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Józef Spałek

MAGNETIC PROPERTIES OF STRONGLY CORRELATED ELECTRONS IN NARROW BANDS

Kraków 1981

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models of strongly correlated electrons in metals and semiconductors

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Contents

"One of my strongest styllistic prejudices in science is that many of the facts Nature confronts us with are so implausible, given the simplicities of non-relativistic quantum mechanics and statistical mechanics, that the mere demonstration of a reasonable mechanism leaves no doubt of the correct explanation. This is so especially if it also correctly predicts unexpected facts... Very often such a simplified model throws more light on the real workings of nature than any number ab initio calculations of individual situations which even where correct often contain so much detail as to conceal rather than reveal reality"

P.W. Anderson, The Nobel Lecture (1977)

Józef Spałek

MAGNETIC PROPERTIES OF STRONGLY CORRELATED ELECTRONS IN NARROW BANDS

Abstract. We review some of our recent work on the problems of kinetic exchange and semiconductor - metal transition in model systems with a narrow band and/or localised moments. It extends the theory of superexchange in the Mott insulator to the case of strongly correlated metals. Beside that, it shows how the derived magnetic interactions influence the stability of various magnetic phases of itinerant electrons andnthe nonmetal - metal (Mott) transition for the half-filled band.

In the first part (Introduction) we give a short summary of underlying problems, both experimental and theoretical which we deal with in the following, and also place our work within the whole subject of itinerant magnetism.

In Part II composed of Sections 4-7 we develop a theory of the kinetic exchange in detail, and discuss a magnetic phase diagram as a function of band filling, both for single and doubly degenerate bands.

In Part III (Sects 8-10) we show how the local moments can be introduced in a translationally invariant system. It shows up under which conditions the narrow band Hamiltonian and s-d (s-f) model are equivalent. The s-d model corresponding to the periodic Anderson-Falicov-Kimball model is also derived (cf.Sect.10).

In Part IV (Sects 11-14) we discuss the extended s-d model and consider briefly its application to itinerant magnetism (Sect.12), to magnetic semiconductors in the double exchange limit (Sect.13), and to mixed valence systems (Sect.14).

Finally, in Part V (Sects 15-17) we first overview our approach, then summarize our results (Sect.16), and conclude on what should be done to make the approach selfcontained.

Part I

INTRODUCTION

Basic problems and the role of models

1. Local Moments in Itinerant Magnetism
2. Band Theory versus Parametrized Models
3. Aim and the Scope of the Work

1. Local Moments in Itinerant Magnetism

The theory of itinerant magnetism may be divided into four areas of activity:

(i) the ground state properties (type of ordering, magnetic moment per atom, cohesive energy, the Fermi surface, ionic radius, etc.);

(ii) the elementary excitations (quasiparticles, and collective excitations: spin waves = magnons, and the Stoner modes);

(iii) the temperature effects (magnetic susceptibility and specific heat, the critical temperature, the temperature dependence of Stoner exchange splitting, spin waves above T_c, etc.);

(iv) transport properties (electron and lattice conductivities, Hall effect and magnetoresistance, thermopower, etc.).

First principles band calculations carried out for transition metals with no adjustable parameters (for review see Moruzzi et al 1978, Eastman et al 1979, and references cited there in [1]), have been remarkably succesful in obtaining a reasonable account of the ground state properties such as magnetisation, neutron form factor, lattice parameter, bulk modulus and cohesive energy. In this respect, the theory of itinerant (3d) ferromagnetism may be regarded as even more succesful than that of localised (Heisenberg) ferromagnets where the first principle calculation of exchange constant is usually not very accurate (Prange 1979 [2]).

The elementary excitations (Stoner modes and magnons calculated by Cooke et al 1978) [3] in the random phase approximation (RPA) and with band and wave-vector dependence of relevant interaction matrix elements taken into account are in good agreement with the neutron scattering experiments of Mook et al (1973) [4] and Lynn (1975) [5], including the intersection of the spin wave dispersion with the Stoner continuum. Moreover, the results had predicted the existence of an optical spin-wave branch in nickel and were subsequently observed [3].

On the other hand, temperature effects, particularly in the paramagnetic phase, are regarded as providing a direct evidence against the present band picture [1] . On the contrary, some results are in a qualitative agreement with expectations derived from the Heisenberg model, and thus lend a support to a picture of partially localised electrons in a degenerate 3d band. Among the striking effects in the high temperature regime are:

a) Persistence of short wavelength spin waves above T_c as observed by Mook et al (1973) [4] ;

b) The Curie-Weiss susceptibility over a wide range of the temperature e.g. for Fe (for the matter see Wohlfarth (1980) [6] ;

c) Temperature independence of the Stoner splitting, and in particular persistence of the Stoner gap above T_c [4,5] , and

d) Applicability of the s-d model in explaining the temperature dependence of resistivity, and, in particular, in the critical region as shown by Balberg (1979) [7] .

The results a) and c) rise a question about the validity of the Stoner -Wohlfarth theory (for recent review see Wohlfarth (1977) [8] , and Shimizu (1977) [9]) , at least for some itinerant ferromagnets, for which local magnetic moments exist in the paramagnetic phase, even though the macroscopic spin polarisation vanishes. The Stoner-Wohlfarth theory assumes that the exchange splitting is proportional to magnetisation (see Fig.1 and the comment beneath), and therefore moments dissolve in the Fermi sea at the Curie temperature T_c, while the result a) points out clearly that the energy of the local moment formation is much larger than k_BT_c which characterizes the energy of the moment-moment interactions. Additionally, it turns out that the exchange splitting calculated within the band theory (Gunnarson 1976 [10]) is too large and gives the estimate of T_c 5-10 times larger than observed. This disagreement points out that some essential fluctuations are missing in the band approach. Many authors have pointed out very recently (Hubbard 1979 [11,12] , You et al 1980 [13] , Hasegawa 1979 [14]) that a part of the spin density fluctuations is beyond the band theory and have tried to incorporate the idea of angular fluctuations into the single-particle picture. The goal of those efforts is to get the correct values of the moment per atoms as determined from the Curie-Weiss susceptibility and of T_c simultaneously. The short range order is expressed either [10-14] through the existence of disordered local moment solutions of the Hubbard (1963) model [15] , or through the assumption that magnetisation changes slowly in space and time (above T_c) and therefore the underlying band structure is affected only weakly by the magnetic transition (Korenman et al 1977 abc [16-18]). The latter assumption brings into existence short-wavelength spin waves in the paramagnetic region even within a simple hydrodynamical approach (Spałek 1979 [19] , cf. Supplement A) .

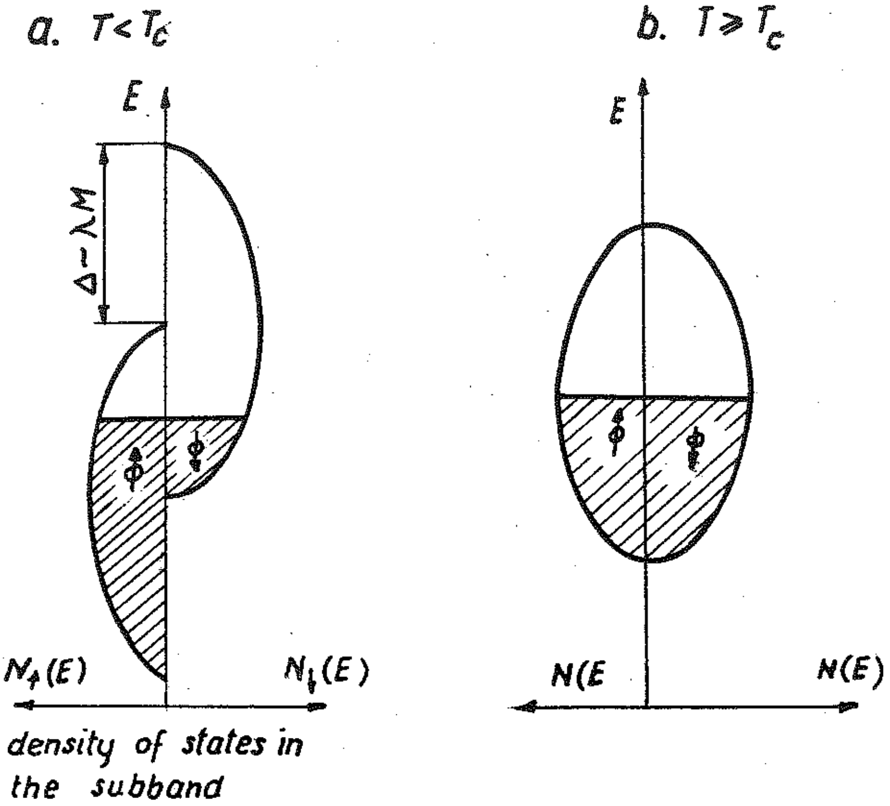

Fig.1. Schematic representation of spin subbands of quasiparticle states. The Stoner splitting Δ is proportional to magnetization M within the Stoner-Wohlfarth theory: a) $T < T_c$; b) $T \geqslant T_c$

While the problem of existence of the local moments has not yet been resolved completely, the dual localised-itinerant nature of magnetic electrons poses a challenge to our microscopic understanding of the quasiparticle states in strongly correlated systems. Obviously, so called "localised moment behaviour" should not violate the fundamental principle that particles in a degenerate band are equivalent and therefore indistinguishable. Therefore, any division into itinerant and localised parts must be done very carefully to preserve the principle and a translational invariance of the system.

The localisation problem in 3d metals shows itself in a full complexity. Hence, it is desirable to find a model system on example of which we can observe a delocalisation of magnetic moments in a more controlled way. In this respect the studies of narrow gap 4f semiconductors under pressure (e.g. SmS, EuO) offer an unique opportunity because well defined 4f moments at ambient pressure are mixed with the conduction band electrons of 5d-6s type (for recent review of the field see Jayaraman 1979, and references therein) [20] . The semiconductor-metal transition to the state with an intermediate (nonintegral) valence is observed. The electron states before and after the transition takes place can be represented in the single-particle terms as in Fig.2.

From a theoretical point of view the transition poses a question: how well defined atomic moments become delocalised when mixed (hybridised) with a wide conduction band? Obviously, an answer to this problem solves it only partially, namely to what extent the wide conduction band destabilizes or delocalises the atomic moment. The principal question why the atomic moment is present in a crystal remains to be answered separately in each case.

Let us list shortly the fundamental questions to be answered by the theory of itinerant magnetism and attach relevant observed facts:

Question 1: Why the concept of localised moment behaviour in a translationally invariant metallic system is so important?

Comment 1: This is because it

(i) gives a connection with atomic physics (shows which of the atomic characteristics are preserved in the solid state);

(ii) explains the insulating behaviour of the (antiferromagnetic) Mott insulator, i.e. the insulating ground state of some systems having a half filled band;

(iii) defines the local moments in metallic magnets, namely:

a) gives metallic state with the magnetic moment equal to the atomic spin of 4f shell (e.g. are earth metals);

b) distinguishes between the itinerant systems with the local

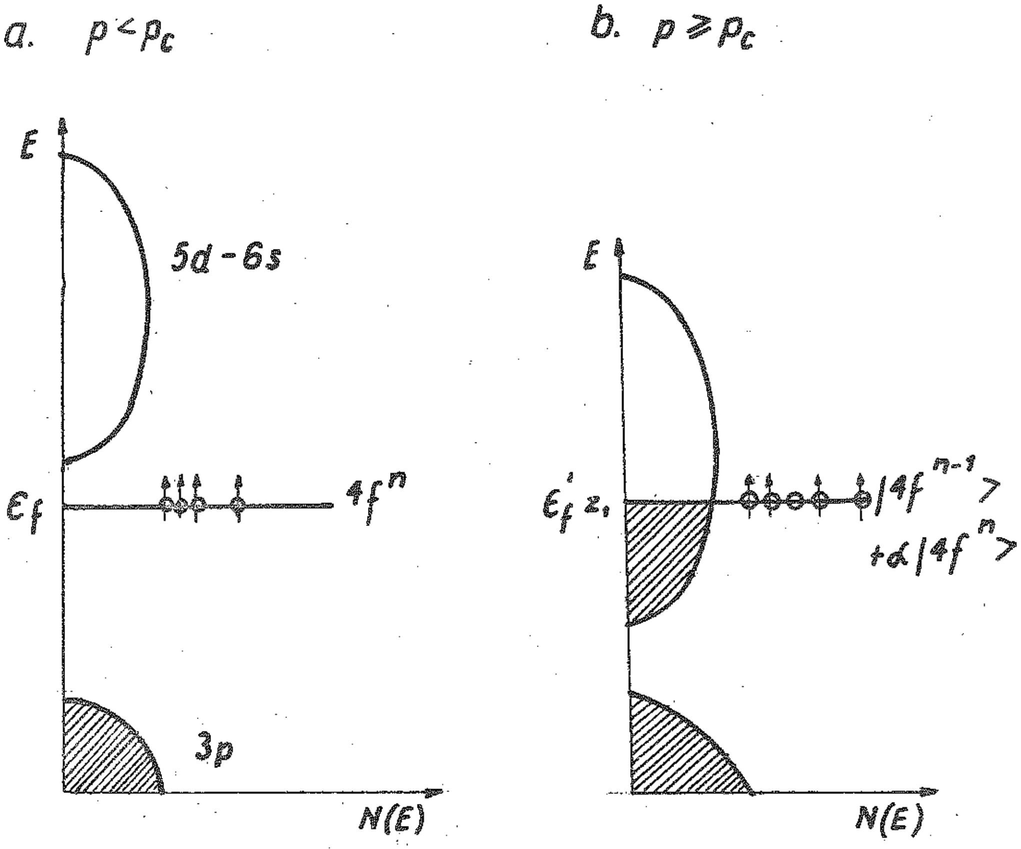

Fig.2. One-electron level structure in 4f ionic semiconductor which exhibits the transition to the intermediate-valence state: a) for static pressure p below critical (p_c) ; b) $p \geqslant p_c$

moment present (e.g. Fe), and the others (e.g. $ZrZn_2$) for which the magnetic moment dissolves entirely in the Fermi sea of conduction electrons, i.e. the Stoner-Wohlfarth theory is qualitatively correct.

Question 2: Can the band electrons be divided into separated itinerant and localised parts? In order words, is the degeneracy of orbitals or multielectron structure essential for observing the local moment behaviour?

Comment 2: This depends on the situation, namely

(i) In rare earth systems the magnetic (4f) electrons are distinguishable from the conduction (5d-6s) electrons and therefore magnetic and metallic properties depend on different sets of electrons;

(ii) In transition metals the electrons are indistinguishable and therefore the dual nature, if present, is an intrinsic property of strongly correlated electrons [11-18] . Thus the degeneracy may not play a principal role [14] .

Question 3: Can a band Hamiltonian representing a strongly correlated itinerant magnet be reduced to the Heisenberg Hamiltonian representing the corresponding Mott insulator for the half-filled band case?

Comment 3: The relevance of such a question is supported by experiments on doped Mott insulators. For example, the system $Co_xNi_{1-x}S_2$ is a metal for $x \neq 0$, while for $x = 0$ (NiS_2) it is a Mott insulator (Ogawa et al 1974, Ogawa 1979) [21,22] .

Question 4: To what extent atomic 4f moments dissolve in the Fermi sea of conduction electrons in the intermediate valence phase? Do they transform into the Fermi liquid (Varma 1977 [21] , Beal-Monod and Lawrence 1980 [22]) ?

Comment 4: The answer to this question clarifies at least the local moment behaviour in an itinerant system composed of two distinguishable parts.

Question 5: Is the canonical (unitary) transformation of a bare many-body Hamiltonian sufficient to provide a definition of localised moments or do they appear only as a well defined concept on the thermodynamic level?

Comment 5: This question suggests vaguely a way of looking at the problem. Various versions of the transformation will be used extensively throughout the present work but a relation to the theory of spin fluctuations as formulated by Moriya and his coworkers (for review see Moriya 1979) [23] is still missing and would be desirable in view of the successes of the latter approach in some cases.

We have tried to arrange the basic questions concerning the local moments hierarchically, from the most general to concrete ones, suggesting ways to get them. Full test of a succesful approach can be done only by studying the temperature effects, because observations at ambient temperatures are the most difficult to understand within the conventional quasiparticle (or elementary excitations) point of view. It has to be pointed out that the hopes attached to the studies of single magnetic impurities (Anderson 1961 Wolff 1961, Krishnamurthy et al 1980 ab) [24-27] in simple metals turned out to be inconclusive because the hopping or correlated scattering of electrons between the magnetic centers via the conduction electron states in many impurities case changes qualitatively the analysis (cf. Part III, mixed valence systems).

It is conceivable, that a new quantum-mechanical representation will be needed to grasp essential features of the duality localised vs. itinerant electrons. Namely, untill now two representations have been used, the Bloch (wave-vector $\vec{k}$) and the Wannier (position $\vec{R}_i$) ones. From the point of view of the uncertainty principle

$$\Delta x_\alpha \cdot \Delta p_\alpha = \hbar \Delta k_\alpha \cdot \Delta x_\alpha \geqslant \hbar , \qquad \alpha = 1,2,3$$

they are the extremal realizations of it because:

a) For the Bloch (band) representation $\vec{p} = \hbar \vec{k}$ is a good quantum number, which means that $\Delta p_\alpha = 0$. Thus, $\Delta x_\alpha = \infty$

b) for the Wannier (atomic) picture the state is specified by the site on which given (atomic-like) function is centered, $\Phi_i = \Phi(\vec{r} - \vec{R}_i)$. Hence now, $\Delta x_\alpha = 0$, and $\Delta p_\alpha = \infty$.

One can invent an intermediate representation, with $\Delta k_\alpha = \Delta x_\alpha^{-1}$ which can prove to be particularly important when $\vec{k}$ is not a good quantum number even in the translationally invariant system (e.g. the Mott insulators, 4f electrons in metals). Such mixed x-p representation has been considered recently by Zak (1980) [28] basing on previous result of McIrvine and Overhauser (1959) [29] , but, as far as we are aware of, it has not been used for the purpose of the localisation problem considered here.

There is a question, closely connected with the fundamental principle of uncertainty used here. Namely, why a nontrivial magnetic ordering is bound to the localised states? At T=0 the answer is simple. For a translationally invariant system the configurational entropy must be zero and system chooses one spin configuration. However, the existence of the order for $T \neq 0$ requires a more detailed knowledge of the interactions between electrons.

We are not interested in the localised state of core electrons which energies change by a negligible amount in the solid state with respect to atomic positions. Nonetheless, the preserved in the solid will be those atomic states for which the energies difference between the nearest excited atomic single-particle states is larger than the bandwidths of the corresponding to them bands. Hence, the most interesting case is the one for which those two energies are comparable.

2. Band Theory versus Parametrized Models

In the current approach to itinerant-electron magnetism two methods can be distinguished. The older one is based on the model Hamiltonian. It is assumed that a magnet can be described by a model with few energy parameters expressing the integrals of all relevant single- and double-particle energies weighted with electron wave functions $\{\Phi_{\alpha}(\vec{r})\}$, chosen as a basis for an expansion of the field operator $\Psi_{\sigma}(\vec{r})$. The dynamical processes are described in terms of transitions between the single-particle states $\{\Phi_{\alpha}(\vec{r})\}$ and pairs of them $(\Phi_{\alpha},\Phi_{\beta})\to(\Phi_{\gamma},\Phi_{\delta})$

Because of their simplicity various models have been studied in detail, and the results have been obtained characterizing both the ground state and thermodynamic properties. The parameters generally need to be taken as adjustable parameters when comparing theoretical results with the experimental data.

Recently [1], as it has been pointed out in the preceding Section there has been a renewed interest in the electron band theory. It has provided a good account of some of the ground state properties for various magnetic systems, often without the need for any adjustable parameter. However, because the band theory cannot explain or is even in contradiction with some of the thermodynamical properties (cf. temperature independent part of the exchange splitting [4], value of T_c [10], existence of sloppy spin waves [4,5]), we have to resort ourselves to the parametrized models which often allow for an intuitive insight in terms of quasiparticles, i.e. relatively long-lived observable single-particle states.

Below we list the three main parametrized models used frequently and characterize shortly each of them. The are: the narrow band model, the Zener-Vonsovskii or s-d model, and the periodic Anderson model. Each of them will be used in a rather non-standard form. Additionally, they can be written both in the Wannier $\{|1j\sigma\rangle\}$ and the Bloch $\{|1k\sigma\rangle\}$ representations, related through the unitary transformation

$$|lj\sigma\rangle = N^{-1/2} \sum_{\vec{k}} \exp\left(-i\,\vec{k}\cdot\vec{R}_j\right)\cdot |l\,\vec{k}\sigma\rangle \qquad (2.1)$$

or its inverse

$$|l\,\vec{k}\sigma\rangle = N^{-1/2} \sum_{j} \exp\left(i\,\vec{k}\cdot\vec{R}_j\right)\cdot |lj\sigma\rangle \qquad (2.2)$$

Accordingly, the two sets of annihilation $\{a\}$ and creation $\{a^+\}$ operators for the corresponding single-particle states can be introduced

$$a_{lj\sigma} = N^{-1/2} \sum_{\vec{k}} \exp\left(-i\,\vec{k}\cdot\vec{R}_j\right) a_{l\,\vec{k}\sigma} \qquad (2.3)$$

$$a^+_{lj\sigma} = N^{-1/2} \sum_{\vec{k}} \exp\left(i\,k\cdot R_j\right) a^+_{l\,\vec{k}\sigma} \qquad (2.4)$$

In (2.1)-(2.4) N is the number of sites, l is the index of orbital quantum number or band, $\vec{k}$ is the wavevector within the first Brillouin zone, j or $\vec{R}_j$ labels the position of sites, and $\sigma/2$ is the spin quantum number of electron, $\sigma = \pm 1$. Beside that $|lj\sigma\rangle = |lj\rangle|\sigma\rangle$, i.e. the spin and space parts are assumed separated.

Narrow band model

The model bases on the tight-binding approximation. This means that the Hamiltonian is written in the Wannier representation and only interactions within the same atom an between the nearest neighbours are included. The Hamiltonian in a degenerate case may written in the form

$$H = \sum_{\substack{ij\sigma\\ ll'}} t_{ij}^{ll'}\, a^+_{li\sigma}\, a_{l'j\sigma} + \sum_{ill'\sigma} V^{ll'}\, a^+_{li\sigma}\, a_{l'i\sigma} + \frac{1}{2} \sum_{\substack{l\,l'l''l'''\\ ijRn\sigma\sigma'}} V_{ijRn}^{ll'l''l'''}\, a^+_{li\sigma}\, a^+_{l'j\sigma'}\, a_{l''R\sigma'}\, a_{l'''n\sigma} \qquad (2.5)$$

where

$$t_{ij}^{ll'} = \langle li|\, V_1 \,|\, l'j\rangle \qquad (2.6)$$

is the Bloch hopping integral with the single-particle potential V of the electron,

$$V^{ll'} = \langle il|\, V_1 \,|\, il'\rangle \qquad (2.7)$$

is the position of atomic level E_l (for $l=l'$) and the overlap between orbitals (for $l \neq l'$) if they are chosen nonorthogonal,

$$V_{ijkn}^{ll'l''l'''} = \langle il|\,\langle jl'|\, V_2 \,|\, nl'''\rangle\,|\, kl''\rangle \qquad (2.8)$$

is the integral of the Coulomb interactions between pair of electrons. In this work we consider two particular nontrivial cases, namely

(i) the extended Hubbard model [15], for which there is only one orbital and only the interactions between the nearest neighbours are included. Then, the Hamiltonian (2.5) reduces to

$$H = \sum_{ij\sigma}{}' t_{ij} a^{+}_{i\sigma} a_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} + \frac{1}{2}\left(K - \frac{J}{2}\right) \sum_{\substack{ij\\ \sigma\sigma'}} n_{i\sigma} n_{j\sigma'}$$
$$- J \sum_{ij}{}' \vec{S}_i \cdot \vec{S}_j + V \sum_{ij\sigma}{}' n_{i-\sigma}\left(a^{+}_{i\sigma} a_{j\sigma} + a^{+}_{j\sigma} a_{i\sigma}\right)$$
$$+ J \sum_{ij}{}' a^{+}_{i\uparrow} a^{+}_{i\downarrow} a_{j\downarrow} a_{j\uparrow} \qquad (2.9)$$

where $t_{ij} = \langle i | V_1 | j \rangle$ is the hopping integral equal to t for nearest neighbours, $U = \langle i,i | V_2 | i,i \rangle$ is the intraatomic Coulomb interaction, $K = \langle i,j | V_2 | i,j \rangle$ is the Coulomb interaction between the nearest neighbours $\langle ij \rangle$, $J = \langle i,j | V_2 | j,i \rangle$ is the exchange constant and $V = \langle i,j | V_2 | i,j \rangle$ is the hopping induced by the Coulomb interactions.

Eqn. (2.9) represents the full tight binding Hamiltonian for a narrow band, with 5 parameters $W = 2z|t|$, U, K, J and V, and with z being the number of nearest neighbours. For the particular case $K=J=V=0$ we get the Hubbard model [15] for which one can study in the simplest way the influence of electron-electron correlations on a formation of stable magnetic phases within a single narrow s-band, as well as the insulator to metal transition as a function of W/U. The full model makes possible to analyse a competition between ferromagnetic intersite exchange $(J > 0)$ and the kinetic exchange coming from correlation and favouring an antiferromagnetic ordering. For details we refer the reader to Part II.

(ii) A model of a degenerate narrow band (cf. Part II) - with the intraatomic pair interactions only. The starting Hamiltonian for this case is of the form

$$H = \sum_{ijl\sigma}{}' t_{ijl} a^{+}_{li\sigma} a_{lj\sigma} + \sum_{ijll'}{}'' t^{12}_{ij} a^{+}_{li\sigma} a_{l'j\sigma}$$
$$+ U \sum_{li} n_{li\uparrow} n_{li\downarrow} + \frac{1}{2}\left(K - \frac{1}{2} J\right) \sum_{\substack{ill'\\ \sigma\sigma'}} n_{li\sigma} n_{l'i\sigma'}$$
$$- J \sum_{ll'i}{}' \vec{S}_{li} \cdot \vec{S}_{l'i} + J \sum_{ll'i} a^{+}_{li\uparrow} a^{+}_{li\downarrow} a_{l'i\downarrow} a_{l'i\uparrow}$$
$$+ V \sum_{ll'i\sigma} \left(n_{li\sigma} + n_{l'i\sigma'} a^{+}_{li-\sigma}\right) a_{l'i-\sigma} , \qquad (2.10)$$

where the single-primed sums exclude terms with either $i=j$ or $l=l'$, while the double-primed one excludes the terms with bot $i=j$ and l=l´. Now, U is intraatomic intraorbital Coulomb interaction, K - is intraatomic interorbital one, J is intraatomic exchange constant (Hund´s rule coupling), and V orbitals´ hybridisation induced by the electrons interactions. Within this model we can study an influence of degeneracy together with the Hund´s rule coupling and the intraatomic correlations onto magnetic ordering of band electrons. It neglects entirely the direct Heisenberg exchange between the atoms. For a detailed analysis we refer the reader to the part two.

In general there are two ways of analysing bare many-body Hamiltonians like (2.9) and (2.10), corresponding to two different physical situations: $U \gg W$ and $U \ll W$. The first of them corresponds to strongly correlated electrons near the atomic limit, and the tight binding approximation should give a good account of underlying states in this case. The second corresponds to the metallic region of weakly correlated electrons. In the latter case the Hartree-Fock approximation should give qualitatively good results in three dimensions, whereas in the former case discussed here more careful treatment is desirable.

The s-d (s-f) model (Vonsovskii (1971) [30], Zener (1951) [31]).

In this model we assume the existence of localised spins $\{\vec{S}_i\}$ coupled to itinerant electrons with spins $\{\vec{S}_i\}$ through the s-d or s-f exchange. The Hamiltonian of the system is composed of the kinetic and Coulomb energies for conduction electrons, the s-d exchange, and the interactions between the localised spins. It is of the form

$$H = {\sum_{ij\sigma}}' t_{ij}\, c^{+}_{i\sigma}\, c_{j\sigma} - 2J \sum_{i} \vec{S}_i \cdot \vec{s}_i + U \sum_{i} n_{i\uparrow}\, n_{i\downarrow} + {\sum_{ij}}' J_{ij}\, \vec{S}_i \cdot \vec{S}_j \qquad (2.11)$$

The conduction electrons are generally regarded as narrow band electrons ($U \neq 0$). In the case of magnetic semiconductor or 4f metal the conduction band is assumed wide and then $U \simeq 0$. Eqn.(2.11) describes a two-component system. In Part III we discuss with some length the conditions under which the more general Hamiltonian (2.10) reduces to (2.11). We also show how the correlations among itinerant electrons produce intersite exchange interactions between resulting localised spins.

Generally, model (2.11) has three parameters: W, U, J. Therefore we can define three well defined asymptotic regimes

(i) $U > J > W$ - called double exchange limit,

(ii) $U > W \gg J$ - regime of strongly correlated electrons, and

(iii) W $\gg$ U $>$ J – weakly correlated s-d system.

In Part IV we review some of our work on the model (2.11) as applied to magnetic semiconductors, itinerant magnets, and (in slightly extended form) to the system with intermediate valence. In order words, the attractive features of (2.11) will be shown first discussing why does it work (Part III) and then, how does it work (Part IV).

(Extended) Periodic Anderson model.

It is represented by the Hamiltonian in which an atomic-like level with energy ϵ_f is hydridised with a wide band. The starting point in this case is given by

$$H = {\sum_{ij\sigma}}' t_{ij}\, c^{+}_{i\sigma} c_{j\sigma} + \sum_{ij\sigma} V_{ij} \left(a^{+}_{i\sigma}\, c_{j\sigma} + c^{+}_{i\sigma}\, a_{j\sigma} \right\rangle + \epsilon_f \sum_{i\sigma} N_{i\sigma} + U \sum_{i} N_{i\uparrow} N_{i\downarrow} + U_{sf} \sum_{i\sigma\sigma'} n_{i\sigma}\, N_{i\sigma'} - 2J \sum_{i} \vec{S}_i \cdot \vec{s}_i \tag{2.12}$$

where $N_{i\sigma} = a^{+}_{i\sigma}\, a_{i\sigma}$ is the particle-number operator for atomic-like (f) electrons, and the whole Hamiltonian has been expressed in the Wannier representation. It is a generalization of the periodic Anderson model in the sense it includes the interorbital Coulomb (U_{sf}), and exchange (J) interactions. In the Bloch representation for the itinerant electrons, it has the usually used form

$$H = \sum_{k} \epsilon_{\vec{k}}\, n_{\vec{k}\sigma} + \frac{1}{\sqrt{N}} \sum_{i\vec{k}\sigma} \left(V_{\vec{k}}\, e^{-i\vec{k}\cdot\vec{R}_i}\, a^{+}_{i\sigma}\, c_{\vec{k}\sigma} + h.c \right) + \frac{U_{sf}}{N} \sum_{ikk'} e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_i}\, N_{i\sigma}\, c^{+}_{\vec{k}\sigma'}\, c_{\vec{k}\sigma'} - \frac{2J}{N} \sum_{\substack{i\vec{k}\vec{k}' \\ \sigma\sigma'}} e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_i} \left(\vec{S}_i \cdot \vec{\tau} \right)_{\sigma\sigma'} a^{+}_{\vec{k}\sigma}\, a_{\vec{k}'\sigma'} \tag{2.13}$$

In (2.12) V_{ij} for $i=j$ contains the intraatomic hybridisation and is nonzero only between the states of the some parity. The quantity V_{ij} for $i \neq j$ may be called off-diagonal hopping because it transfers electron between two sites and between the orbitals simultaneously. The term $\sim U_{sf}$ is so called the Falicov-Kimball 1969 [32] term. It will be important when we will discuss the mixed valence phenomenon in Parts III and IV.

The Hamiltonian (2.12) or (2.13) may be related to the s-d model via the so called Schrieffer-Wolff transformation (1966) [33]. In Part III we discuss the shortcomings of that transformation in the mixed valence limit (i.e. atomic level $\mathcal{E}_f$ is placed near the Fermi level E_F), and propose a new transformation which is not divergent in this limit.

Summarizing, the narrow band model takes into account atomic Coulomb correlations in a band composed of degenerate but otherwise equivalent orbitals, whereas the periodic Anderson model describes a behaviour of hybridised but nonequivalent orbitals (with a different amount of atomic correlations in addition to their location). We are going to show that both of them can be transformed into an extended s-f model in the strongly correlated regime, under some specific conditions. Additionally, two nonequivalent orbital system is a prototype of the mixed (intermediate) valence behaviour since less than one electron per atom on average is transferred to the conduction band in practical situations [20]. The model with equivalent degenerate orbitals is a prototype of magnetism in narrow bands (eg. some 3d systems like CoS_2, NiS_2, V_2O_3) and, in particular, gives a simple description of many-body processes involved [11-12,14,15,16]. It is usually assumed that nonmagnetic (eg. 4s) electrons in a band overlapping with the narrow one play only a passive role in many-body processes. Their role is limited to taking some of the electrons from narrow band (charge transfer) and making them partially filled, without violating the charge neutrality of the whole system.

It is also interesting to note that in principle one could calculate the parameters of the models from the band theory results, and then use them to calculate the contribution due to many-body processes [3]. Unfortunately, such a procedure is usually beyond our possibilities because the realistic band structure is usually not taken into account in the related parametrized models. This problem is also beyond the scope of the work presented here.

3. Aim and the Scope of the Work

The present work proposes a systematic approach to the models listed in the previous Section, in the limit of strong Coulomb interactions. Although our results concerning the ground state and magnetic properties are not rigorous, the effective Hamiltonians derived here can be regarded as starting points of further analysis since they contain principal dynamical processes neglected in the Hartree-Fock approximation.

The purpose of this work is threefold:

1° To derive the magnetic interactions between the correlated itinerant electrons from a bare many-body Hamiltonian and to show their relation to a corresponding situation for the magnetic (Mott) insulators. This will allow us also to see explicitly the difference between the magnetism of insulators in which the orbital motion is frozen and the itinerant magnetism in which the kinetic energy does not commute with the spin part;

2° To present some novel results within the listed parametrized models with inclusion of the derived earlier magnetic interactions between electrons; and

3° To show how and why various models are related among themselves and, in particular, how the well defined localised moments arise from purely itinerant models.

The plan of the paper is as follows. In the next Part we derive the effective Hamiltonian, with a proper form of the kinetic exchange interactions between narrow-band electrons which reduces to the Anderson (1959,1963) kinetic exchange for the Mott insulator [34,35] . The effective Hamiltonian is then used to derive the magnetic phase diagram for an arbitrary band filling, and to discuss criteria for a local moment behaviour.

In Part III we turn over to the question of relation between the s-d model and narrow band represented by Hamiltonian (2-10). It means, we transform both the narrow-band and the periodic Anderson model (2-12) into an effective s-d model, under certain conditions.

In Part IV we consider rather shortly a novel technique of analysis of the derived s-d model, applicable both for itinerant magnetism (Sect.12-13) and intermediate-valence systems (Sect.14).

The present work gives references only to the work directly related to our own and does not pretend to serve as a review of the subject. Therefore, some of the very interesting works concerning the rigorous results for one dimensional narrow s-band (for review see: Ovchinnikov et al 1973 [36], and Coll 1974 [37]), as well as the renormalization group approach (reviewed recently by Solyom 1979 [38], see also Chui and Bray 1978 [39]) will not be touched upon here.

Let us add two additional remarks. Firstly, the present work is a sort of summary and an overview of our papers [19,36-59]. The most important results of that work will not be, however, discussed in detail here and therefore we have supplemented this thesis with the reprints of the most important of our papers (cf. Supplements A-J). Secondly, on the basis of our previous work and the results presented here we draw some general conclusions which may be of some help in understanding distinct classes of mixed itinerant-localised types of magnetism from a common starting point of strongly correlated electrons in a narrow band.

Part II

NARROW BAND

The role of kinetic exchange and the magnetic ground state

4. General Remarks

In this part we concentrate on possible magnetic phases of strongly correlated electrons both in a single and a doubly degenerate narrow bands. In the former case we can study a sole role of Coulomb correlations in a formation of a stable magnetic phase, while in the latter one it is influenced additionally by the intraatomic exchange between the electrons on different orbitals. The correlations introduce the kinetic exchange interactions which are antiferromagnetic. The intraatomic exchange causes indirect exchange of the RKKY type when $J \ll W$, and the double exchange when $J > W$. Additionally, its presence is responsible for the ferromagnetic kinetic exchange for a quarter-filled degenerate band (Kugel and Khomskii 1973 [60], Cyrot and Lyon-Caen 1975 [61]).

Generally, the region of strong correlations $W \ll U$ for a narrow band (called the atomic limit) is complementary to the region $W \gg U$ (the metallic limit) in which the standard approximations like the Hartree-Fock (Langer et al 1969 [63]), Gurtzwiller variational scheme (Brinkman and Rice 1970 [64], Kaplan and Bari 1970 [65], Florencio and Chao 1976 [66]), or many-body perturbation theory (Caron and Kemeny 1971 [67]) are applicable, and therefore the magnetic phase diagram is available (Penn 1966 [68], Cyrot 1972 [69], Caron and Kemeny 1971 [70] Röpke et al 1975 [71]).

The situation in the limit $W \ll U$ is more cumbersome. There exist, however, the well founded results, namely:

1° For half-filled case ground state is antiferromagnetic and insulating (Mott 1974 [72]).

2° Ground state for $U = \infty$ and with one hole in the Mott insulator is ferromagnetic for sc and bcc crystals (Nagaoka 1966 [73]).

3° There exists a critical band filling n_c such that for $n > n_c$ the ground state is ferromagnetic (Kanamori 1963 [74]).

We limit ourselves to the strong correlation limit $U \gg W$ in which we cannot rely on the Hartree-Fock approximation (for review see Robaszkiewicz 1976 [62]). Our approach is based on a canonical transformation of the bare many-body Hamiltonians (2.9) and (2.10) after which magnetic interactions show themselves in the effective Hamiltonian in an explicit form. In such a procedure dynamical processes having a minor influence onto the ground state configuration are removed and replaced by virtual processes of the higher order. The exchange interactions emerging from such processes express a renormalisation procedure of the bare ground state, calculated in an invariant (operator) form and hence, a subsequent approximation scheme in calculating ground state characteristics includes correctly the principal physical processes. A procedure of this type has been formulated previously for a single band (Spałek and Oleś 1976, 1977 [37,36], Chao et al 1977, 1978 [39,46], (Spałek et al 1980 [58]), for a single magnetic impurity Spałek et al 1978ab [44,45]), and for a doubly degenerate band (Chao et al 1977 [40], Spałek and Chao 1980 [59]).

In the present paper we formulate the theory of kinetic exchange in a slightly more general form than in the papers which have been just mentioned. Namely, we start from the full tight-binding Hamiltonian. This will allow us to analyse a competitive nature of direct and kinetic exchange interactions. Beside that, we also analyse the applicability of our results to some concrete systems (cf.Sect.7,5).

The natural question may arise whether the concept of the magnetic Hamiltonian can be useful when considering an itinerant magnet in which orbital and spin degrees of freedom are mutually coupled, i.e. when the kinetic energy term is present and does not commute with the part representing spin-spin interactions*. A clear answer to this question may provide a criterion of localisation of magnetic electrons in a translationally invariant system and, in particular, to give an explanation of the well know fact why some itinerant systems (e.g. Fe) behave in some respects similarly to those described in terms of the Heisenberg model. Unfortunately, a clear answer is not available as yet, although various variants of the theory of local moments behaviour exist [11-18]. We refer the reader to Part III for a detailed discussion of the last problem.

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*The problem has been pointed out to me by J. Hubbard (private communication).

5. Magnetic Interaction and Phases of Electrons in a Narrow Band

The purpose of this Section is threefold:

1° To derive the form of exchange interactions among strongly correlated itinerant electrons with all nearest-neighbour interactions included (full tight-binding Hamiltonian). In particular, we discuss a competitive character of direct and kinetic exchange interactions.

2° To draw a magnetic phase diagram for a model density of states within a realistic description of ferro- and antiferro-magnetic phases, and

3° To discuss the role of the derived kinetic exchange in physical terms, and to formulate a qualitative frame of description of magnetic ground state and border lines between various phases, in accord with the physical insight into the problem.

The method of approach is as follows. After a short illustration of the competitive nature of direct and kinetic exchange interactions on the exactly soluble two-site example in Sect. 5.1, we apply a canonical transformation used previously by us in the particular case of the Hubbard model [15] and derive an effective magnetic Hamiltonian in the second order in W/U (Sect. 5.2). The derived Hamiltonian is further studied within the Green function approach (Sects 5.3 and 5.4, and Appendices A-D). We make us of the two approximations: the Hartree-Fock and the moment-conserving decoupling (MCD) (Tahir-Kheli and Jarrett 1969 [74], Roth 1969ab [75,76]). In the latter case the mean-field type and the self-consistent procedure due to Roth are discussed separately for para-(P), ferro-(F), and antiferromagnetic (AF) phases. The strength and weakness of each approximation under consideration are pointed out. The explicit phase diagram for the rectangular model density of states is also discussed. In Sect. 5.6, based on an intuitive insight into the problem, we discuss our solutions in qualitative but general terms, not limited to the particular density of states. Finally, Sect. 5.6 contains a short summary of whole Section 5 and conclusions.

5.1. Two-site model: exact solution

The many-electron Hamiltonian in the Wannier representation $\left\{\Phi(\vec{r}-\vec{R}_i)\right\}$ where i label the lattice sites, can be expressed in the second quantized form as

$$H = \sum_{ij\sigma} t_{ij}\, a^+_{i\sigma}\, a_{j\sigma} + \frac{1}{2} \sum_{ijkl} V_{ijkl}\, a^+_{i\sigma}\, a^+_{j\sigma'}\, a_{l\sigma'}\, a_{k\sigma} \tag{5.1-1}$$

To illustrate the significance of the various matrix elements of the transfer $\langle i | T | j\rangle = t_{ij}$ and Coulomb $\langle ij | V_2 | kl\rangle = V_{ijkl}$ integrals in determining the magnetic properties of the generalized Hubbard Hamiltonian including all nearest neighbour interactions, we consider a two-site system corresponding to (2.1), which can be solved rigorously. Let these sites be labelled as 1 and 2. Then, for nonequivalent sites H reduces to

$$H = \sum_{i\sigma} E_i\, n_{i\sigma} + t \sum \left(a^+_{1\sigma}\, a_{2\sigma} + a^+_{2\sigma}\, a_{1\sigma}\right) + \sum_i U_i\, n_{i\uparrow}\, n_{i\downarrow} + \left(K - \frac{J}{2}\right) \sum_{\sigma\sigma'} n_{1\sigma}\, n_{2\sigma'} - 2J\vec{S}_1 \cdot \vec{S}_2 + V \sum_\sigma \left(n_{1\sigma} + n_{2\sigma}\right)\left(a^+_{1-\sigma}\, a_{2-\sigma} + a^+_{2-\sigma}\, a_{1-\sigma}\right) + J\left(a^+_{1\uparrow}\, a^+_{1\downarrow}\, a_{2\downarrow}\, a_{2\uparrow} + a^+_{2\uparrow}\, a^+_{2\downarrow}\, a_{1\downarrow}\, a_{1\uparrow}\right) \tag{5.1-2}$$

Where $E_i = t_{ii}$ is the atomic level of i-th atom, $t = t_{12}$ is the hopping integral, $U_i = V_{iiii}$ is the intraatomic Coulomb integral, and $K = V_{1221}{}'$, $V = V_{1112}{}'$ and $J = V_{1221}$ are interside Coulomb integrals. $\vec{S}_i = \left(S_i, S_i^-, S_i^z\right)$ is the spin operator which in the Fock space is represented by $S_i^+ = a^+_{i\uparrow}\, a_{i\downarrow}$, $S_i^- = a^+_{i\downarrow}\, a_{i\uparrow}$, and $S_i^z = \frac{1}{2}\left(n_{i\uparrow} - n_{i\downarrow}\right)$

For a system formed from N atomic sites there are $\binom{2N}{N_e}$ states, where N_e is the number of electrons. For two sites this gives 4 and 6 states for $N = 1$ and 2, respectively. We consider these two cases, corresponding to quarter-and half-filled bands, respectively. In case $N_e = 1$ the doubly degenerate eigenstates can be obtained as

$$|\lambda_{1,2}\rangle = \left[1 + \left(\frac{\lambda_{1,2} - E_{1,2}}{t}\right)^2\right]^{-1/2} \left(a^+_{1\sigma} + \frac{\lambda_{1,2} - E_{1,2}}{t}\, a^+_{2\sigma}\right)|0\rangle \tag{5.1-3}$$

with eigenvalues

$$\lambda_{1,2} = \frac{1}{2}\left(E_1 + E_2\right) \pm \left[\frac{1}{4}\left(E_1 - E_2\right)^2 + t^2\right]^{1/2} \tag{5.1-4}$$

These states are the bonding and antibonding ones, degenerate with respect to spin orientation σ. For two electrons there are three de-zero

generate triplet states with $S^z = S_i^z + S_2^z = \pm 1$ and 0

$$|\lambda_{1,2}\rangle = a^+_{1\sigma}\, a^+_{2\sigma}\, |0\rangle$$
$$|\lambda_3\rangle = \frac{1}{\sqrt{2}} \left(a^+_{1\uparrow}\, a^+_{2\downarrow} + a^+_{2\uparrow}\, a^+_{1\downarrow} \right) |0\rangle \qquad (5.1\text{-}5)$$

with eigenvalue

$$E_t = \lambda_{1,2,3} = 2E + K - J$$

where $E = (E_1 + E_2)/2$. There are also three singlet states, two of them corresponding to the bonding and antibonding states, respectively

$$|\lambda_\mp\rangle = \left[4D\left(D \mp U \pm K\right)\right]^{-1/2} \left[4\,(t+V)\left(a^+_{1\uparrow}\, a^+_{2\downarrow} + a^+_{2\uparrow}\, a^+_{1\downarrow}\right) \mp \left(D \mp U \pm K\right)\left(a^+_{1\uparrow}\, a^+_{1\downarrow} + a^+_{2\uparrow}\, a^+_{2\downarrow}\right)\right] |0\rangle \qquad (5.1\text{-}6)$$

with eigenvalues

$$\lambda_\mp = 2E + J + \frac{1}{2}\left(U + K \mp D\right) \qquad (5.1\text{-}7)$$

and the third one with doubly occupied sites

$$|\lambda_4\rangle = \frac{1}{\sqrt{2}} \left(a^+_{1\uparrow}\, a^+_{1\downarrow} - a^+_{2\uparrow}\, a^+_{2\downarrow} \right) |0\rangle$$

and corresponding eigenenergy

$$\lambda_4 = 2E + U - J \qquad (5.1\text{-}8)$$

where $U = (U_1 + U_2)/2$, and $D = \left[(U-K)^2 + 16\,(V+t)^2\right]^{1/2}$. If U is sufficiently large, $\lambda_4 - \lambda_\pm = (U-K-4J\mp D)/2 > 0$ and the ground state is a triplet if $E_t < \lambda_-$, or equivalently if

$$J > \frac{1}{4}\left(D-U+K\right) \qquad (5.1\text{-}9)$$

For strong intraatomic correlations, i.e. for $U-K \gg 2\,(t+V)$ this condition reduces to

$$J > \frac{2\,(t+V)^2}{U-K} \qquad (5.1\text{-}10)$$

We see that the direct exchange $\sim J$ favours the triplet (ferromagnetic) configuration while the kinetic exchange $\sim \frac{t+V}{U-K}^2$ tends to stabilize the bonding (antiferromagnetic) state. Hence the competition between these two mechanisms plays a very important role in the determination of the magnetic phases of the full narrow band tight binding Hamiltonian (i.e. with all nearest neighbour interactions included), as will be seen in the following section. We should also note that the intersite Coulomb interaction $\sim K$ affects the magnetic conditions (5.2-9) or (5.2-10). Consequently, one expects to see the interplay between the charge fluctuation and spin fluctuation in narrow band systems. Also, one can see that the kinetic exchange does not depend on the position of the atomic level on given site. Therefore we expect that the same type of exchange exists in disordered narrow band systems or in particular, in the narrow band with impurities as it has been discussed in more detail elsewhere [44,45].

5.2. Canonical transformation and effective exchange interactions

Let us now consider the Hamiltonian (5.1-1) for a translationally invariant system ($U_i = U$ and set $t_{ii} = 0$) composed of N sites, containing all interactions between electrons on neighbouring sites. Then we obtain the Hamiltonian which is a straight-forward generalization of (5.1-1).

$$\begin{aligned} H = {} & t \sum_{ij\sigma} a^{+}_{j\sigma} a_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} + \frac{1}{2}\left(K - \frac{J}{2}\right) {\sum_{ij}}' n_{i\sigma} n_{j\sigma'} \\ & - J {\sum_{ij}}' \vec{S}_i \cdot \vec{S}_j + V {\sum_{ij}}' n_{i-\sigma}\left(a^{+}_{i\sigma} a_{j\sigma} + a^{+}_{j\sigma} a_{i\sigma}\right) \\ & + J {\sum_{ij}}' a^{+}_{i\uparrow} a^{+}_{i\downarrow} a_{j\downarrow} a_{j\uparrow} \end{aligned} \tag{5.2-1}$$

where t is the nearest neighbour hopping integral, and K, J and V are defined as in the previous section. All the primed sums run over only those sites which are nearest neighbours of each other. We have also assumed that the Wannier basis $\{\Phi(\vec{r} - \vec{R}_i)\}$ is chosen in such a way that all functions $\Phi(\vec{r} - \vec{R}_i)$ are reals.

In this paper we are interested in the regime of strong intraatomic interactions, namely, U is much larger than $|t|$, K, J and V. In this situation, the spectrum of H is separated into disjoined regions called the Mott-Hubbard subbands. If E_i is the mean energy of the i-th subband then the mean distance between two adjacent E_i´s is U. The structures of the subbands depend on the values of t, K, J and V, and each of them corresponds to the subspace of the Hilbert space, formed from atomic states with a definite number of doubly occupied sites. There is one to one correspondence between the subbands and the subspaces. The former are formed from the latter with the overlap between the nearest neighbours and if $2z|t| \ll U$ (z - number of nearest neighbours) the states in the subbands can be treated as subspaces orthogonal to each other. A thorough analysis of the subspaces and subbands for the Hubbard model has been given by the present author [46] (referred to as I). That analysis applies as well to the generalized case (5.2-1) and the reader is referred to it for details.

As pointed out in I, the magnetic properties at large U and for the number of electrons not exceeding number of sites N is dominated by the lowest subband which contains no doubly occupied atoms and by the first excited subband which contains one doubly occupied site. Let P_1 be the projection operator corresponding to the lowest subband and P_2 the projection operator corresponding to the other. Then we have the projection of the Hamiltonian (5.2-1).

$$\begin{aligned} P_1 H P_1 = P_1 \Big\{ & t \sum_{ij\sigma}{}' a^+_{i\sigma} (1-n_{i-\sigma}) a_{j\sigma} (1-n_{j-\sigma}) \\ & + \frac{1}{2}(K-J) \sum_{ij\sigma\sigma'}{}' n_{i\sigma} (1-n_{i-\sigma}) n_{j\sigma'} (1-n_{j-\sigma'}) \\ & - J \sum_{ij}{}' \vec{S}_i \cdot \vec{S}_j \Big\} P_1 \end{aligned} \tag{5.2-2}$$

$$P_1 H P_2 = (P_2 H P_1)^+ = P_1 \Big\{ (t+V) \sum_{ij}{}' a^+_{i\sigma} (1-n_{i-\sigma}) a_{j\sigma} n_{j-\sigma} \Big\} P_2 \tag{5.2-3}$$

$$\begin{aligned} P_2 H P_2 = P_2 \Big\{ & (t+V) \sum_{ij\sigma} a^+_{i\sigma} n_{i-\sigma} a_{j\sigma} n_{j-\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \\ & - J \sum_{ij}{}' a^+_{i\uparrow} a^+_{i\downarrow} a_{j\downarrow} a_{j\uparrow} \\ & + 2 \left(K - \frac{J}{2}\right) \sum_{ij\sigma}{}' n_{i\sigma} (1-n_{i-\sigma}) n_{j\uparrow} n_{j\downarrow} \Big\} P_2 \end{aligned} \tag{5.2-4}$$

The general rule is that for each site we decompose the single-particle operator A_i as follows (cf. I for details)

$$A_{i\sigma} \equiv A_{i\sigma} (1-n_{i-\sigma}) + n_{i-\sigma}) = A_{i\sigma} (1-n_{i-\sigma}) + A_{i\sigma} n_{i-\sigma}$$

Since the higher lying subbands containing many doubly occupied sites can be ignored for the interest of the present work, the Hamiltonian can be approximated as follows

$$H = \Big(\sum_i P_i\Big) H \Big(\sum_i P_i\Big) = H_o + H_1 \tag{5.2-5}$$

where

$$H_o = P_1 H P_1 + P_2 H P_2 \tag{5.2-6}$$

and

$$H_1 = P_1 H P_2 + P_2 H P_1 \tag{5.2-7}$$

H_o describes the motion of electrons in either lowest or first excited subbands, while H_1 gives the transitions of electrons between the subbands due to the nearest neighbour hopping. Since the subbands are separated by a large energy U, the Hamiltonian H_1 giving rise to intersubband transitions will be treated as a perturbation.

As in I , we consider the canonically transformed effective Hamiltonian

$$H = e^{-iS}\left(H_0 + H_1\right)e^{iS} \quad ; \qquad S = S^{+} \qquad (5.2\text{-}8)$$

where S satisfies

$$H_1 + i\left[H_0, S\right] = 0 \qquad (5.2\text{-}9)$$

Let us discuss with more details the solution of (5.2-9), not included in I . It is a nonstandard solution, since H_0 is not assumed to be diagonal. Additionally, we want to remove only the part of the total hopping processes in the first order (those between subspaces) and thus only part P_iSP_j with $i \neq j$ is important. Indeed, projecting (5.2-9) we have

$$\left[P_iSP_i, \; P_iHP_i\right] = 0 \qquad (5.2\text{-}10)$$

$$iP_iHP_j + P_iSP_j \cdot P_jHP_j - P_iHP_i \cdot P_iSP_j = 0 \qquad (5.2\text{-}11)$$

The first equation has solution $P_iSP_i = f\left(P_iHP_i\right)$ with $f(x)$ being an arbitrary function of $x = P_iHP_i$. We can rewrite the second equation

$$P_1SP_2 = \left[-i\, P_1HP_2 + P_1HP_1 \; P_1SP_2\right]\left(P_2HP_2\right)^{-1} \qquad (5.2\text{-}12)$$

Note that $\left(P_2HP_2\right)^{-1}$ exists only when P_2HP_2 has all eigenvalues different from zero, which means that $U \gg W$. We also assume that to assure the convergence of an iteration procedure which gives rise to the series

$$P_1SP_2 = -i\sum_{n=0}^{\infty}\left(P_1HP_1\right)^{n} P_1HP_2 \left(P_2HP_2\right)^{-(n+1)} \qquad (5.2\text{-}13)$$

where we have started from iteration $P_1S^{(0)}P_2 = 0$. We see that in the transformation (5.2-13) $\left(P_1HP_1\right)^n$ and $\left(P_2HP_2\right)^{-(n+1)}$ correspond to the processes within subbands. Since we include these leading processes of this type already in H_0 the simplest approximation is to average over processes within bands. This leads to the formula for P_1SP_2 derived by us before [46] . But from (5.2-13) we see that the same result can be recovered if we retain in it the terms $\sim t/U$ only. Therefore

$$P_1SP_2 = -i\,\frac{P_1HP_2}{U-K} + O\left(\frac{tJ}{U^2}\right) + O\left(\frac{tV}{U^2}\right) + O\left(\frac{t^2}{U^2}\right) \qquad (5.2\text{-}14)$$

and the effective Hamiltonian H up to the second order $\left(\sim t^2/U-K\right)$ is

$$H = H_0 - \left(P_1HP_2HP_1 - P_2HP_1HP_2\right) / \left(U-K\right) \qquad (5.2\text{-}15)$$

Using (5.2-2) and (5.2-14) we have

$$P_1HP_2HP_1 = (t+V)^2\, P_1\Big\{ \sum_{ij\sigma}{}' \nu_{i-\sigma}\, \nu_{j\sigma} - S_i^{\sigma}\, S_j^{-\sigma} + \sum_{i(j\neq K)}{}''\big(b^+_{k\sigma}\, \nu_{i-\sigma} - b^+_{k-\sigma}\, S_i^{\sigma}\big)\, b_{j\sigma} \Big\}\, P_1 \tag{5,2-16}$$

where $b_{i\sigma} = a_{i\sigma}\,(1-n_{i-\sigma})$, $\nu_{i\sigma} = b^+_{i\sigma}\, b_{i\sigma}$, and $S_i^{\sigma} = a^+_{i\sigma}\, a_{i-\sigma} = b^+_{i\sigma}\, b_{i-\sigma}$.

The double-primed summation includes only these configurations with both the j-th and the k-th sites are nearest neighbours of the i-th site. If we define $c_{i\sigma} = a_{i\sigma}\, n_{i-\sigma}$ then we similarly obtain

$$\begin{aligned} P_2HP_1HP_2 = (t+V)^2\, P_2\Big\{ & \sum_{ij\sigma}{}' (1-n_{i-\sigma})(1-n_{i\sigma})\, n_{j\sigma}\, n_{j-\sigma} \\ & + a^+_{i\sigma}\, a^+_{i-\sigma}\, a_{j-\sigma}\, a_{j\sigma} + \sum_{i(j\neq k)\sigma}{}'' c^+_{k\sigma}\, b_{i\sigma}\, b^+_{i\sigma}\, c_{j\sigma} \\ & + c^+_{i\sigma}\, b_{k\sigma}\, b^+_{j\sigma}\, c_{i\sigma} + c^+_{k-\sigma}\, b_{i-\sigma}\, b^+_{j\sigma}\, c_{i\sigma} \\ & + c^+_{i-\sigma}\, b_{k-\sigma}\, b^+_{i\sigma}\, c_{j\sigma} + \sum_{kl\sigma}{}' \sum_{\substack{ij\sigma' \\ (ij\neq kl)}}{}' c^+_{k\sigma}\, b_{l\sigma}\, b^+_{i\sigma'}\, c_{j\sigma'} \Big\} P_2 \end{aligned} \tag{5,2-17}$$

Part of the processes in (5.2-13) and (5.2-14) which involve three sites correspond to the indirect hopping between more distant neighbours. For example, the term $b^+_{k\sigma}\, \nu_{i-\sigma}\, b_{j\sigma}$ is the indirect hopping from the singly occupied i-th site. Such indirect hoppings have to be neglected for the sake of consistency, since we have excluded direct hopping processes between next nearest neighbours in our tight binding Hamiltonian (3.1). Consequently, we include only two site processes which involve virtual hopping in the second order, both without and with spin-flip. In such a situation the effective Hamiltonian, which can be represented as

$$\tilde{H} = P_1\, \tilde{H}\, P_1 + P_2\, \tilde{H}\, P_2 \tag{5,2-18}$$

with

$$P_1\, \tilde{H}\, P_1 = P_1\Big\{ t \sum_{ij\sigma}{}' b^+_{i\sigma}\, b_{j\sigma} + \frac{1}{2}\Big(\tilde{U}_2 - \frac{\tilde{J}}{2}\Big) \sum_{ij\sigma}{}' \nu_{i\sigma}\, \nu_{j\sigma'} + \tilde{J} \sum_{ij}{}' \vec{S}_i \cdot \vec{S}_j \Big\}\, P_1 \tag{5,2-19}$$

and

$$\begin{aligned} P_2\, \tilde{H}\, P_2 = P_2\Big\{ & (t+V) \sum_{ij}{}' c^+_{i\sigma}\, c_{j\sigma} + U \sum_i n_{i\uparrow}\, n_{i\downarrow} \\ & + \tilde{J} \sum_{ij}{}' a^+_{i\uparrow}\, a^+_{i\downarrow}\, a_{j\downarrow}\, a_{j\uparrow} + 2\Big(K - \frac{J}{2}\Big) \sum_{\substack{ij \\ \sigma\sigma'}}{}' n_{i\sigma}\,(1-n_{i-\sigma})\, n_{j\uparrow}\, n_{j\downarrow} \end{aligned}$$

$$+ \frac{2\left(t+V\right)^2}{U-K} \sum_{ij}{}' \left(1-n_{i\uparrow}\right)\left(1-n_{i\downarrow}\right) n_{j\uparrow} n_{j\downarrow} \Big\} P_2 \tag{5.2-20}$$

with $\tilde{U}_2 = K-J$ and $\tilde{J} = \frac{2\left(t+V\right)^2}{U-K} - J$. This Hamiltonian will be further studied in the following sections for partially filled lowest subband, i.e. for number of electrons per atom $n \leqslant 1$. Comparing (5.2-19) with the condition (5.1-10) for the triplet ground state we see that the competitive character of direct and kinetic exchange interactions is contained in the term $\tilde{J} \sum_{ij} \vec{S}_i \cdot \vec{S}_j$.

5.3. Green function approach and the moment-conserving decoupling

We are interested mainly in the quasiparticle states and the static magnetic properties for the narrow band system represented by the effective Hamiltonian (5.2-19). Since we are interested in the phase diagram at $T = 0$ only, we can disregard the part (5.2-20) of the effective Hamiltonian because from the beginning we have limited ourselves to the region $U > W$. Under these circumstances we have $\langle \nu_{i\sigma} \rangle = \langle n_{i\sigma} \rangle$ and therefore the ground state properties are determined completely in terms of single-particle Green function $\langle\langle b_{i\sigma} | b^+_{j\sigma} \rangle\rangle$ with the equation of motion in the form [74-76]

$$E \langle\langle b_{i\sigma} | b^+_{j\sigma} \rangle\rangle = \frac{1}{2\pi}\left(1-\langle n_{i-\sigma}\rangle\right)\delta_{ij} + \langle\langle \left[b_{i\sigma}\;\; P_1 H P_1\right] | b^+_{j\sigma} \rangle\rangle \tag{5.3-1}$$

or in explicit form

$$\begin{aligned} E \langle\langle b_{i\sigma} | b^+_{j\sigma} \rangle\rangle &= \frac{1}{2\pi}\left(1-\langle n_{i-\sigma}\rangle\right)\delta_{ij} \\ &+ t \sum_{m(i)} \langle\langle b_{m\sigma}\left(1-n_{i-\sigma}\right) + b_{m-\sigma}\, S_i^{-\sigma} | b^+_{j\sigma} \rangle\rangle \\ &+ \tilde{J} \sum_{m(i)} \langle\langle S_m^{-\sigma}\, b_{i-\sigma} - b_{i\sigma}\, \nu_{m-\sigma} | b^+_{j\sigma} \rangle\rangle \\ &+ \tilde{U}_2 \sum_{\substack{m(i)\\ \sigma'}} \langle\langle b_{i\sigma}\, \nu_{m\sigma'} | b^+_{j\sigma} \rangle\rangle \end{aligned} \tag{5.3-2}$$

As usual, the main problem of the equation of motion method is how to decouple the higher-order Green functions on r.h.s. of (5.3-1). We have chosen the moment-conserving decoupling [74-76] for the following reasons. Firstly, the decoupled Green functions which replace the r.h.s. of (5.3-2) are found in a selfconsistent way. Secondly, the average relative shift of the spin subbadns in the ferromagnetic phase is reproduced exactly, which makes this method particularly attractive, since for example, there is no obvious reason why for the Hubbard model (i.e.

for $J = \widetilde{U}_2 = V = 0$) there is a stable ferromagnetic solution as was shown by Nagaoka [73] and Kanamori [74]. Additionally, in the Appendix A we have discussed the simplest decoupling which corresponds to the Hartree-Fock approximation. Those results are used for a comparison with the corresponding ones from the moment-conserving decoupling to conclude what type of correlation, which is missing in the mean-field approximation is essential in a more refined approach to the ferromagnetic case.

In the moment-conserving decoupling we assume that

$$\left[b_{i\sigma} \, , \, P_1 \widetilde{H} P_1\right] = \sum_{l} M_{il} \, b_{l\sigma} \qquad (5.3\text{-}3)$$

where M_{il} is the self-energy part of the mass operator which is determined from the conservation of the first moment of spectral density function $\left\langle\left\{b_{i\sigma}(t) \, , \, b^{+}_{j\sigma}(0)\right\}\right\rangle$, namely

$$\sum_{l} M_{il} \left\langle\left\{b_{l\sigma} \, , \, b^{+}_{j\sigma}\right\}\right\rangle = \left\langle\left\{\left[b_{i\sigma} \, , \, P_1 \widetilde{H} P_1\right] , b^{+}_{j\sigma}\right\}\right\rangle \qquad (5.3\text{-}4)$$

or in explicit form

$$M_{il} = \frac{t}{1-\langle n_{l-\sigma}\rangle}\Big[\langle S^{\sigma}_{l} S^{-\sigma}_{i}\rangle + \langle(1-n_{i-\sigma})(1-n_{l-\sigma})\rangle - JS_{-\sigma} - U_2 S_{\sigma}\Big] + \delta_{il} \frac{zt}{1-\langle n_{i-\sigma}\rangle}\Big\{-S_{-\sigma} + U_2 \langle(1-n_{i-\sigma})(\nu_{m\sigma} + \nu_{m-\sigma})\rangle + J\left[\langle S^{\sigma}_{i} S^{-\sigma}_{m}\rangle - \langle(1-n_{i-\sigma}) \, \nu_{m-\sigma}\rangle\right]\Big\} \qquad (5.3\text{-}5)$$

where $J = \widetilde{J}/t$, $U_2 = \widetilde{U}_2/t$ and the pairs of subscripts (i,l) or (i,m) in the two-particle correlation functions are those of nearest neighbours. Hence, substituting (5.3-5) into (5.3-1) we get the decoupled equation, which for the translationally invariant systems reads as

$$(E-M_1) \left\langle\!\left\langle b_{i\sigma} \middle| \, b^{+}_{j\sigma}\right\rangle\!\right\rangle = \frac{1-\langle n_{i-\sigma}\rangle}{2\pi} + M_2 \sum_{m(i)} \left\langle\!\left\langle b_{m\sigma} \middle| \, b^{+}_{j\sigma}\right\rangle\!\right\rangle \qquad (5.3\text{-}6)$$

where $M_1 = M_{ii}$, and $M_2 = M_{ij}$ for $i \neq j$. Even though the eq. (5.3-6) is diagonalized in the $\vec{k}$ space, we still need to calculate the two-particle correlation functions $\langle S^{\sigma}_{i} S^{-\sigma}_{m}\rangle$ and $\langle n_{i\sigma} n_{m\sigma'}\rangle$. This goal can be achieved with the help of the selfconsistent procedure proposed by Roth [75] for the Hubbard model or, in more general terms, by Kalashnikov and Fradkin [77]. We refer the reader to Appendix B, where the two-particle correlations entering into (5.3-5) are expressed through the one-particle ones determined from the Green function $\left\langle\!\left\langle b_{j\sigma} \middle| \, b^{+}_{j\sigma}\right\rangle\!\right\rangle$ and henceforth eqn. (5.3.1) is solved formally. We point out there also certain ambiguities contained in the Roth method and propose how to resolve them in the simplest way. Furthermore, it is shown there that the decomposition (5.3-3) of higher order Green function $\langle\langle [b_{i\sigma}, P_1\tilde{H}P_1] | b^+_{j\sigma}\rangle\rangle$ conserve first two moments of spectral density function $\langle\langle\{b_{i\sigma}(t), b^+_j(0)\}\rangle\rangle$. This means that if the lowest Hubbard subband splits further into two subbands, then the total number of states within those subbands and the average relative position of them are reproduced exactly. Since in the case of ferromagnetism the system composed of the lowest Hubbard subband splits into two spin-subbands, and in the case of antiferromagnetism into two-spin-independent subbadns due to the formation of superlattice, we think that our method describes properly the most important factors arising from the electron-electron interactions in the strong correlation limit $W \ll U$. If, however, this approach is applied in the region $W \sim U$, it can predict incorrectly the metal-nonmetal transition point, at which the detailed quasiparticle band structure of the merging Hubbard subbands is important. Below, we combine the results (5.3-2)-(5.3-5) and those from Appendices B and C to calculate the quasiparticle states and other ground state properties for the ferro-, para- and antiferromagnetic cases, respectively.

Ferro- and para-magnetic solutions

In the translationally invariant system eq.(5.3-6) can be diagonalized taking the space-Fourier transform to k-space

$$\langle\langle b_{\vec{k}\sigma} | b^+_{\vec{K}\sigma}\rangle\rangle = \frac{1}{N}\sum_{\vec{k}} e^{i\vec{k}(\vec{R}_j-\vec{R}_i)} \langle\langle b_{i\sigma} | b^+_{j\sigma}\rangle\rangle \qquad (5.3\text{-}7)$$

which gives

$$\langle\langle b_{\vec{k}\sigma} | b^+_{\vec{k}\sigma}\rangle\rangle = \frac{1-n_{-\sigma}}{2\pi} \cdot \frac{1}{E-E_{\vec{k}\sigma}} \qquad (5.3\text{-}8)$$

where the quasiparticle energies E_k is

$$E_{\vec{k}\sigma} = \epsilon_{\vec{k}}(1-n_{-\sigma}) + ztW_{1-\sigma} + \epsilon_{\vec{k}} W_{2\sigma} \qquad (5.3\text{-}9)$$

with the band-shift

$$W_{1-\sigma} = -\frac{1}{1-n_{-\sigma}}\Big[S_{-\sigma} + Jn_{-\sigma} - J\langle n_{i-\sigma}\, n_{m-\sigma}\rangle$$
$$- J\langle S_i^{\sigma}\, S_m^{-\sigma}\rangle + U_2\langle n_{i-\sigma}(n_{m\sigma} + n_{m-\sigma})\rangle - U_2 n\Big] \qquad (5.3\text{-}10)$$

and the band-narrowing

$$W_{2\sigma} = \frac{1}{1-n_{-\sigma}}\Big[\langle n_{i-\sigma}\, n_{m-\sigma}\rangle - n^2_{-\sigma} + \langle S_m^{\sigma}\, S_i^{-\sigma}\rangle$$
$$- JS_{-\sigma} - U_2 S_{\sigma}\Big] \qquad (5.3\text{-}11)$$

Comparing (5.3-10)-(5.3-11) with (4.4) determined from the Hartree-Fock approximation one can notice two differences. Firstly, two-particle terms determine both $W_{1\sigma}$ and $W_{2\sigma}$ and secondly, the band-shift and band narrowing factors are multiplied by the factor $(1-n_{-\sigma})^{-1}$ which is very important when $n \to 1$. The former fact reflects the process of "dressing" of a quasi-particle by the other particles present in the system, while the latter one takes into account the conditional probability that the "dressing" process of a particle with spin σ takes place, provided there is a hole with the opposite spin bound to it. This conditional probability is absent in the Hartree-Fock approximation. Substituting either formulas (B.12), (B.13) and (B.15) or (B.16) and (B.17) to (5.3-10) and (5.3-11) we have the solution closed formally. In the rest of this section we will discuss the formulas for ground state properties within the Roth-scheme, which will be discussed further in the next section for model density of states. We refer the reader to the Appendix D for discussion of simpler approach expressed through (B.16) and (B.17). The explicit form of band-shift (5.3-10) and band-narrowing (5.3-11) factors is

$$\begin{aligned} W_{1-\sigma} = & -S_{-\sigma} - Jn_{-\sigma}(1-n_{-\sigma}) - JS^2_{-\sigma}\frac{1-n_{-\sigma}}{1-n} - JS_{\sigma}S_{-\sigma} + U_2 n(1-n_{-\sigma}) \\ & - U_2\frac{S^2_{-\sigma}n_{-\sigma}}{1-n} + U_2 n_{\sigma} n_{-\sigma}(1+R) \end{aligned} \qquad (5.3\text{-}12)$$

and

$$\begin{aligned} W_2(1-n_{-\sigma}) = & -(1-n)^{-1}\left[S^2_{-\sigma}(1-n_{-\sigma}) + S_{\sigma}S_{-\sigma}\right. \\ & \left. + (1-n)(JS_{-\sigma} + U_2 S_{\sigma})\right] \end{aligned} \qquad (5.3\text{-}13)$$

where $R = \frac{1}{2}\sum_{\sigma} S^2_{\sigma} n_{-\sigma}$ and $S_{\sigma} = \langle b^+_{m\sigma} b_{i\sigma}\rangle$ with m and being the pair of nearest neighbours. These results reduce to the derived by Roth in the limit $J = U_2 = 0$, which corresponds to the limit $U = \infty$ in the Hubbard model. Applying to (5.3-8) the fluctuation-dissipation theorem

$$\langle b^+_{\vec{k}\sigma} b_{\vec{k}\sigma}\rangle = \frac{1}{\pi}\int_{-\infty}^{\infty} \mathrm{Im} \langle\langle b_{\vec{k}\sigma} | b^+_{\vec{k}\sigma}\rangle\rangle \; \omega + i\epsilon \; f(\omega - u)\, d\omega \qquad (5.3\text{-}14)$$

where $f(\omega - u)$ is the Fermi-Dirac distribution, and using the property of the inverse space Fourier transform which reads

$$\frac{1}{N}\sum_{\vec{k}} \langle b^+_{\vec{k}\sigma} b_{\vec{k}\sigma}\rangle e^{-i\vec{k}(\vec{R}_m - \vec{R}_j)} = \begin{cases} n_{\sigma} & \text{for } m=i \\ S_{\sigma} & \text{for } (m,i) = \text{n.n.} \end{cases} \qquad (5.3\text{-}15)$$

We have the expression for mean occupation number of electrons per site

$$n_\sigma = \left(1-n_{-\sigma}\right) \frac{1}{N} \sum_{\vec{k}} f\left(E_{\vec{k}\sigma} - \mu\right) \qquad (5.3\text{-}16)$$

and

$$ztS_\sigma = \left(1-n_{-\sigma}\right) \frac{1}{N} \sum_{\vec{k}} \epsilon_{\vec{k}} f\left(E_{\vec{k}\sigma} - \mu\right) \qquad (5.3\text{-}17)$$

Eqns.(5.3-16) and (5.3-17) can be rewritten in the integral form which for T = 0 are

$$n_\sigma = \left(1-n_{-\sigma}\right) \int_{-z|t|}^{\omega_\sigma} \varrho(\omega)\, d\omega \qquad (5.3\text{-}18)$$

and

$$ztS_\sigma = \left(1-n_{-\sigma}\right) \int_{-z|t|}^{\omega_\sigma} \omega \varrho(\omega)\, d\omega \qquad (5.3\text{-}19)$$

where

$$\omega_\sigma = \frac{\mu - ztW_{1-\sigma}}{1-n_{-\sigma} + W_{2\sigma}} \qquad (5.3\text{-}20)$$

and

$$\varrho(\omega) = \frac{1}{N} \sum_{\vec{k}} \delta\left(\omega - \epsilon_{\vec{k}}\right)$$

in the density of states of the bare band /without interactions . Using the formula C.7 from Appendix C we have the expression for the ground state energy

$$e_G = \frac{E_G}{Nz\,|t|} = -\frac{1}{2} \sum_\sigma \left[\left(2-n_{-\sigma}\right) + W_{2\sigma}\right) S_\sigma + n_\sigma W_{1-\sigma}\Big] \qquad (5.3\text{-}21)$$

Antiferromagnetic solution

We decompose now eqn.(5.3-6) into two reflecting the presence of two impenetrable but equivalent sublattices labelled A and B. The system is described by two Green functions $\langle\langle b^A_{\vec{k}\sigma} \mid b^A_{\vec{k}\sigma} \rangle\rangle = \langle\langle b^B_{\vec{k}\sigma} \mid b^{B+}_{\vec{k}\sigma} \rangle\rangle$ and $\langle\langle b^B_{\vec{k}\sigma} \mid b^A_{\vec{k}\sigma} \rangle\rangle = \langle\langle b^A_{\vec{k}-\sigma} \mid b^{B+}_{\vec{k}-\sigma} \rangle\rangle$ which are obtained by the procedure analogical to that in the previous subsection. Namely, from the Fourier transformed Eq.(5.3-6) in this case

$$\left(E - ztW_{1-\sigma}\right) \langle\langle b^A_{\vec{k}\sigma} \mid b^{A+}_{\vec{k}\sigma} \rangle\rangle = \frac{1-n_{-\sigma}}{2\pi} + \epsilon_{\vec{k}} \left(1-n_{-\sigma} + \frac{W_2}{1-n_\sigma}\right) \langle\langle b^B_{\vec{k}\sigma} \mid b^A_{\vec{k}\sigma} \rangle\rangle \qquad (5.3\text{-}22)$$

$$(E-ztW_1)\quad \langle\langle b^B_{\vec{k}\sigma} \,|\, b^A_{\vec{k}\sigma}\rangle\rangle = \epsilon_{\vec{k}}\left(1-n_{-\sigma} + \frac{W_2}{1-n_{-\sigma}}\right)\langle\langle b^A_{\vec{k}\sigma} \,|\, b^{A+}_{\vec{k}\sigma}\rangle\rangle \tag{5.3-23}$$

where now

$$(1-n_{-\sigma})\, W_{1-\sigma} = -S-Jn_\sigma + U_2 n-(U_2-J)\langle n^B_{m\sigma}\; n^A_{i\sigma}\rangle + J\langle S^{B\sigma}_m\; S^{A-\sigma}_i\rangle - U_2\langle n^B_{m\sigma}\, n^A_{-\sigma}\rangle \tag{5.3-24}$$

$$W_2 = \langle n^B_{m\sigma}\; n^A_{i\sigma}\rangle - n_\sigma n_{-\sigma} + \langle S^{B\sigma}_m\; S^{A-\sigma}_i\rangle - (J+U_2)\, S \tag{5.3-25}$$

and $n_\sigma = \langle n^A_{i\sigma}\rangle = \langle n^B_{m-\sigma}\rangle$, we have the following solutions

$$\langle\langle b^A_{\vec{k}\sigma} \,/\, b^{A+}_{\vec{k}\sigma}\rangle\rangle = \frac{1-n_{-\sigma}}{2\pi}\;\frac{E+ztW_{1-\sigma}}{(E-E_{1\,\vec{k}})(E-E_{2\,\vec{k}})} \tag{5.3-26}$$

and

$$\langle\langle b^B_{\vec{k}\sigma} \,|\, b^{A+}_{\vec{k}\sigma}\rangle\rangle = \frac{1}{2\pi}\;\epsilon_{\vec{k}}\;\frac{a^2+W_2}{(E-E_{1\,\vec{k}})(E-E_{2\,\vec{k}})} \tag{5.3-27}$$

where the quasiparticle subbands are given by the dispersion relation

$$E_{1,2\,\vec{k}} = -\frac{1}{2}\,zt\sum_\sigma W_1 \quad \pm\sqrt{\Delta_{\vec{k}}} \tag{5.3-28}$$

with

$$\Delta_{\vec{k}} = (zt/2)^2\left(\sum_\sigma \sigma\, W_{1\sigma}\right)^2 + \epsilon^2_{\vec{k}}\left(\frac{a^2+W_2}{a}\right)^2 \tag{5.3-29}$$

For the particular case $U_2 = 0$, which corresponds to the Hubbard model, our results reduce to those calculated previously [43] . Applying (5.3-14) and (5.3-15) to (5.3-26), and (5.3-27) we obtain mean occupation number per site n and nearest-neighbour hopping correlation function $S = \langle b^B_{m\sigma}\; b^A_{i\sigma}\rangle$, respectively:

$$n_\sigma = \frac{1-n_{-\sigma}}{2}\left\{\frac{1}{N}\sum_{\vec{k}}\left(f_{1\vec{k}}+f_{2\vec{k}}\right) - \sigma\frac{zt}{2}\left(\sum_\sigma \sigma' W_{1\sigma}\right)\frac{1}{N}\sum_{\vec{k}}\frac{f_{1\vec{k}}-f_{2\vec{k}}}{\sqrt{\Delta_{\vec{k}}}}\right. \tag{5.3-30}$$

and

$$ztS = \frac{a^2+W_2}{2}\;\frac{1}{N}\sum_{\vec{k}}\epsilon^2_{\vec{k}}/\sqrt{\Delta_{\vec{k}}}\left(f_{1\vec{k}}-f_{2\vec{k}}\right) \tag{5.3-31}$$

where $f_{1,2\vec{k}} \equiv f(E_{1,2\vec{k}}-\mu)$, $a^2 = (1-n_{-\sigma})\;(1-n_{-\sigma})$ and N is now the number of sites in one sublattice. The proceed further we decompose (5.3-30) into two summing over $\sum_\sigma(\ldots)$ and $\sum_\sigma \sigma(\ldots)$ both of its sides, respectively.

$$n_\sigma = \left(1 - \frac{n}{2}\right) \frac{1}{N} \sum_{\vec{k}} \left(f_{1\vec{k}} + f_{2\vec{k}}\right) - \frac{1}{2}\, zt \left\langle S^z \right\rangle \left(\sum_\sigma \sigma W_{1\sigma}\right) \frac{\sigma}{N} \sum_{\vec{k}} \frac{f_{1\vec{k}} - f_{2\vec{k}}}{\sqrt{\Delta_{\vec{k}}}} \tag{5.3-32}$$

and

$$2\left\langle S^z \right\rangle = \left\langle S^z \right\rangle \frac{1}{N} \sum_{\vec{k}} \left(f_{1\vec{k}} + f_{2\vec{k}}\right) - \frac{1}{2}\, zt \left(1 - \frac{n}{2}\right) \left(\sum_\sigma \sigma W_{1\sigma}\right) \frac{\sigma}{N} \sum_{\vec{k}} \frac{f_{1\vec{k}} - f_{2\vec{k}}}{\sqrt{\Delta_{\vec{k}}}} \tag{5.3-33}$$

From these equations we can derive the equation for the chemical potential

$$\frac{1}{N} \sum_{\vec{k}} \left(f_{1\vec{k}} + f_{2\vec{k}}\right) = \frac{2}{a^2} \left[\frac{n}{2}\left(1 - \frac{n}{2}\right) - \left\langle S^z \right\rangle^2\right] \tag{5.3-34}$$

and for sublattice magnetization $\left\langle S^z \right\rangle = \frac{1}{2}\left(n_\uparrow - n_\downarrow\right) \neq 0$ in the form

$$\left(1-n\right)/a^2 = \frac{1}{2}\, ztB\, \frac{1}{N} \sum_{\vec{k}} \left(f_{2\vec{k}} - f_{1\vec{k}}\right) / \sqrt{\Delta_{\vec{k}}} \tag{5.3-35}$$

with $2B\left\langle S^z \right\rangle = \sum_\sigma \sigma W_{1\sigma}$. To find expression for B we use the eqns.(B.19) - (B.21) for the two-particle correlation functions. The explicit form of W_1 and W_2 is therefore

$$W_{1-\sigma} = \left[U_2 \frac{S^2\left(1 - \frac{n}{2}\right)}{1-n} - J \frac{S^2\left(2 - \frac{n}{2}\right)}{1-n} - S\right] \frac{1-n_\sigma}{a^2} - \left(J-U_2\right) n_\sigma - U_2\left(\frac{S^2}{1-n} - 1\right) \frac{1-n}{a^2}\, n_{-\sigma} - U_2 \frac{1-n_\sigma}{a^2}\, n^2_\sigma \tag{5.3-36}$$

and

$$W_2 = -\frac{S^2\left(2 - \frac{n}{2}\right)}{1-n} - \left(J + U_2\right) S \tag{5.3-37}$$

Furthermore

$$B = -\frac{1}{a^2}\left\{S + \frac{JS^2\left(2 - \frac{n}{2}\right)}{1-n} - U_2 \frac{S^2\left(1 - \frac{n}{2}\right)}{1-n} - \left(J-U_2\right) a^2 + U_2\left(\frac{S^2}{1-n} - 1\right) + U_2\left[\frac{n^2}{4} + \left\langle S^z \right\rangle^2 - n\left(1 - \frac{n}{2}\right)\right]\right\} \tag{5.3-38}$$

Analogically, as in the previous subsection, we can write the equations for the sublattice magnetization and the hopping correlations which for $n > \frac{1}{2}$ and at $T=0$ are

$$\left(1 - \frac{n}{2}\right) \frac{1-n}{a^2} = ztB \int_{\omega}^{z \cdot t} \varrho(\omega) \frac{d\omega}{\sqrt{\Delta(\omega)}} \qquad (5.3\text{-}39)$$

$$ztS = -\left(a^2 + W_2\right) \int_{\omega}^{z|t|} \varrho(\omega) \frac{\omega^2}{\sqrt{\Delta(\omega)}}\, d\omega \qquad (5.3\text{-}40)$$

where $\Delta(\omega) = \left[\left(ztB \langle S^z \rangle\right)^2 + \omega^2 \left(\frac{a^2 + W_2}{a}\right)^2\right]^{1/2}$, and the lower limit of the integrals is determined from the equation

$$-\frac{1}{2} zt \sum_{\sigma} W_{1\sigma} + \sqrt{\Delta(\omega)} - \mu = 0 \qquad (5.3\text{-}41)$$

The chemical potential μ is determined from the integral equation corresponding to $(5.3\text{-}34)$, which reads

$$\frac{1}{a^2}\left[\frac{n}{2}\left(1 - \frac{n}{2}\right) - \langle S^z \rangle^2\right] = \int_{0}^{z\,t} \frac{\varrho(\omega)}{\sqrt{\Delta(\omega)}}\, d\omega + \int_{0}^{\omega} \frac{\varrho(\omega)}{\sqrt{\Delta(\omega)}}\, d\omega \qquad (5.3\text{-}42)$$

In what follows we will solve the equations $(5.3\text{-}39)$ - $(5.3\text{-}42)$ for the model density of states and compare the results with those from the simplified approach presented in Appendices A and D. This will allow us also to draw certain general conclusions about magnetic phases for a class of model Hamiltonians known under the name of the extended Hubbard model.

The ground state energy can be found from $(C.11)$, Appendix C

$$e_G = \frac{E_G}{2Nz|t|} = -S - \frac{1}{8}\left(\sum_{\sigma} W_{1\sigma}\right) \frac{1}{N} \sum_{\vec{k}} \left(f_{2\vec{k}} - f_{1\vec{k}}\right)$$

$$+ \frac{1}{4z|t|} \frac{1}{N} \sum_{\vec{k}} \sqrt{\Delta_{\vec{k}}} \left(f_{1\vec{k}} + f_{2\vec{k}}\right) \qquad (5.3\text{-}43)$$

or, in equivalent form,

$$e_G = -S - \frac{1}{4}\left(\sum_{\sigma} W_{1\sigma}\right) + \frac{1}{2z|t|} \int_{0}^{z\,t} \varrho(\omega)\sqrt{\Delta(\omega)}\, d\omega$$

$$+ \int_{0}^{\omega} \varrho(\omega)\sqrt{\Delta(\omega)}\, d\omega \qquad (5.3\text{-}44)$$

For $n \to 1$ the main contribution comes from the last term, since in this limit $S \to 0$ and $\int_{\omega}^{z|t|}(\ldots) \to 0$.

5.4. Solution for model density of states

To illustrate our general solution we choose the model density of states in the form

$$\varrho(\omega) = \begin{cases} 1/W & \text{for } -\frac{W}{2} < \omega > \frac{W}{2} \\ 0 & \text{otherwise} \end{cases} \qquad (5.4\text{-}1)$$

with $W = 2z|t|$. The same form of $\varrho(\omega)$ has been chosen in the Appendices A and D, where the simplified solutions are given. The purpose of this section is twofold. Firstly, to calculate explicity the magnetic moments in the ground state and the boundary lines between various magnetic phases. Secondly, to compare to what extent the results concerning the AF and F phases depend on the employed decoupling scheme and therefore to establish a simple but general description of magnetic phases, acceptable also on intuitive grounds. We show also that the range of existence of the solutions depends only weakly on $\tilde{J}$ in our limit, but the role played by kinetic exchange term is crucial for the stability of AF phase as $n \rightarrow 1$.

Ferromagnetic solution

Substituting (5.4-1) into (5.3-18) we get the expression for

$$\tilde{\omega}_\sigma \equiv \frac{\omega_\sigma}{z|t|} = \frac{1}{a^2}\left[\left(1 - \frac{n}{2}\right)\left(\frac{3}{2}n - 1\right) - \langle S^z\rangle^2 + 2\langle S^z\rangle(1-n)\sigma\right] \qquad (5.4\text{-}2)$$

On the other hand from (5.4-2) we have

$$\tilde{\omega}_\sigma\left(1 - n_{-\sigma} + W_{2\sigma}\right) = \frac{\mu}{z|t|} + W_{1-\sigma} \qquad (5.4\text{-}3)$$

Summing this equation with respect to spin index σ and substituting (5.3-12) and (5.3-13) for $W_{1-\sigma}$ and $W_{2\sigma}$ respectively, we will get the equation for the magnetic moment $\langle S^z\rangle$ of the form

$$\sum_\sigma \sigma\left[\tilde{\omega}_\sigma\left(1 - n_{-\sigma} + W_{2\sigma}\right) + W_{1\sigma}\right] = 0 \qquad (5.4\text{-}4)$$

To find the correlation function $S_\sigma = \langle b^+_{m\sigma} b_{i\sigma}\rangle$ for nearest neigh bours we have from (5.3-19) and (5.3-18) that

$$S_\sigma = n_\sigma \frac{1-n}{1-n_{-\sigma}} \qquad (5.4\text{-}5)$$

Substituting this expression into (5.4-4) we get the explicit form of equation for $\langle S^z\rangle$

$$a^6 \left(1-J\right) + a^4 \left(1-n\right)\left[U_2 \left(1-\frac{n}{2}\right) - 2J \left(1-n\right)\right] + a^2 \left(1-n\right)^2 \left(7n^2 - 17n + 7\right) + 6U_2 \left(1-n\right)^3 \left(1-\frac{n}{2}\right) = 0 \qquad (5.4\text{-}6)$$

with $a^2 = \left(1-\frac{n}{2}\right)^2 - \left\langle S^z\right\rangle^2$. For the particular case $J = U_2 = 0$ which corresponds to the Hubbard model at $U = \infty$, we obtain the analytic solution

$$a^2 = \left(1-n\right)\left(17n - 7n^2 - 7\right)^{1/2} \qquad (5.4\text{-}7)$$

which gives $\left\langle S^z\right\rangle^2 \simeq \frac{n^2}{4} - 2\left(1-n\right)$ and we have no complete ferromagnetic solution for any $n \neq 1$. This is in contradiction with the previous solution presented in Appendix D and it also illustrates to what extent the ferromagnetic solution is sensitive to the details of approximation scheme involved. We will return to this question in the next section, where we estimate the energy of various magnetic phases and discuss possible solutions on physical grounds.

To complete the solution we have to calculate the energy of the ground state. Substituting (5.4-5) into (5.3-12) and (5.3-13) and next the results into (5.3-21) we get the reduced energy per site

$$\begin{aligned} e_G^{\,F} = \frac{E_G}{Nz|t|} = &-\frac{1}{2} n \left(1-n\right) - \left(1-n\right) \frac{a^2-\left(1-n\right)\left(1-\frac{n}{2}\right)}{a^2} + U_2 n^2 \\ &- \frac{a^2}{2}\left(1-\frac{1-n}{a^2}\right)\left\{-2\left(J+\frac{1-n}{a^2}\right) + 2\left(U_2 R - J\,\frac{1-n}{a^2}\right)\left[1-\left(1-\frac{n}{2}\right)\frac{1-n}{a^2}\right]\right. \\ &\left. + \left(J-U_2\right)\left[3n - 4 + 4\left(1-\frac{n}{2}\right)^2 \frac{1-n}{a^2}\right]\right\} \\ &+ \frac{1}{2}\left(1-\frac{1-n}{a^2}\right)\left(\frac{1-n}{a^2}\right)^2 \left\{2\left[a^2-\left(1-\frac{n}{2}\right)\left(1-n\right) + 3n-4\right.\right. \\ &\left.\left. + 4\left(1-\frac{n}{2}\right)^2 \frac{1-n}{a^2} - 2J\left(1-\frac{n}{2}\right)\right\}\right. \\ &+ U_2 \frac{\left(1-n\right)^2}{a^6}\left\{\left(1-\frac{n}{2}\right)\left[4\left(1-\frac{n}{2}\right)^2 - 3a^2\right]\left(\frac{n^2}{2} + 1-n-a^2\right)\right. \\ &\left. - 2n\left\langle S^z\right\rangle^2\left[4\left(1-\frac{n}{2}\right)^2 - a^2\right]\right\} \end{aligned} \qquad (5.4\text{-}8)$$

For complete ferromagnetic state and $U_2 = 0$ we recover the previous result (I.4) obtained within the simpler approach and presented in Appendix D.

Antiferromagnetic solution and phase diagram

The general solution presented in Section 5.3 for the model density of states (5.4-1) gives us the equation for magnetization (5.3-39), nearest neighbour correlations (5.3-40), and ground state energy (5.3-44) in an explicit form. Namely, we have respectively

$$\frac{1-n}{a^2} = -\frac{B}{2C}\ \ln \frac{[1+(B\langle S^z\rangle^{2}/C^{2}]^{1/2}+1}{[\omega^2+(B\langle S^z\rangle^{2}/C)^2]^{1/2}+\tilde{\omega}} \qquad (5.4\text{-}9)$$

$$S = \frac{a}{4}\Big\{[C^2+(B\langle S^z\rangle)^2]^{1/2} - \frac{\tilde{\omega}}{2}[(C\tilde{\omega})^2+(B\langle S^z\rangle)^2]^{1/2} + \frac{1-n}{a^2}\left(1-\frac{n}{2}\right)\frac{B\langle B^z\rangle}{C}\Big\} \qquad (5.4\text{-}10)$$

and

$$e_G^{AF} = \frac{E_G}{2Nz|t|} = -S - \frac{1}{8}\Big(\sum_{\sigma} W_{1\sigma}\Big)(1-\tilde{\omega}) + \frac{1}{8}\Big\{[(B\langle S^z\rangle)^2 + C^2]^{1/2} + \tilde{\omega}[(B\langle S^z\rangle^{2}+(\tilde{\omega}C)^2]^{1/2} + \frac{1}{8}\frac{B\langle S^z\rangle^{2}}{C}\ln\frac{\{[(B\langle S^z\rangle)^2+C^2]^{1/2}+C\}\{(B\langle S^z\rangle^{2}+(\tilde{\omega}C)^2]^{1/2}+\tilde{\omega}C}{(B\langle S^z\rangle)^2} \qquad (5.4\text{-}11)$$

where B is given by (5.3-38) and

$$C = a - \frac{S^2\left(2-\frac{n}{2}\right)}{a(1-n)} - (J+U_2)\cdot\frac{S}{a} \qquad (5.4\text{-}12)$$

The eqns. (5.4-9) and (5.4-10) form the system of two coupled self-consistent equations for $\langle S^z\rangle$ and S. To first but still quite realistic approximation the term $\sim J$ and U_2 should not influence the nearest neighbour hopping expressed via (5.4-10). From this we can infer that S in the strong coupling limit for the AF and paramagnetic phases should coincide. Furthermore, as will be shown from a general physical picture presented in the next section, the antiferromagnetism is stable only for $n \to 1$ and we expect that $S \simeq (1-n) + O((1-n)^2)$. The same result can be obtained from (5.4-10) if we substitute $\langle S^z\rangle = 0$. This expression for S can help us also to see a qualitative difference between the Hartree-Fock and the moment-conserving decouplings. Namely from (5.4-12) we have

$$C \simeq a - \frac{3}{2}\,\frac{1-n}{a} - (J+U_2)\,\frac{1-n}{a}$$

while from (5.3-38) and for $U_2 = 0$

$$B \simeq -\frac{1-n}{a^2}\left(1+\frac{3}{2}J\right) - J$$

For any nonzero temperature and as $n \to 1$ we have $B \simeq -J$ and $C \simeq a$, which gives the Hartree-Fock results (A.17) presented in Appendix A. Therefore, we conclude that for nearly half-filled band the antiferromagnetism can be described by the mean field type approximation of the effective Hamiltonian (5.2-19), while the onset of ferromagnetism is determined by a more realistic account of bandshift factors for the quasiparticle subbands $E_{\vec{k}\sigma}$. The border line between ferro- and antiferro-magnetic phases is shown schematically in Fig.3. For comparison, the result of Nagaoka [73] is also plotted.

5.5. Discussion: Influence of kinetic exchange on magnetic ground state

In the last two sections we have discussed mainly the ferro- and antiferromagnetic solutions within two approximation schemes: the Hartree-Fock and the moment-conserving decouplings. We have shown that while the latter is not particularly sensitive to an approximation scheme involved, the former one appears only after inclusion of the band-shift (BS) and band-narrowing (BN) factors in a selfconsistent manner. The selfconsistent procedure represented by Eqs.(5.3-3) and (5.3-4) provides the expression for BN and BS through the two-particle correlation functions between nearest neighbours $\langle S_m^+ S_0^- \rangle$ and $\langle n_{m\sigma} \cdot n_{0\sigma'} \rangle$. Hence any subsequent reduction of them to the single-particle correlation functions $S_\sigma = \langle b_{m\sigma}^+ b_{0\sigma} \rangle$ and $n_\sigma = \langle b_{i\sigma}^+ b_{i\sigma} \rangle$ (e.g. by mean-field type decoupling or the Roth procedure) introduces two new unphysical ingredients: part of spin-flip fluctuations, inherent in the Heisenberg type of interactions, and part of two-particle multiple scattering amplitude without spin-flip, are disregarded. This approach therefore can be viewed as an interpolation solution of the mean field type both from the point of view of Kanamori approach as $n \to 0$ [74] and of the Heisenberg model as $n \to 1$ [43]. The same type of interpolation scheme is provided by the Tyablikov decoupling for the Heisenberg model [78], which reduces to spin-wave approximation (without Dyson correction, however) in the low temperature region, and to the mean field approximation as $T \to T_c$. In this section we discuss our interpolation solution on physical grounds. This seems to be particularly useful, because of the differences between ferromagnetic solution from Appendix D and the corresponding one from Section 5.4 for our model density of states.

Let us consider the influence of the kinetic exchange only ($K=J=0$) on the magnetic phases. It lowers the ground state energy of an AF phase (per site) by amount $\Delta E_m \simeq \frac{1}{2z} \frac{W^2}{U} n^2$ and of P state by

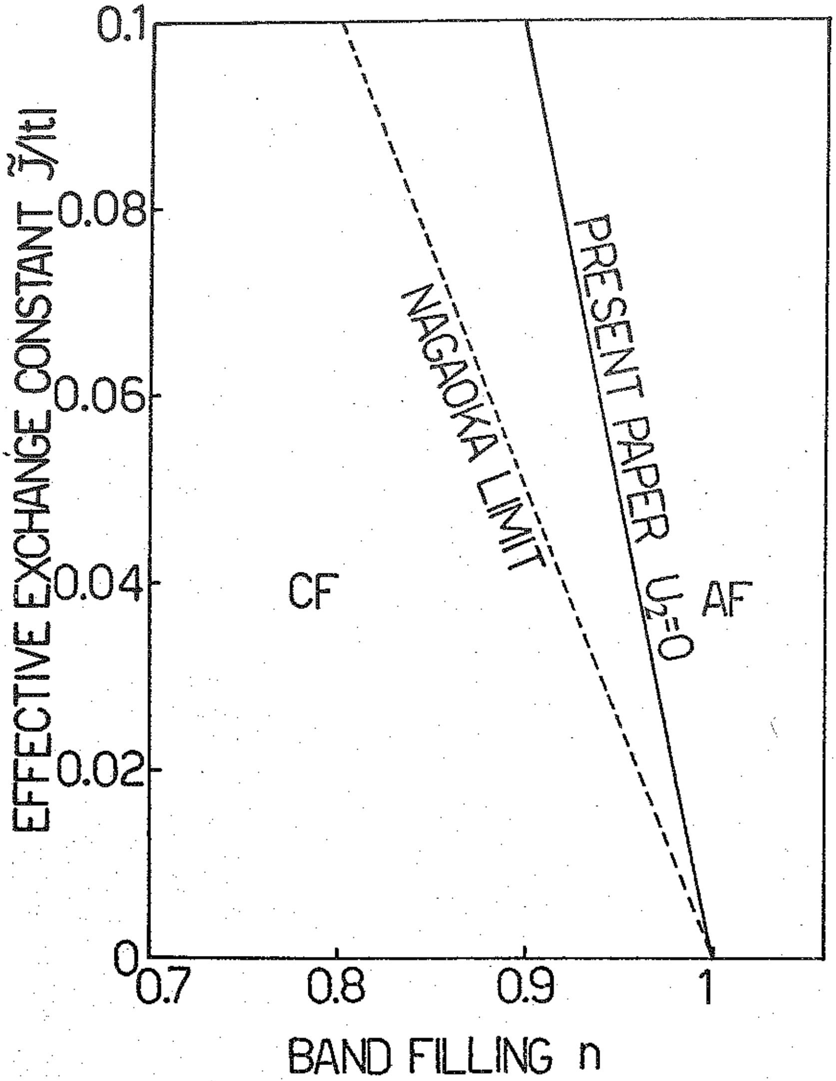

Fig.3. Schematic representation of the phase boundary between complete ferromagnetic (CF) and antiferromagnetic (AF) phases for the model density of states. Mean-field approximation is used. Dashed line: the Nagaoka [14] result (cf. also Sect.5.5).

$\Delta E'_m \simeq \frac{1}{2}\Delta E_{m_1}$. The band energy (per site) of AF and P states is roughly $E_B = -\frac{1}{4} n\,(1-n)\,W$, and for the complete ferromagnetism (CF) $E_B = -\frac{1}{2} W\,(1-n)\,n$. These last formulas can be derived as follows. Firstly, the mean field AF solution is given by $\langle S^z\rangle^2 = n^2/4 - (1-n)^2$, so for $n \to 1$ the moment is almost saturated. So up to order $\sim(1-n)$ $\Delta E_m = J\,z\,\langle \vec{S}_i \cdot \vec{S}_j - \frac{1}{4}\sum_{\sigma\sigma'} n_{i\sigma}\,n_{j\sigma'}\rangle \simeq \frac{1}{2z}\,\frac{W^2}{U}\,n^2$. Secondly, the probability of hopping between the nearest neighbours (one site occupied, the second one empty) is $\sum_\sigma n_\sigma (1-n) = n\,(1-n)$. So the corresponding energy per site in the P or AF phase will be $\frac{1}{2}\,z\,t\,n(1-n)$ ($\frac{1}{2}$ comes from the average over the states in lowest Mott Hubbard subband). For the complete ferromagnetism (CF), however, the quasiparticle states in the lowest subband represented in (5.2-19) by the term $t\sum'_{ij\sigma} b^+_{i\sigma}\,b_{j\sigma}$ are the same as those in the full s-band

$t\sum'_{ij} a^+_{i\sigma}\,a_{j\sigma}$ (i.e. without the doubly occupied sites having projected out) since the Pauli principle automatically excludes a contribution from all upper subbands. So the bandwidth of the quasiparticle states is $W = 2z|t|$ rather than $W/2$ as in the other cases. Therefore, $E_B^{P,AF} = -\frac{1}{4}\,Wn\,(1-n)$ while $E_B^{CF} = -\frac{1}{2}\,Wn\,(1-n)$. Hence the transition from the AF to CF state as n decreases from 1 is caused by the competition between the kinetic exchange and the band energy and is determine by the condition $e_G^{CF} = e_G^{AF}$ which yields

$$n \equiv n_{C1} = \left(1 + \frac{2}{z}\,\frac{W}{U}\right)^{-1} \qquad (5.5\text{-}1)$$

For $(W/U) \ll 1$, $n_{C1} \to 1$ and therefore from (5.5-1) we have that the boundary line CF-AF is given by $(|t|/U) \simeq .25(1-n)$. The same result can be obtained if we take from Appendix D as renormalization factor of band energy in the AF phase $\frac{1}{4}$ instead of $\frac{1}{2}$ and compare it to the energy in AF phase in the mean field approx. $\Delta E_m = \frac{1}{4z}\,\frac{W^2}{U}\cdot n^2$, and is quite close to the result of Nagaoka [73] $(|t|/U) = .246\,(1-n)$. However, our simple picture fails to predict properly the behaviour in the limit $n \to 0$. Indeed, the boundary line P-CF determined from the condition $e_G^P = e_G^{CF}$ gives

$$n \equiv n'_{c2} = \frac{2}{z}\,W/U, \qquad (5.5\text{-}2)$$

and for $U=\infty$ $n'_{c2} = 0$ while Kanamori [74] predicted that $n'_{c2} \simeq .271$ for rectangular density of states. His result is in accord with the intuitive expectation that a ferromagnetism can appear only when the band filling n is larger than $2/z$, reflecting the fact that on average there are at least two electrons on the neighbouring sites. This gives $n_c = \frac{1}{3}$ and $\frac{1}{4}$ for sc and bcc, respectively. Our picture leading to (5.5-2) is valid only above this concentration because effectively only above this concentration the correlations limit the hopping process. So (5.5-2) is modified

$$n \simeq n_{c2} = \frac{2}{z}\left(1 + \frac{W}{U}\right) \qquad (5.5\text{-}3)$$

The numerical solution of Roth [75] for sc structure and $U = \infty$ gives close result $n_{c2} = .36$.

From our simple solutions both for a ferromagnet (cf. Appendix D), and an antiferromagnet (cf. Appendix A) the magnetic moment near $n=1$ is saturated. This means that for nearly half-filled band the electrons are localized from a "magnetic" point of view. Quantitatively, the criterion of localization can be formulated in a following way. The time uncertainty connected with the formation of a quasiparticle CF band is of the order

$$\tau_B \simeq \frac{\hbar}{2\Delta E_B} = \frac{\hbar}{Wn\,(1-n)} \qquad (5.5\text{-}4)$$

while the spin-flip lifetime in the AF phase

$$\tau_m \simeq \frac{\hbar}{2\Delta\, E_m} = \tau_B\ \frac{U}{|t|}\ \frac{1-n}{n} \qquad (5.5\text{-}5)$$

For $n \rightarrow 1$, $\tau_m \ll \tau_B$ and we arrive at the region with slow hopping modulated by fast collective spin fluctuations (induced by virtual hopping between the subbands). Hence the electrons in nearly half-filled band (in the whole region $2U\ 1-n\ z \ll W$) are described essentially by the Heisenberg Hamiltonian. Therefore, to the first approximation, the Mott insulator may be viewed as the Heisenberg antiferromagnet with the renormalized band parameters by the virtual hopping between subbands. In particular, as can be seen from (5.2-14) and (5.2-20) that

$$U \rightarrow U_{ef} = U + \frac{1}{2z}\ \frac{W^2}{U} = U\left[1 + \frac{1}{2z}\left(\frac{W}{U}\right)^2\right] \qquad (5.5\text{-}6)$$

So the simplest generalization (5.5-6) extends the region of validity of our results, since even for $W \simeq U$ the renormalization factor in (5.5-6) is $\simeq \frac{1}{2z} \ll 1$. The magnetic part of energy for the Mott insulator is now

$$\Delta E_m' = \frac{1}{2z}\ \frac{W^2\, U}{U^2 + \frac{1}{2z}\ W^2} \qquad (5.5\text{-}7)$$

It is interesting to note that the last formula gives also qualitatively correct behaviour when interpolated to the region $U \ll W$ where we have $\Delta E_m \sim Un^2$, which is the standard Hartree-Fock result for the Hubbard model [63] . The corrected formula (5.5-7) can thus be used to estimate the condition for the closure of the gap between two lowest subband metal-nonmetal transition

$$U + 2\Delta E_m' = W \qquad (5.5\text{-}8)$$

where factor 2 in $\Delta E_m'$ comes from the increase of quasiparticle energy in the upper subband the lower one is pulled down. Eqn. 5.5-8 has solution approximately at

$$\frac{W}{U} \simeq \frac{z}{2}\left[1 - \left(1 - \frac{4}{z}\right)^{1/2}\right] \qquad (5.5\text{-}9)$$

or more accurately at $(W/U) \simeq 1.09$ and 1.067 for sc and bcc structures, respectively. Hubbard (1964) [79] obtained $(W/U) = 1.15$ for elliptic density of states. Additionally, Eqn.(5.5-9) predicts the metal-nonmetal transition for planar square lattice, but it is absent in the one dimensional chain, in agreement with the exact result of Lieb and Wu (1968) [80].

Hitherto we have turned over the ground state of the system composed of one magnetic phase. We would like to discuss now a possibility of a formation of the mixed phase considered by Visscher (1974) [81]. For $n \rightarrow 1$ tight binding density of states is

$$\rho(\omega) = \frac{V}{4\pi^2 B^{3/2}} \sqrt{\omega} \qquad (5.5\text{-}10)$$

where $B = |t|\, a^2$ and $2\,|t|\, a^2$ for sc and bcc, respectively, and a is the lattice constant. The work done to compress holes from the volume V to $V - \Delta V$ is

$$\Delta L = \frac{1}{10} B\, 6^{5/3} \pi^{4/3} (1-n)^{5/3} N \left[\left(1 - \frac{N_{AF}}{N}\right)^{-2/3} - 1\right] \qquad (5.5\text{-}11)$$

where $N_{AF} = \Delta V/a^3$ is the number of lattice sites free of holes (number of spin ordered antiferromagnetically). The total energy of the mixed state is therefore

$$E_{tot}/N = -z\,|t|\, n\,(1-n) + \frac{\Delta L}{N} - \frac{1}{2z}\,\frac{W^2}{U}\,\frac{N_{AF}}{N} \qquad (5.5\text{-}12)$$

From the condition $\partial E_{tot}/\partial N_{AF} = 0$ we get the portion of sites in the AF phase

$$\frac{N_{AF}}{N} = 1 - \left(\frac{\tilde{a}}{15}\, 6^{5/3} \pi^{4/3}\right)^{3/5} \left(\frac{W}{U}\right)^{3/5} (1-n) \qquad (5,5\text{-}13)$$

with $\tilde{a} = 1,2$ for sc and bcc, respectively. Therefore, the border line between mixed and CF phases is given by the condition $N_{AF} = 0$, or equivalentl y,

$$\frac{W}{U} = \frac{6^{5/3}\pi^{4/3}}{15}\,\tilde{a}\,(1-n)^{5/3} \qquad (5.5\text{-}14)$$

or explicity $|t|/U = .5(1-n)^{5/3}$ for sc structure. This condition replaces the Nagaoka condition (5.5-1). There are minor differences (of factor .5) with the Vischer original result [81] due to the fact that we have assumed that energy of AF state is given by $(-2zt^2/U)\,N_{AF}$ rather than the mean-field value $(-zt^2/U)\,N_{AF}$. Substituting (5.5-13) into (5.5-12) we have the final expression for ground state energy of the mixed state

$$e_G = \frac{E_G}{Nz|t|} = -n(1-n) - \frac{1}{z}\;\frac{W}{U} + \frac{1}{10z}\;\tilde{a}\;6^{5/3}\pi^{4/3}\;(1-n)^{5/3}$$
$$+\frac{1}{z}\left(\frac{W}{U}\right)^{2/5}\left(\frac{\hat{a}}{15}\;6^{5/3}\pi^{4/3}\right)^{3/5}(1-n)$$
$$+\frac{3}{2z}\left(\frac{\tilde{a}}{15}\;6^{5/3}\pi^{4/3}\right)^{3/5}\left(\frac{W}{U}\right)^{2/5}(1-n) \qquad (5.5\text{-}15)$$

The main results of the previous sections together with those from Appendix D enabled us to draw the conceptual phase diagram pictured in Fig.4 for $J = U_2 = 0$. Furthermore, with the help of the renormalization (5.5-6) of U we can draw it on the whole plane $\frac{W}{U}$ vs n. This phase diagram illustrates and summarizes the main physical results obtained quite easily when the concept of kinetic exchange is employed to a partially filled narrow s-band.

5.6. Short summary and conclusions

In this Section our main task was to construct the effective magnetic Hamiltonian from the full tight-binding Hamiltonian (5.2-1), and to prove its usefulness applying it to the description of magnetic phases composed of strongly correlated electrons in a partially filled narrow s-band. We use the equation of motion method for the commutator Green functions and subsequently utilize both the Hartree-Fock and the moment-conserving decouplings (cf. Appendix A and Section 5.3 for details). The latter method reproduces rigorously the average shift of the spin subbands (5.3-4) and hence provides us with a realistic description of ferromagnetism. However, the band shift (BS) and band narrowing (BN) factors (5.3-9) and (5.3-10) contain still nearest neighbour twoparticle correlation functions which have to be calculated independently. To grasp this task Roth [75] has proposed a self-consistent procedure and has expressed the two particle correlations through the single particle ones. This procedure has after all two fundamental defects. Firstly, it violates the spin rotational invariance (cf. the discussion in Appendix B). Secondly, it fails to include the short-range order effects in the nearest neighbour correlations and therefore is of limited importance when generalized to finite temperatures. In Appendix D we have studied a simpler decoupling of two-particle cor-

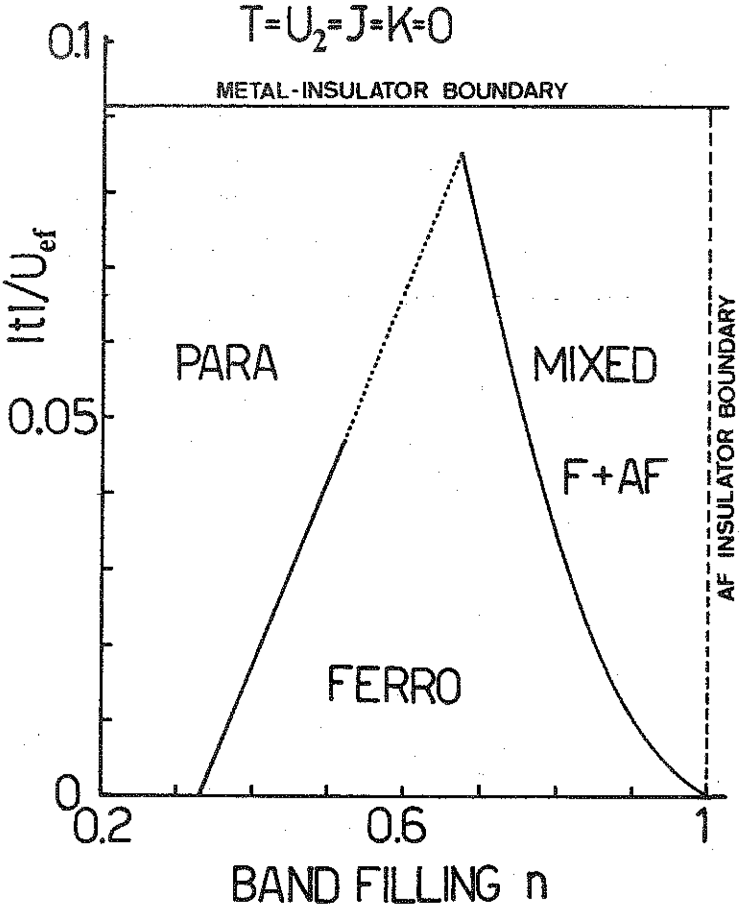

Fig.4. Conceptual phase diagram for sc structure, with the mixed CF-AF phase included. For details see Sect.5.5. The parameters $J = U_2 = 0$

relation functions which does preserve the spin rotation invariance and gives the solution for $n \to 1$ in agreement with the intuitive insight into the nature of single-particle motion of strongly correlated electrons, presented in Sect. 5.5. For a nearly half filled band the ferromagnetism is complete (CF) and there is no band narrowing in this case. This is easy to understand if we notice that in the dynamics of CF phase the correlations are included automatically through the Pauli exclusion principle. We believe that the disagreement between the results of Appendix D and those from Sect. 5.3 which are based on the Roth scheme, is due to the violation of the spin rotation invariance mentioned earlier in the latter case. Unfortunately, our whole approach fails in the limit $n \to 0$ (Roth 1969) [82] . This is due to the fact that in the strong correlation regime the two-particle scattering amplitude [74] $\simeq Un^2$ is not small even for relatively low concentrations.

All approximations produce the solution for the sublattice magnetization $\langle S^z \rangle$ in the antiferromagnetic phase of the same type which can be approximated by the analytical solution $\langle S^z \rangle^2 \simeq \left(1-\frac{n}{2}\right)\left(\frac{3}{2}n-1\right) = n^2/4 - (1-n)^2$. This is caused by the smallness of the prelogarithmic factor in (A.17) or (D.9) since $\langle S^z \rangle \to n/2$ as $n \to 1$ [43] . However, as it is shown in Section 6, antiferromagnetism is unstable against the formation of the mixed CF-AF phase [81] . We think that ferromagnetic polarons in the AF phase considered by Brinkman and Rice [83] and the others [84] may be considered as on excited state of the mixed phase.

In the paper we have limited our considerations to the zero temperature case only. An extension to nonzero temperatures does not show principal difficulties. In fact, a ferromagnetic solution at finite temperatures and for $U = \infty$, and $K=J=0$ has been considered already by Sokoloff (1970-71) [85] . It would be interesting to extend his results to the case with $J \neq 0$. Nevertheless, it seems to be clear that the complete ferromagnetic phase does exist, even though the correlations produce the antiferromagnetic exchange in the second order in t/U .

Appendix A: Hartree-Fock Approximation

Among the simplest decouplings of equation of motion (5.3-2) seems to be the one of a mean-field type

$$\begin{aligned} & b_{m\sigma}\left(1-n_{i-\sigma}\right) \simeq b_{m\sigma}\left(1-\langle n_{i-\sigma}\rangle\right) \\ & b_{i\sigma}\,\nu_{m\sigma'} \simeq \langle \nu_{m\sigma'}\rangle\, b_{i\sigma} - \delta_{\sigma\sigma'}\langle b^{+}_{m\sigma}\, b_{i\sigma}\rangle\, b_{m} \\ & b_{m-\sigma}\, S_i^{-\sigma} \simeq \langle -\, b^{+}_{i-\sigma}\, b_{m-\sigma}\rangle\, b_{i\sigma} = -S_{-\sigma}\, b_{i\sigma} \end{aligned} \tag{A.1}$$

Substituting (A.1) into (5.3-2) we get

$$\left(E + ztS_{-\sigma} + \tilde{J}\sum_{m(i)}\langle \nu_{m-\sigma}\rangle - U_2\sum_{m(i)}\langle \nu_{m\sigma'}\rangle\right)\langle\langle b_{i\sigma} \,|\, b^{+}_{j\sigma}\rangle\rangle = \frac{1-\langle n_{i-\sigma}\rangle}{2\pi}\,\delta_{ij} + \left[t\left(1-\langle n_{i-\sigma}\rangle\right) - \tilde{J}S_{-\sigma} - U_2 S_{\sigma}\right]\sum_{m(i)}\langle\langle b_{m\sigma} \,|\, b^{+}_{j\sigma}\rangle\rangle \tag{A.2}$$

After space Fourier transform this equation can be rewritten as

$$\langle\langle b_{\vec{k}\sigma} \,|\, b^{+}_{\vec{k}\sigma}\rangle\rangle = \frac{1-n_{-\sigma}}{2\pi}\cdot\frac{1}{E - E_{\vec{k}\sigma}} \tag{A.3}$$

with

$$E_{\vec{k}\sigma} = -zt\left(S_{-\sigma} + Jn_{-\sigma} - U_2 n\right) + \epsilon_{\vec{k}}\left(1-n_{-\sigma}\right) \tag{A.4}$$

Applying fluctuation-dissipation theorem we get the expressions for n_{σ} and S_{σ} which can be written down as are (5.3-18) and (5.3-19) with

$$\omega_{\sigma} = \frac{\omega_{\sigma}}{z|t|} = \left(1-n_{-\sigma}\right)^{-1}\left[\mu - \left(S_{-\sigma} + Jn_{-\sigma} - U_2 n\right)\right] \tag{A.5}$$

For the model density of states (5.4-1) this gives the solution for the magnetic moment

$$\langle S^{z}\rangle = \pm\left[\left(1-\frac{n}{2}\right)^{2} - \frac{(1-n)^{2}}{1-J}\right]^{1/2} \tag{A.6}$$

This gives physically meaningful solution for $n \leqslant J$ or for $n=1$. The case $n=1$ corresponds to the Heisenberg magnet and ferromagnetic solution is stable for $J > 0$. The second solution exists only if $J > 0$ which again means that the direct exchange dominates over the kinetic exchange. In particular, there is no ferromagnetic solution for any $n \neq 1$ in the Hubbard model $(J = 2t/U < 0)$ in this approximation which is in disagreement with the results both of Nagaoka [73] and Kanamori [74]. Therefore we conclude that this approximation is inappropriate for the description of ferromagnetism for $n \neq 1$. In Section 5.3 we discuss the above results within the more systematic method of approximation.

For the sake of completeness we reproduce below also the results for the antiferromagnetic case. Eqn.(5.3-2) with (A.1) when decomposed into two sublattices labelled A and B respectively (for details see Section 5.3) and after the Fourier transform to the k-space has the form

$$\langle\langle b_{\vec{k}\sigma} \mid b^{+}_{\vec{k}\sigma} \rangle\rangle = \frac{1-n_{-\sigma}}{2\pi} \frac{\dot{E} + ztS + zJn_{-\sigma} - U_2 zn}{(E-E_{1\vec{k}})(E-E_{2\vec{k}})} \qquad (A.7)$$

and

$$\langle\langle b^{B}_{\vec{k}\sigma} \mid b^{A+}_{\vec{k}\sigma} \rangle\rangle = \frac{1-n_{-\sigma}}{2\pi} \frac{1}{(E-E_{1\vec{k}})(E-E_{2\vec{k}})} \qquad (A.8)$$

where

$$E_{1,2\vec{k}} = -ztS + U_2 zn - \frac{1}{2}\tilde{J}zn \pm \left[\epsilon^2_{\vec{k}} a^2 + (\tilde{J}z\langle S^z\rangle)^2\right]^{1/2} \qquad (A.9)$$

Applying fluctuation-dissipation theorem we obtain, respectively

$$\frac{2n_\sigma}{1-n_{-\sigma}} = \frac{1}{n} \sum_{\vec{k}} \Big[\big(f_{1\vec{k}} + f_{2\vec{k}}\big) - \sigma \tilde{J}z \langle S^z \rangle \big(f_{1\vec{k}} - f_{2\vec{k}}\big) / \sqrt{\Delta_{\vec{k}}} \qquad (A.10)$$

and

$$ztS = \frac{a^2}{2N} \sum_{\vec{k}} \frac{\epsilon^2_{\vec{k}}}{\sqrt{\Delta_{\vec{k}}}} \left(f_{1\vec{k}} - f_{2\vec{k}}\right) \qquad (A.11)$$

where $a^2 = (1-n_\sigma)(1-n_{-\sigma})$, $f_{1,2\vec{k}} = f(E_{1,2\vec{k}} - \mu)$, and

$$\Delta_{\vec{k}} = \epsilon^2_{\vec{k}} a^2 + (Jz\langle S^z\rangle)^2 \qquad (A.12)$$

and now N is the number of sites within the sublattice. Summing Eqn. (A.10) over σ and $\sum_\sigma \sigma(\ldots)$ - we obtain two independent equations for μ and $\langle S^z\rangle$, respectively. The equation for $\langle S^z\rangle$ can be separated from the corresponding one for μ in the following way. For the rectangular density of states we have that

$$\frac{1}{N} \sum_{\vec{k}} \left(f_{1\vec{k}} + f_{2\vec{k}}\right) = 1 + \frac{2\omega}{W} \qquad (A.13)$$

and

$$\frac{1}{N} \sum_{\vec{k}} f\left(f_{1\vec{k}} f_{2\vec{k}} \right) = - \frac{2}{Wa} \ln \frac{\left[(zt)^2 + (b/a)^2 \right]^{1/2} - zt}{\left[\omega^2 + b/a^{\,2} \right]^{1/2} + \omega} \qquad (A.14)$$

where

$$\omega \equiv \tilde{\omega}_{z\,t} = a^{-1} \left\{ \left[zt \left(S + \frac{1}{2} Jn - U_2 n \right) + \mu \right]^2 - \left(\tilde{J}z \langle S^z \rangle \right)^2 \right\}^{1/2}$$

and $b = \tilde{J}z \langle S^z \rangle$. Substituting (A.13) and (A.14) into the equations for μ and $\langle S^z \rangle$ we obtain two equations from which one can determine

$$\omega = \frac{W}{2a^2} \left[\left(\frac{3}{2} n - 1 \right) \left(1 - \frac{n}{2} \right) - \langle S^z \rangle^2 \right] \qquad (A.15)$$

and the selfconsistent equation for $\langle S^z \rangle$ at $T=0$

$$1 = \frac{1}{2} \left(1 + \frac{2\omega}{W} \right) + \tilde{J}z \left(1 - \frac{n}{2} \right) \frac{1}{a \cdot W} \ln \frac{\left[(zt)^2 + (b/a)^2 \right]^{1/2} - zt}{\left[\omega^2 + (b/a)^2 \right]^{1/2} + \omega} \qquad (A.16)$$

Since we have neglected in the effective Hamiltonian (5.2-19) the higher order terms in t/U , so to a first approximation we can retain in the last equation the term $\sim J$ only. Thus finally, the equation for $\langle S^z \rangle$ is

$$2 (1-n) = Ja \ln \tilde{\omega} \qquad (A.17)$$

with $\tilde{\omega} \equiv \omega/(z|t|)$. If the kinetic exchange is dominating, then $J < 0$ and solution exists. Furthermore, since in this case $J \ll 1$ $(|t| \ll U)$ then to a good approximation the (A.17) has the solution

$$\langle S^z \rangle \simeq \left(2n - 1 - \frac{3}{4} n^2 \right)^{1/2} = \left[\frac{n^2}{4} - (1-n)^2 \right]^{1/2} \qquad (A.18)$$

and its nonzero for $n > n_c = \frac{2}{3}$. One can thus see that, in the strong intraatomic interaction limit, the antiferromagnetic solution depends weakly on $\tilde{J}$ and exists also for $\tilde{J} = 0$. The stable solution is given by the minimum of the relative free energy par site which in the present case has the form

$$e_G^{AF} = \frac{E_G^{AF}}{2Nz\,|t|} = -S \left(2 - \frac{n}{2} \right) + \frac{1}{a^2} \left\{ (1-n) \langle S^z \rangle^2 \left(S - U_2 n + J \right) + \left[\frac{n}{2} \left(1 - \frac{n}{2} \right) - \langle S^z \rangle^2 \right] \left[J \langle S^z \rangle^2 + \left(1 - \frac{n}{2} \right) \left(S - U_2 n + \frac{1}{2} Jn \right) \right] \right\} \qquad (A.19)$$

where

$$S = \frac{1}{4} a \left(1 - \tilde{\omega}^2 \right) = \frac{1-n}{a} \left(1 - \frac{n}{2} \right) \left[1 - \left(1 - \frac{n}{2} \right) \frac{1-n}{a^2} \right] \qquad (A.20)$$

For the ferromagnetic case the corresponding quantity is

$$e_G^F = \frac{E_G^F}{2Nz\,|t|} = -\frac{1}{2}\,n\,(1-n) - \frac{1-n}{a^2}\left[a^2-(1-n)\left(1-\frac{n}{2}\right)\right] - \frac{1}{2}\,U_2 n^2 + \frac{1-n}{a^2}\left(1-\frac{n}{2}\right)\left(\frac{n^2}{4}-\langle S^z\rangle^2\right) + J\left(\frac{n^2}{4}-\langle S^z\rangle^2\right) \qquad (A.21)$$

These formulas are used in Sect. 5.4 to draw border lines between AF and P phases for $\tilde{J} > 0$ (cf. Fig.3). In particular case of $n=1$, which corresponds to the Mott insulator, the expressions (A.20) and (A.21) reduce to those for the Heisenberg magnet in the mean-field approximation. Namely, $E_G^{AF} = Nz(U_2-J)$ while for the ferromagnetic one $E_G^F = Nz\,U_2$. Therefore, one can see that for $n=1$ the kinetic exchange lowers the ground state energy of an antiferromagnetic state and does not contribute to the energy of a ferromagnetic state, while the direct exchange acts in the opposite way: lowers the ground state energy for ferro state and does not controbute to the energy of AF state.

Appendix B: Moment-Conserving Decoupling

Ferromagnetic case

To calculate static correlation functions $\langle n_{i+m\sigma}\, n_{i\sigma}\rangle$, $\langle n_{i+m\sigma}\, n_{i-\sigma}\rangle$, and $\langle S^{\sigma}_{i+m}\, S^{-\sigma}_{i}\rangle$ between nearest neighbours $(i,\ i+m)$ we proceed the Roth procedure [76]. Namely, define Green functions $\langle\langle b_{\vec{k}\sigma} \mid B_{1\vec{k}\sigma}\rangle\rangle$ where

$$B_{1\vec{k}\sigma} = N^{-1/2} \sum_{i} \exp\left(-i\,\vec{k}\cdot\vec{R}_i\right) n_{i+m\sigma}\, b^{+}_{i\sigma} \tag{B.1}$$

$$B_{2\vec{k}\sigma} = N^{-1/2} \sum_{i} \exp\left(-i\,\vec{k}\cdot\vec{R}_i\right) n_{i+m-\sigma}\, b^{+}_{i}\sigma \tag{B.2}$$

$$B_{3\vec{k}\sigma} = N^{-1/2} \sum_{i} \exp\left(-i\,\vec{k}\cdot\vec{R}_i\right) S^{\sigma}_{i+m\sigma}\, b^{+}_{i-\sigma} \tag{B.3}$$

Therefore the unknown correlation function may be expressed through these operators in the following way

$$\langle n_{m\sigma}\, n_{0}\rangle = \frac{1}{N} \sum_{\vec{k}} \langle B_{1\vec{k}\sigma}\, b_{\vec{k}\sigma}\rangle \tag{B.4}$$

$$\langle n_{m-\sigma}\, n_{0\sigma}\rangle = \frac{1}{N} \sum_{\vec{k}} \langle B_{2\vec{k}\sigma}\, b_{\vec{k}\sigma}\rangle \tag{B.5}$$

$$\langle S^{\sigma}_{m}\, S^{-\sigma}_{0}\rangle = \frac{1}{N} \sum_{\vec{k}} \langle B_{3\vec{k}\sigma}\, b_{\vec{k}\sigma}\rangle \tag{B.6}$$

To obtain the correlation function on r.h.s. of (B.4)-(B.6) from the fluctuation-dissipation theorem we have to solve the equations of motion for the corresponding Green functions, which are

$$E \langle\langle b_{\vec{k}\sigma} \mid B_{1\vec{k}\sigma}\rangle\rangle = \frac{1}{2\pi} \langle\{b_{\vec{k}\sigma},\, B_{1\vec{k}\sigma}\}\rangle + M_{\vec{k}} \langle\langle b_{\vec{k}\sigma} \mid B_{1\vec{k}\sigma}\rangle\rangle \tag{B.7}$$

where $M_{\vec{k}} = \sum_{m(i)} M_{im} \exp\left[i\,\vec{k}\cdot\left(\vec{R}_m - \vec{R}_i\right)\right]$, or explicity

$$\langle\langle b_{\vec{k}\sigma} | B_{1\vec{k}\sigma} \rangle\rangle = \frac{\langle\{b_{\vec{k}\sigma} , B_{1\vec{k}\sigma}\}\rangle}{2\pi} \cdot \frac{1}{E-E_{\vec{k}\sigma}} \qquad (B.8)$$

Writing the fluctuation-dissipation theorem as contour integral incircling real axis of E and including the poles of retarded Green function and using the notation [76]

$$F_{\omega} \tilde{G}_{\vec{k}\sigma} = \frac{1}{2\pi i} \oint f(\omega) \frac{1}{2\pi} \frac{1}{\omega - E_{\vec{k}\sigma} + i\epsilon} \qquad (B.9)$$

we will have

$$\frac{1}{N} \sum_{\vec{k}} \langle B_{1\vec{k}\sigma} b_{\vec{k}\sigma} \rangle = \frac{1}{N} \sum_{\vec{k}} F_{\omega} \tilde{G}_{\vec{k}\sigma} \langle\{B_{1\vec{k}\sigma}, b_{\vec{k}\sigma}\}\rangle \qquad (B.10)$$

Using the fact that

$$F_{\omega} \langle\langle b_{\vec{k}\sigma} | b^{+}_{\vec{k}\sigma} \rangle\rangle = (1-n_{-\sigma}) F_{\omega} \tilde{G}_{\vec{k}\sigma} \qquad (B.11)$$

and evaluating all summations over $\vec{k}$ explicity we get for $i=0$

$$\langle n_{m\sigma} n_{0\sigma} \rangle = n^{2}_{\sigma} - \frac{s^{2}_{\sigma} (1-n_{\sigma})}{1-n} \qquad (B.12)$$

$$\langle s^{\sigma}_{m} s^{-\sigma}_{0} \rangle = - \frac{s_{\sigma} \cdot s_{-\sigma}}{1-n} \qquad (B.13)$$

$$\langle n_{m\sigma} n_{0-\sigma} \rangle = n_{\sigma} n_{-\sigma} + \frac{s^{2}_{\sigma}}{1-n} n_{-\sigma} \qquad (B.14)$$

We see that for ferromagnetic phase $\langle n_{m\sigma} n_{0-\sigma} \rangle$ depends explicity on σ, which means that it violates the rotational invariance in spin space. It is caused by the fact that the procedure of calculation the Green functions

$$\frac{1}{N} \sum_{\vec{k}} \langle\langle b_{\vec{k}\sigma} | B_{\substack{1\\2}\vec{k}\sigma} \rangle\rangle = \langle\langle b_{i\sigma} | n_{i+m\pm\sigma} b^{+}_{i\sigma} \rangle\rangle$$

from the equation of motion (B.7) involves only processes in which we have hopping from the i-th site and a frazen configuration on $(i+m)$ -th site. Such a procedure does not violate the symmetry - if the spin σ is the same on both sites $\sigma_{i} \neq \sigma_{i+m}$. But it gives incorrect results if $_{i} \neq {}_{i+m}$ because if we want to have the dynamics included correctly in a ferromagnetic case we have to consider simultaneously the dynamics for each σ to have the same degree of approximation. This means that instead of considering Green function $\langle\langle b_{i\sigma} | n_{i+m-\sigma} b^{+}_{i\sigma} \rangle\rangle$ we should calculate

$$\frac{1}{2} \left(\langle\langle b_{i\sigma} | n_{i+m-\sigma} b^{+}_{i\sigma} \rangle\rangle + \langle\langle b_{i-\sigma} | n_{i+m\sigma} b^{+}_{i-\sigma} \rangle\rangle \right)$$

which gives the symmetrized correlation function

$$\langle n_{m\sigma}\; n_{0-\sigma}\rangle_s = \frac{1}{2}\sum_{\sigma}\langle n_{m\sigma}\; n_{0-\sigma}\rangle \tag{B.15}$$

We would like to mention the same defect appears also in the original Roth paper [76] if one calculates explicity correlation function $\langle n_{m\sigma}\; n_{0-\sigma}\rangle$ appearing in calculation as intermediate step. The origin of this defect is caused by the decoupling of the part $[b_{i\sigma}, P_1\tilde{H}P_1]$ of the Green function $\langle\langle [b_{i\sigma}, P_1\,\tilde{H}\,P_1] \,|\, B_{1\vec{k}\sigma}\rangle\rangle$ while leaving without change $B_{1\vec{k}\sigma}$ which is of the same kind. This remark leads us also to the conclusion that the simplest approximation for the static two-particle correlation functions

$$\langle n_{m\sigma}\; n_{0\sigma'}\rangle \simeq n_{\sigma}\, n_{\sigma'} \tag{B.16}$$

$$\langle S_m^{\sigma}\; S_0^{-\sigma}\rangle \simeq 0 \tag{B.17}$$

Both approximations will be used further in Sections 5.4 and 5.5. It should be emphasized, however, that the simplest decoupling (B.16)-(B.17) does not violate the rotational invariance in spin space.

2. Antiferromagnetic case

Now we have two sublattices $\{A,B\}$ and correspondingly, two sets of operators $B^{A,B}_{1\vec{k}\sigma}$. Since we calculate nearest neighbours two-particle correlations via Roth procedure one can expect that the general results will be formally the same apart from that now we have that $\langle n^A_{i\sigma}\rangle \equiv n_{\sigma}$, $\langle n^B_{m\sigma}\rangle = n_{-\sigma}$ and $S_{\sigma} = S_{-\sigma} = S$. This is indeed the case, as can be easily proved within the Roth procedure [76] when we choose the set of operators $\{A_n\} = \{b^A_{\vec{k}\sigma},\, b^B_{\vec{k}\sigma}\}$. The results are

$$\langle n^B_{m\sigma}\; n^A_{0\sigma}\rangle = n_{\sigma}\, n_{-\sigma} - \frac{S^2\,(1-n_{\sigma})}{1-n} \tag{B.18}$$

$$\langle n^B_{m\sigma}\cdot n^A_{0-\sigma}\rangle = n^2_{\sigma} + \frac{S^2}{1-n} \tag{B.19}$$

$$\langle S^B_{m\sigma}\; S^{A-\sigma}_0\rangle = -\frac{S^2}{1-n} \tag{B.20}$$

Once more again, correlation function $\langle n^B_{m\sigma}\; n^A_{0\sigma}\rangle$ as given by (B.18) violates the symmetry $\sigma \rightarrow -\sigma$. This is also not surprising, since calculating the Green function $\langle\langle b^A_{\vec{k}\sigma} \,|\, B^B_{2\vec{k}\sigma}\rangle\rangle$ and decoupling it afterwards we have broken the symmetry between the neighbouring sites. The retain it we have to average it over and hence we get

$$\langle n^B_{m\sigma}\; n^A_{0\sigma}\rangle = n_{\sigma}\, n_{-\sigma} - \frac{S^2\,(1-\frac{n}{2})}{1-n} \tag{B.21}$$

As in previous case we will discuss also the mean field approximation for the second moment

$$\langle n_{m\sigma}^{B}\, n_{0\sigma}^{A}\rangle \simeq n_{\sigma}\, n_{-\sigma} \tag{B.22}$$

$$\langle S_{m}^{B\sigma}\, S_{0}^{A-\sigma}\rangle \simeq 0 \tag{B.23}$$

Appendix C: Expression for the Ground State Energy

1. Ferromagnetic phase

The Hamiltonian (5.2-20) can be rewritten in the form

$$H = \frac{1}{2} \sum_{i\sigma} b^{+}_{i\sigma} \left[b_{i\sigma} , \tilde{H} \right] + \frac{1}{2} t \sum_{ij\sigma} b^{+}_{i\sigma} b_{j\sigma} \tag{C.1}$$

or after space Fourier transform

$$H = \frac{1}{2} \sum_{\vec{k}\sigma} \left\{ b^{+}_{\vec{k}\sigma} \left[b_{\vec{k}\sigma} , \tilde{H} \right] + \epsilon_{\vec{k}} b^{+}_{\vec{k}\sigma} b_{\vec{k}\sigma} \right\} . \tag{C.2}$$

From equation of motion for the single-particle Green function

$$E \langle\langle b_{\vec{k}\sigma} \mid b^{+}_{\vec{k}\sigma} \rangle\rangle = \frac{1-n-\sigma}{2\pi} + \langle\langle \left[b_{\vec{k}\sigma} , \tilde{H} \right] \mid b^{+}_{\vec{k}\sigma} \rangle\rangle \tag{C.3}$$

we have the static correlation function

$$\langle b^{+}_{\vec{k}\sigma} \left[b_{\vec{k}\sigma} , \tilde{H} \right] \rangle = F_{\omega} \left\{ E \langle\langle b_{\vec{k}\sigma} \mid b^{+}_{\vec{k}\sigma} \rangle\rangle \right\} \tag{C.4}$$

where

$$F_{\omega} \left\{ \langle\langle b_{\vec{k}\sigma} \mid b^{+}_{\vec{k}\sigma} \rangle\rangle \right\} = \frac{1}{\pi} \int_{-\infty}^{\infty} \mathrm{Jm} \langle\langle b_{\vec{k}\sigma} \mid b^{+}_{\vec{k}\sigma} \rangle\rangle_{\omega + i0} \, \omega \cdot f(\omega - \mu) \, d\omega \tag{C.5}$$

So the ground state energy $E_G = \langle \tilde{H} \rangle_T$ is

$$E_G = \frac{1}{2} \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} \langle b^{+}_{\vec{k}\sigma} b_{\vec{k}\sigma} \rangle + \frac{1}{2} \sum_{\vec{k}\sigma} F_{\omega} \left. E \langle\langle b_{\vec{k}\sigma} \mid b^{+}_{\vec{k}\sigma} \rangle\rangle \right\} \tag{C.6}$$

or substituting explicit form of

$$\langle\langle b_{\vec{k}\sigma} \; b^{+}_{\vec{k}\sigma} \rangle\rangle = \frac{1-n-\sigma}{2\pi} \; \frac{1}{E - E_{\vec{k}\sigma}}$$

we have that

$$E_G = \sum_{\vec{k}\sigma} \left(E_{\vec{k}\sigma} + \epsilon_{\vec{k}} \right) \left(1 - n_{-\sigma} \right) f \left(E_{\vec{k}\sigma} - \mu \right) \tag{C.7}$$

This is a starting formula to calculate E_G at $T=0$ for the ferromagnetic phase.

2. Antiferromagnetic phase

In this case we decompose the Hamiltonian (5.2-19) into two sublattices with summations over i and j restricted only to one sublattice. The formula which corresponds to (A.1) is

$$\tilde{H} = \frac{1}{2} \sum_{i\sigma} \{ b^{A+}_{i\sigma} \left[b^{A}_{i}, \tilde{H} \right] + b^{B+}_{i\sigma} \left[b^{B}_{i\sigma}, \tilde{H} \right] + \frac{t}{2} \sum_{ij\sigma}{}' \left(b^{A+}_{i\sigma} b^{B}_{j\sigma} + h.c. \right) \tag{C.8}$$

Assuming that the sublattice give an equivalent contribution, we can write

$$\langle \tilde{H} \rangle = 2ztSN + \sum_{\vec{k}\sigma} F_{\omega} \left\{ E \langle\langle b^{A}_{\vec{k}\sigma} | b^{A+}_{\vec{k}\sigma} \rangle\rangle \right\} \tag{C.9}$$

where N is the number of sites within given sublattice, and $S = \langle b^{A+}_{m\sigma} b^{B}_{i\sigma} \rangle$ with m being the nearest neighbour of i. The general form of single-particle Green function is

$$\langle\langle b^{A}_{\vec{k}\sigma} | b^{A+}_{\vec{k}\sigma} \rangle\rangle = \frac{1-n_{-\sigma}}{2\pi} \frac{E-A}{(E-E_{1\vec{k}})(E-E_{2\vec{k}})} \tag{C.10}$$

where

$$E_{1,2\vec{k}} = A \pm \sqrt{\Delta_{\vec{k}}}$$

We have finally,

$$\langle \tilde{H} \rangle = \sum_{\vec{k}} \{ E_{1\vec{k}} \frac{E_{1\vec{k}} - A}{E_{1\vec{k}} - E_{2\vec{k}}} f\left(E_{1\vec{k}} - \mu\right) + E_{2\vec{k}} \frac{E_{2\vec{k}} - A}{E_{1\vec{k}} - E_{2\vec{k}}} f\left(E_{2\vec{k}} - \mu\right) + 2ztSN \, . \tag{C.11}$$

Appendix D: Mean-Field Approximation for First Moment

In this Appendix we will discuss more systematically the mean-field type approximation of the first moment (5.3.4) of the spectral density function or, equivalently, of mass operator 5.3-5 . It is constituted from eqns.(B.16),(B.17) and (B.22),(B.23) from Appendix B, for the ferro- and antiferromagnetic phases, pespectively. This approximation is the simple approach which truncates the chain of Green's functions and does not cause the principal difficulties present in the Roth scheme, as it was shown in Appendix B. Beside that, it gives us comparison of various approximation schemes (see Sect.5.4) and additionally, unlike the mean-field type approximation for the Green function, it yields us the ferromagnetic solution, and in analytical form.

1. Ferromagnetic case

The band-shift and band-narrowing factors (5.3-9)-(5.3-10) have now the form

$$W_{1-\sigma} = -S_{-\sigma} (1-n_{-\sigma})^{-1} - Jn_{-\sigma} + U_2 n \qquad (D.1)$$

$$W_{2\sigma} = -(1 - n_{-\sigma})^{-1} (JS_{-\sigma} + U_2 S_{\sigma}) \qquad (D.2)$$

Substituting these expressions to general formulas (5.3-18)-(5.3-20) for n_{σ} , ω_{σ} , and S_{σ} we obtain the solution for the magnetization $\langle S^z \rangle = \frac{1}{2} \langle n_{1\uparrow} - n_{1\downarrow} \rangle$ in the closed form which for $J < 0$ and for $T=0$ is

$$\langle S^z \rangle^2 = \left(1 - \frac{n}{2}\right)^2 - (1-n) \frac{1+J+U_2}{1+2J} \simeq \frac{n^2}{4} + (1-n)(J-U_2) \qquad (D.3)$$

This solution exists only for $K-2(t+V)^2/(U-K) \leqslant 0$ which means that either $K < 2(t+V)^2/U$ or $K > U-2(t+V)^2/U$. In the particular case $J = U_2 = 0$ we obtain the solution $\langle S^z \rangle = \pm \frac{n}{2}$ which corresponds to the complete ferromagnetism. This particular result can be interpreted as follows. Since $\tilde{J} = 0$ corresponds to the exact cancellation between the kinetic and direct parts of exchange interactions, the system will behave as a paramagnet for $n=1$ which becomes ordered at $T=0$. This solution is stable against paramagnetism, since applying formula (5.3-21) in this case we have ground state energy for ferromagnet

$$e_G^F \left(J=U_2=0\right) = -n\left(1-n\right) \tag{D.4}$$

and for paramagnet

$$e_G^P = -\frac{1}{2}n\left(1-n\right) - \frac{n}{2}\cdot\frac{1-n}{1-n/2} + \frac{n^2}{4}\,\frac{1-n}{\left(1-n/2\right)^2} \tag{D.5}$$

so the difference $e_G^F - e_G^F = -\frac{n^3}{8}\left(1-n\right)/\left(1-n/2\right)^2 < 0$.

The obtained results are also in agreement with the conclusions of Nagaoka about complete ferromagnetism for $n \to 1$ at the atomic limit. They are, however, in disagreement with the results of Kanamori [74] that as $n \to 0$ the ferromagnetism becomes unstable below $n = n_c = 0.271$. But since the difference between energies of these two states is small and $\sim n^3$, our result as an approximate one should not be taken seriously in this region (cf. also [76]).

In general case, $J,\ U_2 \neq 0$ the ground state energy is

$$\begin{aligned} e_G^F = e_G^F \left(J=U_2=0\right) &+ J\left(\frac{n^2}{4} - \langle S^z\rangle^2\right) + J\left(1-\frac{n}{2}\right)\frac{(1-n)^2}{a^4}\left(\frac{n^2}{4} - \langle S^z\rangle^2\right) \\ &+ U_2\left(1-\frac{n}{2}\right)^2 \frac{(1-n)^2}{a^6}\left[-3n\langle S^z\rangle^2 + \left(1-\frac{n}{2}\right)\left(\frac{n^2}{4} + \langle S^z\rangle^2\right)\right] \\ &+ U_2\langle S^z\rangle^2 \frac{(1-n)^2}{a^6}\left[n\langle S^z\rangle^2 + 3\left(1-\frac{n}{2}\right)\left(\frac{n^2}{4} + \langle S^z\rangle^2\right)\right] \end{aligned} \tag{D.6}$$

Therefore the energy of ferromagnetic state is almost without change

$$e_G^F = e_G^F\left(J=U_2=0\right) - \frac{1}{2}U_2 n^2 + 0\left(J^2\right) \tag{D.7}$$

while the difference between the energies of ferromagnetic and paramagnetic phases is

$$e_G^F - e_G^P = -\frac{n^3}{8}\,\frac{1-n}{\left(1-\frac{n}{2}\right)^2} - J\frac{n^2}{4}\left[1 + \frac{(1-n)^2}{1-\frac{n}{2}}\right] \tag{D.8}$$

So the paramagnetism is stable if $J < 0$ for $n \leqslant n_{c1} = 4|J|$ and for $n \geqslant n_{c2} = 1-|J|$. Again the result can be simply interpreted. The stability of paramagnetism above n_{c2} is caused by the kinetic exchange term $\sim J\,n^2/4$ which is absent in the ferro case and which does not vanish as $n \to 1$. All other terms vanish. Hence we expect that the antiferromagnetic phase will be the most stable one as $n \to 1$ because the kinetic exchange contribution to $e_G^{AF} \simeq 2e_G^P$.

2. Antiferromagnetic case

The band-shift and narrowing factors have the same form as (D.1) and (D.2) respectively, apart from the fact that now $S_{\sigma} = S_{-\sigma} = S$ and $n_{\sigma} = \langle n^{A}_{i\sigma} \rangle = \langle n^{B}_{m-\sigma} \rangle$. The solutions for the sublattice magnetization $\langle S^{z} \rangle = \frac{1}{2} \left(\langle n^{A}_{i\uparrow} \rangle - \langle n^{A}_{i\downarrow} \rangle \right)$ and for the nearest neighbour hopping correlation $S = \langle b^{B+}_{m\sigma} b^{A}_{i\sigma} \rangle$ are

$$2 \left(1-n\right) = \frac{Ja^{2} + S}{a^{2} - S \left(J + U_{2}\right)} \cdot a \ln \tilde{\omega} \tag{D.9}$$

and

$$S = \left(1 - \frac{n}{2}\right) \frac{1-n}{a} \left[1 - \left(1 - \frac{n}{2}\right) \frac{1-n}{a^{2}}\right] \tag{D.10}$$

where

$$\tilde{\omega} = 1 - 2 \left(1 - \frac{n}{2}\right) \frac{1-n}{a^{2}} \tag{D.11}$$

and we have assumed the same model density of states for a bare hand as in Sect.5 . In (D.9) and (D.10) we have included only term $\sim J$ since the higher order ones have been neglected already in the starting effective Hamiltonian (5.2-19). They have no solution for any $n \neq 1$ if $\tilde{J} = \tilde{U}_{2} = 0$. In fact, the results derived here are a generalization of those of Sokoloff (1970) [86] and Meyer and Schweitzer (1973) [87] for the case J and $U_{2} \neq 0$.

Using the eqn.(C.11) derived in Appendix C we get the ground state energy per site

$$\begin{aligned} e^{AF}_{G} = \frac{E_{G}}{2Nz|t|} &= - S \left[1 + \left(1 - \frac{n}{2}\right) \frac{a^{2} - S \left(J+U_{2}\right)}{a^{2}}\right] \\ &- \left(1 - \frac{n}{2}\right) \left[U_{2}n - \frac{1}{2} Jn - \left(1 - \frac{n}{2}\right) \frac{S}{a^{2}}\right] \frac{\frac{n}{2} \left(1 - \frac{n}{2}\right) - \langle S^{z} \rangle^{2}}{a^{2}} \\ &+ \left(J - \frac{S}{a^{2}}\right) \langle S^{z} \rangle^{2} \frac{\frac{n}{2} \left(1 - \frac{n}{2}\right) - \langle S^{z} \rangle^{2}}{a^{2}} \\ &- \left(J + \frac{S}{a^{2}}\right) \left(1 - \frac{n}{2}\right) \langle S^{z} \rangle^{2} \frac{1-n}{a^{2}} \\ &+ \left(J - \frac{S}{a^{2}}\right) \left[U_{2}n - \frac{1}{2} Jn - \left(1 - \frac{n}{2}\right) \frac{S}{a^{2}}\right] \langle S^{z} \rangle^{2} \frac{1-n}{a^{2}} \frac{1}{J + \frac{S}{a^{2}}} \end{aligned} \tag{D.12}$$

For the particular case of paramagnet $\langle S^z \rangle = 0$, and this formula is in agreement with (D.6), derived for the ferromagnetic case. Unfortunately, the final results (eqn. D.9 and D.12) are difficult to compare with (D.7) analytically and therefore we analyze in further numerically in Sect. 5.4 to draw a border line between the ferro- and antiferromagnetic phases as $n \rightarrow 1$, for various J.

6. Dynamics of a Single Hole in the Mott Insulator

In Section 5 we have developped a single-particle approach to the extended Hubbard model. This approach gives an overall picture of magnetism as a function of band filling. Here, following the work of Brinkman and Rice (1970) [83] and of Héritier and Lederer (1977) [84] we consider in detail a propagation of a single hole in the (Mott insulator. We are interested in the formation of the self-trapped state called large magnetic polaron Mott 1974 [72]) which is believed to be formed in some transition metal oxides such as NiO or CoO when doped with e.g. Li.

Usually the many-body methods used do not yield the bound states. So, the authors resort themselves to a phenomenological picture to include the self-trapped states as complementary to the quasiparticle ones.

In such a discussion two assumptions are usually made. Firstly, the polaron extends over many lattice sites, so it can be treated within the continuous medium approximation, and secondly, that the spin polarization of the medium surrounding the hole is either completely [72] or almost completely saturated (Héritier (1975), [85]). The first assumption is plausible in the asymptotic region $W \ll U$, while the second should be verified, particularly in the finite temperature region when the binding energy of polaron is comparable to $k_B T$.

The purpose of this Section is twofold. Firstly, we show under which assumptions we can derive microscopically the phenomenological results of Mott [72]. Next, we show how to extend the approach to the case with nonsaturated magnetic moment.

The approach we use is the single-particle one and it is discussed in detail first. Then, we show the correspondence with previous results of Mott [72] which enables us to turn over to the dynamics of the large polaron in the presence of magnetic field.

6.1. Nonlinear Schrödinger equation for the hole

The starting point of our discussion is the Hubbard Hamiltonian (cf. Eqn. (2-9) for $J=K=V=0$) in the strong correlation limit which is from (5.1-19)

$$H = t \sum_{ij\sigma} a^{+}_{i\sigma} (1-n_{i-\sigma})\, a_{j\sigma} (1-n_{j-\sigma})$$

$$+ \frac{2t^2}{U} \sum_{ij}{}' \vec{S}_i \cdot \vec{S}_j - \frac{1}{4} \sum_{\sigma\sigma'} n_{i\sigma} (1-n_{i-\sigma})\, n_{j\sigma'} (1-n_{j-\sigma'}) \tag{6.1-1}$$

t is the overlap integral between the nearest neighbours $\langle ij \rangle$, while the spin operators $\{\vec{S}_i\}$ are as previously

$$\vec{S}_i = (S^z_i , S_i^{+}, S_i^{-}) = ((n_{i\uparrow} - n_{i\downarrow})/2 ,\ a^{+}_{i\uparrow} a_{i\downarrow} ,\ a^{+}_{i\downarrow} a_{i\uparrow})$$

The presence of factors $(1-n_{i-\sigma})$ in (6.1-1) rules out the double occupancy on each site and hence describes the dynamics of a hole in the lowest Mott-Hubbard subband $(n \leqslant 1)$.

It has been shown by Nagaoka (1966) [73] that for alternant lattices and $U = \infty$ the ground state is that of saturated ferromagnet. Therefore, assuming that $|t| \gg t^2/U$ we can expect that in the ground state single hole will be surrounded by an extended in space cloud of spin polarization which decays slowly with distance. To calculate the spacial extent of the cloud, represented by radius R called the polaron radius, we proceed as follows.

Let us define the hole state

$$|\psi\rangle = \sum_{\alpha} \sum_{n\sigma} \varphi^{\alpha}_{n\sigma}\, a_{n\sigma}\, \Gamma(\alpha) \prod_{j} a^{+}_{j\sigma_j} |0\rangle \tag{6.1-2}$$

where $\alpha = (\sigma_1, \ldots, \sigma_{n-1} , \sigma , \sigma_{n+1}, \ldots, \sigma_N)$ is the N-particle configuration, $\Gamma(\alpha)$ is the probability amplitude for this configuration, and $|\varphi^{\alpha}_{n\sigma}|^2$ is the probability to find the hole on site n and configuration α of the Mott insulator so that $|\varphi^{\alpha}_{n\sigma}\Gamma(\alpha)|^2$ is the probability to find $N-1$ -particle configuration $(\sigma_1, \ldots, \sigma_{n-1} , \sigma_{n+1}, \ldots, \sigma_N)$.

Next, we are looking for a solution in the form of a bound state for the hole in the case of finite U . It has to reduce to the extended solution of Nagaoka, e.g. that of the free hole for $U = \infty$. Thus, the simplest approximation is to neglect all spin configurations $\{\alpha\}$ but one, with the perfect alignement of the hole surrounding. In such a situation the tailing effects of wave function will not be reproduced properly We explare this possibility first to establish the connection with the phenomenological approach [72], before resorting to a more refined analysis.

The hole amplitudes $\{\varphi_{n\sigma}\}$ fulfill the condition $\sum_{n\sigma} |\varphi_{n\sigma}|^2 = 1$. To make single-particle approach selfcontained we use the mean-field version of (6.1-1), namely we decouple the spin-spin correlations

$$\vec{S}_i \cdot \vec{S}_j = S_i^z \langle S_j^z \rangle + \langle S_i^z \rangle S_j^z - \langle S_i^z \rangle \langle S_j^z \rangle \qquad (6.1\text{-}3)$$

Neglecting in (6.1-1) the charge fluctuation we get the Schrödinger equation $i \hbar \, \partial_\tau |\Psi\rangle = H|\Psi\rangle$ in the form

$$i \hbar \, \partial_\tau \varphi_{n\sigma} = t \sum_{m(n)} \varphi_{m\sigma} + \frac{t^2 z}{2U} \varphi_{n\sigma} - \frac{t^2}{2U} \varphi_{n\sigma} \sum_{m(n)} \left(|\varphi_{m\sigma}|^2 + |\varphi_{m-\sigma}|^2 \right. \qquad (6.1\text{-}4)$$

The first term is the hole kinetic energy (we have changed t → -t and hence have assumed that the lattice under consideration is alternant: sc or bcc), while the second and third are the losses of the kinetic exchange energy due to presence of the hole in the system. We have also used the fact that the probability of finding electron on site n is $\left(1 - \sum_\sigma |\varphi_{n\sigma}|\right)^2$, and that

$$S_j^z = \frac{1}{2} - \sum_\sigma |\varphi_{j\sigma}|^2 .$$

Assuming further that

$$\varphi_{n\sigma} = \delta_{\sigma\uparrow} \varphi_n \exp\left(- itE/\hbar\right)$$

we get the stationary equation

$$\left(E - zt - \frac{zt^2}{2U}\right) \varphi_{n\sigma} = t \sum_{m(n)} \left(\varphi_m - \varphi_n\right) - \frac{t^2}{2U} \varphi_n \sum_{m(n)} |\varphi_m|^2 \qquad (6.1\text{-}5)$$

In Eqn.(6.1-5) E is <u>not</u> the whole energy of the polaron because is does not contain the exchange energy loss of the cloud surrounding hole. To take into account this effect we proceeds as follows. Firstly, we use the continuum medium version of (6.1-5). This gives for sc structure

$$E = zt + \frac{zt^2}{2U} + ta^2 \int \varphi^* \nabla^2 \varphi \; d^d x - \frac{zt^2}{2U} \int |\varphi|^4 \; d^d x - \frac{ta^2}{2U} \int |\varphi|^2 \nabla^2 |\varphi|^2 \; d^d x \qquad (6.1\text{-}6)$$

where a is the lattice constant. Additionally, the wave function of a bound state will be assumed in the form $\varphi = \varphi(r/R)$ where R is the variational parameter. The normalized function is

$$\varphi(\vec{r}) = \left(\alpha_d R^d\right)^{-1/2} f\,(r/R)$$

where $\int f(x)\, d^d x = 1$, and $\alpha_d = \frac{2d-2}{d}$ is the d-dimensional volume factor $(d = 2$ or $3)$. The energy E in dimensionless units of R $(R \to R/a)$ is then

$$E = zt + \frac{zt^2}{2U} + \frac{|t|\beta}{R^2} - \frac{t^2z}{2U}\gamma + \frac{t^2z}{2U}\gamma' \quad \frac{1}{R^2} \qquad (6.1\text{-}7)$$

with

$$\beta = \int_0^\infty dx \quad x^{d-1} \left|\frac{df}{dx}\right|^2 \qquad (6.1\text{-}7a)$$

$$\gamma = \int_0^\infty dx \quad x^{d-1} \left|f(x)\right|^4 \qquad (6.1\text{-}7b)$$

and

$$\gamma' = \int_0^\infty dx \quad x^{d-1} \left|f'(x)\right|^4 \qquad (6.1\text{-}7c)$$

Now, the exchange energy loss associated with a ferromagnetic cluster surrounding the hole is

$$\frac{t^2}{2U} \sum_{\substack{n\,Q \\ m(n)}} \left(1 - |\varphi_n|^2\right)\left(1 - |\varphi_m|^2 + \frac{t^2z}{2U} \sum_{n\in Q} 1\right) \qquad (6.1\text{-}8a)$$

where Q is the interior of polaron (of volume $\alpha_d R^d$), for which $f_n \neq 0$. If we assume again again that the medium is continous polaron is large then it is

$$\frac{t^2z}{2U}\left(2\alpha_d R^d - 2 + \gamma'' - \gamma'/R^2\right) \qquad (6.1\text{-}8b)$$

where

$$\gamma' = \int_0^\infty dx\, x^{d-1} \,|f|^4 + \int_0^\infty \left(\frac{d}{dx}\,|f|^2\right)^2 d^{d-1}\, dx \qquad (6.1\text{-}8c)$$

Therefore the total energy of hole + cluster is

$$E_t = -z|t| + \frac{zt^2}{2U}\left(\gamma + \gamma'' - 1\right) + \frac{E_0}{R^2} + J'\alpha_d R^d \qquad (6.1\text{-}9)$$

where

$$E_0 = |t|\beta - \frac{t^2z}{2U}\gamma' \ , \quad \text{and} \quad J' = \frac{zt^2}{U} \ .$$

The last formula, apart for the irrelevant constant coincides with that of Mott [72] . It gives the polaron radius from the condition $dE/dR = 0$, which is

$$R = \left(\frac{2E_0}{J'\,\alpha_d\, d}\right)^{1/d+2} \qquad (6.1\text{-}10)$$

and the corresponding energy

$$E_t = -z|t| + \frac{zt^2}{2U}\left(\gamma + \gamma'' - 1\right) + E_o\left(\frac{J'}{E_o}\right)^{\frac{2}{d+2}}\left[\left(\frac{d}{2}\right)^{\frac{2}{d+2}} + \left(\frac{2}{d}\right)^{\frac{d}{d+2}}\right] \tag{6.1-11}$$

So, the variational method applied to Eqn.(6.1-6) that the hole is locally surrounded by the entirely aligned spins yields the previous formulation. It is only valid when the polaron is so large that the boundary region of it with the antiferromagnetic phase gives a negligible contribution to the energy.

6.2. Finite magnetic field

Eqn.(6.1-5) can be easily generalized to the case with the static magnetic field H along the z axis. The wave function is then governed by the equation:

$$\left(E - zt - \frac{zt^2}{U}\right)\varphi = t\left[\nabla^2 - \left(\frac{eH}{2c\hbar}\right)^2 (x^2+y^2)\right]\varphi - \frac{t^2}{2U}|\varphi|^2\varphi - \frac{t^2}{2U}\varphi\nabla^2|\varphi|^2 \tag{6.2-1}$$

The variational function appropriate to the three-dimensional case $(d=3)$ is

$$\varphi(\vec{r}) = \varphi\left(\frac{(x^2+y^2)^{1/2}}{R_\perp}, \frac{z}{R}\right)$$

and it gives the total energy of polaron

$$E_t = \frac{E_o}{3}\left(\frac{2}{R_\perp^2} + \frac{1}{R_\parallel^2}\right) + h^2 R_\perp^2 + \tilde{J}'\alpha_3 R_\parallel R_\perp^2 \tag{6.2-2}$$

with $\tilde{J}' = \frac{1}{2}J'(1-\cos\theta) - \mu_B H\,(1-\cos\theta/2)$, and θ being the angle between the n.n. spins in antiferromagnetic phase. Minimalization with respect to $R_\parallel$ gives

$$R_\perp = \left[\frac{2}{3}\,\frac{E_o}{\tilde{J}' R_\parallel^3 \alpha_3}\right]^{1/2} \tag{6.2-3}$$

and with respect to $R_\perp$, after substitution of (6.2-3)

$$\frac{3}{2}\,\frac{J'\quad{}_3}{E_o}\,R_\parallel^6 - R - \frac{h^2}{\tilde{J}'\alpha_3} = 0 \tag{6.2-4}$$

where $h^2 = |t|\left(\frac{eH}{2c\hbar}\right)^2 \varrho$, and

$$\varrho = \int_0^\infty dx\, x^{d+1}\, |f|^4 .$$

The limit $R_\parallel \to \infty$ defines the field at which the polaron transforms into free vacancies. We can solve (6.2-4) near this value of the field noticing that $R_\perp$ is always finite. Hence, neglecting in (6.2-4) the term $\sim R_\parallel$ we get the value of the field $\mu_B H_c = 2 J$, i.e. at the transition from antiferromagnetic to fully aligned phase.

6.3. Inclusion of partial polarization of the polaron

Guyer (1978) [89] has calculated the band narrowing (BN) factor which depends on the magnetization $\hat{\sigma}$ per spin. His result for the position of the lower band edge $\varepsilon_B(\hat{\sigma})$ of the hole moving in the homogeneously magnetised medium is given by the interpolation formula

$$\varepsilon_B(\hat{\sigma}) = -z\, t\, g_o(\hat{\sigma}) \tag{6.3-1}$$

with

$$g_o(\hat{\sigma}) = \frac{4}{5} + \frac{2}{5}\hat{\sigma}^2 - \frac{1}{3}\hat{\sigma}^4 + \frac{2}{15}\hat{\sigma}^6 \tag{6.3-2}$$

This result bases on the first ten moments of the density of states and contains the closed paths involving few (2-3) spheres of coordination of a given site (cf. also [83]), Hence, if the polaron is large ($R \gg 1$) we can assume that $g_o(\hat{\sigma})$ describes the band edge for the trapped hole within the region of constant magnetisation $\hat{\sigma}$. This means we represent the polaron by a partially saturated cloud which is space homogeneous within it. Thus, instead of (6.1-9) we have

$$E_t = -z|t|\, g_o(\hat{\sigma}) + g_o(\hat{\sigma})\frac{E_o}{R^2} + J'\alpha_d R^d \hat{\sigma}^2 \tag{6.3-3}$$

The polaron is formed at the expence of the antiferromagnetic ordering of the electrons in the Mott insulator surrounding the hole. Thus, the polaron is stable if $E_t < E_{AF}$, where E_{AF} is given by

$$E_{AF} = -z|t|\, g_1(m) - \frac{1}{2} J'\alpha_d R^d m^2 \tag{6.3-4}$$

with m being the sublattice magnetization, and [83]

$$g_1(m) = \frac{4}{5} - \frac{1}{20} m^2 \tag{6.3-5}$$

For finite temperature T we have to replace energies (6.3-3) and (6.3-4) by free energies

$$F_t = -z|t|\, g_o(\hat{\sigma}) + g_o(\hat{\sigma})\frac{E_o}{R^2} + \frac{1}{2} J'\alpha_d R^d \hat{\sigma}^2 + k_B T\left(\frac{1+\hat{\sigma}}{2}\ln\frac{1+\hat{\sigma}}{2} + \frac{1-\hat{\sigma}}{2}\ln\frac{1-\hat{\sigma}}{2}\right) \tag{6.3-6}$$

and

$$F_{AF} = -z|t|\, g_1(m) - \frac{1}{2} J' \alpha_d R^d m^2 + k_B T \left(\frac{1+m}{2} \ln \frac{1+m}{2} + \frac{1-m}{2} \ln \frac{1-m}{2} \right) \qquad (6.3\text{-}7)$$

Therefore, we minimize the difference $F = F_t - F_{AF}$. The quantity can be determined selfconsistently introducing the effective field acting on aligned spins

$$\mu_B H_{ef} = - \frac{1}{\alpha_d R^d} \frac{E}{\partial \hat{\sigma}} = \frac{1}{\alpha_d R^d} \left[z|t|\, g_0'(\hat{\sigma}) - \frac{E_0}{R^2} g_0'(\hat{\sigma}) - J' \alpha_d R^d \hat{\sigma} \right] \qquad (6.3\text{-}8)$$

Then

$$\hat{\sigma} = \tanh \left(\frac{\mu_B H_{ef}}{k_B T} \right) \qquad (6.3\text{-}9)$$

while minimalization with respect to R yields

$$R = \left\{ \frac{4 g_0(\hat{\sigma}) E_0}{J' (\hat{\sigma}^2 + m^2) + 2 k_B T \Delta S} \frac{1}{\alpha_d R^d} \right\}^{1/d+2} \qquad (6.3\text{-}10)$$

where $S = S_{AF} - S_t$. In paramagnetic phase $m=0$, $g_1\ m = \frac{4}{5}$, and $S_{AF} = k_B \ln 2$.

Eqn. (6.3-9) leads to the important conclusion: for $T=0$, $\hat{\sigma}=1$ and hence our results reduce to those of presented previously [72,88] and rederived in Sect. 6.1. To estimate the dependence $\hat{\sigma} = \hat{\sigma}(T)$ we can use instead of (6.3-2) of following interpolation formula for g_0

$$g_0 (\hat{\sigma}) \simeq \frac{4}{5} + \frac{1}{5} \hat{\sigma}^2 \qquad (6.3\text{-}11)$$

Noticing that for $\hat{\sigma} \to 0$ (and for $m=0$) we have

$$R = \frac{16}{15 d\, \alpha_d} \left(\frac{E_0}{J' + k_B T} \right) \hat{\sigma}^{-\frac{2}{d+2}} \equiv B\, \hat{\sigma}^{-\frac{2}{d+2}} \qquad (6.3\text{-}12)$$

Thus, if $\hat{\sigma} \to 0$ R will grow as $T \to T_p$, where T_p is the temperature at which polaron disappears. But then its total moment $\hat{\sigma} \cdot \alpha_d R^d$ diverges for $d=3$ as $\hat{\sigma} \to 0$. Therefore, the only possibility is that polaron disappears at finite $\hat{\sigma}$ and R, when there is only one solution of Eqn. (6.3-8). This is indeed the case. It can be seen substituting (6.3-12) into (6.3-9) and noticing that the effective field acting on spins within polaron is

$$\mu_B H_{ef} = \frac{2}{5}\ \frac{z|t|}{\alpha_d\ B^d}\ \hat{\sigma}^{\frac{2d+1}{d+2}} - \frac{2}{5}\ \frac{E_o}{\alpha_d\ B^{d+2}}\ \hat{\sigma}^2 - J'\hat{\sigma} \tag{6.3-13}$$

is zero for nonzero $\hat{\sigma}$. Expanding the last equation and making use of approximation $\tanh x \simeq x$ we get the value R_p of the radius R at $T=T_p$

$$R_p = \frac{2}{5}\ \frac{z|t|}{J' + k_B T_p}\ \frac{1}{\alpha_d} \tag{6.3-14}$$

which, when substituted to 6.3-10 gives the value $\hat{\sigma} = \hat{\sigma}_p$ at $T=T_p$

$$\sigma_p = \left(\frac{16}{5d\ \alpha_d}\ \frac{E_o}{J' + k_B T_p}\right)^{\frac{d+2}{2}} \left(\frac{5\ \alpha_d}{2}\ \frac{J' + k_B\ T_o}{z|t|}\right)^{\frac{d+2}{2d}} \tag{6.3-15}$$

The value of T_p can be obtained from the condition $d\tanh\ (\beta\mu_B H_{ef})\ /d\hat{\sigma} = 1$, which leads to

$$k_B T_p \quad \frac{2}{5}\left(\frac{2d}{d+2} + 1\right)\frac{z\ t}{\alpha_d} - J' \sim \frac{z\ t}{\pi} - J \tag{6.3-16}$$

The situation is drawn schematically in Fig.5.

We reach the conclusion that the critical value of magnetic moment $\hat{\sigma}_p$ and radius R_p may be estimated analytically and are given by Eqs.(6.3-14) and (6.3-15) respectively. Bound or self-trapped states disappear at temperature T_p of the order of bandwidth $(W/2\pi)$, and its magnitude justifies a posteriori the assumption $(\hat{\sigma} \ll 1)$ we have made to derive $\hat{\sigma}_p$ and R_p . However, our estimate of R_p within the continous medium approximation is only qualitative since $R_p \sim 1$ as can be seen after substituting (6.3-16) to (6.3-14).

The results of the Sect. 6 are complementary to those from Sect. 5.5 concerning the phase separation. Such a separation due to condensation of holes in the lowest Mott-Hubbard subband is possible if the concentration of them is high enough to be treated as a Fermion gas.

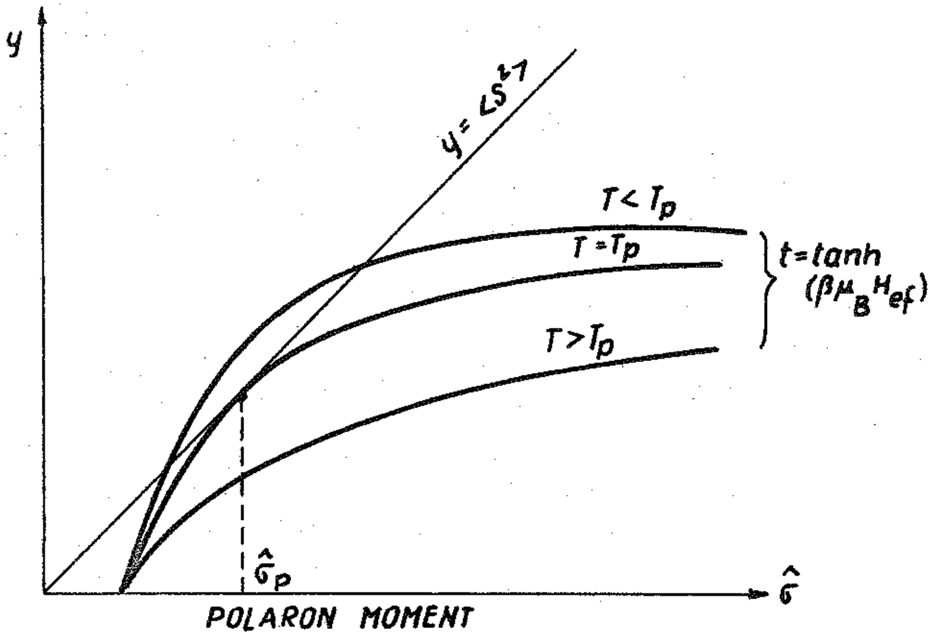

Fig.5. Possible solutions for magnetization $\hat{\sigma}$ of large magnetic polaron for various temperatures. T_p is the temperature at which the polaron disappears

7. Kinetic Exchange Interaction in a Doubly Degenerate Narrow Band

7.1. Introduction

The magnetic properties of a narrow nondegenerate band are largely determined by the electron correlation (Hubbard 1963 [15] , Kanamori 1963 [74] , Nagaoka 1966 [73]) due to the fact that the band narrowing factor is spin-configuration-dependent. Near the metal-insulator transition (Hubbard 1964 [79] , Mott 1974 [72]) the electron correlation also induces the kinetic exchange among itinerant electrons (Brinkman and Rice 1970 [83] , Chao et al 1977 [39]). In the case of a degenerate narrow band one must also consider the important intraatomic exchange interaction in connection to the Hund´s rule, as well as the intraatomic correlation between parallel spin electrons occupying different atomic orbitals (Van Vleck 1953 [90] , Inagaki and Kubo 1973 [91]).

In the strong correlation regime, the above mentioned interactions (the band narrowing factor can be viewed as the itinerant double exchange interaction) either contribute collectively or compete with each other, depending on the band filling. However, explicit forms of the kinetic and the itinerant double exchange contributions are known only for the particular cases (Kugel and Khomskii 1973 [92] , Cyrot and Lyon-Caen 1975 [93] , Inagaki 1975 [94] , Chao et al 1977 [40] referred to as I). In this paper we will derive the proper form of the kinetic exchange starting from the degenerate Hubbard Hamiltonian in rotationally invariant form. We will then obtain the effective magnetic interactions is terms of the global spin and particle number operators. Our results reduce to those obtained by Inagaki (1975) [94] for one electron per atom and to an appropriate form of the Heisenberg Hamiltonian in the case of the Mott insulator. The present work is an extension of our previous work on a nondegenerate narrow band in strong correlation limit

(Spałek and Oleś 1977 [36], Chao et al 1977 [39], 1978 [76], Spałek et al 1980 [59]). Since transition metal disulfides can be described by the doubly degenerate e_g subband, we will discuss the main feature of such system in connection to our theoretical analysis.

7.2. Subband structure and cannonical transformation

We start from the model Hamiltonian in Wannier representation (cf. also Eqn. (2-10))

$$
\begin{aligned}
H = & {\sum_{ijl\sigma}}' t_{ijl} a^{+}_{li\sigma} a_{lj\sigma} + {\sum_{ijll'\sigma}}'' t^{12}_{ij} a^{+}_{li\sigma} a_{l'j\sigma} \\
& + U \sum_{li} n_{li\uparrow} n_{li\downarrow} + \frac{1}{2}\left(K - \frac{1}{2} J\right) {\sum_{ill'\sigma\sigma'}}' n_{li\sigma} n_{l'i\sigma'} \\
& - J {\sum_{ll'i}}' \vec{S}_{li} \cdot \vec{S}_{l'i} + J {\sum_{ll'i}}' a^{+}_{li\uparrow} a_{l'i\downarrow} a_{l'i\downarrow} a_{li\uparrow}
\end{aligned}
\qquad (7.1)
$$

where the single-primed sums exclude terms with either $i=j$ or $l=l'$, while the double-primed sum excludes terms with both $i=j$ and $l=l'$. This Hamiltonian includes the intraatomic intraorbital Coulomb, the intraatomic interorbital Coulomb and the intraatomic interorbital exchange interactions, as well as the intraatomic hopping of two electrons from one orbital to the other ($l=1,2$). The only intraatomic interaction neglected in (1) is

$$
V \sum_{li\sigma} \left\{ \left(n_{li\sigma} + n_{l'i\sigma} \right) a^{+}_{li-\sigma} a_{l'i-\sigma} + \text{h.c.} \right\} , \qquad (7.2)
$$

which corresponds to the intraatomic hopping of only one electron at the presence of another electron. If one atom is doubly occupied, the ground state is a triplet according to the Hund's rule. The energy separation between the ground state triplet and the first excited singlet will be large if J is much larger than $2V^2/(U-K)$. Under this condition, the term (7.2) and the last term in (7.1) contribute negligibly to the thermodynamic properties.

We assume that U and K are much larger than t_{ijl} and t^{12}_{ij}. Therefore, the energy structure of the many-electron system consists of many subbands. The hoppings within a subband are the primary processes while those between subbands are the secondary ones. We can remove the latter from (7.1) by an appropriate cannonical transformation and replace them by higher order virtual hoppings. Similar problem has been treated previously both for a single band (cf. Sect.5) and for a doubly degenerate band (Chao et al 1977 [40]). Here we will briefly outline the analysis.

We first diagonalize the atomic part of (7.1) to obtain the eigenstates $\{|\nu\mu i\rangle\}$ for the ith atom containing electrons and then construct the projection operators $P^{\nu}_{\mu i}$. For $\nu = 0$ the projection operator is simply

$$P^0_{0i} = \prod_{l\sigma} (1-n_{li\sigma}) \quad . \tag{7.3}$$

For one electron $\nu = 1$, we have

$$P^1_{1i} = \sum_{l\sigma} n_{li\sigma} (1-n_{li-\sigma})(1-n_{l'i\uparrow})(1-n_{l'i\downarrow}) \tag{7.4}$$

with the corresponding eigenenergy $\lambda_1 = 0$. The eigenstates of a doubly occupied atom consists of one triplet and three singlets. For the triplet,

$$P^2_{ti} = \frac{3}{4} \sum_{\sigma\sigma'} n_{li\sigma}\, n_{l'i\sigma'} (1-n_{li-\sigma})(1-n_{l'i-\sigma}) + \vec{S}_{l\,i} \cdot \vec{S}_{l'i} \tag{7.5}$$

with $\lambda_t = K-J$. The projection operators for the three singlets are

$$P^2_{si} = \frac{1}{4} \sum_{\sigma\sigma'} \{ n_{li\sigma}\, n_{l'i\sigma'} (1-n_{li-\sigma})(1-n_{l'i-\sigma'}) - \vec{S}_{li} \cdot \vec{S}_{l'i} \tag{7.6a}$$

$$P^2_{\pm i} = \frac{1}{2} \sum_{i} \left\{ n_{li\uparrow}\, n_{li\downarrow} (1-n_{l'i\uparrow})(1-n_{l'i\downarrow}) \pm a^+_{li\uparrow} a^+_{li\downarrow} a_{l'i\downarrow} a_{l'i\uparrow} \right\} \tag{7.6b}$$

with the respective eigenenergies $\lambda_s = K+J$ and $\lambda_{\pm} = U \pm J$. There is only one projection operator for $\nu = 3$ as

$$P^3_{di} = \sum_{l\sigma} n_{li\uparrow}\, n_{li\downarrow}\, n_{l'i\sigma} (1-n_{l'i-\sigma}) \tag{7.7}$$

and the eigenenergy is $\lambda_d = U+2K-J$. Finally, if the atom is fully occupied by four electrons, we have

$$P^4_{li} = \prod_{l\sigma} n_{li\sigma} \tag{7.8}$$

and $\lambda_4 = 2\,U+2K-J$. In (7.4)-(7.7) we have assumed that $l' = 1$.

In terms of $\{P^{\nu}_{\mu i}\}$ we can construct the projection operator P_j corresponding to the jth subband. Since $\sum_j P_j = 1$, we can decompose the Hamiltonian as $H = (\sum_j P_j)\, H\, (\sum_k P_k) = \sum_j P_j H P_j + \sum_{j,k}' P_j H P_k$. While $P_j H P_j$ describes the physical properties of the jth subband, $P_j H P_k$ represents the hopping of electron from the kth to the jth subbands. Since we are interested in the case that U and K are much larger, than t_{ijl} and t^{12}_{ij}, only the few low lying subbands are important. If we define $H_{ijll'\sigma} = t_{ijl}\, a^{+}_{lj\sigma}\, a_{li\sigma}\, \delta_{ll'} + t^{12}_{ij}\, a^{+}_{lj\sigma}\, a_{l'i\sigma}$, then the relevant low lying subbands are

$$P_1HP_1 = \sum_{ij}{}' P^1_{1i}\, P^1_{1j} \Big(\sum_{ll'}{}' H_{ijll'}\Big) P^1_{1j}\, P^1_{1i} \qquad (7.9)$$

for the electron density $n \ll 1$, and

$$P_2HP_2 = \sum_{ij}{}' \Big\{P^2_{ti}\, P^2_{tj} \Big(\sum_{ll'\sigma} H_{ijll'\sigma}\Big) P^2_{tj}P^2_{ti} + P^2_{si}P^2_{sj} \Big(\sum_{ll'\sigma} H_{ijll'}\Big) P^2_{sj}P^2_{si}\Big\} + \frac{1}{2}\Big(K - \frac{1}{2} J\Big) \sum_{\substack{ill' \\ \sigma\sigma'}}{}' n_{li\sigma}\, n_{l'i\sigma'} \big(1-n_{li-\sigma}\big)\big(1-n_{l'i-\sigma'}\big) - J \sum_{il} \vec{S}_{li} \cdot \vec{S}_{l'i} \qquad (7.10)$$

for the electron density $1 < n \ll 2$. By the same taken, the relevant inter-subband hoppings are

$$P_1HP_2 = \sum_{ij}{}' \Big\{P^1_{1i}\, P^1_{1j} \Big(\sum_{ll'\sigma}{}' H_{ijll'\sigma}\Big)\Big(P^2_{tj}+P^2_{sj}+P^2_{+j}+P^2_{-j}\quad P^0_{0i}\Big) = \big(P_2HP_1\big)^{+} \qquad (7.11)$$

for $n \leqslant 1$, and

$$P_2HP_3 = \sum_{ij\gamma\eta}{}' P^2_{\gamma i}\, P^2_{\eta j} \Big(\sum_{ll'\sigma} H_{ijll'\sigma}\Big) P^3_{dj}P^1_{1i} = \big(P_3HP_2\big)^{+} \qquad (7.12)$$

for $1 < n \leqslant 2$.

With a cannonical transformation, we can derive an effective Hamiltonian $\tilde{H} = \exp(-iS)\, H \exp(iS)$. (7.13)
By a proper choice of S, the first order inter-subband hopping can be removed. The detailed mathematical manipulation has been demonstrated earlier (Chao et al 1978 [45]). To the second order in inter-subband hopping, the effective Hamiltonian has the form

$$\tilde{H} = P_1HP_1 - \sum_{ij\gamma}{}' \Big\{P^1_{1i}P^1_{1j} \Big(\sum_{ll'\sigma} H_{ijll'\sigma}\Big) P^2_{\gamma j}\, P^0_{0i} \sum_{ll'\sigma}{}' H_{jill'\sigma}\Big) P^1_{1j}P^1_{1i} \,/\Delta E^{21}_{\gamma} + P^2_{\gamma i}\, P^0_{0j} \Big(\sum_{ll'\sigma} H_{ijll'\sigma}\Big) P^1_{1j}P^1_{1i} \Big(\sum_{ll'\sigma}{}' H_{jill'\sigma}\Big) P^0_{0_j}\, P^2_{\gamma i} \,/\Delta E^{12}\Big\} + \Big\{P_2HP_2 - \sum_{ij\gamma\eta}{}' \Big[P^2_{\gamma i}P^2_{\eta j} \Big(\sum_{ll'\sigma}{}' H_{ijll'\sigma}\Big) P^1_{1i}P^3_{dj} \Big(\sum_{ll'\sigma}\Big) H_{jill'\sigma}\Big) P^2_{\eta j}P^2_{\gamma i} \,/\Delta E^{32} + P^3_{di}P^1_{1j} \Big(\sum_{ll'\sigma} H_{ijll'\sigma}\Big) P^2_{\gamma i}P^2_{\eta j} \Big(\sum_{ll'\sigma}{}' H_{jill'\sigma}\Big) P^1_{1j}P^3_{di} \,/\Delta E^{23}_{\gamma\eta}\Big]\Big\}\, \theta\,(n-1) \qquad (7.14)$$

where $\theta(x) = 1$ if $x > 0$ and $\theta(x) = 0$ if $x < 0$.

The energy denominator $E^{st}_{\gamma\eta}$ or E^{st}_{γ} measures the change of energy from the initial state to the intermediate state in the virtual hopping process. (7.14) is similar to that derived in I but is improved by taking into account the correct local atomic configuration.

7.3. Effective magnetic Hamiltonian

The calculation of the effective Hamiltonian reduces to the calculation of the second order matrix elements of (7.14). We will present the results for various cases.

7.3.1. Case A: $n \leqslant 1$

Let us introduce the global operators representation of Kugel and Khomskii (1973) [92] generalized to the case of partially filled band. We define the orbital ordering operator

$$\vec{T}_i = \frac{1}{2} \sum_{ll'\sigma} (\vec{\tau})_{ll'} a^+_{li\sigma} a_{l'i\sigma} , \qquad l' \neq l \tag{7-15}$$

the global spin operator

$$\vec{S}_i = \frac{1}{2} \sum_{l\sigma\sigma'} (\vec{\tau})_{\sigma\sigma'} a^+_{li\sigma} a_{li\sigma'} , \qquad \sigma \neq \sigma' \tag{7-16}$$

and the global number operator

$$N_i = \sum_{l\sigma} P^1_{1i} n_{li\sigma} P^1_{1i} , \tag{7-17}$$

where $\vec{\tau}$ is the Pauli matrices $\vec{\tau} = (\tau_x, \tau_y, \tau_z)$. Then it is easy to show that

$$P^1_{1i} a^+_{1i\sigma} a_{2i\sigma} P^1_{1i} = T^+_i \left(\frac{1}{2} + \sigma S^z_i\right) N_i , \tag{7-18}$$

$$P^1_{1i} a^+_{2i\sigma} a_{1i\sigma} P^1_{1i} = T^-_i \left(\frac{1}{2} + \sigma S^z_i\right) N_i ,$$

$$\left.\begin{aligned} P^1_{1i} a^+_{1i\sigma} a_{2i-\sigma} P^1_{1i} &= S^{\sigma}_i T^+_i N_i , \\ P^1_{1i} a^+_{2i\sigma} a_{1i-\sigma} P^1_{1i} &= S^{\sigma}_i T^-_i N_i , \end{aligned}\right. \tag{7-19}$$

$$P^1_{1i} n_{1i\sigma} P^1_{1i} = \left(\frac{1}{2} + T^z_i\right) N_i \left(\frac{1}{2} + \sigma S^z_i\right) , \tag{7-20}$$

$$P^1_{1i} S_i P^1_{1i} = \left(\frac{1}{2} + T^z_i\right) S^{\sigma}_i N_i , \tag{7-21}$$

where we have used the notation $\vec{T}_i = (T^+_i , T^-_i , T^z_i)$ with $l=1$ corresponding to $\sigma = +$ and $l=2$ corresponding to $\sigma = -$. When $N_i=1$, (7-18)-(7-21) reduce to the same results of Kugel and Khomskii (1973)

If we define $S_{ij+} = \frac{3}{4} + S_i \cdot \vec{S}_j$, $\vec{S}_{ij-} = \frac{1}{4} \cdot \vec{S}_i \cdot \vec{S}_j$ and $T_{ij\pm} = \frac{1}{4} \pm \vec{T}_i \cdot \vec{T}_j$, and assume $t_{ij1} = t_{ij2} = t_{ij}$, then the effective Hamiltonian can be given explicity as

$$\begin{aligned} \tilde{H} = & \sum_{ij}{}' P^1_{1i} P^1_{1j} \Big(\sum_{ll'\sigma}{}' H_{ijll'\sigma} \Big) P^1_{1j} P^1_{1i} \\ & - \sum_{ij}{}' N_i N_j \Big\{ t^2_{ij} \Big[S_{ij+} T_{ij-} / (K-J) + S_{ij-} \big(T_{i\, j+} - 2T^z_i T^z_j \big) / (K+J) \\ & + 2US_{ij-} T_{ij+} / \big(U^2 - J^2 \big) \Big] + \big(t^{12}_{ij} \big)^2 \Big[S_{ij+} \big(T_{ij+} - 2T^x_i T^x_j \big) / (K-J) \\ & + S_{ij-} \big(T_{ij+} - 2T^y_i T^y_j \big) / (K+J) + S_{ij-} T_{ij-} / (U-J) \\ & + S_{ij-} \big(T_{ij+} - 2T^z_i T^z_j \big) / (U+J) \Big] \Big\} \end{aligned} \tag{7-22}$$

This effective Hamiltonian is a generalization of those derived by Kugel and Khomskii (1973) [92] , Cyrot and Lyon-Caen (1975) [93] and Inagaki (1975) [94] for $n \neq 1$. It also leads to the same form obtained by Roth (1966) [95] for the case of a two-site system. Although (7-22) looks rather complicated, it is a straightforward matter to analyse it. The dominating terms which are $\sim (K-J)^{-1}$ yield a ferromagnetic spin and alternant (or antiferromagnetic) orbital ordering in the ground state. But the antiferromagnetic orbital ordering is only possible if the system can be divided into two interpenetrating sublattices. We notice that the first sum in (7-22) vanishes if $N_i = 1$. Since this sum represents the intra-subband hopping which is the only charge-transfer process in this case, the system becomes an insulator for $N_i = 1$ for temperature below $T_{MI} \sim (K-J-W)/k_B$, where W is the width of the lowest subband. We will return to this discussion in next section.

7.3.2. Case B: $1 \leq n < 2$

In the ground state some atoms will be singly occupied and some atoms will be doubly occupied. We assume that the Hund´s rule is obeyed and so the atomic configuration will be a triplet if it is doubly occupied. The global operators for a singly occupied site have been given by (7-15)-(7-17). Now we introduce the global operators $\vec{S}_{i2} = (S^+_{i2}, S^-_{i2}, S^z_{i2})$, N_{i2} and N'_{i2} for a doubly occupied site via the following equations according to the Hund´s rule

$$N_{i2} = \sum_{\sigma} n_{1i\sigma} (1-n_{1i-\sigma}) \; n_{2i\sigma} (1-n_{2i-\sigma}) \tag{7-23}$$

$$N'_{i2} = \sum_{\sigma} n_{1i\sigma}\left(1-n_{1i-\sigma}\right) n_{2i-\sigma}\left(1-n_{2i-\sigma}\right) \qquad (7\text{-}24)$$

$$P^2_{ti}\, S^{\sigma}_{i}\, P^2_{ti} = \frac{1}{2} N_{i2}\, S^{\sigma}_{i2} \qquad (7\text{-}25)$$

$$P^2_{ti}\, n_{1i\sigma}\, P^2_{ti} = \frac{1}{2} N_{i2}\left(1 + \sigma S^{z}_{i2}\right) + \frac{1}{2} N'_{i2} \qquad (7\text{-}26)$$

In terms of these operators, we have the effective Hamiltonian H = expression given by equation (7-22)

$$+ \sum_{ij}{}' \left\{ P^2_{ti}\, P^2_{tj} \left(\sum_{ll'\sigma} H_{ijll'\sigma} \right) P^2_{tj} P^2_{ti} + P^2_{si} P^2_{sj} \left(\sum_{ll'\sigma} H_{ijll'\sigma} \right) P^2_{sj}\, P^2_{si} \right\} + K \sum_{i} N'_{i2} + (K-J) \sum_{i} N_{i2} - 2 \sum_{ij} \left\{ t^2_{ij} + \left(t^{12}_{ij}\right)^2 \right\} \left(\frac{1}{2} - \vec{S}_i \cdot \vec{S}_{j2} \right) N_i N_{j2} / (U+K) - \sum_{ij}{}' \left\{ t^2_{ij} + \left(t^{12}_{ij}\right)^2 \right\} \left(1 - \vec{S}_{i2} \cdot \vec{S}_{j2} \right) N_{i2}\, N_{j2} / (U+J) \qquad (7\text{-}27)$$

It is helpful to point out here that N_{i2} and N'_{i2} are the number operators for the doubly occupied site with total $S \neq 0$ and $S=0$, respectively.

To summarize, we have expressed the second order inter-subband hopping contribution to the effective Hamiltonian (7-22) and (7-27) in terms of the global charge variables N_i, N_{i2} and N'_{i2}, the global spin variables S_i and S_{i2}, and the global orbital ordering variable $\vec{T}_i$. However, the intra-subband hopping terms in (7-22) and (7-27) are still expressed in terms of the non-global variables. Yet in the next section we will show that this form of the effective Hamiltonian can be easily analyzed by decoupling the charge and the spin fluctuations.

7.4. General features of the magnetic ground state

To describe the magnetic phases of strongly correlated electrons using the effective Hamiltonian, we notice that there are three parameters essential to a degenerate band: the bare band width W, the intraatomic Coulomb energy U (we assume K the same order of magnitude as U) and the intraatomic exchange constant J. Therefore, there are three regimes in the parameter space (W,U,J): (a) $W \gg U > J$ for the weakly correlated regime, (b) $U > W \gg J$ for the strongly correlated regime, and (c) $U > J \gg W$ for the double exchange regime. In this paper we will only treat (b) and (c).

7.4.1. Case A: $n \leqslant 1$

If we assume $t_{ij}^{12} = 0$ and decouple the charge and the spin fluctuations as well as the orbital and the spin degrees of freedom in (7-22), then we have ferromagnetic spin and antiferromagnetic orbital ordering, in agreement with the findings of Inagaki (1975)[94] and Cyrot and Lyon-Caen (1975) [93] for $n=1$. However, since $|t_{ij}^{12}| \sim |t_{ij}| \gg t_{ij}^{2}/(K-J)$, the orbital ordering will be destroyed by the interorbital hopping. Without such long-range orbital order (7-22) can be simplified as

$$\begin{aligned}\tilde{H}_1 = {\sum_{ij\sigma}}' t_{ij}\, a_{1i\sigma}^{+}(1-n_{1i-\sigma})\, a_{1j\sigma}(1-n_{1j-\sigma})(1-n_{1'i\uparrow})(1-n_{1'j\uparrow})(1-n_{1'j\downarrow}) \\ + \sum_{ij11'\sigma} t_{ij}^{12}\, a_{1i\sigma}^{+}(1-n_{1i-\sigma})\, a_{1'j\sigma}(1-n_{1'j-\sigma})(1-n_{1'i\uparrow})(1-n_{1'i\downarrow}) \\ (1-n_{1'j\uparrow})(1-n_{1'j\downarrow}) - {\sum_{ij}}' \tilde{J}_{ij}\, \vec{\Xi}_i \cdot \vec{\Xi}_j\,, \end{aligned} \tag{7-28}$$

where $\vec{\Xi}_i = N_i \vec{S}_i$ and $\tilde{J}_{ij} = \frac{1}{2}\left\{t_{ij}^{2} + (t_{ij}^{12})^{2}\right\}\left\{J/(K^2 - J^2) - U/(U^2-J^2)\right\}$.
If we decouple again the spin and the charge variables $\langle \Xi_i^z \rangle = \langle N_i \rangle \langle S_i^z \rangle = n/2$ (7-28) can be diagonalized as

$$\bar{H}_1 = P_1 \sum_{\vec{k}} \left(E_{\vec{k}}^{+} \alpha_{\vec{k}}^{+} \alpha_{\vec{k}} + E_{\vec{k}}^{-} \beta_{\vec{k}}^{+} \beta_{\vec{k}} \right) P_1\,, \tag{7-29}$$

where $\alpha_{\vec{k}}^{+} = (a_{1\vec{k}\uparrow}^{+} - a_{2\vec{k}\uparrow}^{+})/\sqrt{2}$, $\beta_{\vec{k}}^{+} = (a_{1\vec{k}\uparrow}^{+} + a_{2k\uparrow}^{+})/\sqrt{2}$ and $E_{\vec{k}}^{\pm} = (\epsilon_{\vec{k}} \mp \epsilon'_{\vec{k}})/\sqrt{2}$, with $a_{1k\sigma}^{+}$, $\epsilon_{\vec{k}}$ and $\epsilon'_{\vec{k}}$ being the Fourier transforms of $a_{1i\sigma}^{+}$, t_{ij} and t_{ij}^{12} respectively.

7.4.2. Case B: $1 < n \leqslant 2$ and $W \lesssim J$

Since we have assumed that the Hund's rule is obeyed at the doubly occupied sites, the quantity $\vec{S}_{i2}$ is well defined and so the decoupling of the spin and the charge degrees of freedom in (7-27) is meaningful. Since we have assumed $(K-J) > W$, there is one electron localized at each site while the rest of the electrons are itinerant. In this case we can use the formalism of double exchange developed recently by Cieplak (1978) [96] to obtain from (7-27) the effective spin Hamiltonian

$$\tilde{H}_2 = (2-n)(1-n)\sum_{ij}{}'\left(t_{ij}+t_{ij}^{12}\right)\left(\frac{3}{8}+\frac{1}{2}\vec{S}_i\cdot\vec{S}_j\right)-(2-n)^2\sum_{ij}{}' J_{ij}\vec{S}_i\cdot\vec{S}_j$$
$$+\sum_{ij}\left\{t_{ij}^2+\left(t_{ij}^{12}\right)^2\right\}\frac{2(n-1)(2-n)}{U+K}\vec{S}_i\cdot\vec{S}_{j2}$$
$$+\frac{(n-1)^2}{U+J}\vec{S}_{i2}\cdot\vec{S}_{j2} \qquad (7\text{-}30)$$

For the case of half-filled band $n=2$, this effective Hamiltonian reduces to the Heisenberg antiferromagnet representing the Mott insulator, as it should be. For $n \leqslant 2$ and in the mean field approximation, the intersite spin antiferromagnetic phase becomes stable when

$$\sum_{j}{}'\left\{(2-n)(1-n)\left|t_{ij}+t_{ij}^{12}\right| + (2-n)^2\tilde{J}_{ij} - \left[t_{ij}^2 + \left(t_{ij}^{12}\right)^2\right]\left[\frac{2(n-1)(2-n)}{U+K}+\frac{(n-1)^2}{U+J}\right]\right\} = 0 \qquad (7\text{-}31)$$

In tight-binding approximation with nearest hopping t and t^{12}, this condition reduces to

$$2\left(2U+K+J\right)\left[t^2+\left(t^{12}\right)^2\right] / \left|t+t^{12}\right|(U+K)(U+J) = 2-n \ll 1 \qquad (7\text{-}32)$$

If we set $K=J=t^{12}=0$ (7-32), is just the Nagaoka (1966) [73] result for a single band.

In general, we can not rule the possibility of the onset of other more exotic phases. But such situation will not happen in the mean field approximation.

7.4.3. Case C: $1 < n \leqslant 2$ and $W \gg J$

It is important to note that in this case the rôle of singlet states is no longer negligible, even though the atomic state is a triplet. Thus we can devide the strongly correlated itinerant magnets into two classes:

(1) $U > J \gtrsim W$: Local moments exist and the low lying magnetic excitation is spin wave. This is probably the situation for some transition metal oxides (Mott 1974) [72].

(2) $U \gtrsim W > J$: There is no local moment and the low lying magnetic excitation is spin fluctuations, i.e., the fluactuation of total spin length from site to site (Moriya 1979) [101].

Now the decouplind of E_i into the spin and the charge variables does not help the analysis of (7-27). The standard approach is to use the Hartree-Fock approximation for the intraatomic exchange (Inagaki and Kubo 1973) [91] and to use the mean field approximation for the kinetic exchange terms. Then the ferromagnetic ordering compets with the antiferromagnetic ordering. However, the Hartree-Fock approximation is valid only if $J \ll W(2-n)(n-1)/2$, and so it breaks down as $n \to 2$.

7.4.4. Insulator-metal transitions

The insulator to metal transition can occur when either $W \sim K-J$ (for $n=1$) or $W \sim U-J$ the Mott transition, $n=2$. Since we have assumed $U \gg W$, a direct investigation of the insulator-metal transition is possible. However, we can estimate the conditions under which such transitions take place, following the similar argument for the case of a nondegenerate band (cf. Sect. 5.5).

We consider first the case $n \ll 1$. The band energy per site for the antiferromagnetic and the paramagnetic states is roughly $E_B = -n(1-n)W/4$, while for the complete ferromagnetic (CF) state is $E'_B = -n(1-n)\,W/2$. The energy in the CF state is further lowered by the kinetic exchange with an amount $\Delta E_m = ZJ \sim W^2/4Z(K-J)$. The time uncertainty connected with the formation of a quasiparticle CF band is

$$\tau_B = \hbar/2E_B \simeq \hbar/Wn(1-n) \tag{7-33}$$

while the spin-flip lifetime in the same phase is

$$\tau_m = \hbar/2\Delta E_m = \tau_B\, 2Zn(1-n)(K-J)/W \tag{7-34}$$

For $n \to 1$, $\tau_m \ll {}_B$ indicating a slow intra-subband electron hopping modulated by a fast collective spin fluctuation due to the virtual inter-subband transition. Hence, electrons in nearly quarter-filled band with $(K-J)(1-n)Z \ll W$ are described by a Heisenberg-type Hamiltonian.

In such picture it can be shown that the virtual hopping energy should be renormalized as

$$\Delta E'_m = W^2(K-J)/\left\{4Z(K-J)^2 + 2W^2\right\} \; . \tag{7-35}$$

It is interesting to see that (7-35) also gives the qualitatively correct behaviour at the other limit $W \gg U$ where we should have $\Delta E'_m \sim (K-J)\,n^2$. We can then estimate the insulator-metal transition condition from the mergence of the twolowest subbands when $K-J+2\Delta E'_m = W$. We thus obtain the condition as

$$W/(K-J) = Z\left\{1-(1-4/Z)^{1/2}\right\}/2 \; , \tag{7-36}$$

which is approximately 1.1 for cubic systems. This condition can be satisfied by a square lattice, but not by linear chain.

Using $U-J+2\Delta E_m' = W$ we can estimate the condition for Mott transition as

$$W/\,U-J = Z\left\{1-\left(1-4/Z\right)^{1/2}\right\}/2\ . \tag{7-37}$$

Again there is no Mott transition to the metallic state for linear chain. Our conclusion thus extends the Lieb and Wu (1968) exact solution result, whi ch predicts this type of behaviour for one dimensional nondegenerate bands.

7.5. Analysis of the data for $Fe_{1-x}Co_xS_2$ and $Co_{1-y}Ni_yS_2$

The above derived results can be directly applied to the transition metal disulfides FeS_2, CoS_2 and NiS_2, since these materials can be described by the doubly degenerate e_g subband with 0, 1 and 2 electrons per atom respectively Jarrett et al 1968 [97] , Ogawa et al 1974 [21] , Ogawa 1979 [22] . Therefore, the solid solutions $Fe_{1-x}Co_xS_2$ and $Co_{1-x}Ni_xS_2$ as well as $CoS_{2-x}Se_x$ (Adachi et al 1979 [98] , Yasuoka et al 1979 [94]) are ideal systems for studying the magnetism of a partially filled doubly degenerate band. Here we should mention that Sokoloff (1971) [85] , Abito and Schweitzer (1975) [100] , Moriya (1978) [101] , Inagaki (1979) [102] and Mabatah et al (1980) [103] have investigated such systems, but using only a single nondegenerate band.

Since CoS_2 is a metal, we can not assume $W < (K-J)$ and so the result derived in Sect. 7.3.1 should be modified in such a way that the renormalized kinetic exchange interaction must be used. From the description in Sect. 7.4.4, the $\tilde{J}_{ij}$ defined in Sect. 7.3.1 (now $\frac{1}{K-J}$ is the dominating term) is renormalized as $\tilde{J}_{ij} = \left\{t_{ij}^2 + \left(t_{ij}^{12}\right)^2\right\}/4\left\{K-J+2Z\left[t_{ij}^2 + \left(t_{ij}^{12}\right)^2\right]/(K-J)\right\}$. With this renormalized kinetic exchange interaction, (7-22) can be applied to CoS_2 . We should notice that the ferromagnetic interaction in (7-22) dominates only if there is AF orbital ordering. However, the cations in CoS_2 have FCC structure. Therefore, as $n=1$ the AF orbital ordering is destroyed by frustration (Alexander and Pincus 1980) [103] . In this case, (7-22) predicts a state with ferromagnetic orbital ordering and antiferromagnetic spin ordering. Consequently, the low magnetic moment state of Co atoms is caused at least partially by frustration effect on the spin and the orbital orderings.

Since $W > K-J$ for CoS_2, the addition of Se atoms broadens the band without changing the intraatomic interaction, we expect $W > K$ for $Co\left(S_xSe_{1-x}\ _2\right)$. Under this situation, there is finite probability to have singlet atomic configuration with two antiparallel spin electrons on the same atom. Such singlet pairs of electrons have been seen as non-magnetic Co atoms in the recent NMR experiments (Yasuoka et al 1979 [99]). The presence of the singlet state is one of the reasons causing the disappearance of the magnetic moments in $\mathrm{Co}\,(S_x Se_{1-x\;2})$ for $x < 0.88$. The possibility to have singlet-triplet transitions also provides a physical picture for the local spin fluctuations developed by Moriya (1978,1979) [101]. Finally, the possibility of having singlet components should give rise to a high temperature Curie-Weiss susceptibility.

The bandwidth in the paramagnetic phase is narrower than that in the complete ferromagnetic phase by a factor $\frac{1}{4}$ (Brinkman and Rice 1970 [83], Guyer 1978 [84], Spałek et al 1980 [59]). Therefore, the gain of band energy in the ferromagnetic phase is $W\,(n-n_c)(1-n)\,/8$, where $n_c = 0.05$ is the upper limit of n below which ferromagnetism is absent. The temperature dependence of the magnetization can thus be derived as

$$m = 2\langle S_i^{\,z}\rangle = n \tanh\left\{\beta(n-n_c)\left[\frac{1}{8}\,(1-n)\,W+Z\tilde{J}\right]m\right\}\,, \qquad (7\text{-}38)$$

where $\tilde{J}$ is the nearest neighbour value of $\tilde{J}_{ij}$. Such magnetization yields a Curie-Weiss susceptibility with the Curie temperature

$$T_c = (n-n_c)\left\{\frac{1}{2}\,(1-n)\,W+Z\tilde{J}\right\}/4k_B\,. \qquad (7\text{-}39)$$

The correction terms $Z\tilde{J}$ in (7-38) and (7-39) are essential in order to fit the experimental data (Sokoloff 1971 [85]). Using the maximum value of T_c at $n=0.85$ (Ogawa et al 1974) [21] we can estimate $\tilde{J}/W = 0.03$.

However, there are two sources of error in our estimation (7-38) and (7-39). Firstly, as $n \to 1$ the frustration effects will reduce the effective exchange constant and so the magnetic moment. Secondly, since $W > K-J$ the first excited subband will overlap with the lowest lying subband and therefore will also contribute to m and T_c. Taking these two factors into account, we can conclude that while n increases, T_c will reach its maximum value before m does. This is due to the fact that as n increases, more triplet states will be occupied when double occupancy is allowed. The decrease of m above $n=0.95$ suggests a saturated singlet state occupancy and the frustration works very effectively to destroy the magnetic order. If this is true, the system $Ni_yCo_{1-y}S_2$ should exhibit typical spin glass susceptibility cusp for $y > 0.1$.

If we again assume $U > W > K-J$, the overlap of the two lowest subbands can explain the band filling variation of the linear specific heat coefficient γ (Inagaki 1978 [102]). Condition $U > W$ is necessary for the existence of the Mott-Hubbard gap in NiS_2. The frustration effects in the insulating phase will lead to a weak ferromagnetism, or more generally, to the noncollinear structure observed (Ogawa et al 1974 [21]). The metamagnetic behaviour of $Co_{1-y}Ni_yS_2$ for $0.1 < y < 0.8$ strongly suggests the importance of singlet pairs when the band energy dominates the intraatomic exchange and so destroys the magnetic ordering (Ogawa 1979 [22]). But further studies on this problem are necessary.

7.6. Conclusions

In Section 7 we have formulated a more general treatment on the problem of narrow band systems as compared to the existing works in this area. Here we emphasize that earlier works considered either only a nondegenerate band (Sokoloff 1971, [98], Abito and Schweitzer 1975 [100], Moriya 1978 [101], Inagaki 1978 [102]) or only the Ising part of the intraatomic exchange in a doubly degenerate band (Chao et al 1977 [40]). Our purpose is to explain the observed magnetic behavior of transition metal disulfides $Fe_{1-x}Co_xS_2$ and $Co_{1-y}Ni_yS_2$. The interpretation presented in Sec. 7.5 forms the basis for a more quantitative analysis. The frustration effects and the presence of singlet electron pairs complicate such an analysis enormously.

Essentially new features appear when degeneracy is included in the Hubbard model. Among them are the following ones:

1° The predominant contribution to the kinetic exchange for the quarter filled band ($n=1$) is ferromagnetic;

2° The ground state is orbitally ordered and the structure is alternant in this case;

3° The state for $n=1$ is insulating when $W < (U-J)$;

4° There are spin fluctuations (singlet-triplet transitions) present even for strongly correlated electrons ($U > W$) if $J \ll W$ and $n > 1$;

5° The intraatomic exchange can induce an indirect exchange between electrons.

The problems $1^{\circ} - 4^{\circ}$ have been analysed in this Section.

The last one will be on of the subjects of the next Part.

Part III

FROM NARROW BAND TO s-d MODEL

Existence of localised moments in strongly correlated narrow bands

8. Introduction: Systems with Localised Moments

There are two physically distrinct classes of itinerant magnetic systems for which the concept of localised (atomic) magnetic moment is relevant, namely:

a) 4f systems for which the position of the atomic level of 4f electrons is well below the conduction band edge (usually of 5d-6s character) and

b) 3d or 4f systems for which the states of magnetic electrons overlap considerably with the states in a much wider conduction band. In other words, the systems in which the magnetic electrons contribute to the Fermi surface of a metal.

In the former case the magnetic (atomic-like) states are distinguishable from the conduction states because of the different character of the wave function in each of these states. The conduction-band electrons having quasiparticle energies larger than those of 4f electrons leave them unpaired because the energy of the doubly occupied of orbital exceeds the bandwidth W of the conduction electrons.

On the other hand, the local-moment behaviour in the case b) is not at all obvious since the d or f electrons form a band by themselves which is partially filled. We are particularly interested in this case since it is nontrivial and attracted a considerable amount of attention recently [11-18] .

There are two kinds of systems belonging, to class b , namely some itinerant magnets (e.g. Fe) and intermediate valence systems. Each of them has been shortly discussed in Section 1 together with the relevant phenomena. On the side of theory the localised moments have been introduced as a separate solution, existence of which has been proved on an example of narrow s-band electrons in the limit of sufficiently strong correlations (Hasegawa 1979 [14] , Evenson et al 1970 [104] , Cyrot 1970,1972 [105,69] , Roth 1977 [106] , Pettifor 1980 [107]). Such a solution characterized by the moment $\mu_i = \pm 1$ on each site (for half-filled band) cannot be obtained within a standard band theory.

In this work we consider an easier to analyse problem of localisation of a part of electrons filling a degenerate band. The number of electrons on average is not less than one per atom. All electrons in the narrow band are equivalent (Sect.9) or mixed with a wide conduction band (Sect.10). In each case we prove that the system under consideration may be regarded as a form of s-d model which we derive explicitly.

9. Localised-Moment Behaviour of Narrow-Band Electrons

The simplest model of degenerate narrow-band electrons is based on the parametrized Hamiltonian of identical degenerate orbitals

$$H = \sum_{ijl\sigma} t_{ij} a^{+}_{li\sigma} a_{lj\sigma} + U \sum_{li} n_{li\uparrow} n_{li\downarrow} + \frac{U'}{2} \sum_{\substack{l\neq l' \\ \sigma\sigma'}} n_{li\sigma} n_{li\sigma'} - J \sum_{l\neq l'} \vec{S}_{li} \cdot \vec{S}_{l'i} \qquad (9\text{-}1)$$

We have assumed that orbitals labelled by $l=1,2,\ldots,d$ are equivalent so the overlap integral (t_{ij}), intraorbital (U), interorbital (U') Coulomb interactions, as well as the intraatomic exchange constant (J) do not depend on the particular choice of orbitals. Also, $U' = U-J/2$.

Suppose we have $n = p+x$ electrons per atom, where p is integer $(p \leq d)$, and $0 < x < 1$. Then, if electrons are strongly correlated, i.e. $U > W$ the p electrons on each site will be always present because the hopping processes involving transition $p \rightarrow (p-1)$ require the energy loss exceeding the bare bandwidth W .

The decomposition onto p localised and x itinerant ones is in accord with the fact that the particles are indistinguishable if the time uncertain connected with the band motion which is of the order $\hbar / [Wx(1-x)]$ (cf. Sect. 5.5) is much smaller than the time $\hbar/U'$ required to rearrange and reach a stable atomic configuration after the hopping with formation of doubly occupied orbital (violating the Hund's rule) has taken place. However, the corresponding virtual hopping processes are taking place on the time scale $\hbar U/2t^2x^2$ (cf. Sect. 7.3) which can be comparable with the hopping (particularly if $x \rightarrow 0$ and $x \rightarrow 1$) . Hence, the kinetic exchange must be incorporated into the description. More formally, we represent the Coulomb terms through the spin field $\vec{S}_{li}$ Schrieffer 1969 [108] , Gomes and Ledeyer 1977 [109]

$$\sum_{l} n_{li\uparrow} n_{li\downarrow} = \frac{1}{2} \sum_{l\sigma} n_{li\sigma} - \frac{2}{3} U \sum_{li} (\vec{S}_{li})^2 \qquad (9\text{-}2)$$

and

$$\sum_{\substack{l\neq l'\\ \sigma\sigma'}} n_{li\sigma}\, n_{l'i\sigma'} = \Big(\sum_{l\sigma} n_{li}\Big)^2 - 2\sum_{l} n_{li\uparrow}\, n_{li\downarrow} - \sum_{l\sigma} n_{li\sigma}, \qquad (9\text{-}3)$$

while the exchange part

$$\sum_{l\neq l'} \vec{S}_{li}\cdot\vec{S}_{l'i} = \Big(\sum_{l} \vec{S}_{li}\Big)^2 - \sum_{l}\big(\vec{S}_{li}\big)^2 \qquad (9\text{-}4)$$

Now, employing the Hund's rule we can define the itinerant $\{\vec{s}_i\}$ and localised $\{\vec{S}_i\}$ parts

$$\sum_{l} \vec{S}_{li} = \vec{S}_i + \vec{s}_i \qquad (9\text{-}5)$$

with $\vec{S}_i^{\,2} = (p/2)(p/2+1)$, while the principle of minimum polarity [90] yields [*]

$$\sum_{l} n_{li\sigma} = p + n_{i\sigma} \qquad (9\text{-}6)$$

Eqs. (9-5) and (9-6) may be regarded as definitions of $s_{i\sigma}$ and $n_{i\sigma}$. Hence

$$\Big(\sum_{l\sigma} \vec{S}_{li}\Big)^2 = p\,(p+1) + \vec{s}_i^{\,2} + 2\vec{S}_i\cdot\vec{s}_i$$

$$\sum_{l} \vec{S}_{li}^{\,2} = \frac{3}{4}p + \vec{s}_i^{\,2}$$

Thus, the intraatomic part of (9-1) reduces to

$$U\sum_{i} n_{i\uparrow} n_{i\downarrow} - 2J\sum_{i} \vec{S}_i\cdot\vec{s}_i + \text{const}$$

The band part of (9-1) can be transformed introducing the projection operators $\{P_{pi}\}$ specifying the configuration with p particles on given site i. The are defined through the identity

$$\prod_{l\sigma}\Big[y n_{li\sigma} + (1-n_{li-\sigma}) = \sum_{n=1}^{d} P_{ni}\cdot y^n \qquad (9\text{-}7)$$

where y is an arbitrary variable, d is the degeneracy of the band consideration. P_{ni} projects atomic state $|\mu_i i\rangle$ onto the subspace with n singly occupied orbitals. In our case we have either p or $(p+1)$ electrons on given site only. Others (e.g. with doubly occupied orbitals) are accessible only in virtual processes. Beside that, we can write

$$P_{p+1\ i} = P_{pi}\sum_{\sigma} n_{i\sigma}\,(1-n_{i\,-\sigma})$$

---

[*] We do not discuss here the conditions under which the Hund's rule and minimum polarity principles hold. Full microscopic theory requires a justification of those two facts as well.

The projector P_{pi} restricts the change of the number of electrons $Ni = \sum_{l\sigma} n_{li\sigma}$ on given site to one, so we put

$$a^{+}_{i\sigma}\, a_{j\sigma}\,(1-n_{i-\sigma})\,(1-n_{j-\sigma}) = P_{pi}P_{pj}\Big(\sum_{l} a^{+}_{li\sigma}\, a_{lj\sigma}\Big)\, P_{pi}\, P_{pj}$$

and thus

$$\sum_{l\sigma} a^{+}_{li\sigma}\, a_{lj\sigma} = \sum_{\sigma} a^{+}_{i}\,(1-n_{i-\sigma})a_{j\sigma}\,(1-n_{j-\sigma}) + H'_{ij}$$

where H'_{ij} contains the hoppings with the formation of doubly occupied orbitals, etc. Therefore, in new representation we have

$$H = \sum_{ij}{}' \, t_{ij}\, a^{+}_{i\sigma}\, a_{j\sigma}\,(1-n_{i-\sigma})(1-n_{j-\sigma}) - 2J\sum_{i} \vec{S}_i \cdot \vec{s}_i + H_{ex}\left\{\vec{S}_i + \vec{s}_i\right\} \qquad (9\text{-}8)$$

where $H_{ex}\{\cdot\}$ expresses the kinetic exchange interactions for d-fold degenerate band with n electrons per atom. The explicit calculations of H_{ex} for doubly degenerate band are given in Sect. 7.

For $n \leqslant 1$ the localised part $\vec{S}_i$ is absent. Therefore, our theory is applicable only for $n > 1$. For less than half-filled band we have then

$$H_{ex} = -\sum_{ij}{}' \frac{t^2_{ij}}{U}\left[\frac{1}{2} - \vec{S}_i\,(\vec{S}_j + \vec{s}_j)\right] - \sum_{ij}{}' \frac{t^2_{ij}}{U+J}\left[1-(\vec{S}_i + \vec{s}_i)\cdot(\vec{S}_i + \vec{s}_j)\right] \qquad (9\text{-}9)$$

$\vec{S}_i$ is the Heisenberg spin 1/2, and $\vec{S}_i N_i = \vec{s}_i$ is the itinerant electron spin. In Eqn. (9-9) we have antiferromagnetic interaction both between the spins belonging to the same and different subsystems. All couplings are of equal strength. For $n=2$ (half-filled band) $n_{i\uparrow} + n_{i\downarrow} = 1$, $N_{12} = 1$, $N_i = 0$, and H_{ex} reduces to the Hamiltonian of the Heisenberg antiferromagnet with $S=1$, as it should be.

It is a tedious task to construct the Hamiltonian H_{ex} for higher degeneracies $(d > 2)$ but, in principle, method is straightforward. Some remarks on the kinetic exchange for an arbitrary d the reader can find in Part V.

10. Relation Between the Periodic Anderson-Falicov-Kimball Model of Intermediate Valence and the s-d Model

10.1. Introduction

There have been various attempts to describe systems with space-homogeneous intermediate valence (IV). Falicov and Kimball (1969)[32] introduced a two-band model, one of finite width W, and the other one of zero width and thus represented by the atomic level ϵ_f. The two subsystems, carriers and the localised electrons (herein referred to as f electrons) interact with one another through the intraatomic Coulomb interactions. The role of this interorbital interaction is to provide a gain in energy due to a redistribution of electrons between the subsystems. The Hamiltonian of such system is

$$H = \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} n_{\vec{k}\sigma} + \epsilon_f \sum_{i\sigma} N_{i\sigma} + U_{sf} \sum_{i\sigma\sigma'} n_{i\sigma} N_{i\sigma'} \qquad (10\text{-}1)$$

where the first term describes conduction electron carriers with energy $\epsilon_{\vec{k}}$, while the second describes the f electrons. The third term is the interorbital Coulomb interaction on the same site. The ground state of (10-1) is nonmagnetic and the last term can drive a transition from an insulating phase (with $N_i = \sum_\sigma N_{i\sigma} = 1$) to a metallic one with number of carriers $n_c = N^{-1}\sum_{\vec{k}\sigma} \langle n_{\vec{k}\sigma} \rangle < 1$. In the limit of zero band-width $W=0$ the model can be solved exactly (Spałek 1980c [54], cf. Supplement G).

The second model considered as a more basic is the periodic Anderson model (Leder and Mühlschlegel 1978 [110], Coqblin et al 1980 [111]). It is represented by the parametrized Hamiltonian

$$H = \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} n_{\vec{k}\sigma} + \epsilon_f \sum_{i\sigma} N_{i\sigma} + U \sum_i N_{i\uparrow} N_{i\downarrow}$$
$$+ N^{-1/2} \sum_{\vec{k}i\sigma} \left(V_{\vec{k}} e^{-i\vec{k}\vec{R}_i} a^+_{i\sigma} c_{\vec{k}\sigma} + V_{\vec{k}} e^{i\vec{k}\vec{R}_i} c^+_{\vec{k}\sigma} a_{i\sigma} \right) \qquad (10\text{-}2)$$

where the first two terms have the same meaning as in (10-1); the third one represents the short-range intraatomic Coulomb interaction between f electrons ($N_{i\sigma} = a^+_{i\sigma} a_{i\sigma}$), while the last one the single-particle hybridization introduced by Anderson (1961) to express the nonorthogonality between the conduction band and f states. When hybridization is of intraatomic nature, it takes place between the states of the same parity only and $V_{\vec{k}} = V$.

Apart from these two Hamiltonians, some authors start from the periodic Kondo Hamiltonian (Jullien et al 1979 [112] , Lacroix and Cyrot 1979 [113])

$$H = \sum_{\vec{k}\sigma} \epsilon_{\vec{k}}\, n_{\vec{k}\sigma} + J \sum_{i} \vec{S}_i \cdot \vec{s}_i \qquad (10\text{-}3)$$

where $\{\vec{S}_i\}$ are the localized (atomic) spins, and $\{\vec{s}_i\}$ are the itinerant carriers spin in the Wannier representation

$$\vec{s}_i = \left(s_i^{z},\, s_i^{+},\, s_i^{-}\right) = \left\{\frac{1}{2}\left(c^{+}_{i\uparrow} c_{i\uparrow} - c^{+}_{i\downarrow} c_{i\downarrow}\right),\; c^{+}_{i\uparrow} c_{i\downarrow},\; c^{+}_{i\downarrow} c_{i\uparrow}\right\} \qquad (10\text{-}4)$$

It should be established to what extent the spin coupling $(J\vec{S}\cdot\vec{s})$ between the subsystems can exhibit the Kondo lattice behaviour and IV properties. However, in view of the fact that in the mixed valence limit $\epsilon_f \rightarrow 0$ the Schrieffer-Wolff (1966) [114] transformation is not directly applicable to (2), the meaning of the Hamiltonian (3) is not obvious. It has been proved very recently (Krishna-murthy et al 1980ab [26,27]) with the help of the renormalization group approach that the Anderson Hamiltonian (2) for a single f level can be mapped onto the Kondo Hamiltonian even in the mixed valence limit under the condition $U > \pi |V|^2 \rho(E_F)$, where $\rho(E_F)$ is the density of states at the Fermi energy E_F .

The purpose of this paper is to show how a general model which is a combination of (1) and (2), namely one with the Hamiltonian

$$\begin{aligned} H = {} & \sum_{\vec{k}\sigma} \epsilon_{\vec{k}}\, n_{\vec{k}\sigma} + \epsilon_f \sum_{i\sigma} N_i + U \sum_{i} N_{i\uparrow} N_{i\downarrow} \\ & + N^{-1/2} \sum_{\vec{k}i} \left(V_{\vec{k}}\, e^{-i\vec{k}\cdot\vec{R}_i}\, a^{+}_{i\sigma}\, c_{\vec{k}\sigma} + \text{h.c.} \right) \\ & + \frac{U_{sf}}{N} \sum_{\substack{\vec{k}\,i \\ \sigma\sigma'}} N_{i\sigma}\, C^{+}_{\vec{k}\sigma'}\, c_{\vec{k}'\sigma'}\, e^{i(\vec{k}-\vec{k}')\vec{R}_i} \end{aligned} \qquad (10\text{-}5)$$

can be transformed into an effective s-f Hamiltonian which shows the Fermi-liquid nature of the f electrons. This will enable us to discuss the jutual relations among the models (10-1)-(10-3) and, in particular, the band nature of f electrons.

for $V_{ij} = 0$. It can be calculated going back to the Bloch representation for the conduction electrons which gives

$$P_2HP_1 = \frac{i}{\sqrt{N}} \sum_{\vec{k}i\sigma} \left(\frac{V_{\vec{k}}\, e^{-i\vec{k}\cdot\vec{R}_i}}{\epsilon_f + U - U_{sf} - \epsilon_{\vec{k}}} \; a^+_{i\sigma} N_{i-\sigma} c_{\vec{k}} - h.c. \right) \tag{10-13}$$

In calculating the denominator of (13) we have neglected the contribution of the conduction electron Coulomb scattering (last term of (5) with $\vec{k} \neq \vec{k}'$) to the quasiparticle states. The inclusion of the terms $V_{\vec{k}}$ in (9a), as well as of the Coulomb scattering onto (the quasiparticle states the denominator in (13)) would extend the region of validity of our results and thus make possible a comparison with the renormalization group results [26,27] but this problem will not be discussed any further here.

Taking into account the electrons from the Fermi level only (cf. Schrieffer and Wolff 1966 [114] , Spałek et al 1978ab [44,45]) we get

$$P_2SP_1 = i \sum_{ij\sigma} \left(\frac{V_{ij}}{\epsilon_f + U - U_{sf}} \; a^+_{i\sigma} \; N_{i-\sigma} \; c_{j\sigma} - h.c. \right) \tag{10-14}$$

Then the effective Hamiltonian up to second order is

$$\tilde{H} = \tilde{H}(1) + \tilde{H}(2) + \tilde{H}_{exc} + \tilde{H}_{fl} + \tilde{H}_h \tag{10-15}$$

where

$$\begin{aligned} \tilde{H}(1) = {} & \sum_{ij\sigma}{}' c^+_{i\sigma} \left\{ t_{ij} - \sum_l V_{il} V^*_{ij} \frac{N_{l-\sigma}}{\epsilon_f + U - U_{sf}} \right\} c_{j\sigma} \\ & + \epsilon_f \sum_{i\sigma} N_{i\sigma} \left(1 - N_{i-\sigma}\right) + \sum_{ij\sigma} V_{ij} \left(a^+_{i\sigma} c_{j\sigma} + \right. \\ & \left. + c^+_{j\sigma} a_{i\sigma} \right) \left(1 - N_{i-\sigma}\right) + U_{sf} \sum_{i\sigma\sigma'} n_{i\sigma} N_{i\sigma'} \left(1 - N_{i-\sigma'}\right) \end{aligned} \tag{10-15a}$$

describes the dynamics of the lowest subband P_1 , including hopping within the band and onto singly occupied f level,

$$\begin{aligned} \tilde{H}(2) = {} & \sum_i \Big\{ 2\, \epsilon_f + U + \frac{2}{\epsilon_f + U - U_{sf}} \sum_j \left| V_{ij} \right|^2 \quad N_{i\uparrow} N_{i\downarrow} \\ & + 2U_{sf} \sum_{i\sigma} n_{i\sigma} N_{i\uparrow} N_{i\downarrow} \end{aligned} \tag{10-15b}$$

corresponds to the subspace P_2 of doubly occupied f levels, with a shifted energy,

$$H_{ex} = \frac{2}{\epsilon_f + U - U_{sf}} \sum_{ij} |V_{ij}|^2 \left\{ \vec{S}_i \cdot \vec{s}_j - \frac{1}{4} \sum_{\sigma\sigma'} N_{i\sigma} (1 - N_{i-\sigma}) \, n_{j\sigma'} \right\} \tag{10-15c}$$

contains the s-f (kinetic) exchange and Coulomb interactions between the subsystems of conduction and f electrons,

$$H_{fl} = \frac{1}{\epsilon_f + U - U_{sf}} {\sum_{ijl\sigma}}' V^{*}_{lj} V_{ji} S^{\sigma}_j c^{+}_{l-\sigma} c_{i\sigma} \tag{10-15d}$$

represents spin-flip scattering of conduction electrons on f electrons and

$$\begin{aligned} H_h = &- \frac{1}{\epsilon_f + U - U_{sf}} \sum_{ijl\sigma} V^{*}_{lj} V_{ji} a^{+}_{l\sigma} N_{l-\sigma} a_{i\sigma} N_{i-\sigma} \\ &+ \frac{1}{\epsilon_f + U - U_{sf}} \sum_{ijl\sigma} V^{*}_{lj} V_{ji} a^{+}_{l-\sigma} N_{l-\sigma} a_{i\sigma} N_{i-\sigma} s^{\sigma}_j \end{aligned} \tag{10-15e}$$

reflects the hopping between the doubly occupied f levels on neighbouring atoms, without and with the spin-flip respectively. We have neglected mixing between the subspaces in the second order because it leads to the renormalization of the subbands P_i in the higher orders.

The results obtained may be interpreted as follows. We have assumed that U is large. Hence, the only relevant contributions to (10-15) are given by (10-15a) and (10-15cd). In other words only the subspace of P_1HP_1 is important. This is made out of the conduction band still mixed with the renormalized but atomic f states through the term

$$\sum_{ij\sigma} V_{ij} \left(a^{+}_{i\sigma} c_{j\sigma} + c^{+}_{j\sigma} a_{i\sigma} \right) (1 - N_{i-\sigma}) \tag{10-16}$$

Besides, the subsystems are exchange and Coulomb coupled through (10-15c).

10.2.2. Second transformation: Complete elimination of mixing up to the second order

Let us assume that together with $|\epsilon_f + U - U_{sf} - \epsilon_{\vec{k}}| \gg |V_{ij}|$ we have also $|\epsilon_f - U_{sf} - \epsilon_{\vec{k}}| \gg |V_{ij}|$. Then defining the projection operators

$$P_{0i} = (1 - N_{i\uparrow})(1 - N_{i\downarrow}) \; ; \quad P_{1i} = \sum_{\sigma} N_{i\sigma} (1 - N_{i-\sigma}) \, , \quad \text{and} \quad P_{2i} = N_{i\uparrow} N_{i\downarrow}$$

we can rewrite our Hamiltonian (10-5) as $H = H_o + H_1$, where now

$$H_1 = P_o H P_1 + P_1 H P_o + P_1 H P_2 + P_2 H P_1 \tag{10-17}$$

The term $(P_1HP_2 + P_2HP_1)$ has been removed by the first transformation. Now, we would like to get rid of the term $(P_oHP_1 + P_1HP_o)$ as well. Noting that

$$P_oHP_o = \sum_{ij\sigma}{}' t_{ij} c^+_{i\sigma} c_{j\sigma} \; ; \quad P_1HP_o = \sum_{ij\sigma} V_{ij} a^+_{i\sigma} c_{j\sigma} (1-N_{i-\sigma}) \tag{10-18}$$

and

$$P_1HP_1 = P_oHP_o + \epsilon_f \sum_{i\sigma} N_{i\sigma}(1-N_{i-\sigma}) + U_{sf} \sum_{i\sigma\sigma'} n_{i\sigma} N_{i\sigma'} \tag{10-19}$$

we see that the whole procedure is similar to that from Section 10.2.1, where now

$$P_1SP_o = \frac{1}{\sqrt{N}} \sum_{\vec{k}\; i\sigma} \frac{V_{\vec{k}}\, e^{-i\,\vec{k}\cdot\vec{R}_i}}{\epsilon_f - U_{sf} - \epsilon_{\vec{k}}} \left[a^+_{i\sigma}(1-N_{i-\sigma})\, c_{\vec{k}\sigma} - \text{h.c.} \right]$$

$$\simeq i \sum_{ij\sigma} \frac{V_{ij}}{\epsilon_f - U_{sf}}\, a^+_{i\sigma}(1-N_{i-\sigma})\, c_{j\sigma} - \text{h.c.}] \tag{10-20}$$

Therefore, the effective Hamiltonian up to the second order in V_{ij} is finally

$$\tilde{H} = \tilde{H}(0) + \tilde{H}(1) + \tilde{H}(2) + \tilde{H}_{exc} + \tilde{H}_{fl} + \tilde{H}_h \tag{10-21}$$

where

$$\tilde{H}(0) = \sum_{ij\sigma}{}' a^+_{i\sigma} \left\{ t_{ij} - \sum_{l} V_{il} V^*_{lj} \left[\frac{N_{l-\sigma}}{\epsilon_f + U - U_{sf}} + \frac{1-N_{l-\sigma}}{\epsilon_f - U_{sf}} \right] \right\} a_{j\sigma}$$

$$- \frac{1}{\epsilon_f - U_{sf}} \sum_{ij\sigma} |V_{ij}|^2\, n_{j\sigma} \tag{10-21a}$$

describes the renormalized hopping within the band and the shift of the reference level of the conduction band (can be taken as zero),

$$\tilde{H}(1) = \sum_i \left\{ \epsilon_f + \frac{1}{\epsilon_f + U_{sf}} \sum_j |V_{ij}|^2 \right\} N_{i\sigma}(1-N_{i-\sigma}) \tag{10-21b}$$

is the renormalized position of the atomic (f) level when singly occupied

$$\tilde{H}(2) = \sum_i \left\{ 2\epsilon_f + U + \frac{2}{U + \epsilon_f - U_{sf}} \sum_j |V_{ij}|^2 \; N_{i\uparrow} N_{i\downarrow} \right.$$

$$+ 2U_{sf} \sum_{i\sigma} n_{i\sigma} N_{i\uparrow} N_{i\downarrow} \tag{10-21c}$$

corresponds to effective electron-electron interactions when f level is doubly occupied (can be neglected),

$$H_{exc} = - \frac{2U}{(\epsilon_f - U_{sf})(\epsilon_f - U_{sf} + U)} \sum_{ij} |V_{ij}|^2 \, \vec{S}_i \cdot \vec{s}_j$$

$$+ \left\{ U_{sf} - \frac{U + 2\epsilon_f - 2U_{sf}}{2(\epsilon_f - U_{sf})(\epsilon_f + U - U_{sf})} \right\} \sum_{\substack{ij \\ \sigma\sigma'}} |V_{ij}|^2 \, n_{i\sigma} \, N_{j\sigma'} (1 - N_{j-\sigma}) \qquad \text{10-21d}$$

are the exchange and Coulomb interactions as before,

$$H_{fl} = - \frac{U}{(\epsilon_f - U_{sf})(\epsilon_f + U - U_{sf})} \sum_{ijl\sigma} V^*_{lj} V_{li} \, S^{\sigma}_i \, c^+_{i-\sigma} c_{j\sigma} , \qquad (10\text{-}21e)$$

is the hopping in the conduction band with simultaneous spin flip, and

$$H_h = - \frac{1}{\epsilon_f - U_{sf}} \sum_{ijl\sigma} V^*_{lj} V_{li} \, a^+_{l\sigma} (1 - N_{l-\sigma}) \, a_{i\sigma} (1 - N_{i-\sigma})(1 - n_{j\sigma})$$

$$+ \frac{1}{\epsilon_f - U_{sf}} \sum_{ijl\sigma} V^*_{lj} V_{li} \, a^+_{l-\sigma} (1 - N_{l\sigma}) \, a_{i\sigma} (1 - N_{i-\sigma}) \, s^{\sigma}_j , \qquad (10\text{-}21f)$$

which represents the hopping between the singly occupied neighbouring f orbitals, without and with spin-flip respectively. The first term of (10-21f) changes the atomic levels into a narrow band. Thus, the system is composed of two bands. The hopping between the f electrons is nonzero only if the mixing between the nearest neighbours is not vanishingly small. Hence, the model with intraatomic mixing only (Leder and Mühlschegel 1978 [110], Foglio and Falicow 1979 [115]) does not yield the itinerant f electrons in any order of V_{ii} alone. It can leand only finite f band-width in the third order, involving processes $\sim V_{ii} t_{ij} V_{jj}$. The band-width of the f states is of the same order or less than the effective s-f exchange coupling constant (cf. 21d and (10-21f)) and hence we can regard the f-f magnetic interactions as due to double exchange (Cieplak 1978 [96], Varma 1979 [116]). However, in a true 4f system situation, the double exchange takes place between the localised electrons and is mediated by strongly exchange coupled to them itinerant electrons. Since in all practical cases less than one electron is transferred to the conduction band (Jayaraman 1979 [20]) then (n-1)f electrons present on f shell both in semiconducting and metallic phases form essentially localized moments coupled via Hund´s rule exchange with the f electrons which are delocalized in IV state. Then, the double exchange will be operative if only the Hund´s rule intraatomic exchange J exceeds the f bandwidth. The double exchange competes with the Kondo effects caused by the kinetic exchange (10-21d).

When

$$J < \frac{2U}{(\epsilon_f - U_{sf})\,(\epsilon_f - U_{sf} + U)}$$

then the system may condense into the Kondo lattice, while in the opposite limit the transition into the ferromagnetic IV state may occur (provided the concentration of itinerant f electrons is large enough so the double exchange can dominate the antiferromagnetic kinetic and indirect exchange interactions).

The hopping term (10-21f) may be calculated in the Bloch representation

$$H_h = -\frac{1}{\epsilon_f - U_{sf}}\,\frac{1}{N}\sum_{ij\vec{k}\sigma} |V_{\vec{k}}|^2\, e^{i\vec{k}(\vec{R}_i-\vec{R}_j)}\, a^+_{i\sigma}\,(1-N_{i-\sigma})\,a_{j\sigma}\,(1-N_{j-\sigma})\,(1-n_{\vec{k}\sigma}) - a^+_{i-\sigma}\,(1-N_{i\sigma})\,a_{j\sigma}\,(1-N_{j-\sigma})\,s^{\sigma}_{\vec{k}} \tag{10-22}$$

which means that the hopping without spin-flip between the neighbouring f states is nonzero only at the Fermi level. Two kinds of electrons are present in the system: ordinary carriers and the extremely narrow band composed of the lattice of resonant states located at E_F (Kaplan et al 1978, in particular the remark by P.W.Anderson during the discussion).

Summarizing, the simplest nontrivial model which in the limits $U > W > U_{sf} \gg |V_{ij}|$ and $U_{sf} + \epsilon_f \gg |V_{ij}|$ represents the same properties as the periodic Anderson model (5), is of the form

$$\tilde{H} = \sum_{\vec{k}\sigma} \epsilon_{\vec{k}}\, n_{\vec{k}\sigma} + \tilde{\epsilon}_f \sum_{i\sigma} N_{i\sigma}\,(1-N_{i-\sigma}) + N^{-1}\sum_{\substack{i\vec{k}\vec{k}\\ \sigma\sigma'}} J(\vec{k},\vec{k}')\,(\vec{S}_i\cdot\vec{\tau})_{\sigma\sigma'}\, c^+_{\vec{k}\sigma}\, c_{\vec{k}'\sigma'}\, e^{i(\vec{k}-\vec{k})\vec{R}_i} + N^{-1}\sum_{\substack{i\vec{k}\vec{k}\\ \sigma\sigma'}} K(\vec{k},\vec{k}')\, N_{i\sigma}\,(1-N_{i-\sigma})\, c^+_{\vec{k}\sigma}\, c_{\vec{k}'\sigma'}\, e^{i(\vec{k}-\vec{k}')\vec{R}_i} - \frac{1}{\epsilon_f - U_{sf}}\, N^{-1} \sum_{ij\vec{k}\sigma} |V_k|^2\, e^{i\vec{k}(\vec{R}_i-\vec{R}_j)}\, a^+_{i\sigma}\,(1-N_{i-\sigma})\,a_{j\sigma}\,(1-N_{j-\sigma})\,(1-n_{\vec{k}\sigma}) \tag{10-23}$$

with

$$\tilde{\epsilon}_f = \epsilon_f + \frac{1}{\epsilon_f - U_{sf}} \sum_{j(i)} |V_{ij}|^2 \tag{10-23a}$$

$$J(\vec{k},\vec{k}') = -\frac{U}{(\epsilon_f - U_{sf})\,(\epsilon_f - U_{sf} + U)}\, V_{\vec{k}}\, V_{\vec{k}'} \tag{10-23b}$$

and

$$K(\vec{k}, \vec{k}') = U_{sf} - \frac{U+2\,\epsilon_f - 2U_{sf}}{2\,(\epsilon_f - U_{sf})\,(\epsilon_f + U - U_{sf})} \qquad (10\text{-}23c)$$

Thus, neglecting the $\vec{k}$ dependence and J and K, our model in the nonmagnetic phase is a generalized version of the Falicov-Kimball (1969) [32] mo del. Additionally, (23) reduces to the Kondo lattice Hamiltonian (10-3) exactly if the number of f electrons on each site is conserved, i.e. $N_{i\uparrow} + N_{i\downarrow} = 1$. Therefore, the Kondo lattice Hamiltonian (10-3) is rather inappropriate as a starting model Hamiltonian of discussing the intermediate-valence phase.

Beside that, our canonical transformation introduces two new ingredients to current models of mixed valence. Firstly, the atomic characteristic of the bare Hamiltonian (10-5) are renormalized by the virtual hopping processes (cf. Eq. 10-23a). Secondly, what is more important, the f electrons form a narrow band (true lattice of resonant state). The hopping integral for this band is of the order

$$t_{ij} = \frac{1}{N} \sum_{\vec{k}} \frac{|V_{\vec{k}}|^2}{\epsilon_f - \epsilon_{\vec{k}} - U_{sf}} \left(1 - \langle n_{\vec{k}\sigma} \rangle\right) \; e^{i\,\vec{k}(\vec{R}_j - \vec{R}_i)} \qquad (10\text{-}24)$$

which is nonzero only near the Fermi surface. At $T=0$ $\langle n_{\vec{k}\sigma} \rangle =$ $= \Theta\,(k_f - k)$ and f electrons may be still regarder as atomic.

The hopping (10-24) gives the bandwidth of f states not larger than the value of the s-f exchange constant (cf. 10-23b). Therefore, it yields the contribution to the double exchange if more than one f electrons are present (cf. Cieplak 1978 [96]). The value of exchange constant is

$$b = \sum_{j(i)\sigma} t_{ij\sigma}\, n_f\,(1-n_f) \quad .$$

Part IV

THE EXTENDED s-d MODEL

Influence of localised moments onto single-particle states and magnetic interactions

11. Old versus New Problems in the s-d Model

In the last two sections we have shown how to decompose an itinerant system into localised moments and carriers coupled to them through the s-d exchange interaction. In the next Sections we show how to extract from it physically relevant information concerning itinerant magnetism: quasiparticle states $E_{k\sigma}$, the Stoner splitting Δ, and for an intermediate-valence phase, a degree of mixing for the ground state.

In this Section we characterize rather briefly the major problems which are studied within the model. They correspond to three physical situations, namely:

1° d or f electrons are well localised in the magnetically ordered phase. The conduction electrons are of a different type (s or s-d) and their bandwidth does not exceed the magnitude ϵ_f+U where ϵ_f is the position of d (or f) atomic level and U the magnitude of intraatomic f-f (d-d) Coulomb interaction on them. To avoid the direct influence of the s-d or s-f hybridisation it is assumed that ϵ_f lies deeply below the Fermi level $E_F = \mu$.

2° The f-electrons atomic level is close to the Fermi level but the correlations on f level are strong anough, so the hybridised model Hamiltonian can be still transformed into the s-d model (for example see Sect.10 and Refs. [26,27]).

3° The electrons in a degenerate (or not [11-14]) band are strongly correlated and we have more than one electron per atom (cf. Sect.9). The residual itinerant electrons are then strongly correlated and ultimately form a magnetic Fermi liquid.

The situation 1° describes the magnetism of the heavy rare-earth metals (cf. Sinha 1979 [117]) basing on the indirect (RKKY) type of exchange. Such an analysis is possible if the s-d exchange constant J is much smaller than the carriers bandwidth W.

The situation 2^o bears its origin from the paper of Schrieffer and Wolff (1966) [33] who transformed the Anderson (1961) model of magnetic impurity [24] into the Kondo Hamiltonian, i.e. the s-d Hamiltonian for single magnetic impurity in a simple metal, and with the antiferromagnetic s-d coupling. The simplest generalization of the Kondo problem is the Kondo lattice, i.e. a lattice of localised spins coupled antiferromagnetically to free electrons [112,113]. The realistic solution of the Kondo lattice Hamiltonian (10-3) is not available as yet as well as its relation to the intermediate-valence phenomenon.

The situation 3^o is regarded as the one reflecting an itinerant magnet with both the Hund´s rule and the minimum polarity principle fulfilled. In the asymptotic regime $J > W$ it yield the double exchange between the localised moments (Anderson and Hasegawa 1955 [118], De Gennes 1961 [119], Cieplak 1978 [96]).

The special class of materials form magnetic semiconductors in which magnetic 4f or 3d electrons are well localised but can be thermally excited to conduction band (e.g. EuO:Eu, and HgTe:Mn). A simple model for such materials together with an application to EuO:Eu has been given by Spałek et al 1977 [54] and by Spałek and Tarnawski 1979 [55]. We refer the reader to Supplements H and I respectively, where the details of this work have been reproduced.* Here we present only some new results focusing mainly on a role of itinerant electrons in case 3^o and, on the role of s-d interaction in formation of a magnetic phase of a system with the non-integral valence (case 2^o).

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* In Supplement J we have presented some results concerning the polaronic effects for the case of a shallow donor level.

12. The Zener-Vonsovskii Model: U>W≫J

Let us start from the effective Hamiltonian (9-7) representing the transformed degenerate narrow-band model

$$H = \sum_{ij\sigma}{}' t_{ij}\, a^{+}_{i\sigma}\, a_{j\sigma}\, (1-n_{i-\sigma})(1-n_{j-\sigma}) - 2J \sum_{i} \vec{S}_i \cdot \vec{s}_i + H_{ex} \left\{ \vec{S}_i + \vec{s}_i \right\} \qquad (12\text{-}1)$$

We group together the residual hopping, the s-d term and the part of the kinetic exchange representing itinerant electrons

$$H_1 = \sum_{ij\sigma} t_{ij}\, a^{+}_{i\sigma}\, a_{j\sigma}\, (1-n_{i-\sigma})(1-n_{j-\sigma}) - 2J \sum_{i} \vec{S}_i \cdot \vec{s}_i + \sum_{ij}{}' \frac{2t_{ij}^{2}}{U} \left[\vec{s}_i \cdot \vec{s}_j - \frac{1}{4} \sum_{\sigma\sigma'} n_i\, (1-n_{i-\sigma'})\, n_{j\sigma'}\, (1-n_{j-\sigma'}) \right. \qquad (12\text{-}2)$$

The first term can be regarded as the Hubbard model at $U = \infty$ [86, 85,82] . It has a ferromagnetic solution in a wide concentration range even if (the kinetic exchange (the last term in (12-2) is included (cf. Sect. 5.3) . We rewrite down (12-2) in the diagonal form with respect to correlations

$$H_1 = \sum_{\vec{k}\sigma} E_{\vec{k}\sigma}\, \tilde{n}_{\vec{k}\sigma} - 2J \sum_{i} \vec{S}_i \cdot \vec{s}_i \qquad (12\text{-}3)$$

where (cf. Eqs. (5.3-9)-(5.3-11)) , $\tilde{n}_{\vec{k}\sigma} = b^{+}_{\vec{k}\sigma}\, b_{\vec{k}\sigma}$,

$$E_{\vec{k}\sigma} = (1-n_{-\sigma} + W_{2\sigma})\, \epsilon_k + ztW_{1-\sigma} \qquad (12\text{-}4)$$

and $n_\sigma = (1-n_{-\sigma})\, N^{-1} \sum_{\vec{k}} f(E_{\vec{k}\sigma})$ with $f(E_{\vec{k}\sigma})$ being the Fermi-Dirac distribution.

Next, we transform spins $\vec{s}_i$ in the s-d term to the Bloch representation

$$-J \sum_i \vec{S}_i \cdot \vec{s}_i = -\frac{J}{N} \sum_{\substack{i\,\vec{k}\,\vec{k}' \\ \sigma\,\sigma'}} (\vec{S}_i \cdot \vec{\tau})_{\sigma\sigma'} \, a^+_{\vec{k}\sigma} \, a_{\vec{k}'\sigma'} \exp\left[i\,(\vec{k}-\vec{k}')\, R_i \right],$$

and divide it into two parts: the diagonal H_d containing the terms with $\vec{k} = \vec{k}'$ only, and the nondiagonal H_{nd} containing all others, with $\vec{k} \neq \vec{k}'$. Since we are interested in the quasiparticle states only we remove the part H_{nd} containing scattering processes $\vec{k} \to \vec{k}' \neq \vec{k}$ and replace it by terms with the virtual transitions $\vec{k} \to \vec{k}'$, $\vec{k}'' = \vec{k}$ in the second order.[*] This can be done with the help of transformation presented in Sect. 5.2 provided the eigenvalues $\lambda_{\alpha\vec{k}\sigma}$, eigenstates $|\lambda_{\alpha\vec{k}\sigma}\rangle$, and the corresponding projection operators

$P_{\alpha\vec{k}\sigma} = |\lambda_{\alpha\vec{k}\sigma}\rangle \langle \lambda_{\alpha\vec{k}\sigma}|$ of the Hamiltonian

$$H_o = \sum_{\vec{k}\sigma} E_{\vec{k}\sigma} \tilde{n}_{\vec{k}\sigma} + H_d \tag{12-5}$$

are given.

12.1. Diagonal part of s-d model

To diagonalise (12-5) we proceed as follows. We consider only singly occupied states $|E_{\vec{k}\sigma}\rangle$. Therefore we can replace $\tilde{n}_{\vec{k}\sigma}$ by $n_{\vec{k}\sigma} = a^+_{\vec{k}\sigma} a_{\vec{k}\sigma}$ and rewrite H_o as

$$H_o = N^{-1} \sum_{\vec{k},i} H_{\vec{k}i}$$

where the summations over $\vec{k}$ and i are over quasiparticle (itinerant) and atomic ($\vec{S}_i$) states, respectively. Because $\left[H_{\vec{k},n}, \; H_{\vec{k}'n'} \right] = 0$ we have

$$\left[H_{\vec{k}n}, \; H_o \right] = 0$$

and thus diagonalizing $H_{\vec{k}n}$ we get the eigenvalues of H_o. The lowest eigenvalues of $H_{\vec{k}n}$ are

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[*] Strictly speaking, such an approach gives meaningful results only for $|J| \ll E_F$.

$$\begin{cases} \lambda_{1\vec{k}\uparrow} = E_{\vec{k}\uparrow} - JS \,, \\ \lambda_{\substack{2\\3}\vec{k}\downarrow} = \frac{1}{2}\left(E_{\vec{k}\downarrow} + E_{\vec{k}\uparrow} + J\right) \pm \frac{1}{2}\left\{\left[E_{\vec{k}\downarrow} - E_{\vec{k}\uparrow} + J\left(2S-1\right)\right]^2 + 8J^2S^2\right\} \\ \lambda_{4\vec{k}} = E_{\vec{k}\uparrow} - J\left(S-1\right) \,, \quad \text{etc.} \,, \end{cases} \tag{12-6}$$

while the corresponding eigenstates of $H_{\vec{k}n}$

$$\begin{cases} \left|\lambda^{(n)}_{1\vec{k}\uparrow}\right\rangle = a^+_{\vec{k}\uparrow}\left|0\right\rangle \,, \\ \left|\lambda^{(n)}_{\substack{2\\3}\vec{k}\downarrow}\right\rangle = \cos\theta_{2,3}\, a^+_{\vec{k}\downarrow}\left|0\right\rangle + \frac{\sin\theta_{2,3}}{\left(2S\right)^{1/2}}\, a^+_{\vec{k}\uparrow} S^-_n \left|0\right\rangle \\ \left|^{(n)}_{4\vec{k}\downarrow}\right\rangle = \left(2S\right)^{-1/2} a^+_{\vec{k}\downarrow} S^-_n \left|0\right\rangle \,, \quad \text{etc.,} \end{cases} \tag{12-7}$$

where the reference state $\left|0\right\rangle = \left|S^z_n = S,\ 0_{\vec{k}}\right\rangle$, and

$$\tan\theta_{2,3} = \left\{\frac{E_{\vec{k}\downarrow} + JS - \lambda_{2,3\,\vec{k}}}{E_{\vec{k}\uparrow} - J\left(S-1\right) - \lambda_{2,3\,\vec{k}}}\right\}^{1/2} \tag{12-8}$$

For $S = \frac{1}{2}$ the sets (12-6) and (12-7) are complete. Otherwise, the are the characteristics of the states with given $\vec{k}$ and $S_n{}^z = S$ or $\left(S-1\right)$. For the particular case of the s-d model $\left(U=0\right)$ $E_{\vec{k}\sigma} = \epsilon_{\vec{k}}$, and

$$\begin{aligned} \lambda_{1\vec{k}\uparrow} &= \lambda_{2\vec{k}\uparrow} = \epsilon_{\vec{k}} - JS \\ \lambda_{3\vec{k}\downarrow} &= \epsilon_{\vec{k}} + J\left(S+1\right) \\ \lambda_{4\vec{k}\downarrow} &= \epsilon_{\vec{k}} + J\left(S-1\right) \end{aligned} \tag{12-9}$$

which is the standard result in the first order. Beside that Eqs. (12-7) and (12-8) combined together supply an attractive interpretation of the carrier's states. Namely, the Hamiltonian H_o can be written as

$$H_o = \sum_{\mu k\sigma} \lambda_{\mu\vec{k}\sigma}\, P_{\mu\vec{k}\sigma} \tag{12-10}$$

with

$$P_{\mu k\sigma} = \frac{1}{N}\sum_n \left|\lambda_{\mu\vec{k}\sigma}\right\rangle\left\langle\lambda_{\mu\vec{k}\sigma}\right| \tag{12-11}$$

is composed of $2(2S+1)$ subbands labelled by μ and, even when the conduction band is uncorrelated $(U=0)$, the transition $|\lambda_{1\vec{k}\uparrow}\rangle \rightarrow |\lambda_{2\vec{k}\uparrow}\rangle$ corresponding to spin-flip of the conduction electron has a gap $\Delta = J(2S+1)$. In the case of a correlated magnet $(U\neq 0)$ $\Delta = \lambda_{2\vec{k}\uparrow} - \lambda_{1\vec{k}\uparrow}$ and the transition provides the Stoner splitting for wavevector $\vec{k}$. Its value $\Delta = J(2S+1)$ in the paramagnetic phase is nonzero (even in the paramagnetic phase!) i.e. for $E_{\vec{k}\uparrow} = E_{\vec{k}\downarrow}$. This is due to the fact that the spin-flip state $a^+_{\vec{k}\downarrow}|0\rangle$ of the carrier is coherently mixed with the state $\sum_n \alpha_n S_n^- a^+_{\vec{k}\uparrow}|0\rangle$, which is the state non-magnon with wavevector $\vec{k}_m = 0$ in the subsystem of localised moments.* The temperature dependent part of the Stoner splitting is given by the difference $E_{\vec{k}\uparrow} - E_{\vec{k}\downarrow}$. The eigenvalues $\lambda_{\mu\vec{k}\sigma}$ the many-body nature of the ground state of H_o. This can be easily seen if we rewrite H_o in the form

$$H_o = \sum_{\vec{k}\sigma}\Big(E_{\vec{k}\sigma} - JN^{-1}\sum_n S_n^z\sigma\Big)\, n_{\vec{k}\sigma} - JN^{-1}\sum_{\vec{k}\sigma} a^+_{\vec{k}\sigma} a_{\vec{k}-\sigma}\sum_n S_n^{-\sigma} \qquad (12\text{-}12)$$

and thus only the magnons with $\vec{k}_m = 0$ influence the dynamics of the itinerant electrons. If we replace in the brackett $N^{-1}\sum_n S_n^z$ by the thermodynamical average $\langle S^z\rangle$ and neglect the last term then (12-12) gives the Stoner-Wohlfarth or the Hartree-Fock model. However, such an approximation in unjustified because the total magnetic moment within the subsystems is not conserved and the quantum fluctuations in the state $a^+_{\vec{k}\downarrow}|0\rangle$ produce coupling to the state $\frac{1}{N}\sum_n S_n^- a^+_{k\uparrow}|0\rangle$ with unit change of spin quantum number in both subsystems. The conserved quantity is the total spin

$$\sum_n(\vec{S}_n + \vec{s}_n)$$

and the ground state is with total spin either $NS + N_e/2$ or $NS - N_e/2$. The former corresponds to $J>0$ (ferromagnetic s-d exchange), while the latter to $J<0$ (antiferromagnetic s-d exchange). For number of carriers $N_e = N$ we have either totally aligned ground state or the

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* The coherent mixture of the states considered here bears a close resemblance to the zero-point motion in antiferromagnet.

Kondo lattice, i.e. the state with total spin $S_t = 0$.

12.2. Indirect exchange

The nondiagonal part H_{nd} influences both the quasiparticles states and the magnetic interactions in higher orders. Applying the canonical transformation of the type derived in Sect. 5.3 for the nondiagonal part we obtain in the second order

$$H^{(2)} = \sum_{\mu,\mu'} \frac{P_\mu H_{nd} P_{\mu'} H_{nd} P_\mu}{E_\mu - E_{\mu'}}$$

which in our case is

$$H^{2} = \sum_{\vec{k} \neq \vec{k}'} \sum_{\substack{\mu\mu' \\ \mu_1\mu_1'}} \sum_{\substack{\sigma\sigma' \\ \sigma_1\sigma_1'}} \frac{P_{u\vec{k}\sigma} (H_{nd})^{\vec{k}\vec{k}'}_{\sigma\sigma'} P_{\mu'\vec{k}'} \; P_{\mu_1\vec{k}'\sigma_1} (H_{nd})^{\vec{k}'\vec{k}}_{\sigma_1'\sigma_1} P_{\mu_1\vec{k}\sigma_1}}{\lambda_{\mu\vec{k}\sigma} - \lambda_{\mu'\vec{k}'\sigma'}} \tag{12-13}$$

where

$$H_{nd} = \sum_{\vec{k} \neq \vec{k}'} \sum_{\sigma\sigma'} (H_{nd})^{\vec{k}\vec{k}'}_{\sigma\sigma'} \tag{12-14}$$

We are interested in the second order contribution. Hence, we put $\lambda_1 = \lambda_3 = E_{\vec{k}\uparrow}$, and $\lambda_2 = \lambda_4 = E_{\vec{k}\uparrow}$, and (in $|\lambda_{2,3\vec{k}\downarrow}|$)$\cos\theta_{2,3} = 0$ and 1 respectively. The effective Hamiltonian of the whole system becomes

$$\tilde{H} = \sum_{\mu\vec{k}\sigma} \lambda_{\mu\vec{k}\sigma} P_{\mu\vec{k}\sigma} + H^{(2)} \tag{12-15}$$

with

$$H^{(2)} = -\left(\frac{J}{N}\right)^2 \sum_{n,m\sigma} \sum_{\vec{k}} \sum_{\vec{q}\neq 0} \exp(i\vec{q}\cdot\vec{R}_{mn}) \times$$

$$\left\{ \frac{\tilde{n}_{\vec{k}\sigma}(1-\tilde{n}_{\vec{k}+\vec{q}\sigma})}{E_{\vec{k}\sigma} - E_{\vec{k}+\vec{q}\sigma}} S^z_m S^z_n + \frac{\tilde{n}_{\vec{k}\sigma}(1-\tilde{n}_{\vec{k}+\vec{q}-\sigma})}{E_{\vec{k}\sigma} - E_{\vec{k}+\vec{q}-\sigma}} S^\sigma_m S^{-\sigma}_n \right\} \tag{12-16}$$

This expression reduced to the ordinary RKKY interaction (Ruderman and Kittel 1954 [120] , Kasuya 1956 [121] , Yosida 1957 [122] , Van Vleck 1962 [123]) in case U=0 , i.e. $E_{\vec{k}\sigma} = \varepsilon_{\vec{k}}$ and if we average over carriers' degrees of freedom. To order $\sim J^2$ we can assume that

$$\tilde{n}_{\vec{k}\sigma}\left(1-\tilde{n}_{\vec{k}+\vec{q}\sigma}\right) S_m^z\, S_n^z \simeq \left\langle \tilde{n}_{\vec{k}\sigma}\left(1-\tilde{n}_{\vec{k}+\vec{q}\sigma}\right)\right\rangle S_m^z\, S_n^z$$

$$+\, \tilde{n}_{\vec{k}\sigma}\left(1-\tilde{n}_{\vec{k}+\vec{q}\sigma}\right) \left\langle S_m^z\, S_n^z\right\rangle - \left\langle \tilde{n}_{\vec{k}\sigma}\left(1-\tilde{n}_{\vec{k}+\vec{q}\sigma}\right)\right\rangle \left\langle S_m^z\, S_n^z\right\rangle \tag{12-17}$$

Decoupling analogously the term

$\tilde{n}_{\vec{k}\sigma}\left(1-\tilde{n}_{\vec{k}+\vec{q}-\sigma}\right) S_m^{\sigma}\, S_n^{-\sigma}$ we get finally

$$\tilde{H} = \sum_{\mu\vec{k}\sigma} \lambda_{\mu\vec{k}\sigma}\, P_{\mu\vec{k}\sigma} + H_i^{(2)} + H_l^{(2)} + H_{ex}\left\{\vec{S}_i\right\} \tag{12-18}$$

The localised part

$$H_l^{(2)} = \sum_{\vec{q}\neq 0} \sum_{\alpha=1}^{3} J^{\alpha}(\vec{q})\, S_{\vec{q}}^{\alpha}\, \left(S_{\vec{q}}^{\alpha}\right)^{+} \tag{12-19}$$

in an anisotropic $(\alpha = z, \pm)$ indirect exchange, with

$$J^{\alpha}(\vec{q}) = -\left(\frac{J}{N}\right)^2 \sum_{\vec{k}\sigma} \left\{ \delta_{\alpha z}\, \frac{\left\langle \tilde{n}_{\vec{k}\sigma}\left(1-\tilde{n}_{\vec{k}+\vec{q}\sigma}\right)\right\rangle}{E_{\vec{k}\sigma} - E_{\vec{k}+\vec{q}\sigma}} \right.$$

$$\left. +\, \delta_{\alpha\sigma}\, \frac{\left\langle n_{\vec{k}\sigma}\left(1-n_{\vec{k}+\vec{q}-\sigma}\right)\right\rangle}{E_{\vec{k}\sigma} - E_{\vec{k}+\vec{q}-\sigma}} \right. \tag{12-20}$$

The itinerant part

$$H_i^{(2)} = \sum_{\vec{k}\sigma} E_{\vec{k}\sigma}^{(2)}\, \tilde{n}_{\vec{k}\sigma} + \sum_{\vec{k}} \sum_{\vec{q}\neq 0} f_{\vec{k}\vec{q}}^{\sigma\sigma'}\, \tilde{n}_{\vec{k}\sigma}\, \tilde{n}_{\vec{k}+\vec{q}\sigma} \tag{12-21}$$

gives a contribution to the quasiparticle states (first term) and the Landau interactions introduced in his theory of the Fermi liquid (Landau 1956 [124]), where

$$f_{\vec{k}\vec{q}}^{\sigma\sigma'} = \left(\frac{J}{N}\right)^2 \frac{\left\langle S_{\vec{q}}^{\sigma}\, S_{-\vec{q}}^{-\sigma}\right\rangle \delta_{\sigma' -\sigma} + \left\langle S_{\vec{q}}^{z}\, S_{-\vec{q}}^{z}\right\rangle \delta_{\sigma\sigma'}}{E_{\vec{k}} - E_{\vec{k}+\vec{q}\sigma'}}, \tag{12-22}$$

and

$$E_{\vec{k}}^{(2)} = \sum_{\vec{q}\neq 0} f_{\vec{k}\vec{q}}^{\sigma\sigma}$$

Our effective Hamiltonian (12-18) contains the anisotropic RKKY-type and kinetic exchange interactions among the localised spins, as well as the Landau Fermi liquid picture for itinerant electrons. The Fermi liquid is ferromagnetic with the coupling parameters $f^{\sigma\sigma'}_{\vec{k}\vec{q}}$ which depend on spin correlation functions. Conversely, the exchange constant $J^{\alpha}(\vec{q})$ depends on the distribution of carriers through the averages $\langle \tilde{n}_{\vec{k}\sigma} \rangle = (1-n_{-\sigma}) f(E_{\vec{k}\sigma})$. Hence, the Zener-Vonsovskii model is more complicated than both the RKKY and the Fermi liquid theories. Except, the function $f^{\sigma\sigma'}_{\vec{k},\vec{q}}$ is given explicitly, and thus solving the problem, a number of the phenomenological Fermi liquid parameters need not to be introduced. We would like to emphasize once more again that our result (12-18), which is a transformed version of the Zener-Vonsovskii model (12-1), is obtained under the assumption we know the quasiparticle energies $E_{\vec{k}\sigma}$ of the Hubbard Hamiltonian. This is because we transform (2.1) in two steps. Firstly, the itinerant part is written as a quasiparticle Hamiltonian, and then the s-d model projected onto the subspace of singly occupied sites.

There are two well-known results which are reproduced also correctly. Namely, for uncorrelated conduction band electrons (i.e. U=0) interactions between the localised spins are ordinary RKKY interaction, and in the second order the contribution to the quasiparticle states given by spin-spin correlation function (Rys et al 1967 [125]). However, there is one principal difference with respect to the perturbation theory. The Hamiltonian H_o composed of kinetic energy $\sum_{\vec{k}\sigma} \epsilon_{\vec{k}} n_{\vec{k}\sigma}$ and of the diagonal part H_d gives rise to the eigenstates (12-6) which differ remarkably from the spin-split subband picture $\lambda_{1\vec{k}\sigma} = \epsilon_{\vec{k}} - J\langle S^z \rangle \sigma$ [121,125]. This effect can give rise to the partial polarisation of the carriers even at T=0, but this problem which has a direct relation to the photoemission results, will be discussed in detail separately (cf. discussion of recent results given by Nolting 1979 [126]).

The final remark concerns the universality of our results. Since it it possible to represent the itinerant part through the quasiparticle Hamiltonian for any U we can say that results obtained in this Section hold for an arbitrary U if only $J \ll W$.

Of course, our results need further analysis to estimate relative contributions of kinetic and direct exchange to the value of the Curie temperature T_c for an itinerant magnet. But, even without a detailed analysis we can draw a conclusion that there is no direct relation between the values of the Stoner splitting Δ and T_c. If indirect exchange dominates the kinetic exchange than $\Delta \gg T_c$, since, as we have shown, $\Delta \sim J$, while the indirect exchange gives $k_B T_c \sim J^2/E_F$, where E_F is the Fermi energy. This is in agreement with what is observed for 3d metals Fe, Co and Ni [1].

13. The Zener-Vonsovskii Model: U > J > W

Now we would like to turn over to the double-exchange limit. The natural starting point of analysis in this limit is the diagonalization of the s-d part in the atomic limit $(W=0)$. Then the only important atomic states are those with one itinerant electron per site. The corresponding eigenvalues are

$$\lambda_{1,2} = -JS, \quad \lambda_3 = J(S+1), \quad \lambda_4 = -J(S-1), \quad \text{etc.} \tag{13-1}$$

while the corresponding eigenvalues

$$|\lambda_1^{(i)}\rangle = a^+_{i\uparrow} \, |0\rangle \quad , \tag{13-2}$$

$$|\lambda_2^{(i)}\rangle = (2S+1)^{-1/2} \left(a^+_{i\downarrow} - S^-_i \, a^+_{i\uparrow}\right) \quad |0\rangle \quad , \tag{13-3}$$

$$|\lambda_3^{(i)}\rangle = \left[2S/(2S+1)\right]^{1/2} \left(a^+_{i\downarrow} + S^-_i \, a^+_{i\uparrow} \,/\, \sqrt{2S}\right) \, |0\rangle \tag{13-4}$$

$$|\lambda_4^{(i)}\rangle = a^+_{i\downarrow} \; S^-_i \,/\, \sqrt{2S} \; |0\rangle \qquad \text{etc.} \tag{13-5}$$

Therefore we get result (12-6) for $E_{\vec{k}\sigma} = 0$, and the atomic ground state is a coherent mixture of $|\lambda_4^{(i)}\rangle$ and $|\lambda_2^{\,i}\rangle$.

We introduce also the projection operators $P_{ni} = |\lambda_n^{(i)}\rangle \langle\lambda_n^{(i)}|$. Their explicit form is

$$P_{1i} = n_{i\uparrow} \left(1-n_{i\downarrow}\right) \; |S_i^{\,z} = S\rangle \langle S_i^{\,z} = S| \tag{13-6}$$

$$P_{2i} = \frac{1}{2S+1}\Big\{\Big[\vec{S}_i \cdot \vec{s}_i + 2S_i^z\, s_i^z + n_{i\downarrow}\,(1-n_{i\uparrow})\Big]\,|S_i^z = S\rangle\langle S_i^z = S|$$

$$+\, n_{i\uparrow}\,(1-n_{i\downarrow})\; S_i^-\,|S_i^z = S\rangle\langle S_i^z = S|\, S_i^+ \tag{13-7}$$

$$P_{3i} = \frac{2S}{2S+1}\Big\{\Big[\frac{1}{S}\big(\vec{S}_i \cdot \vec{s}_i - S_i^z\, s_i^z\big) + n_{i\downarrow}\,(1-n_{i\uparrow})\Big]|S_i^z = S\rangle\,\langle S_i^z = S|$$

$$+\, \frac{1}{2S}\; n_{i\uparrow}\,(1-n_{i\downarrow})\; S_i^-\,|S_i^z = S\rangle\langle S_i^z = S|\, S_i^+ \tag{13-8}$$

$$P_{4i} = n_{i\downarrow}\,(1-n_{i\uparrow})\,|S_i^z = S-1\rangle\,\langle S_i^z = S-1| \quad , \qquad \text{etc.} \tag{13-9}$$

The eigenstate $|\lambda_4\rangle$ is only approximate since for $S > \frac{1}{2}$ it should contain also a term $a_i^+\,(S_i^-)^2|\,S_i^z = S\rangle$. It is easy to correct it but we will not consider it here since it does not influence our conclusions.

The lowest manifold is characterized by the projector $P_i = P_{1i} + P_{2i}$. Since the distance on energy scale between this manifold and the next one exceeds bandwidth W we have to project hopping onto the lowest physically accessible manifold. This means that the restricted hopping term plays the role of the effective Hamiltonian of the system

$$\tilde{H} = {\sum_{ij\sigma\sigma'}}' \; t_{ij}\; a_{i\sigma}^+\,(1-n_{i-\sigma})(\tilde{P}_i\tilde{P}_j)_{\sigma\sigma'}\; a_{j\sigma'}\,(1-n_{j-\sigma'}) + \sum_{i\mu} \lambda_\mu^{(i)}\; P_{i\mu} \tag{13-10}$$

In case we include in $P_{1i} + P_{2i}$ only * the states with $|S_i^z = S\rangle$ we have (Kubo and Ohata 1972 [127])

$$\tilde{P}_i\,\tilde{P}_j = \frac{1}{(2S+1)^2}\Big[\vec{S}_i \cdot \vec{S}_j\,\delta_{\sigma\sigma'} + (\vec{S}_i + \vec{S}_j)\vec{\tau}\;\; S+1 + i(\vec{S}_i \wedge \vec{S}_j)\vec{\tau}$$

$$+\, (S+1)^2\Big] \tag{13-11}$$

and

$$\tilde{P}_i = \frac{1}{2S+1}\Big[\vec{S}_i \cdot \vec{\tau} + (S+1)\,\delta_{\sigma\sigma'}\Big] \tag{13-12}$$

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* For temperature $k_BT \ll W$. We also neglect the virtual hopping processes with formation of the singlet intermediate state c.f. kinetic exchange Hamiltonian in Sect. 7 and 9.

where $\vec{\tau}=(\tau^x, \tau^y, \tau^z)$ are Pauli matrices $(\tau^\alpha)_{\sigma\sigma'}$.

For spin $S = \frac{1}{2}$ the projector (13-12) is exact. Taking as a reference level $(t_{ii} - JS/2)$ we reduce (13-10) to

$$\tilde{H} = \sum_{ij\sigma\sigma'}' t_{ij}\, a^+_{i\sigma}(1-n_{i-\sigma})(\tilde{P}_i \tilde{P}_j)_{\sigma\sigma'}\, a_{j\sigma'}(1-n_{j-\sigma'}) \qquad (13\text{-}13)$$

Therefore, the double exchange may be viewed as a band narrowing process for the itinerant electrons. For $S=0$ we recover the Hubbard model for $U = \infty$ (cf. Sect. 5). In general, (13-13) should be supplemented with the kinetic exchange part as it is shown in Sect. 9. Thus, the total double exchange Hamiltonian $W < J$ for doubly degenerate band with $n > 1$ or s-d system with localised spin $S = \frac{1}{2}$ is

$$H = \sum_{ij\sigma\sigma'}' t_{ij}\, a^+_{i\sigma}(1-n_{i-\sigma})(\tilde{P}_i \tilde{P}_j)_{\sigma\sigma'}\, a_{j\sigma'}(1-n_{j-\sigma'}) + H_{ex}\{\vec{S}_i + \vec{s}_i\} \qquad (13\text{-}14)$$

where H_{ex} is given by Eqn.(9-8). We would like to emphasize that our Hamiltonian (13-14) preserves the quantum nature of both carriers and localised spins. Hence, it can be regarded as a microscopic version of the treatment of Cieplak (1978)[96] and Karpenko (1976) [128] who where interested in the intersite coupling among the localised spins only. However, if we are interested in the carrier states and in particular, whether spin-split quasiparticle picture for carriers is correct, then we have to consider full form (13-14).

This and connected problems will be considered separately and the results published shortly.

14. s-d Model of Intermediate-Valence Systems

We start from the parametrized Hamiltonian, which has the form in the Wannier representation

$$H = \sum_{ij\sigma} t_{ij} c^{+}_{i\sigma} c_{j\sigma} + \sum_{i\sigma\sigma'} \left\{ U_{sf} n_{i\sigma} N_{i\sigma'} + \frac{1}{4} U N_{i\uparrow} N_{i\downarrow} - \frac{1}{2} J \vec{S}_i \cdot \vec{s}_i \right\}$$

$$+ \sum_{i\sigma} \epsilon_i N_{i\sigma} + \sum_{ij}{}' J_{ij} \vec{S}_i \cdot \vec{S}_j \qquad (14\text{-}1)$$

This Hamiltonian is close to the one derived in Sect. 10 (cf. Eq.(10-23)) but with $\vec{k}$ dependence of the coupling constants omitted. For the sake of simplicity we consider the f electrons as atomic (it does not influence the conclusions for $T=0$).

We have two sets of orbitals, one of them composes the conduction electron (carriers) band represented by the creation operators $\{c^{+}_{i\sigma}\}$, particle number operators $\{n_{i\sigma} = c^{+}_{i\sigma} c_{i\sigma}\}$ and with spins $\{\vec{s}_i\}$; the corresponding quantities for the other one (composed of localised or f electrons) are $\{a^{+}_{i\sigma}\}$, $\{N_{i\sigma}\}$ and $\{\vec{S}_i\}$. In general, the carrier concentration per site

$$n_c = N^{-1} \sum_{i\sigma} \langle n_{i\sigma} \rangle \quad ,$$

as well as the occupation of the localised orbital

$$n_f = N^{-1} \sum_{i\sigma} \langle N_{i\sigma} \rangle$$

are regarded as fractional, although we assume that $n_f + n_c = 1$, i.e. we have on average one electron per atom. Hence, the spin averages

$$N^{-1} \sum_i \langle \vec{S}_i^{\,2} \rangle = \frac{3}{4} n_f$$

and $N^{-1} \sum_i \langle S_i^z \rangle = n_f \langle S_f^z \rangle$, where $S_i^z = 0, \pm \frac{1}{2}$ is the spin quantum number at site i.

The first term of (14-1) represents the conduction band energy, the other ones give the position of f level (ϵ_f), interorbital (U_{sf}), intraorbital (U), and s-f (J) Coulomb interactions within the same atom, as well as intersite exchange $(\sim J_{ij})$ between f electrons.

We assume the following hierarchy of parameters

$$U > W > U_{sf} > J > J_{ij} \qquad \text{and} \qquad |\epsilon_f| < U_{sf} \tag{14-2}$$

where W is the carriers bandwidth. Hence, we can say that we approach the limit $U \to \infty$ and thus the intraatomic correlations on the f level must be treated carefully, whereas the other intraatomic terms to the first-order of approximation can be treated within the mean-field approximation. The mean-field version of (14-1) for the case with the longitudinal spin density wave

$$\langle S_i^{\alpha} \rangle = \delta_{\alpha z} \langle S_f^z \rangle \; n_f \exp(i \vec{Q} \cdot \vec{R}_i)$$

is

$$\begin{aligned} H_{MFA} = \sum_{\vec{k}\sigma} & \Big[(\epsilon_{\vec{k}} + U_{sf} n_f) \, n_{\vec{k}\sigma} - J \langle S_f^z \rangle n_f \; c^+_{\vec{k}\sigma} c_{\vec{k}+\vec{Q}\sigma} \Big] \\ + \sum_{i\sigma} & \Big[\big(\epsilon_f + U_{sf} n_c - J \langle s_i^z \rangle \sigma - J(\vec{Q}) e^{i\vec{Q}\cdot\vec{R}_i} \big) N_{i\sigma} \\ & + \frac{U}{2} N_{i\uparrow} N_{i\downarrow} \Big] \end{aligned} \tag{14-3}$$

where

$$J(\vec{Q}) = n_f \langle S_f^z \rangle \sum_{j(i)} J_{ij} \exp\left[i\vec{Q} \cdot (\vec{R}_j - \vec{R}_i) \right].$$

We see that the spin density wave induces a similar wave in the conduction band, i.e.

$$\langle s_i^z \rangle = \langle s^z \rangle \; \exp(i \vec{Q} \cdot \vec{R}_i)$$

We are interested in the antiferro- and para-magnetic solutions only, and thus $\vec{Q} = \vec{\tau}/2$ or 0 respectively. In the former case we can introduce the reduced Brillouin-zone scheme: the original zone is halved in the presence of the antiferromagnetic structure. The procedure is rather standard and the canonical transformation

$$\begin{pmatrix} c_{\vec{k}\sigma} \\ c_{\vec{k}+\vec{Q}\sigma} \end{pmatrix} = \begin{pmatrix} \cos\theta_{\vec{k}\sigma} , & -\sin\theta_{\vec{k}\sigma} \\ \sin\theta_{\vec{k}\sigma} , & \cos\theta_{\vec{k}\sigma} \end{pmatrix} \begin{pmatrix} \alpha_{1\vec{k}} \\ \alpha_{2\vec{k}} \end{pmatrix} \qquad (14\text{-}4a)$$

with

$$\tan 2\theta_{\vec{k}\sigma} = \frac{J \langle S_f^z \rangle n_f \sigma}{\epsilon_{\vec{k}+\vec{Q}} - \epsilon_{\vec{k}}} ,$$

gives the quasiparticle energies in the form of the slater´s split-sub-bands

$$E_{\vec{k}\,{}^1_2} = U_{sf}\, n_f + \frac{\epsilon_{\vec{k}} + \epsilon_{\vec{k}+\vec{Q}}}{2} \pm \left[\left(\frac{\epsilon_{\vec{k}} - \epsilon_{\vec{k}+\vec{Q}}}{2} \right)^2 + \left(J \langle S_f^z \rangle n_f \right)^2 \right]^{1/2} \qquad (14\text{-}5)$$

For $\vec{Q} = \vec{\tau}/2$, $\epsilon_{\vec{k}+\vec{Q}} = -\epsilon_{\vec{k}}$, and $J(\vec{Q}) = -J(0)$.

The carriers´ polarisation $\langle s^z \rangle$ is determined from the equation

$$\langle s^z \rangle = N^{-1} \sum_{\vec{k}\sigma} \sigma \langle c^+_{\vec{k}\sigma}\, c_{\vec{k}+\vec{Q}\sigma} \rangle \exp\left(i\, \vec{k} \cdot \vec{R}_i\right) \qquad (14\text{-}6a)$$

which is of the form

$$\langle s^z \rangle = \frac{J \langle S_f^z \rangle n_f}{N} \sum_{\vec{k}\sigma} \frac{f_{2\vec{k}} - f_{1\vec{k}}}{\left[\epsilon_{\vec{k}}^2 + \left(J \langle S_f^z \rangle n_f \right)^2 \right]^{1/2}} \qquad (14\text{-}6b)$$

where

$$f_{ik} = \left\{ \exp\left[\beta \left(E_{i\vec{k}} - E_F \right) \right] + 1 \right\}^{-1} = \langle d^+_{i\vec{k}}\, d_{i\vec{k}} \rangle$$

is the Fermi-Dirac distribution for the quasiparticles.

The system of f electrons in (14-3) is essentially a two-sublattice entiferromagnet in the molecular-field approximation. The equation for $\langle S_f^z \rangle$ is therefore given by

$$\langle S_f^z \rangle = \frac{1}{2} \tanh\left(\frac{\beta}{2}\, g\, \mu_B\, H_{eff} \right) \qquad (14\text{-}7a)$$

where the effective magnetic field acting on the spine of the sublattice A (i.e. the one with $\exp\left(i\,\vec{Q}\cdot\vec{R}_i\right)=+1$) is

$$g\mu_B H_{eff} = 2\left\langle S_f^z\right\rangle n_f \sum_{j(i)} J_{ij} + 2J\left\langle s_i^z\right\rangle \tag{14-7b}$$

The Eqs. (14-6b) and (14-7a) form a system of selfconsistent equations for $\left\langle S_f^z\right\rangle$ and $\left\langle s^z\right\rangle$. To get the conditional for the chemical potential we have to calculate the occupation probability n_f of the f level. We assume that we have one electron per atom, so $n_c = 1-n_f$. The quasiparticle energies of f electrons on the atom belonging to the sublattice A are

$$\begin{aligned} E_{1,2} &= \epsilon_f + U_{sf}n_c \pm \tfrac{1}{2}\, g\mu_B H_{eff} \\ E_3 &= 2\left(\epsilon_f + U_{sf}\, n_c\right) + U \\ E_4 &= 0 \end{aligned}$$

and correspond to the atomic states at site i : $|\,i\uparrow\rangle$, $|\,i\downarrow\rangle$, $|\,i\uparrow\downarrow\rangle$ and $|0\rangle$ respectively. Therefore, the partition function Z can be calculated exactly, even though the intraatomic Coulomb interactions are present. The average number of f electrons is

$$\begin{aligned} h_f = 2Z^{-1}\Big\{&\cosh\left(\beta g\mu_B H_{eff}/2\right)\exp\left[-\beta\left(\epsilon_f + U_{sf}\, n_c - E_F\right)\right] \\ &+ \exp\left[-2\beta\left(\epsilon_f + \frac{U}{2} + U_{sf}\, n_c - E_F\right)\right]\Big\} \end{aligned} \tag{14-8}$$

where

$$\begin{aligned} Z = 1+2\cosh&\left(\beta g\mu_B H_{eff}/2\right)\exp\left[-\beta\left(\beta_f + U_{sf}n_c - E_F\right)\right] \\ &+ \exp\left[-2\beta\left(\epsilon_f + \frac{U}{2} + U_{sf}n_c - E_F\right)\right] \end{aligned} \tag{14-9}$$

In particular and interesting us case when $U\to\infty$ we get the result for the occupation of a single electron donor in the magnetic semiconductor (cf. Appendix G). The carrier concentration is then

$$n_c = \left\{1+2\cosh\left(\beta g\mu_B H_{eff}/2\right)\exp\left[-\beta\left(\epsilon_f + U_{sf}n_c - E_F\right)\right]\right\}^{-1} \tag{14-10}$$

Hence as temperature $T\to 0$ $(\beta\to\infty)$ we approach the limit (if $\left\langle S_f^z\right\rangle \neq 0$)

$$n_c = \begin{cases} 0 & \text{for } E_F < E_2 \\ \frac{1}{2} & \text{for } E_F = E_2 \\ 1 & \text{for } E_F > E_2 \end{cases} \tag{14-11}$$

Therefore the ration of mixing in the ground state with mixed valence is 50:50. From (14-8) we get also the degree of mixing in the paramagnetic state at $T=0$ $n_f : n_c = 67:33$. Obviously the change of valence is connected with the change of the number of holes on the f level . Corresponding to (14-11) change of holes can be found from Eqn.(14-8) treating the creation of electron as an annihilation of a hole with the opposite spin, and vice versa. Then, the change of valence in P state correspondes to change of the hole number $n_h = 1-n_c = \frac{2}{3}$, instead of $\frac{1}{3}$ for the case of electrons. This is the ratio observed for some nonmagnetic systems (see e.g. Jayaraman 1979 [20]). Also, the results for mixed-valent antiferromagnet match with the experimental results of Haen et al. 1979 [129] , who have observed that the residual resistivity is divergent for Tm_xSe as x 1 , and that $n_f : n_c = 1:1$ in that limit. In our approach the insulating nature of TmSe is due to fact that the lowest Slater subband is filled and the higher one is empty. The localised level is pinned down to the Fermi level. This picture will be also true if f level is replaced by a narrow band since the Brillouin zone of this band is also halved in the ground state and if only the Slater splitting between subbands is greater than the f-band width the ground state will remain insulating. This indeed the case because due to factor $(1-n_{k\bar{\sigma}})$ in (10-22) the f bandwidth will be smaller than the gap which is of order J .

We have also calculated the static magnetic susceptibility for our system represented by the two-band Hamiltonian (14-1). The result is

$$\chi = \frac{1}{3}(g\mu_B)^2 \varrho(E_F) + n_f \frac{(g\mu_B)^2}{4k_B} \frac{[1+J\varrho(E_F)]^2}{T+n_f\left[J(0)-J^2\varrho(E_F)\right]/4k_B} \tag{14-12}$$

The first term is the Pauli susceptibility of carriers; the second one is the Curie-Weiss due to f electrons. The s-f exchange influences both the value of the paramagnetic Curie temperature $\theta = -J(0) + J^2\varrho(E_F)$ reducing it, and the Curie constant $C_m = \frac{1}{3} n_f S(S+1)\left[1+\varrho(E_F)J\right]^2$. In the latter quantity the magnitude of localised moment $\frac{1}{3} n_f S(S+1) = n_f/4$ is strongly reduced for $J<0$, particularly when $-J\varrho(E_F) \rightarrow 1$. In this limit the magnetic moment of f electrons is totally compensated by the conduction electrons. Since the same sort of compensation occurs in the Kondo effect, we can say that if $-J\varrho(E_F) \rightarrow 1$ the state is that of the Kondo lattice [112,113] . It is characterized by $\theta < 0$ and a small localised moment. In the opposite limit $|J|\varrho(E_F) \ll 1$ the presence of carriers reduces only partially the moment. It seems that the latter case reflects the situation encountered in TmSe. Then, the paramagnetic Curie temperature changes only a little with change $n_f : n_c$.

In conclusions, the presented attractive features of our mean-field version of the s-f model represented by (14-1) follow from the hybridised Hamiltonian for U_{sf} sufficiently large. It gives rise to the hopping between neighbouring f orbitals with the hopping (Bloch) integral

$$t_{ij\sigma} = \frac{1}{N} \sum_{\vec{k}} \frac{|V_{\vec{k}f}|^2}{\epsilon_f - \epsilon_{\vec{k}} - U_{sf}} \left(1 - \langle n_{\vec{k}\sigma} \rangle\right) e^{i \vec{k} \cdot (\vec{R}_i - \vec{R}_j)}$$

and is essentially nonzero only for carriers near the Fermi surface. Due to factor $(1 - \langle n_{\vec{k}\sigma} \rangle)$ the hopping between the f states can be treated as perturbation of the atomic part of (14-1), and thus can be represented through the Heisenberg Hamiltonian of the double exchange. The intersite exchange in (1) has therefore a ferromagnetic part increasing with concentration n_f through the factor $t_{ij\sigma} \, n_f \, (1 - n_f)$.

Finally, it would be interesting to construct a more realistic model including the many-electron nature of f electrons. The localised spin skeleton $\{\vec{S}_i\}$ is then composed of two parts. One of them is localised both in the metallic and insulating phases. The other one, due to a transfer of one f electron ($n_c \leqslant 1$ experimentally [20]) and coupled to the former one via the Hund's rule. The situation is schematically represented in Fig.6. Essentially, it is a model of minimum polarity [90] applied to f electrons, and with inclusion of the s-f coupling to carriers from a wide conduction band. In such an approach the only difference with the magnetism of 3d metals is due to the atomic nature of f spins and additionally, now $U \gg W$. The Kondo lattice state corresponds to the case when $n_c = 1$ $(n_f = 0)$. Work along this line is in progress.

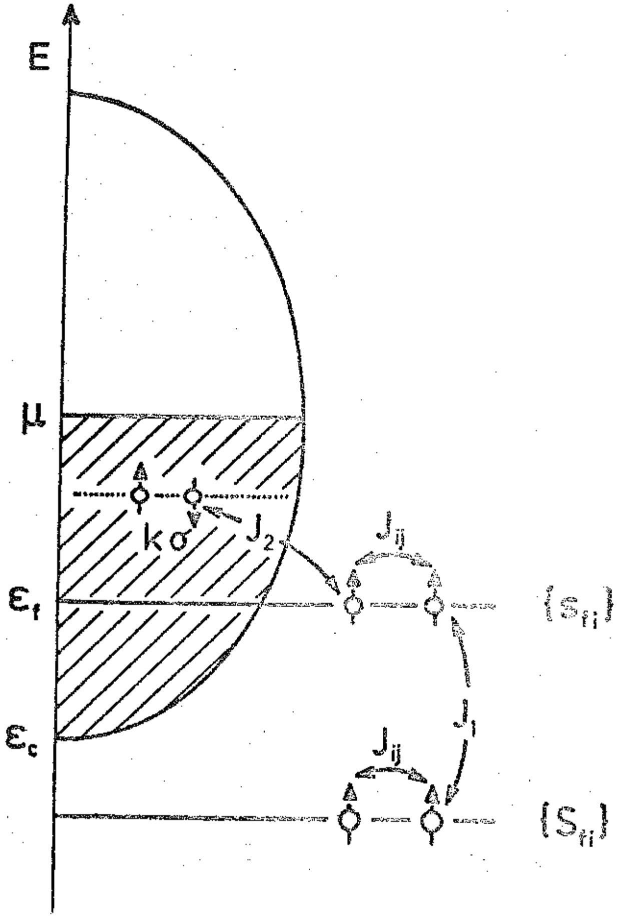

Fig.6. Schematic representation of a system with many 4f electrons. Localised spins $\left\{\vec{S}_i\right\}$ are coupled to additional ones $\left\{\vec{s}_i\right\}$ via the Hund´s rule. The additional one is also of the 4f type but it is the one which undergoes a transition to the conduction band due to valence fluctuation. The others are localised because the transfer of second electron costs energy which exceeds by far the Fermi energy $E_F = \mu$.

Part V

SUMMARY AND CONCLUSIONS

Towards an unification of various models and types of exchange

15. An Overview of the Approach

The discovery of insulating properties of transition-metal oxides with odd number of 3d electrons posed a challenge to the band theory for a long time. Two alternative explanations of the fact have been proposed by Mott and Slater respectively.

The first of them stresses the role of electron-electron interactions. It is these interactions which prevent a formation of a stable metallic ground state if the band energy grain due to delocalization of electron is smaller than the loss in the Coulomb energy. Quantitatively, Mott argues that hydrogen-like bound states at each site cannot be formed if the screening is such that the Bohr radius of this state exceeds the lattice constant.

In the Slater´s model the insulating ground state is created through a split-band superstructure induced by an antiferromagnetic ordering or, more generally, a spin-density wave. The Brillouin zone is halved into two parts separated by a gap which disappears at the Neél temperature T_N.

Experimentally, it is observed that temperature of insulator-metal transition T_{MI} is either much higher-or coincides with T_N (for review see: Mott 1974 [72]). Observations of the electronically driven transitions in systems which do not order magnetically speak in favour of the Mott mechanism.

The Mott concepts were subsequently developped on a model with short-range Coulomb interactions. Such a model has been introduced by Anderson (1959)[34] to explain the exchange interactions and magnetic ordering of insulating 3d compounds (now called the Mott insulators). The ideas of Anderson were reformulated in a narrow band context by Hubbard (1963, 1964) [15,79] who concentrated on a formulation of the approach to nonmetal-metal transition. This model contains one additional parameter, the magnitude of intraatomic Coulomb interactions U between two electrons positioned on the same atomic (Wannier) orbital. Therefore, it has no obvious connection with the original Mott approach to the problem.

Paradoxically enough, the Anderson approach gives correctly magnetic interactions (called kinetic exchange) but is unable to give the insulator-metal transition if the bare bandwidth $W \ll U$; conversely, the Hubbard approach gives a continuous transition to the metallic phase with increasing W/U , but does not give a magnetic solution as it has been proved by subsequent authors (Fukuyama and Ehrenreich 1972 [130] , Mehrohta and Viswanathan 1973 [131] , Ducastelle et al. 1976 [132] , Ducastelle 1977 [133]).

The lack of a reliable solution of the Hubbard and related models challenges undertaken extensive efforts for more than a decade. The situation in the metallic limit $U \ll W$ is quite clear since the Hartree-Fock and its diagrammatical generalization (Penn 1966 [68] , Langer et al. 1969 [63] , Kanamori 1963 [74] Caron and Kemeny 1971 [70] are applicable and give reliable results. However, the situation in the strong correlation limit $U \gg W$ is more cumbersome. There are, nonetheless, well founded results in this limit as well (Kanamori 1963 [74] , Nagaoka 1966 [73] , Brinkman and Rice 1970 [83] , Vischer 1974 [81] , Guyer 1978 [89] , Chao et al 1977 [43]) . We have listed them at the end of Sect.4. There have also attempts to bridge those two limits (Economu et al 1980 [134] ; see also reviews by Adler 1968 [135] and Khomskii 1970 [136]) but the results does not seem to be conclusive as yet. The Green function and the Gurtzwiller variational techniques seem to be the best ones for interpolating between weakly and strongly correlated regimes but the error involved in a decoupling procedure is difficult to estimate unless the whole procedure is selfconsistent like that presented in Sect.5.

The purpose of Part II of this work was to analyse in detail the limit $U \gg W$. In particular, we formulate the theory in such a way that for a particular case of the Mott insulator our results reduce to those derived by Anderson [24] . This gives us two things. Firstly, it incorporates the results which have been known before, for the Mott insulators, into the approach to strongly correlated metals. Secondly, we can see clearly the role of the kinetic exchange in the formation of an antiferromagnetic metallic phase.

Generally, the following circumstances force us to conclude that only strongly correlated electrons are described properly by the models of the type considered in Part II. It is simply because the tight-binding approximation is based on the assumption that the overlap of neighbouring atomic wave-functions is small and thus the long-range part of the Coulomb interactions can be neglected in this representation. Hence, it seems purely academic to consider the metallic limit $U \ll W$ and simultaneously use the tight-binding scheme.

We emphasise, that in a narrow s-band (cf. Sect.5) we have started from a full tight-binding Hamiltonian (i.e. with all n.n. interactions included), while for a doubly degenerate band (cf. Sect.7) we have taken all intraatomic interactions. Various magnetic phases for temperature $T=0$ have been obtained as a function of band filling n. Though our method of approach seems to be well justified in the strong correlation limit $U \gg W$, the following extension of our results to the whole region $U \gtrsim W$ (cf. Sects. 5.5 and 7.4), although appealing to a physical insight into the nature of virtual hopping, seems to be qualitative.

It should be also underlined that the term "partially filled band" should not be taken too literally. The physical situation underlying the existence of the partially filled band is such, that to assure charge neutrality of the whole system some of the electrons have been taken out from the narrow band and placed in a band overlapping with it but completely passive magnetically. The other way is to alloy two elements having number of d or f electrons differing by one. The latter situation is the cases for $Fe_{1-x}Co_xS_2$ and $Eo_{1-x}Ni_xS_2$ which were discussed in Sect. 7.5.

In Part III we have turned our attention to the two simplest many-band situations: a system composed from degenerate equivalent orbitals, and a system composed of localised (atomic) electrons mixed with a wide band. Those two situations are the extremal ones. Most of practical cases lie somewhere in between. However, it is a purpose of material science rather than of condensed matter physics to analyse systematically different materials by superposing distinct physical mechanisms to get the correct numbers. We have shown how a proper form of s-d (s-f) model can be brought into existence in each of the extremal situations and then, in Part IV, analysed the effective Hamiltonian.

Our approach bases on the concept of the effective Hamiltonian, derived from a bare many-body Hamiltonian. Appart from a derivation presented in Sect. 9, the effective Hamiltonian is obtained in each case (Sects. 5,7 and 10) via canonical transformation. Therefore, it contains physically equivalent information to the bare one. But, in subsequent calculations the approximations are used and it is better to use the effective Hamiltonian because it yields a better intuitive insight into the nature of the processes leading to the relevant interaction determining a collective behaviour we are interested in. In this respect, the same situation is encountered in the theory of superconductivity where the electron-phonon interaction is first transformed out (Bardeen and Pines 1955 [137]), and then the effective

Hamiltonian treated within approximate (BCS) theory. In our case, the transformed Hamiltonian allows for introduction of the concept of molecular field in the context of strongly correlated itinerant magnetism, i.e. in the case when the Stoner-Wohlfarth or Hartree-Fock approximations are not correct.

Let as recapitulate this Section with historical remarks. The theory of itinerant magnetism went through three main phases. The first one is characterized by the papers discussing purely quantitatively the factors which determine magnetic properties of metals. The concept of molecular field acting on band electrons (so called Stoner-Wohlfarth theory, see Wohlfarth 1977, 1980 [6,8]) was the only quantitative theory of that period. The roles of the Hund's rule (Slater 1953 [138]) and of correlations through the principle of minimum polarity (Van Vleck 1953 [90]) have been discussed. Approximately at the same time Zener(1951)[31] brought into consideration the s-d model in which itinerant and localized electrons coexist and interact through the intraatomic exchange $-J\,\vec{S}_i\cdot\vec{s}_i$. This model has been elaborated in detail by Ruderman and Kittel 1954 [120] , Kasuya 1956 [121] , and Yosida 1957 [122] and subsequently applied to explain both magnetic and transport properties of 3d and 4f metals.

The lack of a success of Landau theory of the Fermi liquids (Landau 1956 [124]) as well as of the theory of interacting electron gas (see Brueckner 1957 [139]) in describing collective magnetism in metals has induced a series of parametrized models starting from these of Anderson (1961)[24] and Hubbard(1963)[15] . Interest in field-theoretical models was exchanced further by spectacular achievements of the s-d model in explaining properties of heavy rare-earth metals and of magnetic semiconductors, particularly if proper crystal field levels were taken into account (for reviews see: Elliott 1972 [140] , Methfessel and Mattis 1968 [141]) . Let us remark that the last success was mainly due to the canonical transformation of the s-d Hamiltonian into RKKY exchange Hamiltonian which is equivalent to perturbation expansion (in the operator form) for the s-d interaction, calculated up to second order. So, the second phase of the development may be characterized by field-theoretical approach to model systems unlike transition metals. The value of models can be illustrated also through a semiquantitative description of insulator-metal transition in concrete systems (Askenazy and Weger 1972 [142] , Adler 1968 [135] , Ray and Kajzar 1980 [143]).

The often cited review by Harring (1966)[144] may be placed on the border between the first two phases.

There were, however specific features of the field-theoretical models not explained for a long time. In the s-d model the Kondo problem for magnetic impurities in simple metals was difficult to solve. The relations between various models have been suggested (see e.g. the Schrieffer-Wolff 1966 [36], transformation of the Anderson model into the s-d model). Additionally, the existence of localised moments in a narrow s-band (translationally invariant system with no a priori localised moments!) has been predicted (Cyrot 1972 [69], Evenson et al 1970 [145] Kimball and Schrieffer 1972 [143]), and even the indirect exchange of the RKKY type has been derived (Cyrot and Lyon-Caen 1974 [61]). The last results have risen hopes of understanding experimentally observed local moment behaviour of some itinerant systems (cf. Sect.1).

The stage three of the theory can be characterized as the one in which a full quantitative solution of the models introduced in the stage two (Anderson, Hubbard, Zener-Vonsovskii models) is expected to come out. The Kondo and the Anderson model for a magnetic impurity have been solved with the help of the renormalization group approach (Wilson 1975 [147], Krishnamurthy et al 1980 ab [26,27]), while the Hubbard model is under intensive study at the moment [11-14, 16-18]. This is due to the fact that the first principle band calculations carried out recently without any adjustable parameters [1,10] give correctly ground state characteristics but predict incorrectly the value of the Curie temperature (cf. Sect.1).

In view of these rather long remarks, our work may be characterized shortly as a contribution clarifying the role of various type of exchange interactions (kinetic, s-d, double and indirect exchange), together with a definition of local moments, for various harrow band situations. Furthermore, we develop a novel technique of analysis of the s-d model, from with the temperature independent part of the Stoner splitting comes out naturally.

16. Short Summary of Results

Let us specify more explicity the new results presented here.[*] They can be divided into three classes: those concerning the narrow-band electrons, the ones concerning the s-d systems, and those relating the two. Below we list the most important results from each class of problems.

1. Narrow band electrons: nondegenerate case (Sect. 5).
Results:

1° Theory of the kinetic exchange for the full tight-binding Hamiltonian,

2° Phase diagram including mixed ferro-antiferromagnetic phase,

3° Discussion of the role of the kinetic exchange for local moment behaviour and in the Mott transition.

2. Narrow band electrons: doubly degenerate case (Sect. 7).
Results:

4° Theory of the kinetic exchange for arbitrary band filling,

5° Discussion of an interplay between the kinetic exchange and the double exchange,

6° Qualitative discussion of the phase diagram and of the Mott transitions,

7° Qualitative discussion of experimental results for transition-metal disulfides.

3. From a narrow band to s-d model (Sects. 9 and 10).
Results:

8° Transformation of the narrow band Hamiltonian into the Zener-Vonsovskii model,

9° Transformation of the periodic Falicov-Kimball-Anderson model into an extended s-d model.

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[*] We disregard the Supplements A-J which consist of reprints of published already results.

4. The extended s-d model (Sect. 12-14.)

Results:

10° Derivation of the temperature independent part of the Stoner splitting,

11° Theory of indirect exchange for $J \ll W$ (for weakly exchange-coupled, strongly correlated magnets),

12° Derivation of the effective Hamiltonian of the double exchange (full quantum theory),

13° Derivation of an universal degree of mixing for the mixed valence systems and of static magnetic susceptibility in the paramagnetic region

17. Concluding Remarks

The natural question arises: has the problem of strongly correlated electrons been covered fully? The answer is, of course, not. What we have presented here is rigorous as for as the construction of the effective Hamiltonian is concerned. However, the presented solutions, while quantitatively correct, are far from being rigorous!

Such a rigour is not even needed if the model cannot be directly tested on concrete systems. Personally, we think that more work is needed for the doubly degenerate band case in a direction of a possible application to the doped Mott insulators (e.g. NiO:Li). Work along this line is planned in the near future.

Also, a further study of the indirect exchange presented in Sect.12 is necessary to make our ideas more quantitative. A systematic discussion of the Curie temperature as a function of band filling and of the magnitude of localised spin $\vec{S}_i$ is required to draw a conclusion on applicability of the results to 3d metals.

Furthermore, a detailed analysis of the double exchange Hamiltonian may provide required but not entirely known structure of carriers quasiparticle states in magnetic semiconductors (cf. Nolting 1979 [126]).

Finally, an extension of the model of mixed-valence systems, presented in Sect.14, needs a full analysis of the stability of various magnetic solutions as well as a systematic study of fitite temperature effects.

We have concentrated our attention mainly on the magnetic interactions and quasiparticle states in systems with either strongly correlated electrons alone or mixed with ordinary carriers. It would be of prime importance to supplement them with calculations of the static magnetic susceptibility and of transport properties such as resistivity or the Hall effect. This is because the mentioned quantities are the simplest characteristics measured for such systems. However, to reach this goal a generalization to finite temperatures of our formalism is needed.

The conclusion we would like to draw from our whole approach to exchange interactions in a narrow band is that various types of them (kinetic, indirect, double) can show themselves in the same system (i.e. with the same parameters), with changing band filling. The crucial quantities are the position of the Fermi level E_F , the magnitude of Coulomb correlations U , and of the intraatomic exchange J .

Additionally, basing on the theory of kinetic exchange one can draw a general rule about the sign of kinetic exchange for system with d-fold degenerate magnetic (narrow) band. Namely, if the band is less than quarter filled (the number of electrons per atom $n \leq \frac{d}{4}$ or more than $\frac{3}{4}$ filled), then the ferromagnetic kinetic exchange dominates. For fillings $\frac{d}{4} < n < \frac{d-1}{d}$ and $\frac{d+1}{d} < n < \frac{3}{4} d$ the ferro- and antiferromagnetic interactions compete, while for $\frac{d-1}{d} < n < \frac{d+1}{d}$ the antiferromagnetic kinetic exchange is the only present in the system. However, we should not forget that the residual part of hopping which is also present in the effective Hamiltonian for a partially filled band favours additionally ferromagnetic ordering. If the intraatomic exchange constant exceeds bare bandwidth then the hopping can be expressed through an equivalent Hamiltonian of double exchange for filling $n > \frac{1}{d}$ (or less than $\frac{d-1}{d}$). The detailed analysis of this point will be given elsewhere.

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Streszczenie

Własności magnetyczne silnie skorelowanych elektronów w wąskich pasmach:

Przyczynek do teorii oddziaływań wymiennych, przejścia niemetal-metal oraz występowania zlokalizowanych momentów magnetycznych w układach wąskopasmowych; rozpatrywane z punktu widzenia modeli teoriopolowych silnie skorelowanych elektronów w metalach i półprzewodnikach.

Niniejsza rozprawa podzielona jest na pięć części. Oprócz tego zawiera 10 suplementów w postaci odbitek prac autora, ściśle związanych z tematyką rozprawy, nie omawianych jednak szczegółowo w jej zasadniczym tekście.

Celem pracy jest podanie metody systematycznego opisu skorelowanych elektronów w układach wąskopasmowych, tzn. układów, w których energia korelacji kulombowskich jest porównywalna lub większa od energii w paśmie. Dla takich układów stosowane często przybliżenia Hartree-Focka lub podobnego typu nie mogą być stosowane.

Cały problem opisu stanów elektronowych w silnie skorelowanych układach może być podzielony na dwie części. W pierwszej konstruujemy hamiltonian efektywny, który zawiera podstawowe procesy dynamiczne występujące w tych układach, w postaci jawnej. Osiąga to się poprzez transformację kanoniczną wyjściowego hamiltonianu wielociałowego, zastępując procesy mało prawdopodobne poprzez odpowiadające im procesy wirtualne w wyższych rzędach. W drugiej części natomiast diagonalizujemy otrzymany wcześniej hamiltonian efektywny i wprowadzamy do opisu stany quasicząstkowe odpowiadające silnie oddziaływującym cząstkom wyjściowym. Quasicząstki są cząstkami niezależnymi, ale posiadającymi zrenormalizowane charakterystyki takie jak masa efektywna, szerokość i kształt pasma oraz degeneracja spinowa stanów pasmowych. Oprócz tego dostarczają opisu natury stanu podstawowego, a więc w szczególności

natury magnetyzmu kolektywnego w tych układach.

Nowymi charakterystykami ilościowymi specyficznymi dla silnie skorelowanych elektronów w kryształach są takie pojęcia jak: podpasma Hubbarda /czyli pasmo rozszczepione pod wpływem korelacji/, izolator Motta czyli izolator odpowiadający układowi z do połowy wypełnionym pasmem, gdy zaniedbamy korelacje, czy pojęcie kinetycznej wymiany - specyficznej dla silnie skorelowanych elektronów. Poza tym należy rozważyć problem do jakiego stopnia zachowane są charakterystyki atomowe w układach pasmowych, gdyż determinują one całą gamę zjawisk specyficznych dla magnetyków Heisenberga, tj. takich, które posiadają dobrze określone momenty spinowe i mało się różniące od sumy momentów atomowych.

W niniejszej pracy rozpatrujemy po kolei wszystkie wyżej wymienione specyficzne charakterystyki ilościowe i to w jednolitym formaliźmie. Zatem celem niniejszej rozprawy jest nie tylko otrzymanie konkretnych rezultatów ilościowych w różnego rodzaju sytuacjach modelowych, ale także próba scalenia różnych sposobów podejścia, znajdujących swój wyraz w wyborze hamiltonianu wyjściowego.

Podział całości na poszczególne zagadnienia przedstawia się następująco.

W części pierwszej formułujemy podstawowe fakty świadczące o obecności momentów atomowych lub zlokalizowanych w układach wąskopasmowych z silnymi korelacjami. W szczególności, dyskutujemy dlaczego takie fakty są nietrywialne z punktu widzenia teorii stanów elektronowych. Najogólniej można powiedzieć, iż fakty te zmuszają nas do stwierdzenia, iż różnica pomiędzy stanami pasmowymi będącymi wyrazem translacyjnej niezmienniczości układu, a stanami atomowymi nie jest tak ostra w przypadku silnie skorelowanych elektronów. W związku z tym start z modelu posiadającego jasny obraz intuicyjny w granicy atomowej jest bardziej atrakcyjny.

Przykładem takiego modelu jest rozszerzony model Hubbarda rozważany szczegółowo w części drugiej i to zarówno w przypadku pasma niezdegenerowanego, jak i podwójnie zdegenerowanego. I tak w paragrafie 5 omówiono szczegółowo metodę konstrukcji hamiltonianu efektywnego zawierającego oddziaływania wymiany tzw. kinetycznej w przypadku wąskiego pasma typu s. Zaprezentowana metoda pozwala na uogólnienie teorii wymiany kinetycznej wprowadzonej przez Andersona dla przypadku izolatorów Motta. Poza tym w paragrafie tym przeprowadzamy szczegółową dyskusję stanów quasicząstkowych stosując do tego celu rozszczepienie z zachowaniem pierwszych czterech momentów dla jednocząstkowej funkcji Greena. Rozwiązanie to pozwala na dyskusję diagramu faz magnetycznych w funkcji stopnia wypełnienia pasma dla tego przypadku. W paragrafie 6 omawiamy najprostszy typ stanu związanego, tzw. dużego polaronu magnetycznego, który jest poza opisem quasicząstkowym, a który może się realizować w przypadku małej koncentracji dziur w izolatorze Motta.

W paragrafie 7 omawiamy szczegółowo teorię oddziaływania wymiany kinetycznej w przypadku prostej struktury pasmowej. Pokazujemy, że wymiana kinetyczna dla pasma wypełnionego w 1/4 może prowadzić do ferromagnetyzmu spinowego z antyferromagnetycznym uporządkowaniem orbitalnym, podczas gdy dla do połowy wypełnionego pasma otrzymujemy antyferromagnetyczną wymianę Andersona. Otrzymane rezultaty posłużyły za podstawę analizy jakościowej magnetyzmu związków $Fe_{1-x}Co_xS_2$ oraz $Co_{1-x}Ni_xS_2$, które mogą być opisane przez pojedyncze pasmo typu $3de_g$. Dokładniejsza analiza wymagać będzie uwzględnienia nieporządku podstawieniowego w tych układach dla $0 \leqslant x \leqslant 1$.

W części trzeciej rozpatrujemy relację pomiędzy modelem elektronów w wąskich pasmach a modelem s-d (s-f) zakładającym obecność zlokalizowanych momentów spinowych w układzie. Relację tego typu pokazujemy najpierw na przykładzie elektronów ze zdegenerowanego wąskiego pasma zawierającego więcej niż jeden elektron na atom; a następnie dla periodycznego modelu Andersona, przy uwzględnieniu także kulombowskiego oddziaływania pomiędzy dwoma typami elektronów: s oraz d . W przypadku elektronów w zdegenerowanym wąskim paśmie, nasz rezultat winien być uważany raczej jako ilościowe sformułowanie zasady minimum polarności Van Vlecka oraz reguły Hunda, aniżeli pełna teoria mikroskopowa. Odpowiada on w sposób oczywisty granicy mikroskopowej, w której energia pasmowa przypadająca na cząstkę nie przekracza energii wymiany wewnatrzatomowej. Jednakże można przypuszczać, iż jest on słuszny w znacznie szerszym zakresie.

W części czwartej przedyskutowano wpływ istniejących momentów zlokalizowanych na stany nośników w układach ze sprzężeniem s-d. Ograniczono się przy tym do rozpatrzenia dwóch przypadków: modelu Zenera-Wonsowskiego dla metalicznego magnetyka oraz do modelu s-d dla układów wykazujących przejście do stanu z mieszaną walencyjnością. W pierwszym przypadku przedyskutowano charakter wielociałowy stanów nośników oraz oddziaływanie wymiany pośredniej w przypadku, gdy nośniki wnoszą wkład do kolektywnego magnetyzmu tego układu. Prowadzi to do procesów z odwróceniem spinu nośnika, które mogą być zinterpretowane jako niezależne od temperatury rozszczepienie Stonera. Natomiast w drugim przypadku otrzymano uniwersalne stosunki mieszania elektronów walencyjnych ze stanami nośników oraz zależność temperaturową statycznej podatności magnetycznej w obszarze paramagnetycznym.

Część piąta, podsumowująca, zawiera ogólną charakterystykę podejścia wraz z pewnymi uwagami historycznymi na temat rozwoju teorii stanów skorelowanych elektronów, krótkie podsumowanie rezultatów tej rozprawy, a także uwagi końcowe, których celem jest wyszczególnienie nierozwiązanych problemów, ściśle związanych z tą pracą. Większość z nich jest obecnie przedmiotem naszych badań.

Dziesięć suplementów stanowiących rezultaty prac opublikowanych w całości w czasopismach fizycznych, nie są analizowane szczegółowo w tekście. Stanowią one ilustrację metod podanych w ogólniejszej postaci w niniejszej rozprawie.

Supplements

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