

Thomas-Fermi Model

TF Kinetic Functional

In 1927, Thomas and Fermi realized that the ground state energy of the Homogeneous Electron Gas (HEG) is a function of electron density alone. Imagine an infinite suspanse of HEG, if we study a small chunk of it, say a box with side l , then we can solve the familiar particle in a periodic box problem and get

$$\epsilon_n = \frac{h^2}{2ml^2}n^2 \quad (1)$$

In the grand scheme of things, we need to add up the energies of all such boxes of volume $dV = l^3$ to get the total energy of HEG. Thus let's say there are dN electrons in this region, then the Fermi level

$$\begin{aligned} 2 \cdot \frac{4}{3}\pi n_F^3 &= dN \Rightarrow \\ n_F &= \left(\frac{3dN}{8\pi}\right)^{1/3} \end{aligned} \quad (2)$$

The total energy of the particles inside is then

$$\begin{aligned} dE &= 2 \cdot \int_0^{2\pi} \int_0^\pi \int_0^{n_f} \epsilon_n n^2 \sin\theta dn d\theta d\phi = 8\pi \int_0^{n_F} \frac{h^2}{2ml^2} n^4 dn = \frac{8\pi h^2}{10m} \frac{n_F^5}{l^2} \\ &= \frac{8\pi h^2}{10m} \frac{3}{8\pi} \left(\frac{3}{8\pi}\right)^{2/3} \frac{dN^{5/3}}{l^2} = \frac{3h^2}{10m} \left(\frac{3}{8\pi}\right)^{2/3} \left(\frac{dN}{dV}\right)^{5/3} dV \end{aligned} \quad (3)$$

Notice $\rho = \frac{dN}{dV}$ is the density of electrons inside the box. Call $C_F = \frac{3h^2}{10m} \left(\frac{3}{8\pi}\right)^{2/3}$, the total energy (which is just kinetic energy) of HEG

$$T(\rho) = \int dE = C_F \int \rho dV \quad (4)$$

While this is correct for HEG, it is not obvious if this relation will hold for inhomogeneous electron gas. Therefore Thomas and Fermi had to throw in little magic called *Local Density Approximation*(LDA), which says the properties of an inhomogeneous electron gas is locally identical to those of HEG. Thus they introduced the famous *Thomas-Fermi kinetic energy functional*

$$\boxed{T_{TF}[\rho] = \int dE = C_F \int \rho(\vec{r}) d\vec{r}} \quad (5)$$

and said it's a good first approximation for everything.

TF Model of Atom

Recall the energy of a bunch of electrons in terms of electron density

$$E = T + \int v(\vec{r})\rho(\vec{r})d\vec{r} + \frac{1}{2} \iint \frac{1}{r_{12}}\rho(\vec{r}_1)\rho(\vec{r}_2)d\vec{r}_1d\vec{r}_2 + \frac{1}{2} \iint \frac{1}{r_{12}}\rho(\vec{r}_1)\rho_{XC}(\vec{r}_1, \vec{r}_2)d\vec{r}_1d\vec{r}_2 \quad (6)$$

where T is kinetic energy, $v(\vec{r})$ is external potential and $\rho_{XC}(\vec{r}_1, \vec{r}_2)$ is the exchange-correlation hole density. Thomas and Fermi apply LDA to the above model and further ignore exchange-correlation effect to obtain

$$\boxed{E_{TF}[\rho]} = T_{TF}[\rho] + \int v(\vec{r})\rho(\vec{r})d\vec{r} + \frac{1}{2} \iint \frac{1}{r_{12}}\rho(\vec{r}_1)\rho(\vec{r}_2)d\vec{r}_1d\vec{r}_2$$

$$\boxed{= C_F \int \rho(\vec{r})d\vec{r} + \int v(\vec{r})\rho(\vec{r})d\vec{r} + \frac{1}{2} \iint \frac{1}{r_{12}}\rho(\vec{r}_1)\rho(\vec{r}_2)d\vec{r}_1d\vec{r}_2} \quad (7)$$

which can be minimized with the constraint

$$\int \rho(\vec{r})d\vec{r} = N \quad (8)$$

to obtain the approximate ground state electron density of an atom. While this is an OK model for calculating atomic ground state energies, its accuracy is quite low compared to other methods at the time. More importantly, no molecular bonding is predicted whatsoever. As a consequence, it was dismissed as a cute toy model that employed too many approximations to have any physical significance. The theory was forgotten, and the dream of reducing electronic energy to pure functional of the simple and physical electron density seemed lost... At least for almost 4 decades.

In 1964, Hohenberg and Kohn resurrected this dream.