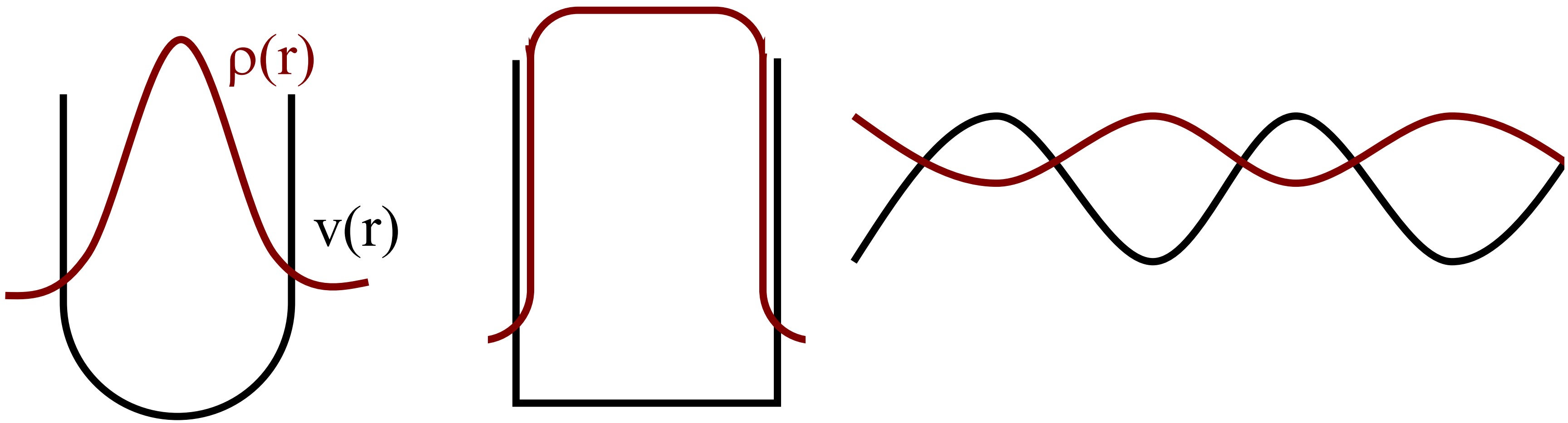
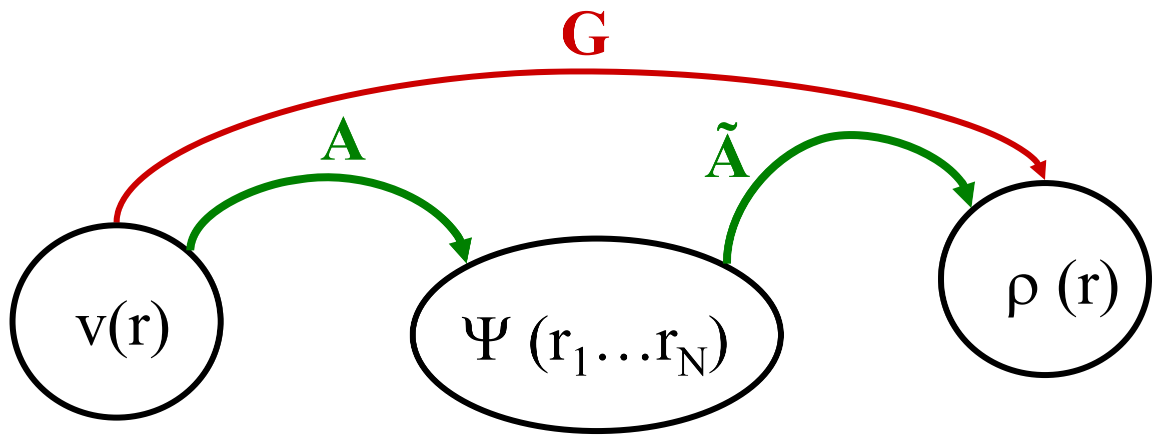
Static Density Functional Theory: An Overview

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

<u>Hohenberg-Kohn-Theorem (1964)</u>

$$\boxed{G: v(r) \rightarrow \rho(r) \quad \text{is invertible}}$$

Proof

Step 1: Invertibility of map A

Solve many-body Schrödinger equation for the external potential:

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

$$\sum_{j=1}^{N} v\left(r_j\right) = -\frac{\hat{T}\Psi}{\Psi} - W_{ee}\left(\vec{r}_1 \ldots \vec{r}_N\right) + \text{constant}$$

This is manifestly the inverse map: A given Ψ uniquely yields the external potential.

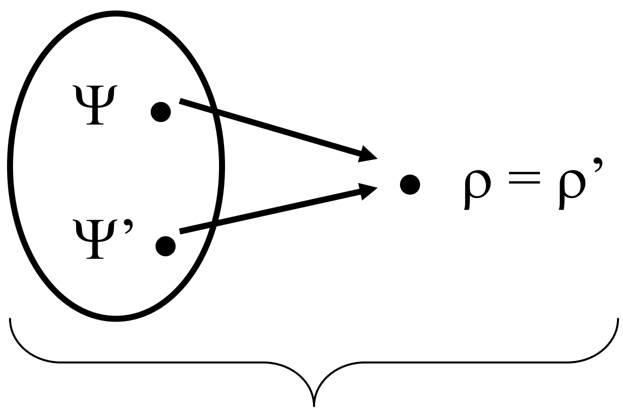
Step 2: Invertibility of map Ã

Given: two (nondegenerate) ground states Ψ, Ψ' satisfying

$$\hat{H}\Psi = E\Psi \qquad \text{with} \qquad \hat{H} = \hat{T} + \hat{W} + \hat{V}$$

$$\hat{H}'\Psi' = E'\Psi' \qquad \qquad \hat{H}' = \hat{T} + \hat{W} + \hat{V}'$$

to be shown: $\Psi \neq \Psi' \quad \Rightarrow \quad \rho \neq \rho'$



cannot happen

Use Rayleigh-Ritz principle:

⅄ $$E = \left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle < \left\langle \Psi' \middle| \hat{H} \middle| \Psi' \right\rangle = \left\langle \Psi' \middle| H' + V - V' \middle| \Psi' \right\rangle$$

$$= E' + \int d^3r \rho'(r) \left[v(r) - v'(r) \right]$$

✶ $$E' = \left\langle \Psi' \middle| \hat{H}' \middle| \Psi' \right\rangle < \left\langle \Psi \middle| \hat{H}' \middle| \Psi \right\rangle$$

$$= E + \int d^3r \rho(r) \left[v'(r) - v(r) \right]$$

<u>Reductio ad absurdum:</u>

Assumption $\rho = \rho'$. Add ⅄ and ✶ $\Rightarrow$ $E + E' < E + E'$ ϟ

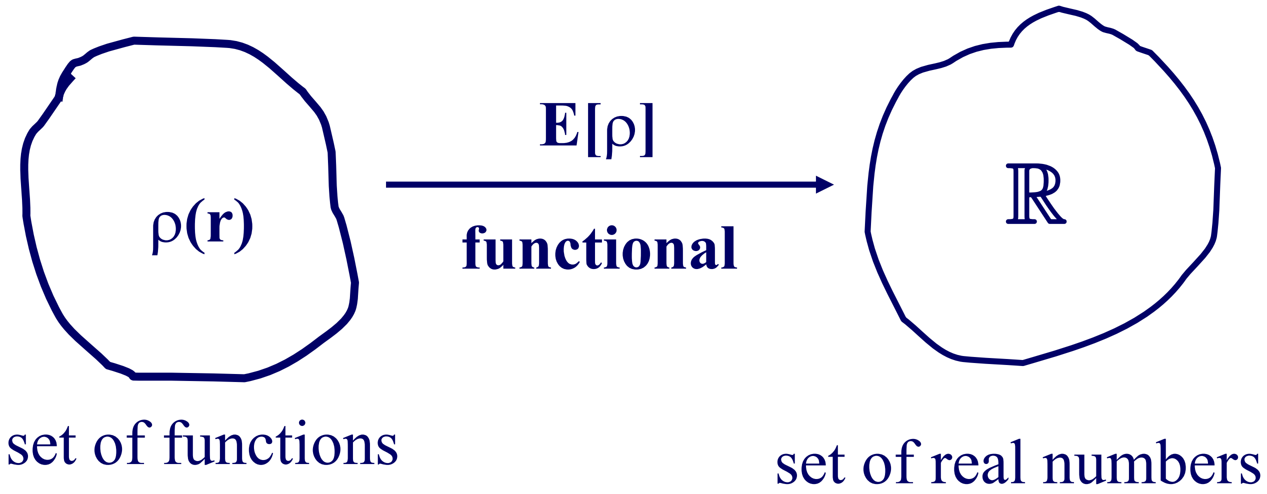
Consequence

Every quantum mechanical observable is completely determined by the ground state density.

$$\text{Proof:} \quad \rho \xrightarrow{G^{-1}} v[\rho] \xrightarrow{\text{solve S.E.}} \Phi_{\mathbf{i}}[\rho]$$

$$\text{observables } \hat{B}\text{:} \ B_{\mathbf{i}}[\rho] = \left\langle \Phi_{\mathbf{i}}[\rho] \middle| \hat{B} \middle| \Phi_{\mathbf{i}}[\rho] \right\rangle$$

What is a FUNCTIONAL?



Generalization:

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

$$\psi_{\vec{r}_1 \ldots \vec{r}_N}[\rho] = \psi[\rho](\vec{r}_1 \ldots \vec{r}_N)$$ or on $(\vec{r}_1 \ldots \vec{r}_N)$

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

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

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

where E_o = exact ground state energy of the system

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

yields exact ground state density ρ_o.

proof:

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

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

define: $\boxed{E_{HK}[\rho] \equiv \langle \Psi[\rho] \,|\hat{T} + \hat{W} + \hat{V}_o| \Psi[\rho]\rangle}$

$> \mathbf{E_o}$ **for** $\rho \neq \rho_o$

$= \mathbf{E_o}$ **for** $\rho = \rho_o$ q.e.d.

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

F[ρ] is $\boxed{\textbf{universal}}$

HOHENBERG-KOHN THEOREM

1. $v(r) \xleftrightarrow{1-1} \rho(r)$

   one-to-one correspondence between external potentials v(r) and ground-state densities ρ(r)

2. Variational principle

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

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

   yields the exact ground-state energy $\mathbf{E_0}$ and ground-state density $\boldsymbol{\rho_0}\mathbf{(r)}$ of this system

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

   F[ρ] is UNIVERSAL. **In practice,** F[ρ] **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 <u>non</u>-interacting particles)

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

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

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

By construction, the HK mapping is well-defined for all those functions ρ(r) that are ground-state densities of some potential (so called V-representable functions ρ(r)).

QUESTION: Are all "reasonable" functions ρ(r) V-representable?

V-representability theorem (**Chayes, Chayes, Ruskai, J Stat. Phys. 38, 497 (1985)**)

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

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

In the worst case, the potential has degenerate ground states such that the given ρ(r) is representable as a linear combination of the degenerate ground-state densities (ensemble-V-representable).

$$\mathbf{v}_{ext}[\rho](\mathbf{r}) \;\overbrace{\longleftrightarrow}^{\text{HK 1-1 mapping for interacting particles}}\; \rho(\mathbf{r}) \;\overbrace{\longleftrightarrow}^{\text{HK 1-1 mapping for non-interacting particles}}\; \mathbf{v}_s[\rho](\mathbf{r})$$

<u>Kohn-Sham Theorem</u>

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

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

<u>proof</u>: $\mathbf{v}_{s,o}(\mathbf{r}) = \mathbf{v}_s[\rho_o](\mathbf{r})$

Uniqueness follows from HK 1-1 mapping

Existence follows from V-representability theorem

<u>Define</u> $\mathbf{v_{xc}[\rho](r)}$ **by the equation**

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

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

KS equations

$$\boxed{\left(-\frac{\nabla^2}{2} + \underbrace{\mathbf{v_{ext}}[\boldsymbol{\rho}_o](\mathbf{r})}_{\substack{\mathbf{v_o}(\mathbf{r}) \\ \textbf{fixed}}} + \mathbf{v_H}[\boldsymbol{\rho}_o](\mathbf{r}) + \mathbf{v_{xc}}[\boldsymbol{\rho}_o](\mathbf{r})\right)\varphi_j(\mathbf{r}) = \epsilon_j\, \varphi_j(\mathbf{r})}$$

to be solved selfconsistently with $\boldsymbol{\rho}_o(\mathbf{r}) = \sum |\varphi_j(\mathbf{r})|^2$

<u>Note</u>: The KS equations do <u>not</u> 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}:

$$\boxed{\mathbf{v}_{\mathbf{xc}}\left[\boldsymbol{\rho}_{\mathbf{o}}\right](\mathbf{r})=\left.\frac{\delta \mathbf{E}_{\mathbf{xc}}[\boldsymbol{\rho}]}{\delta \boldsymbol{\rho}(\mathbf{r})}\right|_{\boldsymbol{\rho}_{\mathbf{o}}}}$$

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

<u>Consequence</u>:
Approximations can be constructed either for $E_{xc}[\rho]$ or directly for $v_{xc}[\rho](r)$.

Proof: $\mathbf{E_{HK}\left[\rho\right] = T_s\left[\rho\right] + \int \rho\left(r\right) v_o\left(r\right) d^3r + E_H\left[\rho\right] + E_{xc}\left[\rho\right]}$

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

δT_s = change of T_s due to a change $\delta\rho$ which corresponds to a change δv_s

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

$$= \delta\sum_j \int \varphi_j^*\left(r\right)\left(\in_j - v_s\left(r\right)\right)\varphi_j\left(r\right) d^3r = \delta\left(\sum_j \in_j - \int \rho\left(r\right) v_s\left(r\right) d^3r\right)$$

$$= \underbrace{\sum_j \delta\in_j}_{\cancel{\sum_j \left\langle\varphi_j\left(r\right)\middle|\delta v_s\left(r\right)\middle|\varphi_j\left(r\right)\right\rangle}} - \int \delta\rho\left(r\right) v_s\left(r\right) d^3r - \cancel{\int \rho\left(r\right)\delta v_s\left(r\right) d^3r}$$

$$= -\int \delta\rho\left(r\right) v_s\left(r\right) d^3r \quad \Rightarrow \quad \boxed{\frac{\delta T_s}{\delta\rho\left(r\right)} = -v_s\left[\rho\right]\left(r\right)}$$

$$\Rightarrow 0 = -v_s[\rho_o](r) + v_o(r) + v_H[\rho_o](r) + \left.\frac{\delta E_{xc}}{\delta \rho(r)}\right|_{\rho_o}$$

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