Chapter 1

Thomas-Fermi Theory

The Thomas-Fermi theory provides a functional form for the kinetic energy of a non-interacting electron gas in some known external potential $V(r)$ (usually due to impurities) as a function of the density. It is a local density functional and is based on a semiclassical approximation. The formulation becomes exact for a uniform electron gas.

In a uniform system of Fermions of spin $S = 1/2$ in 3 dimensions, the Fermi momentum k_F is related to the density via the following relation:

$$\frac{4\pi}{3}k_F^3/\frac{(2\pi)^3}{\Omega} = \frac{N}{2} \Longrightarrow 3\pi^2 n = k_F^3$$

The kinetic energy of the uniform system is given by:

$$\begin{aligned} T &= \sum_{k<k_F}\sum_{\sigma}\frac{\hbar^2k^2}{2m} = 2\frac{\Omega}{(2\pi)^3}\int_0^{k_F} 4\pi k^2 dk\,\frac{\hbar^2k^2}{2m} \\ &= \frac{\Omega}{\pi^2}\frac{\hbar^2}{10m}k_F^5 \end{aligned} \tag{1.1}$$

The total electron number can be obtained in a similar fashion:

$$N = \sum_{k<k_F}\sum_{\sigma} 1 = 2\frac{\Omega}{(2\pi)^3}\int_0^{k_F} 4\pi k^2 dk = \frac{\Omega}{3\pi^2}k_F^3 \tag{1.2}$$

One can thus calculate the kinetic energy per unit volume or per particle:

$$T = \Omega\;\frac{3}{5}\frac{\hbar^2k_F^2}{2m}n = N\;\frac{3}{5}\frac{\hbar^2k_F^2}{2m} \tag{1.3}$$

In a non-uniform system where the density is a function of the position $n(r)$, one assumes the same functional form (the semiclassical approximation) and thus the Fermi momentum becomes position-dependent:

$$n(r) = \frac{k_F^3(r)}{3\pi^2} \tag{1.4}$$

and the kinetic energy within TF becomes

$$T[n] = \int d^3r \frac{3}{5} \frac{\hbar^2 k_F^2(r)}{2m} n(r) \tag{1.5}$$

The relationship between the external potential and the density is obtained by minimizing the total (here the kinetic plus external) energy with respect to the density with the constraint of constant electron number:

$$\delta(T + \int n(r)V(r)\, d^3r - \mu \int n(r)\, d^3r)/\delta n = 0$$

In the semi classical approximation, the local Fermi momentum is obtained by solving the above minimization equation:

$$\mu = \frac{\hbar^2 k_F^2(r)}{2m} + V(r) \tag{1.6}$$

where the Lagrange multiplier μ is identified as the equilibrium chemical potential of the system. This semiclassical approximation is valid if the variations in the external potential are weak in the scale of the Fermi wavelength: $|\nabla V(r)|/V(r) \ll k_F(r)$. Eliminating k_F in both equations 1.4 and 1.6, one can find the relationship between the external potential $V(r)$ and the ground state density $n(r)$ without any need to solve the Schrödinger equation!

$$n(r) = \frac{1}{3\pi^2\hbar^3}\{2m[\mu - V(r)]\}^{3/2} \tag{1.7}$$

This equation is the central result of the Thomas-Fermi theory in 3 dimensions. The result is a very simple local analytical relation between the external potential and the ground state density of a non-interacting electron gas.

From equation 1.4, one can also deduce the form of the total kinetic energy as a function of density in the Thomas-Fermi approximation (exact for a uniform system), resulting in a kinetic energy per particle :

$$T/N = \frac{3\hbar^2}{10m}[3\pi^2 n]^{2/3}$$

or a kinetic energy density

$$\tau_{\rm TF}(r) = \frac{3\hbar^2}{10m}[3\pi^2]^{2/3}\, n(r)^{5/3}$$

For an **interacting system**, if the form of the interaction potential is known as a function of the ground state density, such as in the density functional theory, one can also add this contribution to the external potential $V(r)$, and solve the non-linear equations again, now with an effective potential $V_{\rm eff} = V + V_H + V_{xc}$:

$$n(r) = \frac{1}{3\pi^2\hbar^3}\{2m[\mu - V(r) - e^2\int dr'\frac{n(r')}{|r-r'|} - v_{xc}[n](r)]\}^{3/2} \tag{1.8}$$

Here, the newly added terms are respectively the Coulomb interaction (Hartree potential) and the exchange-correlation potential seen by an electron. The latter has a simple expression in the local density approximation (LDA) of the density functional theory. Within the Hartree-Fock theory, the exchange energy of the Jellium model was derived as the function of the density (see Eq.**??**). From this functional, it is possible to deduce an exchange-only potential which is obtained by differentiating the exchange energy with respect to n. Using this potential in the TF equation above yields the **Thomas-Fermi-Dirac** equation:

$$\mu = V(r) + e^2\int dr'\frac{n(r')}{|r-r'|} - \alpha n(r)^{1/3} + \frac{\hbar^2 k_F^2(r)}{2m} \tag{1.9}$$

Note that now, for a given μ and a given external potential, the solution needs to be found iteratively as the equation has become an integral equation.

1.1 Generalizations to other dimensions and spin-polarized systems

The above results can trivially be generalized to other spatial dimensions and arbitrary spins: equation 1.4 must be replaced by: $n = (2S+1)\, \upsilon_d\, k_F^d/(2\pi)^d$ where υ_d is the volume of a hypersphere of radius 1 in d dimensions. Furthermore, for a spin-polarized system, the external as well as the exchange-correlation potentials will be spin-dependent. Equation 1.7 becomes:

$$n_\sigma(r) = \frac{1}{(2\pi\hbar)^d}\,\upsilon_d\,\{2m[\mu - V_\sigma(r)]\}^{d/2} \tag{1.10}$$

The total kinetic energy is now:

$$T = \sum_{k<k_F} \sum_{\sigma} \frac{\hbar^2 k^2}{2m} = \sum_{\sigma} \int_0^{k_{F\sigma}} s_d k^{d-1} dk \, \frac{\hbar^2 k^2}{2m} = \sum_{\sigma} \frac{s_d \, \hbar^2}{2m(d+2)} [\frac{(2\pi)^d n_\sigma}{\upsilon_d}]^{(d+2)/3} \tag{1.11}$$

where $s_d = d\upsilon_d$ is the surface of the hypersphere of radius 1 in d dimensions. The following table summarizes the formulas for υ_d and s_d in 1,2 and 3 dimensions.

d	υ_d	s_d
1	2	2
2	π	2π
3	$4\pi/3$	4π

Here $2S+1$ is the spin degeneracy, and $\Omega = L^d$ is the system volume. The kinetic energy of the uniform system is given by:

$$\begin{aligned} T &= \sum_{k<k_F} \sum_{\sigma} \frac{\hbar^2 k^2}{2m} = (2S+1) \frac{\Omega}{(2\pi)^d} \int_0^{k_F} s_d k^{d-1} dk \, \frac{\hbar^2 k^2}{2m} \\ &= (2S+1) \frac{\Omega}{(2\pi)^d} \frac{s_d}{d+2} \frac{\hbar^2 k_F^2}{2m} k_F^d \end{aligned} \tag{1.12}$$

One can thus calculate the kinetic energy as a function of the density by combining the above equation with Eq.(**??**) to obtain:

$$T = \Omega \, \frac{\hbar^2 k_F^2}{2m} \frac{d}{d+2} n = N \frac{d}{d+2} \frac{\hbar^2 k_F^2}{2m} \tag{1.13}$$

In a non-uniform system where the density is a function of the position $n(r)$, one assumes the same functional form (the semiclassical approximation) and thus the Fermi momentum in equation **??** becomes position-dependent:

$$n(r) = (2S+1) \frac{\upsilon_d}{(2\pi)^d} \, k_F^d(r); \text{ in 3D} : n(r) = \frac{(2S+1)}{6\pi^2} k_F^3(r) \tag{1.14}$$

and the kinetic energy within TF becomes

$$T[n] = \int d^d r \frac{\hbar^2 k_F^2(r)}{2m} \frac{d}{d+2} \, n(r) \tag{1.15}$$

1.2 Finite temperature generalization

More generally, the particle density can be obtained from the integration of the distribution function:

$$n_\sigma(r) = \frac{1}{\Omega}\sum_k f_\sigma(r,k) = \int \frac{d^dk}{(2\pi)^d}\frac{1}{1+e^{\beta(\varepsilon_{k\sigma}+V_\sigma(r)-\mu)}} \tag{1.16}$$

The band energy $\varepsilon_{k\sigma}$ is used in this equation, but for uniform systems, one can use $\hbar^2k^2/2m$ instead, and recover equation 1.7 in the zero temperature limit. The total charge and magnetization are defined respectively as:

$$n(r) = n_\uparrow(r) + n_\downarrow(r); \;\; m(r) = -g\mu_B[n_\uparrow(r) - n_\downarrow(r)]$$

The k integration maybe performed analytically if the band energy is quadratic; it leads to a special function. Otherwise, if the band structure is given, the integration within the first Brillouin zone can be performed numerically. The concept of spin-dependent kinetic energy density can be similarly defined in this general case.

$$\tau_\sigma^{\mathrm{TF}}(r) = \frac{1}{\Omega}\sum_k \frac{\hbar^2k^2}{2m} f_\sigma(r,k) = \int \frac{d^dk}{(2\pi)^d}\frac{1}{1+e^{\beta(\frac{\hbar^2k^2}{2m}+V_\sigma(r)-\mu)}}\frac{\hbar^2k^2}{2m} \tag{1.17}$$

1.3 Linear screening

1.3.1 Non-interacting susceptibility

If a perturbation $\delta V(r)$ is added to the existing potential, then a change in the density $\delta n(r)$ results. To lowest order in δV, the correction in the density is linear in the perturbation, and it is easy to compute the coefficient of proportionality within TF by using equation 1.7:

$$n(r) + \delta n(r) = \frac{(2S+1)}{6\pi^2\hbar^3}\{2m[\mu - V(r) - \delta V(r)]\}^{3/2} \tag{1.18}$$

Equating the first order terms from both sides, one obtains the susceptibility function χ defined by $\delta n(r) = \int dr'\chi(r,r')\delta V(r')$:

$$\begin{aligned}\chi^0_{\mathrm{TF}}(r,r') &= \frac{\partial n(r)}{\partial V(r')} = -\frac{(2S+1)}{4\pi^2\hbar^3}(2m)^{3/2}[\mu - V(r)]^{1/2}\,\delta(r-r') \\ &= -DOS(\mu - V(r))\,\delta(r-r')\end{aligned} \tag{1.19}$$

The susceptibility within the TF theory is thus local. Again, the same can be done for a spin polarized system; the susceptibility becomes a 2×2 matrix defined as: $\delta n_\sigma(r) = \sum_{\sigma'} \int dr' \, \chi^0_{\sigma\sigma'}(r, r') \, \delta V_{\sigma'}(r')$

$$n_\sigma(r) + \delta n_\sigma(r) = \frac{1}{6\pi^2\hbar^3}\{2m[\mu - V_\sigma(r) - \delta V_\sigma(r)]\}^{3/2} \tag{1.20}$$

It is therefore diagonal with $\chi^0_{\sigma\sigma'}(r, r') = -DOS_\sigma(\mu - V_\sigma(r)) \, \delta(r - r')\delta_{\sigma\sigma'}$.

The purpose of the linear screening theory is to treat non-uniform perturbations which are harder to solve analytically. Therefore, it is usually used when the potential $V(r)$ is a constant, or in other words, omitted; so that the reference system is the uniform electron gas. In this case, the susceptibility does not depend on the location r anymore, and is a constant (besides its delta function dependence which becomes unity in the k-space.

1.3.2 Interacting susceptibility

The above result (χ^0) was for a non-interacting system; for an interacting system, however, one can also compute, within the mean-field approximation, the response function χ which is still defined as the response of the density to an **external potential**. This time, the equation 1.9 must be linearized.

$$\begin{aligned} \chi_{\sigma\sigma'}(r, r') &= \frac{\partial n_\sigma(r)}{\partial V^{\text{ext}}_{\sigma'}(r')} = \sum_{\sigma''} \int dr'' \frac{\partial n_\sigma(r)}{\partial V^{\text{tot}}_{\sigma''}(r'')} \frac{\partial V^{\text{tot}}_{\sigma''}(r'')}{\partial V^{\text{ext}}_{\sigma'}(r')} \\ &= \sum_{\sigma''} \int dr'' \, \chi^0_{\sigma\sigma''}(r, r'')[\delta(r' - r'')\delta_{\sigma'\sigma''} \\ &+ \sum_{\sigma'''} \int dr'''(\frac{e^2}{|r'' - r'''|}\delta_{\sigma''\sigma'''} + f^{\text{xc}}_{\sigma''\sigma'''}(r'', r'''))]\chi_{\sigma'''\sigma'}(r''', r') \end{aligned} \tag{1.21}$$

where we have used a chain rule for differentiation of $V^{\text{tot}} = V^{\text{ext}} + V^{\text{Coulomb}}[n] + V^{\text{xc}}[n]$ with respect to the density, and $f^{\text{xc}} = \partial V^{\text{xc}}/\partial n$. This equation can be formally solved for χ and yields the final result:

$$\begin{aligned} \chi_{\sigma\sigma'}(r, r') &= \sum_{\sigma''} \int dr'' \, \chi^0_{\sigma\sigma''}(r, r'')[\delta(r' - r'')\delta_{\sigma'\sigma''} \\ &- \sum_{\sigma'''} \int dr'''(\frac{e^2}{|r'' - r'''|}\delta_{\sigma''\sigma'''} + f^{\text{xc}}_{\sigma''\sigma'''}(r'', r'''))\chi^0_{\sigma'''\sigma'}(r''', r')]^{-1} \end{aligned} \tag{1.22}$$

This relation as presented above (in the r space representation) might not be very helpful, but gives the idea on how to compute the interacting susceptibility function in a given representation within the RPA or mean field approximation. More symbolically and simply, omitting the spin and coordinates indices, one finds that the non-interacting susceptibility becomes renormalized; it can be written as:

$$\chi = [1 - \chi^0 U]^{-1}\chi^0 = \chi^0[1 - U\chi^0]^{-1} \tag{1.23}$$

where U represents the interaction kernel $\frac{e^2}{|r-r'|} + f^{\mathrm{xc}}(r, r')$, and the spin-dependent dielectric function can be defined as $\epsilon = [1 - U\chi^0]$. Note that in the momentum representation, for a uniform system, this equation is correct, and only χ and U become momentum dependent.

For a uniform system, it is convenient to represent these functions in the reciprocal space. Furthermore, the exchange-correlation kernel is usually short ranged, and can be approximated by $f^{\mathrm{xc}}_{\sigma\sigma'}(r, r') \simeq J\delta(r - r')(1 - 2\delta_{\sigma\sigma'})$, where $J > 0$. Thus it is equal to $-J$ for parallel spins and J for antiparallel spins located at the same point. Physically, this means, as it should due to Pauli principle, that the Coulomb interaction between parallel spin electrons is weaker than that between two antiparallel spin electrons located at the same positions. If the Coulomb or more generally, the pair interaction between the Fermions is represented by the function $v(q)$ in the reciprocal space, the Coulomb interaction kernel matrix can be written as:

$$U_{\sigma\sigma'}(q) = \begin{bmatrix} v(q) - J & v(q) + J \\ v(q) + J & v(q) - J \end{bmatrix}$$

The interacting susceptibility within the RPA becomes:

$$\chi_{\sigma\sigma'}(q) = \begin{bmatrix} \chi^0_\uparrow(q) & 0 \\ 0 & \chi^0_\downarrow(q) \end{bmatrix} \begin{bmatrix} 1 - \chi^0_\uparrow(q)(v(q) - J) & -\chi^0_\downarrow(q)(v(q) + J) \\ -\chi^0_\uparrow(q)(v(q) + J) & 1 - \chi^0_\downarrow(q)(v(q) - J) \end{bmatrix}^{-1} \tag{1.24}$$

Within TF, it was shown that in the absence of an external potential, the non interacting susceptibility χ^0 is $q-$independent and equal to $\chi^0_\sigma = -DOS_\sigma(\mu) = -D_\sigma$. Using this substitution, we find for the dielectric function and the interacting susceptibility:

$$\epsilon_{\sigma\sigma'}(q) = \begin{bmatrix} 1 + D_\uparrow(v(q) - J) & D_\downarrow(v(q) + J) \\ D_\uparrow(v(q) + J) & 1 + D_\downarrow(v(q) - J) \end{bmatrix} \tag{1.25}$$

and

$$\chi_{\sigma\sigma'}(q) = \frac{\begin{bmatrix} -D_\uparrow[1 + D_\downarrow(v(q) - J)] & D_\uparrow D_\downarrow(v(q) + J) \\ -D_\downarrow D_\uparrow(v(q) + J) & -D_\downarrow[1 + D_\uparrow(v(q) - J)] \end{bmatrix}}{1 + (D_\uparrow + D_\downarrow)(v - J) - 4D_\uparrow D_\downarrow vJ} \tag{1.26}$$

respectively.

In conclusion, the Thomas-Fermi theory, in addition to providing a kinetic energy functional of the density, which is exact in the uniform system limit, allows one to bypass the much involved task of solving the Schroedinger equation altogether. Indeed, the density can be written down explicitly, even at nonzero temperatures, as a function of the external and Fermion pair-interaction potentials, whereas, if one had to diagonalize the Hamiltonian matrix, one needed then to add up all the densities due to each eigenstate up to the Fermi energy in order to obtain the ground state density. The key equation is 1.17 which works for finite temperatures, spin polarized and even non uniform systems. Its zero temperature limit, equation 1.7, however, is most well-known and works for uniform, paramagnetic systems, at zero temperature.

1.4 Beyond the Thomas-Fermi theory: Gradients expansion

The previous kinetic energy functional is exact for uniform systems. One can thus expect it to work rather well for metals where the electron density is almost uniform due to strong screening. To go beyond this theory, one can add correction terms in powers of the higher derivatives of the density. This is a perturbative idea first used by Kirznits[2] who first derived the lowest order quantum corrections to the Thomas-Fermi kinetic energy. Within this theory, the next correction term in the kinetic energy density is:

$$T_W[n] = A\frac{1}{2}\int dr|\nabla\sqrt{n(r)}|^2 = A\frac{1}{8}\int dr\frac{|\nabla n(r)|^2}{n(r)} \tag{1.27}$$

which is also called the von-Weizsacker[1] functional. It was later shown that the best coefficient for the gradient term is neither the Weizsacker value of $A = 1$ nor the Kirznits value of $A = 1/9$, but somehow the averaged value of $A = 1/5$. It is possible to go beyond this formula by using perturbation theory to first and also second order[3]. This was done by Wang and Teter. Here, we will only give the result for the first order perturbation correction to the wavefunctions from which one can extract the corrected kinetic energy functional:

$$T_{WT}[n] \;=\; \frac{48}{125}(3\pi^2)^(2/3)\int dr\,dr'\,n^{5/6}(r)\,n^{5/6}(r')\,w(r-r') \tag{1.28}$$

$$
\begin{aligned}
- & \quad \frac{21}{250}(3\pi^2)^{(}2/3) \int dr\, n^{5/3}(r) \\
- & \quad \frac{1}{2} \int dr\, n^{1/2}(r)\, \nabla^2 n^{1/2}(r)
\end{aligned}
$$

This is the first reasonable step towards a real density functional theory of materials which, combined with gradient corrected exchange-correlation functionals, allows a rather correct description of slightly non uniform systems such as metals. In this case, to solve for the ground state, an in principle much simpler minimization will replace the more involved task of diagonalizing a Kohn-Sham Hamiltonian and making it self-consistent.

Bibliography

[1] CF von Weizsacker, Z. Phys. **96**, 431 (1935).

[2] DA Kirznitz, Sov. Phys. JETP **5**, 64 (1957).

[3] LW Wang, and MP Teter, Phys. Rev. B **45**, 13196 (1992).