# Ferromagnetism continued

So far: Qualitative understanding –
Interacting discrete local moments

Have: - Mean-field theory

- Heisenberg Hamiltonian

$$H^{\text{Heisenberg}} = -\sum_{ij} \frac{J_{ij}}{\mu_B^2} \, \underline{m}_i \cdot \underline{m}_j$$

But nothing yet about origin of $J_{ij}$ !

Estimate $J_{ij}$ via mean-field theory:

- nearest-neighbor only
- mean-field
- fcc lattice

$$H = -\sum_i \underline{m}_i \cdot \underbrace{\sum_j \frac{J_{ij}}{\mu_B^2} \cdot \underline{m}_j}_{\underline{B}_{mol, i}}$$

Mean-field $\underline{B}_{mol, i} \xrightarrow{\text{average}} \underline{B}_{mol} = \mu_0 \cdot \lambda \cdot \underline{M}$

but $\underline{M} = \frac{N}{V} \langle \underline{m_i} \rangle_{\text{average}}$

magnetisation density

$$\Rightarrow \quad \underline{B}_{mol} = \frac{\sum_j J_{ij}}{\mu_B^2} \cdot \frac{V}{N} \cdot \underline{M}$$

$$= \frac{\sum_j J_{ij}}{\mu_B^2} \cdot \overline{m}_s$$

in principle (for, 12 NN): $\quad J_{NN} = \frac{\mu_B^2 \cdot B_{mol}}{12 \, \overline{m}_s} \sim 10^{-2} \, eV$
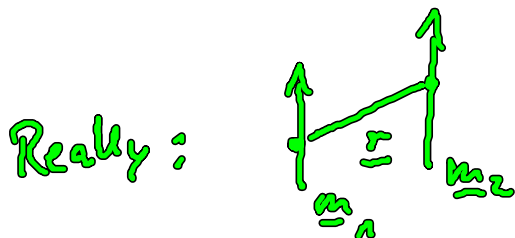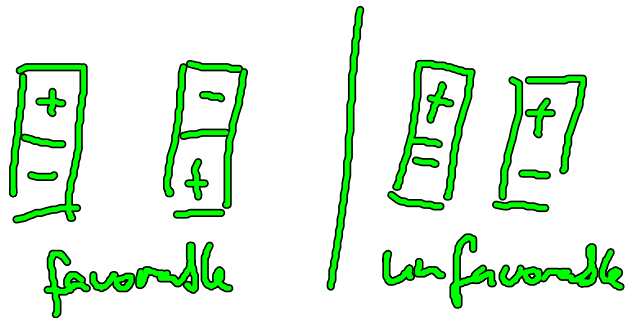
(order $kT$)
(for TM, Fe, Co, Ni)

Excursion : Other (weaker, but long-ranged) magnetic interactions

Heisenberg : $\quad J > 0 \quad$ should always yield macroscopic ferromagnetism.

(Which other (longer-ranged?) interactions must we consider?

① Dipolar interaction



favorable          unfavorable

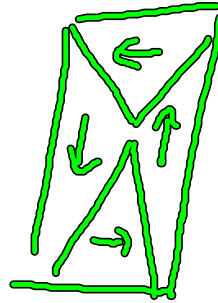Really : $\uparrow_{\underline{m}_1} \xrightarrow{\underline{r}} \uparrow_{\underline{m}_2}$
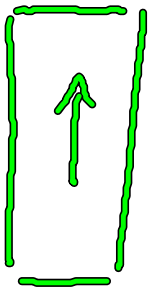
Interaction (electrostatics)

$$U^d = \frac{1}{r^3}\left[ \underline{m}_1 \cdot \underline{m}_2 - 3(\underline{m}_1 \cdot \hat{r})\cdot(\underline{m}_2 \cdot \hat{r}) \right]$$

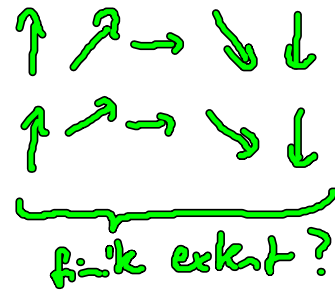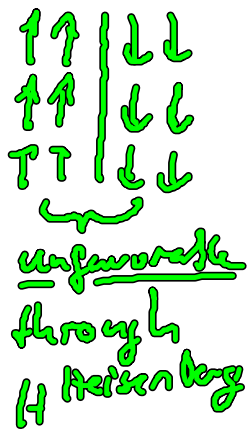$$\sim 10^{-4} \, eV \quad \text{at distances } O(\mathring{A})$$

$$\ll J^{Heisenberg}$$

However: $\frac{1}{r^3}$ is weak decay $\rightarrow$ at large distances, overcomes all other interactions



domains where $\underline{M}$ approx. cancel each other

Domain walls



unfavorable through $H^{Heisenberg}$

$\longrightarrow$



finite extent?

Domain wall extent: restricted through (weak) interaction with lattice

"magnetic anisotropy" – connects $\underline{S}$, lattice orientation

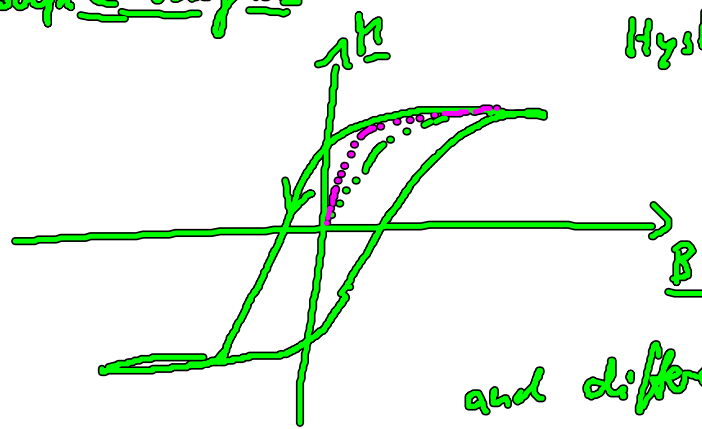However, weak: through $\underline{L}$-$\underline{S}$ coupling

( in Pauli Hamiltonian : $\sim \frac{1}{r} \frac{dV}{dr} \underline{\sigma} \cdot \underline{L}$   near nuclei

$\longrightarrow$ "magnetostriction": typically : collinear $\underline{\sigma}, \underline{L}$

in solid

and orientation dependence (weak)

because $\underline{L}$ still couples to

the lattice

$\longrightarrow$ "magnetic anisotropy"

in total : domains + anisotropy determine

macroscopic magnets



Hysteresis ( domains

and different orientations of

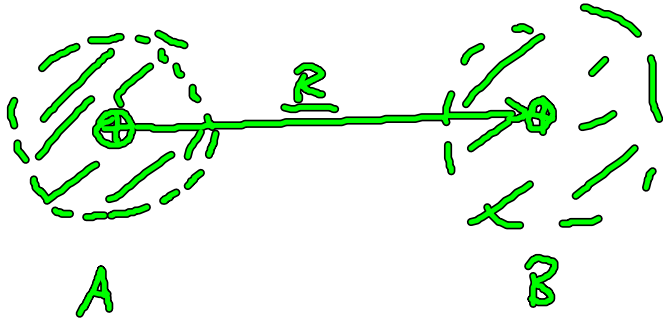$\underline{B}$ compared to lattice give

easy axes
hard axes

Back to the microscopic scale :

How parallel spins can be favorable :

"Exchange interaction" in $H_2$     (Heitler-London)

A                         B

one atom:    $h_0 |\phi\rangle = \epsilon_0 |\phi\rangle$

with    $|\phi\rangle \equiv \langle r, \sigma |\phi\rangle$

two atoms, bring together

$$H|\bar{\Phi}\rangle = \left(h_0(A) + h_0(B) + h_{int}\right)|\bar{\Phi}\rangle$$

$|\bar{\Phi}\rangle$ : two-electron wave function

since $H$ does not depend on spin :

Separate  $\bar{\Phi}(r_1 \sigma_1 ; r_2 \sigma_2) =$

$$= \bar{\psi}_{orb}(r_1 ; r_2) \cdot \chi_{spin}(\sigma_1, \sigma_2)$$

Spin part : four spin "basis functions"

$$|\uparrow\uparrow\rangle, \quad |\uparrow\downarrow\rangle, \quad |\downarrow\uparrow\rangle, \quad |\downarrow\downarrow\rangle$$

but for Pauli principle, require symmetry properties

of $\bar{\Phi}$

$\rightarrow$ to get defined symmetry, choose eigenstates

of $\quad \underline{S}^2 = (\underline{S}_1 + \underline{S}_2)^2$

can solve (try!)

$\rightarrow \quad \chi_0 = \frac{1}{\sqrt{2}} \left( |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right)$

$(\underline{S}^2 \chi_0 = 0)$

$S = 0, \quad S_z = 0 \quad$ "singlet"

<u>antisymmetric</u> spin function

$\chi_{1,1} = |\uparrow, \uparrow\rangle$

$\chi_{1,0} = \frac{1}{\sqrt{2}} \left( |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \right)$

$\chi_{1,-1} = |\downarrow, \downarrow\rangle$

$\underline{S}^2 \chi_{1,\mu} = 1 \cdot \chi_{1,\mu}$

"triplet state"

symmetric

$\rightarrow \quad$ singlet : $|\bar{\Psi}_{orb}\rangle$ must be symmetric

triplet : $|\bar{\Psi}_{orb}\rangle$ must be antisymmetric

and $\quad E_S - E_T \quad$ gives an effective

spin interaction

How to get $|\bar{\Psi}_{orb}\rangle$ (1) solvable

(2) into a picture that allows to connect

to Heisenberg?

Key : - choice of single-particle basis functions
       - variational principle


In finitely separated atoms :

$$\phi_A(\underline{r}) = \frac{1}{\sqrt{N}} e^{-a(\underline{r} - \underline{R}_A)}$$

$$\phi_B(\underline{r}) \quad \text{equivalent}$$

$$\Rightarrow \quad \overline{\psi}_{orb, sym} = \frac{1}{\sqrt{2}} \left[ \phi(1A) \cdot \phi(2B) + \phi(2A) \phi(1B) \right]$$

$$\overline{\psi}_{orb, asym} = \frac{1}{\sqrt{2}} \qquad -$$

but  $\infty$  separation  $\longrightarrow E = 2 G_0$   for both singlet, triplet

Key step ( Heitler - London )
    vary basis for finite separation.

$$\phi_A = \frac{1}{\sqrt{N'}} e^{-a r} \cdot \left( 1 + \beta \frac{\underline{r} \cdot \underline{R}}{r} \right)$$

$$r = |\underline{r} - \underline{R}_A|$$
$$\underline{R} = |\underline{R}_A - \underline{R}_B|$$

and equiv. for $\phi_B$ , with $-\beta$ !

Since $\phi_A, \phi_B$  sym w.r.t. each other:

$$| \psi_{orb, sym} \rangle = \frac{1}{\sqrt{2(1 + S^2)}} \left[ |\phi(1A)\rangle |\phi(2B)\rangle + |\phi(2A)\rangle |\phi(1B)\rangle \right]$$

$$| \bar{\Psi}_{orb, asym} \rangle =$$

$$S = \int d^3\vec{r}\, \phi_A(\vec{r})\, \phi_B(\vec{r})$$

$$E_T,\ E_S \rightarrow \text{compute} \quad \langle \bar{\Psi}_{orb} | H | \bar{\Psi}_{orb} \rangle$$

$$H = \sum_{i=n}^{2} \frac{\vec{p}_i^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \sum_{i=n}^{2} \left( \frac{1}{|\vec{r}_i - \vec{R}_A|} + \frac{1}{|\vec{r}_i - \vec{R}_B|} \right)$$

$$+ \frac{1}{|\vec{r}_1 - \vec{r}_2|} + \frac{1}{|\vec{R}_A - \vec{R}_B|}$$

So:
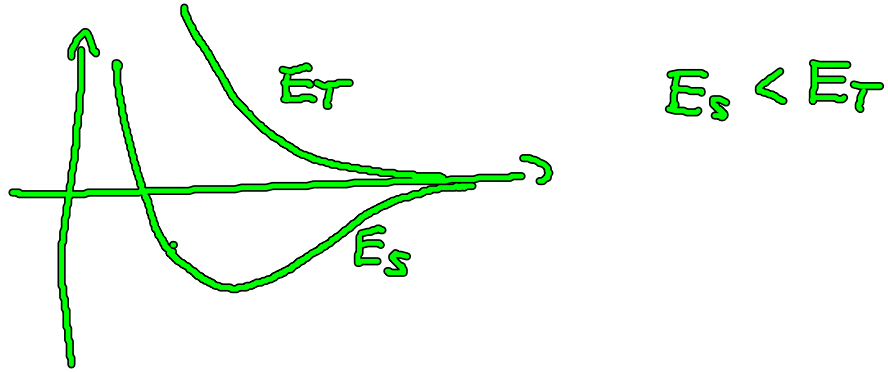$$E_S = \frac{1}{1+S^2} \left( \langle 1,2 | H | 1,2 \rangle + \langle 1,2 | H | 2,1 \rangle \right)$$

$$E_T = \frac{1}{1-S^2} \left( \langle 1,2 | H | 1,2 \rangle - \langle 1,2 | H | 2,1 \rangle \right)$$

$$J := E_S - E_T \sim \frac{2}{1-S^4} \left( \langle 1,2 | \frac{1}{|\vec{r}_1 - \vec{r}_2|} | 2,1 \rangle \right.$$

<span style="color:magenta">Exchange term</span>

$$\left. - S^2 \langle 1,2 | \frac{1}{|\vec{r}_1 - \vec{r}_2|} | 1,2 \rangle \right)$$

<span style="color:magenta">Coulomb term</span>

Very roughly: $\underline{\text{Exchange}}$ would favor triplet spin state

in $H_2$ (Heitler – London, vary $\alpha$, $\beta$)

$E_S < E_T$

- can extend this model to map

$$H \longrightarrow H(\underline{s}_1, \underline{s}_2) = -J \, \underline{s}_1 \cdot \underline{s}_2 + const$$

- can also extend this to generalized picture of local orbitals that interact qualitatively: "Hubbard Hamiltonian"

$$H = \sum_{ij} t_{ij} \, c_{j\sigma}^+ c_{i\sigma}$$

$$+ U \sum_i n_{i\uparrow} n_{i\downarrow}$$

sites $i$ with orbitals
$e^-$ in orbitals created, destroyed by
$c_{j\sigma}^+$, $c_{i\sigma}$

But what about band structure?

Impact of exchange

Homogeneous electron gas

We had
$$\bar{E}/N = T_s + E_x$$

$$= \frac{30.1\,eV}{\left(\frac{r_s}{a_B}\right)^2} - \frac{12.5\,eV}{\left(\frac{r_s}{a_B}\right)}$$

kinetic e.　　　　exchange

remember:
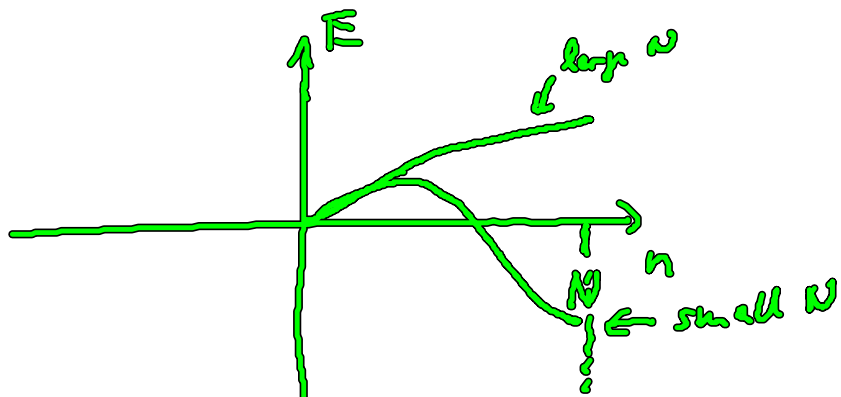
- $r_s = \frac{3}{4\pi}\left(\frac{V}{N}\right)^{1/3}$

- $T_{s_1}\quad E_x$　came from separate spin channels

$$\Rightarrow E_{jellium} = \left[78.2\,eV\left(\left(\frac{N^\uparrow}{V}\right)^{5/3} + \left(\frac{N^\downarrow}{V}\right)^{5/3}\right)\right]$$

$$- \left[20.1\,eV\left(\left(\frac{N^\uparrow}{V}\right)^{4/3} + \left(\frac{N^\downarrow}{V}\right)^{4/3}\right)\right]$$

$$= \frac{78.2\,eV}{2^{5/3}}\left[\left(\frac{N+n}{V}\right)^{5/3} + \left(\frac{N-n}{V}\right)^{5/3}\right]$$

$$- \frac{20.1\,eV}{2^{4/3}}\left[\left(\frac{N+n}{V}\right)^{4/3} + \left(\frac{N-n}{V}\right)^{4/3}\right]$$

$$\Rightarrow$$



$E$ can have a minimum

$$n = 0$$
$$n = N$$

Limiting case : $\dfrac{r_s}{a_B} = 5.45$

$\longrightarrow$ but in reality, correlation
reduces this tendency to $\dfrac{r_s}{a_B} \sim 50$

unfortunately, this does not apply to real materials!

## Band structure considerations

(1) Flashback to chapter 3
Density functional theory

$$E = E[n] = E[n^\uparrow, n^\downarrow] \qquad \text{spin density functional theory}$$

$$= T_s[n^\uparrow, n^\downarrow] + E^{ion}[n]$$
$$+ E_{Hartree}[n]$$
$$+ E_{xc}[n^\uparrow, n^\downarrow]$$

$\longrightarrow$ we can parametrize $E_{xc}$
for spin-polarized electron gas : LSDA
(local spin density approx.)

## Stoner model of itinerant ferromagnetism

Observation : • Real DOS's have peaks

• otherwise $N^{\uparrow}(\epsilon) \approx N^{\downarrow}(\epsilon + shift)$

qualitatively :

$$V_{xc}^{\uparrow\downarrow}(\underline{r}) = \frac{\delta E_{xc}[n^{\uparrow}, n^{\downarrow}]}{\delta n(\underline{r})}$$

$$\approx \underbrace{V_{xc}^{0}(\underline{r})}_{unpolarized} \pm \underline{m}(\underline{r}) \cdot \tilde{v}(\underline{r}) + \dots$$

$$\longrightarrow V_{xc}^{0}(\underline{r}) \pm I \cdot M$$

$$\underline{M} = \int_{unitcell} d^{3}r \, \underline{m}(\underline{r})$$

$$I: \quad \text{"Stoner parameter"}$$
$$(\text{"exchange intgral"})$$

$$\Rightarrow \quad \epsilon_{i}^{\uparrow\downarrow} = \epsilon_{i}^{0} \pm \frac{1}{2} I M \qquad \text{for Kohn-Sham eq.'s}$$

$$\text{and:} \quad M = \int^{\epsilon_{F}(M)} d\epsilon \left[ N^{0}(\epsilon + \tfrac{1}{2}IM) - N_{0}(\epsilon - \tfrac{1}{2}IM) \right] =: F(M)$$

Graphical:
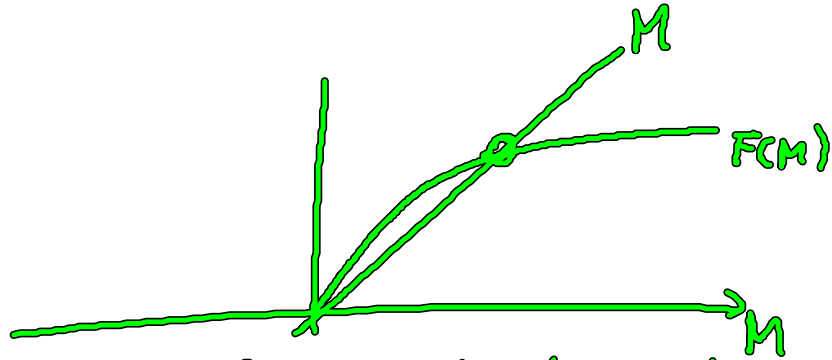


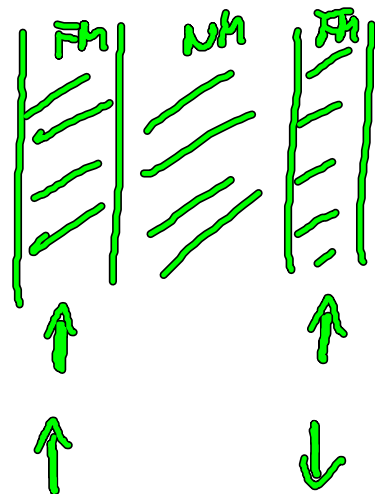if M intersects F(M) ⟹ solution
with finite M

possible if $F'(M=0) > 1$

$$\left.\frac{\partial F}{\partial M}\right|_{M=0} = I \cdot N_0(\varepsilon_F) > 1$$

$$\boxed{\text{Stoner criterion !}}$$

⟶ $I$ can be calculated from ground-state DFT
by looking at electron-gas response to a small
perturbation

Outlook : magnetism today

o Giant magnetoresistance



FM coupling between layers

↑ ↓ AFM

• FM coupling : conduction $e^-$ belong to 1 spin channel
predominantly, travel equally well through

both FM layers

- AFM coupling: $e^-$ that travel well in ↑
  don't travel well for ↓

⟹ electrical resistivity difference!

"spin valve"