ANALYTIC BOUND ON THE EXCESS CHARGE FOR THE HARTREE MODEL

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Abstract. We prove an analytic bound on the excess charge for the Hartree equation in the atomic case.

1. Introduction

The ability of atoms and molecules to catch or give electrons is one of the fundamental pillars of chemistry and biology, and it has somewhat attracted attention since the late XVIIIth century with the birth of modern chemistry. Given a neutral atom, one can extract one electron by providing enough energy. The energy needed to remove one electron is called its ionization energy (e.g., the energy needed to extract the electron of the Hydrogen atom in its ground state is approximately 13.6 eV). One can continue this process of removing electrons by providing increasing amounts of energy (a fact that seems intuitively obvious but yet to be proven), up to stripping the atom completely of all its electrons. On the other hand, the question up to what extent one can add electrons to a neutral atom is not yet completely understood. 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 variational principle of E. Hylleraas, he proved the existence of a bound state for $H^-$ [7], and computed quite accurately the ionization energy of the first electron to be 17 kcal/mol (i.e., approximately 0.74 eV, whereas its present value is approximately 0.75 eV). With the discovery of Rupert Wildt [47] 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 [8], [18], and the monograph [14], pp. 404–ff). A rigorous proof that $H^-$ has only one bound state (i.e., the ground state) and no singly excited states had to wait approximately fifty years, until the work of Robert Hill [15, 16]. For a review of the physics literature on the Hydrogen anion up to 1996, we refer the reader to the article of Rau [35].

In the last half a century there has been a big effort in trying to determine the maximum number of electrons an atomic nucleus or a molecule can bind. These efforts come from three different fronts. From one side, in experimental physics, there has been an intensive search for dianions (i.e., doubly ionized atoms and molecules). On another front, there has been an
intensive numerical search for the possibility of stable atomic dianions [17] giving strong evidence that stable atomic dianions do not exist. Finally, in mathematical physics there has been an interesting quest to solve this problem. Based on the knowledge coming from these three fronts, we expect 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 very much related to the mathematical properties of the Coulomb interaction between charged particles. In particular, a crucial role is played by Newton’s theorem. 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., more precisely with the fact that electrons obey Fermi statistics).

We have seen above that the first rigorous results (of Bethe and Hill) on negative ions dealt with \( H^- \). Concerning the more general situation of \( N \) electrons and \( K \) (usually fixed) nuclei interacting via Coulomb potentials the first results were obtained by Zhislin (see [48, 49]) 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. Upper bounds on the number of bound states for bosonic matter above neutrality were obtained later in [1, 38]. At the beginning of the 80’s, Ruskai and Sigal [36] [37] [40] [41], 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 1983, Benguria and Lieb [5] proved that the Pauli principle is crucial when considering the problem of the maximum number of electrons an atom can bind. In fact, they proved that \( N_c(Z) - Z \geq cZ \), where \( c \) is obtained by solving the Hartree equation (which is equation (2) below). Here we denote by \( N_c(Z) \) the maximum number of electrons a nucleus of charge \( Z \) can bind. Then, Baumgartner [3] solved numerically the Hartree equation to find \( c \approx 0.21 \). Later, Solovej [32] obtained an upper bound which showed that \( N_c(Z) = 1.21 \) \( Z \) is the appropriate asymptotic formula for large \( Z \). In 1984, Lieb obtained the simple upper bound \( N_c(Z) \leq 2Z + K \) independently of statistics [21] [22], and Lieb, Sigal, Simon and Thirring proved that fermionic matter is asymptotically neutral (i.e., \( N_c(Z)/Z \to 1 \) as \( Z \) goes to infinity [25] [26]). In 1990, Fefferman and Seco [10] 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 [39] who established a connection between the ionization energy and the excess charge \( N_c(Z) - Z \), and estimated asymptotically the ionization energy. More recently P.-T. Nam [32] proved...
that the maximum number $N_c$ of non-relativistic electrons that a nucleus of charge $Z$ can bind is less than $1.22 Z + 3 Z^{1/3}$, 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 \cite{27, 30} 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 \cite{43} proved that $N_c(Z) - Z \leq c$ for some constant $c$ for a reduced Hartree–Fock model. Finally, Solovej in 2003 \cite{44} 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., \cite{9, 11, 12, 13, 19}) We also refer the reader to the monograph of Lieb and Seiringer \cite{24}, chapter 12, for a more complete summary on the maximum ionization.

In this manuscript, using Nam’s technique, we prove an analytic bound on the excess charge for the solution of the Hartree equation. Our main result is given in Theorem 3.1 below, where we prove that $N < 1.5211 Z$. In his original article \cite{32} Nam showed that his technique only gives better results for fermions. In view of our result we expect that it could also give better results for an atomic system of $N$ bosons.

We dedicate this paper to Elliott Lieb, in admiration, for his many outstanding contributions in Physics, Analysis and Mathematical Physics.

2. The Hartree Functional and the Hartree Equation

The Hartree atomic model is defined by the energy functional,

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

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 (1) 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 \cite{1, 20}, by setting $p = 5/3$ and $\gamma = 0$, see also \cite{2, 28, 29, 45, 46}). It also follows
from [4, 20] that the minimizer $\psi$ is such that $\int_{\mathbb{R}^3} \psi^2 \, dx < \infty$. Using the convexity of $\mathcal{E}[\psi]$ in $\rho = \psi^2$ (see, e.g., [4], Lemma 4, or [23], 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),

$$- \Delta \psi = \phi(x) \psi, \quad (2)$$

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

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

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

$$K = \int_{\mathbb{R}^3} (\nabla \psi)^2 \, dx, \quad (4)$$

$$A = \int_{\mathbb{R}^3} \frac{Z}{|x|} \psi^2 \, dx, \quad (5)$$

and,

$$R = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \psi^2(x) \frac{1}{|x - y|} \psi^2(y) \, dx \, dy. \quad (6)$$

Then we have the following identities.

**Theorem 2.1 (Virial Theorem).** If $\psi$ is the unique minimizer of $\mathcal{E}[\psi]$, and $K$, $A$ and $R$ are defined by (4), (5), and (6) respectively, then we have

$$2K - A + R = 0, \quad (7)$$

**Proof.** Let $\psi_\mu(r) = \mu^{3/2} \psi(\mu r)$, then,

$$E(\mu) = \mathcal{E}[\psi_\mu] = \mu^2 K - \mu A + \mu R. \quad (8)$$

Because of the minimization property of $\psi$,

$$\frac{dE}{d\mu} (1) = 0, \quad (9)$$

and therefore (7) follows. \hfill \Box

Moreover we have the following relation.

**Theorem 2.2.** If $\psi$ is the unique minimizer of $\mathcal{E}[\psi]$, and $K$, $A$ and $R$ are defined by (4), (5), and (6) respectively, then we have

$$K - A + 2R = 0. \quad (10)$$

**Proof.** Multiply (2) by $\psi(x)$ and integrate over $\mathbb{R}^3$. Integrating by parts the left side and using the definition of $K$, $A$, and $R$, (10) follows. \hfill \Box
It follows from (7) and (10) that $3K = A$, i.e., if $\psi$ satisfies the Hartree equation (2) one has
\[ \int_{\mathbb{R}^3} (\nabla \psi)^2 \, dx = \frac{1}{3} \int_{\mathbb{R}^3} \frac{Z}{|x|} \psi^2 \, dx. \] (11)

A key inequality to estimate $A$ is the well known Coulomb Uncertainty Principle.

**Theorem 2.3.** For any $\psi \in H^1(\mathbb{R}^3)$ one has,
\[ \int_{\mathbb{R}^3} \frac{1}{|x|} \psi(x)^2 \, dx \leq \|\nabla \psi\|_2 \|\psi\|_2, \] (12)
with equality if and only if $\psi(x) = B e^{-c|x|}$ for any constants $B$ and $c > 0$.

For a proof see, e.g., [31], Theorem 1, p. 14, or [24], Equation (2.2.18), p. 29.

In fact, we have,

**Lemma 2.4 (An upper bound on $A$).** If $\psi \in H^1(\mathbb{R}^3)$ is the unique minimizer of (7) (i.e., $\psi$ is the positive solution of the Hartree equation (2)), one has,
\[ A \leq \frac{1}{3} N Z^2. \] (13)

**Proof.** Using (11) and (12) one has,
\[ A = 3 \|\nabla \psi\|_2^2 \geq \frac{3}{Z^2} A^2 \frac{1}{N}, \] (14)
and from here (13) immediately follows. \qed

To conclude this section, we will prove an estimate on
\[ J \equiv \int_{\mathbb{R}^3} |x| \psi^2 \, dx, \] (15)
where $\psi$ is the solution to the Hartree equation (2).

**Lemma 2.5 (A lower bound on $J$).** If $\psi$ is the unique positive solution of the Hartree equation (2), one has,
\[ J \geq 3 \frac{N}{Z}. \] (16)

**Proof.** Using the Schwarz inequality, one has
\[ N^2 = \left( \int_{\mathbb{R}^3} \psi^2(x) \, dx \right)^2 \leq \left( \int_{\mathbb{R}^3} |x| \psi^2(x) \, dx \right) \left( \int_{\mathbb{R}^3} \frac{1}{|x|} \psi^2(x) \, dx \right), \] (17)
i.e.,
\[ N^2 \leq J \frac{A}{Z} \leq \frac{1}{3} J N Z, \] (18)
where we used (13) to get the last inequality in (18). Finally the lemma follows from (18). \qed
3. Upper bound on the critical charge for the Hartree equation.

In this section we prove the main result of our manuscript namely,

**Theorem 3.1 (Upper bound on $N$).** If $\psi \in H^1(\mathbb{R}^3)$ is the unique positive solution to the Hartree equation (3), we have

$$N \leq \frac{5}{4\beta} Z \leq \frac{5}{4 \times 0.8218} Z \approx 1.5211 Z,$$

where $\beta$ is given by (26) below.

**Remarks.**

i) The proof that $N > Z$ is given in [4], Lemma 13, or in [20], Theorem 7.16. In both cases take $p = 5/3$ and $\gamma = 0$.

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

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

Before we go into the proof of Theorem 3.1, we recall that using the Benguria Lieb strategy one can prove the upper bound,

$$N \leq 2Z.$$  \hfill (20)

For completeness, we recall the proof of (20) (see, [20], Theorem 7.22, p. 633, for details). Multiplying (2) by $|x| \psi(x)$ and integrating over $\mathbb{R}^3$, we get

$$\int_{\mathbb{R}^3} (-|x|\psi(x) \Delta \psi) \, dx = Z \int_{\mathbb{R}^3} \psi^2(x) \, dx - \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \psi^2(x) \frac{|x|}{|x-y|} \psi^2(y) \, dx \, dy$$  \hfill (21)

Symmetrizing the second term in (21), and using the triangular inequality we get,

$$\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \psi^2(x) \frac{|x|}{|x-y|} \psi^2(y) \, dx \, dy = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \psi^2(x) \frac{|x| + |y|}{|x-y|} \psi^2(y) \, dx \, dy \geq \frac{1}{2} N^2,$$  \hfill (22)

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

$$\int_{\mathbb{R}^3} (-|x|\psi(x) \Delta \psi) \, dx \geq 0.$$  \hfill (23)

(see, [20], or [21] [22]). Finally from (21), (22) and (23), the bound (20) follows.

Now, using the strategy introduced by Nam in [32] (see also [33] [34]) we prove Theorem 3.1.
Proof of Theorem 3.1. Multiplying this time (2) by $|x|^2 \psi(x)$, integrating over $\mathbb{R}^3$, and symmetrizing as before, we get

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

(24)

In this case, the integral on the left of (24) is not non–negative. However, we can use the fact that for any real $f \in H^1(\mathbb{R}^3)$, one has that

$$
(x^2 f, -\Delta f) \geq -\frac{3}{4} (f, f),
$$

(25)

(see, e.g. [32], pp. 431, equation (9)) to bound the left side from below by $-3 N/4$.

Following Nam [32] we define,

$$
\beta = \inf \frac{1}{2} \left( \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \psi^2(x) \frac{|x|^2 + |y|^2}{|x-y|} \psi^2(y) \, dx \, dy \right) \left( \int_{\mathbb{R}^3} |x| \psi^2(x) \, dx \right) \left( \int_{\mathbb{R}^3} \psi^2(x) \, dx \right)
$$

(26)

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, $0.8218 \leq \beta \leq 0.8705$ ([32], Proposition 1).

It follows from (26) that

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

(27)

where we have used (15). It follows from (24), (25), and (27) that

$$
\beta J N \leq Z J + \frac{3}{4} N \leq Z J + \frac{1}{4} Z J,
$$

(28)

where the last inequality in (28) follows from (16). Finally, dividing both sides of (28) by $J$, and using the lower bound $\beta \geq 0.8218$ (see, [32]) the Theorem follows. \qed

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