Frustration, ring exchange, and the absence of long-range order in EtMe$_3$Sb[Pd(dmit)$_2$]: from first principles to many-body theory

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We parameterize Hubbard and hence spin models for EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ from broken symmetry density functional calculations. This gives a scalene triangular model where the largest net exchange interaction is three times larger than the mean interchain coupling. The chain random phase approximation shows that the difference in the interchain couplings is equivalent to a bipartite interchain coupling, favoring long-range magnetic order. This competes with ring exchange, which favors quantum disorder. Ring exchange wins.

EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ (EtMe$_3$Sb) is a quantum spin liquid (QSL) candidate shrouded in mystery. It lacks magnetic ordering down to the lowest temperatures measured [1–3], but the physics that results in a quantum disordered state remains under debate. EtMe$_3$Sb shares important structural motifs with the quantum spin liquids κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ (κ-Cu) and κ-(BEDT-TTF)$_2$Ag$_2$(CN)$_3$ (κ-Ag). A crucial question is: how closely related are their ground states?

EtMe$_3$Sb, κ-Cu, and κ-Ag all form structures with alternating layers of organic molecules and counter-ions. In all three materials, the organic molecules dimerize with one unpaited electron found on each dimer in the insulating phase. The main structural difference between them is the spacial arrangement the dimers. Within κ-Cu and κ-Ag, neighboring dimers are almost perpendicular to one another, whereas in EtMe$_3$Sb, the dimers (gray circles in Fig. 1a) form quasi-one-dimensional stacks (along the horizontal in Fig. 1a).

κ-Cu and κ-Ag are Mott insulators. In the strong coupling limit, where the Hubbard $U$ is much greater than the largest interdimer hopping integral, $t$, their insulating phase is described by the isosceles triangular Heisenberg model (Fig. 1a). This model has two candidate QSL phases. Firstly, a QSL has been suggested in the region $0.6 \lesssim J'/J \lesssim 0.9$ [4–6,8], for which the ground state remains controversial. Secondly, the large $J'/J$ limit is adiabatically connected to the Tomonaga-Luttinger liquid (TLL) expected for uncoupled chains, $J'/J \gtrsim 1.4$ [6,11]. Theories in this regime show an emergent ‘one-dimensionalization’ whereby the many-body state is more one-dimensional than the underlying Hamiltonian [12–15]. However, the validity of the strong coupling limit in these materials is uncertain because both materials undergo a Mott metal-insulator transition under moderate pressures. This motivates the inclusion of higher order terms, most importantly ring exchange, in the spin model. It has been shown that these can also cause QSL phases [16–20].

Many early studies explored the possibility that the spin liquid in EtMe$_3$Sb can be explained by one of the above theories. However, the lower symmetry of EtMe$_3$Sb means that all three exchange interactions are different, i.e., it is described by a scalene triangular lattice, Fig. 1a,b. EtMe$_3$Sb is also close to a Mott transition and so ring exchange is likely to be important.

In this Letter we parameterize the spin model of EtMe$_3$Sb including both the scalene Heisenberg and ring exchange interactions from broken symmetry density functional theory (BS-DFT) calculations [21-24]. We find that the strongest exchange coupling is along the dimer stacking direction ($J_B$; cf. Fig. 1a). We solve our model via the chain random phase approximation (CRPA) around the large $J_B$ limit. In this approach the single electron problem is solved exactly and the effective one-dimensional magnetic susceptibility of a Heisenberg spin-1/2 chain, and treats interchain interactions via the RPA [25,26]. On an isosceles triangular lattice, the interchain interactions are perfectly frustrated. Within the CRPA, this prevents ordering at any temperature [26,27]. In EtMe$_3$Sb, we find that the anisotropy in the interchain coupling leads to an effective unfrustrated interchain interaction, given by the difference in the two interchain couplings $(\delta J_y = J_x - J_B)$. This favors long-range order. On the other hand, ring exchange favors quantum disorder [16–20]. Combining our BS-DFT and CRPA results shows that the absence of long-range magnetic order in EtMe$_3$Sb springs from the interplay of one-dimensionalization and ring exchange, leading us to propose that the ground state of EtMe$_3$Sb is adiabatically connected to the TLL.

The low-energy physics of the insulating phase of EtMe$_3$Sb
is described by an extended Hubbard model \[28,30\].

\[
H_{\text{Hubbard}} = \sum_{ij} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + \frac{1}{2} \sum_{ij} \left[ \left( \sum_{\nu \rho} V_{ij}^\nu c_{i\nu}^\dagger c_{j\rho} c_{j\rho}^\dagger c_{i\nu} \right) + \left( J_{ij}^{\text{DE}} + J_{ij}^{\text{SP}} \right) \mathbf{S}_i \cdot \mathbf{S}_j - \frac{J_{ij}^{\text{DE}}}{2} c_{i\uparrow}^\dagger c_{i\downarrow} c_{j\uparrow} c_{j\downarrow} \right],
\]

where \( c_{i\sigma}^\dagger \) (\( c_{i\sigma} \)) creates (destroys) an electron with spin \( \sigma \) on site \( i \), \( t_{ij} \) is the hopping between sites, \( U \) is the effective on-site Coulomb repulsion, \( n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma} \) is the electron density, \( V_{ij} = V_{ij} + (J_{ij}^{\text{DE}} / 4) \), \( V_{ij} \) is the Coulomb repulsion between electrons on different dimers, \( J_{ij}^{\text{DE}} \) is the interdimer direct exchange, and \( J_{ij}^{\text{SP}} \) is the interdimer spin polarization.

While there have been a number of calculations of \( t_{ij} \) \[4,31–33\], only Nakamura et al. \[30\] have previously estimated \( U \) and \( V_{ij} \). They also calculated the direct exchange \( J_{ij}^{\text{DE}} \). Although \( |J_{ij}^{\text{SP}}| \ll U, V_{ij} \), Nakamura et al.’s parameters show that \( J_{ij}^{\text{DE}} \) is non-negligible on the scale of the superexchange interaction, \( J_{ij}^{\text{SE}} \).

We construct an effective low-energy spin model of the Mott insulating phase for \( t_{ij} \ll U_{\text{eff}} \). As well as the usual superexchange interactions, we also retain the three- and four-site ring exchange, illustrated in Fig. 1h.

\[
H = \frac{J_{\text{sp}}}{2} \sum_{ij} \hat{P}_{ij} + \frac{J_{\text{sp}}}{4} \sum_{ijkl} \hat{P}_{ijkl} + \frac{1}{4} J_{S_2} \sum_{ij} \hat{P}_{ij} + \frac{1}{4} J_{S_3} \sum_{ijkl} \hat{P}_{ijkl}
\]

\[
+ \frac{K_{ij}}{2} \sum_{ijkl} \left( \hat{P}_{ijk} + \hat{P}_{ikj} \right) + \frac{K_{ijkl}}{2} \sum_{ijkl} \left( \hat{P}_{ijkl} + \hat{P}_{iklj} + \hat{P}_{ijkl} + \hat{P}_{ijlk} \right)
\]

where \( J_{ij}^{\text{SE}} = 4t_{ij}^2 / U_{\text{eff}} \), \( U_{\text{eff}} = U - V_{ij}^2 / 4 \), \( J_{ij} = J_{ij}^{\text{SE}} + J_{ij}^{\text{DE}} + J_{ij}^{\text{SP}} \) [we retain only \( \{i, j\} \in \{B, S, r\} \) (cf. Fig. 1a,b)], \( K_4 = 3t_{ij} t_{ik} t_{jk} / U_{\text{eff}}^2 \), \( K_3 = 80t_{ij}^2 t_{ik} / U_{\text{eff}}^3 \), \( K_4' = 80t_{ij}^2 t_{ik} / U_{\text{eff}}^3 \), \( K_{ijkl} = 80t_{ij}^2 t_{ik} t_{jk} / U_{\text{eff}}^4 \), \( \hat{P}_{ij} = 2S_i \cdot S_j + \hat{P}_{ikj} + \hat{P}_{ijk} \), \( \hat{P}_{ijkl} = \hat{P}_{ij} \hat{P}_{jk} \hat{P}_{kl} \), and \( \hat{P}_{ijkl} \) and \( \hat{P}_{ikj} \) cyclically permute spin states around the plaquettes shown (with dashing to match Figs. 1a,b).

Significant effort has been expended parameterizing tight-binding models for EtMe₃Sb from DFT \[4,31–33\]. However, these calculations do not give a direct parameterization of the spin model [Eq. (2)] because they do not enable the calculation of \( U, V_{ij}, J_{ij} \), or \( J_{ij}^{\text{SP}} \). Nakamura et al. \[30\] have addressed this by performing constrained RPA calculations, which do provide estimates of the Coulomb interactions. However, all of the calculations mentioned above are based on pure density functionals, i.e., the local density approximation (LDA) or generalized gradient approximations (GGA), which are known to perform poorly for parameterizing magnetic interactions \[36–39\]. In particular, they underestimate \( J_{ij}^{\text{SE}} \). LDA+U calculations are not straightforward in these molecular systems as, like many inorganic and organometallic magnets, the spins are delocalized over a dimer rather than being centered on a single atom. However, hybrid functionals have been shown to provide similar accuracy the LDA+U calculations in many molecular systems \[36,40\].

Tight-binding models based on either the monomer or dimer models of EtMe₃Sb \[4,28,30,32\] necessarily neglect the contributions to the net exchange interactions from states outside of a small window near the Fermi energy. However, BS-DFT allows for the direct calculation of exchange interactions from the full atomistic Hamiltonian. Furthermore, recent advances \[22,24\] have made it possible to isolate distinct physical contributions to the total exchange and even the parameters of the Hubbard model from this approach. Thus, EtMe₃Sb provides a valuable opportunity for comparison of BS-DFT with constrained RPA. BS-DFT calculations are based on a cluster, rather than an infinite crystal. This is a double-edged sword. Finite size effects need to be considered, but the finite size makes hybrid functionals, which include exact exchange interactions, computationally tractable.

In light of these considerations, we calculated \( J_{ij}^{\text{SE}}, J_{ij}^{\text{DE}}, J_{ij}^{\text{SP}}, t_{ij}, \) and \( U - V_{ij} \) for each nearest neighbor pair of dimers from a series of BS-DFT calculations. We utilize the frozen orbital capabilities of the local self-consistent field method \[21,24\]. We use the “quasi-restricted” orbital (QRO) approach \[41\] with LANDL2DZ effective core potential and basis set for palladium and antimony \[42,43\] and 6-31+G* basis set \[44–47\] for other atoms and with hybrid B3LYP functional \[48\] in ORCA \[49\]. We included the six nearest cations to each Pd(dmit)₂ tetramer; benchmarking calculations show that the calculated exchange interactions are well converged at this cluster size. We use the experimental crystal structure measured at 4 K \[50\].

As illustrated in Fig. 2, we start with a triplet state in the quasi-restricted open-shell formalism (T,QRO). We split the high spin dimer one-electron orbitals into two different sets, (i) the two same spin localized magnetic orbitals and (ii) the remaining (non-magnetic) ones. A first BS solution is found by flipping the individual spin state of one magnetic orbital (BS,QRO in Fig. 2), allowing us to calculate the direct exchange, \( J_{ij}^{\text{DE}} \). Then we relax (i.e. delocalize) the magnetic orbitals (while keeping the non-magnetic ones frozen) in the BS solution (BS,UFM in Fig. 2), which allows us to calculate the kinetic exchange (superexchange) \( J_{ij}^{\text{SE}} \) as well as the Hubbard model parameters \( t_{ij} \) and \( U - V_{ij} \), as described in \[22\]. The magnetic orbitals are then kept frozen in both the triplet and BS states while the non-magnetic ones are relaxed (T,UFM and BS,UFM in Fig. 2), eventually giving the spin-polarization contribution, \( J_{ij}^{\text{SP}} \).

Our BS-DFT results are shown in Table I. We calculate small values for the spin-polarization contribution, \( J_{ij}^{\text{SP}} \sim 0.05J_{ij} \), and henceforth neglect this term. The unfrustrated
interlayer coupling is $J_z = 0.06$ K.

Our values for the total Heisenberg exchange ($J_{ij}$) between dimers reveal that the exchange coupling in the dimer stacking direction, $J_B$ (see Fig. 1a), is significantly larger than the couplings in the other directions; $J_x/J_B = 0.35$ and $J_y/J_B = 0.30$. In what follows, it will be convenient to make a change of variables into the average of the interchain couplings, $J_y = \frac{1}{2}(J_y + J_x) = 135$ K, and the difference between them, $\delta J_y = J_y - J_x = 22$ K.

In the limit $\delta J_y$ and $J_z \to 0$, the lattice becomes a quasi-one-dimensional isosceles model (c.f. Fig. 1b), which is highly frustrated (a regime explored by Bocquet et al. [26]). Numerical studies have shown that this model remains quasi-one-dimensional for $J_y/J_B < 0.7$ [8, 9, 51, 55]. The unfrustrated limit (explored by Schulz [25]) occurs when $J_y \to 0$ or $J_x \to 0$ in which case the magnitude of the unfrustrated interchain coupling is $|\delta J_y|$. This model is quasi-one-dimensional for $|\delta J_y| + |J_z|/J_B < 0.3$ [56]. In EtMe$_3$Sb, both the frustrated component of the interchain coupling, $J_y/J_B = 0.33 \ll 0.7$, and the total unfrustrated component, $(|\delta J_y| + |J_z|)/J_B = 0.05 \ll 0.3$, are comfortably within quasi-one-dimensional limits.

We determine the ring exchange parameters (c.f. Eq. 2) using our values of $t_{ij}$ and $U - V_{ij}$. The three-site ring exchange, $K_1 = 18$ K, simply renormalizes the Heisenberg couplings in each direction within the Pd(dmit)$_2$ planes; $J_B \to J_B + K_3$ and $J_y \to J_y + K_3$ [19]. The four-membered ring exchange terms are slightly larger: $K_4 = 23$ K, $K_4' = 76$ K, $K_4'' = 66$ K.

These terms are also more consequent due to effective interactions in additional directions within the lattice. To include them in an effective Heisenberg model, we use a leading order mean-field approximation [17], $(S_{\alpha} \cdot S_{\beta}) = S^2 \cos(k \cdot r_{\alpha\beta})$, where $r_{\alpha\beta}$ is the vector from site $\alpha$ to site $\beta$. This leads to

$$
\frac{1}{S^2} (S_{\alpha} \cdot S_{\beta})(S_{\gamma} \cdot S_{\delta}) = \cos(k \cdot r_{\alpha\beta}) S_{\gamma} \cdot S_{\delta} + \cos(k \cdot r_{\gamma\delta}) S_{\alpha} \cdot S_{\beta} - 2 \cos(k \cdot r_{\alpha\beta}) \cos(k \cdot r_{\gamma\delta}).
$$

This results in renormalised exchange couplings $J_{ij}$ in the $x$, $y$, $z$ directions (see axes in Fig. 1). The Néel ordering temperature, $T_N$, of a lattice of weakly coupled chains can be calculated using the CRPA expression for the three-dimensional dynamical magnetic susceptibility, $\chi(\omega, k, t) = \chi_{\text{chain}}(\omega, k_x, t)/(1 - 2\tilde{J}_\perp(k)\chi_{\text{chain}}(\omega, k_x, t))$, where $t = k_B T/(J_B + K_3)$ is the reduced temperature, $\tilde{J}_\perp(k)$ is the Fourier transform of the interchain coupling and $k = (k_x, k_y, k_z)$ is the crystal momentum along the axes in Fig. 1 in units of the inverse lattice spacing. The dynamical susceptibility for a single Heisenberg chain, calculated from a combination of the Bethe ansatz and field theory techniques, is $59, 63$

$$
\chi_{\text{chain}}(\omega, k_0, t) = \Phi(t) \left( \frac{1}{\Gamma} - i \frac{\omega - u_0}{4 \pi \Gamma} \right) \left( \frac{1}{\Gamma} - i \frac{\omega + u_0}{4 \pi \Gamma} \right) \left( \frac{1}{\Gamma} - i \frac{\omega - u_0}{4 \pi \Gamma} \right) \left( \frac{1}{\Gamma} - i \frac{\omega + u_0}{4 \pi \Gamma} \right),
$$

where $u_0 = k_x - \pi$, $\Gamma(x)$ is the Euler gamma function, $u = \frac{\pi}{2} J_x b_0$ is the spin velocity, $b_0$ is the interdimer separation along the quasi-one-dimensional stack, $\Phi(t) = -\sqrt{\ln(\Lambda/t)/[2t(2\pi)^{3/2}]}$, and $\Lambda = 24.27$ [64]. The Néel temperature, $T_N$, corresponds to the zero frequency pole in $\chi(\omega, k, t)$ when $2\tilde{J}_\perp(k)\chi_{\text{chain}}(0, k_x)|_{T = T_N} = 1$. The instability occurs at the maximum of $\tilde{J}_\perp(k)\chi_{\text{chain}}(0, k_x)$.

Numerical exploration of our system for a range of coupling values reveals that $T_N$ is affected only negligibly by $J_y$, $K'$, $K''$, but significantly by $J_x$, $J_z$, $K_3$. We also find, analytically, that only the magnitudes of each interaction affect the value of $T_N$. In light of this, Fig. 3 shows a numerical calculation of $T_N$ as a function of the unfrustrated couplings and $K_4$. In the white region of Fig. 3 there are no solutions with positive real $T_N$. This implies that there is no long-range magnetic order, and that this state is in the same phase as the TLL.

| $i$ | $j$ | $t_{ij} (K)$ | $J_{ij}^{SE} (K)$ | $J_{ij}^{DE} (K)$ | $t_{ij} (meV)$ | $U - V_{ij} (meV)$ |
|-----|-----|--------------|----------------|----------------|--------------|----------------|
| B   | r   | 414          | 481            | -67            | 80           | 565           |
| S   | 146 | 168          | -22            | 47             | 600          | 519           |
|     | 124 | 168          | -44            | 44             | 519          |               |

TABLE I. Calculated nearest neighbour interactions between dimers of EtMe$_3$Sb, as shown in Figure 1. The full Heisenberg exchange ($J_{ij}$) is a sum of the superexchange ($J_{SE}$) and the direct exchange ($J_{DE}$), $t_{ij}$ is the effective hopping between dimers and $U - V_{ij}$ is the effective Coulomb interaction on each dimer.
isolated chain, similar to the state observed above in Cs
$^{3}$ $^{19.4}$ mK [1].

The quasi-one-dimensionality of the spin Hamiltonian derived from band structure calculations has been previously noted [30][32], although detailed many-body calculations have not previously been performed in this regime of the scalone triangular lattice. It has also been reported that the mean free path of quasi-particles using thermal conductivity measurements “...bears a striking resemblance to the 1D Heisenberg system” [67].

In conclusion, we have used an atomistic approach to parametrize an extended Hubbard model, and hence a spin model, for the spin-liquid candidate EtMe$_3$Sb. This revealed a frustrated scalone triangular lattice where the largest coupling along the stacking direction is nearly three times larger than the others. We showed that, in the quasi-one-dimensional limit relevant to EtMe$_3$Sb, the difference in the interchain coupling acts identically to an unfrustrated interchain coupling and favors long-range magnetic order. This interaction competes with ring exchange, which promotes quantum disorder. Our DFT calculations show that, in EtMe$_3$Sb, $2|\delta J| > |J_z|$ and we therefore predict that EtMe$_3$Sb does not reveal gapless excitations from the ground state. This is consistent with the gapless spinon excitations expected in a TLL [68]. The $^{13}$C nuclear spin-lattice relaxation rate shows a peak at 1 K [1]. We propose that this could be explained by short range correlations caused by the unfrustrated interactions within the lattice ($\delta J_y$ and $J_z$), which are of this order of magnitude. This hypothesis could also explain the broad hump structure found in the heat capacity around 3.7 K [66].
not order magnetically even at $T = 0$. Thus, we propose that the ‘spin-liquid’ behaviour is a remnant of TLL behavior in weakly coupled 1D spin chains, giving a natural explanation for many of the experimental observations.

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SUPPLEMENTARY INFORMATION

Previous *ab initio* parametrisations of a Hubbard model also fit within a quasi-1D picture, as indicated in Table II. Previous DFT studies parametrized monomer or dimer tight-binding models on the basis band structure calculations; either by fitting to models or via Wannier functions [3, 4, 30–32]. This approach yields less anisotropy tight-binding models than our BS-DFT, as summarized in Table II and very weak hopping between the layers [32].

As most of these calculations only parameterize the tight-binding model direct comparison with our values of $J_{ij}$ are not possible. But, $U_{\text{eff}}$ cancels from the ratio of superexchange parameters, e.g., $J_{y}^{SE}/J_{B}^{SE} \approx 2t_{B}^{2}/(t_{r}^{2} + t_{S}^{2})$, allowing this to be calculated. The values in Table II all lie within the weakly coupled chain regime ($J_{y}^{SE}/J_{B}^{SE} \lesssim 0.7; \delta J_{y}^{SE}/J_{B}^{SE} \lesssim 0.3$).

| Ref. | $t_{B}$ (meV) | $t_{r}$ (meV) | $t_{S}$ (meV) | $J_{y}^{SE}/J_{B}^{SE}$ | $\delta J_{y}^{SE}/J_{B}^{SE}$ |
|------|---------------|---------------|---------------|-------------------------|-----------------------------|
| [30] | 54            | 40            | 45            | 0.62                    | 0.14                        |
| [31] | 57            | 40            | 47            | 0.59                    | 0.19                        |
| [32] | 49            | 42            | 37            | 0.65                    | 0.16                        |
| [4]  | 49            | 38            | 46            | 0.74                    | 0.28                        |

TABLE II. Past results for inter-dimer hoppings based on DFT band-structure calculations. To estimate the ratio of exchange couplings, we use the superexchange in the large $U$ limit, $J_{y}^{SE} \approx \frac{4}{U} t_{B}^{2} t_{r}^{2} + t_{S}^{2}$, $\delta J_{y} \approx \frac{4}{U} t_{B}^{2} t_{r}^{2}$ and $J_{B}^{SE} \approx 4t_{B}^{2}/U$, which leads to $J_{y}^{SE}/J_{B}^{SE} \sim 2t_{B}^{2}/(t_{r}^{2} + t_{S}^{2})$. All of these models lie in or close to a weakly coupled chain regime ($J_{y}^{SE}/J_{B}^{SE} \lesssim 0.7; \delta J_{y}^{SE}/J_{B}^{SE} \lesssim 0.3$) which gives rise to a gapless spin-liquid state [6–11].