# The Energy Asymptotics of Large Coulomb Systems


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## Introduction.

Consider a molecule consisting of $N$ quantized electrons at positions $x_i$, and $M$ nuclei of charges $Z = (Z_1, \ldots, Z_M)$ fixed at positions $y = (y_1, \ldots, y_M)$. The Schrödinger Hamiltonian of such a system is given by

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

$$V_{\text{Coulomb}}(x) = -\sum_{j=1}^{M} \frac{Z_j}{|x_- y_j|}$$

acting on $\mathcal{H} = \wedge_{i=1}^{N} L^2\left(\mathbf{R}^3 \times \mathbf{Z}_q\right)$; in this exposition, in order to simplify notation, we neglect spin by putting $q = 1$. Define the ground state of such a system by

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

When $M = 1$, this system is an atom. In this case we can assume $y = 0$ and we denote its energy simply by $E_{\text{atom}}(Z)$.

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

**Theorem 1**

$$E(Z, y; |Z|) = -c_0 Z^{7/3} + \tfrac{1}{8} Z^2 + O\big(Z^{2-a}\big) \qquad a > 0$$
$$E_{\text{atom}}(Z) = -c_0 Z^{7/3} + \tfrac{1}{8} Z^2 - c_1 Z^{5/3} + O\Big(Z^{\frac{5}{3} - \frac{1}{2835}}\Big)$$

*In the molecular case, the formula holds for all $y$ such that $|y_j - y_k| > Z^{-\frac{2}{3}+\epsilon}$, and for $Z \to \infty$ along a given direction.*

Note that in the molecular case, the asymptotics are asserted for the neutral molecule, whereas in the atomic case, we use the lowest possible energy. The problem of whether both energies are the same is a very subtle one, and although much research has been done about it, not much is known about it. In our setting, however, given the relatively large degree of error we allow ourselves in the energy asymptotics as compared with the delicate phenomenom of neutrality, it is just a technical point. We refer the reader to (4, 5, 20, 23, 27, 28) and references thereof for information on the neutrality problem. We also refer the reader to the contribution of Ruskai and Solovej to appear elsewhere in this same proceedings.

The first term above was conjectured by Thomas (29) and Fermi (14), and proved rigorously by Lieb-Simon (19). Their proof holds for atoms as well as molecules. The second term was conjectured by Scott (22) and proved rigorously by Hughes-Siedentop-Weikard (15 , 24, 25 and 26) in the atomic case; its proof for molecules appears in (16). The third term was conjectured by Schwinger (21), based on the fundamental work of Dirac (3); its proof for the atomic case was announced in (6), and the complete details of it appear in (7, 8, 9, 10, 11, 12 and 13). The proof of the third term for molecules remains open.

The purpose of this paper is to give a brief joint expository presentation of the proof of Theorem 1. We refer the reader to (7, 8, 9, 10, 11, 12, 13 and 16) 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 (17) for a comprehensive review.

We denote the Thomas–Fermi density by $\rho_{\text{TF}}^Z(x)$. It satisfies the perfect scalling property

$$\rho_{\text{TF}}^Z(x) = Z^2 \rho_{\text{TF}}^1(Z^{1/3} x)$$

The Thomas–Fermi potential

$$V_{\text{TF}}^Z(x) = \sum_{j=1}^{M} \int \frac{\rho_{\text{TF}}(y_j)}{|x - y_j|}\, dy$$

is smooth away from the origin, and vanishing at infinity. In the atomic case, $V_{\mathrm{TF}}^{Z}$ is radially symmetric: this will be of crucial importance for our current proof of the atomic energy asymptotics.

The screened Thomas–Fermi potential

$$W_{\mathrm{TF}}^{Z}(x) = \sum_{j=1}^{M} \frac{Z_j}{|x - y_j|} - V_{\mathrm{TF}}^{Z}(x) \geq 0$$

satisfies the Thomas–Fermi equations

$$6\pi^2 \rho_{\mathrm{TF}}^{Z}(x) = \left| W_{\mathrm{TF}}^{Z}(x) \right|^{3/2} \qquad \Delta W_{\mathrm{TF}}^{Z}(x) = 4\pi \rho_{\mathrm{TF}}^{Z}(x).$$

In the atomic case $W_{\mathrm{TF}}^{1}$ can be written as $u(\gamma r)/r$, with an appropiate constant $\gamma$, and $u$ satisfying the Thomas–Fermi Ordinary Differential Equation (ODE)

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

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## 1 Mean Field Theory.

The first step in understanding $E(Z)$ is to simplify $H_{Z,N}$. We start by describing Lieb's inequality (18), which was used in (15 , 16 and 25) to prove the Scott term.

Start with the elementary identity

$$\frac{1}{|x-y|} = \frac{1}{\pi} \iint \chi_{B(z,R)}(x) \chi_{B(z,R)}(y) \, \frac{dz\, dr}{R^5}$$

which, except for the constant $\frac{1}{\pi}$, is forced on us by dilation and translation invariance. Summing over pairs of electrons, we arrive at

$$\tfrac{1}{2} \sum_{i \neq j} \frac{1}{|x_i - x_j|} = \frac{1}{2\pi} \iint \mathcal{N}\Big(\mathcal{N} - 1\Big) \, \frac{dz\, dR}{R^5}$$

where

$$\mathcal{N} = \mathcal{N}(x_1, \ldots, x_N; z, R) = \sum_{i=1}^{N} \chi_{B(z,R)}(x_i)$$

represents the number of $x_i$ in the ball of center $z$ and radius $R$.

Let us pick now

$$\bar{\mathcal{N}}(z, R) = \int_{B(z,R)} \rho_{\mathrm{TF}}^{Z}(x)\, dx$$

to write

$$\tfrac{1}{2} \sum_{i \neq j} \frac{1}{|x_i - x_j|} = \frac{1}{2\pi} \iint \left( \left(\mathcal{N} - \bar{\mathcal{N}}\right)^2 + \mathcal{N}\left(2\bar{\mathcal{N}} - 1\right) - \bar{\mathcal{N}}^2 \right) \frac{dz\, dR}{R^5}$$

Since $\bar{\mathcal{N}}$ is independent of the $x_i$, of the three terms in the integrand above, the first is a two–body potential, the second is one–body and the last is a constant. The two–body part is hard to understand, but its contribution is non–negative. Therefore, dropping the two–body part, we arrive at

$$\tfrac{1}{2} \sum_{i \neq j} \frac{1}{|x_i - x_j|} \geq \sum_{i=1}^{N} V(x_i) - C$$

where $V$ is essentially $V_{\mathrm{TF}}^{Z}$. This suggests that we should consider the following Schrödinger operator

$$H^{\mathrm{ind}} = \sum_{i=1}^{N} \left( -\Delta_{x_i} - \frac{Z}{|x_i|} + V_{\mathrm{TF}}^{Z}(x_i) \right)$$

This operator describes $N$ independent particles in the effective external potential $-Z/|x| + V_{\mathrm{TF}}^{Z}(x)$, i.e., the nuclear potential screened by the Thomas–Fermi charge density.

To understand the error that such an inequality sacrifices, take a ball of radius $R \sim C\, Z^{-2/3}$, $C$ large, which is expected to contain a fixed, large number of electrons. The term dropped, $(\mathcal{N} - \bar{\mathcal{N}})^2$ is approximately the variance of $\mathcal{N}$, which, if electrons were independent, would be like $\bar{\mathcal{N}} \sim$ large constant. For this ball, $\frac{dz\, dR}{R^5}$ contributes with approximately $R^{-1}$, this giving an error of about $Z^{2/3}$. Since there are about $Z$ of these balls, the total error is like $Z^{5/3}$.

## 2 Correlations.

The error obtained in the previous section is acceptable for the asymptotics we announced for molecules, but for the refined atomic asymptotics, we have to do better. The improvement will come from the analysis of electron–electron correlations.

**Theorem 2** *Let $\psi$ be the gound state of $H_{Z,N}$. Then*

$$\left\langle \psi, \tfrac{1}{2}\sum_{i\neq j}\frac{1}{|x_i-x_j|}\psi\right\rangle \geq \left\langle \sum_{i=1}^{N} V_{\mathrm{TF}}^{Z}(x_i)\psi,\psi\right\rangle \\ -\tfrac{1}{2}\iint \frac{\rho_{\mathrm{TF}}(x)\rho_{\mathrm{TF}}(y)}{|x-y|}\,dx\,dy - c_D\int \rho_{\mathrm{TF}}^{4/3}(x)\,dx + O\left(Z^{\frac{5}{3}-\frac{1}{2835}}\right)$$

The complete proof of this theorem for the atomic case appears in (7). The proof for molecules follows after trivial modifications.

In preparation for the proof of Theorem 2, 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. Precisely,

$$d = \min(Z^{-\frac{2}{3}+a_0}, c|x|) \qquad c \text{ small}$$

Now, in view of the above calculation, 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 $\psi$ 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 $L=Z^{-\frac{2}{3}+a_1}$. Consider also $\Lambda(L)=\frac{2\pi}{L}\mathbf{Z}^3$, the lattice dual to $Q$. For simplicity, we impose on $\psi$ periodic boundary conditions at $\partial Q$. This condition on $\psi$ will have to be de–localized, in order to allow $\psi$'s of arbitrary support, but this will be entirely omitted in the present exposition.

Furthermore, we assume that $\psi$ satisfies the crucial estimate

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

where $c_{\mathrm{TF}}=(\frac{4\pi}{3})^{-5/3}\cdot\frac{4\pi}{5}\cdot(2\pi)^2$ is the semiclassically correct constant, and $a_2$ is a positive constant to be carefully picked during the proof. Note that if one takes

$$\psi = e^{ix_1\cdot\xi_1}\wedge\cdots\wedge e^{ix_p\cdot\xi_p}$$

for $\xi_j \in B(0,R)\cap\Lambda(L)$ distinct, and as close as possible to the origin to minimize the kinetic energy, then

$$\|\nabla\psi\|^2 \sim \tfrac{4\pi}{5}\left(\tfrac{L}{2\pi}\right)^3 R^5$$

$$p = \#B(0,R)\cap\Lambda(L) \sim \tfrac{4\pi}{3}R^3\left(\tfrac{L}{2\pi}\right)^3$$

for $p$ large, which shows

$$R \sim R_{\mathrm{F}} = 2\pi(4\pi/3)^{-1/3}p^{1/3}L^{-1}$$

We call $R_{\mathrm{F}}$ the Fermi radius, and $B(0,R_{\mathrm{F}})$ the Fermi ball for $p$ particles.

It follows, as a consequence of Lieb–Simon's theorem, that if $\psi$ 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 $\psi$ 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 $\{\varphi_\alpha\}_{\alpha=1}^{N_{\mathrm{TF}}}$ 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 $\partial Q_0$. Here, $N_{\mathrm{TF}}$ is the number of $\xi_\alpha$ inside the Fermi ball for $K$ particles $B(0,2\pi(4\pi/3)^{-1/3}K^{1/3}L^{-1})$. We extend this orthonormal set to a basis for $L^2(Q)$, thus extending $\alpha$ to all integers. Consider also the translates $\varphi_\alpha^z$ of $\varphi_\alpha$ to $z\in Q$. Then, in this situation, the following holds:

**Lemma 3** *Let $\psi$ satisfy (1). Then, for most $z\in Q$, we can write*

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

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

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

*for all $i$, $j$, and all $y_l$, $x_n$ with $l \neq j$ and $n \neq i$; $\phi^z_{\mathrm{error}}$ is 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 $\psi$, 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 $\mu$ measures how much $\psi$ differs from being an antisymmetric product of the $\psi_\alpha$, errors of interest in what follows will be bounded by $\mu(z,\alpha)$. We make this *a little* more precise:

If we Fourier–expand $\psi$, 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 $\xi_j$ are inside the Fermi ball; on the other hand, since the $\varphi_\alpha$ are almost equal to $e^{i\xi_j\cdot x}$, stationary phase implies the term in brackets above is close to zero for all $\xi_j$ in the Fermi ball, when $1 \le \alpha \le N_{\mathrm{TF}}$. 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

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

Thus,

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

as stated. The size of $\psi^z_{\mathrm{error}}$ 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 $\phi^z_{\mathrm{error}}$ from now on. However, $\phi^z_{\mathrm{extra}}$ 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. 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 $\phi^z_{\text{basic}}$ and $\phi^z_{\text{extra}}$.

In orther words, in order to prove Theorem 2, we can assume that $\psi$ correlates at short distances like the Hartree–Fock wave function $\phi^z_{\text{basic}}$. 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 explicitly the density and correlation function of $\phi_{\text{basic}}$. 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 $\varphi^z_\alpha$, 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, $\rho^z$ is very nearly equal to $N_{\text{TF}}$. Therefore,

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

This last inequality becomes Theorem 2 in passing from $\psi$ supported on cubes $Q$ to arbitrary $\psi$.

This finishes the exposition of the proof of Theorem 2.

**Corollary** *Denote by $E^{\text{ind}}(Z,N)$ the lowest eigenvalue of*

$$H^{\text{ind}} = \sum_{i=1}^{N} \left( -\Delta_{x_i} - \frac{Z}{|x_i|} + V^Z_{\text{TF}}(x_i) \right)$$

*Then*

$$E_{Z,N} \geq E^{\mathrm{ind}}(Z) - \tfrac{1}{2} \iint \frac{\rho_{\mathrm{TF}}(x)\rho_{\mathrm{TF}}(y)}{|x-y|}\,dx\,dy \\ - c_D \int \rho_{\mathrm{TF}}^{4/3}(x)\,dx + O\Big(Z^{\frac{5}{3}-\frac{1}{2835}}\Big) \tag{3}$$

Note that if $E_k$ are the $N$ lowest negative eigenvalues of

$$-\Delta_x - \frac{Z}{|x|} + V_{\mathrm{TF}}^Z(x)$$

then

$$E^{\mathrm{ind}}(Z,N) = \sum_k E_k.$$

## 3 Upper Bound.

In order to obtain an upper bound for $E(Z,y;N)$ we use the ground state of $H^{\mathrm{ind}}$ as a test function. Precisely, if we denote by $\psi_k$ the normalized eigenfunctions of $-\Delta - W_{\mathrm{TF}}^Z(x)$, for $W_{\mathrm{TF}}^Z$ the screened Thomas–Fermi potential, and we put $\psi = \wedge\psi_k$, then the variational principle yields

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

A simple computation shows that

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

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, at least in the atomic case, these upper and lower bounds agree up to an error $O\Big(Z^{\frac{5}{3}-a}\Big)$ with $a>0$. Indeed, the following lemma holds:

**Lemma 4** *In the atomic case,*

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

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

Inequality (5a) is a consequence of rather rough asymptotics, and can be obtained by a modification of a result in (16). We remark that in the case of a smooth potential, the formula for the exchange (5a) was previously known (2). Equation (5b) is much more subtle, and requires control of the periodic orbits at zero energy for the classical Hamiltonian.

Combining this lemma with (3), (4) and (5), we note that Theorem 1 is reduced to obtaining the asymptotic formula for the sum of the eigenvalues $E_k$ that implies the expression for $E_{\rm atom}(Z)$. Note that our result also implies that the Hartree–Fock energy is accurate through the $Z^{5/3}$ term.

The proof of the equivalent of the corollary in the previous section, and of Lemma 4 for molecules remains open. However, there is a recent independent proof of the accuracy of the Hartree–Fock model through the $Z^{5/3}$ term due to V. Bach (1). His proof also holds for molecules, is very concise and, in the atomic case, leads to better error terms than ours. He also obtains some of the correlation estimates of the previous section.

## 4 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 potential, which is allowed Coulomb singularities, and that our screened Thomas–Fermi potential belongs to this class.

In the present exposition we will take care of the eigenvalue sum only. At exactly this point, the proofs for atoms and molecules start to be very different: for molecules, one does not have radial symmetry. For atoms, one has radial symmetry, but one wants to go beyond $Z^2$ and obtain the $Z^{5/3}$ term. A common feature, however, remains to be the presence of singularities in the potential.

### 4.1 Quasiclassical Asymptotics: General Case.

We consider in this section the negative eigenvalue sum for a Schrödinger operator with symbol

$$h(x,\xi) = |\xi|^2 - W_{\mathrm{TF}}^{Z}(x)$$

It follows by the perfect scaling of the Thomas–Fermi potential, that this problem can be viewed as a quasiclassical limit for the Operator

$$P = -\hbar^2 \Delta - \phi(x) \qquad \phi(x) = W_{\mathrm{TF}}^{1}(x)$$

for $\hbar = Z^{-1/3}$. We denote the symbol of $P$ by $p(x,\xi) = |\xi|^2 - \phi(x)$.

If $\phi$ were smooth, then one can use standard results based on the pseudo–differential calculus to obtain sharp spectral asymptotic for this problem. This smooth case is related to the work of Duistermaat, Guillemin, Helffer, Hörmander, Ivrii, Melrose, Petkov, Robert, among many others. Our problem is that $\phi$ is has singularities.

**Theorem 5** *Let $Z \to \infty$ along a given direction and let the mutual distances between the $y_j$'s $\geq$ $\mathrm{const}|Z|^{-\frac{2}{3}+\epsilon}$. Then*

$$\sum_{i=1}^{N} E_i \;=\; \mathrm{Weyl} + \mathrm{Scott} + o(|Z|^2) \;,$$

*where*

$$\mathrm{Weyl} \;=\; \iint_{p\leq 0} h(x,\xi)\, dx\, d\xi$$

*and*

$$\mathrm{Scott} \;=\; \frac{1}{8}\sum Z_j^2 \;.$$

*Proof.* There are two ingredients in our proof.

**Microlocal Spectral Analysis.** We estimate global quantities through local ones. For instance, we study

$$\mathrm{tr}\big(\psi(x) g(P)\big) \tag{6}$$

where $g(\lambda) = \lambda$ for $\lambda \leq 0$ and $0$ for $\lambda \geq 0$. If $\psi \equiv 1$, then the trace above is just the sum of negative eigenvalues of $P$. We take for $\psi$ smooth functions localized outside of the singularities of the potentials. Then it is not difficult to obtain asymptotic expansion in the quasiclassical parameter $\hbar$ of the trace (6).

The traditional approach to obtaining spectral information, is first, to study a particular P.D.E. $f(P,t)$, and then use a tauberian theorem to pass information to the eigenvalues, Different P.D.E.'s and the corresponding tauberian techniques that one can use are summarized in the following table:

| **P.D.E.** | **Tauberian Technique** |
|---|---|
| Heat | Laplace Transform |
| Wave Eqn. | sin transform |
| Schrödinger Eqn. | Fourier Transform |
| Stationary Schrödinger Eqn. | Hilbert Transform |
| Powers $H^z$ | Mellin Transform |

The tauberian analysis is generally easy and sharp, while the P.D.E. analysis is generally hard and subject to improvement. This justifies the choice in our approach of the best tauberian technique (Fourier Transform) and the corresponding –hardest– P.D.E., the Schrödinger Equation. In general, this equation is very hard to study for second order operators, which is our case, due to the infinite speed of the propagation of singularities. However, microlocally, we have

$$|\xi| \sim \sqrt{E + \phi(x)}$$

and since we are interested only in the negative eigenvalues, we obtain the bound –always microlocally–

$$|\xi| \leq \sup |\phi_+(x)|^{1/2}$$

where the sup ranges over the support of $\psi$. This gives us a bound for speed of propagation of singularities. And as a result we are left with a domain in phase space given by

$$\{(x, \xi) \mid |\xi| \leq |\phi_+(x)|^{1/2} \quad x \in \text{supp } \psi\}$$

outside of which we get a negligible contribution to the negative part of the spectrum. We denote by $\varphi(x, \xi)$ a smooth cut–off function adapted to a small neighborhood of such domain.

Pseudodifferential calculus provides convenient tools for carrying out our program. Adapting a standard technique, one represents $g(P)$ as

$$g(P) \;= \frac{1}{2\pi\hbar} \int \hat{g}(t) e^{-iPt/\hbar}\, dt$$

where $\hat{g}(t)$ is the $\hbar$–Fourier transform of $g$,

$$\hat{g}(t) = \int e^{-it\lambda/\hbar}\, g(\lambda)\, d\lambda \tag{7}$$

The evolution operator $e^{-iPt/\hbar}$ is then approximated locally to any power in $\hbar$ by Fourier integral operators in the spirit of the geometrical optics

$$e^{-iPt/\hbar} \approx F_t$$

on the appropiate part of phase space, for

$$F_t u = \hbar^{-d} \iint e^{i\left(S(t,x,\xi)-z\cdot\xi\right)/\hbar} a(t,x,\xi,\hbar)\, u(z)\; dz\, d\xi \tag{8}$$

where $S$ satisfies the Hamilton–Jacobi equation

$$\left.\begin{aligned} \partial_t S + p(x, \nabla_x S) = 0 \\ S(0,x,\xi) = x\cdot\xi \end{aligned}\right\}$$

and

$$a = \sum_{j=0}^{N} \hbar^j a_j(t,x,\xi)$$

where the $a_j$ satisfy the transport equations

$$\partial_t a_j + \nabla_x S \cdot \nabla_x a_j + \tfrac{1}{2}\Delta_x S\, a_j = -\tfrac{i}{2}\Delta_x a_{j-1} \qquad a_{-1} \equiv 0$$

$$a_j\big|_{t=0} = \delta_{j,0}\varphi(x,\xi)$$

The initial conditions on the $a_j$ imply that $F_0 = \varphi(x, -i\partial_x)$ and since $\varphi \equiv 1$ on the support of $\psi$, we have that $\psi F_t \approx F_t$ for small enough time. For sufficiently small time, the classical trajectories starting in supp$\varphi$ do not reach the singularities of $\phi(x)$. Thus, the singularities of $\phi(x)$ are decoupled, and all the objects we are dealing with are smooth.

Expressions like the one in (8) allow us to analyze the trace in (6) by the method of stationary phase. Note that after the localization introduced with $\varphi$, all integrals are absolutely convergent, so that the analysis involved is rather easy. Since in this part of the analysis we stay away from the singularities, this analysis is quasiclassical in nature and in our asymptotics we will obtain only the contribution to the Weyl term, with a good error bound. The problem here is that the remainder estimates here depend on supp $\psi$ and on estimates of $\partial^\nu \phi$ on supp $\psi$. To remedy this we introduce the second ingredient of our analysis.

**Multiscale Analysis.** There are three scales in the problem: momentum scale determined by the quasiclassical parameter $\hbar = O(|Z|^{-\frac{1}{3}})$, space scale, $\ell(x)$, determined by the behavior of the potential under differentiation, and the energy scale, $f(x)^2$, determined by the size of the potential. The first scale is constant while the other two depend on $x$. Specifically, assume there are positive functions $f(x)$ and $\ell(x)$ such that

1. $|\nabla \ell(x)| \leq M$.
2. $cf(y) \leq f(x) \leq Cf(y)$ for $x \in B\big(y, \ell(y)\big)$.
3. $|\partial_x^\alpha \phi(x)| \leq C_\alpha f(x)^2 \ell(x)^{-|\alpha|}$.

In dealing with the Coulomb singularities of $\phi(x)$ we set

$$\ell(x) \;=\; \text{dist of } x \text{ to the singularities}$$

and $f(x) = \ell(x)^{-1/2}$. At each point outside of the singularities we rescale the problem using the scales at this point in such a way that the problem is mapped into a model one, i.e. the one with a potential $U$ obeying $|\partial^\alpha U(x)| \;\le\; C_\alpha$ on a unit ball, with the effective quasiclassical parameter

$$\hbar_{\text{eff}}(x) \;=\; \frac{\hbar}{\ell(x) f(x)}$$

which depends on all the scales.

What is important here is that quantities of interest (eigenvalues, traces, density) commute with rescalings and that the new –rescaled– problem admits a quasiclassical expansion discussed above with a remainder bound independent of the singular structure of $\phi(x)$. This implies an expansion for the original problem outside of small balls around the singularities. The term “singularity” now has to be understood in a broad sense, since the singularities in the flow caused by stationary points also affect our error bounds. We are thus confronted with two kinds of singularities: those coming from the points where $\nabla_x \phi$ vanishes, and the Coulomb singularity. The choice of $\ell(x)$ and $f(x)$ is different in these cases.

Away from the Coulomb singularities, we have the following result:

**Theorem 6** *Consider the Schrödinger operator $P$ in $\mathbf{R}^d$, $d \ge 2$, and for $0 \le s \le 1$ let*

$$g_s(\lambda) = \begin{cases} (-\lambda)^s & \text{if } \lambda < 0 \\ 0 & \text{otherwise} \end{cases}$$

*Then*

$$\left| \operatorname{tr}\left(\psi g_s(P)\right) - (2\pi\hbar)^{-d} \iint \psi(x)\, g_s\big(p(x,\xi)\big)\, dx\, d\xi \right| \le C\hbar^{-d+1+s} \int_\Omega f(x)^{d+s-1} \ell(x)^{-s-1}\, dx$$

*for any $\psi$ smooth supported in $\{x \mid \ell(x) f(x) \ge \hbar\}$ and such that*

$$\partial_x^\alpha \psi(x) = O\Big(\ell(x)^{-|\alpha|}\Big)$$

*and for any $\Omega$ which is a union of balls $B(y, \ell(y)$ covering supp $\psi$.*

Using the scales we can see that the critical points of the Hamiltonian have essentially no effect on the eigenvalue asymptotics when $d \ge 2$.

Inside those balls around the Coulomb singularities, we analyze the problem differently. Namely, we replace the potential by its leading term near the singularity, which is pure Coulomb, and solve the quasiclassical problem for this truncated operator more accurately. Since the Schrödinger for the Coulomb potential admits an exact solution, we can analyze the crucial part of this problem explicitly. Leading terms near and outside the singularities combine into a single Weyl term over $\mathbf{R}^3$ which gives the Thomas-Fermi energy. Precise expansion of low-lying eigenvalues of the truncated problem near the singularities yields the Scott correction.

### 4.2 Quasiclassical Asymptotics: Radial Case.

As before, consider the Schrödinger Operator given by

$$H = -\Delta - W(x)$$

with negative eigenvalues $E_k$. Our next task is to obtain the next term for the sum of the negative eigenvalues. It is known that this problem is related to the presence of periodic orbits for the hamiltonian flow, in contrast with the previous asymptotic analysis where no dynamical properties of $H$ where required. In addition to this, as before, we also have to deal with the singularities of the potential.

The main theorem we try to proof now is the following:

**Theorem 7** *Let $W$ be radial. Denote by $E_k$ the negative eigenvalues of $H$. Then,*

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

*assuming that zero–energy 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

$$\frac{d^2}{dr^2} + p_E(r,l) = 0 \tag{9}$$

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

in the sense that if we can find a solution of (9) 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 7 is the following eigenvalue formula.

**Theorem 8** *If $l \geq Z^{a_4}$, $a_4$ small,*

$$\phi(E_{k,l}) + \tfrac{1}{48}\psi(E_{k,l}) = \pi(k+\tfrac{1}{2}) + O\Big(\|p\|^{-1+\epsilon_2}\Big) \tag{10}$$

*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 (8). We also refer the reader to (8) 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

$$F''(x) + p(x)F(x) = 0 \tag{11a}$$

$$A''(y) + V(y)A(y) = 0 \tag{11b}$$

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

$$(y')^2\, V(y) + \{y,x\} = p(x) \qquad \{y,x\} = -\tfrac{3}{4}\left(\frac{y''(x)}{y'(x)}\right)^2 + \tfrac{1}{2}\frac{y'''(x)}{y'(x)} \tag{12}$$

makes (11a) and (2) equivalent via the transformation law

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

What we will do then is, first, take $V$ a simple potential for which (2) admits an explicit solution; then, a virtue of (12) 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 (11a). The choices of $V$ will be as follows:

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

b. When $p > 0$, we take $V = \lambda^2$. When $V < 0$, we take $V = -\lambda^2$, $\lambda$ 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 (2) 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 and 7. 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.

When performing the WKB approximation, one needs to estimate error terms carefully, and understand their dependence on $E$ and $l$, so that we can see that in all cases discussed above, they are small. An effective way of doing this is, as in the previous section, to introduce functions $f(x)^2$ and $\ell(x)$, which, following the notation in (8) we denote by $S(x)$ and $B(x)$, and assume the estimates

$$\left| \left( \frac{d}{dx} \right)^n p(x) \right| \le C_n S(x)\, B(x)^{-n}$$

on a suitable interval $I$ where we intend to perform the WKB approximation.

For instance, if $p(x) = \lambda^2 p_0(x)$, then we can take

$$S(x) = \lambda^2 \qquad B(x) = 1$$

If $p(x) = \frac{1}{x} - \frac{l(l+1)}{x^2}$, then we can take

$$S(x) = \frac{1}{x} \qquad B(x) = x \qquad \text{on } \left( \tfrac{l(l+1)}{10}, \infty \right)$$

Then our error bounds for the eigenvalue equation will essentially be given in terms of the effective semiclassical parameter

$$\hbar = \int_I \frac{dx}{S^{1/2}(x)\, B^2(x)}$$

In the case that $p(x) = \lambda^2 p_0(x)$, note that $\hbar \sim \lambda^{-1}$, and this makes the WKB approximation optimal. However, if $p(x) = \frac{1}{x} - \frac{l(l+1)}{x^2}$, then $\hbar \sim l^{-1}$.

This expresses the fact that for large $l$, one expects the first eigenvalue formula in the statement of Theorem 8 to be accurate, whereas one expects to obtain only the second crude eigenvalue formula for $l$ a small integer (the case $l = 0$ is a hybrid). This is no surprise, since the exact eigenvalues for the Hydrogen Hamiltonian satisfy the relation

$$\phi(E_k, l) = \pi(k + l - \sqrt{l(l+1)})$$

in clear violation of formula (10) for $l$ small.

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

The next step is to lift Theorem 8 in order to say something about *radial* potentials in $\mathbf{R}^3$. We do this by summing Theorem 8 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

$$\sum_{l=1}^{l_{\max}} \frac{2l+1}{n_l}\beta(\phi_l)$$

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

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

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

Define

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

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 $\pi$, then all classical orbits at zero energy are periodic, our term $G(W)$ is oscillating, and has the same size as the third term in the formula in Theorem 7, 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 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 at zero energy 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 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 $V_{\mathrm{TF}}$ in a natural topology allow $F''$ to vanish as many times as we want. The analysis of $F''$ is taken care of in (13).

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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