Low ordered magnetic moment by off-diagonal frustration in undoped parent compounds to iron-based high-$T_c$ superconductors

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Abstract

A Heisenberg model over the square lattice recently introduced by Si and Abrahams to describe local-moment magnetism in the new class of Fe-As high-$T_c$ superconductors is analyzed in the classical limit and on a small cluster by exact diagonalization. In the case of spin-1 iron atoms, large enough Heisenberg exchange interactions between neighboring spin-1/2 moments on different iron 3$d$ orbitals that frustrate true magnetic order lead to hidden magnetic order that violates Hund’s rule. It accounts for the low ordered magnetic moment observed by elastic neutron diffraction in an undoped parent compound to Fe-As superconductors. We predict that low-energy spin-wave excitations exist at wavenumbers corresponding to either hidden Néel or hidden ferromagnetic order.
The recent discovery of a new class of high-$T_c$ superconductors that are notably composed of iron-arsenic layers has reinvigorated the search for new superconductors \[1\]. Iron is usually detrimental to conventional superconductivity because its magnetic moment breaks up Cooper pairs \[2\]. Electronic conduction is confined primarily to the Fe-As layers in the new class of high-$T_c$ superconductors, on the other hand \[3\]. The nature of the magnetic moments in the iron atoms that make up the new class of materials may then be critical to the superconductivity that these systems display.

As in the copper-oxide high-$T_c$ superconductors, the new Fe-As superconductors are obtained by doping stoichiometric parent compounds. Elastic neutron diffraction measurements on the parent compound LaOFeAs reveal the presence of long-range spin-density wave (SDW) order at low temperature that is commensurate with the square lattice of Fe atoms that make up each layer \[4\]. The magnetic moment associated with this collinear type of magnetic order is only a fraction of the Bohr magneton, however. Hund’s rule is therefore violated in the iron 3$d$ orbitals of this new parent compound for high-$T_c$ superconductivity.

In this Letter, we identify a route to low ordered magnetic moments in frustrated two-dimensional magnets composed of local moments of spin one or higher. It is based on linear spin-wave analysis and exact diagonalization of a Heisenberg model over a square lattice of iron atoms that includes local Hund’s rule coupling \[5\]. We find that Heisenberg spin exchange between different 3$d$ orbitals on neighboring iron atoms leads to either hidden Néel or hidden ferromagnetic order if the exchange interaction is sufficiently frustrating. This may account for the low moment associated with collinear/SDW order that is observed in LaOFeAs \[4\]. Low-energy spin-wave excitations are a natural consequence of the hidden magnetic order, however. We predict that they collapse to the ground-state energy at the respective Néel and ferromagnetic wave numbers. Last, we identify a quantum phase transition into hidden order from a more familiar frustrated magnetic groundstate that obeys Hund’s rule.

Recent transport measurements indicate that parent compounds to iron-based high-$T_c$ superconductors are bad insulators (metals) close to a transition into a metallic (insulating) state \[3\]. Further, classical spin-wave frequencies obtained from near-neighbor Heisenberg models can be used to fit the measured spin-wave spectra in such parent compounds \[6\]. We believe, therefore, that a local-moment description of magnetism in parent compounds to iron-based high-$T_c$ superconductors is valid at low temperature. Following Si and Abrahams,
we then consider a spin-1/2 Hamiltonian that contains near-neighbor Heisenberg exchange among local iron moments within isolated layers plus Hund’s-rule coupling:

\[ H = \frac{1}{2} J_0 \sum_i \left[ \sum_{\alpha} S_i(\alpha) \right]^2 + \sum_{(i,j)} \sum_{\alpha,\beta} J_{1,\alpha,\beta} S_i(\alpha) \cdot S_j(\beta) + \sum_{\langle\langle i,j \rangle\rangle} \sum_{\alpha,\beta} J_{2,\alpha,\beta} S_i(\alpha) \cdot S_j(\beta). \]  

(1)

Above, \( S_i(\alpha) \) is the spin operator that acts on the spin-1/2 state of orbital \( \alpha \) in the iron atom at site \( i \). The latter runs over the square lattice of iron atoms that make up an isolated layer. The application of Hund’s rule is controlled by a negative local Heisenberg exchange constant \( J_0 < 0 \), while nearest neighbor and next-nearest neighbor Heisenberg exchange across the links \( \langle i, j \rangle \) and \( \langle\langle i, j \rangle\rangle \) is controlled by the tensor exchange constants \( J_{1,\alpha,\beta} \) and \( J_{2,\alpha,\beta} \), respectively. The strength of the crystal field at each iron atom compared to Hund’s rule determines the number of orbitals per iron atom above. It can be as low as two for strong crystal fields, and as high as four for weak crystal fields. We shall now search for groundstates of the \( J_0-J_1-J_2 \) model above (1) that exhibit low ordered magnetic moments that violate Hund’s rule. It is useful to first consider the special case where all nearest-neighbor and next-nearest-neighbor exchange coupling constants are equal, respectively: \( J_{1,\alpha,\beta} = J_1 \) and \( J_{2,\alpha,\beta} = J_2 \). The Hamiltonian then reduces to \( H = \frac{1}{2} J_0 \sum_i S_i \cdot S_i + J_1 \sum_{(i,j)} S_i \cdot S_j + J_2 \sum_{\langle\langle i,j \rangle\rangle} S_i \cdot S_j \), where \( S_i = \sum_{\alpha} S_i(\alpha) \). Observe now that \( S_i + S_j \) commutes with \( S_i \cdot S_i \), and hence that the latter commutes with the Hamiltonian. This means that the total spin at a given site \( i \) is a good quantum number. The groundstate then obeys Hund’s rule in the classical limit because states with maximum total spin at a given site minimize both the Hund’s-rule energy \( (J_0 < 0) \) and the Heisenberg exchange energies in such a case.

A violation of Hund’s rule will therefore require a strong variation in the Heisenberg exchange coupling constants among the different iron orbitals. This can be easily seen if we confine ourselves to the case of two 3d-wave orbitals per site and choose off-diagonal exchange coupling constants that lead to frustration when Hund’s rule is obeyed: \( J_{1,\alpha,\alpha} = 0 = J_{2,\alpha,\alpha} \), while \( J_{1,\alpha,\beta} = J_1 \) and \( J_{2,\alpha,\beta} = J_2 \) if \( \alpha \neq \beta \), with \( J_2 > 0 \). In the limit of weak Hund’s-rule coupling, \( J_0 \to 0 \), the classical ground state per orbital is a Néel state for \( J_1 < 0 \) and a ferromagnet for \( J_1 > 0 \). The spins at a given iron atom are equal and opposite across the two orbitals, however. (See fig. 1) The moment associated with any type of true magnetic order must therefore vanish! It is important to observe that the hidden magnetic order shown in fig. 1 is stabilized by the addition of diagonal Heisenberg exchange coupling constants that are opposite in sign to the corresponding off-diagonal ones.
Extremely low ordered moments are therefore possible at weak enough Hund’s rule coupling, \( J_0 < 0 \), when off-diagonal frustration exists: \( J_2^\alpha,\beta > 0 \) at \( \alpha \neq \beta \). The hidden order that is responsible for it is antiferromagnetic, showing two sublattices (see fig. 1). Two spin-wave quanta per momentum \( \hbar \mathbf{k} \) are then expected at \( \hbar \omega_{\text{sw}} \) above the groundstate energy. Here, \( \omega_{\text{sw}} \) is the natural frequency, which is obtained by linearizing the dynamical equation for classical precession by each spin-1/2 moment, \( \dot{S}_i(\alpha) = S_i(\alpha) \times \partial H/\partial S_i(\alpha) \). In the simple case where all diagonal Heisenberg exchange coupling constants are null, it has the form:

\[
\omega_{\text{sw}}(\mathbf{k}) = (\Omega_+ + \Omega_-)^{1/2},
\]

where \( \mathbf{k}' = \mathbf{k} \) or \( \mathbf{k} - (\pi/a, \pi/a) \) and where cfn = cos or sin, respectively, in the case of hidden ferromagnetic order or hidden Néel order per orbital, at off-diagonal \( J_1 > 0 \) or \( J_1 < 0 \). Above, \( k'_n = k'_x + k'_y, a \) denotes the square lattice constant, and \( s \) is the electron spin. Figure 1 depicts these spectra at maximum off-diagonal frustration \( J_2 = |J_1|/2 \). The spin-wave velocity is then equal to \( c_{\text{sw}} = s a[2(|J_1| + 2J_2)(J_0 + 4 \theta(J_1)J_1 + 4J_2)]^{1/2} \). It collapses to zero at \( J_0 = -4(J_1 + J_2) \) for off-diagonal \( J_1 > 0 \) and at \( J_0 = -4J_2 \) for off-diagonal \( J_1 < 0 \), which serve as stability bounds for hidden ferromagnetic and Néel order, respectively.

The above results indicate that large enough off-diagonal frustration in the \( J_0-J_1-J_2 \) model induces a quantum phase transition into hidden magnetic order that is unfrustrated, but that violates Hund’s rule. We shall now study how the low-energy spectrum of states for the \( J_0-J_1-J_2 \) model, with two spin-1/2 moments per site, evolves with the strength of the Hund’s rule coupling by applying the Lanczos technique numerically on a 4 by 4 square lattice with periodic boundary conditions. As usual, we restrict the Hilbert space to states with equal numbers of up and down spins. Next, translational invariance is exploited to reduce the Hamiltonian to block diagonal form, with each block labeled by a momentum quantum number. The allowed wave numbers, \( (k_x a, k_y a) \) are then \((0, 0), (\pi, 0), (\pi, \pi), (\pi/2, 0), (\pi/2, \pi/2) \) and \( (\pi, \pi/2) \), plus their symmetric counterparts. The associated translational symmetry reduces the dimension of each block to a little under 38,000,000 states. Spin-flip symmetry can then be exploited to further block-diagonalize the Hamiltonian at such momenta into two blocks that are respectively even and odd under it. The dimension
of each of these subspaces is then a little under 19,000,000 states. Each term in the Hamiltonian (1) permutes these Bloch-wave type states, and the permutations are stored in memory. Also, the value of the matrix element for Bloch waves that are composed of configurations of spin up and spin down that display absolutely no non-trivial translation invariance is stored in memory, while it is calculated otherwise. This speeds up the application of the Hamiltonian operator tremendously because the vast majority of Bloch waves lie in the first category. The application of the Hamiltonian $H$ on a given state is accelerated further by enabling shared-memory parallel computation through OpenMP directives. Last, we use the ARPACK subroutine library to apply the Lanczos technique on the block-diagonal Hamiltonian operator just described [9].

Figures 2 and 3 show how the low-energy spectrum of the $J_0$-$J_1$-$J_2$ model (1) evolves with the strength of the Hund’s rule coupling in the case of maximum off-diagonal frustration: $J_1^{\alpha,\alpha} = 0 = J_2^{\alpha,\alpha}$, while $J_1^{\alpha,\beta} = J_1$ and $J_2^{\alpha,\beta} = |J_1|/2$ for $\alpha \neq \beta$. Respectively, they correspond to ferromagnetic and to antiferromagnetic nearest-neighbor Heisenberg exchange, $J_1 < 0$ and $J_1 > 0$. Notice first the coincidence at weak Hund’s rule coupling, $J_0 = 0$, between the previous linear spin-wave approximation about hidden-order shown in fig. 1 with the present exact-diagonalization results. It suggests that long-range hidden magnetic order indeed exists. Second, notice that the lowest energy spin-1 excitation is not the first but the second excited state at strong Hund’s rule coupling. This suggests that a nonzero spin gap exists at maximum magnetic frustration. We have checked that the low-energy spectrum of the corresponding $J_1$-$J_2$ model at spin $s = 1$ is very similar by setting $J_1^{(1(2)} = J_1^{(2)}$. Both a spin-wave analysis at large spin $s$ [10] and series-expansion studies [11] at $s = 1/2$ find a spin gap at maximum frustration for the $J_1$-$J_2$ model. The spin gap then likely persists at $s = 1$, which argues in favor of a spin gap in the present off-diagonal case. Both sets of spectra are then consistent with a transition from a magnetically frustrated state that shows a spin gap, but that obeys Hund’s rule, to an unfrustrated hidden-order state that violates Hund’s rule. Figures 4 (A) and 5 (A) display level crossings of the lowest-energy spin excitations, which are consistent with such a quantum phase transition. It can be shown that a transition into hidden magnetic order from true magnetic order of collinear or of Néel type is expected at $J_0 = -2|J_1|$ for maximum frustration, $J_2 = |J_1|/2$, in the classical limit at large spin $s$.

Figures 4 (B) and 5 (B) also show the evolution of relevant magnetic order parameters with Hund’s rule coupling. They further confirm the interpretation that a quantum phase
transition into hidden order takes place near $J_0 = -2|J_1|$. The ordered moment is obtained here by computing the autocorrelation $\langle O(k)_{\pm} \cdot O(-k)_{\pm} \rangle_0$ of the order parameter

$$O(k)_{\pm} = \sum_i e^{i k \cdot r_i} [S_i(1) \pm S_i(2)]$$

over the groundstate. Figure 4 (B), in particular, displays how the square of the ordered moment for true collinear/SDW order (+) decays once the system transits into hidden order at off-diagonal $J_1 < 0$. Figure 5 (B) displays how the same occurs for true Néel order ($\times$) at off-diagonal $J_1 > 0$. The former is notably consistent with the low ordered moment that is observed by elastic neutron diffraction in an undoped parent compound to the recently discovered Fe-As high-$T_c$ superconductors. It must be emphasized, however, that the low-energy spectrum of hidden order contains observable spin-wave excitations with energies that collapse to the groundstate energy either at the Néel wave number ($\pi, \pi$), or at the ferromagnetic wave number (0, 0). (See figs. 1 - 3.)

Recent inelastic neutron scattering measurements on an undoped parent compound of Fe-As superconductors find a small spin gap at the collinear/SDW wave number ($\pi, 0$) on the other hand. Figures 4 and 6 (A) are consistent with both a reduced moment for collinear/SDW order and a small spin gap at ($\pi, 0$) at the transition into hidden Néel order for off-diagonal $J_1 < 0$. The undoped parent compounds of Fe-As superconductors could then lie at the transition point into hidden magnetic order.

In conclusion, we have identified a route to low ordered magnetic moments in the undoped parent compounds of the recently discovered Fe-As superconductors that is based on the weakening of Hund’s rule by frustrating Heisenberg exchange interactions between different 3$d$ orbitals in neighboring iron atoms. We predict, however, that the spin-wave excitation energy vanishes either at the wave number ($\pi, \pi$) or at the wave number (0, 0) deep inside the respective hidden-order phases where Hund’s rule is violated. (Cf. ref. [6].)

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FIG. 1: The linear spin-wave spectrum for the Hamiltonian (1) is displayed in units of $|J_1|$ at off-diagonal $J_1 < 0$ and $J_1 > 0$ respectively, at off-diagonal $J_2 = |J_1|/2$, and with no Hund’s rule coupling acting on two orbitals per site. Hereafter, we set $\hbar \to 1$. 
FIG. 2: Shown is the low-energy spectrum for $4 \times 4 \times 2$ spin-$1/2$ moments that experience off-diagonal ferromagnetic and frustrating Heisenberg exchange at weak and at moderately strong Hund’s rule coupling. The lowest-energy spin-1 state at momentum $(\pi, \pi)$ is used as the reference for the linear spin-wave approximation.
FIG. 3: Shown is the low-energy spectrum for $4 \times 4 \times 2$ spin-1/2 moments that experience off-diagonal anti-ferromagnetic and frustrating Heisenberg exchange at weak and at moderately strong Hund’s rule coupling. The lowest-energy spin-1 state at momentum $(0, 0)$ is used as the reference for the linear spin-wave approximation.
FIG. 4: The evolution of the spin gap with Hund’s rule coupling at wave numbers that correspond to collinear and to Néel order is shown for off-diagonal $J_1 < 0$ and off-diagonal $J_2 = |J_1|/2$. Also shown is the autocorrelation $\langle \mathbf{O}(\mathbf{k})_\pm \cdot \mathbf{O}(-\mathbf{k})_\pm \rangle_0$ of the order parameter (2) for true (+) and for hidden (-) magnetic order as a function of Hund’s rule coupling. It is normalized to its value in the true ferromagnetic state.
FIG. 5: The spin gap at wavenumbers corresponding to ferromagnetic and to Néel order are displayed as a function of Hund’s rule coupling for off-diagonal $J_1 > 0$ and off-diagonal $J_2 = J_1/2$. Also displayed is the autocorrelation of the order parameter $\langle \sigma \rangle^2$ versus Hund’s rule coupling. It is normalized to its value in the true ferromagnetic state.
FIG. 6: Shown is the low energy spectrum for $4 \times 4 \times 2$ spin-$1/2$ moments that experience maximum off-diagonal frustration near the transition point into hidden order.