# Density Functional Theory with Quantum Espresso

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# Basics of Density Functional Theory, Part 1

- Multi-particle Hamiltonian for an atomic system

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N_e} \nabla_i^2 + \frac{1}{2}\sum_{i\neq j}^{N_e} \frac{1}{|\vec{r}_i - \vec{r}_j|} + \sum_{i=1}^{N_e}\sum_{I=1}^{N_n} \frac{Z_I}{|\vec{r}_i - \vec{R}_I|}$$

- First term: Electronic kinetic energy
- Second term: Electron-electron interaction (Coulomb)
- Third term: Nucleus-electron interaction (Coulomb)

# Basics of Density Functional Theory, Part 1

- Multi-particle Schrödinger equation

$$\hat{H}\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = E\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$$

- For very small systems, solving this equation is feasible.
- For larger systems, prohibitively complex.
- Shift focus from the wave function to the electronic density

$$n(\vec{r}) = N \int |\Psi(\vec{r}, \vec{r}_2, \ldots, \vec{r}_N)|^2 d\vec{r}_2 \ldots d\vec{r}_N$$

# Basics of Density Functional Theory, Part 1

**Hohenberg-Kohn Theorems**

The theoretical foundation of DFT is provided by two theorems published in 1964 (Physical Review, 136 (3B): B864B871)

**Theorem 1:** A given charge density uniquely determines the external potential. Thus, the total energy can be expressed as a functional of the density.

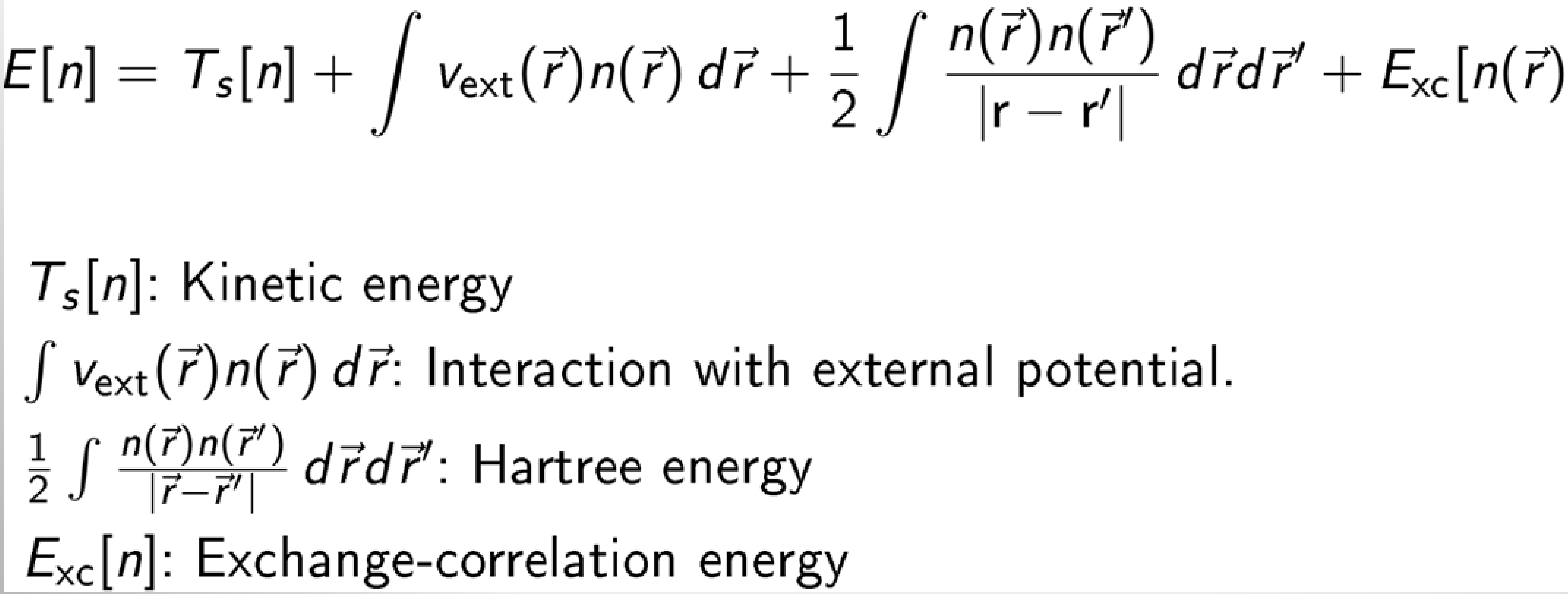
$$E = E[n(\vec{r})]$$

**Theorem 2:** The minimum energy with respect to charge density is the ground state energy. The density that provides this minimum is the ground state density ($n_0$ ).

$$\left.\frac{\delta E}{\delta n(\vec{r})}\right|_{n_0} = 0$$

# Basics of Density Functional Theory, Part 1

## Energy Functional



$$E[n] = T_s[n] + \int v_{\mathrm{ext}}(\vec{r})n(\vec{r})\,d\vec{r} + \frac{1}{2}\int \frac{n(\vec{r})n(\vec{r}')}{|\mathrm{r}-\mathrm{r}'|}\,d\vec{r}d\vec{r}' + E_{\mathrm{xc}}[n(\vec{r})$$

$T_s[n]$: Kinetic energy

$\int v_{\mathrm{ext}}(\vec{r})n(\vec{r})\,d\vec{r}$: Interaction with external potential.

$\frac{1}{2}\int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|}\,d\vec{r}d\vec{r}'$: Hartree energy

$E_{\mathrm{xc}}[n]$: Exchange-correlation energy

# Next: Introduction to DFT, Part 2

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# Basics of Density Functional Theory, Part 2

## The Kohn-Sham Ansatz

The second derivative in the kinetic energy term prevents it from being written as an explicit expression of the density. Instead, the expression proposed by Kohn and Sham in 1965 is used:

$$n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2.$$

Here, $\{\phi_i\}$ are single-electron orbitals, whose forms are to be determined later.

# Basics of Density Functional Theory, Part 2

**The Kohn-Sham Equations**

The system of equations that determines the Kohn-Sham orbitals minimizing the energy functional is written as:

$$\left[-\frac{1}{2}\nabla^2 + V_{\mathrm{ext}}(\vec{r}) + \int \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|}\,d\vec{r}' + V_{\mathrm{xc}}(\vec{r})\right]\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r})$$

- Here, $V_{ext}$ defines the external potential.
- $V_{xc}$ is the exchange-correlation potential, which is not exact and can only be expressed through various approximations.
- $\{\epsilon_i\}$ are the so-called Kohn-Sham orbital energies

# Basics of Density Functional Theory, Part 2

## Common XC Approximations

**Local Density Approximation (LDA):** LDA bases the exchange-correlation energy density only on the local value of the density:

$$E_{\mathrm{xc}}^{\mathrm{LDA}}[n] = \int n(\vec{r})\epsilon_{\mathrm{xc}}(n(\vec{r}))\, d\vec{r},$$

**Generalized Gradient Approximation (GGA):** GGA also takes into account the gradient of the density ($\nabla n(\vec{r})$):

$$E_{\mathrm{xc}}^{\mathrm{GGA}}[n] = \int f(n(\vec{r}), \nabla n(\vec{r}))\, d\vec{r},$$

- $f(n, \nabla n)$: The function defining the exchange-correlation energy density.

# Next: Practicalities, Part 1

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