

At zero temperature all energy levels below the Fermi energy are occupied:

$$f(E) = \begin{cases} 1 & E \leq F \\ 0 & E > F \end{cases}$$

Consequently the total energy of the electrons in one cell will be

$$E = \int_0^F E f(E) g(E) dE \\ = \frac{4\pi}{h^3} (2m)^{3/2} l^2 \int_0^F E^{3/2} dE$$

$$E = \frac{8}{5} \left(\frac{2l}{h}\right)^3 (2m)^{3/2} E^{5/2} \quad \text{--- (5)}$$

The Fermi energy F can be obtained from the total number of electrons in a cell.

$$\Delta N = 2 \int_0^F f(E) g(E) dE = \frac{\pi}{h^3} \left(\frac{2l}{h}\right)^3 (2m)^{3/2} F^{3/2} \quad \text{--- (6)}$$

Combine equ. (5) and (6)

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

→ $\frac{\Delta N}{l^3} = n$
from (6)

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

(2)

where

$$C_F = \frac{3}{10} (3\pi^2)^{2/3} = 2.871 \quad \text{--- (7)}$$

$e = h = m_0 = 1$ are in atomic unit.

The electron density is a smooth function in a real space. Now adding the contributions from all cells with energies within F , is.

$$T_{HF}[\rho] = C_F \int \rho^{5/3}(\mathbf{r}) d^3\mathbf{r} \quad \text{--- (8)}$$

The equ (8) represents the well-known Thomas-Fermi kinetic energy functional, which is a function of the local electron density. This could be applied to electrons in atoms encountering the most important idea of the modern DFT.

The equ. (8) shows that the total K.E of the electrons can be expressed in terms of only spatially varying electron.

21a density $\rho(\vec{r})$, according to this model.

They calculate the energy of an atom using this model by incorporating the \vec{V}_{Ne} and \vec{V}_{ee} terms (which can both also be represented in terms of the electron density).

Potential Energy

The potential energy of an atomic electrons, due to the electric attraction of the positively charged nucleus is

$$V_{eN} = \int \rho(\vec{r}) \bar{V}_N(\vec{r}) d^3r$$

where $\bar{V}_N(\vec{r})$ is the potential energy of the n -electron at \vec{r} , due to field produce by nucleus, which is

$$\bar{V}_N(\vec{r}) = -\frac{Ze^2}{r}$$

& The potential energy of the electrons due to their mutual repulsion

is -

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•). Complete neglect. The electron-correlation

•). The energy of any molecule is calculated with TF theory is higher than the sum of the energies of the constituent atoms.

Density Functional Theory :-

Density functional theory is a quantum mechanical approach - used in chemistry and physics to calculate the electronic structure - specifically the ground state of the system. For many body (atoms, molecules and the condensed phases). The properties of many electron system can be determined by using functional functions of another function, which is spatially dependent electron density. Hence, the name comes DFT - ~~comes~~ from the use of functional of the electron density.

$$\bar{V}_{ee} = \frac{1}{2} e^2 \int \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r'$$

Total Energy:

The total energy of the electrons is the sum of their K.E and P.E.

$$E = T + \bar{V}_{en} + \bar{V}_{ee}$$

$$E = C_F \int (n(\vec{r}))^{5/3} d^3r + \int n(\vec{r}) V_N(\vec{r}) d^3r + \frac{1}{2} e^2 \int \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r'$$

Deficiencies.

Although it was a good first step, but this model TF equations accuracy is limited because the K.E is only the approximates and the method does not attempt to represent the exchange energy of an atom.

1) A term of -exchange energy is added by Dirac in 1928.

Hohenberg-Kohn Theorems

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The basis of DFT is provided by.

The Hohenberg-Kohn Theorem. The conventional formulation of the two theorems of Hohenberg and Kohn is as follows:

Theorem 1: "The non-degenerate ground state electron density ρ appropriately determines the external potential V_{ext} ."

The consequence is that the external potential is a well-defined functional of the exact ground state electron density $V_{ext}[\rho]$.

Theorem 2: "The ground state total energy functional $E_{ext}[\rho]$ reaches its minimal value (equal to the ground state total energy) at the correct ground state