

ATOMIC ORBITAL, CRYSTAL FIELD THEORY AND DEGENERATE PERTURBATION THEORY

BASICS FOR MICROSCOPIC ORIGIN OF COUPLINGS BETWEEN PSEUDOSPINS

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The is part of the appendices of my Master's thesis. Short notes like this is not my original discovery, but I still uploaded them for pedagogical purposes of my own. This note contains many immature expressions of physics in that period, so revision and additional detail of the statements are necessary.

1 Atomic Orbitals and Crystal Field Theory

In quantum mechanics, we've learned the exact solution of a hydrogen atom, i.e., single electron wave function with a centrifugal potential $V(r)$. The general form of its eigenfunction is written as

$$\psi_{nlm}(\vec{r}) = R_{nl}(r)Y_{lm}(\theta, \phi), \quad (1)$$

where $Y_{lm}(\theta, \phi)$ is the spherical harmonics. For $\alpha\text{-RuCl}_3$, the outer electrons share the same principal quantum number ($n=4$) and orbital angular momentum quantum number ($l=2$), simplifying the complexity of the total wave function in the atomic level. The list of the spherical harmonics is in Table 1.

(n, l, m)	symbol	mathematical form $Y_{lm}(\theta, \phi)$
$(4, 2, 2)$	$ 2\rangle$	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta e^{2i\phi}$
$(4, 2, 1)$	$ 1\rangle$	$-\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta e^{i\phi}$
$(4, 2, 0)$	$ 0\rangle$	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$
$(4, 2, -1)$	$ -1\rangle$	$\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta e^{-i\phi}$
$(4, 2, -2)$	$ -2\rangle$	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta e^{-2i\phi}$

Table 1. Spherical harmonics with $n = 4$, $l = 2$.

Combine these functions to form two sets of modes

$$\begin{aligned} e_g &= \{|x^2 - y^2\rangle, |z^2\rangle\}, \\ t_{2g} &= \{|xy\rangle, |yz\rangle, |xz\rangle\}, \end{aligned} \quad (2)$$

where

$$\begin{aligned} |x^2 - y^2\rangle &= \frac{1}{\sqrt{2}}(|2\rangle + |-2\rangle) \\ |z^2\rangle &= |0\rangle \\ |xy\rangle &= -\frac{i}{\sqrt{2}}(|2\rangle - |-2\rangle) \\ |yz\rangle &= -\frac{1}{\sqrt{2}}(|1\rangle - |-1\rangle) \\ |xz\rangle &= \frac{i}{\sqrt{2}}(|1\rangle + |-1\rangle) \end{aligned} \quad (3)$$

are all real eigenfunctions. In crystal field theory where ligands appear around an atom, the degenerate eigenstates split into two groups e_g and t_{2g} with higher and lower energy, respectively. This energy difference comes from the distance between the outer shell electrons and the ligands. See Fig. 1 and 2.

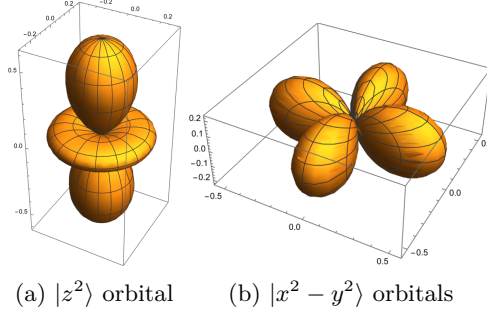


Figure 1. e_g orbitals. By convention, we put the ligands on the x, y and z axis. The distances between the orbitals and the ligands are shorter compared with that in Fig.2. This notation e_g means it is doubly degenerate (e) and symmetric under inversion (g).

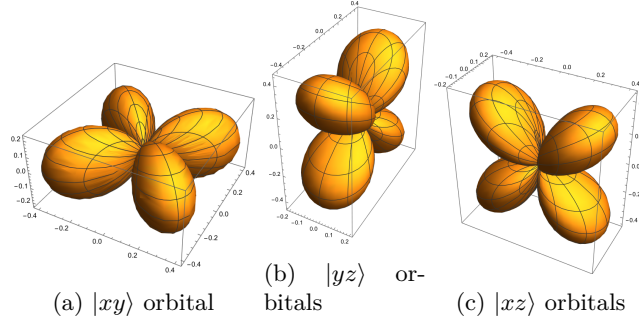


Figure 2. t_{2g} orbitals. By convention, we put the ligands on the x, y and z axis. The distances between the orbitals and the ligands are longer compared with that in Fig.1. This notation t_{2g} means it is triply degenerate (t) and symmetric under inversion (g).

2 Degenerate Perturbation Theory

2.1 1D crystal with a half-filled band

Before we discuss the Hubbard potential $U \sum_i n_{i\uparrow} n_{i\downarrow}$, which describes the Coulomb interaction of two electrons in the same orbitals, we first construct a bound state approximation model, i.e., a tight-binding model, of 1D crystal. The form of the tight-binding model is

$$H_{tb} = -t \sum_{\langle ij \rangle, \sigma} c_{i,\sigma}^\dagger c_{j,\sigma}, \quad (4)$$

which describes the hopping of an electron from one orbital of the site j to that of the site i . Notice that the orbitals that an electron resides in are atomic orbitals, and that's the reason I call the tight-binding model a "bound state approximation"¹.

Now add the Hubbard potential to the tight binding model

$$H = -t \sum_{\langle ij \rangle, \sigma} c_{i,\sigma}^\dagger c_{j,\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \quad (5)$$

When $U \ll t$, we can *imagine* that the original band of the tight-binding model is unchanged, the Hubbard potential U only redistributes the electrons in the band² in order

¹Of course we can always consider the mixing of orbitals (or any form of deformation) to make this approximation closer to the real case.

²I haven't estimated the effect of U as a perturbative term. Let's suppose that when U is large, the

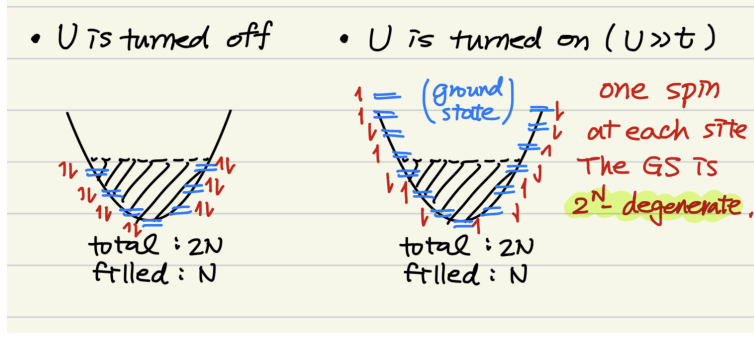


Figure 3. Left: Spin localized when U is turned off. Right: Large U will make spins localized one at a site, forming a spin chain (or spin lattice for 2D).

to minimize the total energy.

Consider a band with $2N$ states with spins degenerate in each state. When the system is in zero temperature, according to Fermi-Dirac distribution, the electrons will be localized in the lowest energy states, which we can see in the picture (Fig. 3, Left). It's easy to imagine that when U is large, the spins tend to leave each other and therefore no longer stay in the lowest states of the band. When U is large enough, a large enough energy difference will make the band *split* into two sub-bands and form a **Mott insulator**. Each of them will contain part of the original states (total $2N$ states), and this is called the **spectral weight transfer**, which is the characteristic of a Mott insulator.

2.2 Degenerate perturbation theory

We need perturbation theory to help us analyze the eigen-energies and eigenvectors of a new H which is slightly deviated from H_0 by H_1 , i.e.,

$$H = H_0 + \lambda H_1. \quad (6)$$

For instance in the next section, we will discuss the limit $U \gg t$, which has a degenerate spectrum for $H_0 = U \sum_i n_{i\uparrow} n_{i\downarrow}$.

Suppose we have an orthonormal basis $\{|j\rangle\}$ for the Hamiltonian H_0 , where $j = 1, 2, \dots, g$ and for $j = 1, 2, \dots, g_0$, the energy is degenerate,

$$\begin{aligned} H_0|\alpha\rangle &= E_\alpha|\alpha\rangle, \quad \alpha = 1, \dots, g_0 \\ H_0|\mu\rangle &= E_\mu|\mu\rangle, \quad \mu = g_0 + 1, \dots, g. \end{aligned} \quad (7)$$

The subspace spanned by $\{|\alpha\rangle\}$ is denoted as Ω_0 . The problem is to find the perturbed spectrum in Ω_0 . Notice that we require

$$|\lambda\langle\alpha|H_1|\mu\rangle| \ll |E_\alpha - E_\mu|, \quad (8)$$

which is the condition for perturbation. And whether the spectrum outside Ω_0 is degenerate or not doesn't matter. Write down the eigenstates $|a\rangle$, which stem from $|\alpha\rangle$, for the total Hamiltonian H

$$|a\rangle = \sum_{\alpha} c_{\alpha}|\alpha\rangle + \sum_{\mu} d_{\mu}|\mu\rangle, \quad (9)$$

band will not be altered (we can still use the tight-binding band).

where c_α and d_μ are of $\mathcal{O}(1)$ and $\mathcal{O}(\lambda)$, respectively. Use the form $(H - E_a)|a\rangle = 0$,

$$(H_0 + \lambda H_1 - E_a)|a\rangle = \sum_\alpha c_\alpha (E_\alpha - E_a + \lambda H_1)|\alpha\rangle + \sum_\mu d_\mu (E_\mu - E_a + \lambda H_1)|\mu\rangle = 0. \quad (10)$$

Project it onto some state $|\beta\rangle$ in Ω_0 and another state $|\nu\rangle$ outside Ω_0 ,

$$\begin{aligned} c_\beta (E_\beta - E_a) + \lambda \sum_\alpha c_\alpha \langle \beta | H_1 | \alpha \rangle + \lambda \sum_\mu d_\mu \langle \beta | H_1 | \mu \rangle &= 0, \\ \lambda \sum_\alpha c_\alpha \langle \nu | H_1 | \alpha \rangle + d_\nu (E_\nu - E_a) + \lambda \sum_\mu d_\mu \langle \nu | H_1 | \mu \rangle &= 0. \end{aligned} \quad (11)$$

Remember that d_μ is of order $\mathcal{O}(\lambda)$. So the last term of the second equation can be eliminated and we have

$$d_\nu = \frac{1}{E_a - E_\nu} \lambda \sum_\alpha c_\alpha \langle \nu | H_1 | \alpha \rangle \quad (12)$$

Put it back into the first equation,

$$\begin{aligned} c_\beta (E_\beta - E_a) + \sum_\alpha c_\alpha \left(\lambda \langle \beta | H_1 | \alpha \rangle + \lambda^2 \sum_\mu \frac{1}{E_a - E_\mu} \langle \beta | H_1 | \mu \rangle \langle \mu | H_1 | \alpha \rangle \right) &= 0, \\ c_\beta (E_a - E_\beta) = \langle \beta | \left(\lambda H_1 + \lambda^2 \sum_\mu \frac{H_1 | \mu \rangle \langle \mu | H_1}{E_a - E_\mu} \right) \left(\sum_\alpha c_\alpha | \alpha \rangle \right). \end{aligned} \quad (13)$$

If you look at this equation carefully, you will find that it is an expression of the elements of the effective Hamiltonian³

$$H_{eff} = \lambda P H_1 P + \lambda^2 P H_1 \frac{1 - P}{E_a - H_0} H_1 P, \quad (14)$$

which operates only on the subspace Ω_0 , and $P = \sum_\alpha |\alpha\rangle \langle \alpha|$ is a projection operator. To make a matrix form of H_{eff} , we substitute E_a with \bar{E}_a , which is the mean energy in Ω_0 .

As for the replacement of E_μ by H_0 , I kind of realized its meaning, but **I haven't understood it** in a careful way and made myself confident enough to say this substitution is suitable.

2.3 The limit $U \gg t$

When t is turned off, we expect the spins to be localized at each site (Fig. 3, right) since two spins occupying the same sites will contribute energy U . To estimate the effect of tight-binding term when $U \gg t$, we are going to treat $-t \sum_{\langle ij \rangle, \sigma} c_{i, \sigma}^\dagger c_{j, \sigma}$ with perturbation theory. Due to the form of these operators, It might be better to discuss the perturbation in the Fock space (particle number space). First, let's consider the spins arranged in a parallel / anti-parallel ordering. Parallel ordering prevents electrons from hopping to their nearest neighbor because of the Pauli exclusion principle. On the other hand, the anti-parallel ordering allows a transition to an intermediate state and back to the original anti-parallel ordering.

³In fact this expression for elements does not form an ordinary matrix since the index for this matrix will be $\mathbf{H}_{eff}(\beta a')$. β and $a' = \sum_\alpha c_\alpha |\alpha\rangle$ are two different bases for the same subspace Ω_0 .

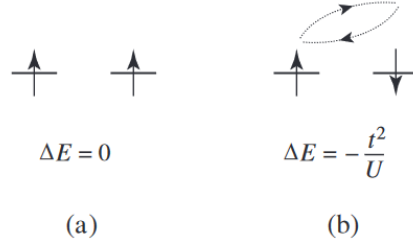


Figure 4. From Khomskii, "Transition metal compounds". (a) the perturbed energy of parallel ordering = 0. Remember that we're discussing the electron behaviors on a half-filled band. (b) The second-order perturbation gives a nonzero value. $\Delta E = \sum_n \frac{|\langle 0 | H_1 | n \rangle|^2}{\bar{E}_a - E_n}$ should count over all possible states. But remember H_1 is simply one hopping, only $\bar{E}_a - E_n = -U$ is allowed.

Notice that these localized spin chains form a 2^N -degenerate subspace of H_0 . We use perturbation theory to find the 2^{nd} -order perturbation⁴, the energy scale is like Fig.??, which matches our imagination for the behaviors.

The formal way to construct an effective Hamiltonian is using the expression eq14. Here let's take advantage of the physical picture of an effective Hamiltonian. An effective Hamiltonian H_{eff} is an approximation focusing on the degenerate subspace, i.e., H_{eff} operates on the degenerate subspace Ω_0 . So the trick is to find the components of $H_1 H_1$ that operate on Ω_0 ⁵. Then things will become much easier:

$$\begin{aligned}
 H_1 H_1 &= t^2 \left(\sum_{i,j,\sigma} c_{i\sigma}^\dagger c_{j\sigma} \right) \left(\sum_{l,m,\sigma'} c_{l\sigma'}^\dagger c_{m\sigma'} \right) = t^2 \left(\sum_{i,j,\sigma} c_{i\sigma}^\dagger c_{j\sigma} \right) \left(\sum_{j,i,\sigma} c_{j\sigma'}^\dagger c_{i\sigma'} \right) \\
 &= \left(\sum_{i,j} c_{i\uparrow}^\dagger c_{j\uparrow} + c_{i\downarrow}^\dagger c_{j\downarrow} \right) \left(\sum_{j,i} c_{j\uparrow}^\dagger c_{i\uparrow} + c_{j\downarrow}^\dagger c_{i\downarrow} \right).
 \end{aligned} \tag{15}$$

2.4 Mapping electron to spin operator

Clearly when wandering around the low-energy subspace of a Mott insulator (with perturbation), we don't need the whole Fock space and c^\dagger, c to describe our problem⁶. Let's introduce a transformation from the electron operators to the spin operators,

$$\begin{aligned}
 c_{i\uparrow}^\dagger c_{i\uparrow} &\Rightarrow \frac{1}{2} + S_i^Z, \\
 c_{i\downarrow}^\dagger c_{i\downarrow} &\Rightarrow \frac{1}{2} - S_i^Z, \\
 c_{i\uparrow}^\dagger c_{i\downarrow} &\Rightarrow S_i^+, \\
 c_{i\downarrow}^\dagger c_{i\uparrow} &\Rightarrow S_i^-.
 \end{aligned} \tag{16}$$

Put this back into eq.15, we will have

$$H_1 H_1 = 2t^2 \sum_{i,j} \left(\frac{1}{4} + S_i \cdot S_j \right). \tag{17}$$

⁴The diagonal elements of tight-binding terms are zero with the basis of particle numbers at each site.

⁵It might go wrong, but it is worth a shot, not to mention that we might have another physical picture to support this "reckless" try.

⁶symmetry approach?

and the effective Hamiltonian for the tight-binding terms is

$$H_{eff} = \frac{2t^2}{U} \sum_{i,j} \left(\frac{1}{4} + S_i \cdot S_j \right). \quad (18)$$

3 Application in Large- U -Limit Hubbard Model

3.1 The Second Quantization

When dealing with more than one indistinguishable particle, the second quantization picture simplifies the description of our many-body state. Let \bar{N} represent the total number of Ru^{3+} ions in the crystal. By second-quantizing the Hamiltonian $H_\Delta + H_\lambda$, which originally operates on $\mathcal{H}_{0,i}^{\otimes \bar{N}}$, we transform it into an operator acting on the Fock space \mathcal{F} .

$$H_{\mathcal{F}} = (H_\Delta + H_\lambda)_{\mathcal{F}} = \sum_{i'=i} \Psi_{i', (E_{\varepsilon'}, (\alpha'))}^\dagger [H_{0,i'}]_{(E_{\varepsilon'}, (\alpha')), (E_{\varepsilon}, (\alpha))} \Psi_{i, (E_{\varepsilon}, (\alpha))}, \quad (19)$$

$$\Psi_{i, (E_{\varepsilon}, (\alpha))} = (c_{i, E_{0, (1)}}, c_{i, E_{0, (2)}}, c_{i, E_{0, (3)}}, c_{i, E_{0, (4)}}, c_{i, E_{1, (1)}}, c_{i, E_{1, (2)}})^T.$$

where \mathcal{F} indicates that the Hamiltonian is written in Fock space, $\varepsilon' = 0, 1$ denotes the ε'^{th} lowest eigenenergy, while $\alpha' = 0, 1, 2, \dots$ represents the α'^{th} degenerate eigenstate corresponding to the ε'^{th} lowest eigenenergy. $[H_{0,i'}]_{(E_{\varepsilon'}, (\alpha')), (E_{\varepsilon}, (\alpha))}$ is diagonalized. The many-body state is

$$|n_{E_{0, (1)}}, n_{E_{0, (2)}}, n_{E_{0, (3)}}, n_{E_{0, (4)}}, n_{E_{1, (1)}}, n_{E_{1, (2)}}\rangle^{\otimes \bar{N}} \quad (20)$$

where $|n_{E_{0, (1)}}, n_{E_{0, (2)}}, n_{E_{0, (3)}}, n_{E_{0, (4)}}, n_{E_{1, (1)}}, n_{E_{1, (2)}}\rangle$ denotes the occupation representation of electrons on a single ion.

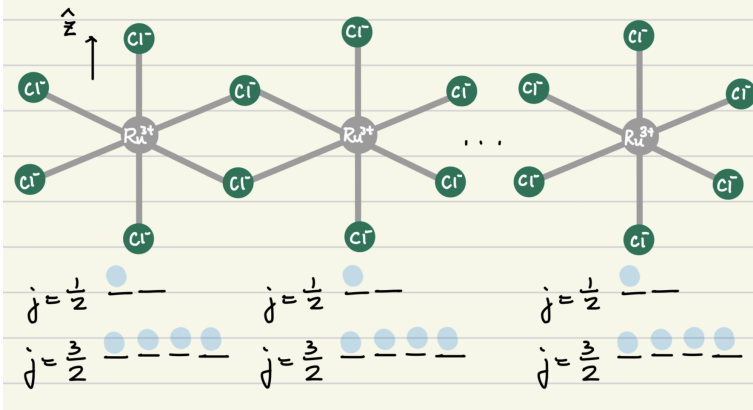


Figure 5. One of the many-body ground states of a crystal composed of edge-shared tetrahedra, where each site has 5 valence electrons (blue circles), is illustrated. This depiction uses the occupation representation. When a single electron occupies a certain eigenstate, a many-body state is automatically reconstructed to satisfy the symmetrization/anti-symmetrization rule for bosons/fermions. The \hat{z} -axis labeled at the top-left corner is a local axis for a tetrahedron, perpendicular to the plane containing the shared chlorides and bonds.

If we allow hopping from the orbitals at site j to those nearest site i , the electrons are no longer bound states. we write the H_1 in the 2^{nd} quantization language,

$$H_1 = \sum_{i,j,\sigma} [\Psi_{i,\sigma}]_{\eta'}^\dagger [H_{t,ij\sigma}]_{\eta'\eta} [\Psi_{j,\sigma}]_{\eta},$$

where i, η, σ are the indices for the basis vectors with orbital η , spin σ at site i . The H_1 comes from the overlap of orbitals, so first, it is independent of spin degrees of freedom σ , i.e., $H_{ij\uparrow} = H_{ij\downarrow}$. We sum over σ and rewrite the expression, then

$$\begin{aligned} H_1 &= \sum_{ij} [\Psi_i]_{\eta'\sigma'} [H_{1,ij}]_{\eta'\sigma'\eta\sigma} [\Psi_i]_{\eta\sigma}, \\ [H_{1,ij}]_{\eta'\sigma'\eta\sigma} &= \begin{bmatrix} a & 0 & b^* & 0 & c^* & 0 \\ 0 & a & 0 & b^* & 0 & c^* \\ b & 0 & d & 0 & e^* & 0 \\ 0 & b & 0 & d & 0 & e^* \\ c & 0 & e & 0 & f & 0 \\ 0 & c & 0 & e & 0 & f \end{bmatrix}, \\ [\Psi_i]_{m\sigma} &= \begin{pmatrix} d_{i,xy,\uparrow} \\ d_{i,xy,\downarrow} \\ d_{i,yz,\uparrow} \\ d_{i,yz,\downarrow} \\ d_{i,xz,\uparrow} \\ d_{i,xz,\downarrow} \end{pmatrix}. \end{aligned} \quad (21)$$

d and d^\dagger are the creation and annihilation operators, respectively.

To find the possible hopping, we choose to start with the basis of real orbitals $\eta = xy, yz, xz$, so we can cross out those hoppings with zero orbital overlaps,

$$\int \langle i, \eta', \sigma | x \rangle \langle x | j, \eta, \sigma \rangle dx = 0. \quad (22)$$

These hoppings with zero overlaps can be identified by examining the relative signs of the neighboring orbitals, which are determined by the structure of crystals, i.e., the relative positions and angles of sites. For the edge-shared tetrahedrons, electrons at site j can only hop from the orbital $|xz(yz)\rangle$ to the p_z at shared ligands, then from the p_z to the orbital $|yz(xz)\rangle$ at the neighboring site i [1]. Therefore in the Eq.(21), only $e \neq 0$.

$$[H_{1,ij}]_{\eta'\sigma'\eta\sigma} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & t^* & 0 \\ 0 & 0 & 0 & 0 & 0 & t^* \\ 0 & 0 & t & 0 & 0 & 0 \\ 0 & 0 & 0 & t & 0 & 0 \end{bmatrix},$$

where we replace e with a symbol t which means hopping by convention. This agrees with the conclusion in the previous paper[2].

3.2 The Second-Order Effective Hamiltonian

α - $RuCl_3$ is a Mott insulator (see Appendix (2) for more details). Electrons cannot hop freely in the crystal; once they hop to a neighboring site, they quickly return due to strong Coulomb repulsion between electrons. This short-range Coulomb interaction is referred to as the Hubbard term.

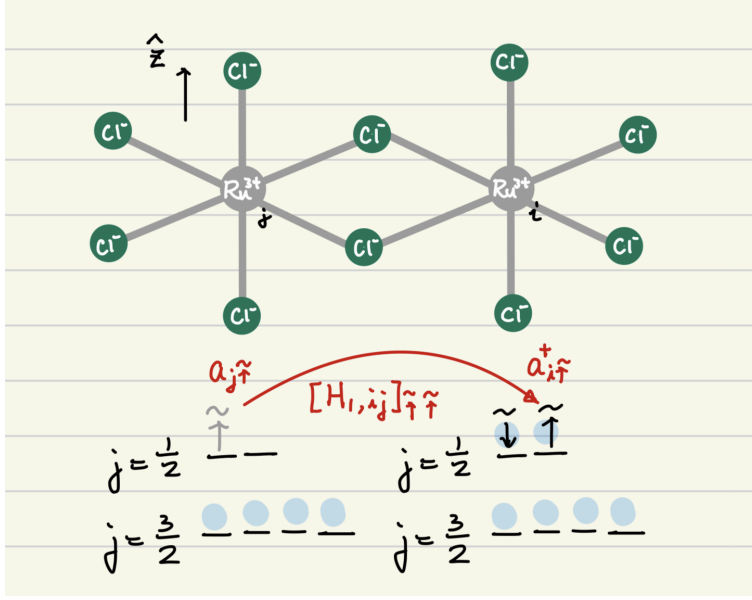


Figure 6. One possible hopping between the nearest neighboring edge-shared tetrahedrons. The z axis is local and perpendicular to the shared chlorides and their bonds.

Recall that $H_{1,ij}$ is the many-body hopping term between nearest neighbors (Equation 21). If the system evolves under H_1 , on single site i the occupation representation of the onsite electrons can be

$$|1, 1, 1, 1, 1, 1\rangle_i \quad (23)$$

which should be suppressed by the Hubbard terms (Coulomb interaction). To estimate the hoppings after Hubbard terms are turned on, change the basis of $H_{1,ij}$,

$$[H_{1,ij}]_{\nu'\nu} = \begin{bmatrix} \frac{2}{3}(Im(t)) & 0 & \frac{1}{3}\sqrt{2}(Im(t)) & 0 & 0 & \sqrt{\frac{2}{3}}(Re(t)) \\ 0 & -\frac{2}{3}(Im(t)) & 0 & i\sqrt{\frac{2}{3}}(Re(t)) & \frac{1}{3}\sqrt{2}(Im(t)) & 0 \\ \frac{1}{3}\sqrt{2}(Im(t)) & 0 & \frac{1}{3}(Im(t)) & 0 & 0 & \frac{1}{\sqrt{3}}(Re(t)) \\ 0 & -i\sqrt{\frac{2}{3}}(Re(t)) & 0 & (Im(t)) & \frac{i}{\sqrt{3}}(Re(t)) & 0 \\ 0 & \frac{1}{3}\sqrt{2}(Im(t)) & 0 & -\frac{i}{\sqrt{3}}(Re(t)) & -\frac{1}{3}(Im(t)) & 0 \\ \sqrt{\frac{2}{3}}(Re(t)) & 0 & \frac{1}{\sqrt{3}}(Re(t)) & 0 & 0 & -(Im(t)) \end{bmatrix}, \quad (24)$$

with ordered basis $\{\psi_{E_1}^{(1)}, \psi_{E_1}^{(2)}, \psi_{E_0}^{(1)}, \psi_{E_0}^{(2)}, \psi_{E_0}^{(3)}, \psi_{E_0}^{(4)}\}$. This basis comes from the eigenstates of $(H_\Delta + H_\lambda)$ (See Equation(??-??)). It helps us to build proper low-energy effective Hamiltonian using degenerate perturbation theory. For instance, for a single site i , a many-body state $|\psi_{\bar{N}}\rangle$ with 5 electrons has the lowest energy when

$$|\psi_{\bar{N}}\rangle = (|0, 1, 1, 1, 1, 1\rangle, |1, 0, 1, 1, 1, 1\rangle)^{\otimes \bar{N}}. \quad (25)$$

we use the degenerate perturbation theory which gives the perturbed term H_{eff}

$$H_{eff} = \lambda P H_1 P + \lambda^2 P H_1 \frac{1 - P}{\bar{E}_a - H_0} H_1 P + \dots, \quad (26)$$

where P is the projection operator

$$P = \sum_{\Psi_{\bar{N}} \in \mathcal{M}} |\Psi_{\bar{N}}\rangle \langle \Psi_{\bar{N}}|. \quad (27)$$

$|\psi_{\bar{N}}\rangle = (|0, 1, 1, 1, 1, 1\rangle, |1, 0, 1, 1, 1, 1\rangle)^{\otimes \bar{N}}$. The first term in Eq.(26) vanishes. In the second term, The sequentially ordered operators P , $1 - P$, and P describes the hoppings from the subspace \mathcal{M} to $\bar{\mathcal{M}}$ then back to \mathcal{M} . $\bar{\mathcal{M}}$ is the orthogonal complement of \mathcal{M} with fixed total particle number $5\bar{N}$.

With Equation (24), we can derive the second-order effective Hamiltonian which is of an energy scale $\pm \frac{t_{(1)}^2}{U}$. Remember that our $5\bar{N}$ -particle ground states are

$$|n_{E_{0,(1)}}, n_{E_{0,(2)}}, n_{E_{0,(3)}}, n_{E_{0,(4)}}, n_{E_{1,(1)}}, n_{E_{1,(2)}}\rangle^{\otimes N} = (|0, 1, 1, 1, 1, 1\rangle \text{ or } |1, 0, 1, 1, 1, 1\rangle)^{\otimes N}.$$

If we only consider the nearest neighbor hopping with energy increase U , i.e., the hopping that only changes the occupation representation of one set of neighboring sites from

$$(|0, 1, 1, 1, 1, 1\rangle, |1, 0, 1, 1, 1, 1\rangle)^{\otimes \bar{N}} \quad (28)$$

to

$$\begin{aligned} & |0, 0, 1, 1, 1, 1\rangle, |1, 1, 1, 1, 1, 1\rangle)^{\otimes \bar{N}} \\ & \text{or } |1, 1, 1, 1, 1, 1\rangle, |0, 0, 1, 1, 1, 1\rangle)^{\otimes \bar{N}} \end{aligned} \quad (29)$$

with total particle number $5\bar{N}$. Thus we should focus only on the top-left 2×2 submatrix of Equation(24). We denote

$$\frac{2}{3}(Im(t)) \equiv t_{(1)}, -\frac{2}{3}(Im(t)) \equiv -t_{(1)}$$

and the second-order effective Hamiltonian $PH_1 \frac{1-P}{E_a - H_0} H_1 P$ can be simplified as

$$\begin{aligned} H_{eff} &= -\frac{1}{U} \left(\sum_{\langle i,j \rangle, \mu} [H_{1,ij}]_{\mu\mu} d_{i\mu}^\dagger d_{j\mu} \right) \left(\sum_{\langle k,l \rangle, \mu} [H_{1,kl}]_{\mu'\mu'} d_{k\mu'}^\dagger d_{l\mu'} \right) \\ &= -\frac{1}{U} \left(\sum_{\langle i,j \rangle, \mu'\mu} [H_{1,ij}]_{\mu\mu} [H_{1,ji}]_{\mu'\mu'} d_{i\mu}^\dagger d_{j\mu} d_{j\mu'}^\dagger d_{i\mu'} \right), \end{aligned} \quad (30)$$

where $\mu = \psi_{E_1}^{(1)}, \psi_{E_1}^{(2)}$ are the single-site isospin ground states. $H_{1,ij}$ is Hermitian, so $H_{1,ji} = H_{1,ij}^*$. Since the elements in the top-left 2×2 matrix are all real, in this part

$$H_{1,ji} = H_{1,ij}^* = H_{1,ij}.$$

$$\begin{aligned}
H_{eff} &= -\frac{1}{U} \sum_{\langle i,j \rangle, \mu' \mu} [H_{1,ij}]_{\mu\mu} [H_{1,ij}]_{\mu' \mu'} d_{i\mu}^\dagger d_{i\mu'} d_{j\mu} d_{j\mu'}^\dagger \\
&= -\frac{1}{U} \sum_{\langle i,j \rangle, \mu' = \mu} [H_{1,ij}]_{\mu\mu}^2 \left(d_{i\mu}^\dagger d_{i\mu'} d_{j\mu} d_{j\mu'}^\dagger \right) - \frac{1}{U} \sum_{\langle i,j \rangle, \mu' \neq \mu} [H_{1,ij}]_{\mu\mu} [H_{1,ij}]_{\mu' \mu'} \left(d_{i\mu}^\dagger d_{i\mu'} d_{j\mu} d_{j\mu'}^\dagger \right) \\
&= \sum_{\langle i,j \rangle} -\frac{t_{(1)}^2}{U} \left(d_{i\uparrow}^\dagger d_{i\uparrow} d_{j\uparrow} d_{j\uparrow}^\dagger + d_{i\downarrow}^\dagger d_{i\downarrow} d_{j\downarrow} d_{j\downarrow}^\dagger \right)_{\mu' = \mu} + \frac{t_{(1)}^2}{U} \left(d_{i\uparrow}^\dagger d_{i\downarrow} d_{j\uparrow} d_{j\downarrow}^\dagger + d_{i\downarrow}^\dagger d_{i\uparrow} d_{j\downarrow} d_{j\uparrow}^\dagger \right)_{\mu' \neq \mu} \\
&= \sum_{\langle i,j \rangle} -\frac{t_{(1)}^2}{U} \left(d_{i\uparrow}^\dagger d_{i\uparrow} (1 - d_{j\uparrow}^\dagger d_{j\uparrow}) + d_{i\downarrow}^\dagger d_{i\downarrow} (1 - d_{j\downarrow}^\dagger d_{j\downarrow}) \right)_{\mu' = \mu} - \frac{t_{(1)}^2}{U} \left(d_{i\uparrow}^\dagger d_{i\downarrow} d_{j\downarrow}^\dagger d_{j\uparrow} + d_{i\downarrow}^\dagger d_{i\uparrow} d_{j\uparrow}^\dagger d_{j\downarrow} \right)_{\mu' \neq \mu} \\
&= \sum_{\langle i,j \rangle} \frac{t_{(1)}^2}{U} \left(d_{i\uparrow}^\dagger d_{i\uparrow} d_{j\uparrow}^\dagger d_{j\uparrow} + d_{i\downarrow}^\dagger d_{i\downarrow} d_{j\downarrow}^\dagger d_{j\downarrow} \right)_{\mu' = \mu} - \frac{t_{(1)}^2}{U} \left(d_{i\uparrow}^\dagger d_{i\downarrow} d_{j\downarrow}^\dagger d_{j\uparrow} + d_{i\downarrow}^\dagger d_{i\uparrow} d_{j\uparrow}^\dagger d_{j\downarrow} \right)_{\mu' \neq \mu} \\
&\quad - \frac{t_{(1)}^2}{U} \left(d_{i\uparrow}^\dagger d_{i\uparrow} + d_{i\downarrow}^\dagger d_{i\downarrow} \right).
\end{aligned} \tag{31}$$

In the above derivation, we use the anti-commutation relation of the d operators,

$$\begin{aligned}
\{d_{i\mu}, d_{j,\nu}^\dagger\} &= \delta_{ij} \delta_{\mu\nu}, \\
\{d_{i\mu}, d_{j,\nu}\} &= \{d_{i\mu}^\dagger, d_{j,\nu}^\dagger\} = 0.
\end{aligned} \tag{32}$$

3.3 The Mapping of Electron Operators to Local Spin Operators

Due to the energy scales of $\frac{t_{(1)}^2}{U}$, when the system deviates from the ground-state subspace with the effective Hamiltonian H_{eff} , we can restrict ourselves from using the entire Fock space \mathcal{F}^{6N} and d^\dagger, d to describe our system. Instead, we introduce a transformation from the electron operators d^\dagger, d to the spin operators S^+, S^-, S^Z ,

$$\begin{aligned}
d_{i\uparrow}^\dagger d_{i\uparrow} &\Rightarrow \frac{1}{2} + S_i^Z, \\
d_{i\downarrow}^\dagger d_{i\downarrow} &\Rightarrow \frac{1}{2} - S_i^Z, \\
d_{i\uparrow}^\dagger d_{i\downarrow} &\Rightarrow S_i^+, \\
d_{i\downarrow}^\dagger d_{i\uparrow} &\Rightarrow S_i^-,
\end{aligned} \tag{33}$$

we can rewrite the Eq.(31)

$$\begin{aligned}
\rightarrow H_{eff, s} &= \frac{t_{(1)}^2}{U} \sum_{\langle i,j \rangle} \left(\left(\frac{1}{2} + S_i^Z \right) \left(\frac{1}{2} + S_j^Z \right) + \left(\frac{1}{2} - S_i^Z \right) \left(\frac{1}{2} - S_j^Z \right) \right. \\
&\quad \left. - (S_i^+ S_j^- + S_i^- S_j^+) - \left(\frac{1}{2} + S_i^Z + \frac{1}{2} - S_i^Z \right) \right).
\end{aligned} \tag{34}$$

Because each term in the above equation is

$$\left(\frac{1}{2} + S_i^Z \right) \left(\frac{1}{2} + S_j^Z \right) + \left(\frac{1}{2} - S_i^Z \right) \left(\frac{1}{2} - S_j^Z \right) = 2S_i^Z S_j^Z + \frac{1}{2}, \tag{35}$$

$$\begin{aligned}
S_i^+ S_j^- + S_i^- S_j^+ &= (S_i^X + iS_i^Y)(S_j^X - iS_j^Y) + (S_i^X - iS_i^Y)(S_j^X + iS_j^Y) \\
&= 2(S_i^X S_j^X + S_i^Y S_j^Y),
\end{aligned} \tag{36}$$

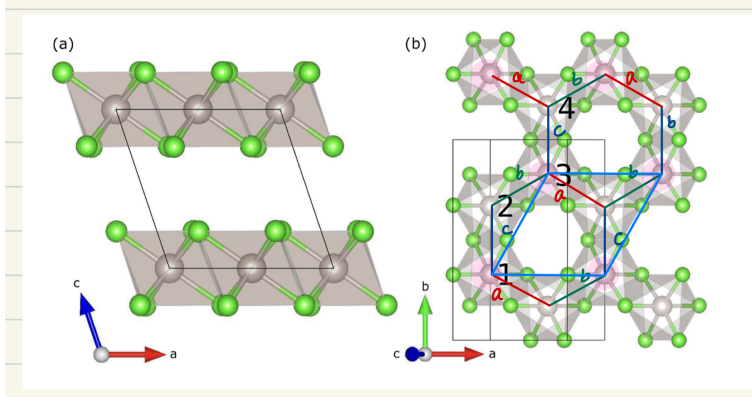


Figure 7. $\alpha - RuCl_3$ structure. Such stacking makes $\alpha - RuCl_3$ be of the space group $C_{2/m}$.

$$\frac{1}{2} + S_i^Z + \frac{1}{2} - S_i^Z = 1, \quad (37)$$

We can simplify the Eq.(34),

$$\begin{aligned} H_{eff,s} &= \frac{t_{(1)}^2}{U} \sum_{\langle i,j \rangle} 2(S_i^Z S_j^Z - S_i^X S_j^X - S_i^Y S_j^Y) - \frac{1}{2} \\ &= const(N) + \frac{2t_{(1)}^2}{U} \sum_{\langle i,j \rangle} 2S_i^Z S_j^Z - \vec{S}_i \cdot \vec{S}_j. \end{aligned} \quad (38)$$

Now we have our simplest spin Hamiltonian. Notice that the Z superscript indicates the local z -axis.

Result 3.1. The effective spin Hamiltonian from second-order degenerate perturbation theory in $\frac{t_{(1)}}{U}$ describing $\alpha - RuCl_3$ is $H_{eff,s} = const(N) + \frac{2t_{(1)}^2}{U} \sum_{\langle i,j \rangle} 2S_i^Z S_j^Z - \vec{S}_i \cdot \vec{S}_j$. The axis is local for each bond between $\langle i, j \rangle$.

For monolayer $\alpha - RuCl_3$ in Fig.(7), if we choose the direction of the dark green bond c to the *global* z -axis, the spin Hamiltonian in Eq.(38) will become

$$H_{eff,s} = const(N) + \frac{2t_{(1)}^2}{U} 2 \sum_{\langle i,j \rangle} S_i^\gamma S_j^\gamma - \vec{S}_i \cdot \vec{S}_j, \quad (39)$$

γ labels the global coordinate components.

$S_i \cdot S_j$ is unchanged. Since each tetrahedron $RuCl_6$ has cubic symmetry, the local z axis is parallel to the global coordinate axis and $\gamma = x, y, z$.

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