Deriving the Thomas-Fermi-Dirac Equation

For an atom in a given state, assuming \( P(\mathbf{r}) \) is the maximum momentum of an electron in a volume \( V \), there is an octant of spherical momentum space with a radius of \( P \).

\[ \langle P \rangle = \frac{3kT}{\pi} \]

It can be shown that the momentum as a function of the electron density is

\[ P = \frac{1}{\alpha} \frac{3kT}{\pi} \]

If we define the energy of one electron classically, the Hamiltonian is then

\[ E = \frac{P^2}{2m} + V(\mathbf{r}) = \frac{1}{2m} \left( \frac{3kT}{\pi} \right)^2 + V(\mathbf{r}) \]

Now consider the total energy of the whole electron distribution. With kinetic energy density \( t(\mathbf{r}) \), the kinetic energy \( T \) is defined as

\[ T = \int t(\mathbf{r})d\mathbf{r} \]

When evaluated at the maximum momentum \( P \) defined earlier,

\[ \frac{3kT}{\pi} \]

The potential energy \( V(\mathbf{r}) \) is due to the interaction of the electron density from the nuclei and the electrostatic interaction of the electron density with itself. So the total energy of the electron system is

\[ E_{tot} = T + V(\mathbf{r}) = \int t(\mathbf{r})d\mathbf{r} + \int V(\mathbf{r})d\mathbf{r} \]

To find the density functional that minimizes the total energy, we can use the calculus of variations:

\[ \delta (E_{tot} - \lambda N_e) = 0 \]

We can calculate the electric field of an ionic sheet:

\[ E = \frac{\rho}{\epsilon_0} \]

The Thomas-Fermi-Dirac equation is not sufficient for determining interlayer forces, because it does not have a minimum. However, upon adding the Kirzhnits correction, the functional does have a minimum a distance away from the slab. In our case the correction is

\[ U_k = \frac{\alpha}{\beta} \int \frac{d^2q}{(2\pi)^2} \left[ \frac{1}{\beta} + (1 + \frac{2\pi^2}{\beta^2}) \right] \]

The Kirzhnits Correction

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Many-body problem

DFT electron density

ion

Mathematically Modeling Graphite

To determine the width of an ionic slab, normalize a boundary around a single carbon atom so that it encloses 5 of its electrons, excluding the outermost 2p electrons. The electron density around a carbon atom can be thought of as a superposition of wave functions. These were determined from empirical data and are spherically symmetric

\[ \rho(\mathbf{r}) = \frac{n(\mathbf{r})}{4\pi \alpha^2} \]

where

\[ \alpha^2 = \frac{e^2}{\epsilon_0 E_{Fermi}} \]

With coefficients and effective nuclear charge \( A_1 \) (all in atomic units):

\[ A_1 = 27.76 \quad C = 3268 \quad \frac{A_1}{A_2} = 1.505 \]

Evaluating this integral and solving for \( z \) yields \( z = 1.1826 \) a.u., the width of a slab is \( 2z \).

Determining the Electric Field of an Ionic Sheet is straightforward. Experimentally, we know that the distance between nuclei is \( d = 1.42 \) Å.

The area of a hexagon, \( A = \frac{3\sqrt{3}}{2} a^2 \).

Area/Atom \( \frac{A}{atom} = 4 \times \frac{3\sqrt{3}}{2} a^2 \alpha^2 = 3.18 \times 10^{-10} \) atom/square meter.

Surface Charge Density \( \sigma = 3.18 \times 10^{-10} \alpha^2 = 0.1076 \) a.u.

Then, exploiting symmetry and using Gauss’s law, we can calculate the electric field at the surface of the sheet:

\[ E = \frac{2m_e}{\epsilon_0} \]

Calculating Interlayer Force

Upon obtaining the solution to the Thomas-Fermi-Dirac equation and plugging it into the total energy functional, the energy is now a functional of the distance between layers. Integrating the total energy functional along with both corrections for different values of \( R \) allows the calculation of the equilibrium distance, and the force constant by adjusting a suitable second order polynomial near the minimum.

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