Ground state ferromagnetism in a doubly orbitally degenerate model

L. Didukh, Yu. Skorenkyy, V. Hankevych, and O. Kramar
Ternopil State Technical University, Department of Physics,
56 Rus’ka Str., Ternopil UA-46001, Ukraine
(October 31, 2018)

In the present paper the ground state of a double orbitally degenerate model at weak intra-atomic interaction is studied using the Green functions method. Beside the diagonal matrix elements of electron-electron interactions the model includes correlated hopping integrals and inter-atomic exchange interaction. The influence of orbital degeneracy with Hund’s rule coupling, correlated hopping and inter-atomic direct exchange on the ferromagnetic ordering is investigated. The expressions for ground state energy and magnetization, the criterion of transition from paramagnetic to ferromagnetic ground state as functions of the model parameters are obtained. The obtained results are compared with some experimental data for magnetic materials.

I. INTRODUCTION

The problem of an origin of the metallic ferromagnetism, in spite of the variety of theoretical attempts to solve it, still remains open. Nowadays we can distinguish a few ways to obtain the ferromagnetic solution. First, one can consider the Hubbard model which describes itinerant electrons in a single non-degenerate band interacting via on-site Coulomb repulsion $U$. Within this model the ferromagnetic solution has been obtained by means of some approximations, also the exact result of Nagaoka shows that the ground state of a band with exactly one electron above or below half-filling is ferromagnetic at $U = \infty$. However, in spite of the large number of papers (for recent reviews see Refs. [4,7]) the question of an existence of ferromagnetic ordering in the Hubbard model is still under discussion. Second, one can include in a model Hamiltonian, in addition to the intra-atomic Coulomb repulsion, also other matrix elements of electron-electron interaction, which can provide new mechanisms of ferromagnetism stabilization. Third, one can take into consideration the orbital degeneracy with the intra-atomic Hund’s rule exchange interaction which forms atomic magnetic moments. Taking into consideration the orbital degeneracy is essentially important: in the case of strong intra-atomic interactions the kinetic superexchange has a ferromagnetic nature, in contrast with the single-band Hubbard model where it has an antiferromagnetic one. We believe that at least for understanding of the ferromagnetism origin in crystals with narrow energy bands it is enough to consider other matrix elements of electron correlations (in addition to the intra-atomic Coulomb repulsion) and orbital degeneracy with intra-atomic Hund’s rule exchange.

The importance of orbital degeneracy and Hund’s rule exchange interaction for ferromagnetism was first suggested by Slater and van Vleck: the presence of orbital degeneracy and Hund’s rule exchange interaction leads to so-called “atomic ferromagnetism”; in such a situation translational motion of electrons forces the spins of electrons on nearest-neighbour atoms to align in parallel. This mechanism of ferromagnetism based on a microscopic model was studied by Roth considering the Hubbard model with double orbital degeneration. In Refs. [4,5] it was found that ferromagnetism in such two-band Hubbard model coexists with orbital ordering for the case of a quarter-filled band and strong intra-atomic interactions. Moreover, recently Spa/suppress lek with co-workers have proposed the mechanism of a coexisting ferromagnetism and spin-triplet paired state in a doubly orbitally degenerate band due to the intra-atomic Hund’s rule coupling. The problem of metallic ferromagnetism in the two-band Hubbard model has attracted much attention of researchers in a series of papers by means of the dynamical mean-field theory, the slave boson method and the Gutzwiller variational wave function approximation. They all find ferromagnetism to be stabilized by intra-atomic Hund’s rule coupling at intermediate and strong intra-atomic Coulomb interactions. On the other hand, the authors have obtained that intra-atomic Hund’s rule exchange does not play the important role in ferromagnetic ordering of crystals with narrow energy bands, and even may destabilize ferromagnetism. In particular, Hirsch suggests that orbital degeneracy and intra-atomic exchange interaction are not likely to play a significant role in the ferromagnetic ordering of Ni or Ni-Cu and Ni-Zn alloys, and a single-band model with inter-atomic direct exchange contains the essential physics of metallic ferromagnetism of transition metal compounds. Nolting and co-workers have obtained that magnetization of the doubly orbitally degenerate Hubbard model strongly decreases with increasing intra-atomic Hund’s rule exchange for a wide range of model parameters, namely the intra-atomic exchange coupling substantially suppresses ferromagnetic order.

In the cited above papers the authors have not took into consideration so-called “off-diagonal” matrix elements of electron-electron interaction which are one of the possible mechanisms of ferromagnetism in narrow energy bands as mentioned above. The importance of these matrix elements in a single-band case was pointed out in many
works [16,26,33]. Here we note the special role of direct exchange interaction and correlated hopping (taking into account of the inter-atomic density-density Coulomb interaction which plays the essential role in charge ordering goes beyond the goal of this article). Last ten years the problem of importance of inter-atomic exchange interaction for the metallic ferromagnetism again is under discussion in number of works [16,26,33], where it was concluded that the inter-atomic exchange interaction \( J \) plays a fundamental role for the stabilization of ferromagnetic ordering in a single-band model. The authors found that the inter-atomic direct exchange \( J > 0 \) stabilizes ferromagnetic ordering in the single-band Hubbard model at intermediate to strong intra-atomic Coulomb interactions [16,26,33]. In the case of weak interactions the inter-atomic exchange is important for the stabilization of incomplete ferromagnetism [27,30]. Hirsch [31] argued that the inter-atomic exchange interaction is the main driving force for metallic ferromagnetism in systems like iron, cobalt and nickel. Also for the special cases of generalized Hubbard models it has been found [22,33] by means of exact techniques that inter-atomic exchange plays a dominant role in the occurrence of ferromagnetism.

The importance of correlated hopping for understanding of the metallic ferromagnetism in narrow energy band was discussed in Refs. [6,26,27,28,29,30,33,35]. In particular, a generalization of Nagaoka’s theorem has been proved [33], and it has been shown [30,31] that in strong coupling regime close to half-filling correlated hopping favours ferromagnetism stronger for electron-like carriers than for hole-like carriers (the reverse situation occurs at weak interactions [33]). Note, that due to an additional mechanism of correlated hopping [27] at weak intra-atomic interactions the situation, which is analogous to that of strong interactions, can be realized: correlated hopping favours ferromagnetism stronger for electron-like carriers versus hole-like carriers (see also Section 3).

In this connection, the necessity of a further study of the metallic ferromagnetism problem in narrow energy bands is obvious. Firstly, it is interesting and important to find how the orbital degeneracy with intra-atomic Hund’s rule coupling and “off-diagonal” matrix elements of electron-electron interaction (correlated hopping and inter-atomic direct exchange interaction) in the aggregate show itself. Note that these studies were performed partially in Ref. [24] by means of exact diagonalization, in particular, for the case of small one-dimensional chains and strong intra-atomic Coulomb repulsion the role of orbital degeneracy with intra-atomic Hund’s rule coupling and inter-atomic exchange interaction for the ferromagnetic ordering was studied. However, the results depend sensitively on the number of lattice sites and the boundary conditions, on the one hand, and the study is restricted to the one-dimensional case, on the other hand. Secondly, there is a contradiction about the role of intra-atomic Hund’s rule interaction for the stabilization of ferromagnetic ordering, as mentioned above. Therefore, the present paper is devoted to the study of the metallic ferromagnetism problem.

The structure of the paper is the following. In Section 2 we formulate the Hamiltonian of the doubly orbitally degenerate Hubbard model which is generalized by taking into account correlated hopping and inter-atomic exchange interaction. For the case of weak intra-atomic interactions the single-particle Green function and energy spectrum at arbitrary values of electron concentration are derived by means of the mean-field approximation. In Section 3 the ferromagnetism in ground state of the model is investigated. The role of orbital degeneracy with intra-atomic Hund’s rule coupling, of correlated hopping, and of inter-atomic direct exchange interaction for the stability of ferromagnetic ordering is studied. The expressions for ground state energy and magnetization as functions of the model parameters, the criterion of transition from paramagnetic to ferromagnetic ground state are derived by means of the mean-field approximation. In Section 3 the ferromagnetism in ground state of the model is investigated. The role of orbital degeneracy with intra-atomic Hund’s rule coupling, of correlated hopping, and of inter-atomic direct exchange interaction for the stability of ferromagnetic ordering is studied. The expressions for ground state energy and magnetization as functions of the model parameters, the criterion of transition from paramagnetic to ferromagnetic ground state are found. Finally, Section 4 is devoted to the conclusions from the obtained results.

II. GREEN FUNCTION AND ENERGY SPECTRUM OF THE MODEL IN THE CASE OF WEAK INTERACTION

Let us generalize the Hamiltonian proposed in work [37] by taking into account the inter-atomic exchange interaction:

\[
H = -\mu \sum_{i\gamma\sigma} a_{i\gamma\sigma}^+ a_{i\gamma\sigma} + \sum_{ij\gamma\sigma} t_{ij}(n) a_{i\gamma\sigma}^+ a_{j\gamma\sigma} + \sum_{ij\gamma\sigma} (t'_{ij} a_{i\gamma\sigma}^+ a_{j\gamma\sigma} n_{i\bar{\gamma}} + h.c.) \\
+ \sum_{ij\gamma\bar{\sigma}} (t''_{ij} a_{i\gamma\sigma}^+ a_{j\gamma\bar{\sigma}} n_{i\bar{\gamma}} \bar{\sigma} + h.c.) + U \sum_{i\gamma} n_{i\gamma\uparrow} n_{i\gamma\downarrow} + U' \sum_{i\sigma} n_{i\sigma\sigma} n_{i\bar{\sigma}} \\
+ (U'' - J_0) \sum_{i\sigma} n_{i\sigma\sigma} n_{i\bar{\sigma}} + J_0 \sum_{i\sigma} a_{i\sigma\sigma}^+ a_{i\bar{\sigma}}^+ a_{i\sigma\bar{\sigma}} a_{i\bar{\sigma}} \\
+ \frac{J}{2} \sum_{i\gamma\gamma'\sigma\sigma'} a_{i\gamma\sigma}^+ a_{i\gamma'\bar{\sigma}}^+ a_{i\gamma\bar{\sigma}} a_{i\gamma'\sigma},
\]

where \( \mu \) is the chemical potential, \( a_{i\gamma\sigma}^+ \), \( a_{i\gamma\sigma} \) are the creation and destruction operators of an electron of spin \( \sigma \) \((\sigma = \uparrow, \downarrow); \bar{\sigma} \) denotes spin projection which is opposite to \( \sigma \) on \( i \)-site and in orbital \( \gamma \) \((\gamma = \alpha, \beta \) denotes two possible orbital
states), $n_{i\gamma\sigma} = a_{i\gamma\sigma}^+ a_{i\gamma\sigma}$ is the number operator of electrons of spin $\sigma$ and in orbital $\gamma$ on $i$-site, $n_{i\gamma} = n_{i\gamma\uparrow} + n_{i\gamma\downarrow}$; $t_{ij}(n)$ is the effective concentration-dependent hopping integral of an electron from $\gamma$-orbital of $j$-site to $\gamma$-orbital of $i$-site (we neglect the electron hoppings between $\alpha$- and $\beta$-orbitals), $t_{ij}'$ includes influence of an electron on $\gamma$-(\(\gamma\)')-orbital of $i$- or $j$-site on hopping process ($\gamma = \beta$ if $\gamma = \alpha$, and $\gamma = \alpha$ when $\gamma = \beta$), the primes at sums in Eq. (2.1) signify that $i \neq j$, $U$ is the intra-atomic Coulomb repulsion of two electrons of the opposite spins at the same site (we assume that it has the same value at $\alpha$- and $\beta$-orbitals), $U'$ is the intra-atomic Coulomb repulsion of two electrons of the opposite spins at the different orbitals, $J_0$ is the intra-atomic exchange interaction energy which stabilizes the Hund’s states forming the atomic magnetic moments, and $J$ is the inter-atomic exchange interaction. The effective hopping integral $t_{ij}(n)$ is concentration-dependent in consequence of taking into account the correlated hopping $[38]$ of electron.

The peculiarities of the model described by the Hamiltonian (2.1) are taking into consideration the influence of the site occupation on the electron hoppings (correlated hopping), and the direct exchange between the neighbouring sites. In this model an electron hopping from one site to another is correlated both by the occupation of the sites involved in the hopping process and the occupation of the nearest-neighbour sites. The correlated hopping, firstly, renormalizes the initial hopping integral (it becomes concentration- and spin-dependent) and, secondly, leads to an independent on quasiimpulse shift of the subband center, dependent on magnetic and orbital orderings. To characterize the value of correlated hopping we introduce dimensionless parameters $\tau = \frac{t_{ij}(n)}{|t_{ij}|} - 1$, $\tau' = \frac{t_{ij}'}{|t_{ij}|}$, and $\tau_2 = \frac{t_{ij}''}{|t_{ij}|}$ where $t_{ij}$ is the band hopping integral.

The single-particle Green function satisfies the equation

$$\begin{align*}
&E + \mu \langle \langle a_{p\gamma\sigma}^+ | a_{p\gamma\sigma}^\dagger \rangle \rangle E = \frac{\delta_{pp'}}{2\pi} + \sum_{i} t_{ip}(n) \langle \langle a_{i\gamma\sigma}^+ | a_{p\gamma\sigma}^\dagger \rangle \rangle E \\
&+ \sum_{i'\sigma'} t'(ip) \left[ \langle \langle a_{p\gamma\sigma}^+ | a_{p\gamma\sigma}^\dagger | a_{i'\gamma\sigma}^+ \rangle \rangle E + \langle \langle a_{p\gamma\sigma}^+ | a_{i'\gamma\sigma}^\dagger | a_{p\gamma\sigma}^\dagger \rangle \rangle E \right] \\
&+ \langle \langle a_{i'\gamma\sigma}^\dagger a_{i\gamma\sigma}^\dagger | a_{p\gamma\sigma}^\dagger \rangle \rangle E + \langle \langle a_{i'\gamma\sigma}^\dagger a_{i\gamma\sigma}^\dagger | a_{p\gamma\sigma}^\dagger \rangle \rangle E \\
&+ U \langle \langle n_{p\gamma\sigma} | a_{p\gamma\sigma}^\dagger \rangle \rangle E + U' \langle \langle n_{p\gamma\sigma} | a_{p\gamma\sigma}^\dagger \rangle \rangle E + (U' - J_0) \langle \langle n_{p\gamma\sigma} | a_{p\gamma\sigma}^\dagger \rangle \rangle E \\
&+ J_0 \langle \langle a_{i'\gamma\sigma}^\dagger a_{i\gamma\sigma}^\dagger | a_{p\gamma\sigma}^\dagger \rangle \rangle E + \sum_{i'\sigma'} J \langle \langle a_{i'\gamma\sigma}^\dagger a_{i\gamma\sigma}^\dagger | a_{p\gamma\sigma}^\dagger \rangle \rangle E.
\end{align*}
$$

Let us consider the system at weak intra-atomic Coulomb interaction ($U$, $U'$ are smaller than the bandwidth $w = 2z|t_{ij}|$ where $z$ is the number of nearest neighbours to a site). In this case we can take into account electron-electron interactions in the Hartree-Fock approximation:

$$\begin{align*}
&\langle \langle a_{p\gamma\sigma}^+ | a_{p\gamma\sigma}^\dagger \rangle \rangle \approx \langle a_{p\gamma\sigma}^+ | a_{p\gamma\sigma}^\dagger \rangle \langle \langle a_{p\gamma\sigma}^+ | a_{p\gamma\sigma}^\dagger \rangle \rangle E; \\
&\langle \langle a_{i'\gamma\sigma}^\dagger a_{i\gamma\sigma}^\dagger | a_{p\gamma\sigma}^\dagger \rangle \rangle \approx \langle a_{i'\gamma\sigma}^\dagger a_{i\gamma\sigma}^\dagger \rangle \langle \langle a_{p\gamma\sigma}^\dagger | a_{p\gamma\sigma}^\dagger \rangle \rangle E.
\end{align*}
$$

We assume that averages $\langle a_{i\gamma\sigma}^\dagger a_{i\gamma\sigma} \rangle = n_{i\gamma\sigma}$ are independent of the number of a site, i.e. we limit ourselves to a uniform charge and electronic magnetic moment distribution (the problems of antiferromagnetic, orbital and charge orderings will be studied elsewhere).

After the transition to Fourier representation we obtain for the Green function

$$\langle \langle a_{p\gamma\sigma}^+ | a_{p\gamma\sigma}^\dagger \rangle \rangle_k = \frac{1}{2\pi} \frac{1}{E - E_{\gamma\sigma}(k)},$$

where the single particle energy spectrum is

$$E_{\gamma\sigma}(k) = -\mu_{\gamma\sigma} + t_k(n_{\gamma\sigma}),$$

with the shifted chemical potential

$$\mu_{\gamma\sigma} = \mu - \beta'_{\gamma\sigma} - \beta''_{\gamma\sigma} - n_{\gamma\sigma}U - n_{\gamma\sigma}U' - n_{\gamma\sigma}(U' - J_0) + zJ \sum_{\sigma'} n_{\gamma\sigma'},$$
here the shifts of the subband centers are

\[ \beta'_{\gamma} = \frac{2}{N} \sum_{ij\sigma} t'(ij) \langle a_{i\gamma\sigma}^+ a_{j\gamma\sigma} \rangle, \]  \hspace{1cm} (2.7)

\[ \beta''_{\gamma\sigma} = \frac{2}{N} \sum_{ij} t''(ij) \langle a_{i\gamma\sigma}^+ a_{j\gamma\sigma} \rangle ; \]  \hspace{1cm} (2.8)

and the spin- and concentration-dependent hopping integral is

\[ t_k(n_{\gamma\sigma}) = t_k(1 - \tau n - 2\tau' n_{\gamma\sigma} - 2\tau_2 n_{\gamma\bar{\sigma}} - \frac{zJ}{w} \sum_{\sigma'} \langle a_{i\gamma\sigma'}^+ a_{j\gamma\sigma} \rangle), \]  \hspace{1cm} (2.9)

t_k is the Fourier transformant of the hopping integral \( t_{ij} \).

The dependence of effective hopping integral on electron concentration and magnetization, a presence of the spin-dependent shift of subband center are the essential distinctions of single-particle energy spectrum of the model described by Hamiltonian (2.1) from the spectrum of the Hubbard model in the case of weak interaction.

III. FERROMAGNETISM IN THE GROUND STATE OF THE MODEL

The concentration of electrons with spin \( \sigma \) on \( \gamma \) orbital is

\[ n_{\gamma\sigma} = \int_{-\infty}^{+\infty} \rho(\epsilon) f(E_{\gamma\sigma}(\epsilon)) d\epsilon. \]  \hspace{1cm} (3.1)

Here \( \rho(\epsilon) \) is the density of states, \( f(\epsilon) \) is the Fermi distribution function, \( E_{\gamma\sigma}(\epsilon) \) is obtained from respective formula (2.5) substituting \( t_k \rightarrow \epsilon \). Let us assume the rectangular density of states:

\[ \rho(\epsilon) = \frac{1}{N} \sum_k \delta(\epsilon - \epsilon(k)) = \frac{1}{2w} \theta(\epsilon^2 - w^2). \]  \hspace{1cm} (3.2)

In the case of zero temperature we obtain:

\[ n_{\gamma\sigma} = \frac{\epsilon_{\gamma\sigma} + w}{2w}, \]  \hspace{1cm} (3.3)

where the value \( \epsilon_{\gamma\sigma} \) is the solution of the equation \( E_{\gamma\sigma}(\epsilon) = 0 \), from which we obtain \( \epsilon_{\gamma\sigma} = \frac{\mu_{\gamma\sigma}}{a_{\gamma\sigma}}, \) where \( a_{\gamma\sigma} = 1 - \tau n - 2\tau' n_{\gamma\sigma} - 2\tau_2 n_{\gamma\bar{\sigma}} - \frac{zJ}{w} \sum_{\sigma'} n_{\gamma\sigma'}(1 - n_{\gamma\sigma'}). \)

The shifts of subband centers are

\[ \beta'_{\gamma} = \frac{2}{N} \sum_{ij\sigma} t'(ij) \langle a_{i\gamma\sigma}^+ a_{j\gamma\sigma} \rangle = -2\tau' w \sum_{\sigma} n_{\gamma\sigma} (n_{\gamma\sigma} - 1), \]  \hspace{1cm} (3.4)

\[ \beta''_{\gamma\sigma} = \frac{2}{N} \sum_{ij} t''(ij) \langle a_{i\gamma\sigma}^+ a_{j\gamma\sigma} \rangle = -2\tau_2 w n_{\gamma\bar{\sigma}} (n_{\gamma\bar{\sigma}} - 1). \]  \hspace{1cm} (3.5)

From equation (3.3) we obtain for the magnetization \( (m < n) \):

\[ m = \sum_{\gamma} (n_{\gamma\uparrow} - n_{\gamma\downarrow}) \]

\[ = \pm 2 \left( \frac{zJ}{2w} \right)^{\frac{1}{2}} \left( \frac{zJ}{8w} (8 + n(4 - n)) + \frac{U + J_0}{2w} + \tau_1 n + \frac{\tau_2}{2} (4 - n) - 1 \right)^{\frac{1}{2}}, \]  \hspace{1cm} (3.6)

where \( \tau_1 = \tau + \tau' \), here we have assumed that the orbital distribution of electrons is uniform. Note that magnetization (3.6) does not depend on the parameter of intra-atomic Coulomb interaction \( U' \), which leads to the independent on magnetic moment renormalization of the chemical potential (it can be seen also from the expression for ground
state energy). Similarly, in the work \cite{25} is has been argued that this parameter does not play the decisive role in metal ferromagnetism of the transition metal compounds.

The magnetization defined by Eq. \cite{10} is plotted in Fig. 1 as a function of electron concentration \( n \) at different values \( J_0/w \). These dependencies qualitatively agree with results of works \cite{29,30} obtained by use of the Gutzwiller variational functions method. From Fig. 1 one can see that nature of the ground state of the system strongly depends on the values of system parameters; the small changes of \( J_0 \) can lead to the transition from a paramagnetic state to a ferromagnetic one at some values of electron concentration and energy parameters (this result agrees with the results of works \cite{24,27}); note that at some values of parameters the system can be fully polarized. The transition to ferromagnetic state is also possible with the increase of \( n \). Similar transition with the increase of electron concentration has been found by the authors of work \cite{39}.

Taking into account correlated hopping leads to the appearance of a peculiar kinetic mechanism of ferromagnetic ordering stabilization. This mechanism is caused by the presence of the spin-dependent shift of the subband centers being the consequence of correlated hopping (which are similar to the shift of subband centers in consequence of inter-atomic direct exchange interaction).

The influence of correlated hopping on behaviour of the system is illustrated on Fig. 2. In distinction from the two-band Hubbard model there is an asymmetry of the cases \( n < 2 \) and \( n > 2 \). With the increase of parameter \( \tau_1 \) the region of ferromagnetic ordering moves towards larger values of electron concentration \( n \), and with increasing \( \tau_1 \) to smaller values of \( n \). Let us also note that taking into account the correlated hopping significantly enriches the set of curves (illustrating the \( m(n) \) dependencies), which qualitatively describe the experimental Slater-Pauling curves \cite{40} for ferromagnetic alloys.

The peculiarity of degenerate band models is taking into account Hund’s exchange interaction \( J_0 \). The importance of \( J_0 \) is shown in Fig. 3. One can see that intra-atomic exchange stabilizes ferromagnetism in orbitally degenerate band (the behaviour of \( m \) with the increase of \( J_0 \) qualitatively agrees with the dependence of magnetic moment on the intra-atomic correlation strength obtained in work \cite{37}). To describe the real narrow-band materials we have to take into account the correlated hopping which allows to obtain the transition from paramagnetic to ferromagnetic phase at realistic values of \( J_0 \). Fig. 4, which is plotted with use of Eq. \cite{10} at \( \frac{t_1}{w} = 1.2, \frac{t_2}{w} = 0.06 \) and \( \frac{t_2}{w} = 0.2, \tau_1 = 0, \tau_2 = 0.15 \), reproduces the behaviour of the magnetization observed in the systems \( \text{Fe}_{1-x}\text{Co}_x\text{S}_2 \) and \( \text{Co}_{1-x}\text{Ni}_x\text{S}_2 \) with the change of electron concentration in 3\( d \)-band \cite{47}. In these crystals the same subsystem of electrons is responsible both for conductivity and for the localized magnetic moment formation. The noted compounds have the cubic pyrite structure, then 3\( d \)-band is split into two subbands: a doubly degenerate \( e_g \) band and a triply degenerate \( t_{2g} \) band; \( t_{2g} \) band is completely filled and \( e_g \) band is partially filled (the \( e_g \) band filling changes from 0 to 1 in the compound \( \text{Fe}_{1-x}\text{Co}_x\text{S}_2 \) and from 1 to 2 in the compound \( \text{Co}_{1-x}\text{Ni}_x\text{S}_2 \)). One should describe \( e_g \) band of these compounds by a doubly orbitally degenerate model.

The unusual peculiarity of the system \( \text{Fe}_{1-x}\text{Co}_x\text{S}_2 \) is the presence of ferromagnetic ordering at very small values of electron concentration \( n = x \simeq 0.05 \) \cite{11}. Ferromagnetism in this compound has been studied within a single-band model in Refs. \cite{24,43}. The authors of work \cite{24} have proposed an approximation for the description of \( \text{Fe}_{1-x}\text{Co}_x\text{S}_2 \) in the non-degenerate Hubbard model with \( U = \infty \) which provides the ferromagnetic solution even at very small electron concentration (in this connection see also Ref. \cite{3}). However, in accordance with the Kanamori theory \cite{3} at very small \( n \) we should obtain the gas limit where ferromagnetism does not occur. We also believe that the degeneracy of \( e_g \) band is essential for the description of ferromagnetic ordering in this system. Our results allow to obtain the ferromagnetism for small values of electron concentration induced by correlated hopping \( \tau_2 \) in a presence of the inter-atomic exchange interaction (see Fig. 4). Thus, we believe that the correlated hopping mechanism in a presence of the inter-atomic exchange interaction allows the more natural explanation of the origin of ferromagnetism in the system \( \text{Fe}_{1-x}\text{Co}_x\text{S}_2 \) at very small \( x \).

To calculate the ground state energy of the model per site we use the formula

\[
E_0 = \frac{1}{2N} \sum_{\gamma\sigma} \left[ \int_{-\infty}^{+\infty} (t_{k}(n) + E) J^\gamma_{k}(E) dE \right] \tag{3.7}
\]

Here

\[
J^\gamma_{k}(E) = \delta(E - E_{\gamma\sigma}(k))\theta(-E) \tag{3.8}
\]

is the spectral intensity of Green function \cite{24,20}; \( \theta(-E) \) is the step-wise function. From Eq. \cite{3.7} one can obtain for the ground state energy the expression

\[
E_0 = -\frac{1}{2} \sum_{\gamma\sigma} (\mu_{\gamma\sigma} n_{\gamma\sigma} - (1 - \tau_1 n + \alpha_{\gamma\sigma}) n_{\gamma\sigma} (1 - n_{\gamma\sigma}) w) . \tag{3.9}
\]
Expression (3.9) can be rewritten in the form

$$E_0 = E^{(0)}_0 + E^{(2)}_0 + E^{(4)}_0,$$

$$E^{(0)}_0 = \frac{\mu n}{2} \left( -U + 2U' - J_0 - \frac{zJ}{8} \left( 16 - (4 - n)^2 \right) - \left( 1 - \tau_1 n - \frac{n}{2}\tau_2 \right) (4 - n) \frac{w}{2} \right),$$

$$E^{(2)}_0 = \left( 2(1 - \tau_1 n - \tau_2 (4 - n)) \right) \frac{U}{w} - \left( J_0 \frac{w}{w} + \frac{2zJ}{w} (1 + \frac{n(4 - n)}{8}) \right) \frac{w}{8m^2},$$

$$E^{(4)}_0 = \frac{zJ}{64} m^4.$$ 

The position of the minimum of ground state energy depends on values of model parameters. In Fig. 5 the energy difference $\Delta E_0$ between paramagnetic and ferromagnetic states is plotted as a function of the magnetization. At some values of the parameters a ferromagnetic ordering with $m \neq 0$ is energetically gainful. As it has been noted above the intra-atomic exchange is an important factor leading to ferromagnetism in an orbitally degenerate band. The increase of $J_0/w$ leads both to the increase of magnetic moment and to the decrease of the ferromagnetic ground state energy.

The dependence of the ground state energy of the model on the electron concentration is plotted in Fig. 6. One can see that with the increase of $n$ Coulomb correlation becomes more and more important and the value of the ground state energy rapidly increases, as well as at the rise of the intra-atomic Coulomb repulsion parameters. As the value of intra-atomic exchange increases the ground state energy decreases (Fig. 7); at some critical value $J_0/w$ the transition of the system from a state of paramagnetic metal to a state of ferromagnetic metal occurs. It appears that the ferromagnetic ordering can be more favourable than the paramagnetic one in orbitally degenerate model without singularities of the density of states even if the inter-atomic exchange and correlated hopping are absent (in the work [20] similar result is obtained only at the presence of density of states singularities). Let us also note that at increase of $U$ the critical value of $J_0$, at which the transition to ferromagnetic state occurs, decreases. The qualitatively similar picture has been obtained by the authors of work [13].

In Fig. 8 the energy difference between the paramagnetic and ferromagnetic states (Fig. 8b) and the value of magnetization (Fig. 8a) as functions of band filling are plotted at different values of correlated hopping. Depending on the value of $n$ (and the relation between the energy parameters) the state of the system can be para- or ferromagnetic, polarization can be full or partial. The curves 1 correspond to the case when correlated hopping is absent. With increase of $n$ the transition from para- to ferromagnetic state occurs, in the region $n > 2$ the inverse transition takes place (symmetrical behaviour of the concentration dependence relative to half-filling is observed). The correlated hopping leads to the decrease of the ground state energy, in particular, the increase of $\tau_1$ (curves 3) has stronger influence at $n > 2$ (as a result the region of ferromagnetic ordering moves towards larger values of $n$), the increase of $\tau_2$ (curves 2) at $n < 2$ (the region of ferromagnetic ordering moves towards smaller values of $n$). These effects are the manifestation of electron-hole asymmetry being the property of the systems with correlated hoppings (see [37,38]). At some values of correlated hopping in the system electron-hole symmetry retrieves (curves 4 in Fig. 8).

The condition of ferromagnetic ordering stability $\frac{dE_0}{dm} < 0$ can be obtained as

$$\frac{U + J_0}{2w} + \frac{zJ}{8w} (8 + n(4 - n)) + n\tau_1 + \frac{1}{2}\tau_2 (4 - n) > 1.$$  

(3.11)

From expressions for ground state energy (3.10) and magnetization (3.4) one can see that for the values of inter-atomic exchange interaction $J > 0$ at the point of transition from a paramagnetic metal to a ferromagnetic metal the magnetization changes continuously, and for $J = 0$ it has a jump, namely, in the former case the transition from a paramagnetic state to a partially polarized ferromagnetic state occurs, in the later one the transition from a paramagnetic state to a fully polarized ferromagnetic state (saturated ferromagnetic state, $m = n$) is obtained. The similar results have been obtained in a single-band model [20,27]. Thus, taking into account the inter-atomic exchange interaction allows to obtain a partially polarized ferromagnetic state in two-band Hubbard model with symmetrical density of states; the partially polarized ferromagnetic state has been obtained by the authors of work [23], using the special feature of the density of states.

For the case of $J = 0$ from Eq. (3.11) we obtain a generalization of the Stoner criterion which takes into account the orbital degeneracy and correlated hopping

$$(U + J_0)\rho(\epsilon_F) > 1 - n\tau_1 - \frac{1}{2}\tau_2 (4 - n).$$  

(3.12)

From the condition of the minimum of ground state energy $\frac{dE_0}{dm} = 0$ one can also obtain the condition of partial spin polarization...
The condition of full spin polarization \((m = n)\) is
\[
\frac{U + J_0}{2w} + \frac{zJ}{8w} \left( 8 + n(4 - n) - 8n^2 \right) + n\tau_1 + \frac{1}{2}\tau_2(4 - n) > 1.
\]

Eqs. (3.11)-(3.14) coincide with the conditions which can be derived from Eq. (3.10).

From these conditions one can see that both mechanisms of correlated hopping favour ferromagnetism but their concentration dependences are different; if \(\tau_2 > \tau_1\) then the systems with the electron concentration \(n < 1\) are more favourable to ferromagnetism than the systems with \(n > 1\), and vice versa (see Figs. 2, 8, 9).

In Fig. 9 the critical values of inter-atomic exchange are plotted as a function of band filling. The lower curve corresponds to the critical value for the partial polarization, the upper one – for the full polarization; the region below the lower curve corresponds to paramagnetic ordering of spins, between the curves – to the partial polarization, above the curves – to the full polarization of spins. It can be seen that correlated hopping essentially changes the condition of ferromagnetic ordering. Let us also note that the region of partial polarization is narrowed with a deviation from the curves – to the full polarization of spins. It can be seen that correlated hopping essentially changes the condition of ferromagnetic ordering. Let us also note that the region of partial polarization is narrowed with a deviation from half-filling (similarly to the case of non-degenerate band \([24]\)).

In Fig. 10 the dependencies of critical values of \(J_0/w\) on electron concentration at different values of \(zJ/w\) are plotted. It is important to note that at \(zJ = 0\) the critical value of \(J_0/w\) does not depend on the electron concentration. It can be explained by the next arguments: in the absence of inter-atomic exchange the mechanism which stabilizes ferromagnetism is a translational motion of electrons which enhances the spins of sites, involved in the hopping process, to align in parallel because of Hund’s rule coupling.

Note also the essential difference of the situation where the system is described by non-zero values of correlated hopping: since correlated hopping renormalizes the bandwidth and makes it dependent on the concentration, the behaviour of the critical value of \(zJ/w\) becomes asymmetrical relative to half-filling.

The critical value of \(J_0/w\) as a function of \(zJ/w\) is plotted on Fig. 11. As one can see the increase of \(zJ/w\) significantly decreases the critical value of \(J_0/w\) (in the same way the correlated hopping does). It shows the importance of taking into account the inter-atomic exchange and correlated hopping for the description of ferromagnetism in the systems with orbital degeneracy. The inverse dependence of critical values of \(zJ/w\) and \(J_0/w\) (what indicates the destabilization of ferromagnetic ordering at the increase of \(J_0/w\)) has been obtained in work \([24]\) with use of the exact diagonalization method for the even number of sites in one-dimensional chains, but that result depends sensitively on the number of lattice sites and the boundary conditions.

IV. CONCLUSIONS

In this paper we have investigated the ground state of a doubly orbitally degenerate model. Taking into consideration the orbital degeneracy allows to analyse the influence of intra-atomic exchange interaction (Hund’s rule coupling), which is responsible for the formation of local magnetic moments, on the possibility of ferromagnetism realization. Beside the diagonal matrix elements of electron-electron interactions the model includes the off-diagonal ones – correlated hopping integrals, which describe the influence of site occupancy on the hopping of electrons. The model under consideration also includes the inter-atomic exchange interaction \(J\).

The study of the model ground state, carried out in this work, shows that the stability of ferromagnetism strongly depends on the model parameters. In particular, it has been found that the relationship between correlated hopping parameters determines the criterion of ferromagnetism. At \(\tau_2 > \tau_1\) in the system with concentration of electrons \(n < 2\) the situation for ferromagnetic ordering is more favourable than for the system with \(n > 2\); at \(\tau_2 < \tau_1\) the opposite behaviour is obtained. At some values of correlated hopping parameters the retrieval of the electron-hole symmetry is possible. Taking into account the correlated hopping leads to the appearance of the specific mechanism which stabilizes ferromagnetic ordering, and this is due to the spin-dependent shift of the subband centers. In the absence of inter-atomic exchange interaction the ferromagnetic ordering is stabilized by the translational motion of electrons between sites with “atomic ferromagnetism” formed by Hund’s rule coupling.

It is important to note that the transition of the system from paramagnetic to ferromagnetic state can occur at the values of interaction parameters, which are of the same order that bandwidth, and with density of states without peculiarities. The important role for the ferromagnetism stabilization in weak interaction regime \((U < 2w)\) is played
by the intra- and inter-atomic exchange interactions as well as correlated hopping that allows to describe the metallic paramagnetic-ferromagnetic transition with realistic relationship between above mentioned exchange interactions.

For the values of inter-atomic exchange interaction $J > 0$ at the point of the transition from a paramagnetic metal to a ferromagnetic metal the magnetization changes continuously, and for $J = 0$ it has a jump, namely, in the former case the transition from a paramagnetic state to a partially polarized ferromagnetic state occurs, in the later one the transition from a paramagnetic state to a fully polarized ferromagnetic state (saturated ferromagnetic state) is obtained.

The obtained dependencies of magnetization on concentration of electrons qualitatively describe the experimental Slater-Pauling’s curves for ferromagnetic alloys. At some values of the model parameters the experimental dependence of magnetization for the systems Fe$_{1-x}$Co$_x$S$_2$ and Co$_{1-x}$Ni$_x$S$_2$ with changing electron concentration in $e_g$ band is reproduced theoretically. The correlated hopping mechanism of ferromagnetism stabilization allows to explain the ferromagnetism in the systems Fe$_{1-x}$Co$_x$S$_2$ at small concentrations $x \simeq 0.05$.

ACKNOWLEDGMENTS

V.H. is grateful to Prof. W. Nolting (Humboldt-Universität, Berlin) for the hospitality during the workshop “242. WE-Heraeus-Seminar on Ground-State and Finite-Temperature Bandferromagnetism” (4-6 October, 2000, Berlin), where the part of the results considered in the present paper was discussed. The authors thank to Prof. D. Vollhardt and Prof. W. Weber for valuable discussions.

* Electronic address: didukh@tu.edu.te.ua
[1] J. Hubbard, Proc. Roy. Soc. A 276, 238 (1963).
[2] J. Kanamori, Prog. Theor. Phys. 30, 275 (1963).
[3] M. C. Gutzwiller, Phys. Rev. Lett. 10, 159 (1963).
[4] D. Vollhardt et al., Adv. in Sol. St. Phys. 38, 383 (1999).
[5] T. Herrman and W. Nolting, J. Magn. Magn. Mater. 170, 253 (1997).
[6] Y. Nagaoka, Phys. Rev. 147, 392 (1966).
[7] H. Tasaki, Progr. Theor. Phys. 99, 489 (1998).
[8] J. C. Slater, Phys. Rev. 49, 537 (1936).
[9] J. H. van Vleck, Rev. Mod. Phys. 25, 220 (1953).
[10] L. M. Roth, hys. Rev. 149, 306 (1966).
[11] K. I. Kugel’ and D. I. Khomskii, Sov. Phys.- JETP 37, 725 (1973).
[12] M. Cyrot and C. Lyon-Caen, J. Phys. C 36, 253 (1975).
[13] W. Gill, D. J. Scalapino, Phys. Rev. B 35, 215 (1987).
[14] J. Kuei, R. T. Scalettar, Phys. Rev. B 55, 14968 (1997).
[15] A. Kleinberg and J. Spalek, J. Phys.: Condens. Matter 11, 6553 (1999); Phys. Rev. B 61, 15542 (2000).
[16] D. Vollhardt et al., Z. Phys. B 103, 283 (1997).
[17] K. Held and D. Vollhardt, Eur. Phys. J. B 5, 473 (1998).
[18] T. Momoi and K. Kubo, Phys. Rev. B 58, R567 (1998).
[19] R. Fresard, G. Kotliar, Phys. Rev. B 56, 12909 (1997).
[20] K. A. Chao, Phys. Rev. B 4, 4034 (1971).
[21] J. Bünemann, W. Weber, Physica B 230-232, 412 (1997).
[22] J. Bünemann, W. Weber, F. Gebhard, Phys. Rev. B 57, 6896 (1998).
[23] T. Okabe, J. Phys. Soc. Jpn. 65, 1056 (1996).
[24] J. E. Hirsch, Phys. Rev. B 56, 11022 (1997).
[25] D. Meyer, W. Nolting, J. Phys.: Condens. Matter 11, 5811 (1999).
[26] L. Didukh, Sov. Phys. Solid State 19, 711 (1977).
[27] L. Didukh, O. Kramar and Yu. Skorenkyy, cond-mat/0012402.
[28] S. Kivelson, W.-P. Su, J. R. Schrieffer and A. J. Heeger, Phys. Rev. Lett. 58, 1899 (1987).
[29] D. K. Campbell, J. T. Gammel, E. Y. Loh, Phys. Rev. B 42, 475 (1990).
[30] J. E. Hirsch, Phys. Rev. B 40, 2354 (1989); Phys. Rev. B 40, 9061 (1989).
[31] J. C. Amadon and J. E. Hirsch, Phys. Rev. B 54, 6364 (1996).
[32] R. Strack and D. Vollhardt, Phys. Rev. Lett. 72, 3258 (1994).
[33] M. Kollar, R. Strack, and D. Vollhardt, Phys. Rev. B 53, 9225 (1996).
[34] J. Wahle et al., Phys. Rev. B 58, 12749 (1998).
[35] M. Kollar and D. Vollhardt, Phys. Rev. B 63, 045107 (2001).
[36] L. Didukh, L. Pryadko, I. Stasyuk, Correlation Effects in Materials with Narrow Energy Bands, Vyshcha Shkola, Lviv (1978) (in Russian).
[37] L. Didukh, Yu. Skorenky, Yu. Dovhopaty, and V. Hankevych, Phys. Rev. B 61, 7893 (2000).
[38] L. Didukh, Cond. Matt. Phys. 1, 125 (1998).
[39] M. Acquarone, D. K. Ray and J. Spalek, J. Magn. Magn. Mater. 47-48, 388 (1985); M. Acquarone, J. Spalek and D. K. Ray, J. Magn. Magn. Mater. 54-57, 985 (1986).
[40] F. Gautier, in Magnetism of Metals and Alloys, edited by M. Cyrot (North-Holland, Amsterdam, 1982), Chap. 1.
[41] H. S. Jarrett et al., Phys. Rev. Lett. 21, 617 (1968).
[42] M. I. Auslender, V. Yu. Irkhin, M. I. Katsnelson, J. Phys. C 21, 5521 (1988).
[43] L. Didukh, Ukr. Phys. Journ. 33, 449 (1988) (in Russian).
[44] V. Ivanov, Ukr. Phys. Journ. 36, 751 (1991) (in Russian).
FIG. 1. The magnetization $m$ as a function of $n$ at $U/w = 1.5$ and $\tau_1 = \tau_2 = 0$, $zJ/w = 0.1$. Upper curve corresponds to $J_0/w = 0.27$, middle curve corresponds to $J_0/w = 0.25$, lower one corresponds to $J_0/w = 0.23$.

FIG. 2. The magnetization $m$ as a function of $n$ at $U/w = 1.5$, $zJ/w = 0.1$ and $J_0/w = 0.22$. Curve 1 corresponds to $\tau_1 = \tau_2 = 0$, curve 2 – to $\tau_1 = 0$, $\tau_2 = 0.015$ curve 3 – to $\tau_1 = 0.015$, $\tau_2 = 0$.

FIG. 3. The magnetization $m$ as a function of $J_0/w$ at $n = 0.9$, $U/w = 1.5$ and $zJ/w = 0.1$. Left curve corresponds to $\tau_1 = 0$, $\tau_2 = 0.01$, middle curve corresponds to $\tau_1 = 0.01$, $\tau_2 = 0$, right one corresponds to $\tau_1 = \tau_2 = 0$.

FIG. 4. The magnetization $m$ as a function of $n$ at $U/w = 1.2$, $zJ/w = 0.06$ and $J_0/w = 0.2$, $\tau_1 = 0$, $\tau_2 = 0.15$. 
FIG. 5. The energy difference between ferro- and paramagnetic ground states as a function of magnetization \( m \) at \( n = 1.2, U/w = 1.2, zJ/w = 0.2 \) and \( \tau_1 = \tau_2 = 0 \): upper curve corresponds to \( J_0/w = 0 \), middle curve corresponds to \( J_0/w = 0.3 \) and lower curve corresponds to \( J_0/w = 0.4 \).

FIG. 6. The energy of ferromagnetic ground state as a function of \( n \) at \( U/w = 1.2, zJ/w = 0.1, \tau_1 = \tau_2 = 0 \): \( J_0/w = 0.1 \) for upper curve, \( J_0/w = 0.2 \) for lower one.

FIG. 7. The ferromagnetic (curves 1,3) and paramagnetic (curves 2,4) ground state energies as a function of \( J_0/w \): \( n = 1.2, zJ/w = 0.05, \tau_1 = \tau_2 = 0.1 \); curves 1,2 correspond to \( U/w = 1 \), curves 3,4 correspond to \( U/w = 1.2 \).
FIG. 8. The magnetization $m$ (panel a) and the energy difference between ferro- and paramagnetic ground states (panel b) as a function of $n$ at $U/w = 0.9$, $J_z/w = 0.3$, $J_0/w = 0.3$: curve 1 correspond to $\tau_1 = \tau_2 = 0$, curve 2 - to $\tau_1 = 0$, $\tau_2 = 0.02$, curve 3 - to $\tau_1 = 0.01$, $\tau_2 = 0$ and curves 4 to $\tau_1 = 0.01$, $\tau_2 = 0.02$. 
FIG. 9. The critical values of $zJ/w$ as a function of $n$ at $J_0/w = 0.1$. Upper curves correspond to $U/w = 0.9$, $\tau_1 = \tau_2 = 0$, lower curves - to $U/w = 1.2$, $\tau_1 = 0.05$.

FIG. 10. The critical values of $J_0/w$ as a function of $n$ at $U/w = 0.9$, $\tau_2 = 0$. Curve 1 corresponds to $zJ/w = 0$, $\tau_1 = 0$, curves 2 - to $zJ/w = 0.1$, $\tau_1 = 0$, curve 3 - to $zJ/w = 0$, $\tau_1 = 0.01$, and curves 4 correspond to $zJ/w = 0.1$, $\tau_1 = 0.01$.

FIG. 11. The critical value of $J_0/w$ vs $zJ/w$ at $U/w = 1$ and $\tau_1 = \tau_2 = 0.1$ Upper curve corresponds to $n = 0.5$, middle curve - to $n = 2$, lower curve - to $n = 3.5$. 