

Ground-state DFT, an unconventional overview



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Many-Body Schrödinger Equation

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

$$\hat{H} = \hat{T} + \hat{V} + \hat{W}$$

$$\hat{T} = \sum_{j=1}^N -\frac{\hbar^2 \nabla_j^2}{2m}$$

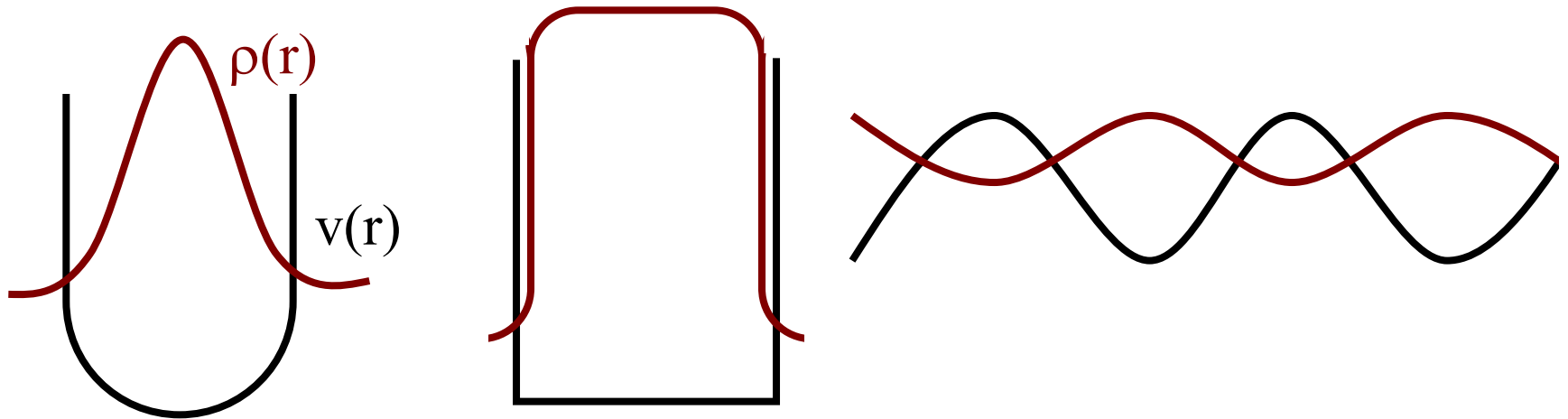
$$\hat{V} = \sum_{j=1}^N v(\mathbf{r}_j)$$

$$\hat{W} = \frac{1}{2} \sum_{\substack{j,k=1 \\ j \neq k}}^N \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_k|}$$

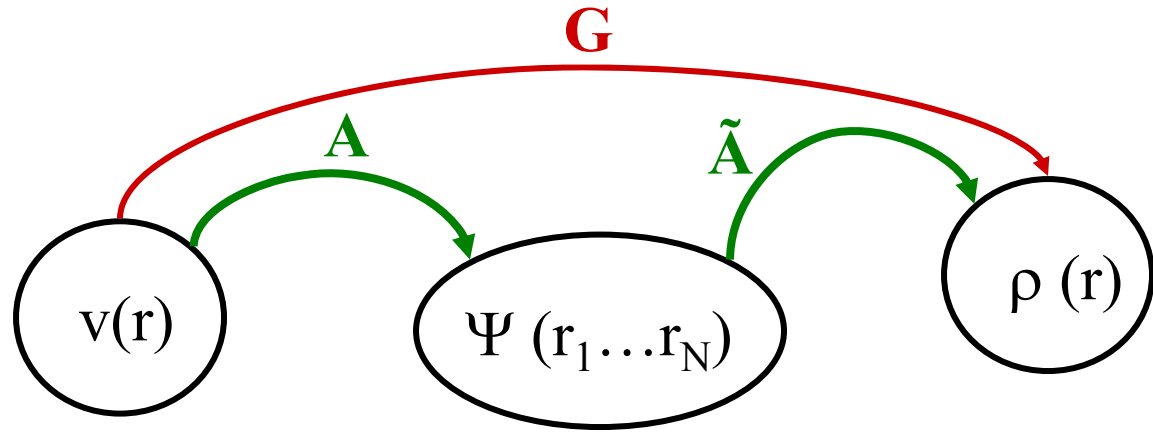
ESSENCE OF DENSITY-FUNCTIONAL THEORY

- **Every observable quantity of a quantum system can be calculated from the ground-state density of the system ALONE**
- **The ground-state density of particles interacting with each other can be calculated as the ground-state density of an auxiliary system of non-interacting particles**

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)

$G: v(r) \rightarrow \rho(r)$ is invertible

Proof

Step 1: Invertibility of map A

Solve many-body Schrödinger equation for the external potential:

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

$$\sum_{j=1}^N v(\mathbf{r}_j) = -\frac{\hat{\mathbf{T}}\Psi}{\Psi} - W_{ee}(\vec{\mathbf{r}}_1 \dots \vec{\mathbf{r}}_N) + \text{constant}$$

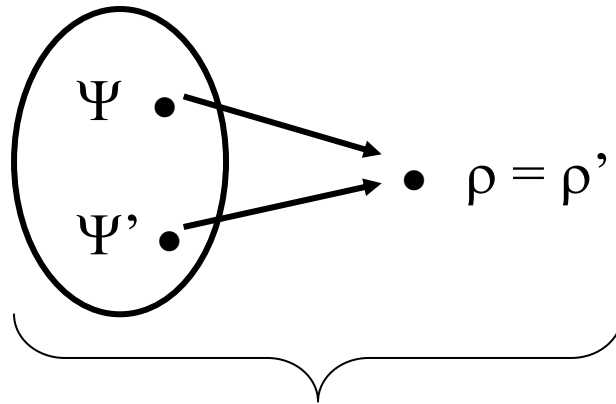
This is manifestly the inverse map: A given Ψ uniquely yields the external potential.

Step 2: Invertibility of map \tilde{A}

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

$$\begin{array}{lcl} \hat{H}\Psi = E\Psi & & \hat{H} = \hat{T} + \hat{W} + \hat{V} \\ \hat{H}'\Psi' = E'\Psi' & \text{with} & \hat{H}' = \hat{T} + \hat{W} + \hat{V}' \end{array}$$

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



cannot happen

Use Rayleigh-Ritz principle:

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

$$\begin{aligned} \star E' &= \langle \Psi' | \hat{H}' | \Psi' \rangle < \langle \Psi | \hat{H}' | \Psi \rangle \\ &= E + \int d^3r \rho(r) [v'(r) - v(r)] \end{aligned}$$

Reductio ad absurdum:

Assumption $\rho = \rho'$. Add \blacktriangle and $\star \Rightarrow E + E' < E + E'$



Consequence

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

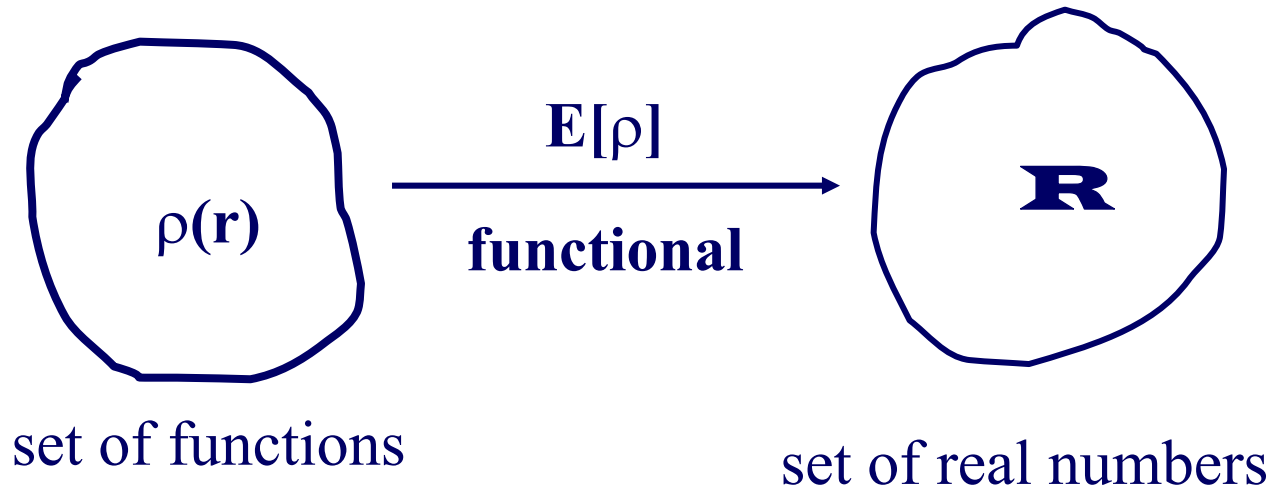
$$\text{Proof: } \rho \xrightarrow{G^{-1}} v[\rho] \xrightarrow{\text{solve S.E.}} \Phi_i[\rho]$$

Hermitian operator \hat{B}

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

e.g. excitation spectrum: $E_i[\rho]$

What is a FUNCTIONAL?



Generalization of terminology:

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

$$\Psi_{\vec{r}_1 \dots \vec{r}_N}[\rho] = \Psi[\rho](\vec{r}_1 \dots \vec{r}_N) \quad \text{depending parametrically on } (\vec{r}_1 \dots \vec{r}_N)$$

Explicit construction of the HK map $v_s \longleftrightarrow \rho$ for non-interacting particles

$$\left(-\frac{\hbar^2 \nabla^2}{2m} + v_s(\mathbf{r}) \right) \varphi_i = \epsilon_i \varphi_i \quad \left| \sum_i \varphi_i^* \cdot \right.$$

$$\sum_{i=1}^N \varphi_i^* \left(-\frac{\hbar^2 \nabla^2}{2m} \right) \varphi_i + v_s(\mathbf{r}) \rho(\mathbf{r}) = \sum_{i=1}^N \epsilon_i |\varphi_i(\mathbf{r})|^2$$

$$\Rightarrow v_s(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})} \cdot \sum_{i=1}^N \left(\epsilon_i |\varphi_i(\mathbf{r})|^2 - \varphi_i^* \left(-\frac{\hbar^2 \nabla^2}{2m} \right) \varphi_i \right)$$

Iterative procedure

$\rho_0(\mathbf{r})$ given (e.g. from experiment)

Start with an initial guess for $v_s(\mathbf{r})$ (e.g. GGA potential)

solve $\left(-\frac{\hbar^2 \nabla^2}{2m} + v_s(\mathbf{r}) \right) \varphi_i = \epsilon_i \varphi_i$

$$v_s^{\text{new}}(\mathbf{r}) = \frac{1}{\rho_0(\mathbf{r})} \cdot \sum_{i=1}^N \left(\epsilon_i |\varphi_i(\mathbf{r})|^2 - \varphi_i^* \left(-\frac{\hbar^2 \nabla^2}{2m} \right) \varphi_i \right)$$

solve SE with v_s^{new} and iterate, keeping $\rho_0(\mathbf{r})$ fixed

QUESTION:

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

Theorem:

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

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

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

where E_o = exact ground state energy of the system

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

yields exact ground state density ρ_o .

proof:

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

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

define:

$$E_{\text{HK}}[\rho] \equiv \langle \Psi[\rho] | \hat{T} + \hat{W} + \hat{V}_0 | \Psi[\rho] \rangle$$

$$> E_0 \quad \text{for } \rho \neq \rho_0$$

$$= E_0 \quad \text{for } \rho = \rho_0 \quad \text{q.e.d.}$$

$$E_{\text{HK}}[\rho] = \int d^3r \rho(\mathbf{r}) v_0(\mathbf{r}) + \underbrace{\langle \Psi[\rho] | \hat{T} + \hat{W} | \Psi[\rho] \rangle}_{\text{F}[\rho] \text{ is universal}}$$

F[ρ] is universal

HOHENBERG-KOHN THEOREM

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

one-to-one correspondence between external potentials $v(\mathbf{r})$ and ground-state densities $\rho(\mathbf{r})$

2. Variational principle

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

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

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

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

$F[\rho]$ is UNIVERSAL. **In practice, $F[\rho]$ needs to be approximated**

**Can one approximate the functional $F[\rho]$
in a systematic (controlled) way?**

YES!

Expansion of $F[\rho]$ in powers of e^2

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

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

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

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

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

Systematic approach to construct E_{xc} using KS-MBPT

$H_{KS} \longrightarrow$ unperturbed system

$$H = H_{KS} + \lambda H_1,$$

where $H_1 = W_{ee} - \int d^3r \rho(r)(v_H(r) + v_{xc}(r))$

$$E_x^{\text{exact}}[\rho] = \text{diagram} \\ = -\frac{1}{2} \sum_{\sigma=\uparrow\downarrow} \sum_{j,k}^{N_\sigma} \int \frac{\varphi_{k\sigma}^*(r') \varphi_{k\sigma}(r) \varphi_{j\sigma}^*(r) \varphi_{j\sigma}(r')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r'$$

$E_c[\rho]$ = sum of all higher-order diagrams in terms of the Green's function

$$G_{s\sigma}(\mathbf{r}, \mathbf{r}') = \sum_k \frac{\varphi_{k\sigma}(\mathbf{r}) \varphi_{k\sigma}^*(\mathbf{r}')}{\omega - \varepsilon_{k\sigma}} \Rightarrow \text{The exact } E_{xc}[\rho] \text{ is an orbital functional}$$

TOWARDS THE EXACT FUNCTIONAL

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

1st generation of DFT: Use approximate functionals (LDA/GGA) for T_s , E_x and E_c e.g.

$$T_s[\rho] = \int d^3r \left(a\rho(\mathbf{r})^{5/3} + b \frac{(\nabla\rho)^2}{\rho} + \dots \right)$$

⇒ Thomas-Fermi-type equation has to be solved

2nd generation of DFT: Use exact functional $T_s^{\text{exact}}[\rho]$ and LDA/GGA for E_x and E_c

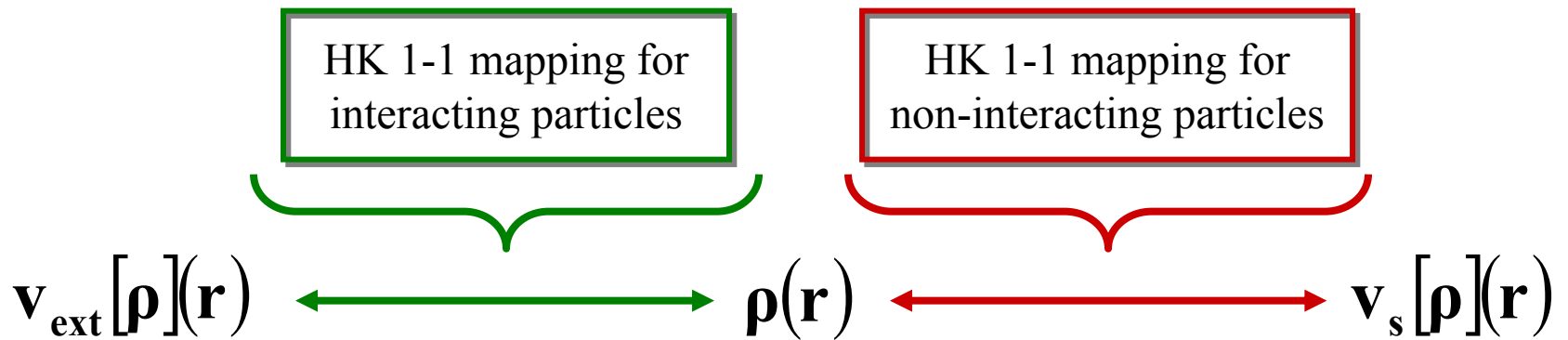
$$T_s^{\text{exact}}[\rho] = \sum_{j_{\text{occ}}} \int d^3r \varphi_j^*[\rho](\mathbf{r}) \left(-\frac{\nabla^2}{2} \right) \varphi_j[\rho](\mathbf{r})$$

⇒ KS equations have to be solved

3rd generation of DFT: Use $T_s^{\text{exact}}[\rho]$, and an orbital functional $E_{xc}[\varphi_1, \varphi_2, \dots]$ e.g.

$$E_x^{\text{exact}}[\rho] = - \sum_{\sigma=\uparrow\downarrow} \sum_{j,k}^{N_\sigma} \int \frac{\varphi_{k\sigma}^*[\rho](\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}) \varphi_{j\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r'$$

⇒ KS equations have to be solved self-consistently with OEP integral equation



Kohn-Sham Theorem

Let $\rho_0(\mathbf{r})$ be the ground-state density of interacting electrons moving in the external potential $v_0(\mathbf{r})$. Then there exists a unique local potential $v_{s,0}(\mathbf{r})$ such that non-interacting particles exposed to $v_{s,0}(\mathbf{r})$ have the ground-state density $\rho_0(\mathbf{r})$, i.e.

$$\left(-\frac{\nabla^2}{2} + v_{s,0}(\mathbf{r}) \right) \varphi_j(\mathbf{r}) = \epsilon_j \varphi_j(\mathbf{r}) , \quad \rho_0(\mathbf{r}) = \sum_{j(\text{with lowest } \epsilon_j)}^N |\varphi_j(\mathbf{r})|^2$$

proof: $v_{s,0}(\mathbf{r}) = v_s[\rho_0](\mathbf{r})$

Uniqueness follows from HK 1-1 mapping

Existence follows from V-representability theorem

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

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

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

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

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

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

Define $v_{xc}[\rho](\mathbf{r})$ by the equation

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

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

KS equations

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

$v_o(\mathbf{r})$
fixed

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

Note: The KS equations do not follow from the variational principle. They follow from the HK 1-1 mapping and the V-representability theorem.

Time-dependent density-functional formalism (first: electrons only, nuclei are fixed or treated classically)

(E. Runge, E.K.U.G., PRL 52, 997 (1984))

Basic 1-1 correspondence:

$v(\mathbf{r}t) \xleftrightarrow{1-1} \rho(\mathbf{r}t)$ The time-dependent density determines uniquely the time-dependent external potential and hence all physical observables for fixed initial state.

KS theorem:

The time-dependent density of the interacting system of interest can be calculated as density

$$\rho(\mathbf{r}t) = \sum_{j=1}^N \left| \varphi_j(\mathbf{r}t) \right|^2$$

of an auxiliary non-interacting (KS) system

$$i\hbar \frac{\partial}{\partial t} \varphi_j(\mathbf{r}t) = \left(-\frac{\hbar^2 \nabla^2}{2m} + v_s[\rho](\mathbf{r}t) \right) \varphi_j(\mathbf{r}t)$$

with the local potential

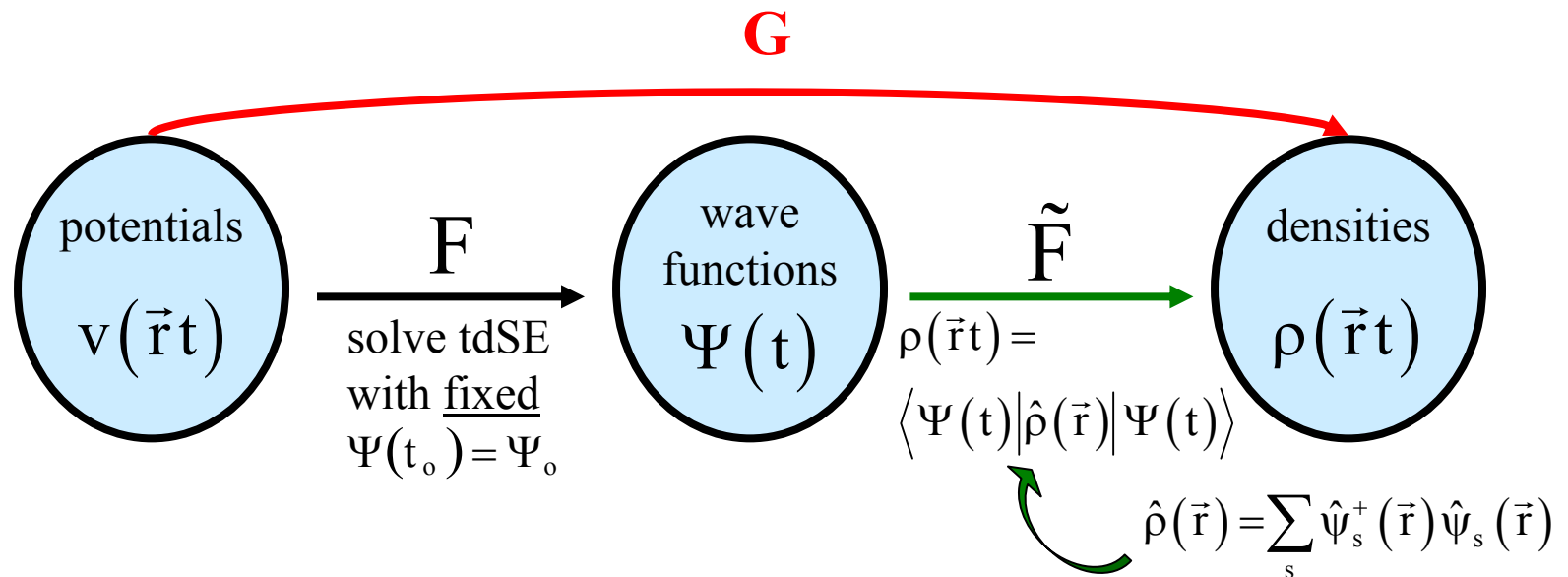
$$v_s[\rho(\mathbf{r}'t')](\mathbf{r}t) = v(\mathbf{r}t) + \int d^3r' \frac{\rho(\mathbf{r}'t')}{|\mathbf{r}-\mathbf{r}'|} + v_{xc}[\rho(\mathbf{r}'t')](\mathbf{r}t)$$

Proof of basic 1-1 correspondence between $v(\vec{r}t)$ and $\rho(\vec{r}t)$

define maps

$$F: v(\vec{r}t) \mapsto \Psi(t)$$

$$\tilde{F}: \Psi(t) \mapsto \rho(\vec{r}t)$$



$$G: v(\vec{r}t) \mapsto \rho(\vec{r}t)$$

The TDKS equations follow (like in the static case) from:

- i. the basic 1-1 mapping and**
- ii. the TD V -representability theorem (R. van Leeuwen, PRL 82, 3863 (1999)).**

A TDDFT variational principle exists as well, but this is more tricky (R. van Leeuwen, PRL 80, 1280 (1998)).

complete 1 - 1 correspondence not to be expected!

$$i \frac{\partial}{\partial t} \Psi(t) = \left(\hat{T} + \underline{\hat{V}(t)} + \hat{W} \right) \Psi(t) \quad \Psi(t_0) = \Psi_0$$

$$i \frac{\partial}{\partial t} \Psi'(t) = \left(\hat{T} + \underline{\hat{V}'(t)} + \hat{W} \right) \Psi'(t) \quad \Psi'(t_0) = \Psi_0$$

$$\hat{V}'(t) = \hat{V}(t) + C(t) \Leftrightarrow \Psi'(t) = e^{-i\alpha(t)} \Psi(t)$$

↑
“no operator”

with

$$\dot{\alpha}(t) = C(t)$$

$$\Rightarrow \underline{\underline{\rho'(\vec{r}t) = \rho(\vec{r}t)}}$$

$$\text{i.e. } \{ \hat{V}(t) + C(t) \} \rightarrow \rho(\vec{r}t)$$

If G invertible up to within time-dependent function $C(t)$

$\Rightarrow \Psi = FG^{-1}\rho$ fixed up to within time-dependent phase

i.e. $\Psi = e^{-i\alpha(t)}\Psi[\rho]$

For any observable \hat{O}

$$\langle \Psi | \hat{O} | \Psi \rangle = \langle \Psi[\rho] | \hat{O} | \Psi[\rho] \rangle = O[\rho]$$

is functional of the density

THEOREM (time-dependent analogue of Hohenberg-Kohn theorem)

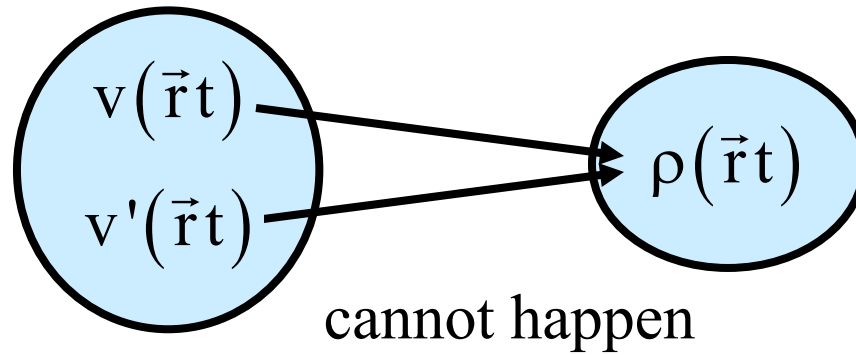
The map

$$G : v(\vec{r}t) \mapsto \rho(\vec{r}t)$$

defined for all single-particle potentials $v(\vec{r}t)$ which can be expanded into a Taylor series with respect to the time coordinate around t_0

is invertible up to within an additive merely time-dependent function in the potential.

Proof:
to be shown:



i.e. $\hat{v}(\vec{r}t) \neq \hat{v}'(\vec{r}t) + c(t) \stackrel{!}{\Rightarrow} \rho(\vec{r}t) \neq \rho'(\vec{r}t)$

potential expandable into Taylor series

$$\exists k \geq 0 : \frac{\partial^k}{\partial t^k} [v(\vec{r}t) - v'(\vec{r}t)]_{t=t_0} \neq \text{constant}$$

step 1

$$\vec{j}(\vec{r}t) \neq \vec{j}'(\vec{r}t)$$

step 2

$$\rho(\vec{r}t) \neq \rho'(\vec{r}t)$$

Step 1: Current densities

$$\vec{j}(\vec{r}t) = \left\langle \Psi(t) \left| \hat{j}(\vec{r}) \right| \Psi(t) \right\rangle$$

$$\text{with } \hat{j}(\vec{r}) = -\frac{1}{2i} \sum_s \left(\left[\vec{\nabla} \hat{\psi}_s^+(\vec{r}) \right] \hat{\psi}_s(\vec{r}) - \hat{\psi}_s^+(\vec{r}) \left[\vec{\nabla} \hat{\psi}_s(\vec{r}) \right] \right)$$

Use equation of motion:

$$i \frac{\partial}{\partial t} \left\langle \Psi(t) \left| \hat{O}(t) \right| \Psi(t) \right\rangle = \left\langle \Psi(t) \left| i \frac{\partial}{\partial t} \hat{O}(t) + \left[\hat{O}(t), \hat{H}(t) \right] \right| \Psi(t) \right\rangle$$

$$\Rightarrow i \frac{\partial}{\partial t} \vec{j}(\vec{r}t) = \left\langle \Psi(t) \left[\hat{j}(\vec{r}), \hat{H}(t) \right] \right| \Psi(t) \right\rangle$$

$$i \frac{\partial}{\partial t} \vec{j}'(\vec{r}t) = \left\langle \Psi'(t) \left[\hat{j}(\vec{r}), \hat{H}'(t) \right] \right| \Psi'(t) \right\rangle$$

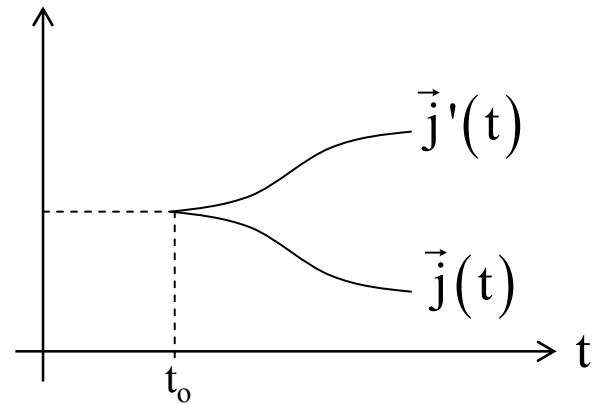
note: $\vec{j}(\vec{r}\underline{t}_0) = \vec{j}'(\vec{r}\underline{t}_0) = \left\langle \Psi_0 \left| \hat{j}(\vec{r}) \right| \Psi_0 \right\rangle \equiv \vec{j}_0(\vec{r})$

$$\rho(\vec{r}\underline{t}_0) = \rho'(\vec{r}\underline{t}_0) = \left\langle \Psi_0 \left| \hat{\rho}(\vec{r}) \right| \Psi_0 \right\rangle \equiv \rho_0(\vec{r})$$

$$\begin{aligned}
i \frac{\partial}{\partial t} [\vec{j}(\vec{r}t) - \vec{j}'(\vec{r}t)]_{t=t_0} &= \left\langle \Psi_0 \left[\left[\hat{j}(\vec{r}), \hat{H}(t_0) - \hat{H}'(t_0) \right] \right] \Psi_0 \right\rangle \\
&= \left\langle \Psi_0 \left[\left[\hat{j}(\vec{r}), V(t_0) - V'(t_0) \right] \right] \Psi_0 \right\rangle \\
&= i \rho_0(\vec{r}) \vec{\nabla} (v(\vec{r}t_0) - v'(\vec{r}t_0))
\end{aligned}$$

if $\frac{\partial^k}{\partial t^k} [v(\vec{r}t) - v'(\vec{r}t)]_{t=t_0} \neq \text{constant}$ holds for $k=0$

then $i \frac{\partial}{\partial t} [\vec{j}(\vec{r}t) - \vec{j}'(\vec{r}t)]_{t=t_0} \neq 0$



$\Rightarrow \underline{\underline{\vec{j}(\vec{r}t) \neq \vec{j}'(\vec{r}t)}} \quad \text{q.e.d.}$

if $\frac{\partial^k}{\partial t^k} [\mathbf{v}(\vec{r}t) - \mathbf{v}'(\vec{r}t)]_{t=t_0} \neq \text{constant}$ holds for $k > 0$

→ use equation of motion k+1 times:

$$\begin{aligned} \left(i \frac{\partial}{\partial t} \right)^2 \vec{j}(\vec{r}t) &= i \frac{\partial}{\partial t} \left\langle \Psi(t) \left[\hat{\vec{j}}, \hat{H}(t) \right] \Psi(t) \right\rangle \\ &= \left\langle \Psi(t) \left| i \frac{\partial}{\partial t} \left[\hat{\vec{j}}, \hat{H}(t) \right] + \left[\left[\hat{\vec{j}}, \hat{H}(t) \right], \hat{H}(t) \right] \right| \Psi(t) \right\rangle \end{aligned}$$

$$\begin{aligned} \left(i \frac{\partial}{\partial t} \right)^3 \vec{j}(\vec{r}t) &= i \frac{\partial}{\partial t} \left\langle \Psi(t) \left| i \frac{\partial}{\partial t} \left[\hat{\vec{j}}, \hat{H}(t) \right] + \left[\left[\hat{\vec{j}}, \hat{H}(t) \right], \hat{H}(t) \right] \right| \Psi(t) \right\rangle \\ &= \dots \end{aligned}$$

$$\left(i \frac{\partial}{\partial t} \right)^{k+1} \left[\vec{j}(\vec{r}t) - \vec{j}'(\vec{r}t) \right]_{t=t_0} = i \rho_0(\vec{r}) \vec{\nabla} \underbrace{\left(\left(i \frac{\partial}{\partial t} \right)^k \left[\mathbf{v}(\vec{r}t) - \mathbf{v}'(\vec{r}t) \right]_{t_0} \right)}_{\neq \text{constant}} \neq 0$$

⇒ $\vec{j}(\vec{r}t) \neq \vec{j}'(\vec{r}t)$ q.e.d.

Step 2: densities

Use continuity equation:

$$\frac{\partial}{\partial t} [\rho(\vec{r}t) - \rho'(\vec{r}t)] = -\text{div} [\vec{j}(\vec{r}t) - \vec{j}'(\vec{r}t)]$$

$$\begin{aligned} \Rightarrow \frac{\partial^{k+2}}{\partial t^{k+2}} [\rho(\vec{r}t) - \rho'(\vec{r}t)]_{t=t_0} &= -\text{div} \frac{\partial^{k+1}}{\partial t^{k+1}} [\vec{j}(\vec{r}t) - \vec{j}'(\vec{r}t)]_{t=t_0} \\ &= -\text{div} \rho_o(\vec{r}) \underbrace{\vec{\nabla} \left(\frac{\partial^k}{\partial t^k} [\mathbf{v}(\vec{r}t) - \mathbf{v}'(\vec{r}t)]_{t=t_0} \right)}_{\neq \text{constant}} \end{aligned}$$

remains to be shown:

$$\text{div} [\rho_o(\vec{r}) \vec{\nabla} u(\vec{r})] \neq 0 \quad \text{if} \quad u(\vec{r}) \neq \text{constant}$$

Proof: by reductio ad absurdum

Assume: $\operatorname{div}[\rho_o(\vec{r})\vec{\nabla}u(\vec{r})] = 0$ with $u(\vec{r}) \neq \text{constant}$

$$\begin{aligned} & \int d\vec{r}^3 \rho_o(\vec{r}) (\vec{\nabla}u(\vec{r}))^2 \\ &= -\int d\vec{r}^3 u(\vec{r}) \underbrace{\operatorname{div}[\rho_o(\vec{r})\vec{\nabla}u(\vec{r})]}_0 + \underbrace{\oint \rho_o(\vec{r})u(\vec{r})\vec{\nabla}u(\vec{r}) \cdot d\vec{S}}_0 = 0 \end{aligned}$$

$$\Rightarrow \rho_o(\vec{r})(\vec{\nabla}u(\vec{r}))^2 \equiv 0 \quad \longrightarrow \quad \begin{array}{l} \text{contradiction to} \\ u(\vec{r}) \neq \text{constant} \end{array}$$

Thanks !