# Density Functional Theory (DFT) : What Does It Mean?

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# Regular Approach to Solving System

$\Psi$ : Wavefunction for total system

e.g. One electron system

<u>Schrödinger Equation</u> : $\widehat{H}\Psi = E\Psi$ for system Hamiltonian $\widehat{H}$

$\widehat{H} = \widehat{\mathrm{T}} + \hat{V}$ (kinetic energy operator, potential term e.g. nuclear potential)

$\hat{T} = -\frac{\hbar^2}{2m}\nabla^2; \quad \hat{V} = -\frac{\mathrm{Z_B}}{\left|\vec{r}-\vec{R}_B\right|}$

# Regular Approach to Solving System

*N*-electron system : $\Psi = \Psi(\vec{r}_1, \sigma_1; \vec{r}_2, \sigma_2; \dots; \vec{r}_N, \sigma_N)$

Now the Hamiltonian consists of more parts:

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \sum_i^N V(\vec{r}_i)$$

$\hat{T}, \hat{V}_{ee}$ are independent of particular system, while $V$ is system dependent

Try to calculate *N*-electrons for *M* points in space $\Longrightarrow M^N$ values to calculate. Any realistic system cannot be solved even by computers

# Motivation for New Procedure

Function vs Functional :

Function assigns number(s) to number(s)

Functional assigns function(s) to number(s)

Often see in context of calculus of variations, e.g. Lagrangians

<u>Wavefunction variational principle</u>: extrema of functional

$h[\Psi] = \langle \Psi | \widehat{H} | \Psi \rangle$ gives stationary states; $\min\{h[\Psi]\}$ gives ground state

# Hohenberg-Kohn Theorems

(1) There exists an electron-density functional $F[n]$ such that the ground-state energy and density for *N* electrons within external potential $V(\vec{r})$ is:

$$E_{GS} = \min\left\{F[n] + \int d^3r\, V(\vec{r})n(\vec{r})\right\},$$

where minimization is taken over all $n(\vec{r}) \geq 0$ satisfying constraint $\int d^3r\, n(\vec{r}) = N$.

→ $F[n]$ is “universal functional” of the density : totally independent to the details of external potential $V$

# Hohenberg-Kohn Theorems

(2) The external potential $V(\vec{r})$ (and hence the Hamiltonian) are determined to within an additive constant by $n(\vec{r})$

→ Opposite of how we normally think about solving: rather than going from potential to electron density we can instead get external potential from electron density.

# Constructing the Functional

Kohn-Sham Scheme : construct one-electron orbitals which give reasonable enough approximations to $F[n]$.

$$\Phi_n : \widehat{H}_s \Phi_n = E_s \Phi_n \text{ (s: single-electron)}$$

$$F[n] = \left\langle \Psi_n \middle| \hat{T} + \hat{V}_{ee} \middle| \Psi_n \right\rangle = \left\langle \Phi_n \middle| \hat{T} + \hat{V}_{ee} \middle| \Phi_n \right\rangle + E_c[n]$$

$$T_s[n] = \left\langle \Phi_n \middle| \hat{T} \middle| \Phi_n \right\rangle \;\&\; \left\langle \Phi_n \middle| \hat{V}_{ee} \middle| \Phi_n \right\rangle = U[n] + E_x[n]$$

$$\Longrightarrow F[n] = T_s[n] + U[n] + E_{xc}[n]$$

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$$\Longrightarrow F[n] = \underbrace{T_s[n] + U[n]}_{\boxed{\text{Treated exactly}}} + \underbrace{E_{xc}[n]}_{\boxed{\text{Approximated}}}$$