Herbertsmithite ($\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$) is often discussed as the best realization of the highly frustrated antiferromagnetic kagomé lattice known so far. We employ density functional theory calculations to determine eight exchange coupling constants of the underlying Heisenberg Hamiltonian. We find the nearest neighbour coupling $J_1$ to exceed all other couplings by far. However, next-nearest neighbour kagomé layer couplings of $0.019J_1$ and interlayer couplings of up to $-0.035J_1$ slightly modify the perfect antiferromagnetic kagomé Hamiltonian. Interestingly, the largest interlayer coupling is ferromagnetic even without Cu impurities in the Zn layer. In addition, we validate our DFT approach by applying it to kapellasite, a polymorph of herbertsmithite which is known experimentally to exhibit competing exchange interactions.

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Quantum spin liquids have fascinated physicists for decades as this exotic ground state constitutes a novel state of matter. The magnetic moments in a spin liquid do not order even at extremely low temperature due to a high degree of frustration in the magnetic system. Typical examples for lattices that lead to frustration of antiferromagnetic interactions are triangular, pyrochlore and kagomé lattices. While experimental realizations of quantum spin liquids have long been scarce, in particular the discovery of the perfect kagomé lattice realization in herbertsmithite has led to considerable excitement. In the eight years since the discovery of the $S = \frac{1}{2}$ kagomé antiferromagnet nature of $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$, numerous experiments have been performed to ascertain the spin liquid ground state of herbertsmithite, its properties and excitations. In particular, measurements of the magnetic susceptibility show antiferromagnetic couplings of the order $J \approx 17$ meV ($\sim 190$ K) and no magnetic ordering down to 50 mK. Muon spin rotation measurements confirm the absence of magnetic ordering and inelastic neutron scattering experiments find that fractionalized quantum excitations are present in $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$. More recently, non-ideality of the realization of the kagomé Heisenberg Hamiltonian in herbertsmithite due to additional interactions and in the form of site disorder has been the focus of many studies. While defects within the kagomé layer are detected in nuclear magnetic resonance but not in recent x-ray scattering measurement, Cu impurities on interlayer Zn sites seem to play a role. Low temperature deviations between theory for the kagomé antiferromagnet and experimental susceptibilities as well as anisotropies in thermodynamic quantities point to a small nonzero Dzyaloshinskii-Moriya interaction. Evidence of this interaction has been found in electron spin resonance measurements. However, the experimental and theoretical discussion about the Hamiltonian correctly describing herbertsmithite is far from settled.

Therefore, we undertake an effort to determine the parameters of the underlying Heisenberg Hamiltonian using all-electron density functional theory methods. We will show in this Letter that the exchange coupling constants from first principles corroborate that $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ is a near perfect realization of a kagomé antiferromagnet with a dominant coupling of $J_1 = 182$ K. However, there are small corrections to this picture: A next-nearest

![Image](https://www.example.com/figure1.png)

FIG. 1: (Color online) (a) Crystal structure of kapellasite, viewed along the c direction. (b) Kagomé lattice formed by the Cu sites in (a). Note that $J_d$ and $J_4$ exchange paths both correspond to a distance of 6.3 Å but while $J_4$ points precisely along a nearest neighbour bond, $J_d$ cuts diagonally across a Cu hexagon with nonmagnetic Zn in the center.

Quantum spin liquids have fascinated physicists for decades as this exotic ground state constitutes a novel state of matter. The magnetic moments in a spin liquid do not order even at extremely low temperature due to a high degree of frustration in the magnetic system. Typical examples for lattices that lead to frustration of antiferromagnetic interactions are triangular, pyrochlore and kagomé lattices. While experimental realizations of quantum spin liquids have long been scarce, in particular the discovery of the perfect kagomé lattice realization in herbertsmithite has led to considerable excitement. In the eight years since the discovery of the $S = \frac{1}{2}$ kagomé antiferromagnet nature of $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$, numerous experiments have been performed to ascertain the spin liquid ground state of herbertsmithite, its properties and excitations. In particular, measurements of the magnetic susceptibility show antiferromagnetic couplings of the order $J \approx 17$ meV ($\sim 190$ K) and no magnetic ordering down to 50 mK. Muon spin rotation measurements confirm the absence of magnetic ordering and inelastic neutron scattering experiments find that fractionalized quantum excitations are present in $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$. More recently, non-ideality of the realization of the kagomé Heisenberg Hamiltonian in herbertsmithite due to additional interactions and in the form of site disorder has been the focus of many studies. While defects within the kagomé layer are detected in nuclear magnetic resonance but not in recent x-ray scattering measurement, Cu impurities on interlayer Zn sites seem to play a role. Low temperature deviations between theory for the kagomé antiferromagnet and experimental susceptibilities as well as anisotropies in thermodynamic quantities point to a small nonzero Dzyaloshinskii-Moriya interaction. Evidence of this interaction has been found in electron spin resonance measurements. However, the experimental and theoretical discussion about the Hamiltonian correctly describing herbertsmithite is far from settled.

Therefore, we undertake an effort to determine the parameters of the underlying Heisenberg Hamiltonian using all-electron density functional theory methods. We will show in this Letter that the exchange coupling constants from first principles corroborate that $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ is a near perfect realization of a kagomé antiferromagnet with a dominant coupling of $J_1 = 182$ K. However, there are small corrections to this picture: A next-nearest
FIG. 2: (Color online) (a) Crystal structure of herbertsmithite ZnCu$_3$(OH)$_6$Cl$_2$, viewed along the c direction. (b) Kagomé lattice formed by the Cu sites in (a). Exchange paths between nearest, next nearest and third nearest neighbours within the kagomé lattice are shown. (c)-(e) show three inter-kagomé layer exchange pathways.

TABLE I: Exchange coupling constants for ZnCu$_3$(OH)$_6$Cl$_2$ (kapellasite) determined from total energies of five different spin configurations in a $2 \times 2 \times 1$ supercell.

| name | $d_{Cu-Cu}$ | type         | $J_i$ (K) | $U = 6$ eV |
|------|-------------|--------------|-----------|------------|
| $J_1$ | 3.15        | kagomé nn    | -14.2     |            |
| $J_2$ | 5.45596     | kagomé 2nd nn| -0.7      |            |
| $J_4$ | 6.3         | kagomé 3rd nn| -0.3      |            |
| $J_d$ | 6.3         | kagomé 3rd nn| 24.0      |            |

neighbour coupling in the kagomé layer of $0.019J_1$ and in particular some interplanar couplings between $-0.035J_1$ and $0.029J_1$ could actually be relevant for the nature and excitations of the spin liquid ground state in herbertsmithite.

We perform density functional theory calculations with the full potential local orbital (FPLO) basis set using generalized gradient approximation (GGA) and GGA+U functionals. The exchange couplings, $J_i$, are obtained from total energy calculations for different Cu spin configurations in supercells of various sizes. Before proceeding to herbertsmithite, we test our methods on kapellasite, a polymorph of herbertsmithite, which has been investigated before, both theoretically and experimentally. We use the structure of kapellasite as given in Ref. 22 and determine the hydrogen position by relaxation. The structure is shown in Figure 1. We create two different supercells: A $2 \times 2 \times 2$ supercell with $P \bar{1}$ symmetry and 10 inequivalent Cu positions with the purpose of resolving four interlayer couplings, and a $2 \times 2 \times 1$ supercell.

FIG. 3: (Color online) Band structure and density of states of ZnCu$_3$(OH)$_6$Cl$_2$ calculated with GGA exchange correlation functional. High symmetry points of the $P\bar{3}m$ space group are $M = (1/2, 0, 0)$, $K = (1/3, 1/3, 0)$ and $A = (0, 0, 1/2)$ in units of the reciprocal lattice vectors. DOS is given in states per eV per unit cell (containing 3 formula units).
TABLE II: Exchange coupling constants for ZnCu$_3$(OH)$_6$Cl$_2$ (herbertsmithite) determined from total energies of nine different spin configurations. Energies were calculated with GGA+U functional at $U = 6$ eV, $J = 1$ eV and with atomic limit double-counting correction.

| name            | $d_{Cu-Cu}$ | type          | $J_1$ (K) $U=6$eV |
|-----------------|-------------|---------------|-------------------|
| **kagomé layer couplings** |             |               |                   |
| $J_1$           | 3.4171      | kagomé nn     | 182.4             |
| $J_2$           | 5.91859     | kagomé 2nd nn | 3.4               |
| $J_3$           | 6.8342      | kagomé 3rd nn | -0.4              |
| **interlayer couplings** |       |               |                   |
| $J_4$           | 5.07638     | interlayer 1st nn | 5.3             |
| $J_5$           | 6.11933     | interlayer 2nd nn | -1.5            |
| $J_6$           | 7.00876     | interlayer 3rd nn | -6.4             |
| $J_7$           | 8.51328     | interlayer 4th nn | 3.0             |
| $J_8$           | 9.17347     | interlayer 6th nn | 2.5             |
discuss the kagomé lattice Heisenberg model and show coupling along the diagonal of the Cu hexagon (see Appendix B). This method has been very useful to discuss the kagomé lattice Heisenberg model as well as various additional terms. We find that at least in the region of applicability of this method the effect of interlayer couplings is noticeable. We hope that our results inspire more precise manybody calculations that could establish the consequences of interlayer couplings for the low temperature properties of herbertsmithite.

In summary, our \textit{ab initio}-based analysis of the Cu-Cu exchange coupling constants in kapellasite and herbertsmithite provides a detailed description of these materials. Our results for the dominant interactions are in excellent agreement with experiments. Moreover, we are able to resolve the strength and sign of weaker, but not negligible, exchange interactions that were not known up to now and are important for understanding the behavior of these materials at low temperatures. Both polymorphs, even though they are realizations of a perfect kagomé lattice, show a few remarkable differences. The nearest neighbor Cu-Cu exchange interaction is strongly antiferromagnetic in herbertsmithite (\(\sim 190\) K) and weakly ferromagnetic in kapellasite (\(\sim -13\) K) due to the fact that the Cu-O-Cu angle in herbertsmithite is 119° compared to 106° in kapellasite. Kapellasite shows a significant antiferromagnetic 4th nearest neighbor coupling along the diagonal of the Cu hexagon (\(J_d\)) which is negligible in herbertsmithite since the exchange path in kapellasite is through the in-plane Zn situated in the center of the hexagons. Also, the stacking of the kagomé layers in both polymorphs is crucial for understanding the interlayer exchange couplings. In kapellasite, the kagomé layers are stacked in a similar fashion as in the layered TiOC\(_3\) or Cs\(_2\)CuCl\(_4\) where interactions are mostly of van der Waals nature. In this situation, the interlayer couplings are comparatively small (see Appendix B). In contrast, in herbertsmithite the interlayer Cu-Cu couplings are partly through Zn orbitals. This leads to relatively significant antiferromagnetic (\(J_2\)) and ferromagnetic (\(J_6\)) interlayer couplings. Nevertheless, the ratio between the dominant intralayer coupling \(J_1\) and the dominant interlayer coupling remains large enough for this system to be considered a very good realization of a two-dimensional kagomé lattice and only at low temperatures should the smaller \(J_i\) become important. This and the importance of couplings other than the dominant ones for the spin-liquid behavior in these materials should be investigated in the future. In particular, it would be interesting to determine also the couplings of the Dzyaloshinskii-Moriya and ring exchange terms in the Hamiltonian from first principles.

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**Appendix A: Details for exchange constants of kapellasite**

In Tables III and IV we provide the results of total energy calculations with GGA+U functional using different values of U. The \(2 \times 2 \times 2\) supercell used in the calculation for Table IV allows resolution of four interlayer couplings of kapellasite. They are all very small which is not surprising considering the van der Waals gap between the layers of kapellasite (see Figure 3). This is a significant difference to the polymorph herbertsmithite that has kagomé layers coupled in the third dimension via O-Zn-O bonds (see Figure 5).

**Appendix B: Details for exchange constants of herbertsmithite**

In Table V we provide the results of total energy calculations with GGA+U functional using different values of U for ZnCu\(_3\)(OH)\(_6\)Cl\(_2\).

| name | \(d_{Cu-Cu}\) | type | \(J_1\) (K) | \(J_2\) (K) | \(J_4\) (K) |
|-------|---------------|------|-------------|-------------|-------------|
| \(U = 6\) eV | \(U = 7\) eV | \(U = 8\) eV |
| \(J_d\) | 3.15 | kagomé mn | -14.2 | -13.4 | -12.6 |
| \(J_2\) | 5.45956 | kagomé 2nd mn | -0.7 | -0.7 | -0.6 |
| \(J_4\) | 6.3 | kagomé 3rd mn | -0.3 | -0.3 | -0.3 |
| \(J_d\) | 6.3 | kagomé 3rd mn | 24.0 | 19.8 | 16.3 |

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TABLE IV: Exchange coupling constants for kapellasite determined from total energies of eight different spin configurations in a $2 \times 1 \times 2$ supercell. Note that here, kagomé 3rd nearest neighbours are symmetry equivalent so that $J'_d = \frac{1}{3}J_d + \frac{2}{3}J'_d$.

| name $d_{Cu-Cu}$ | type | $J_1$ (K) | $J_2$ (K) | $J_3$ (K) |
|------------------|------|-----------|-----------|-----------|
| $U = 6$ eV       |      | $-11.3$   | $-12$     | $-10.9$   |
| $U = 7$ eV       |      | $-11.8$   | $-1.2$    | $-0.9$    |
| $U = 8$ eV       |      | $-10.8$   | $8.8$     | $7.3$     |

**kagomé layer couplings**

| $J_1$ | $J_2$ | $J_3$ | $J_4$ |
|-------|-------|-------|-------|
| $5.733$ | $6.54139$ | $7.91421$ | $8.51806$ |
| $-0.4$ | $0.04$ | $0.04$ | $0.03$ |
| $-0.3$ | $0.04$ | $0.04$ | $0.03$ |

**interlayer couplings**

| $J_1$ | $J_2$ | $J_3$ | $J_4$ |
|-------|-------|-------|-------|
| $3.4171$ | $5.91859$ | $6.8342$ | $9.17347$ |
| $182.4$ | $3.4$ | $-0.4$ | $2.5$ |
| $155.4$ | $2.9$ | $-0.5$ | $2.1$ |
| $131.8$ | $2.3$ | $-0.4$ | $1.7$ |

FIG. 4: (Color online) (a) Side view of the crystal structure of kapellasite (approximately along $b$ direction). (b) Interlayer exchange paths for the Cu sites in (a).

FIG. 5: (Color online) Side view of the crystal structure of herbertsmithite (approximately along $b$ direction).

TABLE V: Exchange coupling constants for ZnCu$_3$(OH)$_2$Cl$_2$ (herbertsmithite) determined from total energies of nine different spin configurations. Energies were calculated with GGA+U functionals at $J = 1$ eV with different values of $U$ and with atomic limit double counting correction.

| name $d_{Cu-Cu}$ | type | $J_1$ (K) | $J_2$ (K) | $J_3$ (K) |
|------------------|------|-----------|-----------|-----------|
| $U = 6$ eV       |      | $-0.4$    | $-1.5$    | $-6.4$    |
| $U = 7$ eV       |      | $5.3$     | $-1.1$    | $-5.4$    |
| $U = 8$ eV       |      | $4.5$     | $-0.5$    | $-4.4$    |

**kagomé layer couplings**

| $J_1$ | $J_2$ | $J_3$ | $J_4$ |
|-------|-------|-------|-------|
| $5.07638$ | $6.11933$ | $7.00876$ | $8.51328$ |
| $5.3$ | $-1.5$ | $-6.4$ | $3.0$ |
| $4.5$ | $-1.1$ | $-5.4$ | $2.5$ |
| $3.7$ | $-0.8$ | $-4.4$ | $2.1$ |

**interlayer couplings**

| $J_1$ | $J_2$ | $J_3$ | $J_4$ |
|-------|-------|-------|-------|
| $9.17347$ | $5.91859$ | $6.8342$ | $3.4171$ |
| $2.5$ | $2.9$ | $-0.4$ | $182.4$ |
| $2.1$ | $2.3$ | $-0.5$ | $155.4$ |
| $1.7$ | $2.3$ | $-0.4$ | $131.8$ |

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