ON SOME BASIC PROPERTIES OF DENSITY FUNCTIONALS FOR ANGULAR MOMENTUM CHANNELS

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We investigate some basic properties of the Hellmann and the Hellmann–Weizsäcker energy functional, density functionals, which use densities for angular momentum channels as trial functions, and investigate their relation to the ground state energy of an atomic N-electron system. Furthermore, various scaling properties are shown, the virial theorem, and in the case of no electron–electron interaction the dependence on the nuclear charge.

1. Introduction

Already in the early period of quantum mechanics the Thomas–Fermi theory (Thomas [1], Fermi [2], Lenz [3]) has been derived as an approximation scheme for the ground state energy and ground-state density of N electrons for large particle number in the field of some nuclei of total charge Z. The Thomas–Fermi energy $E_Z^{TF}(N)$ has for $N = cZ$ a relatively simple dependence on the total charge

$$E_Z^{TF}(N) = E_1^{TF}(c)Z^{7/3}. \tag{1.1}$$

Since the Thomas–Fermi model has been heuristically derived under the assumption of a large particle number, the right-hand side of (1.1) has been considered as the leading asymptotic term for the quantum mechanical ground state energy $E_Q(Z, N)$ (see e.g. March [4]). Lieb and Simon [5] showed that this heuristics can be turned into a proof. They obtained for $N = cZ$

$$E_Q(Z, N) = E_1^{TF}(c)Z^{7/3}+o(Z^{7/3}). \tag{1.2}$$

Later, Lieb [6] refined this result to

$$E_Q(Z, N) = E_1^{TF}(c)Z^{7/3}+O(Z^{7/3-1/30}). \tag{1.3}$$

Thirring [7] improved the lower bound for the infimum of the spectrum of the Coulomb hamiltonian which implies that the error term in (1.3) may be chosen of order $O(Z^{7/3-2/33})$. Scott [8], however, and later Schwinger [9] and Englert and Schwinger [10] gave arguments that the next correction should be of order Z^2. The constant should be given as $q/8$, where q is the number of spin states, for the electron two. The purpose of the present paper is to develop a tool for the first part of this conjecture.

Hellmann [11] introduced a functional, which uses the densities of the angular momentum channels as trial functions. We shall investigate the Hellmann and the Hellmann–Weizsäcker functional, which will be used in later papers to bound the quantum mechanical ground state energy in order to improve (1.3) towards Scott's conjecture.

In Chapter 2 we shall define the model to be investigated. Chapter 3 deals with uniqueness and existence questions of minimizing densities and thus with the uniqueness and existence of solutions for the corresponding Euler–Lagrange equation. Moreover, the critical particle number, i.e. the number of electrons that can be bound by an atom with nuclear charge Z, is discussed. In Chapter 4 we mention some scaling properties of the Hellmann and Hellmann–Weizsäcker functional for the case with and without electron–electron interaction. Chapter 5 generalizes a previous bound of one of the authors [12] to the case of non-integer occupation numbers of the various angular momentum subchannels.

2. Definition of the Hellmann and the Hellmann–Weizsäcker functional and their infima

We first define a set of functions. Let

$$G = \left\{\varrho \in L^1(\mathbf{R}^+) \cap L^3(\mathbf{R}^+) \,\middle|\, \frac{\varrho}{r^2} \in L^1(\mathbf{R}^+),\ \varrho \geqslant 0\right\}. \tag{2.1}$$

If $\varrho \in G$, then $\int_0^\infty \frac{\varrho(r)}{r}\,dr$ is finite, too, since

$$\int_0^\infty \frac{\varrho(r)}{r}\,dr \leqslant \int_0^1 \frac{1}{r}\varrho(r)\,dr + \int_1^\infty \frac{1}{r}\varrho(r)\,dr \leqslant \left\|\frac{1}{r^2}\varrho\right\|_1 + \|\varrho\|_1. \tag{2.2}$$

Thus

$$\varepsilon^H_{l,Z}\colon G \to \mathbf{R}, \qquad \varepsilon^H_{l,Z}(\varrho) = \int_0^\infty \left(\frac{1}{3}\alpha_l \varrho^3(r) + \left(\frac{\beta_l}{r^2} - \frac{Z}{r}\right)\varrho(r)\right)dt \tag{2.3}$$

is well defined, where l denotes the angular momentum channel. The positive constants α_l are bounded from above while the numbers β_l are bounded from below by a positive constant. They will be chosen subsequently to be $\left(\frac{\pi}{q(2l+1)}\right)^2$ and $(l+\frac{1}{2})^2$, respectively. We remark that $\varepsilon^H_{l,Z}$ is strictly convex on G. This follows from the strict convexity of x^3 for $x > 0$ and the linearity in ϱ of the second term of the functional.

Furthermore, if $\varepsilon^H_{l,Z}$ is restricted onto $G_N = \{\varrho \in G \mid \|\varrho\|_1 \leqslant N\}$ or $G_{\partial N} = \{\varrho \in G \mid \|\varrho\|_1 = N\}$, it is bounded from below:

$$\varepsilon^H_{l,Z}(\varrho) \geqslant \int_0^1 \left(\frac{\beta_l}{r^2} - \frac{Z}{r}\right)\varrho(r)\,dr - Z\int_1^\infty \varrho(r)\,dr \geqslant \left(\inf\left\{\frac{\beta_l}{r^2} - \frac{Z}{r}\,\middle|\, r \in (0, 1]\right\} - Z\right)N \geqslant \text{const}\, N. \tag{2.4}$$

If we neglect the electron–electron interaction for the moment, we may interpret $\varepsilon^H_{l,Z}(\varrho)$ with $\int \varrho\,dr = N$ as the quasi-classical energy of N electrons with radial density ϱ in the angular momentum channel l (Thomas–Fermi functional for these electrons in the effective radial potential). If α_l is chosen to be π^2 and $\int \varrho\,dr = N$, it may be interpreted as the quasi-classical energy of N electrons with radial density ϱ in the angular momentum subchannel with indices l, m, s.

Let $\boldsymbol{\varrho}$ denote $(\varrho_0, \ldots, \varrho_l, \ldots)$ and $\alpha(\boldsymbol{\varrho}) = (\sum_{l=0}^\infty \alpha_l \int_0^\infty \varrho_l^3\,dr)^{1/3}$ be the norm, in which $X = L^3(\boldsymbol{R}^+ \times \boldsymbol{N}_0, d\mu)$ is a reflexive Banach space. Here $d\mu$ is the Lebesgue measure in the first coordinate and the counting measure weighted by α_l in the second coordinate. Furthermore, define the following sets:

$$\begin{aligned}
M &= \left\{\boldsymbol{\varrho} \in X \,|\, \boldsymbol{\varrho} \geqslant 0,\ \sum_{l=0}^\infty \beta_l \int_0^\infty \frac{\varrho_l}{r^2}\,dr < \infty,\ \sum_{l=0}^\infty \int_0^\infty \varrho_l\,dr < \infty\right\},\\
M_N &= \left\{\boldsymbol{\varrho} \in X \,|\, \boldsymbol{\varrho} \geqslant 0,\ \sum_{l=0}^\infty \beta_l \int_0^\infty \frac{\varrho_l}{r^2}\,dr < \infty,\ \sum_{l=0}^\infty \int_0^\infty \varrho_l\,dr \leqslant N\right\},\\
M_{\partial N} &= \left\{\boldsymbol{\varrho} \in X \,|\, \boldsymbol{\varrho} \geqslant 0,\ \sum_{l=0}^\infty \beta_l \int_0^\infty \frac{\varrho_l}{r^2}\,dr < \infty,\ \sum_{l=0}^\infty \int_0^\infty \varrho_l\,dr = N\right\},
\end{aligned} \tag{2.5}$$

where $\boldsymbol{\varrho} \geqslant 0$ is an abbreviation for $\varrho_0, \ldots, \varrho_l, \ldots \geqslant 0$. Then the quasi-classical functional $\tilde{\varepsilon}^H_Z$: $M \to \boldsymbol{R}$, which restricted onto $M_{\partial N}$ is the functional of the total energy of N non-interacting electrons in the filed of a nucleus of charge Z, is given by

$$\tilde{\varepsilon}^H_Z(\boldsymbol{\varrho}) = \sum_{l=0}^\infty \varepsilon^H_{l,Z}(\varrho_l). \tag{2.6}$$

This is obviously well defined which follows from the properties of each $\varepsilon^H_{l,Z}$ and from the fact that $\sum_{l=0}^\infty \alpha_l \|\varrho_l\|_3^3$, $\sum_{l=0}^\infty \|\varrho_l\|_1$, $\sum_{l=0}^\infty \beta_l \left\|\frac{\varrho_l}{r^2}\right\|_1$ and $\sum_{l=0}^\infty \left\|\frac{\varrho_l}{r}\right\|_1$ are all finite. The latter follows analogously to (2.2), since the β_l are bounded from below by a positive constant. Again for $\boldsymbol{\varrho} \geqslant 0$ and $\int_0^\infty \sum_{l=0}^\infty \varrho_l(r)\,dr \leqslant N$ the functional $\tilde{\varepsilon}^H_Z$ is bounded from below: Using (2.4) we get

$$\tilde{\varepsilon}_Z^H(\mathbf{\varrho}) \geqslant \int_0^1 \sum_{l=0}^{\infty} \left(\frac{\beta_l}{r^2} - \frac{Z}{r}\right) \varrho_l \, dr - Z \int_1^{\infty} \sum_{l=0}^{\infty} \varrho_l(r) \, dr \geqslant (\mathrm{const} - Z) N. \tag{2.7}$$

In order to treat interacting electrons we, introduce the quadratic form

$$D(\varrho, \sigma) = \int_0^{\infty} dr \int_0^{\infty} ds \frac{\varrho(r)\sigma(s)}{\max\{r, s\}}. \tag{2.8}$$

$D(\varrho, \sigma)$ may be bounded by $\int_0^{\infty} dr \frac{\varrho(r)}{r} \int_0^{\infty} ds \sigma(s) + \int_0^{\infty} dr \varrho(r) \int_0^{\infty} ds \frac{\sigma(s)}{s}$ and this is well defined on G^2. Thus the Hellmann functional

$$\begin{gathered} \varepsilon_Z^H \colon M \to \mathbf{R}, \\ \varepsilon_Z^H(\mathbf{\varrho}) = \tilde{\varepsilon}_Z^H(\mathbf{\varrho}) + \tfrac{1}{2} \sum_{l,l'=0}^{\infty} D(\varrho_l, \varrho_{l'}) \end{gathered} \tag{2.9}$$

is obviously well defined, and, since $\varepsilon_Z^H(\mathbf{\varrho}) \geqslant \tilde{\varepsilon}_Z^H(\mathbf{\varrho})$ for $\mathbf{\varrho} \geqslant 0$, it is also bounded from below, if $\sum_{l=0}^{\infty} \int_0^{\infty} \varrho_l \, dr \leqslant N$. Later we shall show that this last condition is not necessary. Physically speaking, the atom described by the Hellmann functional can bind only finitely many electrons, which is obvious and has its source in the electron–electron repulsion. Indeed the repulsion will be essential for the corresponding mathematical argument, too. Both ε_Z^H and $\tilde{\varepsilon}_Z^H$ are strictly convex.

Given $N \geqslant 0$, the infima of the functionals (2.3), (2.6) and (2.9) are denoted by

$$e_{l,Z}^H(N) = \inf\{\varepsilon_{l,Z}^H(\varrho) \mid \varrho \in G_N\}, \tag{2.10}$$

$$\tilde{e}_Z^H(N) = \inf\{\tilde{\varepsilon}_Z^H(\mathbf{\varrho}) \mid \mathbf{\varrho} \in M_N\}, \tag{2.11}$$

$$e_Z^H(N) = \inf\{\varepsilon_Z^H(\mathbf{\varrho}) \mid \mathbf{\varrho} \in M_N\}. \tag{2.12}$$

For every fixed Z these functions are convex and monotone decreasing. We are interested in these infima only because of technical reasons. Later on, they will allow us to make connections with the well known techniques of the calculus of variations to establish the existence of minimizing solutions for

$$E_{l,Z}^H(N) = \inf\{\varepsilon_{l,Z}^H(\varrho) \mid \varrho \in G_{\partial N}\}, \tag{2.13}$$

$$\tilde{E}_Z^H(N) = \inf\{\tilde{\varepsilon}_Z^H(\mathbf{\varrho}) \mid \mathbf{\varrho} \in M_{\partial N}\}, \tag{2.14}$$

$$E_Z^H(N) = \inf\{\varepsilon_Z^H(\mathbf{\varrho}) \mid \mathbf{\varrho} \in M_{\partial N}\}. \tag{2.15}$$

The distinction between the two types of infima, however, is superficial, since the corresponding infima are equal.

THEOREM 2.1.

$$e^H_{l,Z}(N) = E^H_{l,Z}(N), \quad \tilde{e}^H_Z(N) = \tilde{E}^H_Z(N), \quad e^H_Z(N) = E^H_Z(N).$$

Proof: We prove only the third equation, since the other are proven by similar arguments. The inequality $e^H_Z(N) \leqslant E^H_Z(N)$ is trivial. To prove the converse we note that ε^H_Z is continuous in the norm $\|\varrho\|^* = (\sum_{l=0}^{\infty} \alpha_l \|\varrho_l\|_3^3)^{1/3} + \sum_{l=0}^{\infty} \beta_l \left\|\frac{\varrho_l}{r^2}\right\|_1 + \sum_{l=0}^{\infty} \left\|\frac{\varrho_l}{r}\right\|_1$. Let $\varrho_n \to \varrho$ in the *-norm, then

$$|\varepsilon^H_Z(\varrho) - \varepsilon^H_Z(\varrho_n)| \leqslant \sum_{l=0}^{\infty} \left\{\frac{\alpha_l}{3} \int_0^{\infty} |\varrho_l^3(r) - \varrho_{n,l}^3(r)|\, dr + \beta_l \int_0^{\infty} \frac{|\varrho_l(r) - \varrho_{n,l}(r)|}{r^2}\, dr + \right.$$
$$\left. + Z \int_0^{\infty} \frac{|\varrho_l(r) - \varrho_{n,l}(r)|}{r}\, dr \right\} + \frac{1}{2} \sum_{l,l'=0}^{\infty} |D(\varrho_l, \varrho_{l'}) - D(\varrho_{n,l}, \varrho_{n,l'})|. \tag{2.16}$$

The second and the third term tend to zero by definition of the *-norm. For the first term we get

$$\sum_{l=0}^{\infty} \alpha_l \int_0^{\infty} |\varrho_l^3(r) - \varrho_{n,l}^3(r)|\, dr \leqslant \sum_{l=0}^{\infty} \alpha_l \int_0^{\infty} |\varrho_l(r) - \varrho_{n,l}(r)|^3\, dr +$$
$$+ 3 \sum_{l=0}^{\infty} \alpha_l \int_0^{\infty} |\varrho_l(r)\, \varrho_{n,l}(r) (\varrho_l(r) - \varrho_{n,l}(r))|\, dr. \tag{2.17}$$

Again the first term on the right-hand side of (2.17) converges to zero by definition. The second term on the right-hand side of (2.17) may be bounded as follows by Hölder's inequality

$$\sum_{l=0}^{\infty} \alpha_l \int_0^{\infty} |\varrho_l(r)\, \varrho_{n,l}(r) (\varrho_l(r) - \varrho_{n,l}(r))|\, dr$$
$$\leqslant (\sum_{l=0}^{\infty} \alpha_l \int_0^{\infty} \varrho_l^3(r)\, dr)^{1/3} (\sum_{l=0}^{\infty} \alpha_l \int_0^{\infty} \varrho_{n,l}^3(r)\, dr)^{1/3} (\sum_{l=0}^{\infty} \alpha_l \int_0^{\infty} |\varrho_l(r) - \varrho_{n,l}(r)|^3\, dr)^{1/3}$$
$$\leqslant \text{const} (\sum_{l=0}^{\infty} \alpha_l \|\varrho_l - \varrho_{n,l}\|_3^3)^{1/3} \to 0. \tag{2.18}$$

Finally, we estimate the last term of (2.16)

$$\sum_{l,l'=0}^{\infty} |D(\varrho_l, \varrho_{l'}) - D(\varrho_{n,l}, \varrho_{n,l'})|$$

$$\leqslant \sum_{l,l'=0}^{\infty} \left(|D(\varrho_l, \varrho_{l'}) - D(\varrho_{l'}, \varrho_{n,l})| + |D(\varrho_{n,l}, \varrho_{l'}) - D(\varrho_{n,l}, \varrho_{n,l'})|\right)$$

$$\leqslant \sum_{l,l'=0}^{\infty} \left(\int_0^{\infty} \varrho_{l'}(r)\,dr \int_0^{\infty} \frac{|\varrho_l(r) - \varrho_{n,l}(r)|}{r}\,dr + \int_0^{\infty} \varrho_{n,l}(r)\,dr \int_0^{\infty} \frac{|\varrho_{l'}(r) - \varrho_{n,l'}(r)|}{r}\,dr\right) \to 0. \tag{2.19}$$

Next we claim that each element $\boldsymbol{\varrho} \in M$ with $\sum_{l=0}^{\infty} \|\varrho_l\|_1 \leqslant \lambda$ can be approximated by functions $\boldsymbol{\varrho}_n$ with $\sum_{l=0}^{\infty} \|\varrho_{n,l}\|_1 = \lambda$. Choose $\varrho_{n,l} = \varrho_l + \frac{1}{n} f_{n,l}$, where the $f_{n,l}$ are non-negative functions with $[0, (1+\beta_l)n) \cap \operatorname{supp} f_{n,l} = \emptyset$, $\sum_{l=0}^{\infty} \int_0^{\infty} f_{n,l}\,dr = n(\lambda - \sum_{l=0}^{\infty} \int_0^{\infty} \varrho_l\,dr)$, $\sum_{l=0}^{\infty} \int_0^{\infty} \chi_{\operatorname{supp} f_{n,l}}\,dr \leqslant 2n\lambda$, and $f_{n,l} \leqslant 1$. Then

$$\|\boldsymbol{\varrho} - \boldsymbol{\varrho}_n\|^* = \frac{1}{n}\left\{\left(\sum_{l=0}^{\infty} \alpha_l \int_0^{\infty} f_{n,l}^3\,dr\right)^{1/3} + \sum_{l=0}^{\infty} \beta_l \left\|\frac{f_{n,l}}{r^2}\right\|_1 + \sum_{l=0}^{\infty} \left\|\frac{f_{n,l}}{r}\right\|_1\right\}$$

$$\leqslant \frac{1}{n}\left(\operatorname{const}(2n\lambda)^{1/3} + \frac{2n\lambda}{n^2} + \frac{2n\lambda}{n}\right) \to 0, \tag{2.20}$$

since the α_l are bounded from above. Thus we can find a sequence $\boldsymbol{\varrho}_n$ with $\sum_{l=0}^{\infty} \int_0^{\infty} \varrho_{n,l}\,dr = \lambda$ so that $\varepsilon_Z^H(\boldsymbol{\varrho}_n)$ approaches $e_Z^H(\lambda)$ in the *-norm. Thus

$$E_Z^H(\lambda) \leqslant \lim_{n\to\infty} \varepsilon_Z^H(\boldsymbol{\varrho}_n) = e_Z^H(\lambda). \quad \blacksquare \tag{2.21}$$

Remark. The above argument has its origin in a similar argument of Lieb and Simon [5] for the case of Thomas–Fermi theory.

The second type of functionals we wish to consider are analogues of the Thomas–Fermi model with gradient term. We call them Hellmann–Weizsäcker functionals. For these functionals we choose $\alpha_l = \left(\frac{\pi}{q(2l+1)}\right)^2$ and $\beta_l = l(l+1)$. First we treat the functional for one angular momentum channel. Let $H_0^1(0, \infty)$ be the local Sobolev space of order one (completion of $C_0^\infty(0, \infty)$ in the norm $\|\varphi\|_{2,1} = \|\varphi'\|_2 + \|\varphi\|_2$ and let

$$F = \{\varrho \mid \varrho \geqslant 0, \sqrt{\varrho} \in H_0^1(0, \infty)\}. \tag{2.22}$$

Define

$$\varepsilon_{l,Z}^{HW}: F \to \boldsymbol{R},$$

$$\varepsilon_{l,Z}^{HW}(\varrho) = \int_0^\infty \left(\sqrt{\varrho(r)}'^2 + \frac{\alpha_l}{3}\varrho^3(r) + \left(\frac{\beta_l}{r^2} - \frac{Z}{r}\right)\varrho(r)\right) dr. \tag{2.23}$$

By Lieb–Thirring's inequality [13] $\|\varrho\|_3 \leqslant c\|\sqrt{\varrho}\|_{2,1}^2$ holds. Moreover, $\int_0^\infty \frac{\beta_l}{r^2}\varrho\, dr$ can be bounded by const $\int_0^\infty \sqrt{\varrho}'^2\, dr$ using Hardy's inequality. Thus, in view of the result for $\varepsilon_{l,Z}^{H}$ the functional $\varepsilon_{l,Z}^{HW}$ is well defined on F, bounded from below for $\int_0^\infty \varrho\, dr \leqslant N$, and strictly convex which follows immediately from the proof of the convexity of the Thomas–Fermi–Weizsäcker functional (Lieb [6]).

To treat the functionals of the total energy we define $\bigoplus_{l=0}^{\infty} H_0^1(0,\infty)$ to be the Hilbert space direct sum of H_0^1. Then with $\sqrt{\boldsymbol{\varrho}} = (\sqrt{\varrho_0}, \ldots, \sqrt{\varrho_l}, \ldots)$ let

$$W = \left\{ \boldsymbol{\varrho} \mid \boldsymbol{\varrho} \geqslant 0,\ \sqrt{\boldsymbol{\varrho}} \in \bigoplus_{l=0}^{\infty} H_0^1(0,\infty),\ \sum_{l=0}^{\infty} \beta_l \int_0^\infty \frac{\varrho_l(r)}{r^2}\, dr < \infty \right\},$$

$$W_N = \left\{ \boldsymbol{\varrho} \in W \mid \sum_{l=0}^{\infty} \int_0^\infty \varrho_l\, dr \leqslant N \right\}, \tag{2.24}$$

$$W_{\partial N} = \left\{ \boldsymbol{\varrho} \in W \mid \sum_{l=0}^{\infty} \int_0^\infty \varrho_l\, dr = N \right\}.$$

Again one shows that

$$\tilde{\varepsilon}_Z^{HW}: W \to \boldsymbol{R},$$

$$\tilde{\varepsilon}_Z^{HW}(\boldsymbol{\varrho}) = \sum_{l=0}^{\infty} \int_0^\infty \left(\sqrt{\varrho_l(r)}'^2 + \frac{\alpha_l}{3}\varrho_l^3(r) + \left(\frac{\beta_l}{r^2} - \frac{Z}{r}\right)\varrho_l(r)\right) dr, \tag{2.25}$$

and

$$\varepsilon_Z^{HW}: W \to \boldsymbol{R},$$

$$\varepsilon_Z^{HW}(\boldsymbol{\varrho}) = \sum_{l=0}^{\infty} \int_0^\infty \left(\sqrt{\varrho_l(r)}'^2 + \frac{\alpha_l}{3}\varrho_l^3(r) + \left(\frac{\beta_l}{r^2} - \frac{Z}{r}\right)\varrho_l(r)\right) dr + \frac{1}{2}\sum_{l,l'=0}^{\infty} D(\varrho_l, \varrho_{l'}) \tag{2.26}$$

are well defined on W, bounded from below on W_N and on $W_{\partial N}$, and strictly convex. We introduce

$$e_Z^{HW}(N) = \inf\{\varepsilon_Z^{HW}(\boldsymbol{\varrho}) \mid \boldsymbol{\varrho} \in W_N\}, \tag{2.27}$$

and

$$E_Z^{HW}(N) = \inf\{\varepsilon_Z^{HW}(\boldsymbol{\varrho}) \mid \boldsymbol{\varrho} \in W_{\partial N}\}. \tag{2.28}$$

As for the case without gradient correction one proves:

THEOREM 2.2.

$$e_{l,Z}^{HW}(N) = E_{l,Z}^{HW}(N), \quad \tilde{e}_Z^{HW}(N) = \tilde{E}_Z^{HW}(N), \quad e_Z^{HW}(N) = E_Z^{HW}(N).$$

Here we used notations analogous to those in Theorem 2.1.

3. Uniqueness and existence of minimizing densitions. Critical particle numbers

First we show the uniqueness of minimizing densities:

THEOREM 3.1. *If there exists a minimizing density for one of the above defined functionals, then it is unique.*

Proof: Suppose this were not the case, i.e. there were two distinct ϱ and σ with $\varepsilon(\varrho) = \varepsilon(\sigma) = e(N)$. Then by strict convexity for $0 < \alpha < 1$

$$\varepsilon(\alpha\varrho + (1-\alpha)\sigma) < \alpha\varepsilon(\varrho) + (1-\alpha)\varepsilon(\sigma) = e(N), \tag{3.1}$$

which is a contradiction. ∎

Next we investigate the existence of minimizing densities and the maximal number of electrons which can be bound for the Hellmann functional. First we treat the relation of the Euler–Lagrange equations to the Hellmann functional. The following theorem and its proof are analogues of the corresponding result of Lieb and Simon [5] for Thomas–Fermi theory.

THEOREM 3.2. (a) *If $\varrho \in M_{\partial N}$ obeys the Hellmann equations*

$$\varrho_l(r) = \alpha_l^{-1/2}\left[\varphi(r) + \lambda - \frac{\beta_l}{r^2}\right]_+^{1/2}, \quad l = 0, 1, 2, \ldots, \tag{3.2}$$

where φ is either

$$\varphi(r) = \frac{Z}{r} - \sum_{l=0}^{\infty} \int_0^{\infty} \frac{\varrho_l(r')}{\max\{r, r'\}} dr' \tag{3.3}$$

or

$$\varphi(r) = \frac{Z}{r}, \tag{3.4}$$

then ϱ minimizes ε_Z^H respectively $\tilde{\varepsilon}_Z^H$ on M_N, $E_Z^H(x)$ and $\tilde{E}_Z^H(x)$ are differentiable at $x = N$, and

$$\lambda = \left.\frac{dE_Z^H(x)}{dx}\right|_{x=N} \quad \text{respectively} \quad \lambda = \left.\frac{d\tilde{E}_Z^H(x)}{dx}\right|_{x=N}. \tag{3.5}$$

In particular, λ is zero (in the interacting case), if ϱ minimizes ε_Z^H on M.

(b) *Conversely, if* $\varrho \in M_{\partial N}$ *minimizes* ε_Z^H *or* $\tilde{\varepsilon}_Z^H$ *on* $M_{\partial N}$, *then* ϱ *obeys the Hellmann equations* (3.2) *and* (3.3) *or* (3.2) *and* (3.4), *respectively, where* λ *is given by* (3.5).

Proof: As mentioned above, the proof is analogous to the proof of Theorem II.10 of [5] with the definition $\delta\varepsilon/\delta\varrho_l = \alpha_l \varrho_l^2 - \varphi(r) + \beta_l/r^2$. ∎

Next we come to the existence of a minimum. The strategy is the usual one of calculus of variations: Show weak lower semicontinuity of the functional on a suitable weakly compact set. For the Hellmann functional this is unfortunately not straightforward because of two reasons: The high singularity at the origin of the β_l/r^2 term and the lack of decrease in the variable l in the Z/r term. We start with $\varepsilon_{l,Z}^H$ where only the first problem occurs.

THEOREM 3.3. $\varepsilon_{l,Z}^H$ *has a unique minimizing element in* G_N.

Proof: Let ϱ_n be any sequence in G_N such that $\lim_{n\to\infty} \varepsilon_{l,Z}^H(\varrho_n) = e_{l,Z}^H(N)$. Furthermore, let r_l be the zero of $\frac{\beta_l}{r^2} - \frac{Z}{r}$, i.e. $r_l = \frac{\beta_l}{Z}$. We then see that $\tilde{\varrho}_n = \varrho_n \chi_{[r_l, \infty)}$ is also a minimizing sequence, since $\int_0^\infty \tilde{\varrho}_n \, dr \leqslant N$ and

$$\varepsilon_{l,Z}^H(\varrho_n) = \int_0^\infty \left(\frac{\alpha_l}{3}\varrho_n^3 + \left(\frac{\beta_l}{r^2} - \frac{Z}{r}\right)\varrho_n\right) dr \geqslant \int_{r_l}^\infty \left(\frac{\alpha_l}{3}\varrho_n^3 + \left(\frac{\beta_l}{r^2} - \frac{Z}{r}\right)\varrho_n\right) dr = \varepsilon_{l,Z}^H(\tilde{\varrho}_n),$$

where we used the property that $\frac{\beta_l}{r^2} - \frac{Z}{r}$ is positive for $r \in (0, r_l)$. Next, we remark that $\|\tilde{\varrho}_n\|_3$ is bounded: $-\int_0^\infty \frac{Z}{r}\tilde{\varrho}_n \, dr$ is bounded from below on G_N by $-\frac{Z}{r_l}N$, thus

$$0 \leqslant \|\tilde{\varrho}_n\|_3^3 \leqslant \frac{3}{\alpha_l}\left(\int_0^\infty \left(\frac{\alpha_l}{3}\tilde{\varrho}_n^3 + \left(\frac{\beta_l}{r^2} - \frac{Z}{r}\right)\tilde{\varrho}_n\right) dr + \frac{Z}{r_l}N\right) = \frac{3}{\alpha_l}\left(\varepsilon_{l,Z}^H(\tilde{\varrho}_n) + \frac{Z}{r_l}N\right). \quad (3.6)$$

The right-hand side of (3.6) is convergent as we showed above and therefore bounded in n. Thus, since $L^3(\boldsymbol{R}^+)$ is reflexive, we may use the Banach–Alaoglu theorem and extract from $\tilde{\varrho}_n$ a $L^3(\boldsymbol{R}^+)$-weakly convergent subsequence, whose limit is denoted by $\tilde{\varrho}$. We denote this subsequence by $\tilde{\varrho}_n$ too. We get

$$\int_0^\infty \tilde{\varrho}^3 \, dr = \lim_{n\to\infty} \int_0^\infty \tilde{\varrho}^2 \tilde{\varrho}_n \, dr \leqslant \underline{\lim}_{n\to\infty} \left(\int_0^\infty \tilde{\varrho}^3 \, dr\right)^{2/3} \left(\int_0^\infty \tilde{\varrho}_n^3 \, dr\right)^{1/3},$$

and thus

$$\frac{\alpha_l}{3}\int_0^\infty \tilde{\varrho}^3\,dr \leqslant \varliminf_{n\to\infty}\frac{\alpha_l}{3}\int_0^\infty \tilde{\varrho}_n^3\,dr. \tag{3.7}$$

Since $\left(\frac{\beta_l}{r^2}-\frac{Z}{r}\right)\chi_{(r_l,\infty)}\in L^{3/2}(\boldsymbol{R}^+)$, we obtain

$$\lim_{n\to\infty}\int_0^\infty\left(\frac{\beta_l}{r^2}-\frac{Z}{r}\right)\tilde{\varrho}_n\,dr = \int_0^\infty\left(\frac{\beta_l}{r^2}-\frac{Z}{r}\right)\tilde{\varrho}\,dr. \tag{3.8}$$

Combining (3.7) and (3.8) we have

$$\varepsilon_{l,Z}^H(\tilde{\varrho}) \leqslant \varliminf_{n\to\infty}\varepsilon_{l,Z}^H(\tilde{\varrho}_n) = e_{l,Z}^H(N).$$

This proves the theorem provided we can show $\tilde{\varrho}\in G_N$:

(i) $\tilde{\varrho}\geqslant 0$ a.e., since otherwise $\int_0^\infty f(\tilde{\varrho}_n-\tilde{\varrho})\,dr$ would not converge to zero for every $f\in L^{3/2}$, e.g. $f=\chi_A$ with $A=\{r\,|\,\tilde{\varrho}(r)<0,\ r\leqslant R\}$ for some large enough R.

(ii) $\int_0^\infty \tilde{\varrho}\,dr\leqslant N$, since $\int_0^\infty\tilde{\varrho}\,dr = \lim_{m\to\infty}\int_0^\infty \chi_{(0,m)}\tilde{\varrho}\,dr = \lim_{m\to\infty}\lim_{n\to\infty}\int_0^\infty\chi_{(0,m)}\tilde{\varrho}_n\,dr\leqslant N$.

(iii) $\int_0^\infty\frac{\tilde{\varrho}}{r^2}\,dr<\infty$, since $\int_0^\infty\frac{\tilde{\varrho}}{r^2}\,dr=\int_{r_l}^\infty\frac{\tilde{\varrho}}{r^2}\,dr\leqslant\frac{N}{r_l^2}$.

Uniqueness follows from Theorem 3.1. ■

Next we come to the functionals of total energy. Let k be some non-negative integer and $\varepsilon_Z^{H,k}(\tilde{\varepsilon}_Z^{H,k})$ the restriction of $\varepsilon_Z^H(\tilde{\varepsilon}_Z^H)$ onto $M^k=\{\boldsymbol{\varrho}\in M\,|\,\varrho_{k+1}=\varrho_{k+2}=\ldots=0\}$. Analogously one defines M_N^k, $M_{\partial N}^k$. A simple corollary to the proof of Theorem 3.3 is

THEOREM 3.4. *$\varepsilon_Z^{H,k}$ and $\tilde{\varepsilon}_Z^{H,k}$ have uniquely determined minimizing elements on M_N^k.*

Proof: We remark that the r_l are bounded from below by $1/(4Z)$ and that $D(\varrho,\sigma)$ as a positive quadratic form is weakly lower semicontinuous. The rest follows as in the proof of Theorem 3.3. ■

THEOREM 3.5. (a) *The following holds*

$$f(k)=\inf\{\varepsilon_Z^{H,k}(\boldsymbol{\varrho})\,|\,\boldsymbol{\varrho}\in M_N^k\}\geqslant\inf\{\varepsilon_Z^{H,k+1}(\boldsymbol{\varrho})\,|\,\boldsymbol{\varrho}\in M_N^{k+1}\}=f(k+1),$$

i.e. the infima are monotone decreasing functions in k.

(b) *There is a critical k_c such that $f(k)=f(k_c)$ for $k\geqslant k_c$, and in this case the uniquely determined minimizing $\boldsymbol{\varrho}^k$ has $\varrho_{k_c+1}=\varrho_{k_c+2}=\ldots=0$.*

Proof: (a) is immediate.

(b) Let ϱ^k be the uniquely determined minimum of $\varepsilon_Z^{H,k}$ on M_N^k. Then ϱ^k fulfils the Euler–Lagrange equations for some non-positive μ_k

$$\varrho_l^k = \alpha_l^{-1/2}\frac{1}{r}[\Psi^k(r)-\beta_l]_+^{1/2} \quad \text{for } l = 0, 1, \ldots, k,$$

where

$$\Psi^k(r) = r^2\left(\frac{Z}{r} - \sum_{l=0}^{k}\int_0^\infty \frac{\varrho_l^k(r')}{\max\{r, r'\}}dr' + \mu_k\right).$$

Since $\Psi^k(r)/r^2$ is monotone decreasing on $S = \{r \mid \Psi^k(r)/r^2 > 0\}$, we have

$$\frac{\Psi^k(r)}{r^2} \leqslant \frac{\Psi^k(r')}{r'^2} \leqslant \frac{\Psi^k(r_1)}{r_1^2}$$

for $r \geqslant r' \geqslant r_1$.

Given $\varepsilon > 0$ we distinguish two cases:

(1) Ψ^k is bounded by $(1+\varepsilon)\beta_0$.

(2) Ψ^k is not bounded by $(1+\varepsilon)\beta_0$. Then we define for every r with $\Psi^k(r) > (1+\varepsilon)\beta_0$ the point $r_1 = r\left(\frac{(1+\varepsilon)\beta_0}{\Psi^k(r)}\right)^{1/2}$. Let $r' \in [r_1, r]$. Then we obtain

$$\Psi^k(r') \geqslant \left(\frac{r'}{r}\right)^2 \Psi^k(r) \geqslant \left(\frac{r_1}{r}\right)^2 \Psi^k(r) = \frac{(1+\varepsilon)\beta_0}{\Psi^k(r)}\Psi^k(r) = (1+\varepsilon)\beta_0.$$

Thus

$$N \geqslant \sum_{l=0}^{k}\int_0^\infty \varrho_l^k(r')\,dr' \geqslant \int_{r_1}^{r} \varrho_0^k(r')\,dr' = \alpha_0^{-1/2}\int_{r_1}^{r}\frac{1}{r'}[\Psi^k(r')-\beta_0]_+^{1/2}\,dr'$$

$$\geqslant \sqrt{\varepsilon\frac{\beta_0}{\alpha_0}}\ln\frac{r}{r_1} = \sqrt{\varepsilon\frac{\beta_0}{\alpha_0}}\,\frac{1}{2}\ln\frac{\Psi^k(r)}{(1+\varepsilon)\beta_0},$$

and therefore

$$\Psi^k(r) \leqslant (1+\varepsilon)\beta_0\exp\left(2\sqrt{\frac{\alpha_0}{\varepsilon\beta_0}}N\right).$$

Combining both cases and choosing $\varepsilon = 1$, we get

$$\Psi^k(r) \leqslant \frac{1}{2}\exp\frac{4\pi N}{q}. \tag{3.9}$$

The right-hand side of (3.9) is independent of k and r. Therefore, independently of k, we obtain at least for all l with $\beta_l \geqslant \frac{1}{2}\exp\frac{4\pi N}{q}$ that $\varrho_l = 0$ which proves (b). The proof of (3.9) is essentially due to Sölter [14]. ∎

We remark that for the non-interacting case the analogue can be proven in a similar way. Therefore we have as an immediate corollary:

THEOREM 3.6. *ε_Z^H and $\tilde{\varepsilon}_Z^H$ have uniquely determined minimizing elements in M_N which are equal to those of ε_Z^{H,k_c} and $\tilde{\varepsilon}_Z^{H,k_c}$, respectively, on $M_N^{k_c}$ and the corresponding minima are equal.*

Now we discuss the critical particle number. Let N_c be that particle number, where the energy ceases to decrease further. We call N_c the critical particle number. Since the infima of both the Hellmann and the Hellmann–Weizsäcker functional are monotone decreasing in the particle number, as Theorem 2.1 and 2.2 show, and convex, $N_c \in [0, \infty]$ is well defined. Because of the monotonicity of the infimum and the uniqueness of the minimizing ϱ we have $\sum_{l=0}^{\infty} \|\varrho_l\|_1 = N$ for $N \leqslant N_c$. Our goal is to show that $N_c = Z$ in the interacting case. We begin with the following theorem.

THEOREM 3.7. *For $N \leqslant Z$ the minimizing ϱ for ε_Z^H on M_N has $\sum_{l=0}^{\infty} \int_0^{\infty} \varrho_l \, dr = N$.*

Proof: Suppose that the minimizing ϱ has $\sum_{l=0}^{\infty} \int_0^{\infty} \varrho_l \, dr = N_0 < N$. Then the Lagrange multiplier λ is zero, thus

$$\alpha_l \varrho_l^2(r) = \left[\frac{Z}{r} - \int_0^{\infty} \frac{\sum_{l=0}^{\infty} \varrho_l(r')}{\max\{r, r'\}} dr' - \frac{\beta_l}{r^2} \right]_+ .$$

Thus there exist two positive constants c and R such that

$$\varrho_l(r) \geqslant c \sqrt{\frac{1}{r}} \quad \text{for } r \geqslant R.$$

Hence

$$\int_0^{\infty} \varrho_l \, dr \geqslant c \int_R^{\infty} r^{-1/2} \, dr = \infty .$$

Such densities, however, are excluded, which proves the theorem. ∎

THEOREM 3.8. *If $N \geqslant Z$, then for the ϱ that minimizes ε_Z^H on M_N the following equality holds*:

$$\sum_{l=0}^{\infty} \int_0^{\infty} \varrho_l(r) \, dr = Z .$$

Proof: We first remark that $\sum_{l=0}^{\infty} \int_0^{\infty} \varrho_l(r)\,dr$ cannot be smaller than Z because of Theorem 3.7. Now suppose $\sum_{l=0}^{\infty} \int_0^{\infty} \varrho_l(r)\,dr > Z$. Then by Newton's theorem, for r large enough,

$$\varphi(r) = \frac{Z}{r} - \int_0^{\infty} \frac{\sum_{l=0}^{\infty} \varrho_l(r')}{\max\{r, r'\}}\,dr' \tag{3.10}$$

becomes negative. We therefore have a closer look at

$$T = \{r \in \boldsymbol{R} \mid r \geqslant 0,\ \varphi(r) < 0\}.$$

First we remark that φ is continuous away from zero. Zero, however, does certainly not belong to T, since φ diverges to infinity as r approaches zero from the right. Thus Z as the preimage of an open set under a continuous function is open. Furthermore by the Euler–Lagrange equation

$$\alpha_l \varrho_l^2(r) = \left[\varphi - \frac{\beta_l}{r^2} + \lambda\right]_+$$

ϱ_l is zero on T, since $\lambda \leqslant 0$. Hence on T: $\sum_{l=0}^{\infty} \varrho_l = 0$ and since

$$r\frac{d^2}{dr^2} r\varphi = \sum_{l=0}^{\infty} \varrho_l(r) = 0,$$

$\varphi = a + b/r$. Because φ vanishes on the boundary of T and $\varphi(r) \to 0$ for $r \to \infty$, φ is identical to zero on T. Hence $T = \emptyset$ and $\varphi \geqslant 0$ everywhere, which is a contradiction. ∎

Both proofs are characteristic of the Hellmann functional and cannot be transscribed to the case with gradient correction. The following theorem summarizes the above results.

THEOREM 3.9. (a) *If $N \leqslant Z$, then ε_Z^H assumes its minimum on $M_{\partial N}$ for a unique element. The minimizing density fulfils the Euler–Lagrange equations* (3.2) *and* (3.3) *with $\lambda = \left.\frac{dE_Z^H(x)}{dx}\right|_{x=N}$. Particularly, if $N = Z$, then $\lambda = 0$, and if $N < Z$, then $\lambda < 0$.*

For $N > Z$ there exists no minimizing element for ε_Z^H in $M_{\partial N}$ and no solution of the Euler–Lagrange equations. In M_N, however, a unique minimizing element $\boldsymbol{\varrho}$ exists which fulfils $\sum_{l=0}^{\infty} \int_0^{\infty} \varrho_l\,dr = Z$.

(b) *For $\tilde{\varepsilon}_Z^H$ a unique minimizing density in $M_{\partial N}$ exists for all N. This density fulfils the Euler–Lagrange equations* (3.2) *and* (3.4) *with* $\lambda = \left.\frac{d\tilde{E}_Z^H(x)}{dx}\right|_{x=N} < 0$.

Proof: For the non-interacting case $N_c = \infty$ remains to be proved. This follows analogously as in the proof of Theorem 3.7. ∎

Now we come to the Hellmann–Weizsäcker functional. For technical purposes we define further functionals and sets of functions, obtained by writing ψ^2 for ϱ:

$$\hat{F} = \{\psi \mid \psi \geqslant 0,\ \psi^2 \in F\},$$

$$\hat{W} = \{\boldsymbol{\psi} \mid \boldsymbol{\psi} \geqslant 0,\ \boldsymbol{\psi}^2 \in W\},$$

and analogously $\hat{F}_N$, $\hat{F}_{\partial N}$ $\hat{W}_N$ and $\hat{W}_{\partial N}$. $\boldsymbol{\psi}^2$ stands here for $(\psi_0^2, \psi_1^2, \ldots)$. These functionals are the following:

$$\mathscr{F}_{l,Z}^{HW}(\psi_l) = \int_0^\infty \left(\psi_l'^2 + \frac{\alpha_l}{3}\psi_l^6 + \left(\frac{\beta_l}{r^2} - \frac{Z}{r}\right)\psi_l^2\right) dr,$$

$$\tilde{\mathscr{F}}_Z^{HW}(\boldsymbol{\psi}) = \sum_{l=0}^\infty \mathscr{F}_{l,Z}^{HW}(\psi_l),$$

$$\mathscr{F}_Z^{HW}(\boldsymbol{\psi}) = \tilde{\mathscr{F}}_Z^{HW}(\boldsymbol{\psi}) + \tfrac{1}{2} \sum_{l,l'=0}^\infty D(\psi_l^2, \psi_{l'}^2).$$

The infima of these functionals are the same as those of the associated density functionals and $\boldsymbol{\psi}$ minimizes $\mathscr{F}_Z^{HW}$ on $\hat{W}_{\partial N}$, if and only if $\boldsymbol{\varrho} = \boldsymbol{\psi}^2$ minimizes ε_Z^{HW} on $W_{\partial N}$. The same holds in the other cases. Therefore we denote the infima of the $\mathscr{F}$-functionals by E, too. Now we come to the relation of the functionals $\mathscr{F}$ to the Euler–Lagrange equations:

THEOREM 3.10. (a) *If $\boldsymbol{\psi} \in \hat{W}_{\partial N}$ obeys the Hellmann–Weizsäcker equations*

$$-\psi_l''(r) + \alpha_l \psi_l^5 + \left(\frac{\beta_l}{r^2} - \varphi(r) - \lambda\right)\psi_l = 0, \qquad l = 0, 1, 2, \ldots, \tag{3.11}$$

where φ is either

$$\varphi(r) = \frac{Z}{r} - \sum_{l=0}^\infty \int_0^\infty \frac{\psi_l^2(r')}{\max\{r, r'\}} dr' \tag{3.12}$$

or

$$\varphi(r) = \frac{Z}{r}, \tag{3.13}$$

then $\boldsymbol{\psi}$ minimizes $\mathscr{F}_Z^{HW}$ respectively $\tilde{\mathscr{F}}_Z^{HW}$ on $\hat{W}_N$, $E_Z^{HW}(x)$ and $\tilde{E}_Z^{HW}(x)$ are differen-

tiable at $x = N$, *and*

$$\lambda = \left.\frac{dE_Z^{HW}(x)}{dx}\right|_{x=N} \quad \textit{respectively} \quad \lambda = \left.\frac{d\tilde{E}_Z^{HW}(x)}{dx}\right|_{x=N}. \tag{3.14}$$

In particular λ *is zero (in the interacting case), if* ψ *minimizes* $\mathscr{F}_Z^{HW}$ *on* $\hat{W}$.

(b) *Conversely, if* $\psi \in \hat{W}_{\partial N}$ *minimizes* $\mathscr{F}_Z^{HW}$ *or* $\tilde{\mathscr{F}}_Z^{HW}$ *on* $\hat{W}_{\partial N}$, *then* ψ *obeys the Hellmann–Weizsäcker equations* (3.11) *and* (3.12), *respectively* (3.11) *and* (3.13) *where* λ *is given by* (3.14).

Proof: The proof imitates that of Theorem 3.2. ∎

Now we are concerned with existence questions.

THEOREM 3.11. $\mathscr{F}_{l,Z}^{HW}$ *has a minimizing element in* D *where* D *is the completion of* $\{\psi \in C_0^\infty(0, \infty) | \psi \geq 0\}$ *in the norm* $\|\psi'\|_2 + \|\psi\|_6$.

Proof: First we remark that $\mathscr{F}_{l,Z}^{HW}$ is finite on D: Because of Hardy's and Hölder's inequalities $\int_0^\infty \frac{\psi^2}{4r^2}\, dr \leq \int_0^\infty \psi'^2\, dr$ holds and for every $\varepsilon > 0$ there exist positive numbers δ and b with

$$\int_0^\infty \frac{Z}{r}\psi^2\, dr \leq \int_0^\delta \left(\frac{Z}{r} - \frac{\varepsilon}{4r^2}\right)\psi^2\, dr + \varepsilon \int_0^\infty \frac{\psi^2}{4r^2}\, dr + \int_\delta^\infty \frac{Z}{r}\psi^2\, dr \leq \varepsilon \int_0^\infty \psi'^2\, dr + b\Big(\int_0^\infty \psi^6\, dr\Big)^{1/3}.$$

Therefore $\mathscr{F}_{l,Z}^{HW}$ is bounded from below on D by

$$\mathscr{F}_{l,Z}^{HW} \geq \|\psi'\|_2^2 + \frac{\alpha_l}{3}\|\psi\|_6^6 + \beta_l \left\|\frac{\psi}{r}\right\|_2^2 - \varepsilon\|\psi'\|_2^2 - b\|\psi\|_6^2 \geq \gamma(\|\psi'\|_2^2 + \|\psi\|_6^6) - C \tag{3.15}$$

with certain positive constants γ and C.

Now let ψ_n be a minimizing sequence. Because of (3.15) we find that $\|\psi_n'\|_2$ and $\|\psi_n\|_6$ are bounded. By the Banach–Alaoglu theorem we can extract a subsequence, also denoted by ψ_n, converging weakly in the norm $\|\psi_n'\|_2 + \|\psi_n\|_6$ to $\psi \in D$. Therefore $\psi_n \to \psi$ weakly in L^6 holds and hence

$$\int_0^\infty \psi^6\, dr \leq \varliminf_{n\to\infty} \int_0^\infty \psi_n^6\, dr. \tag{3.16}$$

Choosing the number a sufficiently small we define the scalar product

$$(f, \psi) = \int_0^\infty \left(f'\psi' - \frac{Z}{r}\chi_{[0,a]}(r) f\psi\right) dr$$

which is continuous in the norm $\|\psi'\|_2+\|\psi\|_6$

$$(f, \psi) \leqslant \|f'\|_2\|\psi'\|_2+\left(\int_0^a\left(\frac{Z}{r}f\right)^2 dr\right)^{1/2}\left(\int_0^a\psi^2\,dr\right)^{1/2}$$
$$\leqslant \|f'\|_2\|\psi'\|_2+\text{const}\,\|f'\|_2\|\psi\|_6 \leqslant \text{const}\,(\|\psi'\|_2+\|\psi\|_6).$$

Therefore, using Schwarz' inequality, we find

$$0 \leqslant \int_0^\infty\left(\psi'^2-\frac{Z}{r}\chi_{[0,a]}(r)\psi^2\right)dr \leqslant \varliminf_{n\to\infty}\int_0^\infty\left(\psi_n'^2-\frac{Z}{r}\chi_{[0,a]}(r)\psi_n^2\right)dr. \tag{3.17}$$

Furthermore $\int_0^\infty \frac{f}{r^2}\psi\,dr$ is a continuous linear functional

$$\int_0^\infty \frac{1}{r^2}f\psi\,dr \leqslant \left(\int_0^\infty\frac{f^2}{r^2}dr\right)^{1/2}\left(\int_0^\infty\frac{\psi^2}{r^2}dr\right)^{1/2} \leqslant 4\|f'\|_2(\|\psi'\|_2+\|\psi\|_6)$$

yielding

$$\beta_l\int_0^\infty\frac{\psi^2}{r^2}dr \leqslant \varliminf_{n\to\infty}\beta_l\int_0^\infty\frac{\psi_n^2}{r^2}dr. \tag{3.18}$$

The term $\int_a^\infty -\frac{Z}{r}\psi^2\,dr$ remains. Since $\psi_n\to\psi$ weakly in L^6, $\psi_n\to\psi$ weakly in L^2_{loc} and therefore in $H^1_{0,\text{loc}}$. Since for any $R>0$ the space $H^1(0, R)$ may be compactly imbedded in $L^3(0, R)$ (Adams [15] Theorem 6.2), we find $\psi_n^2\to\psi^2$ strongly in L^3_{loc}. Therefore we have

$$\left|\int_a^\infty\frac{1}{r}(\psi_n^2-\psi^2)\,dr\right| \leqslant \left|\int_a^{R_0}\frac{1}{r}(\psi_n^2-\psi^2)\,dr\right|+\left|\int_{R_0}^\infty\frac{1}{r}(\psi_n^2-\psi^2)\,dr\right|$$
$$\leqslant \left(\int_a^{R_0} r^{-3/2}\,dr\right)^{2/3}\left(\int_a^{R_0}|\psi_n^2-\psi^2|^3\,dr\right)^{1/3}+2^{2/3}R_0^{-1/3}\left(\int_{R_0}^\infty|\psi_n^2-\psi^2|^3\,dr\right)^{1/3}.$$

The first and the third integral are finite. The second integral tends to zero as n approaches infinity, whereas all the other terms remain bounded. Taking then the limit R_0 to infinity yields zero for the remaining term. Thus we have

$$\int_a^\infty\frac{Z}{r}\psi^2\,dr = \lim_{n\to\infty}\int_a^\infty\frac{Z}{r}\psi_n^2\,dr. \tag{3.19}$$

Combining (3.16), (3.17), (3.18) and (3.19) we finally arrive at

$$\mathscr{F}^{HW}_{l,Z}(\psi) \leqslant \varliminf_{n\to\infty}\mathscr{F}^{HW}_{l,Z}(\psi_n). \quad\blacksquare$$

Again, as in the Hellmann case, we can generalize this result to the case where finitely many angular momentum channels are taken into account. We define the functionals $\mathscr{F}_Z^{HW,k}$ and $\tilde{\mathscr{F}}_Z^{HW,k}$ and the sets $\hat{W}^k$, $\hat{W}_N^k$ and $\hat{W}_{\partial N}^k$ analogously to the Hellmann case and we arrive at

THEOREM 3.12. *$\mathscr{F}_Z^{HW,k}$ and $\tilde{\mathscr{F}}_Z^{HW,k}$ have minimizing elements in*

$$\mathbf{D}^k = \{\boldsymbol{\psi} | \psi_0, \psi_1, \ldots, \psi_k \in D,\ \psi_{k+1} = \psi_{k+2} = \ldots = 0\}.$$

Now we consider the critical particle number. Of course $N_c = \infty$, if there is no interaction. Our goal is to show that $N_c < \infty$ for each functional $\mathscr{F}_Z^{HW,k}$ and $N_c > Z$.

THEOREM 3.13. *The $\boldsymbol{\psi}$ that minimizes $\mathscr{F}_Z^{HW,k}$ on $\mathbf{D}^k$ fulfils $\sum_{l=0}^{k} \int_0^\infty \psi_l^2\, dr < \infty$.*

Proof: Suppose $\int_0^\infty \sum_{l=0}^{k} \psi_l^2\, dr = \infty$. Then there will be a point r_1 with $\int_0^{r_1} \sum_{l=0}^{k} \psi_l^2\, dr = Z + \delta$ for some positive δ. Therefore $\varphi(r) \leqslant -\frac{\delta}{r}$ holds for $r \geqslant r_1$. Since $\boldsymbol{\psi}$ fulfils the Euler–Lagrange equations (3.11) for $l = 0, 1, \ldots, k$ we have

$$-\psi_l'' + \frac{\delta}{r}\psi_l \leqslant 0 \quad \text{for } r \geqslant r_1.$$

The function $\tilde{\psi}_l = Mre^{-2\sqrt{\delta r}}$ fulfils the inequality

$$-\tilde{\psi}_l'' + \frac{\delta}{r}\tilde{\psi}_l \geqslant 0 \quad \text{for } r \neq 0.$$

Thus we have for $r \geqslant r_1$

$$-(\psi_l - \tilde{\psi}_l)'' + \frac{\delta}{r}(\psi_l - \tilde{\psi}_l) \leqslant 0. \tag{3.20}$$

Choose M such that $\psi_l(r_1) \leqslant \tilde{\psi}_l(r_1)$. Now fix $\zeta \in C_0^\infty[0, \infty)$ with $0 \leqslant \zeta \leqslant 1$ and

$$\zeta(r) = \begin{cases} 1 & \text{for } r \leqslant 1 \\ 0 & \text{for } r > 2 \end{cases}$$

and define $\zeta_n(r) = \zeta\left(\frac{r}{n}\right)$. Multiplying (3.20) by $\zeta_n[\psi_l - \tilde{\psi}_l]_+$ and integrating over the interval $[r_1, \infty)$ yields

$$\int_{r_1}^\infty (\psi_l - \tilde{\psi}_l)'(\zeta_n'[\psi_l - \tilde{\psi}_l]_+ + \zeta_n[\psi_l - \tilde{\psi}_l]_+')\, dr + \int_{r_1}^\infty \frac{\delta}{r}[\psi_l - \tilde{\psi}_l]_+^2\, \zeta_n\, dr \leqslant 0$$

and hence

$$\int_{r_1}^{\infty} \frac{\delta}{r} [\psi_l - \tilde{\psi}_l]_+^2 \zeta_n dr \leqslant \int_{r_1}^{\infty} -(\psi_l - \tilde{\psi}_l)' \zeta_n' [\psi_l - \tilde{\psi}_l]_+ dr = \tfrac{1}{2} \int_{r_1}^{\infty} \zeta_n'' [\psi_l - \tilde{\psi}_l]_+^2 dr.$$

We may estimate the latter integral by

$$\frac{1}{2} \int_{r_1}^{\infty} \zeta_n'' [\psi_l - \tilde{\psi}_l]_+^2 dr \leqslant \frac{1}{2} \int_{n}^{2n} \zeta_n'' \psi_l^2 dr \leqslant \frac{c}{n^2} \int_{n}^{2n} \psi_l^2 dr \leqslant cn^{-4/3} \|\psi_l\|_6^2,$$

which tends to zero as $n \to \infty$. However, $\zeta_n \to 1$ as n approaches infinity and therefore $\int_{r_1}^{\infty} \frac{\delta}{r} [\psi_l - \tilde{\psi}_l]_+^2 dr = 0$ yielding $\psi_l(r) \leqslant \tilde{\psi}_l(r)$ for $r \geqslant r_1$. Since $\tilde{\psi}_l$ is square integrable, we find $\psi_l \in L^2$, too, and hence $\int_0^{\infty} \sum_{l=0}^{k} \psi_l^2 dr < \infty$, which contradicts our assumption and proves the theorem. ∎

THEOREM 3.14. *If* $\boldsymbol{\psi}$ *minimizes* $\mathscr{F}_Z^{HW}$ *or* $\mathscr{F}_Z^{HW,k}$ *on* $\mathbf{D}^\infty$ *or* $\mathbf{D}^k$, *respectively, then* $\sum_{l=0}^{\infty} \int_0^{\infty} \psi_l^2 dr > Z$.

Proof: Again we suppose that the contrary is true: $\sum_{l=0}^{\infty} \int_0^{\infty} \psi_l^2 dr \leqslant Z$. Then we find easily that $\varphi(r) \geqslant 0$ for $r \neq 0$. Therefore, since a minimizing $\boldsymbol{\psi}$ fulfils the Euler–Lagrange equations, we have particularly for $r \neq 0$

$$-\psi_0'' + \alpha_0 \psi_0^5 \geqslant 0.$$

The function $\tilde{\psi}_0 = cr^{-1/2}$ fulfils for $r > 1$ the inequality

$$-\tilde{\psi}_0'' + \alpha_0 \tilde{\psi}_0^5 \leqslant 0,$$

if the constant c is chosen such that $c^4 \leqslant \frac{3q^2}{4\pi^2}$ holds. Therefore we have for $r > 1$

$$-(\psi_0 - \tilde{\psi}_0)'' + \alpha_0 (\psi_0^5 - \tilde{\psi}_0^5) \geqslant 0. \tag{3.21}$$

Since $\psi_0 \in H_{\text{loc}}^1$, ψ_0 is continuous on a compact set Ω using Theorem 5.4 of Adams [15]. Therefore we can choose c such that $\tilde{\psi}_0(1) \leqslant \psi_0(1)$. Moreover, $\psi_0'' = \alpha_0 \psi_0^5 - \varphi(r)\psi_0$ is continuous and consequently $\psi_0 \in C^2(\Omega)$. Now define the function $f = \psi_0 - \tilde{\psi}_0$ and the open set $A = \{r > 1 \mid f(r) < 0\}$. Using (3.21) we find on A that $f'' < 0$, i.e. f is concave. This is impossible, since $f(1) \geqslant 0$ and $\psi_0 \geqslant 0$. Hence A is empty and $\tilde{\psi}_0(r) \leqslant \psi_0(r)$ for $r \geqslant 1$. Therefore we have

$$\sum_{l=0}^{\infty} \int_0^{\infty} \psi_l^2 \, dr \geqslant \int_1^{\infty} \psi_0^2 \, dr \geqslant \int_1^{\infty} \tilde{\psi}_0^2 \, dr = c^2 \int_1^{\infty} r^{-1} \, dr = \infty,$$

which yields a contradiction, thus proving the theorem. ∎

We remark that the proofs of the Theorem 3.11, 3.13 and 3.14 are suggested by Benguria, Brezis and Lieb [16].

In a final theorem we summarize the results for the Hellmann–Weizsäcker functionals.

THEOREM 3.15 (a) *For every* $k \in N_0$ *there exists a number* N_c *with* $Z < N_c < \infty$ *such that for* $N \leqslant N_c$ *the functional* $\varepsilon_Z^{HW,k}$ *assumes its minimum on* $W_{\partial N}^k$ *for a unique element* $\boldsymbol{\varrho}$. $\boldsymbol{\psi} = \sqrt{\boldsymbol{\varrho}}$ *fulfils the Euler–Lagrange equations* (3.11) *and* (3.12) *with* $\lambda = \left.\dfrac{dE^{HW,k}(x)}{dx}\right|_{x=N}$. *Particularly, if* $N = N_c$, *then* $\lambda = 0$, *and if* $N < N_c$, *then* $\lambda < 0$.

For $N > N_c$ *there exists no minimizing element for* $\varepsilon_Z^{HW,k}$ *in* $W_{\partial N}^k$ *and no solution of the Euler–Lagrange equations. In* W_N^k, *however, a unique minimizing element* $\boldsymbol{\varrho}$ *exists which fulfils* $\sum_{l=0}^{k} \int_0^{\infty} \varrho_l \, dr = N_c$.

(b) *For every* $k \in N_0$ *the functional* $\tilde{\varepsilon}_Z^{HW,k}$ *assumes its minimum on* $W_{\partial N}^k$ *for a unique element* $\boldsymbol{\varrho}$. $\boldsymbol{\psi} = \sqrt{\boldsymbol{\varrho}}$ *fulfils the Euler–Lagrange equations* (3.11) *and* (3.13) *with* $\lambda = \left.\dfrac{dE^{HW,k}(x)}{dx}\right|_{x=N} < 0$.

4. Scaling properties of the Hellmann and the Hellmann–Weizsäcker functional

In this chapter we collect some scaling properties of the Hellmann and the Hellmann–Weizsäcker functional. Let us start with the interaction free case. We scale

$$\begin{aligned} r &\mapsto Zr = \tilde{r}, \\ \varrho(r) &\mapsto Z\varrho(Zr) = \tilde{\varrho}(r). \end{aligned} \tag{4.1}$$

Then

$$\varepsilon_{l,Z}^{HW}(\tilde{\varrho}) = \int_0^{\infty} \left\{ \left(\frac{\partial}{\partial r} \sqrt{Z\varrho(Zr)} \right)^2 + \frac{\alpha_l}{3} Z^3 \varrho^3(Zr) + \frac{\beta_l}{r^2} Z\varrho(Zr) - \frac{Z^2}{r} \varrho(Zr) \right\} dr = Z^2 \varepsilon_{l,1}^{HW}(\varrho). \tag{4.2}$$

Thus we obtain

$$E_{l,Z}^{HW}(N) = Z^2 E_{l,1}^{HW}(N), \tag{4.3}$$

and

$$\tilde{E}_Z^{HW}(N) = Z^2 \tilde{E}_1^{HW}(N). \tag{4.4}$$

The counterpart of (4.2) for the Hellmann functional implies the result analogous to (4.3) and (4.4). For the interacting case this result breaks down, however.

Next we show the virial theorem. Use again the scaling as above. Suppose ϱ minimizes ε_Z^{HW} on W_N. Then for $c > 0$

$$f(c) = \varepsilon_Z^{HW}(c\varrho(c.)) \tag{4.5}$$

assumes its minimal value for $c = 1$. Thus

$$0 = f'(1) = 2\sum_{l=0}^{\infty}\int_0^{\infty}\left(\sqrt{\varrho l}'^2 + \frac{\alpha_l}{3}\varrho_l^3 + \frac{\beta_l}{r^2}\varrho_l\right)dr -$$

$$-\sum_{l=0}^{\infty} Z\int_0^{\infty}\frac{\varrho_l(r)}{r}dr + \frac{1}{2}\sum_{l,l'=0}^{\infty}\int_0^{\infty}dr\int_0^{\infty}dr'\frac{\varrho_l(r)\varrho_{l'}(r)}{\max\{r, r'\}}, \tag{4.6}$$

which implies

$$2T^{HW} + V^{HW} + W^{HW} = 0, \tag{4.7}$$

where we introduced the obvious abbreviations for the first, second, and third term of the right-hand side of (4.6). Again the results for the case without interaction and for the Hellmann functional follow analogously.

5. A bound for the quantum mechanical ground state energy

As shown in [12] one finds for the quantum mechanical ground state energy the following upper bound, whenever some non-negative integers $N_{l,m,s}$ such that $\sum_{l,m,s} N_{l,m,s} = N$ and non-negative functions $\tilde{\varrho}_{l,m,s}$ with $\int_0^{\infty} 4\pi r^2\,\tilde{\varrho}_{l,m,s}(r)\,dr = N_{l,m,s}$ are given:

$$E_Q(Z, N) \leqslant \sum_{l,m,s}\int_0^{\infty} 4\pi r^2\left\{\sqrt{\tilde{\varrho}_{l,m,s}(r)}'^2 + \frac{16\pi^4}{3}\frac{[N_{l,m,s}^2 - 1]_+}{N_{l,m,s}^2}r^4\,\tilde{\varrho}_{l,m,s}^3(r) + \right.$$

$$\left. + \left(\frac{l(l+1)}{r^2} - \frac{Z}{r}\right)\tilde{\varrho}_{l,m,s}\right\}dr + \frac{1}{2}\sum_{l,m,s}\sum_{l',m',s'}\int_0^{\infty}dr 4\pi r^2\int_0^{\infty}dr'\,4\pi r'^2\,\tilde{\varrho}_{l,m,s}(r)\,\tilde{\varrho}_{l',m',s'}(r')$$

$$\times\int d\Omega\int d\Omega'\,|Y_{l,m}(\Omega)|^2\,|Y_{l',m'}(\Omega')|^2\frac{1}{|\mathbf{r}-\mathbf{r}'|}. \tag{5.1}$$

If one introduces $\varrho_l(r) = 4\pi r^2 q(2l+1)\,\tilde{\varrho}_{l,m,s}(r)$ and assumes $N_{l,m,s} = \dfrac{N_l}{q(2l+1)}$ independent of m and s then the right-hand side of (5.1) becomes the functional ε_Z^{HW} with coefficients

$$\alpha_l = \frac{\pi^2}{q^2(2l+1)^2}\left[1 - \frac{1}{N_{l,m,s}^2}\right]_+ \quad\text{and}\quad \beta_l = l(l+1). \tag{5.2}$$

Thus, ε_Z^{HW} is an upper bound on the quantum mechanical ground state energy, if one prescribes the $N_{l,m,s}$ to be integer. Here we will generalize this condition to non-integer values of $N_{l,m,s}$.

In the following we consider the trace class operators d_1 with the additional properties

(i) $0 \leqslant d_1(x, x') = \sum_{j=0}^{\infty} w_j \varphi_j(x) \varphi_j^*(x') \leqslant 1$ and

(ii) $\sum_{j=0}^{\infty} w_j \sum_{\sigma=1}^{q} \int |\nabla \varphi_j|^2 d^3 r < \infty$.

Here x and x' are space-spin variables, i.e. $x = (\mathbf{r}, \sigma)$ and the gradient is to be understood in distributional sense. For this class of operators

$$\mathscr{H}(d_1) = \sum_{\sigma=1}^{q} \int \left(\left[\frac{\partial^2}{\partial \mathbf{r}\, \partial \mathbf{r}'} d_1(x, x') \right]_{x=x'} - \frac{Z}{|\mathbf{r}|} d_1(x, x) \right) d^3 r + \\ + \frac{1}{2} \sum_{\sigma, \sigma'=1}^{q} \int\int \frac{d_1(x, x) d_1(x', x')}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r'$$

may be defined in a natural way. The occurrences of d_1 in the following proof may be interpreted in the same way.

The quantum mechanical ground state energy can be bounded by the Hartree–Fock form of the energy functional independently of whether the one-particle density matrix is derived from a Slater determinant or not using Lieb's theorem [17] and thus, by the positivity of the Coulomb kernel we have

$$E_Q(Z, N) \leqslant h_Z(N) = \inf \{ \mathscr{H}(d_1) | \operatorname{tr} d_1 = N \}, \tag{5.3}$$

where N is the number of particles, i.e. an integer. However, we now relax this condition and allow for non-integer values of N for which $h_Z(N)$ is also well defined, and prove that the condition $\operatorname{tr} d_1 = N$ in (5.3) may be substituted by the condition $\operatorname{tr} d_1 \leqslant N$.

THEOREM 5.1. *The function $h_Z(N)$ is monotone decreasing, i.e. $h_Z(N) \leqslant h_Z(N')$ for $N' < N$.*

Proof: We introduce a seminorm for one-particle density matrices

$$\|d_1\|^* = \sum_{\sigma=1}^{q} \int \left[\frac{\partial^2}{\partial \mathbf{r}\, \partial \mathbf{r}'} |d_1|(x, x') \right]_{x=x'} d^3 r.$$

The functional $\mathscr{H}$ is continuous in this seminorm on each set $\{d_1 | \operatorname{tr} d_1 < c\}$: Let $\|d_{1,n} - d_1\|^* \to 0$, then

$$|\mathscr{H}(d_{1,n})-\mathscr{H}(d_1)| \leqslant \sum_{\sigma=1}^{q} \int \left\| \left[\frac{\partial^2}{\partial \mathbf{r}\, \partial \mathbf{r}'}(d_{1,n}(x, x')-d_1(x, x'))\right]_{x'=x} \right| d^3 r +$$
$$+\sum_{\sigma=1}^{q} \int_{|r|\leqslant a} \frac{Z}{|\mathbf{r}|} |d_{1,n}(x, x)-d_1(x, x)|\, d^3 r + \sum_{\sigma=1}^{q} \int_{|r|>a} \frac{Z}{|\mathbf{r}|} |d_{1,n}(x, x)-d_1(x, x)|\, d^3 r$$
$$+\frac{1}{2}\sum_{\sigma,\sigma'=1}^{q} \iint \frac{(d_{1,n}(x, x)+d_1(x, x))|d_{1,n}(x', x')-d_1(x', x')|}{|\mathbf{r}-\mathbf{r}'|} d^3 r'\, d^3 r. \tag{5.4}$$

The first term of the right-hand side of (5.4) tends to zero, which follows from the definition of the seminorm. In order to treat the other terms we remark that the following inequalities hold:

$$\sum_{\sigma=1}^{q} \int |d_1^{4/3}(x, x)|\, d^3 r \leqslant \Big(\sum_{\sigma=1}^{q} \int |d_1(x, x)|\, d^3 r\Big)^{1/2} \Big(\sum_{\sigma=1}^{q} \int |d_1|^{5/3}(x, x)\, d^3 r\Big)^{1/2}, \tag{5.5}$$

$$\sum_{\sigma=1}^{q} \int |d_1|^{5/3}(x, x)\, d^3 r \leqslant \text{const} \sum_{\sigma=1}^{q} \int \left[\frac{\partial^2}{\partial \mathbf{r}\, \partial \mathbf{r}'} |d_1|(x, x')\right]_{x'=x} d^3 r, \tag{5.6}$$

where we used Hölder's inequality in (5.5) and Lieb–Thirring's and Jensen's inequalities in (5.6). Since $\frac{1}{|\mathbf{r}|}\chi_{B_a} \in L^{5/2}(\boldsymbol{R}^3)$ and $\frac{1}{|\mathbf{r}|}\chi_{\overline{B_a}} \in L^4(\boldsymbol{R}^3)$ ($B_a = \{\mathbf{r} \mid |\mathbf{r}| \leqslant a\}$) the second and the third integral will tend to zero using Hölder's inequality, (5.5) and (5.6). The fourth integral is estimated by

$$\|d_{1,n}+d_1\|_q \left(\|d_{1,n}-d_1\|_t \left\| \frac{1}{|\mathbf{r}|}\chi_{B_a} \right\|_s + \|d_{1,n}-d_1\|_{t'} \left\| \frac{1}{|\mathbf{r}|}\chi_{\overline{B_a}} \right\|_{s'} \right) \tag{5.7}$$

with $\frac{1}{q}+\frac{1}{t}+\frac{1}{s} = 2$ and $\frac{1}{q}+\frac{1}{t'}+\frac{1}{s'} = 2$ using Hölder's and Young's inequalities. We choose $q = 1$, $s = \frac{5}{2}$, $t = \frac{5}{3}$, $s' = 4$, and $t' = \frac{4}{5}$. Thus we see that (5.7) will tend to zero and hence the functional $\mathscr{H}$ is continuous in the *-seminorm. Now we claim that each one-particle density matrix d_1 with $\operatorname{tr} d_1 = N' < N$ can be approximated by density matrices $d_{1,n}$ with $\operatorname{tr} d_{1,n} = N$. Choose $d_{1,n} = d_1 + \frac{1}{n^3} g\left(\frac{\mathbf{r}}{n}\right) g^*\left(\frac{\mathbf{r}'}{n}\right)$ with $\nabla g \in L^2(\boldsymbol{R}^3)$ and $q\int |g(\mathbf{r})|^2\, d^3 r = N - N'$. Thus $\operatorname{tr} d_{1,n} = N$ and

$$\|d_{1,n}-d_1\|^* = \frac{1}{n^3} \left\| g\left(\frac{\mathbf{r}}{n}\right) g^*\left(\frac{\mathbf{r}'}{n}\right) \right\|^*$$
$$= \frac{q}{n^3} \int \left\| \left[\frac{\partial^2}{\partial \mathbf{r}\, \partial \mathbf{r}'} g\left(\frac{\mathbf{r}}{n}\right) g^*\left(\frac{\mathbf{r}'}{n}\right)\right]_{\mathbf{r}'=\mathbf{r}} \right| d^3 r = \frac{q}{n^2} \int |\nabla g|^2\, d^3 r \to 0$$

as n approaches infinity. Hence we can find a sequence $d_{1,n}$ with $\operatorname{tr} d_{1,n} = N > N'$ so that $\mathscr{H}(d_{1,n})$ approaches $h_Z(N')$ in the *-seminorm:

$$h_Z(N) \leqslant \lim_{n\to\infty} \mathscr{H}(d_{1,n}) = h_Z(N'). \quad \blacksquare$$

From now on let d_1 denote the one particle density matrix with the following kernel:

$$d_1(x, x') = \sum_{v=-\infty}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{s=1}^{q} w_{v,l,m,s} e^{ik_{v,l}\pi\zeta_l(r')} \frac{\sqrt{\zeta_l'(r')}}{r'} \times$$

$$\times Y_{l,m}^*(\Omega')\chi_s(\sigma') e^{-ik_{v,l}\pi\zeta_l(r)} \frac{\sqrt{\zeta_l'(r)}}{r} Y_{l,m}(\Omega)\chi_s(\sigma), \quad (5.8)$$

where $0 \leqslant w_{v,l,m,s} \leqslant 1$, and $\sum_{v,l,m,s} w_{v,l,m,s} \leqslant N$. The χ_s are normalized spin functions, e.g. $\chi_s(\sigma) = \delta_{s,\sigma}$, the $Y_{l,m}$ are spherical harmonics and $\zeta_l(r)$ are monotone increasing functions with ζ_l: $[0, \infty) \to [0, 1)$, $\zeta_l(0) = 0$ and $\zeta_l(r) \to 1$ for $r \to \infty$ i.e.

$$\zeta_l(r) = \int_0^r f_l(t)\, dt$$

for some non-negative function f_l with integral one. For a given index l the difference $k_{v,l} - k_{v',l}$ has to be an integer multiple of 2 because of the orthogonality requirement of the eigenfunctions of d_1. Therefore we choose $k_{v,l}$ to be $2v$ or $(2v-1)$ depending on whatever lowers the energy the most.

By the above we have $E_Q(Z, N) \leqslant \mathscr{H}(d_1)$. This yields

$$E_Q(Z, N)$$

$$\leqslant \sum_{v=-\infty}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{s=1}^{q} w_{v,l,m,s} \int_0^{\infty} \left\{ \sqrt{f_l(r)}'^2 + k_{v,l}^2 f_l^3(r) + \left(\frac{l(l+1)}{r^2} - \frac{Z}{r} \right) f_l(r) \right\} dr +$$

$$+ \frac{1}{2} \sum_{v,v'} \sum_{l,l'} \sum_{m,m'} \sum_{s,s'} w_{v,l,m,s} w_{v',l',m',s'} \int_0^{\infty} dr \int_0^{\infty} dr' f_l(r) f_{l'}(r') \int d\Omega \int d\Omega'$$

$$\times \frac{|Y_{l,m}(\Omega)|^2 |Y_{l',m'}(\Omega')|^2}{|\mathbf{r} - \mathbf{r}'|}. \quad (5.9)$$

If we choose the $w_{v,l,m,s}$ independent of m and s, we are able to carry out the sums over m and s in (5.9). Define the numbers $N_l = \sum_v q(2l+1) w_{v,l,m,s}$ which have to satisfy the requirement $\sum_{l=0}^{\infty} N_l \leqslant N$. Defining $N_{l,m,s} = \dfrac{N_l}{q(2l+1)}$ this is equivalent to $\sum_v w_{v,l,m,s} = N_{l,m,s}$. Since v appears only in $k_{v,l}^2$ and since this term is positive, we prefer those v being closest to zero. Therefore we define $N'_{l,m,s}$, to be the greatest integer less than or equal to $N_{l,m,s}$, and $g_l = N_{l,m,s} - N'_{l,m,s}$. If $N'_{l,m,s}$ is odd, we choose $k_{v,l} = 2v$, otherwise we choose $k_{v,l} = 2v - 1$. The numbers $w_{v,l,m,s}$ are chosen as follows:

$$w_{v,l,m,s} = \begin{cases} 1 & \text{for } |k_{v,l}| \leqslant N'_{l,m,s} - 1, \\ \frac{1}{2} g_l & \text{for } |k_{v,l}| = N'_{l,m,s} + 1, \\ 0 & \text{otherwise.} \end{cases}$$

This choice satisfies the above mentioned condition $\sum_v w_{v,l,m,s} = N_{l,m,s}$, because 1 appears $N'_{l,m,s}$ times in the sum and $g_l/2$ appears twice in the sum.

Next we calculate $\sum_v k_{v,l}^2 w_{v,l,m,s}$. We get for $N'_{l,m,s}$ odd

$$\sum_v k_{v,l}^2 w_{v,l,m,s} = \sum_{v=1}^{(N'_{l,m,l}-1)/2} 2(2v)^2 + 2\tfrac{1}{2} g_l (N'_{l,m,s} + 1)^2,$$

and for $N'_{l,m,s}$ even

$$\sum_v k_{v,l}^2 w_{v,l,m,s} = \sum_{v=1}^{N'_{l,m,s}/2} 2(2v-1)^2 + 2\tfrac{1}{2} g_l (N'_{l,m,s} + 1)^2.$$

In both cases one finds

$$\begin{aligned} \sum_v k_{v,l}^2 w_{v,l,m,s} &= \frac{1}{3} N'_{l,m,s}(N'^2_{l,m,s} - 1) + g_l (N'_{l,m,s} + 1)^2 \\ &= \frac{N_{l,m,s}^3}{3} + N_{l,m,s}\left(-\frac{1}{3} + 2g_l - g_l^2\right) + \frac{2}{3} g_l^3 - 2g_l^2 + \frac{4}{3} g_l, \end{aligned} \tag{5.10}$$

where $N_{l,m,s} - g_l$ was inserted for $N'_{l,m,s}$. Furthermore, we define $\varrho_l(r) = \sum_v w_{v,l,m,s}\, q(2l+1) f_l(r) = N_l f_l(r)$ and carry out the sums over m, s and v in (5.9) using (5.10). This yields

$$\begin{aligned} E_Q(Z, N) \leqslant \sum_{l=0}^{\infty} \int_0^{\infty} \Bigg\{ & \sqrt{\varrho_l(r)}'^2 + \left(\frac{l(l+1)}{r^2} - \frac{Z}{r}\right) \varrho_l(r) + \\ & + \pi^2 \left(\frac{1}{3} N_{l,m,s}^3 + N_{l,m,s}\left(-\frac{1}{3} + 2g_l - g_l^2\right) + \frac{2}{3} g_l^3 - 2g_l^2 + \frac{4}{3} g_l\right) \frac{q(2l+1)}{N_l^3} \varrho_l^3 \Bigg\} dr + \\ & + \frac{1}{2} \sum_{l,l'=0}^{\infty} \int_0^{\infty} dr \int_0^{\infty} dr' \frac{1}{16\pi^2} \varrho_l(r) \varrho_{l'}(r') \int d\Omega \int d\Omega' \frac{1}{|\mathbf{r} - \mathbf{r}'|}. \end{aligned} \tag{5.11}$$

In order to evaluate the interaction term one may use the addition theorem for the spherical harmonics and the expansion of $\frac{1}{|\mathbf{r} - \mathbf{r}'|}$, i.e.

$$\sum_{m=-l}^{l} |Y_{l,m}(\Omega)|^2 = \frac{2l+1}{4\pi},$$

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|}=\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{(\min\{r,r'\})^l}{(\max\{r,r'\})^{l+1}}\frac{4\pi}{2l+1}Y_{l,m}^*(\Omega)\,Y_{l,m}(\Omega').$$

Thus (5.11) can be evaluated to give the right-hand side of the conclusion of the following theorem.

THEOREM 5.2. *Let $E_Q(Z, N)$ denote the infimum of the operator*

$$H=\sum_{j=1}^{N}\left(-\Delta_j-\frac{Z}{|r_j|}\right)+\sum_{i<j}\frac{1}{|r_i-r_j|}$$

in $\bigwedge_{i=1}^{N}(L^2(\mathbf{R}^3)\otimes\mathbf{C}^q)$. *Let* $(\varrho_0,\varrho_1,\ldots)\in W_N$. *Then*

$$E_Q(Z,N)\leqslant\varepsilon_Z^{HW}(\varrho_0,\varrho_1,\ldots)+$$
$$+\sum_{l=0}^{\infty}\frac{\pi^2}{3}\left(\frac{-3g_l^2+6g_l-1}{N_l^2}+q(2l+1)\frac{2g_l^3-6g_l^2+4g_l}{N_l^3}\right)\int_0^{\infty}\varrho_l^3\,dr.$$

Therefore we have the following result. If the condition, that the $N_{l,m,s}$ are integers, is dropped, we find that the Hellmann–Weizsäcker functional is still an upper bound for the quantum mechanical ground state energy provided one adds the correction term in Theorem 5.2, which can be positive or negative. However, the correction for the infimum proves to be of lower order, at least in our applications which will be shown in [18, 19].

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