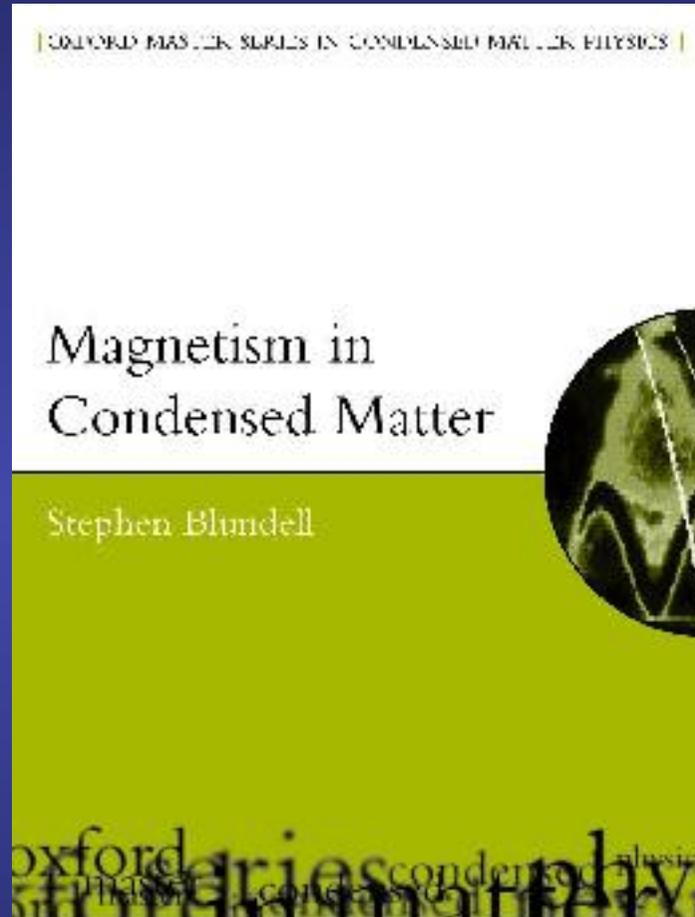


# Introduction to Heisenberg model

**Javier Junquera**



# Most important reference followed in this lecture



**Magnetism in Condensed Matter Physics**  
**Stephen Blundell**  
**Oxford Master Series in Condensed Matter Physics**

# Exchange interactions

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



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

# A look to the hamiltonian: a difficult interacting many-body system.

$$\hat{H} = \sum_i -\frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i,\alpha} \frac{Z_\alpha e^2}{|\vec{r}_i - \vec{R}_\alpha|}$$

Kinetic energy operator for the electrons

Potential acting on the electrons due to the nuclei

$$+ \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

Electron-electron interaction

$$+ \sum_\alpha -\frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2$$

Kinetic energy operator for the nuclei

$$+ \frac{1}{2} \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|}$$

Nucleus-nucleus interaction

# Exchange interactions

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



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



When it is applied to a wavefunction, it does not affect the spinoidal variables



The wave function of a system of particles can be written as a product

$$\Psi(\vec{r}_1, \sigma_1; \vec{r}_2, \sigma_2; \dots) = \chi(\sigma_1, \sigma_2, \dots) \phi(\vec{r}_1, \vec{r}_2, \dots)$$



It depends only on the spin  
variables



It depends only on the  
spatial coordinates of the  
particles

The Schrödinger equation determines only  $\phi$ , leaving  $\chi$  arbitrary

# The indistinguishability of the particles leads to symmetry conditions on the wave function

Despite the fact that the electric interaction is spin-independent, there is a **dependency of the energy of the system with respect the total spin**

Let us consider a system of two identical particles.

After solving the Schrödinger equation, we find a set of energy levels, each of which are associated with a spatial wavefunction  $\phi(\vec{r}_1, \vec{r}_2)$

Since the particles are identical, the Hamiltonian of the system has to be invariant with respect the permutation of the particles

$\phi(\vec{r}_1, \vec{r}_2)$  **has to be symmetric or antisymmetric**

# The possible values of the energy of a system of identical particles depend on the total spin system

Let us assume now that the particles have spin 1/2

**The total wave function** (product of a spatial coordinate wave function and the spinorial wave function) **has to be antisymmetric with respect the permutation of the two particles**

$\phi(\vec{r}_1, \vec{r}_2)$  symmetric  $\implies$   $\chi(\sigma_1, \sigma_2)$  antisymmetric  $\implies$  Total spin = 0  
(spins aligned antiparallel one to the other)

**The energy only depends on  $\phi(\vec{r}_1, \vec{r}_2)$ , that is determined by the total spin**

$\phi(\vec{r}_1, \vec{r}_2)$  antisymmetric  $\implies$   $\chi(\sigma_1, \sigma_2)$  symmetric  $\implies$  Total spin = 1  
(spins aligned parallel one to the other)

# The possible values of the energy of a system of identical particles depend on the total spin system

Let us assume now that the particles have spin 1/2

Consider two electrons which have spatial coordinates  $\vec{r}_1$  and  $\vec{r}_2$

Let us assume that the two particles, without considering their mutual interaction, are in states that can be represented by single electron coordinate wavefunctions  $\phi_1(\vec{r})$  and  $\phi_2(\vec{r})$

The overall wave function of the system for a state with total spin  $S$

$$S = 0 \quad \text{Singlet } (m_S = 0) \quad \implies \Psi_S = \frac{1}{\sqrt{2}} [\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) + \phi_1(\vec{r}_2)\phi_2(\vec{r}_1)] \chi_S$$

$$S = 1 \quad \text{Triplet } (m_S = \{-1, 0, +1\}) \implies \Psi_T = \frac{1}{\sqrt{2}} [\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) - \phi_1(\vec{r}_2)\phi_2(\vec{r}_1)] \chi_T$$

# The possible values of the energy of a system of identical particles depend on the total spin system

The energies of the two possible states are

$$E_S = \int \Psi_S^* \hat{H} \Psi_S d\vec{r}_1 d\vec{r}_2$$

$$E_T = \int \Psi_T^* \hat{H} \Psi_T d\vec{r}_1 d\vec{r}_2$$

We assume that the spin part of the wave function is normalized

The overall wave function of the system for a state with total spin  $S$

$$S = 0 \quad \text{Singlet } (m_S = 0) \quad \implies \Psi_S = \frac{1}{\sqrt{2}} [\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) + \phi_1(\vec{r}_2)\phi_2(\vec{r}_1)] \chi_S$$

$$S = 1 \quad \text{Triplet } (m_S = \{-1, 0, +1\}) \implies \Psi_T = \frac{1}{\sqrt{2}} [\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) - \phi_1(\vec{r}_2)\phi_2(\vec{r}_1)] \chi_T$$

# Mean value of the energy in the singlet and triplet states

The energies of the single state is

$$E_S = \int \Psi_S^* \hat{H} \Psi_S \, d\vec{r}_1 d\vec{r}_2$$

$$\Psi_S = \frac{1}{\sqrt{2}} [\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) + \phi_1(\vec{r}_2)\phi_2(\vec{r}_1)] \chi_S$$

We assume that the spin part of the wave function is normalized

$$\begin{aligned} E_S &= \int \Psi_S^* \hat{H} \Psi_S \, d\vec{r}_1 d\vec{r}_2 \\ &= \int \left[ \frac{1}{\sqrt{2}} (\phi_1^*(\vec{r}_1)\phi_2^*(\vec{r}_2) + \phi_1^*(\vec{r}_2)\phi_2^*(\vec{r}_1)) \right] \hat{H} \left[ \frac{1}{\sqrt{2}} (\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) + \phi_1(\vec{r}_2)\phi_2(\vec{r}_1)) \right] d\vec{r}_1 d\vec{r}_2 \\ &= \frac{1}{2} \int \phi_1^*(\vec{r}_1)\phi_2^*(\vec{r}_2) \hat{H} \phi_1(\vec{r}_1)\phi_2(\vec{r}_2) \, d\vec{r}_1 d\vec{r}_2 \\ &\quad + \frac{1}{2} \int \phi_1^*(\vec{r}_1)\phi_2^*(\vec{r}_2) \hat{H} \phi_1(\vec{r}_2)\phi_2(\vec{r}_1) \, d\vec{r}_1 d\vec{r}_2 \\ &\quad + \frac{1}{2} \int \phi_1^*(\vec{r}_2)\phi_2^*(\vec{r}_1) \hat{H} \phi_1(\vec{r}_1)\phi_2(\vec{r}_2) \, d\vec{r}_1 d\vec{r}_2 \\ &\quad + \frac{1}{2} \int \phi_1^*(\vec{r}_2)\phi_2^*(\vec{r}_1) \hat{H} \phi_1(\vec{r}_2)\phi_2(\vec{r}_1) \, d\vec{r}_1 d\vec{r}_2 \end{aligned}$$

# Mean value of the energy in the singlet and triplet states

The energies of the triplet state is

$$E_T = \int \Psi_T^* \hat{H} \Psi_T d\vec{r}_1 d\vec{r}_2$$
$$\Psi_T = \frac{1}{\sqrt{2}} [\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) - \phi_1(\vec{r}_2)\phi_2(\vec{r}_1)] \chi_T$$

We assume that the spin part of the wave function is normalized

$$\begin{aligned} E_T &= \int \Psi_T^* \hat{H} \Psi_T d\vec{r}_1 d\vec{r}_2 \\ &= \int \left[ \frac{1}{\sqrt{2}} (\phi_1^*(\vec{r}_1)\phi_2^*(\vec{r}_2) - \phi_1^*(\vec{r}_2)\phi_2^*(\vec{r}_1)) \right] \hat{H} \left[ \frac{1}{\sqrt{2}} (\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) - \phi_1(\vec{r}_2)\phi_2(\vec{r}_1)) \right] d\vec{r}_1 d\vec{r}_2 \\ &= \frac{1}{2} \int \phi_1^*(\vec{r}_1)\phi_2^*(\vec{r}_2) \hat{H} \phi_1(\vec{r}_1)\phi_2(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \\ &\quad - \frac{1}{2} \int \phi_1^*(\vec{r}_1)\phi_2^*(\vec{r}_2) \hat{H} \phi_1(\vec{r}_2)\phi_2(\vec{r}_1) d\vec{r}_1 d\vec{r}_2 \\ &\quad - \frac{1}{2} \int \phi_1^*(\vec{r}_2)\phi_2^*(\vec{r}_1) \hat{H} \phi_1(\vec{r}_1)\phi_2(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \\ &\quad + \frac{1}{2} \int \phi_1^*(\vec{r}_2)\phi_2^*(\vec{r}_1) \hat{H} \phi_1(\vec{r}_2)\phi_2(\vec{r}_1) d\vec{r}_1 d\vec{r}_2 \end{aligned}$$

# Mean value of the energy in the singlet and triplet states

The difference in energies between the singlet and the triplet state is

$$E_S - E_T = 2 \int \phi_1^*(\vec{r}_1) \phi_2^*(\vec{r}_2) \hat{H} \phi_1(\vec{r}_2) \phi_2(\vec{r}_1) d\vec{r}_1 d\vec{r}_2$$

(to obtain this expression remembers that the Hamiltonian operator is self-adjoint)

The difference between single and triplet states can be parametrized by

$$\vec{S}_1 \cdot \vec{S}_2$$

# Explanation of this mapping: The coupling of two spins

Consider two spin-1/2 particles coupled by an interaction given by the Hamiltonian

$$\hat{H} = A \hat{S}^a \cdot \hat{S}^b$$

Operator for the spin of particle  $a$

Operator for the spin of particle  $b$

Considered as a joint entity, the total spin can be represented by the operator

$$\hat{S}^{\text{tot}} = \hat{S}^a + \hat{S}^b$$

so that

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

# The coupling of two spins: eigenvalue of different operators

Combining two spin-1/2 particles results in a joint entity with spin quantum number

$$s = 0 \text{ or } 1$$

The eigenvalue of  $(\hat{S}^{\text{tot}})^2$  is  $s(s + 1)$       The eigenvalue of  $(\hat{S}^a)^2$  and  $(\hat{S}^b)^2$  are  $3/4$

$$(\hat{S}^{\text{tot}})^2 = \begin{cases} 2 & \text{if } s = 1 \\ 0 & \text{if } s = 0 \end{cases}$$

Since  $(\hat{S}^{\text{tot}})^2 = (\hat{S}^a)^2 + (\hat{S}^b)^2 + 2\hat{S}^a \cdot \hat{S}^b$       Since  $\hat{H} = A\hat{S}^a \cdot \hat{S}^b$

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

# The coupling of two spins: eigenstates of different operators

Let us consider the following basis

$$|\uparrow\uparrow\rangle$$

$$|\uparrow\downarrow\rangle$$

$$|\downarrow\uparrow\rangle$$

$$|\downarrow\downarrow\rangle$$

First arrow:  $z$ -component of the spin labelled as  $a$

Second arrow:  $z$ -component of the spin labelled as  $b$

The eigenstates of  $\hat{S}^a \cdot \hat{S}^b$  are linear combination of these basis states

**Table 1.1** The eigenstates of  $\hat{S}^a \cdot \hat{S}^b$  and the corresponding values of  $m_s$ ,  $s$  and the eigenvalue of  $\hat{S}^a \cdot \hat{S}^b$ .

Eigenstate	$m_s$	$s$	$\hat{S}^a \cdot \hat{S}^b$
$ \uparrow\uparrow\rangle$	1	1	$\frac{1}{4}$
$\frac{ \uparrow\downarrow\rangle +  \downarrow\uparrow\rangle}{\sqrt{2}}$	0	1	$\frac{1}{4}$
$ \downarrow\downarrow\rangle$	-1	1	$\frac{1}{4}$
$\frac{ \uparrow\downarrow\rangle -  \downarrow\uparrow\rangle}{\sqrt{2}}$	0	0	$-\frac{3}{4}$

The degeneracy of each state of each state is given by

$$2s + 1$$

$$s = 1 \Rightarrow \text{Triplet}$$

$$s = 0 \Rightarrow \text{Singlet}$$

# The coupling of two spins: eigenstates of different operators

Let us consider the following basis

$$|\uparrow\uparrow\rangle \quad |\uparrow\downarrow\rangle \quad |\downarrow\uparrow\rangle \quad |\downarrow\downarrow\rangle$$

First arrow:  $z$ -component of the spin labelled as  $a$

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$ \uparrow\uparrow\rangle$	1	1	$\frac{1}{4}$
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$\frac{ \uparrow\downarrow\rangle -  \downarrow\uparrow\rangle}{\sqrt{2}}$	0	0	$-\frac{3}{4}$

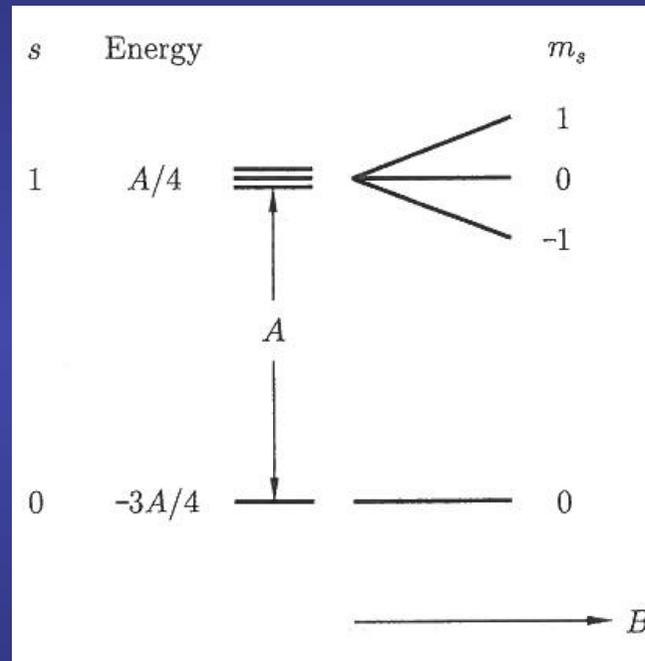
The  $z$  component of the spin of the state,  $m_s$   
Is the sum of the  $z$  components of the individual spins

Because eigenstates are mixtures of states in the original basis, it is not possible in general to know both the  $z$ -component of the original spins and the total spin of the resultant entity

$$s = 1 \Rightarrow \text{Triplet} \quad m_s = -1, 0, +1$$

$$s = 0 \Rightarrow \text{Singlet} \quad m_s = 0$$

# The coupling of two spins: Summary



$A$  assumed to be positive  
in the diagram

# Mean value of the energy in the singlet and triplet states

The difference in energies between the singlet and the triplet state is

$$E_S - E_T = 2 \int \phi_1^*(\vec{r}_1) \phi_2^*(\vec{r}_2) \hat{H} \phi_1(\vec{r}_2) \phi_2(\vec{r}_1) d\vec{r}_1 d\vec{r}_2$$

(to obtain this expression remembers that the Hamiltonian operator is self-adjoint)

The difference between single and triplet states can be parametrized by

$$\vec{S}_1 \cdot \vec{S}_2$$

For a singlet state

$$\vec{S}_1 \cdot \vec{S}_2 = -\frac{3}{4}$$

For a triplet state

$$\vec{S}_1 \cdot \vec{S}_2 = \frac{1}{4}$$

The Hamiltonian can be written in the form of an effective Hamiltonian

$$\hat{H} = \frac{1}{4} (E_S + 3E_T) - (E_S - E_T) \vec{S}_1 \cdot \vec{S}_2$$

# Effective Hamiltonian to describe singlet and triplet states

The Hamiltonian can be written in the form of an effective Hamiltonian

$$\hat{H} = \frac{1}{4} (E_S + 3E_T) - (E_S - E_T) \vec{S}_1 \cdot \vec{S}_2$$

**Constant term:**

Can be absorbed into other constant energy-terms

**Spin-dependent term:**

**Since**

$$E_S - E_T = 2 \int \phi_1^*(\vec{r}_1) \phi_2^*(\vec{r}_2) \hat{H} \phi_1(\vec{r}_2) \phi_2(\vec{r}_1) d\vec{r}_1 d\vec{r}_2$$

**We can define the exchange constant (or exchange integral) as**

$$J = \frac{E_S - E_T}{2} = \int \phi_1^*(\vec{r}_1) \phi_2^*(\vec{r}_2) \hat{H} \phi_1(\vec{r}_2) \phi_2(\vec{r}_1) d\vec{r}_1 d\vec{r}_2$$

**And hence, the spin dependent term in the model Hamiltonian can be written as**

$$\hat{H}^{\text{spin}} = -2J \vec{S}_1 \cdot \vec{S}_2$$

# Effective Hamiltonian to describe singlet and triplet states

And hence, the spin dependent term in the model Hamiltonian can be written as

$$\hat{H}^{\text{spin}} = -2J\vec{S}_1 \cdot \vec{S}_2$$

$J > 0 \Rightarrow (E_S > E_T) \Rightarrow$  the triplet state  $S = 1$  is favoured

$J < 0 \Rightarrow (E_S < E_T) \Rightarrow$  the singlet state  $S = 0$  is favoured

# Generalization for more than two electrons

The spin dependent term in the model Hamiltonian can be written as

$$\hat{H}^{\text{spin}} = -2J\vec{S}_1 \cdot \vec{S}_2$$

Generalizing to a many-body system is far from trivial

Since the early days of Quantum Mechanics, it was recognized that interactions such as the previous one **probably apply between all neighboring atoms**

**This motivates the Hamiltonian of the Heisenberg model**

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

The factor of 2 is omitted because the summation includes each pair of spins twice

$$\hat{H} = -2 \sum_{i>j} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

The factor of 2 appears because the summation on  $i > j$  avoids the double counting

# General features respect the (complicate) calculation of exchange integrals

If the two electrons are on the same atom the exchange integral is usually positive

$J > 0 \Rightarrow (E_S > E_T) \Rightarrow$  the triplet state  $S = 1$  is favoured



**Antisymmetric spatial state**



**Minimizes the Coulomb repulsion between the two electrons by keeping them apart**

**Good agreement with Hund's first rule**

# General features respect the (complicate) calculation of exchange integrals

If the two electrons are on neighboring atoms

Any joint state will be a combination of a state centered on one atom and a state centered on the other



- The correct states to consider are molecular orbitals that can be:
- Bonding (spatially symmetric)  $\Rightarrow$  (asymmetric spin state)
  - Antibonding (spatially asymmetric)  $\Rightarrow$  (symmetric spin state)

Antisymmetric state usually more energetic  
(more curvature that implies larger kinetic energy),  
and the system tends to be in the bonding state

$$J < 0 \Rightarrow (E_S < E_T) \Rightarrow \text{the singlet state } S = 0 \text{ is favoured}$$

**Additional information**

# Direct exchange

**If the electrons in neighboring magnetic atoms interact via an exchange interaction, this is known as direct exchange**

The exchange interaction proceeds directly without the need for an intermediary.

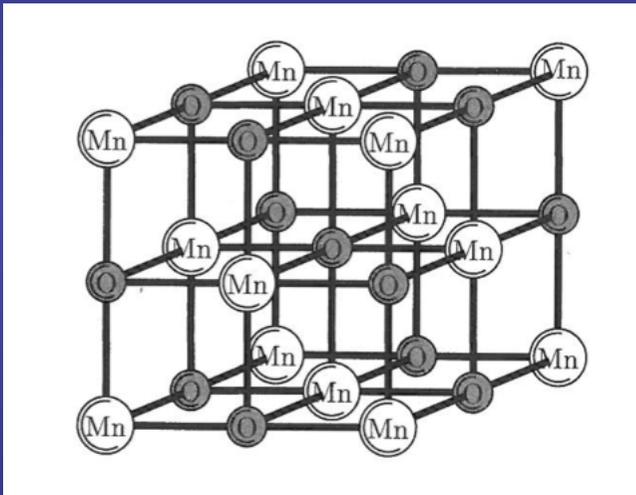
Physical situation is rarely that simple:

**Very often, direct exchange cannot be an important mechanism in controlling the magnetic properties because there is insufficient direct orbital between neighboring magnetic orbitals**

- 4f electrons in rare earths are strongly localized
- 3d transition metals, extremely difficult to justify magnetic properties from direct exchange. Some of these materials (Fe, Co, Ni) are metals, and conduction (delocalized) electrons should not be neglected.

# Indirect exchange in ionic solids: superexchange

Superexchange is defined as an indirect exchange interaction between non-neighboring magnetic ions which is mediated by a non-magnetic ion which is placed in between the magnetic ion



Imagine two transition metal ions separated by an oxygen atom (for instance  $\text{Mn}^{2+}$  manganese ions connected via  $\text{O}^{2-}$  oxygen ions in  $\text{MgO}$ )

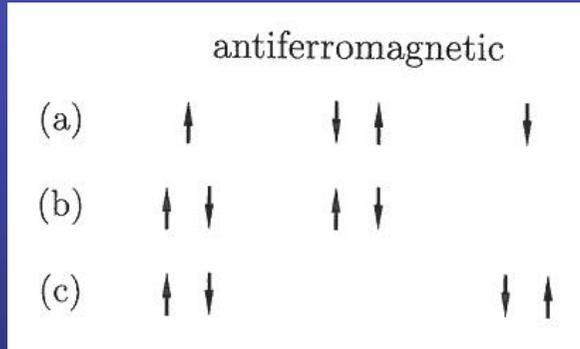
For simplicity, we assume that the magnetic moment on the transition metal ion is due to a single unpaired electron

In the perfectly ionic picture, each metal ion would have a single unpaired electron in a *d*-orbital and the oxygen would have two *p*-electrons in its outermost occupied state

# Indirect exchange in ionic solids: superexchange

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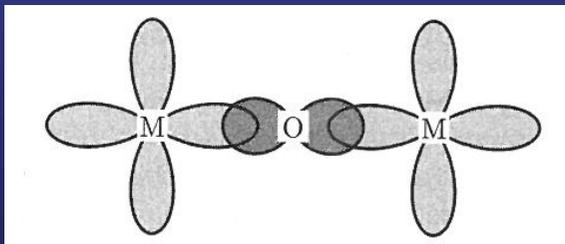
In the perfectly ionic picture, each metal ion would have a single unpaired electron in a  $d$ -orbital and the oxygen would have two  $p$ -electrons in its outermost occupied state



In the antiferromagnetic configuration, two electrons with spin up and two electrons with spin down

The ground state configuration is (a)

But the excited states (b) and (c) are also possible

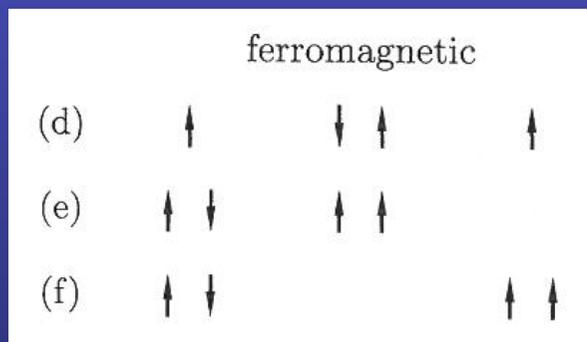


Therefore (a) can mix with the excited states (b) and (c) and the **magnetic electrons can be delocalized over the M-O-M unit, lowering the kinetic energy**

# Indirect exchange in ionic solids: superexchange

Superexchange is defined as an indirect exchange interaction between non-neighboring magnetic ions which is mediated by a non-magnetic ion which is placed in between the magnetic ion

In the perfectly ionic picture, each metal ion would have a single unpaired electron in a  $d$ -orbital and the oxygen would have two  $p$ -electrons in its outermost occupied state



In the ferromagnetic configuration, three electrons with spin up and one electron with spin down

The ground state configuration is (a)

The excited states (b) and (c) are not possible due to exclusion principle

Therefore (a) cannot mix with the excited states (b) and (c).  
The ferromagnetic state is more localized and costs more energy.

# Indirect exchange in ionic solids: superexchange

Superexchange is a second order process and is derived from second order perturbation theory

The energy involved is:

Directly proportional to the square of the matrix element of the transition

$$t$$

Related with the width of the conduction band in a simple tight-binding approach

Inversely proportional to the to the energy cost of making the transition state

$$U$$

Related with the Coulomb energy

$$J \sim -\frac{t^2}{U}$$

# Indirect exchange in ionic solids: superexchange

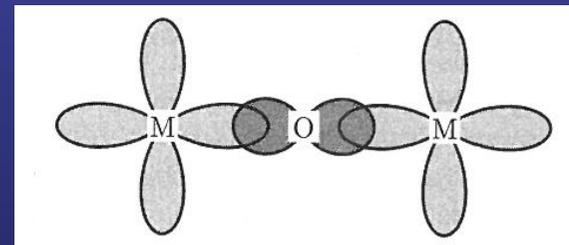
The exchange integral consists of two parts

## Potential exchange term

Represents the electron repulsion.  
Favours ferromagnetic state.  
Small when the atoms are well separated

## Kinetic exchange term

Favours delocalization of the electrons.  
Dominates when the atoms are well separated.  
Strongly dependent upon the angle of the  
M-O-M bond.



# Indirect exchange in metals: RKKY interaction

In metals, the exchange interaction between magnetic ions can be mediated by the conduction electrons

A localized magnetic moment spin polarizes the conduction electrons

This polarization, in turn, couples to a neighbouring localized magnetic moment a distance  $r$  away

The magnetic interaction is indirect because it does not involve direct coupling between magnetic moments.

**Ruderman, Kittel, Kasuya and  
Yoshida interaction**

$$J_{\text{RKKY}} \propto \frac{\cos(2k_{\text{F}}r)}{r^3}$$

- The interaction is long range
- It might be ferro or antiferro depending on the distance
- Oscillatory coupling, with wave length  $\frac{\pi}{k_{\text{F}}}$  because sharpness of Fermi surface

# Double exchange

A ferromagnetic exchange interaction which occurs because the magnetic ion can show **mixed valency**, i.e. that it can exist in more than one oxidation state

Examples: compounds containing the Mn ion which can exist in oxidation state 3 or 4 ( $\text{Mn}^{3+}$  or  $\text{Mn}^{4+}$ )



Sr is divalent ( $\text{Sr}^{2+}$ )  $\implies$  a fraction  $x$  of the Mn ions are  $\text{Mn}^{4+}$

La is trivalent ( $\text{La}^{3+}$ )  $\implies$  a fraction  $(1-x)$  of the Mn ions are  $\text{Mn}^{3+}$

The end members of the series are both antiferromagnetic insulators (as expected for an oxide material in which magnetism is mediated by superexchange through the oxygen)

When  $\text{LaMnO}_3$  is doped with Sr up to  $x = 0.175$ , the Jahn-Teller distortion vanishes and the system becomes ferromagnetic with a Curie temperature around room temperature, below which the system is metallic

# Double exchange

A ferromagnetic exchange interaction which occurs because the magnetic ion can show **mixed valency**, i.e. that it can exist in more than one oxidation state

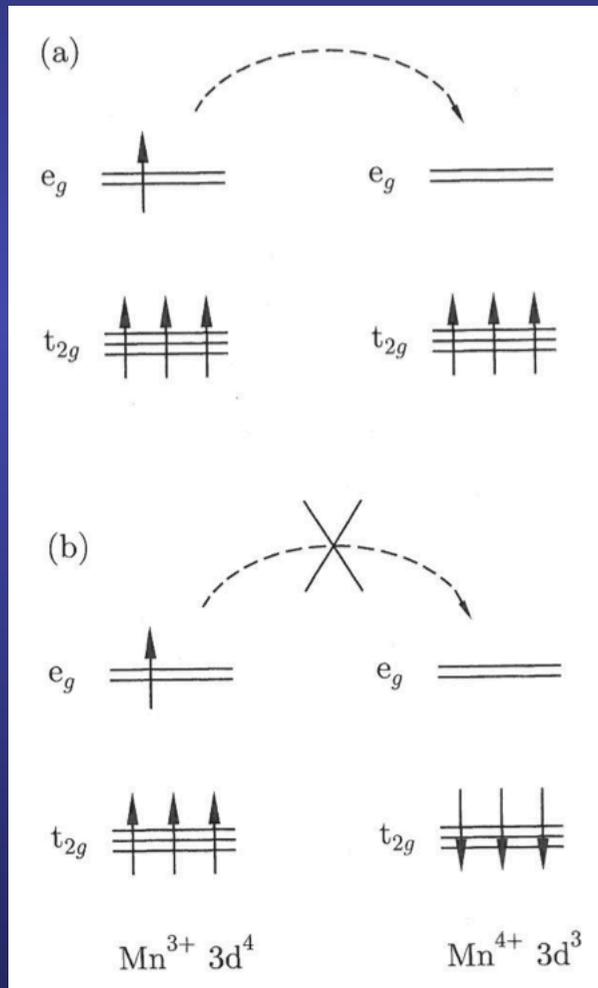


The  $e_g$  electron of a  $\text{Mn}^{3+}$  ion can hop to the neighboring site only if there is a vacancy there with the same spin  
(hopping proceeds without spin flip of the hopping electron)

If the neighboring atom is a  $\text{Mn}^{4+}$  (no electrons in its  $e_g$  shell), this should present no problem

However, there is a strong single-center exchange interaction between the  $e_g$  electron and the  $t_{2g}$  level, which wants to keep them all aligned

Ferromagnetic alignment of neighboring ions is therefore required to maintain the high-spin alignment on the donating and receiving ion



# The Pauli spin matrices

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

**Any two by two matrix can be written in terms of them  
(they are a basis of the Hilbert space of the (2×2) matrices)**

**Any matrix that can be written has four numbers in it**  $M = \begin{pmatrix} a & b \\ c & d \end{pmatrix}$

**It can be written as a linear combination of four matrices**

$$M = a \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + b \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + c \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} + d \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

**One special way of doing this is to choose the Pauli spin matrices as the basis**

$$M = \alpha 1 + \beta \sigma_x + \gamma \sigma_y + \delta \sigma_z \quad \alpha, \beta, \gamma, \delta \quad \text{Are complex numbers}$$

# Products of the Pauli spin matrices

$$\sigma_x^2 = 1 \quad \sigma_y^2 = 1 \quad \sigma_z^2 = 1$$

$$\sigma_x \sigma_y = -\sigma_y \sigma_x = i\sigma_z$$

$$\sigma_y \sigma_z = -\sigma_z \sigma_y = i\sigma_x$$

$$\sigma_z \sigma_x = -\sigma_x \sigma_z = i\sigma_y$$

## Pauli spin matrices as components of a vector of matrices

$$\sigma = (\sigma_x, \sigma_y, \sigma_z)$$

You can use  $\sigma$  in different coordinate systems as though it is a vector

# Definition of the spin angular momentum operator

We define the spin angular momentum operator by

$$\hat{\vec{S}} = \frac{1}{2} \hat{\vec{\sigma}}$$

Or, in components

$$\hat{S}_x = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \hat{S}_y = \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \hat{S}_z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

We are using the convention that the angular momentum is measured in units of  $\hbar$

The angular momentum associated with an electron is  $\hbar \vec{S}$

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Only the operator  $\hat{S}_z$  is diagonal.

If the electron spin points along  $\hat{z}$  the representation is particularly simple

# Representation of the spin operator along $z$ -direction

Eigenstates of  $\hat{S}_z$

Eigenvalues of  $\hat{S}_z$

$$|\uparrow_z\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$m_s = \frac{1}{2}$$

Spin pointing parallel  
to the  $z$ -axis

$$\hat{S}_z |\uparrow_z\rangle = \frac{1}{2} |\uparrow_z\rangle$$

$$|\downarrow_z\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$m_s = -\frac{1}{2}$$

Spin pointing antiparallel  
to the  $z$ -axis

$$\hat{S}_z |\downarrow_z\rangle = -\frac{1}{2} |\downarrow_z\rangle$$

# Eigenstates corresponding to the spin pointing parallel or antiparallel to the $x$ and $y$ axis

$x$  axis

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

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

$y$  axis

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

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

**These eigenstates are normalized**

**All of them have the same magnitude of the eigenvalue:  $\frac{1}{2}$   
positive if pointing parallel to the axis  
negative if pointing antiparallel**

## Spinor representation: the two-component representation of the spin wave function

$$|\psi\rangle = \begin{pmatrix} a \\ b \end{pmatrix} = a|\uparrow_z\rangle + b|\downarrow_z\rangle$$

Where  $a$  and  $b$  are complex numbers and it is conventional to normalize the state

$$|a|^2 + |b|^2 = 1$$

# Total spin angular momentum operator

$$\hat{\vec{S}} = \begin{pmatrix} \hat{S}_x \\ \hat{S}_y \\ \hat{S}_z \end{pmatrix} = \vec{i}\hat{S}_x + \vec{j}\hat{S}_y + \vec{k}\hat{S}_z$$

The spin square operator is given by

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

Since the eigenvalues of  $\hat{S}_x^2$ ,  $\hat{S}_y^2$ , and  $\hat{S}_z^2$  are always

$$\frac{1}{4} = \pm \left(\frac{1}{2}\right)^2$$

So we have the result that for any spin state,

$$\hat{\vec{S}}^2 |\psi\rangle = \left(\hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2\right) |\psi\rangle = \left(\frac{1}{4} + \frac{1}{4} + \frac{1}{4}\right) |\psi\rangle = \frac{3}{4} |\psi\rangle$$

# Commutation relations between the spin operators

From the commutation relations of the Pauli matrices, it follows immediately that

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

And cyclic permutations thereof.

Besides, each of these components commutes with  $\hat{S}^2$

$$\left[ \hat{S}^2, \hat{S}_z \right] = 0$$

**Thus, it is possible to know simultaneously the total spin and one of the components, but it is impossible to know more than one component simultaneously**

# Raising and lowering operator

Raising operator

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

Lowering operator

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

They are not Hermitian operators (not observables)

$$\hat{S}_+^\dagger = \hat{S}_-$$

$$\hat{S}_-^\dagger = \hat{S}_+$$

# Raising and lowering operator effect on spin states

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

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

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

$$\hat{S}_- |\downarrow_z\rangle = 0$$

The raising operator will raise the  $z$  component of the spin angular momentum by  $\hbar$

The lowering operator will lower the  $z$  component of the spin angular momentum by  $\hbar$

If the  $z$  component of the spin angular momentum is already at its maximum (minimum) level, the raising (lowering) operator will annihilate the state