

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

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

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

but $\underline{M} = \frac{N}{V} \langle \underline{m}_i \rangle$ average magnetisation density

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

$$= \frac{\sum_j J_{ij}}{\mu_B^2} \cdot \bar{M}_s$$

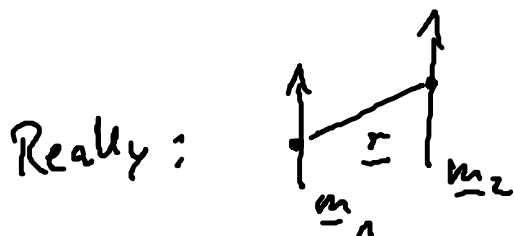
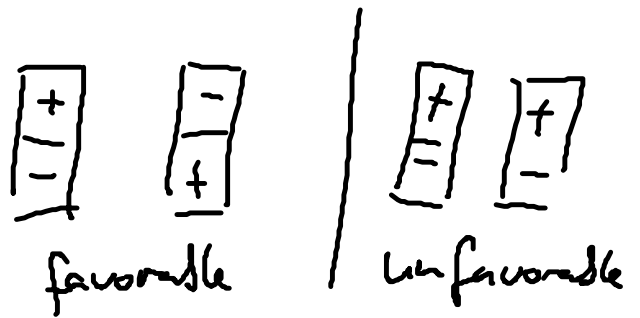
in principle (for, 12 NN): $J_{NN} = \frac{\mu_B^2 \cdot B_{\text{mol}}}{12 \bar{M}_s} \sim 10^{-2} \text{ eV}$
 (order kT)
 (for TM, Fe, Co, Ni)

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

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

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

① Dipolar interaction



Interaction (electrostatics)

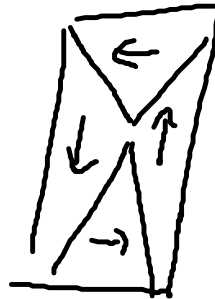
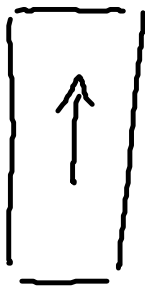
$$U^d = \frac{1}{r^3} [\underline{m}_1 \cdot \underline{m}_2 - 3(\underline{m}_1 \cdot \hat{r})(\underline{m}_2 \cdot \hat{r})]$$

$\sim 10^{-4}$ eV at distances 0 (Å)

$\ll J_{\text{Heisenberg}}$

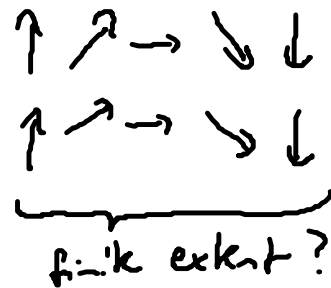
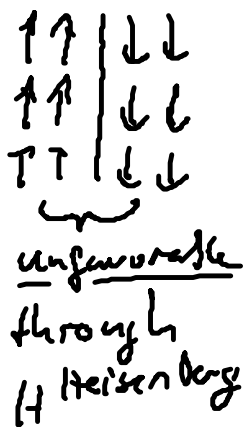
However: $\frac{1}{r^3}$

is weak decay \rightarrow at large distances, overcomes all other interactions



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

Domain walls



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

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

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

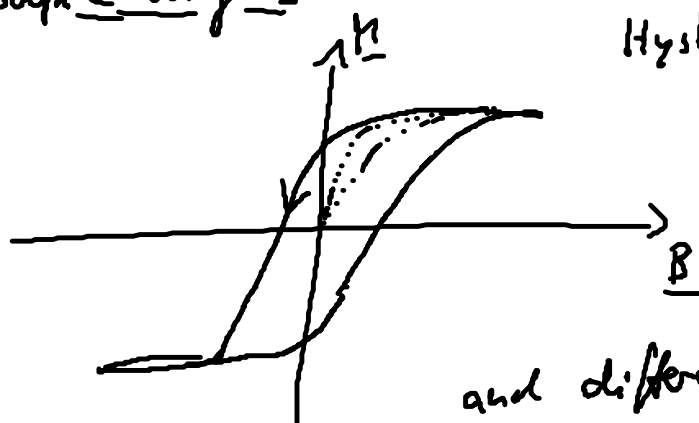
(in Pauli Hamiltonian: $\sim \frac{1}{r} \frac{dV}{dr} \underline{\sigma} \cdot \underline{L}$ near nuclei

→ "magnetostriction": typically: collinear $\underline{\sigma}, \underline{L}$
in solid

and orientation dependence (weak)
because \underline{L} still couples to
the lattice

→ "magnetic anisotropy"

in total: domains + anisotropy determine
macroscopic magnets



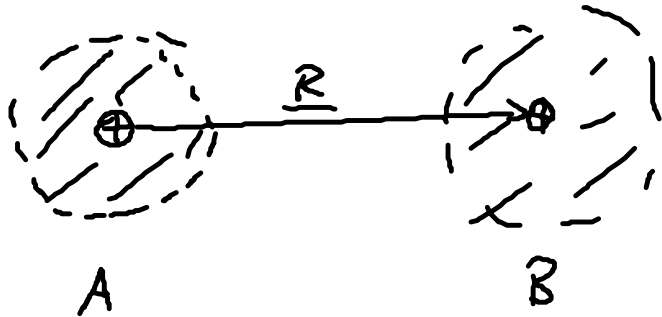
Hysteresis (domains)

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)



one atom: $h_0 |\phi\rangle = \epsilon_0 |\phi\rangle$
 with $|\phi\rangle \equiv \langle \underline{r}, \sigma | \phi \rangle$

two atoms, bring together

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

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

since H does not depend on spin:

$$\begin{aligned} \text{Separate } \bar{\Phi}(\underline{r}_1, \sigma_1; \underline{r}_2, \sigma_2) &= \\ &= \bar{\Psi}_{\text{orb}}(\underline{r}_1, \underline{r}_2) \cdot \chi_{\text{spin}}(\sigma_1, \sigma_2) \end{aligned}$$

Spin part: four spin "basis functions"

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

but for Pauli principle, require symmetry properties

of $\bar{\Phi}$

→ to get defined symmetry, choose eigenstates

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

can solve (try!)

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

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

$$S=0, S_z=0 \text{ "singlet"}$$

antisymmetric spin function

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

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

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

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

"triplet state"

symmetric

→ singlet: $|\bar{\Psi}_{\text{orb}}\rangle$ must be symmetric

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

and $E_S - E_T$ gives an effective spin interaction

How to get $|\bar{\Psi}_{\text{orb}}\rangle$ (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 :

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

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

$$\rightarrow \bar{\Psi}_{\text{orb, sym}} = \frac{1}{\sqrt{2}} [\phi(1A) \cdot \phi(2B) + \phi(2A) \phi(1B)]$$

$$\bar{\Psi}_{\text{orb, asym}} = \frac{1}{\sqrt{2}}$$

but ∞ separation $\rightarrow E = 2\epsilon_0$ for both singlet, triplet

Key step (Heitler - London)

vary basis for finite separation.

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

and equiv. for ϕ_B , with $-\beta$!

$$\begin{aligned} r &= |\underline{r} - \underline{R}_A| \\ R &= |\underline{R}_A - \underline{R}_B| \end{aligned}$$

Since ϕ_A, ϕ_B symmetric w.r.t. each other:

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

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

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

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

$$H = \sum_{i=1}^2 \frac{p_i^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^2 \left(\frac{1}{|\underline{r}_i - \underline{R}_A|} + \frac{1}{|\underline{r}_i - \underline{R}_B|} \right) + \frac{1}{|\underline{r}_1 - \underline{r}_2|} + \frac{1}{|\underline{R}_A - \underline{R}_B|}$$

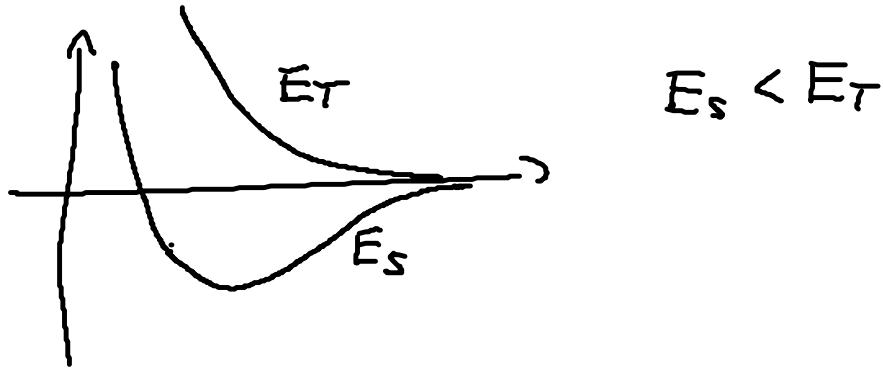
$$\text{So: } E_S = \frac{1}{1+S^2} (\langle 1,2 | H | 1,2 \rangle + \langle 1,2 | H | 2,1 \rangle)$$

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

$$J = E_S - E_T \sim \frac{2}{1-S^4} \left(\underbrace{\langle 1,2 | \frac{1}{|\underline{r}_1 - \underline{r}_2|} | 2,1 \rangle}_{\text{Exchange term}} - S^2 \underbrace{\langle 1,2 | \frac{1}{|\underline{r}_1 - \underline{r}_2|} | 1,2 \rangle}_{\text{Coulomb term}} \right)$$

Very roughly: Exchange would favor triplet spin state

in H_2 (Heitler-London, vary α, β)



• can extend this model to map

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

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

$$H = \sum_{ij} t_{ij} c_{j\sigma}^\dagger c_{i\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

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

But what about band structure?

Impact of exchange

Homogeneous electron gas

We had

$$\begin{aligned} \bar{E}/N &= T_s + E_x \\ &= \frac{30.1 \text{ eV}}{\left(\frac{r_s}{a_B}\right)^2} - \frac{12.5 \text{ eV}}{\left(\frac{r_s}{a_B}\right)} \end{aligned}$$

kinetic e. exchange

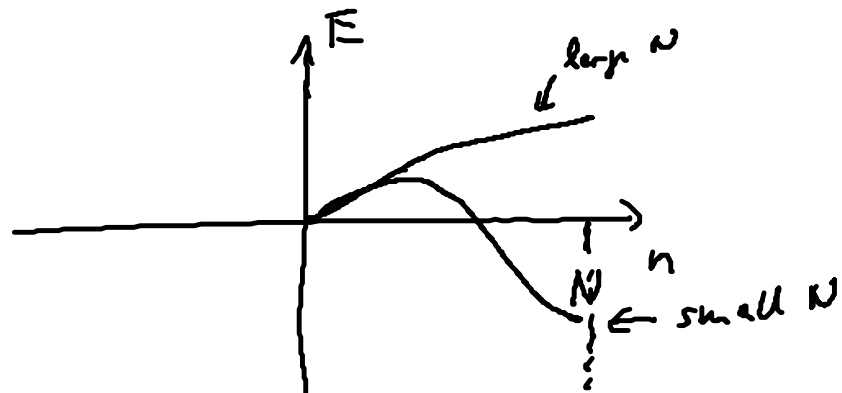
remember:

$$\bullet \quad r_s = \frac{3}{4\pi} \left(\frac{V}{N}\right)^{1/3}$$

• T_s, E_x came from separate spin channels

$$\begin{aligned} \rightarrow E_{\text{Jellium}} &= \left[78.2 \text{ eV} \left(\left(\frac{N^\uparrow}{V}\right)^{5/3} + \left(\frac{N^\downarrow}{V}\right)^{5/3} \right) \right] \\ &\quad - \left[20.1 \text{ eV} \left(\left(\frac{N^\uparrow}{V}\right)^{4/3} + \left(\frac{N^\downarrow}{V}\right)^{4/3} \right) \right] \\ &= \frac{78.2 \text{ eV}}{2^{5/3}} \left[\left(\frac{N+n}{V}\right)^{5/3} + \left(\frac{N-n}{V}\right)^{5/3} \right] \\ &\quad - \frac{20.1 \text{ eV}}{2^{4/3}} \left[\left(\frac{N+n}{V}\right)^{4/3} + \left(\frac{N-n}{V}\right)^{4/3} \right] \end{aligned}$$

\Rightarrow



E can have a minimum

$$n = 0$$

$$n = N$$

Limiting case : $\frac{\Gamma_S}{a_B} = 5.45$

→ but in reality, correlation reduces this tendency to $\frac{\Gamma_S}{a_B} \sim 50$

Unfortunately, this does not apply to real materials!

Band structure considerations

① Flashback to chapter 3

Density functional theory

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

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

→ we can parameterize E_{xc}

for spin-polarized electron gas : LSDA
(local spin density approx.)

Stoner model of itinerant ferromagnetism

- Observation:
- Real DOS's have peaks
 - otherwise $N^\uparrow(\epsilon) \approx N^\downarrow(\epsilon + \text{shift})$

qualitatively:

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

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

$$\rightarrow V_{xc}^0(\epsilon) \pm I \cdot M$$

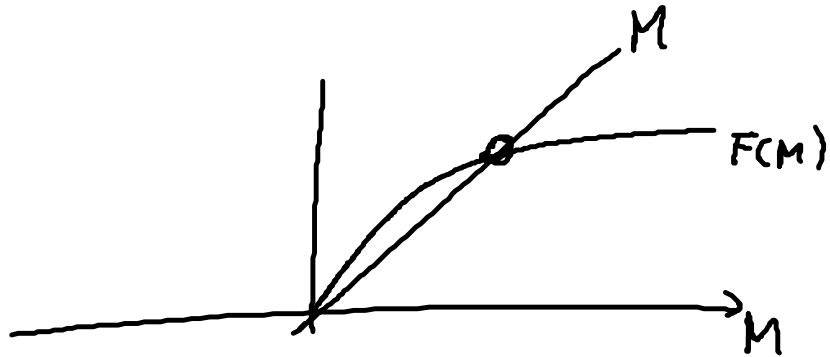
$$\underline{M} = \int_{\text{unit cell}} d^3r \underline{m}(\epsilon)$$

I : "Stoner parameter"
("exchange integral")

$$\Rightarrow \epsilon_i^{\uparrow\downarrow} = \epsilon_i^0 \pm \frac{1}{2} I M \quad \text{from Kohn-Shan eq.'s}$$

$$\text{and: } M = \int_{\epsilon_F(M)} d\epsilon \left[N^0(\epsilon + \frac{1}{2} I M) - N_0(\epsilon - \frac{1}{2} I M) \right] =: F(M)$$

Graphical:



if M intersects $F(M) \Rightarrow$ solution with finite M

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

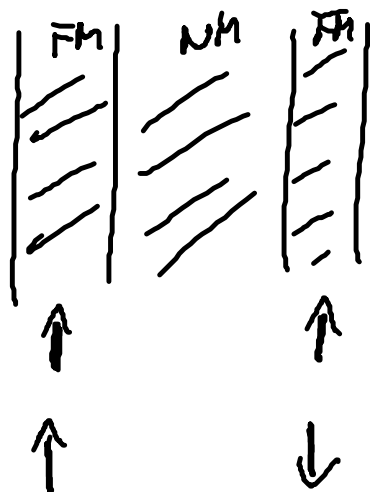
$$\left. \frac{\partial F}{\partial M} \right|_{M=0} = I \cdot N_0(\epsilon_F) > 1$$

Stoner criteria

\rightarrow 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

- AFA coupling: e^- that travel well in \uparrow
do not travel well for \downarrow

\Rightarrow electrical resistivity difference!

"spin valve"