

17a

This term is cancelled with the exchange term. The exchange term comes from inclusion of the Pauli principle and the assumed determinantal form of the wavefunction. The effect of exchange is for electrons of like-spin to avoid each other.

The HF approximation corresponds to the conventional single-electron picture of the electronic structure. The distribution of the N -electrons is given simply by the sum of one electron distributions $|\phi_i|^2$. This allows concept such as labelling of ϵ_i s by angular momenta, but it must be remembered that this is an artifact of the initial trial wavefunction and that in some systems modifications are required to these ideas.

Difficulties & Shortcomings of HFT.

- 1) HF theory, by assuming a single-determinant form for the wavefn, neglects correlation b/w electrons.
- 2) The electrons are subject to an average non-local potential arising from the other electrons, which can lead to a poor description of the electronic structure.
- 3) Although, qualitatively it's a correct approximation in many materials and compounds, but is insufficiently accurate to make accurate quantitative predictions.

18a / Difficulties with when proceeding

with the wave-function.

• Hilbert space grow exponentially with N .

• Many body wavefn is a very complicated

object:- If a grid of q points is used per degree of freedom, then

$B = q^{3N}$ values have to be stored.

eg:-

$q = 3$ (very rough grid) $\rightarrow 3^{30} \approx 10^{15}$

Solution:

Many physical quantities of interest.

such as; Energy (E), Charge

density depend explicitly only on

a small number of variables, e.g.

$$n(\vec{r}) = N \int d^3r_1 \dots d^3r_N \Phi^*(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \Phi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$

Therefore, avoid full many body wavefunction and try to calculate: $n(\vec{r})$ and E directly from some other methods.

Thomas-Fermi Model: (TF)

It is a quantum mechanical approach, in order to calculate the electronic structure of many body systems.

Electronic Structure: is the state of motion of electrons in an electrostatic field created by stationary nucleus.

TF model is being formulated in terms of electronic density alone, instead of ~~over~~ electronic wavefns.

In 1920s, Thomas and Fermi suggested that atoms are uniformly distributed by electrons (negatively charge ^{clouds} clouds) around nuclei in a six dimensional.

19a Phase space (momentum and position coordinates). This is enormous simplification of the actual many-body problem.

The basic idea of T.F approximation is that the total energy of the system could be presented as a functional of electron density ($E[n]$). Each h^3 of the momentum space volume is occupied by two electrons and electrons are moving in an effective potential field that is determined by nuclear charge and by assumed uniform distribution of electrons. The density of ΔN electrons in real space within a cube with a side " l " is given by

$$f(r) = \frac{\Delta N}{l^3} = \frac{\Delta N}{V} \quad \text{--- (1)}$$

Functional:

A functional is a function of a vector space into its underlying scalar field, or a set of real numbers.

The electron energy levels in 3d-infinite well are given by.

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

$$= \frac{h^2}{8mp^2} R^2 \quad \text{--- (2) } n_x, n_y, n_z = 1, 2, 3, \dots$$

Radius $R = R_{max}$ of the sphere in the space (n_x, n_y, n_z) covering all occupied state, determined. The maximum energy of electrons: The Fermi energy F . The maximum of energy levels within this max value at zero temp is.

$$N_F = \frac{1}{2^3} \frac{4\pi}{3} R^3 = \frac{\pi}{6} \left(\frac{8mp^2}{h^2} E \right)^{3/2} \quad \text{--- (3)}$$

Hence, the density of states is defined as

$$g(E) dE = N_F(E + dE) - N_F(E)$$

$$= \frac{\pi}{4} \left(\frac{8mp^2}{h^2} \right)^{3/2} E^{1/2} dE \quad \text{--- (4)}$$

In other words, it is a function that takes a vector as its input argument and returns a scalar.

$$f: \mathbb{R}^n \rightarrow \mathbb{R}$$