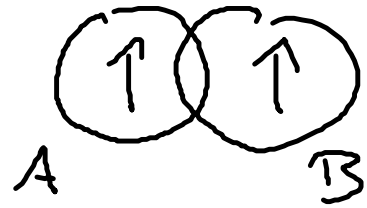
Magnetism: final episode

recap direct exchange:



$S=0$ antiparallel spins $\uparrow\downarrow - \downarrow\uparrow$

$$|\phi\rangle_{singlet} = |\psi_{orb,sym}\rangle |\chi_0\rangle$$

$$= \frac{1}{\sqrt{2(1+S^2)}}\left[\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)\right]|\chi_0\rangle$$

$S=1$ parallel spins $\uparrow\uparrow$ or $\downarrow\downarrow$ or $\uparrow\downarrow + \downarrow\uparrow$

$$|\phi\rangle_{triplet} = |\psi_{orb,anti}\rangle |\chi_{1,\mu}\rangle$$

$$= \frac{1}{\sqrt{2(1-S^2)}}\left[\phi_A(1)\phi_B(2) - \phi_A(2)\phi_B(1)\right]|\chi_{1,\mu}\rangle$$

to know which state is present, consider energies:

$$J := E_S - E_T$$

E_S: antiparallel spins; E_T: parallel spins

$$\approx \frac{2}{1-S^4}\left(\langle\phi_A(1)\phi_B(2)|\frac{1}{|\underline{r}-\underline{r}'|}|\phi_A(2)\phi_B(1)\rangle \right.$$ (exchange)

$$\left. - S^2\langle\phi_A(1)\phi_B(2)|\frac{1}{|\underline{r}-\underline{r}'|}|\phi_A(1)\phi_B(2)\rangle\right)$$ (Coulomb)

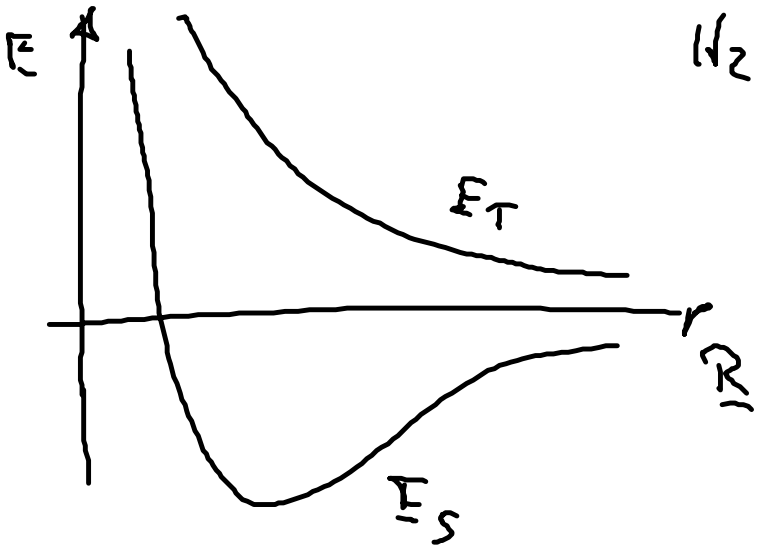
for $E_S < E_T$ singlet ground state antiparallel spins

$J < 0$ $\Longrightarrow$ antiferromagnetic

$E_S > E_T$ triplet ground state parallel spins

$J > 0$ $\Longrightarrow$ ferromagnetic

this is why it makes sense to define $J = E_S - E_T$



for H_2 E_S always lowest because

$\Psi_{orb}^T = |\Psi_{orb, anti}>$

↑

has a node between atoms

- in general E_T can be lower than E_S

to use definition

$$J = E_S - E_T$$

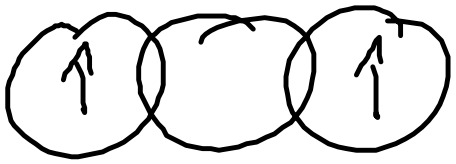
or $J = E_{AFM} - E_{FM}$

can calculate this in DFT

in similar vein:

look at more complex interactions

e.g.



Super exchange

Bandstructure considerations (continuation from yesterday)

- we've seen throughout lecture that DFT gives a good description of many materials → mostly non-magnetic so far
- let's generalize to spin dependence:

$$E = T[n^\uparrow, n_\downarrow] + E^{e\text{-}i}[n] + E^{i\text{-}i}[n] + E^{H}[n] + E^{xc}[n^\uparrow, n^\downarrow]$$

spin dependent

$\Rightarrow$ competition between kinetic energy and exchange-correlation

Simple example:

spin-polarized LDA : SLDA

$$m(\underline{r}) = \left(n^\uparrow(\underline{r}) - n^\downarrow(\underline{r})\right)/\mu_B \qquad \mu = \int d\underline{r}\, m(\underline{r})$$

m: magnetization density

μ: magnetic moment

μ/μ_B	SLDA	exp.
fcc	2.1	2.2
Co	1.6	1.7
Ni	0.6	0.6

- Surprisingly good!
- normal pieces of electronic structure theory (T, E_H, E_{xc}) are enough to trigger FM

DOS:

- real DOS is structured → peaks
- but otherwise $N^{\uparrow}(\epsilon) \approx N^{\downarrow}(\epsilon + \text{shift})$

$$V_{xc}^{\uparrow\downarrow}(\underline{r}) = \frac{\delta E^{\uparrow\downarrow}[n(\underline{r}), m(\underline{r})]}{\delta n(\underline{r})} \approx V_{xc}^{0}(\underline{r}) + m(\underline{r})\,\hat{V}(\underline{r}) + \dots$$

for slowly varying $n(\underline{r})$, $m(\underline{r})\hat{V}(\underline{r})$ also varies slowly

$$\approx V_{xc}^{0}(\underline{r}) \pm \frac{1}{2} J M$$

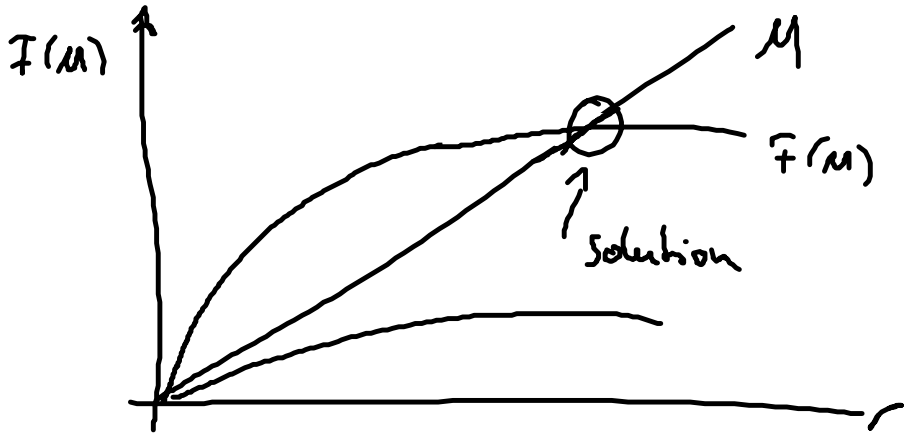
Stoner parameter

$$\Rightarrow \epsilon_i^{\uparrow\downarrow} = \epsilon_i^{0} \pm \frac{1}{2} J M$$

DOS is given by non-polarized DOS (N^0) but shifted

$$M = \int_{}^{\epsilon_F} d\epsilon \left[N^0(\epsilon + \tfrac{1}{2} J M) - N^0(\epsilon - \tfrac{1}{2} J M) \right] =: \mp(M)$$

graphical solution:



we know $F(M)$ is monotonic

Solution only exists if $F'(0) > 1$

$$\Rightarrow \left.\frac{\partial F}{\partial M}\right|_{M=0} = \boxed{J N^2(\epsilon_F) > 1}$$

Stoner criterion

- we can also compute J in DFT using e.g. linear response
- reassuringly only Fe, Co, Ni fullfil Stoner criterion
  but Ca, Sc, Pd come very close

Outlook beyond LDA / GGA:

- they do not capture all magnetism
  - Lo subtle balance between T and E_{xc}
    - but self-interaction
- temperature dependence is not included
- common fix: get parameters for „model" Hamiltonians

e.g. Heisenberg, Ising, etc.

Domain walls

our theories explain magnetism in:

RE: localized-f electrons, atomic like magnetism (in Compounds e.g. oxides)

or exchange coupling (in metals)

TM: itinerant d-electrons, exchange + band structure

- two puzzling exp. facts:
  - not every FM sample shows net macroscopic magnetization below Curie temp.
  - magnetization can be switched by external fields, despite internal fields of $\sim 10^3$ Tesla

explanation:

two different forces:

- exchange force: short ranged and strong
- magnetic dipole: long ranged and weak

$$U^d \sim \frac{1}{r^3}$$

(U^d: dipolar energy)

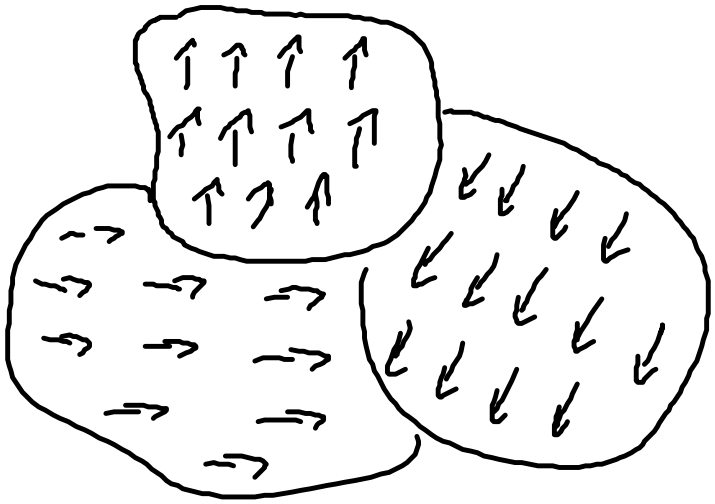
if all spins point in the same direction

U^d can still diverge

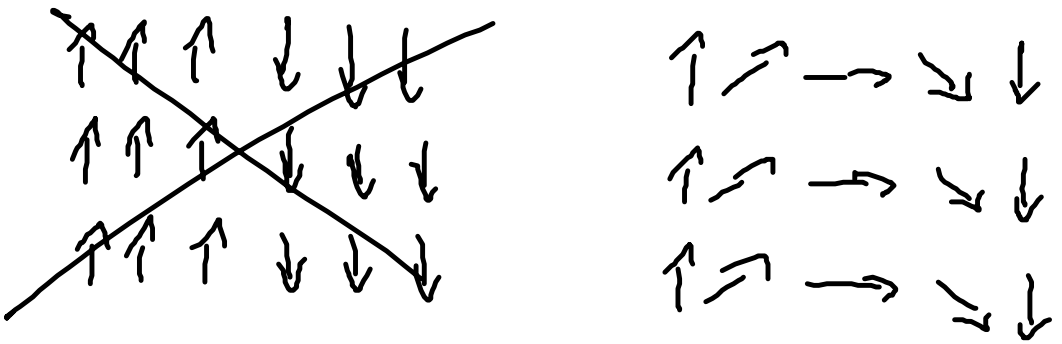
↳ instead system lowers energy by rotating spins

↳ but exchange interaction favors alignment

=> domain formation

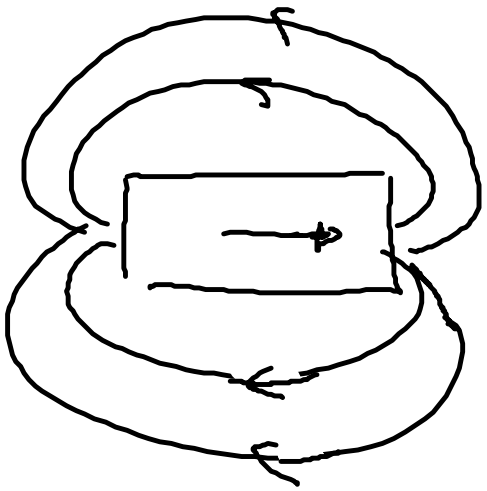


but domain walls are not abrupt but smooth



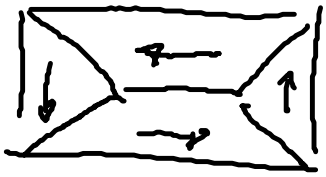
applied fields can therefore smoothly move domain walls

- much cheaper than flipping spins

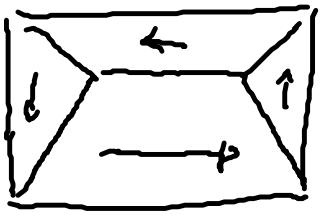


all spins are aligned

→ magnetic field extends outside material

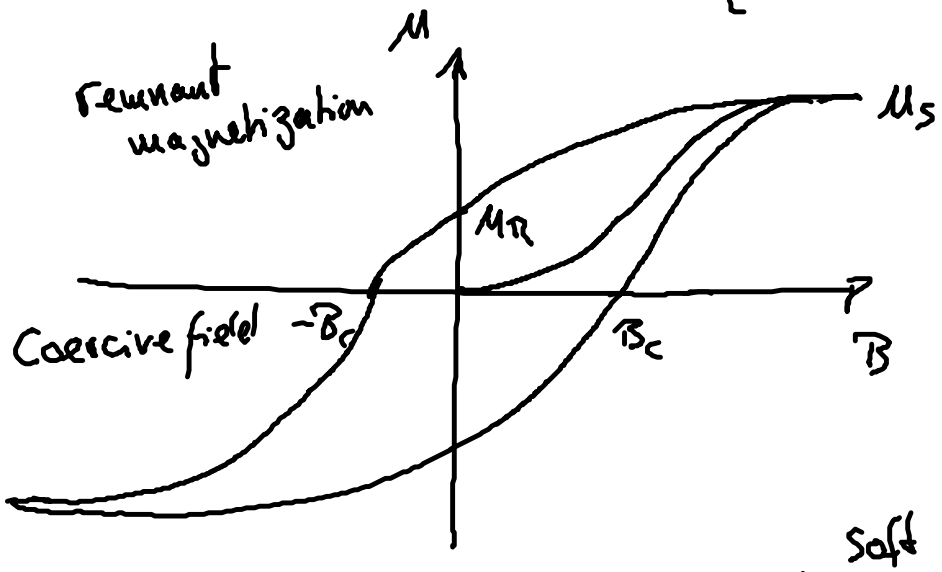


Zero net magnetization

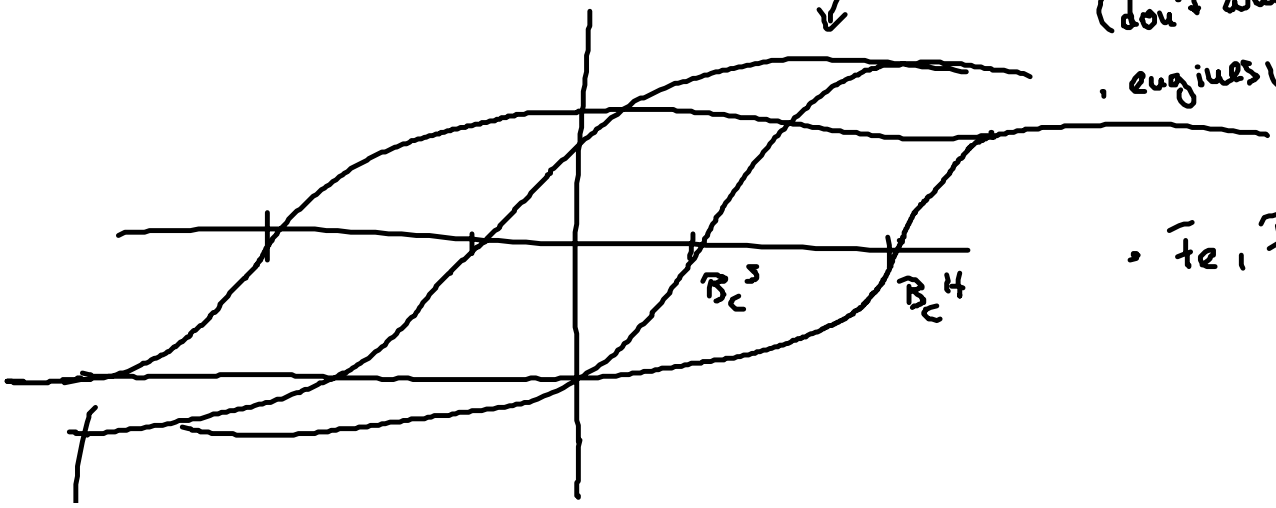


domain walls shift
– develop magnetization

↙ hysteresis loop of FM



Soft magnet → small B_c
. used for fast switching (don't want high field)
. engines, transformers, switches
. Fe, Fe-Ni, Fe-Co



hard magnet → large B_c

- prevent demagnetization of magnetic state
- magnetic storage
- Fe oxide, Cr oxide