Models of Strongly Correlated Systems

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Lectures

- ✓ Spin-orbital exchange in Mott insulators
- Multiferroics and magnetoelectrics

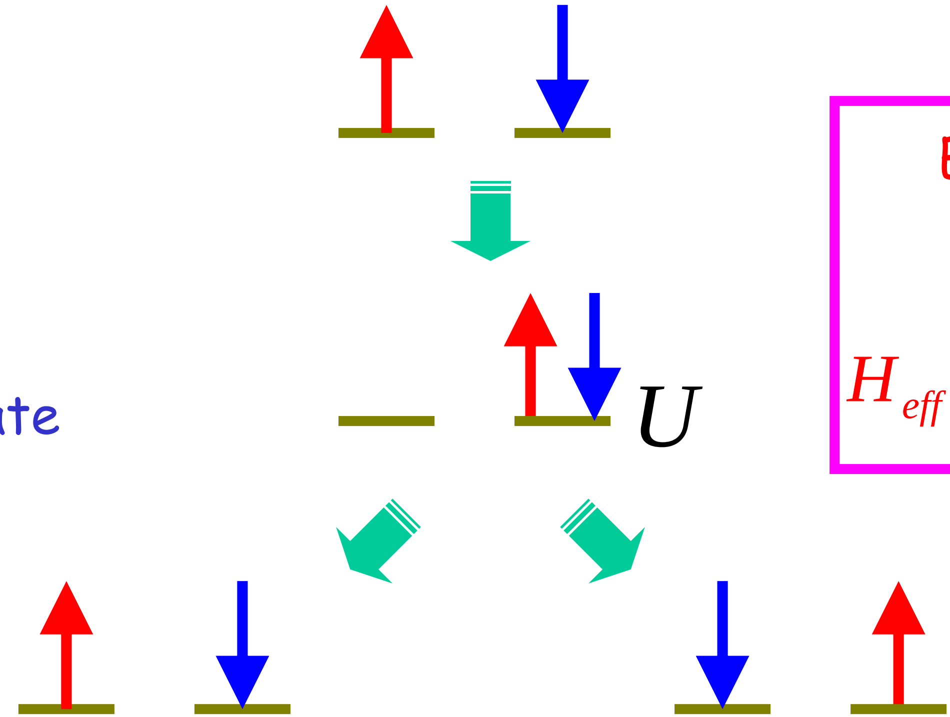
Part I

- Spin & orbital exchange interactions in e_g systems, Kugel-Khomskii Hamiltonian
- Compass models, frustration of orbital ordering
- Jahn-Teller effect
- Spin and orbital fluctuations in t_{2g} systems

Spin exchange in Hubbard model

$$H = -t\sum_{\langle i,j\rangle\sigma}\left(c^{+}_{i\sigma}c_{j\sigma} + c^{+}_{j\sigma}c_{i\sigma}\right) + U\sum_{i} n_{i\uparrow}n_{i\downarrow}$$

$$|i\rangle$$



intermediate state

$$U$$

Effective spin Hamiltonian:

$$H_{eff} = -\frac{2t^2}{U}\left(1 - S_{12}\right)$$

$$|f\rangle$$

$$-\frac{t^2}{U} \qquad\qquad +\frac{t^2}{U}S_{12}$$

Spin-exchange operator: $S_{12}|\sigma_1\rangle|\sigma_2\rangle = S_{12}|\sigma_2\rangle|\sigma_1\rangle$

Spin exchange in Hubbard model

Total spin

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$$

$$\mathbf{S}_1 \cdot \mathbf{S}_2 = \begin{cases} -3/4, & S = 0 \\ +1/4, & S = 1 \end{cases}$$

projector operators

$$P_{S=0} = 1/4 - (\mathbf{S}_1 \cdot \mathbf{S}_2)$$

$$P_{S=1} = (\mathbf{S}_1 \cdot \mathbf{S}_2) + 3/4$$

$S = 1$ spin functions symmetric

$$|1+1\rangle = \uparrow\uparrow$$

$$|10\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \qquad S_{12}\left|1S^z\right\rangle = +\left|1S^z\right\rangle$$

$$|1-1\rangle = \downarrow\downarrow$$

$S = 0$ antisymmetric

$$|00\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$$

$$S_{12}\left|00\right\rangle = -\left|00\right\rangle$$

Spin-exchange operator

$$S_{12} = P_{S=1} - P_{S=0} = 2(\mathbf{S}_1 \cdot \mathbf{S}_2) + \frac{1}{2}$$

Effective Hamiltonian

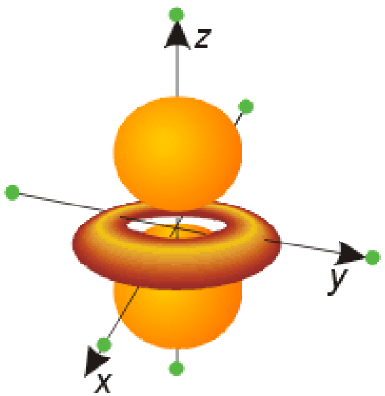
$$H_{eff} = -\frac{2t^2}{U}(1 - S_{12}) = -\frac{4t^2}{U} P_{S=0} = J\left(\mathbf{S}_1 \cdot \mathbf{S}_2 - \frac{1}{4}\right)$$

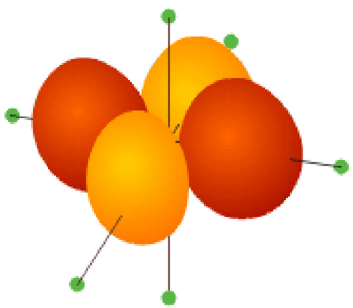
exchange constant

$$J = \frac{4t^2}{U} > 0$$

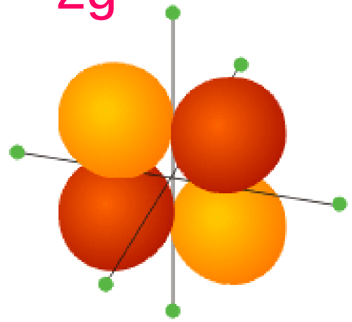
d-orbitals

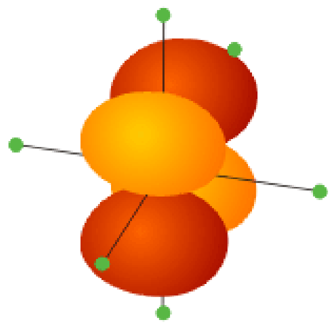
e_g

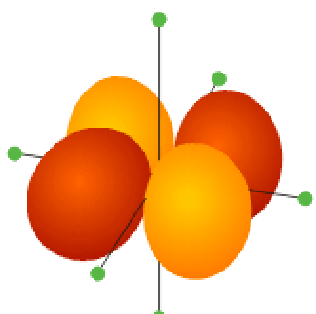




t_{2g}







octahedral crystal field	tetrahedral crystal field
e_g	t_{2g}
t_{2g}	e_g

d-states in cartesian and spherical coordinates

e_g

$$\frac{1}{\sqrt{6}}\left(3z^2 - r^2\right) = kY_{2,0}$$

$$\frac{1}{\sqrt{2}}\left(x^2 - y^2\right) = k\,\frac{\left(Y_{2,+2} + Y_{2,-2}\right)}{\sqrt{2}}$$

$$k = -\sqrt{\frac{8\pi}{15}}\,r^2$$

t_{2g}

$$xy = k'\,\frac{\left(Y_{2,+2} - Y_{2,-2}\right)}{\sqrt{2}}$$

$$xz = k'\,\frac{\left(Y_{2,+1} + Y_{2,-1}\right)}{\sqrt{2}}$$

$$yz = k'\,\frac{\left(Y_{2,-1} - Y_{2,+1}\right)}{\sqrt{2}i}$$

$$k' = -i\sqrt{\frac{4\pi}{15}}\,r^2$$

Orbitally degenerate Hubbard model

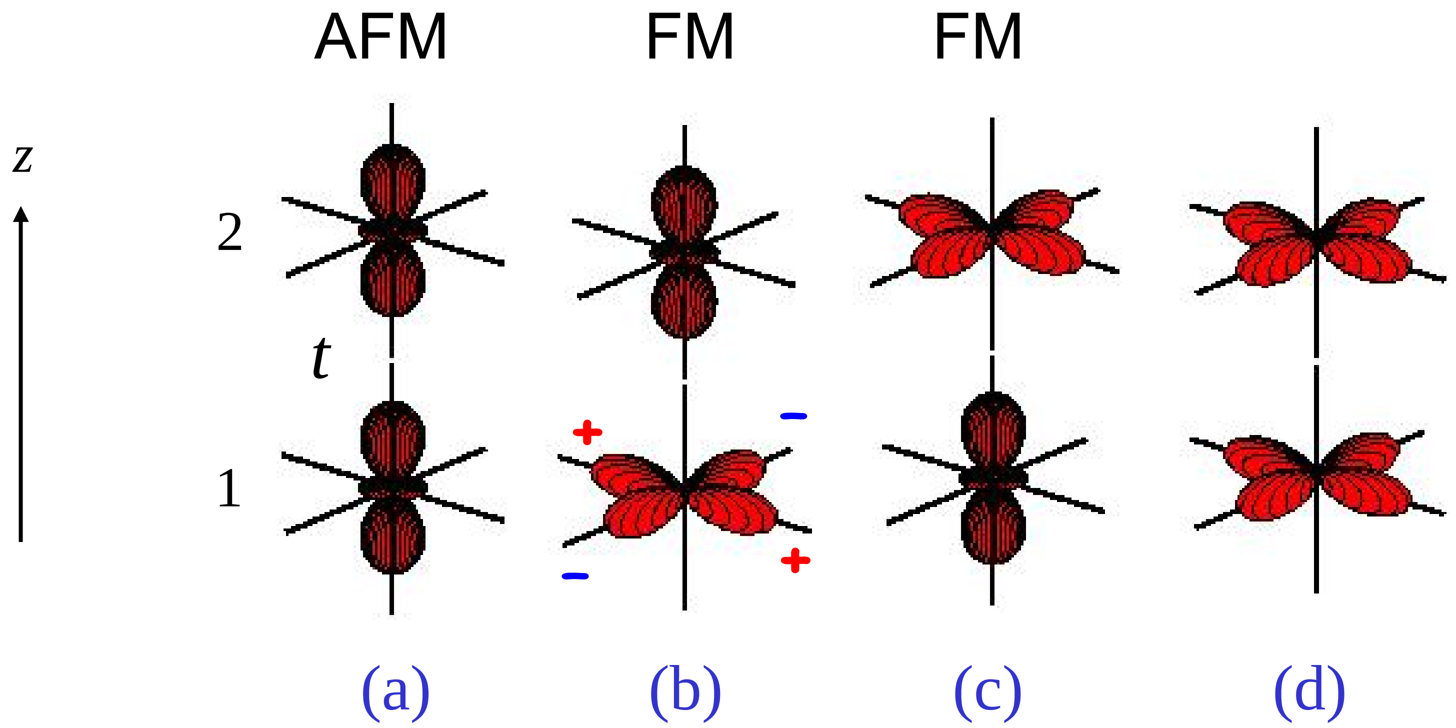
$$H_{dd} = -\sum_{\langle i\alpha, j\beta \rangle} t_{i\alpha, j\beta} \left(d^{+}_{i\alpha} d_{j\beta} + d^{+}_{j\beta} d_{i\alpha} \right) + \sum_{i} H^{C}_{i}$$

On-site Coulomb interaction (Kanamori parameters)

$$H^{C} = \frac{u}{2} \sum_{\alpha\sigma\sigma'} n_{\alpha\sigma} n_{\alpha\sigma'} + \frac{(u - 2j)}{2} \sum_{\substack{\alpha \neq \beta \\ \sigma\sigma'}} n_{\alpha\sigma} n_{\beta\sigma'}$$

$$+ \frac{j}{2} \sum_{\substack{\alpha \neq \beta \\ \sigma\sigma'}} d^{+}_{\alpha\sigma} d^{+}_{\beta\sigma'} d_{\alpha\sigma'} d_{\beta\sigma} + \frac{j}{2} \sum_{\substack{\alpha \neq \beta \\ \sigma \neq \sigma'}} d^{+}_{\alpha\sigma} d^{+}_{\alpha\sigma'} d_{\beta\sigma'} d_{\beta\sigma}$$

Exchange along the *z*-axis

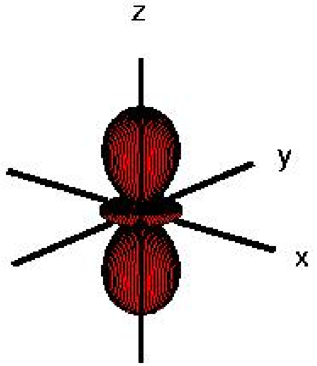


No hopping between $\left|3z^2 - r^2\right\rangle$ and $\left|x^2 - y^2\right\rangle$ orbitals

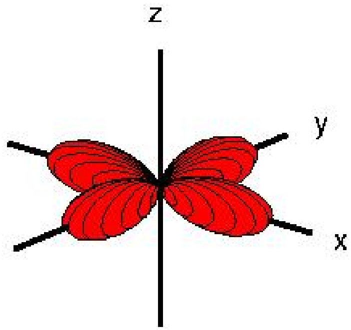
Exchange does not change orbital occupation

Orbitals and isospin

e_g orbitals $\quad T = \frac{1}{2}$



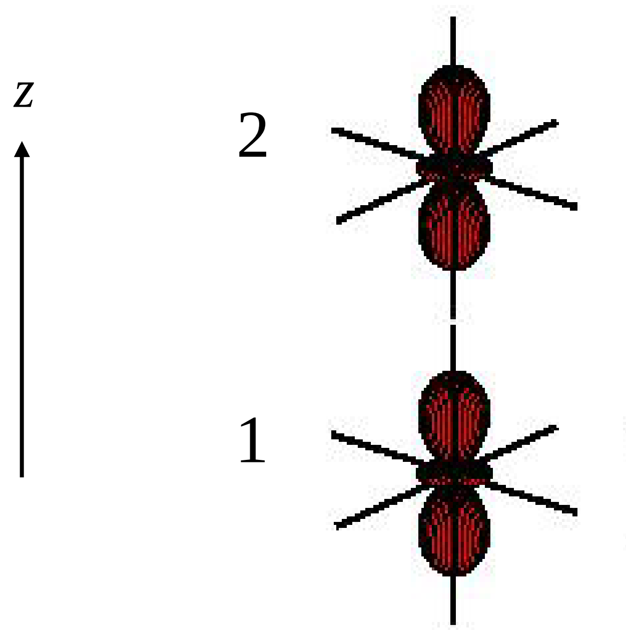
$$|3z^2 - r^2\rangle = |\uparrow\rangle \qquad T^z = +\frac{1}{2}$$



$$|x^2 - y^2\rangle = |\downarrow\rangle \qquad T^z = -\frac{1}{2}$$

AFM interaction

(a)



$$t = \frac{t_{pd}^2}{\Delta}$$

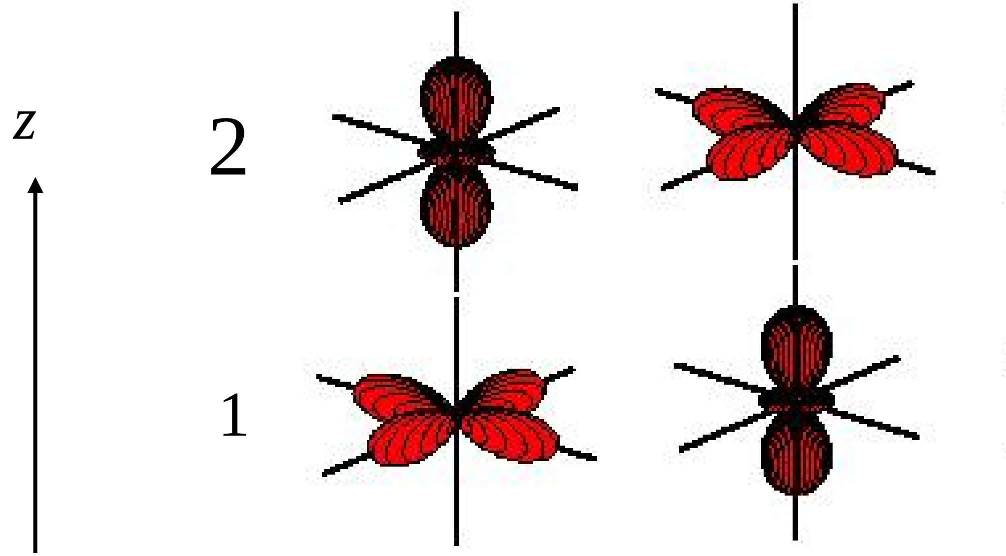
$$H_a = -\frac{4t^2}{U}\left(\frac{1}{2} + T_1^z\right)\left(\frac{1}{2} + T_2^z\right)\left(\frac{1}{4} - \mathbf{S}_1 \cdot \mathbf{S}_2\right)$$

$$T^z = +\frac{1}{2}$$

$$S = 0$$

FM interaction

(b) + (c)



$$U' = u - j$$

$$J_d = 2j$$

$$H_{b+c} = -\frac{t^2}{U' - J_d\left(\frac{3}{4} + \mathbf{S}_1 \cdot \mathbf{S}_2\right)}\left[\left(\frac{1}{2} - T_1^z\right)\left(\frac{1}{2} + T_2^z\right) + \left(\frac{1}{2} + T_1^z\right)\left(\frac{1}{2} - T_2^z\right)\right]$$

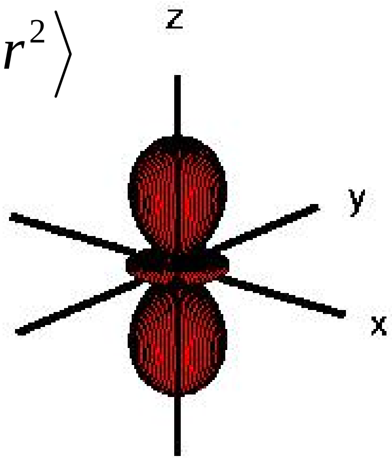
Hund's rule coupling

$S = 1$

$$H_{FM} = -\frac{t^2 J_d}{U'^2}\left[\left(\frac{1}{2} - T_1^z\right)\left(\frac{1}{2} + T_2^z\right) + \left(\frac{1}{2} + T_1^z\right)\left(\frac{1}{2} - T_2^z\right)\right]\left(\frac{3}{4} + \mathbf{S}_1 \cdot \mathbf{S}_2\right)$$

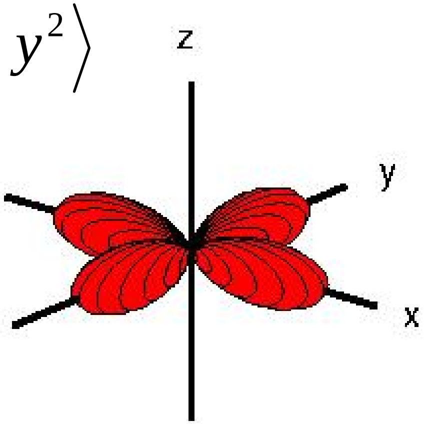
Isospin operator for e_g-orbitals

$|3z^2 - r^2\rangle$



$$T^z = +\frac{1}{2}$$

$|x^2 - y^2\rangle$

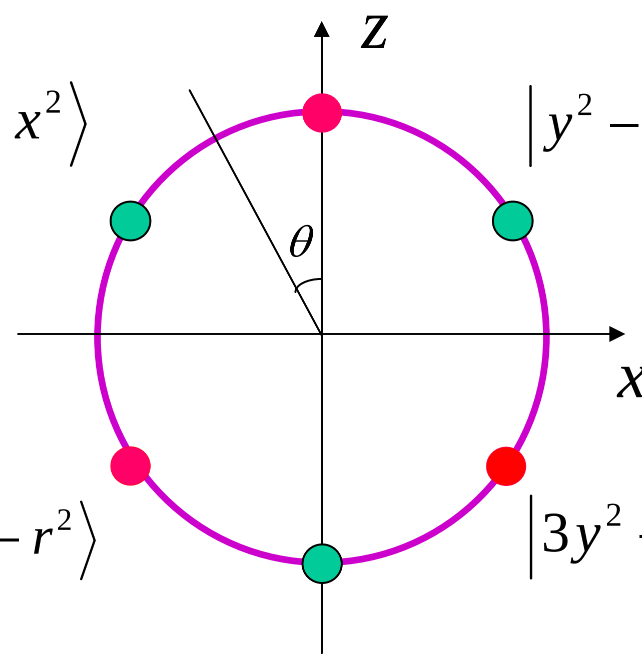


$$T^z = -\frac{1}{2}$$

$$\cos\frac{\theta}{2}|3z^2 - r^2\rangle + \sin\frac{\theta}{2}|x^2 - y^2\rangle$$

$|3z^2 - r^2\rangle$

$|z^2 - x^2\rangle$ $|y^2 - z^2\rangle$



$|3x^2 - r^2\rangle$ $|3y^2 - r^2\rangle$

$|x^2 - y^2\rangle$

I-operators

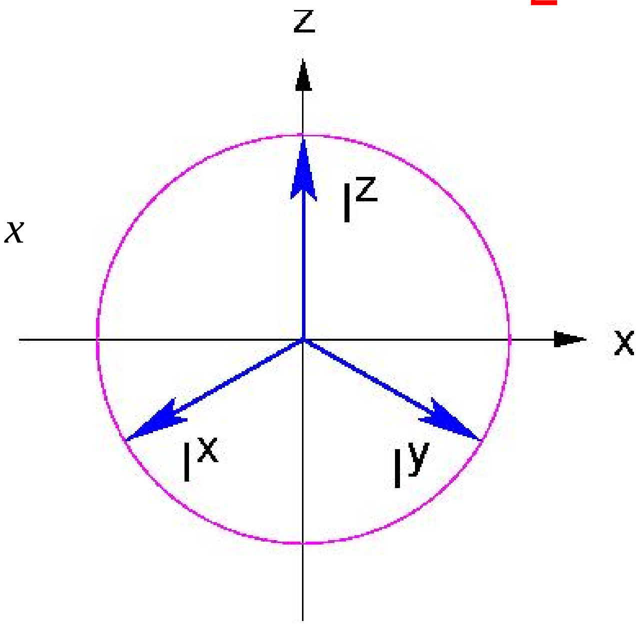
$$T^z = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$I^z = T^z$$

$$\left|3z^2 - r^2\right\rangle \quad I^z = +\frac{1}{2}$$

$$\left|x^2 - y^2\right\rangle \quad I^z = -\frac{1}{2}$$

$$T^x = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$



$$I^x = -\frac{1}{2}T^z - \frac{\sqrt{3}}{2}T^x$$

$$\left|3x^2 - r^2\right\rangle \quad I^x = +\frac{1}{2}$$

$$\left|y^2 - z^2\right\rangle \quad I^x = -\frac{1}{2}$$

$$I^y = -\frac{1}{2}T^z + \frac{\sqrt{3}}{2}T^x$$

$$\left|3y^2 - r^2\right\rangle \quad I^y = +\frac{1}{2}$$

$$\left|z^2 - x^2\right\rangle \quad I^y = -\frac{1}{2}$$

$$I^x + I^y + I^z = 0$$

Kugel-Khomskii Hamiltonian

*K. I. Kugel & D. I. Khomskii, Sov. Phys. JETP **37**, 725 (1973)*

Exchange in x and y directions: $T^z \rightarrow I^x \text{ and } I^y$

$$H_{AFM} = J_1 \sum_{j,a} \left(\frac{1}{2} + I_j^a \right) \left(\frac{1}{2} + I_{j+a}^a \right) \left(\mathbf{S}_j \cdot \mathbf{S}_{j+a} - \frac{1}{4} \right)$$

$$H_{FM} = -J_2 \sum_{j,a} \left(\frac{1}{4} - I_j^a I_{j+a}^a \right) \left(\mathbf{S}_j \cdot \mathbf{S}_{j+a} + \frac{3}{4} \right)$$

- Orbital occupation is not conserved
  orbitals can fluctuate like spins

- Orbital interactions are anisotropic

Infinite degeneracy for $J_H = 0$

Energy of classical AFM is independent of orbital states

$$E = \frac{4t^2}{U}\sum_{j,a}\left(\frac{1}{2}+I_j^a\right)\left(\frac{1}{2}+I_{j+a}^a\right)\left(\mathbf{S}_j\cdot\mathbf{S}_{j+a}-\frac{1}{4}\right)-\frac{2t^2}{U}\sum_{j,a}\left(\frac{1}{4}-I_j^a I_{j+a}^a\right)$$

Classical spins: $\mathbf{S}_1\cdot\mathbf{S}_2 = -\frac{1}{4}$ $\quad$ $\boxed{E = -\frac{3t^2}{U}N}$

- Spin-orbital liquid *L.F. Feiner et al Phys. Rev. Lett.* ***78****, 2799 (1997)*

- Quasi-one-dimensional magnet

G. Khaliullin & V. Oudovenko Phys. Rev. B 56, R14243 (1997)

Energy gain on spin fluctuations $\quad T_1^z, T_2^z \approx \frac{1}{2} \quad \mathbf{S}_1\cdot\mathbf{S}_2 \approx -\frac{3}{4}$

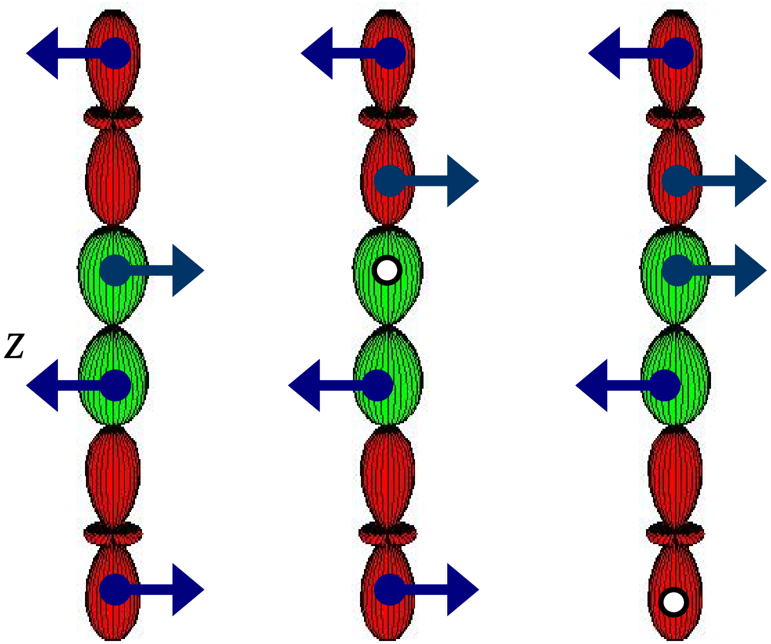
Superexchange

Effective dd-hoping

$$t = \frac{t_{pd}^{2}}{\Delta}$$

$d_{3z^2-r^2}$

p_z



$d_{3z^2-r^2}$

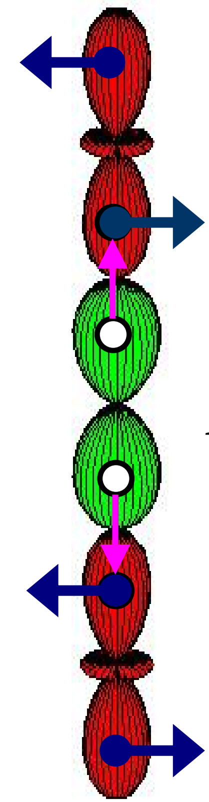
charge transfer energy Δ

Intermediate state with 2 oxygen holes

correction to exchange constant

$$\delta J = \frac{8 t_{pd}^{4}}{\Delta^{2}(2\Delta + U_p)}$$

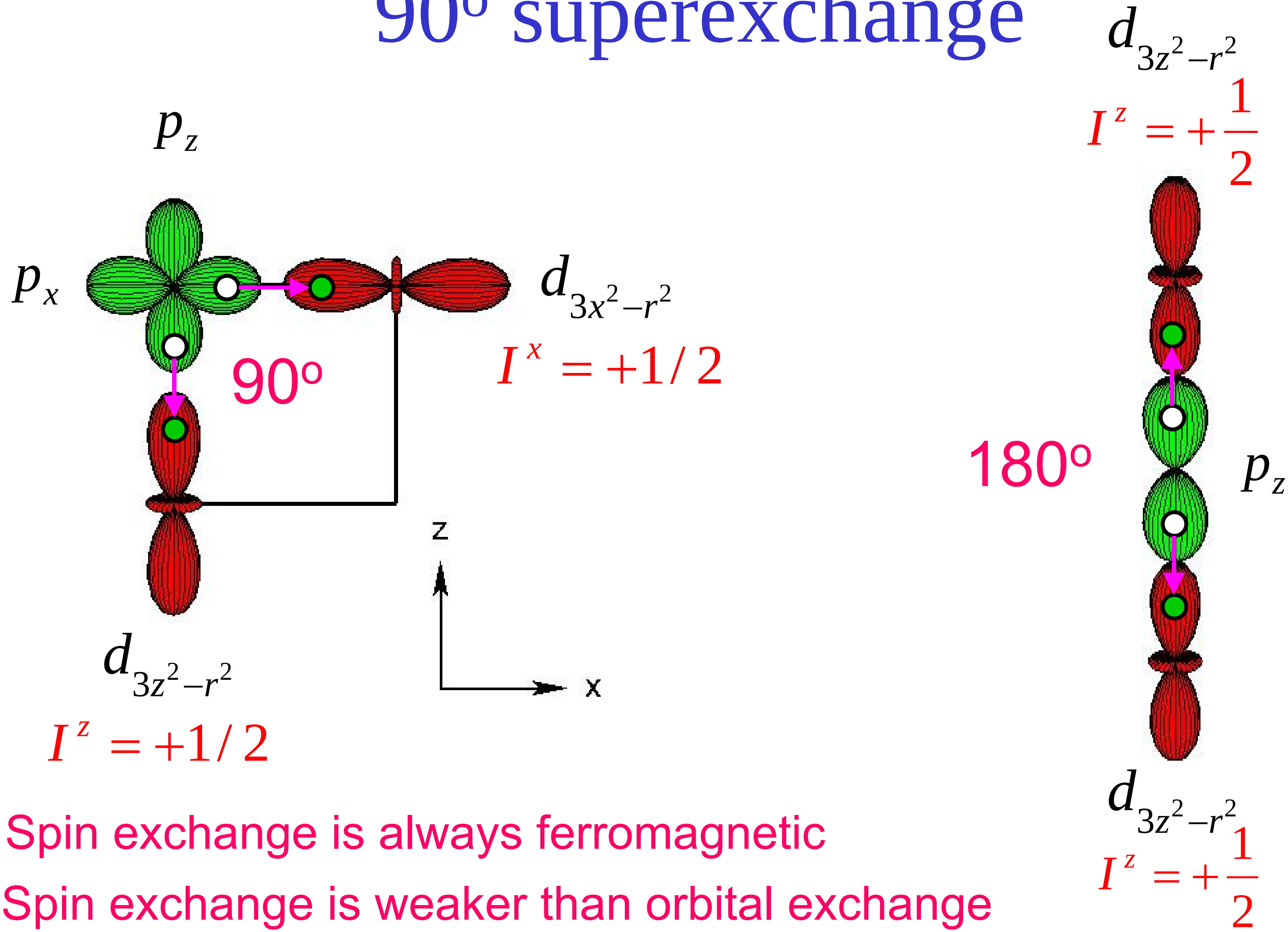
$d_{3z^2-r^2}$



p_z

$d_{3z^2-r^2}$

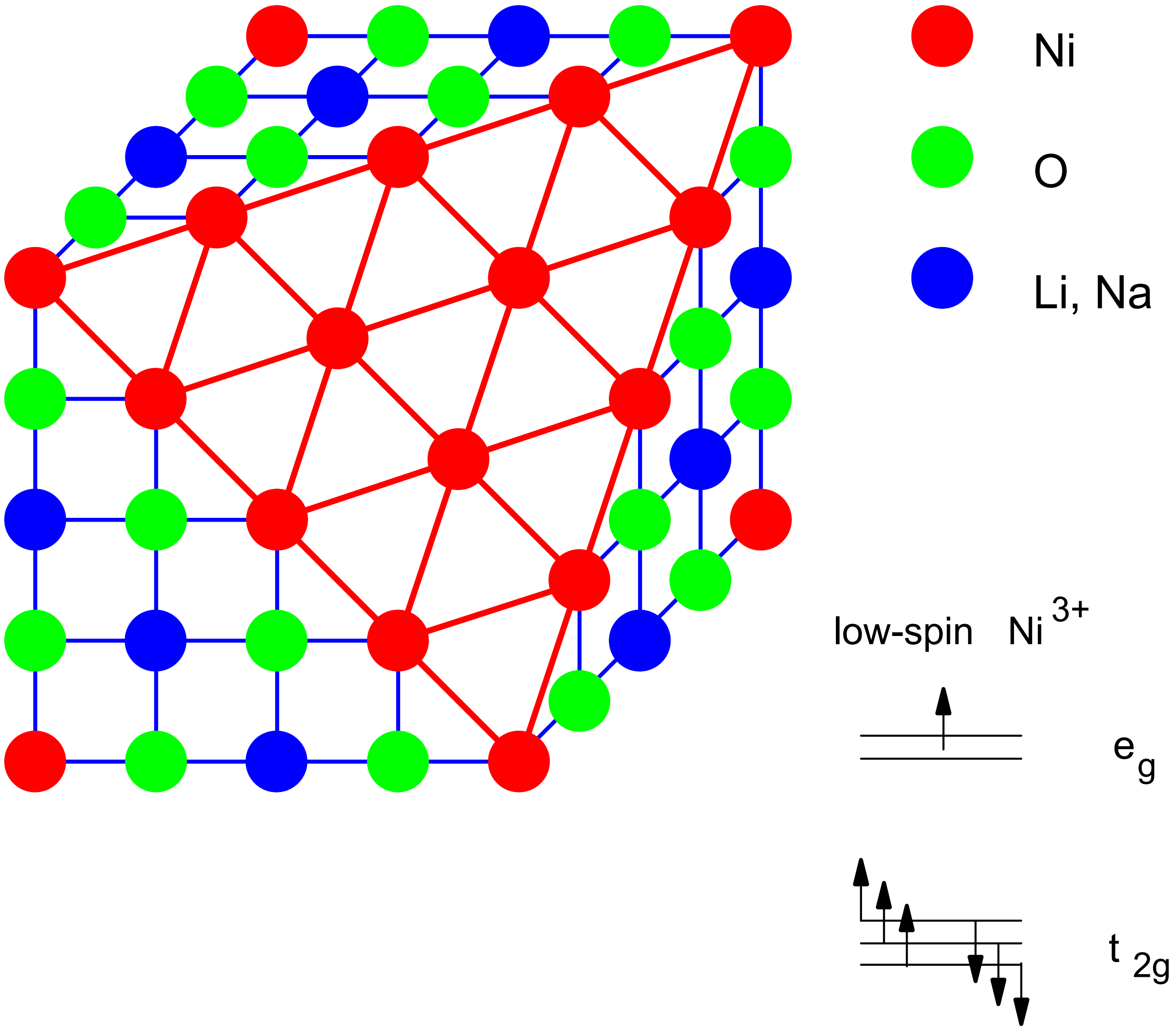
90° superexchange



Spin exchange is always ferromagnetic

Spin exchange is weaker than orbital exchange

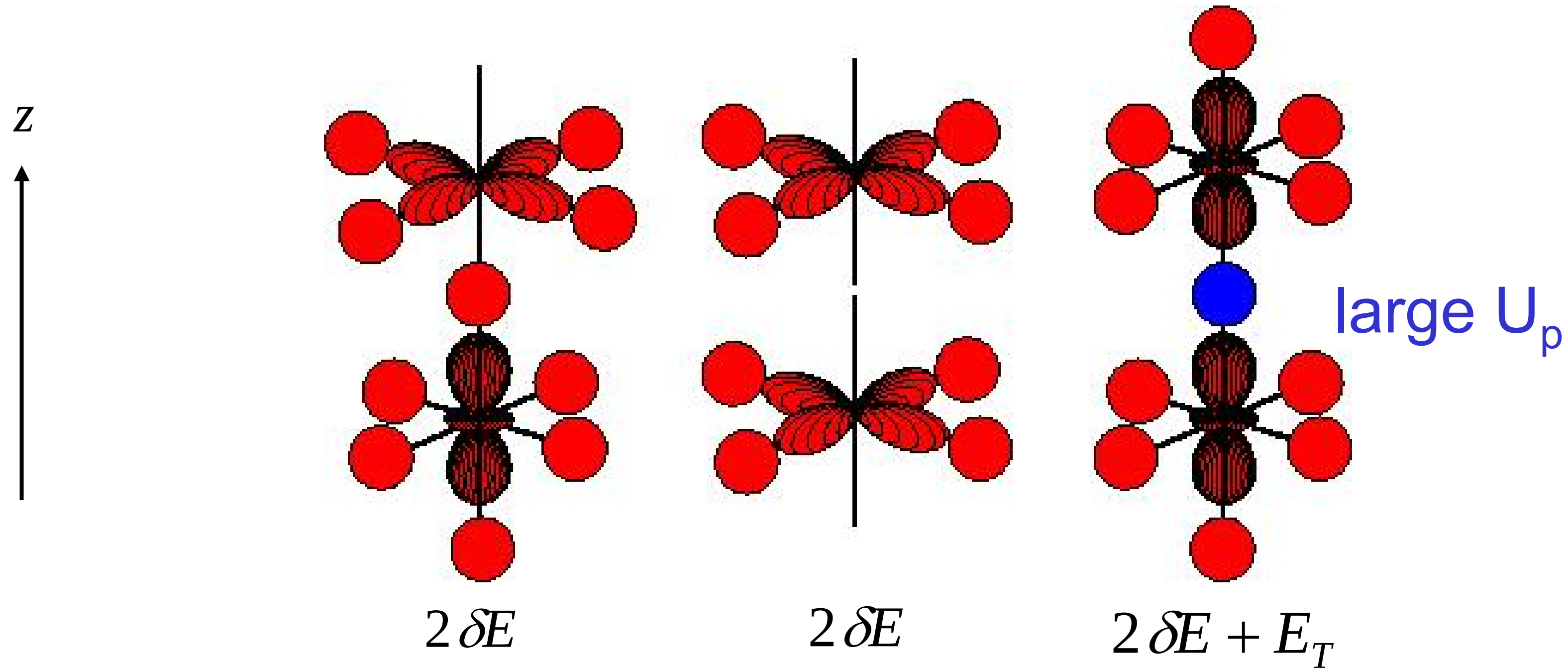
$NaNiO_2$



Orbital Casimir effect

(spin-independent exchange)

*M.M. & D. Khomskii, PRL **89**, 227203 (2002)*



Holes

$$H_T = +\frac{2t_{pd}^4}{\Delta^3}\left(\frac{1}{2}+T_1^z\right)\left(\frac{1}{2}+T_2^z\right)$$

Electrons

$$H_T = +\frac{2t_{pd}^4}{\Delta^3}\left(\frac{3}{2}-T_1^z\right)\left(\frac{3}{2}-T_2^z\right)$$

e_g-orbital compass models

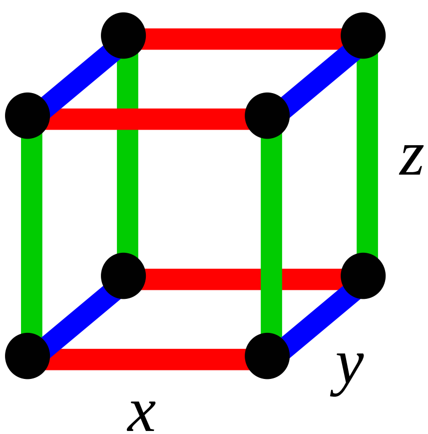
*M.M. & D. Khomskii, PRL **92**,167201 (2004).*

2 orbitals 3 types of bonds

180^o-exchange

cubic

$KCuF_3$



$$I_1^z I_2^z$$

$$I_1^y I_2^y$$

$$I_1^x I_2^x$$

$$I^x + I^y + I^z = 0$$

90^o-exchange

triangular

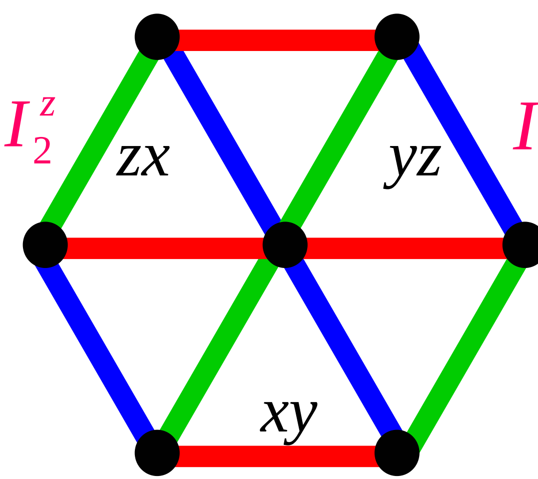
$LiNiO_2$

pyrochlore

$ZnMn_2O_4$

$$I_1^z I_2^x + I_1^x I_2^z$$

$$I_1^y I_2^z + I_1^z I_2^y$$

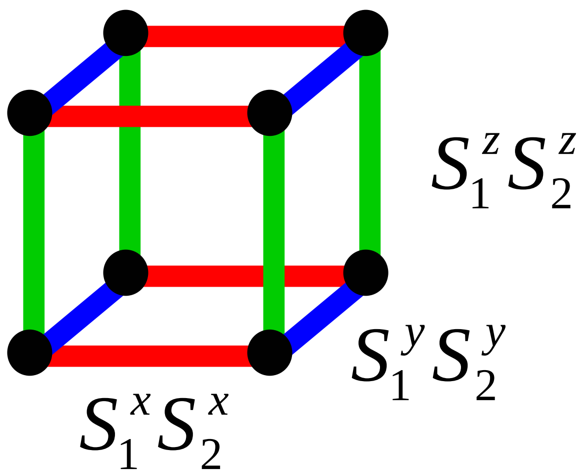


$$I_1^x I_2^y + I_1^y I_2^x$$

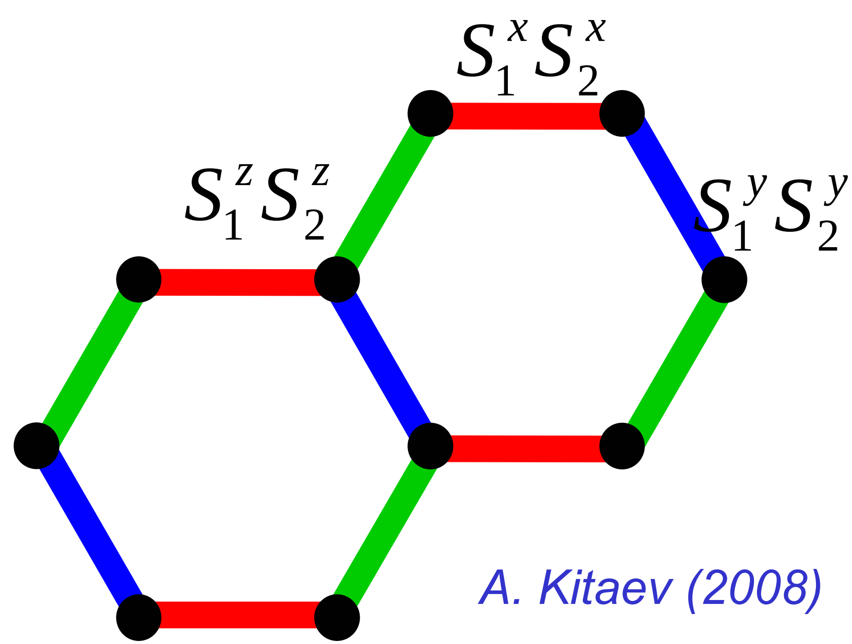
Spin compass models

$$H = J\sum_n \left(S_n^x S_{n+x}^x + S_n^y S_{n+y}^y + S_n^z S_{n+z}^z \right)$$

cubic

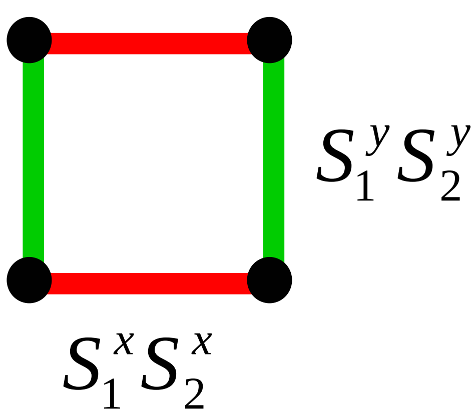


honeycomb

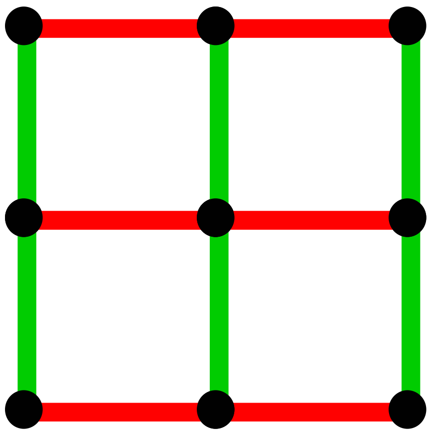


A. Kitaev (2008)

square



2D compass model



$$H = J \sum_n \left(\sigma_n^x \sigma_{n+x}^x + \sigma_n^y \sigma_{n+y}^y \right)$$

*A. Mishra et al, PRL **93**, 207201 (2004)*

*Z. Nussinov & E. Fradkin, PRB **71**, 195120 (2005)*

dual to *p+ip* model of SC arrays

Z_2 symmetries

$$U_x = \prod_{n_x} \sigma^y (n_x, n_y) \qquad \sigma_n^x \to -\sigma_n^x$$ on any horizontal line

$$U_y = \prod_{n_y} \sigma^x (n_x, n_y) \qquad \sigma_n^y \to -\sigma_n^y$$ on any vertical line

Extensive ground state degeneracy

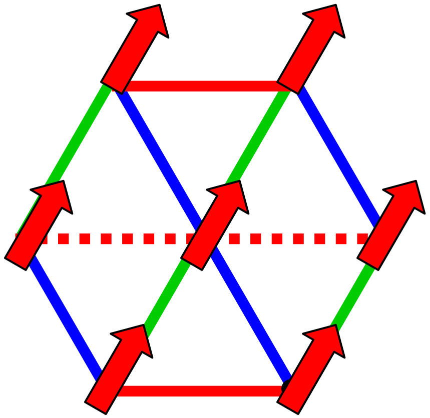
Nematic order $\left\langle \sigma_n^x \sigma_{n+x}^x - \sigma_n^y \sigma_{n+y}^y \right\rangle$

Symmetries of classical orbital models

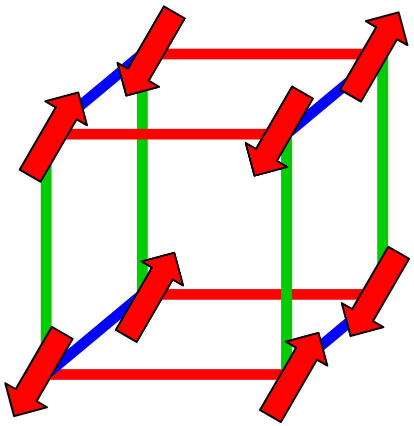
Triangular, pyrochlore
ferroobital

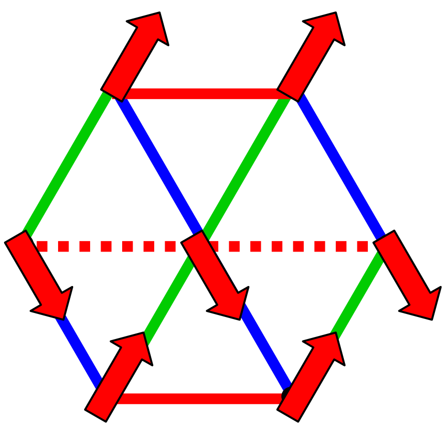
Cubic
antiferroorbital

Rotational isospin invariance



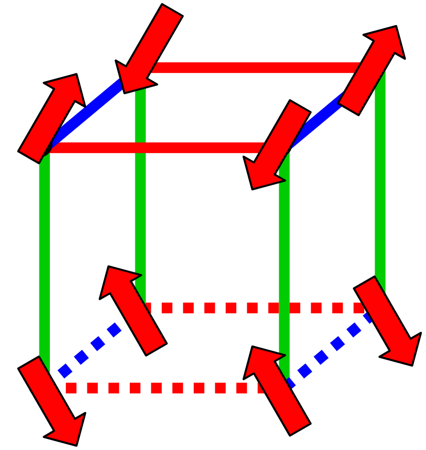
$$\cos\frac{\theta}{2}\left|3z^2 - r^2\right\rangle + \sin\frac{\theta}{2}\left|x^2 - y^2\right\rangle$$





$$T^x \to -T^x$$

$$T^y \to -T^y$$

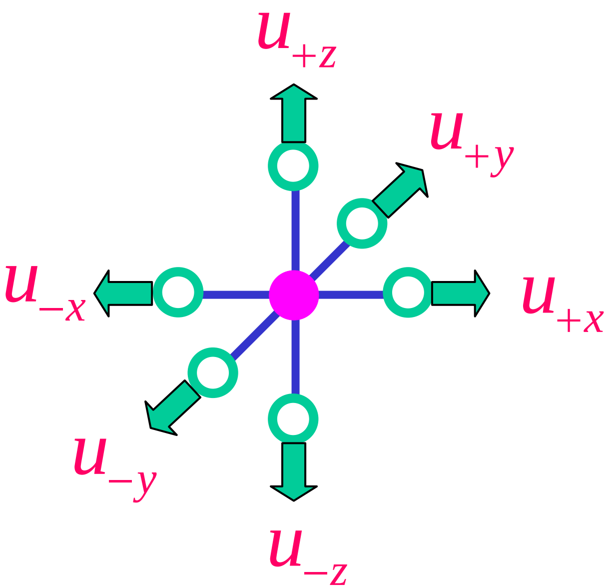


destroyed by fluctuations

Orbital and magnetic ordering in e_g-systems

material	T_{OO} (K)	T_M (K)	JT ion
$LaMnO_3$	780	140	Mn^{3+} d^4
$KCrF_3$	923	46	Cr^{2+} d^4
$NaNiO_2$	480	20	Ni^{3+} d^7
$KCuF_3$	$T_{melting}$	38/22	Cu^{2+} d^9

Octahedron distortions



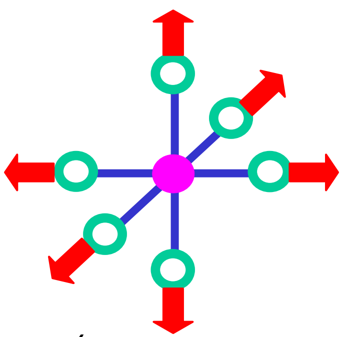
3 ferroelectric modes

$$w_a = \frac{1}{\sqrt{2}}\left(u_{+a} - u_{-a}\right) \qquad a = x, y, z$$

3 non-ferroelectric modes

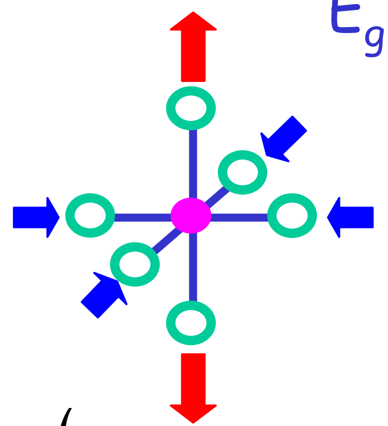
$$\upsilon_a = \frac{1}{\sqrt{2}}\left(u_{+a} + u_{-a}\right)$$

breathing mode

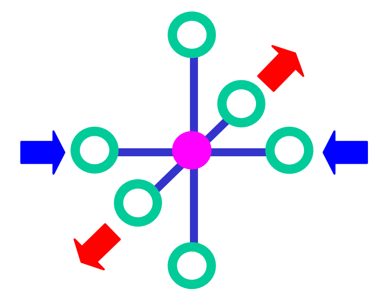


$$Q_1 = \frac{\left(\upsilon_x + \upsilon_y + \upsilon_z\right)}{\sqrt{3}}$$

E_g Jahn-Teller modes



$$Q_z = \frac{\left(2\upsilon_z - \upsilon_x - \upsilon_y\right)}{\sqrt{6}}$$



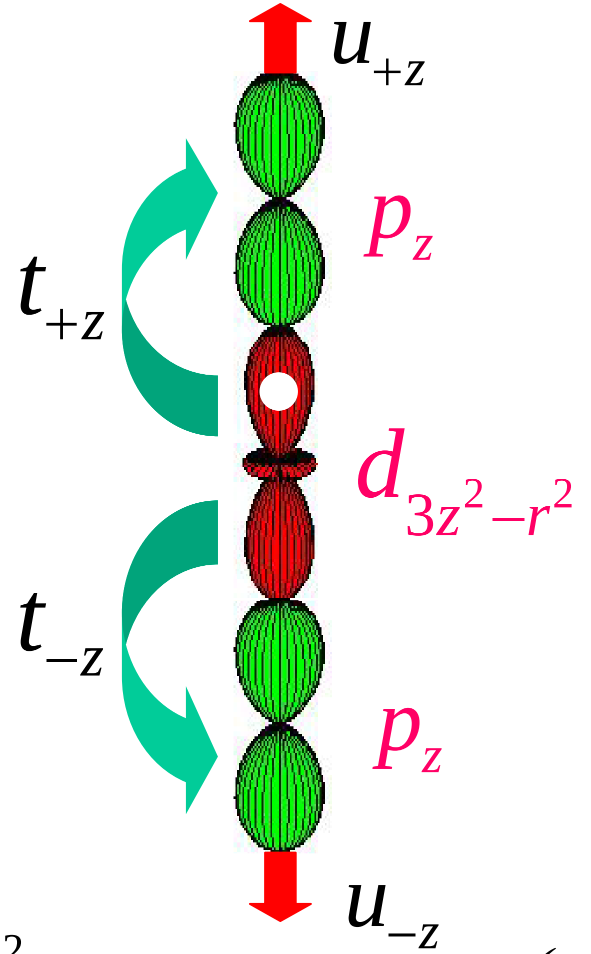
$$Q_x = \frac{\left(\upsilon_y - \upsilon_x\right)}{\sqrt{2}}$$

Electron-lattice interaction

Hopping amplitudes along z axis

$$t_{+z} = t_{pd}\left[1-\alpha u_{+z}\right]$$

$$t_{-z} = t_{pd}\left[1-\alpha u_{-z}\right]$$



Energy gain

$$\Delta E_z = -\frac{\left(t_{+z}^2 + t_{-z}^2\right)}{\Delta}\left(\frac{1}{2}+T^z\right) \approx -2\frac{t_{pd}^{\ 2}}{\Delta}\left[1-\alpha\left(u_{+z}+u_{-z}\right)\right]\left(\frac{1}{2}+T^z\right)$$

Electron-lattice interaction

Energy gain due to hopping in all three directions

$$\Delta E = -2\frac{t_{pd}^2}{\Delta}\sum_{a=x,y,z}\left[1-\sqrt{2}\alpha\upsilon_a\right]\left(\frac{1}{2}+I^a\right)$$

In absence of distortion energy is independent of orbital occupation

$$I^x + I^y + I^z = 0$$

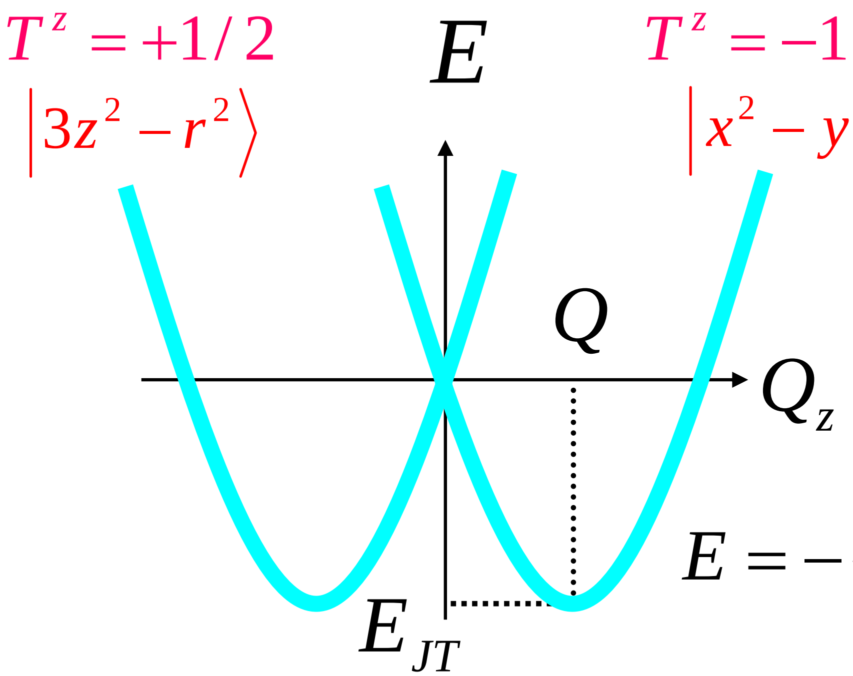
Jahn-Teller coupling

$$\Delta E = g\left[T^z Q_z + T^x Q_x\right] + \frac{g}{\sqrt{2}} Q_1 \qquad g = 2\sqrt{2}\frac{\alpha t_{pd}^2}{\Delta}$$

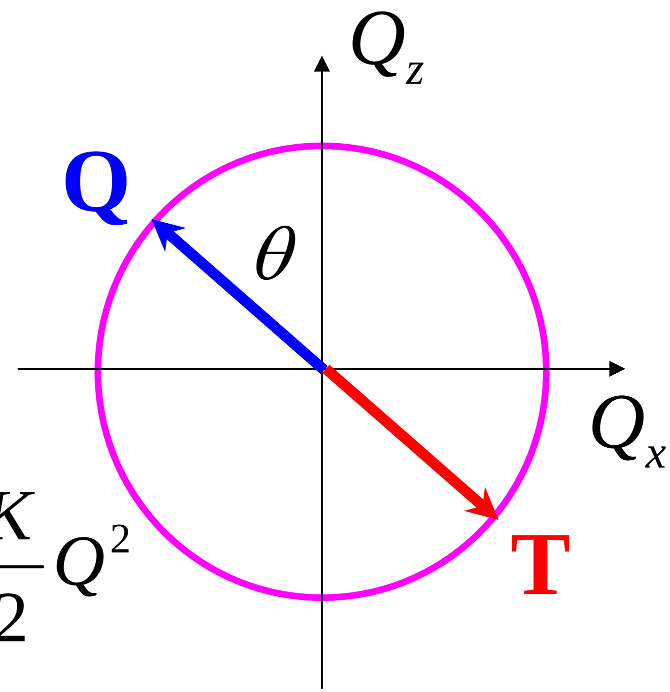
Jahn-Teller effect

JT coupling | harmonic lattice energy

$$E = g\left[T^z Q_z + T^x Q_x\right] + \frac{K}{2}\left(Q_z^2 + Q_x^2\right)$$

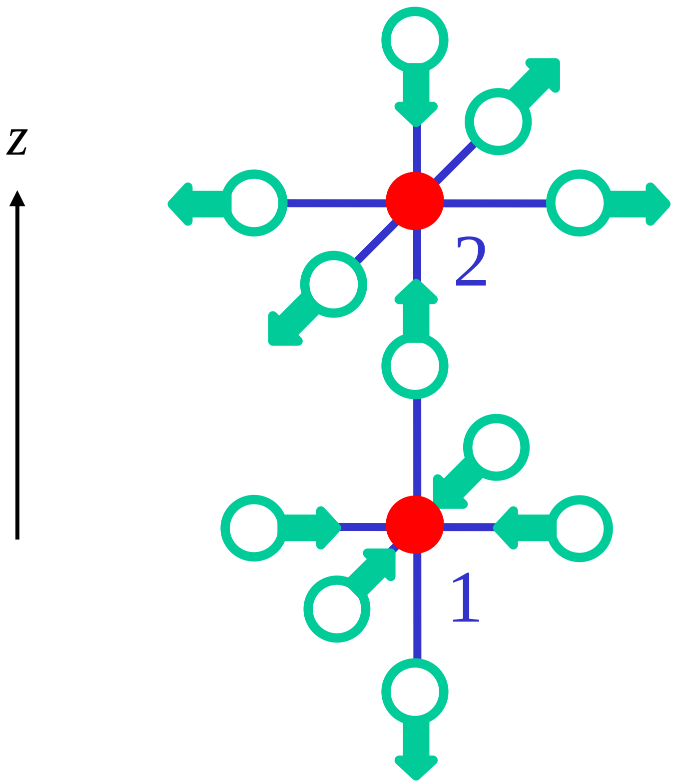


$$E = -\frac{g}{2} Q + \frac{K}{2} Q^2$$



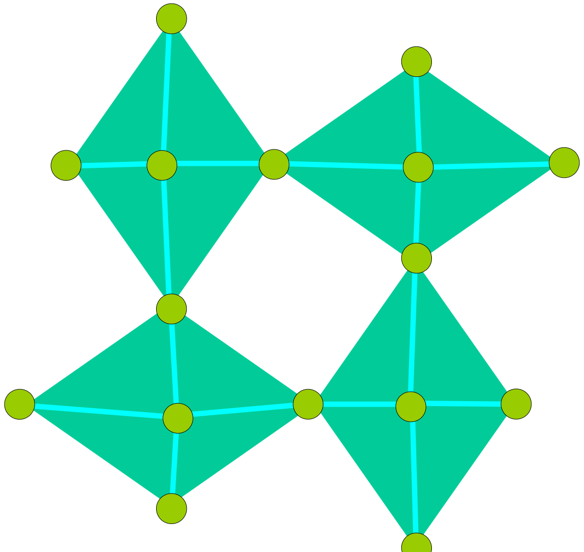
$$Q = \frac{g}{2K} \qquad E_{JT} = \frac{g^2}{8K} \qquad |\theta\rangle = \cos\frac{\theta}{2}|x^2 - y^2\rangle - \sin\frac{\theta}{2}|3z^2 - r^2\rangle$$

Cooperative Jahn-Teller effect

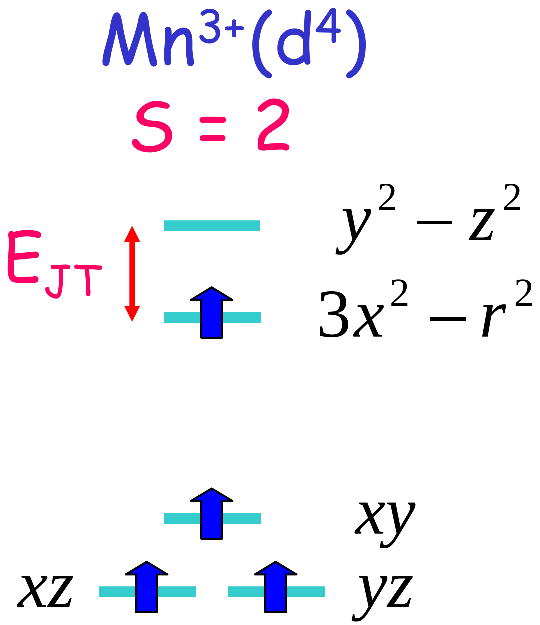


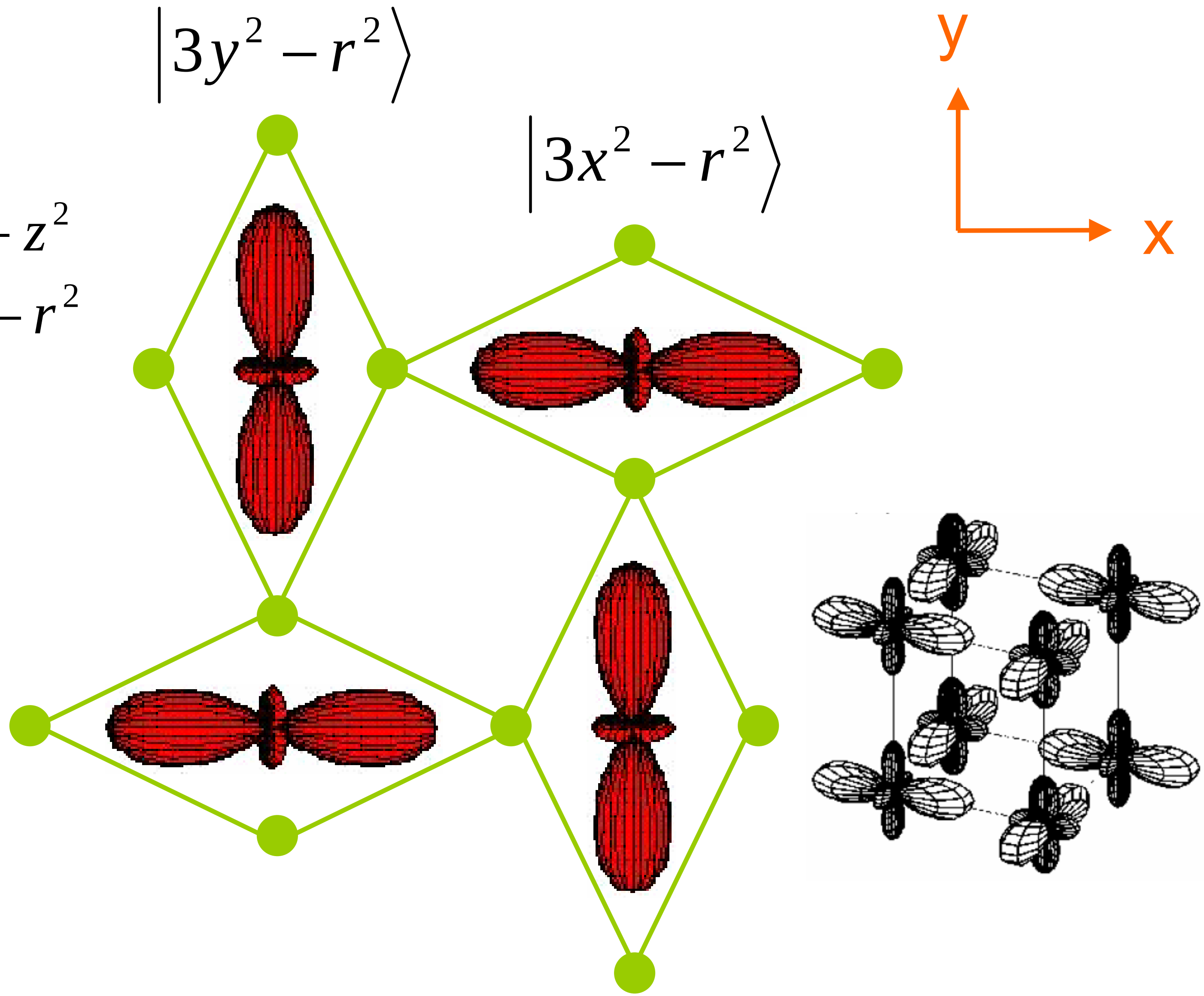
$$H_{12} = \sum_{i=1,2} \left[g T_i^z Q_{3i} + \frac{K Q_{3i}^2}{2} \right]$$

$$H_{eff} = \frac{2g^2}{3K} T_1^z T_2^z$$



$LaMnO_3$

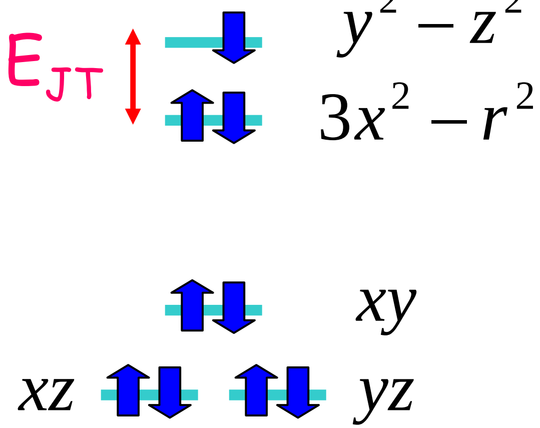




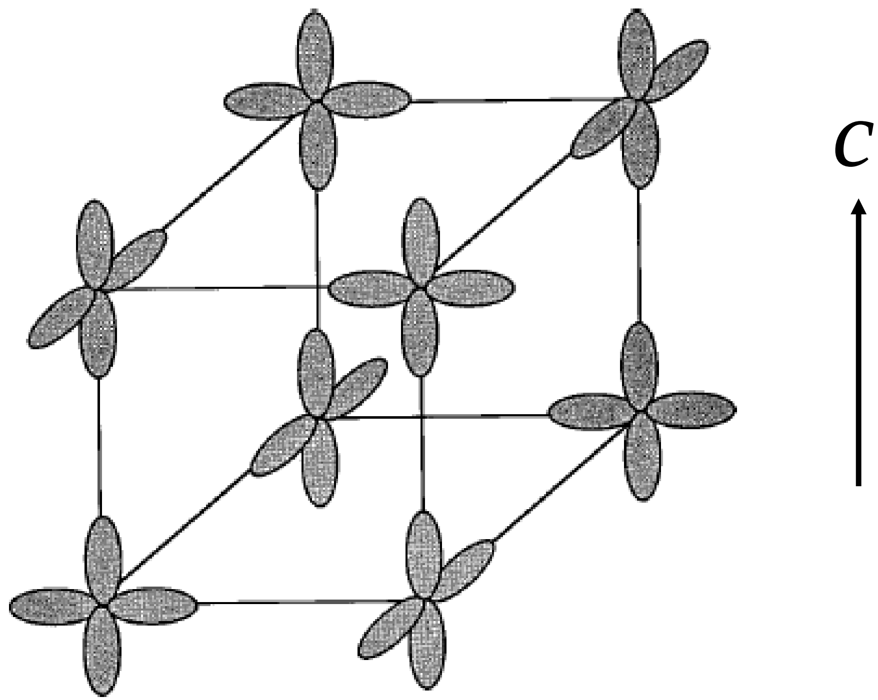
$KCuF_3$

Cu^{2+} (d^9)

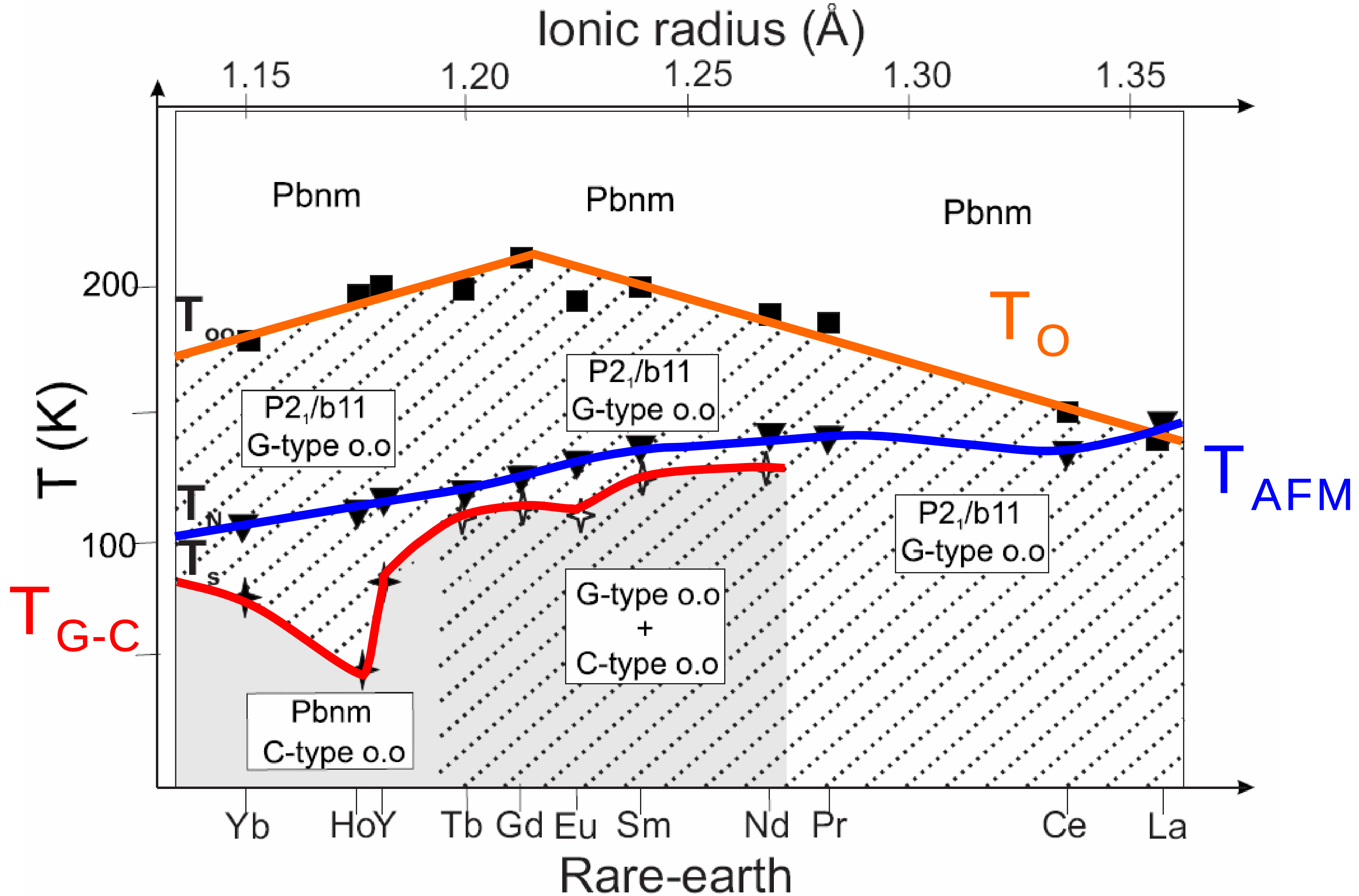
$S = 1/2$



$|z^2 - x^2\rangle$ $|y^2 - z^2\rangle$



RVO_3



Ionic radius (Å)
1.15
1.20
1.25
1.30
1.35
200
100
T (K)
Pbnm
Pbnm
Pbnm
T_{oo}
T_N
T_s
T_{G-C}
T_O
T_{AFM}
$P2_1/b11$
G-type o.o
$P2_1/b11$
G-type o.o
$P2_1/b11$
G-type o.o
G-type o.o
+
C-type o.o
Pbnm
C-type o.o
Yb
Ho
Y
Tb
Gd
Eu
Sm
Nd
Pr
Ce
La
Rare-earth

G-C transition in YVO_3

V^{3+} (d^2)

S = 1

yz / *xz*

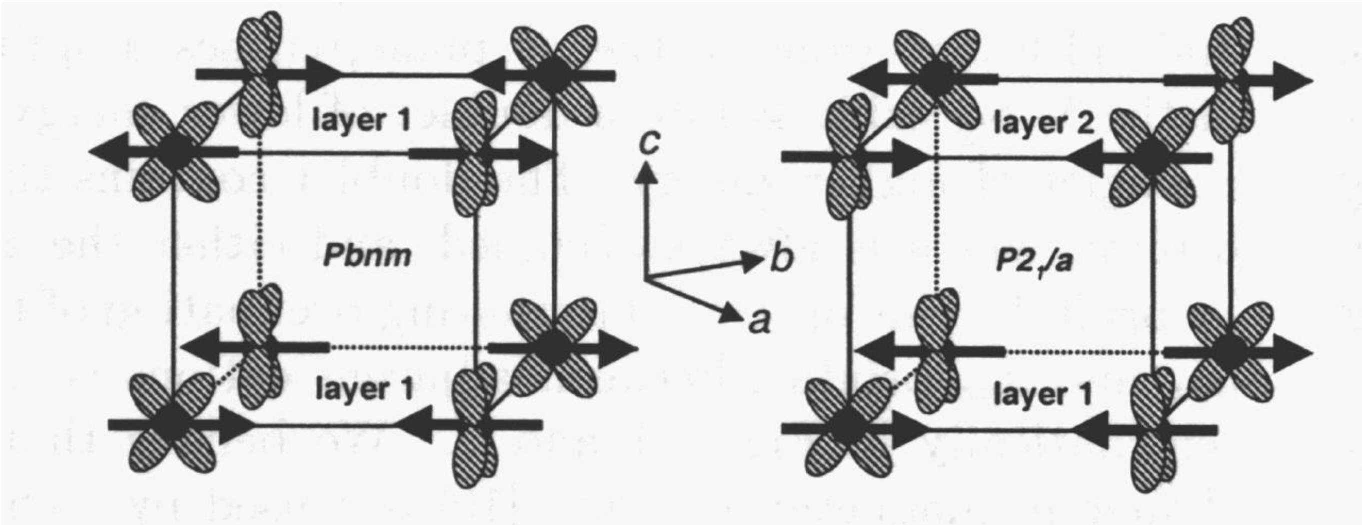
xz / *yz*

xy

occupied on all sites

C-type orbital
G-type magnetic

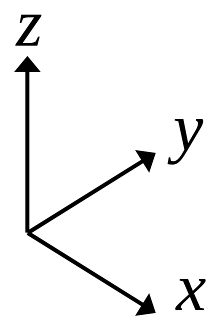
G-type orbital
C-type magnetic



T < 77K

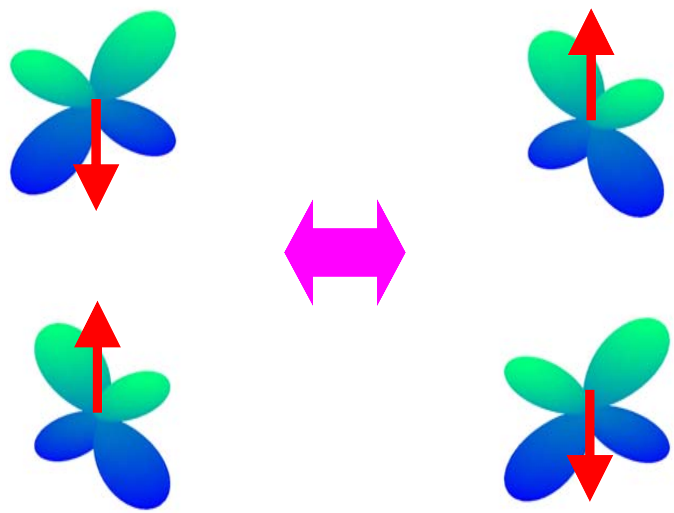
77K < T < 116K

180°-exchange of t_{2g}-electrons



$RTiO_3$, RVO_3

$|yz\rangle = |\downarrow\rangle$ $\quad$ $|xz\rangle = |\uparrow\rangle$



$|xz\rangle = |\uparrow\rangle$ $\quad$ $|yz\rangle = |\downarrow\rangle$

Spin-orbital exchange ($J_H = 0$)

$$H = -\frac{2t^2}{U}\left(1 - T_{12}S_{12}\right)$$

Spin-exchange operator

$$S_{12} = 2\left(\mathbf{S}_1 \cdot \mathbf{S}_2\right) + \frac{1}{2}$$

$$|\uparrow\rangle_1 |\downarrow\rangle_2 \leftrightarrow |\downarrow\rangle_1 |\uparrow\rangle_2$$

Orbital exchange operator
(depends on bond direction)

$$T_{12} = 2\left(\mathbf{T}_1 \cdot \mathbf{T}_2\right) + \frac{1}{2}$$

$$|xz\rangle_1 |yz\rangle_2 \leftrightarrow |yz\rangle_1 |xz\rangle_2$$

Strong ferromagnetic exchange

$$H = \frac{2t^2}{U}\left(2(\mathbf{S}_1 \cdot \mathbf{S}_2) + \frac{1}{2}\right)\left(2(\mathbf{T}_1 \cdot \mathbf{T}_2) + \frac{1}{2}\right)$$

AFO Orbital singlet T = 0 $\leftrightarrow$ Spin triplet S = 1 **FM**

FO Orbital triplet T = 1 $\leftrightarrow$ Spin singlet S = 0 **AFM**

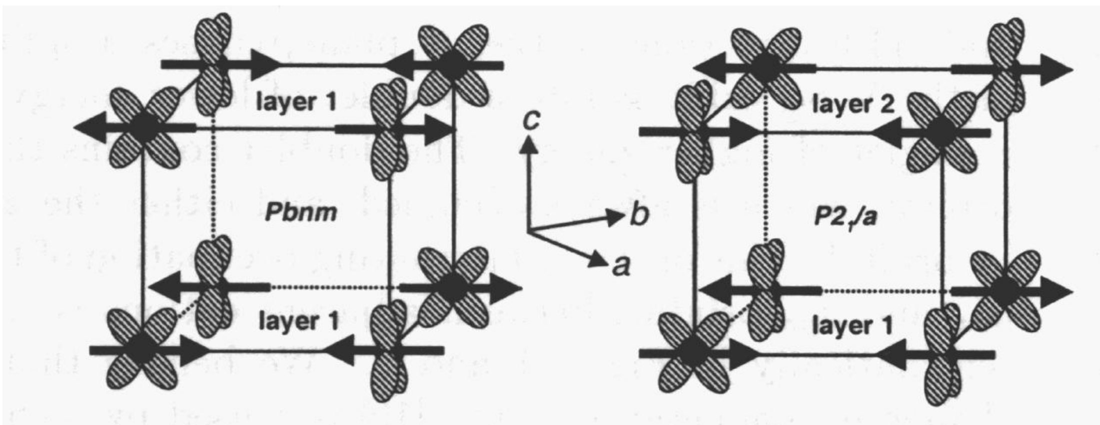
Pauli principle: $\Psi_{21} = -\Psi_{12}$

$$(-)^{S+1}(-)^{T+1} = -1$$

G. Khaliullin et al PRL 86, 3879 (2001)
P. Horsch et al PRL 91, 257203 (2003)

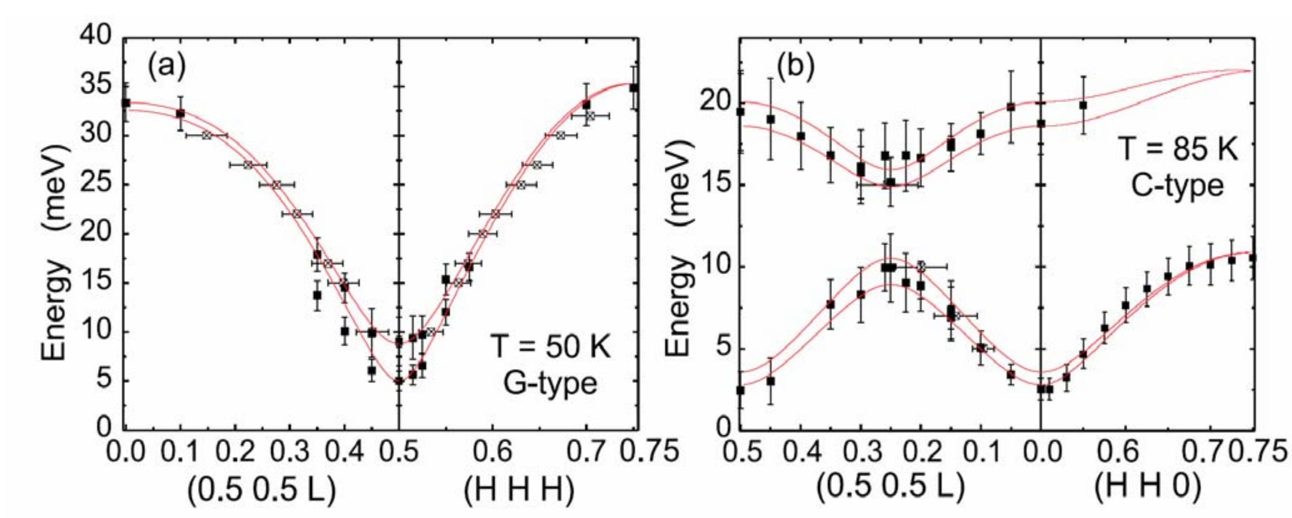
Orbital dimerization in YVO_3

G-type | C-type



G. Blake et al.
PRL **87**, 245501 (2001)

T < 77K | 77K < T < 116K



C. Ulrich et al.
PRL **89**, 167202 (2002)

$$J_{ab} = +2.6\,\mathrm{meV}$$

$$\bar{J}_c = -3.1\,\mathrm{meV}$$

$$J_c = \bar{J}_c(1 \pm 0.35)$$

Beyond AKG rules

For $J_H = 0$ the spin-orbital model has SU(4) symmetry

$$H = \frac{2t^2}{U}\left(2\left(\mathbf{S}_1 \cdot \mathbf{S}_2\right) + \frac{1}{2}\right)\left(2\left(\mathbf{T}_1 \cdot \mathbf{T}_2\right) + \frac{1}{2}\right)$$

15 generators: $S^a,\ T^a,\ S^a T^b$

*B. Sutherland, PRB **12**, 3795 (1975); Y.Q. Li et al, PRL **81**, 3527 (1998);*
*B. Frischmuth et al, PRL **82**, 835 (1999); F. Mila et al, PRL **82**, 3697 (1999)*

Coupled fluctuations of orbitals and spins are large,
MF factorization does not work

$$\left\langle \left(\mathbf{S}_1 \cdot \mathbf{S}_2\right)\left(\mathbf{T}_1 \cdot \mathbf{T}_2\right)\right\rangle \neq \left(\mathbf{S}_1 \cdot \mathbf{S}_2\right)\left\langle\left(\mathbf{T}_1 \cdot \mathbf{T}_2\right)\right\rangle + \left\langle\left(\mathbf{S}_1 \cdot \mathbf{S}_2\right)\right\rangle\left(\mathbf{T}_1 \cdot \mathbf{T}_2\right) - \left\langle\left(\mathbf{S}_1 \cdot \mathbf{S}_2\right)\right\rangle\left\langle\left(\mathbf{T}_1 \cdot \mathbf{T}_2\right)\right\rangle$$

*A. Oleś et al JMMM **272**, 440 (2004)*

Conclusions

- Anisotropy of spin-orbital exchange frustrates orbital ordering
- Jahn-Teller instability quenches orbital fluctuations in e_g systems
- Coupled spin and orbital fluctuations may play a role in t_{2g} systems
- Beautiful models