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The ultrarelativistic Thomas–Fermi–von Weizsäcker model

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Abstract
We consider a possible zero mass limit of the relativistic Thomas–Fermi–von Weizsäcker model of atoms and molecules. We find sharp bounds for the critical atomic number below which there is stability and above which the system collapses.

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1. Introduction

A possible zero mass limit, neglecting logarithmic divergences, of the relativistic Thomas–Fermi–von Weizsäcker (henceforth ultrarelativistic TFW) energy functional for nuclei of charges $z_i > 0$ (which need not be integral) located at R_i, $i = 1, \ldots, k$, is defined by [1–3]

$$\xi(\rho) = a^2 \int (\nabla \rho^{1/3})^2 \, \mathrm{d}x + b^2 \int \rho^{4/3} \, \mathrm{d}x - \int V(x)\rho(x) \, \mathrm{d}x + D(\rho, \rho). \quad (1)$$

Here $x \in \mathbb{R}^3$, $\mathrm{d}x$ denotes the standard Lebesgue measure, $\rho(x) \geqslant 0$ is the electron density,

$$V(x) = \alpha \sum_{i=1}^{k} \frac{z_i}{|x - R_i|} \quad (2)$$

is the electrostatic potential created by the nuclei,

$$D(\rho, \rho) = \frac{\alpha}{2} \int \frac{\rho(x)\rho(y)}{|x - y|} \, \mathrm{d}x \, \mathrm{d}y \quad (3)$$

is the electronic repulsion and $\alpha = e^2/\hbar c \approx 1/137$ is the fine structure constant. The constants a^2 and b^2 in (1) are given respectively by

$$a^2 = \frac{3}{8\pi^2}(3\pi^2)^{2/3}\lambda \quad (4)$$

and

$$b^2 = \tfrac{3}{4}(3\pi^2)^{1/3}. \quad (5)$$

(Whenever we use a and b we consider them to be positive.) The constant λ in (4) has different values according to different approximations. According to the original von Weizsäcker model [8], $\lambda = 1/9$. In the derivation of Tomishima and Yonei [7], $\lambda = 1/5$. Finally, based on energy considerations, Lieb found [4, 5] $\lambda = 0.185$.

Let us first study the atomic case, i.e. the case $k = 1$, $z_1 = z$, $R_1 = 0$. Because of simple scaling considerations, if we minimize the energy functional (1) over all functions ρ for which each of the terms in (1) makes sense, the infimum of the energy functional is either 0 or $-\infty$. In the first case we say the atom is *stable*, otherwise the atom is *unstable*. Our purpose here is to determine the range of values of the atomic number z for which the atom is *stable*. Our main result in the atomic case is the following theorem.

Theorem 1. *Let*

$$\xi(\rho) = a^2 \int (\nabla \rho^{1/3})^2 \, \mathrm{d}x + b^2 \int \rho^{4/3} \, \mathrm{d}x - \int z\alpha \frac{\rho}{|x|} \, \mathrm{d}x + D(\rho, \rho) \tag{6}$$

with $D(\rho, \rho)$ given by (3). Then

$$\inf \xi(\rho) = \begin{cases} -\infty & \text{for} \quad z > \frac{4ab}{3\alpha} + \frac{7\pi a^3}{6b^3} \\ 0 & \text{for} \quad z < \frac{4ab}{3\alpha} \end{cases} \tag{7}$$

where the infimum is taken over all non-negative functions $\rho(x)$ such that $\rho \in L^{4/3}(\mathbb{R}^3)$, $\nabla \rho^{1/3} \in L^2(\mathbb{R}^3)$ and $D(\rho, \rho) < \infty$.

Remarks 1

(i) It follows from (7) that if $z < 4ab/(3\alpha)$ the atom is stable, whereas if $z > 4ab/(3\alpha) + 7\pi a^3/(6b^3)$ the atom is unstable. We do not know, in general, the exact critical value of z (say z_c) separating the region of stability from the region of unstability. However, it turns out that for physical values of the constants, the gap between the upper and lower bounds on z_c is less than 1, and therefore negligible (see the following remarks).

(ii) For the physical values of a and b given by (4) and (5), the atom will be stable if $z < \sqrt{3\lambda/2}/\alpha \approx 167.8\sqrt{\lambda}$. Thus, if $\lambda = 1/9$ (i.e. the original value used by von Weizsäcker [8]) the atom is stable if $z < 56$. If $\lambda = 1/5$ (i.e. the value used by Tomishima and Yonei [7]) the atom is stable if $z < 75$. Finally, using the value of Lieb [4, 5], the atom is stable if $z < 73$.

(iii) As for the value of the gap, using the physical values of the constants, we get $7\pi a^3/(6b^3) = (7/12\pi)\sqrt{3\lambda^3/2} < 0.021 < 1$ for all values of λ considered above. Thus, the gap is negligible from the physical point of view.

The rest of the paper is organized as follows. In section 2 we prove a functional inequality which is the key ingredient in the proof of our main result. This functional inequality is of independent interest. We then proceed with the proof of theorem 1. In section 3 we extend our results to the molecular case.

2. Atomic case

We start this section by proving a functional inequality which plays a crucial role in what follows and is of independent interest.

Lemma 1. *Consider the functional*

$$F(\psi) = \frac{a^2 \int (\nabla \psi)^2 \, \mathrm{d}x + b^2 \int \psi^4 \, \mathrm{d}x}{\alpha \int \psi^3 |x|^{-1} \, \mathrm{d}x} \tag{8}$$

defined on the set

$$\mathcal{D} \equiv \{\psi \mid \psi \in L^4(\mathbb{R}^3), \nabla\psi \in L^2(\mathbb{R}^3), \psi \not\equiv 0, \psi \geqslant 0\}. \tag{9}$$

Then

$$F(\psi) \geqslant \frac{4ab}{3\alpha}. \tag{10}$$

Moreover, equality is attained in (10) if and only if $\psi = (a/b)(|x| + K)^{-1}$, where K is any positive constant.

Proof. We first note that $\psi \in \mathcal{D}$ implies $\int \psi^3/|x|\,\mathrm{d}x < \infty$. In fact, using that $\psi \in \mathcal{D}$, it follows from Sobolev's inequality (see, e.g., [6], theorem 8.3) that $\psi \in L^6(\mathbb{R}^3, \mathrm{d}x)$. Therefore, $\psi \in L^4(\mathbb{R}^3, \mathrm{d}x) \cap L^6(\mathbb{R}^3, \mathrm{d}x)$, i.e. $\psi^3 \in L^{4/3}(\mathbb{R}^3, \mathrm{d}x) \cap L^2(\mathbb{R}^3, \mathrm{d}x)$. On the other hand, $1/|x| \in L^2(\mathbb{R}^3, \mathrm{d}x) + L^4(\mathbb{R}^3, \mathrm{d}x)$. Thus, by Hölder's inequality, $\int \psi^3/|x|\,\mathrm{d}x < \infty$.

The rest of the proof is performed in two steps. We first prove that the functional $F(\psi)$ is decreasing under symmetric rearrangements. Then, it is enough to prove the bound (8) for non-increasing spherically symmetric functions. Finally, the cases of equality will be clear from our proof.

First step. Here we state a few necessary facts about the symmetric-decreasing rearrangement of a function. We follow the recent book by Lieb and Loss [6] (see section 3.3, pp 72ff) which we refer to for details. If $A \subset \mathbb{R}^3$ is a Borel set of finite Lebesgue measure, the set A^*, the symmetric rearrangement of the set A, is defined to be the open ball centred at the origin having the same volume as A. (All results quoted below hold good in all dimensions; because of our functional, here we have restricted ourselves to only $\mathbb{R}^3$.) The symmetric-decreasing rearrangement of a characteristic function of a set is defined as $\chi_A^* \equiv \chi_{A^*}$. Now, if $f\colon \mathbb{R}^3 \to \mathbb{R}$ is a Borel measurable function vanishing at infinity (see [6]), the symmetric-decreasing rearrangement, f^*, of the function f is defined by

$$f^*(x) \equiv \int_0^\infty \chi^*_{\{|f|>t\}}(x)\,\mathrm{d}t.$$

The function f^* is radially symmetric and non-increasing as a function of $|x|$. There are three main properties of symmetric-decreasing rearrangements that we need here. The first one is that they preserve all the L^p norms. In particular, if $f \in L^4(\mathbb{R}^3)$,

$$\int f^4\,\mathrm{d}x = \int (f^*)^4\,\mathrm{d}x. \tag{11}$$

Since the function $1/|x|$ is a symmetric-decreasing one, it also follows from the general properties of symmetric-decreasing rearrangements that

$$\int \frac{f^3}{|x|}\,\mathrm{d}x \leqslant \int \frac{(f^*)^3}{|x|}\,\mathrm{d}x. \tag{12}$$

In fact, if g and h are non-negative functions in $\mathbb{R}^3$ (in general in $\mathbb{R}^N$ for that matter), vanishing at infinity,

$$\int gh\,\mathrm{d}x \leqslant \int g^*h^*\,\mathrm{d}x. \tag{13}$$

(see, e.g., [6], theorem 3.4). Taking g to be f^3 and $h = 1/|x| = h^*$, (12) follows. Finally, if f is such that $\nabla f \in L^2(\mathbb{R}^3, \mathrm{d}x)$, then

$$\int (\nabla f)^2\,\mathrm{d}x \geqslant \int (\nabla f^*)^2\,\mathrm{d}x \tag{14}$$

(see, e.g., [6], lemma 7.17).

It follows immediately from (8), and the properties of the symmetric-decreasing rearrangements embodied in (11), (12), and (14), that

$$F(\psi) \geqslant F(\psi^*) \tag{15}$$

for any $\psi \in \mathcal{D}$, which concludes the first step of our proof.

Second step. We may consider now non-zero radially symmetric functions $\psi(r)$, with non-positive derivative, where $r = |x|$. Denoting $\psi'(r) = \mathrm{d}\psi/\mathrm{d}r$, we can write

$$F(\psi) = \frac{a^2\int_0^\infty (\psi')^2 r^2\,\mathrm{d}r + b^2\int_0^\infty \psi^4 r^2\,\mathrm{d}r}{\alpha\int_0^\infty \psi^3 r\,\mathrm{d}r} \tag{16}$$

for radially symmetric functions in $\mathcal{D}$. After an integration by parts, we obtain

$$\int_0^\infty (\psi)^3 r\,\mathrm{d}r = -\frac{3}{2}\int_0^\infty (\psi)^2\psi' r^2\,\mathrm{d}r = \frac{3}{4ab}\int_0^\infty (-2ab\psi^2\psi')r^2\,\mathrm{d}r. \tag{17}$$

Finally, (10) follows from (16), (17) and

$$-2ab\psi^2\psi' \leqslant a^2(\psi')^2 + b^2\psi^4. \tag{18}$$

The case of equality in (10) is obtained if and only if $a\psi' = -b\psi^2$. Integrating the last equation, we get the equality in (10) if and only if

$$\psi = \bar{\psi}(r) = \frac{a}{b}\frac{1}{r+K} \tag{19}$$

for any positive constant K. □

Given the result of the previous lemma, it is straightforward to prove theorem 1.

Proof (Proof of theorem 1)**.** Setting $\rho = \psi^3 \geqslant 0$ in (6), we get

$$J(\psi) \equiv \xi(\rho) = a^2\int(\nabla\psi)^2\,\mathrm{d}x + b^2\int \psi^4\,\mathrm{d}x - \alpha z\int\frac{\psi^3}{|x|}\,\mathrm{d}x + \frac{\alpha}{2}\int\frac{\psi^3(x)\psi^3(y)}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y. \tag{20}$$

Evaluating $J(\psi)$ for $\psi(x)$ given by (19) (i.e. for the function that minimizes $F(\psi)$), we get

$$J(\bar{\psi}) = \frac{2\pi}{K}\frac{a^3}{b^3}\left(\frac{4}{3}ab - \alpha z + \frac{7}{6}\pi\alpha\left(\frac{a}{b}\right)^3\right). \tag{21}$$

If $z > 4ab/(3\alpha) + (7\pi/6)(a/b)^3$, letting $K \to 0$ in (21), we obtain

$$\inf J(\psi) = \lim_{K\to 0} J(\bar{\psi}) = -\infty \tag{22}$$

i.e. the atom is *unstable*. On the other hand, if $z < \frac{4ab}{3\alpha}$, by lemma 1, we have $J(\psi) \geqslant 0$ for all ψ, i.e. the atom is *stable*. In fact,

$$\inf J(\psi) = \lim_{K\to\infty} J(\bar{\psi}) = 0 \tag{23}$$

in this case. □

3. Molecular case

Lemma 1 is also useful for obtaining estimates of the nuclear charges of a molecule (i.e. the z_i' in (2)) that ensure its stability. As we showed in the proof of lemma 1, $\psi \in \mathcal{D}$ implies $\psi^3 \in L^{4/3}(\mathbb{R}^3, \mathrm{d}x) \cap L^2(\mathbb{R}^3, \mathrm{d}x)$. Since V, given by (2), belongs to $L^2(\mathbb{R}^3, \mathrm{d}x) + L^4(\mathbb{R}^3, \mathrm{d}x)$, using Hölder's inequality we have $\int V(x)\psi^3\,\mathrm{d}x < \infty$. It follows from (13) that

$$\int V\psi^3\,\mathrm{d}x \leqslant \int V^*(\psi^3)^*\,\mathrm{d}x = \int V^*(\psi^*)^3\,\mathrm{d}x. \tag{24}$$

The symmetric-decreasing rearrangement of V is just $V^*(x) = Z\alpha/|x|$, where $Z = \sum_{i=1}^k z_i$. Thus, from (24) and lemma 1, we have

$$\int V\psi^3\,\mathrm{d}x \leqslant \frac{3\alpha}{4ab}\left(a^2\int(\nabla\psi)^2\,\mathrm{d}x + b^2\int\psi^4\,\mathrm{d}x\right) \tag{25}$$

for all $\psi \in \mathcal{D}$. Setting $\rho = \psi^3 \geqslant 0$ in (1), it follows immediately from (25) that

$$\xi(\rho) \geqslant 0 \tag{26}$$

if

$$Z = \sum_{i=1}^k z_i \leqslant \frac{4ab}{3\alpha}. \tag{27}$$

Hence the molecule in the ultrarelativistic TFW model is stable for these values of Z. As in the atomic case we can show in fact that $\inf \xi(\rho) = 0$. For this purpose, we take $\bar\psi(r)$, given by (19), as a trial function. A straightforward computation gives

$$\xi(\bar\psi^3) = \frac{2\pi}{K}\frac{a^3}{b^3}\left(\frac{4}{3}ab - \alpha\sum_{i=1}^k z_i f\left(\frac{R_i}{K}\right) + \frac{7}{6}\pi\alpha\left(\frac{a}{b}\right)^3\right) \tag{28}$$

where

$$f(u) \equiv \frac{2}{u}\log(1+u) - \frac{1}{1+u}. \tag{29}$$

For the last computation note that

$$\int\frac{\bar\psi^3(x)}{|x-R_i|}\,\mathrm{d}x = \frac{a^3}{b^3}\int_0^\infty\frac{r^2\,\mathrm{d}r}{(r+K)^3}\int\frac{\mathrm{d}\Omega}{|x-R_i|} = \frac{2\pi}{K}\frac{a^3}{b^3}f\left(\frac{R_i}{K}\right),$$

where we have used Newton's theorem,

$$\frac{1}{4\pi}\int\frac{\mathrm{d}\Omega(x)}{|x-y|} = \frac{1}{\max(|x|,|y|)}.$$

For $u \geqslant 0$, $0 \leqslant f(u) \leqslant 1$. Moreover, $\lim_{u\to 0} f(u) = 1$. Hence, from (28) we get

$$\inf\xi(\rho) = \lim_{K\to\infty}\xi(\bar\psi^3) = 0 \tag{30}$$

whenever Z satisfies (27). We have thus proved the following stability condition for molecules.

Theorem 2. *Let*

$$\xi(\rho) = a^2\int(\nabla\rho^{1/3})^2\,\mathrm{d}x + b^2\int\rho^{4/3}\,\mathrm{d}x - \int V\rho\,\mathrm{d}x + D(\rho,\rho) \tag{31}$$

with V given by (2) and $D(\rho,\rho)$ given by (3). Then

$$\inf\xi(\rho) = 0 \qquad \textit{if} \quad Z = \sum_{i=1}^k z_i \leqslant \frac{4ab}{3\alpha} \tag{32}$$

where the infimum is taken over all non-negative functions $\rho(x)$ such that $\rho \in L^{4/3}(\mathbb{R}^3)$, $\nabla\rho^{1/3} \in L^2(\mathbb{R}^3)$ and $D(\rho,\rho) < \infty$.

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