Orbital Ordering in materials

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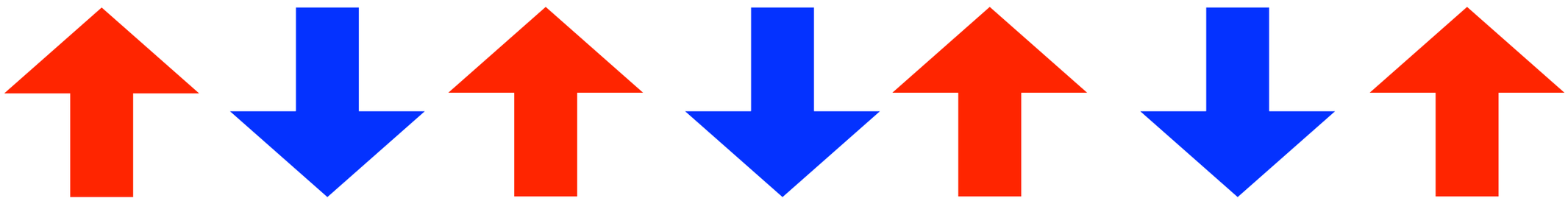
spontaneous spin ordering

spin degrees of freedom: 2S+1

$$H_{SE}^{ii'} = J_{SS} S_i \cdot S_{i'} \qquad H = \frac{1}{2} \sum_{i,i'} H_{SE}^{ii'}$$



S=1/2, degenerate spin states

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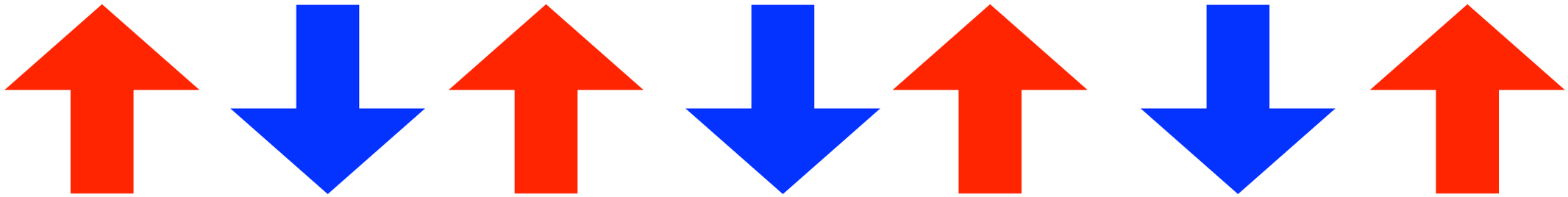
spontaneous spin ordering



MnO

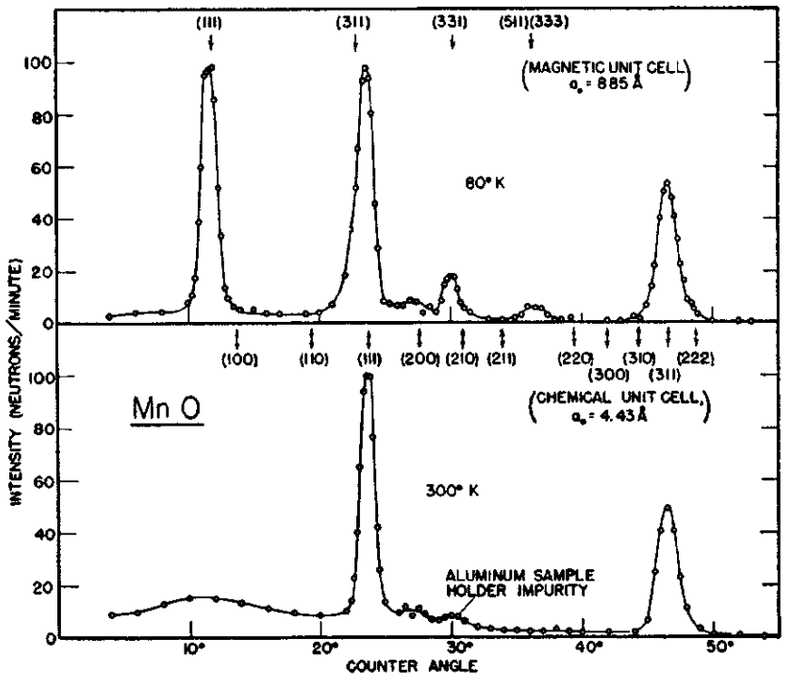


FIG. 1. Neutron diffraction patterns for MnO at room temperature and at 80°K.

T=80K

T=300K

neutron scattering: Shull and Smart (1949)

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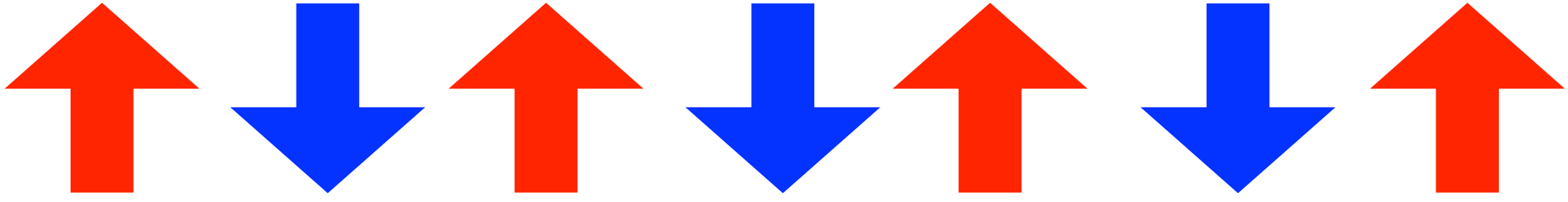
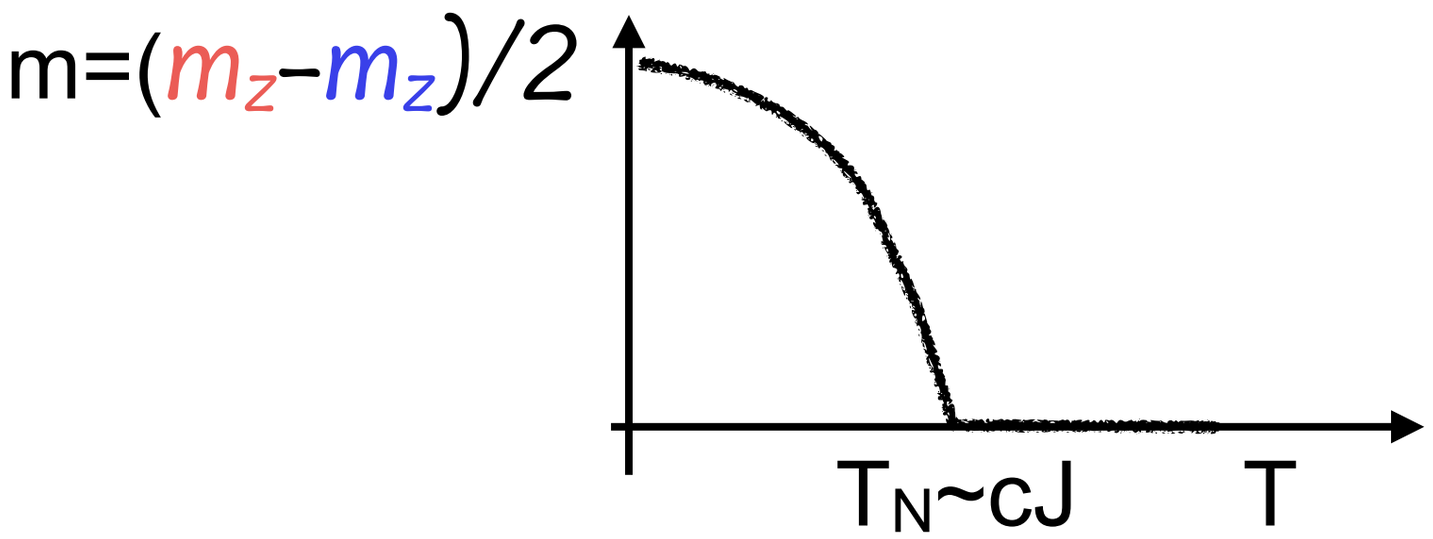
spontaneous spin ordering



phase transition, order parameter



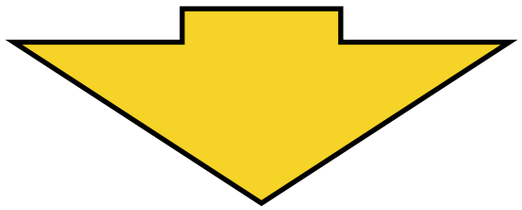
$m_z = \langle S_z \rangle$

strongly-correlated materials

mechanism: super-exchange

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

t/U small



half filling
(one electron per site)

$$H = \frac{1}{2} \sum_{i,i'} H^{ii'}_{SE} \qquad H^{ii'}_{SE} = J_{SS} S_i \cdot S_{i'}$$

S=1/2, $J_{SS}=4t^2/U$

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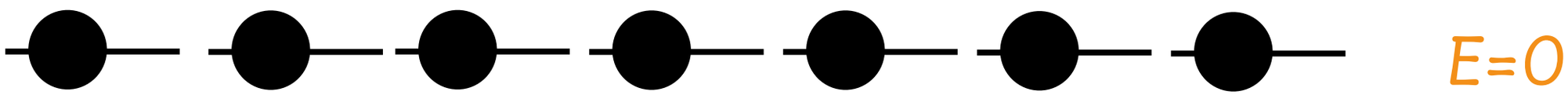
one-band Hubbard model

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

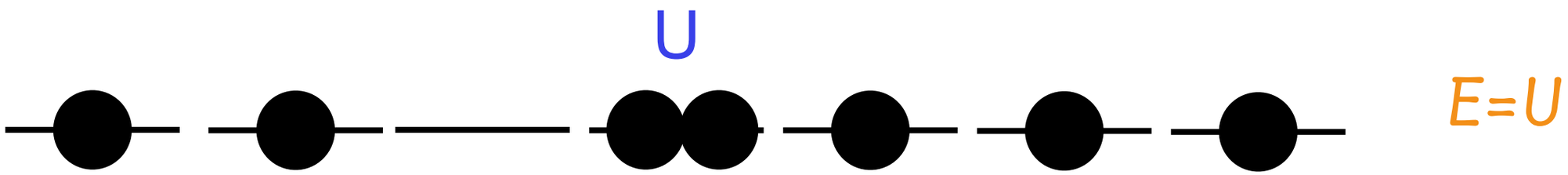
set to zero

ground state *without hopping*



E=0

first excited state *without hopping*



E=U

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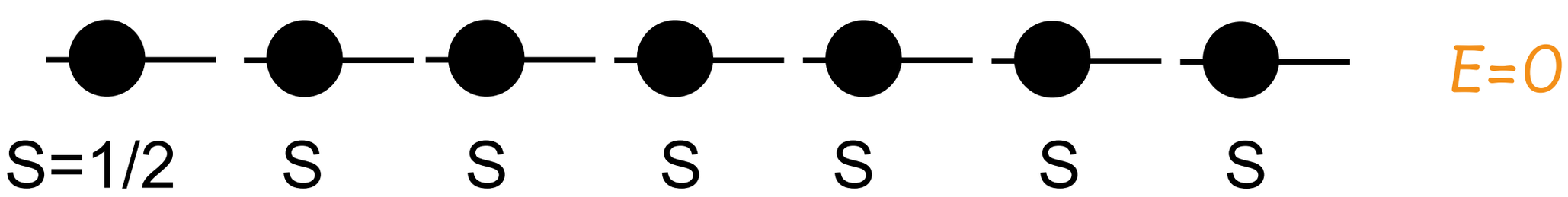
one-band Hubbard model

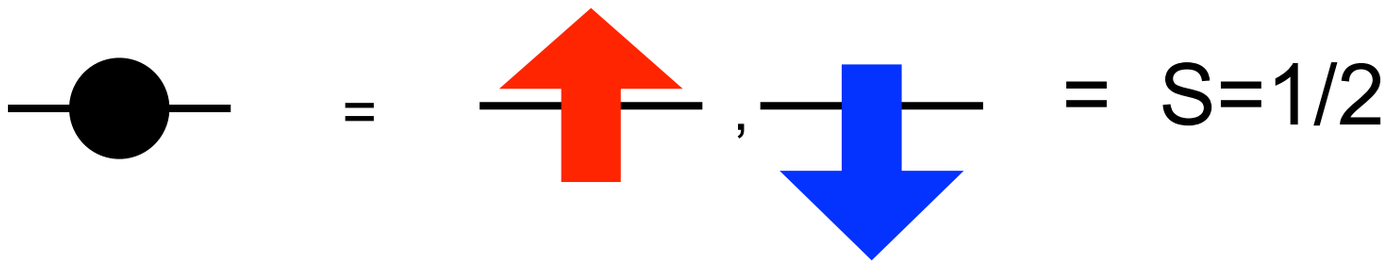
$$\hat{H} = \boxed{-t \sum_{\langle ii' \rangle} \sum_{\sigma} c^{\dagger}_{i\sigma} c_{i'\sigma}} + \boxed{U \sum_{i} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}}$$

set to zero

ground state *without hopping*



E=0



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

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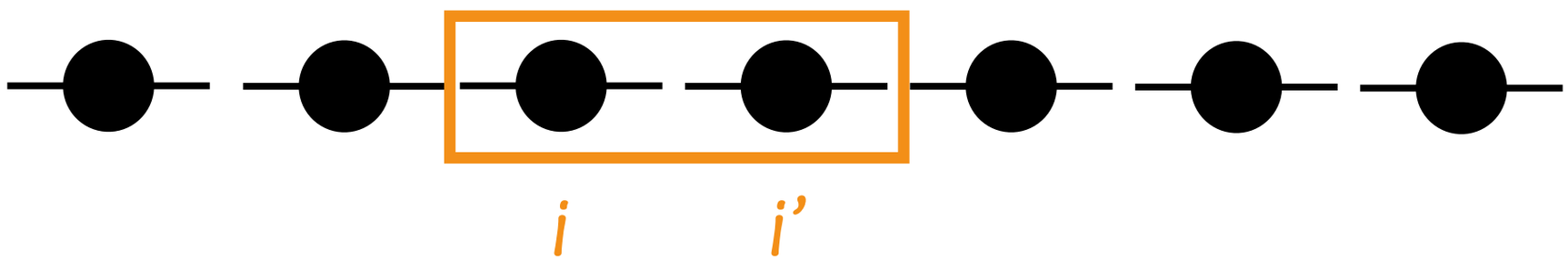
one-band Hubbard model

hopping as perturbation

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



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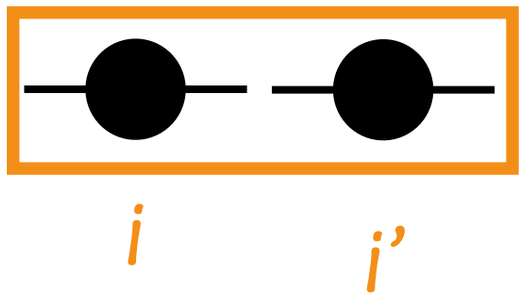
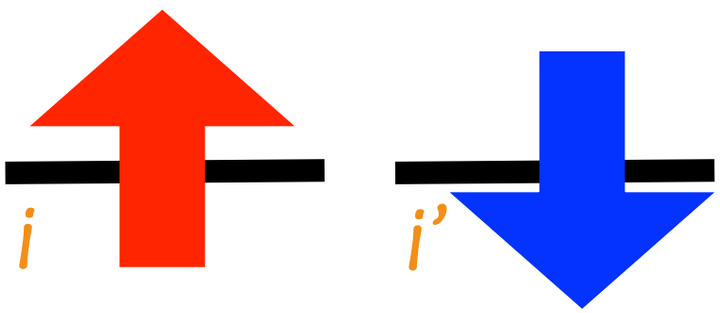
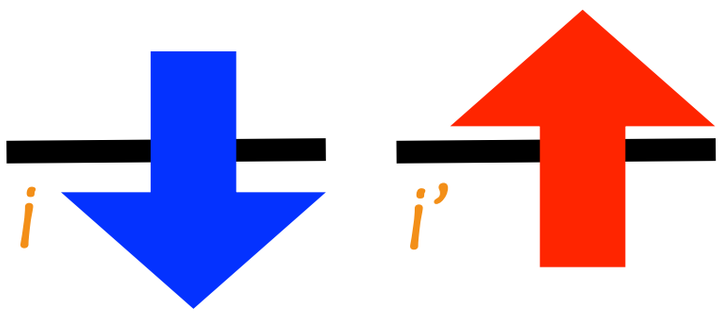
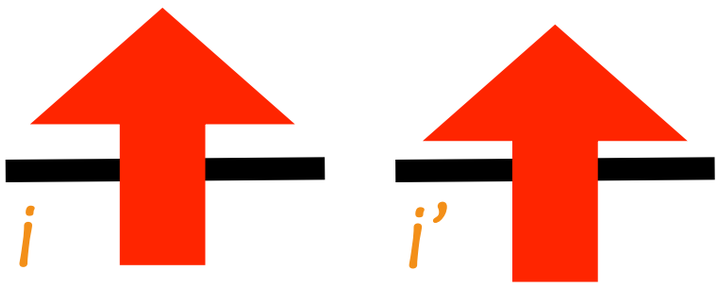
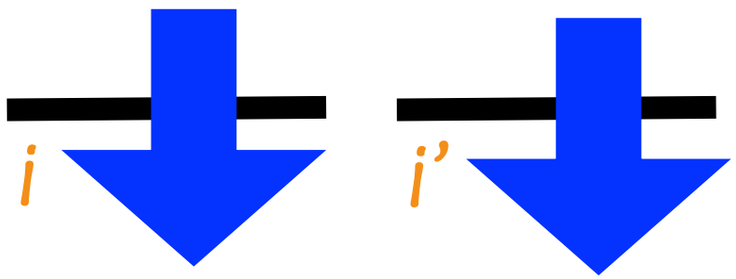
two sites, 4 states with E=0











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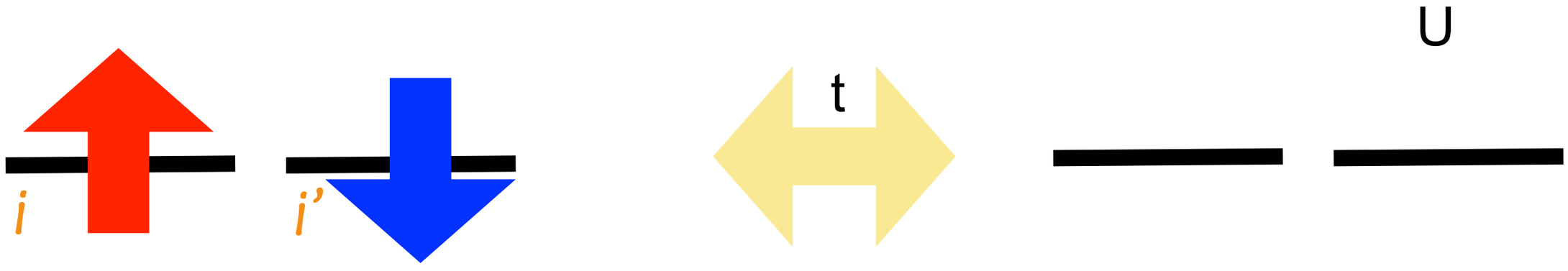
result depends on spin arrangement

hops to doubly occupied states



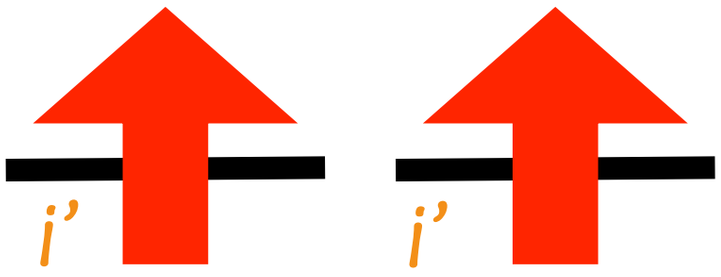
$$\Delta E_{\uparrow\downarrow} \sim -\sum_I \langle\uparrow,\downarrow|H_T|I\rangle\langle I\left|\frac{1}{E(2)+E(0)-2E(1)}\right|I\rangle\langle I|H_T|\uparrow,\downarrow\rangle \sim -\frac{2t^2}{U}.$$

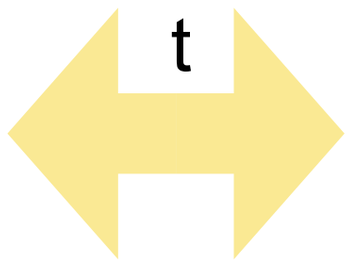
=t	$1/(E_I-E_G)=1/U$	=t

(second-order perturbation theory)

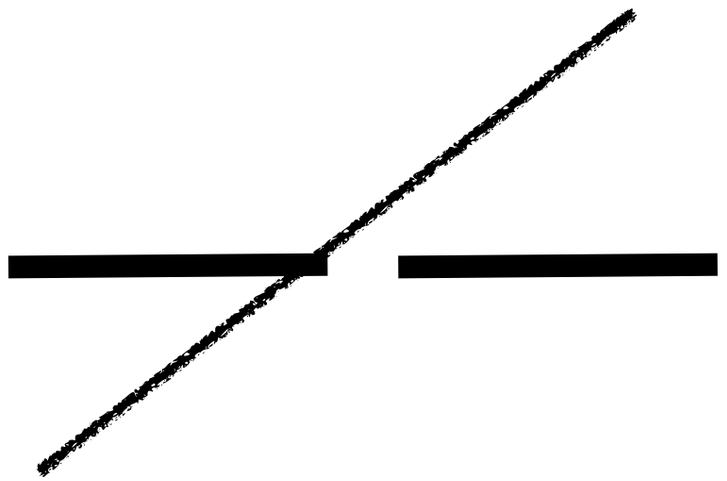
energy gain

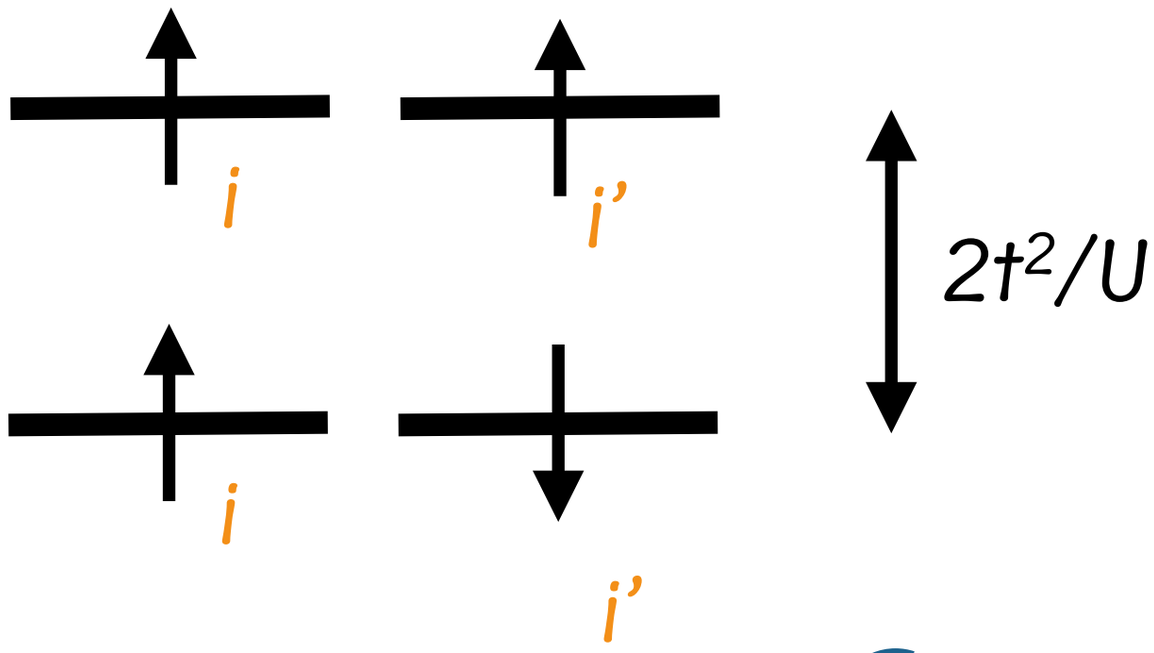
no gain for FM arrangement





No! Pauli principle





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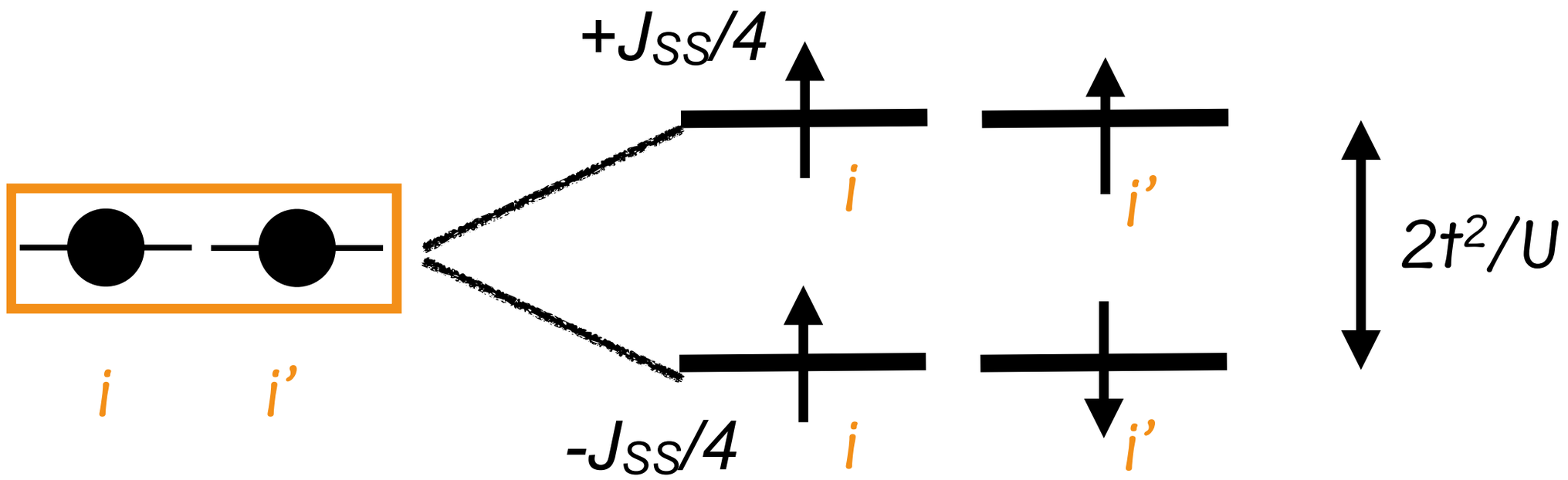
effective spin model

$$H_{SE}^{ii'} = J_{SS} S_i \cdot S_{i'}$$

$S=1/2,\ J_{SS}=4t^2/U$



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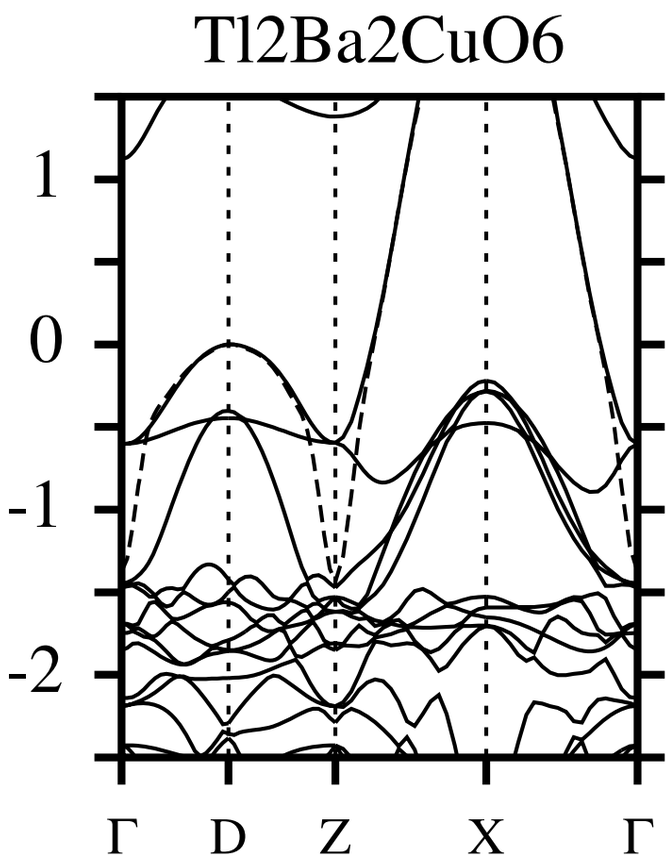
high-T_c superconducting cuprates

VOLUME 87, NUMBER 4 PHYSICAL REVIEW LETTERS 23 JULY 2001

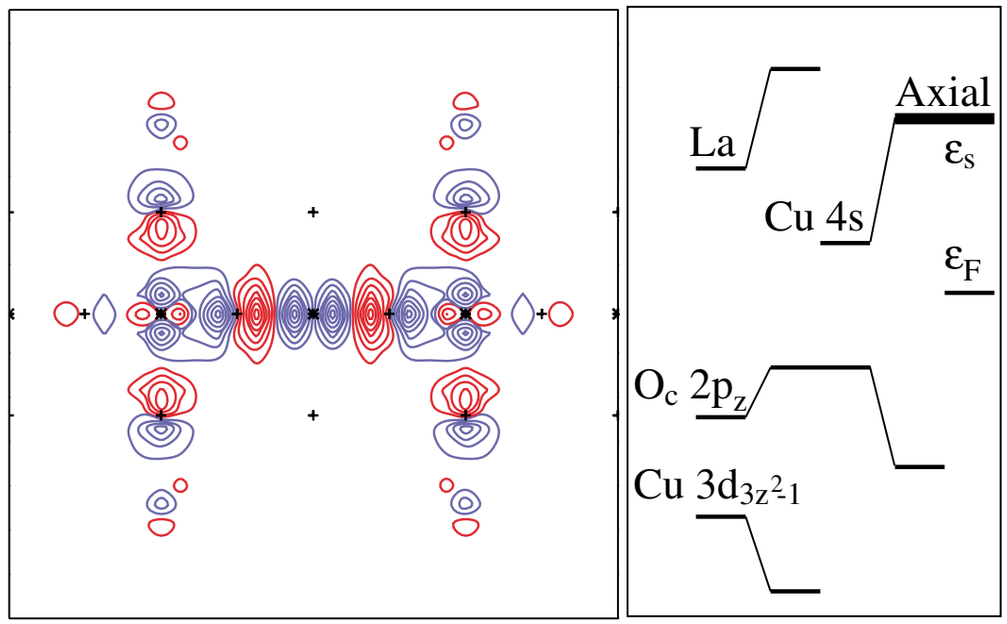
Band-Structure Trend in Hole-Doped Cuprates and Correlation with $T_{c\,\max}$

E. Pavarini, I. Dasgupta,* T. Saha-Dasgupta,† O. Jepsen, and O. K. Andersen
Max-Planck-Institut für Festkörperforschung, D-70506 Stuttgart, Germany
(Received 4 December 2000; published 10 July 2001)

By calculation and analysis of the bare conduction bands in a large number of hole-doped high-temperature superconductors, we have identified the range of the intralayer hopping as the essential, material-dependent parameter. It is controlled by the energy of the axial orbital, a hybrid between Cu $4s$, apical-oxygen $2p_z$, and farther orbitals. Materials with higher $T_{c\,\max}$ have larger hopping ranges and axial orbitals more localized in the CuO_2 layers.



the axial orbital



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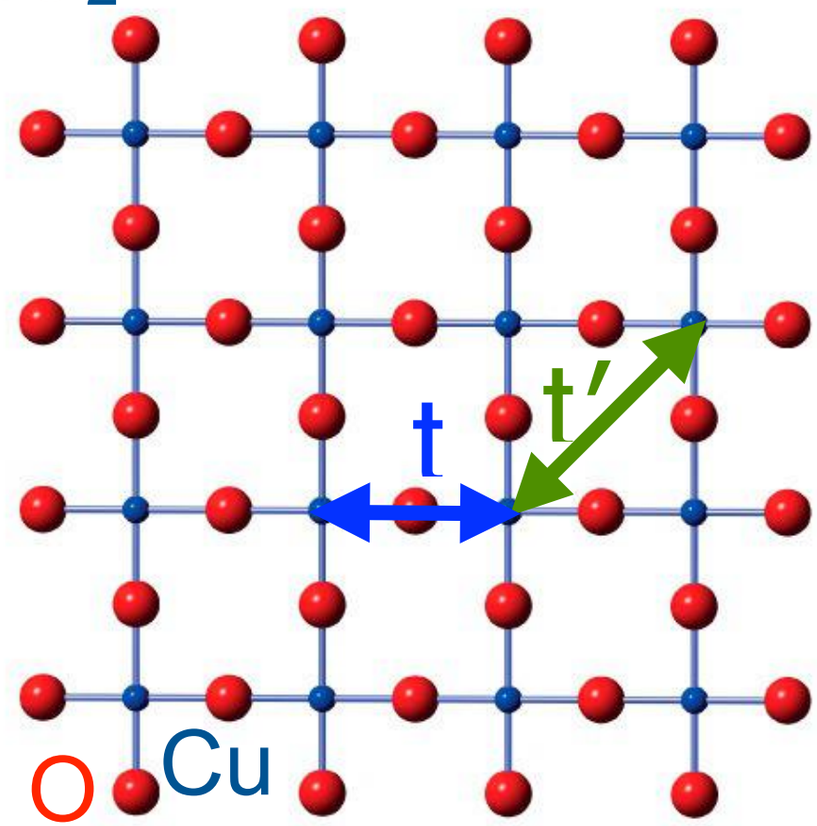
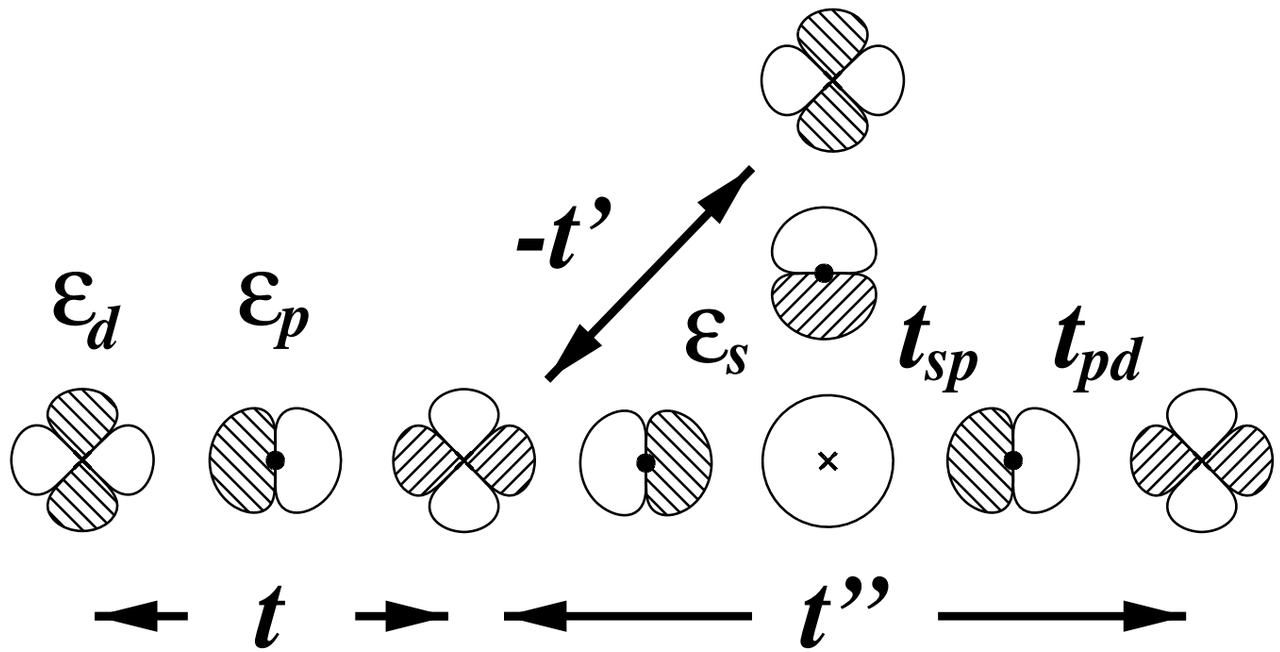
high-T_c superconducting cuprates (e_g^9)

$$H = -\sum_{\sigma} \sum_{\langle ii' \rangle} t_{i,i'} c^{\dagger}_{i\sigma} c_{i'\sigma}$$

CuO_2

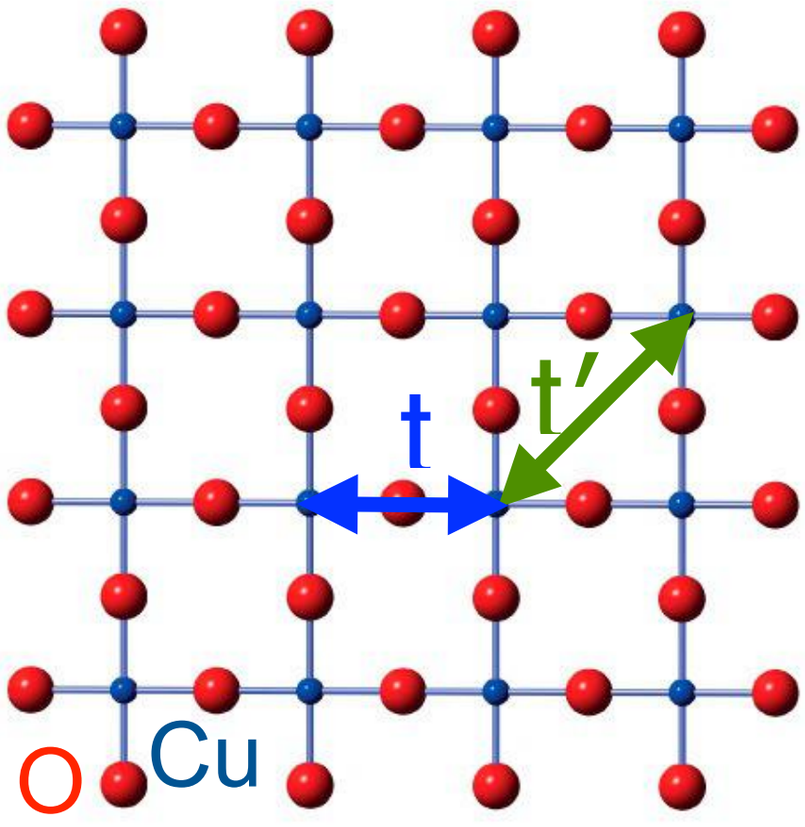




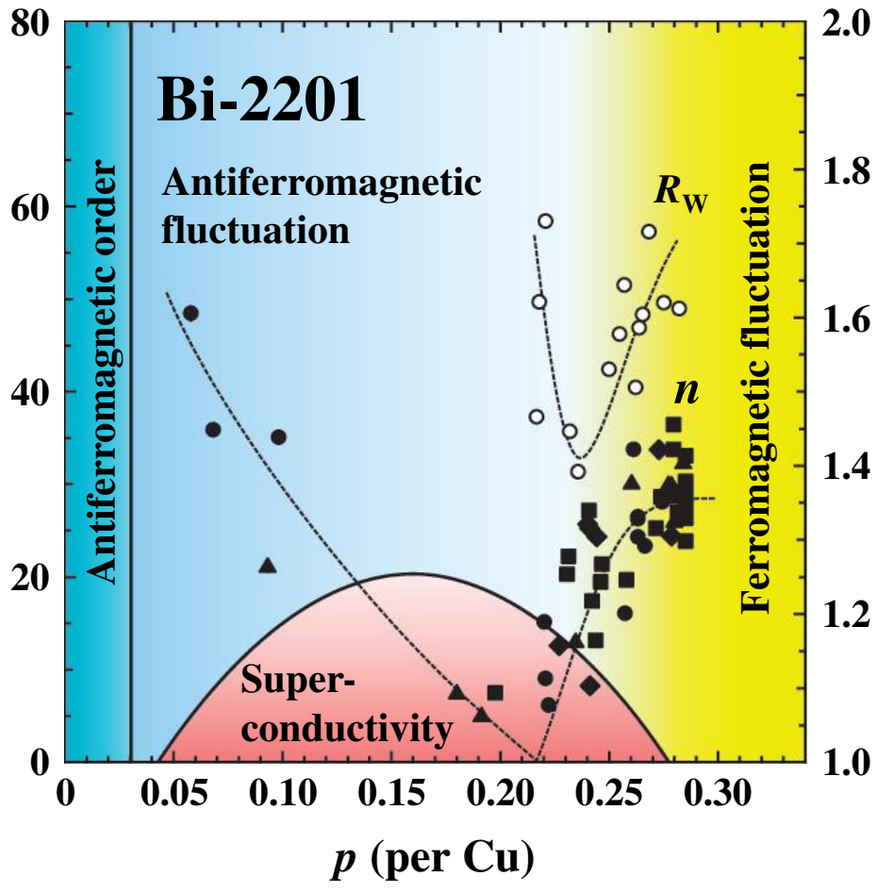
high-T_c superconducting cuprates (e_g^9)

$$H = -\sum_{\sigma}\sum_{\langle ii' \rangle} t_{i,i'} c^{\dagger}_{i\sigma} c_{i'\sigma} + \sum_{i} U n_{i\uparrow} n_{i\downarrow}$$

CuO_2



PRL 121, 057002 (2018)



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effective low-energy models

$$\hat{H}_e = \underbrace{-\sum_{ab} t_{ab} c_a^\dagger c_b}_{\hat{H}_0} + \underbrace{\frac{1}{2} \sum_{aa'bb'} U_{aa'bb'}\ c_a^\dagger c_{a'}^\dagger c_{b'} c_b}_{\hat{H}_U}$$

Hubbard model

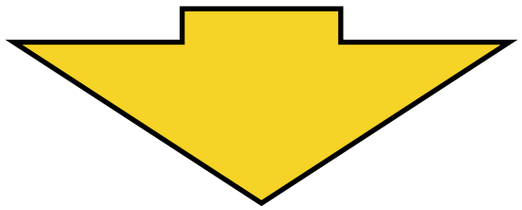
$$H = -\sum_{\sigma} \sum_{\langle ii' \rangle} t_{i,i'} c_{i\sigma}^\dagger c_{i'\sigma} + \sum_i U n_{i\uparrow} n_{i\downarrow}$$

emergent energy scale

mechanism: super-exchange

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

t/U small



half filling
(one electron per site)

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S=1/2, $J_{SS}=4t^2/U$

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spontaneous ordering of orbitals

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.

$KCuF_3$

$LaMnO_3$

strong Coulomb repulsion (the Hubbard U)

+ orbitals degrees of freedom

= orbital super-exchange

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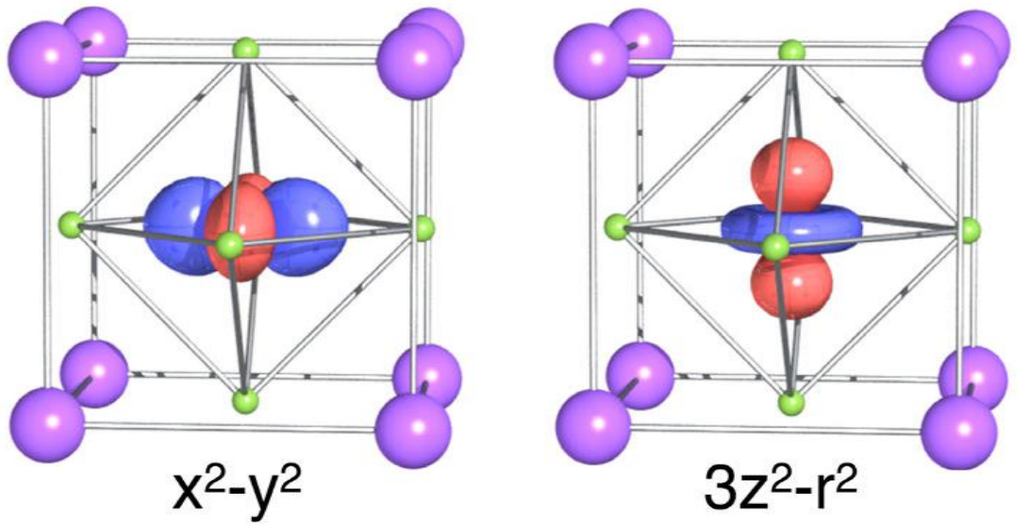
orbital degrees of freedom

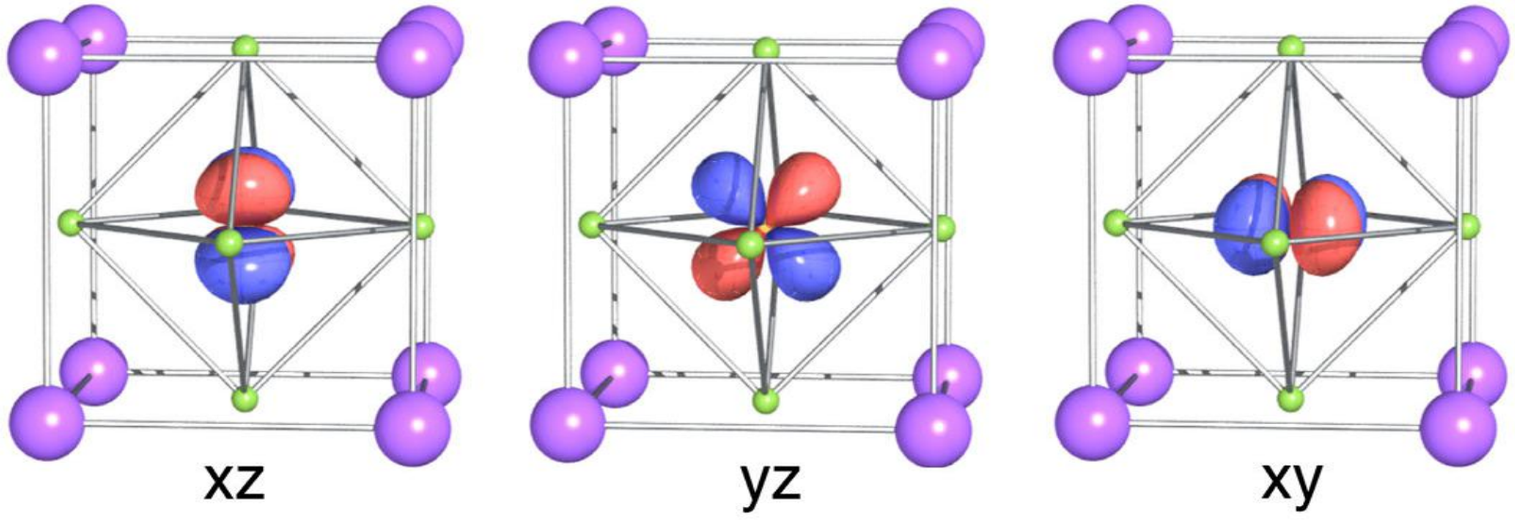
$KCuF_3$

$F^{1-}: 2p^6$

$Cu^{2+}: 3d^9 = t_{2g}^6 e_g^3$

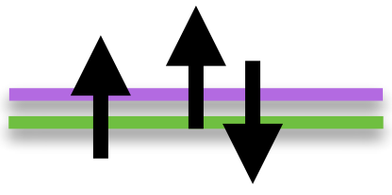
$K^{1+}: 3p^6$



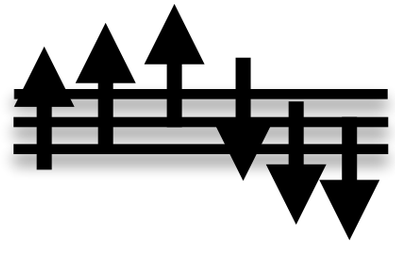


degenerate e_g orbitals

$(e_g)^3$



$(t_{2g})^6$



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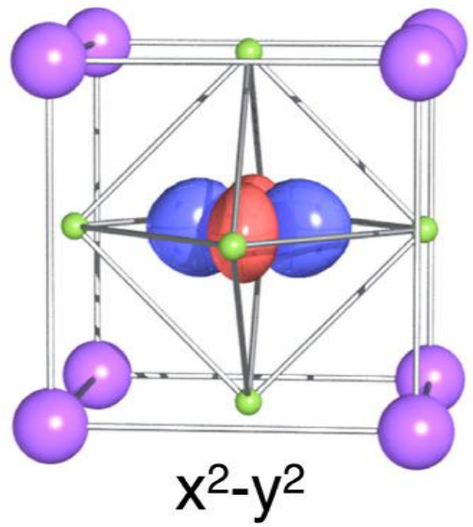
orbital degrees of freedom: holes

$KCuF_3$

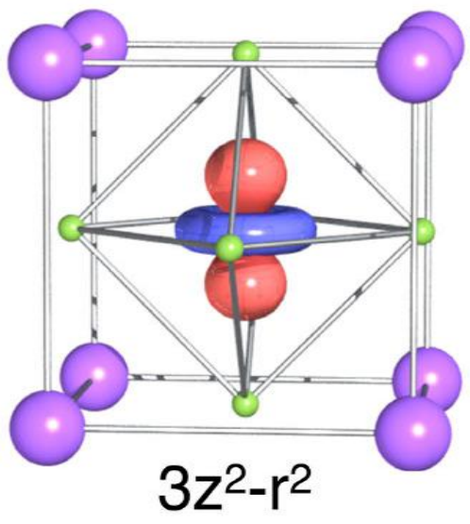
$F^{1-}: 2p^6$

$Cu^{2+}: 3d^9 = t_{2g}^6 e_g^3$

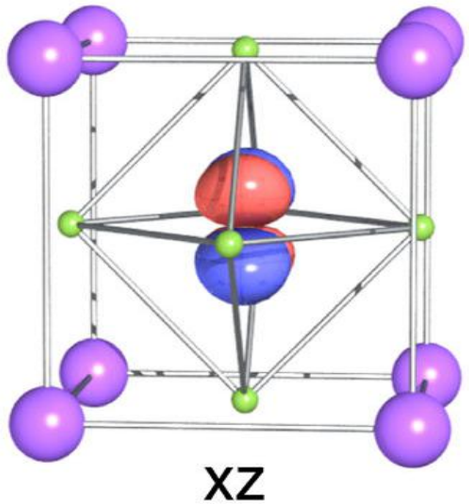
$K^{1+}: 3p^6$



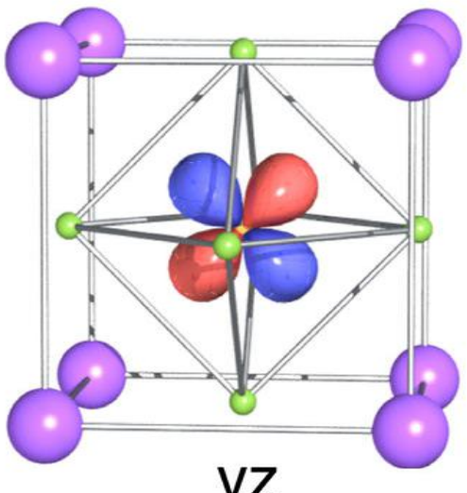
x^2-y^2



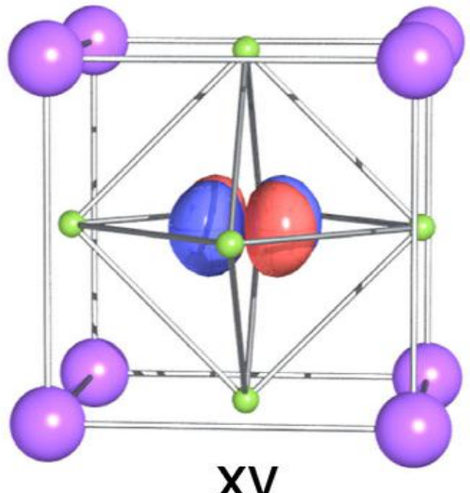
$3z^2-r^2$



xz



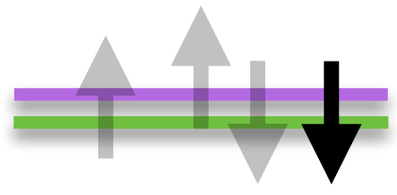
yz



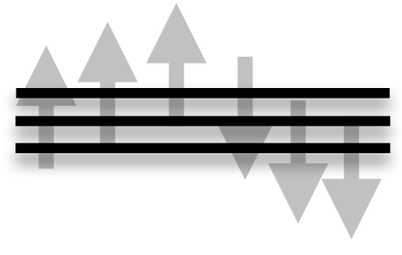
xy

degenerate e_g orbitals

$(e_g)^1$



$(t_{2g})^0$



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$KCuF_3$

$LaMnO_3$

orbital super-exchange

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

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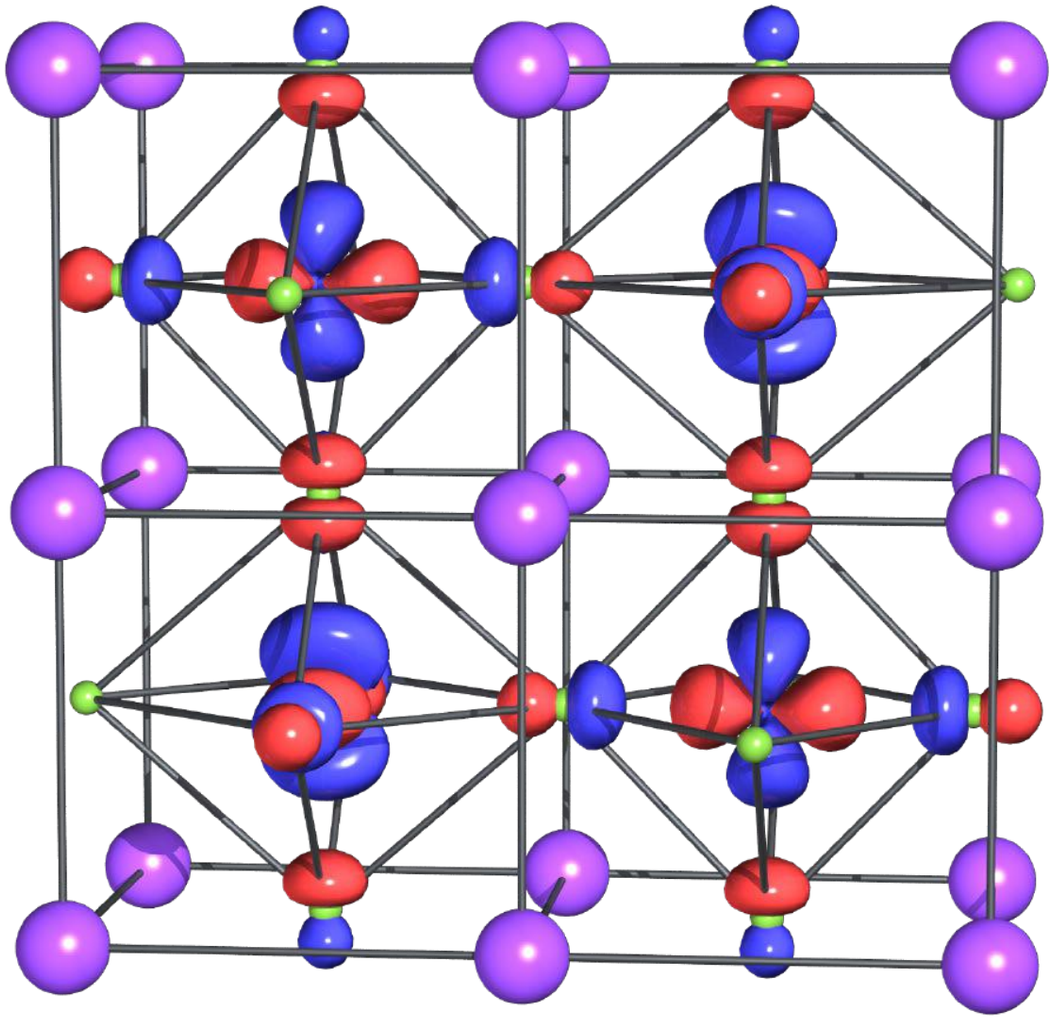
orbital ordering (OO) in $KCuF_3$

orbital degrees of freedom: degenerate Cu e_g orbitals



shown: empty e_g orbital (hole orbital) at each site

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orbital ordering

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
ww.sciencedirect.com/science/.../S0038109812004413 ▾ ScienceDirect ▾
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 ▾
Z Nussinov - Cited by 80 - Related articles
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,

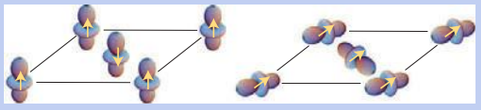

Figure 1 Possible arrangements of Mn^{3+} *d*-orbitals on a square lattice. The patterns are two-dimensional versions of orbitally ordered states actually observed in manganese oxides. The corresponding magnetic states are indicated by yellow arrows.

Article

Photo-induced high-temperature ferromagnetism in $YTiO_3$

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Received: 13 November 2021
Accepted: 16 February 2023
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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orbital physics

Review—Orbital Physics: Glorious Past, Bright Future

D. I. Khomskii[z]

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.

 [DOI: 10.1149/2162-8777/ac6906]

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John Goodenough

orbital ordering

orbital analogous of spin ordering

via orbital (KK) super-exchange

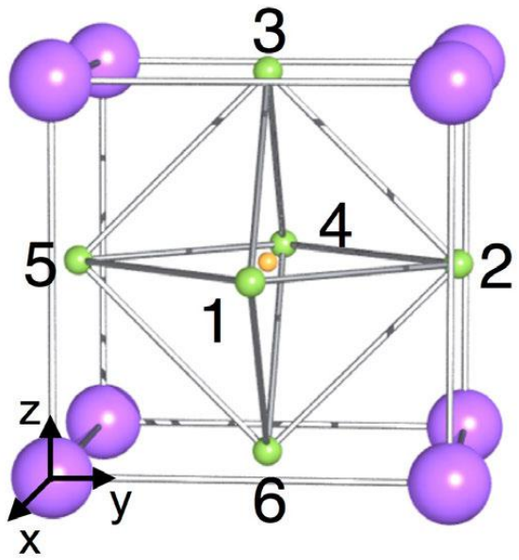
$$H_{SE}^{ii'} = J_{SS} S_i \cdot S_{i'} + J_{OO} O_i O_{i'} + J_{SO} (O_i O_{i'})(S_i \cdot S_{i'})$$

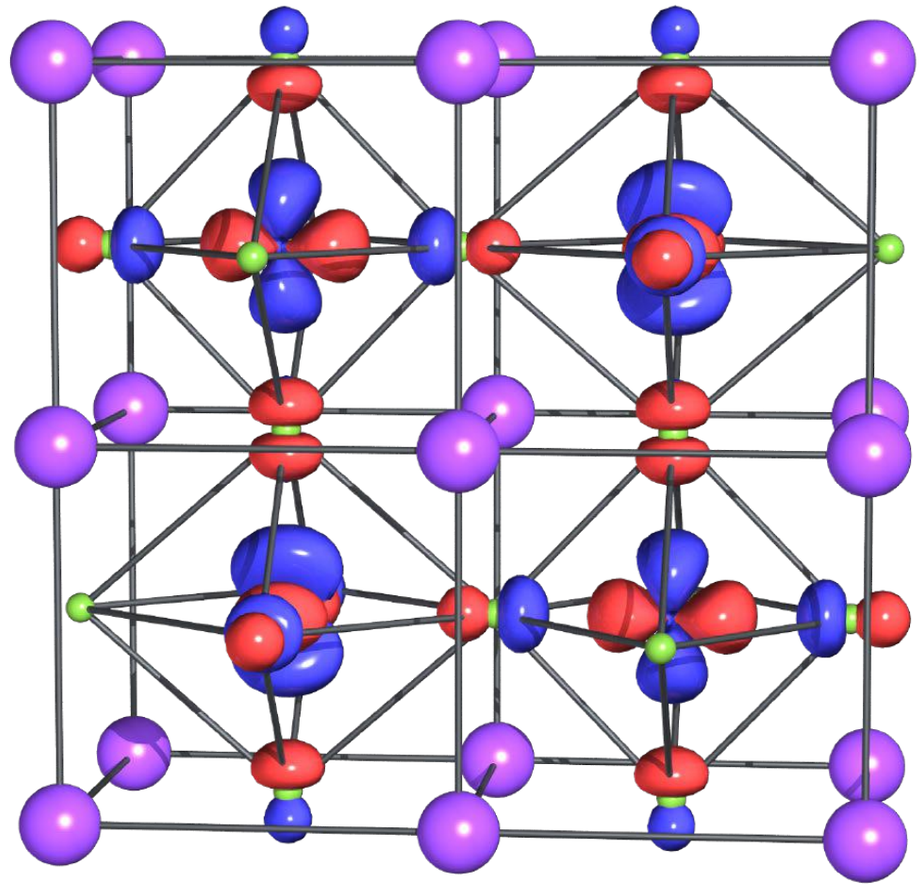
but there is a difference:

orbitals are strongly coupled to the lattice

orbital ordering (OO) in $KCuF_3$

OO can yield lattice distortions





alternating long and short CuF bonds

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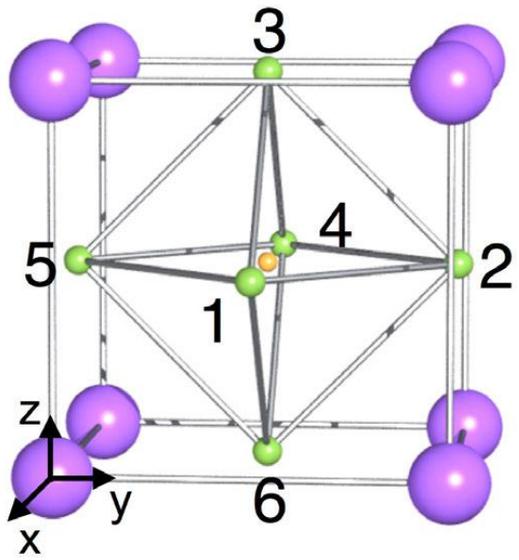
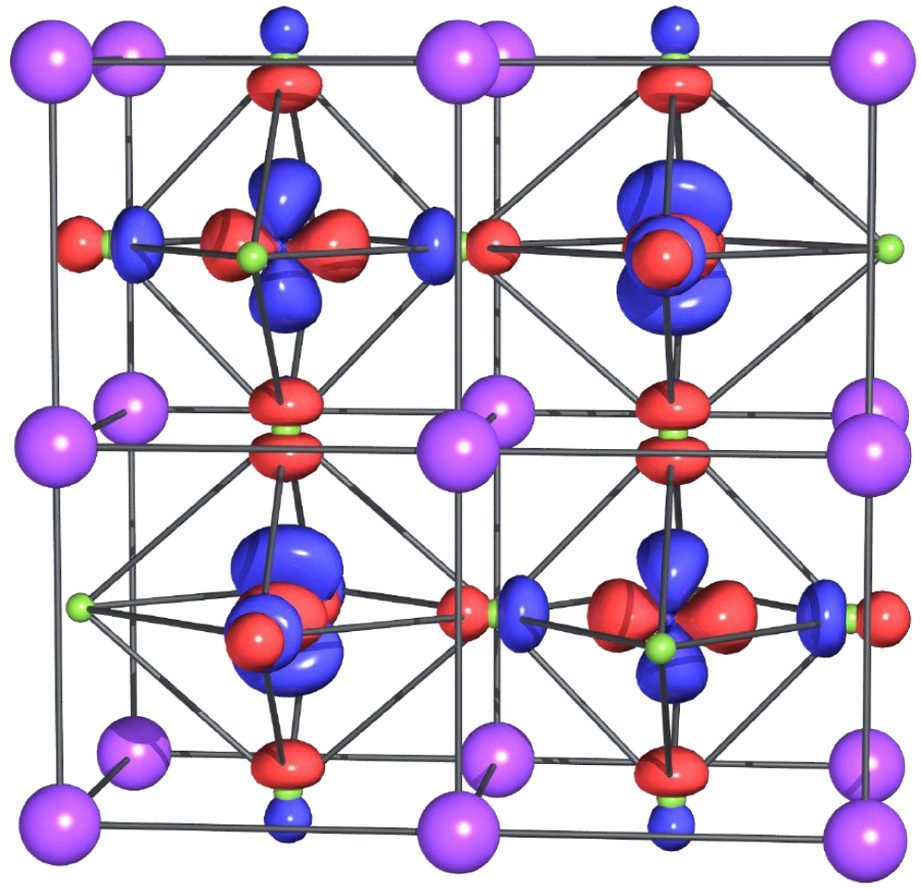
orbital ordering (OO) in $KCuF_3$

the distortion is the hallmark
of orbital ordering





alternating long and short CuF bonds

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orbital ordering (OO) in $KCuF_3$

another possibility: distortions yield order

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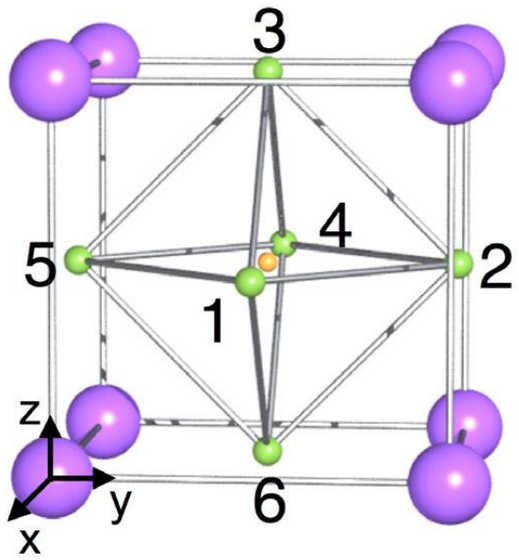
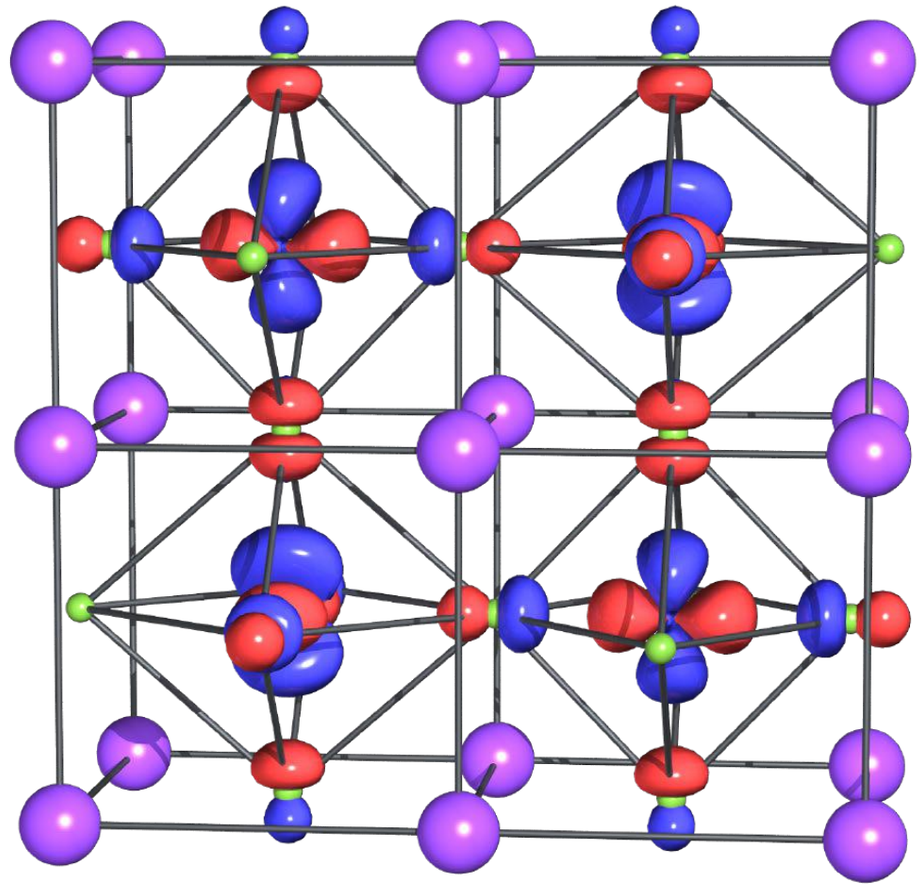
orbital ordering (OO) in $KCuF_3$

the distortion is the hallmark
of orbital ordering





alternating long and short CuF bonds

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why? Jahn-Teller theorem

Stability of Polyatomic Molecules in Degenerate Electronic States

I—Orbital Degeneracy

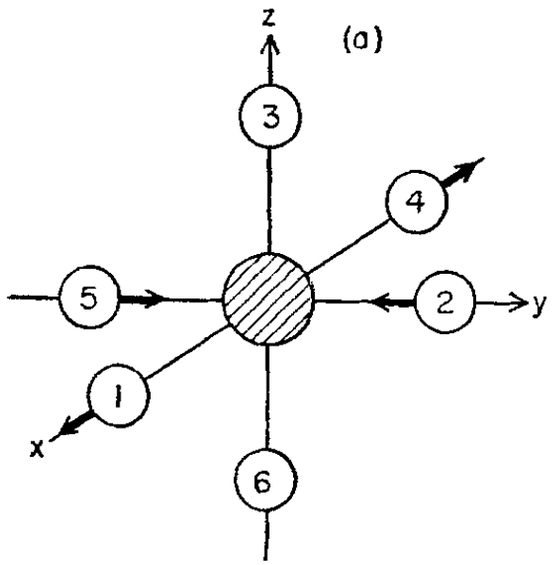
By H. A. Jahn, *Davy-Faraday Laboratory, The Royal Institution*
and E. Teller, *George Washington University, Washington, D.C.**

(*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.

lattice distortions generate 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

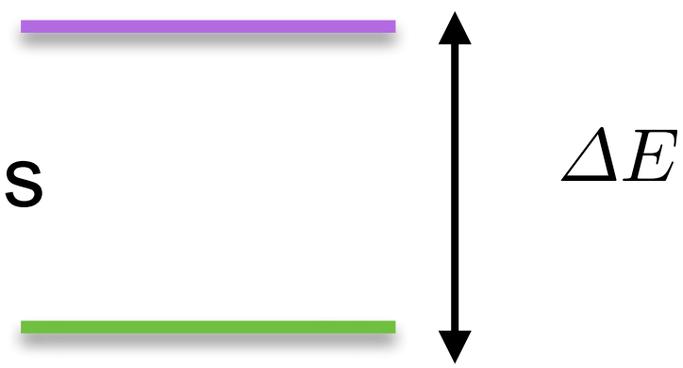
The crystal distortion which arises from the Jahn-Teller effect is discussed in several examples. In the case of compounds containing Cu^{2+} or Mn^{3+} at octahedral sites, the lowest orbital level of these ions is doubly degenerate in the undistorted structure, and there is no spin-orbit coupling in 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)

degenerate Cu e_g orbitals



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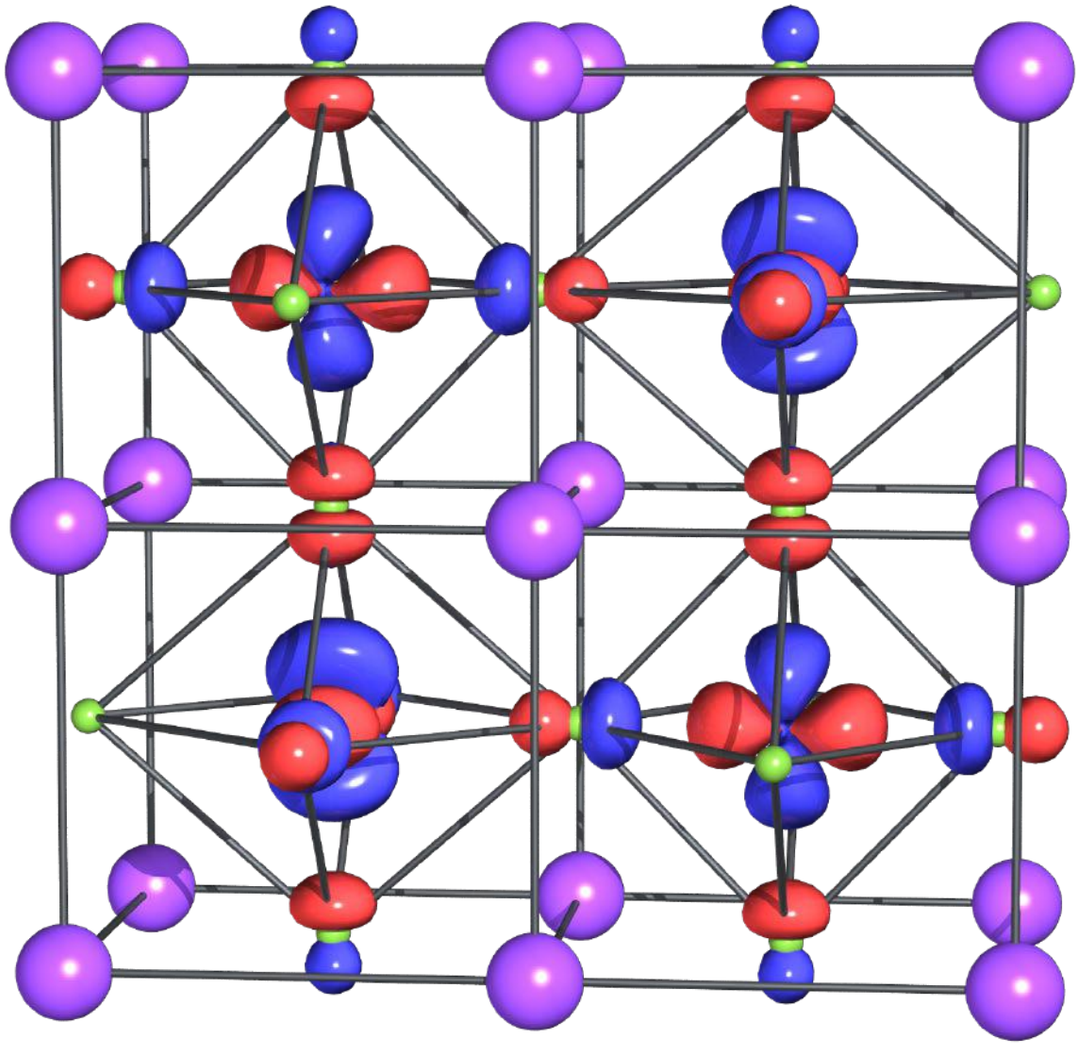
orbital ordering (OO) in $KCuF_3$



shown: empty e_g orbital (hole orbital) at each site

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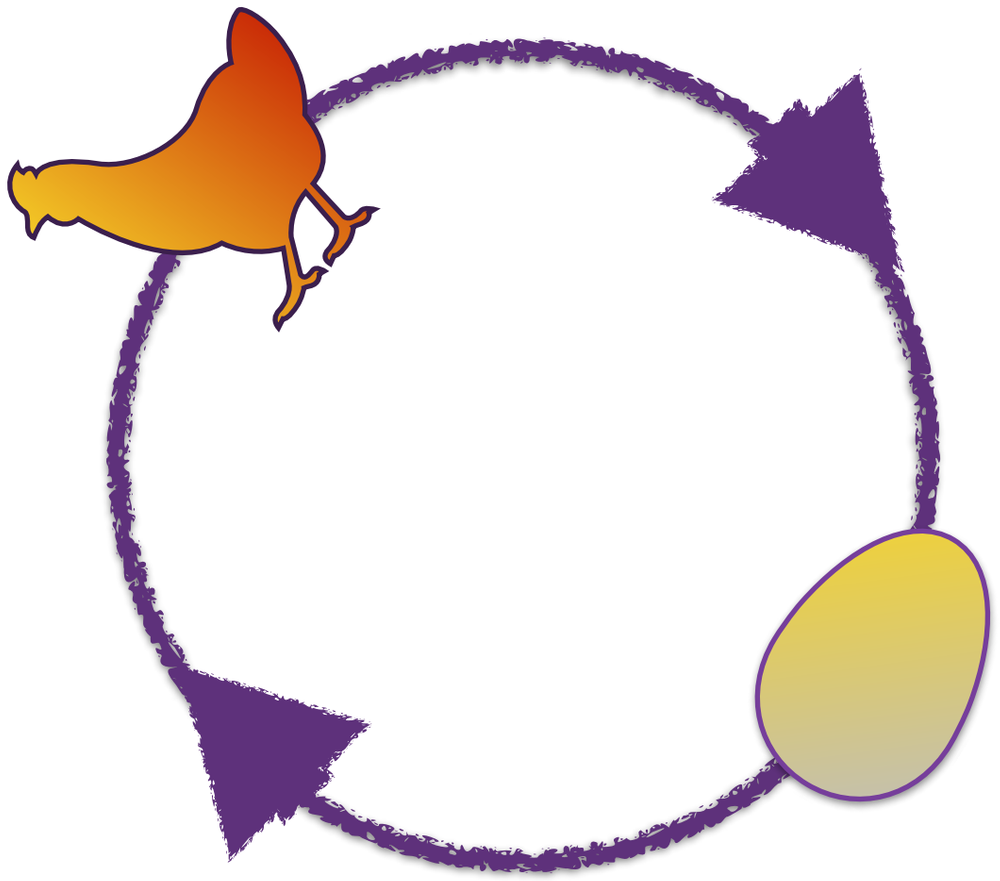
materials: a chicken-and-egg problem

how to disentangle the two?
which mechanism dominates when?

distortions



ordering

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orbital ordering in materials

rest of lecture $KCuF_3$

- introduce KK super-exchange and electron-phonon coupling mechanisms for orbital ordering
- explain how to disentangle them in materials
- thermally-assisted ordering
- are there true KK systems?

Kugel-Khomskii theory

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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orbital ordering from super-exchange

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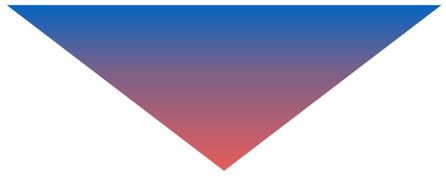
m: degenerate e_g orbitals



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how many orbital degrees of freedom?

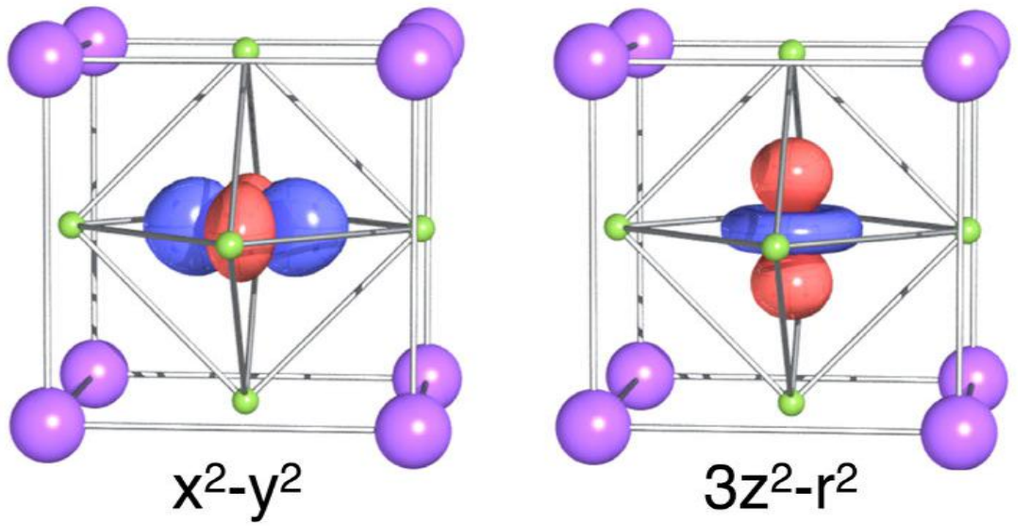
$KCuF_3$

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

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

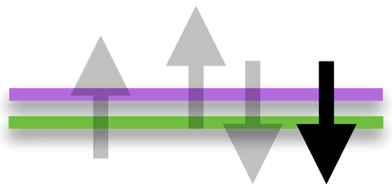
$K^{1+} : p^6$

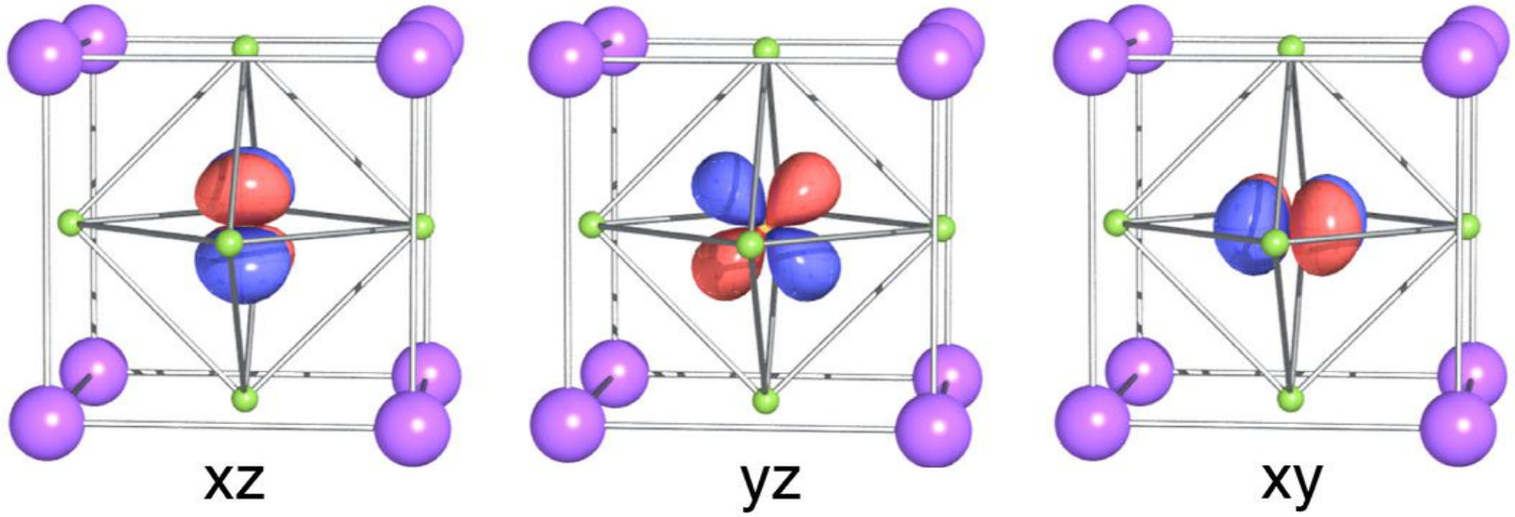
Cu: [Ar]$3d^{10}$ $4s^1$



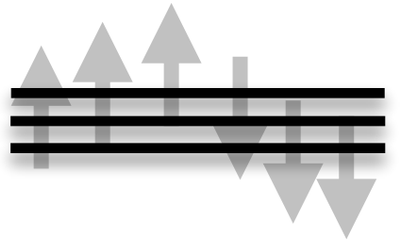
degenerate e_g orbitals

$(e_g)^1$





$(t_{2g})^0$



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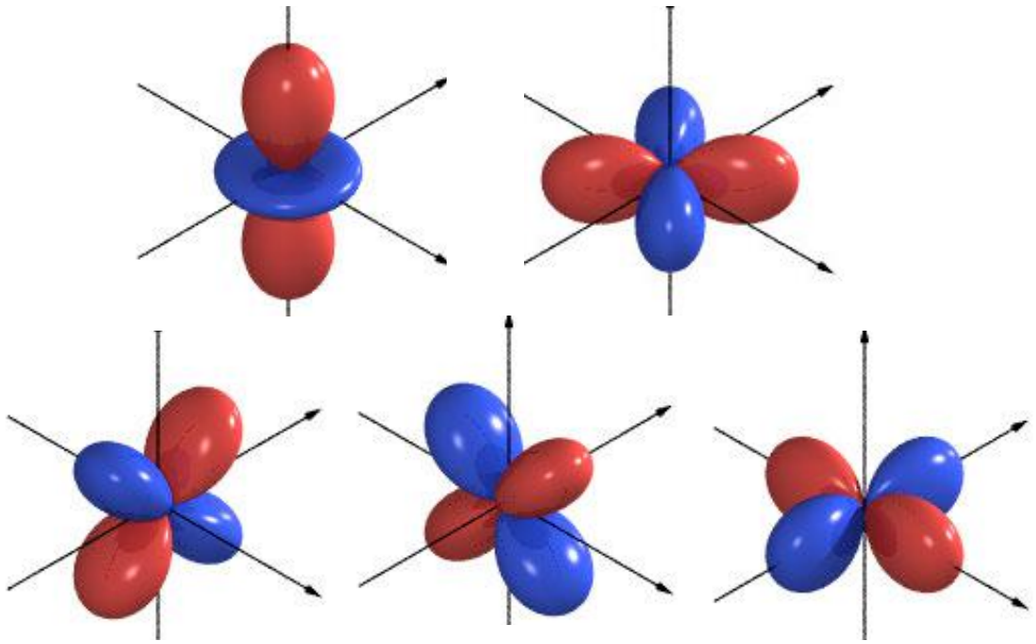
spherical symmetry: d shell



l=2

5 degenerate states

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the cubic crystal field

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

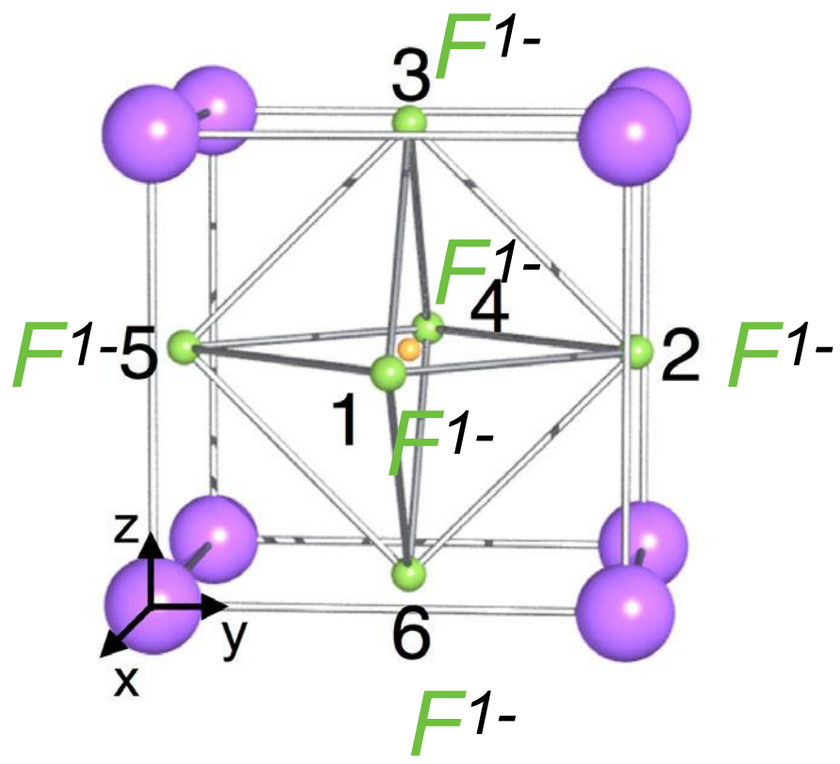
point charge model

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

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

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

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



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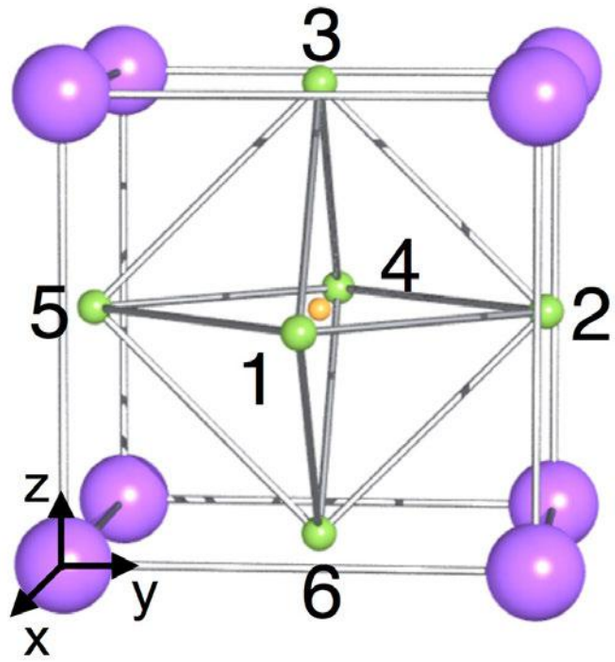
small r=(x,y,z) expansion

F_6 octahedron of negative ions

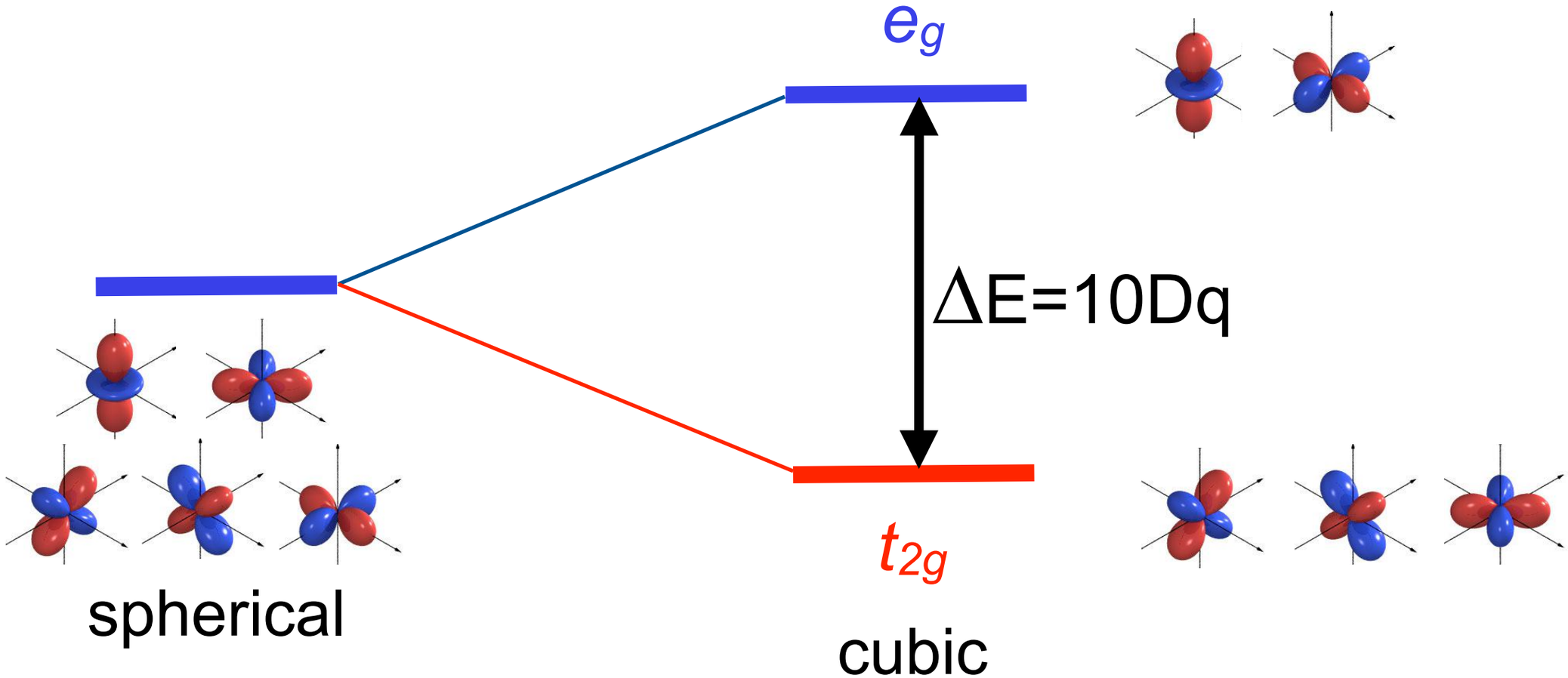
F^{1-}



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

cubic crystal-field

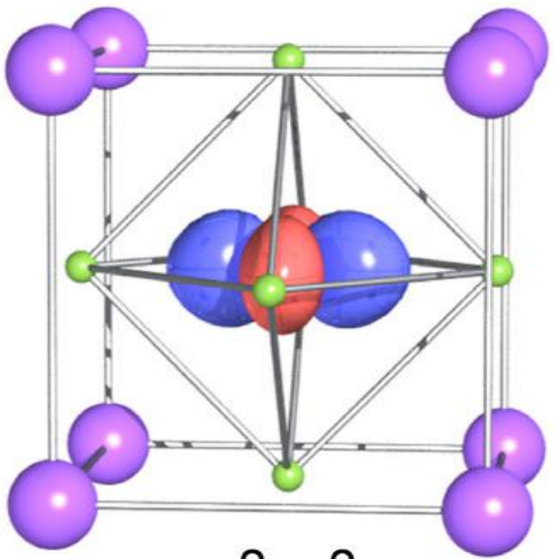
in first order perturbation theory:



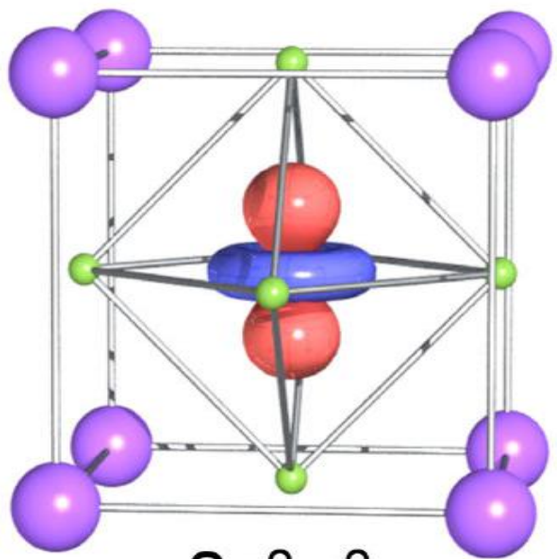
Cu^{2+} $3d^9$ $t_{2g}^6 e_g^3$

d orbitals in cubic symmetry

e_g

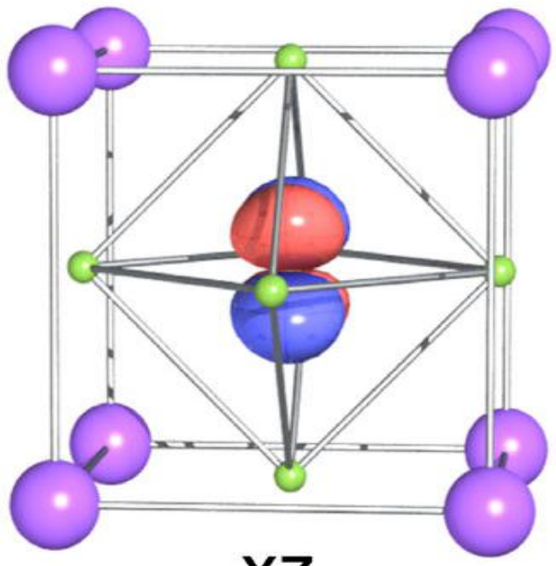


x^2-y^2

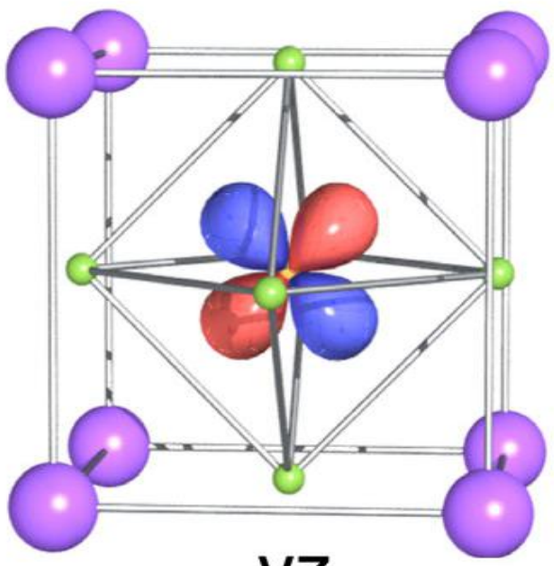


$3z^2-r^2$

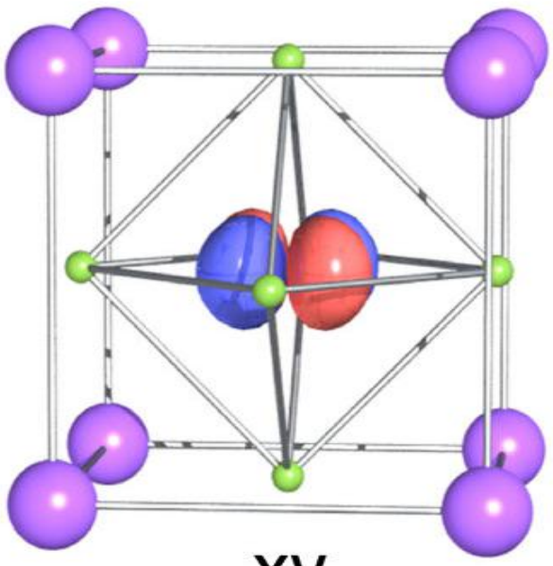
t_{2g}



xz



yz



xy

(exact: group theory)

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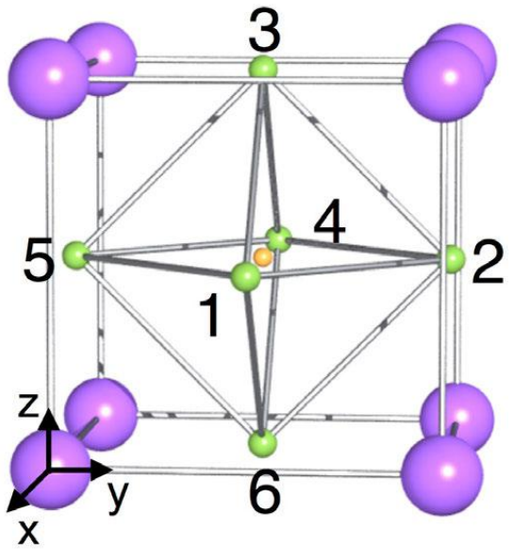
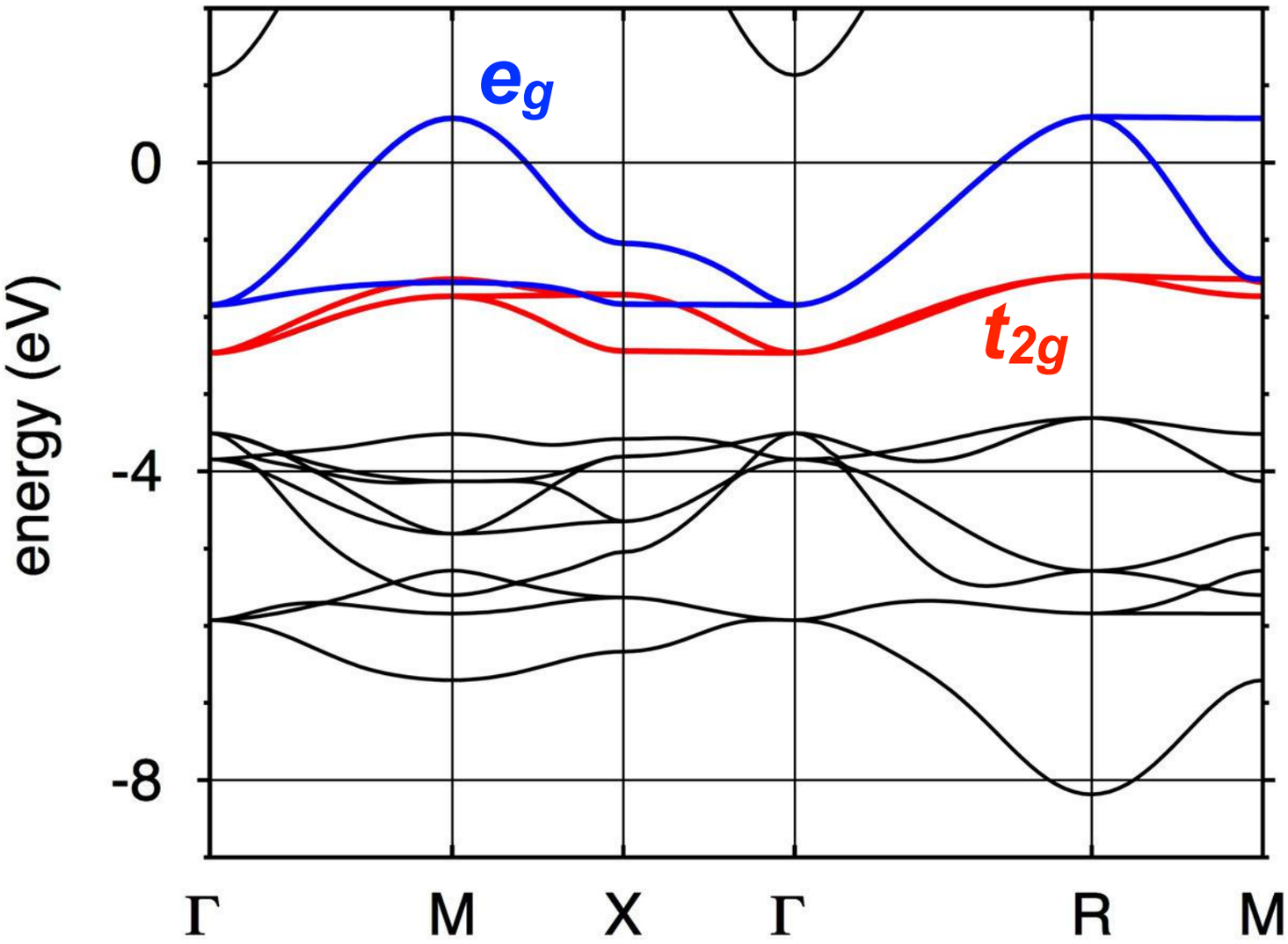
ideal cubic $KCuF_3$: electronic structure



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



Cu d -like

F p-like

large cubic CF splitting (~2 eV)

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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
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m: degenerate e_g orbitals

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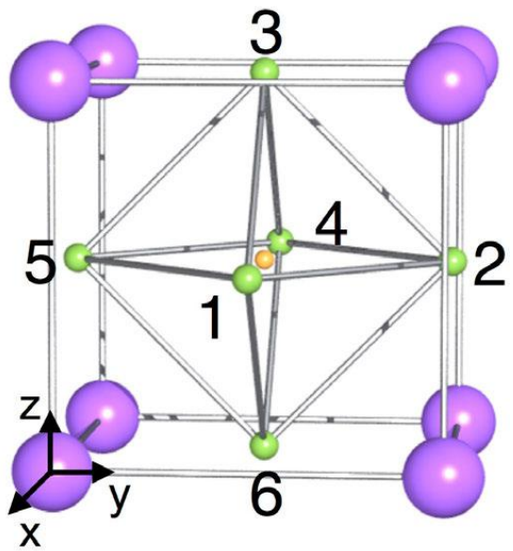
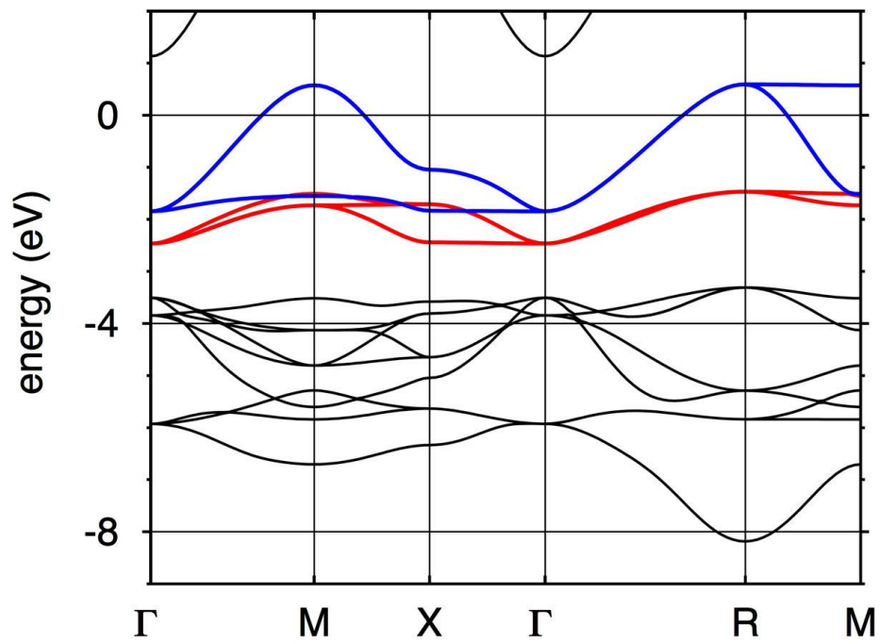
ideal cubic $KCuF_3$: electronic structure





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

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

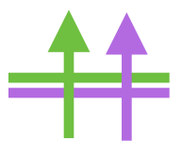
$$+\frac{1}{2}\sum_{i}\sum_{\sigma\sigma'}\sum_{m\neq m'} \left(U - 2J - J\delta_{\sigma,\sigma'}\right)\hat{n}_{im\sigma}\hat{n}_{im'\sigma'}$$

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

U

U-2J

Hund's rule ground state



U-3J

U>3J

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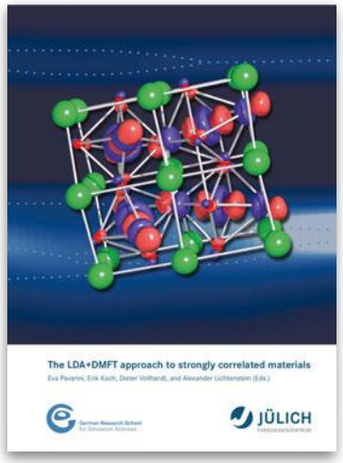
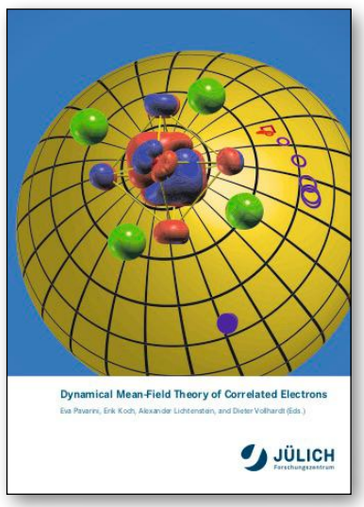
missing: the Hund's rule J

$$\hat{H} = -\sum_{ii'}\sum_{\sigma}\sum_{mm'} t^{i,i'}_{mm'}\, c^{\dagger}_{im\sigma} c_{im'\sigma} + \hat{H}_U$$



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



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orbital ordering from super-exchange

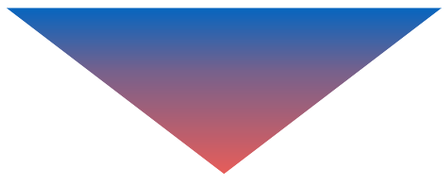
Crystal structure and magnetic properties of substances with orbital degeneracy

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)

$KCuF_3$

$LaMnO_3$

m: degenerate e_g orbitals



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$KCuF_3$

$LaMnO_3$

$$H = -\sum_{ii'}\sum_{mm'}\sum_{\sigma} t^{ii'}_{mm'} c^{\dagger}_{im\sigma} c_{i'm'\sigma} + \hat{H}_U$$

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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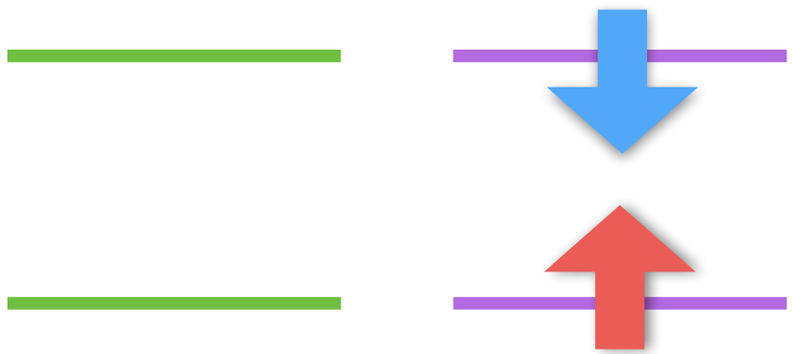
let us set the hoppings to zero

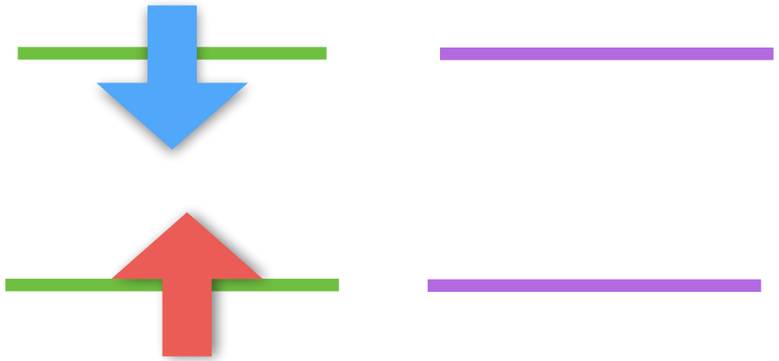
H_T, set to zero

$$H = \boxed{-\sum_{ii'}\sum_{mm'}\sum_{\sigma} t^{ii'}_{mm'} c^{\dagger}_{im\sigma} c_{i'm'\sigma}} + \hat{H}_U$$

ground state: 1 hole per site

4 possible hole states





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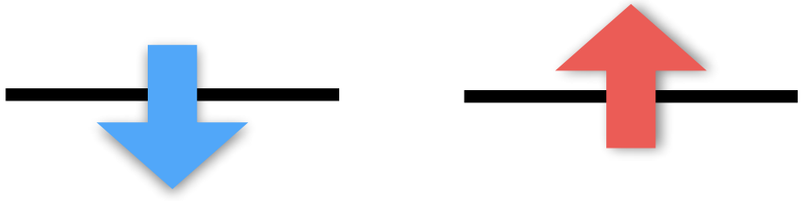
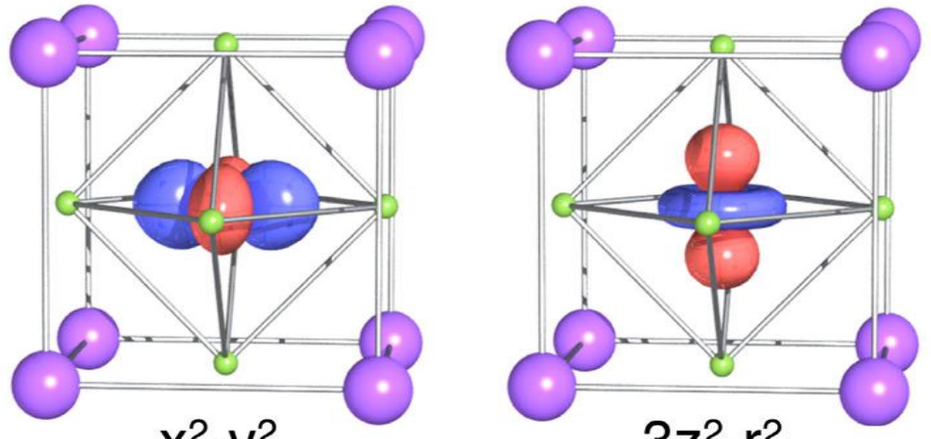
spin and pseudospin representation





eigenstates of:

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

S_i=1/2 m_S=1/2,-1/2

eigenstates of:

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

O_i=1/2 m_O=1/2,-1/2

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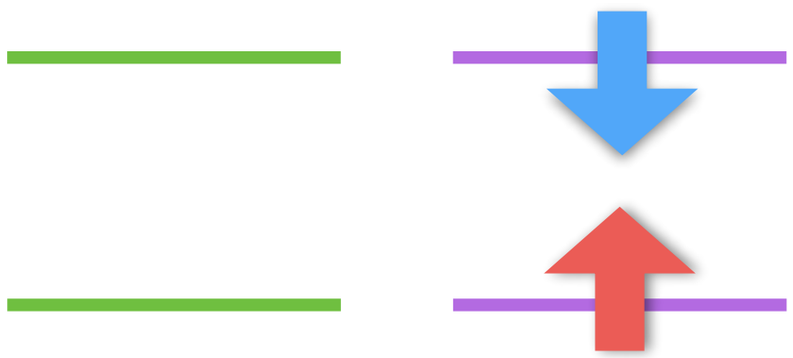
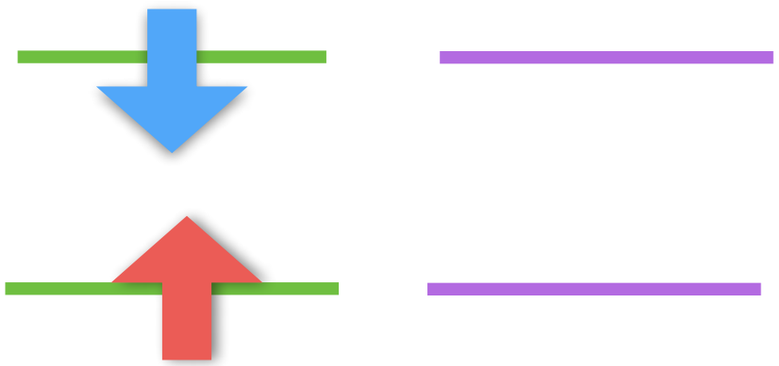
spin and pseudospin representation



$(m_S,m_O)=(-1/2,1/2)$

$(m_S,m_O)=(1/2,1/2)$



$(m_S,m_O)=(-1/2,-1/2)$

$(m_S,m_O)=(1/2,-1/2)$

$S=1/2 \quad O=1/2$

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let us set the hoppings to zero

cubic $KCuF_3$, ground state

4 states per site ($S \times 0 = 1/2 \times 1/2$)

let us switch on the hoppings

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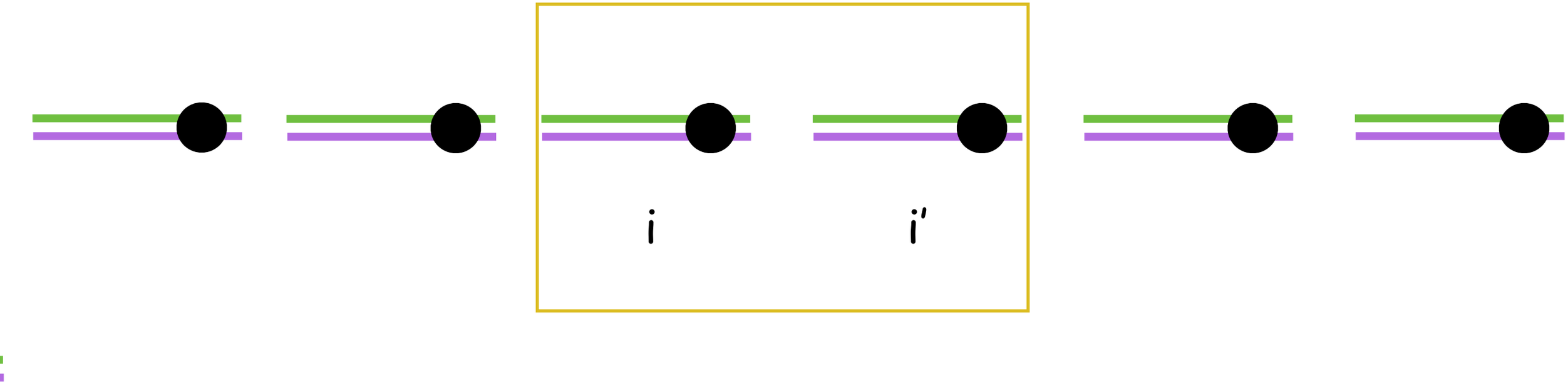
let us set the hoppings to zero

ground state



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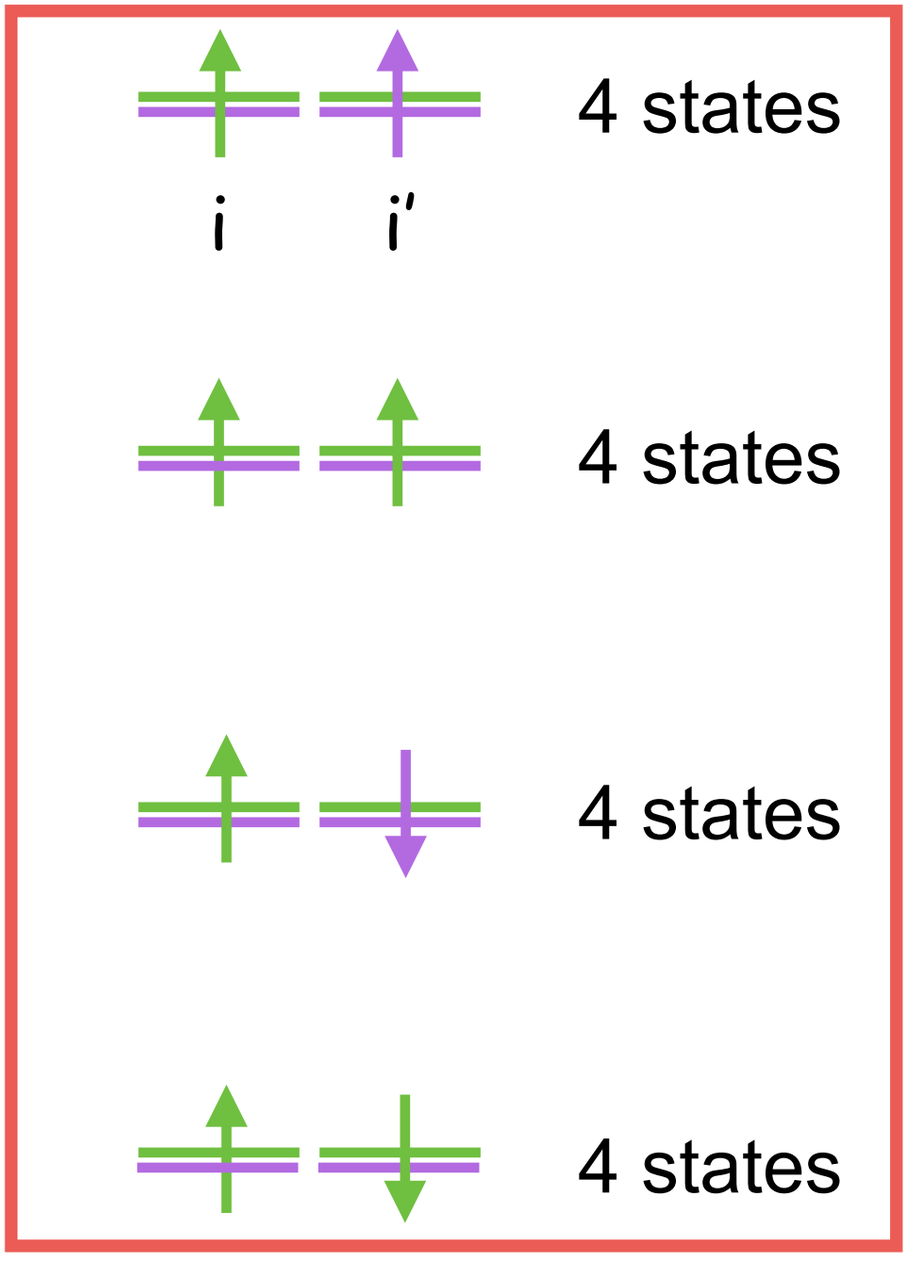
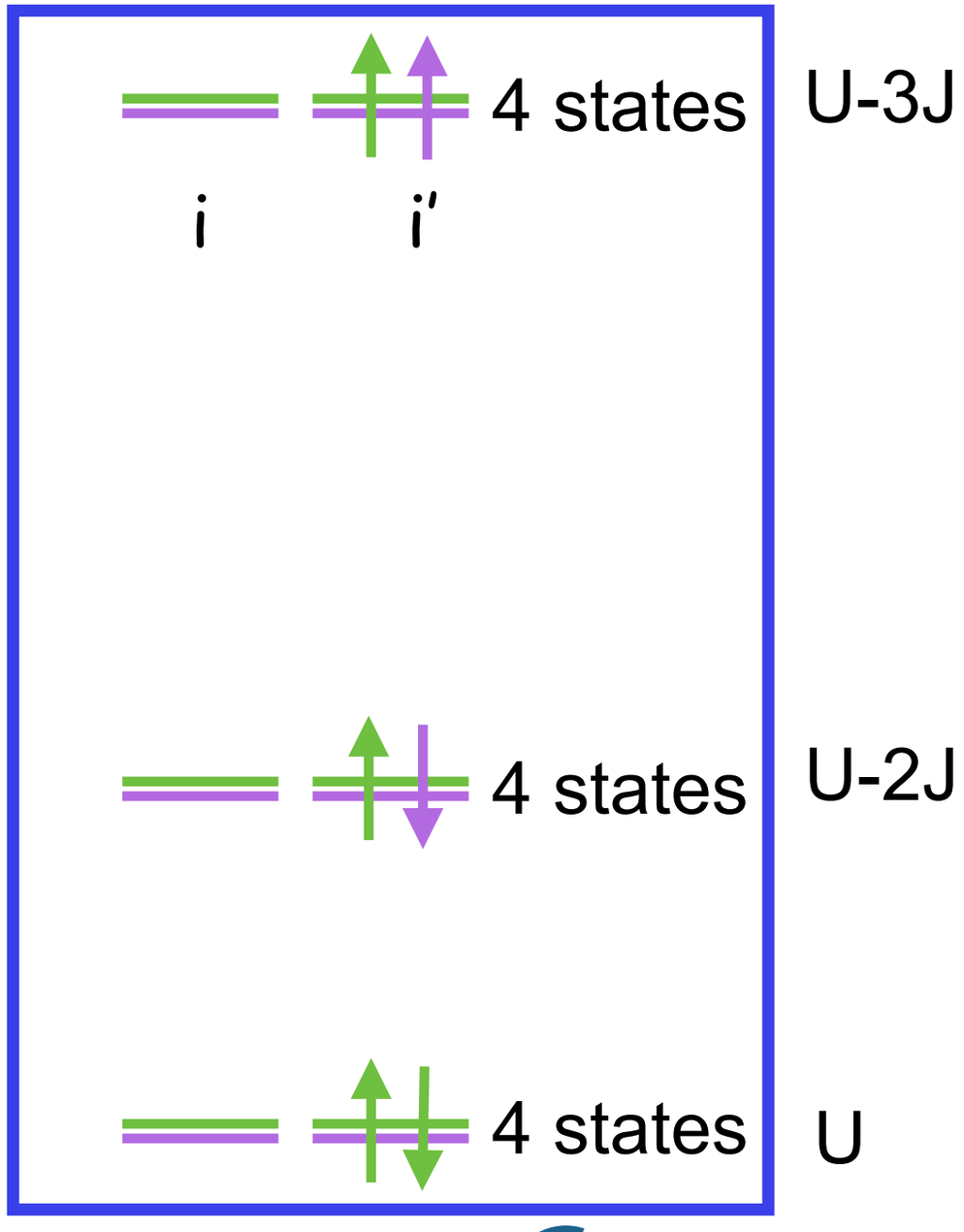
two-site problem, one hole per site

16 states with N_d=0



12 states with N_d=1



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low-energy model: perturbation in t

$$\Delta E_G = -\sum_I \frac{|\langle \Psi_G | H_T | \Psi_I \rangle|^2}{E_I - E_0}$$

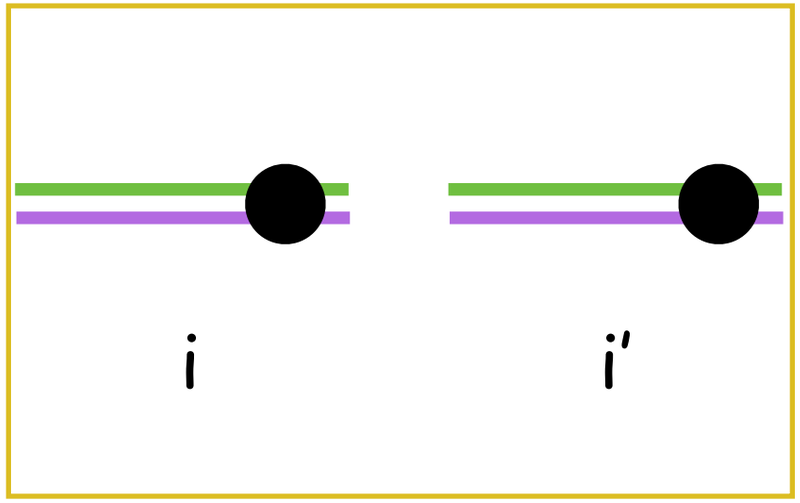
G=16 states with N_d=0

I=12 states with N_d=1

simplified hopping model

(intra-orbital hoppings only)

$$\hat{H}_T = -t \sum_{\sigma} \sum_{m} \sum_{i} c^{\dagger}_{imσ} c_{i'mσ}.$$



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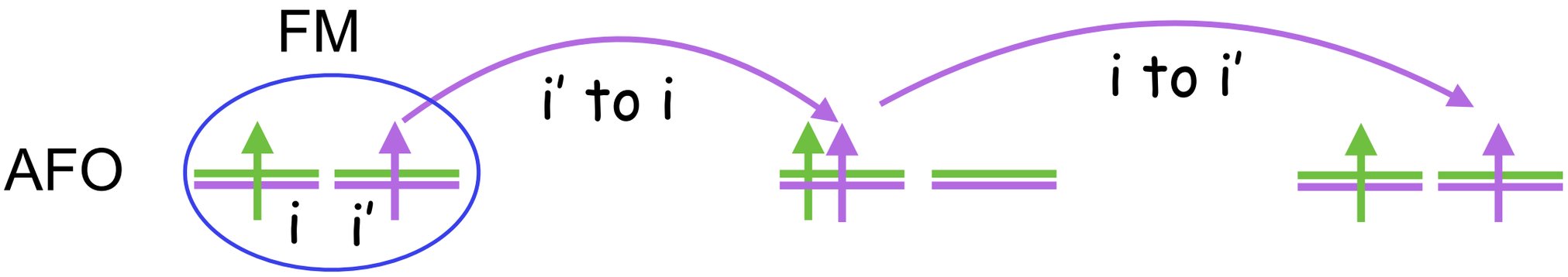
low-energy model: perturbation in t



$$\Delta E = -\frac{2t^2}{U - 3J}$$

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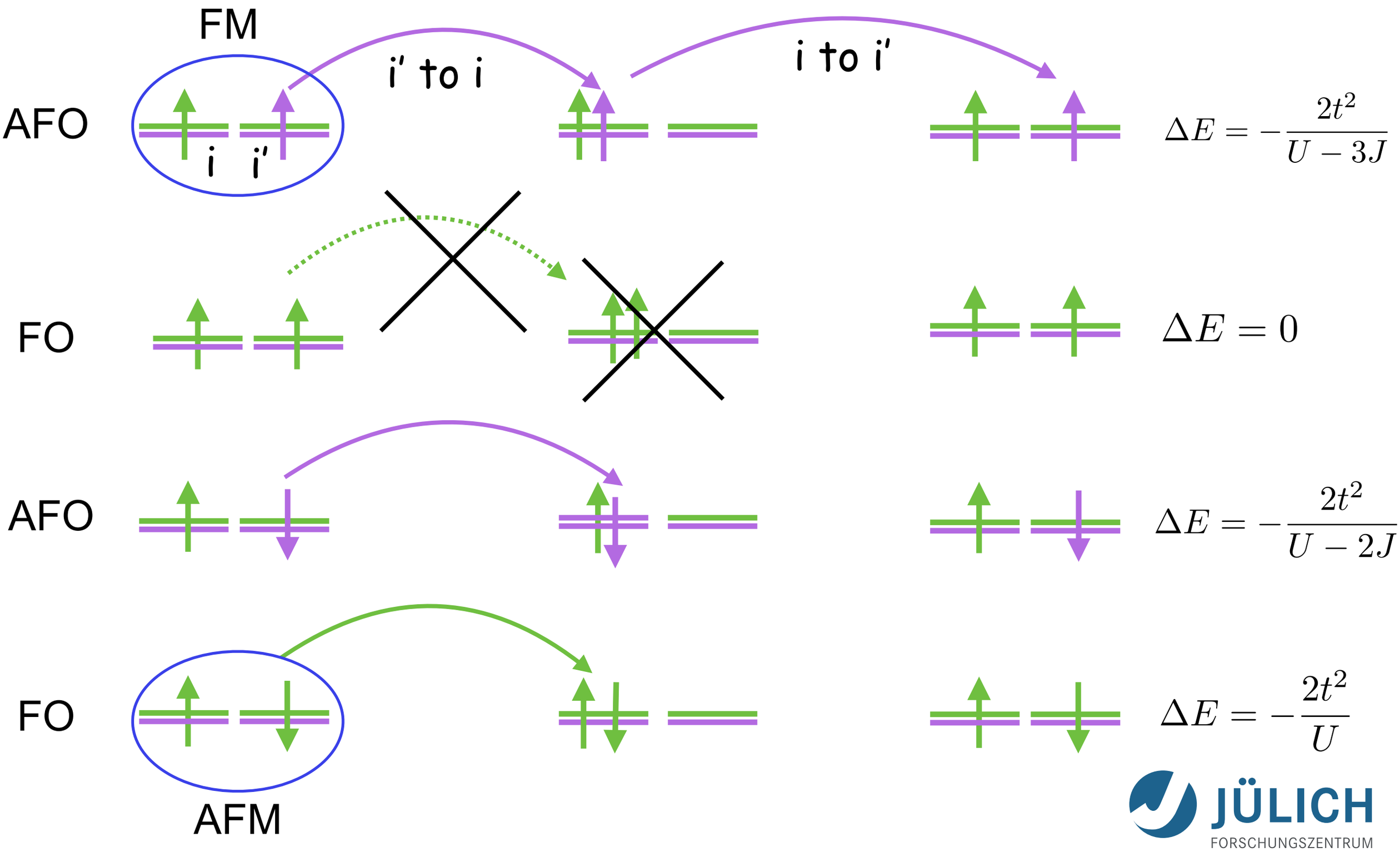
two-site problem, one electron per site



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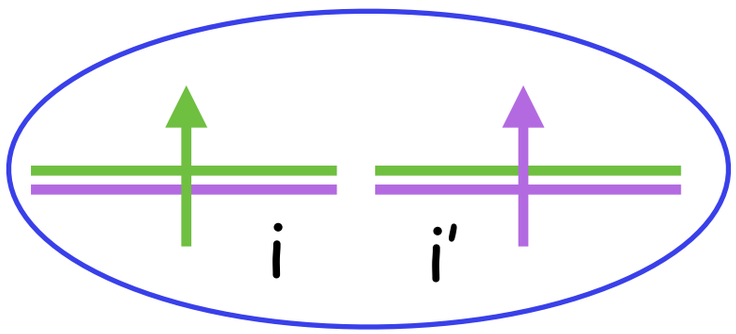
Kugel-Khomskii super-exchange

$$\hat{H}^{i,i'}_{\mathrm{SE}} = 2\Gamma_{-+}\left[\mathbf{S}^i\cdot\mathbf{S}^{i'}-\frac{1}{4}\right]\left[O^i_z\,O^{i'}_z+\frac{1}{4}\right]+2\Gamma_{+-}\left[\frac{1}{4}+S^i_z\,S^{i'}_z\right]\left[\mathbf{O}^i\cdot\mathbf{O}^{i'}-\frac{1}{4}\right]$$
$$+2\Gamma_{--}\left[\left(\mathbf{S}^i\cdot\mathbf{S}^{i'}-S^i_z\,S^{i'}_z\right)\left(\mathbf{O}^i\cdot\mathbf{O}^{i'}-O^i_z\,O^{i'}_z\right)-\left(S^i_z\,S^{i'}_z-\frac{1}{4}\right)\left(O^i_z\,O^{i'}_z-\frac{1}{4}\right)\right]$$

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

FM, AFO



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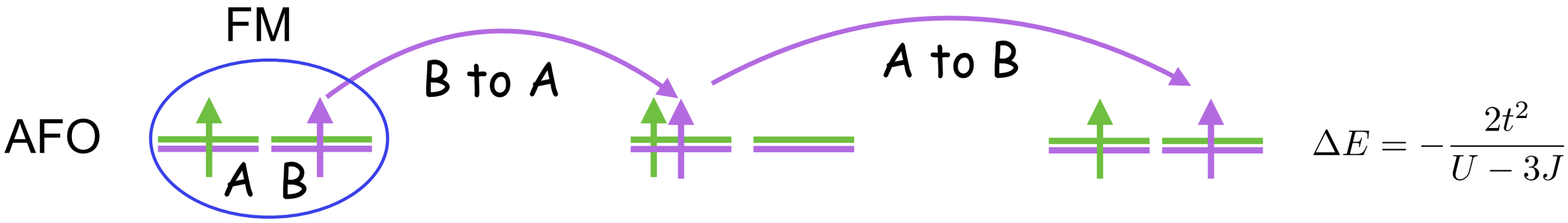
verify it!



G: $(m_{SA},m_{OA})=(1/2,-1/2)$ $(m_{SB},m_{OB})=(1/2,1/2)$

[+1/2*1/2-1/4]=0

2[1/4+1/2*1/2][-1/2*1/2-1/4]=-1/2

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

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

[+1/2*1/2-1/2 1/2]=0

[+1/2*1/2-1/4]=0

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

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G-K rules

$$\hat{H}^{i,i'}_{\mathrm{SE}} = 2\Gamma_{-+}\left[\mathbf{S}^i\cdot\mathbf{S}^{i'}-\frac{1}{4}\right]\left[O^i_z\,O^{i'}_z+\frac{1}{4}\right]+2\Gamma_{+-}\left[\frac{1}{4}+S^i_z\,S^{i'}_z\right]\left[\mathbf{O}^i\cdot\mathbf{O}^{i'}-\frac{1}{4}\right]$$
$$+2\Gamma_{--}\left[\left(\mathbf{S}^i\cdot\mathbf{S}^{i'}-S^i_z\,S^{i'}_z\right)\left(\mathbf{O}^i\cdot\mathbf{O}^{i'}-O^i_z\,O^{i'}_z\right)-\left(S^i_z\,S^{i'}_z-\frac{1}{4}\right)\left(O^i_z\,O^{i'}_z-\frac{1}{4}\right)\right]$$

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

FM, AFO

AF, FO

orbital ordering from super-exchange

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$KCuF_3$

$LaMnO_3$

$$H = \boxed{-\sum_{ii'}\sum_{mm'}\sum_{\sigma} t^{ii'}_{mm'} c^{\dagger}_{im\sigma} c_{i'm'\sigma}} + \boxed{\hat{H}_U}$$

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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$KCuF_3$

realistic hoppings

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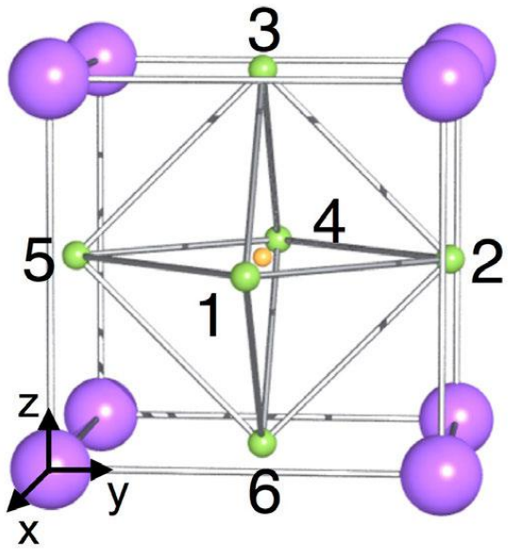
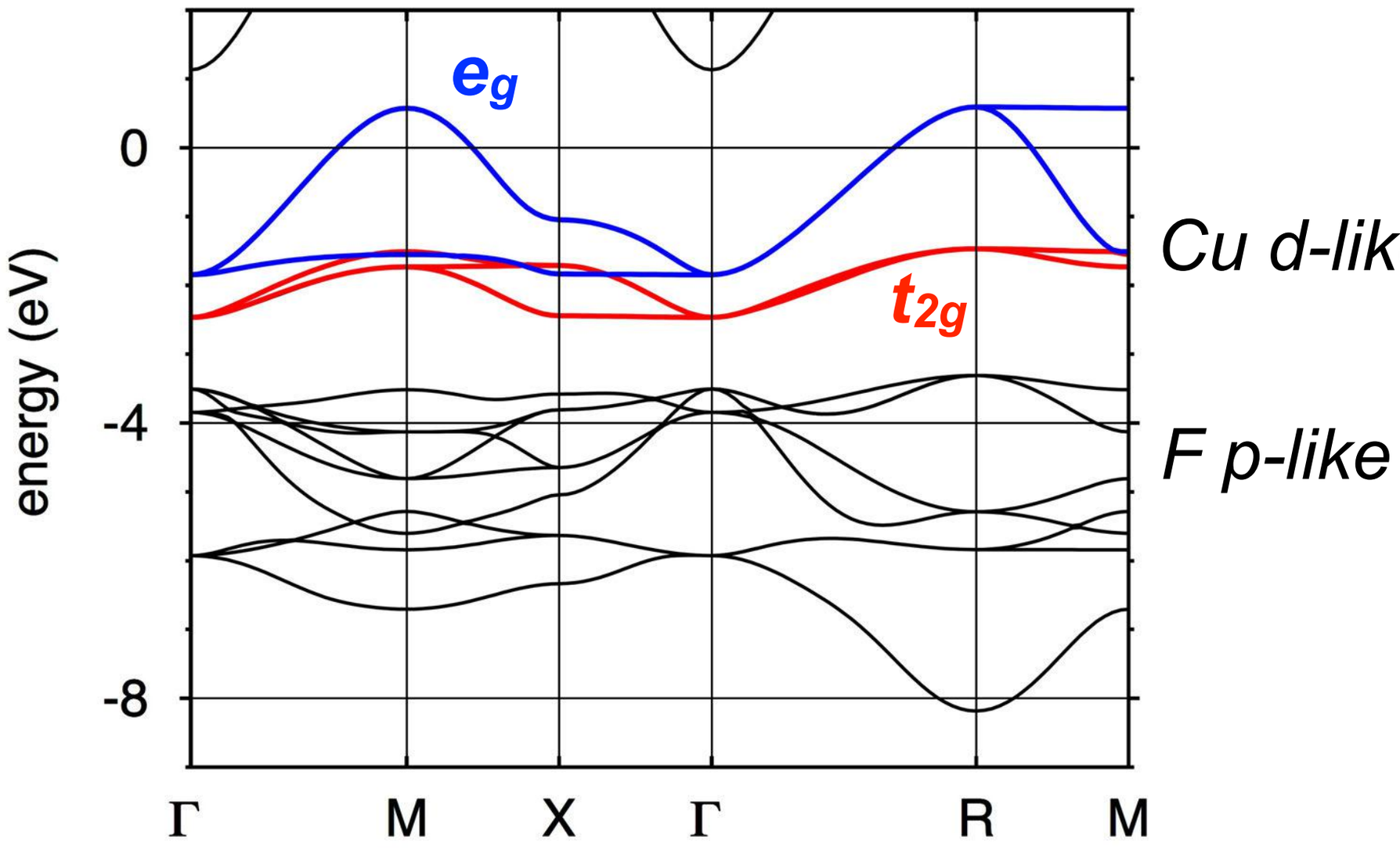
ideal cubic $KCuF_3$

what are the hoppings here?



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



Cu d-like

F p-like

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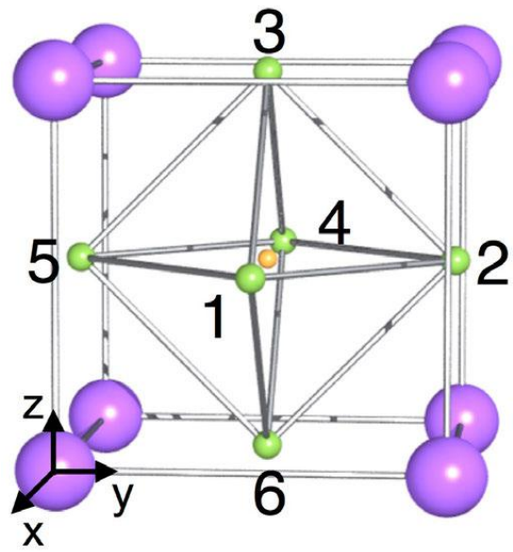
F-mediated hoppings

$$H = - \sum_{ii'} \sum_{mm'} \sum_{\sigma} t^{ii'}_{mm'} c^{\dagger}_{im\sigma} c_{i'm'\sigma} + \hat{H}_U$$

not direct Cu-Cu hoppings



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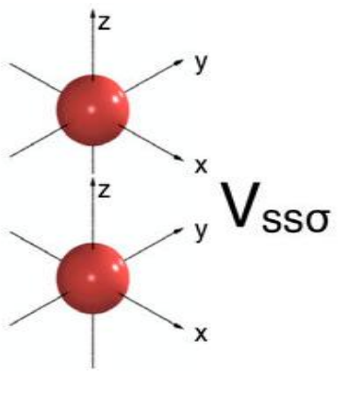
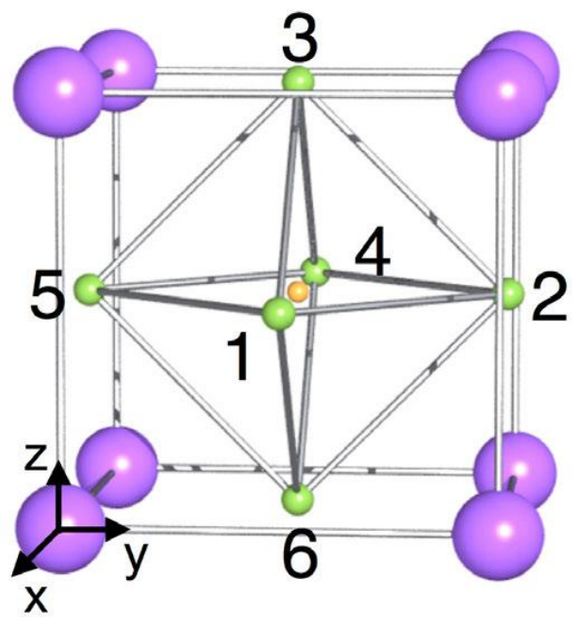
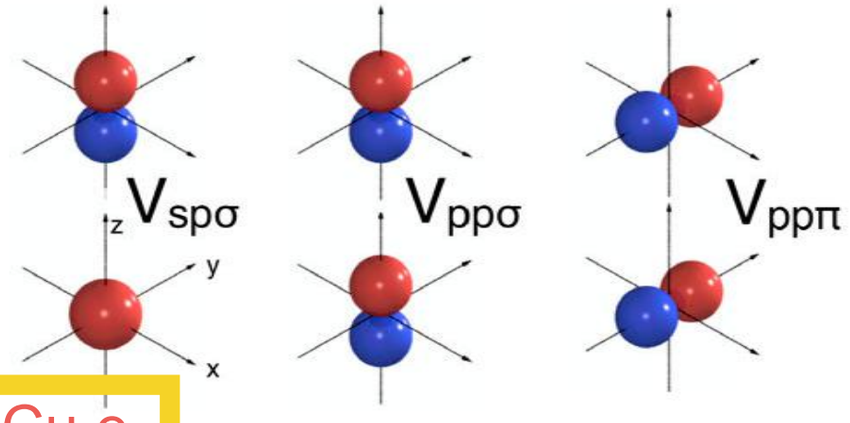
tight-binding two-center integrals

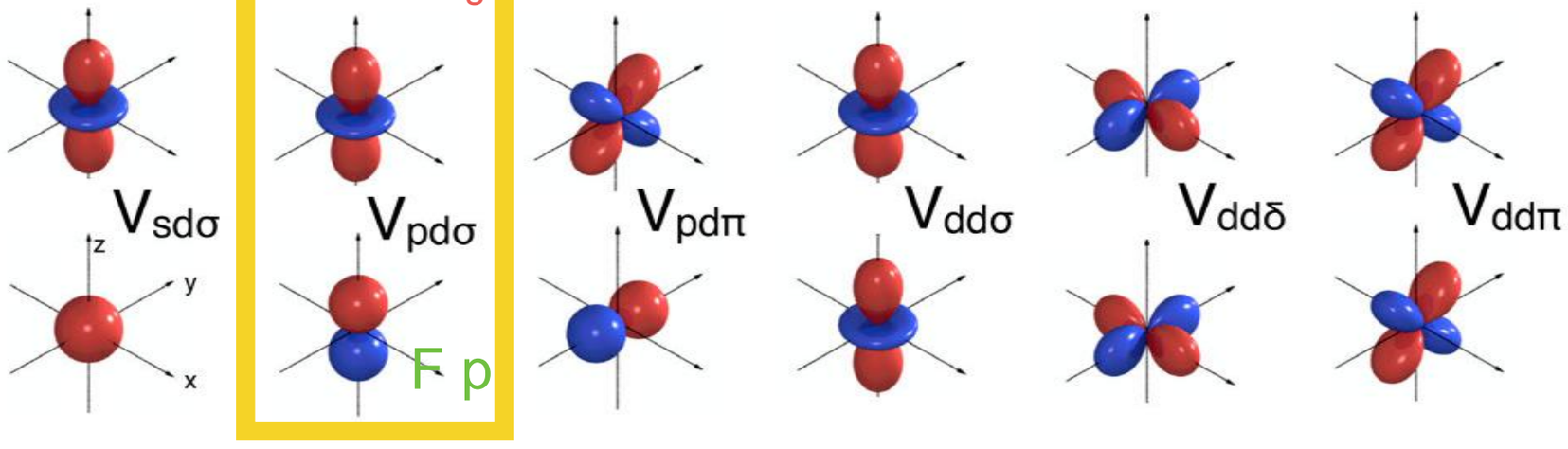
$$t^{i,i'}_{lm,l'm'} = -\int d\mathbf{r}\, \overline{\psi_{lm}}(\mathbf{r}-\mathbf{T}_i)\big(\Delta v(\mathbf{r}-\mathbf{T}_j)\big)\psi_{l'm'}(\mathbf{r}-\mathbf{T}_{i'}).$$

Cu e_g F p









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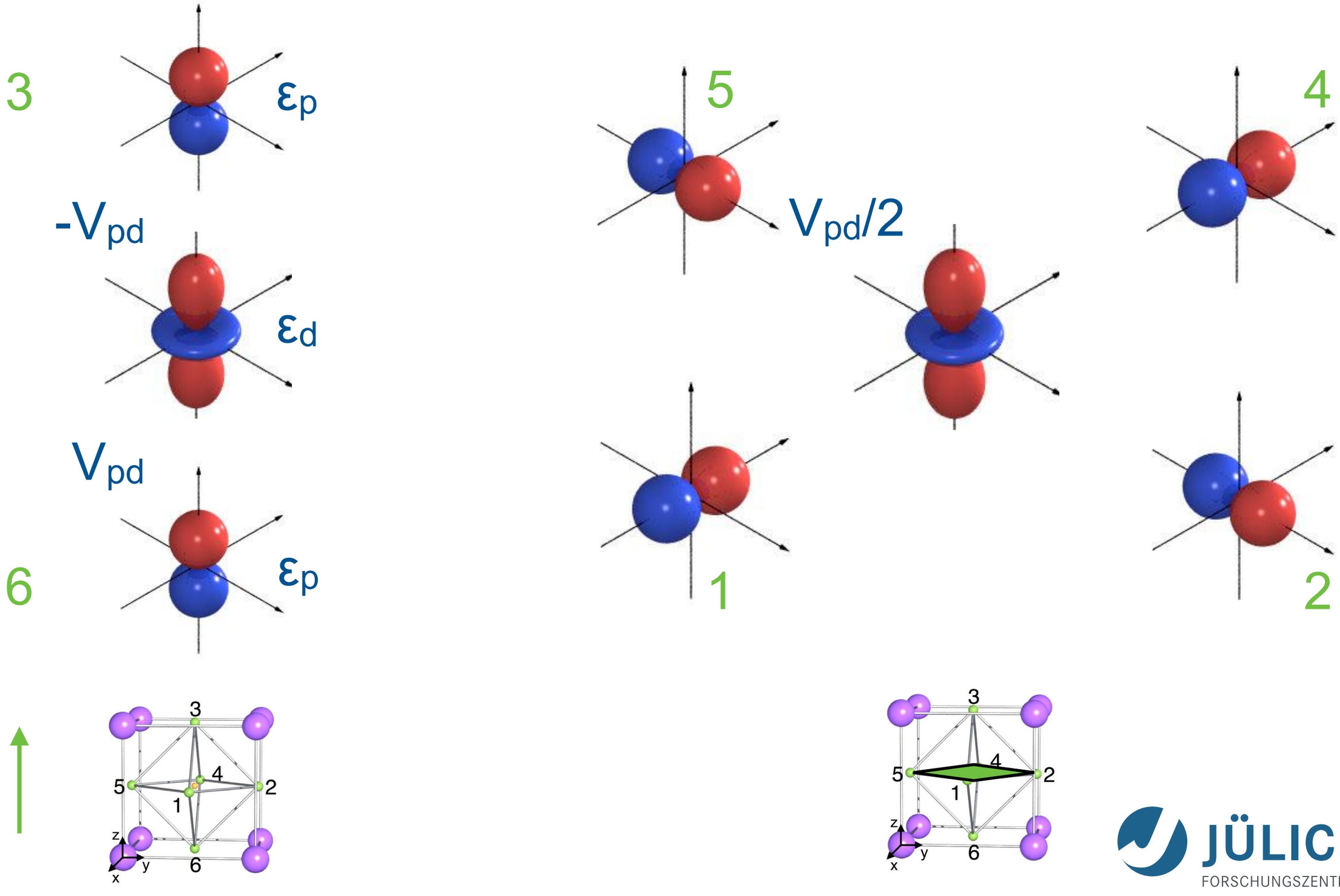
tight-binding model: $3z^2-r^2$



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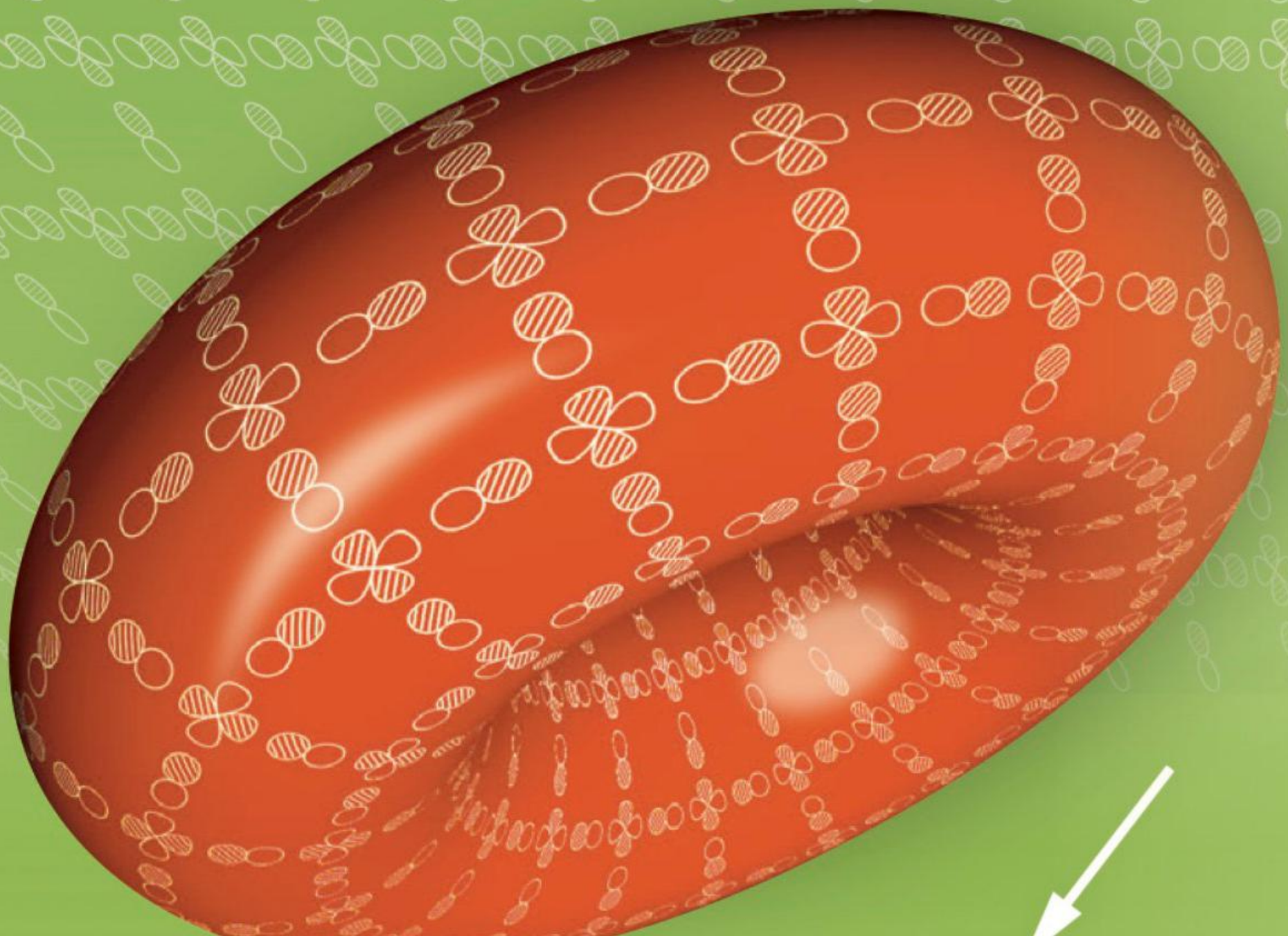
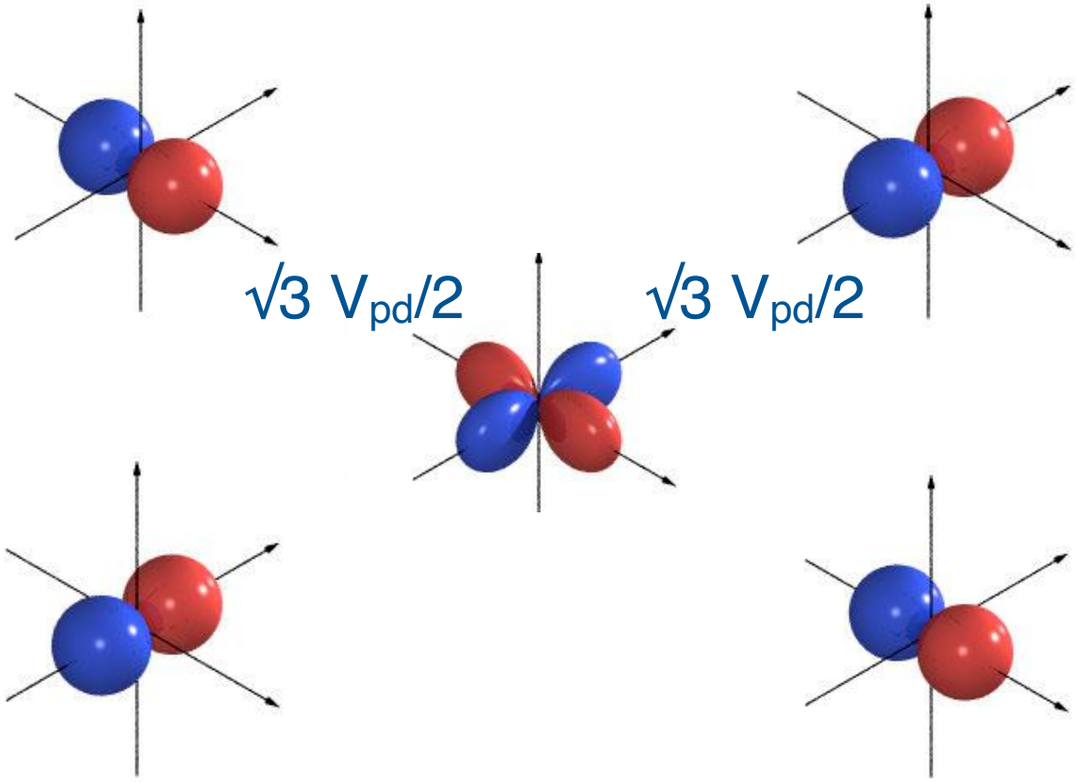
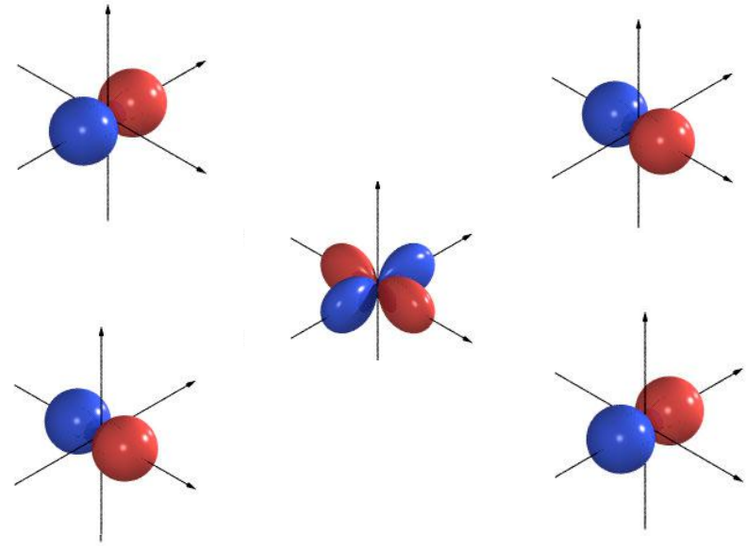
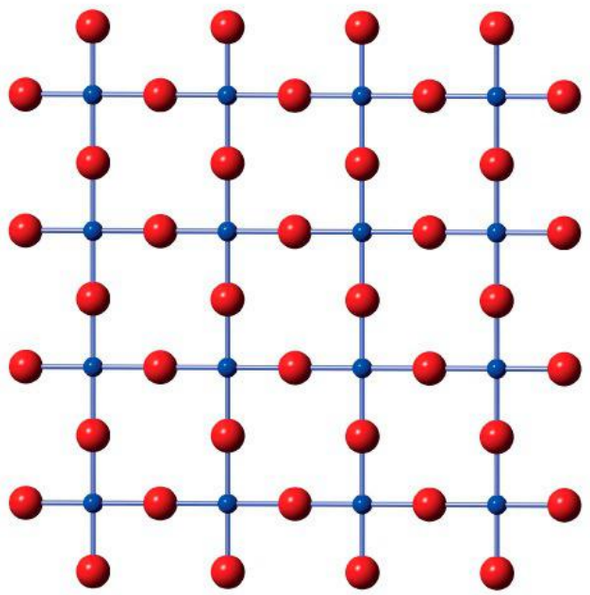


tight-binding model e_g bands: x^2-y^2





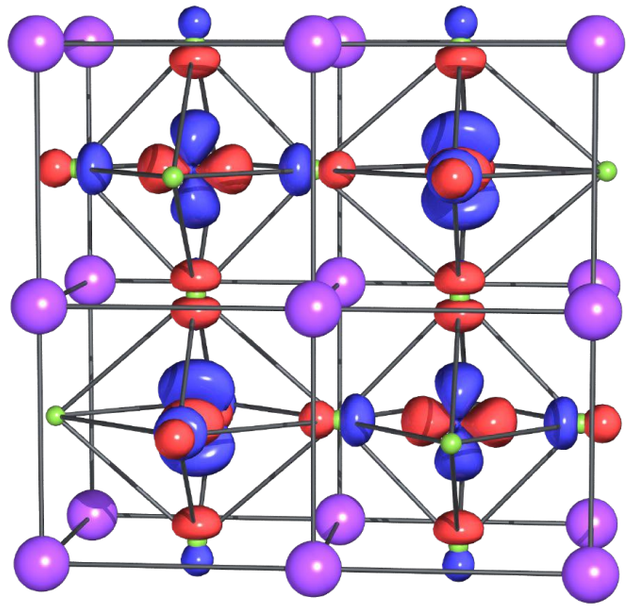


e_g-p tight-binding model

$H^{\mathrm{TB}}_{e_g}$	$\lvert \boldsymbol{k}\ z^c\rangle$	$\lvert \boldsymbol{k}\ x^a\rangle$	$\lvert \boldsymbol{k}\ y^b\rangle$	$\lvert \boldsymbol{k}\ 3z^2-r^2\rangle$	$\lvert \boldsymbol{k}\ x^2-y^2\rangle$
$\lvert \boldsymbol{k}\ z^c\rangle$	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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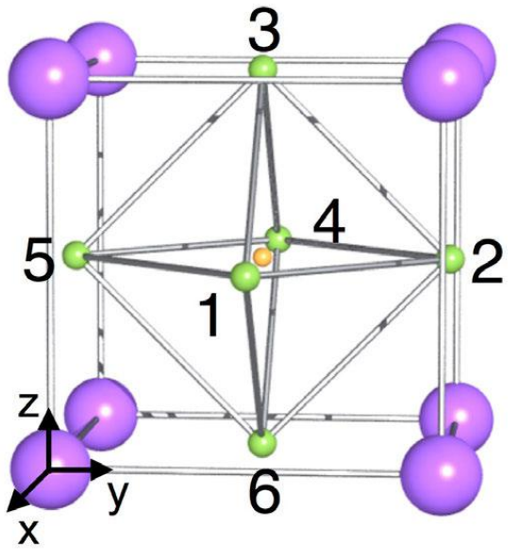
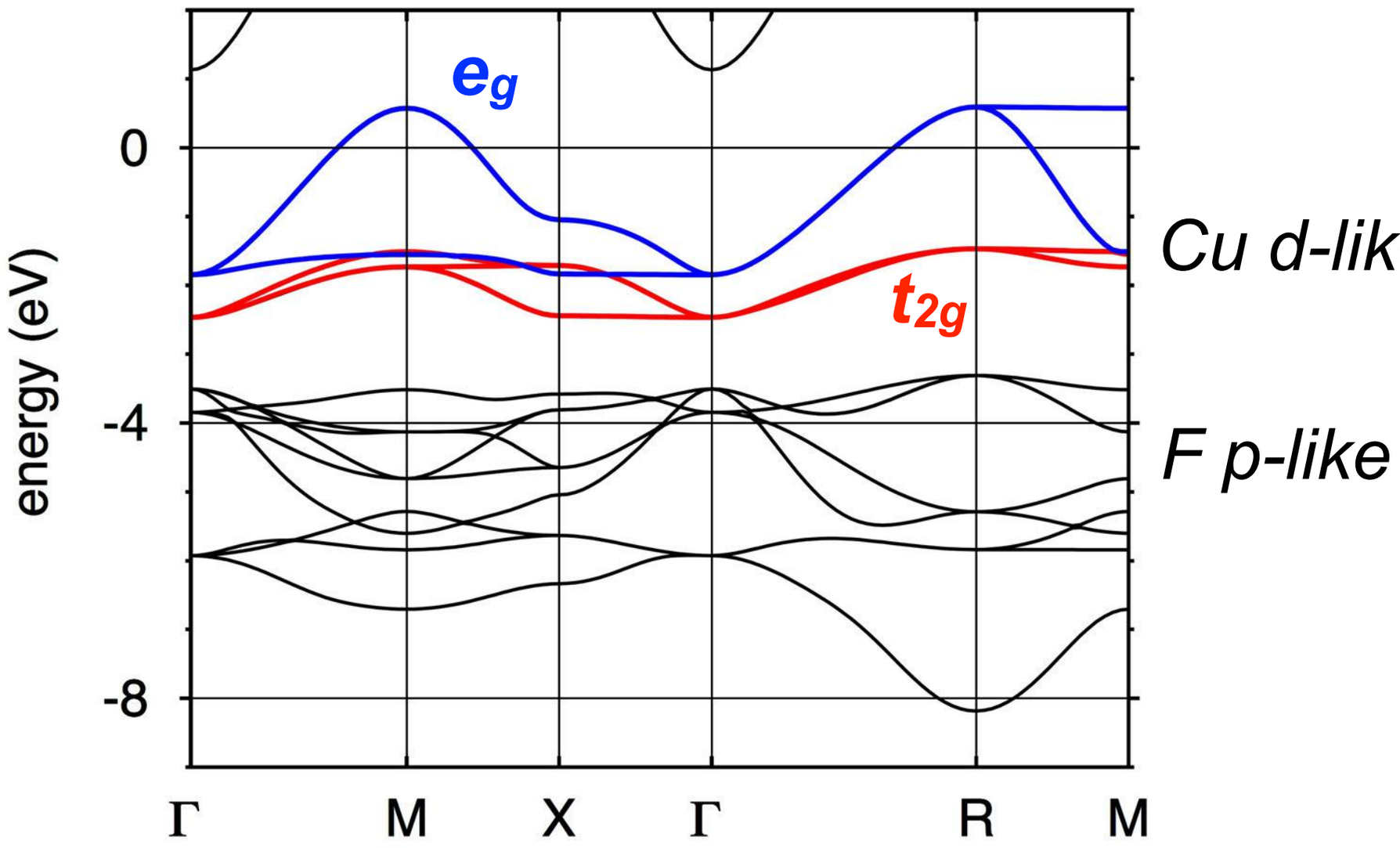
ideal cubic $KCuF_3$

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 (*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

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

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

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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General Super Exchange Hamiltonians

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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.*

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		$\tilde{\mathcal{V}}_0 = -\frac{f_1+2f_{-1}-f_{-3}}{4}$, $\tilde{\mathcal{V}}_1 = -\mathcal{V}_1$, $\tilde{\mathcal{V}}_2 = \frac{f_1+f_{-3}}{4}$, $\tilde{\mathcal{V}}_3 = \frac{f_{-3}+2f_{-1}-f_1}{4}$		

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)

$KCuF_3$

$LaMnO_3$

$$H = \boxed{-\sum_{ii'}\sum_{mm'}\sum_{\sigma} t^{ii'}_{mm'} c^{\dagger}_{im\sigma} c_{i'm'\sigma}} + \boxed{\hat{H}_U}$$

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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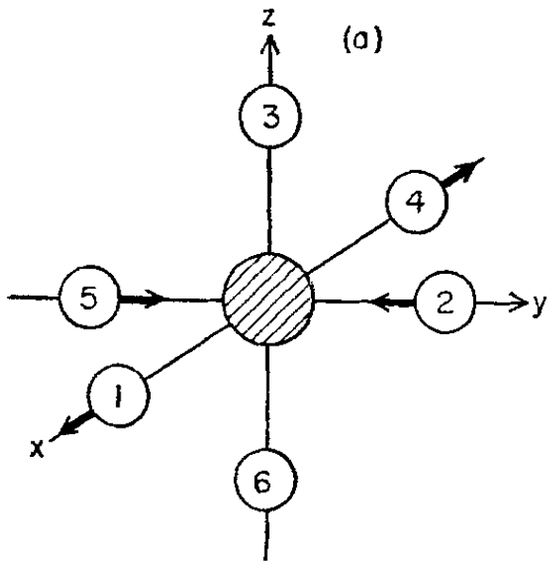
orbital ordering from distortions

lattice distortions generates order



The Normal Mode
Q_2 (Q_2 >0)

Crystal Distortion in Magnetic Compounds

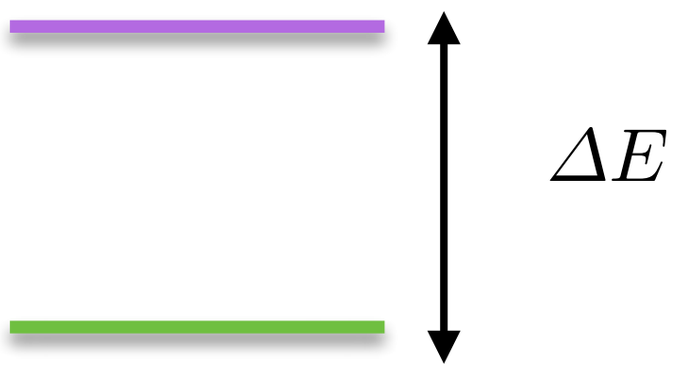
JUNJIRO KANAMORI*
Institute for the Study of Metals, University of Chicago, Chicago 37, Illinois

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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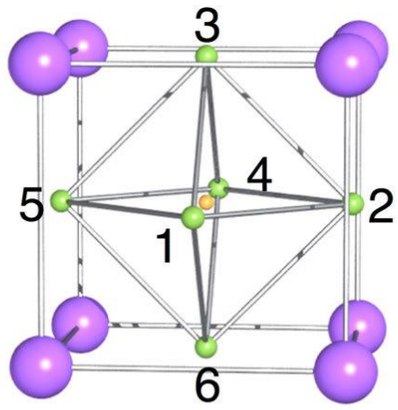
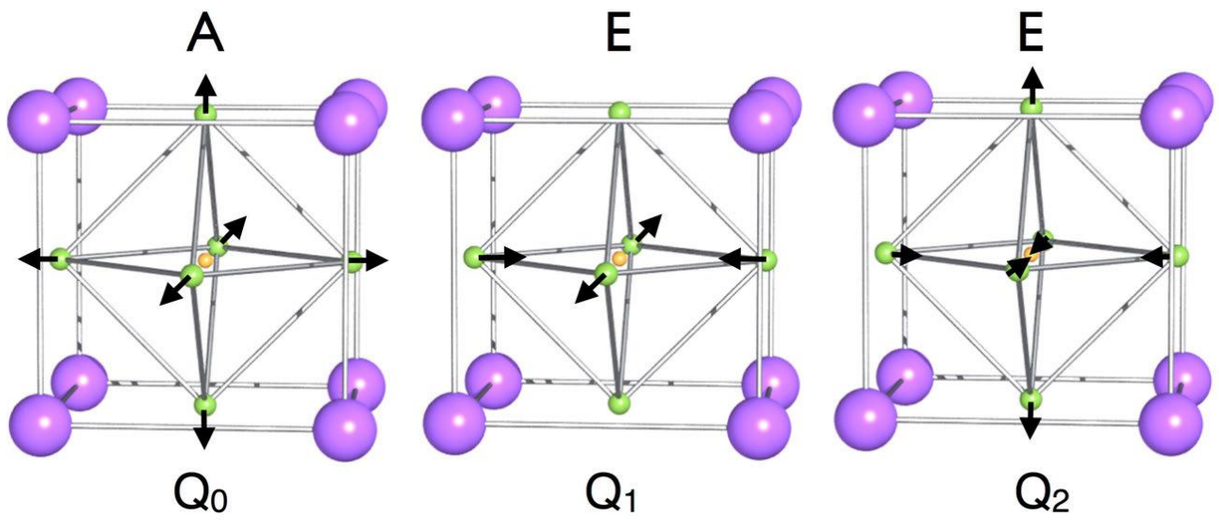
which phononic modes?

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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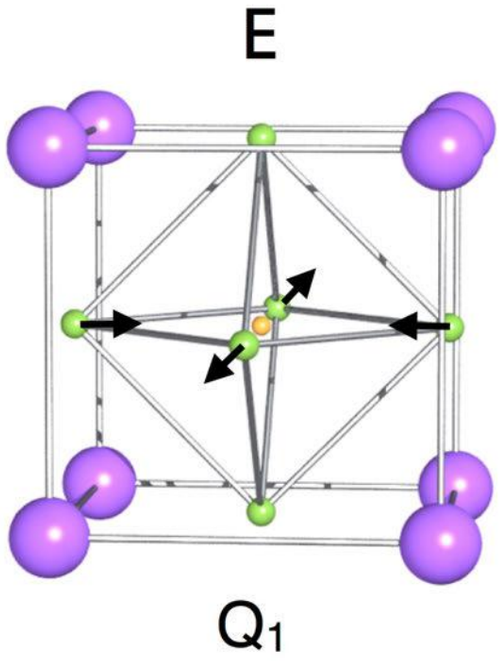
Q_1 mode

$$\boldsymbol{Q}_1 = \boldsymbol{u}_1(q_1) + \boldsymbol{u}_2(q_1) + \boldsymbol{u}_4(q_1) + \boldsymbol{u}_5(q_1)$$



$$\begin{aligned}
\boldsymbol{u}_1(q_1) &= \frac{1}{\sqrt{4}} q_1 (1,0,0) \\
\boldsymbol{u}_2(q_1) &= -\frac{1}{\sqrt{4}} q_1 (0,1,0) \\
\boldsymbol{u}_3(q_1) &= (0,0,0) \\
\boldsymbol{u}_4(q_1) &= -\frac{1}{\sqrt{4}} q_1 (1,0,0) \\
\boldsymbol{u}_5(q_1) &= \frac{1}{\sqrt{4}} q_1 (0,1,0) \\
\boldsymbol{u}_6(q_1) &= (0,0,0)
\end{aligned}$$

$$\hat{U}_n^{\mathrm{P}}$$

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

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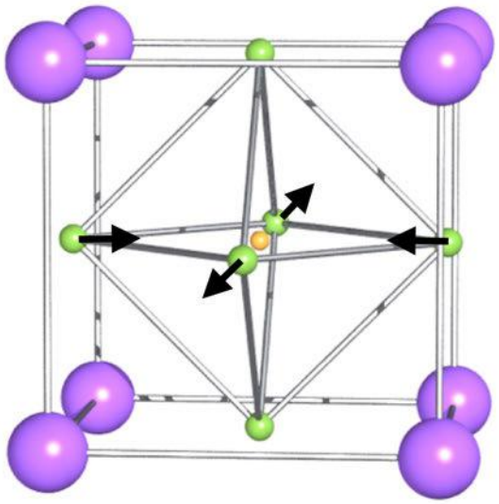
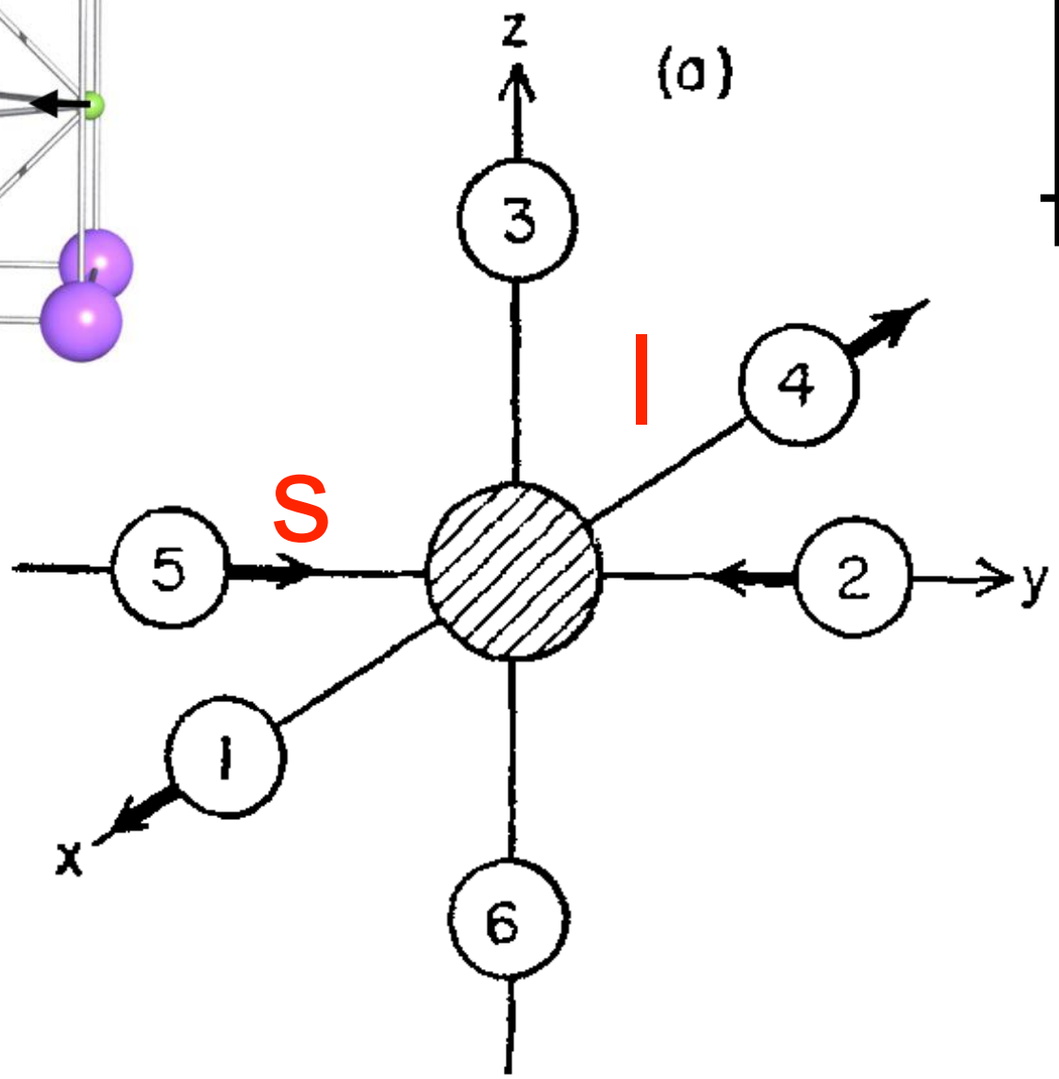
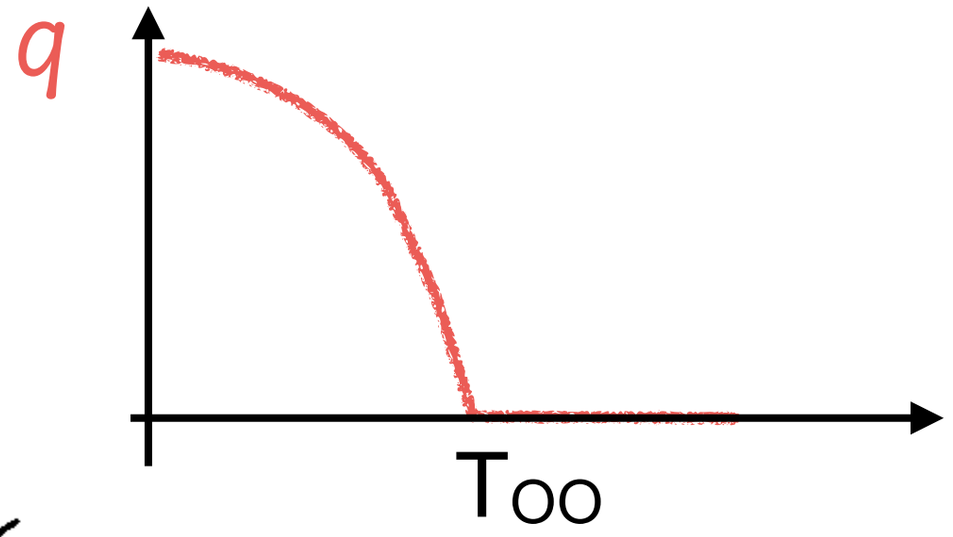
mode Q_1







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

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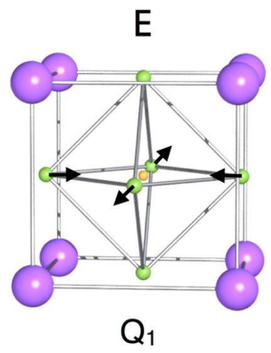
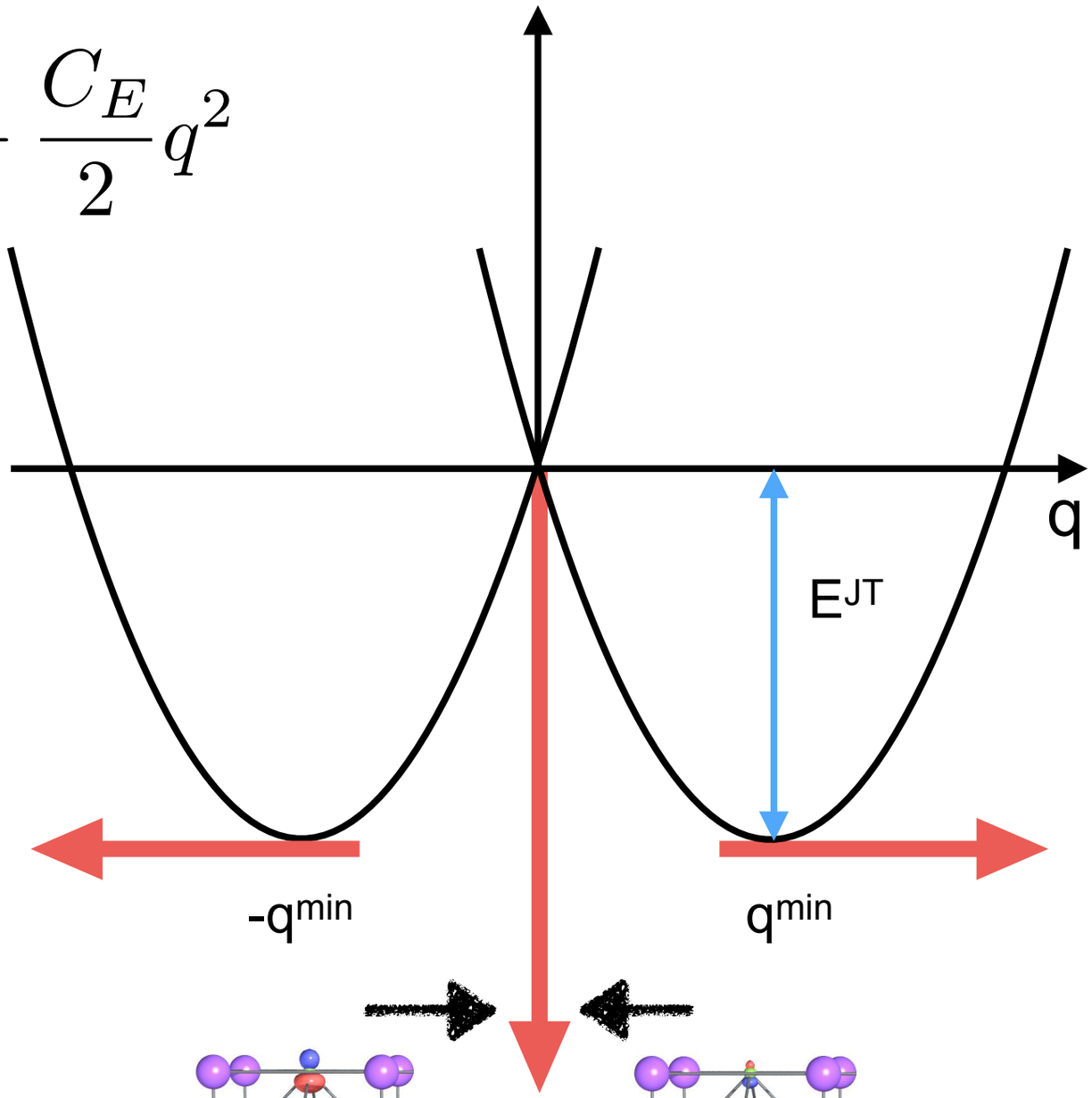
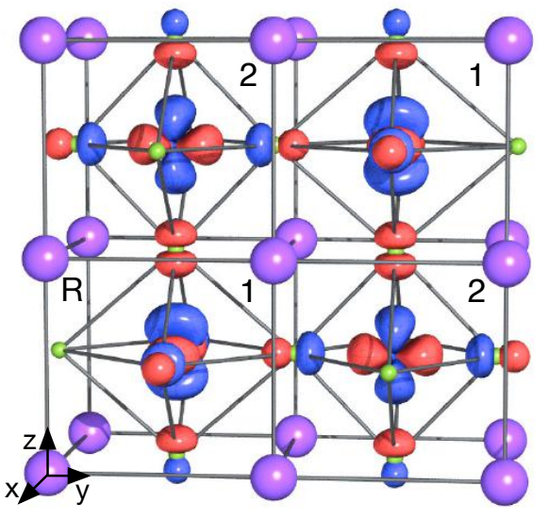
ideal JT potential

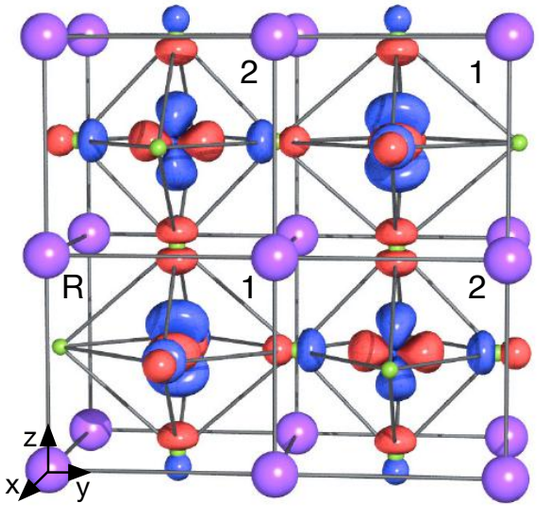
$$E_-(q) = -\lambda q + \frac{C_E}{2} q^2$$





OO





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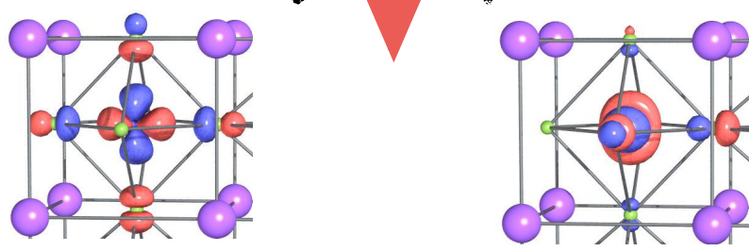
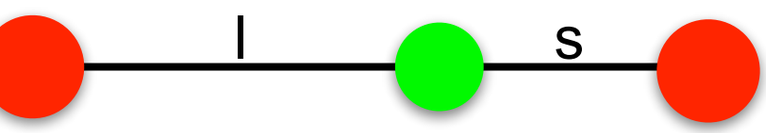
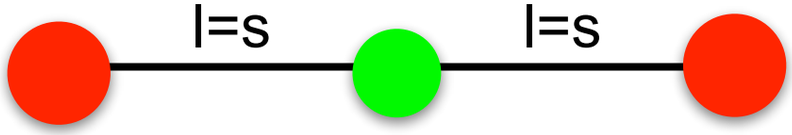


cubic, orbital degeneracy





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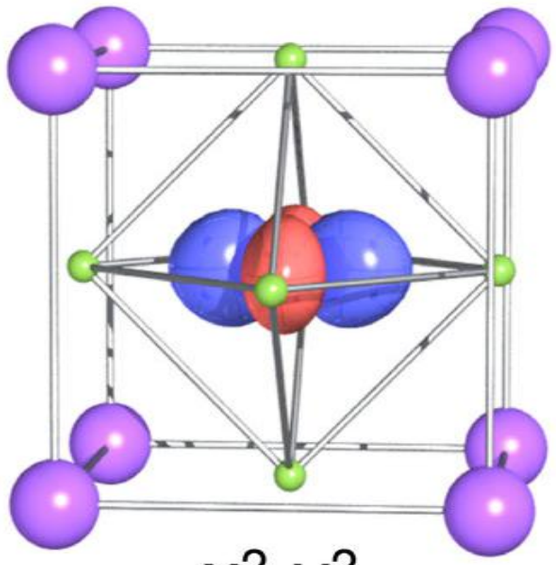
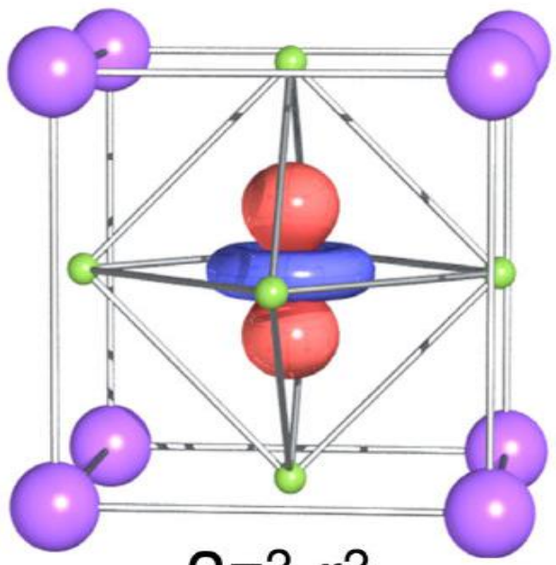
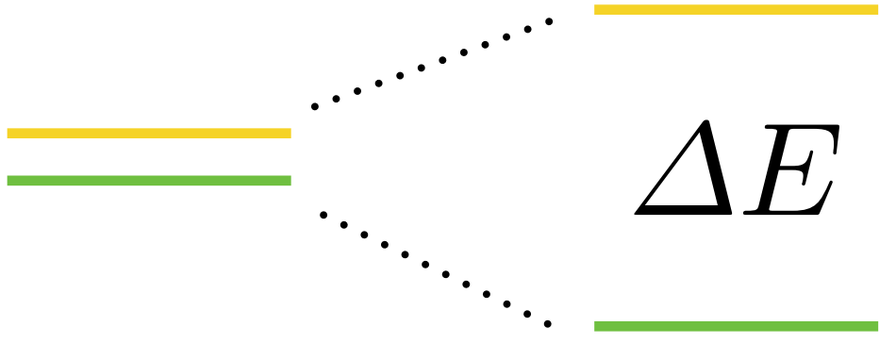
splitting via co-operative distortion

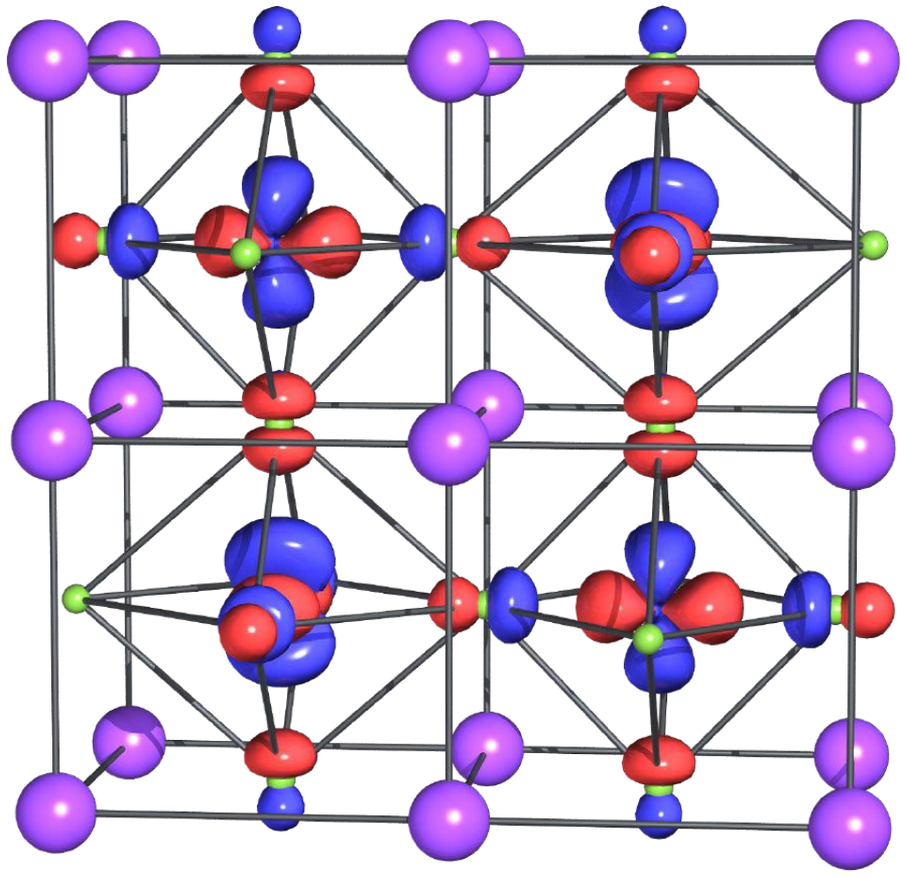


x^2-y^2



$3z^2$-r^2





two-mechanisms, same type of ordering

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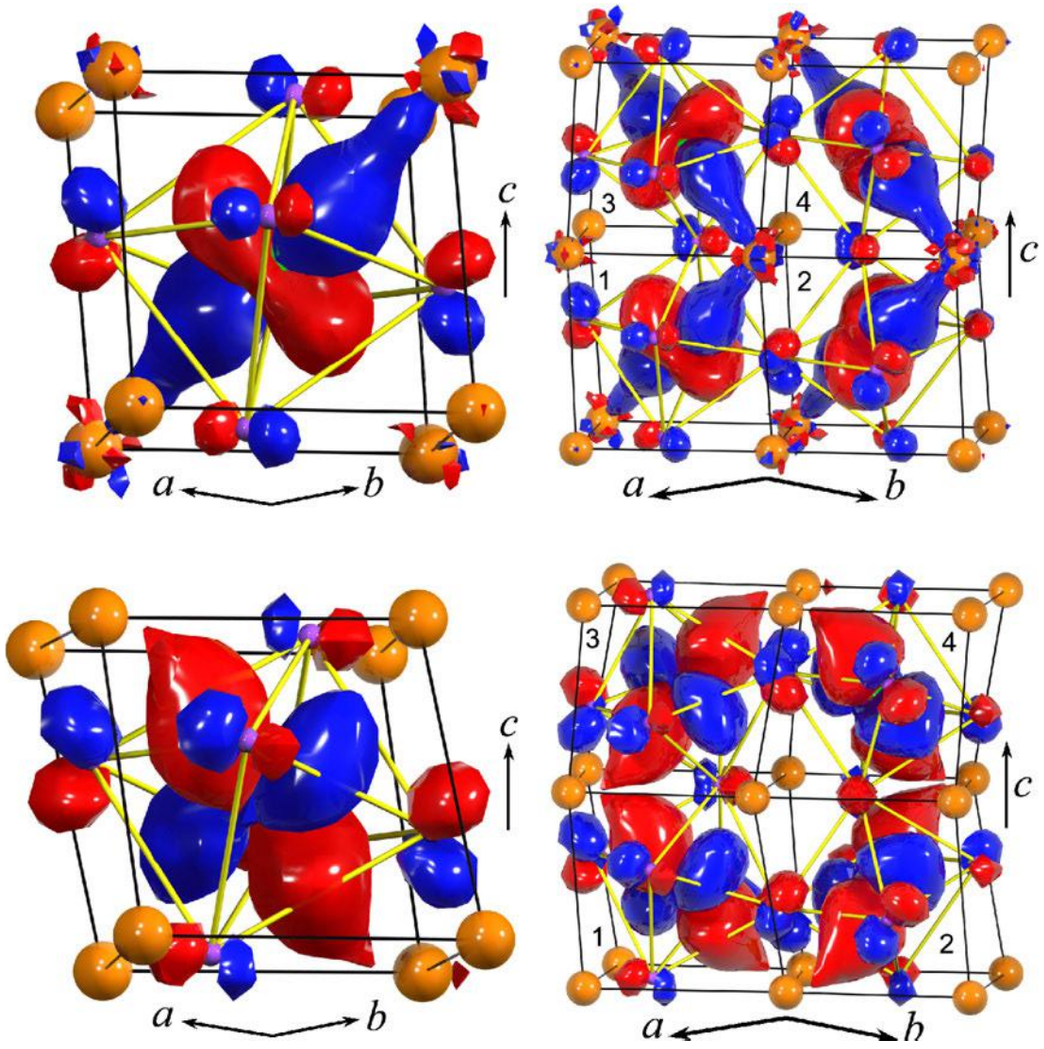
do we need a large crystal-field?

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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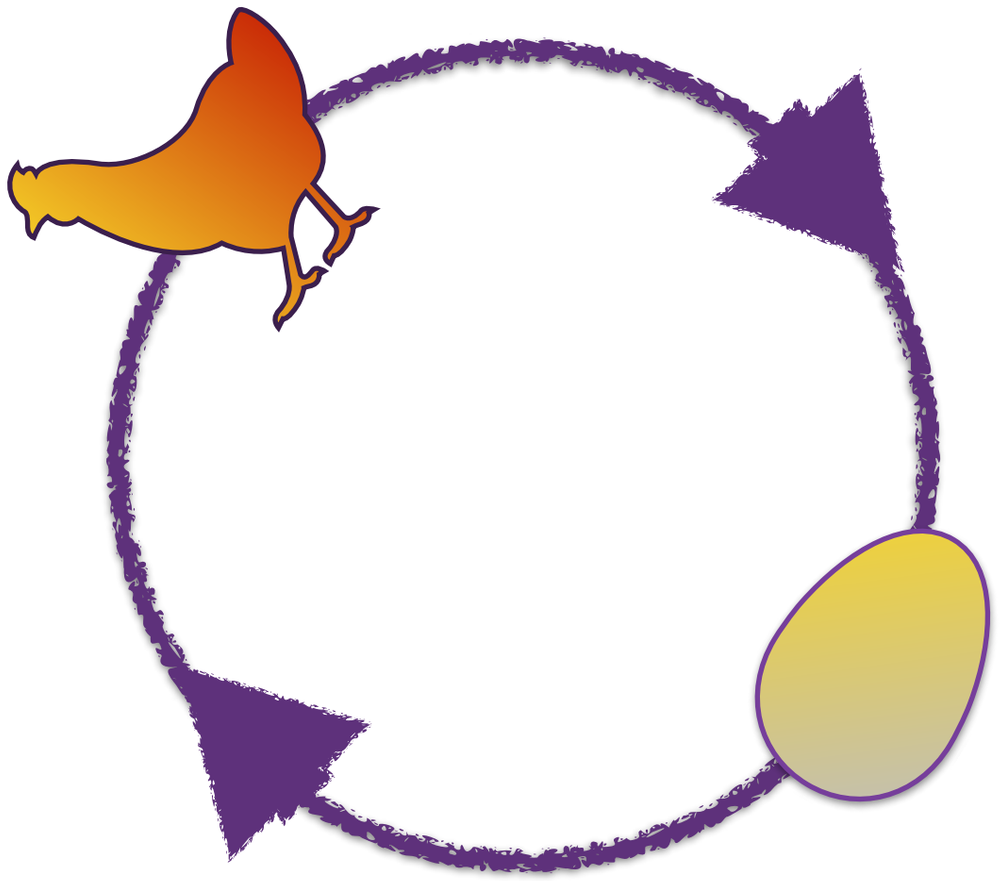
orbital ordering in materials

a chicken-and-egg problem

how to disentangle the two?
which mechanism dominates when?

distortions



ordering

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$KCuF_3$ LDA+U: KK-like mechanism

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

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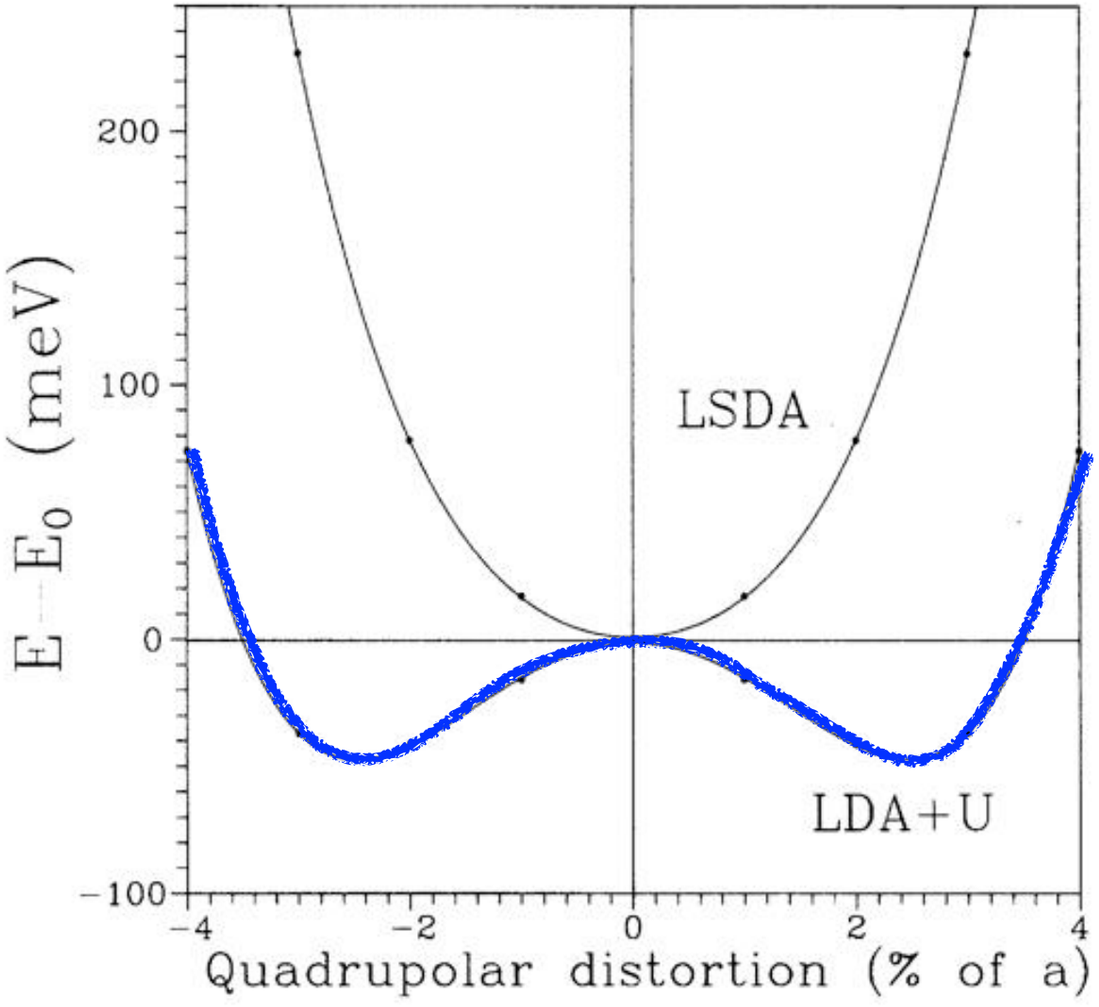
J. Zaanen
Lorentz Institute for the Theoretical Physics, Leiden University, Leiden, The Netherlands
(Received 15 May 1995)



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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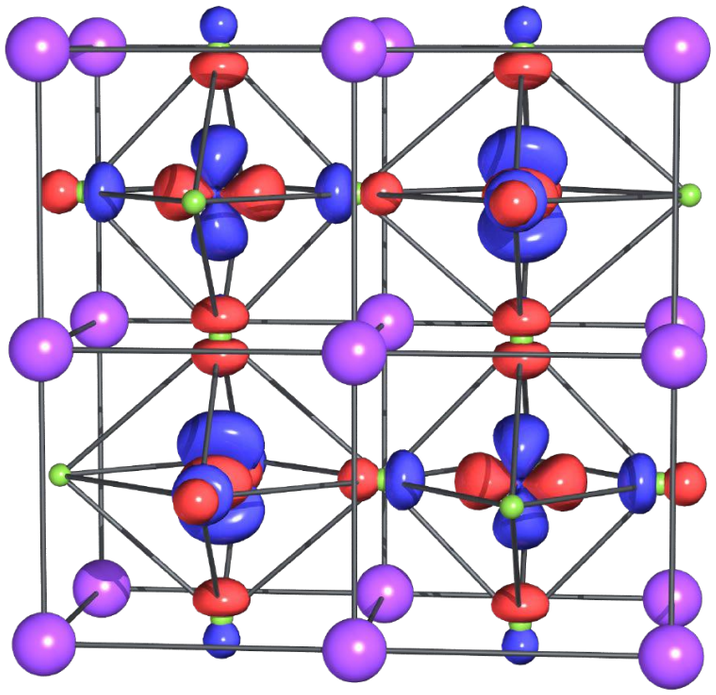
$KCuF_3$ LDA+U: KK-like mechanism



- however LDA+U can only describe magnetic phase

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 $KCuF_3$

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[3]*Institute of Metal Physics, South Kovalevskoy Street 18, 620219 Yekaterinburg GSP-170, Russia*
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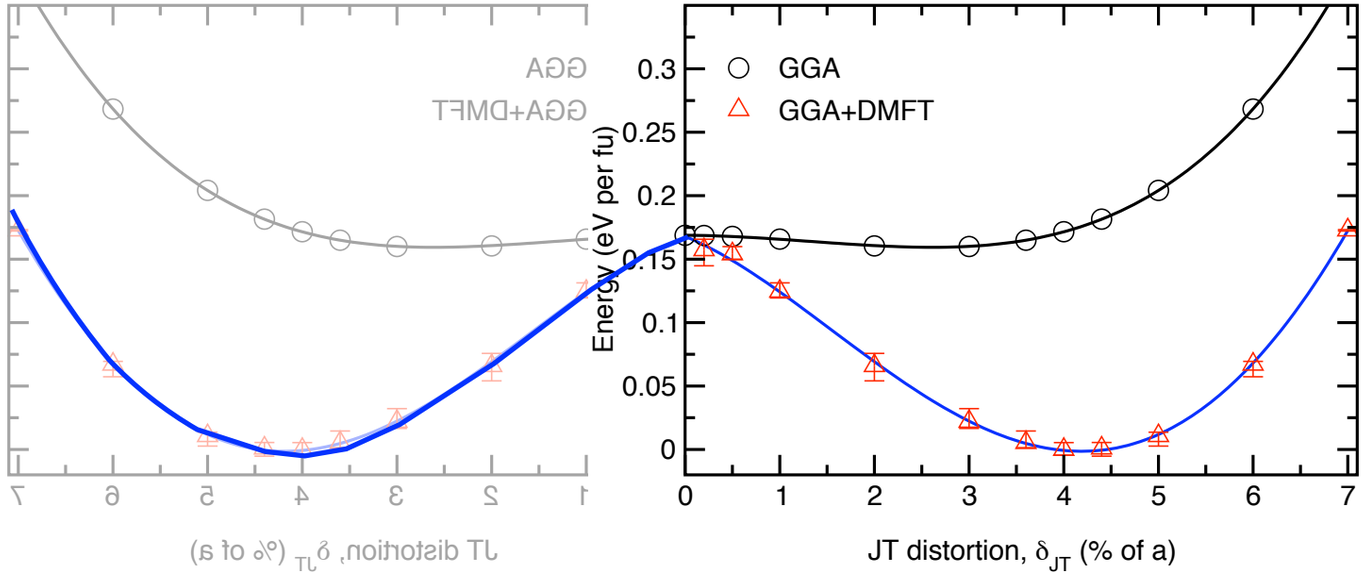
(Received 7 April 2008; published 29 August 2008)



energy gain ~ 175 meV

DMFT para and LDA+U AFM
give similar results

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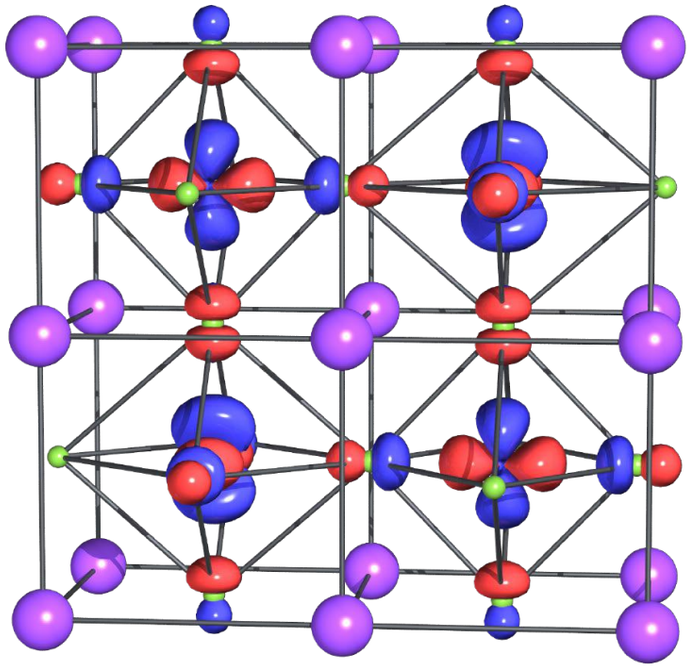
KK is the mechanism: $T_{OO} \sim T_{KK}$



…or, is it ?

- why T_N (40K-140K) much smaller than T_{JT} (800-1400 K) ?
- total energy does not distinguish mechanisms

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 $KCuF_3$

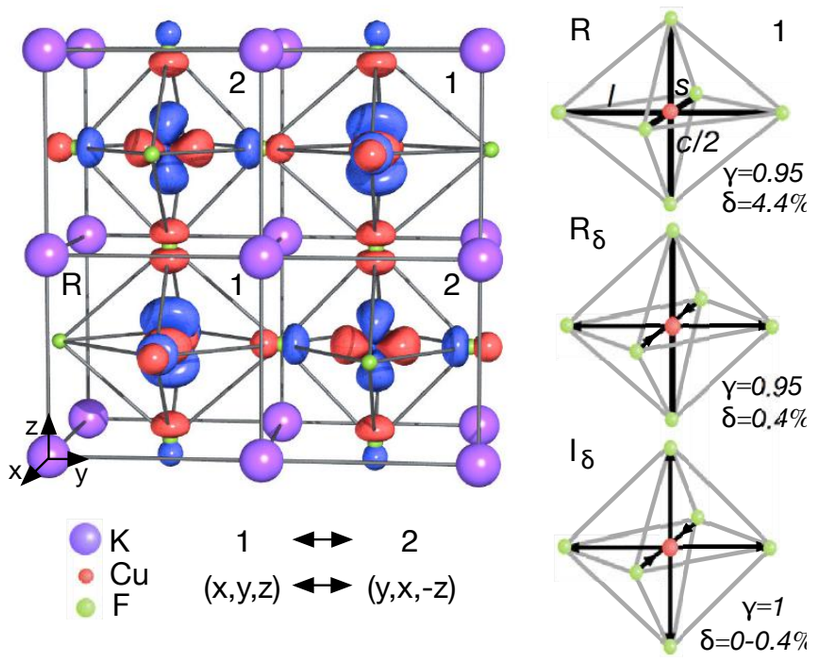
E. Pavarini,[1] E. Koch,[1] and A. I. Lichtenstein[2]

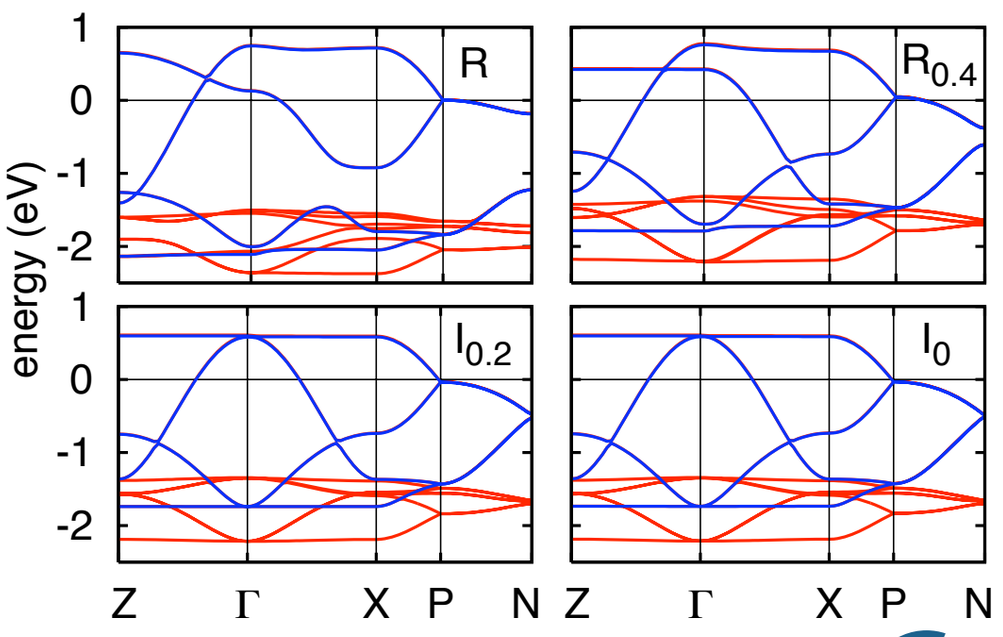
[1]*Institut für Festkörperforschung and Institute for Advanced Simulation, Forschungzentrum Jülich, 52425 Jülich, Germany*
[2]*Institute of Theoretical Physics, University of Hamburg, Jungiusstrasse 9, 20355 Hamburg, Germany*

(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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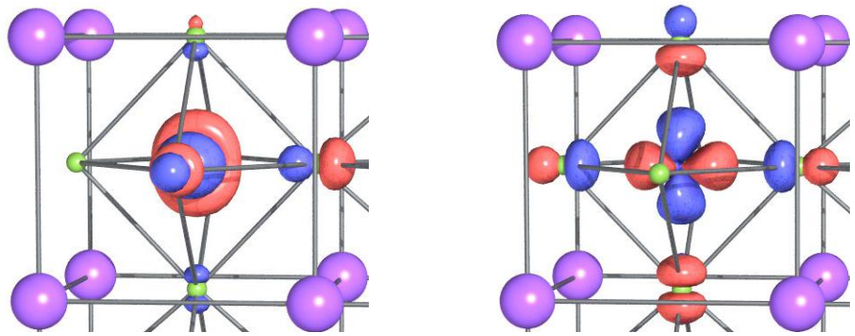
LDA+DMFT with Wannier functions

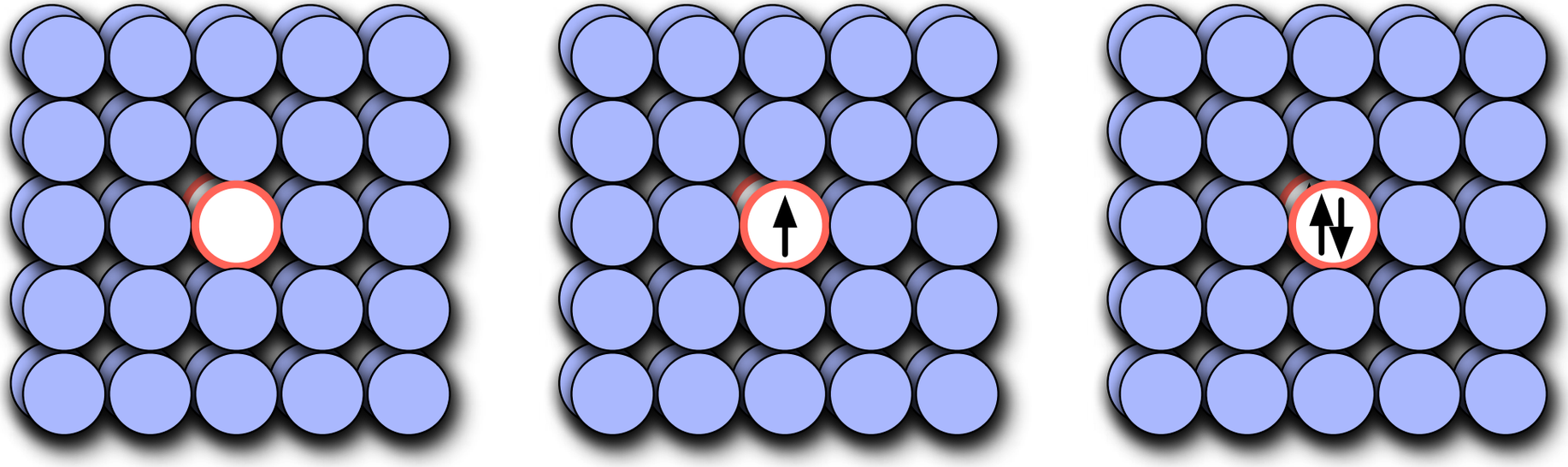
$$
\begin{aligned}
H = & - \sum_{ii'} \sum_{mm'} \sum_{\sigma} t^{ii'}_{mm'} c^{\dagger}_{im\sigma} c_{i'm'\sigma} \\
& + U \sum_{im} n_{im\uparrow} n_{im\downarrow} \\
& + \frac{1}{2} \sum_{im \neq m'\sigma\sigma'} (U - 2J - J\delta_{\sigma\sigma'}) n_{im\sigma} n_{im'\sigma'} \\
& - J \sum_{m \neq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

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

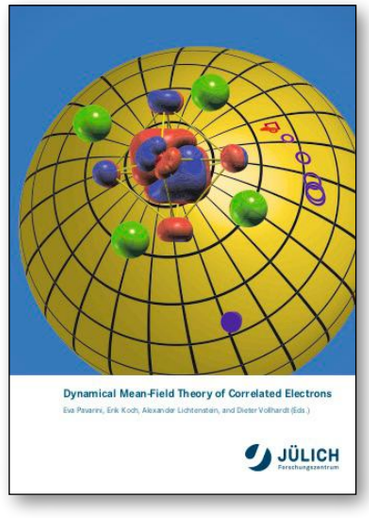
Mott Transition and Suppression of Orbital Fluctuations in Orthorhombic $3d^1$ Perovskites

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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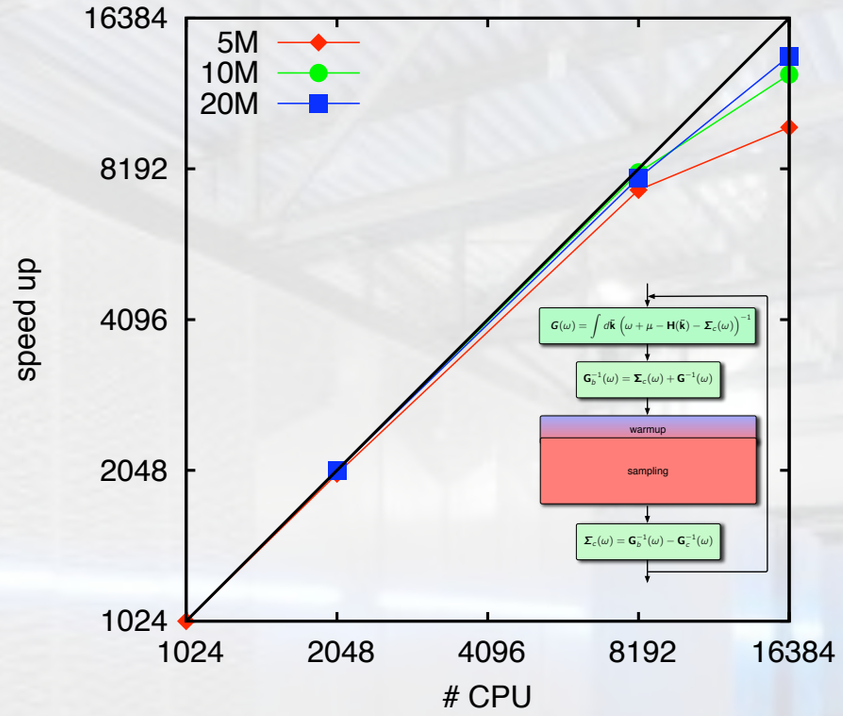
flexible and efficient solvers

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

self-energy matrix in spin-orbital space



DMFT and cDMFT

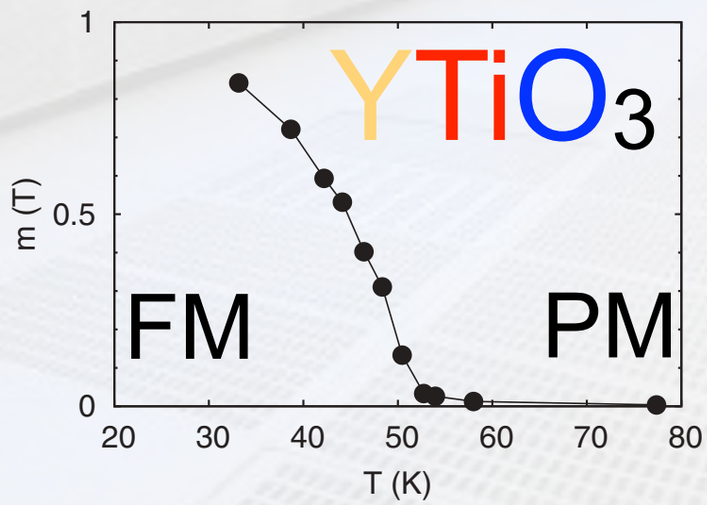
generalized quantum impurity solvers:

general HF QMC

general CT-INT QMC

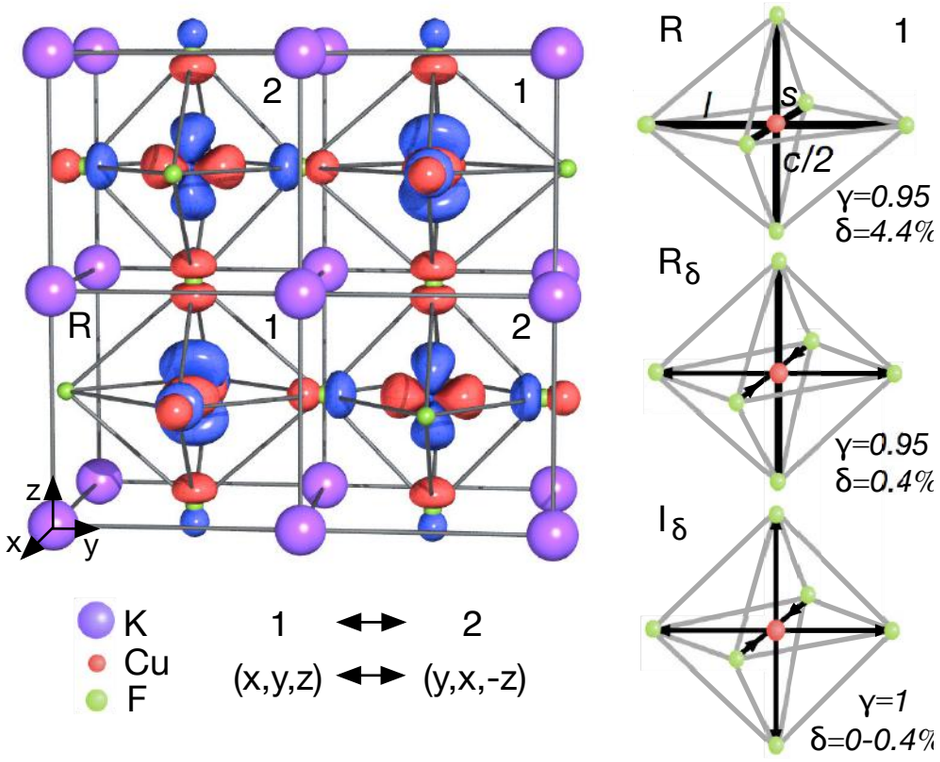
general CT-HYB QMC

- 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)



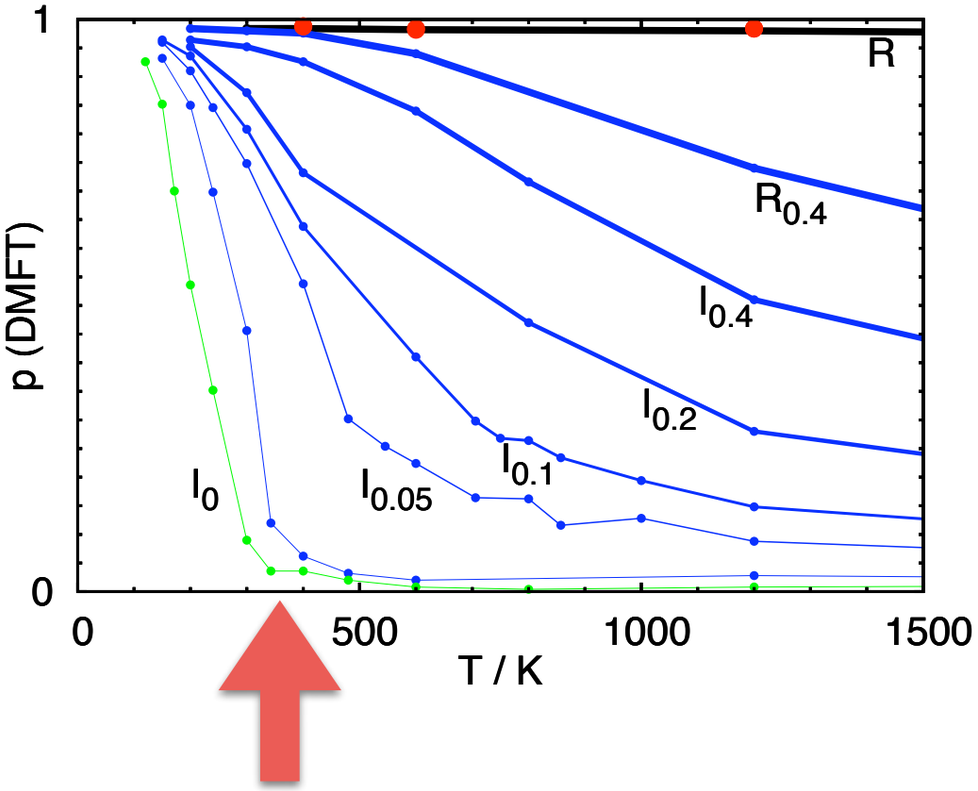
sign problem: smart adapted basis choice

the KK mechanism in $KCuF_3$



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

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



T_{KK}~350 K

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

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

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spontaneous ordering of orbitals

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.

$KCuF_3$

$LaMnO_3$

strong Coulomb repulsion (the Hubbard U)

+ orbitals degrees of freedom

= orbital super-exchange

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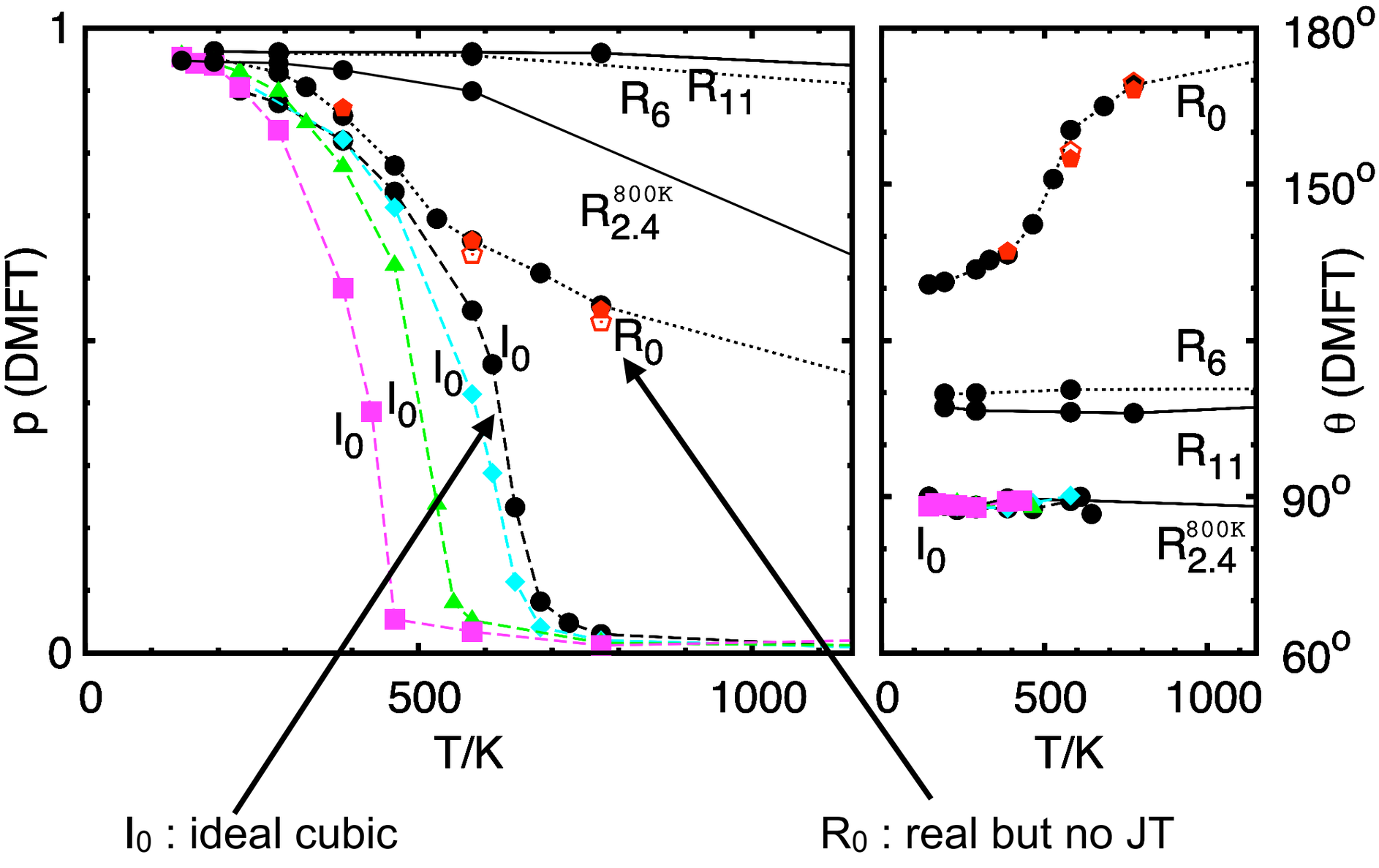
$LaMnO_3$: T_{KK} ~ 600 K !!

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



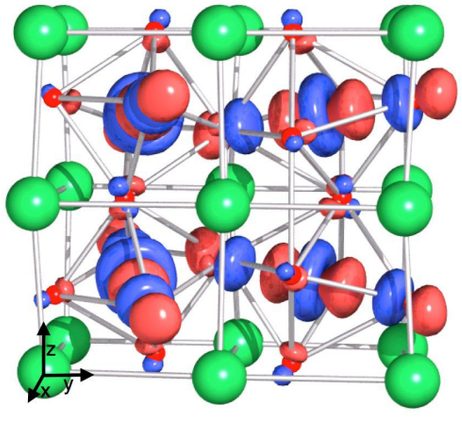
non-JT crystal-field

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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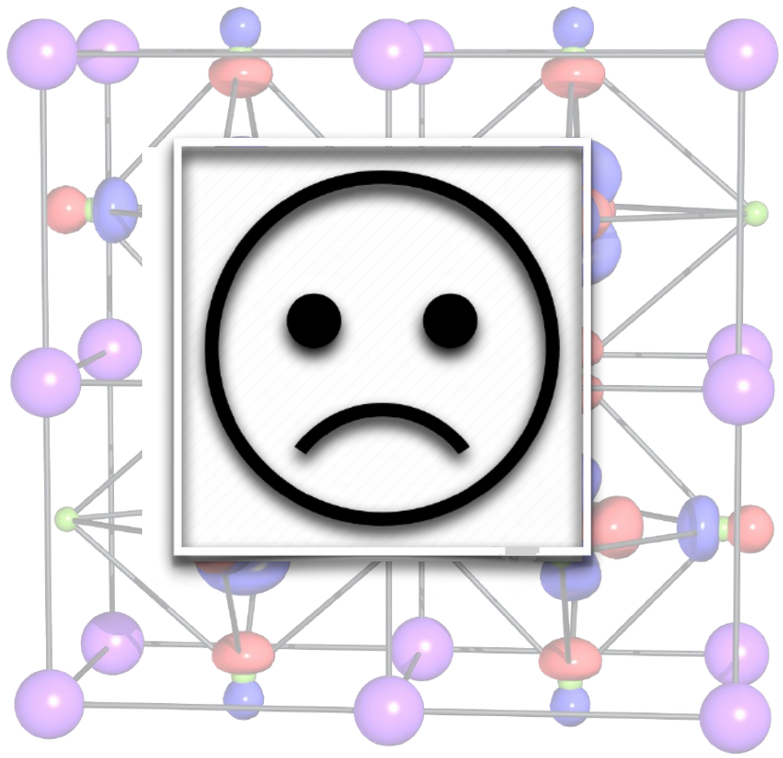
KK-only candidates

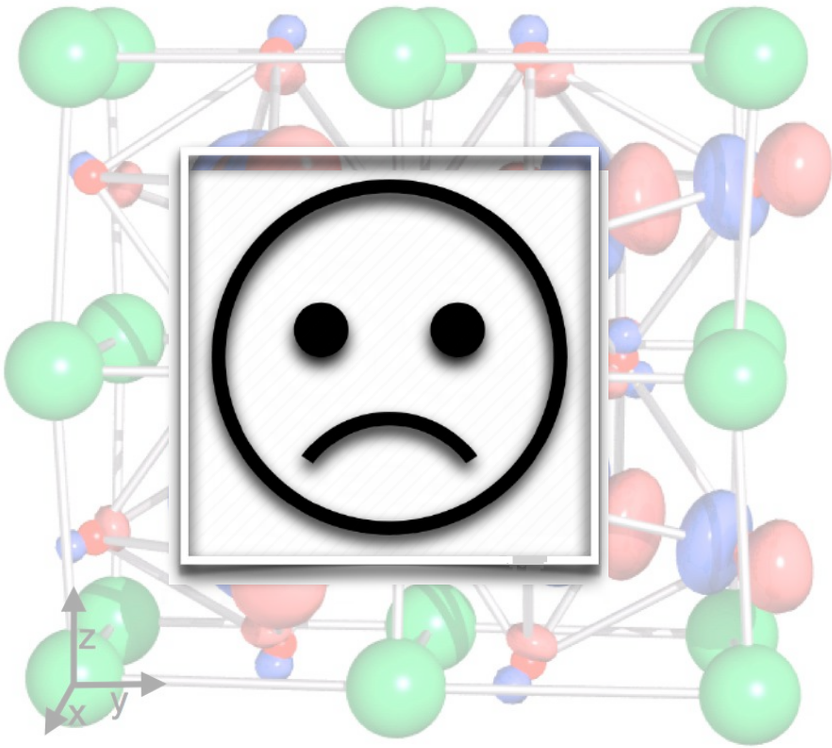
e_g systems

$KCuF_3$



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

$LaMnO_3$



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

$KCrF_3$ $ReMnO_3$

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is $KCuF_3$ really JT?

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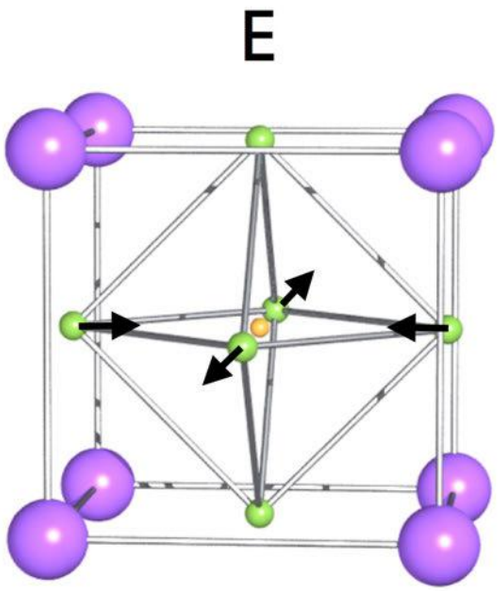
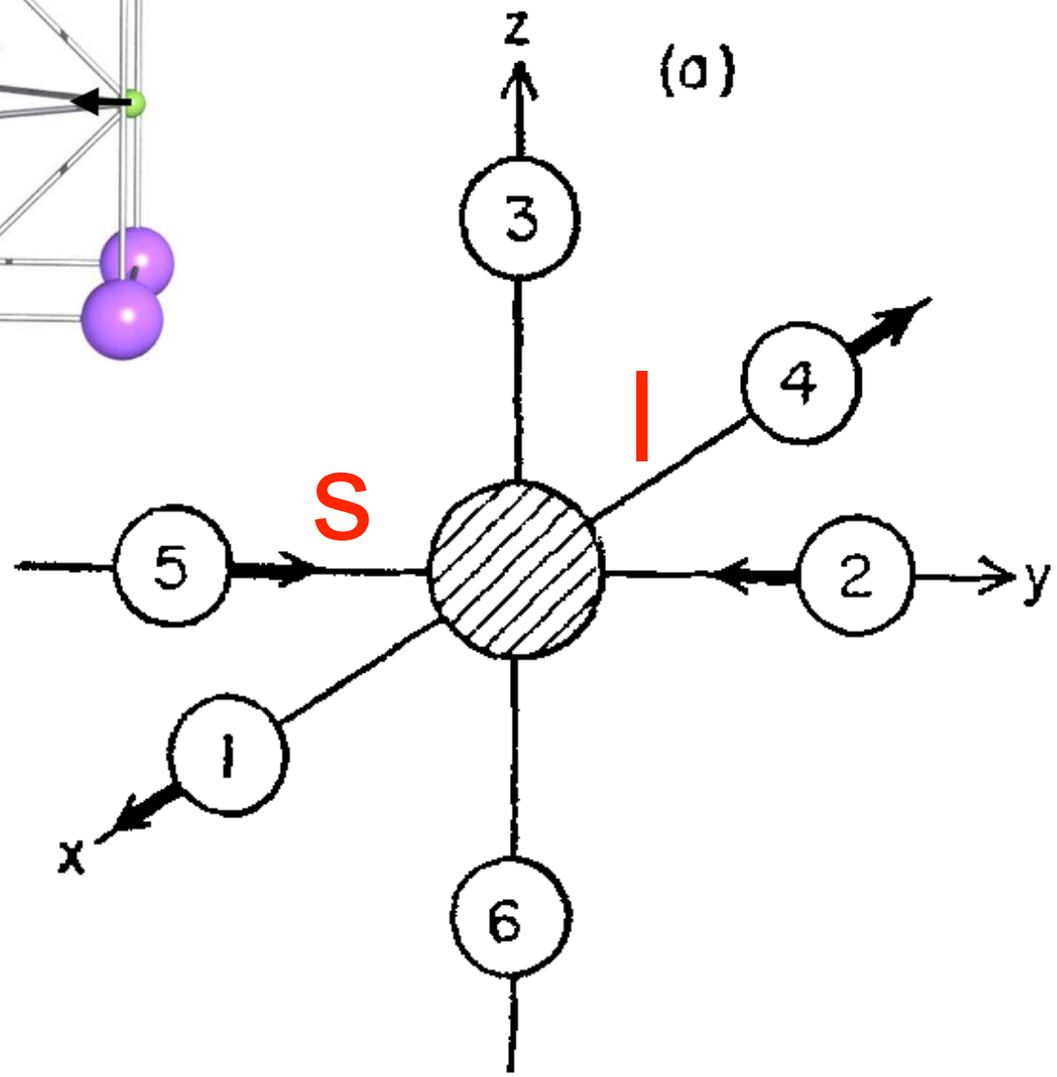
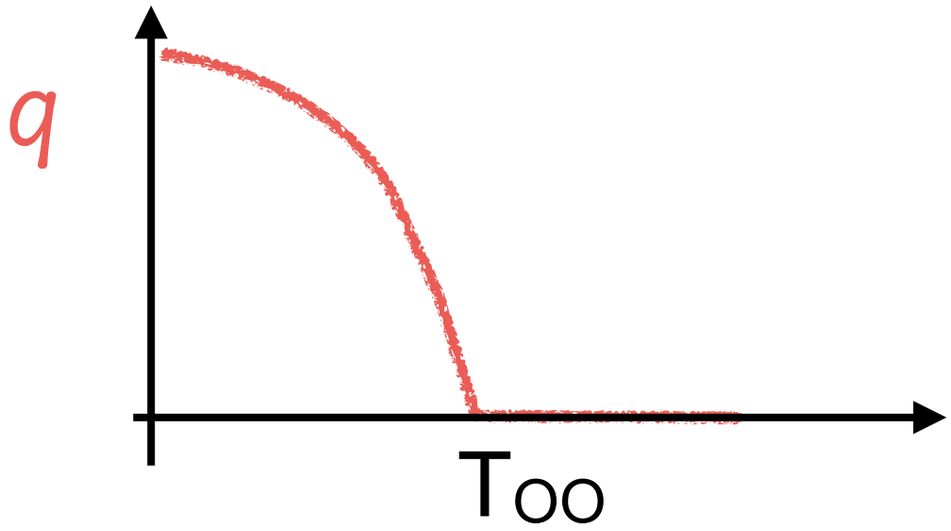
order parameter decreases with increasing T







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

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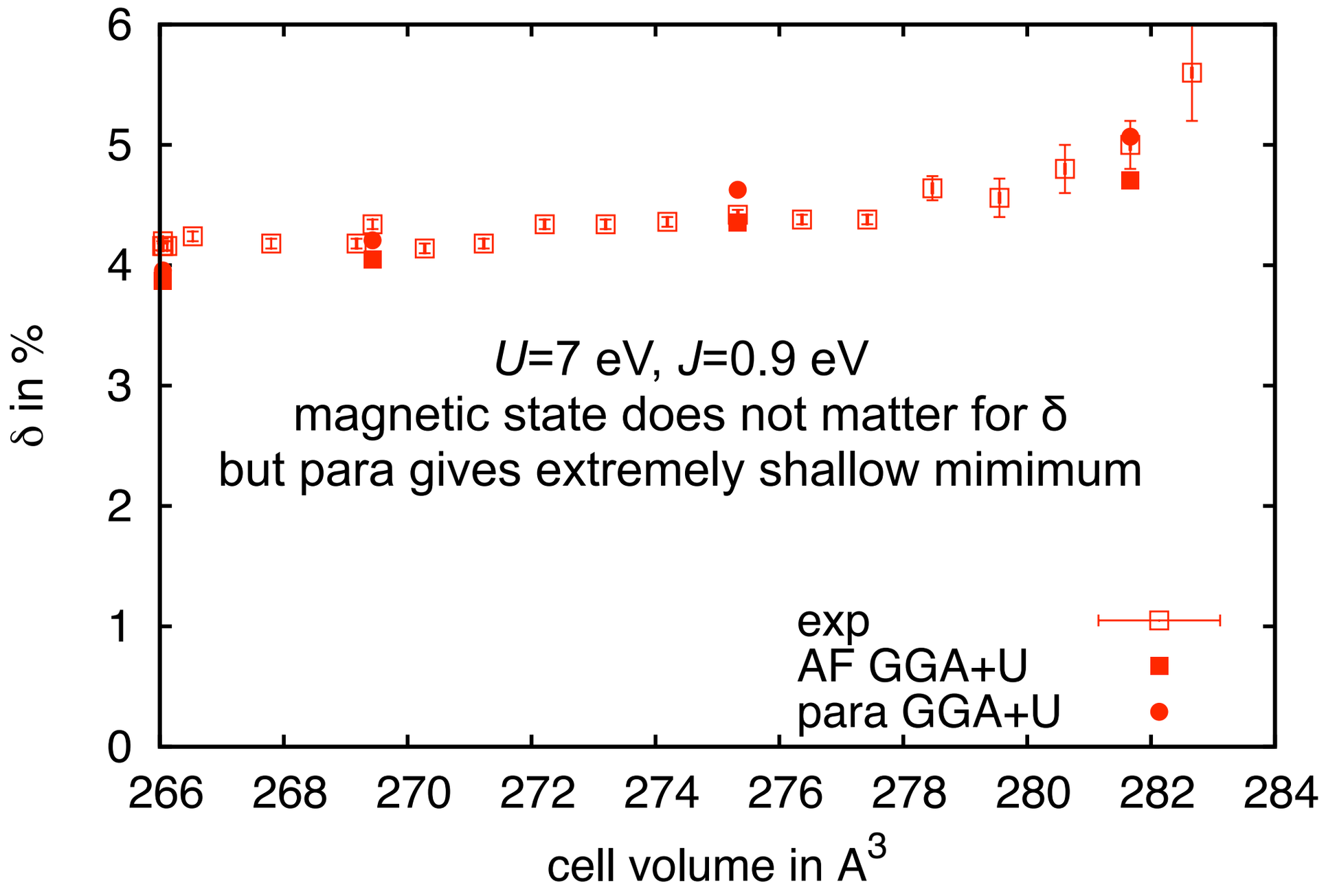
the distortion *q* increases with T

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



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

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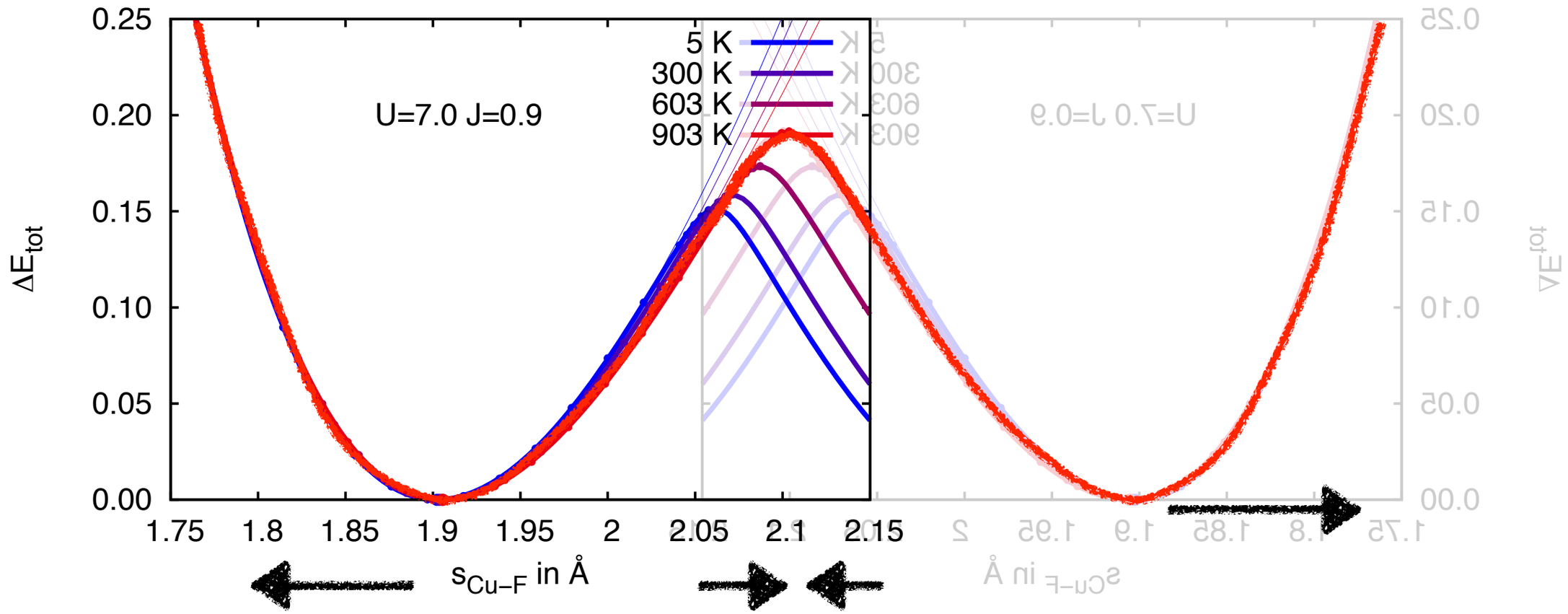
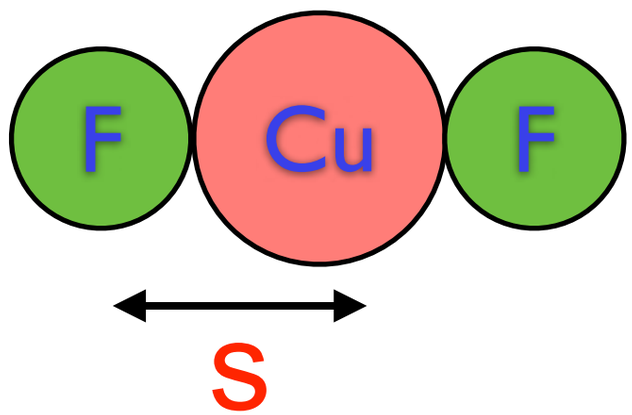
re-plot the (GGA+U) mexican hat

Born-Mayer repulsion !



touching ions



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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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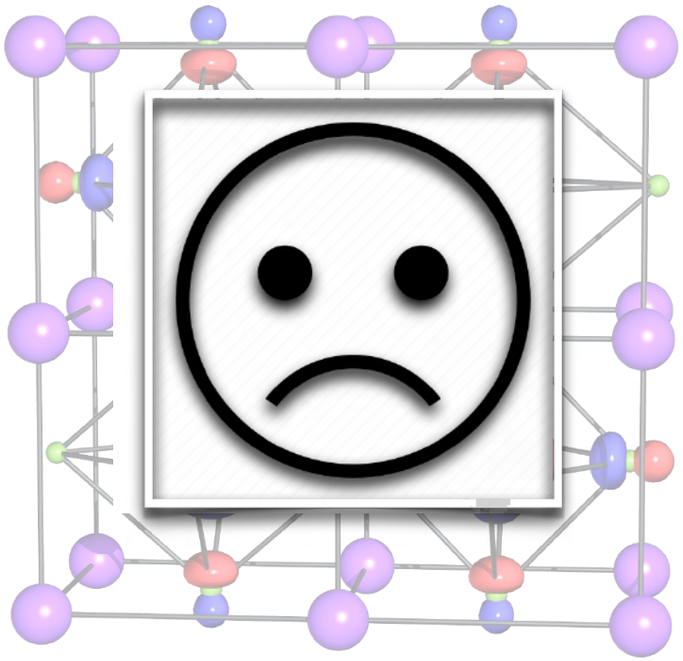
KK-only candidates

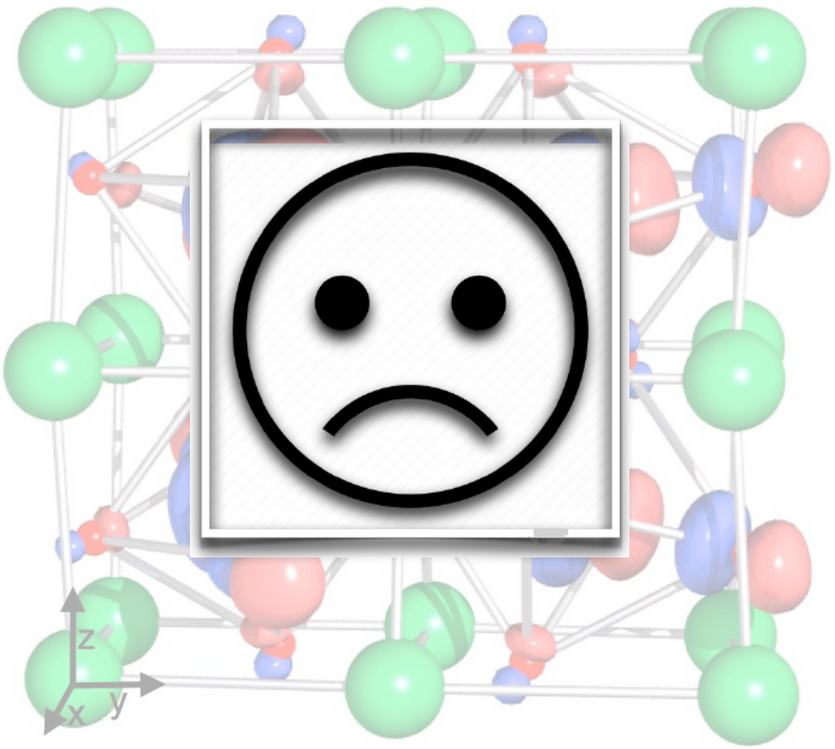
e_g systems

$KCuF_3$



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

$LaMnO_3$



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

$KCrF_3$ $ReMnO_3$

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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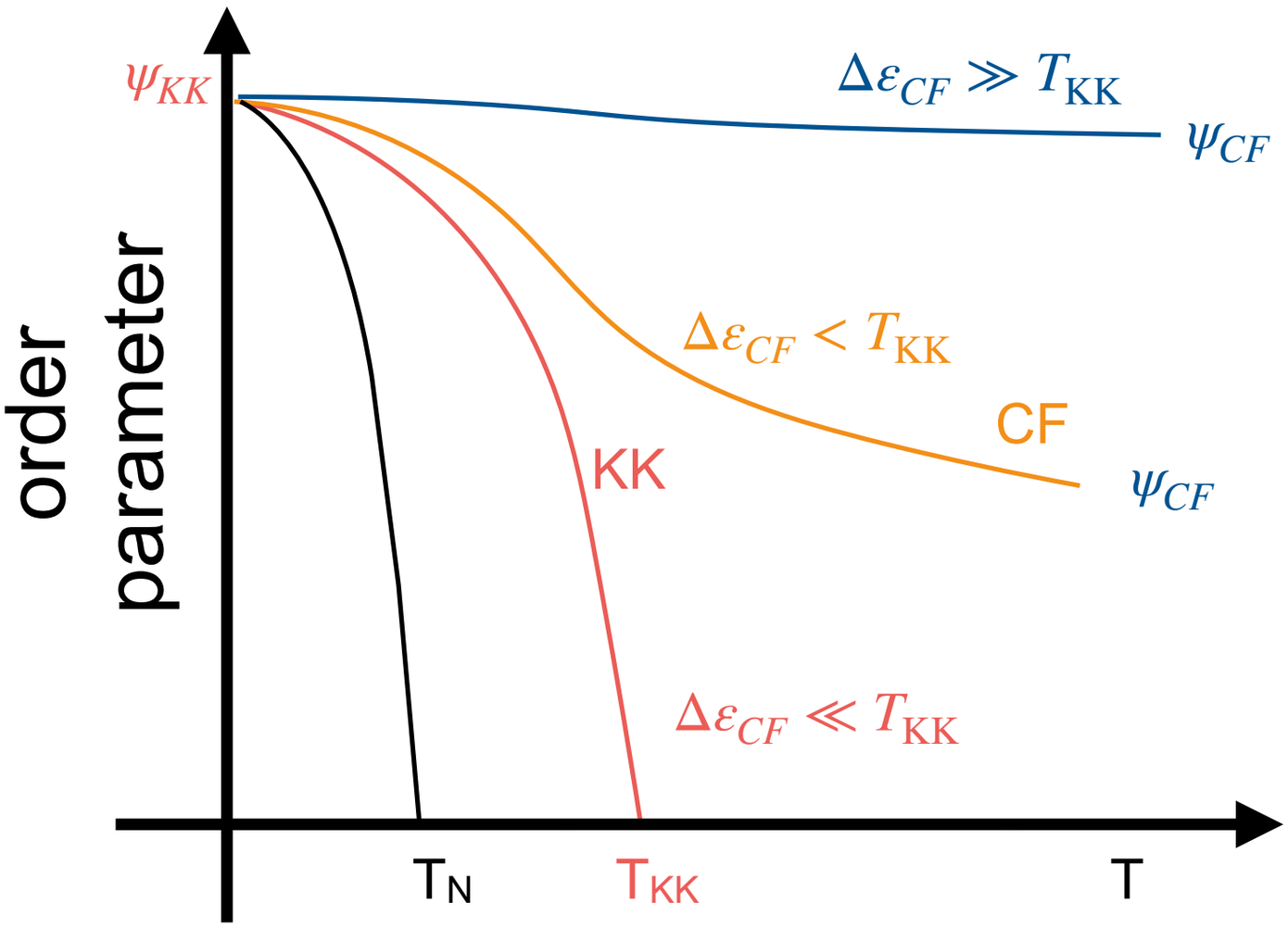
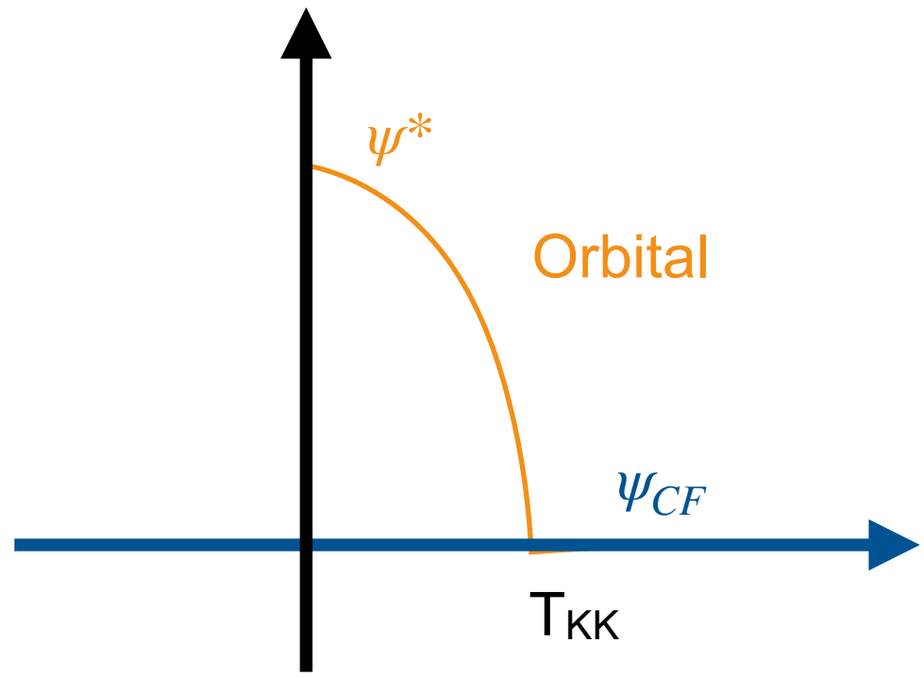
change of orbitals at low T?





ψ = occupied or hole orbital

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

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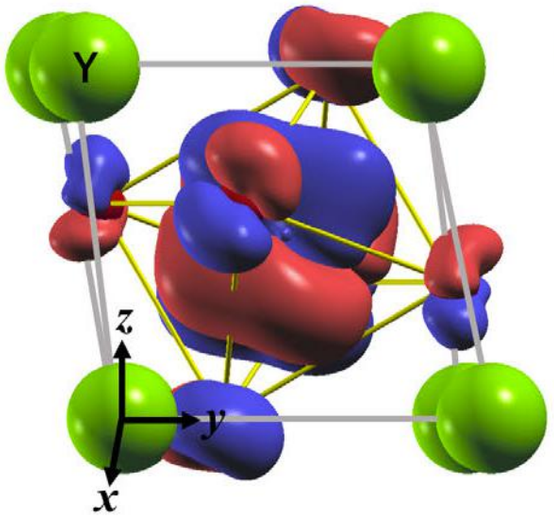
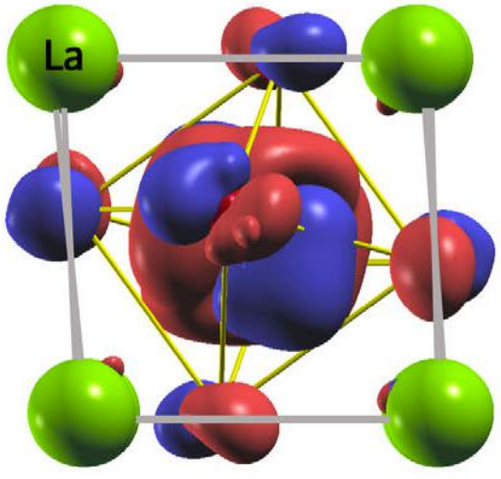
the first clear case: $LaVO_3$

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

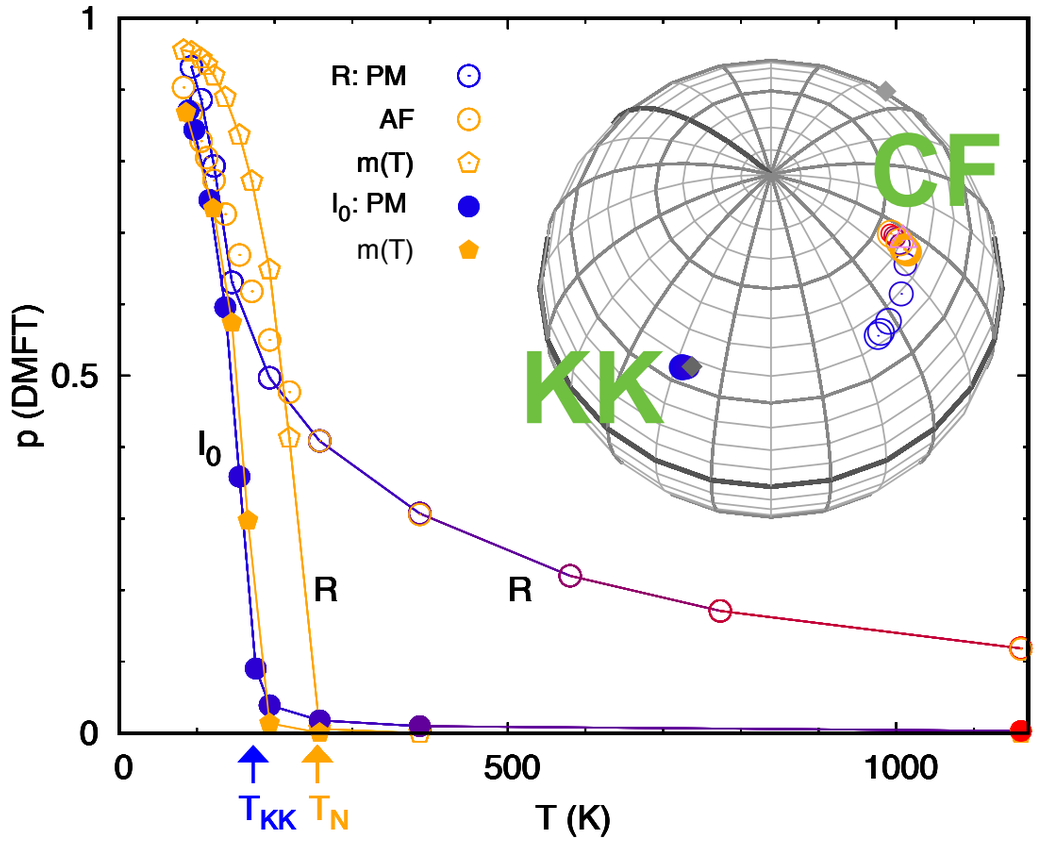
$|\theta,\phi\rangle_{CF}$



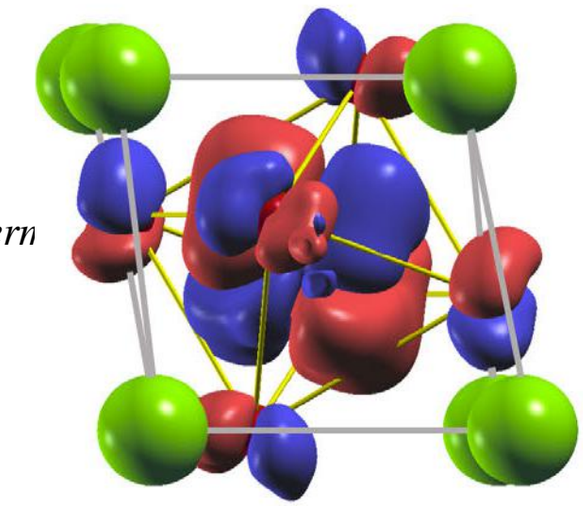


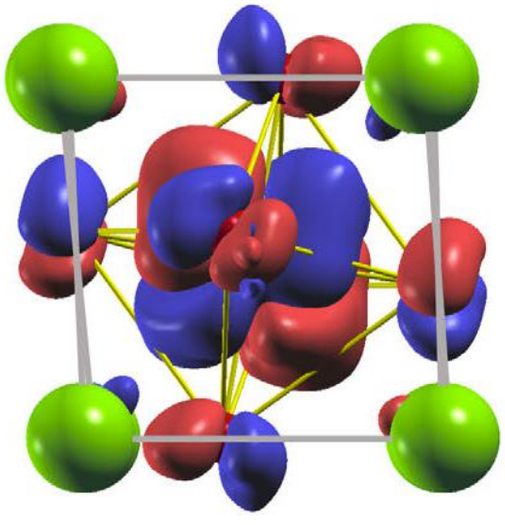
$LaVO_3$: A true Kugel-Khomskii system

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



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





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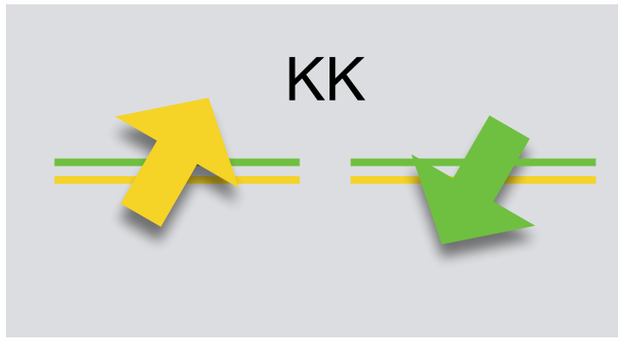
conclusion: mechanisms

super-exchange interaction



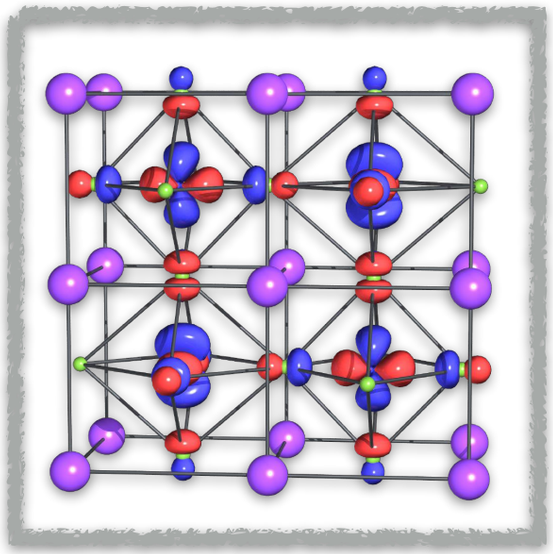
purely electronic coupling $4t^2/U$

lattice distortions

coulomb-enhanced crystal-field splitting

materials: pure KK systems are rare

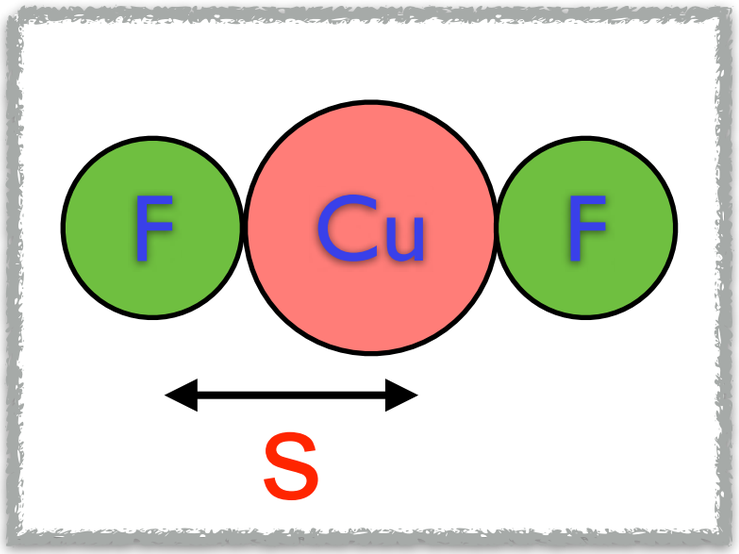
however, materials are complex



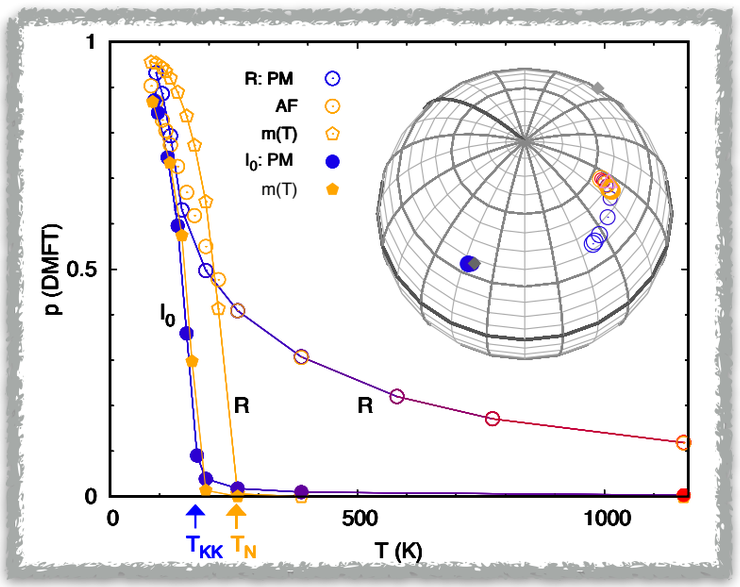
KBF_3 K_2BF_4 $ReMnO_3$ $ReTiO_3$

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

static splitting essential



thermal-assisted ordering



$LaVO_3$

KK system

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thank you!