Optical excitations of transition-metal oxides under the orbital multiplicity effects

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Abstract. We investigated optical excitations of transition-metal (TM) oxides with metal oxygen octahedra taking account of the orbital multiplicity effects. We predicted excitation energies of intersite d–d transitions and p–d transitions of TM oxides. We compared the evaluated excitation energies with reported experimental data, and found that they are in good agreement with each other. Moreover, we could demonstrate possible answers for a few long-standing problems of the low-frequency spectral features in some early 3d TM oxides: (i) the broad and multi-peak structures of the d–d transitions, (ii) the low values (around 2 eV) of the d–d transition energies for some t¹₂g and t²₂g systems, and (iii) the lack of the d–d transition below 4.0 eV region for LaCrO₃, one of the t³₂g systems. These indicate that our approach considering the orbital multiplicity effects could provide good explanations of intriguing features in the optical spectra of some early TM oxides. In addition, we showed that optical spectroscopy can be useful as a powerful tool to investigate spin and/or orbital correlations in the TM ions. Finally, we discussed the implications of the orbital multiplicity in the Zannen–Sawatzky–Allen scheme, which has been used successfully to classify correlated electron systems.

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1. Introduction

Recently, the orbital degree of freedom has emerged as an important physical term in understanding numerous intriguing phenomena occurring in condensed matter systems [1, 2]. It has been found that intriguing physical properties of numerous transition-metal (TM) oxides, including manganites [1, 2], titanates [3], vanadates [4, 5], cobaltates [6], molybdates [7] and ruthenates [8], could be explained by taking account of the orbital degree of freedom. For instance, couplings between the orbital and the other degrees of freedom, such as charge, spin, and/or lattice, are considered as key ingredients in explaining novel phenomena observed in manganites, including colossal magnetoresistance [1], orbital ordering [2], and optical anisotropy [9]. Although the importance of the orbitals has been widely recognized recently, theoretical and experimental efforts to explain such effects are still quite scarce. The single-band Hubbard model, which has been most commonly used to explain the physical properties of strongly correlated electron systems, does not take account of the orbital degeneracy. In addition, there are few experimental techniques to probe this important degree of freedom [10].

Optical spectroscopy has been proven to be a powerful experimental tool to investigate the electronic structure of TM oxides [11]. Similar to experts in other condensed matter experimental fields, most optical spectroscopists have used the single-band Hubbard model as a starting point to explain optical spectra of TM oxides. Owing to this tradition, there have been important spectral features which are difficult to be understood in the single-band Hubbard picture. For example, numerous early transition oxides show absorption features, possibly due to optical
transitions between the lower and the upper Hubbard bands; these features are usually very broad or have multiple peak structures, which cannot be explained using the single-band Hubbard model [12, 13].

Quite recently, we demonstrated that optical spectroscopy could be a very useful and powerful method to investigate certain aspects related to the orbital degree of freedom, especially orbital and spin correlations [14, 15]. Based on the orbitally degenerate Hubbard model, we evaluated the orbital correlations between the nearest-neighbour Ru ions from optical spectra of (Ca,Sr)$_2$RuO$_4$, and proposed a possible orbital ground state [14]. In a similar way, we also estimated the spin correlations between the Mo ions in RE$_2$Mo$_2$O$_7$ (RE = Y, Sm and Nd), and explained the spin ground states of the molybdates [15]. In these studies, we considered the intersite d–d transitions only in the systems of metal oxygen octahedra with two or four $t_{2g}$ electrons on the TM ions.

It should be noted that the new approach considering the orbital multiplicity can be applied to a wealth of optical data for TM oxides, which have been accumulated over the decades. In particular, it can provide new insights on some optical spectral features, which could not have been explained in the single-band Hubbard picture. In this paper, we will take account of the orbital multiplicity effects in both interatomic d–d transitions and charge-transfer p–d excitations for all electronic configurations for systems of metal oxygen octahedra with $t_{2g}$ electrons. We will evaluate all of the possible excitation energies for the d–d and the p–d transitions. We will compare them with reported experimental data and confirm that such an approach could provide a good basis to explain the unusual spectral features observed in early TM oxides. We will also demonstrate how to apply optical spectroscopy as a probing tool for nearest neighbouring spin and/or orbital correlations. Finally, we will discuss the implications of the orbital multiplicity to the Zaanen–Sawatzky–Allen scheme [16].

2. Orbitally degenerate Hubbard model

The single-band Hubbard model has been commonly used as a starting point to explain the physical properties of TM oxides. In this model, the Hamiltonian can be written as

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

where $n_{i\sigma} \equiv c_{i\sigma}^{\dagger} c_{i\sigma}$ and $c_{i\sigma}^{\dagger}$ ($c_{i\sigma}$) is the creation (annihilation) operator for an electron on site $i$ with spin $\sigma (= \uparrow$ or $\downarrow$). And, $t_{ij}$ is the transfer integral between sites $i$ and $j$, which are located as nearest neighbours. $U$ is the on-site Coulomb repulsion. In equation (1), the electrons at the oxygen sites are not included, and only the nearest-neighbouring hopping is included among numerous possible hoppings between the TM ions. In addition, the orbital degeneracies of electrons in TM ions are not included. To explain more realistic physical phenomena occurring in TM oxides, the single-band Hubbard model has been extended to various forms. Some workers considered the multi-band Hubbard model, which takes account of electrons in the oxygen 2p orbitals as well as in the TM d orbitals [17]. Also, many workers extended equation (1) to include hoppings between next-nearest neighbours (and/or third nearest neighbours) [18]. These approaches have been quite useful to explain magnetic and charge correlations, and the shapes of Fermi surfaces of some cuprates [18, 19].
However, to explain phenomena related to orbital degrees of freedom of TM ions, it would be more proper to extend equation (1) by including the orbital degeneracy. In the orbitally degenerate Hubbard model

$$H = - \sum_{\langle i,j \rangle} t_{ij} c_{i,a,\sigma}^\dagger c_{j,b,\sigma} + U \sum_{\sigma,\sigma'} \sum_{\alpha,\beta,\gamma,\delta} \langle \alpha\beta | e^2/r | \gamma\delta \rangle c_{i,a,\sigma}^\dagger c_{i,b,\sigma'}^\dagger c_{i,b,\sigma'} c_{i,\gamma\sigma},$$

(2)

where $\alpha, \beta, \gamma$ and $\delta$ are indices of the involved d orbitals. And, $c_{i,a,\sigma}^\dagger$ ($c_{i,a,\sigma}$) is the creation (annihilation) operator for an electron on site $i$ with orbital $\alpha$ and spin $\sigma = \uparrow$ or $\downarrow$. The non-vanishing matrix elements of the Coulomb interaction are grouped into direct and exchange interactions. There are a diagonal direct coupling, $U = \langle \alpha\alpha | e^2/r | \alpha\alpha \rangle$, an off-diagonal direct coupling, $U' = \langle \alpha\beta | e^2/r | \alpha\beta \rangle$, and an exchange coupling, $J_H = \langle \alpha\beta | e^2/r | \beta\alpha \rangle$. Due to rotational invariance in orbital space, $U' = U - 2J_H$.

3. Optical excitations under the orbital multiplicity effects

Numerous TM oxides have the simple perovskite structure. In this crystal structure, the d orbital states of TM ions are split into the triply degenerate $t_{2g}$ (i.e., $d_{xy}$, $d_{yz}$ and $d_{zx}$) orbital states and the doubly degenerate $e_g$ (i.e., $d_{x^2−y^2}$ and $d_{3z^2−r^2}$) orbital states. Due to electrostatic interaction between the d electrons and the oxygen 2p electrons, the $t_{2g}$ and the $e_g$ states will have the ‘crystal field splitting’, $10Dq$, as schematically shown in figure 1(a). In most TM oxides, values of $10Dq$ are typically located between 1 and 4 eV [20]–[23]. For some perovskite oxides, a strong electron–phonon coupling, called the Jahn–Teller distortion, or the GdFeO$_3$-type distortion results in an additional splitting in the $t_{2g}$ and/or the $e_g$ levels [24]. In most cases, values of the structural distortion energies are much smaller than $10Dq$, so we do not include effects of this energy splitting in this paper.

Optical conductivity spectra of most TM oxides with the perovskite structure are composed of the interatomic transitions. Figure 1(b) shows a schematic diagram of optical transitions in a TM-oxygen-TM network, which is a basic structural unit of the perovskite structure. The oxygen 2p orbitals are fully occupied. As an example, we put only one electron in the $t_{2g}$ orbitals at the TM site. The intra-atomic optical excitations between the oxygen 2p orbitals were not allowed, and those between the d orbitals of the TM ions are generally forbidden by the electric dipole selection rule. The interatomic optical excitations can occur from the occupied oxygen 2p orbitals to the unoccupied $t_{2g}$ orbitals (i.e., the p–d transitions) or between the d orbitals (i.e., the d–d transitions). The transition energy of each excitation is given by the energy difference between the initial and the final states. For the p–d transition, its transition energy corresponds to the so-called charge-transfer energy, $\Delta$. And, for the d–d transition, its transition energy is related to the Coulomb repulsion energy, $U$. Zaannen, Sawatzky and Allen classified many strongly correlated electron systems in terms of $\Delta$ and $U$ [16], and their scheme has been widely used by many workers [25].

Note that these understandings are based on the single-band Hubbard model, which ignores the orbital multiplicity effects. In this simple model, the final d state is defined as a single upper Hubbard band, so energies of the p–d and the d–d transitions can be represented by single quantities, i.e., $\Delta$ and $U$, respectively. When the orbital degeneracy of the involved electrons is included, each of the p–d and the d–d transitions should be understood as a transition from a
Figure 1. (a) The d orbitals of a TM ion in an octahedral site. The left diagram shows the d orbitals having the fivefold degeneracy as the TM ion is in the free space. And, the right diagram shows that d orbitals split into the t$_{2g}$ orbitals and e$_g$ orbitals by the crystal field splitting energy 10D$_q$ under the octahedral field. (b) The schematic diagram of TM-oxygen-TM link and the possible optical excitations. The occupied electrons (spins) are indicated by arrows. There are two interatomic optical transitions: the p–d transition and the d–d transition.

3.1. Eigenstates and eigenenergies under the multiplicity effects

In order to provide a basis for later discussion, we will briefly explain eigenstates and their eigenenergy values of the multiplet states when the orbital degeneracy effects are considered. Let us give an example for the d$^2$ states, i.e., the t$_{2g}^2$ state and the t$_{2g}^1$e$_g^1$ state. Since electrons are elementary particles with spin 1/2, the total wavefunctions of the d$^2$ state should be antisymmetric about the exchange operation of the electrons. Therefore, the multiplet states should be constructed based on this important property.

When the multiplicity effects are considered appropriately, the t$_{2g}^2$ configuration should have four eigenstates for two electrons, which can be written as $^3T_1$, $^1T_2$, $^1E$ and $^1A_1$ in the irreducible representation [26, 27]. The wavefunctions corresponding to each irreducible representation are shown in table 1. Similarly, for the t$_{2g}^1$e$_g^1$ configuration, there are four multiplet states, represented...
Racah parameters between eg orbitals is 4 should be given in more complex ways. That is, the exchange coupling between d$_x^2$ and d$_{yz}$ wavefunctions involved. While the exchange coupling between t$_2g$ orbitals is 3 states.

Table 1. Wavefunctions and energy eigenvalues of the d$_2$ system cited from [25, 26]. By appropriate cyclic permutation of orbitals (d$_{yz}$, d$_{zx}$, d$_{xy}$) and (d$_{z^2-r^2}$, d$_x^2$, d$_{y^2}$), the unlisted components of the wavefunctions can be obtained. Here, $|d_{xy}(\uparrow)d_{yz}(\downarrow)|$ indicates the Slater determinant of two d$_{xy}(\uparrow)$ and d$_{yz}(\downarrow)$ states, and the arrows in parentheses represent the spin state. The subscript M means the magnetic quantum number of the spin $S$ state.

| Wavefunctions | Energy eigenvalues |
|---------------|-------------------|
| t$_2g$ configuration | |
| $\Psi(3T_1(M=1)) = |d_{xy}(\uparrow)d_{yz}(\downarrow)|$ | |
| $\Psi(3T_1(M=0)) = \frac{1}{\sqrt{2}}(|d_{xy}(\uparrow)d_{xy}(\downarrow)| - |d_{xy}(\uparrow)d_{yz}(\downarrow)|)$ | $U - 3J_3$ |
| $\Psi(3T_1(M=-1)) = |d_{zy}(\downarrow)d_{yz}(\downarrow)|$ | |
| $\Psi(3T_2) = \frac{1}{\sqrt{2}}(|d_{xy}(\uparrow)d_{xy}(\downarrow)| + |d_{xy}(\uparrow)d_{yz}(\downarrow)|)$ | |
| $\Psi(E_x) = \frac{1}{\sqrt{2}}(|d_{xy}(\uparrow)d_{xy}(\downarrow)| - |d_{xy}(\uparrow)d_{yz}(\downarrow)|)$ | $U - J_3$ |
| $\Psi(E_y) = \frac{1}{\sqrt{2}}(|d_{xy}(\uparrow)d_{xy}(\downarrow)| - |d_{xy}(\uparrow)d_{yz}(\downarrow)| + 2|d_{xy}(\uparrow)d_{yz}(\downarrow)|)$ | |
| $\Psi(1A_1) = \frac{1}{\sqrt{2}}(|d_{xy}(\uparrow)d_{xy}(\downarrow)| + |d_{xy}(\uparrow)d_{xy}(\downarrow)| + |d_{xy}(\uparrow)d_{yz}(\downarrow)|)$ | $U + 2J_3$ |
| t$_2g$ configuration | |
| $\Psi(3T_2(M=1)) = |d_{xy}(\uparrow)d_{z^2-r^2}(\uparrow)|$ | |
| $\Psi(3T_2(M=0)) = \frac{1}{\sqrt{2}}(|d_{xy}(\uparrow)d_{z^2-r^2}(\downarrow)| + |d_{xy}(\downarrow)d_{z^2-r^2}(\uparrow)|)$ | $U - 3J_4 + 10Dq$ |
| $\Psi(3T_2(M=-1)) = |d_{xy}(\downarrow)d_{z^2-r^2}(\downarrow)|$ | |
| $\Psi(3T_3(M=1)) = |d_{xy}(\uparrow)d_{z^2-r^2}(\uparrow)|$ | |
| $\Psi(3T_3(M=0)) = \frac{1}{\sqrt{2}}(|d_{xy}(\uparrow)d_{z^2-r^2}(\downarrow)| + |d_{xy}(\downarrow)d_{z^2-r^2}(\uparrow)|)$ | $U - 3J_1 + 10Dq$ |
| $\Psi(3T_3(M=-1)) = |d_{xy}(\downarrow)d_{z^2-r^2}(\downarrow)|$ | |
| $\Psi(3T_2) = \frac{1}{\sqrt{2}}(|d_{xy}(\uparrow)d_{z^2-r^2}(\downarrow)| - |d_{xy}(\downarrow)d_{z^2-r^2}(\uparrow)|)$ | $U - J_4 + 10Dq$ |
| $\Psi(3T_1) = \frac{1}{\sqrt{2}}(|d_{xy}(\uparrow)d_{z^2-r^2}(\downarrow)| - |d_{xy}(\downarrow)d_{z^2-r^2}(\uparrow)|)$ | $U - J_1 + 10Dq$ |

as $3T_2$, $3T_1$, $1T_2$, and $1T_1$. The lower part of table 1 shows the wavefunctions of the multiplet states.

The corresponding eigenenergy values of each eigenstate are varied according to the spin configurations and the respective orbitals of each multiplet state. For both t$_2g$ and e$_g$ electrons, their diagonal direct coupling $U$ term is the same as $U = A + 4B + 3C$. Here, $A$, $B$ and $C$ are the Racah parameters [26, 27]. However, the exchange coupling terms can differ depending on the orbital wavefunctions involved. While the exchange coupling between t$_2g$ orbitals is $3B + C$, that between e$_g$ orbitals is $4B + C$. When both t$_2g$ and e$_g$ electrons participate, the exchange couplings should be given in more complex ways. That is, the exchange coupling between d$_{z^2-r^2}$ and d$_{xy}$ (d$_{yz}$, d$_{zx}$) orbitals is $C$ ($3B + C$, $3B + C$), and the exchange couplings between d$_{z^2-r^2}$ and d$_{xy}$ (d$_{yz}$, d$_{zx}$) orbitals is $4B + C$ ($B + C$, $B + C$). For clarity, let us define these exchange interactions as $J_1 \equiv C$, $J_2 \equiv B + C$, $J_3 \equiv 3B + C$ and $J_4 \equiv 4B + C$.

2 Racah parameters $A$, $B$ and $C$ can be written in terms of three Slater integrals, i.e., $F_0$, $F_2$ and $F_4$, as $A = F_0 - 49F_4$, $B = F_2 - 5F_4$ and $C = 35F_4$, and the Slater integrals are given as $F_0 = F^0$, $F_2 = \frac{3}{67}F^2$ and $F_4 = \frac{1}{231}F^4$, where $F^k = \int_0^{\infty} r^{2k} dr_1 \int_0^{\infty} r_2^{2k} dr_2 (r_1/r_2)^{k+1} R_d(r_1)^2 R_d(r_2)^2$. Here, $R_d(r)$ is the radial part of the d orbital wavefunction, and $r_+$ and $r_-$ denote the larger and smaller of $r_1$ and $r_2$, respectively. See [25, 26].
For the \( t^2_{2g} \) configuration, the eigenenergy values are given by \( A - 5B \) for the \( 3T_1 \) state, \( A + B + 2C \) for the \( 1T_2 \) state, \( A + B + 2C \) for the \( 1E \) state and \( A + 10B + 5C \) for the \( 1A_1 \) state \[26, 27\]. Considering that \( U = A + 4B + 3C \) and \( J_3 = 3B + C \), eigenenergy values for the \( t^2_{2g} \) states can be represented as \( U - 3J_3 \) for the \( 3T_1 \) state, \( U - J_3 \) for the \( 1T_2 \) state, \( U - J_3 \) for the \( 1E \) state and \( U + 2J_3 \) for the \( 1A_1 \) state. For the \( t^1_{2g}e^1_g \) configuration, the eigenenergy values are given by \( A - 8B \) for the \( 3T_2 \) state, \( A + 4B \) for the \( 3T_1 \) state, \( A + 2C \) for the \( 1T_2 \) state and \( A + 4B + 2C \) for the \( 1T_1 \) state. As we consider the composing orbital states of each \( t^1_{2g}e^1_g \) state, the corresponding eigenenergy values can be represented as \( U - 3J_4 \) for the \( 3T_2 \) state, \( U - 3J_4 \) for the \( 3T_1 \) state, \( U - J_4 \) for the \( 1T_2 \) state and \( U - J_1 \) for the \( 1T_1 \) state. Due to the crystal field splitting between the \( t_{2g} \) and the \( e_g \) states, there should be an additional energy parameter \( 10Dq \) for the \( t^1_{2g}e^1_g \) configuration. In the second column of table 1, we show the eigenenergy values for both the \( t^1_{2g} \) and the \( t^1_{2g}e^1_g \) configurations.

Since our main attention is focused on \( t_{2g} \) electrons, we define the exchange interaction between \( t_{2g} \) orbitals as \( J_H \), i.e., \( J_H \equiv J_3(= 3B + C) \). For most TM ions, the values of \( B \) are smaller than those of \( C \). With \( 4B \simeq C \ [26, 27] \), \( J_1 \simeq \frac{3}{5}J_H \), \( J_2 \simeq \frac{2}{5}J_H \) and \( J_4 \simeq \frac{3}{5}J_H \). These approximations are useful for evaluating excitation energies to final states containing \( e_g \) electrons.

### 3.2. Intersite \( p-d \) transitions

#### 3.2.1. \( p-d \) transitions using the simple electron configuration.

Before going into a detailed discussion of the optical excitations with consideration of the multiplicity effects, it would be useful to discuss \( p-d \) transitions using the simple electron configuration where we fill each orbital state with one or two electrons without antisymmetrizing the total wavefunction of multiple electrons. Figure 2 shows the \( d^{n+1} \) final states of the \( p-d \) transitions \( d^n \rightarrow Ld^{n+1} \), where \( L \) indicates a ligand hole in the oxygen. The initial \( d^n \) states are supposed to have the \( t^2_{2g} \) configuration. The arrows with the solid triangles display the electrons occupied in the atom before the transition, and the arrows with open triangles indicate the transferred electrons.

In figure 2(a), we consider the \( p-d \) transitions of the \( d^1 \) system, i.e., \( d^1 \rightarrow Ld^2 \). There are five possible \( d^2 \) final states in the \( d^1 \rightarrow Ld^2 \) excitation. We evaluate the excitation energies with the simple consideration of the orbital occupation, and display the results in the first line of each diagram. In figures 2(b)–(e), we give the same consideration to the charge-transfer excitations, \( d^n \rightarrow Ld^{n+1} \) with \( n = 2, 3, 4 \) and 5, respectively. We show possible \( d^{n+1} \) final states for each excitation and the corresponding excitation energy values. It should be noted that in the single-band Hubbard model such various kinds of \( p-d \) transitions for each electron configuration are not expected. In this respect, the approach based on this simple picture can provide at least a qualitatively good insight on how the optical excitations should be understood under consideration of the orbital degeneracy effects.

#### 3.2.2. \( p-d \) transitions under the orbital multiplicity effects.

Now, we discuss the intersite \( p-d \) transitions under the consideration of orbital multiplicity effects. Let us begin with \( p-d \) transitions with one \( t_{2g} \) electron per metal-ion site, i.e., \( d^1 \rightarrow Ld^2 \). As final states, we have to consider \( t^1_{2g}e^1_g \) as well as \( t^2_{2g} \) configurations. For the \( t^2_{2g} \) configuration, there will be four final eigenstates, represented by \( 3T_1, 1T_2, 1E \) and \( 1A_1 \) in the irreducible representation, as shown in table 1 \[26, 27\]. The \( S = 1 \) state, i.e., \( 3T_1 \), will have the lowest energy, so the excitation energy to the \( 3T_1 \) final state is defined as \( \Delta_0(t^1_{2g}) \). Compared to the \( 3T_1 \) state, three \( S = 0 \)
Figure 2. Schematic diagrams for the p–d transitions \( d^n \rightarrow Ld^{n+1} \) of (a) \( n = 1 \), (b) \( n = 2 \), (c) \( n = 3 \), (d) \( n = 4 \) and (e) \( n = 5 \). Each diagram corresponds to the \( d^{n+1} \) final state in each \( d^n \rightarrow Ld^{n+1} \) excitation. We show electrons of the initial \( d^n \) states with solid arrows and indicate an additional electron of the final \( d^{n+1} \) state by open arrows. We display the excitation energies calculated using the simple electron configuration at the upper parts of each diagram. Also, we show the excitation energies together with the corresponding eigenstates in parentheses.
Table 2. Possible p–d transitions of the d^1 system, d^1 → Ld^2, considering the multiplicity effects. The first and the second column show the possible d^2 final states and their energy levels. The third column shows the corresponding energy cost of each excitation. For this, we suppose that J_H ≡ J_3 ≃ 7B, J_1 ≃ 4/7 J_H, J_2 ≃ 2/7 J_H and J_4 ≃ 5/7 J_H. Details of this table are described in the text.

| d^2 | E(d^2) | ΔE(d^1 → Ld^2) |
|-----|--------|-----------------|
| t_{2g}^2(l^1_T_1) | A − 5B (U − 3J_H) | Δ_0(t_{2g}^2) |
| t_{2g}^2(l^1_T_2) | A + B + 2C (U − J_H) | Δ_0(t_{2g}^2) + 6B + 2C (U − 3J_H) |
| t_{2g}^2(l^1_E) | A + B + 2C (U − J_H) | Δ_0(t_{2g}^2) + 6B + 2C (U − J_H) |
| t_{2g}^2(l^1_A_1) | A + 10B + 5C (U + 2J_H) | Δ_0(t_{2g}^2) + 15B + 5C (U + 2J_H) |
| t_{2g}^2(l^1_T_2) | A + 8B + 10Dq (U − 2/7 J_H + 10Dq) | Δ_0(t_{2g}^2) + 3B + 10Dq (U − 4/7 J_H + 10Dq + 5/7 J_H) |
| t_{2g}^2(l^1_T_1) | A + 4B + 10Dq (U − 2/7 J_H + 10Dq) | Δ_0(t_{2g}^2) + 9B + 10Dq (U − 2/7 J_H + 10Dq + 5/7 J_H) |
| t_{2g}^2(l^1_T_2) | A + 2C + 10Dq (U − 2/7 J_H + 10Dq) | Δ_0(t_{2g}^2) + 5B + 2C + 10Dq (U − 2/7 J_H + 10Dq + 5/7 J_H) |
| t_{2g}^2(l^1_T_1) | A + 4B + 2C + 10Dq (U − 2/7 J_H + 10Dq) | Δ_0(t_{2g}^2) + 9B + 2C + 10Dq (U − 2/7 J_H + 10Dq + 5/7 J_H) |

states, i.e., l^1_T_2, l^1_E and l^1_A_1, will have energies higher by 2J_H, 2J_H and 5J_H, respectively. Then the excitation energies to the l^1_T_2, l^1_E and l^1_A_1 states can be written as Δ_0(t_{2g}^1) + 2J_H, Δ_0(t_{2g}^1) + 2J_H and Δ_0(t_{2g}^1) + 5J_H, respectively. For the t_{2g}^1 configuration, there will be four final eigenstates, represented by l^3_T_2, l^3_T_1, l^1_T_2 and l^1_T_1. The excitation energies into these states can be evaluated in a similar manner.

Table 2 summarizes all of the possible d^1 → Ld^2 transitions when the orbital multiplicity effects are fully taken into account. The first column shows all of the possible d^2 final states in the irreducible representation. The second and third columns show the eigenenergy values of the final d^2 configuration E(d^2) and the corresponding p–d transition energy costs ΔE(d^1 → Ld^2), respectively. Both of them are represented in two different ways, i.e., in terms of Racah parameters, A, B and C, as well as in terms of U and J_H.

In table 3, we show excitation energies of the possible p–d transitions, d^n → Ld^{n+1} with n = 2, 3, 4 and 5. We assume that the ground states of the initial d^n states have the low-spin configurations, i.e., t_{2g}^n. The first column shows all of the possible d^{n+1} final states in the irreducible representation. And, the second column shows corresponding p–d transition energy costs ΔE(d^n → Ld^{n+1}). The reference energies Δ_0(t_{2g}^n) are defined as the excitation energies to the t_{2g}^{n+1} final states, shown in the second row of each table. Note that all of the excitation energies can be represented in terms of three energy parameters, Δ_0(t_{2g}^n), J_H and 10Dq.

In the above, we discussed the p–d transitions both using the simple electron configuration and considering the orbital multiplicity effects. Let us begin to compare the possible excitations.
Table 3. Possible p–d transitions of the dⁿ systems (n = 2–5), dⁿ → Ldⁿ⁺¹, considering the multiplicity effects. The first column shows the possible dⁿ⁺¹ final states, and the second column shows the corresponding energy cost of each excitation. Here, Δ₀(t₂ᵍ) are defined as the excitation energies to the t₂ᵍ⁺¹ states shown in the second row of each table, where the energy eigenvalues of the t₂ᵍ⁺¹ states are also shown. In this table also, we suppose that J_H = J_3 ≃ 7B, J₁ ≃ 4/7 J_H, J₂ ≃ 5/7 J_H and J₄ ≃ 8/7 J_H.

\[
\begin{array}{cccc}
\text{d}^3 & \Delta E(\text{d}^3 \rightarrow \text{L}d^3) & \text{d}^4 & \Delta E(\text{d}^4 \rightarrow \text{L}d^4) \\
\hline
t\text{t}_2^g(4\text{A}_2) & \Delta_0(t_2^g) & t\text{t}_2^g(3\text{T}_1) & \Delta_0(t_2^g) \\
(\text{E}^\text{t}^2(\text{A}_2) = 3U - 9J_H) & (\text{E}^\text{t}^2(\text{A}_1) = 6U - 13J_H) \\
t\text{t}_2^g(2E) & \Delta_0(t_2^g) + 2J_H & t\text{t}_2^g(5\text{E}) & \Delta_0(t_2^g) + 10Dq - \frac{26}{7} J_H \\
t\text{t}_2^g(2\text{T}_1) & \Delta_0(t_2^g) + 2J_H & t\text{t}_2^g(5\text{E}) & \Delta_0(t_2^g) + 10Dq - \frac{4}{7} J_H \\
t\text{t}_2^g(2\text{T}_2) & \Delta_0(t_2^g) + 5J_H & t\text{t}_2^g(5\text{E}) & \Delta_0(t_2^g) + 10Dq - \frac{9}{7} J_H \\
t\text{t}_2^g(4\text{T}_2) & \Delta_0(t_2^g) + 10Dq + \frac{12}{7} J_H & t\text{t}_2^g(5\text{E}) & \Delta_0(t_2^g) + 10Dq + \frac{3}{7} J_H \\
t\text{t}_2^g(4\text{T}_1) & \Delta_0(t_2^g) + 10Dq + \frac{1}{7} J_H & t\text{t}_2^g(5\text{E}) & \Delta_0(t_2^g) + 10Dq + \frac{3}{7} J_H \\
\hline
t\text{t}_2^g(2\text{T}_2) & \Delta_0(t_2^g) & t\text{t}_2^g(4\text{A}_1) & \Delta_0(t_2^g) \\
(\text{E}^\text{t}^2(\text{T}_2) = 10U - 20J_H) & (\text{E}^\text{t}^2(\text{A}_1) = 15U - 30J_H) \\
t\text{t}_2^g(4\text{T}_1) & \Delta_0(t_2^g) + 10Dq - \frac{11}{7} J_H & t\text{t}_2^g(4\text{T}_1) & \Delta_0(t_2^g) + 10Dq - \frac{3}{7} J_H \\
t\text{t}_2^g(4\text{T}_2) & \Delta_0(t_2^g) + 10Dq - 3J_H & t\text{t}_2^g(4\text{T}_2) & \Delta_0(t_2^g) + 10Dq - \frac{5}{7} J_H \\
t\text{t}_2^g(4\text{T}_1) & \Delta_0(t_2^g) + 10Dq + \frac{1}{7} J_H & t\text{t}_2^g(4\text{T}_1) & \Delta_0(t_2^g) + 10Dq + \frac{3}{7} J_H \\
t\text{t}_2^g(4\text{T}_2) & \Delta_0(t_2^g) + 10Dq + \frac{5}{7} J_H & t\text{t}_2^g(4\text{T}_2) & \Delta_0(t_2^g) + 10Dq + \frac{7}{7} J_H
\end{array}
\]

with results of the d¹ system. Among the five possible d² final states in the d¹ → Ld² excitation shown in figure 2(a), except for the state in the first diagram, the other four d² states are not eigenstates, but states composed of more than one eigenstate. For example, the second diagram corresponds to a state composed of ⁴T₁ and ¹T₂, whose wavefunctions are shown in table 1 as \(\Psi(t_2^g(1T_1(\text{H}=0))) = \frac{1}{\sqrt{2}}[|d_x(\uparrow)\downarrow d_y(\downarrow)\downarrow | - |d_y(\uparrow)\downarrow d_x(\downarrow)\downarrow |]\) and \(\Psi(t_2^g(1T_2)) = \frac{1}{\sqrt{2}}[|d_x(\uparrow)\downarrow d_y(\downarrow)\downarrow | + |d_y(\uparrow)\downarrow d_x(\downarrow)\downarrow |]\). Referring to the results shown in table 2, the excitation energies to the ³T₁ and ¹T₂ states are \(\Delta_0(t_2^g(1T_1))\) and \(\Delta_0(t_2^g(1T_2)) + 2J_H\), respectively. So, the p–d transition to the state shown in the second diagram of figure 2(a) should have two excitation energies, \(\Delta_0(t_2^g)\) and \(\Delta_0(t_2^g) + 2J_H\), whose averaged value happens to be the same as the excitation energy evaluated using the simple electron configuration.

In the second and subsequent lines above each diagram of figure 2, we display the eigenstates composing each final state and the corresponding energy costs with a parenthesis. Actually, most of the averaged values of all possible transition energies are quite similar to the values evaluated with the simple consideration of the orbital occupation, although there are some differences for the transition to the e₈ states. (Such differences originate mainly from the wide variation of the
Table 4. Possible d–d transitions considering the multiplicity effects. Among the final states of each optical process, we show the states having the multiplicity effect, such as the $t^2_{2g}$ state for the $t^1_{2g}$ system, the $t^3_{2g}$ state for the $t^2_{2g}$ system, and the $t^2_{2g}$ and $t^4_{2g}$ states for the $t^3_{2g}$ system. Also, we display the corresponding energy costs in each optical process.

| Optical process | Multiplet final states and energy costs |
|-----------------|----------------------------------------|
| $t^1_{2g} t^1_{2g} \rightarrow t^0_{2g} t^2_{2g}$ (LaTiO$_3$) | $t^2_{2g}(^3T_1)$, $t^2_{2g}(^1E, ^1T_2)$, $t^2_{2g}(^4T_1)$, $U - 3J_H$, $U - J_H$, $U + 2J_H$ |
| $t^2_{2g} t^2_{2g} \rightarrow t^1_{2g} t^3_{2g}$ (LaVO$_3$) | $t^3_{2g}(^4A_2)$, $t^3_{2g}(^2E, ^2T_1)$, $t^4_{2g}(^2T_2)$, $U - 3J_H$, $U$, $U + 2J_H$ |
| $t^3_{2g} t^3_{2g} \rightarrow t^2_{2g} t^4_{2g}$ (LaCrO$_3$) | $t^2_{2g}(^3T_1)/t^4_{2g}(^4T_1)$, $U$ |
Figure 3. Schematic diagrams showing the optical selection rule. In (a), there are two singly occupied $d_{xy}$ orbitals hybridized with the oxygen $p_y$ orbital in between, and the upward and downward arrows indicating the spin states. The d–d transition is weakly allowed between two d orbitals. In (b), there are two orthogonal $d_{xy}$ and $d_{yz}$ orbitals, and the d–d transition is forbidden between them.

$U$ and $U + 2J_H$, which are similar to those for the $t_{2g}^1$ system. Interestingly, for $t_{2g}^3$ system, its d–d transition appears only at $U + 2J_H$. d–d transitions for the $t_{2g}^4$ and the $t_{2g}^6$ systems are the same as those of the $t_{2g}^2$ and the $t_{2g}^4$ system, respectively, due to the electron–hole symmetry.

3.3.2. Intersite d–d transitions related to the spin and orbital correlations. In this subsection, let us look into the possibility of probing spin and orbital correlations using the intersite d–d transitions. To begin with, it is useful to consider the selection rules for the intersite d–d transitions. In real oxides, the intersite d–d transitions could be allowed due to the hybridization between the O 2p bands and the TM d bands. Figure 3(a) shows an intersite d–d transition from one $d_{xy}$ orbital to other $d_{xy}$ orbitals in the nearest-neighbour TM ions. If their spins are aligned along the same direction, the intersite transition should be forbidden due to the Pauli exclusion principle. On the other hand, if their spins are in opposite directions, the intersite transition could be allowed, since the corresponding matrix element might not be zero due to the finite overlap of the $d_{xy}$ orbitals, hybridized with the O 2p$_y$ orbital. Figure 3(b) shows another intersite d–d transition from one $d_{xy}$ orbital to other $d_{yz}$ orbitals in the nearest-neighbour TM ions. In this case, even when their spins are pointing in opposite directions, the overlap between the d orbitals is negligibly small (even with any O 2p orbital), so the corresponding intersite transition should be almost forbidden.

Let us apply this selection rule to numerous $t_{2g}^n$ transitions. It should be noted that, depending on the spin and orbital arrangements between the nearest-neighbour d metal ions, the allowed transitions could vary. As shown in figure 4, for each $t_{2g}^n$ transition, we can think of four spin/orbital configurations as initial states, i.e., FM/FO, FM/AFO, AFM/FO and AFM/AFO. Here, FM and AFM represent the ferromagnetic and the antiferromagnetic spin configurations between the d electrons, respectively. And, FO (AFO) represents the ferro-orbital (antiferro-orbital) configuration, in which the same (different) $t_{2g}$ orbitals are occupied in neighbouring sites. In each diagram, the allowed transitions are shown with the dotted arrows, and the corresponding excitation energy values are also written with the irreducible representations of the final states in parentheses.

Figure 4(a) shows the d–d transitions for the $t_{2g}^1$ system, namely the $t_{2g}^1_t_{2g}^1 \rightarrow t_{2g}^1t_{2g}^1$ transitions. For the FM/FO configuration, there should be no possible transition due to the aforementioned selection rule. For the FM/AFO configuration, there exists a single d–d transition to the high-spin configuration, which corresponds to the $^3T_1$ final eigenstate. Its excitation energy should be $U - 3J_H$. For the AFM/AFO configuration, the $d^3$ final state is composed of two eigenstates
Figure 4. Schematic diagram showing possible d–d transitions in various spin/orbital configurations of (a) the d^1 system, (b) the d^2 system, and (c) the d^3 system. We assume four spin/orbital configurations, FM/FO, FM/AFO, AFM/AFO and AFM/FO. Possible optical excitations are shown as dotted arrows together with the excitation energies and the corresponding eigenstates.

Table 5. Possible d–d transitions in various spin/orbital configurations of FM/FO, FM/AFO, AFM/AFO and AFM/FO in the t^n_2g systems with n = 1−5. Note that the results for the t^1_2g and t^2_2g systems should be the same as those for the t^3_2g and t^4_2g systems, respectively.

|                | FM/FO | FM/AFO | AFM/AFO | AFM/FO |
|----------------|-------|--------|---------|--------|
| t^1_2g/t^5_2g  | –     | U−3J_H | U−3J_H/U−J_H | U−J_H/U+2J_H |
| t^2_2g/t^4_2g  | –     | U−3J_H | U/U+2J_H  | U/U+2J_H  |
| t^3_2g         | –     | –      | –        | U+2J_H   |

^3T_1 and ^1T_2, as was demonstrated in section 3.2. From table 4, the excitation energies for this configuration could be evaluated to be U−3J_H and U−J_H. For the AFM/FO configuration, d–d transitions should occur to the low-spin configurations, which are composed of the ^1A_1 and ^1E states. Also, their excitation energies should be U−J_H and U+2J_H. Allowed d–d transitions with proper excitation energies for the t^2_2g and t^4_2g systems can be similarly evaluated and are displayed in figures 4(b) and (c), respectively. For the t^3_2g system, we do not have to consider the AFO configuration, since all three t_2g orbitals are already occupied.

Table 5 summarizes the relations between the intersite d–d transitions and the spin/orbital correlation for the t^n_2g systems (n = 1−5). For n = 1, 2 and 3, the possible excitation energies are the same as those shown in table 4, but displayed in terms of the spin and orbital configurations. (As mentioned earlier, the results for n = 4 and 5 should be the same as those for n = 2 and 1, respectively, due to the electron–hole symmetry.) For the t^1_2g (or t^5_2g) system, the lowest excitations at U−3J_H can occur in both the FM/AFO and the AFM/AFO configurations. The other excitation at U−J_H can occur in both the AFM/AFO and the AFM/FO configurations, and the highest U+2J_H excitation can occur solely in the AFM/FO configuration. For the t^2_2g (or t^4_2g) system, the intersite d–d transitions for the FM-spin configuration have the lowest excitation energy, i.e., U−3J_H, but those for the AFM-spin configurations have the higher energies of U and U+2J_H. For the t^3_2g system, the only allowed intersite d–d transitions should occur for the
AFM/AFO configuration. Note that spectral weight of each d–d transition will critically depend on the overlap integral of the orbitals involved.

Using the spectral-weight analysis, we can sometimes probe the spin and/or the orbital correlations between nearest-neighbour d ions. From an experimental optical spectrum, we could analyse its spectral features in terms of the allowed optical transition. For some spectral regions, most of such spectral features might come mainly from the intersite d–d transitions addressed in this section. In such a case, we might be able to analyse the spectrum in terms of the d–d transitions, displayed in figure 4. From the spectral weights estimated from such analysis, we can obtain information on spin/orbital correlations. For example, if we observe the d–d transition for the $t_{2g}^2$ (or $t_{2g}^4$) systems at $U - 3J_H$ and obtained the contribution from such transitions in the total spectral weights, we might be able to get information on the ratio of FM to AFM correlations [15].

4. Discussions

4.1. Comparisons with earlier experimental data

4.1.1. Early 3d TM oxides LaMO$_3$ with a perovskite structure. Arima and Tokura have done pioneering works by investigating the optical conductivity spectra $\sigma(\omega)$ of 3d TM oxides, and showed that some of the early compounds have the Mott insulator character; namely, their optical gaps should be determined by the d–d transitions [12]. Figure 5 shows $\sigma(\omega)$ of some early 3d TM oxides LaMO$_3$ with a perovskite structure, where M = Sc, Ti, V and Cr, obtained by Arima.
and Tokura [12]. Note that each TM ion has zero to three $t_{2g}$ electrons in order. All of the spectra show strong absorption edges around 4–6 eV, whose peaks correspond to the charge-transfer excitations. Accordingly, the spectral weight below such absorption edges should be attributed to the intersite d–d transitions. For LaScO$_3$, the p–d transition appears from around 6 eV, but there is almost no spectral weight below 6 eV. In this d$^0$ band insulator compound, there is no d electron in the valence band, so the intersite d–d transition is not allowed.

There are a few intriguing spectral features in these $\sigma(\omega)$, which have not been explained up to this point. Firstly, $\sigma(\omega)$ of LaTiO$_3$ and LaVO$_3$ showed very broad spectral features below the p–d transitions, which usually cannot be fitted with a single Lorentz oscillator. Secondly, the observed peak positions for the d–d transitions for of LaTiO$_3$ and LaVO$_3$ seem to be much lower than the $U$ values determined by other studies. It can be noted that the observed peak energies of the p–d transitions are consistent with the theoretical values of $\Delta$: namely, around 7.0 eV for LaTiO$_3$ and 6.0 eV for LaVO$_3$ [28, 29]. However, it seems that the d–d transitions appear around 2 eV, which is much lower than the theoretical $U$ values of around 4.0 eV for LaTiO$_3$ and 4.5 eV for LaVO$_3$ [28, 29]. Thirdly, $\sigma(\omega)$ of LaCrO$_3$ does not exhibit any spectral features for the d–d transition. Lack of a d–d transition below the 4.0 eV region indicates that, if it exists, the d–d transition should be located in a higher energy region. This high value of the d–d transition energy is not consistent with the values around 2 eV of the d–d transition energies for LaTiO$_3$ and LaVO$_3$.

Based on the d–d transitions considered in section 3.2.2, let us look into the p–d transitions of these early 3d TM oxides. For LaVO$_3$, since the V$^{3+}$ ion has the $t_{2g}^2$ configuration, as shown in figure 2(b), the charge–transfer excitations have seven different energy costs of $\Delta_0(t_{2g}^2), \Delta_0(t_{2g}^2)+3J_H, \Delta_0(t_{2g}^2)+5J_H, \Delta_0(t_{2g}^2)+10Dq-\frac{3}{7}J_H, \Delta_0(t_{2g}^2)+10Dq+\frac{9}{7}J_H, \Delta_0(t_{2g}^2)+10Dq+\frac{13}{7}J_H$, and $\Delta_0(t_{2g}^2)+10Dq+\frac{20}{7}J_H$. If we adopt the parameter values as $(\Delta_0(t_{2g}^2), J_H, 10Dq) \simeq (5.0 \text{ eV}, 0.7 \text{ eV}, 1.5 \text{ eV})$ [28, 29], then the excitations should appear around $(\Delta_0(t_{2g}^2), \Delta_0(t_{2g}^2)+3J_H, \Delta_0(t_{2g}^2)+5J_H, \Delta_0(t_{2g}^2)+10Dq-\frac{3}{7}J_H, \Delta_0(t_{2g}^2)+10Dq+\frac{9}{7}J_H, \Delta_0(t_{2g}^2)+10Dq+\frac{13}{7}J_H, \Delta_0(t_{2g}^2)+10Dq+\frac{20}{7}J_H) = (5.0 \text{ eV}, 7.1 \text{ eV}, 8.5 \text{ eV}, 6.2 \text{ eV}, 7.4 \text{ eV}, 7.8 \text{ eV}$ and 8.5 eV). These predicted excitation energies are consistent with the experimental results shown in [12], where the strong charge–transfer excitations are observed around 5 and 6–8 eV. With similar energy parameters, the charge–transfer excitations for LaTiO$_3$ and LaCrO$_3$ can also be well understood.

Based on the d–d transitions discussed in section 3.3.2, we could provide a possible answer to the long-standing problems of the low-frequency spectral features in some early 3d TM oxide. Firstly, the broad and multi-peak structures of the d–d transitions could be understood in terms of the multiple intersite d–d transitions due to the orbital multiplicity effects. For LaTiO$_3$, having the $t_{1g}^1$ configuration of the Ti$^{3+}$ ion, the d–d transitions should appear at $U-3J_H$, $U-J_H$, and $U+2J_H$ and for LaVO$_3$, having the $t_{2g}^2$ configuration of the V$^{3+}$ ion, they should appear at $U-3J_H$, $U$ and $U+2J_H$. Accordingly, their d–d transitions should spread over 5$J_H$, which could be around 3–4 eV [28, 29]. Note that these broad spectral features cannot be explained in the optical spectra of LaTiO$_3$, shown in figure 5 (reproduced from [12]), the d–d transition has a very broad spectral weight down to below 0.5 eV, so it is not easy to determine exact peak positions. This might be due to the large bandwidth of the Ti 3d states [30], and/or the intrinsic oxygen off-stoichiometries [31], which are well known to induce the metallic behaviour. On the other hand, note that for YTiO$_3$, which also contains the Ti$^{3+}$ ions with one $t_{2g}$ electron, the lowest peak centre related to the d–d transition can be easily identified around 2 eV [12]. Therefore, we estimated the lowest d–d transition of the titanate to be about 2.0 eV.

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3 In the optical spectra of LaTiO$_3$, shown in figure 5 (reproduced from [12]), the d–d transition has a very broad spectral weight down to below 0.5 eV, so it is not easy to determine exact peak positions. This might be due to the large bandwidth of the Ti 3d states [30], and/or the intrinsic oxygen off-stoichiometries [31], which are well known to induce the metallic behaviour. On the other hand, note that for YTiO$_3$, which also contains the Ti$^{3+}$ ions with one $t_{2g}$ electron, the lowest peak centre related to the d–d transition can be easily identified around 2 eV [12]. Therefore, we estimated the lowest d–d transition of the titanate to be about 2.0 eV.
terms of the single-band Hubbard model. Secondly, the low values of the d–d transition energies for LaTiO3 and LaVO3 can be explained from the fact that the lowest excitation energy of the d–d transitions is not $U$ but $U - 3J_H$ for the $t_{2g}^4$ and $t_{2g}^2$ configurations. Since the $U$ and $J_H$ values of these compounds could be assumed to be around 4.5 and 0.7 eV, respectively [28, 29], $U - 3J_H$ should be around 2.4 eV. This value is quite consistent with the optically observed peak positions for both compounds [12]. Thirdly, the lack of a d–d transition below the 4.0 eV region for LaCrO3 can be explained from the fact that the lowest excitation energy for the half-filled $t_{3g}^3$ orbital configuration is $U + 2J_H$. Since the $U$ and $J_H$ values of LaCrO3 are similar to those of LaTiO3 and LaVO3 [28, 29], the $U + 2J_H$ peak should be located above 6 eV. Consequently, the disappearance of the d–d transition around 2 eV can be understood in terms of the intrinsically forbidden $U - 3J_H$ peak due to the half-filled $t_{3g}^3$ orbital configuration. Considering the orbital multiplicity effects, we could explain the intriguing low-frequency spectral features of some early 3d TM oxides successfully.

4.1.2. Probing spin and orbital correlations using intersite d–d transitions. When we consider the orbital multiplicity effect to gain understanding of the optical excitations, one of the most important merits is that it can provide information on the spin and/or orbital correlations between the neighbouring TM ions in terms of the intersite d–d transitions. Very recently, there have been several studies addressing the spin/orbital correlations using the optical investigations for some $t_{2g}^4$ systems and $t_{2g}^2$ systems, such as LaVO3 [32, 33], YVO3 [34], RE2Mo2O7 [15] and Ca$_{2-x}$Sr$_x$RuO4 [14]. In these cases, the $U - 3J_H$ transition is directly coupled to the FM spin correlation, so its spectral-weight enhancements should be attributed to the increases of the FM correlation as the systems get into the FM state. Similar to our approach, Khalullin et al considered the orbital degeneracy to explain characteristic spectral features of LaVO3, i.e., the anisotropy in the optical absorption and its strong temperature dependence near the magnetic transitions [33]. In terms of the spin and orbital superexchange interactions, they demonstrated a theoretical evidence that the spin/orbital correlations play important roles in determining the optical spectral weights in the Mott insulators. By the way, our systematic approaches on the intersite d–d transitions, demonstrated in section 3.3.2, could extend such spin and/or orbital

4 In our earlier papers on (Ca,Sr)$_2$RuO4 [14] and RE$_2$Mo$_2$O$_7$ [15], we considered diagrams of the $t_{2g}^4$ → $t_{2g}^4$ and $t_{2g}^2$ → $t_{2g}^2$ transitions, respectively, which are similar to figure 4(b). In those papers, we considered a simple argument, so we assigned only one excitation energy for the FO/AFM configuration. However, in this paper, we presented a more refined and correct picture, which takes account of the orbital degeneracy effects fully, and assigned two excitation energies to the configuration. Let us look into the conclusions of [14, 15] based on the more refined picture. If the spectral weight of each peak is linearly proportional to configurations of the initial state, then the relative ratio between contributions from the AFO and the FO configurations to the $U$ (or $U + 2J_H$) peak should be 2:1 (or 1:1). So, the spectral weight decrease of the $U$ peak for the insulating (Ca,Sr)$_2$RuO$_4$, accompanying the spectral weight increase of the $U + 2J_H$ peak, could be related to the reduction of the AFO configuration. And, for the Mo-oxides, since the lowest $U - 3J_H$ excitation is solely attributed to the FM configuration in our modified picture also, its spectral weight enhancement could be attributed to the increase of the FM correlation. It should be noted that, although we adopt the more refined picture for the d–d transitions, the conclusions made in our previous papers should remain valid.

5 In [33] they emphasized the quantum effects beyond the mean-field theory on the optical spectral weights. They argued that even above the magnetic transition temperatures the optical spectral weights should show a finite temperature dependence due to the spin–orbital fluctuation effects.
correlation studies to other \( t_{2g}^{5} \) systems \((n = 1 \text{ and } 5)\). As far as we know, there have been few efforts to obtain spin/orbital correlations in the \( t_{2g}^{1} \) and \( t_{2g}^{5} \) systems using optical studies.

Recently, Lukenheimer \textit{et al} reported the temperature-dependent spectral-weight changes of LaTiO\(_3\), a \( t_{2g}^{1} \) system [35]. They showed that the spectral weight below 2 eV, which should correspond to the \( U - 3J_H \) peak, increases slightly as temperature decreases. The ground state of this titanate is known to have a G-type AFM and orbital liquid state, and the magnetic transition occurs around 140 K [3]. Table 4 shows that the \( U - 3J_H \) peak of the \( t_{2g}^{1} \) system should come from FM/AFO and AFM/AFO configurations. (Note that this is different from the \( t_{2g}^{5} \) system, where the \( U - 3J_H \) peak should come from FM/AFO only.) From this table, it is clear that most of the lowest peak contributions should come from the AFO correlation. In addition, the weak temperature dependence of the peak should be due to the competition between contributions of FM/AFO and AFM/AFO configurations to the \( U - 3J_H \) peak. A further spectroscopic investigation is highly desirable to obtain a more detailed understanding of the spin/orbital correlations for this compound.

4.1.3. Remaining problems in intersite d–d transitions. Our new approach based on the consideration of orbital degeneracy provides a general framework to analyse the spectral features of numerous perovskite oxides. Most importantly, the approach allows us an important merit, i.e. to estimate the contribution of the spin and orbital degree of freedom in optical spectra. However, it should be noted that there remain some controversies and limitations in this approach.

Firstly, it could be controversial in determining the energy scale of \( U \) and \( J_H \). For example, Miyasaka \textit{et al} investigated strongly temperature-dependent optical features in LaVO\(_3\) and YVO\(_3\), and explained them in terms of the Mott–Hubbard gap transition due to spin and orbital ordering [32]. Especially, they observed that multiple peaks appear between 1.8 and 3.0 eV, and the splittings between the peaks are around 0.5 eV. They tried to explain this fine spectral splitting features in terms of different intersite d–d transitions, similar to this work but with a much more limited version [32]. However, such an explanation of the fine splitting may not be correct. Since the value of \( J_H \) is known to be about 0.6 eV for both vanadates [28, 29], the energy differences of the intersite d–d transition, based on our analysis, should be \( 3J_H \) (i.e. 1.8 eV) between the \( U - 3J_H \) and the \( U \) peaks. Moreover, while LaVO\(_3\) and YVO\(_3\) have different spin and orbital ground states, their temperature dependences closely resemble one another. Since the spectral weights of the d–d transition should be strongly affected by the spin and orbital correlations, the observed similar temperature dependences for different spin and orbital ground states cannot be explained in our picture by considering the orbital multiplicity effects. The spectral splitting should come from different physical origins, whose energy scale should be smaller than the exchange energy of the electrons. The origin and the temperature dependences of the spectral features of LaVO\(_3\) and YVO\(_3\) around 2.5 eV remain to be investigated further.

Secondly, our approach could become less realistic under the degeneracy lifting due to the local lattice distortion. Up to this point, we have considered the case when d orbitals have exactly the same energy. When there are physical mechanisms which will result in a higher energy splitting than the characteristic energy scale used in this study, i.e. \( U \) and \( J_H \), our analysis based on the orbital degeneracy cannot be applied. However, when the new interaction results in a smaller energy splitting, we should treat the new term as the perturbing Hamiltonian. For example, in the case of a system with a structural distortion, such as the Jahn–Teller distortion and the

\( \sigma(\omega) \) of LaMnO\(_3\) shows a similar spectral feature, i.e., a fine spectral splitting for the 2.0 eV feature. For examples, see [36]–[38].

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GdFeO$_3$-type distortion [24], it would be easier for us to start from the results demonstrated in this paper. However, the selection rule, addressed in section 3.3.2, for the intersite d–d transition may not hold: for example, the intersite d–d transition from one d$_{xy}$ orbital to another d$_{yz}$ orbital in nearest neighbour TM ions could be allowed, since there might be a hybridization between the orbitals due to the structural symmetry lowering. In such a case, we should consider the possibility of further splitting of the d–d transitions, and, moreover, should be careful in assigning the meaning of the spectral weights of the d–d transitions.\footnote{Related to the degeneracy lifting of t$_{2g}$ orbitals, some materials exhibit exotic orbital orderings. For example, the recent x-ray absorption study for YTiO$_3$ showed that the wave functions of 0.8|d$_{x^2}$⟩ − 0.6|d$_{yz}$⟩ and 0.8|d$_{x^2}$⟩ + 0.6|d$_{yz}$⟩ are alternately arranged at the Ti$^{3+}$ sites (see [39]). In such a case, while the simple approach shown in figure 4 is difficult to be applied directly, a more detailed consideration is needed for supposing the initial states of the d–d transitions.}

Finally, we emphasize that our approach can be more accurate when the band effect is taken into account additionally. In TM oxides, it is well known that the p–d hybridization, which is closely related to the transfer integral or the bandwidth, also plays an important role in determining the energies and the spectral weights of the optical excitations. For the p–d transitions, both of them should increase as the hybridization strength increases [40]–[42]. For the d–d transitions, their excitation energies are determined by $U$ and $J_H$ in our approach, such as $U - 3J_H$, $U - J_H$ and $U + 2J_H$ for the t$_{2g}^1$ systems. As a result, while the offset energies of the d–d transitions could be influenced by the hybridization effect (or the screening effect), their energy separations would not be much affected by the hybridization since $J_H$ usually retains its atomic value even in a solid. For the spectral weight of the d–d transitions, it is supposed to be linearly proportional to the configuration of the initial states. However, in order to address the spectral weight properly, a more thorough analysis is desirable to take account of the transfer integral in estimating the matrix element of the optical transitions [43].

4.2. Extension to the systems with $e_g$ electrons

Up to now, we have focused on t$_{2g}^n$ systems ($n = 1–5$). There are eight other d-orbital configurations which have not been addressed in this paper, i.e., t$_{2g}^3$e$_{g}^1$, t$_{2g}^3$e$_{g}^2$, t$_{2g}^4$e$_{g}^2$, t$_{2g}^4$e$_{g}^1$, t$_{2g}^6$, t$_{2g}^6$e$_{g}^1$, t$_{2g}^6$e$_{g}^2$ and t$_{2g}^6$e$_{g}^3$ systems. Here, we briefly discuss some of important features of their d–d transitions. The lowest excitation energies for t$_{2g}^1$e$_{g}^1$, t$_{2g}^1$e$_{g}^2$, and t$_{2g}^1$e$_{g}^3$ systems are given as $U - 3J_4$, and those for t$_{2g}^2$e$_{g}^2$ and t$_{2g}^2$e$_{g}^3$ systems are given as $U - 3J_3$. All of them are excitation energies to the high-spin final states, and mainly contributed by the FM/AFO configuration. For the t$_{2g}^3$ and t$_{2g}^5$ systems, the lowest excitation energies are given as $U + J_1 + 2J_3 + J_4 (= A + 14B + 7C)$ and $U + J_4$, respectively. (For the t$_{2g}^1$ system, no d–d transition is allowed.) Since these two configurations are in the half-filled state similarly to the t$_{2g}^3$ system, while the transition to the high-spin state is not defined, the d–d transitions are only possible for the AFM/FO-configuration, which has the highest excitation energy among the four spin/orbital configurations. However, in most real perovskite metal oxides with $e_g$ electrons, the charge transfer excitations are dominant in the low-frequency region, so the analysis for the d–d transition could not be easily applicable.

4.3. Revisit to the Zaanen–Sawatzky–Allen scheme

Zaanen, Sawatzky and Allen classified strongly correlated electron systems into charge-transfer type insulators and Mott–Hubbard type insulators in terms of two physical quantities, i.e., on-site
Coulomb interaction and the charge-transfer energy [16]. According to the scheme, while the optical conductivity spectra of the charge-transfer type insulator should have the p–d transition as their lowest optical excitation, that is, $\Delta_{\text{eff}} < U_{\text{eff}}$, $\sigma(\omega)$ of the Mott–Hubbard type insulator should have the d–d transition as its lowest excitation energy, that is, $\Delta_{\text{eff}} < U_{\text{eff}}$. Here, the effective charge-transfer energy $\Delta_{\text{eff}}$ and the effective Coulomb repulsion energy $U_{\text{eff}}$ correspond to the lowest excitation energies of the p–d transitions and the d–d transitions, respectively.

Previously, using photoemission studies, Fujimori et al [25] provided explicit arguments about the orbital multiplicity effects on the electronic structure considering the multiplet corrections to each energy state of the system. However, there have been few optical investigations which take account of such multiplicity effects. In the early works on the optical spectra of the 3d TM oxides, Arima and Torura et al [12] treated the optical gap without considering the orbital multiplicity effects explicitly and used the Zaanen–Sawatzky–Allen scheme. Here, we briefly address the estimated optical excitation energies considering the orbital multiplicity effects. The orbitally degenerate Hubbard model predicts that, except for the half-filled cases, the $U_{\text{eff}}$ values should be smaller by $3J_3$ or $3J_4$ than the $U$ value. For the half-filled cases, such as $t_{2g}^3$, $t_{2g}^3 e_{g}^2$ and $t_{2g}^6 e_{g}^2$ systems, $U_{\text{eff}}$ should be larger by $2J_3$, $\sim 4J_3$ and $J_4$, respectively, than the $U$ value. These differences should be explicitly included to use the Zaanen–Sawatzky–Allen scheme from the optically determined values of the related physical quantities.

5. Summary

We attempted to understand the optical excitations of the perovskite TM oxides with $t_{2g}$ electrons by taking orbital multiplicity effects into consideration. We evaluated the excitation energies of the charge transfer p–d and the intersite d–d optical excitations, and compared them with the previously reported experimental results. We could provide a possible answer to a few intriguing long-standing problems in the optical conductivity spectra of some early 3d TM oxides. We applied these results to understand the optical spectral features of some TM oxides in terms of spin and/or orbital correlations. We also discussed some energy splitting features observed in the intersite d–d transition regions, which are not possible to explain within this model.

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