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The spin of the ground state of an atom

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In this paper we address a question posed by M. and T. Hoffmann-Ostenhof, which concerns the total spin of the ground state of an atom or molecule. Each electron is given a value for spin, $\pm 1/2$. The total spin is the sum of the individual spins.

For a neutral atom, say, of nuclear charge Z, if all Z electrons have the same spin, then the total spin would be $\pm Z/2$. There is a result of Lieb and Mattis [LM] where they show that in one dimension, ground states have lowest possible total spin. Their result also holds for a class of 3-dimensional systems which does not include the quantum atom. A related result [AL] extends this result to positive temperature, and also shows that for systems with certain parity constraints, spin alignment is in fact favored at all temperatures. It is expected that, for the atom, this is not the case, and there is a lot of spin-cancellation among the different electrons. In rigorous mathematical terms, this can be expressed in the form

$$\text{total spin} \ \leq C\, Z^{\gamma}\,, \qquad \gamma < 1\,.$$

The goal of this paper is to prove such a bound. Unfortunately, we do not have control over the constant C, which we only know to be independent of Z.

For a solid, or a molecule with many nuclei, it is expected that the total spin may get as large as the order of magnitude of the number of particles (or perhaps nuclei), which would account for ferro-magnetism.

It is also conjectured that for an atom, the order of magnitude of the spin can be as large as $Z^{1/3}$. For non-interacting radial systems, with degeneracy of the order of $Z^{1/3}$, this is certainly possible. In fact, Hund's rule, well known in chemistry, states that this degeneracy is resolved, after turning on the interaction, into making the spin as large as possible, which agrees with the $Z^{1/3}$ size of spin if one believes in atomic shells. The study of spin is also of interest because it determines qualitative properties of the wave functions (see [HHS]).

Throughout the paper, C will be used to denote any irrelevant large constant, c any irrelevant small constant, and $C_1, C_2, \ldots, c_1, c_2, \ldots$, will denote carefuly chosen large and small constants respectively.

1. Definitions, background and theorem.

Consider the atomic hamiltonian

$$H_{Z,N} = \sum_{i=1}^{N} \left(-\Delta_{r_i} - \frac{Z}{|r_i|} \right) + \sum_{i<j} \frac{1}{|r_i - r_j|} ,$$

and $E(Z,N)$ its lowest eigenvalue when acting on the Hilbert Space

$$\mathcal{H} = \bigwedge_{i=1}^{N} L^2 \left(\mathbb{R}^3 \times \mathbb{Z}_2 \right) .$$

The atomic ground-state energy is defined as

$$E(Z) = \inf_{N \geq 0} E(Z,N) .$$

It is a result of [Ru] and [Si] that $E(Z,N)$, which is decreasing in N, achieves the infimum at a finite N_c, which physically corresponds to the largest number of electrons an atom can bind; by the HVZ theorem (see [CFHS]), the ground state of the atom, which we denote by Ψ, is then defined as the eigenfunction of $H(Z,N_c)$ with eigenvalue $E(Z)$. It was proved in [Zh], [Li1] and [Li2] that

$$Z \leq N_c \leq 2\,Z .$$

Throughout this paper we will consider any N between Z and N_c, (the interesting cases corresponding, of course, to either $N = Z$ or $N = N_c$) and Ψ will denote any ground state of $H_{Z,N}$ with energy $E(Z,N)$.

As a consequence of Lieb's bound for N_c the trivial upper bound for the total spin is Z.

Here, we will use

$$x = (r, \sigma)$$

to denote the variable in $\mathbb{R}^3 \times \mathbb{Z}_2$, with $r \in \mathbb{R}^3$ the space variable and $\sigma = \sigma(x) = \pm 1/2$ the spin variable. The total spin operator is now given by

$$\mathbf{S} = \sum_{i=1}^{N} \sigma^{\uparrow}(x_i) - \sigma^{\downarrow}(x_i)\,,$$

where

$$\sigma^{\uparrow}(x) = \begin{cases} 1/2\,, & \text{if } \sigma(x) = +1/2\,, \\ 0\,, & \text{otherwise,} \end{cases}$$

$$\sigma^{\downarrow}(x) = \begin{cases} 1/2\,, & \text{if } \sigma(x) = -1/2\,, \\ 0\,, & \text{otherwise.} \end{cases}$$

Basic to our strategy is the theory of atomic (spectral) asymptotics, and some version of atomic electric neutrality, all well known, which we now briefly review.

Associated to the atomic hamiltonian there is the Thomas-Fermi energy ([Fe], [Th]), which equals $c_{\mathrm{TF}}\, Z^{7/3}$ for an explicit negative constant c_{TF} and satisfies

$$E(Z) = c_{\mathrm{TF}}\, Z^{7/3} + O\left(Z^{7/3-\varepsilon}\right)\,, \qquad \varepsilon > 0\,, \tag{1}$$

which was proved in [LS]. We also have the Thomas-Fermi density ρ^Z_{TF}, and the Thomas-Fermi potential V^Z_{TF}, which satisfy the perfect scaling conditions

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

for universal functions $\rho(r)$ and $V(r)$, which satisfy the Thomas-Fermi equations

$$\rho(r) = \frac{1}{3\,\pi^2}\, V^{3/2}(r)\,, \qquad \Delta V(r) = 4\pi\, \rho(r)\,.$$

Note that our definition of the Thomas-Fermi potential is the negative of the usual one. We refer the reader to [Li] for a great exposition of Thomas-Fermi theory. We also have the bound [Hi]

$$
\begin{aligned}
& c\,\mathcal{S}(x) \le V^Z_{\mathrm{TF}}(x) \le C\,\mathcal{S}(x)\,, \qquad \mathcal{S}(x) = \min\left\{\frac{Z}{|x|}, \frac{1}{|x|^4}\right\}, \\
& \left|\nabla V^Z_{\mathrm{TF}}(x)\right| \le C\,\mathcal{S}(x)\,|x|^{-1}\,.
\end{aligned} \tag{2}
$$

The expansion (1) can be continued into what is called the Scott asymptotics, namely

$$
E(Z) = c_{\mathrm{TF}}\,Z^{7/3} + \frac{1}{4}\,Z^2 + O(Z^{2-\varepsilon})\,, \qquad \varepsilon > 0\,. \tag{3}
$$

The Z^2 term is not semiclassical; its nature comes from the coulomb singularities and is therefore a genuine quantum effect. This was first realized in [Sc], and proved rigorously (in the atomic case only) in [Hu], [SW1], [SW2] and [SW3]. Its proof for molecules is in [IS].

A refinement of (3) is also known for atoms, and it has the form

$$
E(Z) = c_{\mathrm{TF}}\,Z^{7/3} + \frac{1}{4}\,Z^2 + c_{\mathrm{DS}}\,Z^{5/3} + O\Big(Z^{5/3-\varepsilon}\Big)\,, \qquad \varepsilon > 0\,, \tag{4}
$$

obtained in [Di] and [Sch], and proved rigorously in [FS1], [FS2], [FS3], [FS4], [FS5], [FS6], [FS7] and [FS8]. The corresponding molecular problem remains open, but the techniques in [IS] come very close to proving a similar expression. The expansion in powers of Z almost surely ends here (see [En], [CFS1] and [CFS2]).

Concerning the electronic neutrality problem, we only need the following two facts, which can be found in [FS9] and [SSS]; they depend on a number $b > 0$ which, after the accurate asymptotics in (4), or even (3) with $\varepsilon = 1/3$, can be taken to be $b = 2/3$. They are expressed in terms of the ground state density, which is defined as

$$
\begin{aligned}
& \rho_\Psi(r) = \rho^{\uparrow}_\Psi(r) + \rho^{\downarrow}_\Psi(r), \\
& \rho^{\uparrow}_\Psi(r) = \tfrac{1}{2}N \int_{[\mathbb{R}^3\times\mathbb{Z}_2]^{(N-1)}} \left|\Psi(r,\tfrac{1}{2};x_2;\cdots;x_N)\right|^2 dx_2\cdots dx_N, \\
& \rho^{\downarrow}_\Psi(r) = \tfrac{1}{2}N \int_{[\mathbb{R}^3\times\mathbb{Z}_2]^{(N-1)}} \left|\Psi(r,-\tfrac{1}{2};x_2;\cdots;x_N)\right|^2 dx_2\cdots dx_N.
\end{aligned}
$$

1. The main result in [FS9] and [SSS] is

$$N_c = \int_{\mathbb{R}^3} \rho_\Psi(r)\, dr = Z + O\Big(Z^{1-3b/7}\Big)\,. \tag{5.a}$$

2. The following is the content of estimate (A) or Lemma 2.1 in [FS9], or Lemma 6 in [SSS]:

$$\left| \int_{\mathbb{R}^3} \rho_\Psi(r)\, \chi(r)\, dr - \int_{\mathbb{R}^3} \rho^Z_{\mathrm{TF}}(r)\, \chi(r)\, dr \right| \leq C\, Z^{(7/3-b)/2}\, \|\nabla \chi\|_2\,, \tag{5.b}$$

where χ is a positive function equal to 1 in a ball of radius at least $C\, Z^{-2/3}$, 0 outside of its double, and bounded by 1.

A common feature in both the asymptotic analysis and the neutrality problem is Lieb's inequality which also plays a crucial role in our analysis, and is by now part of the mathematical physics folkore ([Li]; see also [SW2], and for improvements [FS7], [Ba] and [GS]). We will use it in the following precise form,

Theorem (Lieb). *Assume* $\psi(x_1, \ldots, x_N)$, $(Z \leq N \leq 2Z)$ *is such that*

$$\|\nabla \psi\|_2^2 \leq C\, Z^{7/3}\,.$$

Then, we have that

$$\langle H_{Z,N}\, \psi, \psi \rangle \geq \langle H^{\mathrm{ind}}_{Z,N} \psi, \psi \rangle - \frac{1}{2} \iint \frac{\rho^Z_{\mathrm{TF}}(x)\, \rho^Z_{\mathrm{TF}}(y)}{|x-y|}\, dx\, dy - C'\, Z^{5/3}\,,$$

where

$$H^{\mathrm{ind}}_{Z,N} = \sum_{i=1}^{N} \Big(-\Delta_{x_i} - V^Z_{\mathrm{TF}}(x_i) \Big)\,.$$

The proof of this result can be found in Lemma 2 in [SW2], which is stated in a special case, but its proof shows exactly this. The role of this inequality is that it reduces the analysis of systems with interaction to a system without it. Technically, the problem reduces to an asymptotic estimate for the sum of the negative eigenvalues of a fixed Schrödinger operator in $\mathbb{R}^3$ (see below). For convenience, given an operator H, we denote the sum of its negatives eigenvalues by $\mathrm{sneg}\, H$. We denote by

H_N^Ω the corresponding operator with Neumann boundary conditions on Ω.

The asymptotic estimates we need began with the work of Lieb and Simon. Those estimates, more refined ones even, are now also part of the folkore. We reproduce here a variant which suffices for our theorem. This is essentially contained in [LS] and explicitly proven in [FS7]; we include a version of the proof here for the convenience of the reader, and to make this paper as self-contained as possible.

Lemma 1. *If Q is a cube of side L, and K is a number larger than $100\,L^{-2}$, we have that*

$$\text{sneg}\,(-\Delta - K)_N^Q \geq -\frac{1}{15\,\pi^2}\,K^{5/2}\,L^3 - C\,K^2\,L^2\,,$$

for a universal constant C. If $K \leq M\,L^{-2}$ we have trivially

$$\text{sneg}\,(-\Delta - K)_N^Q \geq -M'\,L^{-2}\,.$$

PROOF. If $K\,L^2 \geq 100$,

$$\begin{aligned}\text{sneg}\,(-\Delta - K)_N^Q &= \sum_{\substack{\pi^2(n_1^2+n_2^2+n_3^2)\leq K L^2 \\ n_i \geq 0}} \left(\frac{\pi^2\,(n_1^2+n_2^2+n_3^2)}{L^2} - K\right) \\ &= \frac{1}{8}\int\limits_{|x|\leq\sqrt{K}L/\pi} \left(\left|\frac{\pi\,x}{L}\right|^2 - K\right)\,dx + O(K^2\,L^2)\,.\end{aligned}$$

Lemma 2. *Let W be any potential satisfying*

$$\begin{aligned}&W(x) \sim \mathcal{S}(x)\,, \qquad |\nabla W(x)| \leq C\,\mathcal{S}(x)\,|x|^{-1}\,, \\ &\mathcal{S}(x) = \min\left\{\frac{Z}{|x|}\,, |x|^{-4}\right\}.\end{aligned} \tag{6}$$

Then,

$$\text{sneg}\,(-\Delta - W) \geq -\frac{1}{15\,\pi^2}\int W(x)^{5/2}\,dx - \overline{C}\,Z^{13/6}\,,$$

where $\overline{C}$ only depends on the constants in (6).

PROOF. We break up $\mathbb{R}^3$ into cubes Q_0, Q_ν and Q'_ν with the properties:

1. Q_0 is centered at the origin and has diameter $d_0 = C_1 Z^{-1}$.

2. The Q_ν are centered at x_ν, with $C_1 Z^{-1}/10 \leq |x_\nu| \leq c$, and have diameters d_ν which satisfy

$$d_\nu \sim S^{-1/4}(x_\nu)\,|x_\nu|^{1/2}\,. \tag{7}$$

3. The $Q_{\nu'}$ are centered at $x_{\nu'}$, with $|x_{\nu'}| \geq c'$, and have diameter $d_{\nu'}$ which satisfy

$$10^{-5}\,|x_{\nu'}| \leq d_{\nu'} \leq \frac{1}{100}\,|x_{\nu'}|\,. \tag{8}$$

Let us check that $\mathbb{R}^3$ can be broken into such cubes. We begin with a simple geometric observation: if $Q(r)$ denotes the cube of diameter r centered at 0, then $Q(3r) - Q(r)$ may be decomposed into cubes of diameter r. It follows that $Q(3r) - Q(r)$ may be decomposed into subcubes of diameter between $s/3$ and s, for any given $s \leq r$.

Now let $r_k = C_1 Z^{-1} 3^k$ for $k \geq 0$, and break up $\mathbb{R}^3$ into $Q(r_0) = Q_0$, and $Q(r_{k+1}) - Q(r_k)$ for $k \geq 0$. For $k \geq 0$ such that $r_k \leq c$ we break up $Q(r_{k+1}) - Q(r_k)$ into cubes Q_ν of diameter

$$d_k \sim s_k = \left(\min\left\{\frac{Z}{r_k}, r_k^{-4}\right\}\right)^{-1/4} r_k^{1/2}\,,$$

which is possible since $s_k \leq r_k$.

For $k \geq 0$ such that $r_k > c$, we break up $Q(r_{k+1}) - Q(r_k)$ into cubes $Q_{\nu'}$ of diameter between $r_k/3 \cdot 10^4$ and $10^{-4}\, r_k$. One checks easily that the resulting decomposition into cubes satisfies 1, 2 and 3 above.

Note that, by (8), the number of $Q_{\nu'}$ with centers in a spherical shell of radii R and $2R$, is not more than a fixed large constant and therefore,

$$\text{number } \{Q_{\nu'} : R_1 \leq |x_{\nu'}| \leq R_2\} \leq C \log(R_2/R_1)\,, \tag{9}$$

when $R_2 \geq R_1$. In preparation to use Lemma 1, we denote

$$w_\nu = \max_{x \in Q_\nu} W(x)\,,$$

and we note that, when $x \in Q_\nu$,

$$\begin{aligned}\left|W^{5/2}(x) - {w_\nu}^{5/2}\right| &\le C\,{w_\nu}^{3/2}\,|W(x) - W(x_\nu)| \\ &\le C\,{w_\nu}^{3/2}\,d_\nu \max_{Q_\nu} |\nabla W(x)| \\ &\underset{\text{using (7)}}{\le} C\,\mathcal{S}(x_\nu)^{3/2}\,S^{-1/4}(x_\nu)\,|x_\nu|^{1/2}\,\mathcal{S}(x_\nu)\,|x_\nu|^{-1} \\ &\le C\,\mathcal{S}^{9/4}(x_\nu)\,|x_\nu|^{-1/2}\,.\end{aligned}$$

This implies that

$$\begin{aligned}\left|{w_\nu}^{5/2}\,d_\nu^3 - \int_{Q_\nu} W^{5/2}(x)\,dx\right| &\le C\,\mathcal{S}^{9/4}(x_\nu)\,|x_\nu|^{-1/2}\,d_\nu^3 \\ &\le C\int_{Q_\nu} \mathcal{S}^{9/4}(x)\,|x|^{-1/2}\,dx\,.\end{aligned} \tag{10}$$

For Q_0, we have that

$$\begin{aligned}\operatorname{sneg}\,(-\Delta - W(x))_N^{Q_0} &\ge \operatorname{sneg}\left(-\Delta - \frac{C\,Z}{|x|}\right)_N^{Q_0} \\ &= Z^2\operatorname{sneg}\left(-\Delta - \frac{C}{|x|}\right)_N^{\tilde{Q}_0}\,,\end{aligned}$$

where $\tilde{Q}_0$ is the cube Q_0 dilated by Z, which is therefore of diameter C_1 and makes the sneg term above independent of Z.

After this, we turn to sneg's by writing

$$\begin{aligned}\operatorname{sneg}\,(-\Delta - W(x)) &\ge \operatorname{sneg}\,(-\Delta - W(x))_N^{Q_0} + \sum_\nu \operatorname{sneg}\,(-\Delta - W(x))_N^{Q_\nu} \\ &\quad + \sum_{\nu'} \operatorname{sneg}\,(-\Delta - W(x))_N^{Q_{\nu'}} \\ &\ge -C\,Z^2 + \sum_\nu \operatorname{sneg}\,(-\Delta - w_\nu)_N^{Q_\nu} \\ &\quad + \sum_{\nu'} \operatorname{sneg}\,(-\Delta - W(x))_N^{Q_{\nu'}} \\ &\ge -C\,Z^2 + \sum_\nu \left(w_\nu^{5/2}\,d_\nu^3 - C\,w_\nu^2\,d_\nu^2\right) \\ &\quad + \sum_{\nu'} \operatorname{sneg}\,(-\Delta - W(x))_N^{Q_{\nu'}}\,.\end{aligned} \tag{11}$$

For the $Q_{\nu'}$, we use the trivial part of Lemma 1 to obtain

$$\begin{aligned}\sum_{\nu'} \operatorname{sneg}\,(-\Delta - W(x))_N^{Q_{\nu'}} &\geq -C \sum_{\nu'} {d_{\nu'}}^{-2} \\ &\geq -C \sum_{n=\sim 1}^{\infty} 2^{-2n} \sum_{2^n \leq |x_{\nu'}| \leq 2^{n+1}} 1 \\ &\geq -C\,. \end{aligned} \tag{12}$$

For the Q_ν, we have

$$w_\nu^2\, d_\nu^2 \leq C\, \mathcal{S}^{9/4}(x_\nu)\, |x_\nu|^{-1/2}\ |Q_\nu| \leq C \int_{Q_\nu} \mathcal{S}^{9/4}(x)\, |x|^{-1/2}\, dx\,.$$

Putting this, with (10) and (12) into (11), we obtain

$$\begin{aligned}\operatorname{sneg}\,(-\Delta - W(x)) &\geq -\frac{1}{15\,\pi^2} \int_{\cup_\nu Q_\nu} W^{5/2}(x)\, dx \\ &\quad - C \int_{\mathbb{R}^3} \mathcal{S}^{9/4}(x)\, |x|^{-1/2}\, dx - C \\ &\geq -\frac{1}{15\,\pi^2} \int_{\mathbb{R}^3} W^{5/2}(x)\, dx - C\, Z^{13/6}\,, \end{aligned}$$

as we claimed.

We are now ready to state and prove our main result:

Theorem 3. *If Ψ is the ground state for $H_{Z,N}$ for $Z \leq N \leq N_c$, then we have*

$$|\langle \mathbf{S}\, \Psi, \Psi \rangle| \leq C\, Z^\gamma\,, \qquad \gamma < 1\,.$$

PROOF. Let $\delta > 0$ be a small number to be chosen later, and consider a positive function χ, bounded by 1 and as smooth as possible, such that

$$\chi(r) = \begin{cases} 1\,, & \text{if } |r| < Z^{-1/3+\delta}\,, \\ 0\,, & \text{if } |r| > 2\, Z^{-1/3+\delta}\,. \end{cases}$$

For a real number μ in the range

$$|\mu| \leq c_1\, Z^{-4\delta}\,, \tag{13}$$

consider the hamiltonian given by

$$H_\mu = H_{Z,N} + 2\,\mu\, Z^{4/3} \mathrm{S}_\chi \,,$$

where

$$\mathrm{S}_\chi = \sum_{i=1}^{N} \chi(r_i)\,\big(\sigma^\uparrow(x_i) - \sigma^\downarrow(x_i)\big)\,,$$

and denote by $E_\mu(Z)$ the corresponding ground state energy. Note that

$$\mathrm{S} = \mathrm{S}_\chi + \mathrm{S}_{1-\chi}\,.$$

We will study S_χ first using H_μ; later, $\mathrm{S}_{1-\chi}$ will be easily dominated using (5.).

We define the Thomas-Fermi approximation to E_ν,

$$\begin{aligned}\mathcal{E}_\mu(Z) = -\frac{Z^{7/3}}{15\,\pi^2} \int \Big(&\big(V(r) + \mu\,\chi(Z^{-\delta} r)\big)_+^{5/2} \\ &+ \big(V(r) - \mu\,\chi(Z^{-\delta} r)\big)_+^{5/2} \Big)\, dr \\ - \frac{1}{2} \iint \frac{\rho_{\mathrm{TF}}^Z(x)\,\rho_{\mathrm{TF}}^Z(y)}{|x-y|}\, dx\, dy\,,&\end{aligned}$$

which plays the following role:

Proposition 4. *There is a constant C such that*

$$E_\mu(Z) \geq \mathcal{E}_\mu(Z) - C\, Z^{7/3-\varepsilon_1}\,, \qquad \varepsilon_1 = \frac{1}{6}\,,$$

uniformly for all $|\mu| \leq c_1\, Z^{-4\delta}$.

REMARK. Although the corresponding upper bound is most probably also true, we will have no need for it here, and we ignore the issue.

PROOF. Note first that our assumption (13) on μ implies that

$$|\mu|\, Z^{4/3}\, \chi(x) \leq \frac{1}{2}\, V_{\mathrm{TF}}^Z(x)\,, \qquad \text{for all } x\,. \tag{14}$$

Indeed, this is clear for $|x| < Z^{-1/3}$, and is also obvious for $|x| \geq 2\, Z^{-1/3+\delta}$. For the other x, we have that $|\mu|\, Z^{4/3}\, \chi(x) \leq c_1\, Z^{4/3-4\delta}$,

whereas $V^Z_{\rm TF}(x) \geq c\,|x|^{-4} \geq c\,Z^{4/3-4\delta}$, and (14) then follows by taking c_1 small enough. Estimate (14) in turn implies that

$$\frac{1}{2}\,V^Z_{\rm TF}(x) \leq V^Z_{\rm TF}(x) \pm \mu\,Z^{4/3}\,\chi(x) \leq \frac{3}{2}\,V^Z_{\rm TF}(x)\,. \tag{15}$$

In preparation to use Lieb's inequality, we compute the kinetic energy of a ground state Ψ_μ for E_μ, (or elements of a sequence with energy converging to E_μ) with a virial argument as follows: define

$$\mathrm{KE}(\psi) = \|\nabla\psi\|_2^2\,, \qquad \mathrm{PE}(\psi) = \langle V_{\rm Coulomb}\psi, \psi\rangle\,,$$

with

$$V_{\rm Coulomb}(x_1,\ldots,x_N) = -\sum_{i=1}^{N}\frac{Z}{|r_i|} + \sum_{i\neq j}\frac{1}{|r_i - r_j|}\,,$$

and denote the approximate ground-state sequence by $\Psi_{\mu,k}$. We denote their densities by $\rho_{\mu,k}$.

For $\lambda > 0$, denote

$$\Psi^\lambda_{\mu,k}(x_1,\ldots,x_N) = \lambda^{3N/2}\,\Psi_{\mu,k}(\lambda\,x_1,\ldots,\lambda\,x_N)\,,$$

and note that

$$\begin{aligned} f(\lambda) &= \langle H_\mu\,\Psi^\lambda_{\mu,k}, \Psi^\lambda_{\mu,k}\rangle \\ &= \lambda^2\,\mathrm{KE}(\Psi_{\mu,k}) + \lambda\,\mathrm{PE}(\Psi_{\mu,k}) \\ &\quad + \mu\,Z^{4/3}\int \chi(\lambda^{-1}x)\,\left(\rho^{\uparrow}_{\mu,k}(x) - \rho^{\downarrow}_{\mu,k}(x)\right)\,dx\,, \end{aligned}$$

is a smooth function which satisfies

$$\lim_{\lambda\to 0} f(\lambda) = 0\,, \qquad \lim_{\lambda\to\infty} f(\lambda) = \infty\,.$$

Also, using Ψ as trial function for H_μ and taking k large enough, we see that

$$f(1) \leq \frac{1}{2}\,E(Z) + c_1\,Z^{7/3-\delta}\,.$$

By (1), the right hand side is negative for all Z larger than a certain constant depending on c_1. Therefore f attains its minimum at some $0 < \lambda < \infty$ and, maybe by changing our sequence $\Psi_{\mu,k}$ to another whose energy converges faster to the ground state energy, we can rescale the

$\Psi_{\mu,k}$ so that the minimum of f is attained at $\lambda = 1$ and thus $f'(1) = 0$. This means that

$$2\,\mathrm{KE}(\Psi_{\mu,k}) + \mathrm{PE}(\Psi_{\mu,k}) \leq 2\,|\mu|\,Z^{4/3} \int |\nabla\chi(x)|\;|x|\;\rho_{\Psi_{\mu,k}}(x)\,dx$$
$$\leq C\,Z^{7/3}\,.$$

Using $\Psi_{\mu,k}$ as trial function for $H_{Z,N}$, we see that

$$\mathrm{KE}(\Psi_{\mu,k}) + \mathrm{PE}(\Psi_{\mu,k}) \geq -C\,Z^{7/3}\,.$$

Altogether, we conclude that

$$\mathrm{KE}(\Psi_{\mu,k}) \leq C\,Z^{7/3}\,.$$

In view of Lieb's inequality, it is then quite obvious that

$$E_\mu \geq \mathrm{sneg}\left(-\Delta - V^Z_{\mathrm{TF}} + \mu\,Z^{4/3}\,\chi\right) + \mathrm{sneg}\left(-\Delta - V^Z_{\mathrm{TF}} - \mu\,Z^{4/3}\,\chi\right)$$
$$- \frac{1}{2}\iint \frac{\rho^Z_{\mathrm{TF}}(x)\,\rho^Z_{\mathrm{TF}}(y)}{|x-y|}\,dx\,dy - C\,Z^{5/3}\,.$$

Set

$$W(x) = V^Z_{\mathrm{TF}}(x) - \mu\,Z^{4/3}\,\chi(x)\,,$$

and recall (2) and (15) which, with the equally trivial bound

$$\left|\mu\,Z^{4/3}\,\nabla\chi(x)\right| \leq C\,|x|^{-5}\,,$$

show that W satisfies (6). Lemma 2 then proves our result.

Now, we consider the following lemma:

Lemma 5. *$\mathcal{E}_\mu$, as a function of μ, is concave, and there is a constant C such that*

$$C^{-1}\,Z^{7/3} \leq |\mathcal{E}_\mu(Z)| \leq C\,Z^{7/3}\,, \qquad \left|\frac{\partial^2\mathcal{E}_\mu(Z)}{\partial\mu^2}\right| \leq C\,Z^{7/3+\delta}\,,$$

uniformly for all $|\mu| \leq c_1\,Z^{-4\delta}$.

PROOF. After checking that (15) settles the first bounds in the statement of the lemma, a calculation gives

$$\begin{aligned}\left|\frac{\partial^2 \mathcal{E}_\mu(Z)}{\partial \mu^2}\right| &\leq C\, Z^{7/3} \int_{\mathbb{R}^3} \Big(\big(V(x) + \mu\, \chi(Z^{-\delta}\, x)\big)^{1/2} \\ &\qquad + \big(V(x) - \mu\, \chi(Z^{-\delta}\, x)\big)^{1/2} \Big)\, \chi^2\, (Z^{-\delta}\, x)\, dx \\ &\leq C\, Z^{7/3} \int\limits_{|x| \leq 2\, Z^\delta} V^{1/2}(x)\, dx \\ &\leq C\, Z^{7/3} \int\limits_{|x| \leq 2\, Z^\delta} |x|^{-2}\, dx \\ &\leq C\, Z^{7/3+\delta}\,.\end{aligned}$$

After this, we simply observe that $\mathcal{E}_0(Z) = c_{\mathrm{TF}}\, Z^{7/3}$ (again, see [Li]), and note that $\mathcal{E}_\mu(Z)$ is an even function of μ to conclude that, for μ in our range, we must have

$$\begin{aligned}\mathcal{E}_\mu(Z) &\geq c_{\mathrm{TF}}\, Z^{7/3} - \frac{\mu^2}{2} \sup_\mu \left|\frac{\partial^2 \mathcal{E}_\mu}{\partial \mu^2}\right| \\ &\geq c_{\mathrm{TF}}\, Z^{7/3} - C\, \mu^2\, Z^{7/3+\delta}\,,\end{aligned}$$

which implies

$$E_\mu(Z) \geq c_{\mathrm{TF}}\, Z^{7/3} - C\, \mu^2\, Z^{7/3+\delta} - C\, Z^{7/3-\epsilon_1}\,. \tag{16}$$

On the other hand, if we denote by Ψ any ground state of the atom, we use it as a trial function to conclude that

$$E_\mu(Z) \leq E(Z) + 2\, \mu\, Z^{4/3}\, \langle \mathbf{S}_\chi\, \Psi, \Psi \rangle\,.$$

If we now use as trial function the same Ψ, but with spins reversed, we obtain

$$E_\mu(Z) \leq E(Z) - 2\, \mu\, Z^{4/3}\, \langle \mathbf{S}_\chi\, \Psi, \Psi \rangle\,.$$

Altogether, we obtain

$$E_\mu(Z) \leq E(Z) - 2\, |\mu|\, Z^{4/3}\, |\langle \mathbf{S}_\chi\, \Psi, \Psi \rangle|\,.$$

Since

$$E(Z) = c_{\mathrm{TF}}\, Z^{7/3} + O(Z^2)\,,$$

we conclude that

$$E_\mu(Z) \le c_{\rm TF}\, Z^{7/3} - 2|\mu|\, Z^{4/3}\, |\langle \mathrm{S}_\chi\, \Psi, \Psi\rangle| + O(Z^2)\ .$$

Putting this together with (16), we obtain

$$|\mu|\, \frac{|\langle \mathrm{S}_\chi\, \Psi, \Psi\rangle|}{Z} \le C\, Z^\delta\, |\mu|^2 + C\, Z^{-\varepsilon_1}\,, \qquad |\mu| \le c_1\, Z^{-4\delta}\,.$$

If we choose now

$$|\mu| = c_1\, Z^{-4\delta}\,,$$

we obtain

$$\frac{|\langle \mathrm{S}_\chi\, \Psi, \Psi\rangle|}{Z} \le C\, Z^{-3\delta} + C\, Z^{-\varepsilon_1 + 4\delta}\,. \tag{17}$$

Finally, we have

$$|\langle \mathrm{S}_{1-\chi}\, \Psi, \Psi\rangle| \le N - \int \rho_\Psi(r)\, \chi(r)\, dr\,. \tag{18}$$

Since

$$\left| Z - \int \rho_{\rm TF}^Z(r)\, \chi(r)\, dr \right| \le C\, Z^{1-3\delta}\,,$$

we use (5.b) with $b = 2/3$ to conclude that

$$\begin{aligned} \left| N - \int \rho_\Psi(r)\, \chi(r)\, dr \right| &\le |Z - N_c| + C\, Z^{1-3\delta} + C\, Z^{(4/3+\delta)/2} \\ &\le C\, Z^{5/7} + C\, Z^{1-3\delta} + C\, Z^{(4/3+\delta)/2}\,. \end{aligned}$$

By (18), we conclude that

$$|\langle \mathrm{S}_{1-\chi} \Psi, \Psi\rangle| \le C\, Z^{5/7} + C\, Z^{1-3\delta} + C\, Z^{(4/3+\delta)/2}\,.$$

With $\varepsilon_1 = 1/6$, we choose $\delta = 1/42$ here and in (17) to conclude Theorem 3 with $\gamma = 13/14$.

Our proof of theorem 3 with $\gamma = 13/14$ was kept simple because we used a form of spectral asymptotics in Lemma 2 which is not very involved. If we used the sharper version given by Theorem 6 below, and the sharper atomic energy asymptotics in (4), then we would obtain, with the same arguments, a bound with $\gamma = 5/7$. But we would also

drive the careful reader into the pain and suffering involved in reading the contents of [FS 2-8], which contains the proof of Theorem 6 below and (4). It is interesting to point out that the bound such analysis would yield, $\gamma = 5/7$, is the same as the bound we know for electric neutrality. And this is not because spin neutrality used electric neutrality: if we imposed electric neutrality to our atoms, by studying $H_{Z,Z}$ instead, we would obtain the same exponent.

We end by stating the theorem, proved in [FS5], which we mentioned above. Our potential W is easily checked to satisfy hypothesis (1), (2) and (3) below.

Theorem 6. *Suppose $W(r)$ is defined on $(0,\infty)$ and satisfies the following conditions:*

$$(1) \qquad \left|\left(\frac{d}{dr}\right)^{\alpha} W(r)\right| \leq C_\alpha \, \mathcal{S}(r)\, r^{-\alpha},$$

for all $r \in (0,\infty)$, $\alpha \geq 0$,

$$(2) \qquad \left|\left(\frac{d}{dr}\right)^{\alpha} \left(W(r) - V_{\mathrm{TF}}^{Z}(r)\right)\right| \leq c_0 \, \mathcal{S}(r)\, r^{-\alpha},$$

for all $r \in (0,\infty)$, $\alpha = 0,1,2$, with $c_0 > 0$ determined by the C_α in (1),

$$(3) \qquad \left|\left(\frac{d}{dr}\right)^{\alpha} \left(E_0 - \frac{Z}{r} + W(r)\right)\right| \leq C_\alpha \, Z^{3/2}\, r^{1/2-\alpha},$$

for all $r \in (0, 2\,Z^{-3/5+2\varepsilon})$, $\alpha \geq 0$, with $c\,Z^{4/3} < E_0 < C\,Z^{4/3}$ and $0 < \varepsilon < 10^{-12}$.

Set Ω equal to the positive root of $\Omega(\Omega+1) = \max_{r>0} r^2\, W(r)$,

$$\left.\begin{aligned} \eta_l &= \frac{1}{\pi}\int_0^\infty \left(W(r) - \frac{l(l+1)}{r^2}\right)_+^{-1/2} dr \\ \phi_l &= \frac{1}{\pi}\int_0^\infty \left(W(r) - \frac{l(l+1)}{r^2}\right)_+^{1/2} dr \end{aligned}\right\} \qquad (1 \leq l \leq \Omega).$$

Then,

$$\begin{aligned} \operatorname{sneg}\left(-\Delta + W(|x|)\right) = &-\frac{1}{15\,\pi^2}\int_{\mathbb{R}^3} W^{5/3}(|x|)\, dx + \frac{Z^2}{8} \\ &- \frac{1}{48\,\pi^2}\int_{\mathbb{R}^3} W^{1/2}(|x|)\, \Delta W(|x|)\, dx \\ &+ \sum_{Z^{8/25+10\varepsilon} < l < \Omega} \frac{2l+1}{\eta_l}\mu(\phi_l) + \text{Error}, \end{aligned}$$

with $|\text{Error}| \leq C' Z^{8/5+2\cdot 10^{-9}}$ *and* $\mu(t)$ *denotes the fractional part of* t. *The constant* C' *depends only on* C_α, c_0, C *and* ε *in* (1), (2) *and* (3). *Furthermore, the last sum is easily seen to be bounded by* $C\, Z^{5/3}$.

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