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Determination of magnetic form factors for organic charge-transfer salts: A first-principles investigation

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Organic charge-transfer salts show a variety of complex phases ranging from antiferromagnetic long-range order, spin liquid, bad metal, or even superconductivity. A powerful method to investigate magnetism is spin-polarized inelastic neutron scattering. However, such measurements have often been hindered in the past by the small size of available crystals as well as by the fact that the spin in these materials is distributed over molecular rather than atomic orbitals, and good estimates for the magnetic form factors are missing. By considering Wannier functions obtained from density-functional theory calculations, we derive magnetic form factors for a number of representative organic molecules. Compared to Cu^{2+}, the form factors $|F(\mathbf{q})|^2$ fall off more rapidly as function of q, reflecting the fact that the spin density is very extended in real space. Form factors $|F(\mathbf{q})|^2$ for TMTTF, BEDT-TTF, and $(\text{BEDT-TTF})_2$ have anisotropic and nonmonotonic structures.

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Since the discovery of superconductivity in the Bechgaard salt $(\mathrm{TMTSF})_2\mathrm{PF}_6$ [1], the complex phase diagrams of organic charge-transfer salts have inspired intense research efforts [2]. Among the families of charge-transfer salts with magnetic and superconducting phases, the more one-dimensional Fabre salts [3] and the more two-dimensional salts based on BEDT-TTF molecules in a κ-type structural arrangement [4–7] have attracted a lot of attention. Within the many experimental techniques used to study these organic materials, magnetic inelastic neutron scattering has, to our knowledge, so far not been used. This technique has played an outstanding role in the investigation of cuprate high temperature superconductors [8,9] and its application to organics would mean a significant progress [3]. The sizes of available crystals have limited the application of neutron techniques on charge-transfer salts, and only the phonon response of a few materials such as κ-$(\text{BEDT-TTF})_2\mathrm{Cu(SCN)}_2$ [10] has been studied by inelastic neutron scattering (INS). For the quantitative interpretation of magnetic inelastic neutron scattering spectra, however, besides significant crystal sizes, the knowledge of the magnetic form factor is necessary. In magnetically ordered organic charge-transfer salts, the polarized neutrons are scattered by spins which are not localized on atomiclike Cu $3d_{x^2-y^2}$ orbitals as in cuprates but spin densities which are distributed over extended molecular orbitals. While atomic magnetic form factors are tabulated [11], magnetic form factors for molecular orbitals are often not known. Due to the large spatial extension and inhomogeneity of a molecular orbital, the corresponding magnetic form factor can be expected to exhibit more structure than its atomic counterparts. Walters *et al.* [12] have demonstrated for the one-dimensional cuprate $\mathrm{Sr}_2\mathrm{CuO}_3$ that structure in the spin density distribution beyond the regular Cu $3d_{x^2-y^2}$ shape has important consequences for the quantitative evaluation of magnetic INS. In this Rapid Communication, we will extend this approach to the molecular orbitals carrying the spin in one- and two-dimensional charge-transfer salts. We investigate two representative examples, $(\mathrm{TMTTF})_2\mathrm{SbF}_6$ (where TMTTF stands for tetramethyl-tetrathiafulvalene) and κ-$(\text{BEDT-TTF})_2\mathrm{Hg(SCN)}_2\mathrm{Cl}$ [where BEDT-TTF denotes bis-(ethylenedithio)-tetrathiafulvalene].

Method. In magnetic neutron scattering, neutrons are used to probe the spin density of a material. For a given momentum transfer $\mathbf{q} = \mathbf{k} - \mathbf{k}'$ and energy transfer $\hbar\omega = \frac{\hbar^2}{2m}(k^2 - k'^2)$, the magnetic scattering cross section is given as [13]

$$\frac{d^2\sigma}{d\Omega d\omega} = (\gamma r_0)^2 \frac{k'}{k} |F(\mathbf{q})|^2 e^{-2W(\mathbf{q})} \times \sum_{\alpha\beta} \left(\delta_{\alpha\beta} - \frac{q_\alpha q_\beta}{q^2} \right) S^{\alpha\beta}(\mathbf{q},\omega), \tag{1}$$

with the Debye-Waller factor $e^{-2W(\mathbf{q})}$ and the magnetic scattering function $S^{\alpha\beta}(\mathbf{q},\omega)$. Here, we focus on the static magnetic form factor $F(\mathbf{q})$. This quantity is defined as the Fourier transform of the electronic spin density $\rho_s(\mathbf{r})$,

$$F(\mathbf{q}) = \int d^3r\, e^{i\mathbf{q}\cdot\mathbf{r}} \rho_s(\mathbf{r}). \tag{2}$$

The electronic spin density is given by

$$\rho_s(\mathbf{r}) = \rho_\uparrow(\mathbf{r}) - \rho_\downarrow(\mathbf{r}), \tag{3}$$

where $\rho_\uparrow(\mathbf{r})$ and $\rho_\downarrow(\mathbf{r})$ denote the electronic density with spin up and down, respectively, of the local scatterer. For crystalline systems, these spin densities can be obtained from first-principles solid-state calculations with density-functional theory (DFT). However, within DFT, the eigenstates of the system are Bloch states (characterized by a band index, a wave vector, and spin) which are periodically extended waves. In order to obtain a spin density localized on a given scatterer (atom or molecule), a projection of the Bloch state onto a state localized at the corresponding scatterer must be carried out. The resulting localized orbitals are so-called Wannier orbitals, which we compactly denote by $\Psi_W(\mathbf{r})$. Once $\Psi_W(\mathbf{r})$ is known, the spin density can be readily evaluated via

$$\rho_s(\mathbf{r}) = |\Psi_W(\mathbf{r})|^2, \tag{4}$$

and the magnetic form factor follows from a numerical evaluation of the expressions given above.

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Density-functional theory calculations are performed on the full-potential nonorthogonal local-orbital basis set, as implemented in the FPLO code [14], and the generalized gradient approximation [15] to the exchange-correlation functional is adopted. It should be mentioned that, although one should in principle carry out spin-polarized DFT calculations for half-filled systems such as those examined in this work, it is permissible to carry out a nonmagnetic calculation and consider the unpaired electron occupying the half-filled band at the Fermi level as giving rise to the net spin density [12]. To perform the projection of the (Kohn-Sham) Bloch states onto a localized orbital, we use the projective Wannier functions within the FPLO basis as described in Ref. [16]. In order to avoid charge-leakage issues through the unit-cell boundaries, the Wannier orbitals have been evaluated in large (3 × 3 × 3) supercells. The magnetic form factor is computed from the resulting spin density by means of the fast Fourier transform (FFT).

Results. Magnetic form factors have been calculated for two representative organic charge-transfer salts, κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl and (TMTTF)$_2$SbF$_6$; the crystal structures of these systems are taken from Refs. [17,18], respectively, and are displayed in Figs. 1(a) and 1(b). Whereas the C and S atoms in (TMTTF)$_2$SbF$_6$ are coplanar, κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl exhibits a minor noncoplanarity along the main axis of the molecule. This noncoplanarity is accentuated by the two ethylene end groups, which can have so-called eclipsed and staggered out of plane twists [2]. DFT calculations were performed on 8 × 8 × 8 and 6 × 6 × 6 k meshes for (TMTTF)$_2$SbF$_6$ and κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl, respectively. For (TMTTF)$_2$SbF$_6$, the two bands near the Fermi level shown in Fig. 2(a) (compare also Ref. [17]) are represented by two molecular Wannier functions, one of which is shown in Fig. 1(c). For κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl, the four bands formed by the highest occupied molecular orbital states of the four BEDT-TTF molecules in the unit cell [see Fig. 2(b)], are represented by four Wannier functions such as the one shown in Fig. 1(d). Note that the projection indeed leads to well-localized Wannier orbitals on the relevant molecules, without replicas or contributions elsewhere in the unit cell. We note that the residual electron density which leaks out of the considered molecule into the rest of the unit cell and beyond is negligibly small (two orders of magnitude below the maximum value of the electron density attained within the molecule). Furthermore, the fact that the considered bands exhibit predominantly strong characters of the atomic orbitals of the considered molecule implies that the adopted partitioning scheme leads to a consistent representation in terms of Wannier orbitals. A system of Cartesian coordinates x, y, and z is introduced on the molecule in such a way that x

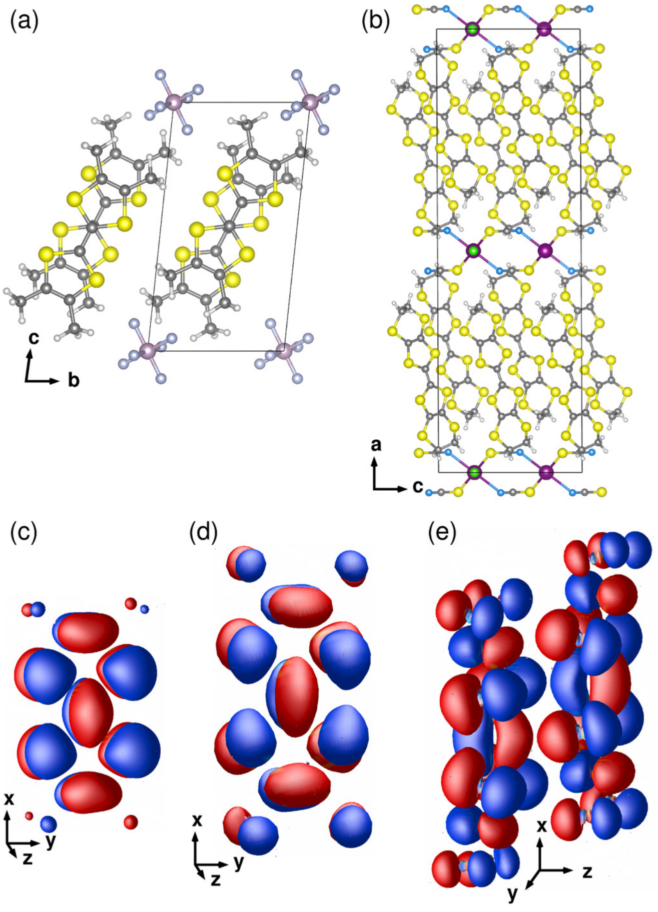

FIG. 1. (Color online) Crystal structures for (a) (TMTTF)$_2$SbF$_6$ and (b) κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl. Wannier orbitals for (c) the TMTTF molecule, (d) the BEDT-TTF molecule, and (e) the (BEDT-TTF)$_2$ dimer, calculated within the crystal structures in (a) and (b), respectively.

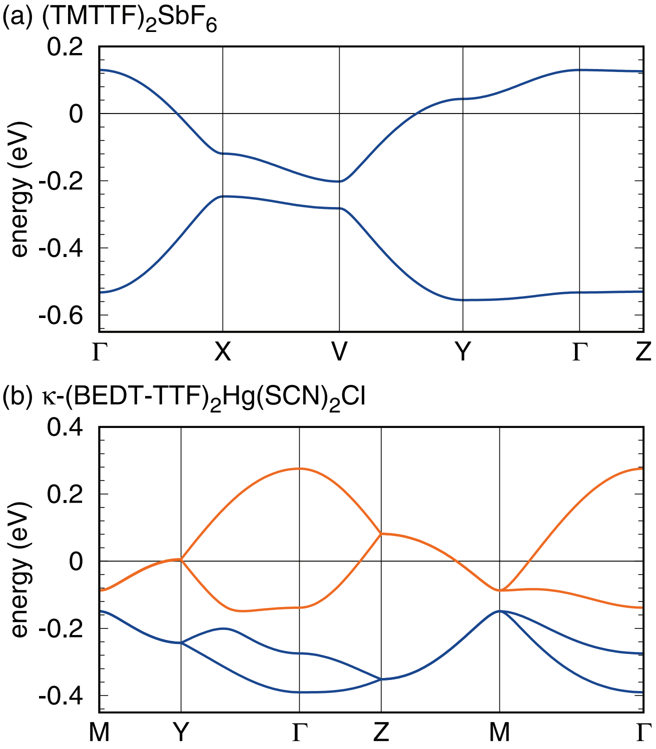

FIG. 2. (Color online) Band structures near E_F for (a) (TMTTF)$_2$SbF$_6$ and (b) κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl. The two bands in (a) originate from the highest occupied molecular orbitals of the two TMTTF molecules in the unit cell, and the four bands in (b) from the highest occupied molecular orbitals of the four BEDT-TTF molecules.

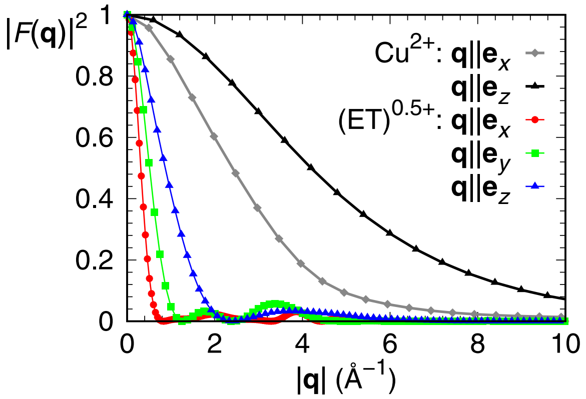

FIG. 3. (Color online) Comparison between magnetic form factors for the Cu^{2+} ion and the (BEDT-TTF)$^{0.5+}$ ion (BEDT-TTF is abbreviated further as ET).

points along the long axis of the molecule, y is on the molecule pointing along the shorter axis, and z is perpendicular to the molecule.

First, we compare in Fig. 3 the magnetic form factor for the Cu^{2+} ion in Sr_2CuO_3 [12] with the magnetic form factor for the (BEDT-TTF)$^{0.5+}$ ion in κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl. Due to the larger spatial extent of the BEDT-TTF Wannier function [see Fig. 1(d)] compared to the Cu $3d_{x^2-y^2}$ Wannier function, the magnetic form factor of (BEDT-TTF)$^{0.5+}$ drops to its first minimum at much lower q values. Figures 4 and 5(a) display the magnetic static form factors for TMTTF molecules in (TMTTF)$_2$SbF$_6$ and for BEDT-TTF molecules in κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl, respectively, as functions of q_x, q_y, and q_z, the Fourier-conjugate variables of x, y, and z. As can be seen in Fig. 1, the charge densities are broad along x and y and rather concentrated along z. Accordingly, the form factors are comparatively narrow for q_x and q_y and broader for q_z. Note that, as opposed to the case of a free atom, the form factor is not a steadily decreasing function: It exhibits marked features. These features reflect the fact that the charge density is strongly modulated over the region in space occupied by the molecule.

Due to the fact that both (TMTTF)$_2$SbF$_6$ and κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl are half-filled systems if we focus on the antibonding bands arising from the highest occupied molecular orbitals only, the dimers (TMTTF)$_2$ and (BEDT-TTF)$_2$, each hosting one hole, can be considered spin-$1/2$ objects. In order to aid in the interpretation of magnetic inelastic neutron scattering data, we also provide in Fig. 5(b) the magnetic form factor associated with a BEDT-TTF dimer. This corresponds to the dimer Wannier function shown in Fig. 1(e). The comparison of this form factor with the form factor for a BEDT-TTF molecule shows that the main peak along q_z becomes narrower (since the spin density is broader along z for the dimer). Also the peak along q_x becomes slightly narrower and its fine-grained structure is also affected, owing to the fact that the dimers are slightly shifted along x. We also investigated the dependence of the form factor of BEDT-TTF on the particular κ-type compound by repeating the calculation for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl [5,19,20]. We found all features of Fig. 5(a) to be robust both on a linear and on a log scale. Finally, we note that the obtained values of $F(q)$ are rather independent of the choice of exchange-correlation potential: Values of $F(q)$ obtained from a calculation employing the local-density approximation to the exchange-correlation potential yielded differences of the order of 1%.

Conclusions. By considering a combination of density-functional theory calculations, Wannier function construction, and numerical Fourier transformations, we have been able to derive form factors for organic molecules in crystalline systems. Such form factors are indispensable for a quantitative analysis of magnetic inelastic neutron scattering experiments of organic materials. We observe a number of differences between form factors for organic molecules and transition metal ions: (i) Due to the large spatial extent of the spin density, the form factor for organic molecules falls to its first minimum at much smaller q values, (ii) due to spatial modulation of the spin density, the form factors show

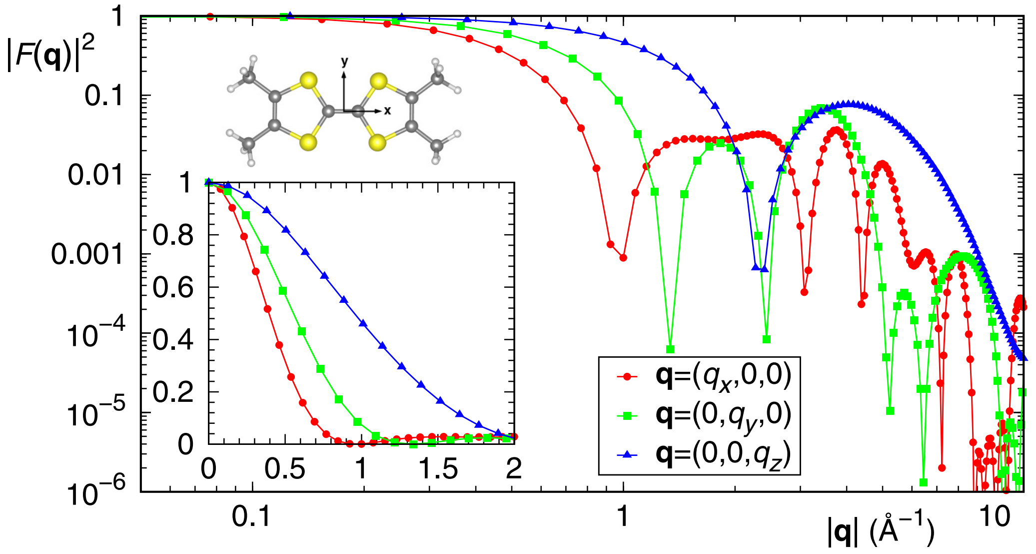

FIG. 4. (Color online) Magnetic form factor for (TMTTF)$_2$SbF$_6$ in log-log scale; the inset shows the same data in linear scale.

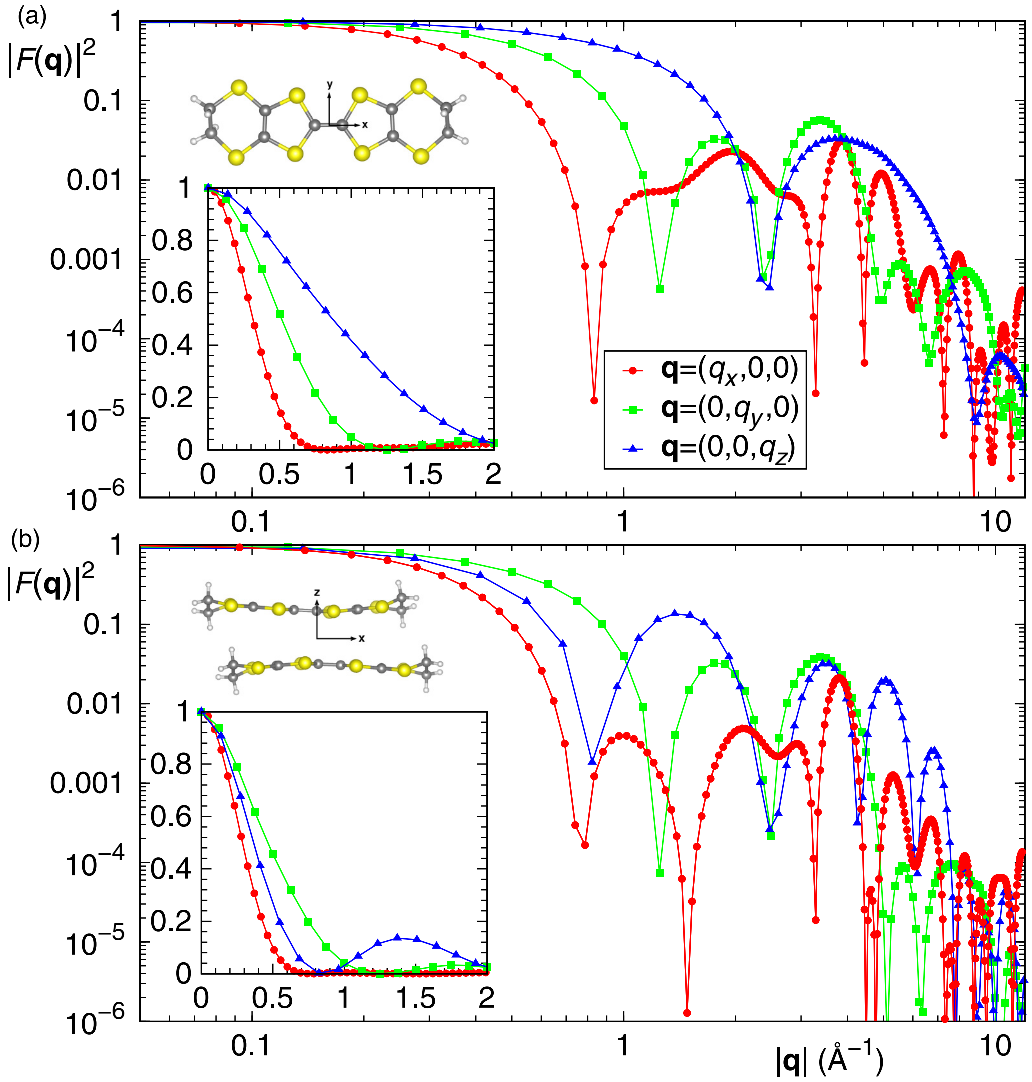

FIG. 5. (Color online) Magnetic form factors for κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl in log-log scale. (a) Form factor for a BEDT-TTF molecule, and (b) form factor for a (BEDT-TTF)$_2$ dimer. The insets show the same data in linear scale.

a richer q-dependent structure, and (iii) the real space shape of the molecular spin density leads to very anisotropic form factors. These consequences of the extended inhomogeneous molecular spin densities can only be captured by accurate first-principles calculations. We hope that this work will help further investigations of the behavior of organic crystals with inelastic neutron scattering experiments.

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