1. Thomas-Fermi method

We consider a system of N electrons in a stationary state, that would obey the stationary Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i\neq j} v(\mathbf{r}_i, \mathbf{r}_j)\right] \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = E_i \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)\ . \tag{1.1}$$

We would try to avoid the complication of searching for the many-electron wavefunction $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$, concentrating on an electron density $\rho(\mathbf{r})$ instead. The electron density is a physical observable, it can be measured, calculated and easily visualized. For just one particle with its corresponding wavefunction $\varphi(\mathbf{r})$, the density is simply a probability amplitude to find a particle near a certain position in space; it reads

$$\rho(\mathbf{r}) = \varphi^*(\mathbf{r})\,\varphi(\mathbf{r})\ . \tag{1.2}$$

For a system with N particles, the definition of the density is the following,

$$\rho(\mathbf{r}) = N\int \Psi^*(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)\Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N) d\mathbf{r}_2 \ldots d\mathbf{r}_N\ , \tag{1.3}$$

i.e., the probability amplitude to find *any* particle near the position $\mathbf{r}$ in space. In principle, one can attempt to solve the equation (1.1) iteratively (subject to certain approximations), i.e. the electron density will be determined by $\Psi(\{\mathbf{r}\})$ and affect, in its turn, the Coulomb potential in Eq.(1.1), and so on till self-consistency. But the essence of the Tomas-Fermi method is to circumvent the discussion of the wavefunction Ψ completely, concentrating on the density $\rho(\mathbf{r})$ as a basic variable to search for.

1.1 Deriving the equation...

The approach has been proposed independently by L. Thomas and E. Fermi in 1927.[1] The Thomas-Fermi approach is semi-classical, i.e., certain ideas will be borrowed from quantum mechanics, but otherwise one operates with normal functions instead of quantum-mechanical operators. The condition for the semi-classical approach to be applicable is that spatial variations of the de Broglie wavelength in a system in question must be small. Specifically, we'll consider momentum p as a spatial function (instead of quantum-mechanical operator) and introduce wave number $k(x) = 1/\hbar p(x)$ (as a function of any spatial coordinate x), then de Broglie wavelength $\lambda(x) = 1/k(x)$, everything being position-dependent, and the condition for the semi-classical approach to be valid reads

$$\xi = \left|\frac{d\lambda(x)}{dx}\right| \ll 1\ . \tag{1.4}$$

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[1] L. H. Thomas, Proc. Camb. Phil. Soc. **23**, 542 (1927); E. Fermi, Rend. Acad. Maz. Lancei **6**, 602 (1927). The method has been since then decribed in many textbooks. For a relatively recent useful review article which covers the history, improvements and applications, see: Larry Spruch, *Pedagogic notes on Thomas-Fermi theory (and on some improvements): atoms, stars, and the stability of bulk matter*, Rev. Mod. Phys. **63**, No.1 (Jan. 1991), pp. 151–209.

From quantum mechanics, one retains two elements:
- the Fermi statistics; all the states up to those with some maximum energy and hence momentum p_{F} – that may vary over space – are occupied;
- the uncertainty principle; every cell in the phase space of volume h^3 may host up to 2 electrons with opposite spin directions.

In the ground state, assuming first that p_{F} over a volume V, one counts the number of electrons N:

$$\underbrace{\frac{4\pi}{3}p_{\mathrm{F}}^3}_{\substack{\text{momentum}\\ \text{space}}} \quad\cdot\quad \underbrace{V}_{\substack{\text{coordinate}\\ \text{space}}} \quad\cdot\frac{2}{h^3} = N\ , \tag{1.5}$$

hence (uniform) electron density is

$$\rho = \frac{N}{V} = \frac{8\pi}{3h^3}\,p_{\mathrm{F}}^3\ , \tag{1.6}$$

or, inverting it:

$$p_{\mathrm{F}} = \left[\frac{3h^3}{8\pi}\,\rho\right]^{1/3}\quad . \tag{1.7}$$

In the following, we assume that both ρ and p_{F} are dependent on $\mathbf{r}$, but so that the quasi-classsical condition (1.4) holds.

We assume that all electrons move as classical particles in a common potential field $V(\mathbf{r})$. The classical energy for the fastest electron will be

$$E_{\mathrm{max.}} = \frac{p_{\mathrm{F}}^2(\mathbf{r})}{2m} + V(\mathbf{r})\ , \tag{1.8}$$

Whereas both kinetic and potential parts may independently depend on $\mathbf{r}$, their sum – at least in equilibrium – must remain constant. Otherwise the electrons will flow from regions with higher maximal energy till $E_{\mathrm{max.}}$ becomes the same everywhere. Substituting Eq. (1.7) into (1.8) yields:

$$E_{\mathrm{max.}} = \frac{1}{2m}\left[\frac{3h^3}{8\pi}\right]^{2/3}\rho^{2/3} + V(\mathbf{r})\ , \tag{1.9}$$

Now, we consider the total energy of the whole electron distribution and in it – kinetic and potential energy parts. With the kinetic energy density t, the kinetic energy T can be recovered as $T = \int t(\mathbf{r})\,\mathbf{dr}$.

$$\begin{aligned} t &= \frac{T}{V} = \frac{1}{V}\int\frac{p^2}{2m}dN = \frac{1}{V}\int_0^{p_{\mathrm{F}}}\frac{p^2}{2m}\cdot\frac{4\pi p^2\cdot V\cdot 2}{h^3}\,dp \\ &= \frac{8\pi}{2mh^3}\int_0^{p_{\mathrm{F}}}p^4dp = \frac{8\pi}{2mh^3}\cdot\frac{p_{\mathrm{F}}^5}{5}\ . \end{aligned} \tag{1.10}$$

Substituting (1.7) into (1.10) yields:

$$t = \frac{8\pi}{2mh^3}\cdot\frac{1}{5}\left[\frac{3h^3}{8\pi}\rho(\mathbf{r})\right]^{5/3} = \underbrace{\frac{3h^2}{10m}\left(\frac{3}{8\pi}\right)^{2/3}}_{C_K}\left[\rho(\mathbf{r})\right]^{5/3}\ . \tag{1.11}$$

The potential energy is due to the interaction with external field $V_{\text{ext.}}(\mathbf{r})$ and electrostatic interaction of the electron density with itself:

$$U = e\int \rho(\mathbf{r})\, V_{\text{ext.}}(\mathbf{r})\, d\mathbf{r} + \frac{1}{2}e^2 \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \ . \tag{1.12}$$

Then the total energy of the electron system is:

$$E_{\text{tot}} = C_K \int [\rho(\mathbf{r})]^{5/3}\, d\mathbf{r} + e\int \rho(\mathbf{r}) V_{\text{ext.}}(\mathbf{r}) d\mathbf{r} + \frac{1}{2}e^2 \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \, . \tag{1.13}$$

We search in the following for such distribution of the electron density that would minimize the total energy, subject to the condition of normalization

$$\int \rho(\mathbf{r}) d\mathbf{r} = N \ : \tag{1.14}$$

$$\delta\left(E_{\text{tot.}} - \mu N\right) = 0 \ , \tag{1.15}$$

introducing a Lagrange multiplier μ. A variation with respect to $\rho(\mathbf{r})$ yields:

$$\begin{aligned} \delta\left(E_{\text{tot.}} - \mu N\right) &= \int \left\{ \frac{5}{3} C_K \left[\rho(\mathbf{r})\right]^{2/3} + eV_{\text{ext.}}(\mathbf{r}) + e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' - \mu \right\} \delta\rho(\mathbf{r}) d\mathbf{r} = 0 \\ &\to \ \frac{5}{3} C_K \left[\rho(\mathbf{r})\right]^{2/3} + eV_{\text{ext.}}(\mathbf{r}) + e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' = \mu \ , \end{aligned} \tag{1.16}$$

that is the Thomas-Fermi equation that determins the equilibrium distribution of the electron density.

Comparing with Eq.(1.9) and taking into account that two last terms on the left side represent the potential energy, we see that μ is the classical energy of the fastest electron, that could be identified with the Fermi energy. On the other side, it follows from Eq.(1.15) that $\mu = \partial E_{\text{tot.}}/\partial N$, i.e. μ has the meaning of the chemical potential.

Eq. (1.16) is the Thomas-Fermi equation for $\rho(\mathbf{r})$ in integral form. Due to the relation between ρ and p_{F}, it can be formulated as that on p_{F}, or k_{F}:

$$\rho^{1/3}(\mathbf{r}) = p_{\text{F}} \left(\frac{8\pi}{3h^3}\right)^{1/3} = \frac{1}{(3\pi^2)^{1/3}} \cdot \frac{p_{\text{F}}}{\hbar} = \frac{1}{(3\pi^2)^{1/3}} k_{\text{F}} \ .$$

With this, Eq. (1.16) transforms into:

$$\frac{5}{3} C_K \frac{1}{(3\pi^2)^{2/3}}\, k_{\text{F}}^2(\mathbf{r}) + eV_{\text{ext.}}(\mathbf{r}) + \frac{e^2}{3\pi^2} \int \frac{k_{\text{F}}^3(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' = \mu \ , \tag{1.17}$$

or

$$\frac{p_{\text{F}}(\mathbf{r})}{2m} + eV_{\text{ext.}}(\mathbf{r}) + \frac{e^2}{3\pi^2} \int \frac{k_{\text{F}}^3(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' = \mu \ .$$

One can transform the Tomas-Fermi equation in the integral form (1.16) into a differential form. The function to search for will be the electrostatic potential generated by $\rho(\mathbf{r})$. We introduce this potential as

$$u(\mathbf{r}) = e \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \ ,$$

it must satisfy the Poisson equation:

$$\Delta u(\mathbf{r}) = -4\pi e\rho(\mathbf{r})\,. \tag{1.18}$$

From Eq.(1.16) one extracts the electron density,

$$\rho(\mathbf{r}) = \left(\frac{3}{5C_K}\right)^{3/2} \left[\mu - eV_{\text{ext.}}(\mathbf{r}) - eu(\mathbf{r})\right]^{3/2}\ , \tag{1.19}$$

and with (1.18) it follows:

$$\begin{aligned}\Delta u(\mathbf{r}) &= -4\pi e\left(\frac{3}{5C_K}\right)^{3/2} \left[\mu - eV_{\text{ext.}}(\mathbf{r}) - eu(\mathbf{r})\right]^{3/2} \\ &= -\frac{32\pi^2 e}{3h^3}\,(2m)^{3/2}\left[\mu - eV_{\text{ext.}}(\mathbf{r}) - eu(\mathbf{r})\right]^{3/2}\ . \end{aligned} \tag{1.20}$$

This is the Thomas-Fermi equation in differential form.

1.2 Thomas-Fermi atom

Let us consider a neutral Thomas-Fermi atom as an example. Then we have

$$N = Z;\quad V_{\text{ext.}}(\mathbf{r}) = -\frac{eZ}{r} \quad\Rightarrow\quad \Delta V_{\text{ext.}}(\mathbf{r}) = 4\pi eZ\delta(\mathbf{r})\ .$$

The energy-minimizing solution of the Thomas-Fermi equation is unique (without proof); we'll seqrch for a spherically symmetric solution that will be *the* solution. Combining extrenal field (of nucleus) and Coulomb field created by the electron density into $V_{\text{eff}}(\mathbf{r})$;

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext.}}(\mathbf{r}) + u(\mathbf{r});\quad \Delta V_{\text{eff}}(\mathbf{r}) = 4\pi eZ\delta(\mathbf{r}) + \Delta u(\mathbf{r})\ .$$

For $r \to \infty$, $\rho(r) \to 0$, then the Coulomb potential created by *spherically symmetric* and *neutral* charge distribution falls down to zero. In Eq.(1.19) all terms approach 0 as $r \to \infty$, then $\mu = 0$ at infinity, hence $\mu = 0$ everywhere in the equilibrium. Eq. (1.20) becomes:

$$\begin{aligned}\Delta V_{\text{eff}}(\mathbf{r}) - 4\pi eZ\delta(\mathbf{r}) &= -\frac{32\pi^2 e}{3h^3}\,(2m)^{3/2}\left[-eV_{\text{eff}}(\mathbf{r})\right]^{3/2} \\ -\Delta V_{\text{eff}}(\mathbf{r}) &= \frac{32\pi^2 e}{3h^3}\,(2m)^{3/2}\left[-eV_{\text{eff}}(\mathbf{r})\right]^{3/2} - 4\pi eZ\delta(\mathbf{r})\ . \end{aligned} \tag{1.21}$$

The δ-function takes care of boundary conditions, $V_{\text{eff}}(r) \to -Z/r$ for $r \to 0$, the other boundary condition is $V_{\text{eff}}(r) \to 0$ for $r \to \infty$, with this the solution of $V_{\text{eff}}(r)$ is unique. For $r \neq 0$, the equation to solve is

$$-\frac{1}{r}\frac{d^2}{dr^2}\,rV_{\text{eff}}(r) = \frac{32\pi^2 e}{3h^3}(2m)^{3/2}\,e^{3/2}\left[-V_{\text{eff}}(r)\right]^{3/2}\ . \tag{1.22}$$

With the *ansatz* $V_{\text{eff}}(r) = -Z/r\chi(\alpha r)$ Eq.(1.22) transforms into:

$$\begin{aligned}
\frac{Z\alpha^3}{x}\frac{d^2\chi(x)}{dx^2} &= \left(\frac{Z\alpha}{x}\right)^{3/2}\frac{32\pi^2\,e}{3h^3}\,(2me)^{3/2}\,[\chi(x)]^{3/2}\ ; \\
\frac{d^2\chi(x)}{dx^2} &= \left(\frac{Z}{x}\right)^{1/2}\alpha^{-3/2}\,\frac{32\pi^2 e}{3h^3}\,(2me)^{3/2}\,[\chi(x)]^{3/2} \\
\frac{d^2\chi(x)}{dx^2} &= \frac{1}{x^{1/2}}\underbrace{\left[Z^{1/2}\,\frac{32\pi^2 e}{3h^3}\,(2me)^{3/2}\,\alpha^{-3/2}\right]}_{=1}[\chi(x)]^{3/2}\ . \qquad (1.23)
\end{aligned}$$

The square bracket can be set to 1 if we choose

$$\alpha = \left(\frac{32\pi^2 e}{3h^3}\right)^{2/3}\cdot 2me\,Z^{1/3}\ , \qquad (1.24)$$

then one arrives so at the universal form of the Thomas-Fermi equation that allows to scale the solution for arbitrary Z and defines $\chi(x)$, the universal Thomas-Fermi function. Let us discuss the asymptotic of the solution. If we assume V_{eff} to behave as

$$V_{\text{eff}} \sim r^{-\nu} \quad \text{for} \quad r \longrightarrow \infty, \quad \text{then} \quad -\frac{1}{r}\frac{d^2}{dr^2}rV_{\text{eff}} \sim r^{-(\nu+2)}\ ;$$

$$\text{on the other side,} \quad [-V_{\text{eff}}(r)]^{3/2} \sim r^{-3\nu/2}\ , \quad \text{hence} \quad \nu + 2 = 3\nu/2 \quad \Rightarrow \quad \nu = 4\ .$$

$$\begin{aligned}
&\text{Then} \quad \rho(r) \sim \Delta V_{\text{eff}}(r) \sim [-V_{\text{eff}}(r)]^{3/2} \Rightarrow \quad \sim r^{-6}\ . \\
&\text{For} \quad r \longrightarrow 0, \quad V_{\text{eff}}(r) \sim -\frac{Z}{r} \quad \text{and} \quad \rho(r) \sim r^{-3/2}\ .
\end{aligned}$$

We summarize below essential properties of a Thomas-Fermi atom:

- There is a solution for neutral or positively charged ion (no bounded solution for negative ions).
- Asymptotic is wrong: $\rho(r) \sim r^{-6}$ for $r \longrightarrow \infty$, in reality $\rho(r) \sim \exp(-r)$. $\rho(r) \sim r^{-3/2}$ (diverges) for $r \longrightarrow 0$, in reality: $\rho(0)$ is finite.
- Total energy is too low, especially for light atoms[2]
- No shell structure of an atom appears.
- There is no chemical binding, the total energy of two close (interacting) atoms is never lower than that of two distant atoms (the Taylor theorem[3]).
- But: the theory is asymptotically exact for $N \longrightarrow \infty$.

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[2] by 54% for hydrogen, by 35% for helium, by ≈15% for heavy elements ($Z \approx 100$).

[3] Edward Teller, *On the Stability of Molecules in the Thomas-Fermi Theory*, Rev. Mod. Phys. **34**, No. 4, 627–631 (Oct. 1962)

1.3 Corrections to the Thomas-Fermi equation

1.3.1 Exchange (Thomas-Fermi-Dirac)

So far, we considered only electrostatic interaction of each electron with the whole background charge. What is wrong with this?

- it includes self-interaction. i.e. the charge distribution related to the electron itself is not excluded:

$$\sum_{i\neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \neq \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' \;;$$

- it neglects the Pauli principle in a sense that there is no preference in electron-electron interaction with respect to spin. The second problem can be corrected for. For an electron with spin, say, “up”, the charge density of spin “down” is reduced in its neighbourhood. Since this “down” density is not due to the electron in question, it can be handled as a smooth distribution of charge, with no problem of self-interaction to care about. As will be discussed larer in relation with the Hartree-Fock formalism, this additional interaction due to the Pauli principle is the exchange interaction; it lowers the total energy (since it puts electrons more apart) and can be casted, at least approximatively, in a form explicitly dependent on density. The incorporation of exchange in the Thomas-Fermi formalism has been done by Dirac.[4] In the following, we discuss only qualitatively what functional dependence on density could be expected, based on dimensions arguments.

Similarly to the kinetic energy density which scales $\sim\ \rho^{5/3}$, one can assume a power low for the exchange energy density. The exchange term arises from electron-electron Coulomb interaction $\sim e^2/r$, so we assume the exchange energy density to scale as $\sim e^2\rho^{\nu}$. The energy density in general must have the dimension $[\mathrm{ML}^{-1}\mathrm{T}^{-2}]$ (M stands for the units of mass, L – length, T – time). In our combination $\sim e^2/r$ considered for the exchange energy density, e^2 has dimension $[\mathrm{ML}^{3}\mathrm{T}^{-2}]$ since e^2/r is energy. ρ is number per unit volume, i.e. its dimensionality is L^{-3}.

$$\mathrm{ML}^{-1}\mathrm{T}^{-2} = \mathrm{ML}^{3}\mathrm{T}^{-2}\mathrm{L}^{-3\nu} \quad \Rightarrow \quad \nu = 4/3.$$

Dirac (1930) suggested a correction term

$$E_{\mathrm{TFD}} = E_{\mathrm{TF}} - C_X \int [\rho(\mathbf{r})]^{4/3}\, d\mathbf{r} \tag{1.25}$$

to be added to the Thomas-Fermi total energy of Eq.(1.13). The Thomas-Fermi-Dirac equation reads:

$$\frac{5}{3} C_K\, [\rho(\mathbf{r})]^{2/3} - \frac{4}{3} C_X\, [\rho(\mathbf{r})]^{1/3} = \mu - eV_{\mathrm{ext}}(\mathbf{r}) - u(\mathbf{r})\ , \tag{1.26}$$

as a substitution to Eq. (1.16). We do not specify the magnitude of the exchange constant C_X here.

Considering the performance of the Thomas-fermi theory with Dirac’s exchange term, one can note that the total energy (already erroneously too low) is lowered even further. There are still no bound negative ions. However, neutral atoms get a finite spatial extension [$\rho(r) = 0$ from certain radius on].

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[4] P. A. M. Dirac, Proc. Cambridge Philos. Soc. **26**, 376 (1930).

1.3.2 Gradient expansions

A more serious problem of the Thomas-Fermi approach is an unsufficiently accurate treatment of kinetic energy. Von Weizsäcker[5] considered modified plane waves $(1 + \mathbf{ar}) \exp(i\mathbf{kr})$ in order to have an inhomogeneous situation and found a gradient correction term

$$K_{\mathrm{W}}[\rho(\mathbf{r})] = \frac{1}{2} \int \left[\nabla \rho^{1/2}(\mathbf{r}) \right]^2 d\mathbf{r} \ .$$

Later on Kirshnitz used systematic expansion and has shown that the 1st order term is $1/9$ of K_{W}. From different points of view, one can achieve coefficients λ, $1/9 \leq \lambda \leq 1$, in front of $K_{\mathrm{W}}[\rho(\mathbf{r})]$.

Results: the electronic density at atomic nuclei becomes finite, and at infinity decays exponentially. Negative ions are formed and molecules may bind. However, it is a problem in attempting to improve the Thomas-fermi theory systematically, based on gradient expansions. It was shown that the 6th order in the gradient exopansion already diverges.

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[5] C. von Weizsäcker, Z. Phys. **96**, 431 (1935).