

Quantum criticality of vanadium chains with strong relativistic spin-orbit interaction

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We study quantum phase transitions induced by the on-site spin-orbit interaction $\lambda\mathbf{L}\cdot\mathbf{S}$ in a toy model of vanadium chains. In the $\lambda\rightarrow 0$ limit, the decoupled spin and orbital sectors are described by a Haldane and an Ising chain, respectively. The gapped ground state is composed of a ferro-orbital order and a spin liquid with finite correlation lengths. In the opposite limit, strong spin-orbital entanglement results in a simultaneous spin and orbital-moment ordering, which can be viewed as an orbital liquid. Using a combination of analytical arguments and density-matrix renormalization-group calculation, we show that an intermediate phase, where the ferro-orbital state is accompanied by a spin Néel order, is bounded on both sides by Ising transition lines. Implications for vanadium compounds CaV_2O_4 and ZnV_2O_4 are also discussed.

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Quasi-one-dimensional (1D) Mott insulators with strongly coupled spin and orbital degrees of freedom have attracted considerable attention recently. A well-studied case is the Kugel-Khomskii Hamiltonian with an $\text{SU}(2)$ symmetry in both spin and orbital sectors.¹ This model is believed to describe the essential physics of quasi-1D compounds $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ and NaV_2O_5 .^{2,3} Extensive numerical and analytical studies have revealed a rich phase diagram.^{4,5} Of particular interest is a $\text{SU}(4)$ symmetric point of the Hamiltonian where the low-energy physics is described by a conformal field theory with a central charge $c=3$, equivalent to a model of three free bosons.

In this paper, we investigate a 1D spin-orbital system which in many aspects is different from the above $\text{SU}(2)\times\text{SU}(2)$ model. The interest is partly motivated by recent experimental progresses on several vanadates including spinel ZnV_2O_4 (Refs. 6 and 7) and quasi-1D CaV_2O_4 .^{8,9} The vanadium chains in these compounds are characterized by frustrated magnetic interactions, Ising-type orbital exchanges, and a large relativistic spin-orbit (SO) interaction. The origin of the first two features can be traced to the lattice geometry of these compounds: vanadium ions in spinel form a three-dimensional (3D) pyrochlore lattice and in CaV_2O_4 they are arranged in weakly coupled zigzag chains (Fig. 1). In both structures the 90° angle between vanadium-oxygen bonds in a network of edge-sharing VO_6 octahedra makes direct exchange the primary mechanism for intersite spin-orbital interaction. An important consequence is that the spin-orbital Hamiltonian only depends on orbitals through the corresponding projection operators. For example, direct $dd\sigma$ exchange takes place along a $[110]$ bond only when one or both of the d_{xy} orbitals are occupied, giving rise to an Ising-type orbital interaction.^{10,11}

Contrary to the anisotropic orbital exchange, magnetic interaction governed by the Heisenberg Hamiltonian preserves the spin-rotational symmetry. The spin exchange constant, however, depends on the underlying orbital occupations. Combined with geometrical frustration, the orbital-dependent spin exchange renders these vanadates essentially quasi-1D spin systems. To see this, we note that the local d_{xy} orbitals are always occupied due to distorted VO_6 octahedron

in both compounds. As a result, the largest spin-spin interaction takes place on bonds parallel to $[110]$ and $[1\bar{1}0]$ directions in spinels [Fig. 1(b)], whereas for CaV_2O_4 the dominant spin exchange occurs along the two rails of a zigzag chain [Fig. 1(a)]. Furthermore, couplings between these spin chains are not only weak but also geometrically frustrated.^{12,13} Since V^{3+} ions in both compounds have spin $S=1$, their magnetic properties thus can be understood from the viewpoint of weakly coupled spin-1 chains (solid lines in Fig. 2).

In both vanadates, one of the two electrons of the V^{3+} ion always occupies the low-energy d_{xy} state, the other one occupies either d_{yz} or d_{zx} orbitals. We introduce a pseudospin-1/2 operator τ to describe this doublet orbital degeneracy, where τ^a are the Pauli matrices. We choose a basis such that $\tau^z = \pm 1$ corresponds to states $|yz\rangle$ and $|zx\rangle$, respectively. The dominant pseudospin interaction is governed by an antiferromagnetic Ising-type Hamiltonian on nearest-neighbor bonds connecting different spin-1 chains^{10,11} (dashed lines in Fig. 2); the relevant orbitals on these bonds are d_{yz} and d_{zx} . Due to the static and three-dimensional nature of the orbital Ising Hamiltonian, the system tends to first develop a long-range orbital order upon lowering the temperature. Figure 2 shows

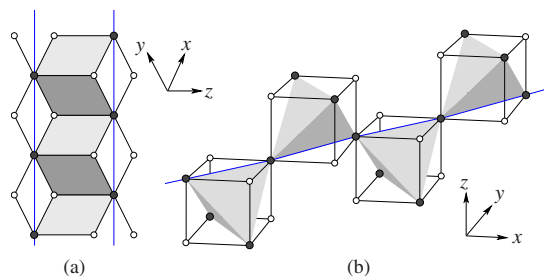


FIG. 1. (Color online) Vanadium chains in (a) CaV_2O_4 and (b) ZnV_2O_4 . The black and white circles denote vanadium and oxygen ions, respectively. The V^{3+} ions are arranged in a zigzag chain of edge-sharing VO_6 octahedra in CaV_2O_4 . On the other hand, V^{3+} ions in spinel form a pyrochlore lattice, which can be viewed as a cross-linking network of vanadium chains. The quasi-1D spin-1 chains are highlighted by solid blue (gray) lines.

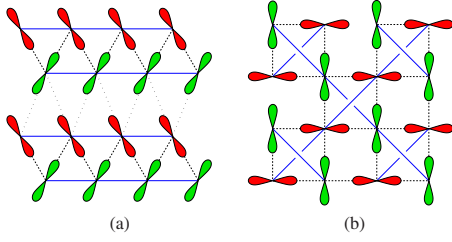


FIG. 2. (Color online) Schematic of antiferro-orbital orders in (a) CaV_2O_4 and (b) ZnV_2O_4 . In both cases, the d_{xy} orbital is occupied at all sites. The interaction between the remaining d_{zx} and d_{yz} orbitals (indicated by red and green symbols, respectively) is governed by an antiferromagnetic Ising-type interaction on the dashed bonds. Also note the *ferro-orbital* order along the quasi-1D spin-1 chains [solid blue (gray) lines].

a schematic of the 3D antiferro-orbital order for the two compounds. It is important to note that orbitals on individual spin-1 chains (solid lines in Fig. 2) are *ferromagnetically* ordered.

The antiferro-orbital order shown in Fig. 2(b), however, is incompatible with the observed crystal symmetry $I4_1/amd$ of tetragonal ZnV_2O_4 .^{6,7} The discrepancy can be attributed to a large SO interaction $\lambda \mathbf{L} \cdot \mathbf{S}$ of vanadium ions. Indeed, the SO term is minimized by a state with simultaneous Néel ordering of spins and orbital angular momenta.¹³⁻¹⁵ The corresponding orbital order consisting of complex $d_{yz} \pm id_{zx}$ orbitals preserves both the mirror inversion m and diamond glide d , and is consistent with the experimental data.

In the absence of SO interaction, the ground state of the spin-1 chain is a nondegenerate spin singlet. This spin liquid phase, also known as the Haldane phase, must be separated from the Néel state favored by a large SO coupling by quantum phase transitions. Since a nonzero L^x requires the electron be in a complex orbital state $\frac{1}{\sqrt{2}}(|zx\rangle \pm i|xy\rangle)$, a fully occupied d_{xy} orbital thus results in the vanishing of L^x and L^y .^{10,13} The nonzero z component of the orbital angular momentum is given by $L^z = -\tau^x$ in our representation. To understand the critical behavior of vanadium chains due to the LS coupling, we consider the following spin-orbital Hamiltonian:

$$H = J \sum_n \mathbf{S}_n \cdot \mathbf{S}_{n+1} - K \sum_n \tau_n^z \tau_{n+1}^z - \lambda \sum_n \tau_n^x S_n^z. \quad (1)$$

This simple model describes two well-studied 1D systems, i.e., an $S=1$ Haldane chain and a ferromagnetic Ising chain (both $J, K > 0$), coupled together by an on-site SO interaction $\lambda \mathbf{L} \cdot \mathbf{S}$. Note that the eigenstates of τ^x , $|yz\rangle \pm i|zx\rangle$, carry an angular momentum $L^z = \mp 1$, respectively. The Hamiltonian [Eq. (1)] has a $U(1) \times Z_2 \times Z_2$ symmetry: the spin $SU(2)$ symmetry is reduced to $U(1) \times Z_2$ by the SO term, whereas an additional Z_2 symmetry comes from the orbital Ising Hamiltonian.

It should be noted that the ferro-orbital order along the quasi-1D chains is stabilized by the interchain antiferro-orbital coupling in real compounds. The ferromagnetic exchange $-K$ in Eq. (1) thus should be regarded as an effective coupling in the mean-field sense.

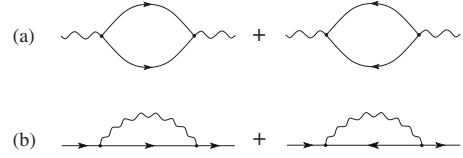


FIG. 3. One-loop corrections to self-energy of (a) magnon and (b) kink. The solid and wavy lines denote the kink and magnon propagators, respectively.

Despite its simplicity, the model contains rather rich physics. It is easy to see that the first-order correction vanishes identically in the ground state of decoupled Haldane and Ising chains. To have a glimpse of the effects of the SO interaction, one needs to go to higher orders and examine the elementary excitations of model [Eq. (1)]. We start with the kink excitations of the Ising chain. Kinks, or domain walls, are topological defects separating the two degenerate ground states of perfectly aligned pseudospins. For classical Ising chains, kinks are static quasiparticles with a constant energy $2K$. To obtain the quasiparticle operators, we first fermionize the Ising chain using Jordan-Wigner transformation¹⁶

$$\tau_n^z = \prod_{m < n} (2c_m^\dagger c_m - 1)(c_n + c_n^\dagger), \quad \tau_n^x = 1 - 2c_n^\dagger c_n. \quad (2)$$

The kink operator γ_q is obtained after subsequent Fourier and Bogoliubov transformations $\gamma_q = u_q c_q - i v_q c_{-q}^\dagger$, where $u_q = \cos(q/2)$ and $v_q = \sin(q/2)$.¹⁶

For spin-1 chain, the lowest excitation above the singlet ground state is a triplet with a dispersion $\omega_k \approx [\Delta_0^2 + v^2(k - \pi)^2]^{1/2}$ near the energy minimum. Here $v = 2.56J$ is the spin-wave velocity and $\Delta_0 \approx 0.4J$ is the Haldane gap.¹⁷ To model the low-energy physics of spin-1 chain, we follow Ref. 18 and introduce three massive magnons a_k^\pm and a_k^z carrying quantum number $S^z = \pm 1$ and 0, respectively. The spin operator is $S_n^z = I_n^z + \frac{1}{2} \sum_k \phi_k e^{ikn} / \sqrt{L}$, where

$$\phi_k = \sqrt{\frac{2v}{\omega_{\pi+k}}} (a_{\pi+k}^z + a_{-\pi-k}^{z\dagger}) \quad (3)$$

and the uniform part I_n^z is quadratic in transverse magnons a_k^\pm . In terms of magnons and kinks, Hamiltonian (1) becomes

$$H = \sum_{k,\sigma} \omega_k a_k^{\sigma\dagger} a_k^\sigma + 2K \sum_q \gamma_q^\dagger \gamma_q + \frac{\lambda}{\sqrt{L}} \sum_{k,q,q'} \left[u_{q+q'} \phi_k \gamma_q^\dagger \gamma_{q'} + \frac{i}{2} v_{q-q'} \phi_k (\gamma_q^\dagger \gamma_{q'}^\dagger - \gamma_{q'} \gamma_q) \right]. \quad (4)$$

The prime on the summation indicates conservation of momentum $k = q \pm q'$. In obtaining the above expression, we have neglected the interaction between kinks and transverse magnons a_k^\pm .

Assuming $\lambda \ll J, K$, we employ a perturbation theory to examine the properties of quasiparticles in the presence of SO coupling. We first evaluate the two-kink bubbles shown in Fig. 3(a),

$$\Pi_1(\omega) = \frac{2\lambda^2 K}{\omega^2 - 16K^2}. \quad (5)$$

It is interesting to note that the particle-hole bubble does not contribute to Π_1 . The above expression for $\Pi_1(\omega)$ diverges as the magnon energy approaches that of a pair of kinks, i.e., $\omega \approx 4K$. In this regime magnons strongly interact with the kinks, and higher order corrections to the interaction vertex have to be taken into account. Assuming $\omega \ll K$ and using random-phase approximation to compute the magnon self-energy, we obtain a renormalized spin gap

$$\Delta_s \approx \Delta_0 - \frac{v\lambda^2}{4\Delta_0 K}, \quad (6)$$

which decreases with increasing λ . At large λ , closing of the spin gap indicates a phase transition into a spin-ordered phase characterized by $\langle a_\pi \rangle \neq 0$.

Figure 3(b) shows the one-loop contribution to the self-energy of magnons. In the $K \gg \Delta_0$ limit, the second term in Fig. 3(b) is negligible compared with the first one, we obtain a self-energy

$$\Sigma_1(q) \approx -\frac{\lambda^2}{\Delta_0} (1 + e^{-\Delta_0/v} \cos 2q). \quad (7)$$

The energy of the kink excitation given by $\varepsilon_q \approx 2K - \Sigma_1(q)$ shows that the kinks become mobile through the mediation of virtual magnons.

The perturbative calculation gives important insight to the elementary excitations in the small λ regime of the spin-orbital model [Eq. (1)]. In particular, the reduced spin and orbital gaps indicate quantum phase transitions at finite λ . To investigate the nature of the phase transitions and the properties of possible new phases, we numerically investigate the spin-orbital model [Eq. (1)] using the infinite-system density-matrix renormalization-group (DMRG) method.¹⁹ The DMRG calculation is known to give a rather accurate description of the ground-state properties for 1D systems. In our calculation we have employed periodic boundary conditions in order to accommodate the staggered ordering of spins and orbital angular momenta.

Noting that $L^z = -\tau^x$ in our representation, we define the following order parameters:

$$\langle \tau_n^z \rangle = \tau, \quad \langle S_n^z \rangle = \mathcal{N}(-1)^n, \quad \langle L_n^z \rangle = -\zeta(-1)^n. \quad (8)$$

The numerical results of a spin-orbital chain with exchange constants $K=0.5J$ are shown in Fig. 4. At small λ , the ground state is characterized by a nonzero ferro-orbital order $\tau \neq 0$ while the spin sector is in the disordered Haldane phase with $\mathcal{N}=0$. At critical point $\lambda_{c1} \approx 0.491J$, the linear chain undergoes a quantum phase transition into a state with simultaneous ordering of staggered spin and orbital moment, characterized by nonzero order parameters \mathcal{N} and ζ , respectively. The ferro-orbital order τ remains finite in the intermediate phase. As we further increase λ , the system undergoes yet another quantum phase transition at $\lambda_{c2} \approx 0.657J$. This critical point is marked by the melting of the ferro-orbital order τ . In the $\lambda \rightarrow \infty$ limit, both order parameters \mathcal{N}, ζ approach 1. The ground state of the spin-orbital chain consists of alter-

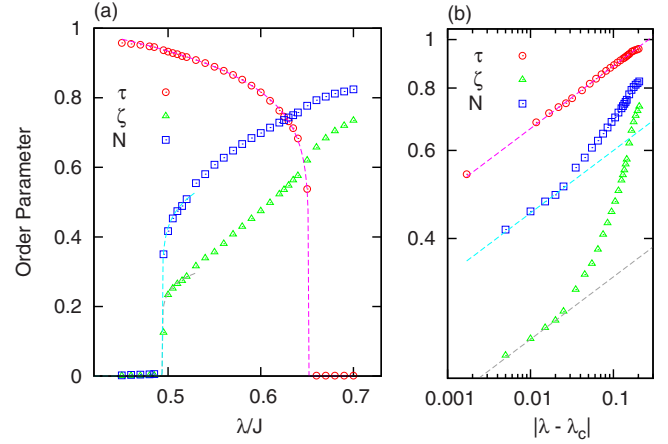


FIG. 4. (Color online) (a) Order parameters as a function of λ/J for a chain with $K=0.5J$. The dashed lines are fittings to 2D Ising transition $m \sim |\lambda - \lambda_c|^{1/8}$, where m is the corresponding order parameter. (b) The same plot in log-log scale.

natively occupied states $|S^z = \pm 1\rangle \otimes |yz\rangle \mp i|zx\rangle$. The orbital occupation numbers $n_{yz} = n_{zx} = 1/2$ are uniform along the chain.

Since the order parameters \mathcal{N} and τ describe, respectively, the broken Z_2 symmetry of the spin and orbital sectors, both critical points λ_{c1} and λ_{c2} are expected to be in the two-dimensional (2D) Ising universality class. Indeed, by fitting the corresponding order parameter m to the Ising scaling relation $m \sim |\lambda - \lambda_c|^{1/8}$, we find agreeable result as shown by the dashed lines in Fig. 4. The Ising nature of the spin Néel transition can be understood in the limit of large orbital gap $K \gg J$. By integrating out orbitals, one obtains an easy-axis spin anisotropy: $-DS_z^2$, where $D = \lambda^2/4K$; the resultant spin gap is reduced in accordance with Eq. (6). As demonstrated numerically in Ref. 20, the spin-1 chain undergoes an Ising transition into a Néel state when $D > D_c$.

Above λ_{c1} , a nonzero \mathcal{N} exerts an effective (staggered) transverse field on the orbitals. By rotating pseudospins an angle π about τ^z axis on odd-numbered sites, the orbital sector is described by a quantum Ising Hamiltonian,

$$H_{\text{orbital}} = -K \sum_n \tau_n^z \tau_{n+1}^z - \Gamma \sum_n \tau_n^x, \quad (9)$$

where the transverse field $\Gamma = \lambda \mathcal{N}$. It is known that the Ising chain reaches a critical state at $\Gamma_c = K$.¹⁶ Numerically, we obtain an Néel order $\mathcal{N} \approx 0.659$ at critical point λ_{c2} . The corresponding critical field $\Gamma_c = \lambda_{c2} \mathcal{N} \approx 0.52J$ is indeed close to the orbital exchange $K=0.5J$ used in the DMRG calculation.

Our main results are summarized in the phase diagram, Fig. 5, which contains three massive phases separated by two Ising transition lines. The spin sector in the $J=0$ limit is extensively degenerate as each spin could be in either $|S^z = +1\rangle$ or $|S^z = -1\rangle$ states, independently; the total degeneracy is 2^L . After applying a π rotation about τ^z axis to those pseudospins at sites where $S_n^z = -1$, the orbital sector is again mapped to a quantum Ising chain Eq. (9) with the transverse field $\Gamma = \lambda$. Since the orbital Ising transition occurs at $\Gamma_c = K$,

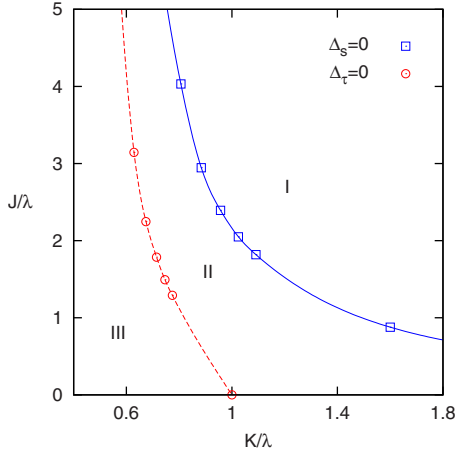


FIG. 5. (Color online) Phase diagram of spin-orbital model [Eq. (1)]. The lines are guide for the eyes. In phase I, the spin sector is in the disordered Haldane phase, $\mathcal{N}=\zeta=0$, while the orbitals are ferromagnetically ordered $\tau \neq 0$. The ground state of phase III is composed of Néel spin order and orbital-moment order, which can be viewed as an orbital liquid, i.e., $\mathcal{N} \neq 0$ and $\tau=0$. In the intermediate phase II, a spin Néel order coexists with the ferro-orbital Ising order.

the phase boundary λ_{c2} hence ends at K on the $J=0$ axis. In the small J limit, one can estimate λ_{c1} for the spin Néel transition using the critical condition $D=D_c \approx 0.05J$,²⁰ which gives $JK \propto \lambda_{c1}^2$. The region of intermediate phase enclosed by boundaries λ_{c1} and λ_{c2} shrinks with increasing spin exchange

J . At very large J , the two Ising lines could merge to form a Gaussian criticality or a first-order transition.

We now discuss implications of our findings to vanadium compounds. As discussed before, the ferro-Ising order parameter τ can also serve as the 3D antiferro-orbital order parameter for both vanadates (see Fig. 2). A nonzero τ thus creates two different orbital chains, hence further lowering the crystal symmetry. However, experiments on both compounds observed a higher symmetry^{6,8} indicating that vanadium chains in both vanadates are likely in the $\tau=0$ orbital liquid state (phase III). Furthermore, the appearance of finite orbital moment $L^z=\zeta$ antiparallel to spin S^z at $\lambda > \lambda_{c2}$ also explains the reduced vanadium moment $\mu=(2S^z+L^z) \mu_B \approx 1 \mu_B$ observed experimentally.^{7,8} On a final note, we caution that the fermionic description of orbital excitations as kinks in an Ising chain is the consequence of using 1D approximation for the orbital system. Furthermore, the Kugel-Khomskii-type spin-orbital terms $(\tau_i^z \tau_j^z)(\mathbf{S}_i \cdot \mathbf{S}_j)$ introduce correlations between orbital and spin excitations. A detailed description of these 3D spin-orbital excitations will be discussed in future publications.

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- ¹Y. Q. Li, M. Ma, D. N. Shi, and F. C. Zhang, *Phys. Rev. Lett.* **81**, 3527 (1998).
- ²E. Axtell, T. Ozawa, S. Kauzlarich, and R. R. P. Singh, *J. Solid State Chem.* **134**, 423 (1997).
- ³M. Isobe and Y. Ueda, *J. Phys. Soc. Jpn.* **65**, 1178 (1996).
- ⁴C. Itoi, S. Qin, and I. Affleck, *Phys. Rev. B* **61**, 6747 (2000).
- ⁵P. Azaria, A. O. Gogolin, P. Lecheminant, and A. A. Nersesyan, *Phys. Rev. Lett.* **83**, 624 (1999).
- ⁶M. Reehuis *et al.*, *Eur. Phys. J. B* **35**, 311 (2003).
- ⁷S.-H. Lee *et al.*, *Phys. Rev. Lett.* **93**, 156407 (2004).
- ⁸O. Pieper *et al.*, *Phys. Rev. B* **79**, 180409(R) (2009).
- ⁹A. Niazzi *et al.*, *Phys. Rev. B* **79**, 104432 (2009).
- ¹⁰S. Di Matteo, G. Jackeli, and N. B. Perkins, *Phys. Rev. B* **72**, 020408(R) (2005).
- ¹¹G.-W. Chern and N. Perkins, *Phys. Rev. B* **80**, 220405(R)

(2009).

- ¹²H. Tsunetsugu and Y. Motome, *Phys. Rev. B* **68**, 060405(R) (2003).
- ¹³O. Tchernyshyov, *Phys. Rev. Lett.* **93**, 157206 (2004).
- ¹⁴T. Maitra and R. Valenti, *Phys. Rev. Lett.* **99**, 126401 (2007).
- ¹⁵G.-W. Chern and N. B. Perkins, *Phys. Rev. B* **80**, 180409(R) (2009).
- ¹⁶B. K. Chakrabarti, A. Dutta, and P. Sen, *Quantum Ising Phases and Transitions in Transverse Ising Models* (Springer-Verlag, Berlin, 1996).
- ¹⁷S. R. White and D. A. Huse, *Phys. Rev. B* **48**, 3844 (1993).
- ¹⁸I. Affleck, *Phys. Rev. B* **41**, 6697 (1990).
- ¹⁹S. R. White, *Phys. Rev. Lett.* **69**, 2863 (1992).
- ²⁰W. Chen, K. Hida, and B. C. Sanctuary, *Phys. Rev. B* **67**, 104401 (2003).