Commun. Math. Phys. 79, 1–7 (1981)

Communications in Mathematical Physics

A Lower Bound with the best Possible Constant for Coulomb Hamiltonians*

W. Thirring
Institut für Theoretische Physik, Universität Wien, A-1090 Wien, Österreich

The reason for stability of matter with Coulomb interactions has become more transparent once it was recognized that the no-binding Theorem of Thomas–Fermi (TF) theory is the key to the problem. In fact, in [1] it was conjectured that TF-theory always gives a lower bound to the ground state energies of Coulomb systems. Unfortunately one inequality on which this conjecture is based has resisted all attempts of proof or disproof. On the other hand one knows that for large nuclear charges Z TF-theory becomes exact and one could hope that at least for large Z the TF-energy is a lower bound. More precisely the question is the following. Suppose we have a neutral system, M nuclei with charges Z, $N = MZ$ electrons. For the ground state energy $E(M, Z)$ one knows [4]

$$\lim_{Z\to\infty} E(M, Z)/Z^{7/3} = -M\varepsilon_{\mathrm{TF}}$$

where

$$\varepsilon_{\mathrm{TF}} = 0.77\, me^4/\hbar^2 = 0.385 \text{ in our units with } 2m = e = \hbar = 1.$$

For stability of matter one considers the other limit $M \to \infty$, $Z =$ fixed. In ref. [1]

$$E(M, Z) \geqq -(4\pi)^{2/3} M\varepsilon_{\mathrm{TF}} Z^{7/3}\,(1 + O(Z^{-2/3}))$$

was proved. (The value $(4\pi)^{2/3}$ was subsequently improved to $(4\pi)^{2/3}/1.5$ [2].) In this note we shall produce a family of inequalities which among other things imply

$$E(M, Z) \geqq -M\varepsilon_{\mathrm{TF}} Z^{7/3}(1 + O(Z^{-2/33})).$$

Thus the constant in front is the best possible, the correction $O(Z^{-2/33})$ is probably not.

Our general strategy is to split the Coulomb potential into a regularized long-range part v_r and a short-range singular part v_s

$$\frac{1}{r} = v_r(r) + v_s(r), \quad v_r = g^2 * \frac{1}{r} * g^2, \quad g^2(x) = e^{-\mu r}\frac{\mu^3}{8\pi} \tag{1}$$

* Work supported in part by Fonds zur Förderung der wissenschaftlichen Forschung in Österreich, Project No. 3569

0010-3616/81/0079/0001/$01.40

For v_r the classical bound with $\varepsilon_{\mathrm{TF}}$ will hold for $Z \to \infty$ whereas the corrections due to v_s go with a lower power of Z. We keep the notation of [1] ($x_i, p_i, \sigma_i =$ coordinate and momentum and spin of the i-th electron, $R_k, Z_k =$ coordinate and charge of the k-th nucleus) but study the family of Hamiltonians

$$H(\alpha) = \sum_i p_i^2 - \sum_{i,k} Z_k(|x_i - R_k|^{-1} + (\alpha - 1)v_s(x_i - R_k)) + \sum_{i>j} (|x_i - x_j|^{-1} + (\alpha - 1)v_s(x_i - x_j)) + \sum_{k>m} Z_k Z_m(|R_k - R_m|^{-1} + (\alpha - 1)v_s(R_k - R_m)). \tag{2}$$

We are actually interested in $H(1)$ and shall use the concavity of the ground state energy [3] $E(\alpha)$ of $H(\alpha)$ in the form

$$E(1) \geqq E(0) + \alpha^{-1}(E(\alpha) - E(0)) \quad \forall \alpha \geqq 1. \tag{3}$$

1. The No-Binding Theorem

For our estimates we shall need the no-binding theorem of TF-theory with Yukawa potentials $e^{-\mu r}/r$. The proof for $\mu > 0$ proceed exactly as for $\mu = 0$[4], the subharmonicity argument being also applicable [5] since $\Delta e^{-\mu r}/r + 4\pi\delta(x) = \mu^2 e^{-\mu r}/r > 0$. The theorem states that the TF-energy is always above the sum of the energies of the isolated atoms and reads in formulae

$$\frac{3\gamma}{5}\int d^3x n^{5/3}(x) - \sum_{k=1}^{M} Z_k \int \frac{d^3x e^{-\mu|x-R_k|}}{|x - R_k|} n(x) + \tfrac{1}{2}\int \frac{d^3x d^3y}{|x-y|} e^{-\mu|x-y|} \cdot n(x)n(y) + \sum_{k>m} Z_k Z_m \frac{e^{-\mu|R_k - R_m|}}{|R_k - R_m|} \geqq - \sum_{k=1}^{M} \varepsilon(\mu, \gamma, Z_k) \tag{4}$$

where

$$-\varepsilon(\mu, \gamma, Z) = \inf_n \left\{ \gamma\frac{3}{5}\int d^3x n^{5/3}(x) - Z\int \frac{d^3x}{|x|} e^{-\mu|x|} n(x) + \frac{1}{2}\int \frac{d^3x d^3y}{|x-y|} e^{-\mu|x-y|} \cdot n(x)n(y) \right\}.$$

By scaling one sees that ε involves only an unknown function of one variable,

$\varepsilon(\mu, \gamma, Z) = \gamma^6 \mu^7 f\left(\dfrac{Z}{\gamma^3\mu^3}\right)$ and TF-theory tells us

$$\varepsilon(0, \gamma, 1) = \frac{1}{\gamma}\varepsilon_{\mathrm{TF}}(3\pi^2)^{2/3} = 3.68/\gamma. \tag{5}$$

$^{+)}$ We adopt the usual mathematical conventions:

$*$ = convolution $(f * g)(x) = \int d^3x' f(x - x')g(x')$,

$\| \|_p = p$-Norm: $\|f\|_p = [\int d^3x |f(x)|^p]^{1/p}$, $L^p = \{f : \|f\|_p < \infty\}$

$|f|_- =$ negative part: $|f|_- = \begin{matrix} -f \text{ where } f \leqq 0 \\ 0 \text{ otherwise} \end{matrix}$,

$\tilde{f} =$ Fouriertransform: $\tilde{f}(k) = \int d^3x e^{ikx} f(x)$

For large μ the repulsion becomes unimportant. Then the bound

$$-f(Z) > \tfrac{3}{5}\|n\|_{5/3}^{5/3} - Z\left\|\frac{e^{-x}}{x}\right\|_{5/2}\|n\|_{5/3} \geqq -Z^{5/2}4(2\pi/5)^{3/2} \equiv -cZ^{5/2} \tag{6}$$

and thus $\varepsilon < c\gamma^{-3/2}\mu^{-1/2}Z^{5/2}$ will be sufficient.

2. Bound for E(0)

Taking (4) for $\mu = 0$, $Z_k = 1$, $M = N$, and integrating with $\int d^3R_1 \ldots d^3R_N g^2(x_1 - R_1)\ldots g^2(x_N - R_N)$. We learn

$$\begin{aligned}\sum_{i>j} v_r(x_i - x_j) &\geqq \sum_i \int d^3x n(x) v_g(x - x_i) - \frac{1}{2}\int \frac{d^3x d^3x'}{|x - x'|} n(x) n(x') \\ &\quad - N\frac{3.68}{\gamma} - \frac{3\gamma}{5}\int d^3x n^{5/3}(x),\end{aligned} \tag{7}$$

$$v_g = \frac{1}{r} * g^2$$

or, upon substitution in (2)

$$\begin{aligned}H(0) &\geqq \sum_i\left\{p_i^2 - \sum_k Z_k v_r(x_i - R_k) + \int d^3x n(x) v_g(x - x_i)\right\} - \frac{3.68}{\gamma}N \\ &\quad - \frac{3\gamma}{5}\int d^3x n^{5/3}(x) + \sum_{k>m} Z_k Z_m v_r(R_k - R_m) - \frac{1}{2}\int\frac{d^3x d^3x'}{|x - x'|}n(x)n(x') \\ &\equiv \sum_i \{h_i\} + C.\end{aligned}$$

Here h_i is the Hamiltonian of the i-th particle in an external field. Using the coherent states $|q, k\rangle$ with wave function $e^{ikx}g(x - q)$ it can be written as [5]

$$h = \int\frac{d^3q d^3k}{(2\pi)^3}\left(k^2 - \sum_k Z_k v_g(q - R_k) + \int d^3x\frac{n(x)}{|q - x|}\right)|q, k\rangle\langle q, k| - \frac{\mu^2}{4}. \tag{8}$$

For spin 1/2-electrons we obviously have

$$\sum h_i \geqq -2tr|h|_- \tag{9}$$

and general trace inequalities [5] tell us

$$tr\left|\int\frac{d^3q d^3k}{(2\pi)^3}h(q, k)|q, k\rangle\langle k, q|\right|_- \leqq \int\frac{d^3k d^3q}{(2\pi)^3}|h(q, k)|_-. \tag{10}$$

In our case the k-integral is easily performed and we find

$$\begin{aligned}H(0) &\geqq -\frac{2}{15\pi^2}\int d^3q\left|-\sum_j Z_j v_s(q - R_j) + \int\frac{d^3x n(x)}{|x - q|}\right|_-^{5/2} - \left(\frac{3.68}{\gamma} + \frac{\mu^2}{4}\right)N \\ &\quad - \tfrac{1}{2}\int\frac{d^3x d^3x'}{|x - x'|}n(x)n(x') + \sum_{j>m} Z_j Z_m v_r(R_j - R_m) - \frac{3\gamma}{5}\int d^3x n^{5/3}(x).\end{aligned} \tag{11}$$

So far the inequality holds for any $n \in L^{5/3}$ and we shall now optimize

$$-\frac{2}{15\pi^2}\int d^3q\left|-\sum_j Z_j v_g(q-R_j)+\int\frac{d^3x n(x)}{|x-q|}\right|_-^{5/2}-\frac{1}{2}\int d^3x d^3y\frac{n(x)n(y)}{|x-y|}.$$

The formal variational derivation vanishes when

$$n(q)=\frac{1}{3\pi^2}\left|-\sum_j Z_j v_g(q-R_j)+\int\frac{d^3x n(x)}{|x-q|}\right|_-^{3/2} \tag{12}$$

and TF-theory guarantees that $\sup_n$ is actually attained. From (12) we learn

$$\begin{aligned}\int d^3q\left|-\sum_j Z_j v_g(q-R_j)+\int\frac{d^3x n(x)}{|x-q|}\right|_-^{5/2} &= \int d^3q\left|-\sum_j Z_j v_g(q-R_j)\right.\\ &\quad\left.+\int\frac{d^3x n(x)}{|x-q|}\right|_- 3\pi^2 n(q)\\ &=(3\pi^2)^{5/3}\int d^3q n^{5/3}(q).\end{aligned}$$

Substituting a linear combination of the two versions back into (11) and using the generalization of (7) for $Z_k \geqq 1$, $N \geqq M$, we find the desired bound:

$$\begin{aligned}H(0) &\geqq \tfrac{3}{5}\left[(3\pi^2)^{2/3}-\gamma\right]\int d^3x n^{5/3}(x)-\sum_j Z_j\int d^3x n(x)v_g(x-R_j)-\left(\frac{3.68}{\gamma}+\frac{\mu^2}{4}\right)N\\ &\quad+\frac{1}{2}\int\frac{d^3x d^3y}{|x-y|}n(x)n(y)+\sum_{k>m}Z_k Z_m v_r(R_k-R_m)\\ &\geqq -\varepsilon_{\mathrm{TF}}\left(\frac{1}{\gamma_1}N+\sum_k Z_k^{7/3}/(1-\gamma_1)\right)-\mu^2 N/4,\quad 0<\gamma_1<1.\end{aligned}$$

3. Correction Due To $\mathbf{v}_s$

Since g^2 has the Fouriertransform $\tilde{g}^2(k)=\dfrac{\mu^4}{(k^2+\mu^2)^2}$, we have

$$\tilde{v}_r(k)=\frac{\mu^8}{(k^2+\mu^2)^4}\frac{4\pi}{k^2}$$

and therefore

$$\tilde{v}_s(k)=\frac{4\pi}{k^2+\mu^2}\left[1+\frac{\mu^2}{k^2+\mu^2}+\frac{\mu^4}{(k^2+\mu^2)^2}+\frac{\mu^6}{(k^2+\mu^2)^3}\right].$$

Thus

$$v_s=\sum_{\rho=1}^{4} f_\rho * \frac{e^{-\mu r}}{r} * f_\rho$$

with

$$f_1=\delta(x),\quad f_2=\mu\int\frac{d^3k e^{ikx}}{(k^2+\mu^2)^{1/2}}=\frac{\mu}{2\pi^2 r^2}\int_{\mu r}^{\infty}d\zeta K_0(\zeta)\zeta,$$

$$f_3=\frac{\mu^2 e^{-\mu r}}{4\pi r},\quad f_4=\frac{\mu^3}{2\pi^2}K_0(\mu r).$$

Since the f_ρ are positive we may again multiply (4) with $\prod_{k=1}^{M} f_\rho(x_k - R_k)$ and integrate: Substituting $n = m * f_\rho$ and using $\| m * f \|_{5/3} \leqq \| m \|_{5/3} \| f \|_1 = \| m \|_{5/3}$ we get a "no-binding" Theorem for the $f_\rho * \frac{e^{-\mu r}}{r} * f_\rho$-potential, however with the binding energy of the Yukawa potential. Adding these four inequalities to the one with $\mu = 0$ gives a no-binding theorem for the $v_r + \alpha v_s$-potential.

$$\begin{aligned}
&\frac{3\gamma}{5}\int d^3x m^{5/3}(x) - \sum_{k=1}^{M} Z_k \int d^3x m(x)(|x - x_k|^{-1} + (\alpha - 1)v_s(x - x_k)) \\
&+ \tfrac{1}{2}\int d^3x d^3y m(x)m(y)(|x - y|^{-1} + (\alpha - 1)v_s(x - y)) + \sum_{k>m} Z_k Z_m (|x_k - x_m|^{-1} \\
&+ (\alpha - 1)v_s(x_k - x_m)) \geqq - \sum_{k=1}^{M}\left\{\frac{3.68}{\gamma - \gamma'} Z_k^{7/3} + 4(\alpha - 1)\varepsilon\left(\mu, \frac{\gamma'}{4(\alpha - 1)}, Z_k\right)\right\} \\
&\forall m \in L^{5/3}, \quad x_k \in \mathbb{R}^3, \quad 0 < \gamma' < \gamma.
\end{aligned} \tag{14}$$

Upon inserting this for $Z_k = 1, M = N$, into (2) we generalize (7) to

$$\begin{aligned}
H(\alpha) \geqq &\sum_i p_i^2 - \sum_{i,k} Z_k(|x_i - R_k|^{-1} + (\alpha - 1)v_s(x_i - R_k)) + \sum_i \int d^3x m(x)(|x - x_i|^{-1} \\
&+ (\alpha - 1)v_s(x - x_i)) + \sum_{k>m} Z_k Z_m(|R_k - R_m|^{-1} + (\alpha - 1)v_s(R_k - R_m)) \\
&- \frac{3\gamma_2}{5}\int d^3x m^{5/3}(x) - \tfrac{1}{2}\int d^3x d^3y m(x)m(y)(|x - y|^{-1} + (\alpha - 1)v_s(x - y)) \\
&- N\left(\frac{3.68}{\gamma_2 - \gamma_3} + 4(\alpha - 1)\varepsilon\left(\mu, \frac{\gamma_3}{4(\alpha - 1)}, 1\right)\right).
\end{aligned} \tag{15}$$

Taking the expectation value of $H(\alpha)$ with any $\psi(x_1, \dots x_N; \sigma_1, \dots \sigma_N)$ the potential will be integrated with the one-particle density

$$\rho(x) = N \sum_{\sigma_1 \dots \sigma_N} \int d^3x_2 \dots d^3x_N |\psi(x, x_2, \dots x_N, \sigma_1, \dots \sigma_N)|^2. \tag{16}$$

For the kinetic energy we employ the inequality [1, 2]

$$\langle \psi | \sum_{i=1}^{N} p_i^2 | \psi \rangle \geqq \frac{3}{5f}(3\pi)^2)^{2/3} \int d^3x \rho^{5/3}, \quad f = (4\pi)^{2/3}/1.5. \tag{17}$$

Thus, setting $m(x) = \rho(x)$, using (14) again and the bound (6) for ε we conclude

$$\begin{aligned}
E(\alpha) = \inf_{\|\psi\| = 1} \langle \psi | H(\alpha) | \psi \rangle \geqq &\frac{3}{5}\left(\frac{(3\pi^2)^{2/3}}{f} - \gamma_2\right)\int d^3x \rho^{5/3}(x) \\
&- \sum_k Z_k \int d^3x \rho(x)(|x - R_k|^{-1} + (\alpha - 1)v_s(x - R_k)) \\
&+ \tfrac{1}{2}\int d^3x d^3y \rho(x)\rho(y)(|x - y|^{-1} + (\alpha - 1)v_s(x - y)) \\
&+ \sum_{k>m} Z_k Z_m(|R_k - R_m|^{-1} + (\alpha - 1)v_s(R_k - R_m))
\end{aligned}$$

$$
\begin{aligned}
&-N\left(\frac{3.68}{\gamma_2-\gamma_3}+4(\alpha-1)\varepsilon\left(\mu,\frac{\gamma_3}{4(\alpha-1)},1\right)\right)\\
&\geqq -\varepsilon_{\mathrm{TF}}\sum_{k=1}^{M}\left\{\frac{fZ_k^{7/3}}{1-f(\gamma_2+\gamma_4)}+\frac{c(4(\alpha-1))^{5/2}Z_k^{5/2}}{3\pi^2\varepsilon_{\mathrm{TF}}\mu^{1/2}\ \gamma_4^{3/2}}\right\}\\
&-N\varepsilon_{\mathrm{TF}}\left(\frac{1}{\gamma_2-\gamma_3}+\frac{c(4(\alpha-1))^{5/2}}{3\pi^2\varepsilon_{\mathrm{TF}}\mu^{1/2}\gamma_3^{3/2}}\right).
\end{aligned}
\tag{18}
$$

At the end we have rescaled the γ's to introduce $\varepsilon_{\mathrm{TF}}$ according to (5). Inserting (18) and (13) into (3) gives the *Lower Bound for the Coulomb Hamiltonian*

$$
\begin{aligned}
H(1)\geqq -\varepsilon_{\mathrm{TF}}\Bigg\{&\sum_{k=1}^{M}Z_k^{7/3}\left(\frac{\alpha-1}{\alpha}\frac{1}{1-\gamma_1}+\frac{1}{\alpha}\frac{f}{1-f(\gamma_2+\gamma_4)}\right)\\
&+\sum_{k=1}^{M}Z_k^{5/2}\frac{c(4(\alpha-1))^{5/2}\alpha^{-1}}{3\pi^2\varepsilon_{\mathrm{TF}}\mu^{1/2}\gamma_4^{3/2}}+N\Bigg(\frac{\alpha-1}{\gamma_1\alpha}+\frac{1}{\gamma_2-\gamma_3}\\
&+\frac{(\alpha-1)\mu^2}{4\alpha\varepsilon_{\mathrm{TF}}}+\frac{c(4(\alpha-1))^{5/2}\alpha^{-1}}{3\pi^2\varepsilon_{\mathrm{TF}}\mu^{1/2}\gamma_3^{3/2}}\Bigg)\Bigg\}
\end{aligned}
\tag{19}
$$

$$
\forall\alpha>1,\ 0<\gamma_1<1,\ 0<\gamma_3<\gamma_2<\frac{1}{f}-\gamma_4,\ \gamma_4>0,\ \mu>0,
$$

$$
f=(4\pi)^{2/3}/1.5=3.6,\quad c=4(2\pi/5)^{3/2}=5.6
$$

Remarks. 1. For $\alpha=1,\gamma_3,\gamma_4\to 0,\gamma_2^{-1}=f(1+(\sum Z_k^{7/3}/N)^{1/2})$ we recover the result of [1]:

$$
E(1)\geqq -f\varepsilon_{\mathrm{TF}}N\left(1+\left(\sum_k Z_k^{7/3}/N\right)^{1/2}\right)^2.
$$

2. Optimizing (19) over all parameters is an extensive numerical job. However, the allegation made at the beginning is obtained easily by putting $\alpha=Z^{2/33}$, $\mu=Z^{7/11}$, and, say, $\gamma_1=Z^{-1/2}$, $\gamma_2=\gamma_4=2\gamma_3=1/3f$. Then the first term is

$$
-\varepsilon_{\mathrm{TF}}\sum_{k=1}^{M}Z_k^{7/3}(1+0(Z^{-2/33}))
$$

and all the others are $0(Z^{-2/33})$.
3. The stability proof can be extended from potentials of the form $\sum_{i>j}e_ie_jv(x_i-v_j)$ to potentials with spin and isospin, f.i. $\sum_{i>j}(\vec{\tau}_i\vec{\tau}_j)\cdot(\vec{\sigma}_i\vec{\sigma}_j)v(x_i-x_j)$. Then (7) would prove stability of nuclear matter with Yukawa potentials but without hard core.
4. If one could prove the no-binding Theorem for v_s in the form that ε is the atomic energy for v_s and not for the Yukawa potential then the numbers in the terms $0(Z^{-2/33})$ could be improved.
5. The physical reason why stability and no-binding requires potentials of positive type is that $\tilde{v}\geqq 0$ implies $v(0)\geqq v(r)\forall r>0$. If $v(r_0)$ were $>v(0)$ for some $r_0>0$

one would easily construct a trial function such that even for fermions

$$\lim_{N\to\infty} \langle \psi | \sum_{i=1}^{N} p_i^2 + \sum_{i>j} e_i e_j v(x_i - x_j) | \psi \rangle / N \to -\infty :$$

Just concentrate $N/2$ positive and $N/2$ negative charges in balls with radius $r_0/10$ and separate them by r_0: For large N the interaction $-e^2 v(r_0) N^{2/4}$ wins over their self-energy $e^2 v(0) N(N-2)/4$ and kinetic energy $N^{5/3}/(r_0/10)^2$.

6. The physical reason why the contribution of v_s does not increase as fast as $Z^{7/3}$ is that $e^{-\mu r}/r$ does not bind as many particles. Even neglecting the electron repulsion the atomic energy is sum of all binding energies $\geqq -c \| v_s \|_{5/2}^{5/2} \sim Z^{5/2} \mu^{-1/2}$. Thus if μ increases faster than $Z^{1/3}$ then v_s does not contribute to the leading order in Z.

Acknowledgement. The author is indebted to John Morgan for carefully reading the manuscript and for valuable suggestions.

References

1. Lieb, D., Thirring, W.: Phys. Rev. Lett. **35**, 681 (1975), and contribution to Essays in Honor of Valentine Bargmann. Lieb, E., Simon, B., Wightman, A. (eds) Princeton: Princeton Univ. Press 1977
2. Lieb, E.: Bull. Amer. Math. Soc. **82**, 751 (1976)
3. Thirring, W.: Quantenmechanik von Atomen und Molekülen, Eq. (3.5, 23). Wien: Springer 1979
4. Lieb, E., Simon, B.: Adv. Math. **23**, 22 (1977)
5. Thirring, W., Quantenmechanik großer System, Eq. (2.2, 11) and (4.1, 46; 3). Wien, Springer 1980

Communicated by E. Lieb

Received March 31, 1980; in revised form June 13, 1980