

# An Introduction to Density Functional Theory

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# Outline

## Basic Formalism

The Kohn-Sham Scheme

Explicit Functionals / LDA

Explicit Functionals / Gradient Approximations

Orbital-Dependent Functionals

Implementation of DFT

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## Litterature I

- ▶ R. van Leeuwen: *Density functional approach to the many-body problem: key concepts and exact functionals*, Adv. Quant. Chem. **43**, 25 (2003).  
(Mathematical foundations of DFT)
- ▶ R. M. Dreizler and E. K. U. Gross: *Density functional theory: An approach to the quantum many-body problem*. (Introductory book)
- ▶ W. Koch and M. C. Holthausen: *A chemist's guide to density functional theory*. (Introductory book, less formal than Dreizler/Gross)
- ▶ E. H. Lieb: Density functionals for Coulomb systems, Int. J. Quant. Chem. **24**, 243-277 (1983). (Mathematical analysis of DFT)



## Litterature II

- ▶ J. P. Perdew and S. Kurth: In *A Primer in Density Functional Theory: Density Functionals for Non-relativistic Coulomb Systems in the New Century*, ed. C. Fiolhais *et al.* (Introductory course, partly difficult, but interesting points of view)
- ▶ E. Engel: In *A Primer in Density Functional Theory: Orbital-Dependent Functionals for the Exchange-Correlation Energy*, ed. C. Fiolhais *et al.* (Introductory lectures, only about orbital-dependent functionals)

# The Hohenberg-Kohn theorem

Assume **Hamiltonian** of many-fermion system

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

or second quantized form

$$\begin{aligned} \hat{H} = & -\frac{\hbar^2}{2m} \int d^3r \hat{\psi}^\dagger(\mathbf{r}) \nabla^2 \hat{\psi}(\mathbf{r}) + \int d^3r \hat{\psi}^\dagger(\mathbf{r}) v(\mathbf{r}) \hat{\psi}(\mathbf{r}) \\ & + \frac{1}{2} \int d^3r \int d^3r' \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}') w(\mathbf{r}, \mathbf{r}') \hat{\psi}(\mathbf{r}') \hat{\psi}(\mathbf{r}), \end{aligned}$$

$\hat{\psi}, \hat{\psi}^\dagger =$  annihilation, creation *field operators*

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## The Hohenberg-Kohn Theorem

Degenerate Ground States

$v$ -Representability and Extensions of  $F_{HK}$

$$\hat{\Psi}(\mathbf{r}) \equiv \sum_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r}) c_{\mathbf{k}}$$

$$\hat{\Psi}^{\dagger}(\mathbf{r}) \equiv \sum_{\mathbf{k}} \psi_{\mathbf{k}}^*(\mathbf{r}) c_{\mathbf{k}}^{\dagger}$$

$\mathbf{k}$  = collection of quantum numbers

$\hat{T}$  = kinetic energy operator

$\hat{V}$  = external single-particle potential operator

$\hat{W}$  = two-particle interaction operator

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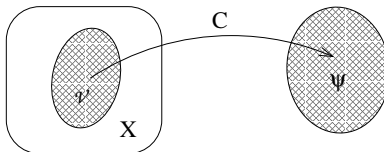
$\mathcal{V}$  = set of external single-particle **potentials**  $v$  s.t.

$$\hat{H}|\phi\rangle = (\hat{T} + \hat{V} + \hat{W})|\phi\rangle = E|\phi\rangle, \quad \hat{V} \in \mathcal{V},$$

gives a **non-degenerate** N-particle ground state  $|\Psi\rangle$

$$\implies C : \mathcal{V}(C) \longrightarrow \Psi \quad \text{surjective,}$$

where  $\Psi$  = set of ground states (GS)  $|\Psi\rangle$



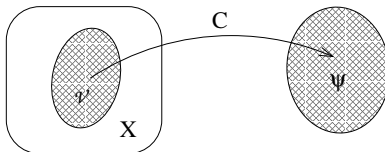
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 $v$ -Representability and Extensions of  $F_{HK}$

The density

$$n(\mathbf{r}) = N \sum_i \int dx_2 \dots \int dx_N |\Psi(\mathbf{r}i, x_2, \dots, x_N)|^2$$

gives a second map

$$D : \Psi \longrightarrow \mathcal{N},$$

where  $\mathcal{N}$  = set of GS densities. The map trivially surjective.

## Lemma

Hohenberg-Kohn states:  $C$  and  $D$  also *injective* (one-to-one;  $x_1 \neq x_2 \Rightarrow Tx_1 \neq Tx_2$ )

$\Rightarrow$   $C$  and  $D$  bijective (surjective and bijective)

$\Rightarrow$   $CD : \mathcal{V}(CD) \longrightarrow \mathcal{N}$  *bijective*

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$$\Rightarrow C \text{ and } D \text{ bijective (surjective and injective)}$$

$$\Rightarrow CD : \mathcal{V}(CD) \longrightarrow \mathcal{N} \quad \text{bijective}$$

## Proof I.

Let us prove  $C : \mathcal{V}(C) \longrightarrow \Psi$  injective:

$$\hat{V} \neq \hat{V}' + \text{constant} \quad \stackrel{?}{\implies} \quad |\Psi\rangle \neq |\Psi'\rangle,$$

where  $\hat{V}, \hat{V}' \in \mathcal{V}$

*Reductio ad absurdum:*

Assume  $|\Psi\rangle = |\Psi'\rangle$  for some  $\hat{V} \neq \hat{V}' + \text{const}$ ,  $\hat{V}, \hat{V}' \in \mathcal{V}$

$$\hat{T} \neq \hat{T}[V], \hat{W} \neq \hat{W}[V] \implies^1$$

$$(\hat{V} - \hat{V}') |\Psi\rangle = (E_{gs} - E'_{gs}) |\Psi\rangle.$$

$$\implies \hat{V} - \hat{V}' = E_{gs} - E'_{gs}$$

$$\implies \hat{V} = \hat{V}' + \text{constant} \quad \text{Contradiction!}$$

<sup>1</sup>Unique continuation theorem:  $|\Psi\rangle \neq 0$  on a set of positive measure

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Let us prove  $D : \Psi \longrightarrow \mathcal{N}$  injective:

$$|\Psi\rangle \neq |\Psi'\rangle \quad \stackrel{?}{\implies} \quad n(\mathbf{r}) \neq n'(\mathbf{r})$$

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Assume  $n(\mathbf{r}) = n'(\mathbf{r})$  for some  $|\Psi\rangle \neq |\Psi'\rangle$

Ritz principle  $\implies$

$$E_{gs} = \langle \Psi | \hat{H} | \Psi \rangle < \langle \Psi' | \hat{H} | \Psi' \rangle$$

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By symmetry

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Previous Lemma:

$$\exists \quad \text{a unique map} \quad D^{-1} : n(\mathbf{r}) \mapsto |\Psi[n]\rangle$$

$\Rightarrow$  first statement of H-K theorem:

For any observable  $\hat{O}$ , the GS expectation value = *unique functional* of  $n$ :

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

In addition,

$$(CD)^{-1} : n(\mathbf{r}) \rightarrow v(\mathbf{r})$$

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Define

$$E_{v_0}[n] := \langle \Psi[n] | \hat{T} + \hat{W} + \hat{V}_0 | \Psi[n] \rangle$$

$\hat{V}_0$  = external potential,  $n_0(\mathbf{r})$  = corresponding GS density,  $E_0$  = GS energy

Rayleigh-Ritz principle  $\implies$  second statement of H-K theorem:

$$E_0 = \min_{n \in \mathcal{N}} E_{v_0}[n]$$

Last statement of H-K theorem:

$$F_{HK}[N] \equiv \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle$$

is universal ( $F_{HK} \neq F_{HK}[\hat{V}_0]$ )

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# Degenerate ground states

Until now: non-degenerate GS

Extension:

$$V \in \mathcal{V} \quad \Rightarrow \quad \Psi_V = \left\{ |\Psi\rangle = \sum_{i=1}^q c_i |\Psi_i\rangle \right\},$$

$|\Psi_i\rangle$  = orthon. degen. GS

$$\Psi = \bigcup_{V \in \mathcal{V}} \Psi_V$$

Corresponding GS densities:

$$\mathcal{N}_V = \{n(\mathbf{r}) | n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle, |\Psi\rangle \in \Psi_V\}$$

$$\mathcal{N} = \bigcup_{V \in \mathcal{V}} \mathcal{N}_V$$

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Corresponding GS densities:

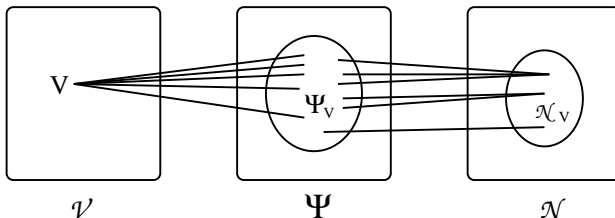
$$\mathcal{N}_V = \{n(\mathbf{r}) | n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle, |\Psi\rangle \in \Psi_V\}$$

$$\mathcal{N} = \bigcup_{V \in \mathcal{V}} \mathcal{N}_V$$

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 $v$ -Representability and Extensions of  $F_{HK}$



$C :$	$\mathcal{V} \longrightarrow \Psi$	not a map
$C^{-1} :$	$\Psi \longrightarrow \mathcal{V}$	proper map
$D :$	$\Psi \longrightarrow \mathcal{N}$	proper map
$D^{-1} :$	$\mathcal{N} \longrightarrow \Psi$	not a map
$(CD) :$	$\mathcal{V} \longrightarrow \mathcal{N}$	not a map
$(CD)^{-1} :$	$\mathcal{N} \longrightarrow \mathcal{V}$	proper map

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**OBS!**

$$\Psi \neq \Psi[n]$$

For variational principle: *unique* functional of  $n$

$$F_{HK}[n] = \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle$$

needed

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$n \implies V[n] \text{ unique} + \text{const.} \implies \text{unique GS energy} + \text{const.}$

$$\implies F_{HK}[n] := E - \int n(\mathbf{r})v([n]; \mathbf{r})d^3r$$

*a unique functional* of  $n$ , even if  $|\Psi\rangle$  is *not a unique functional* of  $n$

$\implies$  Variational principle OK also for degenerate case!

## Let us summarize:

- ▶ We have shown: for non-degen. and degen. GSs  $\exists$  a  $F_{HK} = F_{HK}[n]$
- ▶ If  $\exists v_0(\mathbf{r})$  corresponding to GS  $n(\mathbf{r})$ , then variational principle gives

$$E_0 = \min_{n \in \mathcal{N}} E_{v_0}[n]$$

- ▶ We have assumed:  $\exists v_0(\mathbf{r})$   
Does it exist?  
If not, any solution for “bad” densities  $n(\mathbf{r})$ ?

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## Definition

Density function  $n(\mathbf{r})$  *pure-state  $v$ -representable*:

$n(\mathbf{r})$  (possibly degen.) GS density of a Hamiltonian

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

with some potential  $v_0(\mathbf{r})$ ,

i.e.  $n(\mathbf{r})$  corresponds to some  $v_0(\mathbf{r})$

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## Why care about $v$ -representability?

Our problem: In *implementation* of variational principle

$$E_0 = \min_{n \in \mathcal{N}} E_{v_0}[n]$$

each trial  $n$  must be *pure-state  $v$ -representable*

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A fact: *Not all* reasonably well behaved functions  $\geq 0$  pure-state  $v$ -representable

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Side-remark: Shown in article by van Leeuwen:

$$n(\mathbf{r}) \in L^1 \cap L^3$$

$$v(\mathbf{r}) \in L^{3/2} + L^\infty$$

$$\psi \in H^1(\mathbb{R}^{3N})$$

$f \in L^p$  space:

$$\|f\|_p = \left( \int d^3r |f(\mathbf{r})|^p \right)^{1/p} < \infty$$

Sobolev space  $H^1$ :

$$\|f\| = \left( \int d^3r \left( |f(\mathbf{r})|^2 + |\nabla f(\mathbf{r})|^2 \right) \right)^{1/2} < \infty$$

## Reminder:

- *Density matrix:*  $D = \sum_i p_i |\psi_i\rangle \langle \psi_i|$ ,  
 $p_i$  probability amplitudes of degen. states  $\{|\psi_i\rangle\}_i$
- *Trace:*  $\text{tr } X = \sum_n \langle n| X |n\rangle$ ,  
 $\{|n\rangle\}_i$  arbitr. complete orthon. basis

$$\begin{aligned}
 \text{tr}(DA) &= \sum_n \langle n| \left( \sum_i p_i |\psi_i\rangle \langle \psi_i| \right) A |n\rangle \\
 &= \sum_n \sum_i \langle \psi_i| A |n\rangle \langle n| \psi_i\rangle \\
 &= \sum_i p_i \langle \psi_i| A | \psi_i\rangle \\
 &= \langle A \rangle
 \end{aligned}$$

**First group:**  $|\Psi_1\rangle, \dots, |\Psi_q\rangle$  degen. GSs. Statistical von Neumann density matrix:

$$\hat{D} = \sum_i^q d_i |\Psi_i\rangle \langle \Psi_i|$$

with

$$d_i^* = d_i \geq 0, \quad \sum_{i=1}^q d_i = 1.$$

Corresponding ensemble density

$$n_D(\mathbf{r}) = \text{tr} \left\{ \hat{D} \hat{n}(\mathbf{r}) \right\} = \sum_{i=1}^q d_i n_i(\mathbf{r}),$$

where

$$n_i(\mathbf{r}) = \langle \Psi_i | \hat{n}(\mathbf{r}) | \Psi_i \rangle.$$

Levy and Lieb showed (1982):

- For general coefficients  $d_i$ ,  $n_D(\mathbf{r})$  not pure-state  $v$ -representable

Functions  $n_D(\mathbf{r})$  called **ensemble  $v$ -representable**



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Functions  $n_D(\mathbf{r})$  called **ensemble  $v$ -representable**

## Definition

Density function  $n_D(\mathbf{r}) \geq 0$  **ensemble  $v$ -representable**:

Can write

$$n_D(\mathbf{r}) = \text{tr} \left\{ \hat{D} \hat{n}(\mathbf{r}) \right\} = \sum_{i=1}^q d_i n_i(\mathbf{r}),$$

where

$$n_i(\mathbf{r}) = \langle \Psi_i | \hat{n}(\mathbf{r}) | \Psi_i \rangle$$

$|\Psi_1\rangle, \dots, |\Psi_q\rangle = \text{degen. GSs of Hamiltonian } \hat{H} \text{ with ext. pot. } v_0(\mathbf{r})$

We introduce:

extension of  $F_{HK}[n] \longrightarrow$  ensemble  $v$ -representable densities:

$$F_{EHK}[n] := \text{tr} \left\{ \hat{D}[n] (\hat{T} + \hat{W}) \right\},$$

where density matrix

$$\hat{D} \in \mathcal{D}_V = \left\{ \hat{D} = \sum_{i=1}^q d_i |\Psi_i\rangle \langle \Psi_i| \mid d_i^* = d_i \geq 0, \quad \sum_{i=1}^q d_i = 1 \right\}.$$

$\mathcal{D}_V$  associated with unique  $\hat{V}[n]$  leading to the ensemble  $v$ -representable density  $n(\mathbf{r})$

$\implies$  variational properties of  $E_{V_0}[n]$  OK

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Thus,

$$F_{HK}[n] = \langle \Psi_i[n] | \hat{T} + \hat{W} | \Psi_i[n] \rangle$$

and

$$F_{EHK}[n] = \sum_i d_i \langle \Psi_i[n] | \hat{T} + \hat{W} | \Psi_i[n] \rangle ,$$

with any  $d_i$  satisfying

$$d_i^* = d_i \geq 0, \quad \sum_{i=1}^q d_i = 1.$$

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Unfortunately, *not all* well-behaved functions  $\geq 0$  ensemble  $v$ -representable

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$\exists$  functions that do not correspond to the GS of *any* external potential

Example:

$$n(x) = \left( a + b|x|^{\alpha+1/2} \right)^2, \quad a, b > 0, \quad 0 \leq \alpha < 1/2$$

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Solution: **Constrained search** (Lieb and Levy (1979, 1982)):

$$F_{LL}[n] := \inf_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle .$$

$\Psi \rightarrow n$  = search over all antisymmetric, normalised  $\Psi(x_1, \dots, x_N)$  corresponding to  $n(\mathbf{r})$

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Rayleigh–Ritz principle  $\implies$

$$F_{LL}[n] = F_{HK}[n]$$

for all pure-state  $v$ -representable functions  $n(\mathbf{r})$

Let

$$E_{v_0}[n] := F_{LL}[n] + \int n(\mathbf{r}) v_0(\mathbf{r}) d^3r$$

We need to show:

$$E_0 = \inf_n E_{v_0}[n]$$

correct GS energy



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Let us show:  $E_0 = \inf_n E_{v_0}[n]$  correct GS energy

Rayleigh–Ritz principle  $\implies$

$$\begin{aligned}
 E_0 &= \inf_{\Psi} \langle \Psi | \hat{T} + \hat{W} + \hat{V}_0 | \Psi \rangle \\
 &= \inf_{n(\mathbf{r})} \left[ \inf_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{W} + \hat{V}_0 | \Psi \rangle \right] \\
 &= \inf_{n(\mathbf{r})} \left[ \inf_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle + \int n(\mathbf{r}) v_0(\mathbf{r}) d^3 r \right] \\
 &= \inf_{n(\mathbf{r})} \left[ F_{LL}[n] + \int n(\mathbf{r}) v_0(\mathbf{r}) d^3 r \right] \\
 &= \inf_{n(\mathbf{r})} E_{v_0}[n]
 \end{aligned}$$

$\implies F_{LL}[n]$  a reasonable extension of  $F_{HK}[n]$

Another possibility for extension of domain of  $F_{HK}[n]$ :

The functional

$$F_{EHK}[n] := \text{tr} \left\{ \hat{D}[n] \left( \hat{T} + \hat{W} \right) \right\}$$

replaced by (Lieb (1982) and Valone (1980))

$$F_L[n] := \inf_{\hat{D} \rightarrow n} \text{tr} \left\{ \hat{D}[n] \left( \hat{T} + \hat{W} \right) \right\}$$

Infimum searched over all

$$\hat{D} = \sum_i^{\infty} d_i |\Psi_i\rangle \langle \Psi_i|$$

with

$$d_i^* = d_i \geq 0, \quad \sum_{i=1}^{\infty} d_i = 1$$

which give density

$$n(\mathbf{r}) = \text{tr} \left\{ \hat{D} \hat{n}(\mathbf{r}) \right\} = \sum_{i=1}^{\infty} d_i \langle \Psi_i | \hat{n}(\mathbf{r}) | \Psi_i \rangle$$

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Obviously

$$F_L[n] = F_{EHK}[n]$$

for all ensemble  $v$ -representable  $n(\mathbf{r})$ , and

$$E_0 = \inf_{n(\mathbf{r})} E_{v_0}[n],$$

where

$$E_{v_0} := F_L[n] + \int n(\mathbf{r}) v_0(\mathbf{r}) d^3r.$$

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Lieb showed:  $F_L[n]$  has **advantages** over  $F_{LL}[n]$ :

- ▶  $F_L[n]$  convex
- ▶  $F_L[n]$  Legendre transform

$$F_L[n] = \sup_{v \in \mathcal{V}} \left[ E[v] - \int n(\mathbf{r}) v(\mathbf{r}) d^3r \right]$$

of GS energy  $E[v] = \inf_{\Psi} \langle \Psi | \hat{T} + \hat{V} + \hat{W} | \Psi \rangle$ ,  
 $v(\mathbf{r})$  = external potential

## Definition

**Legendre transform**  $f^*$  of a concave function  $f$ :

$$f^*(p) = \inf_x (px - f(x)),$$

where  $p = df/dx$

$F_L[n]$  convex  $\implies -F_L[n]$  concave  $\implies$  Since one can show

$$\frac{\delta(-F_L)}{\delta n(\mathbf{r})} = v(\mathbf{r}),$$

$\implies$

$$\begin{aligned} (-F_L[n])^* &\equiv F_L^*[v] = \inf_n \left\{ \int n v - (-F_L[n]) \right\} \\ &= \inf_n \left\{ F_L[n] + \int n v \right\} \\ &= E[v] \end{aligned}$$

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$$\begin{aligned} (-F_L[n])^* &\equiv F_L^*[v] = \inf_n \left\{ \int nv - (-F_L[n]) \right\} \\ &= \inf_n \left\{ F_L[n] + \int nv \right\} \\ &= E[v] \end{aligned}$$



The Legendre transform its own inverse:  $(f^*)^* = f$

Thus: When  $(-F_L[n])^* = E[v] \implies$

$$\begin{aligned} -F_L[n] &= E^*[n] \\ &= \inf_v \left\{ \int n v - E[v] \right\} \end{aligned}$$

May write this

$$\begin{aligned} F_L[n] &= -\inf_v \left\{ \int n v - E[v] \right\} \\ &= \sup_v \left\{ - \left( \int n v - E[v] \right) \right\} \\ &= \sup_v \left\{ E[v] - \int n v \right\} \end{aligned}$$

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$F_{LL}[n]$  and  $F_L[n]$  *defined for arbitrary*  $n(\mathbf{r}) \geq 0$ ,  $\int d^3r n(\mathbf{r}) = N$

- ▶ So far:
  - H-K **variational principle**  $\implies$   
exact GS density of many-particle system  
**Practically intractable !!**
- ▶ Next step:
  - Kohn and Sham (1965): **single-particle picture**  
 $\longrightarrow$  equations solved **selfconsistently** (iterative scheme)

Hamiltonian of  $N$  *non-interacting* particles:

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

Hohenberg and Kohn  $\implies \exists$  unique energy functional

$$E_s[n] = T_s[n] + \int v_s(\mathbf{r})n(\mathbf{r})d^3r$$

s. t.  $\delta E_s[n] = 0$  gives GS density  $n_s(\mathbf{r})$  corresp. to  $\hat{H}_s$

## Theorem

Let

$$v_s(\mathbf{r}) = \text{local single-particle pot.},$$

$$n(\mathbf{r}) = \text{GS density of interacting system},$$

$$n_s(\mathbf{r}) = \text{GS density of non-interacting system}$$

$\Rightarrow$  for *any interacting system*,

$$\exists \text{ a } v_s(\mathbf{r}) \text{ s. t. } n_s(\mathbf{r}) = n(\mathbf{r})$$

Proof in book by Dreizler/Gross, Sec. 4.2

In proof:  $F_{HK}[n]$  replaced by  $F_L[n]$

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Proof in book by Dreizler/Gross, Sec. 4.2

In proof:  $F_{HK}[n]$  replaced by  $F_L[n]$

Assume **nondegenerate GS**. Then

$$n(\mathbf{r}) = n_s(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2,$$

where  $\phi_i(\mathbf{r})$  are determined by

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + v_s(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}), \quad \varepsilon_1 \leq \varepsilon_2 \leq \dots$$

If  $\exists v_s(\mathbf{r})$ , then H-K theorem gives *uniqueness* of  $v_s(\mathbf{r})$

Consequently, we may write

$$\phi_i(\mathbf{r}) = \phi_i([n(\mathbf{r})]) \quad !!$$

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Consequently, we may write

$$\phi_i(\mathbf{r}) = \phi_i([n(\mathbf{r})]) \quad !!$$



Assume

$$v_0(\mathbf{r}) = \text{ext. potential}$$

$$n_0(\mathbf{r}) = \text{GS density}$$

of **interacting** system

- Wanted: **single-particle potential**  $v_s(\mathbf{r})$  of **non-interacting** system

# Exchange-correlation functional

Many-particle energy functional:

$$\begin{aligned} E_{v_0}[n] &= F_L[n] + \int d^3r v_0(\mathbf{r})n(\mathbf{r}) \\ &= \left( T_s[n] + \frac{1}{2} \iint d^3r d^3r' n(\mathbf{r})w(\mathbf{r}, \mathbf{r}')n(\mathbf{r}') + E_{xc}[n] \right) + \int d^3r v_0(\mathbf{r})n(\mathbf{r}) \end{aligned}$$

Here **exchange-correlation functional** defined:

$$E_{xc}[n] = F_L[n] - \frac{1}{2} \iint d^3r d^3r' n(\mathbf{r})w(\mathbf{r}, \mathbf{r}')n(\mathbf{r}') - T_s[n]$$

The exchange-correlation functional defined:

$$E_{xc}[n] = F_L[n] - \frac{1}{2} \iint d^3r d^3r' n(\mathbf{r}) w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') - T_s[n]$$

Explicit form of  $F_L[n]$  as functional of  $n$  unknown

- $E_{xc}[n]$  unknown functional, must be approximated  
Otherwise, Kohn-Sham scheme exact

## Definition

Let  $F : B \rightarrow \mathbb{R}$  be a *functional* from normed function space  $B$  to real numbers  $\mathbb{R}$ .

The **functional derivative** (Gâteaux derivative)

$\delta F[n] \equiv \delta F[n]/\delta n(\mathbf{r})$  is defined as

$$\frac{\delta F}{\delta n}[\varphi] = \lim_{\varepsilon \rightarrow 0} \frac{F[n + \varepsilon \varphi] - F[n]}{\varepsilon}$$

Another useful definition of  $\delta F[n]$ :

$$\langle \delta F[n], \varphi \rangle = \left. \frac{d}{d\varepsilon} F[n + \varepsilon \phi] \right|_{\varepsilon=0},$$

where

$$\langle \delta F[n], \varphi \rangle \equiv \int d\mathbf{r} (\delta F[n(\mathbf{r})]) \varphi(\mathbf{r}),$$

$\varphi$  = test function

Let us **derive** expression for **single-particle potential**  $v_s(\mathbf{r})$  of non-interacting system:

H-K variational principle:

$$\begin{aligned} 0 &= \delta E_{v_0} = E_{v_0}[n_0 + \delta n] - E_{v_0}[n_0] \\ &= \delta T_s + \int d^3r \delta n(\mathbf{r}) \left[ v_0(\mathbf{r}) + \int w(\mathbf{r}, \mathbf{r}') d^3r' + v_{xc}([n_0]; \mathbf{r}) \right], \end{aligned} \quad (3)$$

where exchange-coorelation potential

$$v_{xc}([n_0]; \mathbf{r}) = \left. \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \right|_{n_0},$$

$n_0(\mathbf{r})$  = GS density

$n_0(\mathbf{r}) + \delta n(\mathbf{r})$  non-interacting  $v$ -representable  $\implies$  unique representation  
 $\phi_{i,0}(\mathbf{r}) + \delta\phi_i(\mathbf{r})$

$$\begin{aligned}\delta T_s &= \sum_i^N \int d^3r \left[ \delta\phi_i^*(\mathbf{r}) \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \phi_{i,0}(\mathbf{r}) + \phi_{i,0}^*(\mathbf{r}) \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \delta\phi_i(\mathbf{r}) \right] \\ &= \sum_i^N \int d^3r \left[ \delta\phi_i^*(\mathbf{r}) \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \phi_{i,0}(\mathbf{r}) + \delta\phi_{i,0}^*(\mathbf{r}) \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \phi_i(\mathbf{r}) \right] \quad (4)\end{aligned}$$



Green's first identity

Green's first identity:

$$\int_V f \nabla^2 g \, dV = \oint_S f(\nabla g \cdot \mathbf{n}) \, dS - \int_V \nabla f \cdot \nabla g \, dV,$$

where  $V \in \mathbb{R}^3$ ,  $S \equiv \partial V \in \mathbb{R}^2$  and  $f, g = \text{arb. real scalar functions}$

Let surface  $\partial V$  approach infinity w.r.t. origin,

assume  $f, g \longrightarrow 0$  on  $\partial V$ ,

Apply Green's first identity twice  $\implies$

$$\begin{aligned} \int_V f \nabla^2 g \, dV &= 0 - \int_V \nabla f \cdot \nabla g \, dV \\ &= - \left( 0 - \int_V \nabla f \cdot \nabla g \, dV \right) \\ &= \int_V g \nabla^2 f \, dV \end{aligned}$$

The orbitals  $\phi_{i,0}(\mathbf{r})$  in Eq. (4) satisfy

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + v_{s,0}(\mathbf{r}) \right) \phi_{i,0}(\mathbf{r}) = \varepsilon_i \phi_{i,0}(\mathbf{r}), \quad \varepsilon_1 \geq \varepsilon_2 \geq \dots \quad (5)$$

Using this relation, we may rewrite Eq. (4) as

$$\begin{aligned} \delta T_s &= \sum_i^N \int d^3r \left[ \delta \phi_i^*(\mathbf{r}) (\varepsilon_i - v_{s,0}(\mathbf{r})) \phi_{i,0}(\mathbf{r}) + \delta \phi_i(\mathbf{r}) (\varepsilon_i - v_{s,0}(\mathbf{r})) \phi_i^*(\mathbf{r}) \right] \\ &= \sum_{i=1}^N \varepsilon_i \int d^3r \delta |\phi_i(\mathbf{r})|^2 - \sum_{i=1}^N \int d^3r v_{s,0}(\mathbf{r}) \delta |\phi_i(\mathbf{r})|^2. \end{aligned} \quad (6)$$



Since

$$\begin{aligned}\int d^3r \delta |\phi_i(\mathbf{r})|^2 &= \int d^3r \left[ |\phi_{i,0}(\mathbf{r}) + \delta \phi_{i,0}(\mathbf{r})|^2 - |\phi_{i,0}(\mathbf{r})|^2 \right] \\ &= 1 - 1 = 0,\end{aligned}\tag{7}$$

the first term of Eq. (6) vanishes, and we get

$$\delta T_s = - \int d^3r v_{s,0}(\mathbf{r}) \delta n(\mathbf{r}).\tag{8}$$

Combine Eqs. (3) and (8):  $\implies$  total single-particle potential:

$$v_{s,0}(\mathbf{r}) = v_0(\mathbf{r}) + \int d^3r' w(\mathbf{r}, \mathbf{r}') n_0(\mathbf{r}') + v_{xc}([n_0]; \mathbf{r})\tag{9}$$

# The Kohn-Sham scheme I

The **classic Kohn-Sham** scheme:

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + v_{s,0}(\mathbf{r}) \right) \phi_{i,0}(\mathbf{r}) = \varepsilon_i \phi_{i,0}(\mathbf{r}), \quad \varepsilon_1 \geq \varepsilon_2 \geq \dots,$$

where

$$v_{s,0}(\mathbf{r}) = v_0(\mathbf{r}) + \int d^3 r' w(\mathbf{r}, \mathbf{r}') n_0(\mathbf{r}') + v_{xc}([n_0]; \mathbf{r})$$

The density calculated as

$$n_0(\mathbf{r}) = \sum_{i=1}^N |\phi_{i,0}(\mathbf{r})|^2,$$

Equation **solved selfconsistently**

Total energy:

$$E = \sum_{i=1}^N \varepsilon_i - \frac{1}{2} \int d^3 r d^3 r' n(\mathbf{r}) w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') + E_{xc}[n] - \int d^3 r v_{xc}([n]; \mathbf{r}) n(\mathbf{r})$$

# The Kohn-Sham scheme I

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$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{s,0}(\mathbf{r})\right)\phi_{i,0}(\mathbf{r}) = \varepsilon_i\phi_{i,0}(\mathbf{r}), \quad \varepsilon_1 \geq \varepsilon_2 \geq \dots,$$

where

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# The Kohn-Sham scheme II

**Kohn-Sham** scheme for systems with **degenerate** GS:

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + v_{s,0}(\mathbf{r}) \right) \phi_{i,0}(\mathbf{r}) = \varepsilon_i \phi_{i,0}(\mathbf{r}), \quad \varepsilon_1 \geq \varepsilon_2 \geq \dots ,$$

where

$$v_{s,0}(\mathbf{r}) = v_0(\mathbf{r}) + \int d^3 r' w(\mathbf{r}, \mathbf{r}') n_0(\mathbf{r}') + v_{xc}([n_0]; \mathbf{r})$$

and

$$\begin{aligned} v_{xc}([n]; \mathbf{r}) &= \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \\ &= \frac{\delta}{\delta n(\mathbf{r})} \left( F_L[n] - \frac{1}{2} \iint d^3 r d^3 r' n(\mathbf{r}) w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') - T_L[n] \right) \end{aligned}$$

# The Kohn-Sham scheme II

Density of degen. K-S scheme:

$$n_0(\mathbf{r}) = \sum_{i=1}^N \gamma_i |\phi_{i,0}(\mathbf{r})|^2,$$

occupation numbers  $\gamma_i$  satisfy

$$\gamma_i = 1 : \varepsilon_i < \mu$$

$$0 \leq \gamma_i \leq 1 : \varepsilon_i = \mu$$

$$\gamma_i = 0 : \varepsilon_i > \mu$$

and

$$\sum_{i=1}^N \gamma_i = N$$

Hartree-Fock equation:

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + v_0(\mathbf{r}) + \int d^3 r' w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \right) \phi_k(\mathbf{r}) - \underbrace{\sum_{l=1}^N \int d^3 r' \phi_l^*(\mathbf{r}') w(\mathbf{r}, \mathbf{r}') \phi_k(\mathbf{r}') \phi_l(\mathbf{r})}_{\text{exchange term}} = \varepsilon_k \phi_k(\mathbf{r}),$$

**Non-local** exchange term (Pauli exclusion principle)

Kohn-Sham equation:

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + v_0(\mathbf{r}) + \int d^3 r' w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') + \underbrace{v_{xc}([n]; \mathbf{r})}_{\text{exchange + correlation}} \right) \phi_k(\mathbf{r}) = \varepsilon_k \phi_k(\mathbf{r}),$$

**Local** exchange-correlation term

Exchange-correlation energy = Exchange energy + Correlation energy

$$E_{xc}[n] = E_x[n] + E_c[n]$$

From earlier:

$$E_{xc}[n] = F_L[n] - T_s[n] - \frac{1}{2} \iint d^3r d^3r' n(\mathbf{r}) w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}')$$

We want to show:  $E_c[n] \leq 0$

Here we have (assume  $F_L[n] = F_{LL}[n]$ )

$$\begin{aligned} F_L[n] &\equiv \inf_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle \\ &= \left\langle \Psi_n^{min} \left| \hat{T} + \hat{W} \right| \Psi_n^{min} \right\rangle, \end{aligned}$$

and

$$T_s[n] \equiv \inf_{\Psi \rightarrow n} \langle \Psi | \hat{T} | \Psi \rangle = \left\langle \Phi_n^{min} \left| \hat{T} \right| \Phi_n^{min} \right\rangle,$$

$\Psi$  = normalized, antisymm.  $N$ -particle wavefunction,  
 $\Phi_n^{min}$  lin. komb. of Slater determinants of  
single-particle orbitals  $\psi_i(r_j)$



Eq. (4.35) in J. M. Thijssen: *Computational Physics*:

$$\begin{aligned} \langle \Phi_n^{min} | \hat{W} | \Phi_n^{min} \rangle = & \frac{1}{2} \sum_{k,l} \left[ \iint d^3r d^3r' n(\mathbf{r}) w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \right. \\ & \left. - \iint d^3r d^3r' \psi_l^*(\mathbf{r}) \psi_l(\mathbf{r}') w(\mathbf{r}, \mathbf{r}') \psi_k^*(\mathbf{r}') \psi_k(\mathbf{r}) \right] \end{aligned}$$

By definition,

$$E_x[n] \equiv -\frac{1}{2} \sum_{k,l} \iint d^3r d^3r' \psi_l^*(\mathbf{r}) \psi_l(\mathbf{r}') w(\mathbf{r}, \mathbf{r}') \psi_k^*(\mathbf{r}') \psi_k(\mathbf{r})$$

Using expressions from previous pages gives

$$\begin{aligned}
 E_c[n] &= E_{xc}[n] - E_x[n] \\
 &= F_L[n] - T_s[n] - \frac{1}{2} \iint d^3r d^3r' n(\mathbf{r}) w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \\
 &\quad + \frac{1}{2} \sum_{k,l} \iint d^3r d^3r' \psi_l^*(\mathbf{r}) \psi_l(\mathbf{r}') w(\mathbf{r}, \mathbf{r}') \psi_k^*(\mathbf{r}') \psi_k(\mathbf{r}) \\
 &= \langle \Psi_n^{min} | \hat{T} + \hat{W} | \Psi_n^{min} \rangle - \langle \Phi_n^{min} | \hat{T} + \hat{W} | \Phi_n^{min} \rangle
 \end{aligned}$$

Since

$$\langle \Psi_n^{min} | \hat{T} + \hat{W} | \Psi_n^{min} \rangle = \inf_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle,$$

we see that

$$E_c[n] \leq 0$$

We showed:

$$E_c[n] \leq 0$$

In C. Fiolhais *et al*: *A Primer in Density Functional Theory*,  
Sec. 1.3.5 also shown:

$$E_x[n] \leq 0$$

# Exchange-correlation hole

## Definition

**Conditional probability**  $\Omega(\mathbf{x}_2; \mathbf{x}_1)$ :

Probability of finding any electron with spin-position coordinate  $\mathbf{x}_2$  given another electron with coordinate  $\mathbf{x}_1$ :

$$\Omega(\mathbf{x}_2; \mathbf{x}_1) \equiv \frac{\rho_2(\mathbf{x}_1, \mathbf{x}_2)}{\rho(\mathbf{x}_1)} \quad (10)$$

$\rho_2(\mathbf{x}_1, \mathbf{x}_2)$  = probability density for a pair at  $(\mathbf{x}_1, \mathbf{x}_2)$

$\rho(\mathbf{x}_1)$  = probability density for a single particle at  $\mathbf{x}_1$

## Definition

**Exchange-correlation hole:**

$$h_{xc}(\mathbf{x}_1; \mathbf{x}_2) \equiv \Omega(\mathbf{x}_2; \mathbf{x}_1) - \rho(\mathbf{x}_2) \quad (11)$$

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# Exchange-correlation hole

$$h_{xc}(\mathbf{x}_1; \mathbf{x}_2) = h_x(\mathbf{x}_1; \mathbf{x}_2) + h_c(\mathbf{x}_1; \mathbf{x}_2)$$

$$h_x(\mathbf{x}_1; \mathbf{x}_2) = \text{Fermi hole (Pauli principle)}$$

$$h_c(\mathbf{x}_1; \mathbf{x}_2) = \text{Coulomb hole (electrostatic correlation)}$$

- See picture handed out

## The adiabatic connection

Continuous (adiabatic) **transition**: non-interacting  $\longleftrightarrow$  interacting:

$$\hat{H}_\lambda = \hat{T} + V_{\text{ext}}^\lambda + \lambda \sum_{i < j}^N \frac{1}{r_{ij}}, \quad (12)$$

$$0 \leq \lambda \leq 1,$$

$V_{\text{ext}}^\lambda$  chosen s. t. the density for all  $\lambda$  equals that for  $\lambda = 1$

Energy of interacting system:

$$E_{\lambda=1} = \int_0^1 dE_\lambda + E_{\lambda=0} \quad (13)$$

$dE_\lambda$  = expectation value of the operator

$$d\hat{H}_\lambda = dV_{\text{ext}}^\lambda + d\lambda \sum_{i < j}^N \frac{1}{r_{ij}} \quad (14)$$



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# The adiabatic connection

## Theorem

*Exchange-correlation energy:*

$$E_{xc} = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1) \overline{h_{xc}}(\mathbf{r}_1; \mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2, \quad (15)$$

*where*

$$\overline{h_{xc}}(\mathbf{r}_1; \mathbf{r}_2) = \int_0^1 h_{xc}^\lambda(\mathbf{r}_1; \mathbf{r}_2) d\lambda \quad (16)$$

$h_{xc}^\lambda(\mathbf{r}_1; \mathbf{r}_2)$  = xc hole for adiabatically connected system with parameter  $\lambda$

## Proof.

Proof in book by Koch and Holthausen, Sec. 6.2 (short and easy)



# Local density approximation

Uniform electron gas:

$N, V \longrightarrow \infty, \quad N/V \equiv \rho = \text{constant} \quad (= \text{thermodynamic limit})$   
electrons uniformly distributed,  
positive background charge

Local density approximation (LDA):

$$E_{xc}^{LDA}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{xc}(\rho(\mathbf{r})) d\mathbf{r}, \quad (17)$$

$\varepsilon_{xc}(\rho(\mathbf{r})) = \text{xc energy per particle}$   
of a uniform electron gas of density  $\rho(\mathbf{r})$

Analytical *exchange energy* for uniform electron gas:

$$E_x = \int d^3r \varepsilon_x[n(\mathbf{r})] n(\mathbf{r})$$
$$\varepsilon_x[n(\mathbf{r})] = \text{const.} \times n^{1/3}(\mathbf{r}),$$

$$\text{const.} = -3/4(3/\pi)^{1/3}$$

Local *spin* density approximation (LSDA):

$$E_x[n_+, n_-] = -\text{const.} \int d^3r \left[ n_+^{4/3}(\mathbf{r}) + n_-^{4/3}(\mathbf{r}) \right],$$

$$\text{const.} = 3/2(3/4\pi)^{1/3}$$

∃ several parametrizations

of *correlation energy* for uniform electron gas:

E.g.: quantum MC → successful parametrisation

Example (Hedin and Lundqvist (1971)):

$$\epsilon_c[n(\mathbf{r})] = -C \left\{ (1+x)^3 \ln \left( 1 + \frac{1}{x} \right) + \frac{x}{2} - x^2 - \frac{1}{3} \right\},$$

where

$$x = \frac{r_s}{A}, \quad r_s = \left[ \frac{3}{4\pi n(\mathbf{r})} \right]^{1/3} \frac{1}{a_0},$$

$$C = 0.0225[e^2/a_0], \quad A = 21$$

Polarisation:

$$\zeta(\mathbf{r}) = \frac{1}{n(\mathbf{r})} (n_+(\mathbf{r}) - n_-(\mathbf{r}))$$

*Spin dependent* correlation energy  $\varepsilon_c$ :

**Interpolation**

between unpolarised ( $\zeta = 0$ ) and fully polarised ( $\zeta = \pm 1$ )

Interpolation function  $f(\zeta(\mathbf{r}))$

obtained from exchange energy

For Kohn-Sham scheme:

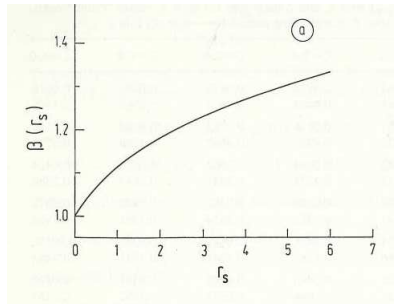
$$v_{xc}[n(\mathbf{r})] = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

needed

Parametrisations  $\longrightarrow$  analytical derivatives

Errors can be increased:

Gunnarsson and Lundqvist (1976) use  
independent parametrisations of  $v_{xc}$



$$\beta(r_s) = v_{xc}(r_s)/v_x(r_s)$$

$r_s \sim$  "distance" between electrons



# LDA

- ▶ LDA works best with slowly varying density
- ▶ But: **surprisingly good**  
for inhomogeneous systems
- ▶ Problem: self-interaction  
mean field  $\implies$  electron has  
Coulomb interaction with itself  
 $\implies$  wrong long-range behaviour

Basic Formalism  
The Kohn-Sham Scheme  
**Explicit Functionals / LDA**  
Explicit Functionals / Gradient Approximations  
Orbital-Dependent Functionals  
Implementation of DFT

Exchange Energy and Correlation Energy  
Exchange-Correlation Hole  
The Adiabatic Connection  
The Local Density Approximation

*Why* does LDA work so well??

- ▶ LDA OK if length scale of density variation  $\gg$  Fermi wavelength  $2\pi/k_F$

But: This condition rarely satisfied in real electronic systems

Other reasons?

## Reason 1

Homogeneous electron gas

⇒ exchange-correlation hole spherical:

$$h_{xc}^{LDA}(\mathbf{r}_1; \mathbf{r}_2) = h_{xc}^{LDA}(|\mathbf{r}_2 - \mathbf{r}_1|)$$

Remember:

$$E_{xc} = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1) \overline{h_{xc}}(\mathbf{r}_1; \mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

⇒ Sufficient that  $h_{xc}^{LDA}$  gives  $\approx$  right **spherical average**

# Reason 1

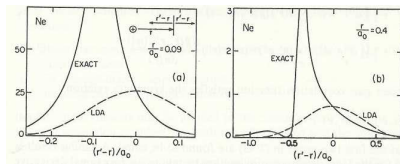


Figure: Exchange holes  $\approx$  "where  $e_1^-$  is excluded, if  $e_2^-$  is at 0"

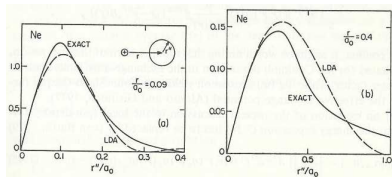


Figure: Spherically averaged exchange holes

## Reason 2

$$\begin{aligned}\int h_{xc}(\mathbf{r}_1; \mathbf{r}_2) d\mathbf{r}_2 &= \int \underbrace{\Omega(\mathbf{r}_2; \mathbf{r}_1)}_{\text{cond. prob.}} d\mathbf{r}_2 - \int \rho(\mathbf{r}_2) d\mathbf{r}_2 \\ &= (N - 1) - N \\ &= -1\end{aligned}$$

Integral constant  $\implies$  **systematic cancellation** of errors

# Gradient expansion

The **gradient expansion approximation (GEA)** – a natural extension of LDA ??

**Taylor expansion** of  $E_{xc}[n]$

around homogeneous electron gas (HEG)

density  $n_0$  ( $(n - n_0)/n_0 \ll 1$ ):

$$E_{xc}[n] = E_{xc}[n_0] + \sum_{m=1}^{\infty} \frac{1}{m!} \int d^3r \frac{\delta^m E_{xc}}{\delta n(\mathbf{r}_1) \dots \delta n(\mathbf{r}_m)} \bigg|_{n=n_0} \delta n(\mathbf{r}_1) \dots \delta n(\mathbf{r}_m)$$

# Gradient expansion

Shown in article by van Leeuwen:

Expansion can be written

$$E_{xc}[n] = E_{xc}^{LDA}[n] + \int d^3r g_1(n(\mathbf{r}))(\nabla n(\mathbf{r}))^2 \\ + \int d^3r g_2(n(\mathbf{r}))(\nabla^2 n(\mathbf{r}))^2 + \dots,$$

$g_i(n)$  uniquely determined by the density response functions of a HEG



Gradient expansion in principle exact, **provided series converges**

Metallic systems:	good convergence
Insulators:	bad convergence
Finite systems:	bad convergece

## Caution!

Numerical tests show:  
Inclusion of second-order gradient term  
may give a considerably worse  $E_{xc}[n]$  than  $E_{xc}^{LDA}[n]$

Why?

$E_{xc}^{LDA}[n]$  provides rather realistic results for atoms, molecules, and solids

But: second-order term (next systematic correction  
for slowly-varying densities) makes  $E_{xc}$  worse

Why does gradient expansion fail?

1. Realistic electron densities not very close to slowly-varying limit
2. LDA: xc hole is the hole of a possible physical system  
     $\Rightarrow$  satisfies exact constraints  
    GEA: xc hole not physical  
     $\Rightarrow$  does not satisfy constraints

Example of constraints:

Physical constraint	LDA	GEA
$E_c < 0$	$< 0$	$> 0$
$E_x < 0$	$< 0$	not restricted
$\int h_{xc}(\mathbf{r}_1; \mathbf{r}_2) d\mathbf{r}_2 = -1$	$-1$	not restricted

⇒ Wrong behaviour of GEA

Method: **Enforce** physical **restrictions** for the xc hole  
 $\Rightarrow$  Generalized gradient approximation (GGA):

$$E_{xc}^{GGA}[n_{\uparrow}, n_{\downarrow}] = \int d^3r f(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow})$$

- ▶  $f(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow})$  not unique,  
but formal features of LDA  $\Rightarrow$  constraints
- ▶ GGA-functionals with/without semiempirical parameters
- ▶ Successful in quantum chemistry
- ▶ No systematic approach to improve GGA-functionals

**Typical errors** for atoms, molecules, and solids (Perdew/Kurth):

Property	LDA	GGA
$E_x$	5% (not negative enough)	0.5%
$E_c$	100% (too negative)	5%
bond length	1% (too short)	1% (too long)
structure	overly favours close packing	more correct
energy barrier	100% (too low)	30% (too low)

- ▶ GGA in most cases better than LDA
- ▶ Typically cancellation of errors between  $E_x$  and  $E_c$
- ▶ "Energy barrier" = barrier to a chemical reaction

Situations where GGA fails:

Unaccurate results for **heavy elements**

Does not predict existence of **negative ions**

Fails to reproduce **dispersion forces** ( $\approx$  van der Waals forces)

Can not describe properly **strongly correlated systems**





GGA does not predict existence of **negative ions**:

For neutral atoms exactly:

$$v_s(\mathbf{r}) \xrightarrow{r \rightarrow \infty} -\frac{1}{r}$$

- ⇒ additional electron feels a Coulomb-like potential
- ⇒ Rydberg series of excited states
- ⇒ necessary criterion for negative ion state fulfilled

In LDA:

$$v_s(\mathbf{r}) \xrightarrow{r \rightarrow \infty} \exp(-\alpha r)$$

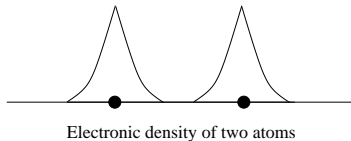
- ⇒ not able to bind additional electron (negative ion)

Same problem with GGA

GGA fails to reproduce **dispersion forces**:

[ Dispersion forces = one type of van der Waals forces ]

Two neutral atoms far apart:



The only attraction between the atoms: virtual dipole interaction

In LDA:

interaction provided by  $E_c$

**requires density overlap**

$\Rightarrow$  no dispersion forces

Same problem with GGA

Generally **both** exact  $E_x$  and exact  $E_c$  are **very nonlocal** (Engel)

Notice: Existence theorems  $\implies$  all physics  
can be obtained from a purely local  $E_{xc}[n]$

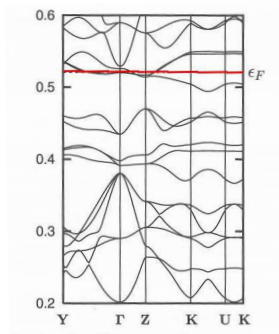
GGA can not describe properly **strongly correlated systems**

Examples: 3d transition metal monoxides MnO, FeO, CoO, and NiO  
(insulating antiferromagnets (Mott insulators))  
wrongly described by LDA and GGA

Mott insulator:

Conventional band theory  
predicts conductor behaviour,  
Electron-electron interactions  
 $\Rightarrow$  insulator behaviour

LDA gives **metallic** behaviour, should be **insulator**!



**Figure:** Band structure of antiferromagnetic FeO calculated with an LDA functional (lectures of Engel). (Same problem with GGA)

The wrong description of Mott insulators not properly understood,  
indications that the problem is **related to self-interaction**

**Orbital-dependent functionals:**  $E_{xc} = E_{xc}[\{\phi_i, \varepsilon_i\}]$

The simplest example the exact exchange:

$$E_x[n] \equiv -\frac{1}{2} \sum_{k,l} \iint d^3r d^3r' \phi_l^*(\mathbf{r}) \phi_l(\mathbf{r}') w(\mathbf{r}, \mathbf{r}') \phi_k^*(\mathbf{r}') \phi_k(\mathbf{r})$$

OBS!  $E_x \neq$  the Hartree-Fock exchange energy  
 (K-S orbitals  $\phi_i(\mathbf{r})$ , not H-F orbitals)

Correlation energy in K-S theory:

$$E_c \equiv E_{xc} - E_x$$

$E_c$  = correlation energy (many-body theory)  
 $+ (E_x^{HF} - E_x^{KS}) + (T[n] - T_s[n])$



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Remember: for Kohn-Sham orbitals,

$$\phi_i(\mathbf{r}) = \phi_i[n(\mathbf{r})]$$

$$\Rightarrow E_{xc}[\{\phi_i\}] = \textit{implicit density functional}$$

Orbital-dependent  $E_{xc}$

can be calculated using **perturbation theory**  
and the **Optimised Potential Method** (OPM)

The  $e^2$ -expansion (see van Leeuwen):

$$E[n] = T_s[n] + \int d^3r n(\mathbf{r}) v(\mathbf{r}) + \frac{e^2}{2} \iint d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \sum_{i=1}^{\infty} e^{2i} E_{xc}^{(i)}$$

Perturbation expansion in  $e^2 \implies$

$E_{xc}^{(1)}$ : exact functional of KS orbitals only (known)

$E_{xc}^{(2)}$ : functional of  $v_{xc}^{(1)}(\mathbf{r}) \equiv \delta E_{xc}^{(1)} / \delta n(\mathbf{r})$

$\vdots$

$E_{xc}^{(i)}$ : functional of  $v_{xc}^{(i-1)}$

Assume  $E_{xc}^{(i)}$  known  $\implies v_{xc}^{(i)}$  can be obtained by solving  
the **Optimised Potential Method** (OPM) integral equation

$$\int d^3 r' \chi_s(\mathbf{r}, \mathbf{r}') v_{xc}(\mathbf{r}') = \Lambda_{xc}(\mathbf{r}),$$

$\Lambda_{xc}(\mathbf{r})$  = functional of KS orbitals  $\phi_k$ , KS eigenvalues  $\varepsilon_k$ ,  
and of  $E_{xc}[\{\phi_k, \varepsilon_k\}]$

$\chi_s(\mathbf{r}, \mathbf{r}')$  = functional of KS orbitals only

OPM equation: a *Fredholm equation* of first kind

Combination of  $e^2$ -expansion and Optimised Potential Method  
 $\implies E_{xc}$  as a perturbation series

- ▶ Rule of thumb: OPM calculations  $\sim 10$ – $100$  times slower than GGA calculations
- ▶ Perturbation series of  $e^2$ -expansion diverges, but low orders give good results

## Wavefunction theory (WFT)

- ▶ Computationally **expensive**
- ▶ **Convergence** to right answer as a function of correlation and basis size

## Density functional theory (DFT)

- ▶ Single-particle equations  $\Rightarrow$  **better** computational **scaling**, possibility to study larger systems
- ▶ Exact  $E_{xc}$  unknown, **no systematic way to improve** calculations
- ▶ Often semi-empirical parametrisations





## Ab initio DFT: Getting the right answer for the right reason

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### Abstract

Some highlights of the WATOC plenary lecture are presented. We discuss what *ab initio dft* is, and that unlike standard density functional methods (DFT) methods, it has to converge to the right answer in the limit of basis and correlation like *ab initio* wavefunction methods. We obtain the correct behavior of the exchange and correlation potentials. In the case of correlation in particular, these are vastly different than those obtained by standard methods like LYP and PBE, and sufficiently different for exchange, that the numerical effect of the correct potentials is quite important. With the correct potentials, the orbital energies in Kohn–Sham DFT are shown to approximately satisfy a kind of Koopmans' theorem, while at the same time, the differences between the occupied orbital energies and the unoccupied orbital energies, offers an excellent zeroth-order approximation to the excitation energy. We demonstrate that we can build a local correlation potential using an optimized effective potential (OEP) strategy, that is equally applicable to non-local Hartree–Fock exchange as it is to local exchange. This makes it possible to create consistent 'hybrid' dft methods at the level of the potential. Some numerical consequences are discussed.

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**Keywords:** Density functional theory; Ab initio dft; Ab initio exchange-correlation functional; Optimized effective potential; Exact exchange; Hybrid functional; correlation potential

Bartlett *et al* state:

”Rather than guessing a functional, we insist upon  
using orbital dependent expressions that *we know are right*.”

*Ab initio* DFT:

1. All calculations done in a basis set
2. Wavefunction theory (WFT)  $\implies E_x[\{\phi_i\}], E_c[\{\phi_i\}]$   
(no explicit WFT calculations)
3. Convergence to the right answer in a basis set and correlation limit
4. KS determinant  $\implies$  correct density

Here: Wavefunction theory, second-order perturbation theory, and Optimised Potential Method  $\implies$  local  $E_{xc}$  functional

Some results... Impressive?

Property	Gradient corrected hybrid methods	<i>ab-initio</i> DFT
Convergence to exact answer	No	Yes
Correct self-interaction	No	Yes
Correct behavior of exchange	No	Yes
Correct behavior of correlation	No	Yes
Approximation for all principal ionization energies (excluding those that are inherently “shake-up” states)	No	Yes
Rydberg excitations	No	Yes
Potential energy curves to dissociation	No	?
Weak interactions	No	Yes

Gradient corrected hybrid methods = example of conventional DFT methods

At least some **drawbacks** compared to conventional DFT:

- Harder to implement, computationally more expensive

*ab initio* DFT:  $\sim N_{it} n^2 N^3$ ,    conventional DFT:  $\sim (n + N)^4$ ,

$n$  = number of electrons,

$N$  = number of basis functions,

$N_{it}$  = number *unspecified* in the article!! (May be large)

Basic Formalism  
The Kohn-Sham Scheme  
Explicit Functionals / LDA  
Explicit Functionals / Gradient Approximations  
**Orbital-Dependent Functionals**  
Implementation of DFT

Implicit Density Functionals  
Optimised Potential Method  
**Ab initio DFT**

Take-home message:

Be *critical* when using DFT methods!

Kohn-Sham equations:

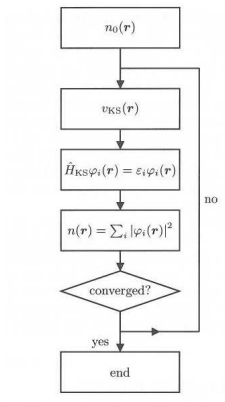
$$\left( -\frac{\nabla^2}{2} + v_{KS}[n(\mathbf{r})] \right) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

or

$$\hat{f}^{KS} \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

with

$$n(\mathbf{r}) = \sum_{i=1}^{\text{occ}} |\phi_i(\mathbf{r})|^2$$
$$v_{KS}[n(\mathbf{r})] = v_{\text{ext}}(\mathbf{r}) + v_{\text{Hartree}}[n(\mathbf{r})] + v_{xc}[n(\mathbf{r})]$$



**Figure:** Flow-chart of the Kohn-Sham procedure (from Nogueira *et al.*: A Tutorial on Density Functional Theory).



K-S orbitals  $\phi_i(\mathbf{r})$  **expanded in basis functions**  $\eta_\mu(\mathbf{r})$ :

$$\phi_i(\mathbf{r}) = \sum_{\mu}^L c_{\mu,i} \eta_{\mu}(\mathbf{r})$$

$\eta_{\mu}$  = plane waves, Gaussians, Slater-type orbitals etc.

In real applications  $L$  finite

$\implies$  crucial to choose good set  $\{\eta_{\mu}\}$

Highly non-linear optimization problem

$\longrightarrow$  linear

Substitution into K-S equation:

$$\hat{f}^{KS}(\mathbf{r}_1) \sum_{\nu=1}^L c_{\nu,i} \eta_{\nu}(\mathbf{r}_1) = \varepsilon_i \sum_{\nu=1}^L c_{\nu,i} \eta_{\nu}(\mathbf{r}_1)$$

Apply integration  $\int d\mathbf{r}_1 \eta_{\mu}(\mathbf{r}_1) \implies$  matrix equation

$$\mathbf{F}^{KS} \mathbf{C} = \mathbf{S} \mathbf{C} \varepsilon$$

$\mathbf{F}^{KS}$ ,  $\mathbf{C}$ ,  $\mathbf{S}$ , and  $\varepsilon$  are  $L \times L$  matrices

For a short and easy first introduction  
to the implementation of DFT ( $\sim$  our last lecture),

read for example Koch and Holthausen:  
*A Chemist's Guide to Density Functional Theory*, Chapter 7