Magnetic Interactions. Magnetic Order.



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I. Introduction.

II. Exchange interaction in the solid: origin and examples.

III. Localized Magnetic Order:III.1 Molecular field theory.III.2 FM, AF, FiM.

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V. Indirect interactions:
V.1 Super and Double exchange.
V.2 RKKY, Spin glasses.
V.3 DMI interactions.

VI. Itinerant magnetism:VI.1 Stoner model.VI.2 Stoner criterion.VI.3 Metal alloys.

If relativistic effects are not considered, then the electric interactions between particles does not depend on their spins.

In absence of a magnetic field, the Hamiltonian of a system of particles in electric interaction does not contain spin operators.

When applied to a wave function, it does not affect spin variables.

$$\Psi(\vec{r}_1 s_1, \vec{r}_2 s_2, \dots) = \psi(\vec{r}_1, \vec{r}_2, \dots) \chi(s_1, s_2, \dots)$$

Depends only on spatial coordinates Depends only on spin variables

The Schrödinger equation determines only $\,\psi(ec{r}_1,\dots)\,$ and not $\,\chi(s_1,\dots)\,$

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_{i,\alpha} \frac{Z_\alpha e^2}{|\mathbf{r}_i - \mathbf{R}_\alpha|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Electron only Schr. Eq.

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Despite electric interaction is spin independent, there is a dependency of the energy on the total spin.

Example: Two identical particles



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Spin 1/2 (fermions): {	\int Spatial coordinates: $ec{r_1}, ec{r_2}$			
	Single particle wave functions: $\varphi_1(ec{r}), \varphi_2(ec{r})$	(eigenfunctions of non-interacting case)		

The total wave function $\Psi(\vec{r_1}, \vec{r_2})$ for the states with total spin S_T will be:

$$\begin{cases} \mathsf{S}_{\mathsf{T}}=\mathsf{0}, \text{ Singlet (m}_{\mathsf{S}}=\mathsf{0}) & \Psi_{S}(\vec{r}_{1},\vec{r}_{2}) = \frac{1}{\sqrt{2}}[\varphi_{1}(\vec{r}_{1})\varphi_{2}(\vec{r}_{2}) + \varphi_{1}(\vec{r}_{2})\varphi_{2}(\vec{r}_{1})]\chi_{S} \\ \\ \mathsf{S}_{\mathsf{T}}=\mathsf{1}, \text{ Triplet (m}_{\mathsf{S}}=\{-\mathsf{1},\mathsf{0}.,+\mathsf{1}\}) & \Psi_{T}(\vec{r}_{1},\vec{r}_{2}) = \frac{1}{\sqrt{2}}[\varphi_{1}(\vec{r}_{1})\varphi_{2}(\vec{r}_{2}) - \varphi_{1}(\vec{r}_{2})\varphi_{2}(\vec{r}_{1})]\chi_{T} \end{cases}$$

The energies will then be different:

$$\begin{cases} \mathsf{S}_{\mathsf{T}}=\mathsf{0}, \text{ Singlet (m}_{\mathsf{S}}=\mathsf{0}) & E_{S}=\langle\Psi_{S}|\,\hat{\mathscr{H}}\,|\Psi_{S}\rangle=\int d\vec{r}_{1}d\vec{r}_{2}\Psi_{S}^{\star}\hat{\mathscr{H}}\Psi_{S} \\ \\ \mathsf{S}_{\mathsf{T}}=\mathsf{1}, \text{ Triplet (m}_{\mathsf{S}}=\{-\mathsf{1},\mathsf{0},+\mathsf{1}\}) & E_{T}=\langle\Psi_{T}|\,\hat{\mathscr{H}}\,|\Psi_{T}\rangle=\int d\vec{r}_{1}d\vec{r}_{2}\Psi_{T}^{\star}\hat{\mathscr{H}}\Psi_{T} \end{cases}$$

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Energy of the singlet state: $|\Psi_S(\vec{r_1}, \vec{r_2})\rangle = \frac{1}{\sqrt{2}}[|\varphi_1(\vec{r_1})\varphi_2(\vec{r_2})\rangle + |\varphi_1(\vec{r_2})\varphi_2(\vec{r_1})\rangle]\chi_S$ (using bra/ket notation as a shorthand)

$$\begin{split} E_{S} &= \langle \Psi_{S} | \,\hat{\mathscr{H}} \, | \Psi_{S} \rangle = \frac{1}{2} \, \langle \varphi_{1}(\vec{r}_{1})\varphi_{2}(\vec{r}_{2}) + \varphi_{1}(\vec{r}_{2})\varphi_{2}(\vec{r}_{1}) | \,\hat{\mathscr{H}} \, | \varphi_{1}(\vec{r}_{1})\varphi_{2}(\vec{r}_{2}) + \varphi_{1}(\vec{r}_{2})\varphi_{2}(\vec{r}_{1}) \rangle \\ &= \frac{1}{2} (\langle \varphi_{1}(\vec{r}_{1})\varphi_{2}(\vec{r}_{2}) | \,\hat{\mathscr{H}} \, | \varphi_{1}(\vec{r}_{1})\varphi_{2}(\vec{r}_{2}) \rangle + \langle \varphi_{1}(\vec{r}_{1})\varphi_{2}(\vec{r}_{2}) | \,\hat{\mathscr{H}} \, | \varphi_{1}(\vec{r}_{2})\varphi_{2}(\vec{r}_{1}) \rangle \\ &+ \langle \varphi_{1}(\vec{r}_{2})\varphi_{2}(\vec{r}_{1}) | \,\hat{\mathscr{H}} \, | \varphi_{1}(\vec{r}_{1})\varphi_{2}(\vec{r}_{2}) \rangle + \langle \varphi_{1}(\vec{r}_{2})\varphi_{2}(\vec{r}_{1}) | \,\hat{\mathscr{H}} \, | \varphi_{1}(\vec{r}_{2})\varphi_{2}(\vec{r}_{1}) \rangle) \\ \\ \end{array}$$
The triplet state:
$$| \Psi_{T}(\vec{r}_{1},\vec{r}_{2}) \rangle = \frac{1}{\sqrt{2}} [| \varphi_{1}(\vec{r}_{1})\varphi_{2}(\vec{r}_{2}) \rangle - | \varphi_{1}(\vec{r}_{2})\varphi_{2}(\vec{r}_{1}) \rangle] \chi_{T}$$

Energy of

$$E_{T} = \langle \Psi_{T} | \hat{\mathscr{H}} | \Psi_{T} \rangle = \frac{1}{2} \langle \varphi_{1}(\vec{r}_{1})\varphi_{2}(\vec{r}_{2}) - \varphi_{1}(\vec{r}_{2})\varphi_{2}(\vec{r}_{1}) | \hat{\mathscr{H}} | \varphi_{1}(\vec{r}_{1})\varphi_{2}(\vec{r}_{2}) - \varphi_{1}(\vec{r}_{2})\varphi_{2}(\vec{r}_{1}) \rangle$$

$$= \frac{1}{2} (\langle \varphi_{1}(\vec{r}_{1})\varphi_{2}(\vec{r}_{2}) | \hat{\mathscr{H}} | \varphi_{1}(\vec{r}_{1})\varphi_{2}(\vec{r}_{2}) \rangle - \langle \varphi_{1}(\vec{r}_{1})\varphi_{2}(\vec{r}_{2}) | \hat{\mathscr{H}} | \varphi_{1}(\vec{r}_{2})\varphi_{2}(\vec{r}_{1}) \rangle$$

$$- \langle \varphi_{1}(\vec{r}_{2})\varphi_{2}(\vec{r}_{1}) | \hat{\mathscr{H}} | \varphi_{1}(\vec{r}_{1})\varphi_{2}(\vec{r}_{2}) \rangle + \langle \varphi_{1}(\vec{r}_{2})\varphi_{2}(\vec{r}_{1}) | \hat{\mathscr{H}} | \varphi_{1}(\vec{r}_{2})\varphi_{2}(\vec{r}_{1}) \rangle)$$

Energy difference (using the hermiticity of H):

$$E_{S} - E_{T} = 2 \langle \varphi_{1}(\vec{r}_{1})\varphi_{2}(\vec{r}_{2}) | \hat{\mathscr{H}} | \varphi_{1}(\vec{r}_{2})\varphi_{2}(\vec{r}_{1}) \rangle = 2 \int d\vec{r}_{1}d\vec{r}_{2}\varphi_{1}^{\star}(\vec{r}_{1})\varphi_{2}^{\star}(\vec{r}_{2})\hat{\mathscr{H}}\varphi_{1}(\vec{r}_{2})\varphi_{2}(\vec{r}_{1})$$

Exchange energy

Energy difference (using the hermiticity of H):

$$E_{S} - E_{T} = 2 \left\langle \varphi_{1}(\vec{r}_{1})\varphi_{2}(\vec{r}_{2}) \right| \hat{\mathscr{H}} \left| \varphi_{1}(\vec{r}_{2})\varphi_{2}(\vec{r}_{1}) \right\rangle = 2 \int d\vec{r}_{1}d\vec{r}_{2}\varphi_{1}^{\star}(\vec{r}_{1})\varphi_{2}^{\star}(\vec{r}_{2})\hat{\mathscr{H}}\varphi_{1}(\vec{r}_{2})\varphi_{2}(\vec{r}_{1})$$

Exchange energy

Objective: rewrite this in terms of the spin operators of the 2 particles

Consider two spin ½ particles (1,2) coupled by the following spin Hamiltonian

$$\begin{split} \hat{\mathscr{K}} &= A\hat{\mathbf{S}}_{1} \cdot \hat{\mathbf{S}}_{2} & \hat{\mathbf{S}} = \hat{\mathbf{S}}_{1} + \hat{\mathbf{S}}_{2} \\ \hat{\mathbf{S}}^{2} &= \hat{\mathbf{S}}_{1}^{2} + \hat{\mathbf{S}}_{2}^{2} + 2\hat{\mathbf{S}}_{1} \cdot \hat{\mathbf{S}}_{2} & \hat{\mathbf{S}}^{2} |\psi\rangle = S(S+1) |\psi\rangle \\ \hat{\mathbf{S}}_{1} \text{ and } \hat{\mathbf{S}}_{2} \text{ act only on particle 1 or 2, respectively.} \\ \hat{\mathbf{S}}^{2} &= \hat{\mathbf{S}}_{1}^{2} + \hat{\mathbf{S}}_{2}^{2} + 2\hat{\mathbf{S}}_{1} \cdot \hat{\mathbf{S}}_{2} & \hat{\mathbf{S}}_{1}^{2} |\psi\rangle = s_{i}(s_{i}+1) |\psi\rangle = \frac{3}{4} |\psi\rangle \\ \hat{\mathbf{S}}_{1} \cdot \hat{\mathbf{S}}_{2} |\psi\rangle &= \frac{1}{2} \left[S(S+1) - \frac{3}{2} \right] |\psi\rangle \Longrightarrow \begin{cases} \mathbf{S}_{\mathsf{T}} = \mathbf{0}, \text{ Singlet } (\mathsf{m}_{\mathsf{S}} = \mathbf{0}) & \hat{\mathbf{S}}_{1} \cdot \hat{\mathbf{S}}_{2} |\psi_{s}\rangle = -\frac{3}{4} |\psi_{s}\rangle , \ E_{s} = -\frac{3}{4}A \\ S_{\mathsf{T}} = \mathbf{1}, \text{ Triplet } (\mathsf{m}_{\mathsf{S}} = \{-1, 0, +1\}) & \hat{\mathbf{S}}_{1} \cdot \hat{\mathbf{S}}_{2} |\psi_{t}\rangle = \frac{1}{4} |\psi_{t}\rangle , \ E_{t} = \frac{1}{4}A \end{split}$$

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Heisenberg Hamiltonian $\hat{\mathscr{H}} = A\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$



Energy difference (using the hermiticity of H):

$$E_{S} - E_{T} = 2 \left\langle \varphi_{1}(\vec{r}_{1})\varphi_{2}(\vec{r}_{2}) \right| \hat{\mathscr{H}} \left| \varphi_{1}(\vec{r}_{2})\varphi_{2}(\vec{r}_{1}) \right\rangle = 2 \int d\vec{r}_{1}d\vec{r}_{2}\varphi_{1}^{\star}(\vec{r}_{1})\varphi_{2}^{\star}(\vec{r}_{2})\hat{\mathscr{H}}\varphi_{1}(\vec{r}_{2})\varphi_{2}(\vec{r}_{1})$$

Exchange energy

Objective: rewrite this in terms of the spin operators of the 2 particles

$$\hat{\mathscr{H}} = -2J_{12}\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2$$

Lecture I: Interactions and Magnetic Order

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Comparing both expressions:

$$E_{S} - E_{T} = 2 \langle \varphi_{1}(\vec{r}_{1})\varphi_{2}(\vec{r}_{2}) | \hat{\mathscr{H}} | \varphi_{1}(\vec{r}_{2})\varphi_{2}(\vec{r}_{1}) \rangle$$
$$\hat{\mathscr{H}} = \frac{1}{4} (E_{s} + 3E_{t}) - (E_{s} - E_{t})\hat{\mathbf{S}}_{1} \cdot \hat{\mathbf{S}}_{2}$$
$$\hat{\mathscr{H}} = -2J_{12}\hat{\mathbf{S}}_{1} \cdot \hat{\mathbf{S}}_{2}$$

Sign of exchange

 $J > 0 \Rightarrow E_s > E_t \Rightarrow$ Triplet favoured, S = 1 $J < 0 \implies E_s < E_t \implies$ Singlet favoured, S = 0

Exchange integral or energy $J_{12} = \langle \varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) | \hat{\mathscr{H}} | \varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1) \rangle$

When the two electrons are in a spin **triplet** state, there can be no chance of finding them at the same point of space. **Electrons** with parallel spins avoid each other.

But if the electrons are in the spin **singlet** state, with antiparallel spins, there is some probability of **finding them in** *the same place*, because the spatial part of the wave function is symmetric under exchange of the electrons.

Can be extended to systems with more spins (e's) and more atoms:

Heisenberg Hamiltonia

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$$\hat{\mathscr{H}} = -\sum_{i,j} J_{ij} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j$$

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(We will come back to it later on...)



Two spins in *different atoms*: Sign of J?? Interatomic exchange

Joint states are linear combinations of a state centered in at.1 and a state centered in at.2



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Anti-symmetric spatial state Ferromagnetic coupling

1st Hund rule Minimize Coulomb repulsion

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Symmetric spatial state Antiferromagnetic coupling

Favour bonding orbitals Save kinetic energy



 $\left\langle \psi_{\pm} \right| \hat{\mathscr{H}} \left| \psi_{\pm} \right\rangle = 2N^2 E_0 + 2\mathcal{J} \pm 2\mathcal{K}$

$$\mathcal{J} \equiv -\left\langle \phi_a \right| \frac{e^2}{4\pi\varepsilon_0 r_b} \left| \phi_a \right\rangle$$

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Coulomb Integral J(R) repulsion e-n

$$\mathscr{K} \equiv -\left\langle \phi_b \right| \frac{e^2}{4\pi\varepsilon_0 r_b} \left| \phi_a \right\rangle$$

> Origin of exchange: the H_2^+ as a toy model

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$$E_{\pm} = \frac{\langle \psi_{\pm} | \hat{\mathscr{H}} | \psi_{\pm} \rangle}{\langle \psi_{\pm} | \psi_{\pm} \rangle} = \frac{1}{N^2} (N^2 E_0 + 2\mathscr{J} \pm 2\mathscr{K}) = E_0 \pm \frac{\mathscr{J} \pm \mathscr{K}}{1 \pm O}$$

$$\begin{split} \mathscr{J} &\equiv -\left\langle \phi_{a}\right| \frac{1}{4\pi\varepsilon_{0}r_{b}} \left|\phi_{a}\right\rangle \quad \begin{array}{l} \text{Coulomb} \\ \text{Integral } \emph{J(R)} \\ \\ \mathscr{K} &\equiv -\left\langle \phi_{b}\right| \frac{e^{2}}{4\pi\varepsilon_{0}r_{b}} \left|\phi_{a}\right\rangle \quad \begin{array}{l} \text{Exchange} \\ \text{Integral } \emph{K(R)} \\ \\ \\ \text{(can be calculated exactly)} \\ \end{split}$$



e_2 r_{2a} r_{1b} r_1 R H_a H_b

$$\mathcal{H} = \mathcal{H}_{atom,1} + \mathcal{H}_{atom,2} + \left(\mathcal{H}_{e1-n2} + \mathcal{H}_{e2-n1} + \mathcal{H}_{e1-e2} + \mathcal{H}_{n1-n2}\right)$$

 $\mathscr{H} \approx \mathscr{H}_{mol,1} + \mathscr{H}_{mol,2} + \mathscr{H}_{e1-e2}$

Neglecting nuclei interaction

$$\begin{aligned} \mathscr{H}_{mol,1} &= -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{e^2}{4\pi\varepsilon_0} \left[\frac{1}{r_1} + \frac{1}{r_{1b}} \right] \\ \mathscr{H}_{mol,2} &= -\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0} \left[\frac{1}{r_2} + \frac{1}{r_{2a}} \right] \end{aligned}$$

$$\mathscr{H}_{e1-e2} = \frac{e^2}{4\pi\varepsilon_0(r_1 - r_2)}$$

 $\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi = \varepsilon\psi$

Remember! $\Psi(\vec{r}_1 s_1, \vec{r}_2 s_2) = \psi(\vec{r}_1, \vec{r}_2)\chi(s_1, s_2) \implies \begin{cases} \psi_{as}(\vec{r}_1, \vec{r}_2)\chi_{sym}(s_1, s_2) \\ \psi_{as}(\vec{r}_1, \vec{r}_2)\chi_{sym}(s_1, s_2) \end{cases}$

Antisymmetric (Pauli principle for fermions)

LCMO (Linear Combination of **Molecular Orbitals**) made up of the $H^{2+}AO's(\psi_A, \psi_B)$

Origin of exchange: the H₂ hydrogen molecule



Origin of exchange: the H₂ hydrogen molecule



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Origin of exchange: the He helium atom



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Ground state is 2 e's in 1s orbital \Rightarrow spatial w.f. has to be symm. \Rightarrow spin w.f. antisymm. \Rightarrow spins $\uparrow\downarrow$

$$\psi_{gs}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} (\phi_{1s}(\vec{r}_1)\phi_{1s}(\vec{r}_2) + \phi_{1s}(\vec{r}_2)\phi_{1s}(\vec{r}_1))\chi_{as}(s_1, s_2) \qquad 1s$$

Excited state: $1 e^{-}$ in 1s orbital and spin \uparrow and:

$$2^{nd} e^{-} \text{ in } 2s \text{ with spin } \downarrow \Rightarrow \text{ spin w.f. antis.} \Rightarrow \text{ spatial w.f. symm.} \Rightarrow \textbf{singlet}$$
$$\psi_{es}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} (\phi_{1s}(\vec{r}_1)\phi_{2s}(\vec{r}_2) + \phi_{1s}(\vec{r}_2)\phi_{2s}(\vec{r}_1))\chi_s(s_1, s_2)$$

 $2^{nd} e^{-} \text{ in } 2s \text{ with spin } \uparrow \Rightarrow \text{ spin w.f. symm.} \Rightarrow \text{ spatial w.f. antis.} \Rightarrow \textbf{triplet}$ $\psi_{et}(\vec{r_1}, \vec{r_2}) = \frac{1}{\sqrt{2}} (\phi_{1s}(\vec{r_1})\phi_{2s}(\vec{r_2}) - \phi_{1s}(\vec{r_2})\phi_{2s}(\vec{r_1}))\chi_s(s_1, s_2)$





$$\begin{aligned} \mathcal{H} &= \mathcal{H}_{e1}(r_1) + \mathcal{H}_{e2}(r_2) + \mathcal{H}_{e1-e2}(r_1, r_2) = \mathcal{H}^0(r_1, r_2) + \mathcal{H}^1(r_1, r_2) \\ \mathcal{H}_{ei} &= \frac{p_i^2}{2m_e} - \frac{2e^2}{4\pi\varepsilon_0 r_i} \quad \text{Kinetic energy + Coulomb attraction of e's to nucleus} \\ \mathcal{H}_{e1-e2} &= + \frac{e^2}{4\pi\varepsilon_0 r_{12}} \quad \text{Coulomb repulsion between e's} \end{aligned}$$

Energies of excited states when in sg. or tr. state:

$$E_{sg} = \langle \psi_{sg} | \mathscr{H}^{0} | \psi_{sg} \rangle + \langle \psi_{sg} | \mathscr{H}^{1} | \psi_{sg} \rangle$$
$$\langle \psi_{sg} | \mathscr{H}^{0} | \psi_{sg} \rangle = \langle \psi_{tr} | \mathscr{H}^{0} | \psi_{tr} \rangle = E_{1s} + E_{2s}$$
$$E_{tr} = \langle \psi_{tr} | \mathscr{H}^{0} | \psi_{tr} \rangle + \langle \psi_{tr} | \mathscr{H}^{1} | \psi_{tr} \rangle$$

The correction comes from the Coulomb repulsion term:

Skipping some details...

Triplet state has lower energy (FM $\uparrow\uparrow$)

$$\mathscr{C} = \langle \phi_{1s}(1)\phi_{2s}(2) | \mathscr{H}^1 | \phi_{1s}(1)\phi_{2s}(2) \rangle \quad \text{Coulomb term (>0)}$$
$$\mathscr{J} = \langle \phi_{1s}(2)\phi_{2s}(1) | \mathscr{H}^1 | \phi_{1s}(2)\phi_{2s}(1) \rangle \quad \text{Exchange term (>0)}$$

> Origin of ferromagnetism?

What is the origin of Ferromagnetism (spontaneous magnetization?



$$E_{dip} = \frac{\mu_0}{4\pi} \left\{ \frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{r^3} - \frac{3(\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r})}{r^5} \right\}$$

$$\mu = 1 \,\mu_B \quad , \quad r = 1 \,\text{\AA}$$

$$E_{dip} \sim \frac{\mu_0 \mu^2}{4\pi r^3} \simeq 8.6 \times 10^{-24} J = 53 \,\mu eV = 0.623 \,K$$

Origin of FM cannot be the dipolar interaction...

Dipolar interactions are long-range: responsible for: demagnetizing fields, magnetic domains.

Important only when exchange interactions are small. (But stay tuned until next lesson...)



FM (Fe, Co, Ni) have spontaneous magnetization up to ~ 1000 K \Rightarrow there must be huge internal magnetic field maintaining magnetism against thermal fluctuations.

For Co: T_c = 1400 K = 120 meV

$$\mu_{Co}$$
 B_{int} > 120 meV, μ_{Co} = 1.6 $\mu_{B} \implies$ B_{int} = 1300 T (!!)

Assuming $a_0 = 0.25 \text{ nm} + B_{int} = \mu_B I/8a \implies I = 4 \text{ A} (!!)$

Then what?

Weiss (1907) – Molecular field theory

Acting on every magnetic ion, there is an *exchange (molecular) field* created by the rest of ions:

 $H_{m} = \lambda M$ $H_{Tot} = H_{a} + \lambda M$

What is its origin? How do we find the thermal dependence of the magnetization?



How do we find the thermal dependence of spontaneous magnetization?

 $H_m = \lambda M$

Recalling average magnetization in *Brillouin paramagnetism*...

N independent magnetic moments μ having angular momentum J and m_J=-J,...+J *in a magnetic field H*

 $E_{m_J} = -\mu_z \mu_0 H = -g\mu_B m_J \mu_0 H , \text{(Zeeman energy)}$

$$M = n \langle \mu_z \rangle = \sum_{m_J = -J}^{m_J = +J} \mu_z e^{-E_{m_J}\beta} / Z$$
$$Z = \sum_{m_J = -J}^{m_J = +J} e^{-E_{m_J}\beta} = \sum_{m=-J}^{m=+J} e^{g\mu_B m_J \mu_0 H\beta} = \frac{\sinh(J + M_J)}{\sinh\frac{y_J}{2}}$$
$$(y \equiv g\mu_B \mu_0 H\beta)$$

$$M = ng\mu_B \frac{1}{Z} \frac{dZ}{dy}$$

 $\mu_{eff} = g\mu_B \sqrt{J(J+1)}$



 $\left(\frac{1}{2}\right)y$



But what happens if no field is applied? If only the internal Weiss field is considered?

If instead of the applied field, we use now the Weiss field in x: $x = g\mu_B J\lambda M\beta \implies M = \frac{k_B T}{g\mu_B \mu_0 \lambda J} x$

This means that, at a given T, the magnetization follows:



Linear function of x T dependent slope

Since both equations have to be accomplished, we find solutions graphically for different temperatures (T=0 is unstable): deduce M(T)





Can we calculate the critical Curie temperature Tc?

T_c: temperature above which the spontaneous magnetization is zero.

Equating the slopes of both functions for small x:





0.4

0.2-

0

0

0.2

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Temperature, T/T_{c}

0.6

0.4

0.8

1.0

0.2

Co, Ni

0.4

0.6

 $T/T_{\rm C}$

0.8

1.0

0.4

0.2

Weiss molecular field theory

What happens with the susceptibility? How is the Curie law modified for a FM?

For T>>T_c, paramagnetic region: Curie law will be valid but with H+ H_m instead of H:



In practice T_c and Θ_p do not coincide (mean field theory not valid near T_c)

Thermal dependence of magnetization and susceptibility





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Curie-Weiss law

for susceptibility

What is the behavior near the critical temperature Tc?

Recall the expansion of the Brillouin function (up to 3rd order):

$$\frac{M(T)}{M_0} = \mathscr{B}(x) \simeq ax - bx^3$$

$$\implies a\left(\frac{T}{T_c}\right)x = ax - bx^3 \Rightarrow x^2 = \frac{a}{b}\left(1 - \frac{T}{T_c}\right) \implies a\left(\frac{T}{T_c}\right)x = ax - bx^3 \Rightarrow x^2 = \frac{a}{b}\left(1 - \frac{T}{T_c}\right)$$

$$\implies \left(\frac{M(T)}{M_0}\right)^2 = \frac{a^3}{b}(1-t)t^2 \simeq \frac{10(J+1)^2}{3(J^2+(J+1)^2)}(1-t)) \implies \frac{M(T)}{M_0} \sim (1-t)^{1/2} \ [T/T_c \to 1]$$



Lecture I: Interactions and Magnetic Order

In an ANTIFERROMAGNET (AF) the exchange constant is negative (J<0) favoring antiparallel alignment of nn spins





Louis Néel 1932

In general: several sublattices, depending on geometry and type of magnetic ions

SC lattices



Triangular lattices



bcc lattices



fcc lattices



 $\begin{aligned} q_{\rm I} &= (2\pi/a)(0,0,1) = \\ q_{\rm II} &= (2\pi/a)(\frac{1}{2},\frac{1}{2},\frac{1}{2}) \\ q_{\rm III} &= (2\pi/a)(1,\frac{1}{2},0) = \\ q_{\rm IV} &= (2\pi/a)(\frac{1}{2},\frac{1}{2},0) \end{aligned}$

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Typical AF materials and Néel ordering temperatures

Element	$T_{\rm N}$ (K)	Compound	$T_{\rm N}$ (K)	Compound	$T_{\rm N}\left({\rm K}\right)$
Cr	311	MnO	118	FeS	593
Mn	100	${\rm FeO}$	185	MnF_2	72
Ce	12.5	CoO	291	FeF_2	79
Nd	19.2	NiO	515	CoF_2	38
\mathbf{Sm}	106	CuO	230	${ m FeF_3}$	394
Eu	90.5	$NdFeO_3$	760	CoF_3	460
Dy	178	$LaFeO_3$	750	K_2NiF_4	97
Ho	132	$\rm KMnF_3$	88	α -Fe ₂ O ₃	948
\mathbf{Er}	84	$KNiF_3$	275	Cr_2O_3	318
Tb	230	$NiCr_2O_4$	65	MnPt	975
Tm	56	$GeFe_2O_4$	10	Mn_3Pt	485

RE hcp

AB oxides (NaCl) ABC₃ perovskites

 AB_2O_4 spinels

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Observed Susceptibility









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 $\chi = \frac{1}{T - (-\theta)}$



Now, we will have 2 molecular fields, one per sublattice:

$$H_{m,a} = \lambda_{aa} M_a - \lambda_{ab} M_b + H = \lambda M_a - \lambda' M_b + H$$
$$H_{m,b} = -\lambda_{ba} M_a + \lambda_{bb} M_b + H = -\lambda' M_a + \lambda M_b + H$$

For simplicity, we will ignore λ :

$$H_{m,a} = -\lambda' M_b + H$$
$$H_{m,b} = -\lambda' M_a + H$$

In the paramagnetic regime: T > T_N the total magnetization will follow the Curie law: $\chi = \frac{M}{H} = \frac{C}{T}$

$$M_{a} = \frac{C'}{T}(H - \lambda'M_{b})$$

$$M = M_{a} + M_{b} = \frac{C'}{T}(2H - \lambda'(M_{a} + M_{b})) = \frac{C'}{T}(2H - \lambda'M)$$

$$M_{b} = \frac{C'}{T}(H - \lambda'M_{a})$$

$$\chi = \frac{M}{H} = \frac{C'}{T}(2 - \lambda'\chi)$$

$$\chi = \frac{2C'}{T + \lambda'C'}$$

$$\chi = \frac{C}{T + \Theta_{p}}$$

$$\chi = \frac{C'}{T + \Theta_{p}}$$

$$M_{a} = C' + \frac{C'}{T + \Theta_{p}}$$

$$M_{a} = \frac{C'}{T} + \frac{C'}{T} + \frac{C'}{T + \Theta_{p}}$$

$$M_{a} = \frac{C'}{T} + \frac{C'}{T + \Theta_{p}}$$

$$M_{a} = \frac{C'}{T} + \frac{C'}{T + \Theta_{p}}$$

$$M_{a} = -\frac{C'}{T + \Theta_{p}}$$

$$M_{a} =$$



Now, we will have 2 molecular fields, one per sublattice:

$$H_{m,a} = \lambda_{aa} M_a - \lambda_{ab} M_b + H = \lambda M_a - \lambda' M_b + H$$
$$H_{m,b} = \lambda_{ba} M_a - \lambda_{bb} M_b + H = \lambda' M_a - \lambda M_b + H$$

For simplicity, we will ignore λ :

$$H_{m,a} = -\lambda' M_b + H$$
$$H_{m,b} = -\lambda' M_a + H$$

In reality $T_N \neq \Theta_p$ because of contribution of nnn. fields λ . Calculations including λ show that:

$$T_c = C'(\lambda - \lambda')$$
, $\Theta_p = C'(\lambda + \lambda')$

For T< T_N, M_a=-M_b and M=0, but application of a field gives a small susceptibility that depends on the direction of the field





 $\chi \uparrow H_2 > H_1$ **(b)** H_2 H_1 $T_{\rm N}$

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IN



Now the magnetic field will increase the sublattice magnetization of one sublattice and decrease the

 $M = M_a + \delta M_a - (M_b - \delta M_b) = \delta M_a + \delta M_b = 2\delta M_a$



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If the applied field is large enough, sublattice magn. will reorient towards field direction:





 $M_a T = \alpha C (H + \lambda_a M_a - \lambda' M_b)$

 $M_b T = \beta C (H + \lambda_b M_b - \lambda' M_a)$

- > A ferrimagnet may be regarded as an antiferromagnet with *two unequal sublattices*: Same ion spices on sites of different symmetry (diff. # of ions in each sublattice). Different ion species in each sublattice with fractions α , β such that α + β =1 and magnetic moments $\mu_{i,a}$, $\mu_{i,b}$
- Sublattice spontaneous magnetizations will have different magnitudes M_a > M_b pointing opposite: finite small spontaneous magnetization (non-compensated AF). $M_a = \alpha n \mu_a$, $M_{\rm b} = \beta n \mu_{\rm b}$
- \succ Examples: Ionic solids, localized electrons, insulators. Ferrites such as Fe₃O₄, Fe₂O₃, Mn_3O_4 , CoFe₂O₄,...Garnets such as YIG (Y₃Fe₅O₁₂)

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We will still have 2 molecular fields, but now intrasublattice molecular fields cannot ignored:

$$H_{m,a} = \lambda_{aa} M_a - \lambda_{ab} M_b + H = \lambda_a M_a - \lambda' M_b + H$$
$$H_{m,b} = -\lambda_{ba} M_a + \lambda_{bb} M_b + H = -\lambda' M_a + \lambda_b M_b + H$$

In the paramagnetic regime: $T > T_c$ each sublattice magnetization will follow the Curie law:

Lenghty

$$\chi_i = \frac{M_i}{H_{m,i}} = \frac{C}{T}$$

$$\frac{1}{\chi_0} = \lambda' \left(2\alpha\beta - \bar{\lambda}_a \alpha^2 - \bar{\lambda}_b \beta^2 \right)$$
$$b = \lambda'^2 C\alpha\beta \left[\alpha (1 + \bar{\lambda}_a) - \mu (1 + \bar{\lambda}_b) \right]^2$$
$$\Theta_p = \lambda' C\alpha\beta (2 + \bar{\lambda}_a + \bar{\lambda}_b)$$

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 $\chi = \frac{M_a + M_b}{H}$ $\frac{1}{\chi} = \frac{T}{C} + \frac{1}{\chi_0} - \frac{b}{T - \Theta_p}$



$$\frac{1}{\chi} = \frac{T}{C} + \frac{1}{\chi_0} - \frac{b}{T - \Theta_p}$$

Equation of an hyperbola.

> Ferrimagnets: Molecular field theory

At high T, 3rd term negligible: Curie-Weiss behavior

$$\chi = \frac{C}{T + (C/\chi_0)}$$

Curie temperature T_c , computed equating $\chi^{-1}=0$:

$$T_C = \frac{\lambda'C}{2} \left[\alpha \bar{\lambda}_a + \beta \bar{\lambda}_a + \left\{ (\alpha \bar{\lambda}_a - \beta \bar{\lambda}_b)^2 + 4\alpha \beta \right\}^{1/2} \right]$$

Condition $T_C > 0 \Rightarrow$ intrasublattice interactions can't be too large ($\lambda'_{\alpha}\lambda'_{\beta}<1$).

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Below : $T < T_c$ each sublattice spontaneous magnetization follows a Brillouin law (H=0):

$$M_a^S = M_{a0} \mathscr{B} \left(\frac{\mu_0 m_a H_{m,a}}{k_B T} \right) \qquad H$$
$$M_b^S = M_{b0} \mathscr{B} \left(\frac{\mu_0 m_b H_{m,b}}{k_B T} \right) \qquad H$$

$$H_{m,a} = \lambda_a M_a - \lambda' M_b + H = (\lambda_a \alpha - \lambda' \beta) M$$
$$H_{m,b} = -\lambda' M_a + \lambda_b M_b + H = (\lambda_b \beta - \lambda' \alpha) M$$

- Coupled system of equations.
- > Solved numerically.



Compensation temperature

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III. Localized Magnetic Order

- Found in rear earths with hcp structure.
- > Helix is perpendicular to the hexagonally close packed planes, along what is usually defined as the c axis
- Exchange is RKKY mediated here (see later on...)



$$E_{exch} = -2S^2 N \sum_n \mathcal{J}_n \cos(\varphi_n)$$
$$\simeq -2S^2 N [\mathcal{J}_0 + \mathcal{J}_1 \cos(\varphi) + \mathcal{J}_1 \cos(2\varphi)]$$

Minimization:

$$\sin(\phi) \left[\mathcal{J}_1 + 4 \mathcal{J}_2 \cos(\phi) \right] = 0$$

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$$\cos\phi = -\mathcal{J}_1/4\mathcal{J}_2$$

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- > J> 0 \Rightarrow FM , J< 0 \Rightarrow AF or competing signs.
- S_i are quantum operators, but (for high S) approx. by classical vector spins.
- S_i can be distributed in a lattice or at random positions n space.
- Usually, only nn or nnn considered.

- Ground state and T_c may depend on lattice dimension and coordination.
- Can be used in MC, LLG atomistic or micromagnetic simulations.
- Hamiltonian is isotropic, has continuous O(3) symmetry (broken in the gr. state).
- Terms other than bilinear may appear (biquadratic...).

Relating Heisenberg exchange to Weiss molecular field...

$$\begin{aligned} \mathscr{H} &= -\sum_{i,j} J_{ij} \vec{S}_i \vec{S}_j = \sum_i \mathscr{H}_i \\ \mathscr{H} &= -\vec{S}_i \cdot \sum_j^z J_{ij} \vec{S}_j = -\vec{S}_i \cdot \vec{H}_i , \text{ with } \vec{H}_i = \sum_j^z J_{ij} \vec{S}_j \end{aligned} \qquad \Longrightarrow \qquad \begin{cases} \mathscr{H} &= -\sum_i^N \vec{S}_i \cdot \vec{H}_i \\ \mathscr{H}_{Zee} &= -g\mu_B \sum_i^N \vec{S}_i \cdot \vec{H}_{eff} \end{cases} \qquad \Longrightarrow \end{aligned}$$

$$\implies g\mu_B \vec{H}_{eff} = \sum_j^z J_{ij} \vec{S}_j \simeq \sum_j^z J_{ij} \langle \vec{S}_j \rangle = z J_0 \langle \vec{S}_j \rangle \qquad \Longrightarrow \qquad \vec{H}_{eff} = \frac{z J_0 \langle \vec{S}_j \rangle}{g\mu_B} \\ \vec{M} = g\mu_B N \langle \vec{S}_j \rangle \qquad \longrightarrow \qquad \vec{H}_{eff} = \frac{z J_0}{N g^2 \mu_B^2} \vec{M} = \lambda_W \vec{M}$$
Molecular field related to

exchange constants.

T -	$2zJ_0S(S+1)$
I_c –	$3k_B$

Exchange constants can be induced from the critical temperature.

Typical values: Fe, Co, NI

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Heisenberg model for atoms

\succ

Variants of Heisenberg model

Ising model
$$\mathscr{H} = -\sum_{i < j} J_{i_{2}}$$
(1925)

$$\mathscr{U} = -\sum_{i < j} J_{ij} \sigma_i \sigma_j \quad (\sigma = \pm 1)$$

XY model

Anisotropic

$$\mathscr{H} = -\sum_{i < j} J_{ij} (S_i^x S_j^x + S_i^y S_j^y)$$

 $\mathscr{H} = -\sum_{i < j} J_{ij} (S_i^x S_j^x + S_i^y S_j^y + \Delta S_i^z S_j^z)$

Ising 1D: No phase transition (order only @ T=0) Quantum case: sigmas are spin Pauli matrices.

- Ising 2D exactly solved (Onsager). k B Tc= 2.269 J
- > XY in 2D: no long-range order KT transition

 $T_{\rm KT} = \frac{\pi J}{2k_{\rm B}}$

Mermin-Wagner theorem: no FM order in <=2D for \geq isotropic Heisenberg model.





 $\overline{i < j}$



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1.5

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Basic assumptions

- Free energy F(m) is continuous and has the symmetries of the Hamiltonian.
- Continuous (2nd order) phase transition: F(m) varies cont. across T_c, 1st derivative too.
- > F(m) is minimum at m_0 , the equilibrium value of the order parameter: $m_0 = 0$ (T> T_c), $m_0 \neq 0$ (T< T_c).
- Ignores correlations and fluctuations (it is mean field).
- Can be expanded as:

 $F(m) = F_0 + A(T)m^2 + B(T)m^4 + \dots$

A(T)=a(T-T_c), changes sign at T_c, B(T)= b > 0

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> Magnetic phase transitions: Landau theory

Landau Theory

Magnetization

$$F(m) = F_0 + A(T)m^2 + B(T)m^4 + \dots$$

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$$\frac{\partial F(m)}{\partial m} = 2Am + 4Bm^3 = 2m(A + 2Bm^2) = 0 \implies \begin{cases} m_0 = 0 \quad T \ge T_c \\ m_0 = \pm \sqrt{\frac{-A}{2B}} \quad T < T_c \end{cases}$$



Susceptibility

$$F(m) = F_0 + A(T)m^2 + B(T)m^4 - \mu_0 Hm$$

$$\frac{\partial F(m)}{\partial m} = 2Am + 4Bm^3 - \mu_0 H = 0$$

$$\begin{cases} T \ge T_c \ 2Am \simeq \mu_0 H \Rightarrow m = \frac{\mu_0 H}{2a(T - T_c)} \\ T < T_c \ 2m\chi + 12m^2\chi = \mu_0 \Rightarrow \chi = \frac{\mu_0}{-4A} = \frac{\mu_0}{4a(T_c - T)} \end{cases}$$



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$F(m) = F_0 + A(T)m^2 + B(T)m^4 + \dots$

Free ene

Critical exponents

Free energy
$$\begin{cases} T \ge T_c, \quad F(m_0) = F_0 - \frac{A^2}{4B} = F_0 - \frac{a^2}{4b}(T - T_c)^2 \\ T < T_c, \quad F(0) = F_0 \end{cases}$$
Specific heat
$$C_P = -T\frac{\partial^2 F}{\partial^2 T} \Rightarrow C_P = \begin{cases} T \ge T_c, \quad \frac{a^2}{2b}T^1 \\ T < T_c, \quad 0 \end{cases}$$

 $\chi = \frac{1}{k_B T} \left(\langle m^2 \rangle - \langle m \rangle^2 \right)$



Magnetization isotherm

$$m = \left(\frac{\mu_0 B}{2b}\right)^{1/3}$$

Diverges at $T_C \Rightarrow$ divergence of fluctuations, clusters of all sizes

Linked to the concept of correlation length ξ

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Susceptibility and

fluctuations:

Critical exponents

Close to T_c: correlation length diverges, scaling properties become universal, independent on microscopic details.

Universality class: systems with same set of critical exponents, independent of details of composition.
Usually, with the same spatial dimensions and order parameter components.

Specific heat	$C_m \sim 1 - T/T_c ^{\alpha}$
Magnetization	$m \sim (1 - T/T_c)^{\beta}$
Susceptibility	$\chi \sim (1 - T/T_c)^{-\gamma}$
Induced magnetization	$m(T=T_c)\sim H^{1/\delta}$
Correlation length	$\xi \sim 1 - T/T_c ^{-\nu}$
Spin-spin correlation	$\Gamma(r) \sim r ^{-(D-2+\eta)}$

Renormalization group theory (links between exponents)

$$2 = \alpha + 2\beta + \gamma$$

$$\gamma = \beta(\delta - 1)$$

$$\alpha = 2 - \nu D$$

$$(2 - \eta)\nu = \nu$$

	Mean Field	Ising	Heisenberg	Ni
$C_m = 1 - T/T_c ^{\alpha}$	0	0.11	-0.115	0.1
$m = (1 - T/T_c)^\beta$	1/2	0.323	0.362	0.42
$\chi = (1 - T/T_c)^{-\gamma}$	1	1.24	1.39	1.32
$m = H^{1/\delta}$	3	4.82	4.82	4.5
$\xi = 1 - T/T_c ^{-\nu}$	2/3	0.63	0.7	0.63*
$\Gamma(r) = r ^{-(D-2+\eta)}$	1/2	0.03	0.03	-0.08*

Critical exponents for Ising model in d dimensions

dimensions	2	3	≥4 **
V	1	0.6301	1/2
Y	7/4	1.2373	1
α	logarithmic	0.110	
β^*	1/8	0.3265	1/2
δ	15	4.789	3
η	1/4	0.0365	

Critical exponents

Close to T_c: correlation length diverges, scaling properties become universal, independent on microscopic details.

Universality class: systems with same set of critical exponents, independent of details of composition. Usually, with the same spatial dimensions and order parameter components.



Dimensionality crossover



3D FM univers. class

We have seen that few materials made of single elements are FM or AF: Fe, Co, Ni, Cr, Mn,... But when it turns to compound materials, we know many others are AF or FM: Magnetic Oxides, Spinels, Manganites,...

What is the origin of negative molecular field (J< 0)?

In these materials magnetism was driven by DIRECT EXCHANGE, mainly due to w.f. overlap between nearest atoms. In compound materials, magnetic ions are separated by non-magnetic ones. Direct exchange cannot explain why are they magnetic.

INDIRECT

EXCHANGE



INDIRECT EXCHANGE

Exchange coupling bw. magnetic atoms is mediated by a non-magnetic atom.

Typical of ionic compounds

Usually non-magnetic atom is O (but can be F,...)

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- 1934 1950
- Two cations of same valence coupled to oxygen anion (Mn²⁺, Fe³⁺).
- Exchange mediated by 2p-orbitals of oxygen.
- Singly occupied or half-filled 3d orbitals.
- > MnO, NiO, CrO_2 , ... MnF_2 , FeF_2 , CoF_2 ,...



Since O orbital is full, this is only possible if an e⁻ is transferred from an O to a Mn orbital.



It gives an **AF Coupling** between metal cations







> Indirect Interactions: Superexchange

> Indirect Interactions: Superexchange



Super exchange depends on:

- Magnitude of magnetic moment of the cations.
- Degree of M-O overlap.
- Angle of the M-O-M bond.

Goodenough-Kanamori rules



For half-filled orbitals: 180° superexchange: strong AF coupling.

For half-filled: 90° direct exchange: weak FM coupling.







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DOUBLE EXCHANGE



- Two cations of *different valence* coupled to oxygen anion (Mn³⁺, Mn⁴⁺).
- Exchange mediated by 2p-orbitals of oxygen.
- Manganites: $La_{1-x}Sr_{x}MnO_{3}$, $La_{1-x}Ca_{x}MnO_{3}$,....





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- Some degree of covalent bonding Mn-O energetically favorable.
- One half-filled and one empty or full.
- Metal cations exchange their valence: metallic conduct +FM

It gives a *weak FM Coupling* between metal cations.



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> Indirect Interactions: Double exchange

Case of Magnetite Fe_3O_4



- Ferrimagnet: Tc= 860 K
- 24 Fe ions/fu: 16 Fe³⁺, 8 Fe²⁺
- 16 Octah: Fe³⁺, Fe²⁺ aligned ↑: O-O Double exchange
- 8 Tetrah: Fe³⁺, aligned \downarrow : T-O Super exchange
- Magnetic moment: μ = (5+4-5) μ _B = 4 μ _B/fu



RKKY interactions



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• Wavelength given by $\lambda=\pi/k_F\sim 3{
m \AA}$

RKKY interactions: examples

If a spin S_2 is placed at distance from S_1



$$\mathscr{H}_{eff} = -2J(r)\vec{S}_1 \cdot \vec{S}_2$$
$$J(r) = \frac{2m_e J_{sd}^2 k_F^4}{(2\pi^3)\hbar^2} F(2k_F r)$$



In metallic multilayers (metal thickness d)

$$J_{12}(z) = J_0 \frac{d^2}{z^2} \sin(2k_F z)$$

Importance for GMR:

Cr film

L ≈ 300–500 μm

Fe whisker



(a) Monolayers

2 nm

200 µm

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5-20 nm







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Z.

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Spin Glasses

- > Instead of a single impurity, we now consider a collection of impurity ions distributed in an electron gas.
- Randomness and competing interactions.
- Below a characteristic spin-glass temperature, T_{sg}, the magnetic moments are so frustrated that they will freeze in random orientations.
- Sharp peak in the low-field susceptibility at T_{sg} and the observation, for T <T_{sg}, of irreversible and time dependent effects on the application of magnetic fields.
- > Order parameter is the replica overlap.
- Low T phase is one of the many possible local minima in a complex energy landscape with many minima separated by large energy barriers.
- Metallic systems such as Au–Fe, Au–Cr, Au–Mn, Cu–Mn, and Ag-Mn at low concentrations 0.1–10%.

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Ising triangular: Wannier (1950)





States in triangular lattice



Spin Glasses

Phase diagram of $Au_{(1-x)}Fe_x$





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Frustrated lattices \succ

Examples of frustrated lattices

Kagomé lattice



- Classical ground state with macroscopic degeneracy, described as cooperative PM.
- Only short-range correlations between spins are found for all temperatures.

Spin ice **Pyrochlore lattice in 3D**



- $Dy_{2}Ti_{2}O_{7}$
- Large classical Ising spins along (111)
- Ice rule: 2 in-2 out.
- Magnetic monopoles.





- Based on elongated nanomagnets.
- Many different lattices.
- Logic gates.
- Neuromorphic computing.



I. Dzyaloshinski



T. Moriya (1957-60)

Dzyaloshinskii-Moriya interaction

- > Previous indirect exchange mechanisms favored collinear configurations.
- > Introduced to explain weak ferromagnetism in typically AF α -Fe₂O₃ hematite crystals.
- It is an antisymmetric and chiral interaction: spiral textures and skyrmions.
- Generated by the *lack of inversion symmetry* + *indirect super exchange* mediated by *spin orbit coupling* (with a 3rd atom).
- Favors perpendicular orientation of magnetic moments.

$$\mathscr{H}_{DMI} = \vec{S}_i \begin{bmatrix} \mathscr{J}^A \end{bmatrix} \vec{S}_j = \vec{S}_i \begin{pmatrix} 0 & D_x & D_y \\ -D_x & 0 & D_z \\ -D_y & -D_z & 0 \end{pmatrix} \vec{S}_j$$

- Magnitude of D proportional to SO coupling.
- Direction for the case of the figure given by: $\vec{D}_{ij} \propto (\vec{r_i} \times \vec{r_j}) = \vec{r_{ij}} \times \hat{x}$

Spin of Bloch state (that has $L \neq 0$) needs to align towards magnetic moment and $L \Rightarrow$ canting of magnetic moments to minimize energy.

 \geq



$$\mathscr{H}_{DMI} = \vec{D}_{ij} \cdot (\vec{S}_i \times \vec{S}_j)$$

DMI Interaction

Dzyaloshinskii-Moriya interaction

Direction of the DMI vector:

Two spins located at R_1 and R_2 . The middle is $R = (R_1 + R_2)/2$.

- Center of inversion is located at R: D = 0.
- Mirror plane perp. to $R_1 R_2$ includes R: $D \perp (R_1 R_2)$.
- > Mirror plane includes R_1 and $R_1 + R_2$: D \perp mirror plane.
- > Two-fold rotation axis perp. to $R_1 R_2$ includes R: D \perp rotation axis.
- > If a n-fold rotation axis (n ≥ 2) includes R_1 and R_2 : D || ($R_1 R_2$).



Skymions





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 $\vec{D}_{ij} \cdot (\vec{S}_i \times \vec{S}_j)$





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Magnetism in metals: motivation \geq



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Mystery of broken Bohr magnetons

If magnetic atomic moments are multiples of μ_B ...

 $\mathbf{m} = (2\mathbf{S} + \mathbf{L})\mu_B/\hbar$

...why measured values for Fe, Co, Ni are not?

	$\mu_s(\mu_B)$	$\mu_m(\mu_B)$
Fe	4	2.216
Co	3	1.715
Ni	2	0.616

The dark side of magnetism



Let us consider an hypothetic metal with electronic density n_0 , quasi-free e's, in absence of external magnetic field.





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> Stoner Criterion

• Increase in Kinetic energy:

• Increase in Kinetic energy:

$$\Delta E_K = \frac{g(\varepsilon_F)}{2} \delta \varepsilon(\delta \varepsilon) = \frac{g(\varepsilon_F)}{2} (\delta \varepsilon)^2$$

• Molecular field energy decrease:

$$\Delta E_{PE} = -\int_0^M d\mathbf{M}' \mu_0 \mathbf{H}_{int} \cdot \mathbf{M}' = -\mu_0 q \mathbf{M}^2 / 2 = -\frac{\mu_0 q}{2} \mu_B^2 (g(\varepsilon_F) \delta \varepsilon)^2$$

• Total energy change:

$$\Delta E = \frac{g(\varepsilon_F)}{2} (\delta \varepsilon)^2 - \frac{\mu_0 q}{2} \mu_B^2 (g(\varepsilon_F) \delta \varepsilon)^2$$

Exchange splitting of bands will occur if $\Delta E < 0$:

 $\mu_0 q \mu_B^2 g(\varepsilon_F) > 1$

$$U = \mu_0 q \mu_B^2$$
, Coulomb energy

STONER CRITERION

$$U g(\varepsilon_F) > 1$$

How can we get a net magnetization?







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Competition between exchange and kinetic energy.

Stoner Criterion

STONER CRITERION U g(

$$\varepsilon_F) > 1$$
 Somet

imes written also as: $I N_0 > 1$



- Only Fe, Co, Ni accomplish it among the 3d TM.
- Sc and Pd are on the verge.
- > FM occurs basically because of the spatial localization of the d orbitals near the top of the d band.
- This localization produces both a large density of states and a relative maximum in the exchange integral *I*.
- \succ IN₀ is large enough for FM at the end of the 3d series, but not the 4d series because the 4d w.f. extends further out from the nucleus, which implies larger interaction bw. the neighbors, a larger bandwidth and thus a smaller density of states.
- > Exchange integral is considerably larger in the light elements than in the 3d series, there is no possibility of FM because of the much smaller density of states.

Susceptibility: even if Stoner criterion is not satisfied, the Stoner field will affect the paramagnetic susceptibility, how?

We add the Zeeman term to the total energy change:

$$\Delta E = \Delta E_K + \Delta E_{PE} + \Delta E_{Zee}$$
$$= \frac{1}{2} (g(\varepsilon_F) \delta \varepsilon)^2 \left[\frac{1}{g(\varepsilon_F)} - U \right] - \mu_0 M H$$
$$= \frac{M^2}{2g(\varepsilon_F) \mu_B^2} \left[1 - Ug(\varepsilon_F) \right] - \mu_0 M H$$

Minimizing with respect to M:

$$\frac{M}{g(\varepsilon_F)\mu_B^2} \left[1 - Ug(\varepsilon_F)\right] - \mu_0 H = 0$$

$$\chi = \frac{\mu_0 g(\varepsilon_F) \mu_B^2}{[1 - Ug(\varepsilon_F)]} = \frac{\chi_{Pauli}}{1 - Ug(\varepsilon_F)}$$

Coulomb interactions (exchange) enhance the Pauli susceptibility.

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STONER CRITERION

 $U g(\varepsilon_F) > 1$

Sometimes written also as: $I N_0 > 1$

- All the previous treatment was done for an s band of free e's.
- But for 3d metal things are not that simple: valence electrons are 4s and 3d.

(1) Band structure matters

- As atoms approach each other, atomic levels broaden into bands.
- 4s (ℓ=0) states have lower energy (closer to nucleus) than 3d (ℓ=2) states.
- But 4s states extend further: begin to bond (broaden) at further distances than 3d (more localized).
 - Lower 3d band: bonding states (delocalized)
 - Upper 3d band: antibonding states (localized)
 - Areas under 4d and 3d bands: 2/10 ratio.
 - Fermi energy ε_F varies with e- concentration.
 - There is a larger # of e's in d bands (magnetism).



STONER MODEL

Postulates the existence of a molecular field *acting on electronic levels* (!!) of 3d TM



- \succ Due to the molecular energy, levels of \uparrow and \downarrow spins are shifted differently.
- > The density of states is shifted by an exchange splitting $\Delta \approx 1$ eV.
- $\blacktriangleright~I_{3d}\!\!>I_{4d}\!\!>I_{5d}$, g(ϵ_{F}) ~ 1/w

(2) Band widths

> Smaller coordination \Rightarrow smaller s-d hybrid. \Rightarrow smaller w \Rightarrow FM boosted in lower dimensions.





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STONER CRITERION

 $U g(\varepsilon_F) > 1$

Sometimes written also as: $I N_0 > 1$

- > All the previous treatment was done for an s band of free e's.
- > But for 3d metal things are not that simple: valence electrons are 4s and 3d.

③ Coulomb repulsion (exchange) vs kinetic energy

- Sub bands are split by Weiss field (exchange interaction).
- For e's in a 3d band, we cannot fill states as 1st Hund rule for atoms, they are non degenerate.
- > High energy cost putting all e's in same band.

- > Pauli's: 2 e-'s with same spin can't be same place.
- > e-'s with $\uparrow\uparrow$ repel less the e-'s with $\uparrow\downarrow$.
- > Parameter I: repulsion of $\uparrow \downarrow$ e's is larger by I than for $\uparrow \uparrow$ e's.



3d band filling as a function of valence electrons



Origin of broken Bohr magnetons

- Some (small fraction) e-'s go into 4s band.
- Filling of 3d band can be any fraction of n_v.
- > Splitting of bands due to exchange is given by Stoner parameter.



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Sign of J: Bethe-Slater-Neél curve

J (or T_c) as a function of a/r₀ (or d band occupancy) where a is lattice spacing and r₀ is radius of e⁻ shell

$$\mathcal{J}_{12} = \iint \Psi_{a}^{*}\left(r_{1}\right) \Psi_{b}^{*}\left(r_{2}\right) \left[\frac{1}{r_{ab}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} - \frac{1}{r_{12}}\right] \Psi_{a}\left(r_{1}\right) \Psi_{b}\left(r_{2}\right) dv_{1} dv_{2}$$



Element	Fe	Co	Ni	Cr	Mn	Gd
a/r _o	3.26	3.64	3.94	2.6	2.94	3.12

- > Slater criterion: FM if $a/r_0 > 3$, AF if $a/r_0 < 3$
- Fe can be FM-AF depending on cryst. struct. (fcc z=12, bcc z= 8)
- Bandwidth also matters (related to z (nn) and hopping): w= 2zt
- Sc, Ti, V... not magnetic because t too big.
- Narrow band, large moments.
- Alloying Mn or Cr may lead also to FM.

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Hopping between neighb. atoms in a 3d metal

Magnetic moments of TM alloys follow these curves for any combination (experimental)



Rigid Band Model

- Bands remain the same.
- Only offect of alloying is to change the band filling with the added electrons.
- Only # of valence e's seem to matter.

$$\mu_m = \mu_B (n_{d,\uparrow} - n_{d,\downarrow})$$



- > Maximum of $2.5\mu_B$ for Fe_{0.7}Co_{0.3} (largest in any material)
- In going from Fe, Co to Ni: reduction expected and observed.
- Mixing with elements to the right of max: reduction.

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VI. Itinerant Magnetism

Magnetic moments of TM alloys follow these curves for any combination (experimental)



Rigid Band Model

- Bands remain the same.
- Only offect of alloying is to change the band filling with the added electrons.
- Only # of valence e's seem to matter.

$$\mu_m = \mu_B (n_{d,\uparrow} - n_{d,\downarrow})$$



- > Maximum of $2.5\mu_B$ for $Fe_{0.7}Co_{0.3}$ (largest in any material)
- In going from Fe, Co to Ni: reduction expected and observed.
- Mixing with elements to the right of max: reduction (?).

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Magnetic moments of TM alloys follow these curves for any combination (experimental)



 $\mu_m = \mu_B (n_{d,\uparrow} - n_{d,\downarrow})$ $n_d = n_{d,\uparrow} - n_{d,\downarrow}$

When adding a strong FM:

Suppose $n_{d\uparrow}$ = 5 (case of Co, Ni added to Fe): adding more e's to the d shell \Rightarrow go to $n_{d\downarrow} \Rightarrow \mu_m$ reduced

$$\mu_{m} = \mu_{B}(5 - n_{d,\downarrow}) \qquad \mu_{m} = \mu_{B}(10 - n_{d})$$

$$n_{d,\downarrow} = n_{d} - 5 \qquad \text{Negative}$$

$$slope -1$$

For
$$Fe_{0.7}Co_{0.3} \Rightarrow n_v = 8.6 \Rightarrow n_{d\downarrow} = 8.6-5=3.6 \Rightarrow \mu_m = 2.4 \ \mu_B \ Ok$$

When adding a weak FM:

Case of V, Cr added to Fe: $n_{d\uparrow} + n_{d\downarrow} = 8$, $n_{d\uparrow} - n_{d\downarrow} = 2.2 \Longrightarrow$ n_{d↓} ≈ 3. $\mu_m = \mu_B(n_d - n_{d,\downarrow} - n_{d,\downarrow}) = \mu_B(n_d - 2n_{d,\downarrow})$

Additional holes reduce the moment.

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 $\mu_m = \mu_B(n_d - 6)$

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