

A Brief Review of Thomas-Fermi Theory

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1 Introduction

It is a great pleasure for me to have the opportunity to contribute to this collection of articles dedicated to Larry Spruch, for many years a friend and colleague . The editor, Ben Bederson, asked me to write about Thomas-Fermi theory because that is one of the subjects Larry and I both find interesting. Larry's review article [SL] is a gem of clear, pedagogical scientific writing and I am afraid the present essay will not reach that level. Also, Larry, together with Mueller and Rau [MRS] was one of the pioneers of the use of Thomas-Fermi type theories to understand atoms in ultra-large magnetic fields. It is, therefore, a good opportunity to try to review the older theory and bring together some recent developments and extensions of the ideas that Thomas and Fermi pioneered about three quarters of a century ago

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and which are still actively pursued to the present day. Some of the newer developments, mentioned in section 5, are, in fact, concerned with atoms in large magnetic fields. This and other aspects of Thomas-Fermi theory are not finished subjects, of course, and I hope Larry will continue to contribute his important insights into these problems.

2 Formulation of Thomas-Fermi Theory

Sometimes called the ‘statistical theory’, it was invented by L. H. Thomas[TH] and E. Fermi [EF], shortly after Schrödinger invented his quantum-mechanical wave equation, in order to describe, approximately, the *electron density*, $\rho(\mathbf{x})$, $\mathbf{x} \in \mathbb{R}^3$, and the *ground state energy*, $E(N)$ for a large atom or molecule with a large number, N , of electrons. Schrödinger’s equation, which would give the exact density and energy, cannot be easily handled when N is large. It has to be remembered that most of the time, in ordinary matter, atoms and molecules are in, or close to their ground states. Therefore, it is of central importance to learn as much as possible about the properties of the ground state and Thomas-Fermi (TF) theory is a remarkably good guide in many respects.

A starting point for the theory is the *TF energy functional*. For a molecule with K nuclei of charges $Z_i > 0$ and *fixed* locations $\mathbb{R}_i \in \mathbb{R}^3$ ($i = 1, \dots, K$), it is

$$\begin{aligned} \mathcal{E}(\rho) := & \frac{3}{5} \frac{\hbar^2}{2m} (3\pi^2)^{2/3} \gamma \int_{\mathbb{R}^3} \rho(\mathbf{x})^{5/3} d^3\mathbf{x} - \int_{\mathbb{R}^3} V(\mathbf{x})\rho(\mathbf{x}) d^3\mathbf{x} \\ & + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(\mathbf{x})\rho(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} d^3\mathbf{x}d^3\mathbf{y} + U \end{aligned} \quad (2.1)$$

in suitable units ($e^2 = 1$). Here,

$$\begin{aligned}
V(\mathbf{x}) &= \sum_{j=1}^K Z_j |\mathbf{x} - \mathbf{R}_j|^{-1}, \\
U &= \sum_{1 \leq i < j \leq K} Z_i Z_j |\mathbf{R}_i - \mathbf{R}_j|^{-1},
\end{aligned}$$

and $\gamma = (3\pi^2)^{2/3} \hbar^2 / 2m$. The constraint on $\rho(\mathbf{x})$ is $\rho(\mathbf{x}) \geq 0$ and $\int_{\mathbb{R}^3} \rho = N$. The functional $\rho \rightarrow \mathcal{E}(\rho)$ is convex.

The justification for this TF functional is this:

- The first term is roughly the minimum quantum-mechanical kinetic energy of N electrons needed to produce an electron density $\rho(\mathbf{x})$. The fact that electrons are fermions is crucial here. This minimum energy is, in fact, the semiclassical energy and is known to be exact in the limit where the shape of $\rho(\mathbf{x})$ is fixed and N goes to ∞ . The first term is also conjectured [LT] to be a lower bound to the electronic kinetic energy when the density is $\rho(\mathbf{x})$.
- The second term is the attractive interaction of the N electrons with the K nuclei, via the Coulomb potential V .
- The third term is approximately the electron-electron repulsive energy.
- U is the nuclear-nuclear repulsion. While it is a constant, it is an important constant because it determines whether or not binding can occur, i.e., whether or not the energy can be lowered by moving the nuclei far apart from each other.

The *TF energy* is defined to be

$$E^{\text{TF}}(N) = \inf \{ \mathcal{E}(\rho) : \rho \in L^{5/3}(\mathbb{R}^3), \int_{\mathbb{R}^3} \rho = N, \rho(\mathbf{x}) \geq 0 \},$$

i.e., the TF energy and density is obtained by minimizing $\mathcal{E}(\rho)$ with $\int_{\mathbb{R}^3} \rho^{5/3}(\mathbf{x}) d^3x < \infty$ and $\int_{\mathbb{R}^3} \rho(\mathbf{x}) d^3x = N$. The *Euler-Lagrange equation*, called the *Thomas-Fermi equation*, is

$$\gamma \rho(\mathbf{x})^{2/3} = [\Phi(\mathbf{x}) - \mu]_+, \quad (2.2)$$

where $[a]_+ \equiv \max\{0, a\}$, $-\mu$ is some constant (*Lagrange multiplier = chemical potential*) and Φ is the *TF potential*:

$$\Phi(\mathbf{x}) = V(\mathbf{x}) - \int_{\mathbb{R}^3} |\mathbf{x} - \mathbf{y}|^{-1} \rho(\mathbf{y}) \, d^3\mathbf{y}. \quad (2.3)$$

The $[\]_+$ in (2.2) is essential. Usually it is omitted. It is only in the neutral case with $\mu = 0$ that the $[\]_+$ is not needed because the right side is never negative in that case. (See below).

The following essential mathematical facts about the TF equation were established in [LS] (*cf.* also the review articles [EL], [SL] and the book [LL]).

1. There is a density $\rho_N^{\text{TF}}(\mathbf{x})$ that minimizes $\mathcal{E}(\rho)$ *if and only if* $N \leq Z := \sum_{j=1}^K Z_j$. This $\rho_N^{\text{TF}}(\mathbf{x})$ is unique and it satisfies the TF equation (2.2) for some $\mu \geq 0$. Every positive solution, $\rho(\mathbf{x})$, of (2.2) is a minimizer of (2.1) for $N = \int_{\mathbb{R}^3} \rho$. If $N > Z$ then $E^{\text{TF}}(N) = E^{\text{TF}}(Z)$ and any minimizing sequence converges weakly in $L^{5/3}(\mathbb{R}^3)$ to $\rho_Z^{\text{TF}}(\mathbf{x})$.
2. $\Phi(\mathbf{x}) \geq 0$ for all \mathbf{x} . (This *need not be so* for the real Schrödinger $\rho(\mathbf{x})$ in an atom.)
3. $\mu = \mu(N)$ is a strictly monotonically decreasing function of N and $-\mu(Z) = 0$ (the *neutral case*). $-\mu$ is the *chemical potential*, namely

$$-\mu(N) = \frac{\partial E^{\text{TF}}(N)}{\partial N}.$$

$E^{\text{TF}}(N)$ is a strictly convex, decreasing function of N for $N \leq Z$ and $E^{\text{TF}}(N) = E^{\text{TF}}(Z)$ for $N \geq Z$. If $N < Z$, $\rho_N^{\text{TF}}(\mathbf{x})$ has compact support.

When $N = Z$, (2.1) becomes $\gamma \rho^{2/3}(\mathbf{x}) = \Phi(\mathbf{x})$. By applying the Laplacian ∇^2 to both sides we obtain

$$-\nabla^2 \Phi(\mathbf{x}) + 4\pi\gamma^{-3/2} \Phi(\mathbf{x})^{3/2} = 4\pi \sum_{j=1}^K Z_j \delta(\mathbf{x} - \mathbf{R}_j),$$

which is the form in which the TF equation is usually stated (but it is valid only for $N = Z$).

An important property of the solution is *Teller's theorem* [ET] (proved rigorously in [LS]) which implies that the TF molecule is always unstable for $K > 1$, i.e., for each $N \leq Z$ there are K numbers $N_j \in (0, Z_j)$ with $\sum_j N_j = N$ such that

$$E^{\text{TF}}(N) > \sum_{j=1}^K E_{\text{atom}}^{\text{TF}}(N_j, Z_j), \quad (2.4)$$

where $E_{\text{atom}}^{\text{TF}}(N_j, Z_j)$ is the TF energy with $K = 1, Z = Z_j$ and $N = N_j$. The presence of U in (1) is crucial for this result. The inequality is strict. Not only does $E^{\text{TF}}(N)$ decrease when the nuclei are pulled infinitely far apart (which is what (2.4) says) but any dilation of the nuclear coordinates ($\mathbf{R}_j \rightarrow \ell \mathbf{R}_j, \ell > 1$) will decrease E^{TF} in the neutral case (*positivity of the pressure*) [EL], [BL]. This theorem plays an important role in the stability of matter.

3 Connection with the Schrödinger Equation

To what extent do the Thomas-Fermi predictions correspond to the quantum mechanical quantities they were meant to approximate? Specifically, how close is $E^{\text{TF}}(N)$ to $E^{\text{Q}}(N)$, the ground state energy (= infimum of the spectrum) of the Schrödinger operator, H . (Note: The bottom of the spectrum of H need not be an eigenvalue; it is not an eigenvalue if there are too many electrons, for example. Thus, the infimum need not be a minimum. The same phenomenon happens in TF theory when $N > Z$.)

$$H = \sum_{i=1}^N \left[-\frac{\hbar^2}{2m} \nabla_i^2 + V(\mathbf{x}_i) \right] + \sum_{1 \leq i < j \leq N} |\mathbf{x}_i - \mathbf{x}_j|^{-1} + U \quad (3.1)$$

which acts on the antisymmetric functions $\wedge^N L^2(\mathbb{R}^3; \mathbb{C}^2)$ (i.e., square integrable functions of space and spin). It used to be believed that $E^{\text{TF}}(N)$ is asymptotically

exact as $N \rightarrow \infty$ but this is *not* quite right; $Z \rightarrow \infty$ is also needed. Simon and I proved [LS] (but a simpler proof was given later in [EL]) that if we fix K and fix Z_j/Z and if we set $\mathbf{R}_j = Z^{-1/3} \mathbf{R}_j^0$, with fixed $\mathbf{R}_j^0 \in \mathbb{R}^3$, and if we set $N = \lambda Z$, with $0 \leq \lambda < 1$ then

$$\lim_{Z \rightarrow \infty} E^{\text{TF}}(\lambda Z)/E^{\text{Q}}(\lambda Z) = 1. \quad (3.2)$$

In particular, a simple change of variables shows that

$$E_{\text{atom}}^{\text{TF}}(\lambda, Z) = Z^{7/3} E_{\text{atom}}^{\text{TF}}(\lambda, 1) \quad (3.3)$$

and hence the true energy of a large atom is asymptotically proportional to $Z^{7/3}$.

Likewise, there is a well-defined sense in which the quantum mechanical density converges to $\rho_N^{\text{TF}}(\mathbf{x})$ (cf. [LS]). The TF density for an atom located at $R = 0$, which is spherically symmetric, scales as

$$\begin{aligned} \rho_{\text{atom}}^{\text{TF}}(\mathbf{x}; N = \lambda Z, Z) &= \\ &Z^2 \rho_{\text{atom}}^{\text{TF}}(Z^{1/3} \mathbf{x}; N = \lambda, Z = 1). \end{aligned} \quad (3.4)$$

Thus, a large atom (i.e., large Z) is *smaller* than a $Z = 1$ atom by a factor $Z^{-1/3}$ in radius. Despite this seeming paradox, TF theory gives the correct electron density in a real atom — as far as the bulk of the electrons is concerned — as $Z \rightarrow \infty$.

The same is true of molecules in this theory. If the scaling of the \mathbf{R}_j with Z are as described above then (3.4) still holds.

This fact about the Thomas-Fermi density is mirrored in the true quantum mechanical density, which we can call $\rho^{\text{Q}}(\mathbf{x})$. Here, it might be noted that the ground state density of an atom might not be unique, e.g., as in the case of Carbon, but as $A \rightarrow \infty$ the density $\rho^{\text{Q}}(\mathbf{x})$ has a well defined limit. The differences among the finite system densities are, like the mountains on earth, unobservable on a large scale.

Equation (3.4) tells us that the length scale on which most of the electrons are to be found is $Z^{-1/3}$. The smaller length scale, Z^{-1} is the highly quantum

mechanical region in which the innermost electrons (K-shell, etc.) reside. The Scott correction, which is the most important correction to TF theory, is concerned with this Z^{-1} region. It gives a correction to the energy of order Z^2 . In the Z^{-1} region one expects the density to be the sum of the squares of the hydrogenic bound state wave functions (appropriately scaled by Z^{-1}). Larry and Shakeshaft also investigated this sum [SS]. The precise evaluation is in [HL] and the fact that the sum is, indeed, the correct electron density near the nucleus of a large atom is proved in [LIS].

Another important fact about the TF density is the large $|\mathbf{x}|$ asymptotics of $\rho_{\text{atom}}^{\text{TF}}(\mathbf{x})$ for a neutral atom. As $|x| \rightarrow \infty$,

$$\rho_{\text{atom}}^{\text{TF}}(\mathbf{x}, N = Z, Z) \sim \gamma^3 (3/\pi)^3 |\mathbf{x}|^{-6},$$

independent of Z . Again, this behavior agrees with quantum mechanics — on a length scale $Z^{-1/3}$, which is where the bulk of the electrons are to be found.

In light of the limit theorem (3.4), Teller’s theorem can be understood as saying that as $Z \rightarrow \infty$ the quantum mechanical binding energy of a molecule is of lower order in Z than the total ground state energy. Thus, Teller’s theorem is *not* a defect of TF theory (although it is sometimes interpreted that way) but an important statement about the true quantum mechanical situation.

For finite Z one can show, using the Lieb-Thirring inequality [LT] and the Lieb-Oxford inequality [LO], that $E^{\text{TF}}(N)(\mathbf{x})$, with a modified γ , gives a lower bound to $E^{\text{Q}}(N)(\mathbf{x})$.

4 Some Improvements

Several ‘improvements’ to Thomas-Fermi theory have been proposed, but none have a fundamental significance in the sense of being ‘exact’ in the $Z \rightarrow \infty$ limit. The *von Weizsäcker correction* consists in adding a term

$$(\text{const.}) \int_{\mathbb{R}^3} |\nabla \sqrt{\rho(\mathbf{x})}|^2 d^3\mathbf{x}$$

to $\mathcal{E}(\rho)$. This preserves the convexity of $\mathcal{E}(\rho)$ and adds $(\text{const.})Z^2$ to $E^{\text{TF}}(N)$ when Z is large (just as the Scott corection does). It also has the effect that the range of N for which there is a minimizing $\rho(\mathbf{x})$ is extend from $[0,Z]$ to $[0,Z + (\text{const.}) K]$.

Another correction, the *Dirac exchange energy*, is to add

$$-(\text{const.}) \int_{\mathbb{R}^3} \rho(\mathbf{x})^{4/3} d^3\mathbf{x}$$

to $\mathcal{E}(\rho)$. This spoils the convexity but not the range $[0,Z]$ for which a minimizing $\rho(\mathbf{x})$ exists *cf.* [LS] for both of these corrections.

5 Large External Magnetic Fields

When a uniform external magnetic field \mathbf{B} is present, the operator $-\nabla^2$ in H is replaced by

$$|i\nabla + \mathbf{A}(\mathbf{x})|^2 + \boldsymbol{\sigma} \cdot \mathbf{B} ,$$

with $\text{curl } \mathbf{A}(\mathbf{x}) = \mathbf{B}$ and with $\boldsymbol{\sigma}$ denoting the Pauli spin matrices. This leads to a modified TF theory that was discovered by Yngvason [JY] and which is asymptotically exact as $Z \rightarrow \infty$ in the first three of the five regions cited below. In this theory, one does *not* try to introduce a complex-valued density in imitation of the quantum mechanical $|i\nabla + \mathbf{A}(\mathbf{x})|^2$. Instead, one computes the energy of a free Fermi gas in a constant field B , which then gives a kinetic energy/unit volume $T_B(\rho)$ as a function of B and density ρ . One then uses $T_B(\rho(\mathbf{x}))$ in place of $\rho(\mathbf{x})^{5/3}$ in the Thomas-Fermi energy functional. More complicated TF-like theories are needed in the last two regions.

The five regions depends on the manner in which $B = |\mathbf{B}|$ varies with Z as Z grows. The five distinct regions are: $B \ll Z^{4/3}, B \sim Z^{4/3}, Z^{4/3} \ll B \ll Z^3, B \sim Z^3, \gg Z^3$. These theories [LSY1], [LSY2] are relevant for neutron stars.

Another class of TF theories with magnetic fields is relevant for electrons confined to two-dimensional geometries (quantum dots) [LSY3]. In this case there

are three regimes. A convenient review of all of these magnetic field theories is [LSY4].

Still another modification of TF theory is its extension from a theory of the ground states of atoms and molecules (which corresponds to zero temperature) to a theory of positive temperature states of large systems such as stars (cf. [JM], [WT]).

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