Thomas-Fermi Theory

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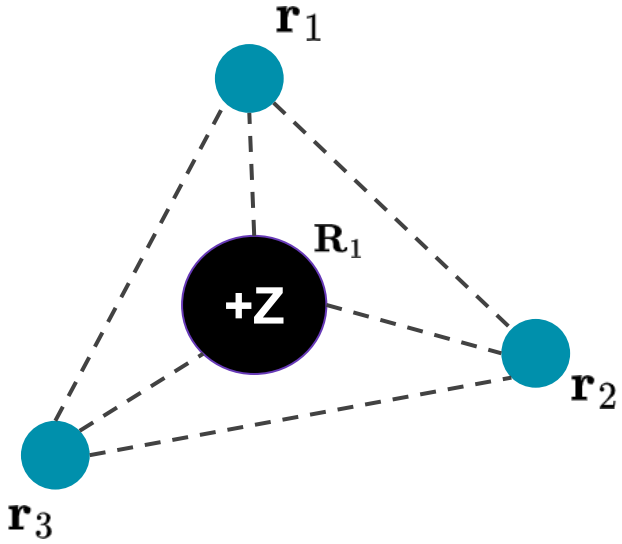
Electronic wavefunction & Electron density



A quantum system with 1 nucleus and 3 electrons. The wavefunction for this systems depend on 9 variables and electron density depend on only 3.

- The electronic wavefunction describe the whereabouts of electrons in a quantum system. It is a highly dimensional function depending on the coordinates of ALL electrons in the system:

$$\Psi(\mathbf{r}_1, \mathbf{r}_1, \cdots, \mathbf{r}_N)$$

$$\mathbf{r_i} = (x_i, y_i, z_i) \quad \rightarrow 3\mathbf{N} \text{ variables!}$$

- Electron density describe the concentration of electrons throughout space. It is therefore merely a function of three variable:

$$\rho(r)$$

$$\mathbf{r} = (x, y, z) \rightarrow \text{only 3 variables!}$$

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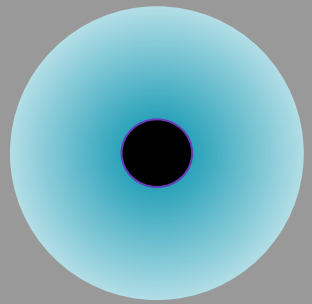
The general idea

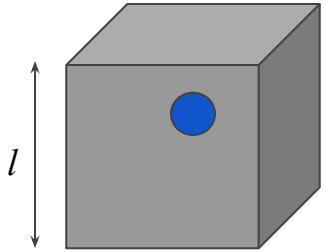
We would like to turn the complex many-electron problem described by the Shrödinger equation into a simpler problem. In Thomas-Fermi theory we try to derive a useful expression for energy in terms of the electron density which depend on only three coordinates instead of 3N.

$$\hat{H}\Psi = E\Psi$$



$$E = F(\rho)$$

Non-interacting uniform electron gas (Fermi gas) - A particle in box



A box with side-length, l, containing an electron.

- A non-interacting uniform electron gas (NUEG) is an ensemble of non-interacting electrons.
- Electrons are Fermions. Therefore we can also refer to NUEG as a Fermi gas.
- Non-interacting electrons can be treated quantum mechanically using the *particle in a box* model. The energy of such an electron is defined by:

$$E = \frac{h^2}{8ml^2}(n_x^2 + n_y^2 + n_z^2)$$

l - side-length of the box
m - mass of the electron
n_x, n_y, n_z - quantum numbers.

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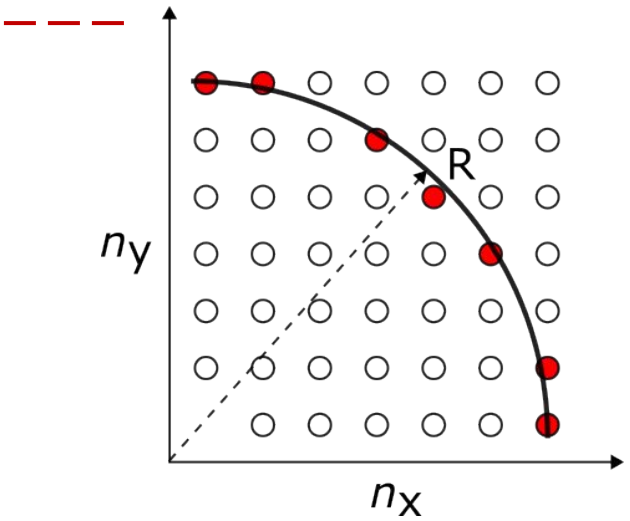
Counting states



A 2D example showing allowed quantum numbers for an electron in a box. Each point in the chart correspond to a quantum state with an energy proportional to the square of distance from origo ($E \propto R^2$). The points marked with red, corresponds to states with a similar energy.

- The square sum of quantum numbers can be interpreted as the square of a radius in the space spanned by the quantum numbers, $\boldsymbol{n_x}$, $\boldsymbol{n_y}$ and $\boldsymbol{n_z}$. We can write:

$$E = \frac{h^2}{8ml^2}(n_x^2 + n_y^2 + n_z^2) = \frac{h^2}{8ml^2}R^2$$

- States with similar energies are found on the surface of a sphere with radius, $\boldsymbol{R}$, in the space spanned by the quantum numbers.

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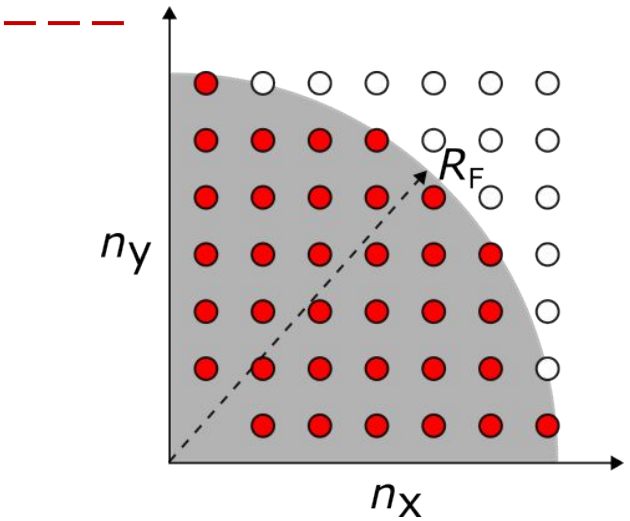
Counting states



A 2D example showing allowed quantum numbers for an electron in a box. Points marked with red color have an energy smaller F.

- The square sum of quantum numbers can be interpreted as the square of a radius in the space spanned by the quantum numbers. We can write:

$$E = \frac{h^2}{8ml^2}(n_x^2 + n_y^2 + n_z^2) = \frac{h^2}{8ml^2}R^2$$

- States with an energy smaller than a certain energy, F, will be found inside a sphere (a circle in the 2D representation in figure) of radius R_F.

- n_x, n_y and n_z must be positive numbers. The number of states, N_F, is therefore ⅛ of the volume (¼ of the area in the 2D example). We can write:

$$N_F = \frac{1}{8}\frac{4\pi R_F^3}{3} = \frac{\pi}{6}\left(\frac{8ml^2F}{h^2}\right)^{3/2}$$

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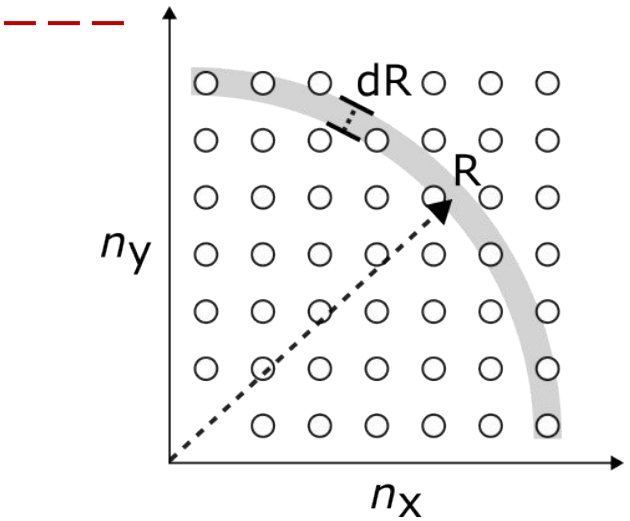
Density of states (DOS) & total energy



A 2D example showing allowed quantum numbers for an electron in a box. The area of the grey shell corresponds to the density of states with energy given by R.

- The density of states, $g(E)$, is defined as the number of states in a infinitely small energy range dE around E. It corresponds to a spherical shell in the space of n_x, n_y and n_z. We can write it as follows:

$$g(E) = \frac{\pi}{4}\left(\frac{8ml^2}{h^2}\right)^{3/2} E^{1/2}$$

- The total energy, E_{tot} ,and the number of states, N_F. can be defined as:

$$E_{tot} = \int_0^F E \cdot g(E) dE$$

$$N_F = \int_0^F g(E) dE$$

F is the energy of highest occupied state and is called the Fermi energy.

$$E_{tot} = \int_0^F E \cdot g(E) dE = \int_0^F \frac{\pi}{4} \left(\frac{8ml^2}{h^2} \right) E^{3/2} dE = \cdots = \frac{\pi}{5} \left(\frac{2l}{h} \right)^3 (2m)^{3/2} F^{5/2}$$

$$N_F = \int_0^F g(E) dE = \int_0^F \frac{\pi}{4} \left(\frac{8ml^2}{h^2} \right) E^{1/2} dE = \cdots = \frac{\pi}{3} \left(\frac{2l}{h} \right)^3 (2m)^{3/2} F^{3/2}$$

The electron density is the concentration of electrons i.e. the number of electrons per volume.

$$\rho = \frac{N_F}{V} = \frac{N_F}{l^3}$$

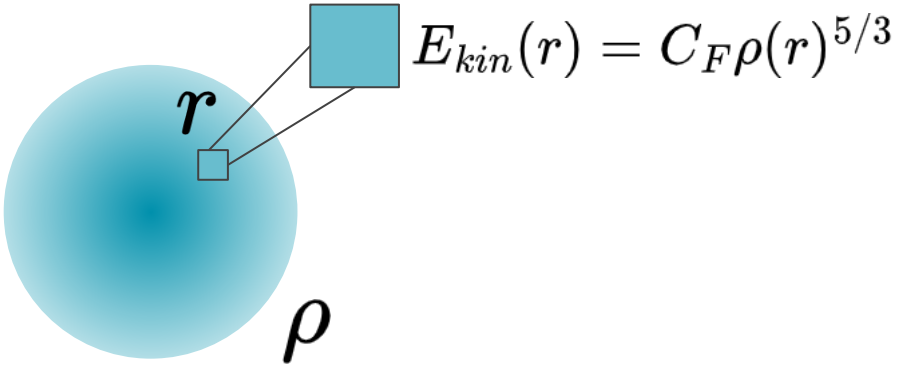
Note that the volume of the box, l^3, appear in the expressions for both electron density and N_F. It can therefore be eliminated, allowing us to find a rather simple energy expression for a non-interacting uniform electron gas.

$$E = \frac{3}{10} (3\pi)^{2/3} \rho^{5/3} = C_F \rho^{5/3}$$

$$C_F \approx 2.871$$

This energy expression correspond to the kinetic energy of the electrons.
Why? Since the system is non-interacting, all other energy contributions are zero by construction!

Energy for a non-interacting non-uniform electron gas

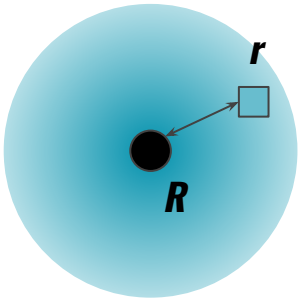


For a non-interacting system of electrons, we can find the kinetic energy by summing up the contribution from each local electron density. In a small volume element around ***r***, the system is uniform and the local energy can therefore be calculated using the expression derived on the previous slide.

- The (kinetic) energy for a non-uniform system can be found from an integral of space using our kinetic energy expression:

$$E_{kin,total} = \int C_F\rho(r)^{5/3}dr$$

Adding the nucleus-electron attraction



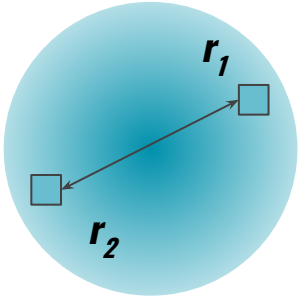
$$E_{Ne}(r) = \frac{-Z}{|r-R|}$$

In a similar spirit, Nucleus-electron attraction can be added by summing up contributions from each volume element of the electron density. The energy for each volume element depend on it's distance to the nucleus.

- We add nucleus-electron attraction by assuming that every small volume element of the electron density interacts with the nucleus via a Coulomb attraction term. We may write:

$$E_{Ne,total} = -\int \frac{Z}{|r-R|} dr$$

Adding electron repulsion



$$E_{ee}(r_1, r_2) = \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|}$$

Electron repulsion is calculated from each unique pairs of two volume elements. For each pair the energy depend on the distance between the volume elements.

- We add electron-electron repulsion in a similar spirit. This time we need consider every unique pair of volume elements. This leads to a double integral and a factor of half in front to avoid double counting:

$$E_{ee,total} = \frac{1}{2} \int\int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2$$

Putting it all together

The total energy expression involving all contributions is the Thomas-Fermi energy and can be written:

$$E_{TF}[\rho] = \int C_F \rho(r) dr - \int \frac{Z}{|r-R|} dr + \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2$$

Kinetic energy *Nucleus attraction* *Electron repulsion*

This is the simplest example of a complete density functional. We use the phrase ***functional**** to emphasize that the energy depend on the electron density which in turn is a function in three-dimensional space.

The approximation is unfortunately rather poor in terms of describing the energy of realistic systems. However it's importance should not be understated since it has inspired to the development of modern Density Functional Theory DFT).

*A "function of a function" is called a functional in mathematics.

Minimizing the energy

$$\min E_{TF}[\rho]$$
$$\text{subject to: } N - \int \rho dr = 0$$

We can find a density ρ corresponding to a given fixed number of electrons that minimize the energy by making use of a Lagrangian multiplier.

$$\mathfrak{L}(\rho, \mu) = E_{TF}[\rho] + \mu \left(N - \int \rho dr\right)$$

Step 1: Define the Lagrangian function.

$$\frac{\delta \mathfrak{L}}{\delta \rho} = \frac{5}{3} C_F \rho^{2/3} - \frac{Z}{|r-R|} + \int \rho(r') dr' - \mu = 0$$

Step 2: Find the minimum by identifying when the derivative is zero.

$$V = -\frac{Z}{|r-R|} + \int \rho(r') dr'$$

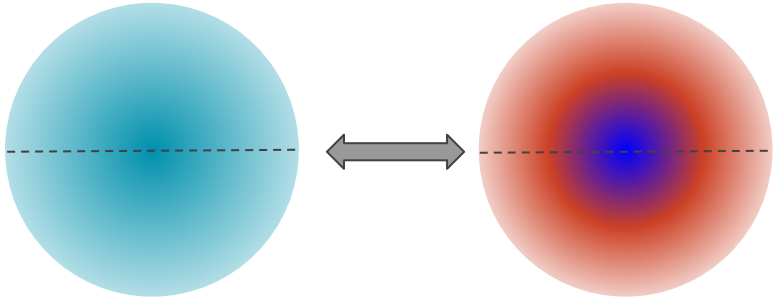
Step 3: Inspect the expression.

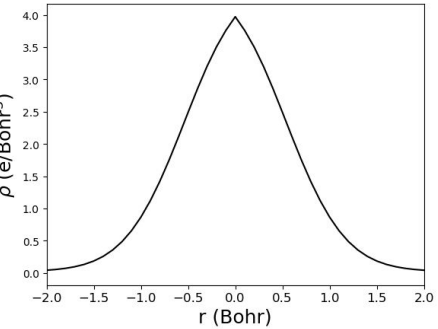
$$\rho = \left(\frac{5}{3} C_F\right)^{-3/2} (\mu - V)^{3/2}$$

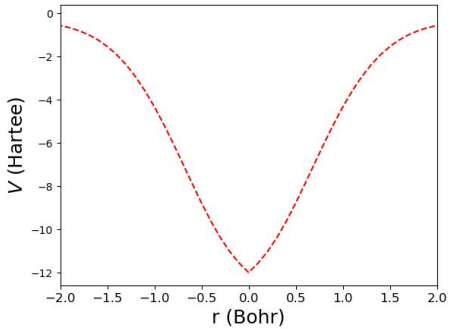
Step 4: Rewrite the expression in a convenient way.

$$E_{TF}[\rho] = \int C_F \rho(r) dr - \int \frac{Z}{|r-R|} dr + \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2$$

An implicit relation between electron density and potential







- In Thomas-Fermi theory, there is a connection between the electron density and the potential in which the electrons are moving.

$$\rho = \left(\frac{5}{3}C_F\right)^{-3/2}(\mu - V)^{3/2}$$

- This connection inspired Walter Kohn in the derivation of density functional theory (DFT).

Summary

- Thomas-Fermi theory allow us to express the energy of system in terms of its electron density
- The method can be derived using the quantum mechanical concept of a *particle in a box*
- The method is a simple example of a Density Functional
- It forms the inspiration to modern Density Functional Theory