

electron density ρ_0 corresponding to
Vext..

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$$E[\rho] \geq E[\rho_0]$$

for every trial electron density ρ . The
ground state total energy functional.

$E_{\text{Vext}}[\rho]$ can be written as

$$E_{\text{Vext}}[\rho] = \langle \psi | T_e + V_{ee} | \psi \rangle \\ + \langle \psi | V_{\text{ext}} | \psi \rangle$$

$$= F_{\text{HK}}[\rho] + \int \rho V_{\text{ext}} d\vec{r}$$

where $F_{\text{HK}}[\rho]$ is the Hohenberg-Kohn
density functional is universal for many
electron system.

Two important results:

1) The one-to-one correspondence

b/w - ground state density and external

Potential $\rho(\vec{r}) \leftrightarrow V_{\text{ext}}$ is important to
note.

It is known ^{given} many electron system has a unique external potential, which yields a unique ground state of many particle wavefn. by the Schrodinger wave eqn. and the Hamiltonian.

$$\hat{H} = T_{ee} + V_{ee} + V_{ext}$$

From the above calculated wavefn. (ground state), the corresponding electron density is easily found.

Hence, an external potential gives a unique ground state density corresponding to it.

From the first theorem, the density contains as much information as the ψ , therefore, all the observables can be written as a functional of the density.

Second, the universality of the $E_{HK}[\rho]$ should be understood. A very well defined expression for the $E_{HK}[\rho]$ is not known. Just check, $E_{HK}[\rho]$ does not contain any information on the nuclei. Therefore, it is a universal functional for any many electrons system, implying that, in principle, there exist an expression for $E_{HK}[\rho]$ which can be used for every atom, molecule or solid.

Now the ground state density corresponding to the V_{ext} can be obtained by using the second theorem.

Now it is easy to understand the meaning of energy functional $E_{ext}[\rho]$.

Let assume,

ρ_i — any other density
(not ground state)

So. f_j - ground state density.

then.

$$E_i = E_{\text{ext.}} [f = f_i]$$

$$E_j = E_{\text{ext.}} [f = f_j]$$

Hence.

$$f_j < f_i$$

therefore ground state energy is always less value than any other density i.e. f_i

So.

$$E_{f_i} > E_{f_j}$$

The Kohn-Sham Equations.

The Hohenberg-Kohn theorem shows that it is possible to use the ground state density to calculate the physical properties of the system, but it does not tell us a way of finding the ground state density.

This problem is solved by the Kohn-Sham equations.

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In the description of Kohn-Sham eqs, we will explain the two important terms, ① The exchange and ② Correlation.

Correlation energy - The correlation energy is defined as this is the part of the total energy which is present in the exact solution, but absent in the Hartree-Fock solution.

The total energy functional $E[\rho]$ and $E_{HF}[\rho]$ corresponding to the exact and Hartree-Fock Hamiltonians are given below.

$$E = T + V \quad \text{--- ①}$$

$$E_{HF} = T_0 + (V_H + V_{ee}) \quad \text{--- ②}$$

In eqn ①; T and V are the kinetic and electron-electron potential energy functional for the exact sol.

while T_0 is for the non-interacting (26)
electron gas and $V_H + V_x = V$, V_H
and V_x are the Hartree and the
exchange contribution; respectively.
Subtract (2) from (1), will get.

$$T - T_0 = V_c \quad (3)$$

The exchange contribution to
the ~~total~~ ^{exchange} energy is defined as the
part which is present in the Hartree-
Fock solution, but absent in the
Hartree solution; so the Hartree
functional is.

$$E_H = T_0 + V_H$$

The exchange functional can be
written as

$$V_x = V - V_H \quad (4)$$

we know the HK-functional

$$E_{HK} = T + V$$

so

$$E_{HK} = T + V + T_0 - T_0$$