

Erratum: Dynamical Reduction of the Dimensionality of Exchange Interactions and the “Spin-Liquid” Phase of κ -(BEDT-TTF) $_2$ X [Phys. Rev. Lett. **119**, 087204 (2017)]

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In this Letter, we presented a general calculation of the superexchange interactions in dimer Mott insulators and compared these results to the title materials. We contrasted the “monomer model,” with one orbital per molecule, to the so-called dimer approximation where the bonding and antibonding combinations of the two orbitals within each dimer are first constructed and the orbitals that are filled in the noninteracting limit are neglected. We showed that intradimer interference effects can lead to qualitative differences between the full monomer model and the dimer approximation. Most dramatically, intradimer interference can cause a quasi-one-dimensional Heisenberg model to arise as an effective low-energy model of a quasi-two-dimensional tight-binding model. We argued that this physics is relevant to the κ -(BEDT-TTF) $_2$ X.

However, we have subsequently discovered an important error in our application of the general theory to the BEDT-TTF salts. We wrote the tight-binding part of the Hamiltonian in the form $-\sum_{ij\sigma} t_{ij} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma}$, where $\hat{c}_{i\sigma}^{(\dagger)}$ annihilates an electron with spin σ in the i th Wannier orbital. We continue to use this convention throughout this Erratum. However, Koretsune and Hotta [1] write such terms in the form $+\sum_{ij\sigma} t_{ij} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma}$. We failed to account for this sign difference when using their first principles parameters for the κ -(BEDT-TTF) $_2$ X salts. This has important consequences for these materials. As discussed below, the general mechanism described in this Letter whereby a one-dimensional superexchange interaction results from a two-dimensional tight-binding model remains correct. However, it does not appear to be relevant to the κ -(BEDT-TTF) $_2$ X salts.

The value of J_1 is independent of the signs of the hopping integrals, but J_2 is not (compare Fig. 2 of this Erratum to Fig. 2 of the original Letter). As emphasized in this Letter, interference effects can dominate the value of J_2 , particularly when electron-electron interactions are large. In this Letter, we analyzed the superexchange interactions analytically, in two limits. We begin this Erratum by clarifying how the superexchange interactions are changed when the signs of the hopping integrals are reversed (the numbering below corresponds to that on pages 2 and 3 of the original Letter).

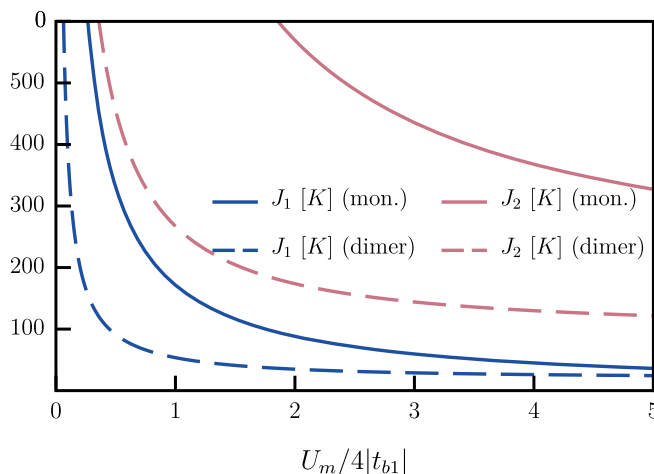


FIG. 2. Superexchange from perturbation theory for the monomer (solid lines) and dimer (dashed lines) models. Tight-binding parameters as calculated from first principles for κ -Cl and $V_m = 0$. With our sign convention, the hopping integrals are $t_{b1} = -207$ meV, $t_{b2} = -67$ meV, $t_p = 102$ meV, and $t_q = 43$ meV.

(i) In the molecular limit, $(U_m - V_m)/|t_{b1}| \rightarrow \infty$, the analytic forms we reported in the Letter are correct regardless of the signs of the hopping integrals. In this limit, the only nonvanishing superexchange interaction is $J_2 = -t_p t_q / 2t_{b1}$. Changing the signs of all three hopping integrals takes $J_2 \rightarrow -J_2$. This is consistent with the differences between Nagaoka ferromagnetism and Haerter-Shastry antiferromagnetism [2–4]. However, the signs of the hopping integrals that Koretsune and Hotta found via density functional theory (DFT) imply that in the molecular limit the κ -phase salts are described by an antiferromagnetic Heisenberg model on a *square lattice* as $J_1 = 0$ and $J_2 > 0$. Thus, in this frequently studied limit, our conclusion that there are important differences between the superexchange interactions calculated from the monomer and dimer models remains valid (the latter yields a Heisenberg model on the anisotropic triangular lattice in this limit [5]).

(ii) For $U_m = V_m$, changing the sign of t_{b1} swaps the bonding and antibonding orbitals relative to the definitions in the original Letter. That is, with $t_{b1} < 0$, the bonding orbital is created by $\hat{b}_{i\sigma}^\dagger = (1/\sqrt{2})(\hat{c}_{i1\sigma}^\dagger - \hat{c}_{i2\sigma}^\dagger)$ and the antibonding orbital is created by $\hat{a}_{i\sigma}^\dagger = (1/\sqrt{2})(\hat{c}_{i1\sigma}^\dagger + \hat{c}_{i2\sigma}^\dagger)$. These signs propagate through and change our analytical results. The general superexchange interaction in this limit for $t_{b1} < 0$ is $J_{\text{gen}} = 2(t_{11} + t_{12} + t_{21} + t_{22})^2 / U_m$, which is importantly different from the expression for $t_{b1} > 0$ given in the original Letter. The expression for J_1 is unchanged, but for $t_{b1} < 0$, we have $J_2 = 2(t_p + t_q)^2 / U_m$, which again differs by a sign from the expression for $t_{b1} > 0$, given in the original Letter. An important consequence of these corrections is that the ratio J_2/J_1 from the dimer approximation is correct when $U_m = V_m$: observe that the monomer and dimer lines in Fig. 4 coincide at $V_m/U_m = 1$ for both materials.

Our error also necessitates the correction of two figures from this Letter. We replot Figs. 2 and 4 with the signs of all the hopping integrals reversed (so as to correctly represent the results of DFT calculations [1]). It can be seen from Fig. 2 that both J_1 and J_2 remain antiferromagnetic (> 0) for all values of U_m . This is in contrast to the case reported in the original Letter, with the signs of all hopping integrals reversed, where J_2 becomes ferromagnetic (< 0) for sufficiently large U_m . This behavior is expected for large U_m as, to leading order in $1/U_m$, we have $J_2 = -t_p t_q / t_{b1}$; changing the signs of all three hopping integrals must change the sign of J_2 in this limit. Figure 4 shows that the superexchange interactions in both CuCN and κ -Cl remain quasi-two-dimensional. Indeed, as one expects $U_m > V_m$, these results suggest that the dimer approximation *underestimates* J_2/J_1 and hence that the magnetic interactions are closer to the square lattice than one would expect from the dimer approximation. This emphasizes that accurate estimates of the interaction parameters are important for determining the ratio J_2/J_1 and hence for understanding the spin-liquid state in CuCN.

Finally, to understand the role of the signs of hopping integrals in molecular Mott insulators more generally, the following observations may be helpful. Considering the pattern of hopping integrals (Fig. 1) given that the sign of t_{ij} is reversed by a π gauge transformation on exactly one of the sites (i or j), changing only the sign of t_{b1} is sufficient to change the results between those described in the Erratum and those given in the original Letter. Secondly, as changing the signs of all hopping integrals is equivalent to a particle-hole transformation, if there is one electron per dimer (rather than three) the formulas given in the original Letter hold. This is the relevant filling for organic anion systems such as the Ni(dmit)₂ salts [6], which do appear to show quasi-one-dimensional magnetism.

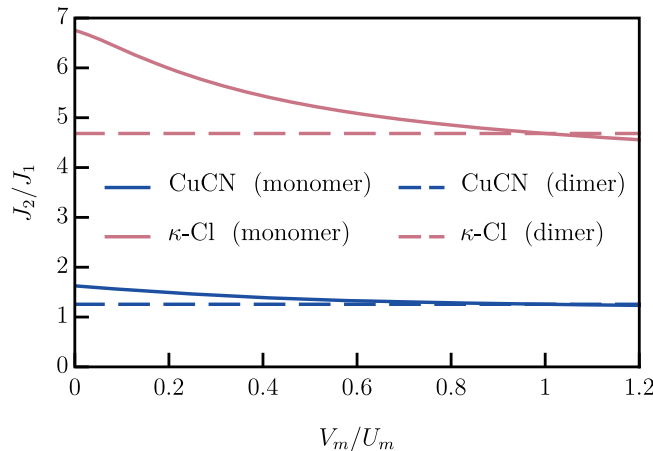


FIG. 4. Comparison of dimer (dashed lines) and monomer (solid lines) models for CuCN and κ -Cl (hopping integrals from [10] and $U_m = 12t_{b1}$). Tight-binding parameters from [1], with our sign convention, these are $t_{b1} = -207$ meV, $t_{b2} = -67$ meV, $t_p = 102$ meV, and $t_q = 43$ meV for κ -Cl and $t_{b1} = -199$ meV, $t_{b2} = -91$ meV, $t_p = 85$ meV, and $t_q = 17$ meV for CuCN.

Thus, we conclude the following: (i) The interference mechanism for realizing a quasi-one-dimensional (q1d) Heisenberg model from a quasi-two-dimensional (q2d) tight-binding model is not relevant to the κ -phase organics, but is possible and may be realized in other materials; (ii) interdimer interference effects are still likely to be relevant to the κ -phase organics, but they tend to drive the system towards the square lattice limit ($J_1/J_2 \rightarrow 0$); (iii) the dimer approximation is only accurate when the Hartree-Fock approximation is reasonable.

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