

Ground-state-DFT

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Hamiltonian for the complete system of N_e electrons with coordinates $(\mathbf{r}_1 \cdots \mathbf{r}_{N_e}) \equiv \underline{\underline{\mathbf{r}}}$ and N_n nuclei with coordinates $(\mathbf{R}_1 \cdots \mathbf{R}_{N_n}) \equiv \underline{\underline{\mathbf{R}}}$

$$\hat{H} = \hat{T}_n(\underline{\underline{\mathbf{R}}}) + \hat{W}_{nn}(\underline{\underline{\mathbf{R}}}) + \hat{T}_e(\underline{\underline{\mathbf{r}}}) + \hat{W}_{ee}(\underline{\underline{\mathbf{r}}}) + \hat{V}_{en}(\underline{\underline{\mathbf{R}}}, \underline{\underline{\mathbf{r}}})$$

with $\hat{T}_n = \sum_{v=1}^{N_n} -\frac{\nabla_v^2}{2M_v}$ $\hat{T}_e = \sum_{i=1}^{N_e} -\frac{\nabla_i^2}{2m}$ $\hat{W}_{nn} = \frac{1}{2} \sum_{\substack{\mu, v \\ \mu \neq v}}^{N_n} \frac{Z_\mu Z_v}{|\mathbf{R}_\mu - \mathbf{R}_v|}$

$$\hat{W}_{ee} = \frac{1}{2} \sum_{\substack{j, k \\ j \neq k}}^{N_e} \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|} \quad \hat{V}_{en} = \sum_{j=1}^{N_e} \sum_{v=1}^{N_n} -\frac{Z_v}{|\mathbf{r}_j - \mathbf{R}_v|}$$

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Stationary Schrödinger equation

$$\hat{H} \Psi(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}) = E \Psi(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}})$$

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Time-dependent Schrödinger equation

$$i \frac{\partial}{\partial t} \Psi(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}, t) = \left(H(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}) + V_{\text{laser}}(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}, t) \right) \Psi(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}, t)$$

$$V_{\text{laser}}(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}, t) = \left(\sum_{j=1}^{N_e} \mathbf{r}_j - \sum_{v=1}^{N_n} Z_v \mathbf{R}_v \right) \cdot \mathbf{E} \cdot \mathbf{f}(t) \cdot \cos \omega t$$

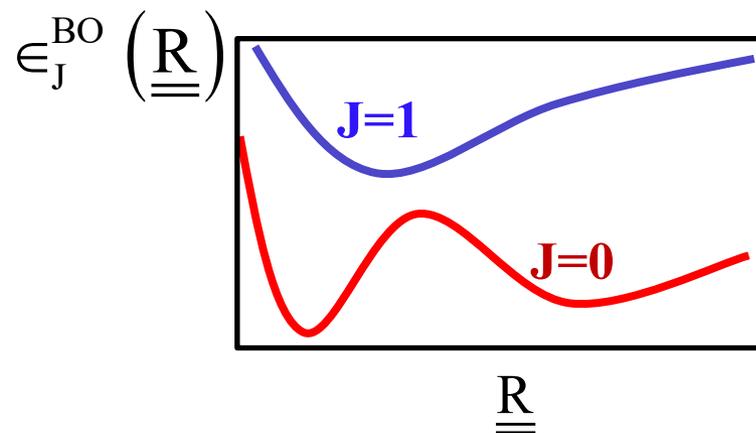
Standard approach to deal with the full e-n problem

1st step: Solve the electronic-structure problem

(obtained from full Hamiltonian H by neglecting T_n)

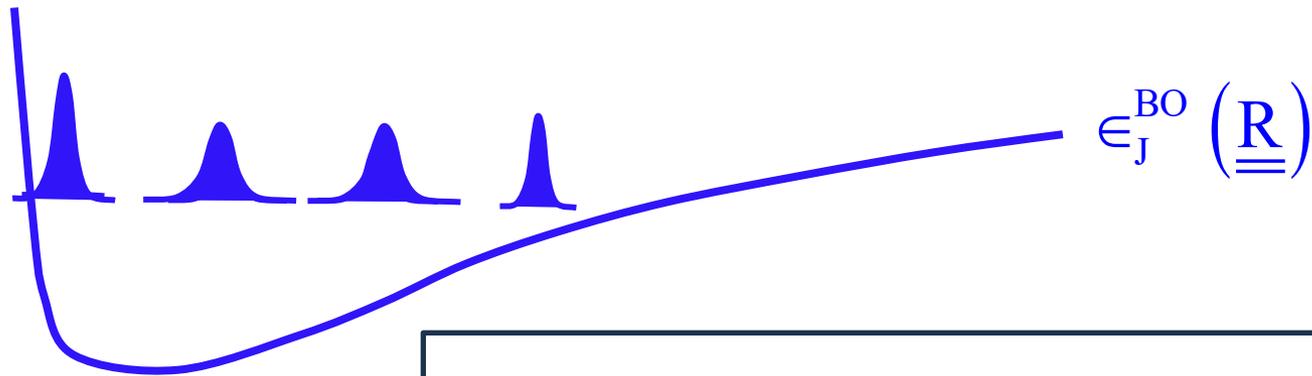
$$\left(\hat{T}_e(\underline{r}) + \hat{W}_{ee}(\underline{r}) + \hat{W}_{nn}(\underline{R}) + \hat{V}_{en}(\underline{r}, \underline{R}) \right) \Phi_{\underline{R}, J}^{\text{BO}}(\underline{r}) = \epsilon_J^{\text{BO}}(\underline{R}) \Phi_{\underline{R}, J}^{\text{BO}}(\underline{r})$$

for fixed nuclear configuration \underline{R} .



2nd step: Adiabatic approximation for the full e-n wave function

$$\Psi^{\text{adiab}}(\underline{\mathbf{r}}, \underline{\mathbf{R}}, t) = \chi(\underline{\mathbf{R}}, t) \Phi_{\underline{\mathbf{R}}, J}^{\text{BO}}(\underline{\mathbf{r}})$$



$$i\partial_t \chi(\underline{\mathbf{R}}, t) = \left(T_n + \epsilon_J^{\text{BO}}(\underline{\mathbf{R}}) \right) \chi(\underline{\mathbf{R}}, t)$$

- achieves approximate separation of electronic and nuclear degrees of freedom, making calculations possible
- represents our intuition of a molecule or solid (the electronic density resulting from the full Hamiltonian H is constant!!)

The “variationally best” adiabatic approximation

Plug the ansatz

$$\tilde{\Psi}^{\text{adiab}}(\underline{\mathbf{r}}, \underline{\mathbf{R}}, t) = \tilde{\chi}(\underline{\mathbf{R}}, t) \Phi_{\underline{\mathbf{R}}}^{\text{BO}}(\underline{\mathbf{r}})$$

into the TD variational principle and determine the “best” nuclear wave function by making the QM action stationary:

$$\begin{aligned} i\partial_t \tilde{\chi}(\underline{\mathbf{R}}, t) &= \left(\tilde{\mathbf{T}}_n + \tilde{\epsilon}(\underline{\mathbf{R}}) \right) \tilde{\chi}(\underline{\mathbf{R}}, t) \\ \tilde{\mathbf{T}}_n &= \sum_v^{N_n} \frac{1}{2M_v} \left(-i\nabla_v + \mathbf{A}_v(\underline{\mathbf{R}}) \right)^2 \end{aligned}$$

$$\mathbf{A}_v(\underline{\mathbf{R}}) = \int d\underline{\mathbf{r}} \Phi_{\underline{\mathbf{R}}}^{\text{BO}}(\underline{\mathbf{r}})^* \left(-i\nabla_{\mathbf{R}_v} \right) \Phi_{\underline{\mathbf{R}}}^{\text{BO}}(\underline{\mathbf{r}}) = \left\langle \Phi_{\underline{\mathbf{R}}}^{\text{BO}} \left| -i\nabla_{\mathbf{R}_v} \Phi_{\underline{\mathbf{R}}}^{\text{BO}} \right. \right\rangle$$

Berry connection

$$\tilde{\epsilon}(\underline{\mathbf{R}}) = \epsilon^{\text{BO}}(\underline{\mathbf{R}}) + \sum_v^{N_n} \left\{ \left\langle \nabla_v \Phi_{\underline{\mathbf{R}}}^{\text{BO}} \left| \nabla_v \Phi_{\underline{\mathbf{R}}}^{\text{BO}} \right. \right\rangle - \mathbf{A}_v(\underline{\mathbf{R}})^2 \right\} / 2M_v$$

“Diagonal correction”

To be kept in mind: Traditional ground-state DFT, as well as Berry-phase effects, are inseparably tied to the adiabatic approximation. We exclusively deal with the electronic-structure Hamiltonian

$$\hat{H}^{\text{BO}}(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}) = \hat{T}_e(\underline{\underline{\mathbf{r}}}) + \hat{W}_{ee}(\underline{\underline{\mathbf{r}}}) + \hat{W}_{nn}(\underline{\underline{\mathbf{R}}}) + \hat{V}_{en}(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}})$$

for fixed nuclear coordinates **R**.

Why don't we just solve the many-particle SE?

Example: Aluminium atom (13 electrons)

$\Psi(\vec{r}_1, \dots, \vec{r}_{13})$ depends on 39 coordinates

rough table of the wavefunction

10 entries per coordinate: $\Rightarrow 10^{39}$ entries

1 byte per entry: $\Rightarrow 10^{39}$ bytes

10^{12} bytes per SSD: $\Rightarrow 10^{27}$ SSDs

20 g per SSD: $\Rightarrow 2 \times 10^{28}$ g SSDs

For Ti atom the required mass of SSDs exceeds mass of the universe

Two fundamentally different classes of ab-initio approaches:

- Wave function approaches
 - Configuration interaction
(also stochastic CI)
 - Tensor networks
- “Functional Theories”

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**Write total energy as functional
of a simpler quantity and minimize**

“Functional Theories”

MBPT

RDMFT

DFT

$$G(\mathbf{r}, \mathbf{r}', t - t') \quad \gamma(\mathbf{r}, \mathbf{r}') = G(\mathbf{r}, \mathbf{r}', 0^+) \quad \rho(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r})$$

“Functional Theories”

MBPT

RDMFT

DFT

$$G(r, r', t - t')$$

$$\gamma(r, r') = G(r, r', 0^+)$$

$$\rho(r) = \gamma(r, r)$$

Functional:

$$\Phi_{xc}[G]$$

or $\Sigma_{xc}[G]$

Functional:

$$E_{xc}[\gamma]$$

Functional:

$$E_{xc}[\rho]$$

or $v_{xc}[\rho]$

“Functional Theories”

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or $\Sigma_{xc}[G]$

easy (e.g. GW)

Functional:

$$E_{xc}[\gamma]$$

difficult

Functional:

$$E_{xc}[\rho]$$

or $v_{xc}[\rho]$

very difficult

“Functional Theories”

MBPT

$$G(r, r', t - t')$$

Functional:

$$\Phi_{xc}[G]$$

or $\Sigma_{xc}[G]$

easy (e.g. GW)

numerically

heavy

RDMFT

$$\gamma(r, r') = G(r, r', 0^+)$$

Functional:

$$E_{xc}[\gamma]$$

difficult

moderate

DFT

$$\rho(r) = \gamma(r, r)$$

Functional:

$$E_{xc}[\rho]$$

or $v_{xc}[\rho]$

very difficult

light

Each of these functional theories comes in two versions:

- **a ground-state (or equilibrium) version**
- **a time-dependent (or non-equilibrium) version**

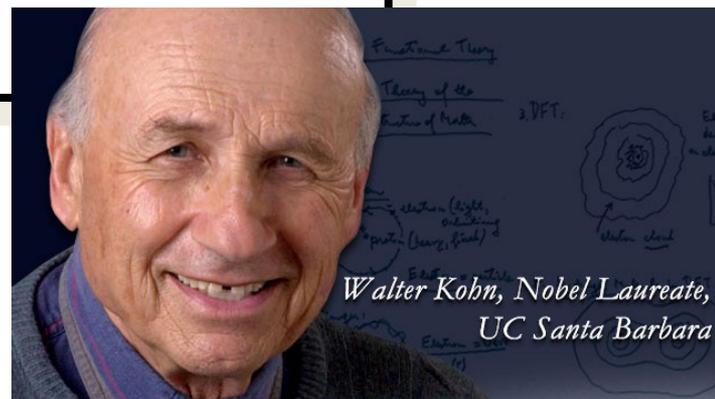
ESSENCE OF DENSITY-FUNCTIONAL THEORY

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

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Hohenberg-Kohn theorem (1964)
Kohn-Sham theorem (1965)
(for the ground state)



*Walter Kohn, Nobel Laureate,
UC Santa Barbara*

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 $\rho(\mathbf{r})$. Consequence: Many-body WF is uniquely determined by the density, $\Psi = \Psi[\rho]$, and hence all expectation values w.r.t. $\Psi[\rho]$ are functionals of $\rho(\mathbf{r})$.

2. Variational principle

Given a particular system characterized by the external potential $\mathbf{v}_0(\mathbf{r})$. There exists a functional, $E_{\text{HK}}[\rho]$, such that the solution of the Euler-Lagrange equation

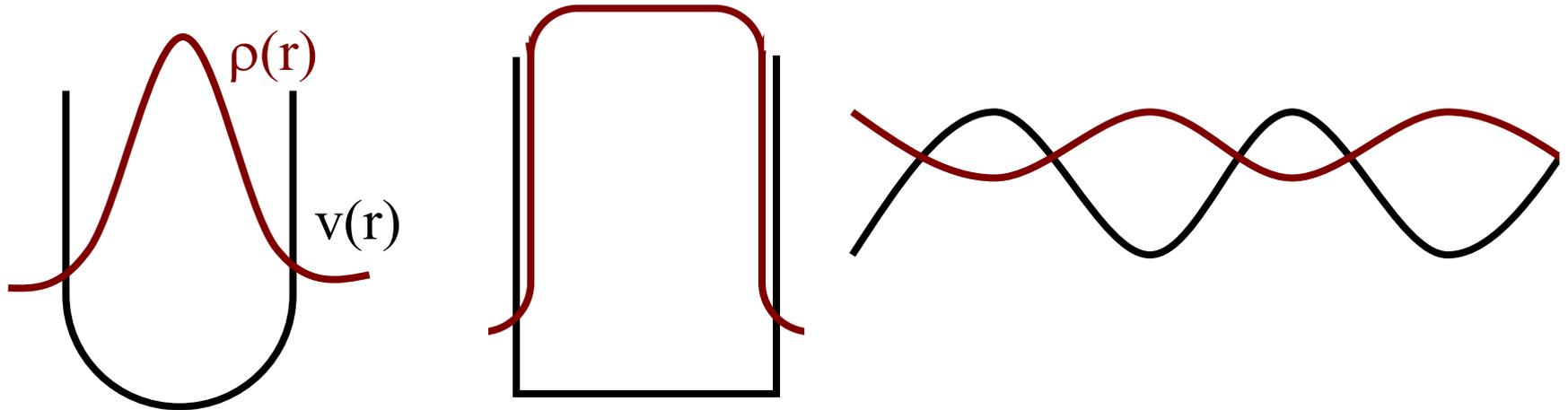
$$\frac{\delta}{\delta\rho(\mathbf{r})} E_{\text{HK}}[\rho] = 0$$

yields the exact ground-state energy \mathbf{E}_0 and ground-state density $\rho_0(\mathbf{r})$ of this system

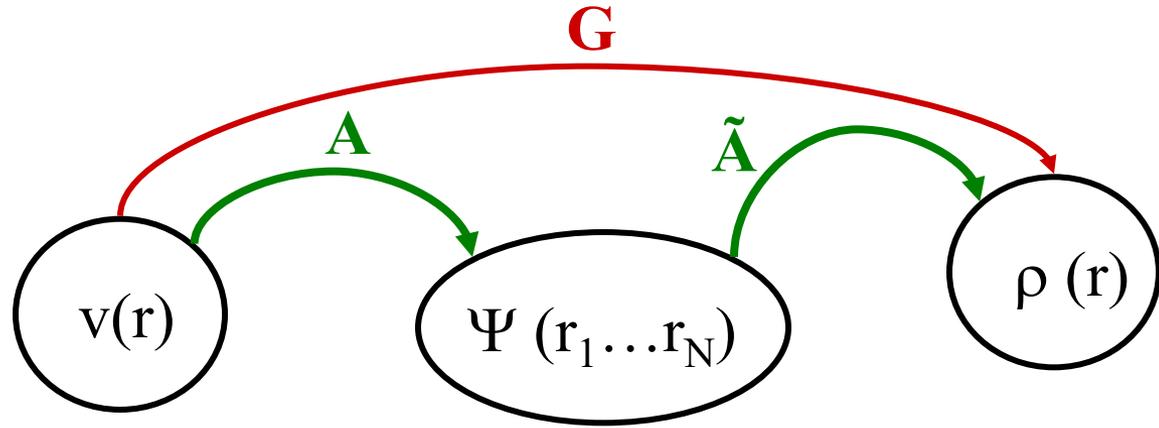
3. $E_{\text{HK}}[\rho] = \langle \Psi[\rho] | T + V_{\text{ee}} + \mathbf{V}_0 | \Psi[\rho] \rangle = F[\rho] + \int \rho(\mathbf{r}) \mathbf{v}_0(\mathbf{r}) d^3r$

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

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)

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

Proof

Step 1: Invertibility of map A

Solve many-body Schrödinger equation for the external potential:

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

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

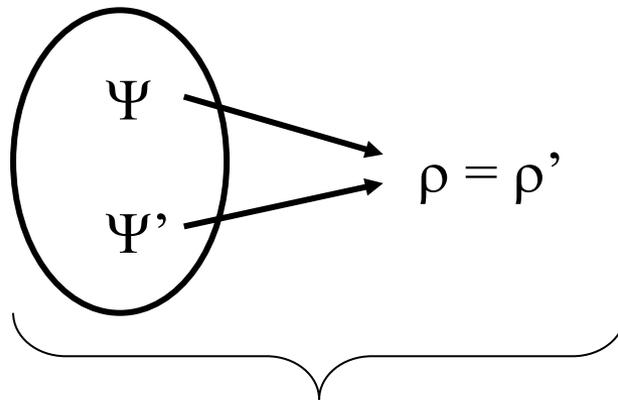
This is manifestly the inverse map: A given Ψ uniquely yields the external potential.

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:

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

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

Proof by reductio ad absurdum:

Assumption $\rho = \rho'$. Add the two inequalities $\Rightarrow E + E' < E + E'$



Consequence

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

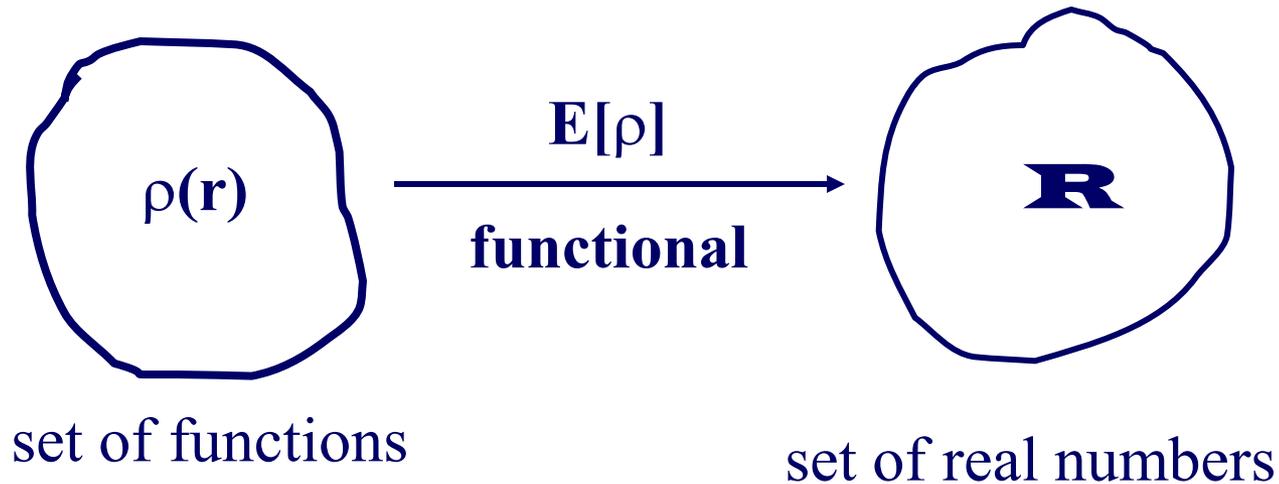
Proof: $\rho \xrightarrow{G^{-1}} v[\rho] \xrightarrow{\text{solve S.E.}} \Phi_i[\rho]$

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:

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

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

QUESTION:

How to calculate ground state density $\rho_o(\vec{r})$ of a given system (characterized by 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:

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

$$> E_o \quad \text{for } \rho \neq \rho_o$$

$$= E_o \quad \text{for } \rho = \rho_o \quad \text{q.e.d.}$$

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

F[ρ] is universal

An Example: Explicit algorithm to construct the HK map

$v_s \longleftrightarrow \rho$ for non-interacting particles

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

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

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

Iterative procedure

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

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

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

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

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

Consequence: The orbitals are functionals of the density: $\varphi_i[\rho]$

KOHN-SHAM EQUATIONS

Rewrite HK functional: $E_{\text{HK}}[\rho] = T_{\text{S}}[\rho] + \int \rho(\mathbf{r}) v_0(\mathbf{r}) d^3r + E_{\text{H}}[\rho] + E_{\text{xc}}[\rho]$

where $T_{\text{S}}[\rho] = \sum \int d^3r \phi_j^*[\rho](\mathbf{r}) \left(-\nabla^2 / 2 \right) \phi_j[\rho](\mathbf{r})$
is the kinetic energy functional of non-interacting particles

$\frac{\delta}{\delta \rho(\mathbf{r})} E_{\text{HK}}[\rho] = 0$ yields the Kohn-Sham equations:

$$\left(-\nabla^2 / 2 + v_0(\mathbf{r}) + v_{\text{H}}[\rho](\mathbf{r}) + v_{\text{xc}}[\rho](\mathbf{r}) \right) \phi_j(\mathbf{r}) = \epsilon_j \phi_j(\mathbf{r})$$

The orbitals from these equations yield the true density of the interacting system

Walter Kohn: “The KS equations are an exactification of the Hartree mean-field equation”

$E_{\text{xc}}[\rho]$ is a universal functional of the density which, in practice, needs to be approximated.

The functional $E_{xc}[\rho]$ is universal:

Curse or blessing?

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Functional can be systematically improved, i.e. results will improve -on average- for all systems. Systematic improvement for a single given system is not possible.

EXTENSIONS

Relativistic KS equations:

$$\left[\vec{\gamma} \cdot \left(-i\hbar \vec{\nabla} - \vec{\mathbf{A}}_s(\mathbf{r}) \right) + mc^2 + \gamma_0 \mathbf{v}_s(\mathbf{r}) \right] \psi_n(\mathbf{r}) = \varepsilon_n \gamma_0 \psi_n(\mathbf{r})$$

$$\vec{\mathbf{A}}_s(\mathbf{r}) = -e \left\{ \vec{\mathbf{A}}_{\text{ext}}(\mathbf{r}) + \int d^3r' \frac{\vec{\mathbf{j}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}[\rho, \vec{\mathbf{j}}]}{\delta \vec{\mathbf{j}}(\mathbf{r})} \right\}$$

$$\mathbf{v}_s(\mathbf{r}) = -e \left\{ \underbrace{A_{\text{ext}}^0(\mathbf{r})}_{V_{\text{nuc}}(\mathbf{r})} + \int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}[\rho, \vec{\mathbf{j}}]}{\delta \rho(\mathbf{r})} \right\}$$

KS orbitals are Dirac spinors

EXTENSIONS

Finite temperature KS equations:

$$\left(-\frac{\nabla^2}{2m} + v_{\text{nuc}}(\mathbf{r}) + \int \frac{\rho_{\text{T}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r' + v_{\text{xc}}^{\text{T}}[\rho_{\text{T}}](\mathbf{r}) \right) \varphi_j(\mathbf{r}) = \varepsilon_j \varphi_j(\mathbf{r})$$

$$\rho_{\text{T}}(\mathbf{r}) = \sum_j \underbrace{f_{\text{T}}(\varepsilon_j)}_{\text{Fermi-Dirac distribution}} \times |\varphi_j(\mathbf{r})|^2$$

Approximations for the exchange-correlation functional

Local density approximation (LDA)

$E_{xc}[\rho]$ = smallest part of total energy

simplest approximation : $E_{xc}[\rho] \equiv 0 \Rightarrow$ Hartree approach

Result: lattice constants and bonding distances much too large (20%-50%)

$\Rightarrow E_{xc} =$ "Nature's glue"

LDA (Kohn and Sham, 1965)

$$E_{xc}^{\text{LDA}}[\rho] = \int d^3r \rho(\vec{r}) \varepsilon_{xc}^{\text{unif}}(\rho(\vec{r}))$$

$\varepsilon_{xc}^{\text{unif}}(\rho)$ xc energy per particle of a uniform electron gas of density ρ
(known from quantum Monte-Carlo and many-body theory)

Result: decent lattice constants, phonons, surface energies of metals

<u>Quantity</u>	<u>Typical deviation</u> (from expt)
• Atomic & molecular ground state energies	< 0.5 %
• Molecular equilibrium distances	< 5 %
• Band structure of metals, Fermi surfaces	few %
• Lattice constants	< 2 %

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Systematic error of LDA: Molecular atomisation energies too large and bond lengths and lattice constants too small

One would expect the LDA to be good only for weakly inhomogeneous systems, i.e., systems whose density satisfies:

$$\frac{|\nabla\rho|}{\rho} \ll k_F = (3\pi^2\rho)^{1/3} \quad \text{and} \quad \frac{|\nabla\rho|}{\rho} \ll k_{TF} = 4(3\rho/\pi)^{1/6}$$

Why is the LDA good also for strongly inhomogeneous systems?

Answer: Satisfaction of many exact constraints (features of exact xc fct!)

$$E_{xc}^{LDA}[\rho] = \frac{1}{2} \int d^3r \rho(\vec{r}) \int d^3r' \frac{\bar{n}_{xc}^{LDA}(\vec{r}, \vec{r}')}{|\vec{r}' - \vec{r}|}$$

$\bar{n}_{xc}(\vec{r}, \vec{r}')$ coupling-constant-averaged xc hole density $n_{xc} = n_x + n_c$

Important constraints:

$$\int d^3r' n_x(\vec{r}, \vec{r}') = -1 \quad \int d^3r' \bar{n}_c(\vec{r}, \vec{r}') = 0 \quad n_x \leq 0$$

are satisfied in LDA

Generalized Gradient Approximations (GGA)

$$E_{xc}^{\text{GGA}}[\rho] = \int d^3r f(\rho(\vec{r}), |\nabla\rho(\vec{r})|)$$

Langreth, Mehl (1983), Becke (1986), Perdew, Wang (1988)
PBE: Perdew, Burke, Ernzerhof (1996)

Construction principle: Satisfaction of exact constraints
(important lesson from LDA and from gradient expansion of E_{xc})

Results: GGAs reduce the LDA error in the atomisation energy significantly (but not completely) while LDA bond lengths are over-corrected (i.e. are in GGA too large compared with expt)

Detailed study of molecules (atomization energies)

B. G. Johnson, P. M. W. Gill, J. A. Pople, *J. Chem. Phys.* 97, 7847 (1992)

32 molecules (all neutral diatomics from first-row atoms only and H₂)

Atomization energies (kcal/mol) from:

	$E_x^B + E_c^{VWN}$	$E_x^B + E_c^{LYP}$	HF
mean deviation from experiment	0.1	1.0	-85.8
mean absolute deviation	4.4	5.6	85.8

for comparison: MP2
-22.4
22.4

LIMITATIONS OF LDA/GGA

- **Not free from spurious self-interactions: KS potential decays more rapidly than r^{-1} for finite systems**

Consequences:

- no Rydberg series
- negative atomic ions not bound
- ionization potentials (if calculated from highest occupied orbital energy) too small

- **Dispersion forces cannot be described**

$W_{\text{int}}(\mathbf{R}) \longrightarrow e^{-R}$ (rather than R^{-6})

- **band gaps too small: G**

$$E_{\text{gap}}(\text{LDA/GGA}) \approx 0.5 E_{\text{gap}}(\text{expt})$$

- **Energy-structure dilemma of GGAs**

atomisation energies too large

bond lengths too large

(no GGA known that gets both correct!!)

- **Wrong ground state for strongly correlated solids, e.g. CoO, La₂CuO₄ predicted as metals (in the KS equations)**

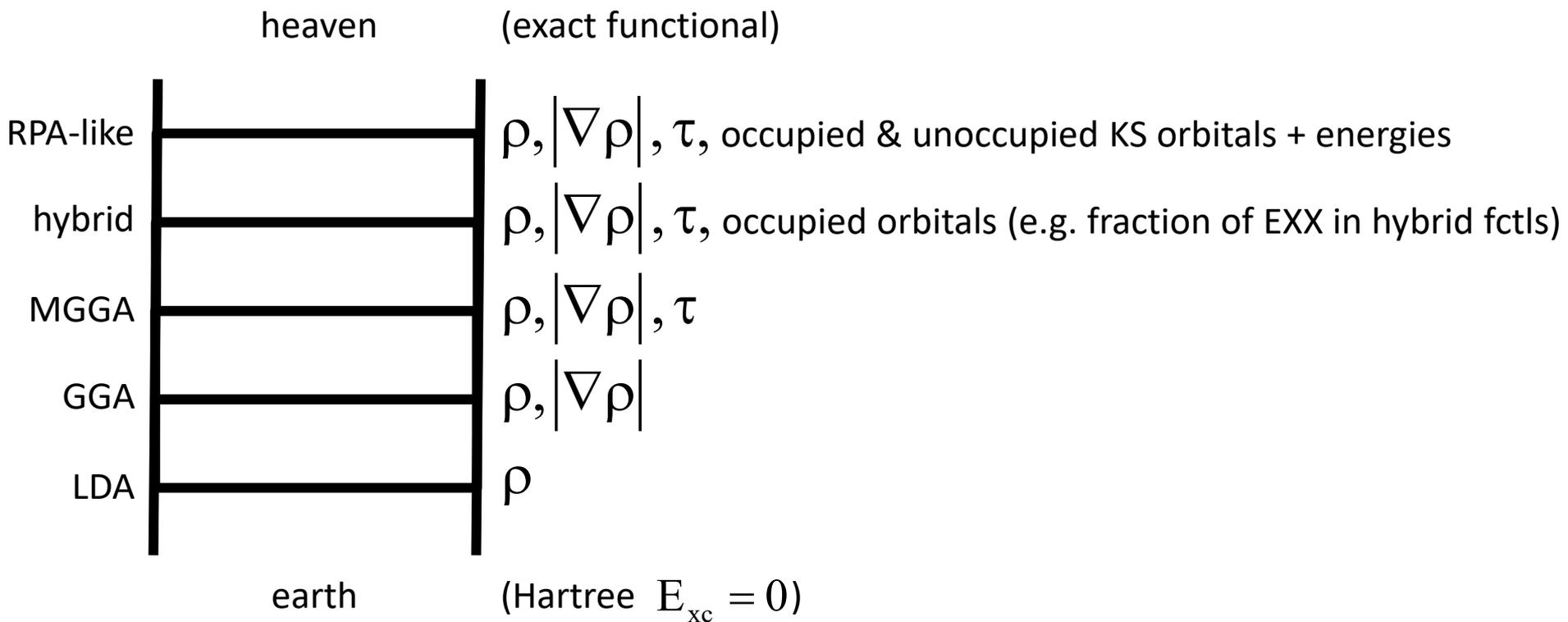
Meta Generalized Gradient Approximations (MGGA)

$$E_{\text{xc}}^{\text{MGGA}}[\rho] = \int d^3r \rho(\vec{r}) \varepsilon_{\text{xc}}^{\text{MGGA}}(\rho(\vec{r}), |\nabla\rho(\vec{r})|, \tau(\vec{r}))$$

$$\tau(\vec{r}) = \frac{1}{2} \sum_{\alpha, \sigma}^{\text{occup}} |\nabla \psi_{\alpha, \sigma}(\vec{r})|^2 \quad T_s[\mathbf{n}] = \int d^3r \tau(\vec{r})$$

Result: Solves energy-structure dilemma of GGAs

Jacob's ladder of xc functionals (John Perdew)



DFT of Magnetism and Superconductivity

DFT of Magnetism and Superconductivity

Spontaneously-broken-symmetry phases:

Formation of a non-vanishing order parameter

Order parameter of magnets: spin magnetization density

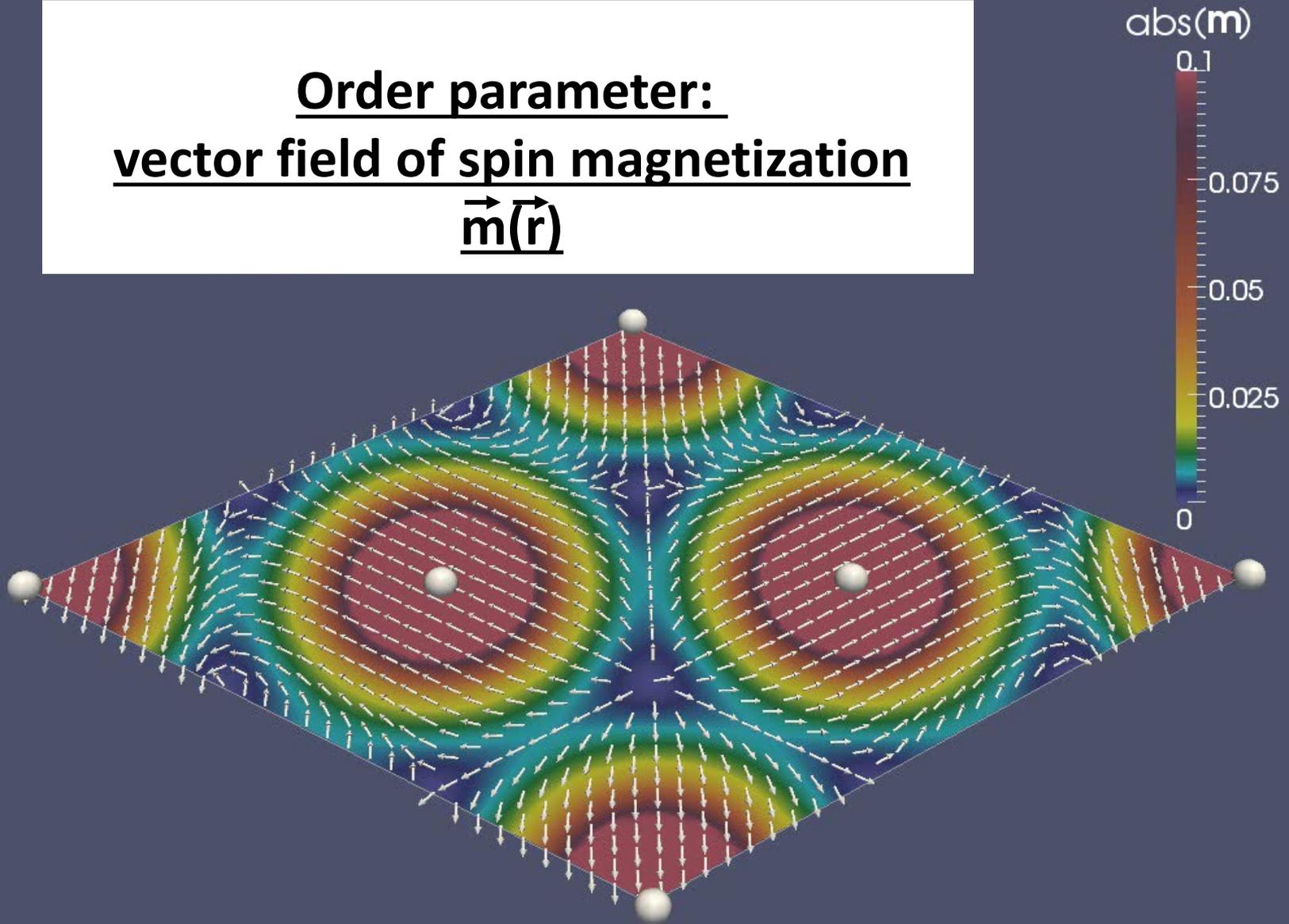
$$\hat{\mathbf{m}}(\mathbf{r}) = \mu_0 \sum_{\alpha\beta} \hat{\psi}_{\alpha}^{+}(\mathbf{r}) \vec{\sigma}_{\alpha\beta} \hat{\psi}_{\beta}(\mathbf{r})$$

Order parameter of superconductors:

$$\hat{\chi}(\mathbf{r}, \mathbf{r}') = \hat{\psi}_{\uparrow}(\mathbf{r}) \hat{\psi}_{\downarrow}(\mathbf{r}')$$

Order parameter:
vector field of spin magnetization
 $\vec{m}(\vec{r})$

Order parameter:
vector field of spin magnetization
 $\vec{m}(\vec{r})$



Cr monolayer in the ground state (obtained with non-collinear LSDA)

In principle, Hohenberg-Kohn theorem guarantees that $m(\mathbf{r})$ is a functional of the density: $m(\mathbf{r}) = m[\rho](\mathbf{r})$.

In practice, very few approximations for the functional $m[\rho]$ are known.

Notable exceptions: Callow, Pearce, Gidopoulos, JCP **156**, 111101 (2022); C. Ullrich, PRA **100**, 012516 (2019).

Standard procedure: Include $m(\mathbf{r})$ as additional ‘density’ in the formalism (in addition to the density $\rho(\mathbf{r})$).

Start from fully interacting Hamiltonian with Zeeman term:

$$\hat{H}_{v,\vec{B}} = \hat{T} + \hat{V}_{ee} + \int \hat{\rho}(\mathbf{r}) v(\mathbf{r}) d^3r - \mu_B \int \hat{\vec{m}}(\mathbf{r}) \cdot \vec{B}(\mathbf{r}) d^3r$$

$$\text{with } \hat{\vec{m}}(\mathbf{r}) = \sum_{\alpha\beta} \hat{\psi}_{\alpha}^{\dagger}(\mathbf{r}) \vec{\sigma}_{\alpha\beta} \hat{\psi}_{\beta}(\mathbf{r})$$

HK theorem

$$[\rho(\mathbf{r}), \vec{m}(\mathbf{r})] \xleftrightarrow{1-1} [v(\mathbf{r}), \vec{B}(\mathbf{r})]$$

U. von Barth, L. Hedin, J. Phys C 5, 1629 (1972), N. Gidopoulos, PRB 75, 134408 (2007)

total energy:

$$E_{v,\vec{B}}[\rho, \vec{m}] = F[\rho, \vec{m}] + \int d^3r (v(\mathbf{r})\rho(\mathbf{r}) - \mu_B \vec{B}(\mathbf{r}) \cdot \vec{m}(\mathbf{r}))$$

↑
universal

KS scheme: Orbitals are Pauli spinors

$$\left(-\frac{\nabla^2}{2m} + [v(\mathbf{r}) + v_H(\mathbf{r}) + \mathbf{v}_{xc}(\mathbf{r})] - \sigma [\mu_B \mathbf{B}(\mathbf{r}) + \mathbf{B}_{xc}(\mathbf{r})] \right) \varphi_j(\mathbf{r}) = \varepsilon_j \varphi_j(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_{j=1}^N \varphi_j^\dagger(\mathbf{r}) \varphi_j(\mathbf{r})$$

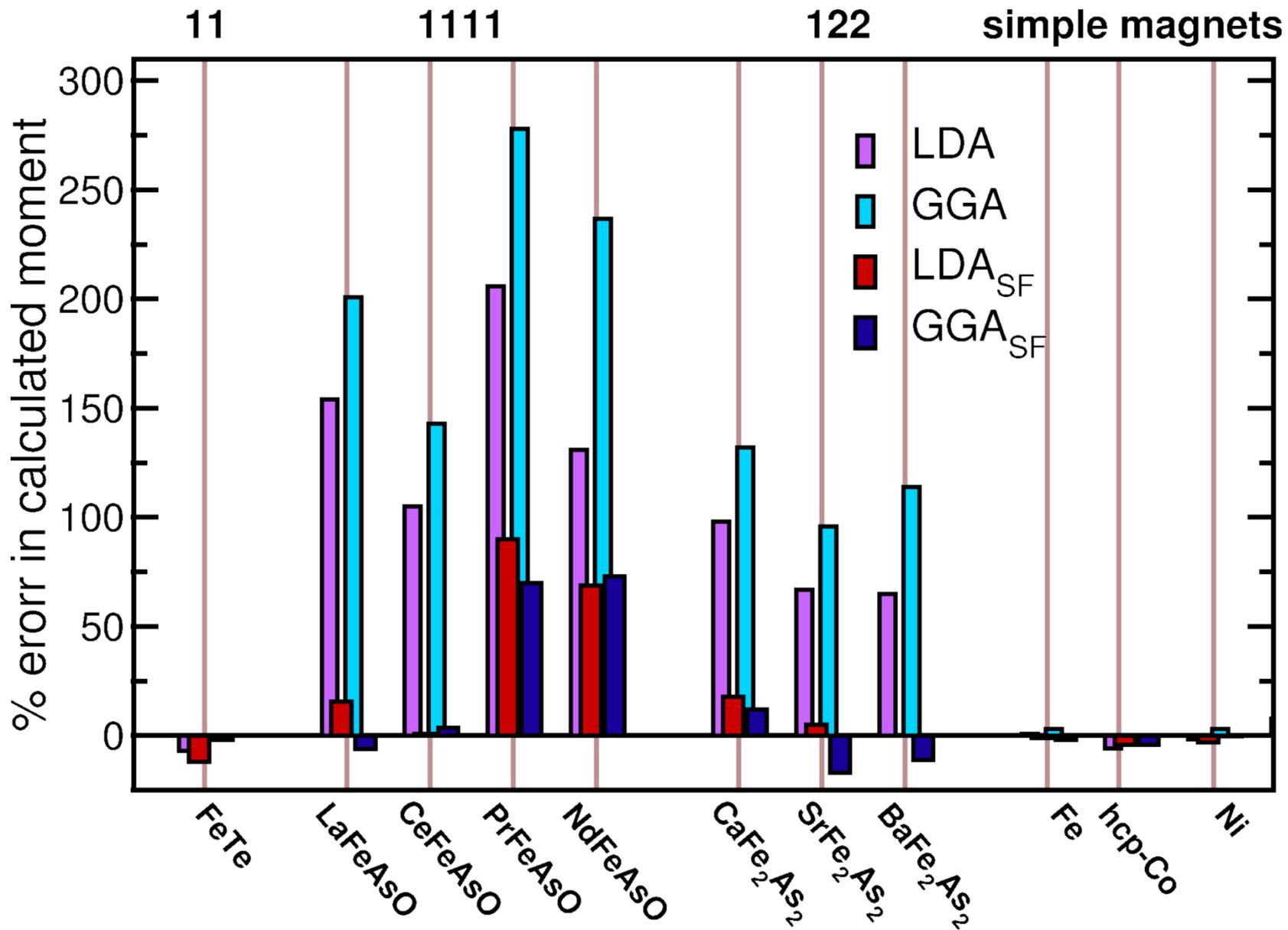
$$\vec{m}(\mathbf{r}) = \sum_{j=1}^N \varphi_j^\dagger(\mathbf{r}) \vec{\sigma} \varphi_j(\mathbf{r})$$

$$\mathbf{v}_{xc}[\rho, \mathbf{m}] = \delta E_{xc}[\rho, \mathbf{m}] / \delta \rho$$

$$\mathbf{B}_{xc}[\rho, \mathbf{m}] = \delta E_{xc}[\rho, \mathbf{m}] / \delta \mathbf{m}$$

B → 0 limit

These equations do not reduce to the original KS equations for $\mathbf{B} \rightarrow 0$ if, in this limit, the system has a finite $\mathbf{m}(\mathbf{r})$.



Construction of a novel xc functional for non-collinear magnetism

Enforce property of the exact xc functional:

$$\mathbf{B}_{\text{xc}}^{\text{exact}}(\mathbf{r}) = \nabla \times \mathbf{A}_{\text{xc}}^{\text{exact}}(\mathbf{r})$$

K. Capelle, E.K.U. Gross, PRL 78, 1872 (1997)

This condition is violated by all standard functionals (LDA, GGAs,...), i.e. the approximate xc magnetic field is produced by magnetic monopoles

By virtue of Helmholtz' theorem, any vector field can be decomposed as:

$$\mathbf{B}_{\text{xc}}^{\text{GGA}}(\mathbf{r}) = \nabla \times \mathbf{A}_{\text{xc}}(\mathbf{r}) + \nabla \varphi(\mathbf{r})$$

Enforce exact property by subtracting source term!

Explicit construction:

S. Sharma, E.K.U. Gross, A. Sanna, K. Dewhurst, JCTC14, 1247 (2018)

$$\nabla^2 \varphi(\mathbf{r}) = 4\pi \nabla \times \mathbf{B}_{\text{xc}}^{\text{GGA}}(\mathbf{r})$$

$$\tilde{\mathbf{B}}_{\text{xc}}(\mathbf{r}) := \mathbf{B}_{\text{xc}}^{\text{GGA}}(\mathbf{r}) - \frac{1}{4\pi} \nabla \varphi(\mathbf{r})$$

$$\mathbf{B}_{\text{xc}}^{\text{SF}}(\mathbf{r}) = s \tilde{\mathbf{B}}_{\text{xc}}(\mathbf{r})$$

Scaling factor, s, only depends on underlying functional (GGA/LSDA), nothing else. (s = 1.14 for GGAs)

