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*, $\rho(x)$, $x \in \mathbf{R}^3$, 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.

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

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

in suitable units. Here,

$$\begin{aligned} V(x) \quad &= \quad \sum_{j=1}^{K} Z_j |x - r_j|^{-1} \ , \\ U \quad &= \quad \sum_{1 \le i < j \le K} Z_i Z_j |R_i - R_j|^{-1} \ , \end{aligned}$$

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

$$E^{\mathrm{TF}}(N) = \inf\{\mathcal{E}(\rho) : \rho \in L^{5/3}, \int \rho = N, \rho \geq 0\} \ ,$$

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

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

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

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

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 ρ_N^{TF} that minimizes $\mathcal{E}(\rho)$ if and only if $N \leq Z := \sum_{j=1}^{K} Z_j$. This ρ_N^{TF} is unique and it satisfies the TF equation (2) for some $\mu \geq 0$. Every positive solution, ρ, of (2) is a minimizer of (1) for $N = \int \rho$. If $N > Z$ then $E^{\mathrm{TF}}(N) = E^{\mathrm{TF}}(Z)$ and any minimizing sequence converges weakly in $L^{5/3}(\mathbf{R}^3)$ to ρ_Z^{TF}.

2. $\Phi(x) \geq 0$ 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*). μ is the *chemical potential*, namely

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

$E^{\mathrm{TF}}(N)$ is a strictly convex, decreasing function of N for $N \leq Z$ and $E^{\mathrm{TF}}(N) = E^{\mathrm{TF}}(Z)$ for $N \geq Z$. If $N < Z$, ρ_N^{TF} 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* [ET] (proved rigorously in [LS]) 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

$$E^{\mathrm{TF}}(N) > \sum_{j=1}^{K} E^{\mathrm{TF}}_{\mathrm{atom}}(N_j, Z_j) \ , \qquad (4)$$

where $E^{\mathrm{TF}}_{\mathrm{atom}}(N_j, Z_j)$ 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^{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^{TF} in the neutral case (*positivity of the pressure*) [EL], [BL]. This theorem plays an important role in the *stability of matter*.

An important question concerns the connection between $E^{\mathrm{TF}}(N)$ and $E^{\mathrm{Q}}(N)$, 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 $\wedge^N L^2(\mathbf{R}^3; \mathbf{C}^2)$ (i.e., functions of space and spin). It used to be believed that E^{TF} is asymptotically exact as $N \to \infty$ but this is not quite right; $Z \to \infty$ is also needed. Lieb and Simon [LS] proved that if we fix K and Z_j/Z and we set $R_j = Z^{-1/3} R^0_j$, with fixed $R^0_j \in \mathbf{R}^3$, and set $N = \lambda Z$, with $0 \leq \lambda < 1$ then

$$\lim_{Z \to \infty} \ E^{\mathrm{TF}}(\lambda Z)/E^{\mathrm{Q}}(\lambda Z) = 1 \ . \qquad (5)$$

In particular, a simple change of variables shows that $E^{\mathrm{TF}}_{\mathrm{atom}}(\lambda, Z) = Z^{7/3} E^{\mathrm{TF}}_{\mathrm{atom}}(\lambda, 1)$ 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 ρ^{TF}_N (*cf.* [LS]).

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

$$\rho^{\mathrm{TF}}_{\mathrm{atom}}(x; N = \lambda Z, Z) \quad = \quad Z^2 \rho^{\mathrm{TF}}_{\mathrm{atom}}(\quad Z^{1/3} x; \quad N = \lambda, Z = 1) \ .$$

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 $\rho^{\mathrm{TF}}_{\mathrm{atom}}$ for a neutral atom. As $|x| \to \infty$,

$$\rho^{\mathrm{TF}}_{\mathrm{atom}}(x, N = Z, Z) \sim \gamma^3 (3/\pi)^3 |x|^{-6} \ ,$$

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 [LT] and the Lieb-Oxford inequality [LO], that $E^{\mathrm{TF}}(N)$, with a modified γ, gives a lower bound to $E^{\mathrm{Q}}(N)$.

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

$$(\mathrm{const.}) \int_{\mathbf{R}^3} |\nabla \sqrt{\rho(\mathrm{x})}|^2 \ \mathrm{dx}$$

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

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

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

to $\mathcal{E}(\rho)$. This spoils the convexity but not the range [0,Z] for which a minimizing ρ exists *cf.* [LS] 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 σ 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: $B \ll Z^{4/3}, B \sim Z^{4/3}, Z^{4/3} \ll B \ll Z^3, B \sim Z^3, \gg Z^3$. 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 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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