Static Density Functional Theory: An Overview
compare ground-state densities $\rho(r)$ resulting from different external potentials $v(r)$.

**QUESTION:** Are the ground-state densities coming from different potentials always different?
single-particle potentials having nondegenerate ground state

ground-state wavefunctions

ground-state densities

**Hohenberg-Kohn-Theorem (1964)**

\[ G: v(r) \rightarrow \rho (r) \text{ is invertible} \]
Proof

Step 1: Invertibility of map \( A \)

Solve many-body Schrödinger equation for the external potential:

\[
\hat{V} = \left( \frac{E - \hat{T} - \hat{W}_{ee}}{\Psi} \right) \Psi
\]

\[
\sum_{j=1}^{N} v(r_j) = - \frac{\hat{T} \Psi}{\Psi} - W_{ee} (\vec{r}_1...\vec{r}_N) + \text{constant}
\]

This is manifestly the inverse map: A given \( \Psi \) uniquely yields the external potential.
Step 2: Invertibility of map $\tilde{A}$

Given: two (nondegenerate) ground states $\Psi, \Psi'$ satisfying

$\hat{H}\Psi = E\Psi$  \hspace{1cm} \text{with} \hspace{1cm} $\hat{H} = \hat{T} + \hat{W} + \hat{V}$

$\hat{H}'\Psi' = E'\Psi'$  \hspace{1cm} $\hat{H}' = \hat{T} + \hat{W} + \hat{V}'$

to be shown: $\Psi \neq \Psi' \implies \rho \neq \rho'$

\[\text{cannot happen}\]
Use Rayleigh-Ritz principle:

\[ E = \langle \Psi | \hat{H} | \Psi \rangle < \langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | \hat{H} + V - V' | \Psi' \rangle \]
\[ = E' + \int d^3r \rho'(r) [v(r) - v'(r)] \]

\( \text{①} \quad E' = \langle \Psi' | \hat{H} | \Psi' \rangle < \langle \Psi | \hat{H} | \Psi \rangle \]
\[ = E + \int d^3r \rho(r) [v'(r) - v(r)] \]

Reductio ad absurdum:
Assumption \( \rho = \rho' \). Add \( \diamond \) and \( \text{①} \) \implies \( E + E' < E + E' \)́
Every quantum mechanical observable is completely determined by the ground state density.

Proof: \( \rho \xrightarrow{G^{-1}} \psi[\rho] \xrightarrow{\text{solve S.E.}} \hat{\Phi}_i[\rho] \)

Observables \( \hat{B}: B_i[\rho] = \langle \Phi_i[\rho] | \hat{B} | \Phi_i[\rho] \rangle \)
What is a FUNCTIONAL?

\[ \rho(\mathbf{r}) \xrightarrow{E[\rho]} \mathbb{R} \]

set of functions \quad set of real numbers

Generalization:

\[ v_r[\rho] = v[\rho](\mathbf{r}) \quad \text{functional depending parametrically on } \mathbf{r} \]

\[ \psi_{\mathbf{r}_1...\mathbf{r}_N}[\rho] = \psi[\rho](\mathbf{r}_1...\mathbf{r}_N) \quad \text{or on } (\mathbf{r}_1...\mathbf{r}_N) \]
QUESTION:

How to calculate ground state density $\rho_o(\vec{r})$ of a given system (characterized by external potential $V_o = \sum v_o(\vec{r})$) without recourse to the Schrödinger Equation?

Theorem:

There exists a density functional $E_{HK}[\rho]$ with properties

i) $E_{HK}[\rho] > E_o$ for $\rho \neq \rho_o$

ii) $E_{HK}[\rho_o] = E_o$

where $E_o = \text{exact ground state energy of the system}$

Thus, Euler equation $\frac{\delta}{\delta \rho(\vec{r})} E_{HK}[\rho] = 0$

yields exact ground state density $\rho_o$. 
proof:

formal construction of $E_{HK}[\rho]$:

for arbitrary ground state density $\rho(\vec{r}) \xrightarrow{\hat{\Lambda}^{-1}} \Psi[\rho]$,

define:

$$E_{HK}[\rho] \equiv \left\langle \Psi[\rho] | \hat{T} + \hat{W} + \hat{V}_o | \Psi[\rho] \right\rangle$$

- $> E_o$ for $\rho \neq \rho_o$
- $= E_o$ for $\rho = \rho_o$  

q.e.d.

$$E_{HK}[\rho] = \int d^3 r \rho(r) V_o(r) + \left\langle \Psi[\rho] | \hat{T} + \hat{W} | \Psi[\rho] \right\rangle$$

$F[\rho]$ is universal
HOHENBERG-KOHN THEOREM

1. \( v(r) \leftrightarrow \rho(r) \)
   
   one-to-one correspondence between external potentials \( v(r) \) and ground-state densities \( \rho(r) \)

2. **Variational principle**

   Given a particular system characterized by the external potential \( v_0(r) \). Then the solution of the Euler-Lagrange equation

   \[
   \frac{\delta}{\delta \rho(r)} E_{\text{HK}}[\rho] = 0
   \]

   yields the exact ground-state energy \( E_0 \) and ground-state density \( \rho_0(r) \) of this system

3. \( E_{\text{HK}}[\rho] = F[\rho] + \int \rho(r) v_0(r) d^3r \)

   \( F[\rho] \) is **UNIVERSAL**. \( \text{In practice, } F[\rho] \text{ needs to be approximated} \)
Expansion of $F[\rho]$ in powers of $e^2$

\[ F[\rho] = F^{(0)}[\rho] + e^2 F^{(1)}[\rho] + e^4 F^{(2)}[\rho] + \cdots \]

where: $F^{(0)}[\rho] = T_s[\rho]$ (kinetic energy of non-interacting particles)

\[ e^2 F^{(1)}[\rho] = \frac{e^2}{2} \int \int \frac{\rho(r) \rho(r')}{|r-r'|} \, d^3r \, d^3r' + E_x[\rho] \] (Hartree + exchange energies)

\[ \sum_{i=2}^{\infty} (e^2)^i F^{(i)}[\rho] = E_c[\rho] \] (correlation energy)

\[ \Rightarrow F[\rho] = T_s[\rho] + \frac{e^2}{2} \int \int \frac{\rho(r) \rho(r')}{|r-r'|} \, d^3r \, d^3r' + E_x[\rho] + E_c[\rho] \]
By construction, the HK mapping is well-defined for all those functions $\rho(r)$ that are ground-state densities of some potential (so called V-representable functions $\rho(r)$).

**QUESTION**: Are all “reasonable” functions $\rho(r)$ V-representable?


On a lattice (finite or infinite), any normalizable positive function $\rho(r)$, that is compatible with the Pauli principle, is (both interacting and non-interacting) ensemble-V-representable.

In other words: For any given $\rho(r)$ (normalizable, positive, compatible with Pauli principle) there exists a potential, $v_{\text{ext}}[\rho](r)$, yielding $\rho(r)$ as interacting ground-state density, and there exists another potential, $v_s[\rho](r)$, yielding $\rho(r)$ as non-interacting ground-state density.

In the worst case, the potential has degenerate ground states such that the given $\rho(r)$ is representable as a linear combination of the degenerate ground-state densities (ensemble-V-representable).
**Kohn-Sham Theorem**

Let \( \rho_o(r) \) be the ground-state density of interacting electrons moving in the external potential \( v_o(r) \). Then there exists a local potential \( v_{s,o}(r) \) such that non-interacting particles exposed to \( v_{s,o}(r) \) have the ground-state density \( \rho_o(r) \), i.e.

\[
\left(-\frac{\nabla^2}{2} + v_{s,o}(r)\right)\varphi_j(r) = \epsilon_j \varphi_j(r), \quad \rho_o(r) = \sum_{j \text{ (with lowest } \epsilon_j)}^N |\varphi_j(r)|^2
\]

**proof:** \( v_{s,o}(r) \rightarrow v_{s,o}[\rho_o](r) \)

Uniqueness follows from HK 1-1 mapping

Existence follows from V-representability theorem
Define \( v_{xc}[\rho](r) \) by the equation

\[
v_{\rho}[r](\psi) - v_{\text{ext}}[\rho](\psi) + \int \frac{\rho(r')}{|r - r'|} \, d^3r' \psi_{\rho}[r](\psi)
\]

\( v_{s}[\rho] \) and \( v_{\text{ext}}[\rho] \) are well defined through HK.

KS equations

\[
\left( -\frac{\nabla^2}{2} + v_{\text{ext}}[r_0](\psi) + \rho_{\text{H}}[r_0](\psi) + \rho_{xc}[r_0](\psi) \right) r \varphi_j(\psi) = \varepsilon_j r \varphi_j(\psi)
\]

Fixed to be solved selfconsistently with \( \rho_o(r) = \sum |\varphi_j(r)|^2 \)

Note: The KS equations do not follow from the variational principle. They follow from the HK 1-1 mapping and the V-representability theorem.
Variational principle gives an additional property of $v_{xc}$:

$$v_{\rho_e} [\rho \mathbf{r}] (\mathbf{r}) = \left. \frac{\delta E_{xc} [\rho]}{\delta \rho (\mathbf{r})} \right|_{\rho_0}$$

where

$$E_{\rho_e} [\rho] = \rho \left[ \rho \right] - \frac{1}{2} \int \frac{\rho (\mathbf{r}) \rho (\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' - \rho_s [\rho]$$

Consequence:
Approximations can be constructed either for $E_{xc}[\rho]$ or directly for $v_{xc}[\rho](\mathbf{r})$. 
**Proof:** \( E_{HK} \left[ \mathbf{T} \right] = \rho_s \left[ \mathbf{T} \right] + \int \left( \mathbf{v}_o (\mathbf{r}) \mathbf{v}_o (\mathbf{r}) \right) \mathbf{E} + \rho_H \left[ \mathbf{E} \right] + \rho_{xc} \left[ \mathbf{E} \right] \)

\[
0 = \frac{\delta E_{HK}[\rho]}{\delta \rho(\mathbf{r})}\bigg|_{\rho_o} = \frac{\delta T_s}{\delta \rho(\mathbf{r})}\bigg|_{\rho_o} + \mathbf{v}_o(\mathbf{r}) + \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})}\bigg|_{\rho_o}
\]

\( \delta T_s = \text{change of } T_s \text{ due to a change } \delta \rho \text{ which corresponds to a change } \delta \mathbf{v}_s \)

\[
= \delta \sum_j \int \varphi_j[\rho](\mathbf{r}) \left( -\frac{\nabla^2}{2} \right) \varphi_j[\rho](\mathbf{r}) d^3\mathbf{r}
\]

\[
= \delta \sum_j \int \varphi_j^*(\mathbf{r}) (\epsilon_j - \mathbf{v}_s(\mathbf{r})) \varphi_j(\mathbf{r}) d^3\mathbf{r} = \delta \left( \sum_j \epsilon_j - \int \rho(\mathbf{r}) \mathbf{v}_s(\mathbf{r}) d^3\mathbf{r} \right)
\]

\[
= \sum_j \delta \epsilon_j - \int \delta \rho(\mathbf{r}) \mathbf{v}_s(\mathbf{r}) d^3\mathbf{r} - \int \rho(\mathbf{r}) \delta \mathbf{v}_s(\mathbf{r}) d^3\mathbf{r}
\]

\[
\sum_j \langle \varphi_j(\mathbf{r}) | \mathbf{v}_s(\mathbf{r}) | \varphi_j(\mathbf{r}) \rangle
\]

\[
= -\int \delta \rho(\mathbf{r}) \mathbf{v}_s(\mathbf{r}) d^3\mathbf{r}
\]

\[
\Rightarrow \frac{\delta T_s}{\delta \rho(\mathbf{r})} = -\mathbf{v}_o[\mathbf{E}](\mathbf{r})
\]
\[ \Rightarrow 0 = -v_s [ \rho ](r) + v(\rho) \rho + H [ \rho ](\rho) + \left. \frac{\delta E_{xc}}{\delta \rho(r)} \right|_{\rho_o} \]

\[ \Rightarrow v_{\rho_c} [ \sigma ](\rho) = \left. \frac{\delta E_{xc}}{\delta \rho(r)} \right|_{\rho_o} \]