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Approximate Neutrality of Large-Z Ions*

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Abstract. Let $N(Z)$ denote the number of electrons which a nucleus of charge Z can bind in non-relativistic quantum mechanics (assuming that electrons are fermions). We prove that $N(Z)/Z \to 1$ as $Z \to \infty$.

1. Introduction

This paper is a contribution to the exact study of Coulombic binding energies in quantum mechanics. Let $H(N,Z)$ denote the Hamiltonian

$$H(N,Z) = \sum_{i=1}^{N} (-\Delta_i - Z|x_i|^{-1}) + \sum_{i<j} |x_i - x_j|^{-1},$$

and let $E(N,Z)$ denote its minimum over all fermion states (we suppose there are two spin states allowed, although any fixed number could be accommodated). For comparison purpose, we let $E_b(N,Z)$ denote the same minimum, but over all states (taken on a totally symmetric wave function, hence b for boson).

It is a fundamental result of Ruskai [9] for bosons, and Sigal [11] for fermions (see also Ruskai [10]) that there exists $N(Z), N_b(Z)$ so that, for all $j = 0, 1, \ldots,$

$$E(N(Z),Z) = E(N(Z)+j,Z); \quad E_b(N_b(Z),Z) = E_b(N_b(Z)+j,Z).$$

We let $N(Z)$ (respectively $N_b(Z)$) denote the smallest number for which the first (respectively second) equality holds for all j. Sigal [12] showed that

$$\overline{\lim}[N(Z)/Z] \leqq 2, \quad \lim[\ln N_b(Z)/\ln Z] \leqq 1, \tag{1.1}$$

and then Lieb [6, 7] proved the bounds

$$N(Z) < 2Z + 1, \quad N_b(Z) < 2Z + 1 \tag{1.2}$$

which implies, in particular, that a doubly ionized hydrogen atom is unstable.

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Zhislin [15] proved that $N(Z) \geqq Z$ and $N_b(Z) \geqq Z$. A more detailed review of the history and status of this and related problems is given in [7].

Our main goal in this paper is to show that

Theorem 1.1. $\lim\limits_{Z \to \infty} [N(Z)/Z] = 1.$

That is, asymptotically, the excess charge in negative ions is a small fraction of the total charge. While this is physically reasonable, and partially captures the observed fact that in nature there are no highly negative ions, it is not as "obvious" as it might appear at first. For Benguria and Lieb [1] have shown that

$$\lim N_b(Z)/Z > 1.$$

(They actually prove that lim is at least the critical charge for the Hartree equation which is rigorously known to lie between 1 and 2, and numerically [16] is about 1.2.) Thus, the Pauli principle will enter into our proof of Theorem 1.1.

Part of our argument closely follows that in Sigal [12] (see also Cycon et al. [13]). We differ from Sigal in one critical aspect. He gets a factor of 2 in (1.1) by using the obvious fact that if one has $2Z + 1$ electrons surrounding a nucleus of charge Z, one can always gain classical energy by taking the electron farthest from the nucleus to infinity. We will exploit the fact that if you have $Z(1 + \varepsilon)$ electrons and Z is large, classical energy can be gained by taking *some* electron to infinity. We will prove precisely this fact in Sect. 3. Actually, for technical reasons, we will need a slightly stronger result, also proven there. Unfortunately, our proof of this key classical fact is by contradiction, using a compactness result. Hence our proof is non-constructive, which means that we have no estimates on how large Z has to be for $N(Z)/Z$ to be bounded by $1 + \varepsilon$ for any given ε.

The theorem we prove in Sect. 3 says that, with $N = Z(1 + \varepsilon)$ point electrons, one gains classical energy by taking some electron to infinity. We prove this by appealing to an analogous result for a "fluid" of negative charge: if $\int d\rho(x) \geqq Z(1 + \varepsilon)$, then for some x_0 in $\operatorname{supp} \rho$ one has $Z|x_0|^{-1} - \int |x_0 - y|^{-1} d\rho(y) \geqq 0$. This fact is proven in Sect. 2. It is interesting that our results in quantum potential theory require various results in classical potential theory.

In Sect. 4, we construct a partition of unity in $\mathbb{R}^{3N}$-the result of Sect. 3 is needed only to assure that certain sets over $\mathbb{R}^{3N}$. Given this partition, the actual proof of Theorem 1.1. in Sect. 5 follows Sigal [12]. Section 6 provides some additional remarks.

2. Classical Continuum Theorem

Theorem 2.1. *Let ρ be a nonzero finite (positive) measure on $\mathbb{R}^3$ which is not a point mass at* 0, *and let ϕ_ρ be its potential*, i.e.,

$$\phi_\rho(x) = \int |x - y|^{-1} d\rho(y). \tag{2.1}$$

Then, for any $\varepsilon > 0$, the set of points $x \neq 0$ such that

$$\phi_\rho(x) \geqq (1 - \varepsilon)|x|^{-1} \rho(\mathbb{R}^3) \tag{2.2}$$

has positive ρ measure.

Proof. Let T_ε denote the set of points in $\mathbb{R}^3 \setminus \{0\}$ such that (2.2) holds. Our goal is to show that $\rho(T_\varepsilon) > 0$. First, let us eliminate any possible small point mass at 0 by defining $\tilde{\rho} = \rho - c\delta(x)$. For some $0 \leqq c < 1, \tilde{\rho}(\{0\}) = 0$. Additionally, defining $\tilde{\varepsilon} = \varepsilon\rho(\mathbb{R}^3)/\tilde{\rho}(\mathbb{R}^3)$, one sees that proving the theorem for ε and ρ is equivalent to proving it for $\tilde{\varepsilon}$ and $\tilde{\rho}$ with $(1-\tilde{\varepsilon})\rho(\mathbb{R}^3) > c$. It suffices to assume, therefore, that $\tilde{\varepsilon} = \varepsilon, \tilde{\rho} = \rho$ and $\rho(\{0\}) = 0$, and we shall do so henceforth.

Let B denote the set of $x \neq 0$ for which $\phi_\rho(x) = \infty$. If $\rho(B) > 0$ we are trivially done, so assume $\rho(B) = 0$. Since $\rho(\{0\}) = 0$, this means that ϕ_ρ is finite ρ-a.e. and we can apply Baxter's Theorem 2 [17]. If we define the measure $\mu = (1-\varepsilon)\{\int d\rho\}\delta(x)$, this theorem asserts the existence of a (positive) measure γ such that

(a) $\gamma \leqq \rho$ and $\gamma(\mathbb{R}^3) \geqq \rho(\mathbb{R}^3) - \mu(\mathbb{R}^3) = \varepsilon \int d\rho > 0$,
(b) $\phi_\rho(x) = \phi_\gamma(x) + \phi_\mu(x)$ γ.a.e..

(In Baxter's notation, $\rho = \nu, \rho - \gamma = \lambda$ and $\mu = \mu$.) Thus, $\rho(T_\varepsilon) \geqq \gamma(T_\varepsilon) = \gamma(\mathbb{R}^3) > 0$. □

Remark. One can also prove this theorem by appealing to Choquet's theorem [2, 5].

3. Classical-Discrete Theorem

Theorem 3.1. *For any ε, there exists N_0 so that, for all sets $\{\vec{x}_a\}_{a=1}^N$ of $N \geqq N_0$ points, we have*

$$\max_b \left\{ \sum_{a \neq b} \frac{1}{|\vec{x}_a \rightarrow \vec{x}_b|} - \frac{(1-\varepsilon)N}{|\vec{x}_b|} \right\} \geqq 0.$$

Remarks. This is clearly a classical analog of the quantum theorem that we are seeking. It says that if the electron excess over the nuclear charge above Z is more than $\varepsilon(1-\varepsilon)^{-1}Z$, then one gains energy by moving at least one of the electrons off to infinity.

2. Unfortunately, our proof is by contradiction, and therefore non-constructive. The fact that we cannot make our estimates explicit, even in principle, comes from this fact.

Proof. Suppose not. Then, there is $\varepsilon_0 > 0$ and sequences points $\{x_a^{(n)}\}_{a=1}^{N_n}$ with $N_n \rightarrow \infty$ and

$$\sum_{a \neq b} \frac{1}{|x_b^{(n)} - x_a^{(n)}|} < \frac{(1-\varepsilon_0)N_n}{|x_b^{(n)}|} \tag{3.1}$$

for all n and all $1 \leqq b \leqq N_n$.

Equation (3.1) is invariant under rotations and scaling of the x's as well as relabelling. Thus, without loss we can suppose that

$$x_1^{(n)} = (1,0,0) = x_0,$$
$$|x_a^{(n)}| \leqq 1 \quad \text{all} \quad 1 \leqq a \leqq N_n.$$

The measures

$$\rho^{(n)} = N_n^{-1} \sum_{a=1}^{N_n} \delta(x - x_a^{(n)})$$

are probability measures on the unit ball. Thus, by passing to a subsequence if necessary, we can suppose that ρ_n converges in the $C(\mathbb{R}^3)$-weak topology to a probability measure $d\rho$. We will show that $d\rho$ violates Theorem 2.1. If y is a limit point of $x_{i_n}^{(n)}$ and $g(z) = (|z|^2 + M^2)^{-1/2}$, then since g is C^1 with bounded derivatives

$$\lim \int g(x - x_i^{(n)}) d\rho_n(x) = \int g(x - y) d\rho(x).$$

Thus, by (3.1):

$$\int g(x - y) d\rho(x) \leqq (1 - \varepsilon_0)|y|^{-1}.$$

By the monotone convergence theorem, we can take M to zero to obtain

$$\int |x - y|^{-1} d\rho(x) \leqq (1 - \varepsilon)|y|^{-1}. \tag{3.2}$$

We have just proven (3.2) for any y in the limit set of the $\{x_a^{(n)}\}$. Any $y \in \operatorname{supp} \rho$ is such a limit point so (3.2) holds for all $y \in \operatorname{supp} \rho$. Thus we will have a contradiction with Theorem 2.1 if we show that $\rho \neq \delta_0$. But since $x_1^{(n)} = x_0$, we have (3.2) for $y = x_0$, i.e.,

$$\int |x - x_0|^{-1} d\rho(x) \leqq (1 - \varepsilon). \tag{3.3}$$

Since, for $d\rho = \delta_0$, the left side is 1, we can conclude that $d\rho \neq \delta_0$. □

We will actually need an extension of Theorem 3.1 to potentials cut off at short distances, but in a way that may seem unnatural at first. Define

$$G_\alpha(x, y) = \begin{cases} |x - y|^{-1} & \text{if} \quad |x - y| \geqq \alpha|x| \\ \alpha^{-1}|x|^{-1} & \phantom{\text{if}} \quad |x - y| \leqq \alpha|x|. \end{cases} \tag{3.4}$$

For a set of points $\{x_a\}_{a=1}^N$ in $\mathbb{R}^3$, define $|x|_\infty \equiv \sup_a |x_a|$.

Theorem 3.2. *Let $\alpha_N \to 0$ as $N \to \infty$. Then, for any ε, there exists N_0 and $\delta > 0$ so that, for any $N \geqq N_0$ and any set of points $\{x_a\}_{a=1}^N$, there is a point x_a with $|x_a| \geqq \delta|x|_\infty$ and*

$$\sum_{j \neq a} G_{\alpha_N}(x_a, x_j) \geqq \frac{(1 - \varepsilon)N}{|x_a|}. \tag{3.5}$$

Proof. G is defined to be invariant under scaling (which is why we took the cutoff to be $\alpha|x|$, not just α) and rotations. Also, the condition $|x_a| \geqq \delta|x|_\infty$ has the same invariance. Thus, if the result is false, we can find $\varepsilon_0 > 0$, $\delta_N \to 0$ and a sequence with $|x|_\infty = 1$; $x_1^{(n)} = (1, 0, 0)$ so that (3.5) fails. Taking the limit, we get the same contradiction as in the proof of Theorem 3.1. □

4. A Partition of Unity

As noted in Sect. 1, the key element in the proof of Sigal, which we will mimic, is the construction of a partition of unity. Here we will construct such a partition which we will use in the next section. The preliminaries in the last section will be relevant precisely in order to be sure that certain sets cover $\mathbb{R}^{3N}$.

Theorem 4.1. *For all $\varepsilon > 0$, there exists N_0 and $\delta > 0$, and for each $N \geqq N_0$ and each $R > 0$, a family $\{J_a\}_{a=0}^N$ of C^∞ functions on $\mathbb{R}^{3N}$ so that:*

(1) J_0 *is totally symmetric,* $\{J_a\}_{a\neq 0}$ *is symmetric in* $\{x_b\}_{b\neq a}$.
(2) $\sum_a J_a^2 = 1$.
(3) $\operatorname{supp} J_0 \subset \{\{x_a\} \mid |x|_\infty < R\}$.
(4) $\operatorname{supp} J_a \subset \{x \mid |x|_\infty \geqq (1-\varepsilon)R,\ \ |x_a| \geqq (1-2\varepsilon)\delta|x|_\infty$ *and* $\sum_{b\neq a} |x_b - x_a|^{-1} \geqq (1-2\varepsilon)N|x_a|^{-1}\}$.
(5) *For a constant* C, *depending only on* ε, $\sum_a |\nabla J_a|^2 \leqq CN^{1/2}(\ln N)^2 |x|_\infty^{-1} R^{-1}$.

(4.1)

Proof. Without loss, we can take $R=1$ since the result for $R=1$ implies the result for all R by scaling. Moreover, we can prove (4.1) with $|x|_\infty^{-1}$ replaced by $|x|_\infty^{-2}$. For the left-hand side of (4.1) (when $R=1$) is supported in the region where $|x|_\infty \geqq (1-\varepsilon)$, and in that region $|x|_\infty^{-2} \leqq (1-\varepsilon)^{-1}|x|_\infty^{-1}$.

Next, we note that instead of finding J_a's obeying (1)–(5), it suffices to find F_a's obeying (1′), (2′), (3), (4) and (5′):

(2′) $\sum_a F_a^2 \geqq \frac{1}{2}$,

(5′) $\left(\sum_a (\nabla F_a)^2\right) \Big/ \left(\sum_a F_a^2\right) \leqq CN^{1/2}(\ln N)^2 |x|_\infty^{-2}$,

and for any permutation π:

(1′) $F_{\pi(a)}(x_{\pi(1)}, \ldots, x_{\pi(N)}) = F_a(x_1, \ldots, x_N)$.

For if $J_a = F_a \Big/ \left(\sum_a F_a^2\right)^{1/2}$, then J_a has the same symmetry and support properties as F has, and

$$\sum_a (\nabla J_a)^2 \leqq \sum_a (\nabla F_a)2 / \sum F_a^2. \tag{4.2}$$

To understand (4.2), think of $F = (F_0, \ldots, F_N)$ as a function from $\mathbb{R}^{3N}$ to $\mathbb{R}^{N+1}$, in which case J is the "angular" part of F, and (4.2) is a standard inequality on the gradient of the angular part.

Now we concentrate on constructing the F_a's. Let ψ be a C^∞ function on $[0, \infty)$ with

$$\begin{aligned} \psi(y) &= 0 \qquad && y \leqq 1-2\varepsilon \\ &= 1 && y \geqq 1-\varepsilon \\ &\in [0,1] && \text{all } y \end{aligned}$$

and define $\varphi = \psi^2$. Let $\alpha_N \equiv (\ln N)^{-1}$ and choose N_0, δ as given by Theorem 3.2. As a preliminary, take F_0, F_a as follows. These functions are not C^∞, but are continuous and are C^1 off the set $\{x \mid |x_a| = |x_b|$ for some $a \neq b\} \cup \{x \mid |x_a - x_b| = \alpha_N |x_a|$ some $a, b\}$ with discontinuities of the gradients allowed on that set:

$$F_0(x) = 1 - \psi(|x|_\infty),$$

$$F_a(x) = \varphi(|x|_\infty)\varphi(|x_a|/\delta|x_\infty|)\varphi\left(N^{-1}|x_a| \sum_{b\neq a} G_{\alpha_N}(x_a, x_b)\right),$$

where G_α is given by (3.3). The symmetry condition (1) is obvious, and (3) holds since $\varphi(y)=1$ if $y \geqq 1$.

$F_a \neq 0$ implies that $|x|_\infty \geqq 1-2\varepsilon$, $|x_a| \geqq (1-\varepsilon)\delta|x|_\infty$, and

$$\sum_{b \neq a} G_{\alpha_N}(x_a, x_b) \geqq (1-2\varepsilon)N|x_a|^{-1},$$

since $\varphi(y) \neq 0$ implies $|y| \geqq 1-2\varepsilon$. Since $|x-y|^{-1} \geqq G_\alpha(x,y)$, we have proven (4). That leaves the key conditions (5′) and (2′).

For (2′), we use Theorem 3.2. This guarantees us that there is an a where the last two factors in F_a are 1, and so there is an a with $F_a(x)=\varphi(|x|_\infty)$. Since

$$\theta^2+(1-\theta)^2 \geqq \tfrac{1}{2}$$

for all θ, for this a, $F_0(x)^2+F_a(x)^2 \geqq \frac{1}{2}$, proving (2′).

As a preliminary to (5′), we want to note that, for some constant C and all γ:

$$|\varphi'|^2 \leqq \gamma + C\gamma^{-1}|\varphi|^2. \tag{4.3}$$

For

$$|\varphi'|^2 = 4|\psi|^2|\psi'|^2 \leqq \gamma + 4\gamma^{-1}|\psi|^4|\psi'|^4,$$

proving (4.3) with $C=4\|\psi'\|_\infty^4$.

Away from points where $|x_a|=|x_b|$ for some $a \neq b$,

$$\nabla\varphi(|x|_\infty) = \varphi'(|x|_\infty)\nabla|x|_\infty.$$

Since $|x|_\infty$ is some $|x_a|$ and

$$\nabla_a|x_b| = \delta_{ab}x_a/|x_a|,$$

we see that

$$|\nabla\varphi(|x|_\infty)| = \varphi'(|x|_\infty). \tag{4.4}$$

Similarly,

$$\nabla\varphi(|x_a|/\delta|x|_\infty) = \varphi'(|x_a|/\delta|x|_\infty)\left[-\frac{|x_a|}{\delta|x|_\infty^2}\nabla|x|_\infty + \delta^{-1}|x|_\infty^{-1}\nabla|x_a|\right]. \tag{4.5}$$

Finally, if

$$\eta_a = \varphi(N^{-1}|x_a|\sum_{b \neq a} G_{\alpha_N}(x_a, x_b)),$$

then, for $b \neq a$

$$|\nabla_b \eta_a| \leqq \varphi'(N^{-1}|x_a|\sum_{b \neq a} G_{\alpha_N}(x_a, x_b))N^{-1}|x_a|\,|G_{\alpha_N}(x_a, x_b)|^2,$$

since

$$\nabla_b G_\alpha = [G_\alpha^2](x_b - x_a)/|x_b - x_a| \quad \text{or} \quad 0.$$

Recall that $G_\alpha(x,y) \leqq \alpha^{-1}|x|^{-1}$, so since $\alpha_N^{-1} = \ln N$,

$$\sum_{b \neq a}|\nabla_b\eta_a|^2 \leqq \left[\varphi'\left(N^{-1}|x_a|\sum_{b \neq a} G_{\alpha_N}(x_a, x_b)\right)\right]^2 N^{-2}|x_a|^2(\ln N)^3|x_a|^{-3}\sum_{b \neq a} G_{\alpha_N}(x_a, x_b).$$

However, $\operatorname{supp}\varphi' \subset [1-2\varepsilon, 1-\varepsilon]$, so on $\operatorname{supp}\varphi'\left(N^{-1}|x_a|\sum_{b \neq a} G_{\alpha_N}(x_a, x_b)\right)$, we have that

$$\sum_{b\neq a} G_{\alpha_N}(x_a, x_b) \leqq |x_a|^{-1} N.$$

Thus

$$\sum_{b\neq a} |\nabla_b \eta_a|^2 \leqq N^{-1}(\ln N)^3 |x_a|^{-2}\left[\varphi'\left(N^{-1}|x_a|\sum_{b\neq a} G_{\alpha_N}(x_a, x_b)\right)\right]^2. \tag{4.6}$$

As a final gradient estimate,

$$|\nabla_a \eta_a| \leqq \varphi'\left(N^{-1}|x_a|\sum_{b\neq a} G_{\alpha_N}(x_a, x_b)\right)\left[N^{-1}\sum_{b\neq a} G_{\alpha_N}(x_a, x_b) + N^{-1}\sum_{b\neq a}|x_a| G_{\alpha_N}(x_a, x_b)^2\right],$$

since $|\nabla_a |x_a|| = 1$ and

$$|\nabla_a G_\alpha(x_a, x_b)| = G_\alpha(x_a, x_b)^2 \quad \text{or} \quad \alpha G_\alpha(x_a, x_b)^2$$

and $\alpha \leqq 1$. Thus, since $|x_a| \sum_{b\neq a} G_{\alpha_N}(x_a, x_b) \leqq N$ when $\varphi'(\cdot) \neq 0$,

$$|\nabla_a \eta_a| \leqq \varphi'\left(N^{-1}|x_a|\sum_{b\neq a} G_{\alpha_N}(x_a, x_b)\right)(1 + (\ln N))|x_a|^{-1}. \tag{4.7}$$

Since $|x_a| \geqq (1-2\varepsilon)\,\delta |x|_\infty$ on $\operatorname{supp} F_a$, we see that, for $a \neq 0$.

$$\sum_b |\nabla_b F_a|^2 \leqq c_1(\gamma + c_2\gamma^{-1}F_a^2)(\ln N)^2 |x|_\infty^{-2},$$

by using (4.3)–(4.7). Thus

$$\sum_{a,b} |\nabla_b F_a|^2 \leqq c_1\left(\gamma N + c_2\gamma^{-1}\sum_a F_a^2\right)(\ln N)^2 |x|_\infty^{-2} + c_3|x|_\infty^{-2}.$$

Since $\sum F_a^2 \geqq \frac{1}{2}$, we can take $\gamma = N^{-1/2}$ and obtain:

$$\sum_{a,b} |\nabla_b F_a|^2 \leqq c_4 N^{1/2}(\ln N)^2 |x|_\infty^{-2} \sum_a F_a^2,$$

as required.

The J's constructed in this way are continuous but are only piecewise C^1. By convoluting with a smooth, totally symmetric function of very small support, we can arrange for C^∞ J's which still obey the required properties. □

Remark. By using $\varphi = \psi^m$ in the above construction for m suitable, we can reduce $N^{1/2}$ to any desired positive power of N.

5. The Main Theorem

Here we will prove Theorem 1.1. Given the construction in the last section, this follows Sigal [12] fairly closely. Pick $\varepsilon > 0$. We shall prove $\overline{\lim}\, N(Z)/Z \leqq (1-3\varepsilon)^{-1}$.

Let $\{J_a\}$ be as in Theorem 4.1, and let

$$L = \sum_{a=0}^{N} |\nabla J_a|^2.$$

By the IMS localization formula (see Chap. 3 of [3]),

$$H = \sum_{a=0}^{N} J_a H J_a - L = \sum_{a=0}^{N} J_a (H - L) J_a. \tag{5.1}$$

By condition (5) of Theorem 4.1,

$$L \leqq C N^{1/2} (\ln N)^2 |x|_\infty^{-1} R^{-1}.$$

For $a > 0$, $\operatorname{supp} J_a \subset \{x \,|\, |x_a| \geqq (1-2\varepsilon)\delta |x|_\infty\}$, and thus:

$$J_a L J_a \leqq c_1 N^{1/2} (\ln N)^2 |x_a|^{-1} R^{-1} \quad (C_1 = c\delta^{-1}(1-2\varepsilon)^{-1}). \tag{5.2}$$

Since $\cup \operatorname{supp}(\nabla J_a) \subset \{x \,|\, |x|_\infty \geqq (1-2\varepsilon) R\}$:

$$J_0 L J_0 \leqq c_2 N^{1/2} (\ln N)^2 R^{-2} \quad (c_2 = (1-2\varepsilon)^{-1} C) \tag{5.3}$$

Let $H_a(N-1, Z)$ be the $(N-1)$ electron Hamiltonian obtained by removing from $H(N, Z)$ all terms involving x_a, so:

$$H(N, Z) = H_a(N-1, Z) - \Delta_a - |x_a|^{-1} Z + \sum_{b \neq a} |x_b - x_a|^{-1}.$$

Since $H_a(N-1, Z) \geqq E(N-1, Z)$ and $-\Delta_a \geqq 0$, taking into account (5.2) and the support property of J_a, we have that

$$J_a (H(N, Z) - L) J_a \geqq J_a [E(N-1, Z) + |x_a|^{-1} d(Z, N, R)] J_a, \tag{5.4a}$$

where

$$d(Z, N, R) = -Z - c_1 N^{1/2} (\ln N)^2 R^{-1} + (1-2\varepsilon) N. \tag{5.4b}$$

R_N has not been introduced up to now.

By solving for a Bohr atom (and this is where the Pauli principle enters):

$$\sum_{i=1}^{N} (-\Delta_i - Z|x_i|^{-1}) \geqq -c_3 Z^2 N^{1/3},$$

so since $|x_a - x_b| \leqq 2R$ on $\operatorname{supp} J_0$:

$$J_0 (H(N, Z) - L) J_0 \geqq J_0 [-c_3 Z^2 N^{1/3} - c_2 N^{1/2} (\ln N)^2 R^{-2} + \tfrac{1}{4} R^{-1} N(N-1)] J_0. \tag{5.5}$$

Choose $R = N^{-2/5}$. Then, for $N \geqq (1-3\varepsilon)^{-1} Z$ and large Z, $d(Z, N, R) > 0$ since $\frac{1}{2} + \frac{2}{5} < 1$. Moreover, $J_0 (H(N, Z) - L) J_0 \geqq 0 \geqq J_0 E(N-1, Z) J_0$ since $N^{12/5}$ dominats $N^{7/3}$ and $N^{13/10} (\ln N)^2$ and $E(N-1, Z) \leqq 0$.

Thus,

$$H(H, Z) \geqq E(N-1, Z)$$

if $N \geqq (1-3\varepsilon)^{-1} Z$ and Z is large, i.e., for Z large

$$N(Z) \leqq (1-3\varepsilon)^{-1} Z.$$

Since ε is arbitrary:

$$\overline{\lim}\, N(Z)/Z \leqq 1.$$

It is well known (see [15, 13]) that $H(Z,Z)$ has bound states, i.e., that $N(Z) \geqq Z$. $\square$

Remark. Without the Pauli principle, $Z^2 N^{1/3}$ becomes $Z^2 N$, so one must take $R_N = cN^{-1}$, in which case the localization term $N^{1/2}(\ln N)^2 R_N^{-1}$ in (5.4b) becomes uncontrollable. Our proof must, of course, fail without the Pauli principle because of the result in [1].

6. Extensions

Our result extends easily to accommodate arbitrary magnetic fields (the same for all electrons) and/or a finite nuclear mass.

The exact form of the electron kinetic energy entered only in two places: in the IMS localization formula and in the positivity of $-\Delta$, both of which hold in an arbitrary magnetic field. We also used the Bohr atom binding energy, but that only decreases in a magnetic field (i.e., $-c_3 N^2 Z^{1/3}$ is a lower bound for all fields). Thus, we obtain a magnetic field independent bound $\tilde{N}(Z)$ with

$$\tilde{N}(Z)/Z \to 1 \quad \text{as} \quad Z \to \infty.$$

As for finite nuclear mass, let x_0 be the nuclear coordinate, and use $J_a(x_b - x_0)$ in place of $J_a(x_b)$. With this change, the nuclear coordinates pass through all proofs with essentially no change at all.

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