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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 exececss 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]):

$$\mathcal{E}_{TF}(\rho) = \int \frac{3}{5}(\frac{6\pi^2}{q})^{2/3}\rho(r)^{5/3} - \frac{Z}{|r|}\rho(r) + \frac{1}{2}(\rho * \frac{1}{|.|})(r)\rho(r)d^3r \tag{1}$$

$$\rho \geq 0, \int \rho \leq N, \tag{2}$$

q being the number of spin states of one electron, i.e., q=2.

2. The Thomas-Fermi-Weizsäcker model (von Weizsäcker [21]):

$$\mathcal{E}_{TFW}(\rho) = \int (\nabla\sqrt{\rho(r)})^2 + \mathcal{E}_{TF}(\rho) \tag{3}$$

with the conditions (2).

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

$$\begin{aligned}\mathcal{E}_H(\underline{\rho}) &= \sum_{l=0}^{\infty}\int_0^{\infty}\frac{3}{5}\left(\frac{\pi}{2(q+\frac{1}{2})}\right)^2\rho_l(r)^3 + \left(\frac{(l+\frac{1}{2})^2}{r^2}-\frac{Z}{r}\right)\rho_l(r)dr \\ &+\frac{1}{2}\sum_{l,l'=0}^{\infty}\int_0^{\infty}\int_0^{\infty}\frac{\rho_l(r)\rho_{l'}(r')}{\max\{r,r'\}}dr\,dr',\end{aligned} \tag{4}$$

$$\rho_l \geq 0,\ \sum_{l=0}^{\infty}\int_0^{\infty}\rho_l(r)dr \leq N. \tag{5}$$

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

$$\mathcal{E}_{HW}(\underline{\rho}) = \sum_{l=0}^{\infty}\int_0^{\infty}\sqrt{\rho_l}'^2 - \frac{1}{4r^2}\rho_l dr + \mathcal{E}_H(\underline{\rho})) \tag{6}$$

with condition (5).

5. The Schrödinger model

$$E_Q(Z,N) = \inf\{(\psi, H\psi)|\psi \in Q(H), ||\psi|| = 1\} \tag{7}$$

where

$$H = \sum_{i=1}^{N}\left(-\Delta_i - \frac{Z}{|\mathbf{r}_i|}\right) + \sum_{\substack{i,j=1\\ i<j}}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{8}$$

as self-adjoint realization on $\bigwedge_{i=1}^{N}(L^2(\mathbb{R}^3)\otimes\mathbb{C}^q)$.

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 caligraphic $\mathcal{E}$. With this notation we can formulate the following results:

1.

$$E_{TF}(Z,N) = E_{TF}(1,\alpha)Z^{7/3} \tag{9}$$

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 α is fixed.

2.

$$E_{TFW}(Z,N) = E_{TF}(Z,N) + DZ^2 + o(Z^2) \tag{10}$$

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

$$\left(-\Delta + \left(\frac{6\pi^2}{q}\right)^{2/3} |\psi|^{4/3} - Z|.|^{-1}\right)\psi = 0 \tag{11}$$

(Lieb [12]).

3.

$$E_H(Z,Z) = E_{TF}(Z,Z) + O(Z^{5/3}) \tag{12}$$

(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 $\mathcal{E}_H$ fulfills the Euler-Lagrange equation

$$\rho_l(r) = \frac{2q(l+\frac{1}{2})}{\pi}\left[\varphi(r) - \frac{(l+\frac{1}{2})^2}{r^2}\right]_+^{1/2} \qquad l = 0,1,2,\ldots \tag{13}$$

$$\varphi(r) = \frac{Z}{r} - \sum_{l=0}^{\infty}\int_0^\infty \frac{\rho_l(r')}{\max\{r,r'\}}dr'. \tag{14}$$

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

$$\mathcal{F}^H_{Z,\mu}(\psi) = -\frac{1}{2}\int_0^\infty (r\psi)'^2 dr - \frac{2}{3}\sum_{l=0}^{\infty}\frac{2q(l+\frac{1}{2})}{\pi}\int_0^\infty \left[\psi(r) - \frac{(l+\frac{1}{2})^2}{r^2} + \mu\right]_+^{3/2} dr \tag{15}$$

with $(r\psi)' \in L^2(I\!R^+)$, $r\psi(r) \to Z$ 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

$$F_H(Z,\mu) + \mu N = E_H(Z,N); \tag{16}$$

$$N = \sum_{l=0}\frac{q2(l+\frac{1}{2})}{\pi}\int_0^\infty \left[\psi_{max}(r) - \frac{(l+\frac{1}{2})^2}{r^2} + \mu\right]_+^{1/2} dr,$$

where ψ_{max} is the maximizer of (15).

For the proof of (12) one chooses

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

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

4.

$$E_{HW}(Z,Z) = E_{TF}(Z,Z) + O(Z^2) \tag{18}$$

(Siedentop and Weikard [18, 17, 16]).

5.

$$E_Q(Z,N) = E_{TF}(Z,N) + \frac{q}{8}Z^2 + O(Z^{47/24}) \tag{19}$$

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 α 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

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

$$h_{TF,i} = \underbrace{1 \otimes ... \otimes 1}_{i-1 \ factors} \otimes h_{TF} \otimes \underbrace{1 \otimes .... \otimes 1}_{N-i \ factors}$$

$$h_{TF} = -Z^{-2/3}\Delta + \varphi_{TF,1} \tag{21}$$

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 (decompositon 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

$$0 \leq d_1 \leq 1, \qquad d_1 \in \mathcal{I}_1(L^2(I\!R^3) \otimes \mathbb{C}^q), \qquad \operatorname{tr} d_1 \leq N, \tag{22}$$

a so called one-particle density matrix in the inequality

$$E_Q(Z,N) \leq \operatorname{tr}[(-\Delta - Z/|.| + \frac{1}{2}V)d_1] \tag{23}$$

where $V = \rho * |.|^{-1}$, ρ 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

$$E_Q(Z,Z) \leq \mathcal{E}_H(\underline{\rho}) + \frac{q}{8}Z^2 + O(Z^{47/24}). \tag{24}$$

Equation (12) completes the proof.

3 Bounds on the Excess Charge

Let E denote any of the above energies

$$N_c = \inf\{N | E(Z,N) = E(Z,N+k) \text{ for all } k \in I\!N\} \tag{25}$$

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 $N_c \leq Z$. Then

$$\begin{aligned} Z \;&>\; N_c = \int_0^\infty \sum_{l=0}^{\infty} \rho_l \, dr = \sum_{l=0}^{\infty} \frac{q2(l+1/2)}{\pi} \int_0^\infty \left[\varphi(r) - \frac{(l+1/2)^2}{r^2}\right]_+^{1/2} dr \\ &\geq\; \frac{q}{\pi} \int_0^\infty \left[\frac{Z-N_c}{r} - \frac{1}{4r^2}\right]_+^{1/2} dr = \infty \end{aligned} \tag{26}$$

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 φ, $\varphi(r) < 0$ on $I\!R^+$ which cannot hold. The Thomas-Fermi case can be treated analogously.

- For the Thomas-Fermi-Weizsäcker model one has

$$Q_c^{TFW} \leq 178.03 \frac{q}{6\pi^2} \tag{27}$$

(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

$$Q_c^q \leq Z \tag{28}$$

(Lieb [10]) and

$$Q_c^q = O(Z^{47/56}) \tag{29}$$

(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:

$$\varphi_{TF}^Z(r) \leq \min\{\frac{d^2}{r^4}, \frac{Z}{r}\} \tag{30}$$

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

$$\varphi_{TF}^\infty(r) = \frac{d^2}{r^4} \tag{31}$$

This follows immediatly 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.

$$\varphi_{TFW}^Z(r) \leq \chi(\alpha) r^{-4} + \frac{\pi^2}{\alpha^2} r^{-2} \tag{32}$$

where χ is given as

$$\chi(\alpha) = \begin{cases} 9\pi^{-2} + c\alpha^{\tau-4} & 0 \leq \alpha \leq \alpha_0 \\ 25\pi^{-25}(1-\alpha)^{-4} & \alpha_0 < \alpha < 1 \end{cases}$$

and (C,α_0) is choosen sucht that χ is $C^1([0,1))$ and $\tau = \frac{1}{2}+\frac{\sqrt{73}}{2}$. (Benguria and Lieb [3], Solovej [19])

$$\varphi^Z_{TFW}(r) \to \varphi^\infty_{TFW}(r) \tag{33}$$

and

$$\varphi^\infty_{TFW}(r) = 9\pi^{-2}r^{-4} - \frac{27}{4}r^{-2} - \frac{25}{64}\pi^2 - \frac{37}{768}\pi^4 r^2 + O(r^{-\frac{1}{2}+\frac{\sqrt{73}}{2}}). \tag{34}$$

Solovej obtains also the corresponding limit for the density.

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

$$\varphi^Z_H(r) \le \min\left\{\frac{Z}{r}, \left(\frac{d}{r^2}+\frac{1}{2r}\right)^2\right\} \tag{35}$$

There exists some R such that for $r \ge R$ we have

$$\varphi^Z_H(r) \ge \frac{1}{4r^2}. \tag{36}$$

$\varphi^Z_H(r)$ is monotone increasing in Z

$$\varphi^\infty_H(r) = \frac{d^2}{r^4} + O(r^{-5/2}) \qquad \text{at } 0, \tag{37}$$

and

$$\varphi^\infty_H(r) = \frac{1}{4r^2} + o(r^{-2}) \qquad \text{at } \infty. \tag{38}$$

The first inequality in (35) is immediate by writing φ^Z_H in terms of ρ_l. To prove the second inequality we use the following lemma

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

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

$$\begin{aligned} & -\frac{1}{r}(r\varphi)'' + \frac{2q}{3\pi}\varphi^{3/2} - \frac{1}{3}r^{-1/2}\varphi^{3/4}\left(1-\frac{r\varphi^{1/2}}{4}\right)_+ \\ \le\ & -\frac{1}{r}(r\varphi)'' + \sum_{l=0}^\infty \frac{q(2l+1)}{\pi r^2}\left(\varphi(r) - \frac{(l+\frac{1}{2})^2}{r^2}\right)^{1/2}_+ \\ \le\ & -\frac{1}{r}(r\varphi)'' + \frac{2q}{3\pi}\varphi^{3/2} + \frac{5}{4}r^{-1/2}\varphi^{3/4} \end{aligned} \tag{40}$$

This allows the second function of the right hand side of (35) as comparison function, which proves (35).

The monotonicity of φ_Z in Z is immediate by comparison. The convergence of φ_Z to φ_∞ follows also immediatly.

To obtain (37) we use the comparison function

$$\frac{1}{dr} + \frac{2d^{1/2}}{r^{5/2}} + \frac{d^2}{r^4} \tag{41}$$

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

$$\varphi_{TF}(r) - \frac{5}{4} r^{-5/2} \left(d + \frac{r}{2}\right)^{1/2} \tag{42}$$

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 $\sum_{l=0}^{\infty} \rho_l(r) = 0$ for r bigger than R. Denote by R the minimum over all such R. Since

$$\varphi(r) = \frac{Z}{r} - \int_0^\infty \frac{\sum_{l=0}^{\infty} \rho_l(r')}{\max\{r, r'\}} dr' \tag{43}$$

$\varphi(R) = 0$. Because of the continuity of φ we can choose a δ 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 ρ_Q be the ground state density, i.e.,

$$\rho_Q^Z(r) = N \int dr_1^3 \ldots dr_N^3 \sum_{\sigma_1, \ldots, \sigma_N = 1}^{q} |\psi_Z(r, \sigma_1, r_2, \sigma_2, \ldots, r_N, \sigma_N)|^2 \tag{44}$$

where ψ_Z is the ground state of (8). Let ρ_{TF} be the Thomas-Fermi density for charge 1, Ω a measurable set in $I\!R^3$. Then

$$\int_\Omega Z^{-2} \rho_Q^Z(Z^{-1/3} r)\, d^3r \to \int_\Omega \rho_{TF}(r) d^3r \tag{45}$$

holds (Lieb and Simon [13]).

References

[1] Volker Bach. A proof of Scott's conjecture for ions. *To be published*, 1989.

[2] Volker Bach and Heinz Siedentop. Universality of the Fermi-Hellmann model. *To be published*, 1989.

[3] Rafael Benguria and Elliott H. Lieb. The most negative ion in the Thomas-Fermi-von Weizsäcker theory of atoms and molecules. *J. Phys. B.*, 18:1054–1059, 1985.

[4] C. L. Fefferman and L. A. Seco. Asymptotic neutrality of large ions. *To Appear*, 1989.

[5] C. L. Fefferman and L. A. Seco. An upper bound for the number of electrons in a large ion. *Proc. Nat. Acad. Sci. USA*, 86:3464–3465, 1989.

[6] E. Fermi. Eine statistische Begründung zur Bestimmung einiger Eigenschaften des Atoms und ihre Anwendungen auf die Theorie des periodischen Systems der Elemente. *Z. Phys.*, 48:73–79, 1928.

[7] E. Fermi. Un metoda statistico per la determinazione di alcune proprietà dell'atomo. *Atti Reale Accademia Nazionale Dei Lincei, Rendiconti, Classe di Scienza fisiche, matematiche e naturali*, 6:602–607, 1927.

[8] Heinrich Hellmann. Ein kombiniertes Näherungsvefahren zur Energieberechnung im Vielelktronenproblem. II. *Acta Pysicochim. U.S.S.R.*, 4:225–244, 1936.

[9] Webster Hughes. *An Atomic Energy Lower Bound that Gives Scott's Correction.* PhD thesis, Princeton, Department of Mathematics, 1986.

[10] Elliott H. Lieb. Bound on the maximum negative ionization of atoms and molecules. *Phys. Rev. A*, 29(6):3018–3028, June 1984.

[11] Elliott H. Lieb. A lower bound for Coulomb energies. *Phys. Lett.*, 70A:444–446, 1979.

[12] Elliott H. Lieb. Thomas-Fermi and related theories of atoms and molecules. *Rev. Mod. Phys.*, 53:603–604, 1981.

[13] Elliott H. Lieb and Barry Simon. The Thomas-Fermi theory of atoms, molecules and solids. *Adv. Math.*, 23:22–116, 1977.

[14] J. M. C. Scott. The binding energy of the Thomas-Fermi atom. *Phil. Mag.*, 43:859–867, 1952.

[15] Heinz Siedentop and Rudi Weikard. On some basic properties of density functionals for angular momentum channels. *Rep. Math. Phys.*, 28:193–218, 1986.

[16] Heinz Siedentop and Rudi Weikard. On the leading correction of the Thomas-Fermi model: lower bound – with an appendix by A. M. K. Müller. *To appear in Invent. Math.*, 1988.

[17] Heinz Siedentop and Rudi Weikard. On the leading energy correction for the statistical model of the atom: interacting case. *Commun. Math. Phys.*, 112:471–490, 1987.

[18] Heinz K. H. Siedentop and Rudi Weikard. *On the Behavior of the Infimum of the Hellmann-Weizsäcker Functional.* Technical Report, Institut für Mathematische Physik, Carolo-Wilhelmina, 3300 Braunschweig, Federal Republic of Germany, 1986.

[19] Jan Philip Solovej. *Universality in the Thomas-Fermi-von Weizsäcker Model of Atoms and Molecules.* PhD thesis, Princeton, Department of Mathematics, 1989.

[20] L. H. Thomas. The calculation of atomic fields. *Proc. Camb. Phil. Soc.*, 23:542–548, 1927.

[21] C. F. von Weizsäcker. Zur Theorie der Kernmassen. *Z. Phys.*, 96:431–458, 1935.

[22] Rudi Weikard. *Hellmann- und Hellmann-Weizsäcker-Funktionale.* PhD thesis, TU Carolo-Wilhelmina Braunschweig, Naturwissenschaftliche Fakultät, 1987.