Exchange and ordering

e-ESM, an online higher-education Magnetism event

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European School of Magnetism 2020

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Outline

1. Direct exchange
2. Indirect exchange
3. Superexchange
4. Types of magnetic order
5. Molecular field

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2. Indirect exchange
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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

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

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

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

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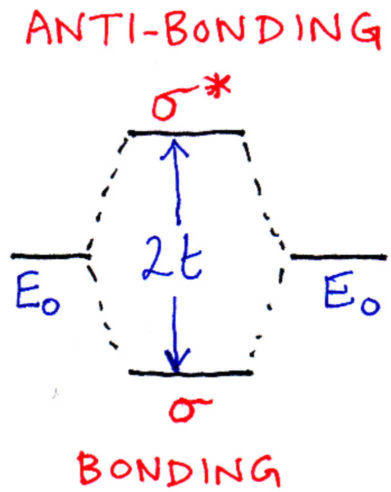
$$\mathcal{H}|\psi\rangle = E|\psi\rangle$$

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

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

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



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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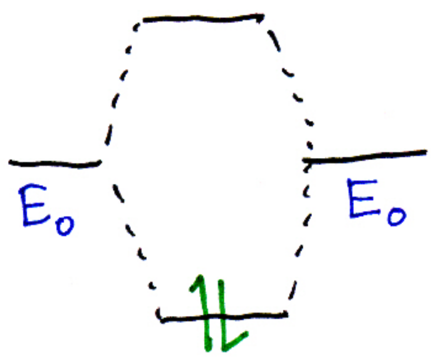
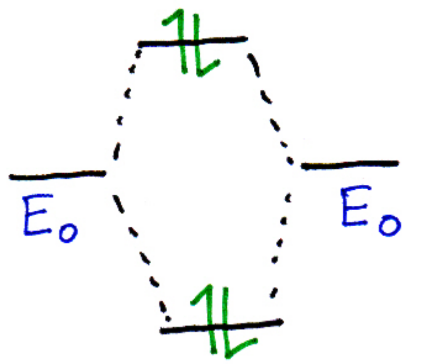
Why do you get H_2 and not He_2?

di-HYDROGEN H_2



Saves energy to bond

di-HELIUM He_2



no saving to bond (in fact, costs energy)

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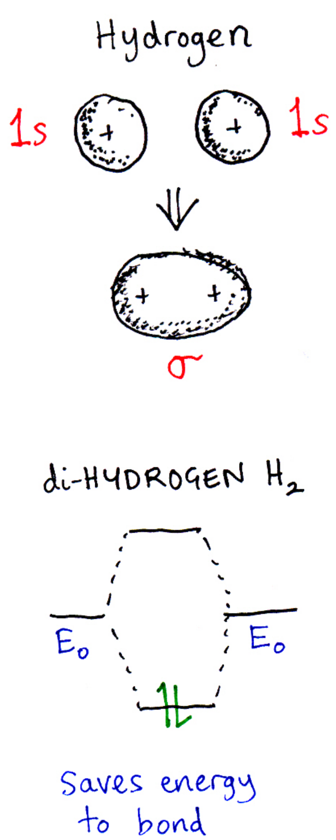
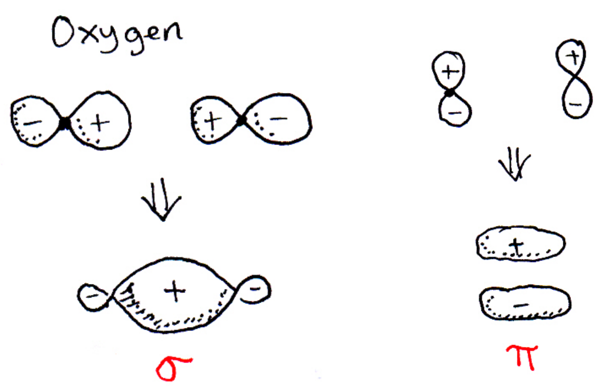
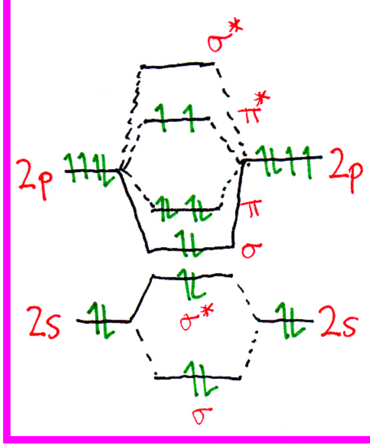






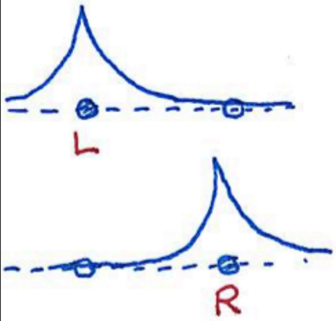
Stable state of O_2 is triplet-O_2 (as drawn)

$\Rightarrow$ magnetic!

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

Why is N–N stronger?

Two-electron model



2 electrons:

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

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

<u>hopping</u> $t = \langle LL|\hat{H}|LR\rangle$

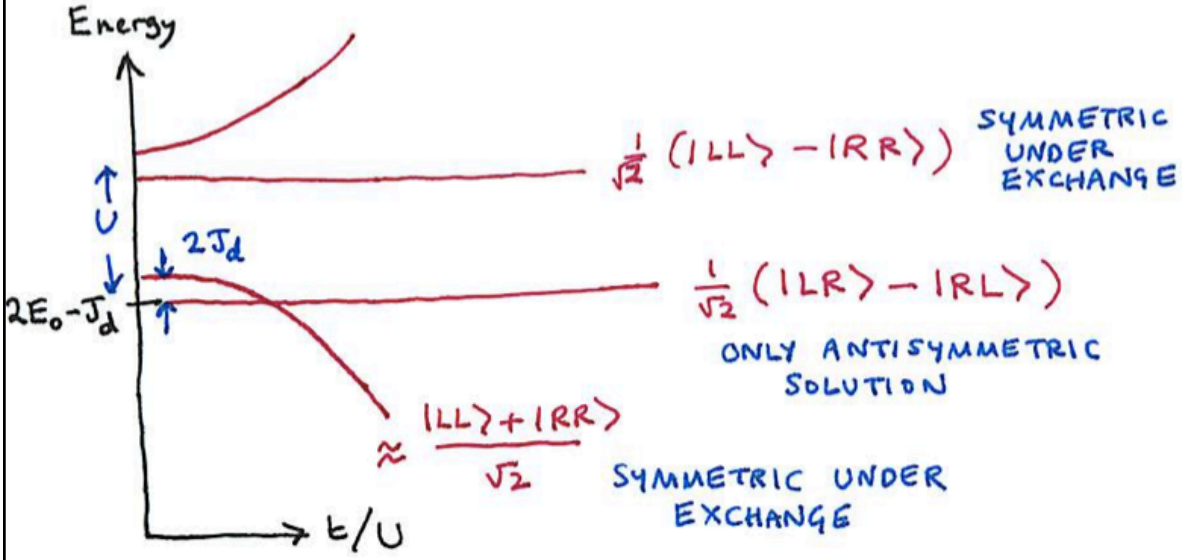
2nd electron hopped

<u>Coulomb</u> $U = \langle LL|\hat{H}|LL\rangle - 2E_0$

penalises double occupancy

<u>direct exchange</u> $J_d = \langle LR|\hat{H}|RL\rangle$

Two-electron model



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

$$\frac{(|LL\rangle + |RR\rangle)}{\sqrt{2}} \sin\chi + \frac{(|LR\rangle + |RL\rangle)}{\sqrt{2}} \cos\chi$$

$\tan 2\chi = -4t/U$

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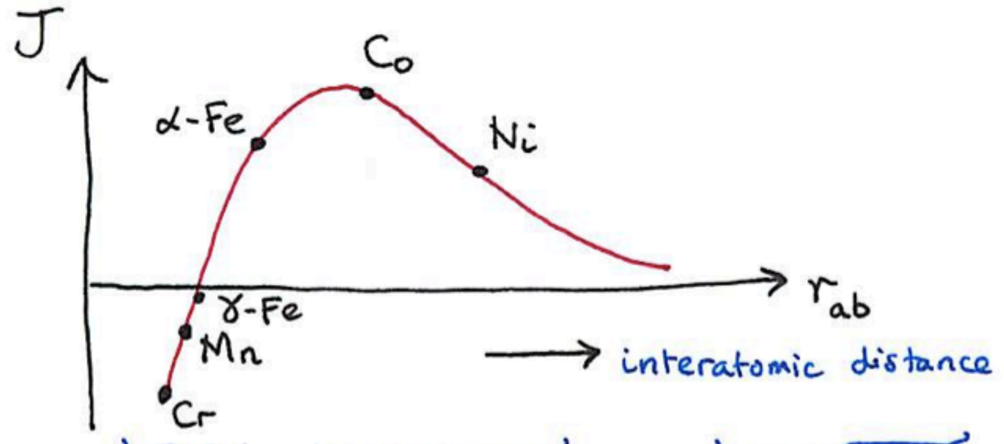
Bethe-Slater curve



Small distances
J_d and t Large
AF dominates

larger distances
J_d, t decrease
F dominates

largest distances
→ paramagnetism

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

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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 $H^{\text{spin}} = -J\mathbf{S_1} \cdot \mathbf{S_2}$.

$$\hat{\mathcal{H}} = A\hat{\mathbf{S}}^a \cdot \hat{\mathbf{S}}^b \qquad \hat{\mathbf{S}}^{\text{tot}} = \hat{\mathbf{S}}^a + \hat{\mathbf{S}}^b$$

$$\Longrightarrow (\hat{\mathbf{S}}^{\text{tot}})^2 = (\hat{\mathbf{S}}^a)^2 + (\hat{\mathbf{S}}^b)^2 + 2\hat{\mathbf{S}}^a \cdot \hat{\mathbf{S}}^b$$

$$\hat{\mathbf{S}}^a \cdot \hat{\mathbf{S}}^b = \begin{cases} \frac{1}{4} & \text{if} \quad s = 1 \\ -\frac{3}{4} & \text{if} \quad s = 0. \end{cases}$$

	Eigenstate	m_s	s	$\hat{\mathbf{S}}^a \cdot \hat{\mathbf{S}}^b$
Triplet: $E = A/4$	$\lvert\uparrow\uparrow\rangle$	1	1	$\frac{1}{4}$
	$\frac{\lvert\uparrow\downarrow\rangle + \lvert\downarrow\uparrow\rangle}{\sqrt{2}}$	0	1	$\frac{1}{4}$
	$\lvert\downarrow\downarrow\rangle$	-1	1	$\frac{1}{4}$
Singlet: $E = -3A/4$	$\frac{\lvert\uparrow\downarrow\rangle - \lvert\downarrow\uparrow\rangle}{\sqrt{2}}$	0	0	$-\frac{3}{4}$

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

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

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

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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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Magnetism and metals

$\underset{\sim}{a}$ Some revision

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

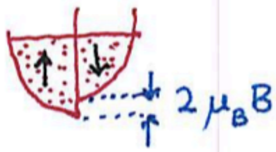
$$n = \frac{N}{V} = \int_0^{k_F} g(k)\,dk = k_F^3/3\pi^2$$

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

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

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

$\underset{\sim}{b}$ Pauli paramagnetism



$$n_\pm = \frac{1}{2}\int_0^\infty g(E \pm \mu_B B)\, f(E)\, dE$$

$$\frac{1}{e^{\beta(E-\mu)}+1}$$

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

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

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

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

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

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

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

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

$$-\frac{\partial f}{\partial E} = \delta(E - E_F)$$

$$\Rightarrow M = \mu_B^2 B\, g(E_F) \Rightarrow \chi = \frac{\mu_0 M}{B} = \mu_0 \mu_B^2\, g(E_F)$$

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

Pauli paramagnetism is small, T-independent

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

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

$$-\frac{\partial f}{\partial E} = \delta(E - E_F)$$

$$\Rightarrow M = \mu_B^2 B\, g(E_F) \Rightarrow \chi = \frac{\mu_0 M}{B} = \mu_0 \mu_B^2\, g(E_F)$$

using $g(E_F) = \frac{3}{5}\frac{n}{E_F}$ $\quad \therefore \chi = \frac{3}{2}\frac{n\mu_0\mu_B^2}{k_B T_F}$

Pauli paramagnetism is small, T-independent

(ii) non-degenerate limit

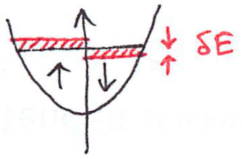
$$f(E) \simeq e^{-(E-\mu)/k_BT} \Rightarrow -\partial f/\partial E = \frac{f}{k_BT}$$

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

$$\Rightarrow \chi = \frac{\mu_0 M}{B} = \frac{n\mu_0\mu_B^2}{k_B T} \propto \frac{1}{T}$$

Curie-like!

c. Spontaneous FM in the absence of B



Reverse $\frac{1}{2} g(E_F)\,\delta E$ electrons from ↓ to ↑, increasing their energy by δE

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

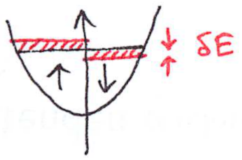
$$n_\pm = \frac{1}{2}\left(n \pm g(E_F)\,\delta E\right)$$

$$n_+ - n_- = g(E_F)\,\delta E \qquad M = (n_+ - n_-)\mu_{\mathrm{B}}$$

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

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

c. Spontaneous FM in the absence of B



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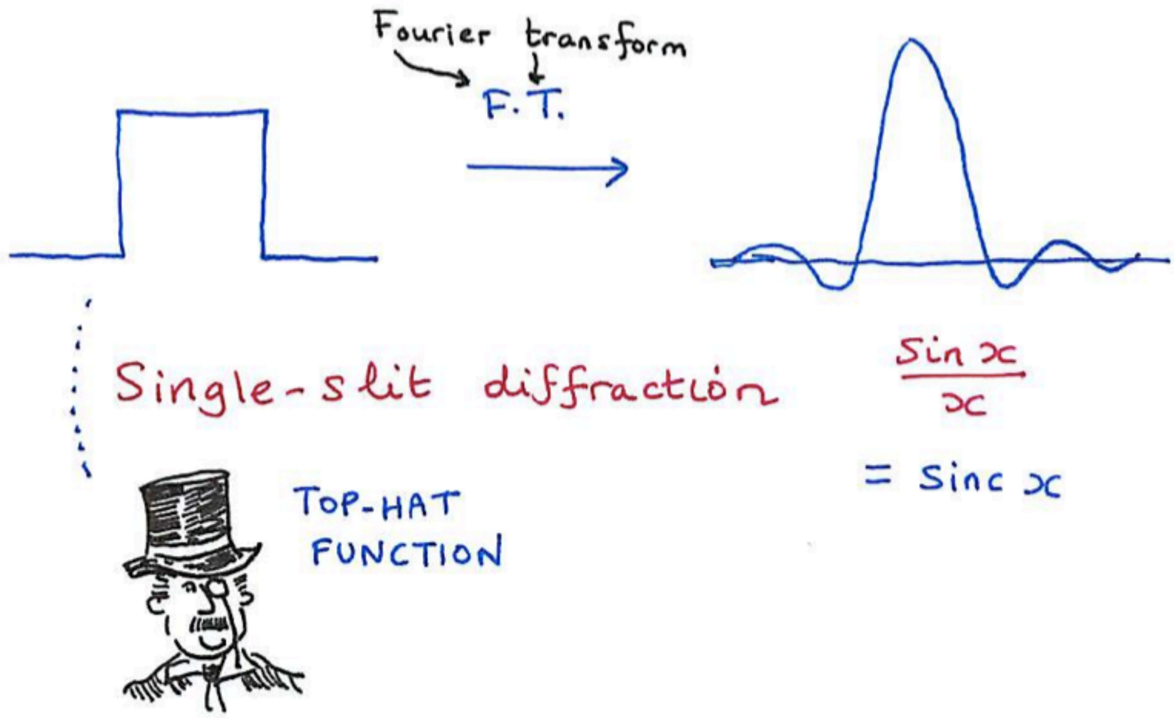
$$\Delta E = ① + ② - MB = \frac{1}{2} g(E_F)(\delta E)^2\left[1 - U g(E_F)\right] - \mu_B g(E_F)\,\delta E$$

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

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

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



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$\underset{\sim}{d}$ 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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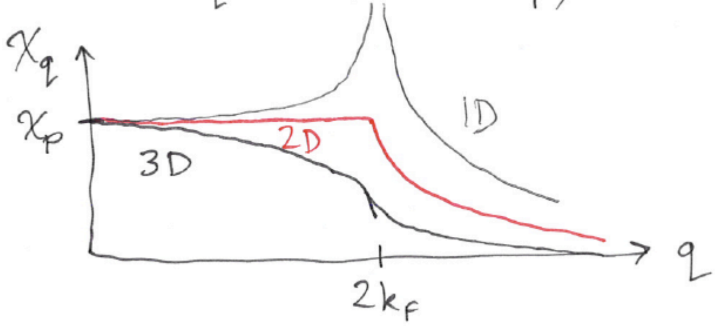
$M_{\underline{q}} = \chi_{\underline{q}} H_{\underline{q}}$

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

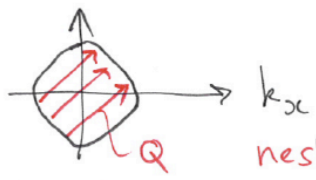


Add interactions

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

no interactions

dimensionless interaction



nesting instability → SDW

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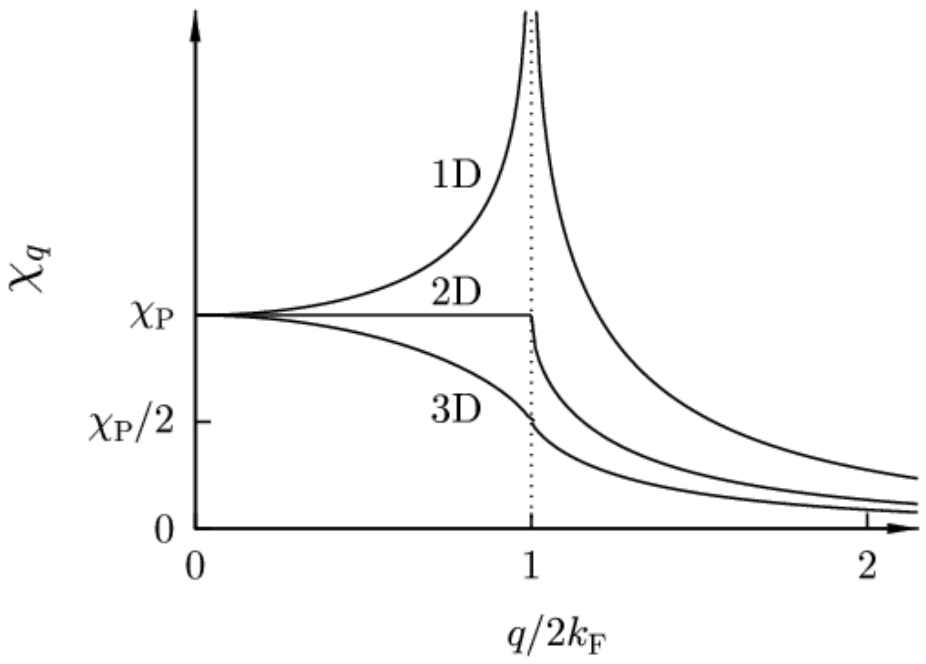
1D electron gas unstable to SDW formation



S. J. Blundell, Magnetism in Condensed Matter (OUP, 2001)

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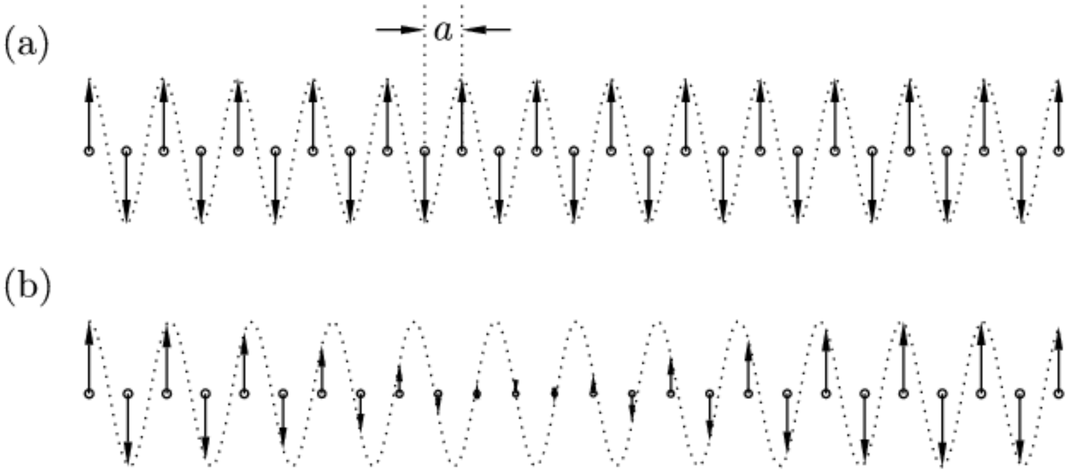
Spin-density wave



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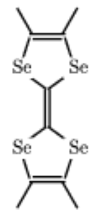
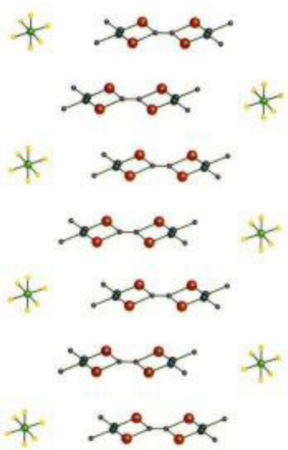
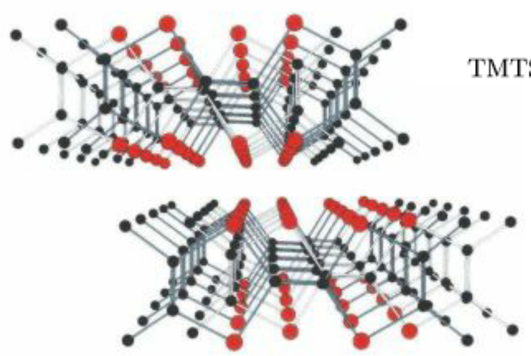
TMTSF salts



TMTSF

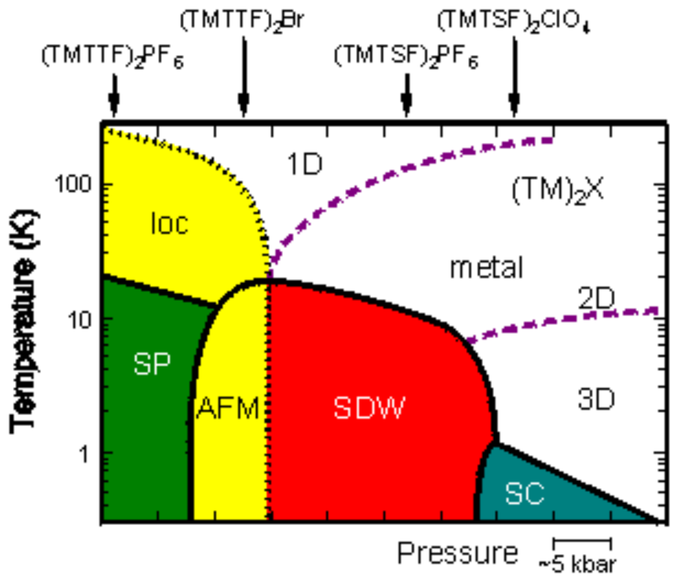




Stacks of TMTSF molecules $\Rightarrow$ 1D chains

TMTSF salts

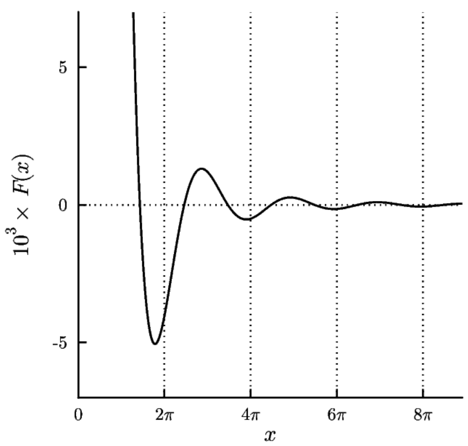
Very rich
phase diagram



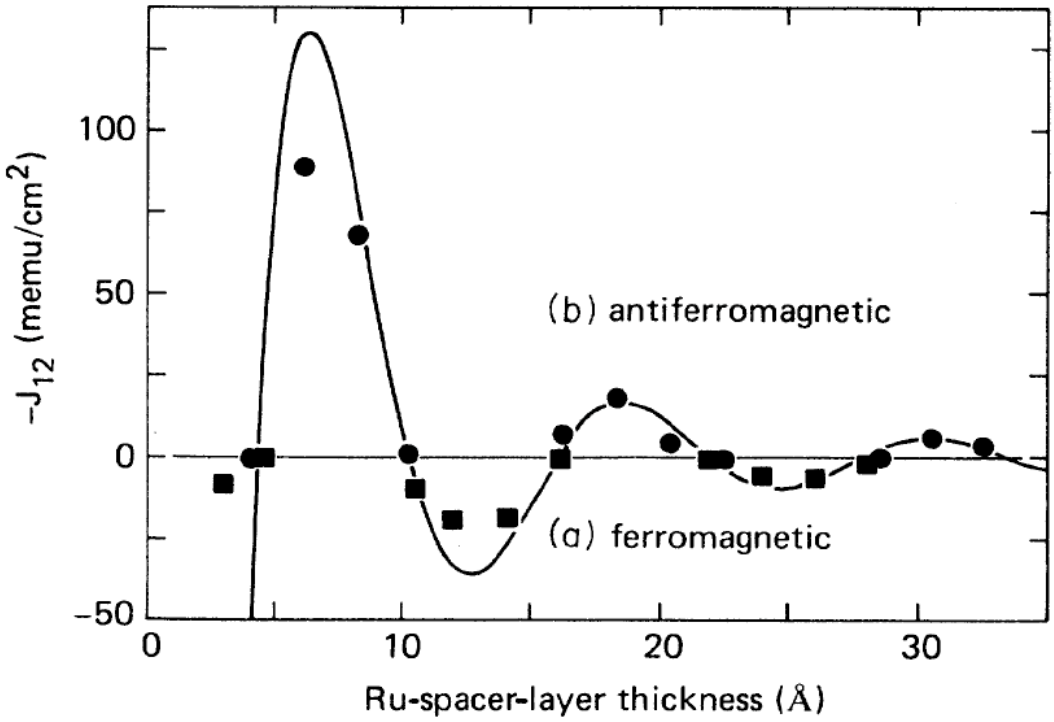
(e) Real space effects – RKKY coupling

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

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



named after Ruderman, Kittel, Kasuya and Yosida



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

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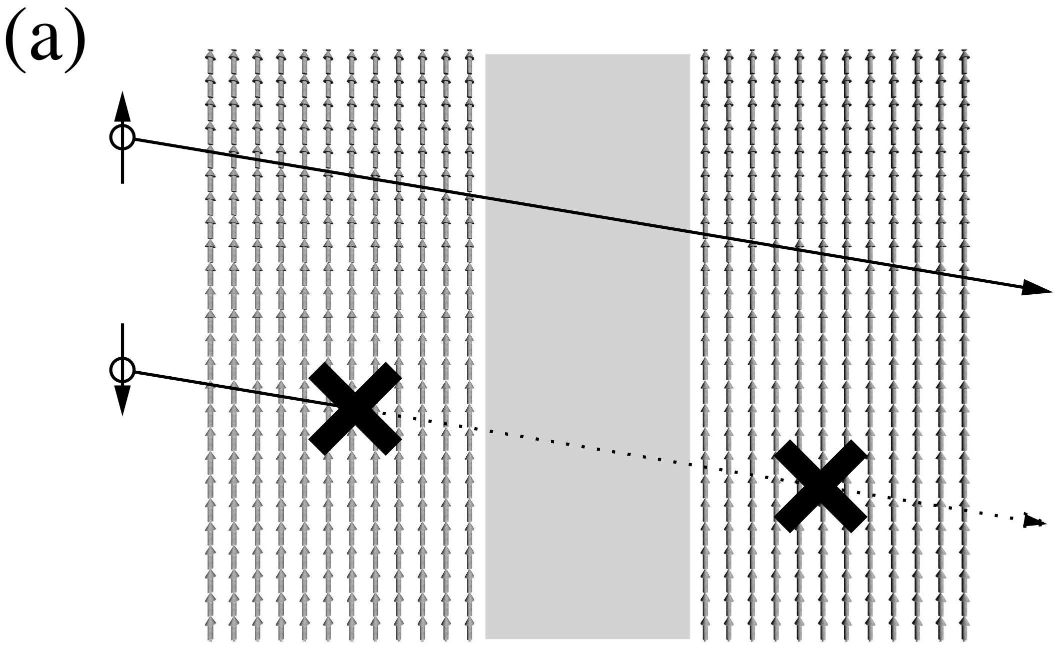
GMR = giant magnetoresistance



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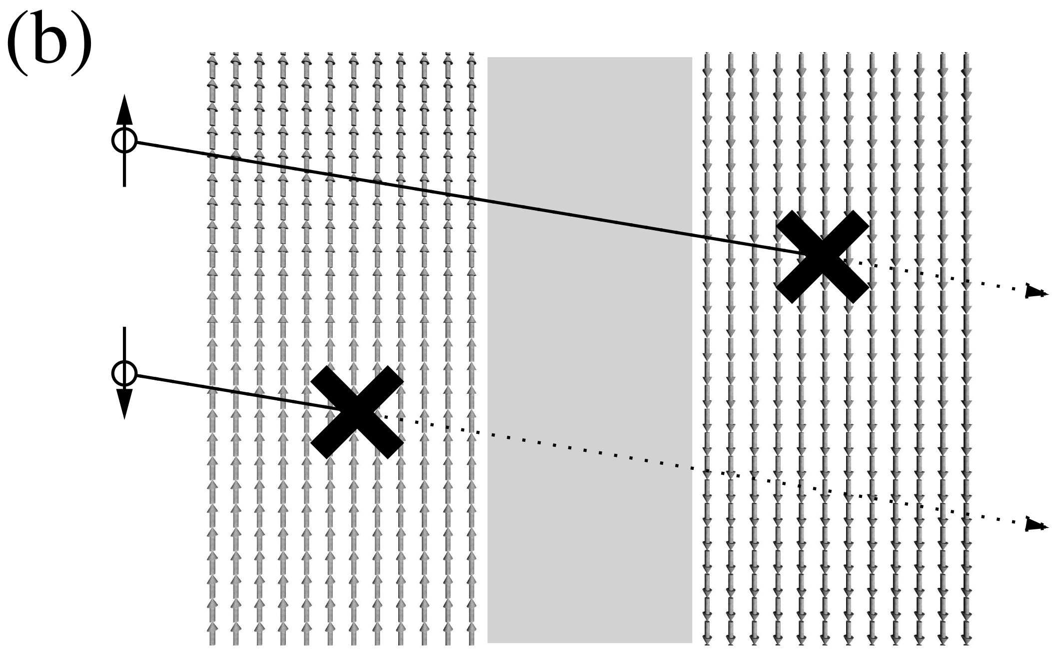

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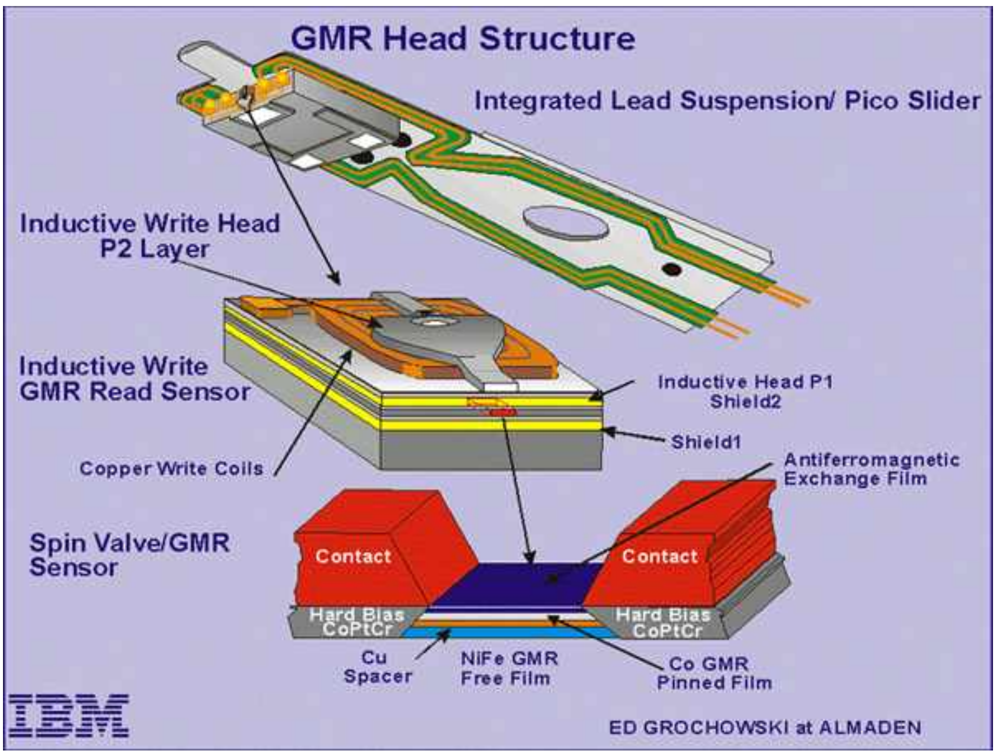

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- Interaction between pair of spins motivates the general form of the Heisenberg model:

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

- *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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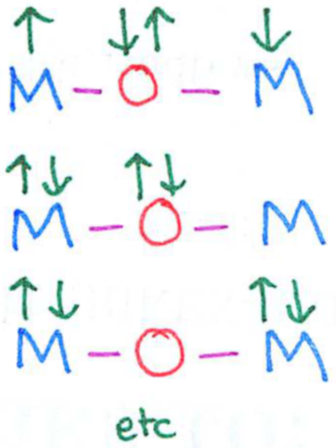
Superexchange

- Case I: AF ordering



ground state ✓

excited states

- Case II: F ordering

ground state ? ✗

- KE advantage for AF ordering

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Toy model for superexchange

Case i/ FM ↑ ↑

penalty U for double occupancy

$E = 0$

hopping t

ii/ AFM

↑	↓	A	0
↓	↑	B	0
↑↓	—	C	U
—	↑↓	D	U

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Toy model for superexchange

$$\mathcal{H} = \begin{bmatrix} 0 & 0 & -t & -t \\ 0 & 0 & -t & -t \\ -t & -t & U & 0 \\ -t & -t & 0 & U \end{bmatrix} \qquad \left(\text{guess } -\frac{2t^2}{U}\right)$$

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

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

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

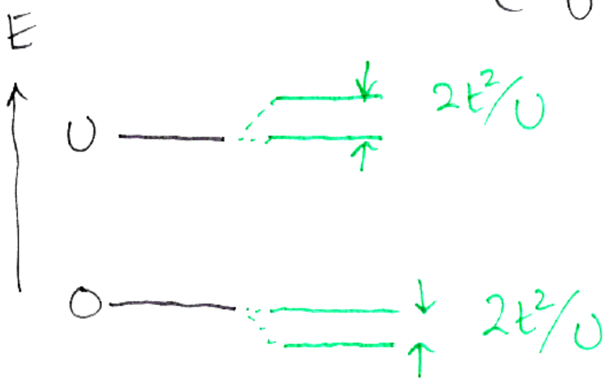
$$\Rightarrow E = 0,\ U,\ \frac{U \pm \sqrt{U^2 + 8t^2}}{2}$$

Toy model for superexchange

$t \ll U$

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

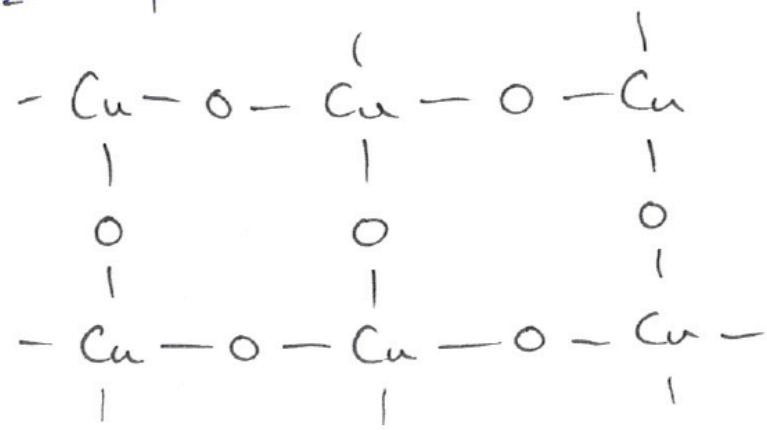
$$\simeq \begin{cases} U + \dfrac{2t^2}{U} \\ 0 - \dfrac{2t^2}{U} \end{cases}$$



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

Toy model for superexchange

La_2CuO_4



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

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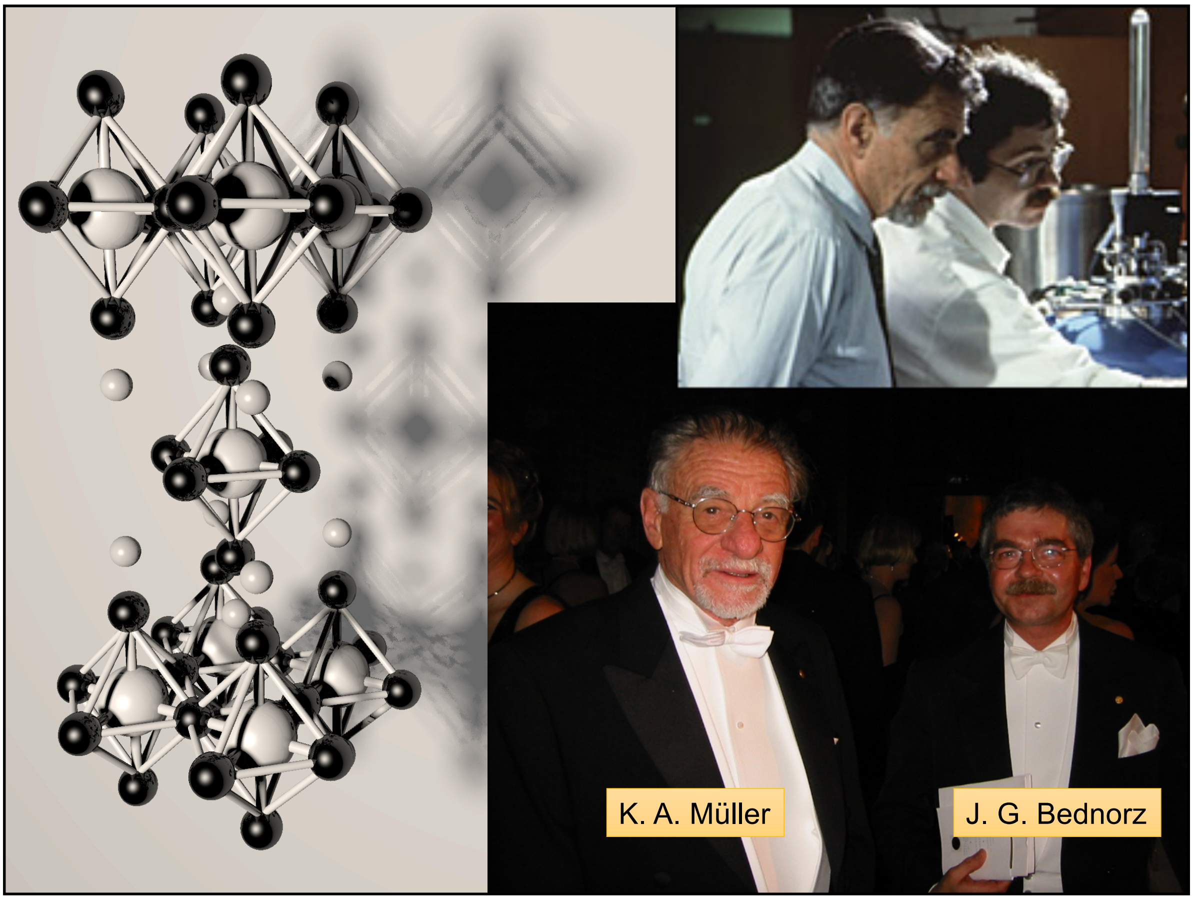

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Outline

1. Direct exchange
2. Indirect exchange
3. Superexchange
4. Types of magnetic order
5. Molecular field

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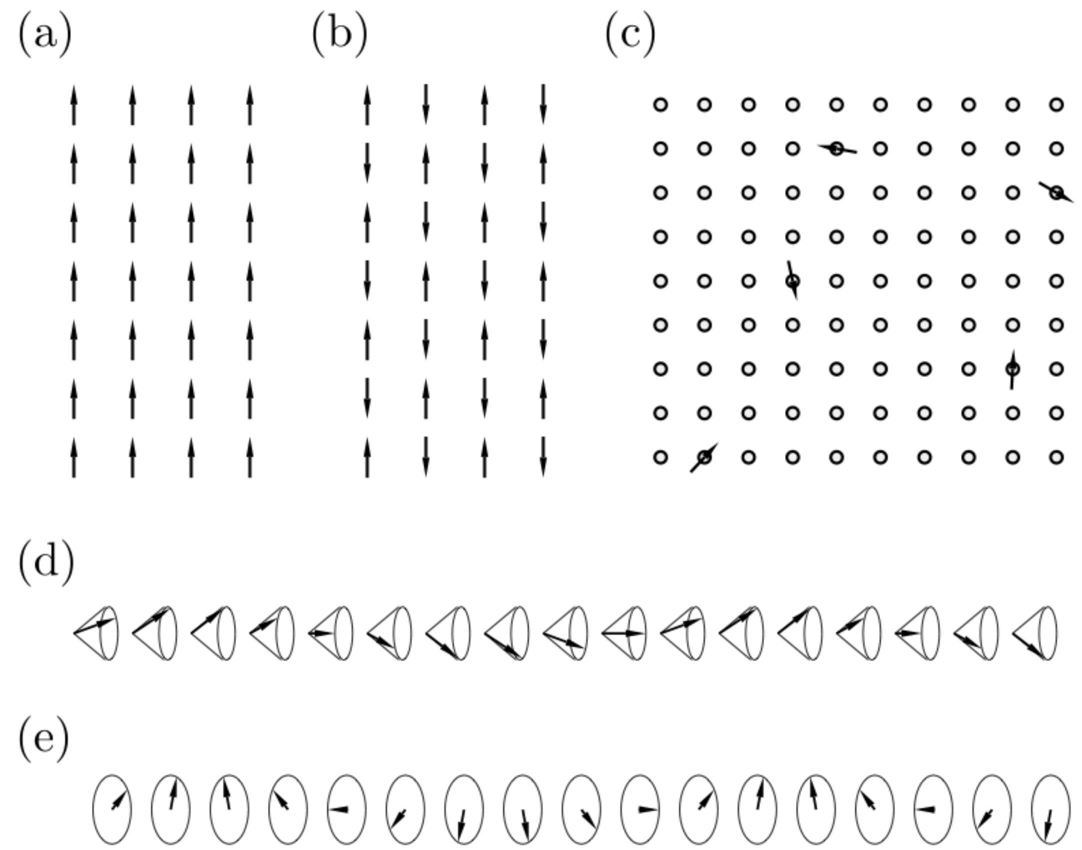
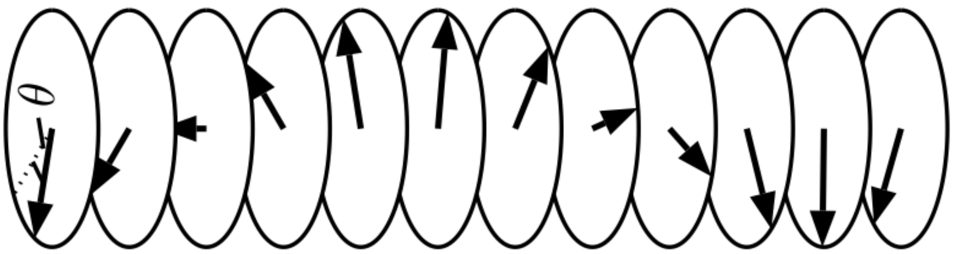


S. J. Blundell, Magnetism in Condensed Matter (OUP, 2001)



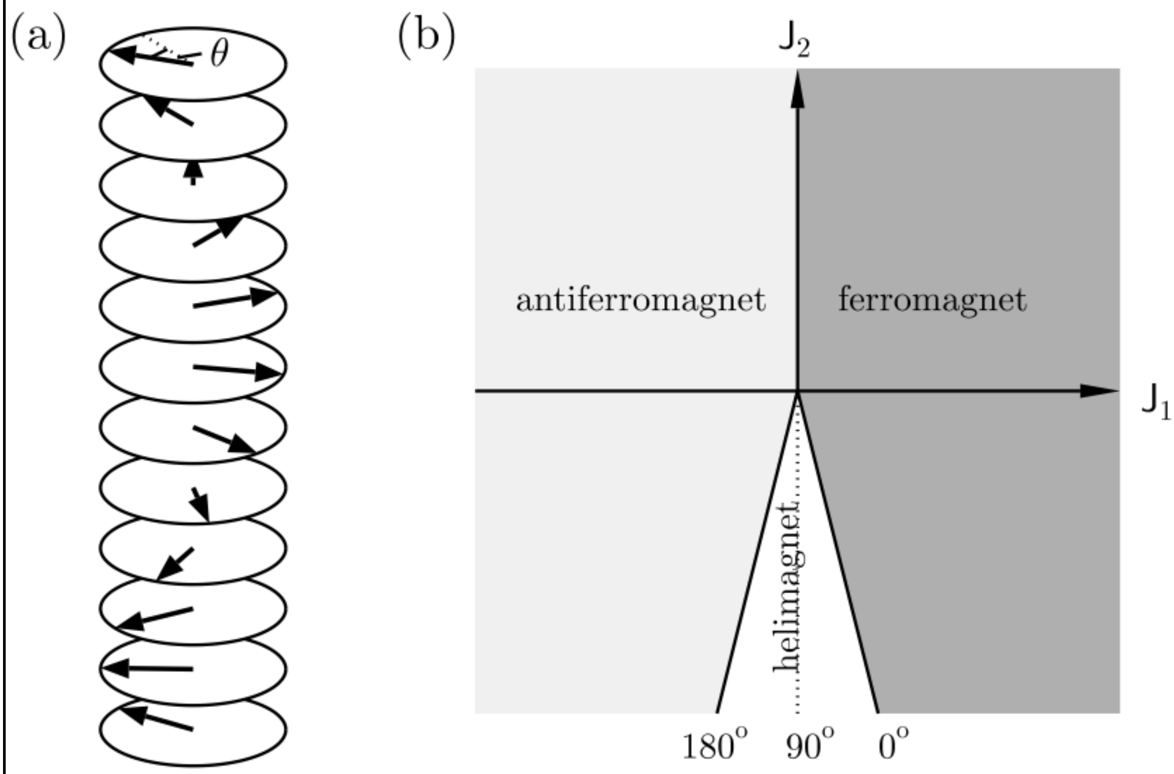
$$E = -2NS^2 (J_1 \cos\theta + J_2 \cos 2\theta)$$

Minimize energy $\quad \dfrac{\partial E}{\partial \theta} = 0$

$$\therefore \quad (J_1 + 4J_2 \cos\theta) \sin\theta = 0$$

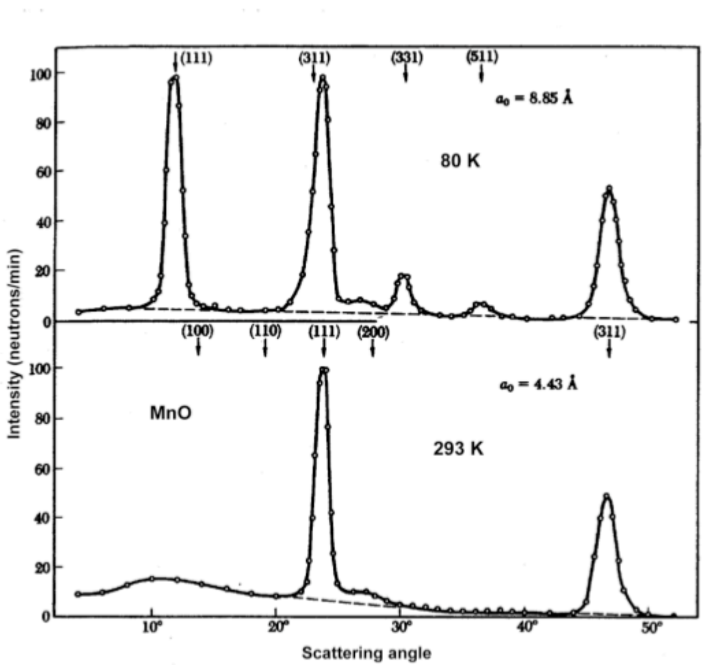
Solutions: $\quad \theta = 0, \quad \pi, \quad \cos^{-1}\left(-\dfrac{J_1}{4J_2}\right)$

FM $\qquad$ AFM $\qquad$ helimagnetism



S. J. Blundell, Magnetism in Condensed Matter (OUP, 2001)

Magnetic neutron diffraction



MnO

C.G. Shull et al. (1951)

see also

A.L. Goodwin et al.
PRL **96,** 047209 (2006)

Outline

1. Direct exchange
2. Indirect exchange
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Mean-field theory

$$\hat{H} = -J \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j + g\mu_B \sum_i \vec{S}_i \cdot \vec{B}$$

spin-$\frac{1}{2}$

Focus on ith spin

$$\hat{H}_i = \underbrace{\left(-J \sum_j \vec{S}_j + g\mu_B \vec{B} \right)}_{g\mu_B \vec{B}_{eff}} \cdot \vec{S}_i$$

Number of nearest neighbours

$$\vec{B}_{eff} = \vec{B} - \frac{Jz}{g\mu_B} \langle \vec{S} \rangle$$

$$\langle \vec{S} \rangle = -\frac{1}{2} \tanh\left(\beta g \mu_B B_{eff}/2 \right) = -\frac{\beta g \mu_B B_{eff}}{4} \quad \text{as } \langle S \rangle \to 0$$

$$B = 0 \Rightarrow \langle \vec{S} \rangle = \underbrace{\frac{\beta g \mu_B}{4} \cdot \frac{Jz}{g\mu_B}}_{=1} \langle \vec{S} \rangle$$

$$\Rightarrow k_B T_c = \frac{zJ}{4}$$

[or ×2 if 2J convention]

Mean-field theory and the Curie-Weiss law

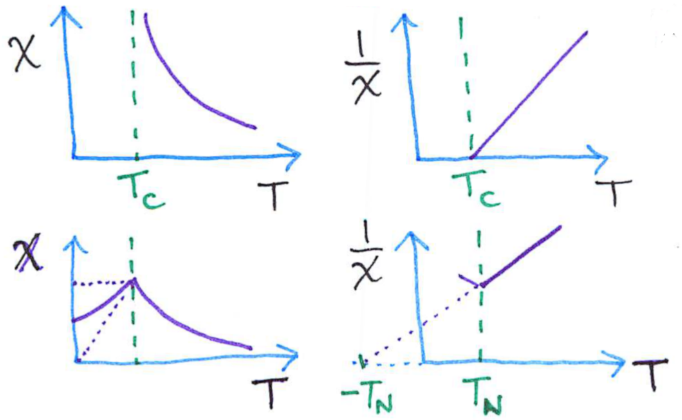
$$\delta\langle S\rangle = -\tfrac{1}{4}\beta g\mu_B\left(\delta B - \frac{Jz}{g\mu_B}\,\delta\langle S\rangle\right)$$ all quantities small

$$\delta M = -n\, g\mu_B\, \delta\langle S\rangle$$

$$\chi = \mu_0 \frac{\delta M}{\delta B} = \frac{\mu_0 n (g\mu_B)^2/4k_B}{T - T_c}$$

$$T_c \quad \frac{zJ}{4k_B}$$

Curie-Weiss law



$$\chi \propto \frac{1}{T - T_c}$$

FERROMAGNET

$$\chi \propto \frac{1}{T + T_N}$$

ANTIFERROMAGNET

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