Orbital Ordering in materials

Eva Pavarini

Institute for Advanced Simulation
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orbital physics

Review—Orbital Physics: Glorious Past, Bright Future

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II. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany

Daniel Khomskii

Transition metal (TM) compounds present a very big class of materials with quite diverse properties. There are insulators, metals and systems with insulator–metal transitions among them; most magnetic systems are TM compounds; there are also (high-T_c) superconductors among them. Their very rich properties are largely determined by the strong interplay of different degrees of freedom: charge; spin; orbital; lattice. Orbital effects play a very important role in these systems—and not only in them! The study of this field, initiated by Goodenough almost 70 years ago, turned out to be very fruitful and produced a lot of important results. In this short review I discuss the basics of orbital physics and summarize the main achievements in this big field, in which Goodenough played a pivotal role, and which are nowadays widely used to explain many properties of TM compounds. In the main part of the text I discuss novel developments and perspectives in orbital physics, which is still a very active field of research, constantly producing new surprises.

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strong Coulomb repulsion (the Hubbard U)

spin, charge, orbitals degrees of freedom

transition metal compounds: d orbitals

John Goodenough

Kugel-Khomskii model

Crystal structure and magnetic properties of substances with orbital degeneracy

K. I. Kugel' and D. I. Khomskiĭ
P. N. Lebedev Physics Institute
(Submitted November 13, 1972)
Zh. Eksp. Teor. Fiz. **64**, 1429-1439 (April 1973)

Exchange interaction in magnetic substances containing ions with orbital degeneracy is considered. It is shown that, among with spin ordering, superexchange also results in cooperative ordering of Jahn-Teller ion orbitals, which, generally speaking, occurs at a higher temperature and is accompanied by distortion of the lattice (which is a secondary effect here). Concrete studies are performed for substances with a perovskite structure ($KCuF_3$, $LaMnO_3$, MnF_3). The effective spin Hamiltonian is obtained for these substances and the properties of the ground state are investigated. The orbital and magnetic structures obtained in this way without taking into account interaction with the lattice are in accord with the structures observed experimentally. The approach employed also permits one to explain the strong anisotropy of the magnetic properties of these compounds and to obtain a reasonable estimate for the critical temperatures.

$KCuF_3$

$LaMnO_3$

ordering of orbitals with no distortion

degenerate e_g orbitals

KK super-exchange

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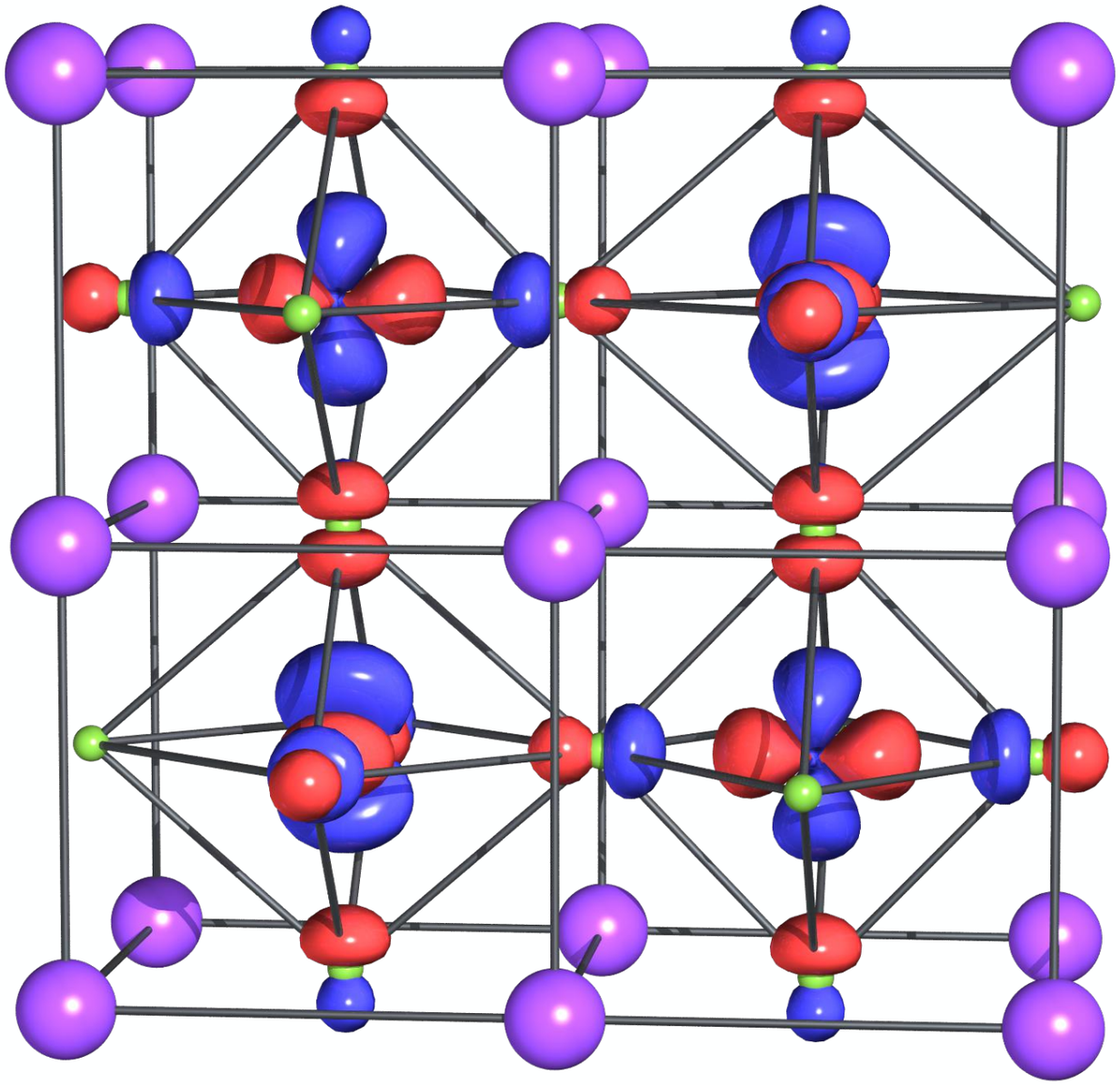
orbital ordering in $KCuF_3$



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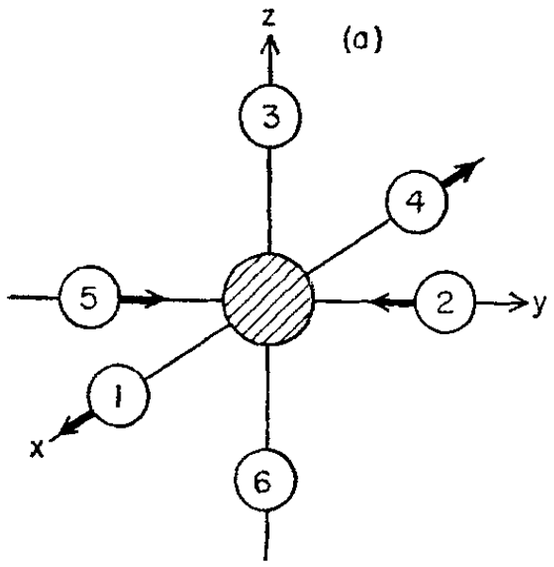
lattice distortions generates order



The Normal Mode
Q_2 (Q_2 >0)

Crystal Distortion in Magnetic Compounds

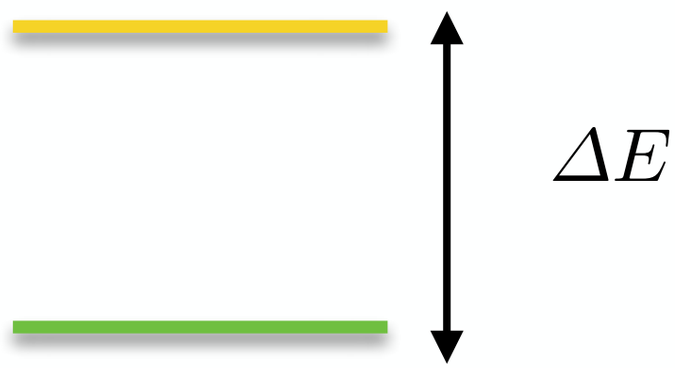
JUNJIRO KANAMORI*
Institute for the Study of Metals, University of Chicago, Chicago 37, Illinois

The crystal distortion which arises from the Jahn-Teller effect is discussed in several examples. In the case of compounds containing Cu^{2+} or Mn^{3+} at octahedral sites, the lowest orbital level of these ions is doubly degenerate in the undistorted structure, and there is no spin-orbit coupling in this level. It is shown that, introducing a fictitious spin to specify the degenerate orbital states, we can discuss the problem by analogy with the magnetic problems. The "ferromagnetic" and "antiferromagnetic" distortions are discussed in detail. The transition from the distorted to the undistorted structure is of the first kind for the former and of the second kind for the latter. Higher approximations are discussed briefly. In compounds like FeO, CoO, and $CuCr_2O_4$, the lowest orbital level is triply degenerate, and the spin-orbit coupling is present in this level. In this case the distortion is dependent on the magnitude of the spin-orbit coupling relative to the strength of the Jahn-Teller effect term. The distortion at absolute zero temperature and its temperature dependence are discussed.

J. Appl. Phys. 31, S14–S23 (1960)

electron-phonon coupling

static crystal-field splitting (symmetry lowering)



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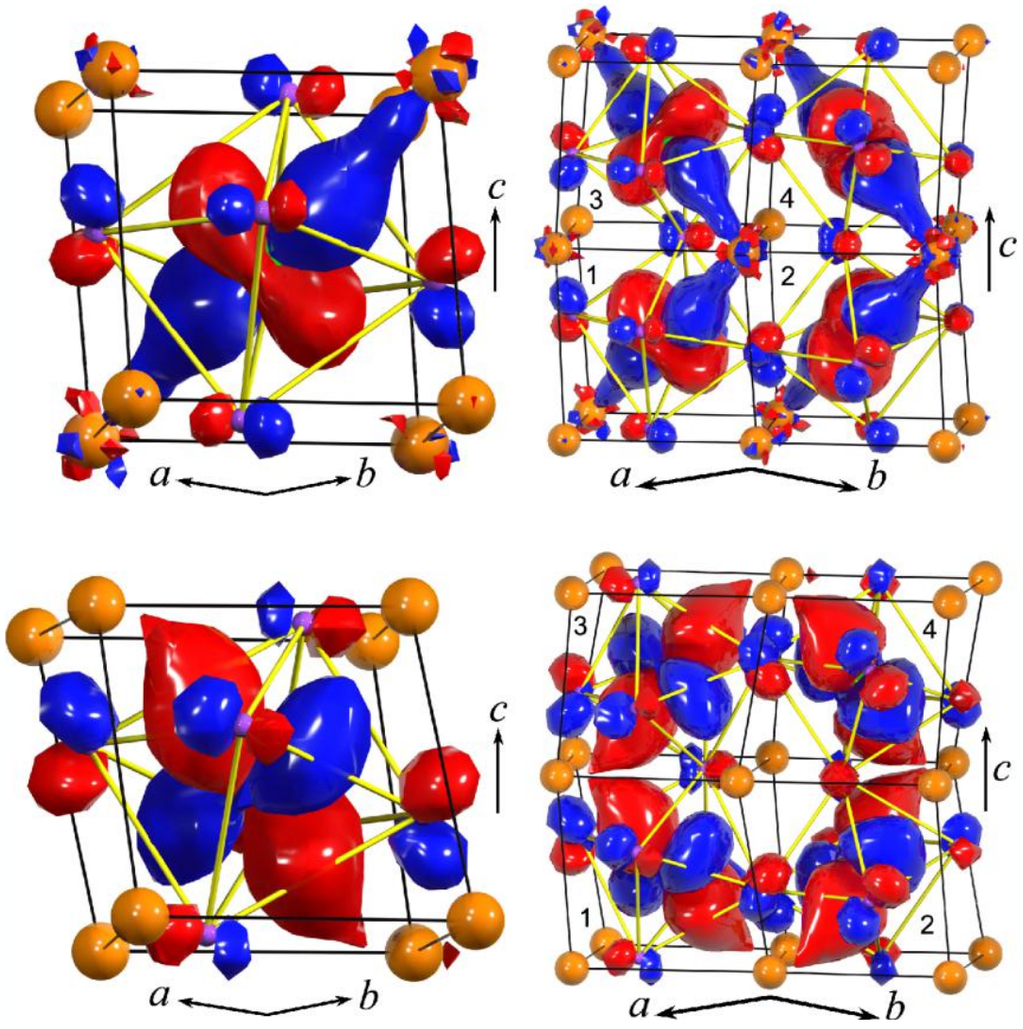
do we need a large crystal-field?

VOLUME 92, NUMBER 17 PHYSICAL REVIEW LETTERS week ending 30 APRIL 2004

Mott Transition and Suppression of Orbital Fluctuations in Orthorhombic $3d^1$ Perovskites

E. Pavarini,[1] S. Biermann,[2] A. Poteryaev,[3] A. I. Lichtenstein,[3] A. Georges,[2] and O. K. Andersen[4]

$LaTiO_3$



$YTiO_3$

t_{2g}^1

LDA+DMFT 770 K

Δ=200-300 meV

No! A 100 meV crystal-field is enough (W~3 eV)

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Orbital Ordering in Materials

aim of lecture

- introduce KK super-exchange and electron-phonon coupling mechanisms for orbital ordering
- explain how they operate in actual materials
- alternative mechanism in specific systems

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orbital ordering & orbital physics

CORRELATED ELECTRON SYSTEMS

REVIEW

Orbital Physics in Transition-Metal Oxides

Y. Tokura[1,2] and N. Nagaosa[1]

An electron in a solid, that is, bound to or nearly localized on the specific atomic site, has three attributes: charge, spin, and orbital. The orbital represents the shape of the electron cloud in solid. In transition-metal oxides with anisotropic-shaped d-orbital electrons, the Coulomb interaction between the electrons (strong electron correlation effect) is of importance for understanding their metal-insulator transitions and properties such as high-temperature superconductivity and colossal magnetoresistance. The orbital degree of freedom occasionally plays an important role in these phenomena, and its correlation and/or order-disorder transition causes a variety of phenomena through strong coupling with charge, spin, and lattice dynamics. An overview is given here on this "orbital physics," which will be a key concept for the science and technology of correlated electrons.

When more than two orbitals are involved, a variety of situations can be realized, and this quantum mechanical process depends on the orbitals (*4, 5*). In this way, the spin $\vec{S}$ and the orbital pseudospin $\vec{T}$ are coupled. In more general cases, the transfer integral t_{ij} depends on the direction of the bond ij and also on the pair of the two orbitals a, b = $(x^2 - y^2)$ or $(3z^2$ – of the well a transfe Mn at

VOLUME 85, NUMBER 18 PHYSICAL REVIEW LETTERS 30 OCTOBER 2000

Orbital Liquid in Three-Dimensional Mott Insulator: $LaTiO_3$

G. Khaliullin[1,2] and S. Maekawa[2]

[1]*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*
[2]*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*

(Received 5 June 2000)

We present a theory of spin and orbital states in Mott insulator $LaTiO_3$. The spin-orbital superexchange interaction between $d^1(t_{2g})$ ions in cubic crystal suffers from a pathological degeneracy of orbital states at the classical level. Quantum effects remove this degeneracy and result in the formation of the coherent ground state, in which the orbital moment of t_{2g} level is fully quenched. We find a finite gap for orbital excitations. Such a disordered state of local degrees of freedom on unfrustrated, simple cubic lattice is highly unusual. Orbital liquid state naturally explains observed anomalies of $LaTiO_3$.

er in ... - arXiv...

2+ 6s6p orbital
reversal of the ...

ital order in ...

each Fermi pocket, the
sults ...

xotic Spin Order due to Orbital Fluctuations
rxiv.org › cond-mat ▾ arXiv ▾
W Brzezicki - 2014
l 8, 2014 - In each case we find strong competition between different types of spin an
rbital order, with entangled spin-orbital phases at the crossover ...

DF] The nature of orbital order in transition-metal oxides
ww.fkf.mpg.de/561365/Pavarini.pdf ▾ Max Planck Society ▾
orbital order in transition-metal oxides. Eva Pavarini (FZ Jülich, Germany). **Orbital**
rder plays a crucial role in the physicis of trasition-metal oxides, and yet its.

rbital order in NaTiO2: A first principles study - ScienceDirect
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M Dhariwal - 2012 - Cited by 1 - Related articles
bstract. The debate over the **orbital order** in the layered triangular lattice system
aTiO2 has been rekindled by the recent experiments of McQueen et al. [Phys.

DF] Orbital order in classical models of transition-metal ...
ww.math.ucla.edu/.../Orbital-Lette... ▾ University of California, Los Angeles ▾
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sonant X-ray scattering techniques in which the 3d **orbital order** is detected by its
ffect on excited 4p states [8]. The case for orbital ordering has been ...

Electronic reconstruction at an interface between a Mott insulator and a band insulator

Satoshi Okamoto & Andrew J. Millis

rtment of Physics, Columbia University 538 West 120th Street, New York, York 10027, USA

face science is an important and well-established branch of erials science involving the study of changes in material

NEWS & VIEWS

TRANSITION METAL OXIDES

Ferroelectricity driven by orbital order

The discovery that the rotation of the orbital arrangement in manganites induces ferroelectricity exposes an intriguing phase transition that could serve as a blueprint for novel applications.

BERNHARD KEIMER
is at the Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany
e-mail: B.Keimer@fkf.mpg.de

Transition metal oxides have fascinated scientists since the 1950s, when the newly developed technique of neutron diffraction was used to show that the compound $La_{1-x}Ca_xMnO_3$ exhibits a rich variety of structural and magnetic phases as the Ca concentration is tuned[1]. The fascination has increased in the wake of the discovery of high-temperature superconductivity in a chemically similar compound,

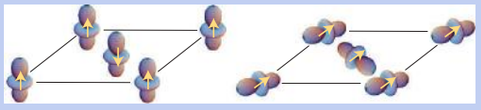

Figure 1 Possible arrangements of Mn^{3+} *d*-orbitals on a square lattice. The patterns are two-dimensional versions of orbitally ordered states actually observed in manganese oxides. The corresponding magnetic states are indicated by yellow arrows.

Article

Photo-induced high-temperature ferromagnetism in $YTiO_3$

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Published online: 3 May 2023

A. S. Disa[1,2]✉, J. Curtis[3,4], M. Fechner[1], A. Liu[1], A. von Hoegen[1], M. Först[1], T. F. Nova[1], P. Narang[3,4], A. Maljuk[5], A. V. Boris[6], B. Keimer[6] & A. Cavalleri[1,7]✉

In quantum materials, degeneracies and frustrated interactions can have a profound

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2023 Autumn School on Correlated Electrons
Orbital Physics in Correlated Matter

www.cond-mat.de/events/correl23

	Mon 18 Sept	Tue 19 Sept	Wed 20 Sept	Thu 21 Sept	Fri 22 Sept
09:00	Orbital Ordering E. Pavarini	Exchange Mechanisms E. Koch	Probing Spin, Charge, Orbital E. Benckiser	Multiplets R. Eder	Coupled Cluster A. Grüneis
10:30	**Coffee Break**				
11:00	Jahn-Teller A. Ceulemans	**Photo**	Oxide Interfaces J. Chakhalian	Kitaev Magnets S.Trebst	Super-QMC A. Lichtenstein
12:30	**Lunch**				
14:00	Imaging Orbitals H. Tjeng	Compass Models J. van den Brink	f-electron systems B. Amadon	Orbital Peierls T. Mizokawa	**Bus to Aachen**
15:30	**Coffee Break**				
16:00	Spin-Orbital Entanglement A. Oleś	Quantum Criticality M. Vojta	Slave-Bosons N. Lanatà	Self-Interaction Correction M. Pederson	
17:30	**Discussion**				
18:00	**Bus to Aachen**		**Poster Session Buffet**	**Bus to Aachen**	
21:00			**Bus to Aachen**		

orbital ordering

Kugel-Khomskii model

Crystal structure and magnetic properties of substances with orbital degeneracy

K. I. Kugel' and D. I. Khomskiĭ
P. N. Lebedev Physics Institute
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Zh. Eksp. Teor. Fiz. **64**, 1429-1439 (April 1973)

$KCuF_3$

$LaMnO_3$

Exchange interaction in magnetic substances containing ions with orbital degeneracy is considered. It is shown that, among with spin ordering, superexchange also results in cooperative ordering of Jahn-Teller ion orbitals, which, generally speaking, occurs at a higher temperature and is accompanied by distortion of the lattice (which is a secondary effect here). Concrete studies are performed for substances with a perovskite structure ($KCuF_3$, $LaMnO_3$, MnF_3). The effective spin Hamiltonian is obtained for these substances and the properties of the ground state are investigated. The orbital and magnetic structures obtained in this way without taking into account interaction with the lattice are in accord with the structures observed experimentally. The approach employed also permits one to explain the strong anisotropy of the magnetic properties of these compounds and to obtain a reasonable estimate for the critical temperatures.

ordering of orbitals with no distortion

degenerate e_g orbitals

KK super-exchange

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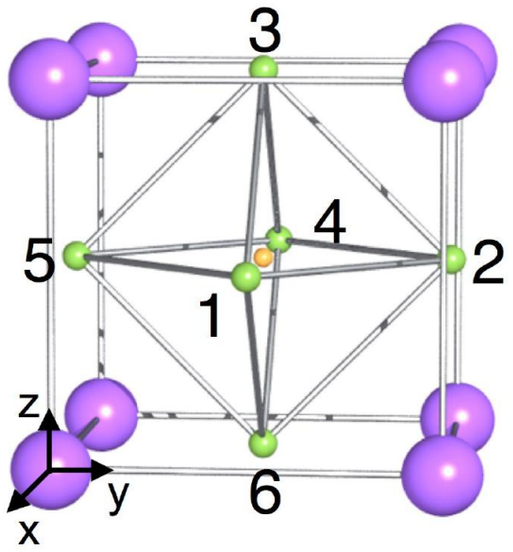
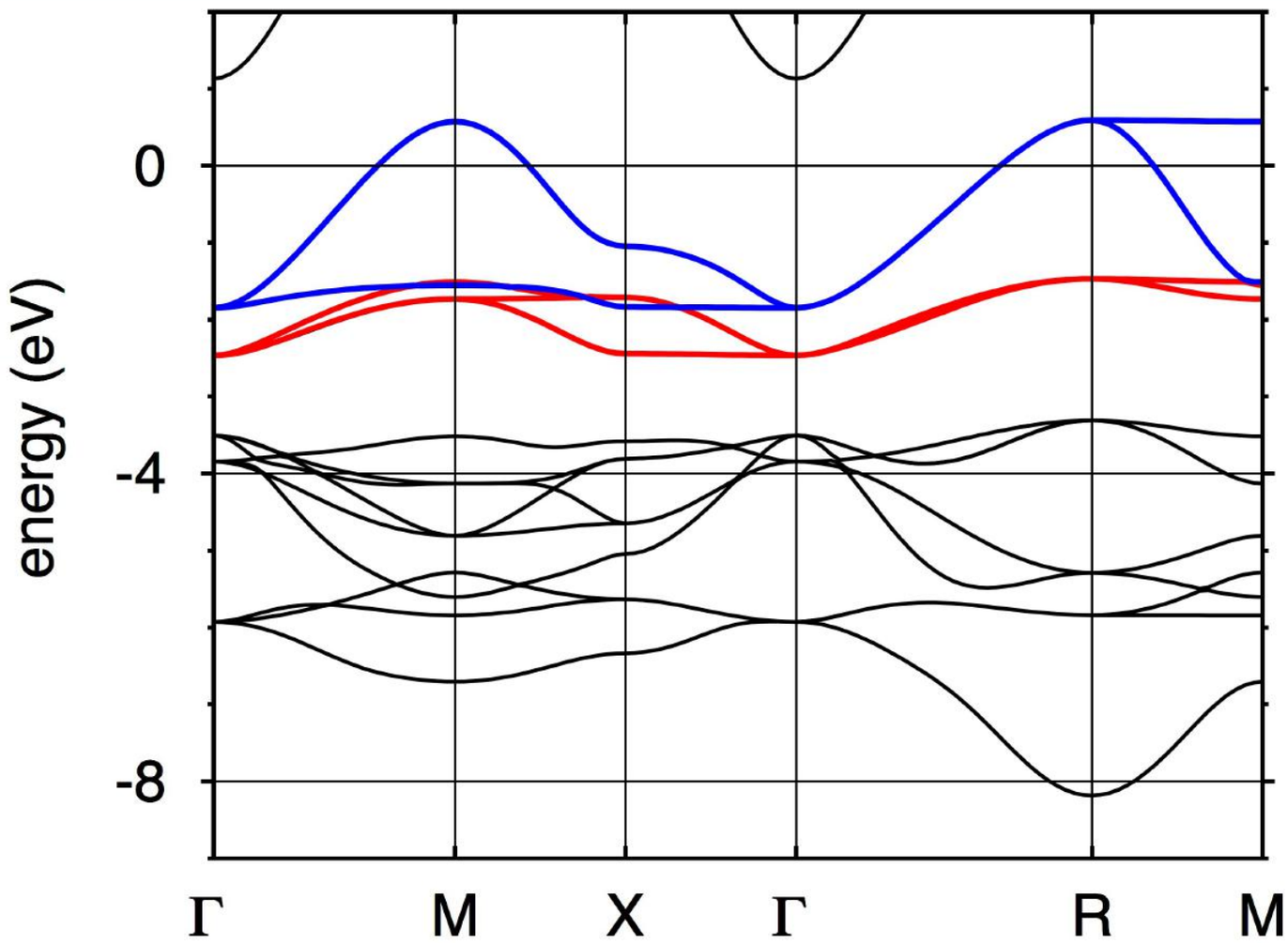
ideal cubic $KCuF_3$: electronic structure



$F^{1-}: p^6$

$Cu^{2+}: t_{2g}^6 e_g^3$

$K^{1+}: p^6$



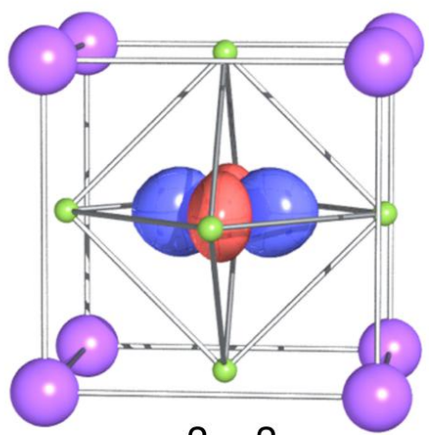
e_g -like

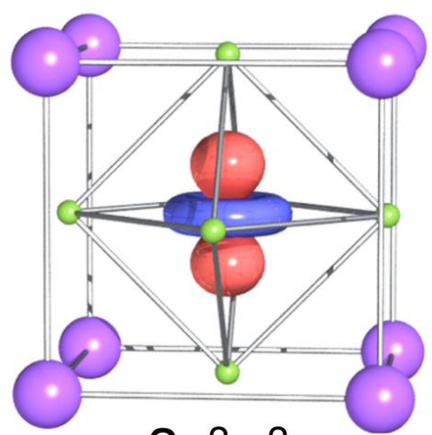
Cu d

t_{2g} -like

F p -like

e_g





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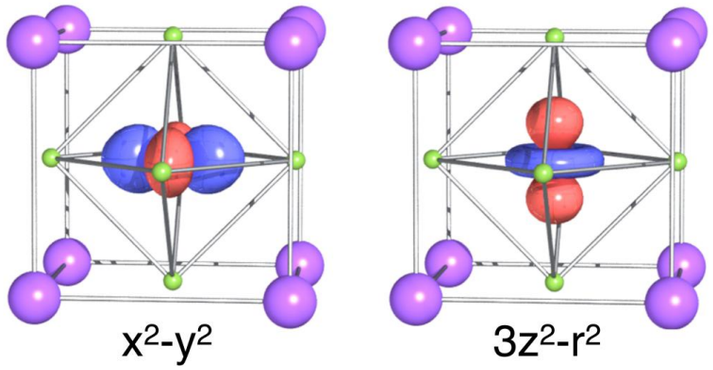
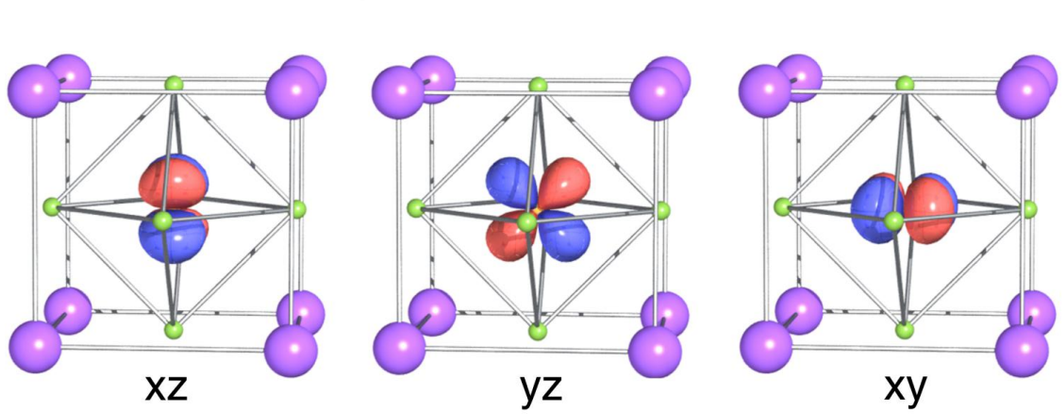
why do e_g and t_{2g} level split ?

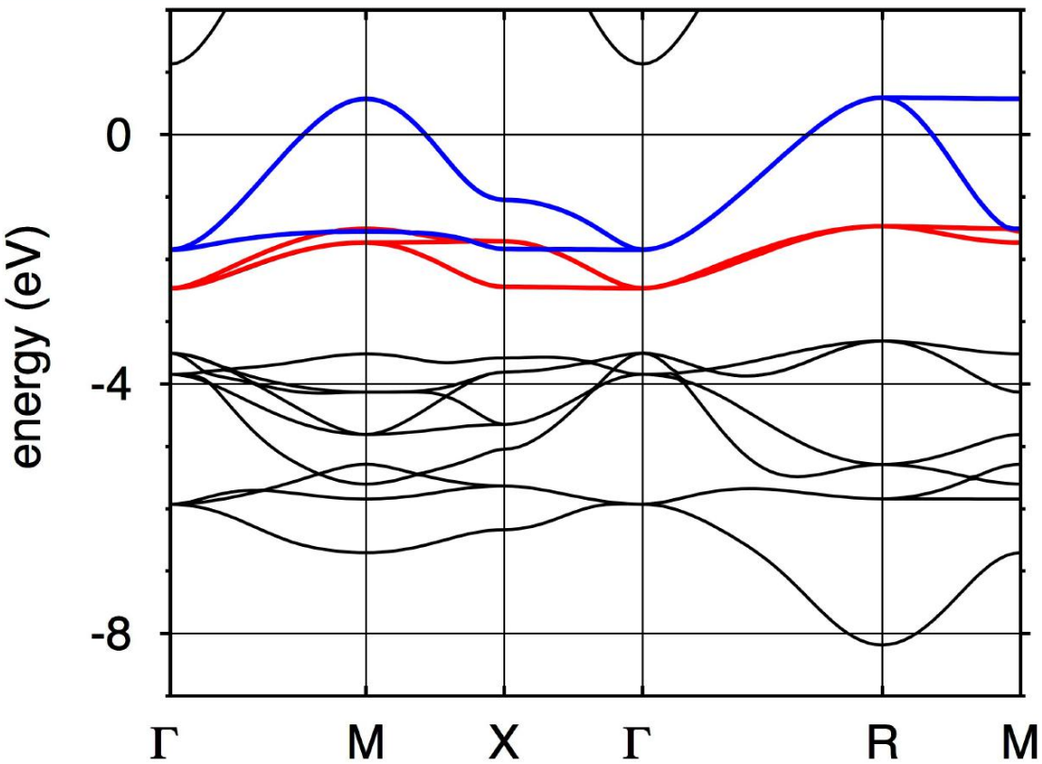
degenerate in atomic limit (spherical symmetry)



e_g



t_{2g}



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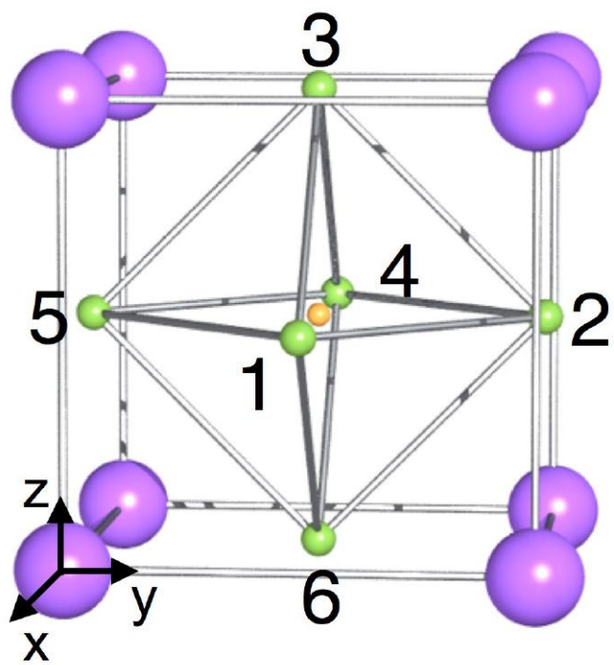
the cubic crystal field

how do *d* levels split at the Cu site?

point charge model

$$v_{\mathrm{R}}(\boldsymbol{r}) = \sum_{\alpha} \frac{q_\alpha}{|\boldsymbol{R}_\alpha - \boldsymbol{r}|} = v_0(r) + \sum_{\alpha \neq 0} \frac{q_\alpha}{|\boldsymbol{R}_\alpha - \boldsymbol{r}|} = v_0(r) + v_c(\boldsymbol{r})$$



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use perturbation theory

$$v_{\mathrm{R}}(\boldsymbol{r}) = \frac{q_B}{r} + \frac{q_C}{d_C}\left[\Delta v\left(\frac{x}{d_C};\frac{r}{d_C}\right) + \Delta v\left(\frac{y}{d_C};\frac{r}{d_C}\right) + \Delta v\left(\frac{z}{d_C};\frac{r}{d_C}\right)\right]$$

$$\Delta v(\xi;\rho) = \frac{1}{\sqrt{1+\rho^2}}\left[\frac{1}{\sqrt{1+\frac{2\xi}{1+\rho^2}}} + \frac{1}{\sqrt{1-\frac{2\xi}{1+\rho^2}}}\right].$$

d_C=a/2=CuF distance

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cubic perovskite

point charge model: F_6 octahedron

$$v_{\mathrm{oct}}(\boldsymbol{r}) = \frac{35}{4}\frac{q_C}{a^5}\left(x^4+y^4+z^4-\frac{3}{5}r^4\right) = D\left(x^4+y^4+z^4-\frac{3}{5}r^4\right).$$

first order perturbation theory

$$H_{\mathrm{CF}} = \begin{array}{c} \begin{array}{ccccc} \text{m=-2} & \text{m=-1} & \text{m=0} & \text{m=1} & \text{m=2} \end{array} \\ \begin{pmatrix} Dq & 0 & 0 & 0 & 5Dq \\ 0 & -4Dq & 0 & 0 & 0 \\ 0 & 0 & 6Dq & 0 & 0 \\ 0 & 0 & 0 & -4Dq & 0 \\ 5Dq & 0 & 0 & 0 & Dq \end{pmatrix} \end{array}.$$

basis: atomic functions

$$\psi_{nlm}(\rho,\theta,\phi) = R_{nl}(\rho)Y_l^m(\theta,\phi)$$

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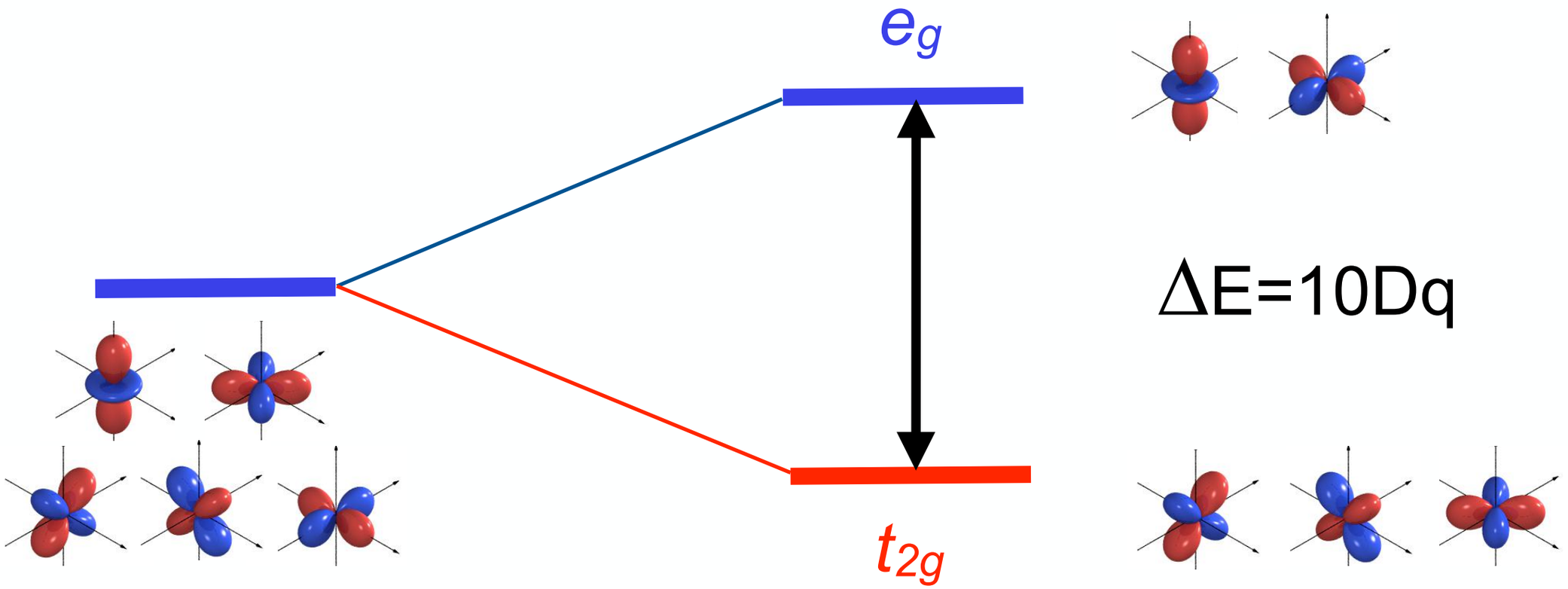
cubic crystal-field

spherical

cubic



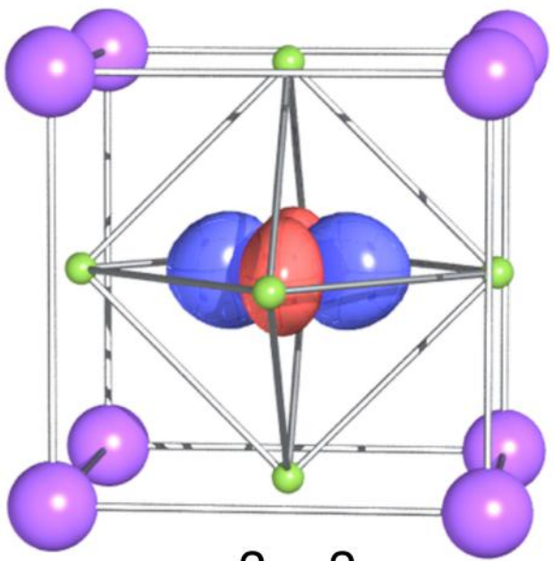
Cu [Ar]3d^{10} 4s^{1}

Cu^{2+} 3d^{9}

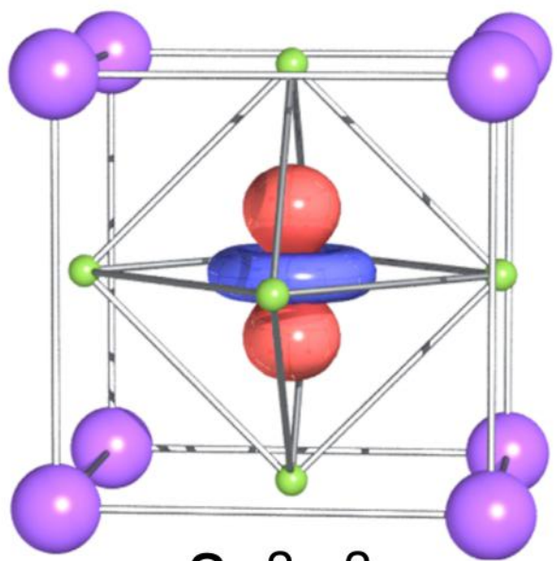
$t_{2g}^{6}e_g^{3}$

d orbitals in cubic symmetry

e_g

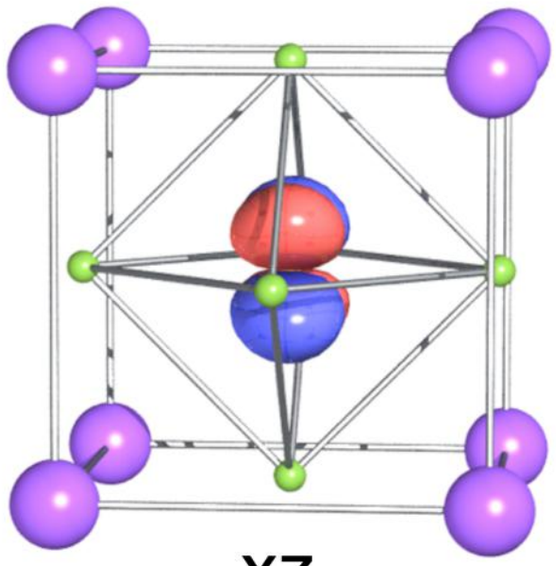


x^2-y^2

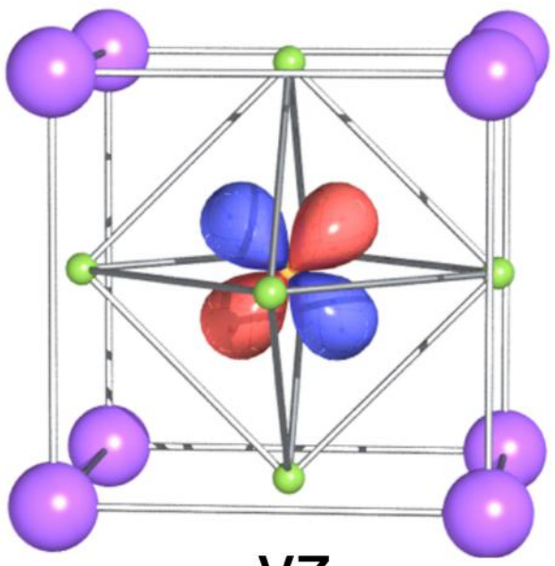


$3z^2-r^2$

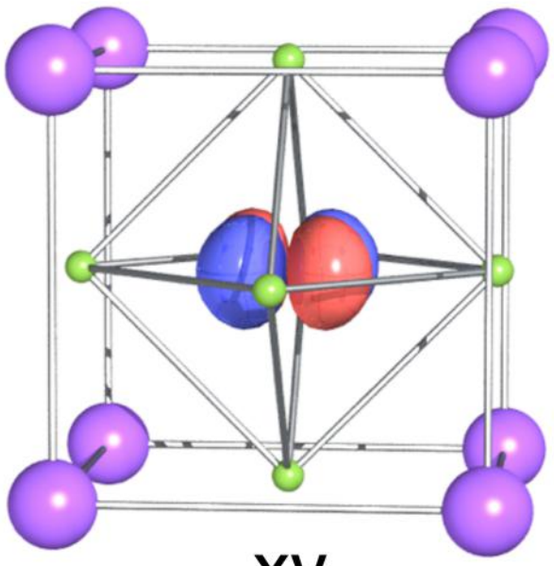
t_{2g}



xz



yz



xy

(exact: group theory)

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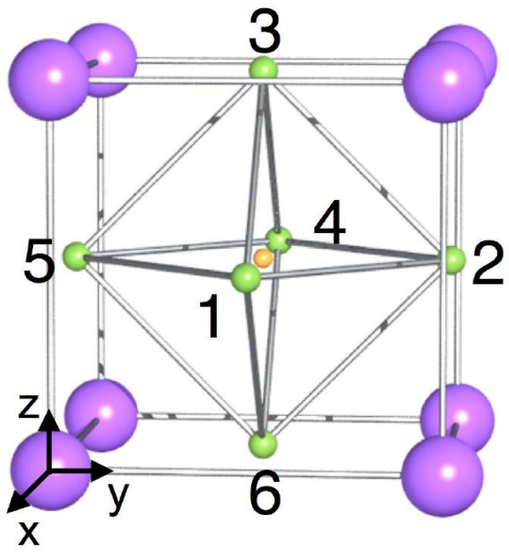
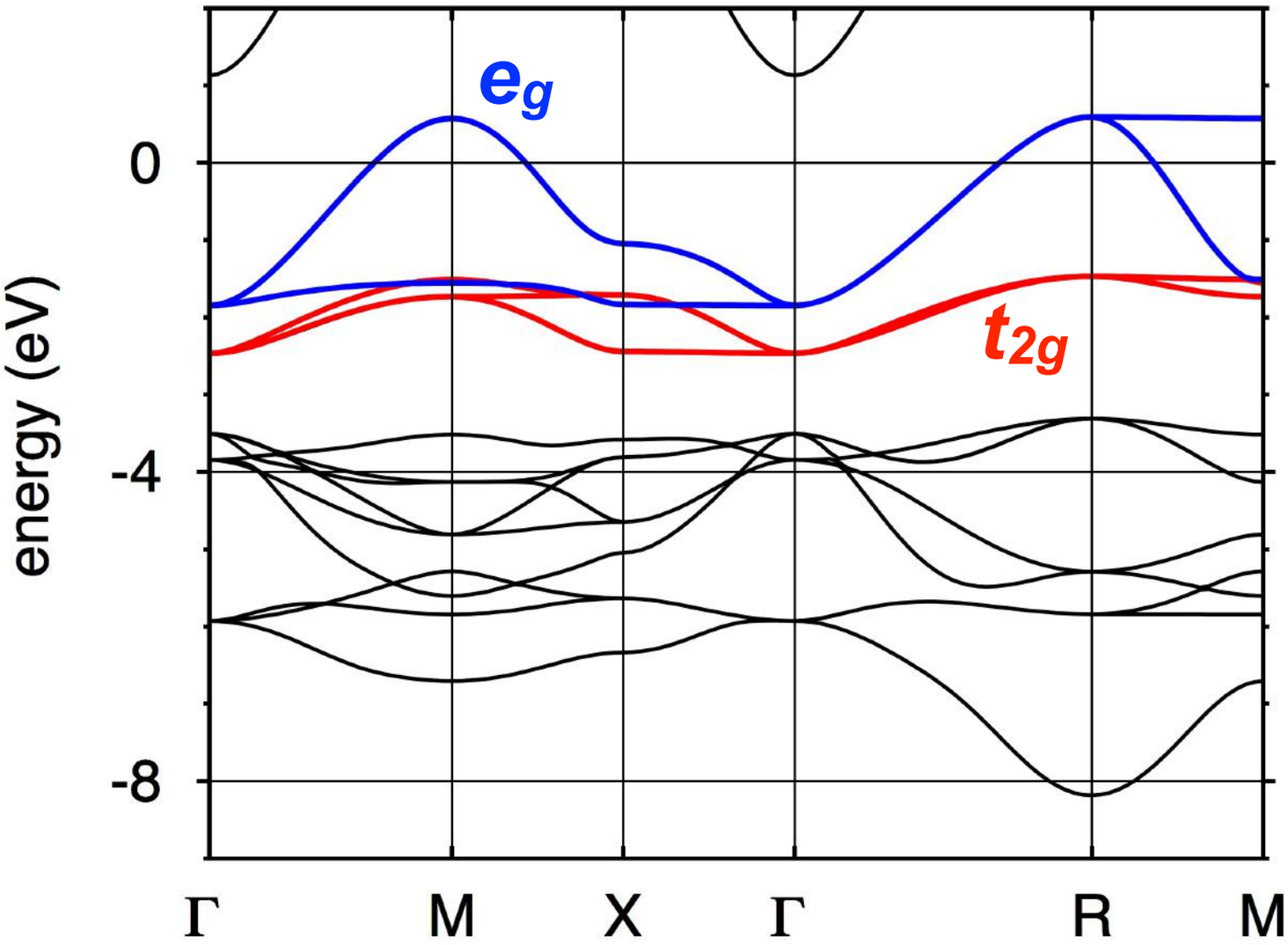
ideal cubic $KCuF_3$: electronic structure



$t_{2g}^6 e_g^3$



Cu d -like

F p-like

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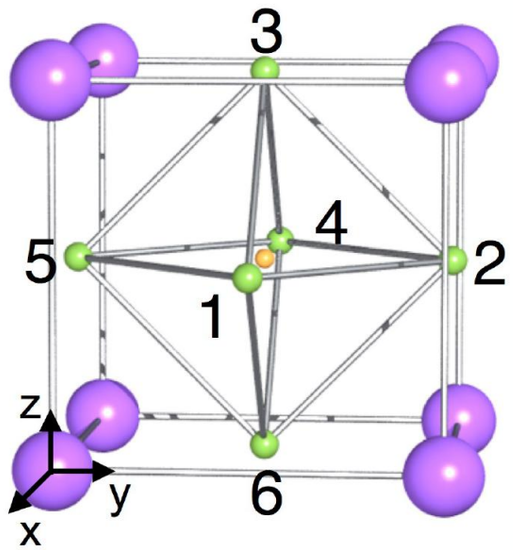
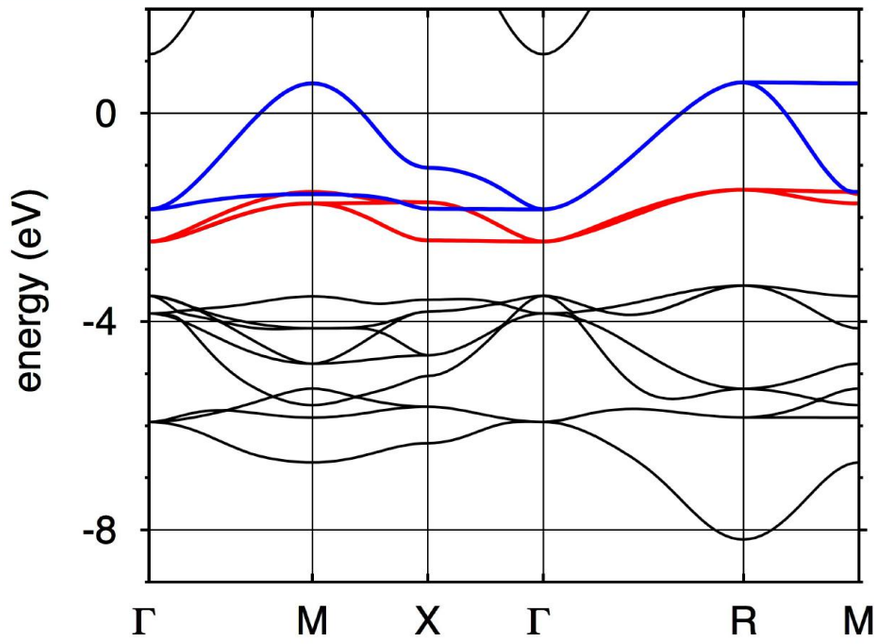
ideal cubic $KCuF_3$: electronic structure





e_g-*like*

.. but is a large gap insulator, paramagnetic above 40 K!

we need the Hubbard U

$$H = -\sum_{ii'}\sum_{mm'}\sum_{\sigma} t^{ii'}_{mm'} c^{\dagger}_{im\sigma} c_{i'm'\sigma} + U \sum_{i} \frac{1}{2} \sum_{m\sigma \neq m'\sigma'} n_{im\sigma} n_{im'\sigma'}$$

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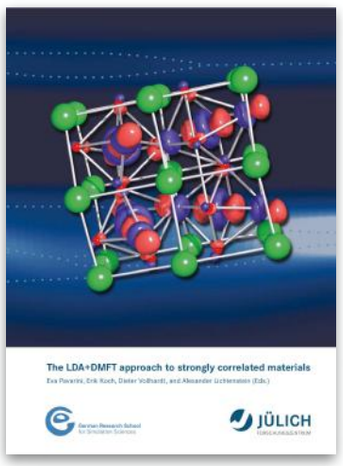
missing: the Hund's rule J

$$\hat{H} = -\sum_{ii'}\sum_{\sigma}\sum_{mm'} t^{i,i'}_{mm'}\, c^{\dagger}_{im\sigma} c_{im'\sigma} + U \sum_{i}\sum_{m} \hat{n}_{im\uparrow}\hat{n}_{im\downarrow}$$

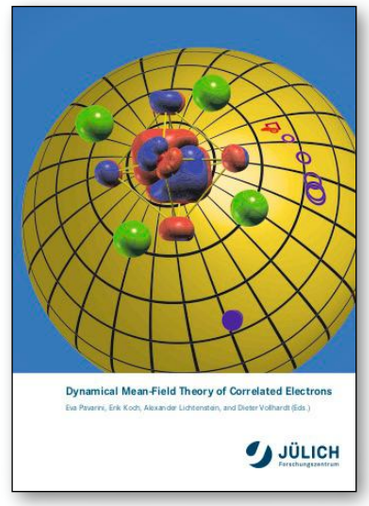
$$+ \frac{1}{2}\sum_{i}\sum_{\sigma\sigma'}\sum_{m\neq m'} \left(U - 2J - J\delta_{\sigma,\sigma'}\right) \hat{n}_{im\sigma}\hat{n}_{im'\sigma'}$$

$$-J \sum_{i}\sum_{m\neq m'} \left[c^{\dagger}_{im\uparrow} c^{\dagger}_{im\downarrow} c_{im'\uparrow} c_{im'\downarrow} + c^{\dagger}_{im\uparrow} c_{im\downarrow} c^{\dagger}_{im'\downarrow} c_{im'\uparrow} \right],$$



$t^{ii}_{mm'}$: crystal-field energies (i=i')
$t^{ii'}_{mm'}$: hopping integrals

U: direct screened Coulomb integral
J: exchange screened Coulomb integral



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orbital ordering from super-exchange

Crystal structure and magnetic properties of substances with orbital degeneracy

K. I. Kugel' and D. I. Khomskiĭ
P. N. Lebedev Physics Institute
(Submitted November 13, 1972)
Zh. Eksp. Teor. Fiz. **64**, 1429-1439 (April 1973)

$KCuF_3$

$LaMnO_3$

$$H = -\sum_{ii'}\sum_{mm'}\sum_{\sigma} t^{ii'}_{mm'} c^{\dagger}_{im\sigma} c_{i'm'\sigma} + U \sum_{i} \frac{1}{2} \sum_{m\sigma \neq m'\sigma'} n_{im\sigma} n_{im'\sigma'}$$

m: degenerate e_g orbitals

Mott insulators (U much larger than t): small t/U limit

$$H^{ii'}_{SE} = J_{SS} S_i \cdot S_{i'} + J_{OO} O_i O_{i'} + J_{SO} (O_i O_{i'})(S_i \cdot S_{i'})$$

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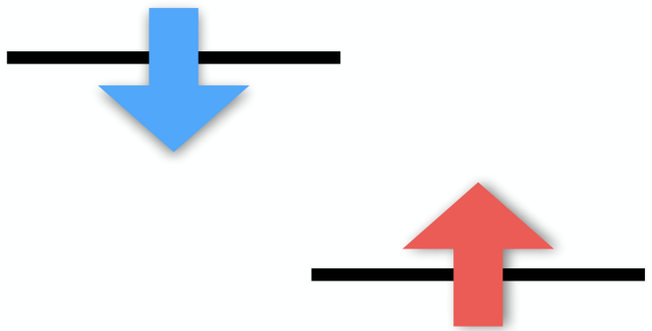
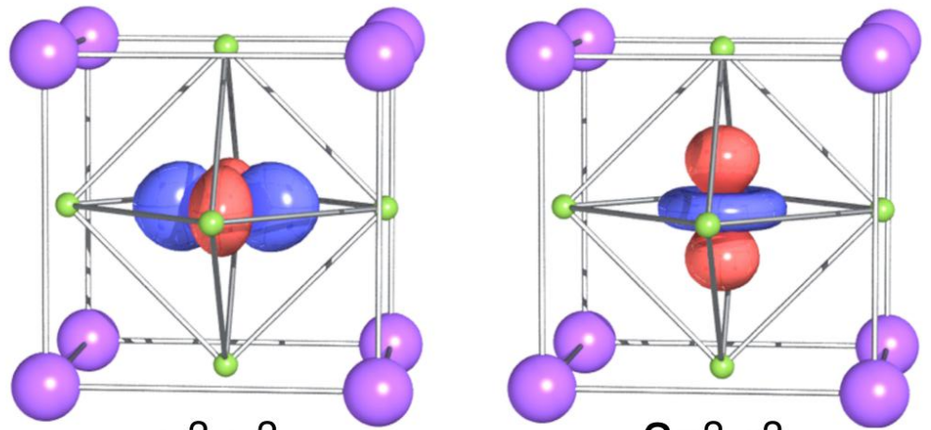
effective operators





$$S_x = \frac{1}{2}\sigma_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$S_z = \frac{1}{2}\sigma_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$S_y = \frac{1}{2}\sigma_y = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$O_x = \frac{1}{2}\tau_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$O_z = \frac{1}{2}\tau_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$O_y = \frac{1}{2}\tau_y = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

S_i=1/2

O_i=1/2

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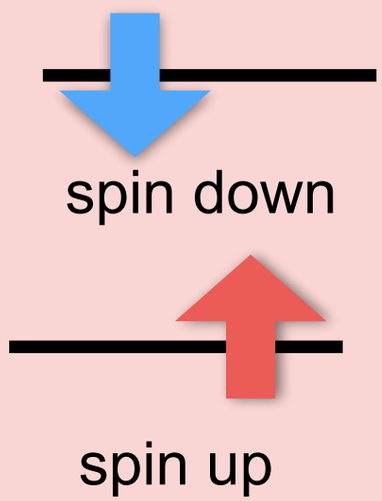
emergence of local spins

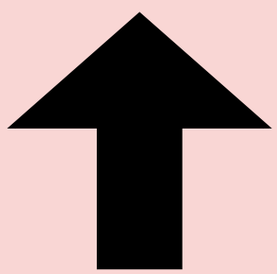
single Hubbard atom

no orbital degrees of freedom

$$H_i = \varepsilon_d \sum_\sigma c^\dagger_{i\sigma} c_{i\sigma} + U n_{i\uparrow} n_{i\downarrow}$$

half filling (one electron)





$S_i = 1/2$

$$H_i = \varepsilon_d \hat{n}_i + U\left(\frac{\hat{n}_i^2}{4} - S_{zi}^2\right)$$

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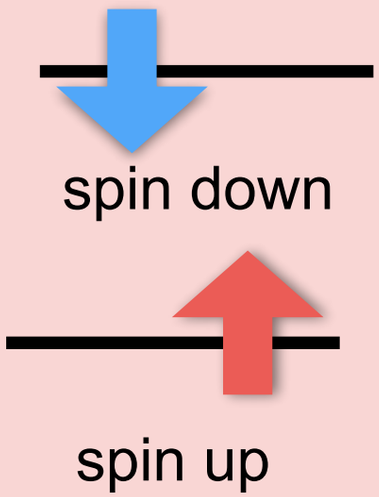
emergence of local spins

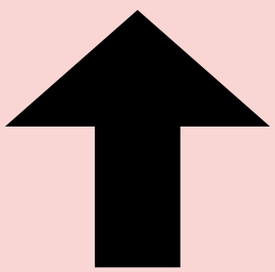
single Hubbard atom

no orbital degrees of freedom

$$H_i = \varepsilon_d \sum_\sigma c^\dagger_{i\sigma} c_{i\sigma} + U n_{i\uparrow} n_{i\downarrow}$$

half filling (one electron)





$S_i = 1/2$

$$H_i = \varepsilon_d + U\left(\frac{1}{4} - S^2_{zi}\right)$$

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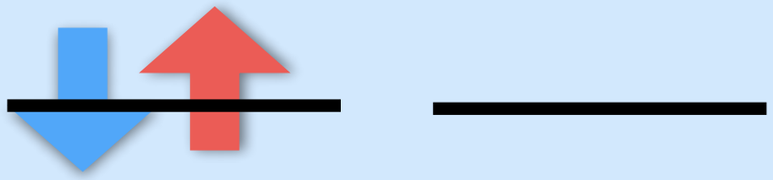
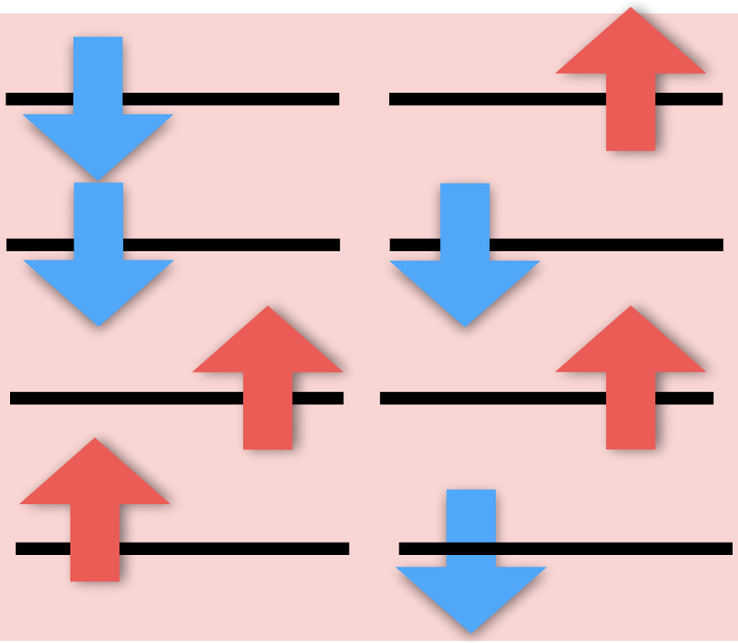
two atoms, N_e=2

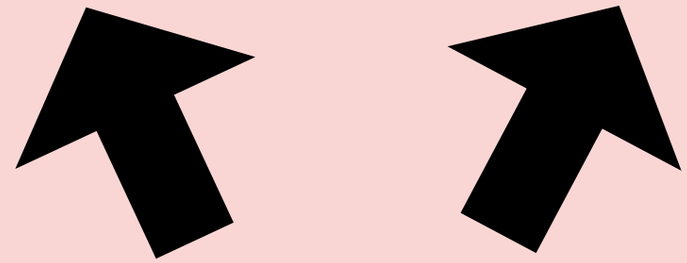
$2\varepsilon_d + U$



no spin degrees of freedom

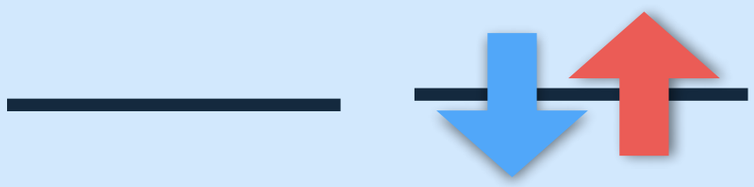
$2\varepsilon_d$





S_A=1/2 S_B=1/2

$2\varepsilon_d + U$



no spin degrees of freedom

site *A* site *B*

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two-level single-site Hubbard model

degenerate levels 

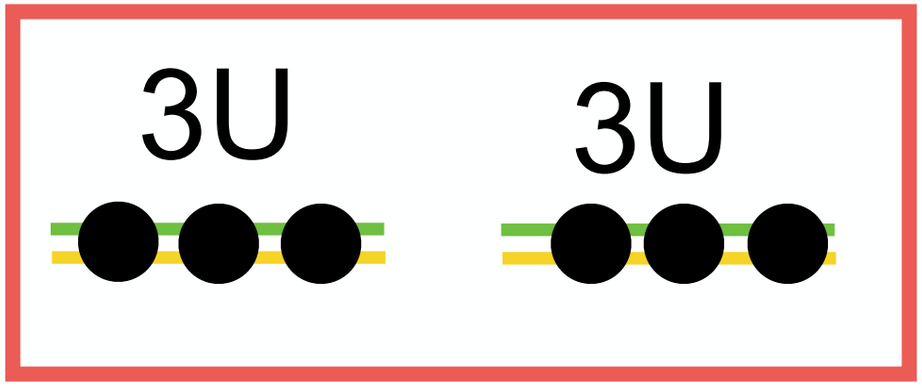
first we consider only direct Coulomb integral U

$$H = \varepsilon_d \sum_{\sigma m} c^\dagger_{im\sigma} c_{im\sigma} + U \, \frac{1}{2} \sum_{m\sigma \neq m'\sigma'} \hat{n}_{im\sigma} \hat{n}_{im'\sigma'}$$

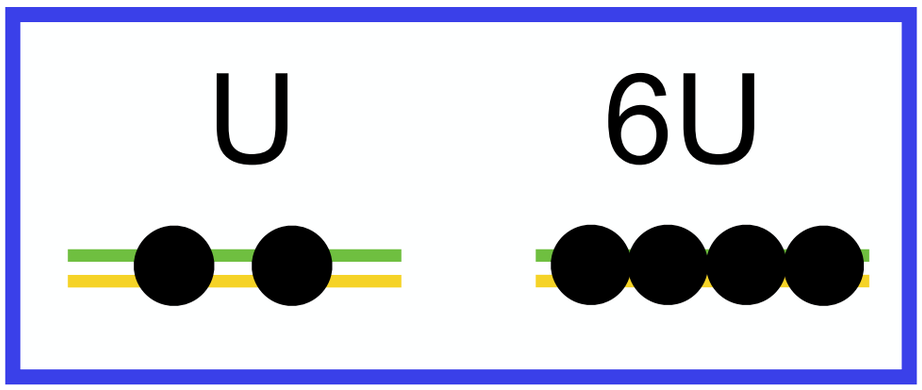
cubic $KCuF_3$: two sites

configuration e_g^3

low-energy



high energy



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cubic $KCuF_3$ and $LaMnO_3$

single site, configuration e_g^3

S=1/2 O=1/2

single site, configuration e_g^1

S=1/2 O=1/2

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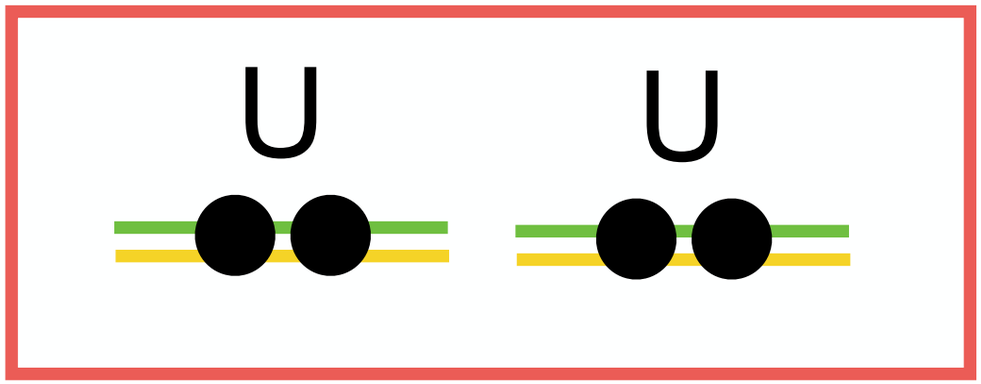
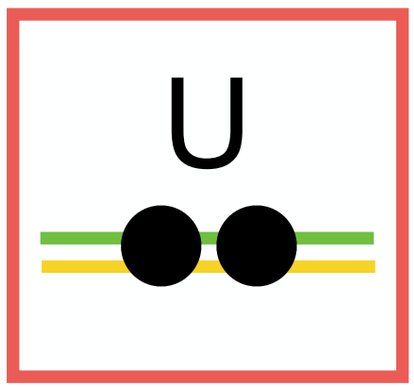
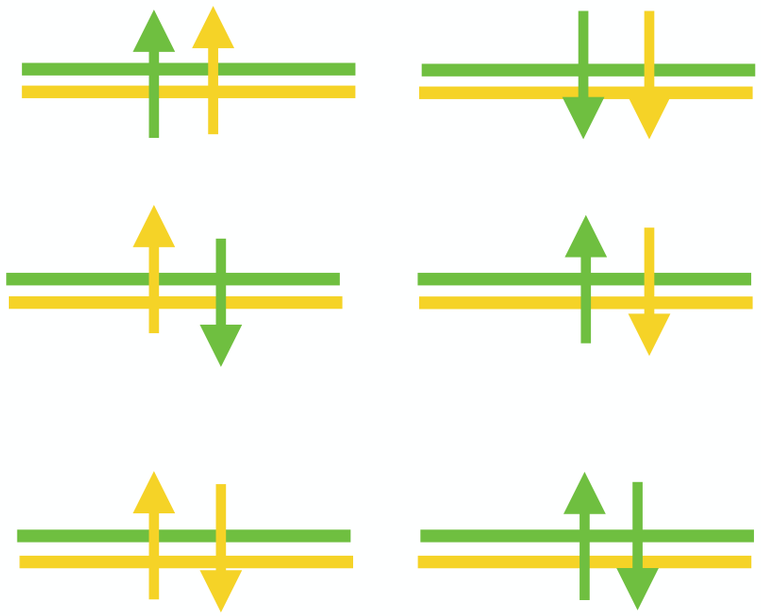
configuration e_g^2 ?

low-energy



possible states for one site:





4 states, S=0 or S=1

2 states, S=0

multiplets: Robert Eder

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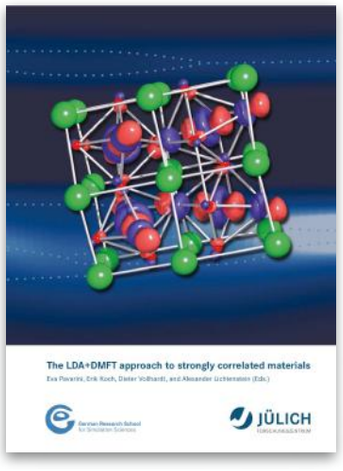
missing: the Hund's rule J

$$\hat{H} = -\sum_{ii'}\sum_{\sigma}\sum_{mm'} t^{i,i'}_{mm'}\, c^{\dagger}_{im\sigma} c_{im'\sigma} + U \sum_{i}\sum_{m} \hat{n}_{im\uparrow}\hat{n}_{im\downarrow}$$

$$+ \frac{1}{2}\sum_{i}\sum_{\sigma\sigma'}\sum_{m\neq m'} (U - 2J - J\delta_{\sigma,\sigma'})\, \hat{n}_{im\sigma}\hat{n}_{im'\sigma'}$$

$$-J\sum_{i}\sum_{m\neq m'}\left[c^{\dagger}_{im\uparrow}c^{\dagger}_{im\downarrow}c_{im'\uparrow}c_{im'\downarrow} + c^{\dagger}_{im\uparrow}c_{im\downarrow}c^{\dagger}_{im'\downarrow}c_{im'\uparrow}\right],$$



$t^{ii}_{mm'}$: crystal-field energies (i=i')
$t^{ii'}_{mm'}$: hopping integrals

U: direct screened Coulomb integral
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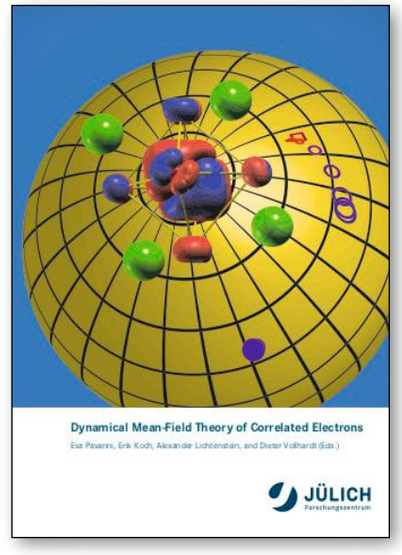

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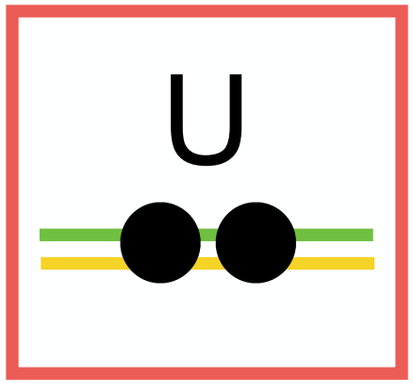
finite J, single site, Ne=2



Hund's rule number one: maximize spin (S=1)

U-3J

O=O S=1

orbital degeneracy is zero!

other multiplets have energy U+J and U-J

multiplets: Robert Eder

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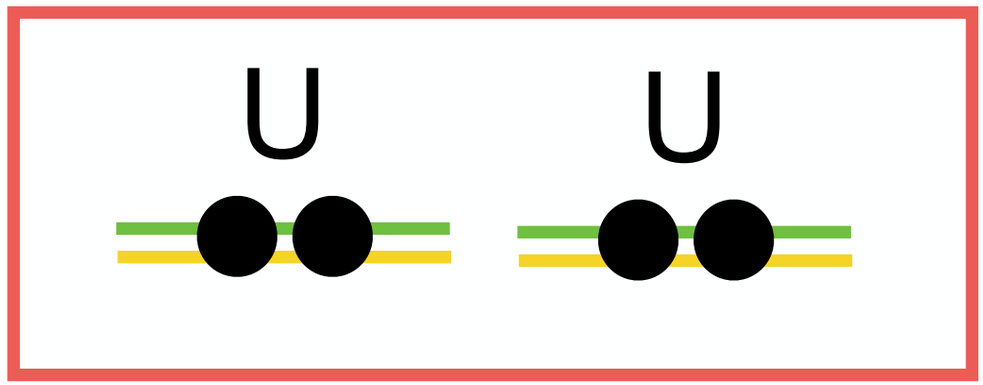
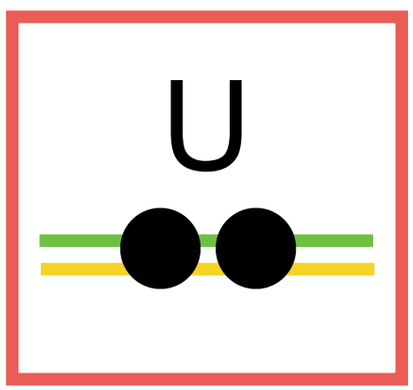
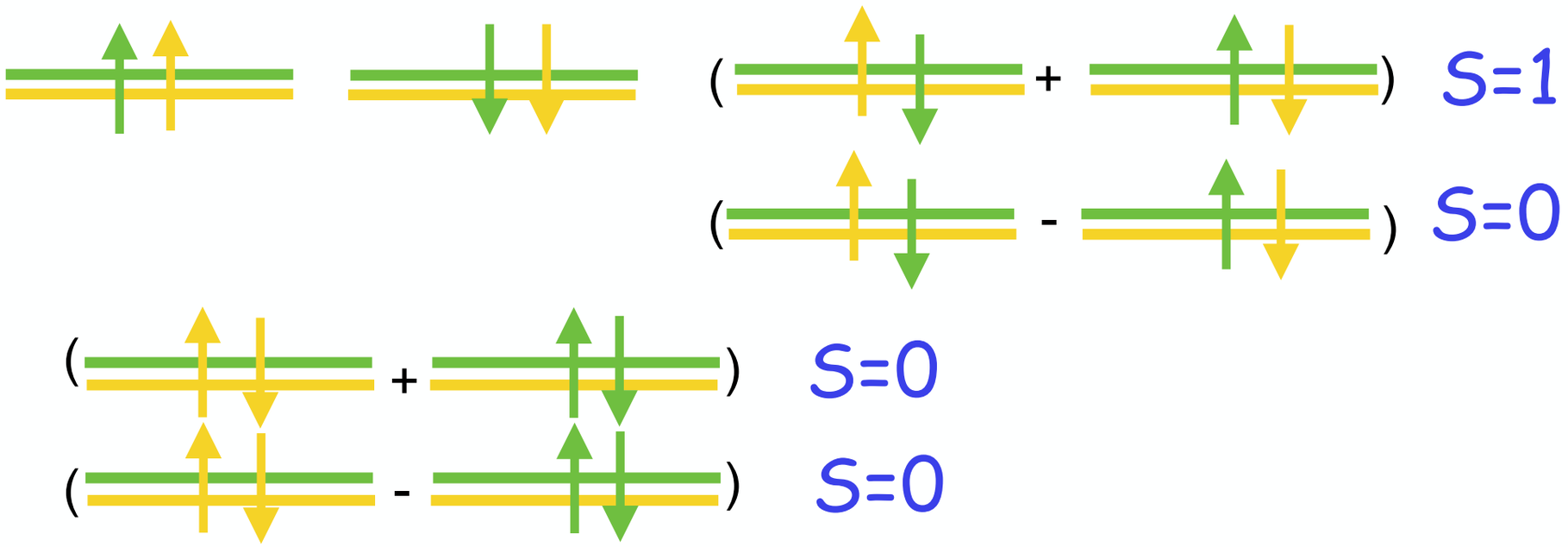
configuration e_g^2 ?

low-energy



possible states for one site:





multiplets: Robert Eder

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local spins and pseudospins

(Hund's rule number 1)

S=1 *O=O* e_g^2

S=1/2 *O=1/2* e_g^3

S=1/2 *O=1/2* e_g^1

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orbital ordering from super-exchange

Crystal structure and magnetic properties of substances with orbital degeneracy

K. I. Kugel' and D. I. Khomskiĭ
P. N. Lebedev Physics Institute
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Zh. Eksp. Teor. Fiz. **64**, 1429-1439 (April 1973)

$KCuF_3$

$LaMnO_3$

$$H = -\sum_{ii'}\sum_{mm'}\sum_{\sigma} t^{ii'}_{mm'} c^{\dagger}_{im\sigma} c_{i'm'\sigma} + U\sum_{i}\frac{1}{2}\sum_{m\sigma\neq m'\sigma'} n_{im\sigma} n_{im'\sigma'}$$

perturbation — *dominant*

small t/U limit (Mott insulator) → e_g *degenerate orbitals*

super-exchange Hamiltonian

$$H^{ii'}_{SE} = J_{SS} S_i \cdot S_{i'} + J_{OO} O_i O_{i'} + J_{SO}(O_i O_{i'})(S_i \cdot S_{i'})$$

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KK super-exchange: ideal case

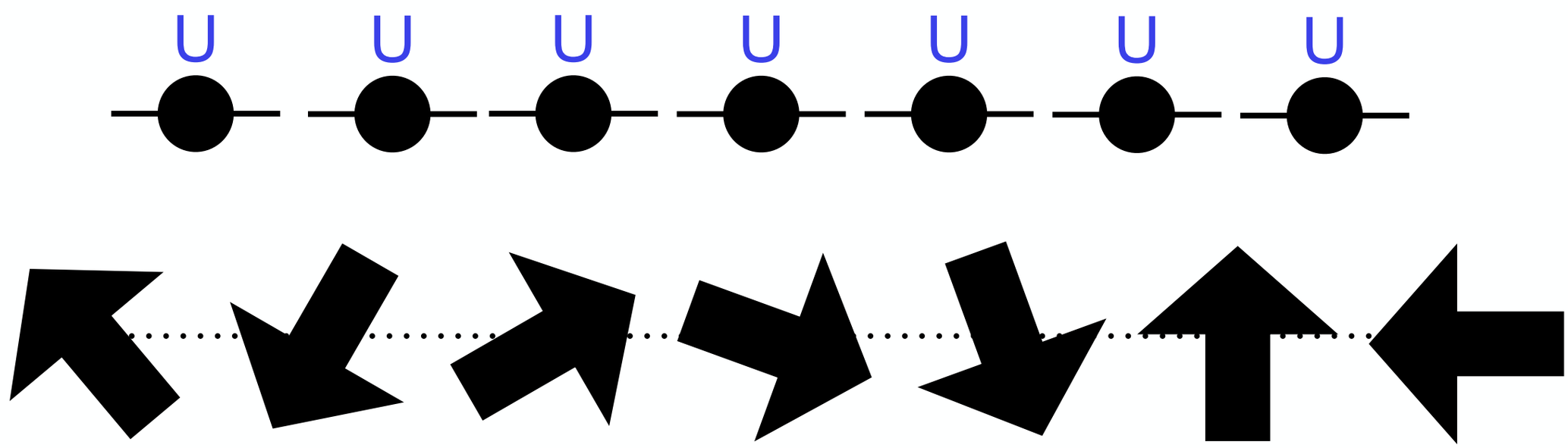
spin ordering: super-exchange

$$H_{SE}^{ii'} = J_{SS} S_i \cdot S_{i'} + J_{OO} O_i O_{i'} + J_{SO} (O_i O_{i'})(S_i \cdot S_{i'})$$

one-band Hubbard model

half filling

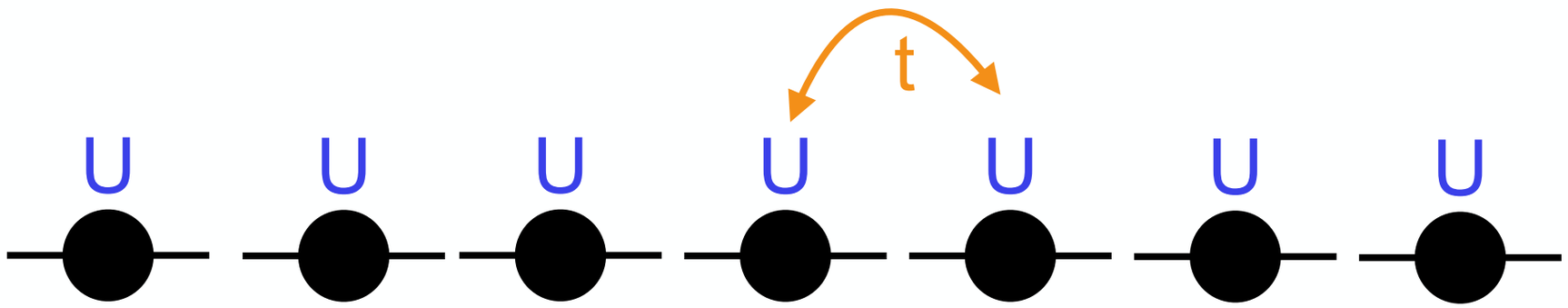
$$\hat{H} = \underbrace{-t \sum_{\langle ii' \rangle} \sum_{\sigma} c^{\dagger}_{i\sigma} c_{i\sigma}}_{\textit{perturbation}} + \underbrace{U \sum_{i} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}}_{\textit{dominant}}$$

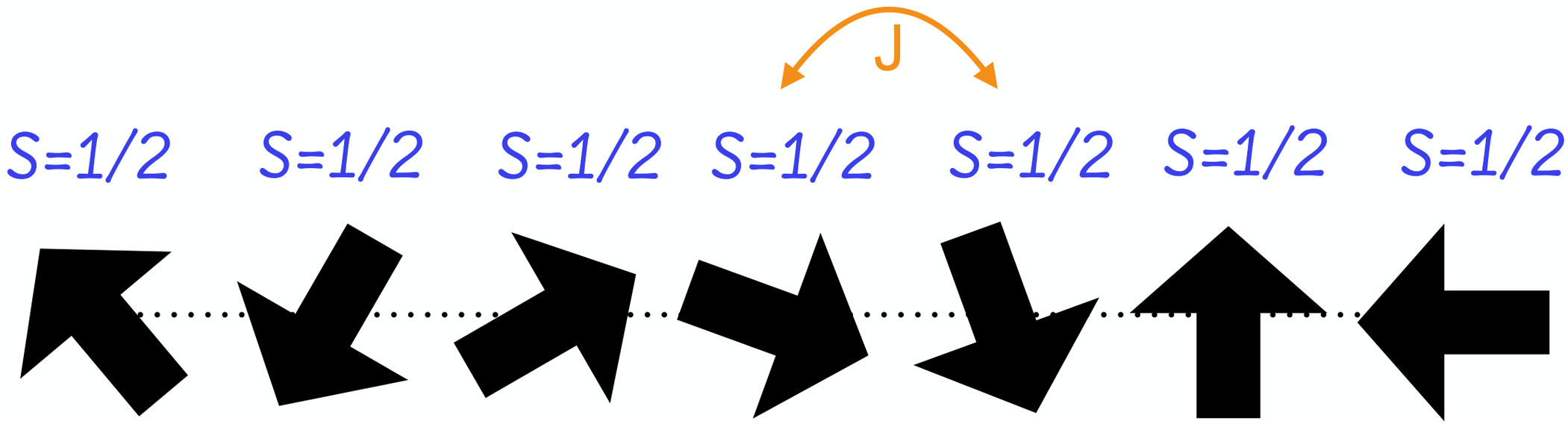


without hopping

local spins interact

let us switch the hopping on…





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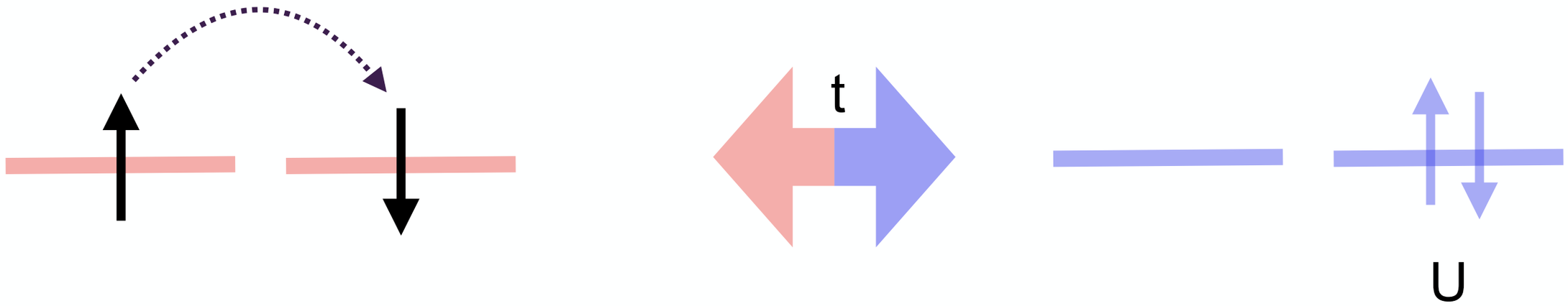
low-energy model: perturbation in t

hops to doubly occupied states



energy gain

$$\Delta E_{\uparrow\downarrow} \sim -\sum_I \langle\uparrow,\downarrow|H_T|I\rangle \langle I \left| \frac{1}{E(2)+E(0)-2E(1)} \right| I\rangle \langle I|H_T|\uparrow,\downarrow\rangle \sim -\frac{2t^2}{U}.$$

=t	=1/U	=t

(second-order perturbation theory)

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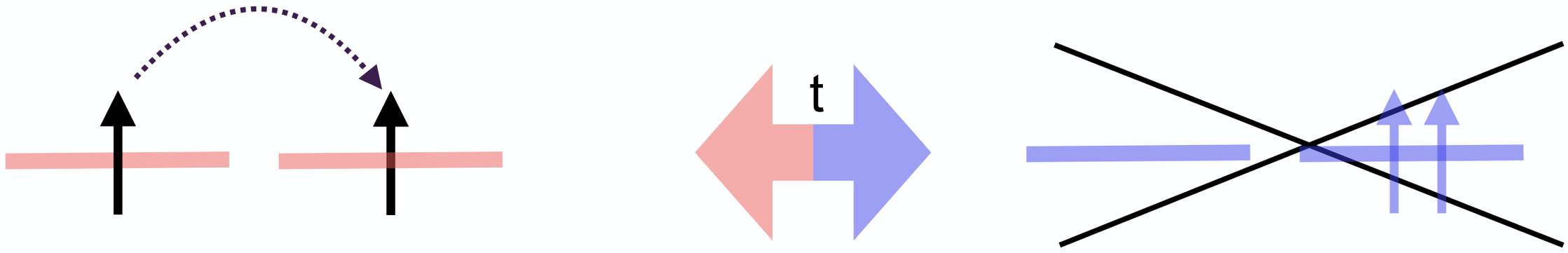
low energy model

energy gain only for antiferromagnetic arrangement



Pauli principle

$$\frac{1}{2}\Gamma \sim (\Delta E_{\uparrow\uparrow} - \Delta E_{\uparrow\downarrow}) = \frac{1}{2}\frac{4t^2}{U}$$

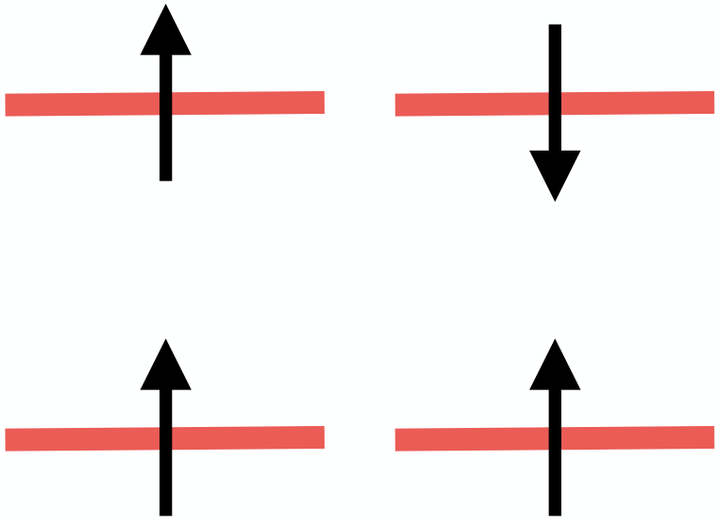
$$H_S = \frac{1}{2}\Gamma \sum_{\langle ii' \rangle} \left[\boldsymbol{S}_i \cdot \boldsymbol{S}_{i'} - \frac{1}{4} n_i n_{i'} \right]$$

super-exchange interaction

(see lecture Erik Koch)

low energy model: let's check it

$$H_S = \frac{1}{2}\Gamma \sum_{\langle ii' \rangle} \left[\boldsymbol{S}_i \cdot \boldsymbol{S}_{i'} - \frac{1}{4} n_i n_{i'} \right]$$



$$E = \frac{1}{2} \times 2 \times \Gamma \left[-\frac{1}{4} - \frac{1}{4} \right] = -\frac{\Gamma}{2} = -\frac{2t^2}{U}$$

$$E = \frac{1}{2} \times 2 \times \Gamma \left[+\frac{1}{4} - \frac{1}{4} \right] = 0$$

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KK super-exchange: ideal case

orbital ordering: super-exchange

$$H_{SE}^{ii'} = J_{SS} S_i \cdot S_{i'} + J_{OO} O_i O_{i'} + J_{SO} (O_i O_{i'})(S_i \cdot S_{i'})$$

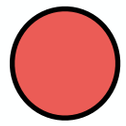
Hubbard-like two-site model, e_g^1

$$\hat{H} = \hat{H}_0 + \hat{H}_T + \hat{H}_U$$

$$\hat{H}_0 = \varepsilon_d \sum_{\sigma} (\hat{n}_{A\sigma} + \hat{n}_{B\sigma})$$

m= 

$$\hat{H}_T = -t \sum_{\sigma} \sum_{m} \left[c^{\dagger}_{Am} c_{Bm} + c^{\dagger}_{Bm} c_{Am} \right].$$

Ne=1/site 

(intra-orbital hoppings only)

$$\hat{H}_U = U \sum_{i=AB} \sum_{m} \hat{n}_{im\uparrow} \hat{n}_{im\downarrow} + \frac{1}{2} \sum_{i=AB} \sum_{\sigma\sigma'} \sum_{m \neq m'} (U - 2J - J\delta_{\sigma,\sigma'}) \hat{n}_{im\sigma} \hat{n}_{im'\sigma'}.$$

(density-density only)

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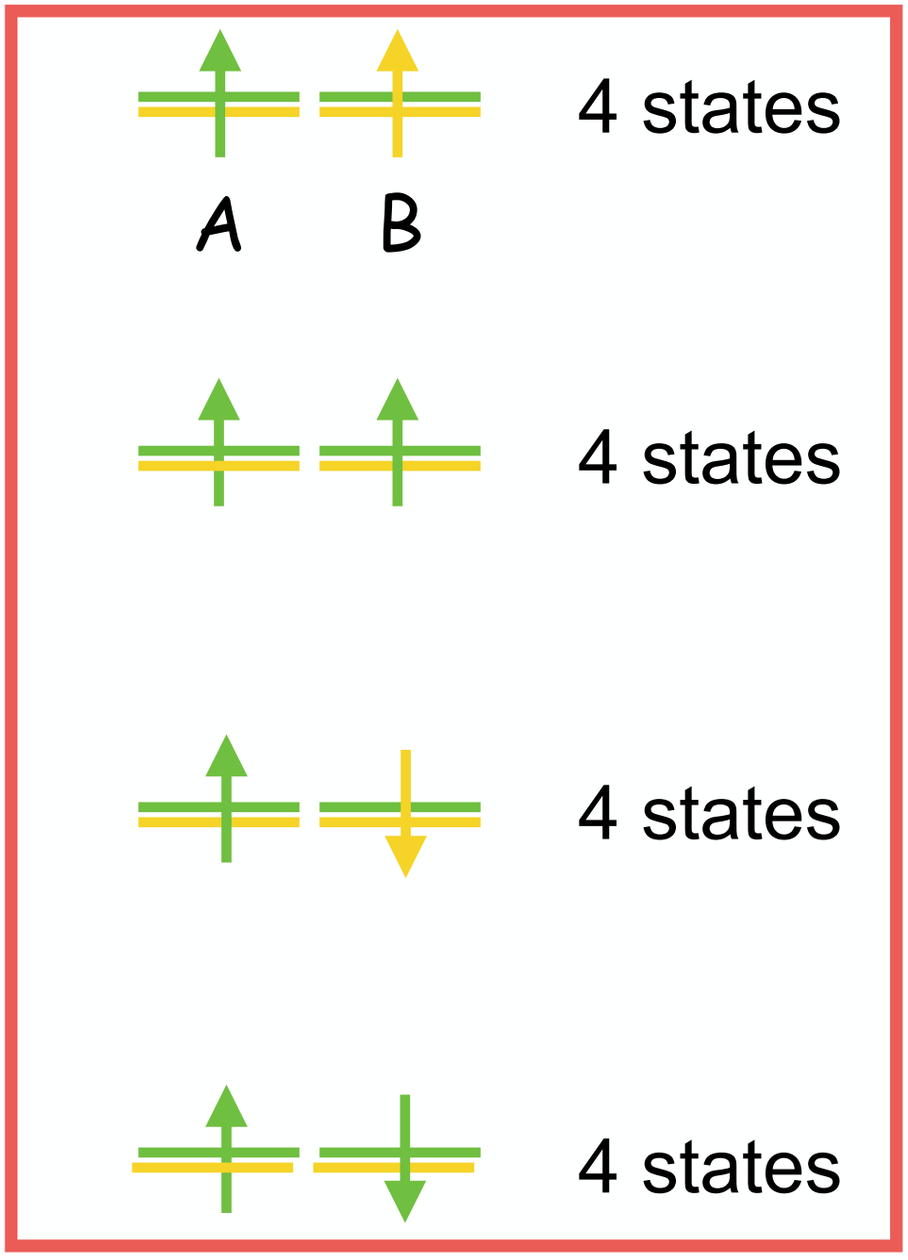
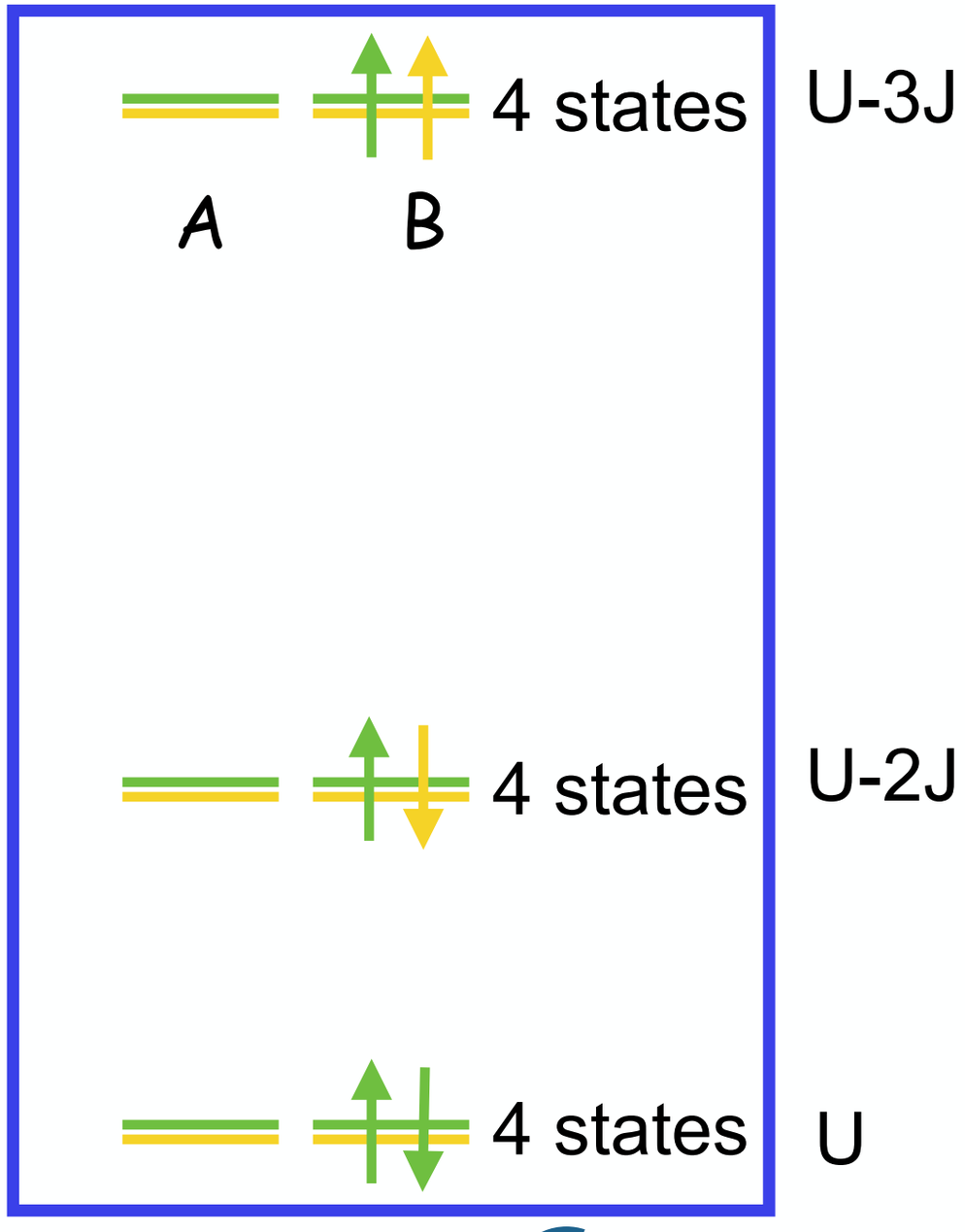
two-site problem, one electron per site

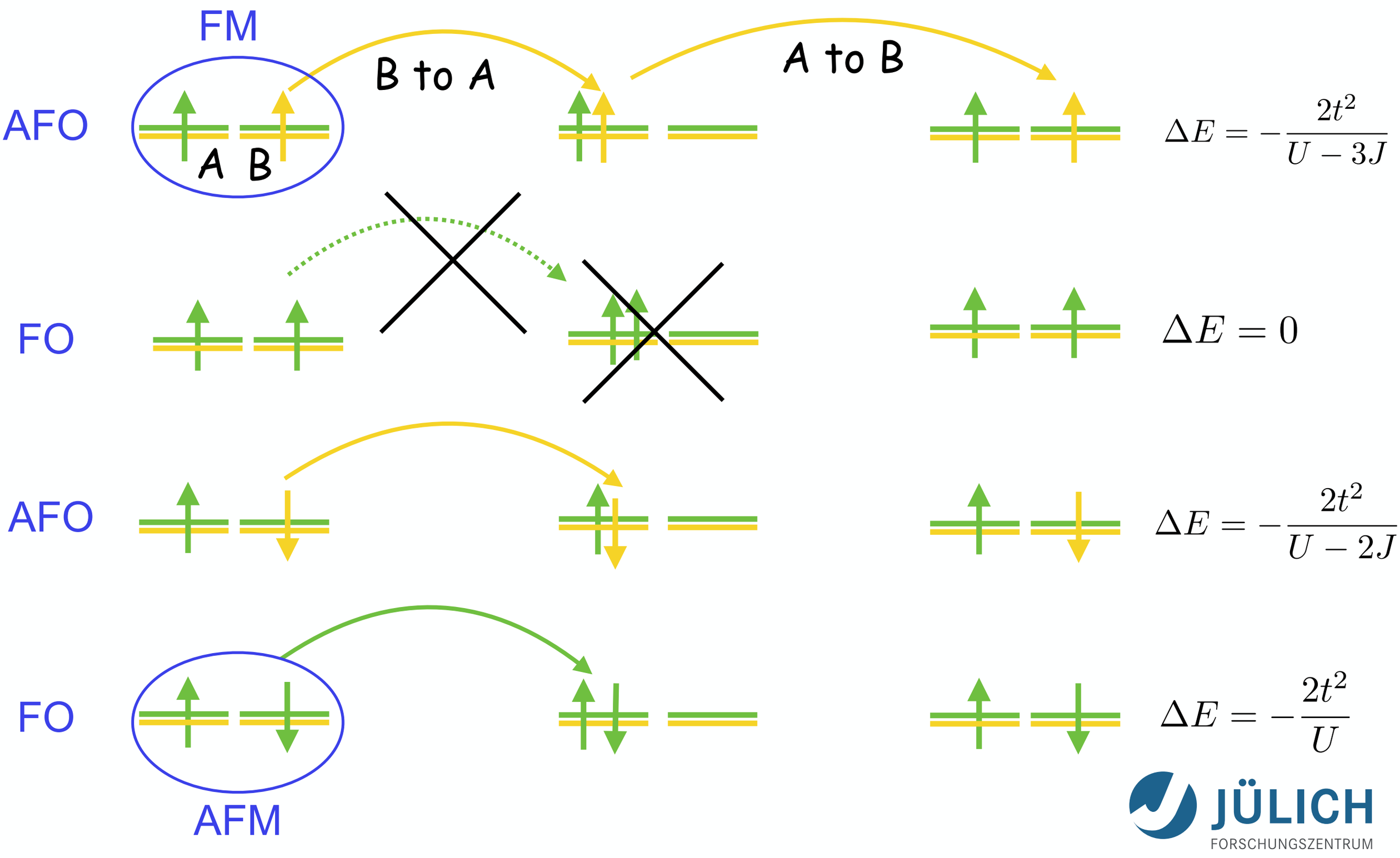
16 states with N_d=0



12 states with N_d=1



two-site problem, one electron per site



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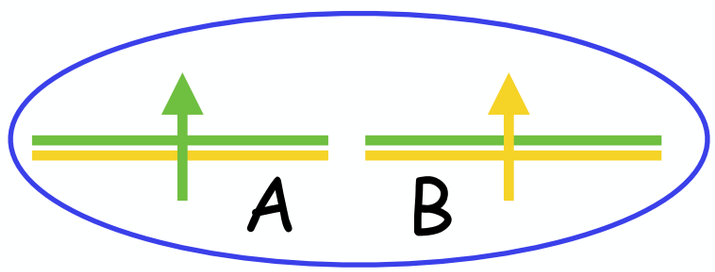
Kugel-Khomskii super-exchange

$$\hat{H}_{\mathrm{SE}} = 2\Gamma_{-+}\left[\boldsymbol{S}^A\cdot\boldsymbol{S}^B-\frac{1}{4}\right]\left[O_z^A\,O_z^B+\frac{1}{4}\right]+2\Gamma_{+-}\left[\frac{1}{4}+S_z^A\,S_z^B\right]\left[\boldsymbol{O}^A\cdot\boldsymbol{O}^B-\frac{1}{4}\right]$$
$$+2\Gamma_{--}\left[\left(\boldsymbol{S}^A\cdot\boldsymbol{S}^B-S_z^A\,S_z^B\right)\left(\boldsymbol{O}^A\cdot\boldsymbol{O}^B-O_z^A\,O_z^B\right)-\left(S_z^A\,S_z^B-\frac{1}{4}\right)\left(O_z^A\,O_z^B-\frac{1}{4}\right)\right]$$

$$\Gamma_{-+}=\frac{4t^2}{U}\qquad \Gamma_{+-}=\frac{4t^2}{U-3J}\qquad \Gamma_{--}=-\frac{4t^2}{U-2J}$$

FM, AFO



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orbital ordering from super-exchange

Crystal structure and magnetic properties of substances with orbital degeneracy

K. I. Kugel' and D. I. Khomskiĭ
P. N. Lebedev Physics Institute
(Submitted November 13, 1972)
Zh. Eksp. Teor. Fiz. **64**, 1429-1439 (April 1973)

$KCuF_3$

$LaMnO_3$

$$H = -\boxed{\sum_{ii'}\sum_{mm'}\sum_{\sigma} t^{ii'}_{mm'} c^{\dagger}_{im\sigma} c_{i'm'\sigma}} + \boxed{U \sum_{i} \frac{1}{2} \sum_{m\sigma \neq m'\sigma'} n_{im\sigma} n_{im'\sigma'}}$$

perturbation *dominant*

small t/U limit (Mott insulator)

e_g degenerate orbitals

super-exchange Hamiltonian

$$H^{ii'}_{SE} = J_{SS} S_i \cdot S_{i'} + J_{OO} O_i O_{i'} + J_{SO} (O_i O_{i'})(S_i \cdot S_{i'})$$

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

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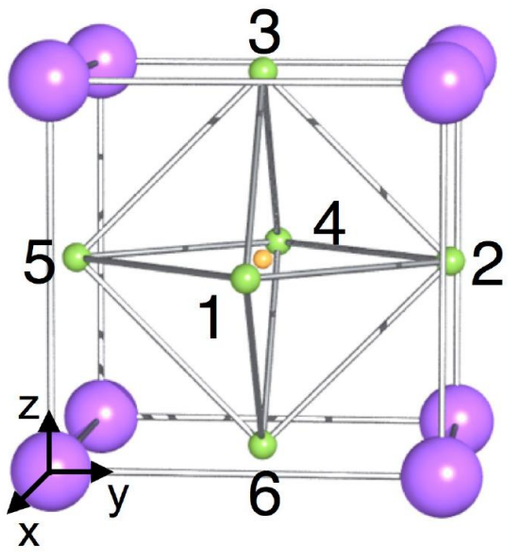
paradigmatic cases: cubic e_g perovskites

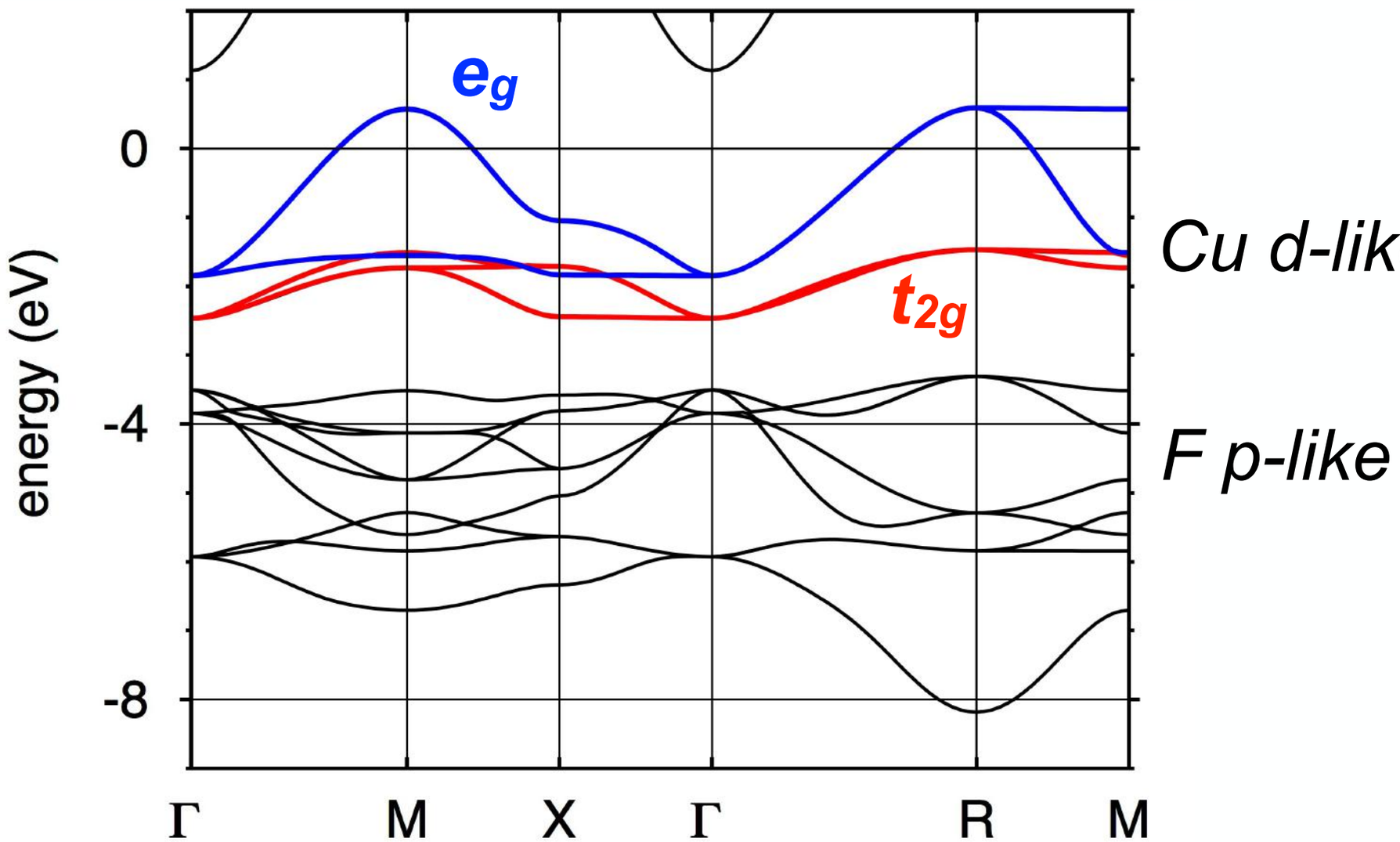
$KCuF_3$ $(t_{2g}^6 e_g^3)$ & $LaMnO_3(t_{2g}^3 e_g^1)$

ideal cubic $KCuF_3$

what are the hoppings here?



$t_{2g}^6 e_g^3$



Cu d-like

F p-like

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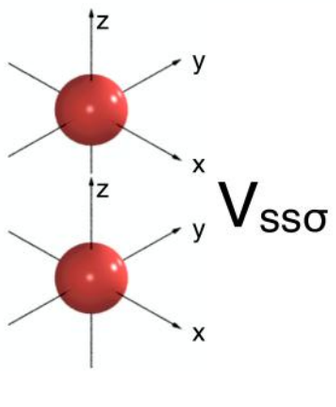
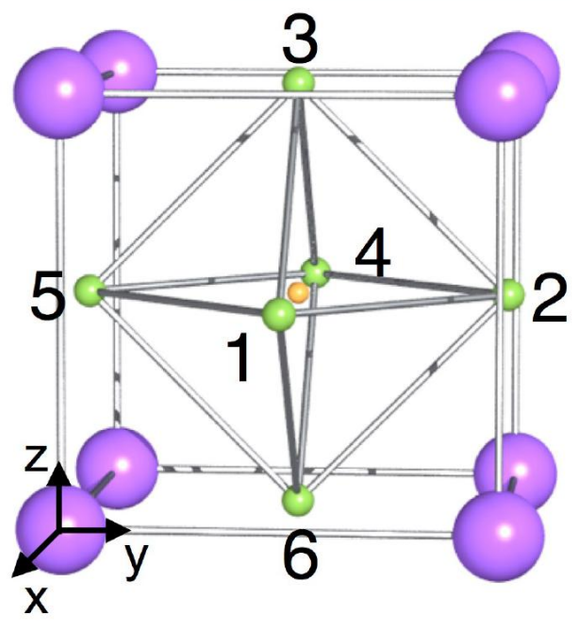
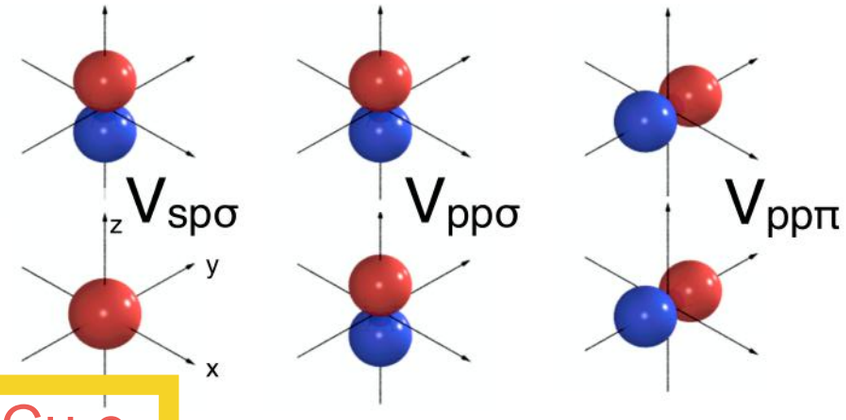
tight-binding two-center integrals

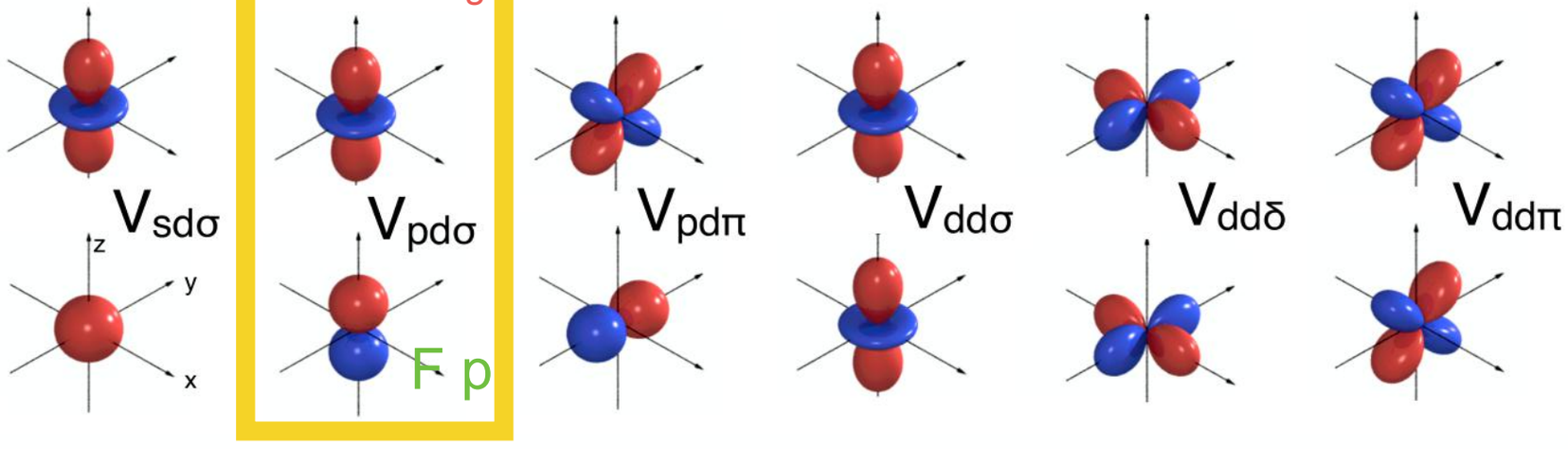
$$t^{i,i'}_{lm,l'm'} = -\int d\mathbf{r}\, \overline{\psi_{lm}}(\mathbf{r}-\mathbf{T}_i)\big(\Delta v(\mathbf{r}-\mathbf{T}_j)\big)\psi_{l'm'}(\mathbf{r}-\mathbf{T}_{i'}).$$

Cu e_g F p









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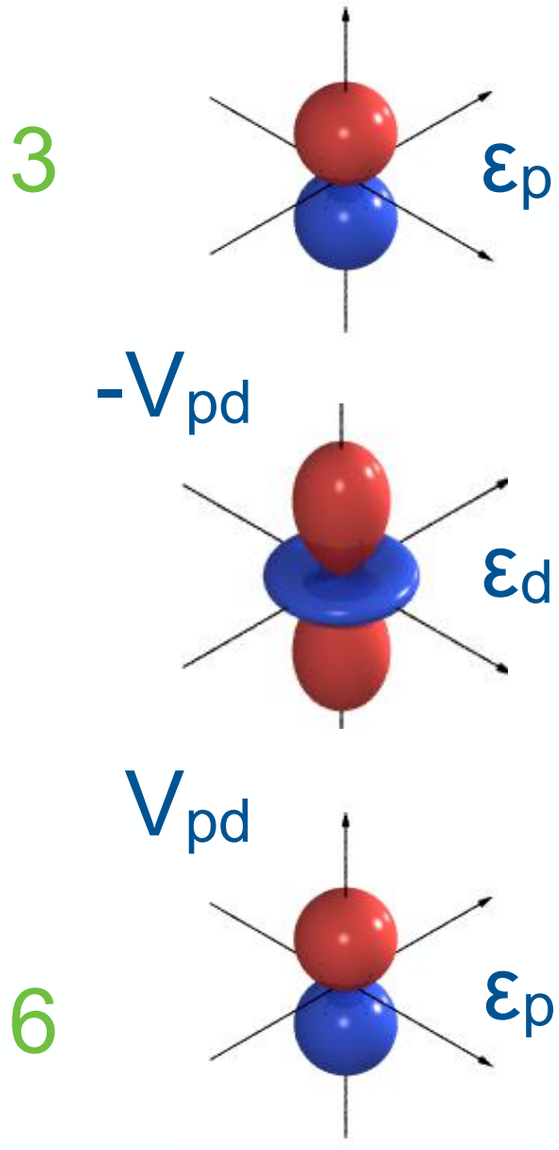
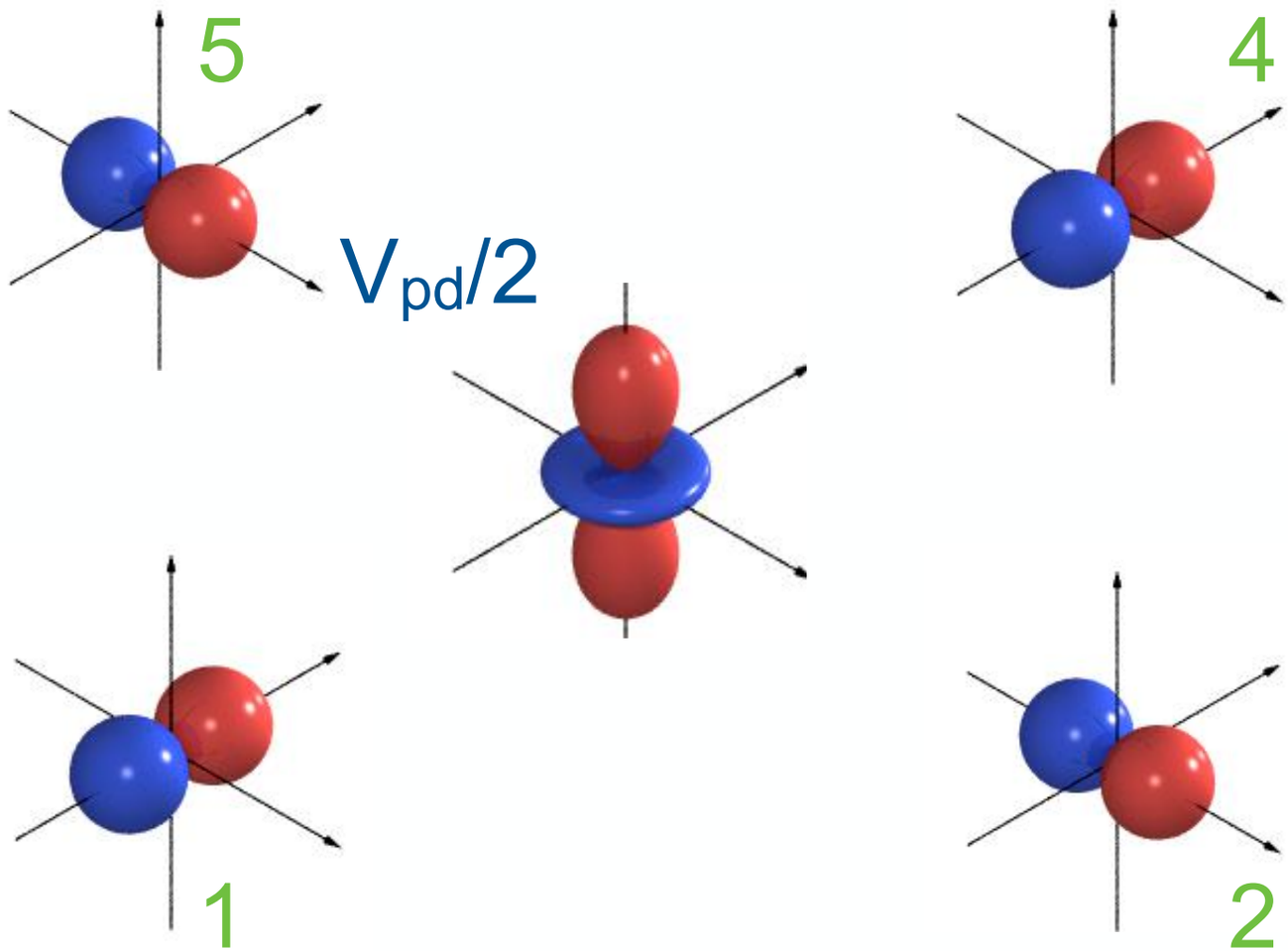
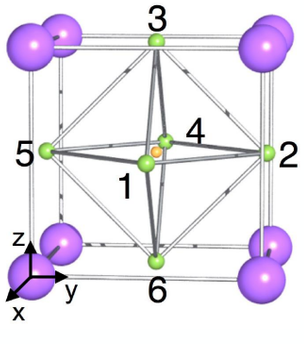
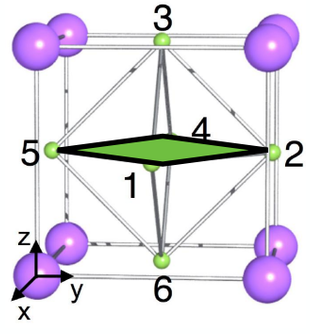
tight-binding model









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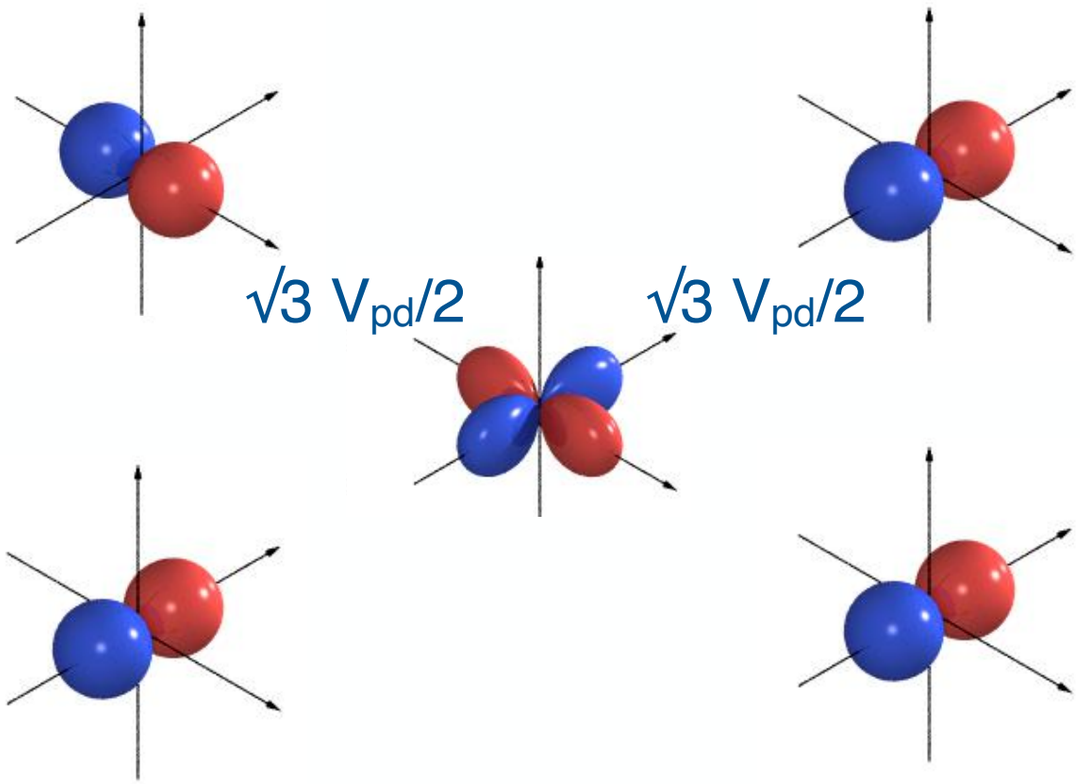
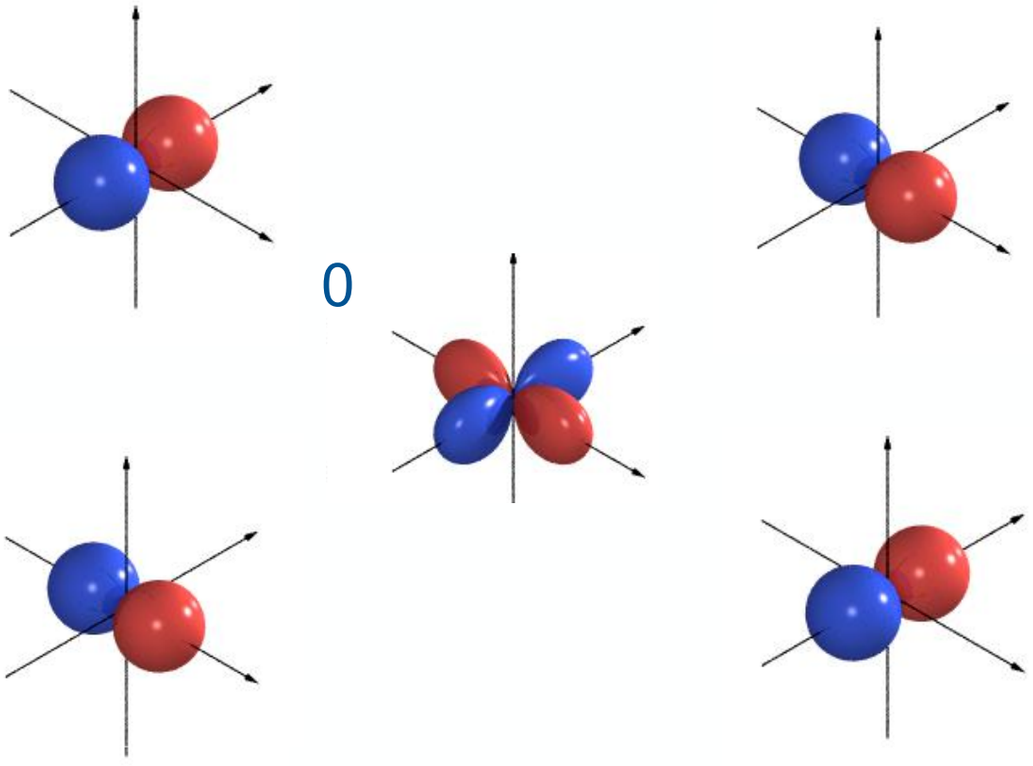
tight-binding model e_g bands



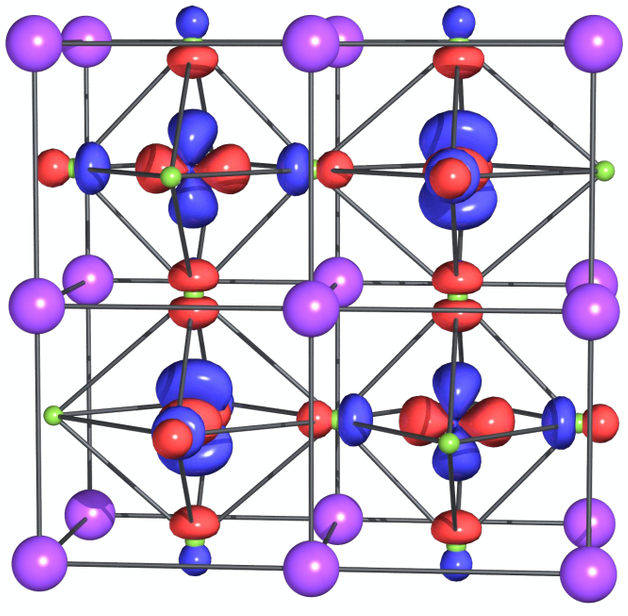


e_g-p tight-binding model

$H^{\mathrm{TB}}_{e_g}$	$\lvert \boldsymbol{k}\ z^c\rangle$	$\lvert \boldsymbol{k}\ x^a\rangle$	$\lvert \boldsymbol{k}\ y^b\rangle$	$\lvert \boldsymbol{k}\ 3z^2-r^2\rangle$	$\lvert \boldsymbol{k}\ x^2-y^2\rangle$
$\lvert \boldsymbol{k}\ z^c\rangle$	ε_p	0	0	$-2V_{pd\sigma}s_z$	0
$\lvert \boldsymbol{k}\ x^a\rangle$	0	ε_p	0	$V_{pd\sigma}s_x$	$-\sqrt{3}V_{pd\sigma}s_x$
$\lvert \boldsymbol{k}\ y^b\rangle$	0	0	ε_p	$V_{pd\sigma}s_y$	$\sqrt{3}V_{pd\sigma}s_y$
$\lvert \boldsymbol{k}\ 3z^2-r^2\rangle$	$-2V_{pd\sigma}\overline{s}_z$	$V_{pd\sigma}\overline{s}_x$	$V_{pd\sigma}\overline{s}_y$	ε_d	0
$\lvert \boldsymbol{k}\ x^2-y^2\rangle$	0	$-\sqrt{3}V_{pd\sigma}\overline{s}_x$	$\sqrt{3}V_{pd\sigma}\overline{s}_y$	0	ε_d

$$H^{\varepsilon}_{dd} = H_{dd} - H_{dp}(H_{pp} - \varepsilon I_{pp})^{-1} H_{pd},$$

$$s_\alpha = e^{-ik_\alpha a}\sin(k_\alpha a/2)$$



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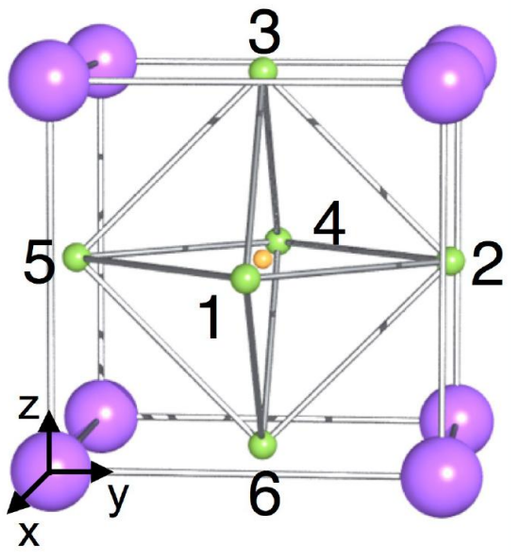
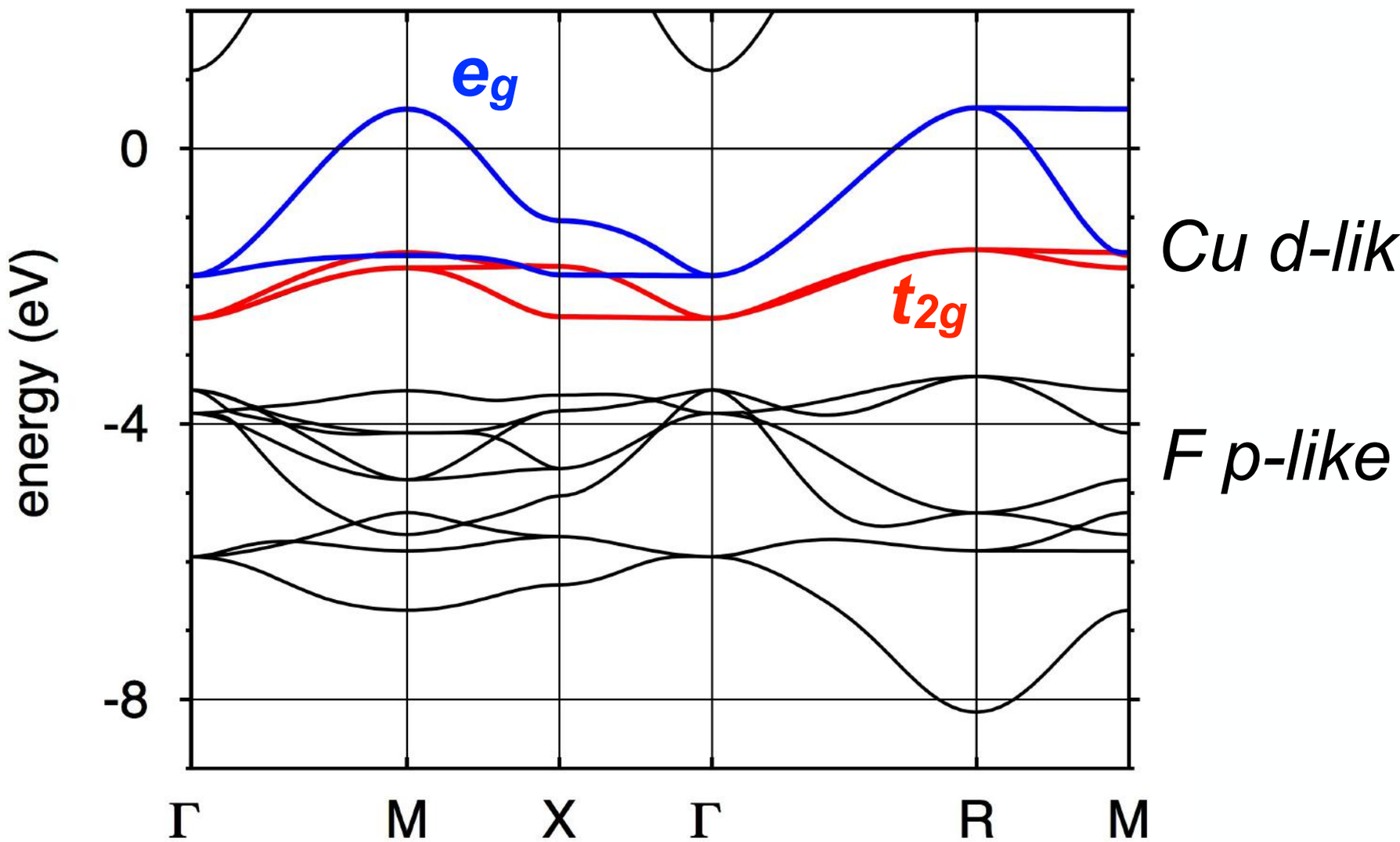
ideal cubic $KCuF_3$

what are the hoppings here?



$t_{2g}^6 e_g^3$



Cu d-like

F p-like

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effective d model

effective d-d hopping integrals

(missing: longer range hoppings) *Cu e_g-like*

$H^{\varepsilon}_{e_g}$	$\lvert \boldsymbol{k}\ 3z^2-r^2\rangle_\varepsilon$	$\lvert \boldsymbol{k}\ x^2-y^2\rangle_\varepsilon$
$\lvert \boldsymbol{k}\ 3z^2-r^2\rangle_\varepsilon$	$\varepsilon'_d-2t^\sigma_\varepsilon[\frac{1}{4}(\cos k_x a+\cos k_y a)+\cos k_z a]$	$2t^\sigma_\varepsilon[\frac{\sqrt{3}}{4}(\cos k_x a-\cos k_y a)]$
$\lvert \boldsymbol{k}\ x^2-y^2\rangle_\varepsilon$	$2t^\sigma_\varepsilon[\frac{\sqrt{3}}{4}(\cos k_x a-\cos k_y a)]$	$\varepsilon'_d-2t^\sigma_\varepsilon[\frac{3}{4}(\cos k_x a+\cos k_y a)]$

$$t^\sigma_\varepsilon=\frac{V^2_{pd\sigma}}{\varepsilon-\varepsilon_p},\quad \varepsilon'_d=\varepsilon_d+3t^\sigma_\varepsilon.$$

$$t^{i,i\pm\hat{z}}_{mm'}=t_\varepsilon\begin{pmatrix}0 & 0\\ 0 & 1\end{pmatrix}\qquad t^{i,i\pm\hat{x}}_{mm'}=t_\varepsilon\begin{pmatrix}\frac{3}{4} & \frac{\sqrt{3}}{4}\\ \frac{\sqrt{3}}{4} & \frac{1}{4}\end{pmatrix}\qquad t^{i,i\pm\hat{y}}_{mm'}=t_\varepsilon\begin{pmatrix}\frac{3}{4} & -\frac{\sqrt{3}}{4}\\ -\frac{\sqrt{3}}{4} & \frac{1}{4}\end{pmatrix}$$

$3z^2$-r^2

x^2-y^2

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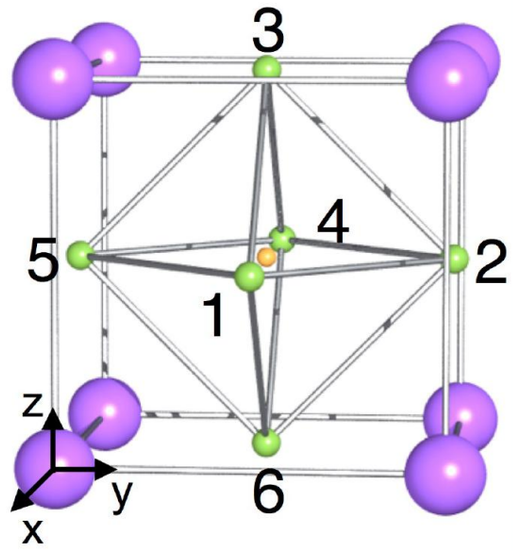
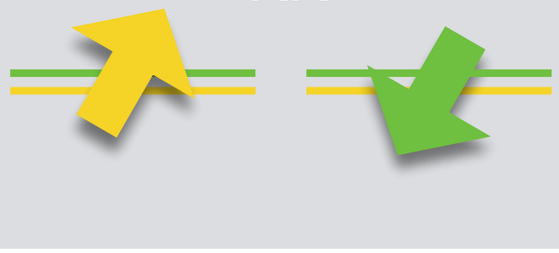


Kugel-Khomskii super-exchange

KK

e_g^1



$$t^{i,i\pm\hat{z}}_{mm'} = t_\varepsilon \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

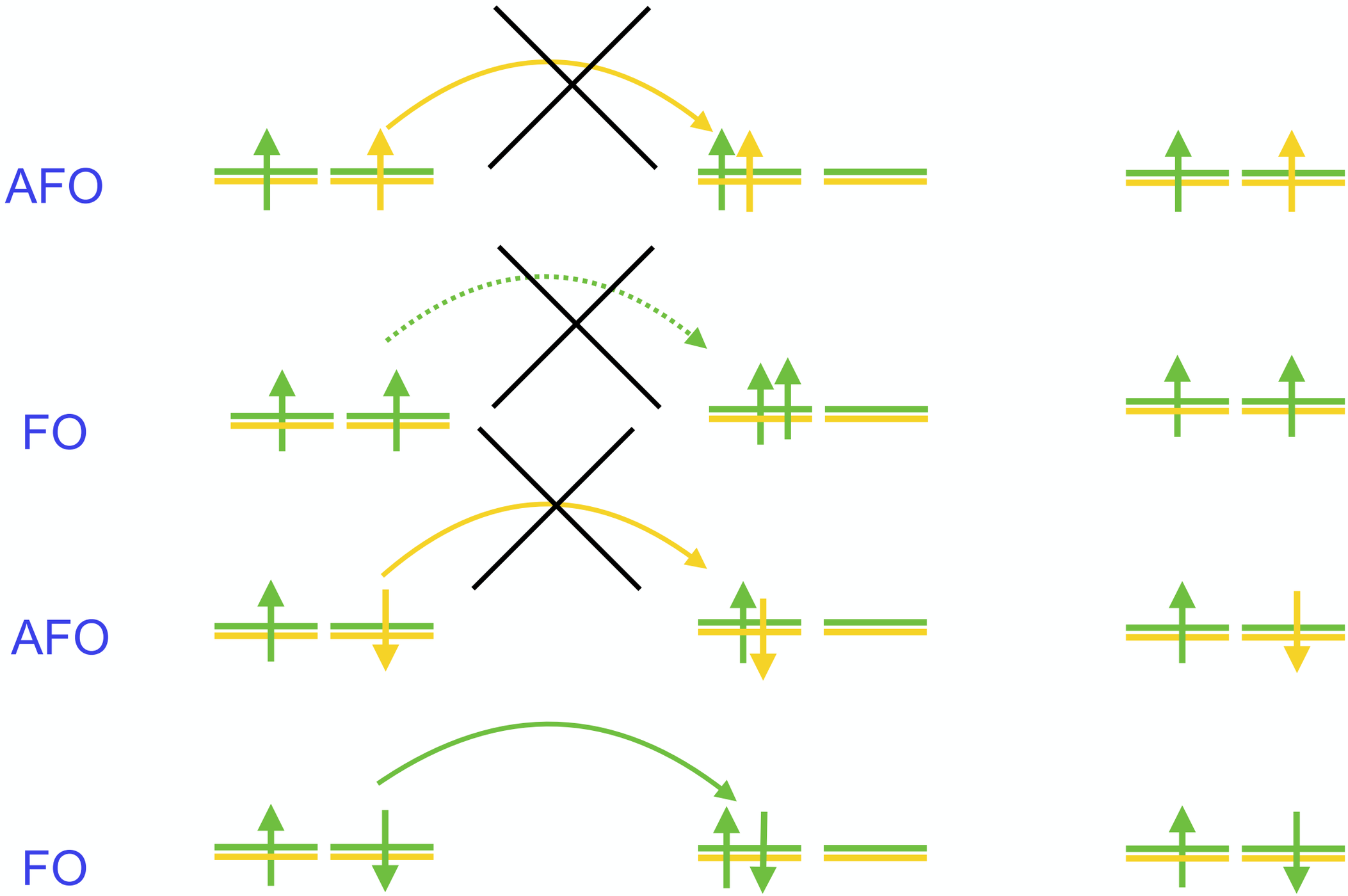
$3z^2\text{-}r^2$

$x^2\text{-}y^2$

$$t^{i,i\pm\hat{x}}_{mm'} = t_\varepsilon \begin{pmatrix} \frac{3}{4} & \frac{\sqrt{3}}{4} \\ \frac{\sqrt{3}}{4} & \frac{1}{4} \end{pmatrix}$$

$$t^{i,i\pm\hat{y}}_{mm'} = t_\varepsilon \begin{pmatrix} \frac{3}{4} & -\frac{\sqrt{3}}{4} \\ -\frac{\sqrt{3}}{4} & \frac{1}{4} \end{pmatrix}$$

Kugel-Khomskii super-exchange: z dir



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Kugel-Khomskii super-exchange (*J=0*)

$$\hat{H}^{\hat{z}}_{\mathrm{SE}} = \frac{\Gamma}{2} \sum_{ii'} \left[\boldsymbol{S}^i \cdot \boldsymbol{S}^{i'} - \frac{n_i n_{i'}}{4} \right] \left[O^i_z - \frac{n_i}{2} \right] \left[O^{i'}_z - \frac{n_{i'}}{2} \right] + \frac{1}{2} \left[O^i_z O^{i'}_z - \frac{n_i n_{i'}}{4} \right],$$

other dirs: rotate axis

$$O^i_z \underbrace{\rightarrow}_{\hat{z}\rightarrow\hat{x}} -\frac{1}{2} O^i_z - \frac{\sqrt{3}}{2} O^i_x$$

$$O^i_z \underbrace{\rightarrow}_{\hat{z}\rightarrow\hat{y}} -\frac{1}{2} O^i_z + \frac{\sqrt{3}}{2} O^i_x$$

same result for e_g^3 configuration

General Super Exchange Hamiltonians

PHYSICAL REVIEW B **105**, 115104 (2022)

General superexchange Hamiltonians for magnetic and orbital physics in e_g and t_{2g} systems

Xue-Jing Zhang,[1] Erik Koch,[1,2] and Eva Pavarini[1,2,*]

[1]*Institute for Advanced Simulation, Forschungszentrum Jülich, 52425 Jülich, Germany*
[2]*JARA High-Performance Computing, 52062 Aachen, Germany.*

(Received 6 December 2021; accepted 16 February 2022; published 3 March 2022)

Material-specific super-exchange Hamiltonians are the key to studying spin and orbital physics in strongly correlated materials. Recently, via an irreducible-tensor operator representation, we derived the orbital superexchange Hamiltonian for t_{2g}^1 perovskites and successfully used it, in combination with many-body approaches, to explain orbital physics in these systems. Here, we generalize our method to e_g^n and t_{2g}^n systems at arbitrary integer filling n, including both spin and orbital interactions. The approach is suitable for numerical implementations based on *ab initio* hopping parameters and realistic screened Coulomb interactions and allows for a systematic exploration of superexchange energy surfaces in a realistic context.

DOI: 10.1103/PhysRevB.105.115104

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TABLE I. Key tensor elements for the e_g^1 and e_g^3 configuration and spin ranks $q = 0$ and 1. The elements for the e_g^3 configuration are obtained setting a minus in front of all linear terms, i.e., those for which $r = 0$, $r' \neq 0$, or $r' = 0$, $r \neq 0$. The elements for imaginary tensors must be multiplied by i (linear terms, involving a single operator) or $i \times i$ (for products of two operators). The prefactors are obtained from the weights: $v_0 = \frac{1}{2}(f_1 - f_{-1})$, $v_1 = \frac{1}{2}(f_1 + f_{-1})$, $v_2 = \frac{1}{4}(3f_{-3} + f_{-1})$, and $v_3 = \frac{1}{2}(3f_{-3} - f_{-1})$. The rest of the matrix elements are given by symmetry: $D^{ij}_{r'\mu',r\mu} = s_\mu s_{\mu'} \overline{D^{ji}_{r\mu,r'\mu'}}$, where $s_\mu = 1$ is for real operators and $s_\mu = -1$ for imaginary ones. Since the model is rotationally invariant for spins, $q = 1$, $v = x, y, z$ elements are identical. They can be obtained from the table for $q = 0$, replacing $\mathcal{V}_0 \longrightarrow \tilde{\mathcal{V}}_0$, $\mathcal{V}_1 \longrightarrow \tilde{\mathcal{V}}_1$, $\mathcal{V}_2 \longrightarrow \tilde{\mathcal{V}}_2$, and $\mathcal{V}_3 \longrightarrow \tilde{\mathcal{V}}_3$. All hopping integrals are defined as $t^{i,j}_{m,m'}$ and are assumed to be real, as typically is the case in the absence of spin-orbit interaction.

r μ	r' μ'	e_g^1	e_g^3	$D^{ij}_{r\mu,r'\mu'} \times U/2$
0 s	0 s	$-\mathcal{V}_0$	$-\mathcal{V}_0$	$\left(t^2_{3z^2-r^2,3z^2-r^2} + t^2_{x^2-y^2,x^2-y^2} + t^2_{3z^2-r^2,x^2-y^2} + t^2_{x^2-y^2,3z^2-r^2}\right)$
0 s	1 z	$-\mathcal{V}_1$	$+\mathcal{V}_1$	$\left(t^2_{3z^2-r^2,3z^2-r^2} - t^2_{x^2-y^2,x^2-y^2} + t^2_{x^2-y^2,3z^2-r^2} - t^2_{3z^2-r^2,x^2-y^2}\right)$
0 s	1 x	$-\mathcal{V}_1$	$+\mathcal{V}_1$	$2(t_{3z^2-r^2,3z^2-r^2}t_{3z^2-r^2,x^2-y^2} + t_{x^2-y^2,x^2-y^2}t_{x^2-y^2,3z^2-r^2})$
1 z	1 z	$+\mathcal{V}_2$	$+\mathcal{V}_2$	$\left(t^2_{3z^2-r^2,3z^2-r^2} + t^2_{x^2-y^2,x^2-y^2} - t^2_{3z^2-r^2,x^2-y^2} - t^2_{x^2-y^2,3z^2-r^2}\right)$
1 x	1 x	$+\mathcal{V}_2$	$+\mathcal{V}_2$	$2(t_{3z^2-r^2,3z^2-r^2}t_{x^2-y^2,x^2-y^2} + t_{3z^2-r^2,x^2-y^2}t_{x^2-y^2,3z^2-r^2})$
1 z	1 x	$+\mathcal{V}_2$	$+\mathcal{V}_2$	$2(t_{3z^2-r^2,3z^2-r^2}t_{3z^2-r^2,x^2-y^2} - t_{x^2-y^2,x^2-y^2}t_{x^2-y^2,3z^2-r^2})$
1 y	1 y	$+\mathcal{V}_3$	$+\mathcal{V}_3$	$2(t_{3z^2-r^2,3z^2-r^2}t_{x^2-y^2,x^2-y^2} - t_{3z^2-r^2,x^2-y^2}t_{x^2-y^2,3z^2-r^2})$
q = 0		$\mathcal{V}_0 = \frac{v_1+2v_2}{2} = \frac{f_1+2f_{-1}+3f_{-3}}{4}$, $\mathcal{V}_1 = \frac{v_1}{2} = \frac{f_1+f_{-1}}{4}$, $\mathcal{V}_2 = \frac{2v_2-v_1}{2} = \frac{3f_{-3}-f_1}{4}$, $\mathcal{V}_3 = \frac{v_0+v_3}{2} = \frac{3f_{-3}-2f_{-1}+f_1}{4}$		
q = 1		$\tilde{\mathcal{V}}_0 = -\frac{f_1+2f_{-1}-f_{-3}}{4}$, $\tilde{\mathcal{V}}_1 = -\mathcal{V}_1$, $\tilde{\mathcal{V}}_2 = \frac{f_1+f_{-3}}{4}$, $\tilde{\mathcal{V}}_3 = \frac{f_{-3}+2f_{-1}-f_1}{4}$		

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orbital ordering from super-exchange

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$KCuF_3$

$LaMnO_3$

$$H = -\sum_{ii'}\sum_{mm'}\sum_{\sigma} t^{ii'}_{mm'} c^{\dagger}_{im\sigma} c_{i'm'\sigma} + U \sum_{i} \frac{1}{2} \sum_{m\sigma \neq m'\sigma'} n_{im\sigma} n_{im'\sigma'}$$

m: degenerate orbitals

small t/U limit (Mott insulator)

$$H^{ii'}_{SE} = J_{SS} S_i \cdot S_{i'} + J_{OO} O_i O_{i'} + J_{SO} (O_i O_{i'})(S_i \cdot S_{i'})$$

super-exchange Hamiltonian

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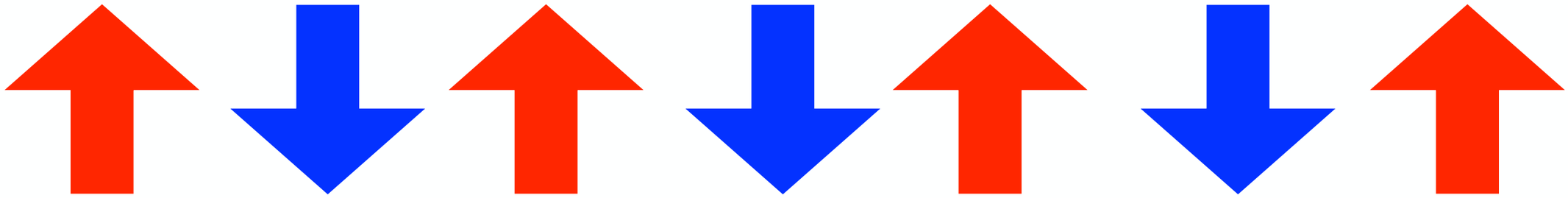
spin ordering via super-exchange



prediction: Néel (1932)

MnO

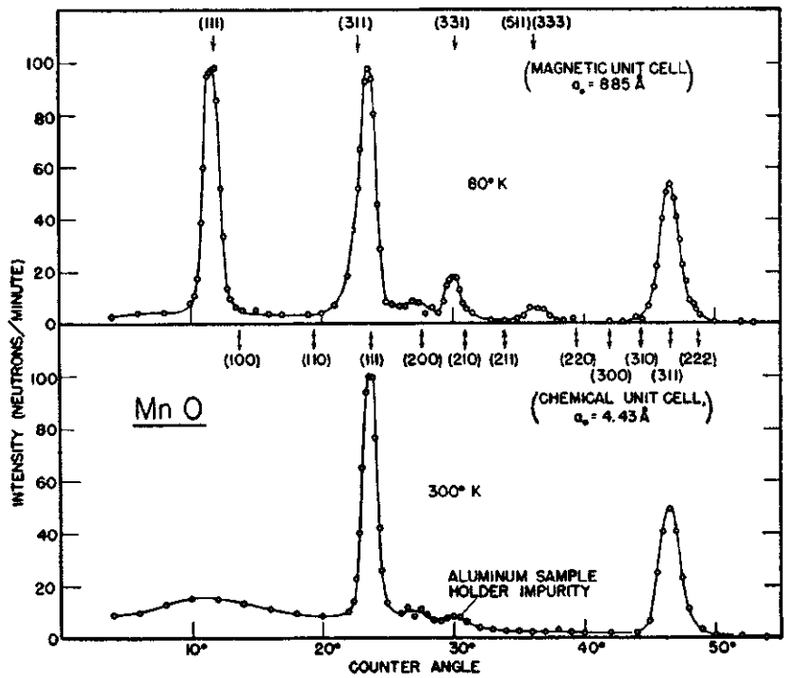


FIG. 1. Neutron diffraction patterns for MnO at room temperature and at 80°K.

T=300K

T=80K

neutron scattering: Shull and Smart (1949)

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super-exchange Hamiltonian

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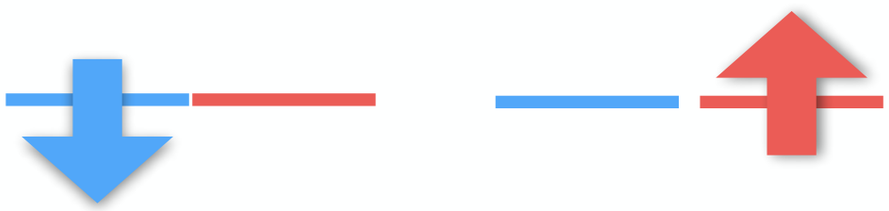
analogy (S=1/2 case)

spin degrees of freedom



effective S=1/2 **spin**

spin 1/2 operators S_x S_y S_z

orbital degrees of freedom

effective O=1/2 **pseudospin**

pseudospin 1/2 operators O_x O_y O_z

spin ordering

orbital ordering

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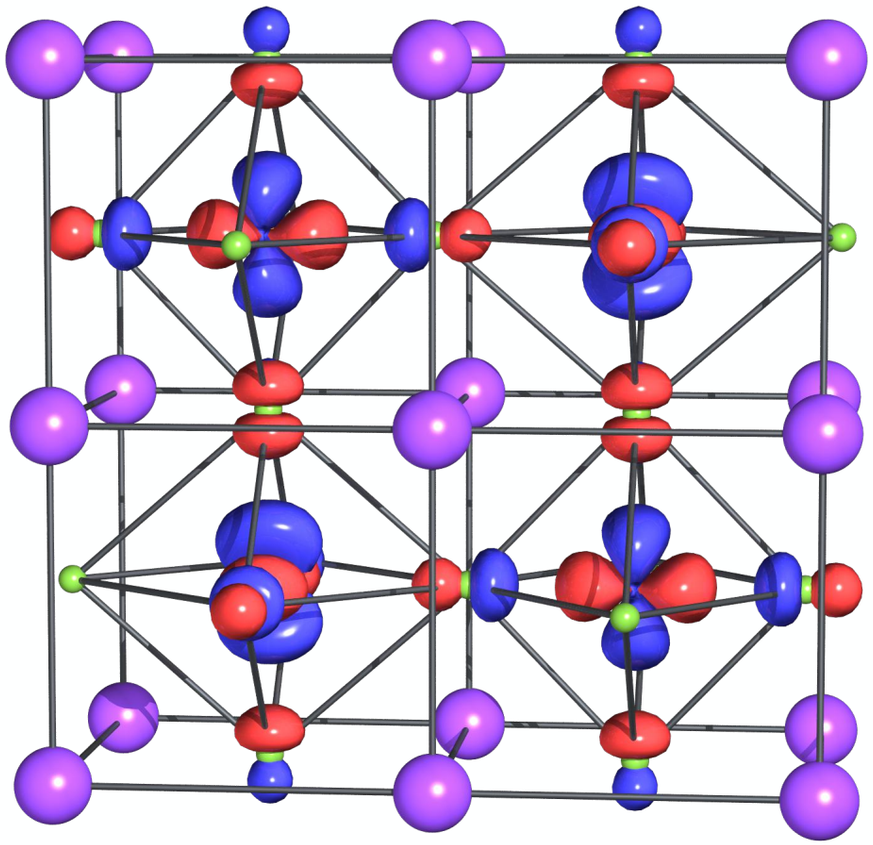
orbital ordering: what is the hallmark?

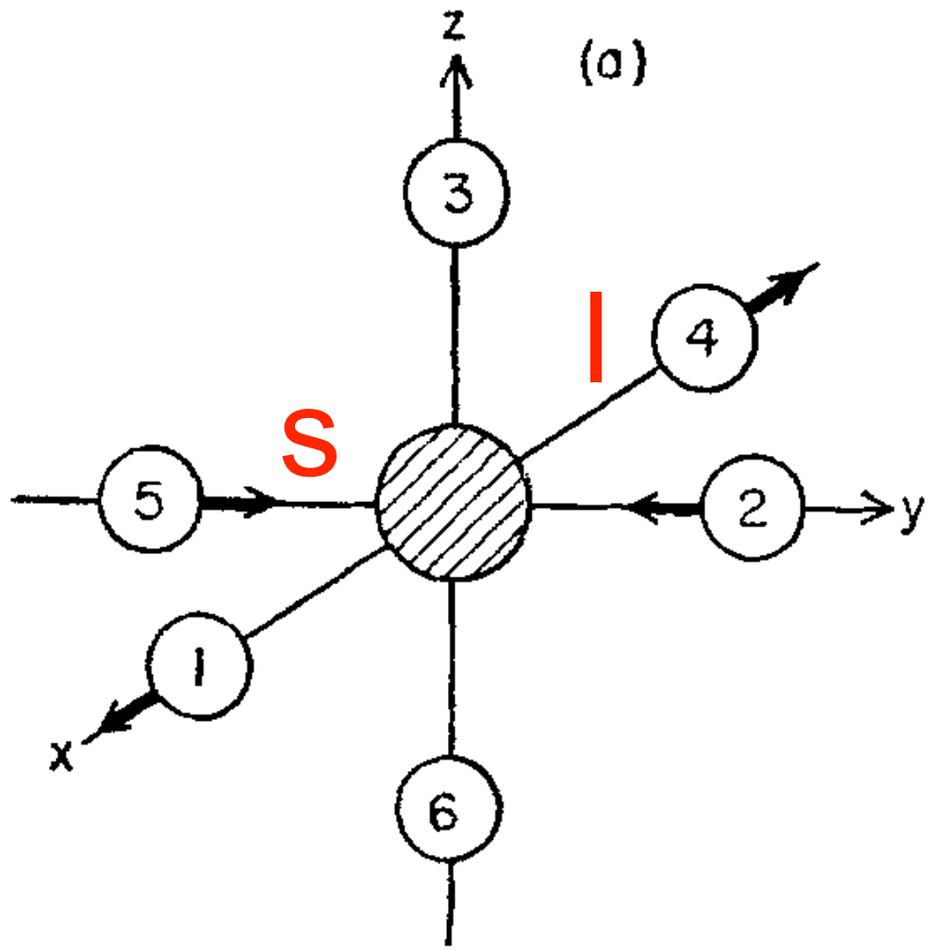
co-operative Jahn-Teller distortion

partially filled e_g levels

$KCuF_3$



$t_{2g}^6 e_g^3$



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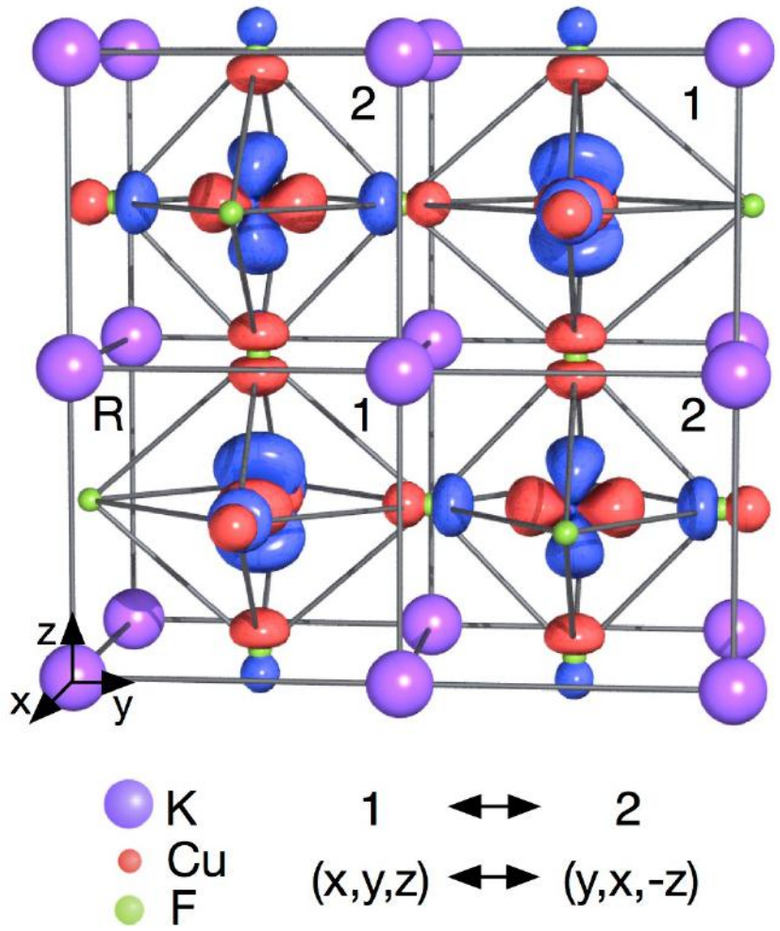
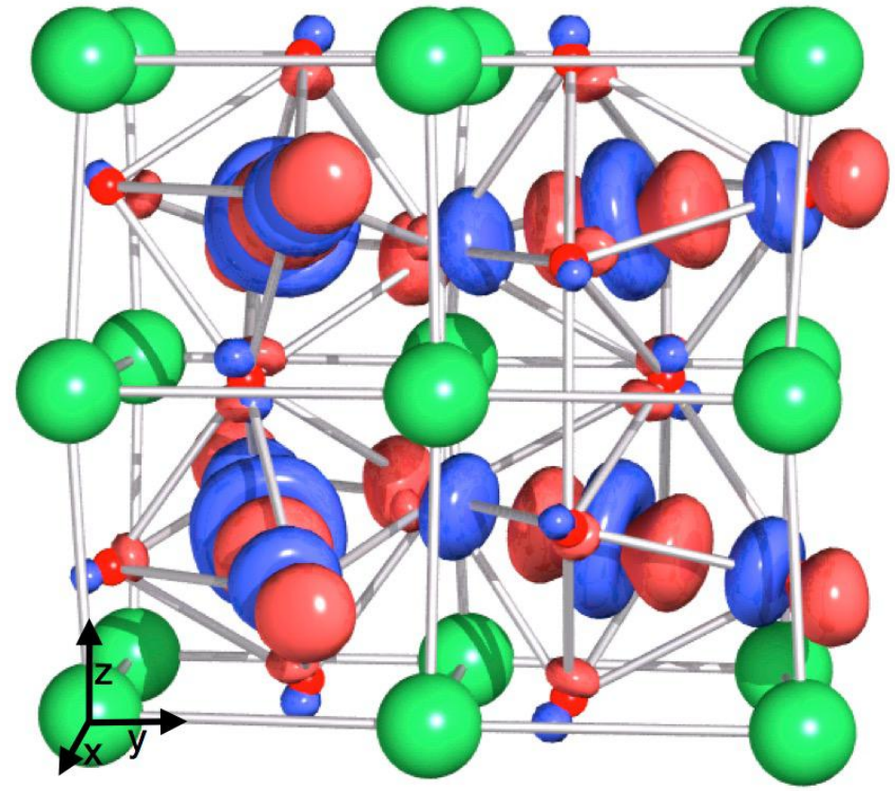
the Jahn-Teller distortion!

$KCuF_3$



$LaMnO_3$



long-range ordering of occupied/empty **local orbitals**
in strongly correlated systems (Mott insulators)
with orbital degrees of freedom

Jahn-Teller theorem

(electron-lattice coupling)

Stability of Polyatomic Molecules in Degenerate Electronic States

I—Orbital Degeneracy

By H. A. Jahn, *Davy-Faraday Laboratory, The Royal Institution*
and E. Teller, *George Washington University, Washington, D.C.**

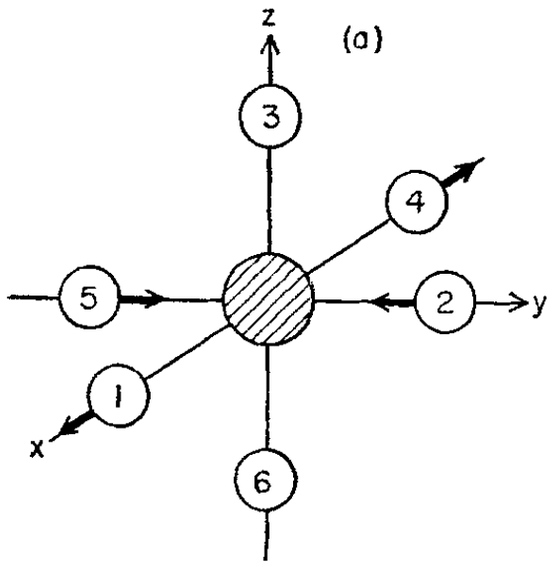
(*Communicated by F. G. Donnan, F.R.S.—Received* 17 *February* 1937)

Introduction

In the following we investigate the conditions under which a polyatomic molecule can have a stable equilibrium configuration when its electronic state has orbital degeneracy, i.e. degeneracy not arising from the spin. We shall show that stability and degeneracy are not possible simultaneously unless the molecule is a linear one, i.e. unless all the nuclei in the equilibrium configuration lie on a straight line. We shall see also that the instability is only slight if the degeneracy is due solely to electrons having no great influence on the binding of the molecule.

see lecture of Arnout Ceulemans

lattice distortions generates order



The Normal Mode
Q_2 (Q_2 >0)

Crystal Distortion in Magnetic Compounds

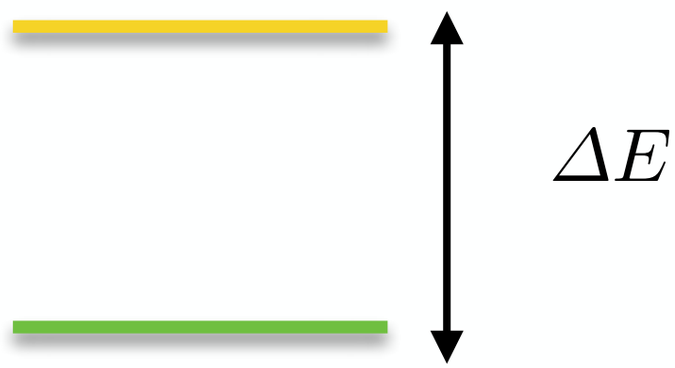
JUNJIRO KANAMORI*
Institute for the Study of Metals, University of Chicago, Chicago 37, Illinois

The crystal distortion which arises from the Jahn-Teller effect is discussed in several examples. In the case of compounds containing Cu^{2+} or Mn^{3+} at octahedral sites, the lowest orbital level of these ions is doubly degenerate in the undistorted structure, and there is no spin-orbit coupling in this level. It is shown that, introducing a fictitious spin to specify the degenerate orbital states, we can discuss the problem by analogy with the magnetic problems. The "ferromagnetic" and "antiferromagnetic" distortions are discussed in detail. The transition from the distorted to the undistorted structure is of the first kind for the former and of the second kind for the latter. Higher approximations are discussed briefly. In compounds like FeO, CoO, and $CuCr_2O_4$, the lowest orbital level is triply degenerate, and the spin-orbit coupling is present in this level. In this case the distortion is dependent on the magnitude of the spin-orbit coupling relative to the strength of the Jahn-Teller effect term. The distortion at absolute zero temperature and its temperature dependence are discussed.

J. Appl. Phys. 31, S14–S23 (1960)

electron-phonon coupling

static crystal-field splitting (symmetry lowering)



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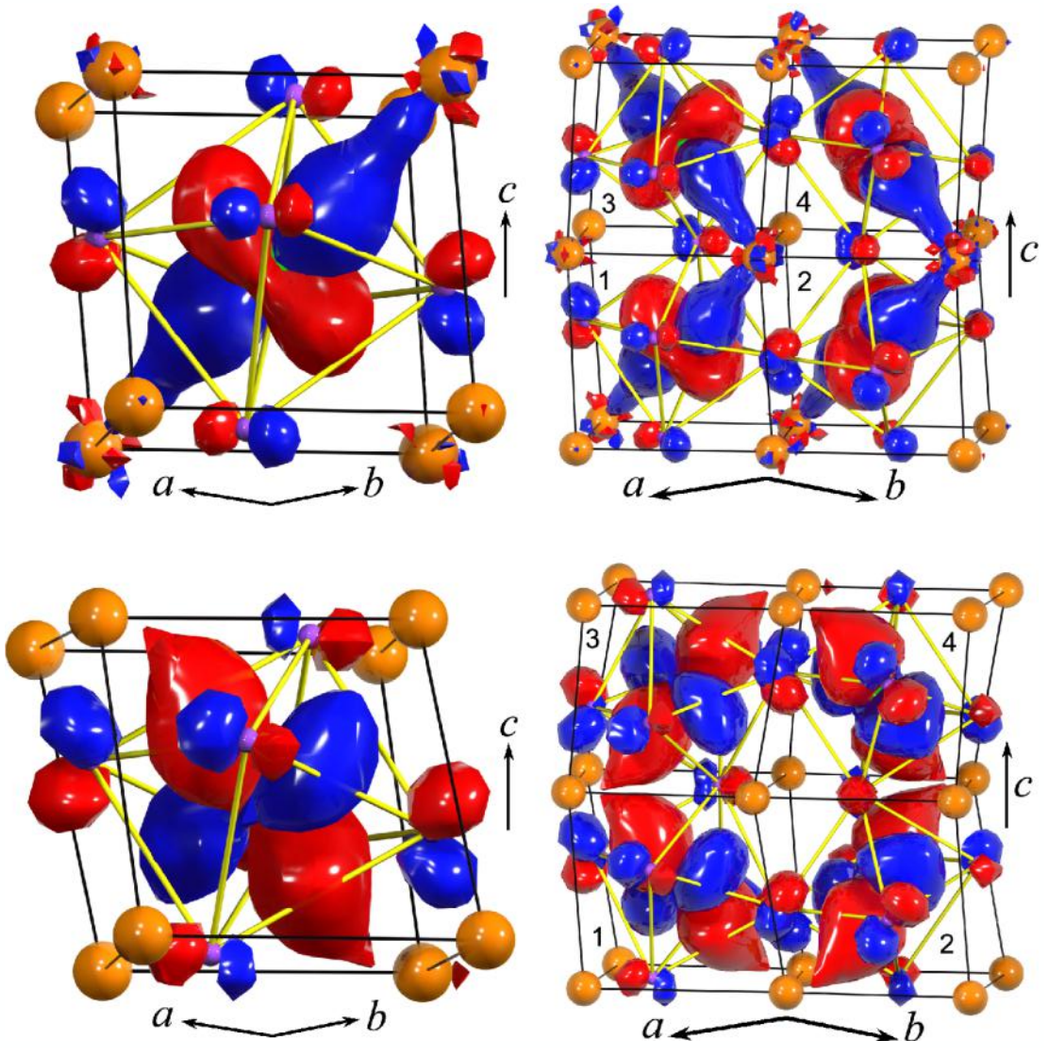
do we need a large crystal-field?

VOLUME 92, NUMBER 17 PHYSICAL REVIEW LETTERS week ending 30 APRIL 2004

Mott Transition and Suppression of Orbital Fluctuations in Orthorhombic $3d^1$ Perovskites

E. Pavarini,[1] S. Biermann,[2] A. Poteryaev,[3] A. I. Lichtenstein,[3] A. Georges,[2] and O. K. Andersen[4]

$LaTiO_3$



$YTiO_3$

t_{2g}^1

LDA+DMFT 770 K

Δ=200-300 meV

No! A 100 meV crystal-field is enough (W~3 eV)

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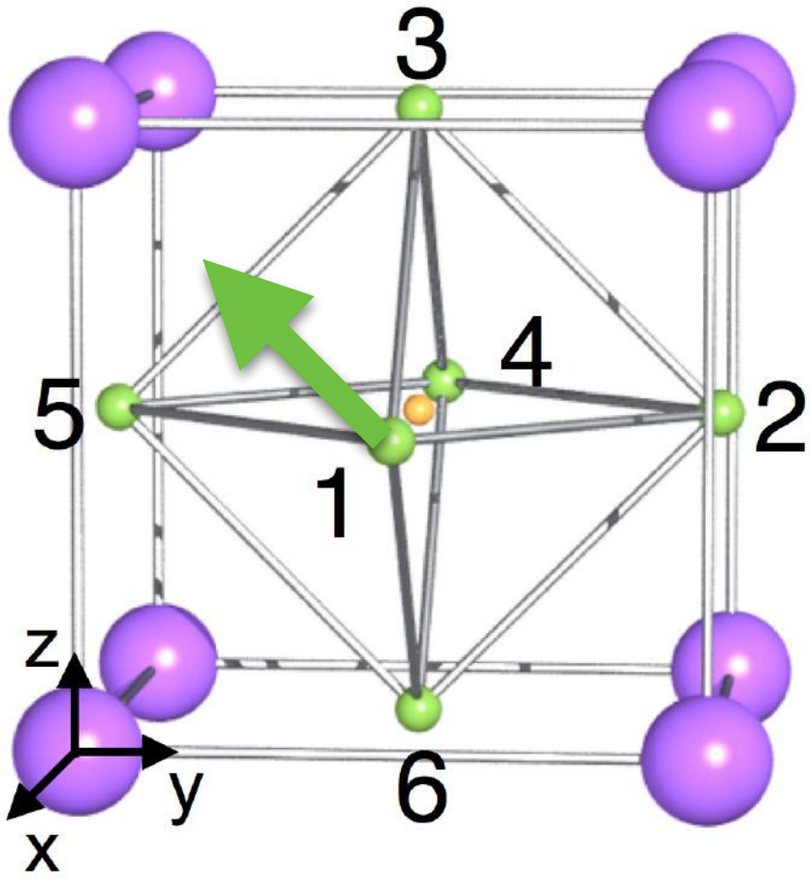
which phononic modes?



displacement vector

6+1=7 atoms, every atom represented by a vector

21 degrees of freedom

-6 (three translations and three rotations)

15 modes

(group theory)

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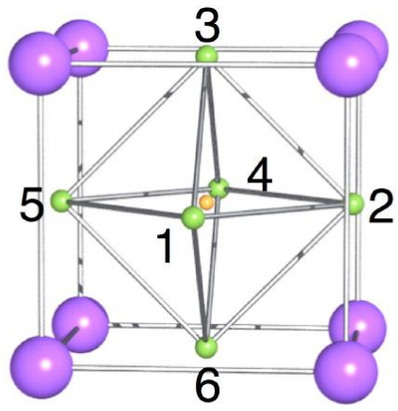
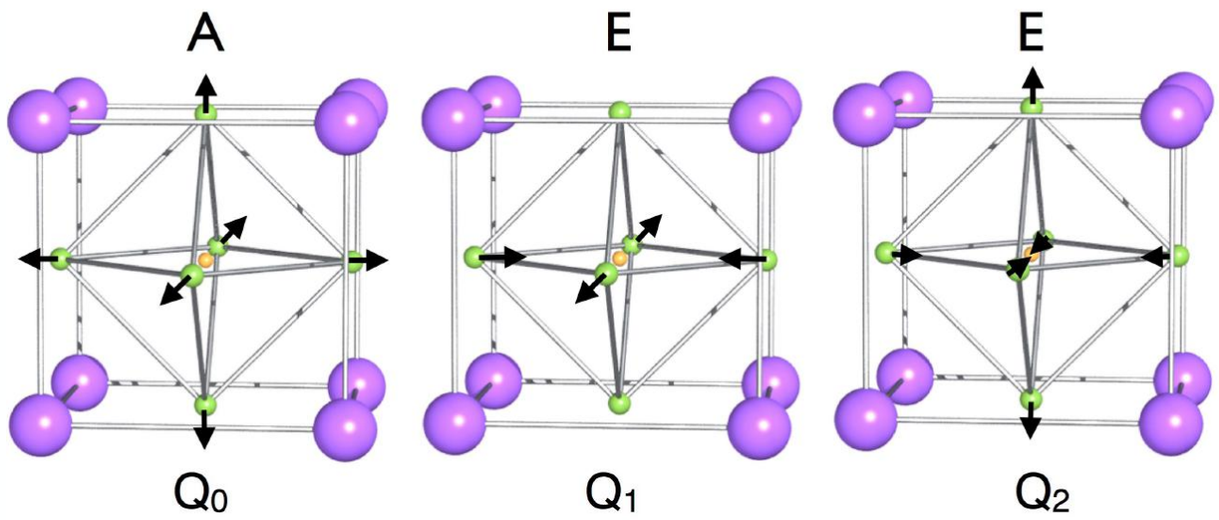
which phononic modes?

modes A and E couple to e_g





$$\hat{U}_n^{\mathrm{PH}} = \frac{1}{2} C_E \left(q_1^2 + q_2^2\right) \hat{I}$$

(group theory)

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electron-phonon coupling E_g with e_g

total energy $E_g \times e_g$

$$\hat{U}(q_1, q_2) = \hat{U}^{\mathrm{JT}} + \hat{U}_n^{\mathrm{PH}} = \lambda \begin{pmatrix} q_2 & q_1 \\ q_1 & -q_2 \end{pmatrix} + \frac{1}{2} C_E \, (q_1^2 + q_2^2) \, \hat{I}$$

$$q_2 = -q \cos\theta, q_1 = -q \sin\theta$$

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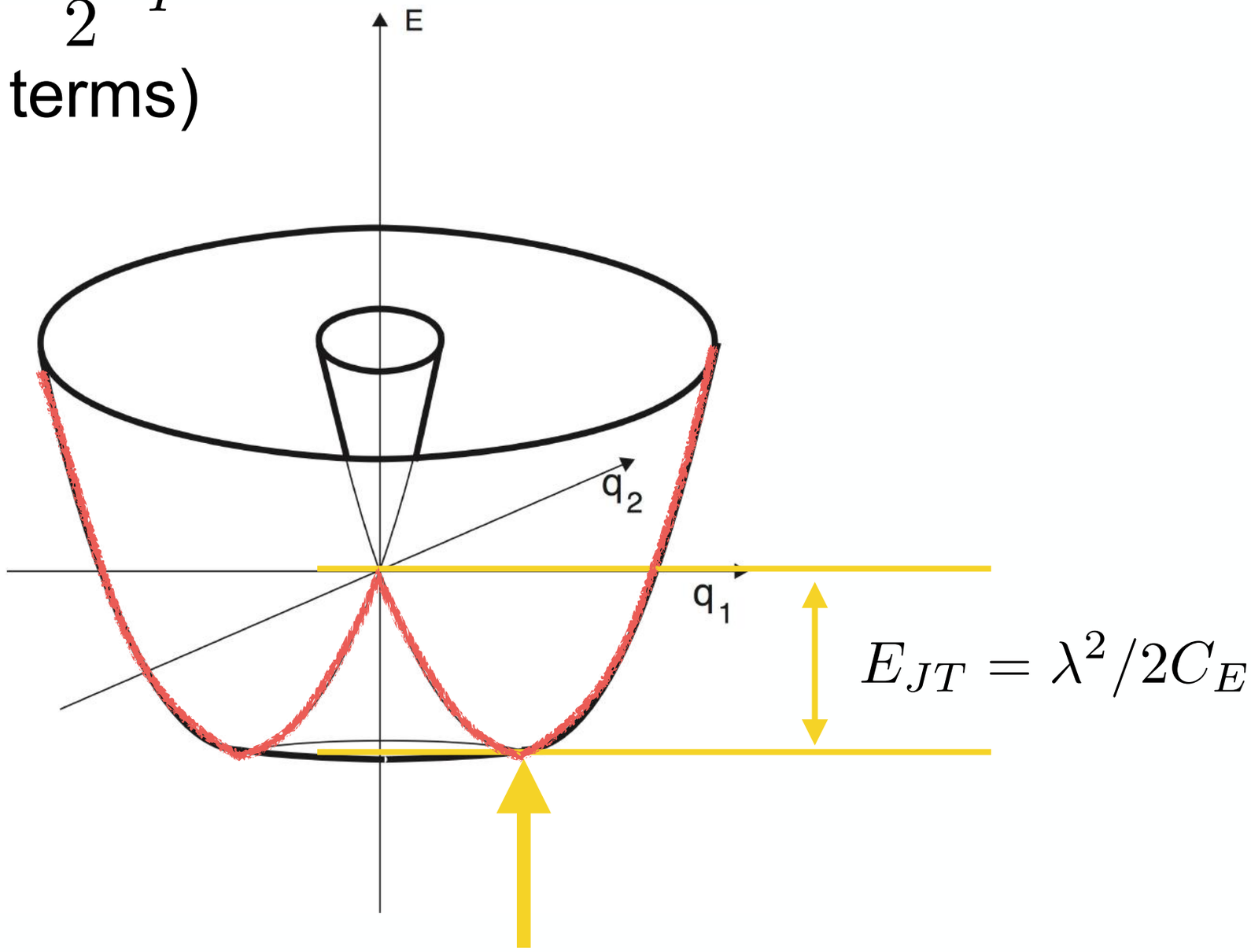
total energy: Jahn-Teller mexican hat

$$E_-(q) = -\lambda q + \frac{C_E}{2} q^2$$

(up to quadratic terms)

$$q_2 = -q\cos\theta, q_1 = -q\sin\theta$$



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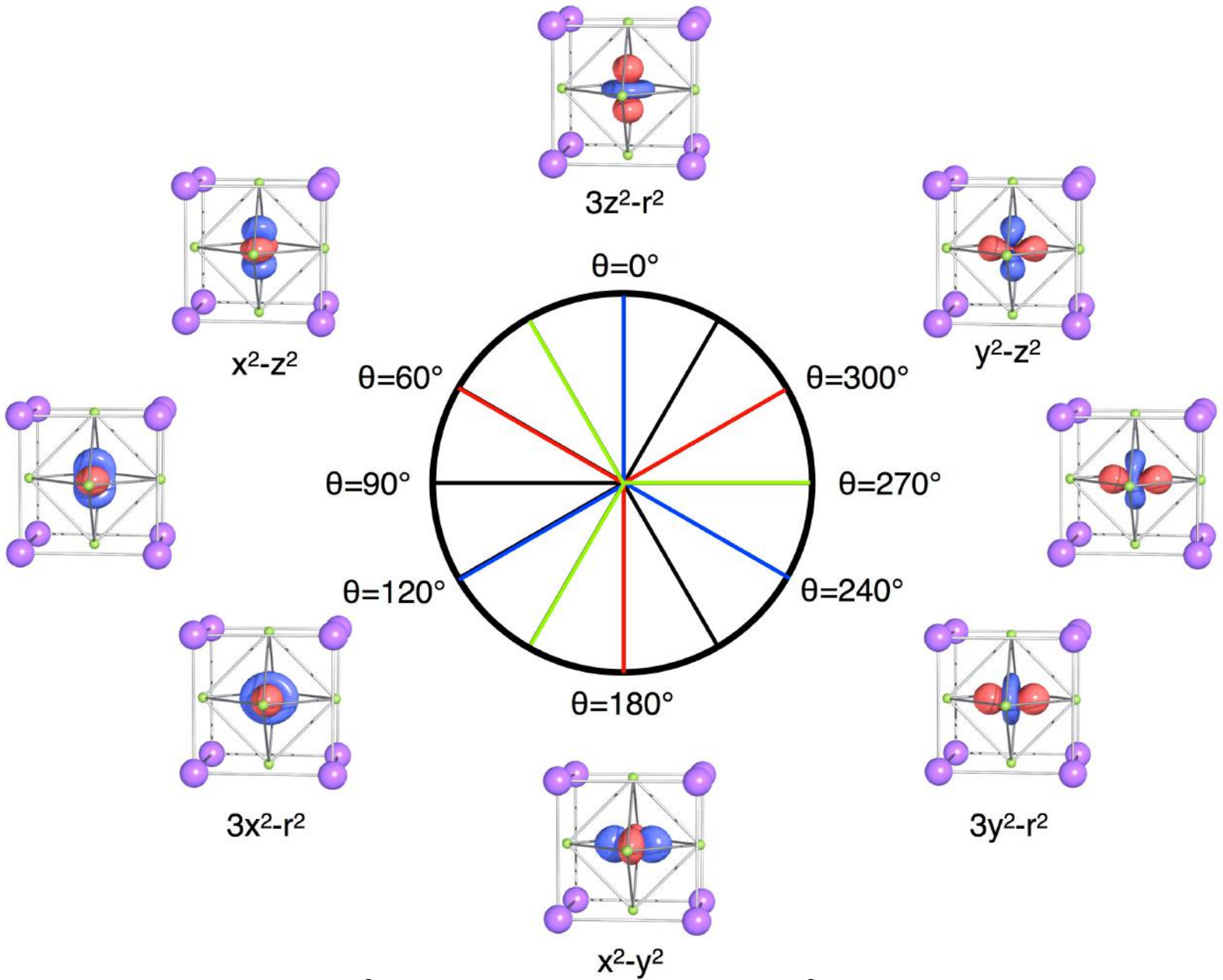
anharmonic effects determine angle



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

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

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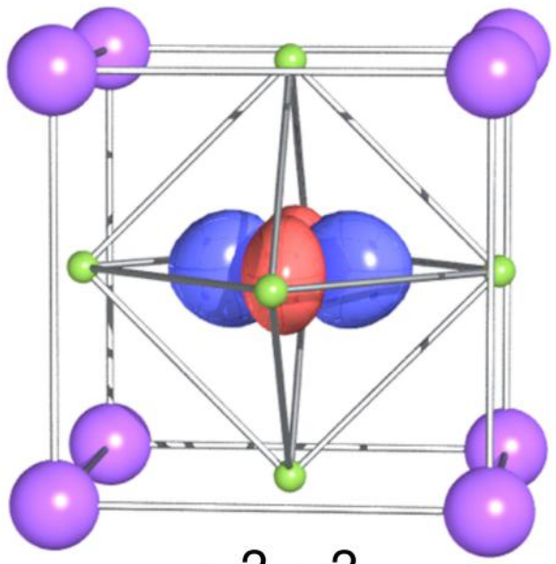
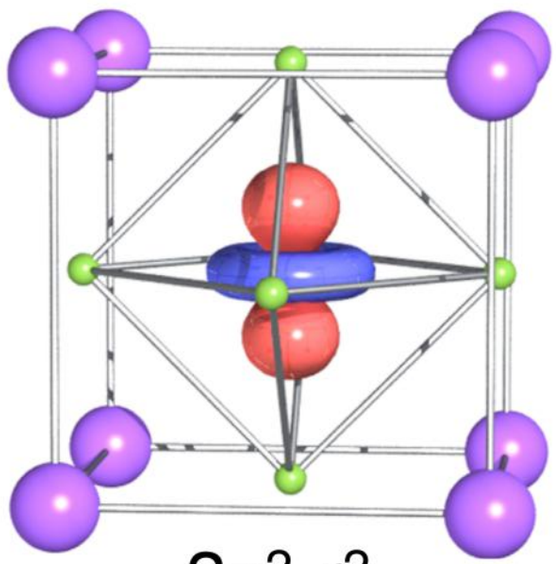
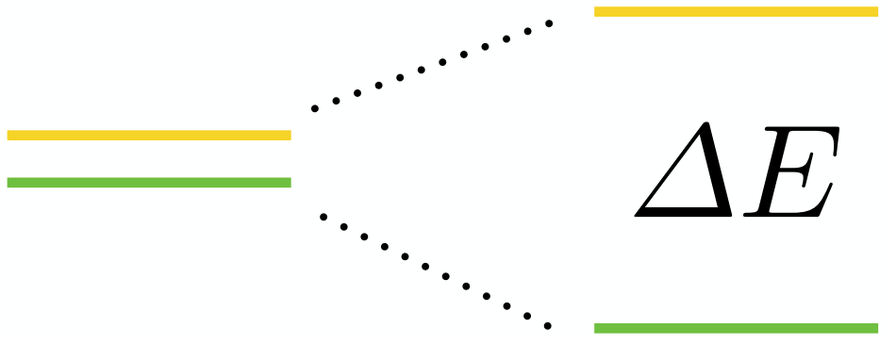
splitting via co-operative distortion

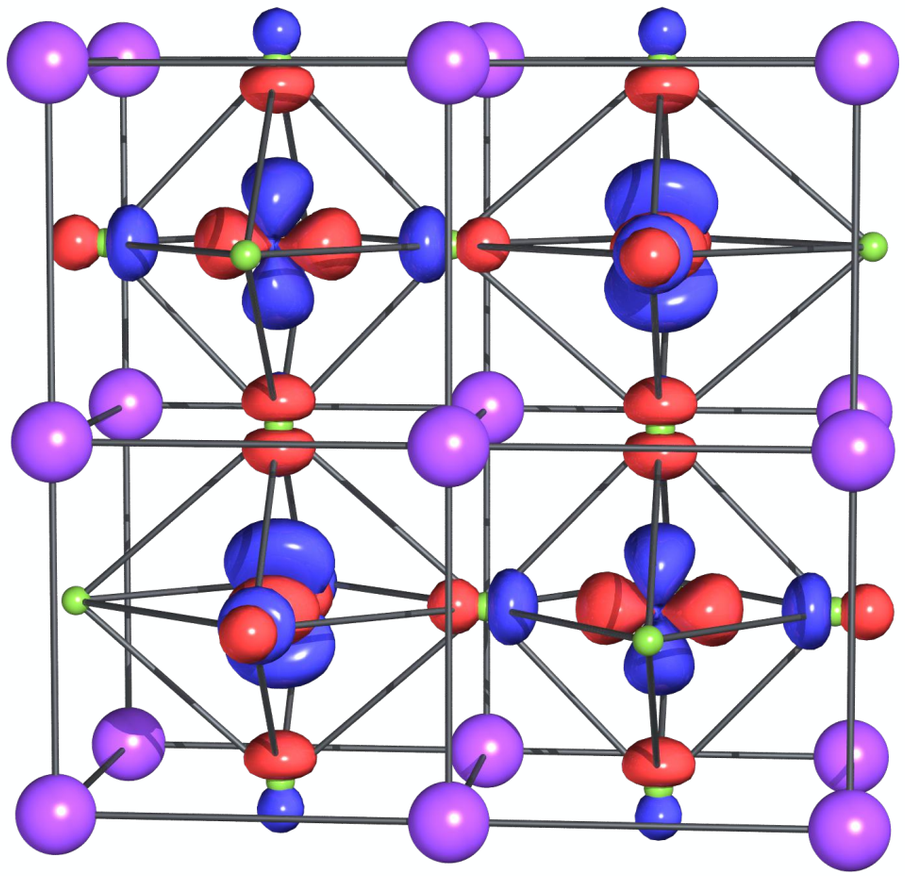


x^2-y^2



$3z^2$-r^2





two-mechanisms, same type of ordering

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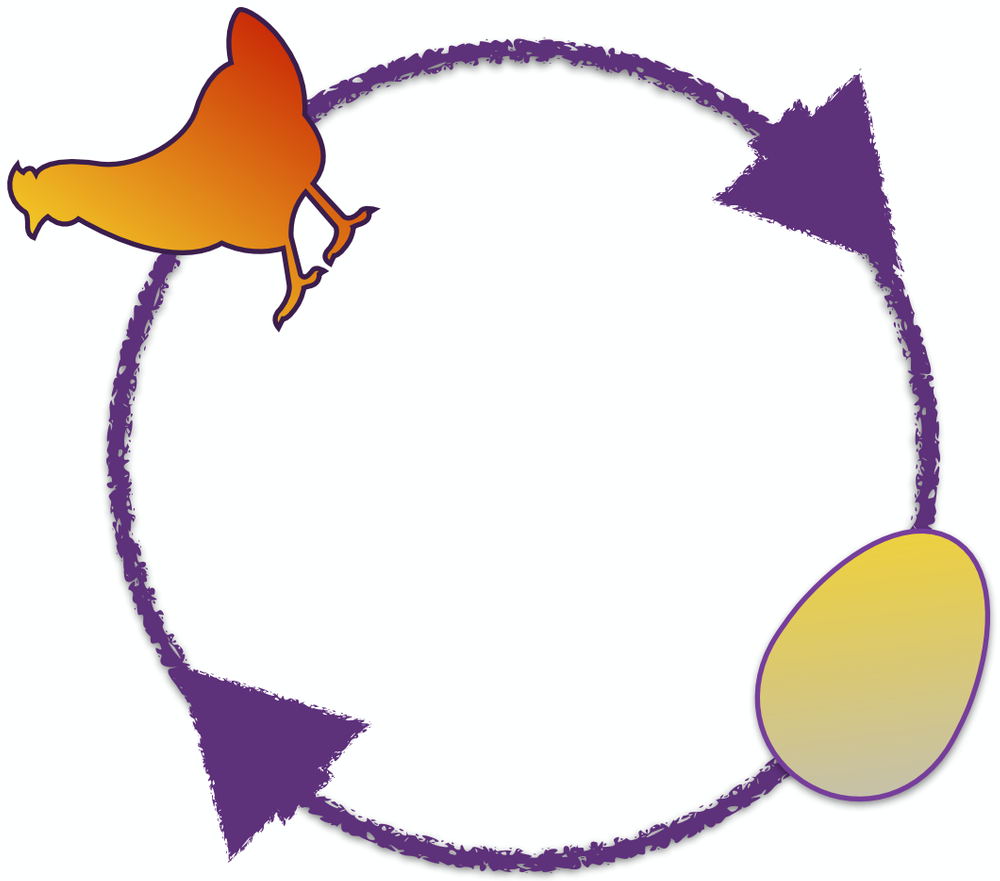
a chicken-and-egg problem

how to disentangle the two?
which mechanism dominates when?

distortions



ordering

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solving the chicken and egg problem in materials

origin of orbital order in real systems

$KCuF_3$ LDA+U: KK-like mechanism

Density-functional theory and strong interactions: Orbital ordering in Mott-Hubbard insulators

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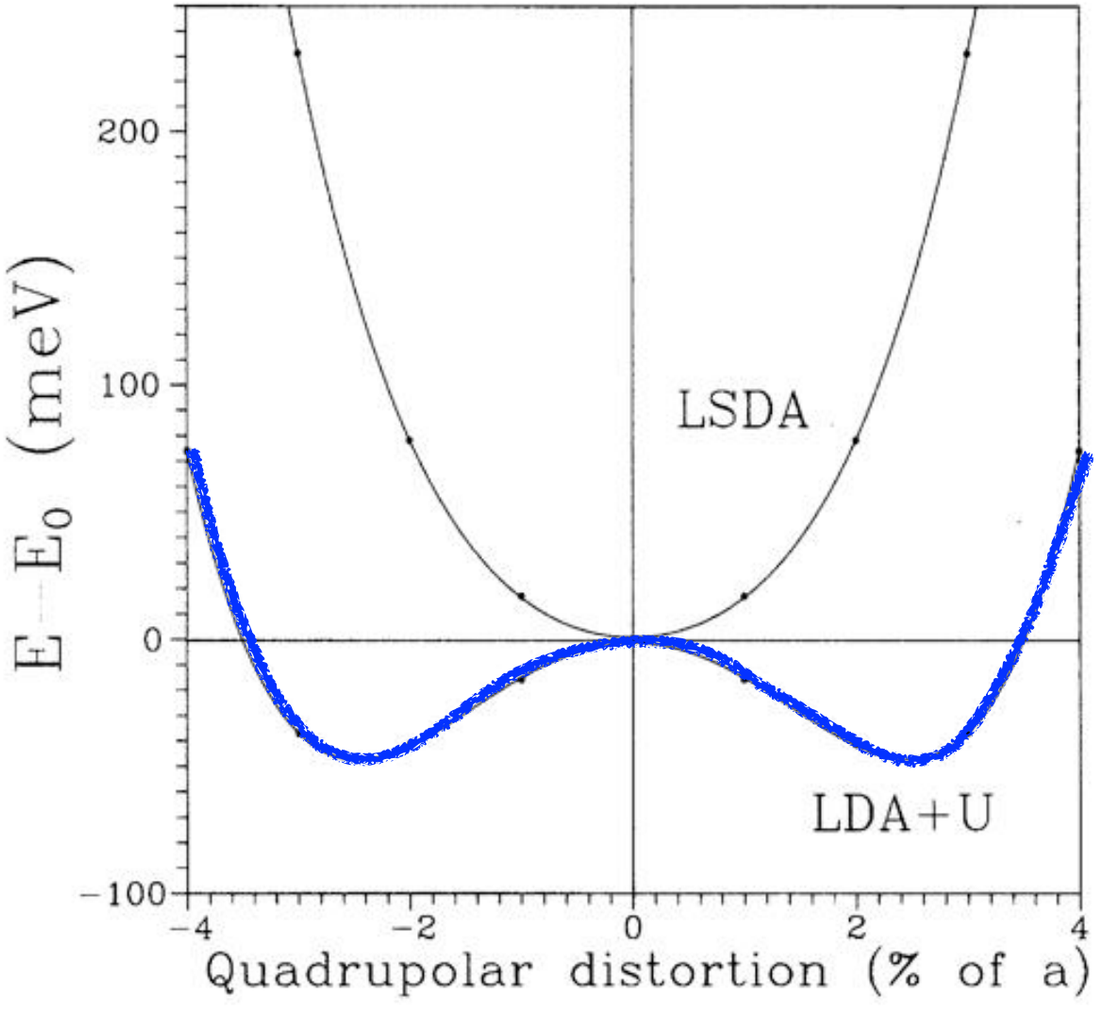
Max-Planck-Institut für Festkörperforschung, D-70506 Stuttgart, Germany

V. I. Anisimov
Institute of Metal Physics, GSP-170 Ekaterinburg, Russia

J. Zaanen
Lorentz Institute for the Theoretical Physics, Leiden University, Leiden, The Netherlands
(Received 15 May 1995)



The situation changes drastically if we allow for orbital polarization. Because U exceeds the bandwidth, the orbital sector is already strongly polarized (as are the spins) before the lattice is allowed to react. Overlooking some unimportant details concerning the coherence of the intermediate states, the well-known rule that electronic MFT in strong coupling maps onto the classical "spin" problem holds also in this case. In other words, we find the quadrupolar orbital-ferromagnetic spin phase to be most stable (for the same reasons as Kugel and Khomskii[6]). Obviously the cubic lattice is unstable in the presence of this orbital order parameter. In fact, despite large-scale changes in the electronic system the deformation is modest, indicating a rather weak electron-phonon coupling.

KK-like mechanism !

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LDA+DMFT confirms LDA+*U*

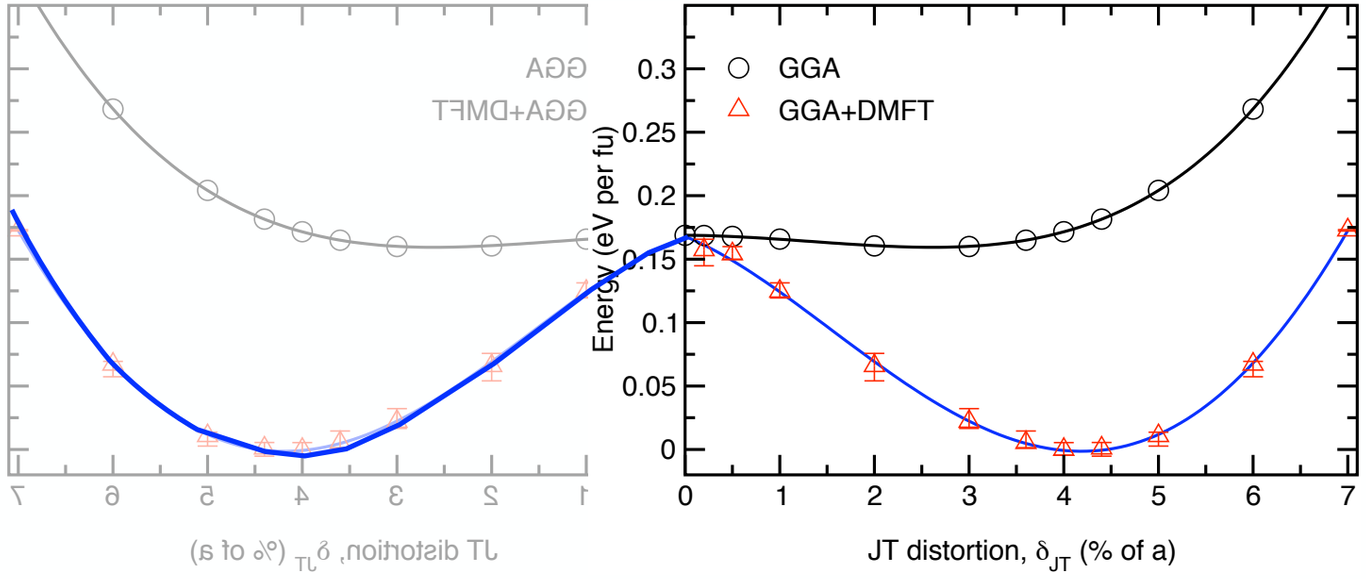
PRL **101,** 096405 (2008) PHYSICAL REVIEW LETTERS week ending 29 AUGUST 2008

Structural Relaxation due to Electronic Correlations in the Paramagnetic Insulator $KCuF_3$

I. Leonov,[1] N. Binggeli,[1,2] Dm. Korotin,[3] V. I. Anisimov,[3] N. Stojić,[4,2] and D. Vollhardt[5]

[1]*Abdus Salam International Center for Theoretical Physics, Trieste 34014, Italy*
[2]*INFM-CNR Democritos, Theory @ Elettra group, Trieste 34014, Italy*
[3]*Institute of Metal Physics, South Kovalevskoy Street 18, 620219 Yekaterinburg GSP-170, Russia*
[4]*International School for Advanced Studies, SISSA, Via Beirut 2/4, 34014 Trieste, Italy*
[5]*Theoretical Physics III, Center for Electronic Correlations and Magnetism, Institute of Physics, University of Augsburg, Augsburg 86135, Germany*

(Received 7 April 2008; published 29 August 2008)



energy gain ~ 175 meV

DMFT para and LDA+U AFM
give similar results

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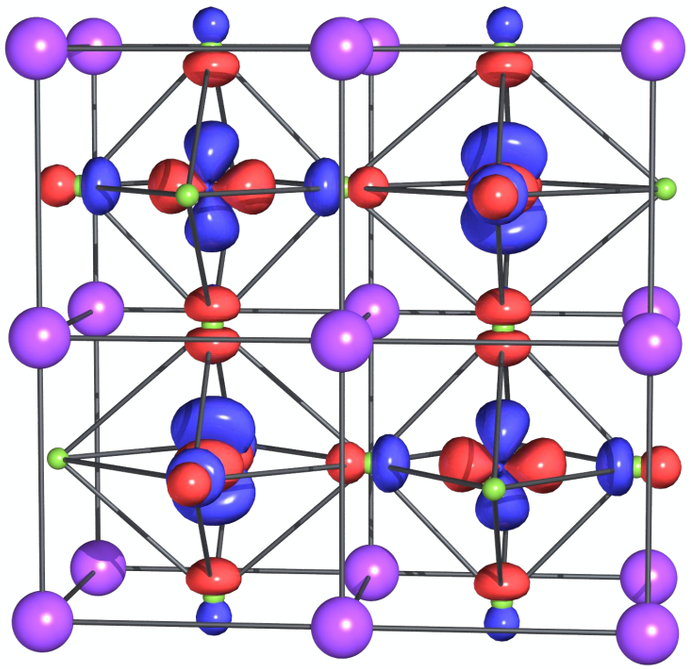
KK is the mechanism: $T_{OO} \sim T_{KK}$



…or, is it ?

Problems:

- why T_N (40K-140K) much smaller than T_{JT} (800-1400 K) ?
- trends with RE, volume, temperature, pressure, in T_{JT}?

Our idea:

- single out Kugel-Khomskii mechanism
- calculate T_{KK} directly

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idea: single out super-exchange

PRL **101,** 266405 (2008) PHYSICAL REVIEW LETTERS week ending 31 DECEMBER 2008

Mechanism for Orbital Ordering in $KCuF_3$

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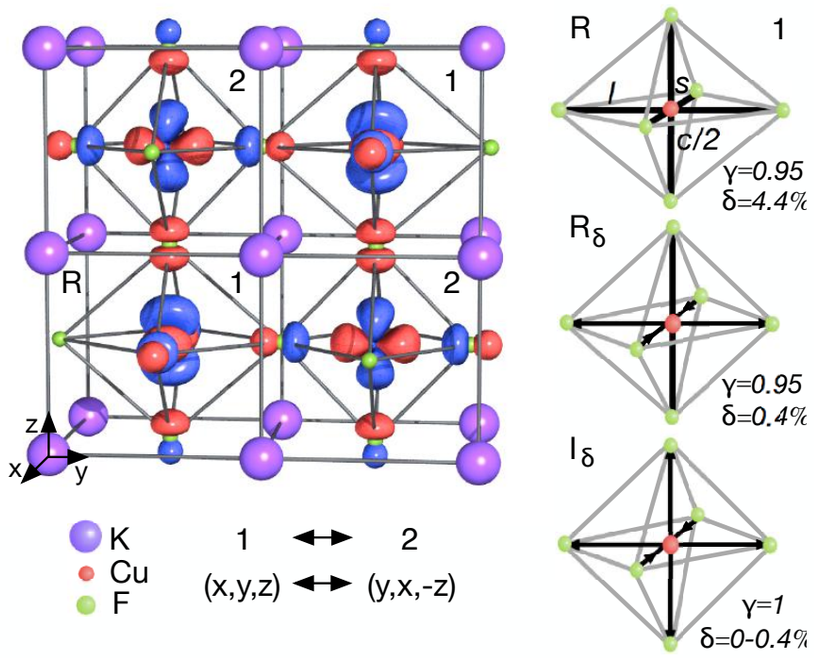
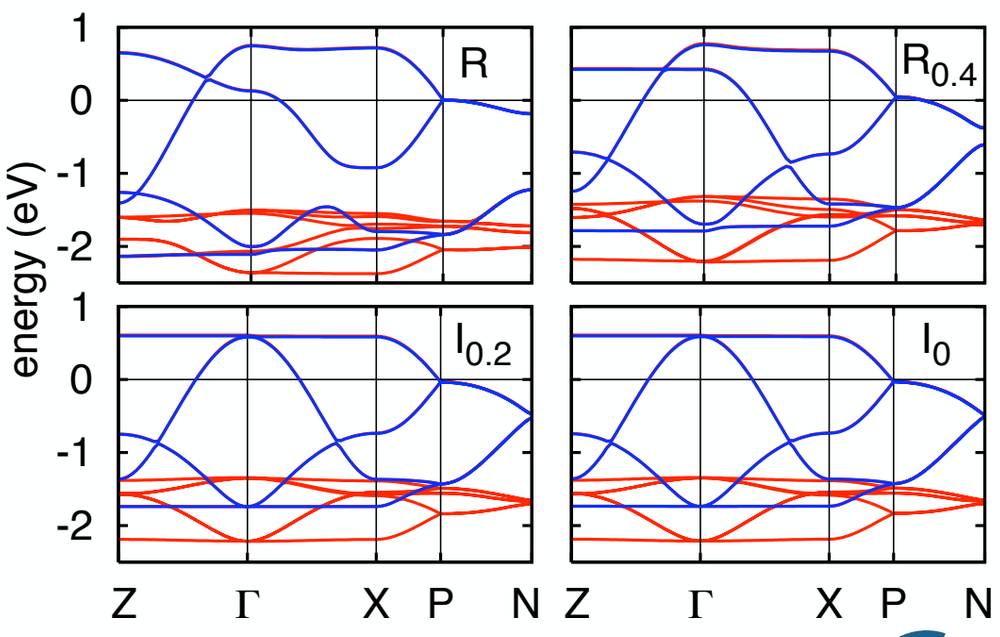
[1]*Institut für Festkörperforschung and Institute for Advanced Simulation, Forschungzentrum Jülich, 52425 Jülich, Germany*
[2]*Institute of Theoretical Physics, University of Hamburg, Jungiusstrasse 9, 20355 Hamburg, Germany*

(Received 18 August 2008; published 31 December 2008)

The Mott insulating perovskite $KCuF_3$ is considered the archetype of an orbitally ordered system. By using the local-density approximation+dynamical mean-field theory method, we investigate the mechanism for orbital ordering in this material. We show that the purely electronic Kugel-Khomskii superexchange mechanism alone leads to a remarkably large transition temperature of $T_{KK} \sim 350$ K. However, orbital order is experimentally believed to persist to at least 800 K. Thus, Jahn-Teller distortions are essential for stabilizing orbital order at such high temperatures.

DOI: 10.1103/PhysRevLett.101.266405 PACS numbers: 71.10.Fd, 71.10.Hf, 71.27.+a





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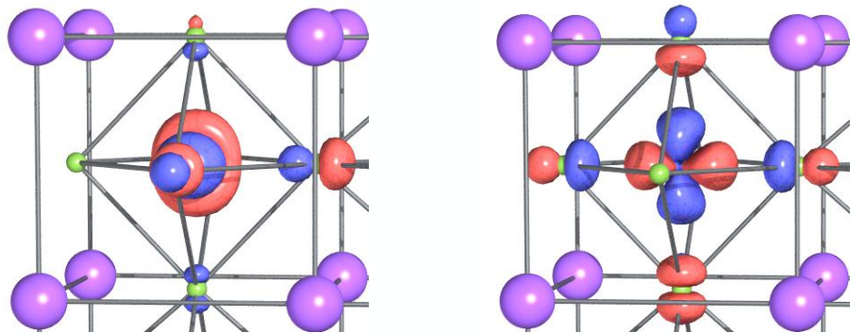
LDA+DMFT with Wannier functions

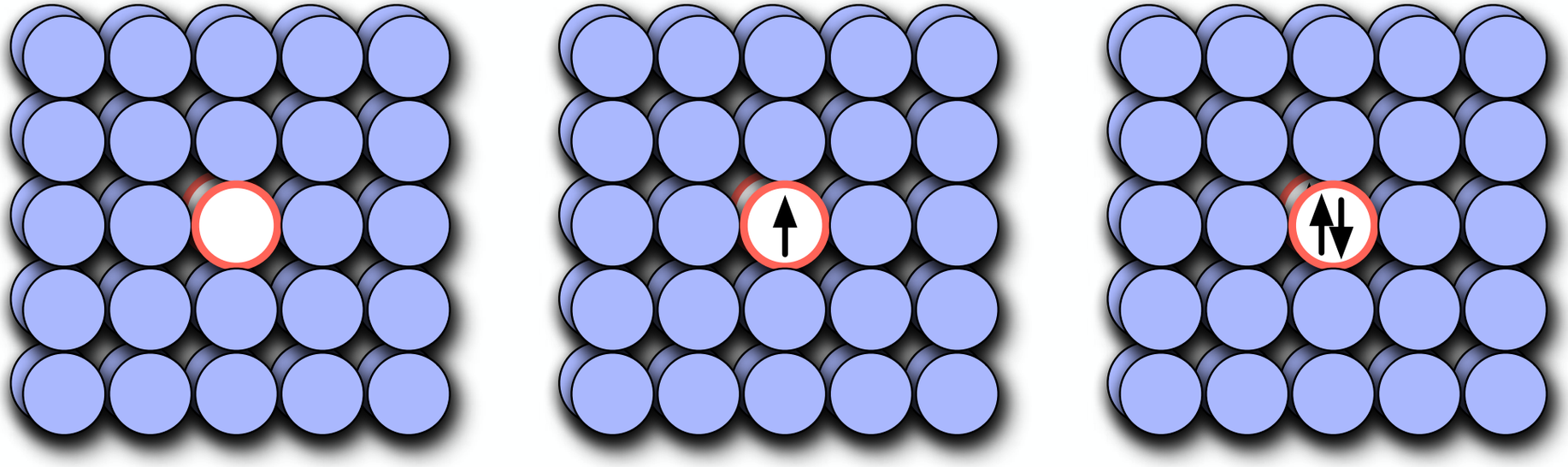
$$
\begin{aligned}
H = & - \sum_{ii'} \sum_{mm'} \sum_{\sigma} t^{ii'}_{mm'} c^{\dagger}_{im\sigma} c_{i'm'\sigma} \\
& + U \sum_{im} n_{im\uparrow} n_{im\downarrow} \\
& + \frac{1}{2} \sum_{im \neq m'\sigma\sigma'} (U - 2J - J\delta_{\sigma\sigma'}) n_{im\sigma} n_{im'\sigma'} \\
& - J \sum_{m \neq m'} (c^{\dagger}_{m\uparrow} c^{\dagger}_{m'\downarrow} c_{m'\uparrow} c_{m\downarrow} + c^{\dagger}_{m\uparrow} c^{\dagger}_{m\downarrow} c_{m'\uparrow} c_{m'\downarrow})
\end{aligned}
$$

VOLUME 92, NUMBER 17 PHYSICAL REVIEW LETTERS week ending 30 APRIL 2004

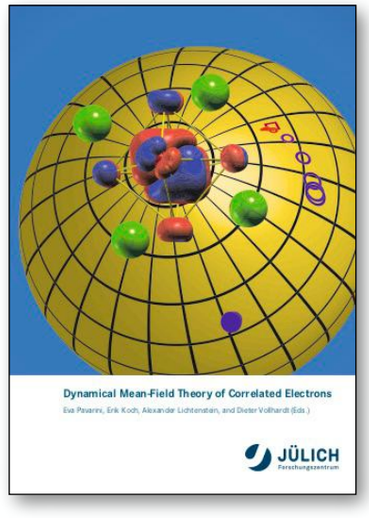
Mott Transition and Suppression of Orbital Fluctuations in Orthorhombic $3d^1$ Perovskites

E. Pavarini,[1] S. Biermann,[2] A. Poteryaev,[3] A. I. Lichtenstein,[3] A. Georges,[2] and O. K. Andersen[4]





$$
G_{m,m'} = \sum_{\mathbf{k},\mathbf{n}} \left[\frac{1}{i\omega_n + \mu - \mathrm{H}_{0\mathbf{k}} - \Sigma(i\omega_n)} \right]_{m,m'}
$$



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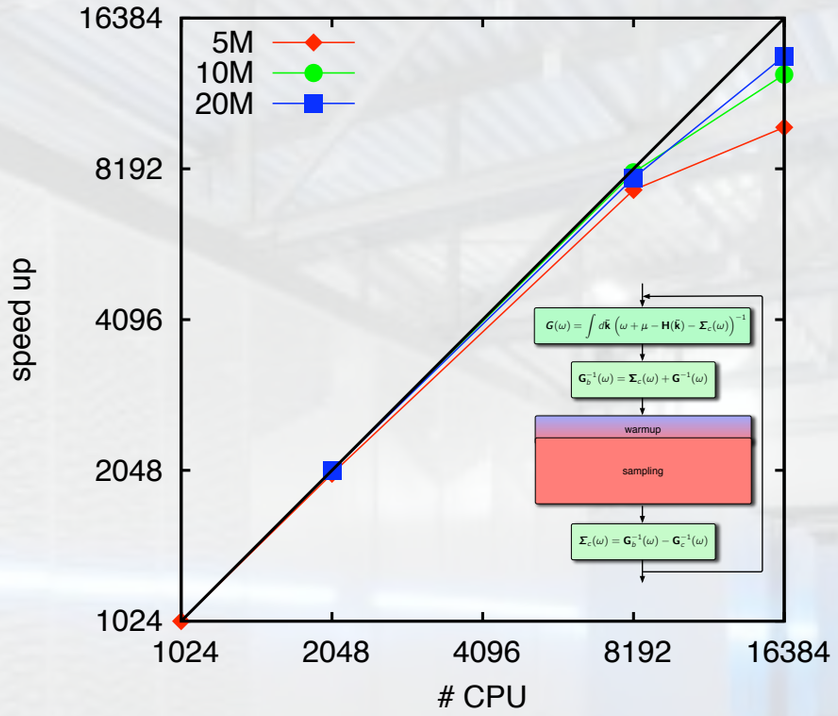
flexible and efficient solvers

$$
\begin{aligned}
H = & - \sum_{ii'} \sum_{mm'} \sum_{\sigma} t^{ii'}_{mm'} c^{\dagger}_{im\sigma} c_{i'm'\sigma} \\
& + U \sum_{im} n_{im\uparrow} n_{im\downarrow} \\
& + \frac{1}{2} \sum_{im \neq m' \sigma\sigma'} (U - 2J - J\delta_{\sigma\sigma'}) n_{im\sigma} n_{im'\sigma'} \\
& - J \sum_{m \neq m'} (c^{\dagger}_{m\uparrow} c^{\dagger}_{m'\downarrow} c_{m'\uparrow} c_{m\downarrow} + c^{\dagger}_{m\uparrow} c^{\dagger}_{m\downarrow} c_{m'\uparrow} c_{m'\downarrow})
\end{aligned}
$$

self-energy matrix in spin-orbital space



DMFT and cDMFT

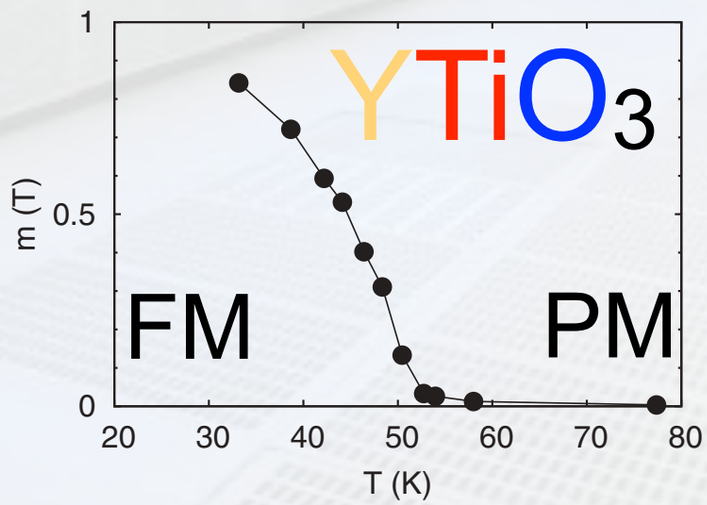
generalized quantum impurity solvers:

general HF QMC

general CT-INT QMC

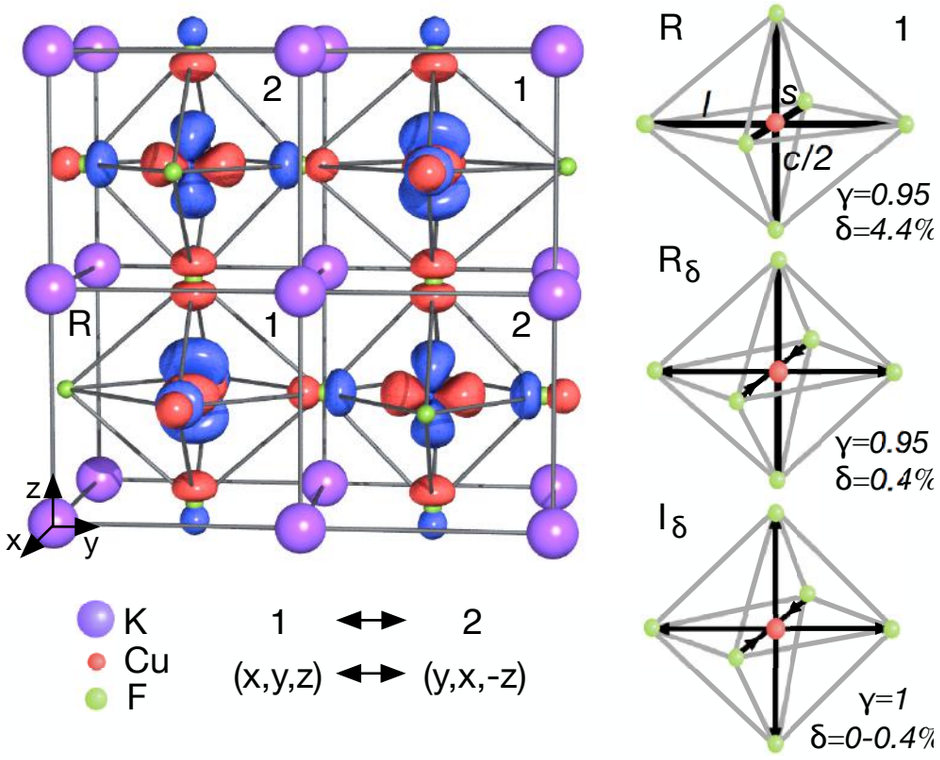
general CT-HYB QMC

- CT-HYB: A. Flesch, E. Gorelov, E. Koch and E. Pavarini
  Phys. Rev. B **87**, 195141 (2013)
- CT-INT: E. Gorelov et al, PRL 104, 226410 (2010)
- CT-INT+SO: G. Zhang, E. Gorelov, E. Sarvestani, and E. Pavarini,
  Phys. Rev. Lett. 116, 106402 (2016)

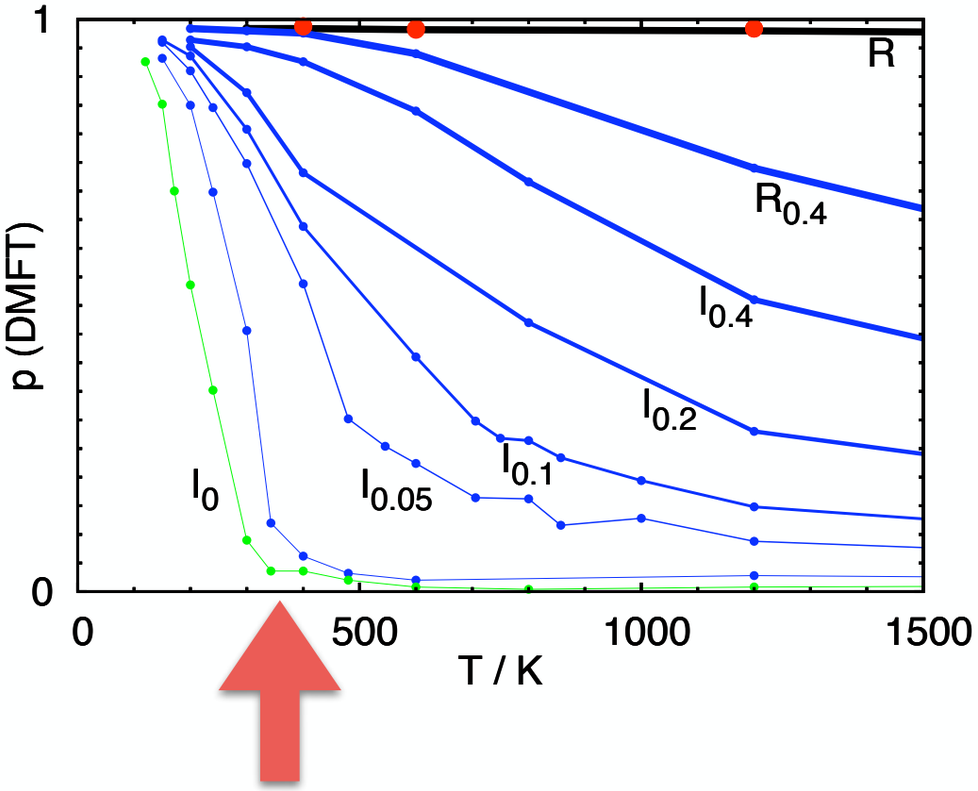


sign problem: smart adapted basis choice

the KK mechanism in $KCuF_3$



$p=n_1-n_2=\langle O \rangle$



Phys. Rev. Lett. **101**, 266405 (2008)

$T_{KK} \sim 350$ K

$T_{KK} \ll T_{OO} > 1400$ K

reminder: mean field theory *overestimates* T_{KK}

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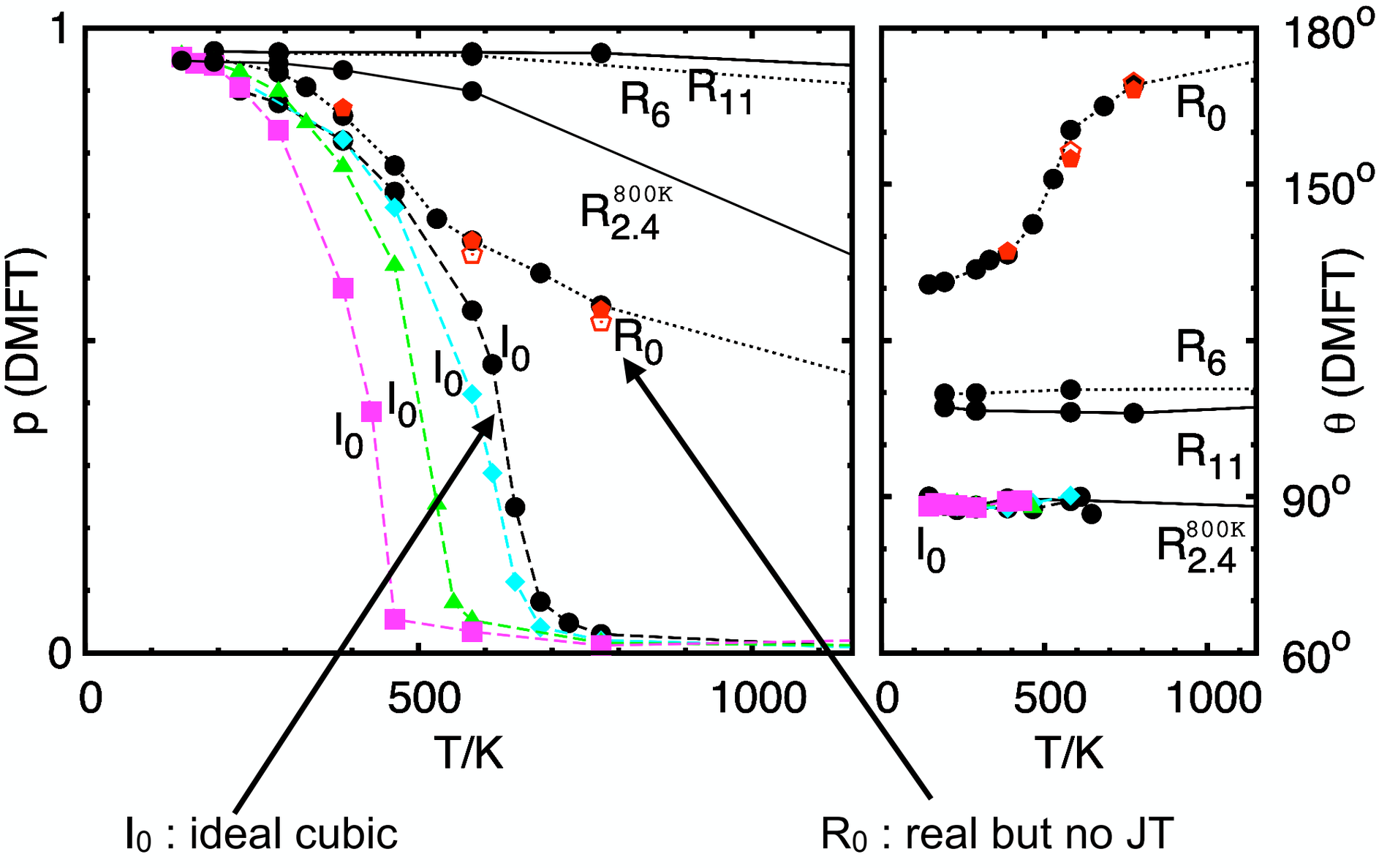
$LaMnO_3$: T_{KK} ~ 600 K !!

Phys. Rev. Lett. **104**, 086402 (2010)



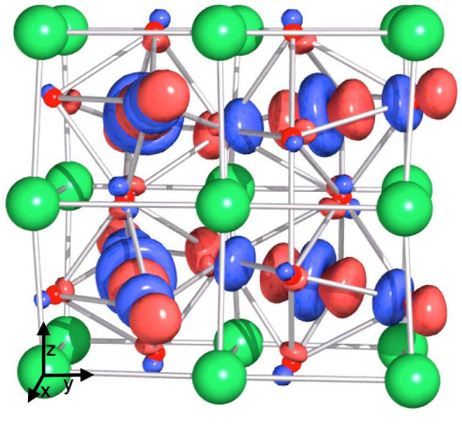
non-JT crystal-field

red: cDMFT 4 sites

black: DMFT

experiments

super-exchange



$$|\theta\rangle = \sin\frac{\theta}{2}|3z^2-1\rangle + \cos\frac{\theta}{2}|x^2-y^2\rangle$$

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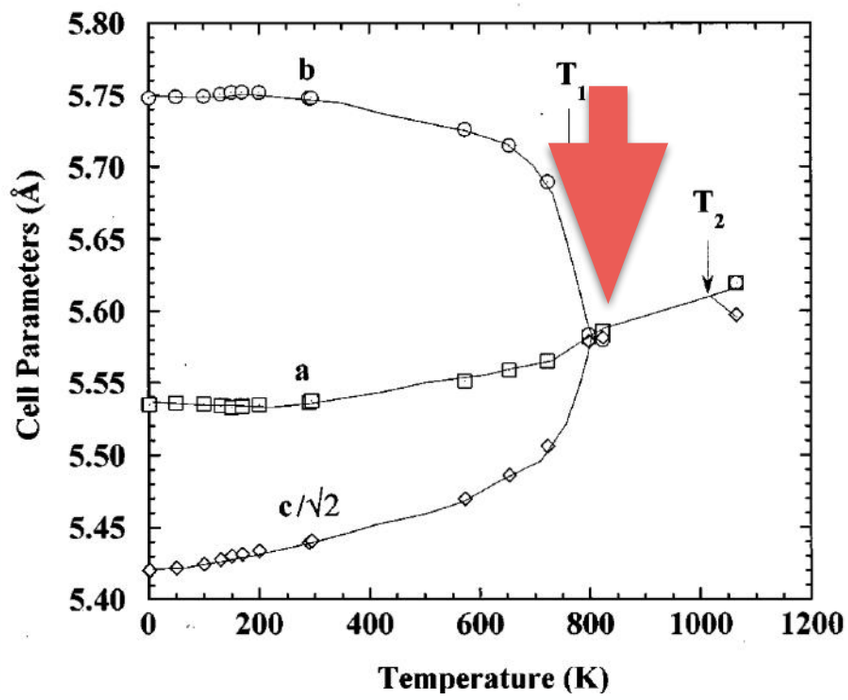
orbital-order transition at T_{OO} in $LaMnO_3$



PHYSICAL REVIEW B VOLUME 57, NUMBER 6 1 FEBRUARY 1998-II

Neutron-diffraction study of the Jahn-Teller transition in stoichiometric $LaMnO_3$

J. Rodríguez-Carvajal,* M. Hennion, F. Moussa, and A. H. Moudden
Laboratoire Léon Brillouin (CEA-CNRS), Centre d'Etudes de Saclay, 91191 Gif sur Yvette Cedex, France

L. Pinsard and A. Revcolevschi
Laboratoire de Chimie des Solides, Université Paris Sud, 91405 Orsay Cedex, France
(Received 2 September 1997)

The parent compound of the giant magnetoresistance Mn-perovskite, $LaMnO_3$, has been studied by thermal analysis and high-resolution neutron-powder diffraction. The orthorhombic *Pbnm* structure at room temperature is characterized by an antiferrodistorsive orbital ordering due to the Jahn-Teller effect. This ordering is evidenced by the spatial distribution of the observed Mn-O bond lengths. $LaMnO_3$ undergoes a structural phase transition at $T_{JT} \approx 750$ K, above which the orbital ordering disappears. There is no change in symmetry although the lattice becomes metrically cubic on the high-temperature side. The MnO_6 octahedra become nearly regular above T_{JT} and the thermal parameter of oxygen atoms increases significantly. The observed average cubic lattice is probably the result of dynamic spatial fluctuations of the underlying orthorhombic distortion. [S0163-1829(98)51706-7]

VOLUME 81, NUMBER 3 PHYSICAL REVIEW LETTERS 20 JULY 1998

Resonant X-Ray Scattering from Orbital Ordering in $LaMnO_3$

Y. Murakami,[1,2] J. P. Hill,[3] D. Gibbs,[3] M. Blume,[3] I. Koyama,[1] M. Tanaka,[1] H. Kawata,[1] T. Arima,[4] Y. Tokura,[5] K. Hirota,[2,6] and Y. Endoh[2,6]
[1]*Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, 305-0801, Japan*
[2]*Core Research for Evolutional Science and Technology (CREST), Tsukuba 305-0047 Japan*
[3]*Department of Physics, Brookhaven National Laboratory, Upton, New York 11973*
[4]*Institute of Materials Science, University of Tsukuba, Tsukuba 305-8573, Japan*
[5]*Department of Applied Physics, University of Tokyo, Tokyo 113-0033, Japan and Joint Research Center for Atom Technology (JRCAT), Tsukuba 305-0046, Japan*
[6]*Department of Physics, Tohoku University, Sendai 980-8578, Japan*
(Received 22 April 1998)

$T_{OO} \sim 800$ K

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T_{OO}: orbital order-to-disorder transition

PRL **94,** 177203 (2005) PHYSICAL REVIEW LETTERS week ending 6 MAY 2005

Orbital Correlations in the Pseudocubic *O* and Rhombohedral *R* Phases of $LaMnO_3$

Xiangyun Qiu,[1] Th. Proffen,[2] J. F. Mitchell,[3] and S. J. L. Billinge[1]

[1]*Department of Physics and Astronomy, Michigan State University, E. Lansing, Michigan 48824, USA*
[2]*Los Alamos National Laboratory, LANSCE-12, MS H805, Los Alamos, New Mexico 87545, USA*
[3]*Material Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA*

(Received 12 August 2004; revised manuscript received 24 February 2005; published 5 May 2005)

The local and intermediate structure of stoichiometric $LaMnO_3$ has been studied in the pseudocubic and rhombohedral phases at high temperatures (300–1150 K). Neutron powder diffraction data were collected and a combined Rietveld and high real space resolution atomic pair distribution function analysis was carried out. The nature of the Jahn-Teller (JT) transition around 750 K is confirmed to be orbital order to disorder. In the high-temperature orthorhombic (*O*) and rhombohedral (*R*) phases, the MnO_6 octahedra are still fully distorted locally. More importantly, the intermediate structure suggests the presence of local ordered clusters of diameter ~16 Å (~4 MnO_6 octahedra) implying strong nearest-neighbor JT antiferrodistortive coupling. These clusters persist well above the JT transition temperature even into the high-temperature *R* phase.

DOI: 10.1103/PhysRevLett.94.177203 PACS numbers: 75.47.Lx, 61.12.−q, 75.47.Gk

$T_{OO} \sim 800$ K $T_{JT} > 1150$ K

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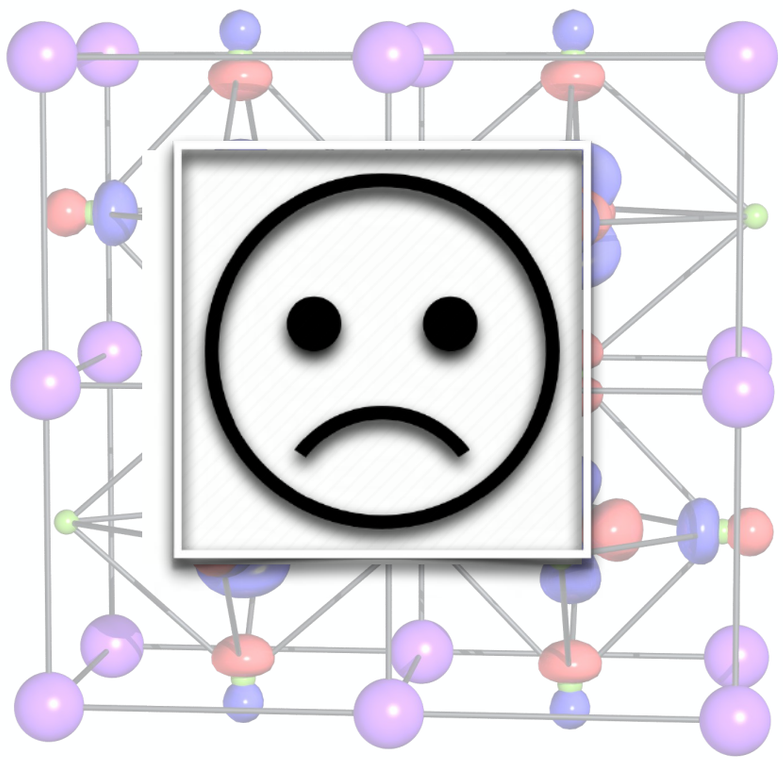
KK-only candidates

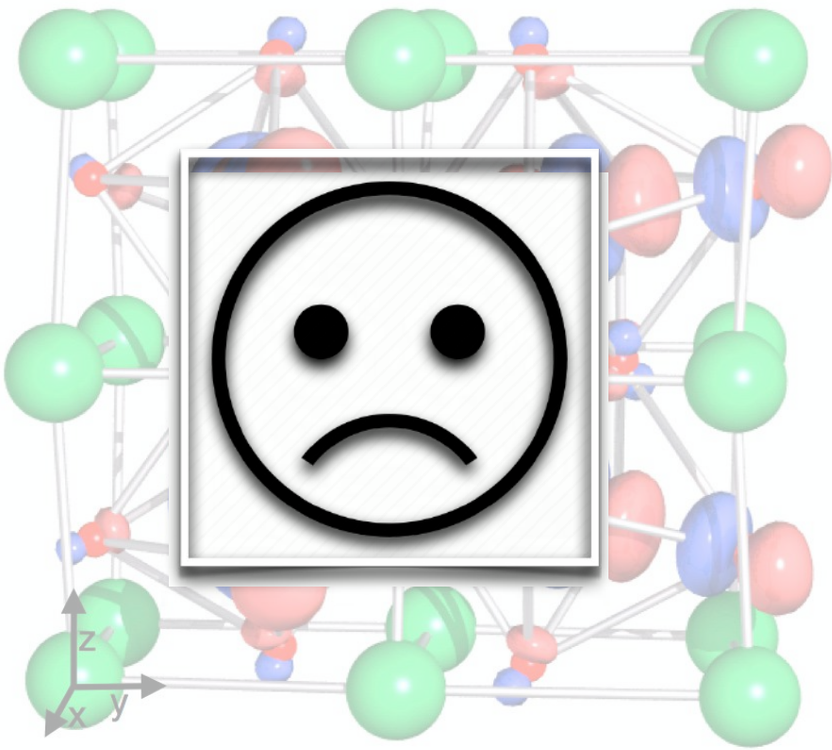
e_g systems

$KCuF_3$



$t_{2g}^6 e_g^3$

$LaMnO_3$



$t_{2g}^3 e_g^1$

$KCrF_3$ $ReMnO_3$

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is $KCuF_3$ really JT?

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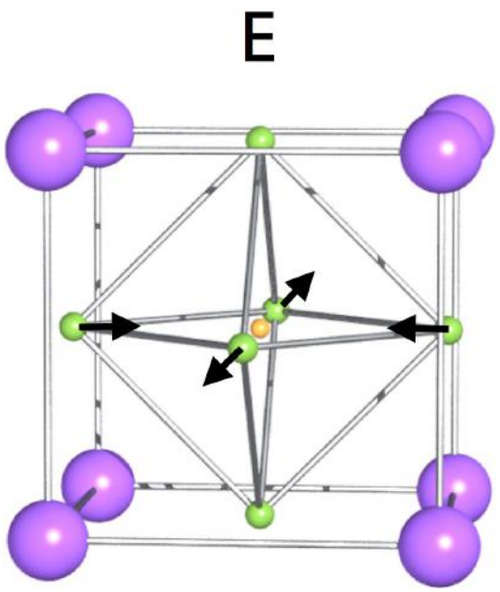
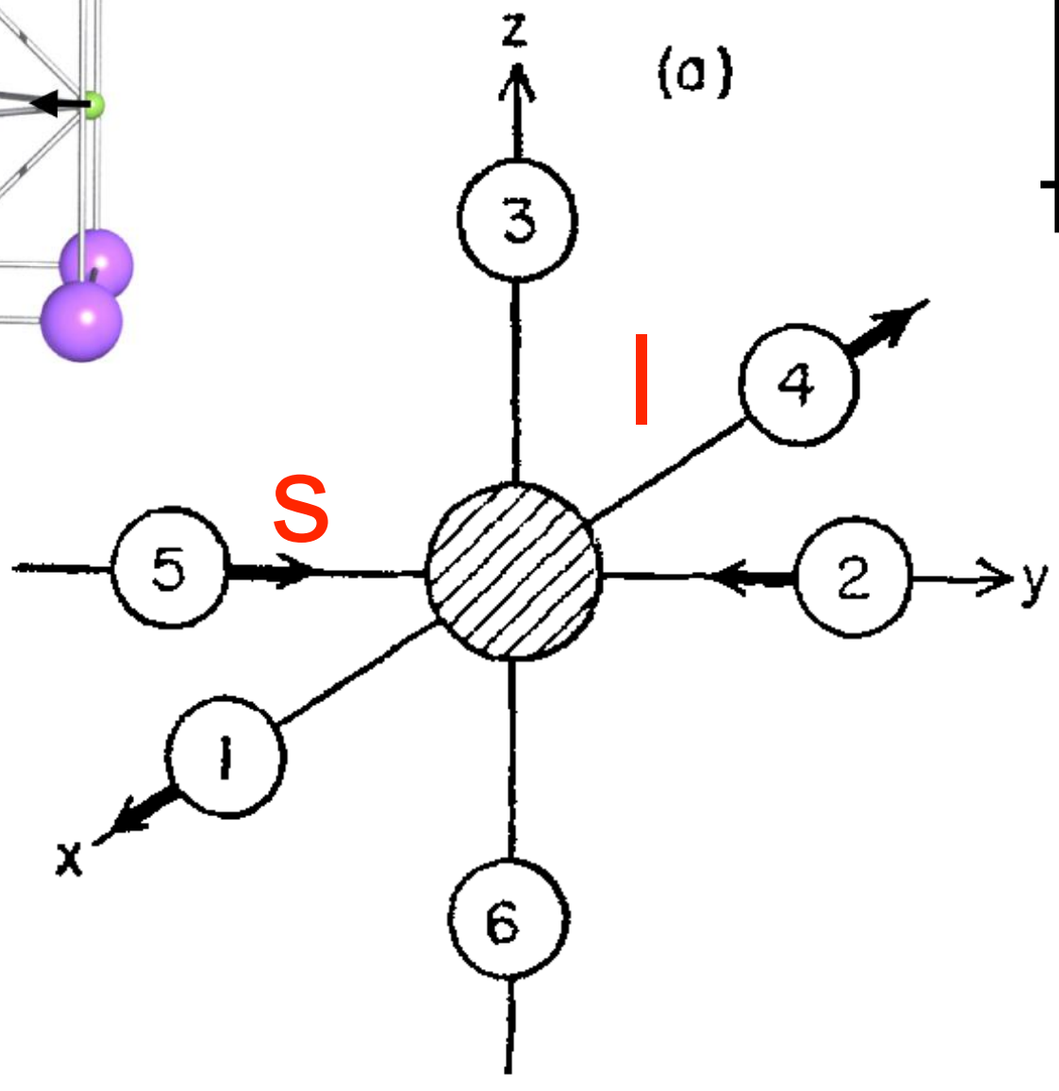
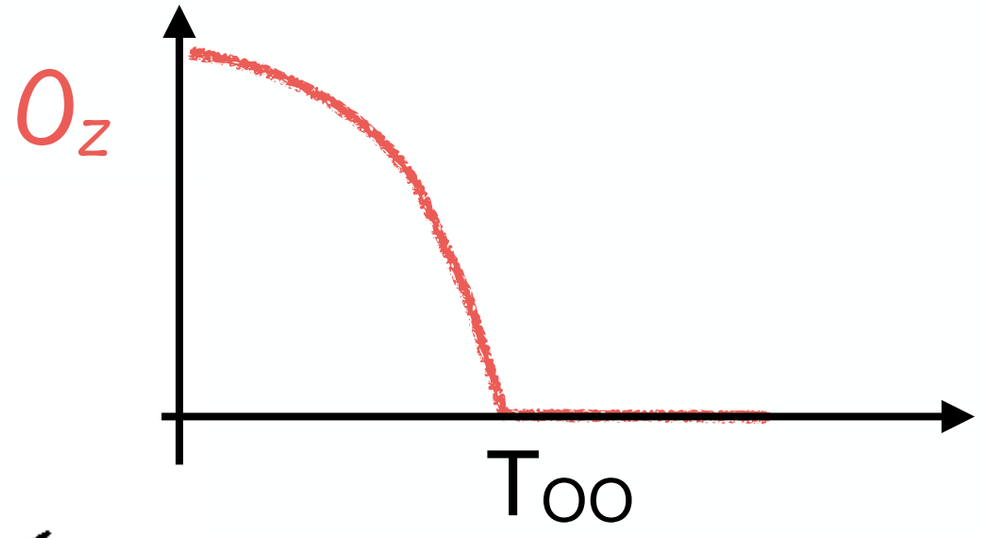
what is the origin of JT distortion?

is the Jahn-Teller distortion really Jahn-Teller?







$$q = \delta = \frac{1}{2}\frac{l-s}{l+s}$$

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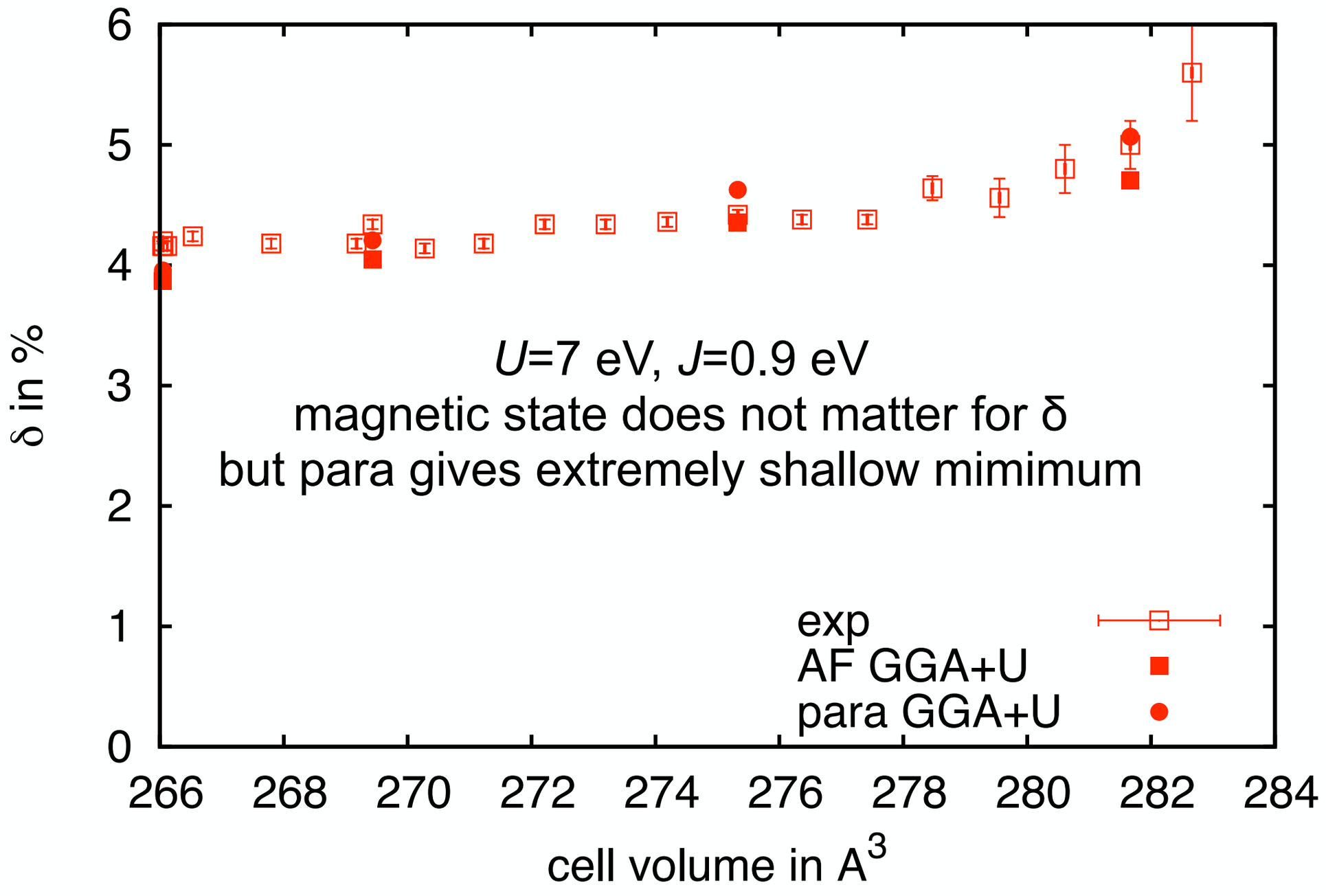
the distortion *q* increases with T

$$q = \delta = \frac{1}{2}\frac{l - s}{l + s}$$



DFT+*U* (same results in DFT+DMFT)

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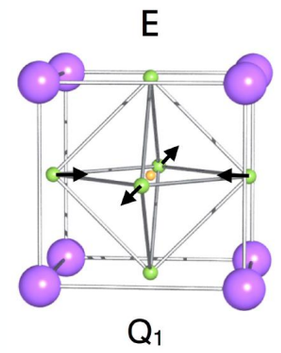
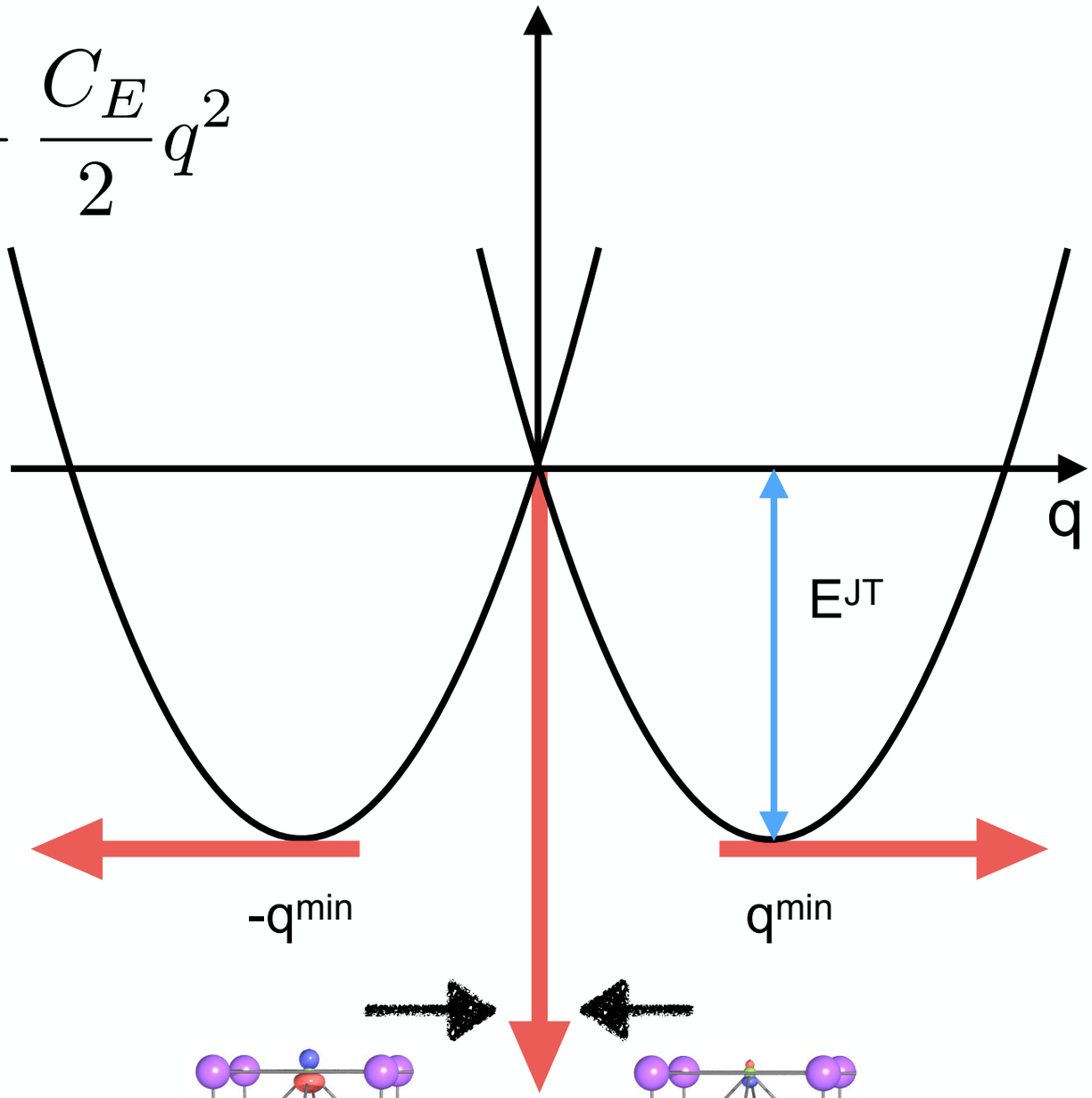
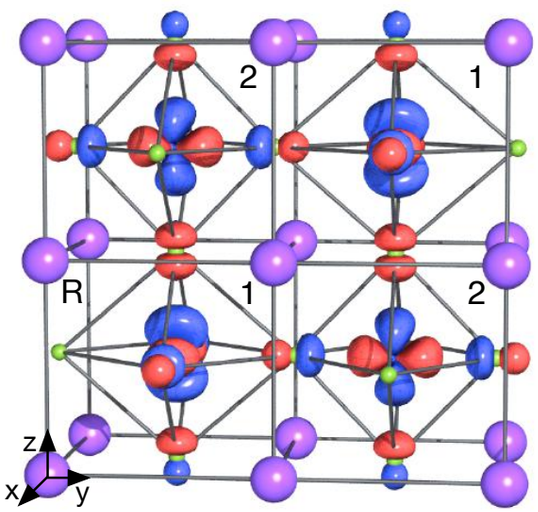
ideal JT potential

$$E_-(q) = -\lambda q + \frac{C_E}{2} q^2$$





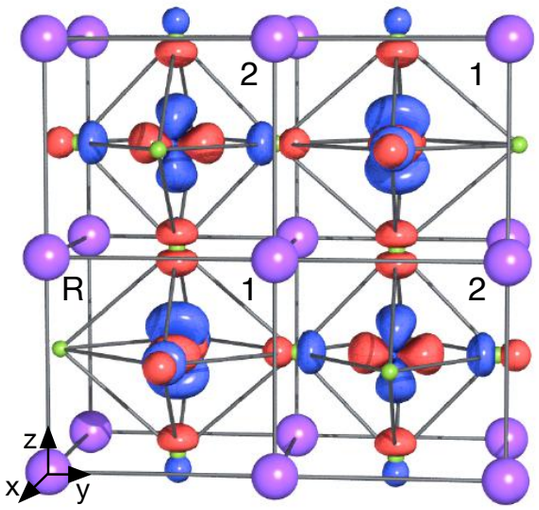
OO



K
Cu
F

1 ↔ 2

(x,y,z) ↔ (y,x,-z)

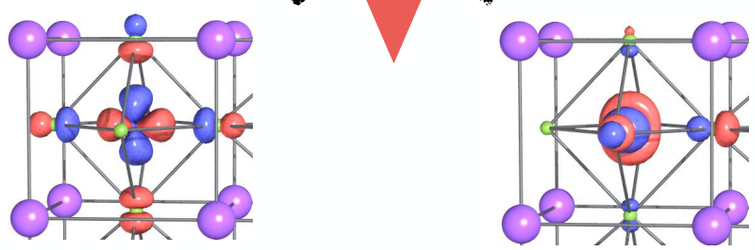


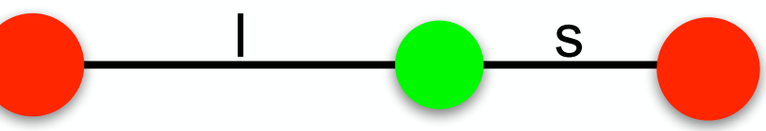
K
Cu
F

1 ↔ 2

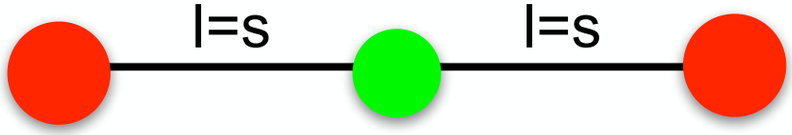
(x,y,z) ↔ (y,x,-z)

OO





cubic, orbital degeneracy



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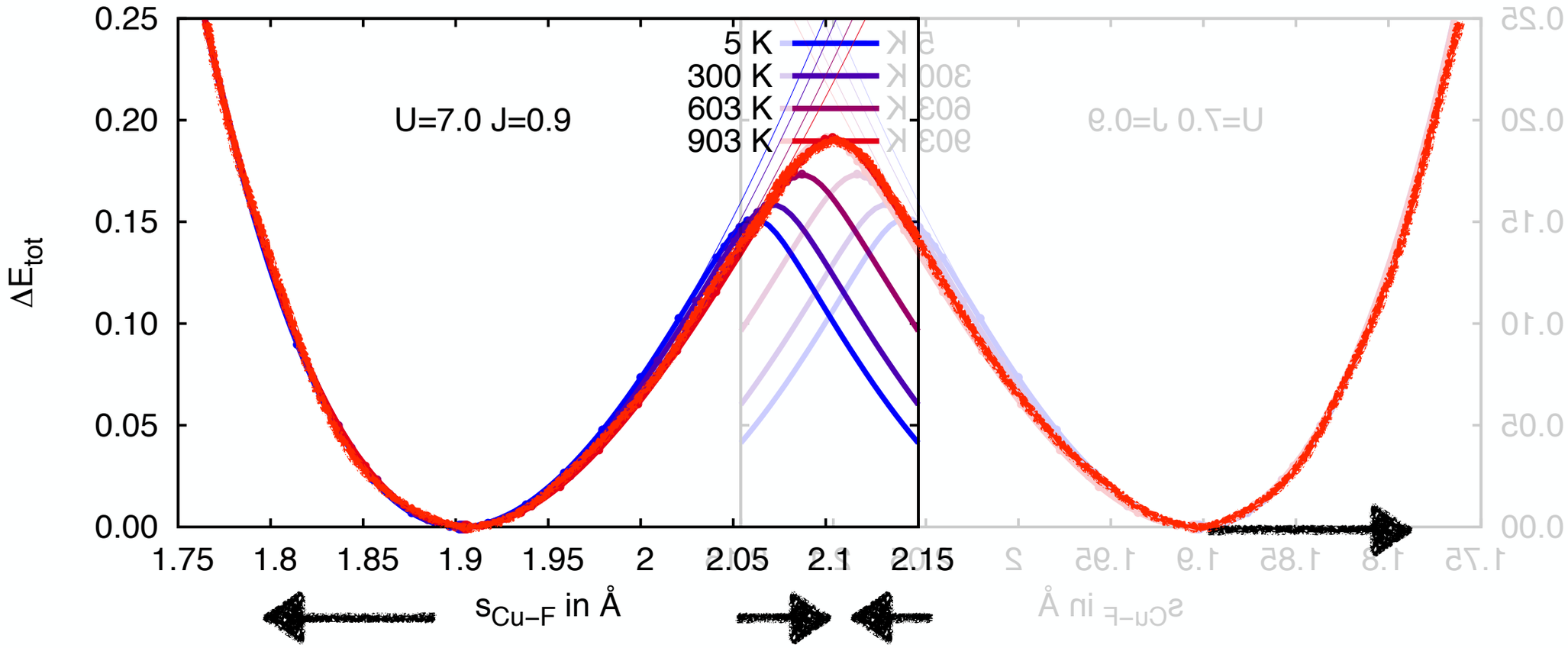
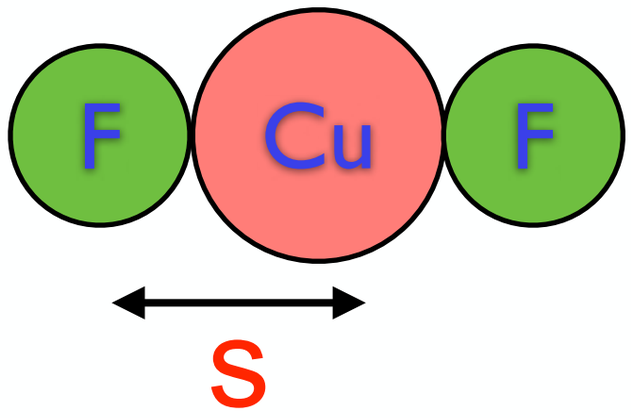
re-plot the (GGA+U) mexican hat



touching ions



Born-Mayer repulsion !

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the T-dependence is via the lattice constant!

PHYSICAL REVIEW B **96**, 054107 (2017)

Thermally assisted ordering in Mott insulators

Hunter Sims,[1] Eva Pavarini,[2,3] and Erik Koch[1,2,3,*]
[1]*Computational Materials Science, German Research School for Simulation Sciences, 52425 Jülich, Germany*
[2]*Institute for Advanced Simulation, Forschungszentrum Jülich, 52425 Jülich, Germany*
[3]*JARA High-Performance Computing, 52425 Jülich, Germany*
(Received 16 November 2016; revised manuscript received 19 July 2017; published 8 August 2017)

Landau theory describes phase transitions as the competition between energy and entropy: The ordered phase has lower energy, while the disordered phase has larger entropy. When heating the system, ordering is reduced entropically until it vanishes at the critical temperature. This picture implicitly assumes that the energy difference between the ordered and disordered phases does not change with temperature. We show that for orbital ordering in the Mott insulator $KCuF_3$, this assumption fails qualitatively: entropy plays a negligible role, while thermal expansion energetically stabilizes the orbitally ordered phase to such an extent that no phase transition is observed. To understand this strong dependence on the lattice constant, we need to take into account the Born-Mayer repulsion between the ions. It is the latter, and not the Jahn-Teller elastic energy, which determines the magnitude of the distortion. This effect will be seen in all materials where the distortion expected from the Jahn-Teller mechanism is so large that the ions would touch. Our mechanism explains not only the absence of a phase transition in $KCuF_3$, but even suggests the possibility of an *inverted* transition in closed-shell systems, where the ordered phase emerges only at high temperatures.

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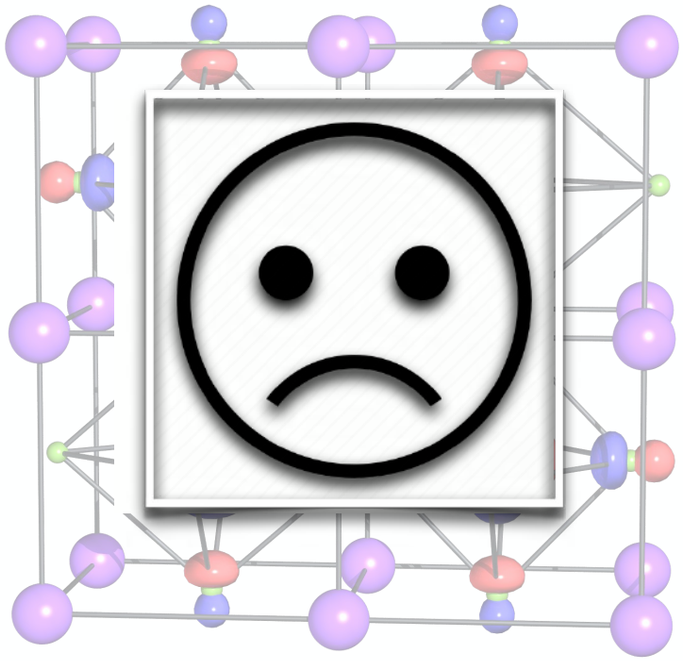
KK-only candidates

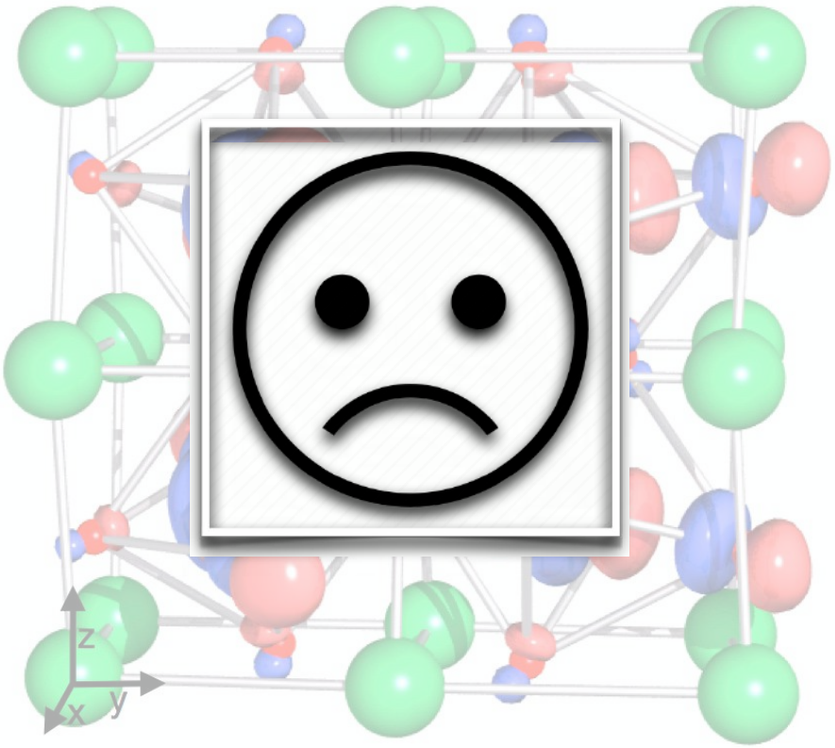
e_g systems

$KCuF_3$



$t_{2g}^6 e_g^3$

$LaMnO_3$



$t_{2g}^3 e_g^1$

$KCrF_3$

$ReMnO_3$

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perhaps we looked in the wrong place..

t_{2g} systems at low temperature?

larger orbital degeneracy, weaker electron-lattice coupling, smaller crystal-field coupling

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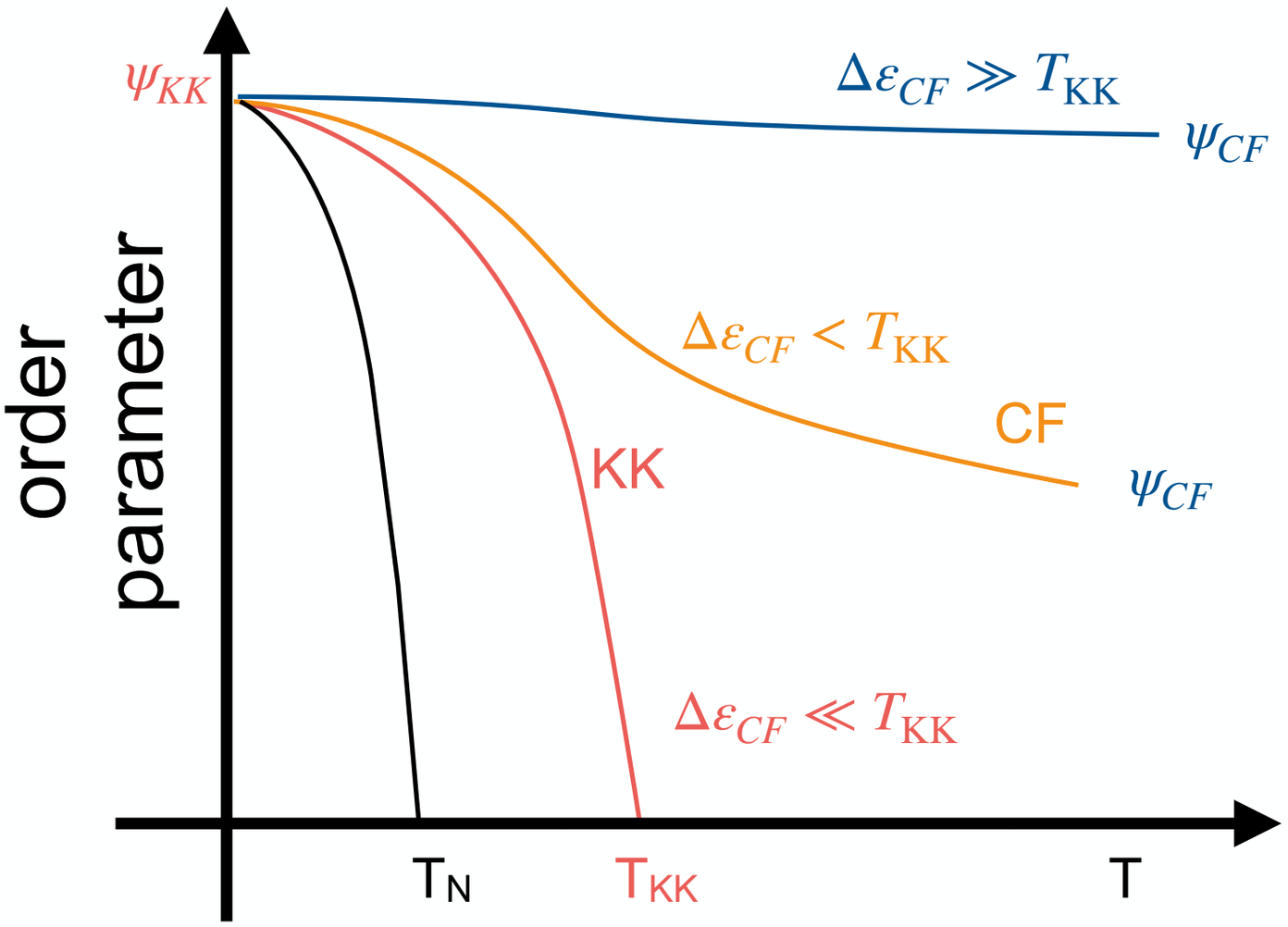
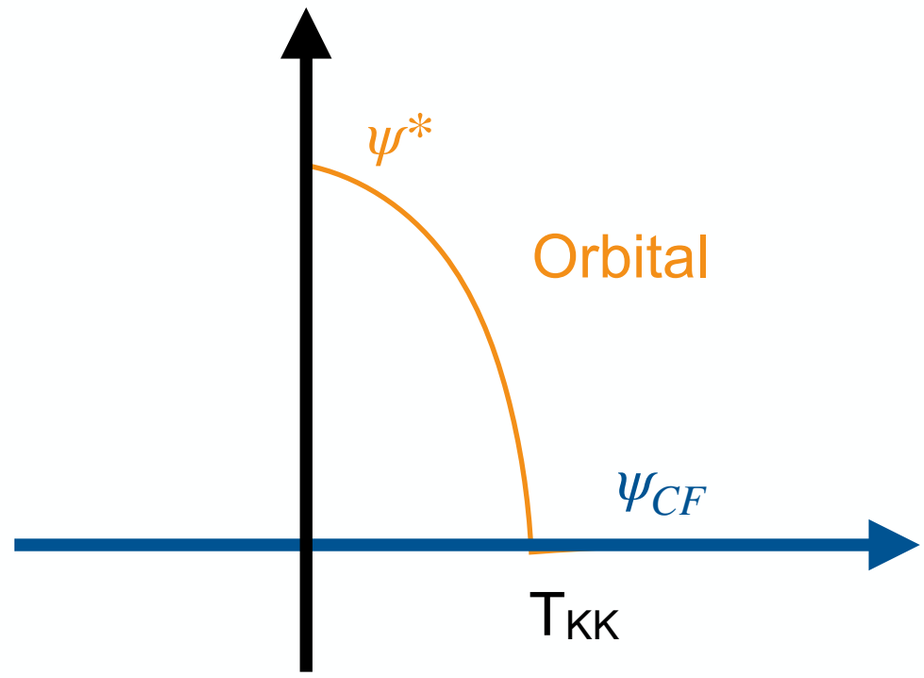
change of orbitals at low T?





ψ = occupied orbital

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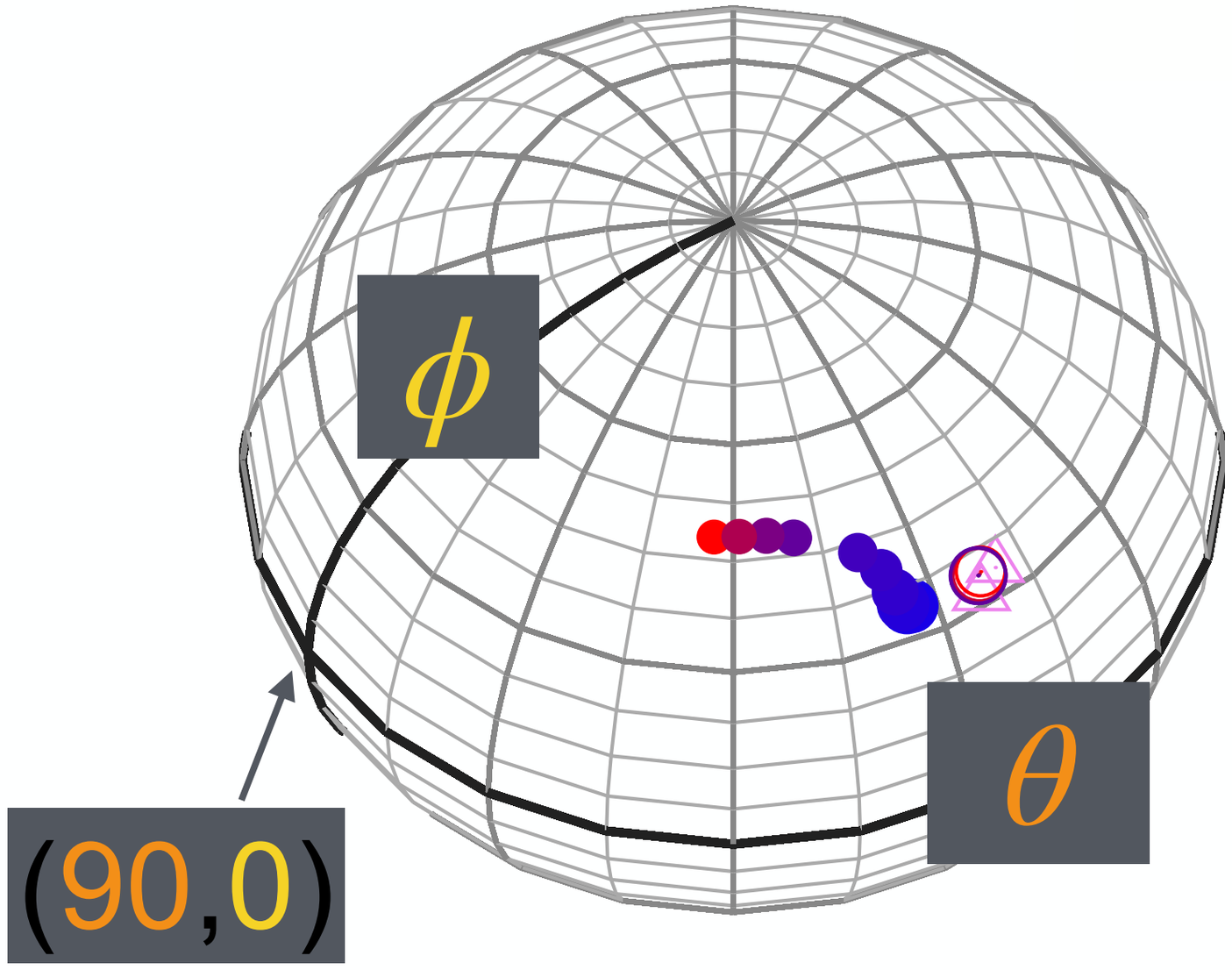
t_{2g} systems: representation of orbital



$$|\theta, \phi\rangle = -|\pi - \theta, \phi \pm \pi\rangle$$

$$= \sin\theta\cos\phi|xz\rangle + \cos\theta|xy\rangle + \sin\theta\sin\phi|yz\rangle.$$

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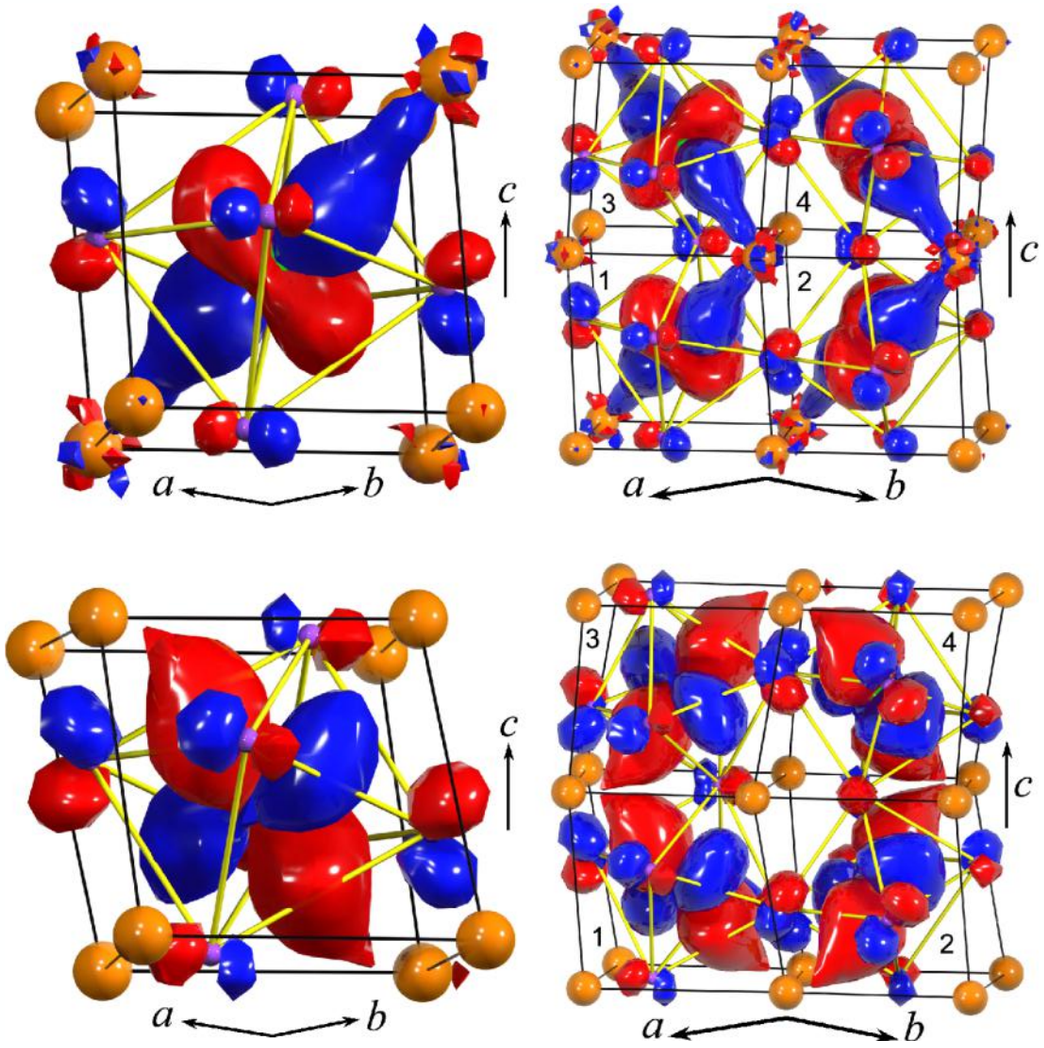
do we need a large crystal-field?

VOLUME 92, NUMBER 17 PHYSICAL REVIEW LETTERS week ending 30 APRIL 2004

Mott Transition and Suppression of Orbital Fluctuations in Orthorhombic $3d^1$ Perovskites

E. Pavarini,[1] S. Biermann,[2] A. Poteryaev,[3] A. I. Lichtenstein,[3] A. Georges,[2] and O. K. Andersen[4]

$LaTiO_3$



$YTiO_3$

t_{2g}^1

LDA+DMFT 770 K

Δ=200-300 meV

No! A 100 meV crystal-field is enough (W~3 eV)

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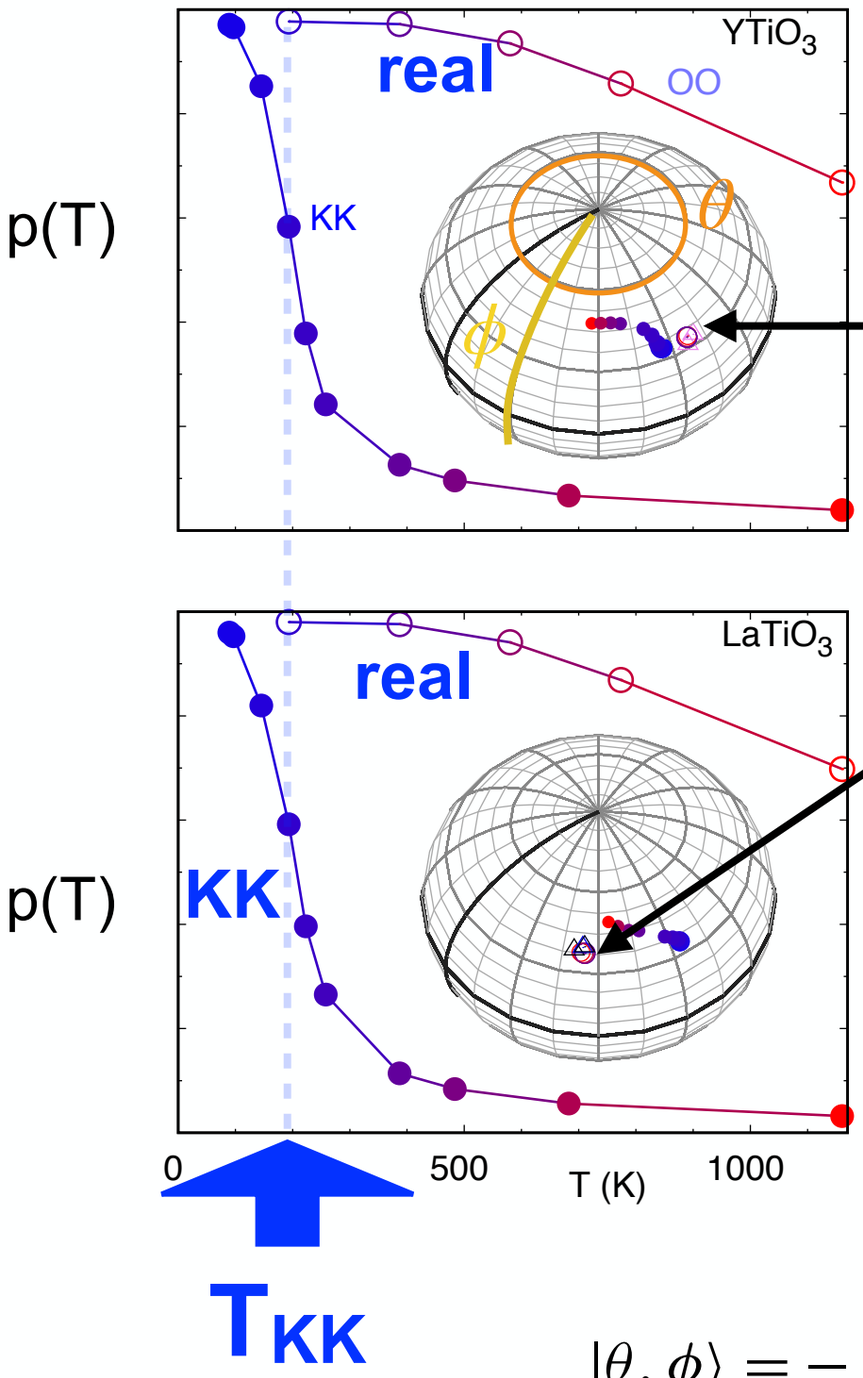
$ReTiO_3$: T_{KK}~300 K



same of CF-orbital

nothing changes at T_{KK}

occupied state temperature-independent!

$$|\theta, \phi\rangle = -|\pi - \theta, \phi \pm \pi\rangle$$
$$= \sin\theta\cos\phi|xz\rangle + \cos\theta|xy\rangle + \sin\theta\sin\phi|yz\rangle.$$

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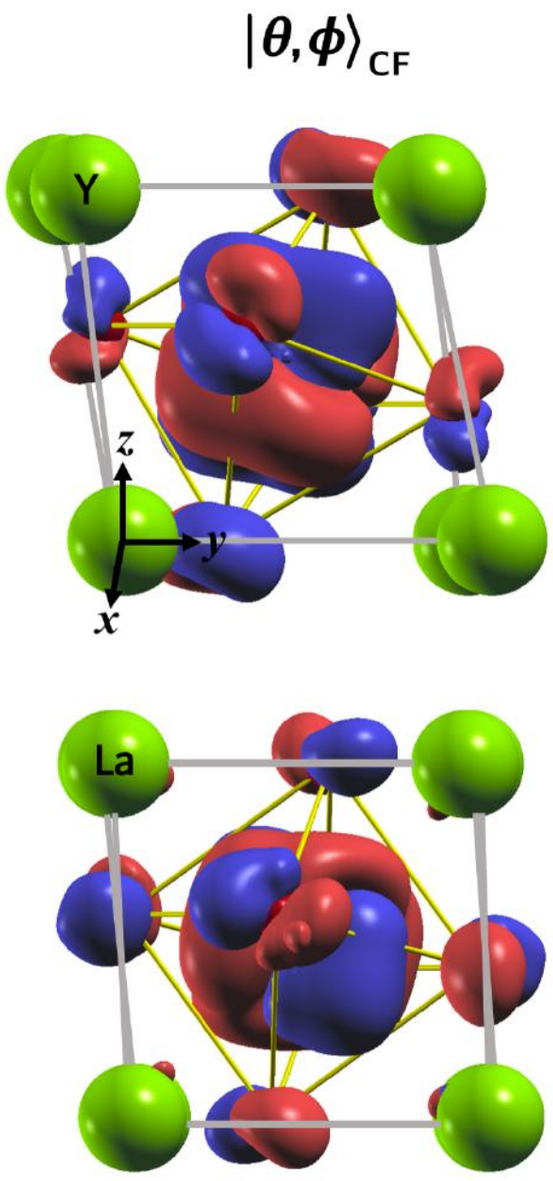
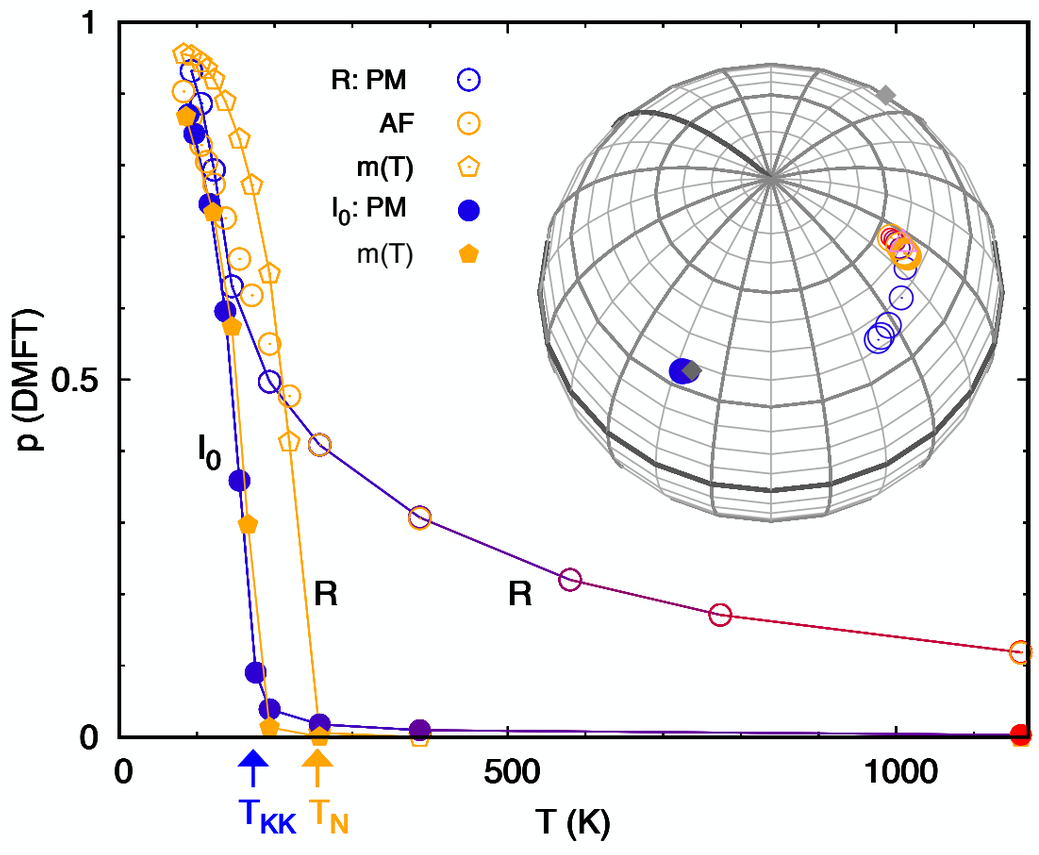
the first clear case: $LaVO_3$

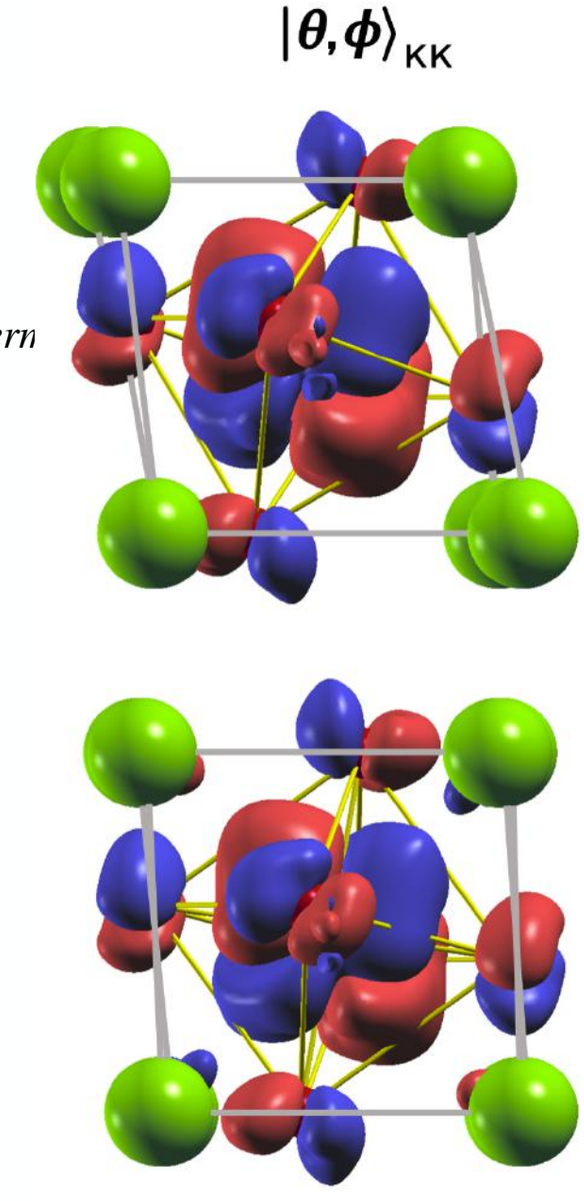
PHYSICAL REVIEW B **106**, 115110 (2022)



$LaVO_3$: A true Kugel-Khomskii system

Xue-Jing Zhang,[1] Erik Koch,[1,2] and Eva Pavarini[1,2]
[1]Institute for Advanced Simulation, Forschungszentrum Jülich, 52425 Jülich, Germ
[2]JARA High-Performance Computing, 52062, Aachen, Germany.





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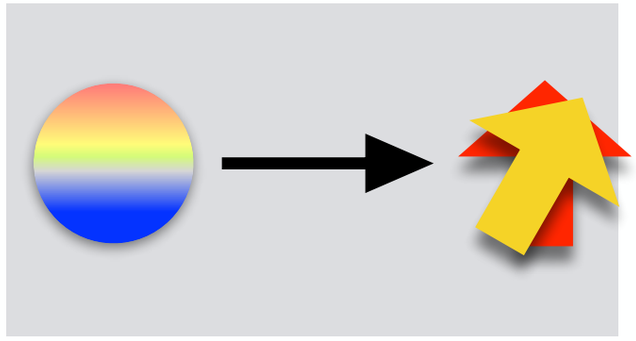
conclusion: mechanisms

emergence of local spins and pseudospins



high energy

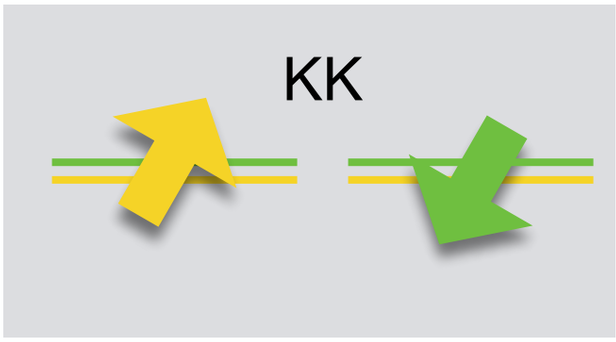
distortions

crystal-field splitting

enhanced by coulomb repulsion

low energy

super-exchange interactions



purely electronic mechanism

coupling $4t^2/U$

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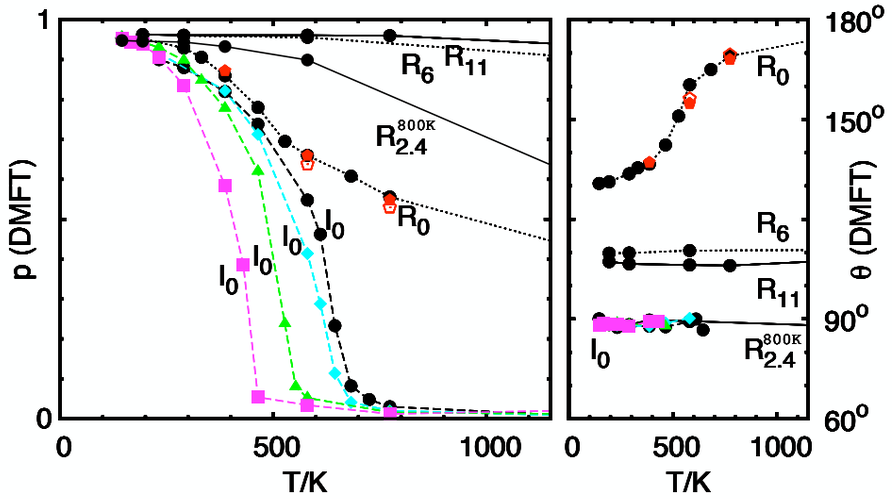
however, materials are complex

KBF_3 K_2BF_4 $ReMnO_3$ $ReTiO_3$

super-exchange strong but alone cannot explain T_{OO}

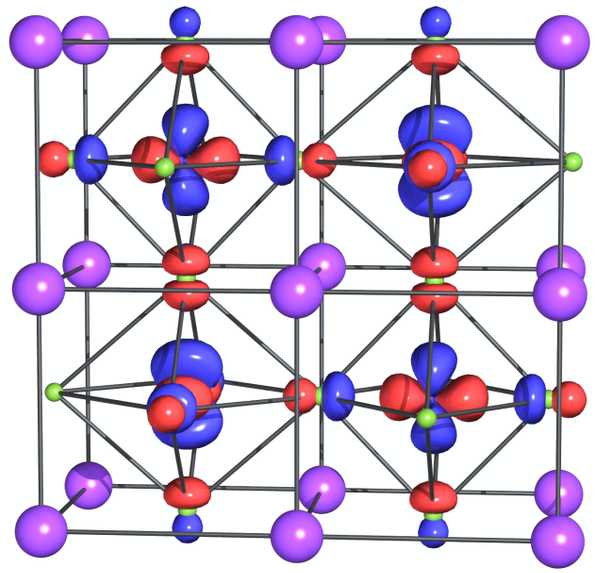
T_{KK} remarkably large



Phys. Rev. Lett. **101**, 266405 (2008)

Phys. Rev. Lett. **104**, 086402 (2010)

but static splitting essential



$T_{KK} \ll T_{OO}$ *and* T_{JT}

KBF_3 : also JT not enough (Born-Mayer repulsion)

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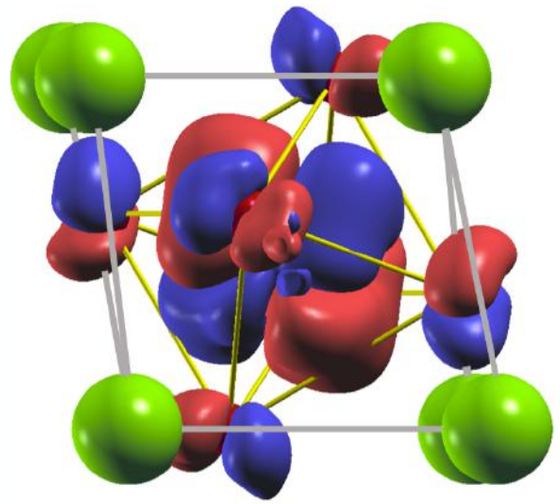
the first clear KK case: $LaVO_3$

X.-J. Zhang, E. Koch and E. Pavarini, Phys. Rev. B **106**, 115110 (2022)

$|\theta,\phi\rangle_{KK}$

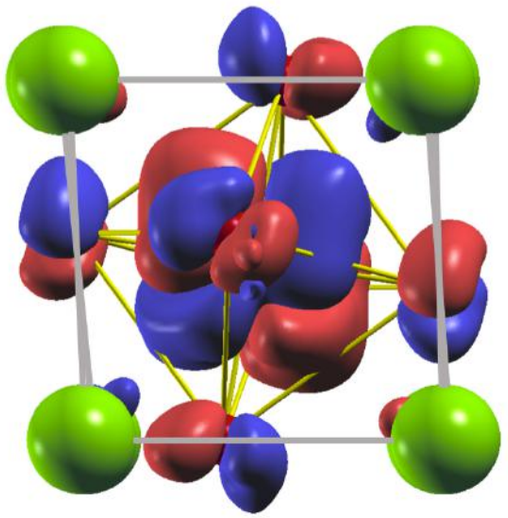


Crystal structure and magnetic properties of substances with orbital degeneracy

K. I. Kugel' and D. I. Khomskiĭ
P. N. Lebedev Physics Institute

(Submitted November 13, 1972)
Zh. Eksp. Teor. Fiz. **64**, 1429-1439 (April 1973)

Exchange interaction in magnetic substances containing ions with orbital degeneracy is considered. It is shown that, among with spin ordering, superexchange also results in cooperative ordering of Jahn-Teller ion orbitals, which, generally speaking, occurs at a higher temperature and is accompanied by distortion of the lattice (which is a secondary effect here). Concrete studies are performed for substances with a perovskite structure ($KCuF_3$, $LaMnO_3$, MnF_3). The effective spin Hamiltonian is obtained for these substances and the properties of the ground state are investigated. The orbital and magnetic structures obtained in this way without taking into account interaction with the lattice are in accord with the structures observed experimentally. The approach employed also permits one to explain the strong anisotropy of the magnetic properties of these compounds and to obtain a reasonable estimate for the critical temperatures.



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FORSCHUNGSZENTRUM

thank you!