Exchange and ordering

Stephen Blundell
University of Oxford

2015 European School of magnetism
Cluj, August 2015

Part 1

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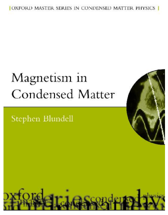
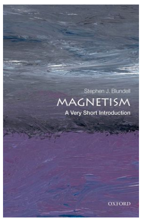
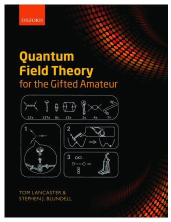
Books

Magnetism in Condensed Matter, S.J. Blundell, OUP (2001)
Magnetism and Magnetic Materials, J.M.D. Coey, CUP (2009)
Basic aspects of the quantum theory of magnetism, D.I. Khomskii, CUP(2010)
Magnetism: A Very Short Introduction, S. J. Blundell, OUP (2012)







Magnetism in Condensed Matter, S.J. Blundell, 36 Euros from amazon.de

Magnetism: VSI S.J. Blundell, 8 Euros

Quantum Field Theory for the Gifted Amateur T. Lancaster and S.J. Blundell, 44 Euros

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Outline

Exchange

1. Direct exchange
2. Indirect exchange
3. Superexchange

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Outline

Exchange

1. Direct exchange
2. Indirect exchange
3. Superexchange

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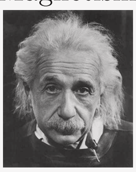
Magnetism is fully relativistic



$$\vec{E} = -\frac{\partial \vec{A}}{\partial t} - \vec{\nabla}\phi \qquad \vec{B} = \vec{\nabla} \times \vec{A}$$

$$F^{\mu\nu} = \begin{bmatrix} 0 & -E_x/c & -E_y/c & -E_z/c \\ E_x/c & 0 & -B_z & B_y \\ E_y/c & B_z & 0 & -B_x \\ E_z/c & -B_y & B_x & 0 \end{bmatrix}$$

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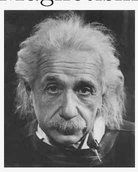
Magnetism is fully quantum mechanical

$$\mathcal{H} = -2\mathcal{J}\mathbf{S}_1 \cdot \mathbf{S}_2$$

Magnetism is fully relativistic



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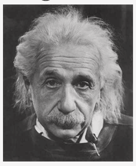
Magnetism is fully quantum mechanical

$$\mathbf{S} = \frac{1}{2}\boldsymbol{\sigma}$$

Magnetism is fully relativistic



$$\vec{E} = -\frac{\partial \vec{A}}{\partial t} - \vec{\nabla}\phi \qquad \vec{B} = \vec{\nabla} \times \vec{A}$$

$$F^{\mu\nu} = \begin{bmatrix} 0 & -E_x/c & -E_y/c & -E_z/c \\ E_x/c & 0 & -B_z & B_y \\ E_y/c & B_z & 0 & -B_x \\ E_z/c & -B_y & B_x & 0 \end{bmatrix}$$

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Louis Néel
(1904-2000)

↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓
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Energy terms:

- Kinetic energy $\frac{\hbar^2}{2m}\frac{\pi^2}{L^2} =$ eV
- Coulomb energy $\frac{e^2}{4\pi\epsilon_0 L} =$ eV
- Size of atom given by balance of these two terms
- Spin-orbit ~ meV
- Magnetocrystalline anisotropy ~ μeV

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Molecular orbitals : H_2

(A)—(B)

$$|\psi\rangle = c_A|\psi_A\rangle + c_B|\psi_B\rangle$$

$$\mathcal{H} = -\frac{\hbar^2}{2m}\nabla^2 + V_A + V_B$$

$$\mathcal{H}|\psi\rangle = E|\psi\rangle$$

↳ energy

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$$E_0 = \langle\psi_A|\mathcal{H}|\psi_A\rangle$$

$$t = \langle\psi_A|\mathcal{H}|\psi_B\rangle$$

↳ resonance integral
[transfer or hopping integral]

$$S_{ij} = \langle\psi_i|\psi_j\rangle$$ overlap integrals

$$= \delta_{ij}$$ (Hückel approx)

$$\mathcal{H}|\psi\rangle = E|\psi\rangle$$

↳ energy

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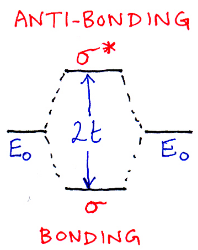
$$\mathcal{H}|\psi\rangle = E|\psi\rangle$$

$$\Rightarrow \quad |H_{ij} - E\,S_{ij}| = 0$$

$$\Rightarrow \quad \begin{vmatrix} E_0 - E & t \\ t & E_0 - E \end{vmatrix} = 0$$

$$\Rightarrow \quad E = E_0 \pm t$$



Eigenfunctions: $\sigma = (|\psi_A\rangle + |\psi_B\rangle)/\sqrt{2}$ (Symmetric, bonding)
$\sigma^* = (|\psi_A\rangle - |\psi_B\rangle)/\sqrt{2}$ (Antisymmetric, antibonding)

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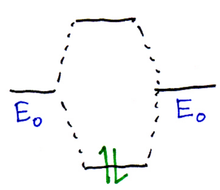
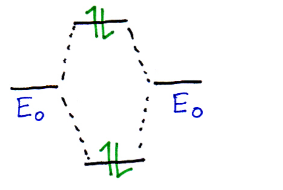
Why do you get H_2 and not He_2?

di-HYDROGEN H_2



Saves energy to bond

di-HELIUM He_2



no saving to bond (in fact, costs energy)

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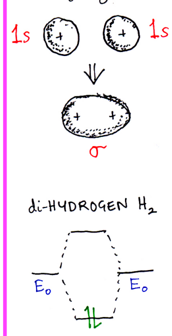
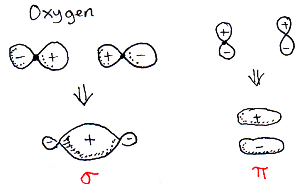
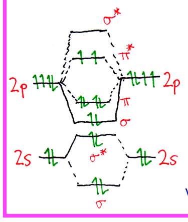
Hydrogen



Saves energy to bond

Oxygen





Stable state of O_2 is triplet-O_2 (as drawn)

⇒ magnetic!

O–O 145 kJ mol^{-1}
N–N 170 kJ mol^{-1}

Why is N–N stronger?

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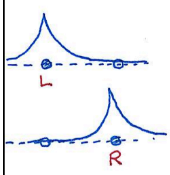
Two-electron model



2 electrons:

states $|LL\rangle, |LR\rangle, |RL\rangle, |RR\rangle$

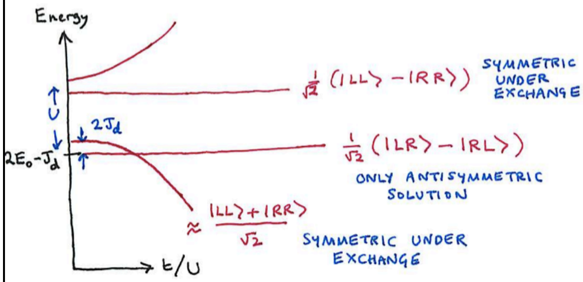
$$\hat{H} = 2E_0 + \begin{pmatrix} U & t & t & J_d \\ t & 0 & J_d & t \\ t & J_d & 0 & t \\ J_d & t & t & U \end{pmatrix}$$

hopping $t = \langle LL|\hat{H}|LR\rangle$ — 2nd electron hopped

Coulomb $U = \langle LL|\hat{H}|LL\rangle - 2E_0$ — penalises double occupancy

direct exchange $J_d = \langle LR|\hat{H}|RL\rangle$

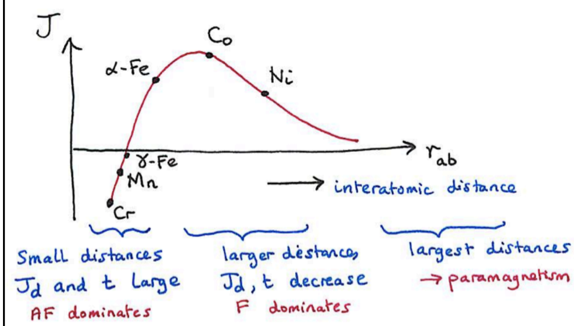
Two-electron model



$$J_{eff} = \frac{\Delta E}{2} = J_d + \frac{U}{4} - \sqrt{t^2 + \left(\frac{U}{4}\right)^2}$$

$$\frac{(|LL\rangle + |RR\rangle)}{\sqrt{2}} \sin\chi + \frac{(|LR\rangle + |RL\rangle)}{\sqrt{2}} \cos\chi \qquad \tan 2\chi = -4t/U$$

Bethe-Slater curve



$$J_{eff} = \frac{\Delta E}{2} = J_d + \frac{U}{4} - \sqrt{t^2 + \left(\frac{U}{4}\right)^2}$$

Consider 2 electrons: their spins can combine to form either an antisymmetric singlet state χ_S ($S = 0$) or a symmetric triplet state χ_T ($S = 1$). The wave function, which is a product of spatial and spin terms, must be antisymmetric overall. Hence:

$$\begin{aligned}\Psi_S &= [\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) + \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1)]\,\chi_S \\ \Psi_T &= [\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) - \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1)]\,\chi_T\end{aligned}$$

The energies of the two possible states are

$$\begin{aligned}E_S &= \int \Psi_S^* \hat{H} \Psi_S \, d\mathbf{r}_1 \, d\mathbf{r}_2 \\ E_T &= \int \Psi_T^* \hat{H} \Psi_T \, d\mathbf{r}_1 \, d\mathbf{r}_2\end{aligned}$$

so that the difference between the two energies is

$$E_S - E_T = 4 \int \psi_1^*(\mathbf{r}_1)\psi_2^*(\mathbf{r}_2)\hat{H}\psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1)\, d\mathbf{r}_1 \, d\mathbf{r}_2.$$

The energy is then $E = \frac{1}{4}(E_S + 3E_T) - (E_S - E_T)\mathbf{S_1} \cdot \mathbf{S_2}$. The spin-dependent term can be written $H^{\text{spin}} = -J\mathbf{S_1} \cdot \mathbf{S_2}$.

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- Interaction between pair of spins motivates the general form of the Heisenberg model:

$$H = -\sum_{ij} J_{ij} \mathbf{S_i} \cdot \mathbf{S_j}$$

- The quantity J_{ij} gives the exchange energy between two spins. Be very careful on the factor of two between different conventions of the definition of *J*.

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"J convention"	**"$2J$ convention"**
$\bullet\overset{J}{\text{——}}\bullet$	$\bullet\overset{2J}{\text{——}}\bullet$
2 spins: $-J\mathbf{S}_1 \cdot \mathbf{S}_2$	**2 spins:** $-2J\mathbf{S}_1 \cdot \mathbf{S}_2$
many spins:	**many spins:**
$-\sum_{i>j} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$	$-2\sum_{i>j} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$
$-\frac{1}{2}\sum_{ij} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$	$-\sum_{ij} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$
$-\frac{J}{2}\sum_{\langle ij\rangle} \mathbf{S}_i \cdot \mathbf{S}_j$	$-J\sum_{\langle ij\rangle} \mathbf{S}_i \cdot \mathbf{S}_j$
$-J\sum_i \mathbf{S}_i \cdot \mathbf{S}_{i+1}$ (1D)	$-2J\sum_i \mathbf{S}_i \cdot \mathbf{S}_{i+1}$ (1D)

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- Interaction between pair of spins motivates the general form of the Heisenberg model:

$$H = -\sum_{ij} J_{ij} \mathbf{S_i} \cdot \mathbf{S_j}$$

- *Direct exchange*: important in many metals such as Fe, Co and Ni
- *Indirect exchange*: mediated through the conduction electrons (RKKY)
- *Superexchange*: exchange interaction mediated by oxygen. This leads to a very long exchange path. Important in many magnetic oxides, e.g. MnO, La_2CuO_4.

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Outline

Exchange

1. Direct exchange
2. Indirect exchange
3. Superexchange

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Magnetism and metals

a Some revision

density of states $\quad g(k)\,dk = \dfrac{2 \times 4\pi k^2\,dk}{(2\pi)^3}$

$$n = \frac{N}{V} = \int_0^{k_F} g(k)\,dk = k_F^3 / 3\pi^2$$

$$\Rightarrow \quad k_F^3 = 3\pi^2 n, \qquad E_F = \frac{\hbar^2 k_F^2}{2m}$$

$$n \propto E_F^{3/2} \quad \therefore \quad \frac{dn}{n} = \frac{3}{2}\frac{dE_F}{E_F}$$

$$\therefore \quad g(E_F) = \left.\frac{dn}{dE}\right)_{E_F} = \frac{3}{2}\frac{n}{E_F}$$

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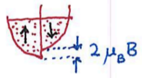
b Pauli paramagnetism



$$n_\pm = \frac{1}{2}\int_0^\infty g(E \pm \mu_B B)\, f(E)\, dE \qquad f(E) = \frac{1}{e^{\beta(E-\mu)}+1}$$

$$n_\pm \simeq \frac{1}{2}\int_0^\infty \left[g(E) \pm \mu_B B \frac{\partial g}{\partial E} \right] f(E)\, dE$$

$$M = \mu_B (n_+ - n_-) \simeq \mu_B^2 B \underbrace{\int_0^\infty \frac{dg}{dE} f(E)\, dE}$$

$$\underbrace{\Big[g(E) f(E) \Big]_0^\infty}_{=0 \ \because\ g(0) = f(\infty) = 0} - \int_0^\infty \frac{df}{dE} g(E)\, dE$$

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$$M = \mu_B^2 B \int_0^\infty \left(-\frac{\partial f}{\partial E} \right) g(E)\, dE$$

$$n = \int_0^\infty f(E)\, g(E)\, dE$$

Two cases

(i) degenerate limit ($T = 0$)

$$-\frac{df}{dE} = \delta(E - E_F)$$

$$M = \mu_B^2 B\, g(E_F)$$

$$\therefore \chi = \frac{\mu_0 M}{B} = \mu_0 \mu_B^2\, g(E_F) \quad \text{(T-independent)}$$

using $g(E_F) = \frac{3}{2}\frac{n}{E_F}$ $\therefore$ $\chi = \dfrac{n \mu_0 \mu_B^2}{\frac{2}{3} k_B T_F}$

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(ii) non-degenerate limit

$$f(E) \simeq e^{-(E-\mu)/k_B T}$$

$$-\frac{df}{dE} = \frac{f}{k_B T}$$

$$M = \frac{\mu_B^2 B}{k_B T} \underbrace{\int_0^\infty f(E)\, g(E)\, dE}_{n} = \frac{n \mu_B^2 B}{k_B T}$$

$$\chi = \frac{\mu_0 M}{B} = \frac{n \mu_0 \mu_B^2}{k_B T} \qquad \text{Curie-like} \propto 1/T$$

Can show that for Pauli sus.

$$\chi(T) = \frac{n \mu_0 \mu_B^2}{\frac{2}{3} k_B T_F} \left(1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 + \ldots \right)$$

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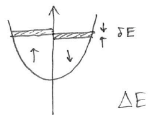
c Spontaneous FM in absence of B?



flip $\frac{1}{2} g(E_F)\,\delta E$ electrons increasing their energy by δE

$$\Delta E_{KE} = \frac{1}{2} g(E_F) (\delta E)^2 \quad ①$$

$$n_\pm = \frac{1}{2}\left(n \pm g(E_F)\,\delta E \right)$$

$$n_+ - n_- = g(E_F)\,\delta E$$

$$\Delta E_{PE} = -\frac{1}{2} U (n_+ - n_-)^2$$

$$= -\frac{1}{2} U \left(g(E_F)\,\delta E \right)^2 \quad ②$$

$$\Delta E = ① + ② - MB = \frac{1}{2} g(E_F) (\delta E)^2 \left[1 - U g(E_F) \right] - MB$$

MB: $\mu_B\, g(E_F)\,\delta E$

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$$\Delta E = \frac{M^2}{2\mu_B^2\, g(E_F)} \left[1 - U g(E_F) \right] - MB$$

minimized when $\dfrac{M}{\mu_B^2\, g(E_F)} \left[1 - U g(E_F) \right] - B = 0$

$$\therefore \chi = \frac{\mu_0 M}{B} = \frac{\chi_P}{1 - U g(E_F)}$$

χ_P ← Pauli susceptibility $\mu_0 \mu_B^2\, g(E_F)$

Stoner criterion: $U g(E_F) > 1$

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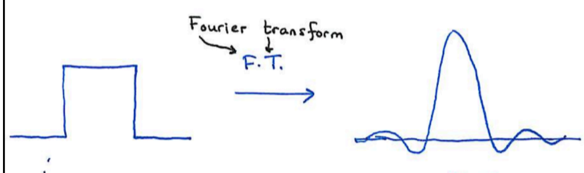

Single-slit diffraction

$$\frac{\sin x}{x} = \operatorname{sinc} x$$

TOP-HAT FUNCTION

d Response of electron gas to $\underline{H}(\underline{r}) = \underline{H}_q \cos \underline{q}\cdot\underline{r}$

$$e^{i\underline{k}\cdot\underline{r}} \longrightarrow e^{i\underline{k}\cdot\underline{r}} \left[1 \pm \frac{g\mu_0\mu_B H_q}{4} \times \left(\frac{e^{i\underline{q}\cdot\underline{r}}}{E_{\underline{k}+\underline{q}} - E_{\underline{k}}} + \frac{e^{-i\underline{q}\cdot\underline{r}}}{E_{\underline{k}-\underline{q}} - E_{\underline{k}}} \right) \right]$$

$$\underline{M}(\underline{r}) = \underline{M}_q \cos \underline{q}\cdot\underline{r}$$

$$M_{\underline{q}} = \chi_{\underline{q}} H_{\underline{q}}$$

where $\chi_q = \chi_P\, f\left(\frac{q}{2k_F}\right)$

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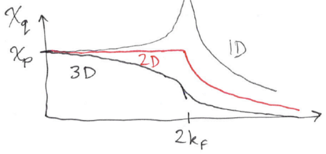
$$M_{\underline{q}} = \chi_{\underline{q}} H_{\underline{q}}$$

where $\chi_q = \chi_P\, f\left(\frac{q}{2k_F}\right)$

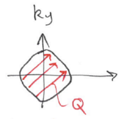


Add interactions

$$\chi_q \longrightarrow \frac{\chi_q^0}{1 - \tilde{U}\chi_q^0}$$

no interactions

dimensionless interaction



nesting instability → SDW

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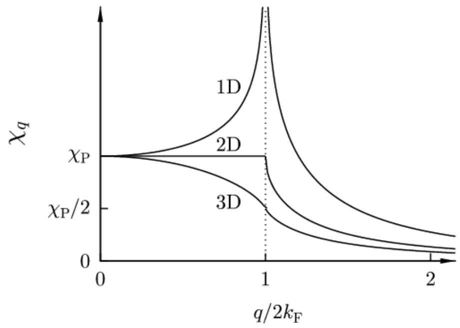
1D electron gas unstable to SDW formation



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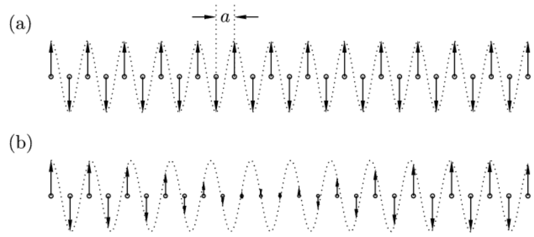
Spin-density wave



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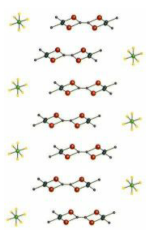
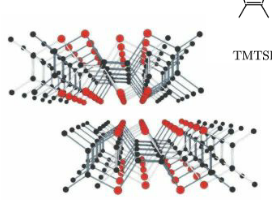
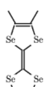
TMTSF salts







TMTSF

Stacks of TMTSF molecules ⇒ 1D chains

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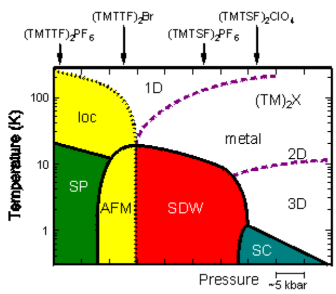
TMTSF salts

Very rich
phase diagram



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Real-space effects

$$\chi(r) = \frac{1}{(2\pi)^3}\int d^3q\, \chi_q\, e^{iq\cdot r}$$

$$= \frac{2k_F^3\chi_P}{\pi}\, F(2k_F r)$$

$$F(x) = -\frac{x\cos x + \sin x}{x^4}$$

$$\sim \frac{\cos 2k_F r}{r^3}$$

RKKY coupling

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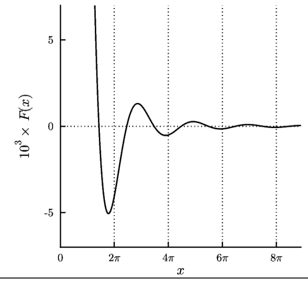
$$\chi(\mathbf{r}) = \frac{1}{(2\pi)^3}\int d^3\mathbf{q}\,\chi_{\mathbf{q}}e^{i\mathbf{q}\cdot\mathbf{r}} = \frac{2k_F\chi_P}{\pi}F(2k_F r)$$

$$F(x) = \frac{-x\cos x + \sin x}{x^4}$$



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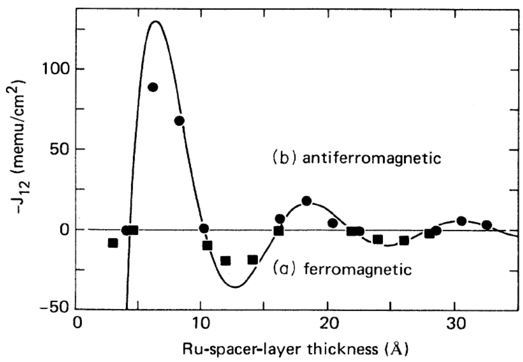

S. S. P. Parkin and D. Mauri, Phys. Rev. B **44,** 7131 (1991)

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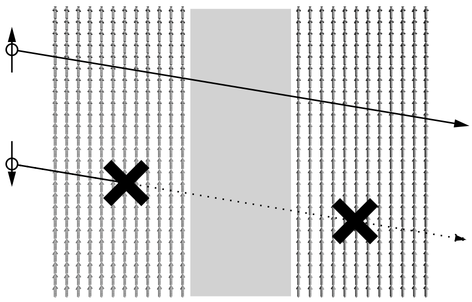
GMR = giant magnetoresistance

(a)



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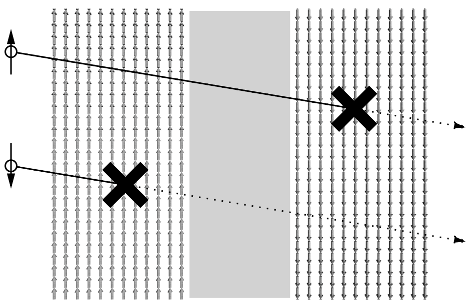
GMR = giant magnetoresistance

(b)



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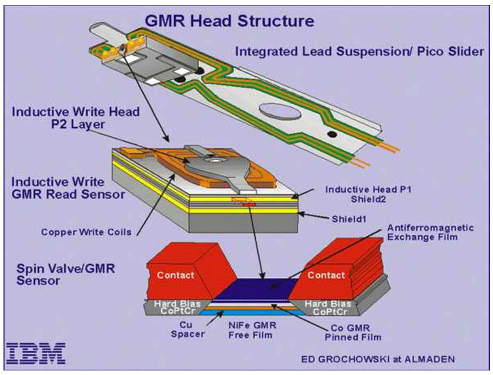

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Outline

Exchange

1. Direct exchange
2. Indirect exchange
3. Superexchange

- Interaction between pair of spins motivates the general form of the Heisenberg model:

$$H = -\sum_{ij} J_{ij}\mathbf{S_i}\cdot\mathbf{S_j}$$

- *Direct exchange*: important in many metals such as Fe, Co and Ni
- *Indirect exchange*: mediated through the conduction electrons (RKKY)
- *Superexchange*: exchange interaction mediated by oxygen. This leads to a very long exchange path. Important in many magnetic oxides, e.g. MnO, La_2CuO_4.

Superexchange

- Case I: AF ordering

$\uparrow$ $\downarrow\uparrow$ $\downarrow$
M O M ground state ✓

$\uparrow\downarrow$ $\downarrow\uparrow$
M O M

$\uparrow\downarrow$ $\downarrow\uparrow$
M O M

excited states

etc

- Case II: F ordering

$\uparrow$ $\downarrow\uparrow$ $\uparrow$
M O M ground state? ✗

- KE advantage for AF ordering

Toy model for superexchange

Case i) FM $\uparrow$ $\uparrow$ penalty U for double occupancy

E = 0 hopping t

ii) AFM

$\uparrow$	$\downarrow$	A	0
$\downarrow$	$\uparrow$	B	0
$\uparrow\downarrow$	—	C	U
—	$\uparrow\downarrow$	D	U

Toy model for superexchange

$$\mathcal{H} = \begin{bmatrix} 0 & 0 & -t & -t \\ 0 & 0 & -t & -t \\ -t & -t & U & 0 \\ -t & -t & 0 & U \end{bmatrix}$$

(guess $-\frac{2t^2}{U}$)

$\det(\mathcal{H}-E) = 0$

$$\begin{vmatrix} -E & 0 & -t & -t \\ 0 & -E & -t & -t \\ -t & -t & U-E & 0 \\ -t & -t & 0 & U-E \end{vmatrix} = 0$$

$E(U-E)\left[-E^2+UE+2t^2\right] = 0$

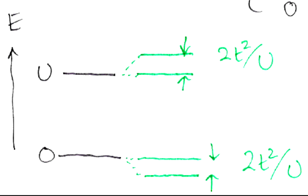
$\Rightarrow E = 0,\ U,\ \frac{U \pm \sqrt{U^2+8t^2}}{2}$

Toy model for superexchange

$t \ll U$

last 2 eigenvalues $= \frac{U}{2} \pm \frac{U}{2}\underbrace{\left(1+\frac{8t^2}{U^2}\right)^{1/2}}_{1+\frac{4t^2}{U^2}}$

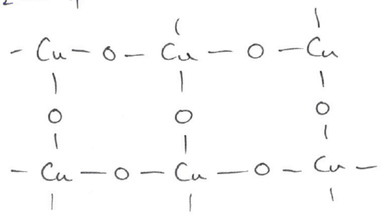
$\simeq \begin{cases} U + \frac{2t^2}{U} \\ 0 - \frac{2t^2}{U} \end{cases}$



$$J \approx \frac{2t^2}{U}$$

Toy model for superexchange

La_2CuO_4



$$J \approx \frac{2t^2}{U}$$

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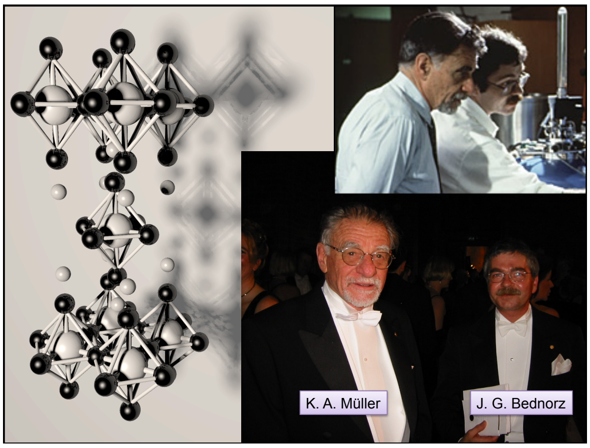

In the next lecture:

- magnetic order
- frustration and triangles

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