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Numerical Calculation of the Thomas-Fermi-von Weizsäcker Function for an Infinite Atom Without Electron Repulsion

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DISCLAIMER

NUMERICAL CALCULATION OF

THE THOMAS-FERMI-VON WEIZSÄCKER FUNCTION

FOR AN INFINITE ATOM WITHOUT ELECTRON REPULSION

by

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ABSTRACT

The Thomas-Fermi (TF) and Thomas-Fermi-von Weizsäcker (TFW) theories of atoms and molecules with electron-electron repulsion are reviewed briefly. The main difference between the energies, $E^{TFW} - E^{TF}$ (for large z), is a term $D^{TFW}z^2$. (It is also believed that $E^Q - E^{TF} \sim D^Q z^2$, where E^Q is the true quantum ground state energy.) To calculate D^{TFW}, it is necessary to find the positive solution to the differential equation

$$\{ - \Delta + |\psi(x)|^{4/3} - |x|^{-1} \} \psi(x) = 0$$

in three dimensions. While this equation arises from TFW theory with electron-electron repulsion, it also has a second interpretation - namely as the TFW equation for an atom without electron-electron repulsion. Hence the title of this report.

The main content of this report is the numerical solution of this equation and the evaluation of D^{TFW}.

I. INTRODUCTION

The main purpose of this report is to present numerically the positive solution to the equation

$$\{ -\Delta + |\psi(x)|^{4/3} - |x|^{-1} \} \psi(x) = 0 \quad . \tag{1.1}$$

This equation is the Thomas-Fermi-von Weizsäcker (TFW) equation (after suitable scaling of the parameters) for a nonrelativistic atom with the nucleus fixed at the origin and <u>without</u> the electron-electron repulsion. However, Eq.(1.1) is also relevant for TFW theory <u>with</u> electron-electron repulsion.

The TFW equation describes the balance of potential and kinetic energies of the electrons in an atom: $-|x|^{-1}$ is potential energy in the field of the nucleus (suitably scaled); $|\psi(x)|^{4/3}$ is the Thomas-Fermi contribution to the kinetic energy (that is, the square of the Fermi momentum); and $-\Delta$ is the von Weizsäcker correction to the kinetic energy.

The electron number,

$$\lambda = \int \psi(x)^2 dx, \tag{1.2}$$

will turn out to be infinity for Eq.(1.1), which is physically reasonable because an atom without repulsion can bind infinitely many electrons. We choose to deal with the case of infinite electron number because it is the appropriate analog of the neutral TFW atom when electron-electron repulsion is included in the sense that it is the case of the maximum electron number.

The only previous numerical study of this modified TFW equation that we are aware of is that of Yonei and Tomishima[1] who studied Eq.(1.1) with zero replaced by $-\mu\psi(x)$ on the right side; μ was adjusted to make λ finite instead of infinite.

Our study of Eq.(1.1) is not merely an exercise in numerical analysis. The equation and its solution play an essential role in the TFW theory[2-4] of large atoms and molecules <u>with</u> electron-electron repulsion. In Sec. II, we briefly outline TF and TFW theory and explain the significance of Eq.(1.1). The reader is referred to a recent review article,[5] especially Sec. VII.C, in which more

details and proofs are given. In Sec. III, some mathematical properties of Eq.(1.1) will be outlined. Proofs will again be omitted; they can be found in Ref. 6. Finally, Sec. IV contains our numerical results.

II. A BRIEF REVIEW OF THE THOMAS-FERMI-VON WEIZSÄCKER THEORY

Everything in this section can be found, with more detail, in Refs. 5 and 6. Notation:

(1) e = electron charge = 1.

(2) $\delta \equiv \hbar^2/2m$, m = electron mass.

(3) L^p (for $1 \leq p < \infty$) is the set of functions, f, such that $||f||_p = [\int |f(x)|^p dx\ ]^{1/p} < \infty$.

(4) H^1 is the set of function, f, such that f and each component of ∇f are in L^2.

(5) We assume there are k fixed nuclei with nuclear charges $z_i > 0$ and located at distinct points $R_i \in \mathbb{R}^3$. These k-tuples will be denoted by $\underline{z}$ and $\underline{R}$. $Z \equiv \sum_{j=1}^{k} z_j$ is the total nuclear charge. In the case of an atom (k = 1), we will assume $R_1 = 0$ and denote z_1 by z.

(6) $V(x) \equiv \sum_{j=1}^{k} z_j |x-R_j|^{-1}$ is the nuclear potential.

(7) q denotes the number of electron spin states. Usually q = 2, but one may wish to consider q = 1 for the ferromagnetic state.

(8) $\gamma_p \equiv (\hbar^2/2m)(6\pi^2/q)^{2/3}$. p stands for "physical."

(9) $y = (x,\sigma)$ denotes a single space-spin pair. $\int dy \equiv \sum_{\sigma=1}^{q} \int dx$. An N-particle function, $\Psi(y_1,\ldots,y_N)$, is always assumed to be antisymmetric (Pauli principle) and $\int |\psi|^2 = 1$ (normalization).

A. The Schrödinger Equation

The Hamiltonian for N electrons is

$$H_N = -\sum_{i=1}^{N} [\delta\Delta_i + V(x_i)] + \sum_{1\leq i<j\leq N} |x_i - x_j|^{-1}. \tag{2.1}$$

The ground state energy (with Q denoting "quantum") is

$$E^Q(N) = \inf \{(\psi, H_N\psi)\}. \tag{2.2}$$

The infinium, as distinct from minimum, in Eq.(2.2) is important because if N is too large, there will be no ψ that minimizes the right side. The ground state density is

$$\rho^Q(N,x) = N \sum_{\sigma=1}^{q} \int \psi((x,\sigma),y_2,\ldots y_N) dy_2,\ldots dy_N \quad , \tag{2.3}$$

where ψ is the ground state, that is, the ψ that minimizes $(\psi, H_N\psi)$. If this ψ is not unique, or if it does not exist, it is still possible to define ρ^Q by means of a sequence of approximating ψ's (see Ref. 5).

B. Thomas-Fermi Theory

The TF energy functional is

$$\mathcal{E}^{TF}(\rho) = \frac{3}{5}\gamma \int \rho(x)^{5/3} dx - \int V(x)\rho(x)dx + J(\rho,\rho) \quad , \tag{2.4}$$

where

$$J(\rho,\rho) \equiv \frac{1}{2} \iint \rho(x)\rho(y) \, |x-y|^{-1} \, dx \, dy. \tag{2.5}$$

$\mathcal{E}^{TF}$ is defined for non-negative ρ's in $L^{5/3} \cap L^1$. $\rho(x)$ is an "electron density." γ is a positive parameter. The TF energy is, for a given electron number that need not be integral,

$$\lambda = \int \rho, \tag{2.6}$$

and

$$E^{TF}(\lambda,\underline{z},\underline{R}) \equiv \inf \{ \mathcal{E}(\rho) \mid \rho \in L^{5/3} \cap L^1, \ \rho(x) \geq 0, \ \int \rho = \lambda \}. \tag{2.7}$$

The important facts about TF theory that will be needed are the following.

F1. Existence and Uniqueness of a Minimum. There is a minimizing ρ for Eq.(2.7) [that is, $\mathcal{E}^{TF}(\rho) = E^{TF}(\lambda,\underline{z},\underline{R})$] if and only if $\lambda \leq \lambda_c = Z$. This ρ is unique (denote it by ρ^{TF}) and satisfies the TF equation

$$\gamma\, \rho^{TF}(x)^{2/3} = \max\, [\, \phi^{TF}(x) - \mu^{TF}, 0], \tag{2.8}$$

for some $\mu^{TF} \geq 0$, where

$$\phi^{TF}(x) = V(x) - \int \rho^{TF}(y)\, |x-y|^{-1} dy. \tag{2.9}$$

Conversely, Eqs.(2.8) and (2.9) have a unique solution pair (ρ,μ) such that $\int \rho = \lambda$ and $\rho \in L^{5/3} \cap L^1$. For $\lambda = \lambda_c = Z$, $\mu^{TF} = 0$ and

$$\gamma\, \rho^{TF}(x)^{2/3} = \phi^{TF}(x), \text{ all } x. \tag{2.10}$$

For $\lambda > \lambda_c$ we define $\rho^{TF}(x)$, $\phi^{TF}(x)$, and μ^{TF} by their values at $\lambda = Z$. Thus, the TF density is defined uniquely for all electron numbers, λ.

F2. The $Z \to \infty$ Limit. Fix $\underline{z}^o$, $\underline{R}^o$, and $\lambda > 0$ and consider the following scaling as N(= integral electron number) $\to \infty$.

$$\text{Let } a_N = N/\lambda\ , \tag{2.11}$$

$$z_j = a_N z_j^o\ , \tag{2.12}$$

$$R_j = a_N^{-1/3} R_j^o,\ (j=1,\ldots,k)\ . \tag{2.13}$$

[Note: Eq.(2.13) can be replaced by $R_j = R_j^o$, in which case we will have isolated atoms as $N \to \infty$.] Take $\gamma = \gamma_p$ in Eq.(2.4) and let $E^{TF}(N,\underline{z},\underline{R})$ denote the

TF energy, Eq.(2.7), with $\int\rho = N$. Likewise, let $\rho^{TF}(N,\underline{z},\underline{R},x)$ denote the TF density. Then

$$\lim_{N\to\infty} a_N^{-7/3}\, E^Q(N,\underline{z},\underline{R}) = \lim_{N\to\infty} a_N^{-7/3} E^{TF}(N,\underline{z},\underline{R})$$

$$= E^{TF}(\lambda,\underline{z^o},\underline{R^o}) \ , \qquad (2.14)$$

$$\lim_{N\to\infty} a_N^{-2}\, \rho^Q(N,\underline{z},\underline{R},a_N^{-1/3}x) = \lim_{N\to\infty} a_N^{-2}\, \rho^{TF}(N,\underline{z},\underline{R},a_N^{-1/3}x)$$

$$= \rho^{TF}(\lambda,\underline{z^o},\underline{R^o},x). \qquad (2.15)$$

This was proved in Ref. 7. The last equalities in Eqs.(2.14) and (2.15) are consequences of the fact that there is a simple scaling in TF theory, namely that $a_N^{-7/3}\, E^{TF}(N,\underline{z},\underline{R})$ and $a_N^{-2}\, \rho^{TF}(N,\underline{z},\underline{R},a_N^{-1/3}x)$ are independent of N. Equations(2.14) and (2.15) state that TF theory (with $\gamma = \gamma_p$) is exact to leading order as Z and N go to infinity with the ratio N/Z fixed. It is important to note that neutrality is not essential for this.

Thus, the leading term in the quantum energy is proportional to $z^{7/3}$ (or $N^{7/3}$). For a neutral atom ($\lambda = z$),

$$E^{TF} = -\, 3.67874\, z^{7/3}/\gamma. \qquad (2.16)$$

The obvious question to ask is "What is the next term in E^Q after the principal (or TF) term?" This is where TFW theory, and ultimately Eq.(1.1), enters.

C. Thomas-Fermi-von Weizsäcker Theory

The TFW energy functional is

$$\mathcal{E}^{TFW}(\rho) = A\delta \int[\nabla\rho^{1/2}(x)]^2 dx + E^{TF}(\rho), \qquad (2.17)$$

where $A > 0$ is an adjustable constant. The additional hypothesis that $\rho^{1/2} \in H^1$ must be made. $E^{TFW}(\lambda)$ is defined in analogy with Eq.(2.6). The important facts about TFW theory[5,8] are the following.

F3. Existence and Uniqueness of a Minimum. There is a minimizing ρ for $\mathcal{E}^{TFW}(\rho)$, with $\int\rho = \lambda$, if and only if $\lambda \leq \lambda_c$. The value of λ_c is not known, but it is known that $Z < \lambda_c < 2Z$, even for a molecule. This ρ is unique and satisfies the TFW equation [wherein $(\psi^{TFW})^2 = \rho^{TFW}$]:

$$\{ - A\delta\Delta + W(x) \} \psi^{TFW}(x) = -\mu \psi^{TFW}(x) , \tag{2.18}$$

where

$$W(x) = \gamma \rho^{TFW}(x)^{2/3} - V(x) + \int\rho^{TFW}(y)|x-y|^{-1}dy \tag{2.19}$$

and $\mu \geq 0$, with $\mu = 0$ for $\lambda = \lambda_c$. Conversely, Eqs.(2.18) and (2.19) have a unique solution pair (ψ,μ) under the conditions that $\psi(x) \geq 0$, $\psi^2 = \rho$, $\int\rho = \lambda$, and $\psi \in H^1$. For $\lambda > \lambda_c$, we define ρ^{TFW} to be its value at λ_c.

F4. The $Z \to \infty$ Limit. The scaling is the same as before, Eqs.(2.11), (2.12), and (2.13). For large N (or Z) and fixed λ and γ,

$$E^{TFW}(N,\underline{z},\underline{R}) = E^{TF}(N,\underline{z},\underline{R}) + D^{TFW} \sum_{j=1}^{k} z_j^2 + o(N^2), \tag{2.20}$$

where D^{TFW} is a constant that depends only on $A\delta$ and γ. The last term in Eq.(2.20) means that $o(N^2)/N^2 \to 0$ as $N \to \infty$. The significance of Eq.(2.20) is the following. The first term, E^{TF}, depends on $\lambda = Z^oN/Z$ and on the configuration of the nuclei in the molecule. It is independent of A, of course. It is strictly proportional to $N^{7/3}$ with our scaling. The second term (which is proportional to N^2) can be said to be a "core effect" because it has the following properties.

P1. It is independent of $\lambda = Z^{o}N/Z$, provided $\lambda > 0$.

P2. It is additive over a molecule, that is, it is a sum of terms corresponding to each atom in the molecule.

P3. The constant, D^{TFW}, does not change if the electron-electron repulsion is removed. Suppose that in Eq.(2.1), the term $\Sigma\ |x_i - x_j|^{-1}$ is deleted. We would then have the Bohr atom, and $E^{Q}(N)$ would be easy to evaluate simply by summing the single particle energies (for an atom, these energies are known explicitly: $-z^2(4\delta n^2)^{-1}$, $n = 1,2,\ldots$). Correspondingly, we would remove the electron-electron repulsion J from $\mathcal{E}^{TF}$. $E^{TF}(\lambda,\underline{z},\underline{R})$ would change (one change being that $\lambda_c = \infty$ in this case), but the limit theorem, Eqs.(2.14) and (2.15), would still be true (with $\gamma = \gamma_p$, of course). The constant D^{TFW} in Eq.(2.20) would not change. All of this is proved by Lieb.[5]

Two obvious questions arise.

Q1. Is the TFW correction to TF theory, given by Eq.(2.20), the same as the quantum correction? In other words, is it true that

$$E^{Q}(N,\underline{z},\underline{R}) = E^{TF}(N,\underline{z},\underline{R}) + D^{Q} \sum_{j=1}^{k} z_j^2 + o(N^2) \qquad (2.21)$$

for some D^{Q}? A similar question can be asked about the relationship between the TFW and the Q corrections to the density, $\rho(x)$.

Q2. What is the value of $D^{TFW}(A,\gamma)$?

These questions can be replied to as follows.

R1. The leading term in $E^{Q} - E^{TF}$ is not known. However, in 1952, Scott[9] conjectured that Eq.(2.21) is true and that property (P3) is satisfied. If this is correct, and it is widely believed to be so, then D^{Q} can be calculated by using (P3) and considering an atom without electron-electron repulsion. For this Bohr atom, E^{Q} and E^{TF} can be evaluated (Ref. 10, p.560), and one finds that

$$D^{Q} = q/8\delta \qquad (2.22)$$

if the Scott conjecture is correct. Hartree-Fock studies[11,12] corroborate Eq.(2.22). In fact, the right side of Eq.(2.21) without the $o(N^2)$ term and with

Eq.(2.22) agrees remarkably well with E^Q (in the Hartree-Fock approximation) for neutral atoms with z down to about 10.

R2. To calculate D^{TFW}, we can remove the electron-electron repulsion [using (P3)], and we can take $\lambda = \infty$ [using (P1)], and we can restrict our attention to an atom [using (P2)]. Equation(2.18) then becomes

$$-A\delta\Delta\psi(x) + [\gamma\rho(x)^{2/3} - z/|x|]\,\psi(x) = 0 \tag{2.23}$$

with $\rho = \psi^2$. In other words, we claim that the TFW energy of this ψ minus the TF energy of an atom (without electron-electron repulsion and with $\lambda = \infty$) is $D^{TFW}z^2$. For this modified TF problem, $\gamma\rho^{TF}(x)^{2/3} = z/|x|$. Both the TFW and TF energies are infinite but the difference is finite, namely

$$F(z,\gamma,A\delta,\psi) = A\delta\int(\nabla\psi)^2 + \int\{\tfrac{3}{5}\gamma\psi(x)^{10/3} - z\psi^2(x)/|x| + \tfrac{2}{5}\gamma(Z/\gamma|x|)^{5/2}\}dx \ . \tag{2.24}$$

[Note that $\frac{3}{5}\gamma\rho^{TF}(x)^{5/3} - Z\rho^{TF}(x)/|x| = \frac{2}{5}\gamma(Z/\gamma|x|)^{5/2}$ in this case.] We shall soon see that $F(z,\gamma,A\delta,\psi)$ is precisely Dz^2, and it has no lower order terms.

The assertion that D^{TFW} is obtained by solving Eq.(2.23) and inserting the result in Eq.(2.24) is proved by Lieb.[5] A further assertion about the correction to the TFW density is also given in Ref. 5. This information is summarized in (R3).

R3. To leading order in N (or Z), ρ^Q and ρ^{TF} agree, and they both have a length scale $Z^{-1/3}$ and an amplitude scale Z^2. This is the content of Eq.(2.15). However, at each nucleus, $\rho^{TF}(x)$ is infinite.

ρ^{TFW} also agrees with ρ^{TF} to leading order. The leading order correction in TFW theory occurs on a scale length Z^{-1} near each nucleus and the "correction" consists in the fact that ρ^{TFW} is finite instead of infinite. This can be precisely stated as follows.

Let $\rho^{TFW} = (\psi^{TFW})^2$, with ψ^{TFW} being the positive solution to Eq.(2.18). Then ρ^{TFW} satisfies an equation similar to Eq.(2.15) for ρ^Q, namely

$$\lim_{N\to\infty} a_N^{-2}\ \rho^{TFW}(N,\underline{z},\underline{R},a_N^{-1/3}x) = \rho^{TF}(\lambda,\underline{z}^o,\underline{R}^o,x). \tag{2.25}$$

This holds for any fixed γ and A.

Now let ψ be the solution to Eq.(2.23) and $\rho = \psi^2$. Fix $y \in \mathbb{R}^3$. Then for all fixed γ and A,

$$\lim_{N\to\infty} z_j^{-3}\ \rho^{TFW}(N,\underline{z},\underline{R},R_j + z_j^{-1}y) = \rho(y). \tag{2.26}$$

In other words, the significance of Eq.(2.23) is that it gives the finite TFW density on a scale length z_j^{-1} near each nucleus in a molecule.

Remark: If the Dirac "exchange correction," $-c\int\rho^{4/3}$, is added to $\mathcal{E}^{TFW}$ it will not affect Eqs.(2.20),(2.25), and (2.26). See Ref. 5. Exchange effects are $O(Z^{5/3})$, not $O(Z^2)$.

What about the quantum density, ρ^Q? A conjecture of Heilmann and Lieb[5] is that an equation similar to Eq.(2.26) holds, namely,

$$\lim_{N\to\infty} z_j^{-3}\ \rho^{Q}(N,\underline{z},\underline{R},R_j + z_j^{-1}y) = \rho^{H}(y)\quad , \tag{2.27}$$

where ρ^H is the density of a quantum Bohr atom with $z = 1$ and infinitely many electrons. This is

$$\rho^H(y) = q \sum_{n,\ell,m} f_{n\ell m}(y)^2\quad , \tag{2.28}$$

where the $f_{n\ell m}$ are all the normalized bound state wave functions of the hydrogen atom with the usual Hamiltonian

$$H = -\delta\Delta - 1/|x|. \tag{2.29}$$

This conjecture about the density, Eq.(2.27), supplements the Scott conjecture, Eqs.(2.21) and (2.22).

In passing, some properties of ρ^H can be mentioned. (1) $\rho^H(y)$ is a function only of $r = |y|$. It is monotone decreasing and displays very little "shell structure." (2) For large $r = |y|$,

$$\rho^H(y) \sim (\gamma_p r)^{-3/2}. \tag{2.30}$$

(Note that the right side is proportional to q.) Thus, $z^3 \rho^H(zx)$ agrees with $\rho^{TF}_{atom}(x)$ for $1 \ll z|x| \ll z^{2/3}$. (3) For $y = 0$, only S-waves contribute in Eq.(2.28). Because $f_{n00}(0)^2 = (8\pi\delta^3 n^3)^{-1}$,

$$\delta^3 q^{-1} \rho^H(0) = \zeta(3)/8\pi = 0.047828325. \tag{2.31}$$

This brief discussion of TF and TFW theories has led us to the following conclusion. The chief effect of the von Weizsäcker correction [the first term on the right side of Eq.(2.17)], both with regard to the energy and the density, is contained in the solution to Eq.(2.23). These corrections parallel what is believed to be the case for Q theory. In the next section, it will be shown that a simple change of variables converts Eq.(2.23) into our starting point--namely, Eq.(1.1).

Anticipating Sec. IV, our main numerical result is the following. With $\gamma = \gamma_p$, A can be chosen so that either D^{TFW} agrees with Eq.(2.22), or it can be chosen so that the right side of Eq.(2.26) agrees with $\rho^H(0)$, Eq.(2.31). For the former

$$A = 0.1859019 \text{ (energy agreement)}. \tag{2.32}$$

For the latter

$$A = 0.4797529 \text{ (density agreement)}. \tag{2.33}$$

von Weizsäcker's original choice[4] was A = 1. Yonei and Tomishima[1] advocated A ≃ 0.2 for z larger than 25, which is close to the value in Eq.(2.32). Kirshnits[13] obtained A = 1/9, assuming a weak perturbing potential (which is not the case for the Coulomb field near a nucleus).

III. PROPERTIES OF EQS. (1.1) AND (2.23)

A. Scaling Properties of Eq.(2.23)

Denote a solution to Eq.(2.23) by $\psi(z,\gamma,A\delta,x)$ and a solution to Eq.(1.1) simply by $\psi(x)$. The two are related by

$$\psi(z,\gamma,A\delta,x) = (z^2/A\delta\gamma)^{3/4}\ \psi(zx/A\delta). \tag{3.1}$$

The densities (namely ψ^2) are related by

$$\rho(z,\gamma,A\delta,x) = z^3\ (A\delta\gamma)^{-3/2}\ \rho(zx/A\delta). \tag{3.2}$$

Define the functional

$$F(\psi) = \int(\nabla\psi)^2 + \int\{\frac{3}{5}\psi(x)^{10/3} - |x|^{-1}\psi^2(x) + \frac{2}{5}\ |x|^{-5/2}\}dx\ . \tag{3.3}$$

The relation between the functional Eqs.(2.24) and (3.3) is, with the scaling Eq.(3.1),

$$\begin{aligned}\Delta E &= F\{z,\gamma,A\delta,(z^2/A\delta\gamma)^{3/4}\psi[z/A\delta)\ \cdot\ ]\} \\ &= z^2(A\delta)^{1/2}\gamma^{-3/2}F[\psi(\cdot)]\ .\end{aligned} \tag{3.4}$$

Note that if we take $\gamma = \gamma_p$, then

$$z^2(A\delta)^{1/2}\gamma_p^{-3/2} = z^2(q/\delta)[A^{1/2}(6\pi^2)^{-1}]. \tag{3.5}$$

Thus,

$$\Delta E = z^2 D \quad , \tag{3.6}$$

and D has the same dependence on the physical parameters q and δ as does D^Q in Eq.(2.22). The fact that $\Delta E \sim z^2$ justifies the claim made after Eq.(2.24).

Our analysis thus simplifies to the study of Eq.(1.1) and the functional F of Eq.(3.3).

B. The Functional F

A word of caution must be said about the last integral, $\int\{\}$, in Eq.(3.3). For the ψ of interest, the three separate terms in $\{\}$ are not integrable, but the sum is integrable.

For any real ψ, not necessarily ≥ 0, let

$$k(\psi,x) = \frac{3}{5}|\psi|^{10/3} - |x|^{-1}\,\psi^2 + \frac{2}{5}|x|^{-5/2} \quad , \tag{3.7}$$

and for any real valued function $\psi(x)$,

$$W(\psi) = \int k(\psi(x), x)dx. \tag{3.8}$$

Note that

$$k(\psi,x) \geq 0 \tag{3.9}$$

and

$$k(\psi,x) = 0 \iff \psi = |x|^{-3/4} \quad . \tag{3.10}$$

Thus, $W(\psi)$ is always well defined, although it may be $+\infty$.

Let us introduce the class of real valued functions

$$G = \{\psi \mid \nabla\psi \in L^2,\ F(\psi) < \infty\}. \tag{3.11}$$

If $\rho(x) \geq 0$, we say $\rho \in G'$ if and only if $\rho^{1/2} \in G$. It is clear from Eq.(3.10) that if $W(\psi) < \infty$, then essentially $\psi(x) \sim |x|^{-3/4}$ for large $|x|$; hence, ψ cannot be in L^2. Thus,

$$\int \rho = \infty \quad \text{if } \rho \in G'. \tag{3.12}$$

Because $F(\psi) \geq 0$, we can ask for its infinium, that is,

$$\Delta E \equiv \inf \{F(\psi) \mid \psi \in G\} \quad . \tag{3.13}$$

Clearly, the formal equation $\delta F/\delta\psi = 0$ is Eq.(1.1).

The following facts can be proved about this minimization problem.[6]

(1) There is a unique ψ that minimizes $F(\psi)$. This $\psi(x)$ is positive for all x and it satisfies Eq.(1.1).

(2) There is precisely one nontrivial solution, ψ, to Eq.(1.1) on $\mathbb{R}^3$ [even if Eq.(1.1) is interpreted in the sense of distributions] with the property that $\psi(x) \geq 0$, all x.

C. Properties of ψ

Henceforth we refer to the unique, positive solution, ψ and $\rho = \psi^2$, mentioned above. The details are in Ref. 6.

(1) Because ψ is unique, it is necessarily spherically symmetric. It is also a monotone decreasing function of $r = |x|$.

(2) ψ is real analytic for $|x| > 0$ and ψ is continuous at $x = 0$.

(3) ψ satisfies the cusp condition[14] at $x = 0$, namely

$$2\,(d\psi/dr)\,(0) = \psi(0). \tag{3.14}$$

$\psi(0)$ is finite.

(4) For large $r = |x|$, ψ has the asymptotic expression

$$\psi(r) = r^{-3/4} - \frac{9}{64}\, r^{-7/4} - \frac{1323}{8192}\, r^{-11/4} + O(r^{-15/4}). \tag{3.15}$$

$$\rho(r) = r^{-3/2} - \frac{9}{32}\, r^{-5/2} - \frac{621}{2048}\, r^{-7/2} + O(r^{-9/2}). \tag{3.16}$$

(5) For all r, $\psi(r) < r^{-3/4}$.

D. Sum Rules

In view of the asymptotic expansion [Eqs.(3.15) and (3.16)], the following integrals are well defined.

$$I_1 = \int(\nabla\psi)^2 = 4\pi \int_0^\infty (d\psi(r)/dr)^2\, r^2 dr = 4\pi \int_0^\infty (d(r\psi(r))/dr)^2\, dr. \tag{3.17}$$

$$I_2 = \int\{|x|^{-5/2} - \rho(x)^{5/3}\}dx = 4\pi \int_0^\infty\{r^{-1/2} - r^2\rho(r)^{5/3}\}dr. \tag{3.18}$$

$$I_3 = \int[\,|x|^{-3/2} - \rho(x)]\;|x|^{-1}dx = 4\pi\int_0^\infty\{r^{-1/2} - r\rho(r)\}dr. \tag{3.19}$$

$$I_4 = \int\{-\rho(x) + |x|^{-3/2} - \frac{9}{32}|x|^{-5/2}\}dx$$

$$= 4\pi\int_0^\infty\{-r^2\rho(r) + r^{1/2} - \frac{9}{32}r^{-1/2}\}dr. \qquad (3.20)$$

Apart from the scaling, Eq.(3.1), I_1 is the contribution of the von Weizsäcker term; $-(3/5)\ I_2$ is the change in the TF kinetic energy, namely $(3\gamma/5)\int\rho^{5/3}$ [note that $\rho^{TF}(r) = r^{-3/2}$ in our units]; and I_3 is the change in the attractive Coulomb energy. Note that to $O(z^2)$, there is no change in the electron-electron repulsion, $J(\rho,\rho)$, which is consistent with property (P3). I_4 is related to the change in the electron number.

If Eq.(1.1) is multiplied by ψ and integrated, the first sum rule is obtained:

$$I_1 + I_3 = I_2. \qquad (3.21)$$

The second sum rule is a "virial theorem," although the coefficients are different from the usual virial theorem:

$$5I_1 + 3I_2 = 5I_3. \qquad (3.22)$$

This is a virial theorem because it is derived by scaling as follows. Given ψ, let $\phi(t,x) \equiv t^{3/4}\ \psi(tx)$, where t is a positive parameter. $F(\psi)$ has its minimum at $t = 1$, whence $[dF(\psi)/dt](1) = 0$. The result is Eq.(3.22). Note that the fact that Eq.(1.1) comes from minimizing F plays a critical role in this derivation. It is difficult to deduce Eq.(3.22) directly from Eq.(1.1).

Combining Eqs.(3.21) and (3.22) yields

$$I_1 : I_2 : I_3 = 1 : 5 : 4\ . \qquad (3.23)$$

This agrees with the usual virial theorem in the following sense. The change in kinetic energy, ΔT, is $I_1 - 3I_2/5$. The change in potential energy, ΔV, is I_3. Then

$$2\Delta T = -\Delta V \tag{3.24}$$

as usual.

Another consequence of Eq.(3.23) is

$$\Delta E \equiv F(\psi) = I_1 - \frac{3}{5}I_2 + I_3 = 2I_1 \quad . \tag{3.25}$$

From this it follows that if we want to have $D^{TFW} = D^Q$, then, using Eq.(3.4) and $\gamma = \gamma_p$, we get

$$A^{1/2}\, qI_1/3\pi^2\delta = D^Q \quad . \tag{3.26}$$

If D^Q is given by Eq.(2.22), then $A = (3\pi^2/8I_1)^2$. This leads to Eq.(2.32). If we want to have $\rho(0) = \rho^H(0)$, then

$$\psi(0)^2/6\pi^2\, A^{3/2} = \zeta(3)/8\pi \quad . \tag{3.27}$$

This leads to Eq.(2.33).

IV. NUMERICAL SOLUTION OF EQ.(1.1)

We want the spherically symmetric solution that is finite at $r = 0$, that is positive everywhere, and that approaches $r^{-3/4}$ for large r.

Usual numerical methods result in difficulties because Eq.(1.1) has a movable singularity: that is, near every radius r_0, there is a solution that behaves like $c|r-r_0|^{-3/2}$ as $r \to r_0$. Efforts to integrate the differential equation numerically result in solutions that show this behavior.

We have turned to a variational method to obtain a solution of good accuracy. It consists in treating Eq.(1.1) differently in different regions and then optimizing the solution with respect to three parameters at our disposal.

For the first region, we use a solution of Eq.(1.1) obtained with an accurate differential equation integrating routine.[15]

$$\psi_1(r) = \psi_0 , \qquad r = 0 ; \tag{4.1}$$

$$\psi(r) = \psi_1(r) , \qquad 0 \leq r \leq R_1. \tag{4.2}$$

Beyond some large radius, R_2, we use the asymptotic form, Eq.(3.15),

$$\psi(r) = \psi_2(r) = r^{-3/4}(1 + C_1/r + C_2/r^2) , \quad R_2 \leq r < \infty , \tag{4.3}$$

where

$$C_1 = -\frac{9}{64} \text{ and } C_2 = -\frac{1323}{8192} . \tag{4.4}$$

In the region between R_1 and R_2, we pass smoothly from the numerical solution ψ_1 to the asymptotic solution by choosing

$$\psi(r) = [\psi_1(r)(R_2 - r) + \psi_2(r)(r - R_1)]/(R_2 - R_1),$$
$$R_1 \leq r \leq R_2. \tag{4.5}$$

Note that $\psi_1(r)$, the numerical solution, is needed in the region $R_1 \leq r \leq R_2$ as well as for $r < R_1$. The three parameters ψ_0, R_1, and R_2 are adjusted to minimize the functional $F(\psi)$ defined by Eq.(3.3).

It was stated above that the solution to Eq.(1.1) minimizes this functional. Our numerical solution achieves a minimum for $F(\psi)$ when the parameters are

$$\psi_0 = 0.9701330 ,$$

$$R_1 = 18 \quad , \text{ and} \tag{4.6}$$

$$R_2 = 33 \quad .$$

At this minimum, we obtain $\Delta E = F(\psi) = 2I_1$ and

$$I_1 = 8.58381 \quad ,$$

$$I_2/I_1 = 4.9998 \quad ,$$

$$I_3/I_1 = 3.9999 \quad , \text{ and} \tag{4.7}$$

$$I_4 = -16.73 \quad .$$

Recall that for the exact solution $I_2/I_1 = 5$ and $I_3/I_1 = 4$. Table I gives $\psi(r)$ for r between 0 and 33. Up to r = 18, $\psi(r)$ is $\psi_1(r)$, the solution obtained from the numerical solution of the differential equation; from r = 18 to r = 33, it is the combination of $\psi_1(r)$ and the asymptotic solution $\psi_2(r)$ given by Eq.(4.5). $\psi(r)$ is shown in Fig. 1 together with the difference $\psi_2(r) - \psi_1(r)$. The radial density $4\pi r^2\rho(r)$, where $\rho(r) = \psi^2(r)$, is shown in Fig. 2. From the value of I_1 and formula (3.26), the value of the von Weizsäcker coefficient, A, given in Eq.(2.32) is obtained.

Table I. Numerical Solution of the TFW Equation.

r	$\psi(r)$	r	$\psi(r)$
0.0	0.970133	6.5	0.23691
0.1	0.92388	7.0	0.22499
0.2	0.88176	7.5	0.21435
0.3	0.84325	8.0	0.20478
0.4	0.80792	8.5	0.19613
0.5	0.77541	9.0	0.18827
0.6	0.74540	9.5	0.18109
0.7	0.71763	10.0	0.17451
0.8	0.69185	10.5	0.16846
0.9	0.66788	11.0	0.16286
1.0	0.64553	11.5	0.15768
		12.0	0.15286
1.2	0.60508		
1.4	0.56950	13.0	0.14416
1.6	0.53796	14.0	0.13653
1.8	0.50984	15.0	0.12978
2.0	0.48461	16.0	0.12375
2.2	0.46186	17.0	0.11833
2.4	0.44124	18.0	0.11344
2.6	0.42248	19.0	0.10899
2.8	0.40534	20.0	0.10493
3.0	0.38961	21.0	0.10120
3.5	0.35547	23.0	0.09459
4.0	0.32720	25.0	0.08891
4.5	0.30341	27.0	0.08396
5.0	0.28313	29.0	0.07961
5.5	0.26562	31.0	0.07576
6.0	0.25035	33.0	0.07231

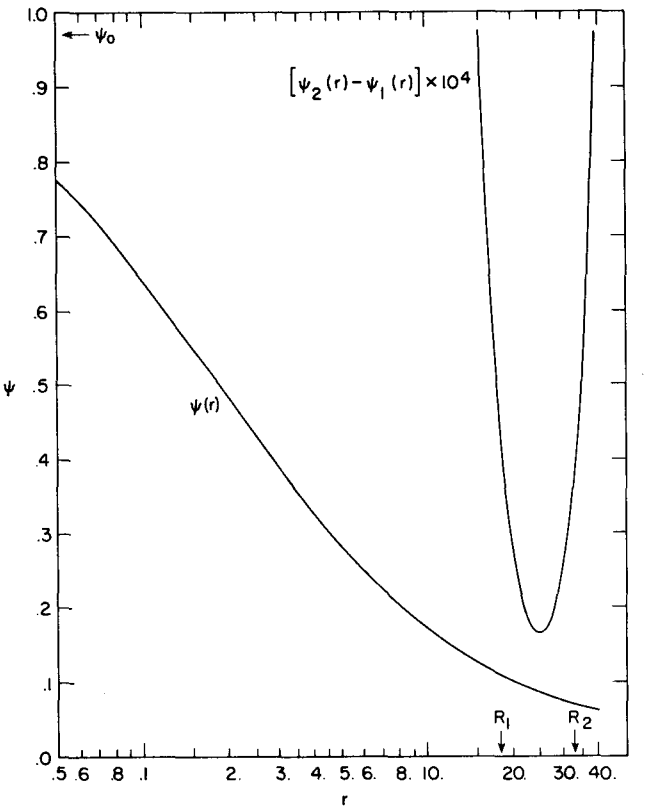

Fig.1

The TFW function $\psi(r)$. Also shown is the difference between the asymptotic expansion, $\psi_2(r)$, and the numerical solution of the differential equation in the range where both are used.

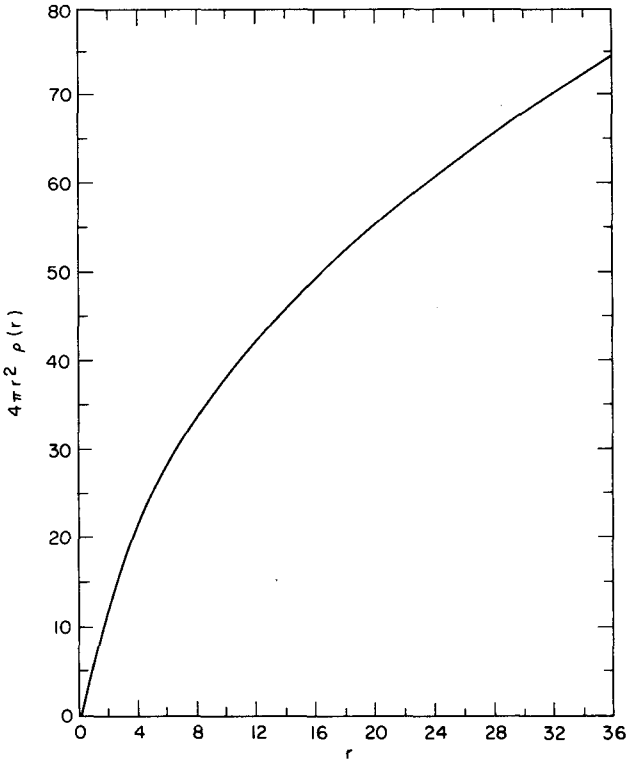

Fig.2

The radial density distribution $4\pi r^2 \rho(r)$.

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