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Asymptotics for Bosonic Atoms

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Abstract. It was proved by Benguria and Lieb that for an atom where the 'electrons' do not satisfy the exclusion principle, the critical electron number N_c, i.e., the maximal number of electrons the atom can bind, satisfies $\liminf_{Z\to\infty} N_c/Z \geqslant 1+\gamma$, where Z is the nuclear charge. Here γ is a positive constant derived from the Hartree model. We complete this result by proving that the correct asymptotics for $N_c(Z)$ is indeed $\lim_{Z\to\infty} N_c/Z = 1+\gamma$.

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1. Introduction

In this Letter, we study the atomic Schrödinger operator

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

acting on $\mathscr{H} = L^2(\mathbb{R}^{3N})$. The ground state energy of $H(N)$ is

$$E(N) = \inf \operatorname{spec}_{\mathscr{H}} H(N). \tag{2}$$

This is the same as if we had restricted $H(N)$ to the space of functions symmetric in the N space variables. $E(N)$ thus corresponds to the energy of an atom where the 'electrons' obey Bose symmetry. We define the ionization energy by

$$I(N) = E(N-1) - E(N) \geqslant 0. \tag{3}$$

There exists $N_c(Z) < 2Z+1$ (see [8]) such that

$$I(N_c(Z)) > 0 \quad \text{and} \quad I(N) = 0 \quad \text{for all } N > N_c(Z). \tag{4}$$

$N_c(Z)$ is the maximal number of Bosonic 'electrons' that can be bound by the nucleus.

We will here study the asymptotics of N_c as $Z\to\infty$. The motivation for this comes from [2], where it was proved by comparison with the Hartree model that

$$\liminf_{Z\to\infty} \frac{N}{Z} \geqslant 1+\gamma \tag{5}$$

for a constant $\gamma > 0$.

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The Hartree model is defined by the functional

$$L_m^H(\rho) = \int \left(m^{-1}(\nabla \sqrt{\rho(x)})^2 - \frac{Z}{|x|}\rho(x) \right) \mathrm{d}x + D(\rho, \rho), \tag{6}$$

where

$$D(f, g) = \tfrac{1}{2} \int f(x)|x - y|^{-1} g(y) \, \mathrm{d}x \, \mathrm{d}y. \tag{7}$$

L_m^H is defined on the set of functions $\rho \geqslant 0$ with $\sqrt{\rho} \in H^1(\mathbb{R}^3)$. The energy in this model is

$$E_m^H(N) = \inf \left\{ L_m^H(\rho) \mid \int \rho(x) \, \mathrm{d}x = N \right\}. \tag{8}$$

Then by scaling we find

$$E_m^H(N) = -mZ^3 e(N/Z), \tag{9}$$

where $e(t)$ is a monotone nondecreasing, concave function. There exists ρ_m^H, such that

$$L_m^H(\rho_m^H) = \min_N E_m^H(N) \equiv m\bar{E}(Z), \tag{10}$$

where $\bar{E}(Z) = -Z^3 \min e$.

It is known (see [7] where the more general Thomas–Fermi–von Weizsäcker (TFW) theory is studied) that if we write $\psi_m^H = \sqrt{\rho_m^H}$, then ψ_m^H is the unique positive solution to

$$-m^{-1} \Delta \psi_m^H - \left(\frac{Z}{|x|} - \rho_m^H * |x|^{-1} \right) \psi_m^H = 0 \tag{11}$$

and

$$\int \rho_m^H(x) \, \mathrm{d}x = (1 + \gamma)Z. \tag{12}$$

This is the same γ as in (5). It was proved by Benguria (for a reference, see [7]) that $0 < \gamma < 1$. The numerical value (see [1]) is $\gamma = 0.21$. If $N \geqslant (1 + \gamma)Z$ then $E_m^H(N) = m\bar{E}(Z)$, i.e., $e(t) = \min e$ when $t \geqslant \gamma + 1$.

Here we complete the result (5) by proving a similar upper bound, i.e.

THEOREM 1.

$$\lim_{Z \to \infty} \frac{N_c(Z)}{Z} = 1 + \gamma. \tag{13}$$

In the case of fermions we have asymptotic neutrality, i.e., the above limit is 1. This was proved in [10] and, recently, by a different method, in [4].

2. Bounds on the Ground State Energy

In this Section we improve the energy bounds from [2]. By choosing a product trial function it is easy to conclude (see [2]) that

$$E(N) \leqslant E^H_{m=1}(N). \tag{14}$$

We will now prove a lower bound to $E(N)$. In fact we will prove a lower bound to the operator H.

For all functions $\varphi \in L^2(\mathbb{R}^{3N})$ symmetric in the N space variables (but not necessarily normalized) we define the one-particle density

$$\rho_\varphi(x) = N \int |\varphi(x, x_2 \ldots, x_N)|^2 \, dx_2 \cdots dx_N$$

and the two-particle correlation

$$\rho^{(2)}_\varphi(x, y) = N(N-1) \int |\varphi(x, y, \ldots, x_N)|^2 \, dx_3 \cdots dx_N.$$

To get the lower bound, we proceed as in [2]. From the simple kinetic energy inequality of Hoffmann-Ostenhof [5] (Lemma 2), we find that for any symmetric function $\varphi \in L^2(\mathbb{R}^{3N})$

$$\langle \varphi | H(N) | \varphi \rangle \geqslant \int \left(\left(\nabla \sqrt{\rho_\varphi(x)} \right)^2 - \frac{Z}{|x|} \rho_\varphi(x) \right) dx + \\ + \sum_{1 \leqslant i < j \leqslant N} \left\langle \varphi \left| \frac{1}{|x_i - x_j|} \right| \varphi \right\rangle.$$

We estimate the last term with the Lieb–Oxford inequality (see [6] and [9])

$$\begin{aligned} &\sum_{1 \leqslant i < j \leqslant N} \left\langle \varphi \left| \frac{1}{|x_i - x_j|} \right| \varphi \right\rangle \\ &\geqslant \|\varphi\|^{-2} D(\rho_\varphi, \rho_\varphi) - (1.68) \|\varphi\|^{-2/3} \int \rho_\varphi^{4/3} \, dx \\ &= \|\varphi\|^{-2} D(\rho_\varphi - \rho^H_m \|\varphi\|^2, \rho_\varphi - \rho^H_m \|\varphi\|^2) + 2D(\rho_\varphi, \rho^H_m) - \\ &\quad - \|\varphi\|^2 D(\rho^H_m, \rho^H_m) - (1.68) \|\varphi\|^{-2/3} \int \rho_\varphi^{4/3} \, dx, \end{aligned}$$

where ρ^H_m was given in (10). If we insert this above we obtain

$$\begin{aligned} &\langle \varphi | H(N) | \varphi \rangle \\ &\geqslant \int \left(\frac{1}{(1+\varepsilon)} (\nabla \sqrt{\rho_\varphi})^2 - \left(\frac{Z}{|x|} - \rho^H_m * |x|^{-1} \right) \rho_\varphi(x) \right) dx - \|\varphi\|^2 D(\rho^H_m, \rho^H_m) + \\ &+ \frac{\varepsilon}{1+\varepsilon} \int (\nabla \sqrt{\rho_\varphi})^2 - (1.68) \|\varphi\|^{-2/3} \int \rho_\varphi^{4/3} \, dx + \\ &+ \|\varphi\|^{-2} D(\rho_\varphi - \rho^H_m \|\varphi\|^2, \rho_\varphi - \rho^H_m \|\varphi\|^2). \end{aligned}$$

Using the Sobolev inequality $\|\nabla g\|_2^2 \geqslant 3(\pi/2)^{4/3}\|g\|_6^2$ and Hölder's inequality

$$\int \rho_\varphi^{4/3} \leqslant \left(\int \rho_\varphi^3\right)^{1/6} \|\varphi\|^{5/3} N^{5/6}$$

we easily get (see also [2])

$$\frac{\varepsilon}{1+\varepsilon}\int (\nabla\sqrt{\rho_\varphi})^2\,\mathrm{d}x - (1.68)\|\varphi\|^{-2/3}\int \rho_\varphi^{4/3}\,\mathrm{d}x \geqslant -a\frac{1+\varepsilon}{\varepsilon}\|\varphi\|^2 N^{5/3},$$

where $a = 0.13$. We now choose $m = 1+\varepsilon$. Since ψ_m^H satisfies the Hartree equation (11) we see that $m\bar{E}(Z) = -D(\rho_m^H, \rho_m^H)$ and since $\psi_m^H \geqslant 0$, ψ_m^H is the ground state of

$$-m^{-1}\Delta - \left(\frac{Z}{|x|} - \rho_m^H * |x|^{-1}\right).$$

This is thus a positive operator. We can therefore conclude that

$$\begin{aligned}\langle\varphi|H(N)|\varphi\rangle \geqslant &\left((1+\varepsilon)\bar{E}(Z) - a\frac{1+\varepsilon}{\varepsilon}N^{5/3}\right)\|\varphi\|^2 + \\ &+ \|\varphi\|^{-2}D(\rho_\varphi - \rho_m^H\|\varphi\|^2, \rho_\varphi - \rho_m^H\|\varphi\|^2).\end{aligned} \tag{15}$$

Using $N < cZ$ and choosing $\varepsilon = cZ^{-2/3}$ we have proved

LEMMA 2. *For all symmetric* $\varphi \in L^2(\mathbb{R}^{3N})$ *we have*

$$\langle\varphi|H(N)|\varphi\rangle \geqslant (\bar{E}(Z) - cZ^{7/3})\|\varphi\|^2 + \|\varphi\|^{-2}D(\rho_\varphi - \rho_m^H\|\varphi\|^2, \rho_\varphi - \rho_m^H\|\varphi\|^2),$$

where $m = 1 + cZ^{-2/3}$.

3. Structure of Ground State

In this section we will prove Theorem 1. The main technical step is (in the fermionic case a similar result is given in [11])

LEMMA 3. *Let* $\chi, \theta \in C^1(\mathbb{R}^3)$ *be nonnegative functions with* χ *compactly supported. If* $N \geqslant (1+\gamma)Z$ *and* $H(N)$ *has a ground state* ψ *we then have the following estimate involving the ground state density* $\rho = \rho_\psi$ *and two point correlation* $\rho^{(2)} = \rho_\psi^{(2)}$

$$\begin{aligned}&\left(\int [\rho^{(2)}(x,y) - \rho_m^H(y)\rho(x)]\theta(x)\chi(y)\,\mathrm{d}x\,\mathrm{d}y\right)^2 \\ &\quad\leqslant C\|\nabla\chi\|^2\left[Z^{7/3}\left(\int \rho(x)\theta(x)\,\mathrm{d}x\right)^2 + Z\|\nabla\sqrt{\theta}\|_\infty^2\int \rho(x)\theta(x)\,\mathrm{d}x\right],\end{aligned}$$

where $m = 1 + cZ^{-2/3}$.

Proof. Since the ground state ψ of $H(N)$ is symmetric we can write

$$\begin{aligned}E(N)\int \rho\theta\,\mathrm{d}x &= \sum_{i=1}^N \langle\psi|\theta(x_i)H(N)|\psi\rangle \\ &= \sum_{i=1}^N \langle\psi|\theta(x_i)^{1/2}H(N)\theta(x_i)^{1/2} - (\nabla\sqrt{\theta(x_i)})^2|\psi\rangle,\end{aligned}$$

where in the last equality we have used a simple commutation identity also used in the IMS formula (see [3]). If we let $H^{(i)}(N-1)$ denote the operator with the ith variable removed and use that the lowest eigenvalue of $-\Delta-(Z/|x|)$ is $-\frac{1}{4}Z^2$ we get

$$E(N)\int\rho\theta\,\mathrm{d}x \geqslant \sum_{i=1}^{N}\langle\psi|\theta(x_i)^{1/2}H^{(i)}(N-1)\theta(x_i)^{1/2}|\psi\rangle - \\ - N\|\sqrt{\theta}\|_\infty^2 - \tfrac{1}{4}Z^2\int\rho\theta\,\mathrm{d}x,$$

where in the ith term we have neglected the repulsion between the ith electron and all the rest. If we now use Lemma 2 for $H^{(i)}(N-1)$ with $\varphi_i=\theta(x_i)^{1/2}\psi$ (here x_i is a parameter) we get

$$E(N)\int\rho\theta\,\mathrm{d}x \geqslant (\bar{E}(Z)-cZ^{7/3})\int\rho\theta\,\mathrm{d}x - N\|\nabla\sqrt{\theta}\|_\infty^2 + \\ + \sum_{i=1}^{N}\int\|\varphi_i\|^{-2}D(\rho^{(i)}-\rho_m^H\|\varphi_i\|^2, \rho^{(i)}-\rho_m^H\|\varphi_i\|^2)\,\mathrm{d}x_i, \qquad (16)$$

here

$$\rho^{(i)}(x)=\rho_{\varphi_i}(x)=N^{-1}\theta(x_i)\rho^{(2)}(x,x_i)$$

and

$$\|\varphi_i\|^2=(N-1)^{-1}\int\rho^{(i)}(x)\,\mathrm{d}x=N^{-1}\theta(x_i)\rho(x_i).$$

We can therefore write

$$\int[\rho^{(2)}(x,y)-\rho_m^H(y)\rho(x)]\theta(x)\chi(y)\,\mathrm{d}x\,\mathrm{d}y \\ = \sum_{i=1}^{N}\int(\rho^{(i)}(y)-\|\varphi_i\|^2\rho_m^H(y))\chi(y)\,\mathrm{d}x_i\,\mathrm{d}y. \qquad (17)$$

We use the Fourier transform (denoted $\wedge$) to estimate the last expression. This idea comes from [4]. It is here that we need some decay of χ.

$$\left(\int(\rho^{(i)}(y)-\|\varphi_i\|^2\rho_m^H(y))\chi(y)\,\mathrm{d}y\right)^2 \\ = \left(\int(\rho^{(i)}-\|\varphi_i\|^2\rho_m^H)^\wedge(p)\hat{\chi}(p)\,\mathrm{d}p\right)^2 \\ \leqslant \int|\hat{\chi}|^2|p|^2\,\mathrm{d}p\int\left|(\rho^{(i)}-\|\varphi_i\|^2\rho_m^H)^\wedge(p)\right|^2|p|^{-2}\,\mathrm{d}p \\ = \mathrm{const}\|\nabla\chi\|^2D(\rho^{(i)}-\rho_m^H\|\varphi_i\|^2, \rho^{(i)}-\rho_m^H\|\varphi_i\|^2)$$

and using Cauchy–Schwarz inequality

$$\left(\int (\rho^{(i)}(y) - \|\varphi_i\|^2 \rho_m^H(y))\chi(y)\, dy\, dx_i\right)^2$$

$$\leqslant \int \left(\int (\rho^{(i)}(y) - \|\varphi_i\|^2 \rho_m^H(y))\chi(y)\, dy\right)^2 \|\varphi_i\|^{-2}\, dx_i \int \|\varphi_i\|^2\, dx_i$$

$$\leqslant C\|\nabla\chi\|^2 \int D(\rho^{(i)} - \rho_m^H\|\varphi_i\|^2, \rho^{(i)} - \rho_m^H\|\varphi_i\|^2)\|\varphi_i\|^{-2}\, dx_i N^{-1} \int \rho\theta\, dx.$$

Since $N \geqslant (1+\gamma)Z$ we know that $E_{m=1}^H(N) = \bar{E}$ and hence from (14), $E(N) \leqslant \bar{E}(Z)$. We can estimate the above expression from (16) where the terms in the sum are independent of i. Inserting this into (17) and noticing again that the terms in the sum of (17) are all the same, we arrive at the final result (recall that $N < 2Z + 1$). □

EXAMPLE. If we choose $\theta = 1$ in the Lemma we find with $m = 1 + cZ^{-2/3}$

$$\left((N-1)\int \rho(y)\chi(x)\, dy - N\int \rho_m^H(y)\chi(y)\, dy\right)^2 \leqslant CN^2 Z^{7/3}\|\nabla\chi\|^2$$

or

$$\left(\int \rho(y)\chi(x)\, dy - \int \rho_m^H(y)\chi(y)\, dy\right)^2 \leqslant CZ^{7/3}\|\nabla\chi\|^2. \tag{18}$$

We can now give the

Proof of Theorem 1. Because of the lower bound in [2], we only have to prove a similar upper bound. We can of course assume that $N_c > (1+\gamma)Z$. We are now concentrating on the case $N = N_c$. Since $I(N_c) > 0$ it follows from the HVZ Theorem (see [3]) that $H(N_c)$ has a ground state.

First choose localizing functions χ_R, θ_R as in the Lemma, but depending on a scale R. χ_R should be supported in a ball of radius R around the origin and be equal to 1 in a ball of radius $\frac{1}{2}R$. Furthermore, we want $\chi_R + \theta_R = 1$. Then

$$\|\nabla\chi_R\|^2 \leqslant cR \quad \text{and} \quad \|\nabla\sqrt{\theta_R}\|_\infty \leqslant cR^{-1}.$$

We will use (18) to give a bound on $\int \rho(x)\chi_R(x)\, dx$. From the scaling of the Hartree model we find that

$$\rho_m^H(x) = m^3 Z^4 \rho^H(mZx),$$

where ρ^H is the Hartree density corresponding to $Z = 1$ and $m = 1$. It follows from the results in [7] on the TFW theory, that ρ^H is exponentially decaying at infinity. Now choose $R = Z^{-7/9}$. Then it follows immediately from (18) that (recall that $m = 1 + cZ^{-2/3}$)

$$\left|\int \rho(x)\chi_R(x)\, dx - (1+\gamma)Z\right| \leqslant CZ^{7/9}.$$

To estimate $\int \rho(x)\theta_R(x)\,dx$ we proceed as in the beginning of the proof of Lemma 3 and use the IMS formula to prove

$$E(N)\int \rho(x)\theta_R(x)|x|\,dx$$
$$\geqslant E(N-1)\int \rho(x)\theta_R(x)|x|\,dx - Z\int \rho(x)\theta_R(x)\,dx +$$
$$+\int \rho^{(2)}(x,y)\theta_R(x)|x|\,|x-y|^{-1}\,dx\,dy - N\|\nabla\sqrt{|x|\theta_R}\|_\infty^2,$$

here we have kept the repulsion between the ith electron and the others but neglected the $-\Delta_i$ term. We choose $0<\lambda<\gamma/2$ and restrict the y-integral above to $|y|\leqslant \lambda R$, i.e., $y\in \operatorname{supp}\chi_{\lambda R}$. If $x\in\operatorname{supp}\theta_R$ and $y\in\operatorname{supp}\chi_{\lambda R}$ then $|x-y|\leqslant |x|+\lambda R\leqslant (1+2\lambda)|x|$. Hence, from (4)

$$0\geqslant -Z\int \rho(x)\theta_R(x)\,dx + \frac{1}{1+2\lambda}\int \rho^{(2)}(x,y)\theta_R(x)\chi_{\lambda R}(y)\,dx\,dy - cNR^{-1}.$$

We then apply Lemma 3 to estimate the second term, again using the results on ρ^H mentioned above

$$0\geqslant\left(-Z+\frac{1+\gamma}{1+2\lambda}Z\right)\int \rho(x)\theta_R(x)\,dx - cNR^{-1} -$$
$$-cR^{1/2}Z^{7/6}\int \rho(x)\theta_R(x)\,dx - cR^{-1/2}Z^{1/2}\left(\int \rho(x)\theta_R(x)\,dx\right)^{1/2}.$$

Since $2\lambda<\gamma$ and $\int \rho\theta_R \leqslant \text{const}\,Z$ we find

$$c(Z-Z^{7/9})\int \rho(x)\theta_R(x)\,dx \leqslant cZ^{16/9}.$$

This then implies the final estimate

$$N_c=\int \rho(x)\,dx = \int \rho(x)\chi_R(x)\,dx + \int \rho(x)\theta_R(x)\,dx \leqslant (1+\gamma)Z + cZ^{7/9}$$

from which Theorem 1 follows. □

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