Time-dependent density-functional formalism

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

Basic 1-1 correspondence:

$$v(rt) \overset{1-1}{\longleftrightarrow} \rho(rt)$$

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

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

of an auxiliary non-interacting (KS) system

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

with the local potential

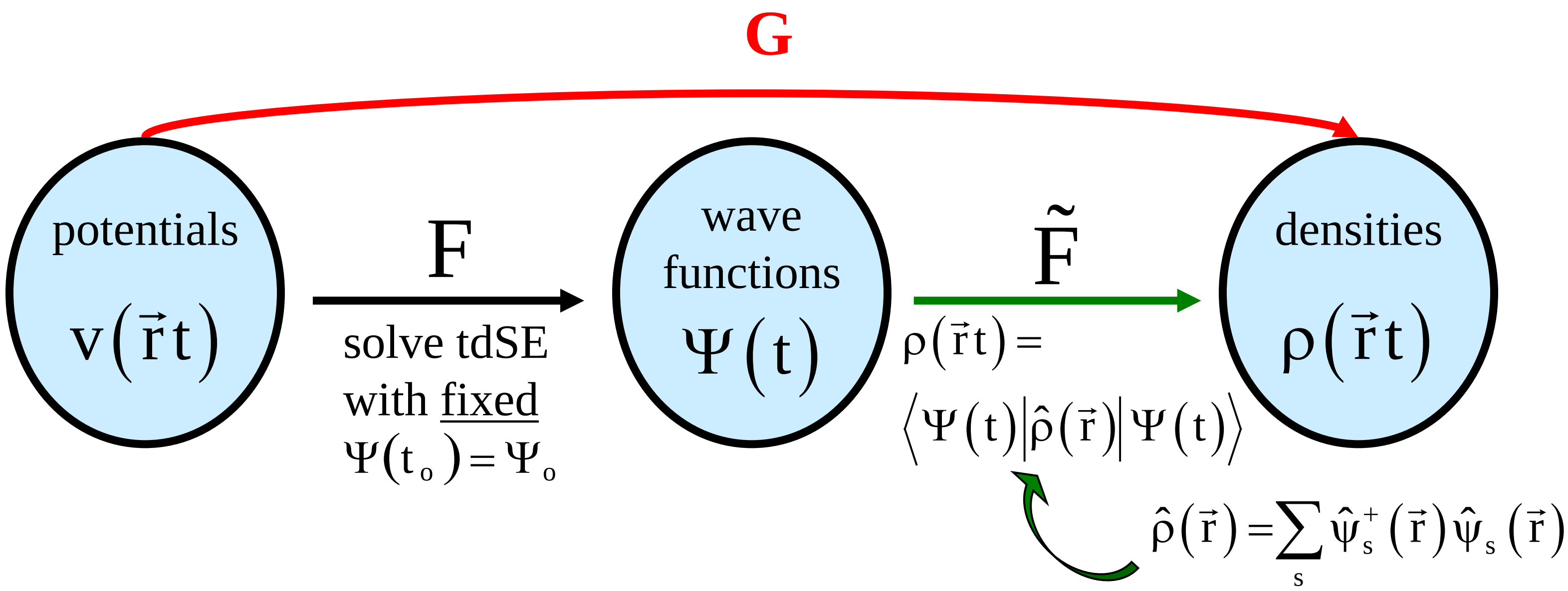
$$v_S\left[\rho(r't')\right](rt) = v(rt) + \int d^3r' \frac{\rho(r't)}{|r-r'|} + v_{xc}\left[\rho(r't')\right](rt)$$

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

define maps

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

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



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

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!

$$i\frac{\partial}{\partial t}\Psi(t) = \left(\hat{T} + \underline{\underline{\hat{V}(t)}} + \hat{W}\right)\Psi(t) \qquad \Psi(t_o) = \Psi_o$$

$$i\frac{\partial}{\partial t}\Psi'(t) = \left(\hat{T} + \underline{\underline{\hat{V}'(t)}} + \hat{W}\right)\Psi'(t) \qquad \Psi'(t_o) = \Psi_o$$

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

"no operator"

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

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

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

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 $\hat{O}$

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

is functional of the density

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

The map

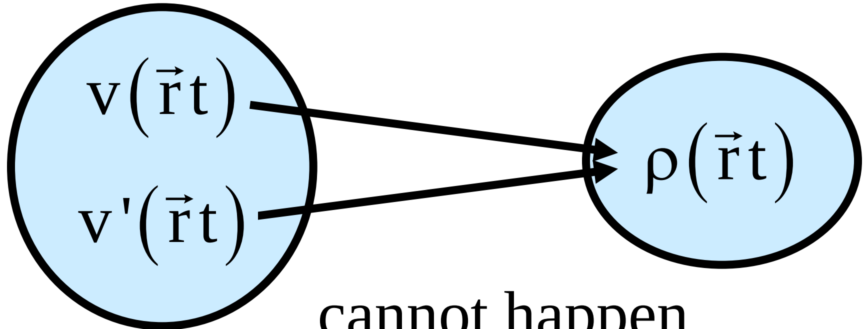
$$G: \ v(\vec{r}t) \mapsto \rho(\vec{r}t)$$

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_o

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

Proof:

to be shown:



cannot happen

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

potential expandable into Taylor series

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

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

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

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

Use equation of motion:

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

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

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

note:

$$\vec{j}(\vec{r}\underline{\underline{t_o}}) = \vec{j}'(\vec{r}\underline{\underline{t_o}}) = \left\langle \Psi_o \middle| \hat{\vec{j}}(\vec{r}) \middle| \Psi_o \right\rangle \equiv \vec{j}_o(\vec{r})$$

$$\rho(\vec{r}\underline{\underline{t_o}}) = \rho'(\vec{r}\underline{\underline{t_o}}) = \left\langle \Psi_o \middle| \hat{\rho}(\vec{r}) \middle| \Psi_o \right\rangle \equiv \rho_o(\vec{r})$$

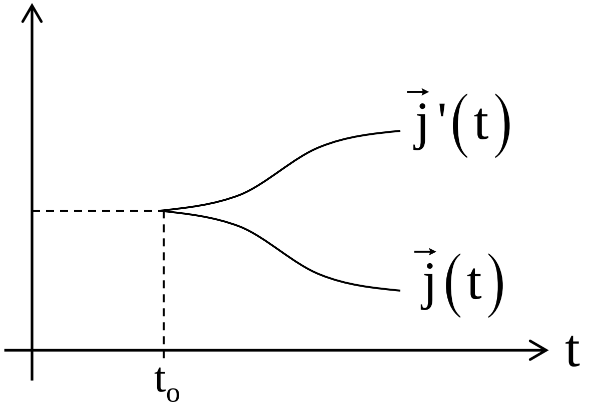
$$i\frac{\partial}{\partial t}\left[\vec{j}(\vec{r}t)-\vec{j}'(\vec{r}t)\right]_{t=t_o}=\left\langle\Psi_o\left\|\left[\hat{\vec{j}}(\vec{r}),\hat{H}(t_o)-\hat{H}'(t_o)\right]\right\|\Psi_o\right\rangle$$

$$=\left\langle\Psi_o\left\|\left[\hat{\vec{j}}(\vec{r}),V(t_o)-V'(t_o)\right]\right\|\Psi_o\right\rangle$$

$$=i\rho_o(\vec{r})\vec{\nabla}\left(v(\vec{r}t_o)-v'(\vec{r}t_o)\right)$$

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

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



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

q.e.d.

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

$\longrightarrow$ use equation of motion k+1 times:

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

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

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

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

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

Step 2: densities

Use continuity equation:

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

$$\Rightarrow \quad \frac{\partial^{k+2}}{\partial t^{k+2}}\left[\rho(\vec r t)-\rho'(\vec r t)\right]_{t=t_o}=-\mathrm{div}\frac{\partial^{k+1}}{\partial t^{k+1}}\left[\vec j(\vec r t)-\vec j'(\vec r t)\right]_{t=t_o}$$

$$=-\mathrm{div}\,\rho_o(\vec r)\vec\nabla\underbrace{\left(\frac{\partial^{k}}{\partial t^{k}}\left[v(\vec r t)-v'(\vec r t)\right]_{t=t_o}\right)}_{\neq\ \mathrm{constant}}$$

remains to be shown:

$$\mathrm{div}\left[\rho_o(\vec r)\vec\nabla u(\vec r)\right]\neq 0 \qquad \text{if} \qquad u(\vec r)\neq \text{constant}$$

Proof: by reductio ad absurdum

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

$$\int dr^3 \rho_o(\vec{r}) \left(\vec{\nabla}u(\vec{r})\right)^2$$

$$= -\int dr^3 u(\vec{r})\, \underbrace{\mathrm{div}\left[\rho_o(\vec{r})\vec{\nabla}u(\vec{r})\right]}_{0} + \underbrace{\int \rho_o(\vec{r})u(\vec{r})\vec{\nabla}u(\vec{r})\cdot d\vec{S}}_{0} = 0$$

$$\Rightarrow \quad \rho_o(\vec{r})\left(\vec{\nabla}u(\vec{r})\right)^2 \equiv 0 \quad \longrightarrow \quad \text{contradiction to } u(\vec{r})\neq \text{constant}$$