

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

$$\boxed{T - T_0 = V_c},$$

then.

$$E_{HK} = T_0 + V + V_c$$

Now. add. and subtract V_H .

$$E_{HK} = T_0 + V_H + V_c + V - V_H$$

but.

$$\boxed{V_{xc} = V - V_H}$$

so.

$$E_{HK} = T_0 + V_H + V_c + V_{xc}$$

$$E_{HK} = T_0 + V_H + V_{xc}$$

where $V_{xc} = V_c + V_x$ is the exchange-correlation energy functional.

If for a moment, we assume that we know the V_{xc} , then we can easily write energy functional as,

$$E_{HK}[\rho] = T_0[\rho] + V_H[\rho] + V_{xc}[\rho] + V_{ext}[\rho]$$

The corresponding Hamiltonian is called the Kohn-Sham Hamiltonian and is

$$\hat{H}_{KS} = \hat{T}_0 + \hat{V}_H + \hat{V}_{xc} + \hat{V}_{ext} \quad (27)$$

Now the energy functional of the interacting system (original problem) can be written as

$$E[\rho] = T_0[\rho] + \int f(\vec{r}) \left(\bar{V}_{ext}(\vec{r}) + \frac{1}{2} \bar{V}_H(\vec{r}) \right) + E_{xc}[\rho] d^3r$$

and the energy functional of the hypothetical non-interacting system:

$$E_0[\rho] = T_0[\rho] + \int d^3r f(\vec{r}) V_{eff}(\vec{r})$$

$V_{eff}(\vec{r})$ — effective potential and has to be chosen such that density

of the non-interacting system is equal to the density of the interacting system

which is.

$$V_{\text{eff}}[\rho(\vec{r})] = V_{\text{ext}}(\vec{r}) + V_H[\rho(\vec{r})] + \frac{\delta E[\rho]}{\delta \rho(\vec{r})}$$

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So the ground state density of the original interacting problem can be calculated from the Kohn-Sham eqs.

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}[\rho(\vec{r})] \right) \phi_n(\vec{r}) = E_n \phi_n(\vec{r})$$

solved self-consistently by iteration

So Now the Kohn-Sham equations theorem.

can be formulated as the exact ground state density ρ for an N electron system,

given by

$$\rho(\vec{r}) = \sum_{n, \text{occ.}} \phi_n^*(\vec{r}) \phi_n(\vec{r})$$

where ϕ_n is the single particle wavefunction, summation over all the occupied states of the N lowest energy sols. of the Kohn-Sham Equation.

$$\boxed{\hat{H}_{KS} \phi_n = \epsilon_n \phi_n}$$

The Exchange-Correlation: ①

The Kohn-Sham equations:

$$-\frac{\hbar^2}{2m} \nabla^2 \phi_n(\vec{r}) + V_{\text{eff}}[\rho(\vec{r})] \phi_n(\vec{r}) = \epsilon_n \phi_n(\vec{r})$$

are thus close to the exact sol, no approximation has been made yet; except that we have simply mapped the fully interacting system onto a non-interacting system that yields the same ground state density.

As mentioned earlier, the KS kinetic energy is not true kinetic energy, as

$$E_{xc}[\rho(\vec{r})] = T[\rho(\vec{r})] - T_s[\rho(\vec{r})] + E_{ee}[\rho(\vec{r})] - E_H[\rho(\vec{r})]$$

where T_s and E_{ee} terms are the

19 exact kinetic energy and electron-electron interaction energies, respectively. Physically, this term can be interpreted as containing the contributions of detailed correlation and exchange to the system energy.

The ~~condition~~ definition above is such that

it ensures that KS-formulation is exact. However, the actual form of E_{xc} is not known, thus we must introduce approximate functionals based upon the electron density to describe this term.

Local Density Approximation;

(2)

The most widely used approximation to the exchange-correlation energy functional is the local density approximation (LDA). In this approximation the exchange-correlation energy is comparable to the value for a homogeneous electron gas having almost constant electron density. (electron density solely varies at each point in the space)

The local exchange-correlation functional in the LDA with a ρ almost constant density " f " is given by

$$E_{xc}^{LDA}[\rho] = \int \rho(\vec{r}) \epsilon_{xc}^{hom}(\rho(\vec{r})) d^3\vec{r} \quad (1)$$

where $\epsilon_{xc}^{hom}(\rho(\vec{r}))$ is the exchange-correlation energy per particle for a uniform electron gas with a constant local density " f ".