Orbital Ordering

Eva Pavarini

Institute for Advanced Simulation Peter Grünberg Institute JARA-HPC Forschungszentrum Jülich



orbital ordering, what is it ?

orbital ordering





LaMnO₃

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

orbital degrees of freedom

CORRELATED ELECTRON SYSTEMS

REVIEW

Orbital Physics in Transition-Metal Oxides

Y. Tokura^{1,2} and N. Nagaosa¹

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 $(3z^2 - r^2)$. This gives rise to the anisotropy of the Hamiltonian in the pseudospin space as well as in the real space. For example, the transfer integral between the two neighboring Mn atoms in the crystal lattice is determined

analogy (S=1/2 case)

spin degrees of freedom



effective S=1/2 **spin** spin 1/2 operators $S_x S_y S_z$

orbital degrees of freedom



effective O=1/2 **pseudospin** pseudospin 1/2 operators O_x O_y O_z

spin ordering



pseudospin ordering



spin and pseudospin interact



Fig. 2. Spin-orbital phase diagram in the perovskite manganese oxide. The top panel shows the orbital and spin order realized in the hole-doped manganese oxides. (A) Temperature dependence

From Tokura and Nagaosa, Science (2001)

overview

• the building blocks

- emergence of local spins and orbital pseudospins
- spin and orbital ordering
- representative systems: KCuF₃ (t_{2g}⁶e_g³) & LaMnO₃ (t_{2g}³e_g¹)
- two mechanisms

• eg Hubbard Hamiltonian

- on-site term, eg orbital degrees of freedom
- hoppings and tight-binding e_g bands

orbital ordering mechanisms

- Jahn-Teller (JT): order via lattice distortion
- Kugel-Khomskii (KK) superexchange: order without distortion
- recent insights



the building blocks

what are local spins and orbital pseudospins?

orbital ordering



atomic d orbitals



eg

t_{2g}

orbital ordering

KCuF₃ and LaMnO₃: *e*^{*g*} two-orbital systems

$$\begin{split} \hat{H} &= -\sum_{ii'} \sum_{\sigma} \sum_{mm'} t_{mm'}^{i,i'} c_{im\sigma}^{\dagger} c_{im'\sigma} + U \sum_{i} \sum_{m} \hat{n}_{im\uparrow} \hat{n}_{im\downarrow} \\ &+ \frac{1}{2} \sum_{i} \sum_{\sigma\sigma'} \sum_{m \neq m'} (U - 2J - J\delta_{\sigma,\sigma'}) \hat{n}_{im\sigma} \hat{n}_{im'\sigma'} \\ &- J \sum_{i} \sum_{m \neq m'} \left[c_{im\uparrow}^{\dagger} c_{im\downarrow}^{\dagger} c_{im'\uparrow} c_{im'\downarrow} + c_{im\uparrow}^{\dagger} c_{im\downarrow} c_{im'\uparrow}^{\dagger} c_{im'\uparrow} \right], \end{split}$$

tⁱⁱmm': crystal-field energies (i=i')
t^{ii'}mm': hopping integrals
U: direct screened Coulomb integral
J: exchange screened Coulomb integral



emergence of local spins and their interaction



emergence of local spins

let us consider an idealized atom (Hubbard model one orbital one site i=A)

$$H = \varepsilon_d \sum_{\sigma} c_{i\sigma}^{\dagger} c_{i\sigma} + n_{i\uparrow} n_{i\downarrow}$$

$ N, S, S_z\rangle$			N	S	E(N)
$ 0,0,0\rangle$	=	0 angle	0	0	0
$ 1,rac{1}{2},\uparrow angle$	=	$c^{\dagger}_{i\uparrow} 0 angle$	1	1/2	$arepsilon_d$
$ 1, \frac{1}{2}, \downarrow \rangle$	=	$c^{\dagger}_{i\downarrow} 0 angle$	1	1/2	$arepsilon_d$
2,0,0 angle	=	$c^{\dagger}_{i\uparrow}c^{\dagger}_{i\downarrow} 0 angle$	2	0	$2\varepsilon_d + U$

emergence of local spins





emergence of local spins

let us consider an idealized atom

$$H = \varepsilon_d \sum_{\sigma} c_{i\sigma}^{\dagger} c_{i\sigma} + n_{i\uparrow} n_{i\downarrow}$$

we can rewrite the Hamiltonian as

$$H = \varepsilon_d n_i + U \left[-\left(S_z^i\right)^2 + \frac{n_i^2}{4} \right]$$

2-atom model

half-filling: one electron per site



$$H = \varepsilon_d \sum_i \sum_{\sigma} c_{i\sigma}^{\dagger} c_{i\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} - t \sum_{\sigma} \left[c_{A\sigma}^{\dagger} c_{B\sigma} + c_{B\sigma}^{\dagger} c_{A\sigma} \right]$$

low- and high-energy states



low energy model



low energy model

energy gain only for antiferromagnetic arrangement

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

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

Pauli principle



Heisenberg model

local spins: effective emergent elementary particles

Heisenberg model: effective interaction

$$H = \frac{1}{2} \Gamma \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j$$



antiferromagnetism

neutron scattering: Shull and Smart (1949)

MnO



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

magnetism & emergence





and what about local orbital pseudospins?



from idealized atom to real atoms

$$H_{e}^{\rm NR} = -\frac{1}{2} \sum_{i} \nabla_{i}^{2} - \sum_{i} \frac{Z}{r_{i}} + \sum_{i>j} \frac{1}{|r_{i} - r_{j}|}$$

one-electron part Coulomb repulsion

self-consistent potential approximation

$$H_e^{
m NR} = -rac{1}{2} \sum_i
abla_i^2 - \sum_i rac{Z}{r_i} + \sum_{i>j} rac{1}{|r_i - r_j|}$$

$$H_e^{\rm NR} = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i v_R(r_i)$$

e.g., DFT/LDA

contains e.g. Hartree term

hydrogen-like atom

$$H_e^{\rm NR} = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_i Z_{\rm eff}/r_i$$

LDA atomic functions



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

$$R_{nl}(\rho) = \sqrt{\left(\frac{2Z}{n}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-\rho/n} \left(\frac{2\rho}{n}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2\rho}{n}\right)$$

(hydrogen-like atom)

Laguerre polynomials

orbital degrees of freedom



many-electron atoms

$$H_{e}^{\rm NR} = -\frac{1}{2} \sum_{i} \nabla_{i}^{2} - \sum_{i} \frac{Z}{r_{i}} + \sum_{i>j} \frac{1}{|r_{i} - r_{j}|}$$

rewrite for one *nl* shell in 2nd quantization

$$H_e^{\rm NR} = \varepsilon_{nl} \sum_{m\sigma} c^{\dagger}_{m\sigma} c_{m\sigma} + \frac{1}{2} \sum_{\sigma\sigma'} \sum_{m\tilde{m}m'\tilde{m}'} U^l_{mm'\tilde{m}m'} c^{\dagger}_{m\sigma} c^{\dagger}_{m'\sigma'} c_{\tilde{m}'\sigma'} c_{\tilde{m}\sigma}$$

kinetic+central

Coulomb

$$U_{mm'\tilde{m}\tilde{m}'}^{iji'j'} = \int d\boldsymbol{r}_1 \int d\boldsymbol{r}_2 \; \frac{\overline{\psi_{im\sigma}}(\boldsymbol{r}_1)\overline{\psi_{jm'\sigma'}}(\boldsymbol{r}_2)\psi_{j'\tilde{m}'\sigma'}(\boldsymbol{r}_2)\psi_{i'\tilde{m}\sigma}(\boldsymbol{r}_1)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}$$

special cases

I=0: Hubbard Hamiltonian of the idealized atom

$$H = arepsilon_d \sum_\sigma c^\dagger_\sigma c_\sigma + U \sum_i n_\uparrow n_\downarrow$$

what about I>0, e.g. I=2?

$$H_e^{\rm NR} = \varepsilon_{nl} \sum_{m\sigma} c^{\dagger}_{m\sigma} c_{m\sigma} + \frac{1}{2} \sum_{\sigma\sigma'} \sum_{m\tilde{m}m'\tilde{m}'} U^l_{mm'\tilde{m}m'} c^{\dagger}_{m\sigma} c^{\dagger}_{m'\sigma'} c_{\tilde{m}'\sigma'} c_{\tilde{m}\sigma}$$

Hund's rules

direct term: the same for all N electron states

$$U_{\rm avg} = \frac{1}{(2l+1)^2} \sum_{mm'} U^l_{mm'mm'}$$

exchange term: 1. Hund's rule

$$U_{\text{avg}} - J_{\text{avg}} = \frac{1}{2l(2l+1)} \sum_{mm'} \left(U_{mm'mm'}^l - U_{mm'm'm'}^l \right)$$

$$egin{aligned} J^l_{m,m'} &= & U^l_{mm'm'm} \ &= & \int dm{r}_1 \! \int dm{r}_2 \; rac{\overline{\psi_{im\sigma}}(m{r}_1) \overline{\psi_{im'\sigma}}(m{r}_2) \psi_{im\sigma}(m{r}_2) \psi_{im'\sigma}(m{r}_1)}{|m{r}_1 - m{r}_2|} \ &= & \int dm{r}_1 \! \int dm{r}_2 \; rac{\phi_{imm'\sigma}(m{r}_1) \overline{\phi_{imm'\sigma}}(m{r}_2)}{|m{r}_1 - m{r}_2|} = rac{1}{V} \sum_{m{k}} rac{4\pi}{k^2} \, |\phi_{imm'\sigma}(m{k})|^2 \,, \end{aligned}$$

Coulomb exchange



positive, hence always ferromagnetic

Friedrich Hund
$$-\frac{1}{2}\sum_{\sigma}\sum_{m\neq m'}J^l_{m,m'}c^{\dagger}_{m\sigma}c_{m\sigma}c^{\dagger}_{m'\sigma}c_{m'\sigma} = -\frac{1}{2}\sum_{m\neq m'}2J^l_{m,m'}\left[S^m_zS^{m'}_z + \frac{1}{4}n_mn'_m\right]$$

two electrons, two levels

1. Hund's rule





first Hund's rule often valid also in solids (with exceptions)

2-level atom, half-filling

because of Hund's rule number one









orbital 1 spin up

orbital 2 spin up

2-level atom, away from half-filling



2-level 2-atom problem

with degenerate levels

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



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

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

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

orbital degrees of freedom



spin ordering pseudospin ordering

effective O=1/2 pseudospin pseudospin 1/2 operators O_x O_y O_z





effective S=1/2 spin spin 1/2 operators S_x S_y S_z

analogy
pseudospin ordering

KCuF₃ and LaMnO₃

$$t_{2g}^6 e_g^3 t_{2g}^3 e_g^1$$

Mn[Ar]3d⁵ 4s²Mn³⁺ 3d⁴ $t_{2g}^3 e_g^1$ Cu[Ar]3d¹⁰ 4s¹Cu²⁺ 3d⁹ $t_{2g}^6 e_g^3$

KCuF₃



LaMnO₃





the hallmark of orbital order

co-operative Jahn-Teller distortion



Y. Tokura^{1,2} and N. Nagaosa¹

When the long-range orbital order exists, i.e., $\langle T_{ix} \rangle \neq 0$ and/or $\langle T_{iz} \rangle \neq 0$, the JT distortion is always present.

the hallmark of orbital order



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



antiferromagnetism

neutron scattering: Shull and Smart (1949)



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

two mechanisms

1. Jahn-Teller: splitting generates order

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.

degenerate states (original symmetry)

static crystal-field splitting (symmetry lowering)







 $Q_2(Q_2 > 0)$

do we need a large crystal-field?

one electron per atom



do we need a large crystal-field?

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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. Andersen⁴



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

2. super-exchange: order without splitting

Crystal structure and magnetic properties of substances with orbital degeneracy

K. I. Kugel' and D. I. Khomskii

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 (KCuF₃, LaMnO₃, MnF₃). The effective spin Hamiltonian is obtained for these substances and the properties of the ground state are investigated. The orbital and magnetic structure tures 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.

super-exchange Hamiltonian

 $H = J_{SS}S_1 \cdot S_2 + J_{OO}O_1O_2 + J_{SO}(O_1O_2)(S_1 \cdot S_2)$

 $J \propto 4t^2/U$ O : pseudospins in orbital space

multi-band Hubbard model

 $H_0 + H_U + H_T$

representative system



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



the LDA electronic structure

cubic KCuF₃



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

unit cell



approximate method

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

point charge model

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



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

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

cubic perovskite

point charge model: F₆ octahedron

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

$$\mathbf{m=-2} \quad \mathbf{m=-1} \quad \mathbf{m=0} \quad \mathbf{m=1} \quad \mathbf{m=2}$$
$$H_{\rm CF} = \begin{pmatrix} Dq & 0 & 0 & 0 & 5Dq \\ 0 & -4Dq & 0 & 0 & 0 \\ 0 & 0 & 6Dq & 0 & 0 \\ 0 & 0 & 0 & -4Dq & 0 \\ 5Dq & 0 & 0 & 0 & Dq \end{pmatrix}.$$

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

atomic functions

atomic d orbitals



exact method: group theory

group O



	0	E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
$(x^2 + y^2 + z^2)$	A_1	1	1	1	1	1
	A_2	1	1	1	-1	-1
$(x^2 - y^2, 3z^2 - r^2)$	E	2	-1	2	0	0
(x,y,z)	T_1	3	0	-1	-1	1
(xy, xz, yz)	T_2	3	0	-1	1	-1



group elements g divided in classes

	0	E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
$(x^2 + y^2 + z^2)$	A_1	1	1	1	1	1
	A_2	1	1	1	-1	-1
$(x^2 - y^2, 3z^2 - r^2)$	E	2	-1	2	0	0
(x,y,z)	T_1	3	0	-1	-1	1
(xy,xz,yz)	T_2	3	0	-1	1	-1

E: identity

Cn: anticlockwise rotation of 360°/n

types of irreducible representations

representation:

set of matrices (one for each operation) of dimensionality d

irreducible representation:

minimal set which plays the role of an orthogonal basis in a linear space for a given Hamiltonian they can be use to label eigenvalues

characters

trace of the matrix corresponding to a given operation within a given representation

characters of A₁

dimensionality; character of E

partner functions



functions that can be used as a basis of an invariant linear space for a given irreducible representation

partner functions of A1

functions that can be used as a basis of an invariant linear space for a given irreducible representation

crystal field and group theory

$$\begin{array}{c|c} O(3) & E & C_{\alpha} \\ \hline & & \\ \Gamma^{l} & 2l+1 & \sin(l+\frac{1}{2})\alpha/\sin\frac{\alpha}{2} \end{array}$$



decomposition formula

$$\Gamma = \oplus_i a_i \Gamma_i,$$

$$a_i = \frac{1}{h} \sum_{g} \left[\chi_i(g) \right]^* \chi(g).$$

h=24

crystal field and group theory



projector

cubic crystal-field



eg Hubbard model



$$\begin{split} \hat{H} &= -\sum_{ii'} \sum_{\sigma} \sum_{mm'} t_{mm'}^{i,i'} c_{im\sigma}^{\dagger} c_{im'\sigma} + U \sum_{i} \sum_{m} \hat{n}_{im\uparrow} \hat{n}_{im\downarrow} \\ &+ \frac{1}{2} \sum_{i} \sum_{\sigma\sigma'} \sum_{m \neq m'} (U - 2J - J\delta_{\sigma,\sigma'}) \hat{n}_{im\sigma} \hat{n}_{im'\sigma'} \\ &- J \sum_{i} \sum_{m \neq m'} \left[c_{im\uparrow}^{\dagger} c_{im\downarrow}^{\dagger} c_{im'\uparrow} c_{im'\downarrow} + c_{im\uparrow}^{\dagger} c_{im\downarrow} c_{im'\uparrow}^{\dagger} c_{im'\uparrow} \right], \end{split}$$

the hopping integrals

 $t_{mm'}^{i,i'} \quad i \neq i'$

the LDA electronic structure

cubic perovskite


let us construct the e_g tight-biding bands

method

$$\hat{h}_{e}(\boldsymbol{r}) = -\frac{1}{2}\nabla^{2} - \sum_{i,\alpha} \frac{Z_{i,\alpha}}{|\boldsymbol{r} - \boldsymbol{T}_{i} - \boldsymbol{R}_{\alpha}|} = -\frac{1}{2}\nabla^{2} + \sum_{i,\alpha} v(\boldsymbol{r} - \boldsymbol{T}_{i} - \boldsymbol{R}_{\alpha}) = -\frac{1}{2}\nabla^{2} + v_{R}(\boldsymbol{r}),$$

Bloch functions

$$\psi_{lm}^{\alpha}(\boldsymbol{k},\boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_{i} e^{i\boldsymbol{T}_{i}\cdot\boldsymbol{k}} \psi_{lm}(\boldsymbol{r}-\boldsymbol{T}_{i}-\boldsymbol{R}_{\alpha}).$$
Wannier functions

$$\begin{aligned} H^{\alpha,\alpha'}_{lm,l'm'}(\boldsymbol{k}) &= \langle \psi^{\alpha}_{lm}(\boldsymbol{k}) | \hat{h}_{e} | \psi^{\alpha'}_{l'm'}(\boldsymbol{k}) \rangle, & \text{Hamiltonian} \\ O^{\alpha,\alpha'}_{lm,l'm'}(\boldsymbol{k}) &= \langle \psi^{\alpha}_{lm}(\boldsymbol{k}) | \psi^{\alpha'}_{l'm'}(\boldsymbol{k}) \rangle. & \text{Overlap} \end{aligned}$$

tight-binding Hamiltonian

$$H_{lm,l'm'}^{\alpha,\alpha'}(\boldsymbol{k}) = \varepsilon_{l'\alpha'}^{0} O_{lm,l'm'}^{\alpha,\alpha'}(\boldsymbol{k}) + \Delta \varepsilon_{lm,l'm'}^{\alpha} \delta_{\alpha,\alpha'} - \frac{1}{N} \sum_{i\alpha \neq i'\alpha'} e^{i(\boldsymbol{T}_{i'} - \boldsymbol{T}_{i}) \cdot \boldsymbol{k}} t_{lm,l'm'}^{i\alpha,i'\alpha'}$$

$$\Delta \varepsilon^{\alpha}_{lm,l'm'} = \int d\boldsymbol{r} \ \overline{\psi_{lm}}(\boldsymbol{r} - \boldsymbol{R}_{\alpha}) \bigg[v_R(\boldsymbol{r}) - v(\boldsymbol{r} - \boldsymbol{R}_{\alpha}) \bigg] \psi_{l'm'}(\boldsymbol{r} - \boldsymbol{R}_{\alpha}) ,$$

$$t_{lm,l'm'}^{i\alpha,i'\alpha'} = -\int d\boldsymbol{r} \ \overline{\psi_{lm}}(\boldsymbol{r} - \boldsymbol{R}_{\alpha} - \boldsymbol{T}_{i}) \bigg[v_{R}(\boldsymbol{r}) - v(\boldsymbol{r} - \boldsymbol{R}_{\alpha'} - \boldsymbol{T}_{i'}) \bigg] \psi_{l'm'}(\boldsymbol{r} - \boldsymbol{R}_{\alpha'} - \boldsymbol{T}_{i'}).$$

keep only two-center integrals

$$V_{lm,l'm'}^{i\alpha,i'\alpha'} = \int d\boldsymbol{r} \ \overline{\psi_{lm}}(\boldsymbol{r} - \boldsymbol{R}_{\alpha} - \boldsymbol{T}_{i})v(\boldsymbol{r} - \boldsymbol{R}_{\alpha} - \boldsymbol{T}_{i})\psi_{l'm'}(\boldsymbol{r} - \boldsymbol{R}_{\alpha'} - \boldsymbol{T}_{i'})$$

two-center integrals



two-center integrals



the LDA electronic structure

cubic perovskite



tight-binding model



tight-binding model *e*^{*g*} bands



tight-binding model



downfolding

$H_{e_g}^{\mathrm{TB}}$	$ m{k} z^c angle$	$ m{k} \; x^a angle$	$ m{k} \; y^b angle$	$ m{k} \; 3z^2 - r^2 angle$	$ m{k} x^2-y^2 angle$
$ m{k} z^c angle$	$arepsilon_p$	0	0	$-2V_{pd\sigma}s_z$	0
$ m{k} x^a angle$	0	$arepsilon_p$	0	$V_{pd\sigma}s_x$	$-\sqrt{3}V_{pd\sigma}s_x$
$ m{k} y^b angle$	0	0	ε_p	$V_{pd\sigma}s_y$	$\sqrt{3}V_{pd\sigma}s_y$
$ m k \; 3z^2 - r^2 angle$	$-2V_{pd\sigma}\overline{s}_z$	$V_{pd\sigma}\overline{s}_x$	$V_{pd\sigma}\overline{s}_y$	$arepsilon_d$	0
$ m{k} x^2 - y^2 angle$	0	$-\sqrt{3}V_{pd\sigma}\overline{s}_x$	$\sqrt{3}V_{pd\sigma}\overline{s}_y$	0	ε_d

$$\frac{H_{dd}^{\varepsilon}}{H_{dd}} = \frac{H_{dd}}{H_{dp}} - \frac{H_{dp}}{H_{pp}} - \frac{\varepsilon I_{pp}}{\varepsilon I_{pp}} - \frac{1}{2}H_{pd}$$

downfolding to *e*_g

$$\begin{array}{c|c} H_{e_g}^{\varepsilon} & |\mathbf{k} \, 3z^2 - r^2 \rangle_{\varepsilon} & |\mathbf{k} \, x^2 - y^2 \rangle_{\varepsilon} \\ \hline |\mathbf{k} \, 3z^2 - r^2 \rangle_{\varepsilon} & \varepsilon_d' - 2t_{\varepsilon}^{\sigma} [\frac{1}{4} (\cos k_x a + \cos k_y a) + \cos k_z a] & 2t_{\varepsilon}^{\sigma} [\frac{\sqrt{3}}{4} (\cos k_x a - \cos k_y a)] \\ \hline |\mathbf{k} \, x^2 - y^2 \rangle_{\varepsilon} & 2t_{\varepsilon}^{\sigma} [\frac{\sqrt{3}}{4} (\cos k_x a - \cos k_y a)] & \varepsilon_d' - 2t_{\varepsilon}^{\sigma} [\frac{3}{4} (\cos k_x a + \cos k_y a)] \end{array}$$

$$t_{\varepsilon}^{\sigma} = \frac{V_{pd\sigma}^2}{\varepsilon - \varepsilon_p}, \quad \varepsilon_d' = \varepsilon_d + 3t_{\varepsilon}^{\sigma}.$$

downfolding to *e*_g

basis $x^2 - y^2$, $3z^2 - r^2$

$$t_{mm'}^{i,i\pm\hat{z}} = t_{\varepsilon} \begin{pmatrix} 0 & 0\\ 0 & 1 \end{pmatrix} \qquad t_{mm'}^{i,i\pm\hat{x}} = t_{\varepsilon} \begin{pmatrix} \frac{3}{4} & \frac{\sqrt{3}}{4}\\ \frac{\sqrt{3}}{4} & \frac{1}{4} \end{pmatrix} \qquad t_{mm'}^{i,i\pm\hat{y}} = t_{\varepsilon} \begin{pmatrix} \frac{3}{4} & -\frac{\sqrt{3}}{4}\\ -\frac{\sqrt{3}}{4} & \frac{1}{4} \end{pmatrix}$$



tight-binding model



the Jahn-Teller mechanism



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 CuCr₂O₄, 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.

the many-body Hamiltonian



Born-Oppenheimer Ansatz

 $\Psi({\mathbf{r}_i}, {\mathbf{R}_\alpha}) = \psi({\mathbf{r}_i}; {\mathbf{R}_\alpha})\Phi({\mathbf{R}_\alpha})$

$$\begin{cases} \hat{H}_e \psi(\{\boldsymbol{r}_i\}; \{\boldsymbol{R}_\alpha\}) &= \varepsilon(\{\boldsymbol{R}_\alpha\})\psi(\{\boldsymbol{r}_i\}; \{\boldsymbol{R}_\alpha\}), & \text{electrons} \\ \\ \hat{H}_n \Phi(\{\boldsymbol{R}_\alpha\}) &= E\Phi(\{\boldsymbol{R}_\alpha\}), & \text{lattice} \end{cases}$$

 $\hat{H}_n = \hat{T}_n + \varepsilon(\{\boldsymbol{R}_\alpha\})$ BO surface

degenerate BO surfaces





is the structure stable?

NO. (apart linear molecules and Kramers degeneracy)

Jahn-Teller theorem

There is always some distortion which lowers the symmetry

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.*

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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.

* This research was carried out when the authors were working in the Sir William Ramsay Laboratories of Inorganic and Physical Chemistry, University College, London.

Jahn-Teller theorem

SUMMARY

It is shown that orbital electronic degeneracy and stability of the nuclear configuration are incompatible unless all the atoms of a molecule lie on a straight line. The proof is based on group theory and is therefore valid only if accidental degeneracy is disregarded. If the electrons causing the degeneracy are not essential for molecular binding, only a slight instability will result. Table I, which is needed to prove the theorem, can also be used to obtain the number of proper vibrations of a given symmetry type for any polyatomic molecule.

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normal modes

$$\hat{H}_n = \hat{T}_n + \sum_{\alpha\mu} \left[\frac{\partial \hat{U}_n}{\partial u_{\alpha\mu}} \right]_{\{\boldsymbol{R}^0_\alpha\}} u_{\alpha\mu} + \frac{1}{2} \sum_{\alpha\mu} \sum_{\alpha'\mu'} \left[\frac{\partial^2 \hat{U}_n}{\partial_{\alpha\mu} \partial_{\alpha'\mu'}} \right]_{\{\boldsymbol{R}^0_\alpha\}} u_{\alpha\mu} u_{\alpha'\mu'} + .$$

$$\tilde{u}_{\alpha\mu} = u_{\alpha\mu}\sqrt{M_{\alpha}}.$$

Dynamical matrix

$$D_{\alpha\mu,\alpha\mu'} = \frac{1}{\sqrt{M_{\alpha}}} \frac{1}{\sqrt{M_{\alpha'}}} \left[\frac{\partial^2 \hat{U}_n}{\partial_{\alpha\mu} \partial_{\alpha'\mu'}} \right]_{\{\boldsymbol{R}^0_{\alpha}\}},$$

Find eigenvalues and eigenvalues

two atoms



$$V(x_1, x_2) = V(R) + \frac{1}{2} x_1 \left. \frac{\partial V}{\partial^2 x_1} \right|_0 \left. x_1 + \frac{1}{2} x_2 \left. \frac{\partial^2 V}{\partial^2 x_2} \right|_0 \left. x_2 + x_2 \left. \frac{\partial^2 V}{\partial x_2 \partial x_1} \right|_0 x_1 \right.$$
$$= V(R) + \frac{1}{2} x_1 \left. K_{11} \left. x_1 + \frac{1}{2} x_2 \right. \left. K_{22} \left. x_2 + \frac{1}{2} x_2 \right. \left(K_{12} + K_{21} \right) x_1 \right.$$

V(R) = 0

change variables

$$x_i = \tilde{x}_i \sqrt{M_i}$$

$$H = \frac{1}{2}(\dot{\tilde{x}}_1^2 + \dot{\tilde{x}}_2^2) + \frac{1}{2}\tilde{x}_1 D_{11} \tilde{x}_1 + \frac{1}{2}\tilde{x}_2 D_{22} \tilde{x}_2 + \frac{1}{2}\tilde{x}_2 (D_{12} + D_{21}) \tilde{x}_1$$

$$D_{ij} = \frac{1}{\sqrt{M_i M_j}} K_{ij}$$

$$D = \begin{pmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{pmatrix} = \begin{pmatrix} D_{11} & D_{12} \\ D_{12} & D_{11} \end{pmatrix}$$

diagonalize D



$$H = \sum_i \left[\frac{1}{2} \dot{Q}_i^2 + \frac{1}{2} \Omega_i^2 \right]$$

but the first is a mere translation, only one normal mode

how many modes?





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

21 degrees of freedom

-6 (three translations and three rotations)

15 modes

which modes are relevant?

only those that can couple to degenerate states

$$\langle \psi_m | \hat{H}_e(\{\boldsymbol{R}_{\alpha}\}) | \psi_{m'} \rangle = \sum_{\alpha \mu} \langle \psi_m | \begin{bmatrix} \partial \hat{H}_e \\ \partial u_{\alpha \mu} \end{bmatrix}_{\{\boldsymbol{R}_{\alpha}^0\}} u_{\alpha \mu} + \dots = \hat{U}_{m,m'}^{\mathrm{JT}} + .$$

$$\hat{U}_{m,m'}^{\mathrm{JT}}$$

$$[\Gamma_m \otimes \Gamma_m] \cap \frac{\Gamma_{ ext{vibrations}}}{\supset A_1},$$

group O, eg states

$$[\Gamma_m \otimes \Gamma_m] \cap \frac{\Gamma_{\mathrm{vibrations}}}{\supset} A_1,$$

 $\Gamma_E \otimes \Gamma_E = A_1 \oplus A_2 \oplus E$

 $[\Gamma_E \otimes \Gamma_E] = A_1 \oplus E$

modes A₁ and E

let us use symmetries







which modes are relevant?

let us use symmetries





effect of operations



effect of operations



 $C_2 u_1 = u_4$

 $C_2 u_1 = u_4$

Effect of operations



 $C_3 u_1 = u_5$

using the projector

$$\hat{\mathcal{P}}_i = \frac{d_i}{h} \sum_g \left[\chi_i(g)\right]^* O(g)$$

$$P_{A1} \mathbf{u}_1 = (4\mathbf{u}_1 + 4\mathbf{u}_2 + 2\mathbf{u}_3 + 4\mathbf{u}_4 + 4\mathbf{u}_5 + 4\mathbf{u}_6)/24$$

let us try different displacements..

let us use symmetries





	0	E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
$(x^2 + y^2 + z^2)$	A_1	1	1	1	1	1
	A_2	1	1	1	-1	-1
$(x^2 - y^2, 3z^2 - r^2)$	E	2	-1	2	0	0
(x,y,z)	T_1	3	0	-1	-1	1
(xy, xz, yz)	T_2	3	0	-1	1	-1

effect of operations





u₁^z=q₀(0,0,1)

u₁^y=q₀(0,1,0)

modes A₁ and E


E modes

$$oldsymbol{Q}_1 = oldsymbol{u}_1(q_1) + oldsymbol{u}_2(q_1) + oldsymbol{u}_4(q_1) + oldsymbol{u}_5(q_1), \ oldsymbol{Q}_2 = oldsymbol{u}_1(q_2) + oldsymbol{u}_2(q_2) + oldsymbol{u}_3(q_2) + oldsymbol{u}_4(q_2) + oldsymbol{u}_5(q_2) + oldsymbol{u}_6(q_2), \ oldsymbol{Q}_2 = oldsymbol{u}_1(q_2) + oldsymbol{u}_2(q_2) + oldsymbol{u}_3(q_2) + oldsymbol{u}_4(q_2) + oldsymbol{u}_5(q_2) + oldsymbol{u}_6(q_2), \ oldsymbol{u}_6(q_2) + oldsymbol{u}_6(q_2) + oldsymbol{u}_6(q_2) + oldsymbol{u}_6(q_2) + oldsymbol{u}_6(q_2), \ oldsymbol{u}_6(q_2) + oldsymbol{u}_6(q_2)$$

 $\frac{1}{\sqrt{12}}q_2(1,0,0)$

 $\frac{1}{\sqrt{4}}q_1(1,0,0)$ $= -\frac{1}{\sqrt{12}}q_2(1,0,0)$ $\boldsymbol{u}_1(q_1)$ $oldsymbol{u}_1(q_2)$ $u_2(q_1) = -\frac{1}{\sqrt{4}}q_1(0,1,0)$ $egin{array}{rll} m{u}_2(q_2) &=& -rac{\sqrt{12}}{\sqrt{12}}q_2(0,1,0) \ m{u}_3(q_2) &=& rac{2}{\sqrt{12}}q_2(0,0,1) \end{array}$ (0, 0, 0)= $u_{3}(q_{1})$ $-rac{1}{\sqrt{4}}q_1(1,0,0) \ rac{1}{\sqrt{4}}q_1(0,1,0)$ $\boldsymbol{u}_4(q_1)$ $oldsymbol{u}_4(q_2) =$ = $\frac{\frac{1}{\sqrt{12}}q_2(0,1,0)}{-\frac{2}{\sqrt{12}}q_2(0,0,1)}$ $oldsymbol{u}_5(q_2) =$ $oldsymbol{u}_5(q_1) ~~=~~~$ (0, 0, 0) $\boldsymbol{u}_6(q_2)$ $u_6(q_1)$ =

Jahn-Teller potential

$$\langle \psi_m | \hat{H}_e(\{\boldsymbol{R}_{\alpha}\}) | \psi_{m'} \rangle = \sum_{\alpha \mu} \langle \psi_m | \begin{bmatrix} \partial \hat{H}_e \\ \partial u_{\alpha \mu} \end{bmatrix}_{\{\boldsymbol{R}_{\alpha}^0\}} u_{\alpha \mu} + \dots = \hat{U}_{m,m'}^{\mathrm{JT}} + \dots$$
$$\hat{U}_{m,m'}^{\mathrm{JT}}$$

perturbation theory

(point charge model)

$$d_C \to d_C + \delta d_C^{\mu}$$

 $v_R \rightarrow v_R + \Delta v_{\rm JT}$

$$\Delta v_{\rm JT} = \frac{q_C}{d_C^6} \frac{25}{14\sqrt{3}} \langle r^4 \rangle \begin{pmatrix} q_2 & q_1 \\ q_1 & -q_2 \end{pmatrix}$$

pseudospin operators

$$\hat{\tau}_{z} |\searrow\rangle = -|\searrow\rangle, \qquad \hat{\tau}_{x} |\searrow\rangle = +|\nearrow\rangle, \qquad \hat{\tau}_{y} |\searrow\rangle = -i|\nearrow\rangle$$

$$\hat{\tau}_{z} |\nearrow\rangle = +|\nearrow\rangle, \qquad \hat{\tau}_{x} |\nearrow\rangle = +|\searrow\rangle, \qquad \hat{\tau}_{y} |\nearrow\rangle = +i|\searrow\rangle$$

$$\hat{\tau}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \hat{\tau}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \hat{\tau}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}.$$

$$\Delta v_{\rm JT} = \lambda \left[q_1 \tau_x + q_2 \tau_z \right]$$

Jahn-Teller potential

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

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

$$\hat{U}^{\rm JT} = -\lambda q \begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix}$$

Jahn-Teller potential



empty state



anharmonic effects determine the angle



Crystal structure and magnetic properties of substances with orbital degeneracy

K. I. Kugel' and D. I. Khomskii

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 (KCuF₃, LaMnO₃, MnF₃). The effective spin Hamiltonian is obtained for these substances and the properties of the ground state are investigated. The orbital and magnetic structure tures 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.

eg Hubbard model

$$\begin{split} \hat{H} &= -\sum_{ii'} \sum_{\sigma} \sum_{mm'} t_{mm'}^{i,i'} c_{im\sigma}^{\dagger} c_{im'\sigma} + U \sum_{i} \sum_{m} \hat{n}_{im\uparrow} \hat{n}_{im\downarrow} \\ &+ \frac{1}{2} \sum_{i} \sum_{\sigma\sigma'} \sum_{m \neq m'} (U - 2J - J \delta_{\sigma,\sigma'}) \hat{n}_{im\sigma} \hat{n}_{im'\sigma'} \\ &- J \sum_{i} \sum_{m \neq m'} \left[c_{im\uparrow}^{\dagger} c_{im\downarrow}^{\dagger} c_{im'\uparrow} c_{im'\downarrow} + c_{im\uparrow}^{\dagger} c_{im\downarrow} c_{im'\downarrow}^{\dagger} c_{im'\uparrow} \right], \end{split}$$

two-site problem, one electron per site

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

$$\hat{H}_{0} = \varepsilon_{d} \sum_{\sigma} (\hat{n}_{A\sigma} + \hat{n}_{B\sigma})$$
$$\hat{H}_{T} = -t \sum_{\sigma} \sum_{m} \left[c^{\dagger}_{Am} c_{Bm} + c^{\dagger}_{Bm} c_{Am} \right].$$
$$\hat{H}_{U} = U \sum_{i=AB} \sum_{m} \hat{n}_{im\uparrow} \hat{n}_{im\downarrow} + \frac{1}{2} \sum_{i=AB} \sum_{\sigma\sigma'} \sum_{m \neq m'} (U - 2J - J\delta_{\sigma,\sigma'}) \hat{n}_{im\sigma} \hat{n}_{im'\sigma'}.$$

two-site problem, one electron per site



energies of doubly occupied states

 $|2,0\rangle_{\alpha'} \qquad E_{\alpha'}(2,0)$ $|2,0\rangle_{i1m} = c^{\dagger}_{im\uparrow}c^{\dagger}_{im\downarrow}|0\rangle \qquad 2\varepsilon_{e_g} + U$ $|2,0\rangle_{i2m} = c^{\dagger}_{im\uparrow}c^{\dagger}_{im'\downarrow}|0\rangle \qquad 2\varepsilon_{e_g} + U - 2J \quad m' \neq m$ $|2,0\rangle_{i3\sigma} = c^{\dagger}_{im\sigma}c^{\dagger}_{im'\sigma}|0\rangle \qquad 2\varepsilon_{e_g} + U - 3J \quad m' \neq m$

classify states in order of N_d

N_d= number doubly occupied sites



second order perturbation theory

$$\Delta E_{\alpha_1,\alpha_2}(1,1) = -\sum_{\alpha'} \alpha_1 \langle 1,1 | \hat{H}_T | 2,0 \rangle_{\alpha'} \frac{1}{E_{\alpha'}(2,0) - E_{\alpha}(1,1)} \alpha_1 \langle 2,0 | \hat{H}_T | 1,1 \rangle_{\alpha_2}$$

$$|2,0\rangle_{\alpha'} \qquad E_{\alpha'}(2,0)$$

$$|2,0\rangle_{i1m} = c^{\dagger}_{im\uparrow}c^{\dagger}_{im\downarrow}|0\rangle \qquad 2\varepsilon_{e_g} + U$$

$$|2,0\rangle_{i2m} = c^{\dagger}_{im\uparrow}c^{\dagger}_{im'\downarrow}|0\rangle \qquad 2\varepsilon_{e_g} + U - 2J \quad m' \neq m$$

$$|2,0\rangle_{i3\sigma} = c^{\dagger}_{im\sigma}c^{\dagger}_{im'\sigma}|0\rangle \qquad 2\varepsilon_{e_g} + U - 3J \quad m' \neq m$$

second order perturbation theory



$$\mathbf{O}_i = \boldsymbol{ au}_i/2$$

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

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

LaMnO₃



$$e_g^1$$

$$t_{mm'}^{i,i\pm\hat{z}} = t_{\varepsilon} \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \qquad t_{mm'}^{i,i\pm\hat{x}} = t_{\varepsilon} \begin{pmatrix} \frac{3}{4} & \frac{\sqrt{3}}{4} \\ \frac{\sqrt{3}}{4} & \frac{1}{4} \end{pmatrix} \qquad t_{mm'}^{i,i\pm\hat{y}} = t_{\varepsilon} \begin{pmatrix} \frac{3}{4} & -\frac{\sqrt{3}}{4} \\ -\frac{\sqrt{3}}{4} & \frac{1}{4} \end{pmatrix}$$

z direction

approximation: *J*=0



$$\hat{H}_{\rm SE}^{\hat{z}} \sim -\frac{1}{U} \sum_{E} \hat{H}_{T} |E\rangle \langle E| \hat{H}_{T}^{\dagger}$$

$$= -\frac{t^2}{U} \frac{1}{2} \sum_{ii'} \sum_{\sigma\sigma'} \sum_{\alpha} \left\{ c^{\dagger}_{i\tau\sigma} |0\rangle^{i\,i} \langle 0|c_{i\tau\sigma'} \left[c_{i'\tau\sigma} |2\rangle^{i'\,i'}_{\alpha\,\alpha} \langle 2|c^{\dagger}_{i'\tau\sigma'} \right] + (i \longleftrightarrow i') \right\} \delta_{\tau,\searrow}$$

$$= -\frac{2t^2}{U} \frac{1}{2} \sum_{ii'} \sum_{\sigma\sigma'} \left\{ (-1)^{-\sigma'-\sigma} P^{i}_{\tau\sigma-\sigma'} P^{i'}_{\tau\sigma'-\sigma} + \frac{1}{2} \left[P^{i}_{\tau\sigma\sigma} P^{i'}_{-\tau\sigma'\sigma'} + P^{i}_{-\tau\sigma\sigma} P^{i'}_{\tau\sigma'\sigma'} \right] \right\} \delta_{\tau,\searrow},$$

$$P^{i}_{\tau\sigma\sigma'} = c^{\dagger}_{i\tau\sigma} |0\rangle \langle 0|c_{i\tau\sigma'} = \hat{o}^{z}_{\tau\tau} \left[\hat{s}^{z}_{\sigma\sigma'} + \hat{s}^{+}_{\sigma\sigma'} + \hat{s}^{-}_{\sigma\sigma'}\right].$$

$$\begin{split} \hat{o}_{\tau\tau'}^z &= \left[\frac{n_i}{2} \ \hat{I} + (-1)^{\tau} O_z^i\right] \delta_{\tau\tau'} & \hat{s}_{\sigma\sigma}^z = \left[\frac{n_i}{2} \ \hat{I} + (-1)^{\sigma} S_z^i\right] \delta_{\sigma\sigma'} \\ \hat{o}_{\tau\tau'}^+ &= O_+^i (1 - \delta_{\tau\tau'}) & \hat{s}_{\sigma\sigma'}^+ = S_+^i (1 - \delta_{\sigma\sigma'}) \\ \hat{o}_{\tau\tau'}^- &= O_-^i (1 - \delta_{\tau\tau'}) & \hat{s}_{\sigma\sigma'}^- = S_-^i (1 - \delta_{\sigma\sigma'}) \,, \end{split}$$

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

other dirs: rotate axis and back

$$O_{z}^{i} \xrightarrow[\hat{z} \to \hat{x}]{} - \frac{1}{2}O_{z}^{i} - \frac{\sqrt{3}}{2}O_{x}^{i}$$
$$O_{z}^{i} \xrightarrow[\hat{z} \to \hat{y}]{} - \frac{1}{2}O_{z}^{i} + \frac{\sqrt{3}}{2}O_{x}^{i}$$

variational approach



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

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

variational approach

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

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

$$\Delta E(\theta) = \frac{\Gamma}{16} \left[3\cos^2(\theta - \pi) - \frac{3}{2} \right]$$

 $\theta = \pi/2$ (Jahn-Teller-like Q_1 distortion).

KCuF₃

eg³: particle-hole symmetry



$$\Delta E(\theta) = \frac{\Gamma}{16} \left[3\cos^2(\theta - \pi) - \frac{3}{2} \right]$$

AFO and FO along z: same variational energy

KCuF₃

eg³: particle-hole symmetry

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

AFO and FO along z: same variational energy

$$\Delta E(\theta) = \frac{\Gamma}{16} \left[3\cos^2(\theta - \pi) - \frac{3}{2} \right]$$

mode Q₁



origin of orbital order

recent insights from our work

Phys. Rev. Lett. 101, 266405 (2008)
Phys. Rev. Lett. 104, 086402 (2010)
Phys. Rev. B 85, 035124 (2012)
Phys. Rev. B 87, 195141 (2013)

LDA+U: KK-like mechanism

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

A. I. Liechtenstein

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

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

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



The situation changes drastically if we allow for orbital polarization. Because U exceeds the bandwidth, the orbital sector is already strongly polarized (as are the spins) before the lattice is allowed to react. Overlooking some unimportant details concerning the coherence of the intermediate states, the well-known rule that electronic MFT in strong coupling maps onto the classical "spin" problem holds also in this case. In other words, we find the quadrupolar orbital-ferromagnetic spin phase to be most stable (for the same reasons as Kugel and Khomskii⁶). 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 !

LDA+DMFT confirms LDA+U

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Structural Relaxation due to Electronic Correlations in the Paramagnetic Insulator KCuF₃

I. Leonov,¹ N. Binggeli,^{1,2} Dm. Korotin,³ V. I. Anisimov,³ N. Stojić,^{4,2} and D. Vollhardt⁵ ¹Abdus Salam International Center for Theoretical Physics, Trieste 34014, Italy ²INFM-CNR Democritos, Theory @ Elettra group, Trieste 34014, Italy ³Institute of Metal Physics, South Kovalevskoy Street 18, 620219 Yekaterinburg GSP-170, Russia ⁴International School for Advanced Studies, SISSA, Via Beirut 2/4, 34014 Trieste, Italy ⁵Theoretical Physics III, Center for Electronic Correlations and Magnetism, Institute of Physics, University of Augsburg, Augsburg 86135, Germany (Received 7 April 2008; published 29 August 2008)



DMFT para and LDA+U AFM give similar results

KK is the mechanism: T_{OO} ~T_{KK}



...or, is it ?

Problems:

- why T_N (40K-140K) much smaller than T_{JT} (800-1400 K)?
- LDA+U,HF,GGA+DMFT results show OO also for no distortion
- trends with RE, volume, temperature, pressure, in T_{JT} ?

Our new approach:

- single out Kugel-Khomskii mechanism
- calculate T_{KK} directly using LDA+DMFT

idea: single out super-exchange



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

two-band model

LDA+DMFT with Wannier functions



LDA+DMFT with Wannier functions



 A. Flesch, E. Gorelov, E. Koch and E. Pavarini Multiplet effects in orbital and spin ordering phenomena: A hybridization-expansion quantum impurity solver study Phys. Rev. B 87, 195141 (2013)

the KK mechanism in KCuF₃



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

reminder: mean field theory overestimates T_{KK}

LaMnO₃ : *T_{KK}* ~ 600 K !!

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



orbital-order transition at T_{OO} in LaMnO₃



PHYSICAL REVIEW B

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1 FEBRUARY 1998-II

Neutron-diffraction study of the Jahn-Teller transition in stoichiometric LaMnO₃

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

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

The parent compound of the giant magnetoresistance Mn-perovskite, LaMnO₃, has been studied by thermal analysis and high-resolution neutron-powder diffraction. The orthorhombic Pbnm structure at room temperature is characterized by an antiferrodistorsive orbital ordering due to the Jahn-Teller effect. This ordering is evidenced by the spatial distribution of the observed Mn-O bond lengths. LaMnO3 undergoes a structural phase transition at $T_{\rm IT} \approx 750$ K, above which the orbital ordering disappears. There is no change in symmetry although the lattice becomes metrically cubic on the high-temperature side. The MnO₆ octahedra become nearly regular above $T_{\rm TT}$ and the thermal parameter of oxygen atoms increases significantly. The observed average cubic lattice is probably the result of dynamic spatial fluctuations of the underlying orthorhombic distortion. [S0163-1829(98)51706-7]

Too ~ 800 K

VOLUME 81, NUMBER 3 PHYSICAL REVIEW LETTERS 20 JULY 1998

Resonant X-Ray Scattering from Orbital Ordering in LaMnO₃

Y. Murakami,^{1,2} J.P. Hill,³ D. Gibbs,³ M. Blume,³ I. Koyama,¹ M. Tanaka,¹ H. Kawata,¹ T. Arima,⁴ Y. Tokura,⁵

K. Hirota,^{2,6} and Y. Endoh^{2,6}

¹Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, 305-0801, Japan

²Core Research for Evolutional Science and Technology (CREST). Tsukuba 305-0047 Japan ³Department of Physics, Brookhaven National Laboratory, Upton, New York 11973 ⁴Institute of Materials Science, University of Tsukuba, Tsukuba 305-8573, Japan ⁵Department of Applied Physics, University of Tokyo, Tokyo 113-0033, Japan and Joint Research Center for Atom Technology (JRCAT), Tsukuba 305-0046, Japan ⁶Department of Physics, Tohoku University, Sendai 980-8578, Japan (Received 22 April 1998)


Too: orbital order-to-disorder transition

PRL 94, 177203 (2005)

PHYSICAL REVIEW LETTERS

week ending 6 MAY 2005

Orbital Correlations in the Pseudocubic O and Rhombohedral R Phases of LaMnO₃

Xiangyun Qiu,¹ Th. Proffen,² J. F. Mitchell,³ and S. J. L. Billinge¹

¹Department of Physics and Astronomy, Michigan State University, E. Lansing, Michigan 48824, USA
²Los Alamos National Laboratory, LANSCE-12, MS H805, Los Alamos, New Mexico 87545, USA
³Material Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA
(Received 12 August 2004; revised manuscript received 24 February 2005; published 5 May 2005)

The local and intermediate structure of stoichiometric LaMnO₃ has been studied in the pseudocubic and rhombohedral phases at high temperatures (300–1150 K). Neutron powder diffraction data were collected and a combined Rietveld and high real space resolution atomic pair distribution function analysis was carried out. The nature of the Jahn-Teller (JT) transition around 750 K is confirmed to be orbital order to disorder. In the high-temperature orthorhombic (*O*) and rhombohedral (*R*) phases, the MnO₆ octahedra are still fully distorted locally. More importantly, the intermediate structure suggests the presence of local ordered clusters of diameter ~16 Å (~4 MnO₆ octahedra) implying strong nearest-neighbor JT antiferrodistortive coupling. These clusters persist well above the JT transition temperature even into the high-temperature *R* phase.

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PACS numbers: 75.47.Lx, 61.12.-q, 75.47.Gk

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

*T*₀₀ ~ 800 K and *T_{KK}* ~ 600 K !!

LaMnO₃



Rodriguez-Carvajal et al., PRB 57, R3189 (1996)

is super-exchange driving oo melting?

is super-exchange driving oo melting?

approach: REMnO₃ series + high pressure data T_{00} ...



.. increases with decreasing ionic radius

.. decreases with increasing pressure

• Raman data $-\Box - T_N$ (Ref. [31])

--- T_n (Ref. [4])

Domains

800

T_{rr} (Ref. [3])

Pnma insulator

900

1000

without distortions



spin flip and pair hopping do not change trends 5 bands yield same result as two bands

Phys. Rev. B 87, 195141 (2013)

conclusion

KBF₃ K₂BF₄ and ReMnO₃

what is the mechanism of orbital-order and orbital-order melting ?



but static splitting essential



The Normal Mode Q₂ (Q₂>0)

super-exchange alone cannot explain trends in Too electron-phonon coupling

 $T_{\kappa\kappa} \ll T_{00}$ and T_{JT}

Phys. Rev. Lett. **101**, 266405 (2008) Phys. Rev. Lett. **104**, 086402 (2010) Phys. Rev. B **85**, 035124 (2012) Phys. Rev. B **87**, 195141 (2013)





conclusion

emergence of local spins and pseudospins



electron-phonon coupling



crustal-field splitting enhanced by coulomb repulsion super-exchange interactions



purely electronic mechanism coupling 4t²/U