1

INTERVAL ARITHMETIC IN QUANTUM MECHANICS

Charles L. Fefferman* and Luis A. Seco**

**Department of Mathematics, Princeton University, Princeton NJ 08544*

***Department of Mathematics, University of Toronto, Toronto, Canada M5S 1A4, email seco@math.toronto.edu*

Quantum mechanics is an area which, over the last ten years or so, has sparked a respectable amount of rigorous computer assisted work (see, for example [9, 13, 20, 39, 38], and their applications in [10, 11, 12, 3, 4, 5, 14, 15, 16, 17, 18, 19, 20]). The purpose of this review is to select a piece of that body of work, and to give a more or less detailed account, both of the quantum mechanical problem surrounding the computer work and of the computer assisted proof itself. We hope this will be enlightening since much of the other computer assisted work in quantum mechanics shares many of the main features presented below.

The underlying theme under discussion here is the proof presented in [14, 15, 16, 17, 18, 19, 20, 21] of a precise asymptotic formula for the ground–state energy of a non–relativistic atom. One of the ingredients of that proof, namely the content of [21], was to establish an elementary inequality that plays a crucial role in the rest of the proof of that formula. This inequality was settled as a computer–assisted proof using interval arithmetic.

The inequality concerns the Thomas–Fermi potential $V_{\mathrm{TF}}(r) = -y(r)/r$, where $y(r)$ is defined as the solution of

$$y''(x) = x^{-1/2} y^{3/2}(x), \quad y(0) = 1, \quad y(\infty) = 0. \tag{0.1}$$

Define

$$F(\Omega) = \int \left(\frac{y(x)}{x} - \frac{\Omega^2}{x^2} \right)_+^{1/2} dx, \qquad \Omega \in (0, \Omega_c),$$

where $a_+ = \max(a, 0)$, and a number Ω_c will be defined at the beginning of Section 2. The function $F(\Omega)$ depends smoothly on Ω [41], and the main result in [21] is as follows:

Theorem 0.1. *$F''(\Omega) \leq c < 0$ for all $\Omega \in (0, \Omega_c)$.*

This is a quantitative form of the non–periodicity of almost all zero–energy orbits for the Hamiltonian $H = |\xi|^2 + V_{\mathrm{TF}}(|x|)$ on $\mathbf{R}^6 = \{(x,\xi) \mid x \in \mathbf{R}^3,\ \xi \in \mathbf{R}^3\}$. In fact, an easy computation shows that a zero–energy orbit with angular momentum Ω is periodic if and only if the derivative $F'(\Omega)$ is a rational multiple of π (see [1].) Hence, Theorem 0.1 shows that closed zero–energy orbits arise for only countably many Ω.

This review will be organized as follows: first, we will present the quantum mechanical picture relevant for this theorem: this gives a meaning to Theorem 0.1, but can be skipped if the reader is not interested in its applications. Afterwards, we will present the basic computer set–up for the proof of Theorem 0.1, which will involve two main things: the rigorous solution to the Thomas–Fermi equation, and the actual computation of the function F above; the final sections of this review will be devoted to these issues.

Our review here will be just a brief sketch of the actual proof. We refer the reader to the original paper [21] for the complete details. The paper itself with the proof of Theorem 0.1, together with the complete programs used in our proof are publicly available by anonymous `ftp` from the machine `math.utexas.edu` (Internet number 128.83.133.215) Our programs are stored in the directory `/pub/papers/seco`.

1 QUANTUM MECHANICS

The ground-state energy $E(N,Z)$ for N electrons and a nucleus of charge Z is defined [1] as the infimum of the spectrum of the Hamiltonian

$$H_{NZ} = \sum_{k=1}^{N} \left(-\Delta_{x_k} - Z|x_k|^{-1}\right) + \sum_{1 \leq j < k \leq N} |x_j - x_k|^{-1},$$

acting on antisymmetric $\Psi(x_1, \ldots, x_N) \in L^2(\mathbf{R}^{3N})$. The ground-state energy of an atom is then defined as

$$E(Z) = \min_{N \geq 1} E(N,Z),$$

and our problem is to compute $E(Z)$ asymptotically for large Z. Building on the previous work of Thomas [43], Fermi [22], Dirac [6] and Scott [37] (see the

[1] In this survey we neglect electron spin to simplify notation.

survey article of Lieb [30]), Schwinger [36] proposed the refined formula

$$E(Z) \approx -c_0 Z^{7/3} + \tfrac{1}{8} Z^2 - c_1 Z^{5/3} \tag{1.1}$$

for some explicitly defined positive constants c_0, c_1. After the early work of Lieb and Simon [31] on molecules, Hughes and Siedentop-Weikard [24, 40, 41, 42] gave a rigorous proof of the "Scott conjecture", namely $E(Z) = -c_0 Z^{7/3} + \frac{1}{8} Z^2 + O(Z^\gamma)$, with $\gamma < 2$. Recently, Ivrii and Sigal [27] proved the analogue of the Scott conjecture for molecules. Our main result, announced in [14] and proved in [15, 16, 17, 18, 19, 20, 21], is as follows.

Theorem 1.1. *$E(Z) = -c_0 Z^{7/3} + \frac{1}{8} Z^2 - c_1 Z^{5/3} + O(Z^{5/3-\varepsilon_0})$ with $\varepsilon_0 = \frac{1}{2835}$.*

The starting point in discussing atoms is an elementary observation on free particles in a box. For N free particles in a box $Q \subset \mathbf{R}^3$, the minimum possible kinetic energy $\mathrm{KE}(N, Q)$ is equal to the lowest eigenvalue of $-\Delta$ acting on antisymmetric $\Psi(x_1, \cdots, x_N) \in L^2(Q^N)$ with appropriate boundary conditions. One computes $\mathrm{KE}(N, Q)$ trivially, by separation of variables. For large N, the answer is

$$\mathrm{KE}(N, Q) \approx c_{\mathrm{TF}} \rho^{5/3} |Q| \tag{1.2}$$

where $\rho = N/|Q|$ is the density of particles in the box, and c_{TF} is a universal constant.

This suggests a way to approximate the energy $\langle H_{NZ} \Psi, \Psi \rangle$ of a wave function $\Psi(x_1, \ldots, x_N)$ in terms of the electron density

$$\rho(x_1) = N \int_{\mathbf{R}^{3(N-1)}} |\Psi(x_1, x_2, \cdots, x_N)|^2 dx_2 \ldots dx_N.$$

In fact, we set

$$\mathcal{E}_{\mathrm{TF}}(\rho) = c_{\mathrm{TF}} \int_{\mathbf{R}^3} \rho^{5/3}(x) dx - \int_{\mathbf{R}^3} \frac{Z}{|x|} \rho(x) dx + \frac{1}{2} \iint_{\mathbf{R}^3 \times \mathbf{R}^3} \frac{\rho(x)\rho(y)}{|x-y|} dx dy. \tag{1.3}$$

Here, the first term on the right is an approximation to the kinetic energy motivated by (1.2), and the remaining terms on the right are simply the classical electric potential energy for a charge density ρ and a nucleus of charge Z. Thomas and Fermi independently proposed that the ground-state energy $E(Z)$ is approximately equal to the minimum of $\mathcal{E}_{\mathrm{TF}}(\rho)$ over all possible densities $\rho(x)$. Moreover, they proposed the minimizing density ρ_{TF} for (1.3) as an approximation to the electron density for an atom in its ground state. This is an immense simplification, since the original problem deals with $\Psi(x_1 \ldots x_N)$ for $N \gg 1$, while Thomas-Fermi theory deals merely with a function on $\mathbf{R}^3$. An elementary computation with the Euler-Lagrange equation for (1.3) leads to an ordinary differential equation for ρ_{TF}, which is essentially (0.1). In particular, Thomas-Fermi theory predicts that

$$E(Z) \approx -c_0 Z^{7/3},$$

which is correct as far as it goes, but much too crude.

A more refined prediction for $E(Z)$ comes from the *Hartree-Fock approximation*[2]. The idea is that since the electron density is approximately ρ_{TF}, each electron behaves as if it was moving in a potential

$$V_{\mathrm{TF}}(x) = -\frac{Z}{|x|} + \int_{\mathbf{R}^3} \frac{\rho_{\mathrm{TF}}(y)dy}{|x-y|}.$$

Therefore it is reasonable to approximate the ground-state of the true Hamiltonian H_{NZ} by that of the much simpler Hamiltonian

$$H_{\mathbf{hf}} = \sum_{k=1}^{N} \left(-\Delta_{x_k} + V_{\mathrm{TF}}(x_k)\right), \text{ acting on antisymmetric } \Psi(x_1,\ldots,x_N). \quad (1.4)$$

Unlike the original Hamiltonian, (1.4) can be diagonalized using separation of variables, and the state of lowest energy can be written explicitly in terms of the eigenfunctions of $-\Delta + V_{\mathrm{TF}}$. So again, the problem is reduced from $3N$ to 3 variables. In fact, suppose E_k are the (negative) eigenvalues of $-\Delta + V_{\mathrm{TF}}$, and let $\varphi_k(x)$ be the corresponding (normalized) eigenfunctions. Then the ground-state wave function for (1.4), which we call $\Psi_{\mathbf{hf}}$, is an antisymmetrized product of the φ_k. As an approximation to the ground-state energy of an atom, it is natural to use

$$E_{\mathbf{hf}}(Z) = \langle H_{NZ}\Psi_{\mathbf{hf}}, \Psi_{\mathbf{hf}}\rangle .$$

Note that we are using the exact Hamiltonian H_{NZ}, even though $\Psi_{\mathbf{hf}}$ arose from the simplified Hamiltonian (1.4). Elementary computation gives the formula

$$\begin{aligned} E_{\mathbf{hf}}(Z) = \operatorname{sneg}(-\Delta + V_{\mathrm{TF}}) - \tfrac{1}{2}\iint_{\mathbf{R}^3\times\mathbf{R}^3} \frac{\rho_{\mathrm{TF}}(x)\rho_{\mathrm{TF}}(y)}{|x-y|}dxdy - \\ \tfrac{1}{2}\iint_{\mathbf{R}^3\times\mathbf{R}^3} \frac{|\mathcal{S}(x,y)|^2}{|x-y|}dxdy \\ +\tfrac{1}{2}\iint_{\mathbf{R}^3\times\mathbf{R}^3} [\rho_{\mathbf{hf}}(x) - \rho_{\mathrm{TF}}(x)][\rho_{\mathbf{hf}}(y) - \rho_{\mathrm{TF}}(y)]\frac{dxdy}{|x-y|}, \end{aligned} \quad (1.5)$$

[2]This is not exactly the same as the usual Hartree-Fock approximation.

with

$$\mathrm{sneg}(-\Delta+V_{\mathrm{TF}}) = \sum_k E_k, \quad \rho_{\mathrm{hf}}(x) = \sum_k |\varphi_k(x)|^2, \quad \mathcal{S}(x,y) = \sum_k \varphi_k(x)\overline{\varphi_k(y)}.$$

To get more explicit information from (1.5), we approximate $\mathrm{sneg}(-\Delta + V_{\mathrm{TF}})$, ρ_{hf} and $\mathcal{S}$. The *semiclassical approximations* for these quantities are as follows.

$$\mathrm{sneg}(-\Delta + V_{\mathrm{TF}}) \approx -\tfrac{1}{15\pi^2} \int_{\mathbf{R}^3} |V_{\mathrm{TF}}(x)|^{5/2} dx, \qquad (1.6a)$$

$$\rho_{\mathrm{hf}}(x) \approx \tfrac{1}{6\pi^2} |V_{\mathrm{TF}}(x)|^{3/2}, \qquad (1.6b)$$

$$\tfrac{1}{2} \iint_{\mathbf{R}^3\times\mathbf{R}^3} |\mathcal{S}(x,y)|^2 \frac{dxdy}{|x-y|} \approx c_D \int_{\mathbf{R}^3} \rho_{\mathrm{TF}}^{4/3}(x) dx, \qquad (1.6c)$$

for a universal constant c_D.

We omit the motivation for (1.6a), (1.6b) and (1.6c) and content ourselves with the remark that they are closely related to Weyl's theorem on eigenvalues of the Laplacian. Formula (1.6c) and its application to atoms are due to Dirac.

Putting (1.6a), (1.6b) and (1.6c) into (1.5), we obtain the semiclassical approximation for $E_{\mathrm{hf}}(Z)$. ¿From the first two terms on the right in (1.5), we recover the Thomas-Fermi energy $-c_0 Z^{7/3}$. The third term on the right of (1.5) takes the form $-c_1' Z^{5/3}$ for a universal constant c_1'. The final term in (1.5) vanishes in the semiclassical approximation. Altogether, we have

$$E_{\mathrm{hf}}(Z) \approx -c_0 Z^{7/3} - c_1' Z^{5/3}. \qquad (1.7)$$

The last term in (1.7) is called the Dirac correction. Comparing (1.7) with the correct formula in Theorem 1.1, we see that the Z^2-term is missing from (1.7), and the $Z^{5/3}$ coefficient is wrong. The trouble is that (1.6a) is only a crude approximation.

A refined form of (1.6a) was proposed by Scott [37] and Schwinger [36]. For potentials V with a Coulomb singularity $V(x) \approx -Z|x|^{-1}$ at the origin, their formula is

$$\mathrm{sneg}(-\Delta + V) \approx -\tfrac{1}{15\pi^2} \int_{V<0} |V|^{5/2} + \tfrac{1}{8} Z^2 + \tfrac{1}{48\pi^2} \int_{V<0} |V|^{1/2} \Delta V. \qquad (1.8)$$

Scott guessed the Z^2-term by working out the elementary example

$$V(x) = E_0 - Z|x|^{-1}.$$

Schwinger deduced the last term in (1.8) from the form of the heat kernel for $e^{-t(-\Delta+V)}$, which in turn he guessed from the known case of the harmonic oscillator. Using (1.8), (1.6b) and (1.6c) to approximate the right-hand side of (1.5), we obtain Schwinger's formula (1.1) for the ground-state energy.

The rigorous comparison of $E_{\rm hf}$ with $E(Z)$ was originally done in [15], but that proof has been greatly simplified first by Bach [2] and then Graf–Solovej in [23]. Theorem 0.1 affects (1.8) as follows: Although (1.8) was guessed by Schwinger and Scott by comparison with the Hydrogen atom and the harmonic oscillator, it is easily seen that (1.8) in fact fails for these two potentials; thus, that it continues to be true for the Thomas–Fermi potential must be a deep fact. This is the aperiodicity described at the beginning of this review, which is the essential content of Theorem 0.1.

Aperiodicity of zero–energy Hamiltonian paths is well-known to play a crucial role in the study of eigenvalues and eigenfunctions. In our setting, Theorem 0.1 enters because our formulas for the eigenvalue sum and density involve expressions of the form

$$S = \sum_{1 \le l < Z^{1/3}\Omega_c} \beta\left(\frac{Z^{1/3}}{\pi} F(Z^{-1/3} l)\right)$$

for elementary functions such as $\beta(t) = t - [t] - \frac{1}{2}$. (Here $[t]$ is the greatest integer in t.) Since β is bounded, we obtain trivially the estimate $S = \mathcal{O}\left(Z^{1/3}\right)$. If $F(\Omega) = \pi\mu\Omega + \nu$ with μ rational, then the trivial estimate for S is easily seen to be the best possible. On the other hand, if $d^2F/d\Omega^2 < c < 0$, then one can prove that the numbers

$$\phi_l = Z^{1/3} F(Z^{-1/3} l)$$

are equidistributed modulo π. (The argument is close to Hardy's estimates on the number of lattice points in a disc.) Since $\beta(t)$ is periodic and has average zero, it follows that $S = \mathcal{O}(Z^{\gamma})$ with $\gamma < \frac{1}{3}$.

Thus, Theorem 0.1 allows us to improve on the trivial estimate for the sum S, which appears in the eigenvalue sum and density for $H_{\rm hf}$.

The proof of Theorem 0.1 is necessarily rather delicate. For small perturbations of $V_{\rm TF}$ in a natural topology, the analog of Theorem 0.1 fails. Therefore, we have to make strong use of the differential equation defining $y(r)$. We remark, however, that without a computer it can also be seen that F'' vanishes at most finitely many times (Proposition 4.8 in [21]; see also the independent proof in [25]), which also implies that zero–energy periodic orbits have measure zero, which in turn also implies the same results stated above for sums S, and therefore our result for atomic energies. Theorem 0.1, however, is better because it implies better error terms for all those formulas. Moreover, if one wants to understand ground–state energies to a greater accuracy, (see [3, 4, 5]), then Theorem 0.1, in its full strength, is unavoidable.

2 COMPUTER–ASSISTED SET–UP

The first issue at hand is a derivation for a formula for $F''(\Omega)$. This is not a trivial matter at first sight, since differentiation twice inside the integral sign gives rise to an unconditionally divergent integral.

To understand the formula for F'', consider the new function $u(x) = x\,y(x)$; this function has a single maximum Ω_c^2 reached at r_c, and for $\Omega \in [0, \Omega_c]$ there are two solutions, denoted by $r_1(\Omega)$ and $r_2(\Omega)$, to the equation $u(r) = \Omega^2$. Then,

$$F''(\Omega) = -\lim_{\delta \to 0} \left(\int_{r_1(\Omega)+\delta}^{r_2(\Omega)-\delta} \left(u(x) - \Omega^2\right)^{-3/2} y(x)\,dx + c(\Omega)\,\delta^{-1/2} \right), \tag{2.1}$$

where $c(\Omega)$ is uniquely specified by requiring the finiteness of the limit. Note here the delicate cancelations taking place in the limit in (2.1). The proof of (2.1) can be found in [21]. There it can also be seen that the function F in fact extends as an analytic function to a complex neighborhood of $(0, \Omega_c]$, and that F blows up like $\Omega^{-\gamma}$ at $\Omega = 0$, for $\gamma = \frac{9-\sqrt{73}}{2}$.

The proof of theorem 0.1 will be done by obtaining strictly negative uniform bounds for (2.1) on a finite number of small intervals Ω_i^* covering $(0, \Omega_c)$. This was done using *interval arithmetic*, which we now briefly review.

Let $\mathcal{R}$ be the set of "representable numbers" in a computer, that is those numbers that the computer can represent exactly. Since computers can only perform arithmetic in an approximate way, 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.

The next step is to perform a similar kind of arithmetic, where objects are functions in some Banach space, not numbers. 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. Occasionally, it will be convenient to switch to genuine real variable theory, for which we will do our work on $C^0[-1,1]$. The reason for this is that inversion of functions in $\mathbf{R}^1$ is a little easier than the complex counterpart, mainly because the domain of definition problem is trivial in the real case.

More precisely, consider the Banach Algebras

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

and

$$C^0 = \{ f(x) \,|\, f \text{ is continuous on } [-1,1] \},$$

with norms

$$\|f\|_1 = \sum_{n=0}^{\infty} |a_n|, \qquad \|f\|_\infty = \sup |f(x)|,$$

respectively. H^1 is a subspace of the set of analytic functions in the unit disk.

Our substitute for intervals in H^1 are sets (sometimes called "neighborhoods", even if they are not actually neighborhoods) $\mathcal{U}^1(I_0, \ldots, I_N; C_h, C_g; k)$ of the form

$$\left\{ f(z) = \sum_{n=0}^{\infty} a_n\, z^n + z^k g(z) \;\middle|\; a_n \in I_n,\ 0 \le n \le N,\ \sum_{n=N+1}^{\infty} |a_n| \le C_h,\ \|g\|_1 \le C_g \right\} \tag{2.2}$$

where C_h and C_g are positive real numbers and the I_n are intervals in the real line. For the computer implementation, C_h and C_g will run over the set of computer–representable numbers, and the intervals will be those with representable endpoints. We refer to C_h and C_g as high and general order error terms respectively, for obvious reasons. The number k will be referred as **type** (set to infinity if $C_g = 0$), and N will be referred to as **order** of $\mathcal{U}$. In our implementation, N will not be fixed, but chosen adaptively during the execution of the programs.

By trivial scaling, we will be able to do analysis on

$$H^1(|z - z_0| \le r) = \left\{ f(z) = \sum_{n=0}^{\infty} a_n \left(\frac{z - z_0}{r} \right)^n \;\middle|\; \sum_{n=0}^{\infty} |a_n| < \infty \right\}$$

a subspace of the set of analytic functions on the disk of center z_0 and radius r.

As for C^0, we will use sets – "neighborhoods" – of the kind

$$\mathcal{U}^0(I_0,\ldots,I_N;C_h,C_g;k;S) = \Bigg\{ f(z) = \sum_{n=0}^{N} a_n\, z^n + z^{N+1}h(z) + z^k g(z) \;\Bigg|$$

$$a_n \in I_n,\ 0 \le n \le N,\ \sup_{z\in S}|h(z)| \le C_h\ ,\ \sup_{z\in S}|g(z)| \le C_g \Bigg\} \qquad (2.3)$$

where S is a subset of $[-1,1]$, and h and g are continuous functions on S. We will use the superscript 0 or 1 whenever we want to emphasize in which topology we are taking these "neighborhoods".

The $\mathcal{U}^0$ will not allow us to perform as many operations –such as differentiation– as the smaller $\mathcal{U}^1$, but we can still add, multiply, raise to fractional powers and integrate (among others) in terms of them; furthermore, the formulas for these neighborhood operations are exactly the same as those for the $\mathcal{U}^1$. We refer the reader to [35, 39] and [21] for a description of some of these operations.

These $\mathcal{U}$ become more useful when they are rescaled appropriately and strung together: in this way, one can have complete local and global control of analytic functions defined over very large sets. This constitutes a mild novelty in this set–up, since a single variable, consisting of a pointer to an array of $\mathcal{U}$ will capture the global behavior of a piecewise analytic function.

Although computer–assisted analysis has become fairly standard, we refer the reader to [34] and [28] for a description of the basic ideas. The technique for solving ODE's is adapted from [39] and [38], and is tailored to handle our particular ODE. See [33] for a thorough discussion on ODE solving techniques, with very good general algorithms. Also, we refer the reader to [7, 8, 13, 29, 32] and [35] for a sample of computer–assisted proofs of a wide variety of problems. Main ideas in our approach go back to those proofs.

Our interval arithmetic package is an adaptation of the one used in [38] and [39], which in turn is an adaptation of the one developed by D. Rana. See [35] and [38] for details on the software.

3 THE THOMAS–FERMI EQUATION

In this section we will be concerned with the problem of getting good bounds for the solution of the Thomas–Fermi equation (0.1). The analysis will be broken into two main parts: the solution of initial value problems, and the solution of the boundary value problem. The first will be further broken into three main problems: initial value problem at 0, at infinity and elsewhere.

We will use the following well known results [26] about y:

$$-w_0 = \lim_{r \to 0} y'(r) < 0, \tag{3.1}$$

exists, and that y admits a power series expansion

$$y(r) = 144\, r^{-3} \Big(\sum_{n=0}^{\infty} b_n r^{-n\alpha} \Big), \tag{3.2}$$

convergent for r large enough, with $b_0 = 1$, $b_1 < 0$ and $\alpha = \frac{1}{2}(\sqrt{73} - 7)$. Also, y is always positive, decreasing, and it is the only such solution of the ODE satisfying (3.1) and (3.2).

The Initial Value Problem Outside the Singularities

In this section we will be concerned with the solution to the Initial Value Problem

$$u''(x) = x^{-1/2} u^{3/2}(x), \quad u(x_0) = u_0 \quad u'(x_0) = u_1 \tag{3.3}$$

for $x_0, u_0 > 0$, which can be viewed as the fixed point of

$$T(u) = u_0 + \int_{x_0}^{x} \left(u_1 + \int_{x_0}^{t} \frac{u^{3/2}(s)}{s^{1/2}}\, ds \right) dt.$$

If we regard u as

$$u(x) = u_0 + u_1 \cdot r \cdot z + z^2 f(z)$$

with $z = (x - x_0)/r$, $f \in H^1$ and r small, we see that T induces in a trivial way an operator $\tilde{T}$ of which f is its fixed point. Thus, the following algorithm is a simple consequence of the fixed point theorem on Banach spaces. The relevant norm – denoted by $\| \; \|$ – throughout this section we will be $\| \; \|_1$.

Algorithm 3.1. *We deduce conditions on u_0, u_1, x_0, r and α under which $\tilde{T}$ is a well–defined contraction in $B(0,\alpha) \subset H^1$, and we compute an upper bound for $\|\tilde{T}\|_{\mathrm{Lip}}$.*

This algorithm is then applied to the following

Algorithm 3.2. *Given appropriate intervals x^*, u_0^* and u_1^*, and representable r, we construct a neighborhood $\mathcal{U}(I_0,\ldots,I_N;0,C_g;0)$ such that for any $x_0 \in x^*$, $u_0 \in u_0^*$, and $u_1 \in u_1^*$, and any solution u of* (3.3) *with any of these initial conditions, we have*

$$u(x) = u_0 + u_1 \cdot (x - x_0) + z^2 f(z), \qquad z = \frac{x - x_0}{r},$$

for some $f \in \mathcal{U}$.

Description. First, we construct, in a heuristic way, a polynomial

$$p(z) = \sum_{i=0}^{N} p_i\, z^i,$$

which approximately solves $\tilde{T}p = p$, and we set α such that $\|p\| \le \alpha$. Next, we look for $\alpha_0 \ge \alpha$ such that the conditions on x_0, u_0, u_1, r and α_0 given by Algorithm 3.1 hold uniformly for all $x_0 \in x^*$, $u_0 \in u_0^*$ and $u_1 \in u_1^*$. Next, since f is the fixed point of $\tilde{T}$, we have

$$\|p - f\| \le \frac{\|p - \tilde{T}p\|}{1 - \|\tilde{T}\|_{\mathrm{Lip}}}$$

We get the required $\mathcal{U}$, by putting $I_i = [\,p_i\,,p_i\,]$ for $i = 0,\ldots,N$ and setting C_g equal to the ratio above. Q.E.D. This has the following easy consequence :

Algorithm 3.3. *Given disjoint intervals x_0^* and x_1^*, and intervals u_0^* and u_1^*, we construct intervals y_0^* and y_1^* such that all solutions u to (3.3) with initial values equal to any $u_0 \in u_0^*$ and any $u_1 \in u_1^*$, for any $x \in x_0^*$ are guaranteed to exist as positive solutions on $[\,x\,,x'\,]$, and furthermore satisfy*

$$u(x') \in y_0^*, \qquad u'(x') \in y_1^*,$$

for all $x' \in x_1^*$.

The Initial Value Problem at 0

It concerns the solution to the Initial Value Problem

$$u''(x) = x^{-1/2} u^{3/2}(x) \quad u(0) = 1 \quad u'(0) = -w \tag{3.4}$$

for $w > 0$, which can be viewed as the fixed point of

$$T(u) = 1 + \int_0^x \left(-w + \int_0^t \frac{u^{3/2}(s)}{s^{1/2}}\, ds \right) dt.$$

If we put

$$u(x) = 1 - w \cdot r \cdot z^2 + z^3 f(z), \tag{3.5}$$

with $z = (x/r)^{1/2}$, $f \in H^1$, and r is small, T induces again an operator $\tilde{T}$ of which f is its fixed point. After this, we just proceed in a similar manner to the previous case.

The Initial Value Problem at Infinity

This is

$$u''(x) = x^{-1/2} u^{3/2}(x) \quad u(\infty) = 0 \quad b_1 = b \tag{3.6}$$

where the last condition is interpreted in the sense of (3.2). The solution will be written as

$$u(x) = \frac{144}{x^3} \left(1 + b\, x^{-\alpha} + z^2 f(z)\right), \tag{3.7}$$

where $f \in H^1$, $z = R^\alpha x^{-\alpha}$, for some R large. If we set

$$T_1(f) = bR^{-\alpha} z + z^2 f(z)$$

$$T_2(g) = (1+g)^{3/2}$$

$$T_3(g) = 12 \sum_{n=2}^{\infty} \frac{a_n z^{n-2}}{(n\alpha+3)(n\alpha+4)}, \quad g(z) = \sum_{n\geq 0} a_n z^n.$$

A solution of (3.6) comes from an f satisfying $\tilde{T} f = f$, with $\tilde{T} = T_3 \circ T_2 \circ T_1$. As before, we would like to go ahead and check that indeed $\tilde{T}$ is a contraction, but the problem here is considerably more subtle than in the previous cases, due to the fact that T_3 does not scale with R. As a consequence, contraction properties of $\tilde{T}$ either hold or don't, and taking large R won't help much. We are lucky, however, that the norm of T_2 is essentially $\frac{3}{2}$, and that the norm of T_3 is essentially

$$\frac{12}{(2\alpha+3)(2\alpha+4)} < \tfrac{1}{2}$$

which says that the Lipschitz norm of $\tilde{T}$ will approximately be $\frac{3}{4}$. The following result is thus crucial.

Lemma 3.4. *Put $\beta = 0.3$. Assume that $|\bar{b}| = R^{-\alpha}|b| \leq 0.23$. Then $\tilde{T}$ is a contraction in $B(0,\beta)$, and $\|\tilde{T}\|_{\mathrm{Lip}} \leq 0.8652$.*

Once this is settled, everything proceeds as before, and we can easily conclude the following:

Algorithm 3.5. *Given b^* (interval) and R (representable), we produce $\mathcal{U}_1$ such that, for any $b \in b^*$, the solution u of (3.6) is given by*

$$y(x) = \frac{144}{x^3}\left(1 + bx^{-\alpha} + z^2 f(z)\right), \qquad z = R^{\alpha}x^{-\alpha},$$

with $f \in \mathcal{U}_1$. Here, $\mathcal{U}_1$ depends only on b^*, i.e., it is independent of which particular b in b^* we are considering. In particular, we can produce two intervals u_0^* and u_1^* such that, if u is the solution to (3.6), we have $u(R) \in u_0^*$ and $u'(R) \in u_1^*$.

The Boundary Value Problem

Next we discuss how to solve

$$u''(x) = x^{-1/2} u^{3/2}(x) \quad u(0) = 1 \quad u(\infty) = 0.$$

Unlike the previous section, we will avoid a serious formulation of the method (which becomes a little technical), and instead we concentrate on the main simple ideas.

What we will be using here is a rigorous variant of the *shooting* method: we will begin making a heuristic guess for, say, $y'(0)$, and we will then follow the solution forward until it violates one of the properties we know to be true for the true Thomas–Fermi function: this will determine whether our choice was an upper bound or a lower bound for the actual value for $y'(0)$. This yields bounds for $-w_0 = y'(0)$. We then carry out a similar procedure at ∞. Let's get into a little more detail:

Pick a value w and, with the aid of the algorithms in the previous section, obtain bounds for the solution of

$$u''(x) = x^{-1/2} u^{3/2}(x) \quad u(0) = 1 \quad u'(0) = -w,$$

around small intervals covering, say, $[0, M]$. If, at some point, we can deduce using these bounds that u is increasing, a trivial ODE analysis shows that this choice w is a *lower* bound for $w_0 = -y'(0)$. If however, the solution vanished, the same trivial ODE analysis yields that $w_0 < w$. The problem here is that the computer alone won't ever be able to tell us that the solution vanishes, since it needs it to be positive to perform the different algorithms above: so, in practice, even if the solution would vanish at some point, the computer will just require, at each step, smaller and smaller intervals to propagate the solution forward, without ever giving negative bounds for $u(x)$. Hence, the following simple lemma is helpful:

Lemma 3.6. *Let u be the solution of* (3.3), *with $u_1 < 0$. If*

$$\frac{2u_0^{5/2}}{x_0^{1/2}} \leq u_1^2, \tag{3.8}$$

then, there exists a point $t > x_0$ such that u can be extended as a well–defined positive solution of the ODE to $[x_0, t)$ and, furthermore, $\inf_{x \in (x_0, t)} u(x) = 0$.

As a consequence, the word *vanishes* used above is simply replaced by the more feasible property (3.8), and we obtain the following

Algorithm 3.7. *Given a representable w, we construct an algorithm that, if successful, will indicate whether $w < w_0$ or $w > w_0$. Hence, given appropriate $x_i \in \mathcal{R}$, we can produce y_i^* and $y'^*_i \in \mathcal{I}$, $i = 0, \ldots, m$, such that*

$$y(x_i) \in y_i^*, \qquad y'(x_i) \in y'^*_i, \qquad i = 0, \ldots, m.$$

We now do the same at infinity.

Algorithm 3.8. *Given a representable b, and assuming bounds for w_0, we construct an algorithm that, if successful, will indicate whether $b < b_1$ or $b > b_1$. Next, we use these bounds to produce $x_i \in \mathcal{R}$, and y_i^*, $y'^*_i \in \mathcal{I}$, $i = 1, \ldots, m$, such that*

$$y(x_i) \in y_i^*, \qquad y'(x_i) \in y'^*_i, \qquad i = 1, \ldots, m.$$

The details are easy. In fact we can use the extra information given by Algorithm 3.3 to detect easily when the test solution goes beyond bounds. Note that afterwards we can take the best of the two sources of information about the Thomas–Fermi function, coming from 0 or from infinity.

A delicate point here is the choice of the x_i above, but we refer the interested reader to [21] for details.

Note also that the refined bounds for u given by Algorithm 3.8, allow us to sharpen our bounds for w_0. These improved bounds for w_0 will in turn improve on the older bounds for b_1, and we are all set for a recursive algorithm, the result of which is quite precise bounds for the Thomas–Fermi function:

Algorithm 3.9. *We can produce x_i, $r_i \in \mathcal{R}$, and*

$$\mathcal{U}_i(I_0^i, \ldots, I_N^i; C_{h,i}, C_{g,i}, 2), \qquad i = 1, \ldots, m,$$

such that

$$y(x_i + z \cdot r_i) \in \mathcal{U}_i(I_0^i, \ldots, I_N^i; C_{h,i}, C_{g,i}, 2), \qquad i = 1, \ldots, m,$$

and

$$\bigcup_{i=1}^{m} (x_i - r_i, x_i + r_i) = (x_1 - r_1, x_m + r_m) \subset (0, \infty)$$

What follows is some rigorous numerical values we obtained for several Thomas–Fermi parameters.

Lemma 3.10. *The following inequalities hold:*

$$1.588071022611278 \leq w_0 \leq 1.588071022611471$$

$$-13.2709738479 \geq b_1 \geq -13.2709738482$$

$$0.486348538043594 \leq \Omega_c^2 \leq 0.486348538046869$$

$$2.104025280219 \leq r_c \leq 2.104025280274$$

4 THE APERIODICITY INEQUALITY

Once we have appropriate bounds for the Thomas–Fermi function, the next step is to use them to prove Theorem 0.1.

There is the straightforward approach of simply computing expression (2.1) for a finite collection of small intervals Ω_i^* which cover all of $(0,\Omega)_c$. As we will see here, this will work with more or less trivial modifications only for for intervals which are not near 0 or Ω_c; intervals near 0 will require a more sophisticated approach to computing (2.1), but near Ω_c we will have to use a completely different approach. This section explains the analysis involved in the computation of F'' for the different Ω_i^*.

Case 1

We begin with the computation of $F''(\Omega^*)$ for Ω^* sufficiently far from 0 and Ω_c. Use (2.1) to write $F(\Omega) = I_1(\Omega) + I_2(\Omega) + I_3(\Omega)$ with

$$I_1 = \int_a^b \left(u(r) - \Omega^2\right)^{-3/2} y(r)\, dr \tag{4.1a}$$

$$I_2 = \lim_{\delta\to 0}\left(\int_{r_1(\Omega)+\delta}^{a} \left(u(r) - \Omega^2\right)^{-3/2} y(r)\, dr - G_1(\Omega)\delta^{-1/2}\right) \tag{4.1b}$$

$$I_3 = \lim_{\delta\to 0}\left(\int_{b}^{r_2(\Omega)-\delta} \left(u(r) - \Omega^2\right)^{-3/2} y(r)\, dr - G_2(\Omega)\delta^{-1/2}\right) \tag{4.1c}$$

with the G_i such that the limit is finite, and $a < b$ carefully chosen.

The computation of I_1 seems to be rather easy at first sight: we just break up

$$I_1 = \sum_{i=1}^{n} \int_{t_i}^{t_{i+1}} \left(u(r) - \Omega^2\right)^{-3/2} y(r)\, dr,$$

with $t_1 = a$ and $t_{n+1} = b$. This involves only basic operations with u and thus feasible with the standard interval arithmetic packages. A deeper issue is that of speed: it turns out that we will be forced to take the intervals Ω_i^* very small, and thus need to compute I_1 many times; in fact, so many that the direct computation approach fails due to time considerations, and we are forced to use a certain amount of trickery which we will omit here.

The computation of I_2 and I_3 is much easier: we use Algorithm 3.2 to compute $\mathcal{U}_1$ such that

$$u(x) = \Omega^2 + z f(z), \qquad z = \frac{x - r_1(\Omega)}{r}, \qquad f \in \mathcal{U}_1, \tag{4.2}$$

where $r \geq |a - r_1(\Omega)|$ and $\mathcal{U}_1$ is uniform for all $\Omega \in \Omega^*$. Therefore,

$$\int_{r_1(\Omega)+\delta}^{a} \left(u(x) - \Omega^2\right)^{-3/2} y(x)\, dx = \int_{r_1(\Omega)+\delta}^{a} z^{-3/2} \tilde{f}(z)\, dx,$$

for a new function $\tilde{f}(z) = y(x) f^{-3/2}(z)$, that can also be enclosed in a computable $\mathcal{U}$. Thus, if

$$\tilde{f}(z) = \sum_{n \geq 0} a_n z^n \in \mathcal{U}(J_0, \ldots, J_N; C_h, C_g; 1),$$

we see that

$$\int_{r_1(\Omega)+\delta}^{a} \left(u(x) - \Omega^2\right)^{-3/2} y(x)\, dx = r \sum_{n \geq 0} \frac{a_n}{n - \frac{1}{2}}\, z^{n-\frac{1}{2}} \Bigg|_{z=\frac{\delta}{r}}^{z=\frac{a-r_1(\Omega)}{r}},$$

which implies

$$I_2 \in r \cdot \sum_{n=0}^{N} \frac{J_n}{n - \frac{1}{2}} \left(\frac{a - r_1(\Omega)}{r}\right)^{n-\frac{1}{2}} \pm \epsilon,$$

with $|\epsilon| \leq r\left(\frac{C_h}{N+\frac{1}{2}} + 2C_g\right)$. I_3 is done in a similar manner.

Case 2

The problem now is that when Ω is small, (4.2) would have to be done either very far (for I_3) of very close to 0 (for I_2), and this is impractical. The answer to this degenerate case goes through the change of variables given by $r(t)$, the inverse of u around 0 for I_2, and around infinity for I_3; we will concentrate here on I_2. This change of variables yields

$$I_2 = \frac{d}{d\Omega}\left(\Omega \int_{r_1(\Omega)}^{a} \left(u(r) - \Omega^2\right)^{-1/2} \frac{dr}{r}\right) = \frac{d}{d\Omega}\left(\Omega \int_{\Omega^2}^{u(a)} \left(t - \Omega^2\right)^{-1/2} w(t)\, dt\right),$$

for $w(t) = r'(t)/r(t)$. The first step is therefore to compute w, which hinges on the following inversion algorithm.

Algorithm 4.1. *Given $N \geq 0$, we produce intervals $a_2^*, \ldots, a_N^*$, and a constant C_N, such that*

$$\left| r(t) - t\Bigl(1 + \sum_{n=2}^{N} a_n \bar{t}^{\,n}\Bigr) \right| \leq C_N\, t \cdot \bar{t}^{\,N+1}, \quad \bar{t} = \left(\frac{t}{x_0}\right)^{1/2},$$

for constants $a_i \in a_i^*$, $i = 2, \ldots, N$, and for $t \leq \eta$.

The point to realize here is that the function $u(x)$ is not analytic either around 0 (where it is still is analytic in $\sqrt{x}$), and is even worse around infinity, where it is a combination of x^{-2} and powers of $x^{(7-\sqrt{73})/2}$. In spite of the fact that this function is not analytic, we can in principle design an algorithm for this case by combining different manipulations with analytic functions. However, it turns out to be more effective to switch here to genuine real variable theory, and to use the Banach algebra C^0 instead of analytic functions. As a consequence, the calculation of the derivatives has to be dealt with in a different manner than before. Of course we omit all details, and simply state the main final result:

Algorithm 4.2. *We produce a neighborhood $\mathcal{U}^0(I_0, \ldots, I_N; C_h, 0; \infty)$ such that*

$$h(t) \stackrel{\text{def}}{\equiv} t\, w'(t) + w(t) = f(\bar{t}), \qquad f \in \mathcal{U}^0,$$

for $t \leq \eta$.

Say then that

$$f_h(\bar{t}) = \sum_{n=0}^{N} a_n \bar{t}^{\,n} + H(\bar{t}), \quad |H(\bar{t})| \leq \varepsilon_h\, |\bar{t}|^{N+1}, \quad 0 < t \leq \eta,$$

for a_n in computable intervals and ε_n bounded by a computable number. Then

$$\frac{d}{d\Omega}\left(\Omega \int_{r_1(\Omega)}^{\delta} \left(u(r) - \Omega^2\right)^{-1/2} \frac{dr}{r}\right) = \frac{d}{d\Omega}\left(\Omega^2 \int_1^{\Omega^{-2}u(\delta)} (t-1)^{-1/2}\, w(t\Omega^2)\, dt\right)$$

$$= 2\Omega \int_1^{\Omega^{-2}u(\delta)} (t-1)^{-1/2}\, h(t\Omega^2)\, dt - 2\left(u(\delta) - \Omega^2\right)^{-1/2} w(u(\delta))u(\delta)$$

$$= 2\Omega \sum_{n=0}^{N} a_n x_0^{-n/2} \Omega^n \int_1^{\Omega^{-2}u(\delta)} (t-1)^{-1/2}\, t^{\frac{n}{2}}\, dt + \tilde{h}(\Omega) - \left(u(\delta) - \Omega^2\right)^{-1/2} \frac{2u(\delta)}{\delta\, u'(\delta)}, \tag{4.3a}$$

with

$$\left|\tilde{h}(\Omega)\right| \leq 2\Omega^{N+2}\epsilon_h x_0{}^{-\frac{(N+1)}{2}} \int_1^{\Omega^{-2}u(\delta)} (t-1)^{-1/2}\, t^{\frac{(N+1)}{2}}\, dt \tag{4.3b}$$

This formula, and a similar formula for I_3, allow us to compute I_2 and I_3 for many small Ω^*. There is a limit again, however, since as $\Omega \to 0$ the integrals above are extended over an intervals spreading to infinity. This calls for a final – but fortunately easy – analysis to control these integrals for very small Ω^*. We simply state that this can be done and refer the interested reader to [21] for all the details.

Case 3

We are finally left with the proof that $F''(\Omega) \leq c < 0$ for Ω sufficiently close to Ω_c. The previous method fails for these Ω mainly because the derivatives of u at the crossing points r_i degenerate to 0. The idea here is to change the approach completely, and consider the change of variables given by $r(t)$, the inverse of $t(r) = \pm\sqrt{\Omega_c^2 - u(r)}$, which allows us to rewrite

$$-F'(\Omega) = \Omega \int_{-1}^{1} (1-t^2)^{-1/2}\, w(Dt)\, dt, \quad w(t) = \frac{r(t)}{r(t)}, \quad D^2 = \Omega_c^2 - \Omega^2. \tag{4.4}$$

The main difficulty here is to gain control over the function $r(t)$ (or $w(t)$), which is done via the following technical lemma in complex variables.

Lemma 4.3. *Let $u \in H^1(|z - r_c| \leq R)$, smooth on the boundary of $B(r_c, R)$, of the form*

$$u(x) = \Omega_c^2 - u_2 R^2\, z^2 + z^3 f(z), \qquad z = \frac{x - r_c}{R}, \qquad f(0) = u_3\, R^3,$$

satisfying

1. $\|f\| \leq h$, $u_2 > 0$ *and* $u_2 R^2 > h$.
2. *For a constant M we have* $\left|u^{(4)}(x)\right| \leq M$ *for* $|z| \leq 1$.

Then, $t(x)$ can be extended analytically to $B(r_c, R)$, and there is an inverse $r(w)$ of $t(x)$, analytic in $|w| < T$, where $T \leq \sqrt{u_2 R^2 - h}$ and

$$\sup_{|w| \leq T} |r'(w)| \leq \frac{2\sqrt{u_2 + hR^{-2}}}{2u_2 - 3\,|u_3|\,R - \frac{1}{6}MR^2}$$

$$\left|\frac{d^{n+1}r}{dw^{n+1}}(0)\right| \leq n!\,T^{-n}\,\frac{2\sqrt{u_2 + hR^{-2}}}{2u_2 - 3\,|u_3|\,R - \frac{1}{6}MR^2} \qquad n \geq 0$$

As a consequence, we obtain the following:

Algorithm 4.4. *Set $u(x) = \Omega_c^2 - z^2 f(z)$, with $z = (x - r_c)/R$. If we know that $f \in \mathcal{U}_0(I_0, \ldots, I_{2N+1}; C_h, 0; \infty)$ and that $A^0 \leq |y(x)| \leq A_0$ when $|x - r_c| \leq R$, for bounds $A^0 < A_0$, we can then construct T and $\mathcal{U}_1$, such that $w(t) = g(t/T)$, with $g \in \mathcal{U}_1$. We use this to compute a bound for F'' sufficiently close to Ω_c.*

Description. The construction of $\mathcal{U}_1$ is rather easy from the lemma above. Therefore, we know that $w(t) = \sum w_n (t/T)^n$ and we have good control on the w_n. We insert this into (4.4) to obtain

$$-\tfrac{1}{\pi}F'(\Omega) = \Omega \sum_{n=0}^{N} w_{2n} \left(\frac{D}{T}\right)^{2n} \alpha_n + \Omega \sum_{n>N} w_{2n} \left(\frac{D}{T}\right)^{2n} \alpha_n,$$

with

$$\alpha_n = \frac{1}{\pi}\int_{-1}^{1} (1 - t^2)^{-1/2} t^{2n}\, dt = \binom{2n}{n} 2^{-2n}. \tag{5.5}$$

The first term above is computed and the second is just an error term, which is easily estimated in absolute value from above. Q.E.D.

Acknowledgements

Charles L. Fefferman was partially supported by an NSF grant at Princeton University.

REFERENCES

[1] V. Arnold, *Mathematical Methods of Classical Mechanics*, Graduate Texts in Math. No. 60, Springer-Verlag, N.Y., 1978.

[2] V. Bach, "Accuracy of Mean Field Approximations for Atoms and Molecules", *Comm. Math. Phys.*, 1993, Vol. 155, No. 2, pp. 295–310.

[3] A. Córdoba, C. Fefferman, and L. Seco, "A Trigonometric Sum relevant to the Non–relativistic Theory of Atoms", *Proc. Nat. Acad. Sci. USA*, June 1994, Vol. 91, pp. 5776–5778.

[4] A. Córdoba, C. Fefferman, and L. Seco, "Weyl Sums and Atomic Energy Oscillations", *Revista Matemática Iberoamericana*, 1995, Vol. 11, No. 1, pp. 167–228.

[5] A. Córdoba, C. Fefferman, and L. Seco, "A Number–Theoretic Estimate for the Thomas–Fermi Density", 1995 (to appear).

[6] P. Dirac, "Note on Exchange Phenomena in the Thomas–Fermi Atom", *Proc. Cambridge Philos. Soc.*, 1930, Vol. 26, pp. 376—385.

[7] J. P. Eckmann, H. Koch, and P. Wittwer, *A computer Assisted Proof of Universality in Area Preserving Maps*, Memoirs A.M.S., Vol 289, American Mathematical Society, Providence, R.I., 1984.

[8] J. P. Eckmann and P. Wittwer, *Computer Methods and Borel Summability Applied to Feigenbaum's equation*, Lecture Notes in Mathematics, Vol. 227, Springer-Verlag, N.Y., 1985.

[9] C. Falcolini, C. Fefferman, and R. Llave, In preparation.

[10] C. Fefferman, "Atoms and Analytic Number Theory", In: *A.M.S. Centennial Publication, Vol. II*, American Math. Society, Providence, RI, 1992, p. 27–36.

[11] C. Fefferman, "The Atomic and Molecular Structure of Matter", *Revista Matemática Iberoamericana*, 1985, Vol. 1, No. 1, pp. 1–44.

[12] C. Fefferman, "The N–Body Problem in Quantum Mechanics", *Comm. Pure and Appl. Math.*, 1986, Vol. 39, No. S, pp. S67–S110.

[13] C. Fefferman and R. Llave, "Relativistic Stability of Matter, I", *Revista Matematica Iberoamericana*, 1986, Vol. 2, No. 1&2, pp. 119–213.

[14] C. Fefferman and L. Seco, "The Ground–State Energy of a Large Atom", *Bull. A.M.S.*, 1990, Vol. 23, No. 2, pp. 525—530.

[15] C. Fefferman and L. Seco, "Eigenvalues and Eigenfunctions of Ordinary Differential Operators", *Adv. Math.*, 1992, Vol. 95, No. 2, pp. 145–305.

[16] C. Fefferman and L. Seco, "The Eigenvalue Sum for a One–Dimensional Potential", *Advances in Math*, Oct. 1994, Vol. 108, No. 2, pp. 263–335.

[17] C. Fefferman and L. Seco, "The Density in a One-Dimensional Potential", *Advances in Math.*, Sept. 1994, Vol. 107, No. 2, pp. 187–364.

[18] C. Fefferman and L. Seco, "The Eigenvalue Sum for a Three–Dimensional Radial Potential", *Advances in Math.*, 1995 (to appear).

[19] C. Fefferman and L. Seco, "The Density in a Three–Dimensional Radial Potential", *Advances in Math.*, 1995 (to appear).

[20] C. Fefferman and L. Seco, "On the Dirac and Schwinger Corrections to the Ground–State Energy of an Atom", *Advances in Math.*, Aug. 1994, Vol. 107, No. 1, pp. 1–185.

[21] C. Fefferman and L. Seco, "Aperiodicity of the Hamiltonian Flow in the Thomas–Fermi Potential", *Revista Matemática Iberoamericana*, 1993, Vol. 9, No. 3, pp. 409–551.

[22] E. Fermi, "Un Metodo Statistico per la Determinazione di alcune Priorieta dell'Atome", *Rend. Accad. Naz. Lincei*, 1927, Vol. 6, pp. 602—607.

[23] G. M. Graf and J. P. Solovej, "A Correlation Estimate with Applications to Quantum Systems with Coulomb Interactions", *Reviews in Math. Phys.*, 1994, Vol. 6, No. 5a, pp. 977–997.

[24] W. Hughes, "An Atomic Energy Lower Bound that Agrees with Scott's Correction", *Advances in Mathematics*, 1990, Vol. 79, pp. 213–270.

[25] B. Helffer, A. Knauf, H. Siedentop, and R. Weikard, "On the Absence of a First Order Correction for the Number of Bound States of a Schrödinger Operator with Coulomb Singularity", *Comm. P.D.E.*, 1992, Vol. 17, No. 3&4, pp. 615–639.

[26] E. Hille, "On the Thomas–Fermi Equation", *Proc. Nat. Acad. Sci. USA*, 1969, Vol. 62, pp. 7—10.

[27] V. Ivrii and I. M. Sigal, "Asymptotics of the Ground State Energies of Large Coulomb Systems", *Annals of Math.*, 1993, Vol. 138, No. 2, pp. 243–335.

[28] E. W. Kaucher and W. L. Miranker, *Self-validating Numerics for Function Space Problems*, Academic Press, N.Y., 1984.

[29] O. Lanford, "A Computer–Assisted Proof of the Feigenbaum Conjecture", *Bull. AMS*, 1986, Vol. 6, pp. 427–434.

[30] E. Lieb, "Thomas–Fermi and Related Theories of Atoms and Molecules", *Reviews of Modern Physics*, 1981, Vol. 53, No. 4, pp. 603–641.

[31] E. Lieb and B. Simon, "Thomas–Fermi Theory of Atoms, Molecules and Solids", *Adv. Math.*, 1977, Vol. 23, pp. 22—116.

[32] R. Llave, "Computer Assisted Bounds in Stability of Matter", *Computer Aided Proofs in Analysis*, IMA Series in Math. and Appl., Vol 28, Springer, Cincinatti, 1989.

[33] R. Lohner, *Einschließung der Lösung gewöhnlicher Anfangs– und Randwertaufgaben und Anwendungen*, Dissertation, Universität Karlsruhe (TH), 1988.

[34] R. E. Moore, *Methods and Applications of Interval Analysis*, SIAM, Philadelphia, PA, 1979.

[35] D. Rana, *Proof of Accurate Upper and Lower Bounds for Stability Domains in Denominator Problems*, Thesis, Princeton University, 1987.

[36] J. Schwinger, "Thomas–Fermi Model: The Second Correction", *Physical Review*, 1981, Vol. A24, No. 5, pp. 2353—2361.

[37] J. M. C. Scott, "The Binding Energy of the Thomas–Fermi Atom", *Phil. Mag.*, 1952, Vol. 43, pp. 859—867.

[38] L. Seco, "Lower Bounds for the Ground State Energy of Atoms", Thesis, Princeton University, 1989.

[39] L. Seco, "Computer Assisted Lower Bounds for Atomic Energies", *Computer Aided Proofs in Analysis*, IMA Series in Math. and Appl., Vol 28, Springer, Cincinatti, 1989, pp. 241—251.

[40] H. Siedentop and R. Weikard, "On the Leading Energy Correction for the Statistical Model of the Atom: Interacting Case", *Communications in Mathematical Physics*, 1987, Vol. 112, pp. 471–490.

[41] H. Siedentop and R. Weikard, "On the Leading Correction of the Thomas–Fermi Model: Lower Bound", and an appendix by A. M. K. Müller, *Inv. Math.*, 1989, Vol. 97, pp. 159–193.

[42] H. Siedentop and R. Weikard, "A New Phase Space Localization Technique with Applications to the Sum of Negative Eigenvalues of Schrödinger Operators", *Ann. Scient. Ecole Normale Superieure*, 1991, Vol. 24, pp. 215–225.

[43] L. H. Thomas, "The Calculation of Atomic Fields", *Proc. Cambridge Philos. Soc.*, 1927, Vol. 23, pp. 542—548.