

Introduction to density-functional theory: discussion on the choice of basic variables in electronic structure theory

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Electronic Hamiltonian, SI and atomic units

- We work within the Born–Oppenheimer approximation (the nuclei are fixed)
- The Hamiltonian describing a N -electron molecule can be written as

$$\hat{H} = \hat{T} + \hat{W}_{ee} + \hat{V}_{ne}$$

$$\hat{T} \equiv \sum_{i=1}^N -\frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 = \sum_{i=1}^N -\frac{\hbar^2}{2m_e} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) \quad \rightarrow \text{kinetic energy}$$

$$\hat{W}_{ee} = \frac{1}{2} \sum_{i \neq j}^N \hat{w}_{ee}(i, j) \quad \text{with} \quad \hat{w}_{ee}(i, j) \equiv \frac{e^2}{4\pi\epsilon_0 r_{ij}} \times \quad \rightarrow \text{electron-electron repulsion}$$

$$\hat{V}_{ne} = \sum_{i=1}^N \hat{v}_{ne}(i) \quad \text{with} \quad \hat{v}_{ne}(i) \equiv - \sum_A^{\text{nuclei}} \frac{Z_A e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_A|} \times \quad \rightarrow \text{electron-nuclei attraction}$$

- A physical N -electron wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ depends on the positions of each electron (spin will be introduced later on) and fulfills the Schrödinger equation $\hat{H}\Psi = E\Psi$.

Electronic Hamiltonian, SI and atomic units

- **Hydrogen atom** ($N = 1$):

$$\hat{H} \rightarrow -\frac{\hbar^2}{2m_e} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{e^2}{4\pi\epsilon_0 \sqrt{x^2 + y^2 + z^2}},$$

$$E \rightarrow E_n = -\frac{E_I}{n^2} \quad \text{where the **ionization energy** equals } E_I = \frac{m_e e^4}{2(4\pi\epsilon_0)^2 \hbar^2} \approx 13.6 \text{ eV.}$$

The ground-state wavefunction ($n = 1$) equals $\Psi_{1s}(x, y, z) = \frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-\sqrt{x^2 + y^2 + z^2}/a_0}$ where

the **Bohr radius** equals $a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} \approx 0.529 \text{ \AA}$.

- Working with so-called "**atomic units**" simply consists in using **unitless** energy $\tilde{E} = E/2E_I$ and coordinates $\tilde{x} = x/a_0$, $\tilde{y} = y/a_0$, $\tilde{z} = z/a_0$.
- The ground-state energy of the hydrogen atom is therefore -0.5 in atomic units.
- Returning to the general N -electron problem, the Schrödinger equation in atomic units is obtained

$$\text{from } \frac{\hat{H}\Psi}{2E_I} = \tilde{E}\Psi$$

Electronic Hamiltonian, SI and atomic units

- **Change of variables** in the wavefunction:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \Psi(a_0 \tilde{\mathbf{r}}_1, a_0 \tilde{\mathbf{r}}_2, \dots, a_0 \tilde{\mathbf{r}}_N) = \tilde{\Psi}(\tilde{\mathbf{r}}_1, \tilde{\mathbf{r}}_2, \dots, \tilde{\mathbf{r}}_N) = \tilde{\Psi}\left(\frac{\mathbf{r}_1}{a_0}, \frac{\mathbf{r}_2}{a_0}, \dots, \frac{\mathbf{r}_N}{a_0}\right)$$

Using $\tilde{\Psi}$ rather than Ψ and the relations $2E_I = \frac{\hbar^2}{m_e a_0^2} = \frac{e^2}{4\pi\epsilon_0 a_0}$ leads to

$$\hat{T}/2E_I \equiv \sum_{i=1}^N -\frac{a_0^2}{2} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) \equiv \sum_{i=1}^N -\frac{1}{2} \left(\frac{\partial^2}{\partial \tilde{x}_i^2} + \frac{\partial^2}{\partial \tilde{y}_i^2} + \frac{\partial^2}{\partial \tilde{z}_i^2} \right),$$

$$\hat{W}_{ee}/2E_I \equiv \frac{1}{2} \sum_{i \neq j}^N \frac{a_0}{r_{ij}} \times = \frac{1}{2} \sum_{i \neq j}^N \frac{1}{\tilde{r}_{ij}} \times,$$

$$\hat{V}_{ne}/2E_I \equiv \sum_{i=1}^N -\frac{Z_A a_0}{|\mathbf{r}_i - \mathbf{R}_A|} \times = \sum_{i=1}^N -\frac{Z_A}{|\tilde{\mathbf{r}}_i - \tilde{\mathbf{R}}_A|} \times$$

- In the following we will simply drop the "tilde" symbol and denote $\hat{T}/2E_I$ as \hat{T} , $\hat{W}_{ee}/2E_I$ as \hat{W}_{ee} , $\hat{V}_{ne}/2E_I$ as \hat{V}_{ne} , and $\hat{H}/2E_I$ as \hat{H} .

Variational principle for the ground state

- Let $\{\Psi_I\}_{I=0,1,2,\dots}$ denote the **exact** orthonormal electronic ground-state ($I = 0$) and excited-state ($I > 0$) wavefunctions:

$$\hat{H}|\Psi_I\rangle = E_I|\Psi_I\rangle, \quad \langle\Psi_I|\Psi_J\rangle = \delta_{IJ}$$

- We assume for clarity that the ground state is non-degenerate: $E_I > E_0$ when $I > 0$.
- We will use **real algebra** in the following (non-relativistic quantum chemistry)

- The exact ground-state energy can be expressed as

$$E_0 = \min_{\Psi} \langle\Psi|\hat{H}|\Psi\rangle = \langle\Psi_0|\hat{H}|\Psi_0\rangle$$

where the minimization is **restricted** to **normalized** wavefunctions Ψ .

Proof: $\forall \Psi, |\Psi\rangle = \sum_I C_I |\Psi_I\rangle$ and $\langle\Psi|\hat{H}|\Psi\rangle - E_0\langle\Psi|\Psi\rangle = \sum_{I>0} C_I^2 (E_I - E_0) \geq 0$.

- Note that, if $\Psi \neq \Psi_0$, then $\langle\Psi|\hat{H}|\Psi\rangle > E_0$ ← important result that will be used later on !
- The **basic variable** is here the electronic wavefunction → **wavefunction theory**
- Once the exact wavefunction Ψ_0 is obtained, the electronic structure is **completely known** (any observable related to electrons can be described)

One-electron wavefunction

- Schrödinger theory: the quantum state of a single electron is written as

$$|\Psi\rangle = \int_{\mathbb{R}^3} d\mathbf{r} \Psi(\mathbf{r}) |\mathbf{r}\rangle$$

where $\Psi(\mathbf{r})$ is the one-electron wavefunction (orbital) and $|\mathbf{r}\rangle$ denotes the quantum state "the electron is at position \mathbf{r} ".

- Pauli theory: the **spin** of the electron is now considered as an additional degree of freedom. The quantum state of a single electron is then written as

$$|\Psi\rangle = \int_{\mathbb{R}^3} d\mathbf{r} \sum_{\sigma=\alpha,\beta} \Psi(\mathbf{r}, \sigma) |\mathbf{r}, \sigma\rangle$$

where $|\mathbf{r}, \alpha\rangle$ denotes the quantum state "electron at position \mathbf{r} with **spin up**" and $|\mathbf{r}, \beta\rangle$ corresponds to the state "electron at position \mathbf{r} with **spin down**"

- In the non-relativistic case, a single electron will have a spin σ_0 which is either up or down. The corresponding wavefunction Ψ^{σ_0} can then be written as a spin-orbital $\Psi^{\sigma_0}(\mathbf{r}, \sigma) = \Psi(\mathbf{r}) \delta_{\sigma\sigma_0}$.

Two-electron wavefunction

- With the notations $X = (\mathbf{r}, \sigma)$ and $\int dX = \int_{\mathbb{R}^3} d\mathbf{r} \sum_{\sigma=\alpha,\beta}$,

the one-electron quantum state in Pauli theory is simply written as

$$|\Psi\rangle = \int dX \Psi(X) |X\rangle$$

- Two-electron case:

$$|\Psi\rangle = \int \int dX_1 dX_2 \Psi(X_1, X_2) |1: X_1, 2: X_2\rangle$$

where the two-electron quantum state $|1: X_1, 2: X_2\rangle$ corresponds to "electron 1 in state $|X_1\rangle$ and electron 2 in state $|X_2\rangle$ "

- Since electrons **cannot be distinguished**, the states

$$|1: X_1, 2: X_2\rangle \quad \text{and} \quad |1: X_2, 2: X_1\rangle$$

are equivalent from the experimental point of view.

Two-electron wavefunction

- According to the Pauli principle, **electron 1** and **electron 2** cannot occupy the same state $|X\rangle$. In other words, the two-electron quantum state $|1: X, 2: X\rangle$ is not physical.
- The latter is automatically removed from the theory when working in the basis of anti-symmetrized two-electron states:

$$|1: X_1, 2: X_2\rangle = |1: X_1, 2: X_2\rangle_{\mathcal{A}} + |1: X_1, 2: X_2\rangle_{\mathcal{S}}$$

where

$$|1: X_1, 2: X_2\rangle_{\mathcal{A}} = \frac{1}{2} \left(|1: \boxed{X_1}, 2: X_2\rangle - |1: X_2, 2: \boxed{X_1}\rangle \right) \longrightarrow \text{anti-symmetric (physical !)}$$

and

$$|1: X_1, 2: X_2\rangle_{\mathcal{S}} = \frac{1}{2} \left(|1: \boxed{X_1}, 2: X_2\rangle + |1: X_2, 2: \boxed{X_1}\rangle \right) \longrightarrow \text{symmetric (not physical !)}$$

Two-electron wavefunction

- Physical two-electron state:

$$\begin{aligned} |\Psi\rangle &\rightarrow |\Psi_{\mathcal{A}}\rangle = \int \int dX_1 dX_2 \Psi(X_1, X_2) |1: X_1, 2: X_2\rangle_{\mathcal{A}} \\ &= \int \int dX_1 dX_2 \Psi_{\mathcal{A}}(X_1, X_2) |1: X_1, 2: X_2\rangle \end{aligned}$$

where the anti-symmetrized wavefunction equals

$$\Psi_{\mathcal{A}}(X_1, X_2) = \frac{1}{2} \left(\Psi(X_1, X_2) - \Psi(X_2, X_1) \right)$$

- Anti-symmetrization** condition: $\Psi_{\mathcal{A}}(X_1, X_2) = -\Psi_{\mathcal{A}}(X_2, X_1)$
- Note that **Slater determinants fulfill this condition**. Consequently a linear combination of Slater determinants (as used in wavefunction theory) will also fulfill this condition.

wavefunction and densities: two-electron case

- A physical two-electron wavefunction should fulfill $\Psi(X_1, X_2) = -\Psi(X_2, X_1)$. In addition we want it to be normalized,

$$\langle \Psi | \Psi \rangle = \int \int dX_1 dX_2 \Psi^2(X_1, X_2) = 1$$

- Expectation value for the **kinetic energy**:

$$\langle \Psi | \hat{T} | \Psi \rangle = -\frac{1}{2} \int_{\mathbb{R}^3} d\mathbf{r} \nabla_{\mathbf{r}'}^2 [n_1(\mathbf{r}, \mathbf{r}')] \Big|_{\mathbf{r}=\mathbf{r}'}$$

where the spin-summed **one-electron density matrix** equals

$$n_1(\mathbf{r}, \mathbf{r}') = 2 \sum_{\sigma_1=\alpha,\beta} \int dX_2 \Psi(\mathbf{r}, \sigma_1, X_2) \Psi(\mathbf{r}', \sigma_1, X_2)$$

- Expectation value for the **nuclear-electron interaction** energy:

$$\langle \Psi | \hat{V}_{ne} | \Psi \rangle = \int_{\mathbb{R}^3} d\mathbf{r} v_{ne}(\mathbf{r}) n(\mathbf{r})$$

where the **electron density** equals $n(\mathbf{r}) = n_1(\mathbf{r}, \mathbf{r})$ ← key quantity in DFT ...

- Expectation value for the **electron-electron** interaction energy:

$$\langle \Psi | \hat{W}_{ee} | \Psi \rangle = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} d\mathbf{r}_1 d\mathbf{r}_2 \frac{n_2(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ and the spin-summed **pair density** equals

$$n_2(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\sigma_1, \sigma_2 = \alpha, \beta} \Psi^2(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2)$$

- **Generalization** to an arbitrary number N of electrons: a physical electronic quantum state should fulfill for $1 \leq i < j \leq N$,

$$\begin{aligned} |\Psi\rangle &= \int \dots \int dX_1 \dots dX_N \Psi(X_1, \dots, X_i, \dots, X_j, \dots, X_N) |1 : X_1, \dots, i : X_i, \dots, j : X_j, \dots, N : X_N\rangle \\ &= \int \dots \int dX_1 \dots dX_N \frac{1}{2} \times \Psi(X_1, \dots, X_i, \dots, X_j, \dots, X_N) \\ &\quad \times \left(|1 : X_1, \dots, i : X_i, \dots, j : X_j, \dots, N : X_N\rangle - |1 : X_1, \dots, i : X_j, \dots, j : X_i, \dots, N : X_N\rangle \right) \end{aligned}$$

thus leading to

$$|\Psi\rangle = \int \dots \int dX_1 \dots dX_N \Psi_{\mathcal{A}}(X_1, \dots, X_i, \dots, X_j, \dots, X_N) |1 : X_1, \dots, i : X_i, \dots, j : X_j, \dots, N : X_N\rangle$$

where the anti-symmetrized wavefunction $\Psi_{\mathcal{A}}(X_1, \dots, X_i, \dots, X_j, \dots, X_N)$ is equal to

$$\frac{1}{2} \left(\Psi(X_1, \dots, X_i, \dots, X_j, \dots, X_N) - \Psi(X_1, \dots, X_j, \dots, X_i, \dots, X_N) \right)$$

- Therefore, for a physical N -electron wavefunction, the so-called "**antisymmetry condition**" associated with the permutation $X_i \longleftrightarrow X_j$ should be fulfilled:

$$\Psi_{\mathcal{A}}(X_1, \dots, X_i, \dots, X_j, \dots, X_N) = \Psi(X_1, \dots, X_i, \dots, X_j, \dots, X_N)$$

that is equivalent to, $\forall X_1, \dots, X_i, \dots, X_j, \dots, X_N,$

$$\Psi(X_1, \dots, X_i, \dots, X_j, \dots, X_N) = -\Psi(X_1, \dots, X_j, \dots, X_i, \dots, X_N)$$

- Using the **antisymmetry condition** leads to

$$\langle \Psi | \hat{T} | \Psi \rangle = -\frac{N}{2} \int \dots \int dX_1 \dots dX_N \Psi(X_1, \dots, X_N) \nabla_{\mathbf{r}_1}^2 \Psi(X_1, \dots, X_N)$$

$$\langle \Psi | \hat{V}_{\text{ne}} | \Psi \rangle = N \int \dots \int dX_1 \dots dX_N v_{\text{ne}}(\mathbf{r}_1) \times \Psi^2(X_1, \dots, X_N)$$

$$\langle \Psi | \hat{W}_{\text{ee}} | \Psi \rangle = \sum_{1 \leq i < j}^N \int \dots \int dX_1 \dots dX_N \frac{1}{r_{12}} \times \Psi^2(X_1, \dots, X_N)$$

- Consequently, **all expectation values can be written exactly like for two electrons**, only the expressions for the densities and the density matrix change:

$$n_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{2} \sum_{\sigma_1, \sigma_2 = \alpha, \beta} \int \dots \int dX_3 \dots dX_N \Psi^2(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, X_3, \dots, X_N)$$

$$n_1(\mathbf{r}, \mathbf{r}') = N \sum_{\sigma_1 = \alpha, \beta} \int \dots \int dX_2 \dots dX_N \Psi(\mathbf{r}, \sigma_1, X_2, \dots, X_N) \Psi(\mathbf{r}', \sigma_1, X_2, \dots, X_N)$$

$$n(\mathbf{r}) = N \sum_{\sigma_1 = \alpha, \beta} \int \dots \int dX_2 \dots dX_N \Psi^2(\mathbf{r}, \sigma_1, X_2, \dots, X_N)$$

- **Important conclusion:** the expectation value for the energy is a **functional** of the one-electron density matrix and the pair density.

electron density and density operator

- It is sometimes convenient to introduce the so-called **density operator**

$$\hat{n}(\mathbf{r}) \equiv \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \times \quad \leftarrow \text{Dirac distribution !}$$

for calculating the electron density.

- Since, by definition, $\int_{\mathbb{R}^3} d\mathbf{r}_i f(\mathbf{r}_i) \delta(\mathbf{r} - \mathbf{r}_i) = f(\mathbf{r})$, we obtain

$$n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle$$

- Consequently, the nuclear potential operator can be rewritten as

$$\sum_{i=1}^N v_{\text{ne}}(\mathbf{r}_i) \times = \int_{\mathbb{R}^3} d\mathbf{r} v_{\text{ne}}(\mathbf{r}) \hat{n}(\mathbf{r})$$

- Thus, we recover the following useful result

$$\left\langle \Psi \left| \sum_{i=1}^N v_{\text{ne}}(\mathbf{r}_i) \times \right| \Psi \right\rangle = \int_{\mathbb{R}^3} d\mathbf{r} v_{\text{ne}}(\mathbf{r}) n(\mathbf{r})$$

Density functions as basic variables

- What about using **density functions** rather than the wavefunction as **basic variables** ?
- If so, how can we reach the exact ground-state energy ? Is there a **variational formulation** ?
- If so, a **constrained minimization** is required in order to obtain physical density functions:

$$\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} d\mathbf{r}_1 d\mathbf{r}_2 n_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{2}$$

$$\int_{\mathbb{R}^3} d\mathbf{r} n_1(\mathbf{r}, \mathbf{r}) = \int_{\mathbb{R}^3} d\mathbf{r} n(\mathbf{r}) = N$$

- We will show in the following that the exact **ground-state energy** E_0 is a **functional of** the exact ground-state **density** $n_0(\mathbf{r})$, *i.e.* the one that is obtained from the exact ground-state wavefunction Ψ_0 (first Hohenberg–Kohn theorem). Moreover, the electron **density** can be used as **basic variable** in order to reach n_0 **variationally** (second Hohenberg–Kohn theorem).

Hohenberg and Kohn theorems

HK1: There is a **one to one correspondence** between the **local potential** $v(\mathbf{r})$, up to a constant, and the non-degenerate **ground-state density** $n(\mathbf{r})$ of the electronic Hamiltonian [*Phys. Rev.* **136**, B864 (1964)]

$$\hat{H}[v] \equiv \hat{T} + \hat{W}_{ee} + \sum_{i=1}^N v(\mathbf{r}_i) \times$$

Proof:

- $v(\mathbf{r}) \rightarrow \Psi[v]$ ground state of $\hat{H}[v] \rightarrow n_{\Psi[v]}(\mathbf{r})$
- $n(\mathbf{r}) \rightarrow$ unique $v(\mathbf{r})$ (up to a constant) so that the density of $\Psi[v]$ equals $n(\mathbf{r})$?

Let us assume that we can find two local potentials $v(\mathbf{r})$ and $v'(\mathbf{r})$ that differ by more than a constant and lead to the same ground-state density:

$$n_{\Psi[v]}(\mathbf{r}) = n_{\Psi[v']}(\mathbf{r}) = n(\mathbf{r})$$

Hohenberg and Kohn theorems

- $\Psi[v]$ **cannot be equal to** $\Psi[v']$ otherwise for **any** values of X_1, \dots, X_N :

$$\hat{H}[v]\Psi[v](X_1, \dots, X_N) = E[v]\Psi[v](X_1, \dots, X_N) \quad \text{and}$$

$$\hat{H}[v']\Psi[v'](X_1, \dots, X_N) = E[v']\Psi[v'](X_1, \dots, X_N)$$

thus leading to

$$\begin{aligned} \left(\hat{H}[v] - \hat{H}[v'] \right) \Psi[v](X_1, \dots, X_N) &= \left(\sum_{i=1}^N v(\mathbf{r}_i) - v'(\mathbf{r}_i) \right) \times \Psi[v](X_1, \dots, X_N) \\ &= \left(E[v] - E[v'] \right) \times \Psi[v](X_1, \dots, X_N) \end{aligned}$$

In the particular case where $\mathbf{r}_1 = \mathbf{r}_2 = \dots = \mathbf{r}_N = \mathbf{r}$ we obtain for any \mathbf{r}

$$v(\mathbf{r}) - v'(\mathbf{r}) = \left(E[v] - E[v'] \right) / N \quad \longrightarrow \quad \text{constant (absurd!)}$$

Hohenberg and Kohn theorems

- Non-degeneracy implies

$$\langle \Psi[v'] | \hat{H}[v] | \Psi[v'] \rangle > E[v] \quad \text{and} \quad \langle \Psi[v] | \hat{H}[v'] | \Psi[v] \rangle > E[v']$$

$$\langle \Psi[v'] | \hat{T} + \hat{W}_{ee} | \Psi[v'] \rangle - \langle \Psi[v] | \hat{T} + \hat{W}_{ee} | \Psi[v] \rangle > \int_{\mathbb{R}^3} d\mathbf{r} v(\mathbf{r}) (n_{\Psi[v]}(\mathbf{r}) - n_{\Psi[v']}(\mathbf{r})) = 0$$

$$\langle \Psi[v'] | \hat{T} + \hat{W}_{ee} | \Psi[v'] \rangle - \langle \Psi[v] | \hat{T} + \hat{W}_{ee} | \Psi[v] \rangle < \int_{\mathbb{R}^3} d\mathbf{r} v'(\mathbf{r}) (n_{\Psi[v]}(\mathbf{r}) - n_{\Psi[v']}(\mathbf{r})) = 0 \quad (!)$$

- Conclusion: $n_{\Psi[v]}(\mathbf{r}) \rightarrow v(\mathbf{r}) \rightarrow \Psi[v] \rightarrow E[v]$

the **ground-state energy** $E[v]$ is a **functional** of the **ground-state density** $n_{\Psi[v]}(\mathbf{r})$

$$E[v] = E[n_{\Psi[v]}]$$

Hohenberg and Kohn theorems

HK2: The exact **ground-state density** $n_0(\mathbf{r})$ of the electronic Hamiltonian

$$\hat{H}[v_{\text{ne}}] \equiv \hat{T} + \hat{W}_{\text{ee}} + \sum_{i=1}^N v_{\text{ne}}(\mathbf{r}_i) \times$$

minimizes the energy density functional $E[n] = F[n] + \int_{\mathbb{R}^3} d\mathbf{r} v_{\text{ne}}(\mathbf{r})n(\mathbf{r})$,

where the Hohenberg–Kohn universal functional $F[n]$ is defined as

$$F[n] = \langle \Psi[n] | \hat{T} + \hat{W}_{\text{ee}} | \Psi[n] \rangle,$$

and the minimum equals the exact ground-state energy E_0 :

$$\boxed{\min_n E[n] = E[n_0] = E_0}$$

Comment: we know from **HK1** that $n(\mathbf{r}) \rightarrow v[n](\mathbf{r}) \rightarrow \Psi[v[n]] = \Psi[n]$

Hohenberg and Kohn theorems

Proof:

- for any density $n(\mathbf{r})$, $\Psi[n]$ is well defined according to **HK1** and

$$\langle \Psi[n] | \hat{H}[v_{\text{ne}}] | \Psi[n] \rangle \geq E_0$$

$$\underbrace{\langle \Psi[n] | \hat{T} + \hat{W}_{\text{ee}} | \Psi[n] \rangle}_{F[n]} + \int_{\mathbb{R}^3} d\mathbf{r} v_{\text{ne}}(\mathbf{r}) \underbrace{n_{\Psi[n]}(\mathbf{r})}_{n(\mathbf{r})} \geq E_0$$

thus leading to $E[n] \geq E_0$

- When $n(\mathbf{r})$ equals the exact ground-state density $n_0(\mathbf{r})$:

$$n_0(\mathbf{r}) \rightarrow v_{\text{ne}}(\mathbf{r}) \rightarrow \Psi[n_0] = \Psi[v_{\text{ne}}] = \Psi_0$$

$$E[n_0] = \langle \Psi_0 | \hat{T} + \hat{W}_{\text{ee}} | \Psi_0 \rangle + \int_{\mathbb{R}^3} d\mathbf{r} v_{\text{ne}}(\mathbf{r}) n_0(\mathbf{r}) = \langle \Psi_0 | \hat{T} + \hat{W}_{\text{ee}} + \hat{V}_{\text{ne}} | \Psi_0 \rangle = E_0$$