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Arithmetic Aspects of Atomic Structures

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Introduction

After the initial success to explain the hydrogen atom, one of the early challenges of quantum mechanics was to study larger atoms. The problems encountered in this process were numerous, and the quest for an understanding quickly became a search for simplified quantum atomic models that would explain different properties of the atom. This study generated a vast theory with ramifications in many areas of physics and specially mathematics, including some which will be reviewed in this presentation: semi-classical asymptotics, field theories, potential theory, computational issues and analytic number theory.

An atom of nuclear charge Z fixed at the origin, and N quantized electrons at positions $x_i \in \mathbf{R}^3$ is described by the hamiltonian

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

acting on antisymmetric functions in $L^2(\mathbf{R}^{3N})$ (in order to simplify our discussion we omit spin considerations). The atomic energies are defined as

$$E(Z, N) = \inf_{\|\psi\|=1} \langle \psi, H_{Z,N} \psi \rangle, \qquad E(Z) = \inf_{N \geq 0} E(Z, N).$$

The energy $E(Z, N)$ is non–increasing as a function of N, and it attains a minimum at some critical N_c, which represents the largest number of electrons an atom can bind (see [Ru], [Si], [L3], [L4], [LSST] and [FS9]).

The ground state Ψ is the eigenfunction with eigenvalue $E(Z)$. Its density is defined as

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

One of the earliest and most successful attempts at a simplified model was Thomas–Fermi theory, which is well–known in the Mathematical Physics community, but which we will nevertheless review later. According to it the atomic energy $E(Z)$ and density $\rho^Z(x)$ of an atom of charge Z behave as

$$E(Z) \approx c_{\mathrm{TF}} Z^{7/3}, \qquad \rho^Z(x) \sim \rho_{\mathrm{TF}}^Z(x) = Z^2 \rho_{\mathrm{TF}}^1 \left(Z^{1/3} x \right), \tag{1}$$

for a suitable explicit constant c_{TF} and universal (Z–independent) function ρ_{TF}^1. In other words, it provides an extremely simple picture of the different atoms, as they are all rescaled versions of each other. While this simple picture is often useful, it has tragic consequences when one takes it too far, such as the no–binding theorem (see [L1] for a complete account of Thomas–Fermi theory).

Associated with the density there is also the Thomas–Fermi potential V_{TF}^Z, satisfying also a perfect scaling condition

$$V_{\mathrm{TF}}^Z(r) = Z^{4/3} V_{\mathrm{TF}}^1 \left(Z^{1/3} \cdot r \right). \tag{2}$$

The problem to understand Thomas–Fermi theory mathematically was tackled in 1973 with the work of Lieb and Simon (see [LS] and [L1]), which is now a central piece in modern mathematical physics. In their setting, large atoms were viewed as a limit $Z \to \infty$. Since then, large–Z asymptotics have become the mathematical paradigm of

large atoms. In particular, the work of Lieb and Simon proves that (1) is the leading expression as $Z \to \infty$.

In this circle of ideas, the result that generated much of the ideas presented in this review is

$$E(Z) = -c_{\mathrm{TF}} Z^{7/3} + \tfrac{1}{8} Z^2 - c_s Z^{5/3} + \mathcal{O}\left(Z^{\frac{5}{3} - a} \right), \qquad a > 0, \tag{3}$$

which is to be understood from the point of view of large–Z asymptotics stated above. The first term in (3) was introduced by Thomas and Fermi in [T], [Fer], and proved rigorously in [LS] as part of their proof of (1) above. The Z^2 term was discovered by Scott in [Sco] and proved to be true in a series of papers by Hughes–Siedentop–Weikard, in [Hug], [SW1], [SW2] and [SW3]. Its generalization to molecules was obtained by Ivrii–Sigal ([IS]). The $Z^{5/3}$ term was obtained by Schwinger in [Sch], and proved to be correct in [FS1], [FS2], [FS3], [FS4], [FS5], [FS6], [FS7] and [FS8].

The purpose of this presentation is to give an updated account of some on–going work related to the theory of large atoms in the context of large–Z asymptotics, which began over the last decade or so, and relate to the proof of (3) above. The goal of that work is to produce a refined version of the Thomas–Fermi theory that accounts for observed physical features such as electronic orbitals or an atomic shell structure. This will present similarities with issues in quantum chaos.

This article contains a combination of rigorous mathematical results with others of a more speculative nature and more physical content. The bibliography, necessarily incomplete, contains numerous missing pieces that this brief overview lacks.

Mean–Field Theory

The analysis of (3) begins with the development of a simplified picture of $H_{Z,N}$ through estimates of the type

$$H_{Z,N} \approx \sum_{j=1}^{N} H_i + \text{constants} + \text{errors},$$

where H_i is a hamiltonian acting only on the i'th electron; *errors* will account for different degrees of approximation. This would be an immense simplification, since

the original N–body hamiltonian is now replaced by a superposition of one particle hamiltonians, and the spectral properties of $H_{Z,N}$ are therefore reduced to those of H_i.

Such inequalities will obviously follow from a rigorous replacement of the repulsion terms by more manageable expressions of the type

$$\frac{1}{2} \sum_{i \neq j} \frac{1}{|x_i - x_j|} \sim \sum_{i=1}^{N} V(x_i) - \text{constants}, \tag{4}$$

modulo small error terms.

Physically, one would argue for such formulas as follows: assume that the electronic distribution of a wave function ψ is given by a density function ρ: one then expects the repulsion term to be approximately

$$\left\langle \psi, \frac{1}{2} \sum_{i \neq j} \frac{1}{|x_i - x_j|} \psi \right\rangle \approx \left\langle \sum_{i=1}^{N} \int_{\mathbf{R}^3} \frac{\rho(y)}{|x_i - y|} \, dy, \psi \right\rangle - \frac{1}{2} \int_{\mathbf{R}^3 \times \mathbf{R}^3} \frac{\rho(x)\,\rho(y)}{|x - y|} \, dx \, dy,$$

where the last term accounts for the non–quantum effect appearing in the right hand side of electrons interacting with themselves: for this reason it is referred to as the self–energy term. This would then be the origin of (4), with

$$V(x) = \int_{\mathbf{R}^3} \frac{\rho(y)\,dy}{|x - y|}.$$

Note that the choice of V depends on ρ, which was assumed to be related to the density of the true atomic ground–state. This self–consistency requirement will be a recurring theme in this review; the Thomas–Fermi theory then appears as the leading resolution of atomic self–consistency issues.

The first such rigorous results in this direction go back to Lieb and his collaborators and are by now well–known in the mathematical physics folklore as Lieb's formulas. In order to understand the significance of the various issues, observe that the rescaling properties (1) and (2) have the following conceptual implications: most electrons are at a distance to the nucleus of about $Z^{-1/3}$, and the distance to the closest electron neighbor is about $Z^{-2/3}$. This is the basic size rescaling of the atom. Based on this, we now introduce one of the different disguises of Lieb's inequality:

Theorem (Lieb's inequality): *Assume* $\psi(x_1, \ldots, x_N)$, $(Z \leq N \leq 2Z)$ *is such that*

$$\|\nabla\psi\|_2^2 \leq C\, Z^{7/3}.$$

Then, we have

$$\langle H_{Z,N}\, \psi, \psi \rangle \geq \langle H_{Z,N}^{\text{ind}}\psi, \psi \rangle - \tfrac{1}{2} \iint \frac{\rho_{\text{TF}}(x)\, \rho_{\text{TF}}(y)}{|x-y|}\, dx\, dy - C'\, Z^{5/3},$$

where

$$H_{Z,N}^{\text{ind}} = \sum_{i=1}^{N} \left\{ -\Delta_{x_i} - V_{\text{TF}}(x_i) \right\}.$$

The proof of this result can be found in Lemma 2 in [SW2]. A recurring theme in the rigorous theory of atomic energies is that upper bounds are comparatively easier than lower bounds, as one can use variational arguments to derive them. Thus, the lower bound in Lieb's inequality is the center issue.

In order to understand what's involved in Lieb's inequalities, and in order to get a feeling for the relevance of improvements of it (which will be crucial for most of the results in this article), we present the following argument.

Begin with the following elementary identity

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

Except for the constant $\frac{1}{\pi}$, which requires a calculation, the rest of the formula is obvious by rotational, translational and dilation invariance. An immediate consequence is

$$\frac{1}{2} \sum_{i \neq j} \frac{1}{|x_i - x_j|} = \frac{1}{2\pi} \iint_{\substack{z \in \mathbf{R}^3 \\ R>0}} \mathcal{N}(\mathcal{N}-1)\, \frac{dz\, dR}{R^5}, \tag{5}$$

where

$$\mathcal{N} = \sum_{i=1}^{N} \chi_{B(z,R)}(x_i), \tag{6}$$

is the number of electrons in the ball $B(z, R)$, and hence a function of all $x_1, \ldots, x_N$, z and R. If we approximate $\mathcal{N}$ by an average of some sort, for instance

$$\bar{N} = \int_{\mathbf{R}^3} \rho_{\mathrm{TF}}(x) \, dx,$$

$\bar{N}$ is now independent of the electron locations $x_1, \ldots, x_N$, and we obtain the rigorous identity

$$\frac{1}{2} \sum_{i \neq j} \frac{1}{|x_i - x_j|} = \frac{1}{2\pi} \iint_{\substack{z \in \mathbf{R}^3 \\ R > 0}} \left\{ (\mathcal{N} - \bar{N})^2 \ + \ 2\mathcal{N}(\bar{N} - 1) \ - \ \bar{N}^2 \right\} \frac{dz \, dR}{R^5},$$

which, dropping the square term, yields

$$\frac{1}{2} \sum_{i \neq j} \frac{1}{|x_i - x_j|} \geq \frac{1}{2\pi} \iint_{\substack{z \in \mathbf{R}^3 \\ R > 0}} \left\{ 2\mathcal{N}(\bar{N} - 1) \ - \ \bar{N}^2 \right\} \frac{dz \, dR}{R^5}. \tag{7}$$

Using (6), this is easily recognized as a version of Lieb's inequality.

The error term in Lieb's inequalities, must therefore be of the order of

$$\mathrm{Error} = \iint_{\substack{z \in \mathbf{R}^3 \\ R > 0}} (\mathcal{N} - \bar{N})^2 \, \frac{dz \, dR}{R^5},$$

If we assumed electrons to be independent, $(\mathcal{N} - \bar{N})^2$ would be a variance, therefore comparable to $\bar{N}$, the expected number of electrons in the ball of radius R about z. Since most electrons are at a distance of about $Z^{-1/3}$ to the nucleus, and the nearest neighbor is at a distance of about $Z^{-2/3}$, we can argue that

$$\mathrm{Error} \approx \frac{N}{\text{distance to nearest neighbor}} \approx Z^{5/3}.$$

This is the size of the error term in Lieb's inequality.

Improvements of Lieb's inequality, thus, amount to the analysis of the variances $(\mathcal{N} - \bar{N})^2$, which in turn reduce to the analysis of inter–electron correlations. If one is interested in first order corrections to Lieb's inequalities, then leading order correlations should suffice.

The work on electronic correlations began with Dirac in 1930 ([D]), when he approximated electronic wave functions with plane waves, which after a calculation yields the term

$$-c_D \int_{\mathbf{R}^3} \rho_{\mathrm{TF}}^{4/3}(x) \, dx,$$

for an explicit constant c_D. The following is a rigorous version of Dirac's estimate:

Theorem thma: *If ψ is the ground–state of the atom,*

$$E(Z) \geq \sum_{i=1}^{N} \langle H^{\text{ind}}\psi, \psi \rangle - \tfrac{1}{2} \iint \frac{\rho_{\text{TF}}(x)\,\rho_{\text{TF}}(y)}{|x-y|}\, dx\, dy - c_D \int_{\mathbf{R}^3} \rho_{\text{TF}}^{4/3}(x)\, dx$$

$$+ \mathcal{O}\!\left(Z^{\frac{5}{3}-a}\right), \qquad a > 0,$$

for

$$H^{\text{ind.}} = -\Delta - V_{\text{TF}}.$$

This theorem was first proved in [FS7], and follows the basic ideas in Dirac's original argument. That proof was soon improved and greatly simplified first by V. Bach [Ba] and then by G. M. Graf and J. P. Solovej in [GS], who exploit the expression of the repulsion terms (5) as a sum of the projection operators

$$\mathcal{N}(\mathcal{N}-1) = \sum_{i \neq j} P_{i,j},$$

where

$$P_{i,j} = \begin{cases} 1 & \text{when } x_i, x_j \in B(x, R), \\ 0 & \text{otherwise,} \end{cases}$$

to which they apply an algebraic inequality.

In what follows, the value of the numerical constant a in the statement of the theorem is important. The proof of [FS7] yields a value of $\frac{1}{2835}$, whereas [Ba] and [GS] improve it to $\frac{2}{21} + \varepsilon$. One would need a value greater than $\frac{1}{6}$ to rigorously justify some of the conclusions in the sections below. This seems to be currently beyond reach, but nevertheless remains a very interesting problem.

We end with the remark that mean field theory can be viewed as a map from densities into potentials: given a density $\rho(x)$, we produce a total effective potential felt by electrons, given by

$$\rho \mapsto -V_\rho^{\text{eff}}(x) = -\frac{Z}{|x|} + \int_{\mathbf{R}^3} \frac{\rho(y)}{|x-y|}\, dy. \tag{8}$$

This will be useful in determining the equations satisfied by the Thomas–Fermi density and improvements on it.

Semiclassical asymptotics

The results of the previous Section, specially Theorem thma, reduce the original problem of estimating $H_{Z,N}$ to the analysis of the much simpler operator $H_{Z,N}^{\text{ind}}$. This hamiltonian can be studied by separation of variables, and one easily sees that

$$E(Z) \geq \text{sneg}\left(-\Delta - V_{\text{TF}}^Z(x)\right) - \tfrac{1}{2} \iint \frac{\rho_{\text{TF}}(x)\,\rho_{\text{TF}}(y)}{|x-y|}\,dx\,dy - c_D \int_{\mathbf{R}^3} \rho_{\text{TF}}^{4/3}(x)\,dx$$

$$+ \mathcal{O}\left(Z^{\frac{5}{3}-a}\right), \qquad a > 0,$$

where sneg denotes the sum of the negative eigenvalues of H. As above, corresponding upper bounds, although still hard, are easier by comparison, as they can rely on variational principles.

We also need estimates for the one-electron density of $H_{Z,N}^{\text{ind}}$:

$$\rho(x) = \sum_k |\psi_k(x)|^2.$$

Note that both problems are doubly singular: first, there are singularities of the Coulomb and Thomas–Fermi potentials; second, and more important, there is the singularity in the energy, due to the non–smooth restriction of the trace to the negative spectrum. More precisely,

$$\text{sneg}\, H^{\text{ind.}} = \text{Trace}\, g(H), \qquad g(\lambda) = \begin{cases} 0 & \text{if } \lambda > 0 \\ -\lambda & \text{otherwise.} \end{cases}$$

Thus, to the singularity of V_{TF}, one has to add the singularity of the energy function g at 0. Moreover, both singularities play a fundamental role in the conclusions that follow.

First, the Coulomb singularity of V_{TF} is responsible for the Z^2 term (the Scott term) in (3): smooth potentials don't have it. This follows from the fact, well known to semiclassical analysts, that such terms (for smooth potentials) come as the contribution from the subprincipal symbol of the Schrödinger operator, which in the case of $H^{\text{ind.}}$

is 0. Therefore, the Scott term is one of the ways the Coulomb singularity makes itself heard in the spectral series.

The second singularity, due to the counting function g at 0, has deeper effects. It is responsible for the relevance of number theoretic terms in the atomic energy series, but goes beyond what one can see in (3), where they are merely one of the error terms. However, there are reasons to believe that they would dominate the other error terms, and therefore are the prime suspects for a continuation of the atomic energy asymptotics.

The situation for densities is even more exciting. Since the Thomas–Fermi density has remained untouched by the series of refinements to the energy asymptotics, number theoretic terms might very well be the first correction to an improved theory beyond Thomas–Fermi.

This section is devoted to the presentation of these arithmetic facts.

The usual semiclassical approximations to sneg and to the density ρ are given by

$$\text{sneg}\,(-\Delta + V) \approx -\tfrac{1}{15\pi^2} \int_{V<0} |V|^{5/2} + \tfrac{1}{8}Z^2 + \tfrac{1}{48\pi^2} \int_{V<0} |V|^{1/2}\Delta V. \qquad (9)$$

$$\rho(x) \approx \tfrac{1}{6\pi^2} |V_{\text{TF}}(x)|^{3/2}. \qquad (10)$$

We omit a discussion of these formulas, which, at least in the case for smooth potentials, are well known to experts in semiclassical asymptotics. Related work can be found in [RS], [HKSW], [HR], [Ro], [He], [IS] and references thereof.

We point out that despite that the formula for sneg was guessed by Schwinger and Scott by comparison with the hydrogen atom and the harmonic oscillator, it is easily seen that in fact they fail for these two potentials; thus, that it continues to be true for the Thomas–Fermi potential is a deep fact. This is rooted in the well-known relation between semiclassical asymptotics and periodic trajectories of classical flows, namely in the fact that aperiodicity of zero–energy Hamiltonian paths plays a role in the study of eigenvalues and eigenfunctions.

In our setting, this relationship shows up as part of the error term in (9) and (10), in the form of trigonometric sums of the type

$$S = Z^{4/3} \sum_{1 \le \ell < Z^{1/3}\Omega_c} \beta\left(\frac{Z^{1/3}}{\pi} F(Z^{-1/3}\ell)\right) \qquad (11)$$

for elementary functions such as

$$\beta(t) = \begin{cases} t - [t] - \frac{1}{2} & \text{for (10),} \\ \text{dist}\,(t, \mathbf{Z})^2 - \frac{1}{12} & \text{for (9),} \end{cases}$$

for $[t]$ the greatest integer in t, and

$$F(t) = \int \left(V(x) - \frac{t(t+1)}{r^2} \right)_+^{1/2} dx.$$

Since β is bounded, we obtain trivially the estimate $S = \mathcal{O}\left(Z^{5/3} \right)$, which falls short of proving a result like (3). If $F(\Omega) = \pi\mu\Omega + \nu$ with μ rational, then the trivial estimate for S is easily seen to be the best possible, and (3) would then be false. On the other hand, if $d^2 F/d\Omega^2 < c < 0$, 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

$$S = \mathcal{O}(Z^\gamma) \qquad \text{with } \gamma < \tfrac{5}{3}. \tag{12}$$

In the case of the hydrogen atom and harmonic oscillator, the function F will degenerate to the case $F(\Omega) = \pi\mu\Omega + \nu$ with μ rational. If this formula for F were also the case for the Thomas–Fermi potential, the oscillating sum would give a contribution comparable with the $Z^{5/3}$–term, and the asymptotic expansion (3) would break down.

Therefore, all estimates hinge on the fundamental inequality

$$|F''(t)| \geq c > 0. \tag{13}$$

This amounts to an aperiodicity result that implies, among other things (see [CFS2]), that the set of periodic trajectories of the classical flow created by the Thomas–Fermi potential has measure zero. This inequality was proved in [FS8], and it is a computer–assisted proof. We refer the interested reader to [FS10] for a review paper on the proof, and of course, we refer to [FS8] for the proof itself.

In the section below we present a brief account of the set of results in number theory which are relevant to the main issues in establishing (12). In the sections beyond the next, we present an overview of the connections of these oscillatory terms with energy asymptotics and density functional theories, which come from interesting mathematical phenomena beyond expansions (9) and (10).

Number Theory

Consider sums of the form

$$S(\lambda) = \sum_{l=1}^{[\lambda]} f\left(\frac{l}{\lambda}\right) \cdot \mu\left(\lambda \cdot \phi\left(\frac{l}{\lambda}\right)\right) \tag{14}$$

where λ is a large number, μ is a periodic function with average 0, f is an amplitude function which can be viewed as constant and ϕ is a smooth function which satisfies the crucial non–degeneracy condition

$$|\phi''(x)| \geq c_0 > 0.$$

Particular cases of sums of this kind give rise to two well–known problems in analytic number theory, namely

1. $f \equiv 1$, $\mu(x) = e^{2\pi i x}$, $\phi(x) = x^2$. In this case, $S(\lambda)$, for λ integer, corresponds to the Gauss sums. The value of S is then known explicitly, and satisfies the estimate

$$S(\lambda) = \mathcal{O}\left(\lambda^{1/2}\right)$$

2. $f \equiv 1$, $\mu(x) = x - [x] - \frac{1}{2}$, $\phi(x) = \sqrt{1 - x^2}$. In this case, S is related to the error $E(\lambda)$ in the lattice point problem for the circle in $\mathbf{R}^2$, which is defined as follows: take a large circle on $\mathbf{R}^2$ of radius λ, and denote by $N(\lambda)$ the number of lattice points in $\mathbf{Z}^2$ which fall inside this circle. Then

$$E(\lambda) = N(\lambda) - \pi\lambda^2$$

and it is an old problem in number theory to prove that

$$E(\lambda) = \mathcal{O}(\lambda^\alpha)$$

for the best possible value of α. It was observed very early, by Gauss and Dirichlet, that one can take $\alpha = 1$ which is an obvious geometric fact, and is also obviously satisfied by $S(\lambda)$. Different probabilistic approaches (as the one by Cramer, for instance) indicate that α above will not be smaller than $\frac{1}{2}$. What follows is a *brief* chronology of the estimates for α (see [GK] for details).

$\alpha = 1$, Gauss–Dirichlet, 1849.

. $\frac{2}{3} = 0.666..$, Voronoi 1904, Hardy, 1917.

. $\frac{66}{100} = 0.6600$, Van der Corput 1922.

. $\frac{163}{247} = 0.659919..$, Walfisz 1927.

. $\frac{27}{41} = 0.6585..$, Nieland–Van der Corput 1928.

. $\frac{15}{23} = 0.6521..$, Tichmarsh 1935.

. $\frac{13}{20} = 0.6500$, Loo Keng Hua 1942.

. $\frac{24}{37} = 0.6486..$, Kolesnik–Yin Wen Lin 1962.

. $\frac{35}{54} = 0.6481..$, Kolesnik 1971.

. $\frac{278}{429} = 0.648018..$, Kolesnik 1985.

. $\frac{7}{11} = 0.636636..$, Iwaniec–Mozzochi 1988.

. $\frac{23}{73} = 0.63014$ Huxley, 1993.

Going back to our main issue of atomic structures, the following question then arises.

Given that the the non–degeneracy condition for ϕ was proved in (13), what is the level of difficulty in analyzing the oscillatory terms (11)? Are they as simple as the analysis of the gauss sums above? Or so hard as the analysis of the lattice point problem?.

The method devised by Van der Corput (or at least, a variant of it), in his attempts to understand the lattice point problem provides the answer: we compute our sum using

Poisson summation, and then we expand each Fourier integral using stationary phase. In doing this, we end up with a sum in which μ is replaced by its Fourier coefficients $\hat{\mu}(n)$. The rate of decay of the Fourier coefficients $\hat{\mu}(n)$ then decides the difficulty of the problem. A decay faster than $|n|^{-3/2}$ gives sharp bounds, as in the case of the Gauss sums, and a decay slower than $|n|^{-3/2}$ gives rise to questions equivalent in difficulty to the lattice point problem. The details of this can be found in [CFS1] and [CFS2].

Translating this ideology to our atomic setup, terms coming from density analysis will be hard to study, whereas we will be able to obtain sharp bounds for oscillatory terms coming from energy–related quantities.

Energy Asymptotics

The aperiodicity result proved by (13) proves the asymptotic expansion in (9), which, jointly with Theorem thma proves (3).

The expansion in powers of Z in (3) almost surely stop there; in fact, in view of [FS 1 – 8], it is naturally conjectured (see [Fef]) that the next term in the energy asymptotics for $E(Z)$ above is given by the following sum

$$\Psi_Q(Z) = \sum_{\ell=1}^{l_{\mathrm{TF}}} \frac{2\ell+1}{\dfrac{1}{\pi} \displaystyle\int \left(V_{\mathrm{TF}}^Z(r) - \frac{\ell(\ell+1)}{r^2} \right)_+^{-1/2} dr} \; \mu\left(\frac{1}{\pi} \int \left(V_{\mathrm{TF}}^Z(r) - \frac{\ell(\ell+1)}{r^2} \right)_+^{1/2} dr \right)$$

(15)

where $\mu(x) = \mathrm{dist}\,(x, \mathbf{Z})^2 - \frac{1}{12}$ and ℓ_{TF} is the greatest integer such that $V_{\mathrm{TF}}^Z(r) - \ell(\ell+1)/r^2$ is positive somewhere.

A calculation shows that the perfect scaling condition (2) of the Thomas–Fermi potential implies that our sum Ψ_Q is –more or less– of the form $S(\lambda)$ as defined in (14), where $\mu(x) = \mathrm{dist}\,(x, \mathbf{Z})^2 - \frac{1}{12}$, $\lambda = Z^{1/3}$, and ϕ is F above.

This sum was studied in [CFS1] and [CFS2], where it was proved that

$$|\Psi_Q| \leq C \sim Z^{\frac{4}{3}+\frac{1}{6}}, \qquad \text{and} \quad \mathrm{Av}_Z \Psi_Q \geq c \sim Z^{\frac{4}{3}+\frac{1}{6}}.$$

In other words, Ψ_Q is of size $Z^{\frac{4}{3}+\frac{1}{6}}$ and this bound is sharp.

More importantly, it was also proved there that Ψ_Q is a sum of classical data taken over all closed trajectories under the Thomas–Fermi potential. This suggests that the expansion for $E(Z)$ is a trace formula which one would expect from a path integral picture.

The validity of these results rests on the (unproved) hypothesis that the error term in Theorem thma is bounded by $Z^{4/3+\varepsilon}$.

The book of Englert ([E]; see also references thereof) contains a discussion of oscillatory terms in the asymptotics of $E(Z)$.

A Density Model

We now investigate the number theoretic implications of the ideas above to the study of atomic densities. The results presented in this section are of an entirely speculative nature, but nevertheless rooted in the rigorous framework developed in the proof of (3) above, and they will result in a new density model of Thomas–Fermi type, which incorporates the arithmetic considerations we reviewed in the section on semiclassical asymptotics.

The main feature that this model introduces is a correction to the Thomas–Fermi density which is, one the one hand, not universal (i.e., varies among the different atoms), and is oscillatory (i.e., reallocates electrons to specially chosen regions in the atom), in what may very well be a ghost of a shell structure showing up in a semiclassical picture of the atom.

From the technical point of view, this refined TF density model will arise from the following two sources:

- A conjectured improvements to (10), as roughly discussed above, which we will present in detail below.

- An improved mean field theory, which, as in the previous section, rests on the (unproved) hypothesis that the error term in Theorem thma is bounded by $Z^{4/3+\varepsilon}$.

We begin by reviewing the derivation of Thomas–Fermi theory according to the guidelines presented above, which will later be perturbed taking into account refined semiclassical formulas to become our proposed new atomic density model.

Self–consistent Mean Fields We now come to the basic issue: our previous discussion was based in a fundamental way on the Thomas–Fermi density and potentials, although their nature has been left intentionally in the dark.

Recall that given a charge density ρ we formed the effective potential it generates V_ρ^{eff} according to the basic recipe of field theory:

$$V_\rho^{\text{eff}} = \int_{\mathbf{R}^3} \frac{\rho(y)\, dy}{|x - y|}. \tag{16}$$

Reciprocally, given a potential V we can consider the density arising from the Schrödinger operator it gives rise to,

$$\rho_V(x) = \sum_k |\psi_k(x)|^2 \tag{17}$$

where ψ_k are the normalized eigenfunctions of the hamiltonian $-\Delta - V$.

A natural requirement for a "reasonable" guess for a charge distribution would be that it satisfies the equation

$$\rho_V = V_\rho^{\text{eff}}. \tag{18}$$

We call this the self–consistent mean field model, which is closely related to Solovej's self–consistent model, which admits a variational description, and has a number of physically interesting properties ([So]).

The Thomas–Fermi density and potentials arise as the solutions to the *semiclassical* self–consistent mean field density: we approximate ρ_V in (17) by its semiclassical approximation (10),

$$\rho_V \approx \frac{1}{6\pi^2} V_+^{3/2}(x), \tag{19}$$

and we note that (16) means

$$\Delta V_\rho(x) = 4\pi\, \rho(x),$$

to arrive at the usual equation for the Thomas–Fermi potential

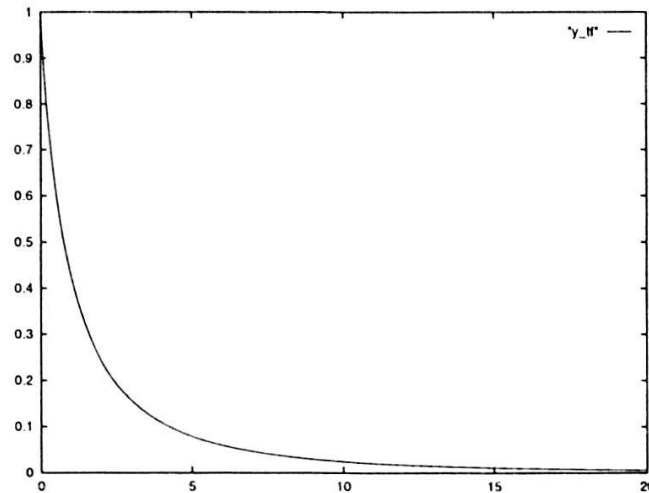$$\Delta V = \tfrac{2}{3\pi} V_+^{3/2}. \tag{20}$$

It is easily seen that

$$V_{\mathrm{TF}}^Z(x) = Z^{4/3} V_{\mathrm{TF}}\left(Z^{1/3} x\right), \qquad V_{\mathrm{TF}}(x) = y(a|x|)/|x|,$$

where y satisfies the ordinary differential equation

$$y''(r) = \frac{y^{3/2}(r)}{r^{1/2}}, \quad \text{with } a = \left(\frac{2q}{3\pi}\right)^{2/3}, \qquad q = 1.$$

The reason to keep the number $q = 1$ above is purely psicological: for real electrons with $q = 2$ spins, the number continues to be a as above.

graph of y_{TF}.

Refined Thomas–Fermi theory. The basic step to obtain the Thomas–Fermi model as an approximation to the self–consistent mean field model was (19).

Based on formulas arising in [FS1 – 7], we are lead to consider the refined version of (19) given by

$$\rho_V(x) = \frac{q}{6\pi^2} V^{3/2}(x) + \rho_{\mathrm{NT}}(V, x),$$

with

$$\rho_{\mathrm{NT}}(V, x) = \frac{1}{4\pi|x|^2} \sum_\ell (V_\ell(x))^{-1/2} \cdot (2\ell + 1)\, \chi(\phi_\ell) \int_0^\infty (V_\ell(r))_+^{-1/2} \, dr, \tag{21}$$

where

$$V_\ell(|x|) = V(x) - \frac{\ell(\ell+1)}{|x|^2}$$

$$\phi_\ell = \frac{1}{\pi} \int_0^\infty (V_\ell(r))_+^{1/2} \, dr,$$

$$\chi(t) = t - [t] - \frac{1}{2},$$

$[t]$ denotes the integral part of t, $q = 2$ is the number of spins.

We omit a derivation of this conjecture (we refer the reader to [FS6]), and simply point out the similarities between (21) and (15) and (11).

The resulting self–consistency relation (18) then yields the refined model

$$\begin{cases} \rho(x) = \dfrac{q}{6\pi^2} V^{3/2}(x) + \rho_{\mathrm{NT}}(V,x), \\[2mm] \Delta V = 4\pi\rho. \end{cases}$$

This model can be studied as a perturbation of the Thomas–Fermi model,

$$V = V_{\mathrm{TF}}^Z + V_1^Z.$$

Elementary analysis shows that V_1 should have as leading expression

$$V_1^Z(x) = Z V_1\left(Z^{1/3} x\right),$$

for a non–universal potential V_1,

$$V_1(x) = y_{\mathrm{cor}}(a|x|)/|x|,$$

for a non–universal function y_{cor} satisfying

$$\begin{cases} y_{\mathrm{cor}}''(r) = \dfrac{a^{-3/2} q}{\pi} \dfrac{y_{\mathrm{TF}}^{1/2}(r)}{r^{1/2}} y_{\mathrm{cor}}(r) + 4\pi r\, a^{-3} Z^{-5/3} \rho_{\mathrm{NT}}\left(a^{-1} Z^{-1/3} r\right), \\[2mm] y_{\mathrm{cor}}(0) = y_{\mathrm{cor}}(\infty) = 0. \end{cases}$$

After grubby manipulations, this takes the form

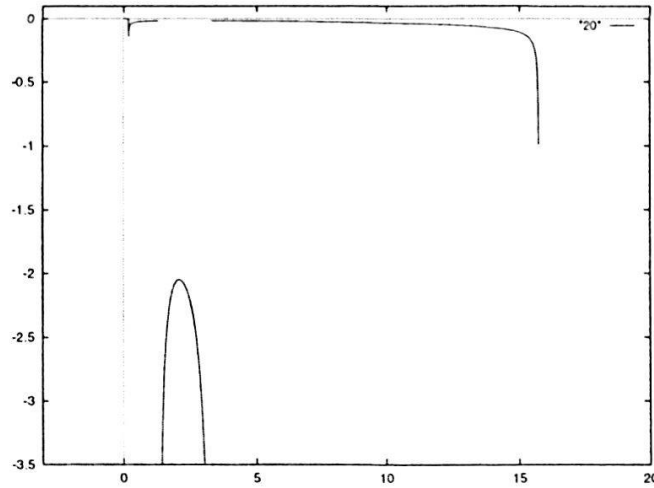$$y_{\mathrm{cor}}''(r) = \frac{3}{2}\left(\frac{y_{\mathrm{TF}}(r)}{r}\right)^{1/2} y_{\mathrm{cor}}(r) + f_Z(r), \tag{22}$$

for

$$f_Z(r) = \frac{Z^{-2/3}}{r} \sum_\ell V_{\Omega_\ell^Z}^{-1/2}(r) \cdot \frac{(2\ell+1)\,\chi(\phi_\ell)}{\int_0^\infty \left(V_{\Omega_\ell^Z}(r)\right)_+^{-1/2}\,dr},$$
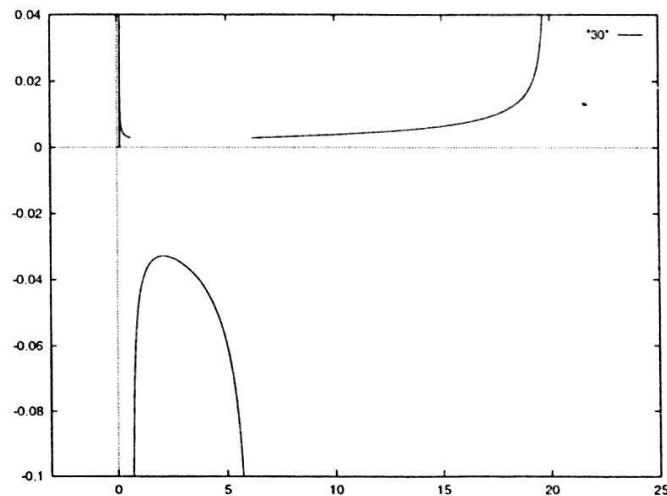
and

$$V_\Omega(r) = \frac{y(r)}{r} - \frac{\Omega^2}{r^2}, \qquad \Omega_\ell^Z = Z^{-1/3}\,\sqrt{a\,\ell\,(\ell+1)}.$$
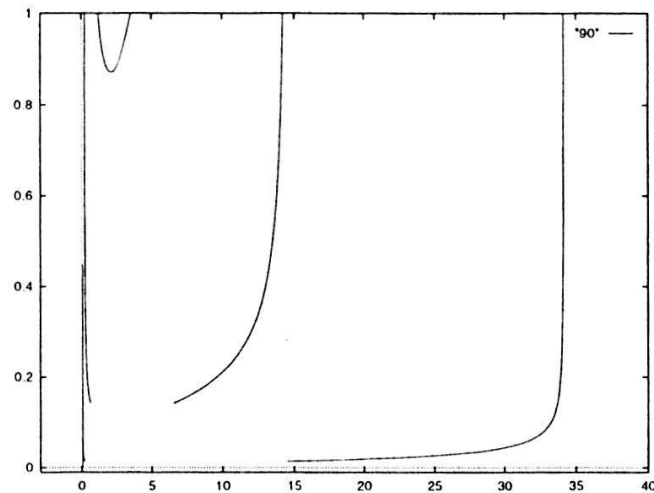
The equation defining y_{cor} is a linearized inhomogenous differential equation of the Thomas–Fermi type. Most of the properties of its solution y_{cor} follow from the source term, f_Z. We present below the graphs of several of these for different atomic numbers Z.
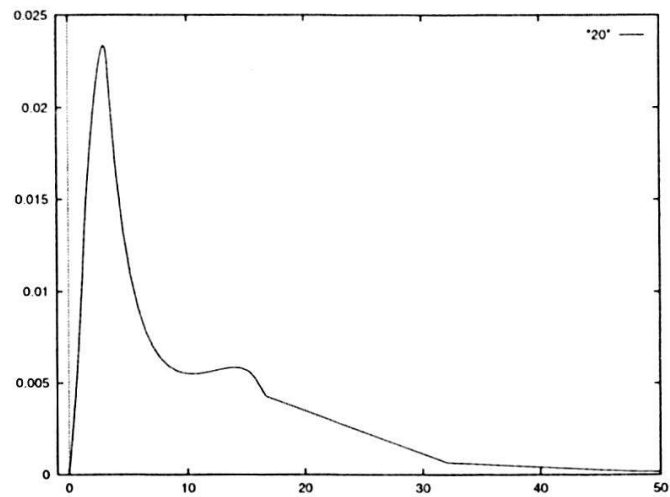

f_Z for $Z = 20$.

f_Z for $Z = 30$.

$$f_Z \text{ for } Z = 90.$$

In the first of these graphs, the function is always negative, in the third it is always positive, and in the second, which is the typical case, it changes sign. If one analyzes the formula defining f_Z, one would realize that the singularities of f_Z appear, precisely, at the places where the Thomas–Fermi potential equals the energy levels predicted by semiclassical arguments. In the typical case, the values of f_Z at its singular points will jump from $+\infty$ and $-\infty$ for a fixed Z. Plugging this into (22), one sees that it will imply that y_{cor} will have arbitrarily large positive and large negative values, which will imply that

$$V = \frac{y(a|x|)}{|x|},$$

for a function y that changes convexity and concavity at the places where the Thomas–Fermi potential equals the semiclassical energy levels. We can view these as electronic shells.

The graph below shows several graphs of y_{cor}:

y_{cor} for $Z = 20$.
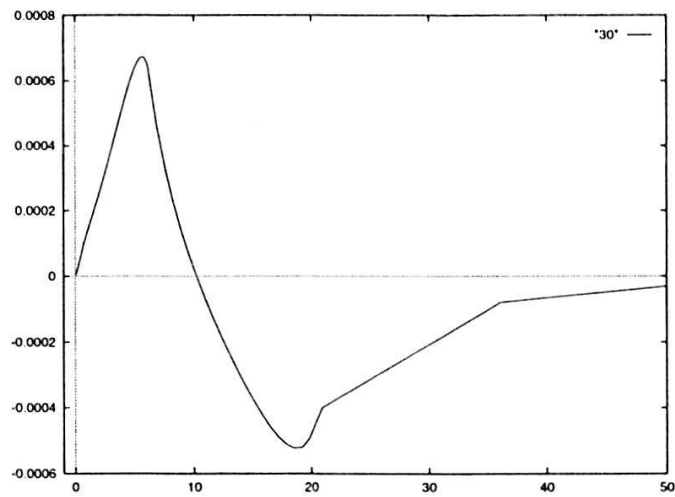
y_{cor} for $Z = 30$.
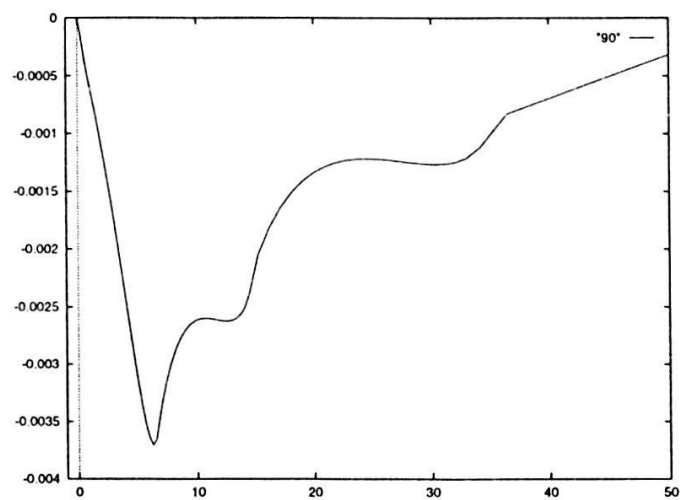
y_{cor} for $Z = 90$.
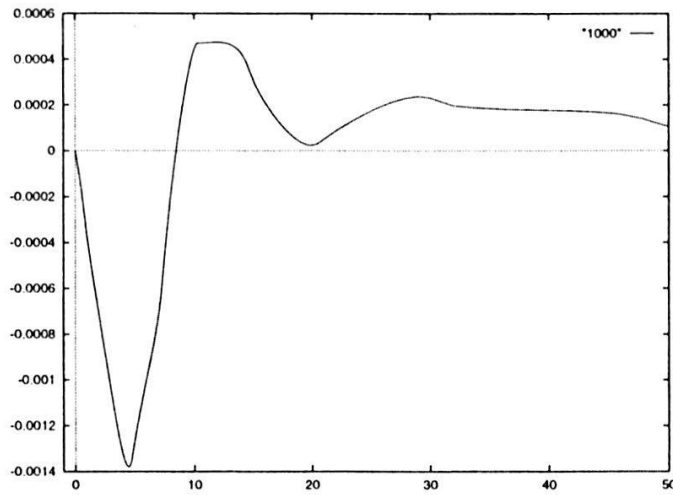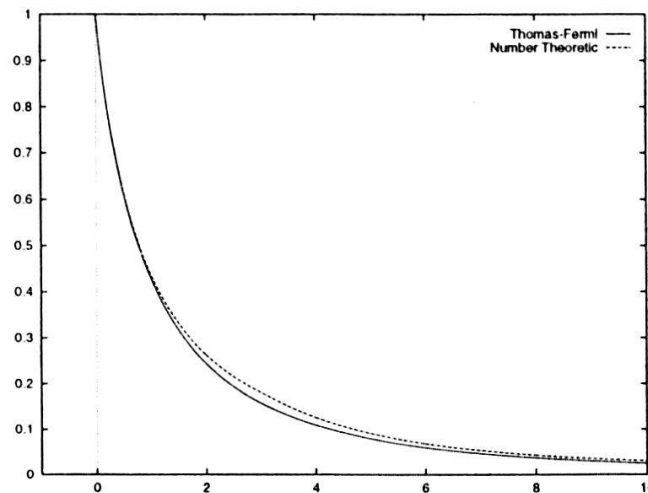
y_{cor} for $Z = 1000$.

The correction that y_{cor} introduces is, however, very small. As an applciation of the number theoretic methods presented above, it was proved in [CFS3] that

$$\int_{\mathbf{R}^3 \times \mathbf{R}^3} \frac{\rho_{\mathrm{NT}}(x)\,\rho_{\mathrm{NT}}(y)}{|x-y|}\,dx\,dy \leq C\,Z^{\frac{13}{9}}\,log^2 Z.$$

This is much smaller than the main term,

$$\int_{\mathbf{R}^3 \times \mathbf{R}^3} \frac{\rho_{\mathrm{TF}}(x)\,\rho_{\mathrm{TF}}(y)}{|x-y|}\,dx\,dy = (\mathrm{const.}) Z^{7/3}.$$

The graph below shows the graph for the resulting function $y_{\mathrm{TF}} + y_{\mathrm{cor}}$ against y_{TF}, for $Z = 20$.

$y_{\mathrm{TF}} + y_{\mathrm{cor}}$ for $Z = 20$.

As a concluding remark, we point out that there are a number of related recent developments which have the common target of understanding atomic densities in rigorous terms. Among these are [HL], [BLLS], [Sie] and [ILS].

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