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On the maximal ionization of atoms in strong magnetic fields

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Abstract

We give upper bounds for the number of spin-$\frac{1}{2}$ particles that can be bound to a nucleus of charge Z in the presence of a magnetic field $\boldsymbol{B}$, including the spin–field coupling. We use Lieb's strategy, which is known to yield $N_c < 2Z + 1$ for magnetic fields that go to zero at infinity, ignoring the spin–field interaction. For particles with fermionic statistics in a homogeneous magnetic field our upper bound has an additional term of the order of $Z \times \min\left\{(B/Z^3)^{2/5}, 1 + |\ln(B/Z^3)|^2\right\}$.

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1. Introduction and main result

Let $H_{N,Z,\boldsymbol{A}}$ be the Hamiltonian for N identical particles with spin-$\frac{1}{2}$ in the Coulomb field of an infinitely massive nucleus of charge Z and in a magnetic field $\boldsymbol{B} = \operatorname{curl} \boldsymbol{A}$,

$$H_{N,Z,\boldsymbol{A}} = \sum_{i=1}^{N} \left(H_{\boldsymbol{A}}^{(i)} - \frac{Z}{|\boldsymbol{x}_i|} \right) + \sum_{i<j} \frac{1}{|\boldsymbol{x}_i - \boldsymbol{x}_j|} \tag{1}$$

with

$$H_{\boldsymbol{A}}^{(j)} = \left[\boldsymbol{\sigma}_j \cdot \left(-\mathrm{i}\nabla_j + \boldsymbol{A}(\boldsymbol{x}_j)\right)\right]^2 = \left(-\mathrm{i}\nabla_j + \boldsymbol{A}(\boldsymbol{x}_j)\right)^2 + \boldsymbol{B} \cdot \boldsymbol{\sigma}_j. \tag{2}$$

Here $\boldsymbol{A} \in \mathcal{L}^2_{\mathrm{loc}}(\mathbb{R}^3; \mathbb{R}^3)$ is the magnetic potential and $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ are the usual Pauli matrices. The Hamiltonian (1) acts on the fermionic (respectively bosonic) subspace of $\bigotimes^N \mathcal{L}^2(\mathbb{R}^3, \mathrm{d}\boldsymbol{x}; \mathbb{C}^2)$. We will assume that the ground state energy

$$E(N, Z, \boldsymbol{B}) = \inf \operatorname{spec} H_{N,Z,\boldsymbol{A}} \tag{3}$$

is finite. (Note that the energy depends only on $\boldsymbol{B}$ because of gauge invariance.) A sufficient condition for this is $\boldsymbol{B} \in \mathcal{L}^{3/2} + \mathcal{L}^\infty$, because is this case $|\boldsymbol{B}| + Z/|\boldsymbol{x}|$ is relatively bounded with respect to $-\Delta$, and $\inf \operatorname{spec} H_{N,Z,\boldsymbol{A}} \geqslant \inf \operatorname{spec} \sum_{i=1}^{N} (-\Delta_i - |\boldsymbol{B}(\boldsymbol{x}_i)| - Z/|\boldsymbol{x}_i|)$ by the diamagnetic inequality [1]. Moreover, we will only consider magnetic fields $\boldsymbol{B}$ such that the energy $E(N, Z, \boldsymbol{B})$ is *monotonically decreasing* in N for fixed Z. That is, we consider fields such that we can add additional particles to spatial infinity with arbitrary small magnetic–kinetic energy. This is in particular the case for a homogeneous magnetic field [2]. We are interested in the maximal number of particles that can be bound, i.e. the largest N such that $E(N, Z, \boldsymbol{B})$ is an eigenvalue. We will denote this 'critical' N by N_c, suppressing the dependence on Z and $\boldsymbol{B}$. For simplicity we will restrict ourselves to considering identical particles.

Alternatively, one could define the critical particle number by

$$\widetilde{N}_c = \max\{N | E(N, Z, \boldsymbol{B}) < E(N-1, Z, \boldsymbol{B})\}. \tag{4}$$

With this definition $E(N, Z, \boldsymbol{B})$ is certainly an eigenvalue if $N \leqslant \widetilde{N}_c$, so $\widetilde{N}_c \leqslant N_c$. Hence any upper bound to N_c is also an upper bound to $\widetilde{N}_c$.

It is well known that magnetic fields, at least homogeneous ones, enhance binding. In [3] it is shown that every once negatively charged ion (i.e. $N = Z + 1$) has an infinite number of bound states in the presence of a homogeneous magnetic field of arbitrary field strength B. And in [2] the lower bound $\liminf_{Z\to\infty}(\widetilde{N}_c/Z) \geqslant 2$ as long as $B/Z^3 \to \infty$ is given, which is in contrast to asymptotic neutrality in the absence of magnetic fields [4].

We will use Lieb's strategy [5] to derive an upper bound on N_c. The difference between our considerations and [5] is the coupling of the spin to the magnetic field, i.e. the term $\boldsymbol{B} \cdot \boldsymbol{\sigma}$ in the Hamiltonian. Without this term, Lieb derived the bound $N_c < 2Z + 1$ for any bounded $\boldsymbol{A}$ that goes to zero at infinity. (The reason why Lieb's bound does not apply to a homogeneous magnetic field is that without spin coupling, the ground state energy in this case is not monotonically decreasing in N since adding a particle at spatial infinity costs at least an energy $|\boldsymbol{B}|$.)

Our result is as follows:

Theorem 1 (Upper bound on N_c). *Under the conditions stated above,*

$$N_c < 2Z + 1 + \frac{1}{2}\frac{E(N_c, Z, \boldsymbol{B}) - E(N_c, kZ, \boldsymbol{B})}{N_c Z(k-1)} \tag{5}$$

for all values of $k > 1$.

Note that since the ground state energy is monotonically decreasing and superadditive in N for fixed Z (because the Coulomb repulsion between the particles is positive), $E(N, Z, \boldsymbol{B})/N$ is bounded by some function independent of N. Moreover, the best bound in (5) is achieved in the limit $k \searrow 1$, which exists since $E(N, Z, \boldsymbol{B})$ is concave in Z (as an infimum over linear functions in Z).

To apply theorem 1 to the case of fermionic electrons in a homogeneous magnetic field $\boldsymbol{B} = (0, 0, B)$, one needs upper and lower bounds to the ground state energy. These were derived in [2, 6] and are given in section 4.1. The result is the following:

Theorem 2 (Maximal ionization for fermions). *Let $H_{N,Z,\boldsymbol{A}}$ be the restriction of (1) to the fermionic subspace, and let $\boldsymbol{B} = (0, 0, B)$. Then, for some constants C_1 and C_2, and for all values of $B \geqslant 0$ and $Z > 0$,*

$$N_c < 2Z + 1 + C_1 Z^{1/3} + C_2 Z \min\left\{(B/Z^3)^{2/5}, 1 + |\ln(B/Z^3)|^2\right\}. \tag{6}$$

Of course we do not believe that these bounds are optimal. One might assume that Lieb's bound $N_c < 2Z+1$ also holds in this case, at least for large Z (compare with the lower bound in [2] stated above), but it remains an open problem to show this. However, theorem 2 improves a result obtained in [7], which states that $N_c < 2Z + 1 + cB^{1/2}$ for the Hamiltonian (1) restricted to some special wavefunctions in the lowest Landau band, which reduces the problem to an essentially one-dimensional one.

One might ask how the Pauli principle affects the result in theorem 2. It turns out that the analogue for bosonic particles is the following:

Theorem 3 (Maximal ionization for bosons). *Let $H_{N,Z,\boldsymbol{A}}$ be the restriction of (1) to the bosonic subspace, and let $\boldsymbol{B} = (0, 0, B)$. Then for some constant C_3 and for all $B \geqslant 0$ and $Z > 0$*

$$N_c < 2Z + 1 + \frac{Z}{2} \min\left\{\left(1 + \frac{B}{Z^2}\right), C_3\left(1 + \left[\ln\left(\frac{B}{Z^2}\right)\right]^2\right)\right\}. \tag{7}$$

In the next section we will give the proof of theorem 1. In section 3 several possible generalizations are stated, and in section 4 the necessary energy bounds for the case of a homogeneous magnetic field are given, which will prove theorems 2 and 3.

2. Proof of theorem 1

Let Ψ be a normalized ground state for $H_{N,Z,\boldsymbol{A}}$. Assume, for the moment, that $\langle\Psi||\boldsymbol{x}_N|\Psi\rangle$ is finite. Then

$$E(N, Z, \boldsymbol{B})\langle|\boldsymbol{x}_N|\Psi|\Psi\rangle = \langle|\boldsymbol{x}_N|\Psi|H_{N,Z,\boldsymbol{A}}\Psi\rangle$$
$$= \left\langle|\boldsymbol{x}_N|\Psi|\left(H_{N-1,Z,\boldsymbol{A}} + H_{\boldsymbol{A}}^{(N)} - \frac{Z}{|\boldsymbol{x}_N|} + \sum_{i=1}^{N-1}\frac{1}{|\boldsymbol{x}_i - \boldsymbol{x}_N|}\right)\Psi\right\rangle. \tag{8}$$

Because $\Gamma = \int \Psi^*\Psi|\boldsymbol{x}_N|\,\mathrm{d}\boldsymbol{x}_N$ is an acceptable trial density matrix, we can use the variational principle to conclude that

$$\langle|\boldsymbol{x}_N|\Psi|H_{N-1,Z,\boldsymbol{A}}|\Psi\rangle \geqslant E(N-1, Z, \boldsymbol{B})\langle|\boldsymbol{x}_N|\Psi|\Psi\rangle. \tag{9}$$

By assumption the energy is monotonically decreasing in N, so

$$\left\langle|\boldsymbol{x}_N|\Psi|\left(H_{\boldsymbol{A}}^{(N)} - \frac{Z}{|\boldsymbol{x}_N|} + \sum_{i=1}^{N-1}\frac{1}{|\boldsymbol{x}_i - \boldsymbol{x}_N|}\right)\Psi\right\rangle$$
$$\leqslant (E(N, Z, \boldsymbol{B}) - E(N-1, Z, \boldsymbol{B}))\langle|\boldsymbol{x}_N|\Psi|\Psi\rangle \leqslant 0. \tag{10}$$

Now using the demanded symmetry of Ψ, we obtain

$$\left\langle\Psi|\frac{|\boldsymbol{x}_N|}{|\boldsymbol{x}_i - \boldsymbol{x}_N|}\Psi\right\rangle = \frac{1}{2}\left\langle\Psi|\frac{|\boldsymbol{x}_N| + |\boldsymbol{x}_i|}{|\boldsymbol{x}_i - \boldsymbol{x}_N|}\Psi\right\rangle > \frac{1}{2} \tag{11}$$

(the strict inequality follows from the fact that $\{(\boldsymbol{x}, \boldsymbol{y}), |\boldsymbol{x} - \boldsymbol{y}| = |\boldsymbol{x}| + |\boldsymbol{y}|\}$ has measure zero), so (10) gives

$$Z > \tfrac{1}{2}(N-1) + \langle|\boldsymbol{x}_N|\Psi|H_{\boldsymbol{A}}^{(N)}|\Psi\rangle. \tag{12}$$

As in [7] we have for any positive function $\varphi(\boldsymbol{x}_N)$

$$\langle\varphi\Psi|H_{\boldsymbol{A}}^{(N)}|\Psi\rangle = \left\langle\varphi^{1/2}\Psi|\left(H_{\boldsymbol{A}}^{(N)} - \left|\frac{\nabla\varphi}{2\varphi}\right|^2\right)\varphi^{1/2}\Psi\right\rangle$$
$$-\mathrm{i}\,\mathrm{Re}\left\langle\varphi^{1/2}\Psi|\frac{\nabla\varphi}{\varphi}\cdot(-\mathrm{i}\nabla + \boldsymbol{A})\varphi^{1/2}\Psi\right\rangle. \tag{13}$$

Now $\langle|\boldsymbol{x}_N|\Psi|H_{\boldsymbol{A}}^{(N)}\Psi\rangle$ is certainly real, because all the other quantities in equation (8) are real. So choosing $\varphi(\boldsymbol{x}_N) = |\boldsymbol{x}_N|$ in equation (13) we obtain

$$\langle|\boldsymbol{x}_N|\Psi|H_{\boldsymbol{A}}^{(N)}\Psi\rangle = \left\langle|\boldsymbol{x}_N|^{1/2}\Psi|\left(H_{\boldsymbol{A}}^{(N)} - \frac{1}{4|\boldsymbol{x}_N|^2}\right)|\boldsymbol{x}_N|^{1/2}\Psi\right\rangle. \tag{14}$$

Using that $H_{\boldsymbol{A}}^{(N)} \geqslant 0$ equation (12) reads

$$N < 2Z + 1 + \tfrac{1}{2}\langle\Psi||\boldsymbol{x}_N|^{-1}\Psi\rangle. \tag{15}$$

Moreover,

$$\begin{aligned}\langle\Psi||\boldsymbol{x}_N|^{-1}\Psi\rangle(k-1) &= \frac{1}{NZ}\langle\Psi|(H_{N,Z,\boldsymbol{A}} - H_{N,kZ,\boldsymbol{A}})\Psi\rangle \\ &\leqslant \frac{1}{NZ}\left(E(N,Z,\boldsymbol{B}) - E(N,kZ,\boldsymbol{B})\right)\end{aligned} \tag{16}$$

so we arrive at the desired bound for N_c.

Throughout, we have assumed that $\langle|\boldsymbol{x}_N|\Psi|\Psi\rangle$ is finite. *A priori*, this need not be the case. However, one could arrive at the same conclusions using the bounded function $\varphi_\varepsilon(\boldsymbol{x}_N) = |\boldsymbol{x}_N|(1+\varepsilon|\boldsymbol{x}_N|)^{-1}$ instead of $|\boldsymbol{x}_N|$ in (8), and letting $\varepsilon \to 0$ at the end (see [5]). Note that

$$\left|\frac{\nabla\varphi_\varepsilon}{\varphi_\varepsilon}\right|^2 = \frac{1}{|\boldsymbol{x}|^2(1+\varepsilon|\boldsymbol{x}|)^2} \leqslant \frac{1}{|\boldsymbol{x}|\varphi_\varepsilon(\boldsymbol{x})} \tag{17}$$

so our conclusions remain valid.

Remark 1. Instead of ignoring the kinetic energy in (14) one could use the operator inequality

$$(-\mathrm{i}\nabla + \boldsymbol{A})^2 - \frac{1}{4|\boldsymbol{x}|^2} \geqslant 0 \tag{18}$$

to conclude that

$$N_c < 2Z + 1 - 2\langle\Psi||\boldsymbol{x}_N|\boldsymbol{B}(\boldsymbol{x}_N)\cdot\boldsymbol{\sigma}_N\Psi\rangle. \tag{19}$$

This may especially be of interest if $|\boldsymbol{B}(\boldsymbol{x})| \leqslant b|\boldsymbol{x}|^{-1}$ for some constant b. And for $\boldsymbol{B} = \boldsymbol{0}$ Lieb's bound $N_c < 2Z + 1$ is reproduced.

3. Generalizations of theorem 1

As in [5] several generalizations of theorem 1 are possible.

- One can allow different statistics from the bosonic or fermionic one, or even consider independent particles. Moreover, the particles could have different masses and charges.
- Hartree and Hartree–Fock theories can be treated in the same manner.
- One can replace the Coulomb interaction (everywhere) by some positive $v(\boldsymbol{x}) = 1/w(\boldsymbol{x})$, with w satisfying

$$w(\boldsymbol{x} - \boldsymbol{y}) \leqslant w(\boldsymbol{x}) + w(\boldsymbol{y}) \tag{20}$$

and for some constant C

$$|\nabla w|^2 \leqslant C. \tag{21}$$

Looking at the proof of theorem 1 we see that these two properties are really what we needed.

4. Application to homogeneous fields

We will now apply theorem 1 to the case of a homogeneous magnetic field $\boldsymbol{B} = (0, 0, B)$, and prove theorems 2 and 3. The magnetic potential, in the symmetric gauge, is given by $\boldsymbol{A} = \frac{1}{2}\boldsymbol{B} \times \boldsymbol{x}$. The energy in this case will be denoted by $E(N, Z, B) \equiv E(N, Z, \boldsymbol{B})$. To derive explicit bounds on N_c, we need upper and lower bounds to the ground state energy of (1). However, since we are not trying to give the optimal constants, the upper bound $E(N, Z, B) \leqslant 0$ will suffice for our purposes. So we will concentrate on the lower bounds. We will distinguish between the fermionic and the bosonic case. Throughout, every fixed constant will be denoted by C, although the various constants may be different.

4.1. The fermionic case

In [2, 6] the following lower bounds on the ground state energy of (1) were derived:

Lemma 1 (Lower bounds on the fermionic energy). *Let $\lambda = N/Z$. The ground state energy of (1) restricted to the fermionic subspace satisfies:*

(a) If $B \leqslant CZ^{4/3}$ then

$$E(N, Z, B) \geqslant -CZ^{7/3}\lambda^{1/3}\left(1 + C\lambda^{2/3}\right). \tag{22}$$

(b) If $B \geqslant CZ^{4/3}$ then

$$E(N, Z, B) \geqslant -CZ^{9/5}\lambda^{3/5}B^{2/5}\left(1 + C\lambda^{-2/5}\right). \tag{23}$$

(c) If $B \geqslant CZ^2$ then

$$E(N, Z, B) \geqslant -CNZ^2\left(1 + \left[\ln\left(\frac{C}{\lambda^{1/2}}\left(\frac{B}{Z^3}\right)^{1/2} + 1\right)\right]^2\right). \tag{24}$$

Remark 2. The conditions in (a) and (b) are not meant to be complementary. The precise meaning of part (a) of the lemma, for instance, is that given a constant C_1, $E(N, Z, B) \geqslant -C_2Z^{7/3}\lambda^{1/3}(1 + C_3\lambda^{2/3})$ for some constants C_2 and C_3 (depending on C_1) as long as $B \leqslant C_1Z^{4/3}$.

Remark 3. Part (c) of lemma 1 follows from omitting the repulsion terms in theorem 1.2 ('confinement to the lowest Landau band') in [2] and then using the bound (4.11) there. Although this theorem is applicable for $B \geqslant CZ^{4/3}$, with an additional error term, the result is simpler for $B \geqslant CZ^2$. However, the bound (24) is only of interest for $B \geqslant CZ^3$, because for smaller B (23) is more useful.

Using (5) with $k = C > 1$ and the bounds in the preceding lemma we find that $\lambda_c \equiv N_c/Z$ satisfies

$$\begin{aligned}
&\lambda_c < 2 + Z^{-1} + C\lambda_c^{-2/3}Z^{-2/3}\left(1 + C\lambda_c^{2/3}\right) && \text{if} \quad B \leqslant CZ^{4/3} \\
&\lambda_c < 2 + Z^{-1} + C\lambda_c^{-2/5}\left(\frac{B}{Z^3}\right)^{2/5}\left(1 + C\lambda_c^{-2/5}\right) && \text{if} \quad B \geqslant CZ^{4/3} \\
&\lambda_c < 2 + Z^{-1} + C\left(1 + \left[\ln\left(\frac{C}{\lambda_c^{1/2}}\left(\frac{B}{Z^3}\right)^{1/2} + 1\right)\right]^2\right) && \text{if} \quad B \geqslant CZ^2.
\end{aligned} \tag{25}$$

Using $\lambda_c \geqslant 1$ (which we can of course assume, since otherwise (6) is trivial) and $\ln(x+1) \leqslant |\ln x| + 1$ for $x > 0$ on the right-hand side of (25) these three bounds imply the result stated in theorem 2. Note that in particular

$$\limsup_{Z\to\infty} \frac{N_c}{Z} \leqslant 2 \qquad \text{if} \quad B/Z^3 \to 0. \tag{26}$$

4.2. The bosonic case

To obtain a lower bound on the bosonic energy we will first omit the positive repulsion terms in (1). By scaling the variables $\boldsymbol{x}_i \to Z^{-1}\boldsymbol{x}_i$ we see that

$$E(N, Z, B) \geqslant NZ^2 e(B/Z^2) \tag{27}$$

where $e(b)$ is the ground state energy of hydrogen in a homogeneous magnetic field of strength b. For small b, we will use the diamagnetic inequality [1], which implies

$$e(b) \geqslant -\tfrac{1}{4} - b. \tag{28}$$

A large-b expansion of $e(b)$ is given in [3]. From there we obtain the following lower bound:

Lemma 2 (Lower bound for the hydrogen energy). *For large enough b the ground state energy of hydrogen, e(b), satisfies*

$$e(b) \geqslant -\tfrac{1}{4}(\ln b)^2 \left(1 + \frac{C}{\ln b}\right). \tag{29}$$

Note that the bosonic energy is at least of the order of NZ^2, even for small B. Therefore, the contribution to (5) is always at least $\mathrm{O}(Z)$, in contrast to fermions, where the energy is of the order of $N^{1/3}Z^2$ for small B (this is the reason for the additional factor of $Z^{1/3}$ in (6)). Setting $k = 2$ we arrive at the bound given in theorem 3.

We note that since the bosonic energy is always less than the fermionic energy, theorem 3 also holds for fermions; but the bound stated there is certainly worse than that given in theorem 2.

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