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 approximately describe the electron density, ρ(x), x ∈ R³, 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.

A starting point for the theory is the TF energy functional. For a molecule with K nuclei of charges Zᵢ > 0 and locations Rᵢ ∈ R³ (i = 1, ..., K), it is

\[ E(\rho) := \frac{3}{\pi^2} \gamma \int_{R^3} \rho^{5/3}(x) \, dx - \int_{R^3} V(x)\rho(x) \, dx + \frac{1}{2} \int_{R^3} \int_{R^3} \rho(x)\rho(y) \frac{dx \, dy}{|x - y|} + U \](1)

in suitable units. Here,

\[ V(x) = \sum_{i=1}^{K} Z_i |x - r_i|^{-1}, \]

\[ U = \sum_{1 \leq i < j \leq K} Z_i Z_j |R_i - R_j|^{-1}, \]

and γ = (3π²)²/³. The constraint on ρ is ρ(x) ≥ 0 and \( \int_{R^3} \rho = N \). The functional ρ → E(ρ) is convex.

The justification for this functional is this:

• The first term is roughly the minimum quantum-mechanical kinetic energy of N electrons needed to produce an electron density ρ.

• The second term is the attractive interaction of the N electrons with the K nuclei, via the Coulomb potential V.

• The third is approximately the electron-electron repulsive energy.

• U is the nuclear-nuclear repulsion and is an important constant.

The TF energy is defined to be

\[ E^{TF}(N) = \inf\{E(\rho) : \rho \in L^{5/3}, \int \rho = N, \rho \geq 0\} , \]
i.e., the TF energy and density is obtained by minimizing E(ρ) with ρ ∈ L⁵/³(R³) and \( \int \rho = N \). The Euler-Lagrange equation, called the Thomas-Fermi equation, is

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

where [a]⁺ = max\{0, a\}, μ is some constant (Lagrange multiplier) and Φ is the TF potential:

\[ \Phi(x) = V(x) - \int_{R^3} |x - y|^{-1} \rho(y) \, dy. \]

The following essential mathematical facts about the TF equation were established by E.H. Lieb and B. Simon [LS] (cf. the review article [EL]).

1. There is a density \( \rho^{TF}_N \) that minimizes E(ρ) if and only if N ≤ Z := \( \sum_{j=1}^{K} Z_j \). This \( \rho^{TF}_N \) is unique and it satisfies the TF equation (2) for some μ ≥ 0. Every positive solution, ρ, of (2) is a minimizer of (1) for N = \( \int \rho \). If N > Z then \( E^{TF}(N) = E^{TF}(Z) \) and any minimizing sequence converges weakly in L⁵/³(R³) to \( \rho^{TF}_Z \).

2. \( \Phi(x) ≥ 0 \) for all x. (This need not be so for the real Schrödinger ρ.)

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

\[ \mu(N) = -\frac{\partial E^{TF}(N)}{\partial N} \]

\( E^{TF}(N) \) is a strictly convex, decreasing function of N for N ≤ Z and \( E^{TF}(N) = E^{TF}(Z) \) for N ≥ Z. If N < Z, \( \rho^{TF}_N \) has compact support.

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

\[ -\Delta \Phi(x) + 4\pi \gamma^{-3/2} \Phi(x)^{3/2} = 4\pi \sum_{j=1}^{K} Z_j \delta(x - R_j) , \]

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 \(\square\) (proved rigorously in \(\square\)) which implies that the TF molecule is always unstable, 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

\[
E^{\text{TF}}(N) > \sum_{j=1}^{K} E^{\text{TF}}(N_j, Z_j),
\]

where \(E^{\text{TF}}(N_j, Z_j)\) 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 \(E^{\text{TF}}\) decrease when the nuclei are pulled infinitely far apart (which is what (4) says) but any dilation of the nuclear coordinates \((R_j \to \ell R_j, \ell > 1)\) will decrease \(E^{\text{TF}}\) in the neutral case (positivity of the pressure) \(\square, \square\). This theorem plays an important role in the stability of matter.

An important question concerns the connection between \(E^{\text{TF}}(N)\) and \(E^{Q}(N)\), the ground state energy (= infimum of the spectrum) of the Schrödinger operator, \(H\), it was meant to approximate.

\[
H = -\sum_{i=1}^{N} [\Delta_i + V(x_i)] + \sum_{1 \leq i < j \leq N} |x_i - x_j|^{-1} + U,
\]

which acts on the antisymmetric functions \(\wedge^{N} L^2(\mathbb{R}^3; \mathbb{C}^2)\) (i.e., functions of space and spin). It used to be believed that \(E^{\text{TF}}\) is asymptotically exact as \(N \to \infty\) but this is not quite right; \(Z \to \infty\) is also needed. Lieb and Simon \(\square\) proved that if we fix \(K\) and \(Z_I / Z\) and we set \(R_j = Z^{-1/3} R_j^0\), with fixed \(R_j^0 \in \mathbb{R}^3\), and set \(N = \lambda Z\), with \(0 \leq \lambda < 1\) then

\[
\lim_{Z \to \infty} E^{\text{TF}}(\lambda Z)/E^{Q}(\lambda Z) = 1.
\]

In particular, a simple change of variables shows that \(E^{\text{TF}}_{\text{atom}}(\lambda, Z) = Z^{7/3} E^{\text{TF}}_{\text{atom}}(\lambda, 1)\) and hence the true energy of a large atom is asymptotically proportional to \(Z^{4/3}\). Likewise, there is a well-defined sense in which the quantum mechanical density converges to \(\rho^{\text{TF}}_N\) (cf. \(\square\)).

The TF density for an atom located at \(R = 0\), which is spherically symmetric, scales as

\[
\rho_{\text{atom}}^{\text{TF}}(x; N = \lambda Z, Z) = Z^2 \rho_{\text{atom}}^{\text{TF}}\left(\frac{z}{Z^{1/3}}; N = \lambda, Z = 1\right).
\]

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 — so far as the bulk of the electrons is concerned — as \(Z \to \infty\).

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

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

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 (5), Teller’s theorem can be understood as saying that as \(Z \to \infty\) 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 \(\square\) and the Lieb-Oxford inequality \(\square\), that \(E^{\text{TF}}(N)\), with a modified \(\gamma\), gives a lower bound to \(E^{Q}(N)\).

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

\[
(\text{const.}) \int_{\mathbb{R}^3} |\nabla \sqrt{\rho(x)}|^2 \, dx
\]

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. It also has the effect that the range of \(N\) for which there is a minimizing \(\rho\) is extend from \(0, Z\) to \(0, Z + (\text{const.}) K\).

Another correction, the Dirac exchange energy, is to add

\[
-(\text{const.}) \int_{\mathbb{R}^3} \rho(x)^{4/3} \, dx
\]

to \(\mathcal{E}(\rho)\). This spoils the convexity but not the range \(0, Z\) for which a minimizing \(\rho\) exists cf. \(\square\) for both of these corrections.
When a uniform external magnetic field $B$ is present, the operator $-\Delta$ in $H$ is replaced by
\[ |i\nabla + A(x)|^2 + \sigma \cdot B(x), \]
with curl $A = B$ and $\sigma$ denoting the Pauli spin matrices. This leads to a modified TF theory that is asymptotically exact as $Z \to \infty$, but the theory depends on the manner in which $B$ varies with $Z$. There are five distinct regimes and theories: $B \ll \frac{Z^4}{3}$, $B \sim \frac{Z^4}{3}$, $\frac{Z^4}{3} \ll B \ll Z^3$, $B \sim Z^3$, $B \gg Z^3$. 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 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. [IM], [WT]).

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Elliott H. Lieb
Departments of Mathematics and Physics
Princeton University