Number Theory and Atomic Densities

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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.

One of the successful attempts was Thomas–Fermi theory. According to it, the atomic energy $E(Z)$ and density $\rho^Z(x)$ of an atom of charge Z (to be defined a little later) behave as

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

for a suitable explicit constant c_{TF} and universal (Z–independent) function ρ^1_{TF}. This is an immense simplification, since it puts all atoms on an equal footing. Associated with the density there is also the Thomas–Fermi potential V^Z_{TF}, satisfying also a perfect scaling condition

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

For the time being, we content ourselves knowing that Thomas–Fermi theory is simpler than the Schrödinger equation. We will postpone the derivation and explanation of the Thomas–Fermi equations until later.

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 $Z \to \infty$.

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. 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, which seem to have connections to quantum chaos. Much of the presentation will be non–rigorous, descriptive, and often incomplete, all for the sake of a quick didactic overview of some of the basic arithmetic issues of the theory. We refer the reader to the references for a more complete, but probably heavy treatment.

Throughout the paper we will use the following definitions:

An atom of nuclear charge Z fixed at the origin, and N quantized electrons at positions $x_i \in \mathbb{R}^3$ 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 $L^2(\mathbb{R}^{3N})$ (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

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

Mean–Field Theory.

The first attempt at a simplification of the original hamiltonian $H_{Z,N}$ involves replacing the repulsion term above by more manageable expressions of the type

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

modulo small error terms.

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

$$\sum_{i=1}^{N} \int_{\mathbb{R}^3} \frac{\rho(y)}{|x_i - y|} \, dy - \tfrac{1}{2} \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho(x) \, \rho(y)}{|x - y|} \, dx \, dy,$$

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. There are several delicate points in this physical argument, one of them being that we need to choose the functions ρ in a clever way. We postpone the discussion of this problem until later, and content ourselves with knowing that the Thomas–Fermi density achieves this purpose very well.

The first such rigorous results go back to Lieb and his collaborators (see, for example, one of the seminal papers [L2]), and are by know well–known in the mathematical physics folklore as Lieb's formulas. Here is one:

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

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

Then, we have that

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

where

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

The proof of this result can be found in Lemma 2 in [SW2]. The role of this inequality is that it reduces the analysis of systems with interaction to a system without it.

We remark that this procedure 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

$$\rho \mapsto -V^{\mathrm{eff}}_{\rho}(x) = -\frac{Z}{|x|} + \int_{\mathbb{R}^3} \frac{\rho(y)}{|x-y|}\,dy. \tag{3}$$

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

In order to obtain a more refined analysis of the interactions, one then needs a better understanding of the electron correlations, which result in improved versions of Lieb's inequality. we refer the reader to [FS7], [Ba] and [GS] for improved estimates, which are in fact crucial to the results presented in this article.

Semiclassical asymptotics.

The most immediate consequence of mean field theory is that the original hamiltonian $H_{Z,N}$ can be replaced by the much simpler $H^{\mathrm{ind}}_{Z,N}$. This is an immense simplification, since this hamiltonian can be studied by separation of variables, and one easily sees that

$$E(Z) \ge \mathrm{sneg}\,\left(-\Delta - V^{Z}_{\mathrm{TF}}(x)\right),$$

where

$$\text{sneg}\,(H) = \text{Trace}\,(H_-),$$

denotes the sum of the negative eigenvalues of H.

We also need estimates for the one-electron density of that same operator. Note that this problem is doubly singular: first, there is a singularity of the Thomas–Fermi potential; second, and more important, there is the singularity in the energy, due to the non–smooth restriction of the trace to the negative spectrum.

The density of $H^{\text{ind}}_{Z,N}$ equals

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

The semiclassical approximations to these quantities are

$$\text{sneg}\,(-\Delta + V) \approx -\tfrac{1}{15\pi^2}\int_{V<0}|V|^{5/2} + \tfrac{1}{8}Z^2 + \tfrac{1}{48\pi^2}\int_{V<0}|V|^{1/2}\Delta V. \tag{4}$$

$$\rho(x) \approx \tfrac{1}{6\pi^2}|V_{\text{TF}}(x)|^{3/2}. \tag{5}$$

We omit a discussion of these formulas, which, at least in the case for smooth potentials, are well known to experts in semiclassical asymptotics. 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 must be a deep fact. This is rooted in the well–known relation between semiclassics and classical periodic trajectories. Aperiodicity of zero–energy Hamiltonian paths is well-known to play a crucial role in the study of eigenvalues and eigenfunctions.

Once this is aperiodicity issue is settled (see [FS8]), the implications of (4) and (5) to the energy asymptotics is that

$$E(Z) = -c_{\text{TF}}Z^{7/3} + \tfrac{1}{8}Z^2 - c_s Z^{5/3} + \mathcal{O}\left(Z^{\frac{5}{3}-a}\right), \qquad a > 0. \tag{6}$$

The first term above was introduced by Thomas and Fermi in [T], [Fer], and proved rigorously in [LS] (See also [L1] for a review of Thomas–Fermi theory). 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].

In this setting we find, as part of the error term in (6), trigonometric expressions of the form

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

for elementary functions such as $\beta(t) = t - [t] - \frac{1}{2}$, (Here $[t]$ is the greatest integer in t) and a certain function F which depends on the potential. 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 $\gamma < \frac{1}{3}$. 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, and the oscillating sum gives a contribution comparable with the last term, and the asymptotic expansion (6) breaks down.

The expansion in powers of Z in (6) almost surely stop there; in fact, interesting mathematical phenomena start to take place in the error terms above. 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

$$\Psi_Q(Z) = \sum_{\ell=1}^{l_{\mathrm{TF}}} \frac{2\ell+1}{\frac{1}{\pi}\int \left(V_{\mathrm{TF}}^Z(r) - \frac{\ell(\ell+1)}{r^2}\right)_+^{-1/2} dr} \, \mu\left(\frac{1}{\pi}\int \left(V_{\mathrm{TF}}^Z(r) - \frac{\ell(\ell+1)}{r^2}\right)_+^{1/2} dr\right) \tag{7}$$

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

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

The sum $\Psi_Q(Z)$ turns out to be an adaptation of similar expressions well–known in analytic number theory, related to the circle and the divisor problem, among others. It was proved in [CFS1] and [CFS2] that this sum Ψ_Q corresponds to a sum of classical data of a certain classical hamiltonian, which would then suggest that the expansion for $E(Z)$ is a trace formula which one would expect from a path integral picture.

Number Theory.

Consider sums of the form

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

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 $\mathbb{R}^2$, which can is defined as follows: take a large circle on $\mathbb{R}^2$ of radius λ, and denote by $N(\lambda)$ the number of lattice points in $\mathbb{Z}^2$ 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* historic overview 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.

Note now that the perfect scaling condition (2) of the Thomas–Fermi potential shows that our sum Ψ_Q is (almost exactly) of the form $S(\lambda)$ as defined above, where $\mu(x) = \operatorname{dist}(x, \mathbb{Z})^2 - \frac{1}{12}$, $\lambda = Z^{1/3}$, and a certain explicit ϕ. The proof of the non–degeneracy condition for ϕ was done in [FS8], and it has the peculiarity that its is a computer assisted proof.

A natural question then arises: what is the level of difficulty in analyzing the size of Ψ_Q?. Is is as simple as the analysis of the gauss sums above? Or so hard as the analysis of the lattice point problem?.

A 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 $\hat{\mu}(n)$. If they decrease fast enough (like $|n|^{-3/2}$, it so happens), the sum is bounded by $\lambda^{1/2}$. In our case, $\mu(n) \sim |n|^{-2}$, therefore, after realizing that the size of our amplitude function is $Z^{4/3}$, we can conclude that $\Psi_Q \sim Z^{\frac{4}{3}+\frac{1}{6}}$.

A density model.

In this section we will present some of the implications of the ideas above to the study of atomic densities. This can be put in the context of some recent improvements of our understanding of atomic densities, which includes also the work in [HL] and [ILS].

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}. Also, given a potential V we constructed the density arising from the Schrödinger operator it gives rise to, ρ_V.

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

$$\rho_V = V_\rho^{\mathrm{eff}}. \tag{8}$$

We call this the self–consistent mean field model, which has been proved by Solovej to have a number of physically interesting properties.

The Thomas–Fermi density and potentials arise as the solutions to the *semiclassical* self–consistent mean field density: we replace ρ_V in (8) by its semiclassical approximation

(5),

$$\rho_V \approx \frac{1}{6\pi^2} V_+^{3/2}(x), \tag{9}$$

and we note that (3) means

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

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

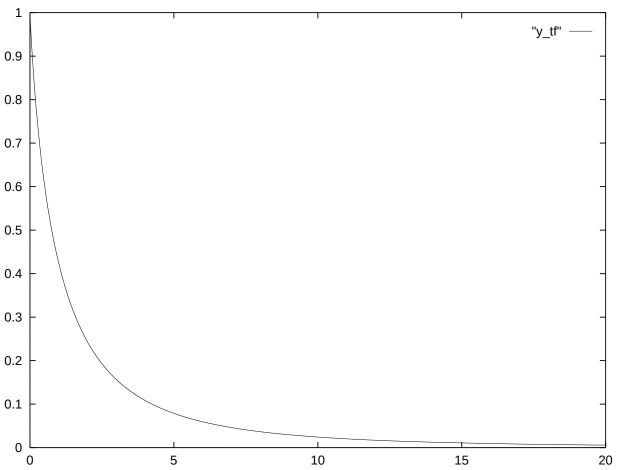
$$\Delta V = \tfrac{3}{2\pi} V_+^{3/2}. \tag{10}$$

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

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



$\boldsymbol{y}_{\mathrm{TF}}$.

We can consider different semiclassical approximations to the mean–field model by considering different semiclassical approximations to ρ_V.

Refined Thomas–Fermi theory. Based on formulas arising in [FS1 – 7], we are lead to consider the refined semiclassical approximation to ρ_V given by

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

with

$$\rho_{\mathrm{NT}}(V,x) = \frac{1}{4\pi|x|^2}\sum_{\ell}\left(V_\ell(x)\right)^{-1/2}\cdot(2\ell+1)\,\chi(\phi_\ell)\int_0^\infty \left(V_\ell(r)\right)_+^{-1/2}\,dr, \qquad (11)$$

where

$$\begin{aligned} V_\ell(|x|) &= V(x) - \frac{\ell(\ell+1)}{|x|^2} \\ \phi_\ell &= \tfrac{1}{\pi}\int_0^\infty \left(V_\ell(r)\right)_+^{1/2}\,dr, \\ \chi(t) &= t-[t]-\tfrac{1}{2}, \end{aligned}$$

and $[t]$ denotes the integral part of t. Note the similarities between (11) and (7).

The self–consistency relation (8) then yields the semiclassical self–consistent approximation to V given by

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

with

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

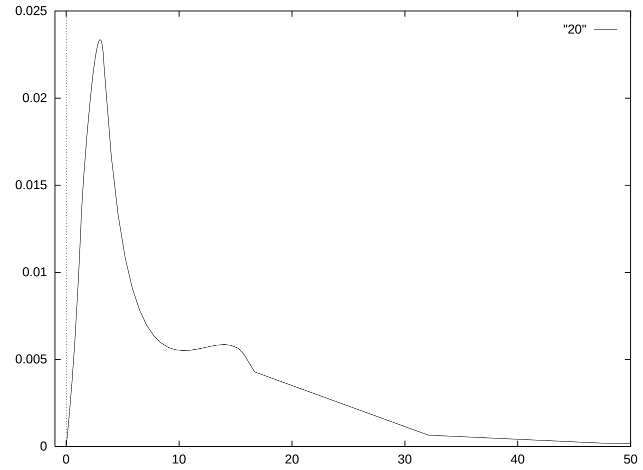
for a non–universal potential V_1,

$$V_1(x) = y(a|x|)/|x|,$$

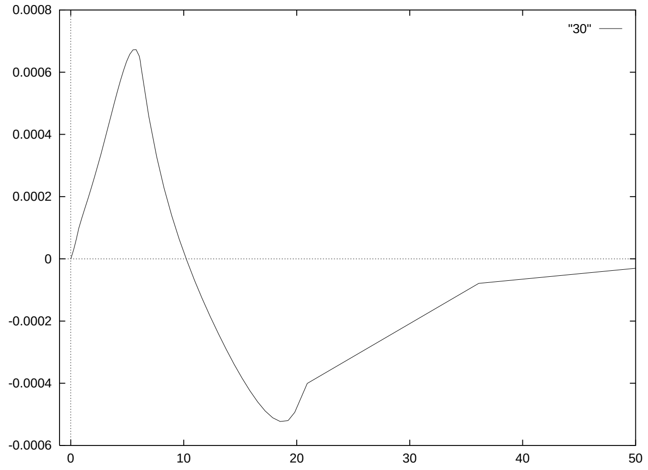
for a non–universal function y satisfying

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

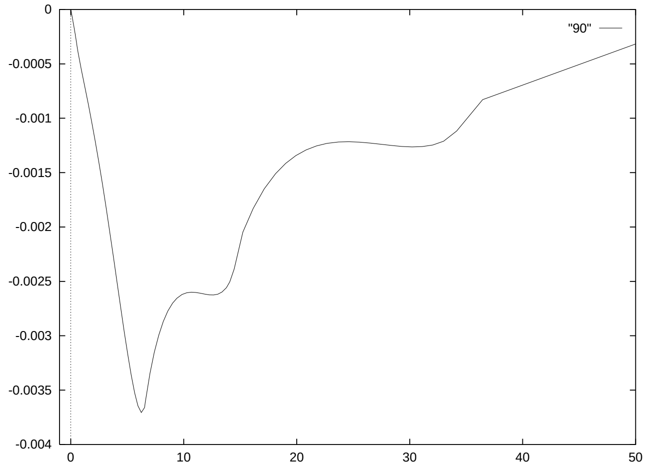
The graph below shows several graphs of y_{cor}:



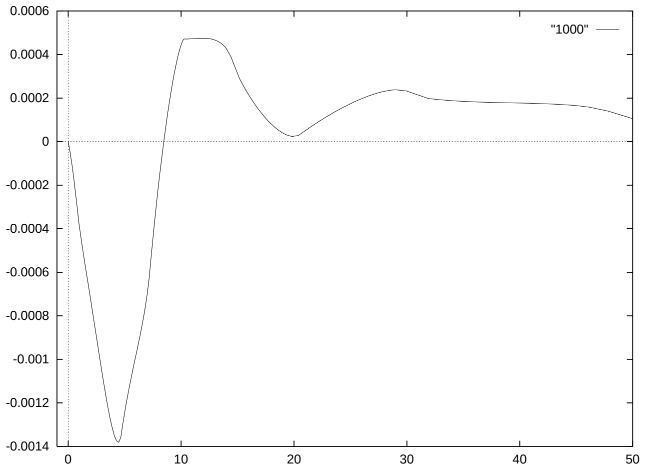
$y_{\rm cor}$ **for** $Z = 20$.



$y_{\rm cor}$ **for** $Z = 30$.



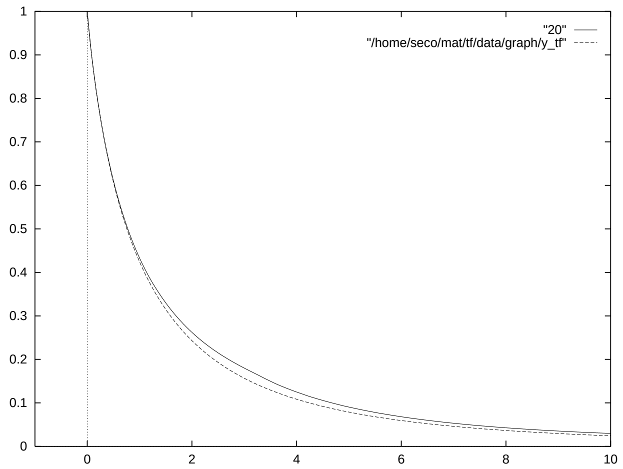
$y_{\rm cor}$ **for** $Z = 90$.



$\boldsymbol{y_{\mathrm{cor}}}$ **for** $\boldsymbol{Z = 1000}$**.**

The main feature of these graphs is the fact that allcorrections are essentially different for each atom, and that the oscillations we clearly observe take place where one would expect to find the electronic shells.

It seems that y_{cor} is in practice very small compared to y_{TF}. The graph below shows the graph for the resulting function $y_{\mathrm{TF}} + y_{\mathrm{cor}}$ against y_{TF}, for $Z = 20$. This, again, is a number–theoretic effect, which was studied in [CFS3], and has to do with the cancellations that take place in (11).



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

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