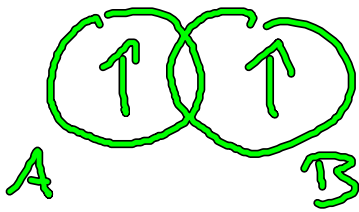


Magnetism: final episode

recap direct exchange:



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

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

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

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

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

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

to know which state is present, consider energies:

$$J := E_S - E_T$$

\nearrow anti parallel spins
 \nwarrow parallel spins
 \swarrow exchange

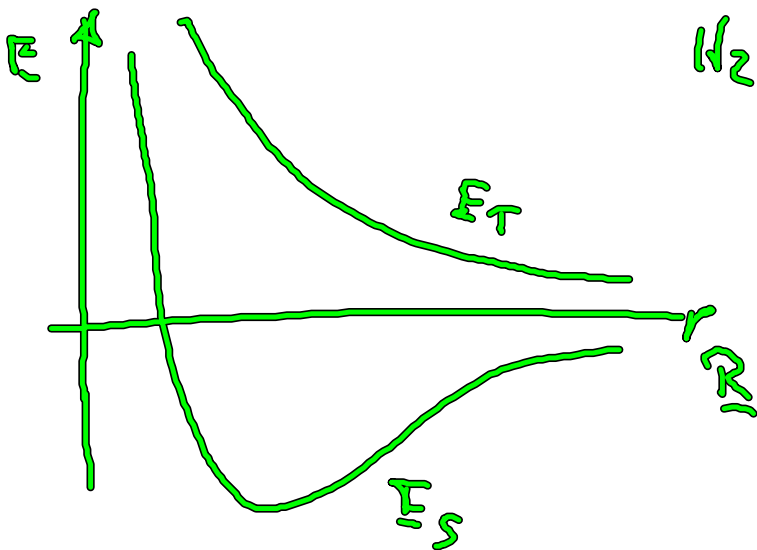
$$\approx \frac{2}{1-S^4} \left(\langle \phi_A(1)\phi_B(2) | \frac{1}{|\underline{r}_- - \underline{r}'_1|} | \phi_A(2)\phi_B(1) \rangle \right. \\ \left. - S^2 \langle \phi_A(1)\phi_B(2) | \frac{1}{|\underline{r}_- - \underline{r}'_1|} | \phi_A(1)\phi_B(2) \rangle \right)$$

\swarrow Coulomb

for $E_S < E_T$ singlet ground state antiparallel spins
 $J < 0 \implies$ antiferromagnetic

$E_S > E_T$ triplet ground state parallel spins
 $J > 0 \implies$ ferromagnetic

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



for H_2 E_S always
 lowest because

$$\psi_{orb}^T = |\psi_{orb, anti}\rangle$$

has a node between atoms

- in general E_T can be lower than E_S
 to use definition

$$J = E_S - E_T$$

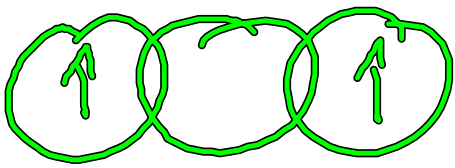
$$\text{or } J = E_{AFM} - E_{FM}$$

can calculate this in DFT

in similar vein:

look at more complex interactions

e.g.

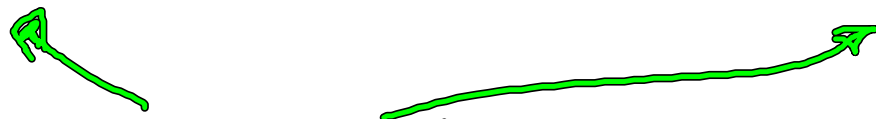


Super exchange

Band structure 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:

$$E = T[n^\uparrow, n^\downarrow] + E^{e-i}[n] + E^{h-i}[n] + E^H[n] + E^K[n^\uparrow, n^\downarrow]$$



spin dependent

⇒ competition between kinetic energy and exchange-correlation

Simple example:

spin-polarized LDA : SLDA

$$m(\underline{r}) = (n^\uparrow(\underline{r}) - n^\downarrow(\underline{r})) / \mu_B$$

↑ magnetization density

$$\mu = \int d\underline{r} m(\underline{r})$$

→ magnetic moment

μ/μ_B	SLDA	exp.
$\overline{\tau}_e$	2.1	2.2
C_0	1.6	1.7
N_i	0.6	0.6

- Surprisingly good
- normal pieces of electronic structure theory ($\overline{\tau}$, \overline{E}_4 , \overline{E}_{xc}) are enough to trigger FM

DOS:

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

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

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

↑
Stoner parameter

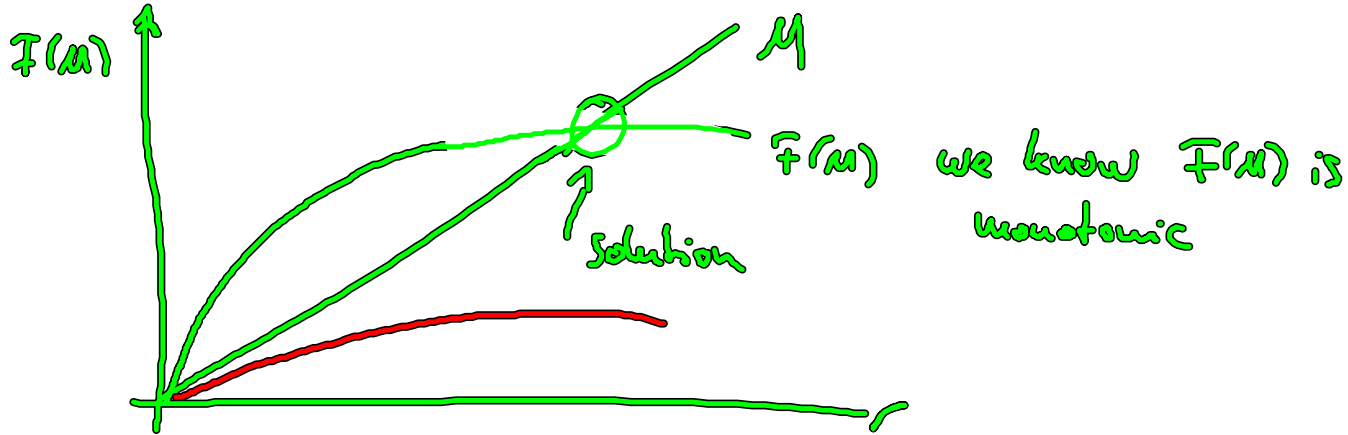
for slowly varying $\overline{m}(\underline{r})$
 $\overline{m}(\underline{r}) \tilde{V}(\underline{r})$ also varies slowly

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

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

$$M = \int_{\epsilon_F} d\epsilon [N^0(\epsilon + \frac{1}{2} J \mu) - N^0(\epsilon - \frac{1}{2} J \mu)] =: \overline{\tau}(\mu)$$

graphical solution:



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

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

Stoner criterion

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

Outlook beyond LDA/GGA:

- they do not capture all magnetism
↳ 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}

IM: 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

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

↑
dipolar energy

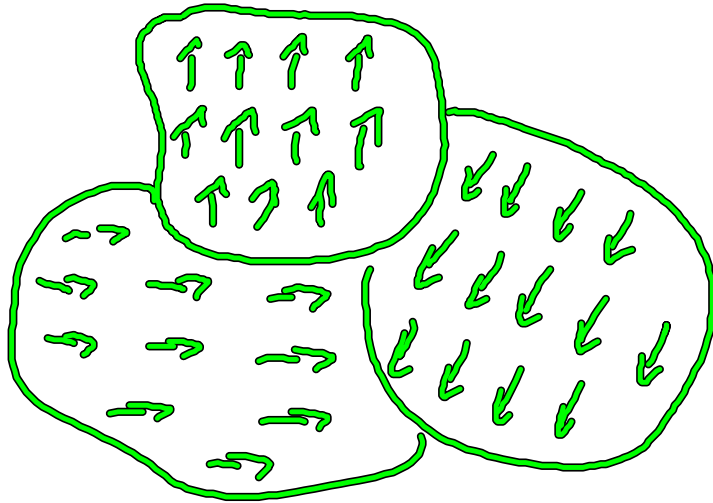
if all spins point in the same direction

U^d can still diverge

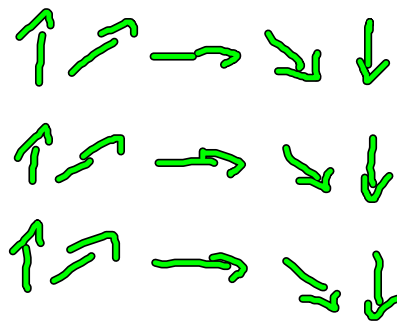
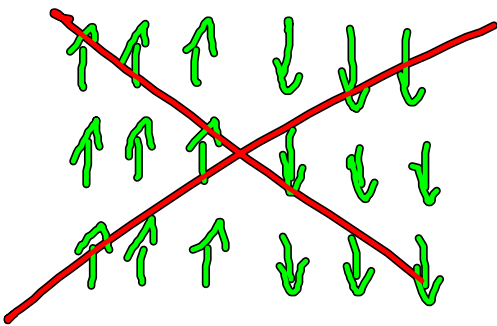
↳ instead system lowers energy by rotating spins

↳ but exchange interaction favors alignment

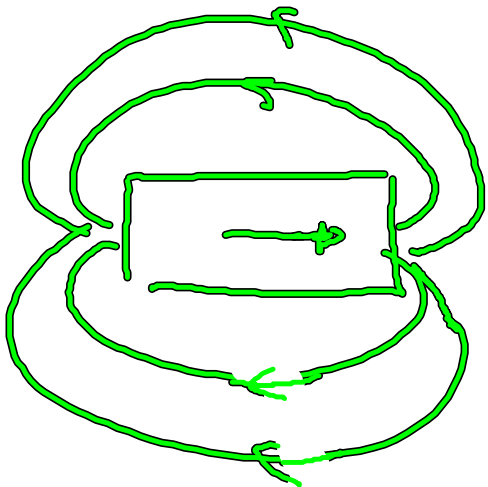
⇒ domain formation



but domain walls are not abrupt but smooth

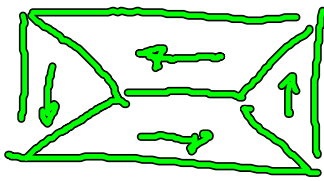


applied fields can therefore smoothly move domain walls
• much cheaper than flipping spins

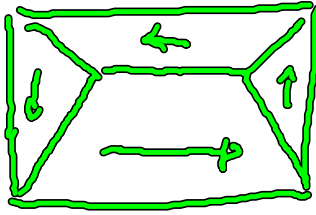


all spins are aligned

→ magnetic field extends outside material

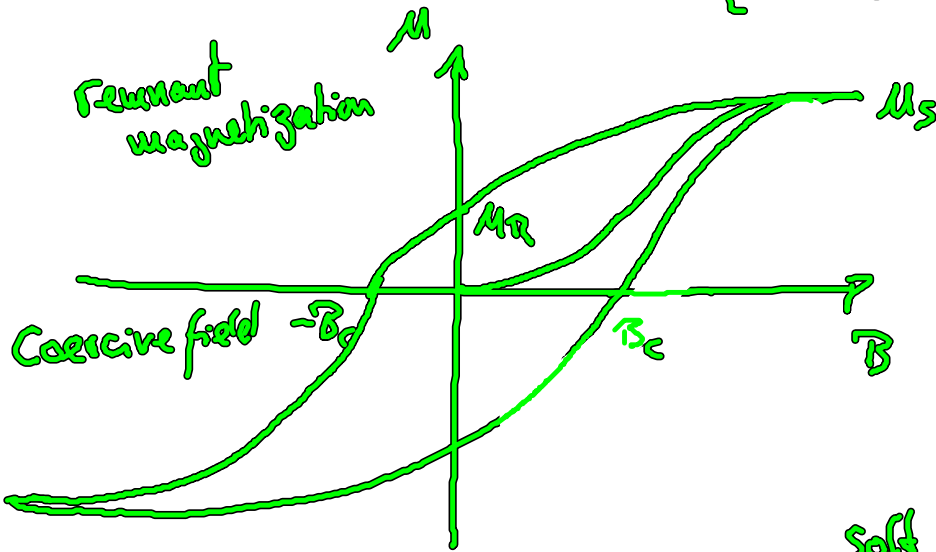


Zero net magnetization



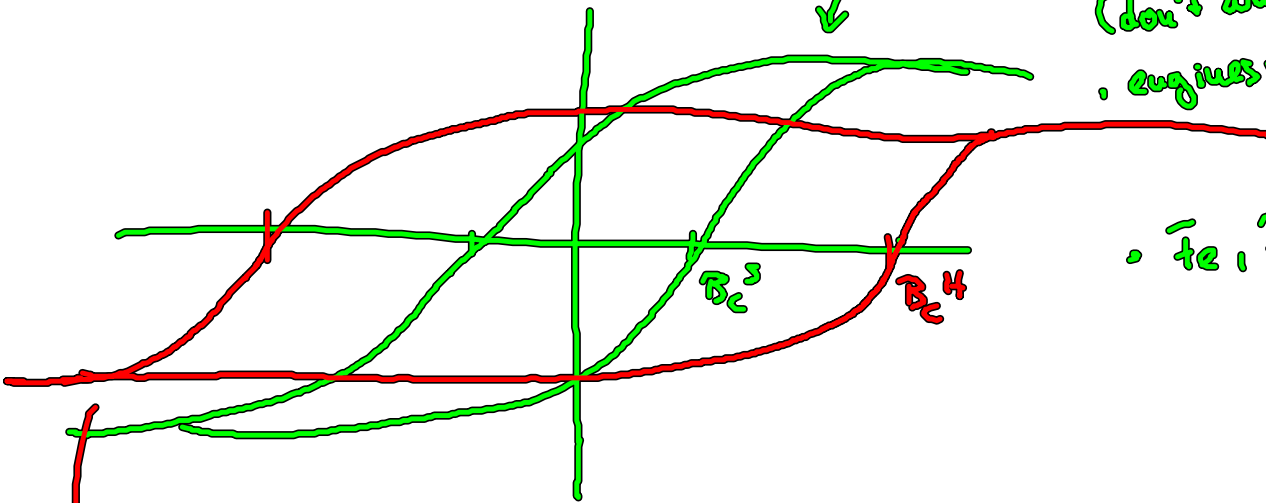
Domain walls shift
- develop magnetization

hysteresis loop of FM



Soft magnet \rightarrow small B_c
 • used for fast switching
 (don't want high field)
 • engines, transformers,
 switches

• Fe, Fe-Ni, Fe-Co



- hard magnet \rightarrow large B_c
- prevent demagnetization of magnetic state
- magnetic storage
- Fe oxide, Cr oxide

