First-principles study of an organometallic S=1/2 kagomé compound

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Cu(1,3-benzenedicarboxylate) [Cu(1,3-bdc)] contains structurally perfect kagomé planes formed by Cu$^{2+}$ ions without the presence of diamagnetic defects. This organometallic compound should have served as a precious platform to explore quantum frustrated magnetism, yet the experimental results so far are mysterious, leading to questions such as “Is Cu(1,3-bdc) just a trivial weak ferromagnet?” Using the the density functional theory (DFT), we have systematically studied the electronic and magnetic properties of Cu(1,3-bdc), putting forth a theoretical basis to clarify this novel material. We present numerical evidences of a dominating antiferromagnetic (AFM) exchange between nearest-neighbor (NN) Cu$^{2+}$ as experimentally extracted from the high-temperature susceptibility data. We further show that beyond the NN AFM exchange, the additional interactions in Cu(1,3-bdc) have similar strength as those in the well-studied kagomé antiferromagnet, Herbertsmithite, by designing a comparative study. In the end, the origin of the phase transition and FM signals observed under low temperature is discussed based on the DFT results.

I. INTRODUCTION

Since Anderson’s proposal in the 70s [1], the concept of quantum spin liquids (QSLs) has now become an indispensable brick laid upon the two milestones of modern condensed matter physics, namely the high-temperature cuprate superconductivity and the fractional quantum Hall effect. Experimental discovery of QSLs in the so-called quantum frustrated materials is a long-sought goal to bring out exotic new quasi-particles and gauge fields never encountered before [2].

After decades of searching, several promising examples have now emerged [3, 4]. The hottest candidate at present is perhaps Herbertsmithite ZnCu$_2$(OH)$_6$Cl$_2$, which realizes the $S = \frac{1}{2}$ AFM Heisenberg model on the 2D kagomé lattice [5]. Extensive theoretical studies have suggested that this model is likely to achieve a QSL ground-state, despite close in energy with other competing phases [6, 12]. Experiments on Herbertsmithite have also shown QSL-like features, such as the absence of any observed magnetic order down to 50 mK [13, 14] and an unusual continuum of spin excitations [15]. However, the inevitable Cu/Zn substitutional defects make the interpretation of experimental data difficult [16]. It remains an open debate whether these defects obscure the intrinsic signals under low temperature [17].

Cu(1,3-bdc), synthesized in the same group three years after Herbertsmithite, also features with structurally perfect Cu$^{2+}$ kagomé planes [18]. A great advantage of Cu(1,3-bdc) is that the substitutional defects are automatically avoided. Unfortunately, Cu(1,3-bdc) has been found to undergo a phase transition at $T_c \sim 2K$ [18, 19], which appears to exclude the possibility of a QSL ground state. This material has thus been largely overlooked. However, given the structural similarity between Cu(1,3-bdc) and Herbertsmithite, a natural question is why the spins behave so differently in these two materials. It is desirable to better understand the electronic properties of Cu(1,3-bdc), as it would in turn help to understand the QSL-like behaviors of Herbertsmithite, and further reveal key factors to achieve QSLs.

An overview on the experimental data of Cu(1,3-bdc) shows puzzling ambiguities. Fitting the high-temperature susceptibility data to the Curie-Weiss law yields a Weiss constant $\theta = -33K$, suggesting a mean NN AFM exchange $J_1 \sim 30K$ [18]. The ratio $|J_1|/T_c > 10$ indicates a strong frustration effect. Later, muon spin relaxation ($\mu$SR) observes persistent spin fluctuation below $T_c$, which further supports the frustration scenario [19]. On the other hand, the magnetization data around $T_c$ displays a ferromagnetic (FM)-like curve [20] and a small hysteresis loop with the coercive field of 10.5 Oe [18]. A recent work starting from the FM hypothesis extracted a mean NN FM exchange $J_{1} \sim -2K$ from the electron spin resonance lineshape, proposing Cu(1,3-bdc) be rather a weak ferromagnet without frustration ($|J_{1}|/T_c \sim 1$) [20]. In addition, there is an unpublished neutron scattering work, which employs this FM scenario to interpret the dynamic structure factor [21].

This Article aims to provide a first-principles description of Cu(1,3-bdc) based on DFT [22] and possibly resolve some lasting controversies. Our primary goal is to
We start from the standard LDA (spinless) band calculation to understand the electronic properties. The result [Fig. 2(a)] shows six bands around the Fermi level, isolated from the other bands. This set of bands exhibits the typical feature of single-orbital hopping on a 2D kagomé lattice, i.e., a flat band and two dispersive bands with a linear crossing. We will refer to these bands as the “kagomé bands” hereafter. Recall that there are two Cu kagomé planes per unit cell, which give rise to two sets of kagomé bands. The flatness of the top bands suggests that except the NN hopping, all the other hopping processes are weak. The Fermi level crosses the middle of the six bands, which corresponds to half-filling of these states. It is well known that LDA cannot properly describe the on-site Coulomb repulsion of 3d orbitals. Hence, the LDA calculation predicts a metallic phase.

FIG. 1: Atomic structure of Cu(1,3-bdc). The white numbers on Cu atoms label the three inequivalent sites of a kagomé plane. (a) Side view of the hexagonal unit cell. (b) Local planar coordination of Cu. (c) 1,3-bdc as a linker; the solid lines show the shortest intra-plane path between two Cu sites; the double lines show the shortest inter-plane path; (d) top view of the hexagonal unit cell; the dashed lines are guide to the eyes for the kagomé geometry formed by the Cu sites.
IV. WANNIER FUNCTION ANALYSIS

FIG. 2: (a) The single-electron (within LDA) band structure of Cu(1,3-bdc). The inset is the Brillouin zone and high-symmetry points of the hexagonal lattice. (b) Wannier function of the kagomé bands [red shaded in (a)] around the Fermi level. The wired surface plots the iso-value contour, and the color (red/blue) denotes the sign.

The single-electron band structure can be understood by considering Cu$^{2+}$ ions under a planar crystal-field splitting, with a single $d_{x^2-y^2}$ at the top. The nine $d$-electrons in one Cu$^{2+}$ ion will fully occupy the bottom four orbitals, leaving an unpaired electron on $d_{x^2-y^2}$, which in the end reduces to a single-orbital degree of freedom around the Fermi level. The low-energy dynamics are primarily determined by this subspace, which is well defined in this case owing a large gap with other occupied bands [$\Delta E_{\text{band}}$ in Fig. 2(a)]. Then, it is helpful to down-fold the full band structure into an effective single-orbital hopping model:

$$H_{\text{hop}} = \sum_{i,j} t_{ij} c_i^\dagger c_j,$$

where $i, j$ label the Cu site, and $t_{ij}$ is the hopping parameter between the two sites. To construct a quantitative basis, we perform Fourier transformation from the Bloch representation to the Wannier representation by using the Wannier90 code [82]. Figure 2(b) plots the spacial distribution of the maximally-localized Wannier function centered at one of the six Cu sites; the others are related via the crystal symmetry. The Wannier function takes the form of a hybridization between the Cu $d_{x^2-y^2}$ orbital and the O $p_{\alpha}$ orbital.

The hopping parameters between these Wannier functions can be rigorously calculated by performing the same Fourier transformation with the same basis. We list three leading terms in Tab. I: the NN hopping $t_1$, the 2nd largest in-plane hopping $t_{\text{in}}^2$, and the largest out-of-plane hopping $t_{\text{out}}^2$. The NN hopping $t_1$ is one order of magnitude larger than the other hopping terms, dominating the hopping dynamics. It is worth noting that $t_1$ has a nontrivial minus sign, which determines the position of the flat band. This sign cannot be simultaneously gauged away on the three Cu sites. When the electron circles the three sites, the minus sign leads to a $\pi$ Berry phase.

Even without information on the spin exchange, the single-electron properties shown above already suggest Cu(1,3-bdc) as an ideal $S = \frac{1}{2}$ kagomé model system: (a) the half-filled Wannier function gives rise to a half spin at each Cu site; (b) beyond the NN coupling, the additional perturbations, such as second neighbor and interplane couplings, are weak. In order to uncover the underlying spin exchange, we need to evaluate the renormalized many-body interactions between the Wannier functions not captured within LDA. The dominating interaction Hamiltonian contains three terms:

$$H_{\text{int}} = \tilde{U}_0 \sum_i n_i \sigma_i + \tilde{U}_1 \sum_{\langle ij \rangle} n_i n_j + \tilde{J}_{\text{ex}} \sum_{\langle ij \rangle \alpha} c_i^\dagger \sigma_i^\dagger, c_j, c_j, c_{\alpha j}, c_{\alpha j}, \alpha, \alpha, \alpha, \alpha,$$

where $\langle ij \rangle$ and $\alpha$ denotes the NN pairs and spin, respectively. $\tilde{U}_0$ is the (renormalized) on-site Hubbard repulsion, $\tilde{U}_1$ is the NN direct repulsion and $\tilde{J}_{\text{ex}}$ is the NN direct exchange. We explicitly include the inter-site direct exchange $\tilde{J}_{\text{ex}}$ to address the possibility of any ligand mediated Hund’s coupling as phenomenologically formulated by the Goodenough-Kanamori rules [33, 34]. A similar Wannier function analysis has successfully explained the ferromagnetism in La$_2$Ba$_2$Cu$_2$O$_{10}$ [29].

A rigorous extraction of these parameters, however, is extremely complicated; the reliability of so-far proposed approximations, e.g. the constraint LDA [33] and the constraint random phase approximation [35] is still under improvement. Fortunately, the uniqueness of Cu(1,3-bdc) is that the downfolded subspace is well separated from the other occupied states [See $\Delta E_{\text{band}}$ labeled in Fig. 2(a)]. Since the renormalization primarily arises from excitations of the electrons outside the downfolded subspace, the effective interactions can be reasonably estimated as the screened Coulomb potential in a large-gap ($\sim \Delta E_{\text{band}} + \tilde{U}_0$) insulator, of which the macroscopic dielectric constant $\epsilon_r$ typically ranges between 2 to 10. Keeping this picture in mind, we proceed by first explicitly evaluating the “bare” Coulomb integrals, and then discussing how screening is going to influence the results.

The interaction parameters are calculated as follows:

$$\tilde{U}_0 = \int d\mathbf{r} d\mathbf{r}' |w_i(\mathbf{r})|^2 |w_i(\mathbf{r}')|^2 \epsilon_r |\mathbf{r} - \mathbf{r}'|^{-1},$$

$$\tilde{U}_1 = \int d\mathbf{r} d\mathbf{r}' |w_i(\mathbf{r})|^2 |w_j(\mathbf{r}')|^2 \epsilon_r |\mathbf{r} - \mathbf{r}'|^{-1},$$

$$\tilde{J}_{\text{ex}} = \int d\mathbf{r} d\mathbf{r}' w_i^\dagger(\mathbf{r}) w_j(\mathbf{r}) w_j^\dagger(\mathbf{r}') w_i(\mathbf{r}') \epsilon_r |\mathbf{r} - \mathbf{r}'|^{-1},$$

in which $w_i$ is the Wannier function centered at site $i$. The values for the “bare” interactions $U_0, U_1$ and $J_{\text{ex}}$ obtained from numerical integration with $\epsilon_r = 1$ are listed in Tab.I.

The condition $U_0 \gg t_0$ indicates a typical Mott insulator at half filling, which is actually intuitively expected from the high transparency of the Cu(1,3-bdc)
crystal. This condition holds even when $U_0$ is screened by an $\epsilon_r \sim 10$. Therefore, the electron model can be safely reduced to a Heisenberg spin model by the standard second-order perturbation:

$$H_{\text{spin}} = J_1 \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j$$

$$J_1 = \frac{4t_1^2}{U_0} - 2 \tilde{J}_{\text{ex}}$$

in which $\mathbf{S}_i$ is the spin $\frac{1}{2}$ operator at site $i$. Note that the $\tilde{U}_1$ term becomes a constant in the spin model and the longer-range exchange terms are of the order $(t_2/t_1)^2 \sim 1/100$ with respect to $J_1$, which are much weaker than the DM interaction as we will see in Sec. V. Substituting the bare parameters into Eq. (4) gives $\frac{4t_1^2}{U_0} = 1.47 \text{meV}$ and $2 \tilde{J}_{\text{ex}} = 0.34 \text{meV}$. Therefore, the AFM superexchange surpasses the FM direct exchange, and the net effective NN spin exchange is $J_1 = 1.13 \text{meV} = 13K$.

With an $\epsilon_r > 1$, the screening effect will enhance the AFM superexchange and suppress the FM direct exchange, resulting in a larger $J_1$, e.g. with $\epsilon_r \sim 2$, $J_1$ will be shifted to $\sim 30K$. The key point here is that we can be sure that the renormalization to the interactions will further favor the AFM exchange rather than reduce it, even though the rigorous calculation is difficult. Therefore, the Wannier function analysis supports an AFM exchange between NN Cu$^{3+}$, and the estimated exchange strength can be reasonably compared with the Weiss constant extracted from the high-temperature susceptibility data [18].

V. DFT+U ANALYSIS

The DFT+U method incorporates at the Hartree-Fock level the strong correlation of localized atomic orbitals, e.g. the Cu 3d orbitals for our case, and describes magnetism in an itinerant picture. In spite of its mean-field nature, this method has been proved to be an efficient tool to provide valuable information on the magnetic properties of Mott insulators. Especially, extensive benchmark calculations have been performed on the parent compounds of high-Tc cuprates, which reproduce the correct AFM ground state [28]. Recently, a DFT+U study on Herbertsmithite has shown that it is possible to even quantitatively describe the NN AFM exchange strength based on the energy differences of the frozen collinear spin configurations [30]. For Cu(1,3-bdc), the ground state are expected to be closer to a frozen configuration than Herbertsmithite. Therefore, it is helpful to see what kind of magnetic ground state the DFT+U method favors.

The calculation involves two parameters $U$ and $J$, describing the average repulsion and Hund’s exchange between the Cu 3d orbitals. Following the previous DFT+U calculations on cuprates and Herbertsmithite [28, 30], we choose a variety of testing $U$ ranging between 6 eV and 8 eV and $J = 1$ eV. The results are found to be nearly independent of the choice of parameters. Note that these parameters should not be confused with those in Eq. (3), which refer to the down-folded Wannier functions. The DFT+U calculations represents an independent analysis based on a full description of the material, rather than a mean-field solution to Eq. (1) + Eq. (2).

FIG. 3: DFT+U energy (per unit cell) of selected spin configurations.

We start from three initial spin configurations of the Cu kagomé plane: (a) collinear, parallel; (b) collinear, one spin antiparallel to the other two; (c) coplanar with relative angles of 120°. We then perform self-consistent calculations to get the mean-field solution and compare the energy of different configurations. As shown in Fig. 3, the FM configuration (a) has the highest energy. Configuration (b) is lower than (a) by $5 \text{ meV}$, and configuration (c) is lower than (b) by another $1 \text{ meV}$. If we assume a classical-spin mapping to Eq. (1), the effective $J_1$ can be extracted according to the energy difference between (a) and (b) as:

$$E_a - E_b = N_p \times 2J_1 \left( \frac{1}{2} \times \frac{1}{2} \right),$$

in which $N_p$ is the number of flipped spin pairs within the unit cell. For our case, each kagomé plane contains 4 flipped pairs, and there are two kagomé planes in the unit cell. Therefore, $N_p = 8$, giving an estimated $J_1 = 1.25 \text{meV} = 14K$, which is close to the Wannier function result with the bare Coulomb parameters.

One interesting point is that after reaching the self-consistency, we notice that configuration (c) slightly deviates from the perfect 120° angles into an asymmetric 130°,130° and 110° configuration. Consequently, the net magnetic moment is nonzero. This observation implies that Cu(1,3-bdc) may have a more complicated magnetic
order than the 120° classical solution and exhibit a weak ferromagnetic signal at the low temperature.

There is no guarantee that configuration (c) is the ground state even within the DFT+U formalism. It is likely that mean-field solutions with lower energy exist in larger periodicity, but a comprehensive searching is computationally expensive - a $\sqrt{3} \times \sqrt{3}$ unit cell already contains 306 atoms. We will therefore leave it for future investigations. Nevertheless, an AFM NN exchange is supported by the present DFT+U results.

VI. EFFECTS OF SOC

The SOC is responsible to various secondary spin anisotropic terms. These terms, especially the DM interaction [37, 38] in quantum frustrated magnets, have attracted a lot of attention, due to their possibly important role in determining the ground state [17, 39, 40]. By including SOC in the DFT(+U) Hamiltonian, we quantify its effects within the first-principles formalism.

The primary effect of SOC on the single-electron band structure is found to open gaps at several degenerate points. In Fig.4 we zoom in around the A point to show a SOC-induced band gap of 6 meV. This gapping mechanism is recently an active topic, because of the nontrivial band topology [31, 41, 42]. A simplified form of SOC on the kagomé lattice can be written down as [42]:

$$H_{soc} = i\tilde{\lambda} \sum_{i,j,\alpha} \eta_{ij} c_{i\alpha}^\dagger \sigma_{\alpha\alpha}^z c_{j\alpha},$$

in which $\tilde{\lambda}$ is the effective strength of SOC and $\sigma^z$ is the z-component Pauli matrix. $\eta_{ij}$ is a sign determined by the hopping direction: $+$, if following the arrows in Fig.4(b); $-$, if opposite. This form of SOC conserves $S_j^z$; i.e., assuming the electric field on each site is in the 2D plane. Intuitively, it pins a nontrivial phase to the electrons when they hop around the lattice. As shown later, this SOC leads to an out-of-plane DM interaction, which is typically the dominant spin anisotropic term.

By fitting the first-principles band splitting to Eq.(7), the value of $\tilde{\lambda}$ can be determined to be 1 meV (Tab.I). We can now add $H_{soc}$ to $H_{hop}$, and do the second-order perturbation again with respect to $H_{int}$. Besides the isotropic Heisenberg exchange, the next largest interaction arises from the $\lambda_1$ cross term:

$$H_{DM} = \sum_{i,j} D_{ij}^z (S_i \times S_j)_z$$

with which is nothing but the out-of-plane DM interaction. Since $2J_{ex} \ll 4t_0^2/U_0$ in Cu(1,3-bdc), the ratio $|D_{ij}^z|/|J_1|$ is simply $2\tilde{\lambda}/|t_0| = 1/25$. Taking $|J_1| \sim 30K$, $|D_{ij}^z|$ is estimated to be of the order of 1K, comparable to the phase transition temperature $T_c$. The pseudo-dipole interaction $H_{aniso} = \sum_{i,j} \Gamma_{\mu\nu} S_i^\mu \cdot S_j^\nu$ arises from the $\lambda^2$ terms, thus one more order smaller than the DM interaction.

Including SOC in the DFT+U calculation is found to have negligible effects. Both the self-consistent spin configuration and the energy difference are the same as described in Sec.V without SOC. When we globally rotate the spins, the spin anisotropic energy can be observed showing an in-plane preference. The magnitude is less than 1 meV per unit cell. In summary, we conclude that the dominant role of SOC in Cu(1,3-bdc) is inducing a DM interaction between NN spins. Despite a weak magnitude, it can induce observable anisotropy as observed in the single-crystal measurement [20], and is possibly related to the phase transition around 2K.

VII. COMPARISON WITH HERBERTSMITHITE

Quoted as the end to the drought of QSL, Herbertsmithite has been extensively studied in the past few years [3]. Some of its properties are carefully determined experimentally, such as a dominant AFM NN coupling $J \sim 180K$ and a z-component DM interaction $D^z \sim 1/10J$ [12]. Being the “siblings”, it is informative to conduct a comparative study on these two materials within the same theoretical framework.

With the rhombohedral (R-3m) space group, Herbertsmithite contains three Cu$^+$ kagomé planes per unit cell [3]. The NN Cu atoms are bonded to one common O atom. The two kagomé planes are bridged by an O-Zn-O three-atom path. Hence, the kagomé planes are much more compact than in Cu(1,3-bdc). We show the single-electron band structure and the Wannier function of Herbertsmithite in Fig.5. A quick comparison between Fig.2 and Fig.5 gives the following information:

(a) For Herbertsmithite, the bands around the Fermi level deviate from the ideal kagomé bands more significantly. Therefore, compared with Cu(1,3-bdc), the addi-
tional hopping terms beyond NN have larger magnitudes, as expected from the more compact structure.

(b) For Herbertsmithite, the flat band resides on the bottom, opposite to the case in Cu(1,3-bdc). As discussed in Sec.III, the position of the flat band is determined by the nontrivial sign of $t_1$. The hopping sign comes from the overlap of the Wannier functions, which depends on the bonding pattern and distance.

(c) The Wannier function is similar as a consequence of the same local CuO$_4$ coordination. With this picture, Cu(1,3-bdc) can be roughly viewed as a loosely-packed Herbertsmithite.

FIG. 5: (a) The single-electron band structure of Herbertsmithite. (b) Wannier function of the kagomé bands [red shaded in (a)] around the Fermi level. The wired surface plots the iso-value contour, and the color (red/blue) denotes the sign.

TABLE I: A comparison of key parameters for Cu(1,3-bdc) and Herbertsmithite derived from the DFT Wannier function analysis

|                  | Cu(1,3-bdc) | Herbertsmithite | Ref. |
|------------------|-------------|-----------------|------|
| $t_1$ (eV)       | $-5.0 \times 10^{-2}$ | $1.8 \times 10^{-1}$ | Eq. (1) |
| $t_2$ (eV)       | $4.8 \times 10^{-3}$ | $2.3 \times 10^{-2}$ | Eq. (1) |
| $t_2'$ (eV)      | $2.3 \times 10^{-3}$ | $3.7 \times 10^{-2}$ | Eq. (1) |
| $\lambda$ (eV)   | $1 \times 10^{-3}$ | $5 \times 10^{-3}$ | Eq. (7) |
| Bare interaction (eV) |            |                  |      |
| $U_0$            | 6.8         | 6.4             | Eq. (2) |
| $U_1$            | 1.0         | 4.1             | Eq. (2) |
| $J_{ex}$ (eV)    | $1.7 \times 10^{-4}$ | $5.6 \times 10^{-2}$ | Eq. (2) |

To provide deeper insights, we list the parameters of Herbertsmithite calculated by the same Wannier function analysis along with Cu(1,3-bdc) for comparison (Tab.I). The hopping amplitudes are in general one order of magnitude larger in Herbertsmithite because of the shorter hopping path, yet the ratios, e.g. $|t_2'|/|t_1|$ and $|\lambda|/|t_1|$ are roughly the same. With regards to the interactions, $U_0$ is almost the same, confirming the similarity of the Wannier functions; $U_1$ and $J_{ex}$ are larger in Herbertsmithite as expected. The experimental value $J_1{=}180$K can be reproduced by assuming an effective dielectric constant $\epsilon_r{=}2.8$, which is slightly larger than the value for Cu(1,3-bdc) as discussed in Sec.IV.

VIII. CONCLUSION AND DISCUSSION

In summary, our DFT calculations suggest that Cu(1,3-bdc) closely reproduces the ideal $S = \frac{1}{2}$ kagomé AFM Heisenberg model. The relative strength of additional interaction terms with respect to the dominant NN AFM exchange is summarized as below.

(a) DM interaction: $\frac{1}{t_1} \sim O(10^{-1})$.

(b) Next NN exchange and inter-plane exchange: $\frac{|t_2'|}{t_1} \sim O(10^{-2})$.

(c) Pseudo-dipolar interaction: $\frac{|\lambda|}{t_1} \sim O(10^{-2})$.

Based on these numerical results, our overall understandings on previous experimental results are as follows. The local spin nature guarantees a nice Curie-Weiss behavior in the high-T range, so the Weiss constant $\theta = -33$K extracted from the high-T susceptibility $\chi^{-1}(T)$ fitting should be respected, which defines a reliable $J_1$ energy. The deviation from the Curie-Weiss law occurs when $T$ is comparable or smaller than $J_1$ because of the breakdown of the molecular field picture, which makes the $\chi^{-1}(T)$ fitting no longer meaningful. Just as observed in Herbertsmithite, the downturn of $\chi^{-1}(T)$ (or equivalently upturn of $\chi(T)$) have complicated origins, leading to a false FM interpretation. The phase transition around $T_c = 2$K may be associated with the additional secondary interactions, such as the DM interaction. The system undergoes an ordering transition, but due to the frustrated lattice and small spin value, quantum fluctuations persist as observed in $\mu$SR. The weak hysteresis after ordering is not from a fully-polarized FM order, but rather a canted Neél order.

It is known that the Schwinger boson mean-field theory (SBMFT) provides a satisfying description on the disorder-order transition of $S = \frac{1}{2}$ kagomé AFM Heisenberg model [2]. Using the SBMFT language, the ordering transition is described as a Bose-Einstein condensation of spinons on the QSL ground state. Following this picture, Cu(1,3-bdc) can be viewed as a condensed QSL. We would like to mention that the SBMFT predicts a flat spinon band at the top of the excitation spectrum [44]. This property is in sharp contrast with the conventional spin-wave theory, which gives a flat magnon band at the bottom of the excitation spectrum [45]. Hence, the inelastic neutron scattering signal of Cu(1,3-bdc) can be very different from that of large-spin kagome AFM materials, such as iron jarosite, which have been found to agree with the spin-wave theory [46].

Unpublished neutron scattering data on Cu(1,3-bdc) has been orally reported, which suggests FM ordering below $T_c$ [21]. The primary evidence, however, appears to be a top flat mode observed in the inelastic spectrum, which is considered to be coincide with the spin-wave theory of a kagomé ferromagnet. We note that this data may need to be re-examined carefully, because if the SBMFT describes Cu(1,3-bdc) correctly, the dynamic structure factor bears many features similar to the
magnon branches of a kagomé ferromagnet, including a top flat peak (For reference, see Fig. 1a in Ref. [47]). This so-called “weather-vane” mode has never been observed in materials before, and thus could be easily interpreted in a wrong way. A distinction between the FM and the AFM scenarios is the energy scale: if Cu(1,3-bdc) turned out to be a ferromagnet, the NN FM exchange could only be of the same order of the phase transition temperature $T_c \sim 2K$ as proposed in Ref. [23], whereas the AFM scenario anticipates a NN exchange one order of magnitude larger. This energy scale will be unambiguously reflected by the width of the neutron scattering spectrum.

The remaining question is why Herbertsmithite can stay in a disorder phase, while the secondary interactions with similar strength induce ordering transition of Cu(1,3-bdc). The only qualitative difference between these two materials shown by our calculations is the non-trivial NN hopping sign. However, this sign does not explicitly enter the Heisenberg model as well as the additional terms we have discussed, because they all arise from the secondary-order perturbation in terms of hopping. Nevertheless, this sign will manifest in higher-order perturbations, and it is interesting to ask whether the sign of these higher-order terms select a specific ground state. Another obvious difference between Cu(1,3-bdc) and Herbertsmithite is that Cu(1,3-bdc) is intrinsically free from the Cu/Zn substitutional defects. Then the open possibility is that these defects indeed play an important role in the low-temperature magnetic properties.

IX. ACKNOWLEDGEMENT

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