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Importance of spin-orbit coupling in layered organic salts

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We investigate the spin-orbit coupling (SOC) effects in α- and κ-phase BEDT-TTF and BEDT-TSF organic salts. Contrary to the assumption that SOC in organics is negligible due to light C, S, and H atoms, we show the relevance of such an interaction in a few representative cases. In the weakly correlated regime, SOC manifests primarily in the opening of energy gaps at degenerate band touching points. This effect becomes especially important for Dirac semimetals such as α-$(ET)_2I_3$. Furthermore, in the magnetic insulating phase, SOC results in additional anisotropic exchange interactions, which provide a compelling explanation for the puzzling field-induced behavior of the quantum spin-liquid candidate κ-$(ET)_2Cu_2(CN)_3$. We conclude by discussing the importance of SOC for the description of low-energy properties in organics.

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Layered organic materials have long served as ideal systems for studying complex physical phenomena such as the interplay between charge and spin order, unconventional superconductivity, and exotic phases emerging from strong electronic correlations [1–4]. In these systems, high compressibility and synthetic versatility allow fine tuning of the underlying interactions via physical and chemical pressure, thus providing access to many different ground states. For example, significant evidence has recently emerged for a quantum spin-liquid (QSL) state in a number of triangular-lattice organics, including κ-$(ET)_2Cu_2(CN)_3$ and κ-$(ET)_2Ag_2(CN)_3$ [5–9]. However, the appearance of very small energy gaps, and field-induced anomalies in the former material, remain essentially unexplained. Likewise, interest has recently grown in the α-phase materials α-$(ET)_2I_3$ [10] and α-$(BETS)_2I_3$ [11]. The former material has been argued to form, under pressure, a zero-gap semimetal (ZGS) with the Fermi energy located at the intersection of a pair of tilted Dirac cones [10,12,13]. However, the low-energy electronic and magnetic response shows a significant departure from theoretical expectations for simple Dirac systems [14,15]. An unexplored aspect is the effect of spin-orbit coupling (SOC) in these systems.

For (inorganic) magnetic insulators, strong SOC may generate large anisotropic magnetic interactions, associated with exotic spin-liquid states discussed, e.g., for the iridates and α-$RuCl_3$ [16–22]. In weakly correlated systems such as BiSb, Bi_2Te_3, etc. [23–26], SOC tends to open a gap in the bulk, and may lead to nontrivial band topology and associated exotic edge states. Such effects have rarely been considered for the organic ET salts, as the light C, S, and H atoms provide only moderate SOC. Nonetheless, it is known that SOC plays a dominant role in the spin relaxation of graphene [27–29] and organic-based semiconductors [30], and may be relatively enhanced for orbitally degenerate systems [31]. Indeed, in this Rapid Communication, we argue, despite a weak relative magnitude, that SOC is relevant for the *low-energy* properties in selected (representative) organic salts. We discuss as primary examples, the α-phase Dirac semimetals and κ-phase spin-liquid materials.

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At first approximation, the effect of SOC is to introduce a spin-dependent, complex hopping [32],

$$\mathcal{H}_{\text{hop}} = \sum_{ij} \mathbf{c}_i^\dagger \left(t_{ij}\mathbb{I}_{2\times 2} + \frac{i}{2}\vec{\lambda}_{ij}\cdot\vec{\sigma} \right)\mathbf{c}_j, \tag{1}$$

in terms of the single particle operators $\mathbf{c}_i^\dagger = (c_{i,\uparrow}^\dagger\, c_{i,\downarrow}^\dagger)$, where $c_{i,\sigma}^\dagger$ creates an electron at molecular site i, with spin $\sigma \in \{\uparrow,\downarrow\}$ and t_{ij} describes hopping between the highest occupied molecular orbital (HOMO) at sites i and j. The vector quantities $\vec{\lambda}_{ij} = -\vec{\lambda}_{ji}$ arise from SOC; $\vec{\sigma} = (\sigma_x,\sigma_y,\sigma_z)$ is the Pauli vector and $\mathbb{I}_{2\times 2}$ is the 2×2 identity matrix. Estimates of t_{ij} and $\vec{\lambda}_{ij}$ (see Table I in the Supplemental Material) were obtained for various ET and BETS salts at the density functional theory (DFT) level using methods implemented in the ORCA code [33]. For sulfur-based ET salts $|\vec{\lambda}_{ij}| \sim$ 1–2 meV, while SOC is stronger in the heavier selenium-based BETS salts and $|\vec{\lambda}_{ij}| \sim$ 5–10 meV. The ratio is governed roughly by $(\zeta_{Se}/\zeta_S) \sim 5$, where ζ_S and ζ_{Se} are the atomic spin-orbit constants of sulfur and selenium, respectively [34,35]. In each case, $\vec{\lambda}_{ij}$ tends to point along the long axis of the ET or BETS molecules, regardless of the details of the crystal packing; $\vec{\lambda}_{ij}$ is also largest for molecules i,j with molecular planes oriented 90° to each other, suggesting the strongest SOC effects occur for, e.g., α- and κ-phase salts. A complete discussion of these issues is provided in the Supplemental Material [33].

We first consider the $t,|\lambda| \gg U$ weakly correlated limit, where SOC alters the dispersion and spin-orbital composition of the single particle band states. Given $|\vec{\lambda}/t| \ll 1$ in the organics, SOC effects are strongest near band-touching $\mathbf{k}$ points, at which the Hamiltonian including SOC can be written most generally as

$$\mathcal{H}_{\mathbf{q}} = (\mathbf{c}_{\mathbf{q},+}^\dagger\, \mathbf{c}_{\mathbf{q},-}^\dagger)\begin{pmatrix} \epsilon_{\mathbf{q}}\mathbb{I}_{2\times 2} & i\vec{\lambda}_{\mathbf{q}}\cdot\vec{\sigma} \\ -i\vec{\lambda}_{\mathbf{q}}^*\cdot\vec{\sigma} & \epsilon_{\mathbf{q}}\mathbb{I}_{2\times 2}\end{pmatrix}\begin{pmatrix}\mathbf{c}_{\mathbf{q},+}\\ \mathbf{c}_{\mathbf{q},-}\end{pmatrix}, \tag{2}$$

where the upper (+) and lower (−) bands become degenerate at $\mathbf{k}=\mathbf{q}$ in the absence of SOC. Equation (2) is obtained from Eq. (1) via Fourier transform, and diagonalization with respect to the nonrelativistic hopping t_{ij}. When SOC is included, the bands are split into two spin-orbital pairs, with an energy difference $\Delta = 2|\vec{\lambda}_{\mathbf{q}}|$. Only the spin component parallel to $\vec{\lambda}_{\mathbf{q}}$ is conserved, which strongly modifies the

TABLE I. Computed exchange interactions J and DM vectors **D** [49]; all values are in units of K. Values for the *Pnma* salts are in the coordinate system (a,b,c), while the $P2_1/c$ values are with respect to (a,b,c^*) (see Fig. 2).

Material	J	J'	**D**
κ-$(ET)_2Cu[N(CN)_2]Cl$	482	165	$(-3.65,-3.58,-0.17)$
κ-$(ET)_2Cu_2(CN)_3$	228	268	$(+3.30,+0.94,+0.99)$
κ-$(ET)_2Ag_2(CN)_3$	250	157	$(-2.93,-0.92,-2.93)$
κ-$(ET)_2B(CN)_4$	131	365	$(+1.03,+4.17,-0.08)$

magnetic response of electrons in the vicinity of such points. For example, in the absence of SOC, an external field **H** induces an energy splitting $\Delta E = g\mu_B|\mathbf{H}|$ between spins aligned parallel and antiparallel to the field. In the presence of SOC, the splitting becomes $\Delta E_{\mathbf{q}} = (C_+ + C_-)/2$, where $C_\pm = \sqrt{(g\mu_B h_{||} \pm |\vec{\lambda}_{\mathbf{q}}|)^2 + (g\mu_B h_\perp)^2}$ and $h_{||}$ and $h_\perp$ are the components of **H** parallel and perpendicular to $\vec{\lambda}_{\mathbf{q}}$, respectively. Defining $g_{\text{eff}} = \lim_{h\to 0}(1/\mu_B)(\partial\Delta E/\partial h)$ yields $g_{\mathbf{q},||} = g \sim 2$ and $g_{\mathbf{q},\perp} = 0$. That is, a perpendicular field imparts *no* Zeeman splitting of the $\mathbf{k} = \mathbf{q}$ states. For this reason, we anticipate an anomalous angular dependence of the spin susceptibility χ_s and related nuclear magnetic resonance (NMR) Knight shift for states close to $\mathbf{k} = \mathbf{q}$. We briefly mention that these observations may be relevant, for example, to the α-phase Dirac semimetals α-$(ET)_2I_3$ and α-$(BETS)_2I_3$ [11–14]. Via Eq. (2), SOC is predicted to open a direct band gap $\Delta \sim 2|\vec{\lambda}_{\mathbf{q}}| \sim$ 1–2 meV for α-$(ET)_2I_3$, and $\Delta \sim$ 5–10 meV for α-$(BETS)_2I_3$, based on the above estimates. The presence of this *direct* gap implies a true Dirac ZGS state is impossible with SOC, although a zero or negative *indirect* gap is possible. For α-$(ET)_2I_3$, the existence of a small gap (or pseudogap) $\sim$1 meV in the semimetal phase is indicated by a suppressed conductivity $\sigma(T)$ [12,36] and spin susceptibility [15] observed over a wide pressure range below 10–20 K. For α-$(BETS)_2I_3$ a constant carrier density was observed below 20 K (above 6 kbars), consistent with an indirect negative gap semimetal [12] instead of a Dirac ZGS. While residual charge-order [37], correlation [15,36], and disorder effects are likely to play an important role in these observations, SOC is also relevant at the energy scale of the observed gaps, and therefore should also be considered in the analysis of the α-phase semimetals.

For the κ-phase salts [Fig. 1(a)], the Fermi level intersects two bands associated with the antibonding combination of HOMOs at each molecular dimer [Fig. 1(c)]. Without SOC, these bands would be degenerate at the Brillouin zone boundary [38–40], but SOC splits the bands. This splitting may be directly observed in quantum oscillation experiments. Such experiments typically reveal two frequencies F_α and F_β with associated amplitude I_α and I_β [Fig. 1(d)] [41,42]. The first corresponds to an orbit around the small hole pocket. The second represents the total area of the first Brillouin zone, and requires tunneling between the hole pockets and open sheets through the spin-orbit gaps at the zone edge. The tunneling rate is given by $\tau = \exp(-H_0/2H)$, where the magnetic breakdown field H_0 is related to the tunneling barrier by $H_0 \propto \Delta_{\text{eff}}^2$. For $H \ll H_0$, $\tau \sim 0$, and only the

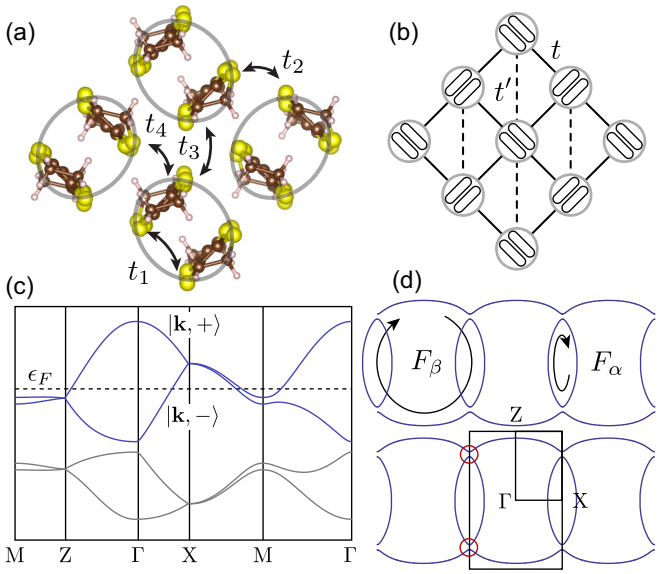

FIG. 1. (a) Definition of molecular hopping integrals $t_{1\text{–}4}$ for κ-phase salts compared to (b) dimer-dimer hopping integrals t,t'. Including SOC modifies the (c) dispersion and (d) Fermi surfaces, opening a gap along the zone edge $X \to M$ and $M \to Z$. In these figures we use hopping parameters for κ-$(BETS)_2Cu[N(CN)_2]Br$, but take $\vec{\lambda}_{\mathbf{q}}$ five times greater than estimated, in order to emphasize the effects.

α orbit is observable ($I_\alpha \gg I_\beta$). For $H \gg H_0$, $\tau \sim 1$, and $I_\alpha \ll I_\beta$. In the absence of SOC, but retaining inversion symmetry, $\Delta_{\text{eff}} \sim 0$, and I_α is expected to vanish at all fields. Nonetheless, F_α oscillations are observed in κ-phase salts, often with $I_\alpha \ll I_\beta$ in ET salts [41,43,44] and $I_\alpha \gtrsim I_\beta$ in Se-based BETS salts [45–47]. Assuming that Δ_{eff} arises primarily from SOC, we expect the ratio of breakdown fields $H_0(\text{BETS})/H_0(\text{ET}) \sim (\zeta_{Se}/\zeta_S)^2 \sim 25$, in terms of the atomic spin-orbit constants of sulfur and selenium [34]. We then may estimate the SOC-induced gap as $\Delta_{\text{eff}} \sim 2|\vec{\lambda}_{\mathbf{q}}| \sim 1$ meV for ET salts corresponding to $H_0(\text{ET}) \lesssim$ 1–2 T, far below typical quantum oscillation fields (larger than 10 T). For BETS salts, $\Delta_{\text{eff}} \sim$ 5–10 meV, suggesting $H_0(\text{BETS}) \lesssim$ 20–50 T, on par with that of κ-$(ET)_2Cu(SCN)_2$, for which inversion symmetry breaking introduces a non-SOC gap [48]. Therefore, the apparent experimental observation that $H_0(\text{BETS}) \gg H_0(\text{ET})$ in a variety of salts is fully consistent with SOC playing a dominant role in the magnetic breakdown behavior of the κ-phase salts.

We now consider the κ-phase materials in the insulating $U,t_1 \gg t_{2\text{–}4}$ limit, where a single hole is localized on each dimer, occupying the antibonding combination of HOMOs. Including SOC, the Hamiltonian for the localized spins up to $O(t^2)$ is

$$\mathcal{H} = \sum_{\langle ij \rangle} J_{ij}\,\mathbf{S}_i \cdot \mathbf{S}_j + \mathbf{D}_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j + \mathbf{S}_i \cdot \Gamma_{ij} \cdot \mathbf{S}_j, \qquad (3)$$

where J_{ij} is the Heisenberg coupling between dimer sites i,j. SOC introduces $\mathbf{D}_{ij}$, the Dzyaloshinskii-Moriya (DM) vector, and Γ_{ij}, the traceless pseudodipolar tensor [50,51]. The ET dimers form an anisotropic triangular lattice; by convention, we label values for the solid bonds in Fig. 1(b) as J, **D**, Γ, and

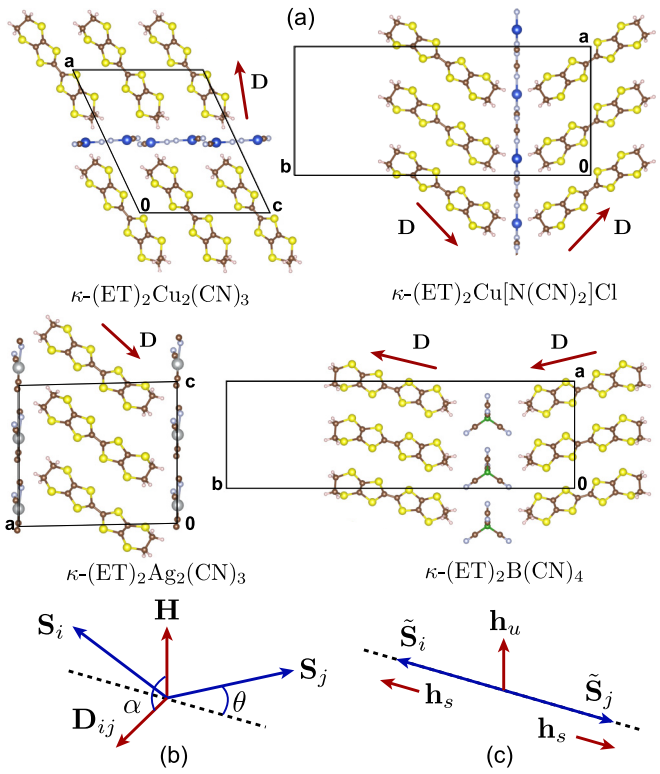

FIG. 2. (a) Computed orientation of **D** in the plane perpendicular to the 2_1 axis for selected ET salts. In each case, **D** is nearly along the long axis of the molecule. The presence of $\mathbf{D}_{ij}$ leads to spin canting by an angle θ, as shown in (b). This canting may be "gauged away" by making local rotations around $\pm\theta$, generating an effective staggered field $\mathbf{h}_s$ (c).

values for the dashed bonds as J', $\mathbf{D}'$, Γ'. Due to the presence of a crystallographic inversion center, $|\mathbf{D}'| = 0$, and $|\Gamma'| \sim 0$. Estimates for J, J', and **D** (Table I) were obtained for selected salts via cluster exact diagonalization [33,49].

Of the salts studied, κ-(ET)$_2$Cu[N(CN)$_2$]Cl exhibits the largest $J/J' \sim 3$, consistent with the observed square lattice Néel order below $T_N = 27$ K [52,53]. The smallest $J/J' \sim 0.3$ belongs to κ-(ET)$_2$B(CN)$_4$, which exhibits quasi-one-dimensional (1D) (spin-liquid) behavior down to $T = 5$ K [54]. The two-dimensional (2D) spin-liquid candidates κ-(ET)$_2$Cu$_2$(CN)$_3$ [7,55] and κ-(ET)$_2$Ag$_2$(CN)$_3$ [9,56] have $J/J' \sim 0.8$–1.6, close to the triangular limit. The orientation of each DM vector with respect to the ET molecules is shown in Fig. 2(a); in each case **D** is nearly parallel to $\vec{\lambda}_{ij}$, along the long axis of the ET molecules (as would be expected from perturbation theory [33]).

For the κ-phase salts, all local $\mathbf{D}_{ij}$ within a given ET plane are nearly collinear [Fig. 2(a)], since the component along the 2_1 axis direction is typically small. If we initially ignore this component, the anisotropic terms can be nearly "gauged away" by making local rotations of $\mathbf{S}_i$ around $\mathbf{D}_{ij}$ by a canting angle $\theta = \frac{1}{2}\eta \tan^{-1}(|\mathbf{D}|/J)$, where $\eta = +1(-1)$ for different sublattices [Figs. 2(b) and 2(c)]. The rotated Hamiltonian is thus

$$\mathcal{H} = \sum_{\langle ij \rangle} \tilde{J}_{ij} \tilde{\mathbf{S}}_i \cdot \tilde{\mathbf{S}}_j + g\mu_B \sum_i (\mathbf{h}_u + \eta \mathbf{h}_s) \cdot \tilde{\mathbf{S}}_i, \qquad (4)$$

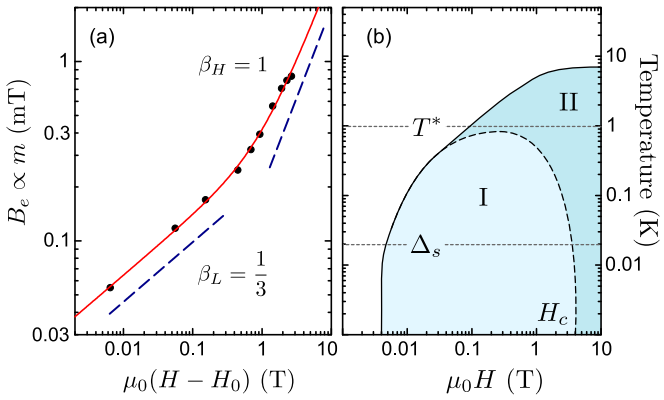

FIG. 3. (a) Fit of the 0.8 K μSR linewidth of κ-(ET)$_2$Cu$_2$(CN)$_3$ from Ref. [66] to $B_e \propto \int d\Omega\, m$, yielding $\beta_L = \frac{1}{3}$ and $\beta_H = 1$. The slope change near 1 T corresponds to a crossover between the staggered-field dominated region (I) at low field to the uniform-field dominated region (II) at high field, as shown in (b). The energy scales T^*, Δ_s, and H_c are discussed in the text.

with weakly modified exchange couplings $\tilde{J} = J + O(|\mathbf{D}|^2/J)$ and $\tilde{J}' = J'$ [57], an effective uniform external field $\mathbf{h}_u \approx \mathbf{H}$, and a staggered field $\mathbf{h}_s(\perp \mathbf{h}_u)$ with periodicity $\mathbf{q} = (\pi,\pi)$ that goes as $\mathbf{h}_s = \frac{1}{2J}(\mathbf{H} \times \mathbf{D})$. Anisotropy in the local g tensor also contributes to $\mathbf{h}_s$ with periodicity (π,π). As pointed out by many previous works [52,53,58], the staggered DM interaction promotes a canted moment in the plane perpendicular to **D** for Néel (π,π) order, as observed in κ-(ET)$_2$Cu[N(CN)$_2$]Cl. For this case, detailed NMR and electron spin resonance (ESR) measurements below T_N suggested that **D** lies close to the ab plane, making an angle of $\phi_a \sim 45^\circ$ from the a axis [59–61]. ESR measurements further provided a magnitude $|\mathbf{D}| \sim 5.0$ K, and $J \sim 600$ K [61]. These values are in good agreement with the computed values of $\phi_a = 44.5^\circ$, $|\mathbf{D}| = 5.1$ K, and $J = 482$ K.

The effects of the staggered field $\mathbf{h}_s$ on the purported 2D quantum spin-liquid (QSL) states of κ-(ET)$_2$Cu$_2$(CN)$_3$ and κ-(ET)$_2$Ag$_2$(CN)$_3$ have not yet been considered. Intuition can be gained by recalling the effect in 1D antiferromagnetic (AFM) chains [62–65], for which $\mathbf{h}_s$ has been studied in great detail. For the purpose of discussion, we first ignore the components of **D** along the 2_1 axis, and consider the effects of a staggered field at $\mathbf{q} = (\pi,\pi)$. In 1D QSLs, the staggered susceptibility $\chi_s \sim H^{\gamma_s}$, $\gamma_s \sim -\frac{2}{3}$ is typically divergent at low field, and greatly exceeds the uniform susceptibility $\chi_u \sim H^{\gamma_u}$, $\gamma_u \sim 0$. Assuming the magnetizations follow $\mathbf{m}_s \perp \mathbf{m}_u$, then the magnitude of the local moment at each site goes as $m = \sqrt{|\mathbf{m}_u|^2 + |\mathbf{m}_s|^2}$, with $|\mathbf{m}_s| \sim (C_s H \sin\alpha)^{\frac{1}{3}}$ and $|\mathbf{m}_u| \sim C_u H$. Here, C_s, C_u are some constants, and α is the angle between **H** and **D**. This finding implies the existence of an angle-dependent crossover field $H_c \sim \sqrt{C_s/C_u^3} \propto \sqrt{J|\mathbf{D}|}$. For $H < H_c$ the local magnetization is dominated by the staggered component and $m \propto H^{\beta_L}$, $\beta_L \sim \frac{1}{3}$, while for $H > H_c$ the uniform component dominates and $m \propto H^{\beta_H}$, $\beta_H \sim 1$. We argue that recent powder μSR studies [66] of κ-(ET)$_2$Cu$_2$(CN)$_3$ under magnetic field detected exactly this behavior; a fit of the 0.8 K μSR linewidth B_e to the powder-averaged expression $B_e \propto \int d\Omega\, m$ [Fig. 3(a)] yields $C_s/C_u = 0.91$, $\beta_L = 0.33$, and $\beta_H = 1.01$, in exact agreement with the expected (1D)

exponents. These exponents are not exotic; $\beta_L \sim 1/\delta$, where $\delta = 3$ is the mean-field value, while constant χ_u is typical of both ordered and disordered AFM systems. Previous NMR measurements at high field also suggested $\beta_H \sim 1$, consistent with this picture [67], while the value of $\beta_H \sim 0.83$ extracted from the μSR data in Ref. [66] was measured within the crossover region, and therefore may be anomalously low. In κ-$(ET)_2Cu_2(CN)_3$, the existence of this crossover requires only that the low-field susceptibilities follow $\chi_s \gg \chi_u$, i.e., $\chi(\pi,\pi) \gg \chi(0,0)$, which is expected since the QSL borders Néel order [68–71]. Upon increasing temperature, $\chi_s(T)$ is expected to decrease much more rapidly than $\chi_u(T)$, so that the $\mathbf{h}_s$ dominated region forms a dome in the H-T plane below some temperature $T^* \propto |\mathbf{D}|$ [region I, Fig. 3(b)], as observed experimentally. Thus, while H_c has been identified as an exotic quantum critical point [66], consideration of the staggered field $\mathbf{h}_s$ due to the DM interaction suggests a more conventional interpretation. In fact, together with $\mathbf{D}$, an applied field generally promotes spinon confinement through $\mathbf{h}_s$ [72–74], i.e., field-induced (π,π) order with a small value of $\mathbf{m}_s \perp \mathbf{H}$. Such induced order has been observed in κ-$(ET)_2Cu[N(CN)_2]Cl$ for $T > T_N$ [75]. This effect may also explain the field-induced broadening of the NMR lines, which was previously attributed to short-range order generated by impurities [67]. In contrast, field-induced order may be long range, and therefore provide well-defined antiferromagnetic resonance modes, making low-T ESR measurements of great interest [49].

Finally, we consider the residual effects not included in the staggered-field picture above; for a nonzero component of $\mathbf{D}$ along the 2_1 axis direction, the anisotropic terms cannot be completely gauged away. This leads to residual Ising-like terms associated with zero-field spin gaps on the order of $\Delta_s \sim \Gamma \sim |\mathbf{D}|^2/J \sim 10$–$50$ mK. For κ-$(ET)_2Cu[N(CN)_2]Cl$, for example, the zero-field magnon gap can be estimated from $\Delta_s \sim \mu_B H_{sf} \sim 50$ mK, where $H_{sf} \sim 0.1$ T is the spin-flop field [52,58]. Spinon gaps of smaller size have been suggested for the spin-liquid candidate κ-$(ET)_2Cu_2(CN)_3$ from μSR measurements ($\Delta_s = 3.5$ mK) [66]. While a complete description of SOC effects on the QSL is beyond the scope of this work, we emphasize that any complete theory of these very small spin gaps cannot ignore SOC effects. The large separation of energy scales $J \gg T^* \gg \Delta_s$ is naturally explained by the relative weakness of SOC without requiring another small emergent energy scale. These observations are generic to light-element magnets, and relevant also to, e.g., the Cu-based kagome antiferromagnet herbertsmithite $ZnCu_3(OH)_6Cl_2$, which shows similar field-induced behavior [76].

We conclude by questioning the common assumption that SOC is sufficiently weak in organics to be safely ignored by asking *weak compared to what?* We have highlighted several cases where there are no relevant energy scales to compete with SOC other than k_BT or $g\mu_BH$, and therefore SOC cannot be ignored *a priori*. We have presented a simple description of SOC effects in such materials, and an intuitive picture of the orientation of the DM vectors. In the organics, SOC is most relevant for the κ- and α-phase salts. For κ-phase BETS salts, a large spin-orbit gap at the zone edge would provide large magnetic breakdown fields observable in quantum oscillation experiments. Similar spin-orbit gaps may also render impossible the realization of a true zero-gap Dirac state in α-$(ET)_2I_3$ and α-$(BETS)_2I_3$, in addition to correlation effects. For the insulating state of κ-phase ET salts, SOC manifests as anisotropic exchange. This results in spin canting through the DM interaction, introduces zero-field magnon or spinon gaps, and provides a promising explanation of field-induced effects in the QSL candidate κ-$(ET)_2Cu_2(CN)_3$.

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