

Russian Science Foundation

Орбитальные степени свободы в непроводящих соединениях переходных металлов

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Materials under consideration

Insulators

- localized electrons
- not-completely filled *d*or *f*-shell

Or materials with the metal-insulator transition

Examples: NiO, LaMnO₃, La₂CuO₄ etc.

Introduction: *d*-orbitals in a crystal, **cubic harmonics**

Directed **away** from ligands

Orbital degrees of freedom

Spin degrees of freedom

Math: spin operators $\hat{\vec{S}}$ $\langle \uparrow | \hat{S}^z | \uparrow \rangle = 1/2$ for $s = 1/2$ $\langle \downarrow | \hat{S}^z | \downarrow \rangle = -1/2$ **Orbital degrees of freedom**

̂ pseudospin operators *τ*

e.g. Cu^{2+} $\langle x^2 - y^2 | \hat{\tau}^z | x^2 - y^2 \rangle = -1/2$ e_g $\frac{1}{3z^2 - r^2}$ $\langle z^2 | \hat{\tau}^z | z^2 \rangle = 1/2$

t2g

Ligands

Orbital degrees of freedom

3. Spin-orbit coupling - lecture on Sunday

Interplay of different degrees of freedom:

Jahn-Teller effect

Jahn-Teller effect in a nutshell

Thus, the system aims to spontaneously lift orbital degeneracy by distorting surrounding

"Orbital-lattice" coupling

Normal vibration modes (octahedron)

$$
E_{JT} = \pm g |\delta| + \frac{B\delta^2}{2}
$$

Introduction: Jahn-Teller *e* **⊗** *E* **problem** for an isolated octahedron

Harmonic approximation: Highly degenerate ground state

Introduction: Jahn-Teller *e* **⊗** *E* **problem** for an isolated octahedron

Harmonic approximation

$$
|\theta\rangle = \cos(\theta)Q_3 + \sin(\theta)Q_2
$$

$$
|\theta\rangle = \cos(\theta/2)|z^2\rangle + \sin(\theta/2)|x^2 - y^2\rangle
$$

Distortion
$$
\longleftrightarrow
$$
 Orbital

*^Q*³ **Anharmonicity**

NaMn₇O₁₂ Nature Mat. 3, 48 (2004) PRB 89, 201115 (2014) **Cs2CuCl2Br2** Cryst. Gr. Des. 10, 4456 (2010) PRB 86, 035109 (2012)

Claimed compressed Turned out elongated

 Q_2 ⁻

E

Elongated octahedra! Most of octahedra with *eg***-ions (Cu2+, Mn3+) are elongated!**

Cooperative Jahn-Teller distortions

(electron-lattice mechanism of orbital ordering)

Interplay of different degrees of freedom:

Exchange interaction Kugel-Khomskii-like models

Mott-Hubbard transition in a nutshell

Localized electrons and correlation effects

Many-band Hubbard model:

$$
H_K = U \sum_m n_{m\uparrow} n_{m\downarrow} + U' \sum_{m \neq m'} n_{m\uparrow} n_{m'\downarrow} + (U' - J_H) \sum_{m < m',\sigma} n_{m\sigma} n_{m'\sigma}
$$

$$
-J_H \sum_{m \neq m'} c_{m\uparrow}^{\dagger} c_{m\downarrow} c_{m'\uparrow}^{\dagger} c_{m'\uparrow} + J_H \sum_{m \neq m'} c_{m\uparrow}^{\dagger} c_{m'\downarrow}^{\dagger} c_{m'\uparrow}
$$

$$
H_U = \left(4J_H - \frac{U}{2} \right) \hat{N} + (U - 3J_H) \frac{\hat{N}^2}{2} - J_H \left(2\hat{S}^2 + \frac{\hat{L}^2}{2} \right)
$$

Polar model (Shubin-Vonsovski)

Electron correlations in narrow energy bands

BY J. HUBBARD Theoretical Physics Division, A.E.R.E., Harwell, Didcot, Berks

(Communicated by B. H. Flowers, F.R.S.—Received 23 April 1963)

 W and W and W and W YHVWLJDWHWKLVVLWXDWLRQD VLPSOHDSSUR[LPDWHPRGHOIRUWKHLQWHUDFWLRQRIHOHFWURQVLQ

 $W(x) = \sum_{\alpha} w_{\alpha}$ which contains the planet of w

On the Electron Theory of Metals.

DEADLERGYLOGICAL SET IS SURFIDE ASSOCIATELY AND INCREMENTAL SURFACE IS A MONSOW SKY .

V. Irkhin, S.S. Sverdlovsk Phys \mathcal{L} structure, \mathcal{D} , \mathcal{D} , *JSNM 35, 2135 (2022)* (Communicated by R. H. I

WKHFRUUHODWLRQSUREOHPIRUWKLVREWDLQHG7KLVREWDLQHG7KLVR **Sverdlovsk Physical Technical Institute.**

(Communicated by R. H. Fowler, F.R.S.—Received December 29, 1933.)

$$
U \xrightarrow{\text{#}} \text{same orbital}
$$
\n
$$
U' \xrightarrow{\text{#}} \text{otherwise}
$$
\n
$$
U' - J_H \xrightarrow{\text{#}} \text{differential}
$$
\n
$$
J_H - \text{Hund's exchange!}
$$
\n
$$
J_O
$$

In Hubbard

$\left(\frac{2}{2}\right)$ 3-band model in non-standard notations

Introduction: Orbitals and spins

Heisenberg model:

 $\hat{H} = J \sum \hat{\vec{S}}_i \hat{\vec{S}}_j$ $i\neq j$

strong **AFM**

AntiFerro-orbital order

Modification of magnetic structure by orbitals

Goodenough - Kanamori - Anderson rules connect orbitals and spins

Ferro-orbital \Rightarrow AFM

900 via orthogonal *p*-orbitals \Rightarrow FM

John Goodenough 1922-2023 Nobel prize 2019

Junjiro Kanamori 1930-2012

Philip Anderson 1923-2020 Nobel prize 1977

Goodenough - Kanamori - Anderson rules connect orbitals and spins

Important general trend in insulating transition metal oxides

TAT

This is the reason why most of insulating transition metal oxides with localized electrons are AFM

Orbitals and spins: Kugel-Khomskii model and exchange mechanism of orbital ordering

Two levels with hoppings between the same orbitals

Pseudo-spin operators:

 $\hat{\tau}^z | 1 \rangle = 1/2 | 1 \rangle$ $\hat{\tau}^z | 2 \rangle = -1/2 | 2 \rangle$

Kugel-Khomskii Hamiltonian:

 $J^S =$ $\hat{H}_{KK} = \sum_{U} J_{ij}^S \hat{S}_i \cdot \hat{S}_j + J_{ij}^{\tau} \hat{\tau}_j \hat{\tau}_j + 4 J_{ij}^{S \tau} (\hat{S}_i \cdot \hat{S}_j)(\hat{\tau}_i \hat{\tau}_j), \quad J^S = \frac{2t^2}{U} \left(1 - \frac{J_H}{U}\right),$ *i*≠*j* $J_{ij}^S \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j + J_{ij}^{\tau} \hat{\tau}_j \hat{\tau}_j + 4 J_{ij}^{S \tau} (\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j) (\hat{\tau}_i \hat{\tau}_j), \quad J^S = \frac{2I^2}{II} \left(1 - \frac{J_H}{II} \right), \quad J^{\tau} = J^{S \tau} =$ $2t^2$ $\frac{1}{U}$ (1+ J_H *U*)

The maximum energy gain is when electrons occupy different orbitals

Electrons can decide by themselves (without lattice), which orbitals to occupy

Exchange mechanism of orbital order

Hubbard model:

$$
\hat{H} = \sum_{\substack{i \neq j}} t_{ij}^{ab} c_{ia\sigma}^{\dagger} c_{jb\sigma} + \frac{1}{2} \sum_{i} U_{ab} n_{ia\sigma} n_{ib\sigma'} (1 - \delta_{ab} \delta_{\sigma\sigma'})
$$

$$
- \sum_{i,a \neq b} J_H^{ab} \left(c_{ia\sigma}^{\dagger} c_{ia\sigma'} c_{ib\sigma}^{\dagger} c_{ib\sigma} + c_{ia\sigma}^{\dagger} c_{ib\sigma} c_{ia\sigma'}^{\dagger} c_{ib\sigma'} \right)
$$

Kugel-Khomskii model derivation

 $\tau^z \lambda$

Let's consider a lattice with two orbitals at each site

Hamiltonian describing exchange interaction can by obtained by the 2nd order of perturbation theory with respect to electron hopping

Approximations:

A.

$$
\mp \frac{}{t_{++}} = t_{--} = t
$$

$$
\lambda = \lambda', \quad \lambda'' = \lambda'''
$$

B. $\langle \hat{H}_1 \rangle = \tilde{U}$ we don't distinguish energies of different excited states

Kugel-Khomskii model derivation

$$
\hat{H}_{eff} = -\sum_{i \neq j} \sum_{\lambda \lambda'} \sum_{\sigma \sigma'} \frac{t^2}{\tilde{U}} c_{i\lambda \sigma}^{\dagger} c_{j\lambda \sigma}^{\dagger} c_{j\lambda' \sigma'}^{\dagger} c_{i\lambda' \sigma'} = -\sum_{i \neq j} \sum_{\lambda \lambda'} \frac{t^2}{\tilde{U}} \left(\sum_{\sigma} c_{i\lambda \sigma}^{\dagger} c_{i\lambda' \sigma} (1 - c_{j\lambda' \sigma}^{\dagger} c_{j\lambda \sigma}) - \sum_{\sigma \neq \sigma'} c_{i\lambda \sigma}^{\dagger} c_{i\lambda' \sigma'}^{\dagger} c_{j\lambda \sigma}^{\dagger} c_{j\lambda \sigma}^{\dagger} c_{j\lambda \sigma}^{\dagger} c_{j\lambda \sigma'}^{\dagger} c_{j\
$$

 $c_{i\uparrow}^{\dagger} c_{i\uparrow} = \hat{n}_{i\uparrow} = 1/2 + \hat{S}_{i}^{z}, \quad c_{i\uparrow}^{\dagger} c_{i\downarrow} = \hat{S}_{i}^{+}$ $c_{i\downarrow}^{\dagger} c_{i\downarrow} = \hat{n}_{i\downarrow} = 1/2 - \hat{S}_{i}^{z}, \quad c_{i\downarrow}^{\dagger} c_{i\uparrow} = \hat{S}_{i}^{-}$ *Spin space (spins)* $c_{i+}^{\dagger} c_{i+} = \hat{n}_{i+} = 1/2 + \hat{\tau}_i^z$ z, $c_{i+}^{\dagger} c_{i-} = \hat{\tau}_i^+$ *i* c_{i-}^{\dagger} $c_{i-} = \hat{n}_{i-} = 1/2 - \hat{\tau}_i^z$ z, $c_{i-}^{\dagger} c_{i+} = \hat{\tau}_i^$ *i Orbital space (pseudospins)*

i.e. e.g. what $c_{i\uparrow}^{\dagger}$, $c_{i\downarrow}$ does? It **acts in both spin and** \longrightarrow \longrightarrow $c_{i\uparrow}^{\dagger}$ **orbital spaces** raising both spin and pseudospin

 $\hat{H}_{\textit{eff}} = \sum \hat{H}_{++} + \hat{H}_{+-} + \hat{H}_{-+} + \hat{H}_{--}$ *i≠j* $λ = +, λ' = +$

Expand the sum over orbitals explicitly

$$
\hat{H}_{\pm\pm} = -\frac{t^2}{\tilde{U}} \left(\frac{1}{2} \pm \hat{\tau}_i^z \right) + \frac{t^2}{\tilde{U}} \left(\frac{1}{2} \pm \hat{\tau}_i^z \right) \left(\frac{1}{2} \pm \hat{\tau}_j^z \right) \left[\frac{1}{2} + 2 \hat{\vec{S}}_i \hat{\vec{S}}_j \right], \quad \hat{H}_{\pm\mp} = \frac{t^2}{\tilde{U}} \hat{\tau}_i^{\pm} \hat{\tau}_j^{\mp} \left[\frac{1}{2} + 2 \hat{\vec{S}}_i \hat{\vec{S}}_j \right]
$$

Highly (and not really) symmetric Kugel-Khomskii model

$$
\hat{H}_{KK} = \frac{t^2}{\tilde{U}} \sum_{i \neq j} \left(\frac{1}{2} + 2\hat{\vec{\tau}}_i \hat{\vec{\tau}}_j \right) \left[\frac{1}{2} + 2\hat{\vec{S}}_i \hat{\vec{S}}_j \right] + C
$$

so-called *SU(4)* symmetric Kugel-Khomskii model

Reproduces **GKA rules** Assume spins are coupled ferromagnetically, i.e. $\langle \hat{S}_i^z \hat{S}_j^z \rangle = 1/4$ In a mean-field E_{AFM} = *t* 2 $\overline{\tilde{U}}$ $\overline{\tilde{U}}$ $\overline{\tilde{U}}$ $\overline{ }$ 1 2 $+ 2\langle \hat{\tau}_i^z \hat{\tau}_j^z \rangle \bigg)$ Minimum at *z i τ*̂ *z* $\langle \xi \rangle = -1/4$ i.e. antiferro-orbital ordering*

Kugel-Khomskii model (perovskite with *eg***-electrons)**

$$
H_{\text{sub}} = \frac{t^2}{U} \sum_{(i, j)_z} \left\{ 8S_i S_j \left[\tau_i^* \tau_j^* \left(1 + \frac{J_H}{U} \right) + \tau_j^* + \frac{1}{4} \left(1 - \frac{J_H}{U} \right) \right] + \frac{t^2}{U} \left[\tau_i^* \tau_j^* \left(1 + \frac{J_H}{U} \right) - \tau_j^* \right] \right\} + \frac{t^2}{U} \sum_{(i, j)_z} \left\{ 2S_i S_j \left[\tau_i^* \tau_j^* \left(1 + \frac{J_H}{U} \right) - 2\tau_j^* + \left(1 - \frac{J_H}{U} \right) \pm 2 \right\} \left(1 + \frac{J_H}{U} \right) \tau_i^* \tau_j^* + 2 \right\} \overline{\sigma}_j^* + \frac{1}{2} \left\{ 1 + \frac{J_H}{U} \right\} \tau_i^* \tau_j^* \right\} + \frac{1}{2} \left[\tau_i^* \tau_j^* \left(1 + \frac{J_H}{U} \right) - \frac{2\tau_j^*}{U} \pm 2 \right\} \overline{\sigma}_j^* + \frac{1}{2} \left[\tau_i^* \tau_j^* \left(1 + \frac{J_H}{U} \right) - \frac{2\tau_j^*}{U} \pm 2 \right\} \overline{\sigma}_j^* \pm 2 \right\} \overline{\sigma}_j^* + \frac{1}{2} \left\{ 1 + \frac{J_H}{U} \tau_i^* \tau_j^* \right\}
$$

* Mean-field approximation is a very poor approach in a general case, see e.g. PRL 82, 836 (1998) σ , t \sim 0 σ (10 σ

Kugel-Khomskii model: realization of a highly symmetric model

$$
\hat{H}_{\text{eff}} = \sum_{i \neq j, k \neq l} \sum_{\{\lambda\}} \sum_{\sigma \sigma'} \frac{t_{\lambda \lambda'} t_{\lambda'' \lambda'''}}{E_0 - \langle H_1 \rangle} c^{\dagger}_{i \lambda \sigma} c_{j \lambda' \sigma} c^{\dagger}_{k \lambda'' \sigma'} c_{l \lambda'''\sigma'}
$$

Excited level spectrum $\langle H_1 \rangle$ and a hopping structure $t_{ij}^{\lambda\lambda'}$ are the origin of all complications!

M. Yamada et al., PRL 121, 97201 (2018)

Note also possibility of dimerization *A. Ushakov, I. Solovyev, S.S., JETP Letters 112, 642 (2020)*

Interplay of different degrees of freedom:

Some examples

Example 1: 3-band Hubbard model with 1 electron on the square lattice (= Sr2VO4)

P. Igoshev, V. Irkhin, S.S. arXiv:2406.07386

Example 2: Reduction of dimensionality Modulation of the exchange interaction

Ferro-orbital => AFM **strong**

Antiferro-orbital => FM $J_F\approx-\frac{2t^2J_H}{H^2}$ *U*² **weak**

 $J_{A}=% {\textstyle\sum\nolimits_{\alpha}} g_{\alpha}\gamma_{\alpha}^{\dag}\gamma_{\alpha} \label{c1c1}%$

 $2t^2$

U

 $J_F\approx-\frac{2t^2J_H}{H^2}$ *U*² **weak** 900 via orthogonal p -orbitals

Example 2: Reduction of dimensionality Modulation of the exchange interaction

KCuF3 - One of the best 1D antiferromagnet !!!

Orbitals reduce dimensionality: $3D \rightarrow 1D$

Example 3: Dimerization driven by orbital ordering

Orbitals reduce dimensionality: 1D \longrightarrow **0D**

Example 4: Formation of a Haldane chain due to orbital ordering

S. Lee, S.S. et al., Nature Material 5, 471 (2006)

Orbitals reduce dimensionality: 3D - 1D

 $Ru⁴⁺$

\overline{a} 2 **Directional character of orbitals:**

ture of the excited levels. Most importantly, the very form of the exchange interaction depends on the spatial orientation of a given bond. We label a bond ij laying in the %& plane perpendicular to the 'ð¼ x; y; zÞ axis by a (')-bond. With this in mind, the Hamiltonian can be written as \overline{y}

cally, the anisotropy corrections are obtained in powers of (B) A 90" bond: There are again only two orbitals active on a given bond, e.g., jxzi and jyzi orbitals along a bond in $\mathbf x$ nondiagonal elements, and there are two possible paths for a charge transfer [via upper or lower oxygen, see Fig. 2(b)]. This peculiarity of a 90" bond leads to an exchange the animal periodic structure of a 90" bond leads to an exchange

Electronic structure: Orbital-selective Mott transitionshared octahedra as in Fig. 2(a), and (B) a 90"-bond Heisenberg plus a pseudodipolar interaction, \vdash $\ddot{}$ \mathbf{r} \mathbf{I} intermediate organizations for the Council of the Council $\overline{}$ **2** very form of the exchange Hamiltonian depends on bond geometry through a density profile of Kramers states, as we

Directional character of orbitals

t_{2g} orbitals on the square lattice

10

Orbitals can have a very different dispersion, which can be reflected on e.g. transport properties

2.59 μ μ **Orbital-selective Mott (OSM) transition**

tiva Matt transitian: Matt transitians
. *xy* and two with mixed *{xz, yz}* character. Their shape and volume agreement the definition of $\mathsf{f}\cap\mathsf{f}$. The definition of $\mathsf{f}\cap\mathsf{f}$ for different orbitals settion can occur congratoly prion can occul separately sign of the energy splitting between the (*xy*)- and (*xz, yz*) orbitals, so that now the *xy*-orbital lies lower in energy ion can occur congratoly **Orbital-selective Mott transition:** Mott transition can occur separately

orbitals. If we denote the occupancy of the *{xz, yz}* and (*xy*)-orbitals by (*n*(α*,*β)*, n*γ), then Sr2RuO⁴ has the frac-1.5 eV for xz/yz orbitals *Anisin* α r α or α is in the endanglement mass in the endanglement mass in the end of α 2.5 eV for xy orbital $\frac{2\pi}{3}$ **Critical** U_c : 1.5 eV for xz/yz orbitals Anisimov et al., Eur. Phys. J. B 25, 191 (2002) $\overline{25}$

 μ at all $F_{\mu\nu}$ D_{lang} I R 25, 101 (200 al $F_{\mu\nu}$ p_{hys} I R 25 101 (2002) formulates the problem in terms of an effective Anderson

Orbital-selectivity: effect of Hund's coupling and orbital mixing The possibility of a phase where some *d* orbitals give **2. And Metal and m** α mechanism for \mathbf{f} . orbital-selective motion is conceptually equivalent to \mathbf{r} the Kondo breakdown in heavy-fermion systems [26], where \blacklozenge \mathbf{col} $\overline{\mathbf{z}}$ of $\overline{\mathbf{t}}$ \mathbf{v} \mathbf{t} *α σ* H *^α α σ α σ t c c* h.c., *i j* $I_{\alpha\alpha}$ λ $\bm \phi$ r \mathcal{L} , \mathcal{L} , *nd's coupling and orbital mixi* $\alpha = 1, 2$ and t_α driving mechanism for particles \mathcal{A} . Moreover, the particle \mathcal{A} orbital-selective Motor Motor is conceptually equivalent to \mathbf{C} \mathbf{f} $\mathbf{$ the localized **field** $\mathbf{S} \triangleleft \mathbf{U}$ with the stop to \mathbf{F} conducting $\alpha =$ where † *α σ ci*, , (*α σ ci*, ,) creates (destroys) an electron with spin *σ* numerical results obtained by using variational Monte Carlo $\alpha = 1, 2$ *t*_α is the nearest-neighborhood *a* is the nearest-neughborhood *a* hopping amplitude with orbital index *α*. We defne *R* = *t t* 2 1 / , 2 as t_{α} is two hopping parameters and without parameters and without parameters and, without parameters and without parame ferent band dispersions [17]. The presence of a crystal-feld splitting in the Hamiltonian is also responsible for the appearfor *J* Dimension $\mathcal{I}(\mathcal{A})$ ^c of Hu

functions that are used to study it; in section 3, we present the

 \mathcal{L}_{max} and two-band model definition \mathcal{L}_{max}

for *J* = 0 and *J*/*U* = 0.1; fnally, in section 4 we draw our

 $\overline{R} = t_2 / t_1$ $R = t_2/t_1$ $R \leq 1$

⟨ ⟩ , , ,

2D Square lattice, two orbitals, half-filling (2 electrons/site) \overline{C} expinding and metal- $2D$ Square fails $\mathcal{H}_{\mathbf{F}}$ H \mathcal{H}_{HP} \mathcal{H}_{HP} algorithment late where the term $\mathcal H$ describes $\mathcal H$ describes $\mathcal H$ conducting *c* electrons and no longer contribute to the Fermi 2D Square lattice, α the ratio between the two hopping parameters and ρ vo orbitals, half-filling ^{c_{lin}g} electrons/site) \mathcal{H} and \mathcal{H} are fact that for \mathcal{H} this respectively. This respectively, a sign-problem-free model with one in $\mathcal{H} = \mathcal{H}_1$ zD Square lattice, two orbitals, half-fil lowing, we also fx *t*1 = 1. We would like to stress the fact that $\frac{t}{n}$ orbital index and index and $\frac{t}{n}$ in the orbital index and, the orbital index and, the orbital index and, the orbital index and, the orbital index and $\frac{t}{n}$ \mathbf{t} no a direct hybridization between different orbitals. The possibility of a phase where some *d* orbitals give rise to delocalize to delocalize attice, two-orbitals, it is not the two-

volume (which is determined by *c* electrons only) [27] 2 . In

rise to delocalized bands while some others remain local-

ized has been discussed in connection with Ca2−*^x*Sr*x*RuO4,

the localized *f* electrons suddenly stop to hybridize with the

33 electrons within the two orbitals: the kinetic term is diagonal in the orbital index and, therefore, As mentioned, the issue of MITs in multi-orbital models H = + H H kin int, (1) $\langle i,j \rangle$ $\mathcal{H}_{\mathbf{k}}\mathcal{H} = -\sum_{\alpha,\beta} \; \; t_{\alpha} c^{\dagger}_{i,\alpha,\sigma} c^{}_{j,\alpha,\sigma} + \text{h.c.},$ α *, σ i j* $, j \rangle, \alpha,$ $\mu_{\rm al}$ *c*_{*a*} *c* $\mathcal{H}_{\rm int} = U \sum_i n_{i,\alpha,\uparrow} n_{i,\alpha,\downarrow} + U' \sum_i n_{i,1,\sigma} n_{i,2,\sigma'}$ $\begin{pmatrix} 1 & 2 & 1, a \\ 0 & 1 & 1 \end{pmatrix}$ and $\begin{pmatrix} 1 & 1 & a \\ b & 1 & a \end{pmatrix}$ is the nearest-nearest-nearest-nearest-nearest-nearest-nearest-nearest-nearest-nearest-nearest-nearest-nearest-nearest-nearest-nearest-nearest-nearest-nea $-\int_H \sum_i c_{i,1,\sigma}^i c_{i,1,\sigma}^i c_{i,2,\sigma}^i c_{i,2,\sigma} - \int_H \sum_i (c_{i,1,\sigma}^i c_{i,2,\sigma}^i c_{i,2,\sigma}$ $\alpha \overline{\emptyset}$ as α, σ_1 between the two hopping parameters and α , α , σ' $\alpha = 1, 2$ and t_{α} and $R \leq 1$. **lowing** \mathbf{F} **that** \mathbf{F} **the fact of orbital mixing** $\mathbf{A} = t_2 / t_1^{\alpha} \mathbf{A}^{\alpha}$ the kinetic term is diagonal in the orbital index and, the orbital index and, the orbital index and, the same $\frac{N_{\text{t}}}{N_{\text{t}}}$ $U_{\text{MIT}}/t_1 = (5.5) \pm 100 \text{ eV}^{-1}$ at the Orbital- $\frac{1}{\sqrt{1-\frac{1$ *EITECT OF THE FIURA S COUPHING: (2)* Stabilization of t $J_{\text{max}}\left(\begin{array}{c} 2 \\ 0 \\ 0 \\ 0 \end{array}\right)$ (1) Stabilization *i* $-\int_{[D\cap\mathcal{M}]} 20, 105602(2016))$ int $U/W \simeq 1.3 \left(\frac{U}{V} \right)$ Stabilization of Mott ph ² (2) Stabilization of the Orbital-sele $\frac{1}{2}$ a direct hybridization between different orbitals. $\mathcal{L}_{\text{Kfil}} = -\sum_{(i,j)\in\mathbb{Z}} \iota_{\alpha} c_{i,\alpha,\sigma} c_{j,\alpha,\sigma} + \text{in.c.,}$ $U \sum_i n_{i,\alpha,\uparrow} n_{i,\alpha,\downarrow} + U' \sum_i n_{i,1,\sigma} n$ $J_{\rm H} \sum c_{i,1,\sigma}^{\dagger} c_{i,1,\sigma}^{\dagger} c_{i,\sigma}^{\dagger} c_{i,\sigma}^{\dagger} c$ f_{α} *I* $R \leq 1$ *i* $_{i,\alpha,\uparrow}$ n $_i$ *i* $\hat{p}_{\text{int}} = U \sum_i n_{i,\alpha,\uparrow} n_{i,\alpha,\downarrow} + U' \sum_i n_{i,1,\sigma} n_{i,\downarrow}$ *i* $i, 1, \sigma^C$ _{*i*}, $1, \sigma^{\prime C}$ *i*, $2, \sigma^{\prime C}$ *i* $R \leq \frac{1}{l}$ *t*_{α} $R \leq \frac{1}{l}$ $R \leq \frac{1}{l}$ $R \leq \frac{1}{l}$, $, \alpha, \, \restriction{\mathcal{H}_{l,\alpha}},$ $, \sigma$, $\overline{\psi}=U\sum\limits_{i}n_{i,\alpha,\uparrow}n_{i,\alpha,\downarrow}+U'\sum\,n_{i,1,\sigma}n_{i,2,\uparrow}$ $, \sigma,$ $,1,\sigma^C i,1,\sigma^{\prime C} i,2,\sigma^{\prime C} i,2,$ $-\int_{H}\sum c^{\dagger}_{i,1,\sigma}c^{\phantom\dagger}_{i,1,\sigma'}c^{\dagger}_{i,1}$ *α* $_{\alpha, \,} \uparrow \!\! n_{i, \alpha}$ σ, σ $\gamma n_{i,\alpha,\downarrow} + \,C^{\gamma}\, \geq\, n_{i,1,\sigma} n_{i,2,\sigma}$ σ, σ σ^{C} _{*i*},1, σ^{C} *i*,2, σ^{C} *i*,2, σ ′ \overrightarrow{B} 6 ′ ${}_{i}c_{i,2,\sigma}^{\dagger}c_{i,2,\sigma} - J_{H}\sum_{i} (c_{i,1,\uparrow}^{\dagger}c_{i,1,\downarrow}^{\dagger}c_{i,2,\uparrow}c_{i,2,\downarrow} + \text{h.c.})$ $U_{\text{MIT}}/t_1 = 4 \pm 0.5 \quad R \approx 0$
 $V_{\text{MIT}}/t_1 = 4 \pm 0.5 \quad R \approx 0$ **s** ^{*b*}_{MIT¹⁴ (*A*. *A*. *A.* These four terms represent to the interaction of the i} $U_{\text{MIT}}/t_1 \sim 4$ *U'*, the Hunder-orbital inter-orbital inter-orbi *L*, *and the pair and the pair and and, the Hund's coupling:* 10 Mott Insulator and $\mathcal{H}_{\bf k}$ \mathcal α - orbital index $n_{i,2,\sigma'}$ *i* $-J_H \sum (c^{\dagger}_{i,1, \uparrow} c^{\dagger}_{i,1, \downarrow} c_{i,2, \uparrow} c_{i,2, \downarrow} + \text{h.c.})$ $\mathbf{1}_{,\sigma}$ $n_{i,2,\sigma}$ \ldots al mixing $\left(t_{mm'}^{-\nu/2/2} \neq 0\right)$ $U_{\text{MIT}}/t_1 = 4 \pm 0.5$ $R \approx 0$ U' , the ± 0.5 $R \approx 0$ U' pling *J*, and the pair hopping *J*′. ⟨ ⟩ α σ $\sum_{i,\alpha}^{i} \sum_{i,\alpha}^{i} n_{i,\alpha,1} n_{i,\alpha,1}$ \mathcal{H} α *α* $\sum_{i,\alpha}$ **c** $\sum_{i,\alpha}^{i} \sum_{i}^{i} a_{i,\alpha,i}$ *c*_{*i*}, *c*_{*i*}, *c*_{*i*}, *c*_{*i*} $\left\{ \begin{array}{ccc} \alpha & \sigma & \sum & i, \alpha \end{array} \right.$ \rightarrow , , , , (2) $\alpha \ \overline{\emptyset}$ *c*_{$\alpha \ \overline{\emptyset}$ *c*₁, α, σ_1 **c**₁, σ, σ'} $\alpha = 1, 2$ and $\alpha = 1, 2$ and r_{α} is the nearest-neughbor $R \leq 1$ **hompion is a multipular index** *a***.** We define $R = t_2 / t_1^t$ μ_{in} between the ratio between the two hopping parameters and, with μ_{in} with μ_{in} and, without μ_{in} and, with μ_{in} and μ_{in} and μ_{in} and μ_{in} and μ_{in} and μ_{in} loss of generality, we focus of the Orb. $U_{\text{MIT}}/t_1 \sim 4$ I ¹ T_{total} interaction of the Ω \sum_i \sum_i \sum_i σ_i $\frac{1}{2}$ c*c* $\frac{1}{2}$ c_c $\frac{1}{2}$ c $\frac{1}{\sqrt{2}}$ *i i* σ *i* $\frac{1}{2}$ *α σ σ* ′ *Tocchio et al., JPCM 28, 105602 (2016) σ σ* $K \leqslant 1$ that \mathbf{r} is no longer index in the $R = t_i$ **Effect of orbital mixing (** $\{t_{mm'}=t_{2'}\}\neq 0$) $t_{\text{MIT}}/t_1 = 4 \pm 0.5$ $R \approx 0$ $U_{\text{MIT}}/t_1 = (5] 5 + 10$ estabilizatikos b[†] the O1 missing in the DMFT picture where the transition to the Mott $U_{\text{MIT}}/t_1 \sim 4$ **Effect of the Hund's coupling:** $U/W \simeq 1.3 \frac{1}{11}$ $\sum_{\alpha=1,3}^{\infty}$ (1) Stabilization of Mott phase (2) Stabilization of the Orbital-selective Mott state (11). This outcome is natural, given the fact that \int_{0}^{1} $\frac{1}{4}$ σ *j* σ $\begin{pmatrix} 1 & 1 & 1 \ 1 & 1 & 1 \end{pmatrix}$ is given by the triplet ot al $IPCM$ 28 I_{MIT} as I_{MIT} *DEAUseR IOCCHIO et al., JPCM 28, 105602 (2016)* function of *U*/*t*1 at *R* = 0.5. Three different regimes can be (1) Destabilization of the Orbital-selective Mott state $H____{}^{c_l,1,\sigma\epsilon}$ _{i,1, σ ¹_i,2, σ ¹_i,2, σ ^{$=$}*H*_H}

$A \left(\bigcap_{i=1}^n A_i \right)$ the set of $A \left(\bigcap_{i=1}^n A_i \right)$ where ϵ and ϵ Increase the the two distributions of the two $\mathbf M$ **Orbital-selective Mott (OSM) transition**

per site. Unfortunately in that model both the difference in

bandwidth and the lifted degeneracy are at work and none

on is possible as the driving one. **Exercise 2.0 Externs in the case of the same bandwidths** reduces the orbital correlations. The role of J can be reduced by α **understand in the atomic limits:** \overline{OSM} transition is possible

 $\begin{array}{c|c}\n\hline\n\text{H} & \text{M} \\
\hline\n\text{M} & \text{M} \\
\hline\n\end{array}$ γ and γ are internal reputations and γ is the γ is the γ is the γ Hunder of the densities of the densities of the three bands of the th are semicircular of half-bandwidth D. \mathbf{m} study three-bands three-bands two bands two bands two bands two bands \mathbf{m} With Lyn ingrasse anovay different $\frac{1}{5}$ we mercase energy union **between high-spin and low-spin** $f(x) = \frac{1}{2\pi} \int_0^1 \cos(x) \cos(x) \cos(x) dx$ **diagram under a small splitting of this diagram under a small splitting of the small splitting of the small split** $\hspace{1.6cm}$ (and suppress or and computation in the sum $\overline{\mathbf{b}}$ (SSMF) $\overline{\mathbf{b}}$ With J we increase energy difference **the splitting of the splitting (and suppress orbital fluctuations)** HS LS

regime the effect of J becomes predominant predominant predominant predominant predominant predominant in the effect of μ

h i), "^m is the bare energy level in orbital m. U and U⁰ ¼

 \mathbb{Z}^2

small, signaling a decoupling of the bands which opens the

Si is the S α $\mathbf 1$ **Directional character of orbitals:**

ture of the excited levels. Most importantly, the very form of the exchange interaction depends on the spatial orientation of a given bond. We label a bond ij laying in the %& plane perpendicular to the 'ð¼ x; y; zÞ axis by a (')-bond. With this in mind, the Hamiltonian can be written as \overline{y}

cally, the anisotropy corrections are obtained in powers of (B) A 90" bond: There are again only two orbitals active on a given bond, e.g., jxzi and jyzi orbitals along a bond in $\mathbf x$ nondiagonal elements, and there are two possible paths for a charge transfer [via upper or lower oxygen, see Fig. 2(b)]. This peculiarity of a 90" bond leads to an exchange the animal periodic structure of a 90" bond leads to an exchange

Orbital-selectivity and magnetic properties **S** \mathbf{r} \mathbf{S} \mathbf{S} \mathbf{I} $\frac{1}{2}$ $\mathbf l$ $\overline{\mathbf{C}}$ $\frac{1}{2}$ $\overline{}$ $\begin{array}{c}\n 1 \\
 2\n \end{array}$ Heisenberg plus a pseudodipolar interaction, \overline{a}

Double exchange as an orbital-selective effect

Double exchange is a natural realization of the orbital-selectivity

Itinerant electrons (e.g. e_g electrons)

<u>Localized electrons</u> (e.g. t_{2g} electrons)

 $\begin{array}{ccc} \n\begin{array}{ccc} \n\text{A} & \text{B} & \text{B} & \text{C} \\
\text{C} & \text{D} & \text{D} & \text{A} \\
\text{D} & \text{D} & \text{D} & \text{A} \\
\text{D} & \text{D} & \text{D} & \text{A}\n\end{array}\n\end{array}$ *No energy gain due* $\frac{18}{24}$ *to hoppings!*

AFM

 \rightarrow

11111

FM

 $\delta F \sim -Wr/2$ $\epsilon = \mu_E$. The same ϵ $\delta E_{DE} \sim -Wx/2$

 \cong = \mathcal{C} *zt*

Double-exchange mechanism of ferromagnetism

C. Zener, Phys. Rev. 82, 403 (1951)

Examples: CrO₂, CMR manganates etc.

Orbital-selective behaviour: localized and itinerant magnetism on the same ion $\overline{}$ m on the same ion

Extreme case: Orbital-selectivity in low-dimensional magnets

c and *d* orbitals "work" at different **T** and *a* orbitals work at different

38 \overline{d} d orbitals "work" of different *c* and *d* orbitals "work" at different *B* \mathcal{F}_1 lated in C-DMFT as χ = *M/B*ext, where *M* is magnetization per

Directional character of \mathcal{S} t
1 $\frac{1}{\sqrt{2}}$ ϵ \blacksquare pulsion on the same orbitals. The parameters #1ð2Þ controlling isotropic (anisotropic) couplings are given by \bullet excited states depends solely on the ratio \$ ¼ JH=U of \blacksquare \blacksquare Hamiltonian, with a weak dipolarlike anisotropy term. While the overall form of Eq. (2) could be anticipated from symmetry arguments, the explicit derivation led us $\mathbf{1}$ $\ddot{}$ #1ð2Þ. Hereafter, we use the energy **orbitals:**

Orbitally-induced Peierls transition bond geometries: (A) a 180"-bond for modern formed by connection and formed by cornershared octahedra as in Fig. 2(a), and (B) a 90"-bond \overline{a} and the nearest-this geometry, the nearest-this geometry, the nearest-this geometry, the nearest-the nea neighbor t2g hopping matrix is diagonal in the orbital space and, on a given bond, only two orbitals are active, e.g., jxyi and jxzi orbitals along a bond in x-direction [Fig. 2(a)]. The spin-orbital exchange Hamiltonian for such a system has already been reported: see Eq. (3.11) in Ref. [12]. After enough, its anisotropy is entirely due to the Hund's coupling. This is opposite to a conventional situation: typically, the anisotropy corrections are obtained in powers of (B) $\frac{1}{2}$ and $\frac{1}{2}$ This peculiarity of a 90" bond leads to an exchange Hamiltonian drastically different from that of a 180" geometry. Two transfer amplitudes via upper and lower oxyvery form of the exchange Hamiltonian depends on bond geometry through a density profile of Kramers states, as we Exchange couplings of neighboring Kramers states.— \blacksquare when $\frac{1}{2}$ isospins. The exchange Hamiltonians for isospins are then obtained by projecting the corresponding superexchange spin-orbital models onto the isospin states Eq. (1). First, we ling isotropic (anisotropic) couplings are given by $t = t$ excited states depends solely on the ratio \$ ¼ JH=U of Hund's coupling and U [24]. At small \$, one has #1 ' 1 to an unexpected result: In the limit of strong SO coupling, the magnetic degrees are governed by a nearly Heisenberg model just like in the case of small !, and, surprisingly

gen interfere in a destructive manner and the isotropic part of the Hamiltonian exactly vanishes. The finite, anisotropic interaction appears, however, due to the JH-multiplet structure of the excited levels. Most importantly, the very form of the exchange interaction depends on the spatial orientation of a given bond. We label a bond ij laying in the %& plane perpendicular to the 'ð¼ x; y; zÞ axis by a (')-bond. With this in mind, the Hamiltonian can be written as Hð'Þ ij ¼ 'JS'

enough, its anisotropy is entirely due to the Hund's coupling. This is opposite to a conventional situation: typically, the anisotropy corrections are obtained in powers of while the Hund's coupling is not essential. (B) A 90" bond: There are again of two orbitals active active active active active active active active active on a given bond, e.g., jxzi and jyzi orbitals along a bond in the xy-plane. However, the hopping matrix has now only nondiagonal elements, and there are two possible paths for a charge transfer λ This peculiarity of a 90" bond leads to an exchange

Peierls transition - simplest case of $1D + half-filling (1 electron/site)$

Instability at $|Q| = 2k_F$ Half-filling: $|k_F| = \pi/2a$, $|Q| = \pi/a$ Gain in kinetic energy: $\sim - |\Delta|^2 \ln |\Delta|$ Loss in elastic energy: $\sim |\Delta|^2$

Physical mechanism: nesting of the Fermi surface

$$
\chi'_0(\overrightarrow{Q}, \omega = 0) =
$$

=
$$
\frac{1}{\Omega} \sum_{\vec{k}} \frac{f(\varepsilon(\vec{k})) - f(\varepsilon(\vec{k} + \overrightarrow{Q}))}{\varepsilon(\vec{k}) - \varepsilon(\vec{k} + \overrightarrow{Q})}
$$

Factor I: lattice deformations are possible for other fillings!

Peierls transition - away from half-filling

Peierls transition: 1D chain

quarter-filling (**1/2 electron/site**):

π π $|k_F|$ = |*Q*| = 4*a* 2*a ε*(*k*) \blacksquare $\frac{1}{1}$ *k π π* $\frac{\pi}{a}$ −*a*− *π π* $rac{\mu}{4a}$ $-\frac{\pi}{4a}$ Tetramerization *a*

Instability at $|Q| = 2k_F$

1/3 electron/site:

$$
|k_F| = \frac{\pi}{3a} \quad |Q| = \frac{2\pi}{3a}
$$

Peierls transition - importance of orbital degrees of freedom

Factor II: Orbital-selectivity with respect to Peierls transition

E.g. edge-sharing geometry

xy

kx

- Wide nearly 1D bands susceptible to Peierls transition
- Localized bands susceptible to *U*;
- Crystal-field can strongly change position of the band;

Orbitally-induced Peierls effect: Kagome lattice Na2Ti3Cl8: Ti2+: *d2 (S=1)*

43 D. Khomskii, T. Mizokawa, S.S. PRL 127, 049701 (2021) D. KHOMSKII, I. MIZOKI

Orbitally-induced Peierls: another lattice, but again trimerization

Orbitally-induced Peierls effect: Triangular lattice ReS₂: diamond necklace

and the

Band filling: 1/2

$$
k_F = \frac{\pi}{2a}, Q = \frac{\pi}{a}
$$

Dimerization in three directions!

"diamond necklace" *D. Khomskii, S.S. Chem. Rev. 121, 2992 (2021)*

Reduction of dimensionality Orbitally-induced Peierls effect

and the set

Spinels (3D structure): AB2O4

Natural formation of 1D bands due to orbitals…

red Peierls effect: \overline{a} r amerization in sninel C_{11} F₂S₄ **Orbitally induced Peierls effect:** When When When Weights and When When When we have a set of the US Tetramerization in spinel CuIr₂S₄

4+

Tetramerization!

 \overline{a} *Khomskii and Mizokawa, PRL 94, 156402 (2005)*

 $\overline{15}$

47

nation of this apparently complicated structure becomes

Orbitally induced Peierls effect: Tetramerization in spinel CuIr₂S₄ !"##"\$% #& '(#)\$"

Reduction of dimensionality due to orbital degrees of freedom

Other examples

D. Khomskii, *S.S.* Chem. Rev. 121, 2992 (2021)

17 M

Take-home messages

Fig. 1. (a), (b) Single-crystal x-ray-different patterns of LiVO-crystal x-ray-different patterns of LiVO-crystal and

R p 4 *.*621%,

*.*5821. The inset shows powder-diffraction patterns above

 $2 + 300$ K, assuming the space group

c

R e

*P*31

*/*presence of long-range ordering

 \bullet direction.

2

m. The obtained

• Orbitals can **affect the** crystal structure crystal x-ray-diffraction experiment was performed using \bullet (Drbitals can affect the **Example 19 keV were performed at the EV started at 19 keV were performed at 19 keV were at 19 keV were exampled a** $\overline{\mathbf{v}}$

*/*V are 1.00(3) for LiVS

2, respectively. Both samples were confirmed to exhibit clear transitions at the reported temperatures using the synchrotron powder x-ray-diffraction experiment. A single-

- Orbitals can define magnetic **properties** *S* Extending the data for the data for $\frac{1}{2}$ properties \mathbf{a} \mathbf{C} Power-diffraction path \mathbf{C} perature of approximately 490 K in Livox. (d) Rietveld refinements and refinements of approximately approximately approximately approximately approximately approximately approximately approximately approximately approximat
	- There are plenty of **orbital-selective** effects: Mott transition, magnetic **A. X-ray diffraction analysis** properties **B. Crystallographic considerations** \blacksquare

² and 0.97(1)

• Orbitals may **reduce dimensionality** of a magnetic subsystem perstructure spots appearing at (1*/*3*,* 1*/*3*,* 0), and the related **positions clearly constructed in Fig. 1.** Orbitals may reduce din $s = s = s = s$ \mathcal{C} **ind.** While Lives in a 3^c structure with α structure with α $\sum_{i=1}^{n}$ **c** structure with α

