Thomas-fermi and related theories of atoms and molecules*

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This article is a summary of what is know rigorously about Thomas-Fermi (TF) theory with and without the Dirac and von Weizsäcker corrections. It is also shown that TF theory agrees asymptotically, in a certain sense, with nonrelativistic quantum theory as the nuclear charge z tends to infinity. The von Weizsäcker correction is shown to correct certain undesirable features of TF theory and to yield a theory in much better agreement with what is believed (but as yet unproved) to be the structure of real atoms. Many open problems in the theory are presented.

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I. INTRODUCTION

In recent years some of the properties of the Thomas-Fermi (TF) and related theories for the ground states of nonrelativistic atoms and molecules with fixed nuclei have been established in a mathematically rigorous way. The aim of these notes is to summarize that work to date—at least as far as the author's knowledge of the subject goes. In addition, some open problems in the subject will be stated.

TF theory was invented independently by Thomas (1927) and Fermi (1927). The exchange correction was introduced by Dirac (1930), and the gradient correction to the kinetic energy by von Weizsäcker (1935).

No attempt will be made to summarize the voluminous subject of TF theory. Such a summary would have to include many varied applications, many formulations of related theories (e.g., relativistic corrections to TF theory, nonzero temperature TF theory) and reams of data and computations. Some reviews exist (March, 1957; Gombás, 1949; Torrens, 1972), but they are either not complete or not up to date.

We shall concentrate on nonrelativistic TF and related theories for the ground state with the following goals in mind:

(1) The definition of TF and related theories (i.e., the von Weizsäcker and Dirac corrections). The main question here is whether the theories are well defined mathematically and whether the equations to which they give rise have (unique) solutions.

(2) Properties of TF and related theories. It turns out that, unlike the correct Schrödinger, quantum (Q) theory, the TF and related theories have many interesting physical properties that can be deduced without computation. Some of these properties are physically realistic and some are not, e.g., Teller's no-binding theorem. As will be seen, however, the no-binding result is natural and correct if TF theory is placed in its correct physical context as a large-Z (=nuclear-charge) theory.

(3) The relation of TF theory to Q theory. The main result will be that TF theory is exact in the large-Z (nuclear-charge) limit. For this reason, TF theory should be taken seriously as one of the cornerstones of atomic physics. The only other regime in which it is possible to make simple, exact statements is the one-electron hydrogenic atom. The natural open question is to find the leading correction, in Z, beyond TF theory. This will lead to a discussion of the Scott correction

(Scott, 1952) which, while it is very plausible, has not yet been proved. It turns out that Thomas–Fermi–von Weizsäcker (TFW) theory has precisely the properties that Scott predicts for Q theory. Moreover, TFW theory remedies some defects of TF theory: It displays atomic binding, it gives exponential falloff of the density at large distances, it yields a finite density at the nucleus, and negative ions are stable (i.e., bound).

The work reported here originated in articles by Lieb and Simon, 1973 and 1977 (hereafter LS). Subsequently, the ideas were developed by, and in collaboration with, Benguria and Brezis. I am deeply indebted to these coworkers.

Since many unsolved problems remain, these notes are more in the nature of a progress report than a textbook. The proofs of many theorems are sketchy, or even absent, but it is hoped that the interested reader can fill in the details with the help of the references. Unless clearly stated otherwise, however, everything presented here is meant to be rigorous.

II. THOMAS-FERMI THEORY

The theories will be stated in this section purely as mathematical problems. Their physical motivation from Q theory will be explained in Sec. V. In order to present the basic ideas as clearly as possible, only TF theory will be treated in this section; the variants will be treated in Secs. VI, VII and VIII. However, the basic definitions of all the theories will be given in Sec. II.A, and there will be some mention of Thomas-Fermi-Dirac (TFD) theory in Sec. II.B and Sec. III.

A. The definitions of Thomas-Fermi and related theories

All the theories we shall be concerned with start with some *energy functional* $\mathcal{E}(\rho)$, where ρ is a non-negative function on three-space, $\mathbb{R}^3$. ρ is called a *density* and physically is supposed to be the electron density in an atom or molecule.

The functionals will involve the following function V and constant U:

$$V(x)=\sum_{j=1}^{k} z_j|x-R_j|^{-1}, \tag{2.1}$$

$$U=\sum_{1\le i<j\le k} z_i z_j|R_i-R_j|^{-1}. \tag{2.2}$$

$V(x)$ is the electrostatic potential of k nuclei of charges (in units in which the electron charge $e=-1$) $z_1,\ldots z_k>0$, and located at $R_1,\ldots,R_k\in\mathbb{R}^3$. The R_i are distinct. The positivity of the z_i is important for many of the theorems; while TF theory makes mathematical sense when some $z_i<0$, it has not been investigated very much in that case. U is the repulsive electrostatic energy of the nuclei.

TF-type theories can, of course, be defined for potentials that are not Coulombic, but many of the interesting properties presented here rely on potential theory and hence will not hold for non-Coulombic potentials. This is discussed in Sec. III. There is, however, one generalization of Eqs. (2.1) and (2.2) that can be made without spoiling the theory, namely, that the nuclei can be "smeared out," i.e., the following replacements can be made:

$$z_j|x-R_j|^{-1}\to\int dm_j(y)|x-R_j+y|^{-1}, \tag{2.3}$$

$$z_i z_j|R_i-R_j|^{-1}\to\int dm_i(y)dm_j(w)|y-w-R_i+R_j|^{-1}, \tag{2.4}$$

where m_i is a positive measure (not necessarily spherically symmetric) of mass z_i.

The functional for TF theory is

$$\mathcal{E}(\rho)=\tfrac{3}{5}\gamma\int\rho(x)^{5/3}dx-\int\rho(x)V(x)dx+D(\rho,\rho)+U, \tag{2.5}$$

where

$$D(g,f)=\tfrac{1}{2}\int\int g(x)f(y)|x-y|^{-1}dx\,dy.$$

All integrals are three dimensional.

γ is an arbitrary positive constant, but to establish contact with Q theory we must choose

$$\gamma_p=(6\pi^2)^{2/3}\hbar^2(2mq^{2/3})^{-1}, \tag{2.6}$$

where $\hbar=h/2\pi$, $h=$ Planck's constant, and m is the electron mass. q is the number of spin states ($=2$ for electrons).

U appears in $\mathcal{E}$ as a constant, ρ-independent term. It is unimportant for the problem of minimizing $\mathcal{E}$ with respect to ρ. Nevertheless U will be very important when we consider how the minimum depends on the R_i, e.g., in the no-binding theorem (Sec. III.C).

For the Thomas-Fermi-Dirac (TFD) theory

$$\mathcal{E}^{\mathrm{TFD}}(\rho)=\mathcal{E}(\rho)-\tfrac{3}{4}C_e\int\rho(x)^{4/3}dx, \tag{2.7}$$

with C_e a positive constant. In the original theory (Dirac, 1930), the value $C_e=(6/\pi q)^{1/3}$ was used for reasons which will be explained in Sec. VI. This value is not sacrosanct, however, and it is best to leave C_e as an adjustable constant.

The Thomas–Fermi–von Weizsäcker theory (TFW) is given by (von Weizsäcker, 1935)

$$\mathcal{E}^{\mathrm{TFW}}(\rho)=\mathcal{E}(\rho)+\delta\int[(\nabla\rho^{1/2})(x)]^2dx, \tag{2.8}$$

with $\delta=A\hbar^2/2m$, and A an adjustable constant. Originally, A was taken to be unity, but in Sec. VII.D it will be seen that $A=0.186$ is optimum from one point of view.

The most complicated, and least analyzed, case is the combination of all three (Sec. VIII):

$$\mathcal{E}^{\mathrm{TFDW}}(\rho)=\mathcal{E}(\rho)-\tfrac{3}{4}C_e\int\rho(x)^{4/3}dx+\delta\int[(\nabla\rho^{1/2})(x)]^2dx. \tag{2.9}$$

The first question to face is the following.

B. Domain of definition of the energy functional

Since ρ is supposed to be the electron density we require $\rho(x)\ge 0$ and

$$\int\rho(x)dx=\lambda=\text{electron number} \tag{2.10}$$

is finite. In addition we require $\rho \in L^{5/3}$ in order that the first term in $\mathcal{E}(\rho)$ (called the kinetic energy term) be finite. λ is not necessarily an integer.

Definition. A function f is said to be in L^p if $[\int |f(x)|^p dx]^{1/p} \equiv \|f\|_p$ is finite, $1 \leq p < \infty$. $\|f\|_\infty \equiv \text{ess sup}|f(x)|$ (see Theorem 3.12).

If $f \in L^p \cap L^q$ with $p < q$ then $f \in L^t$ for all $p < t < q$. $\|f\|_t \leq \|f\|_p^{\lambda} \|f\|_q^{1-\lambda}$, where $\lambda p^{-1} + (1-\lambda)q^{-1} = t^{-1}$.

Proposition 2.1. *If $\rho \in L^{5/3} \cap L^1$ then all the terms in $\mathcal{E}$ and $\mathcal{E}^{\text{TFD}}$ are finite. If $\int \rho \leq \lambda$ then $\mathcal{E}(\rho)$ and $\mathcal{E}^{\text{TFD}}(\rho)$ are bounded below by some constant $C(\lambda)$. Furthermore, for all λ, $\mathcal{E}(\rho) > C > -\infty$ for some fixed C.*

Proof. The first part is an easy application of Young's and Hölder's inequalities. The second part requires a slightly more refined estimate of the Coulomb energies (cf. LS). ■

Remark. Although $\mathcal{E}^{\text{TFW}}$ will be seen to be also bounded below by a constant independent of λ, neither $\mathcal{E}^{\text{TFD}}$ nor $\mathcal{E}^{\text{TFDW}}$ is so bounded. This fact leads to an amusing unphysical consequence of the D theories which will be mentioned later.

A very important fact (which, incidentally, is not true for Hartree-Fock theory) is the following.

Proposition 2.2. *$\rho \to \mathcal{E}(\rho)$ is strictly convex, i.e., $\mathcal{E}(\lambda\rho_1 + (1-\lambda)\rho_2) < \lambda\mathcal{E}(\rho_1) + (1-\lambda)\mathcal{E}(\rho_2)$ for $0 < \lambda < 1$ and $\rho_1 \neq \rho_2$.*

Proof. ρ^p is strictly convex for $p > 1$. $\int V\rho$ is linear in ρ and hence convex. $D(\rho,\rho)$ is strictly convex since the Coulomb kernel $|x-y|^{-1}$ is positive definite. ■

Remark. $\mathcal{E}^{\text{TFW}}$ is also strictly convex, but the functionals $\mathcal{E}^{\text{TFD}}$ and $\mathcal{E}^{\text{TFDW}}$ are not convex because of the $-\int \rho^{4/3}$ term. However, $\mathcal{E}^{\text{TFD}}$ can be "convexified" in a manner to be described in Sec. VI.

C. Minimization of the energy functional

The central problem is to compute

$$E(\lambda) = \inf\left\{\mathcal{E}(\rho) \,\middle|\, \rho \in L^{5/3} \cap L^1, \int \rho = \lambda\right\} \tag{2.11}$$

and

$$e(\lambda) = E(\lambda) - U. \tag{2.12}$$

$E(\lambda)$ is the TF energy for a given electron number, λ, and $e(\lambda)$ is the *electronic contribution to the energy*. The "inf" in Eq. (2.11) is important because, as we shall see, the minimum is not always achieved, although the inf always exists by Prop. 2.1.

Theorem 2.3. *$e(\lambda)$ is convex, negative if $\lambda > 0$, nonincreasing and bounded below. Furthermore,*

$$E(\lambda) = \inf\left\{\mathcal{E}(\rho) \,\middle|\, \rho \in L^{5/3} \cap L^1, \int \rho \leq \lambda\right\}. \tag{2.13}$$

Proof. The first part follows from Prop. 2.2 together with the observation that $V(x) \to 0$ as $|x| \to \infty$. This means that if λ increases we can add some $\delta\rho$ arbitrarily far from the origin so that $\mathcal{E}(\rho + \delta\rho) - \mathcal{E}(\rho) < \varepsilon$ for any $\varepsilon > 0$. Equation (2.13) is a simple consequence of the monotonicity of $e(\lambda)$ and $E(\lambda)$. (cf. LS). ■

Equation (2.13) has an important advantage over (2.11), as Theorem 2.4 shows.

Theorem 2.4. *There exists a unique ρ that minimizes $\mathcal{E}(\rho)$ on the set $\int \rho \leq \lambda$.*

Note. Uniqueness means, of course, that ρ is determined only almost everywhere (a.e.).

Proof. (See LS.) Since $\mathcal{E}(\rho)$ is *strictly* convex, a minimum, if there is one, must be unique. Let $\rho^{(n)}$ be a minimizing sequence for $\mathcal{E}$, namely $\mathcal{E}(\rho^{(n)}) \to E(\lambda)$ and $\int \rho^{(n)} \leq \lambda$. It is easy to see that $\int (\rho^{(n)})^{5/3} \leq c$, where c is some constant; this in fact comes out of the simple estimates used in the proof of Prop. 2.1. We should like to extract a convergent subsequence from the given $\rho^{(n)}$. This cannot be done *a priori* in the strong topology, but the Banach-Alaoglu theorem tells us that a $L^{5/3}$ weakly convergent subsequence can be found; this will be denoted by $\rho^{(n)}$. We should like to prove

$$\liminf \mathcal{E}(\rho^{(n)}) \geq \mathcal{E}(\rho). \tag{2.14}$$

Since $\rho^{(n)} \to \rho$ weakly in $L^{5/3}$ we have (by the Hahn-Banach theorem, for example) that

$$\liminf \int [\rho^{(n)}]^{5/3} \geq \int \rho^{5/3}, \tag{2.15}$$

$$\liminf D(\rho^{(n)}, \rho^{(n)}) \geq D(\rho,\rho). \tag{2.16}$$

The term $-\int V\rho$ requires slightly more delicate treatment. Write $|x-R|^{-1} = f(x) + g(x)$, where $f(x) = |x-R|^{-1}$ for $|x-R| \leq 1$ and $f(x) = 0$ otherwise. $f \in L^{5/2}$ and $\int f\rho^{(n)} \to \int f\rho$ by weak convergence. On the other hand, $g \in L^{3+\varepsilon}$ for all $\varepsilon > 0$. $\rho^{(n)}$ is bounded in $L^{5/3}$ and in L^1 (by λ), so it is bounded in all L^q with $1 \leq q \leq \frac{5}{3}$ and therefore $\rho^{(n)} \to \rho$ weakly in L^q as well as in $L^{5/3}$. Fix $\infty > \varepsilon > 0$ and let q be dual to $3+\varepsilon$. Then $\int g\rho^{(n)} \to \int g\rho$. This proves Eq. (2.14) which, since $E(\lambda) = \liminf \mathcal{E}(\rho^{(n)})$ and $E(\lambda) \leq \mathcal{E}(\rho)$, implies that ρ is minimizing provided we can show $\int \rho \leq \lambda$. This follows from the fact that if $\int \rho > \lambda$ then there is a bounded set A such that $\int_A \rho > \lambda$. If α is the characteristic function of A then $\alpha \in L^{5/2}$ and $\lambda \geq \int \alpha\rho^{(n)} \to \int \alpha\rho$ by weak $L^{5/3}$ convergence. ■

Remark. The proof of Theorem 2.4 can be considerably shortened by using Mazur's (1933) theorem. $\rho \to \mathcal{E}(\rho)$ is obviously norm continuous and hence norm lower semicontinuous. Mazur's theorem says that the convexity of $\mathcal{E}(\rho)$ then automatically implies weak lower semicontinuity since norm closed convex sets are automatically weakly closed. The proof given above has the virtue of an explicit demonstration of the weak lower semicontinuity.

Remark. The analogous proof in TFD theory will be harder, since $\rho^{5/3} - \rho^{4/3}$ is not convex, monotone, or positive; hence we cannot say that

$$\liminf \int [\rho^{(n)}]^{5/3} - [\rho^{(n)}]^{4/3} \geq \int \rho^{5/3} - \rho^{4/3}.$$

However, in TFW theory a different strategy, using Fatou's lemma, will be employed to deal with these terms. The strategy also works for TFDW theory. Thus the introduction of the W term (2.8) makes part of the proof easier. It would be desirable to know how to

use Fatou's lemma (which does not require convexity) in the TF and TFD proofs.

Since $E(\lambda)$ is nonincreasing, bounded, and convex (and hence continuous) we can make the following definition in TF theory.

Definition. λ_c, *the critical* λ, is the largest λ with the property that for all $\lambda' < \lambda$, $E(\lambda') > E(\lambda)$. Equivalently, if $E(\infty) = \lim_{\lambda\to\infty} E(\lambda)$ then $\lambda_c = \inf\{\lambda \,|\, E(\lambda) = E(\infty)\}$. In principle λ_c could be $+\infty$, but this will not be the case. In TFD and TFDW theories $E(\lambda)$ is not bounded and the above definition has to be generalized. λ_c is the largest λ with the property that $2E(\lambda) < E(\lambda-\varepsilon) + E(\lambda+\varepsilon)$ for all $0 < \varepsilon < \lambda$. In other words, $E(\lambda) = E(\lambda_c) + (\text{const})(\lambda - \lambda_c)$ for $\lambda \geq \lambda_c$. The j model in TFD theory is bounded, so the first definition is applicable to that model. λ_c will be shown to be $Z = \sum z_j$ in TF and TFD theory, Theorem 3.18. In TFW theory, $\lambda_c > Z$ (Theorem 7.19).

Theorems 2.3, 2.4, and Proposition 2.2 yield the following picture of the minimization problem in TF theory.

Theorem 2.5. *For* $\lambda \leq \lambda_c$ *there exists a unique minimizing* ρ *with* $\int\rho = \lambda$. *On the set* $[0, \lambda_c]$, $E(\lambda)$ *is strictly convex and monotone decreasing. For* $\lambda > \lambda_c$ *there is no minimizing* ρ *with* $\int\rho = \lambda$, *and* $E(\lambda) = E(\lambda_c)$; *the minimizing* ρ *in Theorem 2.4 is the* ρ *for* λ_c.

Proof. For $\lambda \leq \lambda_c$ use the ρ given by Theorem 2.4 and note that if $\lambda' = \int\rho < \lambda$ then $E(\lambda') = \mathcal{E}(\rho) = E(\lambda)$. The strict convexity is trivial: if $\lambda = a\lambda_1 + (1-a)\lambda_2$ use $a\rho_1 + (1-a)\rho_2$ as a trial function for λ. On the other hand, for $\lambda > \lambda_c$ the ρ given by Theorem 2.4 will have $\int\rho = \lambda_c$ because if a minimum existed with $\int\rho = \lambda' > \lambda_c$ then $\tilde{\rho} \equiv (\rho + \rho_c)/2$ (with ρ_c being the ρ for λ_c) would satisfy $\lambda_c < \int\tilde{\rho} = \frac{1}{2}(\lambda' + \lambda_c) < \lambda'$ but, by strict convexity,

$$\mathcal{E}(\tilde{\rho}) < [\mathcal{E}(\rho) + \mathcal{E}(\rho_c)]/2 = E(\lambda_c),$$

which is a contradiction. ■

The general situation is shown in Fig. 1. There Z is shown as less than λ_c; while that is the case for TFW theory, in TF and TFD theory $\lambda_c = Z$. The straight portion to the right of λ_c is horizontal for TF and TFW, but has a negative slope for TFD and TFDW. The slope at the origin is infinite for TF and TFD but finite for TFW and TFDW.

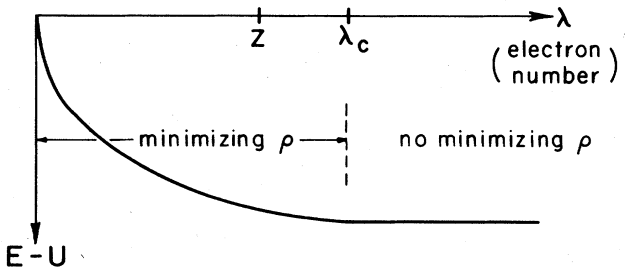

FIG. 1. "The electronic part" of the TF energy, $E-U$, is shown schematically as a function of the "electron number", $\lambda = \int\rho$. For $\lambda \leq \lambda_c$ there is a unique ρ that minimizes the TF energy $\mathcal{E}(\rho)$. For $\lambda > \lambda_c$ there is no such ρ. In TF theory $\lambda_c = Z = \sum_{j=1}^{k} z_j$ = total nuclear charge. $E-U$ is constant for $\lambda \geq \lambda_c$. These features are different for TF, TFD, and TFDW theories (see text).

D. The Thomas-Fermi equation and properties of the density

The variational derivative of $\mathcal{E}(\rho)$ is $\delta\mathcal{E}/\delta\rho = \gamma\rho^{2/3}(x) - \phi_\rho(x)$ where

$$\phi_\rho(x) = V(x) - \int \rho(y)\,|x-y|^{-1}dy\,. \tag{2.17}$$

A Lagrange multiplier μ should be added to $\delta\mathcal{E}/\delta\rho$ to insure that $\int\rho = \lambda$. It is then expected that $\delta\mathcal{E}/\delta\rho + \mu = 0$ if $\rho(x) > 0$, but $\delta\mathcal{E}/\delta\rho + \mu \geq 0$ if $\rho(x) = 0$ because negative variations of $\rho(x)$ are not allowed. The two situations can be written as

$$\gamma\rho^{2/3}(x) = \max[\,\phi_\rho(x) - \mu, 0] \equiv [\,\phi_\rho(x) - \mu\,]_+\,. \tag{2.18}$$

This is *the TF equation.* (Note that the $[\ ]_+$ is very important.) This formal manipulation is, indeed, correct.

Theorem 2.6. *If* ρ *minimizes* $\mathcal{E}(\rho)$ *with* $\int\rho = \lambda \leq \lambda_c$ *then* ρ *satisfies Eq. (2.18) for some (unique)* $\mu(\lambda)$. *Conversely if* ρ, μ *satisfy Eq. (2.18) and* $\rho \in L^1 \cap L^{5/3}$ *then* ρ *minimizes* $\mathcal{E}(\rho)$ *for* $\lambda = \int\rho$. *Hence (2.18) can have at most one solution* ρ, μ *with* $\int\rho = \lambda$. *If* $\lambda = \lambda_c$ *then* $\mu = 0$.

Proof. The first part is standard in the calculus of variations. Now let $\rho_i, \mu_i, i = 1, 2$, satisfy Eq. (2.18) with the same λ. Let $F_i(h) = (3\gamma/5)\int h^{5/3} - \int\phi_i h$. It is easy to check that $F_i(h)$ has a unique minimum, F_i, on the set $\int h = \lambda$, $h \geq 0$; the minimizing h_i is ρ_i. However, $F_1(\rho_2) + F_2(\rho_1) = F_1 + F_2 - D(\rho_1 - \rho_2, \rho_1 - \rho_2)$. This is a contradiction unless $\rho_1 = \rho_2$ (and hence $\mu_1 = \mu_2$). The last part (i.e., $\mu = 0$) follows by considering the absolute minimum of $\mathcal{E}(\rho)$, in which case no μ is necessary. But this is equivalent to setting $\mu = 0$. This minimum occurs for $\lambda \geq \lambda_c$ but as we have shown, only at λ_c is there a minimizing ρ (cf. LS). ■

Remarks. In Sec. III a proof of the uniqueness part of Theorem 2.6 which uses only potential theory will be given. It should be noted that we arrived at the existence of a solution to Eq. (2.18) by first considering the minimization problem. A direct attack on (2.18) is rather difficult. Such a direct approach was carried out by Hille (1969) in the atomic case, but even in that case he did not prove that the spherically symmetric solution is the only one; our uniqueness result guarantees that.

Theorem 2.7. $E(\lambda)$ *is continuously differentiable and* $dE/d\lambda = -\mu(\lambda)$ *if* $\lambda \leq \lambda_c$. $dE/d\lambda = 0$ *if* $\lambda \geq \lambda_c$. *Thus* $-\mu(\lambda)$ *is the* chemical potential.

Proof. The convexity and boundedness of $\mathcal{E}(\rho)$ is used. (See LS, Theorem II.10 and Lemma II.27.) ■

It will be noted that we have not used the fact that V is Coulombic, only that it vanishes at ∞. Likewise, the only property of the kernel $|x-y|^{-1}$ that was used was its positive definiteness. In Sec. III we shall exploit the fact that $|x-y|^{-1}$ is Coulombic and, to a lesser extent, the fact that V is superharmonic. Also, it will be shown that $\lambda_c = Z = \sum_1 z_j$.

Definition. A function $f(x)$ defined on an open set $\Omega \subset \mathbb{R}^3$ is *superharmonic on* Ω if, for almost all $x \in \Omega$ and for almost all spheres centered at x, but contained in Ω, $f(x) \geq$ (the average of f on the sphere), i.e., $f(x) \geq (4\pi)^{-1} \times \int_{|y|=R} f(x+y)dy$. This is the same as $\Delta f \leq 0$ (in the

sense of distributions) in Ω. f is *subharmonic* if $-f$ is superharmonic. f is *harmonic* if it is both subharmonic and superharmonic.

In Sec. III potential theory will shed considerable light on the solution to Eq. (2.18). Here we shall concentrate on some other aspects of (2.18).

Let us assume that $V(x)=\sum z_j|x-R_j|^{-1}$. ϕ denotes ϕ_ρ for the solution to Eq. (2.18). In Sec. III we show $\phi(x)>0$. As a distribution,

$$-\Delta\phi(x)/4\pi=\sum z_j\delta(x-R_j)-\rho(x)$$
$$=\sum z_j\delta(x-R_j)-\gamma^{-3/2}(\phi(x)-\mu)_+^{3/2}. \tag{2.19}$$

This is the TF *differential equation* and is *equivalent* to Eq. (2.18). It involves ϕ alone. Since $\rho\in L^{5/3}\cap L^1$, ϕ is continuous away from the R_j (Lemma 3.1) and goes to zero as $|x|\to\infty$. The fact that ϕ goes to zero at infinity is understood as a boundary condition in Eq. (2.19).

Theorem 2.8 (LS Theorem IV.5).

(*a*) *Near each* R_j

$$\rho(x)=(z_j/\gamma)^{3/2}|x-R_j|^{-3/2}+O(|x-R_j|^{-1/2})$$

(*b*) $\rho(x)\to 0$ *as* $|x|\to\infty$.

(*c*) ρ *and* ϕ *are real analytic on* $A=\{x\,|\,x\neq R_j \text{ all } j,\ \rho(x)>0\}$.

(*d*) *In the neutral case* ($\mu=0$) $\rho(x)>0$, *all* x.

(*e*) *In the ionic case* ($\lambda<Z$, $\mu>0$) ρ *has compact support and* ρ *and* ϕ *are* C^1 *away from the* R_j.

Proof. (a) and (b) follow directly from Eq. (2.18). ϕ continuous $\Rightarrow$ ρ continuous away from the $R_j\Rightarrow\phi$ is C^1 everywhere. Then ρ is C^1 away from the R_j. [Note $(\phi-\mu)^{3/2}$ is C^1 if ϕ is C^1]. By a bootstrap argument ρ is C^∞ on A. By Theorem 5.8.6 in Morrey (1966), ϕ is real analytic away from the R_j and where $\phi>\mu$, namely A. Finally, since $\phi(x)\to 0$ as $|x|\to\infty$, ρ has compact support when $\mu>0$. The positivity of ϕ is established in Sec. III, so $\rho>0$ in the neutral case. ■

In the ionic case ($\lambda<Z$) the set $\Omega=\{x\,|\,\rho(x)>0\}$ is bounded. What can be said about its boundary, $\partial\Omega$? In the atomic case $\partial\Omega$ is, of course, a sphere. In the general case, the TF equation (2.19) is a "free boundary problem" about which Caffarelli and Friedman (1979) have proved the following result among others.

Theorem 2.9. *Consider the generalized TF problem with* $\frac{5}{3}$ *replaced by* p *and* $\frac{3}{2}<p<2$. *There are at most a finite number of open* C^1 *curves* $\Gamma_1,\ldots,\Gamma_l$ *such that* $\partial\Omega\setminus\{\cup_{i=1}^l\bar{\Gamma}_i\}$ *is a* $C^{3+\alpha}$ *manifold with* $\alpha=(2-p)/(p-1)$.

The next question to consider is the asymptotics of ρ, in the neutral case ($\mu=0$), as $|x|\to\infty$. This involves finding universal bounds on ρ. The function $\psi(x)=\gamma^3(3/\pi)^2|x|^{-4}$ satisfies Eq. (2.19) for $|x|>0$ and $x\neq R_j$. It is the only "power law" that does so. This was noted by Sommerfeld, who concluded that $\psi(x)$ is the asymptotic form of ϕ. Hille (1969), who was possibly the first to make a serious mathematical study of the TF equation, proved this asymptotic law in the atomic case. It is remarkable that ψ, the asymptotic form of ϕ, is *independent* of z, and it is just as remarkable that the same form holds even in the molecular case.

Theorem 2.10 (LS Sec. V.2). *Suppose* $\mu=0$ *and* $|R_j|<R$, *for all* j *and some* R. *For* $r=|x|>R$ *let* $\phi_+(r)$ (*resp.* $\phi_-(r)$) *be the max (resp. min) of* $\phi(x)$ *on* $|x|=r$ *and* $C_\pm(r)=\phi_\pm(r)/\psi(r)$ *with* $\psi(r)=\gamma^3(3/\pi r^2)^2$. *Then* $C_\pm(r)\to 1$ *as* $r\to\infty$. *Furthermore, if* $R<r$ *then*

(i) $C_+(R)\geq 1\Rightarrow C_+(r)\leq C_+(R)$,
(ii) $C_+(R)\leq 1\Rightarrow C_+(r)\leq 1$,
(iii) $C_-(R)\leq 1\Rightarrow C_-(r)\geq C_-(R)$,
(iv) $C_-(R)\geq 1\Rightarrow C_-(r)\geq 1$.

Proof. If f,g are continuous, positive functions on $|x|\geq R$ which go to zero as $|x|\to\infty$, and if $\gamma^{3/2}\Delta f\leq 4\pi f^{3/2}$, $\gamma^{3/2}\Delta g\geq 4\pi g^{3/2}$ for $|x|>R$, and if $f(x)\geq g(x)$ for $|x|=R$, then $f(x)\geq g(x)$ for all $|x|>R$. This is easily proved by a "maximum argument" as in Sec. III. ϕ is of this type with $\gamma^{3/2}\Delta\phi=4\pi\phi^{3/2}$. If $C_+(R)\geq 1$, compare $\phi(x)$ with $C_+(R)\psi(x)$. Then $C_+(r)\leq C_+(R)$, all $r>R$. This proves (i) and similarly (iii). To prove (ii) and (iv) compare ϕ with ψ. It remains to show that $C_\pm(r)\to 1$. C_+ is continuous. We shall show that $\limsup C_+(r)\leq 1$; by a similar argument $\liminf C_-(r)\geq 1$. This will complete the proof. If $C_+(R)>1$, let $R_0=\sup\{r\,|\,C_+(r)\geq 1\}$ whence $C_+(r)\geq 1$ for $R\leq r\leq R_0$ and $C_+(r)\leq 1$ for $r\geq R_0$. It is then only necessary to consider $R_0=\infty$. Then, since $C_+(r)$ is decreasing, $C(\infty)=\lim C_+(r)$ exists. Assume $C(\infty)>1$. Pick $\varepsilon>0$ and choose R_1 so that $C_+(R_1)<C(\infty)+\varepsilon$. Consider

$$f(x)=\gamma^3(3/\pi)^2(1+2b/3)^2(|x|-bR_1)^{-4}$$

for $|x|\geq R_1$ and $b<1$. $\gamma^{3/2}\Delta f\leq 4\pi f^{3/2}$. Choose $b<1$ such that $(1+2b/3)^2=C_+(R_1)(1-b)^4$. Then $f\geq\phi$ for $|x|>R_1$ since $f\geq\phi$ when $|x|=R_1$. But this means $C(\infty)\leq(1+2b/3)^2=[C(\infty)+\varepsilon](1-b)^4$. Since $b>B>0$ satisfying $(1+2B/3)^2=C(\infty)(1-B)^4$, and ε is arbitrary, $C(\infty)\leq 1$. For the C_- problem use $g(x)=\gamma^3(3/\pi)^2(1-2b/3)^2(|x|+bR_1)^{-4}$. ■

There are some interesting facts about the possible singularities of TF-type differential equations in a ball. These are related to and complement Theorem 2.10.

Theorem 2.11. *Let* $B=\{x\,|\,0<|x|<R\}$ *and suppose* ϕ *satisfies* $\Delta\phi(x)=G(\phi(x))$ *in the sense of distributions on* B, *and* G *is* C^1. *Then*

(*a*) *If* $\phi\in L^\infty_{\rm loc}(B)$ *and* G *satisfies* $G(t)>\varepsilon t^3$ as $t\to\infty$, $G(t)<\varepsilon t^3$ *as* $t\to-\infty$, $\varepsilon>0$, *there exists a* C^2 *function on* $0\leq|x|<R$ *which agrees with* ϕ *a.e. in* B. *Any singularity is thus removable. In particular* $-\Delta\phi+\phi^3=\delta(x)$ *has no solution in* $B'=\{x\,|\,0\leq x<R\}$.

(*b*) *If* $\phi\in C^2(B)$, $\phi>0$, *and* $G(t)=t^q$, $1<q<3$, *one of the following is true*:

(i) ϕ *has a* C^2 *extension on* B'.
(ii) $\phi(x)\sim C|x|^{-1}$ *as* $|x|\to 0$, $C>0$ *arbitrary*
(iii) $\phi(x)\sim l|x|^{-a}$ *as* $|x|\to 0$ *with* $a=2/(q-1)$, $l^{q-1}=a(a-1)$. *This is called the* "strong singularity."

(*c*) *Let* $q>1$ *and* $B'=\{x\,|\,0\leq|x|<R\}$. *Let* $\phi\in L^\infty_{\rm loc}(B')$ *satisfy* $\Delta\phi=|\phi|^{q-1}\phi$ *in* B' *in the sense of distributions. There is a universal constant* $C_q<\infty$ *such that* $|\phi(0)|\leq C_qR^{-2/(q-1)}$. *This implies that if* $\phi\in L^\infty_{\rm loc}(B)$ *satisfies this equation in* B, *then* $|\phi(x)|\leq C_q|x|^{-2/(q-1)}$ *for* $2|x|<R$. *A stronger bound than this is given by Veron (1979) and Brezis and Veron (1980) for* $1<q<3$.

Proof. (a) is given in Brezis and Veron, 1980, and (b) and (c) are given in Veron, 1979. (c) was given earlier

for $q=\frac{3}{2}$ in Brezis and Lieb, 1979. ■

There are other theorems of this type in Veron, 1979 and Brezis and Lieb, 1979.

See Sec. IV.C for an application of the strong singularity.

There is another property of ρ which can be derived directly from the variational principle, namely,

Theorem 2.12. *In the atomic case $\rho(x)$ is a symmetric, decreasing function.*

Proof. Assume the nucleus is at the origin and let ρ^* be the symmetric, decreasing rearrangement of ρ (for a definition see Lieb, 1977). We claim that if $\rho \neq \rho^*$ then $\mathcal{E}(\rho^*) < \mathcal{E}(\rho)$, thereby proving the theorem. $\int(\rho^*)^p = \int \rho^p$, all p. For the Coulomb terms note that when $\int \rho \leq z$ then $f(x) = z|x|^{-1} - |x|^{-1} * (\rho^*)$ is a symmetric, decreasing function; hence $\int f\rho \leq \int f\rho^*$. Thus $P(\rho) \equiv D(\rho,\rho) - \int V\rho = D(\rho-\rho^*, \rho-\rho^*) - \int \rho f - D(\rho^*,\rho^*)$ and thus $P(\rho) > P(\rho^*)$ if $\rho \neq \rho^*$. ■

Notation. $f*g$ denotes convolution, namely $(f*g)(x) \equiv \int f(x-y)g(y)dy$.

Remarks. (i) The same theorem (and proof) holds for the TFD, TFW, and TFDW theories *provided* $\lambda = \int \rho \leq z$. The only additional fact needed for the W theories is that $\int(\nabla\psi)^2 \geq \int(\nabla\psi^*)^2$ (see Lieb, 1977, appendix). In fact, Theorem 2.12 holds for all λ in TFW theory (Theorem 7.26).

(ii) The spherically symmetric (but not the decreasing) property of ρ also follows from the uniqueness of ρ which, in turn, follows from the strict convexity of $\mathcal{E}$. The decreasing property also follows from Eq. (2.18) since ϕ is decreasing by Newton's theorem.

E. The virial and related theorems

Let us generalize the TF functional $\mathcal{E}$ by multiplying the term $D(\rho,\rho)$ in Eq. (2.5) by a parameter $\beta > 0$. $e(\lambda) = E(\lambda) - U$ in Eq. (2.12) is then a function of γ, $\{z_j\}$, and β. Define

$$K = \tfrac{3}{5}\gamma \int \rho^{5/3}, \quad R = \beta D(\rho,\rho), \quad A = \int V\rho, \tag{2.20}$$

with ρ being the minimizing ρ for $\int\rho = \lambda$ with $\lambda \leq \lambda_c$. [By scaling, $\lambda_c(\beta) = \lambda_c(\beta=1)/\beta$.]

Theorem 2.13. *$e(\lambda,\gamma,\{z_j\},\beta)$ is a C^1 function of its $k+3$ arguments (assuming all are >0, except for β which is ≥ 0, and $\lambda \leq \lambda_c$). e is convex in λ and jointly concave in $(\gamma,\{z_j\},\beta)$. Moreover, $\partial e/\partial\gamma = K/\gamma$, $\partial e/\partial\beta = R/\beta$, $\partial e/\partial\lambda = -\mu$ $\partial e/\partial z_j = -\int \rho(x)|x-R_j|^{-1}dx$. This implies*

$$\partial E/\partial z_j = \lim_{x\to R_j} \{\phi(x) - z_j|x-R_j|^{-1}\}. \tag{2.21}$$

Proof. See LS. The proof uses the convexity of $\rho \to \mathcal{E}(\rho)$. The concavity in the parameters is a trivial consequence of the variational principle and the linearity of $\mathcal{E}$ in the parameters. ■

Now we return to $\beta = 1$.

Theorem 2.14. *(a)* $5K/3 = A - 2R - \mu\lambda$,
(b) for an atom $(k=1)$, $2K = A - R$.

Proof. (a) Simply multiply the TF equation (2.18) by ρ and integrate. Alternatively, note that ρ minimizes $G(\rho) = \mathcal{E}(\rho) + \mu\int\rho$ on all of $L^{5/3} \cap L^1$. Therefore $f(t) \equiv G(\rho_t)$, with $\rho_t(x) = t\rho(x)$, has its minimum at $t=1$. But $df/dt = 0$ gives (a).

(b) Here, scaling is essential. Consider $\rho_t(x) = t^3\rho(tx)$, so that $\int\rho_t = \lambda$. Then $f(t) = \mathcal{E}(\rho_t)$ has its minimum at $t=1$ and $df/dt = 0$ gives (b). ■

Remark. (b) is called the *Virial theorem*. *A priori* there is an analog of (b) for a molecule. Suppose that, with λ fixed, e is stationary with respect to all R_j, i.e., $\nabla_{R_j} e = 0$. Then, by the same scaling argument together with $R_j \to tR_j$, one would conclude that $2K = A - R - U$, equivalently $K + E = 0$. See Fock, 1932 and Jensen, 1933. The difficulty with this is that *there are no stationary points* for $k \geq 2$. The no-binding Theorem 3.23 shows that there are no global minima, and the positivity of the pressure proved in Sec. IV.B shows that there are no local minima (at least for neutral molecules). There it will be shown that for $k \geq 2$, the pressure P satisfies

$$3P = K + E > 0 \quad \text{for neutral molecules}. \tag{2.22}$$

For non-neutral molecules, a sharpening of Theorem 4.7 into a strict inequality for the derivative would suffice to show the absence of local minima.

For a neutral atom, (a) and (b) combine to give the following simple ratios:

$$R : K : -e : A = 1 : 3 : 3 : 7. \tag{2.23}$$

The energy of a neutral atom is

$$e = E = -3.678\,74 z^{7/3}/\gamma.$$

I thank D. Liberman for this numerical value.

Scaling. Suppose the nuclear coordinates R_i are replaced by lR_i with $l > 0$. If $\underline{z}, \underline{R}$ denote the nuclear charges and coordinates, and if $E(\underline{z},\lambda,l\underline{R})$, $-\mu(\underline{z},\lambda,l\underline{R})$, $\rho(\underline{z},\lambda,l\underline{R};x)$, and $\phi(\underline{z},\lambda,l\underline{R};x)$ denote the TF energy, chemical potential, density, and potential with $\int\rho = \lambda$, then

$$\begin{aligned} E(\underline{z},\lambda,l\underline{R}) &= l^{-7}E(l^3\underline{z}, l^3\lambda, \underline{R}), \\ \mu(\underline{z},\lambda,l\underline{R}) &= l^{-4}\mu(l^3\underline{z}, l^3\lambda, \underline{R}), \\ \rho(\underline{z},\lambda,l\underline{R};x) &= l^{-6}\rho(l^3\underline{z}, l^3\lambda, \underline{R}; l^{-1}x), \\ \phi(\underline{z},\lambda,l\underline{R};x) &= l^{-4}\phi(l^3\underline{z}, l^3\lambda, \underline{R}; l^{-1}x). \end{aligned} \tag{2.24}$$

This is a trivial consequence of the scaling properties of $\mathcal{E}(\rho)$.

F. The Thomas-Fermi theory of solids

A solid is viewed as a large molecule with the nuclei arranged periodically. For simplicity, but not necessity, let us suppose that there is one nucleus of charge z per unit cell located on the points of $\mathbb{Z}^3 \subset \mathbb{R}^3$. ($\mathbb{Z}^3$ consists of the points with integer coordinates.) If Λ is a finite subset of $\mathbb{Z}^3$ we want to know if, as $\Lambda \to \infty$ in a suitable sense, the energy/unit volume $|\Lambda|^{-1}E_\Lambda$ has a limit E, and ρ_Λ has a limit ρ, which is a periodic function. Here, $|\Lambda|$ is the volume of Λ. If so, the equation for ρ and an expression for E in terms of ρ is required. Naturally, it is necessary to consider only *neutral* systems, for otherwise $|\Lambda|^{-1}E_\Lambda \to \infty$. Everything works out as expected except for one mildly surprising thing; a

quantity ψ_0 appears in the equation for ρ which, while it looks like a chemical potential, and is often assumed to be one, is not a chemical potential. ψ_0 is the average electric potential in the solid. All of this is proved in LS, Sec. VI.

Definition. A sequence of domains $\{\Lambda_i\}$ in Z^3 is said to *tend to infinity* (denoted by $\Lambda \to \infty$) if

(i) $\cup_{i=1}^{\infty} \Lambda_i = Z^3$, (ii) $\Lambda_{i+1} \supset \Lambda_i$, (iii) $\Lambda_i^h \subset Z^3$ is the set of points not in Λ_i, but whose distance to Λ_i is less than h. Then $|\Lambda_i^h|/|\Lambda_i| \to 0$ for each $h > 0$. $\Gamma = \{x \in R^3 \| x^i| < \frac{1}{2}\}$ is the elementary cube centered at the origin.

Theorem 2.15. *As $\Lambda \to \infty$ the following limits exist and are independent of the sequence Λ_i:*

(i) $\phi(x) = \lim_{\Lambda \to \infty} \phi_\Lambda(x)$.

ϕ is periodic, $\gamma\rho(x)^{2/3} \equiv \phi(x)$, and the convergence is uniform on compacts in R^3.

(ii) $$\phi(x) = \lim_{\Lambda \to \infty} |\Lambda|^{-1} \sum_{y \in \Lambda} \phi_\Lambda(x+y),$$

(iii) $$\lim_{x \to 0} \phi(x) - z|x|^{-1} = \lim_{\Lambda \to \infty} |\Lambda|^{-1} \sum_{y \in \Lambda} \lim_{x \to y} \phi_\Lambda(x) - z \times |x-y|^{-1},$$

(iv) $$\int_\Gamma \rho = \lim_{\Lambda \to \infty} \int_\Gamma \rho_\Lambda = z,$$

(v) $$\int_\Gamma \rho^{5/3} = \lim_{\Lambda \to \infty} |\Lambda|^{-1} \int_{R^3} \rho_\Lambda^{5/3},$$

(vi) $E = \lim_{\Lambda \to \infty} |\Lambda|^{-1} E_\Lambda$.

Definition. $G(x)$ is the *periodic Coulomb potential*. It is defined up to an unimportant additive constant in Γ by $-\Delta G/4\pi = \delta(x) - 1$. A specific choice is

$$G(x) = \pi^{-1} \sum_{\substack{k \in Z^3 \\ k \neq 0}} |k|^{-2} \exp[2\pi i k \cdot x].$$

Theorem 2.16. *ϕ, ρ and E satisfy*

(i) $$E = (\gamma/10) \int_\Gamma \rho^{5/3} + (z/2) \lim_{x \to 0} \{\phi(x) - z|x|^{-1}\}, \quad (2.25)$$

(ii) $$\phi(x) = zG(x) - \int_\Gamma G(x-y)\rho(y) + \psi_0 \quad (2.26a)$$

for some ψ_0. Alternatively,

$$-\Delta\phi(x)/4\pi = \sum_{y \in Z^3} z\delta(x-y) - \rho(x), \quad (2.26b)$$

(iii) *ϕ and ρ are real analytic on $R^3 \setminus Z^3$.*

(iv) *There is a unique pair ρ, ψ_0 that satisfies Eq. (2.26) with $\gamma\rho^{2/3} = \phi$ and $\int \rho = z$ (cf. Theorem 2.6).*

Formula (2.25) may appear strange but it is obtained simply from the TF equation; an analogous formula also holds for a finite molecule.

Equation (2.26), together with $\gamma\rho^{2/3} = \phi$, is the *periodic TF equation*. ψ_0 is *not* a chemical potential. The chemical potential, $-\mu$, is zero because μ_Λ is zero for every finite system. If (2.26) is integrated over Γ we find, since $\int \rho = z$, that $\psi_0 = \int_\Gamma \phi$ = average electric potential. It might be thought that ψ_0 could be calculated in the same way that the Madelung potential is calculated: In each cubic cell there is (in the limit) a charge density $z\delta(x) - \rho(x)$. Therefore if

$$\tilde{\phi}(x) \equiv \sum_{y \in Z^3} g(x-y),$$

with

$$g(x) = z|x|^{-1} - \int_\Gamma \rho(y)|x-y|^{-1} dy,$$

it might be expected that $\tilde{\phi} = \phi$. The correct statement is that $\phi(x) = \tilde{\phi}(x) + d$ and $d \neq 0$ in general. One can show that $\int_\Gamma \tilde{\phi} = 2\pi \int_\Gamma x^2 \rho(x) dx$ (see LS). The fact that $d \neq 0$, precludes having a simple expression for ψ_0. Why is $d \neq 0$, i.e., why is $\phi \neq \tilde{\phi}$? The reason is that the charge density in the cell centered at $y \in Z^3$ is $z\delta(x-y) - \rho(x-y)$ only in the limit $\Lambda \to \infty$. For any finite Λ there are cells near the surface of Λ that do not yet have this charge distribution. Thus $d \neq 0$ essentially because of a neutral double layer of charge on the surface.

In LS asymptotic formulas as $z \to 0$ and ∞ are given for the various quantities.

Theorems 2.15 and 2.16 will not be proved here. Teller's lemma, which implies that $\phi_\Lambda(x)$ is monotone increasing in Λ, is used repeatedly. Apart from this, the analysis is reasonably straightforward.

G. The Thomas-Fermi theory of screening

Another interesting solid-state problem is to calculate the potential generated by one impurity nucleus, the other nuclei being smeared out into a uniform positive background (jellium model). If Λ is any bounded, measurable set in R^3, and if $\rho_B = (\text{const}) > 0$ is the charge density of the positive background in Λ, and if the impurity nucleus has charge $z > 0$ and is located at 0, then the potential is

$$V_\Lambda(x) = z|x|^{-1} + \rho_B \int_\Lambda |x-y|^{-1} dy. \quad (2.27)$$

The TF energy functional, without the nuclear repulsion, and with $\gamma = 1$, is

$$\mathcal{E}_\Lambda(\rho) = \tfrac{3}{5} \int \rho^{5/3} - \int V_\Lambda \rho + D(\rho, \rho). \quad (2.28)$$

The integrals are over R^3, not Λ. Let $\rho_\Lambda(x)$ be the neutral minimizing ρ (so that $\int \rho_\Lambda = z + \rho_B|\Lambda|$).

Definition. A sequence of domains Λ in R^3 is said to *tend to infinity weakly* if every bounded subset of R^3 is eventually contained in Λ.

Remark. This is an extremely weak notion of $\Lambda \to \infty$.

It is intuitively clear that if $\Lambda \to \infty$ weakly and $z = 0$ then $\rho_\Lambda(x) \to \rho_B$. For $z \neq 0$, $\rho_\Lambda(x) - \rho_B$ is expected to approach some function which looks like a Yukawa potential for large $|x|$. This is stated in many textbooks and is correct except for one thing: The coefficient of the Yukawa potential is *not* z but is some smaller number. In TF theory there is *over-screening* because of the nonlinearities.

Theorem 2.17. *Let $\Lambda \to \infty$ weakly and $z = 0$. Then $\phi_\Lambda(x) \to \rho_B^{2/3}$ uniformly on compacts in R^3.*

The theorem is another example of the effects of "surface charge." Since $\rho_\Lambda \to \rho_B$ and $\phi_\Lambda = \rho_\Lambda^{2/3}$, the result is

natural. But it means that the average potential is not zero. If, on the other hand, the integrals in Eq. (2.28) are restricted to Λ then $\rho_\Lambda(x)=\rho_B$ for all Λ and $x\in\Lambda$, and $\phi_\Lambda(x)=0$.

Theorem 2.18. *Let $\Lambda\to\infty$ weakly and $z>0$. Let*

$$f(x)=\lim_{\Lambda\to\infty}\phi_\Lambda(x)-\rho_B^{2/3}$$

and

$$g(x)=\lim_{\Lambda\to\infty}\rho_\Lambda(x)-\rho_B.$$

(i) *these limits exist uniformly on compacts,*
(ii) $g\in L^1\cap L^{5/3}$,
(iii) $0\leq f(x)\leq\phi^{\text{atom}}(x)$,
(iv) *f and g are strictly positive and real analytic away from $x=0$,*
(v) *$f(x)$ is monotone increasing in z,*
(vi) *These limits satisfy the TF equation*

$$f(x)=z|x|^{-1}-\int|x-y|^{-1}g(y)dy\,, \tag{2.29}$$

$$[\rho_B^{2/3}+f(x)]^{3/2}-\rho_B=g(x)\,, \tag{2.30}$$

$$\int g=z\,, \tag{2.31}$$

(vii) *Assuming only that $g\in L^1\cap L^{5/3}$ and $f(x)\geq-\rho_B^{2/3}$ there is only one solution to Eqs. (2.29) and (2.30) [without assuming (2.31)].*

There is a scaling relation:

$$f(x;z)=\rho_B^{2/3}F(\rho_B^{1/6}|x|;\rho_B^{-1/2}z)$$
$$g(x;z)=\rho_B G(\rho_B^{1/6}|x|;\rho_B^{-1/2}z)\,.$$

Let us write $F(r;z)=q(r;z)Y(r)$ where $Y(r)=(1/r)\times\exp\{-(6\pi)^{1/2}r\}$ is the Yukawa potential.

Theorem 2.19. (i) *$q(r;z)$ is monotone decreasing in r and increasing in z;*
(ii) $q(0;z)=z$;
(iii) *$Q(z)=\lim_{r\to\infty}q(r;z)$ exists. $0<Q(z)<z$ and Q is monotone increasing.* $\limsup_{z\to\infty}Q(z)(bz)^{-2/3}<1$ *with* $b=1.039$.

LS contains graphical plots of $Q(z)$ and $q(r;53.7)$. An asymptotic formula for $Q(z)$ has *not* been given. In the linearized approximations found in textbooks, $Q(z)=z$, but we see that this is false.

H. The Firsov variational principle

The problem of minimizing $\mathcal{E}(\rho)$ is a convex minimization problem. It has a dual which we now explore. The advantage of the dual problem is that it gives a *lower bound* to E. The principle was first given and applied in (Firsov, 1957) in the neutral case ($\mu=0$) and was first rigorously justified in that case by Benguria (1979). Here we shall also state and prove the principle for non-neutral systems; furthermore, in the neutral case our (and Benguria's) principle will contain a slight improvement over Firsov's.

The dual functional to be considered is

$$\mathcal{F}_\mu(f)=-(8\pi)^{-1}\int|\nabla f(x)|^2dx$$
$$-\tfrac{2}{5}\gamma^{-3/2}\int[V(x)-f(x)-\mu]_+^{5/2}dx+U, \tag{2.32}$$

where μ is a real parameter. The domain of $\mathcal{F}_\mu$ is $B=\{f\,|\,\nabla f\in L^2,\ |f(x)|<c|x|^{-1}$ for some $c<\infty$ and for $|x|>R$ for some $R\}$. V is assumed to go to zero at ∞ and is such that the TF problem has a minimum for that V, and the minimizing ρ (with $\int\rho\leq\lambda$) satisfies the TF equation (2.18) (for all λ). We define

$$E^F(\mu)=\sup\{\mathcal{F}_\mu(f)\,|\,f\in B\} \tag{2.33}$$

Remark. When $\mu=0$, Firsov imposed the additional constraint $V\geq f$. This, as we shall see, is unnecessary provided $[\ ]_+^{5/2}$ is used as in Eq. (2.32).

Theorem 2.20. *If $\mu<0$ then $E^F(\mu)=-\infty$. If $\mu\geq0$ then there is a unique maximizing f for $\mathcal{F}_\mu$. This f is $f_\mu\equiv|x|^{-1}*\rho_\mu$ where ρ_μ is the unique solution to Eq. (2.18). If $\lambda=\int\rho_\mu$ then (see remark below)*

$$E^F(\mu)=E(\lambda)+\mu\lambda\,. \tag{2.34}$$

Proof. Suppose $\mu<0$. Since V and any $f\in B\to0$ as $|x|\to\infty$, the second term in (2.32) is $-\infty$. Suppose $\mu\geq0$. Let $\tilde{E}_\mu=$ right side of (2.34). Clearly $\mathcal{F}_\mu(f_\mu)=\tilde{E}_\mu$ by the TF equation (2.18). $f\to\mathcal{F}_\mu(f)$ is strictly concave because $\int(\nabla f)^2$ is strictly convex. Thus there can be at most one maximizing f, and we therefore must show that if $f\neq f_\mu$ then $\mathcal{F}_\mu(f)\leq\tilde{E}_\mu$. By Minkowski's inequality ($|ab|\leq2|a|^{5/2}/5+3|b|^{5/3}/5$) we have

$$(\tfrac{2}{5})(V-f-\mu)_+^{5/2}\geq-(\tfrac{3}{5})(V-f_\mu-\mu)_+^{5/2}$$
$$+(V-f-\mu)\,(V-f_\mu-\mu)_+^{3/2}.$$

But $(V-f-\mu)_+\geq V-f-\mu$, so $\mathcal{F}_\mu(f)\leq\tilde{E}_\mu+h(f)$ where

$$h(f)=-(8\pi)^{-1}\int(\nabla f)^2+\int f\rho_\mu-D(\rho_\mu,\rho_\mu)\,.$$

By standard methods (e.g., Fourier transforms), $h(f)\leq0$. Furthermore, $h(f)=0$ only for $f=f_\mu$, which shows once again that the maximizing f is uniquely f_μ. ■

It should be noted that $E^F(\mu)$ is the Legendre transform of $E(\lambda)$. Namely $\lambda\to E(\lambda)$ is convex and

$$E^F(\mu)=\inf_{\lambda\geq0}[E(\lambda)+\lambda\mu]\,,\quad\text{all }\mu\in\mathbb{R}\,. \tag{2.35}$$

This shows that $E^F(\mu)$ is *concave* in μ. On the other hand, Theorem 2.20 displays $E^F(\mu)$ as the supremum (not infimum) of a family of concave functions. Furthermore, since $E(\lambda)$ is convex and bounded it is its own double Legendre transform, viz.

$$E(\lambda)=\sup_\mu[E^F(\mu)-\mu\lambda]\,. \tag{2.36}$$

Theorem 2.21. *Fix $\lambda\geq0$. Then [by Eq. (2.36)]*

$$\sup\{\mathcal{F}_\mu(f)-\mu\lambda\,|\,f\in B,\mu\in\mathbb{R}\}=E(\lambda)\,. \tag{2.37}$$

Remark. In Theorem 2.20 we refer to the unique ρ_μ satisfying Eq. (2.18) for $\mu\geq0$. This requires some explanation. If $V(x)$ is unbounded (e.g., point nuclei), then as μ goes from ∞ to 0, λ goes from 0 to λ_c and $\rho_\mu(\lambda)$ minimizes $\mathcal{E}$ on $\int\rho=\lambda$. If ess sup$V(x)=v<\infty$, then $\rho_\mu\equiv0$ [and $E^F(\mu)=0$] for $\infty>\mu\geq v$. In this range $\lambda(\mu)=0$. Then, as μ goes from v to 0, λ goes from 0 to λ_c, and $\rho_{\mu(\lambda)}$ minimizes $\mathcal{E}$ on $\int\rho=\lambda$. (ess sup is defined in Theorem 3.12).

III. THE "NO-BINDING" AND RELATED POTENTIAL-THEORETIC THEOREMS

The no-binding theorem was discovered by Teller (1962) and is one of the most important facts about the TF and TFD theories of atoms and molecules. It "explained" the absence of binding found numerically by Sheldon (1955). That this crucial theorem was not proved until 1962—after 35 years of intensive study of TF theory—is remarkable. It can be considered to be a prime example of the fact that pure analysis can sometimes be superior to numerical studies.

While Teller's ideas were correct, his proof was questioned on grounds of rigor. Balàzs (1967) found a different proof for the special case of the symmetric diatomic molecule. A rigorous transcription of Teller's ideas was given in LS. In any case, all proofs of the theorem rely heavily on the fact that the potential is Coulombic.

There are really two kinds of theorems. An example of the first kind is "Teller's lemma," which states that the potential increases when nuclear charge is added. The second, "Teller's theorem" is the no-binding Theorem 3.23. The second, but not the first, requires the nuclear repulsion U. If U is dropped then the theorem goes the other way. The proof of Teller's theorem given in LS is complicated in the non-neutral case, but recently Baxter (1980) found a much nicer proof—one which actually produces a variational ρ that lowers the energy for separated molecules. Baxter's proposition (proposition 3.24) will appear again in Lemma 7.22.

In this section we shall consider general V and assume that

$$\mathcal{E}(\rho)=\int j(\rho(x))\,dx-\int V(x)\rho(x)dx+D(\rho,\rho)\,, \tag{3.1}$$

where j is a C^1 convex function with $j(0)=j'(0)=0$. Note that in this section (only) $\mathcal{E}(\rho)$ does not contain U. This is done partly for convenience, but mainly for the reason that since V is not necessarily Coulombic the definition of U would have no clear meaning.

The Euler-Lagrange equation for (3.1) and $\rho(x)\geq 0$ is (with $\phi_\rho=V-|x|^{-1}*\rho$):

$$\begin{aligned}\phi_\rho(x)-\mu&=j'(\rho(x)) \quad \text{a.e. when } \rho(x)>0\,,\\ &\leq 0 \quad \text{a.e. when } \rho(x)=0\,.\end{aligned} \tag{3.2}$$

Any solution to (3.2) is determined only almost everywhere (a.e.).

We could, in fact, allow more general j's of the form $j(\rho,x)$ [and $\int j(\rho(x),x)\,dx$ in $\mathcal{E}$] with $j(\cdot,x)$ having the above properties for all x, but we shall not do so. An annoying case we must consider, however, is $j'(\rho)=0$ for $0<\rho<\rho_0$ and $j'(\rho)>0$ for $\rho>\rho_0$. This is discussed in some detail in Sec. III.C and is needed for TFD theory (Sec. VI). If $j'(\rho)>0$, all $\rho>0$, as it is in TF theory with $j'(\rho)=\gamma\rho^{2/3}$, then Eq. (3.2) can be written as

$$(\phi_\rho(x)-\mu)_+\equiv\max[\,\phi_\rho(x)-\mu,0]=j'(\rho(x))\,, \tag{3.2'}$$

but otherwise (3.2) is stronger than (3.2').

One aim of this section is to study solutions of Eq. (3.2) without considering whether or not (3.2) truly comes from minimizing (3.1) or assuming uniqueness.

Definition. $\mathfrak{C}=\{\rho\,|\,\rho(x)\geq 0,\ \rho\in L^1,$ and $\int\rho(y)\,|x-y|^{-1}dy$ is a bounded, continuous function which goes to zero as $x\to\infty\}$.

We shall be concerned only with solutions to (3.2) in $\mathfrak{C}$.

The following lemma (LS, II.25) is useful, in the cases of interest, to guarantee that $\rho\in\mathfrak{C}$.

Lemma 3.1. *If $f\in L^p, g\in L^{p'}$, $1/p+1/p'=1$, $p,p'>1$ then $f*g$ is a bounded, continuous function which goes to zero as x goes to infinity. In particular, if $\rho\in L^{3/2+\varepsilon}\cap L^1$ then $\rho\in L^{3/2+\varepsilon}\cap L^{3/2-\varepsilon}$. Since $|x|^{-1}\in L^{3+\varepsilon}+L^{3-\varepsilon}$, $\rho\in\mathfrak{C}$.*

It will always be assumed that $V(x)\to 0$ as $|x|\to\infty$ (this always means uniformly with respect to direction). Hence μ cannot be negative in Eq. (3.2), for otherwise $\rho\notin L^1$.

A. Some variational principles and Teller's lemma

At first it will *not* be assumed that V is Coulombic.

Theorem 3.2. *Fix $\lambda>0$ and suppose that ρ_λ, μ_λ satisfy Eq. (3.2) with $\int\rho_\lambda=\lambda$. Let $\phi_\lambda=\phi_{\rho_\lambda}$ and assume that $\rho_\lambda\in\mathfrak{C}$. Then, for all x,*

(a) $$\phi_\lambda(x)-\mu_\lambda=\sup_\rho\Big\{\phi_\rho(x)-\mu\,\Big|\,\phi_\rho(y)-\mu\leq j'(\rho(y))\text{ a.e. } y,\ \int\rho\leq\lambda,\ \rho\in\mathfrak{C}\Big\},$$

(b) $$\phi_\lambda(x)-\mu_\lambda=\inf_\rho\Big\{\phi_\rho(x)-\mu\,\Big|\,\phi_\rho(y)-\mu\geq j'(\rho(y))\text{ a.e. } y \text{ when } \rho(y)>0,\ \int\rho\geq\lambda,\ \rho\in\mathfrak{C}\Big\}$$

(c) $$\phi_\lambda(x)=\sup_\rho\{\,\phi_\rho(x)\,|\,\phi_\rho(y)-\mu_\lambda\leq j'(\rho(y))\text{, a.e. } y,\ \rho\in\mathfrak{C}\,\}$$

(d) $$\phi_\lambda(x)=\inf_\rho\{\,\phi_\rho(x)\,|\,\phi_\rho(y)-\mu_\lambda\geq j'(\rho(y))\text{. a.e. } y \text{ when } \rho(y)>0,\ \rho\in\mathfrak{C}\}\,.$$

Furthermore, in (a) [*resp.* (b)] *there is no ρ satisfying the conditions on the right when $\mu<\mu_\lambda$ [resp. $\mu>\mu_\lambda$]. Note that in* (a) *and* (b) *μ is arbitrary (including $\mu<0$) and ρ is constrained, while in* (c) *and* (d) *the opposite is true [except, of course, $\rho(x)\geq 0$].*

In the following, a statement such as $\Delta\phi/4\pi=\rho$ is always meant in the distributional sense. We shall need Lemma II.26 from LS.

Lemma 3.3. *Let $\rho_1,\rho_2\in L^1$ with $\rho_i(x)\geq 0$ and $\psi_i=|x|^{-1}*\rho_i$. If $\psi_1(x)\geq\psi_2(x)$, all x, then $\int\rho_1\geq\int\rho_2$.*

Proof. Suppose $\int\rho_2-\rho_1=4\varepsilon>0$. There exists a ball, B, of radius R, such that $\int\rho_1(1-\Theta)<\varepsilon$ and $\int\rho_2(1-\Theta)<\varepsilon$, where $\Theta(x)=1$ for $x\leq R$ and zero otherwise. Compute the spherical average of $\psi_2-\psi_1$ on the sphere of radius R; it cannot be positive. The contribution from inside B is, by Newton's theorem, $R^{-1}\int(\rho_2-\rho_1)\Theta>2\varepsilon/R$. The contribution from outside B is at least $-R^{-1}\int\rho_1(1-\Theta)>-\varepsilon/R$. Adding these gives a contradiction. ■

Remark. Even if $\psi_1(x)>\psi_2(x)$ for all x, we cannot conclude that $\int\rho_1>\int\rho_2$.

Proof of Theorem 3.2. (a) will be proved here; (b), (c), and (d) follow similarly. Since ρ_λ gives equality, $\phi_\lambda-\mu_\lambda\leq\sup\{\,\}$. We have to show that if $(\phi_\rho-\mu)_+\leq j'(\rho)$

a.e. and if $\int\rho \le \lambda$ then

(i) $\phi_\lambda(x) - \mu_\lambda \ge \phi_\rho(x) - \mu$,
(ii) $\mu \ge \mu_\lambda$.

First suppose $\mu \ge \mu_\lambda$ and let $\psi(x) = \phi_\rho(x) - \phi_\lambda(x) + \mu_\lambda - \mu$. Let $B = \{x \,|\, \psi(x) > 0\}$. B is open since ψ is continuous. As a distribution $-(4\pi)^{-1}\Delta\psi(x) = \rho_\lambda(x) - \rho(x) \le 0$ a.e. on B since $j'(\rho) \ge \phi_\rho - \mu$, $j'(\rho_\lambda) = \phi_\lambda - \mu_\lambda$ when $\rho_\lambda > 0$ and j' is nondecreasing. Hence ψ is subharmonic on B and takes its maximum on ∂B, the boundary of B, or at ∞. $\psi = 0$ on ∂B. At ∞, $\psi = \mu_\lambda - \mu \le 0$. Hence B is empty and (i) is proved. Suppose now that $\mu_\lambda - \mu = \delta > 0$. Then $j'(\rho) \ge \phi_\rho - \mu > \phi_\rho - \mu_\lambda$ and, by the previous proof (applied to $\mu = \mu_\lambda$), $\phi_\lambda(x) \ge \phi_\rho(x)$. By Lemma 3.3, $\int\rho \ge \int\rho_\lambda = \lambda$. Hence $\int\rho = \lambda$. At this point there are two possible strategies.

(i) If we assume that $\mathcal{E}(\rho)$ has a minimum that satisfies Eq. (3.2) for all $\mu \ge 0$, then we can use the fact [which follows from the strict convexity of $\mathcal{E}(\rho)$] that μ_λ is a continuous decreasing function of λ. Then there exists $\gamma > \lambda$ with $\mu_\lambda > \mu_\gamma > \mu$. Since $j'(\rho) \ge \phi_\rho - \mu_\gamma$, $\int\rho = \gamma$ by what we just proved. But this is a contradiction.

(ii) There is a purely potential theoretic argument without invoking Eq. (3.1). There is a (not necessarily unique) f which satisfies $j'(f(x)) = [\phi_\rho(x) - \mu/2 - \mu_\lambda/2]_-$ and $f(x) = 0$ when $[\ ] = 0$. Hence $f(x) < \rho(x)$ a.e. when $\rho(x) > 0$, and $f(x) = 0$ when $\rho(x) = 0$. Thus $f \in \mathfrak{C}$. Since $\int\rho = \lambda > 0$, $\int f < \lambda$. Let $g = (1-\varepsilon)\rho + \varepsilon f$, $0 < \varepsilon < 1$. Since $|x|^{-1} * \rho$ (and hence $|x|^{-1} * f$) are bounded, $\phi_g(x) \le \phi_\rho(x) + \varepsilon C$ for some constant C. Choose $\varepsilon > 0$ so that $\varepsilon C < \delta/2$. Then $j'(g) \ge j'(f) \ge \phi_g - \mu_\lambda$. Since $\int g < \lambda$, g satisfies the condition in (a) with $\mu = \mu_\lambda$ but, as we have seen, this implies $\int g = \lambda$. ■

Teller's lemma (Theorem 3.4) is closely related to Theorem 3.2.

Definition. We say $V \in \mathfrak{D}$ if $V \not\equiv 0$ and V is superharmonic, vanishing at ∞ (and hence $V > 0$). Moreover, the set $\{x \,|\, V(x) = \infty\} = S_V$ (called the *singularities* of V) is closed, V is continuous on the complement of S_V, and $V(x) \to \infty$ as $x \to S_V$.

Theorem 3.4. *Suppose V is replaced by $V' = V + W$ with $W \in \mathfrak{D}$. (In the case of interest $W = z|x - R|^{-1}$, which means that we add, or increase, a nuclear charge.) Suppose that for some common μ there are solutions to Eq. (3.2) $0 \le \rho$, $\rho' \in \mathfrak{C}$ with V and with V'. Then $\phi'(x) \ge \phi(x)$ all x and, if j' is strictly monotone or if $\phi - \phi' \in H^2$ (i.e., $\phi - \phi'$ and its first two derivatives are in L^2) away from S_W, then $\rho'(x) \ge \rho(x)$, a.e.*

Proof. Let $\psi = \phi' - \phi$ and $B = \{x \,|\, \psi(x) < 0\}$. Clearly $B \cap S_W = \varnothing$ so B is open. As a distribution, $\Delta\psi/4\pi \le \rho' - \rho \le 0$, so ψ is superharmonic on B. Thus B is empty and $\phi' \ge \phi$. The proof that $\rho' \ge \rho$ is trickier. If j' is strictly monotone it is obvious. Otherwise it can be shown (see Benguria, 1979) that for suitable V, W, and j', $\psi \in H^2$ away from S_W. Assuming $\psi \in H^2$, if $\rho'(x) < \rho(x)$ then $x \in C = \{x \,|\, \psi(x) = 0\}$. On C, $\Delta\psi = 0$, a.e. (see Benguria, 1979, Theorems 2.19 and 3.3). Let $D = C \cap \{x \,|\, \rho'(x) < \rho(x)\}$. On D, $0 = \Delta\psi/4\pi \le \rho' - \rho < 0$ a.e., so D has zero measure. ■

Remark. If $j'(s)$ is strictly monotone and $W \not\equiv 0$ then $\phi'(x) > \phi(x)$ for all $x \notin S_W$.

A similar proof yields

Theorem 3.5. *If $V \in \mathfrak{D}$ then $\phi_\lambda(x) \ge 0$. Consequently if $V(x) = \int dM(y)\,|x - y|^{-1}$, $dM \ge 0$, and $\int dM = Z$, then there is no solution if $\lambda > Z$ because then $\phi_\lambda(x) < 0$ for some large x. Cf. Theorem 6.7.*

There are many easy, but important corollaries of Theorem 3.2. We stress that V need not be Coulombic; the important ingredient is that the electron-electron repulsion is Coulombic.

Definition. j' is said to be *subadditive* if $j'(\rho_1 + \rho_2) \le j'(\rho_1) + j'(\rho_2)$. j' is subadditive in the TF case.

Corollary 3.6. *Suppose $V = V_1 + V_2$ and μ is fixed. Let ϕ, ϕ_1, ϕ_2 be solutions to Eq. (3.2) for this μ with V, V_1, V_2, respectively. Suppose $\phi_i \ge 0$ (e.g., $V_i \in \mathfrak{D}$) and suppose j' is subadditive. Then $\phi(x) \le \phi_1(x) + \phi_2(x)$, all x.*

Proof. Use Theorem 3.2 (d) with $\rho_1 + \rho_2$ on the right side. ■

Corollary 3.7. *Let $\lambda > 0$. There can be at most one pair ρ, μ satisfying Eq. (3.2) with $\rho \in \mathfrak{C}$ (in particular for $\rho \in L^{5/3} \cap L^1$) and $\int\rho = \lambda$.*

Proof. If ρ_1, ρ_2 are two solutions, use Theorem 3.2(a) twice with ρ_1 and ρ_2 to deduce $\phi_1 - \mu_1 = \phi_2 - \mu_2$. This implies $\mu_1 = \mu_2$ and hence $\phi_1 = \phi_2$. But then $0 = \Delta(\phi_1 - \phi_2) = 4\pi(\rho_2 - \rho_1)$. ■

This uniqueness result was proved earlier, Theorem 2.6, using the strict convexity of $\mathcal{E}(\rho)$.

Corollary 3.8. *If $0 < \lambda' < \lambda$ then*
(i) $\phi_{\lambda'} \ge \phi_\lambda$
(ii) $\mu_{\lambda'} \ge \mu_\lambda$
(iii) $\phi_{\lambda'} - \mu_{\lambda'} \le \phi_\lambda - \mu_\lambda$.

Proof. For (iii) use Theorem 3.2(b) with ρ_λ, μ_λ as trial function for the λ' problem. (iii) $\Rightarrow$ (ii). For (i) use (c) with ρ_λ as variational function for the λ' problem. ■

Corollary 3.9. *Suppose ρ_1, μ and ρ_2, μ (same μ) are two solutions to Eq. (3.2) with $\int\rho_1$, $\int\rho_2 > 0$. Then $\phi_1 = \phi_2$ and $\rho_1 = \rho_2$ a.e. Therefore, by Corollary 3.8, whenever $\lambda_2 > \lambda_1$ then $\mu_2 < \mu_1$ (i.e., $\mu_2 = \mu_1$ cannot occur).*

Proof. Using Theorem 3.2(d), $\phi_1 = \phi_2$. Then

$$0 = \Delta(\phi_1 - \phi_2)/4\pi = \rho_1 - \rho_2 \text{ a.e.} \quad ■$$

Corollary 3.10. *Suppose $j_1'(\rho) \le j_2'(\rho)$, all ρ. Let $\rho_\lambda^1, \mu_\lambda^1$ and $\rho_\lambda^2, \mu_\lambda^2$ be corresponding solutions to Eq. (3.2) with fixed λ, and ρ^1, ρ^2 solutions with fixed μ. $\phi^i_{(\lambda)}(x)$ are the corresponding potentials. Then*
(i) $\phi_\lambda^1 - \mu_\lambda^1 \le \phi_\lambda^2 - \mu_\lambda^2$,
(ii) $\mu_\lambda^1 \ge \mu_\lambda^2$,
(iii) $\phi^1 \le \phi^2$.

Proof. For (i) use Theorem 3.2(a) with ρ_λ^1, μ_λ^1 as trial function for the 2 problem. (i) $\Rightarrow$ (ii). For (iii) use (d) with ρ_2 as trial function for the 1 problem. ■

Lemma 3.11. *When $\mu > 0$, ρ has compact support.*

Remark. As will be seen in Sec. VI, ρ has compact support in TFD theory even when $\mu = 0$. See Theorem 6.6.

Among the most important consequences of Theorem

3.2 are the *variational principles for the chemical potential* [LS].

Theorem 3.12. *Define the functionals*

$$T(\rho)=\operatorname{ess\,sup}_x\{\phi_\rho(x)-j'(\rho(x))\},$$
$$S(\rho)=\operatorname*{ess\,inf}_{x:\rho(x)>0}\phi_\rho(x)-j'(\rho(x))\}. \tag{3.3}$$

(ess sup *means supremum modulo sets of measure zero*). *Then, whenever there is a solution to (3.2) with* $\int\rho=\lambda>0$,

$$\mu_\lambda=\inf\left\{T(\rho)\,|\,\rho\in\mathfrak{C},\int\rho\le\lambda\right\} \tag{3.4}$$

$$\mu_\lambda=\sup\left\{S(\rho)\,|\,\rho\in\mathfrak{C},\int\rho\ge\lambda\right\}. \tag{3.5}$$

Corollary 3.13. *If* $j'(\rho)$ *is concave (as in TF theory with* $j'=\rho^{2/3}$*) then* μ_λ *and* $\mu_\lambda-\phi_\lambda(x)$*, for each* x*, are jointly convex functions of* V *and* λ.

Corollary 3.14. *If* λ *is fixed and* $V_1(x)\ge V_2(x)$*, all* x*, then* $\mu_\lambda(1)\ge\mu_\lambda(2)$.

By Corollaries 3.9 and 3.14 we know that increasing V increases μ while increasing λ decreases μ. What happens if V and λ are both increased, in particular if we scale up the size of a molecule by $V\to\alpha V$, $\lambda\to\alpha\lambda$? A partial answer is given by the following two corollaries.

Corollary 3.15. *Let* $V_1, V_2\in\mathfrak{D}$ *and* $V=V_1+V_2$. *Assume* j' *is subadditive and suppose Eq. (3.2) has solutions to the three problems* (V_1,λ_1), (V_2,λ_2), (V,λ) *with* $\lambda=\lambda_1+\lambda_2$. *Then* $\mu\ge\min(\mu_1,\mu_2)$.

Proof. In general, if $W\in\mathfrak{D}$ and ρ is a solution to (3.2) with W then $\phi_\rho(x)-j'(\rho(x))=\mu$ a.e. if $\rho(x)>0$ and ≥ 0 a.e. if $\rho(x)=0$ (Theorem 3.5). From this remark it follows that $S_V(\rho_1+\rho_2)\ge\min(\mu_1,\mu_2)$. [Here, $S_V(\rho)$ refers to Eq. (3.3) with V.] ■

Corollary 3.16. *Let* $\alpha>1$ *and suppose Eq. (3.2) has solutions with* (V,λ,μ) *and* $(\alpha V,\alpha\lambda,\mu(\alpha))$. *Assume* j' *satisfies* $j'(\alpha t)\le\alpha j'(t)$*, all* t *(this holds in TF theory). Then* $\mu(\alpha)\ge\alpha\mu$.

Proof. If ρ is the solution to (V,λ,μ) then $S_V(\rho)=\mu$. But $S_{\alpha V}(\alpha\rho)\ge\alpha S_V(\rho)$. ■

Corollary 3.17. *Suppose there is a solution to Eq. (3.2) for all* $\lambda\in(a,b)$ *with* $a<b$. *Then* μ_λ *is continuous on this interval.*

Proof. Let $\lambda_2=\lambda_1+\varepsilon$. By Corollary 3.9, $\mu_1>\mu_2$. Let $\rho=\rho_1+\varepsilon\chi$ with $\int\chi=1$, $0\le\chi(x)\le b$ for some b, $\chi(x)=0$ if $\rho_1(x)=0$, and $\chi(x)=0$ if $\rho_1(x)>a$ for some a. Then $\chi\in\mathfrak{C}$. Since j' is continuous, $S(\rho)\ge\mu_1-Q(\varepsilon)$ where $Q(\varepsilon)\downarrow 0$ as $\varepsilon\downarrow 0$. ■

Theorem 3.18. *Let* $V\in\mathfrak{D}$, $V(x)=\int dM(y)\,|y-x|^{-1}$, $dM\ge 0$, $\int dM=Z>0$. *Suppose that for large* t, $j'(t)>ct^{(1/2)+\varepsilon}$*, with* $c,\varepsilon>0$. *By a simple modification of the method of Theorems 2.4, 2.5, and 2.6,* $\mathcal{E}(\rho)$ *has a unique minimum on the set* $\mathfrak{C}$ *with* $\int\rho\le\lambda$. *This* ρ *satisfies Eq. (3.2) and* $\int\rho=\lambda$ *if* $\lambda\le\lambda_c$*, whereas* $\int\rho=\lambda_c$ if $\lambda>\lambda_c$. *Now assume, in addition, that* $j'(t)<dt^{\varepsilon+1/3}$, $\varepsilon>0$, *for small* t *(this is true in all cases of interest). Then* $\lambda_c=Z$.

Proof. If $\lambda>Z$ there is no solution by Theorem 3.5. Now suppose $\mu=0$; we claim $\lambda\ge Z$, and hence that $\lambda=Z$. If so, we are done because $\mathcal{E}(\rho)$ has an absolute minimum. This minimum corresponds to $\mu=0$ and has $\lambda=\lambda_c$; but $\mu=0$ implies $\lambda=Z$. Now, to prove that $\lambda\ge Z$, let ϕ be the solution. If $\lambda=Z-3\delta$, let χ be the characteristic function of a ball centered at the origin such that $\int\chi dM>Z-\delta$. Then

$$\phi(x)>\psi(x)=\int[\chi(y)dM(y)-\rho(y)dy]\,|x-y|^{-1}.$$

For $|x|>$ some R, $\psi(x)<2Z|x|^{-1}$. Also $[\psi(x)]=$ (spherical average of $\psi)>2\delta|x|^{-1}$ for $x>R$. For a given $|x|=r>R$ let $\Omega_+(r)$ be the proportion of the sphere of radius r such that $2Z>r\psi(x)>\delta$, and let $\Omega_-(r)$ be the complement. Then $2\delta<r[\psi(x)]<2Z\Omega_+ +\delta\Omega_-=\delta+(2Z-\delta)\Omega_+$. Thus $\Omega_+(r)>\delta/(2Z-\delta)$ for all r. On Ω_+, $\rho^{(1/3)+\varepsilon}>\delta|x|^{-1}$ for large $|x|$, and therefore $\rho\notin L^1$ if $\delta>0$. ■

Brezis and Benilan (Brezis, 1978, 1980) have generalized this. Even if $j(\rho)\sim\rho^{(4/3)-\varepsilon}$ for large ρ there is a solution to Eq. (3.2) if $\lambda\le Z$, and no solution otherwise. This is noteworthy, since if $j(\rho)\sim\rho^a$ for large ρ with $a\le\frac{3}{2}$ then $\mathcal{E}(\rho)$ has no lower bound for point nuclei. There are similar results for other potentials, V, in LS, Theorem II.18.

There is also an "energetic," as distinct from potential theoretic, reason that there is no solution if $\lambda>Z$. A solution to Eq. (3.2) implies a minimum for the functional $\mathcal{E}(\rho)$, by strict convexity. If $\lambda=\int\rho>Z$ then ϕ_ρ is negative in some set A of positive measure. Then it is easy to see that if ρ is decreased slightly in A to $\tilde\rho$, then $\mathcal{E}(\tilde\rho)<\mathcal{E}(\rho)$. But $\int\tilde\rho<\lambda$ and $E(\lambda)$ is nonincreasing.

In the variational principle, Theorem 3.12, ρ_λ gives equality, i.e., $T(\rho_\lambda)=S(\rho_\lambda)=\mu_\lambda$. Is this the only ρ with this property? If $\lambda>Z$ there are many ρ's with $T(\rho)=0$ and no ρ with $S(\rho)=0$ (cf. LS). In Brezis, 1980, Sec. 4, it is shown that if j' is concave (as in TF theory) and V has suitable properties (satisfied for $V\in\mathfrak{D}$) then when $\lambda<Z$ only ρ_λ satisfies either $T(\rho)=\mu_\lambda$ or $S(\rho)=\mu_\lambda$. If $\lambda=Z$ this uniqueness is lost in general!

Asymptotics of the chemical potential.

Theorem 3.12 can be used to obtain bounds on μ_λ. In the TF case with point nuclei, the asymptotic formula

$$\mu_\lambda\sim\gamma^{-1}(\pi^2\textstyle\sum z_j^3/4\lambda)^{2/3} \tag{3.6}$$

holds for λ small (LS, Theorem II.31). For λ near Z LS (Theorems IV.11, 12) find upper and lower bounds for μ_λ of the form $\alpha_\pm(Z-\lambda)^{4/3}$ with $Z=\sum z_j$. Brezis and Benilan (unpublished) have shown that

$$\alpha=\lim_{\lambda\uparrow Z}\mu_\lambda(Z-\lambda)^{-4/3}\ \text{exists} \tag{3.7}$$

and is given by solving some differential equation. α is independent of the number of nuclei and their individual coordinates and charges!

Equation (3.7) implies that there is a well defined *ionization potential* I in TF theory (although it probably has nothing to do with the true Schrödinger ionization energy). First observe that if we start with $\sum z_j=1$ and then replace z_j by Zz_j, R_j by $Z^{-1/3}R_j$, and λ by $Z\lambda$, then by scaling Eq. (2.24),

$$\mu_{Z\lambda}=Z^{4/3}\mu_\lambda\,. \tag{3.8}$$

Therefore, by Eq. (3.7), if we let $\lambda = Z - \varepsilon$ with $\varepsilon > 0$ fixed, and let $Z \to \infty$, then

$$\lim_{Z\to\infty} \mu_{Z-\varepsilon} = \alpha\varepsilon^{4/3}. \tag{3.9}$$

The ionization potential is defined to be

$$I = E(\lambda = Z-1) - E(\lambda = Z). \tag{3.10}$$

By integrating (3.9), and appealing to dominated convergence,

$$I \to 3\alpha/7 \quad \text{as } Z \to \infty. \tag{3.11}$$

Another implication of Eq. (3.7) is that an ionized *atom* has a well defined radius as $Z \to \infty$. This question was raised by Dyson. Suppose $V(x) = Z|x|^{-1}$ and $\lambda = Z - \varepsilon$. The density ρ will have support in a ball of radius $R(Z,\varepsilon)$. At $|x| = R$, $\phi(x) = \mu$. But since ρ is spherically symmetric, $R\phi(x) = Z - \lambda = \varepsilon$ by Newton's theorem. Thus the atomic radius satisfies

$$R = \varepsilon/\mu \quad \text{for all atoms} \tag{3.12}$$

and, by Eq. (3.9),

$$\lim_{Z\to\infty} R(Z,\varepsilon) = (\alpha\varepsilon^{1/3})^{-1}. \tag{3.13}$$

There are other ways in which TF theory yields a well defined atomic radius. See Sec. V.C (6).

B. The case of flat j' (TFD)

In TFD theory, as will be seen in Sec. VI, we have to consider

$$j'(\rho) = 0, \quad 0 \le \rho \le \rho_0 = (5C_e/8\gamma)^3$$
$$= \gamma\rho^{2/3} - C_e\rho^{1/3} + 15C_e^2/4^3\gamma, \quad \rho_0 \le \rho. \tag{3.14}$$

j' satisfies all necessary conditions. It is neither concave nor subadditive, however. Let us consider V of the form

$$V(x) = \int dm(y)\,|x-y|^{-1}, \tag{3.15}$$

with m being a measure that is not necessarily positive. In the primary case of interest, $dm(x) = \sum z_j \delta(x - R_j)$.

The question we address here (and which will be important in Sec. VI) is this: Does $\rho(x)$ [the solution to Eq. (3.2)] take values in $(0,\rho_0)$? It may or may not, depending on m and λ.

Example. Suppose $dm(x) = g(x)dx$ with $g(x) \in (0,\rho_0)$ and $\int g = Z < \infty$. Then $\rho(x) = g(x)$ satisfies Eq. (3.2) with $\lambda = Z$, and thus $\rho(x) \in (0,\rho_0)$. This ρ also clearly minimizes $\mathcal{E}(\rho)$ in Eq. (3.1).

Nevertheless, in some circumstances $\rho \notin (0,\rho_0)$.

Theorem 3.19. *Suppose $j'(\rho) = \alpha = \text{constant for } \rho \in F \equiv (\rho_1,\rho_0]$ with $0 \le \rho_1 \le \rho_0 < \infty$, and $j'(\rho) > c\rho^{(1/2)+\varepsilon}$ for large ρ. Let V be given by Eq. (3.15) and let A be a bounded open set such that as distributions on A either $\rho_0 dx < dm < (\rho_0 + \text{const})dx$ or $dm < \rho_1 dx$. Let $\rho \in \mathfrak{C}$ satisfy Eq. (3.2). Then $\rho(x) \notin F$ a.e. (with respect to Lebesgue measure) on A.*

Proof. Cf Benguria, 1979, Lemmas 2.19, 3.2. First, it can be shown that $\phi_\rho \in H^2(A)$ (Sobolev space). Let $B = \{x \,|\, \rho(x) \in F\} \cap A$. On B, $\phi_\rho - \mu = \alpha$ and since $\phi_\rho \in H^2(A)$, $\Delta\phi_\rho = 0$ a.e. on B. But $\Delta\phi_\rho/4\pi = \rho - dm/dx$. ■

Remark. Since a solution to Eq. (3.2) is determined only a.e., $\rho(x)$ can be chosen $\notin F$ for all $x \in A$.

Corollary 3.20. *Consider the TFD problem (3.14) with $V(x) = \sum z_j|x - R_j|^{-1}$. Then any solution to (3.2) can be modified on a set of measure zero so that $\rho(x) \notin (0,\rho_0]$ for all x.*

C. No-binding theorems

Henceforth it will be assumed, as in Theorem 3.18, that j is such that Eq. (3.1) has a minimum for $\lambda \le \lambda_c$ which satisfies Eq. (3.2). We shall be interested in comparing three (nonzero) potentials, V_1, V_2, and $V_{12} = V_1 + V_2$ with $V_i \in \mathfrak{D}$. At first we shall consider what happens when the repulsion U is absent. As usual we define $e_a(\lambda) \equiv \inf \mathcal{E}_a(\rho)$ with $\lambda = \int\rho$ and $\mathcal{E}_a$ having V_a. There is no U term in $\mathcal{E}_a$, Eq. (3.1). Define

$$\Delta e(\lambda) = e_{12}(\lambda) - \min_{\lambda_1+\lambda_2=\lambda} e_1(\lambda_1) + e_2(\lambda_2). \tag{3.16}$$

Definition. If $\Delta e < 0$ (resp. ≥ 0) we say that *in the absence of the repulsion U there is binding* (resp. *no binding*).

Theorem 3.21. *Suppose j satisfies*

$$j(a+b) \le j(a) + j(b) + aj'(b) + bj'(a), \quad a,b \ge 0. \tag{3.17}$$

[If j' is subadditive then Eq. (3.17) is satisfied. $j(t) = t^{5/3}$ satisfies (3.17).] Then $\Delta e < 0$.

Proof. For $i = 1, 2$ let λ_i minimize in Eq (3.16) and let ρ_i be the minimizing ρ for $\mathcal{E}_i$ with $\int\rho_i \le \lambda_i$. Recall $e_a(\lambda)$ is monotone nonincreasing. Let $\rho \equiv \rho_1 + \rho_2$ be a trial function for e_{12} in $\mathcal{E}_{12}$ and use the variational equations (3.2) for ρ_i and the fact that $\phi_i(x) \ge 0$. ■

Remark. The condition (3.17) is satisfied in TF theory but not in TFD theory.

Theorem 3.21 says we can [and do, if j satisfies Eq. (3.17)] have binding if the repulsion U is absent. The no-binding theorem, which we turn to now, relies on the addition of U which, by itself without $\mathcal{E}$, obviously has the no-binding property.

Proposition 3.22. *If j is convex and $j(0) = 0$, then j has the superadditivity property: $j(a+b) \ge j(a) + j(b)$. If j' is strictly monotone, then the foregoing inequality is strict when $a, b \ne 0$.*

Note. We assumed that j is convex in all cases. Therefore Theorem 3.23 holds in all cases.

Definition. Let

$$V_i = \frac{1}{|x|} * m_i \quad (m_i \text{ a measure})$$

be in $\mathfrak{D}$. Then

$$D(m_1,m_2) \equiv \tfrac{1}{2}\int dm_1(x)dm_2(y)\,|x-y|^{-1}.$$

Theorem 3.23 (no binding). *Let m_i, $i = 1, 2$ be nonnegative measures of finite mass $z_i > 0$ and $V_i \in \mathfrak{D}$. Then*

$$\Delta E(\lambda) \equiv \Delta e(\lambda) + 2D(m_1,m_2) \ge 0. \tag{3.18}$$

If j is strictly superadditive then > 0 holds.

Remarks. Obviously $\Delta E(\lambda)$ is the energy difference when the repulsion U is included. *Binding never occurs.* In particular, if

$$V_1=\sum_{j=1}^{n} z_j|x-R_j|, \qquad V_2=\sum_{j=n+1}^{k} z_j|x-R_j|^{-1}$$

then

$$m_1=\sum_{j=1}^{n} z_j\delta(x-R_j), \qquad m_2=\sum_{j=n+1}^{k} z_j\delta(x-R_j).$$

In TFD theory j is not strictly superadditive. As we shall see in Sec. IV.C, it is possible to have a neutral diatomic molecule for which equality holds in Eq. (3.18).

Proof. We give two proofs. The LS proof in the neutral case $\lambda=z_1+z_2$ is the following: Clearly $\lambda_1=z_1$, $\lambda_2=z_2$, $\mu_1=\mu_2=\mu_{12}=0$. Consider $m_1\to\alpha m_1$, $\lambda_1\to\alpha z_1$, $0\le\alpha\le 1$. By Theorem 2.13 we have

$$\partial e_1/\partial\alpha=-\int V_1\rho_1$$

and

$$\partial e_{12}/\partial\alpha=-\int V_1\rho_{12}.$$

Thus

$$\partial(e_{12}-e_1+2D(\alpha m_1,m_2))/\partial\alpha=\int dm_1(x)[\phi_{12}(x)-\phi_1(x)].$$

But $\phi_{12}(x)\ge\phi_1(x)$, all x (Theorem 3.4 and following remark). When $\alpha=0$, $\Delta E=0$, so this proves the theorem. In the non-neutral case the $\mu_a\neq 0$ and it is necessary to take into account the change of μ_a with α. This is complicated (see LS).

The second proof is due to Baxter (1980). For any ρ_{12} with $\int\rho_{12}=\lambda$ we can, by Prop. 3.24, find g, $0\le g(x)\le\rho_{12}(x)$, and $h(x)\equiv\rho_{12}(x)-g(x)$ such that $\psi_g(x)=\psi_{m_1}(x)=V_1(x)$ a.e. when $h(x)>0$, and $\psi_g(x)\le V_1(x)$ a.e. when $h(x)=0$.

Let $a=\int g$, $b=\int h$. Then

$$\begin{aligned}\min\{e_1(\lambda_1)+e_2(\lambda_2)\,|\,\lambda_1+\lambda_2=\lambda\}&\le e_1(a)+e_2(b)\le\mathcal{E}_1(g)+\mathcal{E}_2(h)\\&\le\mathcal{E}_{12}(\rho_{12})+2D(m_1,m_2)+\int h(V_1-\psi_g)dx-\int(V_1-\psi_g)dm_2\\&\le e_{12}(\lambda)+2D(m_1,m_2).\end{aligned}\tag{3.19}$$

The third inequality uses the superadditivity of j. If j' is strictly monotone this superadditivity is strict (and so is the final inequality) provided $g\neq\rho_{12}$. If $g=\rho_{12}$ a.e. then $\psi_{\rho_{12}}\le V_1$ and hence $\lambda\le z_1$ must hold. Choose $\lambda_1=\lambda$, $\lambda_2=0$ and note that $e_1(\lambda)<\mathcal{E}_1(\rho_{12})$ because ρ_{12} does not satisfy Eq. (3.2) since $V_2\neq 0$. Equation (3.19) then gives strict inequality. ■

Proposition 3.24 (Baxter, 1980). *Let $V\in\mathfrak{D}$ and let $\rho(x)\ge 0$ be a given function with $|x|^{-1}*\rho\equiv\psi_\rho\in\mathfrak{D}$. Assume $\rho\in L^p$ for some $p>\frac{3}{2}$ and $D(\rho,\rho)<\infty$. Then there exists g with $0\le g(x)\le\rho(x)$ such that $\psi_g=|x|^{-1}*g$ satisfies $\psi_g(x)=V(x)$ a.e. when $\rho(x)-g(x)>0$ and $\psi_g(x)\le V(x)$ a.e.*

Proof. Baxter proves this when ρ and g are measures. We give a simpler proof for functions. Consider $\mathcal{E}(g)\equiv D(g,g)-\int Vg$ and $E=\inf\{\mathcal{E}(g)\,|\,0\le g(x)\le\rho(x)\}$. Let g^n be a minimizing sequence. There exists a subsequence that converges weakly in L^p to some g and, by Mazur's theorem (1933), there exists a sequence h^n of convex combinations of the g^n that converges strongly to g in L^p. Then a subsequence of the h^n converges a.e. to g. Clearly, $0\le h^n(x)\le\rho(x)$. Since $\mathcal{E}(\cdot)$ is convex (this is crucial) $\mathcal{E}(h^n)\to E$ but, by dominated convergence, $\mathcal{E}(h)\to\mathcal{E}(g)$. So g minimizes and satisfies (a.e.): $V(x)=\psi_g(x)$ when $0<g(x)<\rho(x)$; $\psi_g(x)\le V(x)$ when $g(x)=\rho(x)$ and $\rho(x)>0$; $\psi_g(x)\ge V(x)$ when $g(x)=0$ and $\rho(x)>0$. We have to eliminate the possibility $\psi_g(x)-V(x)\equiv f(x)>0$ when $g(x)=0$. We claim $\psi_g\in\mathfrak{D}$ and hence f is continuous and goes to zero at ∞. Since $g\le\rho$, $\psi_g\le\psi_\rho$ so $\psi_g\to 0$ at infinity. To examine the continuity at $x=0$, write $\psi_g=h+(\psi_g-h)$ with $h=|x|^{-1}*(\chi g)$ and χ is the characteristic function of the ball $|x|<1$. Clearly ψ_g-h is continuous at $x=0$. Moreover, $\chi g\in L^p\cap L^1$ so $h\in\mathfrak{D}$ by Lemma 3.1. (It is here that $p>\frac{3}{2}$ is used.) Now, since $f\in\mathfrak{D}$, $B=\{x\,|\,f(x)>0\}$ is open and, since $x\in B\Rightarrow g(x)=0$, f is subharmonic on B. But f vanishes on the boundary of B and at infinity, so B is empty. ■

IV. DEPENDENCE OF THE THOMAS-FERMI ENERGY ON THE NUCLEAR COORDINATES

In the previous sections TF theory was analyzed when the nuclear coordinates $\{R_j\}$ are held fixed. The one exception was Teller's theorem (Theorem 3.23) which states that the TF energy is greater than the TF energy for isolated atoms (which is the same as the energy when the R_j are infinitely far apart). Here, more detailed information about the dependence of E on the R_j is reviewed.

Note that in this section (and henceforth) E refers to the total energy, [Eq. (2.11)], including the repulsion U. This is crucial.

Although several unsolved problems remain, a fairly complete picture will emerge. The principal open problem is to prove the positivity of the pressure (Sec. IV.B) for subneutral molecules, and to prove it for deformations more general than uniform dilation. The results of this section have been proved only for TF theory, and it is not known which ones extend to the variants (see the discussion of TFD theory in Sec. IV.C).

A. The many-body potentials

The results here are from Benguria and Lieb, 1978a. As usual, the two-body atomic energy is *defined* to be the difference between the energy of a diatomic molecule (with nuclear separation R) and the energy of iso-

lated atoms. Teller's theorem states that this is always positive. We shall now investigate the k-body energy which can be defined similarly. The three-body energy will be shown to be negative, the four-body positive, etc. In all cases, only neutral systems will be considered; in this case there is a unique way to apportion the electron charge among the isolated atoms, namely, make them all neutral. An interesting problem is to treat the k-body energy for subneutral systems.

Definitions. When $c=\{c_1, c_2, \ldots, c_k\}$ is a finite subset of the positive integers with $|c|=k$ elements, $E(c)$ denotes the TF energy for a neutral molecule consisting of nuclear charges $z_{c_i}>0$ located R_{c_i}. $\phi(c,x)$ denotes the TF potential for this molecule. The z's can all be different.

$$\varepsilon(c)=\sum_{b\subseteq c}(-1)^{|b|+|c|}E(b) \tag{4.1}$$

is the $|c|$ body energy for this molecule. Thus, if $c=\{1,2\}$, $|c|=2$ and the two-body energy is $\varepsilon(1,2)=E(1,2)-E(1)-E(2)$ as explained above. If $c=\{1,2,3\}$, $|c|=3$ and the three-body energy is

$$\varepsilon(1,2,3)=E(1,2,3)-[E(1,2)+E(1,3)+E(2,3)]+E(1)+E(2)+E(3).$$

$E(1), E(2), E(3)$ are atomic energies, of course. From Eq. (4.1)

$$E(c)=\sum_{b\subseteq c}\varepsilon(b). \tag{4.2}$$

It is worth remarking that the many-body energies (4.1) are defined in terms of the *total* energy E. It is equally possible to use $e=E-U$ on the right side of Eq. (4.1). e is the *electronic contribution* to E, so the corresponding ε's would be the *electronic contribution to the many-body potential*. However, note that U contains only two-body pieces, $z_iz_j|R_i-R_j|^{-1}$. Therefore the two sets of ε's agree whenever $|c|\geq 3$, i.e., the three- and higher-body ε's are entirely electronic. As far as the two-body energy is concerned, $\varepsilon(1,2)_{\text{tot}}>0$ (Teller) but

$$\varepsilon(1,2)_{\text{elec}}=\varepsilon(1,2)_{\text{tot}}-U(1,2)<0$$

(Theorem 3.21).

In the following $b\subset c$ means b is a subset of c and $b\neq c$.

Theorem 4.1 (Sign of the many-body potential). *If c is not empty*

$$(-1)^{|c|}\varepsilon(c)>0.$$

More generally, if $b\subset c$ and either $|c\setminus b|\geq 2$ or else $|b|=0$ and $|c|>0$

$$\tilde{E}(b,c)\equiv\sum_{b\subseteq a\subseteq c}(-1)^{|b|+|a|}E(a)>0.$$

Theorem 4.2 (Remainder Theorem). *If $2\leq\beta\leq|c|$ then the sign of*

$$E(c)-\sum_{\substack{b\subset c\\ |b|<\beta}}\varepsilon(b)$$

is $(-1)^{\beta}$. In other words, if, in Eq. (4.2), we sum only over the terms smaller than β-body, the sign of the error is the sign of the first omitted terms.

Theorem 4.3 (Monotonicity of the many-body potential). *Suppose that $b\subset c$ and $|b|\geq 2$. Then*

$$(-1)^{|b|}\varepsilon(b)>(-1)^{|c|}\varepsilon(c).$$

Theorems 4.1 and 4.3 imply, for example,

$$0>\varepsilon(1,2,3)>-\min[\varepsilon(1,2),\varepsilon(1,3),\varepsilon(2,3)].$$

Theorem 4.4. *If $b\subset c$ and c is not empty*

$$\tilde{\phi}(b,c,x)\equiv\sum_{b\subseteq a\subseteq c}(-1)^{|a|+|b|}\phi(a,x)<0.$$

Partial Proof. Basically Theorems 4.1, 4.2, and 4.3 are corollaries of Theorem 4.4 through the relation, for $j\in c$,

$$\frac{\partial E(c)}{\partial z_j}=\lim_{x\to R_j}\{\phi(c,x)-z_j|x-R_j|^{-1}\},\quad\text{(Theorem 2.13).}$$

As an illustration we shall prove here that $\varepsilon(1,2,3)<0$; surprisingly, the proof is much more complicated when $|c|>3$. The proof for $|c|=3$ only uses that the function $(j')^{-1}$ is convex [cf. Eq. (3.1)]. The proof for $|c|>3$ requires that $j(\rho)=\rho^k$ with $\frac{3}{2}\leq k\leq 2$.

First note that $\varepsilon(1,2,3)=0$ when $z_3=0$. Thus it suffices to prove that $\partial\varepsilon(1,2,3)/\partial z_3=F(R_3)<0$, where

$$F(x)\equiv\phi(1,2,3,x)-\phi(1,3,x)-\phi(2,3,x)+\phi(3,x).$$

Now

$$\Delta F=4\pi[\rho(1,2,3,x)-\rho(1,3,x)-\rho(2,3,x)+\rho(3,x)]$$

and $\rho=(\phi/\gamma)^{3/2}$. Let $B=\{x\,|\,F(x)>0\}$. F is continuous, so B is open. We claim F is subharmonic on B, which implies B is empty. What is needed is the fact that $a-b-c+d\geq 0\Rightarrow a^{3/2}-b^{3/2}-c^{3/2}+d^{3/2}\geq 0$ under the conditions that $a\geq b\geq d\geq 0$ and $a\geq c\geq d\geq 0$ (Theorem 3.4). But this is an elementary exercise in convex analysis. Finally, as in the strong form of Theorem 3.4, one can prove that F is strictly negative. ■

It is noteworthy that *all* the many-body potentials fall off at the same rate, R^{-7}. This will be shown in Sec. IV.C.

B. The positivity of the pressure

Teller's theorem (Theorem 3.23) suggests that the nuclear repulsion dominates the electronic attraction and therefore a molecule in TF theory should be unstable under local as well as global dilations.

Let us fix the nuclear charges $\underline{z}=\{z_1,\ldots,z_k\}$ and move the R_i keeping λ fixed. Under which deformations does E decrease? We can also ask when $e=E-U$, *the electronic contribution to the energy*, decreases. A natural *conjecture* is the following: Suppose $R_i\to R_i'$ with $|R_i'-R_j'|\geq|R_i-R_j|$ for every pair i,j. Then

(i) E decreases and e increases.

(ii) Furthermore, if $\lambda_1<\lambda_2$ then the decrease (increase) in $E(e)$ is smaller (larger) for λ_2 than for λ_1.

There is one case in which this conjecture can be proved; it is given in Theorem 4.7 due to Benguria (1981).

One interesting case is that of uniform dilation in

which each $R_i \to lR_i$. For this case we define the *pressure* and *reciprocal compressibility* to be

$$P(l) = -(3l^2)^{-1} dE(l)/dl \tag{4.3}$$

$$\kappa^{-1} = -(l/3) dP(l)/dl\,, \tag{4.4}$$

where $E(l)$ is the energy. This definition comes from thinking of the "volume" as proportional to l^3. If $K(l)$ is the kinetic energy [Eq. (2.20)] then

$$3l^3 P(l) = E(l) + K(l)\,.$$

To see this, define $E(\gamma, l)$ to be the energy with the parameter γ thought of as a variable (but with λ fixed). Then, by setting $\rho(x,l) = l^{-3}\tilde{\rho}(x/l, l)$, one easily sees that $E(\gamma, l) = l^{-1}E(\gamma/l, 1)$ and $K(\gamma, l) = l^{-1}K(\gamma/l, 1)$. Equation (4.4) follows from this and Theorem 2.13.

Note that Eq. (4.4) is true (for the same reason) in Q theory and also in TFD, TFW, and TFDW theories provided K is interpreted as Eq. (2.20) in TFD and as (2.20) $+ \delta\int [\nabla\rho^{1/2}]^2$ in TFDW and TFW.

That $e = E - U$ increases under dilation has also been conjectured to hold in Q theory when $\lambda \leq Z$. It is known to hold for one electron, but an arbitrary number of nuclei (Lieb and Simon, 1978). There is one simple statement that can be made (in all theories): The (unique) minimum of e occurs when $l = 0$ (for any $\lambda > 0$), i.e., all the nuclei are at one point. To prove this, assume $R_1, \ldots, R_k$ are not all identical and let ρ be the minimizing solution. Let $\psi = |x|^{-1} * \rho$. ψ has a maximum at some point R_0. Now place all the nuclei at R_0 and use the same ρ as a variational ρ for this problem. Then, trivially, $e(R_0, \ldots, R_0) < e(R_1, \ldots, R_k)$, with the strict inequality being implied by the fact that this ρ does not satisfy the variational equation for $R_0, \ldots, R_0$.

It is useful to have a formula for the variation of e with R_i. A natural extension of Theorem 2.13 (a "Feynman-Hellman"-type theorem) would be the following: Suppose $V_1, \ldots, V_k \in \mathfrak{D}$ with

$$V_i(x) = \int dm_i(y)\,|y - x|^{-1} \tag{4.5}$$

and with m_i a positive measure of mass z_i. Take

$$V(x) = \sum_{i=1}^{k} V_i(x - R_i)\,.$$

Then e is a C^1 function of the R_i and

$$\nabla_{R_i} e = \int \nabla V_i(x - R_i)\,\rho(x)dx = -\int dm_i(y)\nabla\psi(y + R_i)\,, \tag{4.6}$$

with $\psi = |x|^{-1} * \rho$. Equation (4.6) is clearly true, and easy to prove if the m_i are suitably bounded. Benguria (unpublished) proved (4.6) when $V_i(x) = z_i|x|^{-1}$ for $|x| \geq a$ and $V_i(x) = z_i a^{-1}$ for $|x| \leq a$, with $a > 0$, i.e., $dm_i(y) = z_i(\text{const})\delta(|y| - a)$. In this case, the last equality in Eq. (4.6) follows from LS, Lemma IV.4.

For point nuclei, on the other hand, (4.6) has not been proved; indeed, the quantities in (4.6) are not even well defined. We conjecture that the following is true when $V_i(x) = z_i|x|^{-1}$: e is a C^1 function of the R_i on the set where $R_i \neq R_j$, for all $i \neq j$, and

$$\nabla_{R_i} e = -z_i \lim_{a \downarrow 0} \int_{|x - R_i| > a} (x - R_i)\,|x - R_i|^{-3}\rho(x)\,dx \tag{4.7a}$$

$$= -\lim_{x \to R_i} \nabla_x \{\psi(x) + (z_i/\gamma)^{3/2}(16\pi/3)\,|x - R_i|^{1/2}\}\,. \tag{4.7b}$$

Equation (4.7a) makes sense because, by Theorem 2.8,

$$\rho(x) = (z_i/\gamma)^{3/2}|x - R_i|^{-3/2} + O(|x - R_i|^{-1/2})$$

near R_i; the angular integration over the first term vanishes. This leading term in ρ implies that near R_i, $\psi(x) \approx (\text{const}) - (z_i/\gamma)^{3/2}(16\pi/3)|x - R_i|^{1/2}$. The nondifferentiable, but spherically symmetric term in ψ is subtracted in Eq. (4.7b).

The following theorems have been proved so far. (Theorems 4.5 and 4.6 are in Benguria and Lieb, 1978b; Theorem 4.7 is in Benguria, 1981.)

Theorem 4.5 (Uniform dilation). *Replace each R_i by lR_i and call the energy $E(\lambda, l)$. If $\lambda = Z$ then $E(\lambda, l)$ is strictly monotone decreasing and convex in l. In particular, the pressure and compressibility are positive.*

Remarks. (i) If $\lambda = 0$ the conclusion is obviously also true. In Benguria and Lieb (1978b) it is conjectured that this theorem holds for all λ. That $e = E - U$ is *monotone increasing* is also conjectured there.

(ii) In Benguria and Lieb (1978b) several interesting subadditivity and convexity properties of the energy and potential are also proved.

Theorem 4.6 (Molecule with planar symmetry). *Suppose the molecule is symmetric with respect to the plane $P = \{(x^1, x^2, x^3)\,|\,x^1 = 0\}$ and suppose no nucleus lies in the plane. Neutrality is not assumed. Let R_i^1 denote the 1 coordinate of nucleus i and, for all i, replace R_i^1 by $R_i^1 \pm l$, with $\pm$ if $R_i^1 \geq 0$, and $l \geq 0$. Then for all fixed $\lambda \leq Z$, E is decreasing in l.*

Remark. For a homopolar diatomic molecule the dilations in Theorems 4.5 and 4.6 are the same. Balàzs (1967) first proved Theorem 4.6 in this case. For a general diatomic molecule, Benguria's Theorem 4.7 is the strongest theorem.

Theorem 4.7. *Suppose there exists a plane P containing $R_1, \ldots, R_m$ and such that all the other R_j (with $j = m+1, \ldots, k$) are on one (open) side of P (call this side P^+). Assume the nuclei at $R_1, \ldots, R_m$ are point nuclei, but the nuclei at $R_{m+1}, \ldots, R_k$ are anything in $\mathfrak{D}$ and given by Eq. (4.5) with the supports of $m_i \in P^+$ (this includes point nuclei). Let $\mathbf{n}$ be the normal to P pointing away from P^+. Let $l_1, \ldots, l_m \geq 0$ be given and let $R_i \to R_i + l_i\mathbf{n}$ for $i = 1, \ldots, m$. Let $E(\lambda, l)$ denote the energy for fixed $\lambda \leq Z$ and let $\Delta E(\lambda, l) = E(\lambda, l) - E(\lambda, 0)$ denote the change in energy. Likewise define $\Delta e(\lambda, l) = \Delta E(\lambda, l) - \Delta U$. Then*

(i) $\Delta e(\lambda, l) \geq 0$,

(ii) $\Delta E(\lambda, l) \leq 0$,

(iii) $\Delta E(\lambda_1, l) \leq \Delta E(\lambda_2, l)$ *if* $\lambda_1 \leq \lambda_2$,

(iv) $\Delta e(\lambda_1, l) \leq \Delta e(\lambda_2, l)$ if $\lambda_1 \leq \lambda_2$.

To prove Theorem 4.7 the following Lemma 4.8, which is of independent interest, is needed.

Lemma 4.8. *Assume the plane P, with $R_1, \ldots, R_m$ in P and $R_{m+1}, \ldots, R_k$ in P^+ as in Theorem 4.7. However, point nuclei are not assumed. Instead, assume each V_i*

$\in D$ *and given by Eq. (4.5), with* m_i *required to be spherically symmetric for* $i=1,\ldots,m$. *This includes point nuclei. Assume also that the support of* $m_i \subset P^+$ *for* $i=m+1,\ldots,k$. If $x\in P^+$ *then* x^* *is defined to be the reflection of* x *through* P. *Let* ϕ *be the potential. For* $x\in P^+$, *let* $\phi_-(x)=\phi(x^*)$ *and* $f(x)=\phi(x)-\phi_-(x)$. *Then*

(*i*) $f(x)>0$ *for* $x\in P^+$.

(*ii*) *For each* $x\in P^+$, $f(x)$ *strictly decreases when* λ *increases.*

(*iii*) $\rho(x)-\rho(x^*)\geq 0$ *for* $x\in P^+$.

Question. Is it true that $\rho(x)-\rho(x^*)$ is a monotone increasing function of λ?

Proof. (i) Clearly $f(x)=0$ on $\partial P^+=P$ and at ∞. Let $B=\{x\in P^+ \mid f(x)<0\}$. Since each $V_i(x)$ is symmetric decreasing the singularities of V are not in B. Thus B is open. On B, $-\Delta f(x)/4\pi \geq -\rho(x)+\rho(x^*)>0$. Thus f is superharmonic on B so B is empty. By the strong maximum principle $f(x)>0$, in fact, for $x\in P^+$.

(ii) Let $\lambda'<\lambda$ with corresponding f' and f. We want to prove $B=\{x\in P^+ \mid f(x)-f'(x)>0\}$ is empty. B is open and $f-f'=0$ on P and at ∞. $\Delta(f-f')/4\pi = a_+^{3/2}-b_+^{3/2}-c_+^{3/2}+d_+^{3/2}\equiv h$, where $a=\phi-\mu, b=\phi'-\mu', c=\phi_--\mu$, $d=\phi'_--\mu'$. By (i) and Corollary 3.8, $a\geq b>d$ and $a>c\geq d$ for all $x\in P^+$. In B, $a+d>b+c$. Thus $h\geq 0$ in B, whence $f-f'$ is subharmonic on B and hence B is empty. Again, one can prove the stronger result that $f-f'<0$ for $x\in P^+$. Trivially, (i)$\Rightarrow$ (iii) through the TF equation. ■

Proof of Theorem 4.7. We may assume all the l_i are equal to some common l, for otherwise if $l_1\leq l_2\leq\cdots\leq l_m$ we could first move all the m nuclei by l_1, then move $R_2,\ldots,R_m$ by l_2-l_1, etc. Next, replace all the point nuclei at $R_1,\ldots,R_m$ by smeared potentials given by Eq. (4.5) with $dm_i(x)=z_i g^{(n)}(x)dx$ where $g^{(n)}(x)\in C_0^\infty$ and $g^{(n)}$ is symmetric decreasing and with sufficiently small support such that the supports of dm_i $(i=1,\ldots,m)$ are pairwise disjoint and also disjoint from the supports of dm_i $(i=m+1,\ldots,k)$. Under these conditions, e is C^1 in $R_1,\ldots,R_m$ in some neighborhood of the original $R_1,\ldots,R_m$ with derivatives given by Eq. (4.6). We shall prove

(*i*)′ $\mathbf{n}\cdot\nabla_{R_i}e\geq 0$,

(*ii*)′ $\mathbf{n}\cdot\nabla_{R_i}E\leq 0$,

and that (*iii*) and (*iv*) hold for these derivatives. Then the theorem is proved because the original point potentials $z_i|x|^{-1}$ can be approximated in $L^{5/2}$ norm by these smeared potentials $z_i|x|^{-1}*g^{(n)}$, and the energies $e^{(n)}$ and $E^{(n)}$ converge to e and E by LS, Theorem II.15. If (*i*)′ holds for $e^{(n)}$, then $(d/dl)e^{(n)}(\lambda,l)\geq 0$ with $R_i\to R_i+l\mathbf{n}$, $i=1,\ldots,m$, and, by integration, (*i*) holds for $e^{(n)}$. Then, when $n\to\infty$, (*i*) holds for e. The same applies to (*ii*)–(*iv*). Henceforth the superscript (n) will be suppressed.

Assume $\mathbf{n}=(1,0,0)$, $P=\{x \mid x^1=0\}$, and thus $(R_i)^1=0$ for $i=1,\ldots,m$. Since g is symmetric decreasing,

$$(\partial g/\partial x^1)(x^1,x^2,x^3)=-x^1h(x^1,x^2,x^3)$$

with $h(x)\geq 0$ and

$$h(x^1,x^2,x^3)=h(-x^1,x^2,x^3).$$

Likewise,

$$(\partial V_i/\partial x^1)(x^1,x^2,x^3)=-z_i x^1 p(x^1,x^2,x^3),$$

and p has the same properties as h. To prove (*i*)′ use Eq. (4.6) whence

$$\mathbf{n}\cdot\nabla_{R_i}e/z_i=-\int x^1 p(x-R_i)\rho(x)dx$$

$$=-\int_{x^1\leq 0} p(x-R_i)[\rho(x)-\rho(x^*)]x^1dx\geq 0$$

by Lemma 4.8. To prove (*ii*)′ use the second integral in Eq. (4.6), whence

$$B_i\equiv\mathbf{n}\cdot\nabla_{e_i}E=\int dm_i(y)\mathbf{n}\cdot\nabla\phi(y+R_i),$$

where ϕ is the potential. [Note: $V_i(x-R_i)$ is symmetric in x about R_i, so the term $\nabla V_i(x-R_i)$ does not contribute to this integral.] Since V_i is C^∞ it is easy to see that ϕ is also C^∞ near R_i. Now integrate by parts:

$$B_i=-\int \mathbf{n}\cdot\nabla g(y)\phi(y+R_i)dy$$

$$=\int y^1h(y)\phi(y+R_i)dy$$

$$=\int_{y^1\leq 0} y^1h(y)[\phi(y+R_i)-\phi_-(y+R_i)]\leq 0$$

by Lemma 4.8. To prove (*iii*) note that the last quantity [ ] decreases when λ increases by Lemma 4.8. Clearly (*iii*) is equivalent to (*iv*). ■

Proof of Theorem 4.6. Let $\rho(x)$ be the density when $l=0$. For $l>0$ use the variational $\tilde\rho$ given by $\tilde\rho(x^1,x^2,x^3)=\rho(x^1\mp l,x^2,x^3)$ if $x^1\gtrless l$ and $\tilde\rho(x)=0$ otherwise. Then all terms in the energy $\mathcal{E}(\tilde\rho)$ remain the same except for the Coulomb interaction of the two charge distributions on either side of the plane P. This term is of the form

$$W(l)=\int_{x^1,y^1\geq 0} d^3x\,d^3y\,f(x)f(y)\times[(x^1+y^1+2l)^2+(x^2-y^2)^2+(x^3-y^3)^2]^{-1/2},$$

where $f(x)=-\rho(x)+\sum{}' z_j\delta(x-R_j)$ and the $\sum'$ is over those R_i with $R_i^1>0$. Since the Coulomb potential is reflection positive (Benguria and Lieb, 1978, Lemma B.2), $W(l)$ is a decreasing, log convex function of l. ■

Proof of Theorem 4.5. Let $\underline{z}=(z_1,\ldots,z_k)$ and write $E(\underline{z})$, $K(\underline{z})$, $A(\underline{z})$, and $R(\underline{z})$ for the energy and its components (cf. Sec. II.E) of a neutral molecule. These functions are defined on $\mathbb{R}_+^k$. For an atom $3P=E+K=0$ (Theorem 2.14). By Theorem 3.23, $E\geq\sum_1^k E^{\text{atom}}(z_j)$ and, by Theorem 4.10, $K\geq\sum_1^k K^{\text{atom}}(z_j)$. This shows $P\geq 0$. Likewise, by Theorem 4.12, $\kappa^{-1}\geq 0$ and $E(\underline{z},l)$ is convex in l (equivalently l^2P is decreasing in l). ■

Definition. Let f be a real valued function on $\mathbb{R}_+^k$ and $\underline{z}_1,\underline{z}_2,\underline{z}_3\in\mathbb{R}_+^k$. Then f is

(i) *weakly superadditive* (WSA) $\Leftrightarrow f(\underline{z}_1+\underline{z}_2)\geq f(\underline{z}_1)+f(\underline{z}_2)$ whenever $(z_1)_i(z_2)_i=0$, all i,

(ii) *superadditive* (SA) $\Leftrightarrow f(\underline{z}_1+\underline{z}_2)\geq f(\underline{z}_1)+f(\underline{z}_2)$,

(*iii*) *strongly superadditive* (SSA) $\Leftrightarrow f(\underline{z}_1+\underline{z}_2+\underline{z}_3)+f(\underline{z}_1)\geq f(\underline{z}_1+\underline{z}_2)+f(\underline{z}_1+\underline{z}_3)$.

Theorems 4.9–4.12 are for neutral molecules.

Theorem 4.9. *As a function of* $\underline{z}\in\mathbb{R}_+^k$, *for each fixed*

$x \in \mathbb{R}^3$,

(i) $-\phi(\underline{z}, x)$ *is SSA, convex, and decreasing (the latter is Teller's lemma),*

(ii) $\phi(\underline{z}, x) \in C^1(\mathbb{R}^k_+)$ *and* $\in C^2(\mathbb{R}^k_+ \setminus 0)$,

(iii) $\phi_i(\underline{z}, x)$ *is decreasing in* $\underline{z}$ *and* > 0,

(A subscript i denotes $\partial/\partial z_i$.*)*

(iv) $\phi_{ij}(\underline{z}, x) \leq 0$ *(all* i,j*) and is negative semidefinite as a* $k \times k$ *matrix.*

Remark. It is easy to prove that when $f \in C^2(\mathbb{R}^k_+)$ then SSA is equivalent to $f_{ij} \geq 0$ for all i,j. See Benguria and Lieb, 1978b, for this and similar equivalences.

Theorem 4.10. $K(\underline{z}) \in C^1(\mathbb{R}^k_+)$ *and* $\in C^2(\mathbb{R}^k_+ \setminus 0)$

(i) $K_i(\underline{z}) = 3 \lim_{x \to R_i} \left\{ \phi(\underline{z}, x) - \sum_{j=1}^{k} z_j \phi_j(\underline{z}, x) \right\}$,

(ii) $K_{ij}(\underline{z}) = -3 \sum_{\rho=1}^{k} z_\rho \phi_{ij}(\underline{z}, R_\rho)$,

(iii) $K(\underline{z})$, $R(\underline{z})$, *and* $A(\underline{z})$ *are SSA and SA and convex,*

(iv) $E(\underline{z})$ *is WSA (Teller's theorem).*

Definition. $X(\underline{z}) \equiv 3K(\underline{z}) - \sum_{i=1}^{k} z_i K_i(\underline{z})$.

Theorem 4.11. $X(\underline{z})$ *is SA and SSA and ray convex. I.e.,* $X(\lambda \underline{z}_1 + (1-\lambda)\underline{z}_2) \leq \lambda X(\underline{z}_1) + (1-\lambda) X(\underline{z}_2)$, $0 \leq \lambda \leq 1$, *when* $\underline{z}_1, \underline{z}_2 \in \mathbb{R}^k_+$ *and either* $\underline{z}_1 - \underline{z}_2$ *or* $\underline{z}_2 - \underline{z}_1 \in \mathbb{R}^k_+$.

Theorem 4.12. *(i)* $3l^3 P = E + K$,

(ii) $9l^3 \kappa^{-1} = 6l^3 P + 2E + 3X$,

(iii) P *and* κ^{-1} *are WSA and non-negative,*

(iv) $l^2 P$ *is decreasing in* l. *Equivalently,* E *is convex in* l. *Equivalently,* $2E + 3X \geq 0$

[*note:* $\partial(l^2 P)/\partial l = 2lP - 3l\kappa^{-1} = -(\frac{1}{3})(2E + 3X)$].

Proof of (iv). $2E + 3X = 0$ for an atom. By Theorem 4.10, $2E + 3X \geq 0$. ■

The proofs of Theorems 4.9–4.12 are complicated. However, if all necessary derivatives are assumed to exist, then an easy heuristic proof can be given (see Benguria and Lieb, 1978b). We illustrate this for K being SSA, which is equivalent to $K_{ij} \geq 0$, all i,j. This will then prove $P \geq 0$, since $K(0) = 0$. First we show $\phi_{ij} \leq 0$ and then Theorem 4.10 (ii).

Differentiate the TF differential equation [$\Delta\phi/4\pi = -\sum z_j \delta(x - R_j) + (\phi/\gamma)^{3/2}$, which holds for any *neutral* system] with respect to z_i and then z_j:

$$\mathcal{L}\phi_i = \delta(x - R_i), \tag{4.8}$$

$$\mathcal{L}\phi_{ij} = -(3/4\gamma^{3/2})\phi^{-1/2}\phi_i\phi_j, \tag{4.9}$$

with $\mathcal{L} = -\Delta/4\pi + (3\gamma^{-3/2}/2)\phi(x)^{1/2}$. The kernel for $\mathcal{L}^{-1}$ is a positive function, so $\phi_i \geq 0$. Likewise $\phi_{ij} \leq 0$ and ϕ_{ij} is a negative semidefinite matrix.

Next, $K = (3\gamma^{-3/2}/5)\int \phi^{5/2}$, so

$$K_{ij} = (3\gamma^{3/2}/2)\left\{ \int \phi^{3/2}\phi_{ij} + \tfrac{3}{2} \int \phi^{1/2}\phi_i\phi_j \right\}.$$

Using Eq. (4.9) and integrating by parts,

$$K_{ij} = 3 \int \phi_{ij} [\Delta\phi/4\pi - (\phi/\gamma)^{3/2}]$$

$$= -3 \sum_{\rho=1}^{k} z_\rho \phi_{ij}(R_\rho) \geq 0.$$

C. The long-range interaction of atoms

In Sec. IV.B it was shown that the energy of a molecule decreases monotonically under dilation (at least for neutral molecules). If the $R_i \to lR_i$ then, for small l, E is dominated by U, so $E \approx l^{-1}$. To complete the picture it is necessary to know what happens for large l. We define

$$\Delta E = E^{\text{mol}} - \sum_{j=1}^{k} E^{\text{atom}}. \tag{4.10}$$

For large l it is reasonable to consider only neutral molecules, for otherwise $\Delta E \approx l^{-1}$ because of the unscreened Coulomb interaction. In the neutral case $\Delta E \approx l^{-7}$, as proved by Brezis and Lieb (1979). This result (l^{-7}) is not easy to ascertain numerically (Lee, Longmire, and Rosenbluth, 1974), so once again the importance of pure analysis in the field is demonstrated. Some heuristic remarks about the result are given at the end of this section.

A surprising result is that *all* the many-body potentials are $\approx l^{-7}$. Thus in TF theory it is *not* true that the interaction of atoms may be approximated purely by pair potentials at large distances.

An interesting open problem is to find the long-range interaction of polyatomic molecules of fixed shape. Presumably this is also $\approx l^{-7}$.

Theorem 4.13. *For a neutral molecule, let the nuclear coordinates be* lR_i *with* $\{R_i, z_i\} = (\underline{R}, \underline{z})$ *fixed and* $z_i > 0$. *Then*

$$\Delta E(l, \underline{z}, \underline{R}) \equiv l^{-7} C(l, \underline{z}, \underline{R}),$$

where C *is increasing in* l *and has a finite limit,* $\Gamma(\underline{R}) > 0$ *as* $l \to \infty$. Γ *is independent of* $\underline{z}$. *Furthermore, if* A *denotes a subset of the nuclei (with coordinates* $\underline{R}_A$*), and* $\varepsilon(A)$ *is the many-body potential of Eq. (4.1), then, by (4.1), for* $|A| \geq 2$

$$l^7 \varepsilon(A) \to \sum_{B \subseteq A} (-1)^{|A| - |B|} \Gamma(\underline{R}_B) \tag{4.11}$$

and the right side of Eq. (4.11) *is strictly positive (negative) if* $|A|$ *is even (odd).*

Proof of first part. By scaling, Eq. (2.24), we find that

$$\Delta E(l, \underline{z}, \underline{R}) = l^{-7} \{ E(l^3 \underline{z}, \underline{R}) - \sum_j E^{\text{atom}}(l^3 z_j) \}.$$

Therefore, C increasing is equivalent to $f = E^{\text{mol}} - \sum E^{\text{atom}}$ increasing in $\underline{z}$. But $\partial f/\partial z_j = \lim_{x \to R_j} \phi^{\text{mol}}(x) - \phi^{\text{atom}}(x)$, and this is positive by Teller's lemma. All that has to be checked is that C is bounded above. This is done by means of a variational ρ for E^{mol}. Let B_i be a ball of radius lr_i centered at lR_i; the r_i are chosen so that the B_i are disjoint. Let $\rho_i(x) = \rho^{\text{atom}}(x - lR_i)$ be the TF atomic densities for z_i, and let $\rho(x) = \rho_i(x)$ in B_i and $\rho(x) = 0$ otherwise. Of course $\int \rho < \sum z_j$ but this is immaterial for a variational calculation, since the minimum molecular energy occurs when $\int \rho = \sum z_j$. It is easy to check that $f < (\text{const}) l^{-7}$. Finally, since f is monotone in each z_i, $\lim_{l \to \infty} f$ must be independent of the z_j. ■

Remarks. (i) The variational calculation shows clearly why Γ is independent of the z_j. The long-range interaction comes, in some sense, from the tails of the atomic ρ's, but these tails are independent of z, namely $\rho(x) \approx (3\gamma/\pi)^3 |x|^{-6}$. (See Theorem 2.10.)

(ii) At first sight it might appear counterintuitive that the interaction is $+l^{-7}$ and not $-l^{-6}$, as would be obtained from a dipole-dipole interaction. The following heuristic remark might be useful in this respect. Consider two neutral atoms separated by a large distance R. In the quantum theory, as in all the theories discussed in this paper, there is almost no *static* polarization of the atoms; i.e., there is no polarization of the single-particle density ρ. TF theory is therefore correct as far as the density is concerned. The reason there is no polarization is that the formation of a dipole moment d increases the atomic energy by $+\alpha d^2$ with $\alpha > 0$. The dipole-dipole energy gain is $-(\text{const}) d^2 R^{-3}$. Hence, if R is large enough, the formation of dipoles does not decrease the energy. In quantum theory there is, in fact, a $-R^{-6}$ dipolar energy, but this effect is a correlation, and not a static effect. There are two ways to view it. In second-order perturbation theory there are *virtual* transitions to excited, polarized states. Alternatively, the electrons in each atom are correlated so that they go around their respective atoms in phase, but spherically symmetrically. This correlated motion increases the internal atomic energy only by αd^4, not d^2. In short, the $-R^{-6}$ interaction arises from the fact that the density ρ is not that of a structureless "fluid" but is the average density of many separate particles which can be correlated. This fact poses a serious problem for any "density functional approach." It is necessary to predict a $-R^{-6}$ dipolar interaction, yet predict essentially zero static polarization.

An explicit formula for $\Gamma(\underline{R})$ does not seem to be easy to obtain. Two not very explicit formulas are given in Brezis and Lieb, 1979. One is simply to integrate the formula for $\partial f/\partial l = 3l^2 \sum z_j \partial f/\partial z_j$ given in the above proof. Another is obtained by noting that Γ is related to ϕ in the limit $z \to \infty$. This limiting ϕ can be defined, and satisfies the TF differential equation, but with a *strong singularity* at R_i instead of the usual $z|x - R_i|^{-1}$ singularity. As we saw in Theorem 2.11, the only other singularity allowed for the TF equation is $\phi(x) \approx \gamma^3 (3/\pi)^2 |x - R_i|^{-4}$. Therefore that peculiar solution to the TF equation does have physical interest; it is related to the asymptotic behavior of the interatomic interaction.

TFD theory. Here the interaction for large l is *precisely zero* and not l^{-7}. To be precise, $\Delta E = 0$ when the spacing between each pair $|R_i - R_j|$ exceeds a critical length, $L(z_i) + L(z_j)$. The same is *a fortiori* true for the many-body potentials ε.

The reason is the following. In TFD theory an atomic ρ has compact support, namely a ball of radius $L(z)$. See Theorem 6.6. When $|R_i - R_j| > L(z_i) + L(z_j)$, then $\rho(x) = \sum_j \rho(x - R_j; z_j)$ where $\rho(\cdot\,;\cdot)$ is the TFD atomic ρ. Since each atom is neutral, there is then no residual interaction, by Newton's theorem. One may question whether the ρ just defined is correct. It is trivial to check that it satisfies the TFD equation and, since the solution is unique, this must be the correct ρ.

V. THOMAS-FERMI THEORY AS THE $Z \to \infty$ LIMIT OF QUANTUM THEORY

Our goal in this section is to show that TF theory is the $Z \to \infty$ limit of Q theory and that it correctly describes the cores of heavy atoms. This is the perspective from which to view TF theory, and in this light it is seen to be a cornerstone of many-body theory, just as the theory of the hydrogen atom is an opposite cornerstone useful for thinking about light atoms. We shall not review the stability of matter question here (see Lieb, 1976).

In units in which $\hbar^2/2m = 1$ and $|e| = 1$ the Hamiltonian for N electrons is

$$H_N = \sum_{i=1}^{N} \{-\Delta_i + V(x_i)\} + \sum_{1 \le i < j \le N} |x_i - x_j|^{-1} + U. \quad (5.1)$$

E_N, $\rho_N(x)$, and μ will denote the TF energy, ρ and μ corresponding to this problem with $\lambda = N$ electrons if

$$N \le Z = \sum_{j=1}^{k} z_j .$$

Of course, γ is taken to be γ_p [see Eq. (2.6)]. If $N > Z$ then these quantities are *defined* to be the corresponding TF quantities for $N = Z$. E_N^Q denotes the ground-state energy of H_N (*defined* to be $\inf \operatorname{spec} H_N$) on the physical Hilbert space $\mathcal{H}_N = \wedge_1^N L^2(\mathbb{R}^3; \mathbb{C}^q)$ (antisymmetric tensor product). q is the number of spin states ($= 2$ for electrons), but it is convenient to have it arbitrary, but fixed. The TF quantities also depend on q through γ_p.

A. The $Z \to \infty$ limit for the energy and density

Let us first concentrate on the energy; later on we shall investigate the meaning of $\rho(x)$. For simplicity the number of nuclei is fixed to be k; it is possible to derive theorems similar to the following if $k \to \infty$ in a suitable way (e.g., a solid with periodically arranged nuclei), but we shall not do so here. In TF theory the relevant scale length is $Z^{-1/3}$ and therefore we shall consider the following limit.

Fix $\{\underline{z}^0, \underline{R}^0\} = \{z_j^0, R_j^0\}_{j=1}^k$ and $\lambda > 0$. For each $N = 1, 2, \ldots$, define a_N by $\lambda a_N = N$, and in H_N, replace z_j by $a_N z_j^0$ and R_j by $a_N^{1/3} R_j^0$. Thus $\lambda = Z^0 N/Z$, and a_N is the scale parameter. The TF quantities scale as [Eq. (2.24)]:

$$\begin{aligned} E_{\lambda a}(a\underline{z}^0, a^{-1/3}\underline{R}^0) &= a^{7/3} E_\lambda(\underline{z}^0, \underline{R}^0), \\ \rho_{\lambda a}(a^{-1/3}x, a\underline{z}^0, a^{-1/3}\underline{R}^0) &= a^2 \rho_\lambda(x, \underline{z}^0, \underline{R}^0). \end{aligned} \quad (5.2)$$

In this limit the nuclear spacing decreases as $a_N^{-1/3} \sim N^{-1/3} \sim Z^{-1/3}$. This should be viewed as a refinement rather than as a necessity. If instead the R_j are fixed $= R_j^0$, then in the limit one has isolated atoms. All that really matters are the limits $N^{1/3}|R_i - R_j|$.

Theorem 5.1 (LS Sec. III). *With $N = \lambda a_N$ as above*

$$\lim_{N \to \infty} a_N^{-7/3} E_N^Q(a_N \underline{z}^0, a_N^{1/3} \underline{R}^0) = E_\lambda(\underline{z}^0, \underline{R}^0).$$

The proof is via upper and lower bounds for E_N^Q. The upper bound is greater than the Hartree-Fock energy, which therefore proves that Hartree-Fock theory is correct to the order we are considering, namely $N^{7/3}$.

1. Upper bound for E_N^Q

The original LS proof used a variational calculation with a determinantal wave function; this is cumbersome. Baumgartner (1976) gave a simpler proof (both upper and lower bounds) which intrinsically relied on the same Dirichlet-Neumann bracketing ideas as in LS. Here, we give a new upper bound (Lieb, 1981a) that uses coherent states; these will also be very useful for obtaining a lower bound.

Let $y=(x,\sigma)$ denote a single space-spin pair and $\int dy \equiv \sum_{\sigma=1}^{q}\int dx$. Let $K(y,y')$ be any *admissible single-particle density matrix* for N fermions, namely $0\leq K\leq I$ [as an operator on $L^2(\mathbb{R}^3;\mathbb{C}^q)$] and $\mathrm{Tr}K=N$. Let h be the single-particle operator $-\Delta+V(x)$. Then (Lieb, 1981a)

$$E_N^Q \leq E_N^{\mathrm{HF}} \leq \tilde{E}(K), \tag{5.3}$$

with

$$\tilde{E}(K)=\mathrm{Tr}Kh+\tfrac{1}{2}\int\int dy\,dy'\,|x-x'|^{-1} \times\{K(y,y)K(y',y')-|K(y,y')|^2\}. \tag{5.4}$$

In Eq. (5.3), E_N^{HF} is the Hartree-Fock energy. Since $|x-x'|^{-1}$ is positive we can drop the "exchange term," $-|K|^2$, in Eq. (5.4) for the purposes of an upper bound.

First, suppose $N\leq Z$. To construct K, let $g(x)$ by any function on $\mathbb{R}^3$ such that $\int|g|^2=1$ and let $M(p,r)$ be any function on $\mathbb{R}^3\times\mathbb{R}^3$ such that $0\leq M(p,r)\leq 1$ and $(2\pi)^{-3}\times\int M\,dp\,dr=N/q$. Then the coherent states in $L^2(\mathbb{R}^3)$ which we shall use are

$$f_{pr}(x)=g(x-r)\exp[ip\cdot x] \tag{5.5}$$

and

$$K(y,y')=I_q(2\pi)^{-3}\int dp\,dr\,g(x-r)g(x'-r)^*M(p,r) \times\exp[ip\cdot(x-x')]. \tag{5.6}$$

I_q is the identity operator in spin space. It is easy to check that $\mathrm{Tr}K=N$ and that for any normalized ϕ in L^2, $(\phi,K\phi)\leq 1$ by using Parseval's theorem and the properties of g and M. Thus K is admissible.

We choose [with $\rho=\rho_{\min(N,Z)}$ in Eqs. (5.7)–(5.26)]

$$M(p,r)=\theta(\gamma_p\rho(r)^{2/3}-p^2), \tag{5.7}$$

where $\theta(t)=1$ if $t\geq 0$ and $\theta(t)=0$ otherwise. γ_p is given in Eq. (2.6). One easily computes

$$K(y,y)=q^{-1}I_q\rho_g(x), \tag{5.8}$$

$$\mathrm{Tr}(-\Delta)K=(3\gamma_p/5)\int\rho(x)^{5/3}dx+N\int|\nabla g(x)|^2dx, \tag{5.9}$$

$$\mathrm{Tr}VK=\int V_g(x)\rho(x)dx, \tag{5.10}$$

where $\rho_g=|g|^2*\rho$ and $V_g=V*|g|^2$.

For $g(x)$ we choose

$$g(x)=(2\pi R)^{-1/2}|x|^{-1}\sin(\pi|x|/R) \tag{5.11}$$

for $|x|\leq R$, and $g=0$ otherwise, and with $R=N^{2/5}Z^{-1}$. Then

$$\int|\nabla g|^2=\pi^2/R^2=\pi^2Z^2N^{-4/5}.$$

The electron-electron interaction term in Eq. (5.4) is less than $D(\rho,\rho)$ because, as an operator (and function),

$$[\,|g|^2*|x|^{-1}*|g|^2](x-x')<|x-x'|^{-1}.$$

To see this, use Fourier transforms. Thus

$$E_N^Q\leq\tilde{E}(K)\leq E_N+\pi^2N^{1/5}Z^2 +\int[V(x)-V_g(x)]\rho(x)dx. \tag{5.12}$$

To bound the last term in Eq. (5.12) note that, by Newton's theorem, $|x|^{-1}-|g|^2*|x|^{-1}=0$ for $x\geq R$. Furthermore, with the scaling we have employed, $|R_i-R_j|>2R$ for all $i\neq j$ and N large enough. Since $\gamma_p\rho^{2/3}(x)<V(x)$, then for sufficiently large N and for $|x-R_i|\leq R$ we have $\gamma_p\rho(x)^{2/3}<2z_i|x-R_i|^{-1}$. Thus the last integral in Eq. (5.12) is bounded above for large N by

$$3\gamma_p^{-3/2}\sum_{j=1}^{k}z_j^{5/2}A$$

with

$$A=\int_{|x|\leq R}|x|^{-5/2}dx=8\pi R^{1/2}=8\pi N^{1/5}Z^{-1/2}.$$

If $N\leq Z$, we have established an adequate upper bound, namely,

$$E_N^Q-E_N\leq(\mathrm{const})N^{1/5}Z^2. \tag{5.13}$$

Since $Z\approx N$, this error is $\approx N^{11/5}$, and this is small compared to E, which is $\approx N^{7/3}$.

If $N>Z$ we use $K=K^1+K^\infty$ where K^1 is given above (with $N=Z$) and K^∞ is a density matrix (really, a sequence of density matrices) whose trace is $N-Z$ and whose support is a distance d arbitrarily far away from the origin. K^∞ does not contribute to $\tilde{E}(K)$ in the limit $d\to\infty$. ■

2. Lower bound for E_N^Q

In LS a lower bound was constructed by decomposing $\mathbb{R}^3$ into boxes and using Neumann boundary conditions on these boxes. However, control of the singularities of V caused unpleasant problems. Here we use coherent states again (cf. Thirring, 1981).

Let $\psi(x_1,\ldots,x_N;\sigma_1,\ldots,\sigma_N)$ be any normalized function in $\mathfrak{H}_N$ and let

$$\rho_\psi(x)=N\sum_{\sigma=1}^{q}\int|\psi(x,x_2,\ldots,x_N;\sigma_1,\ldots,\sigma_N)|^2dx_2\cdots dx_N \tag{5.14}$$

$$E_\psi=(\psi,H_N\psi) \tag{5.15}$$

$$T_\psi=\Big(\psi,-\sum\Delta_i\psi\Big). \tag{5.16}$$

It is known that (Lieb, 1979; Lieb and Oxford, 1981)

$$I_\psi=\Big(\psi,\sum_{i<j}|x_i-x_j|^{-1}\psi\Big) \geq D(\rho_\psi,\rho_\psi)-(1.68)\int\rho_\psi(x)^{4/3}dx. \tag{5.17}$$

Choose any $\tilde{\rho}(x)\geq 0$ and $\tilde{\phi}=V-|x|^{-1}*\tilde{\rho}$. Since $D(\rho_\psi-\tilde{\rho},\rho_\psi-\tilde{\rho})\geq 0$, we have for any $0\leq\varepsilon<1$

$$E_\psi \geq \left(\psi, \sum_{i=1}^{N} h_i \psi\right) + U - D(\tilde{\rho},\tilde{\rho}) - (1.68)\int \rho_\psi^{4/3} + \varepsilon T_\psi , \tag{5.18}$$

with

$$h = -(1-\varepsilon)\Delta - \tilde{\phi}(x) \tag{5.19}$$

being a single-particle operator.

We shall choose $\tilde{\rho}$ to be the TF density for the problem with γ_b replaced by $(1-\varepsilon)\gamma_b$, and with the same $\lambda = \min(N, Z)$. $-\tilde{\mu}$ and $\tilde{E}$ are the corresponding chemical potential and energy.

Let $f_{p,r}$ be the coherent states in $L^2(\mathbb{R}^3)$ given by Eq. (5.5) and $\pi_{p,r} =$ (projection onto $f_{p,r}) \otimes I_\sigma$. For any function $m(y) = m(x,\sigma)$ in $L^2(\mathbb{R}^3; \mathbb{C}^q)$ we easily compute:

$$(m,m) = (2\pi)^{-3}\int dp\, dr (m, \pi_{p,r} m),$$

$$\int |\nabla m|^2 dz = (2\pi)^{-3}\int dp\, dr\, p^2 (m, \pi_{p,r} m) - (m,m)\int |\nabla g(x)|^2 dx,$$

$$\int |m|^2 \tilde{\phi}_g(x) dz = (2\pi)^{-3}\int dp\, dr\, \tilde{\phi}(r)(m, \pi_{p,r} m), \tag{5.20}$$

with $\tilde{\phi}_g = |g|^2 * \tilde{\phi}$.

Write $\tilde{\phi} = \tilde{\phi}_g + (\tilde{\phi} - \tilde{\phi}_g)$ and $h^g = -(1-\varepsilon)\Delta - \tilde{\phi}_g(x)$. Let us first concentrate on $e_1 = \inf e_1(\psi)$, where

$$e_1(\psi) = \left(\psi, \sum_{i=1}^{N} h_i^g \psi\right).$$

Since $\sum h^g$ is a sum of single-particle operators we need only consider ψ's which are determinants of N orthonormal single-particle functions. If $m_1, \ldots, m_N$ are such, then

$$M(p,r) = \sum_{i=1}^{N} (m_i, \pi_{p,r} m_i)$$

has the property that $0 \leq M(p,r) \leq q$ and

$$(2\pi)^{-3}\int dp\, dr\, M(p,r) = N.$$

Therefore

$$e_1(\psi) = (2\pi)^{-3}\iint dp\, dr \{(1-\varepsilon)p^2 - \tilde{\phi}(r)\} M(p,r) - N\int |\nabla g|^2. \tag{5.21}$$

The minimum of the right side of Eq. (5.21) over all M with the stated properties is given as follows:

$$M(p,r) = q\theta(\tilde{\phi}(r) - (1-\varepsilon)p^2 - \mu)$$

for some $\mu \geq 0$. μ is the smallest μ such that $(2\pi)^{-3} \times \int M(p,r) \leq N$. Since $\tilde{\phi}$ is the TF potential [for $(1-\varepsilon)\gamma_b$] we see that $\mu = \tilde{\mu}$ and

$$e_1 - D(\tilde{\rho},\tilde{\rho}) + U \geq \tilde{E} - N\int |\nabla g|^2. \tag{5.22}$$

Next, let us consider the missing piece $e_2 = -\int (\tilde{\phi} - \tilde{\phi}_g)\rho_\psi$. The second piece of $\tilde{\phi}$, namely $-\tilde{\psi} = -|x|^{-1} * \rho$, has the property that $\tilde{\psi} - |g|^2 * \tilde{\psi} \geq 0$ since ψ is superharmonic and $|g|^2$ is spherically symmetric. Therefore we can ignore this piece in e_2. $V - V_g$ is bounded above, as before, by

$$\sum z_j |x - R_j|^{-1}\theta(R - |x - R_j|).$$

For large N, $|R_i - R_j| > 2R$ and, using Hölder's inequality,

$$e_2 \geq -\|\rho_\psi\|_{5/3}\left[8\pi R^{1/2}\sum z_j^{5/2}\right]^{2/5} \geq -\|\rho_\psi\|_{5/3}\{(8\pi)^{2/5} R^{1/5} Z\}. \tag{5.23}$$

The negative term e_2 is controlled by the εT_ψ term through an inequality of Lieb and Thirring (1975 and 1976; see also Lieb, 1976):

$$T_\psi \geq L\int \rho_\psi(x)^{5/3} dx, \tag{5.24}$$

with $L = \frac{3}{5}(3\pi/2q)^{2/3}$. Furthermore, by the Schwarz inequality, $\int \rho_\psi^{4/3} \leq \{N\int \rho_\psi^{5/3}\}^{1/2}$. If we write $\int \rho_\psi^{5/3} = X$ then $e_2 \geq -X^{3/5} D$, with $D = \{\}$ in Eq. (5.23), and

$$e_2 + \varepsilon T_\psi - (1.68)\int \rho_\psi^{4/3} \geq \min_{X>0} -DX^{3/5} + \varepsilon L X - (1.68) N^{1/2} X^{1/2} \equiv Y. \tag{5.25}$$

Equation (5.22) contains $\tilde{E}$ instead of E; we must bound the difference. Using $\tilde{\rho}$ as a trial function for E, $E \leq \tilde{E} + [\varepsilon/(1-\varepsilon)]\tilde{K}$, where

$$\tilde{K} = [3(1-\varepsilon)/5]\gamma_b \int \tilde{\rho}^{5/3}.$$

Choose $\varepsilon = Z^{-1/30}$ (this is not optimum). For large Z, $\varepsilon < \frac{1}{2}$ and it is easy to see that $\tilde{K} < (\text{const}) Z^{7/3}$ for all N, Z. Thus

$$0 > \tilde{E} - E > -(\text{const}) Z^{7/3} Z^{-1/30}. \tag{5.26}$$

Choose $R = Z^{-1/2}$, which is a different choice from the upper bound calculation. Then $D \approx Z^{9/10}$ and

$$Y \geq -(\text{const}) Z^{7/3} Z^{-1/30}. \tag{5.27}$$

[It is easy to see that the term $-(1.68) N^{1/2} X^{1/2}$ is negligible as long as N/Z is fixed.]

Finally $-N\int |\nabla g|^2 \approx -NR^{-2} \approx Z^2$. Combining all these bounds, we find

$$E_N^Q - E > -(\text{const}) Z^{7/3 - 1/30}$$

which is the desired result. ■

Clearly there is room for a great deal of improvement, for it is believed that $E^Q - E > 0$ as explained in Sec. V.B. But first let us turn to the correlation functions.

3. Correlation functions

In analogy with Eq. (5.14) we define

$$\rho_\psi^j(x_1, \ldots, x_j) = j! \binom{N}{j} \sum_\sigma \int |\psi(x_1, \ldots, x_N; \sigma_1, \ldots, \sigma_N)|^2 \times dx_{j+1} \cdots dx_N. \tag{5.28}$$

We wish to obtain a limit theorem for ρ_ψ^j when ψ is a ground state of H_N. But there may be no ground state (inf spec H_N may not be an eigenvalue) or there may be

several. In any case, it is intuitively clear that the limit of ρ_ψ^j should not depend upon ψ being exactly a ground state, but only upon ψ being "nearly" a ground state.

Definition. Let $\psi_1, \psi_2, \ldots$ be a sequence of normalized functions with $\psi_N \in \mathcal{H}_N$ for N particles. This *sequence* is called an *approximate ground state* if $|\langle \psi_N, H_N \psi_N \rangle - E_N^Q| a_N^{-7/3} \to 0$ as $N \to \infty$. H_N always has k nuclei.

Theorem 5.2. *Let $\{\psi_N\}$ be an approximate ground state with the scaling given before Eq. (5.2), and let $\rho_N^j(x)$ be given by Eq. (5.28) with ψ_N, and*

$$\hat{\rho}_N^j(x_1, \ldots, x_j) \equiv a_N^{-2j} \rho_N^j(a_N^{-1/3} x_1, \ldots, a_j^{-1/3} x_j).$$

Let $\rho^j(x_1, \ldots, x_j) = \rho(x_1) \cdots \rho(x_j)$ with ρ being the solution to the TF problem for λ and $\{z_j^0, R_j^0\}$. (Note that $\lambda = N/Z$ is now fixed.) Then

$$\left\langle \psi_N, -\sum \Delta_i \psi_N \right\rangle a_N^{-7/3} \to \tfrac{3}{5} \gamma_p \int \rho(x)^{5/3} dx,$$

$$\left\langle \psi_N, \sum V(x_i) \psi_N \right\rangle a_N^{-7/3} \to \int \rho V,$$

$$\left\langle \psi_N, \sum |x_i - x_j|^{-1} \psi_N \right\rangle a_N^{-7/3} \to D(\rho, \rho).$$

Moreover, $\hat{\rho}_N^j(x) \to \rho^j(x)$ in the sense that if Ω is any bounded set in $\mathbb{R}^{3j}$ then

$$\int_\Omega \hat{\rho}_N^j(x) d^{3j}x \to \int_\Omega \rho^j(x) d^{3j}x.$$

If $\lambda \leq Z = \sum z_j$, the restriction that Ω be bounded can be dropped and $\hat{\rho}_N^j \to \rho^j$ in the weak L^1 sense.

Proof. The reader is referred to LS, Theorem III.5 for details. The basic idea is to consider a function $U(x_1, \ldots, x_j) \in C_0^\infty(\mathbb{R}^{3j})$ and add $\alpha \int \rho^j U d^{3j}x$ to the TF functional, $\mathcal{E}(\rho)$. On the other hand, the potential

$$\alpha a_N^{4j/3} \sum_{\substack{i_1, \ldots, i_j \\ \text{unequal}}} U(a_N^{1/3} x_{i_1}, \ldots, a_N^{1/3} x_{i_j})$$

is added to H_N. By the aforementioned methods the energies are shown to converge on the scale of $a_N^{7/3}$. But $\partial E / \partial \alpha|_{\alpha=0} = \int \rho^j U$. By concavity of $E(\alpha)$ the derivatives and the limits $a_N \to \infty$ can be interchanged. Thus, for all such U, $\int \hat{\rho}_N^j U \to \int \rho^j U$. ■

One of the assertions of Theorem 5.2 is that, as $N \to \infty$, correlations among any finite number of electrons disappear. *A posteriori* this is the justification for replacing the electron-electron repulsion $\sum |x_i - x_j|^{-1}$ by $D(\rho, \rho)$ in TF theory.

B. The Scott conjecture for the leading correction

We have seen that $E^{TF} = -CZ^{7/3}$ under the assumption that the nuclear coordinates R_j and charges z_j scale as $Z^{-1/3} R_j^0$ and $Z z_j^0$, $\sum z_j^0 = 1$, and $\lambda = N/Z > 0$ is fixed. C depends on $\lambda, \underline{z}^0, \underline{R}^0$. What is the next correction to the energy? While this question takes us to some extent outside TF theory, we should like to mention briefly the interesting conjecture of Scott (1952) and a generalization of that conjecture. None of these conjectures have been proved.

The basic idea of Scott is that in the *Bohr atom* (no electron repulsion) the electrons close to the nuclei *each* have an energy $\sim -Z^2$. This should also be true in some sense even with electron repulsion. Since TF theory cannot yield exactly the right energy near the singularities of V, the leading correction should be $O(Z^2)$.

The leading correction should have three properties.

(i) It is the *same* with or without electron repulsion because the repulsive part of $\phi(x)$, namely $|x|^{-1} * \rho$, is $O(Z^{4/3})$ for all x.

(ii) It is independent of N/Z, provided $N/Z > 0$ and fixed. This is so because the correction comes from the core electrons whose distance from the nucleus is $O(Z^{-1})$. The number of electrons thus involved is small compared to Z.

(iii) It should be additive over a molecule. If the correction is Dz^2 for an atom then the total leading correction should be

$$\Delta E = D \sum_{j=1}^{k} z_j^2 \tag{5.29}$$

and

$$E^Q = E^{TF} + \Delta E + o(Z^2). \tag{5.30}$$

Of course E^{TF} depends on whether electron repulsion is present or not, but ΔE supposedly does not change. To calculate D let us first calculate E^{TF} for an atom without repulsion. The general theory goes through as before, but now the TF equation is $\gamma \rho^{2/3} = (V - \mu)_+$, $V(x) = z/|x|$, $\int \rho = N$, and $\mu > 0$, even when $N = z$. It is found (Lieb, 1976, p. 560) that $\mu = z/R$, $R = 3\gamma(4N/\pi^2)^{2/3}/5z$, and $E_{\text{Bohr}}^{TF} = -3z^2 N^{1/3} (\pi^2/4)^{2/3}/\gamma$. Using γ_p,

$$E_{\text{Bohr}}^{TF} = -z^{7/3} (3N/z)^{1/3} (2mq^{2/3}/\hbar^2)/4.$$

The quantum energy is computed by adding up the Bohr levels. For each principal quantum number n, the energy is $e_n = m/2\hbar^2 n^2$ and it is qn^2-fold degenerate. The result (Lieb, 1976) is

$$E_{\text{Bohr}}^Q = E_{\text{Bohr}}^{TF} + qz^2/8 + O(z^{5/3}), \tag{5.31}$$

thus

$$D = qz^2/8 \tag{5.32}$$

in the Scott conjecture. Scott's (1952) derivation was slightly different from the above, but his basic idea was the same.

The Scott conjecture about the energy can be supplemented by the following about the density. Let $f_{nlm}(z, x)$ be the normalized *bound-state* eigenfunctions for the hydrogenic atom with nuclear charge z, and define

$$\rho^H(z, x) = q \sum_{nlm} |f_{nlm}(z, x)|^2. \tag{5.33}$$

This sum converges and represents the quantum density for a Bohr atom with *infinitely many electrons*. It is being tabulated and studied by Heilmann and Lieb. It is monotone decreasing and a graphical plot of ρ^H shows that it has almost no discernible shell structure. Clearly $\rho^H(z, x) = z^3 \rho^H(1, zx)$ and is spherically symmetric. By our previous analysis of the $z \to \infty$ limit (which strictly speaking is not applicable when $N = \infty$, but which can be suitably modified)

$$z^{-2} \rho^H(z, z^{-1/3} x) \to z^{-2} \rho_{\text{Bohr}}^{TF}(z, z^{-1/3} x) \tag{5.34}$$

as $z \to \infty$. But

$$\rho^{\mathrm{TF}}_{\mathrm{Bohr}}(z,x) = (z/\gamma_p |x|)^{3/2}$$

when $\mu = 0$, as we have just seen. Thus

$$\rho^H(1,y) \to (\gamma_p |y|)^{-3/2} \tag{5.35}$$

as $y \to \infty$. Equation (5.35) is not obvious, but it can be directly proved from (5.33).

Thus $\rho^H(z,x)$, whose scale length is z^{-1}, agrees nicely with $\rho^{\mathrm{TF}}(z,x)$, whose scale length is $z^{-1/3}$, in the overlap region $z^{-1} \ll |x| \ll z^{-1/3}$. This is true even when electron repulsion is included in ρ^{TF} because of Theorem 2.8(a). The common value is $\rho(z,x) = (z/\gamma_p |x|)^{3/2}$. Because of this we are led to the following.

Conjecture. Suppose the sequence $\{\psi_N\} \in \mathcal{H}_N$ is an *approximate ground state* for a molecule (with repulsion) in the *strong sense* that

$$|(\psi_N, H_N \psi_N) - E^Q_N| a_N^{-2} \to 0 \quad \text{as } N \to \infty .$$

Let $\rho^Q_N(x)$ be given by Eq. (5.14). Recall that $R_j = a_N^{-1/3} R^0_j$. Fix $\lambda = N/Z > 0$ and $x \neq R^0_j$, all j. Then, as $N \to \infty$,

$$a_N^{-2} \rho^Q_N(a_N^{-1/3} x) \to \rho^{\mathrm{TF}}(x) , \tag{5.36}$$

where ρ^{TF} is the TF density for λ, z^0_j, R^0_j. On the other hand, for all fixed y,

$$a_N^{-3} \rho^Q_N(a_N^{-1/3} R^0_j + a_N^{-1} y) \to (z^0_j)^3 \rho^H(1, z^0_j y) . \tag{5.37}$$

Equation (5.36) has already been proved in Sec. V.A.

TFW Theory. It is a remarkable fact that the TFW correaction, which has no strong *a priori* justification, has, as its chief effect, precisely the kind of correction (i), (ii), (iii) above predicted by Scott. If δ is chosen correctly in Eq. (2.8), even the constant D in Eq. (5.32) can be duplicated. This will be elucidated in Sec. VII. TFW theory also (accidentally?) improves TF theory in two other ways: negative ions can be supported and binding occurs.

C. A picture of a heavy atom

With the real and imagined information at our disposal we can view the energy and density profile of a heavy, neutral, nonrelativistic atom as being composed of seven regions.

(1) The inner core. Distances are $O(z^{-1})$ and ρ is $O(z^3)$. For large σ, the number of electrons out to $R = \sigma/z$ is $\sim \sigma^{3/2}$, while the energy $\sim z^2 \sigma^{1/2}$. If $1 \ll zr \ll z^{2/3}$, $\rho(r)$ is well approximated by $(z/\gamma_p r)^{3/2}$. $\rho(r)$ is infinity on a scale of z^2 which is the appropriate scale for the next, or TF region. The leading corrections, beyond TF theory, come from this region. None of this has been proved.

(2) The core. Distances are $O(z^{-1/3})$ and ρ is $O(z^2)$. TF theory is exact to leading order. The energy is $E^{\mathrm{TF}} \sim -z^{7/3}$ and almost all the electrons are in this region. This is proved.

(3) The core mantle. Distances are of order $\sigma z^{-1/3}$ with $\sigma \gg 1$. $\rho(r) = (3\gamma_p/\pi)^3 r^{-6}$, the Sommerfeld asymptotic formula. ρ is still $O(z^2)$. This is proved.

(4) A transition region to the outer shell. This region may or may not exist.

(5) The outer shell. In the Bohr theory, $z^{1/3}$ shells are filled. The outer shell, if it can be defined, would presumably contain $O(z^{2/3})$ electrons and each electron in the shell would "see" an effective nuclear charge of order $z^{2/3}$. This picture would give a radius unity for the last shell and an *average* density $\sim z^{2/3}$ in the shell. On the same basis the *average* electron energy would be $O(z^{2/3})$ and thus the energy in the shell would be $O(z^{4/3})$. All this is conjectural, for reliable estimates are difficult to obtain.

(6) The surface. Here the potential is presumably $O(1)$, and so is the energy of each electron. Chemistry takes place here.

TF theory, which is unreliable in this region, nevertheless predicts a surface radius of $O(1)$. We thank J. Morgan for this remark. His idea is that if the surface radius R_s is defined to be such that outside R_s there is one unit of electron charge, then $R_s = O(1)$ because the TF density is $\rho(r) = (3\gamma_p/\pi)^3 r^{-6}$, independent of z, for large r. Likewise, if R_0 is defined such that between R_0 and R_s there are $z^{2/3}$ electrons, then the average TF density in this "outer shell" is $z^{2/3}$ in conformity with *(5)*. Finally, the energy needed to remove one electron is $O(1)$ as Eq. (3.11) shows. The radius of this ionized atom is also $O(1)$ as Eq. (3.13) shows.

In no sense is it being claimed that TF theory is reliable at the surface, or even that the existence of the surface, as described, is proved. We are only citing an amusing coincidence. It is quite likely that the surface radius of a large atom has a weak dependence on z.

(7) The region of exponential falloff. $\rho(r) \sim K \times \exp[-2(2me/\hbar^2)^{1/2}(r-R)]$, where e is the ionization potential, K is the density at the surface, and R is the surface radius. An upper bound for ρ of this kind has been proved by many people, of whom the first was O'Connor (1973). See also Deift, Hunziker, Simon, and Vock, 1978, and M. Hoffmann-Ostenhof, T. Hoffmann-Ostenhof, R. Ahlrichs, and J. Morgan, 1980, for recent developments and bibliographies of earlier work.

The density profile of a heavy atom, as described above, is shown schematically in Fig. 2.

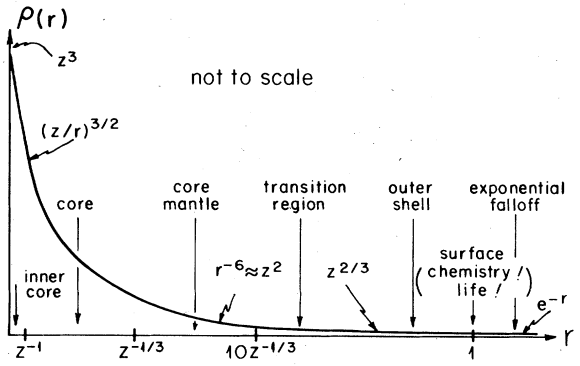

FIG. 2. Schematic plot of the electron density $\rho(r)$ in a neutral heavy atom of charge z. The inner core extends to distances of order z^{-1}; the core to order $z^{-1/3}$; the mantle to $z^{-1/3}$ times a large number. The core and its mantle are correctly described by TF theory. The outer shell extends to distances of order z^p where p is near zero. Finally, there is the surface, and then the region of exponential falloff. The surface thickness is not shown.

VI. THOMAS-FERMI-DIRAC THEORY

The previous sections contain most of the mathematical tools for the analysis of this model; the main new mathematical idea to be introduced here will be the j model and its relation to TFD theory.

The TFD functional is

$$\mathcal{E}^{\mathrm{TFD}}(\rho)=\int J(\rho(x))\,dx-\int V\rho+D(\rho,\rho)+U, \tag{6.1}$$

and

$$J(\rho)=\tfrac{3}{5}\gamma\rho^{5/3}-\tfrac{3}{4}C_e\rho^{4/3}. \tag{6.2}$$

The term $-D=-(3C_e/4)\int\rho^{4/3}$ was suggested by Dirac (1930) to account for the "exchange" energy. The true electron repulsion I in (5.17) is expected to be less than $D(\rho,\rho)$ because the electrons are correlated. For an ideal Fermi gas at constant density, I is computed to be $D(\rho,\rho)-D$ with $C_e=(6/\pi q)^{1/3}$. There is, however, no fundamental justification for the Dirac approximation; it can even lead to unphysical results, as will be seen shortly. In particular, I is always positive but $D(\rho,\rho)-D$ can be arbitrarily negative. As remarked in (5.17), there is a *lower* bound of this form $D(\rho,\rho)-D$ (Lieb, 1979; Lieb and Oxford, 1981) with $3C_e/4=1.68$ (independent of q). In any event, it should be remembered that *D is part of the Coulomb energy* even though it is mathematically convenient to combine it with the kinetic energy as in Eq. (6.2).

For simplicity we assume

$$V(x)=\sum_{i=1}^{k}V_i(x-R_i), \tag{6.3}$$

with $V_i\in\mathfrak{D}$: $V_i=|x|^{-1}*m_i$ (with m_i a non-negative measure) and $|m_i|=z_i$.

Henceforth the superscript TFD will be omitted. All quantities in this section refer to TFD, and not TF, theory, unless otherwise stated.

A. The TFD minimization problem

The function space is the same as for TF theory, namely

$$\mathcal{G}=\{\rho\,|\,\rho\in L^1\cap L^{5/3},\rho(x)\geq 0\}. \tag{6.4}$$

The energy is

$$E(\lambda)=\inf\left\{\mathcal{E}(\rho)\,\middle|\,\int\rho=\lambda,\rho\in\mathcal{G}\right\}. \tag{6.5}$$

Theorem 6.1. *$E(\lambda)$ is finite, nonincreasing in λ, and*

$$E(\lambda)=\inf\left\{\mathcal{E}(\rho)\,\middle|\,\int\rho\leq\lambda,\rho\in\mathcal{G}\right\}. \tag{6.6}$$

Moreover, $e(\lambda)\equiv E(\lambda)-U<0$ when $\lambda>0$.

Proof. Same as Proposition 2.1 and Theorem 2.3. The crucial fact to note is that $J(0)=J'(0)=0$, which permits us to place "surplus charge density" at infinity. ■

It is not immediately obvious that $E(\lambda)$ is convex because J is not convex. The proof of convexity is complicated and will be given later (Theorem 6.9).

A second difficulty is that $E(\lambda)$ is not bounded below for all λ. This is so because J is not positive. This latter difficulty can be dealt with in the following way. Introduce

$$\mathcal{E}_\alpha(\rho)=\mathcal{E}(\rho)+\alpha\int\rho \tag{6.7}$$

with

$$\alpha=15C_e^2(64\gamma)^{-1}. \tag{6.8}$$

This amounts to replacing J by

$$J_\alpha(\rho)=J(\rho)+\alpha\rho. \tag{6.9}$$

Note that $J_\alpha(\rho)\geq 0$ and

$$J_\alpha(\rho_0)=0=J'_\alpha(\rho_0) \tag{6.10}$$

for $\rho_0=(5C_e/8\gamma)^3$. $-\alpha$ and ρ_0 are the minimum value and the minimum point of the function $J(\rho)/\rho$. Correspondingly, introduce

$$E_\alpha(\lambda)=\inf\left\{\mathcal{E}_\alpha(\rho)\,\middle|\,\int\rho=\lambda,\rho\in\mathcal{G}\right\}. \tag{6.11}$$

Theorem 6.2. *$E_\alpha(\lambda)$ is nonincreasing in λ and has a lower bound, independent of λ. Moreover,*

$$E_\alpha(\lambda)=E(\lambda)+\alpha\lambda \tag{6.12}$$

and

$$E_\alpha(\lambda)=\inf\left\{\mathcal{E}_\alpha(\rho)\,\middle|\,\int\rho\leq\lambda,\rho\in\mathcal{G}\right\}. \tag{6.13}$$

$e_\alpha(\lambda)\equiv E_\alpha(\lambda)-U=e(\lambda)+\alpha\lambda<0$ when $\lambda>0$, and $e_\alpha(\lambda)\to\inf_\lambda e_\alpha(\lambda)\equiv e_\alpha(\infty)$ as $\lambda\to\infty$.

Proof. Again the proof is the same as for Proposition 2.1 and Theorem 2.3. Here, however, $J'_\alpha(0)>0$; the fact that $J_\alpha(\rho_0)=J'_\alpha(\rho_0)=0$ is used instead. The fact that $J_\alpha\geq 0$ is responsible for the lower bound. ■

Remark. One consequence of Theorem 6.2 is that $dE(\lambda)/d\lambda\leq-\alpha$ (if the derivative exists). Another is that when λ is large enough so that $e_\alpha(\lambda)=e_\alpha(\infty)$ then $e(\lambda)=e_\alpha(\infty)-\alpha\lambda$. As will be seen, this happens when $\lambda\geq\lambda_c=Z=\sum z_j$. Thus the graph of $e_\alpha(\lambda)$ is similar to that for $e^{\mathrm{TF}}(\lambda)$ in Fig. 1. $e(\lambda)$ then has a negative slope, $-\alpha$, at λ_c and afterwards $e(\lambda)$ has the same constant negative slope. This is a highly unphysical feature of TFD theory which arises from the fact that one can have spatially small "clumps" of density in which $\rho=\rho_0$, arbitrarily far apart. These "clumps" have an energy approximately $-\alpha\rho_0\cdot$(volume) and are physically nonsensical because the $-\rho^{4/3}$ term, which causes this effect, is a gross underestimate of the positive electron repulsion which it is meant to represent. There is no minimizing ρ for these "clumps" because for no ρ is the energy exactly $-\alpha\rho_0\cdot$(volume). The "inf" in Eq. (6.5) is crucial.

B. The j model

Now we must deal with the fact that J_α is not convex. To this end we follow Benguria (1979), who introduced the "convexified" j model. With its aid, Benguria was the first to place the TFD theory on a rigorous basis for a certain class of amenable potentials in Eq. (6.3), which is defined in Sec. VI.C. This class includes the point nuclei. It will turn out that the j model also permits us to analyze TFD theory for all potentials, not just the amenable class. However, for nonamenable potentials, the analysis is complicated and the final result has an unexpected feature, namely, that a minimizing ρ for E may not exist, even if $\lambda<\lambda_c$. The j model is explored in

detail here because, as will be seen in Sec. VI.C, *its energy is the same as* $E_\alpha(\lambda)$ for the TFD model. Moreover, for amenable potentials the density ρ of the two models is also the same.

Definition.

$$j(\rho)=J_\alpha(\rho),\quad \rho\geq\rho_0=(5C_e/8\gamma)^3$$
$$=0,\quad 0\leq\rho\leq\rho_0. \tag{6.14}$$

The derivative of this convex function is given in Eq. (3.14). $\mathcal{E}_j(\rho)$ is given by Eq. (6.1) with J replaced by j. $E_j(\lambda)$ is defined by Eq. (6.5) with $\mathcal{E}$ replaced by $\mathcal{E}_j$.

By the methods of Secs. II and III the j model has many of the same properties as TF theory.

Theorem 6.3. *If V is given by Eq. (6.3) and if $\mathcal{E}$ is replaced by $\mathcal{E}_j$, E by E_j, and e by $e_j=E_j-U$, then the following results of TF theory hold for the j model (they also hold for TF theory, of course, with this V). (Ignore any mention of* TFD *and* TFDW *theory in the cited theorems.):*

Propositions 2.1 and 2.2; Theorems 2.3 and 2.4; the definition of λ_c; Theorem 2.5; Theorem 2.6 [with Eq. (2.18) replaced by (3.2)]; Theorem 2.7; Theorem 2.12 (for a point nucleus); Theorem 2.13 without the γ dependence (for point nuclei; the last two equations in this theorem have an obvious generalization for non-point nuclei.); Theorem 2.14 (for point nuclei) is changed to (a) $5K/3=A-2R-\mu\lambda-\alpha\lambda+4D/3$, (b) $2K=A-R+D$ for an atom, with $D=(3C_e/4)\int\rho^{4/3}$ (note that Theorem 3.19 must be used in the proof); Equation (2.22); Theorem 3.2; Theorems 3.4, 3.5 [Benguria (1979) has shown that if W is the potential of point nuclei then $\phi'-\phi\in H^2$ away from S_W]; Corollaries 3.7, 3.8, 3.9, and 3.10 (note, in particular, that $\phi^{\rm TF}>\phi^{j\ \rm model}$ for fixed μ); Lemma 3.11; Theorem 3.12, Corollaries 3.14 and 3.17; Theorem 3.18 (i.e., $\lambda_c=Z$); Equation (3.6); Sec. III.B; Theorem 3.23 (but note that equality can occur. See remark at the end of Sec. IV.C).

Remarks. (i) Theorem 2.8(a) holds in the sense that $\rho(x)\approx(z_j/\gamma)^{3/2}|x-R_j|^{-3/2}$ near R_j.

(ii) There is no simple scaling for the j model, as in Eq. (2.24) for TF theory.

(iii) We emphasize that a minimizing ρ exists if and only if $\lambda\leq Z$. This ρ is unique and satisfies the *Thomas-Fermi-Dirac equation* (3.2).

(iv) *Question.* Under what conditions do the conclusions of Corollaries 3.13, 3.15, and 3.16 and Theorem 3.21 hold for the j model? *Question.* To what extent do the results of Sec. IV carry over to the j model?

(v) To prove the analogue of Eq. (2.15), Mazur's theorem can be used, as in the proof of Proposition 3.24.

There are some useful additional facts about the j model not mentioned in Theorem 6.3.

Theorem 6.4. *If C_e increases then (i) $\phi(x)-\mu(\lambda)$ decreases and $\mu(\lambda)$ increases, for fixed λ; (ii) $\phi(x)$ decreases for fixed μ.*

Proof. By Corollary 3.10, since $j'(\rho)$ decreases with C_e for fixed ρ. ■

Theorem 6.5. *For all λ, $E^{\rm TF}(\lambda)>E_j(\lambda)>E(\lambda)$ since $J(\rho)<j(\rho)<3\gamma\rho^{5/3}/5$. On the other hand, suppose V is the potential of k point nuclei as in Eq. (2.1). Then for $\lambda\leq\lambda_c=Z$,*

$$E^{\rm TF}(\lambda)\leq E_j(\lambda)-\alpha\lambda+(3C_e/4)\lambda^{1/2}\{(5\varepsilon_1/2\gamma)Z^{7/3}\}^{1/2}$$
$$+27C_e^2\lambda/(10\gamma), \tag{6.15}$$

where $-\varepsilon_1$ is the TF energy for a neutral atom with $z=1$ [see Eq. (7.15)].

Remarks. (i) When $\lambda>Z$ then $(E^{\rm TF}-E_j)(\lambda)=(E^{\rm TF}-E_j)(Z)$.

(ii) Clearly Eq. (6.15) can be improved. But it does show that the effect of the Dirac term is to decrease the energy by $O(Z^{5/3})$ for large Z. (Note: by Theorem 6.8, $E_j-\alpha\lambda=E$.)

Proof. Let ρ be the minimizing density for E_j, and $\rho^{\rm TF}$ that for $E^{\rm TF}$. Use ρ as a trial function for $E^{\rm TF}$. Noting that $\rho(x)\notin(0,\rho_0]$ a.e. (Theorem 3.19), we have $E^{\rm TF}\leq\mathcal{E}^{\rm TF}(\rho)=E_j-\alpha\lambda+(3C_e/4)\int\rho^{4/3}$. By Theorem 3.19, $\gamma\rho^{2/3}-C_e\rho^{1/3}+\alpha=\phi-\mu$ when $\rho>0$. But by Corollary 3.10, $\phi-\mu\leq\phi^{\rm TF}-\mu^{\rm TF}\leq\gamma(\rho^{\rm TF})^{2/3}$. Thus $\rho^{2/3}\leq(\rho^{\rm TF})^{2/3}+C_e/\gamma)\rho^{1/3}$. Squaring this and using $\int(\rho^{\rm TF})^{2/3}\rho^{1/3}\leq\lambda$ (Hölder), and $\int\rho^{2/3}\leq\lambda(\rho_0)^{-1/3}$, and $\int(\rho^{\rm TF})^{4/3}\leq[\lambda\int(\rho^{\rm TF})^{5/3}]^{1/2}$, we obtain Eq. (6.15), but with $5K^{\rm TF}/3\gamma$ in place of $\{\}$. By Theorem 2.14(a), $2K^{\rm TF}/3<-e^{\rm TF}$, and by the remark preceding Eq. (4.5), $e^{\rm TF}>e^{\rm TF}$ (all nuclei at one point). ■

The next theorem states that ρ always has compact support, even when $\lambda=\lambda_c$. When $\lambda<\lambda_c$ this is also true in TF theory (Lemma 3.11). The proof we give seems unnecessarily complicated; a simpler one must be possible.

Theorem 6.6. *Suppose $V=|x|^{-1}*m\in\mathfrak{D}$, with m a nonnegative measure of compact support and $\int dm=Z$. Let ρ be the minimizing j model density for $\lambda\leq\lambda_c=Z$. Then ρ has compact support. Moreover, suppose* supp$(m)\subset B_R$, *the ball of radius R centered at* 0. *Then* supp$(\rho)\subset B_r$ *for some r depending on R and Z, but independent of λ. $r\leq 2R+tZ(\rho_0R^2)^{-1}$ for some universal constant t, independent of all parameters.*

Proof. The strategy is to construct a function f such that supp$(\rho)\subset$ supp(f). Let $S_R=\partial B_R$ be the sphere of radius R. There exists a function (surface charge distribution) σ on S_{2R} such that V_σ, the potential of σ outside B_{2R}, is V, i.e.,

$$V(x)=V_\sigma(x)\equiv 4\pi(2R)^2\int d\Omega\sigma(\Omega)|x-2R\Omega|^{-1}$$

for $|x|>2R$, where Ω denotes a point on S_1 and $\int d\Omega=1$. It is easy to see that σ is a bounded, continuous function since supp$(m)\subset B_R$, and $|\sigma(\Omega)|\leq sZR^{-2}$ for some universal constant s. Let $\Sigma(\Omega)=-\sigma(\Omega)+sZR^{-2}\geq 0$, and let

$$dM(x)=dm(x)+\Sigma(x/2R)\delta(|x|-2R)dx.$$

If $V_M=|x|^{-1}*M$, we see that $V_M(x)\geq V(x)$, all x, and $V_M(x)=Q|x|^{-1}$ for $|x|>2R$, with $0\leq Q\leq(1+16\pi s)Z$. V_M-V is a bounded function in $\mathfrak{D}$. Now let $f(x)=\rho_0$ for $2R<|x|\leq r$ and $f(x)=0$ otherwise, with $\int f=Q$. Let $\psi=|x|^{-1}*\rho$, $g=|x|^{-1}*f$, $\phi=V-\psi$, $h=V_M-g$ where ρ satisfies Eq. (3.2). We claim $u(x)\equiv h(x)-\phi(x)+\mu\geq 0$. If not, let $B=\{x|u(x)<0\}$. B is open since $h-\phi$ is con-

tinuous. $-\Delta u/4\pi \geq -f+\rho$. But $f \leq \rho$ on B since, for $|x| \leq 2R$, $f(x)=0$; for $|x|>2R$, $\rho(x)$ is either 0 or $>\rho_0$ a.e. by Theorem 3.19. If $\rho(x)=0$ then $\phi-\mu \leq 0$ by (3.2) and $h(x)$ is clearly ≥ 0, so $x \notin B$; if $\rho(x) \geq \rho_0$, $\rho - f \geq 0$. Thus u is superharmonic on B and, since $u=0$ on ∂B and $u=\mu \geq 0$ at infinity, B is empty. Now consider $A=\{x \mid r<|x|\}$. In A, $-\Delta u = 4\pi\rho \geq 0$ and $u \geq 0$ on ∂A and at infinity. Therefore either (i) $\rho=0$ a.e. in A or (ii) $u>0$ everywhere in A. In case (ii), $\phi<\mu$ in A because $h=0$ in A. But then, by Eq. (3.2), $\rho=0$ a.e. in A. The bound for r is obtained by $4\pi(r-2R)(2R)^2 < (4\pi/3)[r^3 - (2R)^3] = Q/\rho_0$. ■

Remark. For an atom with nucleus located at the origin, R can be chosen to be any positive number. If the inequality for r is minimized then we find $\rho(x)=0$ for $|x|>3(tZ/\rho_0)^{1/3}$.

Theorem 6.7. *Suppose $V \in \mathfrak{D}$ and $\rho \in \mathfrak{C}$ are such that the second line of Eq. (3.2) holds with $\mu=0$, in the sense that $\phi_\rho(x) \leq 0$ a.e. when $\rho(x)=0$ and $\rho(x)=0$ a.e. when $\phi_\rho(x)<0$. Let A be the complement of the support of ρ. Then $\phi \equiv 0$ on $\bar{A}$, the closure of A.*

Remark. Theorem 6.7 does not mention j. However, the theorem is meaningful only if supp(ρ) is not all of R^3. This does not happen in TF theory when $\mu=0$, but it does happen for the j model if the hypothesis of Theorem 6.6 holds. The significance of Theorem 6.7 is that there is *total shielding* in TFD theory. This is in contrast to TF theory, where there is *under-screening* in the neutral case in the sense that the potential falls off only with a power law. One consequence of Theorem 6.7 is that two or more molecules, each of fixed shape, do not interact when their supports are disjoint. See the remark at the end of Sec. IV.

Proof. Let $B=\{x \mid \phi(x)<0\}$. Clearly the singularities of V are not in B, so B is open. On B, $\Delta\phi \leq 0$ since $\rho=0$ a.e. in B. But $\phi=0$ on ∂B and at infinity so B is empty. Therefore $\phi \geq 0$ everywhere. Let $D=\{x \mid \rho(x)=0\}$. $\phi \leq 0$ a.e. on D. Since $A \subset D$ is open, and ϕ is continuous on $\{x \mid \phi(x)<1\}$, $\phi \equiv 0$ on A, and hence on $\bar{A}$. ■

C. The relation of the *j* model to TFD theory

We shall show that the energy of the j model is exactly $E_\alpha(\lambda)=E(\lambda)+\alpha\lambda$ for the TFD problem. Thus all the facts about the energy in Theorems 6.3 and 6.5 hold for TFD theory. However, the densities may be different!

Let us start with the simplest case studied by Benguria (1979).

Definition. A (non-negative) measure m is said to be *amenable* if

$$dm(x)=\sum_{i=1}^{k} z_i \delta(x-R_i)dx + g(x)dx$$

with $z_i>0$ and g satisfies: (i) $g \geq 0$, (ii) $g \in L^\infty_{\rm loc}$, (iii) If $A=\{x \mid g(x)=0\}$ and $\sim A$ is its complement then $R^3 \setminus [\text{Interior}(A) \cup \text{Interior}(\sim A)]$ has zero Lebesgue measure, (iv) $g(x) \geq \rho_0$ for $x \notin A$. (v) $V=|x|^{-1} * m \in \mathfrak{D}$. m is *strongly amenable* if $g(x)>\rho_0$ for $x \notin A$.

Remark. This amenable class is more restrictive than necessary for Theorem 6.8. Technicalities aside, (iv) is the crucial point. δ measures (corresponding to point nuclei) are strongly amenable.

Theorem 6.8. *Suppose that in Eq. (6.1) $V=|x|^{-1}*m$ and m is amenable. Then $E_\alpha(\lambda)=E(\lambda)+\alpha\lambda$ for the TFD problem equals $E_j(\lambda)$ for the j model. Moreover, there is a minimizing ρ for the TFD problem if and only if $\lambda \leq \lambda_c = Z = \int dm$. This ρ is unique and is the same as the ρ for the j model. It satisfies Eq. (3.2).*

Proof. Clearly $E_\alpha \geq E_j$ since $J_\alpha(\rho) \geq j(\rho)$. First suppose $\lambda \leq \lambda_c = Z$ and let ρ be the unique minimum for the j problem. By Theorem 3.19, $\rho(x) \notin (0, \rho_0)$ so $E_\alpha(\lambda) \leq \mathcal{E}_\alpha(\rho) = \mathcal{E}_j(\rho) = E_j(\lambda)$. Thus $E_\alpha(\lambda)=E_j(\lambda)$. Let ρ satisfy $\int\rho=\lambda$ and $\mathcal{E}_\alpha(\rho)=E_\alpha(\lambda)$. Then since $\mathcal{E}_\alpha(\rho) \geq \mathcal{E}_j(\rho) \geq E_j(\lambda)$ we conclude that ρ minimizes $\mathcal{E}_j(\rho)$. But there is only one such ρ. Next, suppose $\lambda>\lambda_c$. Then $E_j(\lambda)=E_j(\lambda_c)=E_\alpha(\lambda_c)$. But $E_\alpha(\lambda) \leq E_\alpha(\lambda_c)$ by Theorem 6.2, and $E_\alpha(\lambda) \geq E_j(\lambda)$. Hence $E_\alpha(\lambda)=E_j(\lambda)$. By the above argument, any minimizing ρ for $\mathcal{E}_\alpha$ would have to minimize $\mathcal{E}_j$, but no such ρ exists. ■

Remark. By Theorem 3.19, $\rho(x) \notin (0, \rho_0)$ a.e. if m is amenable, and $\rho(x) \neq \rho_0$ a.e. if m is strongly amenable. If ρ is merely amenable, $\rho(x)$ can be ρ_0 with positive measure. An example is $dm(x)=\rho_0 B_R(x)dx$, with B_R being the characteristic function of a ball of radius R centered at 0. Then $\rho_\lambda(x)=\rho_0 B_r(x)$ with $4\pi\rho_0 r^3/3=\lambda$ for $\lambda \leq \lambda_c = 4\pi\rho_0 R^3/3$. This ρ_λ is easily seen to satisfy Eq. (3.2).

If m is not amenable the situation is much more complicated, but more amusing mathematically. First let us consider the energy.

Theorem 6.9. *If $V=|x|^{-1}*m \in \mathfrak{D}$, then $E_\alpha(\lambda)=E_j(\lambda)$ for all λ. In particular, $\lambda_c = Z = \int dm$ and E_α is convex in λ. If there is a minimizing ρ for $E(\lambda)$, it is unique and it is the ρ for the j model.*

A number of lemmas are needed for the proof.

Lemma 6.10. *Let $A \subset R^3$ be a measurable set and let ρ be a function in L^1 with $0 \leq \rho(x) \leq 1$ for $x \in A$, and $\rho(x)=0$ for $x \notin A$. (This implies $\rho \in L^p$, all p.) Then there exists a sequence of functions $f^n \in L^1$ such that (i) $f^n \to \rho$ weakly in every L^p with $1<p<\infty$; (ii) f^n is the characteristic function of some measurable set $F^n \subset A$; (iii) $\int f^n = \int\rho$.*

Proof: For $\delta>0$ and $y \in Z^3$ let $B(\delta, y)=\{x \in R^3 \mid -\delta/2 < x^i - \delta y^i \leq \delta/2\}$ be the elementary cubes of side δ. Let $C(\delta, y)=A \cap B(\delta, y)$. Partition $C(\delta, y)$ into two disjoint measurable sets, C^+ and C^-, such that $|C^+(\delta, y)| = \int B(\delta, y)\rho$. Let $F^\delta = \cup_{y \in Z^3} C^+(\delta, y)$, and let f^δ be the characteristic function of F^δ. Clearly $f^\delta \in L^p$ with norm $(\int\rho)^{1/p}$, and f^δ satisfies (ii) and (iii). Let $1/p+1/q=1$. Since C_0, the continuous functions of compact support, are dense in L^q, and $\|f^\delta\|_p^p = \text{constant}$, it suffices to prove that $I(\delta, g)=\int g(f^\delta-\rho) \to 0$ as $\delta \to 0$ for every $g \in C_0$. But g is uniformly continuous, so for any $\varepsilon>0$, $|g(x)-g(\delta y)|<\varepsilon$ (uniformly) for $x \in B(\delta, y)$ when δ is small enough. Since

$$\int_{B(\delta, y)} (f^\delta - \rho) = 0, \quad |I(\delta, g)| < 2\varepsilon \int \rho\,. \blacksquare$$

Lemma 6.11. *Suppose $\rho \in \mathcal{G}$ and*

$$A(\rho)=\{x\,|\,0<\rho(x)<\rho_0\} \tag{6.16}$$

has positive measure. Then there exists $\tilde{\rho}\in\mathcal{G}$ *satisfying* (*i*) $\mathcal{E}(\tilde{\rho})<\mathcal{E}(\rho)$; (*ii*) $A(\tilde{\rho})$ *is empty*; (*iii*) $\tilde{\rho}(x)=\rho(x)$ *if* $x\notin A(\rho)$; (*iv*) $\int\tilde{\rho}=\int\rho$.

Proof. Apply Lemma 6.10 to the function $h(x)=\rho(x)/\rho_0$ if $x\in A(\rho)$, $h(x)=0$ otherwise. Let $\tilde{\rho}^n(x)=\rho_0 f^n(x)$ if $x\in A(\rho)$, $\tilde{\rho}^n(x)=\rho(x)$ otherwise. Then $\int\tilde{\rho}^n=\int\rho$ and $\int J_\alpha(\tilde{\rho}^n)-\int J_\alpha(\rho)=-K$ with $K>0$ and independent of n [since $J_\alpha(t)>0$ for $0<t<\rho_0$, and $0=J_\alpha(0)=J_\alpha(\rho_0)$]. Now, as in the proof of Theorem 2.4, $\int V\tilde{\rho}^n\to\int V\rho$. $\lim D(\tilde{\rho}^n,\tilde{\rho}^n)=D(\rho,\rho)$ (easy proof). Hence for any $\varepsilon>0$ there is some n such that $\int V\tilde{\rho}^n>\int V\rho-\varepsilon$ and $D(\tilde{\rho}^n,\tilde{\rho}^n)<D(\rho,\rho)+\varepsilon$. ■

The following is a corollary of Lemma 6.11.

Theorem 6.12. (*a*) *If* $\rho\in\mathcal{G}$ *minimizes* $\mathcal{E}(\rho)$ *on* $\int\rho=\lambda$, *then* measure $\{A(\rho)\}=0$. (*b*) *Even if there is no minimizing* ρ, *a minimizing sequence for* $E(\lambda)$ *with* $\int\rho=\lambda$ *can be chosen such that* $A(\rho^n)$ *is empty for all* n.

Theorem 6.13. *Let* ρ *minimize* $\mathcal{E}_j$ *for* $\int\rho=\lambda$. $A(\rho)$ *may not be empty, but for any* $\varepsilon>0$ *there exists a* $\tilde{\rho}$ *such that* $\int\tilde{\rho}=\lambda$, $A(\tilde{\rho})$ *is empty, and* $\mathcal{E}_j(\tilde{\rho})<E_j(\lambda)+\varepsilon$.

Proof. Again, use Lemma 6.10 and mimic the proof of Theorem 6.11. ■

Proof of Theorem 6.9. That $E_\alpha(\lambda)=E_j(\lambda)$ follows from Theorem 6.13 and an imitation of the argument in Theorem 6.8. By Theorem 6.12 any minimizing ρ has $A(\rho)$ empty and thus minimizes $\mathcal{E}_j(\rho)$. There can be only one such ρ, since the minimizing ρ for $\mathcal{E}_j$ is unique. ■

In summary: $E(\lambda)=E_j(\lambda)-\alpha\lambda$ always, but a minimizing ρ may or may not exist for the TFD problem. It exists if and only if the minimizing ρ for the j model (which always exists when $\lambda\leq\lambda_c$) satisfies $\rho(x)\notin(0,\rho_0)$ a.e. A sufficient condition on V for this to occur is that V be amenable; a necessary condition seems to be difficult to find. The example of Sec. III.B illustrates the nonexistence phenomenon: If $dm(x)=g(x)dx$ with $g(x)\in(0,\rho_0)$ and $g\in L^1$, then $\rho_j(x)=g(x)$ in the neutral case, $\lambda=\lambda_c=\int g$. But $g(x)$ does not minimize $\mathcal{E}(\rho)$. A *sequence* of minimizing ρ's for $\mathcal{E}(\rho)$ are functions which on the average locally imitate g but which oscillate rapidly between the two values 0 and ρ_0.

VII. THOMAS-FERMI-VON WEIZSÄCKER THEORY

TFW theory was originally suggested by von Weizsäcker (1935) with $\delta=\delta_1\equiv\hbar^2/2m$ in Eq. (2.8). There is no fundamental justification for TFW theory in the sense that there is for TF theory, i.e., there is no theorem that the correction to the energy or density caused by the Weizsäcker term with $\delta=\delta_1$ agrees with the real quantum problem. We shall see, however, that if $\delta=(0.186)\delta_1$ then the energy correction proposed by Scott (Sec. V.B), but not the density correction conjectured in Eq. (5.37), is realized in TFW theory. If Scott is correct then *a posteriori* TFW theory has some fundamental meaning for atoms and molecules.

We were able to make a great deal of progress with TF and TFD theories essentially because of the pointwise relation between $\phi(x)$ and $\rho(x)$. In TFW theory this relation is lost, and therefore TFW theory is much more difficult mathematically. However, the physical consequences of TFW theory are much richer and *qualitatively* more nearly parallel the physics of real atoms and molecules. In addition to the above mentioned Z^2 energy correction, TFW theory remedies three defects of TF (and TFD) theory:

(i) ρ will be finite at the nuclei.

(ii) binding of atoms occurs and negative ions are stable (i.e., $\lambda_c>Z$). These two facts are closely related.

(iii) ρ has exponential falloff if $\lambda<\lambda_c$, e.g., for neutral atoms and molecules.

The theory presented here was begun by Benguria (1979) and then further developed by Benguria, Brezis, and Lieb (1981) (BBL), to which we shall refer for technical details. Some newer results will also be given, especially that $\lambda_c>Z$ for molecules, the Z^2 correction to the energy (Sec. VII.D), and the binding of equal atoms. Many interesting problems are still open, however.

The TFW energy functional (see Note (iv) below) is

$$\mathcal{E}(\rho)=A\int[\nabla\rho^{1/2}(x)]^2dx+(\gamma/p)\int\rho(x)^p dx-\int V(x)\rho(x)dx+D(\rho,\rho)+U. \tag{7.1}$$

This agrees with Eq. (2.8) in units in which $\hbar^2/2m=1$. A closely related functional, obtained by writing $\psi^2=\rho$, is

$$\mathcal{E}'(\psi)=A\int(\nabla\psi)^2+(\gamma/p)\int\psi^{2p}-\int V\psi^2+D(\psi^2,\psi^2)+U. \tag{7.2}$$

Note. (i) In this section all quantities refer to TFW theory unless otherwise stated.

(ii) Equation (7.1) is defined for $\rho(x)\geq 0$ while in Eq. (7.2) $\psi(x)$ only has to be real.

(iii) As in Sec. VI, we shall assume for simplicity that V is given by Eq. (6.3) *et seq.* Later on a slightly stronger hypothesis (7.12) will be used.

(iv) $p>1$ is a parameter; it will not be indicated explicitly unless necessary. Recall that $E^{\rm TF}$ was finite for point nuclei only if $p>\frac{3}{2}$. E is finite in TFW theory for *all* $p>0$. We need $p>1$ for Theorems 7.1 and 7.2, among other reasons. Even though we are interested in $p=\frac{5}{3}$, we allow p to be arbitrary because the dependence on p is interesting. It will turn out that $p=\frac{5}{3}$, the case of physical interest, is special—at least it is so for the proof that $\lambda_c>Z$.

A. The TFW minimization problem

The function space is

$$G_p'=\{\psi\,|\,\nabla\psi\in L^2,\psi\in L^6\cap L^{2p},D(\psi^2,\psi^2)<\infty\}. \tag{7.3}$$

We say $\rho\in G_p$ if $\rho(x)\geq 0$ and $\rho^{1/2}\in G_p'$. G_p' contains

$$F_p'=G_p'\cap L^2=\{\psi\,|\,\nabla\psi\in L^2,\psi\in L^6\cap L^{2p}\cap L^2\}. \tag{7.4}$$

Even though we are interested in $\rho\in L^1$ (or $\psi\in L^2$), the larger space G_p' is used for technical reasons in order

to prove that $\lambda_c < \infty$; in other words, we shall eventually find that all ρ's of interest are in F_p (defined analogously to G_p).

Remark. By Sobolev's inequality, $\|\nabla\psi\|_2 \geq L\|\psi\|_6$ with $L = 3^{1/2}(\pi/2)^{2/3}$ (cf. Lieb, 1976) when $\psi \in L^q$, $1 \leq q < \infty$. Thus when $\psi \in F_p'$ the restrictions that $\psi \in L^6$ and $\psi \in L^{2p}$ (if $p \leq 3$) are unnecessary. In short, $F_p' = H^1 \cap L^{2p}$, where $H^1 = \{\psi \,|\, \nabla\psi \text{ and } \psi \in L^2\}$.

As usual,

$$E(\lambda) = \inf\left\{\mathcal{E}(\rho)\,|\,\rho \in F_p, \int \rho = \lambda\right\},$$
$$E'(\lambda) = \inf\left\{\mathcal{E}'(\psi)\,|\,\psi \in F_p', \int \psi^2 = \lambda\right\}. \tag{7.5}$$

Theorem 7.1. *$\mathcal{E}(\rho)$ is strictly convex in ρ.*

Proof. The only term that has to be checked is $\int(\nabla\rho^{1/2})^2$. If $\psi_i = \rho_i^{1/2}$, $i = 1, 2$, and $\psi = (\sum \alpha_i^2\rho_i)^{1/2}$, $\sum \alpha_i^2 = 1$, then

$$\psi\nabla\psi = \sum (\alpha_i\psi_i)(\alpha_i\nabla\psi_i)$$

and

$$(\psi\nabla\psi)^2 \leq \left(\sum \alpha_i^2\psi_i^2\right)\left(\sum \alpha_i^2(\nabla\psi_i)^2\right).$$

Assuming $\psi(x) > 0$ everywhere, we are done. Otherwise, the result follows by approximation. ■

Remark. $\mathcal{E}'(\psi)$ is *not convex* in ψ because of the $-\int V\psi^2$ term.

Theorem 7.2. *For all finite λ*

(i) $E(\lambda) = E'(\lambda)$;

(ii) $E(\lambda) = \inf\left\{\mathcal{E}(\rho)\,|\,\rho \in F_p, \int \rho \leq \lambda\right\}$

and similarly for $E'(\lambda)$;

(iii) $E(\lambda)$ is convex and monotone nonincreasing in λ.

Proof. (i) Given ρ, we can always construct $\psi = \rho^{1/2}$, so $E'(\lambda) \leq E(\lambda)$. Conversely, given ψ let $f = |\psi|$. But $\nabla f = (\nabla\psi)(\operatorname{sgn}\psi)$ so $\int(\nabla f)^2 = \int(\nabla\psi)^2$. Thus $\mathcal{E}'(f) = \mathcal{E}'(\psi)$. Choosing $\rho = f^2$, $E(\lambda) \leq E'(\lambda)$. (ii) As before, "excess charge" can be put at "infinity." Here $p > 1$ is essential. (iii) $\mathcal{E}(\rho)$ is convex so $E(\lambda)$ is convex. Monotonicity is implied by (ii). ■

Remark. (i) relates the two problems defined by Eqs. (7.1) and (7.2). To obtain the convexity (iii), $\mathcal{E}$ and Theorem 7.1 were used. We shall use $\mathcal{E}'$ to obtain the existence of a minimum, and then the TFW equation for this minimum.

Lemma 7.3. *Let $V = |x|^{-1} * m$, with m a measure and $|m| = Z < \infty$. Let $\rho(x) \geq 0$. Then there exists a constant C independent of m and ρ such that for every $\varepsilon > 0$*

$$\int V\rho \leq \varepsilon Z\|\rho\|_3 + Z\varepsilon^{-1/2}CD(\rho,\rho)^{1/2}.$$

Proof. By regarding R^3 as the union of balls of unit radius centered on the points of $(\frac{1}{2})Z^3$ it suffices to assume $\operatorname{supp}(m) \subset B_1$, where $B_R = \{x \,|\, |x| \leq R\}$ and χ_R is the characteristic function of B_R. In the following, irrelevant constants will be suppressed. Write $V = V_- + V_+$ where $V_- = V\chi_2$ and similarly for ρ. First consider $I_- = \int V_-\rho_-$. By Young's inequality (and writing $|x-y|^{-1} = |x-y|^{-1}\chi_4(x-y)$ for $x, y \in B_2$) $\|V_-\|_2 \leq Z$. Thus

$$I_- \leq Z\|\rho_-\|_2 \leq Z\|\rho\|_3^{3/4}\|\rho_-\|_1^{1/4} \leq Z\{\|\rho\|_3 + \|\rho_-\|_1\}.$$

But

$$D(\rho,\rho) \geq D(\rho_-,\rho_-) \geq \|\rho_-\|_1^2$$

since $|x-y|^{-1} > \frac{1}{8}$ in B_2. Now, outside B_2, $V(x) < 2Z/|x| \equiv W(x)$. Let $Q = q\chi_2$ be the constant charge distribution such that $|x|^{-1} * Q = W(x)$ outside B_2. Then $I_+ \leq 2D(Q,\rho_+) \leq 2D(Q,Q)^{1/2}D(\rho_+,\rho_+)^{1/2}$. But $D(Q,Q) = Z^2$. Therefore (on the whole of R^3) $I \leq Z\|\rho\|_3 + ZCD(\rho,\rho)^{1/2}$. Now replace $\rho(x)$ by $\varepsilon^3\rho(\varepsilon x)$ and $dm(x)$ by $\varepsilon^3 dm(\varepsilon x)$. Then $\varepsilon I = I_\varepsilon \leq Z\varepsilon^2\|\rho\|_3 + ZC\varepsilon^{1/2}D(\rho,\rho)$. ■

From the Sobolev inequality, the following is obtained:

Corollary 7.4. *There are constants a and $b > 0$ such that for every $\psi \in G_p'$*

$$\mathcal{E}'(\psi) \geq a[\|\nabla\psi\|_2^2 + \|\rho\|_p^p + \|\rho\|_3 + D(\rho,\rho)] + U - b, \tag{7.6}$$

with $\rho = \psi^2$. In particular, $\mathcal{E}'$ is bounded below on G_p' and $E(\lambda)$ is bounded below.

It is obvious that $E(\lambda) \geq E^{TF}(\lambda)$, with the same p. If $p > \frac{3}{2}$, $E^{TF}(\lambda)$ is finite for point nuclei. The following illustrates the sort of lower bound for $E(\lambda)$ that can be obtained with the Sobolev inequality.

Theorem 7.5. *Let $p = \frac{5}{3}$. Let $E^{TFW}(A,\gamma,\lambda)$ denote the TFW energy and $E^{TF}(\gamma,\lambda)$ denote the TF energy. Let $\tilde{L} = 9.578$. Then*

$$E^{TFW}(A,\gamma,\lambda) \geq E^{TF}(\gamma + A\tilde{L}\lambda^{-2/3},\lambda). \tag{7.7}$$

In particular, for an atom with a point nucleus, $E^{TF}(\gamma,\lambda) \sim \gamma^{-1}$ whence, for an atom,

$$E^{TFW}(A,\gamma,\lambda) \geq \gamma(\gamma + A\tilde{L}\lambda^{-2/3})^{-1}E^{TF}(\gamma,\lambda). \tag{7.8}$$

Proof.

$$\int |\nabla\psi|^2 \geq \tilde{L}\left(\int |\psi|^{10/3}\right)\left(\int |\psi|^2\right)^{-2/3}.$$

See Lieb, 1976. ■

Remark. The right side of Eq. (7.8) has two properties: (i) Its slope at $\lambda = 0$ is finite. (ii) It is strictly monotone decreasing for all λ. To some extent, E^{TFW} will be seen to mimic this: E^{TFW} has a finite slope at $\lambda = 0$ and is strictly decreasing up to $\lambda_c > Z$.

Theorem 7.6. *(i) $\mathcal{E}'(\psi)$ has a minimum on the set $\psi \in F_p'$ and $\int\psi^2 \leq \lambda$.*

(ii) $\mathcal{E}'(\psi)$ has a minimum on G_p'.

(iii) The same is true for $\mathcal{E}(\rho)$ on $F_p(\int\rho \leq \lambda)$ and G_p. Furthermore ρ and ψ are related by $\rho(x) = \psi(x)^2$. The minimizing ρ is unique.

Proof. The proof we give is different from the proof of Theorem 2.4 because Fatou's lemma will be used, as stated in the remark after Theorem 2.4. Let ψ^n be a minimizing sequence. By Corollary 7.4 all quantities in Eq. (7.6) are bounded. By passing to a subsequence we can demand, by the Banach-Alaoglu theorem, that $\nabla\psi^n \to f$ weakly in L^2 and $\rho^n \to \rho$ weakly in L^3 and in L^p [where

$\rho^n = (\psi^n)^2]$. Furthermore, for any bounded ball B, $\psi \in L^2(B)$ since $\psi \in L^6(B)$. Moreover, $H^1(B)$ is relatively (norm) compact in $L^2(B)$. Thus, by passing to a further subsequence, we may assume $\psi^n \to \psi$ strongly in $L^2(B)$ for every B and pointwise a.e. Then it is clear that $\rho = \psi^2$ and $f = \nabla\psi$. As before, $\liminf \|\nabla\psi^n\|_2 \geq \|\nabla\psi\|_2$. From the pointwise convergence and Fatou's lemma, $\liminf D(\rho^n, \rho^n) \geq D(\rho,\rho)$ and $\liminf \|\rho^n\|_p \geq \|\rho\|_p$. For the V term we write $m = m_1 + m_2$ with $m_1 = m\chi_R$ and choose R large enough so that $|m_2| < \delta$ (since $|m| = Z < \infty$). If $V_2 = m_2 * |x|^{-1}$ then $\int V_2|\rho - \rho^n| < \delta(\text{const})$ by Lemma 7.3 (with $\varepsilon = 1$). Next, write $V_1 = V_- + V_+$ with $V_- = V_1\chi_r$. If $r > 2R$, $V_+(x) < 2Z/|x|$. Let Q_r be the uniform charge distribution inside B_r so that $Q_r * |x|^{-1} = 2Z/|x|$ outside B_r. Then $\int V_+|\rho - \rho^n| \leq D(Q_r, Q_r)^{1/2} D(|\rho - \rho^n|, |\rho - \rho^n|)^{1/2}$. Choose r large enough so that $D(Q_r, Q_r) < \delta^2$. $V_- \in L^{3/2}$, so $\int V_-(\rho - \rho^n) \to 0$. Since δ was arbitrary, $\int V(\rho - \rho^n) \to 0$. Combining all this, $\liminf \mathcal{E}'(\psi^n) \geq \mathcal{E}'(\psi)$. Finally, if $\int \rho^n \leq \lambda$ then $\int \rho \leq \lambda$ as in the proof of Theorem 2.4 (but using L^3). As remarked in the proof of Theorem 7.2, we can choose $\psi^n(x) \geq 0$ everywhere; hence $\psi(x) \geq 0$ and $\rho(x) = \psi(x)^2$ minimizes $\mathcal{E}(\rho)$. The uniqueness of ρ follows from the strict convexity of $\mathcal{E}(\rho)$. ■

Definition. λ_c can be defined as in Sec. II, namely, $\lambda_c = \sup\{\lambda | E(\lambda) = \lim_{\lambda' \to \infty} E(\lambda')\}$. A simple variational calculation, which exploits the fact that $V(x) \approx -Z/|x|$ for large $|x|$, shows that $\lambda_c > 0$.

Theorem 7.7. *There is a minimizing ρ on F'_p with $\int \rho = \lambda$ if and only if $\lambda \leq \lambda_c$. The minimizing ρ in Theorem 7.6 when $\lambda > \lambda_c$ is the ρ for λ_c. $E(\lambda)$ is strictly convex on $[0, \lambda]$.*

Proof. Same as for Theorem 2.5. ■

Theorem 7.8. *(i) Any minimizing $\psi \in F'_p$ for $\mathcal{E}'(\psi)$ on the set $\int \psi^2 \leq \lambda$ satisfies the* TFW equation *(in the sense of distributions):*

$$[-A\Delta + W_\psi(x)]\psi(x) = -\mu\psi(x), \tag{7.9}$$

where

$$W_\psi(x) = \gamma\psi(x)^{2p-2} - \phi_\rho(x) \tag{7.10}$$

and

$$\phi_\rho = V - |x|^{-1} * \rho \quad \textit{with } \rho = \psi^2.$$

(ii) If ψ minimizes $\mathcal{E}'(\psi)$ on G'_p, then ψ satisfies Eq. (7.9) with $\mu = 0$.

(iii) $E(\lambda)$ is continuously differentiable and $-\mu = dE/d\lambda$ for $\lambda \leq \lambda_c$, while $0 = dE/d\lambda$ for $\lambda \geq \lambda_c$. In particular, $\mu \geq 0$.

(iv) If $\rho \in G_p$ satisfies Eq. (7.9) and $\int \rho = \lambda$ (possibly ∞), then ρ minimizes $\mathcal{E}(\cdot)$ on the set $\int \rho \leq \lambda$.

(v) Fix λ. There can be at most one pair ρ, μ [with $\rho(x) \geq 0$] that satisfies Eq. (7.9) with $\int \rho = \lambda$.

Proof. (i) and (ii) are standard. Just consider $\psi + \varepsilon f$ with $f \in C_0^\infty$ and $(f, \psi) = 0$ and set $d\mathcal{E}/d\varepsilon = 0$. For the absolute minimum we do not require $(f, \psi) = 0$. The proof of (iii) is as in Theorem 2.7 (cf. LS Theorem II.10 and Lemma II.27). The proof of (iv) and (v) imitates that of Theorem 2.6. ■

We shall eventually prove that the minimizing ψ is unique (we already know that ρ, and hence ψ^2 is unique), but Theorem 7.9 is needed first. We also want to prove that $\lambda_c < \infty$, i.e., the ψ that satisfies Eq. (7.9) with $\mu = 0$ satisfies $\int \psi^2 < \infty$. This will be done in Sec. VII.B.

Theorem 7.9. *If $\psi \in G'_p$ satisfies Eq. (7.9) (as a distrubution) and $\psi(x) \geq 0$ for all x, then (i) ψ is continuous. More precisely, $\psi \in C^{0,\alpha}$ for every $\alpha < 1$ [i.e., for every bounded ball B, $|\psi(x) - \psi(y)| < M|x - y|^\alpha$ for some M and all $x, y \in B$]. (ii) If V is C^∞ on some open set Ω, then ψ is C^∞ on Ω. For point nuclei, $\Omega = \mathbb{R}^3 \setminus \{R_i\}$. (iii) Either $\psi \equiv 0$ or $\psi(x) > 0$ everywhere. (iv) $W_\psi \in L^{3-\varepsilon}_{\text{loc}}$ for every $\varepsilon > 0$.*

Proof. Clearly $V \in L^{3-\varepsilon}_{\text{loc}}$ (all $\varepsilon > 0$) and, since $\psi \in L^6$, $-A\Delta\psi \leq f$ with $f = V\psi \in L^{2-\varepsilon}_{\text{loc}}$ (all $\varepsilon > 0$). Choosing $\varepsilon < \frac{1}{2}$, we can apply a result of Stampacchia (1965, Theorem 5.2) to conclude $\psi \in L^\infty_{\text{loc}}$ and hence $\psi^{2p-1} \in L^{3-\varepsilon}_{\text{loc}}$ (all $\varepsilon > 0$). Now, $g = |x|^{-1} * \rho \in L^6$ [since $\Delta g = -4\pi\rho \Rightarrow K\|g\|_6^2 \leq \int (\nabla g)^2 = 8\pi D(\rho,\rho)$]. Therefore $-\Delta\psi \in L^{3-\varepsilon}_{\text{loc}}$ (all $\varepsilon > 0$). Then (Adams, 1975, p. 98) $\psi \in C^{0,\alpha}$. (ii) follows by a bootstrap argument as in Theorem 2.8. For (iii) we note that $-\Delta\psi = b\psi$ and $b \in L^q_{\text{loc}}$, $q > \frac{3}{2}$. The conclusion follows from Harnack's inequality (Gilbarg and Trudinger, 1977). ■

We know that $\rho^{1/2} \geq 0$ satisfies Eq. (7.9), so $\rho^{1/2}$ enjoys the above properties. Since ρ is unique we shall henceforth denote Eq. (7.10) simply by W. We shall also use the notation

$$H = -A\Delta + W. \tag{7.11}$$

Theorem 7.10. *The minimizing ψ is unique up to a sign which is fixed by $\psi(x) = \rho(x)^{1/2} > 0$ everywhere. ψ is also the unique ground-state eigenfunction of $H = -A\Delta + W(x)$ and μ is its ground-state eigenvalue.*

Proof. If ψ is minimizing then $\psi^2 = \rho$ and H are uniquely determined. $f = \rho^{1/2}$ satisfies $Hf = -\mu f$. Since f is nonnegative, it is the ground state of H, and the ground state of H is unique up to sign (cf. Reed and Simon, 1978, Sec. XIII.12). ■

Remarks. (i) It is *not* claimed that the TFW equation (7.9) and (7.10) has no solution other than the positive one. Infinitely many other solutions probably exist. They have been found for certain nonlinear equations which have some resemblance to the TFW equation (Berestycki and Lions, 1980), but the TFW equation itself has not been analyzed in this regard. These other solutions correspond, in some vague sense, to "excited states."

(ii) The interplay between $\mathcal{E}'(\psi)$ and $\mathcal{E}(\rho)$ should be noted. Apart from the somewhat pedantic question of the uniqueness of ψ, $\mathcal{E}$ was used to get the uniqueness of $\rho = \psi^2$ and the convexity of $E(\lambda)$. $\mathcal{E}'$ was used to get the TFW equation in which it is not necessary to distinguish between $\rho(x) > 0$ and $\rho(x) = 0$ as in the TF equation (2.18). The ψ of interest automatically turns out to be positive. For purposes of comparison, the TF equation is $(W + \mu)\psi = 0$ if $\psi > 0$, and $(W + \mu) \geq 0$ if $\psi = 0$. The TFW equation is $(W + \mu)\psi = A\Delta\psi$ everywhere.

(iii) Note that there is a solution even for $\mu = 0$. For this ρ, $H = -A\Delta + W$ has zero as its ground-state eigenvalue with an L^2 eigenfunction, ψ (Theorem 7.12). This is unusual. Zero is also the bottom of the essential spectrum of H.

To complete the picture of $E(\lambda)$ we have to know how $E(\lambda)$ behaves for small λ. Since μ is a decreasing function of λ (by convexity of E), μ has its maximum at $\lambda=0$.

Theorem 7.11. *$\mu(\lambda=0)=-e_0$ where $e_0<0$ is the ground-state energy of the Hamiltonian $H_0=-A\Delta-V(x)$. In particular, for a point nucleus $\mu(\lambda=0)=z^2/(4A)$.*

Proof. $\mu(0)=\lim_{\lambda\to 0}E(0)-E(\lambda)$. $E(0)=U$. Let f be the normalized ground state of H_0: $H_0 f=e_0 f$. Let $\overline{\rho}=\lambda f^2$. Clearly, $\mathcal{E}(\overline{\rho})=\lambda e_0+U+o(\lambda)$, since $p>1$. On the other hand, for any ρ with $\int\rho=\lambda$, $\mathcal{E}(\rho)\geq\lambda e_0+U$. ■

In Sec. VII.B we shall see that $Z<\lambda_c<\infty$. Therefore the behavior of $E(\lambda)$ can be summarized as follows:

$e(\lambda)=E(\lambda)-U$ in TFW theory looks like Fig. 1 with two important changes: (i) $\lambda_c>Z$ (at least for $p\geq\frac{5}{3}$). $e(\lambda)$ is strictly convex for $0\leq\lambda\leq\lambda_c$. (ii) The slope at $\lambda=0$ is finite. [In TF theory $e(\lambda)\approx\lambda^{1/3}$.]

B. Properties of the density and λ_c

Our main concern here will be to estimate λ_c. For energetic reasons, it is intuitively clear that $\lambda_c\geq Z$ for large enough p because otherwise the energy could always be lowered by adding some additional charge far out. Benguria (1979) proved this for $p\geq\frac{4}{3}$. We shall also see that $\lambda_c>Z$ for $p\geq\frac{5}{3}$.

What is far from obvious, however, is that λ_c is finite. There is no energetic reason why $E(\lambda)$ could not steadily decrease (and be bounded, of course). It is easy to construct a $\rho(x)$ with $\int\rho=\infty$ so that all the terms in the energy and also $\phi(x)$, except at the nuclei, are finite. $\rho(x)=(1+x^2)^{-3/2}$ is an example. That $\lambda_c<\infty$ is a subtle fact. The same question arises in quantum theory, and it has only recently been proved there that λ_c is finite. Ruskai (1981) proved this when the "electrons" are bosons. I. M. Sigal later found a proof (by a different method) for fermions (paper in preparation).

In the following, ψ always means $+\rho^{1/2}$. For simplicity we shall henceforth assume the following condition in addition to $V\in\mathfrak{D}$:

$$V(x)\leq C/|x| \tag{7.12}$$

for some $C<\infty$ and for all $|x|>$ some R. The fact that $V=|x|^{-1}*m$ and $|m|=Z$ does not guarantee Eq. (7.12). If, however, m has compact support, then (7.12) holds.

Theorem 7.12. *$\lambda_c<\infty$ for all $p>1$.*

Proof. Let ρ give the absolute minimum of $\mathcal{E}(\rho)$ on G_p. ψ satisfies Eq. (7.9) with $\mu=0$. We shall prove that this ρ has $\lambda=\int\rho<\infty$, thereby proving that $E(\lambda)$ has an absolute minimum at λ, and hence that $\lambda_c=\lambda$. Assume $\lambda=\infty$. Then for $|x|\geq$ some R [which is bigger than the R in Eq. (7.12)], $|x|^{-1}*\rho>2C/|x|$. Thus, for $|x|>R$, $-A\Delta\psi\leq-C\psi/|x|$. Now we use a comparison argument. Let

$$f(x)=M\exp\{-2[C|x|/A]^{1/2}\}$$

with $M>0$. f satisfies $-A\Delta f\geq-Cf/|x|$, for $|x|\neq 0$, so $-A\Delta(\psi-f)\leq-C(\psi-f)/|x|$. Fix M by $f(x)\geq\psi(x)$ for $|x|=R$. If we knew that $\psi(x)\to 0$ as $|x|\to\infty$ we could conclude, from the maximum principle, that $\psi<f$ for $|x|\geq R$. This implies that $\psi\in L^2$. Unfortunately, we only know that $\psi(x)\to 0$ in a weak sense (namely, L^6). This, it turns out, is good enough. See BBL for details. ■

Now that we know $\int\rho<\infty$, even for the absolute minimum ($\mu=0$), we can prove

Theorem 7.13. *ψ is bounded on $\mathbb{R}^3$ and $\psi(x)\to 0$ as $|x|\to\infty$. Also, $\psi\in H^2$ (i.e., $\psi,\nabla\psi$ and $\Delta\psi\in L^2$).*

Proof. $-A\Delta\psi<V\psi$ so $(-A\Delta+1)\psi\leq(V+1)\psi$. Since $(V+1)\psi\in L^2$, $\psi\leq(-A\Delta+1)^{-1}[(V+1)\psi]$ and this is bounded and goes to zero as $|x|\to\infty$ (Lemma 3.1). Finally, $\psi^{2p-1}\leq d\psi$ for some d, and $g=|x|^{-1}*\rho\in L^6$ together with $\psi\in L^6$ imply $g\psi\in L^2$. Hence $\Delta\psi\in L^2$. ■

Theorem 7.14. *If $p\geq\frac{3}{2}$ then, for all x,*

$$\gamma\rho(x)^{p-1}\leq V(x). \tag{7.13}$$

In particular, if $p=\frac{5}{3}$, $\rho(x)<[V(x)/\gamma]^{3/2}$.

Proof. The essential point is that since V is superharmonic, so is V^t for $t\leq 1$. Let $f=\psi-(V/\gamma)^t$ with $t=1/(2p-2)$. Let $B=\{x\,|\,f(x)>0\}$. Since ψ and V are continuous on B, B is open. On B, $W>0$ so $-\Delta f<0$. $f=0$ at ∞ and on ∂B, so B is empty. ■

Remark. The bound in Eq. (7.13) also holds trivially in TF theory from Eq. (2.18).

Theorem 7.15. *If $p\geq\frac{4}{3}$ then $\lambda_c\geq Z$.*

Proof. Suppose $\lambda_c=Z-\varepsilon$. Since $H=-A\Delta+W$ has zero as its ground-state energy, $(f,Hf)\geq 0$ for any $f\in C_0^\infty$. Let $f_1(x)\not\equiv 0$ be spherically symmetric with support in $1\leq|x|\leq 2$, $f_1(x)\leq 1$, and $f_n(x)=f(x/n)$. Then $\int f_n^2\phi=\int f_n^2[\phi]$, where $[\phi]$, is the spherical average of ϕ. It is easy to see that for $|x|\geq$ some R, $[\phi]\geq\varepsilon/2|x|$ since $\int\rho=Z-\varepsilon$. Therefore $\int f_n^2\phi\geq(\text{const})n^2$ for large n. $\int(\nabla f_n)^2=(\text{const})n$. The crucial quantity is $D_n=\int f_n^2\rho^{p-1}$. If $p\geq 2$, $D_n\leq(\text{const})\int\rho$. If $p<2$ use Hölder's inequality: $D_n\leq X_n^{p-1}Y_n^{2-p}$, where $X_n=\int f_n^2\rho$ and $Y_n=\int f_n^2$. Clearly $X_n\to 0$ as $n\to\infty$ since $\rho\in L^1$. $Y_n=(\text{const})n^3$. Now let $n\to\infty$, whence $(f_n,Hf_n)\to-\infty$. ■

Remarks. (i) The basic reason that $p\geq\frac{4}{3}$ is needed in the proof of Theorem 7.15 is that we want to be able to ignore the ρ^{p-1} term in W and thereby obtain a negative-energy bound state for H when $\lambda<Z$. However, if $\rho\in L^1$ then (essentially) $\rho(x)\sim|x|^{-3}f(x)$, where $f(x)$ can be slowly decreasing. Hence we can be certain that ρ^{p-1} is small compared to $|x|^{-1}$ only if $3(p-1)\geq 1$.

(ii) In Theorems 7.16 and 7.19 we prove that $\lambda_c>Z$. The underlying idea is that to have a zero-energy L^2 bound state, $W(x)$ has to be *positive* for large $|x|$. Essentially, $W(x)$ has to be as big as $|x|^{-2}$; this requirement is clear if we assume $\psi(x)\sim|x|^{-a}$ for large $|x|$. If $\lambda_c=Z$, then ϕ is (essentially) positive for large $|x|$, so the repulsion has to come from ρ^{p-1}. But if $p-1\geq\frac{2}{3}$ then ρ^{p-1} cannot be sufficiently big since $\rho\in L^1$. The theorem that $\lambda_c>Z$ when $p\geq\frac{5}{3}$ was proved for an atom in BBL. We give that proof first in Theorem 7.16 in order to clarify the ideas. Then, after Lemma 7.18, we give a proof (which is not in BBL) of the general case in Theorem 7.19. Some condition on p really is needed to have $\lambda_c>Z$. In BBL it is proved that if $p=\frac{3}{2}$, $\gamma=1$, V is given by Eq. (2.1), and $A\leq 1/16\pi$, then $\lambda_c=Z$.

Theorem 7.16. *Suppose $p\geq\frac{5}{3}$ and suppose $V=|x|^{-1}*m$*

where m is a non-negative measure that satisfies the following conditions: (i) m is spherically symmetric; (ii) the support of m is contained in some ball, $B_R = \{x \mid |x| < R\}$. Then $\lambda_c > Z$.

Proof. Assume that $\lambda_c \leq Z$. By Newton's theorem, $\phi(x) \geq 0$ for $|x| > R$. Then when $\lambda = \lambda_c$, $-\Delta\psi \geq -\gamma\psi^{2p-1}$ for $|x| > R$. ψ is spherically symmetric and $\psi(R) > 0$. Let $f(x) = C|x|^{-3/2}$, which satisfies $-A\Delta\psi \geq -\gamma\psi^{2p-1}$ for $|x| \geq R$ provided $0 < C \leq D$ with $D^{2p-2} = (3A/4\gamma)R^{3p-5}$. Let $C = \min[D, \psi(R)]$. Then $\psi(x) \geq f(x)$ for all $|x| > R$, because $-A\Delta(\psi - f) \geq -\gamma(\psi^{2p-1} - f^{2p-1})$, which would imply that $\psi - f$ is superharmonic on the set where $\psi - f < 0$. Since ψ and f go to zero at infinity, and $\psi - f \geq 0$ at $|x| = R$, this is impossible. Hence $\psi \notin L^2$, which contradicts $\|\psi\|_2 \leq Z$. ■

In the foregoing we used a comparison argument which, in turn, relied on the fact that the positive part of W, namely ρ^{p-1}, was simply related to ψ. In the proof of Theorem 7.19 we shall not have that luxury, and so the more powerful Lemma 7.18 is needed.

Lemma 7.17. *Let S_R denote the sphere $\{x \mid |x| = R\}$ and let $d\Omega$ be the normalized, invariant, spherical measure on S_1. For any function h, let $[h](r) = \int h(r, \Omega)d\Omega$ be the spherical average of h. Now suppose $\psi(x) > 0$ is C^2 in a neighborhood of S_R. Let $f(r) = \exp\{[\ln\psi](r)\}$. Then, for all r in some neighborhood of R,*

$$[\Delta\psi/\psi](r) \geq (\Delta f/f)(r)$$

$$= \{d^2f/dr^2 + (2/r)df/dr\}/f(r).$$

Proof. Let $g(x) = \ln\psi(x)$. Then $\Delta\psi/\psi = \Delta g + (\nabla g)^2$. Clearly $[\Delta g] = \Delta[g]$. Moreover, $(\nabla g)^2 \geq \{\partial g(r, \Omega)/\partial r\}^2$, and $[(\partial g/\partial r)^2] \geq (d[g]/dr)^2$ by the Schwarz inequality. Thus $[\Delta\psi/\psi] \geq \Delta[g] + (\nabla[g])^2 = \Delta f/f$. ■

Lemma 7.18. *Suppose $\psi(x) > 0$ is a C^2 function in a neighborhood of the domain $D = \{x \mid |x| > R\}$ and ψ satisfies $\{-A\Delta + W(x)\}\psi(x) \geq 0$ on D. Let $[W]$ be the spherical average of W and write $[W] = [W]_+ - [W]_-$ with $[W]_+(x) = \max([W](x), 0]$. Suppose $[W]_+ \in L^{3/2}(D)$. Then $\psi \notin L^2(D)$. (Note: no hypothesis is made about $[W]_-$.) See note added in proof below.*

Remarks. Simon (1981, Appendix 3) proves a similar theorem for $D = R^3$, except that $[W] = [W]_+ - [W]_-$ is replaced by $W = W_+ - W_-$ with $W_+ = \max(W, 0)$. Simon does not require the technical restrictions that $\psi(x) > 0$ and ψ is C^2. Simon's theorem will be used in our proof. Lemma 7.18 improves Simon's result in two ways: (i) It is sufficient to consider D and not all of R^3. (ii) It is only necessary that $[W]_+$, and not W_+, be in $L^{3/2}$; the latter distinction is important. As an example, suppose that for large $|x|$ the potential W is that of a dipole, i.e., $W(x_1, x_2, x_3) = x_1|x|^{-3}$. $W_+ \notin L^{3/2}$ but, since $[W]_+ = 0$, Lemma 7.18 says that this W cannot have a zero-energy L^2 bound state.

Proof. Let $f = \exp\{[\ln\psi]\}$ as in Lemma 7.17. Then $-A\Delta f/f + [W] \geq [-A\Delta\psi/\psi + W] \geq 0$. By Jensen's inequality $\int f^2 \leq \int \psi^2$, so if $f \notin L^2$ then $\psi \notin L^2$. Therefore it suffices to consider $\{-A\Delta + [W](x)\}f \geq 0$ and to prove $f \notin L^2$ under the stated condition on $[W]$. First, suppose $D = R^3$. Then this is just Simon's (1981) theorem. (However, since we are now dealing with spherically symmetric $[W]$ and f, it is likely that a direct, ordinary differential equation proof can be found to replace Simon's proof.) Next, suppose $R > 0$. Let $g(x) > 0$ be any C^2 function defined in R^3 such that $g(x) = f(x)$ for $|x| \geq R$. Then $\{-A\Delta + U(x)\}g \geq 0$ on R^3 where $U = [W]$ for $|x| \geq R$ and U is bounded for $|x| \leq R$. Clearly $[W]_+ \in L^{3/2}(D)$ if and only if $U_+ \in L^{3/2}(R^3)$. Apply Simon's theorem to U. ■

Note added in proof. H. Brezis (private communication) has found a direct ordinary differential equation proof. Moreover, under the hypotheses of Lemma 7.18, $\psi \notin L^{3-\varepsilon}$ for all $\varepsilon > 0$.

Theorem 7.19. *Let the hypothesis be the same as in Theorem 7.16 except that (i) is omitted. (In other words, a molecule is now being considered.) Then $\lambda_c > Z$.*

Proof. For $|x| > R$, $V(x)$ is C^∞ so $\psi(x) > 0$ and $\psi \in C^2$ by Theorem 7.9. Assume $\lambda_c \leq Z$. The hypotheses of Lemma 7.18 are satisfied with $[-A\Delta + W(x)]\psi = 0$. To obtain a contradiction we have to show $[W]_+ \in L^{3/2}$. Consider ϕ. Even if ϕ is negative somewhere, $[\phi](r) > 0$ in D by Newton's theorem. Therefore it suffices to show $[\rho^{p-1}] \in L^{3/2}$. If $p \geq \frac{5}{3}$ then $p - 1 \geq \frac{2}{3}$ and $[\rho^{p-1}](r) < C[\rho^{2/3}](r)$, since ρ is bounded. But $[\rho^{2/3}](r) \leq \{[\rho](r)\}^{2/3}$, by Hölder, and $\int [\rho]^{(2/3)(3/2)} = \int \rho < \infty$. ■

We know that $\lambda_c > Z$ in the physically interesting case $p = \frac{5}{3}$. *How large is $\lambda_c - Z$?* In other words, *how negative can ions be?* This seems to be a very difficult question, even for an atom. To obtain qualitative agreement with quantum theory, it would be desirable if $\lambda_c - Z \sim 1$, at least for Z up to 100, say. The only available bound, at present, is Theorem 7.23. First Lemmas 7.20, 7.21, and 7.22 are needed. The lemmas were inspired by the work of R. Benguria (private communication), who proved the lemmas and Theorem 7.23 in the spherically symmetric case (which corresponds to the atom in TFW theory).

Lemma 7.20. *Let ψ and f be two real valued functions on R^3 which satisfy $-\Delta\psi = f$ in the sense of distributions. Let r denote the function $|x|$. Suppose $\psi \in L^2$, $f \in L^2$, and $r\psi f \in L^1$. Then, for any constant $d \geq 0$,*

$$\int (|x|^2 + d)^{1/2}\psi(x)f(x)dx \geq 0.$$

Proof. Using dominated convergence, it is sufficient to consider only $d > 0$. Let $R = (r^2 + d)^{1/2} \in C^\infty$. We have $\Delta R = 2R^{-1} + dR^{-3}$ and $|(R/r)\nabla R|^2 = 1$. Suppose $\phi \in C_0^\infty$ (infinitely differentiable functions of compact support). We claim $I = -\int R\phi\Delta\phi \geq 0$. To see this, integrate by parts: $I = A + B$ with $A = \int (\nabla\phi)^2 R$ and

$$B = \int \phi\nabla\phi \cdot \nabla R = \int (\nabla\phi \cdot \nabla R)(R/r)(r/R)\phi.$$

By Schwarz, and $\{(\nabla\phi \cdot \nabla R)(R/r)\}^2 \leq (\nabla\phi)^2$, we have $B^2 \leq AC$ with

$$2C = 2\int \phi^2 r^2 R^{-3} \leq \int \phi^2 \Delta R.$$

However,

$$2B = \int \nabla\phi^2 \cdot \nabla R = -\int \phi^2 \Delta R,$$

and hence $|B| \leq A$, which proves the lemma. Now, suppose ψ and $f \neq C_0^\infty$ have compact support. Given $\varepsilon > 0$ there exists $g \in C_0^\infty$ such that $\|\psi - g\|_2 < \varepsilon$, $\|\nabla\psi - \nabla g\|_2 < \varepsilon$, and $\|\Delta\psi - \Delta g\|_2 < \varepsilon$. (Note: since ψ and $\Delta\psi \in L^2$, so is $\nabla\psi$.) Then $gR \in C_0^\infty$ and

$$\int gRf = -\int gR\Delta\psi \equiv -\int \psi\Delta(Rg)$$
$$= -\int g\Delta(Rg) - M = -\int Rg\Delta g - M,$$

with $M = \int (\psi - g)\Delta(Rg)$. It suffices to show that $M \to 0$ as $\varepsilon \to 0$ because $\int gRf \to \int \psi Rf$. But

$$M = \int (\psi - g)\{g\Delta R + 2\nabla g \cdot \nabla R + R\Delta g\}.$$

We can assume supp(g) is in some fixed ball, independent of ε. Since g, ∇g, and Δg are uniformly L^2 bounded, $M \to 0$. For the general case, let $h \in C_0^\infty$ satisfy $1 \geq h \geq 0$, $(\nabla h)(0) = 0$, $h(0) = 1$, $h(x) = 0$ for $|x| > 1$. Let $h_n(x) = h(x/n)$ and $\psi_n = h_n\psi$. Then, as a distribution,

$$-\Delta\psi_n = h_n f - 2\nabla h_n \cdot \nabla\psi - \psi\Delta h_n \equiv K_n.$$

By the previous result, $T_n \equiv \int R\psi_n K_n \geq 0$. But $\int h_n^2 \psi f R \to \int \psi f R$ by dominated convergence. $Rh_n \Delta h_n = n^{-1}P_n(x/n)$ with

$$P_n(x) = (|x|^2 + dn^{-2})^{1/2}(h\Delta h)(x) < a,$$

so $\int R\psi_n\psi\Delta h_n \to 0$, since $\psi \in L^2$. Similarly, $R\nabla h_n^2 \equiv L_n$ is uniformly bounded and converges pointwise to zero. Since ψ and $\nabla\psi \in L^2$, $\int \psi\nabla\psi L_n \to 0$ by dominated convergence. ■

Remarks. (i) Lemma 7.20 is useful for L^2 solutions to the Schrödinger equation $[-\Delta + W(x)]\psi = -\mu\psi$. Then $\int \psi^2(W + \mu)r \leq 0$ under some mild conditions on W [e.g., $W(x) < c/r$ for large r, $W \in L^2_{\text{loc}}$ and $r\psi^2 \in L^1$ if $\mu \neq 0$].

(ii) The essential properties of R that were used were $R > 0$ and $R\Delta R \geq 2(\nabla R)^2$. Therefore Lemma 7.20 will hold for functions other than $(r^2 + d)^{1/2}$ having these properties. Formally, this means that if $R(x) = 1/V(x)$ then we require $V > 0$ and $\Delta V < 0$. We state this as Lemma 7.21, whose proof imitates the proof of Lemma 7.20.

Lemma 7.21. *Suppose $V = |x|^{-1} * m$, with m a nonnegative measure, $|m| = Z < \infty$, and V satisfies Eq. (7.12). Then if ψ and f satisfy the hypotheses of Lemma 7.20,*

$$\int dx\, \psi(x) f(x)/V(x) \geq 0.$$

Lemma 7.22. *Let $\rho(x) \geq 0$, $\int \rho = \lambda < \infty$, and $V = |x|^{-1} * m$ where m is any non-negative measure with $|m| = Z < \infty$. Then*

$$I \equiv \int \rho(x)\rho(y)|x - y|^{-1}V(x)^{-1}dx\,dy \geq \lambda^2/2Z.$$

Proof. Take $Z = 1$ and let $0 < \varepsilon < 1$. By Proposition 3.24, $\rho = \rho_1 + \rho_2$ with $\rho_1, \rho_2 \geq 0$, and $H_i = |x|^{-1} * \rho_i$ satisfies $H_1 \leq \varepsilon\lambda V$ and $H_1 = \varepsilon\lambda V$ when $\rho_2 > 0$. Clearly, $\int \rho_1 \leq \varepsilon\lambda$ by Lemma 3.3. Then $\int \rho_2 \geq (1 - \varepsilon)\lambda$ and

$$I \geq \int \rho_2(H_1 + H_2)/V \geq \varepsilon(1 - \varepsilon)\lambda^2 + \int \rho_2 H_2/V.$$

Repeat the argument with ρ_2 [using $\int \rho_2 \geq (1 - \varepsilon)\lambda$], and so on *ad infinitum*. Then

$$I \geq \lambda^2\varepsilon(1 - \varepsilon)\sum_{j=0}^{\infty}(1 - \varepsilon)^{2j} = \lambda^2(1 - \varepsilon)/(2 - \varepsilon).$$

Now let $\varepsilon \to 0$. ■

Remark. Benguria proved Lemma 7.22 when $V = 1/r$. In this case one can simply use the fact that $(|x| + |y|)|x - y|^{-1} \geq 1$.

Theorem 7.23. *Assume V satisfies Eq. 7.12. Then $\lambda_c < 2Z$, for all $p > 1$.*

Proof. We know $\lambda_c < \infty$. Let ψ be the minimizing solution of Eq. (7.9) with $\mu = 0$. Then, by Theorem 7.13, ψ and $f = (\gamma\rho^{p-1} - \phi)\psi$ satisfy the hypotheses of Lemma 7.21. Thus $0 < \int \rho\phi/V = \lambda_c - I$ with $I = \int H\rho/V$ and $H = |x|^{-1} * \rho$. But $I \geq \lambda_c^2/2Z$. ■

Remark. This bound does not involve the value of A in Eq. (7.1). It also does not utilize the $\gamma\rho^{p-1}$ term in W. There is considerable room for improvement.

The next two theorems are about the asymptotics of ψ.

Theorem 7.24. *Let ψ be the positive solution to Eq. (7.9), for any p.*

(i) Let $\mu > 0$. Then for every $t < \mu$ there exists a constant M such that

$$\psi(x) \leq M\exp[-(t/A)^{1/2}|x|].$$

(ii) Let $\mu = 0$ (i.e., $\lambda = \lambda_c$), and assume $\lambda_c > Z$, as is certainly the case when $p \geq \frac{4}{3}$. Assume also that m has compact support. Then for every $t < \lambda_c - Z$ there is a constant M such that

$$\psi(x) \leq M\exp[-2(t|x|/A)^{1/2}].$$

Proof. (i) is standard. Since ψ and $V \to 0$ as $|x| \to \infty$, we have $\psi = -(-A\Delta + t)^{-1}(W + \mu - t)\psi$. For $|x| >$ some R, $W + \mu - t > 0$. Therefore, since $\psi > 0$,

$$\psi(x) \leq \int_{|y| \leq R} Y(x - y)[W(y) + \mu - t]\psi(y)dy,$$

where

$$Y(x) = (4\pi A|x|)^{-1}\exp[-(t/A)^{1/2}|x|].$$

The proof of (ii) is the same as the proof of Theorem 7.12. It is only necessary to note that, since m has compact support (in B_R, say), $V(x) \leq Z/(|x| - R)$ for $|x| > R$, and this is $\leq (Z + \varepsilon)/|x|$ for $|x|$ large enough. ■

The next theorem is the well known cusp condition (Kato, 1957).

Theorem 7.25. *Let $V(x) = \sum z_j|x - R_j|^{-1}$ be the potential of point nuclei. Then at each R_j*

$$z_j\psi(R_j) = -2A\lim_{r \downarrow 0}\int_{|x - R_j| = r} r^{-1}(x - R_j)\cdot\nabla\psi(x)d\Omega,$$

where $d\Omega$ is the normalized uniform measure on the sphere. This holds for any λ. In particular, for an atom with nuclear charge z located at the origin, ψ is spherically symmetric and

$$z\psi(0) = -2A\lim_{r \downarrow 0}(d\psi/dr)(r).$$

Proof. Recall that, by Theorem 7.9, ψ is C^∞ away from

the R_j and ψ is Hölder continuous everywhere. The theorem is proved by integrating Eq. (7.9) in a small ball B_r and then integrating by parts. The spherical symmetry in the atomic case is implied by uniqueness. ■

Theorem 7.26. *Let $V(x)=z/|x|$ be the potential of an atom with a point nucleus. Then, for any λ, $\psi(r)$ is a strictly decreasing function of r.*

Proof. In Theorem 2.12 and the remark following it we proved this for $\lambda \leq z$ by using rearrangement inequalities. Here we give a different proof for $\lambda \leq z$ which extends to $\lambda > z$. Recall that ψ is continuous and positive and that ψ is C^∞ for $r>0$. Also, $\mu \geq 0$. Let $Q(r)=\int \chi_r \rho$ be the electronic charge inside the ball B_r. By Newton's theorem, the potential ϕ satisfies:

(i) $\phi(r) \leq [z-Q(r)]/r$.

(ii) $\dot{\phi}=[Q(r)-z]/r^2$ (dots denote d/dr).

(iii) If $\lambda \leq z$, $\phi(r) \geq 0$ and $\phi(r)$ is decreasing.

(iv) If $\lambda > z$ there is a unique $R>0$ such that $\phi(r) \geq 0$ and decreasing for $r \leq R$, and $\phi(r)<0$ for $r>R$. $Q(R)<z$.

$\lambda \leq z$: By Theorem 7.24 $\dot{\psi}(r)<0$ near $r=0$. If ψ is not monotone, then since $\psi(r) \to 0$ as $r \to \infty$, there are two points $0<r_1<r_2$ such that $\psi(r_1) \leq \psi(r_2)$, $\ddot{\psi}(r_1) \geq 0$, $\ddot{\psi}(r_2) \leq 0$, and $\dot{\psi}(r_1)=\dot{\psi}(r_2)=0$. Since ψ does not have compact support, $Q(r)<z$, all r. Hence $W(r_2)>W(r_1)$. Since

$$\ddot{\psi}(r_1)=[W(r_1)+\mu]\psi(r_1) \geq 0\,,$$

we have $W(r_1)+\mu \geq 0$. But then

$$0 \geq \ddot{\psi}(r_2)=[W(r_2)+\mu]\psi(r_2)$$

is impossible.

$\lambda > z$: There is an $\varepsilon>0$ such that $W(r)>0$ for $r>R-\varepsilon$. Let $D_r=\{x \in \mathbb{R}^3 \,|\, |x|>r\}$. Take $r>R-\varepsilon$. On D_r, $-\Delta\psi<0$. Since $\psi>0$ is subharmonic on D_r, ψ has its unique maximum on ∂D_r, namely, $|x|=r$. This proves the theorem on the domain $\{r \,|\, r>R-\varepsilon\}$. To prove the theorem on the domain $\{r \,|\, 0 \leq r<R\}$ the argument in the $\lambda \leq z$ case can be used, since $Q(r)<z$ in this domain. ■

Conjecture. In the point nucleus, atomic case ψ is convex, possibly even log convex.

C. Binding in TFW theory

In TF theory binding never occurs when the repulsion U is included. In TFW theory binding is a common phenomenon. We *conjecture* that every neutral system (molecule or atom) binds to every other neutral system. In the following, the occurrence of binding will be proved in enough cases to render the conjecture plausible. It will also be seen that binding in TFW theory is intimately connected with the existence of negative ions, i.e., $\lambda_c > Z$. We shall assume here that $\lambda_c > Z$ for all the systems under consideration. $p \geq \frac{5}{3}$ guarantees this, but no requirement on p other than $\lambda_c > Z$ will be made. $V=|x|^{-1}*m$, with m a non-negative measure of compact support [so that Eq. (7.12) is satisfied], $|m|=Z$, and m spherically symmetric in the atomic case.

First, let us define what binding means. Suppose we have two systems (not necessarily atoms) with potentials V_1 and V_2 and a combined system with $V(x)=V_1(x)+V_2(x-R)$ for some vector R. The combined system is neutral, i.e., $\lambda=Z \equiv Z_1+Z_2$. Let $E(R)$ denote the energy of the combined system and $E_i(\lambda)$ denote the energies of the subsystems with arbitrary electron charge λ and $E_i=E_i(\lambda=Z_i)$ (note the difference in notation). Then

$$E(\infty) \equiv \min_{0 \leq \lambda \leq Z} E_1(\lambda)+E_2(Z-\lambda)\,. \tag{7.14}$$

Let μ_i be the chemical potentials of the subsystems when they are neutral, i.e., $\lambda_i=Z_i$. We know that $\mu_i>0$. If $\mu_1=\mu_2$ then $E(\infty)=E_1+E_2$. Otherwise, $E(\infty)<E_1+E_2$. In general, λ in Eq. (7.14) is determined by $\mu_1(\lambda)=\mu_2(Z-\lambda)$ if this equation has a solution for $0 \leq \lambda \leq Z$; otherwise, $\lambda=0$ if $\mu_1(0) \leq \mu_2(Z)$ and $\lambda=Z$ if $\mu_2(0) \leq \mu_1(Z)$. (Recall that $\mu_i(\lambda)$ is monotone.)

If $\mu_1 \neq \mu_2$ then the subsystems *spontaneously ionize* when they are infinitely far apart. This is *not* considered to be binding. For real atoms the phenomenon of spontaneous ionization apparently never occurs, because it seems to be the case that the lowest ionization potential among *all* atoms is less than the largest electron affinity. (I thank J. Morgan III for pointing this out to me.) In real atoms, λ and $Z-\lambda$ in Eq. (7.14) are restricted to be integral, but no such restriction occurs in TFW theory. In TF theory the phenomenon never occurs because μ_i is always zero.

In TFW theory it is possible for λ to be zero in Eq. (7.14), i.e., one subsystem is completely stripped of electrons. Let $V_i=z_i/r$ with $z_2 \gg z_1$. If $\mu_1(\lambda=0) \leq \mu_2(\lambda=z_1+z_2)$, then $\lambda=0$ in Eq. (7.14). By Theorem 7.11, $\mu_1(\lambda) \leq \mu_1(0)=z_1^2/4A$. Since $\lambda_c(2)>z_2$ and $\mu_2>0$, the above inequality will hold for any fixed z_2 if z_1 is chosen small enough. This case was cited in BBL as an example where binding occurs (see Theorem 7.27).

Definition. Binding is said to occur if $E(R)<E(\infty)$ for some R.

Theorem 7.27. *Suppose the chemical potentials of the neutral subsystems are unequal, i.e., $\mu_1 \neq \mu_2$. Then binding occurs. (This holds for all $p>1$, even if $\lambda_c=Z$ for one or more of the three systems.)*

Proof. Suppose $\lambda<Z_1$ in Eq. (7.14). Then when $R=\infty$ subsystem 1 is positively charged (with charge $Q=Z_1-\lambda$) and subsystem 2 has charge $-Q$. Let ρ_i be the TFW densities (with λ and $Z-\lambda$, respectively). By Theorem 7.24, ρ_i has exponential falloff. For the combined system (at R) consider the variational ρ defined by $\rho(x)=\rho_1(x)+\rho_2(x-R)$. The first term in Eq. (7.1) is subadditive (by convexity). For large R the total Coulomb energy decreases essentially by $-Q^2/R$ because of the exponential falloff of each ρ_i. The $\int \rho^p$ term is superadditive, but it increases only by a term of order $\exp[-(\text{const})R]$ for large R. We omit the easy proof of these last two assertions. Thus for large enough, but finite, R, $E(R)<E(\infty)$. ■

The difficult case is $\mu_1=\mu_2$. Henceforth we confine our attention to atoms.

Conjecture. If $z_1<z_2$ for two atoms with point nuclei, then $\mu_1(\lambda=bz_1)<\mu_2(\lambda=bz_2)$ for all $b \leq 1$. In particular $\mu_1<\mu_2$. Moreover, $\lambda_c(1)-z_1<\lambda_c(2)-z_2$.

If this conjecture is correct then only the homopolar case has to be considered for point nuclei. In Theorem 7.28 we prove binding for the homopolar molecule, even

for "smeared" nuclei. However, we have already shown that binding occurs if $z_1 \ll z_2$, so it is likely that binding always occurs, even if the conjecture is wrong.

Theorem 7.28. *Binding occurs for two equal atoms for any nuclear charge z and for any $p > 1$ provided $\lambda_c > z$ for the atom.*

Proof. We shall construct a variational $\tilde{\rho}$ for the combined system, with $\int \tilde{\rho} = 2z$, such that $\mathcal{E}(\tilde{\rho})$ for the combined system at some R is less than $E(\infty) = 2E_1$. First, consider the atom with the nucleus at the origin and with $\lambda = z + \varepsilon$, where $z < \lambda < \lambda_c$. Let ρ be the TFW density. Denote E_1 by E and μ_1 by μ. Center the nucleus at the point $(-R, 0, 0)$, where $R > 0$, depending on ε, is such that $\int \chi_- \rho = z$, with χ_- being the characteristic functions of the half space, $H = \{(x_1, x_2, x_3) \mid x_1 \leq 0\}$. Assume, for the moment, that the nuclear m has support in $B_{R/2}$, i.e., the displaced m has support in $\{x_1 \leq -R/2\}$. Center the second atom at $(R, 0, 0)$. Its corresponding density is ρ^*, where the asterisk means reflection through the plane $x_1 = 0$. Choose the variational $\tilde{\rho} = \rho_- + \rho_-^*$ with $\rho_- = \chi_- \rho$. Clearly $\tilde{\rho}$ is continuous across the plane $x_1 = 0$, and $\int \tilde{\rho} = 2z$, so it is a valid variational function. In the following bookkeeping of $\mathcal{E}(\tilde{\rho})$ we use the terminology "energy gain" (resp. "loss") to mean that the contribution to $\mathcal{E}(\tilde{\rho})$ is negative (resp. positive) relative to $2E$. Before the χ_- cutoff, we start with $2E_1(\lambda) \leq 2E - (2\varepsilon)(\mu/2)$ if ε is small enough, so we have gained $\varepsilon\mu$. This linear term in ε is the crucial point; it exists because $\lambda_c > z$. After the cutoff we gain the kinetic energy [first two terms in Eq. (7.1)] contributions from the missing pieces of ρ and ρ^*. Next, we lose on the $-\int V\rho$ term (for each atom separately) because of the missing pieces. Each missing charge is ε and its distance to its atomic origin is R. Since the atomic $V(r) \leq z/r$, the energy loss is at most $2(\varepsilon z/R)$. Clearly we gain on the missing atomic repulsion, $D(\rho, \rho)$ term. Finally, if $dM(x) = dm(x + R) - \rho_-(x)dx$ is the total charge density in H, we lose the atom-atom interaction $\Delta = 2D(M, M^*)$. By reflection positivity, $\Delta \geq 0$. (See Benguria and Lieb (1978b), Lemma B.2.) On balance, the net energy gain is at least $\varepsilon(\mu - 2z/R) - \Delta$.

Now we claim two things: (i) As $\varepsilon \to 0$, $R \to \infty$. (ii) $\Delta < Cz\varepsilon/R$ for some constant C. [Actually, it is possible to prove $\Delta < o(\varepsilon)z/R$.] Using (i) and (ii) we are done, because for sufficiently small ε the gain is positive and the assumption on supp(m) is justified.

Proof of (i). Let ρ_n be the atomic density for $\lambda = z + \varepsilon_n$, with $\varepsilon_n \to 0$. As in the proof of Theorem 7.6, we can find a weakly convergent subsequence, $\rho_n \to \bar{\rho}$, so that $E = \lim \mathcal{E}(\rho_n) \geq \mathcal{E}(\bar{\rho})$. But $\int \bar{\rho} \leq z$, so $\bar{\rho}$ must be ρ_z, the atomic density with $\lambda = z$. If R_n does not tend to ∞ then, for large enough n, $\int \chi_- \rho_n < z$ by the weak convergence, which is a contradiction.

Proof of (ii). This is messy. Let B_r be the ball of radius r centered at $(-R, 0, 0)$ and let χ_r be its characteristic function. Write $\rho = \rho^a + \rho^b$, where $\rho^a = \chi_{3R/2}\rho$. By elementary geometry, $d\int \rho^b \geq \int \rho_-^b$ with $d < 1$. Since

$$\int \rho^b(1 - \chi_-) < \varepsilon, \quad \int \rho^b < \varepsilon/(1 - d).$$

Let $t = d/(1 - d)$. The contribution of ρ^b to Δ is

$$-4D(\rho_-^b, M^*) - 2D(\rho_-^b, \rho_-^{b*}) \leq -4D(\rho_-^b, M^*) \leq 4D(\rho_-^b, \rho_-^*) \leq 4D(\rho^b, \rho_-^*) \leq 2z\Big(\int \rho^b\Big)\Big/R,$$

since the potential of ρ^b is everywhere less than $(3R/2)^{-1}\int \rho^b$. Henceforth we can assume $\rho_- = \rho_-^a$ and $z > \int \rho_-^a > z - t\varepsilon$. This assumption changes M to M^a. Let $d\tilde{M}(x) = dm(x + R) - \rho^a(x)dx$. [Note: supp$(\tilde{M})$ extends outside H, but is inside $\{x_1 \leq R/2\}$.] $\phi \equiv |x|^{-1} * M^{a*}$ is subharmonic on supp$(\tilde{M})$ and harmonic on supp(m) so

$$D(\tilde{M}, M^{a*}) \leq \Big(\int d\tilde{M}\Big) D(\delta, M^{a*}),$$

where δ is a delta function at $(-R, 0, 0)$. This is

$$\leq \Big|\int d\tilde{M}\Big| z/R \leq t\varepsilon z/R,$$

since the distance of supp(M^{a*}) to $(-R, 0, 0)$ is R. Finally,

$$D(M^a - \tilde{M}, M^{a*}) = D(\rho^a - \rho_-^a, M^{a*}) \leq D(\rho^a - \rho_-^a, m^*) = D(\rho^a - \rho_-^a, z\delta^*) \leq 2\varepsilon z/R$$

since $\int \rho^a - \rho_-^a \leq \varepsilon$ and the distance of supp(ρ^a) to $(R, 0, 0)$ is $R/2$. ■

I thank J. Morgan III for valuable discussions about Theorem 7.28. Balâzs (1967) gave a heuristic argument for the binding of two equal atoms with point nuclear charges.

D. The Z^2 correction and the behavior near the nuclei

Here we consider point nuclei with potential given by Eq. (2.1). The question we address is what is the principal correction to the TF energy and density caused by the first term in Eq. (7.1)? This term, $A\int(\nabla\rho^{1/2})^2$, will henceforth be denoted by T. For simplicity we confine our attention to $p = \frac{5}{3}$, the physical value of p.

$E^{\mathrm{TF}} \sim Z^{7/3}$. In particular, for a neutral atom,

$$E^{\mathrm{TF}} = -3.678\,74z^{7/3}/\gamma \tag{7.15}$$

(I thank D. Liberman for this numerical value). At first sight, it might be thought that the leading energy correction is $O(z^{5/3})$. If $\rho^{\mathrm{TF}}(z, r) = z^2\rho^{\mathrm{TF}}(1, z^{1/3}r)$ is inserted into T, then, by scaling, $T(z) = z^{5/3}T(z = 1)$. But $T(z = 1) = \infty$ since $\rho^{\mathrm{TF}} \sim r^{-3/2}$ for small r. Thus, for point nuclei, T cannot be regarded as a small perturbation.

The actual correction is $+O(z^2)$ and bounds of this form can easily be found. The following bounds are for an atom, and can obviously be generalized for molecules.

Upper bound: Use a variational $\tilde{\rho}_{\mathrm{TF}}$ for TFW of the form $\tilde{\rho}(r) = \rho^{\mathrm{TF}}(r)$ for $r \geq 1/z$ and $\tilde{\rho}(r) = \rho^{\mathrm{TF}}(1/z)$ for $r \leq 1/z$.

Lower bound: Let $b > 0$ and write $V(r) = \tilde{V}(r) + H(r)$, where $H(r) = z/r - z^2/b$ for $zr < b$ and $H(r) = 0$ otherwise. For small enough b, $-A\Delta + H > 0$, since $\|H\|_{3/2} \sim b$. Now $\tilde{V} = |x|^{-1} * m$, with $m \geq 0$ and $|m| = z$. Let $\tilde{\rho}$ minimize $\mathcal{E}^{\mathrm{TF}}(\tilde{V}, \rho)$ with energy $E^{\mathrm{TF}}(\tilde{V})$. Then $E^{\mathrm{TFW}} \geq E^{\mathrm{TF}}(\tilde{V})$. But $E^{\mathrm{TF}}(V) \leq \mathcal{E}^{\mathrm{TF}}(V, \tilde{\rho}) = E^{\mathrm{TF}}(\tilde{V}) - \int \tilde{\rho}H$. It is not hard to prove, from the TF equation with $\tilde{V}$, that this last integral is $O(z^2)$.

The foregoing calculations show that the main correc-

tion in TFW theory comes from distances of order z^{-1} near the nuclei. The calculations, if carried out for arbitrary λ, also show that the correction is essentially independent of λ. We now show how this correction can be exactly computed to leading order in z, namely, $O(z^2)$.

Let us begin by considering the atom without electron-electron repulsion. The TF theory of such an atom was presented in Sec. V.B following Eq. (5.30). The analogous TFW equation (with $\delta = A\hbar^2/2m$ and $\hbar^2/2m = 1$) is

$$[-A\Delta + W(x)]\psi = -\mu\psi, \tag{7.16}$$

with $W(x) = \gamma\rho(x)^{2/3} - z/|x|$, and $\rho = \psi^2$. The absolute minimum, which corresponds to $\lambda = \infty$, has $\mu = 0$, namely,

$$(-A\Delta + \gamma|\psi|^{4/3} - z|x|^{-1})\psi = 0. \tag{7.17}$$

The first task is to analyze Eq. (7.17). By simple scaling, any solution scales with A, γ, and z as

$$\psi(z,\gamma,A;x) = (z^2/A\gamma)^{3/4}\psi(1,1,1;zx/A). \tag{7.18}$$

Up to Eq. (7.28) we take $z = \gamma = A = 1$. Consider the functional

$$\mathcal{F}'(\psi) = T(\psi) + P(\psi), \tag{7.19}$$

$$T(\psi) = \int (\nabla\psi)^2, \quad P(\psi) = \int k(\psi(x),x)dx, \tag{7.20}$$

$$k(\psi,x) = 3|\psi|^{10/3}/5 + 2|x|^{-5/2}/5 - |\psi|^2|x|^{-1}. \tag{7.21}$$

Note that $k \geq 0$ and, for each x, k has a minimum at $\psi = |x|^{-3/4}$. The function space for $\mathcal{F}'$ is

$$G' = \{\psi \,|\, \nabla\psi \in L^2, P(\psi) < \infty\}. \tag{7.22}$$

G' is not convex since $0 \notin G'$. Clearly, Eq. (7.17) is the variational equation for $\mathcal{F}'$. We can also define $G = \{\rho \,|\, \rho \geq 0, \rho^{1/2} \in G'\}$ and $\mathcal{F}(\rho) = \mathcal{F}'(\rho^{1/2})$. G is convex and $\rho \to \mathcal{F}(\rho)$ is convex.

Theorem 7.29. *$\mathcal{F}'(\psi)$ has a minimum on G'. This minimizing ψ is unique, except for sign, and satisfies: (i) $\psi > 0$. (ii) ψ is spherically symmetric. (iii) ψ satisfies Eq. (7.17). (iv) ψ is the only non-negative solution to Eq. (7.17) in G'. (v) ψ is C^∞ for $|x| > 0$. (vi) ψ satisfies the cusp condition $2(d\psi/dr)(0) = -\psi(0)$. (vii) for large $r = |x|$, ψ has the asymptotic expansion [which can be formally deduced from Eq. (7.17)],*

$$\psi(r) = r^{-3/4} - \tfrac{9}{64}r^{-7/4} - \tfrac{3}{2}(\tfrac{21}{64})^2 r^{-11/4} + O(r^{-15/4}), \tag{7.23}$$

$$\rho(r) = r^{-3/2} - \tfrac{9}{32}r^{-5/2} - (621/2^{11})r^{-7/2} + O(r^{-9/2}). \tag{7.24}$$

(viii) Any solution f to Eq. (7.17) in G' satisfies $|f(x)| < |x|^{-3/4}$. (ix) By (viii), ψ is superharmonic, and thus $\psi(r)$ is decreasing.

The proof of Theorem 7.29 follows the methods of Secs. VII.A and VII.B, and is given in Lieb, 1981b. The following numerical values, together with a tabulation of ψ, are in Liberman and Lieb, 1981. $\rho = \psi^2$.

$$\begin{aligned} &\psi(0) = 0.970\,133\,0, \\ &I_1 = \int (\nabla\psi)^2 = 8.583\,819\,7, \\ &I_2 = \int \{r^{-5/2} - \rho^{5/3}\} = 42.92, \\ &I_3 = \int [r^{-3/2} - \rho]/r = 34.34. \end{aligned} \tag{7.25}$$

From Eq. (7.17) one has $I_1 + I_3 = I_2$. By dilating $\psi(r) \to t^{3/4}\psi(tr)$ in Eq. (7.19), a "virial theorem" is obtained: $5I_1 + 3I_2 = 5I_3$. Thus

$$I_1 : I_2 : I_3 = 1 : 5 : 4, \tag{7.26}$$

$$\Delta E \equiv \mathcal{F}(\psi) = I_1 - 3I_2/5 + I_3 = 2I_1. \tag{7.27}$$

If the parameters are reintroduced

$$I_1(z,\gamma,A) = A\int (\nabla\psi)^2 = z^2A^{1/2}\gamma^{-3/2}I_1. \tag{7.28}$$

Let us denote the ρ we have just obtained in Theorem 7.29 [with the parameters reintroduced according to Eq. (7.18)] by ρ_∞. The scale length of ρ_∞ is z^{-1} and, for *large* r, $\rho_\infty(r)$ agrees to leading order with $\rho^{\mathrm{TF}}(r)$ for *small* r (on a scale of $z^{-1/3}$), namely, $(z/\gamma r)^{3/2}$. We claim that ρ_∞ can be spliced together with ρ^{TF} in the overlap region, $r = O(z^{-2/3})$, and the result is ρ^{TFW} to leading order in z. The splicing is independent of λ provided $\lambda/z > (\mathrm{const}) > 0$. The change in energy for an atom is then, to leading order, ΔE of Eq. (7.27), and is independent of λ. An analogous situation holds for a molecule; near each nucleus ρ^{TF} is spliced together with ρ_∞ for the appropriate z_j. This is formalized in the following theorem.

Theorem 7.30. *Let $V(x) = \sum z_j|x - R_j|^{-1}$. Consider the $Z \to \infty$ limit with the scaling given before Eq. (5.2), except that the electron charge N is not restricted to be integral. $\lambda = N/Z > 0$ is fixed. $z_j = az_j^0$, $R_j = a^{-1/3}R_j^0$, with $a\lambda = N$. Then, as $N \to \infty$,*

$$(i)\ E^{\mathrm{TFW}}(N) = E^{\mathrm{TF}}(N) + D\sum_{j=1}^{k} z_j^2 + O(a^2), \tag{7.29}$$

with $D = 2A^{1/2}\gamma^{-3/2}I_1$.

$$(ii)\ a^{-4/3}\mu^{\mathrm{TFW}}(N) \to \mu^{\mathrm{TF}}(\lambda, \underline{z}^0, \underline{R}^0). \tag{7.30}$$

(iii) Fix x. Then

$$a^{-2}\rho^{\mathrm{TFW}}(N, \underline{z}, \underline{R}; a^{-1/3}x) \to \rho^{\mathrm{TF}}(\lambda, \underline{z}^0, \underline{R}^0; x), \tag{7.31}$$

with convergence in the sense of weakly in L^1 if $\lambda \leq Z$ and weakly in L^1_{loc} if $\lambda > Z$.

(iv) Fix y. For each j

$$z_j^{-3}\rho^{\mathrm{TFW}}(N, \underline{z}, \underline{R}; R_j + z_j^{-1}y) \to (A\gamma)^{-3/2}\psi^2(y/A), \tag{7.32}$$

where ψ is the solution to Eq. (7.17) with $A = z = \gamma = 1$ given by Theorem 7.29. The convergence is pointwise and in L^1_{loc}. A refinement of Eq. (7.32) is given in Theorems 7.32–7.35.

Before proving Theorem 7.30 let us comment on its significance.

(i) Equation (7.29) states that the energy correction in TFW theory is exactly of the form of the quantum correction conjectured by Scott [Eq. (5.29)]. In particular, since $\gamma^{3/2} \sim q^{-1}$, the q dependence is the same. In order to obtain the conjectured coefficient $\frac{1}{8}$ of Eq. (5.32), with $\gamma = \gamma_p$, we must choose

$$A = q^2\gamma_p^3[16I_1]^{-2} = 0.185\,909\,19. \tag{7.33}$$

This number was mentioned after Eq. (2.8).

Yonei and Tomishima (1965) also realized that $A = 1/5$ is a good choice. They analyzed the TFW atom without electron repulsion, namely Eq. (7.16), and compared the

TFW energy with the quantum Bohr energy, Eq. (5.31), for neutral atoms with z up to 100. They did not seem to notice that this choice for A is valid even if $\lambda = N/z < 1$. Yonei (1971) analyzed TFDW theory with electron repulsion and again advocated $A = 1/5$. This is not surprising since Theorem 7.30 says that the electron repulsion does not affect ΔE to $O(z^2)$ and Theorem 6.5 (suitably modified) says that the Dirac correction changes the energy to $O(z^{5/3})$. Yonei (1971) claims that the dissociation energy and the equilibrium internuclear distance for the nitrogen molecule, calculated with this TFDW theory, are in good agreement with experiment.

(ii) The density, on a length scale $Z^{-1/3}$ agrees with quantum (and TF) theory, Theorem 5.2.

(iii) On a length scale z^{-1} near each nucleus, Eq. (7.32) states that ρ^{TFW} converges to a universal function. This phenomenon is the same as we conjectured in Eq. (5.37) for quantum theory. The universal functions are not exactly the same, but they are very close. For large values of the argument they agree, namely, $(\gamma_p\, y)^{-3/2}$, independent of A. Since the convergence in Eq. (7.32) is *pointwise*, it makes sense to ask what happens at $y = 0$. Using γ_p and A given by Eq. (7.33), the right side of (7.32) is obtained from (7.18) and (7.25) as

$$q^{-1} z_j^{-3} \rho^{\mathrm{TFW}}(x = R_j) \to 0.198\,271\,49\,. \tag{7.34}$$

On the other hand, ρ^H in Eq. (5.33) can be evaluated at $x = 0$, since only S waves contribute. At $x = 0$, $f_{n00}(0)^2 = (8\pi n^3)^{-1}$. Thus Eq. (5.37), if correct, would state that

$$q^{-1} z_j^{-3} \rho^{Q}(x = R_j) \to \zeta(3)/8\pi = 0.047\,828\,325\,. \tag{7.35}$$

To prove Theorem 7.30, Theorems 7.32–7.35, which are independently interesting, are needed. To prove them we need the following comparison theorem which was proved by Morgan (1978) in the spherically symmetric case and by T. Hoffmann-Ostenhof (1980) in the general case.

Lemma 7.31. *Let $B \subset \mathbb{R}^3$ be open, and let f and g be continuous functions on the closure of B that satisfy Δf and $\Delta g \in L^1(B)$ and $f(x)$ and $g(x) \to 0$ as $|x| \to \infty$ if B is unbounded. Assume $\Delta f \leq Ff$ and $\Delta g \geq Gg$ as distributions on B, where F, G are functions satisfying $F(x) < G(x)$ a.e. in B. Assume $f(x) > 0$ in B and $f(x) \geq g(x)$ for all $x \in \partial B$. Then $f(x) \geq g(x)$ for all $x \in B$.*

Theorem 7.32. *Let $V = z/|x|$, and let ψ_∞ be the positive solution to Eq. (7.17) given in Theorem (7.29). Let ψ be the positive solution to the TFW equation, (7.9), for some $\mu \geq 0$ and $p = \frac{5}{3}$. Then, for all x, $\psi(x) \leq \psi_\infty(x)$.*

Proof. Let $B = \{x \,|\, \psi(x) - \psi_\infty(x) > 0\}$. Take $f = \psi_\infty$ and $g = \psi$ in Lemma 7.31. Since f and g are continuous and, by Theorem 7.24, $g(x) < f(x)$ for large $|x|$, B is open and bounded. Hence Δf and $\Delta g \in L^1(B)$. On B, $A\Delta f = Ff$, $A\Delta g > Gg$ with $F = -V + f^{4/3}\gamma$ and $G = -V + g^{4/3}\gamma$. Since $F < G$ in B and $f = g$ on ∂B, $f \geq g$ in B. Therefore, B is empty. ■

For a molecule, an upper bound to ψ, which is not as nice as Theorem 7.32 but which is sufficient for Theorem 7.30, can also be obtained. We always assume $p = \frac{5}{3}$.

Theorem 7.33. *Let V be as in Theorem 7.30 with the scaling given there. Let ψ be the positive solution to the TFW equation for $\mu \geq 0$ and let B be the ball $\{x \,|\, Z^{-2/3} > |x - R_1|\}$. Then, for sufficiently large a,*

$$\psi(x) \leq \psi_\infty(x - R_1) \quad \text{for } x \in B \tag{7.36}$$

where ψ_∞ is the positive solution to Eq. (7.17) with

$$z = z_1 + dZ^{2/3}$$

and

$$d = 1 + 2(Z^0)^{-1/3} / \min\{|R_j^0 - R_1^0| \,|\, j = 2, \ldots, k\}\,.$$

Proof. By Theorem 7.14 and Eq. (7.24), we can choose a large enough so that $\psi_\infty(x - R_1) > \psi(x)$ when $x \in \partial B$ and so that $R_2, \ldots, R_k \notin B$. The proof is then the same as for Theorem 7.32, with $f = \psi_\infty$ and $g = \psi$, provided we can verify that $M(x) \equiv z|x - R_1|^{-1} - V(x) > 0$ when $x \in B$. But M, being superharmonic in B, has its minimum on ∂B. This minimum is positive for large enough a. ■

To obtain a lower bound to ψ, the following is needed.

Theorem 7.34. *Assume the hypothesis of Theorem 7.30 with $\lambda > 0$ and let ψ be the positive solution to the TFW equation. Then there is a constant d, independent of λ, such that*

(i) $h(x) \equiv |x|^{-1} * \rho < da^{4/3}$.

(ii) $\mu < da^{4/3}\lambda^{-2/3}$.

Proof. For (i) we use Theorem 7.14 together with the fact that $\int \rho = a\lambda$. For any x, let B be the ball of radius $a^{-1/3}$ centered at x. The contribution to h from $\chi_B \rho$ is bounded by $(\mathrm{const})(Z^0)^{3/2}a^{4/3}$. The contribution from $(1 - \chi_B)\rho$ is bounded by $a^{1/3}\int \rho$. For (ii), since μ is decreasing in λ, $\mu \leq -e(N)/N$. However, $e(N) > e^{\mathrm{TF}}(N)$. But $-e^{\mathrm{TF}}(N)$ scales as $a^{7/3}f(\lambda)$ and $f(\lambda) \leq (\mathrm{const})\lambda^{1/3}$ by Eq. (3.6). ■

Theorem 7.35. *Assume the same hypothesis as in Theorem 7.33. Then, for sufficiently large a,*

$$\psi(x) \geq \psi_\infty(x - R_1)\sigma(x - R_1) \quad \text{for all } x\,, \tag{7.37}$$

where ψ_∞ is the positive solution to Eq. (7.17) with $z = z_1 - 4ta^{2/3}A$ and

$$\sigma(x) = [1 - a^{2/3}t|x|] \exp(-a^{2/3}t|x|)\,.$$

Here, $At^2 = d(1 + \lambda^{-2/3})$ with d given in Theorem 7.34.

Proof. Let $f = \psi$ and $g =$ right side of Eq. (7.37). We have to verify (7.37) only in $B = \{x \,|\, a^{2/3}t|x - R_1| < 1\}$ because $g \leq 0$ otherwise. Since, by Theorem 7.29, both ψ_∞ and σ are symmetric decreasing, $\Delta g > \sigma\Delta\psi_\infty + \psi_\infty\Delta\sigma$. But

$$(\Delta\sigma)(x) = (a^{4/3}t^2 - 4a^{2/3}t/|x|)\sigma\,,$$

and $\psi_\infty^{4/3} \geq g^{4/3}$ since $\sigma \leq 1$. Therefore, to imitate the proof of Theorem 7.32, it is only necessary to verify that $a^{4/3}At^2 > h(x) + \mu$, but this is clearly true. ■

Proof of Theorem 7.30. (iv) is a trivial consequence of Theorems 7.33 and 7.35. (iii) is proved in the same way as Theorem 5.2 if we note that the energy can be controlled to $O(z^{7/3})$ by the variational upper bound given in the paragraph after Eq. (7.15). (ii) is proved by noting

that, by the proof of (iii) just given,

$$a^{-7/3}E^{\mathrm{TFW}}(a, N=a\lambda) \to E^{\mathrm{TF}}(a=1, \lambda).$$

The limit of the derivative of a sequence of convex (in λ) functions is the derivative of the limit function.

The proof of (i) is complicated. Upper and lower bounds to E of the desired accuracy, $O(Z^2)$, are needed. First, let us make a remark. Consider E as a function of A. By standard arguments used earlier, $E(A)$ is monotone increasing, concave, and hence differentiable almost everywhere for $A>0$. $dE/dA = T/A$ a.e., and $E^{\mathrm{TFW}} - E^{\mathrm{TF}} = \int_0^A (T/A)dA$. If we can find a lower and upper bound to T/A of the form

$$T/A = A^{-1/2}\gamma^{-3/2}I_1 \sum z_j^2 + (\text{lower order})$$

then Eq. (7.29) will be proved. We can, indeed, find a lower bound of this form, and hence a lower bound to E. We cannot find an upper bound of this form and therefore must resort to a direct variational calculation to obtain an upper bound to E.

Upper bound. By the monotonicity of E in N, it is only necessary that $\int\rho \leq N$. There are several ways to construct a variational ρ, which we call f. The details of the calculation of $\mathcal{E}(f)$ are left to the reader. One construction is to define $B = \{x \,|\, \rho^{\mathrm{TF}}(x) > Z^{5/2}\}$. For large a, B is the union of k connected components which are approximately spheres centered at R_j. Call these B_j. Let $\psi_{\infty j}$ be the solution to Eq. (7.17) centered at R_j and with $z = z_j - ta^{2/3}$. Let $C_j = \{x \,|\, \psi_{\infty j} > Z^{5/4}\}$. For large enough, but fixed t, $C_j \subset B_j$ for large a. The variational f is defined by $f(x) = \rho^{\mathrm{TF}}(x)$ for $x \notin B$, $f(x) = Z^{5/2}$ for $x \in B_j \setminus C_j$, and $f(x) = \psi_{\infty j}(x)^2$ for $x \in C_j$.

Lower bound. We construct a lower bound to T/A. Suppose $P_1, \ldots, P_k$ are orthogonal, vector valued functions. Then $T/A \geq \sum_j L_j^2 / \int P_j^2$, where $L_j = \int \nabla\psi \cdot P_j$. We take $P_j(x) = \nabla\psi_{\infty j}(x)\chi_j(x)$, where χ_j is the characteristic function of $D_j = \{x \,|\, |x - R_j| < tz_j^{-2/3}\}$, and t is some fixed constant. For large a, the D_j are disjoint so the P_j are orthogonal. Clearly, $\int P_j^2 = \int \nabla\psi_{\infty j}^2 + o(Z^2)$. Now multiply Eq. (7.17) for $\psi_{\infty j}$ by ψ and integrate over D_j. Then

$$L_j = -A^{-1}\int W_{\infty j}\psi_{\infty j}\psi\chi_j + \int \psi\nabla\psi_{\infty j}\cdot \mathbf{n}ds.$$

By the bound (7.37), the first integral is $(T_{\infty j}/A) + o(Z^2)$. It is not difficult to show that the second integral is $o(Z^2)$. This can be done by using Eq. (7.24), whence, for some $t \in [\frac{1}{2}, 1]$, $d\psi_{\infty j}/dr > -10z_j^{3/4}r^{-7/4}$ at $r = tz_j^{-2/3}$. ■

VIII. THOMAS-FERMI-DIRAC-VON WEIZSÄCKER THEORY

This theory has not been as extensively studied as the other theories. The results presented here are from unpublished work by Benguria, Brezis, and Lieb done in connection with their 1981 paper.

The energy functional is

$$\mathcal{E}'(\psi) = A\int (\nabla\psi)^2 + \int J(\psi^2) - \int V\psi^2 + D(\psi^2, \psi^2) + U \tag{8.1}$$

in units in which $\hbar^2/2m = 1$.

$$J(\rho) = (\gamma/p)\rho^p - (3C_e/4)\rho^{4/3}. \tag{8.2}$$

For convenience we assume $p > \frac{4}{3}$ (not $p>1$). $\mathcal{E}(\rho) \equiv \mathcal{E}'(\rho^{1/2})$. The function space for ψ is the same as for TFW theory, namely, G_p' of Eq. (7.3). Note that $\mathcal{E}(\rho)$ is not convex because of the $-\int\rho^{4/3}$ term.

As in TFD theory Eqs. (6.7)–(6.10), we introduce

$$J_\alpha(\rho) = J(\rho) + \alpha\rho, \tag{8.3}$$

and α is chosen so that $J_\alpha(\rho) \geq 0$ and $J_\alpha(\rho_0) = 0 = J_\alpha'(\rho_0)$ for some ρ_0, namely,

$$\rho_0^{p-4/3} = C_e p[4\gamma(p-1)]^{-1}$$
$$\alpha = (3p-4)[4(p-1)]^{-1}\rho_0^{1/3}C_e. \tag{8.4}$$

The necessity of $p > \frac{4}{3}$ for this construction is obvious. $\mathcal{E}_\alpha'$ and $\mathcal{E}_\alpha$ are defined by using J_α in Eq. (8.1).

The energy for $\lambda \geq 0$ is

$$E(\lambda) = \inf\left\{\mathcal{E}(\rho) \,\middle|\, \rho \in G_p, \int \rho = \lambda\right\}, \tag{8.5}$$

and similarly for $E_\alpha(\lambda)$ and $E'(\lambda)$, $E_\alpha'(\lambda)$ using $\mathcal{E}'$. If the condition $\int\rho = \lambda$ is omitted in (8.5) we obtain E, E_α, E', E_α'.

Theorem 8.1. *(i) The four functions $E(\lambda)$, $E_\alpha(\lambda)$, $E'(\lambda)$, and $E_\alpha'(\lambda)$ are finite, continuous, and satisfy*

$$E(\lambda) = E'(\lambda) = E_\alpha(\lambda) - \alpha\lambda = E_\alpha'(\lambda) - \alpha\lambda. \tag{8.6}$$

(ii) E_α is finite.

(iii) ρ minimizes $\mathcal{E}(\rho)$ on $\int\rho = \lambda$ if and only if $\psi = \rho^{1/2}$ minimizes $\mathcal{E}'(\psi)$ on $\int\psi^2 = \lambda$. This ρ and ψ also obviously minimize $\mathcal{E}_\alpha$ and $\mathcal{E}_\alpha'$.

Proof. The same as for Theorems 2.1, 6.2, and 7.2. Note that $[\int\rho^{4/3}]^{3p-3} \leq [\int\rho]^{3p-4}\int\rho^p$ (by Hölder). ■

Theorem 8.2. *Let ψ minimize $\mathcal{E}'(\psi)$ on the set $\int\psi^2 = \lambda$. Then ψ satisfies the* TFDW equation:

$$[-A\Delta + W(x)]\psi = -\mu\psi, \tag{8.7}$$

in the sense of distributions, with

$$W = \gamma\rho^{p-1} - C_e\rho^{1/3} - \phi + \alpha, \tag{8.8}$$

$\phi = V - |x|^{-1} * \rho$, and $\rho = \psi^2$. Apart from a sign, $\psi(x) > 0$ for all x, and ψ satisfies the conclusions of Theorem 7.9. ψ is the unique ground state of $H = -A\Delta + W(x)$ and μ is its ground-state eigenvalue. E is differentiable at λ and $\mu = -dE_\alpha/d\lambda = -dE/d\lambda - \alpha \geq -\alpha$. $\mu = 0$ if $E_\alpha(\lambda)$ has an absolute minimum at this λ.

Proof. The proof is basically the same as for Theorems 7.8–7.10. Although it is not known that $\rho = \psi^2$ is unique, this is not really necessary. By considering the variation of $\mathcal{E}'(\psi)$, ψ satisfies Eqs. (8.7) and (8.8). If ψ is minimizing, then so is $|\psi|$ (cf. Theorem 7.2). Hence $|\psi|$ satisfies Eq. (8.7) with the same W. But, as in Theorem 7.10, the ground state of $H = -A\Delta + W$ is unique and non-negative and therefore ψ may be taken to be ≥ 0 for all x. The rest follows by the methods of Theorem 7.9. (Note: $\rho^{1/3}\psi \in L^3$ since $\psi \in L^6 \cap L^2$.) ■

Remark. As in Sec. VII, the role of $\mathcal{E}'$, as distinct from $\mathcal{E}$, is solely to prove Eq. (8.7), in which no explicit reference to $\rho \geq 0$ is made.

Remark. Theorem 8.2 does not assert the existence of

a minimizing ψ with $\int \psi^2 = \lambda$.

Now we turn to a difficult and serious problem. We do not know that $E_\alpha(\lambda)$ is monotone nonincreasing. Therefore, if we *define*

$$\hat{E}_\alpha(\lambda) = \inf\left\{\mathcal{E}_\alpha(\rho) \,|\, \rho \in G_p, \int \rho \leq \lambda\right\}, \tag{8.9}$$

we do not know that $E_\alpha(\lambda) = \hat{E}_\alpha(\lambda)$. By definition, $\hat{E}_\alpha(\lambda)$ is monotone nonincreasing. The source of the difficulty is this: Although $J_\alpha(\rho_0) = J'_\alpha(\rho_0) = 0$ (as in TFD theory), we cannot simply add small clumps of charge, of amplitude ρ_0, at ∞. This is so because such a clump would then have $\int(\nabla\psi)^2 = \infty$. Nevertheless, we can add clumps with $\mathcal{E}_\alpha$ energy strictly less than $\alpha\int\rho$, as the following theorem shows.

Theorem 8.3. *Set $V=0$ in $\mathcal{E}'$. There are C^∞ functions of compact support such that $\mathcal{E}'(\psi) < 0$.*

Proof. Let f be any function in C_0^∞ and let $\psi(x) = b^2 f(bx)$. For some sufficiently small, but positive b, $\mathcal{E}'(\psi) < 0$. To see this, note that $\int(\nabla\psi)^2$ scales as b^3, $\int\rho^{5/3}$ as $b^{11/3}$, $D(\rho,\rho)$ as b^3, while $\int\rho^{4/3}$ scales as $b^{7/3}$. ■

As a corollary we have the following.

Theorem 8.4. *$E(\lambda)$ is strictly monotone decreasing in λ. Hence*

$$E(\lambda) = \inf\left\{\mathcal{E}(\rho) \,|\, \rho \in G_p, \int \rho \leq \lambda\right\}. \tag{8.10}$$

$$E = \inf_\lambda E(\lambda) = -\infty.$$

We conjecture that $E(\lambda)$ is convex. Unfortunately, the "convexification" trick of Sec. VI, in which J_α is replaced by j, is not helpful. Because of the gradient term, any minimizing ψ will be continuous, and therefore ψ cannot omit the values $(0, \rho_0)$, even for point nuclei. While the energy for j is, indeed, convex, it is strictly smaller than $E_\alpha(\lambda)$ for all λ.

Theorem 8.5 states that E_α and E_α have absolute minima at some common, finite λ. For all we know, there may be several such λ, but all these λ are bounded. Furthermore, for every λ there is a minimizing ρ for $\hat{E}_\alpha(\lambda)$. Unfortunately, for no λ are we able to infer that $\int\rho = \lambda$.

Theorem 8.5. *(i) There exists a minimizing ρ for $\mathcal{E}_\alpha(\rho)$ on G_p, and $\psi = \rho^{1/2}$ minimizes $\mathcal{E}'_\alpha(\psi)$. Every such $\rho \in L^1$, and $\int\rho \leq$ some constant which is independent of ρ.*

(ii) There exists a minimizing ρ for $\mathcal{E}_\alpha(\rho)$ on the set $\int\rho \leq \lambda$.

Remark. It is not claimed (but it is conjectured) that the minimizing ρ is unique.

Proof. The proofs of (i) and (ii) are the same, so we concentrate on (i). The proof merely imitates the proof of Theorem 7.6. The only new point is that $\rho \in L^1$. Each term in $\mathcal{E}(\rho)$ is finite and, in particular, $I = \int J_\alpha(\rho) < \infty$. But $J_\alpha(\rho) \geq k\rho$ when $0 \leq \rho \leq \beta$ for some k, $\beta > 0$. If χ is the characteristic function of $\{x \,|\, \rho(x) \leq \beta\}$, $k\int\chi\rho < \infty$. On the other hand, $\beta^2(1-\chi)\rho \leq \rho^3$, so $\beta^2\int(1-\chi)\rho \leq \int\rho^3 < \infty$ since $\rho \in L^3$. It is easy to see from Eq. (7.6) that the bound on $\int\rho$ is independent of ρ. ■

Remark. It is surprising that the fact that $\lambda < \infty$ for any absolute minimum is obtained so easily. Recall that in TFW theory the proof of this fact (Theorem 7.12) required analysis of the TFW equation.

An important question is whether λ, for an absolute minimum, always satisfies $\lambda \geq Z$. A few things can be said about the properties of any minimizing ρ on $\int\rho = \lambda$.

Theorem 8.6. *In the atomic case, $V(r) = z/r$, any minimizing ψ is symmetric decreasing when $\lambda \leq z$. (Conjecture: this also holds for all λ.)*

Proof. The rearrangement inequality proof of Theorem 2.12 is applicable. ■

Theorem 8.7. *The conclusions of Theorem 7.13 hold for any minimizing ψ. Moreover, for every $t < \mu + \alpha$ there exists a constant M such that*

$$\psi(x) \leq M\exp[-(t/A)^{1/2}|x|].$$

Proof. Same as for Theorems 7.13 and 7.24. ■

Theorem 8.8. *Every minimizing ψ satisfies Theorem 7.25.*

Plainly, TFDW theory is not in a satisfactory state from the mathematical point of view. In TFD theory we were able to deal with the lack of convexity by means of the J_α trick. In TFW theory, the presence of the gradient term does not spoil the general theory because $\mathcal{E}$ is convex. When taken together, however, the two difficulties present an unsolved mathematical problem.

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L/R refer to left/right column