

Intro - French Meeting on Molecular Magnetic Systems

Fundamentals of Magnetism

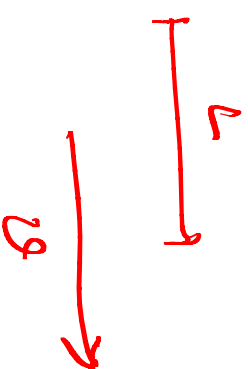


L in a stationary frame

- stationary observer

$$L' = \frac{L}{\gamma} \quad \gamma = \frac{1}{\sqrt{1-v^2/c^2}}$$

c is the velocity of light



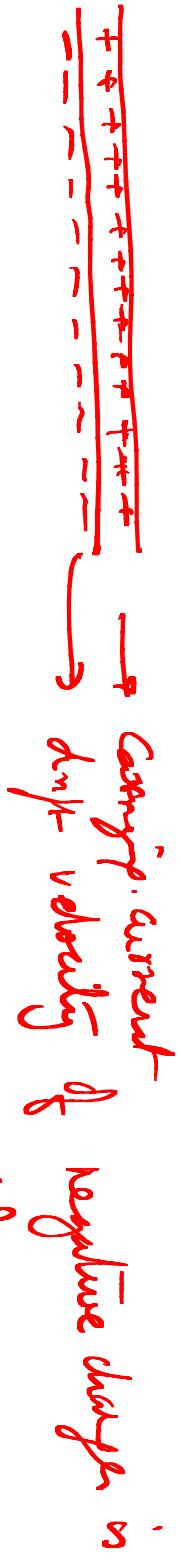
Velocity of light is a constant

$$c = \frac{1}{\sqrt{\mu\epsilon}}$$

↔ Maxwell's equation

μ and ϵ do not depend upon the frame of reference

c must be a constant in all frames of reference



$$q \bullet \quad P_+ = P_-$$

Stationary P_+ and P_- are linear densities of +ve and negative charges

$$\rho_+ = Q_+/l \quad \rho_- = Q_-/l$$



- we change in the wire appear that only while the positive charges appear to fix the wire charge. we moving with velocity v

$$\rho'_- = \frac{Q_-}{L}$$

$$\rho'_+ = \frac{Q_+}{L'}$$

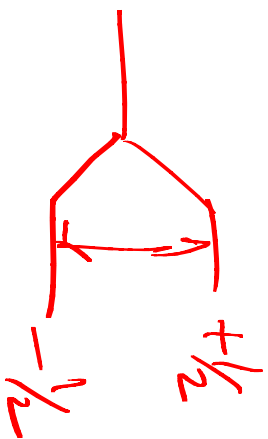
$$L' = L \sqrt{1 - v^2/c^2}$$

Since $L' < L$ $\rho'_+ > \rho'_-$

This leads to an attraction of the electron by the wire
This attractive force is the magnetic force
Lorentz force on a moving charge q with velocity \vec{v} is

Given
$$\vec{F} = q\vec{E} + q\vec{v} \times \vec{B}$$

\vec{B} is the magnetic field and \vec{E} is the electric field
Magnetic force is very weak 1 Tesla of magnetic field (10^4 gauss)
electron in a magnetic field of 1 Tesla the repulsion of the spin
Magnet



$$\Delta E \sim k_B T_n \quad T_n \text{ (172K)} \sim 1.4^\circ \text{K}$$

$$\sim \text{cm}^{-1}$$



there is a current due to the movement of electron around the path
 τ is the time taken for one period

$$I = \frac{e}{\tau}$$

$$\tau = \frac{2\pi r}{v}$$

$$I = \frac{e v}{2\pi r}$$

Magnetic moment is $\vec{\mu} = I \vec{A}$, \vec{A} is the area vector and I is the current.

$$= \frac{e v}{2 \pi r} \cdot \pi r^2 = \frac{e}{2} v r = \frac{e m v r}{2 m} = \frac{e h}{4 \pi m}$$

Bohr Magneton $\frac{e h}{4 \pi m e}$

Associated with every angular momentum

we have a magnetic moment
 $L \propto M$ and the constant of proportionality
is called the gyromagnetic ratio

$M = g_L L$ For orbital angular momentum we have

$$g_L = 1$$

But for spin angular momentum

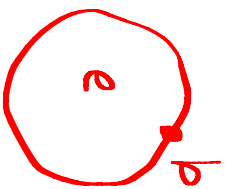
$$g_S = 2$$

Both orbital and spin angular momentum then what happens to g

$$M_{\text{total}} = (g_L L + g_S S) = (L + 2S)$$

When both L and S are nonzero, there is spin-orbit interaction
between the proton and neutron and electron and positron as





Magnetic field produced by the proton
 $\vec{H} = \vec{E} \times \vec{v}$
 \vec{E} is the electric field and \vec{v} is the velocity

$$\vec{E} = -\vec{\nabla} U \quad U = \frac{e^2}{r}$$

$$\vec{E} = \frac{e^2}{r^2} \hat{r}$$

$$\vec{H} = \vec{E} \times \vec{v} = \frac{e^2}{r^2} \hat{r} \times \vec{v}$$

$$= \frac{e^2}{m r^3} (\vec{m} \times \vec{v})$$

where \hat{r} is the unit vector
 $\vec{v} = \gamma \hat{r}$

$$\vec{H} = \frac{e^2}{m r^3} (\vec{r} \times \vec{p}) = \frac{e^2}{m r^3} \vec{L}$$

Spin orbit interaction = $\vec{H} \cdot \vec{S} = \frac{e^2}{m r^3} \vec{L} \cdot \vec{S}$

$\vec{L} \cdot \vec{S}$ is in the Hamiltonian
then the quantum number that is given for the

total angular momentum is $J = L + S, \dots$ $|L - S|$

$$\vec{H} = (L + 2S) = g_J \vec{J}$$

g_J is the g factor for the state J

$(L + 2S)$ and J from spin multiplicity

$$\langle L + 2S \rangle = g_J \langle J \rangle$$

$$= g_J \langle J^2 \rangle$$

$$\langle (L + 2S) \cdot J \rangle = g_J \langle J \cdot J \rangle = g_J J(J+1)$$

$$\langle (L + 2S) \cdot (L + S) \rangle = \langle L^2 + 3L \cdot S + 2S^2 \rangle$$

$$= L(L+1) + 2S(S+1) + 3L \cdot S$$

$$L \cdot S = (L(L+1)^2 - L^2 - S^2) / 2 = (J^2 - L^2 - S^2) / 2$$

$$\begin{aligned} \langle (L+2S) \cdot \vec{J} \rangle &= L(L+1) + 2S(S+1) + \frac{3}{2} (J(J+1) - L(L+1) - S(S+1)) \\ &= \frac{3}{2} J(J+1) - \frac{L(L+1)}{2} + \frac{S(S+1)}{2} = g_J J(J+1) \end{aligned}$$

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

$$H_{\text{map}} = \mu_B (L+2S) \cdot \vec{H}$$

$$H_{\text{map}} = \mu_B (L+2S) \cdot \vec{H} + \lambda L \cdot \vec{S}$$

A perturbation calculation for energy

$$E = E^{(1)} + E^{(2)} + \dots$$

$$E^{(1)} = \mu_B \langle \Phi_g | (\hat{L} + 2\hat{S}^z) | \Psi_g \rangle \cdot \hat{H}^{-1} + \langle \Psi_g | \lambda (\hat{L} \cdot \hat{S}) | \Psi_g \rangle$$

$$E^{(2)} = \mu_B \langle \Phi_g | (\hat{L} + 2\hat{S}^z) \cdot \hat{H} | \Psi_e \rangle \langle \Psi_e | (\hat{L} + 2\hat{S}^z) \cdot \hat{H} | \Psi_g \rangle$$

$$\frac{E_e^{(2)} - E_g^{(2)}}{E_e^{(0)} - E_g^{(0)}}$$

$$+ \lambda^2 \langle \Phi_g | \hat{L} \cdot \hat{S} | \Psi_e \rangle \langle \Psi_e | \hat{L} \cdot \hat{S} | \Psi_g \rangle$$

$$\frac{E_e^{(2)} - E_g^{(2)}}{E_e^{(0)} - E_g^{(0)}}$$

$$E^{(2)} = \frac{\langle \psi_g | \mu_a (\vec{L} + 2\vec{S}) \cdot \vec{H} + \lambda \vec{L} \cdot \vec{S} | \psi_0 \rangle \langle \psi_e | \mu_a (\vec{L} + 2\vec{S}) \cdot \vec{H} + \lambda \vec{L} \cdot \vec{S} | \psi_g \rangle}{E_e^{(0)} - E_g^{(0)}}$$

$$\psi_g = \Phi_g(\vec{r}) \cdot \chi_g$$

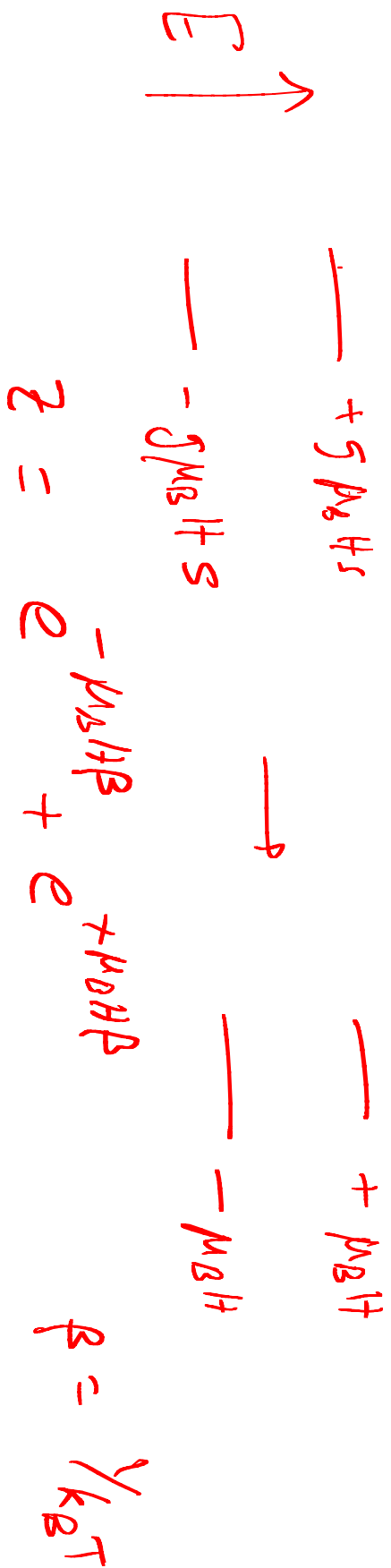
$$J_g^{(2)} = \sum_{i,j} A_{ij} S_i S_j + \sum_i \frac{A'_{ij} H_i H_j S_i S_j}{\dots}$$

A_{ij} are the generalized g factors.

$$g_{\text{matrix}} = \begin{pmatrix} g_{xx} & g_{xy} & g_{xz} \\ g_{yx} & g_{yy} & g_{yz} \\ g_{zx} & g_{zy} & g_{zz} \end{pmatrix} \rightarrow \begin{pmatrix} g_1 & 0 & 0 \\ 0 & g_2 & 0 \\ 0 & 0 & g_3 \end{pmatrix}$$

$$g_1 = g_2 \neq g_3 \rightarrow g_{||} \text{ \& } g_{\perp}$$

E. J. Behrman "Ligand Field Theory"
 Susceptibility of the single ions (interacting) in a magnetic field.
 4-yr electron in a magnetic field.



$$\langle M \rangle = kT \frac{d \ln Z}{dH}$$

$$\langle M \rangle = \frac{-e^{-\mu_B H} + e^{+\mu_B H}}{e^{-\mu_B H} + e^{+\mu_B H}} = \mu_B \tanh(\mu_B H)$$

$$\langle \mu \rangle = \mu_B \text{Tanh}(\mu_B H)$$

Field strengths that can be generated are generally a few Tesla

$$\mu_B H \approx \mu_B H / kT \ll 1$$

and hence we can do a Taylor series expansion.

$$\mu = \frac{\mu_B^2 H}{kT}$$

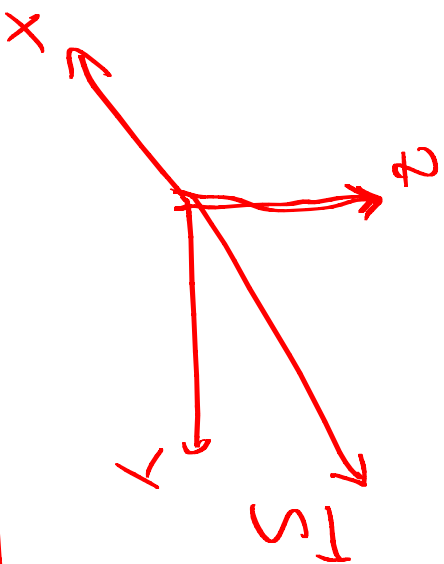
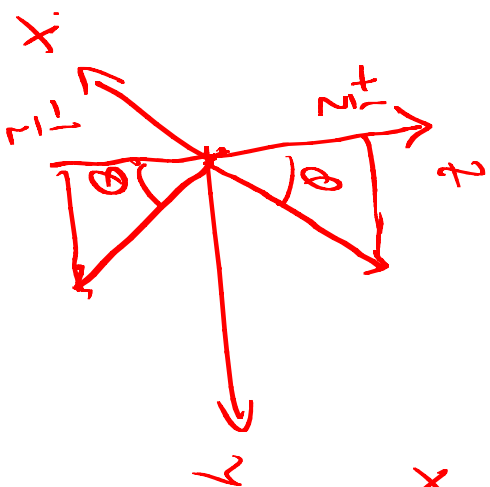
$$\chi = \frac{\mu_B^2}{kT}$$

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

Let μ be very large

$$[S_x, S_y] = i\hbar S_z$$

and cyclic



$|S_z|$, and
one direction

$$S = \sqrt{\frac{1}{2}(\frac{1}{2} + 1)} > \frac{1}{2}$$

$$T_{\text{angular}} = \hbar \chi \hbar \neq 0$$

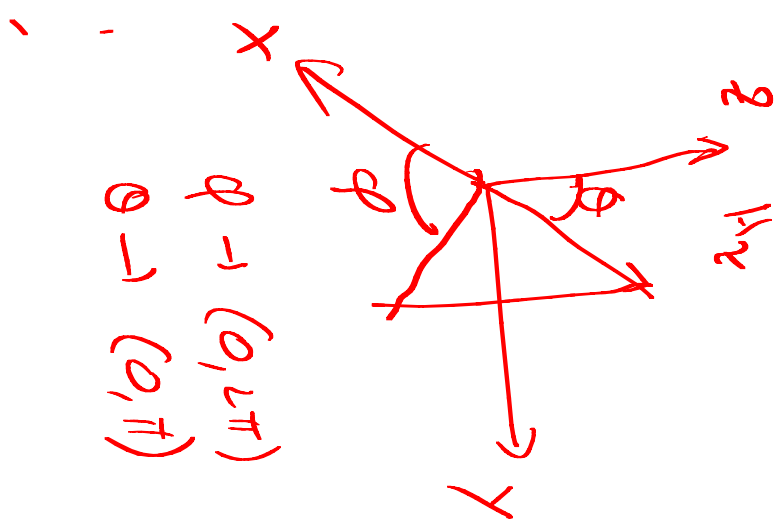
$$E = \mu_B \vec{S} \cdot \vec{H} = \mu H \cos \theta$$

$$\mu = g \mu_B S$$

$$Z = \int_0^\pi e^{\mu H \cos \theta} \int_{\text{mit}} d\Omega$$

$$\mu H \beta = \alpha$$

$$Z = \int_0^\pi e^{\alpha \cos \theta} \int_{\text{mit}} d\Omega$$



$$y = \cos \theta \quad dy = -\sin \theta \, d\theta$$

$$\theta=0 \quad y=1$$

$$\theta=\pi \quad y=-1$$

$$Z = -\int_{-1}^{+1} e^{\alpha y} dy$$

$$Z = \int_{-1}^{+1} e^{\alpha y} dy = \frac{1}{\alpha} e^{\alpha y} \Big|_{-1}^{+1} = \frac{1}{\alpha} (e^{\alpha} - e^{-\alpha})$$

$$M = kT \frac{d \ln Z}{dH}$$

H is the magnetic field

$$M = \mu \cdot kT \frac{d \ln Z}{d\alpha} \cdot \frac{d\alpha}{dH}$$

$$M = \mu \left[\text{cst}h \left(\frac{\mu H}{kT} \right) - \frac{kT}{\mu H} \right]$$

Länge in Funktion

$$L(x) = \left(\text{cst}h(x) - \frac{1}{x} \right)$$

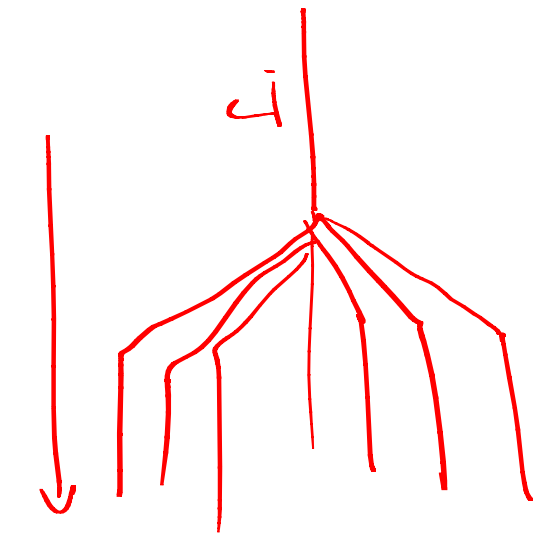
Limit $x \rightarrow 0$ $L(x) = \left(\frac{x}{3} + \frac{1}{x} - \frac{1}{x} \right) = \frac{2}{3}$

$$M = \frac{\mu^2 H}{3kT}$$

$$\chi = \frac{M}{H} = \frac{\mu^2}{3kT}$$

\rightarrow Curie Law $\chi \propto \frac{C}{T}$

What happens when J is large but not necessarily ~~is~~ very large



Partition function:
 $Z =$

$$1 + \mu J 1^{\uparrow}$$

$$\mu = g \mu_B$$

$$e^{-\mu J H \beta} + e^{-\mu (J-1) 1^{\uparrow} \beta} + \dots + e^{\mu J H \beta}$$

Geometric series

$$Z = e^{-\mu J H \beta} \left(1 + e^{-\mu H \beta} + e^{-2\mu H \beta} + \dots + e^{2\mu J H \beta} \right)$$

$$e^{-\mu H \beta} Z = e^{-\mu J H \beta} \left(e^{-\mu H \beta} + e^{-2\mu H \beta} + \dots + e^{2\mu J H \beta - \mu H \beta} \right)$$

$$Z (1 - e^{-\mu H \beta}) = e^{-\mu J H \beta} (1 - e^{-\mu (J+1) H \beta})$$

$$= \frac{\sinh((2J+1)\mu H \beta / 2)}{\sinh(\mu H \beta / 2)} \quad \alpha = J \mu H \beta$$

$$M = kT \frac{d \ln Z}{dH} = kT \frac{d \ln Z}{dx} \cdot \frac{dx}{dH}$$

$$M = \mu \cdot (\mu \gamma \beta) B_J(x\beta)$$

where $B_J(y)$ is

$$B_J(y) = \left[\frac{2^{J+1}}{2^J} \coth \left(\frac{2^{J+1}}{2^J} y \right) - \frac{1}{2^J} \coth \frac{y}{2^J} \right]$$

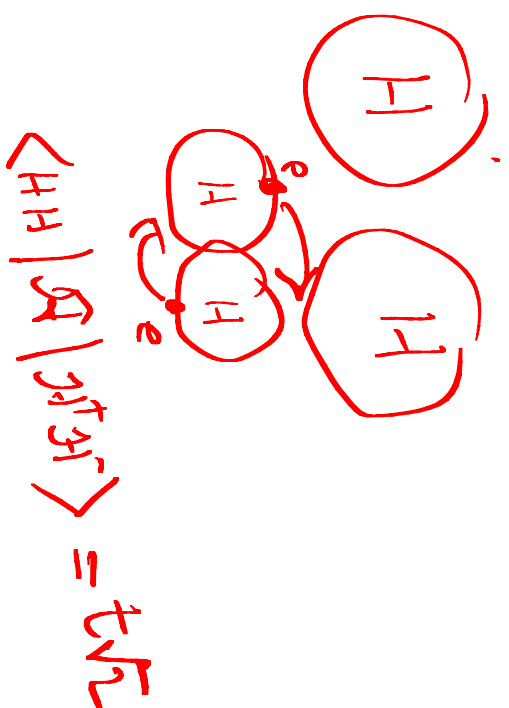
called Brillouin function

$$\chi = \frac{M}{T} = \frac{\mu_B^2 g^2 J(J+1)}{3kT}$$

$$\mu = g \mu_B \sqrt{J(J+1)}$$

$$= \mu^2 / 3kT$$

Temperature Phenomena and Magnetism in metals and insulators



$$\langle \text{Singlet} | \text{Triplet} \rangle = 0$$

$$|S\rangle = \uparrow\downarrow - \downarrow\uparrow$$

$$|T\rangle = \uparrow\uparrow, \downarrow\downarrow, \uparrow\downarrow + \downarrow\uparrow$$

\mathcal{H} does not contain spin

Perturbation \mathcal{H} is a mapping of electron between atoms

$$E^{(1)} = \langle \psi_g | \mathcal{H} | \psi_g \rangle = t \langle H-H | \mathcal{H}^\dagger H^- \rangle \quad \mathcal{H} | H-H \rangle$$

$$= 0 \quad = | \mathcal{H}^\dagger H^- \rangle$$

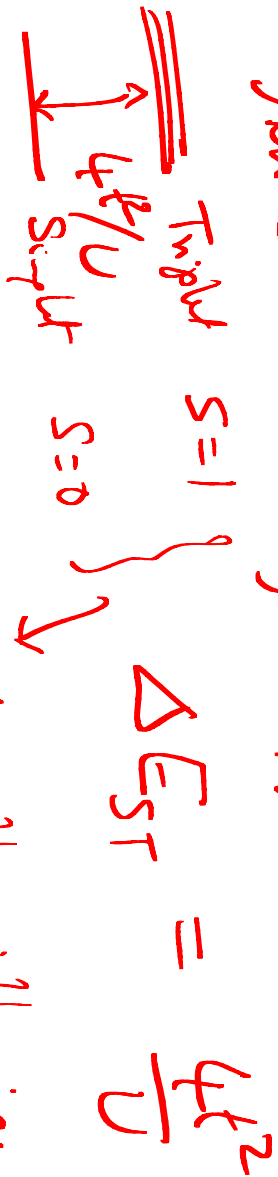
$$= | H^- - \mathcal{H}^\dagger \rangle$$

$$E^{(2)} = \frac{\sum_e \langle \psi_g | \mathcal{H} | \psi_e \rangle \langle \psi_e | \mathcal{H} | \psi_g \rangle}{-E_0 + E_g}$$

$$\begin{aligned}
 &= \frac{\langle H-H | \mathcal{H} | \mathcal{H}^+ \mathcal{H}^- \rangle \langle \mathcal{H}^+ \mathcal{H}^- | \mathcal{H} | \mathcal{H} \mathcal{H} \rangle}{-U} \\
 &+ \frac{\langle H-H | \mathcal{H} | \mathcal{H}^+ \mathcal{H}^+ \rangle \langle \mathcal{H}^+ \mathcal{H}^+ | \mathcal{H} | \mathcal{H}^- \mathcal{H} \rangle}{-U} \\
 &= \frac{2t^2}{U} + \frac{2t^2}{U} = \frac{4t^2}{U}
 \end{aligned}$$

The energy of the triplet state is reduced by $\frac{4t^2}{U}$.
 But the triplet cannot mix with the excited states.

Since nothing happens to them



Want an effective Hamiltonian

$$S_1 \cdot S_2$$

$$S_{\text{tot}}^2 = S_1^2 + S_2^2 = 0, 1$$

$$S_{\text{tot}}^2 = S_1^2 + S_2^2 + 2S_1 \cdot S_2$$

$$S_1 \cdot S_2 = \frac{(S_{\text{tot}}^2 - S_1^2 - S_2^2)}{2}$$

$S_1 \cdot S_2$ for triplet - here the eigenvalue

$$S_1 = 1/2 \text{ and } S_2 = 1/2$$

$$\text{Tryplet } S_{H1} = 1 = \frac{1(1+1) - \frac{1}{2}(\frac{1}{2}+1) - \frac{1}{2}(\frac{1}{2}+1)}{2}$$

$$= \frac{2 - 3/2}{2} = \frac{2}{4}$$

$$S_{H2} = 0 = \frac{(0)(0+1) - \frac{1}{2}(1+1) - \frac{1}{2}(\frac{1}{2}+1)}{2} = -3/4$$

$$(S_1 \cdot S_2^{-1/4}) |S\rangle = -1$$

$$(S_1 \cdot S_2^{-1/4}) |T\rangle = 0$$

$$J_1 = \frac{4t^2}{U} (S_1 \cdot S_2 - 1/4) = J (S_1 \cdot S_2 - 1/4)$$

$$E_T = 0 \quad E_S = -\frac{4t^2}{U}$$

P. W. Anderson

Kinetic Exchange



two degenerate states

ϕ_1 and ϕ_2

Fermion magnetic Exchange ?

Electrons are Fermions & hence the wave function of the many electron system must be antisymmetric

$$\Phi_{\pm}(1,2) = \underbrace{\Phi(x_1, x_2)}_{\text{Symmetric}} \underbrace{\chi(x_1, x_2)}_{\text{antisymmetric}}$$

antisymmetric
symmetric

For triplets
 Asymptotic part is antisymmetric & spin part is symmetric

$$\Phi_{\pm}(1,2) = (\phi_1(x_1) \phi_2(x_2) - \phi_1(x_2) \phi_2(x_1))$$

$$\chi_{\pm}(x_1, x_2) = \alpha_1 \alpha_2$$

$$\Psi_{\pm} = \Phi_{\pm}(1,2) \chi_{\pm}(1,2)$$

$$\begin{aligned} \Psi_S &= \Phi_S(r_1, r_2) \chi_S(r_1, r_2) \\ &= (\phi_1(r_1) \phi_2(r_2) + \phi_1(r_2) \phi_2(r_1)) (\alpha_1 \beta_2 - \beta_1 \alpha_2) \end{aligned}$$

Pauli Spinors is $\frac{e^2}{8\pi^2}$;

Although important had triplets & triplets are degenerate they do not mix & we can carry out non-degenerate P.T.

$$E_T = \langle \Psi_T | \frac{e^2}{8\pi^2} | \Psi_T \rangle ; \quad E_S = \langle \Psi_S | \frac{e^2}{8\pi^2} | \Psi_S \rangle$$

$$A = \int \phi_1^*(1) \phi_1(1) \frac{e^2}{r_{12}} \phi_2^*(2) \phi_2(2) d^3r_1 d^3r_2 d\mathbf{r}_1 d\mathbf{r}_2$$

Antisymmetrisierung

$$= \int \rho_1(1) \rho_2(1) / r_{12} d^3r_1 d^3r_2$$

$$J = \int \phi_1^*(1) \phi_2(1) \frac{e^2}{r_{12}} \phi_2^*(2) \phi_1(2) d^3r_1 d^3r_2 d\mathbf{r}_1 d\mathbf{r}_2$$

Gegenüber $J \rightarrow 0$ für Paared spin because we have opposite spin for electron 1 and 2
 $\int \alpha_1 \beta_2 d\mathbf{r}_1 = 0$ $\int \alpha_2 \beta_1 d\mathbf{r}_2 = 0$

$$E_S = A$$

$$E_T = A - 2J$$

A and J are both positive

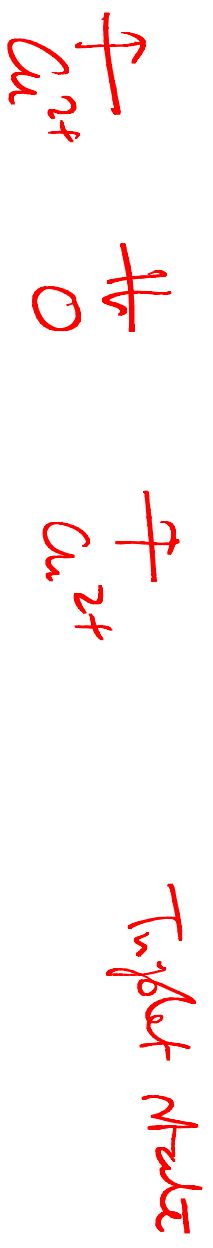
$\therefore E_T$ has lower energy than E_S

\rightarrow Hund's rule

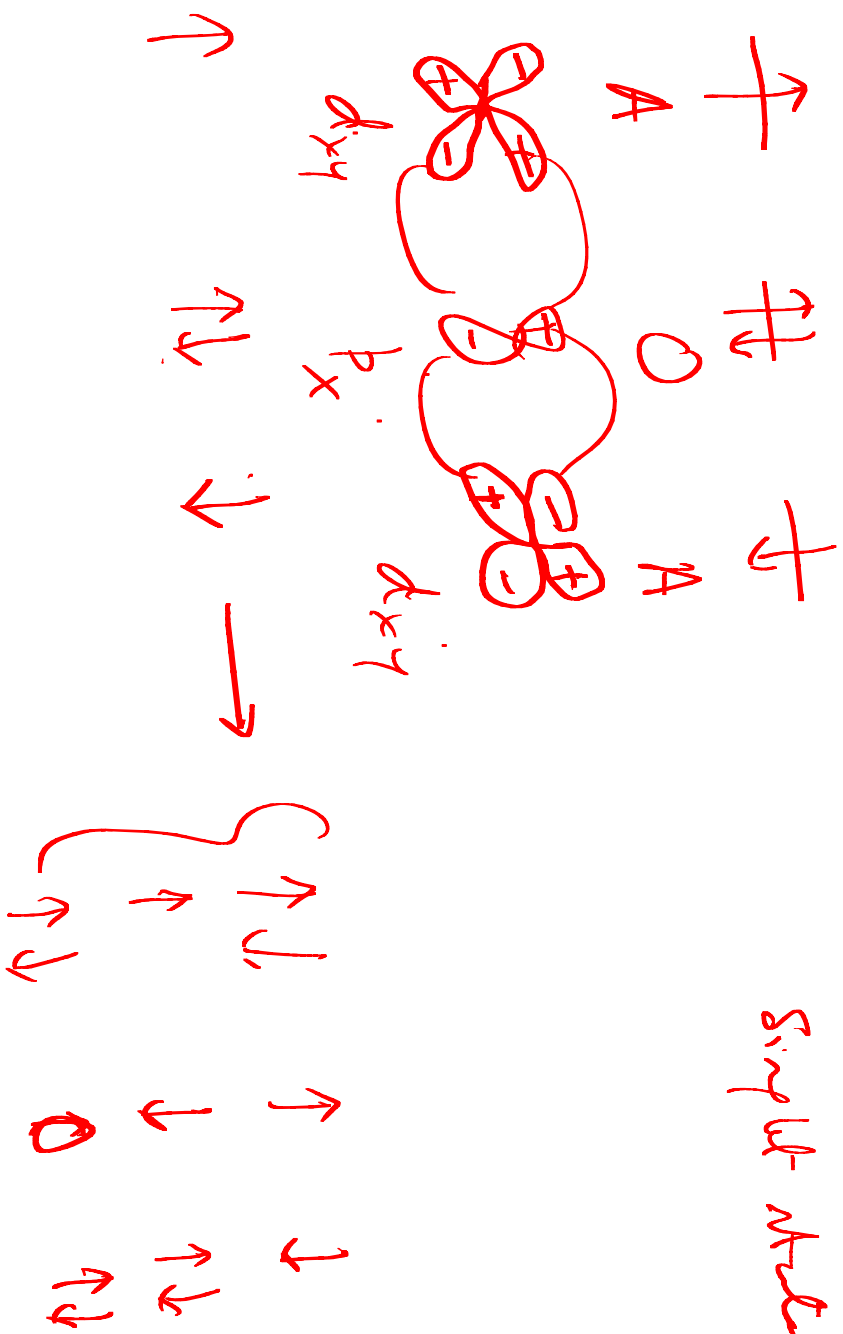
Magnitism is a consequence of direct vs kinetic exchange

$$J_{eff} = A - 2J \left(s_1 s_2^{-1/4} \right) \rightarrow \text{Drac-vanVleck-Heisenberg Exchange}$$

$$L L' \quad Q-N$$

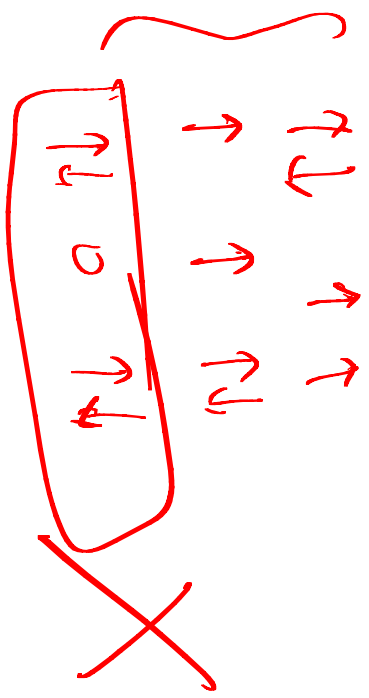


Simplex



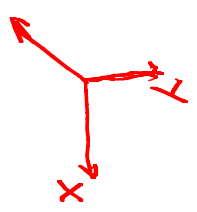
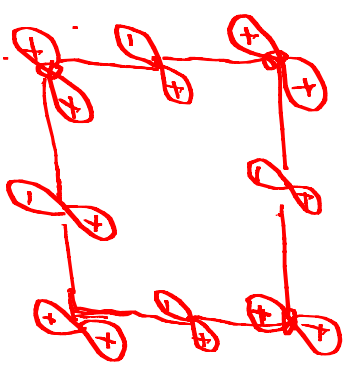
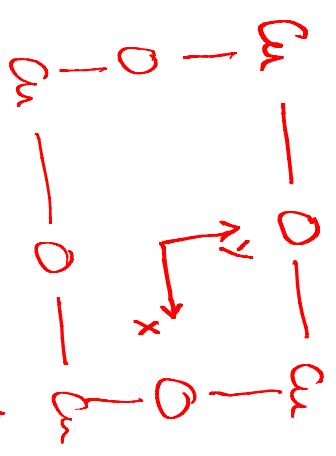
S=0

Anti ferromagnetic exchange is favored



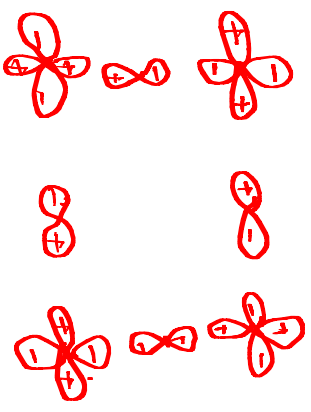
Cu^{2+} in both J-T distortion and the aligned in which the impure is residing in $d_{x^2-y^2}$ and Cu-O-Cu angle is 90° as in CuO_2 plane

1. If the unpaired electron is in the d_{yz}^2 orbital, then

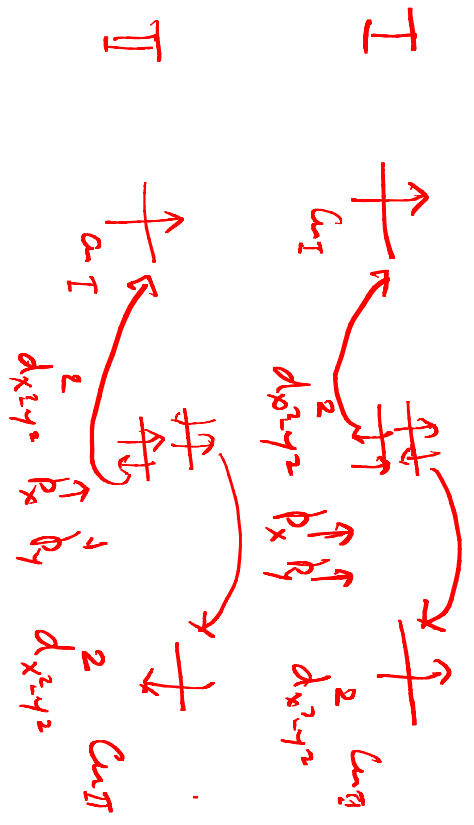
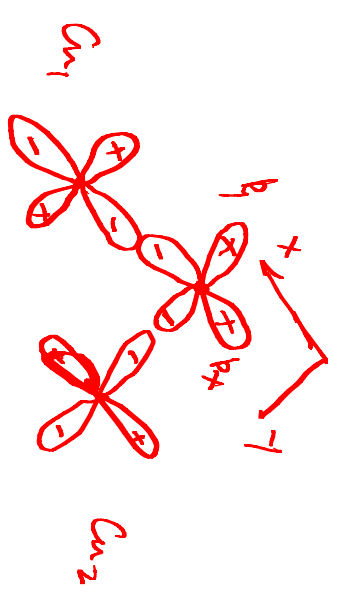


There is no overlap of the d_{yz}^2 and p orbitals on oxygen and the system will be able to form ferromagnetic interactions.

2. If the unpaired electron is in the $d_{x^2-y^2}$ orbital then

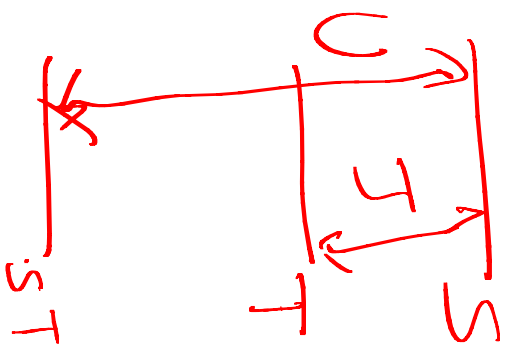


The overlap of the $d_{x^2-y^2}$ orbitals with the p_y orbitals of oxygen in the x-direction and p_x orbitals of oxygen in the y-direction leads to strong antiferromagnetic interactions.

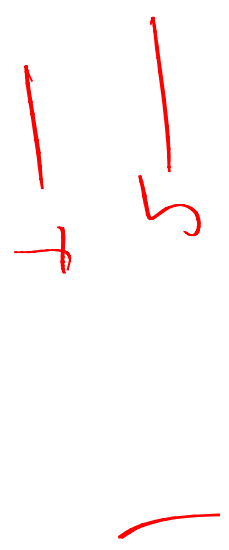


From overlap exchange arises even though overlap is. merge as it is with different p-orbitals.

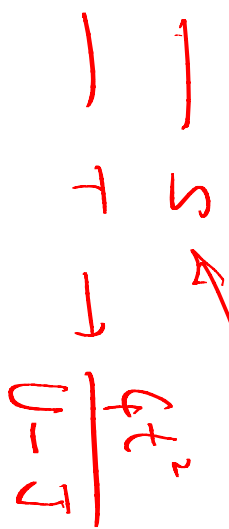
If the Cu-O-Cu is 90° , then the $d_{x^2-y^2}$ orbital of CuI overlaps with the p_x orbital of oxygen while the $d_{x^2-y^2}$ orbital of CuII overlaps with the p_y orbital of the oxygen. Then the antibonding state generated in I or II if electron are parallel, then the antiparallel they are antiparallel, then the antiparallel generated in II. By Hund's rule the intermediate state I is more stable than the intermediate state II.



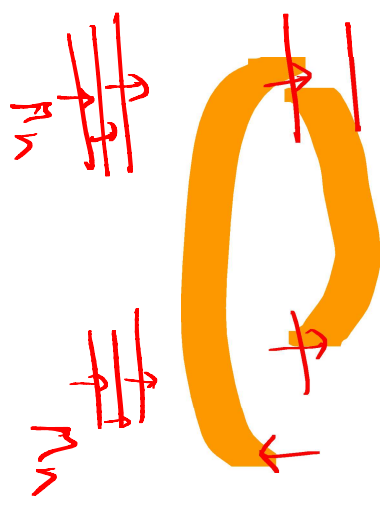
McConnell



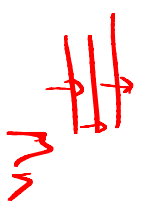
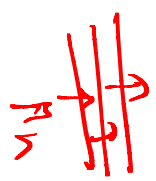
$$\frac{Jt^2}{U}$$



Double exchange interaction



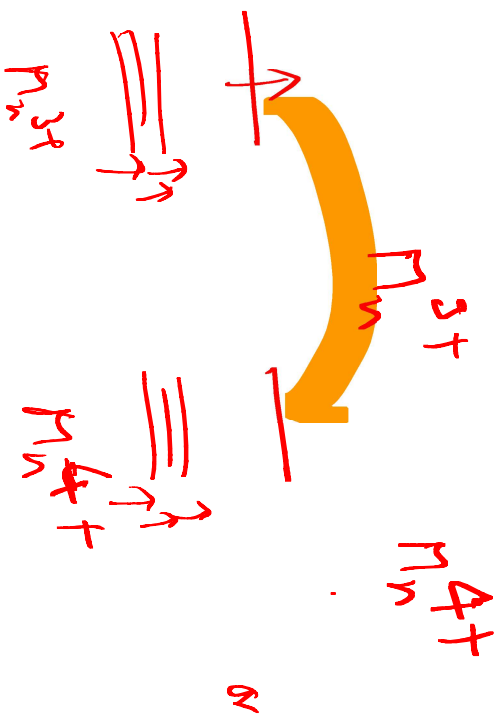
$$M_n^{3f}$$



$$M_n - 0 - iM_n$$

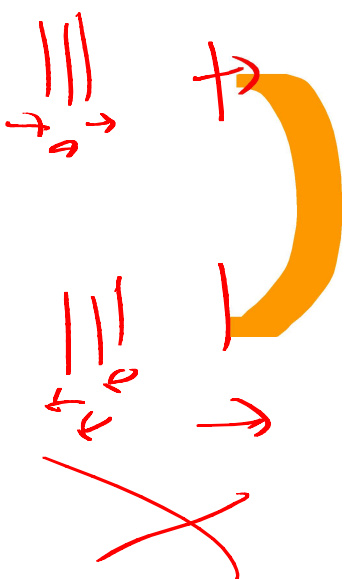
$$L_a M_n O_3$$

M_n-O-M_n is antiferromagnetic
 M_n-M_n interaction



$t \rightarrow t_0 \cos \theta$

Fermion system



Double exchange

$$H = \sum_{i,j} J_{ij} S_i^z \cdot S_j^z$$

Let us consider the interaction in ferromagnets

$$\sum_i J S_i^z \cdot \underline{S_i^z}$$

$\langle S_i^z \rangle$ is an average
 N expected value
 the spin
 at site i

$$J_0 + J_1 = \sum_j (J_0 + J_1) \cdot S_i^z$$

$$\langle S_i^z \rangle = \frac{1}{N} \sum_j \langle S_j^z \rangle$$

at site i

The interest rate $H_{int} = X M$ $M = N < S$

The total field experienced by a spin is

$$(H_a + H_{int}) = (H_a + \lambda M)$$

$$\frac{C}{T} = \frac{M}{(H_a + \lambda M)}$$

$$C H_a + C \lambda M - M T = 0$$

$$M (C \lambda - T) = - C H_a$$

Experimentally \Rightarrow $\left(\frac{M}{H_a} \right) = \frac{C}{T - C \lambda}$

$$\chi = \frac{C}{T - C\chi}$$

$$C\chi = \theta$$

$\chi = \frac{C}{T - \theta}$ is the expression for susceptibility
of a ferromagnet

$$H = \sum_{\langle ij \rangle} J S_i^A \cdot S_j^B$$

i is on sublattice A
and j is on sublattice B

Si^A
Si^B

is in a field of grain on B substrate
and is in a field of grain on A substrate

$$H_A^{Hf} = (\gamma_a - \mu M_B)$$

$$\gamma_B^{Hf} = (\gamma_a - \mu M_A)$$

$$\frac{M_A}{H_A} = \frac{C_A}{T}$$

$$\frac{M_A}{H_B} = \frac{C_B}{T}$$

the field acts against
the field ^{inward} γ_a in the
substrates

$$M_A T = (H_a - \mu M_B) C_A$$

$$M_B T = (H_a - \mu M_A) C_B$$

$$\times \mu C_B$$

$$[M_A T + \mu M_B C_A = H_a C_A] \times \mu C_B$$

$$T$$

$$[M_B T + \mu M_A C_B = H_a C_B]$$

$$= H_a \mu C_A C_B$$

$$M_A T \mu C_B + \mu^2 M_B C_A C_B$$

$$= H_a \mu C_A C_B$$

$$M_B T^2 + \mu M_A C_B T = H_a C_B T$$

$$M_B (-T^2 + \mu^2 C_A C_B) = H_A C_B (\mu C_A - T)$$

$$M_B = \frac{H_A C_B (\mu C_A - T)}{(\mu^2 C_A C_B - T^2)}$$

$$M_A = \frac{H_A C_A (\mu C_B - T)}{(\mu^2 C_A C_B - T^2)}$$

$$\langle M \rangle = M_A + M_B = \frac{H_A [\mu C_B C_A - T C_A + \mu C_A (C_B - T C_B)]}{(\mu^2 C_A C_B - T^2)}$$

$$\frac{\langle M \rangle}{H_L} = \chi = \frac{[2\mu C_B C_A - T(C_A - T C_B)]}{[\mu^2 C_A C_B - T^2]}$$

} is for ferromagnets
} is for antiferromagnets

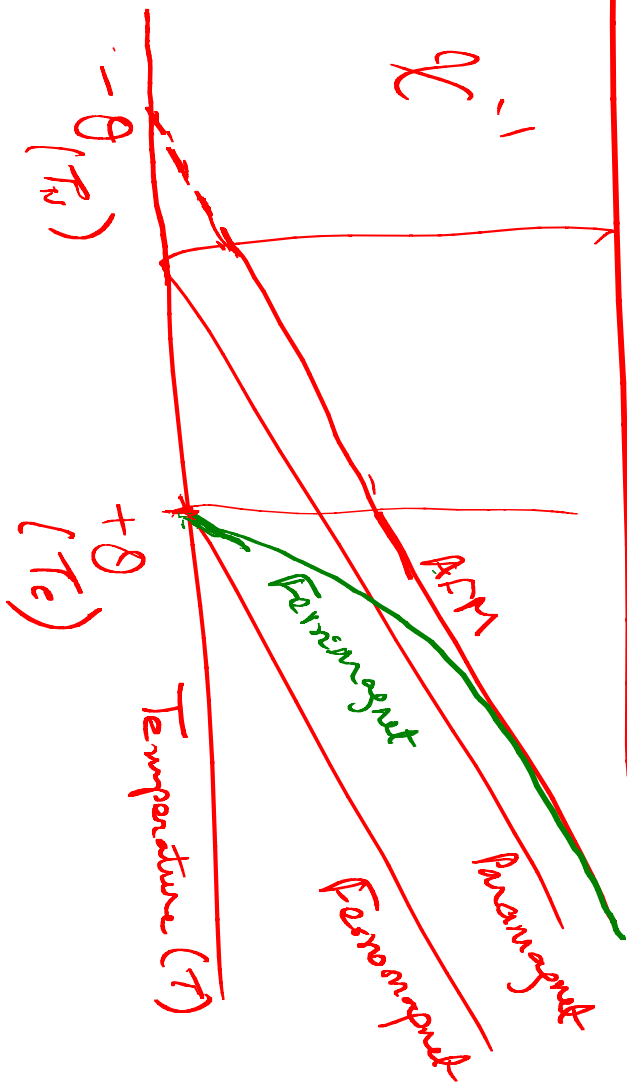
For antiferromagnets $C_A = C_B = C$

$$\chi_{\text{afm}} = \frac{2[\mu C^2 - T C]}{[\mu^2 C^2 - T^2]}$$

$$= \frac{2\mu C \cancel{[T C - T]}}{[\mu C + T] \cancel{[\mu C - T]}} = \frac{2\mu C}{[\mu C + T]}$$

$$\chi_{\text{spin}} = \frac{C}{T + \theta}$$

$$\theta = \mu C$$



$T < +\theta$
 χ^{-1} is not defined
 as μ is $\rightarrow \infty$

