

THE ATOMIC DENSITY ON THE THOMAS–FERMI LENGTH SCALE FOR THE CHANDRASEKHAR HAMILTONIAN

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ABSTRACT. We consider a large neutral atom of atomic number Z , modeled by a pseudo-relativistic Hamiltonian of Chandrasekhar. We study its suitably rescaled one-particle ground state density on the Thomas–Fermi length scale $Z^{-1/3}$. Using an observation by Fefferman and Seco [2], we find that the density on this scale converges to the minimizer of the Thomas–Fermi functional of hydrogen as $Z \rightarrow \infty$ when Z/c is fixed to a value not exceeding $2/\pi$. This shows that the electron density on the Thomas–Fermi length scale does not exhibit any relativistic effects.

1. INTRODUCTION

The energy of heavy atoms as well as the distribution of its electrons are of fundamental interest both in physics and in quantum chemistry. However, as in the classical Kepler problem, one cannot hope for an exact solution of the Schrödinger equation involving more than two particles. For this reason, one needs to devise models for many-body quantum systems which are easier to solve but still describe the system accurately.

Lieb and Simon [10] showed that the atomic ground state density converges on the length scale $Z^{-1/3}$ to the minimizer of the Thomas–Fermi functional of hydrogen. This result is derived by controlling the atomic energy to leading order in Z and its derivative with respect to small perturbations.

However, it is questionable to describe large Z atoms non-relativistically, since the large nuclear charge forces the bulk of the electrons on orbits on the length scale $Z^{-1/3}$ from the nucleus. Thus, electrons close to the nucleus are moving faster than a substantial fraction of the velocity of light c . This suggests that a relativistic description is necessary.

On the other hand, Sørensen [11] showed in the context of the simplest relativistic model, namely the Chandrasekhar operator, that energetically this worry is not justified, at least not to leading order in the energy: the atomic ground state energy of the Chandrasekhar operator is still described by the Thomas–Fermi energy for large Z and $\gamma := Z/c$ fixed to a value not exceeding the critical coupling constant $\gamma_c := 2/\pi$. A similar result for the Brown–Ravenhall operator was proven by Cassanas et al [1].

Schwinger [13] predicted that relativistic effects occur only in sub-leading order. Frank et al [4] and Solovej et al [14] showed, using completely different approaches, that this is indeed the case. In particular, the authors showed that the coefficient of this order is less than the non-relativistic one which reflects the fact that the relativistic kinetic energy is lower than the non-relativistic one, especially for high momenta.

The question arises whether the density on the Thomas–Fermi length scale $Z^{-1/3}$ is also unchanged by relativistic effects. This might be conjectured, since the leading energy correction is generated by the fast electrons close to the nucleus. Our main result is a positive answer to this question: we show that the suitably rescaled density of the atomic Chandrasekhar operator converges for large Z and γ fixed

to a value not exceeding γ_c to the minimizer of the Thomas–Fermi functional of hydrogen.

2. DEFINITION AND MAIN RESULT

Our system consists of a neutral atom, i.e., a nucleus of charge Z located at the origin with $N = Z$ electrons with q spin states whose motion is described by the Chandrasekhar operator. It is given by the Friedrichs extension of the quadratic form associated to

$$(1) \quad C_{c,Z} := \sum_{\nu=1}^N \left(\sqrt{-c^2 \Delta_{\nu} + c^4} - c^2 - \frac{Z}{|x_{\nu}|} \right) + \sum_{1 \leq \nu < \mu \leq N} \frac{1}{|x_{\nu} - x_{\mu}|}$$

in the Fermionic Hilbert space $\bigwedge_{\nu=1}^N (L^2(\mathbb{R}^3) : \mathbb{C}^q)$. (Throughout we use atomic units, i.e., $\hbar = e = m = 1$.) The constant c denotes the velocity of light which in these units is the inverse of Sommerfeld’s fine-structure constant α . Here we focus on $N = Z$. The form is bounded from below, if and only if $\gamma \leq \gamma_c$ (Kato [9, Chapter Five, Equation (5.33)], Herbst [8, Theorem 2.5], Weder [15]). For $\gamma < \gamma_c$, its form domain is $H^{1/2}(\mathbb{R}^{3N} : \mathbb{C}^{q^N}) \cap \bigwedge_{\nu=1}^N (L^2(\mathbb{R}^3 : \mathbb{C}^q))$ by the KLMN theorem. In fact, Hardekopf and Sucher [7] indicated numerically and gave arguments and Raynal et al [12] showed that the one-particle operator is strictly bigger than -1 , even for $\gamma = \gamma_c$.

A general fermionic ground state density matrix can be written as

$$\sum_{\mu=1}^M w_{\mu} |\psi_{\mu}\rangle \langle \psi_{\mu}|$$

where the ψ_{μ} constitute an orthonormal basis of the ground state eigenspace and the w_{μ} are non-negative weights such that $\sum_{\mu=1}^M w_{\mu} = 1$. The corresponding one-particle density ρ is given by

$$\rho_Z(x) := N \sum_{\mu=1}^M w_{\mu} \sum_{\sigma_1, \dots, \sigma_N=1}^q \int_{\mathbb{R}^{3(N-1)}} |\psi_{\mu}(x, \sigma_1; x_2, \sigma_2; \dots; x_N, \sigma_N)|^2 dx_2 \dots dx_N.$$

The ground state energy of this system for fixed γ is written as $E(Z) := \inf \sigma(C_{c,Z})$. Solovej et al [14] and Frank et al [4] determined the first two terms of the expansion of $E(Z)$ for $Z \rightarrow \infty$ and $\gamma \leq \gamma_c$ fixed to be

$$(2) \quad E(Z) = E^{\text{TF}}(Z) + \left(\frac{q}{4} - s(\gamma) \right) Z^2 + O(Z^{47/24})$$

where

$$s(\gamma) := \gamma^{-2} \text{tr} \left[\left(\frac{p^2}{2} - \frac{\gamma}{|x|} \right)_- - \left(\sqrt{p^2 + 1} - 1 - \frac{\gamma}{|x|} \right)_- \right] > 0$$

is the sum of differences between the n -th eigenvalues of

$$\left(-\frac{1}{2} \Delta - \frac{\gamma}{|x|} \right) \otimes \mathbb{1}_{\mathbb{C}^q} \text{ and } \left(\sqrt{-\Delta + 1} - 1 - \frac{\gamma}{|x|} \right) \otimes \mathbb{1}_{\mathbb{C}^q}$$

and $E^{\text{TF}}(Z)$ is the infimum of the atomic Thomas–Fermi functional $\mathcal{E}_Z^{\text{TF}}$ on its natural domain \mathcal{I} , i.e.,

$$E^{\text{TF}}(Z) := \inf(\mathcal{E}_Z^{\text{TF}}(\mathcal{I}))$$

with

$$\mathcal{E}_Z^{\text{TF}}(\rho) := \int_{\mathbb{R}^3} \left(\frac{3}{10} \gamma_{\text{TF}} \rho^{5/3}(x) - \frac{Z}{|x|} \rho(x) \right) dx + D(\rho, \rho)$$

and

$$\mathcal{I} := \{ \rho \in L^{5/3}(\mathbb{R}^3) \mid D(\rho, \rho) < \infty, \rho \geq 0 \}.$$

Here $\gamma_{\text{TF}} := (6\pi^2/q)^{2/3}$ is the Thomas–Fermi constant and $D(\rho, \rho)$ is the electrostatic selfenergy of the charge density ρ , i.e.,

$$D(\rho, \sigma) = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\overline{\rho(x)\sigma(y)}}{|x-y|} dx dy.$$

Note that D defines a scalar product and thus induces a norm, the so-called Coulomb norm $\|\rho\|_C := D(\rho, \rho)^{1/2}$. The minimizer of $\mathcal{E}_Z^{\text{TF}}$ is denoted by ρ_Z^{TF} . It obeys the scaling relation $\rho_Z^{\text{TF}}(x) = Z^2 \rho_1^{\text{TF}}(Z^{1/3}x)$ where ρ_1^{TF} is the Thomas–Fermi density of hydrogen, i.e., $Z = 1$ (Gombas [5]). These scaling relations and the leading order of $E(Z)$ show that the Thomas–Fermi theory is energetically correct in leading order even, if relativistic effects are taken into account. Our result on the convergence of the ground state density shows that it is also a valid model for the density on this length scale.

We write

$$(3) \quad \hat{\rho}_Z(x) := Z^{-2} \rho_Z(Z^{-1/3}x)$$

for the rescaled quantum density on the Thomas–Fermi scale. This allows to formulate our main observation:

Theorem 1. *Let $\gamma \in (0, \gamma_c]$, then $\hat{\rho}_Z \rightarrow \rho_1^{\text{TF}}$ in Coulomb norm. In fact,*

$$\|\hat{\rho}_Z - \rho_1^{\text{TF}}\|_C = O(Z^{-3/16})$$

as $Z \rightarrow \infty$.

Before proving this claim, we remark that the Schwarz inequality implies also weak convergence: suppose σ has finite Coulomb norm, i.e., $\|\sigma\|_C < \infty$. Then

$$D(\sigma, \hat{\rho}_Z - \rho_1^{\text{TF}}) = O(Z^{-3/16}).$$

(Note that the Hardy–Littlewood–Sobolev inequality ensures that this is the case for all $\sigma \in L^{6/5}(\mathbb{R}^3)$ but that this is not exhaustive. For example, σ might also be a uniform charge distribution on a sphere.)

Finally, setting $\sigma := -(1/4\pi)\Delta U$ with U vanishing at infinity gives

$$\int U \rho \rightarrow \int U \rho_1^{\text{TF}} \text{ as } Z \rightarrow \infty$$

for all such U .

Proof of Theorem 1. The basic observation is, that also in this case – as in the non-relativistic case done by Fefferman and Seco [2] – it is useful to keep some positive term in the lower bound in the proof of an asymptotic energy formula: tracing the lower bound, the proof of the Scott conjecture by Frank et al does not only give the Scott formula (2). If one does not drop the positive term in Onsager’s inequality – unlike as is done there, we get for fixed $\gamma \in (0, 2/\pi]$ the two bounds

$$(4) \quad E^{\text{TF}}(Z) + \left(\frac{q}{4} - s(\gamma)\right) Z^2 + \|\rho_Z^{\text{TF}} - \rho_Z\|_C^2 - \text{const } Z^{47/24} \\ \leq E(Z) \leq E^{\text{TF}}(Z) + \left(\frac{q}{4} - s(\gamma)\right) Z^2 + \text{const } Z^{47/24}.$$

We observe that the left and right side have identical terms up to order Z^2 . Subtracting them and rearranging gives

$$(5) \quad \|\rho_Z^{\text{TF}} - \rho_Z\|_C^2 \leq \text{const } Z^{47/24}.$$

Since $\rho_Z^{\text{TF}}(x) = Z^2 \rho_1^{\text{TF}}(Z^{1/3}x)$ and by definition of $\hat{\rho}_Z$ in (3), we obtain by change of variables

$$(6) \quad \|\rho_Z^{\text{TF}} - \rho_Z\|_C^2 = \frac{1}{2} \int dx \int dy \frac{(\rho_Z^{\text{TF}}(x) - \rho_Z(x))(\rho_Z^{\text{TF}}(y) - \rho_Z(y))}{|x-y|} \\ = \frac{Z^{7/3}}{2} \int dx \int dy \frac{(\rho_1^{\text{TF}}(x) - \hat{\rho}_1(x))(\rho_1^{\text{TF}}(y) - \hat{\rho}_1(y))}{|x-y|}.$$

Combining this with (5), dividing by $Z^{7/3}$, and taking the root gives the claimed convergence. \square

We conclude with two remarks:

1. The proof of Solovej et al [14] has the same property as the one used here and yields a generalization for the multi-center case when the distance between nuclei are kept on the Thomas–Fermi scale.

2. Also the proof of the Scott conjecture of the two more elaborate models of atoms, the Brown–Ravenhall operator treated in [3] and the no-pair operator in the Furry picture treated in [6], have the same property that the missing error term in Onsager’s inequality can be added. Repeating the same argument gives the analogues of Theorem 1. One merely needs to adapt the range of allowed constants γ to $(0, 2/(\pi/2 + 2/\pi)]$ and $(0, 1)$ respectively and change the meaning of $\hat{\rho}_Z$ to the respective ground state densities.

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