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The Thomas–Fermi Theory of Atoms, Molecules and Solids

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We place the Thomas–Fermi model of the quantum theory of atoms, molecules, and solids on a firm mathematical footing. Our results include: (1) A proof of existence and uniqueness of solutions of the nonlinear Thomas–Fermi equations as well as the fact that these solutions minimize the Thomas–Fermi energy functional, (2) a proof that in a suitable large nuclear charge limit, the quantum mechanical energy is asymptotic to the Thomas–Fermi energy, and (3) control of the thermodynamic limit of the Thomas–Fermi theory on a lattice.

Contents

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I. Introduction

From the earliest days of quantum mechanics, it has been clear that one could not hope to solve exactly most of the physically interesting systems, especially those with three or more particles. Thus, by 1930 (only 5 years after the advent of the "new" quantum theory), a large variety of approximate methods had been developed such as the time-independent perturbation theory contained in some of Schrödinger's original series of papers [76], the time-dependent perturbation theory developed especially by Dirac [14], the high-accuracy variational methods by Hylleraas [34], the Hartree approximation [28] and its improvement by Fock [19] and Slater [84], the Thomas–Fermi (henceforth TF) approximation [17, 90] and the WKB method [35, 94, 8, 44].

There has been a great deal of work on rigorous mathematical problems in quantum theory, most of it on the fundamentals (beginning with von Neumann's great treatise [62]) and on the relevant operator theory (see [41] for a review up to 1966). Until recently, the only approximation methods treated in the mathematics literature were the variational methods (for which much of the mathematical theory predates quantum mechanics; see the treatise of Stenger and Weinstein [86] for recent developments) and perturbation theory starting from the pioneering work of Rellich [70] on time-independent perturbation theory. (See also [37, 40; 81] for a discussion of time-dependent perturbation theory.) It is not surprising that the other approximation methods have not been so extensively discussed. Perturbation theory is "linear" and variational methods are "basically linear" and the past 40 years have been the age of linear functional analysis. The other techniques are basically nonlinear. They are, in fact, a particularly fascinating class of nonlinear problems. It is not uncommon for one to approximate basic nonlinear equations arising in a physical context by linear ones; in contradistinction the TF and Hartree–Fock methods involve approximating a linear system in a large number of variables by a nonlinear system in a few variables!

Recently, with the popularity of nonlinear functional analysis has come some work on the nonlinear methods. Maslov [57] has studied WKB methods in detail. (See [9, 56, 58, 88, 91] for other WKB results.) The results obtained thus far for the Hartree, Hartree–Fock, and TF methods are of a more meager sort. These methods lead to nonlinear differential and/or integral equations and it is not obvious that these equations even have solutions. For the Hartree equation, this was established for helium by Reeken [69] using a bifurcation analysis. (See [75, 87] for related results.) For general atoms, Wolkowsky [95], using the Schauder fixed point theorem, proved the existence of solutions to the Hartree equation in the spherical approximation. Solutions of the Hartree–Fock equations for a class of potentials *excluding* the Coulomb potentials has been established by Fonte, Mignani, and Schiffrer [23]. Solutions of the time-dependent Hartree–Fock equations have been studied recently by Bove, DaPrato and Fano

[7] and Chadam and Glassey [10]. Using in part methods of the present paper, we have established the existence of solutions of the Hartree and Hartree–Fock equations with Coulomb forces. These results, announced in [50], will appear elsewhere [51].

The TF theory, which is the topic of this paper, has an enormous physics literature (see, e.g., [6, 24, 55]) and few rigorous results. Existence of solutions of the nonlinear *ordinary* differential equation associated with the TF *atom* was shown by Hille [32, 33] (see also Rijnierse [71]) who also established Sommerfeld's asymptotic formula [85] for spherically symmetric solutions (see Sect. IV. 2 below). At least three important questions were left open: (i) the existence of solutions of the nonlinear *partial* differential equation that arises in the TF theory of molecules when rotational symmetry is lacking; (ii) the much more important question of the connection of the TF theory with the original quantum system it was meant to be approximating; (iii) the rigorous connection between the TF equation and the TF energy functional of Lenz [46]. It is these questions, among others, that we wish to answer in this paper. We consider questions (i) and (iii) in Section II and question (ii) in Section III. In Sections IV–VII, we discuss further elements of the theory. Among our most significant additional results are: (iv) extension of Sommerfeld's formula to the molecular case; (v) a rigorous transcription of Teller's result [89] that molecules do not bind in the TF theory; (vi) a proof that the TF theory of a large system with charges at points in a lattice is well approximated by a TF theory in a box with periodic boundary conditions; (vii) a proof of concavity of the chemical potential in TF theory as a function of electron charge.

In the remainder of this introduction, we shall describe the TF approximation, establish some of its formal properties that we need later and summarize our results. Some of our results were announced in [49, 98, 99]. See Note 1.

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I.1. *The* TF *Equation and the* TF *Energy Functional*

We begin by describing the quantum mechanical problem that will concern us. We consider a system of N "electrons" of mass m and charge $-e < 0$ moving about *fixed positive* charges of magnitude $z_1e,\ldots, z_ke$ at positions $R_1,\ldots, R_k \in \mathbb{R}^3$. Then the classical Hamiltonian (energy function) is given by

$$H_C(p_1,\ldots, p_N; r_1,\ldots, r_N) = (2m)^{-1} \sum_{i=1}^{N} p_i^2 + \sum_{i<j}^{N} W(r_i - r_j) - \sum_{i=1}^{N} V(r_i), \qquad (1)$$

where

$$V(r) = e^2 \sum_{j=1}^{k} z_j \,|\, r - R_j \,|^{-1} \qquad (1a)$$

and

$$W(r) = e^2 | r |^{-1}.$$

The corresponding quantum mechanical operator acting on $L^2(\mathbb{R}^{3N})$, with h being Planck's constant, is given by

$$H_Q{}^N = -h^2(8\pi^2 m)^{-1} \sum_{i=1}^{N} \Delta_i - \sum_{i=1}^{N} V(r_i) + \sum_{i<j=1}^{N} W(r_i - r_j). \qquad (2)$$

The Pauli principle for electrons will play a major role in our considerations so we note its form when electron spin is taken into account. The relevant Hilbert space is enlarged from $L^2(\mathbb{R}^{3N})$ to $\mathscr{H} = L^2(\mathbb{R}^{3N}; \mathbb{C}^{2N}) = \otimes_{i=1}^{N} L^2(\mathbb{R}^3; \mathbb{C}^2)$, where $L^2(\mathbb{R}^m; \mathbb{C}^k)$ is the set of square integrable functions on $\mathbb{R}^m$ with values in $\mathbb{C}^k$, i.e., "functions of space and spin." The operator (2) acts on $\mathscr{H}$ and commutes with the natural action of the permutation group $\mathscr{S}_N$ on $\mathscr{H}$. We are interested in the operator H_Q restricted to $\mathscr{H}_{\mathrm{PHYS}}$, the subspace of $\mathscr{H}$ on which each $\pi \in \mathscr{S}_N$ acts as multiplication by ϵ_π, the signature of π. In other words, $\mathscr{H}_{\mathrm{PHYS}}$ is the N-fold antisymmetric tensor product of $L^2(R^3; \mathbb{C}^2)$. We continue to denote $H_Q{}^N \upharpoonright \mathscr{H}_{\mathrm{PHYS}}$ by $H_Q{}^N$ or, when necessary, by $H_Q{}^N(z_1, \ldots, z_k; R_1, \ldots, R_k)$. We shall let $E_N{}^Q$, the "ground state energy," denote the infinum of the spectrum of $H_Q{}^N$. If $N - 1 < \sum_{j=1}^{k} z_j$, this infinum is known to be an eigenvalue of $H_Q{}^N$ [79, 97]. The eigenvector is then called the ground state function. One of the unsolved problems in atomic physics is how large N can be before the infinum stops being an eigenvalue but this question will not concern us here. Among our results (Sect. III) will be limit theorems on the behavior of $E_N{}^Q$ as $N \to \infty$ with z_i/N constant and R_i depending suitably on N; i.e., varying as $N^{-1/3}$. Occasionally, it will be useful to add the constant "internuclear potential energy" $\sum_{i<j} z_i z_j e^2/|R_i - R_j|$ to H_C and $H_Q{}^N$.

We shall introduce the TF equation by describing two "derivations" of it common in the physics literature. The reader may wish to omit these heuristic considerations and merely take Eq. (3) and (7) as the definition of TF theory.

The derivations are essentially the original one of Thomas [90] and Fermi [17] and a slightly later one of Lenz [46]. Both are based on minimization of energy and essentially the same approximate expression for the energy is involved. They differ in their way of deriving the energy formula: One depends on the semiclassical ansatz for counting states while the other depends on a simple approximation in the Rayleigh–Ritz formula for the ground state energy. They also differ in the methods of obtaining the minimizing solution once the energy is given: The second method minimizes by appealing to an Euler–Lagrange equation with subsidiary conditions handled by Lagrange multipliers; the first is a more intuitive Fermi surface argument.

Quantum mechanics enters the first derivation through the mystical postulate that each particle fills up a volume h^3 in the $x - p$ phase space. Allowing for the fact that there are two kinds of electrons ("spin up" and "spin down"), a volume

h^3 in $x - p$ phase space can accommodate two electrons. The TF model views the quantum system as a classical gas filling phase space, and which interacts with itself (via the Coulomb repulsion W) and with the attractive potential V. We suppose that the gas fills a volume of total size $(\frac{1}{2})\,Nh^3$ in such a way that the total energy is minimized. This total energy has three pieces if we include the kinetic energy. Thus, if S is a trial volume in phase space, we want to minimize:

$$(2m)^{-1} \int_S p^2\, d\tau + \int_S \int_S (\tfrac{1}{2}) e^2 \mid x - y \mid^{-1} d\tau_x d\tau_y - \int_S V(x)\, d\tau_r$$

subject to $\int_S d\tau = N$, where $d\tau = (2h^{-3})\, dxdp$. Since the last two terms are only dependent on the volume of the x-dependent slice, $S_x = \{p \mid (x, p) \in S\}$, and the first term is clearly minimized by taking the slice to be a ball, the set S_x is clearly $\{p \mid \mid p \mid \leqslant p_F(x)\}$. Define

$$\rho(x) = 2h^{-3}(4\pi/3)\, p_F(x)^3.$$

Then $\rho(x)$ is the density of electrons at x and we must have

$$\int_{\mathbb{R}^3} \rho(x)\, dx = N. \tag{3a}$$

If we remove a small amount of gas from the surface of the Fermi sphere, S_x, at point x, the change in energy per unit of gas so moved will be

$$(2m)^{-1}\, p_F(x)^2 - \phi(x) \equiv -\psi(x),$$

where

$$\phi(x) = V(x) - \int \rho(y)\, W(x - y)\, dy. \tag{3b}$$

If $\psi(x)$ were not a constant at all points with $p_F(x) > 0$, we could lower the energy of the gas by moving gas from a region of small $\psi(x)$ to a region of larger $\psi(x)$. Thus $\psi(x)$ must be a constant ϕ_0, at least at points with $p_F(x) \neq 0$. If $p_F(x) = 0$, we can demand $-\phi(x) \geqslant -\phi_0$, for otherwise we could lower the energy by moving some gas to x. Thus:

$$\rho(x) = 0 \qquad \text{if } \phi(x) \leqslant \phi_0, \tag{3c}$$

$$c\rho^{2/3}(x) = \phi(x) - \phi_0 \qquad \text{if } \phi(x) \geqslant \phi_0, \tag{3d}$$

where

$$c = h^2(2m)^{-1}\, 3^{2/3}(8\pi)^{-2/3}. \tag{3e}$$

The integral equations (3b–3d) with ϕ_0 adjusted so that (3a) holds are *the TF equations*. Henceforth, we choose units so that $e = 1$ and so that c, given by (3e), is 1. At times we shall introduce $\epsilon_F \equiv -\phi_0$, the *TF chemical potential* or *Fermi energy*.

We note that the nonlinear TF integral equation clearly implies the nonlinear partial differential equation

$$(4\pi)^{-1}\,\Delta\phi = [\max(\phi-\phi_0\,,0)]^{3/2} - \sum_{j=1}^{k} z_j\delta(x-R_j), \tag{3f}$$

and in particular on any open set Ω disjoint from $\{R_1,\ldots,R_k\}$ and on which $\phi>\phi_0$:

$$\Delta\phi = 4\pi(\phi-\phi_0)^{3/2}. \tag{3g}$$

The second derivation of the TF equations is based on a crude variational approximation to $E_N{}^Q$. If we insert any antisymmetric variational wave function $\psi(r_1,\ldots,r_N\,;\sigma_1,\ldots,\sigma_N)$ into the relation $E_N{}^Q \leqslant \langle\psi, H_Q{}^N\psi\rangle$ for any $\|\psi\| = 1$, then only three "partial traces" of ψ enter: the one-body density

$$\begin{aligned}\rho_N^{(1)}(x) &= \sum_{i=1}^{N}\sum_{\substack{\sigma_i=\pm1\\ i=1,\ldots,N}} \int |\psi(x_1,\ldots,x_{i-1}\,,x,x_{i+1}\,,\ldots,x_N\,;\sigma_1\,,\ldots,\sigma_N)|^2\\ &\qquad\times dx_1\cdots dx_{i-1}dx_{i+1}\cdots dx_N\\ &= N\sum_{\substack{\sigma_i\pm1\\ i=1,\ldots,N}}\int|\psi(x,x_2\,,\ldots,x_N\,;\sigma)|^2\,dx_2\cdots dx_N\end{aligned} \tag{4}$$

which enters in the attractive potential energy, the two-body density

$$\rho_N^{(2)}(x,y) = N(N-1)\sum_{\sigma_i=\pm1}\int|\psi(x,y,x_3\,,\ldots,x_N\,;\boldsymbol{\sigma})|^2\,dx_3\cdots dx_N$$

which enters in the interelectron repulsion, and the "off-diagonal one-body distribution":

$$\tilde\rho_N(x,y) = N\sum_{\sigma_i=\pm1}\int\psi^*(x,x_2\,,\ldots,x_N\,;\boldsymbol{\sigma})\,\psi(y,x_2\,,\ldots,;\boldsymbol{\sigma})\,dx_2\cdots dx_N$$

which enters in the kinetic energy term. Thus

$$\begin{aligned}\langle\psi, H_Q{}^N\psi\rangle &= \frac{h^2}{8\pi^2 m}\int_{x=y}\nabla_x\cdot\nabla_y\tilde\rho_N(x,y)\,dx - \int V(x)\,\rho_N^{(1)}(x)\,dx\\ &\qquad+\frac{1}{2}\int\rho_N^{(2)}(x,y)\,W(x-y)\,dx\,dy.\end{aligned}$$

The TF approximation then rests on the ansatz that for ψ that minimizes $\langle\psi, H_Q{}^N\psi\rangle$ (or nearly minimizes it when $E_N{}^Q$ is not an eigenvalue but only the bottom of the continuous spectrum)

$$\rho_N^{(2)}(x,y) \simeq \rho_N^{(1)}(x)\,\rho_N^{(1)}(y) \tag{5}$$

and

$$\frac{h^2}{8\pi^2 m}\int_{x=y} \nabla_x \cdot \nabla_y \tilde{\rho}_N(x, y)\, dx \cong \frac{3}{5}\, c \int [\rho_N^{(1)}]^{5/3}(x)\, dx, \tag{6}$$

where c is the constant (3e).

The ansatz (5) for $\rho_N^{(2)}$ clearly has no hope of being valid except in a large N limit since $\int \rho_N^{(1)}(x)\, dx = N$ while $\int \rho_N^{(2)}(x, y)\, dx\, dy = N^2 - N$, but in the large N limit the idea that $\rho^{(2)}$ has no correlations is quite natural, and so the first half of the ansatz is most reasonable. The assumption (6) is obviously more subtle. It is based on the fact that for a cube of length L, if we take the ρ associated to the ground state of $-\Delta$ (with either Dirichlet, Neumann or a variety of other boundary conditions) then, as $N \to \infty$, the left side of (6) is asymptotic to

$$\tfrac{3}{5} N^{5/3} L^{-2}.$$

We prove this basic result (III.3) where we need it in our proof of the quantum mechanical limit theorem. We will also prove that as $N \to \infty$, the $\rho_N^{(1)}$ associated with the box ground state approaches the constant $\rho_0 = N/L^3$. Thus (6) holds as $N \to \infty$ when ψ is the ground state for $-\Delta$ in a box. The ansatz (6) is not unreasonable if V is "slowly varying" so that we can think of ρ as a "locally constant" density. Of course V is not slowly varying near R_i, and this will present a problem which requires a separate argument (Sect. III. 4). See Note 2.

With the above ansatz and our choice of units so that $c = 1$, the energy is a functional only of ρ of the following form:

$$\mathscr{E}(\rho; V) = \tfrac{3}{5} \int \rho(x)^{5/3}\, dx - \int V(x)\, \rho(x) + \tfrac{1}{2} \iint \frac{\rho(x)\, \rho(y)}{|x - y|}\, dx\, dy. \tag{7a}$$

One recognizes the TF equation (3) as the Euler–Lagrange equations for minimizing (7a) with the subsidiary conditions

$$\int \rho(x)\, dx = N, \tag{7b}$$

$$\rho \geqslant 0. \tag{7c}$$

We shall refer to $\mathscr{E}(\rho; V)$ as *the TF functional.* Notice that in minimizing $\mathscr{E}$ subject to (7b, 7c), ϕ_0 enters as a Lagrange multiplier for the equality (7b); where $\rho(x) > 0$, (7c) is not restricted so the variational derivative $\delta\mathscr{E}/\delta\rho(x)$ must be zero, giving (3d) but when $\rho = 0$, we only have $\delta\mathscr{E}/\delta\rho(x) > 0$ giving (3c).

This variational formulation of the TF equations due to Lenz [46] has several advantages:

(1) It reduces existence questions to establishing that $\mathscr{E}(\cdot; V)$ takes its minimum value subject to (7b, 7c). Alternatively, if we are given ρ_0 and define ϕ by (3b) and then ρ_1 by (3c, d), and thus view the TF equations as a fixed point problem, we have just learned that the map so defined is a gradient map and such maps are known to have special properties.

(2) It links up with the Rayleigh–Ritz principle for the ground state energy, E_N^Q, of the quantum theory thereby providing the basis for the connection with quantum mechanics which we will prove in Section III.

(3) It provides a starting point for a variety of further corrections to the TF theory [55].

I.2. *Scaling and the Quantum Mechanical Limit Theorem*

We define the Thomas–Fermi energy by

$$E^{\mathrm{TF}}(N; V) = \inf_{\rho}\{\mathscr{E}(\rho; V) \mid \int \rho(x)\, dx = N;\ \rho \geqslant 0\}. \tag{8}$$

(We shall be more explicit about restrictions on test functions, ρ, in II.1. where we shall prove that E^{TF} is finite.) As in the quantum case, we shall occasionally write $E^{\mathrm{TF}}(\lambda; z_1, ..., z_k; R_1, ..., R_k)$ if we wish to indicate explicitly that $V(x) = \sum_{j=1}^{k} z_j \mid x - R_j \mid^{-1}$. We shall refer to the ρ that minimizes (8), if it exists, as the TF density, $\rho_{\mathrm{TF}}(x)$.

On the basis of the Lenz derivation of the TF theory, one might expect that as $N \to \infty$, $E_N^Q/E^{\mathrm{TF}} \to 1$, at least if the z_j and R_j are made suitably N dependent. The choice of "suitable" N-dependence is based on:

THEOREM I.1. *Fix $Z > 0$. Let $V_Z(x) = Z^{4/3}\, V(Z^{1/3}x)$ and $\rho_Z(x) = Z^2\rho(Z^{1/3}x)$. Then*:

$$\mathscr{E}(\rho_Z;\ V_Z) = Z^{7/3}\, \mathscr{E}(\rho; V) \tag{9a}$$

and

$$\int \rho_Z(x)\, dx = Z \int \rho(x)\, dx \tag{9b}$$

Remarks. (1) V_Z is so defined that when $V(x) = \sum_{i=1}^{k} z_i \mid x - R_k \mid^{-1}$, then $V_Z(x) = \sum_{i=1}^{k} z_i Z \mid x - Z^{-1/3}R_k \mid^{-1}$. Thus all charges, both nuclear (the z_i's) and electron ($\int \rho_Z$), are scaled up by Z, and distances scaled down by a factor of $Z^{-1/3}$.

(2) This scaling law is certainly not new (see, e.g., [55]). If one did not know about it, it could be discovered quite naturally in the case $V(x) = \mid x \mid^{-1}$ by trying a transformation $\rho \to Z^{\alpha}\rho(Z^{\beta}x)$; $\mid x \mid^{-1} \to Z \mid x \mid^{-1}$. Demanding that each term in (7a) be scaled by the same factor Z^{γ}, one arrives easily at $\alpha = 2$, $\beta = 1/3$, $\gamma = 7/3$.

(3) This theorem clearly implies that

$$\begin{aligned} &E^{\mathrm{TF}}(ZN;\ z_1 Z, ..., z_k Z;\ Z^{-1/3}R_1, ..., Z^{-1/3}R_k) \\ &\quad = Z^{7/3}E^{\mathrm{TF}}(N;\ z_1, ..., z_k;\ R_1, ..., R_k) \end{aligned} \tag{9c}$$

and that

$$\rho_{\text{TF}}(x; z_1 Z, ..., z_k Z; Z^{-1/3}R_1, ..., Z^{-1/3}R_k; ZN)$$
$$= Z^2 \rho_{\text{TF}}(Z^{1/3}x; z_1, ..., z_k; R_1, ..., R_k; N). \quad \text{(9d)}$$

Proof. A direct change of integration variable in each term of (7a). ∎

Equation (9c) suggests what the variation of the R_i should be in the quantum mechanical limit theorem; the main result of Section III will be that $E_{\lambda N}^Q(z_1^{(0)}N, ..., z_k^{(0)}N; R_1^{(0)}N^{-1/3}, ..., R_k^{(0)}N^{-1/3})/N^{7/3}$ approaches the TF energy $E^{\text{TF}}(\lambda; z_1^{(0)}, ..., z_k^{(0)}; R_1^{(0)}, ..., R_k^{(0)})$. Similarly, the appropriately scaled quantum density $N^{-2}\rho^Q(N^{-1/3}r)$ will approach the fixed TF density corresponding to $z_i^{(0)}$ and $R_i^{(0)}$. Moreover, in line with the ansatz of the Lenz derivation, we will prove that the m point quantum density, suitably scaled, approaches a product $\rho(x_1) \cdots \rho(x_m)$ of TF densities.

In the above, if one scales only the z_i's and N but holds the R_i's fixed, then, as will become clear, something trivial happens in the $N \to \infty$ limit. Namely, both the quantum and the TF systems approach that of isolated atoms, at least on the level of *total* energy and density. In other words, in this large N limit, both $\rho_N{}^Q$ and ρ_{TF} become concentrated within a distance $\sim N^{-1/3}$ of the various nuclei.

I.3. *Summary of the Main Results: Open Problems*

Let us conclude this introduction by summarizing the content of the remainder of the paper, and by discussing what we regard as some of the more significant open questions in TF theory and allied subjects, given our work here.

The basic existence and uniqueness theory for the TF equations appears in Section II. The most important result is that when V has the form (1*a*), then the TF equations have a unique solution when $N \leqslant Z = \sum_{i=1}^k z_k$ and no solution when $N > Z$. We prove this by discussing minima and extrema for the TF functional $\mathscr{E}(\rho; V)$ given by (7). After establishing various properties of $\mathscr{E}$ (Sects. II.1–II.3), we prove in Section II.4 that there is a minimizing ρ for $\mathscr{E}$ with the subsidiary condition $\int \rho = N$ replaced by $\int \rho \leqslant N$. The ideas here are similar to methods used by Auchmuty and Beals [1] in their study of equations similar to the TF equations. In Section II.5, we prove that this minimizing ρ has $\int \rho = N$ (resp. $\int \rho < N$) if $N \leqslant Z$ (resp. $N > Z$). The difficulty we overcome in Section II.5 is associated with the infinite volume allowed for the interaction; there is no analog of this problem in the Auchmuty and Beals work where their equation is effectively on a compact set, or in the work of Hertl, *et al.* [30, 31] (discussed below) where their interaction region is explicitly finite. The remainder of Section II concerns itself with various additional techniques of use in studying the TF energy and the chemical potential, $\epsilon_F = -\phi_0$, as a function of $N = \int \rho \, dx$. In particular, we prove that it is monotone, strictly increasing and concave as a function of N.

The basic result of Section III is the quantum mechanical limit theorem which we indicated in Section I.2 above. Precise statements appear in Section III.1 where we also show that the convergence theorem for the energy proved for V's more general than (1a) implies a convergence theorem for the densities, essentially because $\delta E/\delta V(x) = \rho(x)$. Of course, pointwise convergence of E does not imply convergence of the derivative without some additional argument, but a rather simple convexity argument turns out to suffice. The proof of the limit theorem for the energies is found in Section III.5 putting together ideas from Sections III.2–III.4.

The key element in the proof of the quantum mechanical limit theorem is the technique of Dirichlet–Neumann bracketing (III.3). This technique is based on two facts: First, in a quantum mechanical problem, adding a Dirichlet (resp. Neumann) boundary condition on some surface raises (resp. lowers) ground state energies. Second, either type of boundary condition decouples in the sense that if C is a surface in $\mathbb{R}^n$ which divides $\mathbb{R}^n$ into two components, Ω_1 and Ω_2, then $-\Delta$ with Dirichlet (or Neumann) boundary conditions is a direct sum of operators on $L^2(\Omega_1)$ and $L^2(\Omega_2)$. This method of Dirichlet–Neumann bracketing is the basis for a proof of Weyl's theorem on the asymptotic distribution of eigenvalues by Courant and Hilbert [13] and for a variety of other problems: See Lieb [47], Martin [56], Robinson [72], Guerra, Rosen, Simon [26], or Hertl, Narnhofer, and Thirring [30] who have used this technique to prove a quantum limit theorem for the thermodynamics of a large number of particles with gravitational and electrostatic interactions (TF model of White Dwarf stars). Our arguments in Section III are patterned in part on this earlier work. See Note 3.

Dirichlet–Neumann bracketing allows one to reduce the quantum mechanical problem to a problem involving particles in boxes. In all boxes except k, the potentials are approximately constant and can be controlled easily (Sect. III.2). But in the k boxes including some R_i, there is a strong attractive Coulomb singularity. We need a separate argument to show that the system does not collapse into these "central boxes" and this argument appears in Section III.4. We remark that Hertl *et al.* [30, 31] also have a Coulomb singularity to worry about. At first sight, their singularity which is produced by a large number of particles with resulting large gravitational attraction seems less severe than our singularity which is produced by a fixed number, k, of electrostatic attractors which are made large, but their method of controlling the singularity also works in our case. We give a slightly different argument which we feel exhibits the mechanism behind control of the singularity more explicitly, namely, an "angular momentum barrier."

In Section IV we discuss properties of the TF density ρ. In the purely Coulomb case (V given by (1a)) with $N = Z$ we prove that ρ is real analytic away from the R_i and that $\rho(x) - (z_i \mid x - R_i \mid^{-1})^{3/2}$ is continuous at $x = R_i$. We also prove that $\mid x \mid^6 \rho(x) \to 27/\pi^3$ as $\mid x \mid \to \infty$.

In Section V, we give a proof of the theorem of Teller [89] that the sum of the TF energy of a neutral system *plus* the internuclear potential, which we denote by e^{TF} is always lowered by taking any subset of nuclei infinitely far from the others. Our proof is essentially a careful transcription of Teller's with one important difference; since we have been careful in Section II to use methods which allow V to have Coulomb singularities, we do not need to cut off the Coulomb singularities as Teller does. This allows us to avoid criticisms of Teller's proof (mentioned in [3]). We also extend Teller's theorem to the non-neutral case.

In Section VI we consider the following problem. Let Λ be a finite subset of $\mathbb{Z}^3 \subset \mathbb{R}^3$. Place a unit positive charge at each point in Λ. Let ρ_Λ be the TF density for the neutral system and e_Λ the corresponding TF energy. One is interested in letting Λ increase to all of $\mathbb{Z}^3$ and proving that ρ_Λ and $e_\Lambda/|\Lambda|$ have limits. We do this and prove that the limits are associated with a "periodic boundary condition" TF theory in a unit cube. Our results hold when $\mathbb{Z}^3$ is replaced by any lattice in $\mathbb{R}^3$ and when the unit charge at the lattice sites is replaced by any fixed configuration of charges in each occupied cell. In addition to answering a natural question, our work in Section VI provides some justification for an approximation used in applying TF theory to solids under high pressure. However, the problem of solids at high pressure is not the same as solids with infinitely large nuclear charges. There is some question about the validity of TF theory in the former case. We also point out that our results in this case are only in the TF theory itself, i.e., we first take $Z \to \infty$ and then $\Lambda \to \infty$ rather than the other way around. In Section VII, we discuss another problem in solid state physics: the screening of an impurity by electrons.

Let us summarize some of the open problems which are raised by our developments in this paper:

PROBLEM 1. Establish an asymptotic expansion of $E_N{}^Q$ in the atomic case with $Z = N$, to order $Z^{5/3}$. We conjecture that the formalism discussed in [55] is correct in that

$$E_Q{}^N \sim aZ^{7/3} + bZ^{6/3} + cZ^{5/3}, \tag{10}$$

where a is given by TF theory (as we prove), b is an inner shell correction (which we discuss shortly) and c is related to exchange and other possible corrections. The reader can consult [55, Table 1] to see rather impressive agreement between (10) with theoretically computed constants and experimental total binding energies of atoms, even with rather small values of Z. This is much better than the purely $Z^{7/3}$ term which is off by more than 7 % even for $Z = 80$ [29].

The exchange term, $cZ^{5/3}$, has been considered in the physics literature from the very earliest refinements of TF theory (see [15]). The bZ^2 term is more subtle and was first noticed by Scott [77]. The innermost electrons in a large Z atom each makes a contribution of order Z^2 and there is no reason to expect TF theory to get the energy of these inner electrons correctly. In fact, one can explicitly solve the quantum mechanical model in which W is made zero, i.e., electron repulsion is ignored, and find an explicit $b_0 Z^2$ correction to the TF model with $W = 0$. We conjecture with Scott that $b = b_0$, for if the $0(Z^2)$ corrections are, in fact, due to the innermost electrons, these electrons should not be affected by the repulsion of the outer electrons.

We regard Problem 1 as an outstanding problem in the mathematical theory of large Z atoms. We note that since our relative errors in Section III can be seen to be of order $Z^{-\epsilon}$ for some positive ϵ, we have more information than $E^Q/Z^{7/3} \to a$. However, since adding Dirichlet or Neumann boundary conditions automatically introduces $0(Z^{-1/3})$ errors, we cannot hope to see the next term in (10) with our methods, even should we improve control of some of the other errors we make.

Directly related to Problem 1 is:

PROBLEM 2. Prove that the Hartree–Fock total binding energy is correct up to order $Z^{5/3}$ in the large Z limit for E^Q. Essentially by our construction in Section III, we know [51] that the Hartree–Fock energy is correct to leading $Z^{7/3}$ order. Since the Hartree–Fock energy seems to have both exchange and correct inner shells built into it, we expect it to be correct to order $Z^{5/3}$.

PROBLEM 3. Does Hartree–Fock give ionization energies and/or molecular binding energies asymptotically correctly in the $Z \to \infty$ limit? The TF theory does not describe the outer shell correctly so we would not expect it to give ionization or binding energies correctly (see Sect. IV.3). This is seen most dramatically by Teller's theorem (Sect. V.2) that molecules do not bind in the TF model.

PROBLEM 4. In Section II.7, we prove that the TF density maximizes a certain variational problem. Prove that it is the unique maximizing solution.

PROBLEM 5. Prove that the Fermi energy of an ion, $\epsilon_F(\lambda)$, has the property that $\lim \epsilon_F(\lambda)/(Z - \lambda)^{4/3}$ exists as $\lambda \uparrow Z$ (see IV.3).

PROBLEM 6. Prove superadditivity of the TF kinetic energy $\frac{3}{5} \int \rho^{5/3}$ when $V = V_1 + V_2$, each V_i being the attractive potential of a set of nuclei. An affirmative solution of Problem 6 would solve Problems 7 and 8; see Section V.2 for details.

PROBLEM 7. Extend Teller's theorem in the sense that $e^{\mathrm{TF}}(z_1, \ldots, z_k; R_1, \ldots, R_k)$ decreases under dilatation, $R_i \to lR_i$ $(l > 1)$. This was shown to be true by Balazs [3] when $k = 2$ and $z_1 = z_2$.

PROBLEM 8. Show that the pressure and the compressibility are positive for the TF solid.

We wish to note here that TF theory can be extended by using our methods to two additional cases of physical interest. We shall content ourselves with merely pointing out these possibilities here, and will not expand on them further.

The first extension replaces the single TF density $\rho(x)$ by k densities $\rho_1(x),..., \rho_k(x)$. The electrostatic interactions are given as in the usual TF energy with $\rho = \rho_1 + ... + \rho_k$. The kinetic energy $\frac{3}{5} \int \rho^{5/3}\, dx$ is replaced by

$$\tfrac{3}{5}\, 2^{2/3} \sum_{i=1}^{k} \int \rho_i(x)^{5/3}\, dx.$$

The physically interesting case is $k = 2$, where ρ_1 and ρ_2 can be interpreted as "spin up" and "spin down" electrons. One easily sees by convexity that the minimum of this modified energy occurs with $\rho_1 = \rho_2 = \cdots = \rho_k = \rho/k$. This observation expresses the fact that there is *no ferromagnetism in TF theory.*

The second extension allows some of the "nuclear" charges z_j in (1a) to be negative. Of course, real nuclei do not have negative charges. However, in some applications, the "nuclei" are really nuclei together with core electrons and when impurities are present, the total charge of the nucleus and core can be negative; see the discussion in Section VII. The results of Sections II and III carry over to this case with only one major change: It is still true that if $\lambda \leqslant \sum_{i=1}^{k} z_i$, then there is a solution of the TF equations with $\int \rho\, dx = \lambda$, but there can be solutions with $\int \rho > \sum_{i=1}^{k} z_i$. For example, if some $z_i > 0$, there are solutions with $\int \rho > 0$, even if $\sum z_i < 0$. The results of Sections IV, VI, and VII also require a change, namely that the absolute minimizing ρ need not be positive everywhere. Indeed, ρ will vanish identically in a neighborhood of the negative nuclei.

II. The TF Energy Functional

In this section, we study the TF energy functional $\mathscr{E}(\rho; V)$ given by (7a) and use this study to establish existence and uniqueness of solutions of the TF equations. We also present some related results about the chemical potential $\epsilon_F = -\phi_0$. One of our main tools will be the use of the Lebesgue spaces $L^p(\mathbb{R}^3)$, $1 \leqslant p \leqslant \infty$, and we first summarize some of their properties that we will need. If $p < \infty$, $L^p(\mathbb{R}^3)$ is the set of measurable functions from $\mathbb{R}^3$ to $\mathbb{C}$ with the property that

$$\| f \|_p \equiv \left(\int | f(x)|^p\, dx\right)^{1/p} < \infty. \tag{11}$$

$L^\infty(\mathbb{R}^3)$ is the family of essentially bounded functions, i.e., functions which are bounded after modification on a set of measure zero, and $\| f \|_\infty$ is the essential supremum of f. Two useful relations between L^p spaces are Hölder's inequality:

$$\| fg \|_r \leqslant \| f \|_p \| g \|_q \tag{12a}$$

if

$$r^{-1} = p^{-1} + q^{-1}; \qquad 1 \leqslant p, q, r \leqslant \infty, \tag{12b}$$

and Young's inequality:

$$\|f * g\|_r \leqslant \|f\|_p \|g\|_q \tag{13a}$$

if

$$1 + r^{-1} = p^{-1} + q^{-1}; \qquad 1 \leqslant p, q, r \leqslant \infty. \tag{13b}$$

In (12), $(fg)(x) = f(x)\, g(x)$ and in (13)

$$(f * g)(x) = \int f(y)\, g(x - y)\, dy.$$

For any p with $1 \leqslant p \leqslant \infty$, the dual index p' is defined by: $p^{-1} + (p')^{-1} = 1$ or equivalently $p' = p/(p - 1)$.

Two notions of convergence on $L^p(\mathbb{R}^3)$ will concern us. $f_n \to f$ in L^p-norm if and only if $\|f_n - f\|_p \to 0$ as $n \to \infty$. $f_n \to f$ weakly or L^p-weakly for $p \neq \infty$ if and only if for all $g \in L^{p'}$ (p' the dual index of p) $\int f_n(x)\, g(x)\, dx \to \int f(x)\, g(x)\, dx$. Two consequences of Hölder's inequality are useful in this context: First norm convergence implies weak convergence and second if $\sup_n \| f_n \|_p < \infty$, then $f_n \to f$ weakly if $\int f_n(x)\, g(x)\, dx \to \int f(x)\, g(x)$ for all g in some norm-dense subset of $L^{p'}(\mathbb{R}^3)$. For example, if $p \neq 1$, $g \in C_0^\infty(\mathbb{R}^3)$, the C^∞ functions of compact support will do. Note that $f \in L^p \cap L^q$, $p < q$ implies that $f \in L^r$, $p < r < q$.

We need one deep property of the weak topology on $L^p(R^3)$, $p \neq 1$:

THEOREM II.1. *Let $\{f_n\}$ be a sequence of functions in $L^p(\mathbb{R}^3)$ ($p \neq 1$) with $\sup_n \|f_n\|_p < \infty$. Then there is a subsequence $\{f_{n(i)}\}_{i=1}^\infty$ and an $f \in L^p(\mathbb{R}^3)$ so that $f_{n(i)} \to f$ in the weak L^p topology.*

This theorem is a consequence of fairly standard theorems in functional analysis: the duality theory for L^p spaces, the Banach–Alaoglu theorem and the separability of $L^{p'}$. The Banach–Alaoglu theorem can be avoided by appealing to a diagonalization argument. For details of this theorem and other properties of L^p spaces, the reader may consult a variety of functional analysis texts, e.g., [16, 66, 67, 96].

The symbol $L^p + L^q$ denotes those functions which can be written as a sum of an L^p function and an L^q function. For example, $f(x) = |x|^{-1}$ is not in any $L^p(\mathbb{R}^3)$ but it is easily seen to be in $L^p(\mathbb{R}^3) + L^q(\mathbb{R}^3)$ if $p < 3 < q$. If V_n, $V \in L^p + L^q$, we say $V_n \to V$ in $L^p + L^q$-norm if and only if $V_n = V_n^{(1)} + V_n^{(2)}$; $V = V^{(1)} + V^{(2)}$ with $\|V_n^{(1)} - V^{(1)}\|_p \to 0$ and $\|V_n^{(2)} - V^{(2)}\|_q \to 0$.

The main results of Section II are Theorems II.6, II.10, II.14, II.17, II.18, II.20, II.30, II.31.

II.1. *Basic Properties*

We recall that the TF energy functional $\mathscr{E}(\rho; V)$ is given by:

$$\mathscr{E}(\rho; V) = \tfrac{3}{5} \int \rho^{5/3}(x)\, dx - \int V(x)\, \rho(x)\, dx + \tfrac{1}{2} \int \frac{\rho(x)\, \rho(y)}{|x - y|}\, dx\, dy.$$

We emphasize that with our convention, $V > 0$ is *attractive* and $V < 0$ is *repulsive.* It is clear that to define $\mathscr{E}(\rho; V)$ we need $\rho \in L^{5/3}$ and, given the normalization condition $\int \rho(x)\, dx = \lambda$, it is natural to require $\rho \in L^1$. We thus define the sets:

$$\mathscr{I} = \{\rho \in L^1 \cap L^{5/3}(\mathbb{R}^3) \mid \rho \geqslant 0\},$$
$$\mathscr{I}_\lambda = \left\{\rho \in \mathscr{I} \mid \int \rho\, dx \leqslant \lambda\right\},$$
$$\mathscr{I}_{\partial\lambda} = \left\{\rho \in \mathscr{I} \mid \int \rho\, dx = \lambda\right\}.$$

We first have:

THEOREM II.2. *Let* $V \in L^{5/2} + L^\infty$ *and let* $\mathscr{E}(\rho; V)$ *be given by* (7a). Then:

(a) *If* $\rho \in \mathscr{I}$, $\mathscr{E}(\rho; V)$ *exists.*

(b) *If* $\rho_n, \rho \in \mathscr{I}$ *and* $\| \rho - \rho_n \|_{5/3} + \| \rho - \rho_n \|_1 \to 0$ *then* $\mathscr{E}(\rho_n; V) \to \mathscr{E}(\rho; V)$.

(c) *On each* $\mathscr{I}_\lambda$ $(\lambda < \infty)$, $\mathscr{E}(\rho; V)$ *is bounded from below*

(d) *Fix* λ, E_0. *Then there is a* $C < \infty$ *so that* $\rho \in \mathscr{I}_\lambda$ *with* $\mathscr{E}(\rho; V) \leqslant E_0$ *implies that* $\| \rho \|_{5/3} \leqslant C$.

Remarks. (1) Henceforth we shall *always* take $V \in L^{5/2} + L^\infty$. We note that V of the form (1a) is certainly in $L^{5/2} + L^\infty$. We do *not* assume $V > 0$.

(2) For V of the form (1a) we shall shortly see that $\mathscr{E}$ is bounded from below on all of $\mathscr{I}$.

Proof. Write $V = V_1 + V_2$ with $V_1 \in L^{5/2}$ and $V_2 \in L^\infty$. Similarly write $| x |^{-1} = W_1(x) + W_2(x)$ with $W_1 \in L^{5/2}$ and $W_2 \in L^\infty$. Then by Hölder's inequality (12):

$$\int | \rho V |\, dx \leqslant \| V_1 \|_{5/2} \| \rho \|_{5/3} + \| V_2 \|_\infty \| \rho \|_1, \tag{14a}$$

and by Hölder's and Young's inequalities (12, 13):

$$\int (\rho * | x |^{-1})\rho\, dx \leqslant \| \rho \|_1 [\| W_1 \|_{5/2} \| \rho \|_{5/3} + \| W_2 \|_\infty \| \rho \|_1], \tag{14b}$$

and of course:

$$\int \rho^{5/3}\, dx = \| \rho \|_{5/3}^{5/3}. \tag{14c}$$

(a) follows from (14) and (b) follows from similar estimates, e.g.,

$$\left| \int (\rho_n * W)\rho_n - \int (\rho * W)\rho \right| = \left| \int [(\rho_n - \rho) * W](\rho_n + \rho) \right|$$
$$\leqslant \| \rho_n - \rho \|_1 (\| W_1 \|_{5/2} \| \rho_n + \rho \|_{5/3} + \| W_2 \|_\infty \| \rho_n + \rho \|_1).$$

To prove (c), (d), we note that $\int (\rho * |x|^{-1})\rho \geqslant 0$ for any $\rho \in \mathscr{I}$ so, by (14,a,c):

$$\mathscr{E}(\rho; V) \geqslant \tfrac{3}{5} \| \rho \|_{5/3}^{5/3} - c_1 \| \rho \|_{5/3} - c_2 \tag{15}$$

on each $\mathscr{I}_\lambda$, where c_2 is λ dependent $(\lambda \| V_2 \|_\infty)$ and c_1 is λ-independent $(\| V_1 \|_{5/2})$. Since $x^{5/3} - cx$ is bounded from below on $[0, \infty)$, (c) follows. Similarly, (d) follows from (15) and the fact that $\{x \mid x^{5/3} - cx \leqslant d\}$ is bounded for each fixed c,d. ∎

From our eventual analysis of minima for $\mathscr{E}$ on sets of the form $\mathscr{I}_\lambda$, it will follow that when $V = \sum_{j=1}^n z_j \mid x - R_j \mid^{-1}$, $\mathscr{E}(\rho; V)$ has a minimum on all of $\mathscr{I}$ and this occurs for a ρ with $\int \rho d^3x = \sum_{j=1}^n z_j$. In particular, for V of this form, $\mathscr{E}$ is bounded below on all of $\mathscr{I}$. While this will follow from our detailed minimum analysis (Sects. II.4, II.5), it seems advisable to present an elementary proof at this stage. We emphasize that we will not need the following result or its proof in the remainder of this paper.

THEOREM II.3. *Let $V(x) = \sum_{j=1}^k z_j \mid x - R_j \mid^{-1}$ with $z_j \geqslant 0$ and $\sum_{j=1}^k z_j = 1$. Let $\rho \in \mathscr{I}$ with $X = \| \rho \|_{5/3}$. Then*

$$\mathscr{E}(\rho; V) \geqslant \frac{3}{5} X^{5/3} - 3 \left(\frac{2}{5}\right)^{5/6} (8\pi)^{1/3} X^{5/6},$$

$$\inf_{\rho \in \mathscr{I}} \mathscr{E}(\rho; V) \geqslant -\frac{3}{2} \left(\frac{16\pi}{5}\right)^{2/3} = -6.987.$$

Remarks. (1) By scaling (Sect. I.2), there is a result for any $\sum_{j=1}^k z_j$.

(2) This lower bound is not incorrect by an absurd amount. The correct value of the TF energy for an atom ($k = 1$, $Z_1 = 1$), is found numerically[1] to be [22] $-0.7687\ [(3\pi^2)^{2/3}/2] = -3.679$. By Theorem V.4 among all V's and ρ's considered in Theorem II.3, the true minimum occurs in this neutral atomic case.

Proof. It is obviously sufficient to prove that for any $\rho \in \mathscr{I}$ that

$$W(\rho) \equiv -\int \frac{\rho(x)}{|x|} + \frac{1}{2} \int \frac{\rho(x)\,\rho(y)}{|x - y|} \geqslant -3 \left(\frac{2}{5}\right)^{5/6} (8\pi)^{1/3} X^{5/6}. \tag{16}$$

Fix $R > 0$. Let

$$I_+ = \int_{|x|>R} \rho(x)/|x|\, dx; \qquad I_- = \int_{|x|\leqslant R} \rho(x)/|x|\, dx.$$

[1] The first numerical estimate of the energy of a TF atom is in Milne [59] whose answer is off by about 15%. Baker [2] obtained an answer correct to better than 1% and also gave graphs of the TF potential in the neutral case and for several ions.

Let $f(x) = (1/4\pi)\,\delta(|x| - R)$. Then

$$-\frac{1}{2}\iint \frac{f(x)f(y)}{|x-y|} = -\frac{1}{2R}.$$

On the other hand, since

$$\int \frac{f(x)\,dx}{|x-y|} = \frac{1}{|y|} \qquad \text{if} \quad |y| \geqslant R,$$

we have that

$$I_+ = \int_{|y|\geqslant R} \frac{f(x)\,\rho(y)}{|x-y|}\,dx\,dy.$$

Let $\tilde{\rho}(y) = \rho(y)$ if $|y| \geqslant R$; $\tilde{\rho}(y) = 0$ if $|y| \leqslant R$. Then:

$$\frac{1}{2}\int \frac{(\tilde{\rho}-f)(x)\,(\tilde{\rho}-f)(y)}{|x-y|}\,dx\,dy \geqslant 0$$

so

$$-I_+ + \frac{1}{2}\iint \frac{\tilde{\rho}(x)\,\tilde{\rho}(y)}{|x-y|}\,dx\,dy \geqslant -\frac{1}{2}\iint \frac{f(x)f(y)}{|x-y|} = -\frac{1}{2R}.$$

On the other hand, by Hölder's inequality

$$|I_-| \leqslant \left\| \frac{\chi_R}{|x|} \right\|_{5/2} \|\rho\|_{5/3} = (8\pi R^{1/2})^{2/5} X,$$

where χ_R is the characteristic function of the ball of radius R. Thus, for any R:

$$W(\rho) \geqslant -(1/2R) - (8\pi)^{2/5} X R^{1/5}.$$

Choosing $R^{6/5} = (5/2)[(8\pi)^{2/5} X]^{-1}$, (16) results. ∎

Definition. $E(\lambda; V) \equiv \inf\{\mathscr{E}(\rho; V) \mid \rho \in \mathscr{I}_{\partial\lambda}\}$.

Proposition. II.4. *If* $V \in L^{5/2} + L^p$ *for some* $5/2 < p < \infty$, *then* $E(\lambda; V) = \inf\{\mathscr{E}(\rho; V) \mid \rho \in \mathscr{I}_\lambda\}$.

Proof. Note that $|x|^{-1} \in L^{5/2} + L^p$ for some p with $5/2 < p < \infty$ (any $p > 3$ will do!). Hence, by mimicking the proof of Theorem II.2(b), we see that for some $r > 1$ if $\|\rho - \rho_n\|_{5/3} + \|\rho_n - \rho\|_r \to 0$ then $\mathscr{E}(\rho_n; V) \to \mathscr{E}(\rho; V)$. Given $\rho \in C_0^\infty(\mathbb{R}^3) \cap \mathscr{I}_\lambda$, we claim we can find $\rho_n \in \mathscr{I}_{\partial\lambda}$ with $\|\rho_n - \rho\|_{5/3} + \|\rho - \rho_n\|_r \to 0$. Take $\rho_n = \rho + n^{-1}\chi_{A_n}$ where χ_A is the characteristic function of A and A_n is a set disjoint from supp ρ with measure $n(\lambda - \|\rho\|_1)$. Thus

$$\begin{aligned}\inf\{\mathscr{E}(\rho; V) \mid \rho \in \mathscr{I}_{\partial\lambda}\} &\leqslant \inf\{\mathscr{E}(\rho; V) \mid \rho \in \mathscr{I}_\lambda \cap C_0^\infty\}\\ &= \inf\{\mathscr{E}(\rho; V) \mid \rho \in \mathscr{I}_\lambda\}.\end{aligned}$$

The last inequality follows from Theorem II.2(b) and the density of C_0^∞ in $L^1 \cap L^{5/3}$. The inequality

$$\inf\{\mathscr{E}(\rho; V) \mid \rho \in \mathscr{I}_\lambda\} \leqslant \inf\{\mathscr{E}(\rho; V) \mid \rho \in \mathscr{I}_{\partial\lambda}\}$$

is, of course, trivial. ∎

COROLLARY II.5. *$E(\lambda; V)$ is a monotone nonincreasing function of λ whenever V obeys the hypotheses of Proposition* II.4. ∎

Remark. What Corollary II.5 says is that if $V \in L^{5/2} + L^p$ $(p < \infty)$, then increasing λ decreases $E(\lambda; V)$ because one can always place any unwanted piece of ρ "at infinity" without having to increase the energy. If $p = \infty$, this would not necessarily be true. Note that $V \in L^{5/2} + L^p$ $(5/2 < p < \infty)$ implies $V \in L^{5/2} + L^\infty$.

II.2. *Strict Convexity*

The TF functional has an elementary property which has the important consequence of uniqueness of solutions of the TF equation:

THEOREM II.6. *Fix V. Then $\mathscr{E}(\rho; V)$ is a strictly convex function of $\rho \in \mathscr{I}$, that is, if $\rho_1, \rho_2 \in \mathscr{I}$ with $\rho_1 \neq \rho_2$ (by which we mean that $\rho_1 - \rho_2$ is nonzero on a set of positive measure) and* $0 < t < 1$, *then*

$$\mathscr{E}(t\rho_1 + (1 - t)\,\rho_2) < t\mathscr{E}(\rho_1) + (1 - t)\,\mathscr{E}(\rho_2). \tag{17}$$

Proof. Write

$$\mathscr{E}(\rho) = K(\rho) - A(\rho) + R(\rho) \tag{18}$$

corresponding to the three terms in the definition (7a) of $\mathscr{E}(\rho)$. $A(\rho)$ is linear, $K(\rho)$ is clearly strictly convex since $f(x) = x^{5/3}$ is strictly convex on $[0, \infty)$. Finally $R(\rho)$ is strictly convex since $|x|^{-1}$ is strictly positive definite, i.e., its Fourier transform is strictly positive. ∎

Remark. For the theory of Hertl *et al.* [30, 31], where gravitational forces are considered, one loses strict convexity and thus a simple proof of uniqueness.

Theorem II.6 has two immediate corrollaries which will imply uniqueness of solutions of the TF equation once we formally establish the equivalence of stationarity of $\mathscr{E}$ and solutions of the TF equation (see Section II.3).

COROLLARY II.7. *There is at most one $\rho_0 \in \mathscr{I}_\lambda$ with $\mathscr{E}(\rho_0; V) = \inf_{\rho\in\mathscr{I}_\lambda} \mathscr{E}(\rho; V)$. This statement remains true if $\mathscr{I}_\lambda$ is replaced by $\mathscr{I}$, $\mathscr{I}_{\partial\lambda}$ or any convex subset of $\mathscr{I}$.*

COROLLARY II.8. *Suppose that $\rho_0 \in \mathscr{I}_{\partial\lambda}$ is a stationary point of $\mathscr{E}(\rho; V)$ as a functional on $\mathscr{I}_{\partial\lambda}$, i.e., $(d/dt)\,\mathscr{E}(t\rho_0 + (1 - t)\,\rho_1; V)\,|_{t=1} = 0$ for any $\rho_1 \in \mathscr{I}_{\partial\lambda}$.*

Then $\mathscr{E}(\rho_0\,;V) = \inf_{\rho\in\mathscr{I}_{\partial\lambda}} \mathscr{E}(\rho; V)$. *This statement remains true if* $\mathscr{I}_{\partial\lambda}$ *is replaced by* $\mathscr{I}$, $\mathscr{I}_\lambda$ *or any convex subset of* $\mathscr{I}$.

Remark. For convex subsets of $\mathscr{I}$ specified by inequalities, such as $\mathscr{I}_\lambda$, stationarity in the above sense generally implies much more than just minimization on the given convex subset. For example, a stationary point in $\mathscr{I}_\lambda$ is actually a stationary point in $\mathscr{I}$ and thus a minimum in $\mathscr{I}$.

Strict convexity also has implications for the study of $E(\lambda; V)$:

COROLLARY II.9. *Suppose that* $V\in L^{5/2} + L^p$ *with* $p > 5/2$. *Then*:

(a) *If* ρ_0 *minimizes* $\mathscr{E}(\rho; V)$ *on* $\mathscr{I}_{\lambda_0}$ *and* $\int \rho_0 dx < \lambda_0$, *then* $E(\lambda; V) = E(\lambda_0\,; V)$ *for all* $\lambda > \lambda_0$, *when* $p < \infty$.

(b) *If* $\mathscr{E}(\rho; V)$ *has a minimum on* $\mathscr{I}_{\partial\lambda}$ *for all* $\lambda \leqslant \lambda_0$, *then* $E(\lambda; V)$ *is strictly convex on* $[0, \lambda_0]$.

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

Proof. (b) is a direct consequence of strict convexity and (a) follows by noting that ρ_0 must be a minimum for $\mathscr{E}(\rho; V)$ on all of $\mathscr{I}$. ∎

Remarks. (1) For V of the form (1a), this corollary will imply that $E(\lambda; V)$ is strictly convex on $[0, \lambda_0]$ and constant on $[\lambda_0, \infty)$ where $\lambda_0 = \sum_{j=1}^{k} z_j$; see II.5.

(2) For $V(x) = c\,|\,x\,|^{-1}$ (TF atom), one can prove that $-(-\lambda^{-1/3} E(\lambda; V))^{1/2}$ is concave and monotone, nonincreasing. This has been proved for quantum mechanical atoms by Rebane [65] and Narnhofer and Thirring [61]. Thirring (private communication) has remarked that the same proof applies to TF theory.

II.3. *Connection with the TF Equation*

We have already seen a formal connection between the TF equation (3) and stationarity of $\mathscr{E}(\rho; V)$ with the subsidiary condition $\int \rho\, dx = N$. Our goal in this section is to make the formal connection rigorous. This sort of connection is fairly standard in the calculus of variations [60].

THEOREM II.10. (a) *If* ρ *obeys the* TF *equations* (3a–3d) (*with* $W(x) = |\,x\,|^{-1}$) *for some* ϕ_0 *and if* $\int \rho\, dx = N$, *then*

$$\mathscr{E}(\rho; V) = E(N; V).$$

$E(\lambda; V)$ *is differentiable at* $\lambda = N$ *and*

$$-\epsilon_F = \phi_0 = -\partial E(\lambda; V)/\partial\lambda\,|_{\lambda=N}\,. \tag{19}$$

In particular, if $\phi_0 = 0$, *then* ρ *minimizes* $\mathscr{E}$ *on all of* $\mathscr{I}$.

(b) *If* $\rho\in\mathscr{I}_{\partial N}$ *and* $\mathscr{E}(\rho; V) = E(N; V)$, *then* ρ *obeys the* TF *equations* (3a–3d) *and* ϵ_F *is given by* (19).

Remark. It is because of (19) that we interpret $\epsilon_F = -\phi_0$ as a chemical potential.

Proof. For $\rho \in \mathcal{I}$, define

$$(\delta\mathscr{E}/\delta\rho(x)) = \rho^{2/3}(x) - \phi_\rho(x), \tag{20a}$$

where ϕ_ρ is given by (3b), i.e.,

$$\phi_\rho(x) = V(x) - \int |x - y|^{-1} \rho(y)\, dy. \tag{20b}$$

Then (3c), and (3d) are equivalent to

$$(\delta\mathscr{E}/\delta\rho(x)) = -\phi_0 \qquad \text{if } \rho(x) > 0, \tag{21a}$$

$$(\delta\mathscr{E}/\delta\rho(x)) \geqslant -\phi_0 \qquad \text{if } \rho(x) = 0. \tag{21b}$$

Moreover, it is easy to see that for $\rho, \rho' \in \mathcal{I}$:

$$\frac{\partial}{\partial t} \mathscr{E}(t\rho' + (1-t)\rho)|_{t=0} = \int [\rho'(x) - \rho(x)] \frac{\delta\mathscr{E}}{\delta\rho(x)}\, dx, \tag{22}$$

where the derivative on the left side of (22) is a limit as $t \downarrow 0$.

Now suppose that ρ satisfies (21a, 21b). Then since $(\rho' - \rho)(x) \geqslant 0$ whenever $\rho(x) = 0$ we conclude that

$$(\partial/\partial t)\, \mathscr{E}(t\rho' + (1-t)\rho)|_{t=0} \geqslant (-\phi_0) \left[\int (\rho'(x) - \rho(x))\, dx\right]. \tag{23}$$

Let us first apply (23) when $\rho' \neq \rho$ is also in $\mathcal{I}_{\partial N}$. Then (23) implies that the derivative from the right satisfies

$$(\partial/\partial t)\, \mathscr{E}(t\rho' + (1-t)\, \rho)|_{t=0} \geqslant 0.$$

Strict convexity then implies that $\mathscr{E}(\rho') > \mathscr{E}(\rho)$, so we conclude that if ρ obeys (3) and thus (21), then ρ minimizes $\mathscr{E}$ on $\mathcal{I}_{\partial N}$.

To prove (19) we again appeal to strict convexity to deduce

$$\mathscr{E}(\rho') - \mathscr{E}(\rho) \geqslant (-\phi_0) \left[\int (\rho'(x) - \rho(x))\, dx\right]$$

from (23). We conclude that

$$E(\lambda) - E(N) \geqslant (-\phi_0)(\lambda - N) \tag{24}$$

for any λ.

Using (22) with $\rho' = 2\rho$ we see that

$$(\partial/\partial t)\, \mathscr{E}(t\rho' + (1-t)\, \rho)|_{t=0} = (-\phi_0)(2N - N)$$

so $\mathscr{E}(t\rho' + (1-t)\rho) = \mathscr{E}(\rho) + t(-\phi_0)(N) + 0(t^2)$. Thus

$$E((1+t)N) - E(N) \leqslant -t\phi_0 N + 0(t^2). \tag{25a}$$

Similarly taking $\rho' = \frac{1}{2}\rho$, we find that:

$$E((1-t)N) - E(N) \leqslant t\phi_0 N + 0(t^2). \tag{25b}$$

(24) and (25) imply (19). This concludes the proof of (25a).

To begin the proof of (b), we suppose that $\rho \in \mathscr{I}_{\partial N}$ with $\mathscr{E}(\rho; V) = E(N; V)$. Then by (22)

$$\int f(x)[\delta\mathscr{E}/\delta\rho(x)] \geqslant 0 \tag{26a}$$

for f obeying

$$f \in L^1 \cap L^{5/3}, \tag{26b}$$

$$\int f(x)\,dx = 0, \tag{26c}$$

$$\rho + \alpha f \geqslant 0 \qquad \text{for all small positive } \alpha. \tag{26d}$$

Now suppose B is any measurable set obeying:

(i) There are constants $c_1 > 0$, c_2 so that $c_1 \leqslant \rho(x) \leqslant c_2$ for all $x \in B$.

(ii) $|\delta\mathscr{E}/\delta\rho(x)| \leqslant c_2$ for all $x \in B$

(iii) The Lebesgue measure of B is finite.

For any function $f \in L^\infty(B)$ with $\int f\,dx = 0$, both f and $-f$ obey (26b–26d). Thus

$$\int dx\, f(x)(\delta\mathscr{E}/\delta\rho(x)) = 0 \tag{27}$$

for all $f \in L^\infty(B)$ with $\int f\,dx = 0$. Since $\delta\mathscr{E}/\delta\rho(x)$ is bounded on B, (27) holds for any $f \in L^1(B)$ with $\int f\,dx = 0$. Define ϕ_B by:

$$\phi_B = -\int_B \delta\mathscr{E}/\delta\rho(x)\,dx \Big/ \int_B dx.$$

Given $g \in L^1(B)$, let

$$f = g - \chi_B \left[\int g\,dx \Big/ \int \chi_B\,dx\right],$$

where χ_B is the characteristic function of B. Then (27) implies that

$$\int g(x)[\delta\mathscr{E}/\delta\rho(x)]\,dx = -\phi_B \int g(x)\,dx$$

for any $g \in L^1(B)$, i.e.,

$$\frac{\delta\mathscr{E}}{\delta\rho(x)} = -\phi_B \qquad \text{a.e.,} \quad x \in B. \tag{28}$$

Given B_1, B_2 obeying (i)–(iii) above, so does $B_1 \cup B_2$, and $\phi_{B_1} = \phi_{B_1 \cup B_2} = \phi_{B_2}$, i.e., ϕ_B is a constant independent of B. Call it ϕ_0.

Now $\rho \in L^1$ is finite a.e. and, by Young's inequality, $\delta\mathscr{E}/\delta\rho \in L^{5/2} + L^\infty$ so it is finite a.e. It follows that $\{x \mid \rho(x) > 0\}$ is a union of countably many sets obeying (i)–(iii). Thus $\delta\mathscr{E}/\delta\rho(x) = -\phi_0$ for almost all x such that $\rho(x) > 0$.

Given any g in $\mathscr{I}$ with $\int g(x)\, dx = N$, $f = g - \rho$ obeys (26b–26d) so

$$\int g(x)[\delta\mathscr{E}/\delta\rho(x)]\, dx \geqslant -\phi_0 \int \rho(x)\, dx = -\phi_0 \int g(x)\, dx.$$

Thus $\delta\mathscr{E}/\delta\rho(x) \geqslant -\phi_0$ a.e. x. Thus ρ obeys the TF equations. In particular, we can appeal to the argument in (26a) and conclude that (19) holds. ∎

Applying Corollary II.7 and Theorem II.10, we have:

COROLLARY II.11. *Fix N and $V \in L^{5/2} + L^\infty$. Then there cannot be two ρ's in $\mathscr{I}_{\partial N}$ obeying the* TF *equation* (3a–3d) (*with* $W(x) = |x|^{-1}$) *even with distinct values of* ϕ_0.

Using (19), Corrollaries II.5 and II.9, we have:

COROLLARY II.12. *If $V \in L^{5/2} + L^p$ for $5/2 < p < \infty$, then $\phi_0 \geqslant 0$ for any solution of* (7a–7d) *and moreover*:

(i) *If $\phi_0 = 0$, then ρ is an absolute minimum of $\mathscr{E}(\rho; V)$ on $\mathscr{I}$.*

(ii) *If ρ_1, ρ_2 are two solutions of* (3) *with different values of N (say N_1 and N_2) and corresponding values of ϕ_0(say $\phi_0^{(1)}$ and $\phi_0^{(2)}$) then $\phi_0^{(1)} \leqslant \phi_0^{(2)}$ if $N_1 > N_2$.*

Remarks. (1) Once we know that there is a minimizing ρ on each $\mathscr{I}_N$ (see Sect. II.4), Corollary II.9 implies that we can improve (7b) to read $\phi_0^{(1)} < \phi_0^{(2)}$ (see also Sect. II.8).

(2) This corollary is quite natural in terms of the Fermi sea picture (electron gas in phase space) discussed in Section I.

II.4. *Minimization with* $\int \rho \leqslant \lambda$

Due to Theorem II.10, the existence problem for the TF equation is equivalent to finding minimizing ρ's for $\mathscr{E}(\cdot; V)$ as a functional on $\mathscr{I}_{\partial\lambda}$. We shall investigate this existence question in two stages In this section, we shall establish the existence of a minimizing $\rho \in \mathscr{I}_\lambda$, i e., for any λ we shall find ρ with $\mathscr{E}(\rho; V) = E(\lambda; V)$ and $\int \rho\, dx \leqslant \lambda$. In the next section, we shall investigate when this ρ obeys $\int \rho\, dx = \lambda$. This two part approach is natural for two reasons:

(i) If V is given by (21) and $Z = \sum_{j=1}^k z_j$, then folk theorems assert that $\phi_0 = 0$ when $\lambda = Z$. If this folk theorem is valid (and indeed we will prove it in II.5), then our analysis above (especially Corollaries II.9 and II.12) implies there is no $\rho \in \mathscr{I}_{\partial\lambda}$ with $\mathscr{E}(\rho; V) = E(\lambda; V)$ if $\lambda > Z$. But for such a value of λ there is a $\rho \in \mathscr{I}_\lambda$ with $\mathscr{E}(\rho; V) = E(\lambda; V)$, namely, the ρ with $\phi_0 = 0$ and $\int \rho\, dx = Z$. By dividing our existence analysis in two stages, we only have to consider the mechanism distinguishing $\lambda \leqslant Z$ and $\lambda > Z$ after developing some properties of the putative solutions.

(ii) From a mathematical point of view, $\mathscr{I}_\lambda$ is more natural than $\mathscr{I}_{\partial\lambda}$ since $\mathscr{I}_\lambda$ is closed in the weak $L^{5/3}$ topology while $\mathscr{I}_{\partial\lambda}$ is not. We shall use the weak $L^{5/3}$ topology is an essential way.

The natural way of showing that a function has a minimum on a set is to prove that the function is continuous in a topology in which the set is compact. We have already seen that $\mathscr{E}(\cdot; V)$ is continuous in the $L^{5/3} \cap L^1$ norm topology (Theorem II.2b) but alas, $\mathscr{I}_\lambda$ (or even $\{\rho \in \mathscr{I}_\lambda \mid \mathscr{E}(\rho; V) \leqslant E_0\}$) is not compact in this norm topology. On the other hand, by Theorems II.1 and II.2(d), $\{\rho \in \mathscr{I}_\lambda \mid \mathscr{E}(\rho; V) \leqslant E_0\}$ lies in a set which is compact in the weak $L^{5/3}$ topology, but alas, $\mathscr{E}(\cdot; V)$ is not weakly continuous as the following example shows:

Example. Suppose that $V \in L^{5/2} + L^p$; $5/2 < p < \infty$. Pick any $\rho \in \mathscr{I}_\lambda$ and let $\rho_n(x) = \rho(x - r_n)$ where r_n is a sequence of vectors with $r_n \to \infty$. Then $\rho_n \to 0$ weakly in $L^{5/3}$, $\int V\rho_n\, d^3x \to 0$ but $\int \rho_n^{5/3}(x)\, d^3x = \int \rho^{5/3}(x)\, dx$; $\int (\rho_n * |x|^{-1})\, \rho_n\, d^3x = \int (\rho * |x|^{-1})\, \rho\, dx$ for all n. Thus:

$$\mathscr{E}(\rho_n ; V) \to \tfrac{3}{5} \int \rho^{5/3}(x)\, dx + \tfrac{1}{2} \int (\rho * |x|^{-1})\rho\, dx > 0 = \mathscr{E}(0; V).$$

Fortunately, there is a hopeful sign in this example for $\lim_{n\to\infty} \mathscr{E}(\rho_n ; V) \geqslant \mathscr{E}(\lim \rho_n ; V)$ so one might hope for a semicontinuity result which would suffice for establishing existence of a minimum. Such semicontinuity ideas are not uncommon in the calculus of variations [60] and, in particular, have been used in a problem similar to ours by Auchmuty and Beals [1]. In our case, we have:

Theorem II.13. *Let $V \in L^{5/2} + L^p\, (5/2 < p < \infty)$. Then $\mathscr{E}(\cdot, V)$ is lower semicontinuous on each $\mathscr{I}_\lambda\, (\lambda < \infty)$ in the weak $L^{5/3}$ topology, i.e., if $\rho_n \to \rho$ in weak $L^{5/3}$ with* $\sup_n \|\rho_n\|_1 < \infty$, $\rho \in L^1$, $\rho_n, \rho \geqslant 0$, *then*

$$\mathscr{E}(\rho; V) \leqslant \underline{\lim}\, \mathscr{E}(\rho_n ; V). \tag{29}$$

Moreover, if $\mathscr{E}(\rho; V) = \lim \mathscr{E}(\rho_n ; V)$, then $\|\rho_n - \rho\|_{5/3} \to 0$ and each term in $\mathscr{E}(\rho_n ; V)$ converges to the corresponding term in $\mathscr{E}(\rho; V)$.

Proof. By passing to a subsequence, we can suppose that $\lim \mathscr{E}(\rho_n ; V)$ exists and we may as well suppose the limit is finite since (29) is trivial otherwise. Then, by Theorem II.2(d), $\sup_n \|\rho_n\|_{5/3} < \infty$ (alternatively this follows from the weak convergence and the uniform boundedness principle if we only concern ourselves with sequential continuity). We prove (29) by showing

$$\underline{\lim} \| \rho_n \|_{5/3} \geqslant \| \rho \|_{5/3}, \tag{30a}$$

$$\lim \int \rho_n V = \int \rho V, \tag{30b}$$

$$\underline{\lim} \int (\rho_n * | x |^{-1}) \rho_n \geqslant \int (\rho * | x |^{-1}) \rho. \tag{30c}$$

(30a) follows from the fact that balls in $L^{5/3}$ are weakly closed (which, in turn, follows from the Hahn–Banach theorem). Or, we can be more explicit and note that $\rho^{2/3} \in L^{5/2}$, so by the definition of weak convergence and Hölder's inequality,

$$\int \rho^{5/3} d^3x = \lim_{n \to \infty} \int \rho_n \rho^{2/3} \, d^3x$$

$$\leqslant \| \rho \|_{5/3}^{2/3} \underline{\lim} \| \rho_n \|_{5/3} .$$

To prove (30b), write $V = V_1 + V_2$ with $V_1 \in L^{5/2}$, $V_2 \in L^p$ $(5/2 < p < \infty)$. Clearly, $\int V_1 \rho_n$ converges to $\int V_1 \rho$. We claim that since $\sup_n \| \rho_n \|_1 < \infty$, $\rho_n \to \rho$ in weak $L^q (1 < q \leqslant 5/3)$ and, in particular, for q the dual index to p. This claim clearly implies that $\int V_2 \rho_n \to \int V_2 \rho$ completing the proof of (30b). The claim follows by remarking that $L^{5/2} \cap L^{q'}$ is dense in $L^{q'}$ and that $\sup \| \rho_n \|_q < \infty$ by the inequality

$$\| f \|_q \leqslant \| f \|_p^{\alpha} \| f \|_r^{1-\alpha}$$

if $q^{-1} = \alpha p^{-1} + (1 - \alpha) r^{-1}$; $0 < \alpha < 1$.

Finally, to prove (30c), we use positive definiteness of $| x |^{-1}$ and the resulting Schwarz inequality. Since $\rho \in L^1$ and $| x |^{-1} \in L^{5/2} + L^4$, $\rho * | x |^{-1} \in L^{5/2} + L^4$ by Young's inequality. Since $\rho_n \to \rho$ both in weak $L^{5/3}$ and weak $L^{4/3}$ (by the above), $\int (\rho * | x |^{-1}) \rho_n \to \int (\rho * | x |^{-1}) \rho$. Therefore

$$\int \frac{\rho(x) \rho(y)}{| x - y |} dx\, dy = \lim_{n \to \infty} \int \frac{\rho(x) \rho_n(y)}{| x - y |} dx\, dy$$

$$\leqslant \underline{\lim} \left(\left[\int \frac{\rho(x) \rho(y)}{| x - y |} dx\, dy \right]^{1/2} \left[\int \frac{\rho_n(x) \rho_n(y)}{| x - y |} dx\, dy \right]^{1/2} \right)$$

which proves (30c) and so (29).

(30a–30c) imply that if $\mathscr{E}(\rho; V) = \lim \mathscr{E}(\rho_n ; V)$, then each term of $\mathscr{E}(\cdot; V)$ converges and in particular $\lim \| \rho_n \|_{5/3} = \| \rho \|_{5/3}$. Since $L^{5/3}$ is uniformly convex [12, 43] convergence of the norms and weak convergence implies norm convergence. ∎

As a consequence of the lower semicontinuity just proven, we have:

THEOREM II.14. *Let* $V \in L^{5/2} + L^p$ $(5/2 < p < \infty)$. *Then for each* λ, *there exists a unique* $\rho \in \mathscr{I}_\lambda$ *with*

$$\mathscr{E}(\rho; V) = \inf_{\rho' \in \mathscr{I}_\lambda} \mathscr{E}(\rho'; V) \equiv E(\lambda; V).$$

Proof. Pick $\rho_n \in \mathscr{I}_\lambda$ so that $\mathscr{E}(\rho_n; V) \to E(\lambda; V)$. By Theorem II.2(d), $\sup_n \| \rho_n \|_{5/3} < \infty$ so by Theorem II.1 we can find $\rho \in L^{5/3}$ with $\rho_n \to \rho$ in weak $L^{5/3}$. Since $\| g \|_1 = \sup\{\int fg \mid f \in L^{5/2} \cap L^\infty; \| f \|_\infty < 1\}$, $\| \rho \|_1 \leqslant \lim \| \rho_n \|_1 \leqslant \lambda$. Since $g \geqslant 0$ if and only if $\int gf \geqslant 0$ for all $f \in C_0^\infty$ with $f \geqslant 0$, $\rho \geqslant 0$. Thus $\rho \in \mathscr{I}_\lambda$. It follows from Theorem II.13 that

$$\mathscr{E}(\rho; V) \leqslant \underline{\lim}\, \mathscr{E}(\rho_n; V) = E(\lambda; V).$$

Since $\rho \in \mathscr{I}_\lambda$, $\mathscr{E}(\rho; V) \geqslant E(\lambda; V)$. Thus $\mathscr{E}(\rho; V) = E(\lambda; V)$. ∎

The semicontinuity results and the methods employed in their proof can be used to say something about the V dependence of $E(\lambda; V)$ for λ fixed:

THEOREM II.15. *If* $V_n \to V$ *in* $L^{5/2} + L^p$ $(5/2 < p < \infty)$ *then for any fixed* λ, $E(\lambda; V_n) \to E(\lambda; V)$. *Let* ρ *(resp.* ρ_n*) be the unique density that minimizes* $\mathscr{E}(\cdot; V)$ *(resp.* $\mathscr{E}(\cdot; V_n)$*) on* $\mathscr{I}_\lambda$, *then* $\| \rho_n - \rho \|_{5/3} \to 0$ *and* $\| \rho \|_1 \leqslant \lim \| \rho_n \|_1$.

Remarks. (1) Since $\mathscr{E}(\rho; V)$ is linear in V, $E(\lambda; V)$ is a concave function of V and it can be shown to be bounded on bounded subsets of $L^{5/2} + L^p$. This can be used to provide an alternative proof that $E(\lambda; \cdot)$ is continuous.

(2) It can happen that $\| \rho \|_1$ is strictly less than $\lim \| \rho_n \|_1$. For example, if $V_n(x)$ is zero for $|x| \leqslant n$ and $|x|^{-1}$ for $|x| > n$, then our results in Section II.5 below show that for $\lambda = 1$, $\| \rho_n \|_1 = 1$ (all n). But $V_n \to 0$ in $L^{5/2} + L^4$ norm so $\rho = 0$.

Proof. Note first that $\sup_n \| \rho_n \|_{5/3} < \infty$ by arguments similar to those in Theorem II.2. By a simple argument, it is enough to prove that $\| \rho_n - \rho \|_{5/3} \to 0$, $\mathscr{E}(\rho_n; V_n) \to \mathscr{E}(\rho; V)$, and $\| \rho \|_1 \leqslant \lim \| \rho_n \|_1$ for any weak $L^{5/3}$ convergent subsequence ρ_n. Suppose that $\rho_n \to \rho_0$ in weak $L^{5/3}$. Then, as in the proof of the last theorem, $\rho_0 \in \mathscr{I}_\lambda$. By a simple modification of Theorem II.13, $\mathscr{E}(\rho_0; V) \leqslant \lim \mathscr{E}(\rho_n; V_n) \equiv E_\infty$. On the other hand,

$$\mathscr{E}(\rho; V) = \lim_n \mathscr{E}(\rho; V_n) \geqslant \overline{\lim}\, \mathscr{E}(\rho_n; V_n)$$

by the minimizing property of ρ_n. Thus by the minimizing property of ρ:

$$\mathscr{E}(\rho; V) \leqslant \mathscr{E}(\rho_0; V) \leqslant \underline{\lim}\, \mathscr{E}(\rho_n; V_n) \leqslant \overline{\lim}\, \mathscr{E}(\rho_n; V_n) \leqslant \mathscr{E}(\rho; V).$$

It follows that $\mathscr{E}(\rho_n\,;V_n) = E(\lambda; V_n) \to \mathscr{E}(\rho; V) = E(\lambda; V)$ and that $\rho_0 = \rho$. As in Theorem II.13, convergence of $\mathscr{E}(\rho_n\,;V_n)$ to $\mathscr{E}(\rho; V)$ implies $\| \rho_n - \rho \|_{5/3} \to 0$ and, as in Theorem II.14, $\| \rho \|_1 \leqslant \underline{\lim} \| \rho_n \|$. ∎

THEOREM II.16. *Let $V, Y \in L^{5/2} + L^p$ $(5/2 < p < \infty)$. Let ρ_α be the unique minimizing ρ for $\mathscr{E}(\cdot; V + \alpha Y)$ on $\mathscr{I}_\lambda$. Then the function $\alpha \mapsto E(\lambda; V + \alpha Y)$ is continuously differentiable, and the derivative is given by*

$$(\partial E/\partial\alpha) = -\int Y(x)\,\rho_\alpha(x)\,dx. \tag{31}$$

Remarks. (1) Equation (31) is essentially a TF version of the Feynman–Hellman theorem.

(2) Although it is somewhat obscured in the proof, the central reason for differentiability for *all* α is the uniqueness of minima. Concavity of $\alpha \to E(\lambda; V + \alpha Y)$ only implies the existence of the left- and right-hand derivatives everywhere and their equality only a.e. In essence, the left- and right-hand derivatives *should* be of the form $-\int \rho_\alpha^{\pm}(x)\,Y(x)\,dx$ for some minimizing $\rho_\alpha^{\pm}(x)$. Uniqueness then requires that $\rho_\alpha^+ = \rho_\alpha^-$.

Proof. By Theorem II.15, $\alpha \mapsto \rho_\alpha$ is continuous in the $L^{5/3}$ norm topology. Since $\| \rho_\alpha \|_1 \leqslant \lambda$, $\alpha \mapsto \int Y(x)\,\rho_\alpha(x)\,dx$ is continuous so it suffices to prove $\alpha \mapsto E(\lambda; V + \alpha Y)$ is differentiable with derivative (31). Clearly we need only prove differentiability at $\alpha = 0$. Now for $\alpha > 0$:

$$\alpha^{-1}[E(\alpha) - E(0)] \leqslant \alpha^{-1}[\mathscr{E}(\rho_0\,; V + \alpha Y) - \mathscr{E}(\rho_0\,; V)] = -\int Y(x)\,\rho_0(x)\,dx$$

by the minimizing property of ρ_α. By the minimizing property of ρ_0:

$$\alpha^{-1}[E(\alpha) - E(0)] \geqslant \alpha^{-1}[\mathscr{E}(\rho_\alpha\,; V + \alpha Y) - \mathscr{E}(\rho_\alpha\,; V)] = -\int Y(x)\,\rho_\alpha(x)\,dx.$$

Since $\int Y(x)\,\rho_\alpha(x) \to \int Y(x)\,\rho_0(x)$, we have that

$$\lim_{\alpha\downarrow 0} \alpha^{-1}[E(\alpha) - E(0)] = -\int \rho_0(x)\,Y(x)\,dx.$$

A similar argument controls $\lim_{\alpha\uparrow 0}$. ∎

II.5. *Minimization with* $\int \rho = \lambda$

We now examine the question of when the minimizing ρ in $\mathscr{I}_\lambda$ actually lies in $\mathscr{I}_{\partial\lambda}$. Our main results involve potentials of the form

$$V(x) = \sum_{j=1}^{k} z_j\,|x - R_j|^{-1} + V_0(x); \qquad z_j > 0. \tag{32}$$

THEOREM II.17. *Let V have the form* (32) *with $V_0 \in L^{5/2}$ and V_0 of compact support. Then for $\lambda \leqslant Z \equiv \sum_{j=1}^{k} z_j$, the minimizing ρ for $\mathscr{E}(\cdot; V)$ on $\mathscr{I}_\lambda$ has $\int \rho\, dx = \lambda$.*

THEOREM II.18. *Let V have the form* (32) *with $V_0(x) \leqslant 0$ all x, V_0 of compact support and $V_0 \in L^{5/2} + L^p$ $(5/2 < p < \infty)$. Then for $\lambda > Z \equiv \sum_{j=1}^{k} z_j$, the minimizing ρ for $\mathscr{E}(\cdot; V)$ on $\mathscr{I}_\lambda$ has $\int \rho\, dx = Z$.*

Remarks. (1) We shall later present an example showing that $\int \rho\, dx > Z$ is possible if $V_0(x)$ is positive.

(2) The conditions $\lambda > Z$ vs $\lambda \leqslant Z$ enter naturally because the formal large x behavior of $\sum_{j=1}^{k} z_j \mid x - R_j \mid^{-1} - \int \rho(y) \mid x - y \mid^{-1} dy$ is $(Z - \lambda) \mid x \mid^{-1}$.

Proof of Theorem II.17. Suppose that the minimizing ρ has $\int \rho\, dx = \lambda_0 < \lambda$. Then, by Corollary II.9, ρ is a minimizing ρ for $\mathscr{E}(\cdot; V)$ on all of $\mathscr{I}$, so by Theorem II.10, the corresponding ϕ_0 is 0. Thus ρ obeys:

$$\rho(x) = \max(\phi(x), 0)^{3/2}, \tag{33a}$$

$$\phi(x) = V(x) - \int \rho(y) \mid x - y \mid^{-1} dy, \tag{33b}$$

$$\int \rho(x)\, dx = \lambda_0 < Z. \tag{33c}$$

Choose R so that $R > \mid R_j \mid, j = 1,..., k$ and so that supp $V_0 \subset \{x \mid \mid x \mid < R\}$. For $r > R$, define

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

Then, by the well-known formula

$$(1/4\pi) \int_{S_2} \mid r\Omega - y \mid^{-1} d\Omega = [\max(r, \mid y \mid)]^{-1}$$

and (32), (33b),

$$[\phi](r) = Zr^{-1} - \int \rho(y)\, [\max(r, \mid y \mid)]^{-1}\, dy \tag{34}$$

$$\geqslant Zr^{-1} - \int \rho(y) r^{-1}\, dy = (Z - \lambda_0) r^{-1}. \tag{35}$$

Now, let $[\rho](r) = (4\pi)^{-1} \int \rho(r\Omega)\, d\Omega$. Then, by (33a) and Hölder's ineqality, we have for $r > R$:

$$\begin{aligned} [\rho](r) &= \int \max(\phi(r\Omega), 0)^{3/2}\, (d\Omega/4\pi) \\ &\geqslant \left(\int \max(\phi(r\Omega), 0)(d\Omega/4\pi) \right)^{3/2} \\ &\geqslant [\phi](r)^{3/2} \geqslant (Z - \lambda_0)^{3/2} r^{-3/2} \end{aligned}$$

by (35). Thus

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

violating (33c). This establishes a contradiction and thus allows us to conclude, that $\int \rho\,dx = \lambda$. ∎

Proof of Theorem II.18. Suppose that $\int \rho\,dx = \lambda > Z$. As above define $[\phi](r)$. Then, by (34),

$$[\phi](r) \leqslant \left(Z - \int_{|x|<r} \rho(x)\,dx\right) r^{-1}$$

so $[\phi](r) < 0$ if r is sufficiently large. This violates the lemma below. ∎

Lemma II.19. *Let* $\phi(x) = V(x) - \int \rho(y) \mid x - y \mid^{-1}$, *where* V *has the form* (32) *with* $V_0(x) \leqslant 0$, *and suppose* $\rho = \max(\phi - \phi_0, 0)^{3/2}$ *with* $\phi_0 \geqslant 0$. *Then* $\phi(x) - V_0(x) \geqslant 0$ *for all* x.

Proof. Let $\psi = \phi - V_0$. Since $\rho \in L^{5/3} \cap L^1$, $\rho * \mid x \mid^{-1}$ is continuous and goes to zero at infinity (see Theorem IV.1). Hence $\psi \to \infty$ as $x \to$ any R_i and ψ is continuous away from the R_i. Thus $A = \{x \mid \psi(x) < 0\}$ is open and disjoint from the R_i. On A, $\phi = \psi + V_0 < 0$ so $\phi - \phi_0 < 0$. Thus $\rho = 0$ on A, so ψ is harmonic on A. Clearly $\psi(x) \to 0$ as $x \to \infty$ and ψ vanishes on ∂A. It follows that $\psi = 0$ on A, so A is empty. Thus $\psi(x) \geqslant 0$ for all x. ∎

Remarks. (1) The use of harmonic function methods in TF theory goes back at least as far as the work of Teller [89]. We will use these ideas extensively in Sections IV–VI.

(2) Theorem II.18 is false if the restriction $V_0 \leqslant 0$ is removed as the following example shows.

Example. Choose $V_0(x) = \mid x \mid^{-1} \chi_{(a,b)}(x)$, where $\chi_{(a,b)}(x)$ is the characteristic function of the spherical shell $\{x \mid a < \mid x \mid < b\}$. By a simple modification of the argument, V_0 can be made C^∞. As a preliminary consideration, let W be the potential which is $\mid x \mid^{-1}$ if $\mid x \mid < a$ and $2 \mid x \mid^{-1}$ if $\mid x \mid \geqslant a$. By Theorem II.17, there is a $\tilde{\rho}$ minimizing $\mathscr{E}(\cdot; W)$ on $\mathscr{I}_{3/2}$ and $\int \tilde{\rho}\,dx = \frac{3}{2}$. Since there is also a minimizing ρ on $\mathscr{I}_2$ with $\int \rho\,dx = 2$, the ϕ_0 for $\tilde{\rho}$ is strictly positive. Now, by the spherical symmetry of W and uniqueness of solutions, $\tilde{\rho}$ is spherically symmetric, so by our arguments in the proofs of Theorems II.17, II.18, $\tilde{\phi}(r) \to 0$ at infinity. Since $\phi_0 > 0$, and $\tilde{\rho} = 0$ if $\tilde{\phi}(r) < \phi_0$ we see that $\tilde{\rho}$ has compact support. Choose $b > a$ so that $\tilde{\rho}$ has support in $\{x \mid \mid x \mid \leqslant b\}$. We claim that $\tilde{\rho}$ minimizes $\mathscr{E}(\cdot; \mid x \mid^{-1} + V_0)$ on $\mathscr{I}_{3/2}$, thereby exhibiting the need for $V_0 \leqslant 0$ in Theorem II.18. Since $\mid x \mid^{-1} + V_0 \leqslant W$, we have that for any $\rho \in \mathscr{I}_{3/2}$, $\mathscr{E}(\rho; \mid x \mid^{-1} + V_0) \geqslant \mathscr{E}(\rho; W) \geqslant \mathscr{E}(\tilde{\rho}; W) = \mathscr{E}(\tilde{\rho}; \mid x \mid^{-1} + V_0)$.

We close this section by summarizing the situation for V of the form (1a):

THEOREM II.20. *Let* $V(x) = \sum_{i=1}^{k} z_i \mid x - R_i \mid^{-1}$ *with* $z_i > 0$ *and define* $Z = \sum_{i=1}^{k} z_i$. *If* $\lambda \leqslant Z$, *then there is a unique* ρ *with* $\int \rho(x)\, dx = \lambda$ *such that*

$$\rho(x) = \max(\phi(x) - \phi_0, 0)^{3/2}$$
$$\phi(x) = V(x) - \int \mid x - y \mid^{-1} \rho(y)\, dy$$

for some ϕ_0. *Moreover*:

(i) *If* $\lambda = Z, \phi_0 = 0$, *and if* $\lambda < Z, \phi_0 > 0$.

(ii) ϕ_0 *is given by* (19).

(iii) *The function* $E(\lambda; V)$ *is strictly monotone decreasing on* $[0, Z]$, *constant on* $[Z, \infty)$ *and convex on* $[0, \infty)$.

In particular, for all $\rho \in \mathscr{I}$,

$$\mathscr{E}(\rho; V) \geqslant E(Z; V).$$

For V's of the form (1a), we introduce the notation $E^{\mathrm{TF}}(\lambda; z_1, \ldots, z_k; R_1, \ldots, R_k)$ and the notation $\rho_{\mathrm{TF}}(x; z_1, \ldots, z_k; R_1, \ldots, R_k; \lambda)$ for the minimizing E and ρ on $\mathscr{I}_\lambda$ (so $\rho_{\mathrm{TF}}(\ldots; \lambda) = \rho_{\mathrm{TF}}(\ldots; Z)$ if $\lambda \geqslant Z$). We denote the *negative* of the associated ϕ_0 by $\epsilon_F(\lambda; z_1, \ldots, z_k; R_1, \ldots, R_k)$.

II.6. *Components of the Energy*

In this section, we discuss the components of $\mathscr{E}(\rho; V)$, $V \in L^{5/2} + L^p (5/2 < p < \infty)$:

$$K(\rho) = \tfrac{3}{5} \int \rho(x)^{5/3}\, dx; \qquad R(\rho) = \tfrac{1}{2} \int \mid x - y \mid^{-1} \rho(x)\, \rho(y)\, dx\, dy;$$

$$A(\rho; V) = \int \rho(x)\, V(x)\, dx.$$

We also define:

$$E(\kappa, \alpha, \mu; \lambda) = \inf_{\rho \in \mathscr{I}_\lambda} [\kappa K(\rho) - \alpha A(\rho) + \mu R(\rho)].$$

THEOREM II.21. $E(\kappa, \alpha, \mu; \lambda)$ *is* C^1 *for* $\kappa, \mu > 0$, α *real. Moreover*:

$$\left.\frac{\partial E}{\partial \kappa}\right|_{\kappa=\alpha=\mu=1} = K(\tilde{\rho}),$$

$$\left.\frac{\partial E}{\partial \alpha}\right|_{\kappa=\alpha=\mu=1} = -A(\tilde{\rho}),$$

$$\left.\frac{\partial E}{\partial \mu}\right|_{\kappa=\alpha=\mu=1} = R(\tilde{\rho}),$$

where $\tilde{\rho}$ *is the minimizing* ρ *for* $\mathscr{E}(\cdot; V)$ *on* $\mathscr{I}_\lambda$.

Proof. We have already proved $\partial\mathscr{E}/\partial\alpha = -A(\tilde{\rho})$ in Theorem II.16. The method of proof of Theorems II.15, 16 can also be used to prove the remainder of this theorem. ▌

When ρ is the TF density for an atom, molecule, or ion there are some simple relations among $K(\rho)$, $A(\rho)$, and $R(\rho)$. The first of these relations is a virial theorem, first proven by Fock [21]; see also Jensen [36], Gombás [24], and Flügge [22]. The second relation, which is special to TF theory, seems to be due to Gombás [24]; see also Flügge [22]. Our proof of the virial theorem is patterned after one in quantum mechanics [20, 93]. See Note 4.

THEOREM II.22 (TF virial theorem). *If* $V(x) = Z\,|\,x\,|^{-1}$ *and if* ρ *minimizes* $\mathscr{E}(\cdot\,; V)$ *on any* $\mathscr{I}_\lambda$, *then*

$$2K(\rho) = A(\rho) - R(\rho). \tag{36}$$

Proof. Let $\rho_\mu(r) = \mu^3\rho(\mu r)$ so that $\rho_\mu \in \mathscr{I}_\lambda$. Then $K(\rho_\mu) = \mu^2 K(\rho)$, $A(\rho_\mu) = \mu A(\rho)$, $R(\rho_\mu) = \mu R(\rho)$. Now by the minimizing property for ρ, $\mu^2 K(\rho) - \mu A(\rho) + \mu R(\rho)$ has a minimum at $\mu = 1$ from which (36) follows. ▌

The second relation is obtained by Gombás [24] using properties of the TF equation rather than via minimization, as we do:

THEOREM II.23. *Let* ρ *minimize* $\mathscr{E}(\cdot\,; V)$ *on all of* $\mathscr{I}$. *Then, for* V *given by* (1a)

$$\tfrac{5}{3}\,K(\rho) = A(\rho) - 2R(\rho). \tag{37}$$

Proof. Let $\rho_\beta(r) = \beta\rho(r)$. Then the minimizing property of ρ implies that $\beta^{5/3}K(\rho) - \beta A(\rho) + \beta^2 R(\rho)$ has its minimum at $\beta = 1$ from which (37) follows. ▌

COROLLARY II.24 (Gombás [24]). *In the atomic case, let* ρ *minimize* $\mathscr{E}(\cdot\,; Z\,|\,x\,|^{-1})$ *on* $\mathscr{I}$. *Then* $K(\rho) : A(\rho) : R(\rho) = 3 : 7 : 1$.

Proof. The result follows from (36) and (37). ▌

II.7. *Min–Max and Max–Min Principles for the Chemical Potential*

The quantity $\epsilon_F(\lambda) = \partial E(\lambda; V)/\partial\lambda$ is of some importance in the TF theory. It is the chemical potential in the electron gas picture of the TF theory and is the TF prediction for an ionization potential (although we emphasize that the picture we establish for the connection between TF theory and quantum mechanics suggests that the TF theory will not correctly predict ionization energies). Thus far we have seen that $\epsilon_F(\lambda)$ is the negative of the ϕ_0 associated with the minimizing ρ on $\mathscr{I}_\lambda$. This description of ϵ_F is sufficiently complex to be of little direct use. In this section we obtain some alternative characterizations of $\epsilon_F(\lambda)$ in the case where $V(x) = \sum_{j=1}^{k} z_j\,|\,x - R_j\,|^{-1}$ and, in the next section we study the properties of ϵ_F in this case.

Given any putative electron density ρ, we can think of forming an electron gas in phase space by filling a region $\{\langle x, p\rangle \mid |p| \leqslant p_F(x)\}$ such that the associated x-space density is $\rho(x)$. With our units, the energy at the surface of the gas at x is $\rho^{2/3}(x) - \phi_\rho(x)$, where, as usual,

$$\phi_\rho(x) = V(x) - \int \rho(y) \mid x - y \mid^{-1} dy. \tag{38}$$

As we have seen, the TF ρ has $\rho^{2/3}(x) - \phi_\rho(x)$ constant at points where $\rho(x) \neq 0$, and that constant is precisely ϵ_F. Our basic results say that for any other trial ρ, $\rho^{2/3}(x) - \phi_\rho(x)$ has values both larger and smaller than ϵ_F. While this is intuitively obvious for ρ's differing from the TF ρ by a small local perturbation, it is a subtle fact in general. We need three preliminary results.

LEMMA II.25. *If $f \in L^p(\mathbb{R}^3)$, $g \in L^q(\mathbb{R}^3)$ with p, q dual indices different from 1 and ∞ then $f * g$ is a continuous function going to zero at infinity.*

Proof. This result, which improves the Young's inequality result that $f * g \in L^\infty$, is standard. See, e.g., [73]. To prove it, note that if $f, g \in C_0^\infty(\mathbb{R}^3)$, then $f * g \in C_0^\infty$ so, by a density argument and the fact that $\| f * g \|_\infty \leqslant \| f \|_p \| g \|_q$ for any f, g, we know that $f * g$ is in the $\| \cdot \|_\infty$ —closure of C_0^∞. These are precisely the continuous functions going to zero at infinity. ∎

LEMMA II.26. *Let ρ_1, ρ_2 be positive functions in $L^1(\mathbb{R}^3)$. If $\phi_1(x) \geqslant \phi_2(x)$ (with ϕ_i given by* (38) *with $\rho = \rho_i$) for all x, then $\int \rho_2(x)\, dx \geqslant \int \rho_1(x)\, dx$.*

Proof. $(\phi_1 - \phi_2)(x) = \int |x - y|^{-1}(\rho_2 - \rho_1)(y)\, dy$. By the arguments in Section II.5, $\lim_{r\to\infty} r(4\pi)^{-1} \int_{S_2} (\phi_1 - \phi_2)(r\Omega)\, d\Omega = \int (\rho_2 - \rho_1)(y)\, dy$. ∎

LEMMA II.27. *$\epsilon_F(\lambda)$ is a continuous function of λ.*

Proof. Since $\epsilon_F(\lambda) \equiv 0$ on $[Z, \infty)$, it is clearly sufficient to prove ϵ_F continuous on $[0, Z]$. Now, by Corollary II.9, $E(\lambda; V)$ is convex in λ. Thus $E(\lambda)$ has right and left derivatives at each point and the right (resp. left) dervative is continuous from the right (resp. left). This latter fact follows from

$$\begin{aligned} E_R'(0) &= \inf_{x>0} (E(x) - E(0))/x = \inf_{x>0} \{\inf_{y>0} (E(x + y) - E(y))/x\} \\ &= \inf_{y>0} \{\inf_{x>0} (E(x + y) - E(y)/x\} = \inf_{y>0} E_R'(y). \end{aligned}$$

By Theorems II.10 and II.20, $E(\lambda)$ is differentiable on $[0, Z]$ and thus the left and right derivatives are equal for all $\lambda \in [0, Z]$. We conclude that $E(\lambda)$ is continuously differentiable, so by (19), $\epsilon_F(\lambda) = \partial E / \partial \lambda$ is continuous. ∎

THEOREM II.28. *Let $V(x) = \sum_{j=1}^k z_j \mid x - R_j \mid^{-1}$; $z_j > 0$. For $\rho \in \mathscr{I}$, let*

$$T(\rho) = \operatorname*{ess\,inf}_x [\rho^{2/3}(x) - \phi_\rho(x)]. \tag{39}$$

Then

$$\epsilon_F(\lambda) = \sup_{\rho \in \mathscr{I}_{\partial\lambda}} T(\rho). \tag{40}$$

Remarks. (1) The proof will show that $\epsilon_F(\lambda)$ is actually also equal to the sup over all ρ in $\mathscr{I}_\lambda$ (thus providing another proof that ϵ_F is monotone non-decreasing).

(2) Since $\phi_\rho(x) \to 0$ at infinity (by Lemma II.25), $T(\rho) \leqslant 0$ for all ρ thereby proving once more that $\epsilon_F \leqslant 0$.

(3) If $\lambda \leqslant Z$, then clearly the TF ρ has $\epsilon_F(\lambda) = T(\rho)$, so the sup is realized by the TF ρ. We conjecture that for $\lambda \leqslant Z$ this is the unique $\rho \in \mathscr{I}_\lambda$ with $T(\rho) = \epsilon_F$. However, for $\lambda \geqslant Z$, if ρ is the sum of the TF ρ with $\lambda = Z$ and any positive ρ', then $T(\rho) = 0$ so there are many ρ's with $T(\rho) = \epsilon_F$. This is in contrast to the minimization problem for which there is *no* ρ in $\mathscr{I}_{\partial\lambda}$ with $\mathscr{E}(\rho; V) = E(\lambda; V)$ if $\lambda > Z$.

Proof. As we have remarked above, if $\lambda \geqslant Z$, then it is easy to see that $\sup_{\rho \in \mathscr{I}_{\partial\lambda}} T(\rho) = 0 = \epsilon_F(\lambda)$ so we consider the case $\lambda < Z$. Suppose that $T(\rho) > \epsilon_F(\lambda)$. By continuity of $\epsilon_F(\cdot)$, $T(\rho) \geqslant \epsilon_F(\lambda')$ for some $\lambda' \in (\lambda, Z)$. Let ρ_{TF} be the minimizing ρ for $\mathscr{E}(\cdot)$ on $\mathscr{I}_{\partial\lambda'}$. We shall prove that $\int \rho\, dx \geqslant \lambda'$ thereby proving (40) (using Remark 3 above). By Lemma II.26 we need only prove that $\phi_{\text{TF}} \geqslant \phi_\rho$ so let $\psi = \phi_\rho - \phi_{\text{TF}}$ which is continuous by Lemma II.25. Thus $B = \{x \mid \psi > 0\}$ is open. Now, for $x \in B$, either $\rho_{\text{TF}}(x) = 0$ in which case $\rho(x) \geqslant \rho_{\text{TF}}(x)$ or $\rho_{\text{TF}}(x) > 0$ in which case $\rho_{\text{TF}}^{2/3}(x) - \phi_{\text{TF}}(x) = +\epsilon_F(\lambda)$. Thus for almost all $x \in B \cap \{x \mid \rho_{\text{TF}}(x) > 0\}$, $\rho^{2/3}(x) \geqslant \phi_\rho(x) + T(\rho) \geqslant \phi_{\text{TF}}(x) + \psi(x) + \epsilon_F(\lambda) \geqslant \rho_{\text{TF}}^{2/3}(x)$, so $\rho \geqslant \rho_{\text{TF}}$ on almost all of B. It follows that the distributional Laplacian $\Delta\psi = 4\pi(\rho - \rho_{\text{TF}}) \geqslant 0$ on B so that ψ is subharmonic on B. Thus ψ takes its maximum value on $\partial B \cup \infty$. At ∞, $\psi \to 0$ (by Lemma II.25) and by definition, $\psi \to 0$ on ∂B. Thus $\psi \leqslant 0$ on B so B is empty. This establishes that $\phi_{\text{TF}} \geqslant \phi_\rho$. ∎

THEOREM II.29. *Let* $V(x) = \sum_{j=1}^k z_j \mid x - R_j \mid^{-1}$; $z_j > 0$. *For* $\rho \in \mathscr{I}$, *let*

$$S(\rho) = \operatorname*{ess\,sup}_{\{x \mid \rho(x) > 0\}} [\rho^{2/3}(x) - \phi_\rho(x)].$$

Then

$$\epsilon_F(\lambda) = \inf_{\rho \in \mathscr{I}_{\partial\lambda}} S(\rho). \tag{41}$$

Remarks. (1) Our method of proof shows that in (41), $\mathscr{I}_{\partial\lambda}$ can be replaced by $\{\rho \in \mathscr{I} \mid \int \rho \geqslant \lambda\}$.

(2) For $\lambda \leqslant Z$, the TF ρ's obey $S(\rho) = \epsilon_F(\lambda)$ and we conjecture they are the unique such ρ's. For $\lambda > Z$, there is no obvious ρ with $S(\rho) = \epsilon_F(\lambda) = 0$ and our proof shows that there is none.

Proof. We first claim that

$$\epsilon_F(\lambda) \geqslant \inf_{\rho \in \mathscr{I}_{\partial\lambda}} S(\rho). \tag{42}$$

For $\lambda \leqslant Z$, just take ρ to be the TF minimizing ρ. For $\lambda > Z$, proceed as follows. Let $\tilde{\rho}$ be the minimizing ρ for $\lambda = Z$. We can find $\rho \in \mathscr{I}_{\partial\lambda}$ with $\| \rho - \tilde{\rho} \|_\infty$ and $\| \rho - \tilde{\rho} \|_{5/3}$ arbitrarily small. But then, by Young's inequality, $\| \phi_\rho - \phi_{\tilde{\rho}} \|_\infty$ is small so $| S(\rho) - S(\tilde{\rho})|$ can be made arbitrarily small.

Given (42), we need only show that $S(\rho) < \epsilon_F(\lambda)$ implies that $\int \rho \, dx < \lambda$ to complete the proof. Suppose that $S(\rho) < \epsilon_F(\lambda)$. By continuity, we can find $\lambda' < \lambda$ so that $S(\rho) < \epsilon_F(\lambda')$. Let ρ_{TF} be the minimizing ρ on $\mathscr{I}_{\lambda'}$ so that $\int \rho_{\mathrm{TF}} \, dx = \min(\lambda', Z)$. We claim that $\int \rho \, dx \leqslant \int \rho_{\mathrm{TF}} \, dx$. By Lemma II.26, we need only show that $\phi_\rho \geqslant \phi_{\mathrm{TF}}$. Let $\psi = \phi_\rho - \phi_{\mathrm{TF}}$ and let $B = \{x \mid \psi < 0\}$ which is open. Now for $x \in B$ either $\rho(x) = 0$ in which case $\rho_{\mathrm{TF}} \geqslant \rho$, or else $\rho(x) > 0$ in which case (a.e.): $\rho^{2/3}(x) \leqslant \phi_\rho(x) + S(\rho) \leqslant \epsilon_F(\lambda) + \psi(x) + \phi_{\mathrm{TF}}(x) \leqslant \epsilon_F(\lambda) + \phi_{\mathrm{TF}}(x) \leqslant \rho_{\mathrm{TF}}^{2/3}(x)$ since $\rho_{\mathrm{TF}} = \max(\phi_F + \epsilon_F, 0)^{3/2}$. Thus $\rho_{\mathrm{TF}} \geqslant \rho$ on B, so $\Delta\psi = 4\pi(\rho - \rho_{\mathrm{TF}}) \leqslant 0$. ψ is superharmonic and thus takes its minimum value on ∂B. As in the proof of Theorem II.27, B is empty so $\phi_\rho \geqslant \phi_{\mathrm{TF}}$ a.e. ∎

II.8. *Properties of the Chemical Potential*

THEOREM II.30. *Let* $\epsilon_F(\lambda; z_1, ..., z_k; R_1, ..., R_k)$ *be the chemical potential for* $V = \sum_{j=1}^k z_j \, | x - R_j |^{-1}$. *Then:*

(i) *In the region* $0 < \lambda < Z \equiv \sum_{j=1}^k z_j$, $\epsilon_F(\cdot; z_j; R_j)$ *is continuous, negative, strictly monotone increasing and concave, and* $\lim_{\lambda \uparrow Z} \epsilon_F(\lambda) = 0$.

(ii) *For* $\lambda \geqslant Z$, $\epsilon_F \equiv 0$.

(iii) *For fixed* R_j *and* λ, ϵ_F *is monotone decreasing as any* z_i *increases.*

Proof. (i) We have already seen that ϵ_F is negative and monotone increasing. Concavity will imply continuity and, since $\epsilon_F < 0$ for $\lambda < Z$ and $\epsilon_F = 0$ for $\lambda = Z$, strict monotonicity. To prove concavity, let ρ_1, ρ_2 minimize $\mathscr{E}(\cdot; V)$ on $\mathscr{I}_{\partial\lambda_1}, \mathscr{I}_{\partial\lambda_2}$. Let $\rho = t\rho_1 + (1 - t)\rho_2$. Then $\int \rho = t\lambda_1 + (1 - t)\lambda_2$ and for any x:

$$\rho^{2/3}(x) - \phi_\rho(x) \geqslant t(\rho_1^{2/3}(x) - \phi_{\rho_1}(x)) + (1 - t)(\rho_2^{2/3}(x) - \phi_{\rho_2}(x))$$

$$\geqslant t\,\epsilon_F(\lambda_1) + (1 - t)\,\epsilon_F(\lambda_2)$$

since ϕ_ρ is linear in ρ and $x \mapsto x^{2/3}$ is concave. As a result, $T(\rho) \geqslant t\,\epsilon_F(\lambda_1) + (1 - t)\,\epsilon_F(\lambda_2)$, so by Theorem II.27, $\epsilon_F(t\lambda_1 + (1 - t)\lambda_2) \geqslant t\,\epsilon_F(\lambda_1) + (1 - t)\,\epsilon_F(\lambda_2)$.

(ii) follows from Theorems II.10 and II.18.

(iii) As z_i increases, the corresponding ϕ_ρ increases for any fixed ρ. Thus $T(\rho)$ decreases, so by Theorem II.27, ϵ_F decreases. ∎

THEOREM II.31. *Let* $\epsilon_F(\lambda: z_1, \ldots, z_k; R_1, \ldots, R_k)$ *be the chemical potential for* $V = \sum_{j=1}^k z_j \mid x - R_j \mid^{-1}$. *Let* $\alpha = \sum_{j=1}^k z_j^3$, $\beta = \sup_j z_j$ *and* $b = (4\lambda/\pi^2\alpha)^{2/3}$. *Then for small* λ, $\epsilon_F = -b^{-1} + 0(1)$. *More precisely, when* $\lambda \leqslant \alpha\beta^{-2}$ *and* $b \leqslant \min_{i<j} \mid R_i - R_j \mid (z_i + z_j)^{-1}$, *then*

$$\epsilon_F \leqslant b^{-1} \max_i \left\{ -1 + 6\lambda/z_i - \sum_{j \neq i} (z_j - \lambda_j) [\mid R_i - R_j \mid/b + z_i]^{-1} \right\},$$

$$\epsilon_F \geqslant b^{-1} \min_i \left\{ -1 + \lambda/z_i - \sum_{j \neq i} (z_j - \lambda_j) [\mid R_i - R_j \mid/b - z_i]^{-1} \right\},$$

with $\lambda_i = z_i^3/\alpha$. *In the atomic case,*

$$-Z^2(1 - \lambda/Z)(4\lambda/\pi^2)^{-2/3} \leqslant \epsilon_F \leqslant -Z^2(1 - 6\lambda/Z)(4\lambda/\pi^2)^{-2/3}$$

when $\lambda < Z$.

Proof. Atomic case: $(k = 1, z_1 = Z, R_1 = 0)$. For $b > 0$, let

$$\begin{aligned} \rho(x) &= (Z \mid x \mid^{-1} - b^{-1})^{3/2}, \qquad && \mid x \mid \leqslant Zb, \\ &= 0 \qquad , && \mid x \mid \geqslant Zb, \end{aligned}$$

be a trial function. Since $I \equiv \int_0^1 (1 - x)^{3/2} x^{1/2} \, dx = \pi/16$, $\int \rho = Z^3 b^{3/2} \pi^2/4 = \lambda$. Let $\psi(x) = \int \rho(y) \mid x - y \mid^{-1} dy$. $\sup_x \psi(x) = \psi(0) = b^{1/2} Z^2 3\pi^2/2 = 6\lambda(Zb)^{-1}$, since $\int_0^1 (1 - x)^{3/2} x^{-1/2} \, dx = 6I$. For $x \geqslant Zb$, $\psi(x) = \lambda \mid x \mid^{-1}$. Thus

$$\begin{aligned} \epsilon(x) &\equiv \rho^{2/3}(x) - Z \mid x \mid^{-1} + \psi(x) \\ &= -b^{-1} + \psi(x), \qquad && \mid x \mid \leqslant Zb, \\ &= -(Z - \lambda) \mid x \mid^{-1}, && \mid x \mid \geqslant Zb. \end{aligned}$$

Thus, for $\lambda \leqslant Z$,

$$\begin{aligned} T(\rho) &= -(Z - \lambda)(Zb)^{-1}, \\ S(\rho) &= -(Z - 6\lambda)(Zb)^{-1}, \end{aligned}$$

and the theorem is proved using Theorems II.27 and II.28.

Molecular case: Choose $b > 0$ as before and let

$$\rho(x) = \sum_{i=1}^k \rho_i(x - R_i),$$

$$\begin{aligned} \rho_i(x) &= (z_i \mid x \mid^{-1} - b^{-1})^{3/2}, \qquad && \mid x \mid \leqslant z_i b, \\ &= 0, && \mid x \mid \geqslant z_i b, \end{aligned}$$

$$\psi_i(x) = \int \rho_i(y) \mid x - y \mid^{-1} dy.$$

Then $\lambda_i = \int \rho_i = z_i^3 b^{3/2} \pi^2/4$. Choose b such that $\lambda = \sum_{i=1}^k \lambda_i$, i.e., $b = (4\lambda/\pi^2\alpha)^{2/3}$, and suppose that λ is sufficiently small such that the balls $B_i = \{x \mid |x - R_i| < z_i b\}$ are disjoint, i.e., $b \leqslant \min_{i<j} |R_i - R_j|(z_i + z_j)^{-1}$. We also suppose that $\lambda_i \leqslant z_i$, i.e., $\lambda \leqslant \alpha\beta^{-2}$. With $\epsilon(x) = \rho^{2/3}(x) - \phi_\rho(x)$, one has that in $\bar{B}_i$

$$\epsilon(x) = -b^{-1} + \psi_i(x - R_i) - \sum_{j \neq i} (z_j - \lambda_j) \mid x - R_j \mid^{-1}.$$

In $\bar{B}_i$, $|R_i - R_j| - z_i b \leqslant |x - R_j| \leqslant |R_i - R_j| + z_i b$. Therefore,

$$S(\rho) \leqslant b^{-1} \max_i \left\{ -1 + 6\lambda/z_i - \sum_{j \neq i} (z_j - \lambda_j) [| R_i - R_j |/b + z_i]^{-1} \right\}.$$

Turning to $T(\rho)$ we note that $\epsilon(x)$ is superharmonic in B_i and thus has its minimum on ∂B_i. In $K = \mathbb{R}^3 \backslash \bigcup_1^k \bar{B}_i$, $\rho(x) = 0$ and $-\phi_\rho(x)$ is harmonic and thus has its minimum on ∂K. Since $\lambda_i < z_i$, this minimum is again on the boundary of some B_i. Therefore,

$$T(\rho) \geqslant b^{-1} \min_i \left\{ -1 + \lambda/z_i - \sum_{j \neq i} (z_j - \lambda_j) [| R_i - R_j |/b - z_i]^{-1} \right\}.$$

The use of Theorems II.27 and II.28 concludes the proof. ∎

From the properties of $\epsilon_F(\lambda)$, we can read off properties of $E^{\mathrm{TF}}(\lambda; z_j; R_j)$ (we have already proven (i) and (ii) by alternative means):

THEOREM II.32. *$E^{\mathrm{TF}}(\lambda; z_j; R_j)$, the minimum of $\mathscr{E}(\cdot, \sum_{j=1}^k zj \mid x - R_j \mid^{-1})$ on $\mathscr{I}_\lambda$, has the following properties*:

(i) *For $0 \leqslant \lambda \leqslant Z = \sum_{j=1}^k z_j$, $E^{\mathrm{TF}}(\lambda)$ is C^1, negative, strictly monotone decreasing and strictly convex.*

(ii) *$E^{\mathrm{TF}}(\lambda)$ is constant for $\lambda \geqslant Z$ and C^1 near $\lambda = Z$.*

(iii) *For λ small, $E^{\mathrm{TF}}(\lambda) \sim \lambda^{1/3}$ in the sense that* $\lim_{\lambda \downarrow 0} E^{\mathrm{TF}}(\lambda)/\lambda^{1/3} = -3(\pi^2 \sum_{j=1}^k z_j^3/4)^{2/3}$.

Remark. Some results on $E^{\mathrm{TF}}(\lambda; Z)$ for the atomic case when $\lambda \sim Z$ can be found in Theorem IV.12.

III. Quantum Mechanical Limit Theorems

In this section we shall prove a variety of theorems that assert that as the nuclear charges go to infinity, quantum mechanics and TF theory become identical. While we could allow more general potentials than those of the form (1a), in Section III.1 we shall state the limit theorems for the density (44) when V

is of the Coulomb type (1a). We shall reduce the proof of the limit theorems for densities and energies to a single limit theorem for the energy but with V of a more general form than (1a). Baumgartner [5] has recently found an alternative proof of the limit theorem announced in [49] (Theorem III.1 below). His proof uses the Hertl *et al.* bound [29] and Martin's limit theorem [56].

With our choice of units (setting the c of (3e) equal to 1), H_Q (of Eq. (2)) becomes:

$$H_Q{}^N = -(3\pi^2)^{-2/3} \sum_{i=1}^{N} \Delta_i - \sum_{i=1}^{N} V(r_i) + \sum_{i<j} | r_i - r_j |^{-1}, \tag{43}$$

where $V(x) = \sum_{j=1}^{k} z_j \mid x - R_j \mid^{-1}$. We remind the reader that $H_Q{}^N$ is considered on $\mathscr{H}_{\text{PHYS}}$, the space of antisymmetric spinor valued functions described in Section I.1. We introduce the notation $E_N{}^Q(z_1, ..., z_k ; R_1, ..., R_k)$ to denote the infinum of spec($H_Q{}^N$) on $\mathscr{H}_{\text{PHYS}}$. If $\psi(x_1, \sigma_1, ;...; x_N, \sigma_N)$ is any element of $\mathscr{H}_{\text{PHYS}}$ we define $\rho_j(x_1, ..., x_j ; \psi)$ for $j \leqslant N$ by

$$\rho_j(x_1, ..., x_j ; \psi) = j! \binom{N}{j} \sum_{\sigma_i = \pm 1} \int | \psi(x_1, ..., x_j, y_1, ..., y_{N-j} ; \sigma)|^2 \, d^{(N-j)}y. \tag{44}$$

III.1. *Basic Theorems and Reduction to the Energy Theorem*

THEOREM III.1.

$$\lim_{a\to\infty} E^Q_{\lambda a}(az_1, ..., az_k ; a^{-1/3}R_1, ..., a^{-1/3}R_k)/a^{7/3} = E^{\text{TF}}(\lambda; z_j ; R_j). \tag{45}$$

Remarks. (1) In (45) a goes through values with $a\lambda$ integral. More generally if $R_j^{(n)}$, N_n, $z_j^{(n)}$ are given such that $z_j^{(n)}/Z^{(n)} \to z_j$ (with $Z^{(n)} = \sum_{j=1}^{k} z_j^{(n)}$), $R_j^{(n)}[Z^{(n)}]^{-1/3} \to R_j$, $N_n/Z^{(n)} \to \lambda$, and $Z^{(n)} \to \infty$, then $E^Q_{N_n}(z_j^{(n)}; R_j^{(n)})[Z^{(n)}]^{-7/3} \to E^{\text{TF}}(\lambda; z_j ; R_j)$. This result is a consequence of the fact that as our proofs below show, the limit (45) is uniform. All the other limit theorems below have an extension to this more general setting.

(2) As explained in Section I.2, Theorem III.1 says that

$$E^Q_{\lambda a}(z_j a; R_j a^{-1/3})/E^{\text{TF}}(\lambda a; z_j a; R_j a^{-1/3}) \to 1 \text{ as } a \to \infty.$$

(3) As we also explained in Section I our methods also handle the case where the $R_j^{(n)}$ are constant or, more generally, where $(R_j^{(n)} - R_i^{(n)})\, a^{1/3} \to \infty$ (all $i \neq j$). In that case $E^Q_{\lambda a}(z_j a; R_j^{(n)}) \to \min_{\{\lambda_j | \sum \lambda_j = \lambda, \lambda_j \geqslant 0\}} \sum_{j=1}^{k} E^{\text{TF}}(\lambda; z_j ; 0)$. In other words, the system breaks up into isolated atoms or ions.

To state our other theorems we introduce a notion of "approximate ground states."

DEFINITION. Fix z_j, $R_j (j = 1,..., k)$, and λ. For $N = 1,...,...$, let $\lambda\, a_N = N$, and let $H_Q{}^N$ be the Hamiltonian (43) with $z_j^{(N)} = z_j a_N$; $R_j^{(N)} = R_j a_N^{-1/3}$. A sequence of normalized vectors $\psi_N \in \mathscr{H}_{\text{PHYS}}$ is called an approximate ground state if and only if

$$[(\psi_N, H_Q{}^N \psi_N) - E_N{}^Q]\, a_N^{-7/3} \to 0.$$

If $\lambda \leqslant Z = \sum_{j=1}^k z_j$, it is known that $H_Q{}^N$ has an isolated eigenvalue at the bottom of the spectrum [4, 79, 97], and the corresponding eigenvectors form an approximate ground state. This ground state may well be degenerate, however. In interpreting the results below, the reader should keep this example in mind. We consider the more general approximate ground state, first because of the uniqueness question; second to have a result in the case $\lambda > Z$ (where we expect, at least for all large N, that there is not an eigenvalue at the bottom of the spectrum); and third, to be able to say something about excited states where, in a suitable sense, not many electrons are excited.

THEOREM III.2. *Let $\{\psi_N\}$ be any approximate ground state. Write $H_Q{}^N = K_Q{}^N - A_Q{}^N + R_Q{}^N$ corresponding to the three terms in* (44). *Then*

$$(\psi_N, K_Q{}^N \psi_N)\, a_N^{-7/3} \to K(\rho),$$

$$(\psi_N, A_Q{}^N \psi_N)\, a_N^{-7/3} \to A(\rho),$$

$$(\psi, R_Q{}^N \psi_N)\, a_N^{-7/3} \to R(\rho),$$

where ρ is the unique function in $\mathscr{I}_\lambda$ minimizing the TF *energy function $\mathscr{E}(\cdot; \sum_{j=1}^k z_j \mid x - R_j \mid^{-1})$ and K, A, R are the functionals of* §II.6. *In particular, if ψ_N is the ground state of a neutral atom (i.e., N electrons, $V(x) = N \mid x \mid^{-1}$), then as $N \to \infty$:*

$$(\psi_N, K_Q{}^N \psi_N) : (\psi_N, A_Q{}^N \psi_N) : (\psi_N, R_Q{}^N \psi_N) \to 3 : 7 : 1.$$

Remark. The final statement in the theorem follows from the first part of the theorem and Corollary II.24.

THEOREM III.3. *Let $\{\psi_N\}$ be any approximate ground state. Let $\rho_j(x_1, ..., x_j; \psi_N)$ be given by* (44). *Let*

$$_N\hat{\rho}_j(x_1, ..., x_j) = a_N^{-2j} \rho_j(a_N^{-1/3} x_1, ..., a_N^{-1/3} x_j) \tag{46}$$

and let $\rho_{\text{TF}}(x)$ be the minimizing ρ for $\mathscr{E}(\cdot; \sum_{j=1}^k z_j \mid x - R_j \mid^{-1})$ on $\mathscr{I}_\lambda$. Then as $N \to \infty$,

$$_N\hat{\rho}_j(x_1, ..., x_j) \to \rho_{\text{TF}}(x_1)\, \rho_{\text{TF}}(x_2) \cdots \rho_{\text{TF}}(x_j) \equiv \rho_{\text{TF}}^j(x)$$

in the sense that for any bounded set $D \subset \mathbb{R}^{3j}$:

$$\lim_{N \to \infty} \int_D {}_N\hat{\rho}_j(x)\, d^j x = \int_D \rho_{\text{TF}}^j(x)\, d^j x. \tag{47}$$

If $\lambda \leqslant Z \equiv \sum_{j=1}^{k} z_j$, *then the restriction that D be bounded can be removed from* (47) *and*

$$ {}_N\hat{\rho}_j(x) \to \rho^j_{\mathrm{TF}}(x) $$

in the weak-L^1 *sense.*

Remarks. (1) $\hat{\rho}$ is normalized so that

$$ \int_{\mathbb{R}^{3j}} {}_N\hat{\rho}_j(x)\, d^jx = a_N^{-j} j! \binom{N}{j}. $$

As $N \to \infty$, $\int_{\mathbb{R}^{3j}} {}_N\hat{\rho}_j(x)\, d^jx \to \lambda^j$. If $\lambda \leqslant Z$, then $\int_{\mathbb{R}^{3j}} \rho^j_{\mathrm{TF}}(x)\, d^jx = \lambda^j$ (by Theorem II.20), so the part of Theorem III.3 following equation (47) follows from (47) and Lemma III.4 below.

(2) One part of this theorem is the assertion that as $N \to \infty$ there are no correlations among any finite number of electrons; in particular, one has an a posteriori justification of the ansatz (5), just as Theorem III.2 provides an a posteriori justification of the ansatz (6).

(3) For the case of a neutral atom, $V(x) = |x|^{-1}$ and $\lambda = 1$, if we take $j = 1$, then (47) says:

$$ Z^{-1} \int_{x \in Z^{-1/3} D} \rho_Q(x; Z)\, dx \to \int_D \rho_{\mathrm{TF}}(x)\, dx, \tag{48} $$

where $\rho_Q(x; Z)$ is the one-body density in the quantum atom of charge Z and ρ_{TF} is the charge 1 TF atom. Equation (48) of course says that the fraction of charge in $Z^{-1/3} D$ is given by the TF theory, and, in particular it says that in a definite sense the bulk of large Z atoms shrinks as $Z^{-1/3}$ as $Z \to \infty$. We shall say more about this in Section IV.

LEMMA III.4. *Let* $\rho_m, \rho \in L^1(\mathbb{R}^n)$ with $\rho_m(x), \rho(x) \geqslant 0$. *Suppose that*

$$ \int_D \rho_m(x)\, dx \to \int_D \rho(x)\, dx \tag{49} $$

as $m \to \infty$ *for D bounded and for D equal to all of* $\mathbb{R}^n$. *Then* (49) *holds for any D, and* $\rho_m \to \rho$ *in weak* $L^1(\mathbb{R}^n)$.

Proof. Given ϵ, find a bounded D_0 with $\int_{R^n \backslash D_0} \rho(x)\, dx \leqslant \epsilon/4$. By (49) we have that $\int_{R^n \backslash D_0} \rho_m(x)\, dx = \int_{\mathbb{R}^n} \rho_m(x)\, dx - \int_{D_0} \rho_m(x)\, dx \to \int_{R^n \backslash D_0} \rho(x)\, dx$. Hence there exists an M such that $\int_{R^n \backslash D_0} \rho_m(x)\, dx \leqslant \epsilon/3$ for all $m \geqslant M$. Let D be arbitrary and write $D = D_1 \cup D_2$ with $D_1 \subset D_0$ and $D_2 \subset R^n \backslash D_0$. By hypothesis, for suitable M_1, $m \geqslant M_1$ implies that

$$ \left| \int_{D_1} (\rho_m - \rho)\, dx \right| \leqslant \epsilon/3. $$

Since $\int_{D_2} \rho_m \leqslant \int_{\mathbb{R}^n \setminus D_0} \rho_m$ and similarly for ρ, $m \geqslant \max(M, M_1)$ implies that $| \int_D (\rho_m - \rho)\, dx | \leqslant \epsilon$. Since finite linear combinations of characteristic functions are dense in L^∞ and $\sup_m \| \rho_m \|_1 < \infty$, by hypothesis, we have weak L^1 convergence. ∎

In the remainder of this subsection, we want to show how to prove (47) when $j = 1$, from a suitably strengthened version of Theorem III.1. The remainder of Theorem III.3 and also Theorem III.2 follow from different strengthenings of Theorem III.1 which can be proved by our methods in Sections III.2–III.5 (see the remarks below). The strengthened energy theorem we will need is:

THEOREM III.5. *Let V be of the form*

$$V(x) = \sum_{j=1}^{k} z_j \, | x - R_j |^{-1} + U(x), \tag{50}$$

where $z_j > 0$, and $U \in C_0^\infty(\mathbb{R}^3)$. Given λ, N let a_N be defined by $\lambda a_N = N$. Let $E_N{}^Q$ be the infinmum of the spectrum of

$$-(3\pi^2)^{-2/3} \sum_{i=1}^{N} \Delta_i - \sum_{i=1}^{N} V_{a_N}(r_i) + \sum_{i<j} | r_i - r_j |^{-1}, \tag{51a}$$

where

$$V_a(x) = a^{4/3} \, V(a^{1/3} x). \tag{51b}$$

Let $E^{\mathrm{TF}}(\lambda)$ be the minimum on $\mathscr{I}_\lambda$ of $\mathscr{E}(\cdot\,; V)$. Then

$$\lim_{N \to \infty} E_N{}^Q / a_N^{7/3} = E^{\mathrm{TF}}(\lambda).$$

Remarks. (1) This is the theorem we need in order to prove Theorem III.3 when $j = 1$. For general j, one must consider a V of the form $\sum_{l=1}^{k} z_l \, | x - R_l |^{-1}$ and an additional term in (51a) of the form

$$- \sum_{\substack{i_1, \ldots, i_j \\ \text{unequal}}} U_{a_N}(r_{i_1}, \ldots, r_{i_j}),$$

where U is a symmetric function in $C_0^\infty(\mathbb{R}^{3j})$. The TF energy functional is then replaced by

$$\tfrac{3}{5} \| \rho \|_{5/3}^{5/3} - \int \rho(x) \, V(x) \, dx - \int U(x_1, \ldots, x_j) \, \rho(x_1) \cdots \rho(x_j) \, d^j x$$

$$+ \tfrac{1}{2} \int \rho(x) \, \rho(y) \, | x - y |^{-1} \, dx \, dy.$$

With these two changes, Theorem III.5 holds (by the methods of Sects. III.2–III.5) and this new theorem implies Theorem III.3 with j arbitrary (by the methods we discuss immediately below). We note, however, that three points are somewhat more subtle for this modified TF problem. First, the j-body interaction, $I = \int U(x_1, ..., x_j)\, \rho(x_1) \cdots \rho(x_j)$, can destroy convexity of the energy functional in ρ, and consequently the minimizing ρ may not be unique. However, the minimum energy for U replaced by αU is still concave in α and differentiable at $\alpha = 0$. The differentiability follows by the method of Theorem II.16 and the fact that the minimizing ρ is unique when $\alpha = 0$. Second, in proving the existence of a minimizing ρ, we must exploit the fact that if $\rho_m \to \rho$ in weak $L^p(\mathbb{R}^n)$, then $\rho_m(x_1) \cdots \rho_m(x_j) \to \rho(x_i) \cdots \rho(x_j)$ in weak $L^p(\mathbb{R}^{nj})$. This follows from the density of sums of product functions in $L^{p'}(\mathbb{R}^{nj})$ in the norm topology. Third, $|I|$ is bounded by $\| \rho \|_1^j \| U \|_\infty < \infty$ since $U \in C_0^\infty(\mathbb{R}^{3j})$ and $\rho \in \mathscr{I}_\lambda$.

(2) Theorem III.2 follows by the methods below and a theorem of type III.5 but with E_λ^{TF} replaced by $E(\kappa, \alpha, \mu, \lambda)$ (see Sect. II.6) and with

$$H_Q{}^N = -\kappa(3\pi^2)^{-2/3} \sum_{i=1}^{N} \Delta_i - \alpha \sum_{i=1}^{N} \sum_{j=1}^{k} z_j a_N \,| r_i - a_N^{-1/3} R_j |^{-1} + \mu \sum_{i<j} | r_i - r_j |^{-1}.$$

With these two changes Theorem III.5 still holds (by the methods in Sects. III.2–III.5). In obtaining Theorem III.5 from this theorem, the differentiability Theorem II.21 is needed.

(3) By scaling covariance of both the quantum and TF theory we can and shall suppose henceforth that $\lambda = 1$ and hence that $a_N = N$.

Proof of (47), $j = 1$ *from Theorem* III.5. Since ${}_N\hat{\rho}_1$ and ρ^{TF} are both functions with L^1 norm at most 1, it suffices to prove that

$$\int {}_N\hat{\rho}_1(x)\, U(x)\, dx \to \int \rho_{\mathrm{TF}}(x)\, U(x)\, dx \qquad (52)$$

for all $U \in C_0^\infty(\mathbb{R}^3)$. Before giving the proof of (52) let us give the intuition in the special case where ψ_N is a sequence of ground states rather than just approximate ground states and where we suppose each $H_Q{}^N$ has a *simple* isolated eigenvalue at the bottom of its spectrum. After undoing the scale transformation,

$$\int {}_N\hat{\rho}_1(x)\, U(x)\, dx \text{ is equal to } N^{-7/3}(d/d\alpha)\, E_N{}^Q(V_\alpha)$$

where

$$V_\alpha(x) = \sum_{j=1}^{k} z_j \,| x - R_j |^{-1} + \alpha U(x).$$

Now, by Theorem III.5, $N^{-7/3} E_N{}^Q(V_\alpha)$ converges to $E^{\mathrm{TF}}(V_\alpha)$, so (52) is equivalent to the convergence of derivatives of certain functions which we know converge pointwise. In general, of course, pointwise convergence does not imply convergence of derivatives but if all the functions are concave (as they are in this case) and the limiting function is differentiable (as it is by Theorem II.16) then the derivatives do converge (the use of this fact in mathematical physics has been emphasized by Griffiths [25]). It is this mechanism that is central in the proof we now give for approximate ground states.

Let $E_N^Q(\alpha)$ be the infimum of the spectrum of $H_Q^N(\alpha)$ of the form (43) with

$$V_N(x, \alpha) = \sum_{j=1}^{k} z_j N \mid x - R_j N^{-1/3} \mid^{-1} + \alpha N^{4/3} U(N^{1/3} x)$$

and let $f_N(\alpha) = N^{-7/3} E_N^Q(\alpha)$. Let $f_\infty(\alpha)$ be the minimum of the TF functional $\mathscr{E}(\cdot; \sum_{j=1}^k z_j \mid x - R_j \mid^{-1} + \alpha\, U(x))$. We begin by computing $\int {}_N\hat{\rho}_1(x)\, U(x)\, dx$ in terms of expectations with respect to ψ_N.

$$\begin{aligned}(\psi_N, [H_Q^N(\alpha) - H_Q^N(0)]\psi_N) &= \sum_\sigma \sum_{i=1}^{N} \alpha N^{4/3} \int U(N^{1/3} x_i) \mid \psi_N(x_1, \ldots, x_N; \sigma)\mid^2 d^N x \\ &= \alpha N^{4/3} \int U(N^{1/3} x)\, {}_N\hat{\rho}_1(x)\, dx \\ &= \alpha N^{4/3} \int U(N^{1/3} x)\, [N^2\, {}_N\hat{\rho}_1(N^{1/3} x)]\, dx \\ &= \alpha N^{7/3} \int U(y)\, {}_N\hat{\rho}_1(y)\, dy.\end{aligned} \tag{53}$$

Thus by the Rayleigh–Ritz principle, for any $\alpha > 0$:

$$N^{-7/3}\alpha^{-1}[E_N^Q(\alpha) - E_N^Q(0)] \leqslant \int U(y)\, {}_N\hat{\rho}_1(y)\, dy + \alpha^{-1} N^{-7/3}[\delta E(0)], \tag{54}$$

where

$$\delta E(\alpha) = (\psi_N, [H_Q^N(\alpha) - E_N^Q(\alpha)]\psi_N).$$

By definition of approximate ground state, $N^{-7/3}\delta E(0) \to 0$ as $N \to \infty$. Letting $N \to \infty$ in (54) and using Theorem III.5, we have:

$$\alpha^{-1}[E^{\mathrm{TF}}(V_\alpha) - E^{\mathrm{TF}}(V)] \leqslant \underline{\lim} \int U(y)\, {}_N\hat{\rho}_1(y)\, dy; \qquad \alpha > 0. \tag{55a}$$

Similarly for $\alpha < 0$ (using the fact that multiplication by α^{-1} reverses the sign of inequalities):

$$\alpha^{-1}[E^{\mathrm{TF}}(V_\alpha) - E^{\mathrm{TF}}(V)] \geqslant \overline{\lim} \int U(y)\, {}_N\hat{\rho}_1(y)\, dx; \qquad \alpha < 0. \tag{55b}$$

Since $E^{TF}(V_\alpha)$ is differentiable at $\alpha = 0$ with derivative $\int \rho^{TF}(x)\, U(x)\, dx$ by Theorem II.16:

$$\overline{\lim} \int U(y)\, {}_N\hat{\rho}_1(y)\, dy \leqslant \int \rho^{TF}(x)\, U(x)\, dx$$
$$\leqslant \underline{\lim} \int U(y)\, {}_N\hat{\rho}_1(y)\, dy$$

proving (52). ∎

The remainder of this section is devoted to the proof of Theorem III.5 (with $\lambda = 1$, $a_N = N$) and in the remainder of this subsection we want to sketch the overall strategy.

Since the ansatz (6) is based on an intuition of noninteracting particles in boxes, our first step will be to compare the Hamiltonian H_Q^N with certain Hamiltonians which force particles to stay in boxes by adding suitable boundary conditions on the box boundaries. It turns out one can "bracket H_Q^N between operators with Dirichlet and Neumann boundary conditions. (For additional application and pedagogic discussion of the method the reader may consult [68].) Because of the intuition of Section I.2, we choose boxes whose sides shrink as $N^{-1/3}$ as $N \to \infty$.

The second step is controlling the Dirichlet and Neumann boundary condition ground states inside boxes. We prove the necessary estimates in Section III.3.

If the attractive nuclear-electron potentials were bounded below, the proof of Theorem III.5 could be completed on the basis of the two steps just described. The problem is that inside the "central" boxes containing the nuclei the potential becomes very large indeed due to the $N z_j \mid r - R_j \mid^{-1}$ singularity (note the N). We thus will need a separate argument to "pull the Coulomb tooth." We shall first prove the following:

THEOREM III.6. *Fix $\alpha, \delta > 0$ and let $\mid x \mid_\delta^{-1}$ be the function which is $\mid x \mid^{-1}$ if $\mid x \mid > \delta$ and 0 if $\mid x \mid \leqslant \delta$. Theorem* III.5 *remains true with the following changes*:

(i) *Replace the V in* (50) *by*:

$$V_\delta(x) = \sum_{j=1}^{k} z_j \mid x - R_j \mid_\delta^{-1} + U(x) \tag{56}$$

in both the quantum and TF *problems.*

(ii) *Replace the constant* $(3\pi^2)^{-2/3}$ *in front of the kinetic energy term* (*i.e.*, $-\Delta$) *in H_Q^N by* $(3\pi^2)^{-2/3}\alpha$.

(iii) *Replace the term* $3/5 \int \rho^{5/3}$ *in the* TF *energy functional by* $\frac{3}{5}\, \alpha \int \rho^{5/3}$.

This theorem will be proved by the box methods of Sections III.2, III.3. The proof of Theorem III.5 will be completed by showing that by choosing $\delta > 0$

and α suitably, we can make arbitrarily small errors in E^{TF} and $N^{-7/3}E_N{}^Q$ in comparison with the $\delta = 0$, $\alpha = 1$ theory.

III.2. *Insertion of Boxes*

In essence, we prove that $E_N{}^Q/N^{7/3} \to \beta$ as $N \to \infty$ by finding a_N, b_N with $a_N/N^{7/3} \to \beta$ and $b_N/N^{7/3} \to \beta$ such that $a_N \leqslant E_N{}^Q \leqslant b_N$. The basis of the bounds on $E_N{}^Q$ will be the Rayleigh–Ritz principle in the following sense [68]:

PROPOSITION III.7. *Let H be a self-adjoint operator which is bounded from below. Let $Q(H)$ be its quadratic form domain and let C be a form core for H. Then*

$$\inf_{\{\psi\in C\,|\,\|\psi\|\leqslant 1\}} (\psi, H\psi) = \inf \operatorname{spec}(H).$$

Remarks. (1) By definition, $Q(H)$ is those ψ for which $\int |x| \, d(\psi, E_x\psi) < \infty$, where dE_x is the spectral decomposition for H. For $\psi \in Q(H)$, $(\psi, H\psi) = \int x\, d(\psi, E_x\psi)$ (which is equal to the inner product of ψ and $H\psi$ if $\psi \in D(H) = \{\psi \mid \int |x|^2 \, d(\psi, E_x\psi) < \infty\}$).

(2) A form core is a subspace $C \subset Q(H)$ such that for any $\psi \in Q(H)$, there is some sequence $\psi_n \in C$ with $\|\psi - \psi_n\| \to 0$ and $((\psi - \psi_n), H(\psi - \psi_n)) \to 0$.

To apply this version of the principle we need the following technical result which follows from standard operator perturbation theory [40, 67, 80].

PROPOSITION III.8. *If H_0 is $\sum_{i=1}^{N} -\Delta_i$ on $\mathscr{H}_{\mathrm{PHYS}}$ and $V: \mathscr{H}_{\mathrm{PHYS}} \to \mathscr{H}_{\mathrm{PHYS}}$ is a multiplication operator that is a sum of bounded functions and two-body Coulomb forces, then $Q(H) = Q(H_0)$ and any form core for H_0 is a form core for H.*

Remark. In fact, by a classic theorem of Kato [38], one has the stronger result that $D(H) = D(H_0)$ and any operator core for H_0 is an operator core for H.

We could present the upper bound $E_N{}^Q < a_N$ as coming from a suitably clever choice of trial wave function in $Q(H_0)$ for $H_N{}^Q$ but since the lower bound requires us to appeal to connections with classical boundary value problems, we discuss the upper bound in terms of a classical boundary value problem. For simplicity, we discuss the classical boundary value problems only in the case which we shall require, namely, for regions with flat boundary. By a coordinate hyperplane, we mean a plane $\{x \mid x_i = a\}$ in $\mathbb{R}^n$.

DEFINITION. Let $\{\Gamma_i\}_{i\in I}$ be a collection of coordinate hyperplanes in $\mathbb{R}^n$ such that for any compact $\kappa \subset \mathbb{R}^n$ only finitely many Γ_i intersect κ. Let $\Gamma = \bigcup_{i\in I} \Gamma_i$. By $C_{\Gamma;D}$ we denote the C^∞ functions of compact support whose support is disjoint from Γ, and by $C_{\Gamma;N}$ the functions of compact support which are C^∞ on $\mathbb{R}^n/\Gamma$ and which together with their derivatives have boundary values as x approaches Γ_i from either side (but the boundary values from the two sides need not agree).

Thus:

$$C_{\Gamma;D} \subset C_0^\infty(\mathbb{R}^n) \subset C_{\Gamma;N}. \tag{57}$$

DEFINITION. $-\Delta_{\Gamma;D}$ (resp. $-\Delta_{\Gamma;N}$) is the operator obtained by defining $(\psi, A\psi) = \int |\nabla\psi|^2 \, dx$ for $\psi \in C_{\Gamma;D}$ (resp. $C_{\Gamma;N}$) and taking the form closure.

Remark. That every closed positive quadratic form is associated to a self-adjoint operator is a standard theorem; see [40] or [66]. To see that the form $\psi \to \int |\nabla\psi|^2 \, dx$ is closable on $C_{\Gamma;D}$ and $C_{\Gamma;N}$ we note that for $\psi \in C_{\Gamma;N}$ we have $\psi \in D(B^*)$ with $\int |\nabla\psi|^2 \, dx = \| B^*\psi \|^2$, where B is the gradient operator on $C_0^\infty(R^n \backslash \Gamma)$. Since B^* is a closed operator, A is closable as a quadratic form on $C_{\Gamma;N}$ and hence also on $C_{\Gamma;D}$.

One has the following classical boundary value description of $-\Delta_{\Gamma;D}$ and $-\Delta_{\Gamma;N}$ (see [40, 54, 68]):

THEOREM III.9. *Let Γ divide $\mathbb{R}^n$ into open regions $\{R_j\}_{j\in J}$. Let $L^2(\mathbb{R}^n) = \bigoplus L^2(R_j)$ under the association of $f \in L^2(\mathbb{R}^n)$ with $\{f_j\}_{j\in J}$, where $f_j = f \restriction R_j$. Then $-\Delta_{\Gamma;D}$ (resp. $-\Delta_{\Gamma;N}$) leaves each R_j invariant and a core for $-\Delta_{\Gamma;D} \restriction L^2(R_j)$ (resp. $-\Delta_{\Gamma;N} \restriction L^2(R_j)$) is the set of functions of compact support in $\overline{R_j}$ which are C^∞ in R_j, C^∞ up to the boundary and obey $\psi = 0$ on ∂R_j (resp. $\partial_n\psi = 0$ on ∂R_j).*

DEFINITION. $\partial_n\psi$ denotes the normal derivative.

Since C_0^∞ is a core for $-\Delta$ (resp. $C_{\Gamma;D}$ or $C_{\Gamma;N}$ for resp. $-\Delta_{\Gamma;D}$ or $-\Delta_{\Gamma;N}$), (57) immediately implies the basic Dirichlet–Neumann bracketing result:

$$\begin{aligned} \inf \operatorname{spec}(-\Delta_{\Gamma,N} + V) &\leqslant \inf \operatorname{spec}(-\Delta + V) \\ &\leqslant \inf \operatorname{spec}(-\Delta_{\Gamma;D} + V). \end{aligned} \tag{58}$$

Notice that in (58) we have compared $-\Delta + V$ with operators that have boxes built into them.

We are of course interested in operators on $\mathscr{H}_{\text{PHYS}}$ rather than $L^2(\mathbb{R}^n)$ and so we must make some simple additions to the above arguments. Let $\{\gamma_j\}_{j\in J}$ be a collection of hyperplanes in $\mathbb{R}^3$ and $\gamma = \bigcup_j \gamma_j$. Write $\langle r_1, ..., r_N\rangle \in \mathbb{R}^{3N}$ and let Γ be the collection of hyperplanes in $\mathbb{R}^{3N}$ with some r in some γ_j. Then $C_{\Gamma;D}$ and $C_{\Gamma;N}$ are left invariant by permutation of the coordinates in $L^2(\mathbb{R}^{3N}; \mathbb{C}^{2N})$. Thus $-\Delta_{\Gamma;D}$ and $-\Delta_{\Gamma;N}$ leave $\mathscr{H}_{\text{PHYS}}$ invariant. As operators on $\mathscr{H}_{\text{PHYS}}$, let:

$$H_Q^N = -\alpha \sum_{i=1}^N \Delta_i - \sum_{i=1}^N V(r_i) + \sum_{i<j} | r_i - r_j |^{-1}, \tag{59a}$$

$$H_{Q;\gamma,D}^N = -\alpha \sum_{i=1}^N \Delta_{i;\gamma,D} - \sum_{i=1}^N V(r_i) + \sum_{i<j} | r_i - r_j |^{-1}, \tag{59b}$$

$$H_{Q;\gamma,N}^N = -\alpha \sum_{i=1}^N \Delta_{i;\gamma,N} - \sum_{i=1}^N V(r_i) + \sum_{i<j} | r_i - r_j |^{-1}. \tag{59c}$$

Then, as in (58):

THEOREM III.10. *For any N and any γ:*

$$\inf \operatorname{spec}(H^N_{Q,\gamma,N}) \leqslant \inf \operatorname{spec}(H_Q{}^N) \leqslant \inf \operatorname{spec}(H^N_{Q,\gamma,D}).$$

The further development we require involves using product wave functions as trial functions in $(\psi, H\psi)$.

THEOREM III.11. *Let $u_1, \ldots, u_N$ be N orthonormal functions in $Q(-\Delta_{\gamma;D})$. Then:*

$$\inf \operatorname{spec}(H^N_{Q;\gamma,D})) \leqslant -\alpha \sum_{i=1}^{N} (u_i, \Delta u_i) - \sum_{i=1}^{N} (u_i, Vu_i)$$
$$+ \tfrac{1}{2} \sum_{i,j} \int | x - y |^{-1} | u_i(x)|^2 | u_j(y)|^2 \, dx \, dy. \qquad (60)$$

Remark. This theorem and its proof are valid in the Neumann case also but we shall only need the Dirichlet.

Proof. Let Σ_N be the permutation group on $\{1,\ldots, N\}$ and for $\pi \in \Sigma_N$, let $(-1)^\pi$ be its sign. Let

$$\Psi(x_1, \ldots, x_N ; \sigma_1, \ldots, \sigma_N) = (N!)^{-1/2} \sum_{\pi \in \Sigma_N} (-1)^\pi u_{\pi(1)}(x_1 ; \sigma_1) \cdots u_{\pi(N)}(x_N ; \sigma_N).$$

Then $\| \psi \| = 1$ since the u_i are orthonormal and by a simple computation:

$$(\Psi, H^N_{Q;\gamma D}\Psi) = \text{right side of (60)} - \tfrac{1}{2} \sum_{i,j} \int | x - y |^{-1} \overline{u_i(x)}$$
$$\cdot\, u_j(x) \overline{u_j(y)} \, u_i(y) \, dx \, dy.$$

By the positive definiteness of $| x - y |^{-1}$, the exchange term

$$-\sum_{i,j} \int | x - y |^{-1} \overline{u_i(x)} \, u_j(x) \, \overline{u_j(y)} \, u_i(y)$$

is negative so $\inf \sigma(H^N_{Q;\gamma;D})) \leqslant (\Psi, H^N_{Q;\gamma;D}\Psi) \leqslant$ right side of (60). ∎

THEOREM III.12. *Let γ divide $\mathbb{R}^3$ into cubes $\{C_\beta\}_{\beta \in A}$. Suppose that $-V$ is bounded from below, and let $V_\beta = \sup_{x \in C_\beta} V(x)$ and $W_{\gamma\beta} = \inf_{x \in C_\gamma; k \in C_\beta} | x - y |^{-1}$. Let $E_\beta(n)$ be the sum of first n eigenvalues of $-\alpha\Delta_{N;C_\beta}$ as an operator on $L^2(C_\beta ; \mathbb{C}^2)$. Then*

$$\inf \operatorname{spec}(H^N_{Q;\gamma,N}) \geqslant \inf \left\{ E(\{n_\beta\}_{\beta \in A}) \mid \sum_\beta n_\beta = N \right\} \qquad (60a)$$

$$E(\{n_\beta\})_{\beta \in A} = \sum_\beta E_\beta(n_\beta) - \sum_\beta V_\beta n_\beta + \tfrac{1}{2} \sum_{\gamma,\beta} W_{\gamma\beta} n_\gamma n_\beta - \tfrac{1}{2} \sum_\gamma W_{\gamma\gamma} n_\gamma . \qquad (60b)$$

Proof. Let χ_β be the characteristic function of C_β and let $\tilde{H}$ be the operator given by

$$\tilde{H} = -\alpha \sum_{i=1}^{N} \Delta_i - \sum_{i=1}^{N} \sum_{\beta} V_\beta \chi_\beta(r_i) + \sum_{i<j} \sum_{\beta,\gamma} W_{\beta\gamma} \chi_\beta(r_i)\, \chi_\gamma(r_j)$$

on all of $L^2(\mathbb{R}^{3N}; \mathbb{C}^{2N})$ (rather than just the antisymmetric functions). Let $u_1, \ldots, u_N$ be functions in $L^2(\mathbb{R}^3; \mathbb{C}^2)$ with each u_i supported in some C_β and each u_i an eigenfunction of $-\Delta_{N;C_\beta}$ (with say $-\alpha\Delta_{N;C}\, u_i = E_i u_i$). Then $\psi = u_i(x_1\,; \sigma_1) \cdots u_N(x_N\,; \sigma_N)$ is an eigenfunction of $\tilde{H}$ with eigenvalue

$$\sum_{i=1}^{N} E_i - \sum_{\beta} V_\beta n_\beta + \tfrac{1}{2} \sum_{\beta,\gamma} W_{\gamma\beta} n_\gamma n_\beta - \tfrac{1}{2} \sum_{\gamma} W_{\gamma\gamma} n_\gamma$$

and as u_i runs through all possible eigenfunction of $-\Delta_{N;C_\beta}$ we get a basis of eigenfunctions for $\tilde{H}$. Since $\tilde{H}$ commutes with permutations

$$\inf \operatorname{spec}(\tilde{H} \restriction \mathscr{H}_{\text{PHYS}}) = \text{right side of (60a)}.$$

But clearly $H^N_{Q;N;\gamma} \geqslant \tilde{H} \restriction \mathscr{H}_{\text{PHYS}}$. ∎

Theorems III.10–III.12 allow us to bound $E_N{}^Q$ in terms of eigenfunctions for $-\Delta$ in boxes with Dirichlet or Neumann boundary conditions. Note, however, that for Theorem III.12 to be applicable $-V$ must be bounded below. This restriction leads us to the considerations in Section III.4.

III.3. *Estimates for Boxes*

In this section we prove some simple estimates about eigenfunctions of $-\Delta$ in a box of side a with D or N boundary conditions. For convenience we take the box to be $[0, a] \times [0, a] \times [0, a]$.

THEOREM III.13. *Let $E_a{}^D(n)$ (resp. $E_a{}^N$)) be the sum of the first n eigenvalues of $-(3\pi^2)^{-2/3}\Delta$ on $L^2([0, a]^3; \mathbb{C}^2)$ with Dirichlet (resp. Neumann) boundary conditions. Then for some constant C and all n, a:*

$$\left| E_a{}^D(n) - \frac{3}{5} n^{5/3} a^{-2} \right| \leqslant C n^{1/3} a^{-2}, \tag{61a}$$

$$\left| E_a{}^N(n) - \frac{3}{5} n^{5/3} a^{-2} \right| \leqslant C n^{4/3} a^{-2}, \tag{61b}$$

Proof. By scaling covariance $E_a(n) = a^{-2} E_1(n)$ so we need only prove (61) when $a = 1$. In that case, the eigenvalues of $-\Delta_D$ (resp. $-\Delta_N$) are easy to describe. Let $\mathbb{Z}_+$ be the strictly positive integers and let $\mathbb{N} = \mathbb{Z}_+ \cup \{0\}$. Eigenvalues of $-\Delta_D$ (resp. $-\Delta_N$) are associated with points $k \in \mathbb{Z}_+{}^3$ (resp. $\mathbb{N}^3$) and the associated eigenvalue is $\pi^2 \,|\, k\,|^2$. Taking spin into account we consider sets $\{k^{(1)},\ldots,k^{(n)}\}$ in $\mathbb{Z}_+{}^3$ (resp. $\mathbb{N}^3$) with the property that no three k's are equal to each other. Let $A_n{}^D$ (resp. $A_n{}^N$) be the minimum value of $\sum_{j=1}^n |k^{(j)}|^2$ as $\{k^{(1)},...,k^{(n)}\}$ runs through all such sets. Then $E_1{}^D(n) = (3\pi^2)^{-2/3}\pi^2 A_n{}^D$ (and similarly with D replaced by N).

Let K_n, T_n be determined by:

$$n = \pi \int_0^{K_n} k^2\, dk, \tag{62a}$$

$$T_n = \pi \int_0^{K_n} k^4\, dk, \tag{62b}$$

so that

$$T_n = \tfrac{3}{5}(3\pi^2)^{2/3}\pi^{-2} n^{5/3}.$$

Then (61) is equivalent to:

$$|A_n{}^D - T_n| \leqslant cn^{4/3}, \tag{63a}$$

$$|A_n{}^N - T_n| \leqslant dn^{4/3}. \tag{63b}$$

Intuitively, (63) says that A_n is approximately obtained, up to a surface error, in a continuum approximation by an octant of a ball.

Choose $G_n^{(D)}$ (resp. $G_n^{(N)}$) to be a minimizing set for the problem defining $A_n{}^D$ (resp. $A_n{}^N$). Since $G_n^{(D)}$ is an acceptable trial set for the problem defining $A_n{}^N$ we have:

$$A_n{}^D \geqslant A_n{}^N. \tag{64}$$

Next we claim that

$$\sup_{k \in G_n^{(N)}} |k| \leqslant a_1 n^{1/3}$$

for some $a_1 > 0$. This is so because a cube of side $2n^{1/3}$ ($\geqslant [n^{1/3}] + 1$ for all n) contains at least n points of $\mathbb{Z}_+{}^3$. Hence $G_n^{(N)}$ is clearly contained in a sphere of radius $2(3)^{1/2}n^{1/3}$. Since $\{k + (1, 1, 1) \mid k \in G_n^{(N)}\}$ is a valid trial set for $A_n{}^D$ we have that

$$A_n{}^D \leqslant \sum_{k \in G_n^{(N)}} (k + (1, 1, 1))^2$$

$$\leqslant A_n{}^N + (2(3)^{1/2})\, a_1 n^{4/3} + 3n$$

so

$$A_n{}^D \leqslant A_n{}^N + a_2 n^{4/3}. \tag{65}$$

Let $F_n = \bigcup_{k \in G_n^{(N)}} \{l \mid k_i \leqslant l_i \leqslant k_i + 1;\ i = 1, 2, 3\}$ and let $K_n{}^N$ be the radius of the smallest sphere containing F_n. Since $K_n{}^N$ is minimal, some $k \in G_n^{(N)}$ must obey $|k| \geqslant K_n{}^N - 3^{1/2}$, so that any $k \in \mathbb{Z}_+{}^3$ with $|k| < K_n{}^N - 3^{1/2}$ must appear twice in $G_n^{(N)}$ by the minimizing property of $G_n^{(N)}$. Thus F_n must contain the octant of the sphere of radius $K_n^N - 3^{1/2}$, so

$$n \geqslant \pi \int_0^{K_n^N - 3^{1/2}} k^2\, dk$$

from which we conclude that $K_n^N \leqslant K_n + 3^{1/2}$. Now clearly

$$\sum_{k \in G_n^{(N)}} k^2 \leqslant 2 \int_{F_n} k^2 d^3k,$$

so

$$\begin{aligned} A_n^N &\leqslant \pi \int_0^{K_n + 3^{1/2}} k^4\, dk \\ &= T_n(1 + K_n^{-1}(3)^{1/2})^5 \qquad (66) \\ &\leqslant T_n + a_3 n^{4/3}. \end{aligned}$$

Similarly, let $(G_n^{(D)})^*$ be the doubly occupied sites in $G_n^{(D)}$ and let $B_n = \bigcup_{k \in (G_n^{(D)})^*} \{l \mid k_i - 1 \leqslant l_i \leqslant k_i\,;\, i = 1, 2, 3.$ Let K_n^D be the radius of the largest sphere whose upper octant is in B_n. Then some $k \in \mathbb{Z}_+^3$ with $|k| \leqslant K_n^D + 3^{1/2}$ does not appear in $(G_n^{(D)})^*$, and so no k with $|k| > K_n^D + 3^{1/2}$ can appear in $G_n^{(D)}$ by its minimizing property. Thus $G_n^{(D)}$ is clearly contained in the sphere of radius $K_n^D + 3^{1/2}$, so $K_n^D > K_n - 3^{1/2}$. Since $\sum_{k \in G_n^{(D)}} k^2 \geqslant 2 \int_{B_n} k^2 d^3k$:

$$A_n^D \geqslant T_n - a_4 n^{4/3}. \qquad (67)$$

(64)–(67) clearly imply (63). ∎

Choose an orthonormal basis, $\{u_n(x; \sigma)\}$ for $L^2([0, 1]^3; \mathbb{C}^2)$ of eigenfunctions for $-\Delta_D$ ordered so that $-\Delta_D u_n = E_n u_n$ with $E_1 \leqslant E_2 \leqslant \cdots$ (the only choice is that due to the degeneracy of eigenvalues of $-\Delta_D$ and the choice of spin dependence for $u_n(x; \sigma)$). Define:

$$\rho_n(x) = \sum_{m=1}^{n} \sum_{\sigma = \pm 1} |u_m(x; \sigma)|^2. \qquad (68)$$

As $n \to \infty$, we expect that ρ_n should approach a constant, which must be

$$\rho_n^\infty(x) = n. \qquad (69)$$

THEOREM III.14. *Let* $A_p^{(n)} = \| \rho_n - \rho_n^\infty \|_p = (\int_{x \in [0,1]^3} | \rho_n - \rho_n^\infty |^p)^{1/p}$. *Then for all* n, p:

$$\begin{aligned} A_p &\leqslant f n^{5/3}, \qquad 1 \leqslant p \leqslant 2, \qquad (70a) \\ A_p &\leqslant 7^{1-2/p} f^{2/p} n^{1-1/3p}, \qquad 2 \leqslant p \leqslant \infty, \qquad (70b) \end{aligned}$$

for a suitable constant f.

Remarks. (1) A similar result holds with Neumann boundary conditions but we only use the result with Dirichlet boundary conditions below.

(2) If $\rho_{n;a}$ is the density in a box of side a so that

$$\rho_{n;a}^{\infty} = na^{-3} \tag{69'}$$

then by scaling, (70) implies:

$$\| \rho_{n,a}^{\infty} - \rho_{n,a} \|_p \leqslant f n^{5/6} a^{-3+3/p}, \qquad 1 \leqslant p \leqslant 2, \tag{70c}$$

$$\| \rho_{n,a}^{\infty} - \rho_{n,a} \|_p \leqslant 7^{1-2/p} f^{2/p} n^{1-1/3p} a^{-3+3/p}, \qquad p \geqslant 2. \tag{70d}$$

Proof. We can describe the functions u_n by ordering the points in $\mathbb{Z}_+^3$, $k^{(1)}, k^{(2)},\ldots$, with $| k^{(1)} | \leqslant | k^{(2)} | \leqslant \cdots$, with each point in $\mathbb{Z}_+^3$ counted twice. Let $W_n(x) = (2^{1/2})^3 \sin(k_1^{(n)} \pi x) \sin(k_2^{(n)} \pi y) \sin(k_3^{(n)} \pi z)$ and $u_n(x;\sigma) = W_n(x)\, \alpha_n(\sigma)$, where $\alpha_n(\sigma) = (2^{1/2})^{-1}$ for $\sigma = \pm 1$, if $k^{(n)}$ has not appeared in the list already, and $\alpha_n(\sigma) = \sigma(2^{1/2})^{-1}$ if $k^{(n)}$ has appeared once already. Thus, in particular:

$$0 \leqslant \rho_n(x) \leqslant 8n$$

and so

$$\| \rho_n - \rho_n^{\infty} \|_\infty \leqslant 7n. \tag{71}$$

We first claim that given (71) it suffices to prove (70) for $p = 2$, for then when $1 \leqslant p \leqslant 2$ we use

$$\| g \|_p \leqslant \| g \|_2 \, \| 1 \|_{2p/2-p} = \| g \|_2$$

and for $p \geqslant 2$

$$\| g \|_p^p = \int | g |^p = \int g^2 \, | g |^{p-2} \leqslant \| g \|_\infty^{p-2} \, \| g \|_2^2 .$$

Now, for $k, q \in \mathbb{Z}_+$:

$$\int_0^1 \sin^2(\pi kx) \sin^2(\pi qx) = \tfrac{1}{4}(1 + \tfrac{1}{2}\delta_{k,q}),$$

where $\delta_{k,q}$ is the Kronecker δ-function. Thus, since $\int \rho_n(x)\, dx = \rho_n^{\infty}$:

$$A_2^2 = \sum_{i,j=1}^{n} \left[\int W_i^2(x)\, W_j^2(x) - 1 \right]$$

$$= \sum_{i,j=1}^{n} [(\tfrac{3}{2})^{\gamma(i,j)} - 1],$$

where $\gamma(i,j)$ is the number of components which $k^{(i)}$ and $k^{(j)}$ have in common, i.e., $\gamma = 0, 1, 2$ or 3. For each i, let $\beta_n(i) = \#\{j \mid \gamma(i,j) \neq 0\}$. Then

$$A_2^2 \leqslant (\tfrac{3}{2})^3\, n \max_i \beta_n(i).$$

Now $\{k^{(1)},..., k^{(n)}\}$ is a proper choice for the set $G_n^{(D)}$ of the proof of Theorem III.13 and thus $| k^{(i)} | \leqslant Cn^{1/3}$ (for $i = 1,..., n$) by the arguments in that proof. It follows that for any i, $\beta_n(i) \leqslant 3 \cdot 2(Cn^{1/3})^2 \leqslant C_1 n^{2/3}$. As a result

$$A_2{}^2 \leqslant f^2 n^{5/3}$$

from which (70) for $p = 2$ follows. ∎

III.4. *Pulling the Coulomb Tooth*

In Section III.2 we encountered a difficulty occuring when V is not bounded from below. This difficulty is not merely a technicality and must require an additional argument. For by consideration of free Dirichlet and Neumann eigenfunctions alone, one cannot hope to prove that atoms do not shrink at a rate faster than the $Z^{-1/3}$ scale of TF theory. What we shall do to prove this is to show that cutting out the core of the Coulomb potential at a distance $\delta Z^{-1/3}$ produces a small error on the $Z^{7/3}$ scale:

THEOREM III.15. *Let* $V(x; r) = | x |^{-1}$ *if* $| x | \leqslant r$ *and* 0 *if* $| x | \geqslant r$. *Let* $e_n(Z; r; \alpha)$ *be the infinum of the spectrum of the operator*

$$-\alpha \sum_{i=1}^{n} \Delta_i - Z \sum_{i=1}^{n} V(x_i ; r)$$

on $\mathscr{H}_{\mathrm{PHYS}}$. *Then for all* n, Z, r, α:

$$e_n(Z; r; \alpha) \geqslant -Z^2\alpha^{-1} - Z^{5/2}\alpha^{-3/2}r^{1/2}. \tag{72}$$

Remarks. (1) If $r = \delta Z^{-1/3}$, then e_n is very small on the level of $Z^{7/3}$ if δ is very small.

(2) In place of our sharply cut off $V(x; r)$ we could use a Yukawa potential $e^{-\mu r}/r$, for μ small, as is used by Hertel *et al.* [30, 31] (this is in essence a Pauli–Villars [63] regularization of the Coulomb singularity). We emphasize that the angular momentum barrier which is basic to our argument is also basic to theirs.

Proof. Let λ_j be the negative eigenvalues of $h = -\alpha\Delta - ZV(x; r)$. Then for any n:

$$e_n(Z; r; \alpha) \geqslant 2 \sum_j \lambda_j .$$

If we consider h on the subspace of angular momentum l, then h is unitarily equivalent to

$$-\alpha \frac{d^2}{dx^2} + \frac{\alpha l(l+1)}{x^2} - ZV(x; r)$$

on $L^2(0, \infty)$ with boundary condition $\psi(0) = 0$. The total effective potential is clearly positive if $\alpha l(l+1) \geqslant Zr$. Letting L be the smallest integer satisfying this equation we clearly have that

$$L < (Zr/\alpha)^{1/2} + 1 \tag{73}$$

and that h has bound states only for $l < L$. For $l < L$, we have that $-ZV(x; r) \geqslant -Z \mid x \mid^{-1}$ so we can dominate each energy level from below by the corresponding hydrogenic level. Thus a lower bound on $\sum \lambda_j$ can be obtained by taking the energies of hydrogenic levels but with angular momentum $l < L$:

$$\sum \lambda_j \geqslant -\tfrac{1}{4}\alpha^{-1}Z^2 \left\{ \sum_{n=1}^{L} n^{-2}n^2 + \sum_{n=L+1}^{\infty} n^{-2}L^2 \right\}$$
$$\geqslant -\tfrac{1}{2}\alpha^{-1}Z^2 L$$

since $\sum_{n=L+1}^{\infty} n^{-2} \leqslant \int_L^\infty x^{-2}\,dx = L^{-1}$. Therefore

$$e_n(Z; r; \alpha) \geqslant -\alpha^{-1}Z^2 L$$
$$\geqslant -\alpha^{-1}Z^2 - \alpha^{-3/2}Z^{5/2}r^{1/2}. \quad \blacksquare$$

III.5. *Putting It All Together*

We are now prepared to prove Theorem III.5. We first prove the result for cutoff potentials, Theorem III.6:

Proof of Theorem III.6. Take $\lambda = 1$. We first prove that

$$\overline{\lim}\, E_N{}^Q/N^{7/3} \leqslant \inf \left\{ \mathscr{E}(\rho; V) \mid \int \rho \leqslant 1 \right\}. \tag{74}$$

It is clearly sufficient to prove

$$\overline{\lim}\, E_N{}^Q/N^{7/3} \leqslant \mathscr{E}(\rho; V) \tag{75}$$

for a dense set of ρ's. We thus suppose that for some s, ρ is a constant ρ_{n_1,n_2,n_3} on each cube of the form $[n_1 s, (n_1+1)s) \times [n_2 s, (n_2+1)s) \times [n_3 s, (n_3+1)s)$ (for $n_i \in Z$) and that ρ has compact support. For fixed N, let $m(n; N) \equiv m(n_1, n_2, n_3; N) = [N\rho_{n_1,n_2,n_3} s^3]$, where $[x]$ is the largest integer less than x. Thus

$$m_N \equiv \sum_{n \in Z^3} m(n; N) \leqslant N. \tag{76}$$

Let γ be the union of the hyperplanes, $x_i = n_i s N^{-1/3}$ and let $u_1, ..., u_{m_N}$ be the eigenfunctions of the operator $-\Delta_{D;\gamma}$ consisting of the first $m(n; N)$ Dirichlet eigenfunctions in the box of side $sN^{-1/3}$ with lower vertex $nsN^{-1/3}$. Then by Theorem III.11,

$$E_{m_N}^Q \leqslant \sum_{n \in Z^3} \alpha E_{sN^{-1/3}}^D(m(n; N))$$
$$- \int V_N(x)\,\hat\rho_N(x) + \tfrac{1}{2} \int \hat\rho_N(x)\,\hat\rho_N(y) \mid x - y \mid^{-1} dx\,dy, \tag{77}$$

where $E_\alpha^D(n)$ is defined in Theorem III.13 and $\hat\rho_N(x) = \sum_{i=1}^{m_N} | u_i(x)|^2$. Since $m_N \leqslant N$, the general analysis of Schrödinger operators [68] implies that $E_N^Q \leqslant E_{m_N}^Q$. Now

$$\Big| \sum_{n\in\mathbb{Z}^3} E^D_{sN^{-1/3}}(m) - \tfrac{3}{5} N^{7/3} \int \rho(x)^{5/3}\, dx \Big|$$
$$\leqslant \sum_{n\in\mathbb{Z}^3} | E^D_{sN^{-1/3}}(m) - \tfrac{3}{5} m^{5/3}(sN^{-1/3})^{-2} |$$
$$+ \tfrac{3}{5} N^{7/3} \int | \rho(x)^{5/3} - (N^{-1}[N\rho])^{5/3} |\, dx. \tag{78}$$

As $N \to \infty$, the second integral in (78) goes to zero, while by Theorem III.13 the first term is dominated by $C(sN^{-1/3})^{-2} \sum m(n; N)^{4/3} \leqslant Cs^{-2}N^{2/3}(\sum m(n; N))^{4/3} \leqslant Cs^{-2}N^{6/3}$. Thus the first term in (77) divided by $N^{7/3}$ converges to $\frac{3}{5}\,\alpha \int \rho^{5/3}(x)\, dx$. Similarly, using Theorem III.14, and scaling, the other two terms in (77) divided by $N^{7/3}$ converge to $-\int V(x)\,\rho(x)\, dx + \frac{1}{2} \int \rho(x)\,\rho(y)\, | x - y |^{-1}\, dx\, dy$. This proves (75) and so (74). For later purposes we note that this proof of (74) does not use the fact that the V of Theorem III.6 is bounded below and so we also have half of the proof of Theorem III.5.

Now let us prove that

$$\underline{\lim}\ E_N{}^Q/N^{7/3} \geqslant \inf \Big\{\mathscr{E}(\rho;\, V) \mid \int \rho = 1\Big\}. \tag{79}$$

For fixed s, consider the hyperplanes γ described above and write $\mathbb{R}^3\backslash\gamma = \bigcup_\beta C_\beta$. Consider the TF problem obtained by replacing $V(x)$ by $V_s(x) = \Sigma_\beta V_\beta \chi_\beta(x)$ and $| x - y |^{-1}$ by $\sum W_{\beta\gamma}\chi_\beta(x)\,\chi_\gamma(y) = W_s(x, y)$ (where χ_β is the characteristic function of C_β, $V_\beta = \sup_{x\in C_\beta} V(x)$, $W_{\beta\gamma} = \inf\{| x - y |^{-1} \mid x \in C_\beta, y \in C_\gamma\}$). Let $\mathscr{E}_s(\rho)$ be the corresponding TF energy, i.e.,

$$\mathscr{E}_s(\rho) = \tfrac{3}{5} \int \rho^{5/3}(x)\, dx - \int \rho(x)\, V_s(x)\, dx + \tfrac{1}{2} \int \rho(x)\,\rho(y)\, W_s(x, y)\, dx\, dy.$$

The minimizing functions for $\mathscr{E}_s(\rho)$ do not directly concern us, although we remark that by the methods of Section II, minimizing ρ's do exist but they need not be unique. What is critical is that as $s \downarrow 0$

$$\inf \Big\{\mathscr{E}_s(\rho) \mid \int \rho \leqslant 1\Big\} \to \inf \Big\{\mathscr{E}(\rho;\, V) \mid \int \rho \leqslant 1\Big\}.$$

This is proved by the methods of Section II: One first shows that there exists a constant D, independent of s such that $\mathscr{E}_s(\rho) \leqslant 1 + \inf\{\mathscr{E}_s(\rho) \mid \int \rho \leqslant 1\}$ for any s implies that $\| \rho \|_{5/3} \leqslant D$. Next one shows that $\mathscr{E}_s(\rho) \to \mathscr{E}(\rho;\, V)$ uniformly in ρ for all ρ's satisfying $\| \rho \|_{5/3} \leqslant D$ and $\| \rho \|_1 \leqslant 1$. This is done by noting that $\| V - V_s \| \to 0$ and $\| W - W_s \| \to 0$ in $L^{5/2} + L^\infty$. Thus $\inf\{\mathscr{E}_s(\rho) \mid \int \rho \leqslant 1\}$ can be sought among ρ's satisfying $\| \rho \|_{5/3} \leqslant D$ and the uniform convergence implies the convergence of the infimum.

By the above convergence result, it is sufficient to prove that

$$\varliminf E_N{}^Q/N^{7/3} \geqslant \inf \left\{ \mathscr{E}_s(\rho) \mid \int \rho \, dx \leqslant 1 \right\} \tag{80}$$

for each fixed s. Let Γ be the family of hyperplanes $x_i = snN^{-1/3} (n \in \mathbb{Z})$. Now by Theorem III.12 and (58).

$$E_N{}^Q/N^{7/3} \geqslant \inf \left\{ N^{-7/3} E(\{n_\beta\}_{\beta \in B}) \mid \sum n_\beta = N \right\}$$

with $E(\{n_\beta\})$ given by (60b). Now, by scaling,

$$N^{-7/3} E(\{n_\beta\}) = \mathscr{E}_s(\rho) + \text{error}, \tag{81}$$

where ρ is $n_\beta N^{-1} s^{-3}$ on the cube $N^{1/3} C_\beta$. The error term in (81) is

$$N^{-7/3} \left[-\sum_\gamma W_{\gamma\gamma} n_\gamma + \sum_\beta \left(E_\beta(n_\beta) - \tfrac{3}{5} n_\beta^{5/3} (sN^{-1/3})^{-2} \right) \right].$$

Now, for any γ, $W_{\gamma\gamma} = (sN^{-1/3} 3^{1/2})^{-1}$

$$\left| \sum_\gamma W_{\gamma\gamma} n_\gamma \right| \leqslant CN^{4/3}$$

while as above, by Theorem III.13:

$$\left| \sum_\beta E_\beta(n_\beta) - \tfrac{3}{5} n_\beta^{5/3} (sN^{-1/3})^{-2} \right| \leqslant C(sN^{-1/3})^{-2} \sum n_\beta^{4/3} \leqslant \text{const } N^{6/3}.$$

Thus

$$E_N{}^Q/N^{7/3} \geqslant \inf \left\{ \mathscr{E}_s(\rho) \mid \int \rho = 1 \right\} + 0(N^{-1/3})$$

thereby proving (80) and thus (79) as well. ∎

Proof of Theorem III.5. As in the proof of Theorem III.6, $\varlimsup E_N{}^Q/N^{7/3} \leqslant \inf\{\mathscr{E}(\rho; V) \mid \int \rho \leqslant 1\}$. For fixed $\alpha > 0$, $\delta \geqslant 0$, let $E(\alpha; \delta)$ be the TF energy associated with the functional $\alpha \frac{3}{5} \int \rho^{5/3} + \frac{1}{2} \iint |x - y|^{-1} \rho(x) \rho(y) - \int (\sum_{j=1}^k z_j \mid x - R_j \mid_\delta^{-1} + U(x)) \rho(x)$. Then, by the methods of Section II, $\lim_{\alpha \to 1, \delta \downarrow 0} E(\alpha, \delta) = E(1, 0)$, so given ϵ we can find $A < 1$ and D such that $A \leqslant \alpha < 1$, $\delta \leqslant D$ implies that $|E(\alpha, \delta) - E(1, 0)| < \epsilon/2$. Let $E_N{}^Q(\alpha, \delta)$ be the quantum energy which we know obeys $E_N{}^Q(\alpha, \delta)/N^{7/3} \to E(\alpha, \delta)$ by Theorem III.6. Clearly, we need only find $\delta \leqslant D$ such that

$$\varliminf (E_N{}^Q - E_N{}^Q(A, \delta))/N^{7/3} \geqslant -(\epsilon/2) \tag{82}$$

Now, for any operators, G and J we have that

$$\inf \sigma(G + J) \geqslant \inf \sigma(G) + \inf \sigma(J),$$

where $\sigma(B) \equiv$ spectrum of B. Thus

$$E_N{}^Q \geqslant E_N{}^Q(A, \delta) + \sum_{j=1}^{k} \inf \sigma(J_N{}^j),$$

where

$$J_N{}^j = -(1 - A)k^{-1} \sum_{i=1}^{N} \Delta_i - z_j \sum_{i=1}^{N} V(x_i - R_j\,;\, \delta Z^{-1/3})$$

with $V(x_i\,;\, r)$ given in Theorem III.15. By that theorem,

$$\inf \sigma(J_N{}^j) \geqslant -N^2 z_j^2 (1 - A)^{-1} k - k^{3/2}(1 - A)^{-3/2} \delta^{1/2} N^{7/3} z_j^{7/3}.$$

Choose $\delta \leqslant D$ and $\delta \leqslant (\sum_{j=1}^{k} z_j^{7/3})^{-2} k^{-3}(1 - A)^3(\epsilon/2)^2$. Equation (82) follows, thereby completing the proof of the theorem. ∎

IV. Properties of TF Densities

In this section we consider potentials V of the form (1a)

$$V(x) = \sum_{j=1}^{k} z_j \mid x - R_j \mid^{-1} \tag{1a}$$

and study properties of the density ρ which minimizes $\mathscr{E}(\rho; V)$ on $\mathscr{I}_\lambda$. Most of our results concern the *neutral case* where $\lambda = Z \equiv \sum_{j=1}^{k} z_j$, although we do say something about the *ionic case* $\lambda < Z$. We have already proved several facts about ρ:

Theorem IV.1. *The function*

$$\eta(x) = \int \rho(y) \mid x - y \mid^{-1} dy$$

is a bounded continuous function going to zero at infinity with

$$\| \eta \|_\infty \leqslant (12/5)(5\pi^2)^{1/6} \| \rho \|_{5/3}^{5/6} \| \rho \|_1^{1/6}.$$

In particular, $\phi = V - \eta$ and $\rho = [\max(\phi - \phi_0, 0)]^{3/2}$ vanish at infinity and are bounded and continuous on any subset of $\mathbb{R}^3$ which is a nonzero distance from all the R_i.

Proof. The statements about ϕ and ρ follow from those for η. That η is continuous and vanishes at ∞ is a consequence of Lemma II.25. The bound on η follows from Hölder's inequality:

$$\eta(x) = \int_{|y|\leqslant r} |y|^{-1} \rho(x-y)\, dy + \int_{|y|\geqslant r} |y|^{-1} \rho(x-y)\, dy$$

$$\leqslant \left(\int_{|y|\leqslant r} |y|^{-5/2}\, dy\right)^{2/5} \|\rho\|_{5/3} + r^{-1} \|\rho\|_1 .$$

Minimizing over all r leads to the claimed bound on η. ∎

THEOREM IV.2. (a) $\phi = V - \rho * |x|^{-1}$ *is nonnegative.*

(b) *In the ionic case, ρ has compact support.*

Proof. (a) is a special case of Lemma II.19. To prove (b), we need only note that $\rho = [\max(\phi - \phi_0, 0)]^{3/2}$ for some $\phi_0 > 0$ and that $\phi \to 0$ at infinity (by Theorem IV.1). ∎

The main results of this section concern the smoothness of ρ and its behavior at infinity in the neutral case. We shall prove that ϕ is *strictly* positive and that ρ is real analytic away from the R_j in the neutral case and on $\{x \mid \phi(x) > \phi_0, x \neq R_j\}$ in the ionic case. In Section IV.2 we shall prove that $|x|^6 \rho(x) \to 27/\pi^3$ as $|x| \to \infty$ in the neutral case.

IV.1. *Regularity*

We begin with:

THEOREM IV.3. *ϕ is strictly positive and, in the neutral case, ρ is strictly positive.*

Proof. Consider the ionic case first. Since ϕ is continuous, $S = \{x \mid \phi(x) = 0\}$ is closed and, since $\phi > 0$ near the R_i, we need only show S is open to conclude it is empty. But since ϕ is continuous, $\phi(x_0) = 0$ implies that $\phi(x) < \phi_0$ for all x near x_0 since $\phi_0 > 0$. Thus ϕ is harmonic near x_0. A nonnegative harmonic function cannot vanish at an interior point of its domain unless it is identically zero in that domain. It follows that S is open.

Now consider the neutral case where $\phi_0 = 0$. Suppose no R_j is zero and that $\phi(0) = 0$. Given f Borel measurable on $\mathbb{R}^3$, define $[f](r)$ for $r \in [0, \infty)$ by:

$$[f](r) = (1/4\pi) \int f(r\Omega)\, d\Omega.$$

A fundamental formula of potential theory tells us that for $f(x) = |x - x_0|^{-1}$, $[f](r) = [\max(|x_0|, r)]^{-1}$. Thus for $r < \min |R_j|$:

$$[\phi](r) = \sum_{j=1}^{k} z_j |R_j|^{-1} - \int \rho(x)[\max(|x|, r)]^{-1} dx$$

$$= \sum_{j=1}^{k} z_j |R_j|^{-1} - \int_0^\infty [\rho](y) \max(y, r)^{-1} (4\pi y^2) dy.$$

It follows that $[\phi](r)$ is monotone increasing in r for $r < \min |R_j|$. Moreover, since $[\phi](0) = 0$ we see that

$$[\phi](r) = [\phi](r) - [\phi](0)$$

$$= \int_0^r (y^{-1} - r^{-1})[\rho](y)(4\pi y^2) dy.$$

Now, by Theorem IV.1, $\phi(x)$ is bounded, say by C^2, on $\{x \mid |x| < \frac{1}{2} \min |R_j|\}$. Thus for $y < \frac{1}{2} \min |R_j|$:

$$[\rho](y) = (1/4\pi) \int \phi^{3/2}(y\Omega) d\Omega \leqslant C[\phi](y).$$

Since $[\phi]$ is monotone, for $r < \frac{1}{2} \min |R_i|$,

$$[\phi](r) \leqslant C[\phi](r) \int_0^r (y^{-1} - r^{-1})(4\pi y^2) dy$$

$$= \frac{2\pi}{3} Cr^2[\phi](r).$$

It follows that $[\phi](r) = 0$ for $r < \frac{1}{2} \min |R_i|$ and $r < (3/2\pi C)^{1/2}$. Since ϕ is nonnegative and continuous, $[\phi](r) = 0$ implies that $\phi(r\Omega) = 0$ for all Ω. Thus ϕ vanishes near 0. We have just shown $\{x \mid \phi(x) = 0\}$ is open. Therefore, as in the first case, ϕ is strictly positive. Since $\rho = \phi^{3/2}$, ρ is strictly positive. ∎

Lemma IV.4. *Let $p^{-1} + q^{-1} = 1$, $1 < p < \infty$. Let $g \in L^p(\mathbb{R}^n)$ and $f \in L^q(\mathbb{R}^n)$. Suppose that there exist n functions $h = \{h_i\}_{i=1}^n$ in $L^q(\mathbb{R}^n)$ such that as $y \to 0$:*

$$\int \left| \frac{f(x+y) - f(x) - \langle y, h(x)\rangle}{|y|} \right|^q dx \to 0. \tag{83}$$

Then $f * g$ is a C^1 function and

$$\nabla(f * g) = h * g.$$

Proof. Let $F = f * g$ and $H = h * g$. Then by Young's inequality, for any w,

$$\left|\frac{F(w+y) - F(w) - \langle y, H(w)\rangle}{|y|}\right|$$
$$\leqslant \|g\|_p \left[\int\left|\frac{f(x+y) + f(x) - \langle y, h(x)\rangle}{|y|}\right|^q dx\right]^{1/q}$$

so F is differentiable and H is its gradient. H is continuous by Lemma II.25. ∎

THEOREM IV.5. (a) *Near each* R_j

$$\rho(x) = z_j^{3/2} \mid x - R_j \mid^{-3/2} + \beta_j \mid x - R_j \mid^{-1/2} + o(\mid x - R_j \mid^{-1/2})$$

for suitable β_j.

(b) *In the neutral case,* ρ *is* C^∞ *away from the* R_j.

(c) *In the ionic case,* ρ *is* C^1 *away from the* R_j *and* C^∞ *on* $\{x \mid x \neq R_j \text{ all } j, \phi(x) > \phi_0\}$.

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

Proof. Since $\rho \in L^p$ for all p between 1 and $\frac{5}{3}$ and $|x|^{-1} \in L^{3+\epsilon} + L^{3-\epsilon}$, $\rho * |x|^{-1}$ is continuous and goes to zero at infinity by Lemma II.25. In particular $\phi(x) = z_j \mid x - R_j \mid^{-1} + \gamma_j + o(1)$ near R_j from which $\rho(x) = z_j^{3/2} \mid x - R_j \mid^{-3/2} + \beta_j \mid x - R_j \mid^{-1/2} + o(\mid x - R_j \mid^{-1/2})$ near R_j, and ρ is continuous away from all the R_j. This proves (a). Given $x_0 \neq R_j$, choose $\psi \in C_0^\infty$ with support away from all R_j, and with ψ identically 1 near x_0. Let $\rho_1 = \psi\rho$. Then $\phi = V - (\rho - \rho_1) * |x|^{-1} - \rho_1 * |x|^{-1}$. Now $V - (\rho - \rho_1) * |x|^{-1}$ is harmonic near x_0 and thus is C^∞ near x_0. ρ_1 is continuous on supp ψ and so is bounded and thus is in every L^p. Let $\eta \in C_0^\infty$ with $\eta \equiv 1$ near $x = 0$. Then $\eta(x) \mid x \mid^{-1} \in L^1$ with gradient in L^1 in the sense of (83) and $(1 - \eta(x)) \mid x \mid^{-1} \in L^4$ with gradient in L^4 in the sense of (83). Thus $\rho_1 * |x|^{-1} = \rho_1 * \eta(x) \mid x \mid^{-1} + \rho_1 * (1 - \eta) \mid x \mid^{-1}$ is C^1, and so ϕ is C^1. It follows that $\rho = [\max(\phi - \phi_0, 0)]^{3/2}$ is C^1 away from the R_j. Thus ρ_1 is C^1 and $\nabla(\rho_1 * |x|^{-1}) = (\nabla\rho_1) * |x|^{-1}$. Now, as above, $\nabla\rho_1 * |x|^{-1}$ is C^1, so ϕ is C^2. Thus $\rho = [\max(\phi - \phi_0, 0)]^{3/2}$ is C^2 on $\{x \mid \phi(x) > \phi_0\}$. Proceeding inductively, we complete the proof. (d) follows from Theorem IV.1 and the TF equation. ∎

THEOREM IV.6. ρ *and* ϕ *are real analytic away from all the* R_j, *on all of* $\mathbb{R}^3$ *in the neutral case and in* $\{x \mid \phi(x) > \phi_0\}$ *on the ionic case.*

Proof. ϕ obeys the nonlinear elliptic equation $(4\pi)^{-1} \Delta\phi = (\phi - \phi_0)^{3/2}$ in a neighborhood of any $x_0 \neq R_j$ with $\phi(x_0) > \phi_0$. General theorems (see [60 Sect. 5.8]) then assert the real analyticity of ϕ and so also of $\rho = (4\pi)^{-1} \Delta\phi$. ∎

IV.2. *Asymptotics at Infinity*

Our goal in this section is to prove that $|x|^6 \rho(x) \to 27/\pi^3$ as $|x| \to \infty$ for any neutral TF density, *independently* of the distribution of the nuclear charges. In the atomic case, such asymptotics (with different normalizations) were predicted by Sommerfeld [85] partially on the basis that the only solution of $\Delta\phi = 4\pi\phi^{3/2}$ of the form $c|x|^{-\alpha}$ is $\phi(x) = 9\pi^{-2}|x|^{-4}$. In the atomic case, where the TF equation $\Delta\phi^{3/2} = 4\pi(\phi^{3/2} - \delta(x))$ is equivalent to an ordinary differential equation, Hille [32, 33] used methods of ordinary differential equations to prove the correctness of Sommerfeld's prediction. We shall use subharmonic function methods which allow us to handle the molecular case in which V is not spherically symmetric. As we have already mentioned, these methods have been introduced by Teller [89]. We begin with a comparison theorem:

THEOREM IV.7. *Suppose that* ϕ, ψ *are continuous positive functions on* $\{x \mid |x| \geq R\}$ *with the following properties:*

(a) $\phi, \psi \to 0$ *as* $|x| \to \infty$.

(b) $(4\pi)^{-1}\Delta\phi \leq \phi^{3/2}$, $(4\pi)^{-1}\Delta\psi \geq \psi^{3/2}$, *where the derivatives and inequalities are in distributional sense.*

(c) $\phi(x) \geq \psi(x)$ *for all* x *such that* $|x| = R$.

Then $\phi(x) \geq \psi(x)$ *for all* x *such that* $|x| \geq R$.

Remarks. (1) Theorems of this sort have been used by Hartmann and Wintner [27] and Protter and Weinberg [64].

(2) Motivated by our work, one of us has used the idea of this theorem to study asymptotics of Schrödinger eigenfuctions [83].

Proof. Let $S = \{y \mid \phi(y) < \psi(y)\}$, which is open. Let $f(y) = \psi(y) - \phi(y)$ on S. Then on S:

$$(4\pi)^{-1}\Delta f = (4\pi)^{-1}[\Delta\psi - \Delta\phi] \geq \psi^{3/2} - \phi^{3/2} \geq 0.$$

Thus f is subharmonic on S and thus takes its maximum on the boundary of S or at infinity. But by (a), (c), and the definition of S, $f \leq 0$ at infinity and on ∂S. It follows that S is empty and $\phi(x) \geq \psi(x)$ for all x. ∎

THEOREM IV.8. *Let* ϕ *be a spherically symmetric solution of* $\Delta\phi = 4\pi\phi^{3/2}$ *in* $\{x \mid |x| > R_0\}$, *continuous in* $\{x \mid |x| \geq R_0\}$ *and going to zero at* ∞. *Then, if* $R_0^4\phi(R_0) \geq 9\pi^{-2}$ (*resp.* $\leq 9\pi^{-2}$) *then* $r^4\phi(r)$ *is decreasing* (*resp. increasing*) *as* r *increases and* $\lim_{r\to\infty} r^4\phi(r) = 9\pi^{-2}$.

Proof. Let $\psi_c(r) = cr^{-4}$. Then $\Delta\psi_c \leq 4\pi\psi_c^{3/2}$ if $c > 9\pi^{-2}$, $\Delta\psi_c = 4\pi\psi_c^{3/2}$ if $c = 9\pi^{-2}$, and $\Delta\psi_c \geq 4\pi\psi_c^{3/2}$ if $c < 9\pi^{-2}$. Thus, by Theorem IV.7 if $R_0^4\phi(R_0) \geq$

$9\pi^{-2}$ (resp. $\leqslant 9\pi^{-2}$), then $r^4\phi(r) \geqslant 9\pi^{-2}$ (resp. $\leqslant 9\pi^{-2}$) for all r with $r > R_0$ (by the comparison theorem with ψ_c, $c = 9\pi^{-2}$). Thus, it suffices to prove that $r^4\phi(r) \leqslant R_0{}^4\phi(R_0)$ (resp. $\geqslant$) for $r > R_0$. Let $c_0 = R_0{}^4\phi(R_0)$. Then the inequality follows by comparing ϕ and ψ_{c_0}.

Let $\lambda_\infty = \lim_{r\to\infty} r^4\phi(r)$. The limit exists because of the monotonicity. Let $\phi_n(r) = n^4\phi(nr)$. Then $\Delta\phi_n = 4\pi(\phi_n)^{3/2}$ and $\lim_{n\to\infty}\phi_n(r) = \lambda_\infty r^{-4} \equiv \phi_\infty(r)$ uniformly on compacts of $\mathbb{R}^3\backslash\{0\}$. Thus as a distribution on $C_0^\infty(\mathbb{R}^3\backslash\{0\})$, $\Delta\phi_\infty = 4\pi\phi_\infty^{3/2}$, so $\lambda_\infty = 9\pi^{-2}$. ∎

THEOREM IV.9. *Let R_0 and b be given. Then, there is a continuous function, ϕ on $\{x \mid |x| \geqslant R_0\}$, which is spherically symmetric and satisfies $\Delta\phi = 4\pi\phi^{3/2}$ and such that $\phi(R_0) = b$ and* $\lim_{r\to\infty}(r^4\phi(r)) = 9\pi^{-2}$.

Proof. If $bR_0{}^4 = 9\pi^{-2}$, take $\phi(r) = 9\pi^{-2}r^4$. Suppose next that $bR_0{}^4 = c < 9\pi^{-2}$. Let $\eta(r)$ be the neutral TF potential for $V(r) = r^{-1}$. Then, by Theorem IV.5, $r^4\eta(r) \to 0$ as $r \to 0$ and by Theorem IV.8, $r^4\eta(r) \to 9\pi^{-2}$ as $r \to \infty$. Thus for some r_0, $r_0{}^4\eta(r_0) = c$. Take $\phi(r) = (r_0/R_0{}^4)\,\eta(rr_0/R_0)$. Then $\phi(R_0)\,R_0{}^4 = c$ and $\Delta\phi = 4\pi\phi^{3/2}$. Finally, consider the case in which $c = bR_0{}^4 > 9\pi^{-2}$. Consider the problem of minimizing $\mathscr{E}(\rho) = \frac{3}{5}\int \rho^{5/3}\,dx - Z_0\int |x|^{-1}\rho(x) + \frac{1}{2}\int \rho(x)\,\rho(y)\,|x-y|^{-1}$, where $Z_0 = 4\pi c^{3/2}R_0^{-3}/3$ but with the extra requirement that $\rho(x) \equiv 0$ if $|x| < R_0$. By the methods of Section II, the minimizing ρ exists and has $\int \rho\,dx = Z_0$. Moreover, ρ obeys $\rho = \phi_0^{3/2}$, $\phi_0 = Z_0\,|x|^{-1} - \int_{|y|\geqslant R_0} |x-y|^{-1}\rho(y)\,dy$ so that $\Delta\phi_0 = 4\pi\phi_0^{3/2}$. Now, if $r^4\phi_0(r) < c$ for all $r > R_0$, then $\int \rho\,dx < 4\pi\int_{R_0}^\infty (c/x^4)^{3/2}\,x^2\,dx = (4\pi/3)\,c^{3/2}R_0^{-3} = Z_0$. Thus, for some, R_1, $R_1{}^4\phi_0(R_1) = c$. The choice $\phi(r) = (R_1/R_0)^4\,\phi_0(rR_1/R_0)$ solves the problem. ∎

THEOREM IV.10. *Let ρ be the neutral* TF *density for* $V(x) = \sum_{j=1}^k z_j|x-R_j|^{-1}$. *Then $|x|^6\,\rho(x) \to 27\pi^{-3}$ as $|x| \to \infty$, uniformly with respect to direction.*

Proof. Let $R = 2\max_{j=1,\dots,k}|R_j|$. Then $\phi = \rho^{2/3}$ obeys $\Delta\phi = 4\pi\phi^{3/2}$ for $|x| \geqslant R$ and $\phi \to 0$ at infinity. Now ϕ is continuous and strictly positive on $\{x \mid |x| = R\}$ by Theorems IV.3 and IV.5, so there exist numbers $b_\pm > 0$ such that $b_- \leqslant \phi(x) \leqslant b_+$ when $|x| = R$. Let $\phi_\pm$ be the solutions of $\Delta\phi = 4\pi\phi^{3/2}$ which are spherically symmetric and obey $\phi_\pm(R) = b_\pm$ and $r^4\phi_\pm(r) \to 9\pi^{-2}$. Then, by the comparison theorem (Theorem IV.7), $\phi_-(|x|) \leqslant \phi(x) \leqslant \phi_+(|x|)$ for all $|x| \geqslant R$. Thus $|x|^4\,\phi(x) \to 9\pi^{-2}$ and, since $\rho(x) = \phi^{3/2}(x)$, ρ obeys $|x|^6\,\rho(x) \to 27\pi^{-3}$ as $|x| \to \infty$. ∎

IV.3. *"Ionization" Energies in TF Theory*

Consider the Fermi energy $\epsilon_F(\lambda)$ for the TF theory with $V(x) = |x|^{-1}$. As $\lambda \uparrow 1$ we know that $\epsilon_F(\lambda) \uparrow 0$. Using the methods of Section II.7 and the asymptotics of Section IV.2, we can say something about the rate at which $\epsilon_F(\lambda)$ approaches zero.

THEOREM IV.11. *Let $\epsilon_F(\lambda)$ be the chemical potential for the* TF *theory with potential* $V(x) = \sum_{i=1}^{k} z_i \mid x - R_i \mid^{-1}$ $(\sum_{i=1}^{k} z_i = 1)$ *and* $\int \rho(x)\, dx = \lambda < 1$. *Then:*

$$\overline{\lim_{\lambda \uparrow 1}}\ \epsilon_F(\lambda)/(1 - \lambda)^{4/3} \leqslant -3(\pi^2/36)^{1/3}/4,$$

$$\overline{\lim_{\lambda \uparrow 1}}\ \epsilon_F(\lambda)/(1 - \lambda)^{4/3} \geqslant -(\pi^2/36)^{1/3}.$$

Proof. Let ρ_1 be the neutral TF density. Define $R(\lambda)$ by

$$\int_{|x| \geqslant R(\lambda)} \rho_1(x)\, dx = (1 - \lambda).$$

Then, by Theorem IV.10,

$$\lim_{\lambda \uparrow 1} R(\lambda)^3 (1 - \lambda) = 36/\pi^2. \tag{84}$$

Now, let $\rho_\lambda(x)$ be the density which is equal to $\rho_1(x)$ if $\mid x \mid \leqslant R(\lambda)$ and is zero otherwise. Let

$$\psi_\lambda(x) = \rho_\lambda(x)^{2/3} - V(x) + \int \rho_\lambda(y) \mid x - y \mid^{-1} dy$$

so that

$$\begin{aligned} \psi_\lambda(x) &= -\int_{|y| \geqslant R(\lambda)} \rho_1(y) \mid x - y \mid^{-1} dy & &\text{if} \quad \mid x \mid \leqslant R(\lambda), \\ &= -\rho_1(x)^{2/3} - \int_{|y| \geqslant R(\lambda)} \rho_1(y) \mid x - y \mid^{-1} dy & &\text{if} \quad \mid x \mid > R(\lambda). \end{aligned}$$

From the first of these formulas, we find that (see(41))

$$\begin{aligned} S(\rho_\lambda) &= -\min_{|x| \leqslant R(\lambda)} \int_{|y| \geqslant R(\lambda)} \mid x - y \mid^{-1} \rho_1(y)\, dy \\ &\sim -\tfrac{3}{4}(1 - \lambda)/R(\lambda) \end{aligned}$$

by Theorem IV.10. By the second formula (see (39)),

$$T(\rho_\lambda) \sim 4S(\rho_\lambda)/3.$$

The theorem now follows from (84) and Theorems II.28 and II.29. ∎

It is natural to *conjecture*, and we do so (see Sect. I), that

$$\lim_{\lambda \uparrow 1} \epsilon_F(\lambda)/(1 - \lambda)^{4/3} \text{ exists.} \tag{85}$$

Now, let $E(\lambda; Z)$ be the TF energy for $V(x) = Z \mid x \mid^{-1}$ with the subsidiary condition $\int \rho(x)\, dx = \lambda$. Let

$$\delta E(Z) = -[E(Z; Z) - E(Z - 1; Z)].$$

THEOREM IV.12. (a) $\overline{\lim}_{Z\to\infty}\, \delta E(Z) \leqslant (3/7)(\pi^2/36)^{1/3}$

$$\underline{\lim}_{Z\to\infty}\, \delta E(Z) \geqslant (9/28)(\pi^2/36)^{1/3};$$

(b) *if the limit* (85) *exists and is* $-\alpha$, *then*

$$\lim_{Z\to\infty} \delta E(Z) = (3/7)\alpha.$$

Proof. By scaling $E(\lambda; Z) = Z^{7/3}E(\lambda/Z; 1)$, and thus if $\epsilon_F(\lambda)$ is the Fermi energy in the $Z = 1$ problem, then

$$\delta E(Z) = -Z^{7/3} \int_{1-Z^{-1}}^{1} \epsilon_F(\lambda)\, d\lambda.$$

If $\epsilon_F(\lambda) \sim -\alpha(1-\lambda)^{4/3}$, then $\delta E(Z) \sim (3/7)\,\alpha$ from which the theorem follows. ▌

The interesting feature of Theorem IV.12 is that it is contrary to the usual folk wisdom about the TF theory which says that ionization energies (and work functions in solids) are zero. Actually, the correct translation of the folk wisdom is that the ionization energy is zero on the level of $Z^{7/3}$. The more subtle analysis above yields a prediction of nonzero, finite ionization energy. As we shall explain in the next section there is some reason to believe that as $Z \to \infty$, the quantum mechanical ionization energy has a nonzero, finite limit but we see no reason for the TF theory to yield the correct constant.

IV.4. *A Picture of Heavy Atoms*

We want to describe a picture of large Z atoms which helps explain certain apparent paradoxes among which are the following:

(1) In real atoms, the wave function falls off exponentially [82], while, by the above, the TF density falls off as $|x|^{-6}$.

(2) The TF atom shrinks as $Z^{-1/3}$. Atomic diameters as measured, for example, in terms of Van der Waals parameters, tend, if anything, to increase slightly [11].

(3) As we shall show below, molecules do not bind in TF theory but they obviously do bind for real atoms.

(4) In a real atom, the electron density at the nucleus is finite [39, 82], while in TF theory it goes to infinity as $(Z/|x|)^{3/2}$.

We picture the electron density of an atom as varying over five regions. The innermost is the core region which shrinks as $Z^{-1/3}$ and is described by the TF density ρ_{TF} according to Theorem III.3. The next region is the "mantle" of the core which is described by the density $(27/\pi^3)\, Z^2/(Z^{1/3}|x|)^6 = (27/\pi^3)|x|^{-6}$! This density is correct to distances of order infinity on a scale of distance $Z^{-1/3}$, and in this second region the density is still of order Z^2. As $Z \to \infty$, 100 % of the electrons lie in these two regions. What we have said about these two regions has been rigorously proved in Section III and above in Section IV.2. Our remarks about the density outside these regions is largely speculative.

The fourth region is the "outer shell" to which we return shortly. Chemistry takes place in the fourth region. The third region is a transition region between the mantle of the core and the outer shell. The fifth region is the region of exponential falloff outside the bulk of electron density.

It is hard to find really convincing evidence for a prediction of the radius of the outer shell. In a model without electron repulsion, there are $Z^{1/3}$ filled shells and the radius of the outer shell is of order $(Z^{1/3})^2/Z = Z^{-1/3}$. In a model in which we suppose that the nth electron is perfectly shielded by the first $n - 1$ electrons and is put in the Bohr orbit for the nth electron in an atom of charge $Z_{\text{eff}} = Z - n + 1$, the last electron has a radius of order $Z^{2/3}$. Our feeling is that the most reasonable model has the last electrons shielded only imperfectly by the last few shells. Since the outer shell contains order $(Z^{1/3})^2$ electrons, the outermost electrons see an effective nuclear charge of order $Z^{2/3}$ and thus has radius of order $(Z^{1/3})^2/Z^{2/3} = 1$. They have an energy of order 1 however, since the total Coulomb potential is of order 1 at the atomic surface. It is striking that this crude model predicts a constant ionization energy in the limit $Z \to \infty$. This agrees with the prediction of TF theory which has no reason to be a correct picture of the outer shell!

In terms of our picture, the "paradoxes" discussed at the start of this section are easy to understand. The exponential and r^{-6} falloff describe different regions of the atom. The other two "paradoxes" are explained by noting that size and chemistry are determined by the outer shell and not the core which is the region where TF theory is valid.

Paradox (4) is explained by noting that the innermost, or K shell density alone is proportional to Z^3 at the origin. Thus although the density is finite, on the scale of Z^2 which is appropriate for TF theory (see Theorem III.3), it is infinite.

V. The TF Theory of Molecules

In this section we discuss the TF theory of molecules or, more accurately, the nontheory of molecules, since our main result asserts that the TF energy of a collection of fixed nuclei and TF electrons always *strictly* decreases if we arbitrarily separate the nuclei into groups which we then move infinitely far from one another. It is essential that we include the internuclear repulsion $\sum_{1 \leqslant i < j = k} z_i z_j \mid R_i - R_j \mid^{-1}$ in addition to the TF energy. Otherwise, as we shall also prove, the opposite is true. Thus we define

$$e^{\text{TF}}(\lambda; z_1, ..., z_k; R_1, ..., R_k) = E^{\text{TF}}(\lambda; z_1, ..., z_k; R_1, ..., R_k) + \sum_{1 \leqslant i < j = k} z_i z_j \mid R_i - R_j \mid^{-1}.$$

In Sections V.1 and V.2 we prove that:

THEOREM V.1. *For any strictly positive* $\{z_i\}_{i=1}^k$, $\{R_i\}_{i=1}^k$, *and* $j = 1,\dots, k-1$: $e^{\mathrm{TF}}(\lambda = \sum_{i=1}^k z_i; z_1, \dots, z_k; R_1, \dots, R_k) > e^{\mathrm{TF}}(\lambda = \sum_{i=1}^j z_i; z_1, \dots, z_j; R_1, \dots, R_j) + e^{\mathrm{TF}}(\lambda = \sum_{i=j+1}^k z_i; z_{j+1}, \dots, z_k; R_{j+1}, \dots, R_k)$.

In Section V.3, we prove that:

THEOREM V.2. *For any strictly positive* $\{z_i\}_{i=1}^k$, *any* $\lambda > 0$, *any* $\{R_i\}_{i=1}^k$ *and* $j = 1,\dots, k-1$: $e^{\mathrm{TF}}(\lambda; z_1, \dots, z_k; R_1, \dots, R_k) > \min_{0 \leqslant \lambda' \leqslant \lambda}[e^{\mathrm{TF}}(\lambda'; z_1, \dots, z_j; R_1, \dots, R_j) + e^{\mathrm{TF}}(\lambda - \lambda'; z_{j+1}, \dots, z_k; R_{j+1}, \dots, R_k)$.

Remark. Theorem V.1 is obviously a special case of Theorem V.2. We state it separately because it is needed in the proof of Theorem V.2.

These theorems have been stated by Teller [89] whose methods have motivated our work in other parts of this paper. Teller's proof has been questioned on two points [3]: First, his use of infinitesimal charges leaves one uneasy. More seriously, to avoid the nuclear Coulomb singularity, he cuts off the nuclear potential at short distances and this technically invalidates his subharmonic function arguments. Our presentation below is essentially a careful transcription of his arguments into rigorous language and exploits the fact that we have shown how to treat the Coulomb singularity in Section II. We emphasize that our proof in this section of Theorems V.1 and V.2 should be regarded as an exegesis on Teller's work [89].

The inequality in Theorem V.2 is reversed if $e^{\mathrm{TF}}(\lambda; z_1, \dots, z_k; R_1, \dots, R_k)$ is replaced by $E^{\mathrm{TF}}(\lambda; z_1, \dots, Z_k; R_1, \dots, R_k)$:

THEOREM V.3. *For any strictly positive* $\{z_i\}_{i=1}^k$, $\lambda > 0$, $\{R_i\}_{i=1}^k$, *and* $j = 1,\dots, k-1$: $E^{\mathrm{TF}}(\lambda; z_1, \dots, z_k; R_1, \dots, R_k) < E^{\mathrm{TF}}(\lambda'; z_1, \dots, z_j; R_1, \dots, R_j) + E^{\mathrm{TF}}(\lambda - \lambda'; z_{j+1}, \dots, z_1; R_{j+1}, \dots, R_k)$ *whenever* $0 \leqslant \lambda' \leqslant \lambda$.

Proof. As a preliminary, we note that if $x, y \geqslant 0$:

$$(x+y)^{5/3} = (x^2 + y^2 + xy + yx)(x+y)^{-1/3} \leqslant x^{5/3} + y^{5/3} + x^{2/3}y + xy^{2/3}. \tag{86}$$

Since E^{TF} is monotone in λ and takes its minimum value when the molecule is neutral, we may assume that $\lambda' \leqslant \sum_1^j z_i$ and $\lambda - \lambda' \leqslant \sum_{j+1}^k z_i$. Let $\rho^{(i)}(x)$, $\phi^{(i)}(x)$, $E^{(i)}$ $(i = 1, 2)$ be the TF densities, potentials, and energies for the case $V^{(1)}(x) = \sum_1^j z_i \mid x - R_i \mid^{-1}$ and $V^{(2)}(x) = \sum_{j+1}^k z_i \mid x - R_i \mid^{-1}$. Choose $\rho(x) = \rho^{(1)}(x) + \rho^{(2)}(x)$ to be a trial function for the TF problem with $V(x) = \sum_1^k z_i \mid x - R_i \mid^{-1}$. Clearly, $\int \rho(x)\, dx = \lambda$. Using (86), we have:

$$\begin{aligned} &E^{\mathrm{TF}}(\lambda; z_1, \dots, z_k; R_1, \dots, R_k) \\ &\quad \leqslant \mathscr{E}(\rho; V) \leqslant E^{(1)} + E^{(2)} + \int \rho^{(1)}(x)\, [\tfrac{3}{5}\rho^{(2)}(x)^{2/3} - V^{(2)}(x)]\, dx \\ &\qquad + \int \rho^{(2)}(x)\, [\tfrac{3}{5}\rho^{(1)}(x)^{2/3} - V^{(1)}(x)]\, dx \\ &\qquad + \iint \rho^{(1)}(x)\, \rho^{(2)}(y) \mid x - y \mid^{-1} dx\, dy. \end{aligned} \tag{87}$$

By the TF equation (Theorem II.10) and the positivity of ϕ:

$$0 \leqslant \rho^{(i)}(x)^{2/3} \leqslant \phi^{(i)}(x) = V^{(i)}(x) - \int \rho^{(i)}(y) \mid x - y \mid^{-1} dy.$$

Therefore the right side of (87) is at most

$$E^{(1)} + E^{(2)} - (\tfrac{1}{5}) \iint \rho^{(1)}(x) \rho^{(2)}(y) \mid x - y \mid^{-1} dx\, dy$$
$$- \tfrac{2}{5} \int (\rho^{(1)}(x) V^{(2)}(x) + \rho^{(2)}(x) V^{(1)}(x))\, dx < E^{(1)} + E^{(2)}. \quad ∎$$

Notice that the proof of this theorem, unlike that of Theorems V.1 and V.2, *does not use potential theory*.

Theorem V.3 asserts, in particular, that the TF energy, E^{TF}, increases if we have fixed nuclear charges and move them infinitely far from one another. It is an elementary consequence of concavity that if we move all the nuclei to one common point, then E^{TF} decreases, as we now show:

THEOREM V.4. *Fix $\lambda > 0$, $\{z_i\}_{i=1}^k$ positive, and fix R_1. Then $E^{\mathrm{TF}}(\lambda; z_1, \ldots, z_k; R_1, \ldots, R_k)$ is strictly minimized when $R_2 = R_3 = \cdots = R_k = R_1$.*

Proof. Another way of stating this result is that $E^{\mathrm{TF}}(\lambda; z_1, \ldots, z_k; R_1, \ldots, R_k) > E^{\mathrm{TF}}(\lambda; \sum_{i=1}^k z_i, 0, \ldots, 0; R_1, \ldots, R_k)$ as long as some R_j is different from R_1. Fix $R_1, \ldots, R_k$, λ and let

$$f(z_1, \ldots, z_k) \equiv E^{\mathrm{TF}}(\lambda; z_1, \ldots, z_k; R_1, \ldots, R_k).$$

As an infimum of functions linear in z_i, f is jointly concave in $(z_1, \ldots, z_k)$. If $R_j \neq R_1$ it is easy to see that it is strictly concave under changes in z_1 and z_j only, since the minimizing ρ is then nontrivially dependent on z_1/z_j by virtue of the TF equation, Theorem II.10. The required inequality follows. ∎

Remark. Theorem V.1 states an important fact about TF theory, namely, that molecules do not bind. This is not a property of real molecules, i.e., the solution of the true Schrödinger equation. Nevertheless, Theorem V.1 plays an important role in the Lieb–Thirring proof [52, 53] of the stability of real matter. It enters in two ways: (i) It leads to a lower bound on the expectation value of the Coulomb repulsion among charged particles, i.e.,

$$\Big\langle \psi, \sum_{i<j} \mid x_i - x_j \mid^{-1} \psi \Big\rangle$$
$$\geqslant \tfrac{1}{2} \iint \rho_N^{(1)}(x) \rho_N^{(1)}(y) \mid x - y \mid^{-1} dx\, dy - (\text{Const})\, N^{1/2} \| \rho_N^{(1)} \|_{5/3}^{5/6}$$

for any ψ(antisymmetric or not), and where $\rho_N^{(1)}$ is given in the first line of (4); (ii) After first showing that the TF energy (with modified constants) is a lower bound to the true Schrödinger energy, one uses Theorem V.1 to show that this lower bound is greater than a constant times the number of atoms in the system.

V.1. *Teller's Lemma: Neutral Case*

The basis of Theorem V.1 is a set of results of which the simplest is:

THEOREM V.5. (Teller's lemma—neutral case). *Let* ϕ_1, ρ_1 *(resp.* ϕ_2, ρ_2*) to be the* TF *potential and density for a* neutral *system with potential*

$$V(x) = \sum_{i=1}^{k} a_i \mid x - R_i \mid^{-1} \left(\text{resp. } V(x) = \sum_{i=1}^{k} b_i \mid x - R_i \mid^{-1}, \text{ same } R_i\text{'s}\right).$$

Suppose that $b_i \geqslant a_i \geqslant 0$ *for* $i = 1,..., k$. *Then for all* $x \neq \{R_i\}$, $\phi_2(x) \geqslant \phi_1(x)$, $\rho_2(x) \geqslant \rho_1(x)$.

Remarks. (1) We emphasize that $a_i = 0$ is allowed.

(2) ρ_i, which is determined only a.e. by minimization is fixed everywhere by the TF equations.

Proof. By renumbering, suppose $a_1 < b_1,..., a_m < b_m$, $a_{m+1} = b_{m+1},..., a_k = b_k$. Let $S = \{x \mid \phi_2(x) < \phi_1(x)\}$. Then S is disjoint from a neighborhood of $\{R_i\}_{i=1}^m$ since $b_i > a_i (i = 1,..., m)$ and $\phi_2(x) \mid x - R_i \mid$ resp. $\phi_1(x) \mid x - R_i \mid)$ approaches b_i(resp. a_i) as $x \to R_i$. Since ϕ_2 and ϕ_1 are continuous away from the R_i, S is open and $\psi = \phi_2 - \phi_1$ is continuous and negative on S. Its distributional Laplacian $(4\pi)^{-1} \Delta\psi = \phi_2^{3/2} - \phi_1^{3/2} < 0$ on S, so ψ is superharmonic on S and it therefore takes its minimum value on $\partial S \cup \{\infty\}$. But $\psi \to 0$ at ∞ and $\psi = 0$ on ∂S, so $\psi \geqslant 0$ on S. Thus S is empty and $\phi_2 \geqslant \phi_1$ everywhere. ∎

THEOREM V.6. *Under the hypotheses of Theorem* V.5 *suppose that* $b_i > a_i$ *for* some $i = I$. *Then*

(a) $\phi_2(x) > \phi_1(x)$, $\rho_2(x) > \rho_1(x)$

for all $x \neq \{R_i\}$.

(b) *If, in addition,* $b_j = a_j$, *then*

$$\lim_{x \to R_j} (\phi_2(x) - b_j \mid x - R_j \mid^{-1}) > \lim_{x \to R_j} (\phi_1(x) - a_j \mid x - R_j \mid^{-1}).$$

Proof. (a) Clearly $\{x \mid \phi_2(x) = \phi_1(x)\}$ is closed and not all of $\mathbb{R}^3$ since it is disjoint from a neighborhood of R_I. Thus we need only show it is open. Suppose that $0 \neq R_j$ $(j = 1,..., k)$ and that $\psi(x) = \phi_2(x) - \phi_1(x)$ vanishes at $x = 0$. Choose $R_0 < \min\{|R_i|\}$, $R_0 > 0$, and let $M = \max_{|x| \leqslant R_0} \mid \phi_2(x) \mid$. Then, for $\mid x \mid < R_0$:

$$\mid \phi_2(x)^{3/2} - \phi_1(x)^{3/2} \mid \leqslant (\tfrac{3}{2})\, M^{1/2} \psi(x)$$

so $\psi(x)$ obeys

$$0 \leqslant (4\pi)^{-1} \Delta\psi(x) \leqslant (\tfrac{3}{2})\, M^{1/2}\psi(x) \tag{88}$$

for $|x| < R_0$. By mimicking the argument in the proof of Theorem IV.3, we see that ψ vanishes identically near $x = 0$; so S is open. This shows that S is empty.

(b) Suppose that $R_j = 0$. By Theorem IV.5, $\psi(x) = \phi_2(x) - \phi_1(x)$ is continuous at zero and we need only show $\psi(0) \neq 0$. By (a), $\psi(x) \neq 0$ for x near 0. A modification of the argument used in (a) shows then that $\psi(0)$ must be nonzero. This modification consists in replacing the condition $|\phi_2(x)| \leqslant M$ by $|\phi_2(x)| \leqslant A\,|x|^{-1}$, and replacing (88) by

$$0 \leqslant (4\pi)^{-1} \Delta\psi(x) \leqslant (3/2)\, A^{1/2}\, |x|^{-1/2}\, \psi(x). \tag{89}$$

One can still mimic the proof of Theorem IV.3. ∎

V.2. *No Binding: Neutral Case*

Our goal in this section is to prove Theorem V.1. This result of Teller [89] is based in part on suggestions of Sheldon [78] who applied a motification of TF theory, the Thomas–Fermi–Dirac theory, to the N_2 molecule and found numerically that there was no binding. The reader should consult Balàzs [3] for a very different proof of Teller's theorem in the homopolar diatomic case (i.e., $k = 2$, $z_1 = z_2$). Balàzs was able to prove the stronger result that e^{TF} decreased monotonically under dilatations of the molecule. The extension of that result to general molecules was stated as Problem 7 in Section I. At the end of this subsection we discuss the relation of Problem 7 to Problem 6.

Fix $z_1, \ldots, z_k$ strictly positive, $R_1, \ldots, R_k$, and j, and let $e(\alpha) = e^{\mathrm{TF}}(\lambda = \alpha \sum_{i=1}^{k} z_i;\ \alpha z_1, \ldots, \alpha z_k;\ R_1, \ldots, R_k)$, $e^{(1)}(\alpha) = e^{\mathrm{TF}}(\lambda = \alpha \sum_{i=1}^{j} z_i;\ \alpha z_1, \ldots, \alpha z_j;\ R_1, \ldots, R_j)$ and $e^{(2)}(\alpha) = e^{\mathrm{TF}}(\lambda = \alpha \sum_{i=j+1}^{k} z_i;\ \alpha z_{j+1}, \ldots, \alpha z_k;\ R_{j+1}, \ldots, R_k)$. Define $E(\alpha)$, $E^{(1)}(\alpha)$, $E^{(2)}(\alpha)$ similarly. Let ρ_α, $\rho_\alpha^{(1)}$ and $\rho_\alpha^{(2)}$ be the corresponding TF densities and ϕ_α, $\phi_\alpha^{(1)}$, $\phi_\alpha^{(2)}$ the TF potentials. Finally, define

$$\eta_\alpha(i) = \lim_{x \to R_i} [\phi_\alpha(x) - \alpha z_i\, |x - R_i|^{-1}], \qquad i = 1, \ldots, k, \tag{90a}$$

$$\eta_\alpha^{(1)}(i) = \lim_{x \to R_i} [\phi_\alpha^{(1)}(x) - \alpha z_i\, |x - R_i|^{-1}], \qquad i = 1, \ldots, j, \tag{90b}$$

$$\eta_\alpha^{(2)}(i) = \lim_{x \to R_i} [\phi_\alpha^{(2)}(x) - \alpha z_i\, |x - R_i|^{-1}], \qquad i = j+1, \ldots, k. \tag{90c}$$

Then, the strong form of Teller's lemma (Theorem V.6) says that for $\alpha > 0$,

$$\eta_\alpha(i) > \eta_\alpha^{(1)}(i); \qquad i = 1, \ldots, j; \qquad \eta_\alpha(i) > \eta_\alpha^{(2)}(1); \qquad i = j+1, \ldots, k. \tag{91}$$

LEMMA V.7. *As $\alpha \downarrow 0$, $e(\alpha)$, $e^{(1)}(\alpha)$ and $e^{(2)}(\alpha)$ all go to zero. Similarly, $E(\alpha)$, $E^{(1)}(\alpha)$, and $E^{(2)}(\alpha)$ go to zero. Furthermore, $e(\alpha)$ is differentiable in α for $\alpha \geqslant 0$ and*

$de/d\alpha = \sum_{i=1}^{k} z_i \eta_\alpha(i)$ *Similarly* $e^{(i)}(\alpha)$ *is differentiable and* $de^{(1)}/d\alpha = \sum_{i=1}^{j} z_i \eta_\alpha^{(1)}(i)$, $de^{(2)}/d\alpha = \sum_{i=j+1}^{k} z_i \eta_\alpha^{(2)}(i)$.

Proof. We consider $e(\alpha)$; the argument for $e^{(i)}(\alpha)$ and $E(\alpha)$, $E^{(i)}(\alpha)$ is similar. $e(\alpha)$ is the sum of $\alpha^2 \sum_{i<j} z_i z_j \mid R_i - R_j \mid^{-1}$ and a TF energy. By Theorem II.16, the TF energy is differentiable and its derivative is $-\int \rho_\alpha(x) \sum_{i=1}^{k} z_i \mid x - R_i \mid^{-1} dx$. Thus

$$de/d\alpha = 2 \sum_{i<j} \alpha z_i z_j \mid R_i - R_j \mid^{-1} - \sum_i \int \rho_\alpha(x)\, z_i \mid x - R_i \mid^{-1} dx$$

$$= \sum_{i=1}^{k} z_i \left[\sum_{j \neq i} \alpha z_j \mid R_i - R_j \mid^{-1} - \int \rho_\alpha(x) \mid x - R_i \mid^{-1} dx \right] = \sum_{i=1}^{k} z_i \eta_\alpha(i).$$

Differentiability implies continuity.

$e(0)$ is clearly 0 and the corresponding ρ is 0. ∎

Proof of Theorem V.1. By Lemma V.6,

$$(d/d\alpha)[e(\alpha) - e^{(1)}(\alpha) - e^{(2)}(\alpha)] = \sum_{i=1}^{j} z_i(\eta_\alpha(i) - \eta_\alpha^{(1)}(i)) + \sum_{i=j+1}^{k} z_i(\eta_\alpha(i) - \eta_\alpha^{(2)}(i)). \tag{92}$$

By (91), this derivative is strictly positive for $\alpha > 0$. Since $e(\alpha) - e^{(1)}(\alpha) - e^{(2)}(\alpha) \to 0$ as $\alpha \downarrow 0$, we conclude that $e(\alpha = 1) - e^{(1)}(\alpha = 1) - e^{(2)}(\alpha = 1) > 0$. ∎

Remarks. (1) By Theorem II.16,

$$\frac{dE(\alpha)}{d\alpha} - \frac{dE^{(1)}(\alpha)}{d\alpha} - \frac{dE^{(2)}(\alpha)}{d\alpha} = -\sum_{i=1}^{j} \int z_i \mid x - R_i \mid^{-1} (\rho_\alpha(x) - \rho_\alpha^{(1)}(x))\, dx - \sum_{i=j+1}^{k} \int z_i \mid x - R_i \mid^{-1} (\rho_\alpha(x) - \rho_\alpha^{(2)}(x))\, dx$$

which is strictly negative for $\alpha > 0$ by Theorem V.6. We conclude that $E(\alpha) < E^{(1)}(\alpha) + E^{(2)}(\alpha)$, thereby providing an alternative proof of Theorem V.3 in the *neutral* case.

(2) Consider a dilatation of the neutral molecule by l, i.e., $R_i \to lR_i$, $l \in \mathbb{R}^+$. Denoting the energy simply by $e^{\mathrm{TF}}(l)$, a scaling argument shows that $e^{\mathrm{TF}}(l) = l^{-7} e(\alpha = l^3)$. Thus $B \equiv de^{\mathrm{TF}}(l)/dl \mid_{l=1} = -7e(1) + 3de/d\alpha \mid_{\alpha=1}$. Problem 7 is to show that $B \leqslant 0$. With $U = e^{\mathrm{TF}} - E^{\mathrm{TF}} =$ nuclear–nuclear energy, $e(1) = K - A + R + U$ (cf. Sect. II.6) and $de/d\alpha \mid_{\alpha=1} = \sum_{i=1}^{k} z_i \eta_1(i) = 2U - A$ by Lemma V.7. By Theorem II.23, $R = A/2 - 5K/6$. Thus $B = -7K/6 - \frac{1}{2} \sum_{i=1}^{k} z_i \eta_1(i)$. Let $\tilde{\eta}_1(i)$ and $\tilde{K}(i)$ be the values of η_1 and K for an *atom* of nuclear charge z_i located at R_i. By Theorem V.6, $\eta_1(i) \geqslant \tilde{\eta}_1(i)$. $B = 0$ for an atom since $-7\tilde{K}/6 + \tilde{A}/2 = 0$ by Corollary II.24. Thus $\tilde{K}(i) = 3z_i\tilde{\eta}_1(i)/7$, and

therefore $B \leqslant -(7/6)[K - \sum_{i=1}^{k} \tilde{K}(i)]$. We conclude that if $K \geqslant \sum_{i=1}^{k} \tilde{K}(i)$ as stated in Problem 6, then $B \leqslant 0$, and Problem 7 would be solved.

V.3. *Teller's Lemma and No Binding: Positive Ionic Case*

The proper generalization of Teller's lemma, Theorem V.5, to the nonneutral case involves comparing two TF problems with the *same Fermi energy*.

THEOREM V.8. (Teller's lemma: nonneutral case). *Let $\phi^{(1)}$, $\rho^{(1)}$ (resp. $\phi^{(2)}$, $\rho^{(2)}$) solve the equations: $\rho^{(1)}(x) = \max(\phi^{(1)}(x) - \phi_0, 0)^{3/2}$ (resp. $\rho^{(2)}(x) = \max(\phi^{(2)}(x) - \phi_0, 0)^{3/2}$ with the* same ϕ_0), *$\phi^{(1)}(x) = \sum_{i=1}^{k} a_i \mid x - R_i \mid^{-1} - \int \rho^{(1)}(y) \mid x - y \mid^{-1} dy$ (resp. $\phi^{(2)}(x) = \sum_{i=1}^{k} b_i \mid x - R_i \mid - \int \rho^{(2)}(y) \mid x - y \mid^{-1} dy$; same R_i). If $b_i \geqslant a_i$, $i = 1,..., k$ then $\phi^{(2)}(x) \geqslant \phi^{(1)}(x)$ for all x.*

Proof. Identical to the proof of Theorem V.6 once we note that whenever $\phi^{(1)}(x) > \phi^{(2)}(x)$, $\rho^{(1)}(x) \geqslant \rho^{(2)}(x)$. ∎

Remark. The analog of Theorem V.6 does not hold when $\phi_0 > 0$, since $\rho^{(1)}(x) = 0 = \rho^{(2)}(x)$ can occur.

THEOREM V.9. *Let $\rho^{(\lambda)}(x)$, $\phi^{(\lambda)}(x)$, $-\phi_0^{(\lambda)}$, be the* TF *density, potential and Fermi energy for a fixed potential $V(x) = \sum_{i=1}^{k} a_i \mid x - R_i \mid^{-1}$ with subsidiary condition $\int \rho^{(\lambda)}(x)\, dx = \lambda$. Then, as λ increases, $\rho^{(\lambda)}(x)$ increases, $\phi^{(\lambda)}(x)$ decreases and $\phi_0^{(\lambda)}$ decreases.*

Proof. We already know that $-\phi_0^{(\lambda)}$ is monotone increasing (see Theorem II.10 and Corollary II.9). Let $\lambda_1 > \lambda_2$ and let $\rho^{(1)}(x)$, $\phi^{(1)}(x)$, $\phi_0^{(1)}$, and $\rho^{(2)}(x)$, etc. stand for $\rho^{(\lambda)}(x)$, etc. Let $\psi(x) = (\phi^{(1)}(x) - \phi_0^{(1)}) - (\phi^{(2)}(x) - \phi_0^{(2)})$. Then ψ is continuous on all of $\mathbb{R}^3$ including the R_i and $(4\pi)^{-1} \Delta\psi = (\phi^{(1)}(x) - \phi_0^{(1)})_+^{3/2} - (\phi^{(2)}(x) - \phi_0^{(2)})_+^{3/2}$ (distributional derivative). Note that $\psi(x) \to \phi_0^{(2)} - \phi_0^{(1)} > 0$. as $\mid x \mid \to \infty$. Thus, $S = \{x \mid \psi(x) < 0\}$ is an open bounded set. Clearly $\Delta\psi \leqslant 0$ on S, so ψ is superharmonic and thus takes its minimum value on ∂S, where $\psi = 0$. Thus S is empty and $\psi \geqslant 0$ everywhere. It follows that $\rho^{(1)}(x) \geqslant \rho^{(2)}(x)$. But since $\phi^{(\lambda)}(x) = V(x) - \int \rho^{(\lambda)}(y) \mid x - y \mid^{-1} dy$, $\phi^{(1)}(x) \leqslant \phi^{(2)}(x)$. ∎

THEOREM V.10. *Let $V(x) = \sum_{i=1}^{k} z_i \mid x - R_i \mid^{-1}$; $V^{(1)}(x) = \sum_{i=1}^{j} z_i \mid x - R_i \mid^{-1}$; $V^{(2)}(x) = \sum_{i=j+1}^{k} z_i \mid x - R_i \mid^{-1}$. Let $-\phi_0$ (resp. $-\phi_0^{(i)}$) be the Fermi energy for V(resp. $V^{(i)}$) with $\int \rho = \lambda$ (resp. $\lambda^{(i)}$). Suppose that $\lambda = \lambda^{(1)} + \lambda^{(2)}$. Then $-\phi_0 \leqslant \max(-\phi_0^{(1)}, -\phi_0^{(2)})$.*

Proof. Let $\rho^{(1)}$ (resp. $\rho^{(2)}$) be the TF density for the $V^{(1)}$, $\lambda^{(1)}$ (resp. $V^{(2)}$, $\lambda^{(2)}$) problem. Consider $\rho = \rho^{(1)} + \rho^{(2)}$ as a trial function for the V, λ problem in the variational principle, Theorem II.29. Then $-\phi_0 \leqslant \operatorname{ess\,sup}_{\{x \mid \rho(x) \neq 0\}} [\rho(x)^{2/3} - \phi^{(1)}(x) - \phi^{(2)}(x)]$. Now, for a, b positive, $(a + b)^{2/3} \leqslant a^{2/3} + b^{2/3}$, so

$$-\phi_0 \leqslant \operatorname*{ess\,sup}_{\{x \mid \rho(x) \neq 0\}} [\rho^{(1)}(x)^{2/3} - \phi^{(1)}(x) + \rho^{(2)}(x)^{2/3} - \phi^{(2)}(x)]. \tag{93}$$

If $\rho^{(1)}(x) \neq 0 \neq \rho^{(2)}(x)$, then the right side of (93) is $-\phi_0^{(1)} - \phi_0^{(2)}$. If $\rho^{(1)}(x) \neq 0 = \rho^{(2)}(x)$, then $\rho^{(1)}(x)^{2/3} - \phi^{(1)}(x) = -\phi_0^{(1)}$ while $-\phi^{(2)}(x) \leqslant 0$ (by Lemma II.19), so the right side of (93) is at most $-\phi_0^{(1)}$ for such x. Similarly, if $\rho^{(1)}(x) = 0 \neq \rho^{(2)}(x)$, then the right side is at most $-\phi_0^{(2)}$. It follows that $-\phi_0 \leqslant \max(-\phi_0^{(1)}, -\phi_0^{(2)})$. ▮

As a final preparation for our proof of Theorem V.2, we need:

THEOREM V.11. *Let F be a continuous function on $D = [a, b] \times [c, d]$ such that:*

(i) *For every $y \in [c, d]$, $F(\cdot, y)$ is a C^1 function on $[a, b]$, and $\partial F/\partial x$ is bounded on D.*

(ii) *Let $f(x) = \min_{c \leqslant y \leqslant d} F(x, y)$. Suppose that for each $x \in [a, b]$, there is a $y(x) \in [c, d]$ such that*

$$f(x) = F(x, y(x)),$$
$$(\partial F/\partial x)(x, y(x)) \leqslant 0.$$

Then f is continuous and monotone nonincreasing.

Proof. *Let $x_0 \leqslant x_1$* and $y_i = y(x_i)$ $(i = 0, 1)$. Then

$$f(x_0) \leqslant F(x_0, y_1) = f(x_1) - \int_{x_0}^{x_1} (\partial F/\partial x)(x, y_1)\, dx, \tag{94a}$$

$$f(x_1) \leqslant F(x_1, y_0) = f(x_0) + \int_{x_0}^{x_1} (\partial F/\partial x)(x, y_0)\, dx. \tag{94b}$$

By (94):

$$| f(x_1) - f(x_0) | \leqslant | x_1 - x_0 | \sup | \partial F/\partial x |.$$

Let

$$G(x, z) = (1/z) \int_x^{x+z} (\partial F/\partial x)(w, y(x))\, dw$$

for $z > 0$. Then

$$[f(x_1) - f(x_0)]/(x_1 - x_0) \leqslant G(x_0, x_1 - x_0)$$

and G is bounded with the property that, for each fixed x_0, $\lim_{z \downarrow 0} G(x_0, z)$ exists and is nonpositive.

Let $h_\delta(x) = (\pi\delta)^{-1/2} \exp(-x^2/\delta)$ and extend f to $\mathbb{R}$ by making it constant on $(-\infty, a]$ and $[b, \infty)$. Let $f_\delta(x) = \int h_\delta(y) f(x - y)\, dy$. Then, since f is continuous, f_δ converges pointwise as $\delta \downarrow 0$ to f, so we need only show that each f_δ is monotone. f_δ is differentiable so we need only prove that

$$\lim_{x_1 \downarrow x_0} [f_\delta(x_1) - f_\delta(x_0)]/(x_1 - x_0) \leqslant 0$$

for each x_0. But

$$[f_\delta(x_1) - f_\delta(x_0)]/(x_1 - x_0) \leqslant \int h_\delta(y)\, G(x_0 - y, x_1 - x_0)\, dy. \tag{95}$$

The right side of (95) has a nonpositive limit by the dominated convergence theorem. ▮

Proof of Theorem V.2. Fix $\{z_i\}$, $\{R_i\}$, and λ. Let λ' be chosen to minimize $e^{\mathrm{TF}}(\lambda'; z_1, ..., z_j; R_1, ..., R_j) + e^{\mathrm{TF}}(\lambda - \lambda'; z_{j+1}, ..., z_k; R_{j+1}, ..., R_k) \equiv f(\lambda')$. Since $e^{\mathrm{TF}}(\lambda; —)$ is differentiable for $\lambda > 0$ and is $0(\lambda^{1/3})$ at $\lambda = 0$, one has that near $\lambda' = 0$, $f(\lambda') = f(0) - \alpha\lambda'^{1/3} + o(\lambda'^{1/3})$ with $\alpha > 0$. Therefore, the minimizing value of λ' is not at $\lambda' = 0$ or, by a similar argument, at $\lambda - \lambda' = 0$. Thus $df/d\lambda' = 0$ at λ_0', and $-\phi_0^{(1)} = -\phi_0^{(2)}$, where ϕ(resp. $\phi^{(1)}$, $\phi^{(2)}$) and $-\phi_0$ (resp. $-\phi_0^{(1)}$, $-\phi_0^{(2)}$) are the TF potential and Fermi energies for the full problem (resp. λ_0', $\lambda - \lambda_0'$ problems). By Theorem V.10, $-\phi_0 \leqslant -\phi_0^{(1)} = -\phi_0^{(2)}$. Choose $\tilde{\lambda}$ such that the TF potential $\tilde{\phi}$ for $V = \sum_1^k z_i \mid x - R_i \mid^{-1}$ with $\int \tilde{\rho} = \tilde{\lambda}$ has Fermi energy $-\tilde{\phi}_0 = -\phi_0^{(1)}$. Since $-\tilde{\phi}_0 \geqslant -\phi_0$, $\tilde{\lambda} \geqslant \lambda$, by Theorem V.9. Again, by Theorem V.9, $\tilde{\phi}(x) \geqslant \phi(x)$, and, by Theorem V.8, $\tilde{\phi}(x) \geqslant \phi^{(i)}(x)$. Thus

$$\phi(x) \geqslant \phi^{(i)}(x) \qquad \text{all } x,\ i = 1, 2. \tag{96}$$

Now, without loss of generality suppose that $\sum_{i=1}^k z_i > \lambda$, since the theorem follows from the neutral case if $\lambda \leqslant \sum_{i=1}^k z_i$. Define

$$\begin{aligned} G(\alpha, \lambda') &= [e^{\mathrm{TF}}(\lambda'; \alpha z_1, ..., \alpha z_j; R_i) \\ &\quad + e^{\mathrm{TF}}(\lambda - \lambda'; \alpha z_{j+1}, ..., \alpha z_k; R_i) - e^{\mathrm{TF}}(\lambda, \alpha z_1, ..., \alpha z_k; R_i)] \\ g(\alpha) &= \inf_{0 \leqslant \lambda' \leqslant \lambda} G(\alpha, \lambda'). \end{aligned}$$

Then $g(\lambda/\sum_{i=1}^k z_i) < 0$ by the result for the neutral case. As in the proof of Theorem V.1, (96) says that at $\lambda'(\alpha)$, the point where $G(\alpha, \lambda')$ is minimized, $\partial G/\partial\alpha \leqslant 0$. It is easy to verify the other hypothesis of Theorem V.11 for G. As a result, $g(\alpha)$ is monotone on

$$\left[\lambda\Big/\sum_{i=1}^k z_i,\ 1\right] \qquad \text{so that } g(1) < 0. \quad ▮$$

Another application of the foregoing potential theoretic ideas, which will be useful in the study of the TF theory of solids in Section VI, is the following:

THEOREM V.12. *Let* $V^{(1)}(x) = \sum_{i=1}^j z_i \mid x - R_i \mid^{-1}$, $V^{(2)}(x) = \sum_{i=j+1}^k z_i \mid x - R_i \mid^{-1}$ (*all* $z_i > 0$) *and* $V = V^{(1)} + V^{(2)}$. *Let* $\rho^{(i)}, \phi^{(i)}, \rho, \phi$ *be the* TF *densities and potentials for the three* V's *with a common Fermi energy* $-\phi_0$. *Then* $\phi(x) \leqslant \phi^{(1)}(x) + \phi^{(2)}(x)$. *If* $\phi_0 = 0$, *this inequality is strict.*

Proof. Let $\psi = \phi - \phi^{(1)} - \phi^{(2)}$, which is continuous. In the distributional sense, $-(4\pi)^{-1} \Delta\psi = -\rho + \rho^{(1)} + \rho^{(2)}$. Let $B = \{x \mid \psi(x) > 0\}$, which is open. Since $\phi^{(i)}(x) > 0$, $\max(\phi(x) - \phi_0, 0) > \max(\phi^{(1)}(x) - \phi_0, 0) + \max(\phi^{(2)}(x) - \phi_0, 0)$ for $x \in B$. Thus $\rho^{2/3}(x) \geqslant \rho^{(1)}(x)^{2/3} + \rho^{(2)}(x)^{2/3}$ on B and hence $\rho(x) \geqslant \rho^{(1)}(x) + \rho^{(2)}(x)$ on B. Therefore ψ is subharmonic on B and vanishes at infinity, which implies that B is empty. If $\phi_0 = 0$ the methods of Theorem V.6 show that $\psi(x) > 0$. ∎

Remarks. Theorem V.11 is primarily of interest when $\phi_0 = 0$ (neutral case). Then $\rho(x)^{2/3} < \rho^{(1)}(x)^{2/3} + \rho^{(2)}(x)^{2/3}$. It complements Theorem V.6 which asserts that $\rho(x) > \max(\rho^{(1)}(x), \rho^{(2)}(x))$.

VI. The TF Theory of Solids

Thus far we have considered the TF theory of molecules consisting of a finite number of nuclei. Here we wish to extend the theory to infinitely large, periodic molecules; namely, to solids. For simplicity and notational convenience we shall assume that the unit cell of the solid is cubic and contains one nucleus of charge $z > 0$. Our analysis can be extended to more general situations. By scaling (which will be discussed more fully in Sect. VI.3) we may assume the unit cell to have unit volume. Thus the nuclei are situated in $\mathbb{Z}^3 \in \mathbb{R}^3$, the points with integral coordinates.

To each finite subset, Λ of $\mathbb{Z}^3$, we associate the potential

$$V_\Lambda(x) = z \sum_{y \in \Lambda} | x - y |^{-1}. \tag{97}$$

Since we want to take the limit $|\Lambda| \to \infty$, the total electronic charge must cancel the bulk of the nuclear charge, and so we consider *only* the neutral system; consequently, z is the only parameter in the problem. Let e_Λ and $\rho_\Lambda(x)$ be the TF energy and density for the "molecule" Λ. A theory of solids should be based on three facts: (i) $e = \lim_{|\Lambda| \to \infty} e_\Lambda / |\Lambda|$ exists; (ii) $\rho(x) = \lim_{|\Lambda| \to \infty} \rho_\Lambda(x)$ exists; (iii) ρ has the same periodicity as the assumed periodicity of the nuclei. We shall prove this in Section VI.1.

In Section VI.2 we shall prove that ρ is the unique solution of a modified TF equation with a *periodic* Coulomb potential. One of the points to be emphasized is that the constant ψ_0 appearing in this equation is not a chemical potential, as is often assumed because of its similarity to ϕ_0 in (3). Rather, ψ_0 is the average electric potential in the solid. In Section VI.3 some properties of the solution will be discussed.

The TF theory of solids has been applied for many years [18, 92] to obtain equations of state for real solids at high pressures. Our results are relevant to such applications in that we show clearly what equation is to be solved and how the answer is to be interpreted. In most calculations, the proper periodized TF equation is crudely approximated by replacing the cubic cell by a sphere, and the periodic boundary conditions by a vanishing normal derivative. In the absence of numerical evidence, we do not know the accuracy of such an approximation. We also do not know whether the exact solution will yield a positive pressure at all densities, although we believe it does. This is left as a *conjecture.* A positive resolution of the general dilatation conjecture (Problem 7) would, of course, imply positivity of the pressure. A second *conjecture* is that the compressibility is positive; more generally one would expect that the TF energy for molecules is a convex function of the dilatation parameter.

A natural question is whether TF theory correctly describes solids in the limit $|\Lambda| \to \infty$ and then $z \to \infty$. Our results, logically speaking, concern the limit in the reverse order. One reason we cannot discuss the correct limit is that it is unknown how to prove even the existence of the thermodynamic limit, $|\Lambda| \to \infty$, for real quantum mechanical solids. It is, however, possible to establish this limit for "real matter" [45] and for jellium [48], but not for solids in which the rotational symmetry is lost.

Assuming that the interchange of limits can be justified, a more serious question concerns the applicability of TF theory to high density (i.e., high pressure) solids. One wants to let the lattice spacing, a, tend to zero with z fixed, whereas TF theory is presumably justified in the limit $a \to 0$ with $a^3 z$ fixed, as explained in Section III. These are not the same, and we believe that TF theory is largely irrelevant to the $a \to 0$, z fixed limit. In this limit the kinetic energy dominates and ρ tends to a constant. TF theory (with $a \to 0$ and z fixed) correctly describes this principal effect, namely, $e \to (3/5)\,\rho^{5/3}$. See Theorem VI.7. The interesting Coulomb corrections are of a lower order in ρ, and since the error in the kinetic energy alone is $0(\rho^{4/3})$ (cf. Sect. III), it would be fortuitous if TF theory were correct beyond the leading $\rho^{5/3}$ term. If one is content with the statement that TF theory is "approximately correct," instead of "exact in some limit," then possibly TF theory is quite good when a is not too small and z is large.

VI.1. *Existence of the Thermodynamic Limit*

We will use the following notation:

(i) Λ will always denote a finite subset of $\mathbb{Z}^3$ and will be called a domain. $|\Lambda|$ is the number of points in Λ.

(ii) If $y \in \mathbb{Z}^3$, $\Gamma_y = \{x \in \mathbb{R}^3 \mid -\frac{1}{2} < x_i - y_i \leq \frac{1}{2},\ i = 1, 2, 3\}$ is the elementary cube centered at y.

$$\Gamma(\Lambda) = \bigcup_{y \in \Lambda} \Gamma_y . \qquad \mathrm{vol}(\Gamma(\Lambda)) = |\Gamma(\Lambda)| = |\Lambda|.$$

$\sim\Gamma$ denotes the complement of Γ.

(iii) With V_Λ given by (97), $e_\Lambda = e^{\mathrm{TF}}(\lambda = z\,|\Lambda|;\, V_\Lambda)$, cf. section V, and ρ_Λ, ϕ_Λ denote the minimizing TF ρ and potential.

DEFINITION VI.1. A sequence of domains $\{\Lambda_i\}_{i=1}^{\infty}$ is said to tend to infinity if the following holds:

(i) $$\bigcup_{i=1}^{\infty} \Lambda_i = \mathbb{Z}^3, \tag{98}$$

(ii) $$\Lambda_{i+1} \supset \Lambda_i, \tag{99}$$

(iii) If Λ^h is the set of points in $\mathbb{R}^3$ whose distance to $\partial\Gamma(\Lambda)$ is less than h then

$$\lim_{i\to\infty} |\Lambda_i^h|/|\Lambda_i| = 0 \qquad \text{for any } h > 0. \tag{100}$$

We shall write simply $\Lambda \to \infty$ to denote such a sequence and shall write $\lim_{\Lambda\to\infty} f(\Lambda)$ in place of $\lim_{i\to\infty} f(\Lambda_i)$.

Remark. This notion of $\Lambda \to \infty$ is a slightly modified version of Van Hove convergence. Condition (99) is included so that we can use Teller's lemma. It is noteworthy that the proof of the existence of the thermodynamic limit for real matter requires more stringent conditions on the Λ_i. Even for strongly tempered potentials in the continuous case, more stringent conditions than in Definition VI.1 are needed. In Theorem VI.5 we shall in fact show that $e_\Lambda/|\Lambda|$ converges to a limit independent of the sequence for any conventional Van Hove sequence, i.e., any sequence obeying only (100).

THEOREM VI.2. *If $\Lambda \to \infty$, then*

$$\phi(x) = \lim_{\Lambda\to\infty} \phi_\Lambda(x) \tag{101}$$

exists and is independent of the particular sequence of Λ's used. The convergence is monotone increasing and uniform on compacts subsets of $\mathbb{R}^3\backslash\mathbb{Z}^3$. More generally, if $K \subset \mathbb{R}^3$ is compact

$$\phi_\Lambda(x) - \sum_{y\in K\cap\mathbb{Z}^3} z\,|x-y|^{-1} \tag{102a}$$

converges uniformly on K (including $K \cap \mathbb{Z}^3$) to

$$\phi(x) - \sum_{y\in K\cap\mathbb{Z}^3} z\,|x-y|^{-1}. \tag{102b}$$

ϕ is periodic, i.e., $\phi(x+y) = \phi(x)$, $y \in \mathbb{Z}^3$, $x \in \mathbb{R}^3\backslash\mathbb{Z}^3$. Furthermore,

$$\int_{\Gamma_0} \rho = \lim_{\Lambda\to\infty} \int_{\Gamma_0} \rho_\Lambda = z, \tag{103a}$$

$$\int_{\Gamma_0} \rho^{5/3} = \lim_{\Lambda\to\infty} |\Lambda|^{-1} \int_{\mathbb{R}^3} \rho_\Lambda^{5/3}, \tag{103b}$$

$$\phi(x) = \lim_{\Lambda\to\infty} |\Lambda|^{-1} \sum_{y\in\Lambda} \phi_\Lambda(x+y), \tag{104a}$$

and the following limit exists:

$$\lim_{x\to 0}\{\phi(x) - z \mid x \mid^{-1}\} = \lim_{\Lambda\to\infty} \mid \Lambda \mid^{-1} \sum_{y\in\Lambda} \lim_{x\to y}\{\phi_\Lambda(x) - z \mid x - y \mid^{-1}\}. \quad (104b)$$

Proof. By Theorem V.6,

$$\phi_{\Lambda'}(x) > \phi_\Lambda(x) \qquad \text{for all } x, \quad (105)$$

when $\Lambda' \supset \Lambda$. This implies that for any x such that $\lim_{\Lambda\to\infty}\phi_\Lambda(x) \equiv \phi(x)$ exists, $\phi(x)$ must be independent of the sequence. By Theorem V.12,

$$\phi_\Lambda(x) \leqslant \sum_{y\in\Lambda} \phi^{at}(x - y), \quad (106)$$

where ϕ^{at} is the potential for a single atom with nucleus located at $R = 0$. Now $\phi^{at}(x)$ is bounded above by $\sigma \mid x \mid^{-4}$ on all of $\mathbb{R}^3$ by Theorems IV.8 and IV.5, where $\sigma = 9\pi^{-2}$. By extending the sum in (106) to all of $\mathbb{Z}^3$ we see that $\phi_\Lambda(x)$ is bounded, uniformly in Λ, on any subset, K, of $\mathbb{R}^3\backslash\mathbb{Z}^3$ such that the distance of K to Λ is positive. Thus, the limit in (101) exists and is monotonic. To prove the uniformity, we can apply Theorems V.6 and V.12 again when $\Lambda' \supset \Lambda$:

$$0 \leqslant \phi_{\Lambda'}(x) - \phi_\Lambda(x) \leqslant \sum_{y\in\mathbb{Z}^3\backslash\Lambda} \phi^{at}(x - y). \quad (107)$$

As $\Lambda \to \infty$ this sum goes to zero uniformly on K, if K is compact, and hence the functions ϕ_Λ are a Cauchy sequence in the sup norm on K. Equation (107) also implies that $\lim_{x\to 0}\{\phi(x) - z \mid x \mid^{-1}\}$ exists and the uniform convergence of (102a) to (102b). From (105) we see that $\phi(x) = \sup \phi_\Lambda(x)$. For $y \in \mathbb{Z}^3$, however, $\phi_\Lambda(x + y) = \phi_{\Lambda+\{y\}}(x)$ which, together with monotonicity and (98), implies that ϕ is periodic. Likewise, if we define $\tilde{\phi}_\Lambda(x) = \sup_{y\in\mathbb{Z}^3} \phi_\Lambda(x + y)$, then

$$\phi(x) = \lim_{\Lambda\to\infty} \tilde{\phi}_\Lambda(x) \qquad \text{and} \qquad \phi(x) \geqslant \tilde{\phi}_\Lambda(x). \quad (108)$$

Since $\rho_\Lambda = \phi_\Lambda^{3/2}$, $\lim_{\Lambda\to\infty} \rho_\Lambda(x) = \phi^{3/2}(x) \equiv \rho(x)$. By monotone convergence, $I \equiv \int_{\Gamma_0} \rho = \lim_{\Lambda\to\infty} \int_{\Gamma_0} \rho_\Lambda$. Let $\Lambda(a) \subset \mathbb{Z}^3$ be a cube of side $2a + 1$ centered at 0 and let $\rho_a(x)$ be the ρ associated with $\Lambda(a)$. Since each $\Lambda \subset \Lambda(a)$ for some a, and since $\Lambda \supset \Lambda(a)$ eventually for all a, $I = \lim_{a\to\infty} I_a$, where $I_a = \int_{\Gamma_0} \rho_a$. Suppose $I_\Lambda > z$ for some Λ. By monotonicity and (100), $\Gamma(\Lambda(j\Lambda))$ contains $\mid \Lambda(j\Lambda)\mid - o(\mid\Lambda(j\Lambda)\mid)$ elementary cubes Γ for which $\int_\Gamma \rho_{j\Lambda} > z$. But then $\mid \Lambda(j\Lambda)\mid^{-1} \int_{\mathbb{R}^3} \rho_{j\Lambda} > z$ for j sufficiently large, and this is a contradiction. Hence $I \leqslant z$. Similarly, we have that $\int_{\Gamma_0} \rho^{5/3} \leqslant \liminf_{\Lambda\to\infty} \mid \Lambda \mid^{-1} \int_{\mathbb{R}^3} \rho_\Lambda^{5/3}$ and $\phi(x) \leqslant \liminf_{\Lambda\to\infty} \mid \Lambda \mid^{-1} \sum_{y\in\Lambda} \phi_\Lambda(x + y)$ and

$$\lim_{x\to 0}\{\phi(x) - z \mid x \mid^{-1}\} \leqslant \liminf_{\Lambda\to\infty} \mid \Lambda \mid^{-1} \sum_{y\in\Lambda} \lim_{x\to y}\{\phi_\Lambda(x) - z \mid x - y \mid^{-1}\}.$$

The inequalities established thus far use only monotonicity and an elementary "conservation" argument. To prove the opposite inequalities we have to show that ρ_Λ and ϕ_Λ do not "leak out to infinity." The proof of (104) is easy. From (108), $\phi(x) \geqslant \sup_{y\in\Lambda} \phi_\Lambda(x+y)$. Hence

$$\lim_{x\to 0}\{\phi(x) - z \mid x \mid^{-1}\} \geqslant \mid \Lambda \mid^{-1} \sum_{y\in\Lambda} \lim_{x\to y}\{\phi_\Lambda(x) - z \mid x - y \mid^{-1}\},$$

$$\phi(x) \geqslant \mid \Lambda \mid^{-1} \sum_{y\in\Lambda} \phi_\Lambda(x+y)$$

and (104a) and (104b) are proved. To prove (103a) and (103b) we use the bound (106).

$$\int_{\sim\Gamma(\Lambda)} \phi_\Lambda(x) < \int_{\sim\Gamma(\Lambda)} \sum_{y\in\Lambda} \phi^{at}(x-y) \equiv B.$$

Let $c = \int_{\mathbb{R}^3} \phi^{at}$ and let $c_h = \int_{|x|\geqslant h} \phi^{at}(x)\, dx$. Clearly, $c_h \leqslant \delta/h$ for some $\delta < \infty$ because $\phi^{at}(x) \leqslant \sigma \mid x \mid^{-4}$. Thus, for $h \geqslant \frac{1}{2}$, $B \leqslant \mid \Lambda \mid c_h + \mid \Lambda^h \mid c_{1/2}$ and, using (100) together with the fact that h is arbitrary, we have that

$$\limsup_{\Lambda\to\infty} \mid \Lambda \mid^{-1} \int_{\sim\Gamma(\Lambda)} \phi_\Lambda = 0.$$

Likewise, for any $p \geqslant 1$,

$$\limsup_{\Lambda\to\infty} \mid \Lambda \mid^{-1} \int_{\sim\Gamma(\Lambda)} \phi_\Lambda{}^p = 0 \tag{109}$$

because, as was mentioned before, ϕ_Λ is uniformly bounded on $\sim\Gamma(\Lambda)$. Since

$$\phi(x) \geqslant \sup_{y\in\Lambda} \phi_\Lambda(x+y),$$

$$\begin{aligned}
\int_{\Gamma_0} \phi^p &\geqslant \limsup_{\Lambda\to\infty} \mid \Lambda \mid^{-1} \int_{\Gamma(\Lambda)} \phi_\Lambda{}^p \\
&= \limsup_{\Lambda\to\infty} \mid \Lambda \mid^{-1} \left\{\int_{\mathbb{R}^3} \phi_\Lambda{}^p - \int_{\sim\Gamma(\Lambda)} \phi_\Lambda{}^p\right\} \\
&\geqslant \limsup_{\Lambda\to\infty} \mid \Lambda \mid^{-1} \int_{\mathbb{R}^3} \phi_\Lambda{}^p - \limsup_{\Lambda\to\infty} \mid \Lambda \mid^{-1} \int_{\sim\Gamma(\Lambda)} \phi_\Lambda{}^p \\
&= \limsup_{\Lambda\to\infty} \mid \Lambda \mid^{-1} \int_{\mathbb{R}^3} \phi_\Lambda{}^p
\end{aligned}$$

by (109). ∎

Remark. Since ρ_Λ and ϕ_Λ are monotone increasing in Λ, $\rho_\Lambda \to \rho$, $\phi_\Lambda \to \phi$ for *any* sequence of bounded regions with the property that any bounded subset of $\mathbb{Z}^3$ is eventually in Λ. The limit function ϕ is the same as the one in Theorem VI.2.

THEOREM VI.3. *If $\Lambda \to \infty$ and ϕ, ρ are the limiting potential and density, then the limit*

$$\lim_{\Lambda\to\infty} e_\Lambda/|\Lambda| = e(z)$$

exists, and

$$e(z) = \frac{1}{10}\int_{\Gamma_0} \rho^{5/3} + \frac{z}{2}\lim_{x\to 0}\{\phi(x) - z\,|\,x\,|^{-1}\}.$$

Proof. ρ_Λ satisfies the TF equation (3) with $\phi_0 = 0$, i.e., $\phi_\Lambda = \rho_\Lambda^{2/3}$. Hence

$$e_\Lambda = \frac{3}{5}\int \rho_\Lambda^{5/3} - \frac{1}{2}\int \rho_\Lambda\phi_\Lambda - \frac{1}{2}\int \rho_\Lambda V_\Lambda + \frac{1}{2}z^2 \sum_{\substack{x,y\in\Lambda\\ x\neq y}} |\,x-y\,|^{-1}$$

$$= \frac{1}{10}\int \rho_\Lambda^{5/3} + \frac{z}{2}\sum_{y\in\Lambda}\lim_{x\to y}\{\phi_\Lambda(x) - z\,|\,x-y\,|^{-1}\}$$

Theorem VI.2 establishes the result. ∎

Theorem VI.3 can be extended to more general regions by an argument more closely patterned after the usual methods of controlling energies per unit volume in statistical mechanics [74]. The argument does not use Theorem VI.3 and so provides an alternative proof of the convergence of $e_\Lambda/|\Lambda|$ as $\Lambda \to \infty$.

THEOREM VI.4. *As $\Lambda \to \infty$, $e_\Lambda/|\Lambda|$ converges to a limit $e(z)$. Moreover, for* any *region Λ,*

$$e_\Lambda \leqslant |\,\Lambda\,|\,e(z).$$

Proof. Let us make the z-dependence explicit in ϕ_Λ, etc. By Lemma V.7, for any Λ

$$(d/dz)\,e_\Lambda(z) = \sum_{y\in\Lambda}\lim_{x\to y}\{\phi_\Lambda(x;z) - z\,|\,x-y\,|^{-1}\}$$

$$\leqslant |\,\Lambda\,|\lim_{x\to 0}\{\phi(x;z) - z\,|\,x\,|^{-1}\}$$

by monotonicity. By (104b), if $\Lambda \to \infty$,

$$|\,\Lambda\,|^{-1}\,(d/dz)\,e_\Lambda(z) \to \lim_{x\to 0}\{\phi(x;z) - z\,|\,x\,|^{-1}\}.$$

By the dominated convergence theorem it follows that

$$|\,\Lambda\,|^{-1}\,e_\Lambda(z) \to \int_0^z \lim_{x\to 0}[\phi(x;w) - w\,|\,x\,|^{-1}]\,dw$$

and that

$$e_\Lambda \leqslant |\,\Lambda\,|\,e(z) \qquad \text{for any } \Lambda. \ ∎$$

THEOREM VI.5. *Suppose that Λ converges to $\mathbb{Z}^3$ in Van Hove sense* [74], i.e., *only* (100) *is assumed to hold. Then* $|\Lambda|^{-1} e_\Lambda(z) \to e(z)$.

Proof. By theorem VI.4, $\overline{\lim} |\Lambda|^{-1} e_\Lambda(z) \leqslant e(z)$. On the other hand, by a standard argument [24], $\underline{\lim} |\Lambda|^{-1} e_\Lambda(z) \geqslant |\Lambda(a)|^{-1} e_{\Lambda(a)}(z)$ for any cube $\Lambda(a)$. Taking the sup over a, $\underline{\lim} |\Lambda|^{-1} e_\Lambda(z) \geqslant e(z)$. ∎

VI.2. *The Periodic* TF *Equation*

The Periodic Coulomb Potential. There is no Green function for $-\Delta$ on the torus, i.e., there is no periodic function on $\mathbb{R}^3$ satisfying $-\Delta f = \sum_{y\in\mathbb{Z}^3} \delta(\cdot - y)$, essentially because $-\Delta f = g$(periodic) implies that $\hat{g}$ vanishes at $k = 0$ in a Fourier series. However, one can find a function on the unit torus satisfying.

$$-\Delta G = 4\pi(\delta - 1). \tag{110}$$

Equivalently, G: $\mathbb{R}^3 \to \mathbb{R}$ satisfies

$$-(\Delta_x G)(x - y) = 4\pi\left(-1 + \sum_{y\in\mathbb{Z}^3} \delta(x - y)\right)$$

and G is periodic. Obviously, G is determined only up to an additive constant; a specific choice we shall make is

$$G(x) = \pi^{-1} \sum_{\substack{k\in\mathbb{Z}^3\\ k\neq 0}} |k|^{-2} \exp[2\pi i(k, x)]. \tag{111}$$

G is bounded on Γ_0 except for a singularity at $x = 0$, $G(x) = G(-x)$ and

$$M = \lim_{x\to 0} G(x) - |x|^{-1} \tag{112}$$

exists. To see that M exists, we note that $f(x) = \int_{\Gamma_0} |x - y|^{-1} dy$ is continuous and that $G(x) - |x|^{-1} + f(x) = T(x)$ is a distribution whose Laplacian is zero. T is therefore harmonic, and thus C^∞, even at $x = 0$ [67].

THEOREM VI.6. *Let $\Lambda \to \infty$ and let ϕ, ρ be the limit functions of Theorem* VI.2. *Then there exists a constant $\psi_0 > 0$ such that*

$$\phi(x) = zG(x) - \int_{\Gamma_0} G(x - y) \rho(y) + \psi_0 . \tag{113}$$

Alternatively,

$$-(\Delta\phi)(x) = 4\pi\left[z \sum_{y\in\mathbb{Z}^3} \delta(x - y) - \rho(x)\right]. \tag{114}$$

Furthermore, ϕ and ρ are real analytic on $\mathbb{R}^3\backslash\mathbb{Z}^3$.

Proof. Let $\tilde{\phi}$ denote the right side of (113) with $\psi_0 = 0$. As $\rho \in L^{2-\epsilon}(\Gamma_0)$, $G \in L^{3-\epsilon}(\Gamma_0)$, for all $\epsilon > 0$, $G * \rho$ is a well-defined continuous function on

$\mathbb{R}^3\backslash\mathbb{Z}^3$ (cf. Lemma II.25). $\tilde{\phi}$ is periodic and satisfies (114) since $\int_{\Gamma_0} \rho = z$. Let $f \in C_0^\infty(\mathbb{R}^3)$. Then

$$I_\Lambda \equiv 4\pi \int f \left\{ z \sum_{y \in \Lambda} \delta(\cdot - y) - \rho_\Lambda \right\} \xrightarrow{\Lambda \to \infty} 4\pi \int f \left\{ z \sum_{y \in \mathbb{Z}^3} \delta(\cdot - y) - \rho \right\}$$

$$= \int f\{-\Delta\tilde{\phi}\} = \int \{-\Delta f\}\tilde{\phi}.$$

On the other hand,

$$I_\Lambda = \int f\{-\Delta\phi_\Lambda\} = \int \{-\Delta f\}\phi_\Lambda \xrightarrow{\Lambda \to \infty} \int \{-\Delta f\}\phi.$$

Thus, $\psi \equiv \phi - \tilde{\phi}$, which is periodic, bounded, and continuous by Theorem VI.2 and (112), is harmonic. Therefore it is a constant, ψ_0. If we integrate both sides of (113) over Γ_0 we obtain

$$\psi_0 = \int_{\Gamma_0} \phi > 0. \tag{115}$$

By Theorem VI.2, ρ and ϕ are C^1 on $\mathbb{R}^3\backslash\mathbb{Z}^3$ and are strictly positive since $\phi > \phi_\Lambda > 0$. The bootstrap argument of Theorem IV.5 as well as the proof of Theorem IV.6 are applicable here. ∎

Equation (113), together with the conditions

$$\int_{\Gamma_0} \rho = z, \qquad \rho = \phi^{3/2},$$

is the *periodic TF equation* we have been seeking. To establish uniqueness we recast (113) as a variational problem.

Consider the following functional on

$$\mathcal{J}^z = \left\{ \rho \mid \rho \in L^1(\Gamma_0) \cap L^{5/3}(\Gamma_0), \int_{\Gamma_0} \rho = z, \rho \geqslant 0 \right\}:$$

$$\mathscr{E}_p(\rho; z) = \frac{3}{5}\int_{\Gamma_0} \rho^{5/3} - z\int_{\Gamma_0} \rho G + \frac{1}{2}\iint_{\Gamma_0} \rho(x)\,\rho(y)\,G(x-y)\,dx\,dy. \tag{116}$$

Although G is not positive as a function (its integral vanishes), it is nevertheless true that $G(x - y)$ is the kernel of a positive, semidefinite operator. Consequently the arguments and conclusions of Section II apply to $\mathscr{E}_p$. In particular $\rho \mapsto \mathscr{E}_p(\rho; z)$ is strictly convex, so the minimizing ρ is unique. That such a ρ exists follows either from a repetition of the arguments of Section II or else, more directly, from the analog of Theorem II.10 together with the fact that we have already demonstrated at least one solution to the variational equations (113) and (116).

It is important to note that

$$E_p(z) \equiv \min\{\mathscr{E}_p(\rho; z) \mid \rho \in \mathscr{I}^z\}$$

is *not the same* as the limiting energy per cell, $e(z)$. From the definitions, one finds that

$$e(z) = E_p(z) + z^2 M/2, \tag{117}$$

with M defined in (112). ψ_0 does not enter (117). Adding a constant c to $G(x)$ changes none of the quantities or equations except for three things: $M \to M + c$; $\mathscr{E}_p(\rho; z) \to \mathscr{E}_p(\rho; z) - cz^2/2$ on $\mathscr{I}^z$; $E_p(z) \to E_p(z) - cz^2/2$.

VI.3. *General Remarks*

A. *Noncubic Bravais Lattices.* If the underlying Bravais lattice, L, of the crystal is not cubic, but is specified by three primitive, linearly independent translation vectors, $a_1, a_2, a_3 \in \mathbb{R}^3$ then (111) must be replaced by

$$G(x) = (\pi V)^{-1} \sum_{\substack{k \in L^* \\ k \neq 0}} |k|^{-2} \exp[2\pi i(k, x)], \tag{118}$$

where $V = \text{vol}(a_1, a_2, a_3) = |a_1 \cdot (a_2 \times a_3)|$ and L^* is the lattice reciprocal to L, i.e., $L^* = (b_1, b_2, b_3)$ and $(b_i, a_j) = \delta_{i,j}$. With this modification all of our theory goes through as before mutatis mutandis.

In addition, with trivial modification one can allow more than one nucleus per unit cell.

B. *The Madelung Potential and its Significance.* In Γ_0 place a uniform charge distribution of total negative charge one, and also place a positive delta function at the origin. The ordinary potential this charge distribution generates is

$$f(x) = |x|^{-1} - \int_{\Gamma_0} |x - y|^{-1}\, dy. \tag{119}$$

The *Madelung potential*, $F(x)$, in Γ_0 is defined to be the potential of an infinite periodic array of such charges, i.e.,

$$F(x) = \sum_{y \in \mathbb{Z}^3} f(x - y). \tag{120}$$

Since f has no quadrupole moment, $f(x) = 0(|x|^{-4})$ as $|x| \to \infty$, so (120) is absolutely convergent. The Madelung constant, M', is defined by

$$M' = \lim_{x \to 0} F(x) - |x|^{-1}. \tag{121}$$

If the same is done for an arbitrary Bravais lattice, L, $f(x)$ will have a quadrupole moment in general, and the analogous sum for $F(x)$ will not be absolutely convergent, and hence will depend on "shape."

The point we wish to make is that even for the cubic lattice, only differences $F(x) - F(x')$ have significance. Consider the sum in (120) restricted to a large, cubic domain, $\Lambda \in \mathbb{Z}^3$. In the outermost cells of Λ replace the constant negative charge distribution by a nonconstant one of the same charge, -1. As the reader can easily convince himself, in the limit $\Lambda \to \infty$, the sum (120) will converge to $F(x) + c$, where c is a constant depending on the assumed distribution in the outermost cells. Likewise, $M' \to M' + c$, and $\int_{\Gamma_0} F \to \int_{\Gamma_0} F + c$; thus M' is unstable under "changes in the charge at the bounnary."

We mention this fact for two reasons. One is that in the solid state physics literature M' is purported to have some physical significance. The second reason is that TF theory illustrates the foregoing remark insofar as

$$\phi(x) = \sum_{y \in \mathbb{Z}^3} g(x - y) + d, \tag{122}$$

where

$$g(x) = z \mid x \mid^{-1} - \int_{\Gamma_0} \mid x - y \mid^{-1} \rho(y). \tag{123}$$

The constant, d, in (122) is *not zero* precisely because $\rho_\Lambda(x) \neq \rho(x)$ in the outermost cells of Λ, cf. (127) et. seq.

Let us calculate the relation of M' to M. Let $\hat{f}(k)$ be the Fourier transform of $f(x)$. Then the Fourier series coefficients of F are given by

$$\hat{F}(k) = \hat{f}(k), \qquad k = 2\pi n,\ n \in \mathbb{Z}^3. \tag{124}$$

In particular,

$$\begin{aligned} \hat{F}(0) &= \lim_{k \to 0} \hat{f}(k) \\ &= 2\pi \int_{\Gamma_0} x^2 dx = \int_{\Gamma_0} F(x)\, dx. \end{aligned} \tag{125}$$

Since $-(4\pi)^{-1} \Delta F = \delta(x) - 1$ in Γ_0, and $\int_{\Gamma_0} G = 0$,

$$F(x) = G(x) + 2\pi \int_{\Gamma_0} x^2\, dx.$$

Thus

$$M' = M + 2\pi \int_{\Gamma_0} x^2\, dx. \tag{126}$$

Now we shall apply the same analyses to the TF ϕ. Clearly $\phi' = \sum_{y \in \mathbb{Z}^3} g(x - y)$ satisfies $-(4\pi)^{-1} \Delta\phi' = z\delta(x) - \rho = -(4\pi)^{-1} \Delta\phi$, so $\phi = \phi' + d$. Proceeding as in (125),

$$\psi_0 = \int \phi = d + 2\pi \int_{\Gamma_0} \rho(x) x^2\, dx. \tag{127}$$

We wish to show that $d \neq 0$ in general. Otherwise, (127) would give a fortuitously simple expression for ψ_0. As $z \to 0$ it is clear that $\rho \to$ the constant function z, and $\phi \to \rho^{2/3} = z^{2/3}$. We shall prove this later. Thus

$$\psi_0 = z^{2/3} + o(z^{2/3})$$

whereas

$$\int_{\Gamma_0} \rho(x)x^2\, dx = z \int_{\Gamma_0} x^2\, dx + o(z).$$

Hence, $d \neq 0$ for small z.

C. *Significance of* ψ_0. As remarked earlier, $\psi_0 = \int_{\Gamma_0} \phi$ is the average electric potential in the crystal. *It is not the thermodynamic limit of the chemical potential.* The chemical potential, $\epsilon_{F,\Lambda}$, for a finite system is always zero, and hence $\lim_{\Lambda\to\infty} \epsilon_{F,\Lambda} = 0$.

Since $\phi = \rho^{2/3}$, Hölders inequality yields

$$\psi_0 < \left(\int \rho\right)^{2/3} = z^{2/3}. \tag{128}$$

As $z \to 0$, (128) becomes an equality, as we shall prove later.

D. *The Limits* $z \to 0$ *and* $z \to \infty$

THEOREM VI.7. *As* $z \to 0$:

$$z^{-2/3}\psi_0 = 1 + 0(z^{1/3}), \tag{129}$$

$$\| z^{-2/3}\phi - 1 \|_p = 0(z^{1/3}), \qquad 1 \leqslant p < 3, \tag{130}$$

$$\| z^{-1}\rho - 1 \|_p = 0(z^{1/3}), \qquad 1 \leqslant p < 2, \tag{131}$$

where $\| \cdot \|_p$ *is the* $L_p(\Gamma_0)$ *norm. Moreover,*

$$e(z) = (3/5)\, z^{5/3} + 0(z^2). \tag{132}$$

Remark. As we shall see in the next section, the limit $z \to 0$, Γ_0 fixed is the same as z fixed, $|\Gamma_0| \to 0$. This is the *high density* limit and (132) says that the total energy approaches the ideal gas value, namely, $(3/5)\,\rho^{5/3}$. Equation (132) validates the assertion made at the beginning of Section VI that the corrections to TF theory beyond the leading term are of the same order as the quantum mechanical kinetic energy corrections.

Proof. $z^{-2/3}\phi(x) = A(x) + B(x) + C$, where $A(x) = z^{1/3}G(x)$, $B = -z^{1/3}G * (z^{-1}\rho)$, $C = z^{-2/3}\psi_0$. Since $G \in L^{3-\epsilon}$, all $\epsilon > 0$, and $\| z^{-1}\rho \|_1 = 1$ we have that for $1 \leqslant p < 3$, $\| A \|_p = 0(z^{1/3})$ and $\| B \|_p = 0(z^{1/3})$. Hence $\| z^{-2/3}\phi - C \|_p = 0(z^{1/3})$. In particular, taking $p = \frac{3}{2}$ and using the fact that

$\| z^{-2/3}\phi \|_{3/2} = 1$, $C = 1 + 0(z^{1/3})$, thus proving (129), (130). The fact that $\rho = \phi^{3/2}$ implies (131). To prove (132) we use Theorem VI.3. $\int_{\Gamma_0} \rho^{5/3}/10 = z^{5/3}/10 - 0(z^2)$ by (131). $(z/2)\lim_{x\to 0}\{\phi(x) - z\,|\,x\,|^{-1} - zM\} = (z/2)\int_{\Gamma_0} G(-y)\times \rho(y)\,dy + z\psi_0/2$. As $\|\rho\|_{7/4} = 0(z)$ by (131) and $G \in L^{7/3}(\Gamma_0)$, $\int_{\Gamma_0} G(-y)\,\rho(y)\,dy = 0(z)$. Thus $e(z) = [(1/10) + (1/2)]\,z^{5/3} + 0(z^2)$. ∎

THEOREM VI.8. *Let $\phi^{at}(x; z)$, $\rho^{at}(x; z)$, and $e^{at}(z)$ be the* TF *potential, density and energy respectively for a neutral atom with a nucleus of charge z located at $R = 0$. (Recall that $\phi^{at}(x; z) = z^{4/3}\phi^{at}(z^{1/3}x; 1) = \rho^{at}(x; z)^{2/3}$ and $e^{at}(z) = z^{7/3}e^{at}(1)$.) Then there exist $b, c, d < \infty$ such that for all z*

$$\| \phi - \phi^{at} \|_p \leqslant c, \qquad 1 \leqslant p \leqslant \infty, \tag{133}$$

$$\| \rho - \rho^{at} \|_p \leqslant dz^{1/3}, \qquad 1 \leqslant p \leqslant 3, \tag{134}$$

where $\|\cdot\|_p$ is the $L_p(\Gamma_0)$ norm, and

$$\left| \psi_0 - z^{1/3}\int_{\mathbb{R}^3} \phi^{at}(x;\, 1)\,dx \right| \leqslant b. \tag{135}$$

Moreover, as $z \to \infty$,

$$e(z) - e^{at}(z) = 0(z). \tag{136}$$

Remark. This says that as $z \to \infty$ the crystal consists essentially of isolated atoms, in agreement with the fact that $z \to \infty$ is the same as the lattice spacing $\to \infty$, as we shall see in the next section. Equation (134) should be compared with the fact that $\|\rho\|_1 = z$, and (136) should be compared with the fact that $e^{at}(z) \sim z^{7/3}$.

Proof. By Theorems V.6 and V.12,

$$\phi^{at}(x; z) \leqslant \phi(x) \leqslant \sum_{y\in\mathbb{Z}^3} \phi^{at}(x - y;\, z).$$

By Theorems IV.8 and IV.5, $\phi^{at}(x; z) \leqslant \sigma\,|\,x\,|^{-4}$, $\sigma = 9\pi^{-2}$, on all of $\mathbb{R}^3\backslash\{0\}$. These facts imply (133) for $p = \infty$, and, since Γ_0 has finite volume, they imply (133) for all p. Now $\rho = \phi^{3/2}$ and $(a + b)^{3/2} \leqslant a^{3/2} - (3/2)\,b(a + b)^{1/2}$ for $a, b \geqslant 0$. Thus

$$0 \leqslant \rho - \rho^{at} \leqslant (3/2)\,c\phi^{1/2},$$

where c is given by (133). Since $\|\phi^{1/2}\|_3 = z^{1/3}$, and $\|1\|_p = 1$, all p, (134) follows. Since $\psi_0 = \|\phi\|_1$, $|\psi_0 - \|\phi^{at}\|_1| \leqslant c$. However, $\|\phi^{at}\|_1 - \int_{\mathbb{R}^3}\phi^{at} = \int_{\sim\Gamma_0}\phi^{at} \leqslant \sigma\int_{\sim\Gamma_0}|\,x\,|^{-4}\,dx$. This proves (135). To prove (136) use Theorem VI.3. $\|\rho(\phi - \phi^{at})\|_1 \leqslant \|\rho\|_1\|\phi - \phi^{at}\|_\infty \leqslant cz$ and $\|(\rho - \rho^{at})\phi^{at}\|_1 \leqslant \|\rho - \rho^{at}\|_3\|\phi^{at}\|_{3/2} \leqslant dz$. Furthermore, $\int_{\Gamma_0}\rho^{at}\phi^{at} = \int_{\mathbb{R}^3}\rho^{at}\phi^{at} + 0(1)$ since $\rho^{at}(x)\,\phi^{at}(x) \leqslant \sigma^{5/2}\,|\,x\,|^{-10}$. Hence $\|\rho^{5/3}\|_1 = \|\rho\phi\|_1 = \int_{\mathbb{R}_0}(\rho^{at})^{5/3} + 0(z)$. Finally, $z\,|\lim_{x\to 0}\{\phi(x) - z\,|\,x\,|^{-1}\} - \lim_{x\to 0}\{\phi^{at}(x) - z\,|\,x\,|^{-1}\}| = z\,|\lim_{x\to 0}\{\phi(x) - \phi^{at}(x)\}| \leqslant cz$. ∎

E. *Scaling Relations and Pressure.* Suppose the unit cell Γ_0 is isotropically dilated by a factor l, i.e.,

$$\Gamma_0 \to l\Gamma_0 = \{lx \mid x \in \Gamma_0\}.$$

Denote by a subscript l the dependence of the various quantities of interest on l. Note that $e_l(z)$ is the energy per cell, not per unit volume. One easily finds that:

$$\begin{aligned} G_l(x) &= l^{-1}G(l^{-1}x), \\ M_l &= l^{-1}M, \\ \phi_l(x; z) &= l^{-4}\phi(l^{-1}x; l^3z), \\ \rho_l(x; z) &= l^{-6}\rho(l^{-1}x; l^3z), \\ e_l(z) &= l^{-7}e(l^3z). \end{aligned} \tag{137}$$

The *pressure* is, by definition,

$$P \equiv -\lim_{\Lambda\to\infty} (\partial/\partial V)e_\Lambda , \tag{138}$$

where $V = |\Gamma(\Lambda)| = |\Lambda|\, l^3$. We will interpret $\partial/\partial V$ to mean the derivative with respect to isotropic dilatations. Thus

$$P = -(3l^2)^{-1} \lim_{\Lambda\to\infty} (\partial/\partial l)e_{\Lambda,l}/|\Lambda|. \tag{139}$$

If we can interchange the derivative and the limit in (139) then:

THEOREM VI.9.

$$P = -(3l^2)^{-1}\,(\partial/\partial l)\, e_l(z) = [(7/3)\, e(l^3z) - zl^3\dot{e}(l^3z)]\, l^{-6}, \tag{140}$$

where $(\dot{e})(z) = de(z)/dz$.

To validate the interchange in (139) we argue as follows: For a *finite* system, specified by Λ, the scaling relations (137) also hold. Thus, (139) reads

$$P = l^{-6} \lim_{\Lambda\to\infty} |\Lambda|^{-1} [(7/3)\, e_\Lambda(l^3z) - zl^3\, \dot{e}_\Lambda(l^3z)].$$

However,

$$\lim_{\Lambda\to\infty} |\Lambda|^{-1}\, e_\Lambda(l^3z) \equiv e(l^3z)$$

and, by Lemma V.7,

$$\dot{e}_\Lambda(z) = \sum_{y\in\Lambda} \lim_{x\to y}\{\phi_\Lambda(x) - z\,|x-y|^{-1}\},$$

whence

$$\lim_{\Lambda\to\infty} |\Lambda|^{-1}\, \dot{e}_\Lambda(z) = \lim_{x\to 0}\{\phi(x) - z\,|x|^{-1}\} \tag{141}$$

by (104b). Therefore, to complete the justification of (140) we need the following lemma.

LEMMA VI.10. *The energy per cell, $e(z)$, for the periodic* TF *system satisfies*

$$\dot{e}(z) \equiv de(z)/dz = \lim_{x\to 0}\{\phi(x) - z\,|\,x\,|^{-1}\}, \tag{142}$$

where ϕ is the periodic TF *potential.*

Proof. By applying the methods of Section II to the energy functional $\mathscr{E}_p(\rho; z)$, (116), one can prove the analog of Theorem II.16, i.e.,

$$dE_p(z)/dz = -\int_{\Gamma_0} G\rho + \psi_0\,.$$

Using (117),

$$\begin{aligned} de(z)/dz &= zM - \int_{\Gamma_0} G\rho + \psi_0 \\ &= \lim_{x\to 0}\{\phi(x) - z\,|\,x\,|^{-1}\} \end{aligned}$$

by (113) and (112). ∎

Remark. Using Theorems VI.3 and VI.9 we obtain another formula for the energy:

$$e(z) = \frac{1}{10}\int_{\Gamma_0} \rho^{5/3} + \frac{1}{2}\, z\dot{e}(z). \tag{143}$$

This gives us an alternative formula for the pressure:

$$P = l^{-6}[(\tfrac{1}{3})\, e(l^3 z) + (\tfrac{1}{5}) \int_{\Gamma_0} \rho^{5/3}]. \tag{144}$$

From (144) we see that $P > 0$ *whenever* $e > 0$, which proves part of our conjecture.

The *compressibility*, κ, is defined by

$$\begin{aligned} (\kappa)^{-1} &= -\,|\,\Gamma_0\,|\;\partial P/\partial(|\,\Gamma_0\,|) \\ &= -(l/3)\;\partial P/\partial l \\ &= l^{-6}[(14/3)\, e(l^3 z) - (10/3)\, l^3 z\dot{e}(l^3 z) \\ &\qquad + (l^3 z)^2\, \ddot{e}(l^3 z)]. \end{aligned} \tag{145}$$

VII. THE TF THEORY OF SCREENING

Another interesting solid state physics problem is the TF theory of the screening of an impurity in a solid by the electrons in the solid. The simplest model is to treat the impurity as the Coulomb potential of a point charge, and to replace the nuclei of the solid by a uniform background of positive charge.

The electrons are treated as a gas which will partly "screen" the Coulomb potential of the impurity. The TF theory of this problem has been widely studied, see e.g., Kittel [42]. Only the positive impurity case will be discussed although, as in the remark at the end of Section I, we could do the other case as well.

Here we shall put the TF theory on a rigourous basis, but we shall not attempt to justify the TF theory as the limit of a proper quantum theory. We are not certain that a justification is possible, but even if one is, it would not seem to be accessible to our methods of Section III. Those methods depend on energy considerations, and the energy of the impurity is finite while the total energy of the background is infinite. On the other hand, if one considers a large number of impurities, proportional to the size of the solid, the methods of Section III might be applicable. In any event, for real solids the TF theory of screening is not considered to be very realistic; as we shall see, the screened Coulomb field of the impurity falls off exponentially fast with distance, whereas in real solids the fall-off is believed to be much slower and is also oscillatory. This effect is due to the sharpness of the electron Fermi surface [42].

The formulation of the problem is the following. Let Λ be a bounded, measurable set in $\mathbb{R}^3$ in which a uniform charge density $\rho_B > 0$ is placed. In addition, there is a nucleus of positive charge z located at $x = 0$. The total electric potential generated by this configuration is

$$V_\Lambda(x; z) = z \mid x \mid^{-1} + \rho_B \int_\Lambda \mid x - y \mid^{-1} dy. \tag{146}$$

The TF energy functional is

$$\mathscr{E}_\Lambda(\rho; z) = \tfrac{3}{5} \int \rho^{5/3} - \int V_\Lambda(x; z)\rho(x)\, dx + \tfrac{1}{2} \int\int \rho(x)\rho(y) \mid x - y \mid^{-1} dx\, dy \tag{147}$$

These integrals are over all of $\mathbb{R}^3$, and hence the support of ρ is not confined to Λ. We could make a theory in which supp $\rho \subset \Lambda$ but the results, both physical and mathematical, would be the same *apart from an overall shift in the average potential caused by the boundary effects* (cf. Sect. VI.3 and the remark after Theorem VII.2). The formulation (147) is simpler and, on physical grounds, preferable.

We shall only be concerned with the neutral case. Thus, by the methods of Sections II, IV, and V, there is a strictly positive $\rho_\Lambda(x; z)$ which minimizes (147) and satisfies

$$\int \rho_\Lambda(x; z) = \rho_B \mid \Lambda \mid + z, \tag{148}$$

$$\rho_\Lambda(x; z)^{2/3} = \phi_\Lambda(x; z), \tag{149}$$

$$\phi_\Lambda(x; z) = V_\Lambda(x; z) - \int \rho_\Lambda(y; z) \mid x - y \mid^{-1} dy, \tag{150}$$

If $\Lambda \supset \Lambda'$ and $z \geqslant z'$ then $\rho_\Lambda(x; z) \geqslant \rho_{\Lambda'}(x; z')$, (151) with strict inequality if $\Lambda\backslash\Lambda' \neq \varnothing$ or $z > z'$. Equation (151) is Teller's lemma suitably modified for the case of a smeared out background. We use the special notation $\rho_\Lambda(x)$, $V_\Lambda(x)$, and $\phi_\Lambda(x)$ to denote these quantities when $z = 0$.

We shall adopt an extremely weak notion of $\Lambda \to \infty$ and it is remarkable that the theory goes through for such a sequence. One reason for this is that we are not interested in evaluating the total energy.

DEFINITION VII.1. A sequence $\{\Lambda_i\}_{i=1}^\infty$ of bounded measurable domains in $\mathbb{R}^3$ is said to tend to infinity (symbolically $\Lambda \to \infty$) if every bounded subset of $\mathbb{R}^3$ is eventually contained in Λ.

We first study the $z = 0$ case.

THEOREM VII.2. *Let $\Lambda \to \infty$ and $z = 0$. Then*

$$\lim_{\Lambda\to\infty} \phi_\Lambda(x) = \rho_B^{2/3} \tag{152}$$

and the limit is uniform on compact subsets of $\mathbb{R}^3$.

Proof. By monotonicity and the remark after Theorem VI.2, $\lim_{\Lambda\to\infty} \phi_\Lambda(x) = \sup_\Lambda \phi_\Lambda(x) \equiv \phi(x)$ exists. As in the proof of Theorem VI.2 we see that $\phi(x)$ is periodic for *every* period; hence $\phi(x)$ is a constant, ϕ. Let Γ_0 be a cube of side one, centered at 0, as in Section VI, and let ϕ^Γ be the TF potential when $\Lambda = \Gamma_0$. The estimate (106) holds if ϕ^{at} is replaced by ϕ^Γ, and $\phi^\Gamma(x) < \sigma \mid x \mid^{-4}$ by Theorems IV.7, IV.8, IV.9. Thus, as in the proof of Theorem VI.2, $\phi < \infty$ and the limit is uniform on compacta. Taking the limit $\Lambda \to \infty$ in the equation $-\Delta\phi_\Lambda(x) = 4\pi(\rho_B - \rho_\Lambda(x))$, one has that $0 = -\Delta\phi = 4\pi(\rho_B - \phi^{3/2})$. ∎

Remark. When $z = 0$, if (147) is minimized subject to supp $\rho \subset \Lambda$, then it is easy to show that the minimum occurs for $\rho_\Lambda(x) = \rho_B$, all $x \in \Lambda$, and all Λ, and $\phi_\Lambda(x) = 0$. Therefore the boundary effect is precisely to lower the potential by $\rho_B^{2/3}$. Compare the remarks in Section VI.3B.

We next turn to the $z > 0$ case. We want to show that

$$\begin{aligned} \lim_{\Lambda\to\infty} \phi_\Lambda(x; z) - \rho_B^{2/3} &= f(x; z), \\ \lim_{\Lambda\to\infty} \rho_\Lambda(x; z) - \rho_B &= g(x; z) \end{aligned} \tag{153}$$

exist and that they satisfy the obvious TF equation:

$$f(x; z) = z \mid x \mid^{-1} - \int \mid x - y \mid^{-1} g(y; z)\, dy, \tag{154}$$

$$[\rho_B^{2/3} + f(x)]^{3/2} - \rho_B = g(x), \tag{155}$$

$$\int g(x)\, dx = z. \tag{156}$$

Of course, the existence of f implies that of g and also (155).

THEOREM VII.3. *Let $\Lambda \to \infty$ and $z > 0$. Then f exists and* (154)–(156) *hold. Moreover*

(i) $0 \leqslant f(x; z) \leqslant \phi^{at}(x; z)$.

(ii) *The limits in* (153) *are uniform on compact subsets of* $\mathbb{R}^3 \backslash \{0\}$.

(iii) $g \in L^1 \cap L^{5/3}$.

(iv) *f and g are strictly positive and real analytic on* $\mathbb{R}^3 \backslash \{0\}$.

(v) *If $z \geqslant z'$ then $f(x; z) \geqslant f(x; z')$, all x.*

(vi) *Assuming only that $g \in L^1 \cap L^{5/3}$ and that $f(x) \geqslant -\rho_B^{2/3}$, there is only one solution to* (154) *and* (155) (*without assuming* (156)).

Proof. Let $f_\Lambda(x; z)$ (resp. $g_\Lambda(x; z)) = \phi_\Lambda(x; z) - \rho_B^{2/3}$ (resp. $\rho_\Lambda(x; z) - \rho_B$). By monotonicity, f_Λ converges to some f, and by Theorem V.12,

$$\phi_\Lambda(x) < f_\Lambda(x; z) + \rho_B^{2/3} < \phi_\Lambda(x) + \phi^{at}(x; z).$$

This, together with Theorem VII.2 proves (i). By mimicking the proof of Theorem VI.2, (ii) is also proved.

To prove (iii), apply the inequality $(\alpha + \beta)^{3/2} - \alpha^{3/2} \leqslant (\frac{3}{2})\, \beta(\alpha + \beta)^{1/2}$ with $\alpha = \rho_B^{2/3}$, $\beta = f_\Lambda(x; z) \leqslant \phi^{at}(x; z)$. Thus

$$g_\Lambda(x; z) \leqslant (3/2)\, \phi^{at}(x; z)\, [\phi^{at}(x; z) + \rho_B^{2/3}]^{1/2},$$

and g_Λ is dominated by an $L^1 \cap L^{5/3}$ function. The dominated convergence theorem implies (iii). It also implies (156) since $\int g_\Lambda(x; z)\, dx = z$ by neutrality.

Equation (154) follows from the fact that since $g_\Lambda \to g$ in $L^1 \cap L^{5/3}$ we can take the limit $\Lambda \to \infty$ in the distributional equation

$$-\Delta f_\Lambda(x; z) = 4\pi[z\delta(x) - g_\Lambda(x; z)].$$

Then f is given by the right side of (154) plus a harmonic function, h. Since $f \to 0$ as $|x| \to \infty$ by (i), $h = 0$. Condition (iv) follows by the methods of Theorems IV.3, IV.5, and IV.6. Condition (v) follows from the monotonicity property (151).

To prove (vi), suppose that (f', g') is another solution to (154), (155). By the now familiar subharmonicity argument, $B = \{x \mid f'(x; z) > f(x; z)\}$ is empty because $x \in B$ implies that $g'(x; z) > g(x; z)$ which implies that $f' - f$ is subharmonic on B. But both f' and $f \to 0$ as $|x| \to \infty$ by Lemma II.25 and the fact that g and $g' \in L^1 \cap L^{5/3}$. Likewise, $\{x \mid f'(x; z) < f(x; z)\}$ is also empty. ▌

Remark. By the uniqueness of the solution to (154)–(156), both f and g are spherically symmetric functions of x, i.e., $f(x; z) = f(y; z)$ when $|x| = |y|$.

There is a *scaling relation* for this problem. If we write

$$f(x; z) = \rho_B^{2/3} F(\rho_B^{1/6} x; \rho_B^{-1/2} z), \tag{157}$$

$$g(x; z) = \rho_B G(\rho_B^{1/6} x; \rho_B^{-1/2} z), \tag{158}$$

then (154) and (155) become

$$F(x; z) = z\,|\,x\,|^{-1} - \int |\,x - y\,|^{-1}\, G(y; z)\, dy, \tag{159}$$

$$(1 + F)^{3/2} - 1 = G, \tag{160}$$

while (156) becomes

$$\int G(x; z)\, dx = z. \tag{161}$$

Henceforth we shall deal only with the scaled quantities F and G. It is convenient to define $\theta \in \mathbb{R}$ and $Y\colon \mathbb{R}^3 \to \mathbb{R}$ by

$$\theta = (6\pi)^{1/2} \approx 4.342 \tag{162}$$

$$Y(x) = |\,x\,|^{-1} e^{-\theta |x|} \tag{163}$$

whence

$$-(4\pi)^{-1}\, \Delta Y(x) = \delta(x) - (3/2)\, Y(x). \tag{164}$$

It is sometimes said [42] that $f(x; z) \sim zY(x)$ as $|\,x\,| \to \infty$. While the factor Y is correct, the factor z is definitely too large as we shall now show. Physically, one may say that the effect of the nonlinearity of TF theory is to *over screen the impurity*.

THEOREM VII.4. *The real analytic function* $q\colon (0, \infty) \times (0, \infty) \to (0, \infty)$ *defined by*

$$F(x; z) = q(|\,x\,|; z)\, Y(x) \tag{165}$$

satisfies

(i) $q(r; z)$ *is monotone decreasing in* r *and monotone increasing in* z.

(ii) $q(0; z) = \lim_{r\to 0} q(r; z) = z$.

(iii) $Q(z) = \lim_{r\to\infty} q(r; z)$ *exists and* $0 < Q(z) < z$.

(iv) $Q(z)$ *is monotone increasing in* z *and* $\limsup_{z\to\infty} Q(z)(bz)^{-2/3} < 1$, *with* $b = (24/\pi)^{3/4}\,(5 + 5^{1/2})/32 \approx 1.039$.

LEMMA VII.5. *Let* $T\colon \mathbb{R}^3 \to \mathbb{R}$ *be spherically symmetric* (i.e., $|\,x\,| = |\,y\,|$ *implies* $T(x) = T(y)$) *and satisfy* $T(x)|\,x\,|^{-1}\, e^{+\theta|x|} \in L^1(\mathbb{R}^3)$. *Let* $I = Y * T$. *Then* I *is spherically symmetric and*

$$I(x) = I_1(x) - I_2(x),$$

$$I_1(x) = 4\pi(\theta\,|\,x\,|)^{-1}\, e^{-\theta|x|} \int_0^\infty s\, T(s) \sinh(\theta s)\, ds,$$

$$I_2(x) = 4\pi(\theta\,|\,x\,|)^{-1} \int_{|x|}^\infty s\, T(s) \sinh[\theta(s - |\,x\,|)]\, ds.$$

Proof. Use bipolar coordinates, i.e.,

$$\int_{\mathbb{R}^3} f(|x-y|)\, g(|y|)\, dy = 2\pi\, |x|^{-1} \int_0^\infty ds\, s\, f(s) \int_{||x|-s|}^{|x|+s} t\, g(t)\, dt,$$

with $f = T, g = Y$. ∎

Proof of Theorem VII.4. We can rewrite (159) as

$$-(4\pi)^{-1} \Delta F + (3/2) F = z\delta(x) - T,$$

where (166)

$$T(x; z) = G(x; z) - (3/2) F(x; z).$$

As $0 \leqslant (1+a)^{3/2} - 1 - (3/2)\, a \leqslant a^{3/2}$ when $a \geqslant 0$, $0 \leqslant T \leqslant F^{3/2}$. Thus

$$F = zY - Y * T \tag{167}$$

and hence

$$F(x; z) \leqslant zY(x). \tag{168}$$

By (168) $F^{3/2}$ satisfies the hypotheses of Lemma VII.5 and hence

$$(Y * T)(x; z) = A(z)\, Y(x) - H(x; z),$$

where (169)

$$A(z) = (4\pi/\theta) \int_0^\infty s\, \tilde{T}(s; z) \sinh(\theta s)\, ds,$$

and where $\tilde{T}(s; z) = T(x; z)$ for $|x| = s$. H is given by I_2 in Lemma VII.5. Since $0 \leqslant T \leqslant F^{3/2} \leqslant z^{3/2} Y^{3/2}$, a simple estimate I_2 yields $0 \leqslant H \leqslant \beta Y^{3/2}$ with $\beta < \infty$.

Define $Q(z) \equiv z - A(z)$ and $q(r; z)$ by (165). Then we have that

$$q(r; z) = Q(z) + L(r; z)$$

with (170)

$$L(r; z) = (2\pi/\theta) \int_r^\infty s\, \tilde{T}(s; z) \{e^{\theta s} - e^{2\theta r - \theta s}\}\, ds.$$

As $\tilde{T} \geqslant 0$, L is monotone decreasing in r. As $L = H/Y \leqslant \beta Y^{1/2}$, $\lim_{r\to\infty} L(r; z) = 0$. This, together with Theorem VII.3(v) proves (i) and the existence of the limit in (iii) with $Q(z) = z - A(z)$. To prove (ii) it is sufficient to note that by Lemma II.25, $Y * T$, which appears in (167), is continuous and hence finite at $x = 0$.

If $Q(z) = z$, then $A(z) = 0$ and $0 = T + G - (3/2)F$, a.e. Then $F = G = 0$, and (161) would not hold. Now suppose that $Q(z) = 0$. Then $F = H = YL$, whence $T \leqslant F^{3/2} = Y^{3/2}L^{3/2}$. Then from (170) and the monotonicity of L,

$$L(r;\, z) \leqslant (2\pi/\theta) \int_r^\infty s^{-1/2} L(s;\, z)^{3/2}\, e^{-3\theta s/2} \{e^{\theta s} - e^{2\theta r - \theta s}\}\, ds$$

$$\leqslant (2\pi/\theta) \int_r^\infty s^{-1/2}\, e^{-\theta s/2} L(s;\, z)^{3/2}\, ds$$

$$\leqslant (2\pi/\theta)\, L(r;\, z)^{3/2} \int_r^\infty s^{-1/2} e^{-\theta s/2}\, ds.$$

Since $F = YL$, (168) implies that $L \leqslant z$, and since the last integral goes to zero as $r \to \infty$, we conclude that there exists an r_0 such that $L(r;\, z) = 0$ when $r > r_0$. This contradicts Theorem VII.3(iv) and hence (iii) is proved.

The monotonicity of $Q(z)$ is implied by (i). To obtain the bound, we note that $x \to (1 + x)^{3/2} - 1 - 3x/2$ is monotone increasing for $x \geqslant 0$. Thus, since $F \geqslant Q(z)\, Y$, $T \geqslant (1 + Q(z)\, Y)^{3/2} - 1 - 3Q(z)\, Y/2 \equiv T'$. If $Q(z)$ is bounded there is nothing to prove. Otherwise, insert T' into (169) and, by dominated convergence,

$$\liminf_{z \to \infty} A(z)\, Q(z)^{-3/2} \geqslant (4\pi/\theta) \int_0^\infty s^{-1/2} e^{-3\theta s/2} \sinh(\theta s)\, ds = 1/b.$$

Since $A(z) = z - Q(z)$, (iv) is proved. ∎

We are grateful to Dr. J. F. Barnes for providing us with the accompanying two figures. The first is a plot of $Q(z)$ (labeled Q and Z, respectively). The second figure is a plot of the function $q(r;\, z)$ (labeled $ue^{\theta r}$) for $z = 53.6988$. The corresponding $Q(z) = 8.0$.

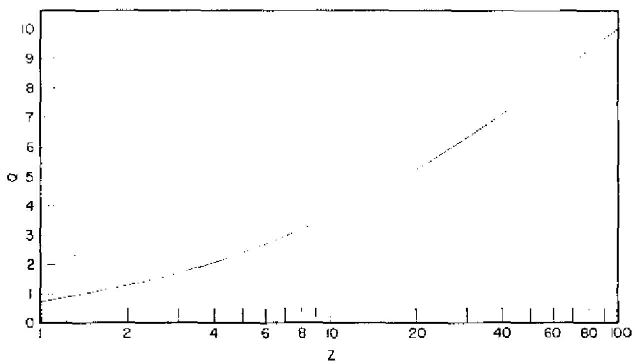

FIGURE 1

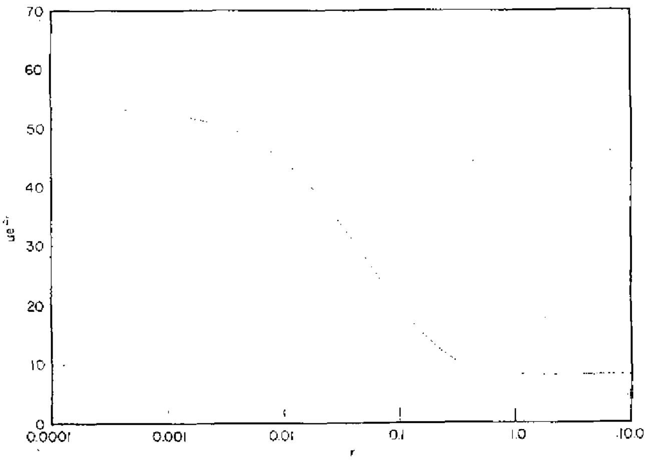

FIGURE 2

Notes Added in Proof.

1. A simplified account of the analytic methods of this paper was given in [98] and a summary of the results, together with some applications, was given in [99].

2. It has been shown [52] that the right side of (6), with a smaller (c), is a lower bound on the left hand side of (6).

3. The reader may consult [68, 100] for further discussion of Dirichlet–Newmann bracketing.

4. In [21, 24, 36], Theorem II.22 is generalized to the molecular case: $2K(\rho) = A(\rho) - R(\rho) + U$, U = internuclear repulsion, *provided* the total energy $e^{\mathrm{TF}}(\lambda) = E^{\mathrm{TF}}(\lambda) + U$ is stationary with respect to variations of the R_i. We do not give this result here, because, as shown in Section V, $e^{\mathrm{TF}}(\lambda)$ has no absolute, and probably no local minimum as a function of the R_i.

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