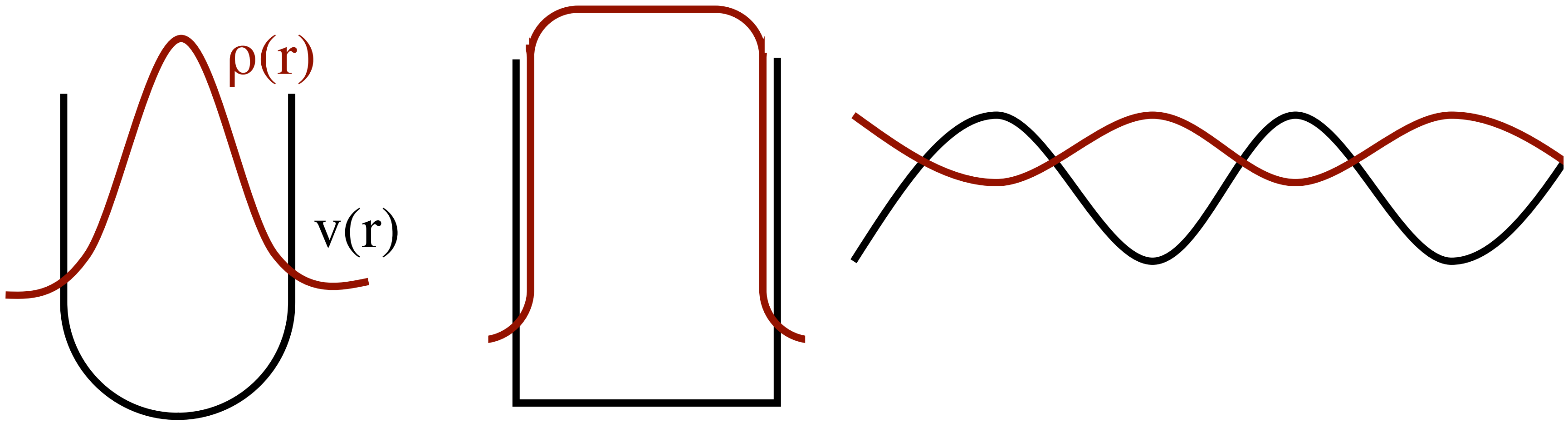
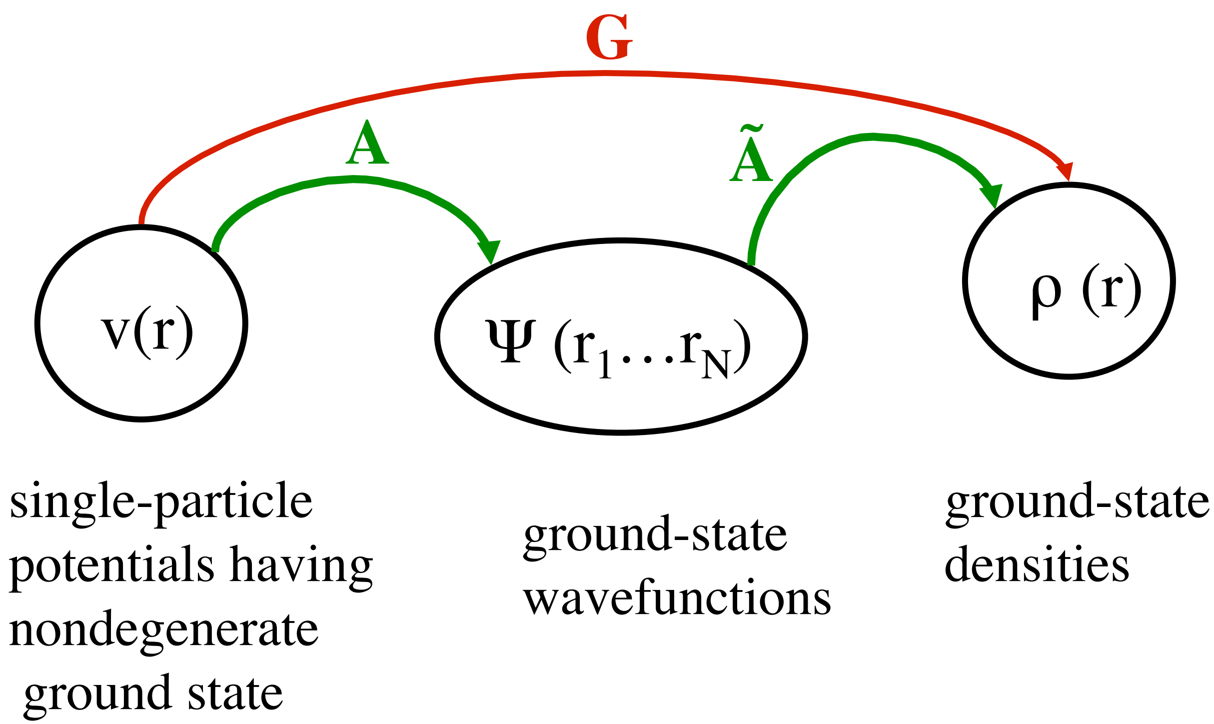
Static Density Functional Theory: An Overview

compare ground-state densities ρ(r) resulting from different external potentials v(r).



QUESTION: Are the ground-state densities coming from different potentials always different?



Hohenberg-Kohn-Theorem (1964)

G: v(r) $\rightarrow$ ρ (r) 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 $\tilde{A}$

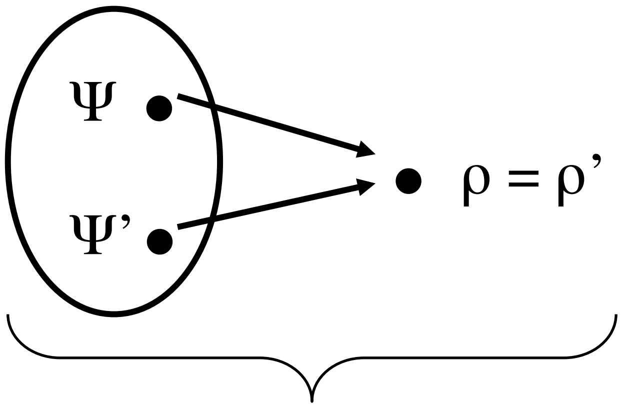
Given: two (nondegenerate) ground states Ψ, Ψ' satisfying

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

with

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

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



cannot happen

Use Rayleigh-Ritz principle:

$$\blacklozenge \quad E = \langle \Psi | \hat{H} | \Psi \rangle < \langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | H' + V - V' | \Psi' \rangle$$

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

$$① \quad E' = \langle \Psi' | \hat{H}' | \Psi' \rangle < \langle \Psi | \hat{H}' | \Psi \rangle$$

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

<u>Reductio ad absurdum:</u>

Assumption ρ = ρ'. Add ♦ and ① ⇒ E + E' < E + E' ↯

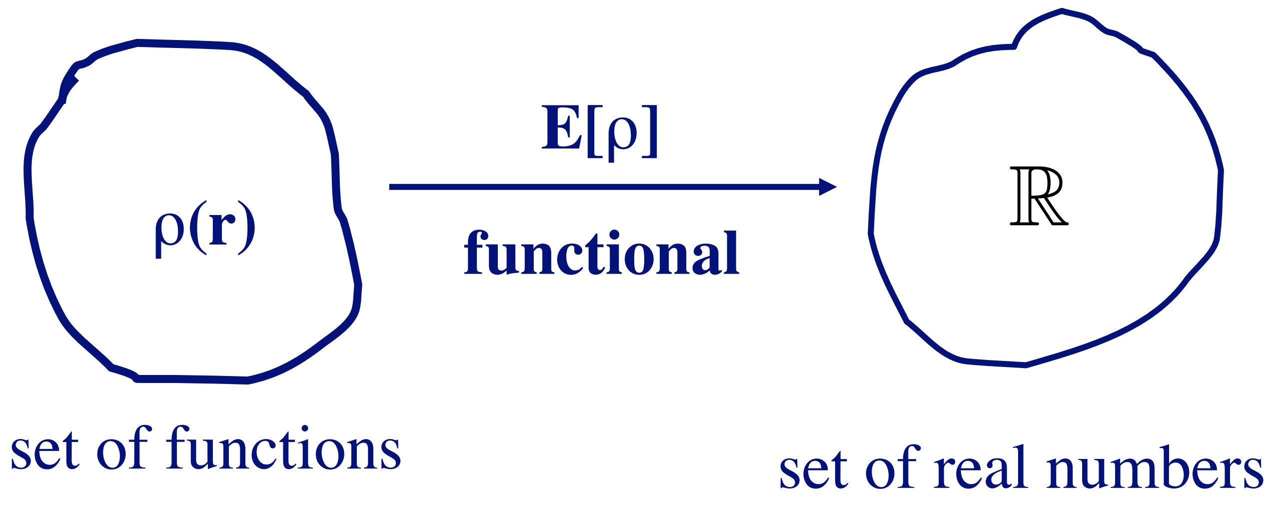
Consequence

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

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

observables $\hat{B}$: $$B_i[\rho] = \langle \Phi_i[\rho] | \hat{B} | \Phi_i[\rho] \rangle$$

What is a FUNCTIONAL?



Generalization:

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

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

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 = 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 ρ_o.

proof:

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

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

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

$> \mathbf{E_o}$ **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 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. <u>Variational principle</u>

   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 <u>UNIVERSAL</u>. **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 non-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)

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

HK 1-1 mapping for interacting particles

HK 1-1 mapping for non-interacting particles

$$v_{ext}[\rho](\mathbf{r}) \longleftrightarrow \rho(\mathbf{r}) \longleftrightarrow v_s[\rho](\mathbf{r})$$

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.

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

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

Uniqueness follows from HK 1-1 mapping

Existence follows from V-representability theorem

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

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

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

KS equations

$$\left(-\frac{\nabla^2}{2} + \underbrace{v_{ext}[\rho_o](r)}_{\substack{v_o(r) \\ \text{fixed}}} + v_H[\rho_o](r) + v_{xc}[\rho_o](r) \right) \varphi_j(r) = \epsilon_j \varphi_j(r)$$

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

<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}:

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

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

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

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

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

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

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

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

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

$$= -\int \delta\rho(r) v_s(r)\, d^3r$$

$$\Rightarrow \quad \boxed{\frac{\delta T_s}{\delta\rho(r)} = -v_s[\rho](r)}$$

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

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