

# Density functionals with spin-density accuracy for open shells

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## Brief Intro to SDFT

SDFT was introduced by U von Barth and Hedin in 1972.  
(Weak/zero external  $B$ :  $H$  includes  $-\int d\mathbf{r} \mathbf{m}(\mathbf{r}) \cdot \mathbf{B}(\mathbf{r})$  term only.)

J. Phys. C: Solid State Phys., Vol. 5, 1972. Printed in Great Britain. © 1972.

### **A local exchange-correlation potential for the spin polarized case: I**

U VON BARTH and L HEDIN  
Department of Theoretical Physics, University of Lund, Lund, Sweden

From the start, it appeared that theoretical foundation of gs DFT was not shared by gs SDFT.

No proof for HK theorem, showing 1-1 correspondence between set of spin potentials and set of gs spin-densities.

Either for collinear or for non-collinear densities.

Traditionally, 1-1 mapping between  $v$  and  $\rho$  is proven in two steps:

- Show that different  $(v^\uparrow, v^\downarrow)$  have different gs  $\Psi$ .
- Show that different  $\Psi$  have different  $(\rho^\uparrow, \rho^\downarrow)$ .

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- Show that different  $(v^\uparrow, v^\downarrow)$  have different gs  $\Psi$ . **Not invertible!**
- Show that different  $\Psi$  have different  $(\rho^\uparrow, \rho^\downarrow)$ . **Invertible**

von Barth & Hedin took ( $N = 1$ ) gs  $\Psi$  of any noncollinear spin potential and constructed a class of different noncollinear spin potentials that admitted  $\Psi$  as their gs.

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**Hence HK theorem could not hold in SDFT.**

**But what about  $N > 1$ ?**

Problem was forgotten ... then, in 2001:

Capelle & Vignale, PRL **86**, 5546 (2001)

Eschrig & Pickett, Solid State Commun. **118**, 123 (2001).

- For collinear  $B$ , Capelle & Vignale gave several examples where the spin potential was not determined uniquely by the spin density.
- Eschrig & Pickett claimed to extend von Barth and Hedin's example to  $N > 1$ .

$\Psi$  can be pure-spin state or impure spin state.

Pure-spin state through local rotation of spin coordinates may be transformed to have a definite number of spin-up and -down electrons.

If  $\Psi$  is a pure-spin state, then  $\Psi$  is also eigenstate of operator  $\hat{O}$ .  
In unrotated spin space,  $\hat{O}$  is a noncollinear magnetic field.

$\Rightarrow$  spin potential in  $H$  cannot be determined by  $\Psi$ .

Actually, things are not too bad for SDFT:

PHYSICAL REVIEW B **75**, 134408 (2007)

**Potential in spin-density-functional theory of noncollinear magnetism determined by the many-electron ground state**

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- For collinear  $B$  mapping  $(v^\uparrow, v^\downarrow)$  &  $\Psi$  is invertible ... but:
  - (a)  $(\rho^\uparrow, \rho^\downarrow)$  must **not** be **fully spin-polarised**.
  - (b)  $(v^\uparrow, v^\downarrow)$  are determined within a **spin-constant**.
- For noncollinear  $B$ , mapping is invertible for  $N > 1$  (explain).



Here we focus on two other questions in DFT vs SDFT when  $B = 0$ :

- Formal link between two exact theories when  $B = 0$ :

When  $B = 0$ , there is only one external potential  $v(\mathbf{r})$ .

So, there must be one conjugate density  $\rho(\mathbf{r})$ .

Should SDFT-KS equations reduce to (some) DFT-KS equations?

**Is it even possible to obtain a spin-potential from a density-functional? (!)**

- Link between approximate results of two theories when  $B = 0$ :

Open shells can be studied with KS-DFT or KS-SDFT.

SDFT-KS equations are used in practice, because its approximations model better the xc functional. **Is this true?**

Textbook by Parr & Yang (“DFT of Atoms and Molecules”):

“Should not the spin-polarized Kohn-Sham results reduce to the spin-compensated results when  $b(\mathbf{r}) = 0$ ? ...

The answer is certainly yes under the condition that the exact xc functionals  $E_{xc}[\rho]$  and  $E_{xc}[\rho^\uparrow, \rho^\downarrow]$  are both known and used, for then both schemes would give the same total density  $\rho$  and energy  $E$ .

But we do not know the exact functionals. . . .

An approximate form of the spin-density functional  $E_{xc}[\rho^\uparrow, \rho^\downarrow]$  can be (and usually is) a better description of the real system than the corresponding approximate  $E_{xc}[\rho]$ .”

**Ghost-exchange error in DFA treatment of open shells.**

(Analogy with HK vs KS DFT for kinetic energy)

For  $B = 0$ , the main error is in (approx.)  $E_x[\rho]$  vs  $E_x[\rho^\uparrow, \rho^\downarrow]$ .

With a local or semi-local DFA it is always assumed:

$$\rho^\uparrow(\mathbf{r}) = \rho(\mathbf{r})/2, \quad \rho^\downarrow(\mathbf{r}) = \rho(\mathbf{r})/2$$

$$E_x[\rho] \simeq E_x[\rho/2, \rho/2], \quad \rho = \rho^\uparrow + \rho^\downarrow.$$

This amounts to mixing partly  $\rho^\uparrow$  with  $\rho^\downarrow$ , leading to the ...  
“ghost exchange energy error”:

$$G_x = E_x[\rho/2, \rho/2] - E_x[\rho^\uparrow, \rho^\downarrow].$$

Part of “static correlation” or “fractional spin error” discussed by Prof. W. Yang and his group.

## The exact x energy as an implicit density functional

$$E_x[\rho^\uparrow, \rho^\downarrow] = -\frac{1}{2} \iint d\mathbf{r}d\mathbf{x} \left\{ \frac{|\rho^\uparrow(\mathbf{r}, \mathbf{x})|^2}{|\mathbf{r} - \mathbf{x}|} + \frac{|\rho^\downarrow(\mathbf{r}, \mathbf{x})|^2}{|\mathbf{r} - \mathbf{x}|} \right\}.$$

$E_x$  separates in two disjoint terms:  $E_x[\rho^\uparrow, \rho^\downarrow] = E_x[\rho^\uparrow, 0] + E_x[0, \rho^\downarrow]$ ,

To avoid cross-exchange the approximate  $E_x$  must also separate.

**Define for any DFA a new ghost-x-error free x-energy DF:**

Analogy with KS-DFT vs HK-DFT:

employ spin-density of virtual KS-DFT system  $(\rho^\uparrow[\rho], \rho^\downarrow[\rho])$   
to model exchange energy  $E_x[\rho]$

in general KS-DFT spin-density  $(\rho^\uparrow[\rho], \rho^\downarrow[\rho]) \neq$  physical spin-density.

**Define for any DFA a new ghost-x-error free x-energy DF:**

- We model  $E_x[\rho]$  using the KS-DFT spin-density  $(\rho^\uparrow[\rho], \rho^\downarrow[\rho])$ .

Still within DFT since  $(\rho^\uparrow[\rho], \rho^\downarrow[\rho])$  is an implicit functional of  $\rho$ :

$$E_x^{\text{iDF}}[\rho] = E_x^{\text{SDF}}[\rho^\uparrow[\rho], \rho^\downarrow[\rho]].$$

iDF: x energy is an *implicit* DF.

To treat xc uniformly, we write  $E_c$  as:

$$E_c[\rho] = E_c^{\text{iDF}}[\rho] + \cancel{\Delta E_c[\rho]},$$

[ $\Delta E_c[\rho] \neq 0$  in exact DFT.]

$$E_c^{\text{iDF}}[\rho] = E_c^{\text{SDF}}[\rho^\uparrow[\rho], \rho^\downarrow[\rho]].$$

In (semi)-local DFAs we omit  $\Delta E_c$  and write for xc:

$$E_{xc}^{\text{iDF}}[\rho] \approx E_{xc}^{\text{SDF}}[\rho^\uparrow[\rho], \rho^\downarrow[\rho]].$$

Hence, total energy DF is:

$$E_{\text{ven}}^{\text{iDF}}[\rho] = T_s[\rho] + \int dr v_{\text{en}}(\mathbf{r})\rho(\mathbf{r}) + U[\rho] + E_{xc}^{\text{iDF}}[\rho],$$



$$v_{xc}[\rho](\mathbf{r}) = \frac{E_{xc}^{\text{iDF}}[\rho]}{\delta\rho(\mathbf{r})}$$

$v_{xc}$  is determined by OEP equation (implicit DF):

$$\int d\mathbf{r}' \left[ \sum_{\sigma} \chi^{\sigma}(\mathbf{r}, \mathbf{r}') \right] v_{xc}[\rho](\mathbf{r}') = \sum_{\sigma} \int d\mathbf{r}' \chi^{\sigma}(\mathbf{r}, \mathbf{r}') v_{xc}^{\sigma}[\rho^{\uparrow}[\rho], \rho^{\downarrow}[\rho]](\mathbf{r}')$$

$v_{xc}$  is the weighted average of  $v_{xc}^{\uparrow}, v_{xc}^{\downarrow}$ .

$$v_{xc}^{\sigma}[\rho^{\uparrow}[\rho], \rho^{\downarrow}[\rho]](\mathbf{r}) = \left. \frac{\partial E_{xc}^{\text{SDF}}[\rho^{\uparrow}, \rho^{\downarrow}]}{\partial \rho^{\sigma}(\mathbf{r})} \right|_{\substack{\rho^{\uparrow} = \rho^{\uparrow}[\rho] \\ \rho^{\downarrow} = \rho^{\downarrow}[\rho]}}$$

$$\chi^{\sigma}(\mathbf{r}, \mathbf{r}') = -2 \sum_{i=1}^{N^{\sigma}} \sum_{a=N^{\sigma}+1}^{\infty} \frac{\phi_i(\mathbf{r})\phi_a(\mathbf{r})\phi_i(\mathbf{r}')\phi_a(\mathbf{r}')}{\epsilon_a - \epsilon_i}$$

Ghost-x-error-corrected  $E_{xc}$ ,  $v_{xc}$  for open shells in (semi)-local DFAs.

$$\int d\mathbf{r}' \left[ \sum_{\sigma} \chi^{\sigma}(\mathbf{r}, \mathbf{r}') \right] v_{xc}[\rho](\mathbf{r}') = \sum_{\sigma} \int d\mathbf{r}' \chi^{\sigma}(\mathbf{r}, \mathbf{r}') v_{xc}^{\sigma}[\rho^{\uparrow}[\rho], \rho^{\downarrow}[\rho]](\mathbf{r}')$$

$$\int d\mathbf{r}' \left[ \sum_{\sigma} \chi^{\sigma}(\mathbf{r}, \mathbf{r}') \right] v_{xc}[\rho](\mathbf{r}') = \sum_{\sigma} \int d\mathbf{r}' \chi^{\sigma}(\mathbf{r}, \mathbf{r}') v_{xc}^{\sigma}[\rho^{\uparrow}[\rho], \rho^{\downarrow}[\rho]](\mathbf{r}')$$

- For closed shells solution reduces to familiar KS xc FD.
- For fully spin-polarised systems (eg spin-up)  $v_{xc}[\rho] = v_{xc}^{\uparrow}[\rho, 0]$ .
- Majority-spin xc potential is an accurate approximation  $v_{xc} = v_{xc}^{\uparrow}$ .

Because HOMO-LUMO gap  $\Delta^{\uparrow} < \Delta^{\downarrow}$ .

- Another approximation:  $v_{xc} \approx \frac{\Delta^{\downarrow} v_{xc}^{\uparrow} + \Delta^{\uparrow} v_{xc}^{\downarrow}}{\Delta^{\uparrow} + \Delta^{\downarrow}}$

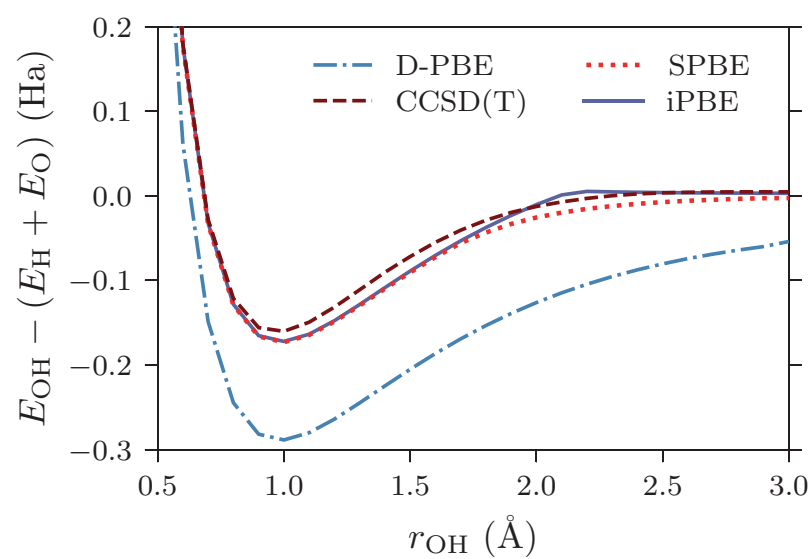
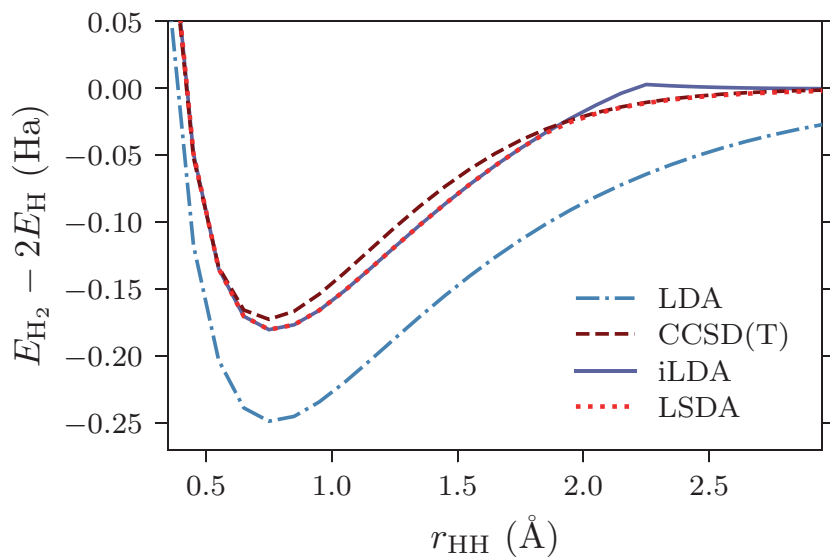
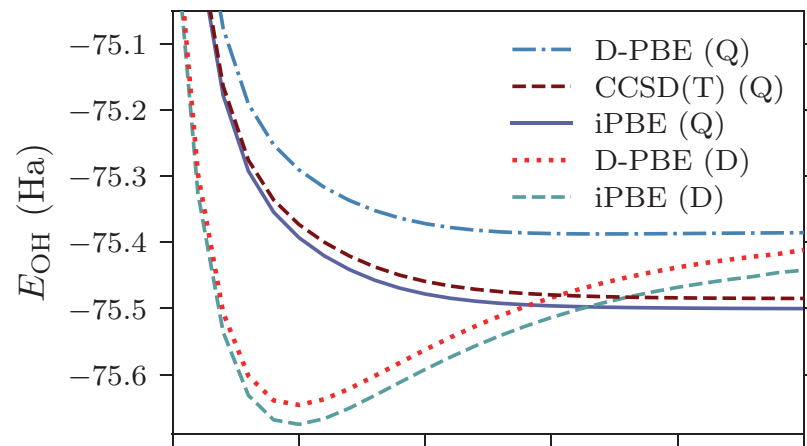
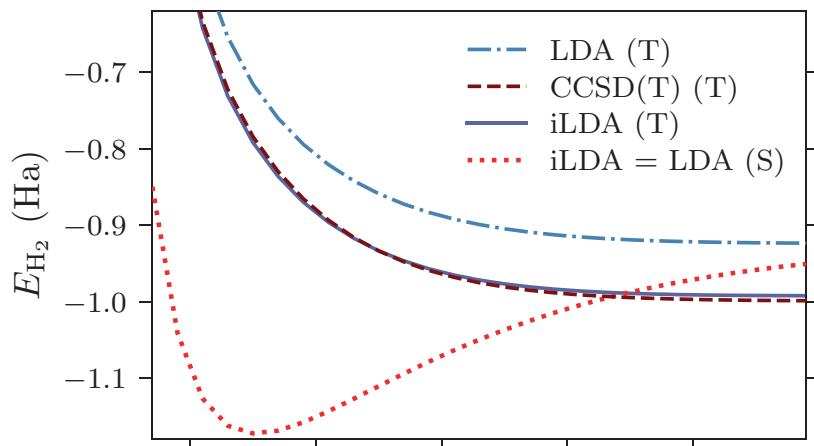
Results: cc-pVTZ orbital basis

L(S)DA gs total energies

	$E_{\text{LDA}}$ (Ha)	$E_{\text{iLDA}}$ (Ha)	$E_{\text{LSDA}}$ (Ha)
Li	-7.388721	-7.398145	-7.398155
B	-24.43315	-24.44669	-24.44747
N	-54.12891	-54.14996	-54.15110
Na	-161.6491	-161.6571	-161.6572
Si*	-288.4640	-288.4905	-288.4910
LiH <sup>+</sup>	-7.652062	-7.685603	-7.685608
O <sub>2</sub> *	-149.6038	-149.6383	-149.6403
OH	-75.34813	-75.37077	-75.37208
NH <sub>4</sub>	-56.79800	-56.80389	-56.80404
Avg diff (mHa)	20.1	0.666	-

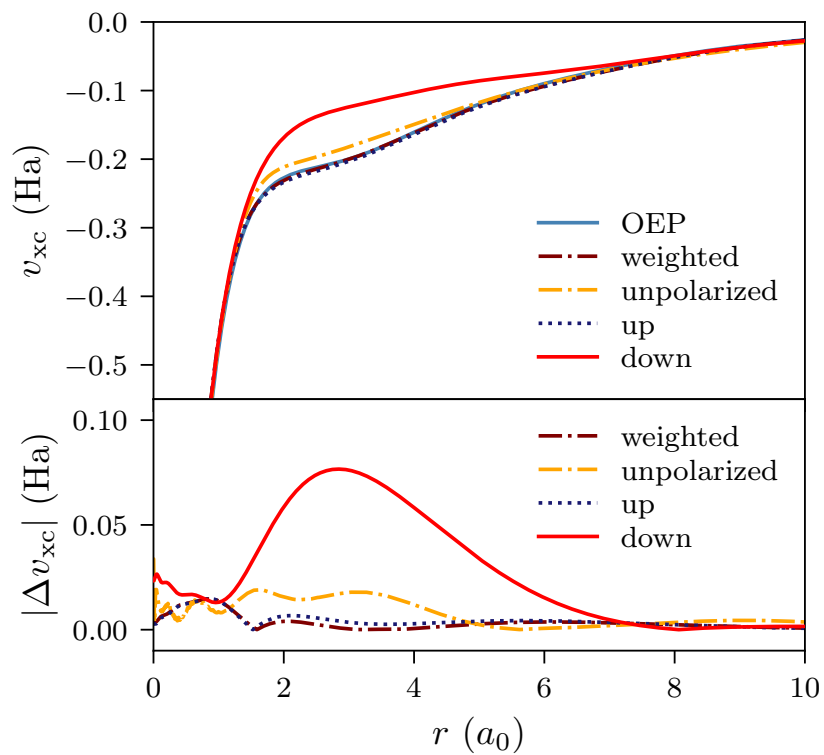
Uncontracted cc-pVTZ aux basis.

\*Triplet state

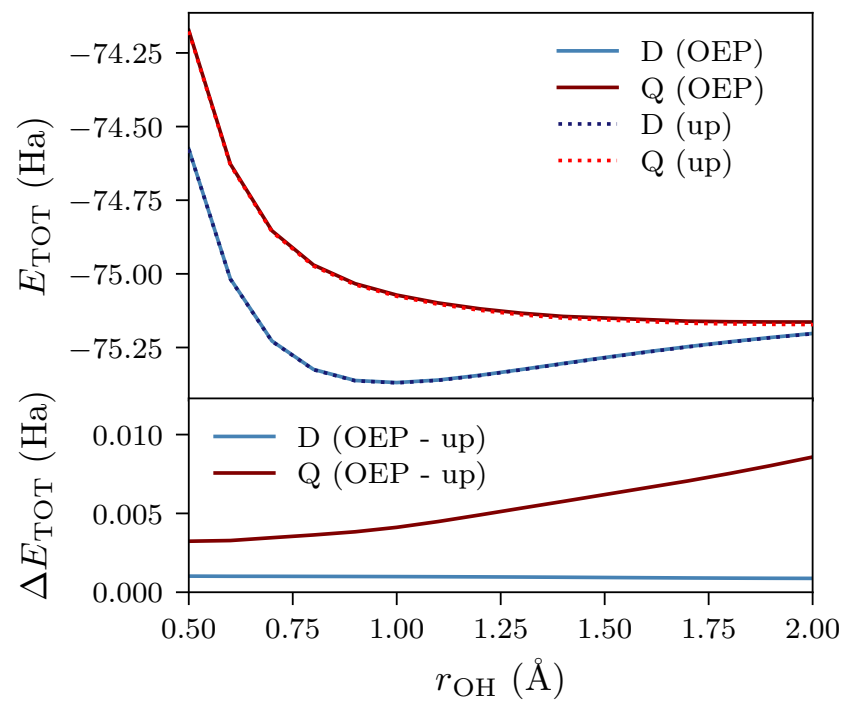


$\text{H}_2$  molecule

OH radical



$v_{xc}$  for Li



OH radical

		$E_{\text{tot}}$ (Ha)	$\Delta E$ (mHa)
iLDA	$v_{xc}^{\text{OEP}}$	-7.398144	0.011
iLDA	$v_{xc}^{\text{W}}$	-7.398135	0.020
iLDA	$v_{xc}^{\uparrow}$	-7.398136	0.019
iLDA	$v_{xc}^{\downarrow}$	-7.396281	1.87
LDA	$v_{xc}[\rho]$	-7.388721	9.43

Total energies for Lithium (doublet), differences relative to LSDA.

## Conclusions so far:

The ghost-x error is a qualitative error in the “restricted” KS equations of DFAs, when open-shell electronic systems are treated as closed shells.

We correct the ghost-x-error by redefining the XC energy as an implicit density functional, in terms of the KS spin-density.

Our restricted KS-DFT results are almost as accurate as the unrestricted KS-SDFT results of the same level of approximation.



**Limit of SDFT-KS equations for  $B = 0$ .**

I restrict to:

Collinear SDFT

(So,  $\hat{N}^\uparrow, \hat{N}^\downarrow$  commute with  $H$  and  $\Psi$  has integer  $N^\uparrow, N^\downarrow$ .)

Pure-state  $v$ -representable densities (interacting, noninteracting)

KS equations of exact SDFT for open shell systems and  $B = 0$ :

$$\left[ -\frac{\nabla^2}{2} + v_{en}(\mathbf{r}) + \int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}^\sigma[\rho^\uparrow, \rho^\downarrow](\mathbf{r}) \right] \phi_i^\sigma(\mathbf{r}) = \epsilon_i^\sigma \phi_i^\sigma(\mathbf{r}), \quad \sigma = \uparrow, \downarrow$$

They do NOT reduce to KS equations of exact DFT:

$$\left[ -\frac{\nabla^2}{2} + v_{en}(\mathbf{r}) + \int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[\rho](\mathbf{r}) \right] \phi_i^\sigma(\mathbf{r}) = \epsilon_i \phi_i^\sigma(\mathbf{r})$$

*Obviously!*

*How could one obtain a spin-potential from a density functional??*

In (S)DFT the value of an observable is a functional of  $\rho$  [or  $(\rho^\uparrow, \rho^\downarrow)$ ].

e.g. for operator  $\hat{O}$ :  $\langle \hat{O} \rangle = \langle \Psi_\rho | \hat{O} | \Psi_\rho \rangle$ .

But this is not useful because  $\Psi_\rho$  unknown and KS determinant not accurate.

⇒ The density-functional for a general observable quantity is not known. (Exceptions:  $E$ , and  $\rho$  or  $(\rho^\uparrow, \rho^\downarrow)$ )

**In DFT the functional for the physical spin-density is unknown.**

**Limit of SDFT-KS equations for  $B = 0$ .**

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle = \langle \Psi_\rho | \hat{T} + \hat{V}_{ee} | \Psi_\rho \rangle$$

The minimising state  $\Psi_\rho$  is the gs of physical system with  $\rho$ .  
[ $\rho$  is pure-state  $v$ -representable.]

**$\Rightarrow$  The physical density and spin-density are given by  $\Psi_\rho$ .**

We separate the minimisation into two separate minimisations:

$$F[\rho] = \min_{(\rho^\uparrow, \rho^\downarrow) \rightarrow \rho} \left[ \underbrace{\min_{\Psi \rightarrow (\rho^\uparrow, \rho^\downarrow)} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle}_{F[\rho^\uparrow, \rho^\downarrow]} \right]$$

$$F[\rho] = \min_{(\rho^\uparrow, \rho^\downarrow) \rightarrow \rho} F[\rho^\uparrow, \rho^\downarrow] = F[\rho_\rho^\uparrow, \rho_\rho^\downarrow]$$

- The minimisation is at fixed  $\rho$ , i.e. within DFT.
- The two minimisations have the same minimum.

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$$F[\rho] = \min_{(\rho^\uparrow, \rho^\downarrow) \rightarrow \rho} \left[ \underbrace{\min_{\Psi \rightarrow (\rho^\uparrow, \rho^\downarrow)} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle}_{F[\rho^\uparrow, \rho^\downarrow]} \right]$$

$$F[\rho] = \min_{(\rho^\uparrow, \rho^\downarrow) \rightarrow \rho} F[\rho^\uparrow, \rho^\downarrow] = F[\rho_\rho^\uparrow, \rho_\rho^\downarrow]$$

- The minimisation is at fixed  $\rho$ , i.e. within DFT.
  - The two minimisations have the same minimum.
  - The minimising  $\rho_\rho^\uparrow, \rho_\rho^\downarrow$  is equal to the spin-density of  $\Psi_\rho$ .
- $\Rightarrow \rho_\rho^\uparrow, \rho_\rho^\downarrow$  is the physical spin-density. (Remember this point!)

Investigate further :  $F[\rho] = \min_{(\rho^\uparrow, \rho^\downarrow) \rightarrow \rho} F[\rho^\uparrow, \rho^\downarrow] = F[\rho_\rho^\uparrow, \rho_\rho^\downarrow]$

Invoke SDFT's KS systems with spin-densities  $(\rho^\uparrow, \rho^\downarrow)$ .

$$F[\rho^\uparrow, \rho^\downarrow] = T_s[\rho^\uparrow, \rho^\downarrow] + E_{xc}[\rho^\uparrow, \rho^\downarrow] + U[\rho^\uparrow + \rho^\downarrow]$$

$$F[\rho] = \min_{(\rho^\uparrow, \rho^\downarrow) \rightarrow \rho} \left\{ T_s[\rho^\uparrow, \rho^\downarrow] + E_{xc}[\rho^\uparrow, \rho^\downarrow] \right\} + U[\rho].$$



*Remember:*

*How could one obtain a spin-potential from a density functional??*

***Definition of (new) generalised KS system***

$$\min_{(\rho^\uparrow, \rho^\downarrow) \rightarrow \rho} \left\{ T_s[\rho^\uparrow, \rho^\downarrow] + E_{xc}[\rho^\uparrow, \rho^\downarrow] \right\}$$

Minimisation under constraint,  $\rho^\uparrow(\mathbf{r}) + \rho^\downarrow(\mathbf{r}) = \rho(\mathbf{r})$ :

$$\min_{(\rho^\uparrow, \rho^\downarrow) \rightarrow \rho} \left\{ T_s[\rho^\uparrow, \rho^\downarrow] + E_{xc}[\rho^\uparrow, \rho^\downarrow] \right\}$$

$$\Rightarrow \min_{\rho^\uparrow, \rho^\downarrow} \left\{ T_s[\rho^\uparrow, \rho^\downarrow] + E_{xc}[\rho^\uparrow, \rho^\downarrow] + \int d\mathbf{r} \lambda(\mathbf{r}) [\rho^\uparrow(\mathbf{r}) + \rho^\downarrow(\mathbf{r})] \right\}$$

The Euler-Lagrange equations for the minimum:  $\sigma = \uparrow, \downarrow$

$$\left. \frac{\partial T_s[\rho^\uparrow, \rho^\downarrow]}{\partial \rho^\sigma(\mathbf{r})} \right|_{\rho_\rho^\uparrow, \rho_\rho^\downarrow} + \left. \frac{\partial E_{xc}[\rho^\uparrow, \rho^\downarrow]}{\partial \rho^\sigma(\mathbf{r})} \right|_{\rho_\rho^\uparrow, \rho_\rho^\downarrow} + \lambda[\rho](\mathbf{r}) = 0$$

$$\Rightarrow v_s^\sigma[\rho_\rho^\uparrow, \rho_\rho^\downarrow](\mathbf{r}) = v_{xc}^\sigma[\rho_\rho^\uparrow, \rho_\rho^\downarrow](\mathbf{r}) + v_H[\rho](\mathbf{r}) + v[\rho](\mathbf{r})$$

*Spin-potential  $v_s^\sigma$  from the minimisation of density functional!*

*$\rho_\rho^\uparrow, \rho_\rho^\downarrow =$  physical spin-density! Density-functional of magnetisation!*

## ***Definition of (new) generalised KS system***

$$\min_{(\rho^\uparrow, \rho^\downarrow) \rightarrow \rho} \left\{ T_s[\rho^\uparrow, \rho^\downarrow] + E_{xc}[\rho^\uparrow, \rho^\downarrow] \right\}$$

- Minimisation searches over SDFT-KS systems with common  $\rho$  and returns that with the correct (physical) spin-density  $(\rho_\rho^\uparrow, \rho_\rho^\downarrow)$ .
- The minimising SDFT-KS system & state  $\Phi_{\rho_\rho^\uparrow, \rho_\rho^\downarrow}$  depend on  $\rho$ .
- The (unrestricted) potential  $v_{xc}^\sigma[\rho_\rho^\uparrow, \rho_\rho^\downarrow](\mathbf{r})$  depends only on  $\rho$ .
- The minimisation defines a *generalised* KS (GKS) system in DFT.
- When  $B = 0$  the SDFT-KS equations reduce to the DFT-GKS equations.

## Conclusions

In the limit  $B = 0$  the SDFT-KS equations reduce to the DFT-GKS equations.

The DFT-GKS state  $\Phi_{\rho_{\uparrow}, \rho_{\downarrow}}$  gives not only the true total density but also the true spin-density.

The elusive exact density functional for the spin-density is the spin-density of the DFT-GKS system.

**Thank you!**