

The European School on Magnetism 2022

LECTURE
2.4

UNIVERSITE DE LA GRANDE REGION
UNIVERSITAT DER GROSSREGION



**Crystal electric field, spin-orbit,
magnetic anisotropy, DMI**

Stephen Blundell
University of Oxford

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**Crystal electric field, spin-orbit,
magnetic anisotropy, DMI**

LECTURE
2.4

1. Orbital magnetism and angular momentum
2. Spin orbit
3. Crystal field and orbital quenching
4. DMI
5. Magnetic anisotropy

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Crystal electric field, spin-orbit, magnetic anisotropy, DMI

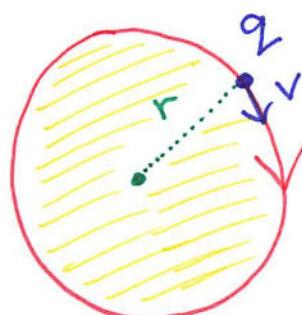
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Orbital magnetism – connection to angular momentum

ORBITAL ANGULAR MOMENTUM



$$I = \frac{qv}{2\pi r}/\nu$$

Magnetic moment $\mu = I\pi r^2 = \frac{q}{2m} L$

GYROMAGNETIC RATIO γ

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Orbital magnetism – connection to angular momentum

LINEAR MOMENTUM

$$\hat{P}_x = -i\hbar \frac{\partial}{\partial x}$$

e^{ikx} eigenfunction
 $\hbar k$ eigenvalue

ANGULAR MOMENTUM

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

$e^{im\phi}$ eigenfunction
 $m\hbar$ eigenvalue

INTEGER

$$\therefore e^{im(\phi+2\pi)} = e^{im\phi}$$

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Orbital magnetism – connection to angular momentum

$$\hat{L} = \hat{r} \times \hat{p} = -i\hbar \hat{r} \times \nabla$$

(see Mike Coey's lecture on
Tuesday on the single electron)

$$\hat{L}_z = i\hbar [y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y}] = -i\hbar \frac{\partial}{\partial \phi}$$

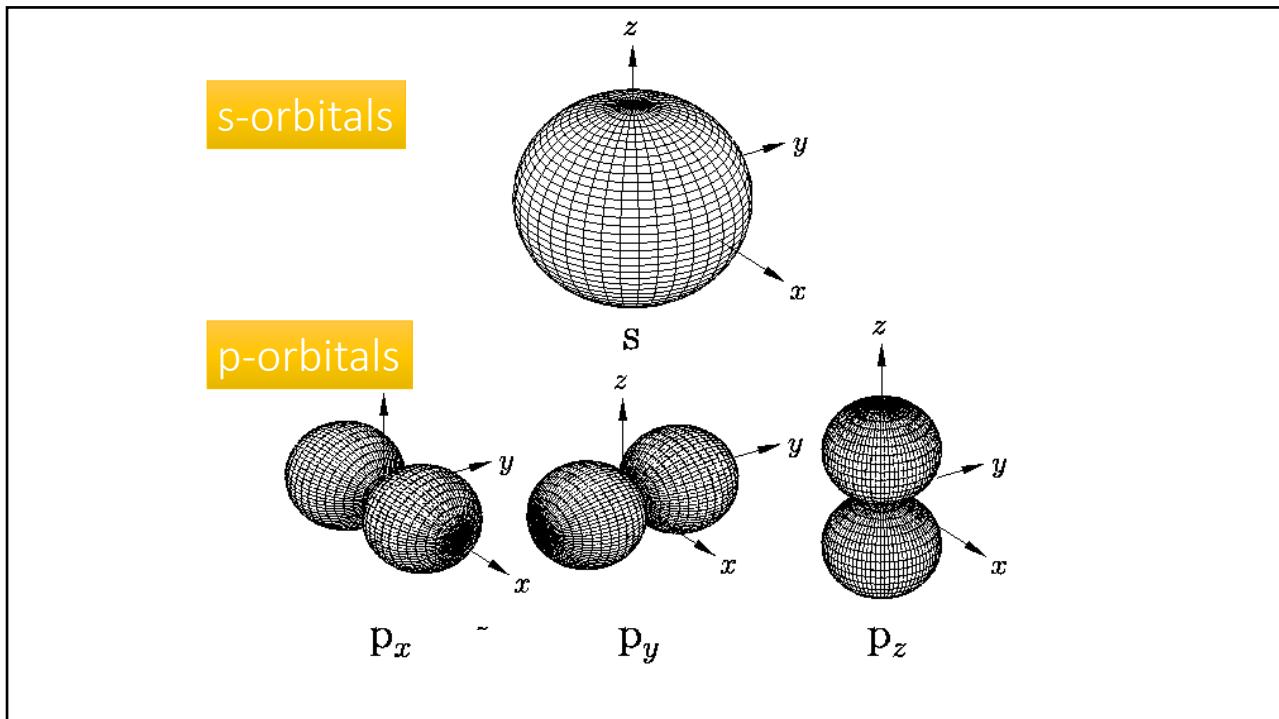
$$\hat{L}_z |l, m\rangle = m\hbar |l, m\rangle \quad \hat{L}^2 |l, m\rangle = l(l+1)\hbar^2 |l, m\rangle$$

$$\langle \theta, \phi | l, m \rangle = Y_l^m(\theta, \phi) \propto P_l^m(\cos \theta) e^{im\phi}$$

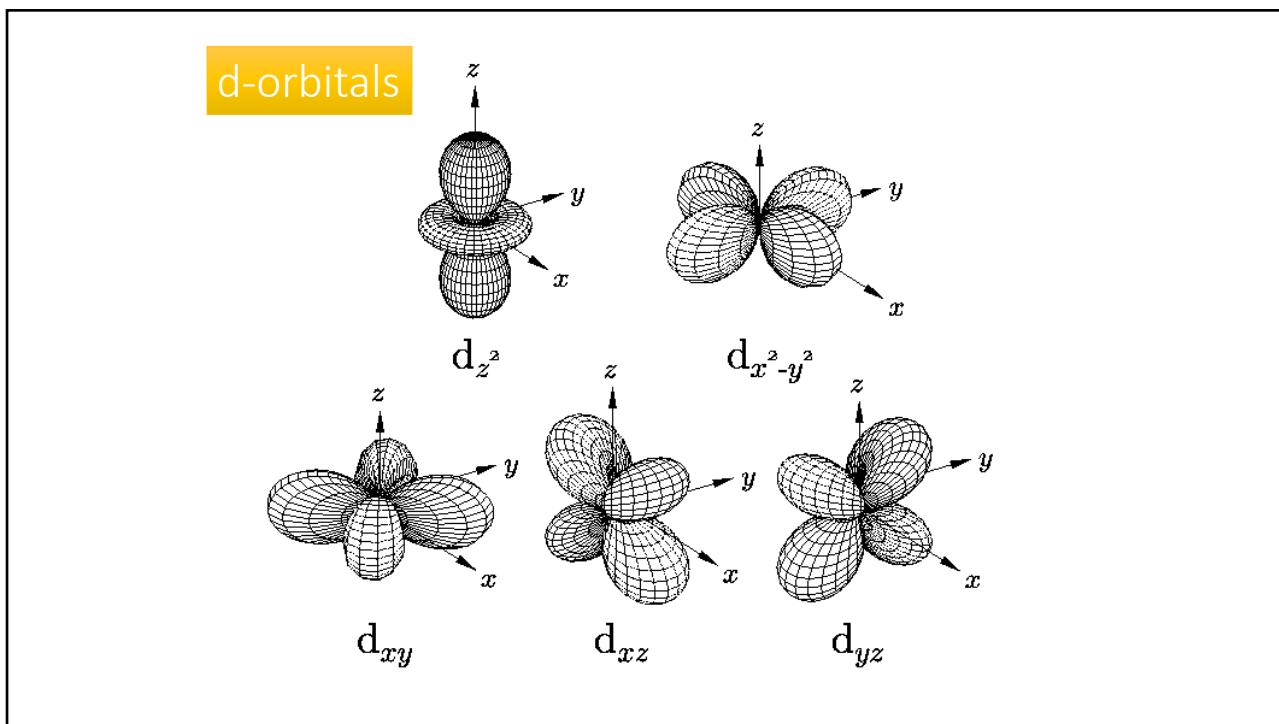
SPHERICAL
HARMONICS

ASSOCIATED
LEGENDRE
POLYNOMIAL

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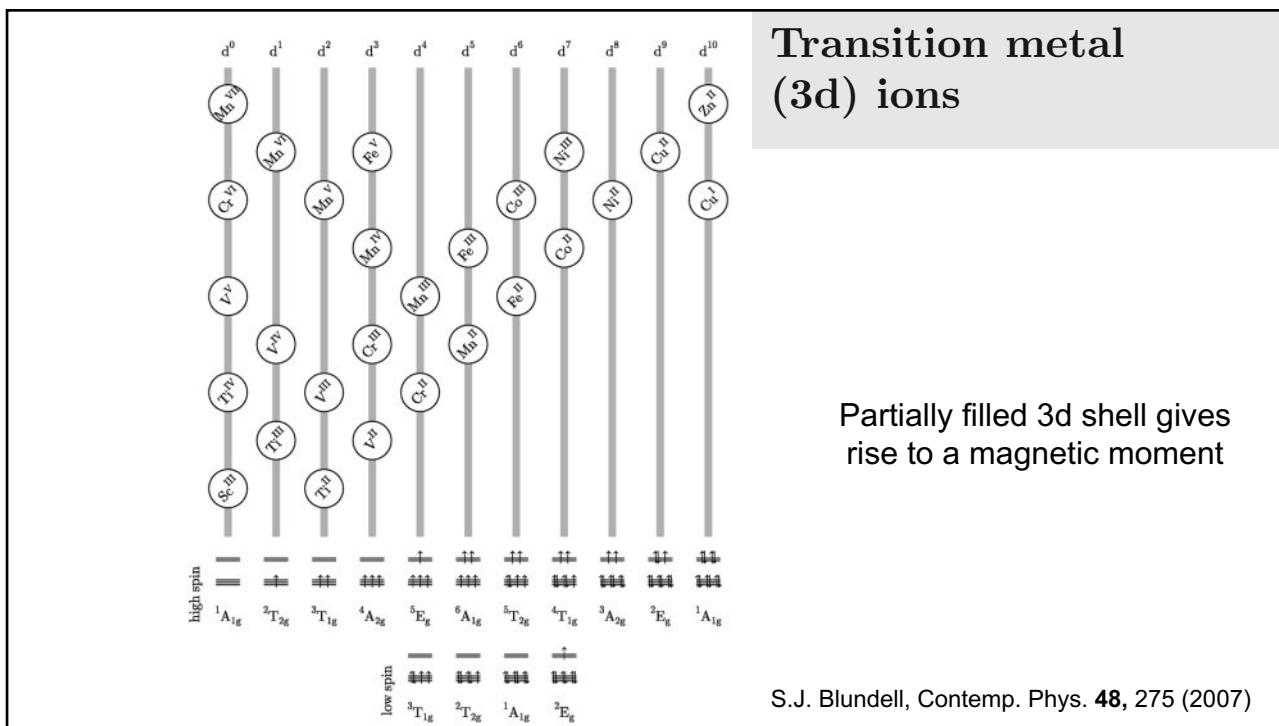
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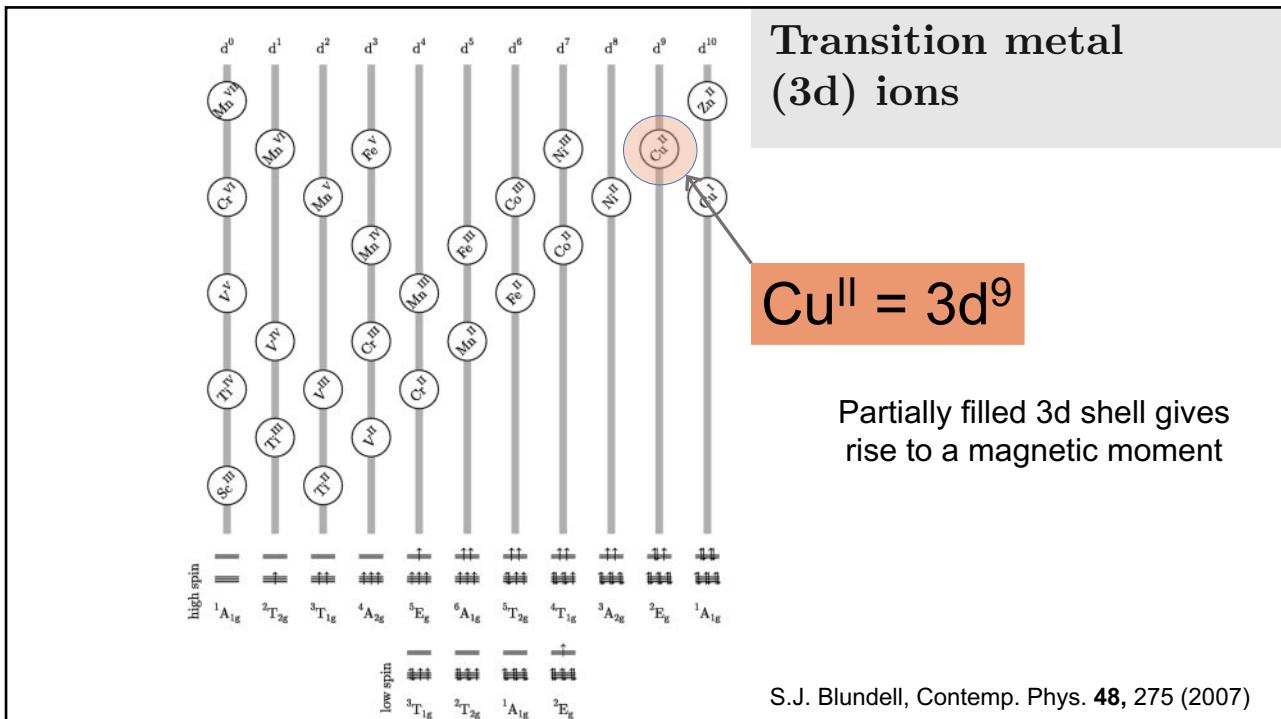
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Magnetic elements and ions																	
¹ H																	² He
³ Li	⁴ Be																⁵ B
¹¹ Na	¹² Mg																⁶ C
¹⁹ K	²⁰ Ca	²¹ Sc	²² Ti	²³ V	²⁴ Cr	²⁵ Mn	²⁶ Fe	²⁷ Co	²⁸ Ni	²⁹ Cu	³⁰ Zn	³¹ Ga	³² Ge	³³ As	³⁴ Se	³⁵ Br	³⁶ Kr
³⁷ Rb	³⁸ Sr	³⁹ Y	⁴⁰ Zr	⁴¹ Nb	⁴² Mo	⁴³ Tc	⁴⁴ Ru	⁴⁵ Rh	⁴⁶ Pd	⁴⁷ Ag	⁴⁸ Cd	⁴⁹ In	⁵⁰ Sn	⁵¹ Sb	⁵² Te	⁵³ I	⁵⁴ Xe
⁵⁵ Cs	⁵⁶ Ba	*	⁷² Hf	⁷³ Ta	⁷⁴ W	⁷⁵ Re	⁷⁶ Os	⁷⁷ Ir	⁷⁸ Pt	⁷⁹ Au	⁸⁰ Hg	⁸¹ Tl	⁸² Pb	⁸³ Bi	⁸⁴ Po	⁸⁵ At	⁸⁶ Rn
⁸⁷ Fr	⁸⁸ Ra	†	¹⁰⁴ Rf	¹⁰⁵ Db	¹⁰⁶ Sg	¹⁰⁷ Bh	¹⁰⁸ Hs	¹⁰⁹ Mt									
* ⁵⁷ La ⁵⁸ Ce ⁵⁹ Pr ⁶⁰ Nd ⁶¹ Pm ⁶² Sm ⁶³ Eu ⁶⁴ Gd ⁶⁵ Tb ⁶⁶ Dy ⁶⁷ Ho ⁶⁸ Er ⁶⁹ Tm ⁷⁰ Yb ⁷¹ Lu																	
† ⁸⁹ Ac ⁹⁰ Th ⁹¹ Pa ⁹² U ⁹³ Np ⁹⁴ Pu ⁹⁵ Am ⁹⁶ Cm ⁹⁷ Bk ⁹⁸ Cf ⁹⁹ Es ¹⁰⁰ Fm ¹⁰¹ Md ¹⁰² No ¹⁰³ Lr																	

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Crystal electric field, spin-orbit, magnetic anisotropy, DMI

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Spin-orbit interaction

(see Mike Coey's lecture on Tuesday on the single electron)

$$\lambda \vec{S} \cdot \vec{L}$$

↑ ↙ acts on $\Psi(\vec{r})$

acts on spin

If states are \approx atomic states, and S.O. acts as a perturbation, can focus on

$$\lambda S^z L^z$$

note $L_z = -i\hbar \frac{\partial}{\partial \phi}$ which has eigenfunctions $e^{im\phi}$

$$\hat{L}_z e^{im\phi} = m\hbar e^{im\phi}$$

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The crystal field is a real potential due to electrostatic fields from neighbouring ions. The eigenfunctions cannot be $e^{im\phi}$ because require real solutions.

Recall: particle in a box



Solutions are real: $\cos kx$ and $\sin kx$
but not e^{ikx} .

∴ make linear combinations: $e^{ikx} \pm e^{-ikx}$

Similarly, crystal field states can be $e^{im\phi} \pm e^{-im\phi}$

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This is the origin of ORBITAL QUENCHING

∴ relevant states are of the form
 $|m\rangle \pm | -m\rangle$, and hence $\langle 4 | \vec{L}^2 | 4 \rangle = 0$.

Notice this in 3d transition metal ions

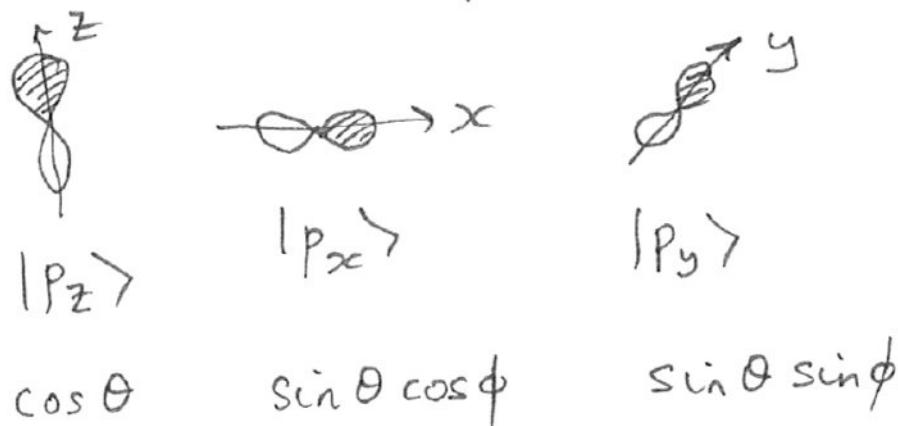
(where $L=0$, $J=S$ and $g=2$), but

NOT in 4f Lanthanide ions.

ion	shell	S	L	J	term	p_1	p_{exp}	p_2
Ti ³⁺ , V ⁴⁺	3d ¹	$\frac{1}{2}$	2	$\frac{3}{2}$	² D _{3/2}	1.55	1.70	1.73
V ³⁺	3d ²	1	3	2	³ F ₂	1.63	2.61	2.83
Cr ³⁺ , V ²⁺	3d ³	$\frac{3}{2}$	3	$\frac{3}{2}$	⁴ F _{3/2}	0.77	3.85	3.87
Mn ³⁺ , Cr ²⁺	3d ⁴	2	2	0	⁵ D ₀	0	4.82	4.90
Fe ³⁺ , Mn ²⁺	3d ⁵	$\frac{5}{2}$	0	$\frac{5}{2}$	⁶ S _{5/2}	5.92	5.82	5.92
Fe ²⁺	3d ⁶	2	2	4	⁵ D ₄	6.70	5.36	4.90
Co ²⁺	3d ⁷	$\frac{3}{2}$	3	$\frac{9}{2}$	⁴ F _{9/2}	6.63	4.90	3.87
Ni ²⁺	3d ⁸	1	3	4	³ F ₄	5.59	3.12	2.83
Cu ²⁺	3d ⁹	$\frac{1}{2}$	2	$\frac{5}{2}$	² D _{5/2}	3.55	1.83	1.73
Zn ²⁺	3d ¹⁰	0	0	0	¹ S ₀	0	0	0

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A parable: p-orbitals



real eigenfunctions, for $V(r)$ which is real

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A parable: p-orbitals

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

$$m = 1 \quad \sin \theta e^{i\phi}$$

$$m = -1 \quad \sin \theta e^{-i\phi}$$

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

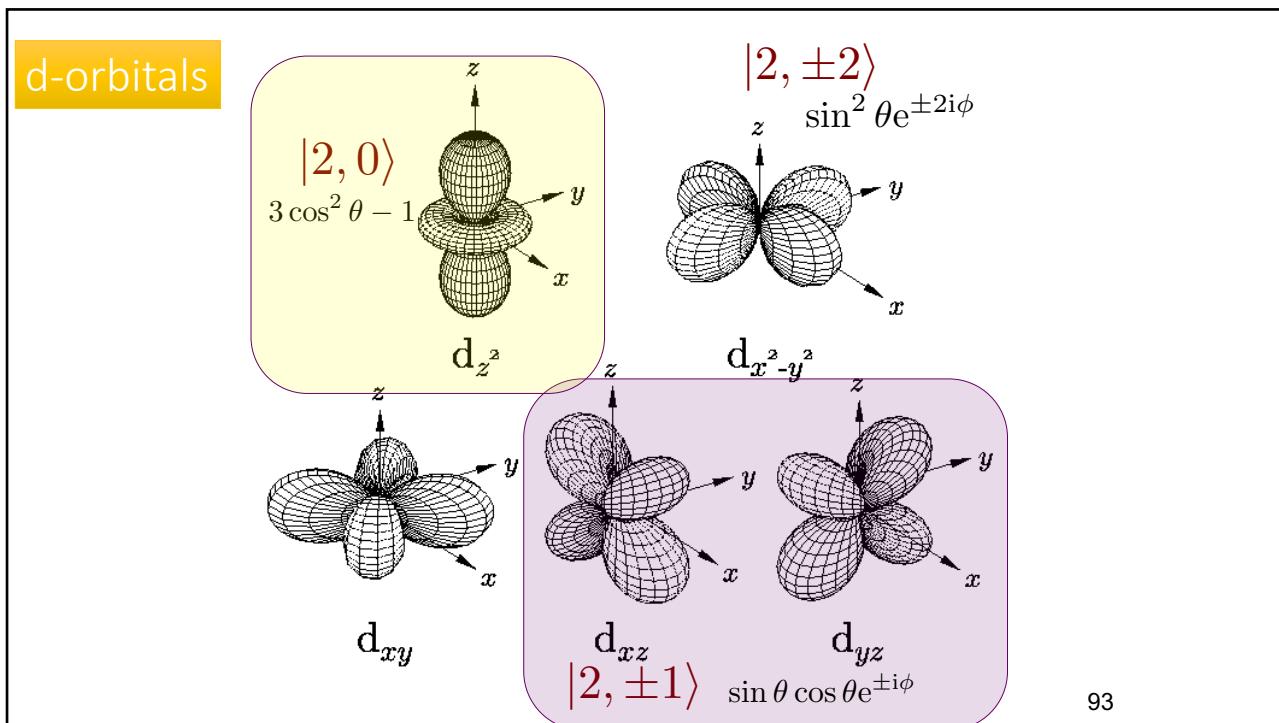
$$|p_z\rangle = |0\rangle$$

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

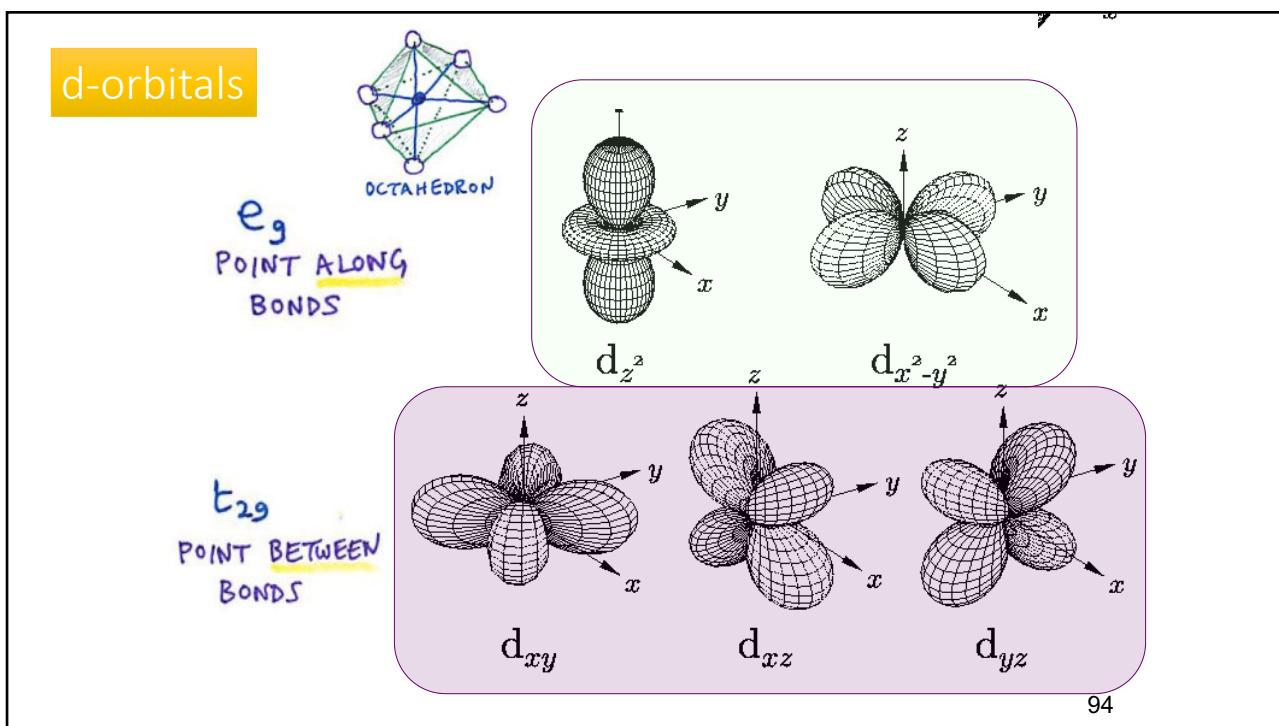
$$|p_y\rangle = \frac{|1\rangle - |-1\rangle}{\sqrt{2}i}$$

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

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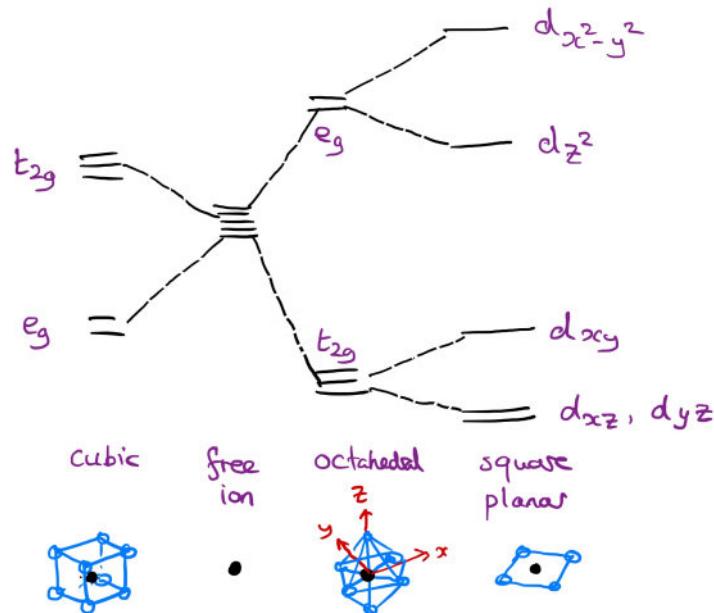


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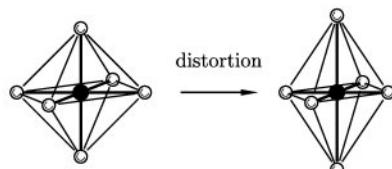
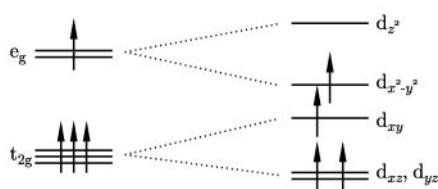
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Effect of crystal field on d electron states



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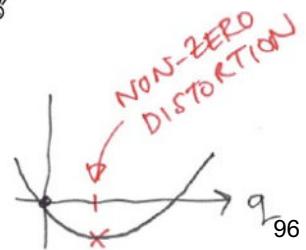
Jahn-Teller distortion in a $3d^4$ ion



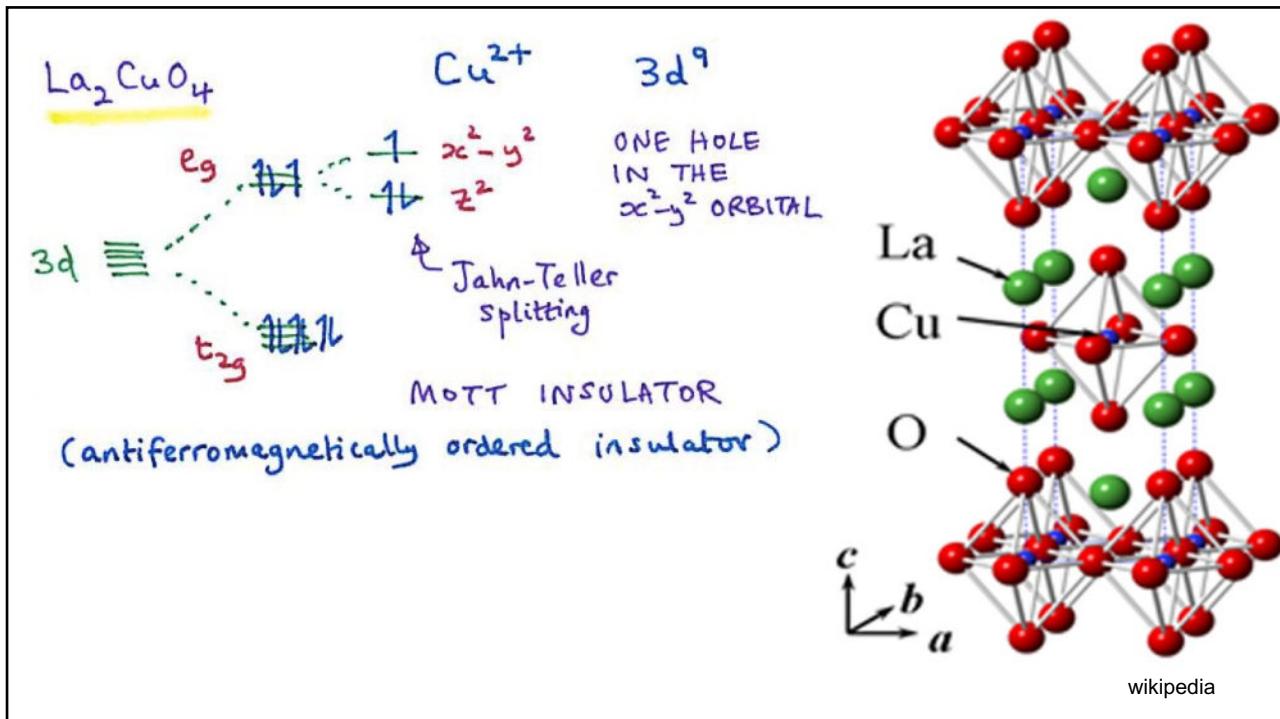
distortion parameter = q

$$\text{energy} = aq^2 - bq$$

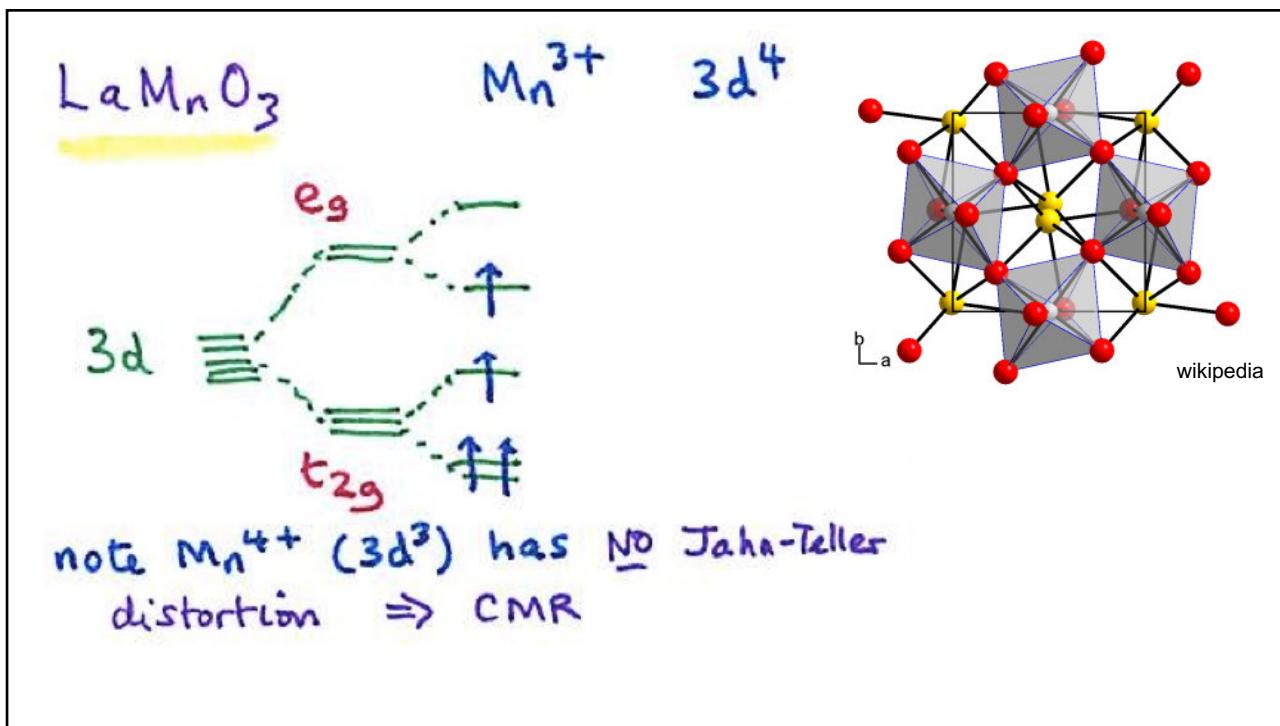
(elastic) (electronic)



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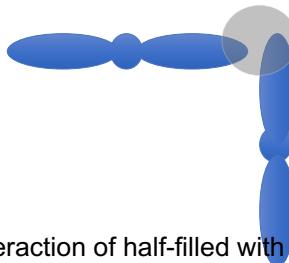
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Goodenough-Kanamori-Anderson (GKA) rules

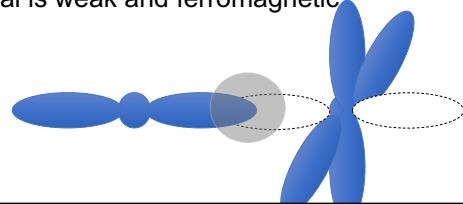
1. Exchange interaction of two half-filled orbitals is strong and antiferromagnetic



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



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



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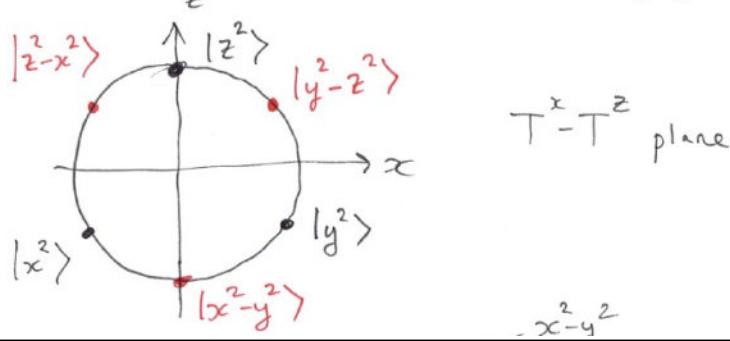
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e_g orbitals

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

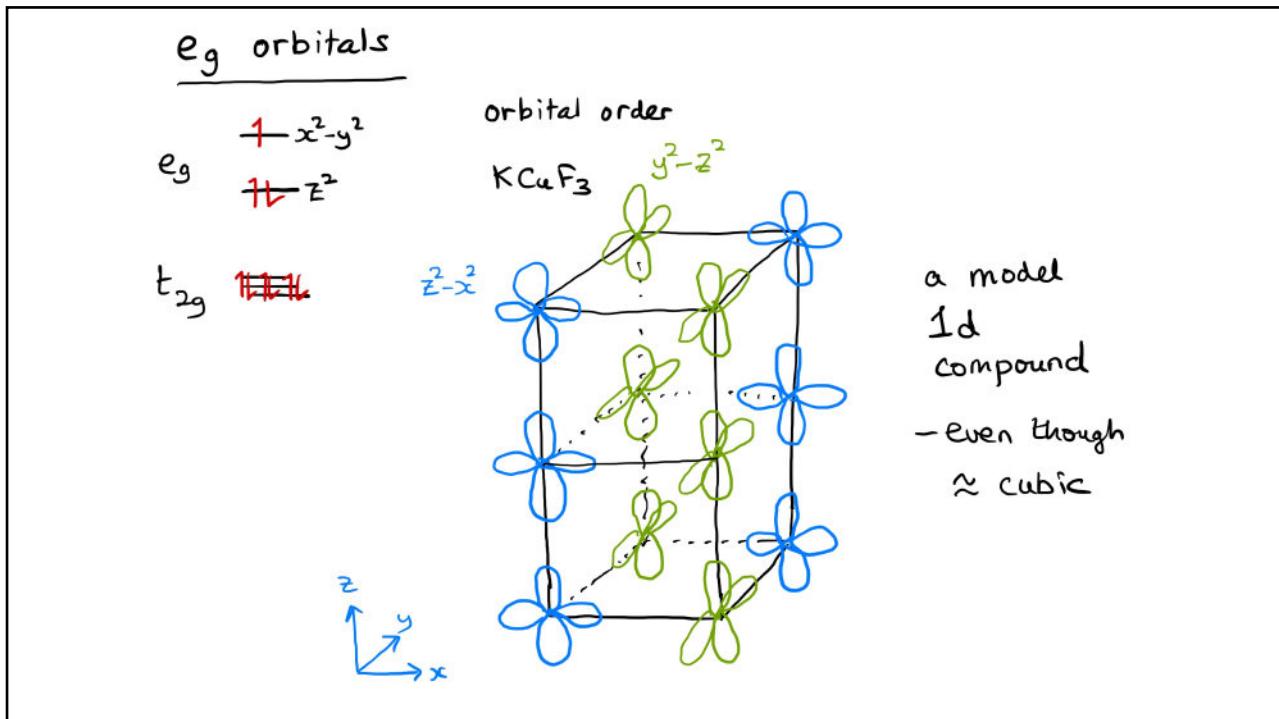
$\stackrel{\uparrow}{| m=0 \rangle}$ $\stackrel{\uparrow}{\frac{1}{\sqrt{2}}(| m=+2 \rangle + | m=-2 \rangle)}$

pseudospin $T = \frac{1}{2}$ ($T^2 = \frac{1}{2}$ d_{z^2}
 $T^2 = -\frac{1}{2}$ $d_{x^2-y^2}$)

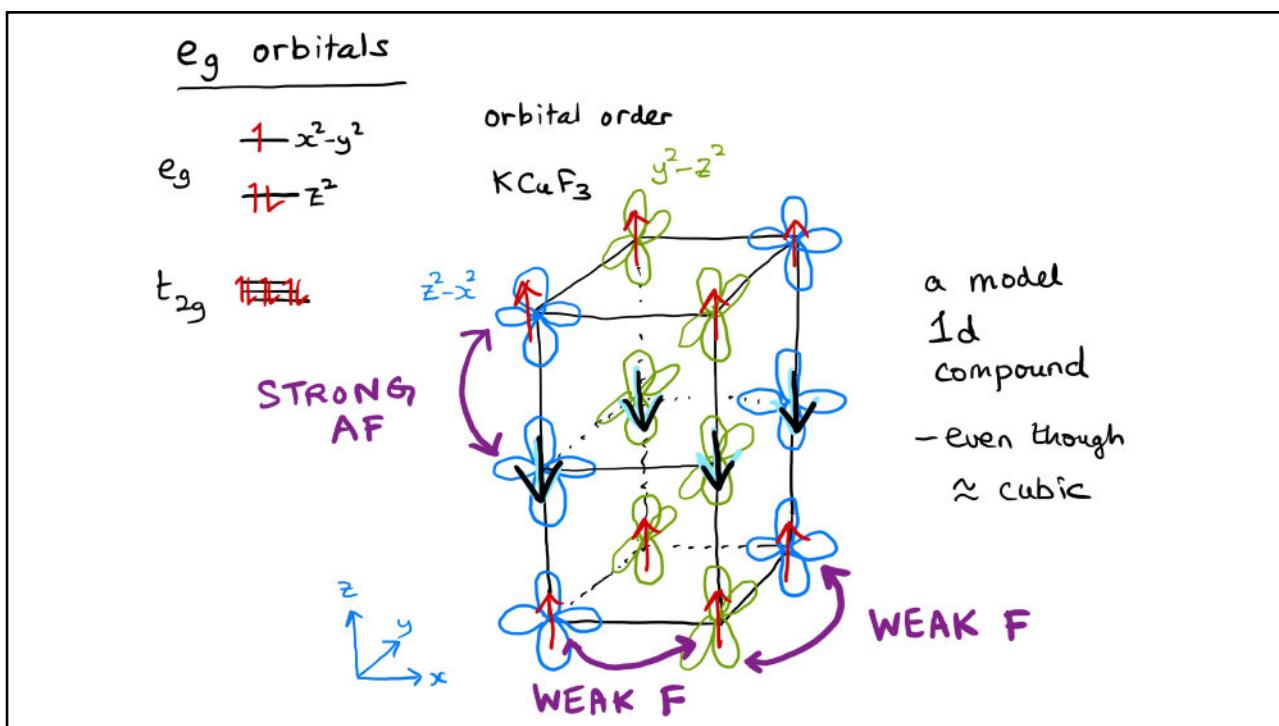


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100



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t_{2g} orbitals

<u>LaTiO₃</u>	Ti^{3+}	$3d^1$
	e_g	x^2-y^2, z^2
$3d \equiv$		ground state $S=\frac{1}{2}$
	$\nparallel t_{2g}$	xy, yz, xz
isospin $T=1$	$ X\rangle = yz\rangle$	$ Y\rangle = zx\rangle$, $ Z\rangle = xy\rangle$

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Na₂IrO₃

	Ir^{4+}	t_{2g}^5
$e_g =$		
t_{2g}	\xrightarrow{SOC}	$\begin{array}{c} \uparrow \\ \text{---} \\ \uparrow \downarrow \end{array} \quad \left\{ J_{eff} = \frac{1}{2} \right.$
		$\begin{array}{c} \uparrow \\ \text{---} \\ \uparrow \downarrow \end{array} \quad \left\{ J_{eff} = \frac{3}{2} \right.$

honeycomb lattice

3 types of bond

Heisenberg-Kitaev model.

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Generalized exchange
 Exchange interaction between \vec{S}_i and \vec{S}_j is

$$\vec{S}_i \cdot \vec{J} \cdot \vec{S}_j = \sum_{\alpha\beta} S_i^\alpha J_{\alpha\beta} S_j^\beta$$

↑ tensorial exchange constant

Can always diagonalize the symmetric part

e.g. $J_{\parallel} S_i^z S_j^z + J_{\perp} (S_i^x S_j^x + S_i^y S_j^y)$

The antisymmetric part can be related to a vector

$$\vec{D}_\alpha = \sum_{\beta\gamma} \epsilon_{\alpha\beta\gamma} J_{\beta\gamma}$$

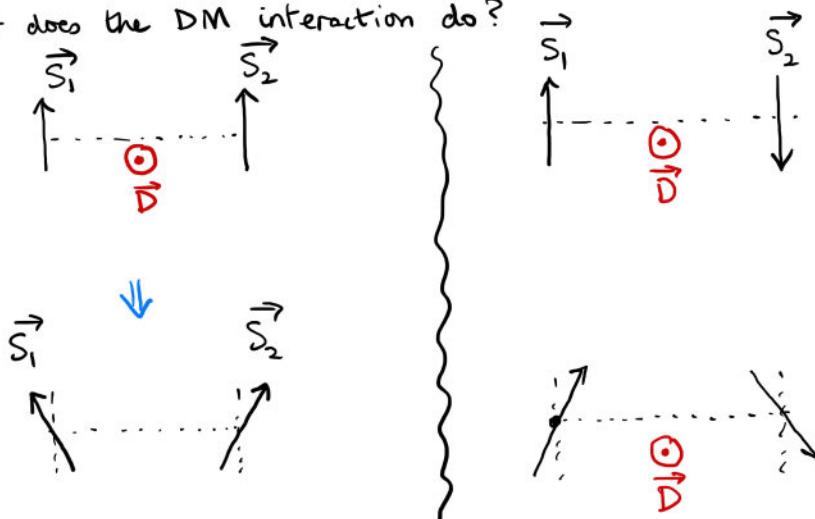
and so the antisymmetric exchange is

$$\vec{D} \cdot \vec{S}_i \times \vec{S}_j$$

And, in general, \vec{D} depends on i and j $\Rightarrow \vec{D}_{ij}$. This is called the DZYALOSHINSKII-MORIYA interaction.

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What does the DM interaction do?



CANTING! WEAK FERROMAGNETISM

$$\delta E_{DM} \sim D \sin \theta \sim D\theta \quad \text{saved}$$

$$\delta E_{exch} \sim \frac{J\theta^2}{2} \quad \text{cost} \Rightarrow \theta \sim D/J \quad (\text{typically } D \sim 10^2 \text{ J})$$

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When do you have the DM interaction?

Answer: symmetry considerations (worked out by Moriya) can rule it out.

e.g. If there is a centre of inversion between \vec{S}_1 and \vec{S}_2 ,
 $\vec{D}_{12} = 0$.

Also:

Mirror plane bisecting \vec{r}_{12} , \vec{D}_{12} in mirror plane.

Mirror plane containing \vec{r}_{12} , $\vec{D}_{12} \perp$ to mirror plane.

2-fold axis bisecting \vec{r}_{12} , $\vec{D}_{12} \perp$ 2-fold axis.

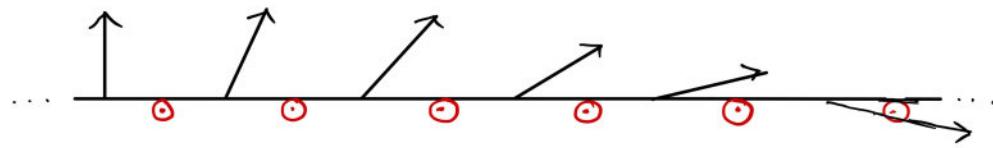
n-fold axis ($n > 2$) along \vec{r}_{12} , \vec{D}_{12} parallel to \vec{r}_{12} .

But, these rules don't tell you about the strength of the DMI.

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Formation of cycloidal spirals

- $D=0 \Rightarrow$ colinear ferromagnet
- $D \neq 0 \Rightarrow$ spiral



angle $\sim D/J$ between neighbouring spins

e.g. MnSi (\rightarrow skyrmions)

BiFeO_3 (ferroelectric transition below 1100K, breaks inversion symmetry and turns a simple two-sublattice AF ordering into a long period [$\sim 70\text{ nm}$] spiral)

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NB Distinguish between $\vec{D}_{1,2}$ between 2 magnetic atoms 1 and 2, and \vec{D} for the crystal as a whole.

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

now refers to sublattices 1 and 2

e.g. La_2CuO_4

(each plane develops a weak FM moment, but the moments from neighbouring planes are OPPOSITE \Rightarrow no net ferromagnetic moment.)

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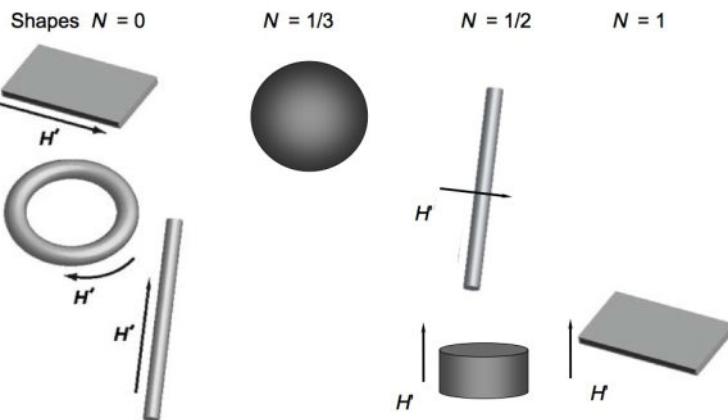
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Compasses work!

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• Shape anisotropy



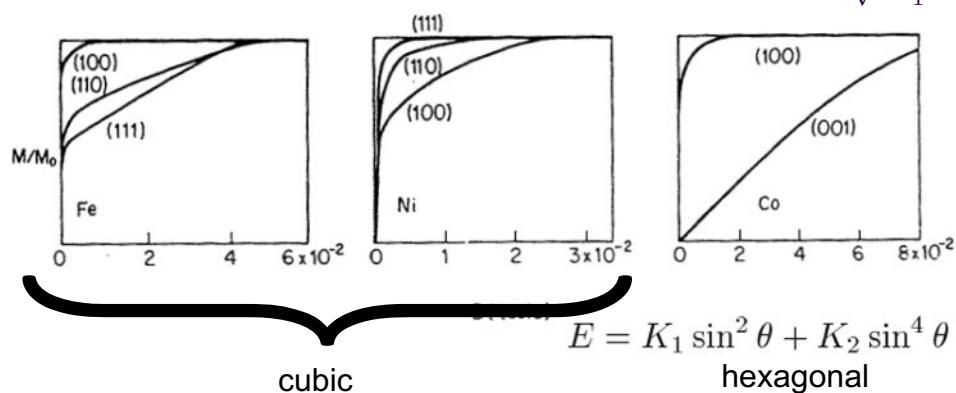
- Volume anisotropy
- Surface anisotropy

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Magnetocrystalline anisotropy in elemental ferromagnets

$$\vec{M} = (M_1, M_2, M_3)$$

$$\alpha_1 = \cos \theta_1 = \frac{M_1}{\sqrt{M_1^2 + M_2^2 + M_3^2}}$$



$$E_a = K_1(\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) + K_2 \alpha_1^2 \alpha_2^2 \alpha_3^2$$

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Magnetocrystalline anisotropy

$$\vec{M} = (M_1, M_2, M_3)$$

Anisotropy energy E_a

$$\alpha_1 = \cos \theta_1 = \frac{M_1}{\sqrt{M_1^2 + M_2^2 + M_3^2}}$$

Cubic crystal: E_a only depends on even powers of α_i direction of \vec{M}
cosinesand must be invariant to interchange of α_i \Rightarrow can't have $E_a = K\alpha_1^2$, must be $K(\alpha_1^2 + \alpha_2^2 + \alpha_3^2)$ BUT $\alpha_1^2 + \alpha_2^2 + \alpha_3^2 = 1$.

$$\text{Also } \alpha_1^4 + \alpha_2^4 + \alpha_3^4 = 1 - 2(\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2)$$

$$\Rightarrow E_a = K_1(\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) + K_2 \alpha_1^2 \alpha_2^2 \alpha_3^2 + K_3 (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2)^2 + \dots$$

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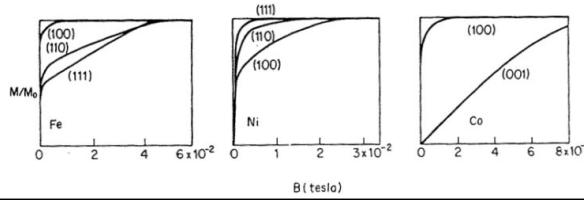
$$E_a = K_1(\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) + K_2 \alpha_1^2 \alpha_2^2 \alpha_3^2 + K_3 (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2)^2 + \dots$$

Direction $\alpha_1 \alpha_2 \alpha_3 E_a$

[100] 1 0 0 0

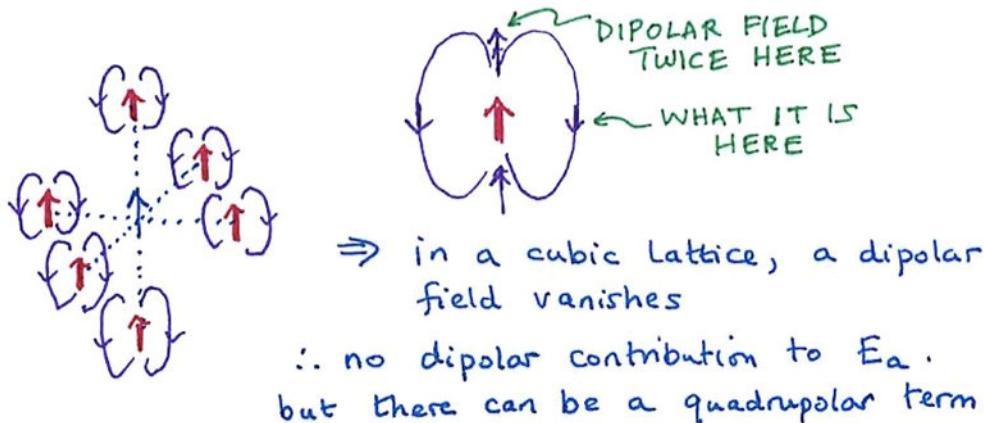
[110] $\frac{1}{\sqrt{2}}$ $\frac{1}{\sqrt{2}}$ 0 $\frac{1}{4}K_1 + \frac{1}{16}K_3 + \dots$ [111] $\frac{1}{\sqrt{3}}$ $\frac{1}{\sqrt{3}}$ $\frac{1}{\sqrt{3}}$ $\frac{1}{3}K_1 + \frac{1}{27}K_2 + \frac{1}{9}K_3 + \dots$

Room T:	$K_1 (\text{Jm}^{-3})$	$K_2 (\text{Jm}^{-3})$	easy axis
Fe	4.7×10^4	-7.5×10^2	[100]
Ni	-5.7×10^3	-2.3×10^3	[111]



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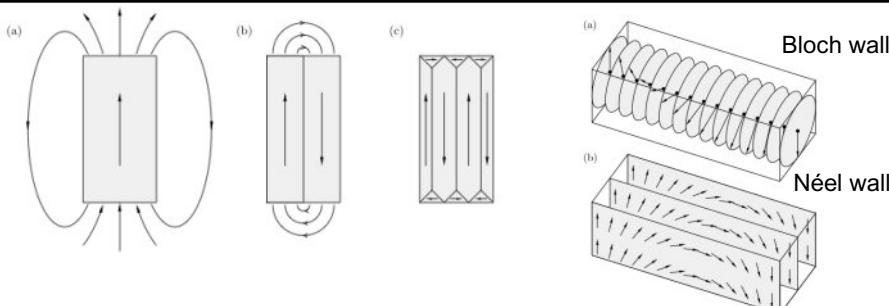
Origin of magnetocrystalline anisotropy: spin pair model



$$\begin{aligned} \text{SPIN PAIR MODEL} \\ E_a &= \sum_i w_i = N \sum_{j=1}^3 d \left(\alpha_j^2 - \frac{1}{3} \right) + q \left(\alpha_1^4 - \frac{6}{7} \alpha_1^2 + \frac{3}{35} \right) + \dots \\ &= -2Nq (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) + \text{const} + \dots \end{aligned}$$

But also have to consider intrinsic single-ion effects (via spin-orbit)

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$$\begin{aligned} E &= \int_{-\infty}^{\infty} \left[A \left(\frac{\partial \theta}{\partial z} \right)^2 + f(\theta) \right] dz, \\ \delta &= \pi \sqrt{A/K} \quad f(\theta) = K \sin^2 \theta \\ E &= 4 \sqrt{AK} \end{aligned}$$

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Thin film case

$$E_a = K \sin^2 \theta$$

Angle between surface normal and \mathbf{M}

$$K = \frac{2K_s}{t} + K_v - \frac{1}{2}\mu_0 M^2$$

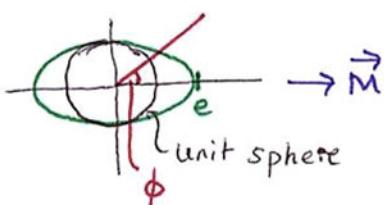
Surface anisotropy Shape anisotropy
Film thickness Volume anisotropy

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Magnetostriction

(Joule 1842)

$$\frac{\Delta l}{l} = e \quad \text{in direction of } \vec{M}$$



elongation in direction at angle ϕ is

$$e \cos^2 \phi$$



\therefore if sample is in many domains $\frac{\Delta l}{l} = \langle e \cos^2 \phi \rangle$

$$\left[\langle \cos^2 \phi \rangle = \int_0^{\pi/2} \cos^2 \phi \sin \phi d\phi = \frac{1}{3} \right]$$

$$\frac{\Delta l}{l} = \frac{e}{3}$$

but if it is saturated $\frac{\Delta l}{l} = e$

$$\text{SATURATION MAGNETO STRACTION} \equiv \lambda_s = e - \frac{e}{3} = \frac{2e}{3}$$

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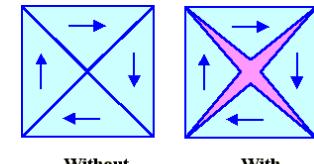
$$\lambda_s = e - \frac{e}{3} = \frac{2e}{3}$$

Rewrite as $e = \frac{3}{2} \lambda_s$ and measuring w.r.t. demagnetized ferromagnet (with $\langle \cos^2 \phi \rangle = \frac{1}{3}$)

$$\frac{\Delta l}{l} = \frac{3}{2} \lambda_s \left(\cos^2 \phi - \frac{1}{3} \right)$$

Fe	-7×10^{-6}	small effect
Ni	-34×10^{-6}	but explains why transformers HUM <small>Joule 1842</small>

[strain induced anisotropy = VILLARI EFFECT]



Does the sample disintegrate when it magnetizes?
No, but magnetization leads to stresses and this an energy contribution that must be considered



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SUMMARY

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