

# ATOMIC ORBITAL, CRYSTAL FIELD THEORY AND DEGENERATE PERTURBATION THEORY

*basics for microscopic origin of couplings between pseudospins*

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## Contents

<b>1</b>	<b>Atomic Orbitals and Crystal Field Theory</b>	<b>1</b>
<b>2</b>	<b>Degenerate Perturbation Theory</b>	<b>2</b>
2.1	1D crystal with a half-filled band	2
2.2	Degenerate perturbation theory	3
2.3	The limit $U \gg t$	4
2.4	Mapping electron to spin operator	5

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This 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  $n = 4, l = 2$ .

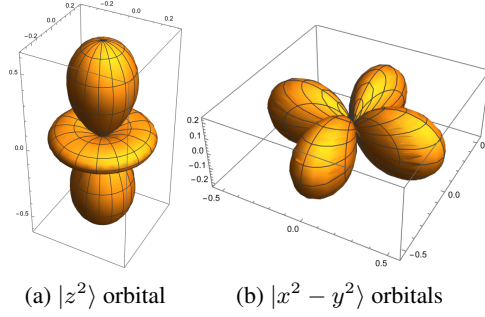
Combine these functions to form two sets of modes

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

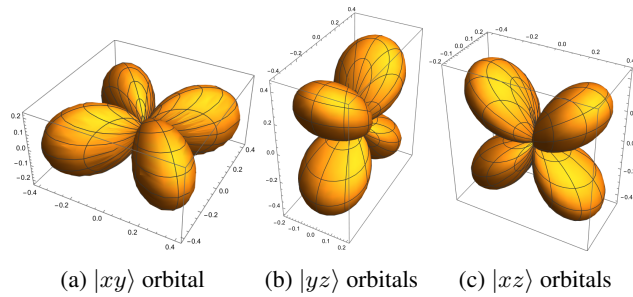
where

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

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"<sup>1</sup>.

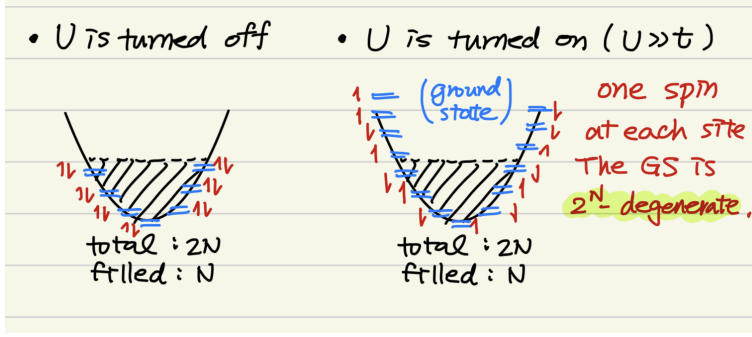
Now add the Hubbard potential to the tight binding model

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

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 band<sup>2</sup> in order to minimize the

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

<sup>2</sup>I haven't estimated the effect of  $U$  as a perturbative term. Let's suppose that when  $U$  is large, the band will not be altered (we can still use the tight-binding band).



**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).

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 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  $\Omega_0$ . The problem is to find the perturbed spectrum in  $\Omega_0$ . 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  $\Omega_0$  is degenerate or not doesn't matter. Write down the eigenstates  $|a\rangle$ , which stem from  $|\alpha\rangle$ , for the total Hamiltonian  $H$

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

where  $c_{\alpha}$  and  $d_{\mu}$  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  $\Omega_0$  and another state  $|\nu\rangle$  outside  $\Omega_0$ ,

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

Remember that  $d_\mu$  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 Hamiltonian<sup>3</sup>

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

which operates only on the subspace  $\Omega_0$ , 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  $\Omega_0$ .

As for the replacement of  $E_\mu$  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 $U \gg t$

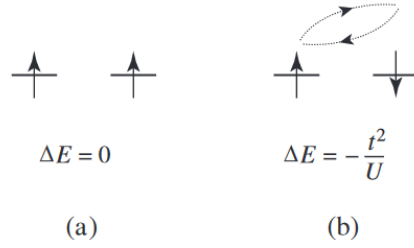
When  $t$  is turned off, we expect the spins to be localized at each site (Fig. 3, right) since two spins occupying the same sites will contribute energy  $U$ . To estimate the effect of tight-binding term when  $U \gg t$ , we are going to treat  $-t \sum_{\langle ij \rangle, \sigma} c_{i, \sigma}^\dagger c_{j, \sigma}$  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.

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 perturbation<sup>4</sup>, the energy scale is like Fig.??, which matches our imagination for the behaviors.

The formal way is 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., A  $H_{eff}$  operates on the degenerate subspace  $\Omega_0$ . So the trick is to find the components of  $H_1 H_1$  that operate on

<sup>3</sup>In fact this expression for elements does not form an ordinary matrix since the index for this matrix will be  $\mathbf{H}_{eff}(\beta a')$ .  $\beta$  and  $a' = \sum_\alpha c_\alpha |\alpha\rangle$  are two different bases for the same subspace  $\Omega_0$ .

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



**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.  $\Delta E = \sum_n \frac{|\langle 0 | H_1 | n \rangle|^2}{E_a - E_n}$  should count over all possible states. But remember  $H_1$  is simply one hopping, only  $E_a - E_n = -U$  is allowed.

$\Omega_0$ <sup>5</sup>. 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 problem<sup>6</sup>. 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

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

and the effective Hamiltonian for the tight-binding terms is

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

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

<sup>6</sup>symmetry approach?