Basics of Quantum Spin Liquids

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Abstract

A quantum spin liquid is a state of matter in which the spins are highly entangled and don't order, even at T = 0. They are predicted to exhibit fractional particle excitations and emergent gauge fields. In this essay, I introduce the basics of quantum spin liquids with an emphasis on their universal features, and cover some experiments done on $ZnCu_3(OH)_6Cl_2$.

1 Introduction

A spin liquid is a state of matter in which the spins are correlated, yet fluctuate strongly, even at low temperatures [1]. For example, consider an Ising antiferromagnet on a hexagonal lattice (see figure 1). Only two of the spins can be antiparallel, leading to six degenerate ground states; thermal fluctuations can drive transitions between these states. This is an example of a classical spin liquid, i.e., a spin ice. Spin ices have been realized experimentally (e.g., $Dy_2Ti_2O_7$) and exhibit magnetic monopoles. At very low temperatures, however, other terms may become relevant in the Hamiltonian (e.g., a stray field) which cause the spins to either order or form a spin glass.

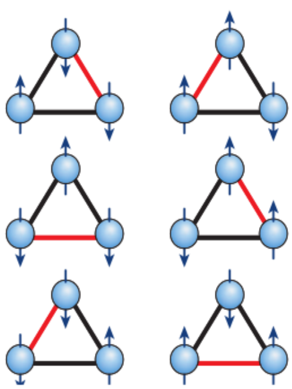


Figure 1: AF Ising spins on a triangle. Figure is from [1].

It's also possible to have quantum fluctuations, which are fluctuations due to the commutation relations of spin operators (i.e., we can no longer represent the spins as vectors). These fluctuations can be strong enough to prevent ordering even at T=0 [1]. If, in addition to a lack of order, the spins are also highly entangled, then we have a quantum spin liquid (QSL) [2]. These states are expected to have fractional, non-local, quasiparticle excitations and emergent gauge fields. Since these states never order, they have no broken symmetries and are not described by Landau's theory of phase transitions.

1.1 History

In 1973, Anderson came up with the idea of QSLs [7]. When two spins interact antiferromagnetically, they can pair into a singlet state, forming a valence bond [1]. If all of the spins in a system form valence bonds, the ground state is given by the product of the valence bonds, i.e., a valence bond solid (VBS) (see figure 2). VBS states are only short-range entangled and can order (e.g, by aligning along an axis), so they are not QSLs. A superposition of VBS states, which Pauling named a *resonating valence bond* (RVB), could form a QSL, however, and Anderson proposed this to be the ground state of the antiferromagnetic Heisenberg model on a hexagonal lattice [7]. This turned out to be incorrect, as the spins order at 120^o [3].

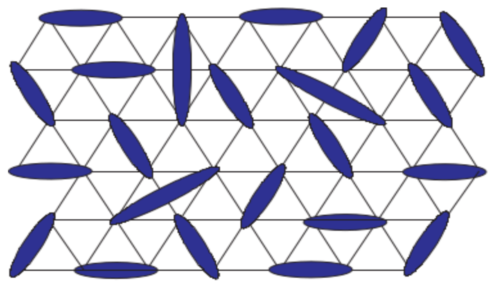


Figure 2: A valence bond solid (VBS) state. The ovals are valence bonds (paired spins). Figure is from [4].

In 1986, Bednorz and Mueller discovered the high-temperature copper oxide superconductors, and in 1987 Anderson proposed that La_2CuO_4 had an RVB ground state [8]. This sparked interest in QSLs, and over the next few years QSLs were connected to topology [2]. In 1989, Wen created our current understanding of *topological order*, when he realized that many different spin liquids have the same symmetry, and that a new order was needed beyond the Landau paradigm [5, 6]. While some QSLs have topological order, many do not [2]. In 2000, Senthil and Fisher discovered QSL quasiparticles could have fractional quantum numbers (i.e, fractionalization). In 2003 Kitaev created his toric code model, and in 2006 created his honeycomb model: these models are exactly solvable and have QSL ground states. This has led to great effort to realize QSL states experimentally, an effort which continues to this day. While there are several QSL candidates, there is no definitive evidence that they are QSLs [2].

In the following sections I shall attempt to elucidate on the terms I've introduced (e.g., topological order), as well as explain the phenomenology of QSLs without focusing on any particular model. I will focus on U(1) gauge fields, as that is electromagnetism on a lattice and therefore familiar. This term paper is based mostly on the 2010 review by Balents [1] and the 2017 review by Savary and Balents [2], which is relatively accessible and recommended to anyone interested in this topic. Additionally, ref. [11] is a book (written in 2011) that has several chapters on QSLs, as well as chapters on experimental techniques such as neutron scattering, NMR, and μSR.

2 Theory

We begin with the parton approach to QSLs, often called the slave-boson or slave-fermion approach. Anderson used this method in 1987 [8]; it has developed since then and is reviewed in refs. [2, 4, 5]. In this approach, we break the spins into parts (partons) which we hope become quasiparticles upon substitution in the Hamiltonian [2]. This isn't necessarily true, but it works exactly in Kitaev's honeycomb model. These partons are chosen to be Schwinger bosons or Abrikosov fermions. Let us use the fermion representation, which is simpler because it avoids Bose Einstein condensation. On our lattice, the spins reside on the bonds between lattice points. We can represent a spin $\vec{S}$ operator as

$$\vec{S} = \sum_{\alpha\beta} \frac{1}{2} f_{\alpha}^{\dagger} \vec{\sigma}_{\alpha\beta} f_{\beta} \tag{1}$$

with constraint $\sum_{\alpha} |f_{\alpha}|^2 = 1$. Assuming they become quasiparticles, these Abrikosov fermions are called *spinons* and are spin 1/2 with no electric charge. Excitations of conventional phases have integer spin, so spinons are *fractional* quasiparticles.

Upon substitution of equation (1) in a Hamiltonian, which for a Heisenberg model depends on terms like $\vec{S}_1 \cdot \vec{S}_2$, we end up with four-fermion terms. To create an effective quadratic Hamiltonian, theorists use mean field theory. This involves many possible groupings of operators; the decoupling scheme is chosen beforehand based on symmetry and energy [2]. Following Savary and Balents[2], we shall just assume the effective Hamiltonian is the Bogoliubov Hamiltonian

$$\sum_{ij} [t_{ij}^{\alpha\beta} f_{i\alpha}^{\dagger} f_{j\beta} + \Delta_{ij}^{\alpha\beta} f_{i\alpha}^{\dagger} f_{j\beta}^{\dagger} + h.c.]. \tag{2}$$

2.1 Gauge fields

This Hamiltonian has a Z_2 symmetry under $f \to -f$. This symmetry is unphysical and occurs as a result of equation (1): the formal Abrikosov fermions have changed, but the physical operator $\vec{S}$ has not [2]. By using this equation, we have expanded our Hilbert space; to create a one-to-one mapping between this enlarged Hilbert space and the physical Hilbert space, the gauge symmetry must be built into the Hamiltonian by introducing a lattice gauge field [5]. The type of gauge symmetry (e.g., Z_2, U(1), or SU(2)) depends on t and Δ.

Suppose $\Delta = 0$. Then equation (2) is invariant under $f \to fe^{i\chi}$ (still unphysical). Introducing a U(1) lattice gauge field, our Hamiltonian becomes

$$\sum_{ij}[t_{ij}^{\alpha\beta} e^{iA_{ij}} f_{i\alpha}^{\dagger} f_{j\beta} + h.c.] + H_g \tag{3}$$

where H_g is a Hamiltonian associated with the lattice gauge field [2].

A U(1) lattice gauge theory is just electromagnetism on a lattice [2]. For a cubic lattice [2],

$$H_g = -K \sum_p \cos(\nabla \times A) + K' \sum_a (\nabla \cdot E)_a^2 + \frac{V}{2} \sum_{<ab>} E_{ab}^2 \tag{4}$$

where we define

$$(\nabla \cdot E)_a = \sum_{b \in nn(a)} E_{ab}$$

$$B_p = (\nabla \times A)_p = \sum_{a \in p} A_{a,a+1}.$$

Here A and E are our 'field' variables which satisfy $[A_{ab}, E_{ab}] = i$, $A_{ab} = -A_{ba}$, and $E_{ab} = -E_{ba}$. The letters a and b refer to lattice points (the field variables are defined on bonds), nn means nearest neighbor, and p refers to plaquette, which is a unit square on the lattice.

Returning to equation (3), the Hamiltonian and its physical states are gauge-invariant under $A_{ij} \to A_{ij} + \chi_i - \chi_j$, $f \to fe^{i\chi}$, and $f^\dagger \to f^\dagger e^{-i\chi}$ [2]. The generator of this symmetry is Q, where

$$Q_i = (\nabla \cdot E)_i - f_{i\alpha}^{\dagger} f_{i\alpha} = -1. \tag{5}$$

Since equation (3) is gauge-invariant, Q is conserved, and when E = 0, our Abrisokov constraint (1) gives -1. According to Savary and Balents [2], this Hamiltonian "corresponds to the mean-field approximation in the limit of large K, in which case fluctuations of A_{ij} are suppressed." Excitations can cause A to fluctuate, however, and in this case the U(1) state is stable in 3D, but not in 2D [2].

For large K we can approximate A = 0, and the Hamiltonian can be diagonalized [2]. This depends on the specific form of t, but in simple cases we expect the spinons to be gapped out. In these cases we obtain a pure U(1) gauge theory described by H_g with equation (5) replaced by Gauss's law

$$Q_i = (\nabla \cdot E)_i.$$

Up to a constant and with renormalized couplings, the Hamiltonian is approximately [2] [1]

$$H_g = K \sum_p B_p^2 + K' \sum_a Q_a^2 + \frac{V}{2} \sum_{<ab>} E_{ab}^2. \tag{6}$$

The Hamiltonian approximation is valid when V $\ll$ K, and is called the (pure) *Coulomb phase* [2].

Before moving on, there are some points I should address. This parton method is a mean field theory, and thus qualitative. It's possible to use variational methods to guess the ground state using partons, but I don't cover that: it is reviewed in refs. [2, 4]. It's also possible for the spinons to be gapless, but that case is more complicated and not fully solved [2].

2.2 Quasiparticles

Consider the Coulomb phase. Since Q is conserved, we can choose our eigenstates to be eigenstates of Q. Let Q = 0. In the continuum limit, the low-energy, long-wavelength physics is given by the electromagnetic energy

$$H = \int d^3x \Big(\frac{\epsilon}{2} |E|^2 + \frac{1}{2\mu} |B|^2 \Big).$$

By analogy to electromagnetism, there are emergent gapless photons.

When Q is non-zero, there are emergent gapped (K') electric charges (not literal charges). There are also magnetic charges, or monopoles, which emerge as topological point defects in 3D [2, 9]. Both of these quasiparticles are bosons, have a 1/r Coulomb potential, and are *non-local* [2]. By non-local, I mean that local operators cannot create just one quasiparticle. Rather, local operators can only create charge-neutral configurations, which means that local operators create particles in pairs. To create a single quasiparticle, a semi-infinite string operator, which is some semi-infinite product of connected (i.e., on neighboring bonds) local operators, is required [2, 9]. The quasiparticles appear at the ends of this 'string.' The electric and magnetic quasiparticles can also pair, or fuse, to form a third quasiparticle, called a dyon, which is a fermion [2].

[1] Savary and Balents [2], page 11: " A naive analysis consists of taking very small but non-zero U, which we expect to introduce *small* fluctuations of B_p." Here U = $\exp(i \sum_a \chi_a Q_a)$. I don't understand how U is small, since it's unitary, or how a gauge transformation can make B non-zero.

2.3 Stability

The Coulomb phase in 3D is stable to weak perturbations, even those which break the gauge symmetry [2]. To paraphrase Savary and Balents, when there are perturbations which break the gauge symmetry yet the QSL phase survives, we say there is an *emergent gauge symmetry* [2]. Strong perturbations can lead to *confinement*. As a reminder, isolated quasiparticles are created by semi-infinite string operators. Confinement is when there is an energy cost to such a string such that the energy to create an isolated quasiparticle, say the electric quasiparticle, is infinite. When this happens the quasiparticles can only be created in pairs and are confined to their antiparticle (oppositely charged particle). The magnetic quasiparticles are also removed, as their energy is set to zero: they can be viewed as a condensate [2]. There is a first-order phase transition from the unconfined phase to the confined phase, which can be viewed as Bose condensation of either the elecric or magnetic quasiparticles.

2.4 Topological phases

Topological phases are defined by topological invariants; for example, Kitaev's toric code model has a topological ground state degeneracy [2]. According to Wen [6], "topological order is defined to describe gapped quantum liquids that cannot be deformed into a product state without gap-closing phase transitions ." Here quantum liquids refers to more than just quantum spin liquids; for example, fractional quantum Hall states have topological order. Topological order is due to long-range entanglement, and therefore different from topological insulators, defects, etc. [6].

The pure Coulomb phase is not a topological phase, as all topological phases only have gapped excitations. It does have non-local excitations, however, which indicates it is a highly entangled phase [2]. Examples of topological QSLs include Kitaev's toric code model, which is a Z_2 gauge phase [2], and the frustrated Coulomb phase on a pyrochlore lattice [9].

2.5 Entanglement entropy

Savary and Balents argue that the fundamental attribute of QSLs is not the absence of symmetry breaking but the presence of a high degree of entanglement [2]. But what does it mean to be 'highly' entangled? The degree of entanglement can be quantified by the von Neumann entanglement entropy. Suppose we have a 2D system split, in real space, into parts A and B. The von Neumann entropy is [2]

$$S(A) = S(B) = -\mathrm{T}r_A(\rho_A \mathrm{log}\rho_A) \sim s_0 L - \gamma. \tag{7}$$

Here ρ_A is the density operator for part A, L is the length of the boundary between the two parts, and γ is the *topological entanglement entropy*; s_0 and γ are constants. For a pure state, the entanglement entropy is zero. For topologically ordered states, γ is quantized and (at least for the toric code) is positive [2]. Since the entropy cannot be negative, it's impossible to have $\mathrm{s}_0 = 0$, and thus a non-zero topological entanglement entropy indicates long-range entanglement.

In the thermodynamic limit, however, the L term dominates. This term is called the area law, since in 3D it is an area, not a length. Savary and Balents [2] acknowledge that in the thermodynamic limit, "quantum-spin-liquid states, including topologically ordered phases, are typically no more entangled than any other ground states." In this sense, the word 'highly' seems meaningless, and I think that the definition Savary and Balents propose is more of a working definition which emphasizes the type of physics they are interested in. They say their definition is vague because entanglement itself is still an active research subject.

For temperatures greater than zero, the entanglement entropy is extensive and no longer a good metric [2]. As a result, most QSLs are only well-defined as T=0, and undergo a smooth crossover to a paramagnetic phase for $T > 0$. An exception is the 3D toric code, which undergoes a second order phase transition unassociated with any local order parameter. For $T > 0$, the physics can be described in terms of a dilute gas of quasiparticles.

3 Experiment

While there are several QSL candidates (see figure 3), none have been proven to be QSLs [2]. This is difficult to do, as QSLs have few experimental signatures and conventional probes focus on local excitations. Thus, it is necessary to study candidate materials with many different probes. Most QSL candidates exhibit no symmetry breaking, which suggests there may be new physics at play.

Table 1 | Some experimental materials studied in the search for QSLs

Material	Lattice	S	Θ_{CW} (K)	R*	Status or explanation
κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$	Triangular†	½	−375‡	1.8	Possible QSL
EtMe$_3$Sb[Pd(dmit)$_2$]$_2$	Triangular†	½	−(375–325)‡	?	Possible QSL
Cu$_3$V$_2$O$_7$(OH)$_2$•2H$_2$O (volborthite)	Kagomé†	½	−115	6	Magnetic
ZnCu$_3$(OH)$_6$Cl$_2$ (herbertsmithite)	Kagomé	½	−241	?	Possible QSL
BaCu$_3$V$_2$O$_8$(OH)$_2$ (vesignieite)	Kagomé†	½	−77	4	Possible QSL
Na$_4$Ir$_3$O$_8$	Hyperkagomé	½	−650	70	Possible QSL
Cs$_2$CuCl$_4$	Triangular†	½	−4	0	Dimensional reduction
FeSc$_2$S$_4$	Diamond	2	−45	230	Quantum criticality

BEDT-TTF, bis(ethylenedithio)-tetrathiafulvalene; dmit, 1,3-dithiole-2-thione-4,5-ditholate; Et, ethyl; Me, methyl. *R is the Wilson ratio, which is defined in equation (1) in the main text. For EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ and ZnCu$_3$(OH)$_6$Cl$_2$, experimental data for the intrinsic low-temperature specific heat are not available, hence R is not determined. †Some degree of spatial anisotropy is present, implying that $J' \neq J$ in Fig. 1a. ‡A theoretical Curie-Weiss temperature (Θ_{CW}) calculated from the high-temperature expansion for an $S = ½$ triangular lattice; $\Theta_{CW} = 3J/2k_B$, using the J fitted to experiment.

Figure 3: Some QSL candidates. The chart is from Balents 2010 [1] and is slightly out of date. $Na_4Ir_3O_8$ has AF order, but may still exhibit residual QSL physics [2].

When looking for new QSLs, there are several features people look for [2]. First, frustration is necessary to avoid ordering. This frustration could be geometric, or it could be due to something else such as next-nearest-neighbor interactions. Second, people look for spin 1/2 systems, since for Heisenberg models the commutator of two spin operators is of order 1/S, which means quantum fluctuations are stronger for smaller spins [2]. But this may not be true for frustrated systems, and theorists are constructing higher spin models [2, 4]. Third, people look for proximity to a Mott transition, as this leads to more quantum fluctuations [2].

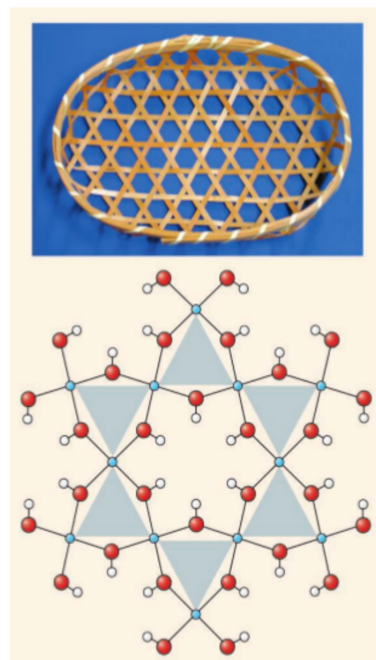
3.1 Herbertsmithite

I shall focus on $ZnCu_3(OH)_6Cl_2$, named herbertsmithite, as this is one of the most well-known and well-characterized QSL candidates. A 2010 experimental review on powder samples is given in ref. [10]; single crystals were grown in 2011, and brief reviews as of 2017 are given in refs. [2, 4]. This material has Cu ions in a kagomé lattice: the lattice was named after a type of Japanese basket weave (see figure 4) [3]. Spins on this lattice have a larger geometric degeneracy compared with spins on hexagonal lattices, and thus the kagomé lattice has a greater potential of realizing a QSL [4].

Herbertsmithite has been shown not to order down to low temperatures by NMR, μSR, neutron scattering, and magnetic susceptibility measurements

[2]. First I shall discuss μSR, which stands for muon spin rotation. Basically, a polarized beam of positively charged muons is produced by proton-proton collisions, then implanted into a sample. The muons then precesses about the local magnetic field before decaying and emitting a positron. This positron is emitted in the direction of the muon spin and can be detected. From this we can measure the muon precession and learn about the local magnetism of a material. Zero field μSR measurements were done by Mendels et al. in 2007, and shows no ordering down to 50 mK for herbertsmithite [10].[2]

NMR is another probe which allows us to learn about local magnetism [2]. The nuclei feel the magnetic field of the nearby electronic spins (i.e., hyperfine interaction), which splits the energy levels of the nuclui. The nuclei can be driven between the levels using an external AC magnetic field. The resonance frequency shifts with temperature, as the field due to the hyperfine interaction is proportional to the local electronic susceptibility: this is known as the Knight shift. Thus NMR measures the local magnetic susceptibility.



Meeting with frustration. (Top) A Kagome basket. **(Bottom)** Structure of $ZnCu_3(OH)_6Cl_2$ (*10*) showing that the Cu ions (blue) occupy a Kagome lattice; O-H is red-white.

Figure 4: Figure is from [3].

The ^{17}O spectra was measured in 2008 by Olariu et al, and the ^{35}Cl spectra measured that same year by Imai et al [10]. The ^{17}O NMR spectra is more sensitive to the kagomé plans, and this shows no ordering down to 0.45 K. It levels off at low temperatures, which indicates herbertsmithite is gapless. It also has a peak which suggests there is there is Cu-Zn disorder: some Zn is in the kagomé planes, and the displaced Cu between planes. This can also be seen in figure 5, as the bulk magnetic susceptibility doesn't match the local susceptibility given by NMR; the bulk susceptibility is interpreted as Curie-Weiss behaviour of the Cu defects, which behave as quasi-free spins.

Neutrons can scatter off both atomic nuclei and magnetic moments, giving information on both structure and bulk magnetic order. For QSLs, elastic scattering can reveal

[2] The cited review says 20 mK, which doesn't match the actual paper.

low-energy excitations; this is because neutrons don't have perfect energy resolution [2]. These low-energy excitaitons (e.g., photons of the Coulumb phase) are expected to be localized in momentum space. Inelastic neutron scattering is used to study the excitations of materials; for QSLs, a smooth continuous signal is usually expected. It's possible for QSL quasiparticles for pair and form a bound state, which could give a sharp peak.

For herbertsmithite, de Vries et al. did structure refinements in 2008 which show 7-10% mixing of Zn and Cu [10]. Inelastic neutron scattering on a single crystal showed smooth spectral weight and no peaks, indicating herbertsmithite is gapless [2]. But the inelastic signal does not agree with any QSL model, which have features at specific momentum points.

The last probe I'll discuss is the specific heat, which reveals phase transitions and, when integrated, can be used to determine the entropy. Specific heat measurements can be used to distinguish gapped and gapless states: the magnetic specific heat is exponentially suppressed for gapped states, and obeys power laws for gapless states [2]. Different gapless QSLs are predicted to have different scalings [2].

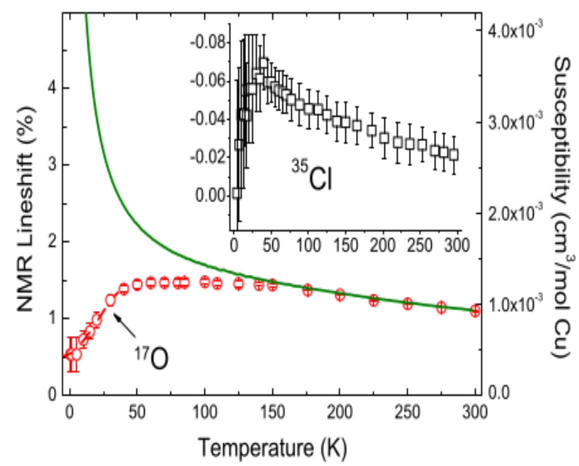


Figure 5: NMR spectra overplotted with bulk susceptibility (solid line). Figure is from [10].

The specific heat for herbertsmithite was measured measured by Helton et al. in 2007, and de Vries et al. in 2008 [4]. The low temperature data shows the specific heat depends on field, and has a field-dependent peak associated with Cu-Zn disorder. The slope is roughly linear at low temperatures in zero field, which is associated with gapless behavior.

In summary, various probes show that herbertsmithite doesn't order down to low temperatures and suggest gapless behavior, but the results are not fully consistent with any model. They also show Cu-Zn disorder, which complicates the analysis. Savary and Balents mention a recent NMR experiment on a single crystal which shows a gap, but that result is unpublished and needs to be reconciled with previous experiments [2].

4 Conclusion

Quantum spin liquids are a state of matter which avoids symmetry breaking and are highly entangled. These states can be approached phenomenologically through an effective Hamiltonian coupled with a gauge field, which leads to emergent non-local quasiparticles with fractional quantum numbers. There are also exactly solvable models, notably Kiteav's toric code and honeycomb model, which have QSL ground states. Gapped QSLs exhibit topological order.

The progress on QSL physics has been largely theoretical, but there is currently a great experimental search for these states. There are some QSL candidates, but none have been proven to be QSLs. Since QSLs have few experimental signatures, their identification is difficult, and, as noted by Savary and Balents, will likely require careful modeling [2].

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