

Emergence of quantum phases in novel materials

Magnetism

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Magnetism is a collective phenomenon

Microscopic description

Magnetic
moments

Interactions

Environment

Macroscopic description

Phases

Dimensionality

Symmetry

Universality

Outline

- Classical Phase Transitions
- Free magnetic ions
- Environment
- Magnetic order and susceptibility
- Interactions
 - Exchange between localized moments
 - Indirect exchange through itinerant electrons
 - Magnetism in metals
- Excitations

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Outline

- Classical Phase Transitions
 - Symmetry
 - Landau theory
 - Order of phase transitions
 - Goldstone theorem
 - Mermin-Wagner Theorem
 - Kosterlitz-Thouless transition

Bibliography

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- Chaikin and Lubensky: Principles of Condensed Matter Physics
- Le Bellac: Quantum and Statistical Field Theory
- Wen: Quantum Field Theory of Many-Body Systems
- Fradkin: Field Theories of Condensed Matter Systems
- J. Negele and H. Orland, Quantum many particle Systems
- Ryder: Quantum Field Theory

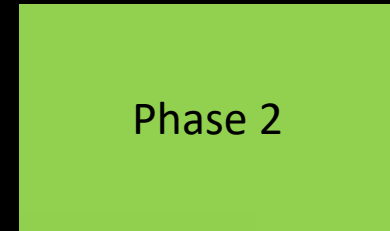
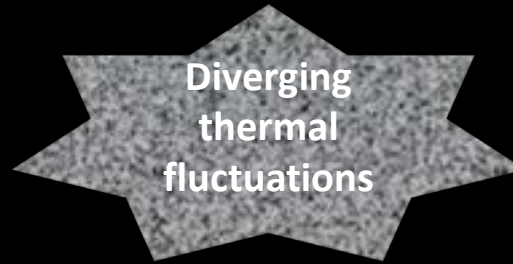
Symmetry

- Invariance of a physical law under transformations: translation symmetry, time reversal, rotation, reflection...
- Symmetries form groups: $O(3)$, $U(1)$...
 - Contains the identity
 - The combination of any pair of elements is also an element of the group.
 - Each element must have an inverse

Kinds of symmetries

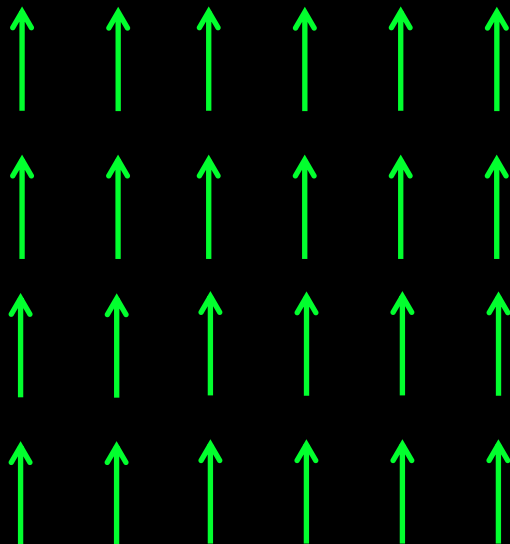
- External (space time) symmetries (Galilean symmetry, rotational symmetry, Lorentz symmetry...)
- Internal symmetries (Gauge symmetries...)
- Global symmetries: act simultaneous in all variables x_i
- Local symmetries: depend on x_i
- Continuous symmetry: rotations $O(n)$
- Discrete symmetry: spin group Z_2

Classical phase transitions



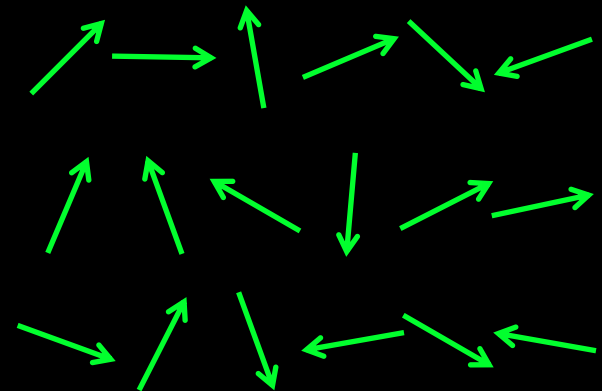
Control parameter: temperature, pressure

Lower symmetry
Lower energy



At T_c :
symmetry
breaking

Uncorrelated, isotropic,
homogeneous, high symmetry
higher entropy

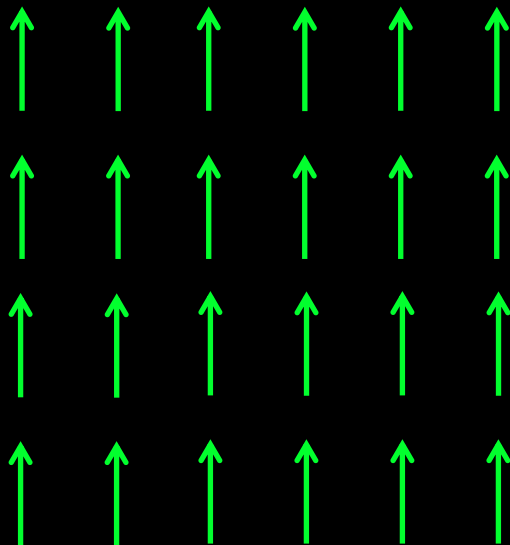


Classical phase transitions

$$H = -J \sum_{ij} S_i S_j$$

The hamiltonian has $O(3)$ symmetry but this symmetry is broken in the ordered phase.

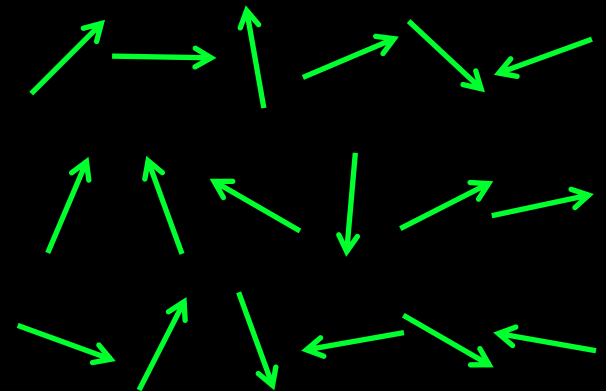
Lower symmetry
Lower energy



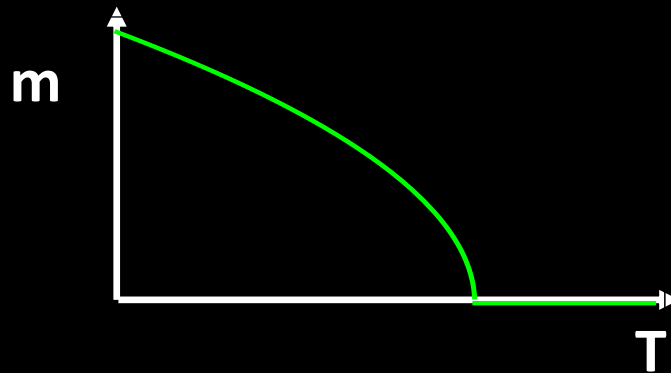
At T_c
spontaneous
symmetry
breaking

(rotation)

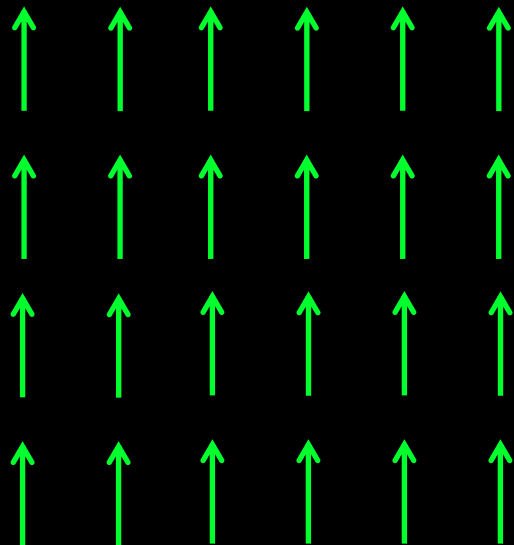
Uncorrelated, isotropic,
homogeneous, high symmetry
higher entropy



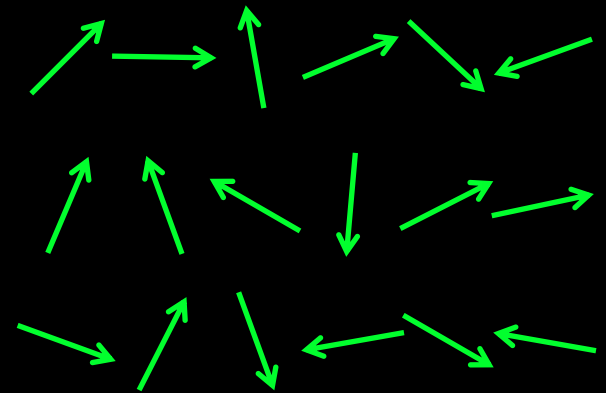
Classical phase transitions



Order parameter $m \neq 0$



Order parameter $m = 0$



Classical phase transitions

Landau mean-field theory (formal connection with the microscopic model through a Hubbard Stratonovic transformation). Express the free energy as a power series expansion in terms of the order parameter.

Example: Ising model (Z_2 symmetry)

$$H = -J \sum_{i,j} \sigma_i \sigma_j \quad \sigma_i = \pm 1$$

The free energy has the symmetries of the hamiltonian (in this case: no odd terms in the expansion)

Simplest expansion (assuming $B > 0$)

$$f(m, h) = Am^2 + Bm^4 - hm$$

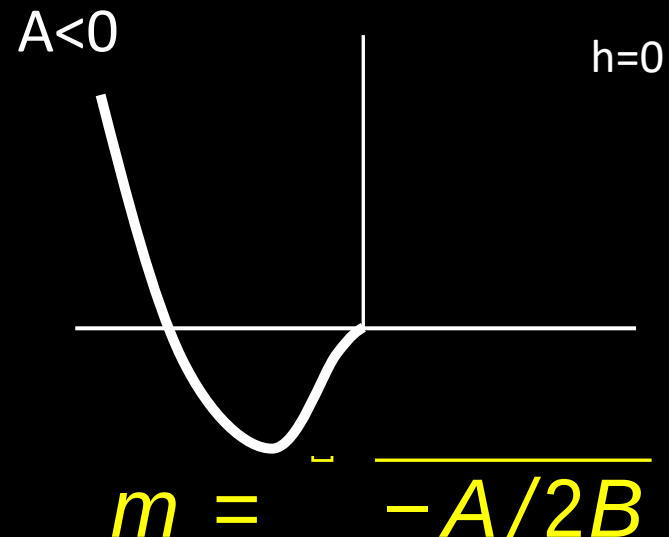
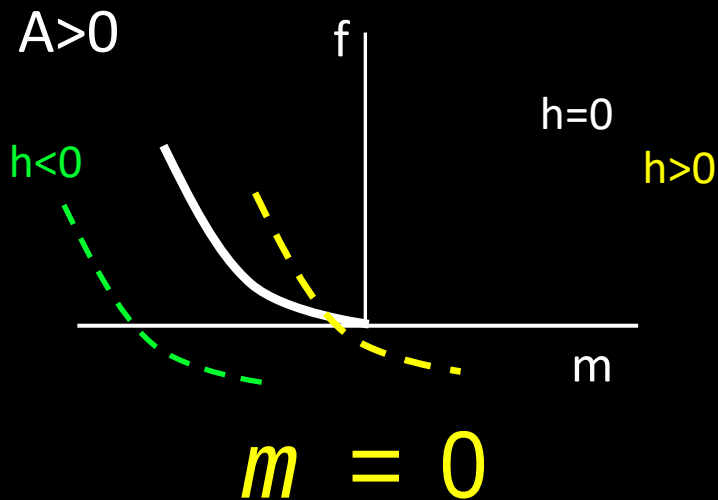
Classical phase transitions

Landau mean-field theory

$$f(m, h) = Am^2 + Bm^4 - hm$$

$$\frac{\partial f(m, h)}{\partial m} = 0$$

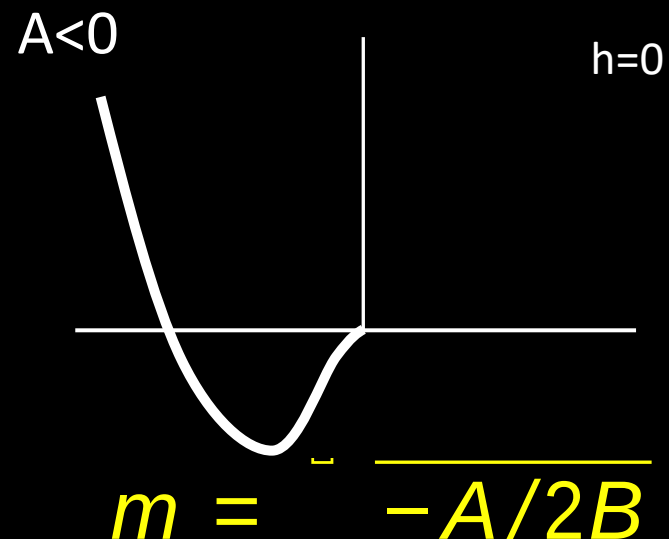
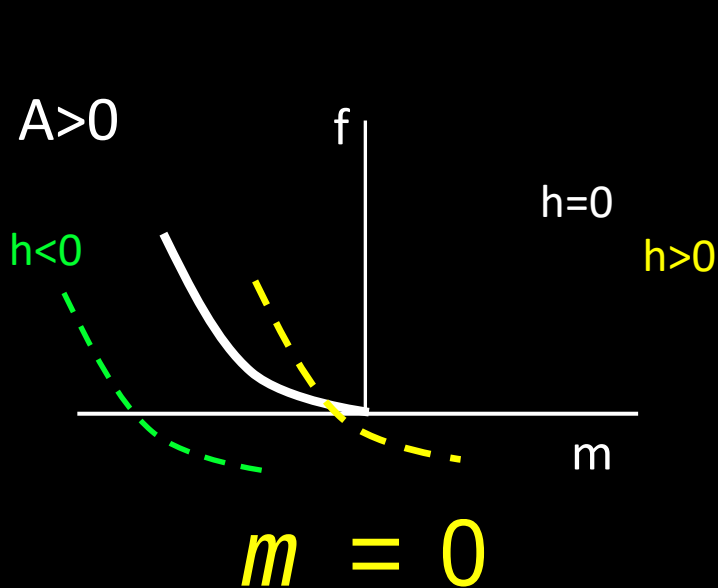
$$2Am + 4Bm^3 - h = 0$$



Classical phase transitions

$$A = (T - T_c)/2T_c$$

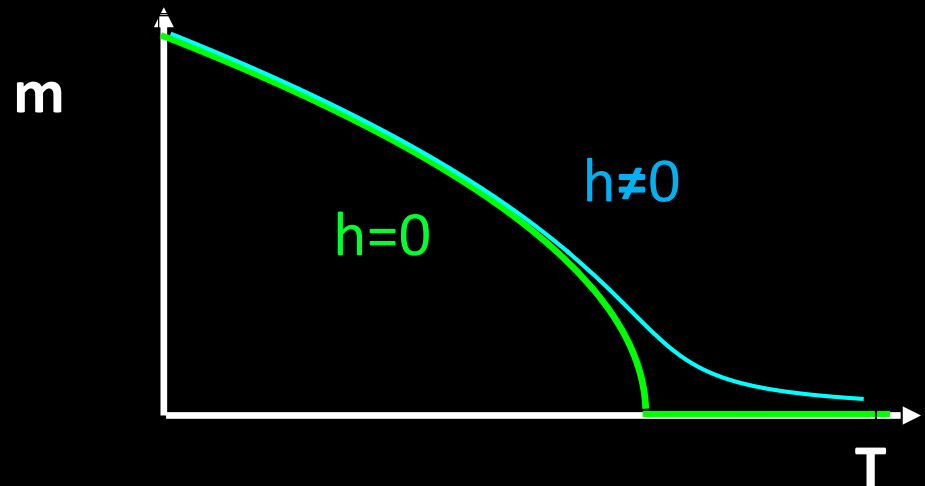
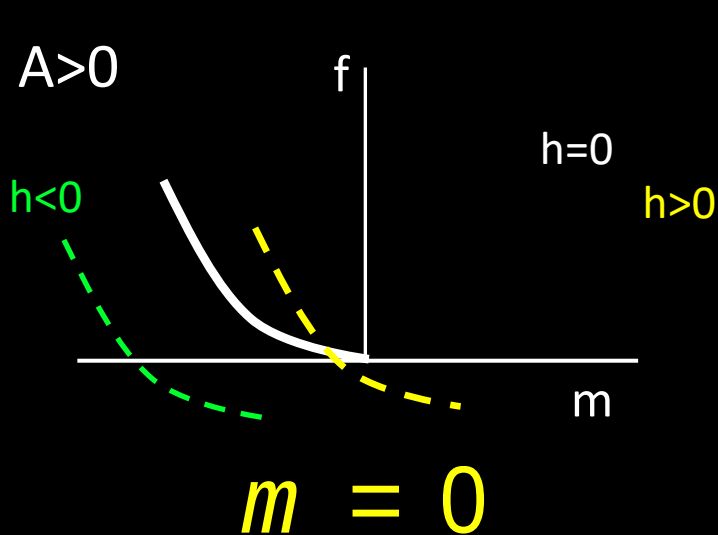
$$m(h=0) = \begin{cases} 0, & T > T_c \\ -\frac{T_c - T}{4T_c B(T)}, & T < T_c \end{cases}$$



Classical phase transitions

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$$m(h=0) = \begin{cases} 0, & T > T_c \\ -\frac{T_c - T}{4T_c B(T)}, & T < T_c \end{cases}$$



Susceptibility

$$\chi = \frac{\partial m}{\partial h} \rightarrow \chi^{-1} = \frac{\partial h}{\partial m}$$

$$f(m, h) = \frac{(T - T_c)}{2T_c} m^2 + Bm^4 - hm$$

$$\frac{(T - T_c)}{T_c} m + 4Bm^3 = h \qquad \frac{\partial h}{\partial m} = \frac{(T - T_c)}{T_c} + 12Bm^2$$

$$\chi^{-1} = \begin{cases} \frac{(T - T_c)}{T_c}, & T > T_c \\ 2\frac{(T_c - T)}{T_c}, & T < T_c \end{cases}$$

The susceptibility diverges at the transition

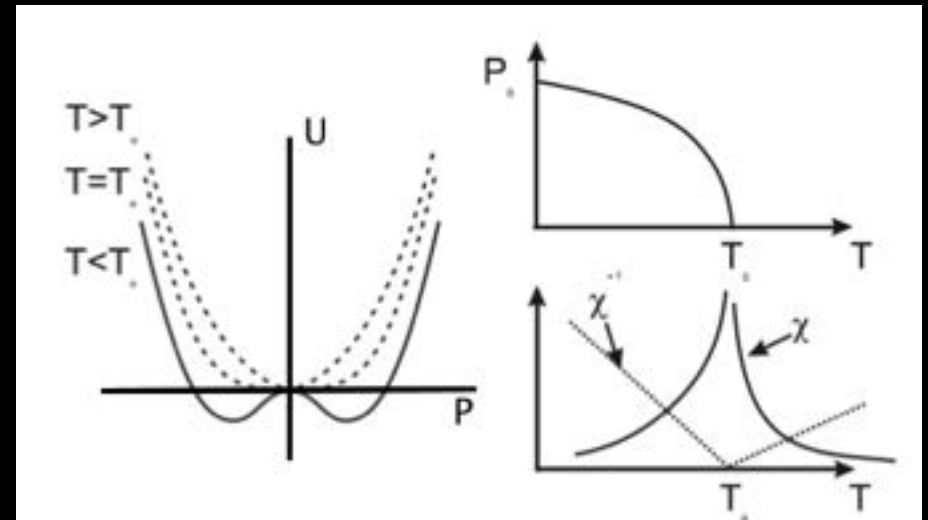
Continuous phase transitions (2nd order)

- Order parameter goes continuously to zero

$$m \sim (T_c - T)^{1/2}$$

- Susceptibility diverges

$$\chi \sim |T - T_c|^{-1}$$

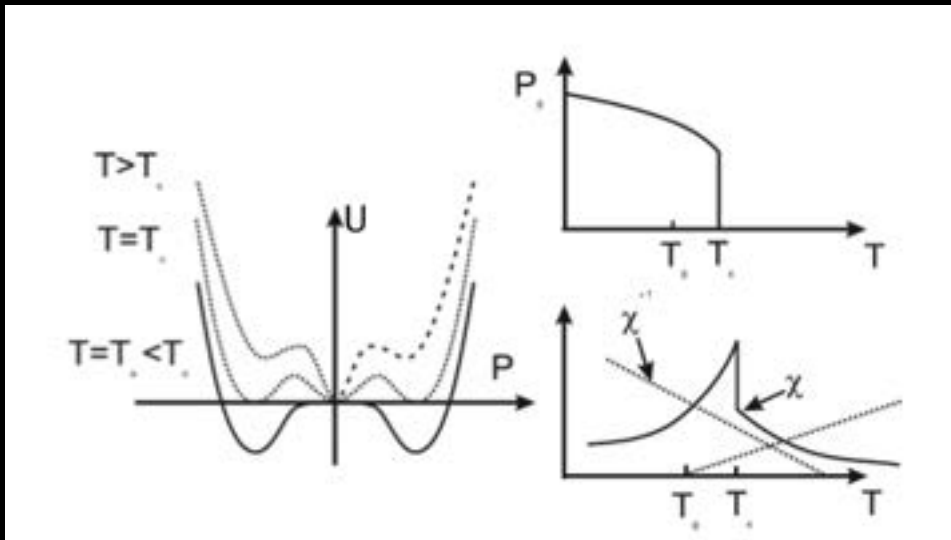


$$f(m, h) = Am^2 + Bm^4 - hm$$

$B > 0$

1st order phase transitions

Both the order parameter and the susceptibility have a jump at T_c



- ✓ Phase separation
- ✓ Hysteresis
- ✓ Latent heat

$$f(m, h) = Am^2 + Bm^4 + Cm^6 - mh$$

$$B < 0$$

Ginzburg Landau

Long-wavelengths fluctuations can be added in Landau theory. $\phi(x)$ is slowly varying. The simplest functional is:

$$f_{GL}[T, \Phi] = \frac{c}{2} (\nabla \Phi)^2 + \frac{r}{2} \Phi^2 + g(T) \Phi^4 - h \Phi$$

A new scale is introduced: Correlation length ξ
(the scale at which the fluctuations of the microscopic degrees of freedom are correlated).
It diverges at T_c in second order transitions.

Correlation and susceptibility

Connected by the fluctuation-dissipation theorem

Correlation function: measure how correlated is the system over a certain range of space

$$G_{ij} = \langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle = \frac{1}{(\beta\mu)^2} \frac{\partial^2 \ln Z}{\partial B_i \partial B_j} \Big|_{B=0}$$

Z is the partition function
B is the magnetic field

Susceptibility

$$\chi = \frac{\partial m}{\partial B} = \frac{1}{\beta} \sum_{ij} \frac{\partial^2 \ln Z}{\partial B_j \partial B_i} = \beta\mu^2 \sum_{ij} \langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle$$

- ✓ Correlations can be measured!
- ✓ At a phase transition χ diverges $\rightarrow$ infinite fluctuations

Universality

The singular behaviour close to the critical point is characterized by critical exponents:

$$\xi \propto (T - T_c)^{-\nu}$$

$$\chi \propto (T - T_c)^{-\gamma}$$

$$C \propto (T - T_c)^{-\alpha}$$

The critical exponents depend on:

- Dimensionality of the space
- Dimensionality of the order parameter
- Symmetries of the local couplings

but not on the details of the interaction (universality).

Universality

The singular behaviour close to the critical point is characterized by critical exponents:

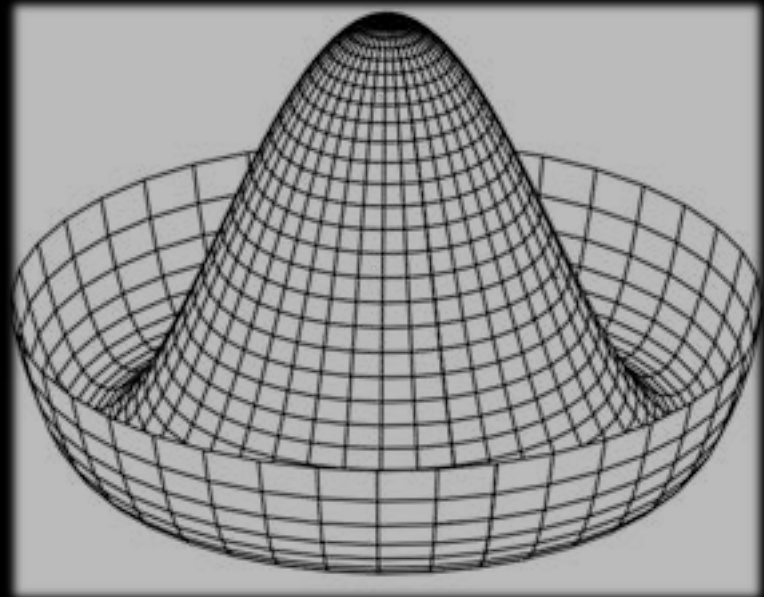
Table 1 Critical behaviour from 2D to 3D			Nature Nanotechnology 14, 408 (2019)	
Model	β	γ	ν	δ
	$M(T < T_c) \propto t ^\beta$	$\chi \propto t ^{-\gamma}$	$\xi \propto t ^{-\nu}$	$M(T_c) \propto B ^{1/\delta}$
2D Ising	1/8	7/4	1	15
3D Ising	0.3265	1.237	0.630	4.789
3D XY	0.348	1.318	0.672	4.787
3D Heisenberg	0.369	1.396	0.711	4.783
Mean field	0.5	1	0.5	3

Goldstone theorem

Low energy excitations are possible in systems with continuous symmetry.

Example: Heisenberg model [invariant under $O(3)$]

$$H = -J \sum_{i,j} \vec{S}_i \vec{S}_j = -J \sum_{i,j} \cos(\theta_{i,j})$$



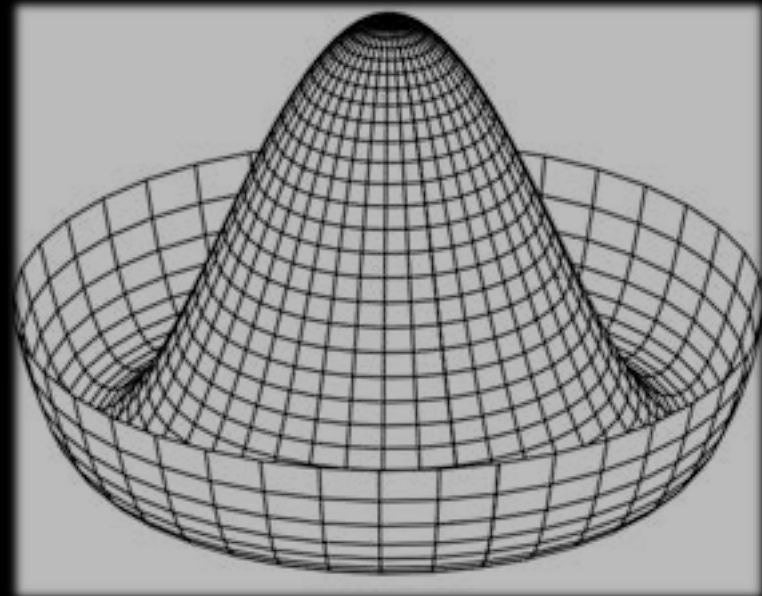
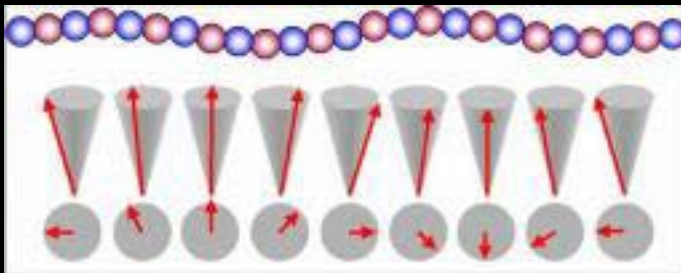
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Excitations:
infinitesimal rotation of a single spin



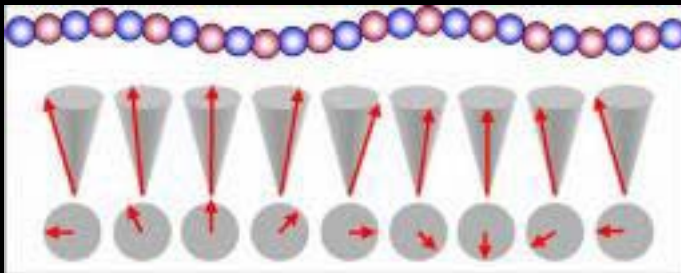
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Excitations:
infinitesimal rotation of a single spin



Gapless excitation
spectrum: Goldstone
modes **Magnons**

Goldstone theorem

Low energy excitations are possible in systems with continuous symmetry.

Example: Heisenberg model [invariant under $O(3)$]

On the other hand:

Ising model (Z_2 symmetry) $H = -J \sum_{i,j} \sigma_i \sigma_j \quad \sigma_i = \pm 1$

An excitation involves flipping a single spin (finite energy $\sim J$).



Mermin-Wagner

Goldstone modes gives rise to large fluctuation effects in low dimensions such that the ordered phase is destroyed.

The number of magnons diverges in 1D and 2D Heisenberg models for any $T > 0$.

In general, there is no phase transition for dimension $d \leq 2$ (for $T > 0$) if we have:

- Spontaneous symmetry of a continuous group
- Short range forces

Mermin, N. D. & Wagner, H. *Phys. Rev. Lett.* **17**, 1133–1136 (1966).

2D magnetic materials

Nature Nanotechnology 14, 408 (2019)

FM in a 2D systems first measured in 2017 on monolayer CrI₃

Mermin-Wagner doesn't apply because of interaction anisotropies.

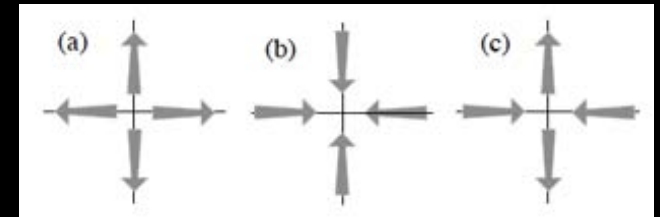
$$H = -\frac{1}{2} \sum_{i,j} (J \mathbf{S}_i \cdot \mathbf{S}_j + \Lambda S_i^z S_j^z) - \sum_i A (S_i^z)^2$$

2D XY model: Berezinskii-Kosterlitz-Thouless transition

The XY model (2D) has continuous symmetry U(1)/O(2).

$$H = -J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j = -J \sum_{\langle i,j \rangle} \cos(\theta_i - \theta_j)$$

Vortices (topological defects)



BKT Transition:

Low T

Vortex-antivortex binding
Correlations show an algebraic decay
(quasi long range order)

High T

Free vortices
Exponential correlation decay
(disorder)

No long range order but a diverging correlation length.

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Free magnetic ions electrons in incomplete shells (d or f orbitals)

Periodic Table of the Elements

1 H Hydrogen																	2 He Helium				
3 Li Lithium	4 Be Beryllium															5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium															13 Al Aluminum	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton				
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon				
55 Cs Cesium	56 Ba Barium	57 La Lanthanum	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium					
72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon							
87 Fr Francium	88 Ra Radium	89 Ac Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium					
			104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium													
			110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 (113)	114 (114)	115 (115)	116 (116)	117 (117)	118 (118)										

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Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Spin angular momentum operator $\hat{S} = \frac{1}{2}\sigma$

Eigenvalues of S_z : $m_s = \pm 1/2$

Eigenvectors: $|\uparrow_z\rangle = \frac{1}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad |\downarrow_z\rangle = \frac{1}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

Spinor
representation

$$|\uparrow_x\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad |\downarrow_x\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$|\uparrow_y\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix} \quad |\downarrow_y\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix}$$

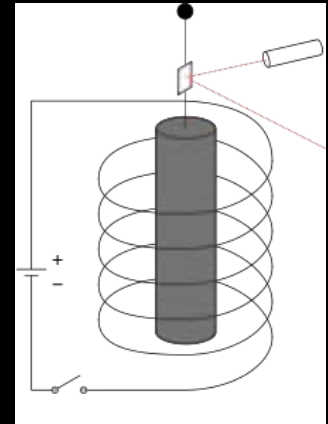
Free magnetic ions

Magnetism originates from the magnetic moment of electrons
(angular momentum: Einstein-de Hass effect)

Intrinsic angular
momentum m_s
(spin quantum number s)

$$\mu_s = -g\mu_B m_s$$

$$m_s = \pm 1/2$$
$$g = 2.0023$$



Orbital angular
momentum m_l
(angular momentum
quantum number l)

$$\mu_O = -\frac{e}{2c}(r \times v) = -\frac{e}{2mc}(r \times p) = -\mu_B m_l$$

Note that for atomic nuclei

$\mu_N \ll \mu_B$ (due to the much larger mass of the proton)

$$\mu_B = \frac{e\hbar}{2mc}$$

Free magnetic ions *electrons in incomplete shells (d or f orbitals)*

Electrons move in the effective potential created by the nucleus plus an average potential from the other electrons (Hartree approx)

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_l^m(\theta, \phi)$$

An ion has a net magnetic moment if it has an incomplete atomic shell (characterized by the atomic numbers n and l). L and S are zero for complete shells.

$$L = \sum_i m_{l_i} \quad S = \sum_i m_{s_i}$$

$(2S+1)(2L+1)$ possible multiplets. L and S are constants of motion in the absence of spin-orbit coupling. The degeneracy is lifted by the correlation energy (deviation of the electron-electron interaction with respect to Hartree): maximize S and maximize L (Hund's rules).

Spin orbit coupling

Interaction between the electron and the magnetic field created by the orbiting nucleus (in the electron frame)

$$\vec{B} = \frac{\vec{E} \times \vec{v}}{c^2} \quad \vec{E} = -\nabla V(r) = -\frac{\vec{r}}{r} \frac{dV(r)}{dr}$$

$$H_{so} = -\frac{1}{2} \vec{m} \cdot \vec{B} = \frac{e\hbar^2}{2m_e c^2 r} \frac{dV(r)}{dr} \vec{S} \cdot \vec{L} = \lambda \vec{S} \cdot \vec{L}$$

For a hydrogen like atom

$$\frac{1}{r} \frac{dV(r)}{dr} = \frac{Z_{\text{eff}} e}{4\pi\epsilon r^3}$$

$$H_{so} \sim Z_{\text{eff}} \langle r^{-3} \rangle \vec{S} \cdot \vec{L}$$

Spin orbit is more important for small r (f-electrons)

For a Hydrogen like atom, $\langle r^{-3} \rangle \sim Z^3$

Free magnetic ions electrons in incomplete shells (d or f orbitals)



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58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium

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Free magnetic ions

Total angular momentum: $\mathbf{J}=\mathbf{L}+\mathbf{S}$

$$|L-S| \leq J \leq L+S$$

$$\sum_{J=|L-S|}^{L+S} 2J+1 = (2L+1)(2S+1)$$

With spin-orbit coupling (λLS),

L and S are not constants of motion but J is.

For Russel-Saunders coupling (SO as a weak perturbation):

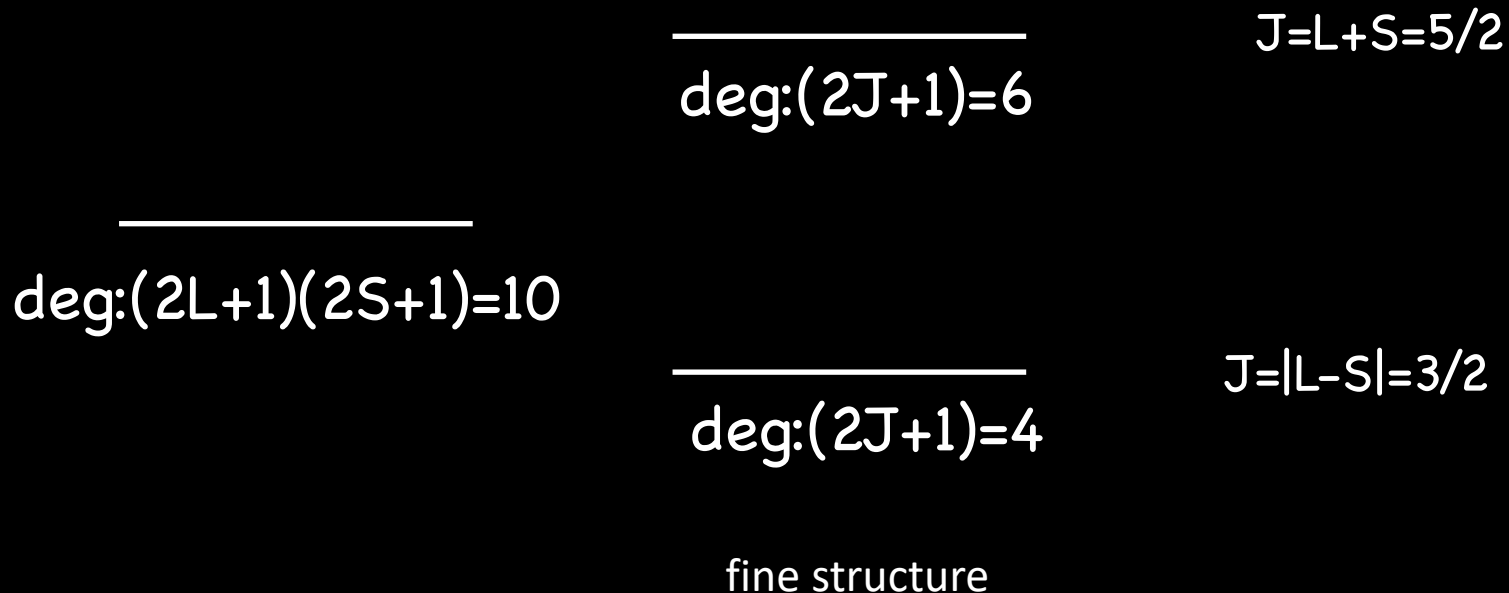
The $(2S+1)(2L+1)$ -fold degenerate level splits into $(2J+1)$ degenerate $(2S+1)$ [for $L>S$] or $(2L+1)$ [for $L<S$] levels.

The lowest energy state is $J=L+S$ if the shell is more than half filled or $J=|L-S|$ otherwise (3rd Hund's rule)

$$\mu_{eff} = g_J \mu_B \sqrt{J(J+1)} \quad g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

Example $d^1: L=2, S=1/2$

$L > S \rightarrow 2S+1=2$ states with degeneracy $2J+1$



Free magnetic ions

Ground state (GS) selection: **Hund's rules**

1. Maximize S
2. Maximize L
3. Minimize spin-orbit energy:
 $J=|L-S|$ if shell is less than half-full
 $J=L+S$ if shell is more than half full

$$2S+1L_J$$

L	0	1	2	3	4	5	6
	S	P	D	F	G	H	I

$$\mu_{eff} = g_J \mu_B \sqrt{J(J+1)} \quad g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

Free magnetic ions

Ground state (GS) selection: **Hund's rules**

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

1. Maximize S
2. Maximize L
3. Minimize spin-orbit energy:
 $J=|L-S|$ if shell is less than half-full
 $J=L+S$ if shell is more than half full

$$2S+1L_J$$

$\text{Mn}^{3+} (3d)^4$

$m_l = 2$

1

0

-1

-2



$S=2$

$L=2$

$J=|L-S|=0$

3D_0

$\mu_{eff}=0$

Free magnetic ions

Ground state (GS) selection: **Hund's rules**

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

1. Maximize S
2. Maximize L
3. Minimize spin-orbit energy:
 $J=|L-S|$ if shell is less than half-full
 $J=L+S$ if shell is more than half full

$$2S+1L_J$$

$Dy^{3+} (4f)^9$

$m_l = 3$

2

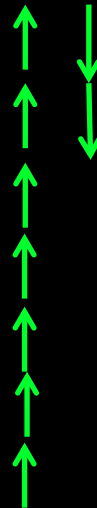
1

0

-1

-2

-3



$S=5/2$

$L=5$

$J=5+5/2=15/2$

${}^6H_{15/2}$

$\mu_{eff}=10.63\mu_B$

Free magnetic ions

Ground state (GS) selection: **Hund's rules**

1. Maximize S
2. Maximize L
3. Minimize spin-orbit energy:
 $J=|L-S|$ if shell is less than half-full
 $J=L+S$ if shell is more than half full

Note

For $(3d)^4$, we got $\mu_{\text{eff}}=0$.
But experimentally (in a solid) $\mu_{\text{exp}}=4.82\mu_B$

In contrast, for $(4f)^9$, $\mu_{\text{eff}} \approx \mu_{\text{exp}}$

Free magnetic ions

Ground state (GS) selection: **Hund's rules**

1. Maximize S
2. Maximize L
3. Minimize spin-orbit energy:
 $J=|L-S|$ if shell is less than half-full
 $J=L+S$ if shell is more than half full

Why $\mu_{\text{eff}} \neq \mu_{\text{exp}}$ for $(3d)^4$ in a solid?

Environment: crystal field

Environment (breaking orbital degeneracy)

- Crystal field (CF):
 - Electrostatic interaction with electrons in surrounding ions. The medium is not isotropic: it has the symmetry of the crystal.
 - More important for d-electrons than for f-electrons because the former are less confined.

Free magnetic ions electrons in incomplete shells (d or f orbitals)

Large CF
Small SO

Small CF
Large SO



Periodic Table of the Elements

atomic number

atomic weight

symbol:

name

black

blue

red

white

solid

liquid

gas

synthetically prepared

not stable isotope

alkali metals

alkaline earth metals

transitional metals

other metals

nonmetals

noble gases

1 H Hydrogen																	2 He Helium	
3 Li Lithium	4 Be Beryllium																	10 Ne Neon
11 Na Sodium	12 Mg Magnesium																	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton	
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon	
55 Cs Cesium	56 Ba Barium	57 La Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon	
87 Fr Francium	88 Ra Radium	89 Ac Actinium	104 Rf Rutherfordium	105 Ha Hassium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium										

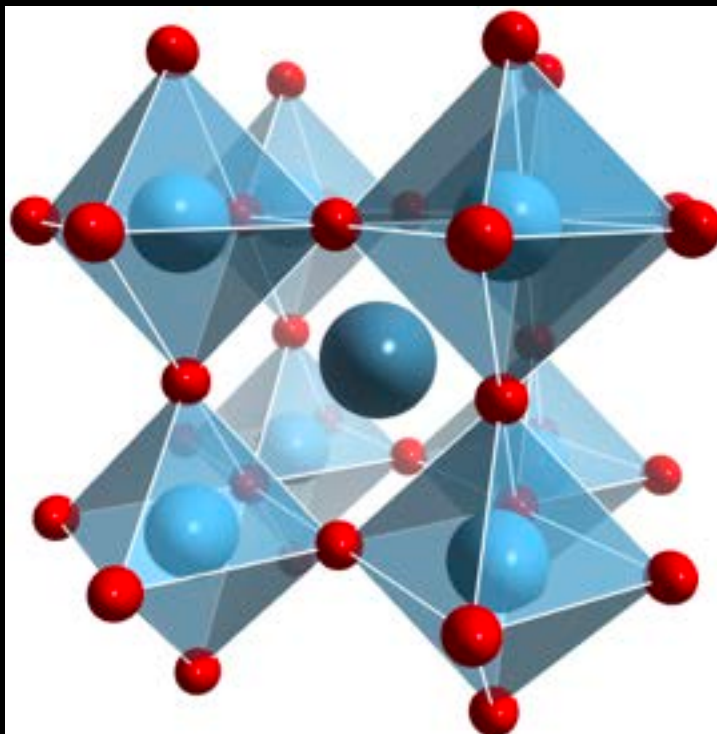
58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium

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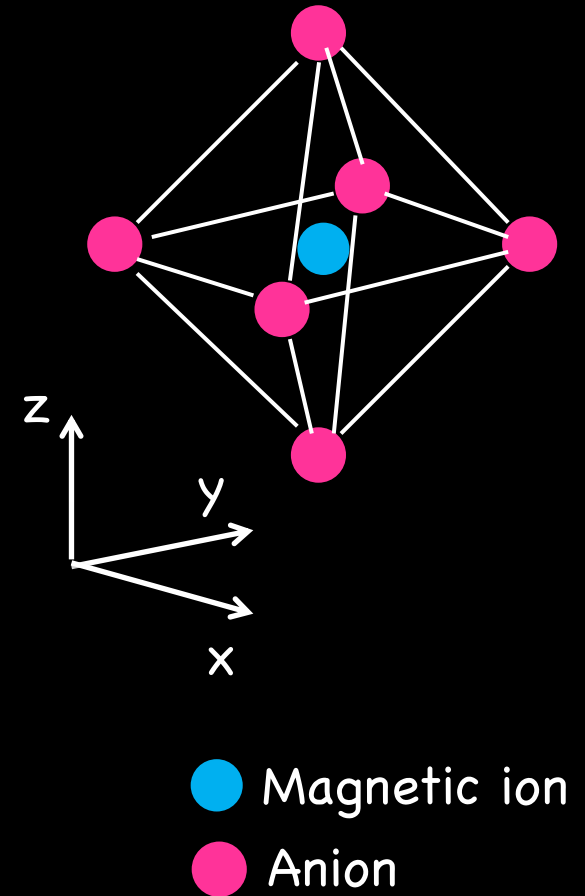
Environment (breaking orbital degeneracy)

- Crystal field

d-electrons in cubic symmetry
(perovskite structure)



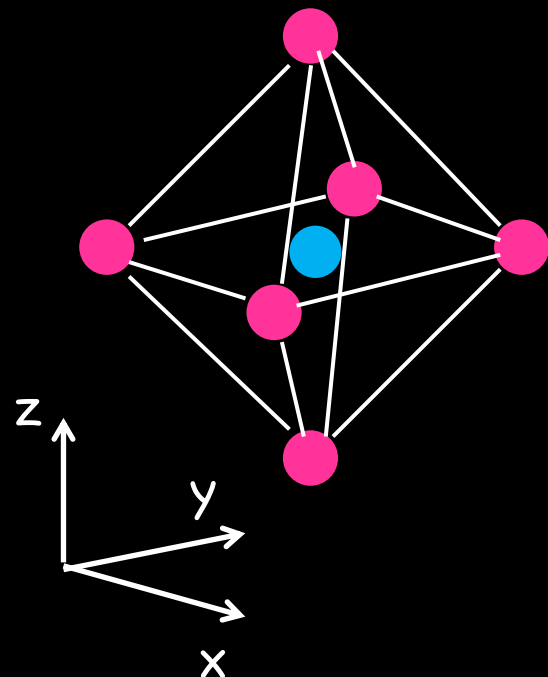
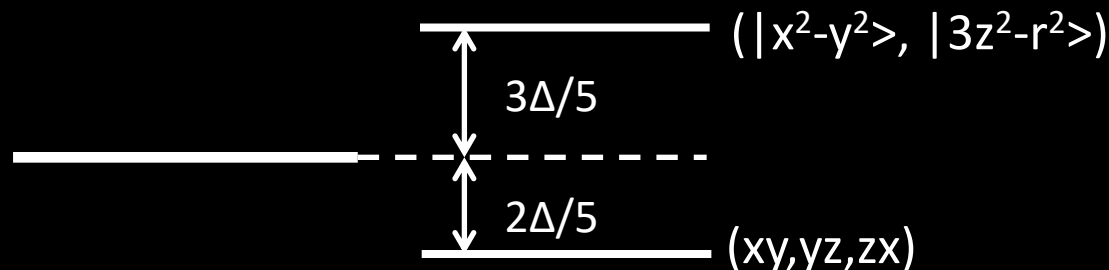
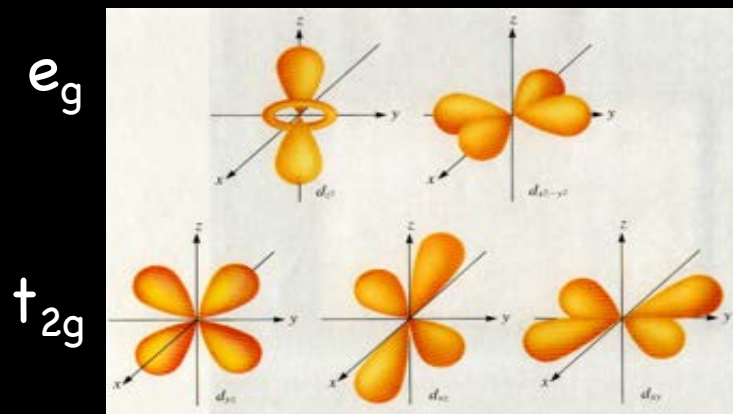
ABO₃



Environment (breaking orbital degeneracy)

- Crystal field

d-electrons in cubic symmetry
(perovskite structure)



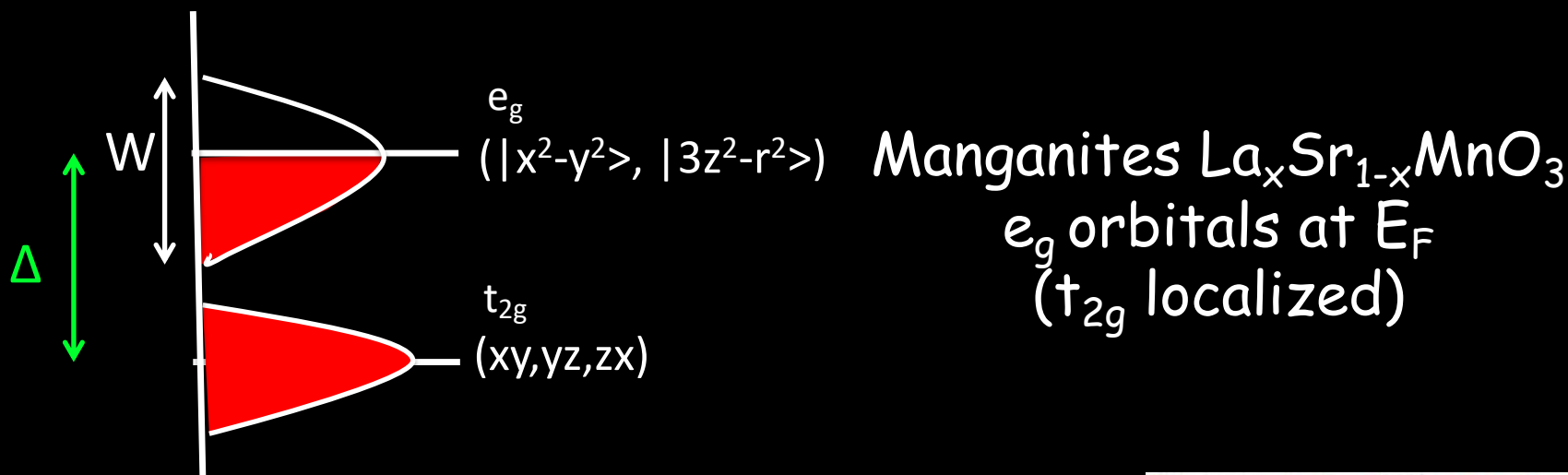
● Magnetic ion

● Anion

Environment (breaking orbital degeneracy)

- Crystal field (splitting Δ)
d-electrons in cubic symmetry
(perovskite structure)

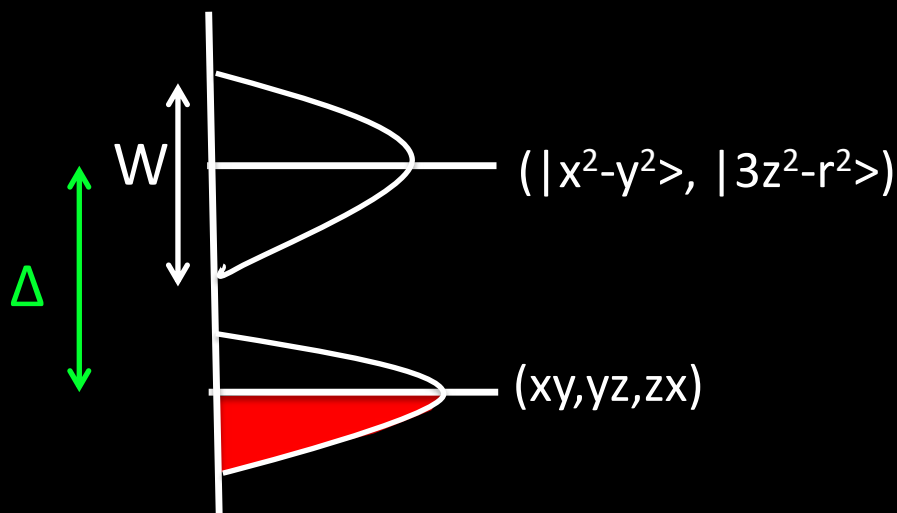
In many cases (manganites, titanates) the splitting Δ is large compared to the bandwidth W .



Environment (breaking orbital degeneracy)

- Crystal field
d-electrons in cubic symmetry
(perovskite structure)

In many cases (manganites, titanates) the splitting Δ is large compared to the bandwidth W .

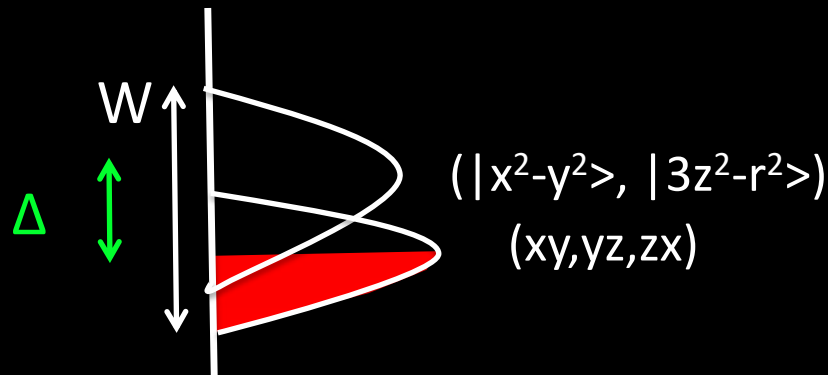


Doped SrTiO_3
 t_{2g} orbitals at E_F

Environment (breaking orbital degeneracy)

- Crystal field
d-electrons in cubic symmetry
(perovskite structure)

If the splitting Δ is small compared to the bandwidth W .

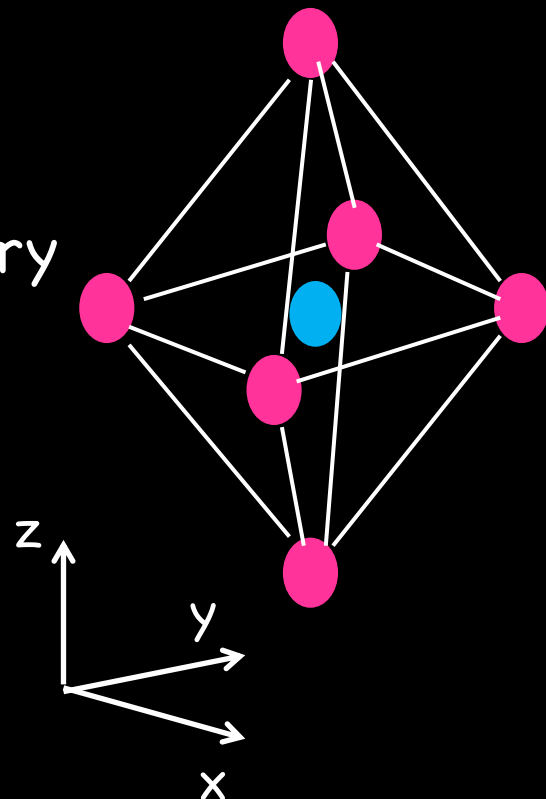
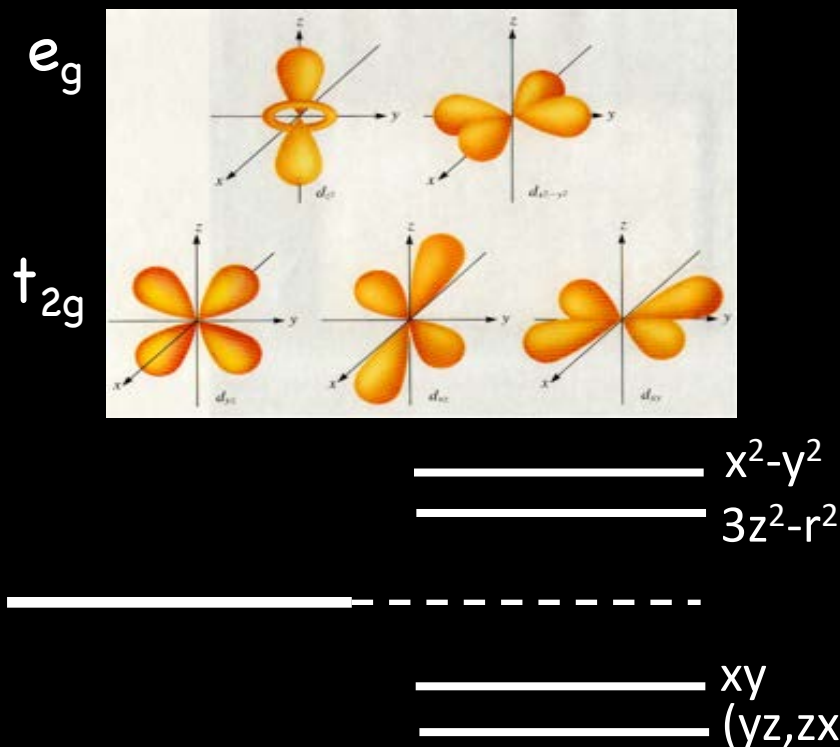


All d-orbitals at E_F

Environment (breaking orbital degeneracy)

- Crystal field

d-electrons in tetragonal symmetry
(perovskite structure)



● Magnetic ion

● Anion

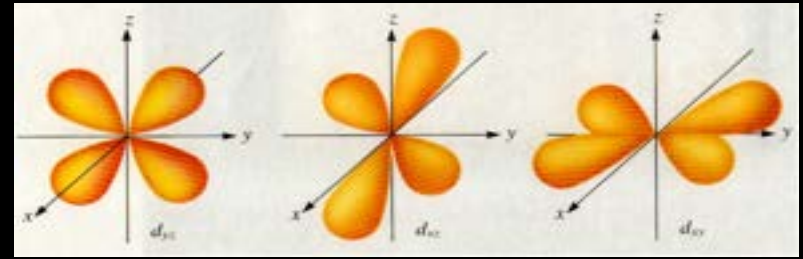
Which orbitals are at E_F is important to determine the bands in the model. (Mott physics in multiorbital systems by Leni Bascones)

Hoppings are determined by the symmetry of the orbitals and the lattice

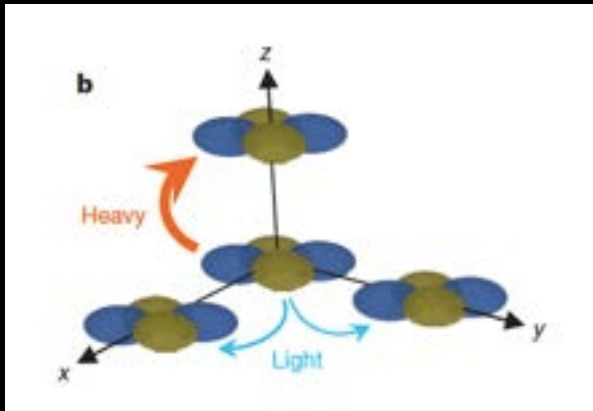
$E_{xy, xy}$	$3l^2m^2(dd\sigma) + (l^2 + m^2 - 4l^2m^2)(dd\pi) + (n^2 + l^2m^2)(dd\delta)$
$E_{xy, yz}$	$3lm^2n(dd\sigma) + ln(1 - 4m^2)(dd\pi) + ln(m^2 - 1)(dd\delta)$
$E_{xy, zx}$	$3l^2mn(dd\sigma) + mn(1 - 4l^2)(dd\pi) + mn(l^2 - 1)(dd\delta)$
E_{xy, x^2-y^2}	$\frac{3}{2}lm(l^2 - m^2)(dd\sigma) + 2lm(m^2 - l^2)(dd\pi) + \frac{1}{2}lm(l^2 - m^2)(dd\delta)$
E_{yz, x^2-y^2}	$\frac{3}{2}mn(l^2 - m^2)(dd\sigma) - mn[1 + 2(l^2 - m^2)](dd\pi) + mn[1 + \frac{1}{2}(l^2 - m^2)](dd\delta)$
E_{zx, x^2-y^2}	$\frac{3}{2}nl(l^2 - m^2)(dd\sigma) + nl[1 - 2(l^2 - m^2)](dd\pi) - nl[1 - \frac{1}{2}(l^2 - m^2)](dd\delta)$
$E_{xy, 3z^2-r^2}$	$\sqrt{3}lm[n^2 - \frac{1}{2}(l^2 + m^2)](dd\sigma) - 2\sqrt{3}lmn^2(dd\pi) + \frac{1}{2}\sqrt{3}lm(1 + n^2)(dd\delta)$
$E_{yz, 3z^2-r^2}$	$\sqrt{3}mn[n^2 - \frac{1}{2}(l^2 + m^2)](dd\sigma) + \sqrt{3}mn(l^2 + m^2 - n^2)(dd\pi) - \frac{1}{2}\sqrt{3}mn(l^2 + m^2)(dd\delta)$
$E_{zx, 3z^2-r^2}$	$\sqrt{3}ln[n^2 - \frac{1}{2}(l^2 + m^2)](dd\sigma) + \sqrt{3}ln(l^2 + m^2 - n^2)(dd\pi) - \frac{1}{2}\sqrt{3}ln(l^2 + m^2)(dd\delta)$
$E_{x^2-y^2, x^2-y^2}$	$\frac{3}{4}(l^2 - m^2)^2(dd\sigma) + [l^2 + m^2 - (l^2 - m^2)^2](dd\pi) + [n^2 + \frac{1}{4}(l^2 - m^2)^2](dd\delta)$
$E_{x^2-y^2, 3z^2-r^2}$	$\frac{1}{2}\sqrt{3}(l^2 - m^2)[n^2 - \frac{1}{2}(l^2 + m^2)](dd\sigma) + \sqrt{3}n^2(m^2 - l^2)(dd\pi) + \frac{1}{4}\sqrt{3}(1 + n^2)(l^2 - m^2)(dd\delta)$
$E_{3z^2-r^2, 3z^2-r^2}$	$[n^2 - \frac{1}{2}(l^2 + m^2)]^2(dd\sigma) + 3n^2(l^2 + m^2)(dd\pi) + \frac{3}{4}(l^2 + m^2)^2(dd\delta)$

Slater and Koster, Phys. Rev. 94, 1498 (1954)

For instance, t_{2g} orbitals:



In a cubic lattice (l,m,n): (1,0,0), (0,1,0), (0,0,1)



Nature 469, 189 (2011)

$$\begin{aligned} t_{xy,xy}^x &= t_{xy,xy}^y \\ &= t_{yz,yz}^y = t_{yz,yz}^z \\ &= t_{zx,zx}^z = t_{zx,zx}^x \end{aligned}$$

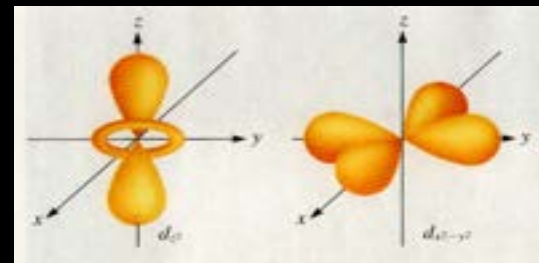
$$t_{\alpha,\beta} = 0$$

t_{2g} orbitals don't mix:
three 2dim bands

If only one t_{2g} orbital
(as for a low crystal
symmetry): 2dim
model

Slater and Koster, Phys. Rev. 94, 1498 (1954)

For e_g orbitals



In a cubic lattice (l,m,n): (1,0,0), (0,1,0), (0,0,1)

$$\begin{aligned}
 t_{3z^2-r^2, 3z^2-r^2}^{x,y} &= 1/4t & t_{x^2-y^2, x^2-y^2}^{x,y} &= 3/4t & t_{x^2-y^2, 3z^2-r^2}^{x,y} &= \pm\sqrt{3}/4t \\
 t_{3z^2-r^2, 3z^2-r^2}^z &= t & t_{x^2-y^2, x^2-y^2}^z &= 0 & t_{x^2-y^2, 3z^2-r^2}^z &= 0
 \end{aligned}$$

e_g orbitals mix.

_____ x^2-y^2
 _____ $3z^2-r^2$

For Cuprates, further
 splitting (tetragonal)
 Cu ($9 \pm x$) electrons.

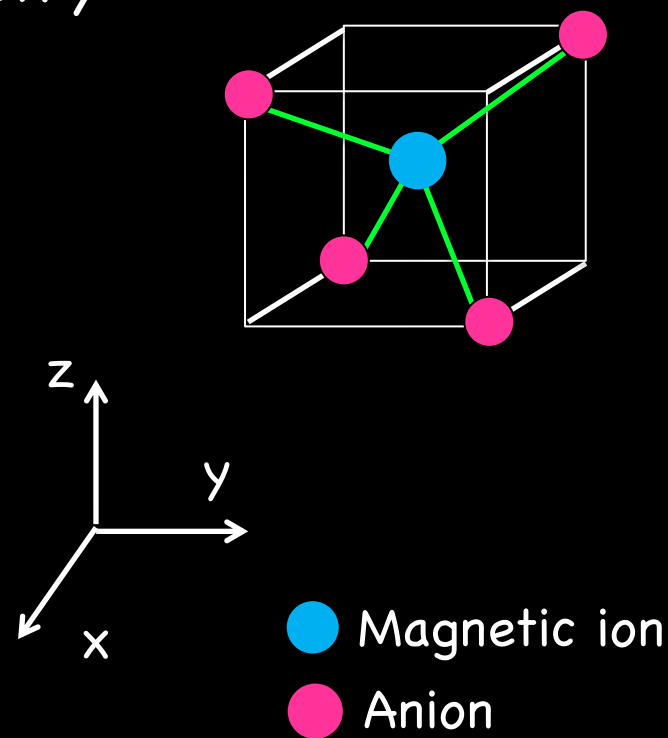
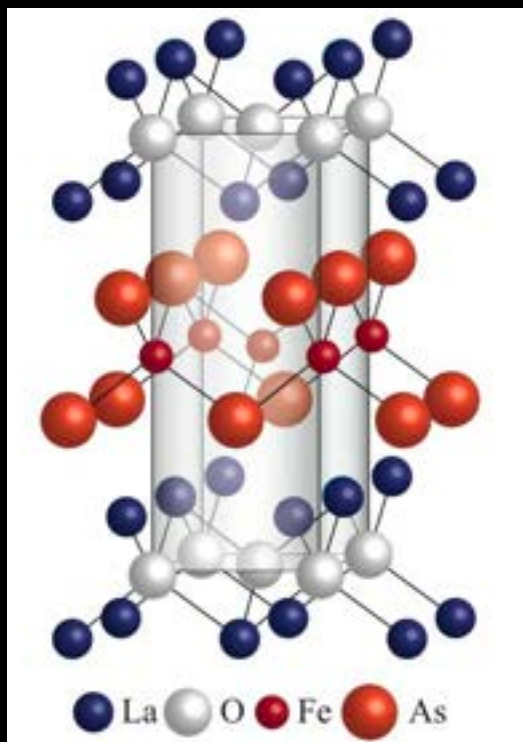
_____ xy
 _____ (yz, zx)

Carriers on x^2-y^2 :
 2dim band

Slater and Koster, Phys. Rev. 94, 1498 (1954)

Environment (breaking orbital degeneracy)

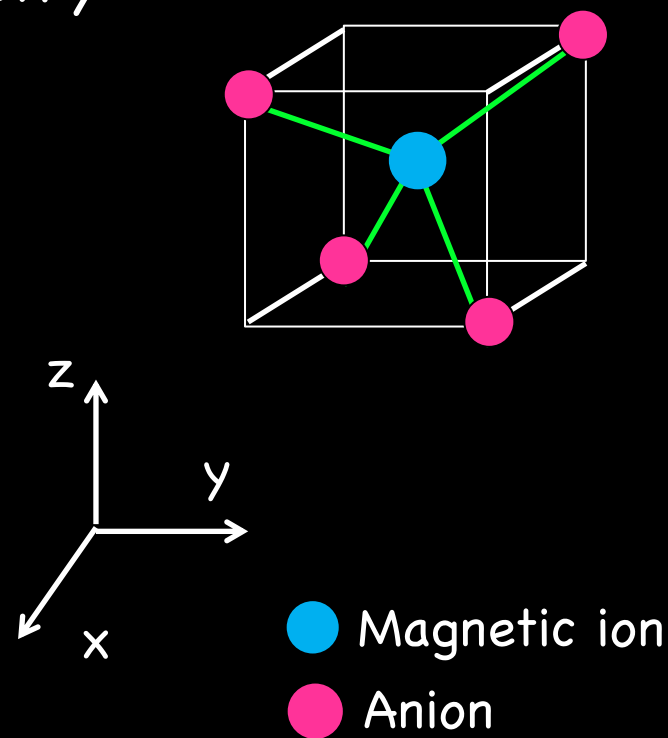
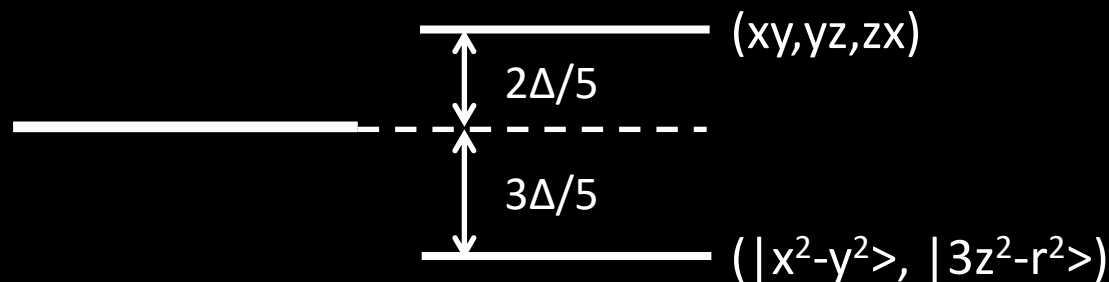
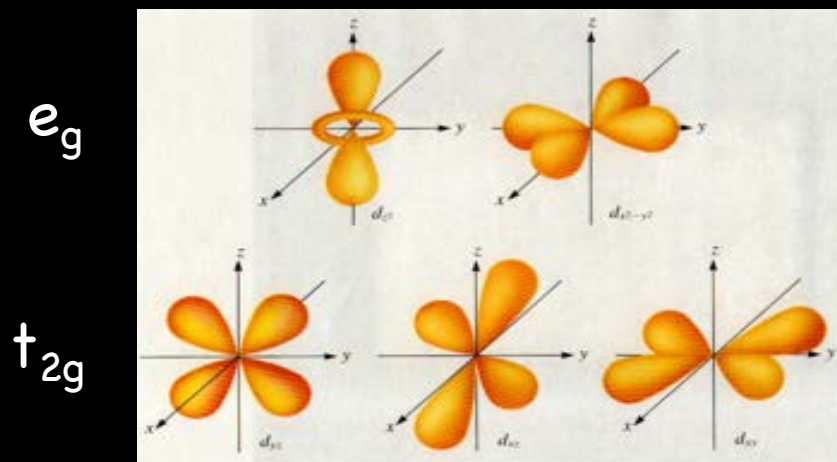
- Crystal field
d-electrons in a tetrahedral symmetry



Environment (breaking orbital degeneracy)

- Crystal field

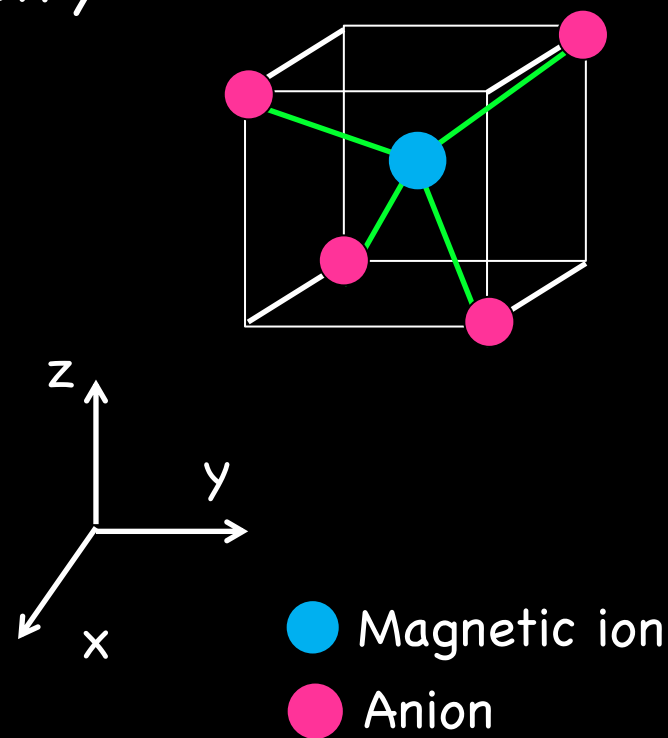
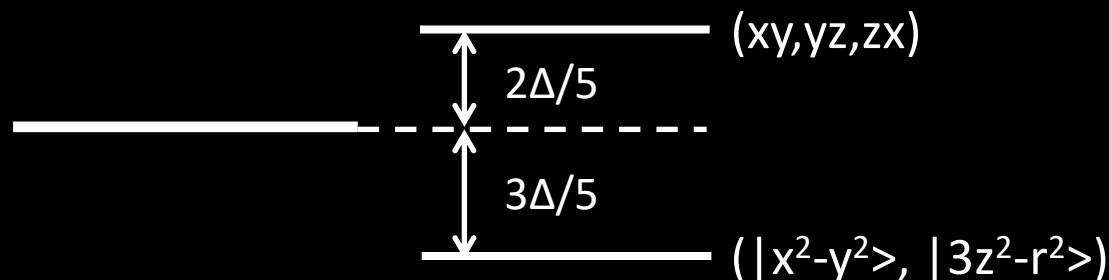
d-electrons in a tetrahedral symmetry



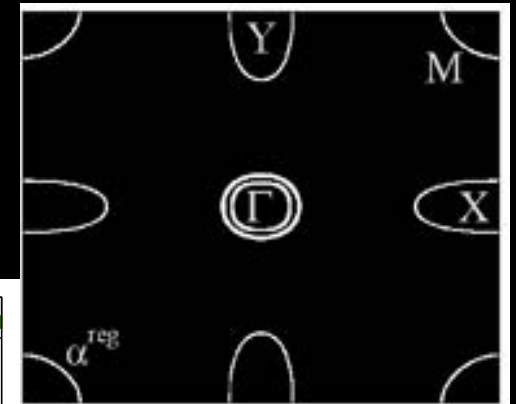
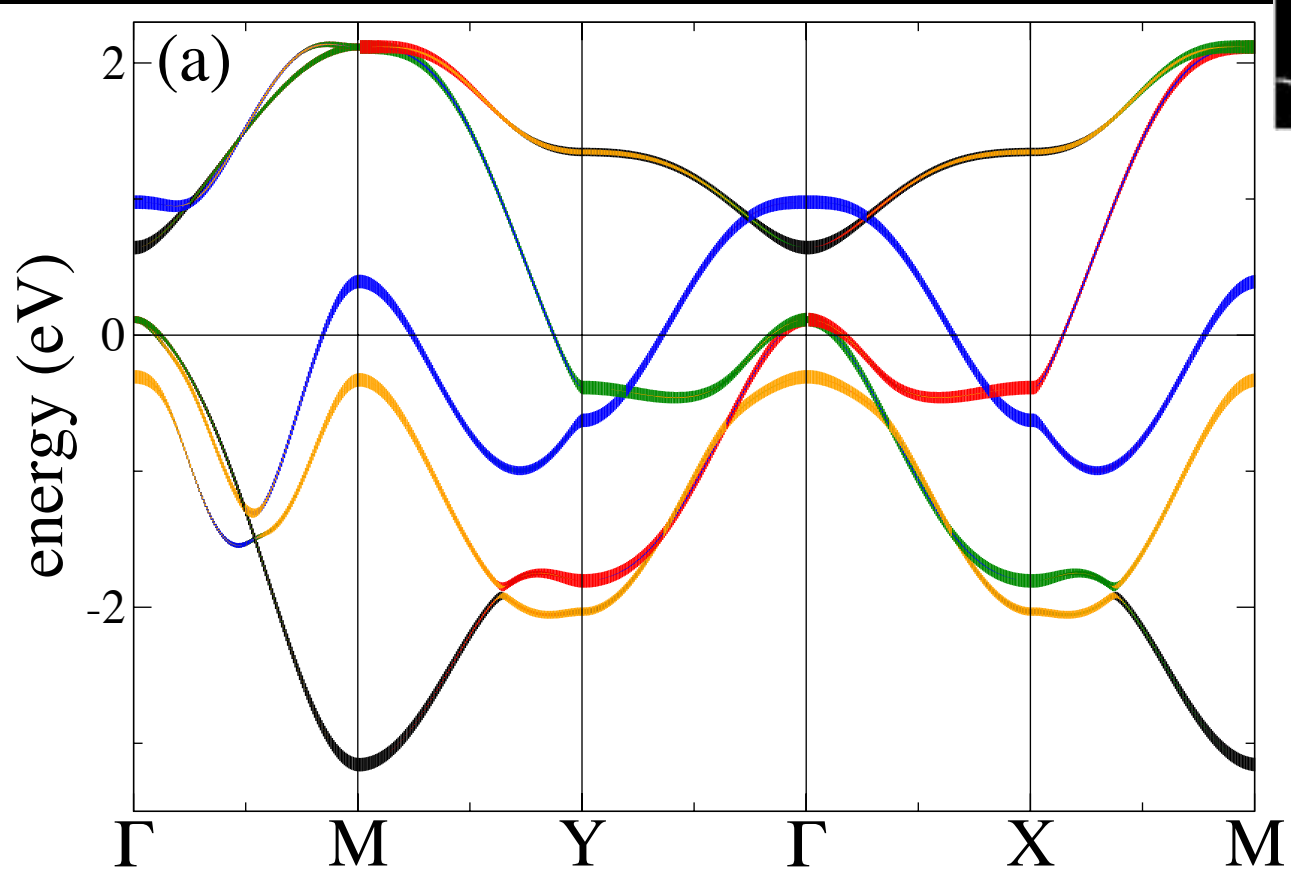
Environment (breaking orbital degeneracy)

- Crystal field
d-electrons in a tetrahedral symmetry

In iron superconductors, the splitting Δ is small compared to the bandwidth so all five orbitals at E_F



d-bands for iron superconductors



PRB 87, 075136

Crystal field



Orbital "selection"



anisotropies

Environment (breaking orbital degeneracy)

- Crystal field. Calculation (sketch)

Treat surrounding ions as point charges

...expand for $r \ll R$

$$V_{cryst} = \sum_i \frac{q_i}{|\mathbf{r} - \mathbf{R}_i|}$$

$$V_{cryst} = \sum_l \sum_{m=-l}^l K_{lm} r^l P_l^{|m|}(\cos\theta) e^{im\varphi}$$

$$K_{lm} = \frac{(l-|m|)!}{(l+|m|)!} \sum_i \frac{q_i}{R_i^{l+1}} P_l^{|m|}(\cos\theta_i) e^{im\varphi_i}$$

R_i has the information of the crystal symmetry

And rewrite as a function of spherical harmonics.

Environment (breaking orbital degeneracy)

- Crystal field. Calculation (sketch)

Treat surrounding ions as point charges

$$V_{cryst} = \sum_i \frac{q_i}{|\mathbf{r} - \mathbf{R}_i|}$$

Calculate expected values of atomic orbitals (also expressed in spherical harmonics)

$$\langle \Psi_{lm}(r) | H_{cryst}(r_i) | \Psi_{lm'}(r) \rangle$$

The calculations involve averages over radial wavefunctions $\langle r^n \rangle$

The results depend on the number of electrons

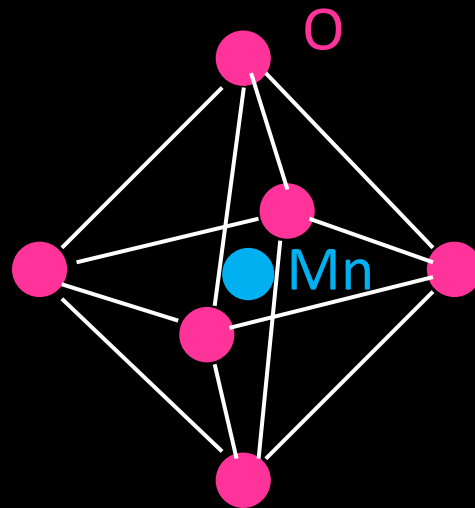
Yosida, Chapter 3.

Environment (breaking orbital degeneracy)

- Jahn-Teller: when the orbital ground state is degenerate, a distortion in the lattice splits orbitals to minimize energy.

For a cubic perovskite lattice:

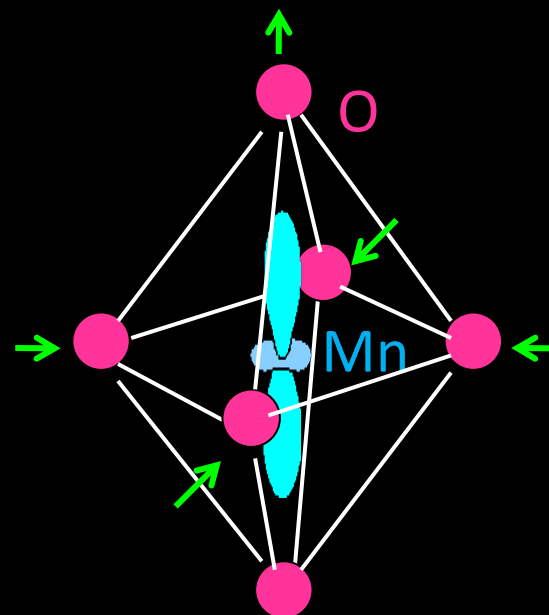
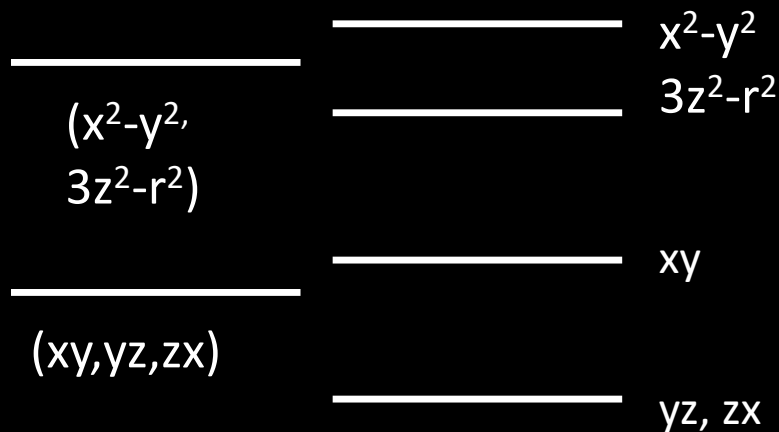
$$(x^2-y^2, 3z^2-r^2)$$

$$(xy, yz, zx)$$


Environment (breaking orbital degeneracy)

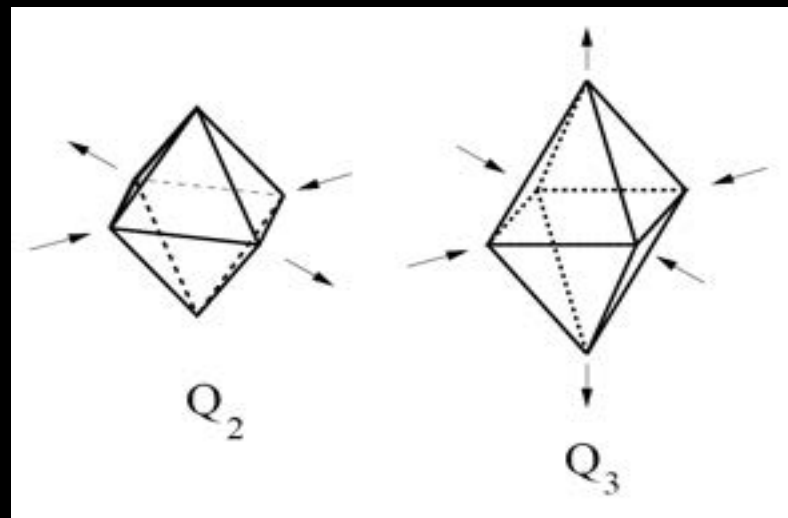
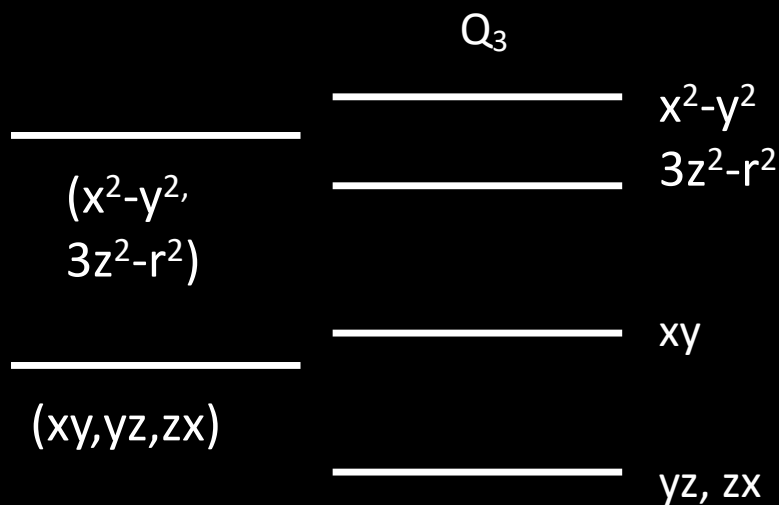
- Jahn-Teller: when the orbital ground state is degenerate, a distortion in the lattice splits orbitals to minimize energy.

For a cubic perovskite lattice:



Environment (breaking orbital degeneracy)

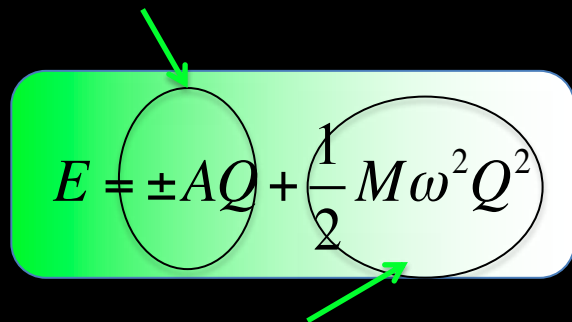
- Jahn-Teller: when the orbital ground state is degenerate, a distortion in the lattice splits orbitals to minimize energy.



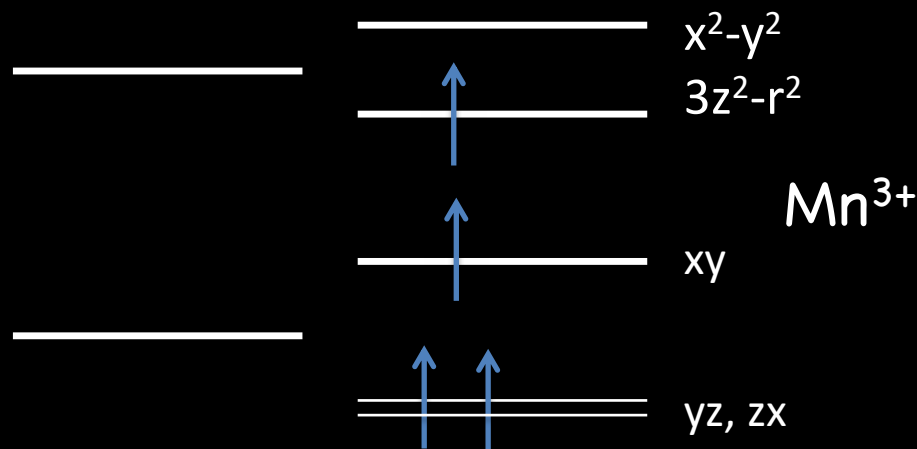
Environment (breaking orbital degeneracy)

- Jahn-Teller: when the orbital ground state is degenerate, a distortion in the lattice splits orbitals to minimize energy.

Electronic energy


$$E = \pm AQ + \frac{1}{2} M \omega^2 Q^2$$

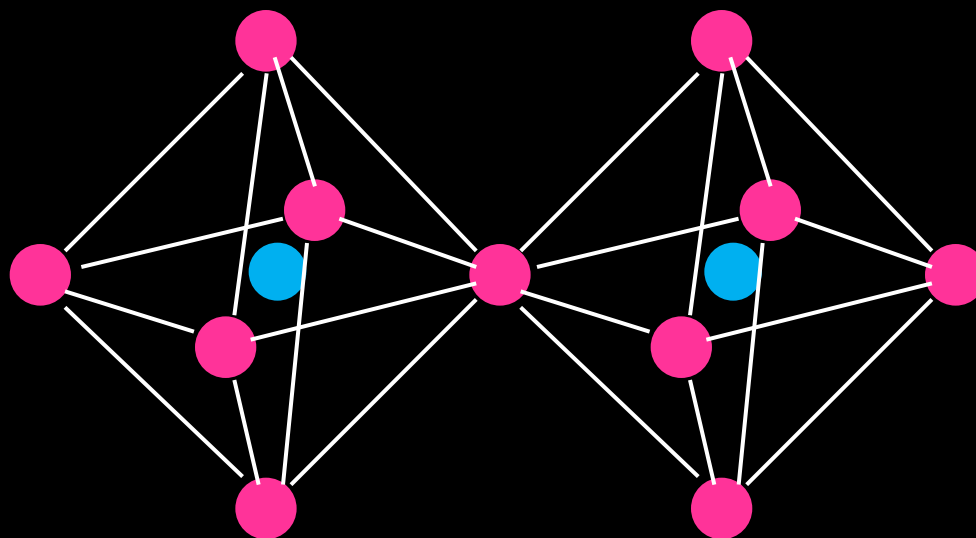
Elastic energy



Note: if you remove (Mn^{4+}) or remove (Mn^{4+}) one electron there is no energy gain by the splitting, hence there is no distortion.

Environment (breaking orbital degeneracy)

Jahn-Teller distortions are cooperative.
They may lead to structural phase transitions



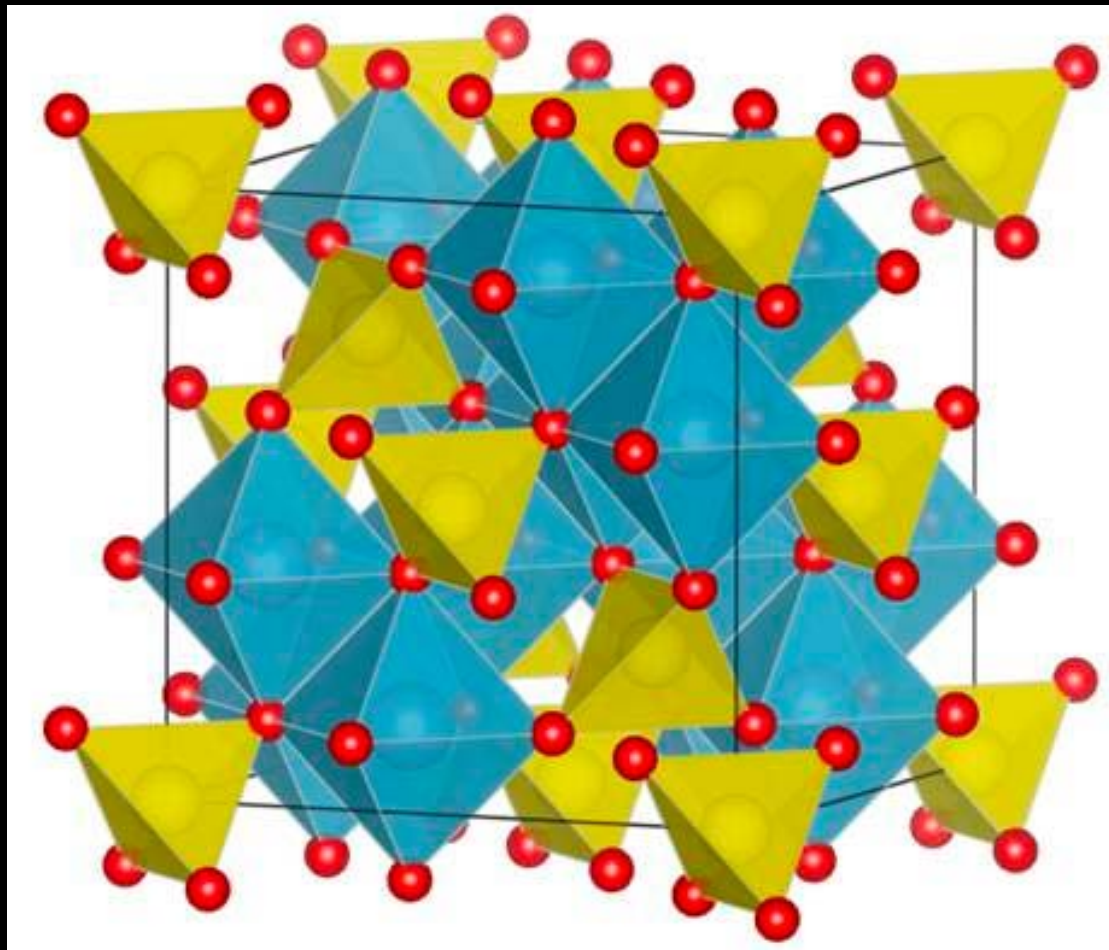
Cubic to tetragonal transitions:

LaMnO_3 ($T_s=800\text{K}$). Perovskite.

CuFe_2O_4 ($T_s=713\text{K}$). Spinel.

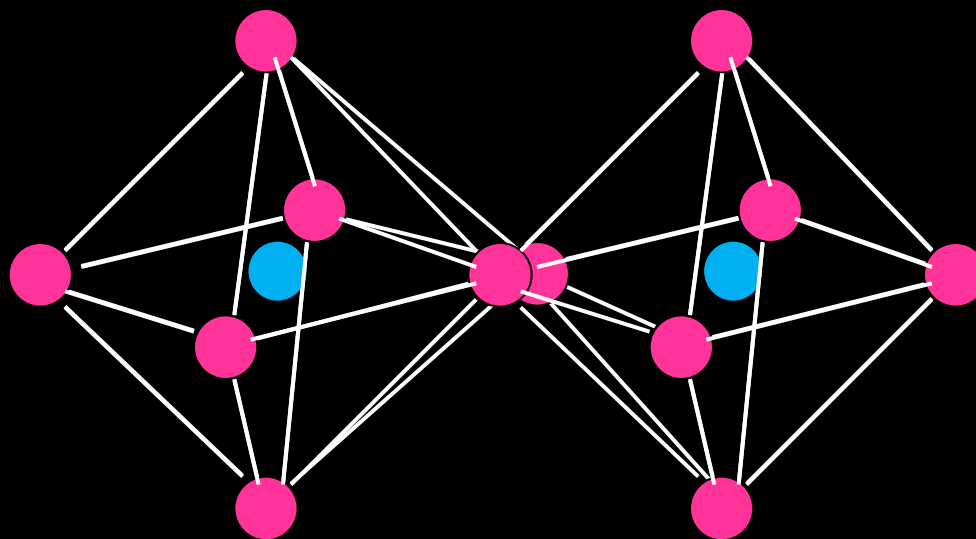
Mn_3O_4 ($T_s=1443\text{K}$). Spinel.

Spinel structure



Environment (breaking orbital degeneracy)

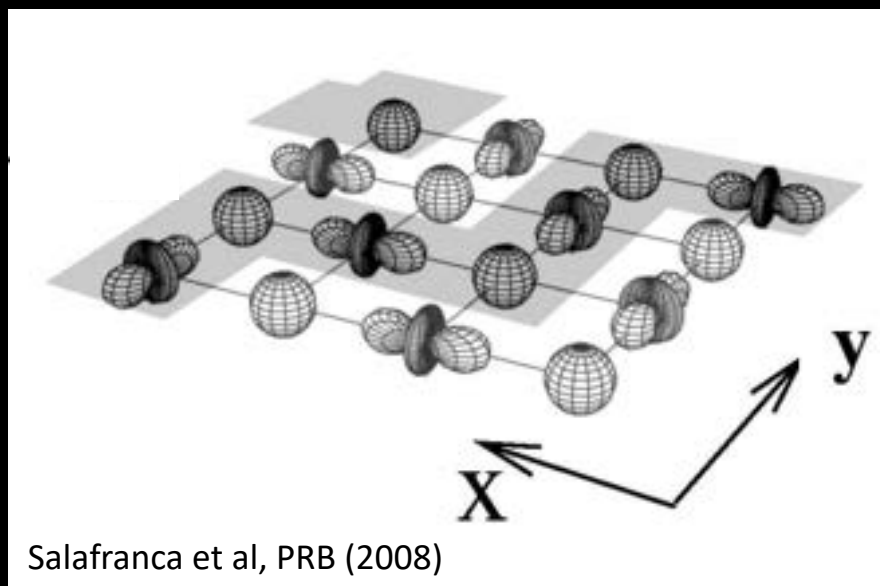
Jahn-Teller distortions are cooperative.
They may lead to structural phase transitions
...and orbital ordering



Environment (breaking orbital degeneracy)

Jahn-Teller distortions are cooperative.
They may lead to structural phase transitions
and orbital ordering

Orbital order in manganites
(0.5 e⁻ per Mn)



Environment (breaking orbital degeneracy)

Jahn-Teller distortions are cooperative.
They may lead to structural phase transitions
and orbital ordering

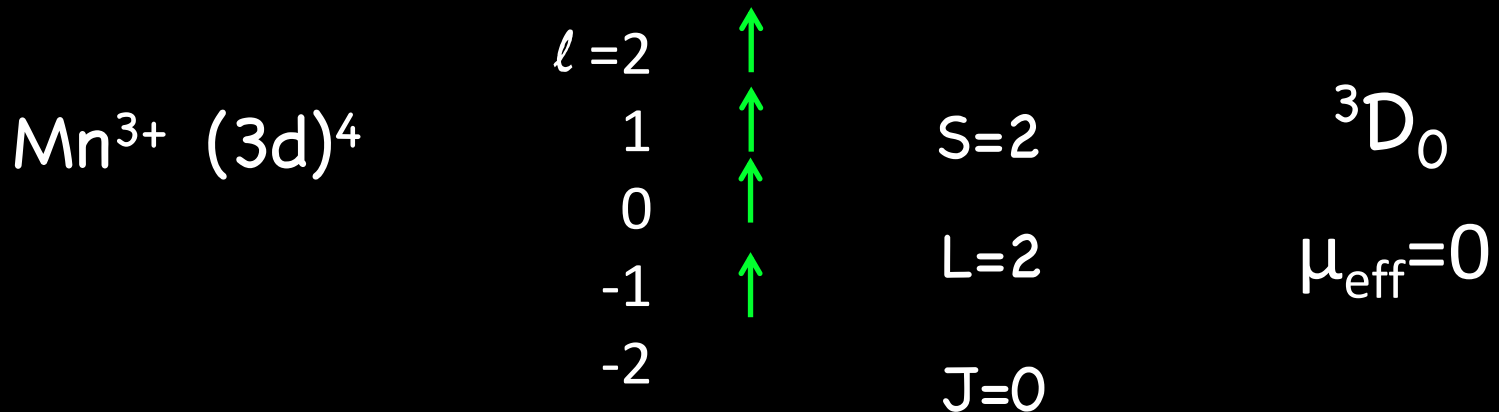
At high temperatures:
dynamic Jahn-Teller effect

Why $\mu_{\text{eff}} \neq \mu_{\text{exp}}$ for $(3d)^4$ in a solid?

Free magnetic ions

Ground state (GS) selection: **Hund's rules**

1. Maximize S
2. Maximize L
3. Minimize spin-orbit energy:
 $J=|L-S|$ if shell is less than half-full
 $J=L+S$ if shell is more than half full

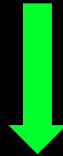


But experimentally $\mu_{\text{exp}}=4.82\mu_B$

Orbital quenching

- If we considered $L=0$ for (3d) ions

$$\mu_{eff} = g_J \mu_B \sqrt{J(J+1)} \quad g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$



$$\mu_{eff} = g_J \mu_B \sqrt{S(S+1)} \quad g_J = 2$$

With $L=0$, for (3d)⁴ we would get $\mu_{eff}=4.89 \mu_B$
(experimentally $\mu_{exp}=4.82 \mu_B$)

(diff between μ_{eff} and μ_{exp} due to finite orbital angular momentum)

Orbital quenching

Experimental observation: When crystal field effects are larger than spin-orbit coupling (as for 3d ions), the ground state is such that $L=0$. *Why?*

$\langle \text{GS} | L | \text{GS} \rangle$ must be real

L is purely
imaginary

Non-degenerate

GS is real

(is an eigenfunction of the crystal field)

$$\langle \text{GS} | L | \text{GS} \rangle = 0$$

Orbital quenching

NOTE:

For degenerate levels, you can define the d-levels in different basis involving any combination of the angular momenta involved.

When the e_g and t_{2g} levels are split by crystal field, you can only make combinations within the restricted set of degenerate levels. In the e_g sector, any combination leads to $L=0$. In the t_{2g} sector, you can choose a combination with $L^z=1$. Therefore, 1 electron in a t_{2g} level has a partially quenched orbital.

Spin-orbit coupling for d-atoms

- Partially restores the quenched orbital momentum
- Induces magnetic anisotropy (the spin feels, through the orbital, the orientation of the crystal axes).

Spin-orbit coupling for d-atoms

Start from a quenched orbital ($L=0$) and introduce LS and magnetic field within second order perturbation theory

$$V = \lambda \mathbf{L} \cdot \mathbf{S} + \mu_B \mathbf{H} \cdot (2\mathbf{S} + \mathbf{L})$$

$$H_S = \sum_{\mu\nu} 2\mu_B H_\mu (\delta_{\mu\nu} - \lambda \Lambda_{\mu\nu}) S_\nu - \lambda^2 S_\mu \Lambda_{\mu\nu} S_\nu - \mu_B^2 H_\mu \Lambda_{\mu\nu} H_\nu$$

$g_{\mu\nu}/2$ (green arrow pointing to $\delta_{\mu\nu}$)
 Induced orbital moment (yellow arrow pointing to $\lambda \Lambda_{\mu\nu}$)
 Anisotropy spin Hamiltonian (blue arrow pointing to $\lambda^2 S_\mu \Lambda_{\mu\nu} S_\nu$)

$$\Lambda_{\mu\nu} = \sum_n \frac{\langle 0 | L_\mu | n \rangle \langle n | L_\nu | 0 \rangle}{E_n - E_0}$$

Spin-orbit coupling for d-atoms

The anisotropy spin Hamiltonian can be written:

$$H = DS_z^2 + E(S_x^2 - S_y^2)$$

- H lifts the $(2S+1)$ degeneracy.
- The first term:
 - For integer S , splitting into doubly degenerate $S_z=\pm S, \pm(S-1)\dots \pm 1$, and non-degenerate 0.
 - For half-integer S , splitting into doubly degenerate $S_z=\pm S, \pm(S-1)\dots \pm 1/2$.
- S_x^2 and S_y^2 produce transitions $\Delta S_z=\pm 2$. Therefore the second term further splits the levels for integer S .
- For half integers ($\Delta S_z=\pm 2$ not possible): Kramers doublet.
- Kramers degeneracy holds as long as the Hamiltonian is invariant under time reversal (and lifted by, for instance, Zeeman energy)

Crystal field for f-atoms

- Crystal field is weak so you have to start from the total angular momentum predicted by third Hund's rule: $(2J+1)$ degeneracy. This degeneracy is usually lifted by the weak crystal field as a $(2J+1)$ degeneracy is too large.
- We have to work with total angular momentum J rather than L . In principle J could be quenched but in practice the crystal field is so small that an external magnetic field or an exchange field can change the relative position of the levels.

Periodic Table of the Elements



Diagram illustrating the periodic table structure and element classification:

Legend:

- alkali metals (grey)
- alkaline earth metals (green)
- transitional metals (yellow)
- other metals (pink)
- nonmetals (blue)
- noble gases (orange)

Diagram Labels:

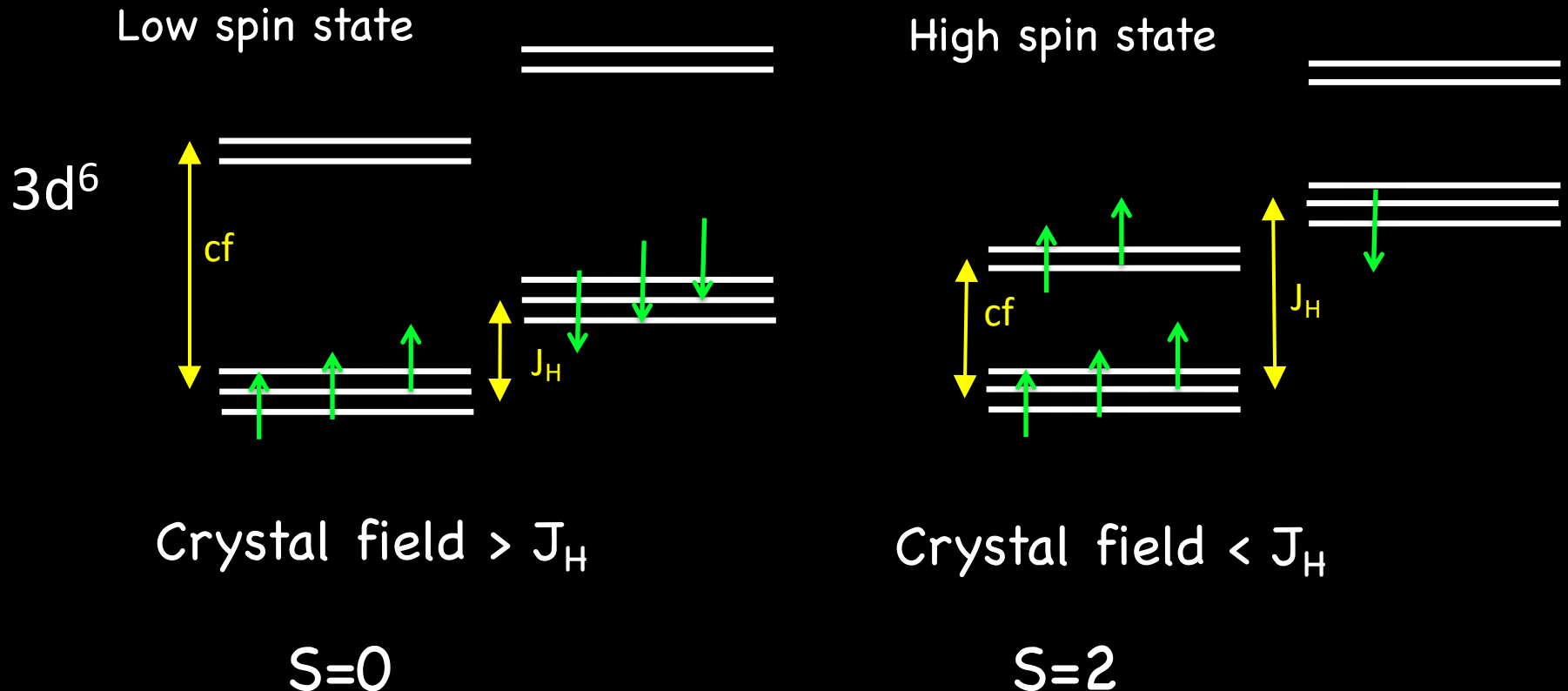
- atomic number (14 for Si)
- atomic weight (28.09 for Si)
- symbol (Si)
- name (Silicon)
- physical state: black solid, blue liquid, red gas
- synthetically prepared (marked with * for synthetic elements)
- most stable isotope (marked with * for synthetic elements)

1	2																	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210	211	212	213	214	215	216	217	218	219	220	221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240	241	242	243	244	245	246	247	248	249	250	251	252	253	254	255	256	257	258	259	260	261	262	263	264	265	266	267	268	269	270	271	272	273	274	275	276	277	278	279	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319	320	321	322	323	324	325	326	327	328	329	330	331	332	333	334	335	336	337	338	339	340	341	342	343	344	345	346	347	348	349	350	351	352	353	354	355	356	357	358	359	360	361	362	363	364	365	366	367	368	369	370	371	372	373	374	375	376	377	378	379	380	381	382	383	384	385	386	387	388	389	390	391	392	393	394	395	396	397	398	399	400	401	402	403	404	405	406	407	408	409	410	411	412	413	414	415	416	417	418	419	420	421	422	423	424	425	426	427	428	429	430	431	432	433	434	435	436	437	438	439	440	441	442	443	444	445	446	447	448	449	450	451	452	453	454	455	456	457	458	459	460	461	462	463	464	465	466	467	468	469	470	471	472	473	474	475	476	477	478	479	480	481	482	483	484	485	486	487	488	489	490	491	492	493	494	495	496	497	498	499	500	501	502	503	504	505	506	507	508	509	510	511	512	513	514	515	516	517	518	519	520	521	522	523	524	525	526	527	528	529	530	531	532	533	534	535	536	537	538	539	540	541	542	543	544	545	546	547	548	549	550	551	552	553	554	555	556	557	558	559	560	561	562	563	564	565	566	567	568	569	570	571	572	573	574	575	576	577	578	579	580	581	582	583	584	585	586	587	588	589	590	591	592	593	594	595	596	597	598	599	600	601	602	603	604	605	606	607	608	609	610	611	612	613	614	615	616	617	618	619	620	621	622	623	624	625	626	627	628	629	630	631	632	633	634	635	636	637	638	639	640	641	642	643	644	645	646	647	648	649	650	651	652	653	654	655	656	657	658	659	660	661	662	663	664	665	666	667	668	669	670	671	672	673	674	675	676	677	678	679	680	681	682	683	684	685	686	687	688	689	690	691	692	693	694	695	696	697	698	699	700	701	702	703	704	705	706	707	708	709	710	711	712	713	714	715	716	717	718	719	720	721	722	723	724	725	726	727	728	729	730	731	732	733	734	735	736	737	738	739	740	741	742	743	744	745	746	747	748	749	750	751	752	753	754	755	756	757	758	759	760	761	762	763	764	765	766	767	768	769	770	771	772	773	774	775	776	777	778	779	780	781	782	783	784	785	786	787	788	789	790	791	792	793	794	795	796	797	798	799	800	801	802	803	804	805	806	807	808	809	810	811	812	813	814	815	816	817	818	819	820	821	822	823	824	825	826	827	828	829	830	831	832	833	834	835	836	837	838	839	840	841	842	843	844	845	846	847	848	849	850	851	852	853	854	855	856	857	858	859	860	861	862	863	864	865	866	867	868	869	870	871	872	873	874	875	876	877	878	879	880	881	882	883	884	885	886	887	888	889	890	891	892	893	894	895	896	897	898	899	900	901	902	903	904	905	906	907	908	909	910	911	912	913	914	915	916	917	918	919	920	921	922	923	924	925	926	927	928	929	930	931	932	933	934	935	936	937	938	939	940	941	942	943	944	945	946	947	948	949	950	951	952	953	954	955	956	957	958	959	960	961	962	963	964	965	966	967	968	969	970	971	972	973	974	975	976	977	978	979	980	981	982	983	984	985	986	987	988	989	990	991	992	993	994	995	996	997	998	999	1000	1001	1002	1003	1004	1005	1006	1007	1008	1009	1010	1011	1012	1013	1014	1015	1016	1017	1018	1019	1020	1021	1022	1023	1024	1025	1026	1027	1028	1029	1030	1031	1032	1033	1034	1035	1036	1037	1038	1039	1040	1041	1042	1043	1044	1045	1046	1047	1048	1049	1050	1051	1052	1053	1054	1055	1056	1057	1058	1059	1060	1061	1062	1063	1064	1065	1066	1067	1068	1069	1070	1071	1072	1073	1074	1075	1076	1077	1078	1079	1080	1081	1082	1083	1084	1085	1086	1087	1088	1089	1090	1091	1092	1093	1094	1095	1096	1097	1098	1099	1100	1101	1102	1103	1104	1105	1106	1107	1108	1109	1110	1111	1112	1113	1114	1115	1116	1117	1118	1119	1120	1121	1122	1123	1124	1125	1126	1127	1128	1129	1130	1131	1132	1133	1134	1135	1136	1137	1138	1139	1140	1141	1142	1143	1144	1145	1146	1147	1148	1149	1150	1151	1152	1153	1154	1155	1156	1157	1158	1159	1160	1161	1162	1163	1164	1165	1166	1167	1168	1169	1170	1171	1172	1173	1174	1175	1176	1177	1178	1179	1180	1181	1182	1183	1184	1185	1186	1187	1188	1189	1190	1191	1192	1193	1194	1195	1196	1197	1198	1199	1200	1201	1202	1203	1204	1205	1206	1207	1208	1209	1210	1211	1212	1213	1214	1215	1216	1217	1218	1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Three **energy scales** to determine local moments in a solid

- Hund's coupling (local exchange)
- Crystal field (environment)
- Spin-orbit coupling

Crystal field vs Hund's coupling

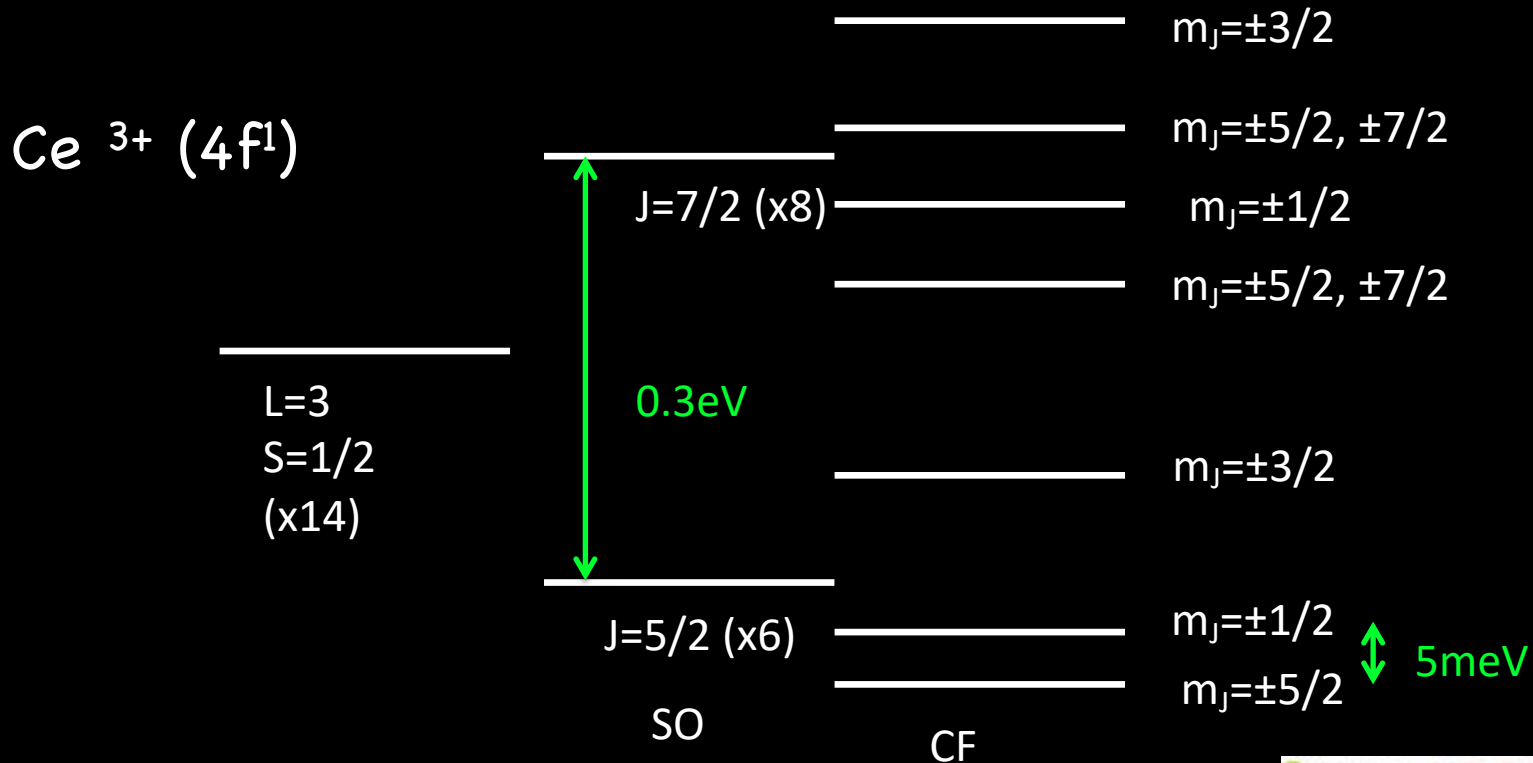


Crystal fields may be changed with pressure

Crystal field vs spin-orbit coupling

3d ions: crystal-field $\gg$ spin-orbit coupling

4f and 5f ions: crystal-field $\ll$ spin-orbit coupling

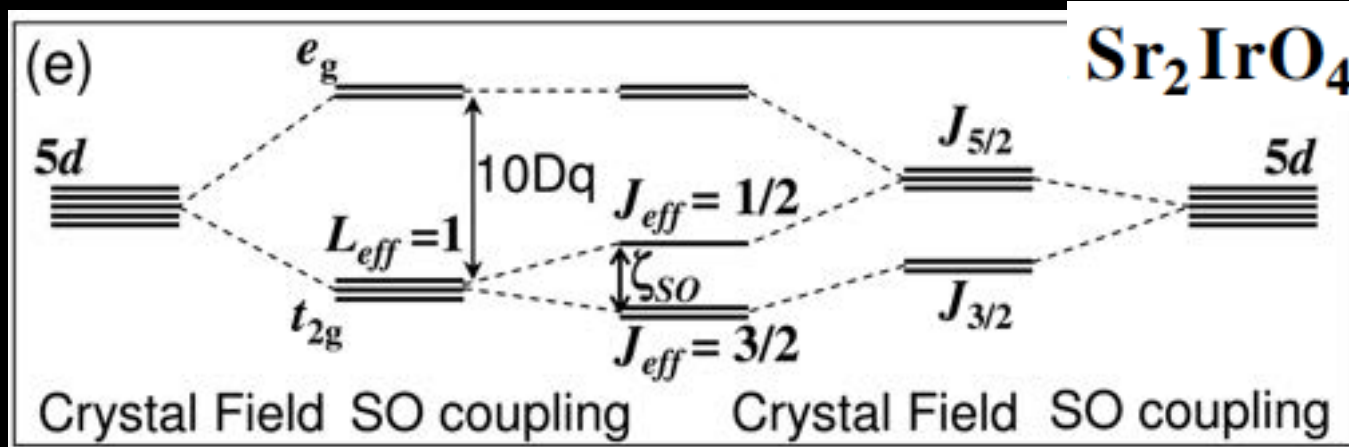


Crystal field vs spin-orbit coupling

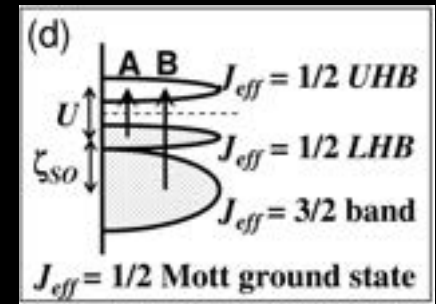
3d ions: crystal-field $\gg$ spin-orbit coupling

4f and 5f ions: crystal-field $\ll$ spin-orbit coupling

4d-5d: crystal-field $\approx$ spin-orbit coupling



5d⁵



Kim et al, PRL 101, 076402

Three **energy scales** to determine local moments

- Hund's coupling (local exchange)
- Crystal field (environment)
- Spin-orbit coupling

3d ions:

- Crystal field $\gg$ spin-orbit coupling
 - orbital quenching ($L=0$)
- Crystal field vs Hund's coupling: low spin–high spin

4f–5f:

- Crystal field $\ll$ spin-orbit coupling
- Large total magnetic moments J

4d–5d: All scales relevant. U competes with LS

Outline

- Free magnetic ions
- Environment
- Magnetic order and phase transitions
- Interactions
 - Exchange between localized moments
 - Indirect exchange through itinerant electrons
 - Magnetism in metals
- Excitations

Susceptibility

Response to a perturbation (e.g. external field).

In general $\chi(r,t)$ [or $\chi(q,\omega)$]

Here: magnetic susceptibility

$$\chi = \frac{\partial M}{\partial H}$$

A measure of correlations

$$\chi_{ij} = \frac{(g\mu_B)^2}{kT} (\langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle)$$

An atom in a magnetic field (non-interacting moments)

$$H = \sum_{i=1}^Z \left(\frac{[\vec{p}_i + e\vec{A}(\vec{r}_i)]^2}{2m_e} + V_i \right) + g\mu_B \vec{B} \cdot \vec{S} =$$
$$\sum_i \left(\frac{p_i^2}{2m_e} + V_i \right) + \mu_B (\vec{L} + g\vec{S}) \cdot \vec{B} + \frac{e^2}{8m_e} \sum_i (\vec{B} \times \vec{r}_i)^2$$

Paramagnetic term. $\chi > 0$

A magnetic field aligns local magnetic moments $\mathbf{J}$

$$\mathbf{A}(\mathbf{r}) = \frac{\mathbf{B} \times \mathbf{r}}{2}$$

$$\hbar \mathbf{L} = \sum_i \mathbf{r}_i \times \mathbf{p}_i$$

Paramagnetic susceptibility

$$\sum_i \left(\frac{p_i^2}{2m_e} + V_i \right) + \mu_B (\vec{L} + g\vec{S}) \cdot \vec{B} + \frac{e^2}{8m_e} \sum_i (\vec{B} \times \vec{r}_i)^2$$

Partition function

$$Z = e^{\mu_B B / k_B T} + e^{-\mu_B B / k_B T}$$

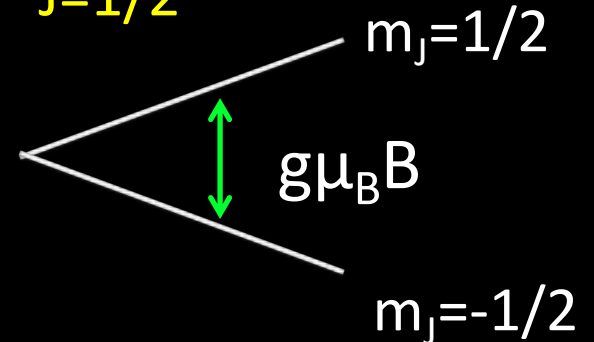
Free energy

$$F = -k_B T \ln Z$$

Magnetization

$$M = - \left(\frac{\partial F}{\partial B} \right)_T$$

$J=1/2$



Magnetic susceptibility

Curie's Law

$$\chi = \frac{\partial M}{\partial H} \propto \frac{1}{T}$$

In 2nd order perturbation theory there is another contribution to the paramagnetic susceptibility (van Vleck). Relevant when $J=0$. Small and independent of T .

An atom in a magnetic field (non-interacting moments)

$$H = \sum_{i=1}^Z \left(\frac{[\vec{p}_i + e\vec{A}(\vec{r}_i)]^2}{2m_e} + V_i \right) + g\mu_B \vec{B} \cdot \vec{S} =$$
$$\sum_i \left(\frac{p_i^2}{2m_e} + V_i \right) + \mu_B (\vec{L} + g\vec{S}) \cdot \vec{B} + \frac{e^2}{8m_e} \sum_i (\vec{B} \times \vec{r}_i)^2$$

Diamagnetic term. $\chi < 0$

- Orbital effect
- Usually weak: relevant when there are no unpaired electrons.

Diamagnetic susceptibility

$$\sum_i \left(\frac{p_i^2}{2m_e} + V_i \right) + \mu_B (\vec{L} + g\vec{S}) \cdot \vec{B} + \frac{e^2}{8m_e} \sum_i (\vec{B} \times \vec{r}_i)^2$$

Apply B_z . For a spherically symmetric atom

$$\Delta E_0 = \frac{e^2 B^2}{8m_e} \sum_{i=1}^Z \langle 0 | (x_i^2 + y_i^2) | 0 \rangle = \frac{e^2 B^2}{12m_e} \sum_{i=1}^Z \langle 0 | r_i^2 | 0 \rangle$$

$$M = -\frac{\partial F}{\partial B} = -\frac{N}{V} \frac{\partial \Delta E_0}{\partial B} = -\frac{Ne^2 B}{6m_e V} \sum_{i=1}^Z \langle r_i^2 \rangle$$

$$\chi \propto -Z_{\text{eff}} r^2$$

- r is the ionic radius
- Independent of T

Magnetic order

Now let the magnetic moments interact...

Broken symmetry: rotational symmetry

But **note**: there can be a magnetocrystalline anisotropy (easy axes/hard axes), originated by spin-orbit coupling, that would reduce the rotational symmetry.

Magnetic order

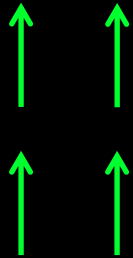
Now let the magnetic moments interact...

Given a pair of magnetic moments, they can interact ferromagnetically (FM) or antiferromagnetically (AF).

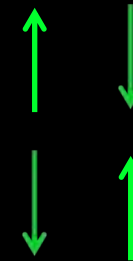
Magnetic order

Different orders

Ferromagnetism FM

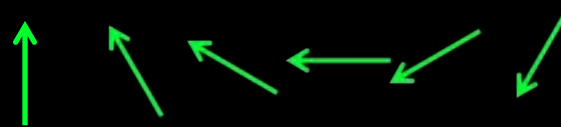


Antiferromagnetism AF

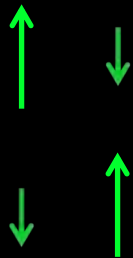


Néel order

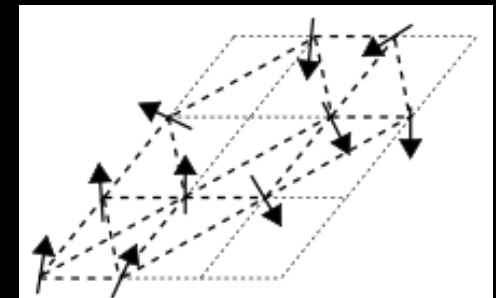
Helical (J_1, J_2)



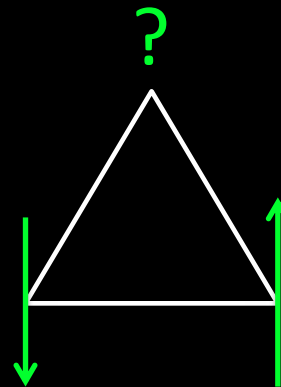
Ferrimagnetism



Spin glass



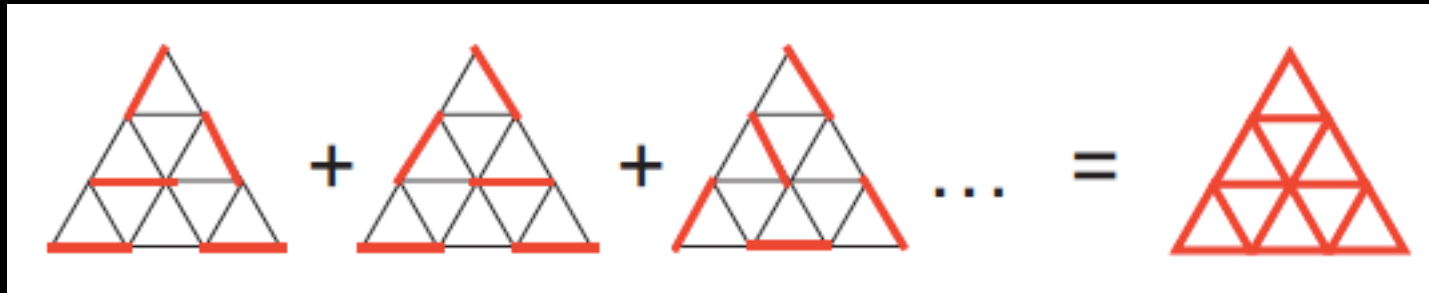
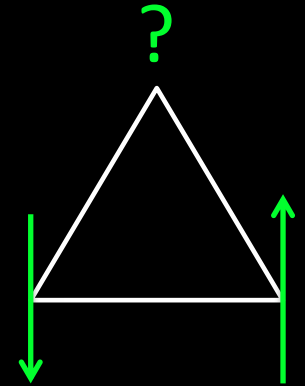
Frustration
(non-bipartite lattice)



Frustration

Anderson proposed quantum spin-liquid
(resonating valence bond)

Pairs of spins correlated in singlets with
no long range magnetic order and no spontaneously
broken symmetry.



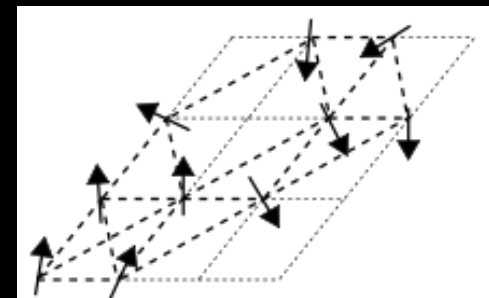
Materials Research Bulletin 8, 153 (1973)

Spin glasses

Due to randomness:

- Site randomness
- Bond randomness (between 2 different magnetic ions which are distributed randomly)
- Random magnetic anisotropies in amorphous materials.

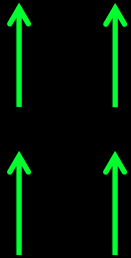
Cooperative freezing transition:
the system freezes in one of its
many possible ground states



Magnetic order

Order parameter

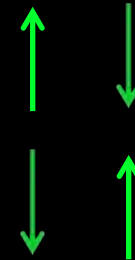
Ferromagnetism FM



Magnetization

$$M^z = \lim_{H \rightarrow 0} \langle S^z \rangle$$

Antiferromagnetism AF



Staggered magnetization

$$M_{st} = \langle \sum_A S^z \rangle - \langle \sum_B S^z \rangle$$

Sublattices A,B

Magnetic order

Order parameter

Ferromagnetism FM

Magnetization

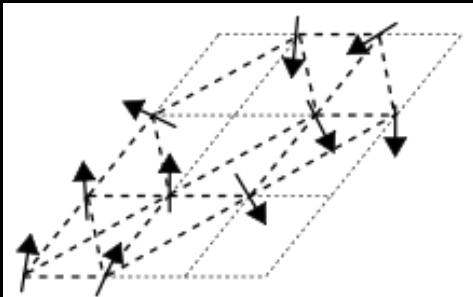
$$M^z = \lim_{H \rightarrow 0} \langle S^z \rangle$$

Antiferromagnetism AF

Staggered magnetization

$$M_{st} = \langle \sum_A S^z \rangle - \langle \sum_B S^z \rangle$$

Spin glass

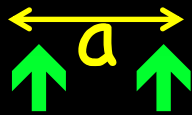


$$q = \lim_{t \rightarrow \infty} \left\langle \left\langle S_i(0) S_i(t) \right\rangle_T \right\rangle_C \quad (\text{freezing})$$

Order parameter $\rightarrow 0$ at phase transitions

The different orders can be characterized by a wave-vector

FM $Q=(0,0)$



$Q=\pi/2a$



$Q=\pi/4a$

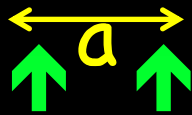


AF $Q=(\pi/a,\pi/a)$



The different orders can be characterized by a wave-vector

FM $Q=(0,0)$



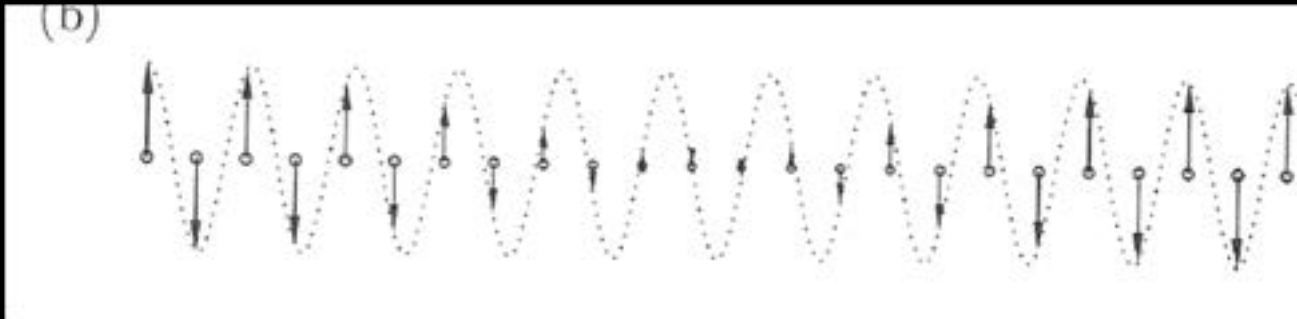
$Q=\pi/2a$



AF $Q=(\pi/a,\pi/a)$



Q can be incommensurate with the lattice



Blundell's book

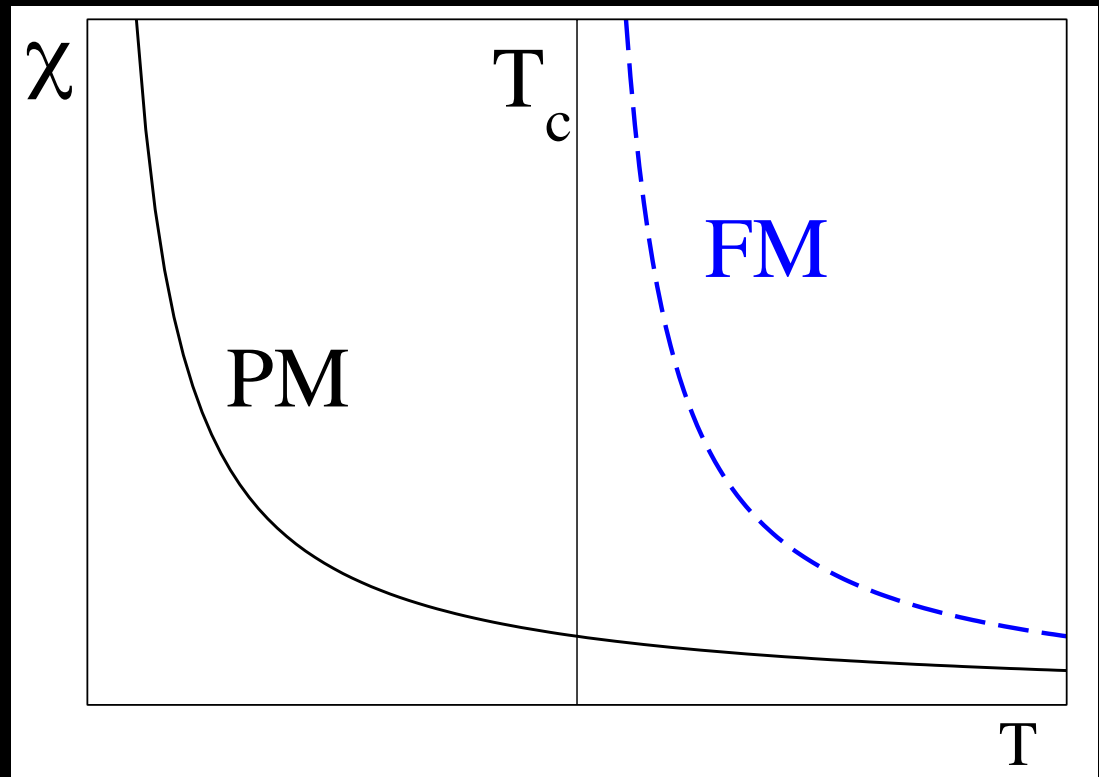
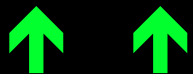
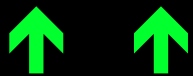
Susceptibility: FM

In mean field, the magnetization of a FM system produces an effective molecular field $B_{mf} = \lambda M$ (typically much larger than any applied field)

For $T > T_c$

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

Curie-Weiss law

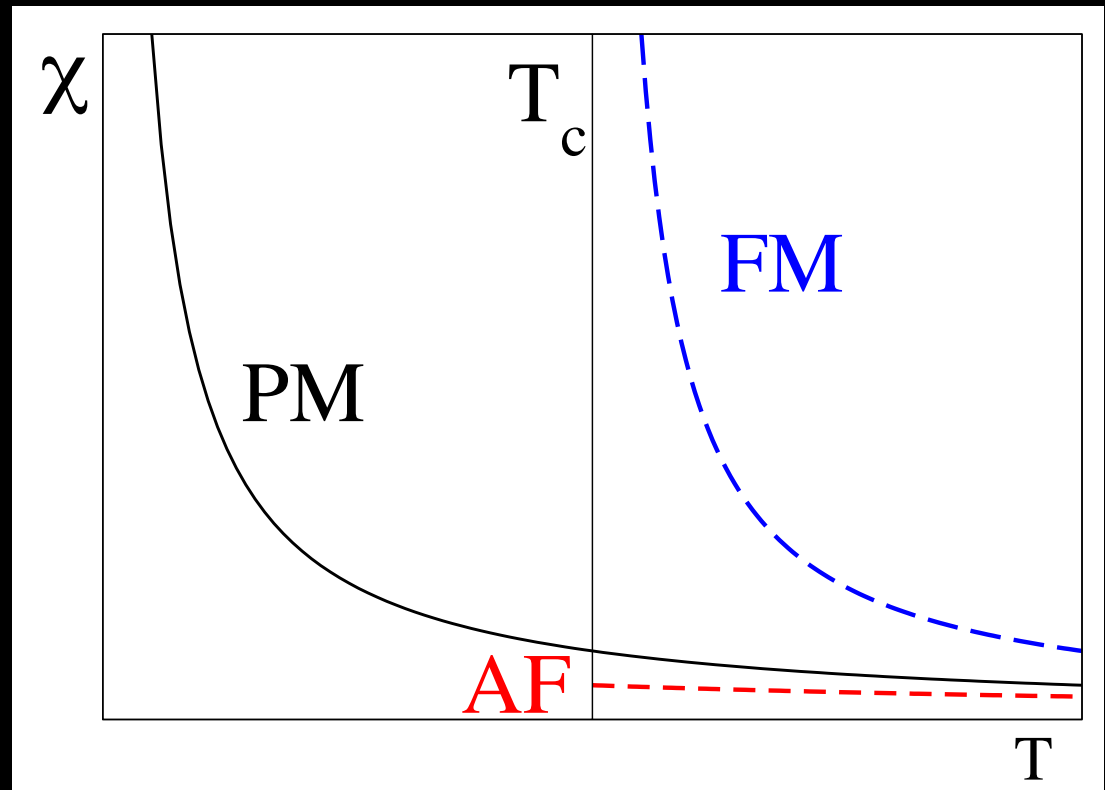
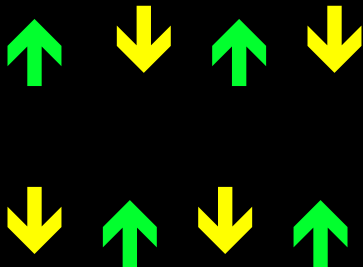


Susceptibility: AF

For an AF there is a different molecular field for each sublattice, B_+ and B_-

For $T > T_N$

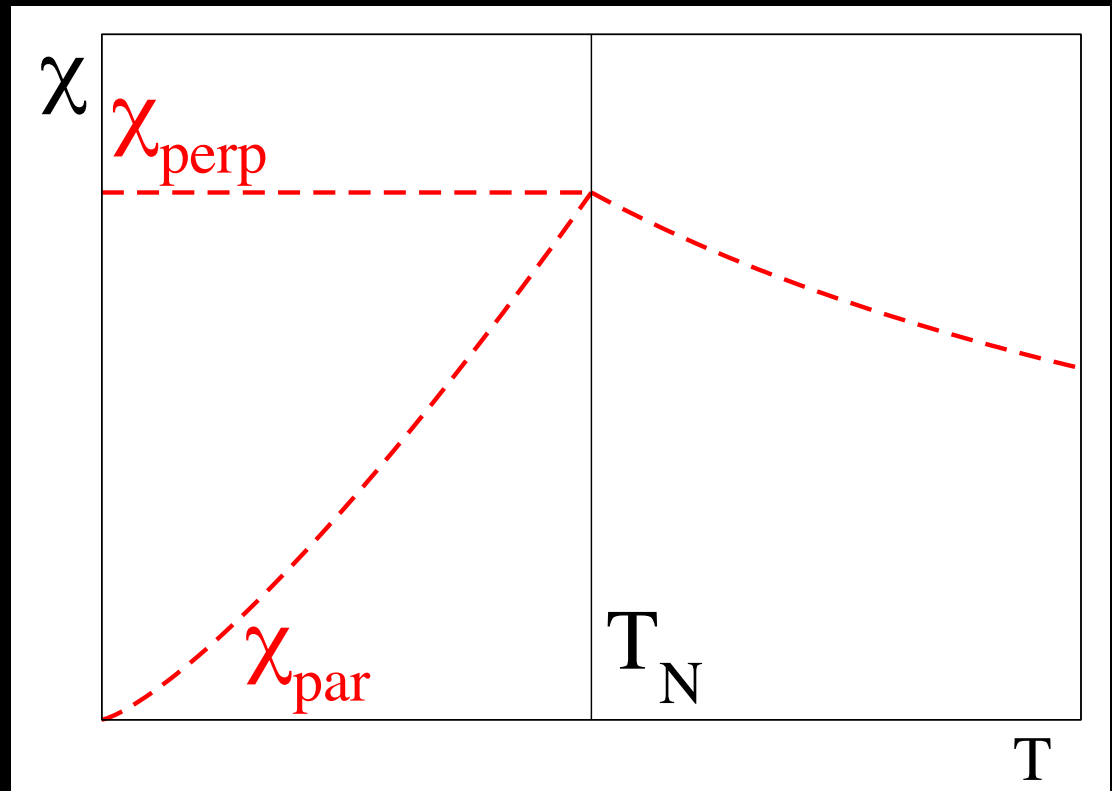
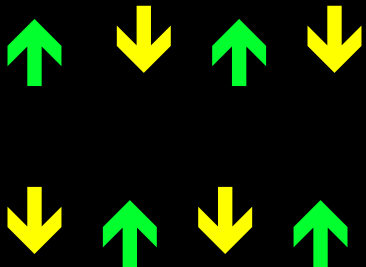
$$\chi \propto \frac{1}{T + T_N}$$



Susceptibility: AF

For an AF there is a different molecular field for each sublattice, B_+ and B_-

For $T < T_N$
 χ depends on the
direction of the
applied field.



Outline

- Free magnetic ions
- Environment
- Magnetic order and susceptibility
- Interactions
 - Exchange between localized moments
 - Indirect exchange through itinerant electrons
 - Magnetism in metals
- Excitations

Interactions

Different mechanisms

1. Localized moments. Heisenberg model.
2. Localized moments + itinerant electrons.
3. Itinerant electrons. Fermi surface instability.

Interaction between localized moments

Magnetic dipolar interactions too weak to explain typical magnetic critical temperatures

Interaction between localized moments

EXCHANGE

Heisenberg model $\sum_{ij} J \mathbf{S}_i \cdot \mathbf{S}_j$

- J is the exchange parameter.
- $J > 0$, AF. $J < 0$, FM.
- Strong interaction: it arises from Coulomb interactions between electrons.
- Intra-atomic exchange: Hund's coupling J_H

Interaction between localized moments

Hamiltonian: electrons in a lattice (bands)
+ electron-electron interaction

$$H = T + V(r) + \frac{e^2}{r_{12}}$$



Heisenberg
model

$$H = J \sum_{i,j} \mathbf{S}_i \cdot \mathbf{S}_j$$

Direct exchange (or potential exchange)

- Basic idea: electron–electron repulsion energy is minimized when two electrons have the same spin (due to Pauli exclusion principle the electrons are as further away as possible).
- Therefore, direct exchange is **ferromagnetic**.
- Between orthogonal orbitals.
- Hund's coupling is an onsite direct exchange.
- Heisenberg 1928.

Direct exchange

$$\iint \Psi^*(r_1) \Psi^*(r_2) \frac{e^2}{r_{12}} \Psi(r_2) \Psi(r_1) d\tau_1 d\tau_2$$

Expand $\Psi(r)$ in terms of orthogonal wave functions localized at the magnetic ions $\phi_n(r)$. No double occupancy is allowed.

Two kinds of terms arise:

$C_{n,n'}$ Coulomb int.
between electrons
at n and n' ions

$$\iint \phi_n^*(r_1) \phi_{n'}^*(r_2) \frac{e^2}{r_{12}} \phi_{n'}(r_2) \phi_n(r_1) d\tau_1 d\tau_2$$

$J_{n,n'}$ Exchange int.
Due to Fermi statistics

$$-\iint \phi_n^*(r_1) \phi_{n'}^*(r_2) \frac{e^2}{r_{12}} \phi_n(r_2) \phi_{n'}(r_1) d\tau_1 d\tau_2$$

Direct exchange

In second quantization $J_{n,n'}$

$$s_z = \frac{1}{2}(a_{\uparrow}^+ a_{\uparrow} - a_{\downarrow}^+ a_{\downarrow})$$

$$s_x + is_y = a_{\uparrow}^+ a_{\downarrow} ; s_x - is_y = a_{\downarrow}^+ a_{\uparrow}$$

Heisenberg:

$$\sum_{s,s'} a_{ns}^+ a_{ns'} a_{n's'}^+ a_{n's}$$

$$-J_{n,n'} \left(\frac{1}{2} + 2s_n \cdot s_{n'} \right)$$

$J_{n,n'}$ is always +ve: Ferromagnetism

Direct exchange

- But **note**: The same mechanism gives antiferromagnetism if the orbitals involved are non-orthogonal !
- The simplest example: The H_2 molecule ground state is a spin-singlet (Wigner's theorem for the 2-electron problem: the ground state does not have a node)

$$H = T_1 - \frac{e^2}{r_{a1}} + T_2 - \frac{e^2}{r_{b2}} - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}} + \frac{e^2}{r_{12}} + \frac{e^2}{r_{ab}}$$

The exchange is the difference between the energy of the spin-singlet and the spin-triplet

S here is the overlap!
 $S=0$ for orthogonal orbitals

$$\text{Exchange} = 2 \frac{S^2 C_{ab} - J_{ab}}{1 - S^4}$$

Direct exchange

- But **note**: The same mechanism gives antiferromagnetism if the orbitals involved are non-orthogonal !
- The simplest example: The H_2 molecule ground state is a spin-singlet (Wigner's theorem for the 2-electron problem: the ground state does not have a node)
- Wigner's theorem does not apply to our magnetic ions because a shell in a $3d^2$ configuration is not a 2-electron problem!

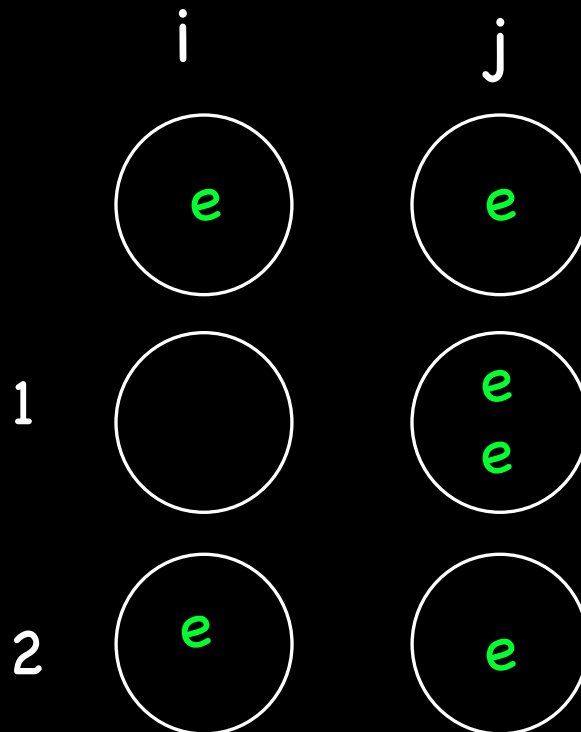
Kinetic exchange

- Basic idea: due to virtual electron transfers. Consider hopping as a perturbation and go to second order perturbation theory.
- Kramers 1934. Formalized by Anderson 1950.
- Kinetic exchange is **antiferromagnetic**.
- Start from single band Hubbard Hamiltonian (on-site interactions) with $U \gg t$. (The strong interacting limit of the Hubbard model is an AF Heisenberg model)

$$H = - \sum_{ij\sigma} t_{ij} (c_{i\sigma}^+ c_{j\sigma} + c_{j\sigma}^+ c_{i\sigma}) + U \sum_j n_{j\uparrow} n_{j\downarrow}$$

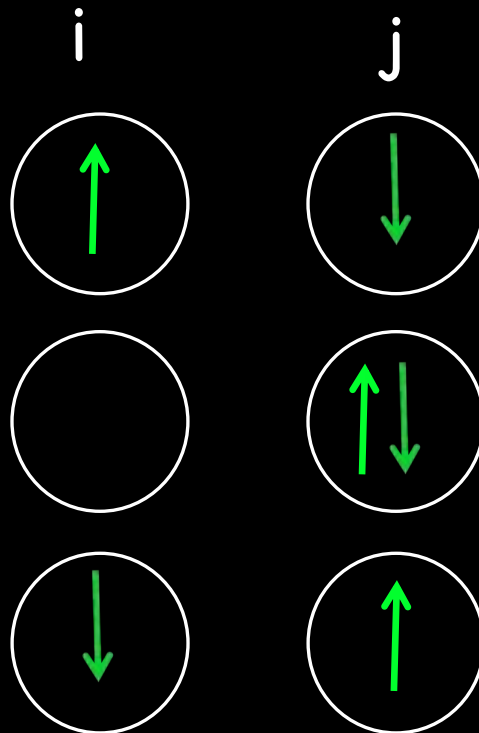
Kinetic exchange

- Treat kinetic energy in second-order perturbation (one band model)



Kinetic exchange

- Treat kinetic energy in second-order perturbation (one band model)



For this process to take place you need antiparallel moments (Pauli principle)

$$\Delta E_2 = - \sum_{\substack{i,j \\ \sigma,\sigma'}} \frac{|t_{ij}|^2}{U} a_{i\sigma}^+ a_{j\sigma} a_{j\sigma'}^+ a_{i\sigma'}$$

Kinetic exchange

$$\Delta E_2 = - \sum_{\substack{i,j \\ \sigma,\sigma'}} \frac{|t_{ij}|^2}{U} a_{i\sigma}^+ a_{j\sigma} a_{j\sigma'}^+ a_{i\sigma'}$$

$$s_z = \frac{1}{2} (a_{\uparrow}^+ a_{\uparrow} - a_{\downarrow}^+ a_{\downarrow})$$

$$s_x + i s_y = a_{\uparrow}^+ a_{\downarrow} ; s_x - i s_y = a_{\downarrow}^+ a_{\uparrow}$$

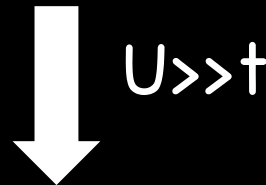
Heisenberg:

$$\Delta E_2 = \sum_{\substack{i,j \\ \sigma,\sigma'}} \frac{|t_{ij}|^2}{U} \left(-\frac{1}{2} + 2s_i \cdot s_j \right)$$

Antiferromagnetic

Hubbard model

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



$U \gg t$

$$J = 4|t|^2/U$$

Heisenberg model

At half-filling
(1 electron per site)

$$J \sum_{i,j} \vec{S}_i \vec{S}_j$$

t-J model

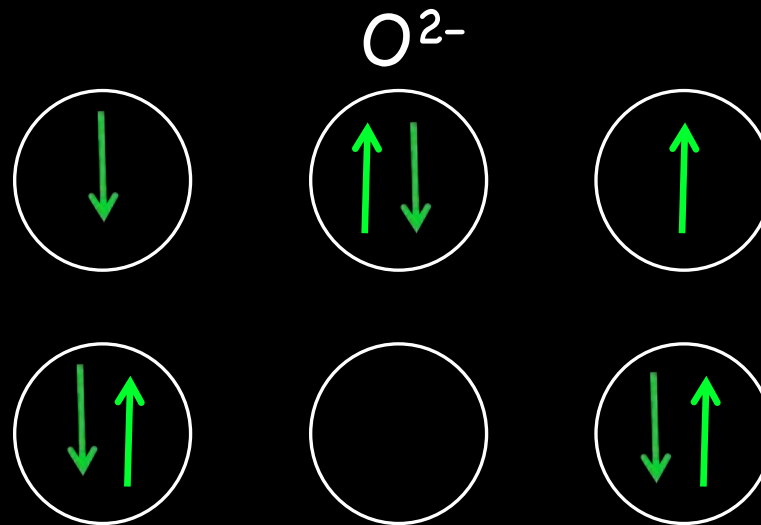
Away from
half-filling

$$- \sum_{ij\sigma} t_{ij} (b_{i\sigma}^{\dagger} b_{j\sigma} + b_{j\sigma}^{\dagger} b_{i\sigma}) + J \sum_{ij} \vec{S}_i \vec{S}_j$$

Hopping only between an empty and a filled site.

Superexchange

Exchange mediated by an anion: $E_{\text{direct}} + E_{\text{kin}}$.



Note that we are assuming half-filling (1 electron per site)

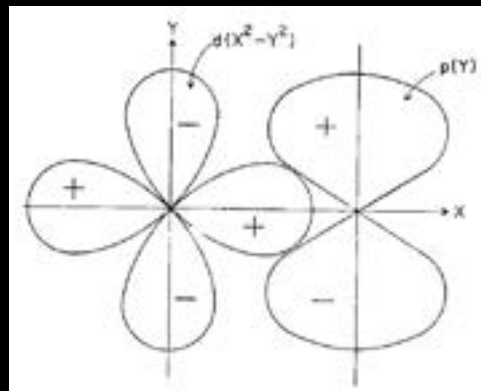
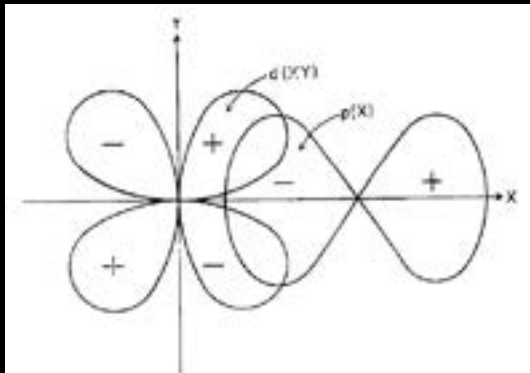
From this, SE is antiferromagnetic but...

Goodenough-Kanamori rule

Superexchange is AF when the virtual hopping involves overlapping half-filled orbitals while it can be FM when:

- overlap is zero: $t_{ij}=0$
(note that t_{ij} depends on the orientation of the M-O-M bonds)

$$E_{kin} = - \sum_{\substack{i,j \\ \sigma,\sigma'}} \frac{|t_{ij}|^2}{U} a_{i\sigma}^+ a_{j\sigma} a_{j\sigma'}^+ a_{i\sigma'}$$



Kanamori,
J. Phys. Chem. Solids 10, 87 (1959)
Goodenough, PR 100, 564 (1955)

http://www.scholarpedia.org/article/Goodenough-Kanamori_rule

Goodenough-Kanamori rule

Superexchange is AF when the virtual hopping involves overlapping half-filled orbitals while it can be FM when:

- overlap is zero: $t_{ij}=0$
- it involves transfers between a half-filled and an empty orbital. Kinetic exchange can be FM because it is not restricted by Pauli principle. (Related to double exchange – see later)

http://www.scholarpedia.org/article/Goodenough-Kanamori_rule

Goodenough-Kanamori rule

Superexchange is AF when the virtual hopping involves overlapping half-filled orbitals while it can be FM when:

- overlap is zero: $t_{ij}=0$
- it involves transfers between a half-filled and an empty orbital.
- **in multiorbital systems:*

* Generalization

http://www.scholarpedia.org/article/Goodenough-Kanamori_rule

For multiorbital systems

$$\begin{aligned}
 H = & H_0 + \bar{U} \sum_{i,l} n_{il\uparrow} n_{il\downarrow} + \bar{U}' \sum_{i,l' < l} n_{il} n_{il'} \\
 & + \bar{J} \sum_{i,l' < l} \sum_{\sigma,\sigma'} c_{il\sigma}^\dagger c_{il'\sigma'}^\dagger c_{il\sigma'} c_{il'\sigma} \\
 & + \bar{J}' \sum_{i,l' \neq l} c_{il\uparrow}^\dagger c_{il\downarrow}^\dagger c_{il'\downarrow} c_{il'\uparrow}
 \end{aligned}$$

Spin rotational invariance:

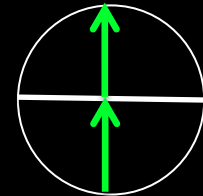
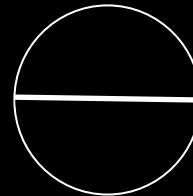
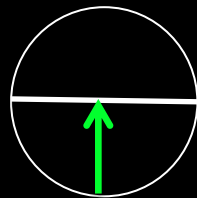
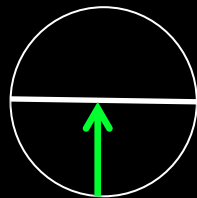
$$U' = U - 2J_H$$

$$J' = J_H$$

Goodenough-Kanamori rule

Superexchange is AF when the virtual hopping involves overlapping half-filled orbitals while it can be FM when:

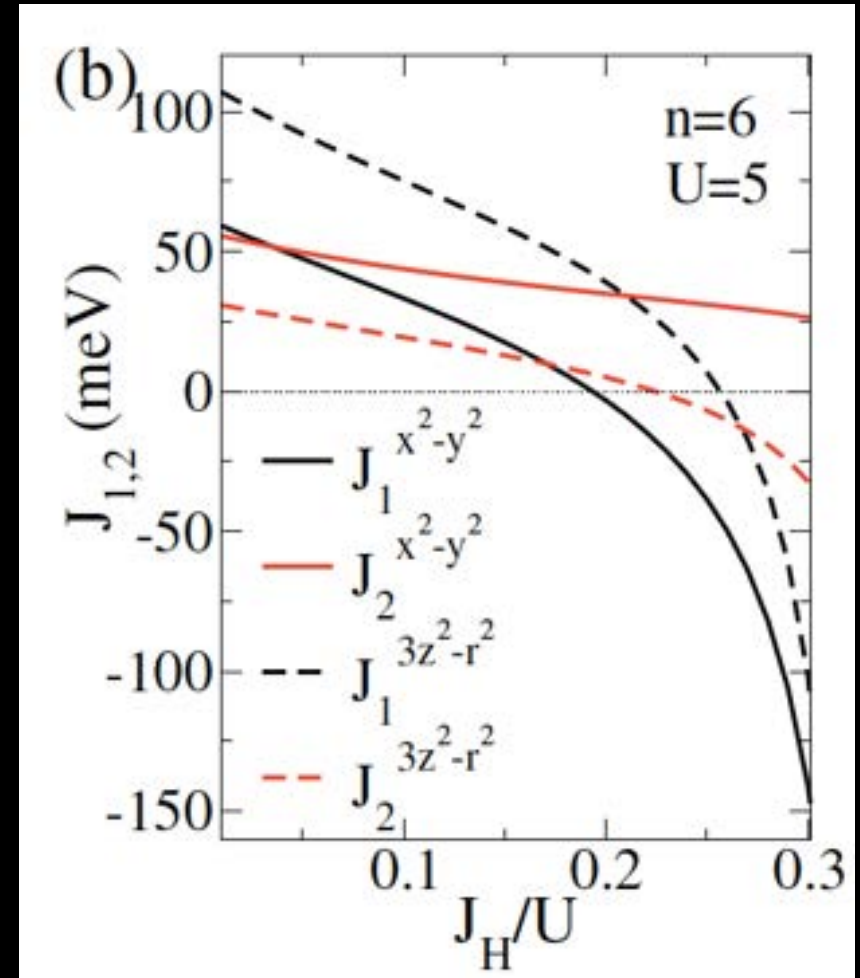
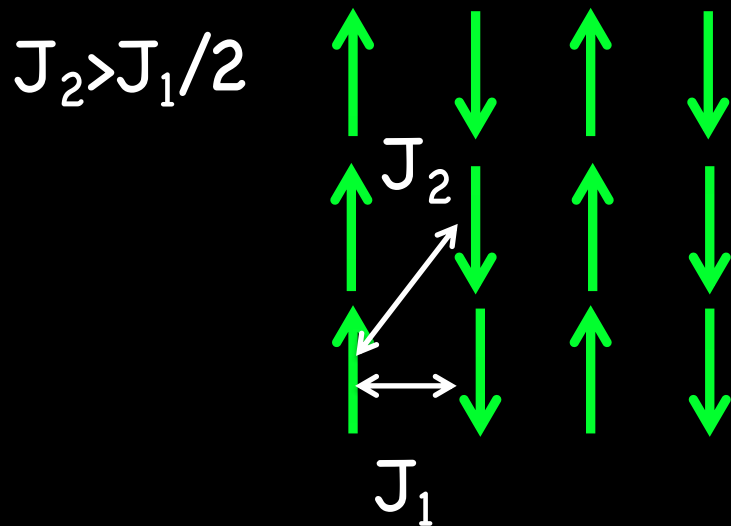
- overlap is zero: $t_{ij}=0$
- it involves transfers between a half-filled and an empty orbital.
- **in multiorbital systems: the onsite interaction for electrons in different orbitals is $U' - J_H$ (and $U'=U-2J_H$), $J_{kin} = -t^2/(U-3J_H)$*



* Generalization

http://www.scholarpedia.org/article/Goodenough-Kanamori_rule

For multiorbital iron superconductors, the sign of exchange depends on the parameters (J_H , U , crystal field). The anisotropies in the hoppings are included).



Physical Review B 86, 104514 (2012).

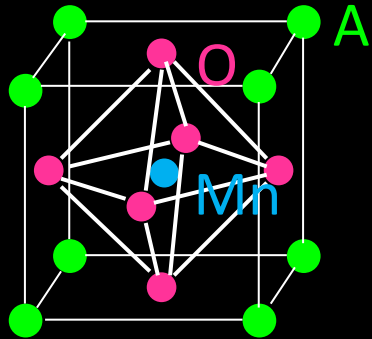
Goodenough-Kanamori rule: consequences

- Superexchange can be of different strengths and signs in the different directions of the crystal. The crystal symmetry and the orbitals symmetry has to be taken into account (Slater-Koster).
- Associated to orbital order (competing sometimes with Jahn-Teller distortions)

Millis, PRB 55, 6405 (1997).

Slater and Koster, Phys. Rev. 94, 1498 (1954)

Example: Manganites

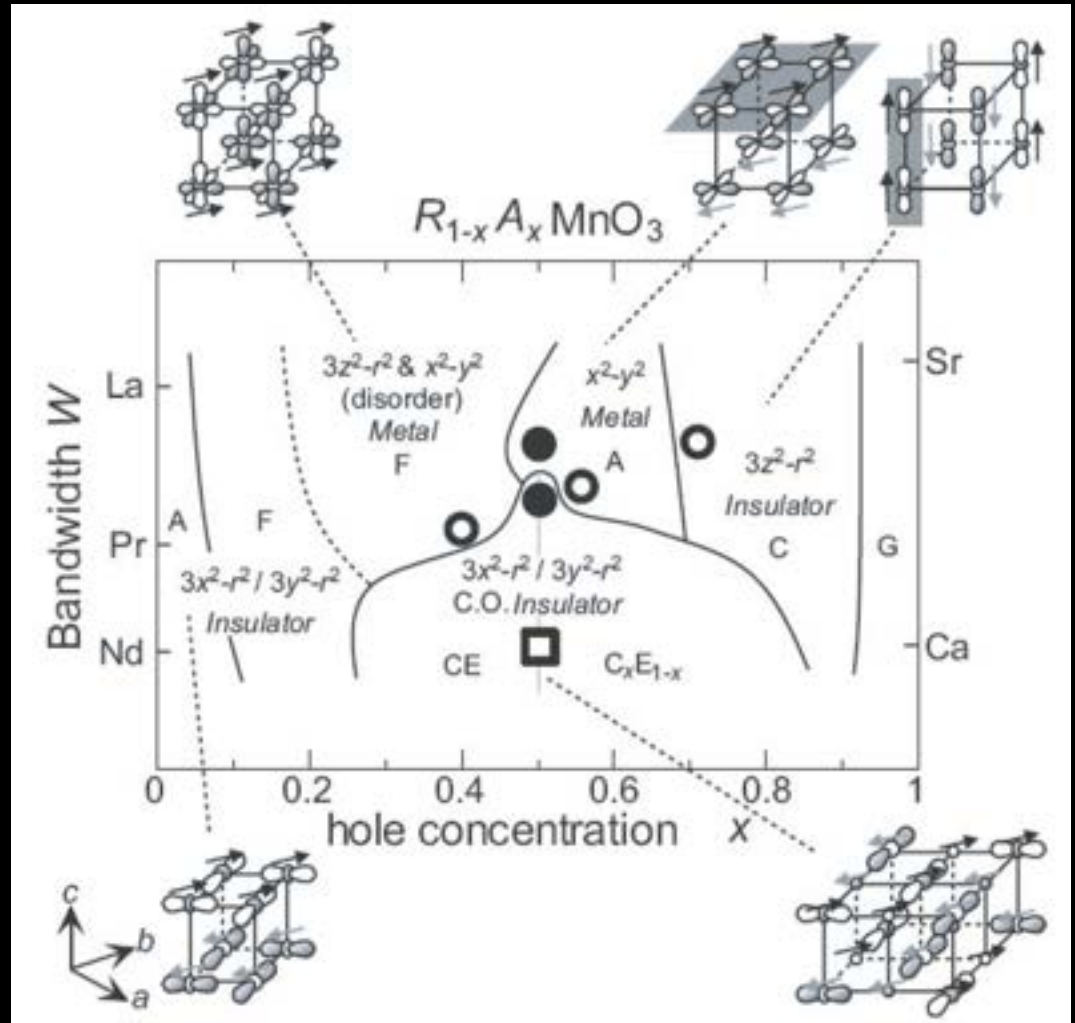


Interplay of spin, orbital and lattice

Kanamori, J. Phys. Chem. Solids 10, 87 (1959)

Goodenough, PR 100, 564 (1955)

Millis, PRB 55, 6405 (1997).



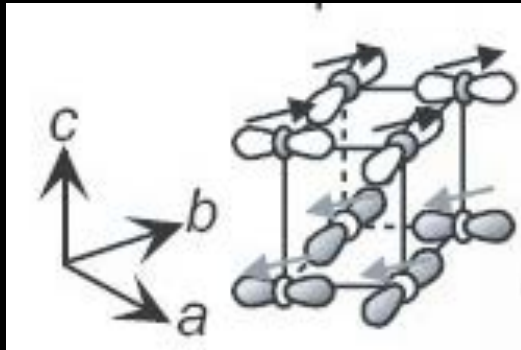
Tokura, Rep. Prog. Phys. 69, 797 (2006)

Example: Manganites

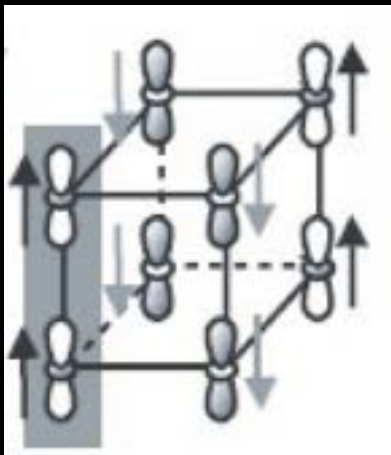
Interplay of spin, orbital and lattice

Kanamori, J. Phys. Chem. Solids 10, 87 (1959)

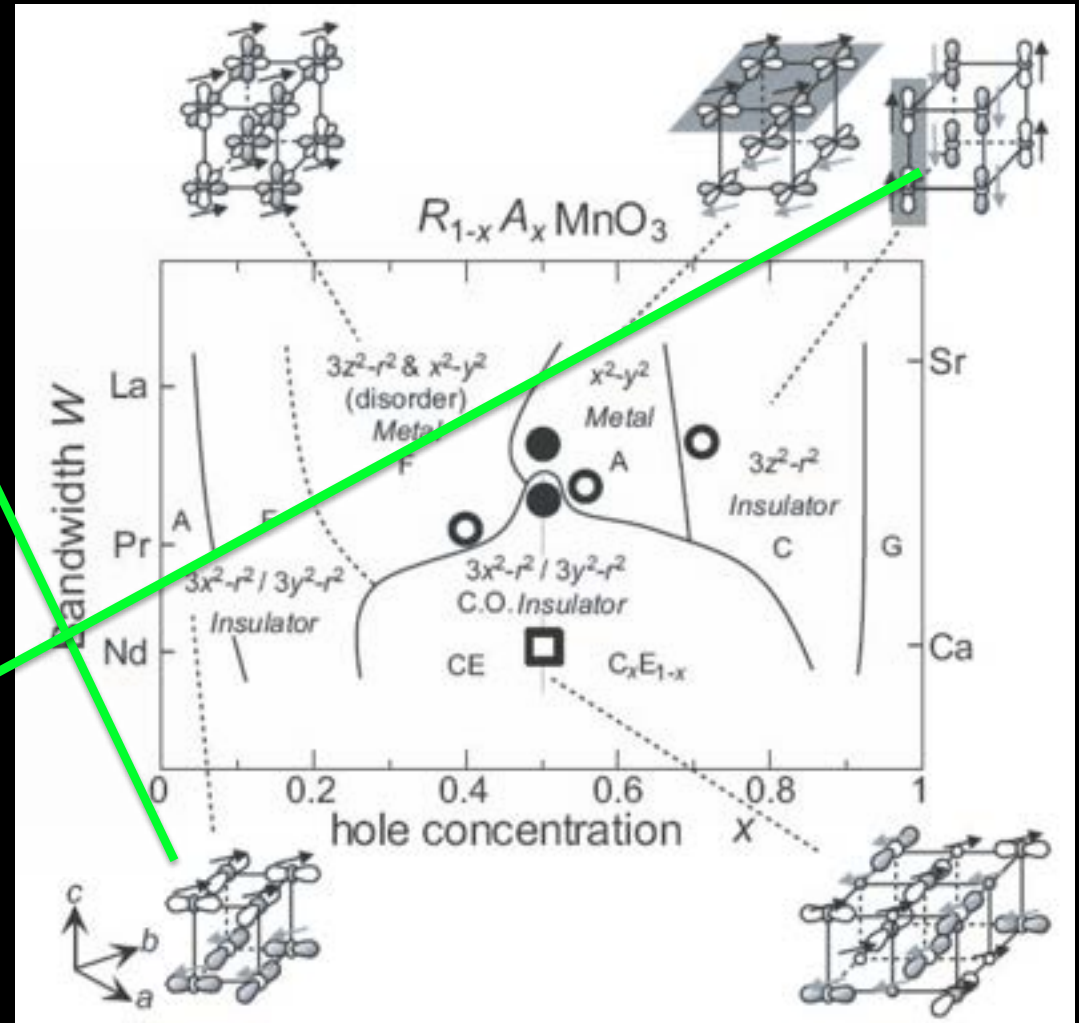
Goodenough, PR 100, 564 (1955)



Type A: $Q=(0,0,\pi)$



Type C: $Q=(\pi, \pi, 0)$



Tokura, Rep. Prog. Phys. 69, 797 (2006)

Anisotropic exchange (for d-orbitals)

It's a kind of superexchange in which the excited intermediate state is not due to an interceding anion but to an excited state produced by spin-orbit interaction in one of the magnetic ions.

$$H' = \lambda(\mathbf{L}_1 \cdot \mathbf{S}_1) + \lambda(\mathbf{L}_2 \cdot \mathbf{S}_2) + V_{exh}$$

Dzyaloshinskii-Moriya

$$H_{DM} = \mathbf{D} \cdot (\mathbf{S}_1 \times \mathbf{S}_2)$$

D=0 with inversion symmetry between the 2 ions

D direction depends on symmetry

Causes AF spins to cant by a small angle: weak ferromagnetism. Examples: $\alpha\text{-Fe}_2\text{O}_3$, MnCoO_3 , RFeO_3 (R: rare-earth).

Interactions

Different mechanisms

1. Localized moments. Heisenberg model.
2. Localized moments + itinerant electrons.
3. Itinerant electrons. Fermi surface instability.

Itinerant electrons coupled to localized moments

- Kondo model (coupling to magnetic impurities)

$$H = - \sum_{i,j,\sigma} t_{ij} (c_{i\sigma}^{\dagger} c_{j\sigma} + c_{j\sigma}^{\dagger} c_{i\sigma}) - J_{local} \mathbf{S} \cdot \mathbf{s}$$

- Kondo Lattice

$$H = - \sum_{i,j,\sigma} t_{ij} (c_{i\sigma}^{\dagger} c_{j\sigma} + c_{j\sigma}^{\dagger} c_{i\sigma}) - J_{local} \sum_i \mathbf{S}_i \cdot \mathbf{s}_i$$

For f-electrons $\mathbf{S} \rightarrow \mathbf{J}$

See Kondo regime in Ramon Aguado's lectures

Itinerant electrons coupled to localized moments

- Kondo model (coupling to magnetic impurities)

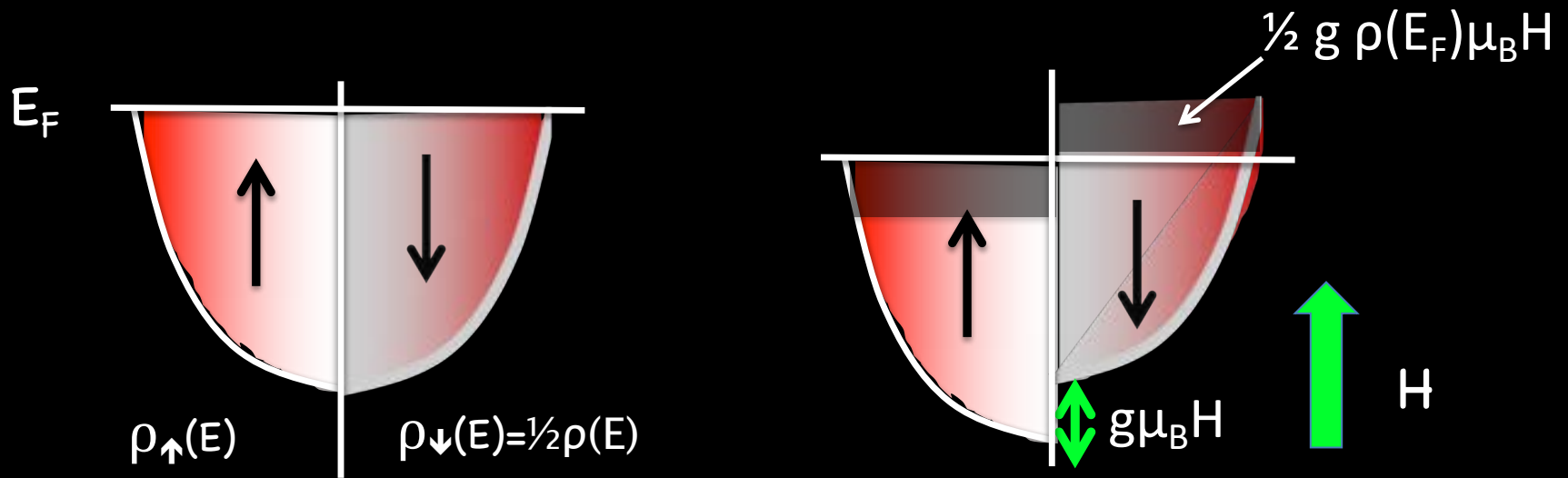
$$H = - \sum_{i,j,\sigma} t_{ij} (c_{i\sigma}^{\dagger} c_{j\sigma} + c_{j\sigma}^{\dagger} c_{i\sigma}) - J_{local} \mathbf{S} \cdot \mathbf{s}$$

Basic idea: the local exchange with an impurity polarizes the surrounding Fermi sea which carries this information to other magnetic impurities.

How effective is this process of the magnetic polarization of the Fermi sea? $\rightarrow$ susceptibility

Paramagnetic susceptibility of conduction electrons

In a uniform magnetic field



$$M = \mu_B (n_{\uparrow} - n_{\downarrow})$$

$$\chi_{\text{Pauli}} = \frac{1}{2} g^2 \mu_B^2 \rho(E_F)$$

Pauli PM only affects electrons close to E_F .
Constant with T .

PM susceptibility in a non-uniform magnetic field

$$H(\mathbf{r}) = \sum_q H_q e^{-i\mathbf{q}\cdot\mathbf{r}}$$

Consider the perturbative effect of H_q on the electron spin

Within first order perturbation theory on a plane wave state

$$\psi_{\mathbf{k}\pm}(\mathbf{r}) = \frac{1}{\sqrt{V}} \left(e^{i\mathbf{k}\cdot\mathbf{r}} \pm \frac{g\mu_0\mu_B \mathbf{H}_q}{4} \left[\frac{e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}}}{E_{\mathbf{k}+\mathbf{q}} - E_{\mathbf{k}}} + \frac{e^{i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}}}{E_{\mathbf{k}-\mathbf{q}} - E_{\mathbf{k}}} \right] \right) |\pm\rangle$$

$$M(\mathbf{r}) = \mu_B (|\Psi_{\mathbf{k}+}(\mathbf{r})|^2 - |\Psi_{\mathbf{k}-}(\mathbf{r})|^2)$$

↓

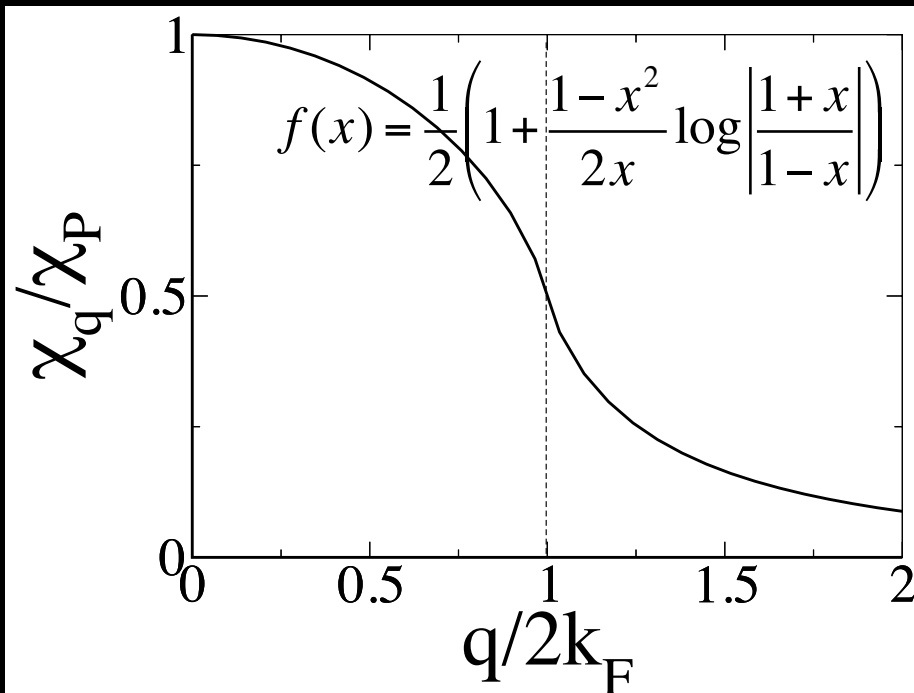
$$M_q$$

$$\chi_q = \chi_{\text{Pauli}} f\left(\frac{q}{2k_F}\right)$$

PM susceptibility in a non-uniform magnetic field

$$H(\mathbf{r}) = \sum_q H_q e^{-i\mathbf{q}\cdot\mathbf{r}}$$

Consider the perturbative effect of H_q on the electron spin



(3dim)
Lindhard function

(in momentum space)

$$\chi_q = \chi_{\text{Pauli}} f\left(\frac{q}{2k_F}\right)$$

Itinerant electrons coupled to localized moments

- Kondo model (coupling to magnetic impurities)

$$H = - \sum_{i,j,\sigma} t_{ij} (c_{i\sigma}^{\dagger} c_{j\sigma} + c_{j\sigma}^{\dagger} c_{i\sigma}) - J_{local} \mathbf{S} \cdot \mathbf{s}$$

Basic idea: the local exchange with an impurity polarizes the surrounding Fermi sea which carries this information to other magnetic impurities.

RKKY exchange

Rudderman-Kittel-Kasuya-Yosida

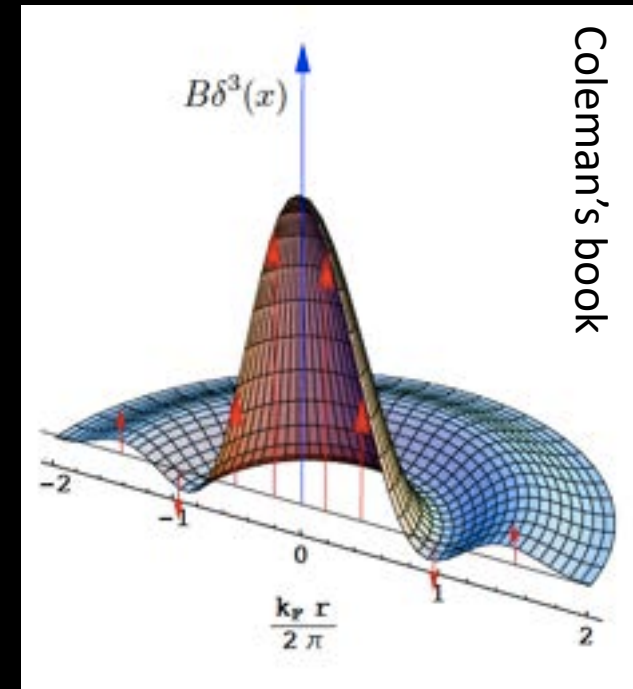
A magnetic impurity with local exchange amounts to having a local external field: $H(r) \sim \delta(r)$
 J_{local} can be J_H or s-d or s-f exchange.

$$H_q = \frac{2J_{\text{local}}}{Ng\mu_B} S_z$$

$$\chi_q = \chi_{\text{Pauli}} f\left(\frac{q}{2k_F}\right)$$

Real space susceptibility:
 Friedel oscillations $\lambda = 2\pi/k_F$

$$\begin{aligned} \chi(r) &= \frac{1}{(2\pi)^3} \int d^3q \chi_q e^{iq \cdot r} \\ &= \frac{2k_F^3 \chi_P}{\pi} F(2k_F r) \end{aligned}$$



RKKY exchange

The conduction electron interacting with the single magnetic impurity suffer a spin polarization that depends on distance

$$|\psi_{\uparrow}|^2 - |\psi_{\downarrow}|^2 \propto J_{local} F(2k_F r)$$

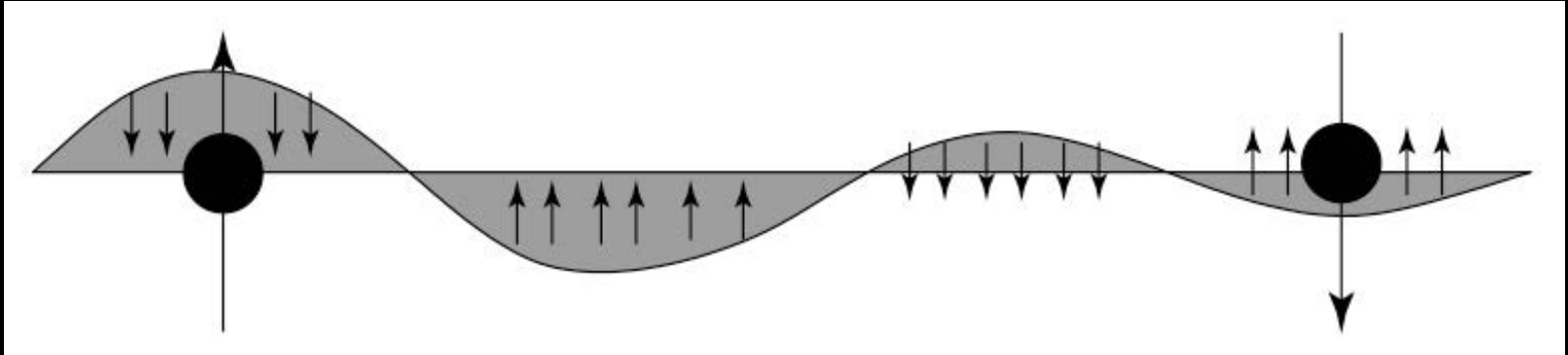
Now this polarized cloud interacts with another magnetic impurity

$$J_{RKKY} \propto J_{local}^2 F(2k_F r)$$

(The sign of J_{local} does not matter)

J_{RKKY} oscillates with distance: A local magnetic moment produces a wave-like local perturbation.

RKKY exchange



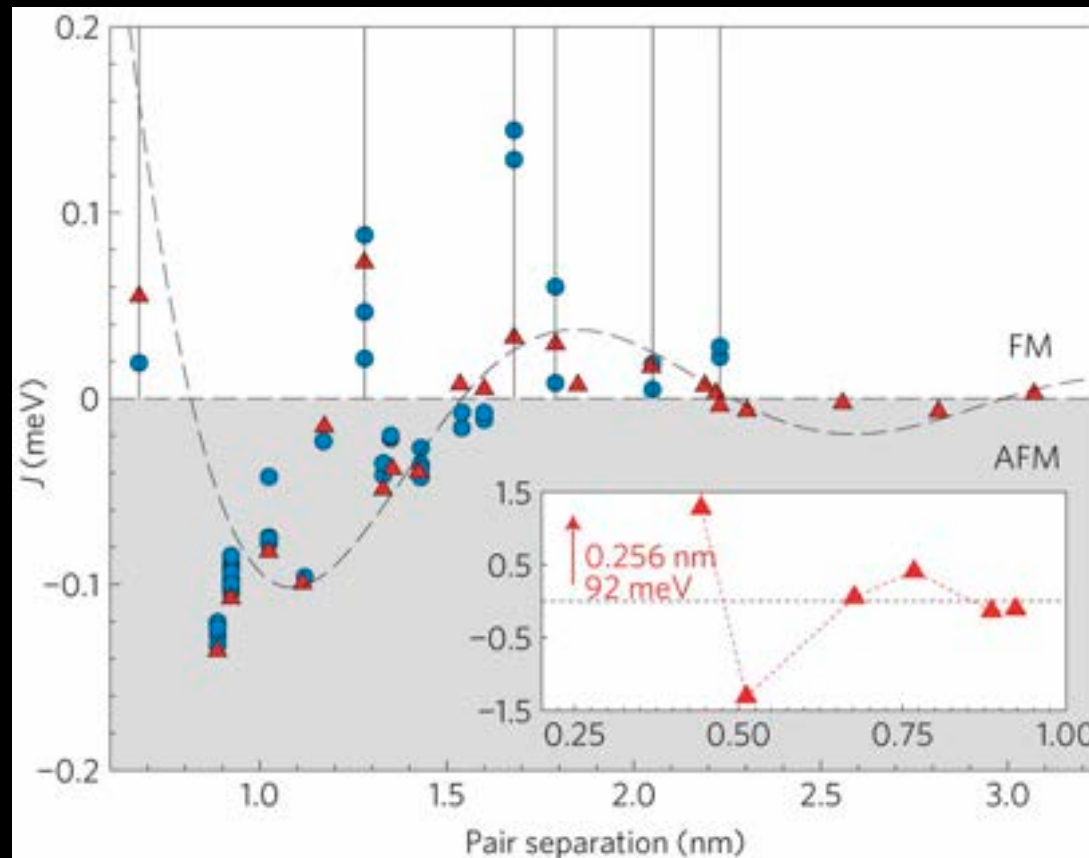
$$J_{RKKY} \propto J_{local}^2 F(2k_F r)$$

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RKKY exchange

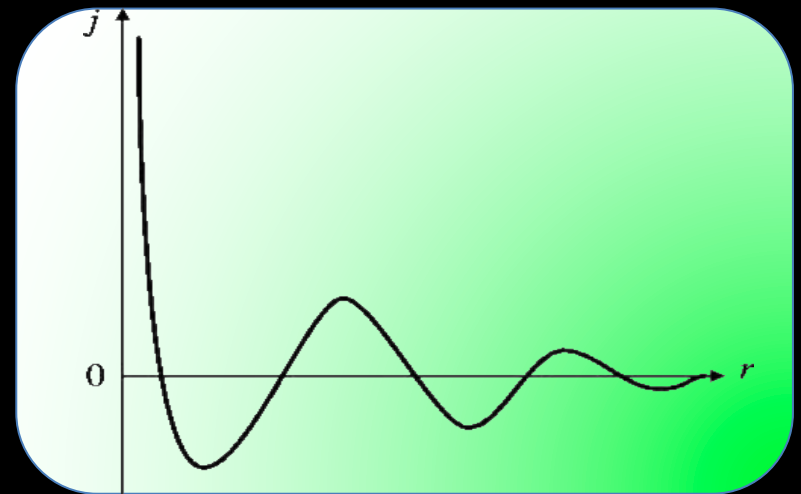
Fe atoms on Cu(111)



Nature Physics 8, 497–503 (2012)

RKKY exchange

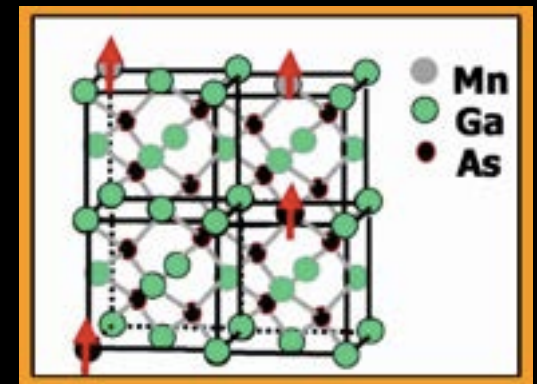
Note that if $k_F r$ is small, J_{RKKY} is FM.



RKKY exchange

- Spin glass in CuMn (Mn is random in Cu lattice).
- FM in diluted magnetic semiconductors, like (Ga,Mn)As or diluted magnetic oxides as (Ti,Co)O₂

(Important for spintronics, where you need carriers to be spin polarized).



RKKY competes with Kondo effect (R. Aguado's Lectures)

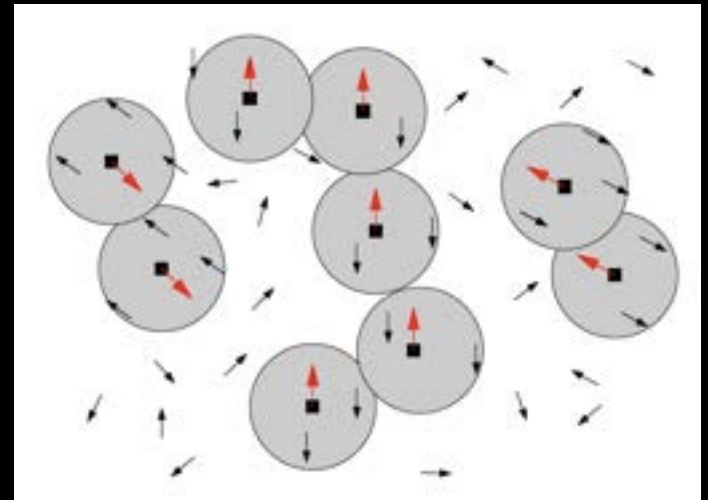
Other effects of local exchange: Bound magnetic polarons

Carriers are bound (not-itinerant!) electrostatically by the Coulomb potential and the spin-polarization is a secondary phenomenon. Polaron: FM cloud.

Proposed for diluted magnetic semiconductors.
Percolation $\rightarrow$ T_c

Due to the local exchange, the size of the bound electron wave-function R_p depends on T as

$$k_B T = |J| (a_0/a_B)^3 S s \exp(-2R_p/a_B)$$



Annals of Physics 322, 2618 (2007)

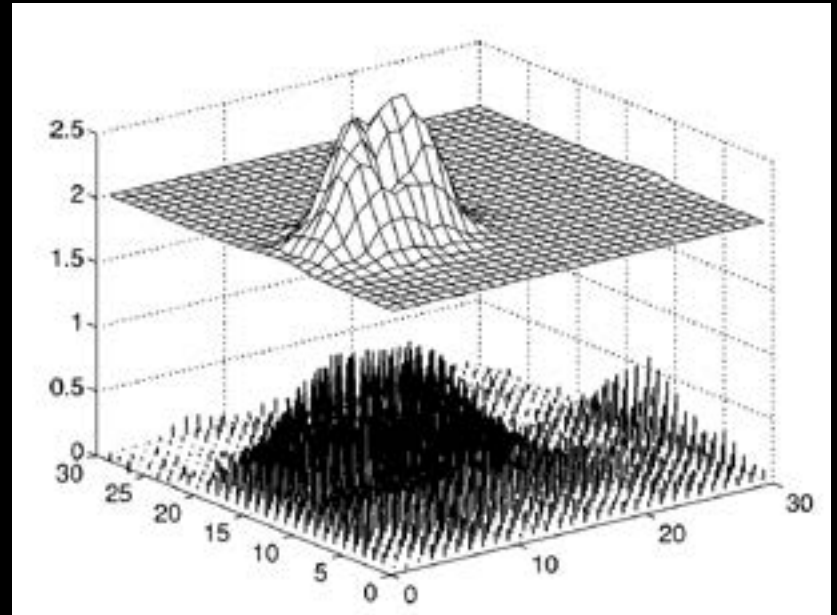
Other effects of local exchange: Free magnetic polarons

Carriers are self-trapped by a FM cloud they have formed themselves in a background of disordered spins (above the FM T_c). Low carrier density is required. Can also form in an AF background

Some pyrochlores

EuB_6

PRB 62, 3368 (2000)

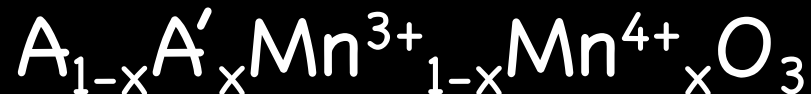


Double exchange ($J_{local} \rightarrow \infty$ limit of Kondo lattice)

$$\sum_{\alpha,\beta} t^{\alpha\beta} \sum_{i,j,\sigma} c_{i,\alpha,\sigma}^\dagger c_{j,\beta,\sigma} + J_H \sum_i S_i S_i \xrightarrow{J_H \rightarrow \infty} \sum_{i,j} \sum_{\alpha,\beta} t_{ij}^{\alpha\beta} d_{i\alpha}^\dagger d_{j\beta}$$

$J_H \rightarrow \infty$ implies the spin of the conduction electrons is always parallel to the localized spin

This model was proposed for manganites



C. Zener, Phys. Rev. **82**, 403, (1951)

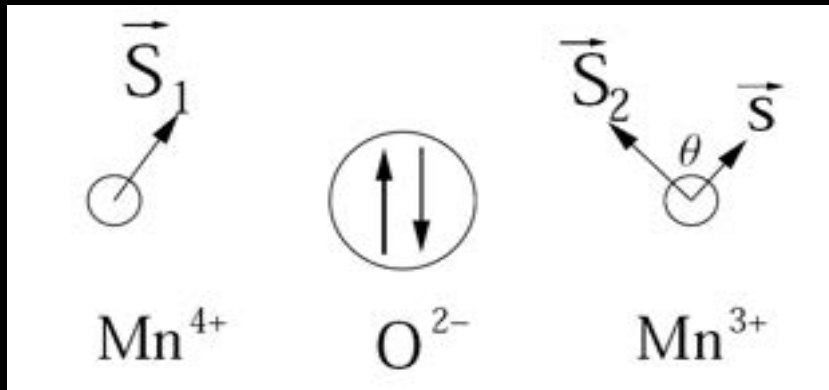
P. W. Anderson y A. Hasegawa, Phys Rev **100**, 675 (1955)

Double exchange

$$\sum_{\alpha,\beta} t^{\alpha\beta} \sum_{i,j,\sigma} c_{i,\alpha,\sigma}^\dagger c_{j,\beta,\sigma} + J_H \sum_i S_i S_i \xrightarrow{J_H \rightarrow \infty} \sum_{i,j} \sum_{\alpha,\beta} t_{ij}^{\alpha\beta} d_{i\alpha}^\dagger d_{j\beta}$$

$$t_{ij}^{\alpha\beta} = t^{\alpha\beta} \cos\left(\frac{\theta_{ij}}{2}\right)$$

Note: spinless Hamiltonian



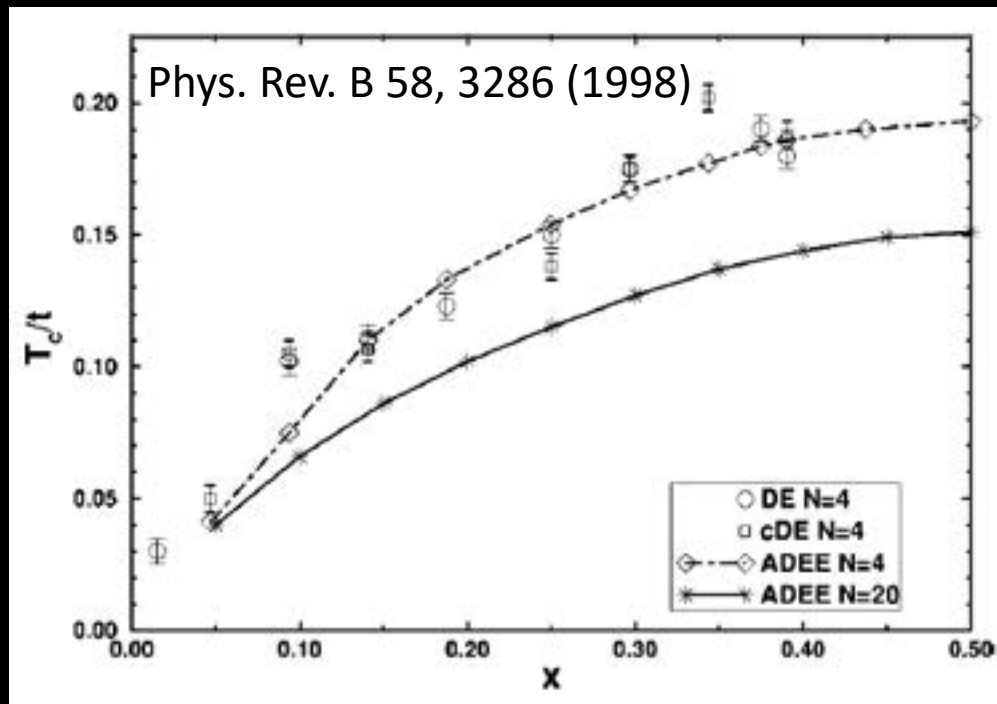
Kinetic exchange with real
(not virtual) electron hopping

Promotes FM with metallicity
(as observed in manganites)

C. Zener, Phys. Rev. **82**, 403, (1951)

P. W. Anderson y A. Hasegawa, Phys Rev **100**, 675 (1955)

Double exchange



T_c proportional to number of carriers

(actually, manganites are governed by a much more complex Hamiltonian and DE competes with AF superexchange)

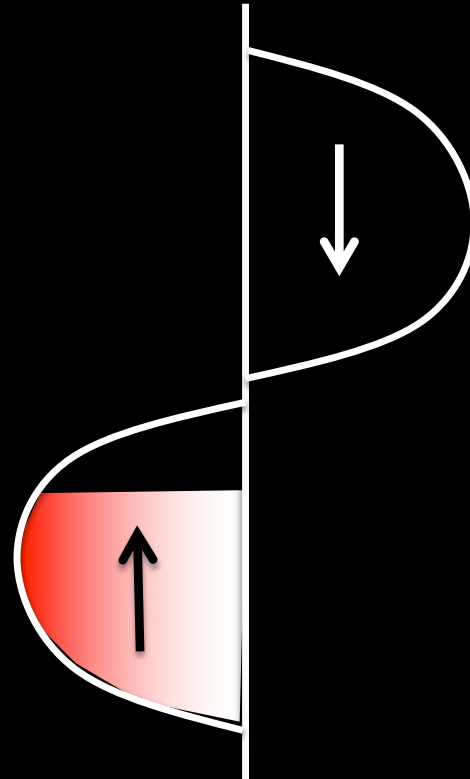
C. Zener, Phys. Rev. **82**, 403, (1951)

P. W. Anderson y A. Hasegawa, Phys Rev **100**, 675 (1955)

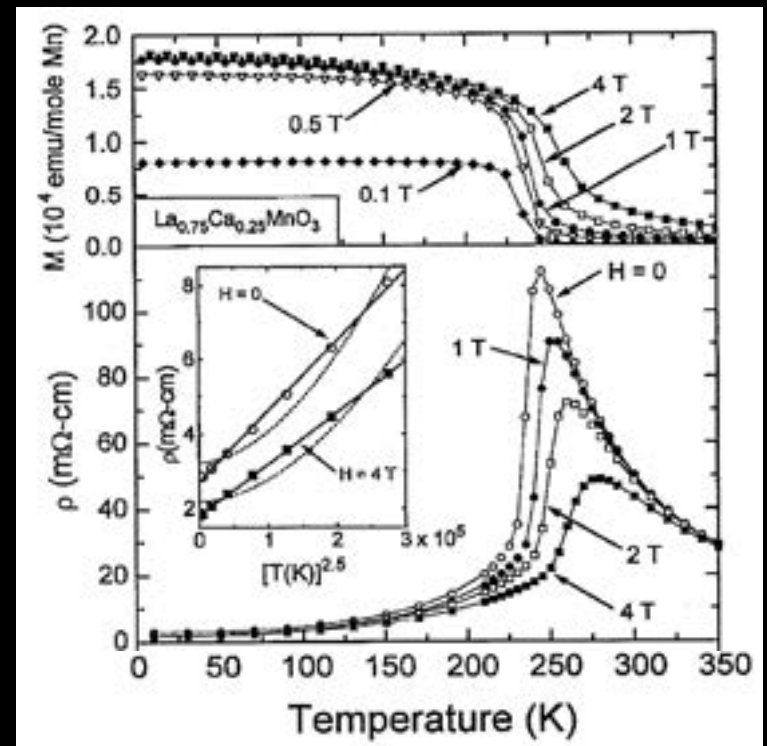
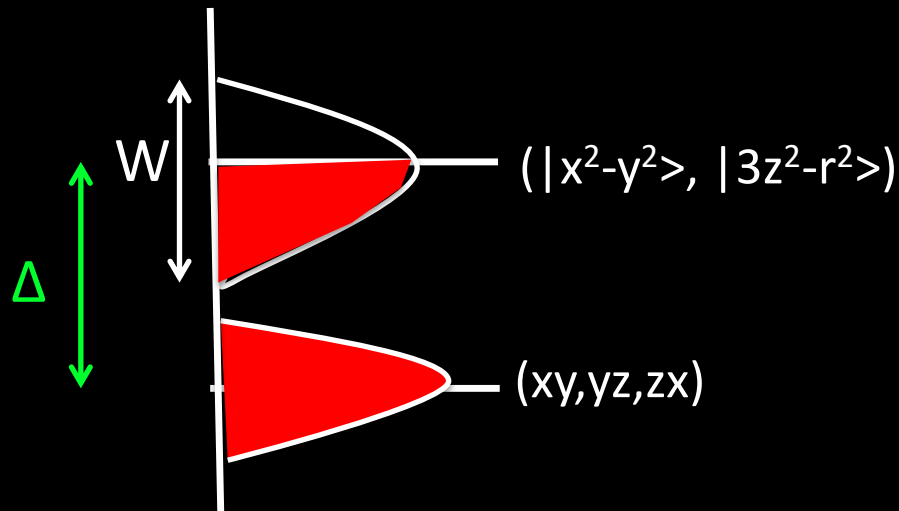
Double exchange

Half-metal: metallic conduction for one spin electrons but insulator for the other spin electrons.

Useful for spintronics.



Manganites



PRL 75, 3336 (1995)

- Double exchange among the e_g electrons.
- AF superexchange among the t_{2g} electrons.
- Jahn-Teller interactions.

Interactions

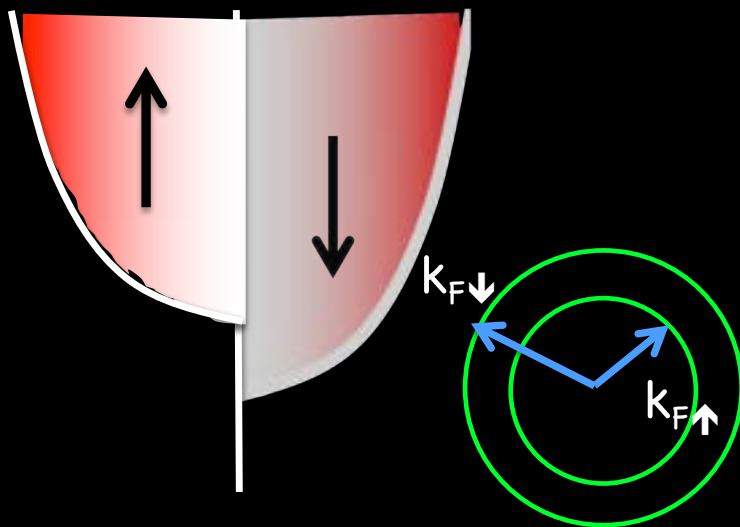
Different mechanisms

1. Localized moments. Heisenberg model.
2. Localized moments + itinerant electrons.
3. Itinerant electrons. Fermi surface instability.

Itinerant ferromagnetism: spontaneously spin-split bands

Question: Is it energetically favourable to have a spin imbalance for the itinerant electrons?

In mean-field, a polarized electron gas produces a molecular field (similar to an external field) which magnetizes the electron gas – Pauli PM).



Spin imbalance is

- non favoured in terms of kinetic energy
- favoured by the interaction with the molecular field.

Itinerant magnetism

Hubbard
model in a
magnetic field

$$H = \sum_{k\sigma} \varepsilon_k n_{k\sigma} + U \sum_j n_{j\uparrow} n_{j\downarrow} - \frac{g\mu_B H}{2} \sum_j (n_{j\uparrow} - n_{j\downarrow})$$

$$\langle n_{j\uparrow,\downarrow} \rangle = \frac{n}{2} \pm m$$

$$n_{j\uparrow} n_{j\downarrow} \rightarrow n_{j\uparrow} \langle n_{j\downarrow} \rangle + n_{j\downarrow} \langle n_{j\uparrow} \rangle - \langle n_{j\uparrow} \rangle \langle n_{j\downarrow} \rangle$$

Energy
density

$$E(m) = \int^{\mu\uparrow} \varepsilon \rho(\varepsilon) d\varepsilon + \int^{\mu\downarrow} \varepsilon \rho(\varepsilon) d\varepsilon + U \left(\frac{n^2}{4} - m^2 \right) - g\mu_B H m$$

At some value of U , $-m^2 U$ will favour a finite magnetization m
(polarizing the spins makes them less likely to meet)

Itinerant magnetism

Hubbard
model in a
magnetic field

$$H = \sum_{k\sigma} \varepsilon_k n_{k\sigma} + U \sum_j n_{j\uparrow} n_{j\downarrow} - \frac{g\mu_B H}{2} \sum_j (n_{j\uparrow} - n_{j\downarrow})$$

Calculate susceptibility

$$\chi = \frac{\chi_{\text{Pauli}}}{1 - U\rho(E_F)}$$

Stoner
enhancement

(Pauli susceptibility is enhanced by electron-electron interaction)

$U \rho(E_F) = 1$ (Stoner criterium for itinerant FM)

Band narrowing and peaks in $\rho(E_F)$ promote FM

Itinerant magnetism

Itinerant FM: Fe, Co, Ni, and alloys YCo_5 , $\text{La}_2\text{Fe}_{14}\text{B}$

If Stoner criterium is marginally satisfied:

- Nearly FM metals (very large susceptibility)
Example: Pd
 $U \rho(E_F) \sim 0.9$.
Alloying with 0.1% Fe or Co, turns Pd FM
- Weak ($m \ll n$) itinerant ferromagnetism
Example: ZrZn_2 (neither Zr nor Zn is magnetic)

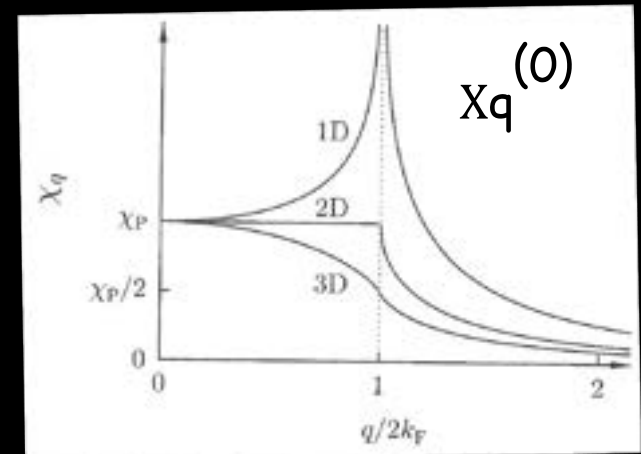
Instabilities with wave-vector $q \neq 0$. Spin density waves. Nesting

Generalized susceptibility: Stoner criterium for finite q . For a non-uniform magnetic field we calculated a q dependent susceptibility

$$\chi_q^{(0)} = \chi_{\text{Pauli}} f\left(\frac{q}{2k_F}\right)$$

In the presence of Coulomb interactions

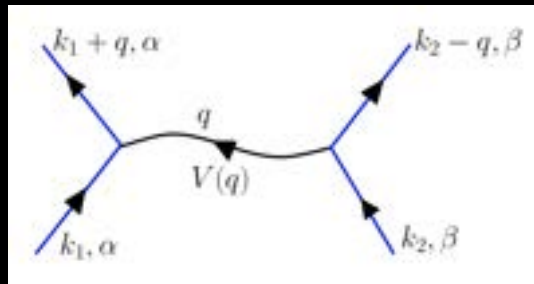
$$\chi_q = \frac{\chi_q^{(0)}}{1 - \alpha \chi_q^{(0)}} = \frac{\chi_{\text{Pauli}} f\left(\frac{q}{2k_F}\right)}{1 - U \rho(E_F) f\left(\frac{q}{2k_F}\right)}$$



S. Blundell, OUP

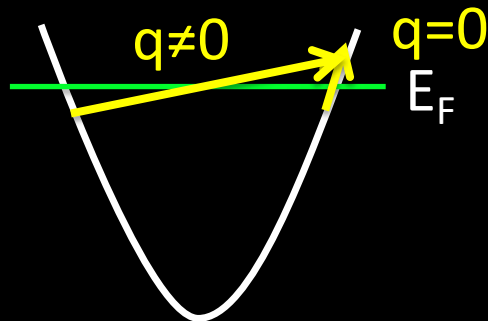
Instabilities with wave-vector $q \neq 0$. Spin density waves. Nesting

If $\chi_q^{(0)}$ diverges, you can have a collective mode even for very weak electron-electron interaction U . The instability that sets in is the one corresponding to the lowest U .



Coleman's book

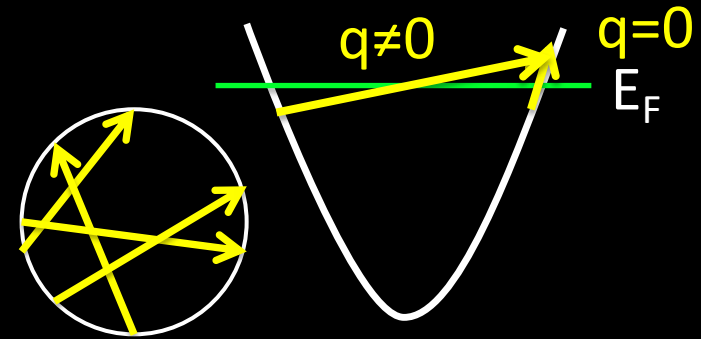
$$V(r) = \sum_q V(q) e^{iqr}$$



Reminder: a metal is in the degenerate limit $T \ll E_F$
Excitations around E_F

Instabilities with wave-vector $q \neq 0$. Spin density waves. Nesting

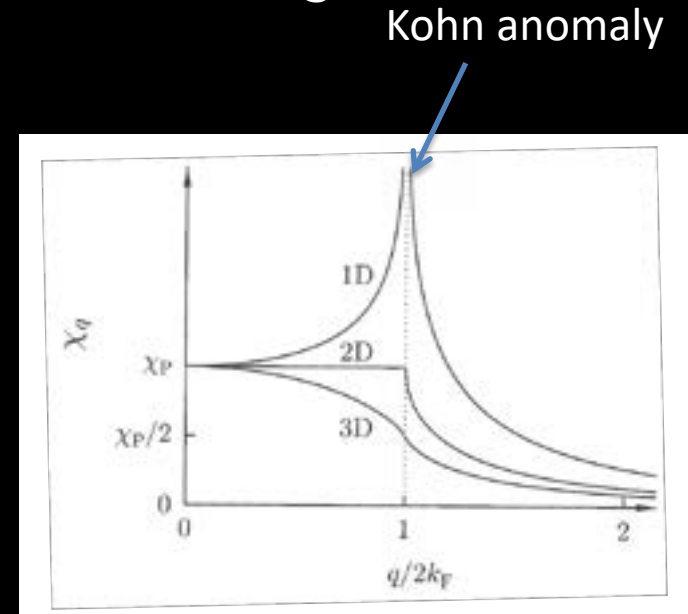
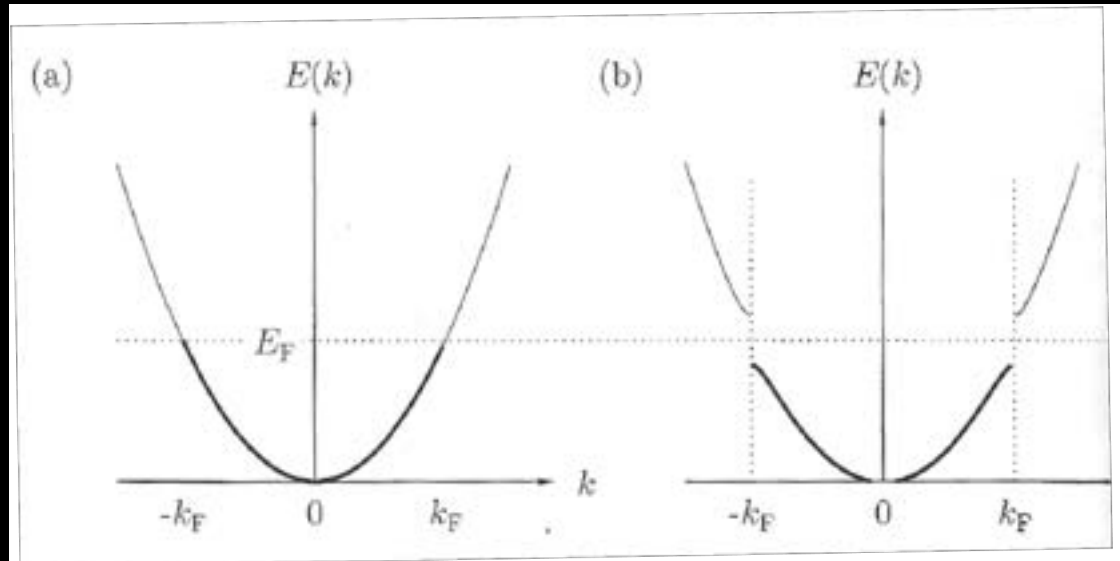
For a parabolic band you can have excitations at all possible q . $q=0$ is going to dominate ($\max \chi$ at $q=0$)



However, if there are sectors of the Fermi surface that are connected by **the same** q , the maximum of the susceptibility can be at that particular q : **nesting**.

Nesting in 1d

In 1d there is always nesting at $q=2k_F$
Peierls instability: dimerization and charge density wave.



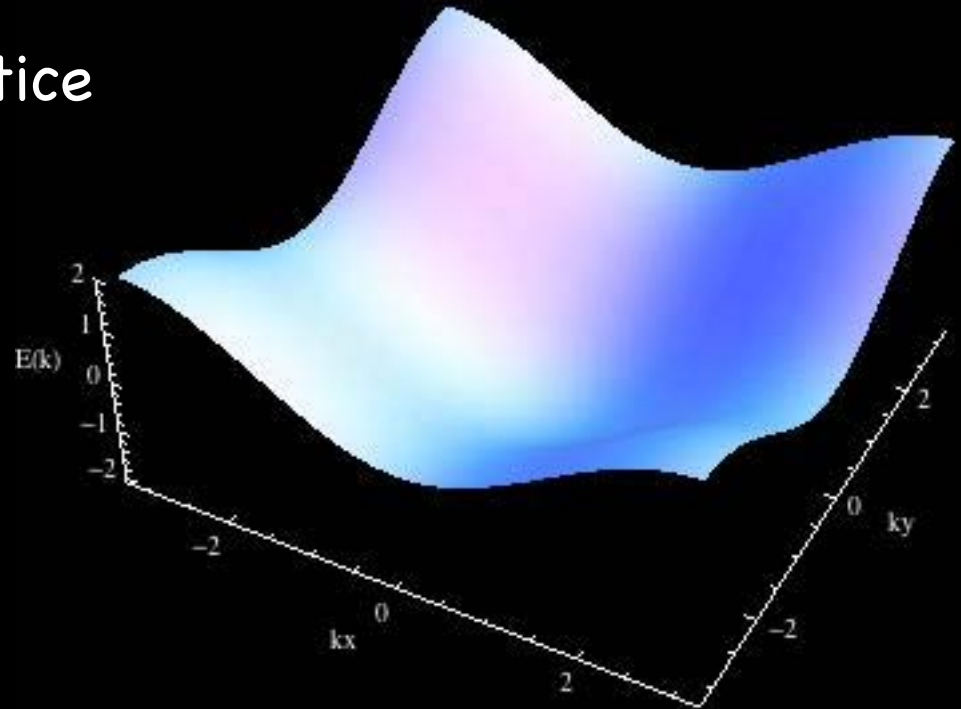
S. Blundell, OUP

For $d>1$, the nesting condition is more restrictive

Instabilities with wave-vector $q \neq 0$. Spin density waves. Nesting

Special case: Square lattice

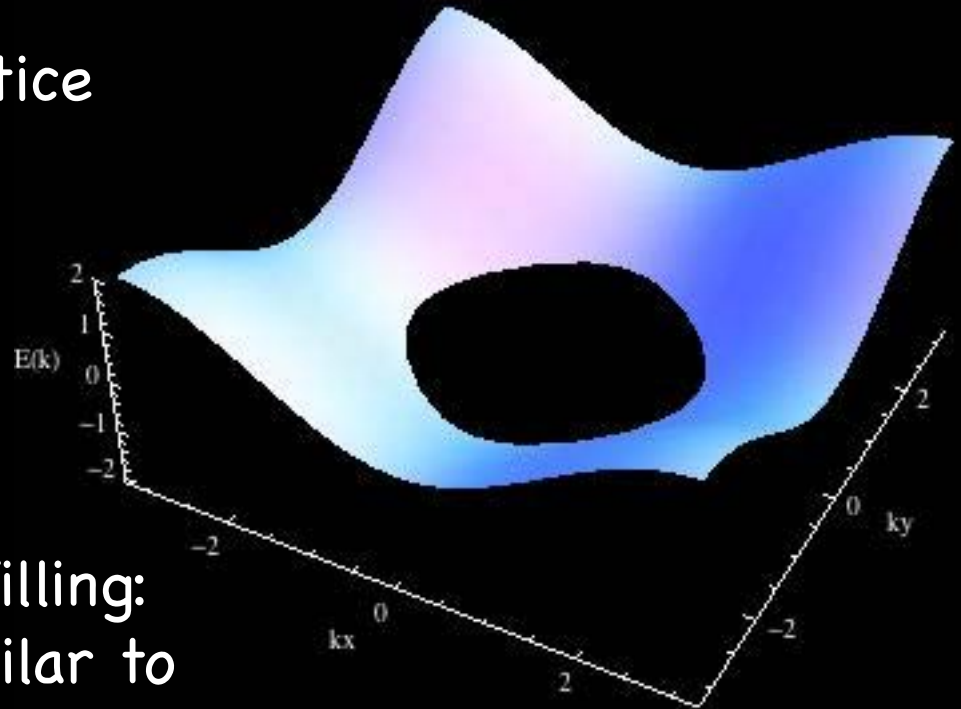
$$\varepsilon(k) = -2t(\cos k_x + \cos k_y)$$



Instabilities with wave-vector $q \neq 0$. Spin density waves. Nesting

Special case: Square lattice

$$\varepsilon(k) = -2t(\cos k_x + \cos k_y)$$



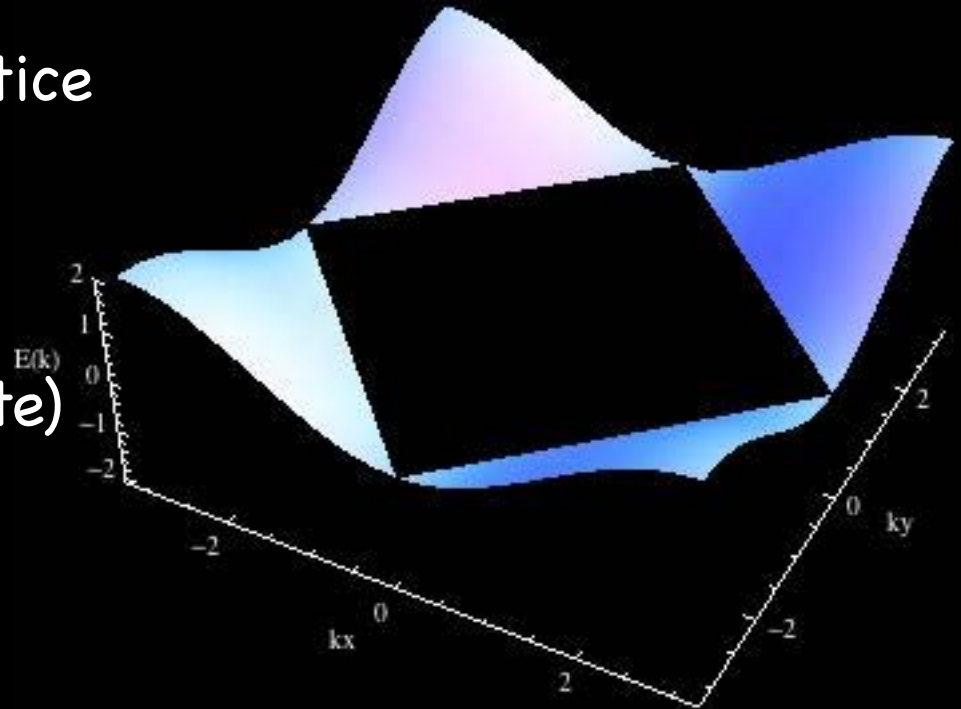
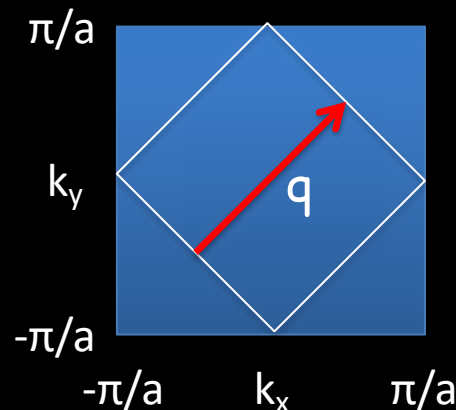
For an incommensurate filling:
The Fermi surface is similar to
the parabolic bands: no nesting

Instabilities with wave-vector $q \neq 0$. Spin density waves. Nesting

Special case: Square lattice

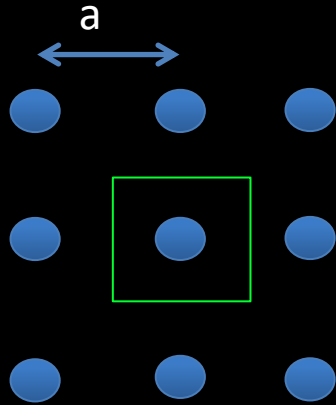
$$\varepsilon(k) = -2t(\cos k_x + \cos k_y)$$

For half filling (1 e⁻ per site)



There is perfect nesting with $q = (\pi/a, \pi/a)$

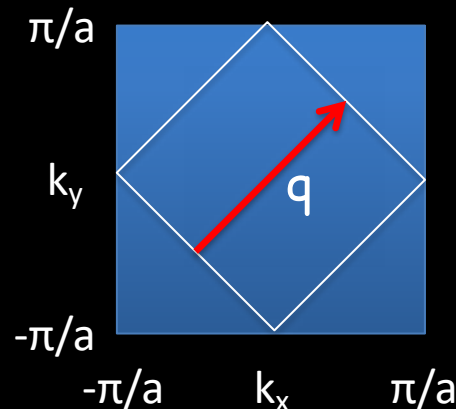
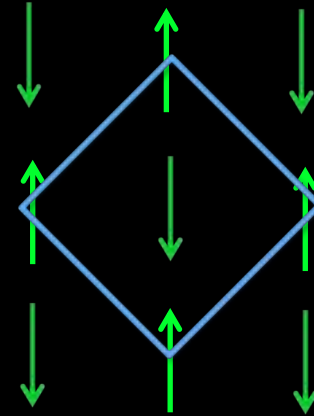
Instabilities with wave-vector $q \neq 0$. Spin density waves. Nesting



AF: Doubling of
unit cell



Folding of
Brillouin zone



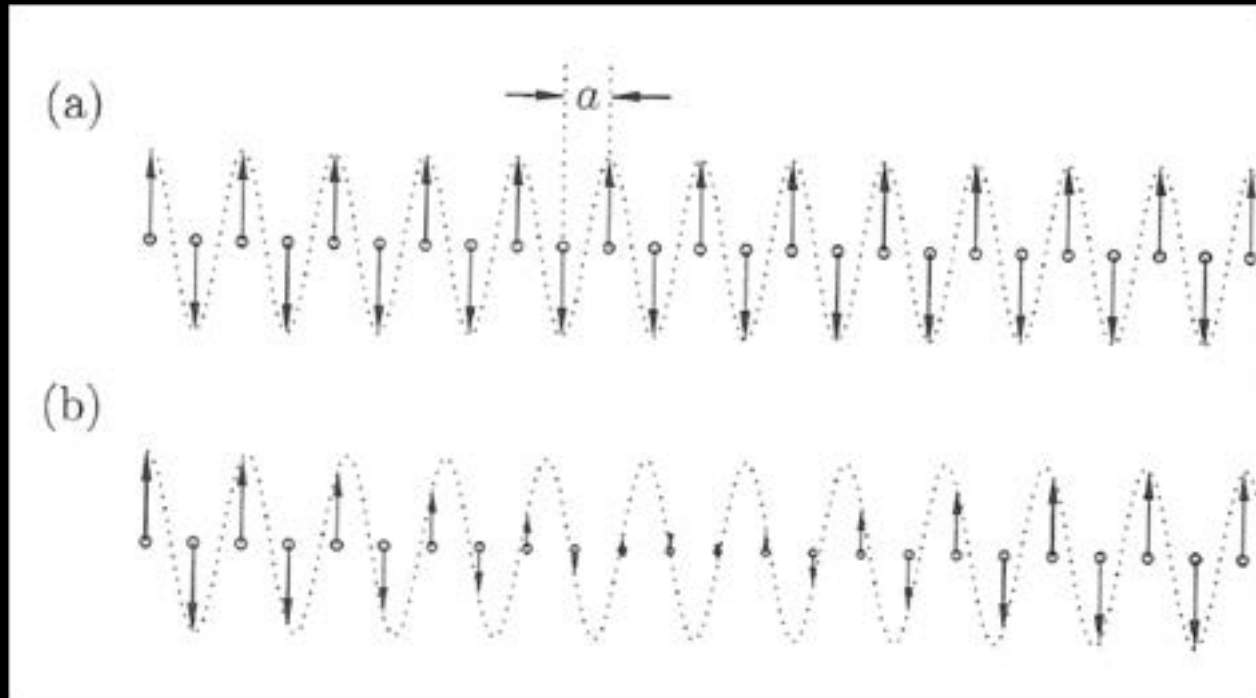
A gap opens at the zone boundary:
the system is insulating at half-
filling even in the weak coupling
regime if there is perfect nesting.

(Slater insulator)

Note that we have used $U=0!!$

Instabilities with wave-vector $q \neq 0$. Spin density waves. Nesting

In general, q can be an incommensurate vector

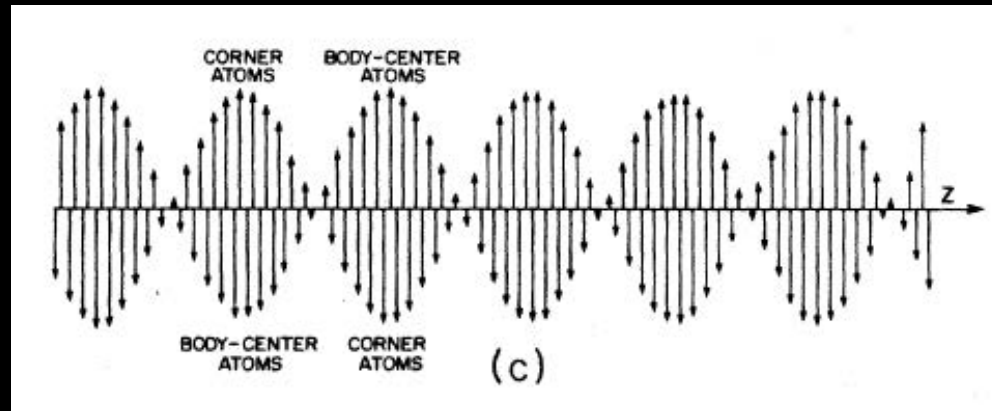
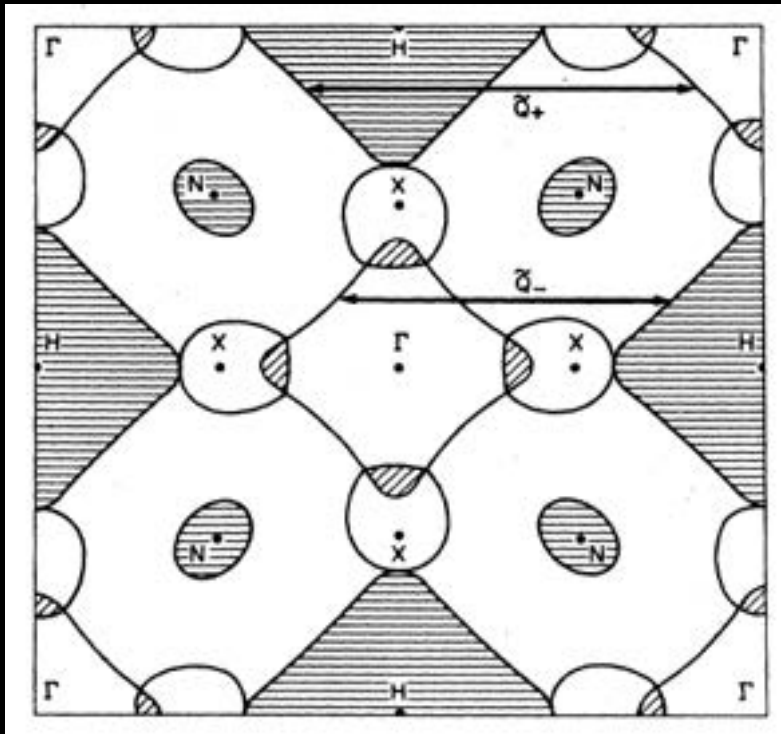


S. Blundell's book

Instabilities with wave-vector $q \neq 0$. Spin density waves. Nesting

Example: SDW in Cr

$$Q = (0, 0, 1 - \delta) \frac{2\pi}{a} \quad (0.037 < \delta < 0.048)$$

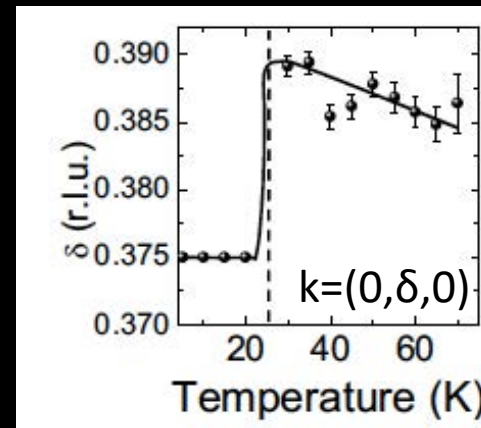


RMP 60, 209 (1988)

The SDW does not open a gap over the entire Fermi surface: the system is metallic

- Nesting can lead to different Fermi surface instabilities (charge density wave, superconducting pairing) that would compete with the spin-density wave.
The one with the largest T_c would set in.
- Incommensurate instabilities sometimes suffer “lock-in” transitions becoming commensurate at low temperatures.

Example: CaFe_4As_3



PRB 81, 184402 (2010)

Lock in transitions

Ginzburg-Landau formalism

Complex order parameter

$$\psi(r) = \rho(r)e^{i(\mathbf{Q}_c \cdot \mathbf{r} + \phi(r))}$$

Free energy

$$\mathcal{F}_\psi = \frac{1}{2} a_\rho (T - T_{CO}) |\psi|^2 + \frac{1}{4} b_\rho |\psi|^4 + \frac{1}{2} \xi_\rho^2 |(\nabla - i \vec{q}_o) \psi|^2 + \frac{1}{n} \eta \Re \left[\psi^n e^{-i \vec{G} \cdot \vec{r}} \right]$$



Elastic term



Umklapp term

Lock in transitions

$$\begin{aligned}\mathcal{F}_\psi &= \frac{1}{2} a_\rho (T - T_{CO}) \rho^2 + \frac{1}{4} b_\rho \rho^4 \\ &+ \frac{1}{2} \xi_\rho^2 (\nabla \rho)^2 + \frac{1}{2} \xi_\rho^2 \rho^2 (\nabla \phi - \vec{q}_0)^2 + \frac{1}{n} \eta \rho^n \cos[n\phi]\end{aligned}$$

q_0 is the incommensurate nesting vector.

n is the period of the lattice

Elastic term favours $\nabla \phi = q_0$ **INCOMMENSURABILITY**

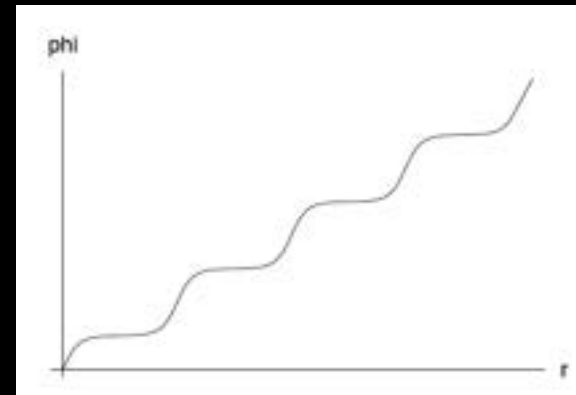
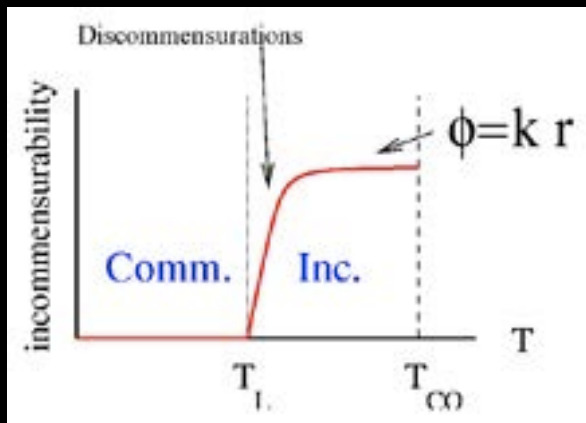
Umklapp term favours
COMMENSURABILITY

$$\phi = \left(\frac{\pi}{n} + \frac{2\pi j}{n} \right) \quad \forall j \in \mathbf{Z}$$

Lock in transitions

$$\mathcal{F}_\psi = \frac{1}{2} a_\rho (T - T_{CO}) \rho^2 + \frac{1}{4} b_\rho \rho^4 + \frac{1}{2} \xi_\rho^2 (\nabla \rho)^2 + \frac{1}{2} \xi_\rho^2 \rho^2 (\nabla \phi - \vec{q}_o)^2 + \frac{1}{n} \eta \rho^n \cos[n\phi]$$

For $n > 2$, at high T , ρ is small and the elastic term wins. At lower T , ρ is large and the Umklapp term wins.



Outline

- Free magnetic ions
- Environment
- Interactions
 - Exchange between localized moments
 - Indirect exchange through itinerant electrons
 - Magnetism in metals
- Excitations

Excitations: spin waves

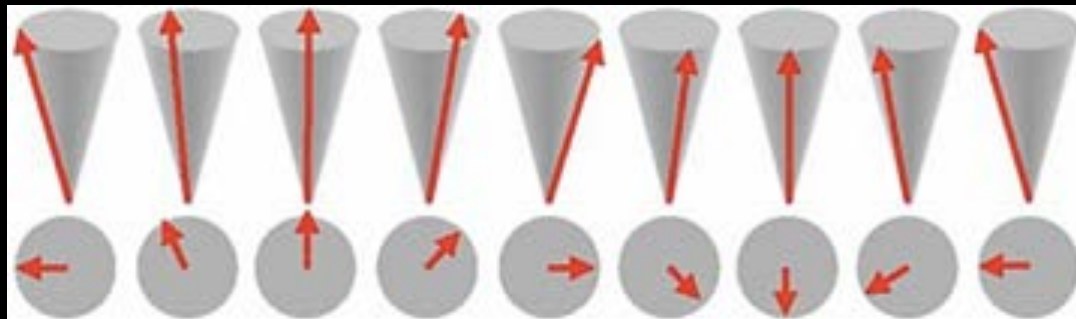
Low T excitations of a Heisenberg model
(localised moments)

Breaking a global continuous symmetry.
(**Goldstone** theorem): it is possible to produce
long-wavelength excitations in the order
parameter with a vanishingly small energy cost.
Excitations are (massless) Goldstone bosons.

Excitations: spin waves

Low T excitations of a Heisenberg model
(localised moments)

In a FM: flip a single spin. The new eigenstate is a state with a wave of spins.



<http://www.uni-muenster.de/>

This excitation can be described as the formation of a bosonic quasiparticle called **magnon**

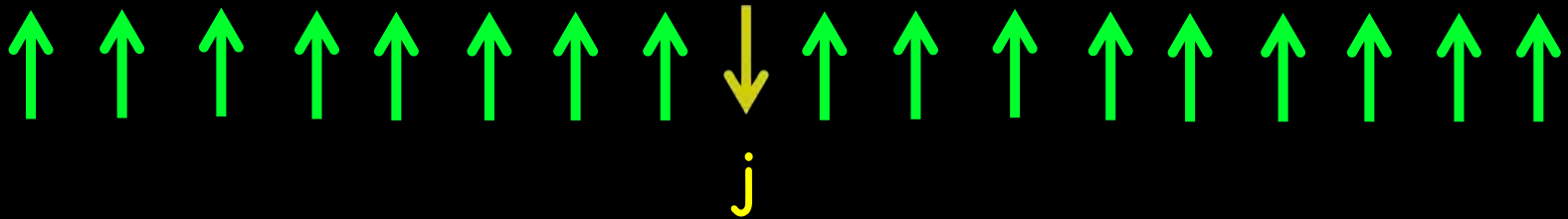
Excitations: spin waves

For a ferromagnetic Heisenberg model

$$H = -2J \sum_i \mathbf{S}_i \mathbf{S}_{i+1} = -2J \sum_i \left[S_i^z S_{i+1}^z + \frac{1}{2} (S_i^+ S_{i+1}^- + S_i^- S_{i+1}^+) \right] \quad S^\pm = S_x \pm iS_y$$

To create an excitation: flip spin j

$$|j\rangle = S_j^- |\phi\rangle$$



Excitations: spin waves

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To create an excitation: flip spin j

$$|j\rangle = S_j^- |\phi\rangle$$

$|j\rangle$ is not an eigenstate of H :
diagonalize the Hamiltonian by
looking for plane-wave solutions

$$|q\rangle = \frac{1}{\sqrt{N}} \sum_j e^{iqR_j} |j\rangle$$

$$E(q) = -2NJS^2 + 4JS(1 - \cos qa)$$

Excitations: spin waves

$$E(q) = -2NJS^2 + 4JS(1 - \cos qa)$$

small q

$$\hbar\omega \approx 2JSq^2a^2$$

Gapless
Goldstone modes

Goldstone theorem: if a continuous symmetry is spontaneously broken and the forces are sufficiently short ranged, there must be a branch of excitations with the property that the energy vanishes for $q \rightarrow 0$.

Excitations: spin waves

$$E(q) = -2NJS^2 + 4JS(1 - \cos qa)$$

small q

$$\hbar\omega \approx 2JSq^2a^2$$

Gapless
Goldstone modes

In 3dim the density
of states is

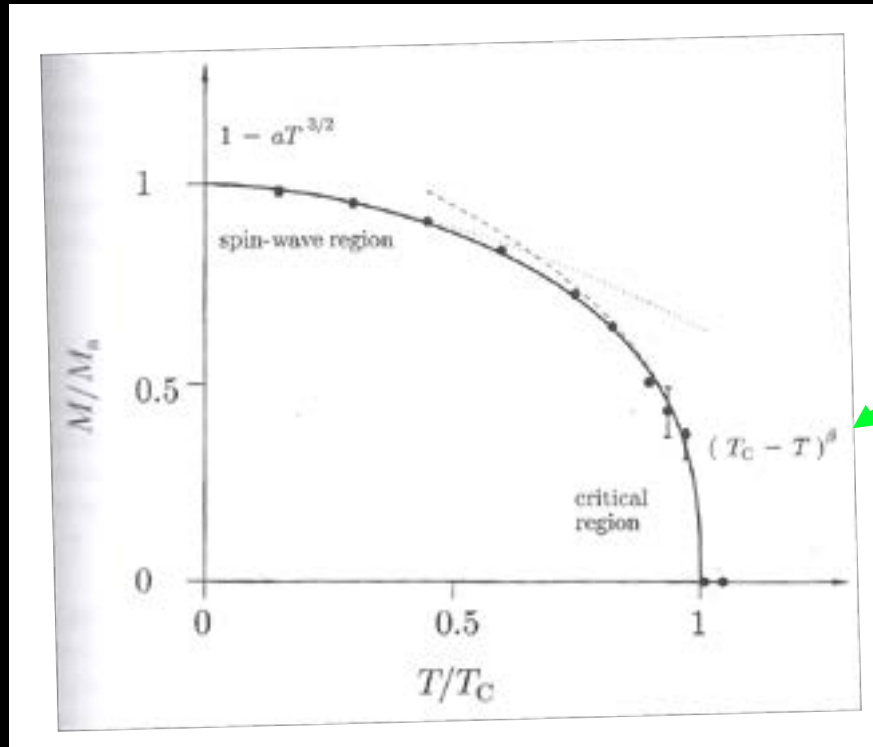
$$\rho(q)dq \propto q^2 dq$$

$$n_{\text{magnon}} = \int_0^\infty \frac{\rho(\omega)d\omega}{\exp(\hbar\omega / k_B T) - 1} \propto T^{3/2}$$

At low T : $M(T) \approx 1 - aT^{3/2}$

Bloch $T^{3/2}$ law

Excitations: spin waves



Blundell's book

Close to T_c , critical exponent 1/2

At low T : $M(T) \approx 1 - aT^{3/2}$

Bloch $T^{3/2}$ law

Excitations: spin waves

$$E(q) = -2NJS^2 + 4JS(1 - \cos qa)$$

small q

$$\hbar\omega \approx 2JSq^2a^2$$

$$n_{\text{magnon}} = \int_0^\infty \frac{g(\omega)d\omega}{\exp(\hbar\omega/k_B T) - 1}$$

In 2dim and 1dim n_{magnon} diverges $\rightarrow$ spontaneous FM is not possible for isotropic 1dim and 2dim Heisenberg models (Mermin-Wagner-Berezinskii theorem)

Excitations: spin waves

But **note**: Anisotropies stabilize FM in low dimensional systems and the spin-wave spectrum acquires a gap

$$H = J \sum_{i,j} (S_i^x S_j^x + S_i^y S_j^y + \underbrace{A}_{A>1 \text{ (easy axes)}} S_i^z S_j^z)$$

$$\Delta E = 4JS(1 - \cos qa) \sim q^2 a^2 \quad (\text{isotropic})$$


$$\Delta E = 4JS(A - \cos qa) \sim (\underbrace{A - 1}_{\text{GAP}} + q^2 a^2)$$

There can also be a gap due to dipole-dipole interactions
(which can be important for f-systems)

Excitations: spin waves

Ground state of the antiferromagnetic Heisenberg model

$$H_{AF} = 2J \sum_i \mathbf{S}_i \mathbf{S}_{i+1} = 2J \sum_i \left[S_i^z S_{i+1}^z + \frac{1}{2} (S_i^+ S_{i+1}^- + S_i^- S_{i+1}^+) \right]$$

$$|\phi_0\rangle = |\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\dots\rangle \quad (\text{classical Néel state})$$

Φ_0 is not an eigenstate of H_{AF} . From this molecular field approximation, you can decrease the energy by letting S^z fluctuate. These quantum fluctuations lower the energy with respect to the Néel state.

$$-NzJS^2 \left(1 + \frac{1}{zS} \right) < E_g < -NzJS^2$$

z : number of neighbors

Excitations: spin waves

$$H_{AF} = 2J \sum_i \mathbf{S}_i \mathbf{S}_{i+1} = 2J \sum_i \left[S_i^z S_{i+1}^z + \frac{1}{2} (S_i^+ S_{i+1}^- + S_i^- S_{i+1}^+) \right]$$

Spin waves have to be defined in the two sublattices. These spin waves are interdependent. The spin wave spectrum is twofold degenerate (± 1 excitations are degenerate)

$$\hbar\omega \approx JzS |q|a$$

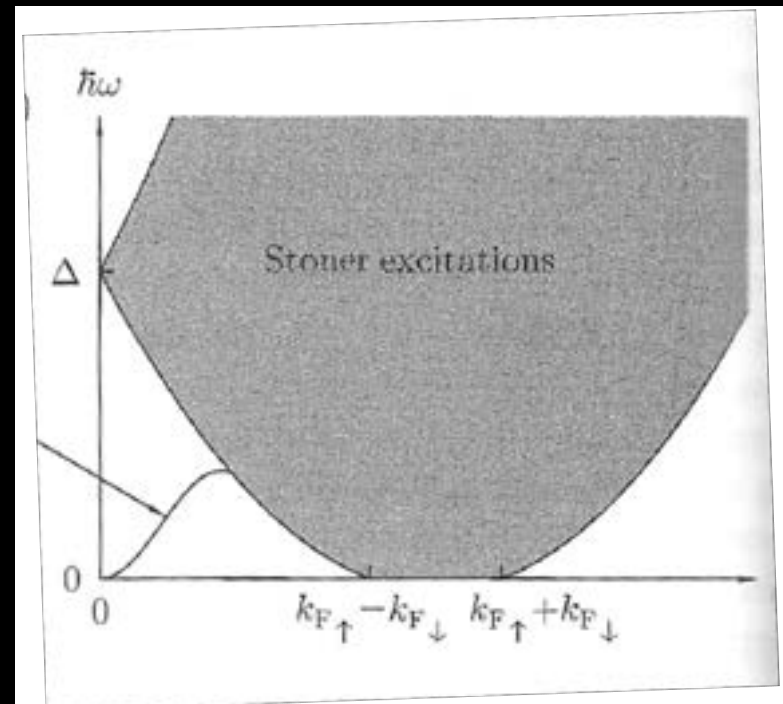
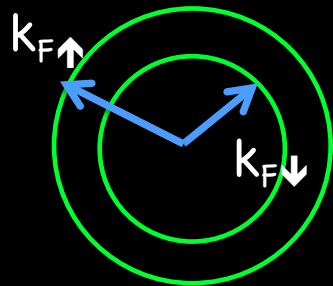
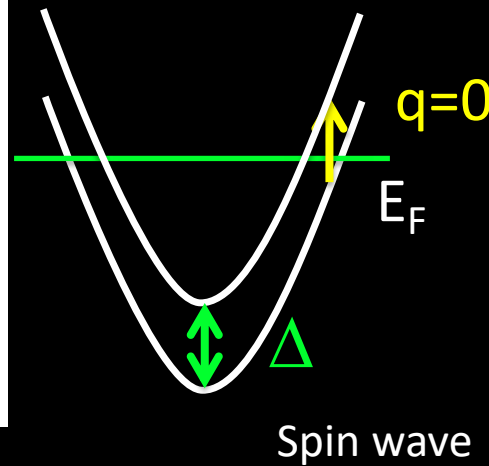
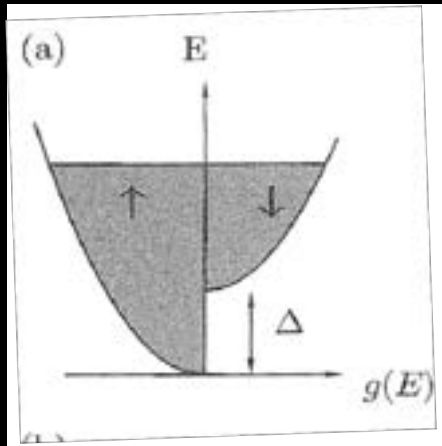
Antiferromagnons
(gapless Goldstone mode)

Excitations in the electron gas

- Also spin waves
- Stoner excitations

$$\hbar\omega = E_{k+q} - E_k + \Delta$$

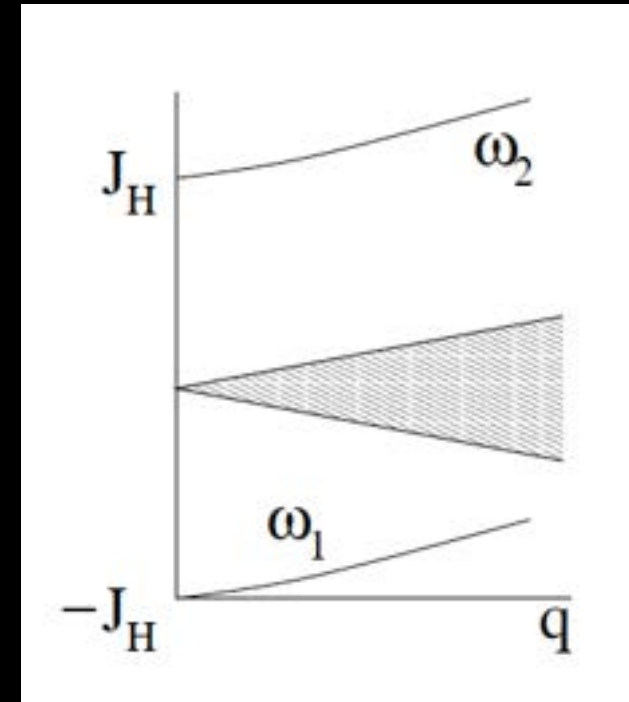
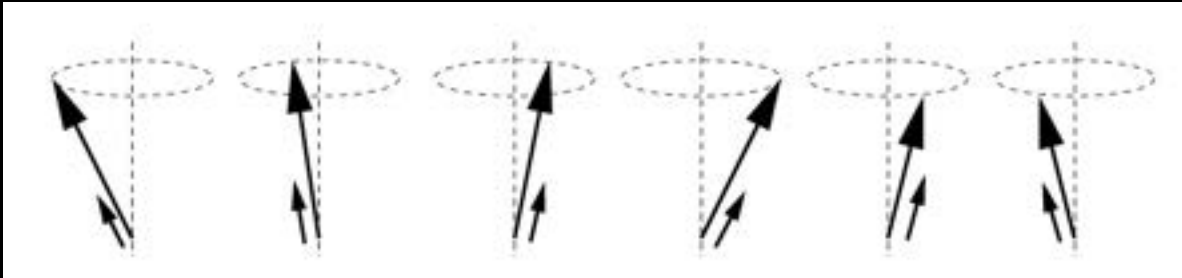
Δ : exchange splitting



Blundell's book

Spin waves in a double exchange system: localized + itinerant

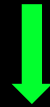
Composite spin waves



PRB 64, 140403

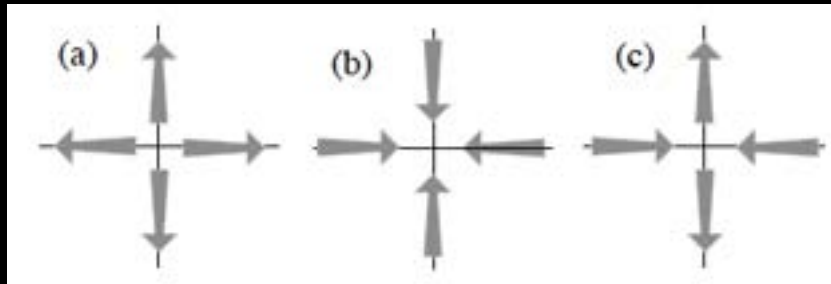
Topological defects

Distortions which cannot be restored into ordering by continuous deformations.



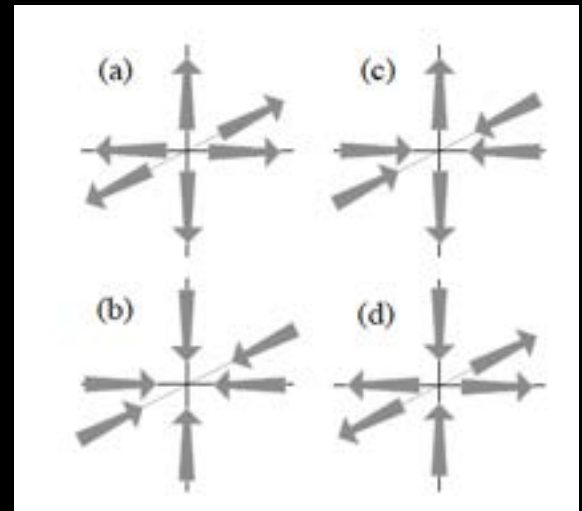
Vortices

XY model in 2dim

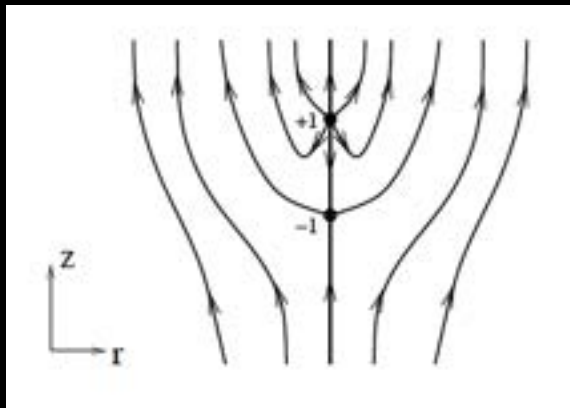
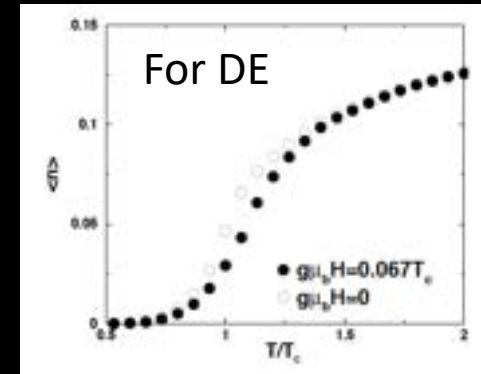
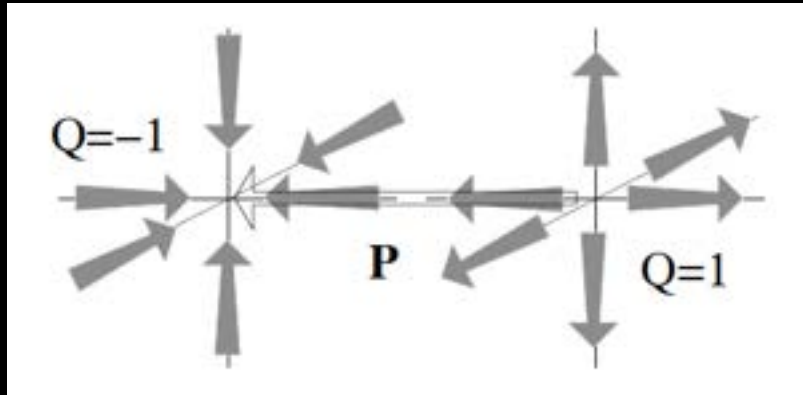


Vortices have a topological charge.

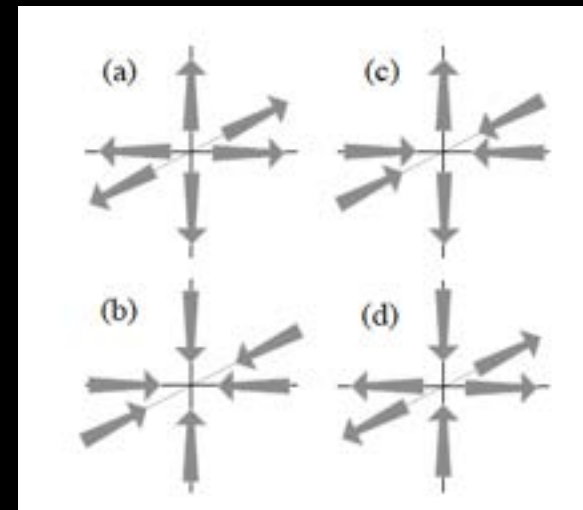
Heisenberg model in 3dim



Topological defects

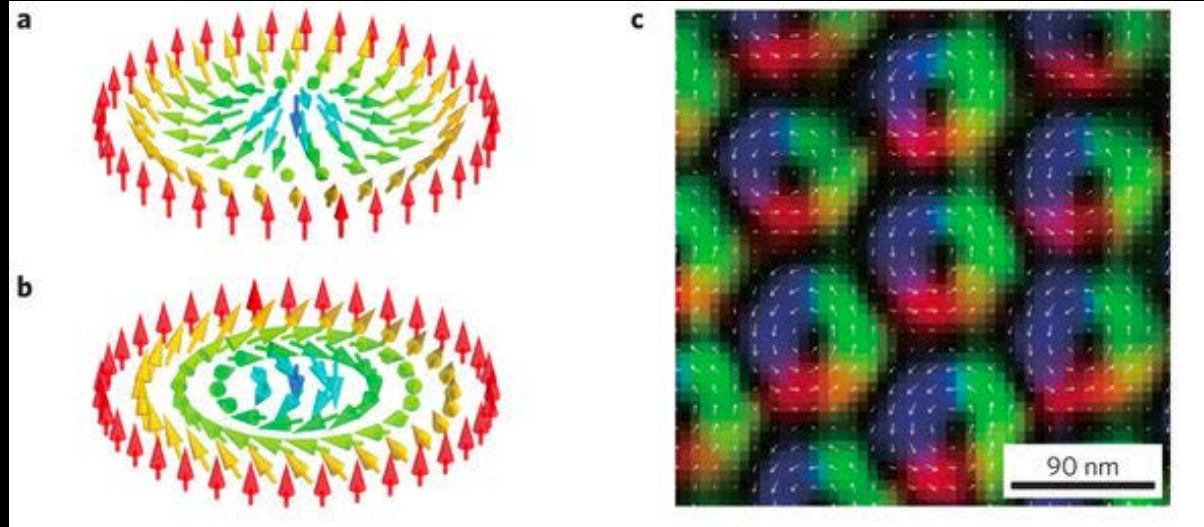


Heisenberg model in 3dim



$$\langle n \rangle = \alpha e^{-\beta E_c}$$

Observation of magnetic skyrmions



- ✓ Induced by Dzyaloshinskii-Moriya interaction (consequence of spin-orbit interaction). Requires no inversion symmetry.
- ✓ Spintronic storage.

$$H_{DM} = \mathbf{D} \cdot (\mathbf{S}_1 \times \mathbf{S}_2)$$

Science **323**, 915–919 (2009).

A. Fert, et al *Nature Nanotechnology* **8**, 152–156 (2013)

Summary

- Classical phase transitions
- Free magnetic ions
- Environment
- Magnetic order and susceptibility
- Interactions
 - Exchange between localized moments
 - Indirect exchange through itinerant electrons
 - Magnetism in metals
- Excitations