On the Atomic Energy Asymptotics

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1 Introduction.

Consider an atom consisting of N quantized electrons at positions x_i, and a nucleus fixed at the origin. The Schrödinger Hamiltonian of such a system is given by

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

acting on $\mathcal{H} = \wedge_{i=1}^{N} L^2\left(\mathbf{R}^3\right)$ (in this exposition, in order to simplify notation, we neglect spin.) Define the ground state of an atom of charge Z by

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

It is a remarkable fact that $E(Z)$ behaves in a very simple way when $Z \to \infty$, as follows:

Theorem 1.1

$$E(Z) = -c_0 Z^{7/3} + \tfrac{1}{8} Z^2 - c_1 Z^{5/3} + O\left(Z^{\frac{5}{3}-a}\right) \qquad a > 0$$

The first term above was conjectured by Thomas ([22]) and Fermi ([11]), and proved rigorously by Lieb-Simon ([16]). Their proof also holds for molecules. The second term was conjectured by Scott ([18]) and proved rigorously by Hughes-Siedentop-Weikard ([12], [19], [20] and [21]); the molecular case was recently proved by Ivrii–Sigal ([13]). The third term was conjectured by Schwinger ([17]), based on the fundamental work of Dirac ([2]); its proof was announced in [3], and the complete details of it appear in [4], [5], [6], [7], [8], [9] and [10].

The purpose of this paper is to give a brief expository presentation of the proof of Theorem 1.1. We refer the reader to [4] – [10] for accurate statements and detailed proofs of what follows.

Before we preceed to the proof, we recall a few basic facts about Thomas–Fermi theory. We refer the reader to [14] for a complete, accurate exposition.

We denote the Thomas–Fermi density by $\rho^Z_{\rm TF}(x)$. It satisfies the perfect scalling property

$$\rho^Z_{\rm TF}(x) = Z^2 \rho^1_{\rm TF}(Z^{1/3} x)$$

The Thomas–Fermi potential

$$V^Z_{\rm TF}(x) = \int \frac{\rho_{\rm TF}(y)}{|x-y|}\, dy$$

is radially symmetric, smooth away from the origin, and vanishing at infinity. The screened Thomas–Fermi potential

$$W^Z_{\rm TF}(x) = \frac{Z}{|x|} - V^Z_{\rm TF}(x) \geq 0$$

satisfies the Thomas–Fermi equations

$$6\pi^2 \rho^Z_{\rm TF}(x) = |W(x)|^{3/2} \qquad \Delta W(x) = 4\pi\rho(x).$$

$W^1_{\rm TF}$ can be written as $y(\gamma r)/r$, with an appropiate constant γ, and y satisfying the Thomas–Fermi Ordinary Differential Equation (ODE)

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

2 Reduction to a One–Electron Problem.

The first step in understanding $E(Z)$ is to simplify $H_{Z,N}$. We do this in the spirit of [12] and [20], but here we need to improve Lieb's inequality (see [14]) to capture the full $Z^{5/3}$ contribution.

Theorem 2.1

$$H_{Z,N} \geq \sum_{i=1}^N \left(-\Delta_{x_i} - \frac{Z}{|x_i|} + V^Z_{\rm TF}(|x_i|) \right)$$
$$-\tfrac{1}{2} \iint \frac{\rho_{\rm TF}(x)\rho_{\rm TF}(y)}{|x-y|}\, dx\, dy - c_D \int \rho^{4/3}_{\rm TF}(x)\, dx + O\left(Z^{\frac{5}{3}-a}\right) \qquad a > 0$$

The complete proof of this theorem appears in [4].

In preparation for the proof of Theorem 2.1, we split the electron–electron repulsion into a short and long range part, as follows

$$\tfrac{1}{2}\sum_{i\neq j}\frac{1}{|x_i-x_j|} = V_L + V_S = \sum_{i<j} K_L(x_i,x_j) + \sum_{i<j} K_S(x_i,x_j)$$

where

$$K_L(x,y) = \frac{1}{|x-y|}\chi_{|x-y|>d}$$
$$K_S(x,y) = \frac{1}{|x-y|}\chi_{|x-y|\leq d}$$

where d is a variable length–scale, approximately equal to $Z^{-\frac{2}{3}+a_0}$, $a_0 > 0$, throughout most of the atom.

Now we point out that, if we apply Lieb's inequality to V_L, the error we expect to obtain will behave like

$$\frac{Z}{\text{distance between electrons}} \leq \frac{Z}{Z^{-2/3+a_0}} = Z^{5/3-a_0}$$

which is good enough for our purposes. Thus, we only need to understand the short range part V_S of the repulsion. This amounts to understanding our wave functions ψ only at short distances. Motivated by this, we put ourselves in the following set–up:

Let $\psi(x_1,\ldots,x_K)$ be an antisymmetric wave function *supported* on $x_i \in Q$, for $i = 1,\ldots,K$, Q being a cube of side $L = Z^{-\frac{2}{3}+a_1}$. For simplicity, we impose on ψ periodic boundary conditions at ∂Q. This condition on ψ will have to be de–localized, in order to allow ψ's of arbitrary support, but this will be entirely omitted in the present exposition.

Furthermore, we assume that ψ satisfies the crucial estimate

$$\|\nabla\psi\|^2 \leq c_{\mathrm{TF}} L^{-2} K^{5/3}\left(1 + Z^{-a_2}\right) \tag{1}$$

where c_{TF} is the semiclassically correct constant, and a_2 is a positive constant to be carefully picked during the proof. It follows, as a consequence of Lieb–Simon's theorem, that if ψ is a ground state, then assumption (1) (or some version of it) must be satisfied for *most* cubes Q, or else, the first term in the energy asymptotics would be wrong. Therefore, we are justified in assuming (1). Our immediate goal is to conclude that if ψ satisfies (1), then it is very nearly equal to an antisymmetric product of "plane waves", in the following sense:

Consider Q_0, a subcube of Q, of side much smaller than L, but still larger than $Z^{-\frac{2}{3}+a_3}$, $a_3 > 0$; next, construct an orthonormal set $\{\varphi_\alpha\}_{\alpha=1}^{N_{\rm TF}}$ of functions supported on Q_0, which are essentially of the form $e^{i\xi_\alpha \cdot x}$, with $\xi_\alpha \in \Lambda(L)$ away from ∂Q_0. Here, $N_{\rm TF}$ is the number of ξ_α inside the Fermi ball $B(0, 2\pi(4\pi/3)^{-1/3}N^{1/3}L^{-1})$. We extend this orthonormal set to a basis for $L^2(Q)$, thus extending α to all integers. Consider also the translates φ_α^z of φ_α to $z \in Q$. Then, in this situation, the following holds:

Lemma 2.2 *Let ψ satisfy (1). Then, for most $z \in Q$, we can write*

$$\psi = \phi^z_{\rm basic} \wedge \phi^z_{\rm extra} + \phi^z_{\rm error} \tag{2}$$

with $\phi^z_{\rm basic} = \wedge_{\alpha=1}^{N_{\rm TF}} \varphi^z_\alpha$, $\phi^z_{\rm extra}$ strongly orthogonal to $\phi^z_{\rm basic}$, i.e.,

$$\int \phi^z_{\rm extra}(y_1, \ldots, y_{K-N_{\rm TF}}) \phi^z_{\rm basic}(x_1, \ldots, x_{N_{\rm TF}}) \delta_{y_j = x_i}\, dx_i\, dy_j = 0$$

for all i, j, and all $y_l \neq y_j$, all $x_n \neq x_i$; $\phi^z_{\rm error}$ is very small in appropriate norms.

Sketch of Proof: We introduce the positive numbers

$$\mu(z, \alpha) = 1 - \sum_{j=1}^{K} \int |\langle \psi, \varphi^z_\alpha \rangle|^2 \; dx_1 \cdots \hat{dx_j} \cdots dx_K$$

where the scalar product is in the x_j variable of ψ, and in the integration we remove the dx_j factor.

These numbers are important mainly for two reasons: first, (1) will imply they are very small. Second, since μ measures how much ψ differs from being an antisymmetric product of the ψ_α, errors of interest in what follows will be bounded by $\mu(z, \alpha)$. We make this *a little* more precise:

If we Fourier–expand ψ, with Fourier coefficients $\xi_i \in \Lambda(L)$, then

$$\mathrm{Av}_{z \in Q} \mu(z, \alpha) = \sum_{\xi_1, \ldots, \xi_K} \left| \hat{\psi}(\xi_1, \ldots, \xi_K) \right|^2 \left(1 - \sum_{j=1}^{K} |\hat{\varphi}^z_\alpha(\xi_j)|^2 \right)$$

Now, (1) implies that $\hat{\psi}(\xi_1, \ldots, \xi_K)$ is negligible unless most of the ξ_j are inside the Fermi ball; on the other hand, since the φ_α are almost equal to $e^{i\xi_j \cdot x}$, stationary phase implies the term in brackets above is close to zero for all ξ_j in the Fermi ball, when $1 \leq \alpha \leq N_{\rm TF}$. Therefore,

$$\mathrm{Av}_{z \in Q} \mu(z, \alpha) = O\big(Z^{-p}\big) \qquad p > 0$$

This implies that for most z, $\mu(z, \alpha)$ is very small. Then, we can obtain (2) by – essentially – setting

$$\phi^z_{\text{error}} = \sum_{\{1,\dots,N_{\text{TF}}\}\not\subset\{1,\dots,K\}} \hat\psi(\xi_1,\dots,\xi_K)\ \varphi^z{}_1 \wedge \cdots \wedge \varphi^z_K$$

Thus,

$$\begin{aligned}\psi - \phi^z_{\text{error}} &= \sum_{\{1,\dots,N_{\text{TF}}\}\subset\{1,\dots,K\}} \hat\psi(\xi_1,\dots,\xi_K)\varphi^z_1 \wedge \cdots \wedge \varphi^z_K \\ &= \phi^z_{\text{basic}} \wedge \phi^z_{\text{extra}}\end{aligned}$$

as stated. The size of ψ^z_{error} is bounded by $\sum_\alpha \mu(z,\alpha)$, and is therefore small. □

This, with some more work that we will omit here, allows us to simply ignore ϕ^z_{error} from now on. However, ϕ^z_{extra} cannot be ignored in such a way. Fortunately, since $K_S \geq 0$, creating electrons should only increase the energy, which is fine with Theorem 2.1. Indeed,

$$\langle V_S(\phi^z_{\text{basic}} \wedge \phi^z_{\text{extra}}), (\phi^z_{\text{basic}} \wedge \phi^z_{\text{extra}})\rangle \geq \langle V_S\phi^z_{\text{basic}}, \phi^z_{\text{basic}}\rangle$$

and this is trivial to prove using the strong orthogonality between ϕ^z_{basic} and ϕ^z_{extra}.

In orther words, in order to prove Theorem 2.1, we can assume that ψ correlates at short distances like the Hartree–Fock wave function ϕ^z_{basic}. Thus, imposing $a_3 < a_0$ we are justified in writing

$$\langle V_S\psi, \psi\rangle \geq \tfrac{1}{2}\sum_{i\neq j} \langle K_S(x_i,x_j)\phi^z_{\text{basic}}, \phi^z_{\text{basic}}\rangle - \text{junk}$$

and the right hand side can be calculated, since we know explicitely the density and correlation function of ϕ_{basic}. This yields

$$\langle V_S\psi, \psi\rangle \geq \tfrac{1}{2}\iint K_S(x,y)\left(\rho^z(x)^2 - |S^z(x,y)|^2\right)\,dx\,dy - \text{junk}$$

for

$$\rho^z(x) = \sum_{\alpha=1}^{N_{\text{TF}}} |\varphi^z_\alpha(x)|^2 \qquad S^z(x,y) = \sum_{\alpha=1}^{N_{\text{TF}}} \varphi^z_\alpha(x)\overline{\varphi^z_\alpha(y)}$$

Recalling the construction of the φ^z_α, note that

$$\begin{aligned}S^z(x,y) &= \sum_{\alpha=1}^{N_{\text{TF}}} e^{i\xi_\alpha(x-y)}\ (1 + \text{tiny errors}) \\ &= \int_{\text{Fermi Ball}} e^{iz(x-y)}\frac{dz}{(2\pi)^3}\ (1 + \text{tiny errors})\end{aligned}$$

and similarly, ρ^z is very nearly equal to N_{TF}. Therefore,

$$\langle V_S\psi,\psi\rangle \geq \tfrac{1}{2}\iint K(x,y)\left(N_{\rm TF}^2 - |\widehat{\chi_{\text{Fermi Ball}}}(x-y)|\right)\,dx\,dy - \text{junk}$$

This last inequality becomes Theorem 2.1 in passing from ψ supported on cubes Q to arbitrary ψ.

This finishes the exposition of the proof of Theorem 2.1

3 The One–Electron Problem.

The goal of this Section is to understand the spectrum of a certain class of operators in $L^2(\mathbf{R}^3)$ given by

$$H = -\Delta - W$$

Again, we omit a detailed description of the conditions on W, and we simply say that W is a large, slowly varying *radial* potential, which is allowed a Coulomb singularity, and that our screened Thomas–Fermi potential belongs to this class.

We start by exhibiting the well–known fact that estimates for the spectrum of H imply bounds for $E(Z)$. Indeed, letting W be the screened Thomas–Fermi potential, if we denote by E_k the negative eigenvalues of H, and by ψ_k the corresponding normalized eigenfunctions, we obtain from the previous section that

$$E(Z) \geq \sum_k E_k - \tfrac{1}{2}\iint \frac{\rho_{\rm TF}(x)\rho_{\rm TF}(y)}{|x-y|}\,dx\,dy - c_D\int \rho_{\rm TF}^{4/3}(x)\,dx + O\left(Z^{\frac{5}{3}-a}\right) \tag{3}$$

Note that the last two constants in the right hand side scale perfectly in Z.

Knowledge of the eigenfunctions ψ_k, on the other hand, provides us with upper bounds by simply setting $\psi = \wedge_k\psi_k$; then, clearly

$$E(Z) \leq \langle H_{Z,N}\psi,\psi\rangle \tag{4}$$

A simple computation shows that

$$\langle H_{Z,N}\psi,\psi\rangle = \sum_k E_k - \tfrac{1}{2}\iint \frac{\rho_{\rm TF}(x)\rho_{\rm TF}(y)}{|x-y|}\,dx\,dy - \iint \frac{|S(x,y)|^2}{|x-y|}\,dx\,dy + \iint \frac{(\rho_{\rm TF}(x)-\rho(x))\,(\rho_{\rm TF}(y)-\rho(y))}{|x-y|}\,dx\,dy$$

where

$$\rho(x) = \sum_k |\psi_k(x)|^2 \qquad S(x,y) = \sum_k \psi_k(x)\overline{\psi_k(y)}$$

Now, it is a very different question whether these bounds (3) and (4) will be any good. It is a remarkable property of the Thomas–Fermi potential that, in fact, these upper and lower bounds agree up to an error $O\left(Z^{\frac{5}{3}-a}\right)$ with $a > 0$. Indeed, the following Lemma holds:

Lemma 3.1

$$\iint \frac{|S(x,y)|^2}{|x-y|}\,dx\,dy \geq c_D \int \rho_{\mathrm{TF}}^{4/3}(x)\,dx + O\left(Z^{\frac{5}{3}-a}\right) \tag{5a}$$

$$\iint \frac{(\rho_{\mathrm{TF}}(x)-\rho(x))\,(\rho_{\mathrm{TF}}(y)-\rho(y))}{|x-y|}\,dx\,dy = O\left(Z^{\frac{5}{3}-a}\right) \tag{5b}$$

Note that this Lemma is also a consequence of an accurate enough knowledge of the spectrum of H. We remark that in the case of a smooth potential, the formula for the exchange (5a) was known ([1]).

Combining this Lemma with (3), (4) and (5), we note that Theorem 1.1 is reduced to obtaining the asymptotic formula for the sum of the eigenvalues E_k that implies the expression for $E(Z)$. Note also that our result also implies that the Hartree–Fock energy is accurate through the $Z^{5/3}$ term.

We start now our analysis of H. In the present exposition we will take care of the eigenvalue sum only. The main theorem we try to proof now is the following:

Theorem 3.2

$$\sum_k E_k = -\tfrac{1}{15\pi^2}\int (W(x))_+^{5/2}\,dx + \tfrac{1}{8}Z^2 + \tfrac{1}{48\pi^2}\int (W(x))_+^{1/2}\,\Delta W(x)\,dx$$
$$+\text{lower order terms}$$

assuming that classical periodic orbits of the Hamiltonian given by $p^2 - W(x)$ *have measure 0.*

A crucial property of H in what follows, is that it is radially symmetric; thus, separation of variables into spherical harmonics yields that, if we denote by $E_{k,l}$ the k'th eigenvalue of

$$H^{\mathrm{ODE}} = -\frac{d^2}{dr^2} - W(r) + \frac{l(l+1)}{r^2}$$

then the eigenvalues of H come in a strightforward way from the $E_{k,l}$, each taken with multiplicity $2l+1$. Here, l is a non–negative integer.

The analysis of H is thus reduced to the analysis of ODE's

$$\frac{d^2}{dr^2} + p_E(r,l) = 0 \tag{6}$$

$$p_E(r,l) = W(r) - \frac{l(l+1)}{r^2} + E \quad E < 0 \quad l = 0, 1, \ldots$$

in the sense that if we can find a solution of (6) which vanishes at 0, at infinity, and at $k-1$ other points, then $E = E_{k,l}$. The main ingredient in the proof of Theorem 3.2 is the following eigenvalue formula.

Theorem 3.3 *If $l \geq Z^{a_4}$, a_4 small,*

$$\phi(E_{k,l}) + \tfrac{1}{48}\psi(E_{k,l}) = \pi(k + \tfrac{1}{2}) + O\Big(\|p\|^{-1+\epsilon_2}\Big)$$

where

$$\phi(E) = \int (p_E(x;l))_+^{1/2}\, dx$$

$$\psi(E) = \lim_{\delta \to 0} \left(\int (p_E(x;l))_+^{-3/2}\, p''(x;l)\, dx - G(E,l)\delta^{-1/2} \right)$$

where $G(E,l)$ is uniquely determined by requiring the finiteness of the limit.

When $l \leq Z^{a_4}$, then

$$\phi(E_{k,l}) = \pi(k + \tfrac{1}{2}) + O(1)$$

The proof of this Theorem is the main content of [5]. We also refer the reader to [5] for the exact meaning of $\|p\|$ above, and for the exact formulation of the Theorem. The strategy of the proof is as follows:

Note first the following change of variables formula for ODE's. Consider two ODE's

$$F''(x) + p(x)F(x) = 0 \tag{7a}$$

$$A''(y) + V(y)A(y) = 0 \tag{7b}$$

Then, the change of variables $y = y(x)$ given by

$$(y')^2\, V(y) + \{y, x\} = p(x) \qquad \{y,x\} = -\tfrac{3}{4}\left(\frac{y''(x)}{y'(x)}\right)^2 + \tfrac{1}{2}\frac{y'''(x)}{y'(x)} \tag{8}$$

makes (7a) and (7b) equivalent via the transformation law

$$F(x) = (y'(x))^{-1/2}\, A(y(x))$$

What we will do then is, first, to take V a simple potential for which (7b) admits an explicit solution; then, a virtue of (8) is that we can understand the change of variables as an explicit formal power series expansion in $\|p\|^{-1}$;

then, we combine both $A(y)$ and $y(x)$ to understand the solution of (7a). The choices of V will be as follows:

a. Near a zero of p, $V(x) = \lambda^2 x$ for λ large. Then, (7b) becomes the well known Airey equation.

b. When $p > 0$, we take $V = \lambda^2$. When $V < 0$, we take $V = -\lambda^2$, λ large.

The previous two choices apply for generic values of l and E. For special values, we need the two additional choices:

c. When l is small, say 1, our two previous choices will not work for x near the Coulomb singularity. The correct choice will be, of course, $V(x) = \frac{\lambda^2}{x}$; then (7b) becomes the well known Hydrogen equation. This is very important, since it gives rise to the non–semiclassical term Z^2 in the energy asymptotics in Theorems 1.1 and 3.2. Smooth potentials don't have it.

d. When E is very near $\min p_0$, then p_E and its first derivative are almost zero when p_E is negative; as a consequence, the previous choices will not work nicely, and we compare in this case with $V(x) = \lambda^2 x^2$, the equation of the Harmonic Oscillator.

Note that this method gives control over the eigenfunctions, too.

The next step is to lift Theorem 3.3 in order to say something about *radial* potentials in $\mathbf{R}^3$. We do this by summing Theorem 3.3 in k and l, recalling the multiplicity of each eigenvalue, obtaining

$$\sum_k E_k = -\tfrac{1}{15\pi^2}\int W(x)_+^{5/2}\,dx + \tfrac{1}{8}Z^2 + \tfrac{1}{48\pi^2}\int W(x)_+^{1/2}\Delta W(x)\,dx \\ +G(W) + \text{junk}$$

where junk is negligible, and $G(W)$ is a term that comes from a careful replacement of sums by integrals: it has the form

$$\sum_l c_l \beta\left(\tfrac{1}{\pi}F_W(l) - \tfrac{1}{2}\right)$$

for $\beta(x) = \{x\}^2 - \frac{1}{12}$, $\{\cdot\}$ meaning the distance to the closest half–integer, and

$$F_W(l) = \int \left(W(r) - \frac{l^2}{r^2}\right)_+^{1/2} dr$$

However, G is far from being just a technical term: it captures the main contribution of classical closed orbits to semiclassical asymptotics.

It is rather easy to see ([Ar]) that a potential W such that $F(t)$ is a linear function of t, with F' a rational multiple of π, then all classical orbits are periodic, our term $G(W)$ is oscillating, and has the same size as the third term in the formula in Theorem 3.2, which would then be wrong in this case; for the atom, this term G would then be of size $O\left(Z^{5/3}\right)$, and therefore Theorem 1.1 would also be wrong if the screened Thomas–Fermi potential were of this type. Potentials of this type are, for example, those of the Hydrogen atom and the Harmonic Oscillator.

The opposite case is a potential W for which $|F''(t)| \geq c > 0$. In this case, classical periodic orbits have measure 0, and $G(W)$ can be seen to be of size $O\left(Z^{\frac{5}{3}-b}\right)$, $b > 0$. An intermediate case of potentials are those for which F'' vanishes to finite order. In this case, closed orbits also have measure 0, and the size of $G(W)$ continues to be $O\left(Z^{5/3-b}\right)$, but the value of b depends on the order of the zeros of F''.

It is therefore very important to determine to which of these classes of potentials the screened Thomas–Fermi potentials belongs to. It is rather easy to see that F'' vanishes only to finite order; therefore, Theorem 1.1 holds, possibly with a bad error term if F'' vanishes very much. However, more is true, and it can be seen that $|F''| \geq c > 0$; this is a very delicate fact since arbitrary small perturbations of V_{TF} in a natural topology allow F'' to vanish as many times as we want. The analysis of F'' is taken care of in [10].

We end by pointing out the similarity between problems in Analytic Number Theory like the Lattice Point Problem, and the effect of the zeros of F'' on the semiclassics for $E(Z)$. In retrospect, this is not so surprising, since the Lattice Point Problem also comes from the semiclassics of a Laplacian on the Thorus.

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