Exchange and ordering

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2011 School - Time-dependent phenomena in magnetism
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Part 1

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Outline

1. Introduction
2. Exchange
3. Superexchange
4. Orbitals

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4. Orbitals

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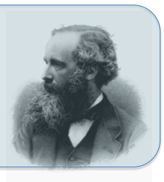
$$\nabla \cdot \mathbf{B} = 0$$

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{J}$$



a problem:

$$\mathbf{J} = \mathbf{J}_{\text{free}} + \mathbf{J}_{\text{bound}}$$

$$\nabla \times \mathbf{M} = \mathbf{J}_{\text{bound}}$$

so define:

$$\boxed{\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})}$$

$$\nabla \times \mathbf{H} = \mathbf{J}_{\text{free}}$$

but:

$$\nabla \cdot \mathbf{H} = -\nabla \cdot \mathbf{M}$$

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Bohr-van Leeuwen theorem

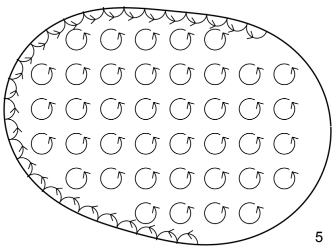
$$\mathbf{p} = m\mathbf{v} + q\mathbf{A}$$

$$\Longrightarrow Z = \int\int \cdots \int \exp(-\beta E(\{\mathbf{r}_i, \mathbf{p}_i\}))\, \mathrm{d}\mathbf{r}_1 \cdots \mathrm{d}\mathbf{r}_N\, \mathrm{d}\mathbf{p}_1 \cdots \mathrm{d}\mathbf{p}_N$$

In a magnetic field, we replace $\mathbf{p}_i$ by $\mathbf{p}_i - q\mathbf{A}$

$$F = -k_{\mathrm{B}} T \log Z$$

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



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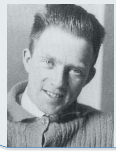
Magnetism is fully quantum mechanical



$$\mathcal{H} = -2\mathcal{J}\mathbf{S}_1 \cdot \mathbf{S}_2$$

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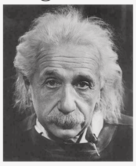
Magnetism is fully quantum mechanical

$$\mathcal{H} = -2\mathcal{J}\mathbf{S}_1 \cdot \mathbf{S}_2$$

Magnetism is fully relativistic



$$\vec{E} = -\frac{\partial \vec{A}}{\partial t} - \vec{\nabla}\phi \qquad \vec{B} = \vec{\nabla} \times \vec{A}$$

$$F^{\mu\nu} = \begin{bmatrix} 0 & -E_x/c & -E_y/c & -E_z/c \\ E_x/c & 0 & -B_z & B_y \\ E_y/c & B_z & 0 & -B_x \\ E_z/c & -B_y & B_x & 0 \end{bmatrix}$$

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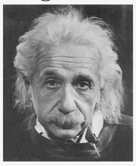
Magnetism is fully quantum mechanical

$$\mathbf{S} = \frac{1}{2}\boldsymbol{\sigma}$$

Magnetism is fully relativistic



$$\vec{E} = -\frac{\partial \vec{A}}{\partial t} - \vec{\nabla}\phi \qquad \vec{B} = \vec{\nabla} \times \vec{A}$$

$$F^{\mu\nu} = \begin{bmatrix} 0 & -E_x/c & -E_y/c & -E_z/c \\ E_x/c & 0 & -B_z & B_y \\ E_y/c & B_z & 0 & -B_x \\ E_z/c & -B_y & B_x & 0 \end{bmatrix}$$

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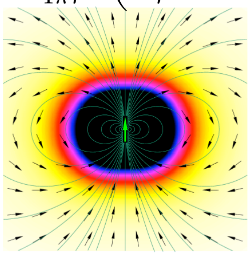
Dipolar fields

$$B^\alpha(\mathbf{r}) = D^{\alpha\beta}(\mathbf{r})m^\beta$$

$$D^{\alpha\beta}(\mathbf{r}) = \frac{\mu_0}{4\pi r^3}\left(\frac{3r^\alpha r^\beta}{r^2} - \delta^{\alpha\beta}\right)$$



$|B|$

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↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓
↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑
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Energy terms:

- Kinetic energy $\quad \dfrac{\hbar^2}{2m}\dfrac{\pi^2}{L^2} = \quad$ eV
- Coulomb energy $\quad \dfrac{e^2}{4\pi\epsilon_0 L} = \quad$ eV
- Size of atom given by balance of these two terms
- Spin-orbit ~ meV
- Magnetocrystalline anisotropy ~ μeV

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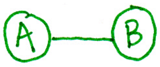
Molecular orbitals : H_2



$$|\Psi\rangle = c_A|\Psi_A\rangle + c_B|\Psi_B\rangle$$

$$\mathcal{H} = -\frac{\hbar^2}{2m}\nabla^2 + V_A + V_B$$

$$\mathcal{H}|\Psi\rangle = E|\Psi\rangle$$

↑ energy

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$$E_0 = \langle\Psi_A|\mathcal{H}|\Psi_A\rangle$$

$$t = \langle\Psi_A|\mathcal{H}|\Psi_B\rangle$$

↑ resonance integral
[transfer or hopping integral]

$S_{ij} = \langle\Psi_i|\Psi_j\rangle$ overlap integrals

$= \delta_{ij}$ (Hückel approx)

$$\mathcal{H}|\Psi\rangle = E|\Psi\rangle$$

↑ energy

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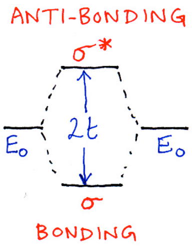
$$\mathcal{H}|\Psi\rangle = E|\Psi\rangle$$

$$\Rightarrow \quad |H_{ij} - E S_{ij}| = 0$$

$$\Rightarrow \quad \begin{vmatrix} E_0 - E & t \\ t & E_0 - E \end{vmatrix} = 0$$

$$\Rightarrow \quad E = E_0 \pm t$$



Eigenfunctions: $\sigma = (|\psi_A\rangle + |\psi_B\rangle)/\sqrt{2}$ (Symmetric, bonding)
$\sigma^* = (|\psi_A\rangle - |\psi_B\rangle)/\sqrt{2}$ (Antisymmetric, antibonding)

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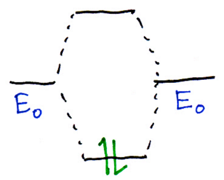
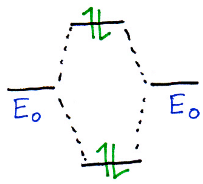
Why do you get H_2 and not He_2?

di-HYDROGEN H_2



Saves energy to bond

di-HELIUM He_2



no saving to bond (in fact, costs energy)

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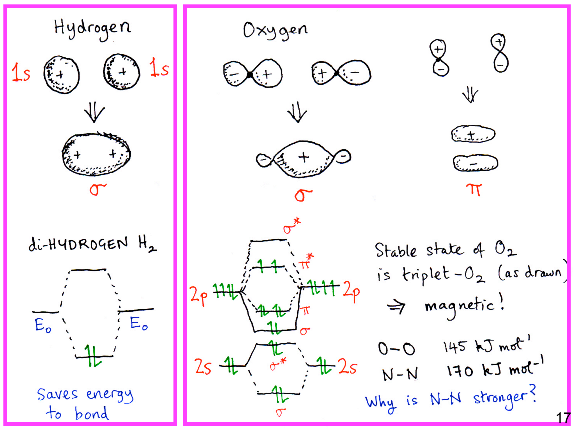

Stable state of O_2 is triplet-O_2 (as drawn)
⇒ magnetic!

O–O 145 kJ mol⁻¹
N–N 170 kJ mol⁻¹

Why is N–N stronger?

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Consider 2 electrons: their spins can combine to form either an antisymmetric singlet state χ_S ($S = 0$) or a symmetric triplet state χ_T ($S = 1$). The wave function, which is a product of spatial and spin terms, must be antisymmetric overall. Hence:

$$\begin{aligned}\Psi_S &= [\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) + \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1)]\,\chi_S \\ \Psi_T &= [\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) - \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1)]\,\chi_T\end{aligned}$$

The energies of the two possible states are

$$\begin{aligned}E_S &= \int \Psi_S^* \hat{H} \Psi_S \, d\mathbf{r}_1 \, d\mathbf{r}_2 \\ E_T &= \int \Psi_T^* \hat{H} \Psi_T \, d\mathbf{r}_1 \, d\mathbf{r}_2\end{aligned}$$

so that the difference between the two energies is

$$E_S - E_T = 4 \int \psi_1^*(\mathbf{r}_1)\psi_2^*(\mathbf{r}_2)\hat{H}\psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1)\, d\mathbf{r}_1 \, d\mathbf{r}_2.$$

The energy is then $E = \frac{1}{4}(E_S + 3E_T) - (E_S - E_T)\mathbf{S_1}\cdot\mathbf{S_2}$. The spin-dependent term can be written $H^{\text{spin}} = -J\mathbf{S_1}\cdot\mathbf{S_2}$.

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- Interaction between pair of spins motivates the general form of the Heisenberg model:

$$H = -\sum_{ij} J_{ij}\mathbf{S_i}\cdot\mathbf{S_j}$$

- The quantity J_{ij} gives the exchange energy between two spins. Be very careful on the factor of two between different conventions of the definition of *J*.

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"J convention"	"$2J$ convention"
$\bullet\overset{J}{—}\bullet$	$\bullet\overset{2J}{—}\bullet$
2 spins: $-J\mathbf{S}_1\cdot\mathbf{S}_2$	**2 spins:** $-2J\mathbf{S}_1\cdot\mathbf{S}_2$
many spins:	**many spins:**
$-\sum_{i>j} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j$	$-2\sum_{i>j} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j$
$-\frac{1}{2}\sum_{ij} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j$	$-\sum_{ij} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j$
$-\frac{J}{2}\sum_{\langle ij\rangle} \mathbf{S}_i\cdot\mathbf{S}_j$	$-J\sum_{\langle ij\rangle} \mathbf{S}_i\cdot\mathbf{S}_j$
$-J\sum_i \mathbf{S}_i\cdot\mathbf{S}_{i+1}$ (1D)	$-2J\sum_i \mathbf{S}_i\cdot\mathbf{S}_{i+1}$ (1D)

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- Interaction between pair of spins motivates the general form of the Heisenberg model:

$$H = -\sum_{ij} J_{ij}\mathbf{S_i}\cdot\mathbf{S_j}$$

- *Direct exchange*: important in many metals such as Fe, Co and Ni
- *Superexchange*: exchange interaction mediated by oxygen. This leads to a very long exchange path. Important in many magnetic oxides, e.g. MnO, La_2CuO_4.

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Superexchange

- Case I: AF ordering

↑ ↓↑ ↓
M O M ground state ✓

↑↓ ↓↑
M O M
↑↓ ↓↑
M O M } excited states

etc

- Case II: F ordering

↑ ↓↑ ↑
M O M ground state? ✗

- KE advantage for AF ordering

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Toy model for superexchange

Case i/ FM $\uparrow \quad \uparrow$ — penalty U for double occupancy

$E = 0$ — hopping t

ii/ AFM

$\uparrow \quad \downarrow$		A	0
$\downarrow \quad \uparrow$		B	0
$\uparrow\downarrow \quad -$		C	U
$- \quad \uparrow\downarrow$		D	U

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Toy model for superexchange

$$\mathcal{H} = \begin{bmatrix} 0 & 0 & -t & -t \\ 0 & 0 & -t & -t \\ -t & -t & U & 0 \\ -t & -t & 0 & U \end{bmatrix} \qquad \left(\text{guess } -\frac{2t^2}{U}\right)$$

$$\det(\mathcal{H} - E) = 0$$

$$\begin{vmatrix} -E & 0 & -t & -t \\ 0 & -E & -t & -t \\ -t & -t & U-E & 0 \\ -t & -t & 0 & U-E \end{vmatrix} = 0$$

$$E(U-E)\left[-E^2 + UE + 2t^2\right] = 0$$

$$\Rightarrow E = 0,\ U,\ \frac{U \pm \sqrt{U^2 + 8t^2}}{2}$$

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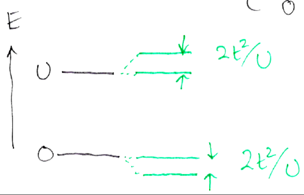
Toy model for superexchange

$t \ll U$

$$\text{last 2 eigenvalues} \simeq \frac{U}{2} \pm \frac{U}{2}\underbrace{\left(1 + \frac{8t^2}{U^2}\right)^{1/2}}_{1 + \frac{4t^2}{U^2}}$$

$$\simeq \begin{cases} U + \frac{2t^2}{U} \\ 0 - \frac{2t^2}{U} \end{cases}$$



$$J \approx \frac{2t^2}{U}$$

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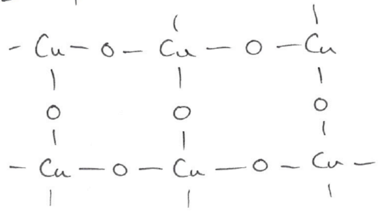
Toy model for superexchange

La_2CuO_4



$$J \approx \frac{2t^2}{U}$$

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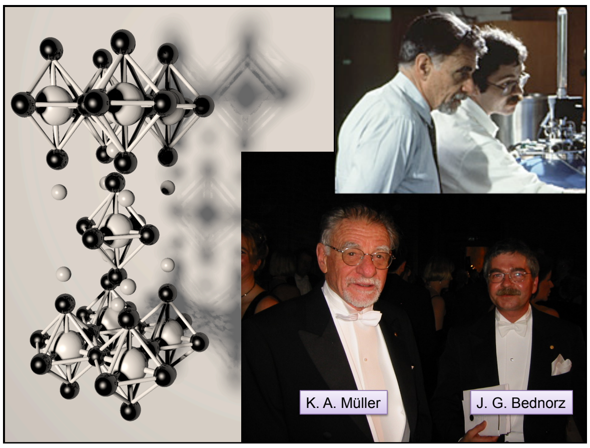

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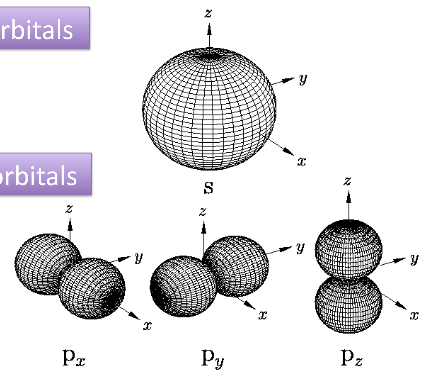
s-orbitals

p-orbitals



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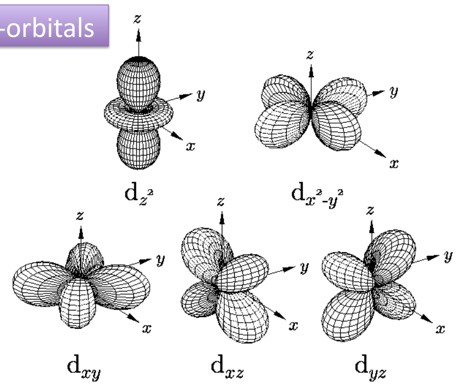
d-orbitals



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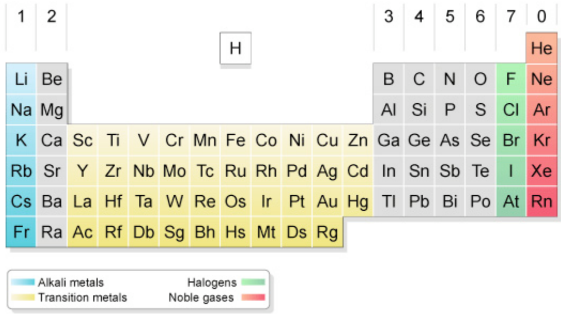
Magnetic elements and ions



traditional technology uses Fe, Co, Ni and alloys – plus the physics of *metals*

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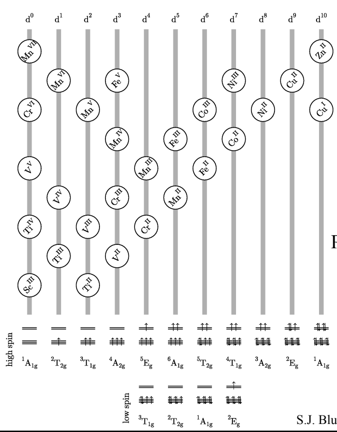
Transition metal (3d) ions



Partially filled 3d shell gives rise to a magnetic moment

S.J. Blundell, Contemp. Phys. **48,** 275 (2007)

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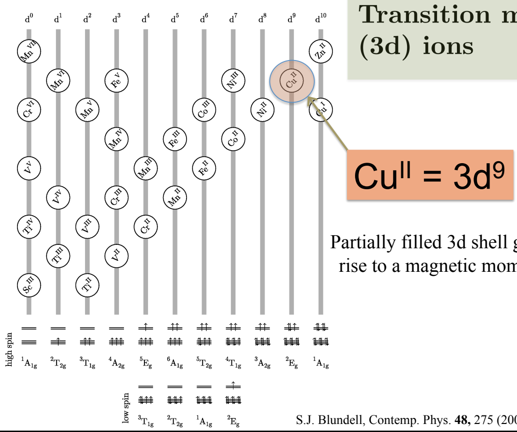
Transition metal (3d) ions



$Cu^{II} = 3d^9$

Partially filled 3d shell gives rise to a magnetic moment

S.J. Blundell, Contemp. Phys. **48,** 275 (2007)

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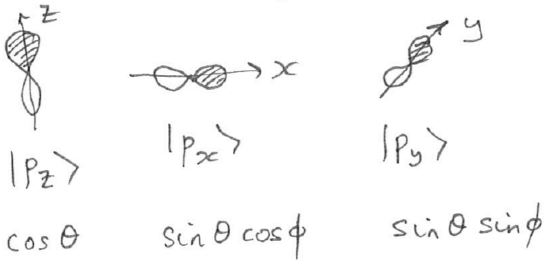
A parable: p-orbitals



real eigenfunctions, for V(r) which is real

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A parable: p-orbitals

$Y_{lm}(\theta,\phi)$ $\quad l=1 \quad$ $m=0 \;\; \cos\theta$

$m=1 \;\; \sin\theta\, \mathrm{e}^{i\phi}$

$m=-1 \;\; \sin\theta\, \mathrm{e}^{-i\phi}$

$\hat{L}_z = -i\hbar \dfrac{\partial}{\partial\phi}$ imaginary, $|m\rangle$ eigenfunctions

$|p_z\rangle = |0\rangle$

$|p_x\rangle = \dfrac{|1\rangle + |-1\rangle}{\sqrt{2}}$

$|p_y\rangle = \dfrac{|1\rangle - |-1\rangle}{\sqrt{2}i}$

note that these contain the eigenfunctions $|m\rangle$ and $|-m\rangle$ in equal mixtures

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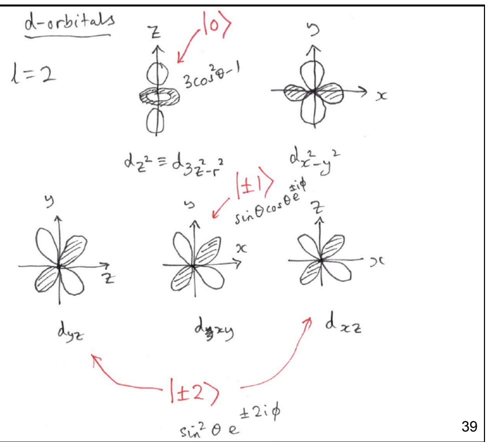

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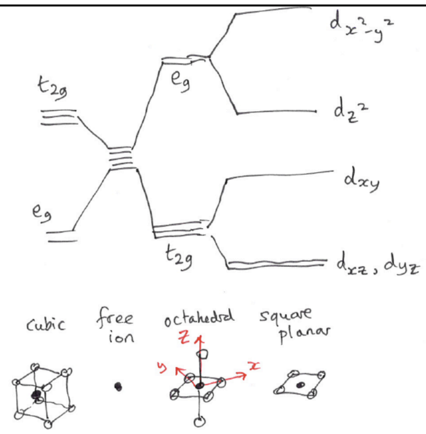

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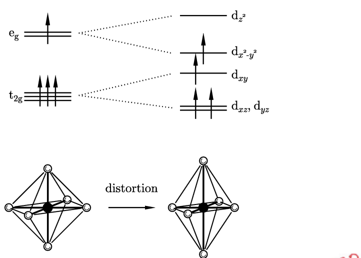
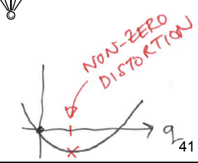
Jahn-Teller distortion in a 3d^4 ion



distortion parameter = q

energy = $a q^2$ − $b q$
(elastic) (electronic)



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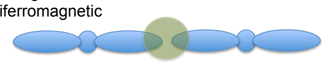
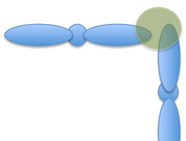
Goodenough-Kanamori-Anderson (GKA) rules

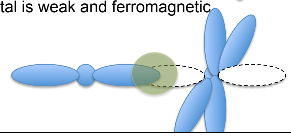
1. Exchange interaction of two half-filled orbitals is strong and antiferromagnetic



2. If this overlap is at 90°, exchange interaction is weak and ferromagnetic



3. Exchange interaction of half-filled with empty (or doubly-occupied) orbital is weak and ferromagnetic



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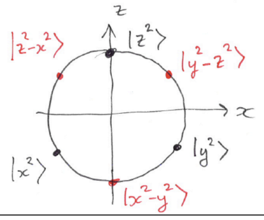
e_g orbitals

$$|\theta\rangle = \cos\frac{\theta}{2}\,|z^2\rangle + \sin\frac{\theta}{2}\,|x^2-y^2\rangle$$

$|m=0\rangle$ $\quad$ $\frac{1}{\sqrt{2}}\left(|m=+2\rangle + |m=-2\rangle\right)$

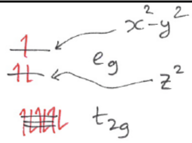
pseudospin $T=\frac{1}{2}$ $\quad$ $\left(T^z=\frac{1}{2} \quad d_{z^2}\right.$; $\left. T^z=-\frac{1}{2} \quad d_{x^2-y^2}\right)$

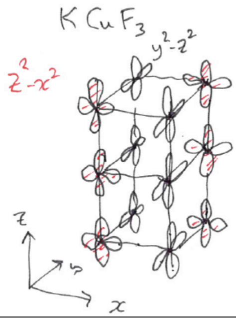


$T^x - T^z$ plane

x^2-y^2

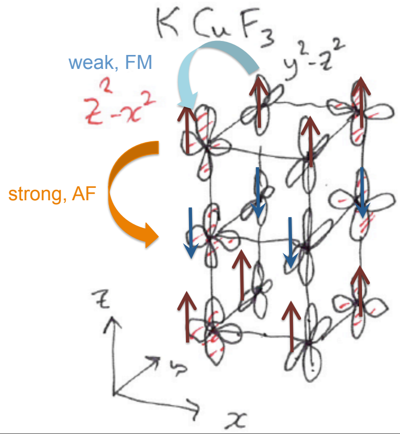
e_g orbitals





orbital order

Model 1D compound even though cubic !!



t_{2g} orbitals

t_{2g} $\quad$ $LaTiO_3$ $\quad$ Ti^{3+} $\quad$ $3d^1$ $\quad$ $S=\frac{1}{2}$

e_g $\quad$ $=$ $\quad$ $x^2-y^2,\ z^2$

orbitally degenerate

t_{2g} $\quad$ $\equiv$ $\quad$ $xy,\ yz,\ xz$

isospin $T=1$ $\quad$ $|X\rangle = |yz\rangle$ $\quad$ $|Y\rangle = |zx\rangle$

$|Z\rangle = |xy\rangle$

In the next lecture:

- spin waves
- frustration
- phase transitions
- metallic magnets