Proof of the Strong Scott Conjecture for Atomic and Molecular Cores

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Abstract

The strong Scott conjecture about the electron density at a distance $1/Z$ from an atomic nucleus of charge $Z$ and its generalization for molecules are proved. The density, suitably scaled, converges to an explicit limiting density as $Z \to \infty$. Both a weak convergence and a pointwise convergence on spheres holds.

1 Introduction

A great deal is known about the ground states of large atoms in the framework of the non-relativistic Schrödinger equation, with fixed (i.e., infinity massive) nuclei. The leading term, in powers of the nuclear charge $Z$, is given exactly by Thomas-Fermi theory, as was proved by Lieb and Simon [12], see [11] for a review. This leading term in the energy is proportional to $Z^{7/3}$, with the proportionality constant depending on the ratio of $N/Z$, which is assumed to be held fixed as $Z \to \infty$. Here, $N$ is the electron number. Neutrality, i.e., $N = Z$, is not required, even though it is the case of primary physical interest. The characteristic length scale for the electron density (in the sense that all the electrons can be found on this scale in the limit $Z \to \infty$) is $Z^{-1/3}$. The fact that the true quantum-mechanical electron density, $\rho_d$, converges (after suitable scaling) to the Thomas-Fermi density, $\rho^{TF}$, as $Z \to \infty$ with $N/Z$ fixed was proved in [12]. The chemical radius, which is another length altogether, is believed, but not proved, to be order $Z^0$ as $Z \to \infty$.

The first correction to the $Z^{7/3}$ law is not, as was formerly supposed, the $Z^{5/3}$ corrections arising from exchange and correlation effects and kinetic energy corrections on the $Z^{-1/3}$ scale. Instead it is $Z^2 = Z^{6/3}$ and arises from extreme quantum mechanical effects on the innermost electrons, which are at a distance $Z^{-1}$ from the nucleus. Among these the most important are the $K$ shell electrons. It was Scott [19] who pointed this out and he also gave a formula for the correction term to the energy,

$$E^{Scott} = \frac{q}{8} Z^2,$$

\[1\]

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where $q$ is the number of spin states per electron (of course $q = 2$ in nature). It is noteworthy that $E^{Scott}$ does not depend on the fixed ratio $N/Z$, provided $N/Z \neq 0$. This fact agrees with the idea that $E^{Scott}$ arises from the innermost electrons, whose energies, in leading order, are independent of the presence of the electrons that are further from the nucleus. The truth of (1) (i.e., the statement that the energy is $E^{TF} + E^{Scott} + o(Z^2)$ for fixed $N/Z \neq 0$) was proved in [22, 23] (upper and lower bound) and by Hughes [3] (lower bound) in the atomic case and by Bach [1] in the ionic case. (For different proofs and extensions of this result see [24], Fefferman and Seco [6, 2, 3, 4, 5, 7], and Ivrii and Sigal [10].)

The “strong Scott conjecture”, which we prove here, was made later in [11], Equation (5.34). It concerns the electron density $\rho_d$ at distances of order $Z^{-1}$ from the nucleus and states that in limit $Z \to \infty$ a suitably scaled $\rho_d$ converges to the sum of the squares of all the hydrogenic bound states. This function is defined in Section 2 below and is extensively analyzed in [3]. (Previously, an upper bound for $\rho_d$ at the origin of the correct form, namely $O(Z^3)$, was derived in [20, 21].) We prove this convergence in several senses, one of which is a “pointwise” convergence on spheres. In fact we go further and show that the individual angular momentum densities converge to the hydrogenic values, thereby giving a somewhat more refined picture of the ground state.

Our main proof strategy is the usual one. We add $\epsilon$ times a one-body test potential to our Hamiltonian and then differentiate the ground state energy with respect to $\epsilon$ at $\epsilon = 0$ in order to find $\rho_d$. To obtain pointwise convergence the test potential is a radial delta-function. To control the energy we rely, in part, on the results and methods in [22, 23].

In the following we shall state and prove our theorems for the neutral case $N = Z$. We do so to avoid the notational complexity and additional discussion required for $N/Z \neq 1$. It is straightforward, however, to generalize our results to $N/Z \neq 1$.

In the next section precise definitions, as well as our main theorems are given. Section 3 contains two lemmata about the difference in energies with and without the test potential. Since there are infinitely many hydrogenic bound states, we need these estimates in order to be able to show that the sum of the derivatives (with respect to $\epsilon$) equals the derivative of the sum. The strong Scott conjecture for atoms is proved in Section 4. Section 5 contains the obvious extension to molecules. The Appendix contains a few needed facts about ground state energies.

2 Definitions and Main Results

The Hamiltonian of an atom of $N$ electrons with $q$ spin states each and a fixed nucleus of charge $Z$ located at the origin is given by

$$H_{N,Z} = \sum_{\nu=1}^{N} \left( -\Delta_{\nu} - \frac{Z}{|r_{\nu}|} \right) + \sum_{1 \leq \mu < \nu \leq N} \frac{1}{|r_{\mu} - r_{\nu}|},$$

in units in which $\hbar^2/2m = 1$ and $|e| = 1$. It is self-adjoint in the Hilbert space $\mathcal{H}_N := \bigwedge_{\nu=1}^{N} (L^2(\mathbb{R}^3) \otimes \mathbb{C}^q)$, i.e., antisymmetric functions of space and spin. A
general ground state density matrix, denoted by \( d \), can be written as

\[
d = \sum_{\nu=1}^{M} w_{\nu} | \psi_{\nu} \rangle \langle \psi_{\nu} |
\]

where the \( \psi_{\nu} \) constitute an orthonormal basis for the ground state eigenspace and where the \( w_{\nu} \) are nonnegative weights such that \( \sum_{\nu=1}^{M} w_{\nu} = 1 \). It is well known that the ground state can be degenerate, e.g., it is for the carbon atom. The corresponding one-electron density is the diagonal part of the one-electron density matrix and is, by definition,

\[
\rho_{d}(r) = N \sum_{\nu=1}^{M} w_{\nu} \sum_{\sigma_1, \ldots, \sigma_N} \int_{\mathbb{R}^{3(N-1)}} | \psi_{\nu}(r, r_{2}, \ldots, r_{N}; \sigma_1, \ldots, \sigma_N) |^2 \, dr_{2} \ldots dr_{N}.
\]

The density \( \rho_{l,d} \) of angular momentum \( l \) electrons at radius \( r \) from the nucleus is given in terms of the normalized spherical harmonics \( Y_{l,m} \).

\[
\rho_{l,d}(r) = N \sum_{m=-l}^{l} \sum_{\nu=1}^{M} w_{\nu} \sum_{\sigma_1, \ldots, \sigma_N} \int_{\mathbb{S}^2} Y_{l,m}(\omega) | \psi_{\nu}(r_{\omega}, r_{2}, \ldots, r_{N}; \sigma_1, \ldots, \sigma_N) |^2 \, d\omega \, dr_{2} \ldots dr_{N}
\]

where we write \( r = r_{\omega} \) and \( d\omega \) denotes the usual unnormalized surface measure on the two dimensional sphere \( \mathbb{S}^2 \) with \( (4\pi)^{-1} \int_{\mathbb{S}^2} d\omega = \int_{\mathbb{S}^2} |Y_{l,m}|^2 d\omega = 1 \).

Throughout the paper we will write \( \varphi_{Z}^{TF}(r) \) for the Thomas-Fermi potential of electron number \( N = Z \) and nuclear charge \( Z \), i.e.,

\[
\varphi_{Z}^{TF}(r) = Z/r - |r|^{-1} \ast \rho_{Z}^{TF},
\]

where \( \rho_{Z}^{TF} \) is the nonnegative minimizer of the Thomas-Fermi functional

\[
\int_{\mathbb{R}^3} \left( \frac{3}{2} (6\pi^2/q)^{2/3} \rho_{Z}^{5/3}(r) - \frac{Z}{|r|} \rho(r) \right) dr + D(\rho, \rho)
\]

under the condition \( \int \rho = N = Z \) and with

\[
D(\rho, \rho) := \frac{1}{2} \int_{\mathbb{R}^6} \frac{\rho(t) \rho(s)}{|t - s|} \, dt \, ds.
\]

Both \( \varphi_{Z} \) and \( \rho_{Z}^{TF} \) are spherically symmetric, i.e., they depend only on \( r = |r| \). There is a scaling relation \( \varphi_{Z}^{TF}(r) = Z^{4/3} \varphi_{1}^{TF}(Z^{1/3}r) \), where \( \varphi_{1}^{TF} \) is the Thomas-Fermi potential for \( Z = 1 \) and “electron number” equal to 1. Similarly, \( \rho_{Z}^{TF}(r) = Z^{2} \rho_{1}^{TF}(Z^{1/3}r) \). This scaling shows that the “natural” length in an atom is \( Z^{-1/3} \). Note that the Thomas-Fermi functional has a unique minimizer.

The Scott conjecture, on the other hand, concerns the length scale \( Z^{-1} \), where we expect the density to be of order \( Z^3 \) instead of \( Z^2 \). In terms of the “true” density defined in (4), we now define

\[
\rho_{Z}(r) := Z^{-3} \rho_{d}(t/Z).
\]
Likewise, we define the angular momentum density

$$\rho_{l,Z}(r) := Z^{-3} \rho_{l,d}(r/Z).$$  

(7)

To formulate the strong Scott conjecture we consider the angular momentum $l$ states of a hydrogen atom ($Z = 1$) with radial Hamiltonian

$$h^H_l := -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \frac{1}{r},$$  

(8)

with normalized eigenfunctions $\psi^H_{l,n}$ (that vanish at 0 and $\infty$) corresponding to negative eigenvalues $e^H_{l,n}$. (The superscript $H$ denotes “Hydrogen” and distinguishes $h^H_l$ from other radial Hamiltonians to be considered later.) The normalization is \( \int_0^\infty |\psi_{n,l}(r)|^2 dr = 1 \). We define the corresponding density in the channel $l$ to be

$$\rho^H_l(r) := q(2l+1) \sum_{n=0}^{\infty} |\psi^H_{l,n}(r)|^2 / (4\pi r^2);$$  

(9)

the total density is then

$$\rho^H(r) = \sum_{l=0}^{\infty} \rho^H_l(r).$$  

(10)

Although we shall not be interested in detailed properties of $\rho^H$, we note the following proved in [8]: The sum over $l$ and $n$ defining $\rho^H(r)$ is pointwise convergent for all $r$. It is monotone decreasing and it decays asymptotically for large $r$ as $1/(6\pi^2 r^{3/2})$. This large $r$ asymptotics meshes nicely with the small $r$ behavior of $\frac{1}{4}\rho^T F^l(r)$.

Note: In [8] the operator $h^H$ is defined using atomic units $\hbar^2/m = 1$, i.e., with $\frac{1}{2}(-d^2/dr^2 + l(l+1)/r^2)$ instead of $-d^2/dr^2 + l(l+1)/r^2$. Note also that we have included the factor $q$ in the definition of $\rho$ which was not done in [8].

Thus some care is needed in comparing formulae there with formulae here.

Various notions for the convergence of the rescaled density are possible. Our precise statements are Theorems 1 and 2 below and Theorem 3 in Section 5.

**Theorem 1 (Convergence in angular momentum channels).** Fix the angular momentum $l_0$.

1. For positive $r$

$$\lim_{Z \to \infty} \rho_{l_0,Z}(r) = \rho^H_{l_0}(r)$$  

(pointwise convergence).

2. Let $V$ be an integrable functions on the positive real line. Then we have the weak convergence

$$\lim_{Z \to \infty} \int_0^\infty rV(r)\rho_{l_0,Z}(r)dr = \int_0^\infty rV(r)\rho^H_{l_0}(r)dr.$$  

(12)
Theorem 2 (Convergence of the total density).

1. Let $W$ be a bounded (not necessarily constant) function on the unit sphere. Then, as $Z \to \infty$,
\[
\int_{S^2} W(\omega) \rho_Z(r\omega) d\omega \to \rho_H(r) \int_{S^2} W(\omega) d\omega
\]  
(pointwise convergence of spherical averages).

2. Let $V$ be a locally bounded, integrable function on $\mathbb{R}^3$. Then, as $Z \to \infty$,
\[
\int_{\mathbb{R}^3} |r| V(r) \rho_Z(r) dr \to \int_{\mathbb{R}^3} |r| V(r) \rho_H(|r|) dr.
\]

Remarks:

1. It is not really necessary to take a sequence of ground state density matrices. We could take just a sequence of states, $d_{N,Z}$, that is an approximate ground state in the sense that
\[
\frac{\text{tr} (H_{N,Z} d_{N,Z}) - E_{N,Z}}{Z^2} \to 0
\]  
as $Z \to \infty$. Here $E_{N,Z}$ is the bottom of the spectrum of $H_{N,Z}$. It might not be an eigenvalue, and it certainly will not be one if $N/Z$ is larger than 2.

2. It is important to note that $W$ and $V$ in (13) and (14) need not be spherically symmetric. It might appear that only the spherical averages of $W$ and $V$ are relevant, but this would miss the point. Theorem 4 says, that in the limit $Z \to \infty$ there is no way to construct a ground state or approximate ground state that is not spherically symmetric on a length scale $Z^{-1}$. For example, in the case of carbon there are ground states that are not spherically symmetric and for which replacing $W$ by its spherical average changes the left side of (13).

3. A word about pointwise convergence. The one-body density matrix $\gamma(r,r')$, which is defined as in (1) but with $|\psi_\nu(\cdots)|^2$ replaced by
\[
\psi_\nu(r,r_2,\ldots,r_N;\sigma_1,\ldots,\sigma_N) \overline{\psi'(r',r_2,\ldots,r_N;\sigma_1,\ldots,\sigma_N)},
\]is easily seen to be in the Sobolev space $H^1(\mathbb{R}^3)$ when $\gamma$ is considered as a function of each variable separately. The trace theorem in Sobolev spaces then implies that the function of $\omega$ on the sphere $S^2$, $\gamma(r\omega,r'\omega')$ is in $L^q(S^2)$ for all $q \leq 4$. Thus, the integrals in (4) are well defined and $\rho_d(r\omega) = \gamma(r\omega,r\omega)$ is in $L^2(S^2)$. It is also easy to see that $\sqrt{\rho_{l,Z}(r)}$ is in $H^1(0,\infty)$ and hence it is a continuous function of $r$. Since $\rho_d(r)$ is in $L^2(S^2)$ the integrals in (13) and (14) are well defined when $W \in L^2(S^2)$.

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infinitely many eigenvalues below the essential spectrum and the ground state eigenspace has finite dimension. This implies that the ground state energy is always a discrete eigenvalue which, in turn, implies exponential decay of the ground state eigenfunctions according to Theorem XIII.42 of [18].

3 Eigenvalue Differences of Schrödinger Operators Perturbed on the Scale 1/Z

It is well known, and will be seen more explicitly in Section 4, that the eigenvalues of $H_{N,Z}$ can be controlled to within an accuracy of $o(Z^2)$ by considering a one-body Schrödinger operator with the spherically symmetric potential given by Thomas-Fermi theory. In the angular momentum $l$ channel, this is

$$h_{l,Z}^{TF} = -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \varphi_{Z}^{TF}(r).$$

(We suppress the dependence on $N$ in $h_{l,Z}^{TF}$ since $N = Z$.) Closely related to $h_{l,Z}^{TF}$ is the unscreened hydrogenic Hamiltonian

$$h_{l,Z}^{H} = -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \frac{Z}{r}.$$  

(16)

In this section we want to study how the spectra of these operators are shifted by the addition of a perturbing potential of the form

$$\epsilon U_Z(r) = \epsilon Z^2 U(Zr)$$

where $\epsilon$ is a small parameter and where $U$ is some fixed function. In particular, $U$ will be a radial delta function, $U(r) = \delta(r-a)$ for some $a > 0$.

Both cases, $h_{l,Z}^{TF}$ and $h_{l,Z}^{H}$, will be considered together and we write

$$h_{l,\epsilon,Z} = -\frac{d^2}{dr^2} + V_{l,Z}(r) - \epsilon U_Z(r),$$

(17)

in which $V_{l,Z} = -Z/r + l(l+1)/r^2$ or $V_{l,Z} = -\varphi_{Z}^{TF}(r) + l(l+1)/r^2$.

Our first lemma estimates the difference in the spectra of $h_{l,0,Z}$ and $h_{l,\epsilon,Z}$ by the difference in the trace (tr) of the negative parts $(h_{l,\epsilon,Z})_-$ or $(h_{l,0,Z})_-$ (i.e., the sums of the negative eigenvalues). This lemma will later on allow us to interchange the limits $Z \to \infty$ and $\epsilon \to 0$ with the $l$ summation.

**Lemma 1** Set $U(r) = \delta(r-a)$, $U_Z(r) = Z^2 U(Zr)$ and assume $|\epsilon| \leq \pi/(16a)$. Then

$$|\text{tr}(h_{l,0,Z})_- - \text{tr}(h_{l,\epsilon,Z})_-| \leq \epsilon \frac{9aZ^2}{(l+1)^2(2l+1)}.$$  

Proof: By the minimax principle we have for $\epsilon > 0$

$$0 \leq s_{\epsilon,l,Z} := \text{tr}(h_{l,0,Z})_- - \text{tr}(h_{l,\epsilon,Z})_- \leq \epsilon \text{tr}(U_Zd_{l,\epsilon,Z}).$$  

(18)

Inserting the identity twice in the right side of (18) we have

$$s_{\epsilon,l,Z} \leq \epsilon \text{tr}(ABC B^*A^*) \leq \epsilon \|A\|_{\infty}^2 \|B\|_{\infty}^2 \text{ tr } C$$

(19)
with
\[
A := d_{l,\epsilon,Z}(h_{l,\epsilon,Z} + c_{l,Z})^{1/2} \geq 0,
B := (h_{l,\epsilon,Z} + c_{l,Z})^{-1/2}(H_{0,l} + c_{l,Z})^{1/2},
C := (H_{0,l} + c_{l,Z})^{-1/2}U_Z(H_{0,l} + c_{l,Z})^{-1/2} \geq 0,
\]
where \(c_{l,Z}\) is any positive number bigger than \(|\inf \sigma(h_{l,\epsilon,Z})|\), where \(\sigma(h)\) denotes the spectrum of \(h\). We also define \(H_{0,l} := -d^2/dr^2 + l(l+1)/r^2\) to be the free operator in the angular momentum channel \(l\). Since \(\varphi_Z^{TF}(r) \leq Z/r\) and since \(\inf \sigma(H_{0,l} - Z/r) = -Z^2/[4(l+1)^2]\) we can take \(c_{l,Z} := Z^2/(l+1)^2\) provided \(\epsilon\) is not too large.

We now estimate these norms individually:

Because \(c_{l,Z}\) is bigger than the modulus of the lowest spectral point of \(h_{l,\epsilon,Z}\) and \(d_{l,\epsilon,Z}\) is the projection onto the negative spectral subspace of \(h_{l,\epsilon,Z}\) we have
\[
\|A\| \leq \sqrt{c_{l,Z}}.
\]

(20)

For \(B\) we get
\[
\|B\|^2 = \|(h_{l,\epsilon,Z} + c_{l,Z})^{-1/2}(H_{0,l} + c_{l,Z})^{1/2}\phi\|^2
= (\phi, (H_{0,l} + c_{l,Z})^{1/2}(h_{l,\epsilon,Z} + c_{l,Z})^{-1}(H_{0,l} + c_{l,Z})^{1/2}\phi)
= (\phi, \frac{1}{1-W_{l,\epsilon,Z}}\phi)
\]
with
\[
W_{l,\epsilon,Z} := (H_{0,l} + c_{l,Z})^{-1/2}(\varphi_Z + \epsilon U_Z)(H_{0,l} + c_{l,Z})^{-1/2}.
\]

We will then have
\[
\|B\| \leq \sqrt{2}
\]
if we can show that \(W_{l,\epsilon,Z}\) is bounded above by \(\frac{1}{2}\). To this end we note that \(H_{0,l} + c_{l,Z}\) is invertible, so that we can write any normalized \(\phi \in L^2(\mathbb{R}^+\) as \(\phi := (H_{0,l} + c_{l,Z})^{1/2}\psi/\|(H_{0,l} + c_{l,Z})^{1/2}\psi\|\) with \(\psi\) in the domain of \(H_{0,l}\). Thus, we have to show that
\[
(\phi, W_{l,\epsilon,Z}\phi) = (\psi, (\varphi_Z + \epsilon U_Z)\psi)/(\psi, (H_{0,l} + c_{l,Z})\psi) \leq \frac{1}{2},
\]
which is equivalent to
\[
\frac{1}{2}(H_{0,l} + c_{l,Z}) - \varphi_Z - \epsilon U_Z \geq 0.
\]

(23)

Since \(\varphi_Z^{TF}(r) \leq Z/r\) and since
\[
(\psi, U_Z\psi) = Z|\psi(a/Z)|^2 \leq Z \int_0^{a/Z} |\psi|^2(r)dr \leq 2Z\Re \int_0^{a/Z} \psi(r)^2\psi'(r)dr
\leq 2Z\|\psi\|_2 \left\{ \int_0^{a/Z} \psi(r)^2dr \right\}^{1/2}
\]

(24)
we have that \((\psi, U_{Z}\psi) \leq (4a/\pi)\|\psi'\|_2^2\). (Here we use the inequality, \(\int_0^L \psi'^2 \leq (\pi/2L)^2 \int_0^L \psi^2\), when \(\psi(0) = 0\).) Thus, (23) is implied by

\[-4 \frac{Z^2}{4(l+1)^2} + c_{l,Z} + \inf \sigma (\frac{1}{4} - \frac{4a}{\pi} H_{0,l}) \geq 0.\]  

(25)

The sum of the first two terms in (25) vanishes because of our choice of \(c_{l,Z}\) and last term in (25) is zero when \(\epsilon \leq \pi/(16a)\). This is true by hypothesis, and the bound on the norm of \(B\) is proved.

Finally the trace of \(C\) is computed easily, since it is of rank one. Since the kernel \((H_{0,l} + c_{l,Z})^{-1}(r, r')\), is a positive, continuous function in both variables, \(\text{tr} C = Z(H_{0} + c_{l,Z})^{-1}(a/Z, a/Z)\). A well known calculation yields

\[(H_{0,l} + c_{l,Z})^{-1}(r, r') = \sqrt{r} K_{l+\frac{1}{2}} (\sqrt{c_{l,Z}} a r) I_{l+\frac{1}{2}} (\sqrt{c_{l,Z}} a r),\]

where \(r_\geq = \max\{r, r'\}\) and \(r_\leq = \min\{r, r'\}\). Thus

\[\text{tr} C = a K_{l+\frac{1}{2}} (\sqrt{c_{l,Z}} a Z) I_{l+\frac{1}{2}} (\sqrt{c_{l,Z}} a Z).\]

The modified Bessel functions \(I_{l+\frac{1}{2}}\) and \(K_{l+\frac{1}{2}}\) are both positive and the following uniform asymptotic expansions hold. (See Olver [14] for a proof of the estimates of the remainder terms, [13], p. 6 for the remainder in the form used here, [17], Chapter 10, Paragraph 7 for a review; see also Olver [16], section 9.7.)

\[K_n(nx) = \sqrt{\frac{n}{2\pi}} e^{-\xi} [1 + \epsilon_{0,2}(n, t)]\]

(26)

\[I_n(nx) = \sqrt{\frac{t}{2\pi n}} e^{\xi} \left[1 + \epsilon_{0,1}(n, 0)\right],\]

(27)

where

\[\xi := \frac{1}{t} - \frac{1}{2} \log \frac{1+t}{1-t}\]

and

\[|\epsilon_{0,1}(n, t)| \leq \frac{n_0}{n - n_0}\]

\[|\epsilon_{0,2}(n, t)| \leq \frac{n_0}{n - n_0}\]

with \(n_0 := \frac{1}{6\sqrt{5}} + \frac{1}{12} \leq 1/6\). Thus,

\[K_n(nx) I_n(nx) \leq \frac{1}{2n(1+x^2)^{1/2}} \frac{n^2}{(n-2n_0)(n-n_0)} \leq \frac{9}{4n},\]

where the last inequality holds for \(n \geq \frac{1}{2}\). Thus

\[\text{tr} C \leq \frac{9}{2} \frac{a}{(2l+1)}.\]  

(28)
Putting (19), (20), (22), and (28) together yields
\[
s_{\epsilon,l,Z} \leq \frac{9c_{l,Z}a}{2(l+1)} \leq \left(\frac{9aZ^2}{(l+1)^2(2l+1)}\right)
\]
which is more than the desired result for \(\epsilon > 0\).

If \(\epsilon\) is negative we have, again by the minimax principle,
\[
0 \geq s_{\epsilon,l,Z} := \text{tr}(h_{l,0,Z}) - \text{tr}(h_{l,\epsilon,Z}) \geq \epsilon \text{tr}(U_Z d_{l,0,Z}). \quad (29)
\]
Similar to the previous analysis, we have
\[
s_{\epsilon,l,Z} \geq \epsilon \text{tr}(DCD^*) \geq \epsilon \|D\|_2^2 \text{tr} C
\]
with
\[
D := d_{l,0,Z}(h_{l,0,Z} + c_{l,Z})^{\frac{1}{2}}.
\]
As for \(A\) above, we have
\[
\|D\|_\infty \leq \sqrt{c_{l,Z}}.
\]
Putting this together with (28) gives
\[
s_{\epsilon,l,Z} \geq \epsilon \frac{9c_{l,Z}a}{2(2l+1)} \geq \left(\frac{9aZ^2}{2(l+1)^2(2l+1)}\right)
\]
which is even better than the desired result for negative \(\epsilon\).

The next result will later on allow us to interchange the limits \(Z \to \infty\) and \(\epsilon \to 0\) with the \(n\) summation for fixed \(l\).

**Lemma 2** Set \(U(r) = \delta(r-a)\) and assume \(|\epsilon| \leq \pi/(4a), a > 0\). Let
\[
h_{l,\epsilon} := -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \frac{1}{r} - \epsilon U(r)
\]  \quad (31)
with form domain \(H^1_0(0, \infty)\). Let \(e_{n,l,\epsilon}\) denote the \(n\)-th eigenvalue of \(h_{l,\epsilon}\). Then
\[
|e_{n,l,0} - e_{n,l,\epsilon}| \leq \frac{1}{(n+l)^2} \frac{\epsilon a}{\pi - 4\epsilon a}
\]  \quad (32)

**Proof:** For any \(\psi\) in \(H^1_0(0, \infty)\) we have
\[
|\psi(a)|^2 \leq \frac{2}{\pi} a \|\psi'\|_2^2,
\]
as proved in (24) of Lemma 1. Thus, for \(\epsilon > 0\),
\[
h_{l,\epsilon} \geq (1 - \frac{4\epsilon a}{\pi}) \left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \frac{1}{r} - (1 - \frac{4\epsilon a}{\pi}) \frac{1}{r}\right].
\]  \quad (33)
This implies
\[
e_{n,l,\epsilon} \geq (1 - \frac{4\epsilon a}{\pi}) \bar{e}_{n,l,0}
\]
where \(\bar{e}_{n,l,0}\) is the \(n\)-th eigenvalue of \(\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \frac{1}{r}\right]\) in (33), i.e., where the potential \(r^{-1}\) is replaced by \((1 - 4\epsilon a/\pi)^{-1} r^{-1}\). Thus,
\[
0 \leq e_{n,l,0} - e_{n,l,\epsilon} \leq \frac{1}{4(n+l)^2} \left(-1 + (1 - \frac{4\epsilon a}{\pi})^{-1}\right) = \frac{1}{(n+l)^2} \frac{\epsilon a}{\pi - 4\epsilon a},
\]
which proves the claim when $0 < \epsilon < \pi/(4a)$.

If $\epsilon$ is negative we have

$$h_{l,\epsilon} \leq (1 - \frac{4ea}{\pi}) \left[ -\frac{d^2}{dr^2} + \frac{l(l + 1)}{r^2} - \frac{1}{(1 - \frac{4ea}{\pi})r} \right]$$

which again proves the claim (by the same argument) when $0 > \epsilon > -\pi/(4a)$.

4 Proof of the Strong Scott Conjecture

We are now able to give the proof of our theorems. We begin with the proof of Theorem I and begin with the first statement:

1. The proof of the convergence of the spherical averages: Set $U(r) := \delta(r-a)$ for $a > 0$ and $U_Z(r) := Z^2 U(Zr) = Z \delta(r - \frac{Z}{2})$. Fix $l_0$ and let

$$H'_{N,Z} := H_{N,Z} - \epsilon \sum_{n=1}^{N} U_Z(r_n) \Pi(l_0)$$

where $\Pi(l_0)$ denotes the projection onto angular momentum $l_0$. We define $\lambda(Z)$ – which does not depend on $\epsilon$ – by

$$\lambda(Z) := a^2 \rho_{l_0}(a) = \frac{\text{tr}(H_{N,Z}d) - \text{tr}(H'_{N,Z}d)}{\epsilon Z^2}.$$  

(35)

Let us define $e_{n,l,\gamma,Z}$ and $e_{n,l,\gamma,Z}$, $n = 1, 2, ..., \epsilon \in \mathbb{R}$, to be the negative eigenvalues of the operators

$$H_{l,\epsilon,Z} := -\frac{d^2}{dr^2} + \frac{l(l + 1)}{r^2} - \frac{Z}{r} - \epsilon U_Z \delta_{l,l_0}$$

(36)

and

$$H'_{l,\epsilon,Z} := -\frac{d^2}{dr^2} + \frac{l(l + 1)}{r^2} - \phi_{TF} - \epsilon U_Z \delta_{l,l_0}$$

(37)

with zero Dirichlet boundary on $(0, \infty)$. To obtain an upper bound for $\lambda(Z)$ we pick $\epsilon$ positive and estimate as follows: by (33) we have the upper bound

$$\text{tr}(H_{N,Z}d) \leq \sum_{l=0}^{L-1} q(2l+1) \sum_n \epsilon_{n,l,0,Z} + \sum_{l=L}^{\infty} q(2l+1) \sum_n e_{n,l,0,Z} - D(\rho_{TF}, \rho_{TF}) + \text{const}Z^{\frac{24}{17}}$$  

(38)

where $L = \lfloor Z^{1/9} \rfloor$.

To obtain a lower bound on $\text{tr}(H'_{N,Z}d)$ we first use the lower bound [55, 11] on the correlations, namely $-\text{const} \lfloor N \int \rho_{d}^{5/3} \rfloor^{1/2}$, to reduce it to a radial problem. Using the fact that $Z/r \geq \phi_{TF}(r)$ for $r > 0$ it follows from this that

$$\text{tr}(H'_{N,Z}d) \geq \sum_{l=0}^{L-1} q(2l+1) \sum_n \epsilon_{n,l,\epsilon,Z} + \sum_{l=L}^{\infty} q(2l+1) \sum_n e_{n,l,\epsilon,Z} - D(\rho_{TF}, \rho_{TF}) - \text{const}Z^{\frac{24}{17}}.$$  

(39)
Note that (39) arises from a relatively simple lower bound calculation. Part of the proof of the Scott conjecture amounts to proving that the right hand of (39) is accurate to \( o(Z^2) \). This proof was carried out in [23] (see also [9, 24]). We are not rederiving the Scott correction for the energy, and it is not necessary for us to do so here.

Define

\[
\theta(n) := \begin{cases} 
1 & n > 0 \\
0 & n \leq 0
\end{cases}.
\]

Since the eigenvalues of the perturbed problem \((\epsilon \neq 0)\) are equal to the unperturbed one \((\epsilon = 0)\) except for \(l = l_0\), we get the inequality

\[
\limsup_{Z \to \infty} \lambda(Z) \leq \liminf_{\epsilon \searrow 0} \limsup_{Z \to \infty} \left[ q(2l_0 + 1) \frac{\text{tr}(H_{l_0,0,Z}^H) - \text{tr}(H_{l_0,\epsilon,Z}^H)}{\epsilon Z^2} \theta(L - l_0) \\
+ \frac{\text{tr}(H_{l_0,0,Z}) - \text{tr}(H_{l_0,\epsilon,Z})}{\epsilon Z^2} \theta(l_0 - L) + \text{const} Z^{- \frac{1}{2}} \epsilon^{-1} \right].
\]

(40)

Because \( L \) eventually becomes larger than the fixed \( l_0 \),

\[
\limsup_{Z \to \infty} \lambda(Z) \leq q(2l_0 + 1) \liminf_{\epsilon \searrow 0} \limsup_{Z \to \infty} \frac{\text{tr}(H_{l_0,0,Z}^H) - \text{tr}(H_{l_0,\epsilon,Z}^H)}{\epsilon Z^2} = q(2l_0 + 1) \liminf_{\epsilon \searrow 0} \frac{\text{tr}(H_{l_0,0,1}^H) - \text{tr}(H_{l_0,\epsilon,1}^H)}{\epsilon},
\]

where the last equation holds since because of the scaling of \( h_{l_0,0,Z}^H \) and \( h_{l_0,\epsilon,Z}^H \).

Therefore

\[
\limsup_{Z \to \infty} \lambda(Z) \leq q(2l_0 + 1) \liminf_{\epsilon \searrow 0} \sum_n \frac{e_{n,l_0,0,1}^H - e_{n,l_0,\epsilon,1}^H}{\epsilon} \]

(42)

\[
= q(2l_0 + 1) \liminf_{\epsilon \searrow 0} \sum_n \frac{e_{n,l_0,0,1}^H - e_{n,l_0,\epsilon,1}^H}{\epsilon} \]

(43)

\[
= a^2 \rho_{l_0}^H(a).
\]

(44)

To exchange the limit \( \epsilon \searrow 0 \) with the summation in (42) we use Lemma 2, which provides a summable majorant for the series that is uniform in \( \epsilon \) and thus allows us to fulfill Weierstraß’ criterion for uniform convergence. Finally, to deduce (44) from (43) we use the fact that the one-dimensional delta potential is a relatively form bounded perturbation, i.e., defines an analytic family in the sense of Kato.

To obtain a lower bound for \( \lambda(Z) \) we pick \( \epsilon \) negative instead of positive and take the limit \( \limsup_{\epsilon \searrow 0} \) and \( \liminf_{Z \to \infty} \) instead of \( \liminf_{\epsilon \searrow 0} \) and \( \limsup_{Z \to \infty} \). Repeating the same steps gives the same result except for reversing the inequalities, thereby yielding the same bound (44) from below. This establishes the first claim of the theorem.
2. Proof of the weak convergence: Because of the linear dependence of the right and left hand side of (12), it suffices to prove the claim for the positive and negative parts of \( V \) separately. Thus we may – and shall – assume that \( V \) is positive. We can now roll the proof back to the previous case as follows: First we pick \( Z \) large enough so that \( l_0 < L \). It is convenient now, to replace \( \epsilon \) be \( \epsilon/a \) in order that the right side of (32) in Lemma 2 is uniformly bounded in \( a \) and \( \epsilon \) for all \( a \in (0, \infty) \) and for \( |\epsilon| \leq \pi/8 \). Then we integrate the inequality

\[
a^2 \rho_{l_0}(a) \leq \frac{\text{tr}(H_{l_0,0,Z})_1 - \text{tr}(H_{l_0,\epsilon/a,Z})_1 - \theta(L - l) + \text{const}/((\epsilon/a)Z^{1/2})}{\epsilon Z^2},
\]

i.e.,

\[
a \rho_{l_0}(a) \leq \frac{\text{tr}(H_{l_0,0,Z})_1 - \text{tr}(H_{l_0,\epsilon/Z})_1 - \theta(L - l) + \text{const}/(Z^{1/2})}{\epsilon Z^2}
\]

against \( V(a) \) from 0 to \( \infty \). Thanks to Lemma 1 the right side of (46) is bounded by \( \text{const} \) and hence the integral is finite. Next we write out the traces appearing in (44) in terms of the eigenvalues and then use Lemma 2 to provide a bound that is summable (over the eigenvalues) and integrable (from 0 to \( \infty \)), if \( |\epsilon| < \pi/8 \). This bound is uniformly bounded in \( \epsilon \), and so, by dominated convergence, we can take the limit \( \epsilon \downarrow 0 \) term by term. Using the result (11), which we established above, Equation (12) is now verified.

Proof of Theorem 2: As was the case in the proof of Theorem 2 we shall assume that \( W \) and \( V \) are nonnegative. For Part 1 we proceed as for Theorem 2 and define \( H_{N,Z} \) as in (34), but with \( \Pi(l_0) \) replaced by \( W(\omega) \). First we treat the case \( W(\omega) = 1 \). We follow the proof of Theorem 1 up to Equations (36) and (37) (with \( \delta_l, l_0 \) replace by \( W(\omega) \)). Then we obtain analogously

\[
\lim \sup_{Z \to \infty} \lambda(Z) \leq \lim \inf_{\epsilon \downarrow 0} \lim \sup_{Z \to \infty} \left[ \sum_{l=0}^{\infty} q(2l + 1) \frac{\text{tr}(H_{l_0,0,Z})_1 - \text{tr}(H_{l_0,\epsilon/Z})_1 - \theta(l - l) + \text{const}Z^{-1/2} \epsilon^{-1}}{\epsilon Z^2} \right]
\]

\[
= \sum_{l=0}^{\infty} q(2l + 1) \lim \inf_{\epsilon \downarrow 0} \lim \sup_{Z \to \infty} \frac{\text{tr}(H_{l_0,0,Z})_1 - \text{tr}(H_{l_0,\epsilon/Z})_1 - \theta(l - L) + \text{const}Z^{-1/2} \epsilon^{-1}}{\epsilon Z^2}
\]

\[
= \sum_{l=0}^{\infty} q(2l + 1) \lim \inf_{\epsilon \downarrow 0} \frac{\text{tr}(H_{l_0,0,1})_1 - \text{tr}(H_{l_0,1})_1 - \theta(l - L) + \text{const}Z^{-1/2} \epsilon^{-1}}{\epsilon Z^2}
\]

\[
= a^2 \rho_{l_0}(a) \leq \frac{a^2 \rho_{l_0}(a) \leq a^2 \rho_{l_0}(a)}{\epsilon}
\]

To obtain (49) we use inequalities (38) and (39). To obtain (50) we use the fact that Lemma 1 provides a majorant uniform in \( \epsilon \) and \( Z \) which is absolutely summable with respect to \( \sum_{l=0}^{\infty} q(2l + 1) \), i.e., fulfills the Weierstraß criterion.
for uniform convergence (or the hypothesis of Lebesgue’s dominated convergence theorem), and therefore allows the interchange of the limit and the summation, and that the second sum tend term by term to zero. To obtain (51) we use the fact that the eigenvalues of the bare problem scale like $Z^2$. Finally, the convergence result of Theorem 2 was used to obtain (52).

To obtain a lower bound we pick $\epsilon$ negative instead of positive and take the limit $\lim_{\epsilon \to 0} \sup_{Z} \rightarrow \frac{\epsilon}{\epsilon Z^2}$ instead of $\lim_{\epsilon \to 0} \inf_{Z} \rightarrow \frac{\epsilon}{\epsilon Z^2}$. Repeating the same steps gives the same result except for reversing the inequalities thereby yielding the bound from below.

Let $W$ now be a general bounded, measurable function on the unit sphere which we may – according to the remarks in the beginning – assume to be positive. We take $\|W\|_{\infty} = 1$.

Let us try to imitate the steps (47) to (53). As before we are faced with estimating the eigenvalues of the one-body operators $H_{\epsilon, Z}^H := -\Delta - Z/|.| - \epsilon Z W \delta_{\frac{\omega}{Z}}$, and $H_{\epsilon, Z}^{TF} := -\Delta - \varphi_{\epsilon Z}^{TF} - \epsilon Z W \delta_{\frac{\omega}{Z}}$ but unlike the previous case these cannot be simply indexed by the angular momentum $l$ when $\epsilon \neq 0$; indeed the one-body operators cannot be reduced to a direct sum of radial Schrödinger operators as in (36) and (37). However, the eigenvalues are real analytic functions of $\epsilon$ and we can label the eigenvalues by the $l$-value they have when $\epsilon$ tends to zero. In short, the only change needed in (47) to (53) is to replace $(2l+1)e_{n,l,\epsilon,Z}$ by the sum of the eigenvalues in the multiplet of $H_{\epsilon, Z}^H$ that converge to $e_{n,l,0,Z}$ as $\epsilon$ tends to zero. Since $W$ is bounded by 1, all our previous bounds for eigenvalue differences (Lemmata 1 and 2) continue to hold and we are finally led to the $\lim_{\epsilon \to 0} \inf_{Z}$ in (51).

The crucial point is this: Even if $W$ is not spherical symmetric, the sum of the eigenvalues in any multiplet is rotationally invariant to first order in $\epsilon$ in the following sense. The only property of $W$ that matters – to first order – is the average $W_{\text{average}} := (4\pi)^{-1} \int W(\omega) d\omega$.

Reversing the sign of $\epsilon$ again gives the lower bound.

2. Proof of the weak convergence: The proof can be rolled back to the previous case as follows: First we assume that $V$ is spherically symmetric and integrate the inequality

$$
a^2 \rho_Z(a\omega) \leq \left[ \sum_{l=0}^{\infty} q(2l+1) \frac{\text{tr}(H_{l,0,Z}^H) - \text{tr}(H_{l,\epsilon,Z}^H)}{\epsilon Z^2} \theta(l - l) \right.
\left. + \sum_{l=0}^{\infty} q(2l+1) \frac{\text{tr}(H_{l,0,Z}^H) - \text{tr}(H_{l,\epsilon,Z}^H)}{\epsilon Z^2} \theta(l - L) \right] + \text{const}/(\epsilon Z^{\frac{1}{4}})
$$

against $aV(a)$ from 0 to $\infty$. Observe that because of Lemma 2, the summand of the sum on the right side of this integrated inequality is uniformly bounded by

$$\frac{9}{(l + 1)^2(2l + 1)} \int_{0}^{\infty} V(a) a^2 da$$

which, when multiplied by $(2l + 1)$, is summable. Again, the same argument holds when expressing the traces as sum over eigenvalues. Thus we are allowed to take the limits term by term for the differences of the eigenvalues giving the desired result as above.

The extension to the non-spherical case is as in Part 1.
5 Extensions to Molecules

The ground state energy of a neutral molecule with nuclear charges \(Z_1 = \lambda z_1,...,Z_K = \lambda z_K\) and positions of the nuclei at \(\mathfrak{R}_1,...,\mathfrak{R}_K\) is given as

\[
E(N, \vec{Z}) = \inf \{\inf \sigma(H_{N,\vec{Z},\vec{R}})|\vec{R} \in \mathbb{R}^{3K}\}
\]

where

\[
H_{N,\vec{Z},\vec{R}} = \sum_{\nu=1}^{N} \left(-\Delta_\nu - \sum_{\kappa=1}^{K} \frac{Z_\kappa}{|r_\nu - \mathfrak{R}_\kappa|}\right) + \sum_{\mu,\nu=1}^{N} \frac{1}{|r_\mu - r_\nu|} + \sum_{\kappa,\kappa'=1}^{N} \frac{Z_\kappa Z_{\kappa'}}{|\mathfrak{R}_\kappa - \mathfrak{R}_{\kappa'}|}
\]

self-adjointly realized in \(\mathcal{H}_N\). Here \(\vec{Z}\) denotes the \(K\)-tuple \((Z_1,...,Z_K)\) and \(\vec{R}\) the \(3K\)-tuple \((\mathfrak{R}_1,...,\mathfrak{R}_K)\). We also set \(\vec{z} := (z_1,...,z_K)\). Solovej \cite{25} showed recently that for arbitrary but fixed \(\vec{z}\) and \(N = Z_1 + ... + Z_K\)

\[
E(N, \vec{Z}) = \sum_{\kappa=1}^{K} E(Z_\kappa, Z_\kappa) + o(\lambda^{\frac{5}{2}})
\]

holds as \(\lambda\) tends to infinity and that the minimizing inter-nuclear distances are of order \(\lambda^{-5/2}\) or bigger. These results imply among other things not only that the atomic Scott correction and Schwinger correction implies the molecular one but allows us to generalize Theorem 2 as well: The molecular density in the vicinity of each nucleus converges in the sense of Theorem 1 to the hydrogen density at each of the centers. Our precise result is:

**Theorem 3** Assume that \(E(N, \vec{Z})\) as defined in (54) is equal to

\[
\inf \{\inf \sigma(H_{N,\vec{Z},\vec{R}})|\vec{R} \in \mathbb{R}^{3K}, \forall 1 \leq \kappa < \kappa' \leq K|\mathfrak{R}_\kappa - \mathfrak{R}_{\kappa'}| \geq \lambda^\gamma\}
\]

with \(\gamma > -1/4\). Assume \(N = Z_1 + ... + Z_K\), \(Z_1 = \lambda z_1,...,Z_K = \lambda z_K\) with given fixed \(z_1,...,z_K\). Furthermore fix \(\kappa_0 \in 1,...,K\) and pick a sequence of ground state density matrices \(d_c\) of \(H_{N,\vec{Z},\vec{R}}\) with densities \(\rho_{d_c}\). Define \(\rho_{\lambda,\kappa_0}(r) := \rho_\lambda((r - \mathfrak{R}_{\kappa_0})/\lambda)/\lambda^\gamma\). Finally assume \(W \in \mathcal{L}(\ell^2(S^2))\). Then

\[
\int \mathbb{S}^2 W(\omega)\rho_{\lambda,\kappa}(r\omega) \to q^H(r) \int \mathbb{S}^2 W.
\]

**Proof.** First note that by suitable relabeling we can always assume that \(\kappa_0 = 1\).

Set \(H_{N,\vec{Z},\vec{R}}' := H_{N,\vec{Z},\vec{R}} - \sum_{\nu=1}^{N} \epsilon \mathcal{U}_\lambda(r - \mathfrak{R}_1)\). Because of (60) it suffices that

\[
\text{tr}(dH_{N,\vec{Z},\vec{R}}') \geq \text{tr}(H_1 - \epsilon \mathcal{U}_\lambda) + \sum_{\kappa=1}^{N} \text{tr}(H_\kappa) - D(\rho_{Z_{\kappa}}^TF, \rho_{Z_{\kappa}}^{TF}) - \text{const} Z^{2-\delta}
\]

for some positive \(\delta\) and an approximate ground state \(d\). To this end let us introduce the localizing functions

\[
u_\kappa(t) := \cos(\psi(|r - \mathfrak{R}_\kappa|/\lambda))
\]

where \(\psi(t)\) is some continuous, piecewise differentiable, monotone decreasing function which vanishes, if \(t < \frac{1}{8}\), and which is \(\pi/2\), if \(t > \frac{1}{2}\). Note that the
supports of these functions have at most finitely many points in common because
\( R \) is the minimal nuclear distance. We also define
\[
v_0 := \sqrt{1 - \sum_{\kappa=1}^{K} v_{\kappa}^2}.
\]

Now pick the density \( \rho(r) := \sum_{\kappa=1}^{K} \rho_{\kappa}^{TF}(|r - \mathfrak{R}_{\kappa}|) \) and denote the one-particle density matrix belonging to \( d \) by \( d_1 \). – By the correlation inequality \([13, 11]\) and the localization formula using the above decomposition of unity we have
\[
\begin{aligned}
\text{tr}(H_{N, Z, R}^{d}) & \geq \text{tr} \left\{ \left[ -\Delta_3 - \sum_{\kappa'}=1^{K} \left( \frac{Z_{\kappa}}{|r - \mathfrak{R}_{\kappa}|} - \rho_{\kappa} \right) - \epsilon U_Z \right] d_1 \right\} - D(\rho, \rho) \\
& \quad + \sum_{\kappa, \kappa'}=1^{K} \left| Z_{\kappa} Z_{\kappa'} \right| - \text{const} \lambda^2 \\
& \geq \text{tr} \left\{ \sum_{\kappa=0}^{K} v_{\kappa} \left[ -\Delta_3 - \sum_{\kappa'}=1^{K} \varphi_{\kappa'}^{TF}(|r - \mathfrak{R}_{\kappa'}|) - \epsilon U_Z \right] d_1 v_{\kappa'} \right\} \\
& \quad - \| \sum_{\kappa=0}^{N} |\text{grad } v_{\kappa}|^2 \|_{\infty} N - \sum_{\kappa'=1}^{K} D(\rho_{\kappa}, \rho_{\kappa'}) - \text{const} \lambda^2. \quad (59)
\end{aligned}
\]

In (59) we used the spherical symmetry of \( \varphi_1, ..., \varphi_K \) to show that \( D(\rho_{\kappa}, \rho_{\kappa'}) \leq Z_{\kappa} Z_{\kappa'} |\mathfrak{R}_{\kappa} - \mathfrak{R}_{\kappa'}|^{-1} \).

Now pick any arbitrary pair of different indices \( \kappa, \kappa' \in \{1, ..., K\} \). On the support of \( v_{\kappa} \) we have
\[
\varphi_{Z_{\kappa}}^{TF}(|r - \mathfrak{R}_{\kappa}|) \leq \frac{2^{2\frac{3}{4}} \pi^2}{q^2 (R/2)^4}
\]
where we use the fact that the Sommerfeld solution of the Thomas-Fermi equation is a pointwise upper bound of the Thomas-Fermi potential \([12, \text{Section V.2}]\). Thus on the support of \( v_{\kappa} \) we have
\[
\sum_{\kappa'=1, \kappa' \neq \kappa}^{K} \varphi_{Z_{\kappa}}^{TF}(|r - \mathfrak{R}_{\kappa}|) \leq \frac{2^{6\frac{3}{4}} (K - 1)}{R^4}.
\]

For the derivative of the \( v_{\kappa} \), which governs the localization error, we have the following uniform estimate: \( \sum_{\kappa=0}^{K} |\text{grad } v_{\kappa}|^2 = |\psi(|r - \mathfrak{R}_{\kappa}|)|^2 / R^2 = 4\pi^2 \) where, for definiteness, we picked \( \psi \) to be the linear functions interpolating between 0 and \( \frac{\pi}{2} \) on the interval \([\frac{1}{2}, \frac{1}{2}]\). Note that outside the annuli of thickness \( R/2 \) centered at the nuclei the derivatives vanish, in fact, whereas in these annuli the bound is actually an equality.
This yields
\[
\text{tr}(H_{N, Z, d}^Z) \geq \sum_{\kappa=1}^{K} \left\{ \text{tr} \left[ \left( -\Delta - \varphi Z_{\kappa}^T \right) - D(\rho_{\kappa}, \rho_{\kappa}) \right] \right\} - D(\rho_{\kappa}, \rho_{\kappa}) - \text{const}\lambda^\frac{5}{3}
\]
\[
\geq \sum_{\kappa=1}^{K} \left\{ \text{tr} \left[ \left( -\Delta - \varphi Z_{\kappa}^T \right) - D(\rho_{\kappa}, \rho_{\kappa}) \right] \right\} - N \left( \frac{4\pi^2}{R^2} + \frac{2^{4}4\pi^2}{R^4} \right) - \text{const}\lambda^\frac{5}{3}
\]
\[
\geq \inf \sigma(H_{Z, Z}^Z) + \sum_{\kappa=2}^{K} \inf \sigma(H_{Z, Z}^Z) - \text{const} \left( \frac{\lambda}{R^3} + \lambda^{5/3} \right)
\]
\[
\geq \inf \sigma(H_{Z, Z}^Z) + \sum_{\kappa=2}^{K} \inf \sigma(H_{Z, Z}^Z) - o(\lambda^2). \quad (60)
\]

Combining this with Solovej’s upper bound reduces the converge question to that of the one-center case.

A Appendix: Facts about the Atomic Ground State Energy

According to [22] we have
\[
E_{Z, Z} \leq E_{TF}(Z, Z) + \frac{q}{8} Z^2 + \text{const} Z^\frac{5}{2}, \quad (61)
\]
and according to [23] (see also [24] and Hughes [9])
\[
E_{Z, Z} \geq \sum_{i=0}^{L-1} q(2l + 1) \text{tr} (H_{i,0,Z}^H) - D(\rho_{TF}, \rho_{TF}) - \text{const} Z^\frac{5}{2}
\]
\[
\geq E_{TF}(Z, Z) + \frac{q}{8} Z^2 - \text{const} Z^\frac{5}{2} \log Z \quad (62)
\]
with \( L = \lfloor Z^{\frac{1}{2}} \rfloor \). Combining (61) and (62) gives
\[
E_{Z, Z} = \sum_{i=0}^{L-1} q(2l + 1) \text{tr} (H_{i,0,Z}^H) - D(\rho_{TF}, \rho_{TF}) + O(Z^\frac{5}{2}). \quad (63)
\]

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