Topological spin liquid phase in a low-dimensional organic molecular compound

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The Landau theory of spontaneous symmetry breaking 1 explains almost all known phase transitions, from simple antiferromagnetism 2 to electroweak symmetry breaking in the early universe via the Higgs mechanism 3. However, it has recently become clear that not all phase transitions are described by Landau theory. Key examples include topological phases of matter, such as fractional quantum Hall fluid 4, and the symmetry protected topological (SPT) phases that are now well understood in free fermion models 5, 6. SPT materials, such as topological insulators 7, topological superconductors 8, and topological superfluids 9, have bulk gaps but the non-trivial topology of their quantum mechanical ground states lead to gapless edge states. However, it is not understood how widespread topological phases of matter are. In particular, it is not known what SPT phases might be caused by interactions between electrons. The Hubbard model, which is paradigmatic for strongly correlated electrons, usually displays a bulk gap only in the Mott insulating phases at half-filling 10. Here we report the discovery of a correlated insulator with a bulk gap at two-thirds filling in a geometrically frustrated Hubbard model that describes the low-energy physics of Mo3S7(dmit)3. We show that the insulating phase is a SPT spin-liquid with fractionalised edge states, hidden order and even degeneracies in the entanglement spectrum, and that this phase is consistent with experiments on Mo3S7(dmit)3. We show that the SPT phase is robust even when the string order vanishes. Our results provide a key step towards an understanding of SPT phases in strongly correlated electrons and suggests new routes to realise such phases via organic chemistry.

The metal-insulator transition is of central importance in the field of strongly correlated electrons 10. For example, a Mott insulator, where strong local interactions drive a half-filled band into an insulating phase, becomes a strongly correlated metal when doped. It has been argued 11, 12 that the physics of doped Mott insulators is fundamental to high temperature superconductivity in the cuprates. Insulating phases that are driven by electronic correlations also play central roles in the physics of many other materials 13.

The central idea of the Landau theory of phase transitions 14 is the existence of a local order parameter, which is zero in the high temperature disordered phases and non-zero in the low temperature ordered phase. However, for the order parameter to be non-zero the quantum mechanical state of the system must spontaneously break a symmetry of the Hamiltonian in the thermodynamic limit 14. However, topological phases of matter cannot be characterised by any local order parameter and therefore no local symmetry of the system is broken. Indeed topological phases are characterised by their long range entanglement 14. For example, the ground state of the spin-one Heisenberg chain, known as the Haldane phase, is an SPT phase 6, 15, 16. In the Haldane a non-local correlation function, known as the hidden order, takes a finite expectation value corresponding to the breaking of a non-local symmetry 17.

Relatively little is known, experimentally, about Mo3S7(dmit)3. It has a charge gap, but neither a spin gap nor long range magnetic order is observed down to 2.1 K 18. Density functional calculations predict that Mo3S7(dmit)3 is a quasi-one-dimensional metal in the absence of magnetic order and a charge gap is only found when long range magnetic order is (counterfactually) assumed 19. On the basis of these calculations and the crystal structure of Mo3S7(dmit)3, Llusar et al. 19 argued that the low energy physics is described by a classical spin model on the ‘triangular necklace lattice’ (Fig. 1a, b), and showed that this model reproduces the observed temperature dependence of the magnetic susceptibility. However, neither this model nor density functional theory are able to explain why the insulating state arises in the absence of long-range magnetic order, as is found experimentally.

Here we study the simplest model of interacting itinerant fermions, viz. the Hubbard model, on the triangular necklace lattice (Fig. 1) at the (two-thirds) filling relevant to Mo3S7(dmit)3, i.e., n = 4 electrons per triangular molecule on average. We find a significant charge gap, but a spin gap too small to have been observed in the experiments on Mo3S7(dmit)3 to date. The insulating state is a SPT spin-liquid that supports hidden order, spin-1/2 edge states, and is adiabatically connected to the ground state of the spin-one Heisenberg model: the Haldane phase. The topologically non-trivial Haldane phase survives even in the presence of significant charge fluctua-
FIG. 1: The triangular necklace model of Mo$_3$S$_7$(dmit)$_3$. a, The Mo$_3$S$_7$(dmit)$_3$ molecule and its schematic representation in the Hubbard model. b, The Hamiltonian for the Hubbard model on the triangular necklace lattice is $H = U \sum \alpha \delta_{\alpha \beta} \hat{c}_{\alpha \sigma} \hat{c}_{\beta \sigma} + t_c \sum_{i \neq j \neq k} \delta_{\alpha, \beta} \hat{c}_{i \alpha \sigma} \hat{c}_{j \beta \sigma} - t \sum_{\sigma} \left( \hat{c}_{i \alpha \sigma} \hat{c}_{(i+1) \sigma} + H.c. \right)$, where \( \hat{c}_{i \alpha \sigma} \) annihilates (creates) an electron with spin \( \sigma \) on the \( \alpha \)th site of the \( i \)th molecule. For the \( t_c > 0 \) and \( n = 4 \), the case relevant to Mo$_3$S$_7$(dmit)$_3$, the system is a topologically trivial metal when \( U = 0 \). Local parity can either be viewed as relabelling sites 2 and 3 on any single molecule or as reflection through the red dotted lines. c, Sketches of the molecular orbitals, \( \hat{c}_{A+} \), \( \hat{c}_{E+} \), and \( \hat{c}_{E-} \), with different colours implying different signs. The labels \( A \) and \( E \) refer to the \( C_3 \) symmetry of the individual molecules and the ‘local parity’ label (±) describes the change in phase of the orbital on relabelling sites 2 and 3 on any single molecule.

The spin sector is even more surprising. There is a spin gap (Fig. 2b), which is orders of magnitude smaller than the charge gap. Furthermore, the degeneracy of the ground state depends on the topology of the lattice. In particular, for periodic boundary conditions the ground state is unique. However, for open boundary conditions a triplet state is degenerate with the singlet ground state; these two states are separated from the remaining excitations by the spin gap. This is precisely the topologically dependent spectra that results from the \( (D_2 \cong Z_2 \times Z_2) \) symmetry of the Haldane phase due to spin-1/2 edge states. Although there is no long range magnetic order, we find a finite expectation value for the string order correlation function (Fig. 3a) in the thermodynamic limit. Collectively these properties indicate that the insulating phase is a topological spin liquid. We stress that none of these phenomena are found in the Luttinger liquid, Mott insulating, phase of the half-filled linear Hubbard chain.

In the remainder of this paper we give a simple explanation of this physics and show that the insulating phase is in the Haldane phase. Understanding the insulating phase is ultimately simpler if one works in the ‘molecular orbital’ basis, shown in Fig. 1c. However, as detailed in the Supplementary Information, the interaction terms take a significantly more complicated form in the molecular orbital basis.

It is helpful to begin by examining the strong coupling \( (U/t_c \rightarrow \infty) \) limit for isolated molecules \( (t = 0) \). Although the Hubbard \( U \) is the same on all sites, the repulsion between two electrons in an \( A_+ \) orbital \( (U/3) \) is less than the repulsion between two electrons in an \( E_+ \) or \( E_- \) orbital \( (U/2) \). For four electrons in three orbitals, there must be (at least) one doubly occupied orbital; clearly in the strong coupling limit this will be the \( A_+ \) orbital. In the molecular orbital basis there is a direct exchange interaction, \( J_N = -U/3 \), between electrons in the \( E_- \) and \( E_+ \) states (cf. Supplementary Information), which stabilises the triplet, as required by Nagaoka’s theorem. Indeed, on the three site cluster this argument holds for all \( U > 0 \) and the exact solution has a triplet ground state.

A non-zero intermolecular coupling \( (t \neq 0) \) means that the 1-sites are no longer equivalent to the 2- or 3-sites. However, the Hamiltonian still retains a ‘local parity’ symmetry under the relabelling of sites 2 and 3 on any individual molecule. Thus the local parity of every molecule is a constant of the motion for the full many-body wavefunction. As \( E_- \) is the only odd parity orbital, this implies that the occupation number of this orbital, \( \hat{n}_{E_-} = \sum \sigma \hat{c}_{E_- \sigma} \hat{c}^\dagger_{E_- \sigma} \) is conserved modulo two. However, we found above that in the strong coupling molecular limit the ground state has exactly one electron in the \( E_- \) orbital on every molecule. It follows that perturbations that do not break the local parity symmetry, such as a finite \( U \) or a non-zero \( t \), will not change the number of electrons in any of the \( E_- \) orbitals unless they drive a phase transition. We find that \( \langle \hat{n}_{E_-} \rangle = 1 \) and the charge gap, \( \Delta_c \), in Fig. 2b.
FIG. 2: Insulating phase at two-thirds filling of the triangular necklace model. a, The charge gap, $\Delta_c = E_0(4L + 2) + E_0(4L − 2) − 2E_0(4L)$, where $E_S(N_s)$ is the energy of the spin $S$ ground state for $N_s$ electrons on $L$ molecules (see Supplementary Information for finite size scaling). As we have an average of four electrons per triangular molecule in the strong coupling limit ($U \rightarrow \infty$) one’s naive expectation is for a strongly correlated metal, with one electron per site and the remaining one-third of an electron per site free to move along the chain. Contrary to this expectation, $\Delta_c$ continues to grow as $U$ is increased, demonstrating that the large $U$ insulating state is highly non-trivial. b, The spin gap, $\Delta_s = E_2(4L) − E_0(4L)$ for $L = 40$ molecules, is orders of magnitude smaller than the charge gap, $\Delta_c$. c, The variance in particle number in each of the molecular orbitals and the total variance in particle number for $t = 0.25t_c$. Even for small $U$ the local parity symmetry means that there are no charge fluctuations in the $E_−$ orbitals for $\langle \hat{n}_{iE_−} \rangle = 1$. In the insulating phase $\langle \hat{n}_{iA_+} \rangle \lesssim 2$ and $\langle \hat{n}_{iE_+} \rangle \gtrsim \langle \hat{n}_{iE_−} \rangle = 1$. As the $A_+$ orbitals are nearly-filled, charge fluctuations in the $A_+$ orbital are significantly smaller than the charge fluctuations in the $E_+$ orbital. In all panels, curves are guides to the eye.

$\langle n^2_{iE_−} \rangle − \langle n_{iE_−} \rangle^2 = 0$ throughout the insulating phase (Fig. 2a), confirming that there are no charge fluctuations in the $E_−$ orbitals.

As the $E_+$ and $A_+$ orbitals have even local parity there is no preclusion of charge fluctuations in these orbitals for finite $U$. Nevertheless, the charge gap indicates that charged excitations are confined in the insulating phase\cite{22}. Thus, we see that a complex interplay of kinetic and potential effects drives the insulating phase of the two-thirds filled triangular necklace model.

In the molecular limit, $t/t_c \rightarrow 0$, the spins on neighboring molecules are coupled by an antiferromagnetic superexchange interaction, $J_s$ (the explicit form is given in the Supplementary Information). As expected from the analysis above the effective spin per molecule, $S \rightarrow 1$ in the strong coupling limit ($U/t_c \rightarrow \infty$), see Fig. 3b. Thus, the low-energy physics of the two-thirds filled Hubbard model on the triangular necklace lattice in the strong coupling molecular limit is captured by the spin-one Heisenberg chain. A corollary to this is that in the strong coupling molecular limit the model is in the Haldane phase, consistent with our numerical results. We show, in the Supplementary Information, that $\Delta_s/J_s$ is of the expected size for the Haldane phase.

However, as we move away from the strong coupling molecular limit an additional complication arises. The charge fluctuations in the $A_+$ and $E_+$ orbitals lead to a suppression of the effective moment on each molecule, cf. Fig 3b. As the physics of the Heisenberg chain is strongly dependent on the magnitude of the spin it is important to ask, particularly for small $U$, whether the charge fluctuations are sufficient to move the system out of the Haldane phase\cite{22}.

In spin-one models the Haldane phase is symmetry protected by the dihedral group ($D_2 \cong Z_2 \times Z_2$), time reversal and (bond) inversion symmetry\cite{13,24}. Charge fluctuations mean that time reversal and the dihedral group do not protect the topological order of fermionic systems\cite{22}. However, the Hubbard model on the triangular necklace lattice is symmetric under inversion about the bonds connecting neighboring molecules. This symmetry protects the Haldane phase meaning that there must be a (quantum) phase transition between it and a topologically trivial phase. It is interesting to note that the string order vanishes for small $U$ (Fig. 3a). However, neither string order nor edge states are required in an SPT phase\cite{13,24}. Nevertheless the entanglement spectrum, i.e., the eigenvalues of the reduced density matrix after tracing out half of the system, may only have even-fold degeneracies in the Haldane phase\cite{24}. Thus, the degeneracy of the entanglement spectrum (Fig. 3c) confirms that the insulating phase remains topologically non-trivial even when the string order vanishes.

Finally we stress the consistency of the above picture with experiment. Llusar et al. have shown that the magnetic susceptibility indicates the presence of doped triplets in the Mo$_3$S$_7$ units, consistent with $S \lesssim 1$ as found in our Hubbard model. No spin gap is observed down to 2 K (the lowest temperature studied)\cite{15}, which is consistent with the very small spin gap predicted for this state. To further test our predictions one could replace Mo$_3$S$_7$(dmit)$_3$ by $S = 1/2$ impurities. ESR experiments could then be used\cite{25} to search for edge excitations, which would provide a signature of SPT order. Furthermore,
the expected finite energy magnon excitations of momentum $k = \pi$ in the Haldane phase could be observed via neutron scattering.

1. Landau, L. D. & Lifschitz, E. M. *Statistical Physics* (Pergamon, London, 1958).
2. Anderson, P. W. *Basic Notions of Condensed Matter Physics* (Reading, Addison-Wesley, 1997).
3. Weinberg, S *The Quantum Theory of Fields, Vol II: Modern Applications* (Cambridge, Cambridge University Press, 1996).
4. Laughlin, R. B. Anomalous quantum Hall effect: An incompressible quantum fluid with fractionally charged excitations. *Phys. Rev. Lett.* 50, 1395-1398 (1983).
5. Chen, X., Gu, Z.-C., Liu, Z.-X., & Wen, X.-G. Symmetry-protected topological orders in interacting bosonic systems. *Science* 338, 1604-1606 (2012).
6. Gu, Z.-C. & Wen, X.-G. Tensor-entanglement-filtering renormalization approach and symmetry-protected topological order. *Phys. Rev. B* 80, 155131 (2009).
7. Moore, J. E. The birth of topological insulators. *Nature* 464, 194-198 (2010).
8. Qi, X.-L. & Zhang, S.-C. Topological insulators and superconductors. *Rev. Mod. Phys.* 83, 1057-1110 (2011).
9. Levin, L. V. et al. Phase Diagram of the spin-1/2 superfluid $^3$He confined in a nanoscale slab geometry. *Science* 340, 841-844 (2013).
10. Lee, P. A, Nagaosa, N. & Wen, X.-G. Doping a Mott insulator: Physics of high-temperature superconductivity. *Rev. Mod. Phys.* 78, 17-85 (2006).
11. Anderson, P. W. The resonating valence bond state in La$_2$CuO$_4$ and superconductivity. *Science* 235, 1196-1198 (1987).
12. Zaanan, J., Sawatzky, G. A. & Allen, J. W. Band gaps and electronic structure of transition-metal compounds. *Phys. Rev. Lett.* 55, 418-421 (1985).
13. Auerbach, A. *Interacting Electrons and Quantum Magnetism* (Springer, New York 1994).
14. Chen, X., Gu, Z.-C. & Wen, X.-G. Local unitary transformation, long-range quantum entanglement, wave function renormalization, and topological order. *Phys. Rev. B* 82, 155138 (2010).
15. Haldane, F. D. M. Nonlinear field theory of large-spin Heisenberg antiferromagnets: Semiclassically quantized solitons of the one-dimensional easy-axis Neel state. *Phys. Rev. Lett.* 50, 1153-1156 (1983).
16. Affleck, I., Kennedy, T., Lieb, E. H. & Tasaki, H. Rigorous results on valence-bond ground states in antiferromagnets. *Phys. Rev. Lett.* 59, 799-802 (1987).
17. Kennedy, T. & Tasaki, H. Hidden $Z_2 \times Z_2$ symmetry breaking in Haldane-gap antiferromagnets. *Phys. Rev. B* 45, 304-307 (1992).
18. Llusar, R. et al. Single-component magnetic conductors based on Mo$_3$S$_7$ trimuclear clusters with outer dithiolate ligands. *J. Am. Chem. Soc.* 126, 12076-12083 (2004).
19. Schollwöck, U. The density-matrix renormalization group in the age of matrix product states. *Ann. Phys.* 326, 96-192 (2011).
20. Nagaoka, Y. Ferromagnetism in a narrow, almost half-filled $s$ band. *Phys. Rev.* 147, 392-405 (1966).
21. Merino, J., Powell, B. J. & McKenzie, R. H. Ferromagnetism, paramagnetism, and a Curie-Weiss metal in
an electron-doped Hubbard model on a triangular lattice. *Phys. Rev. B* **73**, 235107 (2006).

22 Mott, N. F. The basis of the electron theory of metals, with special reference to the transition metals. *Proc. Phys. Soc. London A* **62**, 416-422 (1949).

23 Anfuso, F. & Rosch, A. String order and adiabatic continuity of Haldane chains and band insulators. *Phys. Rev. B* **75**, 144420 (2007).

24 Pollmann, F., Berg, E., Turner, A. M. & Oshikawa, M. Symmetry protection of topological phases in one-dimensional quantum spin systems. *Phys. Rev. B* **85**, 075125 (2012).

25 Hagiwara, M., Katsumata, K., Affleck, I., Halperin, B. I, & Renard, J. P. Observation of S=1/2 degrees of freedom in an S=1 linear-chain Heisenberg antiferromagnet. *Phys. Rev. Lett.* **65**, 3181-3184 (1990).

26 White, S. R. & Huse, D. A. Numerical renormalization-group study of low-lying eigenstates of the antiferromagnetic S=1 Heisenberg chain. *Phys. Rev. B* **48**, 3844-3852 (1993).

27 Girvin, S. M. & Arovas, D. Hidden topological order in integer quantum spin chains. *Physica Scripta* **T27**, 156-159 (1989).

28 Pérez-García, D., Wolf, M. M., Sanz, M., Verstraete, F. & Cirac, J. I. String order and symmetries in quantum spin lattices. *Phys. Rev. Lett.* **100**, 167202 (2008).

**Acknowledgements** We thank Matt Davis, Andrew Doherty, Carlos Gómez-García, Jure Kokalj, Rosa Llusar, Ross McKenzie, Oleg Sushkov, Tom Stace, and Tony Wright for helpful conversations. This work was supported by the Australian Research Council (grants DP0878523, DP1093224, LE120100181, and FT130100161) and MINECO (MAT2012-37263-C02-01).
Supplementary Information

I. DMRG CALCULATIONS

For $U \neq 0$, we apply the density matrix renormalization group (DMRG) using the matrix product state (MPS) ansatz and SU(2) symmetry to obtain the ground state energy and the ground state wave functions for finite size lattices. Most of the results presented below, and in the main paper, are for a lattice size $L = 40$ (where $L$ is the number of molecules, i.e., there are $3L$ sites), with $t/t_c = 0.25$, for varying $U$. Other values of $t/t_c$ give qualitatively similar results and will not be discussed at length for clarity. Whenever required we have implemented finite size scaling. For example, in Fig. S1 we show the finite size scaling of the charge gap. Except where otherwise stated the many body ground state is obtained by keeping up to 1000 states in each DMRG sweep.

For the finite lattices considered here, we find that the lowest energy singlet and triplet states are almost degenerate. This is consistent with the emergent $Z_2$ degrees of freedom expected at the boundary of the spin-one Heisenberg chain. Therefore, in order to avoid the degeneracy due to the edge states, we calculate the spin gap as the difference between the lowest energy spin-two state and the lowest energy spin-zero state.

To calculate the string order parameter we use infinite DMRG algorithm using MPS ansatz. It is well known that since MPS is a very good ansatz for gapped states, the correlation functions obtained naively from MPS appear to show gapped behaviour. However, long range correlations can be obtained by plotting the correlation as a function of the bond dimension, $m$. In Fig. S2 we plot the long range string order parameter. Similarly, the absence of long range antiferromagnetic is clear from the finite correlation length for the spin-spin correlation function (Fig. S3).

II. HUBBARD MODEL IN THE MOLECULAR ORBITAL BASIS

The Hamiltonian for the Hubbard model on the triangular necklace lattice is

$$\hat{H} = U \sum_{i} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} - t_c \sum_{i,\alpha \neq \beta, \sigma} \hat{c}_{i\alpha \sigma}^\dagger \hat{c}_{i\beta \sigma} - t \sum_{i,\sigma} \left( \hat{c}_{i\uparrow \sigma}^\dagger \hat{c}_{(i+1)\downarrow \sigma} + H.c. \right).$$  \hspace{1cm} (S1)

Transforming to the molecular orbital basis, this becomes

$$\hat{H} = \sum_{i m \sigma} \epsilon_m \hat{c}_{i m \sigma}^\dagger \hat{c}_{i m \sigma} + \sum_{i m m' \sigma} \left( \epsilon_{m m'} T_{m m'} \hat{c}_{i \sigma}^\dagger \hat{c}_{i (m+1) \sigma} + H.c. \right)$$

$$+ J_N \sum_i \hat{S}_{iE_-} \hat{S}_{iE_+} + \frac{U}{2} \sum_{i m \neq A_+} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + \frac{U}{3} \sum_i \hat{n}_{iA_+} \hat{n}_{iA_+}$$

$$+ \frac{U}{12} \sum_{i m \neq A_+} \hat{n}_{iE_+\sigma} \hat{n}_{iE_\sigma} - \frac{U}{6} \sum_i \left( \hat{c}_{iE_+\uparrow}^\dagger \hat{c}_{iE_\uparrow} \hat{c}_{iE_+\uparrow} \hat{c}_{iE_\uparrow} + H.c. \right)$$

$$+ \frac{U}{3} \sum_{i m \neq A_+} \hat{n}_{iA_+ \sigma} \hat{n}_{iA_+ \sigma} - \frac{U}{3} \sum_i \left( \hat{c}_{iA_+ \uparrow}^\dagger \hat{c}_{iA_+ \uparrow} \hat{c}_{iA_+ \uparrow} \hat{c}_{iA_+ \uparrow} + H.c. \right)$$

$$- \frac{U}{3 \sqrt{2}} \sum_{i \sigma} \left( \hat{c}_{iA_+ \sigma}^\dagger \hat{c}_{iE_+ \sigma} + H.c. \right) - \frac{U}{3 \sqrt{2}} \sum_{i \sigma} \left( \hat{c}_{iA_+ \sigma}^\dagger \hat{c}_{iE_+ \sigma} + H.c. \right)$$

$$+ \frac{U}{3 \sqrt{2}} \sum_{i \sigma} \left( \hat{n}_{iE_+ \sigma} \hat{c}_{iA_+ \sigma} + H.c. \right) - \frac{U}{3 \sqrt{2}} \sum_{i \sigma} \left( \hat{n}_{iE_+ \sigma} \hat{c}_{iA_+ \sigma} + H.c. \right)$$

$$- \frac{U}{3} \sum_{i \sigma} \hat{n}_{iE_+ \sigma} \hat{c}_{iA_+ \sigma} + \frac{U}{3} \sum_{i \sigma} \hat{n}_{iE_+ \sigma} \hat{c}_{iA_+ \sigma}$$  \hspace{1cm} (S2)

where $m, n \in \{A_+, E_+, E_-\}$, $\sigma \neq \sigma'$, $\hat{S}_{im} = \sum_{\sigma''} \epsilon_{i m \sigma''} \tau_{\sigma''}^0 \hat{c}_{i m \sigma''}$ is the spin of the $m$th molecular orbital on site $i$, $\tau_{\sigma''}^0$ is the vector of Pauli matrices, and $J_N = -U/3$ is the ‘Nagaoka’ exchange interaction.

III. THE MOLECULAR LIMIT

To make further analytical progress, it is helpful to consider the limit of weakly coupled molecules, i.e., $t \ll t_c$ and $U$. To construct a perturbation theory, we
begin by considering the $t = 0$ limit. It can be seen from Eq. (S2) that the repulsion between two electrons in an $A_+$ orbital ($U/3$) is less than the repulsion between two electrons is an $E_+$ or $E_-$ orbital ($U/2$). Therefore for $U \gg t_c$ and $t = 0$, the lowest energy state is to doubly occupy all of the $A_+$ orbitals. Furthermore, the ferromagnetic coupling, $J_N$, cf. Eq (S2), between the $E_+$ and $E_-$ orbitals causes a triplet ground state - this is consistent with Nagaoka’s theorem\cite{5} for $U \to \infty$. For $U = t = 0$ the molecular orbitals are exact eigenstates and the $A_+$ orbital is $3t_c$ lower in energy than the $E$ orbitals, so again the ground state has two electrons in every $A_+$ orbital and one in each $E_+$ and $E_-$ orbital. Explicit calculation shows that this remains the ground state for all $U/t_c$ when $t = 0$.

It is well known that the spin-1/2 Heisenberg model provides an effective low-energy theory of the half-filled Hubbard model in atomic limit, and that this can be shown at second order in a perturbation theory in small $t/U$\cite{6}. We treat the molecular limit of $\tilde{\mathcal{H}}$ in the same manner below and show that the spin-one Heisenberg model...
provides an effective low energy model of the Hubbard model on the triangular necklace lattice at two-thirds filling in the molecular limit. It is helpful to recall that for the two site spin-1 Heisenberg model ($\mathcal{H}_{\text{Heis}} = J_s \Sigma_1 \cdot \Sigma_2$, where $\Sigma_i$ is the spin one operator on the $i^{\text{th}}$ site) has nine possible states: a singlet with energy $-2J_s$, which is the ground state for antiferromagnetic interactions ($J_s > 0$); a triplet with energy $-J_s$; and a quintuplet with energy $J_s$. The molecular limit is rather more complicated than the atomic limit because of the rich internal dynamics of the molecules (for example the calculation of the ground state energy involves the summing over twenty intermediate states). Nevertheless, one can carry out the perturbation theory and we find that the ground state is a singlet with energy
\[
E^{(2)}_{S=0} = -4t_c + 2U - 3 \sum_{n=1}^{4} \frac{4t^2}{9a_n (3t_c + \varepsilon_n)},
\]
where $\varepsilon_1 = U$, and for $n > 1$
\[
\varepsilon_n = \frac{2}{3} \left[ U + \xi \cos \left( \frac{\phi + 2\pi n}{3} \right) \right],
\]
where
\[
\xi = \sqrt{U^2 + 27t_c^2},
\]
and
\[
\phi = \pi + \arccos \left( \frac{U}{\xi} \right)^3
\]
a_1 = 3 and for $n > 1$
\[
a_n = 2|a_n|^2 + |\beta_n|^2 + 1,
\]
where
\[
\beta_n = \frac{U - 3t_c - \varepsilon_n}{U + 3t_c - \varepsilon_n}.
\]
and
\[
E^{(2)}_{S=1} = -4t_c + 2U - \frac{4t^2}{8U_t} - 2 \sum_{n=1}^{4} \frac{4t^2}{9a_n (3t_c + \varepsilon_n)}
\]
and the energy of the lowest energy quintuplet state is
\[
E^{(2)}_{S=2} = -4t_c + 2U - \frac{4t^2}{27t_c}.
\]
Thus, the singlet-triplet energy gap is
\[
J_s \equiv E^{(2)}_{S=1} - E^{(2)}_{S=0} = \sum_{n=0}^{4} \frac{4t^2}{9a_n (3t_c + \varepsilon_n)}
\]
where we have made the defined $\varepsilon_0 = 0$ and $a_0 = -3$ for notational simplicity. Furthermore, the triplet-quintuplet gap $E^{(2)}_{S=2} - E^{(2)}_{S=1} = 2J_s$, as expected for the spin-1 Heisenberg model on two sites. Thus, we find that in the molecular limit the low-energy spectrum of the two-thirds filled Hubbard model on the triangular necklace lattice is identical to that of the spin-one Heisenberg chain. In the strong coupling limit ($U/t_c \to \infty$) we also have $S \to 1$. Therefore, the spin-one Heisenberg model describes the low energy physics of the Hubbard model on the triangular necklace model in the strong coupled molecular limit.

In Fig. [S1], we plot the data for the spin gap, $\Delta_s$, reported in Fig. 2b of the main paper, scaled by $J_s$ for a range of parameters. We find, as expected, that in the strong coupling molecular limit the value of $\Delta_s/J_s$ is comparable to that found for the spin-1 Heisenberg model.

1 Schollwöck, U. The density-matrix renormalization group in the age of matrix product states. *Ann. Phys.* **326**, 96-192 (2011).
2 McCulloch, I. P. Infinite size density matrix renormalization group, revisited. [arXiv:0804.2509].
3 S. R. White, Density-matrix algorithms for quantum renormalization groups. *Phys. Rev. B* **48**, 1034510356 (1993).
4 Affleck, I., Kennedy, T., Lieb, E. H. & Tasaki, H. Rigorous results on valence-bond ground states in antiferromagnets. *Phys. Rev. Lett.* **59**, 799-802 (1987).
5 Nagaoka, Y. Ferromagnetism in a narrow, almost half-filled $s$ band. *Phys. Rev.* **147**, 392-405 (1966).
6 K. A. Chao, J. Spalek, A. M. Oles, Kinetic exchange interaction in a narrow $S$-band J Phys. C **10**, L271-L276 (1977).
7 White, S. R. & Huse, D. A. Numerical renormalization-group study of low-lying eigenstates of the antiferromagnetic $S=1$ Heisenberg chain. *Phys. Rev. B* **48**, 3844-3852 (1993).