









$$H_{He} = \sum_{i=1}^{2} \frac{p_i^2}{2m} - \frac{1}{4\pi\varepsilon_0} \sum_{i=1}^{2} \frac{Ze^2}{r_i^2} + \frac{1}{4\pi\varepsilon_0} \frac{e^2}{|r_2 - r_1|} = H_0 + H_{e-e} \qquad r_2 \qquad He \text{ atom}$$

Ground state -> the two electrons occupy the 1s orbital

-> the spatial part of the wavefunction is symmetric (electrons have identical quantum numbers *nlm*=100) -> the spin part must be antisymmetric (electrons are fermions)

$$\Psi_{\text{ground}} = \Psi_{\text{sym}}(\mathbf{r}_1, \mathbf{r}_2) \chi_{\text{antisym}}(\mathbf{s}_1, \mathbf{s}_2) = \frac{1}{2} [\Psi_{100}(\mathbf{r}_1) \Psi_{100}(\mathbf{r}_2) + \Psi_{100}(\mathbf{r}_1) \Psi_{100}(\mathbf{r}_2)] [\alpha \beta - \beta \alpha]$$

From the previous Hamiltonian we can calculate the energy of the ground state. Because H_{He} does not contain spin terms, the spin part of the wavefunction only needs to satisfy the antisymmetric condition

Excited state -> one electron occupies the 1s orbital (*nlm*=100); the second electron is in an excited state *nlm* 1) the spatial part of the wavefunction is symmetric and the spin part is antisymmetric

$$\Psi_{\text{exci}}^{\text{S}} = \Psi_{\text{sym}}(\mathbf{r}_{1}, \mathbf{r}_{2})\chi_{\text{antisym}}(\mathbf{s}_{1}, \mathbf{s}_{2}) = \frac{1}{2}[\Psi_{100}(\mathbf{r}_{1})\Psi_{\text{nlm}}(\mathbf{r}_{2}) + \Psi_{\text{nlm}}(\mathbf{r}_{1})\Psi_{100}(\mathbf{r}_{2})][\alpha\beta - \beta\alpha] \quad \text{Singlet S=0}$$

2) the spatial part of the wavefunction is antisymmetric and the spin part is symmetric

$$\Psi_{\text{exci}}^{\text{T}} = \Psi_{\text{antisym}}(\mathbf{r}_{1}, \mathbf{r}_{2}) \chi_{\text{sym}}(\mathbf{s}_{1}, \mathbf{s}_{2}) = \frac{1}{2} [\Psi_{100}(\mathbf{r}_{1}) \Psi_{\text{nlm}}(\mathbf{r}_{2}) - \Psi_{\text{nlm}}(\mathbf{r}_{1}) \Psi_{100}(\mathbf{r}_{2})] \chi_{\text{sym}}(\mathbf{s}_{1}, \mathbf{s}_{2})$$
$$\alpha = \frac{1}{2}; \beta = -\frac{1}{2} \qquad \qquad \chi_{\text{sym}}(\mathbf{s}_{1}, \mathbf{s}_{2}) = \alpha \alpha; \beta \beta; \frac{1}{\sqrt{2}} (\alpha \beta + \beta \alpha) \qquad \qquad \text{Tr}$$

Triplet S=1





2-

The singlet and triplet wavefunctions applied to H_0 give the same energy; the H_{e-e} contribution can be calculated with the perturbation theory

I is the Coulomb integral -> electrostatic repulsion between the electrons ($\Psi(r)^2 \rightarrow \rho$ electron density) J is the exchange integral -> energy associated with a change of quantum states between the electrons

Origin of Exchange interaction: -> Coulomb repulsion between electrons -> total anti-symmetric wave function (Pauli exclusion principle)

J is positive J is negative -> triplet ground state S=1 -> singlet ground state S=0

-> parallel spins-> antiparallel spins

Note: we get the exchange energy from an Hamiltonian not including spin terms !!!!!







nonmagnetic ground state

magnetic ground state

Hamiltonian H = H₁ + H₂ + H₁₂, where
$$\begin{cases} H_1 = -\frac{\hbar^2}{2m}\Delta_1 - \frac{Ze^2}{r_1} \\ H_2 = -\frac{\hbar^2}{2m}\Delta_2 - \frac{Ze^2}{r_2} \\ H_{12} = +\frac{e^2}{r_{12}} \end{cases}$$





$$\begin{split} \psi_{1} &= \frac{1}{\sqrt{2 - 2l^{2}}} \left(\phi_{a}(r_{1})\phi_{b}(r_{2}) - \phi_{b}(r_{1})\phi_{a}(r_{2}) \right) \left(\alpha(r_{1})\alpha(r_{2}) \right) \text{ triplet} \\ \psi_{2} &= \frac{1}{\sqrt{2 - 2l^{2}}} \left(\phi_{a}(r_{1})\phi_{b}(r_{2}) - \phi_{b}(r_{1})\phi_{a}(r_{2}) \right) \left(\beta(r_{1})\beta(r_{2}) \right) \text{ triplet} \\ \psi_{3} &= \frac{1}{\sqrt{2 - 2l^{2}}} \left(\phi_{a}(r_{1})\phi_{b}(r_{2}) - \phi_{b}(r_{1})\phi_{a}(r_{2}) \right) \frac{1}{\sqrt{2}} \left(\beta(r_{1})\alpha(r_{2}) + \alpha(r_{1})\beta(r_{2}) \right) \text{ triplet} \\ \psi_{4} &= \frac{1}{\sqrt{2 + 2l^{2}}} \left(\phi_{a}(r_{1})\phi_{b}(r_{2}) + \phi_{b}(r_{1})\phi_{a}(r_{2}) \right) \frac{1}{\sqrt{2}} \left(\beta(r_{1})\alpha(r_{2}) - \alpha(r_{1})\beta(r_{2}) \right) \text{ singlet} \end{split}$$

$$E = \frac{\langle \psi_i | H | \psi_i \rangle}{\langle \psi_i | \psi_i \rangle} = \langle \psi_i | H_1 + H_2 + H_{12} | \psi_i \rangle \quad \text{N.B. } \langle \psi_i | \psi_i \rangle = 1$$

$$= \frac{1}{2 \pm 2l^2} \iint (\phi_a(r_1)\phi_b(r_2) \pm \phi_b(r_1)\phi_a(r_2))^* (H_1 + H_2 + H_{12}) (\phi_a(r_1)\phi_b(r_2) \pm \phi_b(r_1)\phi_a(r_2)) d\mathbf{r}_1 d\mathbf{r}_2$$

$$= \frac{1}{2 \pm 2l^2} (I_1 + I_2 + K_{12} \pm J_{12})$$





$$E = \frac{\langle \psi_i | H | \psi_i \rangle}{\langle \psi_i | \psi_i \rangle} = \langle \psi_i | H_1 + H_2 + H_{12} | \psi_i \rangle \qquad \text{N.B. } \langle \psi_i | \psi_i \rangle = 1$$

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$$= \frac{1}{2 \pm 2l^2} (I_1 + I_2 + K_{12} \pm J_{12})$$

$$I_1 = \underbrace{\int \phi_a^*(\mathbf{r}_1)H_1\phi_a(\mathbf{r}_1)d\mathbf{r}_1}_{e_1 \text{ on atom } a} + \underbrace{\int \phi_a^*(\mathbf{r}_2)H_2\phi_a(\mathbf{r}_2)d\mathbf{r}_2}_{e_2 \text{ on atom } a}$$

$$I_2 = \underbrace{\int \phi_b^*(\mathbf{r}_2)H_2\phi_b(\mathbf{r}_2)d\mathbf{r}_2}_{e_2 \text{ on atom } b} + \underbrace{\int \phi_b^*(\mathbf{r}_1)H_1\phi_b(\mathbf{r}_1)d\mathbf{r}_1}_{e_1 \text{ on atom } b}$$

$$K_{12} = \underbrace{\iint \phi_a^*(\mathbf{r}_1)\phi_b^*(\mathbf{r}_2)H_{12}\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2}_{e_1 - e_2 \text{ interaction, } e_1, e_2 \text{ on different atoms}} + \underbrace{\iint \phi_a^*(\mathbf{r}_2)\phi_b^*(\mathbf{r}_1)H_{12}\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1)d\mathbf{r}_1d\mathbf{r}_2}_{e_1 - e_2 \text{ interaction, } e_1, e_2 \text{ on different atoms}}$$

$$J_{12} = \underbrace{\iint \phi_a^*(\mathbf{r}_1)\phi_b^*(\mathbf{r}_2)H_{12}\phi_b(\mathbf{r}_1)\phi_a(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2}_{e_1 + e_2 \text{ interaction, } e_1, e_2 \text{ on different atoms}} + \underbrace{\iint \phi_a^*(\mathbf{r}_2)\phi_b^*(\mathbf{r}_1)H_{12}\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2}_{e_1 - e_2 \text{ interaction, } e_1, e_2 \text{ on different atoms}}$$







$$\Rightarrow \underline{E}_{s} - \underline{E}_{t} = \frac{1}{4 - 4l^{4}} \left[-4l^{2} \left(I_{1} + I_{2} + K_{12} \right) + 4J_{12} \right]$$

Ground state depends on the relative strength of J_{12} (always > 0) in respect to $-4l^2(I_1+I_2+K_{12})$

 $J_{12} > 4l^2(I_1+I_2+K_{12}) \rightarrow$ ground state is magnetic (triplet)

 $J_{12} < 4l^2(I_1+I_2+K_{12}) \rightarrow$ ground state is non magnetic (singlet)

Ex: H_2 molecule $J_{12} < 0$ -> singlet ground state

The molecule magnetic ground state depends on the interaction between electrons belonging to two different atoms





The Heisenberg Hamiltonian is an effective Hamiltonian extending to larger atoms the electronelectron interaction seen in the He atom

$$\begin{split} H_{\text{Heisenberg}} &= H_0 + H_{\text{Coulomb}} + H_{\text{exchange}} \\ H_{\text{exchange}} &= -2\sum_{i < j}^{N} J_{ij} \mathbf{s}_i \cdot \mathbf{s}_j; \\ J_{ij} &= \int \int \psi_i(\mathbf{r}_i) \psi_j(\mathbf{r}_j) \frac{e^2}{4\pi\varepsilon_0 \left| \mathbf{r}_i - \mathbf{r}_j \right|} \psi_i^*(\mathbf{r}_j) \psi_j^*(\mathbf{r}_i) d\mathbf{r}_i d\mathbf{r}_j \end{split}$$

The Heisenberg Hamiltonian is used to describe: -> coupling of individual spins located on the same atom (intra-atomic exchange)

-> coupling of atomic spin moments on different atoms (inter-atomic exchange)

BUT

Intra-atomic (a,c) and inter-atomic (b) exchange have different energies

a),c) -> intra-atomic V_{e-e} in the isolated atom (Hund's rules) or Stoner band approach





École Polytechnique

Generalization to N-atoms system:

• Coulomb interaction + Pauli's principle → The spins of the electrons are correlated

i.e., there is a magnetic splitting in the energy spectrum of electrons in systems of atoms with open el. shells, true for systems of any size, doesn't tell what type of magnetic coupling

• The energy spectrum is represented by a model system of pairwise interacting spins

$$H = -\sum_{i \neq j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$
 Heisenberg model

 \approx correct to 2nd order in the overlap orbitals, cannot be proven rigorously

• There are many possible exchange-interaction Hamiltonians...

$$H = -J_{z} \sum_{i \neq j} S_{i}^{z} S_{j}^{z} - J_{\perp} \sum_{i \neq j} \left(S_{i}^{x} S_{j}^{x} + S_{i}^{y} S_{j}^{y} \right) \quad \begin{array}{l} \textit{Anisotropic Heisenberg model} \\ \textit{and XY model } (J_{z}=0) \end{array}$$

$$H = -J_z \sum_{i \neq j} \mathbf{S}_i^z \mathbf{S}_j^z$$

Ising model





$$H = -\sum_{i \neq j} J_{ij} \mathbf{S}_{i} \cdot \mathbf{S}_{j} \begin{cases} J > 0 \text{ ferromagnetic coupling} (10-50 \text{ meV in Fe, Co, Ni}) \\ J < 0 \text{ antiferromagnetic coupling} (30-100 \text{ meV in Mn, Cr}; 20 \text{ meV in NiO superexchange}) \end{cases}$$

J < 0, depending on formula unit, system dimensions, topology:

- fully compensated AFM
- ferrimagnetism (uncompensated AFM)
- frustrated AFM

Cr(100) surface



G-type





C-type

A-type













All spins in the grain must be ferromagnetically aligned

exchange energy J coupling spins





Coupling is destroyed and the net magnetic moment is zero

Domain formation -> magnetic moment is strongly reduced



 $H_{exc} = -\sum_{i \neq j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$

S_i is the atomic spin

Gain in the magnetostatic energy at the expenses of the exchange energy





- Which is the origin of the aligned atomic spin moments in a ferromagnetic domain (spontaneous magnetization)?
- Weiss -> molecular field H_W (or mean field theory) of unknown origin
- Heisenberg -> molecular field originating from the interaction of the atomic spin moment with the spin sea of all the other atoms $E = -2s \sum L s = -m H + H = -\frac{2}{2} \sum L s$

$$E_{i} = -2s_{i}\sum_{j}J_{ij}s_{j} = -m_{i}H_{W}; \quad H_{W} = -\frac{2}{g\mu_{B}}\sum_{j}J_{ij}s_{j}$$

Example: Two energy levels: $+/-\mu_B H$ with an occupation probability given by $exp(+/-\mu_B H/kT)$

single spin s=1/2
$$M(H,T) = M^{\uparrow} - M_{\downarrow} = Ng\mu_{B}(\frac{e^{x}}{e^{x} + e^{-x}} - \frac{e^{-x}}{e^{x} + e^{-x}}) = N\mu_{B} \tanh(x); \quad x = \frac{\mu_{B}H}{k_{B}T}$$

Sea of spin s=1/2
$$\longrightarrow x = \frac{\mu_{\rm B}({\rm H} + \beta {\rm M}({\rm T}))}{k_{\rm B}{\rm T}}$$
 $\beta {\rm M}({\rm T}) \rightarrow$ molecular field

Curie temperature: temperature at which the spontaneous magnetization (H=0) goes to zero

$$M(T) \rightarrow 0 \text{ when } \tanh(x) \rightarrow 0$$

$$when x \rightarrow 0 \text{ i.e. } \tanh(x) = x$$

$$M(T_c) \approx N\mu_B x = N\mu_B \frac{\mu_B(\beta M(T_c))}{k_B T_C} \Rightarrow$$

$$T_C = \frac{N\mu_B^2 \beta}{k_B} = \mu_B \frac{\beta M(0)}{k_B}$$

The magnetization goes to zero when the thermal energy $(k_B T_C)$ equals the energy of a single spin in the molecular field $(gs\mu_B H_W = gs\mu_B\beta M(0))$





For a general spin value *s* and moment $m = -g\mu_B s$

$$T_{C} = \frac{2\langle s \rangle^{2} J_{0}}{3k_{B}}; \quad J_{0} = \sum_{j} J_{ij} = NJ_{01}$$
$$H_{W} = \frac{2\langle s \rangle^{2} J_{0}}{3 m}$$
$$H_{W} = \frac{2\langle s \rangle^{2} J_{0}}{3 m}$$

element	$\langle s \rangle^2 J_{01}$ [meV]	N	$\frac{N\langle s\rangle^2 J_{01}}{[\text{meV}]}$	$\langle s \rangle^2 J_0$ [meV]	$T_{ m C}$ [K]	$B_{ m W} = [10^3 { m T}]$
Co (fcc)	14.8	12	178	212	1645	4.3
Ni (fcc)	2.8	12	34	51	397	2.9

Neel temperature: is the equivalent to the Curie temperature for an antiferromagnet







$T_{\rm C}$ depends on the atomic coordination

$$T_{\rm C} = \frac{2\langle s \rangle^2 J_0}{3k_{\rm B}}; \quad J_0 = \sum_j J_{ij} = NJ_{01}$$



 T_c nanostructures $< T_c$ bulk

S. Bornemann et al. Phase Transitions 78, 701 (2005)

J_{ii} as a function of distance



The number of magnetic neighbours (N) is reduced in a thin film

1/*t* dependence





Critical Temperatures of Ising Lattice Films

G. A. T. ALLAN Baker Laboratory, Cornell University, Ithaca, New York 14850

Phys. Rev. B 1, 352 (1970)

$$T_C(\infty) - T_C(t) = t^{-\lambda}, \quad \lambda = 1$$

Experiments and finite-size
scaling model:
$$\frac{T_C(\infty) - T_C(t)}{T_C(\infty)} = \left(\frac{t}{t_0}\right)^{-\lambda}, \quad \lambda' = 1 - 1.6$$

C. Domb, J. Phys. A 1, 1296 (1973); Y. Li et al. Phys. Rev. Lett. 68, 1208 (1992); etc.

This model accounts for the decrease of T_C with t down to a critical thickness $t_0 \approx 4$ monolayers.

t is a continuous parameter -> in the ultra thin limit t becomes discrete (number of atomic layers)

Ultra thin limit: linear decrease

$$\frac{T_{C}(\infty) - T_{C}(t)}{T_{C}(\infty)} = A - (n-1)/2N_{0}$$

N_o is the spin-spin coupling range (typically a few atomic sites) A takes into account the observation that for n=1 ferromagnetism can exist

R. Zhang et al. Phys. Rev. Lett. 86, 2665 (2001)



Curie temperature and band structure



Paramagnet

the magnetic moments are randomly oriented due to thermal fluctuations



T>T_C



Ferromagnet

 $T < T_C$ unlike the moments in a paramagnet, these moments will remain parallel even when a magnetic field is not applied



Antiferromagnet

Adjacent magnetic moments from the magnetic ions align antiparallel to each other without an applied field.



Spin resolved inverse photoemission spectroscopy for 3d bands as a function of temperature for Ni(110)

 $T=T_C \rightarrow spin transition$ from minority and majority states are equal $\rightarrow \Delta = 0$











Curie (Neel temperature)	->	magnetic order in a ferromagnetic (antiferromagnetic) nanostructure
Super-exchange	->	mediated interaction between magnetic atoms
Bias exchange	->	interaction at the interface of FM – AFM structures
Kondo effect	->	interaction between a magnetic impurity and the conduction band electrons
RKKY interaction	->	interaction between magnetic impurities mediated by the conduction band electrons







in many materials (oxides), magnetic atoms are separated by non-magnetic ions (oxygen)



Indirect interactions through oxygen atoms

In the antiferromagnetic configuration, electrons of atoms A and B can both hybridize with 1 p-electron of Oxygen

energy depends on the relative spin orientation







The Kondo interaction J S σ couples itinerant electrons of the host with spin $\sigma = 1/2$ to a magnetic impurity with spin S.

For exchange interaction J < 0, antiferromagnetic (AFM) coupling of the spins of the conduction electrons screens the impurity spin. The ground state at temperatures T below the Kondo temperature T_K is a spin S - σ (red area).

For J > 0, the ferromagnetic (FM) coupling tends to create a cloud of spins aligned parallel to the impurity spin, which becomes asymptotically free at low temperatures.

For $S = \frac{1}{2}$ complete screening For S > 1 under-screening Kondo



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Indirect exchange couples moments (in impurities or magnetic layers) over relatively large distances





Impurity 2 (layer 2)

$$\mathbf{J}(\mathbf{r}) = \mathbf{J}_{0} \cdot \cos(2 \cdot \mathbf{k}_{\mathrm{F}} \cdot \mathbf{r}) / (2 \cdot \mathbf{k}_{\mathrm{F}} \cdot \mathbf{r})^{\mathrm{D}}$$

D represent the system dimensionality

 $\lambda_F = 2\pi/k_F$ Fermi wave length (in metal is of the order of a few nm)



Co/Pt(111): RKKY interaction



distance from monolayer (nm)



F. Meier, et al., Science, 82, 320 (2008)







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Atom-by-atom engineering and magnetometry of tailored nanomagnets

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- a) In an external field and above the Néel temperature T_N , antiferromagnetic spins located at the interface with the ferromagnet are aligned, like the ferromagnet, with the external field.
- b) Once cooled below T_N , these interface spins keep their orientation and appear "pinned" because they are tightly locked to the spin lattice in the bulk of the antiferromagnet, which is not sensitive to external fields. Consequently these pinned spins produce a constant magnetic field at the interface that causes the hysteresis loop of the ferromagnet to shift.
- c) This intuitive picture overestimates the magnitude of the loop shift by orders of magnitude.

 H_b / $H_c \approx W$ / $\xi \approx 2~eV$ / 50 meV ≈ 30

When T < T_N you need several tens of tesla to reverse the AFM coupled spins ("pinning")

J. Nogués et al., J. Magn. Magn. Mater. 192, 203 (1999)





Bias exchange: real case





Applied Field [kOe]

H. Ohldag et al., Phys. Rev. Lett. 91, 017203 (2003)







The exchange break layer is need to decouple the recording layer from the soft underlayer (necessary to close the magnetic flux lines)







R. Araki, *et al.* IEEE Trans. Magn. **44**, 3496 (2008).

D. E. Laughlin, *et al.* J. Appl. Phys. **105**, 07B739 (2009).

Fig. 1. Plan-view TEM image of CoCrPt-SiO₂ with definition of grain size and grain boundary width. White dots in the image show the centroids of each grain.



The inter-grain exchange interaction is stopped by the oxide layer

FIG. 3. (Color online) Schematic of a possible mechanism for tooth growth.



GMR: giant magneto resistance











Available states with the same spin: Low resistance

Absence of states with the same spin: High resistance

Science **282**, 1660 (1998); Nat. mater. **6**, 813 (2007)











The atom spins are coupled together

In non magnetic materials $H_{ex} = J S_i S_j = 0$



Domain wall between two pinned ferromagnetic materials with opposite orientation of the magnetization

- Without the spacer two (negative) scenarios depending on the strength of the exchange force in respect to the pinning force:
- a) The free layer magnetization always aligns parallel to the magnetization of the pinned layer
- b) A domain wall forms which produces the spin current depolarization







Magnetic random access memory (MRAM)

Ferromagnetic (FM) - nonmagnetic (NM) - ferromagnetic (FM) junction



Science 282, 1660 (1998); Nat. mater. 6, 813 (2007)





Reading-writing head in HDD



Reading: the bit stray field defines the magnetization direction of the free layer

Giant Magnetoresistance (GMR)

