Emergence of Quantum Phases in Novel Materials

VIII Edition ICMM School

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EXCELENCIA SEVERO OCHOA

Magnetism is a collective phenomenon in which many spins interact and order.

Important theoretical developments in the context of magnetism have been relevant for other fields (mean-field approaches, Goldstone theorem, critical phenomena)

Many applications.

$q = \lim_{t\to\infty}\langle\langle S_i(0)S_i(t)\rangle\rangle$

Microscopic description (MODELS)

Magnetic moments

Interactions

Environment

Macroscopic description (phase transitions)

Phases

Dimensionality

Symmetry

Universality

Magnetism originates from:

✓The magnetic moment of electrons

✓Electron's kinetic energy

✓Pauli exclusion principle

✓Coulomb repulsion between electrons

Magnetic moment of electrons

Spin magnetic moment:

$$\mu_s = -g\mu_B \boldsymbol{S}$$

The Bohr magneton is $\mu_B = \dfrac{e\hbar}{2mc}$

For free electrons: g=2.0023

Yosida

S=**σ**/2 with

Pauli matrices
(spin operators)

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

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

Eigenvectors:

$$|\uparrow_z\rangle = \frac{1}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix} \;;\; |\uparrow_x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \;;\; |\uparrow_y\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix}$$

$$|\downarrow_z\rangle = \frac{1}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix} \;;\; |\downarrow_x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \;;\; |\downarrow_y\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix}$$

Spin operators

Total spin operator $$\hat{\mathbf{S}} = (\hat{S}_x, \hat{S}_y, \hat{S}_z)$$

$$\hat{\mathbf{S}}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$$

$$\hat{\mathbf{S}}^2|\Psi\rangle = s(s+1)|\Psi\rangle$$

Conmutation relations

$$[\hat{S}_i, \hat{S}_j] = 2i\epsilon_{ijk}\hat{S}_k$$

$$[\hat{S}_x, \hat{S}_y] = i\hat{S}_z$$

$$[\hat{\mathbf{S}}, \hat{S}_i] = 0$$

$$\varepsilon_{ijk} = \begin{cases} +1 & \text{if } (i,j,k) \text{ is } (1,2,3), (2,3,1), \text{ or } (3,1,2), \\ -1 & \text{if } (i,j,k) \text{ is } (3,2,1), (1,3,2), \text{ or } (2,1,3), \\ \;\;0 & \text{if } i = j, \text{ or } j = k, \text{ or } k = i \end{cases}$$

Ladder operators

$$\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y$$

$$\hat{\mathbf{S}} = \frac{1}{2}\left(\hat{S}_+\hat{S}_- + \hat{S}_-\hat{S}_+\right) + \hat{S}_z^2$$

$$\hat{S}_+|\downarrow_z\rangle = |\uparrow_z\rangle$$

$$\hat{S}_+|\uparrow_z\rangle = 0$$

Magnetic moment of electrons

Orbital magnetic momentum:

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

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

The atomic nuclei also have magnetic moment, with nuclear spin I

$$\mu = g_N \mu_N \mathbf{I}$$

Much smaller than the electron's

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

Yosida

OUTLINE

- Free magnetic moments
- Environment
- Magnetic order and susceptibility
- Interactions
  - Between localized moments
  - Localized moments + itinerant electrons
  - Itinerant electrons
- Excitations.
- Altermagnetism → Alberto Cortijo

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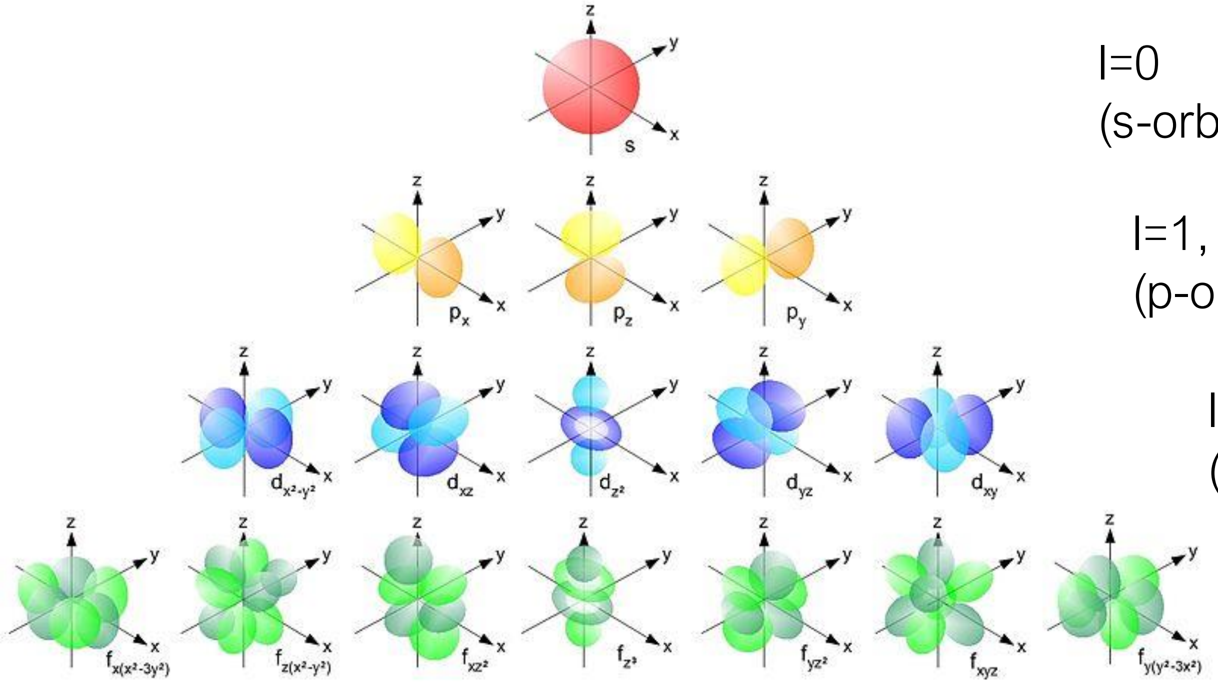
Magnetic atoms/ions

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

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



l=0
(s-orbitals)

2 (2l+1) degeneracy

l=1, m=-1,0,1
(p-orbitals)

l=2, m=-2,-1,0,1,2
(d-orbitals)

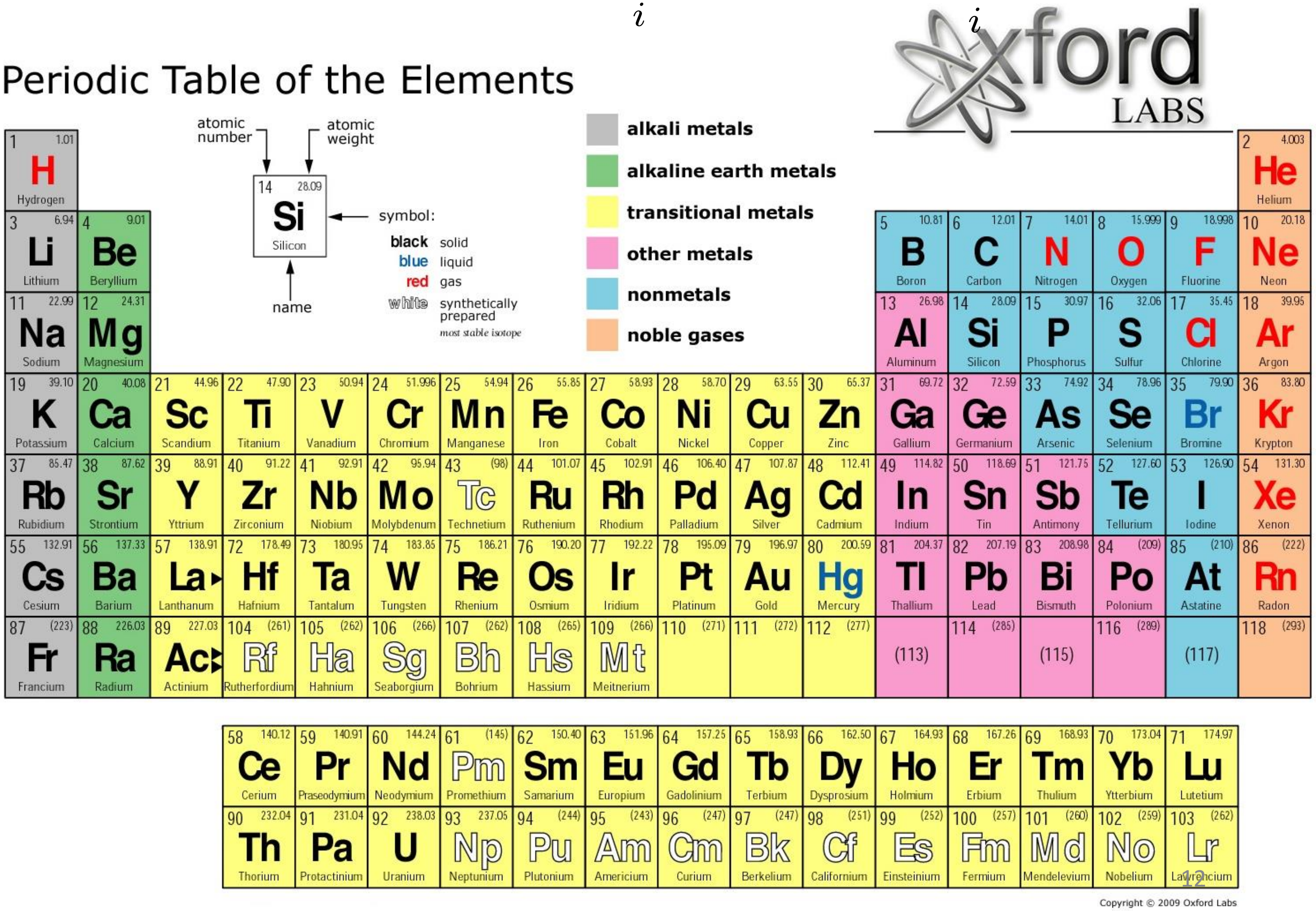
l=3, m=-3,-2,-1,0,1,2, 3
(f-orbitals)

Magnetic atoms/ions

Electrons in incomplete shells (d or f orbitals) $L = \sum_i m_{l_i}$ $S = \sum_i m_{s_i}$

s and p electrons overlap easily and form the conduction bands (large bandwidth W).

d and f electrons have smaller wave-functions. Their overlap is small and the electron-electron interaction may control their behavior.



Spin orbit coupling

Interaction between the electron and the magnetic field created by the orbiting nucleus.

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

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

$$\frac{1}{r}\frac{dV(r)}{dr} = \frac{Z_{\text{eff}}\, e}{4\pi\epsilon r^3} \qquad H_{so} \sim Z_{\text{eff}} \langle r^{-3} \rangle \vec{S} \cdot \vec{L}$$

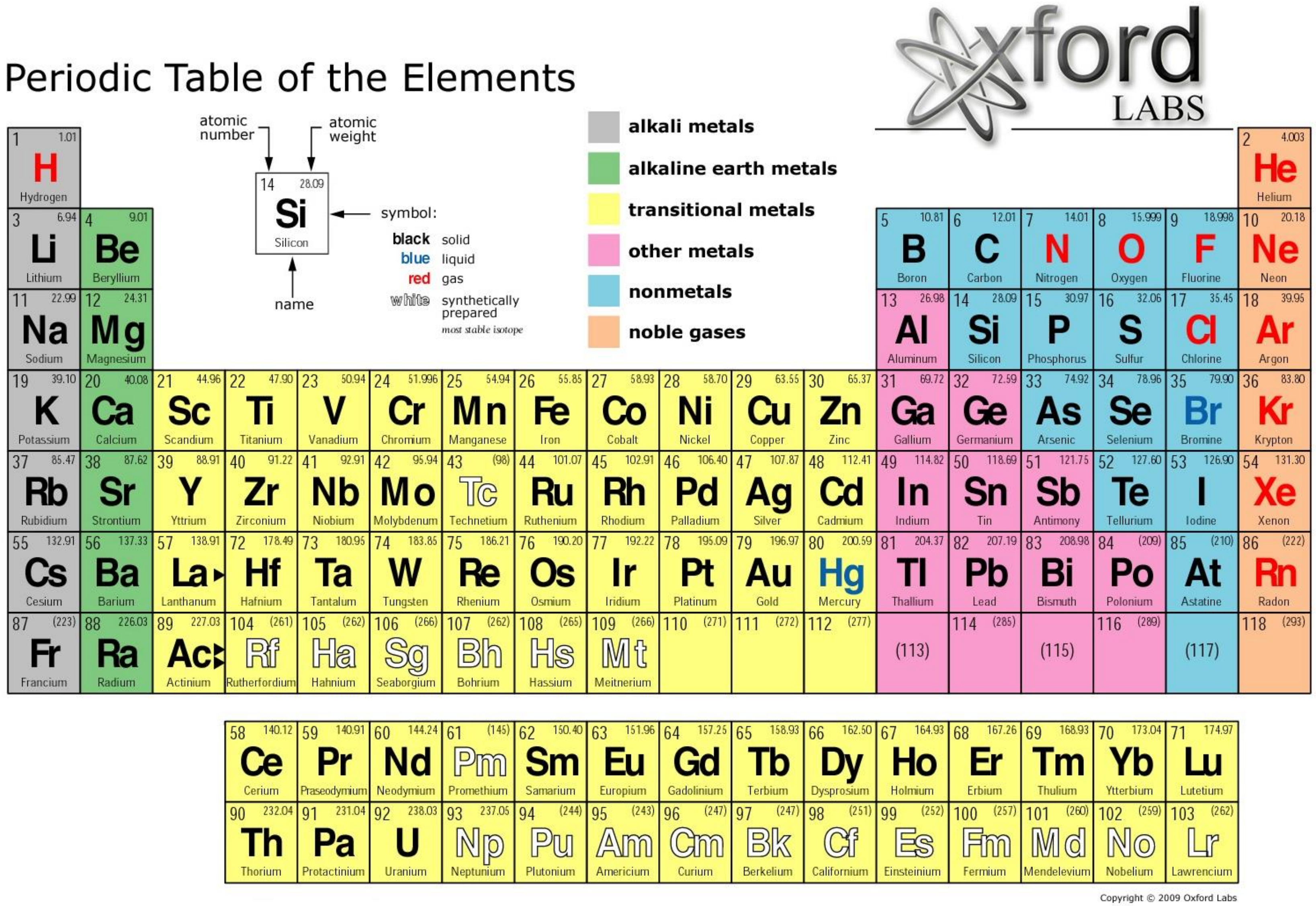
For a Hydrogen like atom,

$$\langle r^{-3} \rangle \sim Z^3$$

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

FREE MAGNETIC IONS

Spin orbit coupling



Increasing SO

Magnetic atoms/ions

Total orbital angular momentum: $L = \sum_i m_{l_i}$

Total spin angular momentum: $S = \sum_i m_{s_i}$

Degeneracy (2S+1)(2L+1)

In the absence of spin orbit coupling, L and S are constants of motion.

However, with spin orbit coupling (λLS): J=L+S is conserved.

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

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

Magnetic atoms/ions

Total angular momentum: **J=L+S**

|L-S| ≤ J ≤ L+S

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

Including SO as a weak perturbation (Russel-Saunders)

- 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)

Example d[1]: L=2, S=1/2

L>S → 2S+1=2 states with degeneracy 2J+1

(x6) J=L+S=5/2

(x10)

(2L+1)(2S+1)

(x4) J=|L-S|=3/2

fine structure

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

Note that the hyperfine interaction with the nuclear moment produces a further splitting: hyperfine structure.

Magnetic atoms/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

$^{2S+1}L_J$

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

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

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

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

m_l	
=2	↑
1	↑
0	↑
-1	↑
-2	

S=2

L=2

J=|L-S|=0

$^3D_0$

$\mu_{\text{eff}}=0$

Magnetic atoms/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

$^{2S+1}L_J$

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

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

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

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

m_l		
=3	↑	↓
2	↑	↓
1	↑	
0	↑	
-1	↑	
-2	↑	
-3	↑	

S=5/2

L=5

J=5+5/2=15/2

$^6H_{15/2}$

$\mu_{\text{eff}}=10.63\mu_B$

Magnetic atoms/ions

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

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

We have to take into account the environment of the atoms: the crystal field

OUTLINE

- Free magnetic moments
- Environment
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  - Between localized moments
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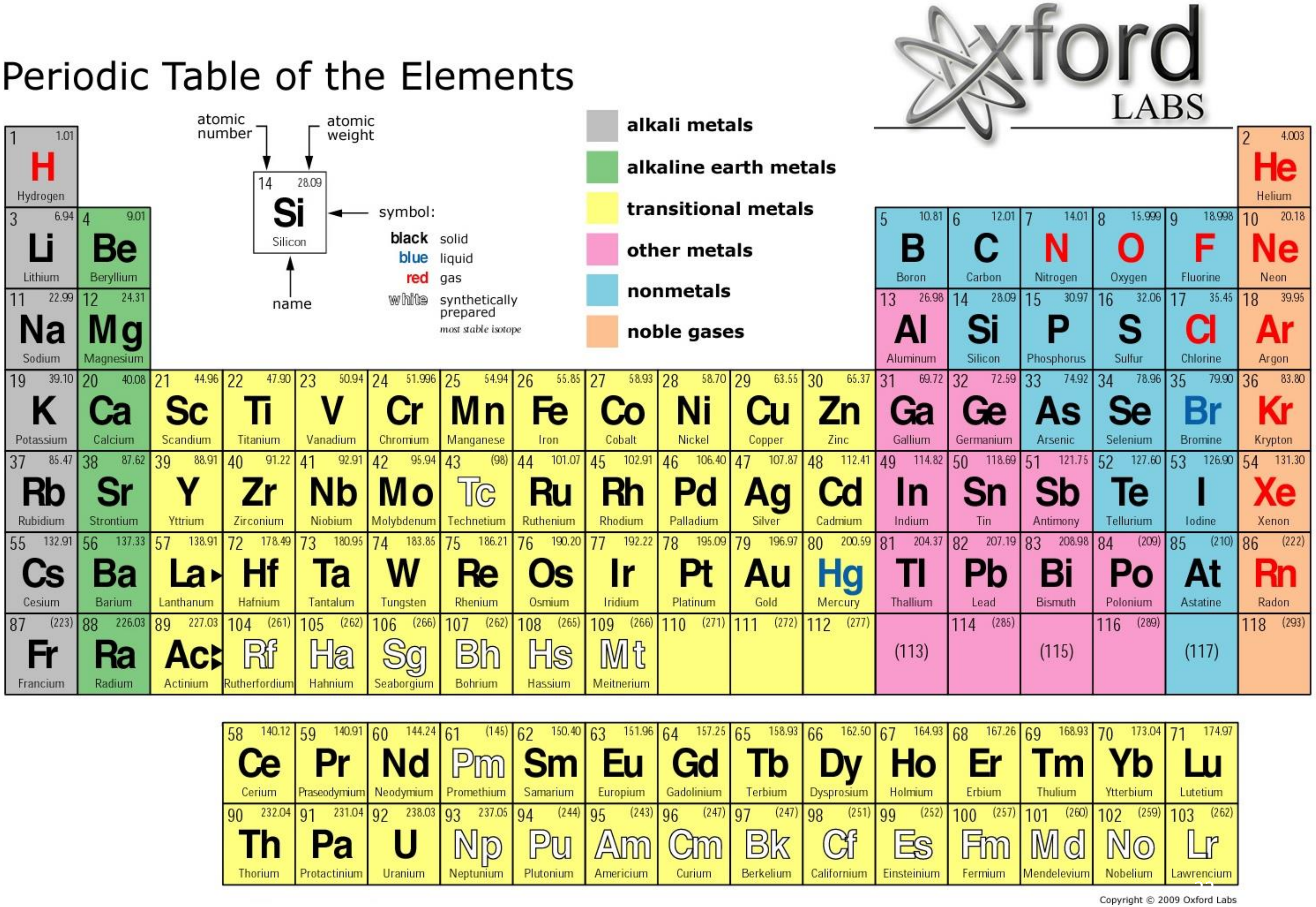
Environment (breaking orbital degeneracy)

Crystal field (CF):

- ➢Electrostatic interaction with electrons in surrounding ions. The medium is not isotropic: it has the symmetry of the crystal or magnetic molecule. It can be affected at surfaces and interfaces.
- ➢More important for less confined electrons.

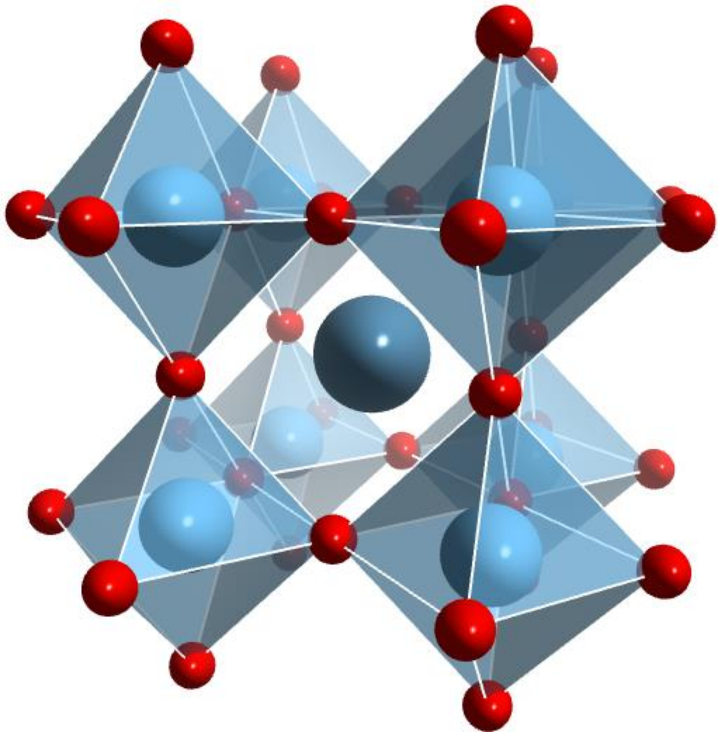
d electrons:
Large CF
Small SO



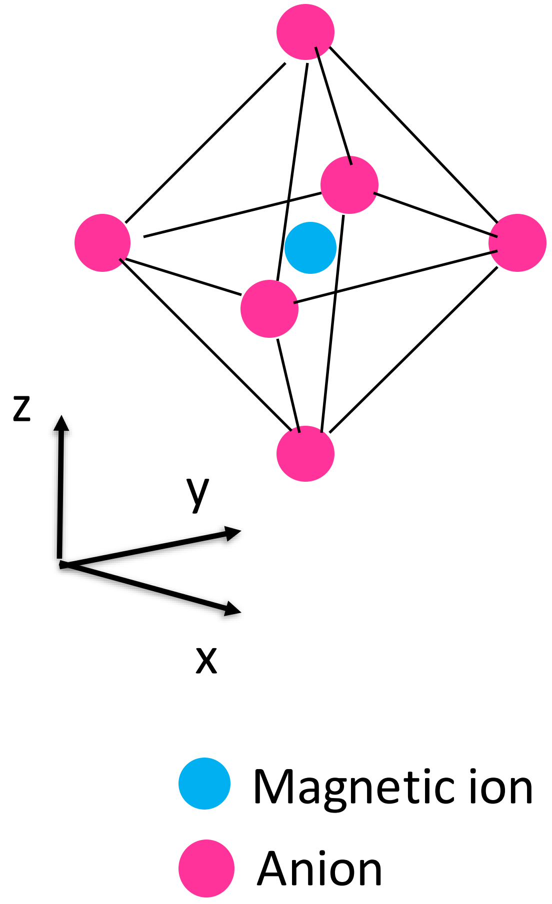
f electrons:
Small CF
Large SO

Crystal field

d-electrons in cubic symmetry
(perovskite structure)



ABO_3



Crystal field

d-electrons in cubic symmetry
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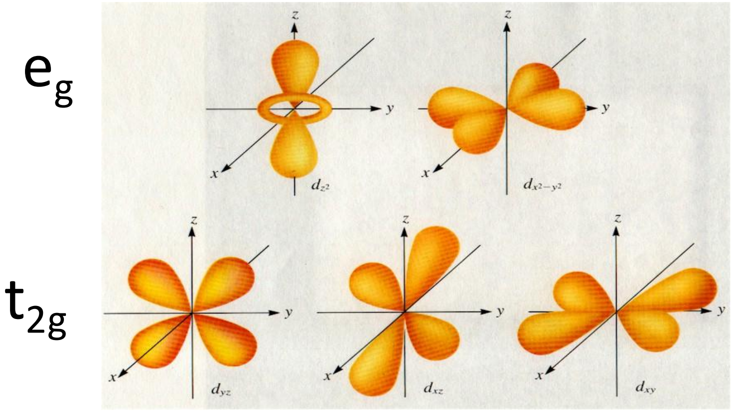
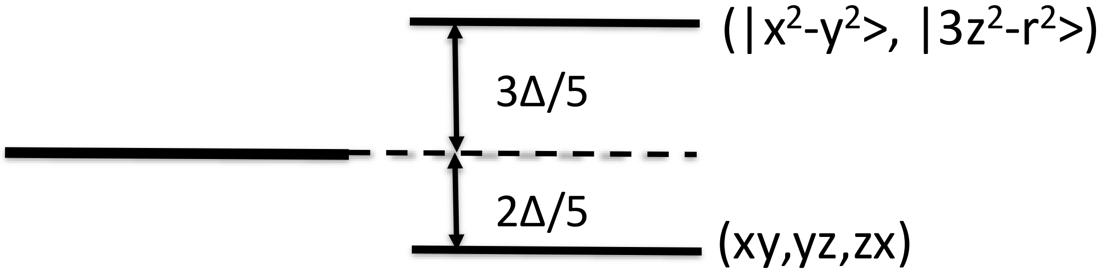
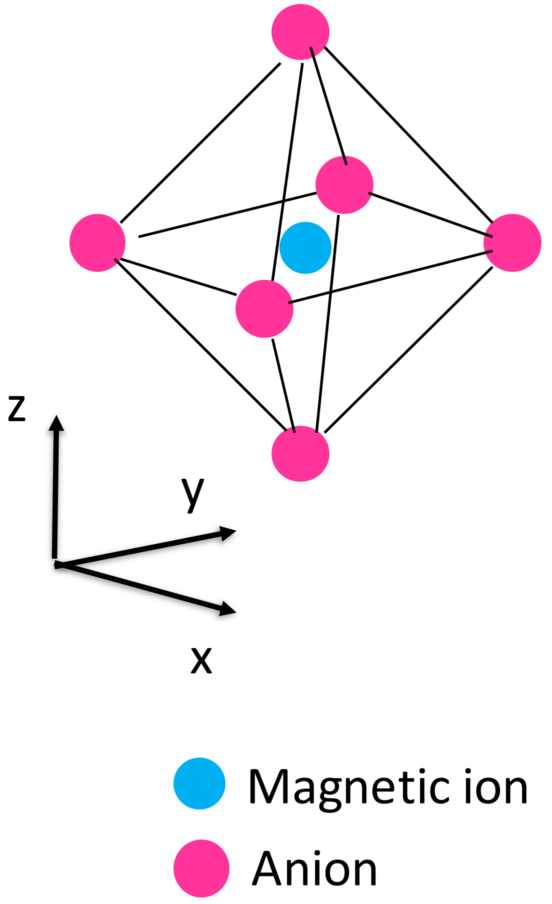


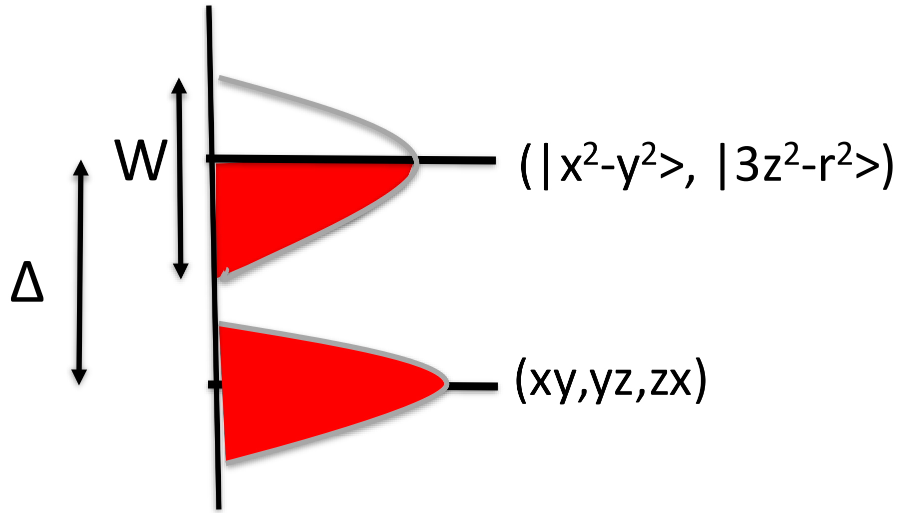




Crystal field

d-electrons in cubic symmetry
(perovskite structure)

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



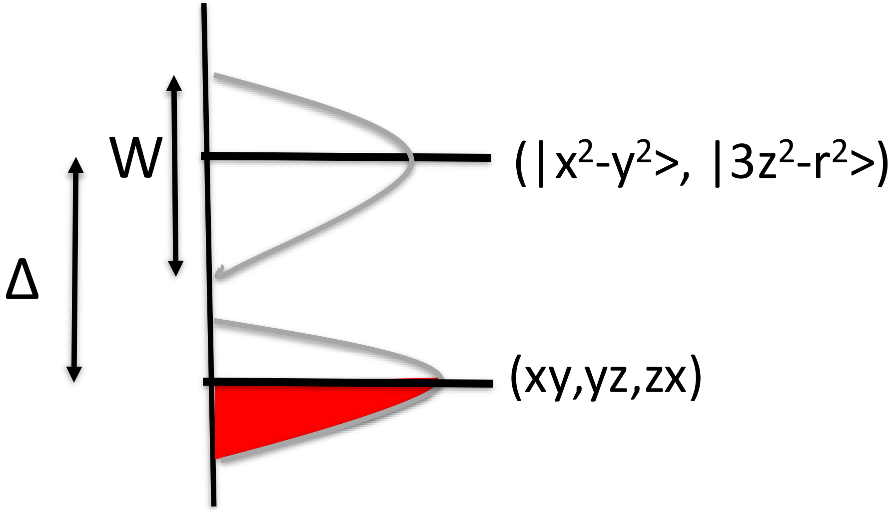
Manganites $La_xSr_{1-x}MnO_3$
e_g orbitals at E_F
(t_{2g} localized)

ENVIRONMENT

Crystal field

d-electrons in cubic symmetry
(perovskite structure)

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

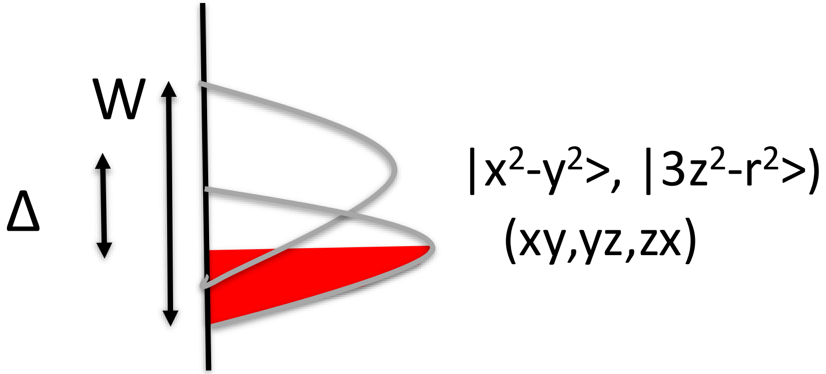


Doped $SrTiO_3$
t_{2g} orbitals at E_F

Crystal field

d-electrons in cubic symmetry
(perovskite structure)

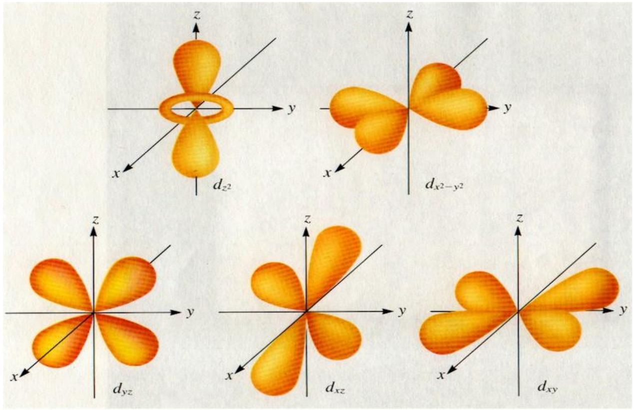
If the splitting Δ is small compared to the bandwidth W.

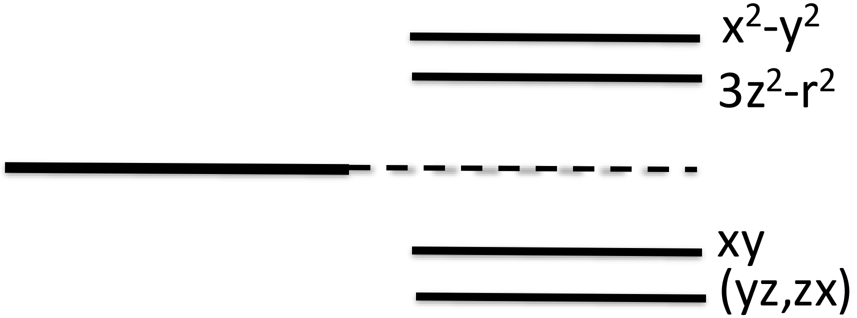


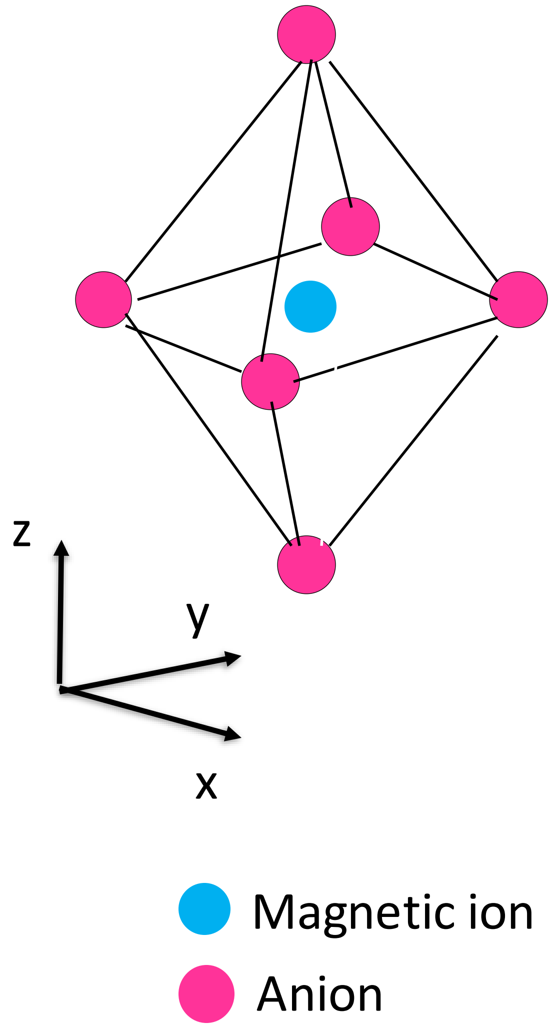
All d-orbitals at E_F

Crystal field

d-electrons in tetragonal symmetry
(perovskite structure)







ENVIRONMENT

Which orbitals are at E_F is important to determine the bands in the model.

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

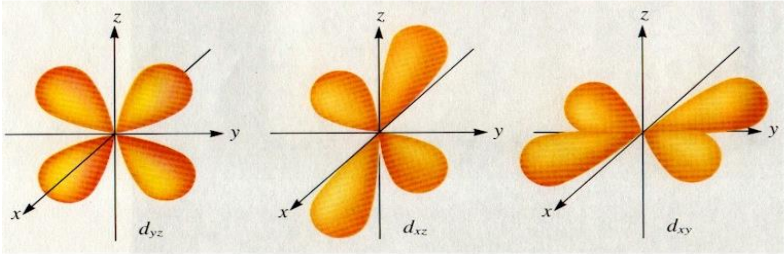
l, m, n are
cosine directors

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

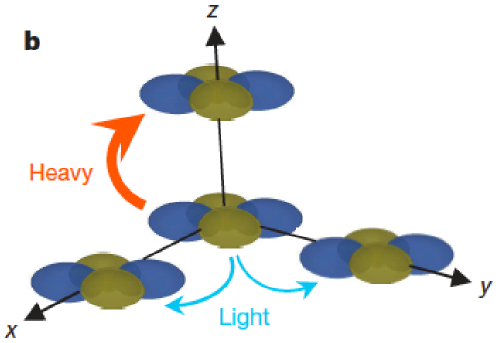
Slater and Koster, Phys. Rev. 94, 1498 (1954)

ENVIRONMENT

For t_{2g} orbitals:



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



Nature 469, 189 (2011)

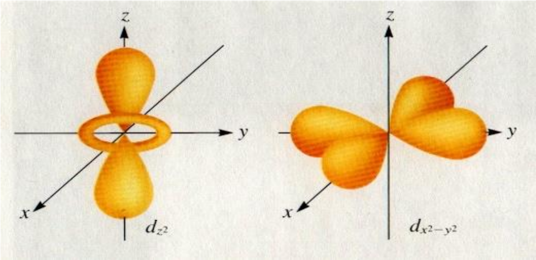
$$t^{x}_{xy,xy} = t^{y}_{xy,xy} = t^{z}_{zx,zx} = t^{x}_{zx,zx} = t^{y}_{yz,yz} = t^{z}_{yz,yz}$$

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

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

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

For e_g orbitals:



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

$$t^{x,y}_{3z^2-r^2,3z^2-r^2} = 1/4t \qquad t^{x,y}_{x^2-y^2,x^2-y^2} = 3/4t \qquad t^{x,y}_{x^2-y^2,3z^2-r^2} = \pm\sqrt{3}/4t$$

$$t^{z}_{3z^2-r^2,3z^2-r^2} = t \qquad t^{z}_{x^2-y^2,x^2-y^2} = 0 \qquad t^{z}_{x^2-y^2,3z^2-r^2} = 0$$

e_g orbitals mix.

x^2-y^2

$3z^2$-r^2

For cuprates, further splitting (tetragonal)

Cu (9±x) electrons.

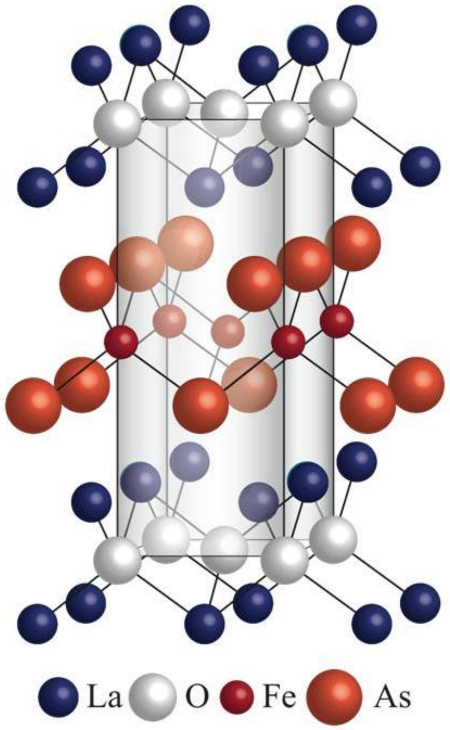
xy

(yz,zx)

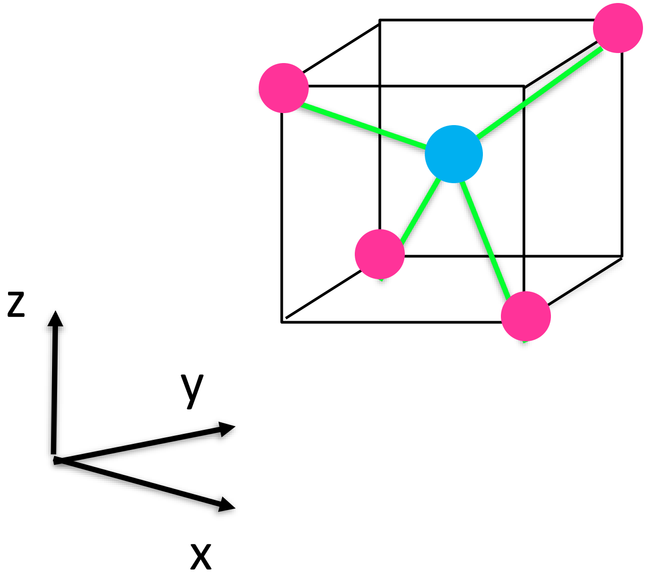
Carriers on x^2-y^2: 2dim band

Crystal field

d-electrons in a tetrahedral symmetry



Crystal structure of an Fe superconductor

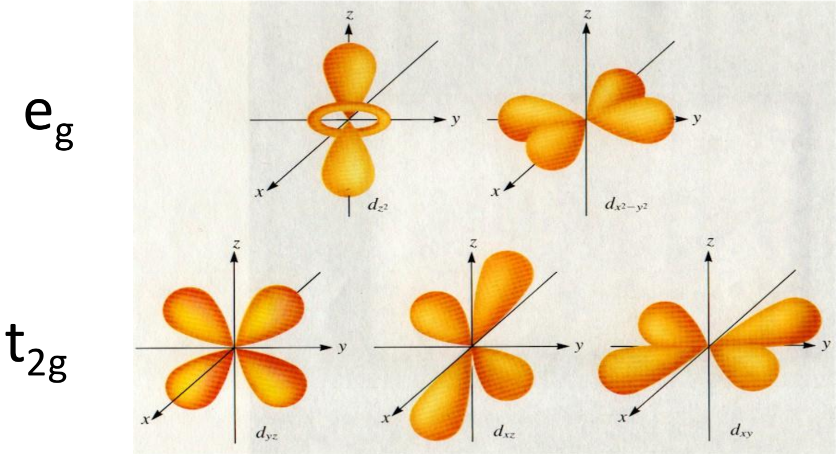


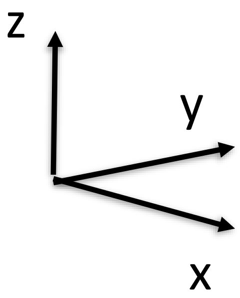
Magnetic ion

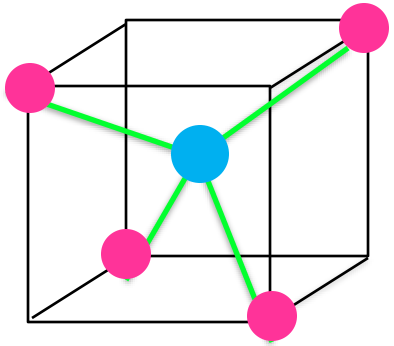
Anion

Crystal field

d-electrons in a tetrahedral symmetry

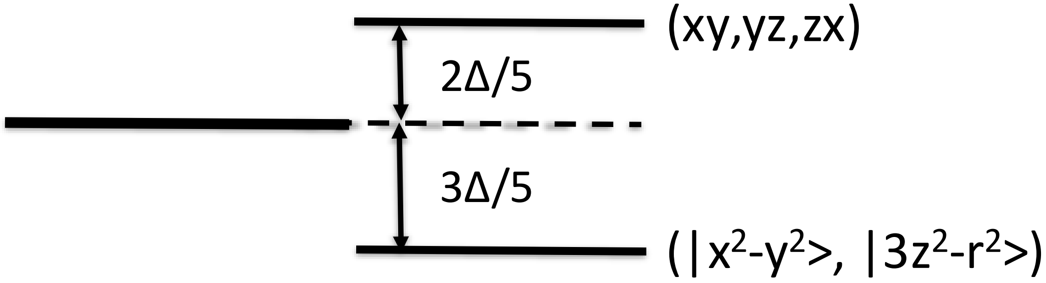






Magnetic ion

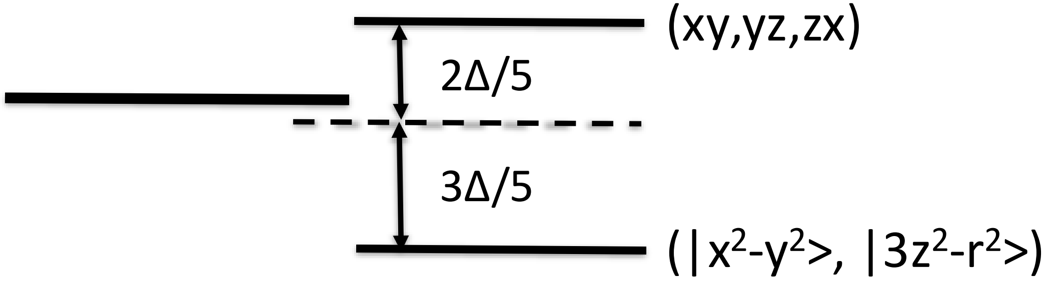
Anion

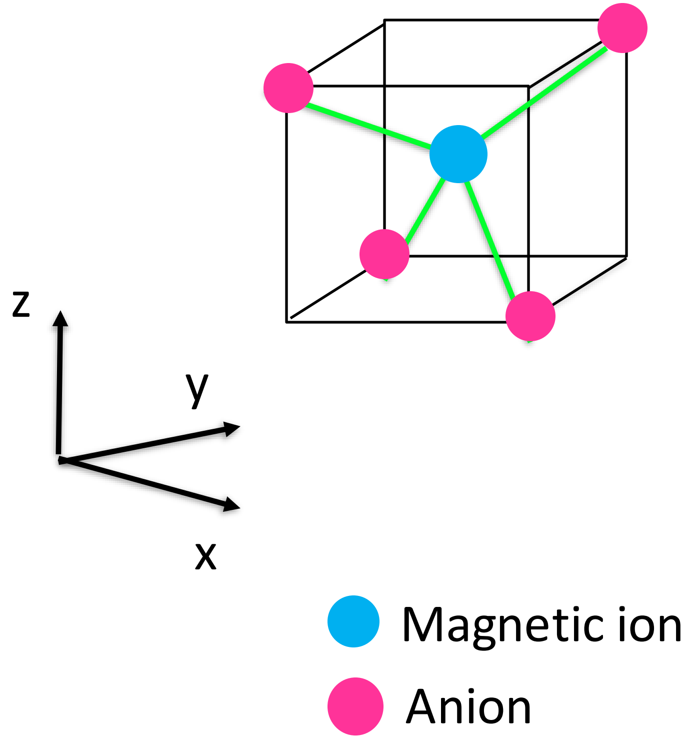


Crystal field

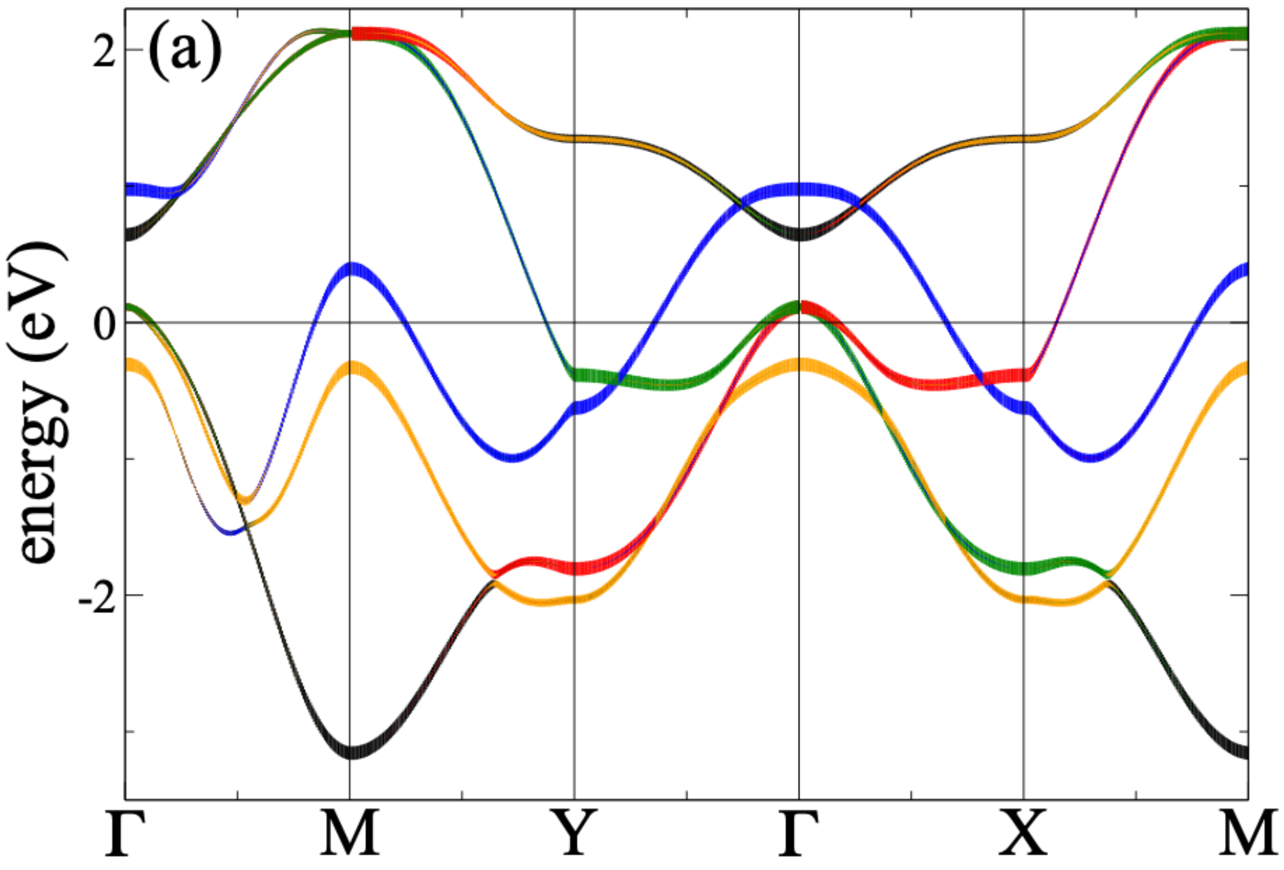
d-electrons in a tetrahedral symmetry

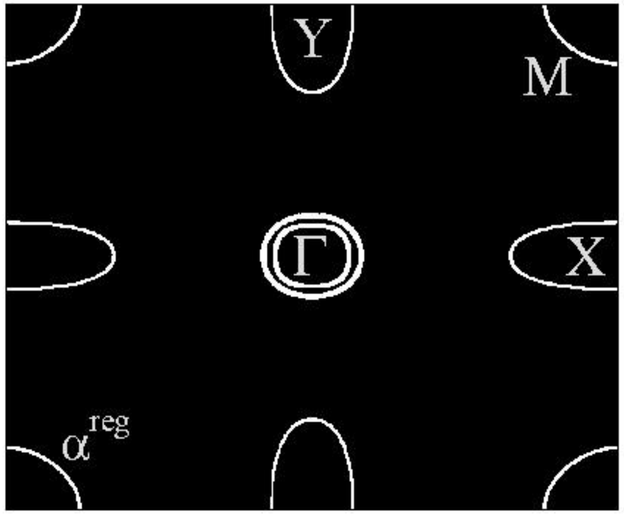
In iron superconductors, the splitting Δ is small compared to the bandwidth so all five orbitals contribute at E_F





d-bands for iron superconductors





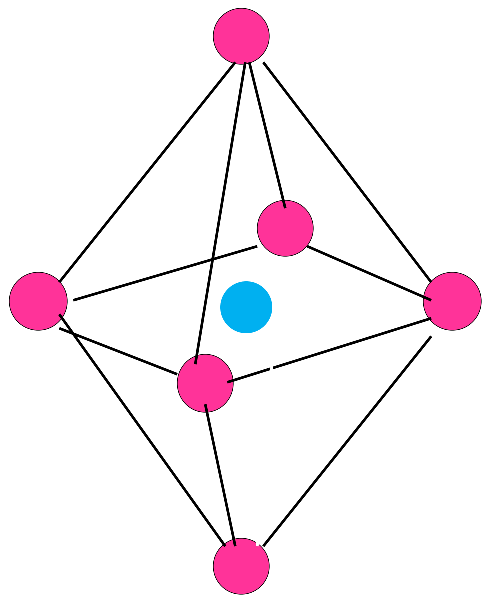
PRB 87, 075136

ENVIRONMENT

Also change the crystal field and lead to orbital splittings:

- strain in thin films
- the presence of interfaces
- surfaces
- pressure

E.g. on a surface:



Environment

Orbital “selection”

anisotropies

Crystal field. Calculation (sketch)

Treat surrounding ions as point charges

Atomic charges

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

Atomic positions

…expand for r<R
and rewrite as a function of spherical harmonics.

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

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

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 wave-functions $\langle r^n \rangle$

The results depend on the number of electrons

Yosida, Chapter 3.

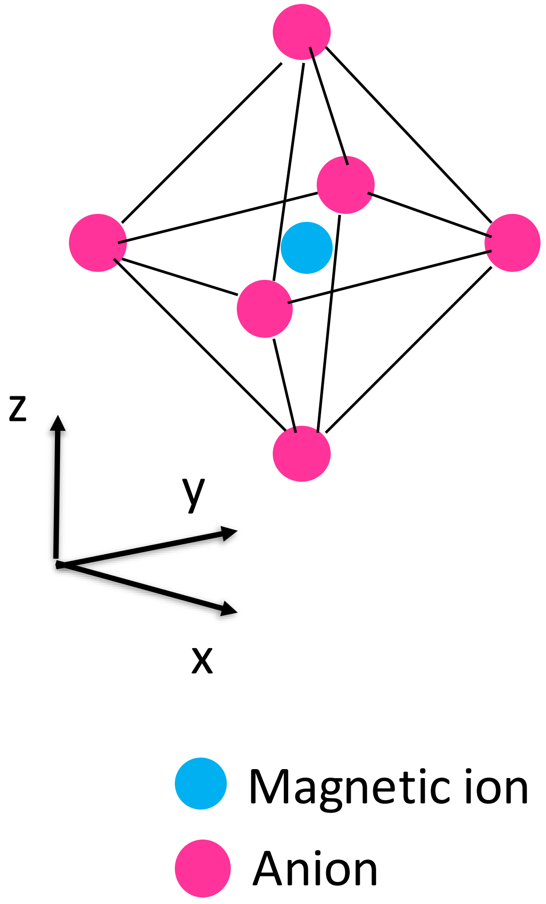
Jahn-Teller distortion

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

For a cubic perovskite lattice. Crystal field:

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

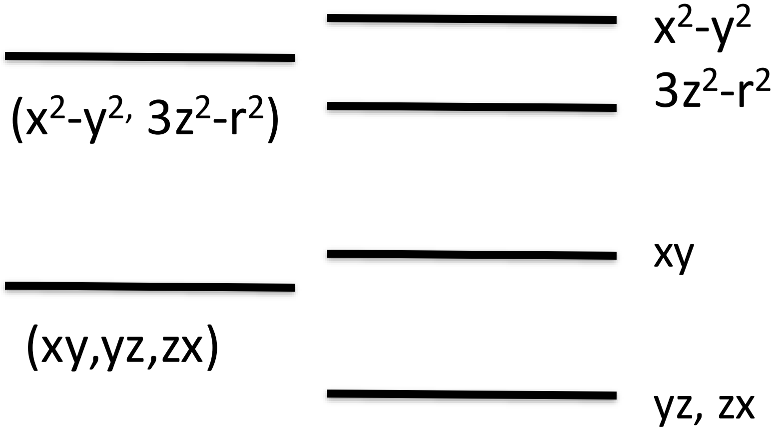
(xy,yz,zx)

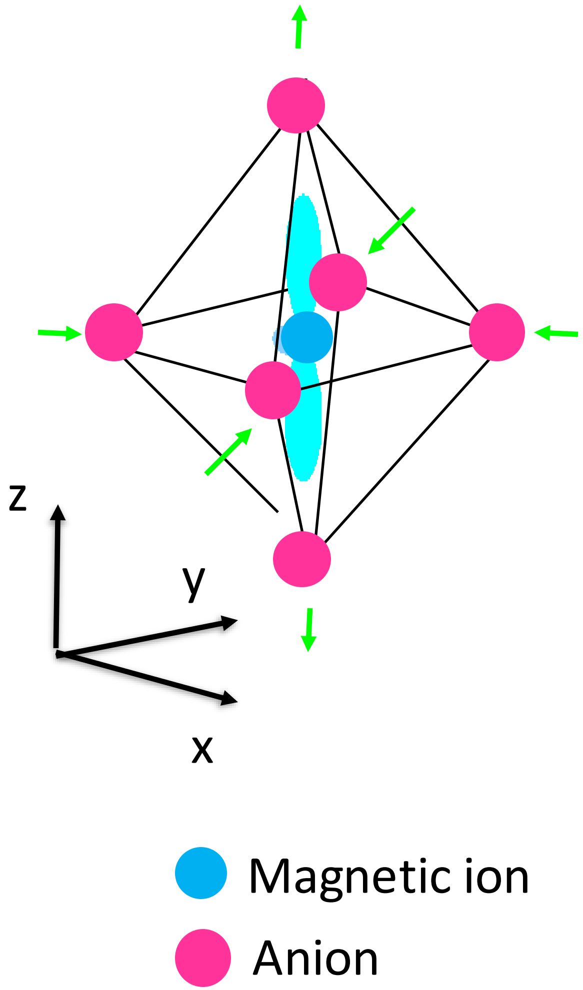


Jahn-Teller distortion

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

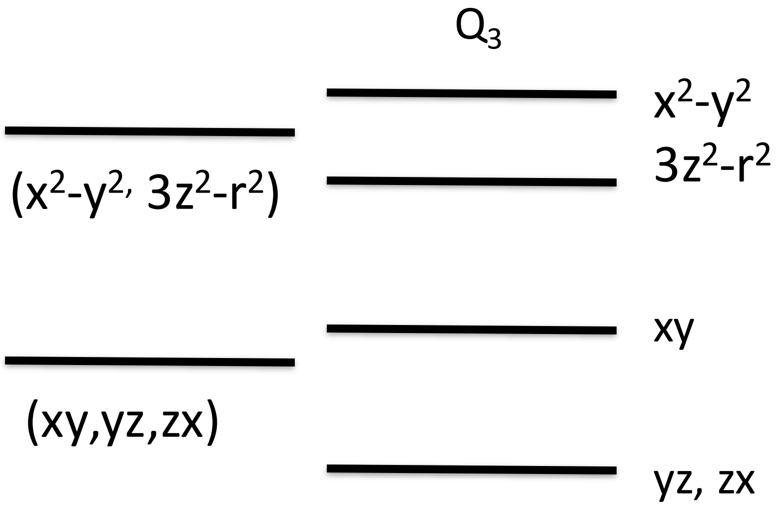
For a cubic perovskite lattice: Crystal field:

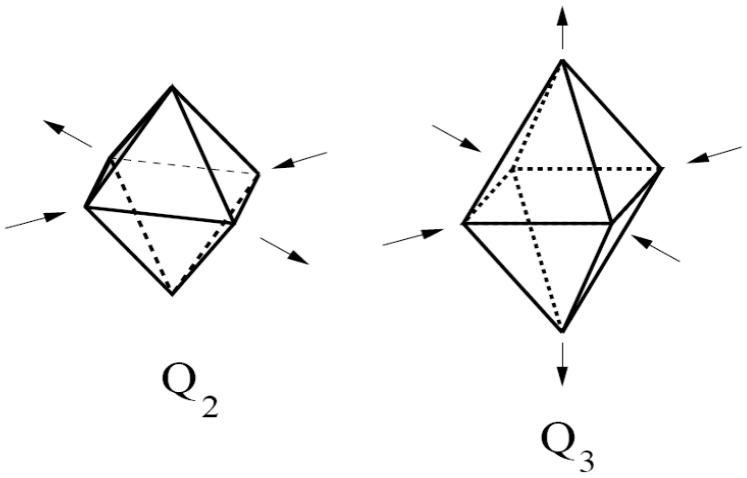




Jahn-Teller distortion

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

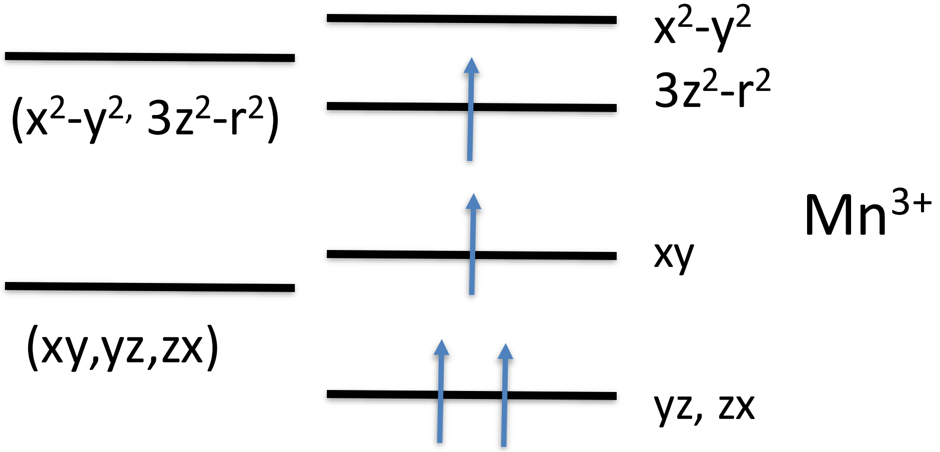




ENVIRONMENT

Jahn-Teller distortion

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



Electronic energy

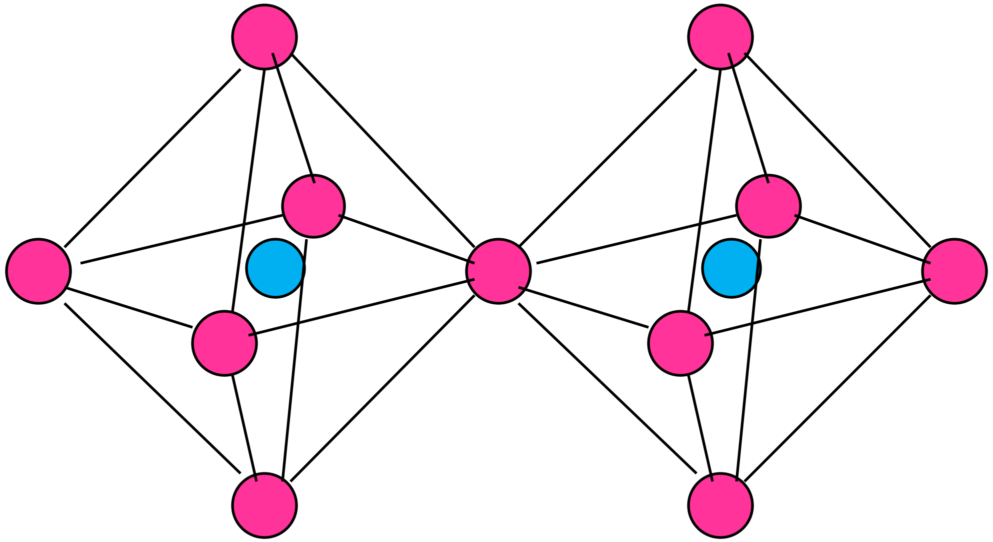
$$E = \pm AQ + \frac{1}{2}M\omega^2Q^2$$

Elastic energy

However, for Mn^{2+} or Mn^{4+} →no energy gain by the splitting → no distortion.

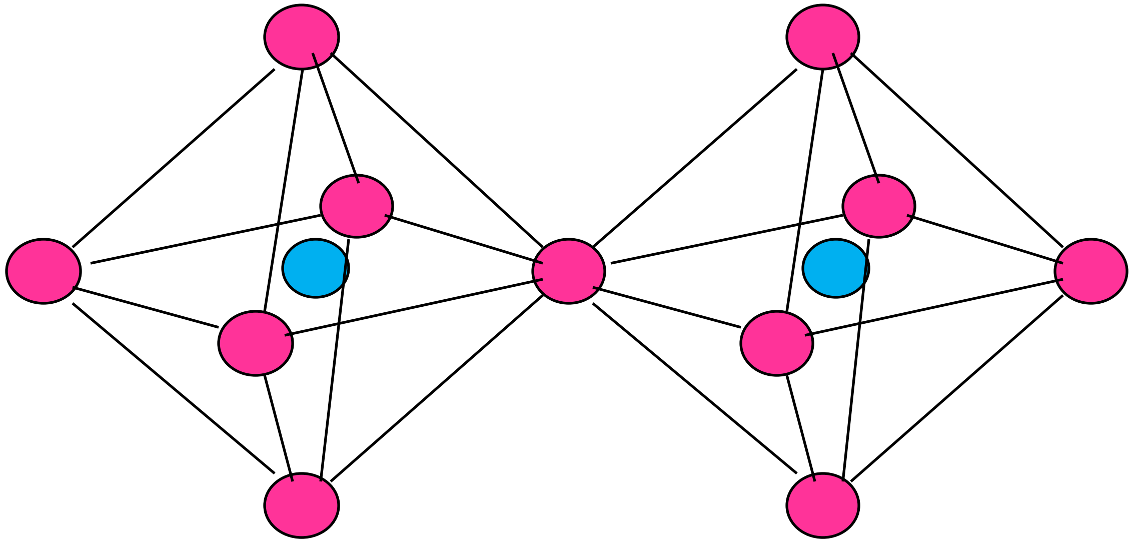
ENVIRONMENT

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

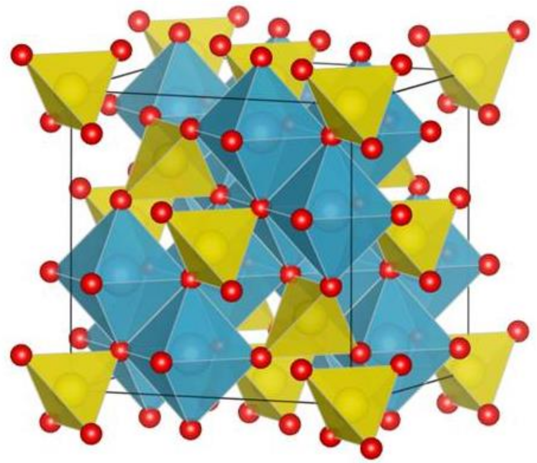


ENVIRONMENT

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

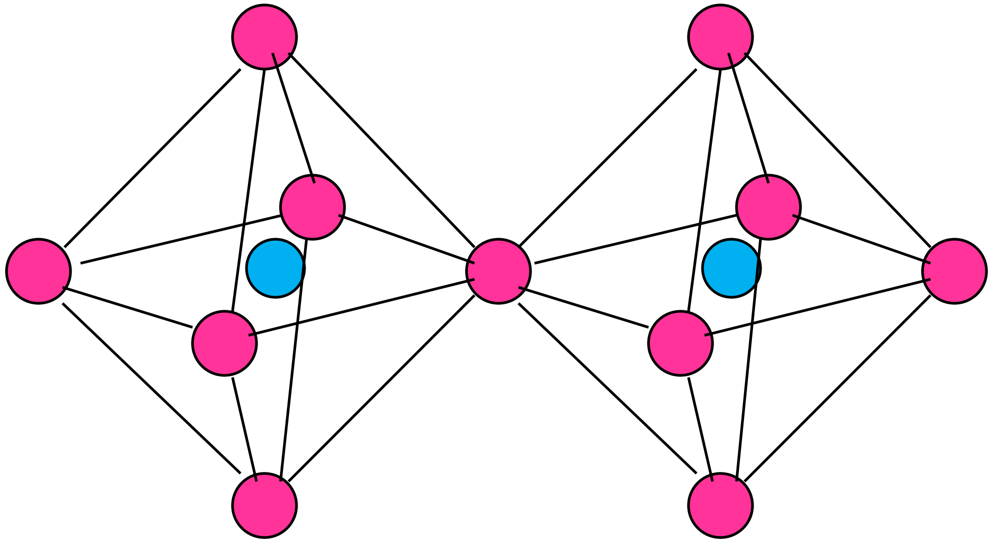


Cubic to tetragonal transitions:
$LaMnO_3$ (T_s=800K). Perovskite.
$CuFe_2O_4$ (T_s=713K). Spinel.
Mn_3O_4 (T_s=1443K). Spinel.

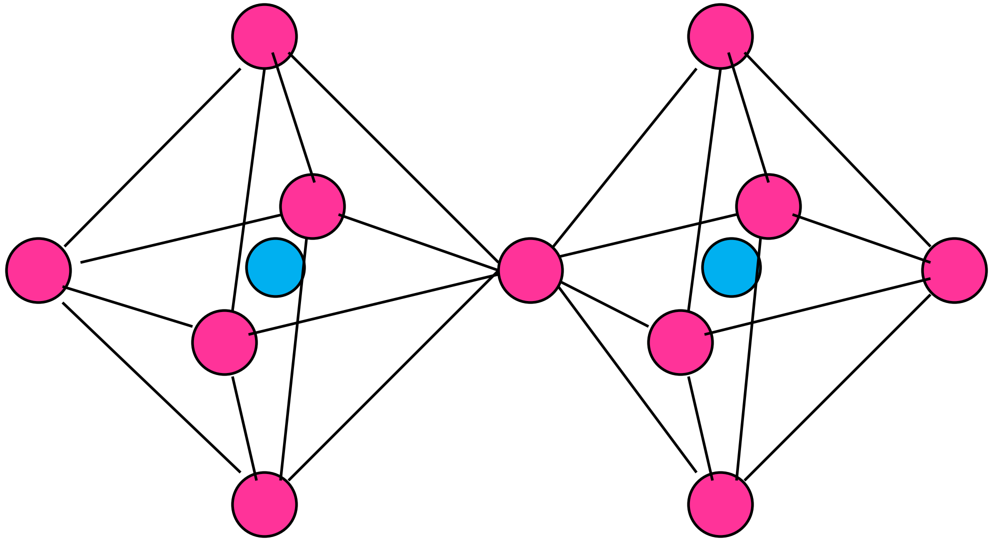


Spinel structure

Jahn-Teller distortions are cooperative. They may lead to orbital order

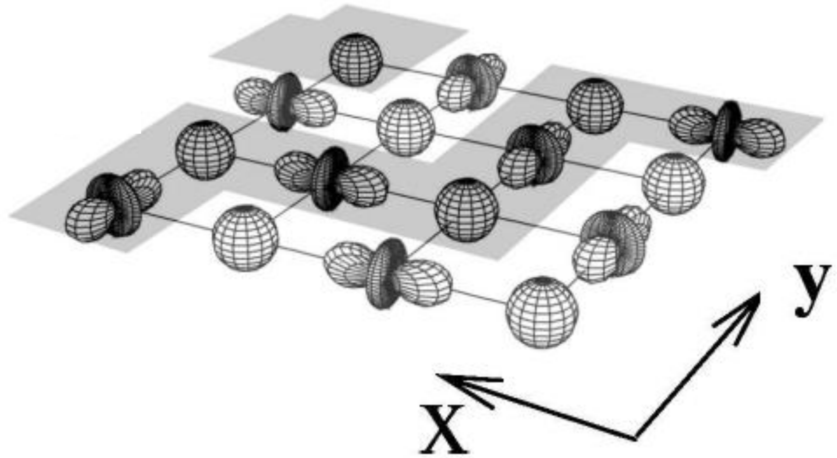


Jahn-Teller distortions are cooperative.
They may lead to orbital order



Jahn-Teller distortions are cooperative.
They may lead to orbital order

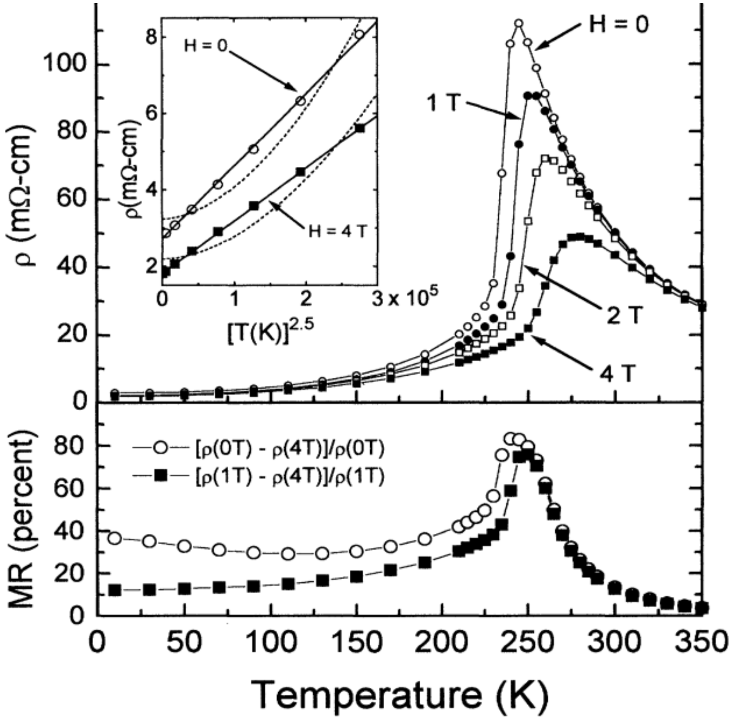
Orbital order in manganites
(0.5 e- per Mn)



Salafranca et al, PRB (2008)

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

At high temperatures:
dynamic Jahn-Teller effect



Manganites
PRL 75, 3336

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

ENVIRONMENT

Magnetic atoms/ions

Ground state (GS) selection: Hund's rules

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

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

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

$^{2S+1}L_J$

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

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

m_l	
=2	↑
1	↑
0	↑
-1	↑
-2	

S=2

L=2

J=|L-S|=0

$^3D_0$

$\mu_{\text{eff}}=0$

Orbital quenching

Assume L=0 for (3d) ions

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

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

With L=0, for $(3d)^4$ we would get μ_{eff}=4.89 μ_B
(experimentally μ_{exp}=4.82 μ_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 non degenerate and L=0. Why?

<GS|L|GS> must be real

L is purely imaginary

Non-degenerate

GS is real

(is an eigenfunction of the crystal field)

<GS|L|GS> =0

Orbital quenching

NOTE

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

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 zero L. 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

Van Vleck orbital PM

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

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

$g_{\mu\nu}/2$

Induced orbital moment

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

Anisotropy spin Hamiltonian

Spin-orbit coupling for d-atoms

The anisotropy spin Hamiltonian can be written:

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

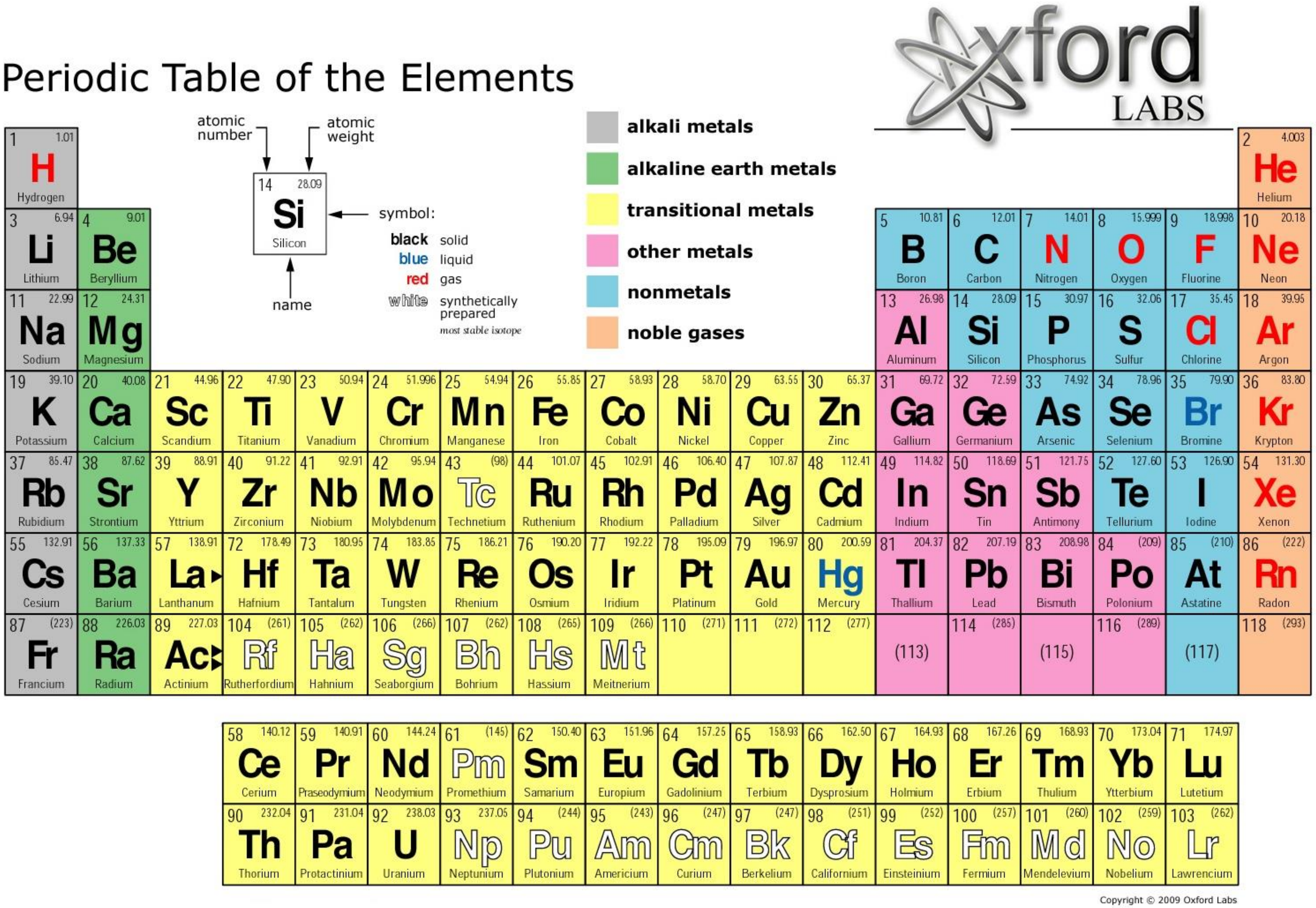
- H lifts the (2S+1) degeneracy.
- The first term:
  - For integer S, splitting into doubly degenerate S_z=±S, ±(S-1)… ±1, and non-degenerate 0.
  - For half-integer S, splitting into doubly degenerate S_z=±S, ±(S-1)… ±1/2.
- S_x^2 and S_y^2 produce transitions ΔS_z=±2. Therefore the second term further splits the levels for integer S.
- For half integers (ΔS_z=±2 can't connect $\pm S$): 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

- The crystal field is weak.
- Due to large SO coupling, total angular momentum is relevant.
- Ground state is (2J+1) degenerate (third Hund’s rule).
- In principle J could be quenched but, due to small crystal field, an external magnetic field or an exchange field can change the relative position of the levels.

ENVIRONMENT

L=0 (orbital quenching)
S relevant



SO coupling
J relevant

Three energy scales to determine local moments in a solid

Crystal field (environment)

Spin-orbit coupling

Hund’s coupling (local exchange)

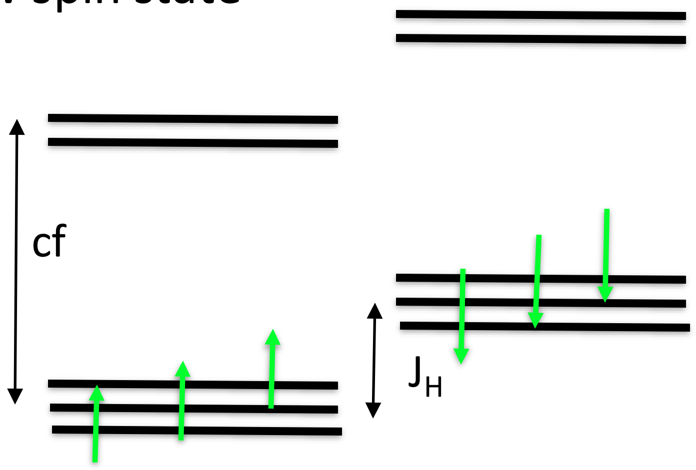
$\Downarrow$

Spin splitting

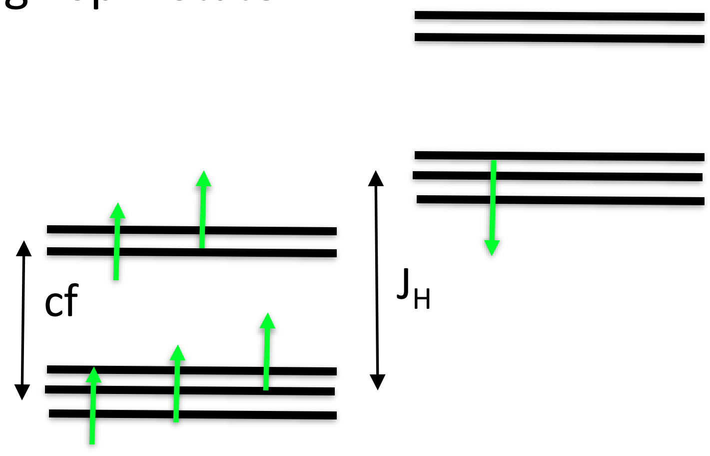
Crystal field vs Hund's coupling

$3d^6$

Low spin state



High spin state



Crystal field > J_H

Crystal field < J_H

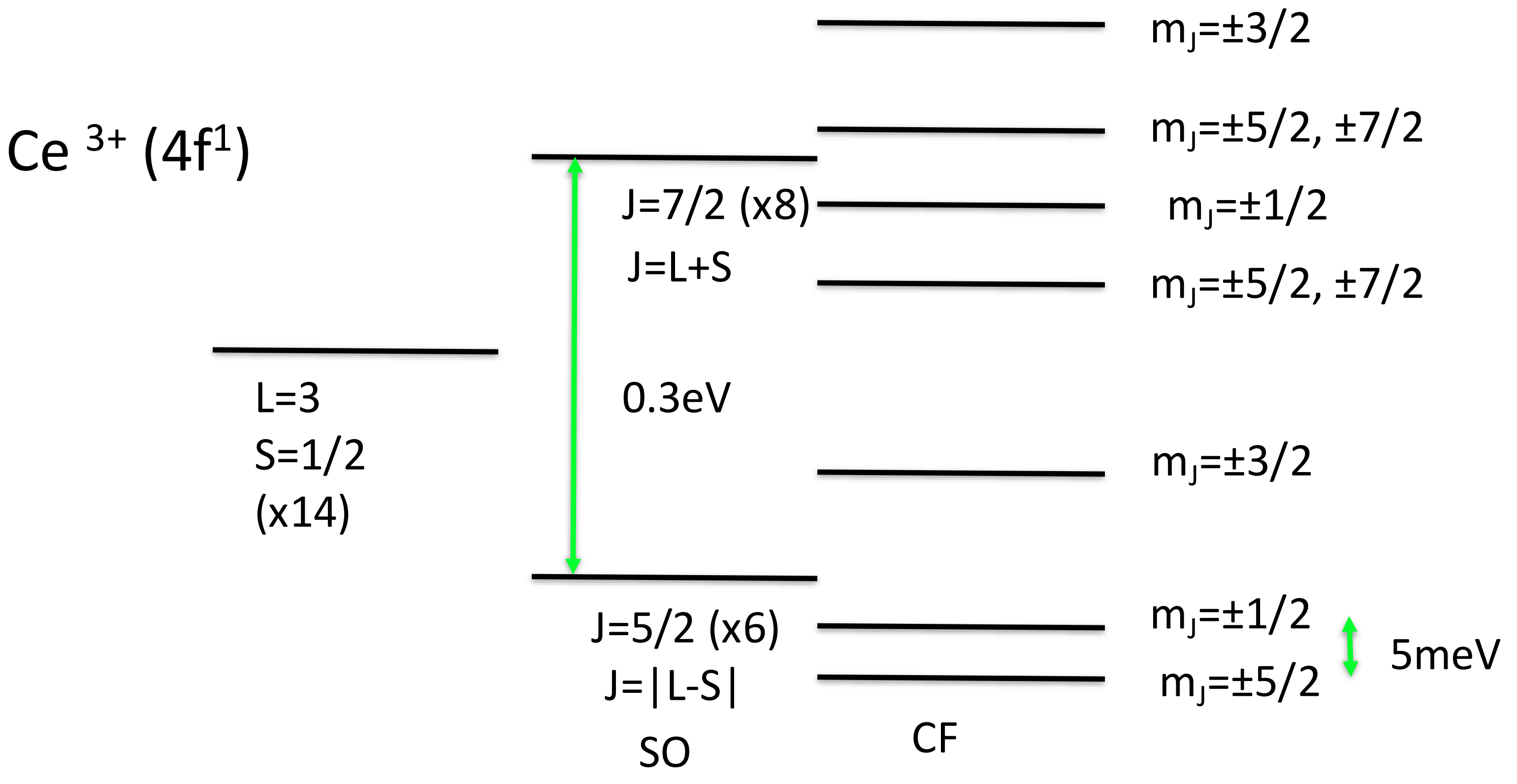
S=0

S=2

Crystal fields may be changed with pressure

Crystal field vs spin-orbit coupling

3d ions: crystal-field >> spin-orbit coupling
4f and 5f ions: crystal-field << spin-orbit coupling

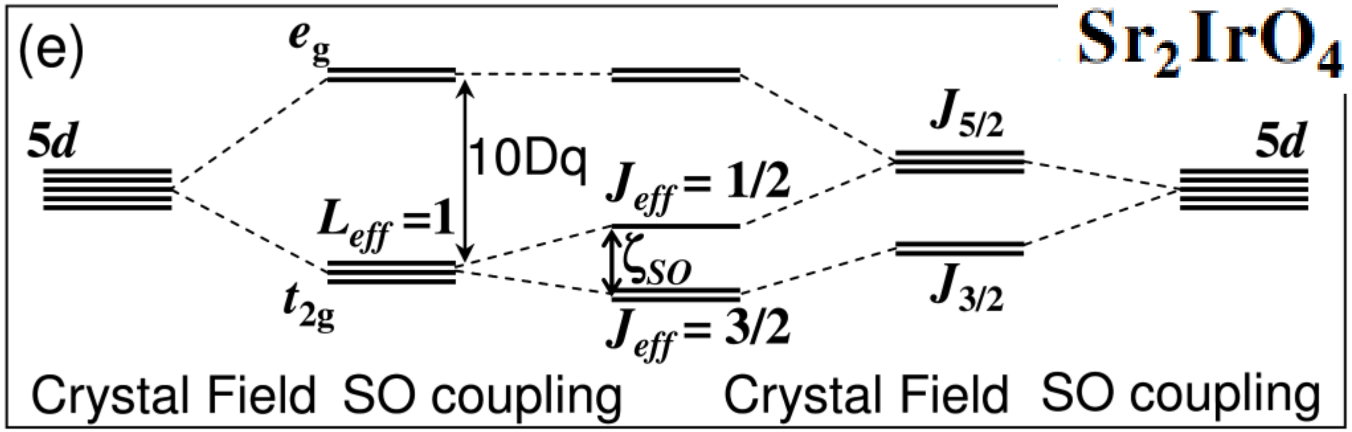


Crystal field vs spin-orbit coupling

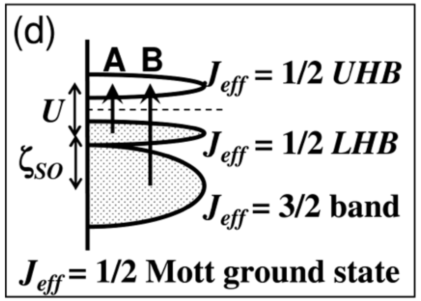
3d ions: crystal-field >> spin-orbit coupling

4f and 5f ions: crystal-field << spin-orbit coupling

4d-5d: crystal-field ≈ spin-orbit coupling



$5d^5$



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 >> spin-orbit coupling
  - orbital quenching (L=0)
- Crystal field vs Hund’s coupling: low spin-high spin

4f-5f:

- Crystal field << spin-orbit coupling
- Large total magnetic moments J

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

OUTLINE

- Free magnetic moments
- Environment
- Magnetic order and susceptibility
- Interactions
  - Between localized moments
  - Localized moments + itinerant electrons
  - Itinerant electrons
- 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

$$\chi_{ij} = \frac{(g\mu_B)^2}{k_B T}\left(\langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle\right)$$

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

$$H = \sum_i \left(\frac{[\vec{p}_i + e\vec{A}(\vec{r}_i)]^2}{2m_e} + V_i \right) + g\mu_B \vec{B} \cdot \vec{S} =$$

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

Paramagnetic term. $\chi > 0$

A magnetic field aligns local magnetic moments J

$$\vec{A}(\vec{r}) = \frac{\vec{B} \times \vec{r}}{2} \qquad \hbar\vec{L} = \sum_i \vec{r}_i \times \vec{p}_i$$

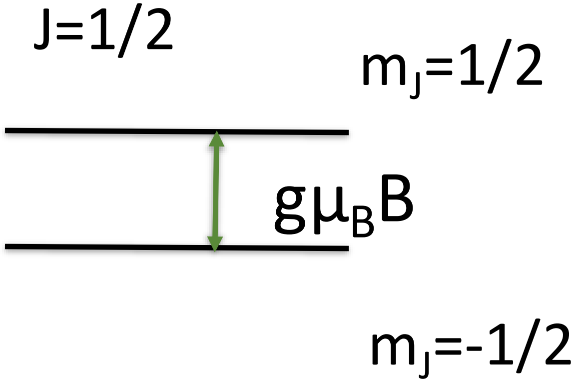
Paramagnetic susceptibility

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

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



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)

$$H = \sum_i \left(\frac{[\vec{p}_i + e\vec{A}(\vec{r}_i)]^2}{2m_e} + V_i \right) + g\mu_B \vec{B} \cdot \vec{S} =$$

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

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

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

$$M = -\frac{\partial F}{\partial B} = -\frac{N}{V} \frac{\partial \Delta E_0}{\partial B} = -\frac{N e^2 B}{6 m_e V} \sum_i \langle r_i^2 \rangle$$

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

- r is the ionic radius
- Independent of T

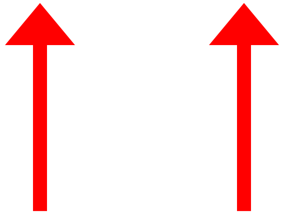
Now let the magnetic moments interact…

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.

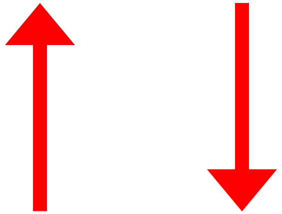
Given a pair of magnetic moments, they can interact ferromagnetically (FM) or antiferromagnetically (AF).

Ferromagnetic (FM) exchange:



$$-J\vec{S}_1\vec{S}_2 \quad (J > 0)$$

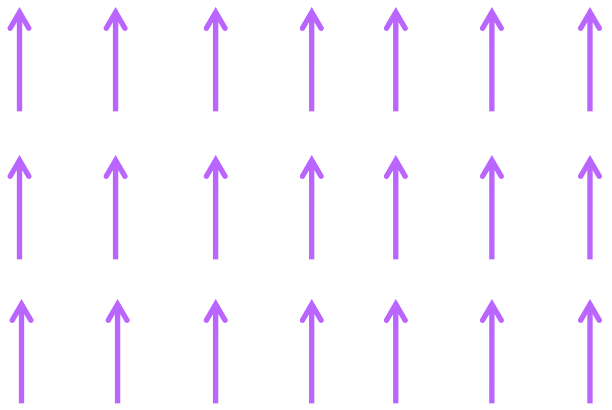
Antiferromagnetic (AF) exchange:



$$-J\vec{S}_1\vec{S}_2 \quad (J < 0)$$

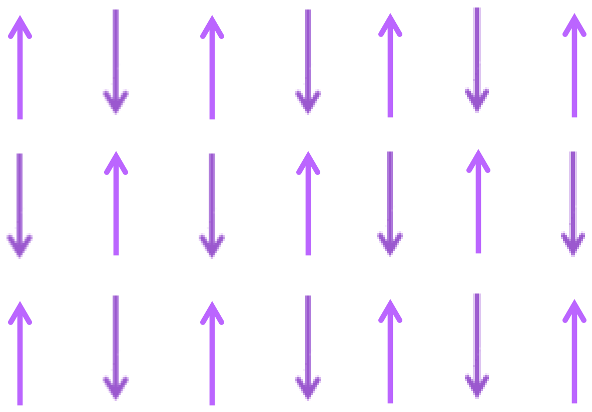
Different orders

Ferromagnetism FM



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

Antiferromagnetism AF



Néel order (bipartite lattice)

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

$M_{st}=\langle\Sigma_A S^z\rangle-\langle\Sigma_B S^z\rangle$

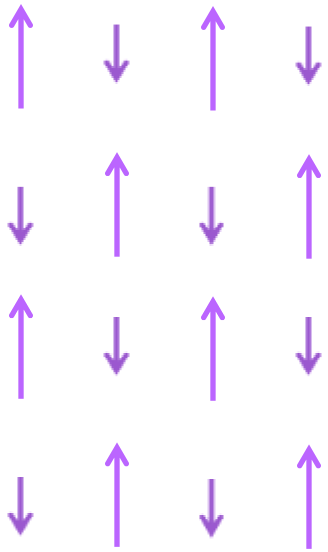
Altermagnetism

- ✓ M=0 (as AF)
- ✓ Broken time-reversal symmetry (as FM)

→ Alberto Cortijo

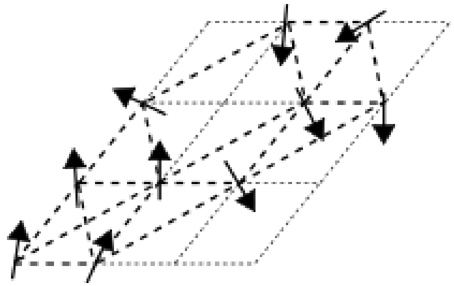
Different orders

Ferrimagnetism



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

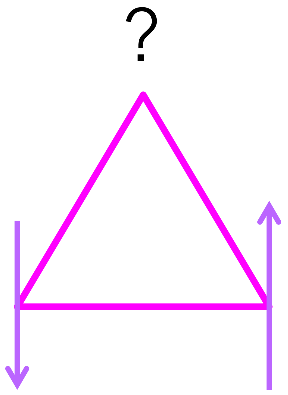
Spin glass



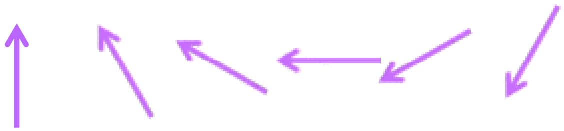
$$q = \lim_{t \to \infty} \langle \langle S_i(0) S_i(t) \rangle \rangle$$

Frustration

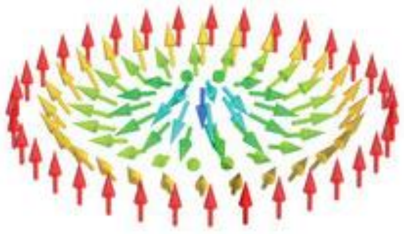
(AF Exchange in a non-bipartite lattice)



Helical

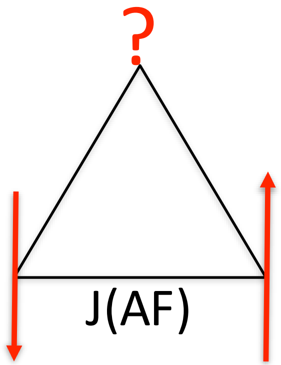


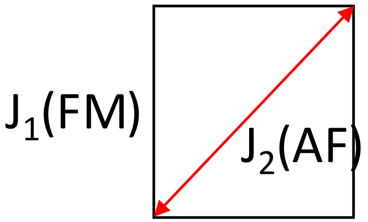
Skyrmions (topological phases)



Science 323, 915–919 (2009).

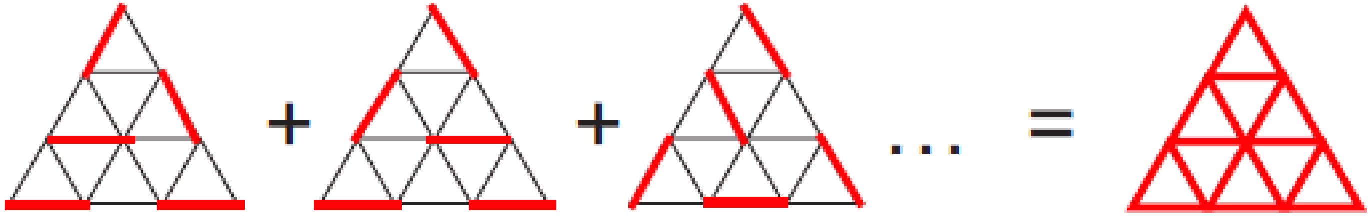
Frustration





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.



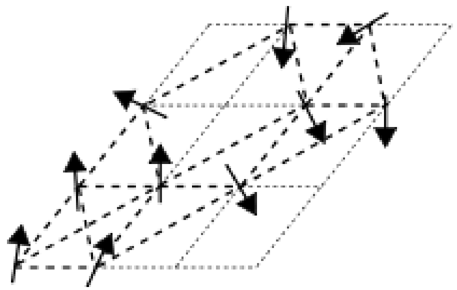
Materials Research Bulleting 8, 153 (1973)

Spin glasses

Due to randomness:

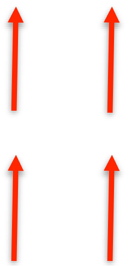
- Site randomness
- Bond randomness (between 2 different magnetic ions which are distributed randomly)
- Random magnetic anisotropies in amorphous materials.

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



Order parameter

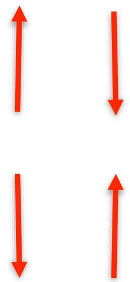
Ferromagnetism FM



Magnetization

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

Antiferromagnetism AF



Staggered magnetization

$M_{st} = \langle \Sigma_A S^z \rangle - \langle \Sigma_B S^z \rangle$

Sublattices A,B

Order parameter

Ferromagnetism FM

Magnetization

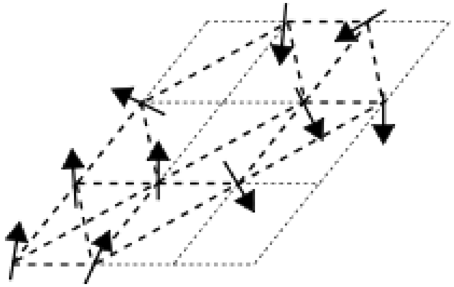
$M^z = \lim_{H\to 0} \langle S^z \rangle$

Antiferromagnetism AF

Staggered magnetization

$M_{st} = \langle \Sigma_A S^z \rangle - \langle \Sigma_B S^z \rangle$

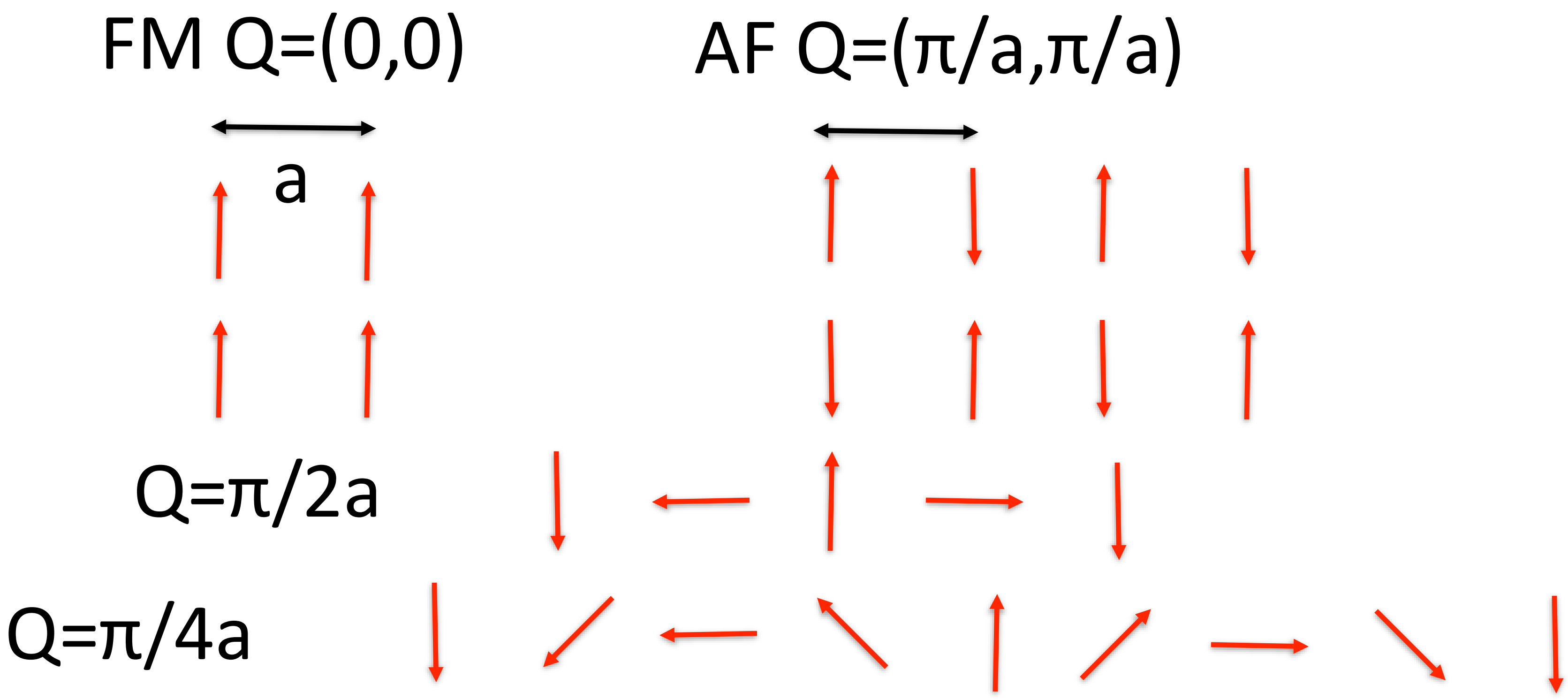
Spin glass



$$q = \lim_{t\to\infty} \langle\langle S_i(0) S_i(t) \rangle\rangle$$ freezing

Order parameter $\to 0$ at phase transitions

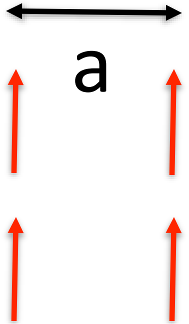
The different orders can be characterized by a wave-vector



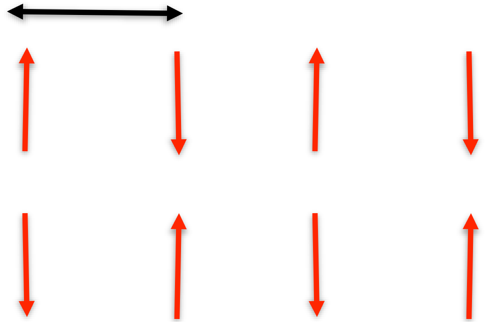
MAGNETIC ORDER

The different orders can be characterized by a wave-vector

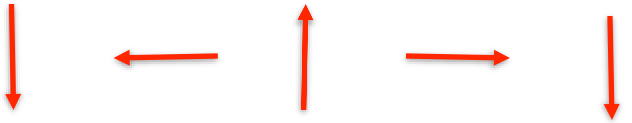
FM $Q=(0,0)$



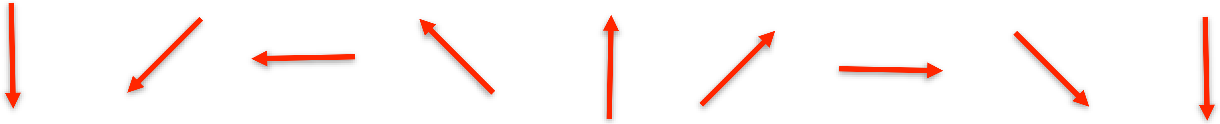
AF $Q=(\pi/a,\pi/a)$



$Q=\pi/2a$



$Q=\pi/4a$



Q can be incommensurate with the lattice

Blundell's book

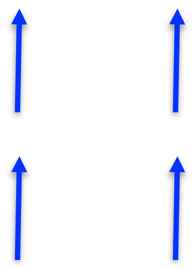
Susceptibility: FM

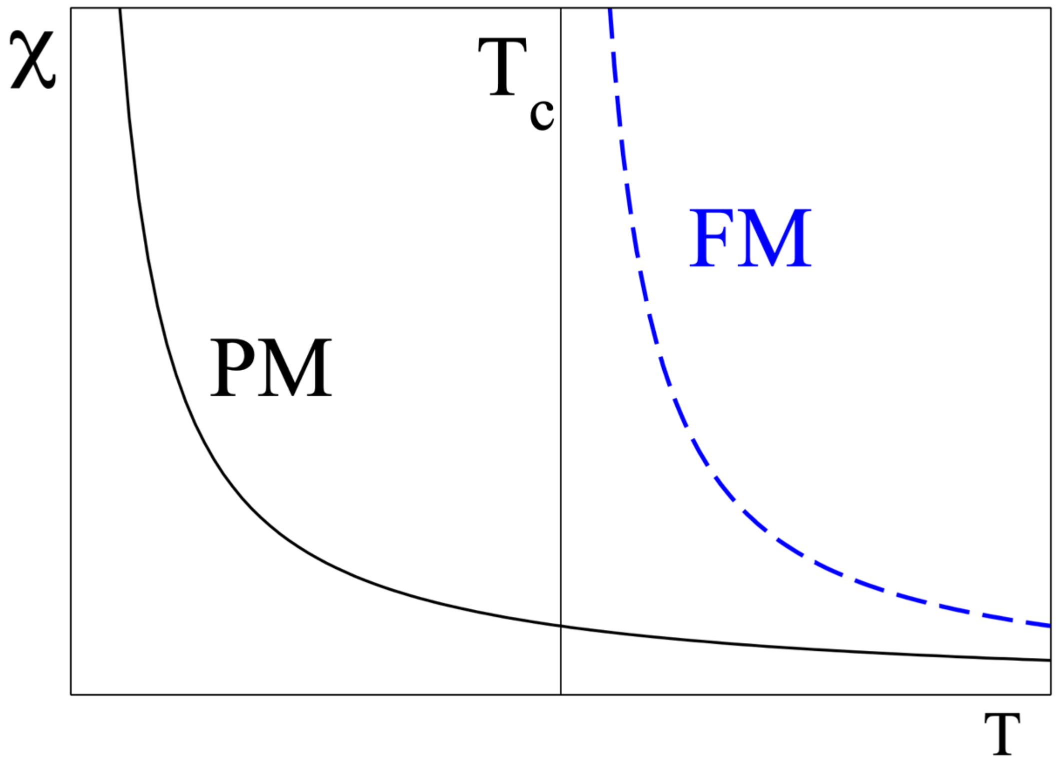
In mean field, the magnetization of a FM system produces an effective molecular field $B_{mf}=\lambda M$ (typically much larger than any applied field)

For T>Tc

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

Curie-Weiss law



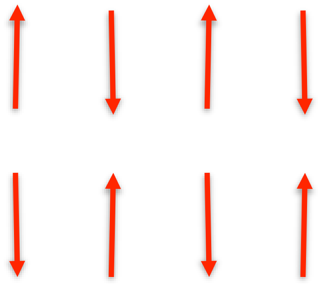


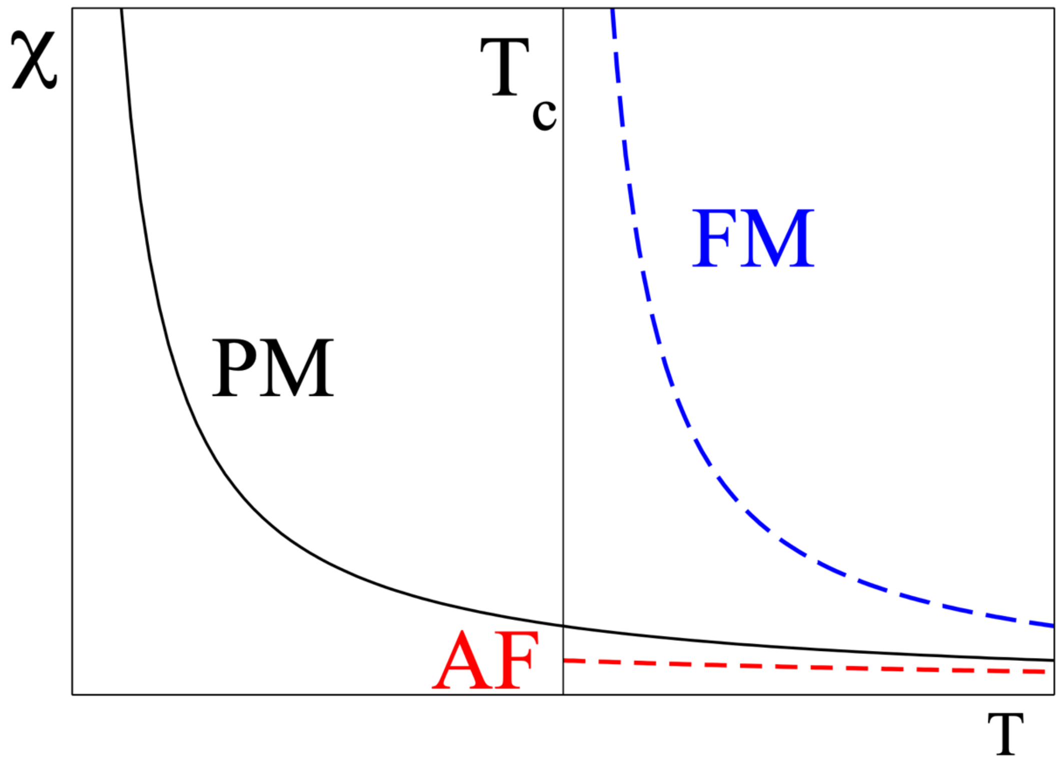
Susceptibility: AF

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

For $T>T_N$

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

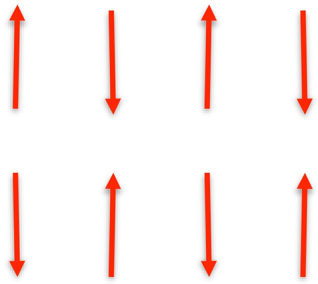


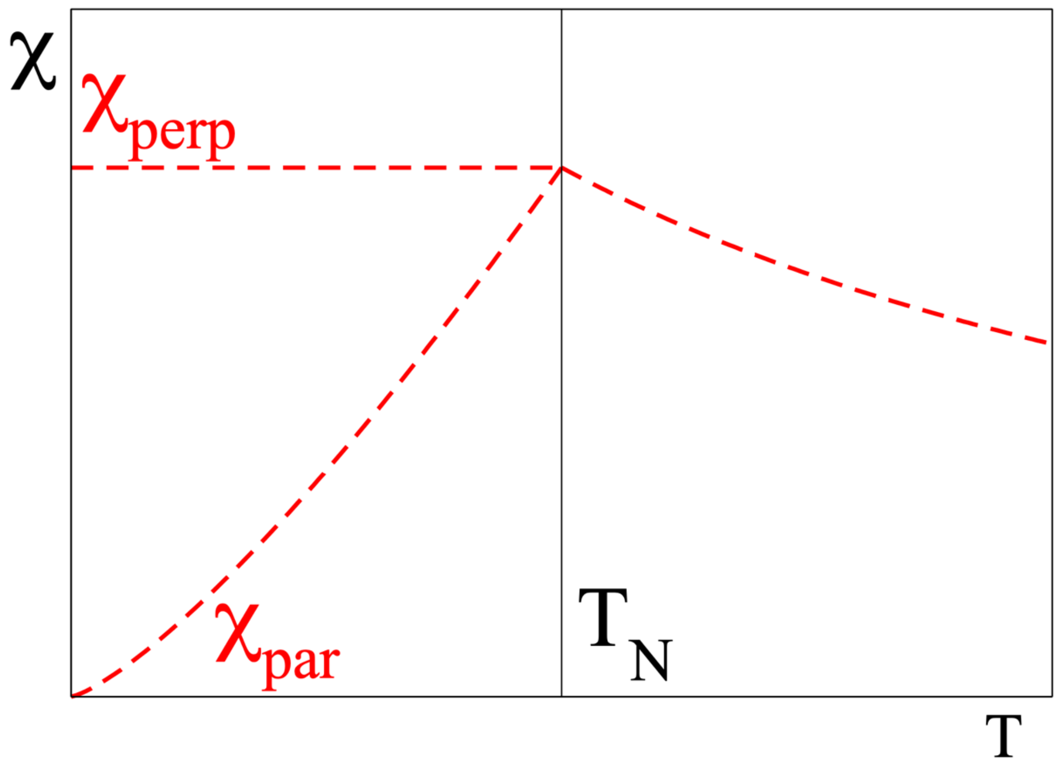


Susceptibility: AF

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 moments
- Environment
- Magnetic order and susceptibility
- Interactions
  - Between localized moments
  - Localized moments + itinerant electrons
  - Itinerant electrons
- Excitations

Different mechanisms

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

Interaction between localized moments

EXCHANGE

Heisenberg model $\Sigma_{ij}\, J\, \mathbf{S}_i\, \mathbf{S}_j$

- 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

Direct 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.
- Proposed by Heisenberg, 1928. Inspired by H_2

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 Ψ(r) in terms of orthogonal wave functions localized at the magnetic ions $\varphi_n(r)$. No double occupancy is allowed (U>>t).

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

Alternatively, the exchange term can be written $\sum_{s,s'} a^+_{ns} a_{ns'} a^+_{n's'} a_{n's}$

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

$$s_x + is_y = a^+_\uparrow a_\downarrow \; ; \; s_x - is_y = a^+_\downarrow a_\uparrow$$

$\Downarrow$

Heisenberg model: $-J_{n,n'}\left(\frac{1}{2} + 2\mathbf{s}_n \cdot \mathbf{s}_{n'}\right)$

$J_{n,n'}$ is always positive: Ferromagnetism

This exchange depends on direct overlap between orbitals → too small to account for experimental T_c

For n and n' two orbitals on the same site, this is the Hund's coupling.

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)

$$\mathrm{Exchange} = 2\frac{\mathrm{overlap}^2 C_{ab} - J_{ab}}{1 - \mathrm{overlap}^4}$$

overlap=0 for orthogonal orbitals

Wigner’s theorem does not apply to our magnetic ions because a shell in a $3d^2$ configuration is not a 2-electron problem!

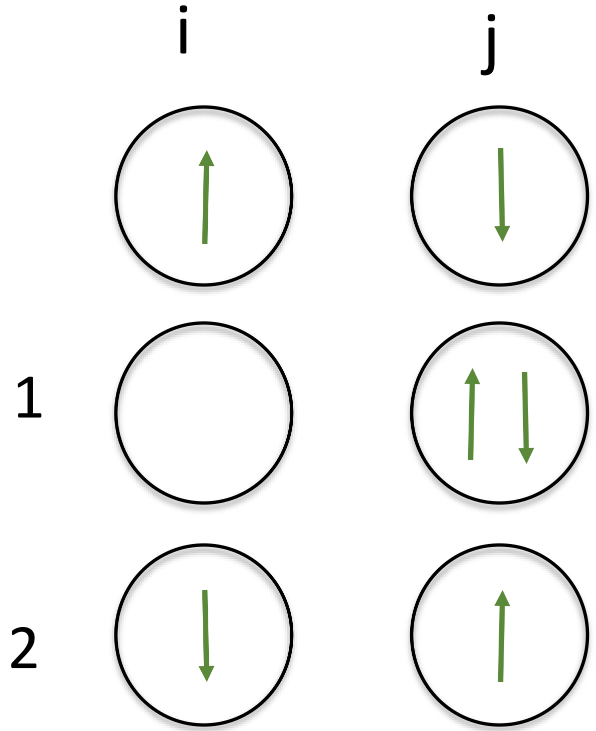
Kinetic exchange

- 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 (more common for insulators).
- Start from single band Hubbard Hamiltonian (on-site interactions) with U>>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)



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

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

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

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 model:

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

Antiferromagnetic

Hubbard model

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

U>>t

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

AF Heisenberg model

At half-filling
(1 electron per site)

$$J\sum_{ij}\vec{S}_i\vec{S}_j$$

t-J model

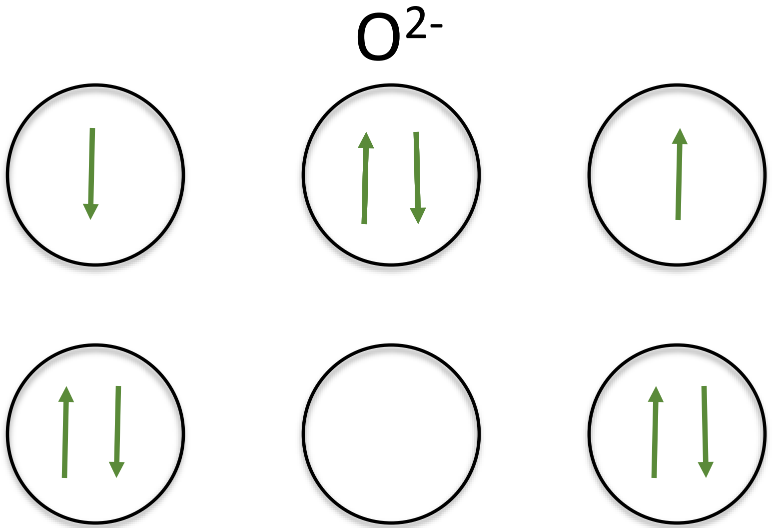
Away from
half-filling

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

Hopping only between an empty and a filled site.

Superexchange

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



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

From this, SE is antiferromagnetic but…

Goodenough-Kanamori rule

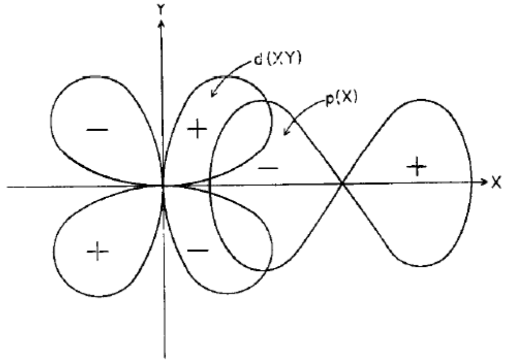
Superexchange is AF when the virtual hopping involves overlapping half-filled orbitals while it can be FM when:

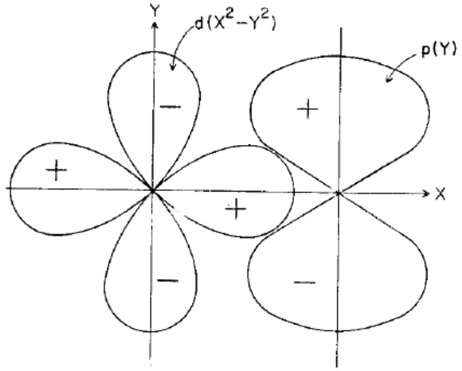
- $t_{ij}=0 \rightarrow E_{kin}=0$

(note that t_{ij} depends on the orientation of the M-O-M bonds)

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

Only direct FM exchange





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:

- $t_{ij}=0$
- 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:

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

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

* Generalization

For multiorbital systems, the model for electron-electron interaction includes more terms:

$$H = H_0 + \bar{U} \sum_{i,\ell} n_{i\ell\uparrow} n_{i\ell\downarrow} + \bar{U}' \sum_{i,\ell'<\ell} n_{i\ell} n_{i\ell'}$$
$$+ \bar{J}_{\mathrm{H}} \sum_{i,\ell'<\ell} \sum_{\sigma,\sigma'} c^{\dagger}_{i\ell\sigma} c^{\dagger}_{i\ell'\sigma'} c_{i\ell\sigma'} c_{i\ell'\sigma}$$
$$+ \bar{J}' \sum_{i,\ell'\neq\ell} c^{\dagger}_{i\ell\uparrow} c^{\dagger}_{i\ell\downarrow} c_{i\ell'\downarrow} c_{i\ell'\uparrow}$$

If 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* $U'=U-2J_H$*),* $J_{kin} = -t^2/(U-3J_H)$

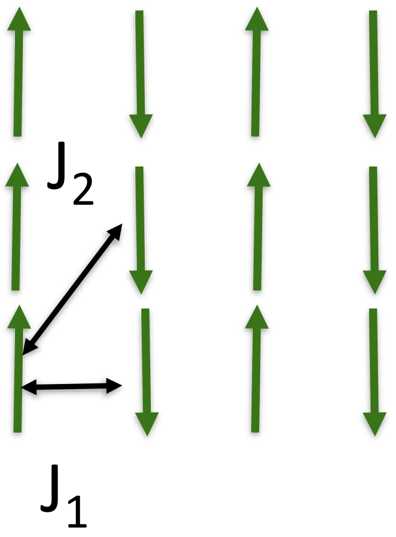
http://www.scholarpedia.org/article/Goodenough-Kanamori_rule

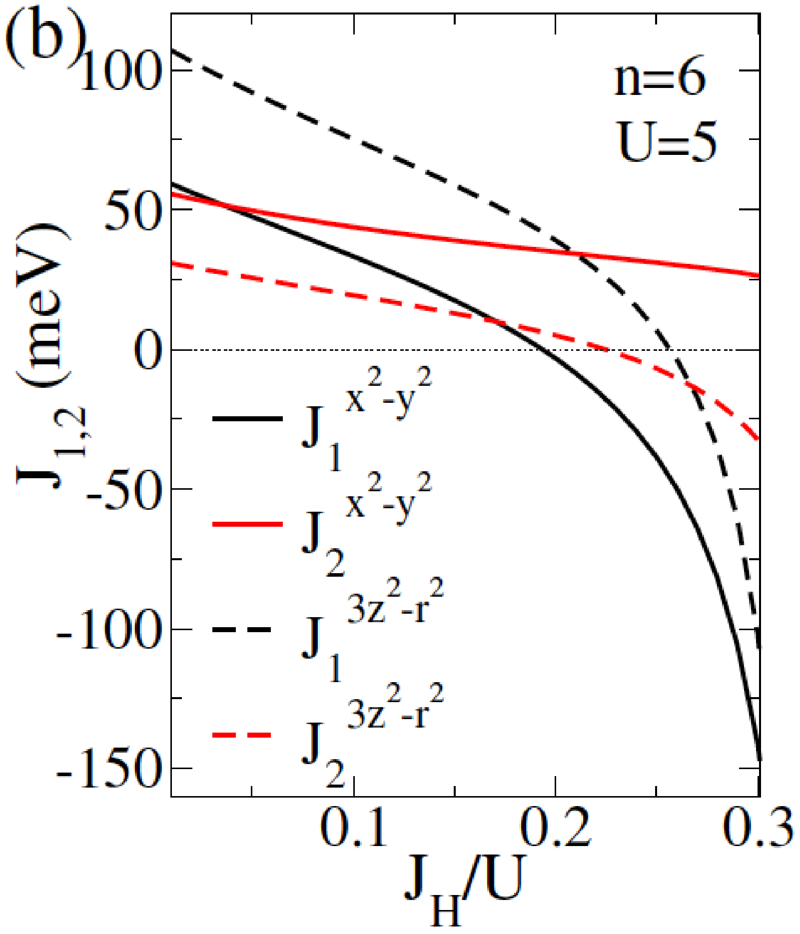
* Generalization

INTERACTIONS

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

$J_2 > J_1/2$





Physical Review B 86, 104514 (2012).

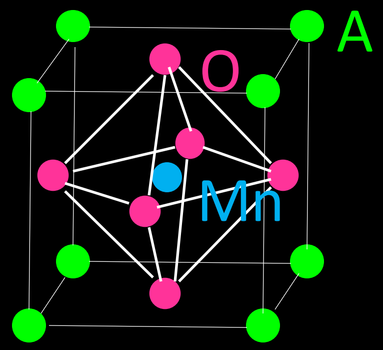
Goodenough-Kanamori rule: consequences

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

- Associated to orbital order (competing sometimes with Jahn-Teller distortions)

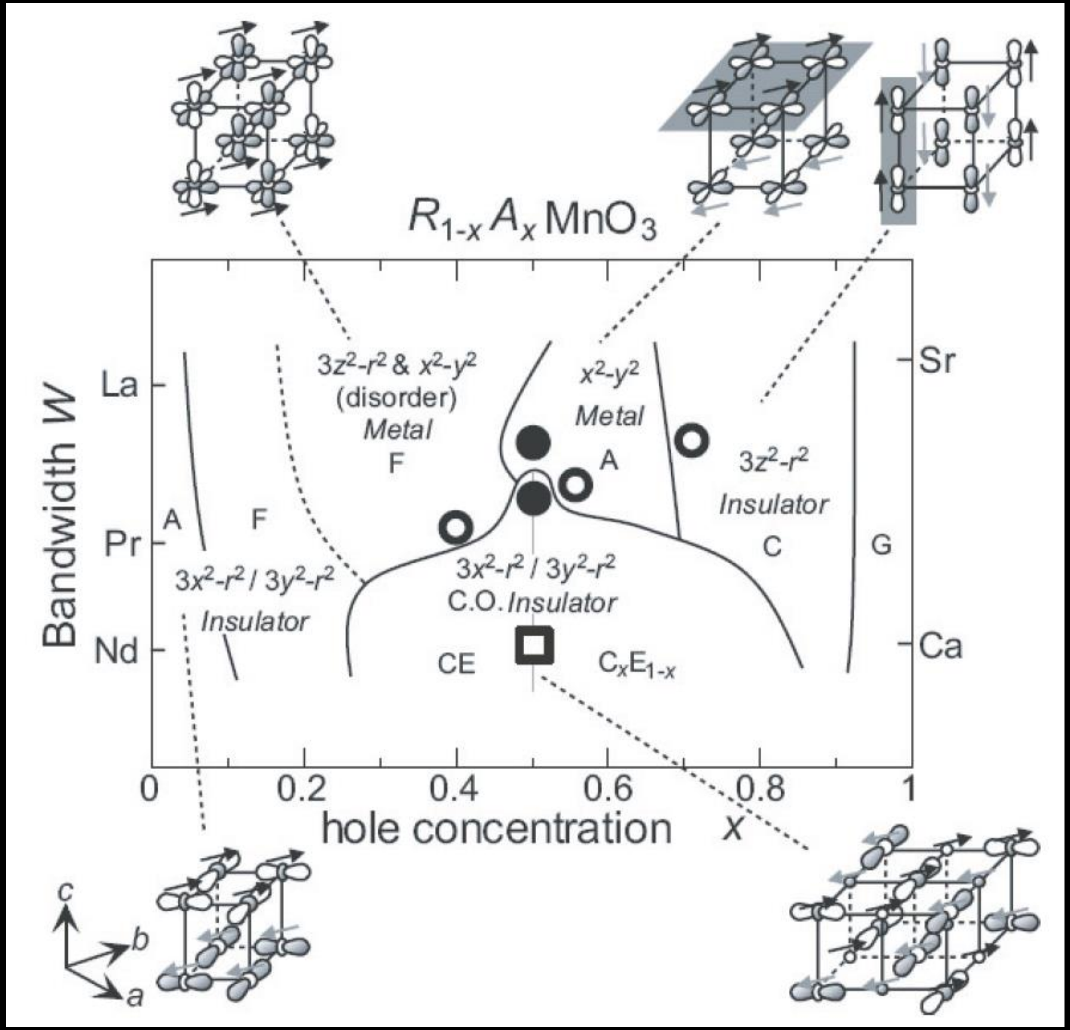
Millis, PRB 55, 6405 (1997).

Example: Manganites



Interplay of spin, orbital and lattice

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



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

Millis, PRB 55, 6405 (1997).

INTERACTIONS

Example: Manganites

Interplay of spin, orbital and lattice

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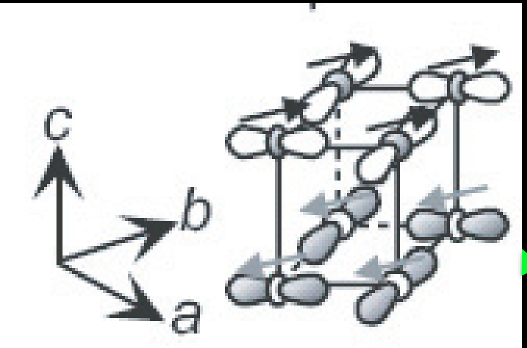
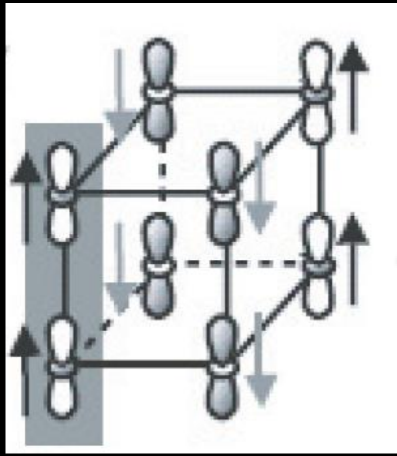
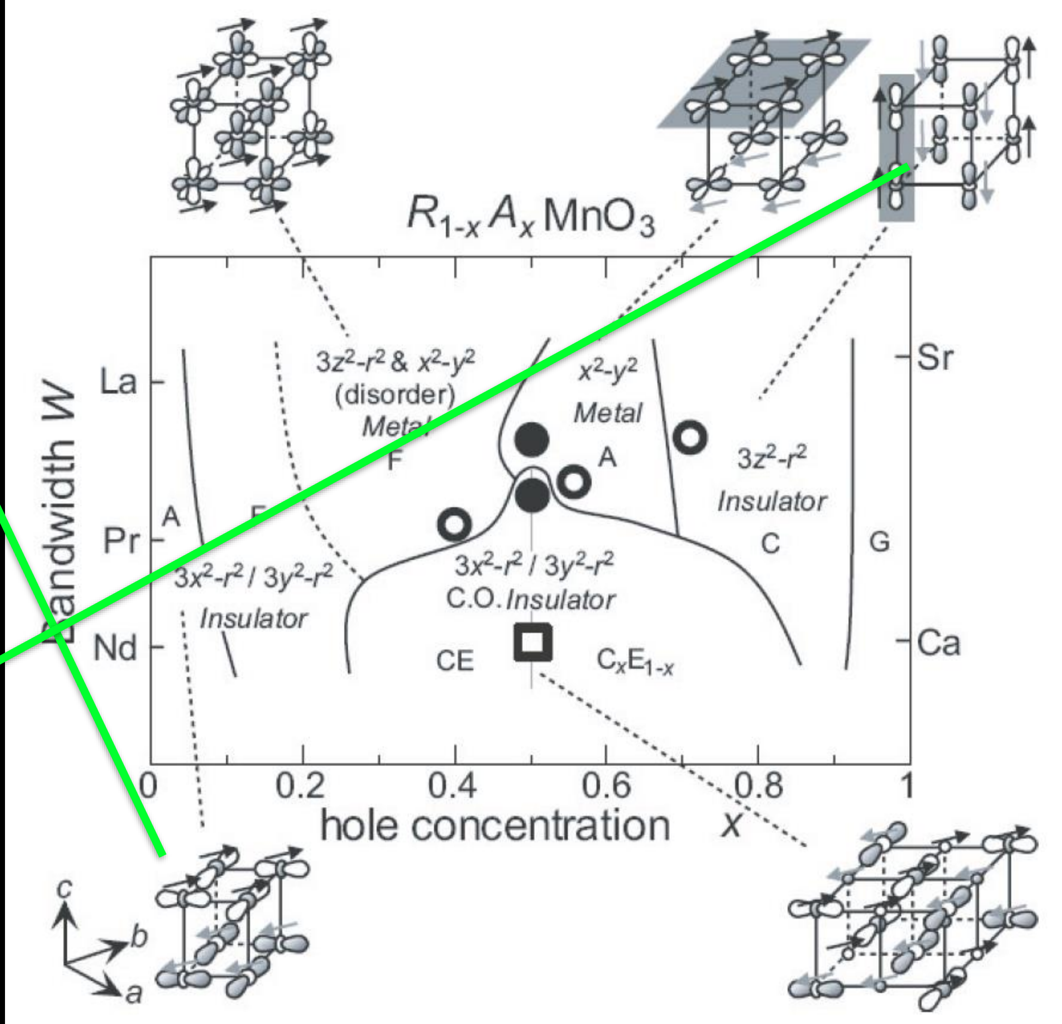


Type A: Q=(0,0,π)



Type C: Q=(π, π,0)



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

Anisotropic exchange

(for d-orbitals)

K. Yosida's book.

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.

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

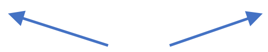
Dzyaloshinskii-Moriya

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

D=0 if there is inversion symmetry between the 2 ions

D direction depends on symmetry

Causes AF spins to cant by a small angle: weak ferromagnetism.



Examples: α-Fe_2O_3, $MnCoO_3$, $RFeO_3$ (R: rare-earth).

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 an impurity

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

Kondo lattice

$$H = -\sum_{ij\sigma} t_{ij}(c_{i\sigma}^{\dagger} c_{j\sigma} + c_{j\sigma}^{\dagger} c_{i\sigma}) - J_{\text{local}} \sum_{i} \mathbf{S_i} \cdot \mathbf{s_i}$$

for f-electrons S →J

See lecture on Kondo effect (Ramón Aguado). Here we are focusing on the regime in which this term gives rise to magnetic order.

Itinerant electrons coupled to localized moments

Kondo model: coupling to an impurity

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

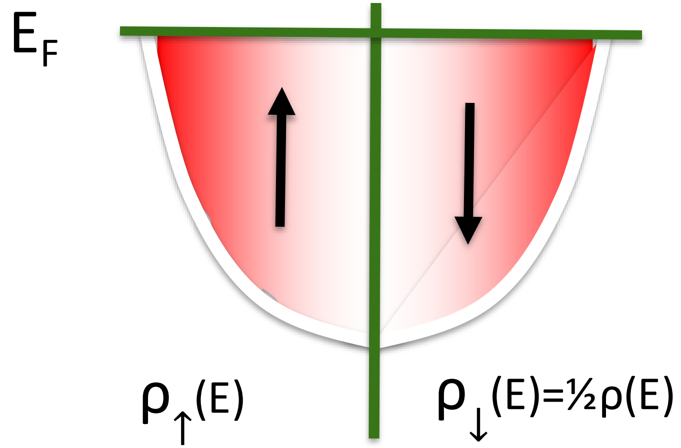
Basic idea: the local exchange with an impurity polarizes the surrounding Fermi sea which carries this information to other magnetic impurities.

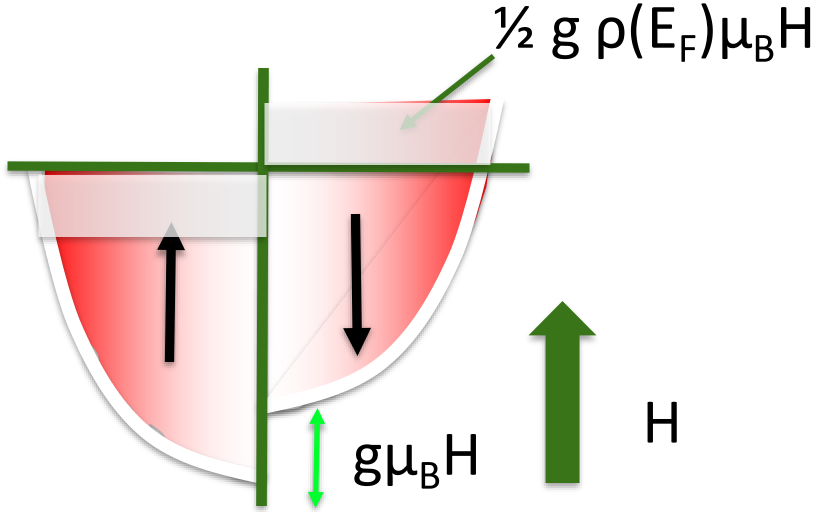
How effective is this process of the magnetic polarization of the Fermi sea? → susceptibility

Paramagnetic susceptibility of conduction electrons

Without magnetic field n↑=n↓

In a uniform magnetic field n↑≠n↓





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

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

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

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

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

$$\downarrow$$

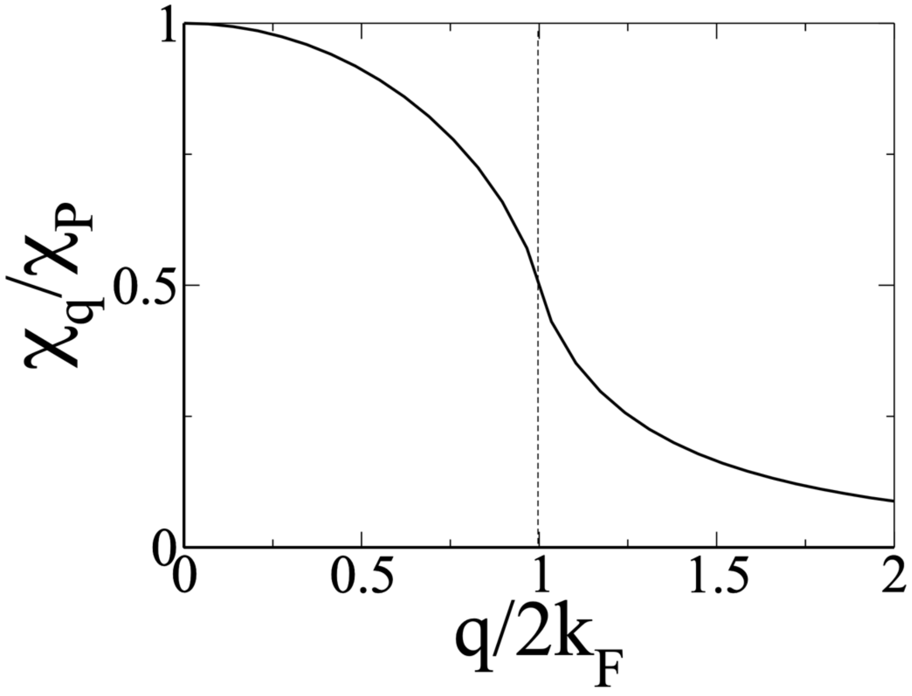
$$M_q$$

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

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)
Linhard function

(in momentum space)

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

RKKY exchange

Rudderman-Kittel-Kasuya-Yosida

For Kondo model: A magnetic impurity with local exchange amounts to having a local external field: H(r) ~ δ(r)

J_{local} : J_H or s-d or s-f exchange.

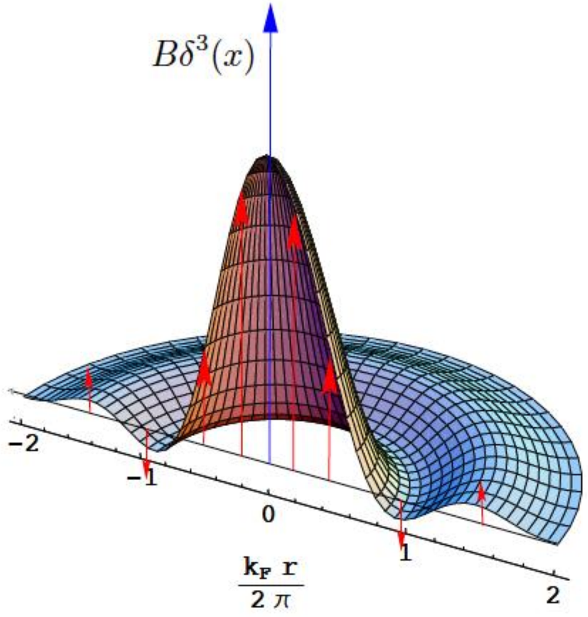
$$H_q = \frac{2J_{local}}{Ng\mu_B} S_z$$

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

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

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

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



Coleman's book

RKKY exchange

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

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

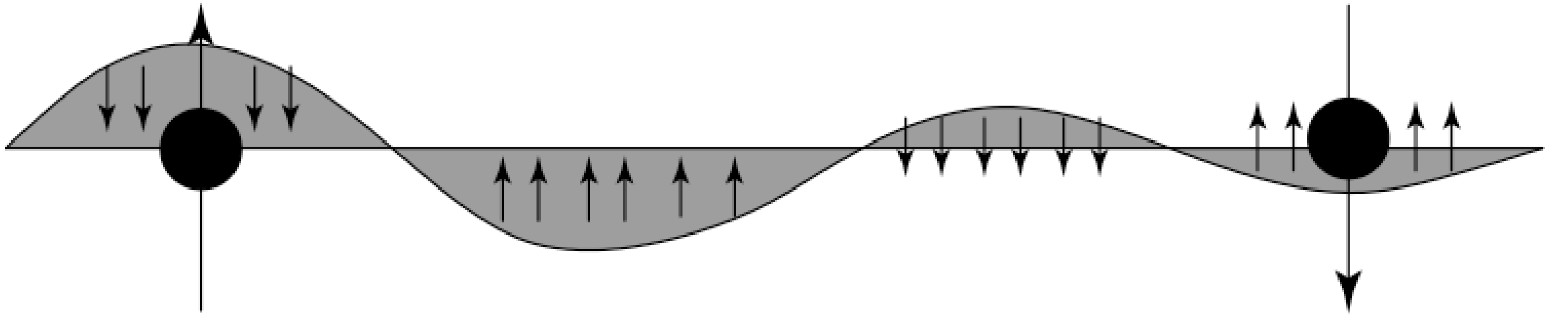
Now this polarized cloud interacts with another magnetic impurity

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

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

J_{RKKY} oscillates with distance: A local magnetic moment produces a wave-like local perturbation, similar to throwing a stone into water.

RKKY exchange



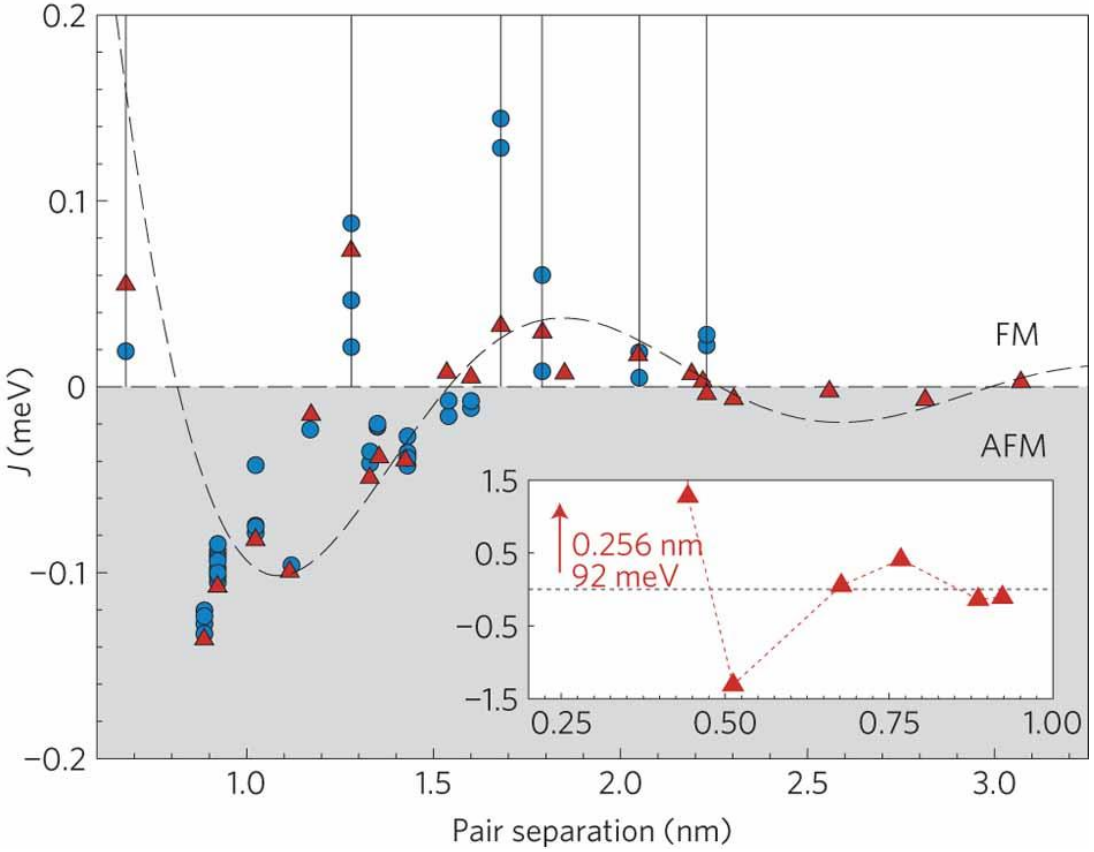
$$J_{RKKY} \propto J_{local}^{2} F(2k_F r)$$

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

J_{RKKY} oscillates with distance: A local magnetic moment produces a wave-like local perturbation, similar to throwing a stone into water.

RKKY exchange

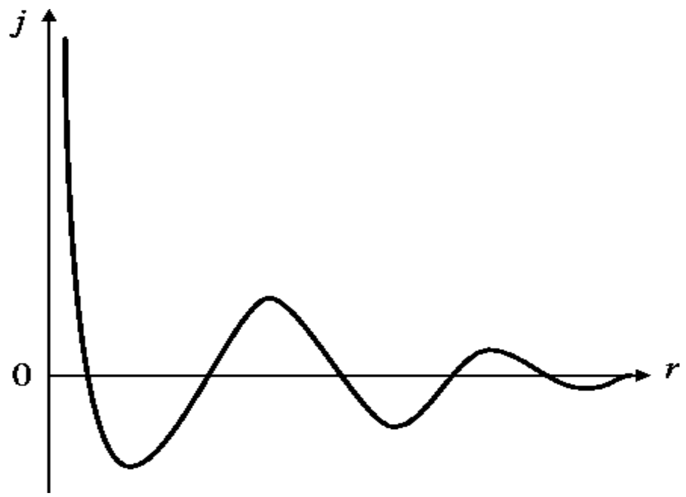
Fe atoms on Cu(111)



Nature Physics 8, 497–503 (2012)

RKKY exchange

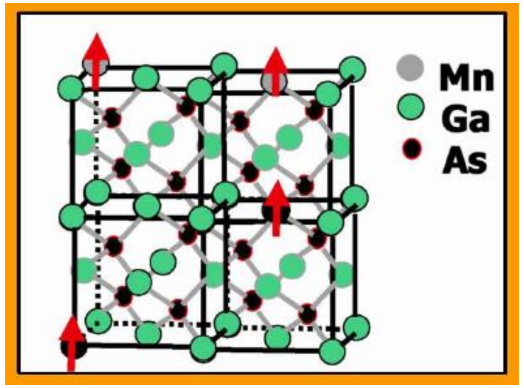
Note that if $k_F r$ is small, J_{RKKY} is FM.



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)O_2

(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

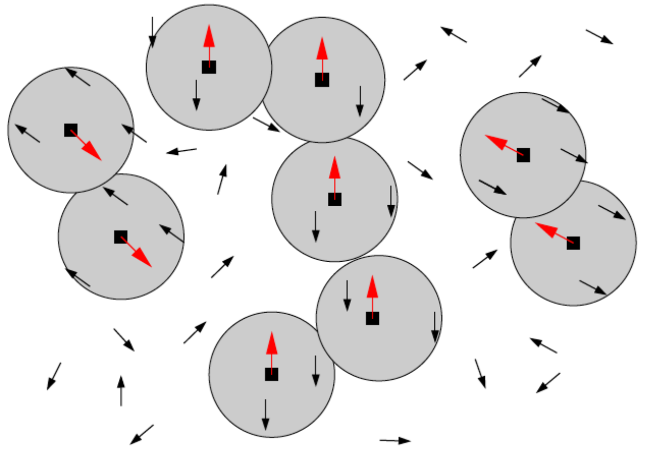
Carriers are bound (not-itinerant!) electrostatically by the Coulomb potential and the spin-polarization is a secondary phenomenon.

Polaron: FM cloud.

Proposed for diluted magnetic semiconductors. Percolation →Tc

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

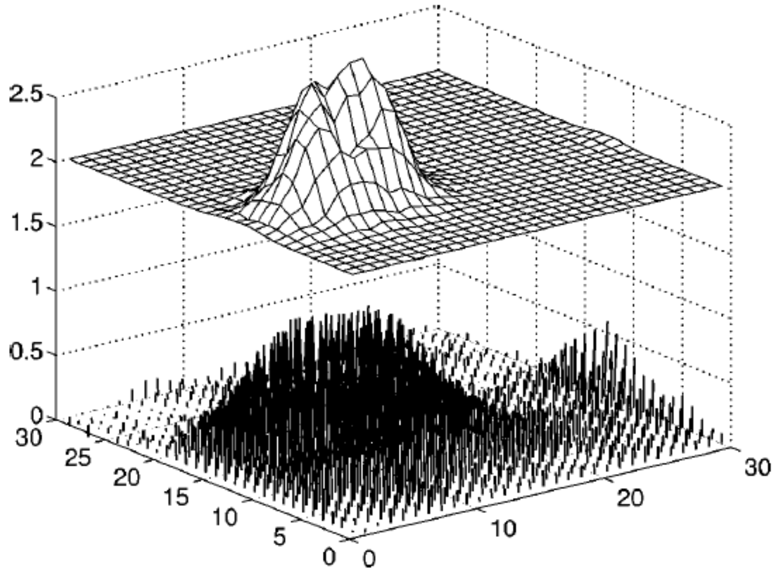
$$k_B T = |J|(a_0/a_B)^3 Ss \exp(-2R_p/a_B)$$



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.



PRB 62, 3368 (2000)

INTERACTIONS

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

$$\sum_{\alpha\beta} t^{\alpha\beta} \sum_{ij\sigma} c^{\dagger}_{i\alpha\sigma} c_{i\beta\sigma} + J_H \sum_i \mathbf{S}_i \mathbf{s}_i \xrightarrow{J_H \rightarrow \infty} \sum_{\alpha\beta} \sum_{ij} t^{\alpha\beta}_{ij} d^{\dagger}_{i\alpha} d_{i\beta}$$

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

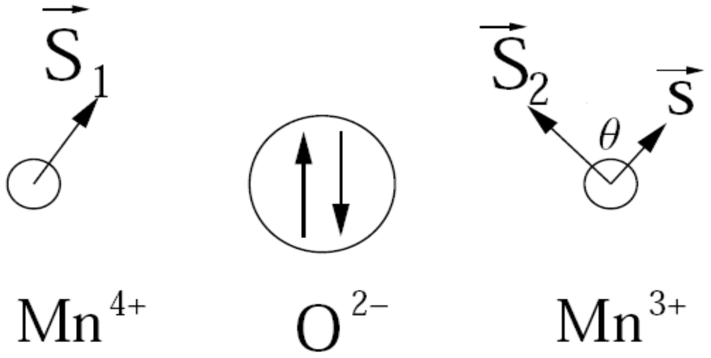
This model was proposed for manganites
$A_{1-x}A'_xMn^{3+}_{1-x}Mn^{4+}_xO_3$

C. Zener, Phys. Rev. **82**, 403, (1951)
P. W. Anderson and A. Hasegawa , Phys Rev **100**, 675 (1955)

Double exchange

$$\sum_{\alpha\beta} t^{\alpha\beta} \sum_{ij\sigma} c^\dagger_{i\alpha\sigma} c_{i\beta\sigma} + J_H \sum_i \mathbf{S}_i \mathbf{s}_i \xrightarrow[J_H \to \infty]{} \sum_{\alpha\beta} \sum_{ij} t^{\alpha\beta}_{ij} d^\dagger_{i\alpha} d_{i\beta}$$

Note: spinless Hamiltonian



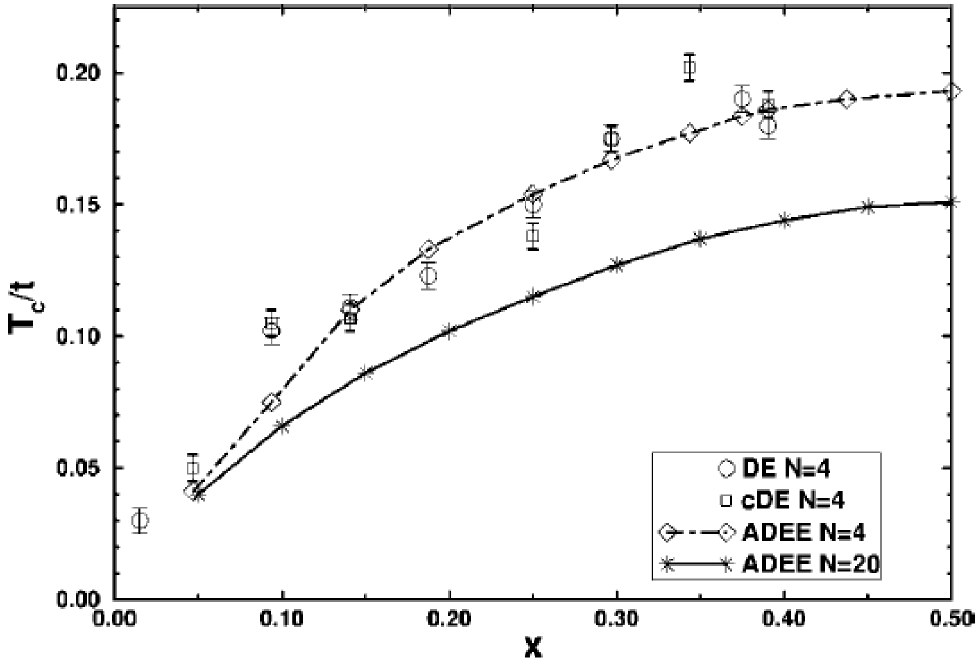
Kinetic exchange with real (not virtual) electron hopping

Promotes FM with metallicity (as observed in manganites)

C. Zener, Phys. Rev. **82**, 403, (1951)
P. W. Anderson and A. Hasegawa , Phys Rev **100**, 675 (1955)

Double exchange

$A_{1-x}A'_xMn^{3+}_{1-x}Mn^{4+}_xO_3$ (x≠0 or 1 → mixed valency)



T_c proportional to the number of carriers

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

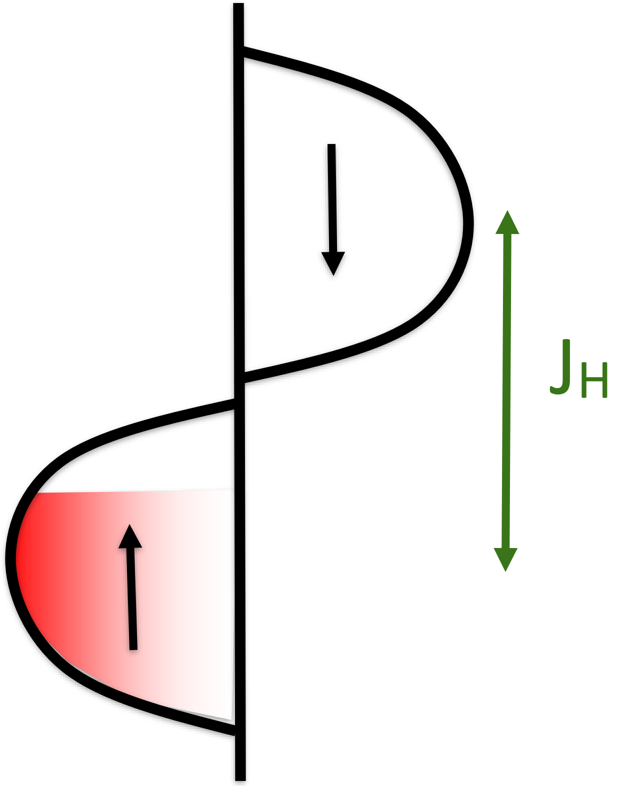
C. Zener, Phys. Rev. **82**, 403, (1951)
P. W. Anderson and A. Hasegawa , Phys Rev **100**, 675 (1955)

Double exchange

<u>Half-metal</u>:

- metallic conduction for spin up
- insulator for spin down

Useful for spintronics.



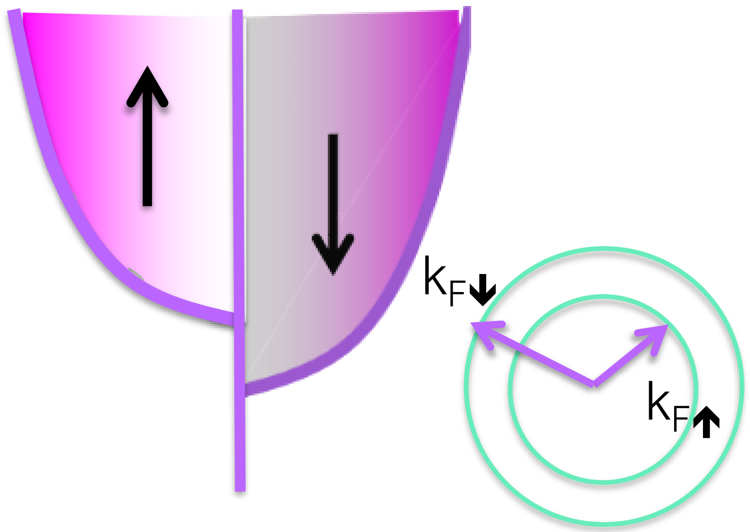
Different mechanisms

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

Itinerant ferromagnetism

Question: Is it energetically favourable to have a spin imbalance for the itinerant electrons? (spontaneously spin-split bands)

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.

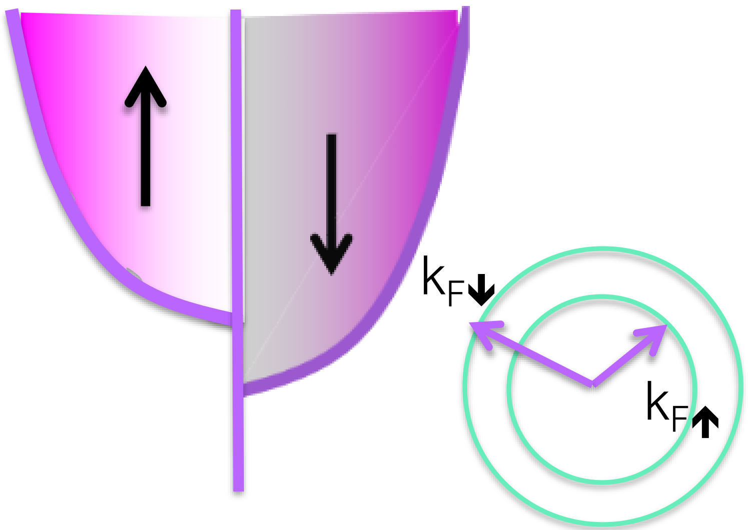
Itinerant ferromagnetism

Hubbard model in a magnetic field

$$H = -\sum_{k\sigma} \epsilon_k n_{k\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} - \frac{g\mu_B H}{2} \sum_i (n_{i\uparrow} - n_{i\downarrow})$$

$$n_{i\uparrow} n_{i\downarrow} \to n_{i\uparrow} \langle n_{i\downarrow} \rangle + \langle n_{i\uparrow} \rangle n_{i\downarrow} - \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle$$

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



$$U \sum_i n_{i\uparrow} n_{i\downarrow} \to U \left(\frac{n^2}{4} - m^2 \right)$$

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

Fazekas

Itinerant ferromagnetism

Hubbard model in a magnetic field

$$H = -\sum_{k\sigma} \epsilon_k n_{k\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} - \frac{g\mu_B H}{2} \sum_i (n_{i\uparrow} - n_{i\downarrow})$$

Calculate susceptibility

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

Stoner enhancement

(Pauli susceptibility is enhanced by electron-electron interaction)

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

Band narrowing and high density of electrons at E_F promote FM

Fazekas

Itinerant magnetism

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<<n) itinerant ferromagnetism
  Example: $ZrZn_2$ (neither Zr nor Zn is magnetic)

Generalised Stoner criterium

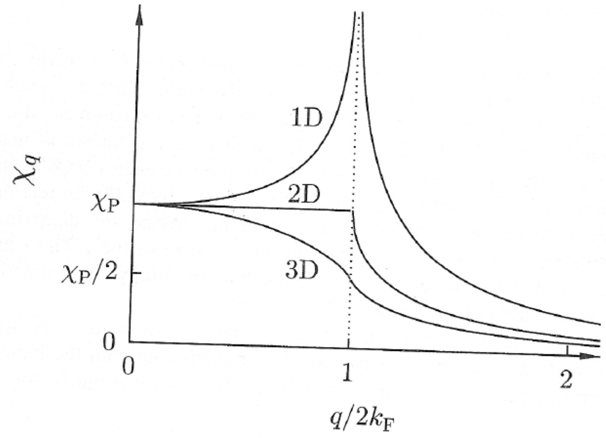
For a non-uniform magnetic field we calculated a q dependent susceptibility:

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

In the presence of Coulomb interactions

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

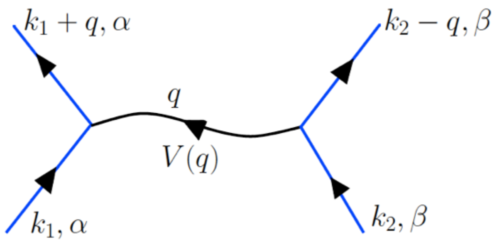
Stoner criterium for finite q



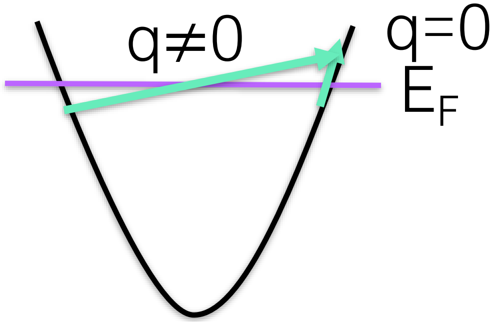
Blundell

Instabilities with wave-vector q≠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.



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

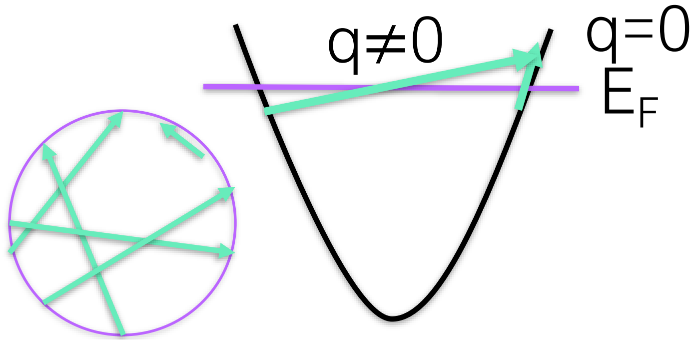


Reminder: a metal is in the degenerate limit $T \ll E_F$

Excitations around E_F

Instabilities with wave-vector q≠0. Spin density waves. Nesting

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

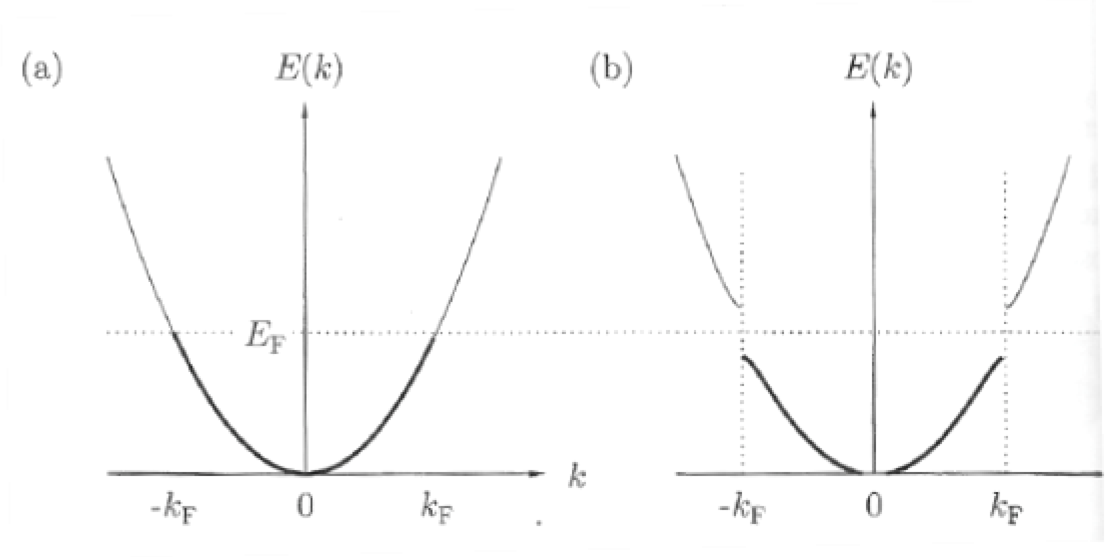


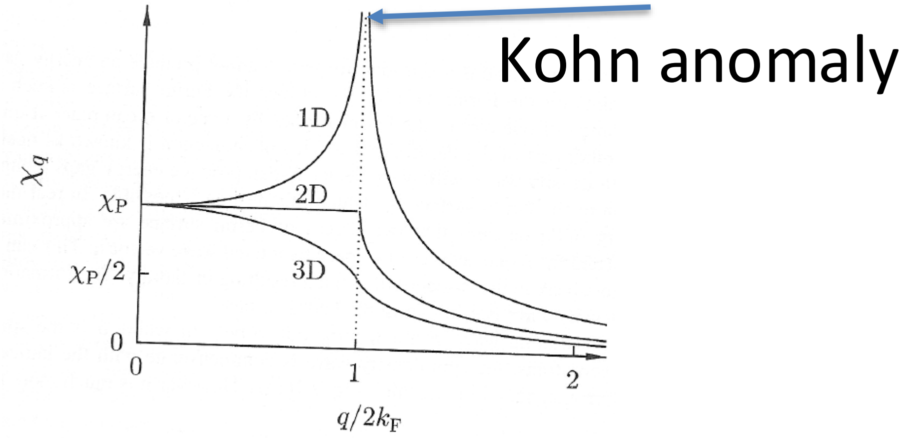
However, if there are sectors of the Fermi surface that are connected by the same q, the maximum of the susceptibility can be at that particular q: nesting.

Nesting in 1d

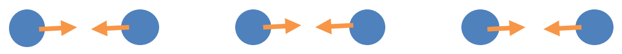
In 1d there is always nesting at $q=2k_F$ leading to AF order ($q=\pi/a$).

A periodic modulation of the magnetization opens a gap, lowering the total energy:





In 1d, the AF order competes with a Peierls instability: dimerization and charge density wave.



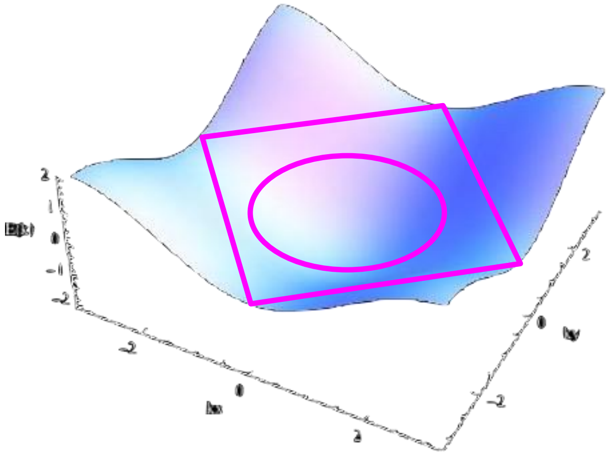
For d>1, the nesting condition is more restrictive

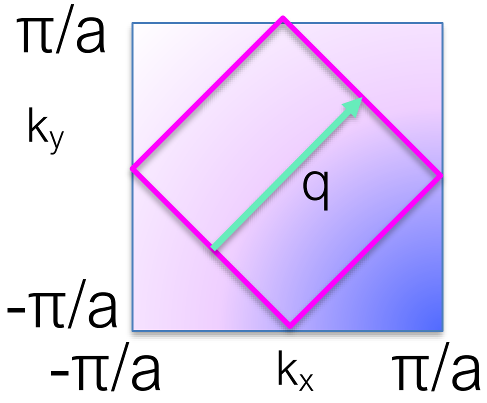
Nesting in 2d

For a 2D square lattice

$$\epsilon(k) = 2t(\cos(k_x a) + \cos(k_y a))$$

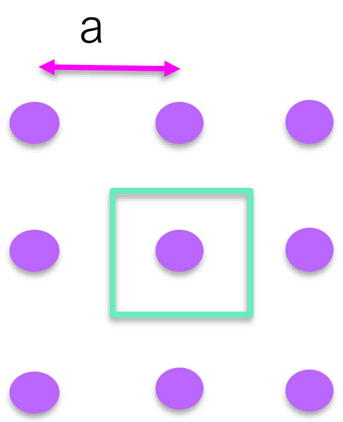
For an incommensurate filling: no nesting





For half-filling (1e- per site):
There is perfect nesting with q=(π/a,π/a)

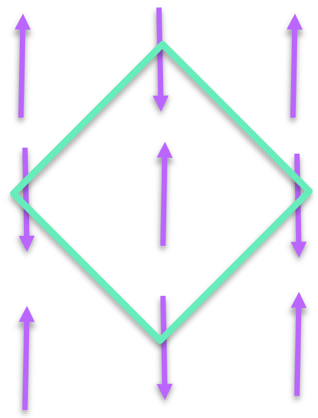
Nesting in 2d

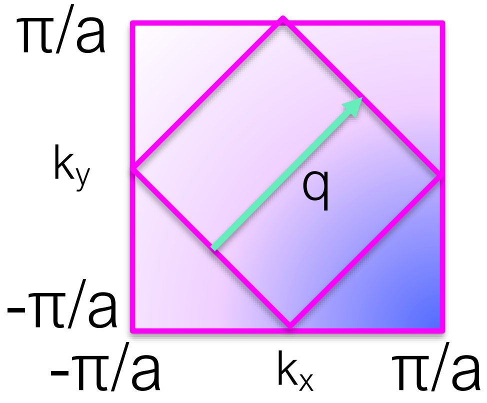


AF: Doubling of unit cell

⬇

Folding of Brillouin zone in the reciprocal space

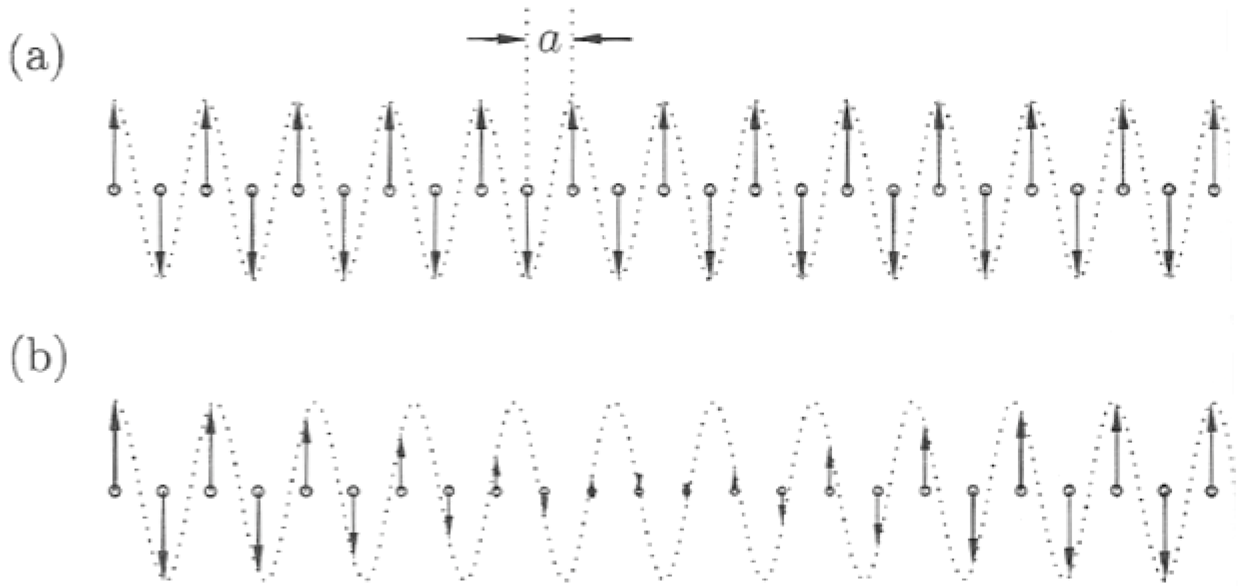




A gap opens at the zone boundary: the system is insulating at half-filling even in the weak coupling regime if there is perfect nesting.
(Slater insulator)
Note that we have used U=0!!

Instabilities with wave-vector q≠0. Spin density waves. Nesting

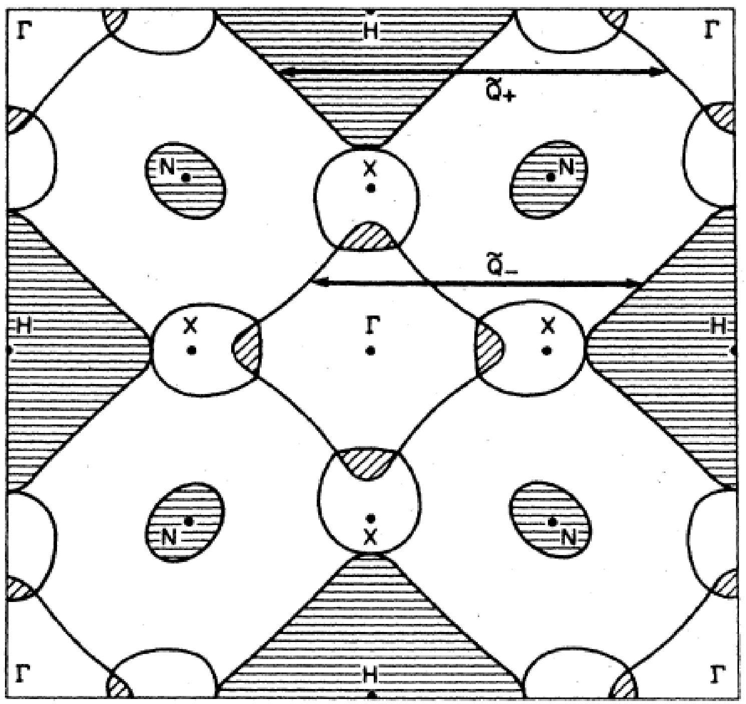
In general, **q** can be an incommensurate vector



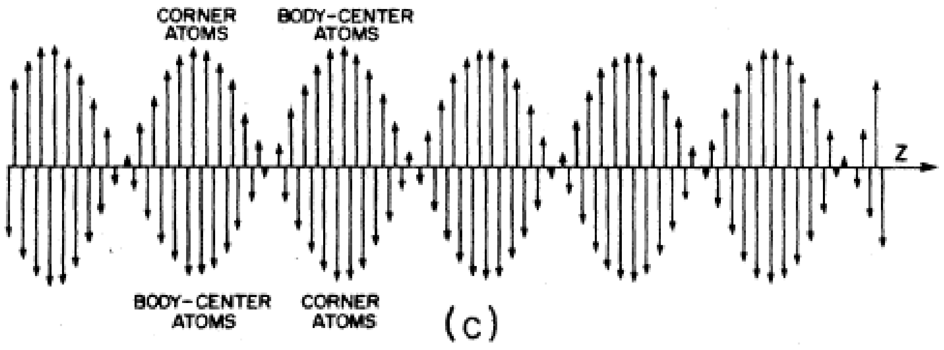
S. Blundell's book

Instabilities with wave-vector q≠0. Spin density waves. Nesting

Example: spin density wave in Cr



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



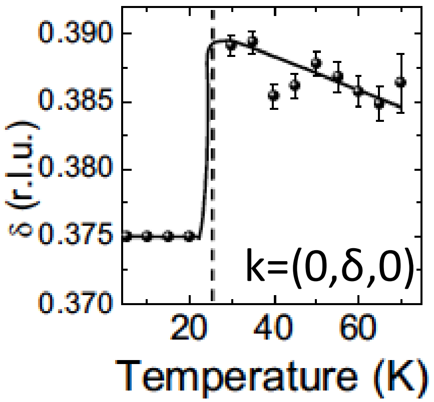
RMP 60, 209 (1988)

Note: In this case the SDW does not open a gap over the entire Fermi surface: the system is metallic.

Nesting can lead to different competing Fermi surface instabilities (charge density wave, superconducting pairing, spin-density wave). The one with the largest Tc sets in.

Incommensurate instabilities sometimes suffer "lock-in" transitions becoming commensurate at low temperatures.

Example: $CaFe_4As_3$



PRB 81, 184402 (2010)

Ginzburg-Landau formalism

Complex order parameter $\psi(r) = \rho(r) e^{i(\mathbf{Q_c}.\mathbf{r}+\phi(r))}$

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

Elastic term

Umklapp term

OUTLINE

- Free magnetic moments
- Environment
- Magnetic order and susceptibility
- Interactions
  - Between localized moments
  - Localized moments + itinerant electrons
  - Itinerant electrons
- Excitations.

Spin waves

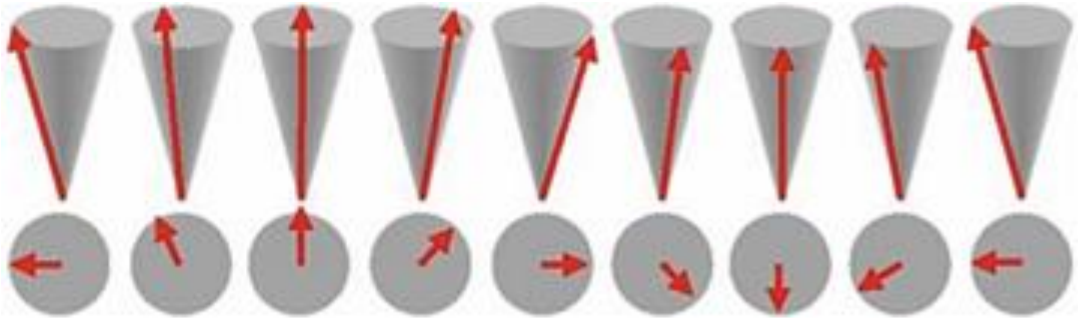
Low T excitations of a Heisenberg model (localised moments)

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.

FM 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

FM spin waves

For a FM Heisenberg model

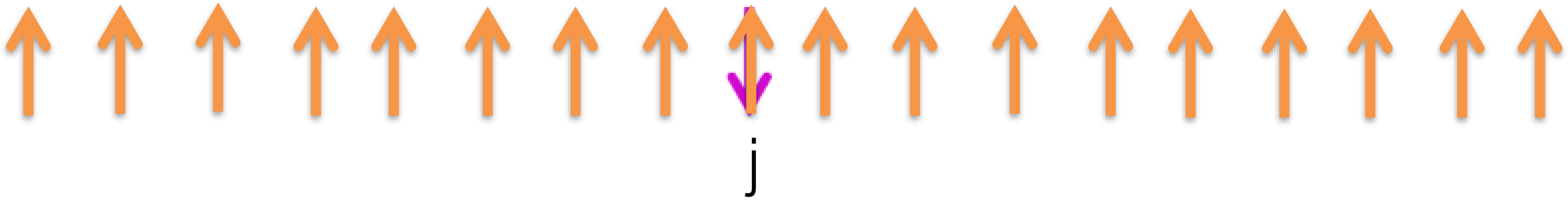
$$S^{\pm} = S_x \pm iS_y$$

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

J>0

To create an excitation: flip spin j

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



|j> is not an eigenstate of H: diagonalize the Hamiltonia by looking for plane-wave solutions

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

$$E(q) = 4JS(1 - \cos(qa))$$

small q

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

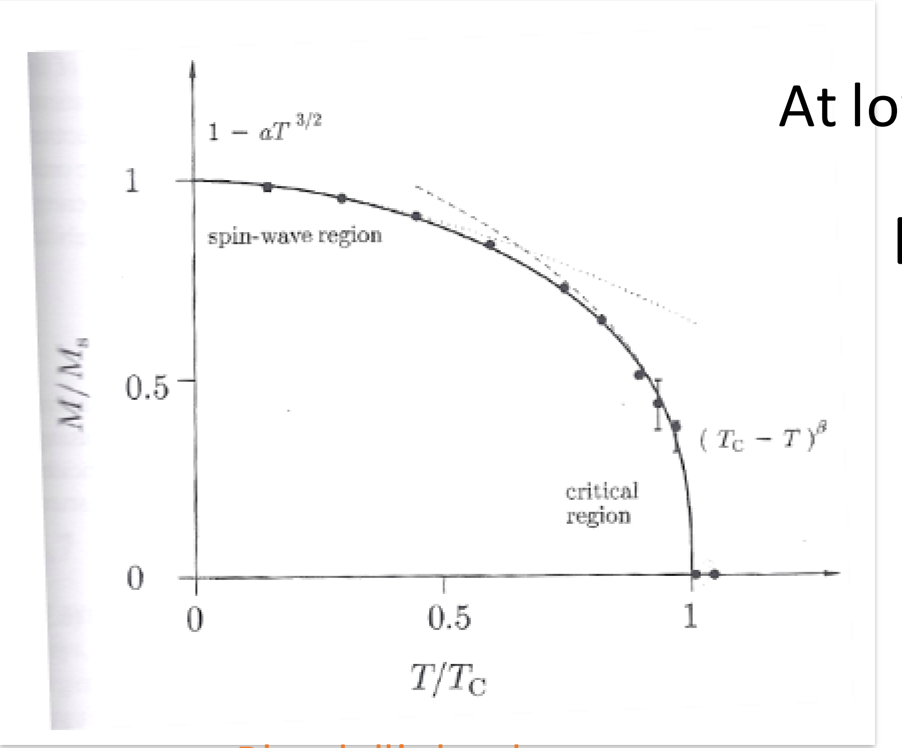
Gapless Goldstone mode

FM spin waves

In 3dim, the density of states is

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

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



Blundell's book

At low T, the number of magnons ∝ M: $M(T) \approx 1 - aT^{3/2}$

Bloch $T^{3/2}$ law

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

2D magnetism

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

$$H = J \sum_{ij} \left(S_i^x S_j^x + S_i^y S_j^y + A S_i^z S_j^z \right)$$

A>1 (easy axes)

$$\Delta E = 4JS(1 - \cos qa) \sim q^2 a^2$$

(isotropic)

$$\Delta E = 4JS(A - \cos qa) \sim A - 1 + q^2 a^2$$

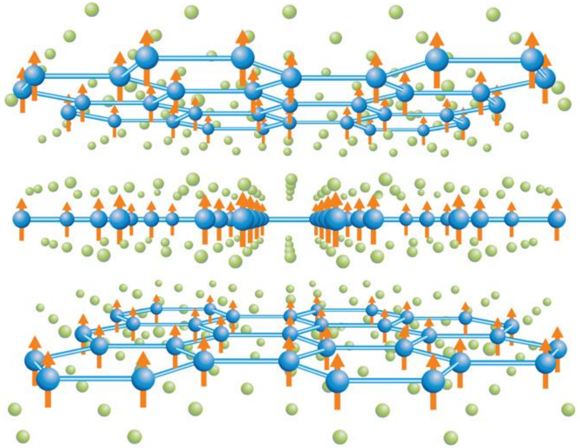
GAP

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

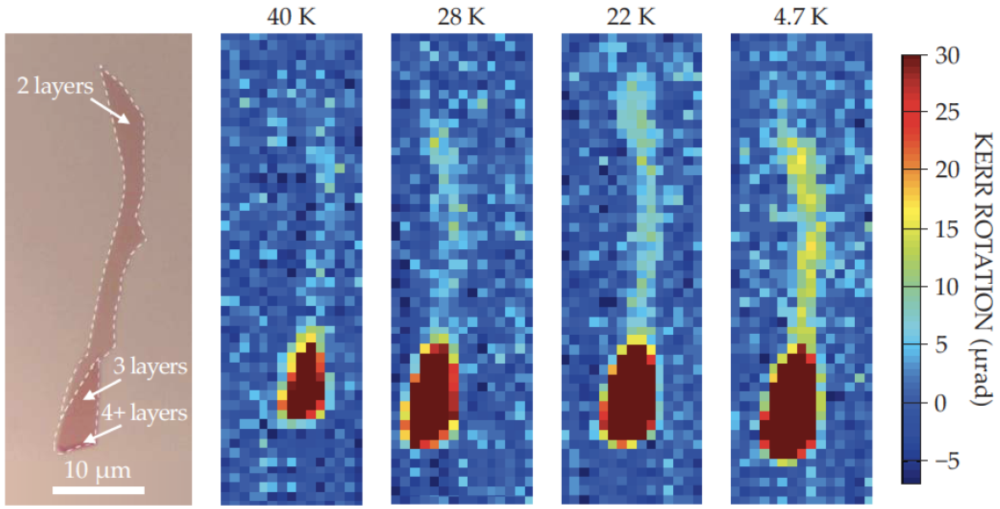
2D magnetism

Found experimentally for the first time in 2017 in Van der Waals materials.

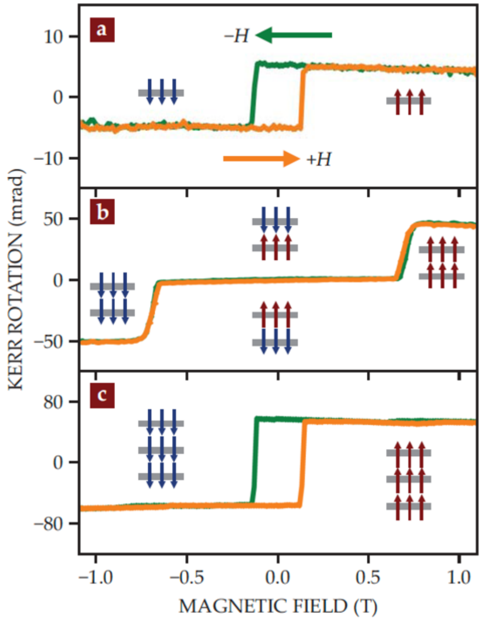
C. Gong et al., Nature 546, 265 (2017).
B. Huang et al., Nature 546, 270 (2017).
Johanna L. Miller, Physics Today 70, 7, 16 (2017)



CrI_3
(bulk T_c=61K)



$CrGeTe_3$ (bulk T_c=70K).



Quantum AF

Antiferromagnetic Heisenberg model J<0

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

$$|\Phi_0\rangle = |\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow \ldots\rangle$$ (classical Néel state)

The ground state has two sublattices: one with all spins up and the other with all spins down with $E=NzS^2J$ (N is the number of spins, z is the number of neighbors). We are only considering the longitudinal part of the exchange.

This energy can be lowered by allowing quantum fluctuations (transverse part of the exchange interaction) leading to

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

Note: For 1d and s=1/2, E_g is doubled by including fluctuations

Yosida

AF spin waves

Antiferromagnetic Heisenberg model $J<0$

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

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)

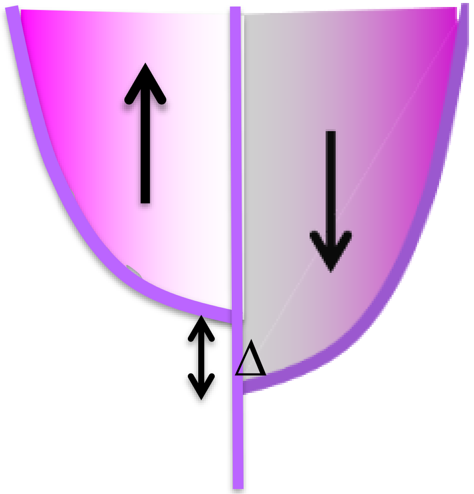
Yosida

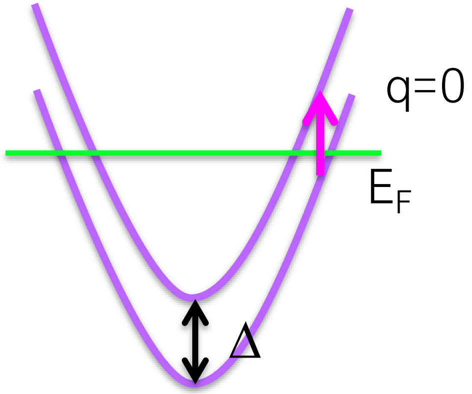
Excitations in the electron gas

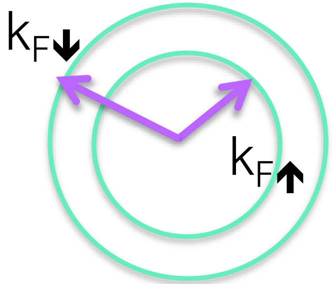
- Also spin waves
- Stoner excitations

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

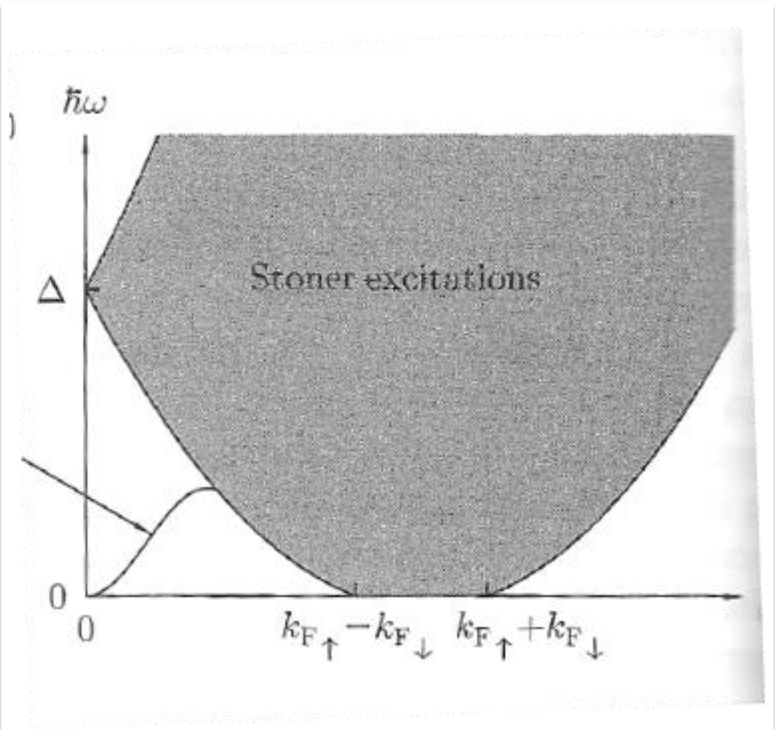
Δ: exchange splitting







Spin wave



Blundell

OUTLINE

- Free magnetic moments
- Environment
- Magnetic order and susceptibility
- Interactions
  - Between localized moments
  - Localized moments + itinerant electrons
  - Itinerant electrons
- Excitations.

HOW TO BUILD A MODEL

1. Focus on transition metals (d-elements), lanthanides (4f), actinides (5f)
2. Given electronic structure of magnetic ion, figure out S, L, J=L+S, posible fine structure (if SO, only J is a good quantum number)
3. Consider dominating energy scales (SO, CF). Large SO → anisotropic μ.
   a) If 3d: SO→0, large CF, JT distortions may break degeneracies and cause orbital selection (afected by strain, at interfaces..).
      Non-degenerate levels: orbital quenching L=0
   b) If 4f: large SO, relevant J, fine structure (|L-S|, L+S). Small CF. JT rare.
      5f: SO, CF, JT enhanced with respect to 4f.
   c) 4d/5d: like 3d + SO.
4. From orbital selection and Slater Koster determine hoppings (hence bandwidth W). Which orbitals are relevant. Dimensionality of bands. Possible changes at interfaces.
5. Include J_H → spin imbalance. Low and high spin states. Significant in many cases.
6. Find the Fermi level. How are magnetic interactions? SO →exchange anisotropies.
a)Filled d-f bands: localized moments. Interactions U, U', J_H, J'. Superexchange $J \sim t^2/U$.
b)Partially filled bands: itinerant electrons. Fermi surface instabilities.
c)Both: Kondo lattice model. RKKY, Double exchange, polarons.