THE VON WEIZSÄCKER AND EXCHANGE CORRECTIONS IN THE THOMAS FERMI THEORY

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A DISSERTATION
PRESENTED TO THE
FACULTY OF PRINCETON UNIVERSITY
IN CANDIDACY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

RECOMMENDED FOR ACCEPTANCE BY THE
DEPARTMENT OF
PHYSICS

June 1979

To Maria Cristina

ACKNOWLEDGEMENTS

It is a pleasure to thank Professor Elliott Lieb. He suggested the problems of this dissertation and provided continuous encouragement as well as many ideas during the period this work was carried out.

I would like to thank Professors Barry Simon for a critical reading of the manuscript, Haïm Brezis for valuable help in some of the technical points of Chapter 3, and Michael Aizenman for valuable discussions.

I also thank Bobbie Cruser for very expert typing.

I wish to thank especially Maria Cristina for her encouragement and understanding.

This publication was supported in part by National Science Foundation grants PHYS-7825390 and MCS 75 21684 A 02 to Princeton University.

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ABSTRACT

Two corrections to the Thomas-Fermi theory of atoms are studied. First the correction for exchange, that is the effect of the Pauli principle in the interaction energy, is considered. The defining variational problem is non-convex and standard techniques to prove existence of a minimizing solution do not apply. Existence and uniqueness of solutions are established by "convexifying" or "relaxing" the energy functional. Properties of minimizing solutions are studied. A second correction due to von Weizsäcker is also discussed. This is an inhomogeneous correction to the kinetic energy density of the form $c_w(\nabla\sqrt{\rho})^2$ which was introduced to obtain the correct behavior of the electron density ρ far away and very close to the nuclei. Existence and uniqueness of solutions in the set $\{\rho \mid \int \rho \leq \lambda\}$ are established. Only in the atomic case existence of solutions in the set $\{\rho \mid \int \rho = \lambda\}$ is determined. There are two major open problems left concerning this correction namely, to establish existence of solutions in the set $\{\rho \mid \int \rho = \lambda\}$ in the molecular case and proving the existence of molecules (binding) within the framework of this theory. (A serious drawback of Thomas-Fermi is the non binding theorem of Teller). Finally the dual principle to the Thomas-Fermi variational problem is studied (only in the neutral case). A dual principle is suggested for the ionic case. Also, a review of recent rigorous results concerning Thomas-Fermi theory is presented.

CHAPTER 1. INTRODUCTION

Since the advent of Quantum Mechanics the impossibility of solving exactly problems involving many particles has been clear. These are of interest in such areas as Atomic and Nuclear Physics.

It was, therefore, necessary from the beginning to introduce approximative methods such as the Hartree-Fock approximation and the Thomas-Fermi theory [16, 47] (henceforth denoted by TF).

Applications of TF to the study of matter under extremal conditions, e.g. high pressures, high temperatures or strong external fields, have achieved particular development. TF is attractive because of its simplicity and universality (the change from one element to another is effected by a simple transformation of scale). However, the applications of TF are quantitatively good only in the limiting situations mentioned above. It is for this reason that after the introduction of TF attempts have continually been made to improve it [13, 49] in order to extend the range of applicability of the model while preserving its achievements. For a review of the physics literature concerning TF and its corrections we refer to [22, 26, 36].

Although the TF theory was introduced a long time ago, it has been only recently that rigorous results have been established [31, 32, 24, 3, 4, 5, 6, 9, 11, 12]. It is the purpose of this thesis to review some of these rigorous results and to derive new ones concerning two of the corrections to TF mentioned before.

The TF theory is defined by the energy functional (in units in which $h^2(8m)^{-1}(3/\pi)^{2/3} = 1$ and $|e| = 1$, where e and m are the electron charge and mass):

$$\xi(\rho) = (3/5)\int\rho(x)^{5/3}dx - \int V(x)\rho(x)dx + \qquad (1.1)$$

$$+ \quad (1/2)\int dx\, dy\; \rho(x)|x-y|^{-1}\rho(y) \quad ,$$

$$V(x) = \sum_{i=1}^{k} z_i |x-R_i|^{-1} \quad , \qquad (1.2)$$

where the $z_1, z_2, \ldots, z_k \geq 0$ are the charges of k fixed nuclei located at $R_1, R_2, \ldots, R_k$. $\int dx$ is always a three dimensional integral. This functional is defined for single particle densities $\rho(x) \geq 0$ (such that $\int\rho$ and $\int\rho^{5/3}$ are finite). The TF energy for λ (not necessarily integral) electrons is defined by

$$E(\lambda) = \inf\{\xi(\rho) \mid \int\rho = \lambda\}. \qquad (1.3)$$

The first term in (1.1) is supposed to approximate the kinetic energy of the electrons. This particular form is suggested by the calculation of the kinetic energy per unit volume for a system of N fermions in a cubic box of volume V, which for large N is proportional to $(N/V)^{5/3}$. This approximation, with an appropriate multiplicative constant, is in fact a lower bound for the kinetic energy [28, 34].

The second term of $\xi(\rho)$, which represents the nucleon-electron attraction, is exact. The third term describes the electronic repulsion and it is only an approximation: it takes into account only the "direct" part of the true Coulomb repulsion (see Chapter 3 below).

It is known [32] that for $\lambda \leq z \equiv \sum_{i=1}^{k} z_i$ there is a unique minimizing ρ for $\xi(\rho)$. It is the unique solution to the TF equation

$$\rho(x)^{2/3} = \max\,[\phi(x) - \phi_o,\, 0]\ , \tag{1.4}$$

for some $\phi_o \geq 0$ and with

$$\phi(x) = V(x) - \int dy\, \rho(y)\, |x-y|^{-1}\ . \tag{1.5}$$

$-\phi_o$ is the chemical potential [32], i.e.

$$\frac{dE}{d\lambda}(\lambda) = -\phi_o\ .$$

For $\lambda \leq z$, $\phi > 0$ all x. $\phi_o = 0$ if and only if $\lambda = z$ and hence for the neutral case the TF equation is

$$\rho^{2/3} = \phi\ . \tag{1.6}$$

If $\lambda > z$ there is no minimizing ρ for (1.3) and $E(\lambda) = E(z)$ in this case. The energy of an isolated atom is $E(z) = -Kz^{7/3}$

where K = 3.678 by numerical computation. It is convenient to introduce the total energy

$$e(\underline{z}, \underline{R}) = e(z_1, \ldots z_k; R_1, \ldots R_k) \equiv E(z) + U,$$

where $U = \sum_{1 \le i < j \le k} z_i z_j |R_i - R_j|^{-1}$ is the nucleon-nucleon repulsion. It is a known, and rather negative, result that molecules in TF do not bind [46, 32]. In fact if one separates the nuclei into clusters and then takes them to infinity the energy $e(\underline{z}, \underline{R})$ decreases. Moreover, there are no local minima of the energy in terms of the nuclei configuration $\underline{R}$. If one dilates uniformly $\underline{R} \longrightarrow \ell\underline{R}$ ($\ell > 0$), the energy always decreases [5]. For a review of additional rigorous results see Section 2.8 below.

The main concern throughout this thesis are the variational problems associated with TF and its corrections. In Chapter 2 a generalization of the functional (1.1) is considered. The kinetic energy density is replaced by a more general local, convex function of the electron density ρ (equation (2.3) below). Most of the results about TF hold for this new functional. In particular the existence of a unique minimizing solution for $\lambda \le z$ is established and, as before, no solution for $\lambda > z$ exists. Moreover, the no-binding theorem also holds. This no-binding theorem is in fact a consequence of the local dependence of the kinetic energy density on ρ. We introduce this general model and discuss its properties because we need them in the discussion of the TF with the correction for exchange. This correction consists in adding a term $-(3/4)\ c_e\int\rho^{4/3}$ (c_e is a positive constant) to the TF functional (1.1), which is meant to be an approximation for the exchange or "indirect" part of the true electronic repulsion (see Chapter 3). In fact all the properties of this theory would follow directly from the results of Chapter 2 if it were not that the introduction of exchange destroys the convexity of the functional. Following known techniques [15], we consider a convex functional instead by replacing $g(\rho) \equiv \frac{3}{5}\ \rho^{5/3} - \frac{3}{4}\ c_e\rho^{4/3}$ by a function $\tilde{g}(\rho)$ whose epigraph (i.e. the set of points above the graph of $\tilde{g}$) is the convex hull of the epigraph of $g(\rho)$. The function $\tilde{g}$ and thus the functional associated with it are convex in ρ. Therefore, this new functional (usually called the relaxed functional) is a particular example of the one studied in Chapter 2 and thus, existence and uniqueness of solutions for this relaxed problem are established at once. We then prove that the minimizing solution $\bar{\rho}$ for the relaxed problem has the property that the set of points where $g(\bar{\rho}(x))$ differs from $\tilde{g}(\bar{\rho}(x))$ has (Lebesgue) measure zero. This implies that $\bar{\rho}$ is also a solution to the original non-convex problem. Finally, some properties of the minimizing solution are proven.

In Chapter 4 another correction is considered. This is a correction to the kinetic energy density of the form $c_w(\nabla\sqrt{\rho})^2$, introduced by von Weizsäcker [49] in order to obtain the correct behavior of the electron density far away and very close to the nuclei. (In the TF theory the electron density falls off as $|x|^{-6}$, rather than exponentially, for large distances [44]. Close to the nuclei behaves as $|x - R_i|^{-3/2}$, which diverges. The fact that the TF density describes very badly the outer shell of the atoms is reflected in the absence of molecules in this theory). The resulting functional is not anymore of the form considered in Chapter 2. It is, however, convex and standard techniques can be applied to prove existence and uniqueness of a minimizing ρ at least on the set $\{\rho | \int\rho \leq \lambda\}$. The question of existence of solutions on the set $\{\rho | \int\rho = \lambda\}$ is harder and it is left as an open problem. In the atomic case ($V(x) = z|x|^{-1}$), however, we show that there is a unique minimizing solution on $\{\rho | \int\rho = \lambda\}$ for $\lambda \leq z$. It also remains as an open problem to determine the largest λ for which this is still true. In the TF von-Weizsäcker theory the kinetic energy density is no longer local in ρ and the no-binding theorem does not apply. It is an important open problem to determine if binding is possible in this theory. There are numerical indications [21] and heuristic arguments [2], that this is indeed so. We do not, unfortunately, present any result concerning binding. The rest of Chapter 4 is spent in discussing regularity and other properties of the minimizing solution.

In Chapter 5 the dual to the TF variational problem is discussed (only the neutral case is considered). This new variational problem, known as Firsov's principle [18], is the dual to TF in the sense that it is a maximization problem rather than a minimization one and that both have the same value, i.e. $\max_f \xi_{FIRSOV}(f) = \min_\rho \xi_{TF}(\rho)$. Here f is the electron potential $f(x) = \int dy\, \rho(y)\, |x-y|^{-1}$. Having this dual principle is very useful in estimating lower bounds to TF energies. It has been particularly used in studying the behavior of the two-body atomic potential [19, 48] for short and long distances. The existence of a unique maximizing solution $\bar{f}$ for $\xi_{FIRSOV}(\cdot)$ is determined by proving that $V-\bar{f}$ satisfies the TF equation (1.6) for the neutral case and appealing to the results of [32]. In the Appendix to Chapter 5 the dual principle for the ionic case is suggested.

To conclude this introduction we note that throughout this thesis the emphasis is on the variational problems defined by TF and its corrections. We have left perhaps the most important question aside namely, to establish the connection between TF, with these corrections included, and the original quantum mechanical system. It is known [32] that the TF theory gives binding energies ($\sim z^{7/2}$) which are asymptotically exact in the large z limit. Is the TF, with the two corrections discussed here included, correct up to order $z^{5/3}$? (This is intimately related to the open problem 2 in [32]).

CHAPTER 2: STUDY OF A VARIATIONAL PRINCIPLE RELATED TO THE TF THEORY

In this chapter we study a variational principle which contains as a particular case the TF theory and which will show to be useful in the discussion of the TF theory with exchange correction (see Chapter 3). The purpose here is twofold. First we want to present a review of the rigorous results related to the TF theory that have appeared in the last few years [3, 4, 5, 6, 9, 11, 12] after the work of Lieb and Simon [31], which set TF in a firm mathematical basis. Second, we want to establish the results needed for the discussion of the TF theory with exchange. Many of the results of this chapter have been already obtained in [6], although the point of view there is the partial differential equation rather than the variational problem. We are more interested in the properties of the energy functional. The main results of this chapter are the existence theorem 2.13 and the no-binding theorem 2.14. In the last section we specialize to the TF theory and review some of its properties.

2.1. Variational Principle

Consider the functional:

$$\xi\ (\rho, V) = \int f(\rho)\ dx - \int V\rho\ dx + \frac{1}{2} \int dx\ dy + \rho(x)\ |x-y|^{-1}\ \rho(y) \tag{2.1}$$

(dx denote the Lebesgue measure in R^3), defined for $\rho \in W$ with

$$W = \{\rho | \rho \geq 0, \ \rho \in L^1 \text{ and } \int f(\rho) < \infty\} .$$

Here $V \in L^{5/2} + L^\infty$. We will be interested mainly in

$$V(x) = \sum_{i=1}^{k} z_i |x-R_i|^{-1} , \ z_i > 0. \tag{2.2}$$

The function $f: R^+ \to R^+$ is assumed to be of the form

$$f(s) = \int_0^s a(t)\, dt, \tag{2.3}$$

with a(t) satisfying the following properties:

(A-1) a(t) is continuous, a(0) = 0 and a(t) is non-decreasing for $t \geq 0$. In particular a(t) is non-negative.

(A-2) There are positive constants c_+ and c_- such that for $t \geq 1$

$$c_+ t^{2/3} \geq a(t) \geq c_- t^{2/3} . \tag{2.4}$$

Note that (A-1) and (A-2) imply the following properties on f:

(F-1) $f \in C^1 (R^+)$.

(F-2) f is convex, non-decreasing and non-negative.

(F-3) $f(s) \geq d\, s^{5/3}$ for $s \geq 1$ and some positive constant d.

(F-4) $\lim_{x \downarrow 0} f(x)/x = a(0) = 0.$

Remarks: i) The exponent 2/3 in (2.4) can be replaced by any $p \in (\frac{1}{2}, 1)$. In [6] more general p's are handled, namely $p > \frac{1}{3}$. However, for $p \le \frac{1}{2}$ $\min \xi(\rho) = -\infty$ and since the object of our interest is the energy $\min \xi(\rho)$, we do not consider those cases.

ii) a function f defined by (2.4) with a(t) satisfying (A-1) and such that $a > 0$ for $t > 0$ is usually called an "N-function" [1]. If moreover a(t) satisfies (A-2) f is said to be "equivalent near infinity" to the N-function $t^{5/3}$. Associated with N-functions, there are Banach spaces called Orlicz-spaces. These spaces are the generalization of the L^p spaces, which can be considered the Orlicz-spaces associated with the N-functions t^p, $p \ge 1$. For a review see [1] or ([15], Chapter VIII, Section 2.4).

Note that if f satisfies the above properties then $W \subset L^{5/3}$. In fact if $\rho \in W$, (F-3) implies

$$\int \rho^{5/3}\, dx = \int_{\rho<1} \rho^{5/3}\, dx + \int_{\rho\ge 1} \rho^{5/3}\, dx \le \int \rho\, dx + d^{-1} \int f(\rho) < \infty \tag{2.5}$$

and therefore $\rho \in L^{5/3}$.

Let us define

$$W_\lambda = \{\rho \in W \mid \int \rho \le \lambda\} \tag{2.6a}$$

and $$W_{\partial\lambda} = \{ \rho \in W \mid \int \rho = \lambda\} \qquad (2.6b)$$

The variational problem that we study here is

$$\min \{\xi(\rho, V) \mid \rho \in W_{\partial\lambda}\} \quad , \qquad (2.7)$$

where $\lambda > 0$ is a fixed number. Even though this seems to be a simple convex minimization problem, it need not have a solution. (Lieb-Simon [32]). The difficulty lies in the fact that, as we shall see, if ρ_n is a minimizing sequence for (2.7), then ρ_n converges weakly to $\bar{\rho}$ in $L^{5/3}$ and $\underline{\lim}\ \xi(\rho_n,V) \geq \xi(\bar{\rho},V)$, but we can only assert that $\int\bar{\rho}dx \leq \lambda$. In fact if $W_{\partial\lambda}$ is replaced by W_λ the problem becomes much simpler [32].

2.2. Minimization of $\xi(\rho,V)$ on W_λ.

The proof of the existence of a solution to the variational problem

$$\min \{\xi\ (\rho,V) \mid \rho \in W_\lambda\} \qquad (2.8)$$

will be based on the following well known theorem.

Theorem 2.1: Suppose $I(u)$ is a bounded functional defined on a (sequentially) weakly closed and non-empty subset M of a reflexive Banach space X. Then, if $I(u)$ is coercive on M (in the sense that $I(u) \to \infty$ whenever $||u||_X \to \infty$ with $u \in M$), and in addition $I(u)$ is weakly lower semicontinuous on M then $c \equiv \inf I(u)$ over M is finite and attained at a point $u_o \in M$.

Proof: This theorem is standard ([7], Theorem 6.1.1; [15], Proposition 1.2, Chapter 2) and its proof is a consequence of the Banach-Alaoglu Theorem ([38], Theorem 4.21). |_|

In the case we are considering the Banach space is $X = L^{5/3}(R^3, dx)$ which is certainly reflexive. In the next two lemmas we prove that $\xi(\rho, V)$ and W_λ satisfy the hypothesis of Theorem 2.1.

Lemma 2.2: (i) $\xi(\rho, V)$ is bounded on $W_\lambda \subset L^{5/3}$ and
(ii) $\xi(\rho, V)$ is coercive on W_λ.

Proof: Since $\rho \in W_\lambda \subset L^{5/3}$, (i) follows from ([32], Theorem II.2). To prove (ii), note that $\int dx\, dy\, \rho(x)\, |x-y|^{-1}\, \rho(y) \geq 0$ because $|x|^{-1}$ is a positive definite kernel. Hence

$$\xi(\rho, V) \geq \int f(\rho) - \int V\rho \geq d\, ||\rho||_{5/3}^{5/3} - \lambda d - \int V\rho,$$

where the last inequality follows from (2.5). Moreover, the decomposition $V = V_1 + V_2$, with $V_1 \in L^{5/2}$, $V_2 \in L^\infty$ and Hölder's inequality imply

$$-\int V\rho \geq -k_1\, ||\rho||_{5/3} - k_2(\lambda)\ ,$$

where k_1, k_2 are constants. Hence

$$\xi(\rho, V) \geq d\ ||\rho||_{5/3}^{5/3} - \lambda d - k_1\ ||\rho||_{5/3} - k_2\ (\lambda)$$

and thus $||\rho||_{5/3} \to \infty$ implies $\xi(\rho, V) \to \infty$. |_|

Since $\xi(\rho, V)$ is bounded on W and $\xi(\rho,V) \to \infty$ as $\int f(\rho)dx \to \infty$, we can restrict our minimization sets W, W_λ to be

$$W' = \{\rho | \rho \geq 0, \rho \in L^1 \quad \int f(\rho) \leq M\}$$

$$W'_\lambda = \{\rho | \rho \in W' \quad , \int \rho \leq \lambda\}$$

for some finite constant M.

<u>Lemma 2.3</u>: The set W'_λ is weakly closed.

<u>Proof</u>: Note first that W'_λ is convex because $f(\cdot)$ is convex. Moreover W'_λ is strongly closed. In fact, let $\{\rho_n\}$ be a sequence in W'_λ with $\rho_n \to \rho$ strongly in $L^{5/3}$. This implies that there exists a subsequence $\rho_{n_i}(x)$ which converges pointwise a.e. to $\rho(x)$. Since f is continuous, $f(\rho_{n_i}(x)) \to f(\rho(x))$ for a.e. x. By Fatou's Lemma $\int f(\rho) \leq M$ and also $\int \rho \leq \lambda$. Therefore W'_λ is strongly closed. W'_λ being strongly closed and convex is weakly closed. |_|

To conclude the proof of existence of a solution to the variational problem (2.8) we need only show

Lemma 2.4: $\xi(\rho, V)$ is weakly lower semicontinuous in W_λ.

Proof: (i) $\int f(\rho)dx$ is weakly lower semicontinuous because $\{\rho | \int f(\rho) \leq M\}$ is weakly closed. (ii) That $\int \rho V dx$ is continuous in the weak $L^{5/3}$ topology is proved in ([32], Theorem II.13). The idea of the proof is the following: denote by $T_R(\rho) \equiv \int dx\, |x|^{-1}\, \theta\, (R-|x|)\rho(x)$, (here θ denotes the step function). The operator $T_R : L^{5/3} \rightarrow R$ is a bounded linear functional so $T_R(\cdot)$ is continuous in the weak $L^{5/3}$ topology.

Moreover, $T_R(\cdot) \rightarrow T(\cdot) \equiv \int |x|^{-1} (\cdot)dx$ uniformly in W_λ (because $|(T_R - T)(\rho)| \leq \lambda R^{-1}$, for all $\rho \in W_\lambda$), hence T is continuous. (iii) $\int \rho(x)\, |x-y|^{-1}\, \rho(y)\, dx\, dy$ is weakly lower semicontinuous because positive quadratic forms are always decreasing under weak limits [43, 32]. $|\overline{\ }|$

Lemma 2.5: If $||\rho_n-\rho||_{5/3} + ||\rho_n-\rho||_1 \rightarrow 0$ as $n \rightarrow \infty$, then $\xi(\rho_n, V) \rightarrow \xi(\rho, V)$.

Proof: Because of ([32], Theorem II.2) we need only check that $\int f(\rho_n) \rightarrow \int f(\rho)$. Since f is convex (F-2) we have

$$|f(\rho) - f(\rho_n)| \leq a(\max\, (\rho,\rho_n)\ (x))\ |\rho-\rho_n|.$$

(because $a(\cdot)$ is non-negative). Thus

$$\int dx\ |f(\rho) - f(\rho_n)| \leq \int a(s_n(x))\ |\rho-\rho_n| dx,$$

with $\quad s_n(x) \equiv \max(\rho,\rho_n)(x)$. Then

$$\int dx\, |f(\rho) - f(\rho_n)| \leq \int_{s_n<1} a(s_n)\, |\rho-\rho_n|$$
$$+ \int_{s_n\geq 1} a(s_n)\, |\rho-\rho_n| \leq a(1)\, ||\rho-\rho_n||_1$$
$$+ c_+ \int_{s_n\geq 1} s_n^{2/3}\, |\rho-\rho_n|$$

(because of (A-1) and (A-2)). Hence, using Hölder's inequality

$$\int dx\, |f(\rho) - f(\rho_n)| \leq a(1)\, ||\rho-\rho_n||_1$$
$$+ c_+ \left(\int_{s_n\geq 1} s_n^{5/3}\right)^{2/5} ||\rho-\rho_n||_{5/3} \to 0$$

as $n \to \infty$. (Since $(\int_{s_n\geq 1} s_n^{5/3}) \leq \int s_n^{5/3} \to \int \rho^{5/3}$ finite). $\square$

Let us now define

$$E(\lambda,V) \equiv \inf\{\xi(\rho,V)\,|\, \rho \in W_{\partial\lambda}\} \tag{2.9}$$

<u>Lemma 2.6</u>: ([32], Proposition 2.4). If $V \in L^{5/2} + L^p$ for some $5/2<p<\infty$, then, $E(\lambda,V) = \inf\{\xi(\rho,V)\,|\, \rho \in W_\lambda\}$.

<u>Proof</u>: Given $\rho \in C_o^\infty(R^3) \cap W_\lambda$, pick $\rho_n = \rho + n^{-1}\chi_{A_n}$ where χ_A is the characteristic function of A and A_n is a set disjoint from supp(ρ) with measure $n(\lambda-||\rho||_1)$. Note that $||\rho_n-\rho||_{5/3} + ||\rho_n-\rho||_r \to 0$ (for every $1<r\leq 5/3$) and therefore

$- \int V\rho_n + \frac{1}{2} \int \rho_n(x)|x-y|^{-1}\rho_n(y) \to -\int V\rho + \frac{1}{2}\int \rho|x-y|^{-1}\rho$ by using Hölder's inequality and the decomposition $V \in L^{5/2} + L^p$. Moreover $\int f(\rho) = \int f(\rho_n) + n\, f(1/n)\; (\lambda - ||\rho||_1)$, so (F-4) implies $\int f(\rho_n) \to \int f(\rho)$ as $n \to \infty$. Thus $\xi(\rho_n, V) \to \xi(\rho, V)$ and

$$\inf\{\xi(\rho,V)|\rho \in W_{\partial\lambda}\} \le \inf\{\xi(\rho,V)|\rho \in W_{\partial\lambda} \cap C_o^\infty\}$$
$$= \inf\{\xi(\rho,V)|\rho \in W_\lambda\}.$$

The last equality follows from Lemma 2.5 and the density of C_o^∞ in $L^1 \cap L^{5/3}$. |_|

<u>Corollary 2.7</u>: $E(\lambda, V)$ is a monotone non-increasing function of λ whenever $V \in L^{5/2} + L^p$, some $5/2 < p < \infty$.

So far we have proven the existence of solutions to the variational problem (2.8) We now show that the solution is in fact unique.

<u>Theorem 2.8</u>: $\xi(\rho, V)$ is strictly convex in $\rho \in W$ and therefore there is a unique solution to problem (2.8).

<u>Proof</u>: $\int f(\rho)$ is convex because $f(\rho)$ is a convex function of ρ. $- \int V\rho + \frac{1}{2} \int dx\, dy\, \rho(x)\, |x-y|^{-1}\, \rho(y)$ is strictly convex because $- \int V\rho$ is linear and $|x|^{-1}$ is a strictly positive definite kernel. |_|

<u>Corollary 2.9</u> ([32], Cor. II.9) Suppose $V \in L^{5/2} + L^p$ with $p > 5/2$. Then,

(a) If ρ_o minimizes $\xi(\rho,V)$ on W_{λ_o} and $\int\rho_o dx < \lambda_o$, then $E(\lambda,V) = E(\lambda_o,V)$ for all $\lambda>\lambda_o$, when $p<\infty$.

(b) If $\xi(\rho,V)$ has a minimum on $W_{\partial\lambda}$ for all $\lambda\leq\lambda_o$, then $E(\lambda,V)$ is strictly convex on $[0,\lambda_o]$.

In particular $E(\lambda,V)$ is convex in λ.

Proof: (b) follows from the strict convexity and (a) follows by noting that ρ_o must be a minimum for $\xi(\rho,V)$ on all W. |_|

2.3 Connection with the Euler equation

Theorem 2.10:

(a) If ρ obeys the (Euler) equations:

$$a(\rho) = \phi - \phi_o \geq 0 \quad \text{if } \rho>0 \tag{2.10a}$$

$$0 = a(\rho) \geq \phi - \phi_o \quad \text{if } \rho=0 \tag{2.10b}$$

where

$$\phi(x) = V(x) - \int dy\ \rho(y)\ |x-y|^{-1} \tag{2.10c}$$

and

$$\int\rho dx = N \tag{2.10d}$$

for some ϕ_o then $\xi(\rho,V) = E(N,V)$; $E(\lambda,V)$ is differentiable at $\lambda=N$, and

$$\phi_o = -\left.\frac{\partial E(\lambda,V)}{\partial\lambda}\right|_{\lambda=N} . \tag{2.11}$$

In particular if $\phi_o = 0$, then ρ minimizes $\xi(\cdot)$ on all of W.

(b) If $\rho \varepsilon W_{\partial N}$ and $\xi(\rho,V) = E(N,V)$, then ρ obeys the Euler equation (2.10) and ϕ_o is given by (2.11).

Proof: Goes in the same way as the proof of ([32], Theorem II.10). The only fact it must be checked (to prove part 6) is that

$$\frac{\delta\xi}{\delta\rho} \equiv a(\rho) - \phi \; \varepsilon \; L^{5/2} + L^{\infty} \; .$$

Note that $\phi \; \varepsilon \; L^{5/2} + L^{\infty}$, because $V \; \varepsilon \; L^{5/2} + L^{\infty}$ and $\rho * |x|^{-1} \varepsilon \; L^{\infty}$. Hence, we need only check that $a(\rho) \; \varepsilon \; L^{5/2} + L^{\infty}$. Decompose $a(\rho)$ as follows: $a(\rho) = a(\rho)\chi_{\rho\geq 1} + a(\rho)\chi_{\rho<1}$ where $\chi_{\rho\geq 1}$ is the characteristic function of the set $\{x|\rho(x) \geq 1\}$. Now $||a(\rho)\chi_{\rho<1}||_{\infty} = a(1) < \infty$, therefore $a(\rho)\chi_{\rho<1} \; \varepsilon \; L^{\infty}$. also, $a(\rho)\chi_{\rho\geq 1} \leq c_{+}\rho^{2/3}$ because of (A-2). Since $\rho \varepsilon W \subset L^{5/3}$ we have $\rho^{2/3} \; \varepsilon \; L^{5/2}$ and therefore $a(\rho)\chi_{\rho\geq 1} \; \varepsilon \; L^{5/2}$. |_|

Remark: This result is also proved in ([9], Proposition 3).

2.4. Minimization with $\int\rho=\lambda$

Let us consider here V of the form

$$V(x) = \sum_{i=1}^{k} z_i \; |x-R_i|^{-1} \; , \quad z_i > 0. \tag{2.12}$$

In this section we deal with two results. First we prove that for $\lambda \leq z = \sum_{i=1}^{k} z_i$, the minimum of $\xi(\cdot,V)$ on W_λ is attained for some $\rho \in W_{\partial\lambda}$. Next we show that for $\lambda \geq z$, the unique minimizing ρ for $\xi(\cdot,V)$ on W_λ has $\int\rho=z$ and therefore there is no solution to the variational problem (2.7) for $\lambda>z$:

Theorem 2.11: Let V be of the form (2.12). Then for $\lambda \leq z$ the minimizing ρ for $\xi(\cdot,V)$ on W_λ has $\int\rho=\lambda$.

Proof: We mimick here the proof of ([32], Theorem II.18). In more generality this theorem is proved in ([9], Theorem 4).

Suppose that the minimizing ρ has $\int\rho dx = \lambda_o < \lambda$. Then by Corollary 2.9, ρ minimizes $\xi(\cdot,V)$ on all of W so, by Theorem 2.10, the corresponding ϕ_o is 0. Thus ρ obeys $a(\rho) = \max(\phi,0)$, where ϕ is given by (2.10c), and also $\int\rho = \lambda_o < z$. Let $R > \max_{j=1,2,\ldots k} |R_j|$. For $r>R$ define

$$[\phi]\ (r) = (4\pi)^{-1} \int_{S_2} \phi(r\Omega)d\Omega.$$

Eq. (2.10c) and $\int\rho=\lambda_o$ imply,

$$[\phi]\ (r) \geq (z-\lambda_o)/r. \tag{2.13}$$

Now let $[\rho]\ (r) = (4\pi)^{-1} \int \rho(r\Omega)\ d\Omega$. Let decompose

$$[\rho]\ (r) = (4\pi)^{-1} \int_{\rho>1} \rho(r\Omega)\,d\Omega + (4\pi)^{-1} \int_{\rho\le 1} \rho(r\Omega)\ d\Omega \geq$$

$$\geq (4\pi)^{-1}\int_{\rho>1} \rho(r\Omega)\,d\Omega \geq c_+^{-3/2}\ (4\pi)^{-1} \int a(\rho)^{3/2}d\Omega,$$

where the last inequality follows from (2.4). Using the Euler equation for ρ and Hölder's inequality we have

$$[\rho]\ (r) \geq (4\pi)^{-1}\ c_+^{-3/2} \int \max(\phi,0)^{3/2}d\Omega \geq$$

$$\geq c_+^{-3/2}\ [\int \max(\phi(r\Omega),0)\ \frac{d\Omega}{4\pi}]^{3/2} \geq$$

$$\geq c_+^{-3/2}\ ([\phi]\ (r))^{3/2} \geq c_+^{-3/2}\ (z-\lambda_o)^{3/2} r^{-3/2},$$

because of (2.13). Thus

$$\int\rho(x)\,dx = 4\pi \int [\rho](r)\ r^2 dr = \infty$$

which contradicts $\int\rho = \lambda_o < z$. We conclude $\int\rho\ dx = \lambda$. |_|

The second result follows after a remarkable theorem of Baxter ([3], eq. (3.2)):

Theorem 2.12: Let V be of the form (2.12). Then for $\lambda > z \equiv \sum_{i=1}^{k} z_i$ the minimizing ρ for $\xi(\cdot,V)$ on W_λ has $\int\rho dx = z$.

Proof: Because of (F-2) (i.e. f non-decreasing) the hypothesis of ([3], equation (3.2)) are satisfied and hence $E(\lambda)$ is non-decreasing on (z,∞). Then the theorem follows from Corollary 2.7 and the uniqueness of the minimizing ρ on W_λ. |_|

Remark: This theorem can also be proven by mimicking the proof of [32, Theorem II.18]. That is, suppose that $\int\rho dx = \lambda > z$. As above define $[\phi](r)$. One can easily see that $\int\rho dx = \lambda > z$ implies $[\phi](r) < 0$ for very large r. This contradicts Lemma 2.18 below.

We can summarize the results of this first 3 sections in the following:

Theorem 2.13: Let $V(x) = \sum_{i=1}^{k} z_i |x-R_i|^{-1}$ with $z_i > 0$ and let $z = \sum_{i=1}^{k} z_i$. If $\lambda \leq z$, there is a unique ρ with $\int\rho dx = \lambda$ such that

$$f'(\rho) = a(\rho) = \max\,(\phi - \phi_o 0),$$

with

$$\phi(x) \equiv V(x) - \int dy\ \rho(y)\ |x-y|^{-1},$$

for some ϕ_o. Moreover:

(i) If $\lambda = z$, $\phi_o = 0$ and if $\lambda < z$, $\phi_o > 0$.

(ii) ϕ_o is given by (2.11)

(iii) $E(\lambda, V)$ is strictly monotone decreasing on $[0,z]$, constant on $[z,\infty)$ and convex on $[0,\infty)$.

2.5. No-binding Theorem

Let us denote by $E(\lambda,\underline{z},\underline{R})$ the minimum of $\xi(\cdot,V)$ on $W_{\partial\lambda}$. Here $\underline{z}$ denotes the k-tuple $(z_1,\ldots,z_k)$ with $z_i \geq 0$. Also $\underline{R} = (R_1,\ldots,R_k)$, $R_i \in R^3$.

Let us define

$$e(\lambda;\underline{z},\underline{R}) \equiv E(\lambda,\underline{z},\underline{R}) + \sum_{1\leq i<j\leq k} z_i z_j |R_i-R_j|^{-1} , \quad (2.14)$$

i.e. e is the total energy, including the internucleon repulsion.

In the TF model there are no molecules. In fact if one separates the nuclei into clusters and then takes them to infinity the energy e decreases. This result was first discovered numerically by Sheldon [42] (who is investigating binding in the TF theory with exchange, see Chapter 3) and then proven by Teller [46]. A rigorous proof, based on Teller's proof, was given by Lieb and Simon [32]. This result extends to a general model like the one decribed by (2.1). A very elegant proof of this fact is given in Baxter ([3], Proposition 2). His proof uses the variational principle rather than the Euler equation used in Teller's proof.

Theorem 2.14: The no-binding theorem of Teller

For any strictly positive $\{z_i\}_{i=1}^k$, any $\lambda>0$, any $\{R_i\}_{i=1}^k$ and $j=1,\ldots,k-1$:

$$e(\lambda;z_1,\ldots,z_k;\ R_1,\ldots,R_k) > \min_{0\le\lambda'\le\lambda} \{e(\lambda';z_1,\ldots,z_j;\ R_1,\ldots,R_j) + e(\lambda-\lambda';z_{j+1},\ldots,z_k;R_{j+1},\ldots,R_k)\} \tag{2.15}$$

Remark: For the TF case ($f(\rho) = \rho^{5/3}$) see ([32], Theorem V.2).

Proof: Since $f(0) = f'(0) = 0$ and $f(\cdot)$ is convex, f is superadditive i.e. $f(\rho_1+\rho_2) \geq f(\rho_1) + f(\rho_2)$. Hence this theorem follows from ([3], Proposition 2). |_|

Since in the true quantum mechanical system molecules do exist, this result of the TF theory is a negative one. However this no-binding result plays an important role in the Lieb-Thirring proof [34,28] of the stability of matter. After first showing that the TF energy with modified constant is a lower bound to the true Schröedinger energy one uses the no-binding theorem to show that this lower bound is greater than a constant times the number of atoms in the system.

The no-binding result is a consequence of the local dependence of the kinetic energy density on ρ. If one includes derivatives of ρ in the kinetic energy density binding may be possible. (see Chapter 4 below).

2.6. Components of the energy, virial theorem, scaling relations and definition of the pressure.

The results of this section are only heuristic. No rigorous proof will be given here. (However for the TF model $f(\rho) = \rho^{5/3}$ all these results are rigorously proven in [32]).

We consider V of the form (2.12). Let us define the components of $\xi(\rho,V)$:

$$K(\lambda,\underline{z},\underline{R}) = \int f(\tilde{\rho})dx. \quad A(\lambda,\underline{z},\underline{R}) = \int \tilde{\rho}(x)V(x)dx.$$

$$R(\lambda,\underline{z},\underline{R}) = \frac{1}{2}\int \tilde{\rho}(x)\ |x-y|^{-1}\tilde{\rho}(y)dx\ dy. \quad U(\lambda,\underline{z},\underline{R}) = \sum_{1\leq i<j\leq k} z_i z_j |R_i - R_j|^{-1}. \tag{2.16}$$

Here $\tilde{\rho}$ denotes the minimizing ρ for $\xi(\cdot,V)$ on W_λ. It is also convenient to define

$$D(\lambda,\underline{z},R) = \int f'(\rho)\rho\ dx. \tag{2.17}$$

"Theorem 2.15": Virial Theorem (one center). (see [32], Theorem II.22).

If $V(x) = z|x|^{-1}$ and if ρ minimizes $\xi(\cdot,V)$ on any W_λ, then

$$+\ 3(K-D) = (R-A). \tag{2.18}$$

Sketch of a proof: set $\rho_\mu(r) = \mu^3\rho(\mu r)$ so that $\rho_\mu \varepsilon W_\lambda$. Then $K(\rho_\mu) = \mu^{-3} \int f(\mu^3\rho)dx$, $A(\rho_\mu) = \mu A(\rho)$ and $R(\rho_\mu) = \mu R(\rho)$. By the minimization property for ρ, $K(\rho_\mu) - \mu A + \mu R$ has a minimum at $\mu=1$.

"Theorem 2.16": Let ρ minimize $\xi(\cdot,V)$ on all of W. Then for V given by (2.12)

$$D= A - 2R \tag{2.19}$$

Sketch of a proof: Let $\rho_\beta(x) = \beta\rho(x)$. By the minimization property of ρ $K(\rho_\beta) - \beta A + \beta^2 R$ has its minimum at $\beta=1$.

Remark: see also ([32], Theorem II.23).

For one atom theorems 2.15 and 2.16 imply

$$\begin{aligned} e &= 4K - 3D \\ A &= 5D - 6K \\ R &= 2D - 3K. \end{aligned} \tag{2.20}$$

In particular, for the TF theory ($f(\rho) = \rho^{5/3}$) $D = {}^{5K}/3$ and we have the result

$$K : A : R = 3: 7 : 1$$

(see [32], Corollary II.24).

We now consider the scaling properties of this TF related models and we get an expression for the pressure. For simplicity we consider here only the neutral case.

Let $a>0$ be a fixed parameter. Consider

$$f_a(\rho) \equiv a^{-5/3} f(a\rho).$$

(This particular dependence on "a" is chosen so that "a" disappears in the TF case. Of course the results are independent of this particular choice.)

Define

$$e(a,\underline{Z},\underline{R}) = \inf \{\xi_a(\rho,V) \mid \rho \varepsilon W\}$$

with

$$\xi_a(\rho,V) \equiv \int f_a(\rho) - \int V\rho + \frac{1}{2} \int \rho(\rho * |x|^{-1}) + U.$$

Then the minimizing $\bar{\rho}$ for $\xi_a(\cdot,V)$ satisfies the following scaling relation:

$$\rho(a,\underline{Z},\ell\underline{R},x) = \ell^{-6}\rho\ (\ell^{-6}a,\ \ell^{3}\underline{Z},\ \underline{R},\ x/\ell) \qquad (2.21)$$

and each of the components of the energy satisfies

$$e(a,\underline{Z},\ell\underline{R}) = \ell^{-7}\ e(\ell^{-6}a,\ \ell^{3}\underline{Z},\ \underline{R}) \qquad (2.22)$$

Let us now consider a dilation of the neutral molecule by ℓ, i.e. $R_i \to \ell R_i$, all i $\ell \varepsilon R^{+}$. We define the pressure

$$P \equiv - \frac{1}{3\ell^2} \frac{\partial e}{\partial \ell} \Big|_{\ell=1} \tag{2.23}$$

where $e(\ell) \equiv e(a,\underline{z},\ell\underline{R})$ (see [5]). Combining the scaling properties with the definition (2.23) we get

$$P = \frac{1}{3} [7e + 6a \frac{\partial e}{\partial a} - 3 \sum z_i \frac{\partial e}{\partial z_i}] \tag{2.24a}$$

Because of the minimization property of $\tilde{\rho}$ we have

$$\sum_{i=1}^{k} z_i \frac{\partial e}{\partial z_i} = - A + 2U \tag{2.24b}$$

$$a \frac{\partial e}{\partial a} = - \frac{5}{3} K + D \tag{2.24c}$$

(these results are only heuristic. One should prove the differentiability of e in z_i and a first. See however ([33], Theorem II.16) for the TF case).

From (2.24a,b,c,) we get

$$P = \frac{1}{3} [e + (3D - 4K)] \; . \tag{2.25}$$

Remarks: (i) Note that for an atom P=0 as it should be!

(ii) In the particular case $f(\rho) = \rho^{5/3}$ one has $D = \frac{5}{3} K$ and, there, $P = (e+K)/3$.

(iii) Theorem (2.14) says that the absolute minimum of e as a function of $\underline{R}$ is attained when all R_i are infinitely apart. If one can prove that $P \geq 0$ one concludes that there is no local minimum. (Because if $\underline{R}$ is a given configuration, $\ell\underline{R}$ for $\ell>1$ has always less energy). In the particular case $f = \rho^{5/3}$ (TF case) this was proven to be true in [5].

2.7 Regularity Properties of the minimizing solution.

Let us consider V of the form (2.2). We establish here some regularity properties of the minimizing ρ for $\xi(\cdot,V)$ and of its respective potential ϕ.

Lemma 2.17: The potential ϕ defined by (2.10c) is continuous away from the R_i's and goes to zero at infinity.

Proof: The convolution $\rho*|x|^{-1}$ is continuous and goes to zero at infinity because $\rho\varepsilon L^1 \cap L^{5/3}$ and $|x|^{-1} \varepsilon L^{5/2} + L^4$ [41], ([32], Lemma II.25). $\Box$

Lemma 2.18: $\phi(x)$ is non-negative, all x.

Proof: Let $S = \{x|\phi(x)<0\}$. Since $\phi\to\infty$ as $x\to R_i$ and ϕ is continuous away from the R_i's then S is open and disjoint from the R_i. On S, $\phi<0$ so $\phi-\phi_o<0$. Thus (2.10b) implies $\rho=0$ on S, hence ϕ is harmonic on S. Because of the previous lemma $\phi=0$ on $\partial S\cup\{\infty\}$. Therefore $\phi\equiv 0$ on S and S is empty (see[32], Lemma II.19). $\Box$

Lemma 2.19: $\phi \varepsilon H^2$ (the Sobolev space s.t. ϕ, $\frac{\partial\phi}{\partial x_i}$, $\frac{\partial^2\phi}{\partial x_i \partial x_j} \varepsilon L^2$) away from R_i.

Proof: Taking the distributional Lapacian in (2.10c) we get

$$- (4\pi)^{-1} \Delta\phi = - \rho + \sum_{i=1}^{k} z_i \, \delta(x-R_i) \tag{2.26}$$

with $\rho = a^{-1} (\max(\phi-\phi_o,0))$. Since a^{-1} is monotone in ϕ, (2.26) is a non-linear elliptic equation (for ϕ) with a monotone non-linearity. Therefore $\phi \in H^2$ away from the R_i by standard regularity theorems for elliptic equations [10]. |_|

Lemma 2.20: ϕ and ρ are analytic on the set $\{x|a(\rho)>0\}$, away from the R_i.

Proof: ϕ obeys the non-linear elliptic equation $(4\pi)^{-1}\Delta\phi = a^{-1} (\phi-\phi_o)$ in the neighborhood of any $x_o \neq R_i$ with $\phi(x_o)>\phi_o$ (or equivalently $x_o \in \{x|a(\rho)>0\}$). General theorems ([37], Section 5.8) then assert the real analyticity of ϕ and so also of $\rho = (4\pi)^{-1} \Delta\phi$. |_|

In the particular case $f(\rho) = \rho^{5/3}$ (i.e. TF theory) additional regularity properties, including asymptotic behavior of ϕ and ρ are proven in [32, Section IV].

2.8. Review of recent developments in the TF theory: $f(\rho) = \rho^{5/3}$.

After the first rigorous work on the (full)[1] TF theory by Lieb and Simon [31,32] many new properties have been studied on rigorous grounds. We will review here

[1]There had been previous rigorous results by E. Hille [24] about the TF equation with spherical symmetry, i.e. $V-Z|x|^{-1}$.

some of the results. (Throughout this section $f(\rho)=\rho^{5/3}$ and V is of the form (2.2)).

(i) <u>Sign of the many-body potentials [4]</u>: The k-body energy $\varepsilon(z_1,\ldots,z_k;\ R_1,\ldots,R_k)$ is defined by successive differences of the total energy e. If $a = \{a_1,\ldots,a_\ell\}$ ($\ell \leq k$) is a subset of the integers $K = \{1,\ldots,k\}$, let e(a) denote $e(z_{a_1},\ldots,z_{a_\ell};\ R_{a_1},\ldots,R_{a_\ell})$, and $|a| = \ell$ be the cardinality of a. Then

$$\varepsilon\ (K) \equiv \sum_{\phi \subseteq a \subseteq K} (-1)^{|K|-|a|} e(a) \tag{2.27}$$

with $e(\phi) \equiv 0$. Thus,

$$\varepsilon\ (\{1,2\}) = e(z_1,z_2;\ R_1,R_2) - e^{at}\ (z_1) - e^{at}\ (z_2)$$

is the two body energy,

$$\varepsilon\ (\{1,2,3\}) = e(\{1,2,3\}) - e(\{1,2\}) - e(\{1,3\})$$
$$- e(\{2,3\}) + e^{at}\ (\{1\}) + e^{at}\ (\{2\}) + e^{at}\ (\{3\})$$

is the three-body energy, and so forth.

It was shown in [4] that the sign of $\varepsilon(K)$ is $(-1)^{|K|}$ for all $\underline{z}$ and $\underline{R}$. This was done by noting that $\varepsilon(K) = 0$ when $z_1 = 0$ and that

$$\partial\varepsilon(K)/\partial z_1 = \lim_{x \to R_1} \psi(K;x)$$

where

$$\psi(K;x) = \sum_{\phi \le a \le K} (-1)^{|K|-|a|} \phi(a;x)$$

(here ϕ is the TF potential corresponding to the configuration a). It was shown that $(-1)^{|a|} \phi(a;x) \geq 0$ all x.

This last result is the finite difference version of the following heuristic result:

If ϕ_i denotes $\frac{\partial \phi}{\partial z_i}(x)$, etc.

$$(-1)^n \phi_{i_1, i_2, \ldots, i_n}(x) \leq 0 \text{ all } x,\ n \geq 1. \qquad (2.28)$$

(see [5] Section 3).

A function satisfying this property is called an alternating function. This kind of result is characteristic of problems related to electrostatics. In fact capacities and Green's function satisfy similar inequalities [35].

This theorem about the sign of the many-body potentials and the inequalities for the TF potential still hold if $f(\rho) = \rho^{5/3}$ is changed by any function satisfying $f, f' \geq 0$, $(-1)^n f^{(n)} \geq 0$, (as long as the minimizing problem still makes sense), i.e. if f' is a Herglotz function.

(ii) Positivity of the pressure (non existence of local minima of the TF energy as a function of the configuration $\underline{R}$) [5]. (neutral case only)

The no-binding theorem of Teller says that the absolute minimum of the TF energy as a function of the configuration $\underline{R}$ is obtained when all R's are infinitely apart from each other. However there could be a configuration of $\underline{R}$'s giving a local minimum for the energy.

Let $e(\underline{R})$ be the TF energy corresponding to the configuration $\underline{R}$. Let us make the uniform dilation $\underline{R} \to \ell\underline{R}$ $(\ell>0)$ and consider $e(\ell) \equiv e(\ell\underline{R})$. Let us define the pressure $P = -\frac{1}{3\ell^2} \frac{\partial e}{\partial \ell}\Big|_{\ell=1}$. Then, it is clear that if p is non-negative there are not any local minima for the energy. This result has been proven in [5]. It was also proven that the compressibility $\kappa^{-1} = -\frac{\ell}{3}\frac{\partial P}{\partial \ell}\Big|_{\ell=1}$ is also non-negative and that, in fact, $e(\ell)$ is a decreasing convex function of ℓ (convexity here is stronger than the statement that κ^{-1} is positive.

The positivity of the pressure and compressibility had been conjectured in [32]. The pressure can be written in terms of the total energy e and the kinetic energy K as $P = \frac{1}{3}(e+K)$. The no-binding theorem 2.14 says that e is superadditive, i.e. if we decompose a system into two clusters the energy of the system is larger than the sum of the energies of the clusters $(e(z_1+z_2) \geq e(z_1) + e(z_2))$. Suppose that K has the same property. Then P would also have it and, therefore, $P \geq \sum P^{at} = 0$, where P^{at} is the pressure of a single atom and is zero because e^{at} does not change under dilation. That K is superadditive follows from the relation

$$\frac{\partial^2 K}{\partial z_i \partial z_j} = -3 \sum_{\ell=1}^{k} z_\ell \frac{\partial^2 \phi}{\partial z_i \partial z_j}(R_\ell)$$

(this kind of relation only holds when $f(\rho)$ is a power of ρ) and equation (2.28).

It has been conjectured [5] that the neutral case is the worst case and therefore the pressure P and compressibility κ^{-1} should be positive for the ionic case ($\lambda<z$) as well.

The only result in the ionic case is the one by Balàzs [2]: (an alternative proof using Reflection Positivity is given in [5]) for a configuration ($\underline{z},\underline{R}$) having a plane of symmetry, the shifting of the charges $\underline{z}$ in each side away from the symmetry plane decreases the energy.

(iii) Asymptotic behavior of the k-body energies [11]: It was proven by Brezis and Lieb [11] that the interaction among neutral atoms in TF theory behaves, for large separation ℓ, like $\Gamma \ell^{-7}$ (Γ is independent of the z's, a consequence of the fact that the asymptotic formula for ρ [32,44] is independent of the z's) but does depend on the relative position of the nuclei. Moreover in TF theory 3 and higher body terms persist into the asymptotic region.

(iv) The Free-Boundary of the TF functional [12]: In the ionic case (i.e. $\lambda<z$) the support of ρ is compact ([32], Theorem IV.2). Let $\Omega = \{x|\rho(x)>0\}$. The boundary $\partial\Omega$ is determined by the TF eqn. (i.e. $\partial\Omega$ is a free boundary). The properties of $\partial\Omega$ have been studied by Cafarelli and Friedman [12]. They proved that $\partial\Omega$ is $C^{3+\frac{1}{2}}$ everywhere except on at most a finite number of C^1 curves.

CHAPTER 3: "THE EXCHANGE CORRECTION"

In the TF functional only the "direct" part of the true quantum mechanical electron-electron repulsion is taken into account. The so called "exchange" energy (the effects of the Pauli principle in the interaction energy) is not considered. Although it is impossible to express this energy only in terms of ρ we seek an approximation to it. A possible approximation is suggested by the calculation of the exchange energy per unit volume for a system of N electrons in a box of volume V. The result of such computation [8,17] is

$$- \frac{3}{4} C_e \, (N/V)^{4/3}, \tag{3.1}$$

with $C_e = e^2(3/\pi)^{1/3}$ ($-e$ is the charge of the electron and we choose units in which $e = 1$). Starting from the Hartree-Fock theory, Dirac [13] derived an approximation to the exchange energy in terms of ρ. He found

$$U_e(\rho) = - (3C_e/4) \int dx \, \rho^{4/3}. \tag{3.2}$$

Finally, it has been recently proven [30] that $U_e(\rho)$, with some appropriate constant replacing C_e, is in fact a lower bound to the true exchange energy (defined as the difference between the quantum mechanical electron-electron repulsion and the direct energy $\frac{1}{2} \int dx \, dy \, \rho(x)|x-y|^{-1}\rho(y)$).

The TF theory with the correction for exchange taken into account (henceforth denoted by TFD) is then defined by the functional

$$\xi_{TFD}(\rho) \equiv \xi_{TF}(\rho) + U_e(\rho)$$

$$= \int g(\rho)\,dx - \int V\rho\,dx + \frac{1}{2}\int dx\,dy\;\rho(x)|x-y|^{-1}\rho(y), \tag{3.3}$$

with

$$g(\rho) = (3/5)\rho^{5/3} - (3/4)\,C_e\rho^{4/3}. \tag{3.4}$$

The addition of the exchange term to the TF energy functional makes it loose its convexity in ρ and therefore we can not apply the usual methods to prove existence and uniqueness of a minimum. In particular TFD does not fall into the category of models studied in the previous chapter.

In the last fifteen years a new technique has been developed to study non-convex variational problems [25,14], namely the "relaxation" of the energy functional: starting with a variational problem which often does not have a solution one tries to formulate a second problem having the same value and such that its optimal solutions are exactly limit points of minimizing sequences of the first. (For a review [15], Chapters VIII-X). This is the method we are going to use here to prove existence of solutions to min $\{\xi_{TFD}(\rho)\;|\int\rho=\lambda\}$ (see Theorem 3.3 below).

In Section 3.1 we formulate the relaxed problem and we study the existence and uniqueness of solutions. This is particularly simple because the relaxed problem is an example of the models studied in Chapter two. In section 3.2 we show that the solution to the relaxed problem also solves the original one. In the last section we discuss some properties of the solution.

3.1. The relaxed problem.

Consider the TFD energy functional defined by (3.3), (3.4). If we are going to minimize $\xi_{TFD}(\rho)$ keeping $\int\rho=\lambda$ fixed, adding a term proportional to $\int\rho$ to $\xi_{TFD}(\rho)$ does not change the minimization problem. For convenience, let us define the functional

$$\xi_k(\rho) \equiv \xi_{TFD}(\rho) + \alpha\int\rho = \int k(\rho)dx - \int V\rho dx + \frac{1}{2}\int dx\, dy\rho(x)|x-y|^{-1}\rho(y), \qquad (3.5)$$

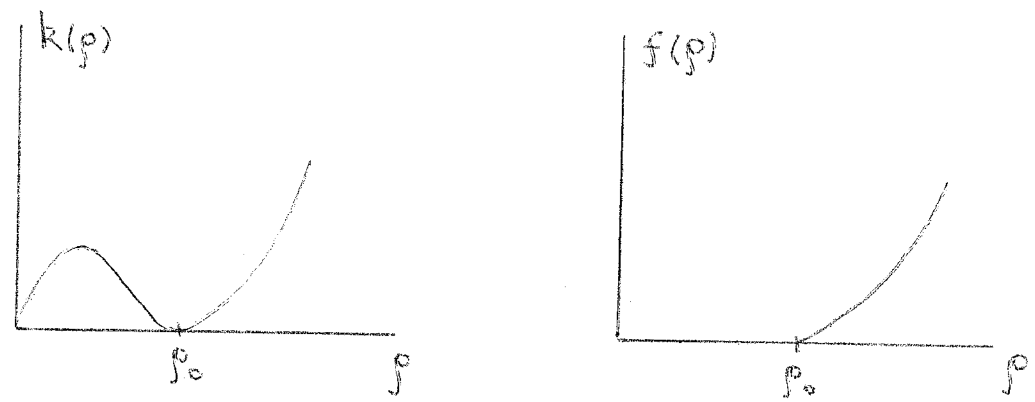
with α chosen to be $15C_e^2/4^3$ so that $k(\rho) \geq 0$ for all ρ. Hence $k(\rho)$ is defined by

$$k(\rho) = (3/5)\rho^{5/3} - (3/4)\, C_e\rho^{4/3} + \alpha\rho \qquad (3.6)$$

with $\alpha = 15C_e^2/4^3$. Let us denote $\rho_o = (5C_e/8)^3$.

The function $k(\cdot)$ is obviously not convex. Let $f(\cdot)$ be the function whose epigraph (i.e. the set $\{(x,y) \mid x \geq 0,\ y \geq f(x)\}$) is the convex hull of the epigraph of $k(\cdot)$ (or in other words f is the second Legendre transform of k). By definition f is a convex function and it is defined by (see figure)

$$\begin{aligned} f(\rho) &= 0 \quad \text{if } \rho < \rho_o \\ f(\rho) &= k(\rho) \text{ if } \rho \geq \rho_o. \end{aligned} \tag{3.7}$$



Corresponding to f let us define the energy functional

$$\xi_f(\rho) = \int f(\rho)dx - \int V\rho dx + \frac{1}{2}\int dx\, dy\ \rho(x)|x-y|^{-1}\rho(y) \tag{3.8}$$

and let us study the following minimization problem,

$$\min\{\xi_f(\rho) \mid \rho \in W_{\partial\lambda}\} \tag{3.9}$$

with $W_{\partial\lambda}$ defined as in (2.6b).

Remark: The variational problem defined by (3.9) is called the relaxation of the original non-convex problem defined by $\xi_k(\rho)$ [15].

The function f defined by (3.7) satisfies all the properties (F-1) through (F-4) and therefore theorem 2.13 applies to the functional $\xi_f(\rho)$. Hence we have:

Theorem 3.1. (Existence of a solution to the relaxed problem): Let $V(x) = \sum_{i=1}^{k} z_i |x-R_i|^{-1}$ with $z_i > 0$ and let $z = \sum_{i=1}^{k} z_i$. Then for $\lambda \leq z$, there is a unique minimizing ρ for (3.9) with $\int \rho dx = \lambda$ such that

$$\phi(x) - \tilde{\phi}_o \leq 0 \quad \text{if } \rho = 0 \tag{3.10a}$$

$$\phi(x) - \tilde{\phi}_o = 0 \quad \text{if } 0<\rho(x)<\rho_o \tag{3.10b}$$

$$\rho(x)^{2/3} - C_e\rho(x)^{1/3} + \alpha = \phi(x) - \tilde{\phi}_o \quad \text{if } \rho(x) \geq \rho_o, \tag{3.10c}$$

with $\phi(x) \equiv V(x) - \int dy\, \rho(y)\, |x-y|^{-1}$, for some $\tilde{\phi}_o$. Moreover if $\lambda = z$, $\tilde{\phi}_o = 0$ and if $\lambda < \bar{z}$, $\tilde{\phi}_o > 0$. $E_f(\lambda,V) = \inf \{\xi_f(\rho) | \rho \varepsilon W_{\partial\lambda}\}$ is strictly monotone decreasing on $[0,z]$ constant on $[z,\infty)$ and convex on $[0,\infty)$. $\tilde{\phi}_o$ is given by $\tilde{\phi}_o = -\frac{\partial E_f}{\partial \lambda}$.

Remark: The tilde over $\tilde{\phi}_o$ is used to distinguish it from the chemical potential for the TFD problem. See Theorem 3.3 below.

3.2. Connection between the relaxed problem and the TFD variational principle.

Since the function f defined by (3.7) is pointwise less or equal than k we have,

$$\xi_k(\rho) \geq \xi_f(\rho)$$

for every $\rho \varepsilon W$. Therefore

$$\min \{\xi_f(\rho) | \rho \varepsilon W_{\partial\lambda}\} \leq \inf \{\xi_k(\rho) | \rho \varepsilon W_{\partial\lambda}\} \qquad (3.11)$$

Here we will show that the minimizing ρ for $\xi_f(\cdot)$ in $W_{\partial\lambda}$ also minimizes $\xi_k(\cdot)$ in that set. Let us denote by $\bar{\rho}$ the function minimizing $\xi_f(\cdot)$ in $W_{\partial\lambda}$ $(\lambda \leq z)$. We start with the following result

Lemma 3.2: If $\bar{\rho}$ is the solution to (3.10) then $\mu \{x | 0<\bar{\rho}(x) \leq \rho_o\} = 0$ where μ is the Lebesgue measure.

Proof: We recall the following property of the Sobolev space H^1 [45]: Let c be an arbitrary constant and $u \varepsilon H^1$, then $\frac{\partial u}{\partial x_i} = 0$ a.e. on the set $\{x | u(x) = c\}$. Iterating this we deduce that if c is a constant and $u \varepsilon H^2$ then $\Delta u = 0$ a.e. on the set $\{x|u(x) = c\}$. Consider now the set $\mathcal{D} = \{x|0<\bar{\rho}(x)\rho_o\}$ $\cup\{x|\rho=0,\ \phi=\tilde{\phi}_o\}$. On $\mathcal{D}$, $\phi=\tilde{\phi}_o$. For x near R_i $\phi(x)$ is very large and thus $\rho>\rho_o$. Hence $\mathcal{D}$ is away from the R_i's. On $\mathcal{D}$ $\phi=\tilde{\phi}_o$ (a constant) and $\phi\varepsilon H^2$ (because of Lemma 2.19). Therefore $\Delta\phi=0$ a.e. on $\mathcal{D}$ and consequently $\rho(x)=0$ a.e. on $\mathcal{D}$. Hence $\mu\{x|0<\bar{\rho}\leq\rho_o\} = 0$. |̅|

Because of Lemma 3.2, $\xi_k(\bar{\rho}) = \xi_f(\bar{\rho})$ and therefore (3.11) implies

$$\xi_f(\bar{\rho}) = \min\{\xi_f(\rho)\ |\ \rho\varepsilon W_{\partial\lambda}\} \leq \inf\{\xi_k(\rho)\ |\ \rho\varepsilon W_{\partial\lambda}\}$$

$$\leq \xi_k(\bar{\rho}) = \xi_f(\bar{\rho}).$$

Thus $\bar{\rho}$ is the unique minimizing ρ for $\xi_k(\cdot)$ in $W_{\partial\lambda}$. (Uniqueness here is implied by the uniqueness of the solution to the relaxed problem).

To conclude this section let us summarize the results about the TFD minimization problem in the following

<u>Theorem 3.3</u>: Let $V(x) = \sum_{i=1}^{k} z_i\,|x-R_i|^{-1}$ with $z_i > 0$ and let $z = \sum_{i=1}^{k} z_i$. For $\lambda \leq z$, there is a unique ρ which minimizes $\xi_{TFD}(\cdot)$ (defined by (3.3)) with $\int\rho dx = \lambda$. The minimizing ρ is such that

$$\rho^{1/3} = \frac{1}{2}\ [C_e + (C_e^2 + 4(\phi-\phi_o))^{\frac{1}{2}}]\ \text{if}\ \phi>\phi_o-\alpha, \qquad (3.12a)$$

$$\rho = \rho_o = (5C_e/8)^3 \qquad \text{if } \phi=\phi_o-\alpha \tag{3.12b}$$

and $$\rho = 0 \qquad \text{if } \phi<\phi_o-\alpha, \tag{3.12c}$$

where $\phi(x) \equiv V(x) - \int dy\, \rho(y)\, |x-y|^{-1}$, for some $\phi_o \geq \alpha \equiv 15C_e^2/4^3$. Moreover if $\lambda=z$, $\phi_o=\alpha$ and if $\lambda<z$ $\phi_o>\alpha$. ϕ_o is given by

$$\phi_o = -\frac{\partial E_{TFD}}{\partial \lambda} \tag{3.13}$$

$E_{TFD}(\lambda)$ is strictly monotone decreasing and convex. If $\lambda>z$ there is no solution.

Remarks: (i) Recall here that $\xi_{TFD}(\rho) = \xi_k(\rho) - \alpha\int\rho$. This is why $\phi_o = \alpha$ in the neutral case.

(ii) Note that $\xi_{TFD}(\rho)$ is not bounded from below in W. In fact, as $||\rho||_1 \to \infty$, $\xi_{TFD}(\rho) \to -\infty$.

3.3. Properties of the minimizing solution.

(i) Properties of ϕ and ρ: Regularity properties of ϕ and ρ are established in section 2.7. In particular ϕ is a continuous function going to zero at infinity. ϕ and ρ are real analytic in the set $\{x|\rho(x)>\rho_o\} = \{x|\phi(x)>\phi_o-\alpha\}$. The TFD density ρ has compact support even in the neutral case and $\mu\{x|0<\rho(x)<\rho_o\} = 0$.

(ii) Dependence on C_e:

Theorem 3.4: Let $\tilde{\phi}_o \equiv \phi_o - 15C_e^2/4^3$ and V be fixed. Let ϕ_1 (respectively ϕ_2) be the TFD potential corresponding to C_e^1 (respectively C_e^2). Then if $C_e^1 > C_e^2$, $\phi_1(x) \leq \phi_2(x)$ for all x. In particular, for neutral systems, $\phi_{TFD}(x) \leq \phi_{TF}(x)$ all x.

Proof: Let $\psi \equiv \phi_2 - \phi_1$. Because of (i) ψ is continuous and goes to zero at infinity. Therefore $S = \{x | \psi(x) < 0\}$ is open and $\psi = 0$ on $\partial S \cup \{\infty\}$. On S

$$-(4\pi)^{-1}\Delta\psi = \rho_1 - \rho_2 \geq 0$$

because, for fixed $\tilde{\phi}_o$, $\rho^{1/3} = \frac{1}{2}(C_e + (C_e^2/16 + 4(\phi - \tilde{\phi}_o))^{\frac{1}{2}})$ is increasing in C_e (on S). Hence ψ is superharmonic on S. Since $\psi = 0$ on $\partial S \cup \{\infty\}$ the maximum modulus principle implies S is empty and therefore $\phi_2(x) \geq \phi_1(x)$ for all x. |_|

(iii) Two-body atomic potential:

- The no-binding theorem 3.14 (Teller's theorem) also holds here. Hence there are no molecules in the TFD model.
- For a one center potential (i.e. $V = z|x|^{-1}$) the solution ρ is spherically symmetric and decreasing in $|x|$ (see Chapter 4, Theorem 4.11)). Therefore the support of the minimizing solution has finite radius R_o. Certainly

$$R_o \leq (3\lambda/4\pi\rho_o)^{1/3} .$$

- In the neutral case ($\lambda=Z$), if one studies two centers separated by a distance $R>R_{o_1} + R_{o_2}$, with $R_{o_i} = (3z_i/4\pi\rho_o)^{1/3}$, the minimizing solution ρ is going to be equal to the one center solution ρ_1 around R_1 and $\rho=\rho_2$ around R_2 and 0 everywhere else. This can be easily seen considering the uniqueness of the solution. This implies that the two-body energy is 0 if the atoms are separated by more than R.
- More (heuristic) information about the TFD interatomic potential can be found in ([48], Section 3.5).

CHAPTER 4: THE THOMAS-FERMI VON WEIZSÄCKER THEORY

The TF and related theories (see Chapter 2), attractive because of their simplicity, are not satisfactory for atomic problems because they yield an electron density with incorrect behavior very close and very far away from the nucleus. Moreover, they do not allow for the existence of molecules. Von Weisäcker [49] suggested the addition of an inhomogeneity correction

$$U_W(\rho) = C_W(\Delta\rho)^2/\rho \quad , \tag{4.1}$$

to the kinetic energy density. Here $C_W \equiv h^2/(32\pi^2 m) = (24\pi^2)^{-2/3}$ in units in which the coefficient of the $\rho^{5/3}$ term is 3/5. The Von Weisäcker correction has been derived in many different ways. It can be obtained as the first order correction to the TF kinetic energy in a quasi-classical approximation to the Hartree-Fock theory via a steepest descent computation [27]. The correction to the TF energy that this additional term yields is of the order $Z^{5/3}$, i.e. of the same order as the exchange correction. Numerical computations using the TF Von Weisacker theory (henceforth TFW) give too high values of the ground state energies of atoms and it has been proposed to reduce the constant C_W by a factor 9 [22,23,27]. We will not discuss that here. Our main concern, however, will be the study of the variational problem defining TFW. The existence of a unique solution minimizing the TFW energy functional (4.2) in the set $\{\rho | \int\rho \leq \lambda, \rho \geq 0\}$ is established [Theorem 4.7 below]. The question of existence of a solution in the set $I_{\partial\lambda} \equiv \{\rho | \int\rho = \lambda, \rho \geq 0\}$ is harder than in the TF case. In the one center case (TFW atom) we show that there is a unique minimizing solution in $I_{\partial\lambda}$ for $\lambda \leq Z$. It remains as an open problem to determine the largest λ for which this is still true. Recall that for the TF related theories the largest λ is Z. Another open problem is to prove the existence of binding within the framework of TFW theory. We do not have any result in this direction. Note, however, that $E_W(\rho) \equiv \int U_W(\rho)dx$ is subadditive as a function of ρ, i.e. $E_W(\rho_1+\rho_2) \leq E_W(\rho_1) + E_W(\rho_2)$ (see Theorem 4.3 below), and therefore does not satisfy the hypothesis of Baxter's Theorem ([3] Proposition 2; Chapter 2 Theorem 2.14). This leaves open the possibility for binding. Gombás [21] applied the TFW theory (including exchange corrections) to study the N_2-molecule and he found numerically that there is binding. He actually computed the distance between the two centers to be 1.39 Å, for the configuration of minimum energy. There is also a non-rigorous argument of Balàzs [2] that indicates the possibility of binding for a homopolar diatomic molecule in the TFW theory.

In sections 4.1 and 4.2 the existence and uniqueness of a minimizing solution in the set I_λ is determined. In section 4.3 it is proven that the minimizing solution is a strong solution to the TFW equation (4.14) and regularity properties of this solution are established. In section 4.4 the TFW atom is studied and in section 4.5 the components of the energy and their properties are discussed.

4.1. The TFW functional

The TFW theory can be defined by the following energy functional

$$\xi(\psi,V) = C_W \int(\nabla\psi)^2 dx + \frac{3}{5}\int(\psi^2)^{5/3}dx - \int V\psi^2 dx$$
$$+ \frac{1}{2}\int dxdy\ \psi(x)^2|x-y|^{-1}\ \psi(y)^2, \tag{4.2}$$

defined on the function space

$$H^1(R^3) \equiv \{\psi|\ \psi\varepsilon L^2,\ \nabla\psi\varepsilon L^2\}\ . \tag{4.3}$$

The Sobolev space $H^1(R^3)$ is a Hilbert space with respect to the inner product $((u,v)) \equiv (u,v) + (\nabla u,\nabla v)$ $((u,v) = \int uvdx)$. In terms of ψ the single particle density ρ is $\rho(x) = \psi(x)^2$. We are interested here on V's of the form

$$V(x) = \sum_{i=1}^{k} z_i \; |x-R_i|^{-1} \quad , \; z_i>0. \tag{4.4}$$

Before we proceed with the proof of existence and uniqueness we claim that if $\psi\varepsilon H^1$

$$\int (\nabla|\psi|)^2 dx \leq \int (\nabla\psi)^2 dx$$

and thus $\xi(|\psi|,V) \leq \xi(\psi,V)$. Therefore we can restrict the function space over which $\xi(\cdot,V)$ is minimized to

$$I = \{\psi| \; \psi\varepsilon H^1, \; \psi\geq 0\} \tag{4.5}$$

The proof of this claim uses the same method as in Kato's theorem [39]: if $\psi_\varepsilon = (\psi^2 + \varepsilon^2)^{\frac{1}{2}}$, then for ψ smooth $\psi_\varepsilon \; \nabla\psi_\varepsilon = \psi\nabla\psi$ and thus $|\nabla\psi_\varepsilon| \leq |\nabla\psi|$. For arbitrary $\psi\varepsilon H^1$, mollify ψ as in the proof of Kato's inequality.

For the same reasons given in the minimization problem of Chapter 2, it is convenient to define

$$I_\lambda = \{\psi\varepsilon I| \int\psi^2 dx \leq \lambda\} \quad , \tag{4.6a}$$

$$I_{\partial\lambda} = \{\psi\varepsilon I| \int\psi^2 dx = \lambda\} \; . \tag{4.6b}$$

Note that $\psi \varepsilon H^1 \Longleftrightarrow \psi \varepsilon L^2$, $\nabla\psi \varepsilon L^2$ and therefore by using Sobolev's inequality [7]

$$\int (\nabla\psi)^2 dx \geq K(\int \psi^6 dx)^{1/3} \tag{4.7}$$

($K = 3\ (\pi/2)^{4/3}$ is known to be the best possible constant) we see that $\psi \varepsilon H^1$ implies $\psi \varepsilon L^6$. Hence $\psi \varepsilon L^P$ for every $2 \leq p \leq 6$. In particular $\psi^2 \varepsilon L^{5/3}$.

<u>Theorem 4.1</u>: Let $V \varepsilon L^{5/2} + L^\infty$ and let $\xi(\psi,V)$ be given by (4.2) then:

(i) If $\psi \varepsilon I$, $\xi(\psi,V)$ exists.

(ii) If ψ_n, $\psi \varepsilon I$ and $||\psi_n - \psi||_{H^1} \to 0$ then $\xi(\psi_n,V) \to \xi(\psi,V)$.

(iii) On each I_λ $(\lambda<\infty)$, $\xi(\psi,V)$ is bounded from below.

(iv) Fix λ, E_o. Then $\exists c<\infty$ such that $\psi \varepsilon I_\lambda$ with $\xi(\psi,V) \leq E_o$ implies $||\psi||_{H^1} \leq c$.

<u>Proof</u>: (i) $\psi \varepsilon H^1$ implies $\psi \varepsilon L^P$ all $p \in [2,6]$ and in particular $\psi^2 \varepsilon L^{5/3}$. Therefore, by ([32], Theorem II.2a)) $\xi(\psi,V) - C_W \int (\nabla\psi)^2$ is finite. Since $\psi \varepsilon H^1$ we have $\xi(\psi,V) < \infty$. (ii) If ψ_n, $\psi \varepsilon I$ and $||\psi_n - \psi||_{H^1} \to 0$ we have $||\psi_n - \psi||_p \to 0$ for $2 \leq p \leq 6$. Hence ([32], Theorem II.2b)) and $||\nabla(\psi_n - \psi)||_2 \to 0$ imply $\xi(\psi_n,V) \to \xi(\psi,V)$. (iii) $\xi(\psi,V) \geq C_W \int (\nabla\psi)^2 dx - \int V\psi^2 dx$, since $\int (\psi^2)^{5/3} \geq 0$ and $\int dxdy\ \psi(x)^2\ |x-y|^{-1}\ \psi(y)^2 \geq 0$. Using Hölder's and Sobolev's inequalities we get

$$||\psi^2||_{5/3} \leq \lambda^{2/5} K^{-3/5} ||\nabla\psi||_2^{6/5} \quad .$$

Since $V = V_1 + V_2$ with $V_1 \in L^\infty$ and $V_2 \in L^{5/2}$, Hölder's inequality and the above estimate yield

$$\xi(\psi,V) \geq C_W Y^2 - \lambda||V_1||_\infty - \lambda^{2/5} K^{-3/5} ||V_2||_{5/2} Y^{6/5}$$

($Y \equiv ||\nabla\psi||_2$), which is certainly bounded from below.

(iv) From (iii) we have $||\nabla\psi||_2 < d$ for some finite d. Since $||\psi||_2 \leq \lambda^{1/2}$ we have $||\psi||_{H^1} < c$. $\square$

<u>Remark</u>: $\xi(\psi,V)$ is also bounded from below in I since $\xi(\psi,V) \geq \xi_{TF}(\psi^2,V)$ which is bounded from below in W [32].

Let us now define

$$E(\lambda,V) \equiv \inf \{\xi(\psi,V) \mid \psi \varepsilon I_{\partial\lambda}\} \quad . \tag{4.8}$$

<u>Theorem 4.2</u>: If $V \varepsilon L^{5/2} + L^P$ for some $5/2<p<\infty$, then $E(\lambda,V) = \inf \{\xi(\psi,V) \mid \psi \varepsilon I_\lambda\}$.

<u>Proof</u>: Given $\psi \varepsilon C_o^1 (R^3) \cap I_\lambda$ we can find $\psi_n \varepsilon I_{\partial\lambda}$ such that $\xi(\psi_n,V) \to \xi(\psi,V)$. In fact let $\psi_n = \psi + \tilde{\Delta}_n$ where $\tilde{\Delta}_n$ is supported in R^3/supp (ψ) and it is the translate of

$$\Delta_n(x) \equiv c\, n^{-\frac{1}{2}} (\lambda - ||\psi||_2^2)^{\frac{1}{2}} \begin{cases} \exp\left(-n^{2/3}(|x|-n^{1/3})^{-2}\right) & \text{if } |x| \le n^{1/3} \\ 0 & \text{if } |x| \ge n^{1/3} \end{cases} \tag{4.9}$$

and $c = 4\pi \int_o^1 \exp\left(-2(1-r)^{-2}\right) r^2 dr$. Note that

$$\begin{aligned} &\text{(i)} \int \Delta_n^2\, dx = (\lambda - ||\psi||_2^2) \quad \forall n>0 \\ &\text{(ii)} \int (\Delta_n)^k dx = a\, n^{(2-k)/2} \\ &\text{(iii)} \int (\nabla\Delta_n)^2 dx = b\, n^{-2/3} \end{aligned} \tag{4.10}$$

for some positive constants a,b and $k>2$. Therefore $\int(\nabla\Delta_n)^2 dx$ and $\int(\Delta_n)^k dx$ go to zero as $n\to\infty$. Hence $\int \psi_n^2 dx = \lambda$ (i.e. $\psi_n \in I_{\partial\lambda}$), $||\psi_n - \psi||_{5/3} \to 0$ and $||\psi-\psi_n||_r \to 0$ as $n\to\infty$ for any $r>2$. Moreover, since $\int(\nabla\Delta_n)^2 dx \to 0$ as $n\to\infty$, by a simple modification of Theorem 4.1 we have

$$\xi(\psi_n, V) \to \xi(\psi, V). \tag{4.11}$$

Thus

$$\begin{aligned} \inf\{\xi(\psi,V) \mid \psi \in I_{\partial\lambda}\} &\le \inf\{\xi(\psi,V) \mid \psi \in I_\lambda \cap C_0^1\} \\ &= \inf\{\xi(\psi,V) \mid \psi \in I_\lambda\}. \end{aligned}$$

The last equality follows from (4.11) and the density of C_0^1 in H^1. $\square$

As a consequence of this theorem we have that $E(\lambda,V)$ is a monotone non-increasing function of λ whenever $V \in L^{5/2} + L^p$, $5/2<p<\infty$. Moreover, $E(\lambda,V)$ is bounded from below (see remark below Theorem 4.1).

<u>Theorem 4.3 (Strict Convexity)</u>: Fix V and let $\psi = (\alpha\psi_1^2 + (1-\alpha)\psi_2^2)^{\frac{1}{2}}$ for $\alpha\varepsilon(0,1)$ with $\psi_1,\psi_2 \in I$ and $\psi_1^2 \neq \psi_2^2$ a.e. Then,

$$\xi(\psi,V) < \alpha\ \xi(\psi_1,V) + (1-\alpha)\ \xi(\psi_2,V).$$

<u>Proof</u>: Because of ([32], Theorem II.6), we need only check

$$(\nabla\psi)^2 \leq \alpha(\nabla\psi_1)^2 + (1-\alpha)\ (\nabla\psi_2)^2. \tag{4.12}$$

This is the same as proving

$$(\alpha\psi_1\nabla\psi_1 + (1-\alpha)\psi_2\nabla\psi_2)^2 \leq (\alpha\psi_1^2 + (1-\alpha)\psi_2^2)\ (\alpha(\nabla\psi_1)^2 + (1-\alpha)\ (\nabla\psi_2)^2)$$

which follows from Schwartz's inequality. |_|

<u>Remark</u>: Let $\alpha = \frac{1}{2}$ in (4.12) and integrate over dx. We get

$$E_W\ (\rho_1+\rho_2) \leq E_W(\rho_1) + E_W(\rho_2),$$

i.e. the von Weizsäcker correction is subadditive in ρ. As we have remarked in the introduction this leaves open the possibility of binding in the TFW theory.

Corollary 4.4: There is at most one $\psi_o \in I_\lambda$ with $\xi(\psi_o,V) = \inf \{\xi(\psi,V) \mid \psi \in I_\lambda\}$. The same is true if I_λ is replaced by I or $I_{\partial\lambda}$.

Corollary 4.5: Suppose $V \in L^{5/2} + L^p$ with $p > \frac{5}{2}$. Then:

a) If ψ_o minimizes $\xi(\psi,V)$ on I_{λ_o} and $\int \psi_o^2 < \lambda_o$, then $E(\lambda,V) = E(\lambda_o,V)$ for all $\lambda<\lambda_o$, when $p<\infty$.

b) If $\xi(\psi,V)$ has a minimum on $I_{\partial\lambda}$ for all $\lambda \le \lambda_o$, then $E(\lambda,V)$ is strictly convex on $[0,\lambda_o]$.

In particular $E(\lambda,V)$ is convex in λ.

Proof: See Corollary 2.9. |_|

4.2. Existence of a solution in I_λ.

To prove existence of solutions in I_λ we use the same technique as in Chapter 2. We first prove that $\xi(\psi,V)$ is lower semicontinuous in the weak H^1 topology. Since $\xi(\lambda,V)$ is coercive (Theorem 4.1) and H^1 reflexive, the proof of existence of solutions follows by the Banach-Alaoglu theorem [38]. Uniqueness follows by Corollary 4.4.

Theorem 4.6 (weak lower semicontinuity of $\xi(\psi,V)$): Let $V \in L^{5/2} + L^p$ $5/2<p<\infty$. Then $\xi(\cdot,V)$ is lower semicontinuous on each I_λ $(\lambda<\infty)$ in the weak H^1 topology, i.e. if $\psi_n \to \psi$ in weak H^1, then

ψ_{n_i} such that $\psi_{n_i} \to \psi_\infty$ in weak H^1. We need only check $||\psi_\infty||_2^2 \leq \lambda$. This follows since $\underline{\lim} \int \psi_n^2 \geq \int \psi_\infty^2$. Therefore by Theorem 4.6 and Corollary 4.4, there is a unique $\psi \in I_\lambda$ with $\xi(\psi,V) = E(\lambda,V)$. $|\overline{\underline{\ }}|$

4.3. Connection with the TFW equation.

In this section we study the Euler equation associated with the TFW variational principle. First we show that the minimizing ψ for $\xi(\cdot,V)$ on $I_{\partial\lambda}$ is a weak solution of the TFW equation (4.13) and then we use elliptic regularity to prove that in fact ψ is a strong solution. This is a standard procedure in the study of variational problems.

Theorem 4.8: Let $V \in L^{5/2} + L^p$ for $p \in (\frac{5}{2},\infty)$.

a) If $\psi \in I_{\partial\lambda}$ and $\xi(\psi,V) = E(\lambda,V)$ then ψ satisfies (in distributional sense) the equation

$$[-C_W\Delta + (\psi^2)^{2/3} - \phi]\ \psi(x) = -\ \phi_o\psi(x), \tag{4.13}$$

for some ϕ_o with $\phi(x) \equiv V(x) - \int \psi(y)^2\ |x-y|^{-1}dy$. Moreover $\phi_o = -\frac{dE}{d\lambda}$ and thus $\phi_o \geq 0$ (because of Theorem 4.2).

b) If $\psi \in H^1$ is any function (not necessarily minimizing) satisfying (4.13) in distributional sense for any ϕ_o then

$$\xi(\psi,V) \leq \underline{\lim}\ \xi(\psi_n,V)$$

Moreover, if $\xi(\psi,V) = \lim \xi(\psi_n,V)$ then each term in $\xi(\psi_n,V)$ converges to the corresponding term in $\xi(\psi,V)$.

Proof: Positive definite quadratic forms are always non-increasing under weak limits [43] therefore

$$\underline{\lim} \int (\nabla\psi_n)^2 \geq \int (\nabla\psi)^2$$

$$\underline{\lim} \int \psi_n(x)^2\ |x-y|^{-1}\ \psi_n(y)^2 dxdy \geq$$

$$\int (x)^2\ |x-y|^{-1}\psi(y)^2\ dx\ dy.$$

That $\lim \int \psi_n^2 V = \int \psi^2 V$ is proved in ([33], Theorem 2.1). That $\underline{\lim} \int \rho_n^{5/3} \geq \int \rho^{5/3}$ is easy (see [32], Theorem II.13 or Chapter 2). |_|

Theorem 4.7 (existence of a unique solution in I_λ): Let $V \varepsilon L^{5/2} + L^P$, with $5/2<p<\infty$. Then for all λ there is a unique $\psi \varepsilon I_\lambda$ with $\xi(\psi,V) = E(\lambda,V)$.

Proof: Pick a minimizing sequence $\psi_n \varepsilon I_\lambda$ so that $\xi(\psi_n,V) \to E(\lambda,V)$. By Theorem 4.1 (iv) $||\nabla\psi_n||_2 < \infty$. Since $||\psi_n||_2 \leq \lambda$ we then have $||\psi_n||_{H^1} < \infty$. Thus by the Banach-Alaoglu theorem [38], there is a subsequence

ψ_{n_i} such that $\psi_{n_i} \to \psi_\infty$ in weak H^1. We need only check $||\psi_\infty||_2^2 \leq \lambda$. This follows since $\underline{\lim} \int \psi_n^2 \geq \int \psi_\infty^2$. Therefore by Theorem 4.6 and Corollary 4.4, there is a unique $\psi \in I_\lambda$ with $\xi(\psi, V) = E(\lambda, V)$. $\square$

4.3. Connection with the TFW equation.

In this section we study the Euler equation associated with the TFW variational principle. First we show that the minimizing ψ for $\xi(\cdot, V)$ on $I_{\partial\lambda}$ is a weak solution of the TFW equation (4.13) and then we use elliptic regularity to prove that in fact ψ is a strong solution. This is a standard procedure in the study of variational problems.

Theorem 4.8: Let $V \in L^{5/2} + L^p$ for $p \in (\frac{5}{2}, \infty)$.

a) If $\psi \in I_{\partial\lambda}$ and $\xi(\psi, V) = E(\lambda, V)$ then ψ satisfies (in distributional sense) the equation

$$[-C_W \Delta + (\psi^2)^{2/3} - \phi]\, \psi(x) = -\, \phi_o \psi(x), \tag{4.13}$$

for some ϕ_o with $\phi(x) \equiv V(x) - \int \psi(y)^2 \, |x-y|^{-1} dy$. Moreover $\phi_o = -\frac{dE}{d\lambda}$ and thus $\phi_o \geq 0$ (because of Theorem 4.2).

b) If $\psi \in H^1$ is any function (not necessarily minimizing) satisfying (4.13) in distributional sense for any ϕ_o then

(i) $\psi \in C^{o}(R^3)$,

(ii) $\chi_\psi \psi \in L^{5/3}$, where $\chi_\psi \equiv (\phi - (\psi^2)^{2/3})$.

Proof: The proof of a) is standard. Simply replace ψ by $\psi + \alpha g$ $g \in \mathcal{S}$ (Schwarz space) and compute the derivative of ξ $(\psi + \alpha g)$ at $\alpha=0$. That $\phi_o = -\frac{dE}{d\lambda}$ follows easily using the convexity of $\xi(\psi,V)$ in $\rho=\psi^2$ (see for example [32], Theorem II.10). To prove b) (i) note that since $\psi \in L^6$, $\psi \in L^p_{loc}$ for any $1 \le p \le 6$ and therefore $(\psi^2)^{2/3} \psi \in L^2_{loc}$. Since $\phi \in L^{5/2} + L^\infty$, $\phi \psi \in L^2_{loc}$. Then, if ψ obeys (4.13), $-\Delta\psi \in L^2(\Omega)$ for any bounded subset of R^3. Therefore ψ belongs to the Sobolev space $W^{2,2}(\Omega)$. By the Sobolev's imbedding theorem $\psi \in C^{o}(\Omega)$ (if Ω is sufficiently regular) and hence $\psi \in C^{o}(R^3)$. (b) (ii): Since $\psi \in H^1$, $\psi \in L^2 \cap L^6$ and thus $\psi^2 \in L^1 \cap L^3$. By Young's inequality $\int dy\ \psi(y)^2\ |x-y|^{-1} \in L^{5/2} + L^{10}$. Therefore $\phi \in L^{5/2} + L^{10}$ and thus $\phi\psi \in L^{5/3}$ by Hölder's inequality. Also $(\psi^2)^{2/3}\psi \in L^{5/3}$ because $\psi \in L^2 \cap L^6$. $\square$

To prove that ψ is in fact a strong solution of equation (4.13) we restrict to V's of the form (4.4).

Theorem 4.9: Let V be of the form (4.4) and let $\psi \in H^1$ be any function (not necessarily minimizing) satisfying (4.13) in distributional sense for $\phi_o > 0$. Then $\psi \in C^\infty$ away from the R_i's and goes to zero at infinity and hence ψ is a strong solution of (4.13).

<u>Proof</u>: The proof that $\psi\epsilon C^\infty$ is a standard bootstrap argument (see [39], section lX.6 for example). Here, we follow Lieb ([29], Theorem 8). If $\phi_o>0$, let $Y = (4\pi|x|)^{-1} \exp(-(\phi_o/C_W)^{\frac{1}{2}}|x|)$ be the kernel for $(-\Delta + (\phi_o/C_W))^{-1}$. $Y\epsilon L^p$ for $1\leq p<3$. We write $\psi = (C_W)^{-1} (\chi_\psi\psi)*Y$, where χ_ψ is defined as in the previous theorem. Since $Y\epsilon L^{5/2}$ and $\chi_\psi\psi\epsilon L^{5/3}$ (by the Theorem 4.8 b(ii)), ψ is bounded and goes to zero at infinity [41]. Now, fix $x_o\epsilon R^3\setminus\{R_i,i=1,\dots,k\}$ and let $f\epsilon C_o^\infty$ be a function which is 1 near x_o. Let $\psi_1 \equiv f\psi$ and $\psi_2 = \psi-\psi_1$. Moreover let $\psi = \psi_a + \psi_b$ where $\psi_a = C_W^{-1} (\chi_\psi\psi_2)*Y$. Since ψ_2 vanishes near x_o, ψ_a is C^∞ near x_o. Assuming that $\psi\epsilon C^k$ $(k\geq 0)$ a neighborhood of x_o we shall prove $\psi\epsilon C^{k+1}$ near x_o. Let $\rho=\rho_1+\rho_2$ with $\rho_1={\psi_1}^2$ and $\rho_2 = (\psi_2)^2 + 2\psi_1 \psi_2$. Since ρ_2 is zero near x_o, $|x|^{-1}*\rho_2$ is harmonic and hence C^∞ near x_o. Since ρ_1 has compact support it is in all L^p and ρ_1 is C^k near x_o. Then $|x|^{-1}*\rho$ is C^k near x_o. Hence χ_ψ is C^k near x_o (recall x_o is away from the R_i's), and therefore $\chi_\psi\psi_1$ is C^k near x_o and has compact support. Hence $\psi_b = (C_W)^{-1} (\chi_\psi\psi_1)*Y$ is C^{k+1} near x_o. |_|

To conclude this section we prove a property of the minimizing ψ which will be useful in the sequel.

Theorem 4.10: Let V be of the form (4.4) and consider $\psi \varepsilon H^1$ such that ψ has compact support and $\int \psi^2 dx = \lambda < z \equiv \sum_{i-1}^{k} z_i$. Then

$$\xi(\psi,V) > \inf \{\xi(\psi,V),\ \psi \varepsilon I\} .$$

Proof: Pick $\tilde{\psi} = \psi + \tilde{\Delta}_n$, $\tilde{\Delta}_n$ defined as in Theorem 4.2. We have

$$\int (\nabla\tilde{\psi})^2 = \int (\nabla\psi)^2 + a'\, n^{-2/3}$$

$$\int (\tilde{\psi}^2)^{5/3} = \int (\psi^2)^{5/3} + b'\, n^{-2/3} ,$$

where a', b' are some positive constants. Also

$$-\int V\tilde{\psi}^2 + \frac{1}{2} \int \tilde{\psi}^2 \,(\tilde{\psi}^2 * |x|^{-1}) = - \int V\psi^2 + \frac{1}{2} \int \psi^2 (\psi^2 * |x|^{-1}) + P$$

with

$$P = - \frac{1}{2} \int \tilde{\Delta}_n^2 \,(V - \psi^2 * |x|^{-1} - \tilde{\Delta}_n^2 * |x|^{-1}) -$$
$$\frac{1}{2} \int \tilde{\Delta}_n^2 \quad (V - \psi^2 * |x|^{-1}) .$$

Since Δ_n is spherically symmetric $\int f\Delta_n^2 = \int [f]\Delta_n^2$ for any function f, where

$$[f](r) \equiv (4\pi)^{-1} \int_{S_2} f(r\Omega)\ d\Omega$$

is the spherical average of f. Since $\int\psi^2 = \lambda$ and $\int\Delta_n^2 = z-\lambda$ we have ([32], Theorem II.17) $[V - \psi^2 * |x|^{-1}] \geq (z-\lambda)/r$ and $[V - \psi^2 * |x|^{-1} - \tilde{\Delta}_n^2 * |x|^{-1}] \geq 0$. Therefore

$$P \leq -\frac{1}{2}\int (z-\lambda) r^{-1} \Delta_n^2 = -d\, n^{-1/3} ,$$

with d a positive constant. Hence

$$\xi(\tilde{\psi},V) \leq \xi(\psi,V) + (a+b) n^{-2/3} - d' n^{-1/3} .$$

Taking n large enough we get $\xi(\tilde{\psi},V) < \xi(\psi,V)$. |_|

Remark: Theorem 4.10 also applies to TF theory. However, it does not hold in the TFD theory because of the $\int\rho$ term of the energy functional (3.5).

4.4. The one-center case: TFW atom.

In this section we restrict ourselves to V of the form $V(x) = z|x|^{-1}$, $z>0$. For this particular V we are able to determine the existence of a minimizing solution in $I_{\partial\lambda}$ for $\lambda<z$ (see Theorem 4.13 below). We think this should also hold for V's of the form (4.4) although we are unable to prove it. Additional properties of the minimizing ψ are established. In particular we prove that the minimizing ψ for $\xi(\cdot,V)$ in $I_{\partial\lambda}$ is a symmetric

decreasing function of $|x|$, for $\lambda \leq z$. It will be necessary to use some inequalities about the symmetric decreasing rearrangement of a function, and we therefore review some of the main facts.

Let $S = \{f:R^3 \to [0,\infty) | f(x) \leq f(y)$ if $|x| \geq |y|\}$ be the symmetric decreasing functions. If χ is the characteristic function of a measurable set in R^3, we define χ^* by

$$\chi^*(x) = 1 \quad \text{if } 4\pi|x|^3/3 \leq ||\chi||_1,$$

$$\chi^*(x) = 0 \quad \text{otherwise.}$$

We see that $\chi^* \varepsilon S$ and $||\chi^*||_1 = ||\chi||_1$. Given $f:R^3 \to [0,\infty)$, let $\chi_a^f(x) = 1$ if $f(x) \geq a$, $\chi_a^f(x) = 0$ otherwise. Then

$$f(x) = \int_0^\infty \chi_a^f(x)\,da. \quad \text{Define}$$

$$f^*(x) \equiv \int_0^\infty \chi_a^{f^*}(x)\;da.$$

Clearly $f^* \varepsilon S$ and for all a, $\mu\{x|f^*(x) \geq a\} = \mu\{x|f(x) \geq a\}$, where μ is Lebesgue measure. Then for all $p \geq 1$

$$||f^*||_p = ||f||_p \tag{4.14}$$

The following two inequalities about symmetric decreasing rearrangements will be needed:

(i) If $f,g: R^3 \longrightarrow [0,\infty)$

$$\int fg\, dx \leq \int f^* g^* dx, \tag{4.15}$$

(ii) If $f \varepsilon H^1$, then $f^* \varepsilon H^1$ and

$$||\nabla f||_2 \geq ||\nabla f^*||_2 \quad . \tag{4.16}$$

<u>Remark</u>: a simple proof of this last inequality is given in ([29], Lemma 5).

The following theorem is due to E. H. Lieb (unpublished):

<u>Theorem 4.11</u>: Let $V(x) = z|x|^{-1}$ and $\rho \;\varepsilon\; L^1 \cap L^{5/3}$. If $\int \rho \leq z$ then

$$-\int V\rho + \frac{1}{2}\int \rho(\rho * |x|^{-1}) \geq -\int V\rho^* + \frac{1}{2}\int \rho^* (\rho^* * |x|^{-1}).$$

<u>Proof</u>: We write,

$$-\int V\rho + \frac{1}{2}\int \rho(\rho * |x|^{-1}) = -\int V\rho^* + \int V(\rho^* - \rho) + \int \rho(|x|^{-1} * \rho^*)$$

$$-\frac{1}{2}\int \rho^* (|x|^{-1} * \rho^*) + \frac{1}{2}\int (\rho - \rho^*) [|x|^{-1} * (\rho - \rho^*)] \geq$$

$$\geq -\int V\rho^* + \frac{1}{2}\int \rho^* (|x|^{-1} * \rho^*) + \int \phi(\rho^* - \rho), \tag{4.17}$$

where $\phi \equiv V - (|x|^{-1} * \rho^*)$. The last inequality in (4.17) follows because $|x|^{-1}$ is a positive definite kernel. Note that ϕ is a function of $|x|$ only and

$$\phi(r) = zr^{-1} - r^{-1}\int_o^r 4\pi s^2\rho^*(s)ds - \int_r^\infty 4\pi s\rho^*(s)ds.$$

Thus

$$\frac{\partial\phi}{\partial r} = \frac{1}{r^2}(-z + \int_o^r 4\pi s^2\rho^*(s)ds) \leq (\lambda-z)r^{-2} \leq 0.$$

Hence $\phi=\phi^*$ and the theorem follows from (4.15) and (4.17). |_|

<u>Corollary 4.12</u>: Let $V = z|x|^{-1}$ and let ψ be the minimizing ψ for $\xi(\cdot,V)$ in I_λ with $\lambda \leq z$. Then $\psi \varepsilon S$, i.e. ψ is a symmetric decreasing function of $|x|$.

<u>Proof</u>: For every $\psi \varepsilon I_\lambda$ $(\lambda \leq z)$ we have $\xi(\psi^*,V) \leq \xi(\psi,V)$ because of (4.14), (4.16) and Theorem 4.11. |_|

We now study the existence of a minimizing solution in $I_{\partial\lambda}$:

<u>Theorem 4.13</u>: Let $V = z|x|^{-1}$. Then for $\lambda \leq z$ the minimizing ψ for $\xi(\cdot,V)$ on I_λ has $\int\psi^2 dx = \lambda$.

<u>Proof</u>: Suppose that the minimizing ψ has $\int\psi^2 dx = \lambda_o < \lambda$. Then by Corollary 4.5 ψ minimizes $\xi(\cdot,V)$ on all of I, so by Theorem 4.8 the corresponding ϕ_o is 0. Thus ψ obeys

$$- C_W \Delta\psi + (\psi^2)^{2/3}\psi - \phi\psi = 0 \ , \tag{4.18}$$

where

$$\phi = z|x|^{-1} - ((\psi^2) * |x|^{-1}). \tag{4.19}$$

Since $\lambda_o < z$, $\phi \geq 0$ and thus (since $\psi \geq 0$)

$$-C_W\Delta\psi + (\psi^2)^{2/3}\psi \geq 0. \tag{4.20a}$$

Let $q = r^{-3/2}$ so that for $r>0$

$$\Delta q = 3q^{7/3}/4. \tag{4.20b}$$

By theorems 4.10 and 4.12, ψ is strictly positive. Let us fix $R>0$. We will show

$$\psi - cq \geq 0 \quad \text{for } r>R, \tag{4.21}$$

where $0<c<\min\ (R^{3/2}\psi(R),\ (3C_W/4)^{3/4})$. Let $D = \{x|\ \psi - cq < 0\} \cap \{r>R\}$. Note that $\psi - cq$ is continuous for $r>R$ because $\psi \varepsilon C^o(R^3)$ (Theorem 4.8 bi)).

Therefore D is open. On D,

$$-C_W\ \Delta\ (\psi - cq) \geq cq^{7/3}\ (\frac{3C_W}{4} - c^{4/3}) \quad\quad 0,$$

i.e. ψ-cq is superharmonic on D and ψ-cq ≥ 0 on $\partial D \cup \{\infty\}$. Hence by the maximum modulus principle it follows that D is empty and $\psi \geq$ cq for r>R. This in turn implies

$$\int \psi^2 dx \geq 4\pi c^2 \int_R^\infty \frac{dr}{r} = \infty$$

which contradicts $\int \psi^2 dx = \lambda_o < z$. |_|

Remark: The only fact that is missing in order to prove this theorem for a general V of the form (4.4) is that ϕ is not necessarily non-negative for those V. However, much less is required to prove this theorem. It is enough to have a bound of the form $\phi \geq -\frac{a}{r^2}$ for some positive constant a. We conjecture this bound is true as long as $\lambda \leq z$.

To conclude this section we give a remark about the chemical potential $-\phi_o$. It is clear from (4.2) that

$$E(\lambda,V) \geq \inf \{C_W \int (\nabla\psi)^2 dx - \int V\psi^2 dx \,|\, \psi \varepsilon I_{\partial\lambda}\} = -\lambda z^2/(4C_W). \quad (4.22)$$

(This is in fact the variational principle for the Hydrogen atom in Quantum Mechanics.) Now, consider the trial function $\psi_A(r) = (\lambda A^3/\pi)^{1/2} \exp(-Ar)$, A>0, so that $\int \psi_A^2 dx = \lambda$. Minimizing the energy with respect to A we get

$$\begin{aligned} E(\lambda,V) &\leq \min\{\xi(\psi_A,V)\,|\,A>0\} \\ &= -(\lambda/4C_W)\,(z - \tfrac{5\lambda}{16})^2 \,/\, (1 + C_o\lambda^{2/3}), \end{aligned} \quad (4.23)$$

which holds for $z \geq 5\lambda/16$. Here $C_o = (3/5)^4 \pi^{-2/3}$. Combining equations (4.22) and (4.23) we get

$$\lim_{\lambda \downarrow o} (E(\lambda,V)/\lambda) = - z^2/(4C_W)$$

i.e. $$\phi_o\ (\lambda=0) = z^2/(4C_W)\ ,$$

Since ϕ_o is decreasing in λ we have $\phi_o \in [0,z^2/(4C_W)]$.

4.5. Components of the Energy, Virial Theorem, Scaling and Pressure

To finish this chapter, we give a brief look at the components of the energy and their relations. Let us denote

$$E_W \equiv C_W \int (\nabla\psi)^2 dx \quad , \tag{4.24}$$

where ψ is the minimizing ψ in I_λ. K, A, R and U are defined as in TF theory (see Chapter 2). Let

$$e(\lambda,V) = E(\lambda,V) + \sum_{1 \leq i < j \leq k} z_i z_j |R_i - R_j|^{-1}. \tag{4.25}$$

First, we remark that e is continuous in the nuclear charges z_i and it has continuous derivatives with respect to the z_i. Moreover,

$$\sum_{i=1}^{k} z_i \frac{\partial e}{\partial z_i} = - A + 2U. \tag{4.26}$$

To prove this fact one proceeds as in the proof of the Feynman-Hellman theorem in TF theory (see [32], Theorem II.16). The same holds for the dependence of e on C_W; namely, e is continuous in C_W and it has continuous derivative. Moreover,

$$C_W \frac{\partial e}{\partial C_W} = E_W. \tag{4.27}$$

<u>Theorem 4.14</u> (<u>Virial theorem for TFW</u>): If $V = z|x|^{-1}$ and ψ minimizes $\xi(\cdot,V)$ on any I_λ then

$$2(E_W + K) = A-R. \tag{4.28}$$

<u>Proof</u>: Proceed as in the proof of the Virial Theorem in TF. Let $\psi_\mu(r) = \mu^{3/2}\psi(\mu r)$. Then $E(\mu) = \mu^2 (E_W + K) - \mu A + \mu R$. Because of the minimization property of ψ, $\left.\frac{\partial E}{\partial \mu}\right|_{\mu=1} = 0$ and therefore (4.28) follows. |_|

<u>Theorem 4.15</u>: Let ψ minimize $\xi(\cdot,V)$ on any I_λ. Then for V given by (4.4),

$$(5/3)K + E_W = A - 2R - \phi_o\lambda. \tag{4.29}$$

Proof: Either use the TFW equation (4.13) or directly the minimization property of ψ as in ([32], Theorem II.23). $\Box$

In particular, for the TFW atom (4.28) implies

$$e = -(K + E_W).$$

Scaling Properties: It is straight forward to check that for $\ell>0$, the minimizing ψ satisfies the following scaling relation,

$$\psi(\underline{z}, C_W, \lambda, \ell R_i; x) = \ell^3 \psi(\ell^3\underline{z}, \ell^2 C_W, \ell^3\lambda, R_i; \frac{x}{\ell}).$$

This in turn implies that under a uniform dilation $R_i \to \ell R_i$ ($\ell>0$) the energy e scales as follows:

$$e(\ell) \equiv e(\underline{z}, C_W, \lambda, \ell R_i) = \ell^{-7} e(\ell^3\underline{z}, \ell^2 C_W, \ell^3\lambda, R_i). \quad (4.30)$$

Pressure: It might be important for the discussion of binding within the TFW theory to have an expression for the pressure. (This was indeed the case in the TF theory. See [5], for example). The pressure corresponding to a uniform dilation is defined by [32,5],

$$P \equiv -\frac{1}{3\ell^2} \left.\frac{\partial e}{\partial \ell}\right|_{\ell=1}$$

Because of the scaling relation (4.30) we can write

$$\left.\frac{\partial e}{\partial \ell}\right|_{\ell=1} = -7e + 3\sum_{i=1}^{k} z_i \frac{\partial e}{\partial z_i} + 2C_W \frac{\partial e}{\partial C_W} + 3\lambda \frac{\partial e}{\partial \lambda} \qquad (4.31)$$

Equations (4.26) and (4.27) and the Theorem 4.8 imply

$$P = \frac{1}{3}(7e - 6U + 3A - 2E_W + 3\phi_o\lambda) \qquad (4.32)$$

Using the virial theorem 4.15 and equation (4.32) we get

$$P = \frac{1}{3}[e + (E_W + K)] \; . \qquad (4.33)$$

Remarks: (i) $P=0$ for an atom, as it should be!

(ii) If $C_W=0$, expression (4.33) reduces to the TF pressure $P = \frac{1}{3}(e + K)$.

CHAPTER 5: THE FIRSOV'S VARIATIONAL PRINCIPLE

It is a well known fact that convex variational principles have a dual variational problem associated with them. The dual P* of a minimization problem P is defined as a maximization problem having the same value, i.e. satisfying min(P) = max(P*). Moreover the function space over which P* is maximized is taken to be the dual of the function space over which P is minimized. There is a systematic procedure to construct a dual problem given the original problem. For a review see [40] and ([15], Chapter III). Dual problems are useful as a variational tool for finding lower bounds to the original minimization problem. These bounds, together with upper bounds provided by the minimization problem itself, allow us to get estimates on the value of min(P).

It is natural, therefore, to ask what is the dual of the TF variational principle. (We consider here only the TF variational principle without the constraint $\int\rho=\lambda$ so that when V is of the form (2.2) the minimum is attained for the neutral configuration). This dual problem was first introduced by Firsov [18] who was interested in computing estimates for the energy of a two-center molecule in TF. The Firsov's variational principle is defined by the functional

$$\mathcal{F}(f) \equiv -(8\pi)^{-1} \int (\nabla f)^2 dx - (2/5) \int (V-f)^{5/2} dx. \quad (5.1)$$

One is interested in sup $\mathcal{F}(f)$, where the sup is taken over all f such that $\int(\nabla f)^2 < \infty$, $\int(V-f)^{5/2}dx < \infty$ and $V-f \geq 0$. The coefficients $(8\pi)^{-1}$ and (2/5) are chosen in such a way that sup $-\mathcal{F}(f) = \inf \xi_{TF}(\rho)$. A heuristic derivation of the Firsov's principle starting from the original TF functional, using the systematic approach of [15], is given in the Appendix to this chapter.

After the first applications by Firsov himself [19], the Firsov's principle has been repeatedly used to compute estimates on the energies of molecules in TF and in particular on the two-body atomic potential. For a review of results in this direction we refer to the book by I. M. Torrens ([48], Chapter II). This principle can also be applied to compute the long range behavior of the two-body atomic potential. (For references to this, see [11]).

In section 5.1 we establish the connection between the Firsov's principle and the TF equation. The existence and uniqueness of solutions to the TF equation [32] will then imply the existence of a unique maximizing f for $\mathcal{F}(\cdot)$. In section 5.2 we study properties of this solution.

5.1. Existence and Uniqueness of a Solution.

Instead of considering the functional (5.1) with the constraint $V \geq f$, we will rather consider

$$\hat{\mathcal{F}}(f) \equiv -(8\pi)^{-1} \int (\nabla f)^2 dx - \frac{2}{5} \int [(V-f)^2]^{5/4} dx \qquad (5.2)$$

without that restriction. It will turn out that the maximizing f for $\hat{\mathcal{F}}(\cdot)$ satisfies $V \geq f$ and therefore it also maximizes (5.1). This also allows one to consider more general trial functions when estimating $\sup \mathcal{F}$.

Let $V(x) = \sum_{i=1}^{k} z_i |x-R_i|^{-1}$, $z_i > 0$. (More general V's can be considered by suitably changing the function space B, below).

Consider the function space

$$B = \{f \mid \nabla f \in L^2, f \in L^4\} .$$

B is a Banach space with respect to the norm

$$||f||_B \equiv ||\nabla f||_2 + ||f||_4.$$

Moreover B is reflexive. (The same proof of the reflexitity of the Sobolev spaces [1] can be applied to B).

We want to maximize $\hat{\mathcal{F}}(\cdot)$ over the set

$$I = \{f \mid f \in B, ||V-f||_{5/2} < \infty \} .$$

Let us first establish the connection between the variational principle and its Euler equation.

Theorem 5.1: If f maximizes $\hat{\mathcal{F}}$ on I then f satisfies (strongly) the Euler equation

$$-(4\pi)^{-1}\Delta f - [(V-f)^2]^{\frac{1}{4}}(V-f) = 0 \quad . \tag{5.3}$$

Proof: By replacing f by f + αh in (5.2), with h ε $\mathcal{S}$ (Schwartz space) and computing the derivative of $\hat{\mathcal{F}}$ (f + αh) at α=0 we prove that a maximizing solution for $\hat{\mathcal{F}}(\cdot)$ satisfies (in distributional sense) the equation (5.3). Since f ε L^4, f ε L^2_{loc}. Also $(V-f)^{3/2}$ ε L^2_{loc} and therefore Δf ε L^2_{loc}. By the Sobolev's imbedding theorem f ε $C^o(R^3)$. Adding and substracting a constant times f in (5.3) we can write

$$f = Y_e * [(V-f)^{3/2} + ef] \ , \tag{5.4}$$

where $Y_e = |x|^{-1}\exp(-(4\pi e)^{\frac{1}{2}}|x|)$ is the kernel for $(-(4\pi)^{-1}\Delta + e)^{-1}$. Since V-f ε $L^{5/2}$, $(V-f)^{3/2}$ ε $L^{5/3}$ and, because Y_e ε $L^{5/2}$, we have that $Y_e * (V-f)^{3/2}$ is continuous and goes to zero at infinity [41]. By the same reason, since f ε L^4 and Y_e ε $L^{4/3}$ f is continuous and goes to zero at infinity. Moreover, by exactly the same analysis of ([32], Theorem IV.5) f is C^∞ away from the R_i's. (See also Theorem 4.9 of this thesis). Hence f is a strong solution to (5.3). $\Box$

Theorem 5.2: There is a unique maximizing solution for $\hat{\mathcal{F}}(\cdot)$ on I.

Proof: Uniqueness follows immediately from the strong concavity of $\hat{\mathcal{F}}$. As for the existence, set $\phi = V-f$. Because of (5.3) ϕ satisfies the TF equation

$$-(4\pi)^{-1} \Delta\phi + \phi^{3/2} = \sum_{i=1}^{k} z_i \ \delta(x-R_i)$$

which has a unique solution ([32], Theorem II.20). Then Theorem 5.2 follows from Theorem 5.1. $\Box$

5.2. Properties of the maximizing solution.

We now check that in fact $0 \leq f \leq V$ and, therefore, the maximizing solution for $\hat{\mathcal{F}}(\cdot)$ also maximizes the Firsov's principle.

Theorem 5.3: The maximizing f for $\hat{\mathcal{F}}(\cdot)$ satisfies:

$$0 \leq f \leq V.$$

Proof: (i) $f \leq V$: Let $g = V-f$. Since $f \in C^0(R^3)$, g is continuous away from the R_i's. Let $S = \{x | g(x) < 0\}$. S is disjoint from the R_i and since g is continuous, S is open. Moreover, $g=0$ on $\partial S \cup \{\infty\}$. On S, $-\Delta g \geq 0$, i.e. g is superharmonic on S. By the maximum modulus principle S is therefore empty and $V \geq f$ everywhere. (ii) $0 \leq f$: As in Chapter 4 (below equation 4.4) $\int(\nabla|f|)^2 \leq \int(\nabla f)^2$. Also $\int(V-|f|)^{5/2} \leq \int(V-f)^{5/2}$. |_|

Finally, an easy computation shows that the TF and Firsov's principles have the same value, i.e.

$$\inf_\rho \xi_{TF}(\rho,V) = \sup_f -\mathcal{F}(f).$$

APPENDIX

We derive here the Firsov's principle from the TF functional by using the approach of Temam and Ekeland [15]. This derivation is heuristic and applies not only to the neutral case but to the subneutral case as well.

Consider the following family of perturbed variational problems:

$$\xi(\rho,p) = \frac{3}{5}\int \rho^{5/3}dx - \int V\rho dx + \frac{1}{2}\int (\rho+p)(x)\ |x-y|^{-1}\ (\rho+p)(y)\,dxdy$$

in such a way that

$$\xi(\rho,p=0) = \xi_{TF}(\rho).$$

Consider the Legendre transform to $\xi(\rho,p)$, namely

$$\xi^*(\rho^*,p^*) = \sup_{\rho,p}\ [\int \rho\rho^* dx + \int pp^* dx - \xi(\rho,p)]\ .^1 \qquad (5.5)$$

Then the dual variational problem (Firsov's principle) is defined by the functional

$$\xi^*_{\text{Firsov}}\ (p^*) \equiv -\ \xi^*(0,p^*)\ . \qquad (5.6)$$

[1] The supremum on ρ is taken only over the set $\{\rho|\rho\geq 0,\ \int\rho=\lambda\}$.

From (5.5) and (5.6) we get,

$$-\xi^*_{\text{Firsov}}(p^*) = \sup_{\rho \geq 0, \int\rho=\lambda} [- \tfrac{3}{5}\int\rho^{5/3} + \int V\rho - \tfrac{1}{2}\int\rho(x)|x-y|^{-1}\rho(y)$$

$$+ I(\rho)] , \tag{5.7}$$

where

$$I(\rho) = \sup_{p} [\int p p^* - \int\rho(x) \ |x-y|^{-1}p(x) - \tfrac{1}{2}\int p(x) \ |x-y|^{-1}p(y)].$$

The supremum of this last expression is attained for p satisfying

$$p^*(x) - \int[\rho(y) + p(y)] \ |x-y|^{-1}dy = 0$$

or equivalently

$$-(4\pi)^{-1} \ \Delta p^* = (\rho + p),$$

and the value of $I(\rho)$ is

$$I(\rho) = \frac{1}{8\pi} \int(\nabla p^*)^2 dx - \int\rho p^* dx + \frac{1}{2} \int\rho(y)|x-y|^{-1}\rho(x)dxdy.$$

Replacing this back into eq. (5.7) we get,

$$-\xi^*_{\text{Firsov}} \ (\rho) = \sup_{\rho \geq 0, \int\rho=\lambda} [- \tfrac{3}{5}\int\rho^{5/3} + \frac{1}{8\pi} \int(\nabla p^*)^2$$

$$\int(V-p^*)\rho] \ .$$

The supremum here is attained for ρ satisfying

$$+\ \rho^{2/3} = (V-p^*-\mu)_+ \quad ,$$

where $(x)_+ = x$ if $x \geq 0$ and $(x)_+ = 0$ if $x<0$.

Finally, the expression for $\xi^*_{Firsov}\ (p^*)$ is

$$-\xi^*_{Firsov}\ (p^*) = \frac{1}{8\pi} \int (\nabla p^*)^2 + \frac{2}{5} \int (V-p^*-\mu)_+^{5/2} + \mu\lambda \quad (5.8)$$

<u>Remarks</u>: (i) For the general model defined by (2.1) the Firsov's functional should read

$$-\xi^*_{Firsov}(p^*) = \frac{1}{8\pi} \int (\nabla p^*)^2 + \int f^*((V-p^*-\mu)_+) + \mu\lambda,$$

where f^* is the Legendre transform of f.

(ii) It remains as an open problem to study the variational principle

$$\sup \xi^*_{Firsov}\ (p^*)$$

for the case $\mu \neq 0$. (The case $\mu=0$ was studied in this chapter), and its connection with the original problem. In particular one should prove

$$\inf_{p} \ \xi_{TF}(\rho) = \sup_{p^*} \ \xi^*_{Firsov}(p^*) \quad .$$

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TO: Physics Department Faculty May 3, 1979

FROM: Val L. Fitch

The final public oral examination of Rafael Benguria will take place on Wednesday, May 9, 1979 at 9:00 a.m. in Room 202 (Chairman's Conference Room). The examination committee will consist of Professors Simon, Treiman, Aizenman and Bennett . Any other member of the University wishing to attend the examination may do so.