The role of Thomas-Fermi theory in mathematical Physics

Jan Philip Solovej
Department of Mathematics
University of Copenhagen

List of Slides

1 The Thomas-Fermi (TF) model

2 The variational formulation

3 Basic results

4 TF energy gives lower bound on quantum energy

5 No binding and stability of matter

6 Validity as approximation; The $Z \to \infty$ limit

7 The structure of a heavy atom

8 The chemical radius

9 Comparison with empirical radii

10 Magnetic Thomas-Fermi Theory

11 The different regimes for atoms in magnetic fields

The Thomas-Fermi (TF) model

A model for the atomic density $\rho(x)$, developed independently by Fermi and Thomas in 1927. Mean field potential ($\hbar = 2m = e = 1$):

$$\varphi(x) = Z|x|^{-1} - \int \rho(y)|x-y|^{-1}dy \tag{1}$$

semiclassical density below Fermi level μ (with spin degeneracy):

$$\begin{aligned} \rho(x) &= 2(2\pi)^{-3}\int_{p^2-\phi(x)<-\mu} 1dpdx \\ &= \gamma^{-3/2}[\phi(x)-\mu]_+^{3/2} \end{aligned} \tag{2}$$

where $\gamma = (3\pi^2)^{2/3}$. Here $[t]_+ = \max\{t, 0\}$. The self-consistent set of equations (1) and (2) define the *TF model*.

For molecules

$$\varphi(x) = \sum_{k=1}^{K} Z_k|x-\mathcal{R}_k|^{-1} - \int \rho(y)|x-y|^{-1}dy.$$

The variational formulation

The equations (1) and (2) are the Euler-Lagrange equations for the Thomas-Fermi energy minimization (μ is the Lagrange multiplier for the constraint $\int \rho = N$):

$$E^{\mathrm{TF}}(N) = \inf \left\{ \mathcal{E}(\rho) : \int \rho = N, \ \rho \geq 0 \right\} \ ,$$

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

$$V(x) \quad = \quad \sum_{j=1}^{K} Z_j |x - \mathcal{R}_j|^{-1}, \quad U = \sum_{1 \leq i < j \leq K} Z_i Z_j |\mathcal{R}_i - \mathcal{R}_j|^{-1} \ ,$$

The nuclear repulsion U has been added to get the correct energy.

Basic results

1927: Fermi solves the atomic case numerically

1969-1970: E. Hille studies the atomic case mathematically

1977: Lieb and Simon proves for the general molecular case:

Existence: There is a density ρ_N^{TF} that minimizes $\mathcal{E}$ under the constraint $\int \rho_N^{\mathrm{TF}} = N$ if and only if $N \leq Z := \sum_{j=1}^{K} Z_j$.

Uniqueness: This ρ_N^{TF} is unique and it satisfies the TF equations (1) and (2) for some $\mu \geq 0$.

TF equation: Every solution, ρ, of (1) and (2) is a minimizer of $\mathcal{E}$ for $N = \int \rho$.

Scaling for neutral atoms: $E_{\mathrm{atom}}^{\mathrm{TF}}(N = Z) = C_{\mathrm{TF}} Z^{7/3}$

Scaling for density: $\rho_Z^{\mathrm{TF}}(x) = Z^2 \rho_1(Z^{1/3} x)$

TF energy gives lower bound on quantum energy

N-particle *fermionic* wave function: Ψ, density: ρ_Ψ.

Lieb-Thirring kinetic energy inequality (1976):

$$-\sum_{i=1}^{N}\int \overline{\Psi}\Delta_i\Psi \geq \frac{3}{5}\widetilde{\gamma}\int \rho_\Psi^{5/3}$$

Lieb-Thirring Conjecture: $\widetilde{\gamma}=\gamma$.

Lieb-Oxford Coulomb inequality (1981) (Lieb 1979):

$$\int\sum_{i<j}|x_i-x_j|^{-1}|\Psi|^2 \geq \frac{1}{2}\int\int\frac{\rho_\Psi(x)\rho_\Psi(y)}{|x-y|}dxdy - 1.68\int\rho_\Psi^{4/3}$$

Consequence for energy: $(\Psi, H_{N,K}\Psi) \geq \mathcal{E}_{\widetilde{\gamma}}(\rho_\Psi) - 1.68\int\rho_\Psi^{4/3}$

$$H_{N,K} = \sum_{i=1}^{N}\left(-\Delta_i - V(x_i)\right) + \sum_{i<j}\frac{1}{|x_i-x_j|} + U$$

No binding and stability of matter

Teller's No-Binding Theorem (Teller 1962, Lieb-Simon 1977)

$$E^{\mathrm{TF}}(N) > \sum_{j=1}^{K} E^{\mathrm{TF}}_{\mathrm{atom}}(N_j, Z_j) \quad \left[\geq \sum_{j=1}^{K} E^{\mathrm{TF}}_{\mathrm{atom}}(Z_j, Z_j)\right]$$

Interpretation: Molecules do not bind in TF theory.

Using this and the fact that TF gives lower bound on the true quantum energy for K nuclei and N electrons Lieb and Thirring (1976) prove **Stability of Matter:** (originally Dyson-Lenard 1967)

$$\begin{aligned}(\Psi, H_{N,K}\Psi) \quad &\geq \quad \mathcal{E}_{\tilde{\gamma}}(\rho_\Psi) - 1.68\int \rho_\Psi^{4/3} \geq E^{\mathrm{TF}}(N) - 1.68\int \rho_\Psi^{4/3} \\ &> \quad \sum_{j=1}^{K} E^{\mathrm{TF}}_{\mathrm{atom}}(Z_j, Z_j) - 1.68\int \rho_\Psi^{4/3} \geq -C(K+N)\end{aligned}$$

Interpretation: Energy *per particle* is bounded independently of the number of particles.

Validity as approximation; The $Z \to \infty$ limit

Main question for atoms: How well does $E^{\mathrm{TF}}(N = Z)$ approximate the true ground state energy $E^{\mathrm{Q}}(N = Z)$ of the Hamiltonian of a neutral atom

$$H = \sum_{i=1}^{Z} -\Delta_i - \frac{Z}{|x_i|} + \sum_{i<j} |x_i - x_j|^{-1} ?$$

Answer: The following asymptotics holds for $Z \to \infty$

$$C_{\mathrm{TF}} Z^{7/3} + \frac{1}{4} Z^2 + C_{\mathrm{Dirac/Schwinger}} Z^{5/3} + o(Z^{5/3})$$

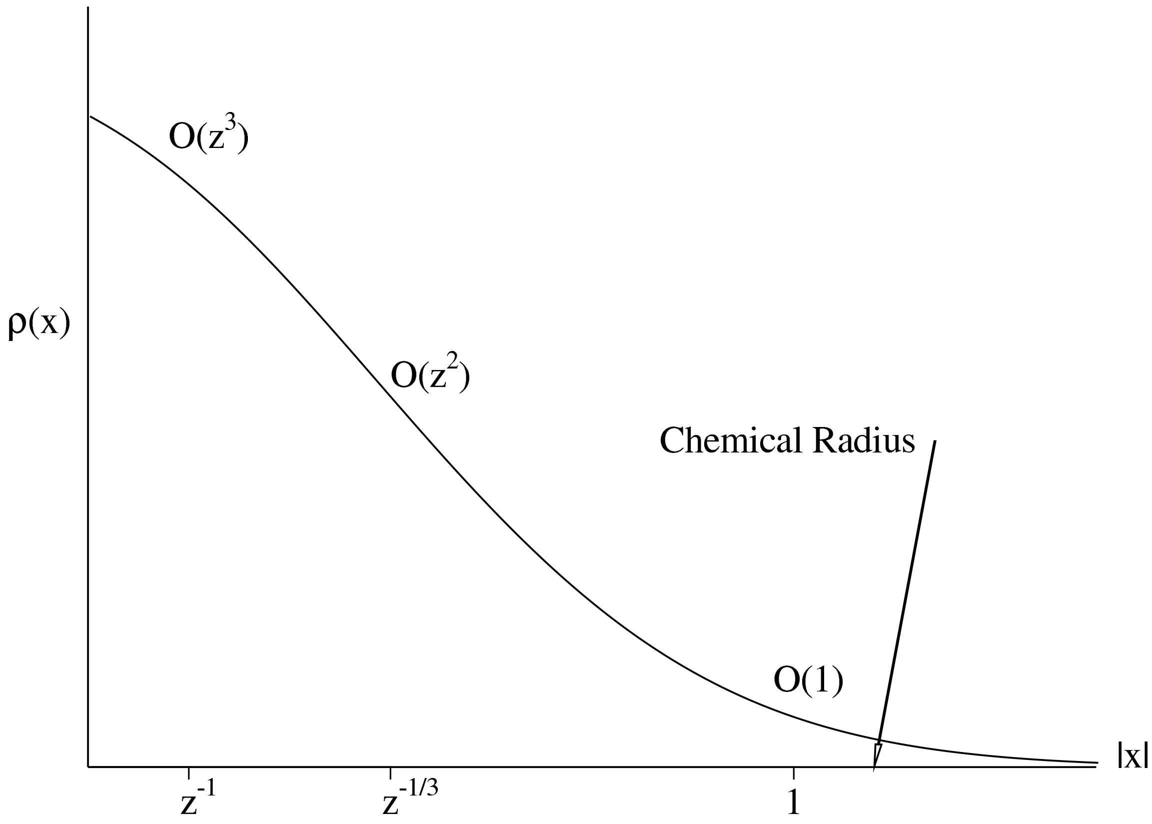
$Z^{7/3}$**:** Lieb and Simon. Semiclassics (originally by DN-bracketing)

$\mathrm{Tr}[(-h^2\Delta - V)_-] = (2\pi h)^{-3} \int (p^2 - V(x))_- dpdx + o(h^-3)$

Z^2 **:** Predicted by Scott (1952). Proved mathematically by Hughes(1990), Siedentop-Weikard (1987)

$Z^{5/3}$**:** One contribution predicted by Dirac (1930) another by Schwinger (1981). Mathematical proof by Fefferman-Seco (90s).

The structure of a heavy atom



The TF scale is $Z^{-1/3}$. The Scott scale is Z^{-1}.

The chemical radius

Question: Can TF theory tell us anything about the chemical radius, which is at a distance independent of Z?
The *energy* cannot be understood to this accuracy!!

A possible definition of radius R_m:

$$\int_{|x|>R_m} \rho = m$$

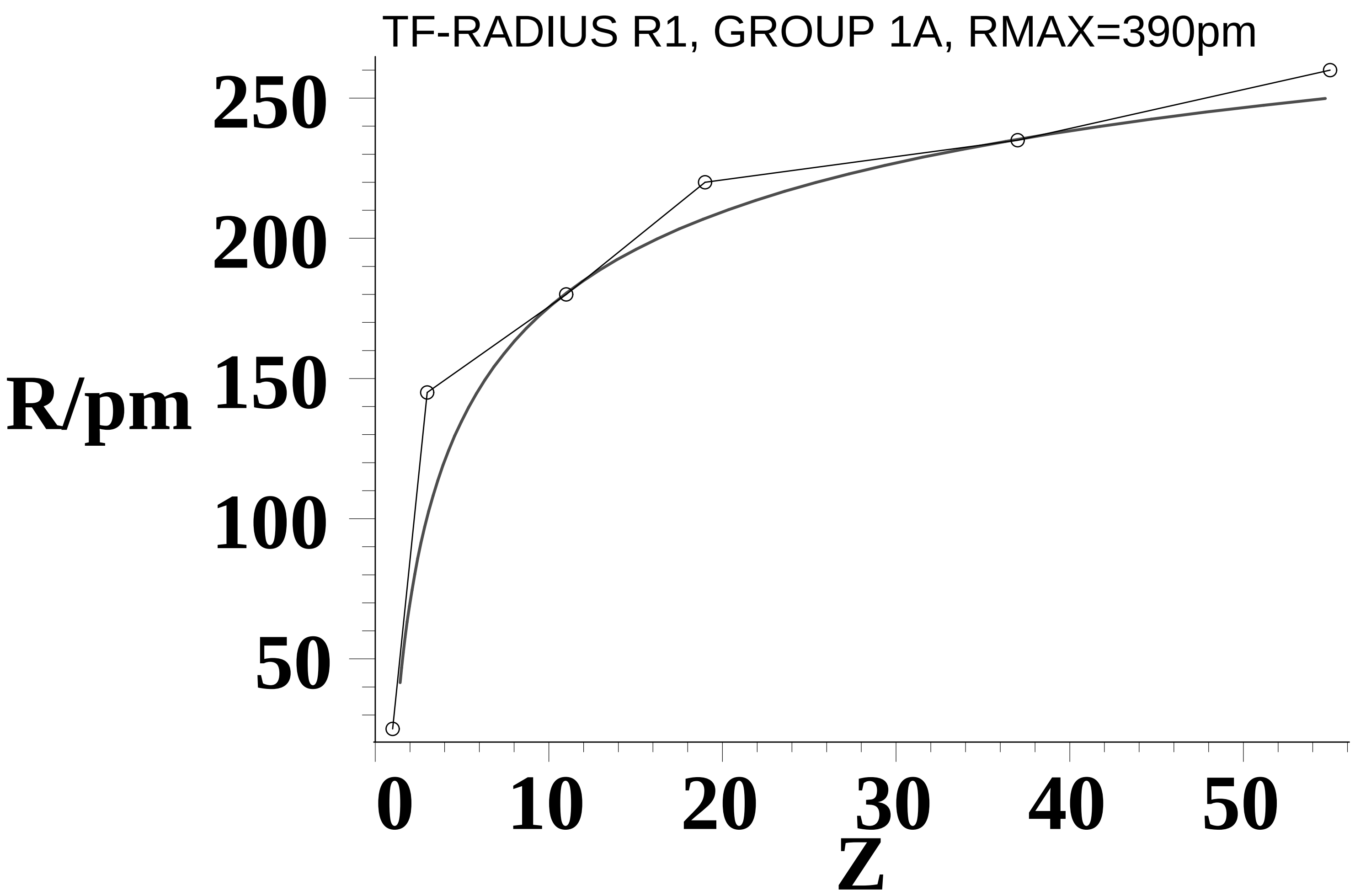
Interpretation: Only m electrons outside ball of radius R_m.

Solovej 2001:

$$\lim_{m\to\infty} \overline{\lim_{Z\to\infty}} \frac{R_m^{\text{Hartree/Fock}} - R_m^{\text{TF}}}{R_m^{\text{TF}}} = 0$$

Testing this result experimentally: The next figure compares R_1 calculated in TF theory with "measured" (*empirical*, Slater 1964) radii in group 1: H, Li, Na, K, Rb, Cs, (Fr).

Comparison with empirical radii



In TF theory an infinite atom ($Z \to \infty$) has radius 390pm.

Magnetic Thomas-Fermi Theory

The structure of matter in the presence of a strong homogeneous magnetic field $\mathbf{B} = \nabla \times \mathbf{A}$ is of interest for neutron stars.

$$H = \sum_{j=1}^{N} \left(\frac{\hbar^2}{2m} \mathcal{D}_{\mathbf{A},j}^2 - \frac{Ze^2}{|x_j|} \right) + \sum_{i<j} \frac{e^2}{|x_i - x_j|}$$

Kinetic energy operator: 3D Euclidean Dirac operator $\mathcal{D}_{\mathbf{A}} = (-i\nabla - \mathbf{A}(x)) \cdot \sigma$, $\sigma = (\sigma_1, \sigma_2, \sigma_3)$ Pauli matrices.

Question: Is there a corresponding Thomas-Fermi theory which is asymptotically exact as $Z \to \infty$?

Answer (Lieb-Solovej-Yngvason 1994-1995): If $B/Z^3 \to 0$ as $Z \to \infty$ then the following Thomas-Fermi theory is accurate:

$$\mathcal{E}_B(\rho) := \int \tau_B(\rho) - \int \frac{Ze^2}{|x|} \rho(x)\ dx + \frac{1}{2} \int\int e^2 \frac{\rho(x)\rho(y)}{|x-y|}\ dxdy$$

The different regimes for atoms in magnetic fields

Here $\tau_B(\rho)$ which has replaced the non-magnetic term $\rho^{5/3}$ is the Legendre transfrom of

$$v \mapsto 2^{-1/2}(3\pi^2)^{-1}B\left[v^{3/2} + 2\sum_{\nu\geq 1}[v - 2B\nu]_+^{3/2}\right].$$

There are 5 different regimes

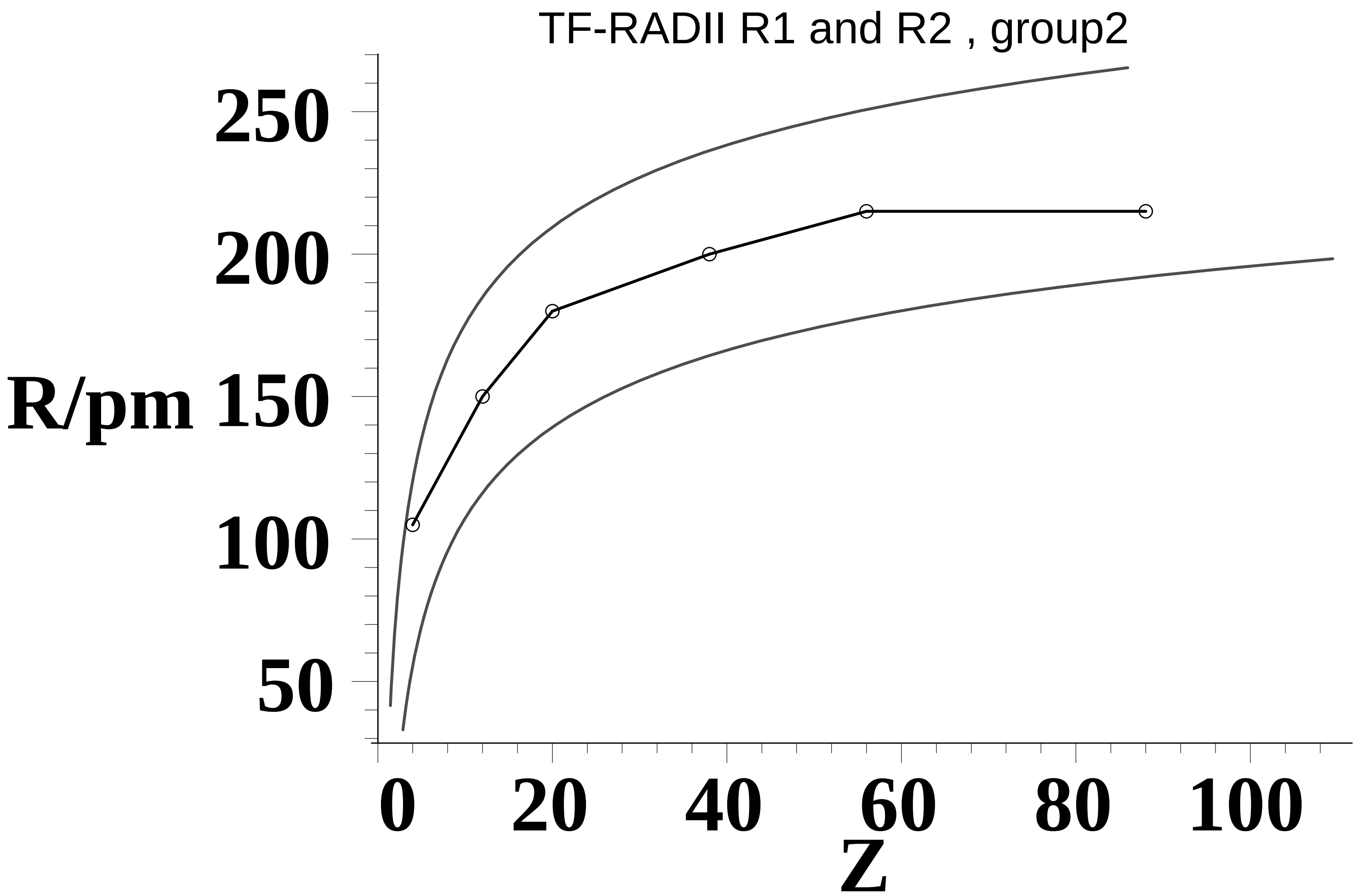
$B \ll Z^{4/3}$: The non-magnetic TF theory applies

$B \sim Z^{4/3}$: The full magnetic TF theory is needed (Yngvason)

$Z^{4/3} \ll B \ll Z^3$: Only the first term above is needed.

$B \sim Z^3$: A more complicated non-TF type theory is needed.
Atoms no longer spherical.

$B \gg Z^3$: Atoms have become effectively one-dimensional.
A TF caricature in 1D applies.


TF-RADII R1 and R2 , group2
R/pm
250
200
150
100
50
0
20
40
60
80
100
Z