Number Theory, Classical Mechanics
and the Theory of Large Atoms

L. A. Seco

A non–relativistic 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

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

which acts on the Hilbert space $\mathcal{H}$ of antisymmetric functions in $L^2(\mathbf{R}^{3N})$. The ground state energy of such a system is given by

$$E(Z) = \inf_{N \geq 0} E(Z,N) \qquad E(Z,N) = \inf_{\substack{\phi \in \mathcal{H} \\ \|\phi\|=1}} \langle H_{Z,N}\phi, \phi \rangle$$

As Z goes to infinity, the energy $E(Z)$ admits an asymptotic expansion of the form

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

The first term above was introduced by Thomas and Fermi in [Th], [Fe], and proved rigorously in [LS] (See also [Li] for a review of Thomas–Fermi theory). The Z^2 term was discovered by Scott in [Sc] and proved to be true in a series of papers by Hughes–Siedentop–Weikard, in [Hu], [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 view of (11 — 18), it is naturally conjectured (see [Feff]) that the next term in the energy asymptotics for $E(Z)$ above is given by the following sum

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

where dist $(x,\mathbf{Z})^2 - \frac{1}{12}$, V_{TF}^Z is the Thomas–Fermi potential for an atom with charge Z (see [Li]), which satisfies the perfect scaling condition

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

where we have

$$V^1_{\mathrm{TF}}(r) = \frac{y(a\cdot r)}{r} \qquad a = \left(\frac{3\pi}{2}\right)^{2/3}$$

and y is the Thomas–Fermi function, solution of the Thomas–Fermi equation

$$\left.\begin{aligned} y''(r) &= \frac{y^{3/2}(r)}{r^{1/2}} \\ y(0) &= 1 \\ \lim_{r\to\infty} y(r) &= 0 \end{aligned}\right\}$$

Finally, l_{TF} is the greatest integer such that $V^Z_{\mathrm{TF}}(r) - l(l+1)/r^2$ is positive somewhere.

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

It was proved in [FSC1] and [FSC2] 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.

The purpose of this paper is to describe the analysis involved in understanding the sum $\Psi_Q(Z)$ as a function of Z, which turns out to be an adaptation of a well–known method in analytic number theory developed mostly by Van der Corput to understand the number of lattice points in a large circle. We begin with a few remarks about analytic number theory.

Number Theory

Consider sums of the form

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

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

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

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 can 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

$$E(\lambda) = O(\lambda^\alpha)$$

for the best posssible 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. Huxley 1992.

Note now that the perfect scaling condition of the Thomas–Fermi potential shows that our sum Ψ_Q is (almost exactly) of the form $S(\lambda)$ as defined above, where $\mu(x) = \text{dist}\,(x, \mathbf{Z})^2 - \frac{1}{12}$, $\lambda = Z^{1/3}$, and

$$\phi(x) = \int \left(\frac{y(r)}{r} - \frac{x^2}{r^2} \right)_+^{1/2} dr \qquad (1)$$

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 analysing 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 $\Psi \sim Z^{\frac{4}{3}+\frac{1}{6}}$.

Classical Mechanics

The Van der Corput method does more than merely tell us the size of Ψ. A mechanical analysis of the result given by the stationary phase expansion shows that the function Ψ is (to leading order) a sum of classical data associated to a certain classical hamiltonian, which displays the relationship between classical and quantum mechanics reminiscent of the Feynmann path integral representation of Schrödinger operators.

In order to explain our main result, consider a classical particle with mass $\frac{1}{2}$, moving in the negative radial potential given by $-V_{\mathrm{TF}}^Z$. Such motion is planar, and we consider the closed orbits at energy 0 which arise for angular momentum M; all such orbits for a fixed M can be obtained by rotations of each other. On each of those orbits, the particle "oscillates" in the sense that the distance to the origin $r(t)$ varies between $r_{\min}(M)$ and $r_{\max}(M)$ and closes after passing $n(M)$ times through, say, $r_{\max}(M)$. We also consider the integer $l(M)$, the winding number of the orbit around 0, the action $S(M)$, the period $T(M)$, and the following locally defined quantity: for a closed trajectory with angular momentum M, and n oscillations, and given ε small, consider a trajectory (not necessarily closed) with angular momentum $M+\varepsilon$ which, after $n(M)$ oscillations between succesive $r_{\max}(M+\varepsilon)$, misses to close by an angle $2\pi\alpha_M(\varepsilon)$, where we take α between 0 and 1. Then, we define

$$D(M) = \lim_{\varepsilon\to 0} \varepsilon^{-1}\alpha_M(\varepsilon)$$

In this classical formalism, the non–degeneracy condition $\phi''(x) \neq 0$ stated amounts to the fact that $D(M) \neq 0$ for all closed trajectories. This means that closed trajectories are isolated once we factor out the trivial symmetry given by the rotation group. Its role in the proof is similar to the non–vanishing curvature of the sphere in the circle problem.

With this notation, our main result is as follows:

Theorem 1:

$$\Psi_Q(Z) = \Psi_0(Z) + o\left(Z^{3/2}\right)$$

where

$$\Psi_0(Z) = 2\pi \cdot Z^{3/2} \cdot \sum_{\substack{\text{closed trajectories} \\ \text{at energy } 0}} \delta \cdot \frac{\hat{\mu}(n)\cdot n \cdot M}{T} \cdot |D(M)|^{-1/2} \cdot e^{i\left(Z^{1/3} S - \pi\cdot(l + \frac{\text{sign } n}{4})\right)}$$

where $\delta = 1$ *except in the case of a perfect circular trajectory, when we have* $\delta = \frac{1}{2}$. *Furthermore, the sum is absolutely convergent.*

We now state precisely the result mentioned in the previous section for the size of $\Psi_Q(Z)$

Theorem 2: *There are universal constants K (large) and κ_0 (small but strictly positive), such that*

$$|\psi_Q(Z)| \leq K \cdot Z^{3/2} \qquad \int_{Z_0}^{Z_0+Z} |\psi_Q(z)|^2 \, \frac{dz}{z^3} \geq \kappa_0 \cdot Z$$

whenever $Z \geq K\, Z_0^{2/3}$. Furthermore,

$$\liminf_{\substack{Z\to\infty \\ Z=1,2,3,\ldots}} \left| Z^{-3/2} \psi_Q(Z) \right| \neq 0$$

The lower bound requires some extra work, and hinges on the fact that a certain number is not zero: the relevance of the non–vanishing of this number is analog to the non vanishing of the $L(\chi, 1)$ in Dirichlet's theorem on the number of primes in arithmetic progressions.

It is interesting to note that the size of the error term above $o\left(Z^{3/2}\right)$ depends on whether a certain number is rational or not. More precisely, let $r_{\max}$ be the radius of the circular closed trajectory corresponding to the maximal angular momentum $M_{\max}$ at energy 0. Then, if

$$\sqrt{1 - \tfrac{1}{2} r_{\max} \cdot M_{\max}}$$

is rational, then the error term can be seen to be $O\left(Z^{\frac{3}{2}-\varepsilon}\right)$. Otherwise, specially if this number is very well approximated by rationals (say, a Louiville number), then in general one cannot improve the o–result. However, if in the sum over closed trajectories above one includes also the trajectories with complex period, then the error term is always of size $O\left(Z^{\frac{3}{2}-\varepsilon}\right)$.

The proofs of theorems 1 and 2 can be found in [FSC2].

The book of Gutzwiller [Gu] contains a discussion of the interplay between classical and quantum mechanics in relation with trace formulas.

Acknowledgements. This reasearch was supported by a N.A.T.O research grant no. CRG921184, by NSERC grants no. OGP0121848 and EQPEQ336, by a CICYT grant and by a Connaught Fellowship.

References

[En] Englert, B. G. "*Semiclassical Theory of the Atom* " Springer Verlag Lecture Notes in Physics, vol 301.

[FS1] Fefferman, C. and Seco, L. "*The Ground–State Energy of a Large Atom* " Bull. A.M.S., Vol **23** no. 2, 525—530, 1990

[FS2] Fefferman, C. and Seco, L. "*Eigenvalues and Eigenfunctions of Ordinary Differential Operators* " To appear in *Adv. Math.*

[FS3] Fefferman, C. and Seco, L. "*The Eigenvalue Sum for a One–Dimensional Potential* " To appear in *Adv. Math.*

[FS4] Fefferman, C. and Seco, L. "*The Density in a One-Dimensional Potential* " To appear in *Adv. Math.*

[FS5] Fefferman, C. and Seco, L. "*The Eigenvalue Sum for a Three–Dimensional Radial Potential* " To appear in *Adv. Math.*

[FS6] Fefferman, C. and Seco, L. "*The Density in a Three–Dimensional Radial Potential* " To appear in *Adv. Math.*

[FS7] Fefferman, C. and Seco, L. "*On the Dirac and Schwinger Corrections to the Ground–State Energy of an Atom* " To appear in *Adv. Math.*

[FS8] Fefferman, C. and Seco, L. "*Aperiodicity of the Hamiltonian Flow in the Thomas–Fermi Potential* " To appear in *Revista Matmemática Iberoamericana*

[Feff] Fefferman, C. "*Atoms and Analytic Number Theory* " Proceedings of the AMS, 1991.

[FSC1] Córdoba, A., Fefferman, C., Seco, L. "*A Trigonometric Sum relevant to the Non–relativistic Theory of Atoms* " To appear, P.N.A.S.

[FSC2] Córdoba, A., Fefferman, C., Seco, L. "*Weyl Sums and Atomic Energy Oscillations* " To appear, Revista Matemática Iberoamericana.

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

[GK] S. W. Graham and G. Kolesnik "*Van der Corput's Method of Exponential Sums* " Cambridge University Press. London Math. Soc. Lecture Notes Series, 126.

[Gu] Gutzwiller, M. "*Chaos in Classical and Quantum Mechanics* " Springer Verlag, 1990.

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

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

[Li] Lieb, E. (1981) "*Thomas–Fermi and Related Theories of Atoms and Molecules*" Reviews of Modern Physics Vol 53 no. 4.

[Sch] Schwinger, J. (1981) "*Thomas–Fermi Model: The Second Correction*" Physical Review A24, **5**, 2353—2361.

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

[SW1] Siedentop, H., Weikard, R. (1987) "*On the Leading Energy Correction for the Statistical Model of* *the Atom: Interacting Case*" Communications in Mathematical Physics **112** 471-490

[SW2] Siedentop, H., Weikard, R. "*On the Leading Correction of the Thomas–Fermi Model: Lower Bound*" and an appendix by A.M.K. Müller. Inv. Math., Vol., 97, pp 159—193, 1989.

[SW3] Siedentop, H., Weikard, R. (1990) "*A New Phase Space Localization Technique with Applications to the Sum of Negative Eigenvalues of Schrödinger Operators.* " Ann. Scient. Ecole Normale Superieure 24, 215 – 225, (1991).

[Th] Thomas, L. H. (1927) "*The Calculation of Atomic Fields*" Proc. Cambridge Philos. Soc. **23** 542—548.