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:

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

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

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

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

\[
\hat{H}\Psi = E\Psi \quad \text{with} \quad \hat{H} = \hat{T} + \hat{W} + \hat{V} \\
\hat{H}'\Psi' = E'\Psi' \quad \text{with} \quad \hat{H}' = \hat{T} + \hat{W} + \hat{V}'
\]

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

\[
\Psi \bullet \\
\Psi' \bullet
\]

\[
\hat{A} \circ \Psi \bullet \rightarrow \bullet \rho = \rho'
\]

cannot happen
Use Rayleigh-Ritz principle:

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

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

**Reductio ad absurdum:**

Assumption \( \rho = \rho' \). Add \( \uparrow \) and \( \star \) \( \Rightarrow E + E' < E + E' \)
Every quantum mechanical observable is completely determined by the ground state density.

**Proof:**

\[ \rho \xrightarrow{G^{-1}} v[\rho] \xrightarrow{\text{solve S.E.}} \Phi_i[\rho] \]

**Consequence**

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

\[ \rho(r) \] is a set of functions set of real numbers

Generalization:

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

\[ \psi_{i_1...i_N}[\rho] = \psi[\rho](\vec{r}_1...\vec{r}_N) \] or on \( (\vec{r}_1...\vec{r}_N) \)
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 $\rho(\vec{r}) \xrightarrow{\tilde{\Lambda}^{-1}} \Psi[\rho]$

define:

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

\[
> E_o \text{ for } \rho \neq \rho_o
\]

\[
= E_o \text{ for } \rho = \rho_o \quad \text{q.e.d.}
\]

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

\[F[\rho] \text{ is universal}\]
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. In practice, \( F[\rho] \) 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)

$$\Rightarrow \quad F[\rho] = T_s[\rho] + \frac{e^2}{2} \int \int \frac{\rho(r)\rho(r')}{|r-r'|} \, d^3r \, d^3r' + E_x[\rho] + E_c[\rho]$$
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?

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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, \( v_{\text{s}}[\rho](r) \), 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.

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

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

Uniqueness follows from HK 1-1 mapping

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

$$v_s[\rho](r) = v_{ext}[\rho](r) + \int \frac{\rho(r')}{|r-r'|} d^3r' + v_{xc}[\rho](r)$$

$$v_H[\rho](r)$$

$v_s[\rho]$ and $v_{ext}[\rho]$ are well defined through HK.

**KS equations**

$$\left( -\frac{\nabla^2}{2} + v_{ext}[\rho_o](r) + v_H[\rho_o](r) + v_{xc}[\rho_o](r) \right) \phi_j(r) = \epsilon_j \phi_j(r)$$

$v_o(r)$ fixed

to be solved selfconsistently with $\rho_o(r) = \sum |\phi_j(r)|^2$

**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 $v_{xc}$:

$$v_{xc}[\rho_o](\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \bigg|_{\rho_o}$$

where

$$E_{xc}[\rho] := F[\rho] - \frac{1}{2} \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' - T_s[\rho]$$

**Consequence:**
Approximations can be constructed either for $E_{xc}[\rho]$ or directly for $v_{xc}[\rho](\mathbf{r})$. 
Proof: \(E_{HK}[\rho] = T_s[\rho] + \int \rho(r)v_o(r)d^3r + E_H[\rho] + E_{xc}[\rho]\)

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

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

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

\[
= \delta \sum_j \int \varphi_j^*(r)(\varepsilon_j - v_s(r))\varphi_j(r)d^3r = \delta \left(\sum_j \varepsilon_j - \int \rho(r)v_s(r)d^3r\right)
\]

\[
= \sum_j \left(\delta \varepsilon_j - \int \delta \rho(r)v_s(r)d^3r - \int \rho(r)\delta v_s(r)d^3r\right)
\]

\[
\sum_j \langle \varphi_j(r)|\delta v_s(r)\varphi_j(r)\rangle
\]

\[
= -\int \delta \rho(r)v_s(r)d^3r \quad \Rightarrow \quad \frac{\delta T_s}{\delta \rho(r)} = -v_s[\rho](r)
\]
\[ \Rightarrow 0 = -v_s[\rho_o](r) + v_o(r) + v_H[\rho_o](r) + \frac{\delta E_{xc}}{\delta \rho(r)} \bigg|_{\rho_o} \]

\[ \Rightarrow v_{xc}[\rho_o](r) = \frac{\delta E_{xc}}{\delta \rho(r)} \bigg|_{\rho_o} \]