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Asymptotic Behavior of the Ground State of Large Atoms

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Abstract

We review some results on the behavior of the ground state energy and the ground state density for large atoms as the nuclear charge Z increases to infinity. Here the atom is described by various models, namely the Thomas-Fermi, the Thomas-Fermi-Weizsäcker, the Fermi-Hellmann, the Hellmann-Weizsäcker model, and the Schrödinger equation.

1 Introduction

The following results for large atoms, i.e., for large nuclear charge Z and large electron number N keeping the ratio Z/N = \( \alpha \) fixed, shall be presented:

• Asymptotic behavior of the ground state energy,
• Bounds on the excess charge,
• Asymptotic behavior of the ground state density.

The results will be presented in the context of the following models ordered roughly according to increasing complexity:

1. The Thomas-Fermi model (Thomas [20], Fermi [7, 6]):

\[
E_{TF}(\rho) = \int \frac{3}{5} \left( \frac{6\pi^2}{q} \right)^{2/3} \rho(r)^{5/3} - \frac{Z}{|r|} \rho(r) + \frac{1}{2}(\rho \ast \frac{1}{|.|})(r) \rho(r) \, d^3r \tag{1}
\]

\[
\rho \geq 0, \quad \int \rho \leq N, \tag{2}
\]

\( q \) being the number of spin states of one electron, i.e., \( q = 2 \).
2. The Thomas-Fermi-Weizsäcker model (von Weizsäcker [21]):

\[ E_{TFW}(\rho) = \int (\nabla \sqrt{\rho(r)})^2 + E_{TF}(\rho) \]  \hspace{1cm} (3)

with the conditions (2).

3. The Fermi-Hellmann model (Fermi [7], Hellmann [8]):

\[ E_{F}(\rho) = \sum_{l=0}^{\infty} \int_{0}^{\infty} \frac{3}{5} \left( \frac{\pi}{2(q + \frac{1}{2})} \right)^2 \rho_l(r)^3 + \left( \frac{(l + \frac{1}{2})^2}{r^2} - \frac{Z}{r} \right) \rho_l(r) dr \]

\[ + \frac{1}{2} \sum_{l,l'=0}^{\infty} \int_{0}^{\infty} \int_{0}^{\infty} \frac{\rho_l(r) \rho_{l'}(r')}{\max\{r, r'\}} dr dr', \]  \hspace{1cm} (4)

\[ \rho_l \geq 0, \sum_{l=0}^{\infty} \int_{0}^{\infty} \rho_l(r) dr \leq N. \]  \hspace{1cm} (5)

4. The Hellmann-Weizsäcker model (Hellmann [8])

\[ E_{HW}(\rho) = \sum_{l=0}^{\infty} \int_{0}^{\infty} \sqrt{\rho_l} \rho_l - \frac{1}{4r^2} \rho_l dr + E_{F}(\rho) \]  \hspace{1cm} (6)

with condition (5).

5. The Schrödinger model

\[ E_Q(Z, N) = \inf\{ (\psi, H \psi) | \psi \in Q(H), ||\psi|| = 1 \} \]  \hspace{1cm} (7)

where

\[ H = \sum_{i=1}^{N} \left( -\Delta_i - \frac{Z}{|r_i|} \right) + \sum_{i,j=1}^{N} \frac{1}{|r_i - r_j|} \]  \hspace{1cm} (8)

as self-adjoint realization on \( L^2(\mathbb{R}^3) \otimes \mathcal{C}^q \).

We remark that basic properties of the first four models – such as existence of minimizers in suitable functions spaces – are well known (Lieb [12] and Siedentop and Weikard [15]). – We shall mention some more results for the models 1, 2, 4, and 5 but shall concentrate mainly on the Fermi-Hellmann equations.

2 Asymptotic Behavior of the Ground State Energy

Denote the infima of the functionals by roman \( E \) – the functionals are denoted by calligraphic \( \mathcal{E} \). With this notation we can formulate the following results:
1. 

\[ E_{TF}(Z, N) = E_{TF}(1, \alpha) Z^{7/3} \]  

where \( \alpha = Z/N \). This is immediate by scaling, i.e., choosing \( \rho(r) = Z^2 \rho_1(Z^{1/3}r) \) in (1) (Fermi [6]). In particular, the Thomas-Fermi energy behaves exactly proportional to \( Z^{7/3} \), if \( \alpha \) is fixed.

2. 

\[ E_{TFW}(Z, N) = E_{TF}(Z, N) + DZ^2 + o(Z^2) \]  

for fixed \( \alpha \) where \( D = \frac{2}{3\pi^2}I_1 \) and \( I_1 = \int (\nabla \psi)^2 \approx 8.583897 \), \( \psi \) being the positive solution of

\[ \left(-\Delta + \left(\frac{6\pi^2}{q}\right)^{2/3} |\psi|^{4/3} - |Z|^{-1}\right) \psi = 0 \]  

(Lieb [12]).

3. 

\[ E_H(Z, Z) = E_{TF}(Z, Z) + O(Z^{5/3}) \]  

(Siedentop and Weikard [17], Weikard [22]).

We indicate the proof of (12). To this end we observe some facts for the Fermi-Hellmann model: The minimizer of \( E_H \) fulfills the Euler-Lagrange equation

\[ \rho_l(r) = \frac{2q(l + \frac{1}{2})}{\pi} \left[ \varphi(r) - \frac{(l + \frac{1}{2})^2}{r^2} \right]^{1/2} \quad l = 0, 1, 2, ... \]  

\[ \varphi(r) = \frac{Z}{r} - \sum_{l=0}^{\infty} \int_0^{\infty} \frac{\rho_l(r')}{\max\{r, r'} dr'. \]  

Moreover by Legendre transform the dual variational principle of the Hellmann principle is

\[ F_H^H(\psi) = -\frac{1}{2} \int_0^{\infty} (r \psi)^2 dr - \frac{2}{3} \sum_{l=0}^{\infty} \frac{2q(l + \frac{1}{2})}{\pi} \int_0^{\infty} \left[ \varphi(r) - \frac{(l + \frac{1}{2})^2}{r^2} + \mu \right]^{3/2} dr \]

with \((r \psi)' \in L^2(\mathbb{R}^+), r \psi(r) \to Z \) for \( Z \to 0 \), and \( \psi(r) = O(1/r) \) as \( r \to \infty \).

For the supremum \( F_H(Z, \mu) \) of this functional we have

\[ F_H(Z, \mu) + \mu N = E_H(Z, N); \]  

\[ N = \sum_{l=0}^{\infty} \frac{2q(l + \frac{1}{2})}{\pi} \int_0^{\infty} \left[ \varphi_{\max}(r) - \frac{(l + \frac{1}{2})^2}{r^2} + \mu \right]^{1/2} dr, \]

where \( \varphi_{\max} \) is the maximizer of (15).
For the proof of (12) one chooses

\[ \psi(r) = \varphi_{TF}(r) = \frac{Z}{r} - \int_0^\infty \frac{\rho_{TF}(r')}{|r - r'|} d^3 r' \quad (17) \]

for the lower bound, where \( \rho_{TF} \) is the minimizer of \( E_{TF} \), in the lower bound and \( \rho_l \) as in (13) substituting \( \varphi \), however, by \( \varphi_{TF} \). The result follows then from the fact that the minimizer of \( E_H \) has always particle number \( \int_0^\infty \sum_{i=0}^\infty \rho_i(r) dr \) smaller than \( Z \) (see Section 3), i.e., we use allowed trial functions, and the explicit summation over the angular momenta \( I \). This may be done by Poisson summation or more directly by using a convexity argument (see equation (39) for a similar result).

4. \( E_{HW}(Z, Z) = E_{TF}(Z, Z) + O(Z^2) \) (Siedentop and Weikard [18, 17, 16]).

5. \( E_Q(Z, N) = E_{TF}(Z, N) + \frac{9}{8} Z^2 + O(Z^{47/24}) \) (19)

where \( Z/N = \alpha \) is fixed.

This has been conjectured by Scott [14]. The first term was established by Lieb and Simon [13]. The proof of (19) has been given by Siedentop and Weikard [17, 16] (see also Hughes [9] for the lower bound) for the neutral case and has been extended to general \( \alpha \) by Bach [1].

We wish to outline the proof for \( Z = N \). A lower bound may be obtained by an estimate on the indirect part of the Coulomb energy (Lieb [11]). It turns out that

\[ E_Q(Z, Z) \geq Z^{4/3} \inf \sigma \left( \sum_{i=1}^N h_{TF,i} \right) - \frac{1}{2} \int \rho_{TF} \star |\cdot|^{-1}(r) \rho_{TF}(r) d^3 r + O(Z^{5/3}) \quad (20) \]

\[ h_{TF,i} = 1 \otimes \ldots \otimes 1 \otimes h_{TF} \otimes 1 \otimes \ldots \otimes 1 \]

\[ h_{TF} = -Z^{-2/3} \Delta + \varphi_{TF,1} \quad (21) \]

where \( \varphi_{TF,1} \) is the Thomas-Fermi potential (17), however for \( Z = 1 \). Thus the first summand on the right hand side of (20) may be estimated from below by \( Z^{4/3} \) times the sum of all negative eigenvalues of \( h_{TF} \). We observe that (21) can be broken up into a set of uncoupled ordinary differential equations (decomposion into angular momentum channels). A carefull WKB analysis for high angular momenta and summing up the “bare” Coulomb eigenvalues for low angular momenta yields the answer up to errors of order \( Z^{17/9} \log Z \).
The upper bound may be obtained by choosing an appropriate "trial" operator 
\[ d_1 \]
\[ 0 \leq d_1 \leq 1, \quad d_1 \in \mathcal{I}_1(L^2(\mathbb{R}^3) \otimes \mathbb{C}^4), \quad \text{tr} d_1 \leq N, \quad (22) \]
a so called one-particle density matrix in the inequality
\[ E_Q(Z, N) \leq \text{tr} [ (-\Delta - Z/|.| + \frac{1}{2} V) d_1 ] \quad (23) \]
where \( V = \rho^{\ast} |.|^{-1} \), \( \rho \) being the density of \( d_1 \), i.e., formally \( \rho(r) = \sum_{\sigma=1}^{q} d_1(r, \sigma, r, \sigma) \).
After some intermediate steps one obtains
\[ E_Q(Z, Z) \leq E_H(\rho) + \frac{q}{8} Z^2 + O(Z^{47/24}). \quad (24) \]
Equation (12) completes the proof.

3 Bounds on the Excess Charge

Let \( E \) denote any of the above energies
\[ N_c = \inf \{ N | E(Z, N) = E(Z, N + k) \text{ for all } k \in \mathbb{N} \} \quad (25) \]
The maximal excess charge is then \( Q_c = N_c - Z \). It may be easily shown that \( Q_c \) is nonnegative in all of the above models. In the following we wish to discuss some upper bounds on \( Q_c \).

- The Thomas-Fermi and Fermi-Hellmann model:
\[ Q_c^{TF} = Q_c^H = 0 \]
(Lieb and Simon [13], Siedentop and Weikard [15]). Here we indicate the proof of this result for the Fermi-Hellmann case. Let \( \rho_1, \rho_2, \ldots \) be the absolute minimizer of the Fermi-Hellmann functional. Assume \( N_c < Z \). Then
\[ Z > N_c = \int_0^\infty \sum_{l=0}^{\infty} \rho_l(r) dr = \sum_{l=0}^{\infty} \frac{q 2 (l + 1/2)}{\pi} \int_0^\infty \left[ \varphi(r) - \frac{(l + 1/2)^2}{r^2} \right]_+^1 dr \]
\[ \geq \frac{q}{\pi} \int_0^\infty \left[ \frac{Z - N_c}{r} - \frac{1}{4r^2} \right]_+^1 dr = \infty \quad (26) \]
which is a contradiction. On the other hand assume \( N_c > Z \). Then there is an \( R \) such that \( \varphi(r) < 0 \) for \( r > R \). Then \( (r \varphi)'' = 0 \) in this region, i.e., \( \varphi(r) = a + \frac{b}{r} \).
Since \( \varphi(\infty) = 0 \) the constant \( a \) is zero and \( b \) negative. Because of the continuity of \( \varphi \), \( \varphi(r) < 0 \) on \( \mathbb{R}^+ \) which cannot hold. The Thomas-Fermi case can be treated analogously.
• For the Thomas-Fermi-Weizsäcker model one has

\[ Q_{c}^{TFW} \leq 178.03 \frac{q}{6\pi^2} \]  

(Benguria and Lieb [3], Solovej [19]) This bound is obtained by an universal (\( Z \) independent) bound on the potential and a bound on the density in terms of the potential.

• In the quantum mechanical case the following bounds are known

\[ Q_{c}^{q} \leq Z \]  

(Lieb [10]) and

\[ Q_{c}^{q} = O(Z^{47/56}) \]  

(Fefferman and Seco [5, 4]). The proof of (29) uses (19) together with the fact that the nucleus is screened out already at small distances.

4 Asymptotic Behavior of the Ground State Density

Let \( d = \frac{18\pi}{q} \). Then:

• Thomas-Fermi model:

\[ \varphi_{TF}^{Z}(r) \leq \min\left\{ \frac{d^2}{r^4}, \frac{Z}{r}\right\} \]  

(30)

for \( Z, r > 0 \), where \( \varphi_{TF}^{Z} \) is the Thomas-Fermi potential for charge \( Z \). Moreover, \( \varphi_{TF}^{Z} \) is monotone in \( Z \) and the limiting function is

\[ \varphi_{TF}^{\infty}(r) = \frac{d^2}{r^4} \]  

This follows immediately from comparison arguments.

• Thomas-Fermi-Weizsäcker model:

In this subsection we use units such that the constant in front of the \( \rho^{5/3} \) term in (3) is 3/5.

\[ \varphi_{TFW}^{Z}(r) \leq \chi(\alpha)r^{-4} + \frac{\pi^2}{\alpha^2}r^{-2} \]  

(32)

where \( \chi \) is given as

\[ \chi(\alpha) = \begin{cases} 
9\pi^{-2} + c\alpha^{-4} & 0 \leq \alpha \leq \alpha_0 \\
25\pi^{-25}(1 - \alpha)^{-4} & \alpha_0 < \alpha < 1 
\end{cases} \]
and \((C, \alpha_0)\) is chosen such that \(\chi\) is \(C^1([0,1])\) and \(\tau = \frac{1}{2} + \frac{\sqrt{3}}{2}\). (Benguria and Lieb [3], Solovej [19])

\[
\varphi_{TFW}^\beta(r) \to \varphi_{TFW}^\infty(r)
\]

and

\[
\varphi_{TFW}^\infty(r) = 9\pi^{-2}r^{-4} - \frac{27}{4} r^{-2} - \frac{25}{64} \pi^2 - \frac{37}{768} \pi^4 r^2 + O(r^{-1+\sqrt{3}/2}).
\]

Solovej obtains also the corresponding limit for the density.

- Fermi-Hellmann model:
  The following results are from Bach and Siedentop [2].

\[
\varphi_H^\beta(r) \leq \min \left\{ \frac{Z}{r}, \left( \frac{d}{r^2} + \frac{1}{2r} \right)^2 \right\}
\]

There exists some \(R\) such that for \(r \geq R\) we have

\[
\varphi_H^\beta(r) \geq \frac{1}{4r^2}.
\]

\(\varphi_H^\beta(r)\) is monotone increasing in \(Z\)

\[
\varphi_H^\infty(r) = \frac{d^2}{r^4} + O(r^{-5/2}) \quad \text{at 0},
\]

and

\[
\varphi_H^\infty(r) = \frac{1}{4r^2} + o(r^{-2}) \quad \text{at } \infty.
\]

The first inequality in (35) is immediate by writing \(\varphi_H^\beta\) in terms of \(\rho_i\). To prove the second inequality we use the following lemma

\[
-\frac{1}{3} \left( \eta - \frac{1}{4} \right)^{3/2} \leq \sum_{l=0}^\infty l(l+1/2) \left[ 1 - (\eta(l+1/2))^2 \right]^{1/2} \eta \leq 5/4 \eta^{3/2} \quad (39)
\]

The proof of (39) uses convexity of \(z(1-x)_{+}^{1/2}\) for \(0 \leq x \leq 1\) and a careful estimate of the error term arising at 0 and 1. (39) yields the following differential inequality for the solution \(\varphi\) of (5)

\[
-\frac{1}{r} (r \varphi)^{''} + \frac{2q}{3\pi} \rho^{3/2} - \frac{1}{3} r^{-1/2} \rho^{3/4} \left( 1 - \frac{r \rho^{1/2}}{4} \right)_{+}
\]

\[
\leq -\frac{1}{r} (r \varphi)^{''} + \sum_{l=0}^\infty \frac{q(2l+1)}{\pi r^2} \left( \varphi(r) - \frac{(l+1/2)^2}{r^2} \right)_{+}^{1/2}
\]

\[
\leq -\frac{1}{r} (r \varphi)^{''} + \frac{2q}{3\pi} \rho^{3/2} + \frac{5}{4} r^{-1/2} \rho^{3/4}
\]
This allows the second function of the right hand side of (35) as comparison function, which proves (35).

The monotonicity of $\varphi_Z$ in $Z$ is immediate by comparison. The convergence of $\varphi_Z$ to $\varphi_\infty$ follows also immediately.

To obtain (37) we use the comparison function

$$\frac{1}{dr} + \frac{2d^{1/2}}{r^{5/2}} + \frac{d^2}{r^4}$$

with $c = \left[\frac{27}{38} + \left(\frac{27}{38} - \frac{2}{9}\right)^{1/2}\right]$ for the bound from above and

$$\varphi_{TF}(r) - \frac{5}{4}r^{-5/2} \left(d + \frac{r}{2}\right)^{1/2}$$

as the comparison function from below. By the limiting function for the Thomas-Fermi model (31) the equation (37) follows. Equation (38) follows from (35) and the following observations. Suppose there was a radius $R$ such that $\varphi(r) = 0$ for $r$ bigger than $R$. Denote by $R$ the minimum over all such $R$. Since

$$\varphi(r) = \frac{Z}{r} - \int_0^\infty \frac{\sum_{i=0}^{\infty} \rho_i(r')}{\max\{r, r'\}} dr'$$

$\varphi(R) = 0$. Because of the continuity of $\varphi$ we can choose a $\delta$ such that for all $x$ with $|x - R| < \delta$, $|\varphi(x)| < 1/8R^2$ holds. Thus $\rho_0, \rho_1, \ldots$ is zero also to the left of $R$, which is a contradiction. Thus there exists a sequence $r_n$ such that $r_n \to \infty$ and $\varphi(r_n) \geq 1/4r_n^2$. Now use a comparison between $r_n$ and $r_{n+1}$ with comparison function $1/4r^2$ to obtain the result.

- The Schrödinger equation

Let $\rho_Q$ be the ground state density, i.e.,

$$\rho_Q^Z(r) = N \int dr_1^3 \ldots dr_N^3 \sum_{\sigma_1, \ldots, \sigma_N=1}^{q} |\psi_Z(r, \sigma_1, r_2, \sigma_2, \ldots, r_N, \sigma_N)|^2$$

where $\psi_Z$ is the ground state of (8). Let $\rho_{TF}$ be the Thomas-Fermi density for charge 1, $\Omega$ a measurable set in $IR^3$. Then

$$\int_\Omega Z^{-2} \rho_Q^Z(Z^{-1/3}r) d^3r \to \int_\Omega \rho_{TF}(r) d^3r$$

holds (Lieb and Simon [13]).
References


