Theory of optical spectral weights in Mott insulators with orbital degrees of freedom

Giniyat Khaliullin  
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany  
and E. K. Zavoisky Physical-Technical Institute of the Russian Academy of Sciences, 420029 Kazan, Russia

Peter Horsch  
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

Andrzej M. Oleś  
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany  
and Marian Smoluchowski Institute of Physics, Jagellonian University, Reymonta 4, PL-30059 Kraków, Poland  

(Dated: 9 June 2004)

Introducing partial sum rules for the optical multiplet transitions, we outline a unified approach to magnetic and optical properties of strongly correlated transition metal oxides. On the example of LaVO$_3$ we demonstrate how the temperature and polarization dependences of different components of the optical multiplet are determined by the underlying spin and orbital correlations dictated by the low-energy superexchange Hamiltonian. Thereby the optical data provides deep insight into the complex spin-orbital physics and the role played by orbital fluctuations.

PACS numbers: 75.30.Et, 75.10.-b, 75.10.Jm, 78.20.-e

I. INTRODUCTION

Charge localization in Mott insulators is not perfect as electrons still undergo virtual transitions to neighboring sites in order to retain partially their kinetic energy. These high-energy virtual transitions across the Mott-Hubbard gap ~ $U$ are crucial for magnetism — this quantum charge motion leads to superexchange (SE) interactions between local degrees of freedom. It is frequently not realized, however, that the same charge excitations are responsible in Mott insulators for the low-energy optical absorption. Therefore, the intensity of the optical absorption and the SE energy are intimately related to each other via the well known optical sum rule, which links the integrated optical conductivity and the kinetic energy. In Mott insulators the latter is due to virtual exchange processes and hence the thermal evolution of spectral weights and SE energy are related.

A qualitatively new situation is encountered in Mott insulators with partly filled $d$ orbitals. Because of orbital degeneracy, virtual charge excitations that are seen in optics reflect the rich multiplet structure of a transition metal ion determined by Hund’s exchange coupling $J_H$, and orbital degrees of freedom contribute then to the SE. When spin and orbital correlations change the individual components of the optical multiplet reflect characteristic spectral weight transfer. Moreover, the cubic symmetry is spontaneously broken by orbital and spin order, and thus one expects anisotropic optical absorption. Indeed, pronounced anisotropy was reported for LaMnO$_3$ for both the A-type antiferromagnetic (AF) phase and for the orbital ordered phase above the Néel temperature $T_N$. Recently, the anisotropy in optical absorption and its strong temperature dependence near the magnetic transitions were found for cubic vanadates. This latter example is even more puzzling as the magnetic properties are anomalous and neutron scattering experiments have revealed nontrivial quasi one-dimensional (1D) correlations of spin and orbital degrees of freedom that are surprising for crystals with nearly cubic symmetry. Indeed, a theory of spin and orbital states in cubic vanadates predicted quasi 1D spin-orbital correlations due to a spontaneous breaking of the cubic symmetry in the SE model.

It is our aim to outline a unified picture that links optical and magnetic properties at orbital degeneracy. Starting from the low-energy spin-orbital model we derive partial sum rules for the different excited states. Thereby we provide a rigorous theoretical basis for the analysis of optical spectral weights and show how the evolution of magnetic coherence manifests itself in optics as intensity transfer between different excitations (upper Hubbard bands). This explains the origin of dramatic variation of the optical absorption and its anisotropy with temperature $T$ in manganites, vanadates, and ruthenates, where at low $T$ the high-spin band carries most spectral weight for the directions with ferromagnetic (FM) spin correlations. We illustrate this idea for the case of C-type AF (C-AF) phase of cubic vanadates with degenerate $t_{2g}$ orbitals. We show that the predicted quasi 1D spin-orbital correlations realized in C-AF phase of LaVO$_3$, are reflected in the $T$-dependence of optical weights derived from the SE model.

The paper is organized as follows. First we present a generic structure of the SE interactions in a Mott insulator with orbital degrees of freedom in Sec. II, and relate them to the intensities in optical absorption. On the example of the SE interactions encountered in LaVO$_3$, we analyze next spin, orbital, and joint spin-and-orbital correlations which determine the optical intensities. In this way, we arrive at a set of self-consistent equations which are solved in Sec. III, where we present the numerical
results for the above sum rules for individual high-spin and low-spin excitations, as well as for the spin and orbital SE interactions. These results and their comparison with experiment are discussed in Sec. IV, where we also give a summary and more general conclusions.

II. THEORY

The SE interaction in a cubic Mott insulator with ions having orbital degrees of freedom has a generic form,

\[ \mathcal{H}_J = H_s + H_r + H_{\sigma r} = \sum_n \sum_{(ij) \parallel \gamma} H_{n,ij}^{(\gamma)}(ij), \]  

and consists of separate spin \( (H_s) \) and orbital \( (H_r) \) interactions, and of a dynamical coupling between them \( (H_{\sigma r}) \). This complex form of \( \mathcal{H}_J \), given by Eq. (1), follows from the terms \( H_{n,ij}^{(\gamma)}(ij) \) for each bond \( (ij) \) along a given cubic axis \( \gamma = a, b, c \), arising from the transitions to various upper Hubbard bands labelled by \( n \). The optical intensity of each band \( n \), for the photon polarization along a cubic axis \( \gamma \), is determined by the respective SE energy:

\[ \frac{a_0 \hbar^2}{c^2} \int_0^\infty \sigma_n^{(\gamma)}(\omega) d\omega = \frac{\pi}{2} K_n^{(\gamma)} = -\pi \left\langle H_n^{(\gamma)}(ij) \right\rangle. \]  

(2)

Here, \( a_0 \) is the distance between magnetic ions (the tight-binding model is implied), and \( \left\langle H_n^{(\gamma)}(ij) \right\rangle \) is the SE interaction for a bond \( (ij) \) along axis \( \gamma \). The first equality in Eq. (2) follows from the optical sum rule for a given transition \( n \), and relates the kinetic energy \( K_n^{(\gamma)} \) to the optical conductivity \( \sigma_n^{(\gamma)}(\omega) \) for this band, while the second equality relates the associated kinetic energy to the SE energy via the Hellman-Feynman theorem.

Experimental data is often presented in terms of an effective carrier number [see, e.g., Eq. (2) of Ref. 7], \( N_{eff,n}^{(\gamma)} = (2m_0v_0^2/e^2) \int_0^\infty \sigma_n^{(\gamma)}(\omega) d\omega \), where \( m_0 \) is the free electron mass, and \( v_0 = a_0^2 \) is the volume per magnetic ion. This gives an optical sum rule as follows:

\[ N_{eff,n}^{(\gamma)} = -\frac{m_0a_0^2}{\hbar^2} K_n^{(\gamma)} = -\frac{m_0a_0^2}{\hbar^2} \left\langle 2H_n^{(\gamma)}(ij) \right\rangle. \]  

(3)

Each level \( n \) of the multiplet represents an upper Hubbard band with its own spin and orbital quantum numbers. The key point is that while full kinetic energy and corresponding total intensity may show only modest \( T \)-dependence and almost no anisotropy, the behavior of the individual transitions is much richer, and directly reflects the ground state correlations via the spin and orbital selection rules.

Hund’s exchange separates the lowest (high-spin) excitation from the next (low-spin) one by: \( \sim 5J_H \) in manganites, \( 3J_H \) in vanadates, and \( 2J_H \) in titanates. When the high-spin excitation, broadened by its propagation in crystal and by many-body effects, has a smaller linewidth than the multiplet splitting, it may show up in optical spectroscopy as a separate band. This is in fact nearly satisfied for typical values of \( J_H \sim 0.6 - 0.7 \text{ eV} \) and hoppings \( t \sim 0.4 \text{ eV} \sim 0.2 \text{ eV} \) for \( eg \) \((t_{2g}) \) orbitals. Higher bands overlap and mix up with \( d - p \) transitions, though.

In a particular case of vanadates, one has three optical bands \( n = 1, 2, 3 \) arising from the transitions to: (i) a high-spin state \( 4A_2 \) at energy \( U - 3J_H \), (ii) two degenerate low-spin states \( 2T_1 \) and \( 2E \) at \( U \), and (iii) \( 2T_2 \) low-spin state at \( U + 2J_H \). Using \( \eta = J_H/U \) we parametrize this multiplet structure by: \( R = 1/(1 - 3\eta) \) and \( r = 1/(1 + 2\eta) \). In LaVO\(_3\) \( xy \) orbitals are singly occupied and one obtains a high-spin contribution \( H_{n}^{(c)}(ij) \) for a bond \( (ij) \) along \( c \) axis:

\[ H_{1}^{(c)} = -\frac{1}{3} JR\left( \hat{S}_i \cdot \hat{S}_j + 2 \right) \left( \frac{1}{4} - \hat{\tau}_i \cdot \hat{\tau}_j \right), \]  

while for a bond in an \((a,b)\) plane:

\[ H_{1}^{(ab)} = -\frac{1}{6} JR\left( \hat{S}_i \cdot \hat{S}_j + 2 \right) \left( \frac{1}{4} - \hat{\tau}_i \cdot \hat{\tau}_j \right). \]  

(4, 5)

In Eq. (4) pseudospin operators \( \hat{\tau}_i \) describe low-energy dynamics of (initially degenerate) \( xz \) and \( yz \) orbital doublet at site \( i \); this dynamics is quenched in \( H_{1}^{(ab)} \). Here \( \frac{1}{2}(\hat{S}_i \cdot \hat{S}_j + 2) \) is the projection operator on the high-spin state for \( S = 1 \) spins. The terms \( H_{n}^{(c)} \) for low-spin excitations \((n = 2, 3)\) contain instead the spin operator \( (1 - \hat{S}_i \cdot \hat{S}_j) \) which guarantees that these terms vanish for fully polarized spins on a considered bond, \( (\hat{S}_i \cdot \hat{S}_j) = 1 \):

\[ H_{2}^{(c)} = -\frac{1}{12} J \left( 1 - \hat{S}_i \cdot \hat{S}_j \right) \left( \frac{7}{4} - \hat{\tau}_i \cdot \hat{\tau}_j - \hat{\tau}_i \cdot \hat{\tau}_j + 5\hat{\tau}_i \cdot \hat{\tau}_j \right), \]  

\[ H_{3}^{(c)} = -\frac{1}{4} Jr \left( 1 - \hat{S}_i \cdot \hat{S}_j \right) \left( \frac{1}{4} + \hat{\tau}_i \cdot \hat{\tau}_j + \hat{\tau}_i \cdot \hat{\tau}_j - \hat{\tau}_i \cdot \hat{\tau}_j \right), \]  

(6)

while again the terms \( H_{n}^{(ab)}(ij) \) differ from \( H_{n}^{(c)}(ij) \) only by orbital operators:

\[ H_{2}^{(ab)} = -\frac{1}{8} J \left( 1 - \hat{S}_i \cdot \hat{S}_j \right) \left( \frac{1}{4} + \hat{\tau}_i \cdot \hat{\tau}_j + \frac{3}{2} \hat{\tau}_i \cdot \hat{\tau}_j \right), \]  

\[ H_{3}^{(ab)} = -\frac{1}{8} Jr \left( 1 - \hat{S}_i \cdot \hat{S}_j \right) \left( \frac{1}{4} + \hat{\tau}_i \cdot \hat{\tau}_j + \frac{3}{2} \hat{\tau}_i \cdot \hat{\tau}_j \right), \]  

(7)

where upper (lower) \( z \) sign corresponds to \( a(b)-axis \) bonds.

First we present a mean-field (MF) approximation for the spin and orbital bond correlations which are determined self-consistently after decoupling them from each other in \( \mathcal{H}_J \). Spin interactions,

\[ H_s = J_{ab}^{(c)} \sum_{(ij)ab} \hat{S}_i \cdot \hat{S}_j - J_{c}^{(c)} \sum_{(ij)c} \hat{S}_i \cdot \hat{S}_j, \]  

(8)

depend on exchange constants:

\[ J_{c}^{(c)} = \frac{1}{2} \left[ \eta R - (R - \eta R - \eta\eta)(\frac{1}{4} + (\hat{\tau}_i \cdot \hat{\tau}_j)) - 2\eta(\hat{\tau}_i \cdot \hat{\tau}_j) \right], \]  

\[ J_{ab}^{(c)} = \frac{1}{4} \left[ -\eta R - (R - \eta R - \eta\eta)(\frac{1}{4} + (\hat{\tau}_i \cdot \hat{\tau}_j)) \right], \]  

(9)
determined by orbital correlations. In the orbital sector one finds

\[ H_\tau = \sum_{\langle ij \rangle_c} \left[ J^c_t \vec{\tau}_i \cdot \vec{\tau}_j - J(1-s_c)\eta \eta^c \vec{\tau}_i \cdot \vec{\tau}_j \right] + J^b_{ab} \sum_{\langle ij \rangle_{ab}} \tau^c_i \tau^c_j, \]

with:

\[ J^c_t = \frac{1}{2} J \left[ (1+s_c)R + (1-s_c)\eta (R+r) \right], \]
\[ J^b_{ab} = \frac{1}{4} J \left[ (1-s_{ab})R + (1+s_{ab})\eta (R+r) \right], \]

depending on spin correlations: \( s_c = \langle \vec{S}_i \cdot \vec{S}_j \rangle_c \) and \( s_{ab} = -\langle \vec{S}_i \cdot \vec{S}_j \rangle_{ab} \). In a classical C-AF state \( s_c = s_{ab} = 1 \), this MF procedure becomes exact, and the orbital problem maps to Heisenberg pseudospin chains along \( c \) axis, weakly coupled (as \( \eta \ll 1 \)) along \( a \) and \( b \) bonds,

\[ H^{(0)}_t = J R \sum_{\langle ij \rangle_c} \vec{\tau}_i \cdot \vec{\tau}_j + \frac{1}{2} \eta \left[ 1 + \left( \frac{r}{R} \right) \right] \sum_{\langle ij \rangle_{ab}} \tau^c_i \tau^c_j, \]

releasing large zero-point energy. Thus, spin C-AF order and quasi 1D quantum orbital fluctuations support each other. 

In addition to spin-orbital SE \( H_{V} \), orbitally degenerate systems experience the Jahn-Teller (JT) interactions — coupling of orbitals to lattice distortions may lead to a structural transition, lifting orbital degeneracy by the term,

\[ H_{V} = V_{ab} \sum_{\langle ij \rangle_{ab}} \tau^c_i \tau^c_j - V_c \sum_{\langle ij \rangle_c} \tau^c_i \tau^c_j, \]

in the present vanadate model.\footnote{Interactions \( V_{ab} > 0 \) originate from the coupling of nearest-neighbor \( t_{2g} \) orbitals in \( (a, b) \) planes to the bond stretching oxygen vibrations in corner-shared perovskite structure. They generate antidistortive oxygen displacements and staggered orbital order (supporting SE), whereas the \( V_c > 0 \) term due to the \( \text{GdFeO}_3 \)-type distortion favors ferro-orbital alignment along \( c \) axis, and thus competes with SE.}

The complete model \( h = h_{J} + h_{V} \) represents a nontrivial many-body problem. Interactions are highly frustrated, leading to strong competition between different spin and orbital states. We leave this complex problem for a future study, and present here the conceptually simpler case of \( \text{LaVO}_3 \) with C-AF order. In this phase spins are FM along the \( c \) axis at low \( T \), and orbitals fluctuate on their own. This justifies \textit{a posteriori} a perturbative treatment of joint spin-orbital correlations and allows one to determine them in a simple analytical way.

We begin with the orbital Hamiltonian \( H_{\tau} + H_{V} \) [Eqs. 10 and 11] which has the form of an \( XYZ \) model. As interchain couplings are weak and of \( \tau^c_i \tau^c_j \) form, the problem is best handled by employing Jordan-Wigner fermion representation\footnote{After decoupling \( \tau^c_i \tau^c_j \) terms in fermionic density and bond-order terms, one finds that the staggered orbital order parameter \( \tau = |\langle \vec{\tau}_i \cdot \vec{\tau}_j \rangle| \), the orbital ordering temperature \( T_{\tau} \), and the temperature dependence of orbital correlations: \( \langle \tau^c_i \tau^c_j \rangle_{c} = -\frac{1}{2} \kappa \), \( \langle \tau^c_i \tau^c_j \rangle_{ab} = -\tau^2 \), do follow from two self-consistent equations:}

\[ \tau = \sum_k \left( \frac{h^2}{2 \epsilon_k} \right) \tanh \left( \frac{\epsilon_k}{2T} \right), \]
\[ \kappa = \sum_k \left( \frac{\vec{J}_c}{2 \epsilon_k} \right) \cos^2 k \tanh \left( \frac{\epsilon_k}{2T} \right), \]

where \( \epsilon_k = \frac{\vec{J}_c}{2} \cos^2 k + (\vec{h}^2)^{1/2} \) is the 1D orbiton dispersion, \( \vec{J}_c = J^c_t + 2\kappa(J^c_r - V_c) \), and \( h^2 = 2\tau(J^c_r + 2J^b_{ab} + 2V_{ab} - V_c) \) is the effective field. We set \( k_B = 1 \).

The short-range spin correlations \( s_q \) determine \( J^c_r \) and are finite also above \( T_N \). We derived them by solving exactly a single bond \( \langle \langle ij \rangle \rangle \) within the mean-field \( \propto (S^2) \) originating from neighboring spins. This is the simplest cluster mean-field theory in the theory of magnetism as Oguchi method.\footnote{For a FM bond along \( c \) axis one finds even an analytic solution: \( s_c = (Z_0 - Z_1 - 2Z_2)/Z \), where \( Z_0 = 1 + 2 \cosh x \cos 2x \), \( Z_1 = (1 + 2 \cosh x) \exp(-2J^c_r/T) \), \( Z_2 = \exp(-3J^c_r/T) \), with \( Z = Z_0 + Z_1 + Z_2 \), \( x = h^2 / T \), \( h^2 = (J^c_r + 4J^b_{ab})^2 / 3 \). The \( s_{ab} \) correlation function for an AF bond can be found numerically.}

Now we turn to the dynamical coupling between orbital and spin sectors, denoted as \( H_{s\tau} \) term in Eq. 11. In the present case of C-AF ground state it contains mainly contributions due to \( c \) axis bonds, and reads as follows:

\[ H_{s\tau} \approx K \sum_{\langle ij \rangle_c} \delta(\vec{S}_i \cdot \vec{S}_j) \delta(\vec{\tau}_i \cdot \vec{\tau}_j). \]

Here, \( K = J(R - \eta R - \eta r) \) and \( \delta(A) = A - \langle A \rangle \) implies the fluctuating part of an operator, which goes beyond the MF decoupling. Treating \( H_{s\tau} \) within the high-temperature expansion, we found that the joint \textit{spin-and-orbital correlations}, \( f_{ij} = \langle \delta(\vec{S}_i \cdot \vec{S}_j) \delta(\vec{\tau}_i \cdot \vec{\tau}_j) \rangle \), are given as follows:

\[ f_{ij} = -\frac{3K}{16T} \left( \langle (\vec{S}_i \cdot \vec{S}_j)^2 \rangle - \langle \vec{S}_i \cdot \vec{S}_j \rangle^2 \right), \]

with \( \langle (\vec{S}_i \cdot \vec{S}_j)^2 \rangle = 1 + 3Z_2 / Z \) in the present Oguchi approximation. This high-temperature expansion for \( f_{ij} \) is valid when spin fluctuations are weak as in the C-AF phase, and one finds that the joint correlations \( f_{ij} \) vanish at \( T \to 0 \) when fully polarized spins decouple from the orbital sector.

### III. NUMERICAL RESULTS

Taking the SE energy scale \( J \sim 40 \text{ meV} \), we set \( T_N = 0.4J \), while \( \eta \approx 0.12 \) follows from spectroscopy.\footnote{It is quite natural in \( t_{2g} \) systems that order and disorder}
in the spin and orbital sectors support each other\textsuperscript{10,19} and indeed \( T_r \simeq T_N \) in \( \text{LaVO}_3 \). While the microscopic reasons of this behavior are subtle, we control \( T_r \) by tuning lattice mediated couplings \( V_γ \) — we found that the orbital transition occurs near \( T_N \) for: \( V_c = 0.9J \) and \( V_{ab} = 0.2J \). Then the energy of the C-AF phase is still lower than that of the G-AF phase, but a slight increase of \( V_c \) (by a factor 1.3) due to a stronger tilting of \( \text{VO}_6 \) octahedra gives the G-AF phase, observed in \( \text{YVO}_3 \)\textsuperscript{16}.

Following Eqs. \textsuperscript{19}, \textsuperscript{11}, \textsuperscript{12}, \textsuperscript{13}, \textsuperscript{14}, and \textsuperscript{16}, we calculated orbital, spin, and joint spin-and-orbital correlations, and next used them to determine the kinetic energies \( K^{(c)}_n \)\textsuperscript{2} due to each Hubbard subband. For instance,

\[
-K_1^{(c)}/2J = \frac{1}{3} R \left[ \langle \vec{S} \cdot \vec{S} \rangle + 2 \left\langle \frac{1}{4} - \vec{\tau} \cdot \vec{\tau} \right\rangle - f_{ij} \right]. \tag{18}
\]

Quantum effects beyond the MF theory are particularly pronounced in \(-K_1^{(c)}\) [see Fig. 1(a)]. In the classical approach \(-K_1^{(c)}\)\textsuperscript{13} increases with decreasing \( T \) only if \( T < T_N \) (when both \( \tau > 0 \) and \( \langle S^z \rangle > 0 \)). This is qualitatively different in the quantum model when the orbitals fluctuate, the orbital order parameter \( \tau \) is not more than half of its classical value, and the spin correlations \( s_c \) are finite above \( T_N \) and decay slowly for \( T > T_N \).

![FIG. 1: (color online) (a) Kinetic energy \( K_1^{(c)} \) for the high-spin excitations within classical and quantum models. Solid (dashed) line with (without) joint spin-orbital fluctuations. (b) Intersite correlations along \( c \) axis: spin \( s_c = \langle \vec{S} \cdot \vec{S} \rangle_c \) orbital \( \langle \vec{\tau} \cdot \vec{\tau} \rangle_c \) and spin-orbital \( f_{ij} \). Orbital order parameter \( \tau \) is also shown. Dotted line (filled circles) for \( G \) and indeed \( T \) of \( V \) reasons of this behavior are subtle, we control \( \tau \) by tun-

![FIG. 2: (color online) Kinetic energy \( K_N^{(c)} \) (solid lines) and total \( K^{(c)} \) (dashed lines) in units of \( 2J \) for: (a) \( c \) axis and (b) \( ab \)-plane polarization. Parameters as in Fig. 1. Filled squares in panel (a) represent the effective carrier number \( N_{\text{eff}}^{(c)} \) in \( \text{LaVO}_3 \) which includes the sum of the peaks 1 and 2 below 3 eV in Fig. 3 of Ref. \textsuperscript{6}. The experimental data follows well the calculated intensity of the high-spin transition, \( n = 1 \). [Fig. 1(b)]. In this case \(-K_1^{(c)} \) is enhanced at \( T = 0 \) by the orbital fluctuations \( \langle \vec{\tau} \cdot \vec{\tau} \rangle_c \simeq -0.43 \), being close to those found for a 1D AF spin 1/2 chain. Kinetic energy gain [Eq. \textsuperscript{19}] gradually decreases with increasing \( T \), and is reduced by half at \( T \sim 2T_N \) from its value at \( T = 0 \) [Fig. 1(a)]. We also note that joint spin-and-orbital fluctuations \( f_{ij} \) develop at finite \( T \) and contribute significantly at \( T > T_N \). An opposite behavior occurs in the limit of large JT orbital splitting that freezes out orbital fluctuations\textsuperscript{2} — then the temperature variation and the anisotropy of optical absorption are quenched, and \( \langle \vec{\tau} \cdot \vec{\tau} \rangle \gamma \) approaches its classical limit \((-0.25)\) in all directions.

The optical intensities \( N_{\text{eff}}^{(c)} \propto K_N^{(c)} \)\textsuperscript{6} exhibit pronounced anisotropy between \( c \) and \( ab \) polarizations (Fig. 2), particularly those of high-spin transitions \( n = 1 \) at low energy \( U - 3J_H \). These low-energy intensities behave here in opposite way for \( c \) and \( ab \) polarizations when temperature increases and the spectral weight is transferred between the high-spin and low-spin bands. The total intensities have a much weaker temperature dependence than individual contributions. The theory reproduces quite well the observed variation of \( N_{\text{eff}}^{(c)} \) with \( T \) [Fig. 2(a)]. We recall that the temperature variation of the kinetic energy \( K_1^{(c)} \) and \( N_{\text{eff}}^{(c)} \) is due to evolution of both spin and orbital correlations; spin-only ordering with frozen orbitals cannot explain a factor of two en-
FIG. 3: (color online) Exchange constants as functions of $T$ along $c$ (a/b) axis: (a) orbital $J^c_s$ and (b) spin $J^s_c$. Parameters: $\eta = 0.12$, $V_c = 0.9J$, $V_{ab} = 0.2J$.

IV. DISCUSSION AND SUMMARY

The basic experimental findings in the optical spectra of LaVO$_3$ such as: (i) pronounced temperature dependence of $c$ axis intensity (changing by a factor of two below 300 K), (ii) large anisotropy between the optical spectral weights along $c$ and a/b axis (both below and above $T_N$), are qualitatively reproduced by our theory (see Fig. 2). This strongly supports the picture of quantum orbital chains in the C-AF phase of vanadates.

The spectral shape of optical absorption in LaVO$_3$ is highly intriguing, developing sharp coherent peak below 3 eV at $T < T_N$. When its two-peak structure is interpreted as following from the multiplet splitting $\sim 3J_H$, the value of $J_H$ would be seriously underestimated, giving $J_H \simeq 0.21$ eV, which is much smaller that the respective value (Kanamori parameter) 0.68 eV in the free ion. Therefore, we suggest that the absorption below 3 eV is arising entirely from high-spin band centered at $U - 3J_H$. The coherent peak emerging at low temperature could be then interpreted as a bound state, similar to what occurs in 1D systems. This is quite natural when spins along the $c$ axis are fully polarized and coherent orbital chains are formed.

While the precise structure of the optical band requires further work, we may already obtain some useful information. Taking the width of $8t$ for the optical band and fitting the position and width of the spectral density in Fig. 2(a) of Ref. 7, one finds $U - 3J_H \simeq 2.3$ eV, $t \sim 0.2$ eV, and thus $JR \sim 70$ meV. As higher bands with $n = 2, 3$ are not resolved in the experiment, we cannot fix $J_H$ directly from the multiplet structure, but considering $\eta = J_H/U \simeq 0.13$ we reproduce basic energy scale $J \simeq 42$ meV, being close to $J \sim 40$ meV deduced from neutron scattering data. In fact, we can also determine $J$ directly from the comparison of the theoretical result $-K^{(c)}_1 \simeq 1.1(2J)$, and the observed $N^{(c)}_{\text{eff}} \simeq 0.21$ at $T = 0$ [see Fig. 2(a)]. Using Eq. (8) with $a_0 = 3.91$ Å one obtains then $J \simeq 48$ meV, a value remarkably consistent with both above estimates. Finally, we remark that the present interpretation of the experimental data of Ref. 7 gives (at $\eta \simeq 0.13$) $J_H \simeq 0.5$ eV and $U \simeq 3.8$ eV, which are somewhat lower than the atomic values. This reduction may be attributed to covalency and/or many-body screening effects in a solid.

Summarizing, we proposed a new approach employing partial optical sum rules in Mott insulators with orbital degeneracy, which provides a theoretical framework for common understanding of the optical and magnetic experiments, both determined by the superexchange. Considering the example of LaVO$_3$ with C-AF order, we have shown that pronounced temperature dependence and strong anisotropy of the optical absorption indeed follow from quasi 1D quantum spin-orbital correlations, being radically different from the classical expectations. A satisfactory agreement between the values of $J$ extracted independently from the magnetic and optical data in LaVO$_3$ demonstrates that superexchange interactions are indeed responsible for the distribution of the optical spectral weight in Mott insulators.

Acknowledgments

We thank B. Keimer and Y. Tokura for insightful discussions and T. Enss for his help on the graphical presentation of the experimental data in Fig. 2. A. M. Oleś would like to acknowledge support by the Polish State Committee of Scientific Research (KBN) under Project No. 1 P03B 068 26.
1. P. W. Anderson, Phys. Rev. 115, 2 (1959).
2. D. Baeriswyl, J. Carmelo, and A. Luther, Phys. Rev. B 33, 7247 (1986).
3. M. Aichhorn, P. Horsch, W. von der Linden, and M. Cuoco, Phys. Rev. B 65, 201101(R) (2002).
4. K. I. Kugel and D. I. Khomskii, Sov. Phys. Usp. 25, 231 (1982); Y. Tokura and N. Nagaosa, Science 288, 462 (2000); Y. Tokura, Physics Today, July 2003, p. 50.
5. K. Tobe, T. Kimura, Y. Okimoto, and Y. Tokura, Phys. Rev. B 64, 184421 (2001).
6. A-type (C-type) AF phase consists of ferromagnetic planes (chains) with AF order between them.
7. S. Miyasaka, Y. Okimoto, and Y. Tokura, J. Phys. Soc. Jpn. 71, 2086 (2002).
8. A. V. Mahajan, D. C. Johnston, D. R. Torgeson, and F. Borsa, Phys. Rev. B 46, 10966 (1992); S. Miyasaka, T. Okuda, and Y. Tokura, Phys. Rev. Lett. 85, 5388 (2000); Y. Ren, T. T. M. Palstra, D. I. Khomskii, A. A. Nugroho, A. A. Menovsky, and G. A. Sawatzky, Phys. Rev. B 62, 6577 (2000); M. Noguchi, A. Nakazawa, S. Oka, T. Arima, Y. Wakabayashi, H. Nakao, and Y. Murakami, ibid. 62, R9271 (2000); G. R. Blake, T. T. M. Palstra, Y. Ren, A. A. Menovsky, and A. A. Menovsky, Phys. Rev. Lett. 87, 245501 (2001).
9. C. Ulrich, G. Khaliullin, J. Sirker, M. Reehuis, M. Ohl, S. Miyasaka, Y. Tokura, and B. Keimer, Phys. Rev. Lett. 91, 257202 (2003).
10. G. Khaliullin, P. Horsch, and A. M. Oleś, Phys. Rev. Lett. 86, 3879 (2001).
11. J. S. Lee, Y. S. Lee, T. W. Noh, S.-J. Oh, Jaejun Yu, S. Nakatsuiji, H. Fukazawa, and Y. Maeno, Phys. Rev. Lett. 89, 257402 (2002).
12. L. F. Feiner and A. M. Oleś, Phys. Rev. B 59, 3295 (1999).
13. G. Khaliullin and S. Maekawa, Phys. Rev. Lett. 85, 3950 (2000).
14. T. Mizokawa and A. Fujimori, Phys. Rev. B 54, 5368 (1996).
15. T. Mizokawa, D. I. Khomskii, and G. A. Sawatzky, Phys. Rev. B 60, 7309 (1999).
16. D. C. Mattis, The Theory of Magnetism II (Springer-Verlag, New York, 1985).
17. We assume that the spin order parameter follows the spin-wave expansion, \( \delta \langle S^z \rangle^\tau \propto (T/T_N)^{\gamma} \) at \( T \ll T_N \), and has a MF behavior \( \langle S^z \rangle \propto (1 - T/T_N)^{1/2} \) when \( T \rightarrow T_N \).
18. T. Oguchi, Progr. Theor. Phys. (Kyoto), 13, 148 (1955); see also: Y. Shibata, S. Nishimoto, and Y. Ohta, Phys. Rev. B 64, 235107 (2001).
19. Y. Motome, H. Sato, Z. Fang, and N. Nagaosa, Phys. Rev. Lett. 90, 146602 (2003).
20. Exact diagonalization of a four-site chain embedded in self-consistent spin and orbital fields gave very similar values of \( f_{ij} \) to those resulting from Eq. (17) [Fig. 1(b)], demonstrating a surprisingly good quality of the high temperature expansion for \( f_{ij} \) in the C-AF phase.
21. Even taking a small JT splitting, these data cannot be explained by a pure orbital model of Ref. 12, and requires consideration of full spin-orbital problem.
22. A quantitative comparison with experiment would require also the spin-orbit coupling \( \propto \lambda \bar{S} \cdot \bar{L} \), which reduces to \( \Delta \bar{S}^\tau \bar{L}^\tau \) when \( xy \) orbital is quenched [P. Horsch, G. Khaliullin, and A. M. Oleś, Phys. Rev. Lett. 91, 257203 (2003)]. Below \( T_N \) this coupling acts as transverse field applied to the orbital chains, competing with both \( \hat{H}_J \) and \( \hat{H}_V \). Possible fluctuations of \( xy \) orbitals, not included in the present theoretical approach, might be also of some importance for a more favorable comparison with experiment.
23. R. Neudert, M. Knupfer, M. S. Golden, J. Fink, W. Stephan, K. Penc, N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. Lett. 81, 657 (1998).
24. For obtained \( U \) and \( J_H \), the low-spin transitions with \( n = 2, 3 \) are expected to be located at \( \sim 3.8 \) eV and \( \sim 4.8 \) eV, respectively. These transitions lose their intensity below \( T_N \) [see Fig. 2(a)], as actually seen in the data of Ref. 7.