Superexchange in the quarter-filled two-leg ladder system NaV$_2$O$_5$

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Abstract

A theory of superexchange in the mixed valent layer compound NaV$_2$O$_5$ is presented which provides a consistent description of exchange both in the disordered and charge ordered state. Starting from results of band structure calculations for NaV$_2$O$_5$ first an underlying electronic model for a ladder unit in the Trellis lattice is formulated. By using the molecular orbital representation for intra-rung electronic states a second-order perturbation procedure is developed and an effective spin-chain model for a ladder is derived. Variation of the resulting superexchange integral $J$ is examined numerically as the ladder system evolves from a charge disordered to the extreme (‘zig-zag’) charge ordered state. It is found that the effective intra-ladder superexchange is always antiferromagnetic.

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I. INTRODUCTION

Since the phase transition into a spin-gapped phase in α’-NaV$_2$O$_5$ was reported\textsuperscript{1} this layered insulating compound has attracted much attention. It was found that the phase transition ($T_c \approx 34$ K) is accompanied both by the lattice distortion\textsuperscript{2} and a charge ordering\textsuperscript{3} in the vanadium layers. Though the details of the low-temperature phase structure in NaV$_2$O$_5$ remain controversial, some main features of this structure are obtained from experiment. For instance, the same low-T lattice superstructure was measured and reported by three groups of researchers\textsuperscript{4–6}. The experiment\textsuperscript{7,8} has also ruled out a hypothetical ‘in-line’ charge ordering (CO) in favour of a ‘zig-zag’ CO. At the same time mechanism of the spin-gap formation is not understood up to now and formulation of adequate spin models for NaV$_2$O$_5$ is required.

The electronic and magnetic properties of NaV$_2$O$_5$ are mainly due to the V ions having in average a mixed valence +4.5. In a particular layer V-ions are arranged to give a sequence of two-leg quarter-filled ladders (one electron per rung) coupled to each other in a Trellis lattice. It is expected that the main properties of vanadium layers are dominated by the ladder physics and the theoretical consideration should start with an analysis of this one-dimensional structure unit. The most important evidence in favour of this point of view is provided by the band structure calculations\textsuperscript{9,10} within the density-functional theory (DFT). These calculations have shown that the overall electronic band structure of NaV$_2$O$_5$ is determined mainly by the large intra-ladder electronic hopping amplitudes while the inter-ladder hopping is rather weak.

Let us now turn to the problem of spin coupling in NaV$_2$O$_5$ and consider a separate quarter-filled ladder. Since the strongest electronic hopping transfers $\sim t_a$ between the basic vanadium $d_{xy}$-orbitals are within the rungs\textsuperscript{9,10} one has to ascribe a spin–1/2 not to a vanadium site but to the intra-rung V-O-V bonding molecular orbital. With strong Coulomb repulsion $\sim U$ on the $d_{xy}$-orbital the lowest electronic bonding orbital cannot be doubly occupied and the problem is naturally reduced to a half-filled chain in the limit of strong electron correlations. The excitation energy of the lowest 2-particle singlet rung state from now on plays a role of an effective Hubbard repulsion parameter which is roughly estimated to be $2t_a$ in the charge disordered state\textsuperscript{9,11}. Horsch and Mack were the first\textsuperscript{11} who derived a quantum Heisenberg spin–1/2 chain model to describe a one dimensional behavior of the ladder systems NaV$_2$O$_5$ in the charge disordered high-T phase.

The superexchange coupling parameters entering into the effective Heisenberg chain model are expected\textsuperscript{12,13} to be strongly reduced as the system undergoes the phase transition into the low-T charge ordered state. It was predicted, for instance, that for neighbouring spins in a ladder the exchange integral $J$, which is antiferromagnetic in high-T phase, may even change the sign to become a ferromagnetic one in the extreme CO phase with a zig-zag charge distribution on the ladder rung\textsuperscript{13}. In the present paper we develop the superexchange theory and obtain estimates for the spin-spin coupling constants in a single ladder both in the charge disordered and in an ordered phase. That allows us to reexamine some earlier statements and estimates\textsuperscript{11–13}. Since the in-line CO is ruled out by experiment the present consideration is restricted to a zig-zag CO state only.

The nature of the CO phase transition in the real NaV$_2$O$_5$ compound is not well understood up to now. Nevertheless, at the first stage (Section III) the analytical expressions for
the superexchange integrals in this system can be derived and analyzed in a rather general context. Next, to reach a quantitative description one has to rely on a particular realistic mechanism driving the charge ordering. We assume that the inter-site Coulomb electron repulsion is responsible for the CO phase transition and the lattice degrees of freedom play a secondary role. The inter-ladder short-range Coulomb interaction is treated in a mean field approximation while intra-ladder charge-charge correlations are considered on a more accurate level. To this end considering at some stage (Section IV) the charge degrees of freedom only we transform the electronic Hamiltonian onto the effective Ising model in the transverse magnetic field \[ \lambda = V_b/2t_a \]. Here \( V_b \) is the characteristic Coulomb repulsion between electrons on neighboring rungs. We adopt this approach which allows us to examine quantitatively how the superexchange coupling varies as the ladder system evolves from a disordered to the charge ordered phase. We expect that besides the quantitative estimates this particular analysis reveals general, mechanism-independent, trends in the behaviour of the superexchange spin-spin coupling in NaV\(_2\)O\(_5\).

II. ELECTRONIC MODEL AND THE EIGENSTATE PROBLEM

We start with the electronic Hamiltonian for a quarter-filled ladder in the following general form

\[
H = \sum_i \left( H_0^{(i)} + H_t^{(i)} \right) + \sum_{<ij>} \left( H_{t,\|}^{(ij)} + H_V^{(ij)} \right)
\]

where \((i)\) and \((ij)\) refer to a particular rung or to a pair of nearest neighbouring \((nn)\) rungs, respectively. The intra-rung interactions involved into \( H_0^{(i)} + H_t^{(i)} \) are described by the electronic hopping amplitude \( t_a \), the Coulomb on-site, \( U \), and inter-site, \( V_a \), parameters. For the \( nn \) inter-rung coupling \( (H_{t,\|}^{(ij)} + H_V^{(ij)}) \), there are two, \( t_b \) and \( t_d \), electronic hopping amplitudes and the corresponding Coulomb repulsion is given by \( V_b \) (see Fig.1). By introducing the creation operator \( d_\alpha^{\dagger} \) for a spin-\( \sigma \) electron on the left (right) \( V \)-ion within the \( i \)-th rung we specify the particular terms in Eq.\((\mathbf{1})\) as follows:

\[
H_0^{(i)} = \varepsilon \sum_{\alpha=L,R} n_\alpha^{(i)} + V_a n_L^{(i)} n_R^{(i)} + U \sum_{\alpha=L,R} n_\uparrow^{(i)} n_\downarrow^{(i)}
\]

\[
H_t^{(i)} = -t_a \sum_{\sigma} \left( d_\alpha^{\dagger} \alpha \sigma d_i \sigma + h.c. \right)
\]

\[
H_{t,\|}^{(ij)} = -t_b \sum_{\alpha=L,R} \sum_{\sigma} \left( d_\alpha^{\dagger} \alpha \sigma d_j \sigma + h.c. \right)
\]

\[
H_V^{(ij)} = -t_d \sum_{\alpha} \left( d_\alpha^{\dagger} L \sigma d_j R \sigma + d_\alpha^{\dagger} R \sigma d_j R \sigma + h.c. \right)
\]

\[
H_V^{(ij)} = V_b \sum_{\alpha=L,R} n_\alpha^{(i)} n_\alpha^{(j)}
\]
where \( n_i^\alpha = \sum_\sigma n_i^{\alpha \sigma} = \sum_\sigma d_{i\sigma}^\dagger d_{i\sigma} \) (\( \alpha = L, R \)) and \( \varepsilon \) is a bare vanadium \( d_{xy} \)-orbital energy in an isolated ladder.

Let us fix now the range of the model parameters. We use the following set of hopping amplitudes [10]: \( t_a = 0.38 \) eV, \( t_b \approx 0.085 \) eV. The proper signs of these amplitudes are adopted in the definition of \( H \). Importance of additional hopping processes \( \sim t_d \), which couple \( d_{xy} \)-orbitals of two V–ions at the opposite ends of \( nn \) rungs of a ladder (Fig. 1), was reported in Ref. [10]. Approximate equality \( t_d \approx t_b \) allows one to explain the pronounced feature of the band structure in \( \text{NaV}_2\text{O}_5 \). Namely, there is almost no dispersion of the antibonding- type molecular orbital states formed by the \( d_{xy} \)-orbitals on a rung. We will consider also another set: \( t_a = 0.38 \) eV, \( t_b = 0.17 \) eV and \( t_d = 0 \), as a more representative one among the sets with \( t_d = 0 \) used by other authors [13]. The value of the on-site Coulomb repulsion \( U \) is fixed from the supercell LDA+U calculations [4] to be \( U = 4 \) eV. The estimates for the magnitudes of intersite Coulomb repulsion \( V_a \) and \( V_b \) (Fig. 1) given in the literature are less accurate. In Ref. [13] for instance, it is claimed that a screening reduces \( V_a \) and \( V_b \) parameters to rather small values \( V_a, V_b < 0.4 \) eV, and hence the inter-rung Coulomb repulsion cannot stabilize CO. To investigate this point we developed a combined analysis by using the results of DFT calculation [4] and more generic multi-orbital Hubbard model for a ladder in the Trellis lattice. We found that inter-orbital vanadium \( d-d \) electron correlations lead to an enhancement for the effective \( V_b \) parameter which enters into the effective single-orbital Hamiltonian Eqs. [11,12]. These results will be presented elsewhere [4]. In the present investigation we take an intermediate value for \( V_a \approx 0.5 \) meV and allow \( V_b \) to vary in a wide range up to 1 eV.

It is worth noting that the validity of the perturbation procedure developed below to the second order in the inter-rung hoppings is based mainly on the smallness of these hoppings, \( t_b \) and \( t_d \), compared to \( 2t_a \) provided the on-site Coulomb repulsion \( U \) is the largest parameter of the theory. This guarantees also that the quarter- filled ladder is in an insulating state [16]. In contrast to the perturbation approach developed in Ref. [13] in our case there are no formal restrictions on the values of \( V_a \) and \( V_b \). Like in Ref. [13] these parameters could be arbitrary small giving a meaningful description of the superexchange in a charge disordered state of \( \text{NaV}_2\text{O}_5 \). Surely, \( V_b \) should be large enough, \( V_b > V_b^{(\text{cr})} \), to sustain a zig-zag CO state and the critical value \( V_b^{(\text{cr})} \) depends on the mechanism chosen for the CO phase transition.

In the perturbation procedure the zeroth order Hamiltonian is defined as \( H_0 = H - \sum_{ij} H_{ij}^{(ij)} \) where the last term is a perturbation mixing electronic states on \( nn \) rungs. As the necessary prerequisite of the superexchange theory the 1- and 2- particle electronic states on a particular rung have to be found explicitly. That can be done by considering the inter-rung Coulomb interaction, the term \( \sum_{ij} H_{ij}^{(ij)} \) in \( H_0 \), in a mean field (MF) approximation. In this case the inter- rung Coulomb interactions lead to the following shift of the on-site orbital energies (\( \alpha = L, R \)):

\[
\varepsilon_{i\alpha} = \varepsilon + V_b \left[ \langle n_{i+1}^\alpha \rangle_g + \langle n_{i-1}^\alpha \rangle_g \right]
\]

(6)

where \( \langle n_{i\pm 1}^\alpha \rangle_g \) are the averages over the lowest singly occupied electronic states of two rungs neighboring to the \( i \)-th rung within the same ladder. Having \( \sum_\alpha \langle n_{i\alpha}^\alpha \rangle_g = 1 \), one obtains \( (\varepsilon_{iL} + \varepsilon_{iR})/2 = \varepsilon + V_b \equiv \bar{\varepsilon} \) and
\[ \varepsilon_{iL} - \varepsilon_{iR} = \Delta \varepsilon_i = (-1)^i \Delta \varepsilon; \quad \Delta \varepsilon = 2V_b \eta \]  

(7)

In Eq. (7) we introduced the parameter \( \eta \) \((0 \leq \eta \leq 1)\) of charge disproportionation \( \langle n_{iR} \rangle_g - \langle n_{iL} \rangle_g = (-1)^i \eta \) in a zig-zag CO state of a ladder.

After applying the approximation given in Eq. (3) the zeroth order Hamiltonian \( H_0 \) becomes a sum over individual rungs, \( H_0 \simeq \sum_i H_0^{(i)} \). From now on each term \( H_0^{(i)} \) can be diagonalised independently. It is worth emphasizing that in this approach the local intra-rung correlations due to \( U \) and \( V_a \) are treated exactly. To specify explicitly a form of \( H_0^{(i)} \) in a particular \( n \)- particle sector of the intra- rung electronic states we invoke an extra subscript like in \( H_{0, n}^{(i)} \) below. For instance, by solving the eigenstate problem in the 1- particle sector one obtains

\[ H_{0,1}^{(i)} = \sum_\sigma \left[ \varepsilon_g g_{i\sigma}^\dagger g_{i\sigma} + \varepsilon_f f_{i\sigma}^\dagger f_{i\sigma} \right] \]  

(8)

where the energy \( \varepsilon_{g/f} \) of the lowest/excited molecular orbital is given by

\[ \varepsilon_{g/f} = \bar{\varepsilon} \mp 1/2 \sqrt{(\Delta \varepsilon)^2 + (2t_a)^2} \]  

(9)

and

\[ g_{i\sigma}^\dagger |0_i\rangle = \left[ u_i d_{iR\sigma}^\dagger + v_i d_{iL\sigma}^\dagger \right] |0_i\rangle \equiv |g_{i\sigma}\rangle \]

\[ f_{i\sigma}^\dagger |0_i\rangle = \left[ -v_i d_{iR\sigma}^\dagger + u_i d_{iL\sigma}^\dagger \right] |0_i\rangle \equiv |f_{i\sigma}\rangle \]  

(10)

The \( u_i \) and \( v_i \) coefficients in Eq. (10) are defined in the following way

\[ u_i = \sqrt{\frac{1}{2} \left[ 1 + \frac{\Delta \varepsilon_i}{\sqrt{(\Delta \varepsilon)^2 + (2t_a)^2}} \right]} \quad v_i = \sqrt{\frac{1}{2} \left[ 1 - \frac{\Delta \varepsilon_i}{\sqrt{(\Delta \varepsilon)^2 + (2t_a)^2}} \right]} \]  

(11)

and for \( \Delta \varepsilon_i \neq 0 \) the values of \( u_i \) and \( v_i \) alternate as \( i \) runs along the ladder. The complete basis for the 2- particle states on the \( i \)-th rung consists of three singlets \( |S_{i,n}\rangle \) \((n = 1, 2, 3)\) and triplet states \( |\tau_i^{(m)}\rangle \) \((m = 0, \pm 1)\). Explicitly, we choose the following definitions for these states (the rung index \( i \) is implied):

\[ |S_1\rangle = 1/\sqrt{2} \left( d_{R\uparrow}^\dagger d_{L\downarrow}^\dagger - d_{R\downarrow}^\dagger d_{L\uparrow}^\dagger \right) |0\rangle \]

\[ |S_{2,3}\rangle = 1/\sqrt{2} \left( \pm d_{R\uparrow}^\dagger d_{L\downarrow}^\dagger + d_{R\downarrow}^\dagger d_{L\uparrow}^\dagger \right) |0\rangle \]  

(12)

\[ |\tau^{(0)}\rangle = 1/\sqrt{2} \left( d_{R\uparrow}^\dagger d_{L\downarrow}^\dagger + d_{R\downarrow}^\dagger d_{L\uparrow}^\dagger \right) |0\rangle \]

\[ |\tau^{(\pm)}\rangle = d_{R\uparrow}^\dagger d_{L\downarrow}^\dagger |0\rangle, \quad d_{R\downarrow}^\dagger d_{L\uparrow}^\dagger |0\rangle \]

One can check that the triplets are degenerate eigenstates of \( H_{0,2}^{(i)} \), i.e. \( H_{0,2}^{(i)}|\tau_i^{(m)}\rangle = \varepsilon_{\tau} |\tau_i^{(m)}\rangle \), with the energy \( \varepsilon_{\tau} = 2\bar{\varepsilon} + V_a \). In the singlet subspace the Hamiltonian \( H_{0,2}^{(i)} \) takes the following form
\[ H_{0,2}^{(i)} = (|S_{i,1}|, |S_{i,2}|, |S_{i,3}|) \left( \begin{array}{ccc} 2\varepsilon + V_a & -2t_a & 0 \\ -2t_a & 2\varepsilon + U & \Delta\varepsilon_i \\ 0 & \Delta\varepsilon_i & 2\varepsilon + U \end{array} \right) \left( \begin{array}{c} \langle S_{i,1}| \\
 \langle S_{i,2}| \\
 \langle S_{i,3}| \end{array} \right) \]  

By diagonalizing the symmetric 3×3 matrix one obtains the eigenstates

\[ |S_i^{(\kappa)}\rangle = \sum_{n=1}^{3} \gamma_{n}^{(\kappa)}(i) |S_{i,n}\rangle \]  

and the corresponding eigenvalues \( \varepsilon_{\kappa} \) (\( \kappa=1,2,3 \)) in the singlet subspace. More precisely, \( \varepsilon_{\kappa} = 2\varepsilon + V_a + (U - V_a)e_\kappa \), where \( e_\kappa(\kappa = 1, 2, 3) \), are the solutions of a cubic characteristic equation reading

\[ e_\kappa \left[ (1 - e_\kappa)^2 - \zeta_i^2 \right] + \mu^2 [1 - e_\kappa] = 0 \]  

where \( \zeta_i = \Delta\varepsilon_i/(U - V_a) \) and \( \mu = 2t_a/(U - V_a) \). Note, that according to Eq.(7) the value of \( \zeta_i^2 \) does not depend on \( i \). Provided Eq.(15) is solved the 3-component vector \( \gamma^{(\kappa)}(i) \) in Eq.(14) can be found by using the following expressions

\[ \gamma_{1}^{(\kappa)} = \pm \frac{|A_{\kappa}|}{R_{\kappa}} \]  
\[ \gamma_{2}^{(\kappa)} = \pm \text{sign}(A_{\kappa}) \frac{\mu(1 - e_\kappa)}{R_{\kappa}} \]  
\[ \gamma_{3}^{(\kappa)}(i) = \mp \text{sign}(A_{\kappa}) \frac{\mu \zeta_i}{R_{\kappa}} \]  

where \( A_{\kappa} = (1 - e_\kappa)^2 - \zeta_i^2 \) and \( R_{\kappa} = [A_{\kappa}^2 + \mu^2 (1 - e_\kappa)^2 + \mu^2 \zeta_i^2]^{1/2} \). Note, that the upper/or the lower signs in Eq.(17) should be taken simultaneously. Like \( \zeta_i \), the third component \( \gamma_{3}^{(\kappa)}(i) \) is staggered along the chain direction. This particular problem, Eqs.(15, 17), can be solved numerically in a wide range of the underlying model parameters provided the order parameter \( \eta \) is fixed from some self-consistent procedure. Most representative results will be discussed in Sec.V.

For further purposes it is helpful to use the projection operators \( X_{i}^{g,\sigma} = |q_i\rangle\langle q_i| \) and the transfer operators \( X_{i}^{q,p} = |q_i\rangle\langle p_i| \) where \( |q_i\rangle \) and \( |p_i\rangle \) are the states defined above on the \( i \)-th rung. More explicitly, for instance, one has

\[ X_{i}^{g_\sigma,g_\sigma} = |g_i\sigma\rangle\langle g_i\sigma|, \quad X_{i}^{0,g_\sigma} = |0_i\rangle\langle g_i\sigma|, \quad X_{i}^{S_\kappa,S_\kappa} = |S_{i}^{(\kappa)}\rangle\langle S_{i}^{(\kappa)}|, \quad X_{i}^{S_\kappa,g_{\sigma}} = |S_{i}^{(\kappa)}\rangle\langle g_{i\sigma}| \]  

etc.

With these notations the approximate zeroth order Hamiltonian \( H_0 \simeq \sum_i H_0^{(i)} \) can be written as

\[ H_0^{(i)} = \varepsilon_v X_0^{0,0} + \varepsilon_g \sum_\sigma X_{i}^{g_\sigma,g_\sigma} + \varepsilon_f \sum_\sigma X_{i}^{f_\sigma,f_\sigma} + \]  
\[ + \sum_{\kappa=1}^{3} \varepsilon_{sk} X_{i}^{S_\kappa,S_\kappa} + \varepsilon_\tau \sum_{m=\pm1,0} X_{i}^{\tau m,\tau m} \]  

(18)
In Eq. (18) the vacuum rung state $|0_i\rangle$ with the reference energy $\varepsilon_v$ is involved for completeness.

At the same time the 3– and 4– particle states are dropped as these states are irrelevant for the present purposes. At the end of this section the following remark is worth to be made. Actually, while solving the intra- rung eigenstate problems we could not avoid the use of a MF treatment of inter- rung Coulomb interactions, the term $\sum_{<ij>} H_V^{(ij)}$ in the original Hamiltonian of Eq. (3). Nevertheless it does not mean the complete neglect of the many body effects due to $H_V^{(ij)}$ in our approach. Further analysis in Secs. IV,V will show that charge-charge correlations between singly occupied $nn$- rungs are important to obtain the estimates for the superexchange coupling between spins in a ladder.

III. PERTURBATION PROCEDURE AND SUPEREXCHANGE ON A LADDER

The superexchange coupling between two singly occupied rungs is established due to the electron hopping transitions with the virtual intermediate 2-particle states in one of two rungs. These transitions are due to the kinetic part of the Hamiltonian, $H_{t,\parallel}$, whose action has now to be represented in terms of the molecular orbital states $|q_i\rangle$ defined in the previous section. In a rather general form one may write:

$$H_{t,\parallel} = \sum_{<ij>} H_{t,\parallel}^{(ij)} = \sum_{<ij>,\sigma} \sum_{qq'} \sum_{pp'} \left[ t_{ij,\sigma}^{(q',q|p',p)} X_{i}^{q',q} X_{j}^{p',p} + h.c. \right]$$

(19)

where

$$t_{ij,\sigma}^{(q',q|p',p)} = -t_b \sum_{\alpha} \langle q_i|d_{i\alpha\sigma}^{\dagger}|q_i\rangle \langle q_j|d_{j\alpha\sigma}|p_j\rangle$$

$$-t_d \left[ \langle q_i|d_{i\alpha\bar{\sigma}}^{\dagger}|q_i\rangle \langle p_j|d_{j\alpha\sigma}|p_j\rangle + (R \leftrightarrow L) \right]$$

(20)

and $(R \leftrightarrow L)$ means the indices interchange. All the necessary amplitudes $\langle q_i|d_{i\alpha\sigma}^{\dagger}|q_i\rangle$ and their conjugates can be now straightforwardly evaluated to give the relevant part of $H_{t,\parallel}$ in the following form

$$H_{t,\parallel} = -\sum_{ij,\sigma} \xi_{ij} \left\{ \frac{(2\sigma)}{\sqrt{2}} \sum_{\kappa=1}^{3} D_{ij}^{(\kappa)} \left( X_{i}^{S_{\kappa},g\bar{\sigma}} X_{j}^{0,g\sigma} + h.c. \right) + \right.$$ \n
$$+ \sum_{\sigma'} \sum_{m=\pm1,0} B_{ij} C_{\sigma'\sigma}^{(m)} \left( X_{i}^{T_{m},g\sigma'} X_{j}^{0,g\sigma} + h.c. \right) \right\}$$

(21)

Here $\xi_{ij} = 1$ if $(ij)$ is a $nn$ pair and equals zero otherwise; $(2\sigma) = +1(\sigma = \uparrow)$, $-1(\sigma = \downarrow)$ and $\bar{\sigma} = -\sigma$. The factor $C_{\sigma'\sigma}^{(m)}$ is defined as

$$C_{\sigma'\sigma}^{(m)} = \delta_{\sigma',\sigma} \delta_{m,2\sigma} + 1/\sqrt{2} \delta_{\sigma',\sigma} \delta_{m,0}.$$  

(22)

The effective transfer amplitudes $D_{ij}^{(\kappa)}$ and $B_{ij}$ can be presented in the following form:
\[ D^{(\kappa)}_{ij} = \sum_{n=1}^{3} \gamma^{(\kappa)}_{n}(i) [t_b a_{ij,n} + t_d \bar{a}_{ij,n}] \]
\[ B_{ij} = t_b b_{ij} + t_d \bar{b}_{ij} \]  

(23)

where \( a_{ij,n}, \bar{a}_{ij,n}, b_{ij} \) and \( \bar{b}_{ij} \) are bilinear functions of the \( u-, v- \) coefficients

\[
\begin{align*}
  a_{ij,1} &= \bar{a}_{ij,2} = u_i v_j + v_i u_j \\
  a_{ij,2} &= \bar{a}_{ij,1} = u_i u_j + v_i v_j \\
  a_{ij,3} &= \bar{b}_{ij} = -u_i u_j + v_i v_j \\
  b_{ij} &= \bar{a}_{ij,3} = -u_i v_j + v_i u_j
\end{align*}
\]  

(24)

To derive the superexchange spin coupling to the second order in the effective hopping amplitudes \( D^{(\kappa)}_{ij} \) and \( B_{ij} \) we use the Schrieffer-Wolff transformation \( \hat{H} = \exp(-\hat{S}) \hat{H} \exp(\hat{S}) \) with the generator \( \hat{S}(= -\hat{S}^\dagger) \) being determined from the condition \([H_0, \hat{S}] = -H_{t,\|} \). Then the second order correction to \( H_0 \) is given by

\[
H_{\text{eff}} = -1/2 \left[ \hat{S}, H_{t,\|} \right]
\]  

(25)

From Eq. (21) we obtain first the form of the generator

\[
\hat{S} = \sum_{ij,\sigma} \xi_{ij} \left\{ \frac{(2\sigma)}{\sqrt{2}} \sum_{\kappa=1}^{3} \frac{D^{(\kappa)}_{ij}}{\varepsilon_{sk} + \varepsilon_{v} - 2\varepsilon_{g}} X^{S_{k,g\sigma}}_i X^{0,g\sigma}_j + \right.
\]

\[
+ \sum_{\sigma', m} \frac{B_{ij} C^{(m)}_{\sigma' \sigma}}{\varepsilon_{\tau} + \varepsilon_{v} - 2\varepsilon_{g}} X^{\tau m,g\sigma'}_i X^{0,g\sigma}_j - h.c. \left\}
\]  

(26)

One can see, that there are two perturbation channels, (s) and (\( \tau \)), with the singlet and triplet intermediate virtual states, respectively. Finally we obtain from Eq. (25) the superexchange Hamiltonian

\[
H_{\text{eff}} = \sum_{<ij>} \left( J^{(s)}_{ij} + J^{(\tau)}_{ij} \right) \vec{S}_i \cdot \vec{S}_j
\]  

(27)

with the exchange constants in the singlet and triplet channel given by

\[
J^{(s)}_{ij} = \frac{3 \left[ D^{(\kappa)}_{ij} \right]^2 + \left[ D^{(\kappa)}_{ji} \right]^2}{\varepsilon_{sk} + \varepsilon_{v} - 2\varepsilon_{g}}
\]  

(28)

\[
J^{(\tau)}_{ij} = -\frac{B_{ij}^2 + \bar{B}_{ji}^2}{\varepsilon_{\tau} + \varepsilon_{v} - 2\varepsilon_{g}}
\]  

(29)

In Eq. (27) the spin- \( \frac{1}{2} \) operators \( S_i^\alpha = 1/2 \sum_{\sigma\sigma'} |g_{i\sigma}\rangle \sigma_{\sigma'}^{\alpha} \langle g_{i\sigma'}| \) and \( \sigma_{\sigma'}^{\alpha} \) are the Pauli matrices (\( \alpha = x, y, z \)); the notation \( <ij> \) means that each pair of the \( nn \) rungs is taken only once.
Note that already at this stage the expressions Eq.(28) and Eq.(29) together with the definitions in Eqs. (23, 24), formulate a complete scheme to estimate \( J_{(ij)}^{(s)} \) and \( J_{(ij)}^{(r)} \) both in a disordered and a zig-zag CO state. That can be done, at least numerically, by solving first the eigenstate problems of Sec.II for given parameters of the model and with the order parameter \( \eta \) varying in the range \( 0 \leq \eta \leq 1 \). In this approach the effects of charge ordering upon spin coupling in a ladder can be examined in its main features without specifying a mechanism driving the CO transition in a quarter- filled ladder system. Preliminary analysis shows that the total superexchange coupling \( J_{(ij)} = J_{(ij)}^{(s)} + J_{(ij)}^{(r)} \) is reduced as the ladder develops from a disordered to a zig-zag CO state. That is in accordance with a prediction in Ref.(12). A more satisfactory quantitative description could be done if one relies on a specific mechanism responsible for CO phase transition. In the next section we pursue one possibility by noting that the underlying model, Eqs.(1 - 5) contains the expected instability without invoking extra degrees of freedom like charge-phonon coupling. Further analysis is based on the pseudospin description of the charge correlations. Before turning to the pseudospin model itself (Sec.IV) we use this representation to present the main results of this section given in Eqs.(23, 24, 28, 29) in a more condensed form.

In the pseudospin representation the molecular ground state of the \( i \)-th rung \( |g_{i\sigma}⟩ = |g_i⟩ \otimes |\sigma_i⟩ \) is given by

\[
|g_i⟩ = [u_i | \uparrow⟩_i + v_i | \downarrow⟩_i]; \quad u_i^2 + v_i^2 = 1 \tag{30}
\]

By using the pseudo- spin \( (T = \frac{1}{2}) \) operators \( T^{[\alpha]}_i, (\alpha = x, y, z) \) we define now several pair correlation functions and expectation values in the ground state of a ladder as follows

\[
Q^{(\|)}_{ij} = \langle T^{z}_i T^{z}_j \rangle_g, \quad Q^{(\perp)}_{ij} = \langle T^{x}_i T^{y}_j + T^{y}_i T^{x}_j \rangle_g \quad R^{(x)}_{ij} = \langle T^{z}_i - T^{z}_j \rangle_g \quad R^{(z)}_{ij} = \langle T^{x}_i T^{x}_j - T^{x}_i T^{x}_j \rangle_g \tag{31}
\]

By using the above definitions and Eqs.(23, 24) one may write the numerators in the expressions of Eqs.(28, 29) in the following form:

\[
\left[D^{(\kappa)}_{ij}\right]^2 + (i \leftrightarrow j) = 4t^2 \left\{ \sum_{n=1}^{3} [\gamma^{(n)}_n]^2 K^{(n)}_{ij} + 2\gamma^{(1)}_1 \gamma^{(2)}_2 K^{(12)}_{ij} + \gamma^{(1)}_1 [\gamma^{(3)}_3 (i) - \gamma^{(3)}_3 (j)] K^{(13)}_{ij} + \gamma^{(2)}_2 [\gamma^{(3)}_3 (i) - \gamma^{(3)}_3 (j)] K^{(23)}_{ij} \right\} \tag{32}
\]

\[
B^2_{ij} + (i \leftrightarrow j) = 4t^2 \kappa^{(4)}_{ij} \tag{33}
\]

where

\[
K^{(1,2)}_{ij} = (1 + \nu^2) \left[ \frac{1}{4} + Q^{(\perp)}_{ij} \right] \pm (1 - \nu^2) Q^{(\|)}_{ij} + 2\nu R^{(z)}_{ij} \]
\[
K^{(3,4)}_{ij} = (1 + \nu^2) \left[ \frac{1}{4} - Q^{(\perp)}_{ij} \right] \pm (1 - \nu^2) Q^{(\|)}_{ij} \]
\[
K^{(12)}_{ij} = 2\nu \left[ \frac{1}{4} + Q^{(\perp)}_{ij} \right] + (1 + \nu^2) R^{(x)}_{ij} \tag{34}
\]
\[
K_{ij}^{(13)} = \nu^2 R_{ij}^{(xx)} - \frac{1}{2} \nu R_{ij}^{(z)}
\]
\[
K_{ij}^{(23)} = \nu R_{ij}^{(xx)} - \frac{1}{2} \nu^2 R_{ij}^{(z)}
\]

and we defined \(\nu = t_d/t_b\). It is worth noting that the antisymmetric property, \(K_{ij}^{(13)} = -K_{ji}^{(13)}\) and \(K_{ij}^{(23)} = -K_{ji}^{(23)}\), makes the complete expression of Eq.(32) to be symmetric.

**IV. PSEUDO- SPIN MODEL FOR THE LADDER**

The effective Hamiltonian in Eq.(27) describes spin-spin interactions in the low- energy subspace spanned by the vector charge- spin manifold \(|G \{g \}, \{\sigma \}\rangle = \prod_i |g_i \rangle \otimes |\sigma_i \rangle\). Our aim now is to project the electronic model, Eqs.(1-5) onto the charge sector within this manifold. The projection procedure was discussed several times \(^{14},^{12}\), it results in the following zeroth- order effective Hamiltonian for a ladder

\[
H_{\text{eff}}^{(0)} = -2t_a \sum_i T_i^{x} + 2V_b \sum_{<ij>} [T_i^{z}T_j^{z} + 1/4] - \Delta \varepsilon_0 \sum_i (-1)^i T_i^{z}
\]

In this one- dimensional (1D) model the effective longitudinal field \(\sim \Delta \varepsilon_0\) expresses in a condensed form effects of Coulomb interactions due to higher dimensionality of the real NaV\(_2\)O\(_5\) compound (see Appendix).

We proceed further in the spirit of the coupled quantum spin chain approach \(^{17}\) which involves a MF treatment of the inter-chain coupling and a more sophisticated treatment of the intra-chain, i.e. intra-ladder, interactions. The intra- ladder problem enters into the expressions for the superexchange constants, Eqs.(28, 29) and Eqs.(31-34), in the form of pair correlation functions for the \(nn\) pseudospins. Having the final aim of calculating these constants we rely on properties of the exact solution for the 1D Ising model in a transverse field.

The term \(\sim \Delta \varepsilon_0\) in Eq.(35) breaks explicitly the Z(2) symmetry of the 1D transverse Ising model which results in a non-zero longitudinal magnetisation \(\langle T_i^{z} \rangle_g = (-1)^i \eta/2\) if the coupling constant \(\lambda = V_b/2t_a\) exceeds some critical value, \(\lambda > \lambda_c\). One may write

\[
\eta = \left[1 - \left(\frac{\lambda_c}{\lambda}\right)^2\right]^{\beta}
\]

and choose for the exponent \(\beta = 1/8\) since the presence of a weak longitudinal field does not change the universality class of the 1D Ising model in the transverse field. Note, that for this exactly solvable model \(\lambda_c = 1\) (Ref. \(^{18,19}\)) and we keep this value in the subsequent numerical analysis. The open problem that still remains are unknown dependencies of \(\beta\) and \(\lambda_c\) on details of the inter- ladder Coulomb interaction if one goes beyond a mean field treatment of these interaction in the Trellis lattice.
Let us now turn to a discussion of the superexchange constants, Eqs. (28, 29). We estimate the inter-rung pseudospin correlation functions entering into Eq. (31) at two different levels of sophistication. The simplest one is to decouple the pair correlation functions as follows:

\[ Q_{ij}^{(\parallel)} \simeq -\langle T_z^i \rangle^2 = - \left( \frac{\eta}{2} \right)^2 \]

\[ Q_{ij}^{(\perp)} \simeq \langle T_x^i \rangle^2 = \frac{1}{4} \left( 1 - \eta^2 \right) \]

\[ R_{ij}^{(xz)} \simeq -\langle T_z^i - T_z^j \rangle \langle T_x^i \rangle = (-1)^{i+1} \frac{\eta}{2} \sqrt{1 - \eta^2} \]

In Eq. (37) we take into account that \( i \) and \( j \) are refered to \( nn \) rungs and, hence, \( \langle T_z^j \rangle = -\langle T_z^i \rangle \) while \( \langle T_x^j \rangle = \sqrt{1 - \eta^2}/2 \) does not depend out the rung index \( i \). Within this first approximation the superexchange constants will be calculated in the next section. The only signatures of the exact solution in Eqs. (36, 37) are due to the choice of the values for \( \beta \) and \( \lambda_c \), while the inter-rung fluctuations are ignored. To gain an impression how these fluctuations may change the superexchange constants we adopt some more properties of the exact solution for the 1D transverse Ising model. For this purpose let us consider the pair correlation functions \( (j = i \pm 1) \):

\[ \langle T_z^i T_j \rangle_g = k_z; \quad \langle T_x^i T_j \rangle_g = m_x^2 + k_x; \quad \langle T_y^i T_j \rangle_g = k_y \]

In particular, one has

\[ k_z = -\frac{1}{4\pi} \int_0^\pi dq \frac{\lambda \cos(q)}{\Lambda_q}; \quad m_x = \frac{1}{2\pi} \int_0^\pi dq \frac{1 + \lambda \cos(q)}{\Lambda_q} = \langle T_x^i \rangle_g \]  

(39)

where \( \Lambda_q = \sqrt{1 + \lambda^2 + 2\lambda \cos(q)} \). The expressions for \( k_{x,y} \) can be found in Refs. (18, 19) as well. We use the property \( |k_z|, |k_y| \ll m_x, |k_z| \) and drop the weak transverse fluctuations, which means \( k_{x,y} \simeq 0 \). Breaking of the Z(2) symmetry allows us to write also

\[ R_{ij}^{(xz)} \simeq (-1)^{i+1} \eta m_x \]  

(40)

We use the Eqs. (30, 38) and (39) together with the approximation in Eq. (40) as the basis of our second approach to calculate the superexchange constants.

**V. ANALYSIS OF SUPEREXCHANGE INTEGRALS, NUMERICAL RESULTS**

The starting point of our analysis is the exact diagonalisation of the single-rung Hamiltonian in the 1- and 2-particle sectors. The excited singlet and triplet states provide the intermediate states for the superexchange mechanism of magnetic coupling between neighbouring singly occupied rungs. From now on we drop the irrelevant lower indices at \( J \). The excitation energies \( E_{sk} = \varepsilon_{sk} + \varepsilon_v - 2\varepsilon_g \) and \( E_r = \varepsilon_x + \varepsilon_v - 2\varepsilon_g \) which enter as the denominators into the perturbative expressions for \( J^{(s)}, J^{(r)} \), are determined by the eigenvalues due to Eqs. (9) and (13). These eigenvalues depend on the degree of charge order via the intra-rung d-orbital levels shifts \( \Delta \varepsilon \) which is proportional to the CO parameter \( \eta \) in Eq. (8).
The symmetry breaking source is assumed to be arbitrary small. The excitation energies in the singlet and triplet channels as function of $\Delta \varepsilon$ are shown in Fig.(2), $\varepsilon_v = 0$. There is a crossing of two singlets at very high values of $\Delta \varepsilon$. For realistic values of $V_b$ however this crossing point is not reached.

While solving the eigenvalue problem in the singlet sector the components of the vectors $\vec{\gamma}^{(s)}(i)$, Eq.(17), are calculated as well. These vector components together with pseudospin correlation functions determine the numerator, Eq.(22), in the expression for $J^{(s)}$, Eq.(23). The pseudospin pair correlation functions are calculated either in the modified MF approximation, Eq.(37), or by using a more accurate approach based on Eqs.(38)-(40). In the latter case the most pronounced charge fluctuation contributions to the superexchange are involved. This requires evaluation of only two pair correlation functions, namely, $\langle T_i^z T_{i+1}^z \rangle_g = k_z$ and $\langle T_i^x T_{i+1}^x \rangle_g \simeq m^2$ which are given by Eq.(38),(39). Both of them are shown in Fig.(3) as function of $\lambda^{-1} = 2t_a/V_b$. It is seen that the intra-chain fluctuations of the order parameter described by the 'longitudinal' correlation function $k_z$ extend far above the critical value $\lambda_c^{-1} = 1$ where the CO vanishes. Since in our approximation $k_z \simeq 0$ the 'transverse' correlation function is reduced to the square of the 'covalency' of each rung $m_x = \langle T_i^x \rangle_g$. The latter approaches one half for $\lambda^{-1} \to \infty$. It shows the opposite behaviour compared to the complementary charge order parameter $m_z = \langle |T_i^z| \rangle_g = \eta/2$. The latter is shown in Fig.(3) as given by Eq.(36) with the exact 1D Ising exponent $\beta = 1/8$.

With these necessary ingredients it is now straightforward to calculate the superexchange integrals $J^{(s)}$, $J^{(r)}$ as function of the microscopic model parameters according to Eqs.(28), (29). The hopping and interaction parameters fixed from LDA+U calculations are discussed in Sec. II where definite values for $t_a$, $t_b$, $t_d$ and $U$ were given. The intra-rung repulsion $V_a$ was assumed to lie close to 0.5 eV and the inter-rung repulsion $V_b$ is allowed to vary in a wide range up to 1 eV. The dimensionless control parameter for CO is $\lambda = V_b/2t_a$ with $\lambda_c = 1$ at the CO transition.

The dependence of $J^{(s)}$, $J^{(r)}$ on $V_b$ is shown in Fig.(4) for two cases: The dashed line corresponds to exchange integrals calculated in the modified MF approach, Eq.(37), with the Ising exponent $\beta = 1/8$. For $\lambda < 1$ ($V_b < V_b^{\text{(CR)}} = 2t_a = 0.76$ eV) in the disordered ladder the exchange constants are independent of $V_b$ and the total value $J = J^{(s)} + J^{(r)}$ amounts to $J_{\text{MF}} = J_{\text{MF}}^{(s)} \simeq 80$ meV since $J_{\text{MF}}^{(r)} = 0$ in this region. At $V_b = V_b^{\text{(CR)}}$ a sharp drop in the singlet exchange constant is observed whose shape is determined by the order parameter $m_z$ (Fig.(3)). The most important reason for the reduction of superexchange is the reduced effective hopping between adjacent rung bonding states caused by charge order. The full line in Fig.(4) shows the same exchange integrals with the effect of charge fluctuations included, as described by the pseudo-spin formalism of the previous chapter, Eqs.(38)-(40). In the disordered regime the inclusion of charge fluctuations strongly reduces the exchange constants compared to the MF value. The total superexchange integral falls now into the region $70 \text{ meV} > J > 55 \text{ meV}$, which is somewhat lower than the theoretical value obtained in Ref.(11) for the disordered phase while it is somewhat higher than the value $J^{\text{(EXP)}} \simeq 50$ meV estimated in Ref.(10). Fig.4 shows that in the CO regime ($V_b > V_b^{\text{(CR)}}$), where charge fluctuations are strongly suppressed, both approximations give very similar results. Above the critical region at, for instance, $V_b \simeq 1.3V_b^{\text{(CR)}}$ (i.e. at $V_b = 1$ eV), where CO is nearly complete, $m_z \simeq 0.43$, the superexchange integral reaches the value $J \simeq 0.22$ meV.
In Fig.(5) we show $J^{(s)}$ and $J^{(r)}$ as function of $V_b$, with charge fluctuation effects included, for various intermediate values of the intra-rung Coulomb repulsion $V_a$. Moreover, by varying $V_a$ in a wider range from zero up to rather high values, $V_a \sim 4t_a$, a regular behaviour of the exchange constants is found, which is already seen from Fig.(5). First, the triplet contribution $J^{(r)}$ is almost negligible as compared to the singlet part $J^{(s)}$ for the model with $t_d = t_b$. In the case $t_d = 0$ however $J^{(r)}$ gives a sizeable (negative) contribution to the total $J$. Secondly, with increasing $V_a$, the total superexchange integral $J$ decreases and remains antiferromagnetic ($> 0$), it never changes its sign. This is true for both models considered ($t_d = t_b$ or $t_d = 0$). These observations are at strong variance with the results of Ref.(13).

It is instructive to examine also both the limit of the extreme CO, $m_z \rightarrow 1/2$, which is reached at $\lambda^{-1} \rightarrow 0$, i.e. at unphysically high values of $V_b$, and the the opposite limit $\lambda^{-1} \rightarrow \infty$, i.e. at $V_b = 0$. To check these limits a variation of the total superexchange integral $J$ is examined in a wide range of $\lambda^{-1}$, Fig.6(a). Two curves there correspond to two sets of the hopping parameters used: (1) $t_a = 0.38eV$, $t_b = t_d = 0.085eV$ and (2) $t_a = 0.38eV$, $t_b = 0.17eV$ and $t_d = 0$. The second set is the most representative one among the sets with $t_d = 0$ used by other authors. First, at $\lambda^{-1} \rightarrow 0$ the curve (1) reaches the value $J = 7.2meV$ which coincide exactly with the estimate based on the standard expression $J = 4t_a^2/U$. The latter estimate is due to the superexchange coupling between two vanadium ions located at the opposite ends of $nn$ rungs. From Fig.6 one can see that in the case of finite $t_d$ the superexchange is regularly enhanced as compared to the case with $t_d = 0$. In fact we found numerically that if $\lambda^{-1} \rightarrow \infty$, the two dependences, i.e. the curves (1) and (2) in Fig.6, approach the same value $J = 80meV$ which is nothing than the MF value of $J$ depicted in Fig.4. In this limit ($V_b = 0$) the general formulas, Eqs.(28), (29), can be easily treated analytically to give the following expression for the total superexchange integral

$$J = 2t^2 \left\{ \frac{(1 + \mu)^2}{1 + \mu^2} \cdot \frac{1}{2t_a - J_a + V_a} + \frac{(1 - \mu)^2}{1 + \mu^2} \cdot \frac{1}{2t_a + J_a + U} \right\}$$

(41)

where $\mu = 2t_a/(U - V_a)$; $J_a = (2t_a)^2/(U - V_a)$ and $t = t_b + t_d$ for the set (1) or $t = t_b$ for the set (2). By using the same parameter values as in Fig.6 one finds that Eq.(11) reproduces completely the above mentioned numerical value for $J$. A large change in $J$ seen in Fig.6(a) at $\lambda = \lambda_c$ is provoked by a sharp behaviour of the order parameter $m_z$ as the system undergoes the CO phase transition. Considering now the CO regime only ($\lambda^{-1} < 1$) we reproduce in Fig.6(b) the same variation of $J$, however, with respect to the order parameter $m_z$. Fig.6(b) shows a rather smooth behaviour with almost linear decrease of $J$ in the regime of weak charge disproportionation, $m_z < 0.2$.

**VI. DISCUSSION AND CONCLUSION**

In Sec.II we formulated the underlying electronic model for the compound NaV$_2$O$_5$ with most of the model paremeters ($t_a, t_b, t_d$ and $U$) fixed from known results of the DFT calculations. By using this model in Sec.III we developed the superexchange theory and derived the second-order perturbation expression (in the effective $V$-$V$ hopping amplitudes $t_b$ and...
for the intra-ladder exchange integral $J$ both in the charge disordered and in the zig-zag charge ordered state. Assuming that the Coulomb mechanism drives the charge ordering (Sec.IV) the exchange integral $J$ is calculated in a wide range of the variable $V_b$ and $V_a$ parameters. Since qualitative results are presented in details in Sec.V we summarize here most important qualitative findings.

(i) In the intra-ladder superexchange mechanism the triplet channel is of minor importance for the model with $t_d = t_b$ and the resulting exchange integral is dominated by the singlet channel, $J \simeq J^{(s)}$ (Figs.4,5). For the model with $t_d = 0$, $J^{(\tau)}$ also gives a sizeable (negative) contribution to $J$.

(ii) In the charge disordered state inter-rung charge-charge correlations within a ladder cause a strong reduction of the exchange integral value (Fig.4).

(iii) With increasing of the zig-zag charge ordering the exchange integral $J$ reduces strongly but never changes sign, i.e. $J$ remains antiferromagnetic ($> 0$) for the whole parameter range, Figs.4-6.

(iv) Variation of the underlying electronic model due to different choices of the hopping amplitude $t_d$ (either $t_d \neq 0$ or $t_d = 0$) may lead to a considerable quantitative change in the value of $J$, especially in the extreme CO limit where $J$ stays finite or vanishes respectively (Fig.6).

In common, Figs.4-6 reveal a general trend. That is the decrease of the total exchange integral $J$ as the inter-rung charge-charge correlations within a ladder increase. We believe this trend together with less obvious properties (i)-(iv) are of general significance not restricted to the particular mechanism we used to describe the CO phase transition in the ladder system.

In the present paper we concentrated on a study of the the intra-ladder superexchange in NaV$_2$O$_5$. To derive a more complete spin model in the Trellis lattice a thorough analysis of the inter-ladder magnetic interactions is required. Such an analysis for the charge disordered phase in NaV$_2$O$_5$ was done in Ref.(11). There the authors claimed that due to the almost perfect cancellation of the triplet- and singlet-interactions in a-direction the ladders are effectively decoupled to give essentially 1D magnetic behavior of the entire spin system. In support of this conjecture we recall also that in the charge disordered Trellis lattice the inter-ladder Heisenberg spin-spin interactions are strongly frustrated. These arguments, however, cannot be transfered directly to a zig-zag CO state. The DFT calculation$^{10}$ of the exchange integrals in a zig-zag CO state have shown, for instance, a rather considerable ferromagnetic (FM) inter-ladder coupling$^{10}$. The opposite sign of this coupling is not surprising in view of different symmetry of V-O-V bonds connecting neighbouring ladders. It is a a challenging problem to reveal the microscopical origins and estimate a value of the resulting FM coupling between neighbouring ladders, which can be done in a properly developed superexchange theory taking into account also effects of direct V-V exchange.
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APPENDIX:

In this Appendix we exploit an extended model including inter-rung Coulomb interactions. Our aim is to show that these interactions lead to the symmetry breaking term $\sim \Delta \varepsilon^0$ in Eq. (35).

We choose the notation $V_{ab}$ for the Coulomb repulsion between the electrons on the diagonal V-V bond, i.e. on a pair of $nn$ V-ions belonging to adjacent ladders (Fig. (1)). We assume the parameter $V_{ab}$ to be not too large otherwise the instability with respect to the in-line charge ordering would be the dominant one. Now the necessary addition to the single ladder model, Eq. (1), can be presented in a form $H_{ab} = \sum_{\{ij\}} H_{ab}^{\{ij\}}$, where the summation is over the pairs $\{ij\}$ of $nn$ rungs belonging to adjacent ladders. For a particular $\{ij\}$ pair one has

$$H_{ab}^{\{ij\}} = V_{ab}(i_L, j_R)n_i^L n_j^R = V_{ab}(i_R, j_L)n_i^R n_j^L$$

(A1)

where the composite index $i_L$ ($i_R$) means the position of V-ion on the left (right) side of the $i$-th rung; the definitions for the electron density operators $n_\alpha^i$ ($\alpha = L, R$) are the same as in the main text. In the pseudospin representation the term $H_{ab}$ takes the following form

$$H_{ab} = -\sum_i \Delta \varepsilon_i^0 T_i^z + \sum_{\{ij\}} V_{ab}(i_L, j_R) \left( \frac{1}{4} - T_i^z T_j^z \right)$$

$$= H_{ab,1} + H_{ab,2}$$

(A2)

where

$$\Delta \varepsilon_i^0 = \frac{1}{2} \sum_{j \in i} [V_{ab}(i_L, j_R) - V_{ab}(i_R, j_L)]$$

(A3)

and summation in (A3) runs over the rungs neighbouring to the $i$–th rung.

Without distortion in the Trellis lattice all the diagonal bonds are identical, $V_{ab}(i_L, j_R) = V_{ab}(i_R, j_L) = V_{ab}(|\vec{r}_0|)$. In this case $\Delta \varepsilon_i^0 = 0$ and the inter-ladder coupling is given by the bilinear term $H_{ab,2}$. Assuming a zig-zag charge ordering in the ladders one may check that in the mean field approximation this term is averaged to zero due to a special geometry of the ladder stacking. It means that on the mean field level the ladders in the non-distorted Trellis lattice are disconnected. Below we argue briefly that a symmetry breaking source appears if the lattice symmetry is lowered as reported, for instance, in Refs. (4, 6) for NaV$_2$O$_5$.

Lüdecke et al. (4) proposed for the low- $T$ lattice superstructure of NaV$_2$O$_5$ two species of ladders, denoted as A and B in Fig.1. In each A- ladder there is a weak transverse, along the a-axis, modulation of the rung positions while the lattice structure of the B-ladders remain symmetric as in the high-$T$ phase. The doubling of unit cell means, in particular, that in the A-B-A’-B .. array the rung’s position modulation in the A- and A’-ladders are of opposite signs. In the modulated Trellis lattice a shortening/lengthening ($\pm \delta$) of the diagonal V-V bonds leads to a special spatial pattern for the intersite Coulomb
parameter variation $V_{ab}(|\vec{r}_0 + \vec{\delta}|) \simeq V_{ab}(|\vec{r}_0|) \mp \nabla V_{ab}\vec{\delta} \equiv V_{ab}^{(\mp)}$ (see Fig.1). By using Eq.(A3) one can easily check that this pattern produces in the A-ladders an effective longitudinal field which is staggered along the ladder b-direction, $\Delta \varepsilon_{0,i,A} = (-1)^i \Delta \varepsilon_{0,A}$, with the amplitude $\Delta \varepsilon_{0,A} \simeq 2|\nabla V_{ab}\vec{\delta}|$. Moreover, the field $\Delta \varepsilon_{0,A}^i$ is also staggered along a-direction, which sustains the zig-zag CO state with the A- and A'-ladders being ordered in the antiphase manner. Due to smallness of the lattice distortion, $|\vec{\delta}|/|\vec{r}_0| \approx 10^{-2}$, we expect that $\Delta \varepsilon_{0,A} \ll V_b$ for the actual values of $V_b$ providing the CO phase transition.

It follows from Eq.(A3) that a symmetry breaking field is not present explicitly in the B-subsystem, i.e. $\Delta \varepsilon_{0,B} = 0$, for the spatial pattern in Fig.1. Strictly speaking, a presence of non-zero field $\Delta \varepsilon_{0,B}$ is not necessary since the long-range zig-zag CO in B-ladders, if it is present, can be explained due to spontaneous symmetry breaking if $\lambda > \lambda_c$.

Note that besides the extracted staggered field term the inter-ladder bilinear interaction, $H_{ab,2}$, is still present. With a zig-zag ordering in A-/or both in A- and B- subsystems this term being considered in the MF- approximation is averaged to zero even in the modulated Trellis lattice structure.
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FIG. 1. Schematic representation of the crystal structure of a vanadium layer of NaV$_2$O$_5$. The vanadium ions are denoted by open circles, the hopping amplitudes ($t_a$, $t_b$ and $t_d$) and Coulomb repulsion parameters ($V_a$, $V_b$) are ascribed to the intra-ladder bonds; the on-site Coulomb repulsion $U$ is also shown. Arrows indicate the weak modulation (not in scale) of V-ion positions in the low-T phase. The single (double) dashed lines are associated with $V_{ab}^{(+)}$ ($V_{ab}^{(-)}$) which are the inter-ladder Coulomb repulsion parameters modulated in the low-T phase.
FIG. 2. The excitation energies in the singlet ($s$) and the triplet ($\tau$) channels as functions of $\Delta \varepsilon$. The model parameters used are (in eV): $t_a = 0.38$, $t_b = t_d = 0.085$, $U = 4$, $V_a = 0.5$.

FIG. 3. Pseudospin correlation functions $\langle T^z_i T^z_{i+1} \rangle_g = k_z$ and $\langle T^z_i T^x_{i+1} \rangle_g \simeq m^2_x$ as functions of $\lambda^{-1} = 2t_a/V_b$. The order parameter $m_z = |\langle T^z_i \rangle_g| = \eta/2$ calculated with the exact 1D Ising exponent $\beta = 1/8$ is shown with a dashed line.
FIG. 4. Variation of the exchange integral $J^{(s)}$ and $J^{(\tau)}$ with respect to $V_b$ (the other model parameters are the same as in Fig.1 and $\beta = 1/8$). The integrals are calculated either in the modified MF approach (dashed lines) or with the effect of charge fluctuations included (solid lines).

FIG. 5. The exchange integrals $J^{(s)}$ and $J^{(\tau)}$ as functions of $V_b$ for various values of $V_a$. 

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{fig4}
\caption{Variation of the exchange integral $J^{(s)}$ and $J^{(\tau)}$ with respect to $V_b$ (the other model parameters are the same as in Fig.1 and $\beta = 1/8$). The integrals are calculated either in the modified MF approach (dashed lines) or with the effect of charge fluctuations included (solid lines).}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{fig5}
\caption{The exchange integrals $J^{(s)}$ and $J^{(\tau)}$ as functions of $V_b$ for various values of $V_a$.}
\end{figure}
FIG. 6. Variation of the total exchange integral $J = J^{(s)} + J^{(\tau)}$ in the wide range of the varying parameter $\lambda^{-1} = 2t_a/V_b$ (a) and in the ordered state as function of the order parameter $m_z$ (b). The curves (1) and (2) correspond to two sets of the hopping amplitudes with $t_d = t_b > 0$ and $t_d = 0$ respectively (see Sec. V).