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Counting Lattice Points and Atomic Energies Oscillations. A Plan to Explain the Periodic Table from First Principles of Quantum Mechanics

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Counting Lattice Points and Atomic Energies Oscillations. A Plan to Explain the Periodic Table from First Principles of Quantum Mechanics

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Mathematicians are by nature reductionist and often we dream, and also pretend, of being able to deduce rigorously the laws of Science from a small set of first principles. The main purpose of this talk will be to present a plan to accomplish such dream in the case of the periodic table of chemical elements.

The plan is a result of a collaboration with Charles Fefferman (Princeton University) and Luis Seco (University of Toronto) and was motivated by their previous work on the Dirac–Schwinger's term in the asymptotic expansion of the energy of the fundamental state of an atom. Our results were published in the Proceedings of the National Academy of Science, Revista Matem´atica Iberoamericana and Communications on Partial Differential Equations (see references). Pedro Balodis and Fernando Chamizo are two of my collaborators with whom I have worked on related subjects, stability of matter and lattice point problems, and Pablo Fern´andez has always helped me improving substantially the quality of my presentations. I am deeply indebted to all of them.

THE BORN–OPPENHEIMER MODEL FOR A NON-RELATIVISTIC MOLECULE

Consider:

- M nuclei of positive charges $Z_1e,\dots,Z_Me$, placed at positions $y_1,\dots,y_M \in \mathbb{R}^3$.
- $Z = \{Z_1,\dots,Z_M\}$, $\mathbf{y} = (y_1,\dots,y_M)$.
- N quantized electrons in positions $x_1,\dots,x_N \in \mathbb{R}^3$.
- $-e$ = electron charge; m = electron mass; $\hbar$ = Planck's constant.

Following the Born–Oppenheimer model, a non-relativistic molecule is described by the Hamiltonian:

$$H_{\mathbf{y},Z,N} = -\sum_{j=1}^{N}\Big(\frac{\hbar}{2m}\,\Delta_{x_j} + \sum_{k=1}^{M}\frac{Z_k\,e^2}{|x_j-y_k|}\Big) + \sum_{1\le j<k\le N}\frac{e^2}{|x_j-x_k|} + \sum_{1\le m<n\le M}\frac{Z_nZ_m\,e^2}{|y_n-y_m|}\,,$$

where the jth Laplacian represents the quantized kinetic energy of the jth electron, and we have also the Coulombian interactions: attraction between the nuclei and the electrons, and two repulsion terms corresponding to the nuclei, one of them, and the electrons, the other.

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This Hamiltonian acts on

$$\mathcal{H} = \Lambda_{j=1}^{N} L^2(\mathbb{R}^3 \otimes G), \quad G = \{+1, -1\}.$$

Here, the symbol Λ denotes the antisymmetric tensor product and encodes thePauli exclusion principle (electron are fermions satisfying the statistic of Fermi– Dirac); while +1 (spin up) and −1 (spin down) denote the two kind of electronic spin.

The *ground state energy* is given by

$$E(Z) = \inf_N \inf_Y \inf_{\substack{\Psi \in \mathcal{H}, \\ ||\Psi||=1}} \langle \Psi, H_{Y,Z,N} \Psi \rangle.$$

To achieve the dream of explaining mathematically chemical phenomena, one would need a very precise calculation of those energies, a task that is several order of diffculty beyond what can be obtained today.

In the following we will confront the more "modest" goal of explaining the periodic table considering only the Hamiltonian of *neutral atoms*.

NEUTRAL ATOMS. HARTREE–FOCK AND THOMAS–FERMI THEORIES

Consider a neutral atom with Z protons placed at the origin $y = 0$, and choose units such that $e^2 = 1$ and $\hbar/2m = 1$.

Then

$$H_Z = -\sum_{j=1}^{Z} \left(\Delta_{x_j} + \frac{Z}{|x_j|} \right) + \sum_{1 \le j < k \le Z} \frac{1}{|x_j - x_k|} \, .$$

Some standard considerations with the symmetric group allows us to eliminate the spin in the discussion, so that the Hilbert space of states is much more easily described:

$$\begin{aligned} \mathcal{H} &= \Lambda_{j=1}^{Z} L^2 \ (\mathbb{R}^3) \\ &= \{\Psi(x_1,\ldots,x_Z), x_j \in \mathbb{R}^3 : \ \Psi \in L^2(\mathbb{R}^{3Z}), \Psi \text{ antisymmetric}\}. \end{aligned}$$

Antisymmetry means that $\Psi(x_{\sigma(1)},\ldots, x_{\sigma(Z)}) = (-1)^{\mathrm{sig}(\sigma)} \Psi(x_1,\ldots, x_Z)$ for every permutation σ.

The *electronic density* is given by

$$\rho(x) = \int_{\mathbb{R}^{3(Z-1)}} |\Psi(x, x_2 \ldots, x_Z)|^2 \ dx_2 \cdots dx_Z,$$

and so,

$$\int_\Omega \rho(x) \, dx$$

is the expected number of electrons in $\Omega \subset \mathbb{R}^3$.

The *ground state energy* reads now

$$E(Z) = \inf_{\substack{\Psi \in \mathcal{H} \\ ||\Psi||=1}} \langle \Psi, H_Z \Psi \rangle.$$

Therefore, the task is to obtain the lowest eigenvalue of the Hamiltonian H_Z acting on antisymmetric square integrable functions in the 3Z-dimensional Euclidean space. But this is still a very hard problem, mainly due to the Coulombian interaction of the electrons.

If our Hamiltonian had the form

$$\widetilde{H}_Z = \sum_{k=1}^{Z} \big(-\Delta_{x_k} + V(x_k) \big)$$

for a one electron potential V, then by separation of variables the problem would reduce from $3Z$ to 3 dimensions. Furthermore, exploiting the radial symmetry it would become merely one dimensional (i.e., an ordinary differential equation), and would be easily solved.

The main idea introduced to study atoms in Quantum Theory (Physics and Chemistry) is to approximate H_Z by $\tilde{H}_Z$, where the potential $V(x)$ is chosen as follows: let us pretend for a moment that we know the electronic density ρ; then a good candidate for such one-electron potential would be the following:

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

It is easy to deduce that the ground state eigenfunction and the ground state electronic density for $\tilde{H}_Z$ are given by

- $\Psi_{\mathrm{HF}}(x_1,\dots, x_Z)$ = antisymmetrized product (Slater's determinant) of the eigenfunctions $\phi_1(x),\dots, \phi_Z(x)$ for the three dimensional Schrödinger operator $-\Delta + V(x)$.
- $\rho_{\mathrm{HF}}(x) = \sum_{k=1}^{Z} |\phi_k(x)|^2$.

The method (Hatree-Fock) is a great simplification of the original problem, because now we are confronting just a 3-dimensional calculation instead of a 3Z-dimensional one. The system is closed asking the consistency condition (Hartree–Fock equation) that the obtained density equals the starting one:

$$\rho_{\mathrm{HF}} = \rho.$$

It is a remarkable and strange equation (neither a partial differential equation or an integral equation), and it is solved by iteration: starting with an initial density ρ_0, we produced the Hartree–Fock ρ_1, which taken as a new initial datum produce ρ_2, and so on. The limit density, in the hypothesis that it exists, would be the solution that we are looking for.

It is not obvious that the method will work and, in any case, the convergence will depend on the choice of an appropriate initial density. Here the Thomas–Fermi theory, also called statistical theory of atoms, came to help providing us with good approximations or both, the density and the eigenvalue sum, of a three dimensional Schrödinger operator.

In this setting, it is easily deduced that the Hartree–Fock ground state is given by the antisymmetrized product of the eigenfunctions, and that the sum of the negative eigenvalues is the lowest possible energy of the Hamiltonian. The so-called semi classical approximation (Hermann Weyl's formulas, Lieb-Thirring's inequalities) allows us, under reasonable conditions upon the potential $V(x)$, to rewrite the Hartree–Fock equation in a much more amenable form.

Let E_k denote the negative eigenvalues of $-\Delta + V(x)$, and let ϕ_k be the corresponding eigenfunctions. We want to approximate

$$E_{\mathrm{HF}}(Z) = \langle \widetilde{H}_Z \Psi_{\mathrm{HF}}, \Psi_{\mathrm{HF}} \rangle = \sum_k E_k \qquad \text{and} \qquad \rho_{\mathrm{HF}}(x) = \sum_k |\phi_k(x)|^2.$$

Then the semiclassical approximation provides us with the formulas:

$$\rho^Z_{\mathrm{TF}}(x) = (Const.)(-V^Z_{\mathrm{TF}}(x))^{3/2},$$

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

Applying the Laplacian to the second equality above and substituting in the resulting equation the value of the density in terms of the potential given by the first equality, we arrive to the more familiar form of the Thomas–Fermi equation:

$$\Delta V^Z_{\mathrm{TF}} = Const.\, (-V^Z_{\mathrm{TF}})^{3/2}.$$

Under the hypothesis of radial symmetry, the equations become a nonlinear ordinary differential equation which can be solved, showing that the dependence on the parameter Z can be removed by a trivial scaling:

$$\rho^Z_{\mathrm{TF}}(x) = Z^2\, \rho(Z^{1/3}\, x); \qquad V^Z_{\mathrm{TF}}(x) = Z^{4/3}\, V(Z^{1/3}\, x),$$

where the density ρ and the potential V are some perfectly determined functions. These formulas have a natural interpretation in terms of the "atomic radius" $Z^{-1/3}$, and the average distance $Z^{-2/3}$ between the electrons.

THE GROUND STATE ENERGY OF THE ATOM

The lines above are just a crude impressionistic view of the Hartree–Fock and Thomas–Fermi theories needed for the presentation of the main point in this talk, that is the rigorous (mathematical theorems) results for the ground state energy of the atom, which can be summarized in the following (asymptotic) expansion:

$$E(Z) = C_{\mathrm{TF}}\, Z^{7/3} + C_{\mathrm{S}}\, Z^2 + C_{\mathrm{SD}}\, Z^{5/3} + \Psi_Q(Z) + \cdots$$

- The term $C_{\mathrm{TF}}\, Z^{7/3}$ was suggested by Thomas–Fermi in 1927, and proved by Lieb–Simon [9] in 1973.
- The term $C_{\mathrm{S}}\, Z^2$ appeared first in numerical computations, was explained in 1950 by Scott [11], and proved rigorously by Hughes–Siedentop–Weikard in 1985-89 ([8], [12]). It reflects the fact that electrons near the nucleus behave as if they have not electronic interactions (screaming effect).
- The term $C_{\mathrm{SD}}\, Z^{5/3}$ was conjectured by Dirac [6] in 1930, and Schwinger [10] in 1981. It was proved by Fefferman–Seco [7] in 1990. It represents a small effect due to delicate electronic correlations.

The next term $\Psi_Q(Z)$ is oscillatory, and is given by the formula

$$\Psi_Q(Z) = \sum_{l=1}^{l_{\mathrm{TF}}} \frac{2l+1}{\frac{1}{\pi}\int \mathcal{F}(r)^{-1/2} dr} \cdot \mu\Big(\frac{1}{\pi}\int \mathcal{F}(r)^{1/2}\, dr\Big),$$

where

$$\mathcal{F}(r) := \Big(V_{\mathrm{TF}}^{Z}(r) - \frac{l(l+1)}{r^2}\Big)_+,$$

with the convention $(x)_+^{-1/2} = 0$ if $x \le 0$, and where

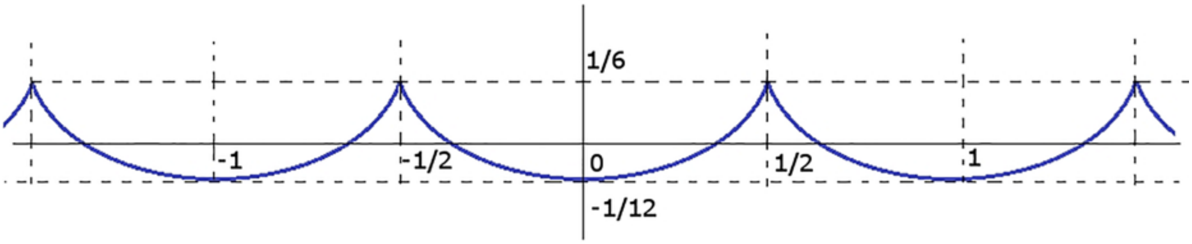
$$V_{\mathrm{TF}}^{Z}(r) = Z^{4/3}\, V(Z^{1/3} r)$$

is the Thomas–Fermi potential, and

l_{TF}= {greatest integer l such that $V_{\mathrm{TF}}^{Z}(r) - \frac{l(l+1)}{r^2} > 0$ somewhere}.

Finally,

$$\mu(x) = \mathrm{dist}(x, Z)^2 - \frac{1}{12}.$$



The oscillatory (almost periodic) character of Ψ_Q is very interesting, and there is a reasonable chance that it encodes the contribution to the energy of the electrons of valence. Our analysis of that term is contained in the following theorem.

Theorem 1 ([4], [5]).

$$-c_1 Z^{3/2} \le \Psi_Q(Z) \le c_1 Z^{3/2},$$
$$\Big(\frac{1}{Z}\int_1^Z |\Psi_Q(u)|^2\, du\Big)^{1/2} \ge c_2\, Z^{3/2},$$

where $0 < c_1, c_2 < \infty$ *are universal constants.*

In particular, we have that

$$\text{Average of } |\Psi_Q| \approx Z^{3/2}.$$

It is not the in the purpose of this talk to present the details of the proof. Let me simply add that the guess of the precise formula for that oscillatory term appears in the work of Fefferman–Seco regarding the Dirac–Schwinger correction to the atomic energy asymptotic. In our analysis we first decode its expression emphasizing the analogies with some classical formulas of Number Theory, namely those appearing in the problem of counting lattice points inside regions of Euclidean space. Then we can make use of the tools introduced by number theorists to deal with trigonometric sums (Van der Corput and Weyl methods: stationary phase, Poisson summation formula) to achieve the proof of the theorem.

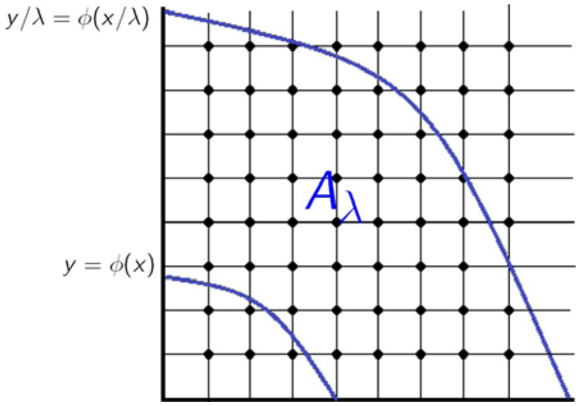
Number Theory is concerned with the estimation of sums of the following type:

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

where $\phi''(x) \geq c_0 > 0$, μ is a periodic function of average 0, and f is of slow variation.

As examples, we have

- f $\equiv 1$, $\mu(x) \equiv e^{2\pi i x}$, $\phi(x) = x^2$. It corresponds to Gaussian sums appearing in the law of quadratic reciprocity.
- f $\equiv 1$, $\mu(x) = x - [x] - 1/2$. Then S represents the error term in counting lattice points under the curve $y = \phi(x)$, dilated by λ.



If $N(\lambda)$ denotes the number of lattice points,

$$N(\lambda) = \text{area}(A_\lambda) + S(\lambda) = C\lambda^2 + S(\lambda),$$

then one expects to have good estimates for the growth of the error term $S(\lambda)$.

Van der Corput proved that, in general, for ϕ convex we have

$$S(\lambda) = O(\lambda^{2/3}),$$

an estimate that has been only slightly improved by several authors. But it is a hard open problem to decide if

$$S(\lambda) = O(\lambda^{1/2+\varepsilon})$$

for every $\varepsilon > 0$, even in the particular case when the curve is a circle.

In [2] it is proved that for "most" curves, the lattice error term in the area approximation is $O(\lambda^{1/2+\varepsilon})$ for every $\varepsilon > 0$. The meaning of "almost all curves" in that paper is coming from Feynman's path integral formulation of Quantum Mechanics, and gives another interesting connection between lattice points counting in Number Theory and quantum mechanical theories.

The analysis of the precise order of magnitude of the error term in lattice point problems is still an open problem. Fortunately, in our atomic case the periodic function μ has Fourier coeffcients decaying faster that the corresponding to the lattice point problem, making the computation easier. However, the nature of the phase function ϕ is much more complicated in the atomic case: the estimate $\phi'' > 0$ was obtained with the help of a computer using intervals arithmetic, becoming one of the first known examples of a computer assisted proof.

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