Thomas Fermi model

Let us consider an almost uniform electron gas. The first step is to neglect the electron-electron interaction and consider the kinetic energy only.

Independent electron gas

Here we consider an electron in a box of volume L^3. The kinetic energy is given by

$$T = 2 \times \frac{1}{2} \sum_{n_x, n_y, n_z} \left(\left(\frac{\pi n_x}{L}\right)^2 + \left(\frac{\pi n_y}{L}\right)^2 + \left(\frac{\pi n_z}{L}\right)^2 \right) \simeq \int_0^{n_{\max}} \frac{\pi^2}{L^2} 4\pi n^4 dn = \frac{\pi^3}{L^2} \frac{4}{5} n_{\max}^5,$$

and the number of electrons is

$$N \simeq 2 \times \int_0^{n_{\max}} 4\pi n^2 dn = \frac{8\pi}{3} n_{\max}^3.$$

Then

$$\frac{T}{V} = \frac{3^{\frac{5}{3}} \pi^{\frac{4}{3}}}{40} \left(\frac{N}{V}\right)^{\frac{5}{3}}.$$

The kinetic energy density and the number density are related by this equation.

When considering an inhomogeneous system, we approximate as

$$T = \int d\boldsymbol{r} \, \frac{3^{\frac{5}{3}} \pi^{\frac{4}{3}}}{40} \left(n(\boldsymbol{r})\right)^{\frac{5}{3}}.$$

This is validated when the de Broglie wavelength has negligible spatial variations, e.g., potential variation is much smaller than inverse of the wave number. The piecewise addition of local quantity is the basic concept of Thomas Fermi.

Classical Coulomb

When the electrons in a piece interact with others in a different piece, the Coulomb energy will be given as

$$\frac{1}{2} \int \frac{n(\boldsymbol{r}) n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d\boldsymbol{r} d\boldsymbol{r}'.$$

This way the total energy of the system will be given as

$$E = \int d\boldsymbol{r} \, \frac{3^{\frac{5}{3}} \pi^{\frac{4}{3}}}{40} \left(n(\boldsymbol{r})\right)^{\frac{5}{3}} + \frac{1}{2} \int \frac{n(\boldsymbol{r}) n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d\boldsymbol{r} d\boldsymbol{r}' + \int v(\boldsymbol{r}) n(\boldsymbol{r}) d\boldsymbol{r}.$$

When E is minimized under the constraint

$$\int n(\boldsymbol{r}) d\boldsymbol{r} = N,$$

we get

$$\frac{5}{3}\frac{3^{\frac{5}{3}}\pi^{\frac{4}{3}}}{40}\left(n(\boldsymbol{r})\right)^{\frac{2}{3}}+\int\frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}'+v(\boldsymbol{r})=\mu.$$

This is called as the Thomas Fermi equation.

Exchange and gradient correction

There are many modifications of the Thomas Fermi model. The Dirac exchange term

$$E_x=-\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\int n^{\frac{4}{3}}(\boldsymbol{r})d\boldsymbol{r}$$

and the von Weizäcker term

$$T_w=\frac{\lambda}{8}\int\frac{|\nabla n(\boldsymbol{r})|^2}{n(\boldsymbol{r})}d\boldsymbol{r}$$

are well-known examples. The energy functional

$$E=\int d\boldsymbol{r}\,\frac{3^{\frac{5}{3}}\pi^{\frac{4}{3}}}{40}\left(n(\boldsymbol{r})\right)^{\frac{5}{3}}+\frac{\lambda}{8}\int\frac{|\nabla n(\boldsymbol{r})|^2}{n(\boldsymbol{r})}d\boldsymbol{r}+\frac{1}{2}\int\frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}d\boldsymbol{r}'-\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\int n^{\frac{4}{3}}(\boldsymbol{r})d\boldsymbol{r}$$
$$+\int v(\boldsymbol{r})n(\boldsymbol{r})d\boldsymbol{r}$$

is constructed in a semilocal way. This is sometimes called as the density functional theory of the first generation.

Note that, in the same spirit, one can incorporate the correlation energy like

$$E_c=\int\epsilon_c[n(\boldsymbol{r})]d\boldsymbol{r}$$

by using the result of quantum Monte Carlo simulation done for a uniform electron gas model.