Z) \otimes \mathbf{C}^2 \right) \tag{2.1}$$

with "$\wedge$" denoting antisymmetric product.
The ground state energy is then defined to be the infimum of the spectrum of H_Z:

$$E(Z) = \inf_{\lambda \in Spec(H)} \lambda = \inf_{\substack{\psi \in \mathcal{H} \\ \|\psi\|_2 = 1}} \langle H_Z \psi, \psi \rangle$$

It is known that this infimum is achieved, and the functions that give this infimum value are usually called "ground states".

Upper bounds can be obtained by using trial functions. Lower bounds for E will be found as follows:

If we have an inequality of the form:

$$\frac{1}{2} \sum_{i \neq j} \frac{1}{|x_i - x_j|} \geq \sum_{i=1}^{Z} V(x_i) - C \tag{2.2}$$

with V radially symmetric decreasing function vanishing at infinity, we have an operator inequality

$$H_Z \geq \sum_{i=1}^{Z} \left(-\tfrac{1}{2}\Delta_{x_i} - \frac{Z}{|x_i|} + V(x) \right) - C \stackrel{\text{def}}{=} H_{LB}$$

Let now $\lambda_1 < \lambda_2 < \cdots < 0$ be the negative eigenvalues of

$$H^{1 \text{ electron}} = -\tfrac{1}{2}\Delta_x - \frac{Z}{|x|} + V(x)$$

acting on $L^2\left(\mathbf{R}^3\right)$. Then, the eigenvalues of

$$H_{LB} = \sum_{i=1}^{Z} \left(-\tfrac{1}{2}\Delta_{x_i} - \frac{Z}{|x_i|} + V(x) \right)$$

are then given by sums of the type

$$\lambda_{i_1} + \lambda_{i_2} + \cdots + \lambda_{i_Z}$$

were the eigenfunctions are given by the tensor products of the corresponding eigenfunctions of each λ_{i_k}. The antisymmetry condition (2.1) implies that no more than two of these λ_{i_k} can be equal. Therefore,

$$E \geq \begin{cases} 2\displaystyle\sum_{i=1}^{Z/2} \lambda_i - C & Z \text{ even} \\ \\ 2\displaystyle\sum_{i=1}^{\frac{Z-1}{2}} \lambda_i + \lambda_{\frac{Z+1}{2}} - C & Z \text{ odd} \end{cases}$$

The way to determine the eigenvalues of $H^{1 \text{ electron}}$ is standard, and follows from decomposition into spherical harmonics; as a result, the eigenvalues of $H^{1 \text{ electron}}$ are the same as the eigenvalues of the ODE operator

$$-\tfrac{1}{2}u'' - \left(\frac{Z}{r}u - \frac{l(l+1)}{2r^2} - V(r)\right)u$$

acting on

$$\mathcal{H}_{\text{ode}} = \left\{u \,:\, r^{-1}u(r) \in L^2(0,\infty)\right\}$$

for $l = 0, 1, 2, \ldots$. Every eigenvalue of (2.3) corresponds to an eigenvalue of $H^{1\text{ electron}}$ with multiplicity $2l+1$. Note that if u is a solution of (2.3), then $u \in \mathcal{H}_{\text{ode}}$ iff $u(0) = u(\infty) = 0$.

From now on, we will consider the ODE problem associated with

$$-u'' - \left(\frac{2Z}{r}u - \frac{l(l+1)}{r^2} - 2V(r)\right)u \tag{2.3}$$

and we will remember that there is a factor 2 affecting the results.

These eigenvalues can be worked out explicitly if $V = 0$, and they are given by the formula

$$\lambda_n = -\frac{Z^2}{2(n+l)^2} \tag{2.4}$$

but for general V the ODE cannot be solved explicitly. We will, still, however be able to estimate accurately its eigenvalues. For this we will use computer assisted techniques. This will be done roughly as follows:

First, we will see how to obtain rigorous upper and lower bounds for the Taylor coefficients of our function V, up to any finite order, as well as upper bounds for the high order terms.

Next, we will use these upper and lower bounds (that we will refer simply as "intervals") to obtain upper and lower bounds (intervals) for the Taylor coefficients of the solution of the ODE, and this, at least in principle, is trivial, by matching powers. This will give equations for the Taylor coefficients of the solution —up to some finite order— in terms of those of the equation, and will also provide bounds the high order terms.

Thus, to obtain bounds for the solution of initial value problems is reduced to a finite number of manipulations with intervals. Chapter 4 explains how this can be done using the capabilities of a computer.

To go from here to estimating the eigenvalues we will use comparison theorems for Sturm-Liouville problems.

The next issue is is how to obtain *good* lower bounds for the energy of atoms with this method:
First, it is important to obtain good functions V in inequality (2.2). Some care will be taken to optimize the choice of V.

Next, for every choice of a function V, we will obtain a constant C, but it will not be optimal. It is also important to improve the inequality by choosing C as small as possible. This will lead to the problem of ball packings in $\mathbf{R}^3$.

Finally, observe that what we really needed in the original problem is not the strong assertion

$$\frac{1}{2}\sum_{i\neq j}\frac{1}{|x_i - x_j|} \geq \sum_{i=1}^{Z} V(x_i) - C$$

but only

$$\left\langle \frac{1}{2}\sum_{i\neq j}\frac{1}{|x_i - x_j|}\psi, \psi \right\rangle \geq \sum_{i=1}^{Z}\langle V(x_i)\psi, \psi\rangle - C$$

for ψ equal to the ground state of the atom.

Note that, even if

$$E(x_1, \ldots, x_Z) = \frac{1}{2}\sum_{i\neq j}\frac{1}{|x_i - x_j|} - \sum_{i=1}^{Z} V(x_i) + C \tag{2.5}$$

is smallest possible pointwise, $\langle E\psi, \psi\rangle$ might still be big.

Obviously, if $E = 0$ at some point, then there is no hope that $\langle E\psi, \psi\rangle$ can be bounded from below with something strictly positive for all ψ, since you can take ψ more and more concentrated around that point. However, in this problem, this would cause the laplacian term to grow very much (roughly as the square of the inverse of the diameter of the support); this means that the ψ that play a role are to some extent "smeared out" and cannot concentrate too much on the points were (2.2) is sharp; this argument will imply that $\langle E\psi, \psi\rangle$ is in fact positive. As a consequence, if $\tilde{E}(Z)$ is the lower bound obtained using inequalities of type (2.2), then

$$E(Z) \geq \tilde{E}(Z) + \langle E\psi, \psi\rangle \tag{2.6}$$

for ψ the ground state of the atom, which is a strictly better lower bound.

Chapter 3 will be devoted to obtain all formulas involved in the calculation of V and C in (2.2).

Chapter 4 will explain how the computer can be used to prove certain rigorous mathematical statements related to out problem.

Chapter 5 contains the necessary results in theory of Ordinary Differential Equations to reduce the sharp estimates for the eigenvalues of the ODE problem (2.3) to a finite number of computations.

Chapter 6 discusses several techniques used to obtain good lower bounds for the energy, and lists the actual results that were obtained.

Chapter 7 shows how the lower bounds can be obtained by leaving the realm of pointwise inequalities of type (2.2) and using inequalities of type (2.6) in two different ways: first, by obtaining an a priori constant lower bounds for $\langle E\psi, \psi\rangle$ and, second, by obtaining a lower bound as a sum of one particle potentials.

Finally, Chapter 8 will take care of improving the constant C in (2.2). This analysis leads to ideas coming from the problem of ball packings in $\mathbf{R}^3$.

An announcement of our results appeared in [Se].

Chapter 3: The Potential

3.1 The Definition

The method to obtain inequalities (2.2) has its origin in the elementary formula first used in [FL]:

$$\frac{1}{|x-y|} = \frac{1}{\pi}\int_{R>0}\int_{z\in\mathbf{R}^3} \chi_{B(z,R)}(x)\cdot\chi_{B(z,R)}(y)\,\frac{dz\,dR}{R^5}$$

that implies

$$\frac{1}{2}\sum_{i\neq j}\frac{1}{|x_i-x_j|} = \frac{1}{2\pi}\int_{R>0}\int_{z\in\mathbf{R}^3} N(N-1)\frac{dzdR}{R^5}$$

where N is the number of x_i that belong to $B(z,R)$:

$$N = N(x_1,\ldots,x_Z;z,R) = \sum_{i=1}^{Z}\chi_{B(z,R)}(x_i)$$

Observe that

$$N(N-1) = (N-\bar{N})^2 + (2\bar{N}-1)N - \bar{N}^2$$

for *any* number $\bar{N} = \bar{N}(z,R)$; and, since $(N-\bar{N})^2 \ \geq \ 0$ we get

$$\begin{aligned}\frac{1}{2}\sum_{i\neq j}\frac{1}{|x_i-x_j|} &\geq \frac{1}{2\pi}\iint (2\bar{N}-1)N\,\frac{dz\,dR}{R^5} - \frac{1}{2\pi}\iint \bar{N}^2\,\frac{dz\,dR}{R^5}\\ &= \frac{1}{2\pi}\sum_{i=1}^{Z}\iint (2\bar{N}-1)\chi_{x_i\in B(z,R)}\,\frac{dz\,dR}{R^5} - \frac{1}{2\pi}\iint \bar{N}^2\,\frac{dz\,dR}{R^5}\\ &= \sum_{i=1}^{Z} V(x_i) - C.\end{aligned}$$

with

$$\begin{aligned}V(x_i) &= \frac{1}{2\pi}\iint_{\substack{|z-x|<R\\ R>0}} 2(\bar{N}(z,R)-1)\,\frac{dz\,dR}{R^5}\\ C &= \frac{1}{2\pi}\iint \bar{N}^2(z,R)\,\frac{dz\,dR}{R^5}.\end{aligned}$$

What we throw away here is the quantity $(N-\bar{N})^2$; thus, we should take $\bar{N}$ to be close to the expected number of electrons in $B(z,R)$ in some approximate ground state. Also, observe that if $\bar{N} = k+\frac{1}{2}$ for k integer, then, since N is also an integer, we can sharpen the inequality by observing that $(N-\bar{N})^2 \geq \frac{1}{4}$, and thus, we may take

$$C = \frac{1}{2\pi}\iint (\bar{N}^2 - \tfrac{1}{4})\,\frac{dz\,dR}{R^5}$$

Observe that this inequality is sharp for every ball in which $\bar{N} = k+\frac{1}{2}$ and that contains either k or $k+1$ electrons.

The method to select a particular half–integer valued function $\bar{N}(z,R)$ will be as follows:

Select a "charge density"

$$\rho(x) \geq 0, \qquad \int_{\mathbf{R}^3}\rho(x)dx = Z$$

that we believe (but need not prove) is close to the real one; then, choose $\bar{N}$ according to the following rule:
Define functions $R_i(z)$, $1 \leq i \leq Z-1$, such that

$$\int_{B(z,R_i(z))} \rho(x)dx = i \tag{3.1}$$

Then, given (z, R), put

$$N(z,R) = \begin{cases} \frac{1}{2} & \text{if } R < R_1(z) \\ i + \frac{1}{2} & \text{if } R_i(z) < R < R_{i+1}(z) \\ Z - \frac{1}{2} & \text{if } R > R_{Z-1}(z) \end{cases}$$

In practice we will take $R_i(z)$ to be piecewise linear, for that closely approximates the functions (3.1). Observe that this does not affect the correctness of our estimates.

The following Lemma proves useful

Lemma 3.1: *Let $\rho(x)$ be a radial function defined on $\mathbf{R}^3$; then, if $\rho(x) = f(|x|)$, we have*

$$\int_{B(z,R)} \rho(x)\,dx = \pi \int_{|R-x|}^{R+x} yf(y)\frac{R^2-(x-y)^2}{x}\,dy + 4\pi \int_0^{R-x} y^2 f(y)\,dy$$

where $|z| = x$, and the second integral does not appear if $x > R$.

Corollary:

$$|B(0,M) \cap B(x,R)| = \begin{cases} 0 & \text{if } M < |x| - R \\ \frac{4\pi}{3}M^3 & \text{if } R > M + |x| \\ \frac{4\pi}{3}R^3 & \text{if } M > R + |x| \\ H(x,R,M) & \text{otherwise} \end{cases}$$

for

$$\frac{1}{\pi}H(x,R,M) = -\frac{(M^2-R^2)^2}{4x} + \frac{4}{3}\frac{R^3+M^3}{2} - |x|\frac{R^2+M^2}{2} + \frac{1}{12}|x|^3 \qquad (3.2)$$

The following Lemma lists some of the properties of the functions R_i.

Lemma 3.2a: *Let R_i be defined as in (3.1), for ρ integrable, radially symmetric, decreasing function. Thus, R_i will take values in $\mathbf{R}^1$ from now on.*

1. *R_i is a radially symmetric, continuous increasing function.*
2. *If we define b_i to be*

$$\int_{b_i}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\rho(x_1,x_2,x_3)\,dx_1\,dx_2\,dx_3 = i$$

Then

$$\lim_{|x|\to\infty} R_i(x) - (x-b_i) = 0$$

3. $R_i(x) \le x + R_i(0)$.

It will also be useful to consider the inverse functions

$$M_i(R) = \begin{cases} R_i^{-1}(R) & \text{if } R \ge R_i(0) \\ 0 & \text{if } R < R_i(0) \end{cases} \qquad (3.3)$$

The properties for R_i then translate into properties for M_i as follows.

Lemma 3.2b: *Let M_i be defined as before.*

1. *M_i is a radially symmetric, continuous increasing function.*
2. $\lim_{|x|\to\infty} M_i(x) - (x+b_i) = 0$
3. *$M_i(R) \ge R - R_i(0)$ for all R.*

Note that the freedom in choosing $\bar{N}$ translates in the freedom to choose any set of functions R_i, or M_i. This will be of importance later.

3.2 The Formulas

Given functions $M_i(R)$, we will describe all the calculations involved in the computation of $V(x)$ and C:

$$V(x) = \frac{1}{2\pi} \iint_{|z-x|<R} \left(2\bar{N}(z,R) - 1\right) \frac{dz\, dR}{R^5}$$
$$C = \frac{1}{2\pi} \iint \left(\bar{N}^2 - \tfrac{1}{4}\right) \frac{dz\, dR}{R^5}$$

First, we will introduce the functions

$$\bar{N}_i(z,R) = \begin{cases} \frac{3}{2} \text{ if } R > R_i(z) \\ \frac{1}{2} \text{ if } R < R_i(z) \end{cases}$$

and call

$$V_i(x) = \frac{1}{2\pi} \iint (2\bar{N}_i(z,R) - 1) \frac{dz\, dR}{R^5}$$
$$= \frac{1}{\pi} \iint_{R>R_i(z)} \frac{dz\, dR}{R^5}$$

Clearly,

$$V(x) = \sum_{i=1}^{Z-1} V_i(x)$$

since

$$\bar{N}(z,R) = \sum_{i=1}^{Z-1} \bar{N}_i(z,R)$$

If we do the same with the constant C, then

$$C = \sum_{i=1}^{Z-1} i \cdot C_i$$

for

$$C_i = \frac{1}{2\pi} \iint \left(\bar{N}_i^2 - \tfrac{1}{4}\right) \frac{dz\, dR}{R^5}$$
$$= \frac{1}{\pi} \iint_{R>R_i(z)} \frac{dz\, dR}{R^5}$$

In order to see this, we have to check that

$$\sum_{j=1}^{Z-1} j \cdot \left(\bar{N}_j^2 - \tfrac{1}{4}\right) = \bar{N}_i^2 - \tfrac{1}{4}$$

or, equivalently

$$\sum_{j=1}^{Z-1} j \cdot \left(\bar{N}_j^2 - \tfrac{1}{4}\right) = i^2 + i \qquad \text{for} \quad R_i(z) < R < R_{i+1}(z)$$

Since

$$\bar{N}_j^2 - \tfrac{1}{4} = \begin{cases} 0 & \text{for } j \geq i+1 \\ 2 & \text{for } j \leq i \end{cases}$$

we have

$$\sum_{j=1}^{Z-1} j \cdot \left(\bar{N}_j^2 - \tfrac{1}{4}\right) = 2 \sum_{j=1}^{i} j = i^2 + i$$

as claimed

Thus, it is enough to calculate $V_i(x)$ and C_i. Let's put $M_i(R) = M(R)$.

Observe that

$$2\bar{N}_i - 1 = \begin{cases} 2 & \text{if } |z| < M(R) \\ 0 & \text{if } |z| \geq M(R) \end{cases}$$

therefore,

$$
\begin{aligned}
V_i(x) &= \frac{1}{2\pi} \iint_{\substack{|z|<M(R)\\ |z-x|<R}} 2 \ \frac{dz\, dR}{R^5} \\
&= \frac{1}{\pi} \int_{R>0} \big|B(0,M(R)) \cap B(x,R)\big| \frac{dR}{R^5} \\
&= \int_{\substack{R+M(R)>|x|\\ |x|+R<M(R)}} \frac{4}{3} R^3 \frac{dR}{R^5} + \int_{\substack{R+M(R)>|x|\\ R-|x|>M(R)}} \frac{4}{3} M^3(R) \frac{dR}{R^5} \\
&\quad + \int_{\substack{R+M(R)>|x|\\ |x|+R>M(R)\\ R-|x|<M(R)}} H(x,R,M(R)) \frac{dR}{R^5}
\end{aligned}
$$

where H is as in (3.2).
At this point, a difficulty appears when trying to solve the equations

$$
|x| + R = M(R), \qquad R - |x| = M(R), \qquad |x| - R = M(R) \tag{3.4}
$$

For this reason, since we are free to choose M as we please, we will take functions $M_i(R)$ that are piecewise linear, i.e.:

Pick numbers a_i, b_i, n for $0 \le i \le n$, such that

$$
\begin{aligned}
R_i(0) = r_0 &< r_1 < \cdots < r_n \\
a_0 &> a_1 > \cdots > a_n = 1 \\
b_0 &< b_1 < \cdots < b_n
\end{aligned} \tag{3.5}
$$

and take $M(R) = a_i R + b_i$ for $r_i < R < r_{i+1}$.

We will limit our attention to *convex* piecewise linear M_i, to ensure that equations (3.4) have unique solutions, which simplifies the problem.
Call $|x|$ simply x. Let's consider two cases: $x < R_i(0)$ and $x > R_i(0)$.

case I: $x < R_i(0)$

The straight line $R - x$ will cross $M(R)$ at a point $\bar{R}$ where

$$
r_{i_0} \le \bar{R} \le r_{i_0+1}
$$

In this case,

$$\bar{R} = \frac{x + b_{i_0}}{1 - a_{i_0}}$$

Similarly, $R + x$ will cross $M(R)$ for $\bar{R} = \frac{-x+b_{i_1}}{1-a_{i_1}}$ for $r_{i_1} \leq \bar{R} < r_{i_1+1}$.
Therefore, we have:

$$\begin{aligned}
V_i(x) &= \int_{R_i(0)}^{\frac{x+b_{i_0}}{1-a_{i_0}}} \frac{4}{3} M^3(R) \frac{dR}{R^5} + \int_{\frac{x+b_{i_0}}{1-a_{i_0}}}^{\frac{-x+b_{i_1}}{1-a_{i_1}}} H(x, R, M(R)) \frac{dR}{R^5} + \int_{\frac{-x+b_{i_1}}{1-a_{i_1}}}^{\infty} \frac{4}{3} R^3 \frac{dR}{R^5} \\
&= \sum_{k=0}^{i_0-1} \int_{r_k}^{r_{k+1}} \frac{4}{3}(a_k R + b_k)^3 \frac{dR}{R^5} + \int_{r_{i_0}}^{\frac{x+b_{i_0}}{1-a_{i_0}}} \frac{4}{3}(a_{i_0} R + b_{i_0})^3 \frac{dR}{R^5} \\
&\quad + \int_{\frac{x+b_{i_0}}{1-a_{i_0}}}^{r_{i_0+1}} H(x, R, a_{i_0} R + b_{i_0}) \frac{dR}{R^5} \\
&\quad + \sum_{k=i_0+1}^{i_1-1} \int_{r_k}^{r_{k+1}} H(x, R, a_k R + b_k) \frac{dR}{R^5} \\
&\quad + \int_{r_{i_1}}^{\frac{-x+b_{i_1}}{1-a_{i_1}}} H(x, R, a_{i_1} R + b_{i_1}) \frac{dR}{R^5} + \int_{\frac{-x+b_{i_1}}{1-a_{i_1}}}^{\infty} \frac{4}{3} R^3 \frac{dR}{R^5}.
\end{aligned}$$

Now, define functions:

$$\begin{aligned}
G_1(a, b; R) &= \int \frac{4}{3}(aR + b)^3 \frac{dR}{R^5} = -\left[\frac{4}{3}\frac{a^3}{R} + 2\frac{a^2 b}{R^2} + \frac{4}{3}\frac{ab^2}{R^3} + \frac{1}{3}\frac{b^3}{R^4}\right]. \\
G_2(R) &= \int \frac{4}{3}\frac{dr}{R^2} = \frac{-4}{3R}. \\
G_3(a, b, x; R) &= \int H(x, R, aR + b) \frac{dR}{R^5}.
\end{aligned}$$

All integrals are taken to be indefinite integrals. So,

$$
\begin{aligned}
V_i(x) = &\sum_{k=0}^{i_0-1}\Big[G_1(a_k,b_k;r_{k+1}) - G_1(a_k,b_k;r_k)\Big] \\
&+ G_1\left(a_{i_0},b_{i_0};\frac{x+b_{i_0}}{1-a_{i_0}}\right) - G_1(a_{i_0},b_{i_0};r_{i_0}) \\
&+ G_3(a_{i_0},b_{i_0},x;r_{i_0+1}) - G_3\left(a_{i_0},b_{i_0},x;\frac{x+b_{i_0}}{1-a_{i_0}}\right) \\
&+ \sum_{k=i_0+1}^{i_1-1}\Big[G_3(a_k,b_k,x;r_{k+1}) - G_3(a_k,b_k,x;r_k)\Big] \\
&+ G_3\left(a_{i_1},b_{i_1},x;\frac{-x+b_{i_1}}{1-a_{i_1}}\right) - G_3(a_{i_1},b_{i_1},x;r_{i_1}) - G_2\left(\frac{-x+b_{i_1}}{1-a_{i_1}}\right).
\end{aligned}
$$

Since all these functions are always evaluated at points of the form $\alpha x+\beta$, the functions we really need are

$$
\begin{aligned}
F_1(a,b,\alpha,\beta;x) &= G_1(a,b,\alpha x+\beta) \\
&= -\left[\frac{4}{3}\frac{a^3}{(\alpha x+\beta)} + 2\frac{a^2 b}{(\alpha x+\beta)^2} + \frac{4}{3}\frac{ab^2}{(\alpha x+\beta)^3} + \frac{1}{3}\frac{b^3}{(\alpha x+\beta)^4}\right] \\
&= \left[\frac{d_1}{(\alpha x+\beta)} + \frac{d_2}{(\alpha x+\beta)^2} + \frac{d_3}{(\alpha x+\beta)^3} + \frac{d_4}{(\alpha x+\beta)^4}\right]. \qquad (3.6)
\end{aligned}
$$

$$
F_2(\alpha,\beta;x) = G_2(\alpha x+\beta) = \frac{-4}{3(\alpha x+\beta)}. \qquad (3.7)
$$

$$
\begin{aligned}
F_3(a,b,\alpha,\beta;x) &= G_3(a,b,x;\alpha x+\beta) \\
&= \frac{p_4(x)}{(\alpha x+\beta)^4} + \frac{p_3(x)}{(\alpha x+\beta)^3} + \frac{p_2(x)}{(\alpha x+\beta)^2} + \frac{p_1(x)}{(\alpha x+\beta)} \\
&\quad + p_0(x)\log(\alpha x+\beta). \qquad (3.8)
\end{aligned}
$$

where

$$p_0(x) = \frac{-(a^2-1)^2}{4x} \tag{3.9a}$$

$$p_1(x) = \frac{ab(a^2-1)}{x} - \frac{2}{3}(1+a^3) \tag{3.9b}$$

$$p_2(x) = \frac{b^2(1-3a^2)}{-4x} - a^2b + \frac{(1+a^2)}{4}x \tag{3.9c}$$

$$p_3(x) = \frac{ab^3}{3x} - \frac{2}{3}ab^2 + \frac{ab}{3}x \tag{3.9d}$$

$$p_4(x) = \frac{b^4}{16x} - \frac{b^3}{6} + \frac{b^2}{8}x - \frac{1}{48}x^3 \tag{3.9e}$$

So,

$$\begin{aligned}
V_i(x) = &\sum_{k=0}^{i_0-1}\Big[F_1(a_k,b_k,0,r_{k+1};x) - F_1(a_k,b_k,0,r_k;x)\Big] \\
&+ F_1\left(a_{i_0},b_{i_0},\frac{1}{1-a_{i_0}},\frac{b_{i_0}}{1-a_{i_0}},x\right) \\
&- F_1(a_{i_0},b_{i_0},0,r_{i_0},x) + F_3(a_{i_0},b_{i_0},0,r_{i_0+1};x) \\
&- F_3\left(a_{i_0},b_{i_0},\frac{1}{1-a_{i_0}},\frac{b_{i_0}}{1-a_{i_0}};x\right) \\
&+ \sum_{k=i_0+1}^{i_1-1}\Big[F_3(a_k,b_k,0,r_{k+1};x) - F_3(a_k,b_k,0,r_k;x)\Big] \\
&+ F_3\left(a_{i_1},b_{i_1},\frac{-1}{1-a_{i_1}},\frac{b_{i_1}}{1-a_{i_1}};x\right) - F_3(a_{i_1},b_{i_1},0,r_{i_1};x) \\
&- F_2\left(\frac{-1}{1-a_{i_1}},\frac{b_{i_1}}{1-a_{i_1}};x\right).
\end{aligned} \tag{3.10}$$

Given a, b, α, β all three functions F_1, F_2 and F_3 are analytic functions in x in some fixed common neighborhood of some x_0. All singularities come from terms of the form $\frac{1}{x(\alpha x+\beta)^k}$ or $\log(\alpha x+\beta)$; therefore the radius of convergence of F_i around x_0 is

$$\min\left(x, x+\frac{\beta}{\alpha}\right).$$

The values for $\frac{\beta}{\alpha}$ are either b_{i_0} or $-b_{i_1}$; thus, if either b_{i_0} or b_{i_1} are very close to x, the radius of convergence of V will be very small; this will happen if the piecewise linear pieces $M(R)$ is made of, have slopes very close to 1.

case 2: $x > R_i(0)$

As in the previous case, consider the intersection of $M(R)$ with $x - R$ and $R + x$. The crossing points are respectively

$$y_0 = \frac{x - b_{i_0}}{1 + a_{i_0}} \quad \text{and} \quad y_1 = \frac{-x + b_{i_1}}{1 - a_{i_1}}$$

We thus have

$$\begin{aligned}
V_i(x) &= \int_{y_0(x)}^{y_1(x)} H(x, R, M(R)) \frac{dR}{R^5} + \int_{y_1(x)}^{\infty} \frac{4}{3} R^3 \frac{dR}{R^5} \\
&= \int_{y_0(x)}^{r_{i_0+1}} H(x, R, M(R)) \frac{dR}{R^5} + \sum_{k=i_0+1}^{i_1-1} \int_{r_k}^{r_k+1} H(x, R, M(R)) \frac{dR}{R^5} \\
&\quad + \int_{r_{i_1}}^{y_1(x)} H(x, R, M(R)) \frac{dR}{R^5} + \int_{y_1(x)}^{\infty} \frac{4}{3} R^3 \frac{dR}{R^5} \\
&= -F_3\left(a_{i_0}, b_{i_0}, \frac{1}{1 + a_{i_0}}, \frac{-b_{i_0}}{1 + a_{i_0}}; x\right) + F_3(a_{i_0}, b_{i_0}, 0, r_{i_0}; x) \\
&\quad + \sum_{k=i_0+1}^{i_1-1} \Big[F_3(a_k, b_k, 0, r_{k+1}; x) - F_3(a_k, b_k, 0, r_k; x)\Big] \\
&\quad - F_3(a_{i_1}, b_{i_1}, 0, r_{i_1}; x) \\
&\quad + F_3\left(a_{i_1}, b_{i_1}, \frac{-1}{1 - a_{i_1}}, \frac{b_{i_1}}{1 - a_{i_1}}; x\right) \\
&\quad - F_2\left(\frac{-1}{1 - a_{i_1}}, \frac{b_{i_1}}{1 - a_{i_1}}; x\right).
\end{aligned} \tag{5.15}$$

The considerations for the radius of convergence in this case are similar to those of the previous section.

We point out that all the radii of convergence of V are bounded below by

$$\min\Big(\frac{R(0)}{a_{n-1} - 1}, x\Big)$$

because $\alpha x + \beta$, being the intersection point of $M(R)$ and $R + x$, has to be at least $R(0)$, and α is at most $\frac{1}{a_{n-1}-1}$, since $\{a_i\}$ is a decreasing sequence.
However, the singularity at 0 is unavoidable, and this is inconvenient. What we will do is pick a small number, η, and for $x < \eta$ just set $V(x) = V(\eta)$; since V is decreasing, this will still give a lower bound to the correct potential; moreover, it is not wasteful, for two reasons: first, $V'(0) = 0$, therefore V is close to a constant around 0; second, since the solution of the ODE vanishes at 0, first order perturbation theory says that the effect of the potential around 0 is not important.

Therefore, the ODE (2.3) takes the form

$$u'' + \left(\frac{a}{r} + \frac{l(l+1)}{r^2} + c\right) u = 0 \tag{3.12}$$

around zero
Also, if $x > 2r_n + b_n$ then

$$V(x) = \frac{1}{3}\left(-\frac{1}{x} + \frac{4}{x - b_n}\right) \tag{3.13}$$

and so, we may take (since we are only looking for lower bounds)

$$V_i(x) = \frac{c}{x} \qquad \text{for} \qquad c = \min\left(1, \frac{3x - b_n}{3(x - b_n)}\right)$$

and in particular, given $\lambda > 0$ and $l \geq 0$, we can find a positive integer

$$k = k(\lambda) = \left[\frac{Z - \sum c_i}{\lambda}\right] + 1 \tag{3.14}$$

(where [ ] denotes "largest integer smaller than"), such that

$$\sum_i V_i(x) \geq \frac{Z - \lambda k}{r} - \frac{l(l+1)}{2r^2} \tag{3.15}$$

This will be useful in order to bound our ODE (2.3) by means of the easier to study ODE's

$$u'' + \left(\frac{2k\lambda}{r} - \lambda^2\right) u = 0 \tag{3.16}$$

and

$$u'' + \left(\frac{2(k+1)\lambda}{r} - \lambda^2 \right) u = 0$$

at infinity.

This completes the description of $V_i(x)$. The upshot is that for every $x_0 > 0$ we can write the potential

$$V(x) = \sum_{n=0}^{N} a_n \left(\frac{x - x_0}{r} \right)^n + H$$

where r is the radius of convergence and is bounded below. H is a function with small norm in a sense to be made precise later; it contains all the high order terms. The values of a_n and estimates for $\|H\|$ can be obtained from x_0 by a finite computation.

V_i, as defined by this procedure, is a piecewise analytic function; that is: there are points $\{x_i\}$ (where in fact each x_i is of the form either $r_i + M(r_i)$ or $r_i - M(r_i)$, such that V_i has a power series expansion around every point $0 < x < \infty$, and it agrees with this power series except at the x_i, where it only agrees to the left of x_i. V_i is continuous everywhere, and has continuous first derivatives except at the smallest and largest of the $\{x_i\}$.

The fact that V has so many singularities has as a consequence that a regularity theory analysis of the ODE (2.3) (for example, reducing the problem to a finite dimensional one via a clever orthonormal family) will not be appropriate. Also, the fact that V introduces a perturbation which is unbounded as Z grows implies that you can expect trouble if you try to analyse the ODE as a perturbation of — for instance— the Hydrogen atom ($V \equiv 0$). It seems then that the ODE problem has to be dealt with using the powerful machinery of computing the solution of the ODE everywhere with very good bounds.

Chapter 4: The Computer

In this chapter, we explain the basic techniques used in proving rigorous results with a computer. All of this is becoming quite standard. For similar and more detailed analysis see [Mo], [KM], [EW], [EKW] and [Ra].

4.1 Arithmetic

Let $\mathcal{R}$ be the set of "representable numbers" in a computer, that is those numbers that the computer can represent exactly. Depending on the specific machine, they are usually real numbers with some finite binary expansion.

It is well known that computers can only perform arithmetic in an approximate way: the addition —for example— of two representable numbers is another representable number that will probably be close to the true sum, but is not exactly the true sum.

The idea to perform rigorous arithmetic is to instruct the computer on how to produce upper and lower bounds to the true results of arithmetic operations between representable numbers; in other words, we work with intervals with endpoints in $\mathcal{R}$, and we implement arithmetic operations on intervals in such a way that given two intervals, the computer will produce a third that is guaranteed

to contain the result of all arithmetic operations between points in the initial intervals. This is usually called "interval arithmetic".

As an example, let's consider one possible interval arithmetic implementation of the sum. This is fact the one that was used in our programs.

The computer manufacturer provides two operations on representables, a_1 and a_2 with the property that

$$\forall r, s \in \mathcal{R} a_1(r,s) \leq r + s \leq a_2(r,s)$$

Then, given two intervals, $I_1 = [r_1, s_1]$ and $I_2 = [r_2, s_2]$, the sum of these two intervals is defined to be

$$I_3 = [a_1(r_1, r_2), a_2(s_1, s_2)]$$

It is then clear that for all *real numbers* $x \in I_1$ and $y \in I_2$ we have that $x + y \in I_3$

Another possible implementation, that was also occasionally used in our programs, is as follows:

We construct two functions on representables *up* and *dn*, with the property that

$$up(r) \geq \inf_{s \in \mathcal{R}} \{s > r\}$$
$$dn(r) \leq \inf_{s \in \mathcal{R}} \{s < r\}$$

The computer manufacturer again provides us with a function a, which is in fact floating point addition for the computer we used, with the property that $a(r,s)$ is the closest representable number to $r + s$. This implies that, again, given two intervals, $I_1 = [r_1, s_1]$ and $I_2 = [r_2, s_2]$, if we define the sum of these two intervals to be $I_3 = [r_3, s_3)]$ with $r_3 = dn(a(r_1, r_2))$ and $s_3 = up(a(s_1, s_2))$ then for all *real numbers* $x \in I_1$ and $y \in I_2$ we have that $x + y \in I_3$

4.2 Functional Analysis

A convenient Banach space to use in this theory is the space of piecewise analytic functions, with a lower bound on the size of the domains of analyticity. The purpose of this section is to formalize definitions and set up the framework for computer assisted analysis in function space.

Consider the Banach space

$$H^1 = \left\{ f(z) | f(z) = \sum_{n=0}^{\infty} a_n \, z^n, \quad \sum_{n=0}^{\infty} |a_n| < \infty \right\}$$

with norm

$$\| f \| = \sum_{n=0}^{\infty} |a_n|$$

This is a subspace of the set of analytic functions in the unit disk. It becomes a Banach Algebra with $\| \, \|$.
We consider a neighborhood basis for the topology induced by $\| \, \|$ consisting of sets $\mathcal{U}(I_1, \ldots, I_N; C)$ of the form

$$\left\{ f(z) = \sum_{n=0}^{\infty} a_n \, z^n \middle| a_n \in I_n, \quad 0 \leq n \leq N, \sum_{n=N+1}^{\infty} |a_n| \leq C \right\} \tag{4.1}$$

where C is a positive real number and I_n are intervals in the real line. For the computer implementation, C will run over the set of computer-representable numbers, and the intervals will be those with representable endpoints.

The reason why this is a convenient space to work in is because elementary operations, such as addition, product, integration, differentiation (composed with a slightly contracting dilation), evaluation at a point and integration of initial value problems in ordinary differential equations can be conveniently bounded by elementary formulas in terms of this set of neighborhoods.

Observe that if we have a function $f(z)$ which is analytic in some disk, $|z-z_0| < r$, then, for any $\tilde{r} < r$, it is clear that if we define the normalized version of f

$$\tilde{f}(\tilde{z}) = f(\frac{\tilde{z} - z_0}{\tilde{r}})$$

then $\tilde{f} \in H^1$. In the real analytic case, $H^1[a,b]$ will denote H^1 of the disc with center a and radius $|b-a|$.

In the previous section, we saw that we will have to deal with functions with are sums of rational expressions. It is possible to produce neighborhoods of type (4.1) that contain those functions locally.

Chapter 5: The ODE

In this chapter, we will see how our ODE problem (2.3) can be dealt with the functional analysis introduced in the previous chapter, and therefore, how one can obtain computer assisted results about ODE's.

The discussion will be divided into two parts: the solution of initial value problems and the localization of eigenvalues. The presentation is taylored to deal with our special problem, but it can be modified, at the expense of complication, to deal with more general problems.

5.1 Initial Value Problems

Lemma 5.1 below takes care of the solutions of an IVP with analytic coefficients. Lemmas 5.2 and 5.3 take care of the expansion of the solutions at the singularities of the ODE, around 0 and ∞.

Lemma 5.1: *Consider the ODE:*

$$\left.\begin{aligned} u'' + qu &= 0 \\ u(0) &= u_0 \\ u'(0) &= u_1 \end{aligned}\right\} \tag{5.1}$$

where $q(x) \in \mathcal{U}\,(q_0, \cdots, q_N; \delta)$.
Then, $u \in \mathcal{U}(u_0, \cdots, u_{N+2}; C)$ *where*

$$u_{n+2} = -\frac{1}{(n+2)(n+1)} \sum_{i=0}^{n} u_i q_{n-i} \qquad 0 \le n \le N \tag{5.2}$$

and

$$C \le \frac{\displaystyle\sum_{i=0}^{N+2} \Big\{ \sum_{k=N+1-i}^{N} \frac{|q_k|}{(k+i+2)(k+i+1)} + \frac{\delta}{(N+3+i)(N+2+i)} \Big\} |u_i|}{\left(1 - \left(\displaystyle\sum_{k=0}^{N} \frac{|q_k|}{(k+N+5)(k+N+4)} + \frac{\delta}{(2N+6)(2N+5)} \right) \right)_+} \tag{5.3}$$

Operations are performed in the set–theoretic sense.

Proof: For simplicity in the formulas, put q_{-1}, $q_{-2}, \cdots = 0$.
The first part can be obtained by matching powers. For the estimate for C, note that

$$\sum_{n>N+2} |u_n| \le$$

$$
\begin{aligned}
&\leq \sum_{n>N} \sum_{i=0}^{n} \frac{|u_i q_{n-i}|}{(n+2)(n+1)} \\
&= \sum_{n>N} \left\{ \sum_{i=0}^{N+2} \frac{|u_i q_{n-i}|}{(n+2)(n+1)} + \sum_{i>N+2}^{n} \frac{|u_i q_{n-i|}}{(n+2)(n+1)} \right\} \\
&= \sum_{i=0}^{N+2} \sum_{n>N} \frac{|u_i q_{n-i}|}{(n+2)(n+1)} + \sum_{i>N+2} \sum_{n\geq i} \frac{|u_i q_{n-i}|}{(n+2)(n+1)} \\
&= \sum_{i=1}^{N+2} |u_i| \sum_{n=N+1}^{i+N} \frac{|q_{n-i}|}{(n+2)(n+1)} + \sum_{i=0}^{N+2} |u_i| \sum_{n=i+N+1}^{\infty} \frac{|q_{n-i}|}{(n+2)(n+1)} \\
&\quad + \sum_{i>N+2} |u_i| \sum_{n\geq i} \frac{|q_{n-i}|}{(n+2)(n+1)} \\
&= \sum_{i=1}^{N+2} |u_i| \sum_{k=N+1-i}^{N} \frac{|q_k|}{(k+i+2)(k+i+1)} \\
&\quad + \sum_{i=0}^{N+2} |u_i| \sum_{k=N+1}^{\infty} \frac{|q_k|}{(k+i+2)(k+i+1)} \\
&\quad + \sum_{i>N+2} |u_i| \sum_{n\geq i} \frac{|q_{n-i}|}{(n+2)(n+1)} \\
&\leq \sum_{i=0}^{N+2} \left\{ \sum_{k=N+1-i}^{N} \frac{|q_k|}{(k+i+2)(k+i+1)} + \frac{\delta}{(N+3+i)(N+2+i)} \right\} |u_i| \\
&\quad + \left(\sum_{k=0}^{N} \frac{|q_k|}{(k+N+5)(k+N+4)} + \frac{\delta}{(2N+6)(2N+5)} \right) \left(\sum_{i>N+2} |u_i| \right)
\end{aligned}
$$

This yields the result. $Q.E.D.$

Note that if q is analytic in a disk $D(z, R)$ other that the unit disk, it is possible to apply the lemma to its normalized version, $\tilde{q}$, with initial conditions u_0 and $R \cdot u_1$, and the solution obtained is, then, $\tilde{u}$, the normalized version of the true solution u. Also note that by doing this, the coefficients q_i are multiplied by a

factor shrinking with the radius, thus improving the estimate for C; in particular, note that the denominator in the expression for C, equation (5.3), may very well be negative (in which case the lemma does not claim any result, although one clearly exists); however, this denominator becomes positive and if fact goes to one when you take smaller and smaller radius for q. In other words, it is unavoidable (in this formulation) to take small steps when solving the ODE.

We point out, for the sake of completeness, an alternative argument to solve the problem in Lemma 5.1:

A solution to ODE (5.1) is characterized as the fixed point in H^1 of the functional

$$\mathcal{T}[f](x) = u_0 + \int_0^x \left(u_1 - \int_0^t q(s)\, f(s)\, ds \right) dt$$

By using the recursion formula (5.2) for the coefficients of u up to any finite order we want, we can obtain a polynomial $u^\sharp$ that we believe to be close to the true solution u.

It is possible to compute a neighborhood of type (4.1) containing $\mathcal{T}[u^\sharp]$, and, therefore, we can compute an upper bound for $\left\| \mathcal{T}[u^\sharp] - u^\sharp \right\|_{H^1}$, that if our guess was good, will be small. Also, it is elementary to compute upper bounds to the Lipschitz norm of $\mathcal{T}$, $\|\mathcal{T}\|_{\Lambda_1}$. All this upper bounds have to be rigorous; they can be implemented using interval arithmetic.

Finally, the contraction theorem in Banach Spaces tells us that that if $\|\mathcal{T}\|_{\Lambda_1} < 1$, then there is a fixed point u of $\mathcal{T}$, and thus a solution of ODE (5.1), and moreover (this is the important thing)

$$\left\| u^\sharp - u \right\|_{H^1} \leq \frac{\left\| \mathcal{T}[u^\sharp] - u^\sharp \right\|}{1 - \|\mathcal{T}\|_{\Lambda_1}} \tag{5.4}$$

and this gives us very good control over the solution u. Note the close resemblance of this estimate with estimate (5.3). However, there is one difference which is that in our approach, all the approximation error goes into the "high order terms",

whereas in this method, it goes into what is called "general error" (we don't know which Taylor coefficients it hits), and this makes it more convenient to work with a slightly different type of neighborhoods in H^1 that control this general error.

These procedures based on the contraction theorem is unavoidable (as far as I know) to study questions in which existence is not given. Note that this method proves existence, as a consequence of the fixed point theorem. This was used in fact to study very deep questions in [LL], [EW], [EW] and [EKW]. Also, in other problems (see [FL]), in which one has to study dependence on parameters, the contraction method is better since the recursive computation of the coefficients leads to explosive growth of the intervals.

We now deal with the singularities of the ODE at zero and infinity.

Lemma 5.2: *Consider the ODE*

$$u'' + \left(\frac{2\lambda k}{r} - \lambda^2 \right) u = 0$$

for k a positive integer, $\lambda > 0$, then, the only solution of the ODE that vanishes at ∞ is

$$u = e^{-\lambda r} \sum_{n=0}^{k} a_n r^n \tag{5.5}$$

where a_k is an arbitrary constant, and

$$a_n = a_{n+1} \frac{n(n+1)}{2\lambda(n-k)} \qquad n \leq k-1$$

Proof: Clearly (5.5) is a solution of the ODE. The lemma follows by observing that the solution that is linearly independent from it is

$$u = e^{\lambda r} \sum_{n=0}^{k} \tilde{a}_n r^{-n}$$

where

$$\tilde{a}_{n+1} = -\tilde{a}_{n+1} \frac{n(n+1)}{2\lambda(k-n-1)} \qquad n \leq k$$

and from here, any solution which is not (5.5) will grow exponentially at ∞. $Q.E.D.$

Lemma 5.3: *Consider the ODE*

$$u'' + \left(a + \frac{b}{r} - \frac{n(n+1)}{r^2}\right) u = 0$$

for n a positive integer. Then, the only solution of the ODE that vanishes at 0 belongs to $\mathcal{U}(u_0, \cdots, u_{N+2}; C)$ for u_{n+1} any constant, and

$$\begin{aligned} u_k &= 0 && k \leq n \\ u_{n+2} &= -\frac{b \cdot u_{n+1}}{(n+2)(n+1) - n(n+1)} \\ u_{k+2} &= -\frac{b \cdot u_{k+1} - a \cdot u_k}{(k+2)(k+1) - n(n+1)} && k \geq n+1 \end{aligned}$$

$$C \leq \frac{\dfrac{|b \cdot u_{N+2}| + |a \cdot u_{N+1}|}{(N+3)(N+2) - n(n+1)} + \dfrac{|a \cdot u_{N+2}|}{(N+4)(N+3) - n(n+1)}}{\left(1 - \dfrac{|b|}{(N+4)(N+3) - n(n+1)} - \dfrac{|a|}{(N+5)(N+4) - n(n+1)}\right)_+}$$

If a and b are sets of numbers, operations are performed in the set–theoretic sense.

Proof: The first part of the lemma follows from the theory of regular singular

points. For the estimate for C, note that the recursion formula gives

$$\begin{aligned}\sum_{k>N+2} |u_k| \leq & \frac{|b|}{(N+3)(N+2)-n(n+1)}|u_{N+2}| \\ & + \frac{|b|}{(N+4)(N+3)-n(n+1)}\left(\sum_{k>N+2}|u_k|\right) \\ & + \frac{|a|}{(N+3)(N+2)-n(n+1)}|u_{N+1}| \\ & + \frac{|a|}{(N+4)(N+3)-n}|u_{N+2}| \\ & + \frac{|a|}{(N+5)(N+4)-n(n+1)}\left(\sum_{k>N+2}|u_k|\right)\end{aligned}$$

So, the result follows. $Q.E.D.$

From these lemmas, and from the remarks of Chapter 4, we can solve initial value problems and evaluate the solution and its derivative at any point within its domain of analyticity. For its derivative it turns out that it convenient to use the formula

$$u'(x) = u_1 - \int_0^x q(t) \cdot u(t)\, dt$$

This formula allows us to evaluate the derivative up to including the boundary of the circle inside which q is in H^1 (we do not need to contract it a little).

5.2 Eigenvalues

A crucial device in the study of eigenvalue problems is the "*match*" function, $M(\lambda)$ associated with the ODE operator $-u'' + q \cdot u$ acting on $\mathcal{H}_{ode}$.

Here we will in fact consider general one–parameter boundary value problems

$$\left.\begin{aligned} u''(x) + p(x,\lambda)\, u(x) &= 0 \\ u(0) &= 0 \\ u'(\infty) &= 0 \end{aligned}\right\}$$

for which we will say that $-\lambda^2$ is an eigenvalue iff the previous equation has a solution for this value of λ. For the case

$$p(x,\lambda) = q(x) - \lambda^2$$

the two definitions of eigenvalue agree. Recall that our boundary condition $u \in \mathcal{H}_{\text{ode}}$ was equivalent to $u(0) = u(\infty) = 0$, by virtue of Lemmas 5.2 and 5.3.

We define the match function then as follows:
Take any point $0 < y < \infty$, and consider on the one hand, u_0, one solution of the ODE which vanishes at 0, and on the other hand, u_∞, one solution vanishing at ∞. Then, define

$$M(\lambda) = \frac{u_0'(y)\cdot u_\infty(y) - u_0(y)\cdot u_\infty'(y)}{\sqrt{u_0^2(y) + {u_0'}^2(y)}\cdot\sqrt{u_\infty^2(y) + {u_\infty'}^2(y)}}.$$

Then, $-\lambda^2$ is an eigenvalue iff $M(\lambda) = 0$.

In our analysis we will be considering two different "eigenvalue" problems, associated with the functions $p(x,\lambda)$ given respectively by

$$p_0(x,\lambda) = \frac{Z}{x} - \frac{l(l+1)}{x^2} - V(x) - \lambda^2 \tag{5.6}$$

$$p_k^*(x,\lambda) = \begin{cases} \dfrac{Z}{x} - \dfrac{l(l+1)}{x^2} - V(x) - \lambda^2 & \text{for } x \le x_0 \\[2ex] \dfrac{2k\lambda}{x} - \lambda^2 & \text{for } x \ge x_0 \end{cases} \tag{5.6up}$$

They will give rise to match functions M_0 and M^* respectively.

The reason is that, for $k = k(\lambda)$ as in (3.16), we have

$$p^*_{k(\lambda)}(x, \lambda) \geq p_0(x, \lambda) \tag{5.7}$$

In fact, when the subscript k is missing we will understand it is this p^* that we are talking about.
(5.7) will have as a consequence that M^* will act as a maximal problem for M_0, and it is easier to study by virtue of Lemma 5.2.

Observe that the problem associated with p^* is not even a generalized eigenvalue problem since it is not guaranteed that

$$\frac{\partial p(x, \lambda)}{\partial \lambda} \leq 0$$

and, even worse, it is not even continuous, since $k(\lambda)$ isn't. This can be remedied as follows:

We will only estimates for $M^*(\lambda)$ for a finite number of values of λ, $\lambda_1 > \cdots > \lambda_n$. Define

$$G_i = -\frac{k(\lambda_i) - k(\lambda_{i+1})}{\lambda_i - \lambda_{i+1}}$$

and

$$\bar{k}(\lambda) = \frac{Z - V(x_0)}{\lambda}$$

Recall that $k(\lambda)$ was defined to be the smallest integer above $\bar{k}(\lambda)$. Since the graph of $\bar{k}$ is convex, given $\epsilon > 0$ we can find a differentiable function $k^*(\lambda)$ such that

1. $k^*(\lambda) \geq \bar{k}(\lambda)$, what implies that $p^*_{k^*}(x, \lambda) \geq p(x, \lambda)$
2. $k^*(\lambda_i) = k(\lambda_i)$ for all i.
3. $\frac{dk^*}{d\lambda}(\lambda) < G_i + \epsilon$ for $\lambda_{i+1} \leq \lambda \leq \lambda_i$.

We then define M^* to be the match function associated with $p^*_{k^*}$. The two definitions of M^* agree at those λ_i and as long as

$$\frac{G_i \cdot \lambda_i + k(\lambda_{i+1})}{x_0} < \lambda_{i+1}$$

we have that $\frac{\partial p_{k*}^*}{\partial \lambda} < 0$, and M^* will be a generalized eigenvalue problem.

The discussion then will deal with the two different cases, one in which the previous condition is fulfilled, and thus, we are dealing with generalized eigenvalue problems, and, two, when this conditions is not fulfilled, in which case, and therefore, we can not use any properties of eigenvalue problems on M^*.

The fact that M^* is not an eigenvalue problem will give rise to certain technical complications; but M^* still is an easier problem to study because the most delicate part of the whole proof is to obtain good bounds for the solution of the ODE.

Define the "phase" of a function u to be the point in the unit circle given by

$$\Phi_u(x) = \frac{(u'(x), u(x))}{\sqrt{u(x)^2 + u'(x)^2}} \tag{5.8}$$

and define its angle $\theta_u(x)$ such that

$$\Phi_u(x) = \big(\cos\big(\theta_u(x)\big), \sin\big(\theta_u(x)\big)\big) \tag{5.9}$$

It is well known ([CL]) that if

$$\theta_u'(x) = \cos^2\left(\theta_u(x)\right) + p(x,\lambda)\sin^2\left(\theta_u(x)\right)$$

and therefore

$$\theta_u(x_0) \equiv 0 \pmod{\pi} \Rightarrow \theta_u'(x_0) > 0 \tag{5.10}$$

Note that the phase is invariant under multiplication of u by a nonzero constant, and it is only defined for functions that do not vanish to order two: since our functions will be nonzero solutions to an ODE problem, their phase is defined.

Note also that

$$\begin{aligned} M(\lambda) &= \det\left(\Phi_{u_0}(y), \Phi_{u_\infty}(y)\right) \\ &= \sin\left(\theta_\infty(y) - \theta_0(y)\right) \end{aligned}$$

Recall the Comparison theorem for Sturm-Liouville problems.

Theorem 5.4 (Sturm-Liouville Comparison Theorem):
Consider two ODE's

$$u'' + q_1 \cdot u = 0$$

$$v'' + q_2 \cdot v = 0$$

on some interval (a, b)*, with*

$$q_2(x) \geq q_1(x), \qquad a \leq x \leq b$$

Then
1. *v has to vanish between any two zeros of u.*
2. *If $\theta_u(a) \leq \theta_v(a)$, then*

$$\theta_u(x) \leq \theta_v(x) \qquad \text{for} \quad a \leq x \leq b$$

And this holds if q_1 and q_2 are Lipschitz. If they have a simple pole at a, the lemma also holds provided $u(a) = v(a) = 0$.

For a proof of this see [CL].

Define θ_λ such that

$$\frac{(-\lambda, 1)}{\sqrt{1+\lambda^2}} = (\cos(\theta_\lambda), \sin(\theta_\lambda)) \qquad (\frac{\pi}{2} < \theta_\lambda < \pi) \tag{5.11}$$

Note that θ_λ is increasing in λ.

Lemma 5.5: *Let u be any solution of*

$$\left.\begin{aligned} u''(x) + q(x)\, u(x) = 0 \\ u(\infty) = 0 \end{aligned}\right\}$$

with

$$\lim_{x\to\infty} q(x) = -\lambda^2$$

Then, we have

$$\lim_{x\to\infty} \theta_u(x) \equiv \theta_\lambda \pmod{2\pi}$$

Proof: Since q is negative for large x, u has only finitely many zeros. Assume

$$\liminf_{x\to\infty} \frac{-u'(x)}{u(x)} = \alpha < \lambda$$

Clearly $\alpha \geq 0$, since otherwise u cannot be zero at infinity.
This means that for $\{x_n\}$ going to infinity, and for ϵ small enough but fixed

$$-u'(x_n) < (\lambda - \epsilon)u(x_n)$$

for n large enough, which by continuity implies

$$-u''(x_n) < (\lambda - \epsilon)^2 u(x_n) < (\lambda^2 - \lambda\epsilon)u(x_n)$$

Since for n large enough

$$q(x_n) = -\lambda^2 \pm \tfrac{\lambda\epsilon}{4}$$

we see that u cannot be a solution of the ODE. Doing the same for lim sup we get the conclusion of the lemma. QED

Lemma 5.6: *Let u_∞ and u^*_∞ be the solutions of*

$$\left.\begin{aligned} u'' + p(x,\lambda)u = 0 \\ u(\infty) = 0 \end{aligned}\right\}$$

with p equal to p_0 and p^* respectively. Then

$$\theta_{u^*_\infty} \leq \theta_{u_\infty}$$

everywhere, where the two angles are normalized so that their limit at infinity is equal to θ_λ.

Proof: Let $w = \theta_{u^*_\infty} - \theta_{u_\infty}$. The ODE that θ satisfies implies that

$$w'(x) = f(x)w(x) + h(x)$$

with

$$f(x) = \big(p(x,\lambda) - 1\big)\left(\sin(\theta_{u^*_\infty}) + \sin(\theta_{u_\infty})\right) \cdot \frac{\sin(\theta_{u^*_\infty}) - \sin(\theta_{u_\infty})}{\theta_{u^*_\infty} - \theta_{u_\infty}}$$

and

$$h(x) = \big(p^*(x,\lambda) - p_0(x,\lambda)\big)\sin^2\left(\theta_{u^*_\infty}\right) \geq 0$$

For x large enough, since $\frac{\pi}{2} \leq \theta_\lambda \leq \pi$, we have that $f > 0$. This implies that $w'(x) > 0$, and thus, if for some y the statement of the lemma is false we have that for all $x > y$

$$\theta_{u^*}(x) - \theta_u(x) > \theta_{u^*}(y) - \theta_u(y)$$

what would imply

$$\lim_{x\to\infty} \theta_u(x) < \lim_{x\to\infty} \theta_{u^*}(x)$$

which is not true because we are normalizing the phases to have the same limit at infinity. Q.E.D.

Let's say that $\lambda_1 > \lambda_2 > \cdots$ are the zeros of M_0.

Lemma 5.7: *For the true eigenvalue problem associated with p_0 as in* (5.6)*, if $u_\infty(\lambda^*, x)$ has strictly less that k zeros in $(0,\infty)$, then*

$$\lambda_k \leq \lambda^*$$

Proof: Assume $\lambda_k > \lambda^*$. Since this is the true eigenvalue problem, we have on the one hand

$$p(\lambda_k, x) < p(\lambda^*, x)$$

and by Lemma 5.5, for x large enough we have that

$$\theta_{u_\infty}(\lambda^*, x) < \theta_{u_k}(\lambda, x)$$

where again the angles are normalized so their limit at infinity is between 0 and π.
By the comparison theorem then

$$\theta_{u_\infty}(\lambda^*, x) < \theta_{u_k}(\lambda, k) \quad \text{for all } x$$

Since by Lemma 5.3 $\theta_{u_k}(\lambda_k, 0) = 0$ and it vanishes $k-1$ times in $(0, \infty)$ (because it is an eigenvalue problem), $\theta_{u_\infty}(\lambda^*, x)$ vanishes mod π at least k times, and therefore u_∞ has to vanish at least k times, which contradicts the hypothesis of the Lemma. Q.E.D.

Lemma 5.8: *Assume that λ_k^* is a zero of M^* and the corresponding eigenfunction u_k^* has at most $k-1$ zeros in $(0, \infty)$.*
Then

$$\lambda_k \leq \lambda_k^*$$

Proof: By Lemma 5.6 we have that

$$\theta_{u_\infty}(\lambda_k^*, x) \geq \theta_{u_\infty^*}(\lambda_k^*, x)$$

with the usual normalization. By (5.10) then $\theta_{u_\infty}(\lambda_k^*, x)$ vanishes mod π at most $k-1$ times, and by the previous Lemma then we get

$$\lambda_k \leq \lambda_k^*$$

as claimed. Q.E.D.

Lemma 5.9: *Define*

$$M = \det\left(\Phi_{u_0}, \Phi_{u_\infty}\right)$$

for the eigenvalue problem associated to either p_0 *or* p^**. Then*

$$M(\lambda) > 0 \quad \text{for } \lambda > \lambda_1$$

where λ_1 *is the largest zero of the problem.*
In particular,it will follow from the proof that the zeros of M *are bounded above.*

Proof: Since M does not change sign in (λ_1, ∞) (that's why $-\lambda_1^2$ is the smallest eigenvalue), it is enough to prove that $M(\lambda) > 0$ for λ large enough.

Take v satisfying

$$\left.\begin{aligned} v''(x) + \frac{Z}{x}\, v(x) &= 0 \\ v(0) &= 0 \\ v'(0) &= 1 \end{aligned}\right\}$$

By Lemma 5.3, $v(x) = x + O\left(x^2\right)$, what implies that $\theta_v(0) = 0$
and, for small enough y,

$$0 \le \theta_v(x) \le \frac{\pi}{2} \qquad \text{for } 0 \le x \le y$$

Pick u_0 so that

$$\left.\begin{aligned} u_0'(0) &= 1 \\ u_0(0) &= 0 \end{aligned}\right\} \tag{5.12}$$

Clearly $\theta_u(0) = 0$ and $\theta'(0) > 0$, which implies that $\theta_{u_0}(x) \ge 0$ for $0 \le x \le \epsilon$
Lemma 5.8 (to be proved later) implies that

$$u(x) \neq 0 \qquad \text{for} \quad 0 < x < Z^{-1} \tag{5.13}$$

which implies that

$$\theta_{u_0}(x) \geq 0 \qquad \text{for} \quad 0 \leq x \leq Z^{-1}$$

Since $p(x) < Z/x$, Theorem 5.4 and the previous estimates imply that

$$0 \leq \theta_{u_0}(x) \leq \theta_v(x) \leq \frac{\pi}{2} \qquad \text{for} \quad 0 \leq x \leq y$$

what means that, for y independent of λ,

$$u_0(y) > 0 \qquad \text{and} \qquad u_0'(y) > 0 \tag{5.14}$$

Since M is invariant under multiplication of u by a constant, we can assume that $u_\infty(y) > 0$. Take λ so big that $p(x)$ as defined in (5.6) is negative in the range $y < x < \infty$ (recall that $k(\lambda) = 1$ for λ large enough). This implies that if $u_\infty'(y) > 0$, u_∞ would be increasing and this would contradict the fact that it vanishes at infinity. Therefore,

$$u_\infty(y) > 0 \qquad \text{and} \qquad u_\infty'(y) > 0$$

This, with (5.14), implies

$$\text{sign } M = (+) \cdot (+) - (+) \cdot (-) > 0$$

as claimed. Q.E.D.

Lemma 5.10: *Assume there is a number λ such that $M^*(\lambda) > 0$, u_λ^∞ vanishes $k-1$ times in (Z^{-1}, ∞), with k an even number, and there are $\lambda_1^*, \cdots, \lambda_{k-1}^*$ zeros of M^* bigger that or equal to λ. Assume that M^* is a generalized eigenvalue problem.*
Then

$$\lambda_k^* \leq \lambda$$

and moreover

$$\lambda_k \leq \lambda$$

Proof: Assume $\lambda_k^* > \lambda$. We know that that $u_{\lambda_k^*}$ has $k-1$ zeros in $(0,\infty)$.

Also, by Lemma 5.9 we know that

$$\frac{d}{d\lambda} M^*(\lambda_k^*) < 0$$

Thus, since $M^*(\lambda) > 0$, then in fact $\lambda < \lambda_{k+1}^*$.

Since $u_{\lambda_{k+1}^*}$ has k zeros in $(0,\infty)$ u_λ^∞ must have $k+1$ zeros in $(0,\infty)$, and by hypothesis, we know that it vanishes $k-1$ times in (Z^{-1},∞), what implies that it vanishes twice in $(0,Z^{-1})$ which is impossible by Lemma 5.12 (to be proved later).

Therefore, $\lambda_k^* \leq \lambda$. This implies in particular that u_λ^∞ has $k-1$ zeros in $(0,\infty)$ and by Lemma 5.8 we have also that

$$\lambda_k \leq \lambda$$

as claimed. $Q.E.D.$

The hypothesis in the Lemma can be reversed to $M^*(\lambda) < 0$ and k odd, with the same conclusions.

In view of the preceding lemmas, the match function M^* will provide us with bounds for the eigenvalues in (2.3). Let's denote the zeros of M^* by $\lambda_1^* > \lambda_2^* > \cdots$.

We will now consider a computer bound for M^*

$$\mathcal{M} : \mathcal{R} \to \mathcal{I}$$

that will satisfy the property that for any representable r,

$$M^*(r) \in \mathcal{M}(r) \tag{5.15}$$

This can be implemented as follows:

For each positive $\lambda \in \mathcal{R}$ our ODE problem is

$$\left.\begin{aligned} u^{*\prime\prime}(x) + p^*(x)u^*(x) = 0 \\ u^*(0) = u^*(\infty) = 0 \end{aligned}\right\}$$

where p is as (5.6up) From section 1, we have a finite set of real numbers, $x_0 > x_1 > \cdots > x_n > 0$ such that the coefficients of the ODE are in $H^1[x_i, x_{i+1}]$ for $0 \leq i \leq n-1$, and (3.8) and (3.10) say that the ODE takes the special form dealt with in lemmas 5.2 and 5.3 around 0 and ∞. Elsewhere, it takes the form dealt with in Lemma 5.1.

As explained in the previous Chapter, we can obtain intervals that contain $u^*_\infty(x_0)$ and ${u^*}'_\infty(x_0)$ and we can, therefore, give bounds for $\Phi_{{u^*}_\infty}(x_0)$.

With the aid of Lemma 5.1, we can solve the initial value problem at x_0, thus obtaining another neighborhood of type (3.7) of $H^1[x_0, x_1]$ that contains ${u^*}_\infty$, and again obtain intervals that contain $\Phi_{{u^*}_\infty}(x_1)$.
Repeating this argument, we can obtain bounds for $\Phi_{{u^*}_\infty}(x_n)$.

With the aid of Lemma 5.3, we can determine bounds for $\Phi_{{u^*}_0}(x_n)$.

Then, we define

$$\mathcal{M}(\lambda) = \det\left(\Phi_{{u^*}_0}(x_n), \Phi_{{u^*}_\infty}(x_n)\right)$$

where the determinant is taken in the interval arithmetic sense.

It is just clear that $M^*(\lambda) \in \mathcal{M}(\lambda)$ for $y = x_n$.

To obtain bounds on the eigenvalues, we produce heuristic (e. g. using numerical analysis) representable numbers

$$\lambda_1^{\mathrm{up}} > \lambda_1^{\mathrm{dn}} > \lambda_2^{\mathrm{up}} > \lambda_2^{\mathrm{dn}} > \cdots \lambda_k^{\mathrm{up}} > \lambda_k^{\mathrm{dn}} > 0$$

such that we believe that the true zeros λ_i^* are contained in the intervals $\bar{\lambda}_i = (\lambda_i^{\mathrm{dn}}, \lambda_i^{\mathrm{up}})$, and these intervals are small. The way this was done in the real implementation is by applying the floating point approximation to the previous

procedure to compute the match function, and then use numerical analysis to "find" its zeros in an approximate way. For this, it is important to notice that, by (2.4)

$$\lambda_n \leq \frac{Z}{\sqrt{2}(n+l)} \tag{5.16}$$

Then compute $\mathcal{M}(\lambda_i^{\text{up, dn}})$. We make the assumption that

$$\begin{aligned} &\mathcal{M}(\lambda_i^{\text{up}}) > 0 \quad \mathcal{M}(\lambda_i^{\text{dn}}) < 0 \quad i = 1, 3, \dots \\ &\mathcal{M}(\lambda_i^{\text{up}}) < 0 \quad \mathcal{M}(\lambda_i^{\text{dn}}) > 0 \quad i = 2, 4, \dots \end{aligned} \tag{5.17}$$

and that, in the case M^* is not a generalized eigenvalue problem, we impose the condition that k does not jump in each interval $\bar{\lambda}_i$.

If we can prove (5.17), (5.15) and the fact that M^* is continuous would prove that each interval $\bar{\lambda}_i = (\lambda_i^{\text{dn}}, \lambda_i^{\text{up}})$ contains at least one eigenvalue. If we fail to prove this we look for other choices of $\lambda_i^{\text{up,dn}}$.
Note that here we are not using condition (5.6) to full power, but only the fact that

$$\text{sign } M(r) = \text{sign } \mathcal{M}(r) \qquad \text{for} \quad r \in \mathcal{R}$$

where the sign of an interval is defined to be $+1$ if the interval is completely to the right of 0, -1 if it is completely to the left and is left undefined if it contains the value 0.

The reason why we impose condition (5.17) is because expect M to change sign between zeros. The fact that we assume that

$$\mathcal{M}(\lambda_i^{\text{up}}) > 0$$

has to do with the fact that we defined

$$\mathcal{M} = \det(\Phi_{u_0}, \Phi_{u_\infty})$$

and not

$$\mathcal{M} = \det(\Phi_{u_\infty}, \Phi_{u_0})$$

and with Lemma 5.9.

It is interesting to point out that to expand the phase in time does not work if we substitute the phase by the vector $(u(x), u'(x))$; the reason is that interval arithmetic estimates are far to conservative and the bounds we obtain are very bad after a few steps. The reason why the previous algorithm in fact manages to prove good bounds for the eigenvalues lies in the fact that the solution of this particular ODE is of the form $e^{-\lambda x}$ with a factor out front small compared to the exponential. This has as a consequence that the normalizing factor in the phase has a contractive effect that provides stability of the bounds: that's why we expand from ∞ towards 0. In other words, if you look at the time flow

$$T_t\left(\Phi_u(x)\right) = \Phi_u(x+t)$$

it turns out for the particular ODE we are working with, the phases of the eigenfunctions are almost always in the unstable manifold, and expansion of the phase backward in time gives good answers. If the phase happened to be in the stable manifold, the previous procedure would also if we expand forward in time, for the same reason. In the general case that solutions to the ODE can have significant projections in both the stable and unstable manifolds, one sided shooting is not enough: you need to consider these two projections separately. For this important generalization see [LR].

All this tells us that, for the maximal problem M^*, there are negative eigenvalues $-\lambda^{*2}$, with ${\lambda^*}_i \in \bar{\lambda}_i^*$, $i = 1, \cdots, k$, with eigenfunctions u_k^*; but in order to proof that these eigenvalues are lower bounds to the eigenvalues for the true problem (2.3) we proceed as follows:

If M^* is a true eigenvalue problem, then it would suffice to prove that the solution to the ODE corresponding to λ_k^{up} has $k-1$ zeros in $(0, \infty)$, with k of the right parity, in view of Lemma 5.10.

In the case M^* is not a generalized eigenvalue problem, we need to show that u_k^* has $k-1$ zeros in $(0,\infty)$, in view of Lemma 5.8. In order to see this, we use the following Lemma:

Lemma 5.11: *Assume*

$$\lambda^{\mathrm{dn}} \cdot \Big(k(\lambda^{\mathrm{up}}) + 2 \Big) > \lambda^{\mathrm{up}} \cdot k(\lambda^{\mathrm{dn}})$$

and that the solution of

$$\left.\begin{aligned} u''(x) + p_{k(\lambda^{\mathrm{up}})+2}(x, \lambda_d n) \cdot u(x) u = 0 \\ u(\infty) = 0 \end{aligned}\right\} \tag{5.18}$$

with $p_{k(\lambda^{\mathrm{up}})+2}(x, \lambda^{\mathrm{dn}})$ as in (5.6up), has $k-1$ zeros.
Then, for any $\lambda^{\mathrm{dn}} \le \lambda \le \lambda^{\mathrm{up}}$, the solution of

$$\left.\begin{aligned} u(x)'' + \left(\frac{2\lambda \cdot k(\lambda)}{x} - \lambda \right) \cdot u(x) = 0 \\ u(\infty) = 0 \end{aligned}\right\}$$

has at most $k-1$ zeros.

Proof: Since $k(\lambda)$ is decreasing in λ, the first hypothesis in the lemma simply says that

$$p^*(x,\lambda) \le p_{k(\lambda^{\mathrm{up}})+2}(x, \lambda^{\mathrm{dn}}) \quad \forall \lambda \in (\lambda^{\mathrm{dn}}, \lambda^{\mathrm{up}})$$

and the rest just follows by the usual argument. Q.E.D.

Call $u^m(x)$ the solution of (5.18), or $u^{\infty}_{\lambda_k^{\mathrm{up}}}$. Note that u^m is the solution of one of those ODE's we can solve via the lemmas in the IVP section. In particular, we know intervals that contain the values of the solution at certain points. We will now see that under very mild conditions on the thickness of the partition $x_0, \cdots, x_n$, the number of zeros of u^m is essentially the same as the number of sign changes in

$$u^m(x_0), \cdots, u^m(x_n)$$

Lemma 5.13: *Consider any solution of*

$$u'' - \left(V(x) + \frac{l(l+1)}{x^2} - \frac{Z}{x} + \lambda^2 \right) u = 0$$

on $[a,b]$, *with* $0 < a < b < \infty$, *and* V *decreasing.*
Define

$$k(a,b) = \frac{Z}{b} - V(a)$$

Then, the following holds:

1. *if*

$$b - a \leq \max\left(Z^{-1}, \pi \big(k(a,b) \big)_+^{-1/2} \right)$$

then u *cannot have two zeros in* $[a,b]$.

2. *If* $u(0) = 0$,

$$u \neq 0 \qquad \text{for} \qquad 0 < x < Z^{-1}$$

3. *If* $u(\infty) = 0$, *then*

$$u \neq 0 \qquad \text{for} \qquad \frac{2k}{\lambda} < x < \infty$$

where k *is defined as in* (3.15), *and* x_0 *is the largest point at which* V *is singular.*

Proof: Consider the equation

$$\left.\begin{aligned} v'' + \frac{b}{x} v = 0 \\ v(0) = 0 \end{aligned}\right\} \tag{5.19}$$

By Lemma 5.3 we know that

$$v > x - \frac{6b}{12 - 2b} x^2 \quad (b < 6)$$

which implies that $v(x) > 0$ for $0 < x < \frac{12-2b}{6b}$. Thus, if $w(x)$ is a solution of

$$\left.\begin{aligned} w'' + \frac{Z}{x} w = 0 \\ w(0) = 0 \end{aligned}\right\}$$

then $v(x) = w(\epsilon x)$ is a solution of (5.19) with $b = \epsilon Z$; thus

$$v(x) \neq 0 \qquad \text{for} \quad x \in \left(0, \frac{12 - 2\epsilon Z}{6\epsilon Z}\right)$$

what implies

$$w(x) \neq 0 \qquad \text{for} \quad x \in \left(0, \frac{12 - 2\epsilon Z}{6\epsilon Z}\right) \quad (\epsilon Z < 6)$$

Taking the limit as $\epsilon \to 0$, we get

$$w(x) \neq 0 \qquad \text{for} \quad x \in \left(0, \frac{2}{Z}\right)$$

Since $p(x) > Z/x$, we have that u cannot vanish in $0 < x < 2Z^{-1}$, thus proving 2.

This argument implies that u cannot vanish twice between two zeros of w anywhere, and since Z/x is decreasing, the zeros of w never get any closer than Z^{-1}, which proves the first half in 1.

For the other statement in 1., note that

$$p(x) < \frac{Z}{b} - V(a) - \frac{l(l+1)}{a^2} - \lambda^2 \ < k(a,b) \qquad \text{for} \quad a < x < b$$

If $k(a,b) < 0$, the distance between neighboring zeros of u is bigger that for the solution of

$$u'' + k(a,b) \cdot u = 0 \tag{5.20}$$

which happens to be $e^{\pm\sqrt{-k(a,b)}x}$ and has no zeros. So, u cannot vanish twice in (a,b).

If $k(a,b) > 0$, then the solution of (5.20) is $\sin\left(\sqrt{k(a,b)}x\right)$, whose zeros are at a distance

$$\pi k(a,b)^{-1/2}$$

which proves 1.

For 3., since by (3.15)

$$p(x) = \frac{2k\lambda}{x} - \lambda^2 \qquad \text{for} \quad x \geq x_0$$

the condition says that p is negative in the range $x \geq x_0$ and $x \geq 2k/\lambda$. Assume then that $u(t) = 0$ and, say, $u'(t) = 0$; then u is positive a little to the right of t and since

$$u''(x) = -p(x) \cdot u(x)$$

u grows and cannot vanish at infinity. QED

We assume that the partition $x_0, \cdots, x_n$ introduced at the end of Chapter 3 is fine enough so that every interval (x_i, x_{i-1}) satisfies the hypothesis of this lemma. This can always be arranged from the start since our potential (5.6) is bounded above.

Note that property 3. in the lemma allows us to count the number of zeros to the right of x_0 (which is useful if x_0 happens to be less that $2k/\lambda$); simply recall that we know the solution is a polynomial with a non-zero factor, so we only have to count the number of zeros of this polynomial between x_0 and $2k/\lambda$. Since these zeros cannot get any closer that

$$\pi\left(k(x_0, \infty)\right)_+^{-1/2} = \pi\left(\frac{2k}{\lambda x_0} - \lambda^2\right)_+^{-1/2}$$

we can take points at a distance less that half this amount from each other and evaluate intervals containing the value of the polynomial at these points; make the assumption that none of these intervals contains the value 0; then the number of zeros of u in (x_0, ∞) is exactly the number of sign changes of these intervals. Note that this does not involve to solve any ODE, except at x_0.

In this way, everything is reduced to counting the number of sign changes in

$$u^m(x_n), \cdots, u^m(x_0)$$

and adding up the zeros the previous procedure gives. The following argument takes care of the fact that we only know an interval bound to the true values of u^m at those points.

Lemmas 5.1 and 5.2 give us intervals $\{I_i\}$ that contain $u^m(x_i)$. We now make the assumption (otherwise we quit the proof) that

$$0 \in I_i \Rightarrow \begin{cases} I_{i-1} < 0 < I_{i+1} \\ \quad \text{or} \\ I_{i-1} > 0 > I_{i+1} \end{cases}$$

in which case we remove I_i from the collection. Therefore, we have a collection of intervals $\{I_i\}$ all of which are always either above or below 0. Let's now count the number of pairs (I_i, I_{i+1}) such that $I_i \cdot I_{i+1} < 0$. It is clear that every such pair is associated with one zero of u^m. Note also that there can be no more; this can be seen as follows:

1. If I_i and I_{i+1} were neighbors before we removed intervals, then

    a. If $I_i \cdot I_{i+1} < 0$, because u^m is continuous, there is one zero, and only one, by Lemma 5.4, and this is the one we accounted for.

    b. If $I_i \cdot I_{i+1} > 0$, then we are counting no zeros. Now, u^m must have an even number of zeros in (x_{i+1}, x_i), and by Lemma 5.4 can have at most one. So it has no zeros in this interval.

2. If there was some interval between them that we removed, then they have different sign, and therefore we are accounting for one zero. Let y be the point x_j corresponding to the interval we removed:

    a. If $u^m(y) > 0$, by Lemma 5.4 we have no zeros in (y, x_i), and an odd number less than two of them in (x_{i+1}, y). So, we have one zero in (x_{i+1}, x_i). If $u^m(y) < 0$ argue the same way.

    b. If $u^m(y) = 0$, by Lemma 5.4 we have no other zeros either in (x_{i+1}, y) or in (y, x_i), so again, one zero in total.

This proves that the number of zeros of u^m is the same as the number of sign changes of the intervals $\{I_i\}$, which is trivial to compute.

It is clear that with the control we have over the solutions of ODE's it is possible to bound the number of zeros without using Sturm-Liouville theory, but comparison theorems simplify the algorithm enormously since everything is reduced to counting sign changes in a sequence of intervals.

With the previous procedure, given l, we can obtain lower bounds for the k smallest eigenvalues of $H^{1 \text{ electron}}$:

$$E_{1,l} < E_{2,l} < \cdots < E_{k,l}$$

Recall that each eigenvalue has to be taken with multiplicity $2(2l+1)$. But remember that what we really needed was the smallest eigenvalues among all these $E_{n,l}$ for all values of $l = 0, 1, \ldots$. Although it is trivial to arrange this once we know enough $E_{n,l}$, since calculating eigenvalues turns out to be quite time–consuming, it is important to have a good procedure. One possibility is as follows:

Chemistry predicts that for $1 \leq Z \leq 86$, the eigenvalues $E_{n,l}$ will be ordered as follows

$$\begin{aligned} E_{1,0} \leq E_{2,0} \leq E_{1,1} \leq E_{3,0} \leq E_{2,1} \leq E_{4,0} \leq E_{1,2} \leq E_{3,1} \leq E_{5,0} \leq E_{2,2} \\ \leq E_{4,1} \leq E_{6,0} \leq E_{1,3} \leq E_{3,2} \leq E_{5,1} \end{aligned}$$

and transitions occur at the following values of Z

$$Z = 2, 4, 10, 12, 18, 20, 30, 36, 38, 48, 54, 56, 70, 86$$

Each $E_{n,l}$ corresponds to the orbital ks, kp, kd, kf,... depending on the value of l, for $k = l + n$.
Since $E_{n,l} \leq E_{n,l+1}$, in order to check that the chemical predictions are correct, it is enough to do as follows:

Given $1 \leq Z \leq 86$, let $E_{\bar{n},\bar{l}}$ be the largest eigenvalue corresponding to a non–empty shell predicted by chemistry. For each l, let $E_{n_l,l}$ be the largest eigenvalue that appears before $E_{\bar{n},\bar{l}}$; let l_0 be the first l such that E_{0,l_0} does not appear before $E_{\bar{n},\bar{l}}$; then

check 1. $E_{\bar{n},\bar{l}} \leq E_{n_l+1,l}$

check 2. $E_{\bar{n},\bar{l}} \leq E_{0,l_0}$

Occasionally, these checks will not be satisfied: electrons will arrange themselves in shells differently from chemical predictions; in this case, we simply replace all unknown eigenvalues by the smallest one known. In practice this only happened for the outermost shells, which correspond to the largest eigenvalues, which happen to be very similar from each other and therefore didn't have any noticeable change in the results.

Chapter 6: The Numerics

As remarked before, how good a lower bound for the energy we obtain depends on how good a "charge density guess" we make, or equivalently, how good functions R_i we select.

Equivalently, all the parameters we need for carrying out the algorithm described in Chapters 2—5 are given by the functions R_i that; since they are chosen to be piecewise linear, we are left with only a finite number of parameters, $\alpha = (\alpha_1, \cdots, \alpha_n)$, which are essentially the numbers is (3.5). Thus, we write the potential as $V_\alpha(x)$ and we write the lower bound for the energy that we obtain with our algorithm as $E(\alpha; Z)$; we then have

$$E(\alpha; Z) \geq E(Z) \quad \forall \alpha$$

and in this way, the problem of finding a good lower bound is reduced to the purely numerical problem of finding a good α. This was done as follows:

Following [HLT], we use as $\rho(x)$ an empirical approximation to TF density introduced in [Ti]

$$\rho(x) = \frac{6\left(\frac{9}{2}\right)^{2/3}}{4\pi|x| \cdot \left(|x| + \left(\frac{9}{2}\right)^{1/3}\right)^4}$$

(note that $\int \rho = 1$), and then for each Z, take

$$\rho_Z(x) = Z^2 \rho\left(Z^{1/3} x\right)$$

With this charge density, apply the algorithm from the previous chapters. This gives a lower bound for the energy, and also, it provides us with a new charge guess in the following way:

Let $f_{n,l}$ the solution to our ODE (2.3) for each value of l, corresponding to the n'th eigenvalue, normalized so that it has L^2 norm 1. As a consequence, a ground state for $H^{1\text{ electron}}$ is given by

$$\Psi_{lb}(x_1, \cdots, x_Z) = \bigwedge_{n,l,m} f_{n,l}(r_i)\, Y_{l,m}(\theta_i) \tag{6.9}$$

where $x_i = r_i \cdot \theta_i$, with $0 \leq r_i \leq \infty$, and θ_i a point in the unit sphere in $\mathbf{R}^3$; $Y_{l,m}(\theta)$ is a normalized spherical harmonic of degree l, the antisymmetric product contains Z factors and by the normalization of the $f_{n,l}$ Ψ has L^2 norm 1. This means that for atoms with an incomplete orbital we make a random choice of which $Y_{l,m}$ we take into the product. This ground state has a density

$$\begin{aligned}\rho(x) &= \int |\Psi(x, x_2, \cdots, x_Z)|^2 \, dx_2 \cdots dx_Z \\ &= \sum_{l,m,n} f_{n,l}^2(r) \cdot Y_{m,l}^2(\theta)\end{aligned}$$

For incomplete orbitals, then, ρ is not radially symmetric. It will be radial, however, if we as ground state the average over all possible choices of $Y_{m,l}$ (the average of a ground state is still a ground state). Thus, since

$$\sum_m Y_{m,l}^2(\theta) = 2l + 1$$

we can take

$$\rho(x) = \sum_{n,l} w(n,l) f_{n,l}^2(r)$$

where the weight $w(n,l)$ is equal to $2(2l+1)$ except in the last orbital $\bar{n}, \bar{l}$, where it is

$$w(\bar{n}, \bar{l}) = Z - \sum_{(n,l)<(\bar{n},\bar{l})} 2(2l+1)$$

a number between 1 and $2(2l+1)$.

We take then this charge density as a new charge guess for the algorithm of finding lower bounds for $E(Z)$. This gives rise to a recursive procedure, that maybe converges to some special value, but I don't know this.

This procedure was carried out with one iteration (it was checked numerically that more iterations will not help much).

Another possible way of optimizing these parameters α is to compute $\nabla_\alpha E(\alpha; Z)$, which, by first order perturbation theory is

$$\int \sum_{i=1}^{Z} \nabla_\alpha V_\alpha(x_i) |\Psi(x_1, \ldots, x_Z)|^2 \, dx_1 \cdots dx_Z$$

for Ψ as in (6.9), which arguing as before is equal to

$$\sum_{n,l} w(n,l) \int \nabla_\alpha V_\alpha(x) f_{n,l}(x) \, dx$$

One possible alternative is then to use the numerical method of steepest descent, which is known not to be very good. It basically amounts to solving the ODE

$$\frac{d\alpha}{dt} = \nabla_\alpha E(\alpha(t); Z)$$

using Euler's method. Since the solution to this ODE will converge to a maximum value as $t \to \infty$, one idea is to solve the ODE using better methods, like Runge-Kutta of high order.

These gradient methods have one clear shortcoming: they are dependent of the choice of coordinates in $\mathbf{R}^n$, and as such they will work well or bad depending mainly on luck.

Another method which works better is to compute the Hessian of $E(\alpha; Z)$, $H_\alpha E$,

which can be approximated roughly by

$$H_\alpha E = \sum_{n,l} \int (H_\alpha V_\alpha(\alpha, x)) \cdot f_{n,l}(x)\, dx$$

and then put

$$\tilde{E}(\alpha) = E(\alpha_0) + \tfrac{1}{2}(\alpha - \alpha_0)^{\mathrm{T}} \cdot H_\alpha E \cdot (\alpha - \alpha_0) \tag{6.24}$$

This is reasonable, because when you are close to the optimum value, $E(\alpha; Z)$ is essentially quadratic in α, and the previous formula is exact for quadratic functions.

The level sets of (6.24) are ellipsoids, and a possible optimization procedure consists in given an initial point α_0, optimize the value of $E(\alpha)$ along the line that passes through the denter of the ellipsoid; precisely

$$\alpha_1 = \alpha_0 - t_0 \left(H_\alpha E\right)^{-1} \cdot \nabla_\alpha E$$

for a cleverly chosen *real number* t.

This method is equivalent to applying the gradient method with respect to the metric in $\mathbf{R}^n$ introduced by the inverse of the Hessian. The previous procedure finds the minimum of quadratic functions after a finite number of steps.

We refer to the reader to [FMM] and [Br] for a discussion of optimization techniques.

This last procedure was actually done, and it improved results a little for small atoms ($1 \leq Z \leq 10$), but it is hard to make it work beyond there due to the fact that the space of acceptable α is not all of $\mathbf{R}^n$: the fact that the R_i are convex imposes some geometric constraint on α, and with growing Z, since $n \sim 15Z$, the geometry becomes very complicated and it is hard to keep this method within the constraints.

The computer programs were written in **C**, and run on a SUN 3/60 workstation. The interval arithmetic package was supplied to me by D. Rana, and is the one he used in [Ra]. The program was divided into parts with a more general scope in mind than this particular problem, and most of them apply to more general situations. Execution time for the heuristics is of about two days for the largest atom, and the rigorous part takes about a couple of weeks. A feature of the program is that most of the memory allocation is done during execution, and disposed of when no longer needed. This is done for two reasons: one, is to allow the degree of the Taylor expansions to be chosen adaptatively, and second, because it requires too much memory otherwise. Freeing memory, the program uses about 3Mb of memory, and without freeing memory it cannot run after a few hours.

The following is a sample of the results obtained for some values of the atomic charge Z; due to obvious time–limitations, the rigorous program was not run for all atoms, but just for some of them. Starred results correspond to rigorous results; all others must be understood as numerical with a good chance of being right.

E_{lb} stands for the lower bounds obtained by the previous method; E_{ub} stands for known numerical —non–rigorous— upper bounds to the energy using Hartree-Fock methods (see [FF]).

Z	E_{lb}	E_{ub}	error (%)
3	-8.33^*	-7.43	11.30
4	-16.06^*	-14.57	9.72
5	-26.76^*	-24.53	8.68
6	-40.86^*	-37.68	8.06
7	-58.73^*	-54.40	7.64
8	-80.75^*	-74.81	7.62
9	-107.33^*	-99.40	7.66

Z	E_{lb}	E_{ub}	error (%)
10	-138.90^*	-128.54	7.73
11	-173.58^*	-161.85	6.98
12	-212.92^*	-199.61	6.44
13	-256.90^*	-241.87	6.02
14	-305.86^*	-288.85	5.71
15	-359.78^*	-340.70	5.44
16	-418.90^*	-397.50	5.23
17	-483.60^*	-459.50	5.10
18	-553.62^*	-526.81	4.96
19	-628.22^*	-599.16	4.73
20	-707.65^*	-676.75	4.47
21	-793.57^*	-759.73	4.35
22	-885.37^*	-848.40	4.24
23	-982.98^*	-942.88	4.15
24	$-1{,}086.21$	$-1{,}043.30$	4.03
25	$-1{,}196.55$	$-1{,}149.86$	3.98
26	$-1{,}313.57$	$-1{,}262.44$	3.97
27	$-1{,}436.21$	$-1{,}381.41$	3.89
28	$-1{,}565.08$	$-1{,}506.87$	3.79
29	$-1{,}702.10$	$-1{,}638.95$	3.78
30	$-1{,}854.83^*$	$-1{,}777.84$	4.17
31	$-2{,}002.95^*$	$-1{,}923.26$	4.02
32	$-2{,}156.22^*$	$-2{,}075.36$	3.81
33	$-2{,}318.33^*$	$-2{,}234.24$	3.69
34	$-2{,}487.53^*$	$-2{,}399.86$	3.58
35	$-2{,}665.08^*$	$-2{,}572.44$	3.53
36	$-2{,}848.65^*$	$-2{,}752.05$	3.45
37	$-3{,}037.25^*$	$-2{,}938.35$	3.30
38	$-3{,}237.45^*$	$-3{,}131.54$	3.32
39	$-3{,}443.75$	$-3{,}331.68$	3.30
40	$-3{,}652.33^*$	$-3{,}538.99$	3.15
41	$-3{,}875.68$	$-3{,}753.55$	3.20
42	$-4{,}102.74$	$-3{,}975.44$	3.15
43	$-4{,}337.42$	$-4{,}204.78$	3.10
44	$-4{,}579.82$	$-4{,}441.87$	3.06
45	$-4{,}482.20^*$	$-4{,}685.80$	2.86

Z	E_{lb}	E_{ub}	error (%)
46	−5,079.65*	−4,937.78	2.82
47	−5,345.25*	−5,197.52	2.80
48	−5,618.94	−5,465.11	2.77
49	−5,897.28	−5,740.16	2.69
50	−6,185.38*	−6,022.93	2.66
51	−6,480.44	−6,313.48	2.61
52	−6,835.21	−6,661.78	2.57
53	−7,095.25	−6,917.98	2.53
54	−7,414.48	−7,232.13	2.49
55	−7,742.07	−7,553.93	2.45
56	−8,072.62	−7,883.54	2.37
57	−8,419.08	−8,221.06	2.37
58	−8,773.26	−8,566.91	2.37
59	−9,136.60	−8,921.18	2.37
60	−9,509.28*	−9,283.88	2.38
61	−9,882.34	−9,655.09	2.32
62	−10,270.32	−10,034.95	2.31
63	−10,667.60	−10,423.54	2.31
64	−11,075.70	−10,820.61	2.33
65	−11,492.38	−11,226.57	2.33
66	−11,918.28	−11,641.45	2.34
67	−12,358.37	−12,065.29	2.39
68	−12,804.31	−12,498.15	2.41
69	−13,261.14	−12,940.17	2.44
70	−13,719.54	−13,391.45	2.45
71	−14,193.98	−13,851.81	2.43
72	−14,666.20	−14,321.25	2.38
73	−15,153.26	−14,799.81	2.35
74	−15,644.81	−15,287.54	2.30
75	−16,142.51	−15,784.53	2.24
76	−16,654.23	−16,290.65	2.20
77	−17,178.24	−16,806.11	2.18
78	−17,705.83	−17,330.94	2.13
79	−18,249.85	−17,865.21	2.12

Z	E_{lb}	E_{ub}	error (%)
80	−18,812.97	−18,408.99	2.11
81	−19,356.51	−18,961.83	2.05
82	−19,928.40	−19,524.01	2.04
83	−20,507.70	−20,095.58	2.02
84	−21,093.76	−20,676.50	1.99
85	−21,692.17	−21,266.88	1.98
86	−22,292.92	−21,866.77	1.92

Chapter 7: The Fuzz

The purpose of this Chapter is to understand, as explained at the end of Chapter 2, why the error E in inequality (2.2) or (2.5), although it may be zero at some points (or a whole manifold of non–zero codimension), when integrated against the ground state or any other function of bounded kinetic energy, is in fact strictly positive and of the right order of magnitude; this is theorem 7.1.

In section 7.6 we will translate the ideas used in proving this lower bound into a practical algorithm that can be used to improve the results obtained with inequalities of type (2.2).

The technique we am going to use will replace the points x_i by small charge clouds: in other words, you take a function ϕ with integral 1 living in a small neighborhood of the origin in R^3, namely a ball of radius $\eta = cZ^{-2/3}$, with c a very small constant, and form the product

$$\Phi(y_1, ..., y_Z) = \phi(y_1) \cdot ... \cdot \phi(y_Z)$$

Then we will show that $E * \Phi$ is strictly positive pointwise, and of the order of $Z^{5/3}$, and the error $E - E * \Phi$, as quadratic forms, will be bounded by some close relative of the laplacian, which in the ground state has an expected value of the order of $cZ^{5/3}$, with c small enough so $\langle E\psi, \psi \rangle$ is positive.

7.1 The Set-up

Let $\rho(x)$ be a radially symmetric decreasing function in $\mathbf{R}^3$, that behaves like the Thomas-Fermi density for an atom of charge Z, in the sense that

$$\rho(x) = Z^2 \rho_0 \left(Z^{1/3} x \right) \tag{7.3}$$

for $\rho_0(x)$ a fixed function of total integral one, smooth outside the origin, and such that $|x|\rho(x)$ is analytic in $|x|$ around the origin, and non–zero at 0.

Define $Z-1$ functions $R_1(x), ..., R_{Z-1}(x)$ as in (3.1), with their inverse functions $M_i(R)$ defined by the formula:

$$\int_{B(z,R)} \rho(x)dx = i \quad \text{if} \quad |z| = M_i(R)$$

Then, for each ball $B(z,R)$, take $\bar{N}$ equal to $i + \frac{1}{2}$ if $R_i(z) < R < R_{i+1}(z)$, or equivalently, if $M_{i+1}(R) < |z| < M_i(R)$. For convenience, we agree that $M_0(R) = \infty$ and $M_Z(R) = 0$ for all R. Also, put

$$S_i = \{z \ : \ M_i(R) \leq |z| < M_{i-1}(R)\} \tag{7.2}$$

Now, we consider the function in $\mathbf{R}^{3Z}$ defined by

$$E(x_1, ..., x_Z) = \frac{1}{2\pi} \int_{R>0} \int_{z \in \mathbf{R}^3} \left((N - \bar{N})^2 - \tfrac{1}{4} \right) \frac{dz \ dR}{R^5} \tag{7.3}$$

where N is the number of x_i that fall inside $B(z,R)$. In Chapter 3 we used the estimate $E \geq 0$ and we simply threw it away. What we want to prove here is the following Sobolev–type inequality.

Theorem 7.1:
Let ψ be a function satisfying

$$\|\nabla\psi\|_2 \leq C_{KE} Z^{7/3}.$$

for some constant C_{KE}. Then, there exists a constant C_E such that

$$\langle E\psi, \psi\rangle \geq C_E Z^{5/3}$$

And this theorem has as a consequence the result stated in the introduction

Corollary: *Let*

$$\tilde{E}(Z) = \inf_{\substack{\psi\in\mathcal{H} \\ \|\psi\|_2=1}} \langle H_{LB}\psi, \psi\rangle$$

Then

$$E(Z) \geq \tilde{E}(Z) + C_E Z^{5/3}$$

Proof: Let ψ_Z be a normalized ground state for H_Z. By the virial theorem, we know that

$$\langle -\Delta\psi_Z, \psi_Z\rangle = -E(Z)$$

where $-\Delta$ means the laplacian in $\mathbf{R}^{3Z}$.
From TF theory, we know (see [Li] or [LS]) that

$$E(Z) = C_{TF} Z^{7/3} + o\left(Z^{7/3}\right)$$

which implies that ψ_Z satisfies the hypotheses of Theorem 7.1; therefore,

$$\begin{aligned} E(Z) &= \langle H_Z\psi_Z, \psi_Z\rangle \\ &= \langle H_{LB}\psi_Z, \psi_Z\rangle + \langle E\psi_Z, \psi_Z\rangle \\ &\geq \tilde{E}(Z) + C_E Z^{5/3} \end{aligned}$$

In order to prove Theorem 7.1, first note that

$$E = \frac{1}{2\pi} \int_{R>0} V(R) \, \frac{dR}{R^5}$$

where $V(R)$ (that has nothing to do with the potential V of Chapter 3) is defined as

$$V(R) = \int_{z \in \mathbf{R}^3} \left((N - \bar{N})^2 - \tfrac{1}{4} \right) \, dz$$

and has the following geometrical interpretation:

define

$$\left.\begin{aligned} \Omega^k(R) &= \{z : N(x_1, \ldots, x_Z; z, R) = k\} \\ \Omega_i(R) &= \{z : N(x_1, \ldots, x_Z; z, R) \neq i, i-1\} \\ &= \bigcup_{k \neq i, i-1} \Omega^k \\ \Omega(R) &= \bigcup_{i=1}^{Z} (\Omega_i(R) \cap S_i(R)) \end{aligned}\right\} \tag{7.4}$$

Note that

$$(N - i + \tfrac{1}{2})^2 - \tfrac{1}{4} = 0 \quad \text{for} \quad z \in \Omega_i(R) \tag{7.5}$$

Therefore,

$$E = \frac{1}{2\pi} \int V(R) \, \frac{dR}{R^5}$$

with

$$\begin{aligned} V(R) &= \sum_{i=1}^{Z} \int_{S_i(R)} \left((N - i + \tfrac{1}{2})^2 - \tfrac{1}{4} \right) \, dz \\ &= \sum_{i=1}^{Z} \sum_{k=1}^{Z} \int_{S_i(R) \cap \Omega^k(R)} \left((k - i + \tfrac{1}{2})^2 - \tfrac{1}{4} \right) \, dz \\ &= \sum_{i=1}^{Z} \sum_{k=1}^{Z} \text{ Vol } \left(S_i(R) \cap \Omega^k(R) \right) \cdot \left((k-i)^2 + (k-i) \right) \end{aligned} \tag{7.6}$$

It will also be of importance to consider the simpler version of $V(R)$ and E, defined as

$$\tilde{V}(R) = \sum_{i=1}^{Z} \text{ Vol } (S_i(R) \cap \Omega_i(R)) = \text{ Vol } \Omega$$
$$\tilde{E} = \frac{1}{2\pi} \int \tilde{V}(R) \, \frac{dR}{R^5}$$

It is clear by (7.4) and (7.6) that

$$V(R) \geq \tilde{V}(R)$$
$$E \geq \tilde{E}$$

A moment's thought reveals that $V(R)$ is strictly positive, independently of the set of points x_i, due to the geometry of balls in $\mathbf{R}^3$ (although the corresponding function may be zero in $\mathbf{R}^2$!); to study this is the purpose of Chapter 8. Here, we will use a different approach that works even if E attains the value 0 on a thin set. As a result, the inequality is sharper than the one you can obtain by pointwise estimates.

7.2 Notation

Let $H(x, y, R)$ denote the volume of the intersection of the ball with center x and radius R, and the ball of center y and same radius. Recall that

$$H(x,y,R) = \begin{cases} \frac{4\pi}{3}R^3 - \pi|x-y|R^2 + \frac{\pi}{12}|x-y|^3 & \text{if } R \geq \frac{|x-y|}{2} \\ \\ 0 & \text{if } R < \frac{|x-y|}{2} \end{cases}$$

Given points $x_1, ..., x_Z$, define

$$\delta(x_i) = \min_{i \neq j} |x_i - x_j|$$

and call $x_{\delta(i)}$ to one of its closest neighbors.
Also,

$$R_Z = R_{\frac{3}{4}Z}(0)$$

the radius of a ball that we expect contains a fixed percentage of all the electrons, and

$$R_0 = R_1(x) \qquad \text{for} \qquad |x| = R_Z$$

Note by (7.3) that $R_{\frac{5}{8}Z}(0) \sim CZ^{-1/3}$ and $R_Z \sim C_Z Z^{-1/3}$.
The following Lemma shows that $R_0 \geq cZ^{-2/3}$.

Lemma 7.2: *If $|x| \geq cZ^{-1/3}$ then*

$$R_1(x) = C\left(Z^{5/3}|x|\right)^{1/3} \cdot (1 + o(()\, Z))$$

and in particular

$$R_1(x) \geq C_0 Z^{-2/3}$$

Proof: Let

$$\rho_0(x) = \frac{\tilde{\rho}(x)}{|x|}$$

with $\tilde{\rho}(x)$ analytic. Assume that $R_1(x) \leq |x|$ otherwise there is nothing to prove. Then, by definition of R_1 we have

$$\begin{aligned} 1 &= Z^2 \int_{B(x, R_1(x))} \rho_0\left(Z^{-1/3}x\right)\, dx \\ &= Z \int_{B(Z^{1/3}x, Z^{1/3}R_1(x))} |z|^{-1} \tilde{\rho}(z)\, dz \\ &= Z\pi \int_{Z^{1/3}(x - R_1(x))}^{Z^{1/3}(x + R_1(x))} \tilde{\rho}(y) \cdot \frac{Z^{2/3}R_1(x)^2 - (y - Z^{1/3}x)^2}{Z^{1/3}|x|}\, dy \end{aligned}$$

$$= Z\pi \int_{Z^{1/3}(x-R_1(x))}^{Z^{1/3}(x+R_1(x))} (\tilde{\rho}(0) + O(y)) \cdot \frac{Z^{2/3} R_1(x)^2 - (y - Z^{1/3}x)^2}{Z^{1/3}|x|}\, dy$$
$$= \tfrac{5}{3} Z^{5/3} \pi \tilde{\rho}(0) \frac{R_1^3(x)}{|x|} \cdot \left(1 + O\left(Z^{-1/3}\right)\right)$$

Thus

$$R_1(x) \leq C \left(Z^{-5/3} \cdot |x|\right)^{1/3}$$

and the result follows. Q.E.D.

7.3 Pointwise Estimates

The aim of this section is to prove that if electrons are not arranged as you expect, then E is big pointwise. Roughly, electrons are expected to be at a distance $Z^{-2/3}$ of the closest neighbor and most of them are within $Z^{-1/3}$ of the nucleus. This is what Thomas-Fermi theory predicts. This implies that we only have to analyze the smeared out potential over a very precise configuration: elsewhere its big pointwise.

Lemma 7.3: *If for some i, $\delta(x_i) < \frac{R_1(0)}{10}$, then:*

$$E > \frac{C}{R_1(0)}$$

Moreover, if there are k such points, then

$$E > \frac{C}{\delta(x_i)} k$$

Proof:

Observe that when $R < R_1(0)$, since $M_i(R) = 0$ for all R, $S_1(R) = \mathbf{R}^3$ and thus

$$\begin{aligned} V(R) &= \sum_{i=1}^{Z} \text{ Vol } \left(\Omega_1^k(R)\right) \left(k^2 - k\right) \\ &= \frac{1}{2} \sum_{i \neq j} \text{ Vol } \left(B(x_i, R) \cap B(x_j, R)\right) \\ &\geq \frac{1}{2} \sum_{i=1}^{Z} H(x_i, x_{\delta(i)}, R) \end{aligned}$$

Let x and y be one such pair of closest neighbors. Note that $H(x, y, R)$ increases with R; in particular for $R > \frac{2}{3}|x - y|$,

$$H(x, y, R) \geq H\left(x, y, \frac{2}{3}|x - y|\right) = \frac{11\pi}{324}|x - y|^3$$

therefore,

$$\begin{aligned} E &\geq \frac{11}{648} \sum_{\substack{i=1 \\ \delta(x_i) < \frac{R_1(0)}{10}}}^{Z} |x_i - x_{\delta(i)}|^3 \int_{\frac{2}{3}|x_i - x_{\delta(i)}|}^{R_1(0)} \frac{dR}{R^5} \\ &= \frac{11}{2592} \sum_{\substack{i=1 \\ \delta(x_i) < \frac{R_1(0)}{10}}}^{Z} \left(\frac{81}{16|x_i - x_{\delta(i)}|} - \frac{|x_i - x_{\delta(i)}|^3}{R_1(0)^4} \right) \\ &\geq \frac{11}{1296} \sum_{\delta(x_i) \leq \frac{R_1(0)}{10}} \left(\frac{810}{16\delta(x_i)} - \frac{10^{-3}}{R_1(0)} \right) \\ &\geq C \sum_{\delta(x_i) \leq \frac{R_1(0)}{10}} \delta(x_i)^{-1} \end{aligned}$$

Q.E.D.

Lemma 7.4: *If for some x_i, $\delta(x_i) \leq \frac{R_1(x_i)}{10}$, then*

$$E \geq \frac{C}{R_1(x_i)}$$

and in general

$$E \geq \sum_{\delta(x_i) \leq \frac{R_1(x_i)}{10}} \frac{C}{R_1(x_i)}$$

Proof: Let $R_1(x)/2 \leq R \leq R_1(x)$.
Note that $z \in B(x,R) \cap B(y,R)$ implies $x, y \in B(z,R)$.
Note also that

$$B\left(x, \frac{R}{10}\right) \subset B(x,R) \cap B(y,R)$$

since for $z \in B(x, \frac{R}{10})$,

$$|z-y| \leq |z-x| + |x-y| \leq \frac{3R}{10}$$

Thus, for all $z \in B(x, \frac{R}{10})$, $x, y \in B(z,R)$.
If $|z| \geq |x|$, we have $R_1(z) \geq R_1(x)$, since R_1 is increasing. Thus, since $R \leq R_1(x)$ we have

$$\bar{N}(z, R; x_1, \ldots, x_Z) = \tfrac{1}{2}$$

and since $N(z,R) \geq 2$

$$\begin{aligned} E &\geq \frac{1}{\pi} \int_{\substack{B(x, \frac{R}{10}) \\ |z| \geq |x|}} \int_{\frac{R_1(x)}{2}}^{R_1(x)} \frac{dz\, dR}{R^5} \\ &\geq \frac{C}{R_1(x)} \end{aligned}$$

If there are N disjoint pairs of closest neighbors, $(x_i, x_{\delta(i)})$, with $\delta(x_i) \leq \frac{R_1(x_i)}{10}$, then $N(z,R) \geq 2$ for

$$z \in B\left(x_i, \frac{R_1(x_i)}{10}\right) \quad (|z| \geq |x_i|) \qquad \text{and} \qquad \frac{R_1(x)}{2} \leq R \leq R_1(x_i)$$

for some i, and since

$$(N-\tfrac{1}{2})^2-\tfrac{1}{4}\geq N\cdot\chi_{N\geq 2}$$

we have that

$$\begin{aligned}E&\geq\frac{1}{\pi}\sum_i\int_{\substack{B(x_i,\frac{R}{10})\\|z|\geq|x_i|}}\int_{\frac{R_1(x_i)}{2}}^{R_1(x_i)}\frac{dz\,dR}{R^5}\\&\geq\sum_i\frac{C}{R_1(x_i)}\end{aligned}$$

Q.E.D.

Lemma 7.5: *Consider $x_1,...,x_Z$ ordered in such a way that $|x_1|\leq\cdots\leq|x_Z|$. For each x_i, $(1\leq i\leq Z-1)$, let's call R_{x_i} the solution of the equation*

$$|x_i|=R+M_i(R) \tag{7.7}$$

If, for some $i\leq Z-1$

$$R_{x_i}>10R_i(0)$$

then

$$E>\frac{C}{R_i(0)}.$$

Observe that this allows one of the x_i to go off to ∞.

Proof: For all $R<R_{x_i}$ we have that $B(x_j,R)$ does not intersect $B(0,M_i(R))$ for $j\geq i$. Thus, all points in $S_{i+1}(R),\cdots,S_Z(R)$ belong to at most $i-1$ of the B_k, that is, one less B_k than they should, and so

$$V(R)\geq\left|\cup_{j=i+1}^{Z}S_j(R)\right|=|B(0,M_i(R)|$$

From Lemma 3.2b we know that $M_i(R) > R - R_i(0)$ for $R \geq R_i(0)$; therefore, we have:

$$\begin{aligned}
E &\geq \int_{R_i(0)}^{R_{x_i}} V(R)\frac{dR}{R^5} \\
&\geq C\int_{R_i(0)}^{R_{x_i}} (M_i(R))^3\frac{dR}{R^5} \\
&\geq C\int_{2R_i(0)}^{R_{x_i}} (R - R_i(0))^3\frac{dR}{R^5} \\
&\geq CR_i(0)^3\int_{2R_i(0)}^{R_{x_i}} \frac{dR}{R^5} \\
&\geq CR_i(0)^3\left(\frac{1}{16R_i(0)^4} - \frac{1}{R_{x_i}^4}\right) \\
&\geq C\left(\frac{1}{16R_i(0)} - \frac{10^{-4}}{R_i(0)}\right) \\
&\geq \frac{C}{R_i(0)}
\end{aligned}$$

The previous lemma seems to indicate that it is hard to pull out an innermost electron, but not so hard to pull out an outer electron.

The way to measure how far x_i is by solving the equation $|x_i| = R + M_i(R)$; this may seem a little cavalier; note that if $i > Z/2$, then $M_i(R) < R$ and so $R_{x_i} > 10R_i(0)$ if $|x_i| > 20R_i(0)$, and thus this strange condition can be replaced by simply $|x| > 20R_i(0)$.

As before, the lemma can be applied to the case in which different x_i that are too far out, and add up the conclusions. But in this case much more is true, taking in to account the multiplicity in the error.

Lemma 7.6: *As before, let's have $|x_i|$ arranged in increasing order. Assume that for some $n < Z - 1$, and for some $p > 0$,*

$$|R_{x_{n-p}}| > 10\, R_n(0)$$

Then,

$$E > C\frac{(p+1)^2}{R_n(0)}$$

Proof: For each i between $n-p$ and n, every point in $B(0, M_i(R))$ belongs to $p+1$ less of the B_k than it should. The rest is like the previous lemma.

Lemma 7.7:

a. *Consider $B(0, 20R_Z)$ If $\frac{1}{4}Z + k$ points are outside of this ball, then*

$$E > C\frac{(k-1)^2}{R_Z}$$

b. *If $B(0, \frac{1}{10}R_{\frac{5Z}{8}}(0)$ contains $(\frac{5}{8} + \epsilon)Z$ electrons then*

$$E \geq \frac{C\epsilon Z}{R_{\frac{5Z}{8}}(0)}$$

The proof is again straightforward.

This last lemma in particular implies that if cZ points leave a ball of radius $Z^{1/3}$, with $c > \frac{1}{4}$, then E will be of the order of $Z^{5/3}$.

Lemmas 7.3 and 7.4 told us that electrons cannot have very close neighbors. Let us now prove that most of them cannot have very distant neighbors either.

Set

$$\tilde{\delta}(x_i) = \delta(x_i) Z^{2/3}$$

We would like $\tilde{\delta}(x_i)$ to be bounded from above and below for all x_i unless E gets very big. That it is bounded below, we saw already; that it is bounded above is only true for most of the electrons. The following lemma states it precisely.

Lemma 7.8: *Assume that there are $N \geq 2$ electrons in $B(0, 20R_Z)$. Then,*

$$\frac{1}{N} \sum_{i=1}^{N} \tilde{\delta}(x_i)^3 \leq C' Z \cdot N^{-1}$$

Proof: Let $B_i = B(x_i, \frac{\delta(x_i)}{2})$. These balls do not intersect. Since $N \geq 2$, we know that $\delta(x_i) \leq 10 R_Z$, therefore

$$\bigcup_{i=1}^{N} B(x_i, \frac{\delta(x_i)}{2}) \subset B(0, 25 R_Z)$$

what implies that

$$\sum_{i=1}^{N} \left| B\left(x_i, \frac{\delta(x_i)}{2}\right) \right| \leq C' R_Z^3$$

or, since $R_Z \sim C_Z Z^{-1/3}$,

$$\sum_{i=1}^{N} \left(\frac{\tilde{\delta}(x_i)}{Z^{2/3}} \right) \leq C' Z^{-1}$$

Now, divide by N and we are done. Q.E.D.

Lemma 7.9: *At least 1% the points x_i will satisfy*

$$\left.\begin{aligned} C_1 \le \tilde{\delta}(x_i) \le C_2 \\ |x_i| < C_2 Z^{-1/3} \end{aligned}\right\}$$

or else

$$E(x_1, \ldots, x_Z) \ge C_{7.9}\, Z^{5/3}$$

Proof: By Lemma 7.7, we can assume that there are $\frac{2}{3}Z$ electrons inside $B(0, 20R_Z)$ and $B(0, \frac{1}{10}R_{\frac{5Z}{8}}(0))$ contains less than $(\frac{5}{8} + \frac{1}{48})Z$ electrons; so, we can assume that at least $\left(\frac{2}{3} - (\frac{5}{8} + \frac{1}{48})\right) Z = \frac{1}{48}Z$ electrons are in $B(0, 20R_Z) - B(0, \frac{1}{10}R_{\frac{5Z}{8}}(0))$; therefore, there are at least $\frac{Z}{48}$ electrons satisfying

$$CZ^{-1/3} \le |x| \le C'Z^{-2/3}$$

Lemma 7.2 implies that $R_i(x_i) \sim Z^{-2/3}$ for these electrons.

If 10% of these $\frac{Z}{48}$ electrons have closest neighbors at a distance less than $\frac{R_1(x_i)}{10}$, Lemma 7.4 says that $E \ge cZ^{5/3}$.

Therefore, there are at least $\frac{3}{160}Z$ electrons inside $B(0, 20R_Z)$ with $\tilde{\delta}(x_i) \ge C_1$ for a constant C_1.

Assume that 1% of these satisfy $\tilde{\delta}(x_i) \ge C_2$, for C_2 to be picked in a moment; then

$$\begin{aligned} \frac{3}{2Z} \sum \tilde{\delta}(x_i)^3 &\ge \frac{3}{2Z} \sum_{\tilde{\delta}(x_i) \ge C_2} \tilde{\delta}(x_i)^3 \\ &\ge \frac{54}{6000} C_2^3 \end{aligned}$$

which contradicts Lemma 7.8 for C_2 large enough. Therefore, at least $\frac{297}{16000}Z$ electrons satisfy the conclusion of the lemma.

7.4 Fuzzed Estimates

In this section we will develop the theory that unless E is big pointwise by the previous section, when you average E over a small ball of radius like $Z^{-2/3}$, you get something strictly positive.

For this section we will not need the multiplicity in the definition of $V(R)$, and therefore it will be easier to work with $\tilde{V}$. Recall that $\tilde{V}(R)$ represents the volume of some set Ω. Consider now a ball of any center z and radius

$$R_* = 10C_2 Z^{-2/3} \tag{7.8}$$

and define

$$V_z(R) = \text{ volume of } (\Omega \cap B(z, R_*))$$

and

$$E_z = \frac{1}{2\pi} \int_{R>0} V_z(R) \frac{dR}{R^5}$$

Clearly

$$\tilde{E} = \frac{C}{(R_*)^3} \int_{\mathbf{R}^3} E_z \, dz$$

This is convenient because, by the pointwise estimates, unless E is very big, V_z depends only on a fixed finite number of variables.
One more modification. Define

$$V_z^*(R) = \min\left(V_z(R), C_3\eta^2 \cdot R_*\right)$$

$$E_z^* = \begin{cases} \dfrac{1}{2\pi} \displaystyle\int_{10^{-6}R_0}^{10^6 R_*} V_z^*(R) \, \frac{dR}{R^5} & \text{if } \delta(x_i) > \frac{R_0}{100} \text{ all } i \\ \\ C'' Z^2 \eta^2 & \text{otherwise} \end{cases}$$

for C_3 to be picked later.

Clearly,

$$E \geq \frac{C}{R_*^3} \int_{\mathbf{R}^3} E_z^* \, dz$$

This is more convenient because the supremum of E_z^* will be comparable with its minimum smeared out value independently of η, and this will allow us to use Sobolev estimates.

The purpose of this section is to prove that averaging $E_z^*(x_1, \ldots, x_Z)$ over two of the electrons taking values over a ball, you get something which is bounded below by $Z^{2/3}$. We will however need this result when we average only over a certain certain cone of directions, because we will like to apply this result to E_z^* restricted to a subset of $\mathbf{R}^{3Z}$, which has nice geometric features but, averaging over balls, would cause E_z^* to take values outside of this set: this would be bad because it would cause an overlapping which would be unbounded as $Z \to \infty$.

Definition: *We say that a set $U \times V \subset \mathbf{R}^6$ has property P_η, if given any two points $x \in U$ and $y \in V$, there exist cones Γ_x^η and Γ_y^η contained in U and V respectively, centered at x and y, with solid angle at least some fixed constant, height η .*

Note that, given any $(u, v) \in U \times V$

$$\left| \{(x, y) \ : \ (u, v) \in \Gamma_{x,y}^\eta\} \right| \leq C\eta^6$$

Lemma 7.10: *Given x and y belonging to a set U that satisfies P_η, with $x, y \in B(z, \frac{1}{10} R_*)$, we have*

$$\frac{1}{|\Gamma_{x,y}^\eta|} \int_{\Gamma_{x,y}^\eta} E_z^*(x', y', x_3, ..., x_n) \, dx' \, dy' \geq C_{7.10} \eta^2 Z^2$$

for η sufficiently small, where the cones are like in the definition of P_η.

Proof: We can assume that $|x-y| > \frac{R_0}{1000}$, for otherwise $|x'-y'| < \frac{R_0}{100}$ for all $(x',y') \in \Gamma^{\eta}_{x,y}$ and so we have directly

$$E^*_z(x',y',x_3,\cdots,x_Z) \geq CZ^2\eta^2$$

Although, as remarked before, it is impossible, let's start assuming that $V_z = 0$. This means that all points inside $B(z,R_*)$ belong to the correct number of B_k. If this is so, consider real numbers r and s, smaller than $\frac{1}{2}$. Then,

$$V_z(x+r(y-x),y+s(x-y),x_3,...,x_n;R) \geq \tfrac{1}{4}rs|x-y|^3$$

or equivalently,

$$V_z(x+u,y+v,x_3,...,x_n;R) \geq \tfrac{1}{4}|u|\cdot|v|\cdot|x-y|$$

for u and v vectors in the direction between x and y with norm less than $|x-y|/2$. This is so because, when you move x and y closer, all those points in the new intersection that were not in the old union

$$W(x,y,r,s,R) = B(x+r(y-x),R) \cap B(y+s(x-y),R) \\ -B(x,R) \cup B(y,R)$$

increased their quota of B_k by two!. Therefore, we count the volume of all those points, and say that $V_z(R)$ is bigger than that. Now, this volume is exactly

$$\begin{aligned} |W(x,y,r,s,R)| &= H(x+r(y-x),y+s(x-y),R) - H(x+r(y-x),y,R) \\ &\quad - H(x,y+s(x-y),R) + H(x,y,R) \\ &= \tfrac{1}{12}\left((1-r-s)^3+1-(1-r)^3-(1-s)^3\right)|x-y|^3 \\ &= \tfrac{1}{4}sr|x-y|^3 \end{aligned}$$

because $|u|, |v| < \frac{1}{2}$.

Note that if you just fuzz one the electrons, then you don't gain anything; the quota is modified only by one, and since points are allowed to belong to two

different number of balls, they could just be shifting from one to the other. In other words, it seems that there is very little one–electron information in E, and you have to use essentially two–electron analysis.

If, instead, we translate x and y by arbitrary vectors, u and v, with

$$|u| < \tfrac{1}{2}|x-y| \qquad \text{and} \qquad |v| < \tfrac{1}{2}|x-y| \qquad \text{(cond. 1)}$$

almost the same thing as before is still true. We can see it as follows:
Consider a coordinate system centered at x, with basis vectors e_1, e_2, e_3 orthogonal to each other and $e_1 = \frac{y-x}{|x-y|}$. Consider only those vectors u, v with coordinates:

$$(r,+,+), (-s,+,+) \qquad r,s \geq 0 \tag{7.9}$$

then, we claim that all those points

$$w = (w_1, w_2, w_3) \in W(x,y,r,s,R), \text{ with } w_2, w_3 \geq 0 \tag{7.10}$$

are also in

$$W(x,y,u,v,R) = B(x+u,R) \cup H(y+v,R) - B(x,R) \cap B(y,R)$$

For that we only have to check that

$$w \in B(x+u,R) \cap B(y+v,R)$$

since it already is not in their intersection. This will follow if

$$|w-(x+u)| \leq |w-(x+re_1)|$$

and

$$|w-(y+v)| \leq |w-(y-se_1)|$$

In order to see this, we will write

$$u = (r, u_2, u_3), \text{ with } u_2, u_3 \geq 0$$

$$v = (-s, v_2, v_3), \text{ with } v_2, v_3 \geq 0$$

So, the condition to be checked amounts to

$$|(w_1 - r, w_2 - u_2, w_3 - u_3)| \leq |(w_1 - r, w_2, w_3)|$$

and

$$|(w_1 - |x-y| + s, w_2 - u_2, w_3 - u_3)| \leq |(w_1 - |x-y| + s, w_2, w_3)|$$

which are trivial, since by (7.10), w_2, $w_3 \geq 0$.

The volume of points represented by (7.10) is exactly $\frac{|W(x,y,r,s,R)|}{4}$; this implies

$$|W(x,y,u,v,R)| \geq \tfrac{1}{16} rs|x-y| \qquad \text{for} \quad (u,v) \in \Gamma^{\eta}_{x,y}$$

and so, we have for this subset of directions u and v

$$\text{Vol } (\Omega(x+u, y+v, x_3, \cdots, x_Z; R)) \geq \tfrac{1}{16} rs|x-y|$$

where r and s are the projection of u and v in the direction $x - y$.

Assuming

$$B(x, R+\eta) \cup B(y, R+\eta) \subset B(z, R_*) \qquad \text{(cond. 2)}$$

all these points whose volume we are estimating are inside $B(z,R)$, and thus

$$V_z(x+u, y+v, x_3, ..., x_Z; R) \geq \tfrac{1}{16} rs|x-y|$$

and if $C_3 \geq \frac{1}{16}$, this proves

$$V^*_z(x+u, y+v, x_3, ..., x_Z; R) \geq \tfrac{1}{16} rs|x-y|$$

Now, if the cones $\Gamma^{\eta}_{x,y}$ are contained in this set of directions (7.9), we have

$$\begin{aligned} \frac{1}{|\Gamma^{\eta}_{x,y}|} \int_{\Gamma^{\eta}_{x,y}} V^*_z(x', y', x_3, ..., x_n; R)\, dx'\, dy' &\geq C|x-y|\eta^{-6} \int_{u \in \Gamma^{\eta}_x} \int_{v \in \Gamma^{\eta}_y} rs\, du\, dv \\ &\geq C\eta^2 |x-y| \end{aligned}$$

Otherwise, pick $(x_0, y_0) \in \Gamma^\eta_{x,y}$ such that

$$B(x_0, c\eta) \subset \Gamma^\eta_x \qquad \text{and} \qquad B(y_0, c\eta) \subset \Gamma^\eta_y$$

where c is a constant that depends only on the aperture of the cones; since x_0 and y_0 then have cones in every possible direction and aperture contained in our set U, we can apply the previous result to $\Gamma^{c\eta}_{x_0,y_0}$ to obtain

$$\begin{aligned}
\frac{1}{|\Gamma^\eta_{x,y}|}\int_{\Gamma^\eta_{x,y}} V^*_z(x', y', x_3, ..., x_n; R)\, dx'\, dy' \geq \\
&\geq \frac{C'}{|\Gamma^{c\eta}_{x_0,y_0}|}\int_{\Gamma^{c\eta}_{x_0,y_0}} V^*_z(x', y', x_3, ..., x_n; R)\, dx'\, dy' \\
&\geq C''|x-y|\eta^{-6}\int_{u\in\Gamma^{c\eta}_{x_0}}\int_{v\in\Gamma^{c\eta}_{y_0}} rs\, du\, dv \qquad (7.11)\\
&\geq C_4\eta^2|x-y|
\end{aligned}$$

If $V^*_z(R) = \alpha$, for α in the range

$$0 < \alpha < 10^{-6}C_4\eta^2|x-y| \qquad (7.12)$$

note that the previous argument says that when you move x and y by vectors u and v as in (7.9), there are points whose total volume is at least $\frac{1}{16}rs|x-y|$ that change their quota of B_k by two. Thus, making $C_3 > C_4$, (7.12) implies

$$\text{Vol}\,(\Omega(x, y, x_3, \cdots, x_Z)) = \alpha$$

and therefore

$$\text{Vol}\,(\Omega(x+u, y+v, x_3, \cdots, x_Z)) \geq \left(\frac{1}{16}rs|x-y| - \alpha\right)_+$$

what implies, if $C_3 < \frac{1}{16}$, that

$$V^*_z(x+u, y+v, x_3, ..., x_Z; R) \geq \left(\tfrac{1}{16}rs|x-y| - \alpha\right)_+$$

And arguing as before, and using the fact that

$$\mathrm{Av}(f)_+ \geq (\mathrm{Av} f)_+$$

we see by (7.12) and (7.11) that

$$\frac{1}{|\Gamma^\eta_{x,y}|}\int_{\Gamma^\eta_{x,y}} V^*_z(u,v,x_3,\cdots,x_Z;R)\,du\,dv \geq \left(C_4\eta^2|x-y|-\alpha\right)_+ \geq \frac{C_4}{2}\eta^2|x-y|$$

If however $\alpha > 10^{-6}C_4\eta^2|x-y|$, then, if there is a pair of vectors

$$(u_0,v_0)\in\Gamma^{\eta/2}_{x,y}$$

such that

$$V^*_z(u_0,v_0,x_3,\cdots,x_Z;R) < 10^{-6}C_4\eta^2|x-y|$$

apply the previous estimate to any of the cones

$$\Gamma^{\eta/2}_{u_0,v_0}\subset\Gamma^\eta_{x,y}$$

to obtain

$$\begin{aligned}\frac{1}{|\Gamma^\eta_{x,y}|}\int_{(x',y')\in\Gamma^\eta_{x,y}} & V^*_z(x',y',x_3,...,x_n;R)\,dx'\,dy' \geq \\ &\geq \frac{1}{|\Gamma^\eta_{x,y}|}\int_{(x',y')\in\Gamma^{\eta/2}_{u_0,v_0}} V^*_z(x',y',x_3,...,x_n;R)\,dx'\,dy' \\ &\geq \frac{\left|\Gamma^{\eta/2}_{u_0,v_0}\right|}{|\Gamma^\eta_{x,y}|}C_4\frac{\eta}{2}^2|x-y| - 10^{-6}C_4\eta^2|x-y|\end{aligned}$$

which, since

$$\left|\Gamma^{\eta/2}_{u_0,v_0}\right| \geq \frac{1}{10}\left|\Gamma^\eta_{x,y}\right|$$

implies (7.11) also in this case

If no such pair of u_0 and v_0 exist, then

$$V_z^*(x+u, y+v, x_3, \cdots, x_Z; R) \geq 10^{-6} C_4 \eta^2 |x-y| \qquad \text{for} \quad u \in \Gamma_x^{\eta/2},\ v \in \Gamma_y^{\eta/2}$$

which implies directly that (7.11) holds in all cases, probably with a different constant C_4, as long as conditions (cond. 1) and (cond. 2) are satisfied. This will be the case if

$$B(x, R+u) \cup B(y, R+v) \subset B(z, R_*)$$

and

$$10\eta < |x-y| < 2R$$

which holds by hypothesis and whenever $5R_* > R > \frac{|x-y|}{2}$

Integrating (7.11) over this set of $R's$, (note that $\frac{|x-y|}{2} \geq 10^{-6} R_0$) we get:

$$\begin{aligned}
\text{Av } E_z^* &\geq \int_{\frac{|x-y|}{2}}^{\frac{R_*}{5}} \text{Av} V_z(R)\, \frac{dR}{R^5} \\
&\geq C\eta^2 |x-y| \left(\frac{16}{|x-y|^4} - \frac{625}{R_*} \right) \\
&\geq \frac{C\eta^2 |x-y|}{{R_*}^4} \\
&\geq \frac{C\eta^2 R_0}{(R_*)^4}
\end{aligned}$$

Recalling that both R_* and R_0 are bounded above and below by constant multiples of $Z^{-2/3}$, we get the conclusion of the lemma.

η will be like $Z^{-2/3}$; this will make $\text{Av} E_z$ of the order of $Z^{2/3}$. Later, we will be able to superimpose the estimates for E_{z_i} for a number of z_i of the order of Z, what will give that the smeared out error is of the order of $Z^{5/3}$.

Also, note that, by the way E_z^* was defined, it is trivial that

$$\|E_z^*\|_\infty \leq C_\infty Z^2 \eta^2 \tag{7.13}$$

7.4 Real Variables

Recall

$$R_* = 10C_2 Z^{-2/3} \quad \eta = C_\eta Z^{-2/3}$$

We will chose how small C_η has to be according to our needs.

Starting with the cube Q_0 with center the origin and diameter $C_2 Z^{-1/3}$, consider all dyadic subcubes of size to be determined later, Q_ν.
Put

$$\int_{\mathbf{R}^{3Z}} E(x_1, ..., x_Z)|\psi(x_1, ..., x_Z)|^2 dx_1, ..., x_Z =$$

$$= \sum_\nu \int_{Q_{\nu_1} \times ... \times Q\nu_Z} E(x_1, ..., x_Z)|\psi(x_1, ..., x_Z)|^2 dx$$

Let's put $E_{Q_{\nu_1}, ..., Q_{\nu_Z}}$ equal to E restricted to this product of cubes. Given one Q_ν, we call Q_ν^* its only dyadic ancestor with size C_7 times bigger, with

$$C_7 > \max\left(C_1, 10^7\right) \tag{7.14}$$

Lemma 7.11: *Either*

$$\min E_{Q_{\nu_1}, ..., Q_{\nu_Z}} \geq C_{7.9}\, Z^{5/3}$$

or, there exist $c_1 Z$ of these cubes $\{Q_{\nu_i}\}$, that we call $\{\tilde{Q}_\alpha\}$, with c a small constant, such that

1. *$\tilde{Q}_\alpha^* \cap \tilde{Q}_{\alpha'}^* = \emptyset$, for $\alpha \neq \alpha'$.*
2. *Every $\tilde{Q}_\alpha$ has a neighbor among the rest of the Q_ν: call it $Q_{\delta(\alpha)}$.*

   By neighbor we mean that it is either equal to itself or one of the 26 cubes adjacent to it.

Proof: Assume that there are $(x_1, \ldots, x_Z)$ such that $E(x_1, \ldots, x_Z) < C_{7.9}\, Z^{5/3}$. By Lemma 7.9, there are N of these x_i, (call them $\{\tilde{x}_\alpha\}$), with $N > Z/100$, such that

$$\left.\begin{aligned} C_1 Z^{-2/3} \leq \delta(\tilde{x}_\alpha) \leq C_2 Z^{-2/3} \\ |\tilde{x}_\alpha| < C_2 Z^{-1/3} \end{aligned}\right\} \tag{7.15}$$

Assume that no one of the x_i belongs to any of the sides of any dyadic subcube of Q_0. This is OK since E is continuous. Perform then a dyadic subdivision to Q_0 such that

1. If at some point, one subcube contains no $\tilde{x}_\alpha$, we throw it away.

2. If for one subcube Q, we have that Q^* contains less that C_8 of these $\tilde{x}_\alpha$, we store it away.

Note that by (7.15), this is a finite procedure. Call $\{Q^\sharp\}$ the set of cubes we stored. There are at least N/C_8 of these cubes. Note also that $\{Q^{\sharp *}\}$ has a fixed finite overlapping, since

$$\sum \chi_{Q^{\sharp *}} \leq C_8$$

so we can extract a maximal disjoint subfamily that contains at least N/C_8 cubes, and take the corresponding family $\{Q^\sharp\}$.

Note that by property 2 of these cubes, if $2Q^\sharp$ is its dyadic predecessor, $(2Q^\sharp)^*$ contains at least C_8 of the $\tilde{x}_\alpha$'s, so by (7.15),

$$(2C_7)^3 \text{ Vol } \left(Q^\sharp\right) = \text{ Vol } \left(2Q^{\sharp *}\right) \geq \frac{4\pi}{3} C_8 \left(C_1/2\right)^3 Z^{-2}$$

what implies

$$\text{diam } Q^\sharp \geq 10^{-6} \left(C_1/C_7\right) C_8^{1/3} Z^{-2/3}$$

Now we pick the size of the Q_ν to be largest dyadic size smaller than the size in the previous expression. Thus, each $Q^\sharp$ contains one of the initial Q_ν, and statement 1 of the lemma follows by property 1 of the $\{Q^\sharp\}$ and the properties of dyadic subdivisions.

For statement 2, simply realize that by (7.15) again, points $\tilde{x}_\alpha$ have a close neighbor at a distaince $C_1 Z^{-2/3}$. By picking C_8 an integer so that

$$\tfrac{1}{4} C_1 Z^{-2/3} \leq 10^{-6} C_1 C_8^{1/3} Z^{-2/3}/C_7 < C_1 Z^{-2/3} \tag{7.16}$$

(such an integer exists by (7.14)) these selected cubes (or any other containing $\tilde{x}_\alpha$'s) has a neighbor in the collection.

Let's consider now one such product of cubes that satisfies the second alternative in the previous Lemma. Let's select one such pair of neighboring cubes, say Q_{ν_1} and Q_{ν_2}. Make $x = (x_1, x_2)$ and $w = (x_3, ..., x_Z)$, and define

$$Q = Q_{1,2} = Q_{\nu_1} \times Q_{\nu_Z}$$
$$W = W_{1,2} = Q_{\nu_3} \times \cdots \times Q_{\nu_Z}$$

Note that Q satisfies property P_η.

Consider also centers z satisfying

$$|z - c_{\nu_1}| < \frac{C_1 Z^{-2/3}}{10} \tag{7.17}$$

Note that by (7.16)

$$\text{diam } Q \leq 10 C_1 Z^{-2/3}$$

and by (7.8)

$$Q \subset B\left(z, \frac{R_*}{10}\right) \tag{7.18}$$

(We can take $C_2 > 10C_1$ in Lemma 7.9).
Then, argue as follows:

We know already that, by (7.18) and Lemma 7.10,

$$C_{7.10}\, \frac{\eta^2}{{R_*}^3} \int_W \int_S |\psi(x,w)|^2 \, dx\, dw \leq$$
$$\leq \int_W \int_S \frac{1}{|\Gamma_x^\eta|} \int_{\Gamma_x^\eta} E_z^*(x', w)\, |\psi(x,w)|^2 \, dx'\, dx\, dw \tag{7.19}$$

The last term in the previous inequality differs from

$$\int_W \int_S \frac{1}{|\Gamma_x^\eta|} \int_{\Gamma_x^\eta} E_z^*(x', w) |\psi(x', w)|^2 \, dx'\, dx\, dw \tag{7.20}$$

by at most

$$\begin{aligned}
&\int_W \int_Q \frac{1}{|\Gamma_x^\eta|} \int_{\Gamma_x^\eta} E_z^*(x',w) \left| |\psi(x,w)|^2 - |\psi(x',w)|^2 \right| \, dx' \, dx \, dw \leq \\
&\qquad \leq C\eta^{-6} \|E_z^*\|_\infty \int_W \int_Q \int_{\Gamma_x^\eta} \left| |\psi(x,w)|^2 - |\psi(x',w)|^2 \right| dx' \, dx \, dw \\
&\qquad = C\eta^{-6} \|E_z^*\|_\infty \\
&\qquad\qquad \cdot \int_W \int_Q \int_{\Gamma_x^\eta} \left| \psi(x,w) + \psi(x',w) \right| \cdot \left| \psi(x,w) - \psi(x',w) \right| dx' \, dx \, dw \\
&\qquad \leq C\eta^{-6} \|E_z^*\|_\infty \left(\int_W \int_Q \int_{\Gamma_x^\eta} \left| \psi(x,w) + \psi(x',w) \right|^2 dx' \, dx \, dw \right)^{1/2} \\
&\qquad\qquad \cdot \left(\int_W \int_Q \int_{\Gamma_x^\eta} \left| \psi(x,w) - \psi(x',w) \right|^2 dx' \, dx \, dw \right)^{1/2} \\
&\qquad \leq C\eta^{-6} \|E_z^*\|_\infty \\
&\qquad\quad \cdot \left(C\eta^3 \|\psi\|_{L^2(Q\times W)} + \left(\int_W \int_Q \int_{\Gamma_x^\eta} |\psi(x',w)|^2 \, dx' \, dx \, dw \right)^{1/2} \right) \\
&\qquad\quad \cdot \left(\int_W \int_Q \int_{\Gamma_x^\eta} \int_0^1 |\nabla_x \psi(x + t(x'-x), w)|^2 \, |x-x'|^2 \, dt \, dx' \, dx \, dw \right)^{1/2} \\
&\qquad \leq C\eta^{-6}\eta \|E_z^*\|_\infty \\
&\qquad\quad \cdot \left(C\eta^3 \|\psi\|_{L^2(Q\times W)} + \left(\int_W \int_Q \int_{B(x',\eta)} |\psi(x',w)|^2 \, dx \, dx' \, dw \right)^{1/2} \right) \\
&\qquad\quad \cdot \left(\int_W \int_0^1 \int_{B(0,\eta)} \int_Q |\nabla_x \psi(u,w)|^2 \, du \, dy \, dt \, dw \right)^{1/2} \\
&\qquad \leq C\eta \|E_z^*\|_\infty \|\psi\|_{L^2(Q\times W)} \cdot \|\nabla_x \psi\|_{L^2(Q\times W)}
\end{aligned}$$

and by (7.13) this is less than

$$CZ^2\eta^3 \|\psi\|_{L^2(Q\times W)} \cdot \|\nabla_x \psi\|_{L^2(Q\times W)} \tag{7.21}$$

Note that

$$\int_W \int_Q \frac{1}{|\Gamma_x^\eta|} \int_{\Gamma_x^\eta} E_z^*(x', w)|\psi(x', w)|^2 \, dx' \, dx \, dw \leq$$

$$\leq C\eta^{-6} \int_W \int_Q \int_{B(0,\eta)} E_z^*(x', w)|\psi(x', w)|^2 \, dx \, dx' \, dw \leq$$

$$\leq C' \int_W \int_Q E_z^*(x, w)|\psi(x, w)|^2 \, dx \, dw$$

which, with (7.19) and (7.21) implies that

$$\int_W \int_Q E_z^*(x, w)|\psi(x, w)|^2 \, dx \, dw \geq C_{7.10} Z^2 \eta^2 \int_W \int_Q |\psi(x, w)|^2 \, dx \, dw$$
$$- C_{10} Z^2 \eta^3 \, \|\psi\|_{L^2(Q\times W)} \cdot \|\nabla\psi\|_{L^2(Q\times W)}$$

for some constant C_{10}.
So, if

$$\|\nabla_x \psi\|_{L^2(Q\times W)} \leq C_9 Z^{2/3} \, \|\psi\|^2_{L^2(Q\times W)} \tag{7.21}$$

for

$$C_9 = 4 \left(\frac{C_{KE}}{c_1} \right)^{1/2} \tag{7.23}$$

we have

$$\int_{Q_{\nu_1}\times\cdots\times Q_{\nu_Z}} E_z(x_1, \cdots, x_Z)|\psi(x_1, \cdots, x_Z)|^2 \, dx_1 \, \cdots \, dx_Z \geq$$
$$\geq Z^2\eta^2 \left(C_{7.10} - C_\eta \cdot C_{10} \cdot C_9\right) \|\psi\|^2_{L^2\left(Q_{\nu_1}\times\cdots\times Q_{\nu_Z}\right)} \tag{7.24}$$

and, taking C_η small enough, we get

$$\int_{Q_{\nu_1}\times\cdots\times Q_{\nu_Z}} E_z(x_1, \cdots, x_Z)|\psi(x_1, \cdots, x_Z)|^2 \, dx_1 \, \cdots \, dx_Z \geq$$
$$\geq C_{11} Z^{2/3} \, \|\psi\|^2_{L^2\left(Q_{\nu_1}\times\cdots\times Q_{\nu_Z}\right)} \tag{7.25}$$

for another constant C_{11}, provided (7.21) holds for these cubes.

Recall that this holds for $|z - c_{\nu_1}| < \frac{C_1 Z^{-2/3}}{10}$; thus, integrating (7.25) over this set of z's, we get

$$\int_{Q_{\nu_1}\times\cdots\times Q_{\nu_Z}} \int_{|z-c_{\nu_1}|<\frac{C_1 Z^{-2/3}}{10}} E_z(x_1,\cdots,x_Z)|\psi(x_1,\cdots,x_Z)|^2\,dz\;dx_1\;\cdots\;dx_Z \geq$$
$$\geq \tfrac{4}{3}\pi C_{11} Z^{2/3}\left(\frac{C_1 Z^{-2/3}}{10}\right)^3 \int_{Q_{\nu_1}\times\cdots\times Q_{\nu_Z}} |\psi(x_1,\ldots,x_Z)|^2\;dx_1\;\cdots\;dx_Z$$

By Lemma 7.11, we can do the same for $c_1 Z$ different pairs of electrons, provided we have (7.21) for them, and since the disks $B(c_{\nu_i}, C_1 Z^{-2/3})$ associated with each pair of electrons are disjoint (also by Lemma 7.11 and (7.14)) we conclude that for all cubes $Q_{\nu_1}\times\cdots\times Q_{\nu_Z}$, where ν is not in either of the sets

$$J = \{\nu\ :\ E_{Q_{\nu_1}\times\cdots\times Q_{\nu_Z}} \geq C_{7.9} Z^{5,3}\}$$

or

$$G = \Big\{\nu \notin J\ |\ \left\|\nabla_{x_i,x_j}\psi\right\|_{L^2(Q_{\nu_1}\times\cdots\times Q_{\nu_Z})} \geq C_9 Z^{2/3}\|\psi\|^2_{L^2(Q\times W)}$$
$$\text{for half of those } c_1 Z \text{ pairs of } (i,j)\Big\}$$

we have

$$\int_{Q_{\nu_1}\times\cdots\times Q_{\nu_Z}} E(x_1,...,x_Z)|\psi(x_1,...,x_Z)|^2\,dx_1\;\cdots\;dx_Z \geq$$

$$
\begin{aligned}
&\geq \left(\frac{C}{{R_*}^3}\right) \int_{Q_{\nu_1}\times\cdots\times Q_{\nu_Z}} \int_{z\in\mathbf{R}^3} E_z(x_1,...,x_Z)|\psi(x_1,...,x_Z)|^2\,dz\;dx_1\cdots dx_Z \\
&\geq \left(\frac{C}{{R_*}^3}\right) \int_{Q_{\nu_1}\times\cdots\times Q_{\nu_Z}} \sum_{i=1}^{\frac{c_1}{2}Z} \\
&\qquad \int_{|z-c_{\nu_i}|<\frac{C_1 Z^{-2/3}}{10}} E_z(x_1,...,x_Z)|\psi(x_1,...,x_Z)|^2\,dz\;dx_1\cdots dx_Z \\
&\geq \tfrac{4}{3}\pi C_{11} Z^{2/3}\frac{c_1 Z}{2}\left(\frac{C}{{R_*}^3}\right)\left(\frac{C_1 Z^{-2/3}}{10}\right)^3 \\
&\qquad \cdot \int_{Q_{\nu_1}\times\cdots\times Q_{\nu_Z}} |\psi(x_1,\ldots,x_Z)|^2\;dx_1\cdots dx_Z \\
&\geq C_{12} Z^{5/3} \int_{Q_{\nu_1}\times\cdots\times Q_{\nu_Z}} |\psi(x_1,\ldots,x_Z)|^2\;dx_1\cdots dx_Z
\end{aligned}
\tag{7.26}
$$

Now, (7.21) may not be true for all cubes, but it has to be true for some fixed portion of them; to see this, note that, if ψ is normalized to have L^2 norm 1, by the hypothesis in Theorem 7.1,

$$
\begin{aligned}
C_{KE} Z^{7/3} &\geq \|\nabla\psi\|^2_{L^2(\mathbf{R}^{3Z})} \\
&\geq \sum_{\nu\in G} \|\nabla\psi\|^2_{L^2\left(Q_{\nu_1}\times\cdots\times Q_{\nu_Z}\right)} \\
&\geq c\sum_{\nu\in G}\sum_{i=1}^{cZ} \left\|\nabla_{x_i,\delta(i)}\psi\right\|^2_{L^2\left(Q_{i,\delta(i)}\times W_{i,\delta(i)}\right)} \\
&\geq \frac{cZ}{2} C_9^2 Z^{4/3} \sum_{\nu\in G} \|\psi\|^2_{L^2(Q\times W)} \\
&\geq 2C_{KE} Z^{7/3} \sum_{\nu\in G} \|\psi\|^2_{L^2(Q\times W)}
\end{aligned}
$$

by (7.23). This shows that

$$
\|\psi\|_{L^2(\cup_{\nu\in G} Q_{\nu_1}\times\cdots\times Q_{\nu_Z})} \leq \tfrac{1}{2} \tag{7.27}
$$

Finally, we have, by Lemma 7.11, (7.27) and (7.26)

$$\int_{\mathbf{R}^{3Z}} E(x_1,\cdots,x_Z)|\psi(x_1,\cdots,x_Z)|^2\,dx_1\cdots dx_Z =$$

$$= \sum_{\nu\in J}\int_{Q_{\nu_1}\times\cdots\times Q_{\nu_Z}} E(x_1,\cdots,x_Z)|\psi(x_1,\cdots,x_Z)|^2\,dx\cdots dx_Z$$

$$+ \sum_{\nu\in G}\int_{Q_{\nu_1}\times\cdots\times Q_{\nu_Z}} E(x_1,\cdots,x_Z)|\psi(x_1,\cdots,x_Z)|^2\,dx\cdots dx_Z$$

$$+ \sum_{\nu\notin J\cup G}\int_{Q_{\nu_1}\times\cdots\times Q_{\nu_Z}} E(x_1,\cdots,x_Z)|\psi(x_1,\cdots,x_Z)|^2\,dx\cdots dx_Z$$

$$\geq C_{7.9}Z^{5/3}\sum_{\nu\in J}\int_{Q_{\nu_1}\times\cdots\times Q_{\nu_Z}} |\psi(x_1,\cdots,x_Z)|^2\,dx\cdots dx_Z$$

$$+ C_{12}Z^{5/3}\sum_{\nu\notin G\cap J}\int_{Q_{\nu_1}\times\cdots\times Q_{\nu_Z}} |\psi(x_1,\cdots,x_Z)|^2\,dx\cdots dx_Z$$

$$\geq (C_{7.9}+C_{12})Z^{5/3}\left(1-\|\psi\|^2_{L^2\left(\cup_{\nu\in G}Q_{\nu_1}\times\cdots\times Q_{\nu_Z}\right)}\right)$$

$$\geq C_E Z^{5/3}$$

what proves Theorem 7.1

7.6 The Implementation.

Although Theorem 7.1 has the right behavior as $Z\to\infty$, it is clearly wasteful.

The purpose of this section is to organize the ideas from the previous section in order to obtain an effective algorithm to improve the lower bounds.

The idea is to replace estimates of the kind

$$\langle E\psi,\psi\rangle \geq cZ^{5/3} \quad \text{if} \quad \|\nabla\psi\|_2^2 \leq \mathrm{C_{KE}}\,\mathrm{Z}^{7/3}$$

by inequalities of the type

$$\varepsilon \|\nabla\psi\|_2^2 + \langle E\psi, \psi\rangle \geq \sum_{i=1}^{Z} V_\varepsilon(x_i) - C_\varepsilon$$

for some potential V_ϵ and constant C_ϵ, where the last inequality is expected to provide a contribution of $cZ^{5/3}$; the new potential and constant can be then incorporated to the analysis of Chapter 2, by putting

$$\sum_i \left(-\Delta_{x_i} - \frac{Z}{|x_i|}\right) + \frac{1}{2}\sum_{i\neq j}\frac{1}{|x_i - x_j|} \geq$$
$$\geq \sum_i \left(-(1-\varepsilon)\Delta_{x_i} - \frac{Z}{|x_i|} + V(x_i) + V_\varepsilon(x_i)\right) - C - C_\varepsilon$$

We proceed as follows:

Fix the center of a ball z.
Let's start with two numbers $T_1(z)$ and $T_2(z)$ such that

$$\alpha T_1(z) < R_1(z)$$
$$R_2(z) > \alpha T_2(z) > R_1(z)$$

for α in some range $(\alpha_0(z), \alpha_1(z))$ that will become a parameter of the solution — together with a whole bunch of other constants and functions— and

$$\delta_1(z) < \frac{T_2(z)}{T_1(z)} < \delta_2(z)$$

Then

$$\begin{aligned}
E &\geq \frac{1}{2\pi}\iint \left((N-\bar{N})^2 - \tfrac{1}{4}\right)\ \frac{dz\,dR}{R^5} \\
&\geq \frac{1}{2\pi}\int_z\int_\alpha \left(\left(N(z,\alpha T_1(z)) - \tfrac{1}{2}\right)^2 - \tfrac{1}{4}\right)\ \frac{d\alpha}{\alpha^5 T_1(z)^4}\,dz \\
&\quad + \frac{1}{2\pi}\int_z\int_\alpha \left(\left(N(z,\alpha T_1(z) - \tfrac{3}{2}\right)^2 - \tfrac{1}{4}\right)\ \frac{d\alpha}{\alpha^5 T_1^4(z)}\,dz \\
&\geq \frac{1}{2\pi}\int_z T_2^{-4}(z)\int \left(\left(N(z,\alpha T_1(z)) - \tfrac{1}{2}\right)^2 - \tfrac{1}{4}\right) \\
&\quad + \left(\left(N(z,\alpha T_2(z)) - \tfrac{3}{2}\right)^2 - \tfrac{1}{4}\right)\ \frac{d\alpha}{\alpha^5}\,dz
\end{aligned}$$

Let's put

$$W(z,\alpha;x_1,\ldots,x_Z) = \begin{cases} 1 & \text{if } B(z,\alpha R_2) \text{ is empty} \\ 1 & \text{if } B(z,\alpha R_1) \text{ has two points} \\ 0 & \text{otherwise} \end{cases}$$

Clearly,

$$\left(\left(N(z,\alpha T_1(z)) - \tfrac{1}{2}\right)^2 - \tfrac{1}{4}\right) + \left(\left(N(z,\alpha T_2(z)) - \tfrac{3}{2}\right)^2 - \tfrac{1}{4}\right) \geq 2W$$

so

$$E \geq \frac{1}{\pi} \int T_2^{-4}(z) \int W(z,\alpha)\, \frac{d\alpha}{\alpha^5}\, dz$$

Define a function $G_{z,\alpha}(x;\delta)$ such that

$$G_{z,\alpha}(x;\delta) = \begin{cases} z + \delta(x-z) & \text{if } |x-z| > c_0 \alpha T_1(z) \\ x & \text{if } |x-z| < c_1 \alpha T_1(z) \end{cases}$$
$$|\nabla_\delta G_{z,\alpha}(x;\delta)| \leq c_3 \alpha T_2(z)$$
$$\det |\partial_x G_{z,\alpha}(x;\delta)| \geq c_4 \delta^3$$

Fix a constant $c_5 < 1$.

Lemma 7.12: *If*

$$x_2 \in B(z,\alpha T_1(z))$$
$$x_1 \in B(z,\alpha T_2(z)) - B(z,\alpha T_1(z)) \stackrel{\text{def}}{=} S(z,\alpha)$$

then

$$\int_{\frac{c_5}{\delta_2}}^1 W(z,\alpha; G_{z,\alpha}(x_1;\delta), x_2, \cdots, x_Z)\, d\delta \geq \frac{1-c_5}{\delta_2}$$

Proof:
Note that for $\delta < \delta_2^{-1}(z)$

$$\begin{aligned} |z - G(x_1;\delta)| &\le |z - (z - \delta(x_1 - z)| \\ &\le \delta\alpha T_2(z) \\ &< \alpha T_1(z) \end{aligned}$$

so

$$G(x_1;\delta) \in B(z, \alpha T_1)$$

and so

$$W(z, \alpha; G(x_i;\delta), x_2, \cdots, x_Z) \ge 1$$

thus

$$\begin{aligned} \int_{\frac{c_5}{\delta_2}}^{1} W(z,\alpha; G(x_1;\delta), x_2, \cdots, x_Z)\, d\delta \ge & \\ &\ge \int_{\frac{c_5}{\delta_2}}^{\frac{1}{\delta_2}} W(z,\alpha; G(x_1;\delta), x_2, \cdots, x_Z)\, d\delta \\ &\ge \frac{1 - c_5}{\delta_2(z)} \end{aligned}$$

Q.E.D.

Lemma 7.13: *There exist a function $w(z,R)$ and a constant F such that*

$$F\,\langle -\Delta\psi, \psi\rangle + \langle E\psi, \psi\rangle \ge \iint w(z,R)\,\big\langle \big(N(z,R) - 1\big)\psi, \psi\big\rangle\ \frac{dz\,dR}{R^5}$$

Proof: For the moment, we fix z and α and we drop the dependence of parameters on (z, α).

Let

$$E_{i,j} = \big\{(x_1, \ldots, x_Z) \mid x_i \in B(z, \alpha T_2) - B(z, \alpha T_1(z)) \\ x_j \in B(z, \alpha T_1(z)), x_k \notin B(z, \alpha T_2)\ k \neq i, j\big\}$$

and

$$E = \big\{(x_1, \ldots, x_Z) \mid N_{B(z,\alpha T_2)} > 2\big\}.$$

Then

$$\begin{aligned} \int W(z, \alpha; x_1, \ldots, x_z) \left|\psi(x_1, \ldots, x_Z)\right|^2 \, dx_1 \cdots dx_Z \\ \geq \int_E W(x_1, \ldots, x_Z) \left|\psi(x_1, \ldots, x_Z)\right| \, dx_1 \cdots dx_Z \\ + \sum_{i,j} \int_{E_{i,j}} W(x_1, \ldots, x_Z) \left|\psi(x_1, \ldots, x_Z)\right| \, dx_1 \cdots dx_Z \end{aligned} \tag{7.28}$$

Let's deal with the term in the previous sum corresponding to $E_{1,2}$. The other terms are treated in the same manner.

Let's introduce the following notation:

$$\begin{aligned} u = u(x; \delta) &= (u_1, \ldots, u_Z) = (G(x_1; \delta), x_2, \cdots, x_Z) \\ x = x(u; \delta) &= (x_1, \ldots, x_Z) = \left(G^{-1}(u_1; \delta), u_2, \cdots, u_Z\right) \\ U(\delta) &= \{u \mid x(u; \delta) \in E_{1,2}\} \\ S &= \{x \in E_{1,2} \mid x \neq u(x; \delta) \qquad \text{for} \quad \delta \neq 1\} \\ \Delta(u; \delta) &= \left|\det(\mathcal{J}_{x_1} G)\left(G^{-1}(u; \delta); \delta\right)\right| \end{aligned}$$

where $\mathcal{J}$ denotes Jacobian matrix.

By the previous Lemma, we know that

$$\int_{E_{1,2}} \mathrm{Av}_{\left(\frac{c_5}{\delta_2}\leq\delta\leq 1\right)} W(z,\alpha;G(x_i;\delta),x_{k\neq i})\,|\psi(x_1,\ldots,x_Z)|^2\,dx \geq$$
$$\geq \frac{1-c_5}{\delta_2-c_5}\int_{E_{1,2}} |\psi|^2\,(x_1,\ldots,x_Z)\,dx_1\,\cdots\,dx_Z \quad (7.29)$$

Changing variables and applying Fubini's theorem, we get that the left hand side of (7.29) is equal to

$$\left(1-\frac{c_5}{\delta_2}\right)^{-1}\iint_{\substack{U(\delta)\\ \frac{c_5}{\delta_2}\leq\delta\leq 1}} W(z,\alpha;u)\,\left|\psi\big(x(u;\delta)\big)\right|^2\,\frac{du\,d\delta}{\Delta(u;\delta)}$$

We proceed as in the previous section; the integral in this last expression differs from

$$\iint_{\substack{U(\delta)\\ \frac{c_5}{\delta_2}\leq\delta\leq 1}} W(z,\alpha;u)\,|\psi\,(u)|^2\,\frac{du\,d\delta}{\Delta(u;\delta)} \quad (7.30)$$

by at most (note that $W\leq 1$)

$$\iint \Big||\psi\,(u)|^2-|\psi\,(x(u,\delta))|\Big|^2\,\frac{du\,d\delta}{\Delta(u;\delta)}$$
$$=\iint_{\substack{u\neq x(u;\delta)\\ U(\delta)}} |\psi\,(u)-\psi\,(x(u;\delta))|\cdot|\psi\,(u)+\psi\,(x(u;\delta))|\,\frac{du\,d\delta}{\Delta(u;\delta)}$$
$$\leq\Bigg\{\left(\iint|\psi\,(u)|^2\,\frac{du\,d\delta}{\Delta(u;\delta)}\right)^{1/2}+$$
$$+\left(\iint|\psi\,(x(u;\delta))|^2\,\frac{du\,d\delta}{\Delta(u;\delta)}\right)^{1/2}\Bigg\}$$
$$\cdot\left(\iint_{u\neq x\in E_{1,2}}|\psi\,(u)-\psi\,(x(u;\delta))|^2\,\frac{du\,d\delta}{\Delta(u;\delta)}\right)^{1/2}$$

Since the range of u we are integrating over is included in $E_{1,2}$ for any $\delta\leq 1$, we can expand the domain in the first integral in the last expression to $E_{1,2}$, and

changing variables back to x in the second and third integrals we obtain

$$\leq \left\{ \|\psi\|_{L^2(E_{1,2})} \cdot \left(\int_{\frac{c_5}{\delta_2}}^1 \frac{d\delta}{\inf_u \Delta(u,\delta)} \right)^{1/2} + \left(\iint |\psi(x)|^2 \, dx \, d\delta \right)^{1/2} \right\}$$
$$\cdot \left(\iint_{u \neq x \in E_{1,2}} |\psi(u(x;\delta)) - \psi(x)|^2 \, du \, d\delta \right)^{1/2} \tag{7.31}$$

Note that

$$\begin{aligned} \psi(x) - \psi(u(x;\delta)) &= \psi(u(x;1)) - \psi(u(x;\delta)) \\ &= -\int_\delta^1 \frac{d}{dt} \psi(u(x;t)) \, dt \\ &= -\int_\delta^1 \nabla_{x_1} \psi(u(x,t)) \cdot \frac{d}{dt} u_1(x_1;t) \, dt \\ &= -\int_\delta^1 \nabla_{x_1} \psi(u(x,t)) \cdot \nabla_\delta G(x_1;t) \, dt \end{aligned}$$

Therefore, we have

$$\begin{aligned} (7.31) &\leq \|\psi\|_{L^2(E_{1,2})} \left(\left(\int_{\frac{c_5}{\delta_2}}^1 \frac{d\delta}{\inf_u \Delta(u,\delta)} \right)^{1/2} + \left(1 - \tfrac{c_5}{\delta_2}\right)^{1/2} \right) \\ &\quad \cdot \left(\sup_{c_5 \delta_2^{-1} \leq \delta \leq 1} \|\nabla_\delta G(x_1;\delta)\|_\infty \right) \\ &\quad \cdot \left(\int_S \int_{c_5\delta_2^{-1}}^1 \int_\delta^1 |\nabla_{x_1} \psi(u(x;t))| \, dt \, d\delta \, dx \right)^{1/2} \\ &\leq \|\psi\|_{L^2(E_{1,2})} \left(\left(\int_{\frac{c_5}{\delta_2}}^1 \frac{d\delta}{\inf_u \Delta(u,\delta)} \right)^{1/2} + \left(1 - \tfrac{c_5}{\delta_2}\right)^{1/2} \right) \\ &\quad \cdot \left(1 - \tfrac{c_5}{\delta_2}\right)^{1/2} \left(\sup_{c_5 \delta_2^{-1} \leq \delta \leq 1} \|\nabla_\delta G(x_1;\delta)\|_\infty \right) \\ &\quad \cdot \left(\int_S \int_{c_5\delta_2^{-1}}^1 |\nabla_{x_1} \psi(u(x;t))| \, dx \, dt \right)^{1/2} \end{aligned}$$

$$\leq \|\psi\|_{L^2(E_{1,2})} \left(\left(\int_{\frac{c_5}{\delta_2}}^1 \frac{d\delta}{\inf_u \Delta(u,\delta)} \right)^{1/2} + \left(1 - \tfrac{c_5}{\delta_2}\right)^{1/2} \right)$$
$$\cdot \left(1 - \tfrac{c_5}{\delta_2}\right)^{1/2} \left(\sup_{c_5\delta_2^{-1} \leq \delta \leq 1} \|\nabla_\delta G(x_1;\delta)\|_\infty \right)$$
$$\cdot \left(\int_{x(u;\delta)\in S} \int_{c_5\delta_2^{-1}}^1 |\nabla_{x_1}\psi(u)| \frac{dx\, d\delta}{\Delta(u;\delta)} \right)^{1/2}$$
$$\leq \|\psi\|_{L^2(E_{2,1})} \left(\left(\int_{\frac{c_5}{\delta_2}}^1 \frac{d\delta}{\inf_u \Delta(u,\delta)} \right)^{1/2} + \left(1 - \tfrac{c_5}{\delta_2}\right)^{1/2} \right)$$
$$\cdot \left(\left(\int_{\frac{c_5}{\delta_2}}^1 \frac{d\delta}{\inf_u \Delta(u,\delta)} \right)^{1/2} \cdot \left(1 - \tfrac{c_5}{\delta_2}\right)^{1/2} \right)$$
$$\cdot \left(\sup_{c_5\delta_2^{-1} \leq \delta \leq 1} \|\nabla_\delta G(x_1;\delta)\|_\infty \right) \|\nabla_{x_1}\psi\|_{L^2(S)}$$

since $u(S;\delta) \subset S$.

Let's introduce the following notation

$$\varepsilon = \varepsilon(\delta_2, c_5) = 1 - \tfrac{c_5}{\delta_2}$$
$$p = p(G, c_5, \delta_2) = \int_{\frac{c_5}{\delta_2}}^1 \frac{d\delta}{\inf_u \Delta(u,\delta)}$$
$$\eta = \eta(G, c_5, \delta_2) = \sup_{c_5\delta_2^{-1} \leq \delta \leq 1} \|\nabla_\delta G(x_1;\delta)\|_\infty$$

Thus, we have

$$(7.31) \leq \left(\varepsilon^{1/2} + p^{1/2}\right) \cdot (p\varepsilon)^{1/2} \cdot \eta \cdot \|\psi\|_{L^2(E_{1,2})} \cdot \|\nabla_{x_1}\psi\|_{L^2(S)}$$
$$\leq \tfrac{1}{2} \left(\varepsilon^{1/2} + p^{1/2}\right) \cdot (p\varepsilon)^{1/2} \cdot \eta \cdot \left(M^{-1} \|\psi\|^2_{L^2(E_{1,2})} + M \|\nabla_{x_1}\psi\|^2_{L^2(S)} \right)$$

for any M.
Note also that

$$(7.30) \leq p\,(G, c_5, \delta_2) \int_{E_{1,2}} W(z,\alpha;x) \,|\psi(x)|^2 \, dx$$

to conclude that

$$p\,(G,c_5,\delta_2)\int W(z,\alpha;x_1,\ldots,x_Z)\,|\psi(x_1,\ldots,x_Z)|^2\;dx_1\cdots dx_Z\geq$$
$$\geq\varepsilon\int_{E_{1,2}}|\psi|^2\,(x_1,\ldots,x_Z)\,dx_1\cdots dx_Z$$
$$-\tfrac{1}{2}\left(\varepsilon^{1/2}+p^{1/2}\right)\cdot(p\varepsilon)^{1/2}\cdot\eta\cdot$$
$$\cdot\left(M^{-1}\,\|\psi\|_{L^2(E_{1,2})}+M\,\|\nabla_{x_1}\psi\|_{L^2(S)}\right)$$

Doing the same for all $E_{i,j}$ and adding the results, we obtain

$$\int_{\cup E_{i,j}}W(z,\alpha;x_1,\ldots,x_Z)\,|\psi(x_1,\ldots,x_Z)|^2\;dx_1\cdots dx_Z\geq$$
$$\geq\left(\varepsilon p^{-1}-\tfrac{1}{2}M^{-1}\left(\varepsilon^{1/2}+p^{1/2}\right)\cdot\left(p^{-1}\varepsilon\right)^{1/2}\cdot\eta\right)$$
$$\cdot\int_{\cup E_{i,j}}|\psi|^2\,(x_1,\ldots,x_Z)\,dx_1\cdots dx_Z$$
$$-\tfrac{1}{2}M\left(\varepsilon^{1/2}+p^{1/2}\right)\cdot(p\varepsilon)^{1/2}\cdot\eta\cdot\sum_{i,j}\|\nabla_{x_i}\psi\|_{L^2(S_{i,j})}$$

Note that the fact that G is a contraction, implies that $p>\epsilon$. Since

$$W(x_1,\ldots,x_Z)\geq 1\qquad\text{for}\quad(x_1,\ldots,x_Z)\in E$$

the last inequality and (7.28) give

$$\int_{\mathbf{R}^{3Z}}W(z,\alpha;x_1,\ldots,x_Z)\,|\psi(x_1,\ldots,x_Z)|^2\;dx_1\cdots dx_Z\geq$$

$$
\begin{aligned}
&\geq \left(\varepsilon p^{-1} - \tfrac{1}{2}M^{-1}\left(\varepsilon^{1/2} + p^{1/2}\right)\cdot\left(p^{-1}\varepsilon\right)^{1/2}\cdot\eta\right) \\
&\qquad \cdot \int_{E\cup E_{i,j}} |\psi|^2 (x_1,\ldots,x_Z)\,dx_1\cdots dx_Z \\
&\quad - \tfrac{1}{2}M\left(\varepsilon^{1/2} + p^{1/2}\right)\cdot(p\varepsilon)^{1/2}\cdot\eta\cdot\sum_{i,j}\|\nabla_{x_i}\psi\|_{L^2(S_{i,j})} \\
&\geq \left(\varepsilon p^{-1} - \tfrac{1}{2}M^{-1}\left(\varepsilon^{1/2} + p^{1/2}\right)\cdot\left(p^{-1}\varepsilon\right)^{1/2}\cdot\eta\right) \\
&\qquad \cdot \int_{\mathbf{R}^{3Z}} \big(N(z,\alpha T_2(z)-1\big)\,|\psi|^2 (x_1,\ldots,x_Z)\,dx_1\cdots dx_Z \\
&\quad - \tfrac{1}{2}M\left(\varepsilon^{1/2} + p^{1/2}\right)\cdot(p\varepsilon)^{1/2}\cdot\eta\cdot\sum_{i,j}\|\nabla_{x_i}\psi\|_{L^2(S_{i,j})} \\
&= w_1(z,\alpha;G,c_5,\delta_2)\int_{\mathbf{R}^{3Z}}\big(N(z,\alpha T_2(z))-1\big)\,|\psi|^2(x_1,\ldots,x_Z)\,dx_1\cdots dx_Z \\
&\quad - w_2(z,\alpha;G,c_5,\delta_2)\sum_{i,j}\|\nabla_{x_i}\psi\|_{L^2(S_{i,j})}
\end{aligned}
$$

Recall that all parameters are taken to be functions of the specific ball we are studying.

If we multiply the previous estimate by $T_2(z)^{-4}$ and integrate against

$$\pi^{-1}\alpha^{-5}\,dzd\alpha$$

we obtain

$$
\begin{aligned}
\langle E\psi,\psi\rangle &\geq \iint w_1(z,\alpha)\left\langle\big(N(z,\alpha T_2(z))-1\big)\psi,\psi\right\rangle\,\frac{dz\,d\alpha}{T^{-4}(z)\alpha^5} \\
&\qquad - \iint w_2(z,\alpha)\sum_{i,j}\|\nabla_{x_i}\psi\|_{L^2(S_{i,j}(z,\alpha T(z)))}\,\frac{dz\,d\alpha}{T^{-4}(z)\alpha^5} \\
&\geq \iint w_1(z,R)\left\langle\big(N(z,R)-1\big)\psi,\psi\right\rangle\,\frac{dz\,dR}{R^5} - F\,\langle-\Delta\psi,\psi\rangle
\end{aligned}
$$

for

$$F = \sup_{x_1,\ldots,x_Z}\sum_{i,j}\iint_{(x_1,\ldots,x_Z)\in S_{i,j}(z,R)} w_2(z,R)\,\frac{dz\,dR}{R^5}$$

what proves the Lemma. $Q.E.D.$

Note that the lower bound in this Lemma can be trivially improved to

$$\iint w(z,R) \left\langle \big(N(z,R)-1\big)_+ \psi, \psi \right\rangle \frac{dz\, dR}{R^5}$$

but although this is a better estimate, it does not give rise to one–electron potentials, which is our goal.

The inequality that the Lemma proves depends on a large number of parameters. In this case, like in the case of the potential V in Chapter 3, some optimization is called for.

Crudely speaking, the lower bound obtained in the Lemma will be like

$$\big(1 - \tfrac{c_5}{\delta}_2\big)\, Z^{5/3}$$

whereas the price we pay, $F\,\langle -\Delta\psi, \psi\rangle$, since F represents a volume, will be like

$$\big(1 - \tfrac{c_5}{\delta}_2\big)^3\, Z^{2/3}$$

This implies that for an appropriate choice of the parameters, this method will give a contribution to the energy of $cZ^{5/3}$.

Note also that this in this section, we are fuzzing with respect to the group of dilations, whereas in the previous ones we were dealing with translations. This is because before, the integration dz was done first, and translations are natural for this measure. This was useful to superimpose estimates for different balls. In this section however, we are only looking for lower bounds as one–particle potentials, and we let the ODE solver take care of extracting any estimates that they yield, and thus it is more convenient to do the $\frac{dR}{R^5}$ integration first.

Chapter 8: The Ball Packing

Lemma 8.1: *Assume there are at least two disjoint balls $B_k = B(c_k, R_k)$ with c_i in a ball $S \subset \mathbf{R}^3$, with the property that*

$$\delta \leq \frac{R_i}{R_j} \leq \frac{1}{\delta} \qquad\qquad 0 < \delta < 1$$

Then, for some universal constant C_0 we have that

$$\text{Vol}\,(S) \geq (1 + C_0\delta^3) \sum |B_k|$$

Proof: Divide S into disjoint sets

$$E_k = \{x \in S \mid \text{dist}\,(x, B_k) \leq \text{dist}\,(x, B_i) \quad i \neq k\}$$

If we can prove that

$$|E_k| \geq \left(1 + C_0\delta^3\right) |B_k| \tag{8.1}$$

summing over all k we would have proved the Lemma.

Observe that (8.1) would follow if we can find a ball $B(x_0, r_0)$ of radius comparable to δR_k, disjoint from B_k and totally contained in E_k.

Given any three balls B_1, B_2 and B_3, take $v \in \mathbf{R}^3$ to be any point equidistant from them, that is

$$|v - c_i| - R_i = d$$

for d the same for all three balls. We denote

$$d = d(c_1, R_1; c_2, R_2; c_3, R_3) = d(c_i, R_i)$$

Define

$$d_0(R) = \inf \left\{ d(c_i, R_i) \mid |c_i - c_j| \geq R_i \geq R \quad \delta \leq R_i \cdot R_j^{-1} \leq \delta^{-1} \right\}$$

and note that in fact

$$d_0(R) = \inf \left\{ d(c_i, R_i) \mid R_i = R \quad |c_i - c_j| \geq R \right\}$$

In order to see this, note that, for general balls, if, say

$$R_1 > R_2 \geq R_3$$

then, defining $\tilde{B}_1 = B(\tilde{c}_1, \tilde{R}_1)$ with

$$\begin{aligned} \tilde{c}_1 &= c_1 + (R_1 - R_2) \cdot \frac{d - c_1}{|d - c_1|} \\ \tilde{R}_1 &= R_2 \end{aligned}$$

we have that $\tilde{B}_1$ continues to be disjoint from the two other balls, has a strictly smaller radius that B_1, and $v(c_i, R_i) = v(\tilde{c}_i, \tilde{R}_i)$.

It is known (see [Ro]) that

$$d_0(R) \geq C_R \cdot R \geq C_R \cdot \delta \cdot R_1$$

Consider now B_k and a closest neighboring ball B_j. Let's denote the plane of equidistant points from them by $P_{k,j}$, and $c_{k,j}$ the point in this plane closest to c_k.

If dist $(c_{k,j}, B_k) \geq \frac{1}{3} C_R \delta R_k$, then dist $(c_{k,j} - B_i) \geq \frac{1}{3} C_R \delta R_k$ for any $i \neq k, j$, and therefore, one of the hemispheres of $B(c_{k,j}, \frac{1}{3} C_R \delta R_k)$ is closer to B_k than any other B_i.

The fact that S is a sphere that contains c_k, c_j and $c_{k,j}$ implies that

$$B(c_{k,j}, \delta R_k) \subset S$$

and therefore the former hemisphere is in fact contained in E_k, what implies (8.1).

Suppose that, on the contrary, $\text{dist}\,(c_{k,j} - B_k) \leq \frac{1}{3} C_R \delta R_k$. Our bound on d_0 implies that the circle with center $c_{k,j}$

$$C_{k,j} = B\left(c_k, R_k(1 + \tfrac{1}{2} C_R \delta)\right) \cap P_{k,j}$$

does not intersect any ball B_i with $i \neq k, j$.

Moreover, given any $\tilde{c} \in C_{k,j}$, $B(\tilde{c}, \frac{1}{4} C_R \delta R_k)$ also does not intersect any ball other than B_k or B_j, since for any $z \in B(\tilde{c}, \frac{1}{4} C_R \delta R_k)$, we have that

$$\begin{aligned} |z - c_k| &\leq \tfrac{1}{4} C_R \delta R_k + |c_k - \tilde{c}| \\ &< C_R \delta R_k + R_k \end{aligned}$$

Also,

$$B(\tilde{c}, \tfrac{1}{4} C_R \delta R_k) \cap B_k = \emptyset$$

since for any $z \in B(\tilde{c}, \frac{1}{4} C_R \delta R_k)$, we have that

$$\begin{aligned} |z - c_k| &\geq |\tilde{c} - c_k| - \tfrac{1}{4} C_R \delta R_k \\ &= R_k + \tfrac{1}{2} C_R \delta R_k - \tfrac{1}{4} C_R \delta R_k \\ &> R_k \end{aligned}$$

Finally, since $\tilde{c} \in P_{k,j}$, half the points in $B(\tilde{c}, \frac{1}{3} C_R \delta r_k)$ are closer to B_k that any other ball. Also, for δ small enough, this ball will be contained in any ball that contains c_k and c_j and therefore in S and (8.1) follows. Q.E.D.

The following corollary follows from the proof of the previous Lemma.

Corollary: *Let $\{B_k\}$ be a system of balls with centers in a ball S, with n disjoint families, each family consisting of two closest–neighboring balls disjoint from all others; assume also that*

$$\delta \leq R_i R_j^{-1} \leq \delta^{-1}$$

for those balls in families.
Then

$$|K - \cup B_k| \geq Cn\delta^3 R^3$$

where R is the smallest of the R_i.

We will use these results to prove the following theorem

Theorem 8.2: *Let E be defined as in* (7.3). *Then*

$$\inf_{x_1,\ldots,x_Z} E(x_1,\ldots,x_Z) \geq CZ^{5/3}$$

Proof: Consider

$$C_1 Z^{-1/3} \leq |z_0| \leq C_2 Z^{-1/3} \tag{8.2}$$

and

$$R_{i+1}(z) \leq R_0 \leq R_i(z)$$

for $c_1 Z \leq i \leq c_2 Z$, for a constant c_1 small enough and c_2 to be picked later.

Clearly, for all $x \in B(z_0, R_0)$ we have $|x| \geq cZ^{-1/3}$, and, as a consequence,

$$\forall x \in B(z_0, R_0) \quad C_4 Z^{-2/3} \leq R_1(x_i) \leq C_3 Z^{-2/3}$$

Set

$$\begin{aligned} B_k &= B\left(x_k, R_1(x_k)\right) \\ B_k^* &= B\left(x_k, R_1(x_k) - C_0 Z^{-2/3}\right) \\ \tilde{B}_k &= B\left(x_k, R_1(x_k) - \tfrac{C_0}{2} Z^{-2/3}\right) \end{aligned}$$

for C_0 a constant to be picked later.

Since $\rho_{TF}(x) \geq cZ^2$ inside $B(z_0, R_0)$, we have

$$\begin{aligned} \int_{B_k - B_k^*} \rho_{TF}(x)\, dx &\leq cC_0^3 \\ \int_{B_k - \tilde{B}_k} \rho_{TF}(x)\, dx &\leq cC_0^3 \end{aligned} \tag{8.3}$$

Assume

$$\tilde{B}_i \cap \tilde{B}_j \neq \emptyset \qquad \text{for} \quad i \neq j \tag{8.4}$$

and consider

$$z \in \Omega_{i,j} = B_i^* \cap B_j^* \qquad \text{and} \qquad R_1(z) - \tfrac{C_0}{4} Z^{-2/3} \leq R \leq R_1(z)$$

Since $z = |x_{i,j}| \cdot (1 + O(Z^{-\epsilon}))$ by Lemma 7.2 we have

$$R_1(z) = R_1(x_i) + O\big(Z^{-1}\big) = R_1(x_j) + O\big(Z^{-1}\big)$$

then

$$\begin{aligned} |z - x_i| &\leq R_1(x_i) - C_0 Z^{-2/3} \\ &\leq R_1(z) \cdot \big(1 + O\big(Z^{-1}\big)\big) - C_0 Z^{-2/3} \\ &\leq (R + \tfrac{C_0}{4} Z^{-2/3}) \cdot (1 + O\big(Z^{-1}\big)) - C_0 Z^{-2/3} \\ &\leq R \end{aligned}$$

so $x_i, x_j \in B(z, R)$, and therefore

$$\begin{aligned} E &\geq \frac{1}{\pi} \int_{\Omega_{i,j}} \int_{R_1(z)(1 - cZ^{-\epsilon})}^{R_1(z)} \frac{dz\, dR}{R^5} \\ &\geq \frac{c}{\pi} \text{ Vol } (\Omega_{i,j})\, Z^{8/3} \\ &\geq cZ^{-2} \left(Z^{8/3}\right) \\ &= cZ^{2/3} \end{aligned}$$

Note also that if there are k disjoint pairs satisfying (8.4), then

$$E \geq ckZ^{2/3}$$

So, if $c_3 Z$ pairs —for c_3 very small to be picked later— satisfy (8.4), then

$$E \geq cZ^{5/3}$$

and thus we can assume from now on that there are at most c_3 intersecting balls $\tilde{B}_k$, and in particular, at most c_3 intersecting balls B_k^*.

If $N(z_0, R_0) \leq \frac{c_1}{2} Z$, then, since $\bar{N}(z_0, R_0) \geq c_1 Z - 1$ we have that

$$\left(N(z_0, R_0) - \bar{N}(z_0, R_0)\right)^2 - \tfrac{1}{4} \geq cZ^2 \tag{8.5}$$

Otherwise, since all the radii $R_1(x_i)$ are comparable, by taking c_3 small compared to c_1 we can find n balls in families of disjoint balls like in the corollary, and the number of balls not in families is only like $c_3 Z$. In this case

$$\text{Vol } (B(z_0, R_0) - \cup B_k^*) \geq c' n Z^{-2}$$

and since $\rho_{TF}(x) \geq CZ^2$ inside $B(z_0, R_0)$, we have

$$\int_{B(z_0,R_0) - \cup B_k^*} \rho_{TF}(x)\, dx \geq C_b n \tag{8.6}$$

where C_b depends only on the geometric constant in the corollary, on Thomas–Fermi theory and on the different $R_i(x_i)$, which in turn, by Lemma 7.2, depend only on C_3 and C_4.

Now, recall that

$$\int_{B_k} \rho_{TF}(x)\, dx = 1$$

and by our hypothesis on R

$$\int_{B(z_0,R_0)} \rho_{TF}(x)\, dx \leq c_2 Z$$

which, with (8.3), implies that,

$$\int_{B(z_0,R_0)-\cup B_k^*} \rho_{TF}(x)\,dx \le c_2 Z - n\cdot\left(1+cC_0^3\right)$$

This estimate, together with (8.6), implies that

$$n \le \frac{c_2}{(1+C_b+cC_0^3)}\cdot Z$$

We now choose C_0, c_2 and c_3 so that, although $c_2 > c_1$, we have

$$\frac{c_2}{(1+C_b+cC_0^3)} + c_3 < c_1$$

what implies

$$N = n + c_3 Z \le c_4 Z$$

for some constant $c_4 < c_1$. This implies (8.5) with a possibly different constant.

(8.5) in turn would imply that

$$\begin{aligned} E &\ge \iint cZ^2\,\frac{dz\,dR}{R^5} \\ &\ge cZ^{7/3} \end{aligned}$$

concluding that in all cases

$$E \ge cZ^{5/3}$$

Q.E.D.

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