NEW BOUNDS ON THE EXCESS CHARGE FOR ATOMIC SYSTEMS

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ABSTRACT. In this manuscript, using a technique introduced by P. T. Nam in 2012 and the Coulomb Uncertainty Principle, we prove new bounds on the excess charge for non relativistic atomic systems, independent of the particle statistics. These new bounds are the best bounds to date for bosonic systems for all values of the atomic number $Z$ and they are also the best bounds for fermionic systems with $Z \leq 26$ (i.e., up to the chemical element iron)

MSC2020–Mathematics Subject Classification System: 81V73, 81V45, 35A15, 35A01.

Keywords. Ionization, Atoms, Coulomb Uncertainty Principle

1. INTRODUCTION

Since the beginning of Quantum Mechanics there has been interest in determining the existence of anions, i.e., negative ions. After the introduction of the Schrödinger equation in 1926, Hans Bethe was the first to study the possibility of having the negative Hydrogen ion $H^-$. Using the Rayleigh–Ritz variational principle and elliptic coordinates, following a technique introduced earlier by E. Hylleras to study the ground state energy of Helium, Bethe proved the existence of a bound state for $H^-$ [10]. In fact, Bethe computed quite accurately the ionization energy of the first electron to be approximately 0.74 eV (its present value is approximately 0.75 eV). With the discovery of Rupert Wildt [52] that the presence of $H^-$ in the solar atmosphere is the main cause of its opacity (in the visible, but specially in the infrared) there was a renewed interest in the spectral properties of the $H^-$ anion (see, in particular, the review articles [11], [22], and the monograph [18], pp. 404–ff). Almost fifty years after the article by Bethe, Robert Hill [19, 20] proved that $H^-$ has only one bound state (i.e., the ground state) and not a single excited state. For a review of the physics literature on the Hydrogen anion up to 1996, we refer the reader to the article of Rau [42]. More recently, associated with the space exploration of the solar system, there has been a renewed interest on the existence and properties of anions in Astrophysics (see, e.g., [37]).
In the last forty years there has been a vast literature in mathematical physics concerning the maximum number of electrons an atom or a molecule can bind. It has been conjectured that an atom of atomic number $Z$ can bind at most $Z + 1$ electrons, while a molecule of $K$ nuclei of total nuclear charge $Z$ can bind at most $Z + K$ electrons.

There are two main ingredients involved in this question: the fact that the maximum number of electrons an atom of nuclear charge $Z$ can bind is at least $Z$ (i.e., that neutral atoms do exist) is related to the mathematical properties of the Coulomb interaction between charged particles. On the other hand, the expected fact that at most $Z + 1$ electrons can be bound has to do with Pauli’s Exclusion Principle (i.e., with the fact that electrons obey Fermi statistics). In fact, Benguria and Lieb [6] proved that the Pauli principle is crucial when considering the problem of the maximum number of electrons an atom can bind: they proved that $N_c(Z) - Z \geq cZ$ as $Z \rightarrow \infty$, where $c$ is obtained by solving the Hartree equation (which is equation (10) below). Here, $N_c(Z)$ stands for the maximum number of electrons a nucleus of charge $Z$ can bind. In 1984, Baumgartner [3] solved numerically the Hartree equation to find $c \approx 0.21$. Later, Solovej [49] obtained an upper bound which showed that $N_c(Z) = 1.21Z$ is the appropriate asymptotic formula for large $Z$.

For a system of $N$ electrons and $K$ fixed nuclei interacting via Coulomb potentials the first results were obtained by Zhislin (see [53, 54]) who proved that below neutrality (i.e., when the total number of electrons is strictly less than the total nuclear charge) the corresponding Hamiltonian in non-relativistic quantum mechanics has an infinite number of bound states, whereas at neutrality or above it, the number of possible bound states is at most finite. At the beginning of the 80’s, Ruskai and Sigal [43, 44, 47, 48], using the IMS localization formula and appropriate partitions of unity obtained the first actual upper bounds on the maximum number of electrons an atom or molecule can bind. In 1984, Lieb obtained the simple upper bound $N_c(Z) < 2Z + K$ independently of statistics [26, 27], and Lieb, Sigal, Simon and Thirring proved that fermionic matter is asymptotically neutral (i.e., $N_c(Z)/Z \rightarrow 1$ as $Z$ goes to infinity [31, 32]). In fact, Lieb’s result [26, 27] implies that $H^{--}$ does not exist, settling the conjecture for $Z = 1$.

In 1990, Fefferman and Seco [13] obtained a correction term to this asymptotic neutrality, namely they proved that $N_c(Z) \leq Z + cZ^{1-\alpha}$, for some constant $c$, with $\alpha = 9/56$. The proof of this result was later simplified by Seco, Sigal and Sovolej [46] who established a connection between the ionization energy and the excess charge $N_c(Z) - Z$, and estimated asymptotically the ionization energy. In their work, Seco, Sigal and Sovolej give the better exponent, $\alpha = 2/7$ (see, Note added in proof in [46]). In fact, as remarked in [46] (page 309), $\alpha = 3b/7$ where $b$ comes from the proof of
the Scott conjecture. In \[13, 16\] they took \(b \geq 3/8\), but the optimal choice \(b = 2/3\) was proved in a separate work of Fefferman and Seco \[14\].

More recently P.-T. Nam \[38\] proved that the maximum number \(N_c\) of non-relativistic electrons that a nucleus of charge \(Z\) can bind is less than \(1.22Z + 3Z^{1/3}\), which improves Lieb’s upper bound \(N_c < 2Z + 1\) when \(Z \geq 6\).

The conjecture we mentioned at the beginning to the effect that the excess charge \(N_c(Z) - Z \leq 1\) for an atom is still open. However, for semiclassical models (including the Thomas–Fermi model and its extensions, the Hartree–Fock theory, and others) there are sharper results. It was proven by Lieb and Simon \(\[33, 36\]\) that \(N_c(Z) = Z\) for the Thomas–Fermi model, whereas for the gradient correction (i.e., for the Thomas–Fermi–Weizsäcker model) Benguria and Lieb proved that \(N_c(Z) - Z \leq 1\). In 1991, Solovej \[50\] proved that \(N_c(Z) - Z \leq c\) for some constant \(c\) for a reduced Hartree–Fock model. Finally, Solovej in 2003 \[51\] proved a similar bound for the full Hartree–Fock model. In the last few years there have been several articles on the excess charge of different models (see, e.g., \[12, 15, 16, 17, 23\]) We also refer the reader to the monograph of Lieb and Seiringer \[30\], chapter 12, for a more complete summary on the maximum ionization.

In this manuscript, using Nam’s technique \[38\] and the \textit{Coulomb Uncertainty Principle} we prove new bounds on the excess charge of non relativistic atomic systems, independent of the particle statistics. Our results are given in Theorem 2.1 below. These new bounds are the best bounds to date for bosonic systems for all values of \(Z\) and they are also the best bounds for fermionic systems with \(Z \leq 26\) (i.e., up to the chemical element iron). We recall that Nam’s result \[38\] only holds for fermions, and one of the main tools he uses to get his bound are the Lieb–Thirring inequalities. On the other hand, our result is valid for fermions and bosons and, instead of using the Lieb–Thirring inequalities we use the \textit{Coulomb Uncertainty Principle}.

The rest of the paper is organized as follows. In section 2 we state the main results. In section 3 we give some mathematical preliminaries that we use in the proof of the main result. A key element in the proof of our main result is the fact that one can bound the expectation energy of the \(N\)–particle non relativistic hamiltonian by a variational principle that defines the \textit{Hartree model}. In section 4 we review the results obtained recently by two of us (RB and TT) on the excess charge for the Hartree model. Finally in section 5 we give the proof of the main result. In the appendix we review the properties of a particular Gagliardo–Nirenberg inequality which we use in the main body of the paper to estimate error bounds.
2. Main Result

The main purpose in this manuscript is to prove the following bound on the excess charge, \( N - Z \) of an atom.

**Theorem 2.1** (Bound on the Excess Charge for bosonic atoms). Consider the \( N \)-body Hamiltonian,

\[
H_{N,Z} = -\sum_{i=1}^{N} \Delta_i - \sum_{i=1}^{N} \frac{Z}{|x_i|} + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|},
\]

acting on the symmetric tensor product of \( N \) copies of \( L^2(\mathbb{R}^3) \) (Bosonic Atom). Then, the maximum number of particles, \( N \), for which the Hamiltonian has a bound state satisfies,

\[
N < 1.5211 + 1 + a Z^{1/3},
\]

with \( a = 0.29363 \), for \( Z \geq 6 \).

On the other hand, for integer values of \( Z \), with \( 1 \leq Z \leq 5 \) we have:

- for \( Z = 1 \), \( N < 2.9489 < 3 \);
- for \( Z = 2 \), \( N < 4.4824 < 5 \);
- for \( Z = 3 \), \( N < 6.0286 < 7 \);
- for \( Z = 4 \), \( N < 7.5741 < 9 \);
- for \( Z = 5 \), \( N < 9.1180 < 11 \).

**Remarks.**

i) This improves Lieb’s result \([26, 27]\) for all systems, independent of particle statistics.

ii) This also improves Nam’s result \([38]\) for fermionic systems for \( 1 \leq Z \leq 26 \), i.e., up to iron.

3. Mathematical Preliminaries

In this section we gather a series of well known results concerning the behavior of \( N \)-particle systems in Quantum Mechanics. We need these results in order to bound the expectation of the \( N \)-particle hamiltonian in terms of the energy functional that defines the Hartree Model. This is a key ingredient in the proof of our main result.

**Theorem 3.1** (Kinetic Energy Bound in terms of the density, M. and T. Hoffmann–Ostenhof \([21]\)). For any \( N \)-particle wave–function \( \psi \in H^1(\mathbb{R}^{3N}) \) one has

\[
\langle \psi, \sum_{i=1}^{N} -\Delta_i \psi \rangle \geq \langle \sqrt{\rho_\psi}, -\Delta \sqrt{\rho_\psi} \rangle.
\]

Here,

\[
\rho_\psi(x) = N \int_{\mathbb{R}^{3(N-1)}} |\psi|^2(x, x_2, \ldots, x_N) \, dx_2 \ldots dx_N,
\]

is the single particle density associated to the wave function \( \psi \).
Remarks. i) This result proved by M. and T. Hoffmann–Ostenhof [21] is known as "Schrödinger inequalities". Its proof relies on the positivity of the Fourier transform of $\exp(t\Delta)$.

ii) A general version of this theorem, including relativistic and magnetic hamiltonians, is given by Lemma 8.4 in [30].

iii) The Pauli exclusion principle does not play any role in this theorem.

**Theorem 3.2** (Bound on the Coulomb energy in terms of the density; E. H. Lieb and S. Oxford [29]). For any $N$–particle wave–function $\psi \in H^1(\mathbb{R}^{3N})$ with density $\rho_\psi$ (3) one has

$$\langle \psi, \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|} \psi \rangle \geq \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \rho_\psi(x) \frac{1}{|x - y|} \rho_\psi(y) \, dx \, dy - C_{LO} \int_{\mathbb{R}^3} \rho_\psi(x)^{4/3} \, dx.$$  

(4)

Remarks. Originally $C_{LO} = 1.68$ [29], while the best constant to date is $C_{LO} = 1.57$ [24].

Moreover, it is straightforward to show that for any $N$–particle wave–function $\psi \in H^1(\mathbb{R}^{3N})$ with density $\rho_\psi$,

$$\langle \psi, \sum_{i=1}^N \frac{Z}{|x_i|} \psi \rangle = \int_{\mathbb{R}^3} \frac{Z}{|x|} \rho_\psi(x) \, dx.$$  

(5)

Summarizing, putting all this together, one has that for any $N$–particle wave–function $\psi \in H^1(\mathbb{R}^{3N})$ with density $\rho_\psi$

$$\langle \psi, H_{N,Z} \psi \rangle \geq \mathcal{E}(\sqrt{\rho_\psi}) - C_{LO} \int_{\mathbb{R}^3} \rho_\psi(x)^{4/3} \, dx,$$

(6)

with,

$$\mathcal{E}(\psi) = \int_{\mathbb{R}^3} (\nabla \psi)^2 \, dx - \int_{\mathbb{R}^3} \frac{Z}{|x|} \psi^2 \, dx + \frac{1}{2} \int_{\mathbb{R}^3} \psi^2(x) \frac{1}{|x - y|} \psi^2(y) \, dx \, dy.$$  

(7)

Moreover, we will use the following inequality (a Gagliardo-Nirenberg inequality):

$$\int_{\mathbb{R}^3} \psi^{8/3} \, dx \leq C_{GN} \left( \int_{\mathbb{R}^3} (\nabla \psi)^2 \, dx \right)^{1/2} \left( \int_{\mathbb{R}^3} \psi^2 \, dx \right)^{5/6},$$

(8)

where the best constant is found numerically to be,

$$C_{GN} = 0.2793...$$

For a discussion on this inequality see the Appendix.
4. Analytic bound on the excess charge in the Hartree model

The strategy we follow to prove our main result is to bound the expectation of the N-particle Hamiltonian in terms of the energy functional that defines the Hartree Model, and then use a recent result obtained by two of us \[8\] on the excess charge for the Hartree Model. To make this manuscript self contained we will summarize in this section the results obtained in \[8\].

The Hartree atomic model is defined by the energy functional,

\[
E[\psi] = \int_{\mathbb{R}^3} (\nabla\psi)^2 \, dx - \int_{\mathbb{R}^3} \frac{Z}{|x|} \psi^2 \, dx + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \psi^2(x) \frac{1}{|x-y|} \psi^2(y) \, dx \, dy.
\]

(9)

This functional is defined for functions \(\psi \in H^1(\mathbb{R}^3)\). Since \(\psi \in H^1(\mathbb{R}^3)\), it follows from Sobolev’s inequality that \(\psi \in L^2(\mathbb{R}^3) \cap L^6(\mathbb{R}^3)\), and one can readily check that the second and third integral of (9) are finite. Using the direct calculus of variations one can prove that there is a minimizer of \(E[\psi]\) in \(H^1(\mathbb{R}^3)\) (one can obtain the existence of solutions directly from \([5, 25]\), by setting \(p = 5/3\) and \(\gamma = 0\), see also \([31, 35]\)). Moreover, by Kato’s inequality, one can show that the minimizer does not change sign, so one can always work with a nonnegative \(\psi\). It also follows from \([31, 25]\) that the minimizer \(\psi\) is such that \(\int_{\mathbb{R}^3} \psi^2 \, dx < \infty\). Using the convexity of \(E[\psi]\) in \(\rho = \psi^2\) (see, e.g., \([5]\), Lemma 4, or \([28]\), Theorem 7.8, p. 177), it follows that the minimizer is unique. Since the minimizer is unique and the potential \(V(x) = Z/|x|\) is radial (atomic case) we have that the minimizer \(\psi(x)\) is radially symmetric. Moreover, the minimizer \(\psi\) satisfies the Euler equation (in this case known as the Hartree equation),

\[-\Delta \psi = \phi(x)\psi,\]

(10)

where the potential \(\phi(x)\) is given by

\[
\phi(x) = \frac{Z}{|x|} - \int_{\mathbb{R}^3} \frac{1}{|x-y|} \psi^2(y) \, dy.
\]

(11)

In what follows we need to look at the components of the energy and their relations. Let \(\psi\) be the unique minimizer of \(E[\psi]\), and denote by

\[
K = \int_{\mathbb{R}^3} (\nabla \psi)^2 \, dx,
\]

(12)

\[
A = \int_{\mathbb{R}^3} \frac{Z}{|x|} \psi^2 \, dx,
\]

(13)
and,

\[ R = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \psi^2(x) \frac{1}{|x-y|} \psi^2(y) \, dx \, dy. \]  \tag{14}

Then we have the following identities.

**Theorem 4.1** (Virial Theorem). If \( \psi \) is the unique minimizer of \( E[\psi] \), and \( K, A \) and \( R \) are defined by (12), (13), and (14) respectively, then we have

\[ 2K - A + R = 0, \]  \tag{15}

and,

\[ K - A + 2R = 0. \]  \tag{16}

**Proof.** One can prove both identities at once by considering \( \psi_{\lambda, \mu}(r) = \lambda^{1/2} \mu^{3/2} \psi(\mu r) \). We find that

\[ E(\lambda, \mu) = E[\psi_{\lambda, \mu}] = \lambda \mu^2 K - \lambda \mu A + \lambda^2 \mu R, \]

has a minimum at \( \lambda = \mu = 1 \). Thus, \( (d/d\mu)E(1, 1) = 0 \) gives (15), while \( (d/d\lambda)E(1, 1) = 0 \) gives (16). \( \square \)

It follows from (15) and (16) that \( 3K = A \), i.e., if \( \psi \) satisfies the Hartree equation (10) one has

\[ \int_{\mathbb{R}^3} (\nabla \psi)^2 \, dx = \frac{1}{3} \int_{\mathbb{R}^3} \frac{Z}{|x|} \psi^2 \, dx. \]  \tag{17}

A key inequality to estimate \( A \) is the well known **Coulomb Uncertainty Principle**.

**Theorem 4.2.** For any \( \psi \in H^1(\mathbb{R}^3) \) one has,

\[ \int_{\mathbb{R}^3} \frac{1}{|x|} \psi(x)^2 \, dx \leq \| \nabla \psi \|_2 \| \psi \|_2, \]  \tag{18}

with equality if and only if \( \psi(x) = Be^{-c|x|} \) for any constants \( B \) and \( c > 0 \).

For a proof see, e.g., [30], Equation (2.2.18), p. 29.

In fact, we have,

**Lemma 4.3** (An upper bound on \( A \)). If \( \psi \in H^1(\mathbb{R}^3) \) is the unique minimizer of (9) (i.e., \( \psi \) is the positive solution of the Hartree equation (10)), one has,

\[ A \leq \frac{1}{3} NZ^2. \]  \tag{19}

**Proof.** Using (17) and (18) one has,

\[ A = 3 \| \nabla \psi \|_2^2 \geq \frac{3}{Z^2} A^2 \frac{1}{N}, \]  \tag{20}

and from here (19) immediately follows. \( \square \)
Corollary 4.4 (A lower bound on $E(\psi)$). For any $\psi \in H^1(\mathbb{R}^3)$

$$E(\psi) \geq -\frac{1}{9}NZ^2.$$  \hfill (21)

*Proof.* If we let $E = \min E(\psi)$, where the minimum is taken over all $\psi \in H^1(\mathbb{R}^3)$, we have that $E = K - A + R = -K$, in view of Theorem 4.1. Moreover, since $K = A/3$ and $A \leq NZ^2/3$ (see, (19)), we conclude that

$$E \geq -\frac{1}{9}NZ^2,$$

which in turn implies (21). \hfill \Box

We will later need an estimate on

$$J \equiv \int_{\mathbb{R}^3} |x|\psi^2 \, dx,$$ \hfill (22)

where $\psi$ is the solution to the Hartree equation (10).

**Lemma 4.5 (A lower bound on $J$).** If $\psi$ is the unique positive solution of the Hartree equation (10), one has,

$$J \geq 3 \frac{N}{Z}.$$ \hfill (23)

*Proof.* Using the Schwarz inequality, one has

$$N^2 = \left( \int_{\mathbb{R}^3} \psi^2(x) \, dx \right)^2 \leq \left( \int_{\mathbb{R}^3} |x|\psi^2(x) \, dx \right) \left( \int_{\mathbb{R}^3} \frac{1}{|x|}\psi^2(x) \, dx \right),$$ \hfill (24)

i.e.,

$$N^2 \leq J \frac{A}{Z} \leq \frac{1}{3}JN,$$ \hfill (25)

where we used (19) to get the last inequality in (25). Finally the lemma follows from (25). \hfill \Box

The main result in [8] is the following analytic upper bound on the excess charge of the Hartree model.

**Theorem 4.6 (Upper bound on $N$ for the Hartree model [8]).** If $\psi \in H^1(\mathbb{R}^3)$ is the unique positive solution to the Hartree equation (10), we have

$$N \leq \frac{5}{4\beta}Z \leq \frac{5}{4(0.8218)}Z \approx 1.5211Z,$$ \hfill (26)

where $\beta$ is given by (33) below.
Remarks. i) By scaling properties of the variational principle \([9]\), \(N/Z\) is independent of \(Z\), so the proof can be written for \(Z = 1\). However, we prefer to leave the dependence on \(Z\) explicitly.

ii) The proof that \(N > Z\) is given in \([5]\), Lemma 13, or in \([25]\), Theorem 7.16. In both cases take \(p = 5/3\) and \(\gamma = 0\).

iii) It is also known that \(N < 2Z\) (see the comments and references immediately below).

iv) B. Baumgartner (see, \([3]\), Section 4) computed numerically that \(N \approx 1.21Z\).

Before we go into the proof of Theorem 4.6, we recall that using the Benguria–Lieb strategy one can prove the upper bound,

\[ N \leq 2Z. \]  

(27)

For completeness, we recall the proof of (27) (see, \([25]\), Theorem 7.22, p. 633, for details). Multiplying (10) by \(|x|\psi(x)\) and integrating over \(\mathbb{R}^3\), we get

\[
\int_{\mathbb{R}^3} (-|x|\psi(x)\Delta\psi) \, dx = Z \int_{\mathbb{R}^3} \psi^2(x) \, dx - \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \psi^2(x) \frac{|x|}{|x - y|}\psi^2(y) \, dx \, dy
\]

(28)

Symmetrizing the second term in (28), and using the triangular inequality we get,

\[
\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \psi^2(x) \frac{|x|}{|x - y|}\psi^2(y) \, dx \, dy = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \psi^2(x) \frac{|x| + |y|}{|x - y|}\psi^2(y) \, dx \, dy \geq \frac{1}{2}N^2,
\]

(29)

where, as before, \(N \equiv \int_{\mathbb{R}^3} \psi^2(x) \, dx\). One can prove that

\[
\int_{\mathbb{R}^3} (-|x|\psi(x)\Delta\psi) \, dx \geq 0.
\]

(30)

(see, \([25]\), or \([26, 27]\)). Finally from (28), (29) and (30), the bound (27) follows.

Now, using the strategy introduced by Nam in \([38]\) (see also \([39, 40]\)) we prove Theorem 3.1.

Proof of Theorem 4.6. Multiplying this time (10) by \(|x|^2\psi(x)\), integrating over \(\mathbb{R}^3\), and symmetrizing as before, we get

\[
\int_{\mathbb{R}^3} (-|x|^2\psi(x)\Delta\psi) \, dx = Z \int_{\mathbb{R}^3} |x|^2\psi^2(x) \, dx - \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \psi^2(x) \frac{|x|^2 + |y|^2}{|x - y|} \psi^2(y) \, dx \, dy
\]

(31)
In this case, the integral on the left of (31) is not non-negative. However, we can use the fact that for any real \( f \in H^1(\mathbb{R}^3) \), one has that
\[
(x^2 f, -\Delta f) \geq -\frac{3}{4} (f, f),
\] (32)
(see, e.g. [38], pp. 431, equation (9)) to bound the left side from below by \(-3N/4\).

Following Nam [38] we define,
\[
\beta = \inf \frac{1}{2} \left( \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \psi^2(x) \left| \frac{|x|}{|x-y|} \psi^2(y) \right| dx \, dy \right)
\] (33)
where the infimum is taken over all \( \psi \), such that \( \int_{\mathbb{R}^3} \psi^2(x) dx < \infty \). The exact numerical value of \( \beta \) is not known, however, \( 0.8218 \leq \beta \leq 0.8705 \). (38), Proposition 1).

It follows from (33) that
\[
\frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \psi^2(x) \left| \frac{|x|}{|x-y|} \psi^2(y) \right| dx \, dy \geq \beta \int_{\mathbb{R}^3} |x| \psi^2(x) dx \int_{\mathbb{R}^3} \psi^2(x) dx = \beta JN.
\] (34)
where we have used (22). It follows from (31), (32), and (34) that
\[
\beta JN \leq ZJ + \frac{3}{4}N \leq ZJ + \frac{1}{4}ZJ,
\] (35)
where the last inequality in (35) follows from (23). Finally, dividing both sides of (35) by \( J \), and using the lower bound \( \beta \geq 0.8218 \) (see, [38]) the Theorem follows.

5. PROOF OF THE MAIN RESULT

Proof of Theorem 2.1. Assume that \( E(N, Z) \) is an eigenvalue of \( H_{N,Z} \) corresponding to some normalized eigenfunction \( \psi_{N,Z} \), i.e.,
\[
(H_{N,Z} - E(N, Z)) \psi_{N,Z} = 0.
\] (36)
Following Nam [38], multiply (36) by \( |x_N|^2 \psi_{N,Z} \) and integrate. We get,
\[
0 = \langle |x_N|^2 \psi_{N,Z}, (H_{N-1,Z} - E(N, Z)) \psi_{N,Z} \rangle + \langle |x_N|^2 \psi_{N,Z}, -\Delta N \psi_{N,Z} \rangle
\]
\[
+ \langle \psi_{N,Z}, (-Z|x_N| + \frac{1}{N} \sum_{1 \leq i < j \leq N} \frac{|x_i|^2 + |x_j|^2}{|x_i - x_j|} \psi_{N,Z} \rangle
\] (37)
Here we used the symmetry of \( |\psi_{N,Z}|^2 \) under interchange of particle coordinates, which is true for both fermions and bosons. The first term on the right side of (37) is nonnegative since
\[
H_{N-1,Z} \geq E(N - 1, Z) \geq E(N, Z),
\]
which follows from the assumption that $E(N, Z)$ is an eigenvalue of $H_{N, Z}$ corresponding to the eigenfunction $\psi_{N, Z}$. Hence, we have from (37) that,

$$0 \geq \langle |x_N|^2 |\psi_{N, Z}, -\Delta_N |\psi_{N, Z}\rangle + \langle \psi_{N, Z}, (-Z + \alpha_N (N - 1)) |x_N| \psi_{N, Z}\rangle$$

(38)

Here, following [38], we have introduced,

$$\alpha_N \equiv \inf_{x_1, \ldots, x_N \in \mathbb{R}^3} \frac{\sum_{1 \leq i < j \leq N} |x_i|^2 + |x_j|^2}{(N - 1) \sum_{i=1}^N |x_i|} \geq \beta.$$  

(39)

As before, we also use Nam’s result,

$$\text{Re} \langle x^2 f, -\Delta f \rangle \geq -\frac{3}{4} \langle f, f \rangle,$$

(40)

with $f = \psi_{N, Z}$. Putting all this together we get,

$$\beta (N - 1) - Z \leq \frac{3}{4} \frac{N}{I},$$

(41)

where we have introduced

$$I = N \langle \psi_{N, Z}, |x_N| \psi_{N, Z}\rangle.$$  

(42)

Using the definition of the single particle density [3] we can write $I$ as,

$$I = \int_{\mathbb{R}^3} |x| \rho_\psi(x) \, dx.$$  

(43)

Notice that $I$ plays a role analogous to the one played by $J$, defined in (22), in the Hartree model. In fact, $I/N$ is the average distance of the particles to the nucleus. A key step in our proof is to bound this distance from below using the Coulomb Uncertainty Principle.

We conclude the proof using the following steps:

**First step.** Use the Schrödinger inequalities and the Lieb–Oxford bound to get (5), i.e.,

$$\langle \psi, H \psi \rangle \geq \mathcal{E}(\sqrt{\rho_\psi}) - C_{LO} \int_{\mathbb{R}^3} \rho_\psi(x)^{4/3} \, dx.$$  

(44)

**Second step.** Use the appropriate Gagliardo–Nirenberg inequality,

$$\int_{\mathbb{R}^3} \rho_\psi(x)^{4/3} \, dx \leq C_{GN} \left( \int_{\mathbb{R}^3} \left( \nabla \sqrt{\rho_\psi(x)} \right)^2 \, dx \right)^{1/2} \left( \int_{\mathbb{R}^3} \rho_\psi(x) \, dx \right)^{5/6}.$$  

(45)

to estimate the error bound in (44) in terms of the $L^2$ norm of $\nabla \sqrt{\rho_\psi(x)}$. See the Appendix. The best bound for $C$ is $C = 0.279271$. 

Third step. Use the many-body virial theorem,
\[ \langle \psi, H \psi \rangle = -K_\psi = -\langle \psi, -\sum_{i=1}^{N} \Delta_i \psi \rangle. \] (46)

Fourth step. Use the Corollary 4.6 (21), i.e.,
\[ \mathcal{E}(\sqrt{\rho}) \geq -\frac{1}{9} N Z^2, \] (47)
the Schrödinger Inequalities, i.e., \( K_\psi \geq K_{\rho_\psi} \) (see equation (2) in Theorem 3.1), equations (46), (44) and (45) to conclude that,
\[ K_{\rho_\psi} \leq \frac{1}{9} N Z^2 + D K_{\rho_\psi}^{1/2} N^{5/6}. \] (48)
Here,
\[ D = C_{LO} \cdot C_{GN} \leq 0.4403. \] (49)

Fifth step. Using the **Coulomb Uncertainty Principle**, we get
\[ \int_{\mathbb{R}^3} \frac{1}{|x|} \rho_\psi(x) \, dx \leq \sqrt{N K_{\rho_\psi}}, \]
(Here, think of \( \rho_\psi \geq 0 \) as being \( g^2 \) for some \( g \)). Then, we use Schwarz’s inequality, as before,
\[ N^2 = \left( \int_{\mathbb{R}^3} \rho_\psi(x) \, dx \right)^2 \leq \int_{\mathbb{R}^3} \frac{1}{|x|} \rho_\psi(x) \, dx \int_{\mathbb{R}^3} |x| \rho_\psi(x) \, dx = I \sqrt{N K_{\rho_\psi}}, \] (50)
where \( I \) is given by (43). Notice that If \( D \) were zero, from here we would get \( I \geq 3 N/Z \), which in turn would imply
\[ N \leq 1 + \frac{5}{4\beta} Z \leq 1.5211 Z + 1, \]
as in the Hartree model.

Taking into account the error term, i.e., \( D \neq 0 \), we can prove
\[ N \leq 1.5211 Z + 1 + a Z^{1/3} \] (51)
where
\[ a = \frac{3D}{8\beta} \left( \frac{N}{Z} \right)^{1/3} + \frac{9D^2}{32\beta} \left( \frac{N}{Z^2} \right)^{2/3}. \] (52)
In fact, introducing \( u \) so that \( K_{\rho_\psi} = \sigma^2 u^2 \), with \( \sigma = Z^{N^{1/2}/3} \), we can write (48) as,
\[ u^2 \leq 1 + \delta u, \] (53)
where
\[ \delta = D \frac{3}{Z} N^{1/3}. \] (54)
It follows from (53) that \( u \leq u_0 \), where \( u_0 \) is the positive root of \( u^2 - \delta u - u = 0 \), i.e.,

\[
\frac{1}{2} \left( \delta + \sqrt{\delta^2 + 4} \right) \leq \frac{1}{2} \left( \delta + 2 + \frac{\delta^2}{4} \right) = 1 + \frac{\delta}{2} + \frac{\delta^2}{8}. \tag{55}
\]

From (50), the definitions of \( u \) and \( \sigma \), and (55) we conclude,

\[
\frac{3N}{4I} \leq \frac{Z}{4} \left( 1 + \frac{\delta}{2} + \frac{\delta^2}{8} \right). \tag{56}
\]

Finally, (51) follows from (41), (56), and (54). To conclude the proof of the theorem, one can estimate \( a \) using Lieb’s bound (see, e.g., [26, 27]), i.e.,

\[
N < \frac{2}{Z} + 1. \tag{57}
\]

Clearly, \( h(Z) \) is a decreasing function of \( Z \), and \( h(6) \leq 0.29363 \). Moreover, computing \( 1.5211 Z + 1 + Z^{1/3} h(Z) \) for \( 1 \leq Z \leq 5 \) we get the upper bounds on \( N \) for \( Z = 1, 2, 3, 4, 5 \). This concludes the proof of the main theorem. \( \square \)

6. Appendix: A Gagliardo–Nirenberg Inequality

In order to estimate the error bound in (5), in terms of the \( L^2 \) norm of \( \nabla \sqrt{\rho} \), we need to consider the following inequality

\[
\int_{\mathbb{R}^3} |\psi(x)|^{8/3} \, dx \leq C_{GN} \left( \int_{\mathbb{R}^3} (\nabla \psi(x))^2 \, dx \right)^{1/2} \left( \int_{\mathbb{R}^3} \psi(x)^2 \, dx \right)^{5/6}. \tag{58}
\]

Here we are interested in the best possible constant \( C_{GN} \). The inequality (58) is a particular case of a Gagliardo-Nirenberg type inequality given by

\[
||u||_{\rho + 2} \leq k(\rho, d) ||\nabla u||_2^2 ||u||_{2}^{1-\alpha}, \tag{59}
\]

that characterizes the embedding of \( H^1(\mathbb{R}^d) \) in \( L_{\rho + 2}(\mathbb{R}^d) \). Here,

\[
\alpha = \frac{d}{2} \frac{\rho}{\rho + 2}. \tag{60}
\]

The inequality (59) holds for any \( \rho \in (0, \rho_0) \), where \( \rho_0 = 4/(d - 2) \), if \( d \geq 3 \), and \( \rho_0 = \infty \) if \( d = 1, 2 \) (see, e.g., [9, 11], and references therein). Except for particular values of the parameters, the optimal constant \( k(\rho, d) \) for (59) is not known. The best estimates to date for \( k(\rho, d) \) are the ones obtained by Nasibov in [41], namely,

\[
k(\rho, d) \leq k_N(\rho, d) \equiv \frac{1}{\chi} \left( \frac{|S^{d-1}| B\left(\frac{d}{2}, \frac{d(1-\alpha)}{2\alpha}\right)}{2} \right)^{\alpha/d} k_{BB} \left( \frac{\rho + 2}{\rho + 1} \right). \tag{61}
\]

In (61),

\[
\chi = \sqrt{\alpha^\alpha (1-\alpha)^{1-\alpha}}, \tag{62}
\]
and $B(x, y)$ is the Euler Beta function, i.e., $B(x, y) = \Gamma(x)\Gamma(y)/\Gamma(x + y)$. Moreover,

$$k_{BB}(p) = \left( \frac{p^2}{2\pi} \right)^{1/p} \left( \frac{p'}{2\pi} \right)^{1/p'} d/2,$$

(63)

for $1 < p < \infty$ and $1/p + 1/p' = 1$, is the optimal constant for the Hausdorff–Young inequality, as it was proven by Babenko [1] and Beckner [4].

Hence, the inequality (58) corresponds to the case $d = 3$, $\rho = 2/3$, and $\alpha = 3/8$ of (59). From here, we have that

$$C_{GN} = k \left( \frac{2}{3}, 3 \right)^{8/3} \leq k_N \left( \frac{2}{3}, 3 \right)^{8/3},$$

(64)

Using (61), (62), and (63), in (64), we get that,

$$k_N \left( \frac{2}{3}, 3 \right) = \left( \frac{3^3 2^{15}}{\pi 5^{10}} \right)^{1/8},$$

(65)

Finally, from (64) and (65), we have that,

$$C_{GN} \leq \frac{96}{125} (5\pi)^{-1/3} \approx 0.306658 \ldots$$

(66)

On the other hand, solving numerically the Euler equation associated to the variational principle embodied in (58), we have,

$$C_{GN} \approx 0.279271 \ldots$$

(67)

Acknowledgments

This work has been supported by Fondecyt (Chile) Project # 120–1055. JMG thanks ANID (Chile) for their support through a Becas de Doctorado Nacional (Folio 21212245). TT, thanks the Instituto de Física of the Pontificia Universidad Católica de Chile for their support through a Summer Research Fellowship.

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