Antiferromagnetic order in multi-band Hubbard models for iron-pnictides

T. Schickling, F. Gebhard, and J. Bünnemann

Fachbereich Physik, Philipps Universität, Renatnof 6, 35032 Marburg, Germany
Institut für Physik, BTU Cottbus, P.O. Box 101344, 03013 Cottbus, Germany
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We investigate multi-band Hubbard models for the three iron 3d-\(t_{2g}\) bands and the two iron 3d-\(e_g\) bands in LaOFeAs by means of the Gutzwiller variational theory. Our analysis of the paramagnetic ground state shows that neither Hartree–Fock mean-field theories nor effective spin models describe these systems adequately. In contrast to Hartree–Fock-type approaches, the Gutzwiller theory predicts that antiferromagnetic order requires substantial values of the local Hund’s-rule exchange interaction. For the three-band model, the antiferromagnetic moment fits experimental data for a broad range of interaction parameters. However, for the more appropriate five-band model, the iron \(e_g\) electrons polarize the \(t_{2g}\) electrons and they substantially contribute to the ordered moment.

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Since their recent discovery, the iron-based high-\(T_C\) superconductors have attracted tremendous attention both in theory and experiment. From a theoretical point of view, these systems are of particular interest because their conduction electrons are less correlated than those of other high-\(T_C\) superconductors. In contrast to the cuprates, the pnictides’ undoped parent compounds are antiferromagnetic metals at low temperatures, not insulators. However, the electronic mass is enhanced by a factor of two which indicates that electronic correlations are quite substantial in the pnictides, too.

The theoretical description of the pnictides’ normal phase turned out to be a difficult problem. Standard density-functional theory (DFT) grossly overestimates the size of their magnetic moment in the antiferromagnetic ground state. For example, in LaOFeAs experiment finds a staggered moment of \(m = (0.4 \ldots 0.8)\mu_B\) whereas DFT calculations predict moments of \(m \approx 1.8\mu_B\) or larger \([4,5]\). For other pnictide compounds, the comparison is equally unfavorable.

Perturbative many-electron theories for the pnictides face the problem that all five iron 3d-bands contribute significantly to the band structure near the Fermi energy. Even when the effective Hubbard interaction \(U\) between pairs of electrons on the same iron atom is smaller than the effective 3d bandwidth \(W\), \(U \lesssim W/2\), atomic charge fluctuations with ionization degree \(\Delta N > U/W\) are improbable in the ground state. The description of itinerant antiferromagnetism in such correlated multi-band systems is beyond perturbative mean-field approximations such as Hartree–Fock (HF) theory. In studies based on dynamical mean-field theory (DMFT), only the paramagnetic phases of these models could be investigated so far, see e.g., Ref. \([6]\).

In this work, we employ the Gutzwiller variational theory (GT) which describes the ground state and quasiparticle excitations of multi-band Fermi liquids; for an application to nickel, see Refs. \([3,5]\). As compared to DMFT, our method is numerically much less costly. This enables us to resolve the small energy differences between the paramagnetic and antiferromagnetic phases in the pnictides (Néel temperature \(T_N \approx 140\) K). From our study of a five-band model for the iron 3d-\(t_{2g}\) and 3d-\(e_g\) bands we find that the paramagnetic phase is much more stable than predicted by DFT or HF calculations. Only for large values of the local exchange interaction, an antiferromagnetic ground state is found; in a related study \([3]\), only paramagnetic states were examined.

We investigate the two-dimensional five-band Hubbard model

\[
\hat{H} = \sum_{i,j,b,b',\sigma} t_{i,j}^{b,b'} c_{i,b,\sigma}^\dagger c_{j,b',\sigma} + \sum_i \hat{H}_{C,i} \equiv \hat{H}_0 + \hat{H}_{\text{loc}},
\]

where \(\hat{H}_0\) describes the transfer of electrons with spin \(\sigma = \uparrow,\downarrow\) between iron atoms on lattice sites \(i, j\) in the 3d-\(e_g\)-\(t_{2g}\) orbitals \(b, b'\). The transfer parameters \(t_{i,j}^{b,b'}\) are taken from Ref. \([10]\). The bare bandwidth of the 3d electrons is \(W = 4.8\) eV, and there are, on average, six electrons on every iron atom. The local Hamiltonian \(\hat{H}_{C,i}\) describes the Coulomb interaction of the iron electrons. Frequently the following form for the Hubbard interaction is employed,

\[
\hat{H}_{C}^{(3)} = \hat{H}_{\text{dens}}^{C} + \hat{H}_{\text{Coul}}^{C},
\]

\[
\hat{H}_{\text{dens}}^{C} = \sum_{b,\sigma} U(b,b) \hat{n}_{b,\sigma} \hat{n}_{b,\sigma} + \sum_{b(b')\sigma,\sigma'} \tilde{U}_{\sigma,\sigma'}(b,b') \hat{n}_{b,\sigma} \hat{n}_{b',\sigma'},
\]

\[
\hat{H}_{\text{Coul}}^{C} = \sum_{b(b')\sigma,\sigma'} J(b,b') \left( \hat{c}_{b,\sigma}^\dagger \hat{c}_{b',\sigma'} + \text{h.c.} \right) + \sum_{b(b')\sigma,\sigma'} J(b,b') \hat{c}_{b,\sigma}^\dagger \hat{c}_{b',\sigma} + \text{h.c..}
\]

Here, we dropped the lattice-site indices and introduced the abbreviations \(\hat{\uparrow} = \downarrow = \uparrow\), and \(\tilde{U}_{\sigma,\sigma'}(b,b') = U(b,b') - \delta_{\sigma,\sigma'} J(b,b')\), where \(U(b,b')\) and \(J(b,b')\) are the local Coulomb and exchange interactions.
Even in cubic symmetry, however, the Hamiltonian (2) is incomplete. The full Hamiltonian reads \( \hat{H}_C = \hat{H}_C^{(1)} + \hat{H}_C^{(2)} \) with

\[
\hat{H}_C^{(2)} = \left[ \sum_{t, \sigma, \sigma'} (T(t) - \delta_{\sigma, \sigma'} A(t)) \hat{n}_{t, \sigma} \hat{c}_{u, \sigma}^\dagger \hat{c}_{v, \sigma'} \right. \\
+ \sum_{t, \sigma} A(t) \left( \hat{c}_{t, \sigma}^\dagger \hat{c}_{t', \sigma} \hat{c}_{u, \sigma} \hat{c}_{v, \sigma'} + \hat{c}_{t, \sigma}^\dagger \hat{c}_{t', \sigma} \hat{c}_{u, \sigma} \hat{c}_{v, \sigma'} \right) \\
+ \sum_{t \neq t' \neq t'' \neq t'''} S(t; t'; t''; e) \hat{c}_{t, \sigma}^\dagger \hat{c}_{t', \sigma} \hat{c}_{v', \sigma'} \hat{c}_{v, \sigma'} + \text{h.c.}
\]

Here, \( t \) and \( e \) are indices for the three \( 2g \) orbitals with symmetries \( xy, xz, \) and \( yz \), and the two \( eg \) orbitals with symmetries \( u = 3z^2 - r^2 \) and \( v = x^2 - y^2 \). The parameters in (3) are of the same order of magnitude as the exchange interactions \( J(b, b') \) and, hence, there is no a-priori reason to neglect them. Of all the parameters \( U(b, b'), J(b, b'), A(t), T(t), S(t, t'; t''; e) \) only ten are independent in cubic symmetry. In a spherical approximation, they are all determined, e.g., by the three Racah parameters \( A, B, C \). For details on the multiplet structure of \( d \)-shells we refer to Sugano’s textbook [11].

In this work, we work with the orbital averages \( J \propto \sum_{b \neq b'} J(b, b') \) and \( U' \propto \sum_{b \neq b'} U(b, b') \) of the exchange and the inter-orbital Coulomb interaction. They are related to the intra-orbital interaction \( U = U(b, b) \) via \( U' = U - 2J \). Due to this symmetry relation, the three values of \( U, U' \), and \( J \) do not determine the Racah parameters \( A, B, C \) uniquely. Therefore, we further assume that the approximate atomic relation \( C/B = 4 \) is satisfied in solids, too. In this way, the three Racah parameters and, consequently, all parameters in \( \hat{H}_C \) are functions of \( U \) and \( J \). This permits a meaningful comparison of our results with those of previous work which, as an additional approximation, the parameters \( U(b, b'), J(b, b') \) were assumed to be orbital independent, see, e.g., Ref. [6].

We note that the Gutzwiller method is applicable to the general form (1) of the atomic Hamiltonian. We approximate the true ground state of \( \hat{H} \) in (1) by the Gutzwiller variational wave function

\[
|\Psi_G\rangle = \hat{P}_G |\Psi_0\rangle = \prod_i \hat{P}_i |\Psi_0\rangle ,
\]

where \( |\Psi_0\rangle \) is a single-particle product state, and the local ‘Gutzwiller correlator’ is defined as

\[
\hat{P}_i = \sum_{\Gamma} \lambda_\Gamma |\Gamma\rangle_i \langle \Gamma | .
\]

Here, we introduced variational parameters \( \lambda_\Gamma \) for each of the atomic multiplet states \( |\Gamma\rangle_i \), i.e., the eigenstates of \( \hat{H}_{C,i} \). Note that the single-particle state \( |\Psi_0\rangle \) is also a variational object which we determine from the minimization of the variational energy functional that results from the wave functions (1). The Hartree–Fock theory is a special case of the Gutzwiller theory which we obtain by setting \( \lambda_\Gamma = 1 \) for all \( |\Gamma\rangle \).

The evaluation of expectation values with respect to (1) poses a difficult many-particle problem. As shown in Refs. [12, 13], it can be solved exactly in the limit of infinite spatial dimensions. The analytic energy functional derived in this limit can be used as an approximation for finite dimensional systems. On top of the approximate ground-state description which is provided by the Gutzwiller wave function one can also calculate quasi-particle band structures for a comparison with data from single-resolved photoemission spectroscopy (ARPES) [14].

The Gutzwiller energy functional contains two different sets of variational parameters. The local multiplet occupations are governed by the parameters \( \lambda_\Gamma \) in the correlation operator \( \hat{G}_\Gamma \). As shown in Refs. [13, 14], the single-particle wave function \( |\Psi_0\rangle \) is the ground state of an effective single-particle Hamiltonian

\[
\hat{H}_0^{\text{eff}} = \sum_{i,j,b,b'} \eta_{i,j}^{b,b'} \hat{c}_{i,b,\sigma}^\dagger \hat{c}_{j,b',\sigma} + \sum_{i,b,b';\sigma} \eta_{i,b}^{b,b'} \hat{c}_{i,b,\sigma}^\dagger \hat{c}_{i,b',\sigma} + \sum_{i,j,b,b'} \tilde{\eta}_{i,j}^{b,b'} \hat{c}_{i,b,\sigma}^\dagger \hat{c}_{j,b',\sigma}
\]

with renormalized electron transfer parameters \( \tilde{\eta}_{i,j}^{b,b'} \) and variational parameters \( \eta_{i,b}^{b,b'} \) which govern the orbital and spin dependent local densities. There are \( N_\Delta = 2^{10} = 1024 \) parameters \( \lambda_\Gamma \) while the number of parameters \( \eta_{i,b}^{b,b'} \) is much smaller, \( N_{\eta,b} = 5 \) for the paramagnetic case and \( N_{\eta,b} = 10 \) for the antiferromagnetic case. Nevertheless, the minimization of the energy functional with respect to the parameters \( \eta_{i,b}^{b,b'} \) is numerically expensive because any change of these parameters results in a minimization cycle with a full momentum-space integration. In order to obtain the required energy resolution, these integrals have been calculated on a momentum-space grid with up to \( 3 \cdot 10^5 \) triangles in the Brillouin zone.

In order to test the reliability of our approach for the five-band model, we first compare our results for the partial densities with those from paramagnetic DMFT calculations. In Fig. 1 we show the density of electrons in each orbital as a function of \( U \) for fixed ratio \( U/J = 4 \). The full symbols give the GT result for the simplified local Hamiltonian (2), \( \hat{H} = \hat{H}_0 + \hat{H}_C^{(1)} \); open symbols give the DMFT results. Obviously, the agreement between the GT and DMFT is very good despite the fact that the particle number is not perfectly conserved in the DMFT calculations [15].

Fig. 1 shows a common feature of multi-band model systems. The local Coulomb interaction induces a substantial charge flow between the bands because, for the local Coulomb interaction, it is energetically more favorable to distribute electrons equally among the bands. However, the bands described by \( \hat{H}_0 \) are usually extracted from a DFT calculation whose predictions for
the Fermi surface reproduce experimental data reasonably well. Therefore, we argue that the artificial charge flow as seen in Fig. 1 is a consequence of the double counting of Coulomb interactions. Since the (paramagnetic) Fermi surface found in DFT reproduces its experimentally determined shape, we assume that the same holds for the paramagnetic orbital densities. For each value of the interaction parameters we therefore choose orbital on-site energies \( \epsilon_i = t_{i,i} \) which lead to a paramagnetic ground state with the same orbital densities as in DFT.

Next, we investigate the local charge distribution and spin distribution in the paramagnet. In Fig. 2, we show the probabilities to find an atom with \( 0 \leq n \leq 10 \) electrons in \(|\Psi_G^{\text{opt}}\rangle\) for \( U = 2.6 \) eV and \( J = 0.4 \) eV. As seen from Fig. 2, local charge fluctuations with \( \Delta N = |N - 6| > 2 \) are essentially forbidden. Hartree–Fock-type mean-field approximations cannot describe this effect properly. The probabilities to find the local spins \( 0 \leq s \leq 5/2 \) in \(|\Psi_G^{\text{opt}}\rangle\) are shown in in Fig. 2. The broad spin distribution in Gutzwiller theory is very similar in Hartree–Fock theory and shows that the system is far from the local-moment situation where we would solely find atoms with Hund’s-rule spin \( s = 2 \). Consequently, the elementary excitations of the five-band Hamiltonian \(|\Psi\rangle\) with parameters from Ref. [10] and \((U = 2.6 \) eV, \( J = 0.4 \) eV) are not well approximated by an effective spin model.

We now turn to the magnetic properties of our five-band model \(|\Psi\rangle\). As seen in Fig. 3, Hartree–Fock theory predicts an antiferromagnetic phase for moderate \( 2.2 \) eV \( \leq U \leq 3.0 \) eV for all \( J > 0 \). The HF moments are strongly orbital dependent. For small values of \( J \), these moment are anti-aligned which leads to a phase with a small total moment. At critical values \( J = J_c(U) \), the HF moments align which results in a large-moment phase. Similar phases have been reported in LDA+U calculations [10].

Our Gutzwiller theory shows that the correlated paramagnetic state is stable over a wide range of Coulomb and exchange-interaction parameters, e.g., \( J \lesssim 0.4 \) eV for \( 2.2 \) eV \( \leq U \leq 3.0 \) eV in Fig. 3. The small-\( J \) phase with orbital-dependent moments as seen in Hartree–Fock theory is absent. The robustness of the paramagnetic phase against symmetry breaking is in agreement with earlier findings [17] that Hartree–Fock theory generally overrates the importance of orbitally ordered phases in the ground state of multi-band systems.

In Gutzwiller theory, the transition to an antiferromagnet with a large moment, \( m \gtrsim 2 \mu_B \), is as abrupt as in Hartree–Fock theory. As seen in Fig. 3 we find an antiferromagnetic state with a small moment \( m = 0.4 \mu_B \) only in a small region of parameter space, e.g., \( U = 2.2 \) eV and \( 0.42 \) eV \(< J < 0.45 \) eV. Since this region in the \( U-J \) parameter space is fairly small, we do not consider it very likely that the iron pnictides fall into this parameter region. The explanation for their small antiferromagnetic moment should have a more natural explanation.

We have extended our analysis to a broader class of variational wave functions where we included the mixing of atomic configurations in the Gutzwiller correlator \(|\Gamma\rangle\) of the form \( \lambda_{\Gamma,\Gamma'} |\Gamma\rangle_i |\Gamma'\rangle_j \) for \( \Gamma \neq \Gamma' \). In order to keep the problem numerically tractable, we considered the dom-
inent 500 couplings for which $|\langle \Psi_{\text{opt}}^{G} | \Gamma_{ii} \langle \Gamma' | \Psi_{\text{opt}}^{G} \rangle |^2$ is largest in the paramagnetic Gutzwiller state $| \Psi_{\text{opt}}^{G} \rangle$. The inclusion of these additional variational parameters lowered the energies of the paramagnetic and the antiferromagnetic optimal states by almost equal amounts so that the phase diagram does not change noticeably. In particular, the region in phase space with a low magnetic moment increases only marginally.

Our findings for the five-band model contrast those of a recent study of a three-band model for the pnictides \cite{18} where the authors report a small magnetic moment over a large region of Coulomb and exchange interactions. In that study, the two 3$d$-$e_g$-bands and their interactions $H_C^{(2)}$ with the 3$d$-t$_{2g}$-bands, eq. \eqref{2}, were not considered. Moreover, the spin-flip and pair-exchange terms in the local Hamiltonian, the terms $H_C^{\text{sf}}$ in eq. \eqref{2}, have been neglected.

In Fig. 4 we show the Gutzwiller prediction for the magnetic moments of the three-band model as a function of $J$ for $U = 2.2 \text{ eV}, 2.6 \text{ eV}, 3.0 \text{ eV}$. Full symbols: GT with the full local interaction $H_C = H_C^{(1)} + H_C^{\text{sf}}$, \eqref{2}; open symbols: GT with density-interactions only, $H_C = H_C^{\text{dens}}$, cf. \cite{18}.

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