orbital ordering, what is it?
orbital ordering

KCuF$_3$

LaMnO$_3$

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

Y. Tokura\textsuperscript{1,2} and N. Nagaosa\textsuperscript{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 \(\hat{S}\) and the orbital pseudospin \(\hat{T}\) 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

\[t_{ij} = \frac{1}{2} \left\{ v_1 \left( \frac{a + b}{2} \right) + v_2 \right\}.

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analogy (S=1/2 case)

spin degrees of freedom

effective S=1/2 spin

spin 1/2 operators $S_x, S_y, S_z$

orbital degrees of freedom

effective O=1/2 pseudospin

pseudospin 1/2 operators $O_x, O_y, O_z$

spin ordering

pseudospin ordering
Spin and pseudospin interact

Local spins & local orbital pseudospins

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 measurements. However, the anisotropic or–

From Tokura and Nagaosa, Science (2001)
overview

- **the building blocks**
  - emergence of local spins and orbital pseudospins
  - spin and orbital ordering
  - representative systems: KCuF$_3$ ($t_{2g}^6e_g^3$) & LaMnO$_3$ ($t_{2g}^3e_g^1$)
  - two mechanisms

- $e_g$ Hubbard Hamiltonian
  - on-site term, $e_g$ 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

KCuF$_3$

the LDA electronic structure
(cubic)
atomic d orbitals

$e_g$

$x^2-y^2$

$3z^2-r^2$

$t_{2g}$

$xz$

$yz$

$xy$
orbital ordering

KCuF₃ and LaMnO₃: $e_g$ two-orbital systems

$$\hat{H} = - \sum_{ii'} \sum_{\sigma} \sum_{mm'} t_{ii'}^\sigma_{mm'} c_{im\sigma}^\dagger c_{im'\sigma} + U \sum_i \sum_m \hat{n}_{im\uparrow} \hat{n}_{im\downarrow}$$

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

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

$t_{ii'}^\sigma_{mm'}$: crystal-field energies \( (i=i') \)

t_{ii'}^\sigma_{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 | 0 | 0 |
| \( |1, \frac{1}{2}, \uparrow\rangle \) | 1 | 1/2 | \( \varepsilon_d \) |
| \( |1, \frac{1}{2}, \downarrow\rangle \) | 1 | 1/2 | \( \varepsilon_d \) |
| \( |2, 0, 0\rangle \) | 2 | 0 | \( 2\varepsilon_d + U \) |
emergence of local spins

- $2e_d + U$ for $N=2$, no spin degrees of freedom
- Partially filled spin states for $N=1$, spin up and spin down, $S=1/2$
- $e_d$ for $N=0$, no spin degrees of freedom
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

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

N=2 sites

N_e=2 electrons

\[ 2\varepsilon_d + U \]

2\varepsilon_d

degeneracy \(2^N\) or \(N\) spin \(S=1/2\)
low energy model

eliminate states with a doubly occupied site

virtual hopping

energy gain

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

energy gain only for antiferromagnetic arrangement

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

Pauli principle

super-exchange interaction

\[ H_S = \frac{1}{2} \Gamma \sum_{\langle ii' \rangle} \left[ S_i \cdot S_{i'} - \frac{1}{4} n_i n_{i'} \right] \]
Heisenberg model

local spins: effective emergent elementary particles

Heisenberg model: effective interaction

\[ H = \frac{1}{2} \Gamma \sum_{\langle ij \rangle} S_i \cdot S_j \]
Materials exhibiting the characteristics described above have been designated "antiferromagnetic." Up to the present time the phenomenon has been qualitatively verified by experimental investigators. At densities around $10^{15}/cc$, $T$ attained values of the order of $10^{-4}$ seconds for MnO and $10^{-3}$ seconds for Fe$_2$O$_3$. However, the magnetization directions for the two sub-lattices have been indirect, e.g., determination of Curie points by susceptibility and specific heat anomalies. It has occurred to one of us to present the neutron diffraction peaks at forbidden reflection positions for MnO and MnF$_2$ and MnSO$_4$ respectively at $122'K$ and $950'K$.

The low temperature pattern also presents. The early work is reviewed in reference 6. In the latter paper (as well as in that of Biebermans), the transport of magnetic ions is formed and the interaction of the neutron magnetic and nuclear scattering amplitudes of a paramagnetic substance. (MnO, MnF$_2$, MnSO$_4$ and Fe$_2$O$_3$) was observed by Zemansky who measured the time of decay, $T$, of the regular face-centered cubic reflection positions and the liquid type of magnetic scattering.

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magnetism & emergence

from electrons emerge local spins

local spins interact

cooperative state

local spins as effective elementary entities
and what about local orbital pseudospins?
from idealized atom to real atoms

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

one-electron part   Coulomb repulsion
self-consistent potential approximation

\[ H^{\text{NR}}_e = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_{i>j} \frac{1}{|r_i - r_j|} \]

e.g., DFT/LDA contains e.g. Hartree term

hydrogen-like atom

\[ H^{\text{NR}}_e = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i v_R(r_i) \]

\[ H^{\text{NR}}_e = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i Z_{\text{eff}}/r_i \]
LDA atomic functions

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

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

(hydrogen-like atom)

Laguerre polynomials
orbital degrees of freedom

spherical potential

eigenvalues: $n$
eigenvectors: $n, l, m$

$l=0$

$l=1$

$l=2$

$xy$
$yz$
$3z^2-r^2$
$xz$
$x^2-y^2$
many-electron atoms

\[ H_{eNR}^{NR} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_{i>j} \frac{1}{|r_i - r_j|} \]

rewrite for one \( nl \) shell in 2nd quantization

\[ H_{eNR}^{NR} = \varepsilon_{nl} \sum_{m\sigma} c_{m\sigma}^\dagger c_{m\sigma} + \frac{1}{2} \sum_{\sigma\sigma'} \sum_{m m' \tilde{m} \tilde{m}'} U_{mm'\tilde{m}\tilde{m}'}^{ij} c_{m\sigma}^\dagger c_{m'\sigma'}^\dagger c_{\tilde{m}\sigma'} c_{\tilde{m}\sigma} \]

kinetic+central

Coulomb

\[ U_{mm'\tilde{m}\tilde{m}'}^{ij} = \int dr_1 \int dr_2 \frac{\psi_i \psi_j \psi_{m\sigma}(r_1) \psi_{m'\sigma'}(r_2) \psi_{i'\tilde{m}\sigma}(r_1) \psi_{j'\tilde{m}'\sigma'}(r_2)}{|r_1 - r_2|} \]
special cases

$l=0$: Hubbard Hamiltonian of the idealized atom

\[ H = \varepsilon_d \sum_{\sigma} c_{\sigma}^\dagger c_{\sigma} + U \sum_i n_{\uparrow} n_{\downarrow} \]

what about $l>0$, e.g. $l=2$?

\[ H_{eNR} = \varepsilon_{nl} \sum_{m\sigma} c_{m\sigma}^\dagger c_{m\sigma} + \frac{1}{2} \sum_{\sigma\sigma'} \sum_{mm'm'm'} U_{mm'm'm'} c_{m\sigma}^\dagger c_{m'\sigma'}^\dagger c_{m'\sigma'} c_{m\sigma} \]
Hund’s rules

direct term: the same for all N electron states

\[
U_{\text{avg}} = \frac{1}{(2l + 1)^2} \sum_{mm'} U_{mm'mm'}^l
\]

exchange term: 1. Hund’s rule

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

\[
J_{m,m'}^l = U_{mm'm'm}^l = \int dr_1 \int dr_2 \frac{\psi_{im\sigma}(r_1)\bar{\psi}_{im'\sigma}(r_2)\psi_{im\sigma}(r_2)\bar{\psi}_{im'\sigma}(r_1)}{|r_1 - r_2|}
\]

\[
= \int dr_1 \int dr_2 \frac{\phi_{imm'\sigma}(r_1)\phi_{imm'\sigma}(r_2)}{|r_1 - r_2|} = \frac{1}{V} \sum_k \frac{4\pi}{k^2} |\phi_{imm'\sigma}(k)|^2,
\]
Coulomb exchange

positive, hence **always ferromagnetic**

Friedrich Hund

\[-\frac{1}{2} \sum_\sigma \sum_{m \neq m'} J_{m,m'}^{l} c_m^\dagger \sigma c_m c_{m'}^\dagger \sigma c_{m'} = -\frac{1}{2} \sum_{m \neq m'} 2J_{m,m'}^{l} \left[ S_{z}^{m} S_{z}^{m'} + \frac{1}{4} n_{m} n_{m}' \right] \]

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
2-level atom, away from half-filling
2-level 2-atom problem

with degenerate levels

\[ \hat{H} = \hat{H}_0 + \hat{H}_T + \hat{H}_U \]

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

\[ \hat{H}_T = -t \sum_{\sigma} \sum_{m} \left[ c_{Am}^{\dag} c_{Bm} + c_{Bm}^{\dag} c_{Am} \right] \]

\[ \hat{H}_U = U \sum_{i=AB} \sum_{m} \hat{n}_{im\uparrow} \hat{n}_{im\downarrow} + \frac{1}{2} \sum_{i=AB} \sum_{\sigma\sigma'} \sum_{m \neq m'} (U - 2J - J\delta_{\sigma,\sigma'}) \hat{n}_{im\sigma} \hat{n}_{im'\sigma'} \]
orbital degrees of freedom

<table>
<thead>
<tr>
<th></th>
<th>Site A</th>
<th>Site B</th>
<th>N per atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>4e_d+ 6U</td>
<td><img src="source" alt="Diagram" /></td>
<td><img src="source" alt="Diagram" /></td>
<td>N=4</td>
</tr>
<tr>
<td>3e_d+ 3U</td>
<td><img src="source" alt="Diagram" /></td>
<td><img src="source" alt="Diagram" /></td>
<td>N=3   d_o=2</td>
</tr>
<tr>
<td>2e_d+ U</td>
<td><img src="source" alt="Diagram" /></td>
<td><img src="source" alt="Diagram" /></td>
<td>N=2   d_o=2</td>
</tr>
<tr>
<td>2e_d+ U</td>
<td><img src="source" alt="Diagram" /></td>
<td><img src="source" alt="Diagram" /></td>
<td>N=2   d_o=2</td>
</tr>
<tr>
<td>e_d</td>
<td><img src="source" alt="Diagram" /></td>
<td><img src="source" alt="Diagram" /></td>
<td>N=1   d_o=2</td>
</tr>
</tbody>
</table>

violates first Hund's rule
analogy

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

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

spin ordering

pseudospin ordering
### pseudospin ordering

#### KCuF$_3$ and LaMnO$_3$

<table>
<thead>
<tr>
<th>Element</th>
<th>Configuration</th>
<th>$t_{2g}^6 e_g^3$</th>
<th>$t_{2g}^3 e_g^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>[Ar]3d$^5$ 4s$^2$</td>
<td>Mn$^{3+}$ 3d$^4$</td>
<td>t$_{2g}^3 e_g^1$</td>
</tr>
<tr>
<td>Cu</td>
<td>[Ar]3d$^{10}$ 4s$^1$</td>
<td>Cu$^{2+}$ 3d$^9$</td>
<td>t$_{2g}^6 e_g^3$</td>
</tr>
</tbody>
</table>
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

co-operative Jahn-Teller distortion

KCuF$_3$

LaMnO$_3$

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

$t_{2g}^3e_g^1$
Materials exhibiting the characteristics described above have been designated as antiferromagnetic. Up to the present time the only methods of detecting antiferromagnetism experimentally have been indirect, e.g., determination of Curie points by susceptibility and specific heat anomalies. It has occurred to one of us that neutron diffraction studies of antiferromagnetic substances would provide a new and important method of investigating the exchange coupling of magnetic ions. The technique of neutron scattering has been developed by Neel, I. Bitter, and Van Vleck for one of the sub-lattices is that for an ordinary ferromagnetic material. However, the magnetization directions for the two interpenetrating lattices such that atoms on one lattice have nearest neighbors only on the other lattice. Examples are simple cubic lattices for MnO and MnF2, and the regular face-centered cubic lattice for MnSO4.

For MnF2 and MnSO4, (2) a liquid type of magnetic scattering has been qualitatively verified by experimental investigators. At absolute zero all of the atoms on one lattice have their magnetic moments parallel to each other. This last condition is required in order that spin parallel pairs occur. An approximate theory of such substances has been developed by Neel, I. Bitter, and Van Vleck. Theory then predicts that the integral for nearest neighbors be negative and consider only nearest neighbor interactions. Theory then predicts that the exchange integrals are negative. In such cases the lowest energy is sufficient to overcome the tendency of the atoms to be scattered. Halpern and Johnson have shown that the coherent nuclear scattering amplitudes for MnO and o.-Fe2O3 are respectively 122°K and 950°K. The spectral line shape of the resonance radiation, as pointed out earlier by Kenty explicit results were obtained for the case of MnO and MnF2 and MnSO4, (3) the presence of strong coherent magnetic scattering (no coupling of the atomic moments) to exist for MnO and (4) the presence of strong coherent magnetic and nuclear scattering amplitudes of a paramagnetic substance. The neutron diffraction patterns for various paramagnetic substances (MnO, MnF2, MnSO4 and Fe2O3) were recently, unpublished calculations have extended the analysis to enclosed and to a variety of line shapes.

The early work is reviewed in reference 6. In the latter paper (as well as in that of Biebermans), the transport of excited 6'PI atom. The later paper (as well as in that of Biebermans), the transport of excited 6'PI atom. The later paper (as well as in that of Biebermans), the transport of excited 6'PI atom. The later paper (as well as in that of Biebermans), the transport of excited 6'PI atom.

*This work was supported in part by the ONR.

In conclusion it appears that neutron diffraction studies of antiferromagnetic materials should provide a new and important method of investigating the exchange coupling of magnetic ions. In order that spin parallel pairs occur. In order that spin parallel pairs occur. In order that spin parallel pairs occur. In order that spin parallel pairs occur. In order that spin parallel pairs occur.

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$_2$O$_4$, 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.
do we need a large crystal-field?

one electron per atom

$\Delta E$

atomic sites

$W \sim 2t$
do we need a large crystal-field?

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

E. Pavarini, S. Biermann, A. Poteryaev, A. I. Lichtenstein, A. Georges, and O. K. Andersen

No! A 100 meV crystal-field is enough ($W\sim3$ 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 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.

super-exchange Hamiltonian

\[ H = J_{SS} S_1 \cdot S_2 + J_{OO} O_1 O_2 + J_{SO} (O_1 O_2)(S_1 \cdot S_2) \]

\[ J \propto 4t^2/U \]

O : pseudospins in orbital space
multi-band Hubbard model

$H_0 + H_U + H_T$
representative system

\[ \text{KCuF}_3 \quad t_{2g}^6e_g^3 \]
the LDA electronic structure

cubic KCuF$_3$
why do $e_g$ and $t_{2g}$ level split?
approximate method

how do \( d \) levels split at the Cu site?

point charge model

\[
v_R(r) = \sum_{\alpha} \frac{q_\alpha}{|R_\alpha - r|} = v_0(r) + \sum_{\alpha \neq 0} \frac{q_\alpha}{|R_\alpha - r|} = v_0(r) + v_c(r)
\]

crystal field
use perturbation theory

\[ v_R(r) = \frac{q_B}{r} + q_C \frac{d}{d_C} \left[ \Delta v \left( \frac{x}{d_C}; \frac{r}{d_C} \right) + \Delta v \left( \frac{y}{d_C}; \frac{r}{d_C} \right) + \Delta v \left( \frac{z}{d_C}; \frac{r}{d_C} \right) \right] \]

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

point charge model: $F_6$ octahedron

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

\[
\begin{align*}
H_{\text{CF}} &= \begin{pmatrix}
Dq & 0 & 0 & 0 & 5Dq \\
0 & -4Dq & 0 & 0 & 0 \\
0 & 0 & 6Dq & 0 & 0 \\
0 & 0 & 0 & -4Dq & 0 \\
5Dq & 0 & 0 & 0 & Dq
\end{pmatrix}.
\end{align*}
\]

\[ \psi_{nlm}(\rho, \theta, \phi) = R_{nl}(\rho)Y_{lm}^m(\theta, \phi) \]
atomic d orbitals

\[x^2-y^2\]

\[3z^2-r^2\]

\[xz\]

\[yz\]

\[xy\]
exact method: group theory

group O
# Character Table of Group $O$

<table>
<thead>
<tr>
<th></th>
<th>$O$</th>
<th>$E$</th>
<th>$8C_3$</th>
<th>$3C_2$</th>
<th>$6C_2$</th>
<th>$6C_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(x^2 + y^2 + z^2)$</td>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$A_1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(x^2 - y^2, 3z^2 - r^2)$</td>
<td>$E$</td>
<td>2</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$(x, y, z)$</td>
<td>$T_1$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$(xy, xz, yz)$</td>
<td>$T_2$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

[Diagram of a crystalline structure with labels 1, 2, 3, 4, 5, 6]
character table of group $O$

group elements $g$ divided in classes

<table>
<thead>
<tr>
<th>$(x^2 + y^2 + z^2)$</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$E$</th>
<th>$8C_3$</th>
<th>$3C_2$</th>
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<th>$6C_4$</th>
</tr>
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<tbody>
<tr>
<td>$(x^2 - y^2, 3z^2 - r^2)$</td>
<td>$E$</td>
<td>2</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
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<td>$T_1$</td>
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<td>0</td>
<td>-1</td>
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<td>1</td>
<td></td>
</tr>
<tr>
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<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td></td>
</tr>
</tbody>
</table>

$E$: identity

$C_n$: anticlockwise rotation of $360^\circ/n$
types of irreducible representations

<table>
<thead>
<tr>
<th>Character</th>
<th>$O$</th>
<th>$E$</th>
<th>$8C_3$</th>
<th>$3C_2$</th>
<th>$6C_2$</th>
<th>$6C_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(x^2 + y^2 + z^2)$</td>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$(x^2 - y^2, 3z^2 - r^2)$</td>
<td>$E$</td>
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<td>-1</td>
<td>2</td>
<td>0</td>
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</tr>
<tr>
<td>$(x, y, z)$</td>
<td>$T_1$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$(xy, xz, yz)$</td>
<td>$T_2$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

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 used to label eigenvalues
## character table of group O

### characters

<table>
<thead>
<tr>
<th>((x^2 + y^2 + z^2))</th>
<th>(O)</th>
<th>(E)</th>
<th>(8C_3)</th>
<th>(3C_2)</th>
<th>(6C_2)</th>
<th>(6C_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_1)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(A_2)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>((x^2 - y^2, 3z^2 - r^2))</td>
<td>(E)</td>
<td>2</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>((x, y, z))</td>
<td>(T_1)</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>((xy, xz, yz))</td>
<td>(T_2)</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

**trace of the matrix** corresponding to a given operation within a given representation
## character table of group O

### characters of A₁

<table>
<thead>
<tr>
<th>Character</th>
<th>Description</th>
<th>O</th>
<th>E</th>
<th>8C₃</th>
<th>3C₂</th>
<th>6C₂</th>
<th>6C₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x² + y² + z²)</td>
<td>A₁</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(x² - y², 3z² - r²)</td>
<td>A₂</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>(x, y, z)</td>
<td>E</td>
<td>2</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(xy, xz, yz)</td>
<td>T₁</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(xy, xz, yz)</td>
<td>T₂</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
</tbody>
</table>
character table of group O

dimensionality; character of E

<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>E</th>
<th>8C₃</th>
<th>3C₂</th>
<th>6C₂</th>
<th>6C₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>((x^2 + y^2 + z^2))</td>
<td></td>
<td>A₁</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A₂</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>((x^2 - y^2, 3z^2 - r^2))</td>
<td></td>
<td>E</td>
<td>2</td>
<td>-1</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>(x, y, z)</td>
<td></td>
<td>T₁</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>(xy, xz, yz)</td>
<td></td>
<td>T₂</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
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</tbody>
</table>
functions that can be used as a basis of an invariant linear space for a given irreducible representation
### character table of group O

**Partner functions of $A_1$**

<table>
<thead>
<tr>
<th></th>
<th>$O$</th>
<th>$E$</th>
<th>$8C_3$</th>
<th>$3C_2$</th>
<th>$6C_2$</th>
<th>$6C_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(x^2 + y^2 + z^2)$</td>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$(x^2 - y^2, 3z^2 - r^2)$</td>
<td>$E$</td>
<td>2</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$(x, y, z)$</td>
<td>$T_1$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
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<tr>
<td>$(xy, xz, yz)$</td>
<td>$T_2$</td>
<td>3</td>
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<td>-1</td>
</tr>
</tbody>
</table>

Functions that can be used as a basis of an invariant linear space for a given irreducible representation.
## crystal field and group theory

### $O(3)$ Table

<table>
<thead>
<tr>
<th>$O(3)$</th>
<th>$E$</th>
<th>$C_\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma^l$</td>
<td>$2l + 1$</td>
<td>$\sin(l + \frac{1}{2})\alpha / \sin \frac{\alpha}{2}$</td>
</tr>
</tbody>
</table>

### $O$ Table

<table>
<thead>
<tr>
<th>$O$</th>
<th>$E$</th>
<th>$8C_3$</th>
<th>$3C_2$</th>
<th>$6C_2$</th>
<th>$6C_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma^s$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma^p$</td>
<td>3</td>
<td>0</td>
<td>$-1$</td>
<td>$-1$</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma^d$</td>
<td>5</td>
<td>$-1$</td>
<td>1</td>
<td>1</td>
<td>$-1$</td>
</tr>
<tr>
<td>$\Gamma^f$</td>
<td>7</td>
<td>1</td>
<td>$-1$</td>
<td>$-1$</td>
<td>$-1$</td>
</tr>
</tbody>
</table>
\[ \Gamma = \bigoplus_i a_i \Gamma_i, \]

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

\[ h=24 \]

<table>
<thead>
<tr>
<th>( O )</th>
<th>( E )</th>
<th>( 8C_3 )</th>
<th>( 3C_2 )</th>
<th>( 6C_2 )</th>
<th>( 6C_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma^s )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( \Gamma^p )</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>( \Gamma^d )</td>
<td>5</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>( \Gamma^f )</td>
<td>7</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
</tbody>
</table>

\[
\begin{array}{c|cccccc}
O & E & 8C_3 & 3C_2 & 6C_2 & 6C_4 \\
\hline
A_1 & 1 & 1 & 1 & 1 & 1 \\
A_2 & 1 & 1 & 1 & -1 & -1 \\
E & 2 & -1 & 2 & 0 & 0 \\
T_1 & 3 & 0 & -1 & -1 & 1 \\
T_2 & 3 & 0 & -1 & 1 & -1 \\
\end{array}
\]
crystal field and group theory

\[
\begin{array}{c|cccccc}
O & E & 8C_3 & 3C_2 & 6C_2 & 6C_4 \\
\hline
\Gamma^s & 1 & 1 & 1 & 1 & 1 \\
\Gamma^p & 3 & 0 & -1 & -1 & 1 \\
\Gamma^d & 5 & -1 & 1 & 1 & -1 \\
\Gamma^f & 7 & 1 & -1 & -1 & -1 \\
\end{array}
\]

\[
\Gamma = \bigoplus_i a_i \Gamma_i,
\]

\[
a_i = \frac{1}{\hbar} \sum_g [\chi_i(g)]^* \chi(g).
\]

\[
\Gamma^d = e \oplus t_2
\]
cubic crystal-field

spherical

cubic

\[ \Delta \]

\[ e_g \]

\[ t_{2g} \]

Mn  \[ [\text{Ar}]3d^5 \, 4s^2 \]

Mn\(^{3+}\) 3d\(^4\)

\[ t_{2g}^3 e_g^1 \]

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

Cu\(^{2+}\) 3d\(^9\)

\[ t_{2g}^6 e_g^3 \]
$\hat{H} = - \sum_{ii'} \sum_{\sigma} \sum_{mm'} t_{mm'}^{i,i'} c_{im\sigma}^{\dagger} c_{im'\sigma} + U \sum_i \sum_m \hat{n}_{im\uparrow} \hat{n}_{im\downarrow}$

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

$$- J \sum_i \sum_{m\neq m'} \left[ c_{im\uparrow}^{\dagger} c_{im\downarrow}^{\dagger} c_{im'\uparrow} c_{im'\downarrow} + c_{im\uparrow}^{\dagger} c_{im\downarrow}^{\dagger} c_{im'\downarrow} c_{im'\uparrow} \right],$$
the hopping integrals

\[ t^{i,i'}_{m m'} \quad i \neq i' \]
the LDA electronic structure
cubic perovskite
let us construct the $e_g$ tight-biding bands
method

\[ \hat{h}_e(r) = -\frac{1}{2}\nabla^2 - \sum_{i,\alpha} \frac{Z_{i,\alpha}}{|r - T_i - R_\alpha|} = -\frac{1}{2}\nabla^2 + \sum_{i,\alpha} v(r - T_i - R_\alpha) = -\frac{1}{2}\nabla^2 + v_R(r), \]

Bloch functions

\[ \psi_{lm}^\alpha(k, r) = \frac{1}{\sqrt{N}} \sum_i e^{i T_i \cdot k} \psi_{lm}(r - T_i - R_\alpha). \]

Wannier functions

\[ H_{lm,l'm'}^{\alpha,\alpha'}(k) = \langle \psi_{lm}^\alpha(k) | \hat{h}_e | \psi_{l'm'}^{\alpha'}(k) \rangle, \]

\[ O_{lm,l'm'}^{\alpha,\alpha'}(k) = \langle \psi_{lm}^\alpha(k) | \psi_{l'm'}^{\alpha'}(k) \rangle. \]

Hamiltonian

Overlap
tight-binding Hamiltonian

\[ H_{lm,l'm'}^{\alpha,\alpha'}(k) = \varepsilon_{l',\alpha'}^0 \: O_{lm,l'm'}^{\alpha,\alpha'}(k) + \Delta\varepsilon_{lm,l'm'}^{\alpha} \: \delta_{\alpha,\alpha'} - \frac{1}{N} \sum_{i \alpha \neq i' \alpha'} e^{i(T_{i'} - T_i) \cdot k} \: t_{lm,l'm'}^{i \alpha, i' \alpha'} \]

\[ \Delta\varepsilon_{lm,l'm'}^{\alpha} = \int d\mathbf{r} \: \overline{\psi_{lm}}(\mathbf{r} - \mathbf{R}_\alpha) \left[ v_R(\mathbf{r}) - v(\mathbf{r} - \mathbf{R}_\alpha) \right] \psi_{l'm'}(\mathbf{r} - \mathbf{R}_\alpha), \]

\[ t_{lm,l'm'}^{i \alpha, i' \alpha'} = -\int d\mathbf{r} \: \overline{\psi_{lm}}(\mathbf{r} - \mathbf{R}_\alpha - T_i) \left[ v_R(\mathbf{r}) - v(\mathbf{r} - \mathbf{R}_{\alpha'} - T_{i'}) \right] \psi_{l'm'}(\mathbf{r} - \mathbf{R}_{\alpha'} - T_{i'}). \]

keep only two-center integrals

\[ V_{lm,l'm'}^{i \alpha, i' \alpha'} = \int d\mathbf{r} \: \overline{\psi_{lm}}(\mathbf{r} - \mathbf{R}_\alpha - T_i)v(\mathbf{r} - \mathbf{R}_\alpha - T_i)\psi_{l'm'}(\mathbf{r} - \mathbf{R}_{\alpha'} - T_{i'}). \]
two-center integrals
two-center integrals

\[ V_{sp\sigma} = \cos \theta + \sin \theta \]
the LDA electronic structure
cubic perovskite
tight-binding model

\[ \epsilon_p, \epsilon_d, -V_{pd}, V_{pd}/2 \]
tight-binding model $e_g$ bands

$\sqrt{3} V_{pd}/2$

$0$


| $H_{eg}^{TB}$ | $|k\ z^c\rangle$ | $|k\ x^a\rangle$ | $|k\ y^b\rangle$ | $|k\ 3z^2 - r^2\rangle$ | $|k\ x^2 - y^2\rangle$ |
|---------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $|k\ z^c\rangle$ | $\varepsilon_p$ | 0 | 0 | $-2V_{pd\sigma s_z}$ | 0 |
| $|k\ x^a\rangle$ | 0 | $\varepsilon_p$ | 0 | $V_{pd\sigma s_x}$ | $-\sqrt{3}V_{pd\sigma s_x}$ |
| $|k\ y^b\rangle$ | 0 | 0 | $\varepsilon_p$ | $V_{pd\sigma s_y}$ | $\sqrt{3}V_{pd\sigma s_y}$ |
| $|k\ 3z^2 - r^2\rangle$ | $-2V_{pd\sigma \bar{s}_z}$ | $V_{pd\sigma \bar{s}_x}$ | $V_{pd\sigma \bar{s}_y}$ | $\varepsilon_d$ | 0 |
| $|k\ x^2 - y^2\rangle$ | 0 | $-\sqrt{3}V_{pd\sigma \bar{s}_x}$ | $\sqrt{3}V_{pd\sigma \bar{s}_y}$ | 0 | $\varepsilon_d$ |
**downfolding**

\[
H_{e_g}^{TB} = H_{dd} - H_{dp} (H_{pp} - \varepsilon I_{pp})^{-1} H_{pd},
\]

| \(H_{e_g}^{TB}\) | \(|k\ z^c\rangle\) | \(|k\ x^a\rangle\) | \(|k\ y^b\rangle\) | \(|k\ 3z^2 - r^2\rangle\) | \(|k\ x^2 - y^2\rangle\) |
|---|---|---|---|---|---|
| \(|k\ z^c\rangle\) | \(\varepsilon_p\) | 0 | 0 | \(-2V_{pd\sigma s_z}\) | 0 |
| \(|k\ x^a\rangle\) | 0 | \(\varepsilon_p\) | 0 | \(V_{pd\sigma s_x}\) | \(-\sqrt{3}V_{pd\sigma s_x}\) |
| \(|k\ y^b\rangle\) | 0 | 0 | \(\varepsilon_p\) | \(V_{pd\sigma s_y}\) | \(\sqrt{3}V_{pd\sigma s_y}\) |
| \(|k\ 3z^2 - r^2\rangle\) | \(-2V_{pd\sigma s_z}\) | \(V_{pd\sigma s_x}\) | \(V_{pd\sigma s_y}\) | \(\varepsilon_d\) | 0 |
| \(|k\ x^2 - y^2\rangle\) | 0 | \(-\sqrt{3}V_{pd\sigma s_x}\) | \(\sqrt{3}V_{pd\sigma s_y}\) | 0 | \(\varepsilon_d\) |
downfolding to $e_g$

\[
\begin{align*}
H_{e_g}^\varepsilon & & |k \ 3z^2 - r^2\rangle_{\varepsilon} & & |k \ x^2 - y^2\rangle_{\varepsilon} \\
|k \ 3z^2 - r^2\rangle_{\varepsilon} & & \varepsilon_d' - 2t^\sigma \left[ \frac{1}{4} (\cos k_x a + \cos k_y a) + \cos k_z a \right] & & 2t^\sigma \left[ \frac{\sqrt{3}}{4} (\cos k_x a - \cos k_y a) \right] \\
|k \ x^2 - y^2\rangle_{\varepsilon} & & 2t^\sigma \left[ \frac{\sqrt{3}}{4} (\cos k_x a - \cos k_y a) \right] & & \varepsilon_d' - 2t^\sigma \left[ \frac{3}{4} (\cos k_x a + \cos k_y a) \right] 
\end{align*}
\]

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

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

\[
\begin{align*}
    t_{mm'}^{i,i\pm\hat{z}} &= t_\varepsilon \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \\
    t_{mm'}^{i,i\pm\hat{x}} &= t_\varepsilon \begin{pmatrix} 3/4 & \sqrt{3}/4 \\ \sqrt{3}/4 & 1/4 \end{pmatrix} \\
    t_{mm'}^{i,i\pm\hat{y}} &= t_\varepsilon \begin{pmatrix} 3/4 & -\sqrt{3}/4 \\ -\sqrt{3}/4 & 1/4 \end{pmatrix}
\end{align*}
\]
tight-binding model

- \( V_{pd} \)
- \( \epsilon_p \)
- \( \epsilon_d \)
- \( -V_{pd} \)
- \( V_{pd}/2 \)
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 CuCr$_2$O$_4$, 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.
the many-body Hamiltonian

\[ \hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq i'} \frac{1}{|\mathbf{r}_i - \mathbf{r}_{i'}|} - \sum_{i\alpha} \frac{Z_{\alpha}}{|\mathbf{r}_i - \mathbf{R}_\alpha|} - \sum_\alpha \frac{1}{2M_\alpha} \nabla^2_\alpha + \frac{1}{2} \sum_{\alpha \neq \alpha'} \frac{Z_{\alpha}Z_{\alpha'}}{|\mathbf{R}_\alpha - \mathbf{R}_{\alpha'}|}. \]

Born-Oppenheimer Ansatz

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

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

\[ \hat{H}_n = \hat{T}_n + \varepsilon(\{\mathbf{R}_\alpha\}) \quad \text{BO surface} \]
degenerate BO surfaces

\[ \varepsilon_m(\{R^0_{\alpha}\}) = \varepsilon(\{R^0_{\alpha}\}) \]
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.
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.

References

Mulliken, R. S. 1933 Phys. Rev. 43, 279.
Placzek, G. 1934 Handbuch der Radiologie, 6, II, 205.
Tisza, L. 1933 Z. Phys. 82, 48.
normal modes

\[
\hat{H}_n = \hat{T}_n + \sum_{\alpha \mu} \left[ \frac{\partial \hat{U}_n}{\partial u_{\alpha \mu}} \right] \{R_\alpha^0\} u_{\alpha \mu} + \frac{1}{2} \sum_{\alpha \mu} \sum_{\alpha' \mu'} \left[ \frac{\partial^2 \hat{U}_n}{\partial \alpha \mu \partial \alpha' \mu'} \right] \{R_\alpha^0\} u_{\alpha \mu} u_{\alpha' \mu'} + \ldots.
\]

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

Dynamical matrix

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

Find eigenvalues and eigenvalues
two atoms

\[ H = \frac{1}{2} M_1 \dot{x}_1^2 + \frac{1}{2} M_2 \dot{x}_2^2 + V(x_1, x_2) \]

\[ V(x_1, x_2) = V(R) + \frac{1}{2} x_1 \left. \frac{\partial V}{\partial^2 x_1} \right|_0 x_1 + \frac{1}{2} x_2 \left. \frac{\partial^2 V}{\partial^2 x_2} \right|_0 x_2 + x_2 \left. \frac{\partial^2 V}{\partial x_2 \partial x_1} \right|_0 x_1 \]

\[ = V(R) + \frac{1}{2} x_1 K_{11} x_1 + \frac{1}{2} x_2 K_{22} x_2 + \frac{1}{2} x_2 (K_{12} + K_{21}) x_1 \]

\[ V(R) = 0 \]
change variables

\[ x_i = \tilde{x}_i \sqrt{M_i} \]

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

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

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

\[ Q_1 = (\tilde{x}_1 + \tilde{x}_2)\sqrt{2} \]

\[ Q_2 = (\tilde{x}_1 - \tilde{x}_2)\sqrt{2} \]

\[ \Omega_1^2 = (D_{11} + D_{12})/2 \]

\[ \Omega_2^2 = (D_{11} - D_{12})/2 \]

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

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

\[
\langle \psi_m | \hat{H}_e (\{ R_\alpha \}) | \psi_{m'} \rangle = \sum_{\alpha \mu} \langle \psi_m | \begin{bmatrix} \frac{\partial \hat{H}_e}{\partial u_{\alpha \mu}} \end{bmatrix} | \psi_{m'} \rangle u_{\alpha \mu} + \cdots = \hat{U}^{JT}_{m,m'} + .
\]

\[
\Gamma_m \otimes \Gamma_m \cap \Gamma_{\text{vibrations}} \supset A_1,
\]
group $O$, $e_g$ states

\[ [\Gamma_m \otimes \Gamma_m] \cap \Gamma_{\text{vibrations}} \supset A_1, \]

\[ \Gamma_E \otimes \Gamma_E = A_1 \oplus A_2 \oplus E \]

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

<table>
<thead>
<tr>
<th>$O$</th>
<th>$E$</th>
<th>$8C_3$</th>
<th>$3C_2$</th>
<th>$6C_2$</th>
<th>$6C_4$</th>
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<tbody>
<tr>
<td>$x^2 + y^2 + z^2$</td>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$x^2 - y^2, 3z^2 - r^2$</td>
<td>$E$</td>
<td>2</td>
<td>-1</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>$x, y, z$</td>
<td>$T_1$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$xy, xz, yz$</td>
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<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
</tr>
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modes $A_1$ and $E$

let us use symmetries

$u_1 = q_1(1,0,0)$

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<td>1</td>
<td>$-1$</td>
</tr>
</tbody>
</table>
which modes are relevant?

let us use symmetries

\[ u_1 = q_0(1,0,0) \]

\[ E \ u_1 = u_1 \]

\[ u_2 = C_4 \ u_1 = q_0(0,1,0) \]

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<td>( E )</td>
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<td>-1</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
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effect of operations

$C_4 u_1 = u_2$
$C_4 u_1 = u_3$
$C_4 u_1 = u_1$
$C_4^3 u_1 = u_6$
$C_4^3 u_1 = u_5$
$C_4^3 u_1 = u_1$
$C_4^2 u_1 = u_4$
$C_4^2 u_1 = u_4$
$C_4^2 u_1 = u_1$

$E u_1 = u_1$
effect of operations

\[ E \ u_1 = u_1 \]

\[ C_2 \ u_1 = u_2 \]
\[ C_2 \ u_1 = u_5 \]
\[ C_2 \ u_1 = u_3 \]
\[ C_2 \ u_1 = u_6 \]
\[ C_2 \ u_1 = u_4 \]
\[ C_2 \ u_1 = u_4 \]
Effect of operations

$E \ u_1 = u_1$

$C_3 \ u_1 = u_2$

$C_3 \ u_1 = u_3$

$C_3 \ u_1 = u_2$

$C_3 \ u_1 = u_5$

$C_3 \ u_1 = u_6$

$C_3 \ u_1 = u_6$

$C_3 \ u_1 = u_3$

$C_3 \ u_1 = u_5$
using the projector

\[ \hat{P}_i = \frac{d_i}{\hbar} \sum_g [\chi_i(g)]^* O(g) \]

\[ P_{A1} u_1 = (4u_1 + 4u_2 + 2u_3 + 4u_4 + 4u_5 + 4u_6)/24 \]

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</tr>
<tr>
<td>( E )</td>
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<td>( -1 )</td>
<td>( 2 )</td>
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<tr>
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<td>( 3 )</td>
<td>( 0 )</td>
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</tr>
</tbody>
</table>
let us try different displacements..

let us use symmetries

\[ u_{1z} = q_0(0,0,1) \]
effect of operations

\[ \hat{\mathcal{P}}_i = \frac{d_i}{\hbar} \sum_g [\chi_i(g)]^* O(g). \]

\[ \begin{align*}
E & \quad u_1^z = u_1^z \\
C_4^2 & \quad u_1^z = -u_1^z \\
C_4 & \quad u_1^z = u_1^y \\
C_4^3 & \quad u_1^z = -u_1^y
\end{align*} \]

\[ \begin{align*}
u_1^z &= q_0(0,0,1) \\
u_1^y &= q_0(0,1,0)
\end{align*} \]
modes $A_1$ and $E$
$Q_1 = u_1(q_1) + u_2(q_1) + u_4(q_1) + u_5(q_1),$ \\
$Q_2 = u_1(q_2) + u_2(q_2) + u_3(q_2) + u_4(q_2) + u_5(q_2) + u_6(q_2),$ \\

$u_1(q_1) = \frac{1}{\sqrt{4}} q_1(1, 0, 0) \quad u_1(q_2) = -\frac{1}{\sqrt{12}} q_2(1, 0, 0)$ \\
$u_2(q_1) = -\frac{1}{\sqrt{4}} q_1(0, 1, 0) \quad u_2(q_2) = -\frac{1}{\sqrt{12}} q_2(0, 1, 0)$ \\
$u_3(q_1) = (0, 0, 0) \quad u_3(q_2) = \frac{2}{\sqrt{12}} q_2(0, 0, 1)$ \\
$u_4(q_1) = -\frac{1}{\sqrt{4}} q_1(1, 0, 0) \quad u_4(q_2) = \frac{1}{\sqrt{12}} q_2(1, 0, 0)$ \\
$u_5(q_1) = \frac{1}{\sqrt{4}} q_1(0, 1, 0) \quad u_5(q_2) = \frac{1}{\sqrt{12}} q_2(0, 1, 0)$ \\
$u_6(q_1) = (0, 0, 0) \quad u_6(q_2) = -\frac{2}{\sqrt{12}} q_2(0, 0, 1)$
Jahn-Teller potential

\[
\langle \psi_m | \hat{H}_e (\{R_\alpha\}) | \psi_{m'} \rangle = \sum_{\alpha \mu} \langle \psi_m | \frac{\partial \hat{H}_e}{\partial u_{\alpha \mu}} \rangle_{\{R_\alpha^0\}} | \psi_{m'} \rangle u_{\alpha \mu} + \cdots = \hat{U}^\text{JT}_{m,m'} + .
\]
perturbation theory

(point charge model)

\[ d_C \rightarrow d_C + \delta d_C^\mu \]

\[ \nu_R \rightarrow \nu_R + \Delta \nu_{\text{JT}} \]

\[ \Delta \nu_{\text{JT}} = \frac{q_C}{d_C^6} \frac{25}{14\sqrt{3}} \langle r^4 \rangle \left( \begin{array}{cc} q_2 & q_1 \\ q_1 & -q_2 \end{array} \right) \]
pseudospin operators

\[ \hat{\tau}_z | \downarrow \rangle = - | \downarrow \rangle, \quad \hat{\tau}_x | \downarrow \rangle = + | \uparrow \rangle, \quad \hat{\tau}_y | \downarrow \rangle = -i | \uparrow \rangle \]
\[ \hat{\tau}_z | \uparrow \rangle = + | \uparrow \rangle, \quad \hat{\tau}_x | \uparrow \rangle = + | \downarrow \rangle, \quad \hat{\tau}_y | \uparrow \rangle = +i | \downarrow \rangle \]

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

\[ \Delta v_{JT} = \lambda \left[ q_1 \tau_x + q_2 \tau_z \right] \]
Jahn-Teller potential

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

\[ q_2 = -q \cos \theta, \quad q_1 = -q \sin \theta \]

\[ \hat{U}^{JT} = -\lambda q \left( \begin{array}{cc} \cos \theta & \sin \theta \\ \sin \theta & -\cos \theta \end{array} \right) \]
Jahn-Teller potential

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

\[ E_{JT} = \frac{\lambda^2}{2C_E} \]

\[ q_{JT} = \frac{\lambda}{C_E} \]
empty state

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

anharmonic effects determine the angle
Kugel-Khomskii 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)

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 ($\text{KCuF}_3$, $\text{LaMnO}_3$, $\text{MnF}_3$). 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.
$\hat{H} = - \sum_{ii'} \sum_{\sigma \sigma'} \sum_{mm'} t_{mm'}^{i,i'} c_{i m \sigma}^{\dagger} c_{i m' \sigma'} + U \sum_{i} \sum_{m} \hat{n}_{i m \uparrow} \hat{n}_{i m \downarrow}$

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

$- J \sum_{i} \sum_{m \neq m'} \left[ c_{i m \uparrow}^{\dagger} c_{i m \downarrow}^{\dagger} c_{i m' \uparrow} c_{i m' \downarrow} + c_{i m \uparrow}^{\dagger} c_{i m \downarrow} c_{i m' \uparrow}^{\dagger} c_{i m' \downarrow} \right]$,
two-site problem, one electron per site

\[ \hat{H} = \hat{H}_0 + \hat{H}_T + \hat{H}_U \]

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

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

\[ \hat{H}_U = U \sum_{i=AB} \sum_{m} \hat{n}_{im\uparrow} \hat{n}_{im\downarrow} + \frac{1}{2} \sum_{i=AB} \sum_{\sigma\sigma'} \sum_{m \neq m'} (U - 2J - J\delta_{\sigma,\sigma'}) \hat{n}_{i\sigma\sigma} \hat{n}_{i m'\sigma'}. \]
two-site problem, one electron per site

16 states with $N_d=0$

12 states with $N_d=1$

\[ E = 2\varepsilon_d \]

\[ E = 2\varepsilon_d + U + E_J \]
energies of doubly occupied states

\[
\begin{align*}
|2, 0\rangle_{\alpha'} & = \; E_{\alpha'}(2, 0) \\
|2, 0\rangle_{i1m} & = \; c_{im\uparrow}^\dagger c_{im\downarrow}^\dagger |0\rangle \quad 2\varepsilon_{eg} + U \\
|2, 0\rangle_{i2m} & = \; c_{im\uparrow}^\dagger c_{im'\downarrow}^\dagger |0\rangle \quad 2\varepsilon_{eg} + U - 2J \quad m' \neq m \\
|2, 0\rangle_{i3\sigma} & = \; c_{im\sigma}^\dagger c_{im'\sigma}^\dagger |0\rangle \quad 2\varepsilon_{eg} + U - 3J \quad m' \neq m
\end{align*}
\]
classify states in order of $N_d$

$N_d =$ number doubly occupied sites
second order perturbation theory

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

| \[2, 0\]_{\alpha'} | \[2, 0\]_{i1m} = c_{im}^\dagger c_{im}^\dagger |0\rangle |2\varepsilon_{eg} + U| \[2, 0\]_{i2m} = c_{im}^\dagger c_{im'}^\dagger |0\rangle |2\varepsilon_{eg} + U - 2J | m' \neq m| \[2, 0\]_{i3\sigma} = c_{im\sigma}^\dagger c_{im'\sigma}^\dagger |0\rangle |2\varepsilon_{eg} + U - 3J | m' \neq m
|
second order perturbation theory

\[ \Delta E = \frac{-2t^2}{(U-3J)} \]

\[ \Delta E = 0 \]

\[ \Delta E = \frac{-2t^2}{(U-2J)} \]

\[ \Delta E = \frac{-2t^2}{U} \]
Kugel-Khomskii super-exchange

\[ \hat{H}_{\text{SE}} = 2\Gamma_{++} \left[ S^A \cdot S^B - \frac{1}{4} \right] \left[ O_A^z O_B^z + \frac{1}{4} \right] + 2\Gamma_{+-} \left[ \frac{1}{4} + S^A_z S^B_z \right] \left[ O^A \cdot O^B - \frac{1}{4} \right] \\
+ 2\Gamma_{--} \left[ \left( S^A \cdot S^B - S^A_z S^B_z \right) \left( O^A \cdot O^B - O_A^z O_B^z \right) - \left( S^A_z S^B_z - \frac{1}{4} \right) \left( O_A^z O_B^z - \frac{1}{4} \right) \right] \\
\]

\[ \Gamma_{++} = \frac{4t^2}{U} \quad \Gamma_{+-} = \frac{4t^2}{U - 3J} \quad \Gamma_{--} = -\frac{4t^2}{U - 2J}. \]
LaMnO$_3$

\[
\begin{align*}
  t^{i,i\pm \hat{z}}_{mm'} &= t_\varepsilon \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \\
  t^{i,i\pm \hat{x}}_{mm'} &= t_\varepsilon \begin{pmatrix} \frac{3}{4} & \frac{\sqrt{3}}{4} \\ \frac{\sqrt{3}}{4} & \frac{1}{4} \end{pmatrix} \\
  t^{i,i\pm \hat{y}}_{mm'} &= t_\varepsilon \begin{pmatrix} \frac{3}{4} & -\frac{\sqrt{3}}{4} \\ -\frac{\sqrt{3}}{4} & \frac{1}{4} \end{pmatrix}
\end{align*}
\]
Kugel-Khomskii super-exchange

\[ \hat{H}^z_{SE} \sim -\frac{1}{U} \sum_E \hat{H}_T |E\rangle \langle E| \hat{H}^\dagger_T \]

\[ = -\frac{t^2}{U} \frac{1}{2} \sum_{ii'} \sum_{\sigma}\sum_{\sigma'} \sum_{\alpha} \left\{ c^\dagger_{i\tau\sigma} |0\rangle_i i \langle 0| c_{i'\tau\sigma'} \left[ c_{i'\tau\sigma'} |2\rangle_{\alpha'} i' \langle i'| c^\dagger_{i'\tau\sigma'} \right] + (i \leftrightarrow i') \right\} \delta_{\tau,\lambda} \]

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

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

\[ \hat{o}_{\tau\tau'}^z = \left[ \frac{n_i}{2} \hat{I} + (-1)^\tau O_z^i \right] \delta_{\tau\tau'}, \]
\[ \hat{o}_{\tau\tau'}^+ = O_+^i (1 - \delta_{\tau\tau'}) \]
\[ \hat{o}_{\tau\tau'}^- = O_-^i (1 - \delta_{\tau\tau'}) \]

\[ \hat{s}_{\sigma\sigma'}^z = \left[ \frac{n_i}{2} \hat{I} + (-1)^\sigma S_z^i \right] \delta_{\sigma\sigma'}, \]
\[ \hat{s}_{\sigma\sigma'}^+ = S_+^i (1 - \delta_{\sigma\sigma'}) \]
\[ \hat{s}_{\sigma\sigma'}^- = S_-^i (1 - \delta_{\sigma\sigma'}), \]
Kugel-Khomskii super-exchange

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

other dirs: rotate axis and back

\[ O_z^i \xrightarrow{\hat{z} \rightarrow \hat{x}} - \frac{1}{2} O_z^i - \frac{\sqrt{3}}{2} O_x^i \]

\[ O_z^i \xrightarrow{\hat{z} \rightarrow \hat{y}} - \frac{1}{2} O_z^i + \frac{\sqrt{3}}{2} O_x^i \]
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

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

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

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

\[ \theta = \pi/2 \text{ (Jahn-Teller-like } Q_1 \text{ distortion).} \]
KCuF$_3$

e_g^3$: 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
$\text{KCuF}_3$

$e_g^3$: 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 $Q_1$

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

recent insights from our work

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

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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[9]). 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!
Structural Relaxation due to Electronic Correlations in the Paramagnetic Insulator KCuF₃

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In conclusion, by formulating GGA+DMFT—the merger of the GGA and DMFT—is formulated within a computational scheme [9], whereas the lower and upper Hubbard bands are seen to interact in contradiction to experiment since the extremely shallow hybridization at about 3 eV corresponds to the fully occupied 3⁡g⁡ orbitals. We note that even without a JT distortion for δJT = 0 yields a symmetric orbital polarization with the experimental value of 4.4% [20]. This clearly shows that the JT distortion in paramagnetic KCuF₃ ≃ 5% would imply that KCuF₃ does not have any JT distortion for δJT = 0.

The spectral density of paramagnetic KCuF₃ computed by GGA and GGA+DMFT(QMC) for diatomic-sphere approximation used in the L(N)MTO method is not suitable since it cannot determine atomic-sphere approximation used in the L(N)MTO method is not suitable since it cannot determine atomic correlations among the partially filled Cu⁡g⁡ orbitals. We note that even without a JT distortion for δJT = 0 yields a symmetric orbital polarization with the experimental value of 4.4% [20]. This clearly shows that the JT distortion in paramagnetic KCuF₃ ≃ 5% would imply that KCuF₃ does not have any JT distortion for δJT = 0.

However, for investigations going beyond equilibrium volume, electronic correla-tions play a role. Extensions of LDA, e.g., for solids with long-range order. Hence the computation of results, e.g., the band gap value and local moment, but only such contributions and can thus fully describe the effect of the limitations of the L(N)MTO scheme in the direct equilibrium Jahn-Teller distortion and δJT (% of a) is a wealth of ordering phenomena and complex doping also make them highly attractive for technological applications. Here the recently developed combination of band-structure methods and DMFT is able to calculate lattice relaxation effects caused by the T > 5% would imply that KCuF₃ does not have any JT distortion for δJT = 0.

The electronic structure of materials can often be de-scritized around the atoms. By contrast, the plane-wave distribution along the axis [inset (a)] i.e., the Cu⁡g⁡ orbitals are almost equally occupied and hence are not fully filled. The sharply defined orbital polarization is obtained for all elements in the so-called Mott metal-insulator transition as encountered in the prototypical JT system K⁡g⁡CuF₃.

The sharp feature in the spectral density at about 3 eV and the high minimum at about 98% for δJT ≃ 7 eV and 2% respectively. The electronic correlations were also found to be responsible for the antiferro-orbital ordering, agree well with experiment. This antiferro-orbital order is found in GGA+DMFT. This is the case that, in contrast to the GGA+DMFT, the GGA charge density is more or less the same along the axis [inset (a)], i.e., the Cu⁡g⁡ orbitals are almost equally occupied and hence are not fully filled. The sharply defined orbital polarization is obtained for all elements in the so-called Mott metal-insulator transition as encountered in the prototypical JT system K⁡g⁡CuF₃.

Additionally, the total energies as a function of the JT distortion (JT) effect—the spontaneous lifting of the degeneracy of the JT distortions play a role. Extensions of LDA, e.g., structural properties of materials where electronic correlations. To this end, the framework is able to allow us to calculate lattice relaxation effects caused by the T > 5% would imply that KCuF₃ does not have any JT distortion for δJT = 0.

The total energies as a function of the JT distortion (JT) effect—the spontaneous lifting of the degeneracy of the JT distortions play a role. Extensions of LDA, e.g., structural properties of materials where electronic correlations. To this end, the framework is able to allow us to calculate lattice relaxation effects caused by the T > 5% would imply that KCuF₃ does not have any JT distortion for δJT = 0.
KK is the mechanism: \( T_{OO} \sim T_{KK} \)

...or, is it?

Problems:

- why \( T_N \) (40K-140K) much smaller than \( T_{JT} \) (800-1400 K)?
- 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

\[ H = - \sum_{ii'} \sum_{mm'} \sum_{\sigma} t_{mm'}^{ii'} c_{im\sigma}^\dagger c_{i'm'\sigma} \]
\[ + U \sum_{im} n_{im\uparrow} n_{im\downarrow} \]
\[ + \frac{1}{2} \sum_{im \neq m' \sigma \sigma'} (U - 2J - J \delta_{\sigma \sigma'}) n_{im\sigma} n_{im'\sigma'} \]
\[ - J \sum_{m \neq m'} (c_{m\uparrow}^\dagger c_{m\downarrow}^\dagger c_{m'\uparrow} c_{m'\downarrow} + c_{m\uparrow}^\dagger c_{m\downarrow} c_{m'\uparrow}^\dagger c_{m'\downarrow}^\dagger) \]

two-band model
LDA+DMFT with Wannier functions

\[ H = - \sum_{im} \sum_{\sigma} t_{im}^{\uparrow \downarrow} c_{im}^{\dagger} c_{im^\prime}^{\sigma} c_{im^\prime}^{\dagger} c_{im}^{\sigma} + U \sum_{im} n_{im} n_{im^\downarrow} \]
\[ + \frac{1}{2} \sum_{im \neq m^\prime} (U - 2J - J_{\delta\sigma\sigma'}) n_{im^\sigma} n_{im^\prime\sigma'} \]
\[ - J \sum_{m \neq m^\prime} \left( c_{m^\uparrow}^{\dagger} c_{m^\downarrow}^{\dagger} c_{m^\prime}^{\uparrow} c_{m^\downarrow} + c_{m^\uparrow}^{\dagger} c_{m^\downarrow}^{\dagger} c_{m^\prime}^{\downarrow} c_{m^\uparrow} \right) \]

\[ G_{m,m'} = \sum_{k,n} \left[ \frac{1}{i \omega_n + \mu - H_{0k} - \Sigma(i \omega_n)} \right]_{m,m'} \]
LDA+DMFT with Wannier functions

\[
H = - \sum_{ii'} \sum_{mm'} \sum_{\sigma} t_{mm'}^{ii'} c_{im\sigma}^\dagger c_{im'\sigma}
+ U \sum_{im} n_{im\uparrow} n_{im\downarrow}
+ \frac{1}{2} \sum_{im\neq m'\sigma\sigma'} (U - 2J - J\delta_{\sigma\sigma'}) n_{im\sigma} n_{im'\sigma'}
- J \sum_{m\neq m'} (c_{m\uparrow}^\dagger c_{m'\uparrow} c_{m\downarrow} + c_{m\uparrow}^\dagger c_{m\downarrow} c_{m'\uparrow} + c_{m'\uparrow}^\dagger c_{m\downarrow} + c_{m\downarrow}^\dagger c_{m'\uparrow})
\]

self-energy matrix spin-orbital space

DMFT and cDMFT

quantum impurity solvers:
- general HF QMC
- general CT-INT QMC
- general CT-HYB QMC

• A. Flesch, E. Gorelov, E. Koch and E. Pavarini
  *Multiplet effects in orbital and spin ordering phenomena: A hybridization-expansion quantum impurity solver study*
the KK mechanism in KCuF$_3$


\[ T_{KK} \ll T_{OO} > 1400 \text{ K} \]

reminder: mean field theory overestimates \( T_{KK} \)
LaMnO$_3$ : $T_{KK} \sim 600$ K !!


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

non-JT crystal-field
red: cDMFT 4 sites
black: DMFT

experiments
super-exchange

$I_0$ : ideal cubic
$R_0$ : real but no JT

LaMnO$_3$ crystal structure

$\theta$ : angle of crystal-field axis

$T_{KK}$ : Kramers-Kronig temperature
Neutron-diffraction study of the Jahn-Teller transition in stoichiometric LaMnO$_3$

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(Received 2 September 1997)

The parent compound of the giant magnetoresistance Mn-perovskite, LaMnO$_3$, has been studied by thermal analysis and high-resolution neutron-powder diffraction. The orthorhombic Pnam structure at room temperature is characterized by an antiferrodistorsive orbital ordering due to the Jahn-Teller effect. This ordering is evidenced by the spatial distribution of the observed Mn-O bond lengths. LaMnO$_3$ undergoes a structural phase transition at $T_N$~750 K, above which the orbital ordering disappears. There is no change in symmetry although the lattice becomes metrically cubic on the high-temperature side. The MnO$_6$ octahedra become nearly regular above $T_N$ 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. [S0163-1829/98/57106-7]
Orbital Correlations in the Pseudocubic O and Rhombohedral R Phases of LaMnO$_3$

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The local and intermediate structure of stoichiometric LaMnO$_3$ has been studied in the pseudocubic and rhombohedral phases at high temperatures (300–1150 K). Neutron powder diffraction data were collected and a combined Rietveld and high real space resolution atomic pair distribution function analysis was carried out. The nature of the Jahn-Teller (JT) transition around 750 K is confirmed to be orbital order to disorder. In the high-temperature orthorhombic (O) and rhombohedral (R) phases, the MnO$_6$ octahedra are still fully distorted locally. More importantly, the intermediate structure suggests the presence of local ordered clusters of diameter $\sim$16 Å ($\sim$4 MnO$_6$ octahedra) implying strong nearest-neighbor JT antiferrodistortive coupling. These clusters persist well above the JT transition temperature even into the high-temperature R phase.

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$T_{oo} \sim 800 \text{ K}$

$T_{JT} > 1150 \text{ K}$
$T_{oo} \sim 800$ K and $T_{KK} \sim 600$ K !!

LaMnO$_3$

Is super-exchange driving $oo$ melting?

Rodriguez-Carvajal et al., PRB 57, R3189 (1996)
is super-exchange driving oo melting?

approach: REMnO₃ series + high pressure data

$T_{oo}$ ...

.. increases with decreasing ionic radius

.. decreases with increasing pressure
without distortions

\( T_{KK} \) decreases with IR

\( T_{OO} \) in experiments

\( T_{KK} \)
- from orbital polarization
- from total energy

\( T_{KK} \)

LaMnO\(_3\)

KCuF\(_3\)

KCrF\(_3\)


Using our general CT-HYB code we could show that

spin flip and pair hopping do not change trends

5 bands yield same result as two bands

Conclusion

KBF$_3$, K$_2$BF$_4$ and ReMnO$_3$

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

$T_{KK}$ remarkably large

but static splitting essential

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

Super-exchange alone cannot explain trends in $T_{OO}$
Elecron-phonon coupling


emergence of local spins and pseudospins

high energy

low energy

electron-phonon coupling

crystal-field splitting enhanced by coulomb repulsion

super-exchange interactions

purely electronic mechanism coupling $4t^2/U$