Ground-State DFT

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Many-Body Schrödinger Equation

$$\hat{H}\Psi(r_1, r_2, ..., r_N) = E\Psi(r_1, r_2, ..., r_N)$$

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

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

$$\hat{V} = \sum_{j=1}^{N} v(r_j)$$

$$\hat{W} = \frac{1}{2} \sum_{\substack{j,k=1 \\ j \neq k}}^{N} \frac{e^2}{|r_j - r_k|}$$

Why don't we just solve the SE?

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Example: Oxygen atom (8 electrons)

$$\Psi\left(\vec{r}_1, \cdots, \vec{r}_8\right) \text{ depends on 24 coordinates}$$

rough table of the wavefunction

10 entries per coordinate:	$\Rightarrow 10^{24}$ **entries**
1 byte per entry:	$\Rightarrow 10^{24}$ **bytes**
5×10^9 bytes per DVD:	$\Rightarrow 2\times10^{14}$ **DVDs**
10 g per DVD:	$\Rightarrow 2\times10^{15}$ **g of DVDs**
	$= 2\times10^9$ **t of DVDs**

Two fundamentally different classes of ab-initio approaches:

- ## Wave function approaches

    -- Quantum Monte Carlo
    -- Configuration interaction
    -- Tensor product decomposition

- ## "Functional Theories"

Two fundamentally different classes of ab-initio approaches:

- ## Wave function approaches

    -- Quantum Monte Carlo
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- ## "Functional Theories"

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

"Functional Theories"

MBPT	RDMFT	DFT

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

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

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

"Functional Theories"

MBPT	RDMFT	DFT
$G(r, r', t - t')$	$\gamma(r, r') = G(r, r', 0^+)$	$\rho(r) = \gamma(r, r)$

Functional: $\qquad$ Functional: $\qquad$ Functional:

$\Phi_{xc}[G]$ $\qquad$ $E_{xc}[\gamma]$ $\qquad$ $E_{xc}[\rho]$

or $\Sigma_{xc}[G]$ $\qquad\qquad\qquad$ or $v_{xc}[\rho]$

"Functional Theories"

MBPT

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

Functional:
$\Phi_{xc}[G]$
or $\Sigma_{xc}[G]$
easy (e.g. GW)

RDMFT

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

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

difficult

DFT

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

Functional:
$E_{xc}[\rho]$
or $v_{xc}[\rho]$
very difficult

"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 $\Sigma_{xc}[G]$
easy (e.g. GW)
numerically
heavy

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

difficult

moderate

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-FUNTIONAL 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 <u>non</u>-interacting particles**

ESSENCE OF DENSITY-FUNTIONAL THEORY

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Hohenberg-Kohn theorem (1964)
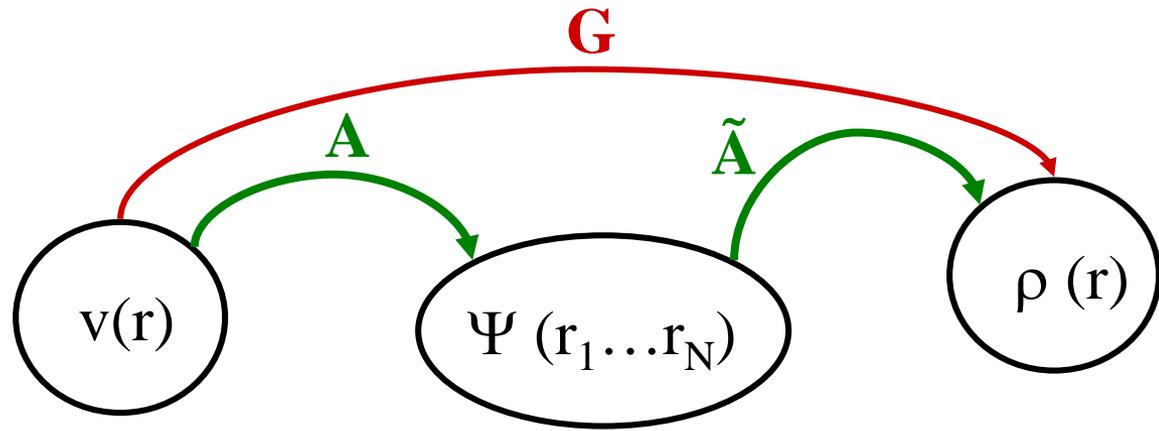**Kohn-Sham theorem (1965)**
(for the ground state)
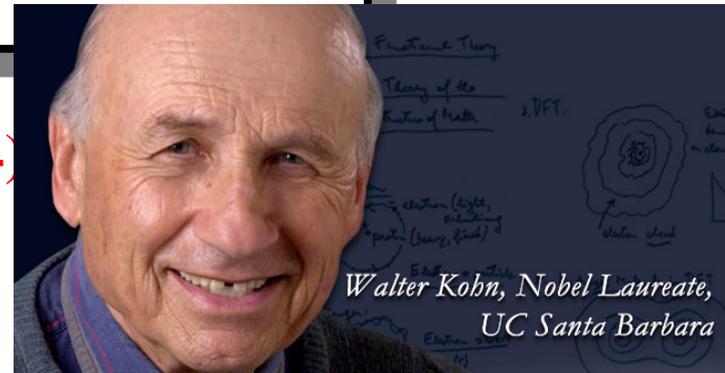
Walter Kohn, Nobel Laureate,
UC Santa Barbara

compare ground-state densities $\rho(r)$ resulting from different external potentials $v(r)$.

$\rho(r)$

$v(r)$
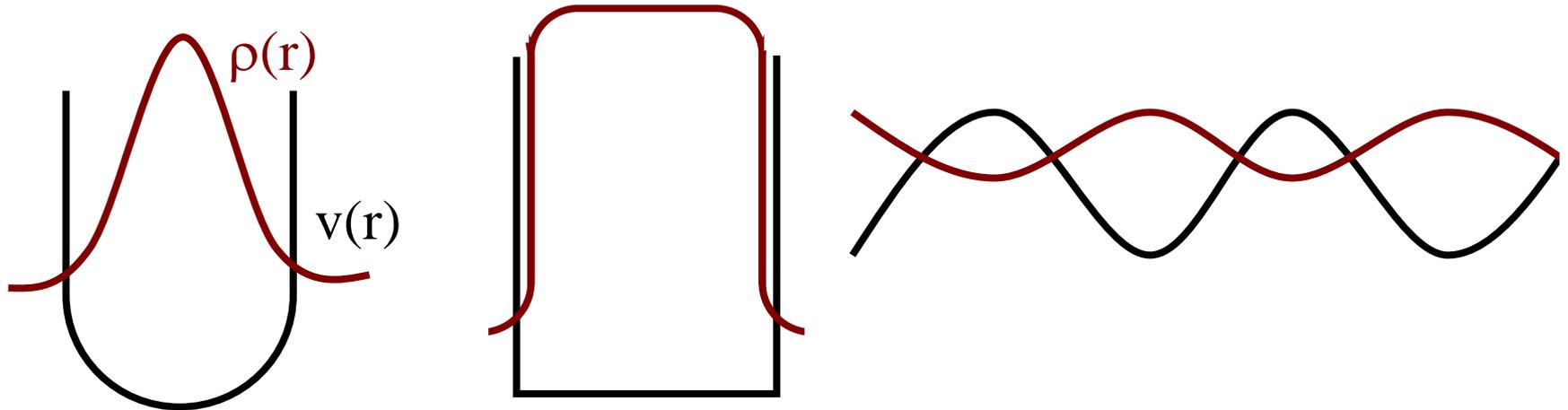
QUESTION: **Are the ground-state densities coming from different potentials always different?**

G

A   **Ã**

$v(r)$

$\Psi(r_1 \dots r_N)$

$\rho(r)$

single-particle
potentials having
nondegenerate
ground state

ground-state
wavefunctions

ground-state
densities

Hohenberg-Kohn-Theorem (1964)

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

Proof

<u>Step 1: Invertibility of map A</u>

Solve many-body Schrödinger equation for the external potential:

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

$$\sum_{j=1}^{N} v(r_j) = -\frac{\hat{T}\Psi}{\Psi} - W_{ee}\left(\vec{r}_1 ... \vec{r}_N\right) + \text{constant}$$

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

Step 2: Invertibility of map Ã

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

$$\hat{H}\Psi = E\Psi \qquad\qquad \hat{H} = \hat{T} + \hat{W} + \hat{V}$$

with

$$\hat{H}'\Psi' = E'\Psi' \qquad\qquad \hat{H}' = \hat{T} + \hat{W} + \hat{V}'$$

to be shown: $\quad \Psi \neq \Psi' \implies \rho \neq \rho'$
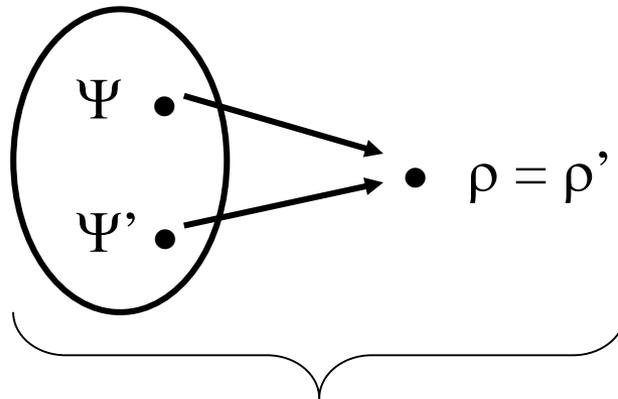
cannot happen

Use Rayleigh-Ritz principle:

$$\text{\Lightning}\quad E = \left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle < \left\langle \Psi' \middle| \hat{H} \middle| \Psi' \right\rangle = \left\langle \Psi' \middle| H' + V - V' \middle| \Psi' \right\rangle$$

$$= E' + \int d^3r \rho'(r)\left[v(r) - v'(r)\right]$$

$$\star\quad E' = \left\langle \Psi' \middle| \hat{H}' \middle| \Psi' \right\rangle < \left\langle \Psi \middle| \hat{H}' \middle| \Psi \right\rangle$$

$$= E + \int d^3r \rho(r)\left[v'(r) - v(r)\right]$$

Reductio ad absurdum:

Assumption $\rho = \rho'$. Add $\text{\Lightning}$ and $\star \Rightarrow E + E' < E + E'$

$$\boxed{\text{Consequence}}$$

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

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

Hermitian operator $\hat{B}$ $B_i[\rho] = \left\langle \Phi_i[\rho] \middle| \hat{B} \middle| \Phi_i[\rho] \right\rangle$

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

What is a FUNCTIONAL?

$$\rho(\mathbf{r}) \quad \xrightarrow{\;\mathbf{E}[\rho]\;} \quad \mathbb{R}$$

functional

set of functions   set of real numbers
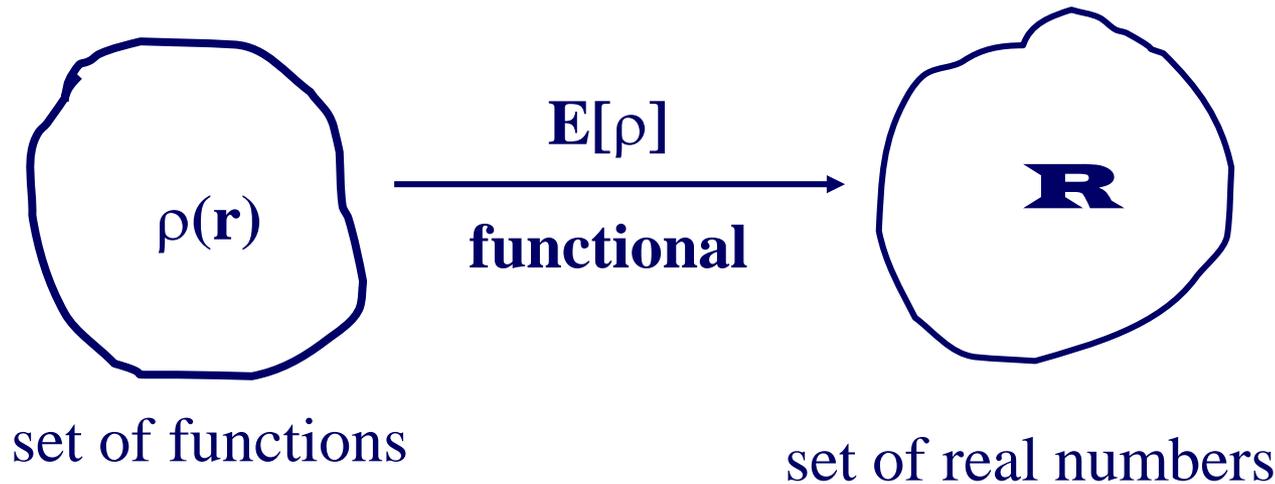
Generalization:

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

$$\psi_{\vec{r}_1...\vec{r}_N}[\rho] = \psi[\rho](\vec{r}_1...\vec{r}_N) \quad \text{or on} \quad (\vec{r}_1...\vec{r}_N)$$

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

$$\left(- \frac{h^2 \nabla^2}{2m} + v_s(r) \right) \varphi_i = \epsilon_i \varphi_i \qquad \Big| \sum_i \varphi_i^* \cdot$$

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

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

Iterative procedure

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

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

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

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

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

QUESTION:

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

<u>Theorem:</u>

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

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

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

where E_o = exact ground state energy of the system

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

yields exact ground state density ρ_o.

proof:

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

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

define:

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

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

$$E_{HK}[\rho] = \int d^3r \, \rho(r) \, v_o(r) \ + \underbrace{\left\langle \Psi[\rho] \middle| \hat{T} + \hat{W} \middle| \Psi[\rho] \right\rangle}$$

$$F[\rho] \ \text{is} \ \boxed{\text{universal}}$$

HOHENBERG-KOHN THEOREM

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

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

2. <u>Variational principle</u>

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

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

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

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

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

<u>Four steps needed</u>

<u>Step 1</u>: Basic Theorems, exact features

<u>Step 2</u>: Find approximate functionals for $v_{xc}\left[\rho(r')\right](r)$

<u>Step 3</u>: Write code that solves the equations

<u>Step 4</u>: Run code for interesting systems/questions

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

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

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

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

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

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

TOWARDS THE EXACT FUNCTIONAL

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

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

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

⇒ **Thomas-Fermi-type equation has to be solved**

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

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

⇒ **KS equations have to be solved**

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

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

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

DF correlation energy versus traditional QC correlation energy

$$E_c^{QC} := E_{tot} - E_{tot}^{HF}[\varphi_j^{HF}]$$

$$E_c^{DFT} = F - T_s - \frac{1}{2} \iint \frac{\rho(r)\,\rho(r')}{|r - r'|}\, d^3r\, d^3r' - E_x^{HF}[\varphi_j^{KS}]$$

$$+ \int \rho\, v_{ext} - \int \rho\, v_{ext}$$

$$E_c^{DFT} := E_{tot} - E_{tot}^{HF}[\varphi_j^{KS}]$$

$$E_{tot}^{HF}[\varphi_j^{HF}] \le E_{tot}^{HF}[\varphi_j^{KS}]$$

$$\Rightarrow E_c^{DFT} \le E_c^{QC}$$

	E_c^{DFT}	E_c^{QC}
H^-	-0.04195	-0.039821
He	-0.042107	-0.042044
Be^{2+}	-0.044274	-0.044267

in Hartree units

details see: E.K.U.G., M.Petersilka, T.Grabo, in: Chemical Applications of Density Functional Theory, B.B. Laird, R.B. Ross, T. Ziegler, eds., ACS Symposium Series 629, 42 (1996).
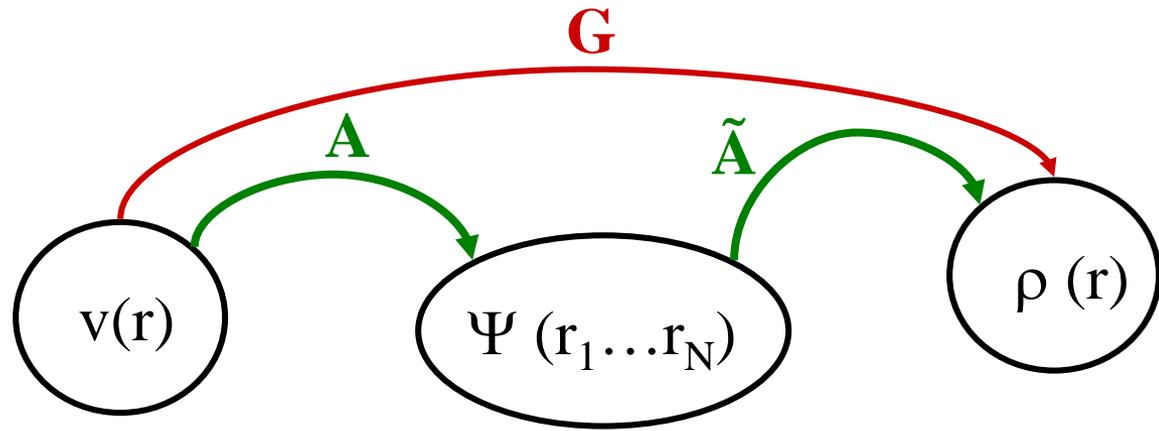
Hohenberg-Kohn-Theorem (1964)

G: v(r) → ρ (r)   is invertible

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

QUESTION: Are all "reasonable" functions $\rho(r)$ V-representable?

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

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

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

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

$$v_{ext}[\rho](r) \longleftrightarrow \rho(r) \longleftrightarrow v_s[\rho](r)$$
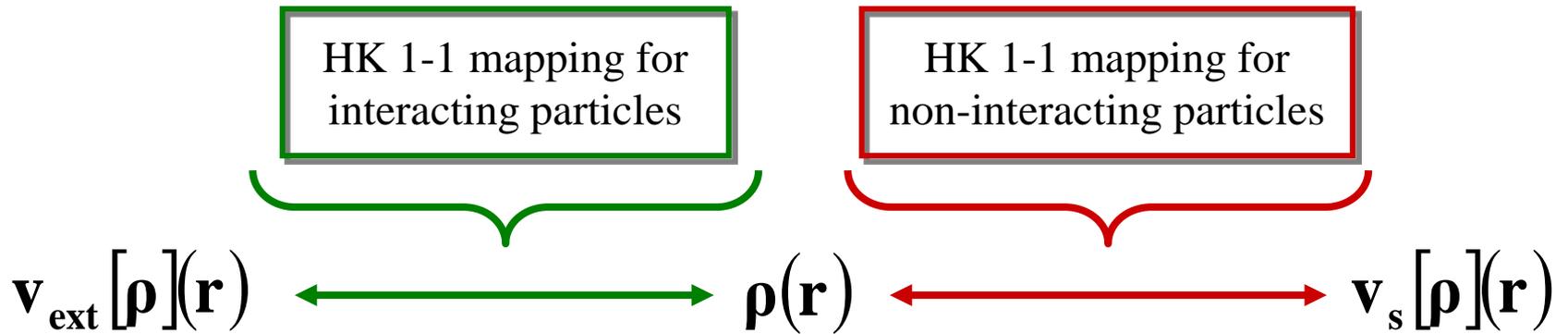
Kohn-Sham Theorem

Let $\rho_o(r)$ be the ground-state density of <u>interacting</u> electrons moving in the external potential $v_o(r)$. Then there exists a unique local potential $v_{s,o}(r)$ such that non-interacting particles exposed to $v_{s,o}(r)$ have the ground-state density $\rho_o(r)$, i.e.

$$\left(-\frac{\nabla^2}{2} + v_{s,o}(r) \right) \varphi_j(r) = \in_j \varphi_j(r) \; , \qquad \rho_o(r) = \sum_{\substack{j\,(\text{with} \\ \text{lowest}\,\in_j)}}^{N} \left| \varphi_j(r) \right|^2$$

proof: $\quad v_{s,o}(r) = v_s[\rho_o](r)$

Uniqueness follows from HK 1-1 mapping

Existence follows from V-representability theorem

<u>Define</u> $v_{xc}[\rho](r)$ **by the equation**

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

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

KS equations

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

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

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

Variational principle gives an additional property of v_{xc}:

$$\boxed{v_{xc}\left[\rho_o\right](r) = \left.\frac{\delta E_{xc}\left[\rho\right]}{\delta\rho(r)}\right|_{\rho_o}}$$

where $\quad E_{xc}\left[\rho\right] := F\left[\rho\right] - \frac{1}{2}\int\frac{\rho(r)\rho(r')}{\left|r-r'\right|}d^3r\,d^3r' - T_s\left[\rho\right]$

Consequence:
Approximations can be constructed either for $E_{xc}[\rho]$ or directly for $v_{xc}[\rho](r)$.

Proof: $E_{HK}[\rho] = T_s[\rho] + \int \rho(r) v_o(r) d^3r + E_H[\rho] + E_{xc}[\rho]$

$$0 = \frac{\delta E_{HK}[\rho]}{\delta \rho(r)}\bigg|_{\rho_o} = \frac{\delta T_s}{\delta \rho(r)}\bigg|_{\rho_o} + v_o(r) + v_H[\rho_o](r) + \frac{\delta E_{xc}}{\delta \rho(r)}\bigg|_{\rho_o}$$

δT_s = change of T_s due to a change $\delta\rho$ which corresponds to a change δv_s

$$= \delta \sum_j \int \varphi_j[\rho](r) \left(-\frac{\nabla^2}{2} \right) \varphi_j[\rho](r) d^3r$$

$$= \sum_j \delta \in_j - \int \delta\rho(r) v_s(r) d^3r - \int \rho(r) \delta v_s(r) d^3r$$

$$\underbrace{}$$

$$\sum_j \langle \varphi_i(r) | \delta v_s(r) | \varphi_j(r) \rangle$$

$$= -\int \delta\rho(r) v_s(r) d^3r \qquad \Rightarrow \qquad \boxed{\frac{\delta T_s}{\delta \rho(r)} = -v_s[\rho](r)}$$

$$\Rightarrow 0 = -v_s \left[\rho_o\right](r) + v_o(r) + v_H \left[\rho_o\right](r) + \left.\frac{\delta E_{xc}}{\delta\rho(r)}\right|_{\rho_o}$$

$$\Rightarrow v_{xc} \left[\rho_o\right](r) = \left.\frac{\delta E_{xc}}{\delta\rho(r)}\right|_{\rho_o}$$

Approximations of the xc functional

Three generations of approximations

1. Local Density Approximation (LDA):

$$E_{xc}[\rho] = \int d^3r \, e_{xc}^{hom}(\rho(r))$$

2. Generalized Gradient Approximation (GGA):

$$E_{xc}[\rho] = \int d^3r \, g_{xc}(\rho, \nabla\rho, \ldots)$$

3. Orbital functionals (Meta-GGA, hybrid functionals, hyper-GGA…)

$$E_{xc} = E_{xc}[\varphi_1 \ldots \varphi_N]$$

SUCCESSES OF LDA

Quantity	Typical deviation from expt
• Atomic & molecular ground state energies	$< 0.5\ \%$
• Molecular equilibrium distances	$< 5\ \%$
• Band structure of metals Fermi surfaces	few %
• Lattice constants	$< 2\ \%$

Generalized Gradient Approximation (GGA)

Detailed study of molecules (atomization energies)

32 molecules (all neutral diatomic with first-row atoms only + H_2)

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}**

  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**

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

- **band gaps too small:**

  $$E_{gap}^{LDA} \approx 0.5 \ E_{gap}^{exp}$$

- **Cohesive energies of bulk metals not satisfactory**

  in LDA overestimated
  in GGA underestimated

- **Wrong ground state for strongly correlated solids, e.g. FeO, La_2CuO_4 predicted as metals**

More "densities"

DENSITY-FUNTIONAL THEORY OF MAGNETIC SYSTEMS

Quantity of interest: Spin magnetization m(r)

In principle, Hohenberg-Kohn theorem guarantees that m(r) is a functional of the density: m(r) = m[ρ](r). In practice, m[ρ] is not known.

Include m(r) as basic variable in the formalism, in addition to the density ρ(r).

DFT for spin-polarized systems

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

$$\vec{m} = \text{spin magnetization}: \quad \hat{\vec{m}}(r) = -\mu_o \sum_{\alpha\beta} \hat{\psi}_\alpha^+(r)\vec{\sigma}_{\alpha\beta}\hat{\psi}_\beta(r)$$

HK theorem

$$\left[\rho(r),\vec{m}(r)\right] \xleftrightarrow{\text{1-1}} \left[\psi\right]$$

total energy:

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

universal

KS scheme

For simplicity:
$$\vec{B}(r) = \begin{pmatrix} 0 \\ 0 \\ B(r) \end{pmatrix} \quad , \quad \vec{m}(r) = \begin{pmatrix} 0 \\ 0 \\ m(r) \end{pmatrix}$$

$$\left(-\frac{\nabla^2}{2m} + \left[v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \right] \pm \mu_o \left[B(\mathbf{r}) - B_{xc}(\mathbf{r}) \right] \right) \varphi_\pm^j(\mathbf{r}) = \epsilon_\pm^j \varphi_\pm^j(\mathbf{r})$$

$$v_{xc}[\rho,m] = \delta E_{xc}[\rho,m]/\delta\rho \qquad B_{xc}[\rho,m] = \delta E_{xc}[\rho,m]/\delta m$$

$$\rho(\mathbf{r}) = \rho_+(\mathbf{r}) + \rho_-(\mathbf{r}) \; , \; m(\mathbf{r}) = \rho_+(\mathbf{r}) - \rho_-(\mathbf{r}) \; , \; \rho_\pm = \Sigma \left| \varphi_\pm^j \right|^2$$

$B \longrightarrow 0$ limit

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

Traditional DFT: $E_{xc}[\rho]$ $v_{xc}(r) = \dfrac{\delta E_{xc}[\rho]}{\delta \rho(r)}$

Traditional DFT: $E_{xc}[\rho]$ $v_{xc}(r) = \dfrac{\delta E_{xc}[\rho]}{\delta\rho(r)}$

Collinear SDFT: $E_{xc}[\rho,m]$ $v_{xc}(r) = \dfrac{\delta E_{xc}[\rho,m]}{\delta\rho(r)}$ $B_{xc}(r) = -\dfrac{\delta E_{xc}[\rho,m]}{\delta m(r)}$

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$$\vec{A}_{xc}(r) = c\,\dfrac{\delta E_{xc}[\rho,m,\vec{j_p}]}{\delta \vec{j_p}(r)}$$

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$$\vec{A}_{xc}(r) = c\,\dfrac{\delta E_{xc}[\rho,\vec{m},\vec{j_p}]}{\delta \vec{j_p}(r)}$$

Most general magnetic situation: KS equation of non-collinear Current-Spin –DFT (CSDFT):

$$\left[\frac{1}{2}\left(-i\vec{\nabla} + \frac{1}{c}\vec{A}_s(r) \right)^2 + v_s(r) + \mu_B \vec{\sigma}\cdot\vec{B}_s(r) \right]\Phi_i(r) = \varepsilon_i \Phi_i(r)$$

$$v_s(r) = v_0(r) + v_H(r) + v_{xc}(r) + \frac{1}{2c^2}\left[A_0^2(r) - A_s^2(r) \right]$$

$$\vec{B}_s(r) = \vec{B}_0(r) + \vec{B}_{xc}(r) \qquad \vec{A}_s(r) = \vec{A}_0(r) + \vec{A}_{xc}(r)$$

$$\rho(r) = \sum_{i=1}^{N}\Phi_i^\dagger(r)\Phi_i(r) \qquad \vec{m}(r) = -\mu_B \sum_{i=1}^{N}\Phi_i^\dagger(r)\vec{\sigma}\,\Phi_i(r)$$

$$\vec{j}_p(r) = \frac{1}{2i}\sum_{i=1}^{N}\left[\Phi_i^\dagger(r)\vec{\nabla}\Phi_i(r) - \left(\vec{\nabla}\Phi_i^\dagger(r)\right)\Phi_i(r) \right]$$

Functionals available:

Ordinary LSDA yields <u>GLOBAL</u> collinearity

$$\vec{B}_{xc}(r) = \begin{pmatrix} 0 \\ 0 \\ B_{xc}(r) \end{pmatrix} \qquad \vec{m}(r) = \begin{pmatrix} 0 \\ 0 \\ m(r) \end{pmatrix}$$

$\vec{B}_{xc}, \vec{m}$ parallel to $\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$ everywhere in space

$$\int \rho(r)v(r)d^3r - \int \vec{m}(r) \cdot \vec{B}(r)d^3r$$

$$\equiv \sum_{\alpha,\beta=\uparrow\downarrow} \rho_{\alpha,\beta}(r)v_{\alpha,\beta}(r)$$

$\{\rho(r),\vec{m}(r)\}$: 4 independent functions

$\rho_{\alpha\beta}$ is Hermitian $\Rightarrow$ 4 independent functions

<u>Non-collinear LSDA</u>:
(Kübler, Sandratskii '80s)

$\vec{r}$ given point in space:

① Find unitary matrix U(r) such that

$$U^+(r)(\rho_{\alpha\beta})U(r) = \begin{pmatrix} n_\uparrow(r) & 0 \\ 0 & n_\downarrow(r) \end{pmatrix}$$

② Calculate $v_{xc}^\uparrow(r)$ and $v_{xc}^\downarrow(r)$ from $\{n_\uparrow, n_\downarrow\}$
    using the normal LSDA expressions

③ $(v_{xc}^{\alpha\beta}) = U(r)\begin{pmatrix} v_{xc}^\uparrow(r) & 0 \\ 0 & v_{xc}^\downarrow(r) \end{pmatrix}U^+(r)$
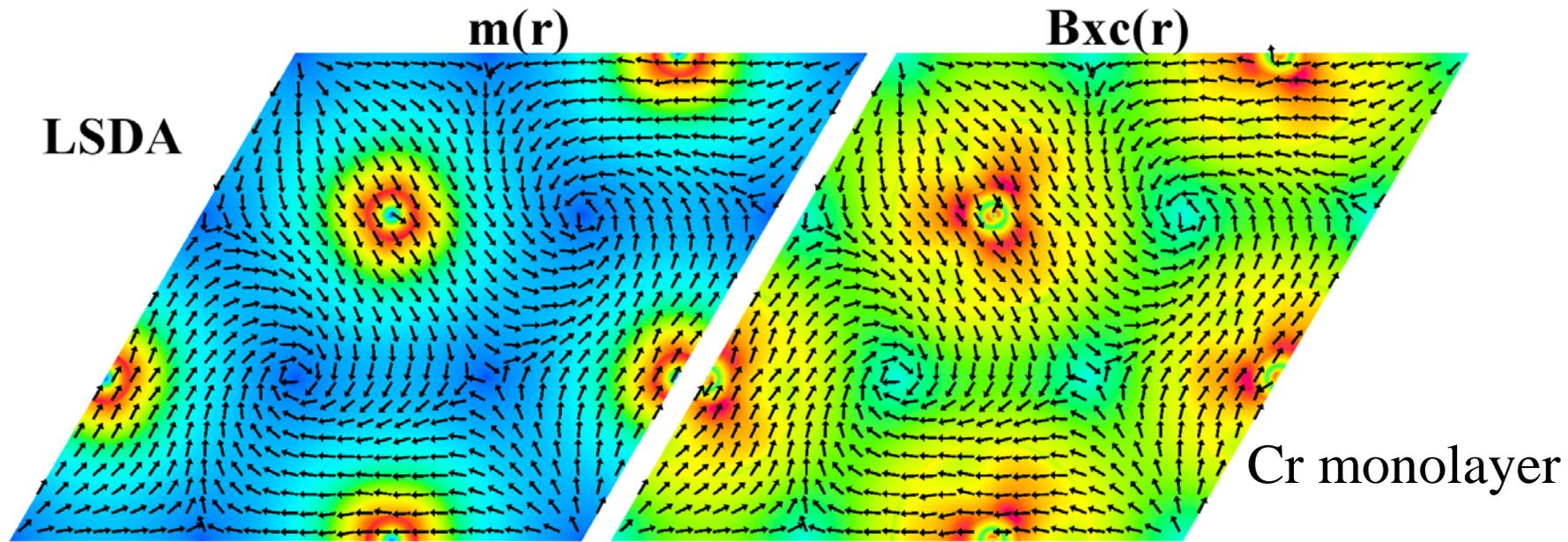
m(r) Bxc(r)

LSDA

Cr monolayer

S. Sharma, J.K. Dewhurst, C. Ambrosch-Draxl, S. Kurth, N. Helbig, S. Pittalis, S. Shallcross, L. Nordstroem E.K.U.G., Phys. Rev. Lett. 98, 196405 (2007)

m(r)   **Bxc(r)**

LSDA

Cr monolayer
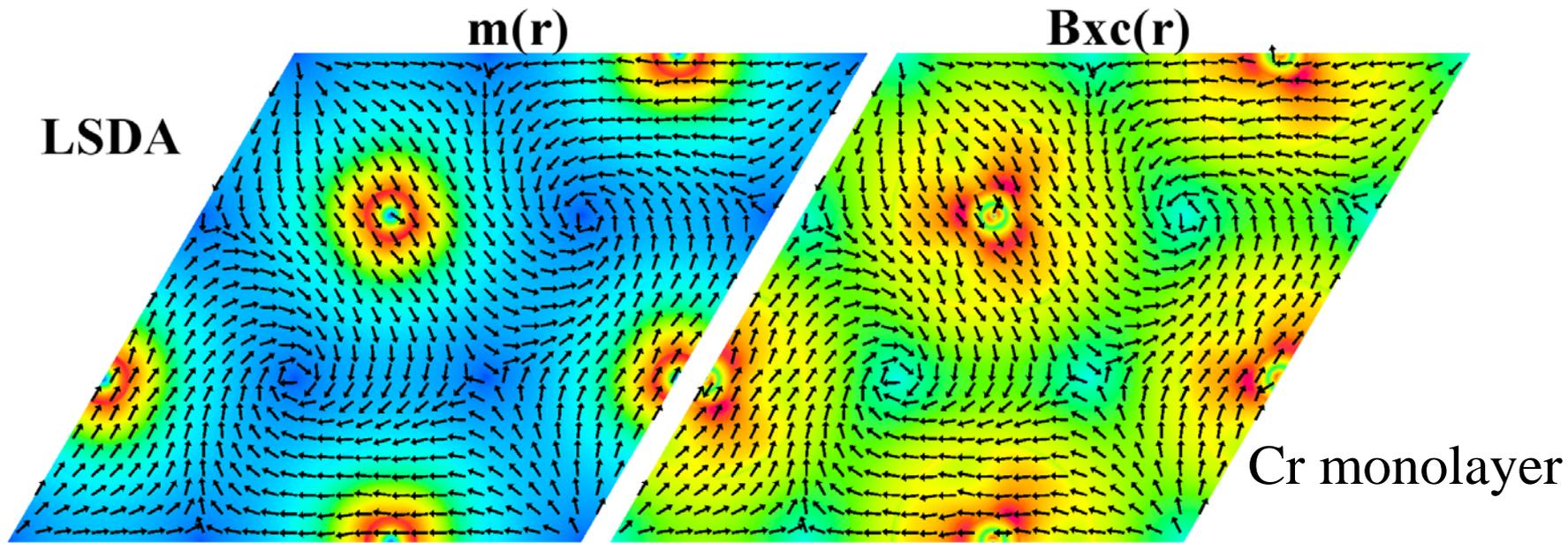
S. Sharma, J.K. Dewhurst, C. Ambrosch-Draxl, S. Kurth, N. Helbig, S. Pittalis, S. Shallcross, L. Nordstroem E.K.U.G., Phys. Rev. Lett. 98, 196405 (2007)

in this approximation $\vec{B}_{xc}(r)$ and $\vec{m}(r)$ may change their direction in space, but locally they are always parallel

Why is that important?

Ab-initio description of spin dynamics:

microscopic equation of motion (following from TDSDFT)

$$\dot{\vec{m}}(\vec{r},t) \; = \; \vec{m}(\vec{r},t) \times \vec{B}_{XC}(\vec{r},t) \; - \; \vec{\nabla} \cdot \overset{\leftrightarrow}{J}_S(\vec{r},t) + SOC$$

in absence of external magnetic field

Consequence of local collinearity: $m \times B_{xc} = 0$:
→ possibly wrong spin dynamics (e.g. spurious
    dynamics in ground state with non-vanishing J_s)

Construction of a novel GGA-type functional

Traditional LSDA: Start from uniform electron gas in collinear magnetic state. Determine $e_{xc}(n,m)$ from QMC or MBPT and parametrize this function to use in LSDA.

New non-collinear functional: Start from spin-spiral phase of e-gas. Determine $e_{XC}[n,\vec{m}]$ from MBPT and parametrize $e_{XC}[n,\vec{m}]$ to use as non-collinear GGA.

F.G. Eich and E.K.U. Gross, Phys. Rev. Lett. 111, 156401 (2013)
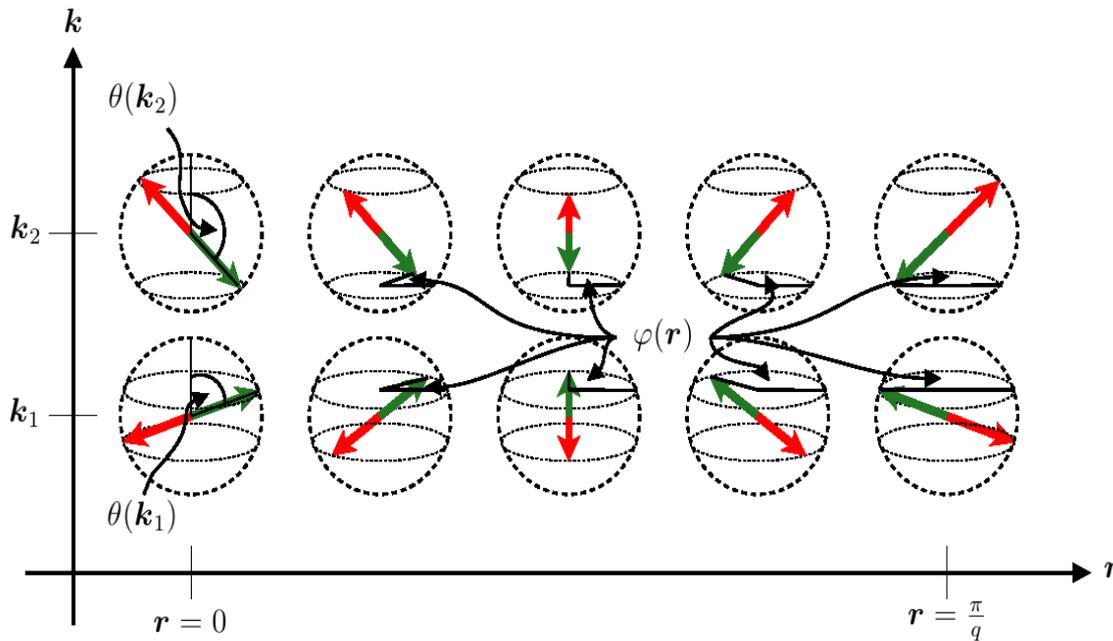
Illustration of spin spiral waves along one spatial coordinate for two different choices of wavevector $q=k_{1/2}$.

Magnetisation of a spin-spiral state in the uniform electron gas

$$m(\mathbf{r}) = m \begin{pmatrix} s\cos(\mathbf{q}\cdot\mathbf{r}) \\ s\sin(\mathbf{q}\cdot\mathbf{r}) \\ \sqrt{1-s^2} \end{pmatrix} \qquad \varepsilon_{xc}^{SSW} = \varepsilon_{xc}^{SSW}(n,m,q,s)$$

$$E_{xc}^{GGA}\left[n,\vec{m}\right]=\int d^3r\,n(\mathbf{r})\,\varepsilon_{xc}^{SSW}\left(n(\mathbf{r}),m(\mathbf{r}),q(\mathbf{r}),s(\mathbf{r})\right)$$

$$s^2(\mathbf{r})=\frac{D_T^2(\mathbf{r})}{D_T^2(\mathbf{r})+m^4(\mathbf{r})d_T(\mathbf{r})}\qquad q^2(\mathbf{r})=\frac{D_T^2(\mathbf{r})+m^4(\mathbf{r})d_T(\mathbf{r})}{m^4(\mathbf{r})D_T(\mathbf{r})}$$

$$D_T(\mathbf{r})=\left|\vec{m}(\mathbf{r})\times\left(\nabla\otimes\vec{m}(\mathbf{r})\right)\right|^2\qquad d_T(\mathbf{r})=\left|\vec{m}(\mathbf{r})\times\left(\nabla^2\vec{m}(\mathbf{r})\right)\right|^2$$

F.G. Eich and E.K.U. Gross, Phys. Rev. Lett. 111, 156401 (2013)

$\mathbf{m} \times \mathbf{B}_{xc}$

in non-coll. functional
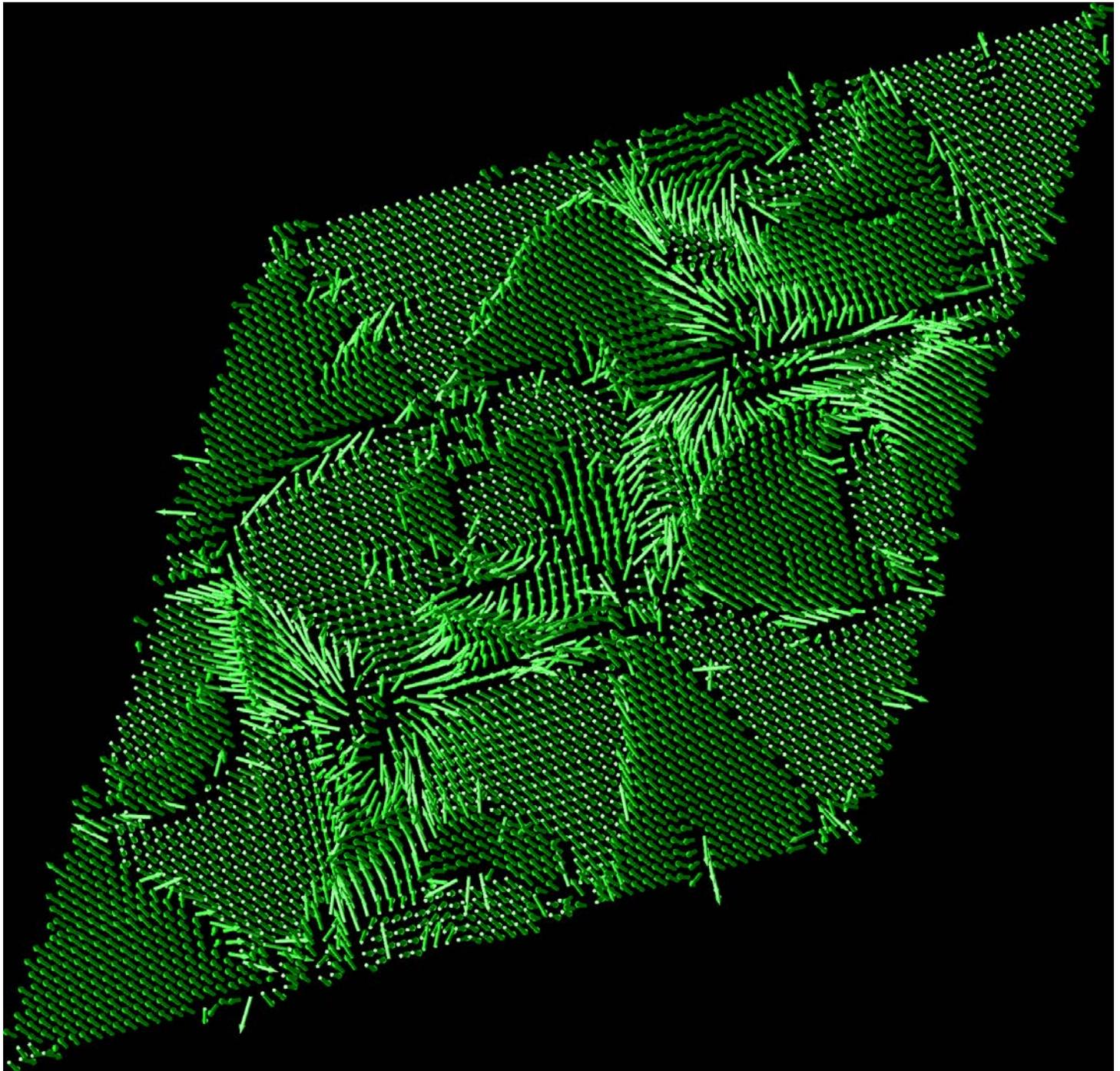
EXTENSIONS

1. Relativistic systems

KS equations:

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

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

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

KS orbitals are Dirac spinors

Local spin-density approximation and EXX-OPM available

2. Finite temperature

KS equations:

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

$$\rho(r) = \sum_j \underbrace{f_T(\varepsilon_j)}_{\text{Fermi distribution}} \cdot |\varphi_j(r)|^2$$

3. Superconductors

$$E = E[\rho, \chi]$$

Superconductig order parameter

DENSITY-FUNTIONAL THEORY OF CONVENTIONAL SUPERCONDUCTORS

BASIC IDEA:

- **Include order parameter, χ , characterising superconductivity as additional "density"**
  L.N. Oliveira, E.K.U.G., W. Kohn, PRL **60**, 2430 (1988)

- **Include N-body density matrix, Γ, of the nuclei as additional "density"**
  T. Kreibich, E.K.U.G., PRL **86**, 2984 (2001)

Electronic KS equation

$$\left(-\frac{\nabla^2}{2} - \mu + v_s[\rho,\chi,\Gamma](r)\right)u(\boldsymbol{r}) + \int \Delta_s[\rho,\chi,\Gamma](r,r')\, v(\boldsymbol{r}')d^3\boldsymbol{r}' = Eu(\boldsymbol{r})$$

$$\int \Delta_s^*[\rho,\chi,\Gamma](\boldsymbol{r},\boldsymbol{r}')\, u(\boldsymbol{r}')d^3\boldsymbol{r}' - \left(-\frac{\nabla^2}{2} - \mu + v_s[\rho,\chi,\Gamma](\boldsymbol{r})\right)v(\boldsymbol{r}) = Ev(\boldsymbol{r})$$

Nuclear KS equation

$$\left(\sum_{\alpha=1}^{N_n} -\frac{\nabla_\alpha^2}{2M_\alpha} + W_s[\rho,\chi,\Gamma](\underline{\underline{R}})\right)\psi(\underline{\underline{R}}) = E\psi(\underline{\underline{R}})$$

3 KS potentials: $\mathbf{v_s}$ $\mathbf{\Delta_s}$ $\mathbf{W_s}$

KS theorem: There exist functionals $v_s[\rho,\chi,\Gamma]$, $\Delta_s[\rho,\chi,\Gamma]$, $W_s[\rho,\chi,\Gamma]$, such that the above equations reproduce the exact densities of the interacting system

No approximation yet!

In a solid, the ions remain close to their equilibrium positions:

$$W_s\left(\underline{\underline{R}}\right) = W_s\left(\underline{\underline{R}}_0 + \underline{\underline{U}}\right)$$

$$= W_s\left(\underline{\underline{R}}_0\right) + \underbrace{\left(\underline{\underline{\nabla}}\, W_s\right)\Big|_{\underline{\underline{R}}_0}}_{} \cdot \underline{\underline{U}}$$

0 (because forces vanish at equilibrium positions)

$$+ \frac{1}{2}\sum_{ij}^{3}\sum_{\mu\nu}^{N_n}\left(\partial_i^{\mu}\partial_j^{\nu}W_s(\underline{\underline{R}})\right)\Big|_{\underline{\underline{R}}_o} U_i^{\mu}U_j^{\nu} + \cdots$$

$$\Rightarrow \quad \hat{H}_{n,KS} = \cdots = \sum_q \Omega_q\left(\hat{b}_q^{+}\hat{b}_q + \frac{3}{2}\right) + O\left(U^3\right)$$
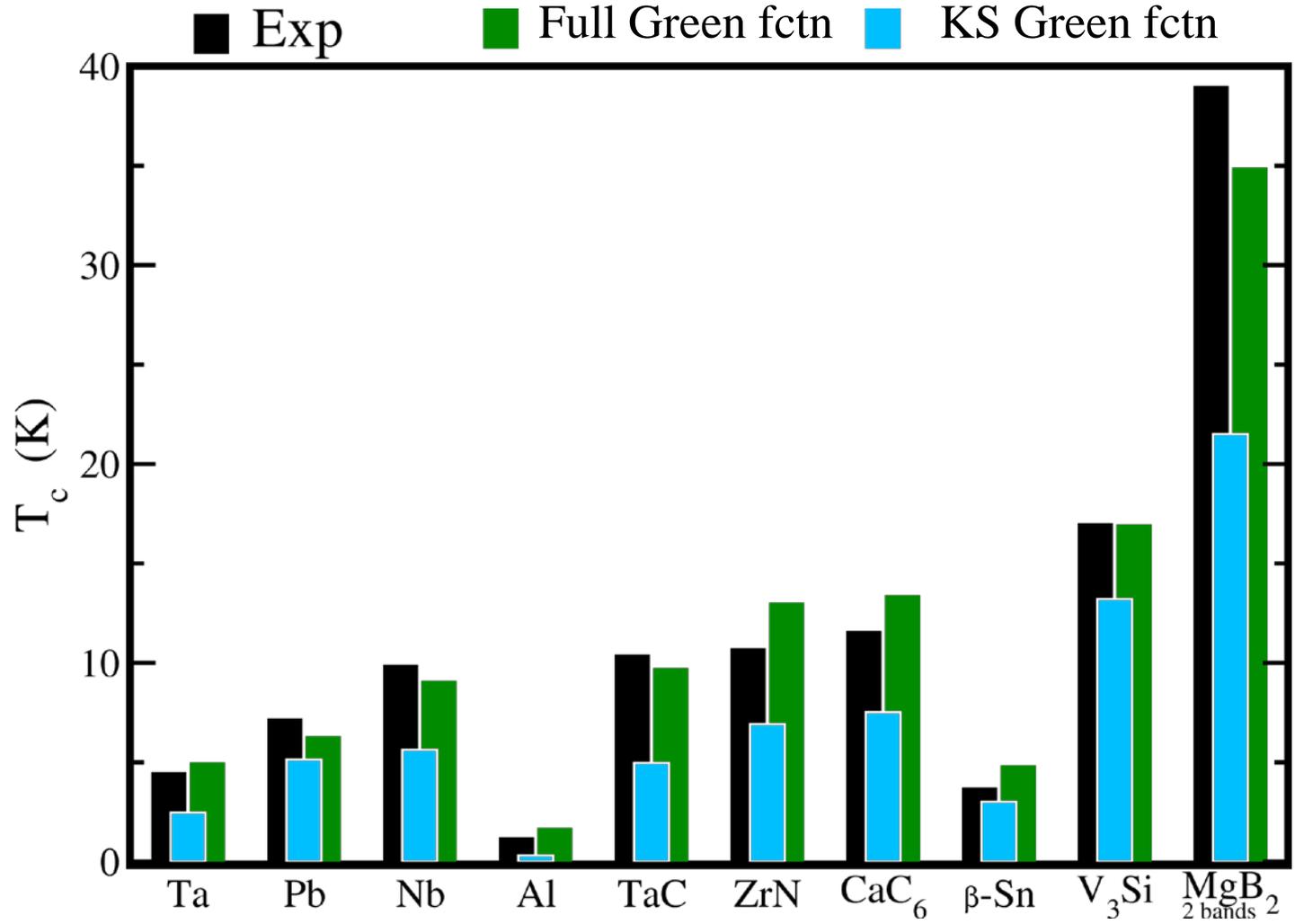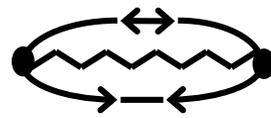
	Isotope effect:		$T_c \propto M^{-\alpha}$

	Calculations		Experiment	
Pb	0.47		0.47	
Mo	0.37		0.33	

The deviations from BCS value
α=0.5 are correctly described

Jump of specific heat at T_c

	Theory	Experiment
Pb	2.93	3.57-3.71
Nb	2.87	2.8-3.07
Ta	2.64	2.63
Al	2.46	2.43

MgB_2

MgB₂ — MgB_2

$T_c = 39.5\ K$

2-D σ-bonding hole pockets
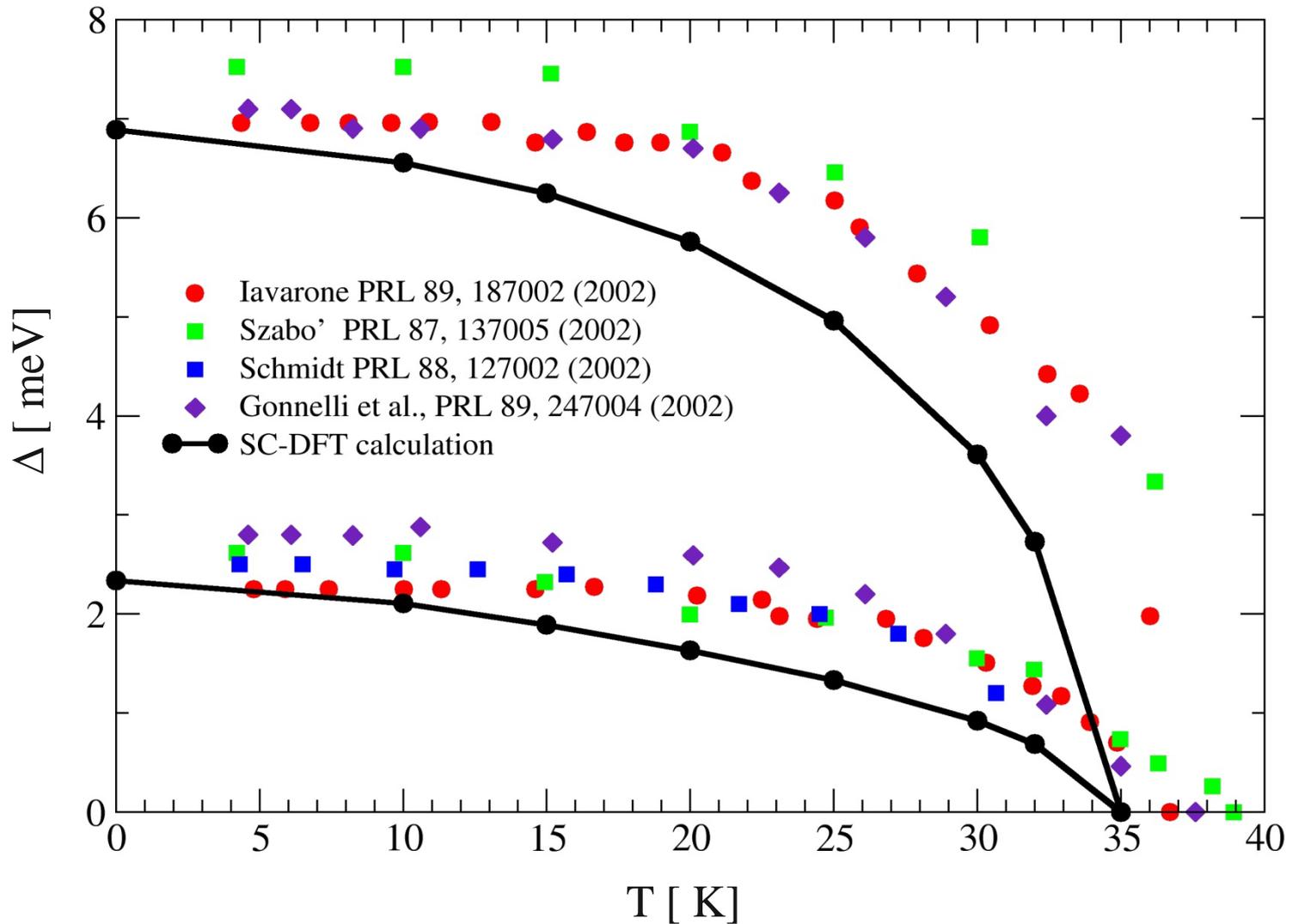**3-D π and π* Fermi surfaces**
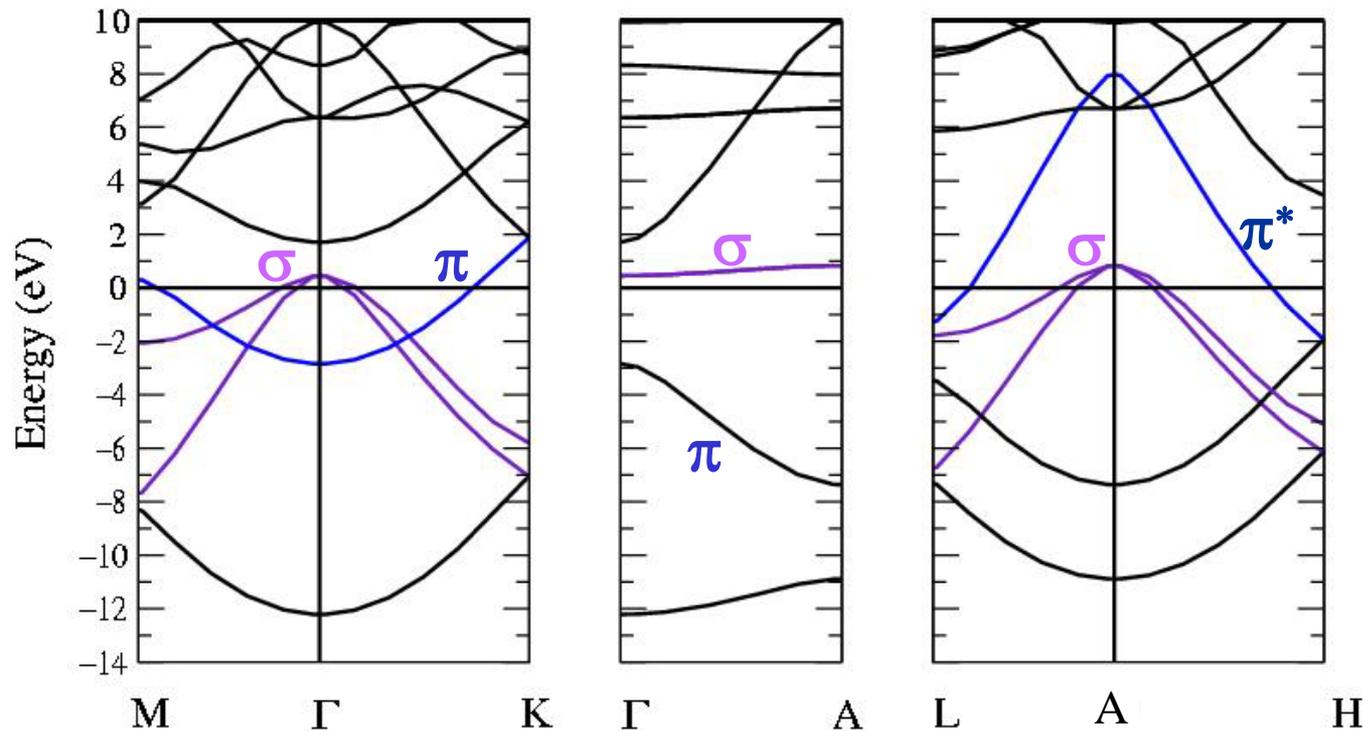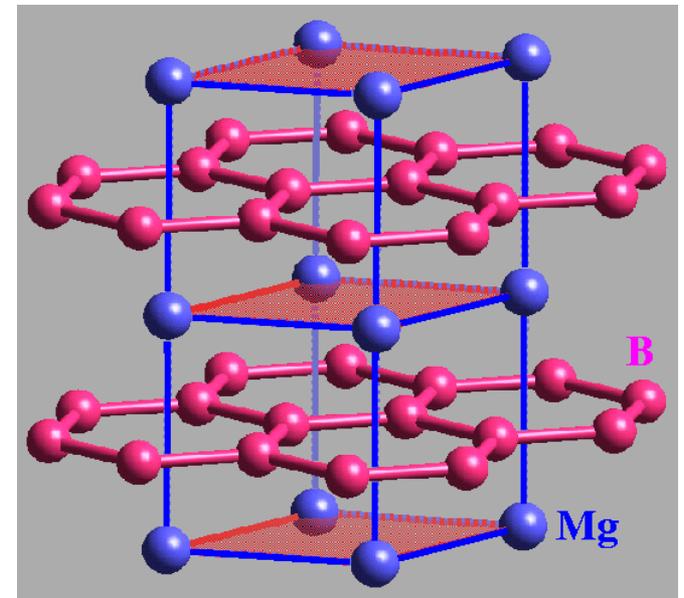
Fermi Surface of MgB$_2$
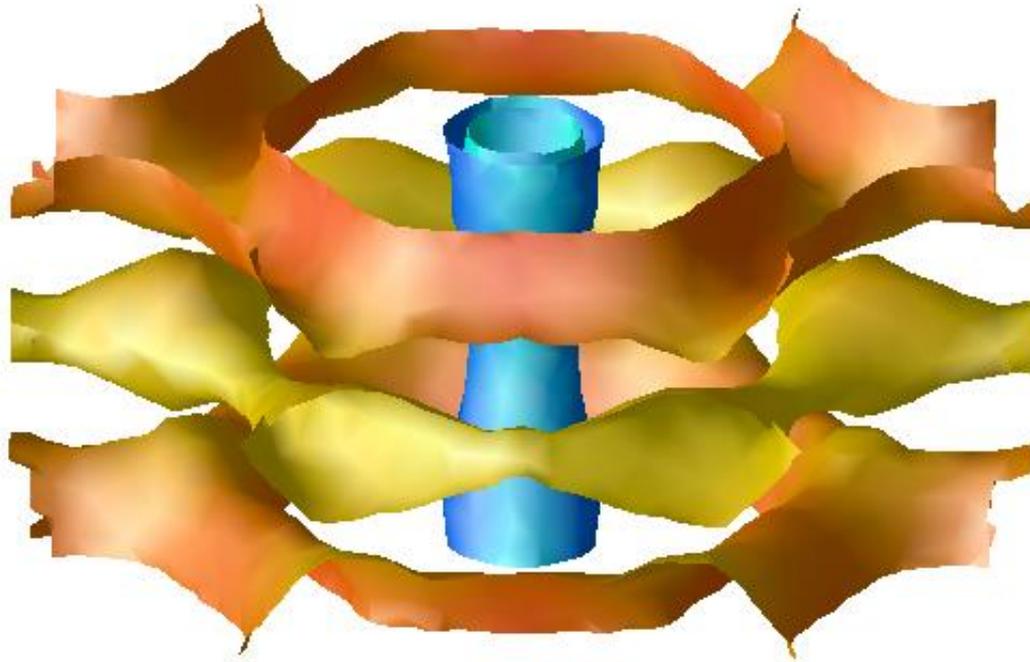
Specific heat of MgB₂
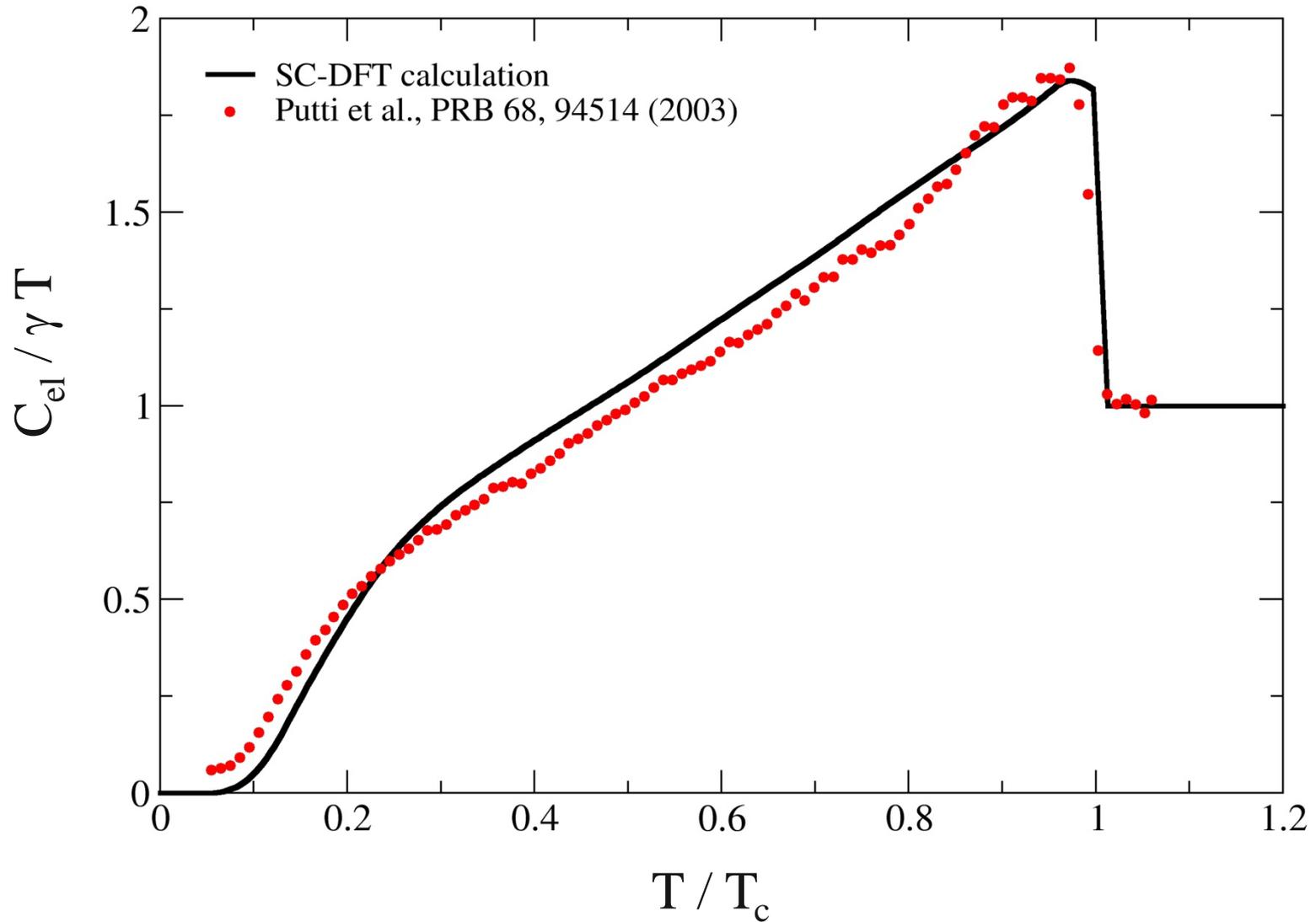
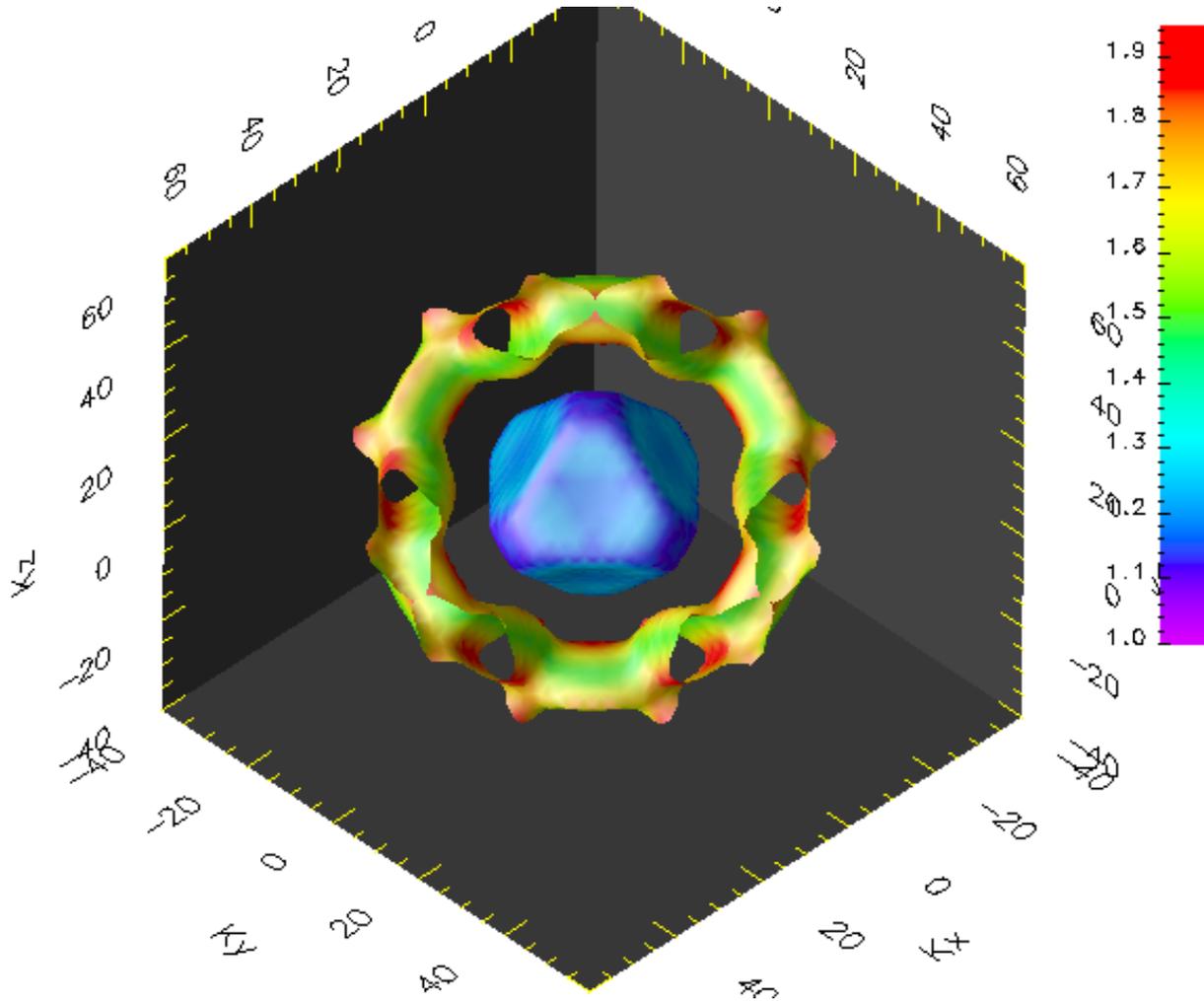**A. Floris et al, Phys. Rev. Lett. <u>94</u>, 037004 (2005)**

MgB₂
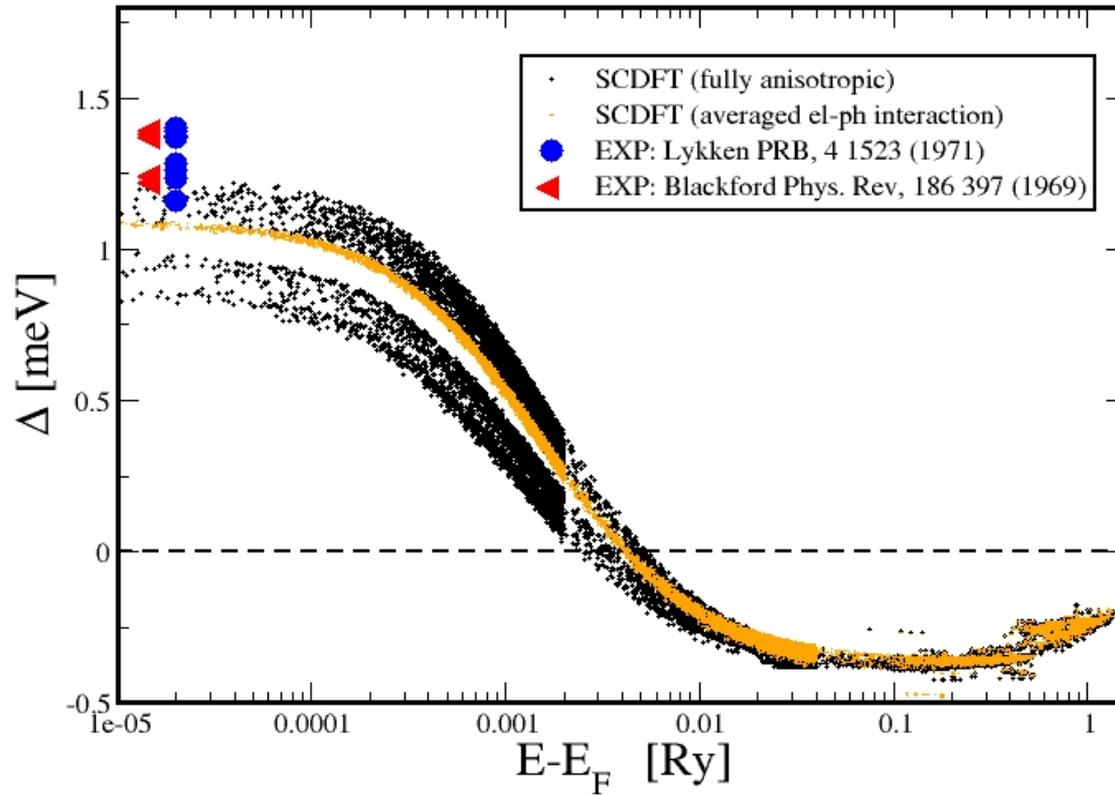

A. Floris et al, Phys. Rev. Lett. 94, 037004 (2005)
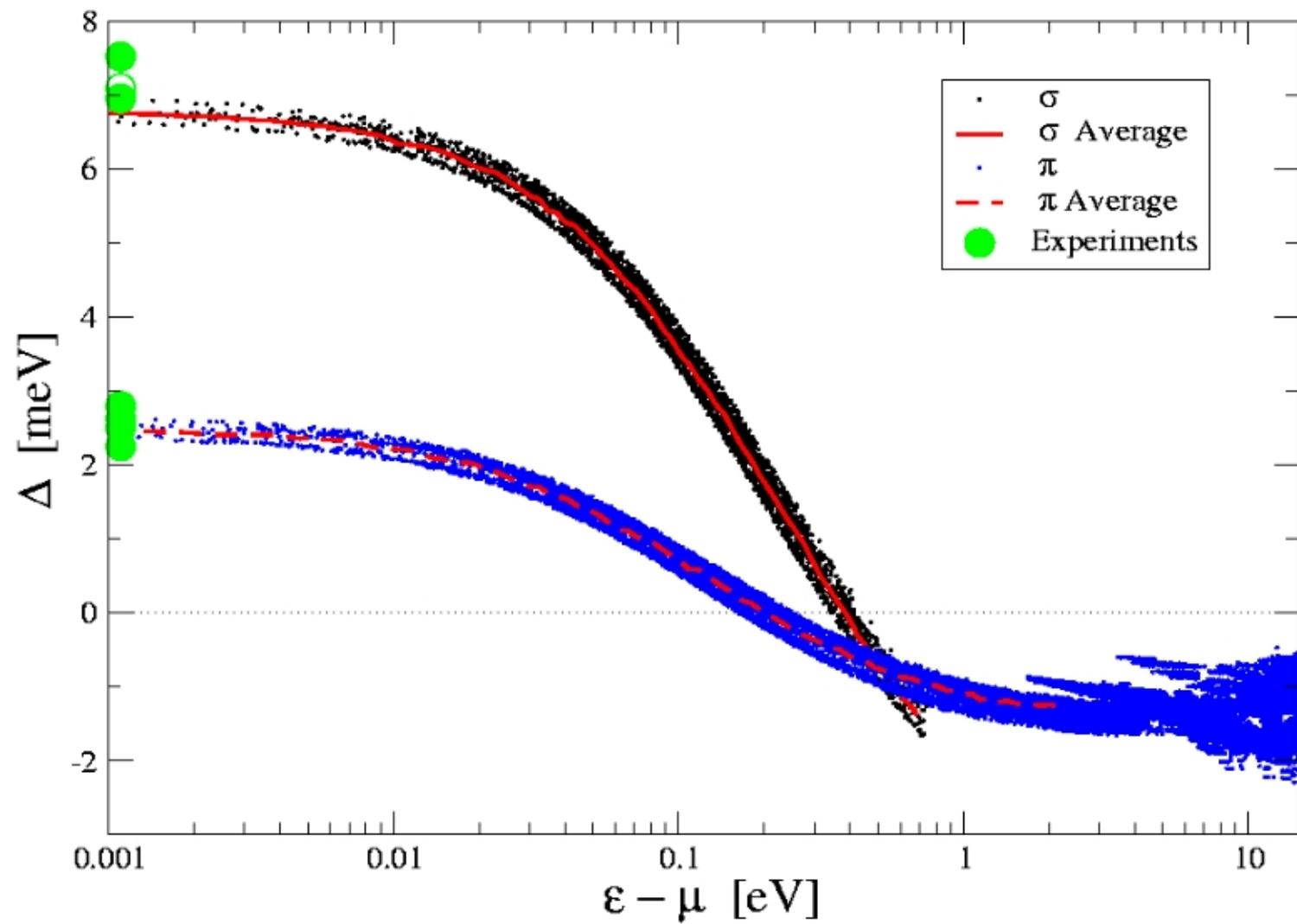
Pb: Gap on the Fermi surface

Pb   (Gap at T = 0.01 K)