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Abstract. – We review the recent progress in the theory of electron correlations in transition metals. Both qualitative picture and the quantitative results obtained for the magnetic moments, exchange splittings, Stoner parameter and magnetovolume effect of Fe, Co and Ni are presented and discussed in detail.

1. Introduction

In spite of considerable progress in recent years, a satisfactory description of electronic and magnetic properties of 3d transition metals is still a challenging problem. There is no doubt that electron correlations are important and thus itinerant and localized degrees of freedom have to be treated simultaneously. The modern theory of magnetism of transition metals at finite temperature replaces the interaction between electrons by the interaction of a moving electron with external fluctuating fields treated within the functional integral method [1]. However, the calculations are made usually within the static approximation which reduces to the ground state of independent electrons at $T = 0$ [2].

There are two ways to include correlations in the ground state. First of them is based on the local spin density approximation (LSDA) [3] within the density functional method [4]. It avoids calculating the wave function and has been remarkably successful in determining binding energies, lattice constants and magnetic moments of transition metals [5]. But going into details, one notices also its certain shortcomings. There are deviations in the binding energy of 1-2 eV, the calculated lattice constants are too short by $\sim 2\%$ and the calculated magnetic moment of Fe is by $\sim 5\%$ larger than the observed one for the *experimental* lattice constants [2]. Experiments indicate that the anisotropy in the populations and the exchange splittings (ES) for different 3d states is underestimated both for bulk Ni [6] and for Ni(001) surface [7]. It is also well known that the values of the ferromagnetic (F) transition temperatures T_c which are predicted from the energy difference between nonmagnetic (NM) and F phase as obtained in the calculations making use of LSDA, are by a factor of 3-5 larger than those observed experimentally [8]. Clearly, all these shortcomings have to do with the unsatisfactory treatment of electron correlations by the LSDA. It cannot describe correctly nonlocal short-range correlations which are absent in the homogeneous electron gas.

Another way to deal with electron correlations is to calculate their effects directly, starting from the respective Slater determinant. At present this is not possible on an *ab initio* level, so one has to use a model Hamiltonian. This approach to the correlation problem has been started in late seventies by formulating the second order perturbation (SOP) expansion [9]. It demonstrated the stabilization of NM phase by correlation effects and explained qualitatively the dependence of cohesive energy on electron density [9-11]. The correlation energy is then, however, seriously overestimated due to the missing saturation effects between the intra- and interorbital correlations which arise from higher order processes and may be considered as screening effects [12]. This difficulty has been removed by a variational method to determine the ground state wave function, known as a *local approach* (LA) [13-17]. The advantage of LA lies in its transparency which allows to identify the energy contributions coming from different correlation processes and to understand which of them are poorly treated by the LSDA, as well as in the possibility of calculating various two-particle correlation functions.

2. Model Hamiltonian and local approach

We describe the 3d states of a transition metal by a model Hamiltonian [15]

$$H = \sum_{mi\sigma} \varepsilon_{mi} n_{mi\sigma} + \sum_{mnij\sigma} t_{mi,nj} a^+_{mi\sigma} a_{nj\sigma}$$
$$+ \frac{1}{2} \sum_{mij\sigma\sigma'} (U_{ij} n_{mi\sigma} n_{mj\sigma'} + J_{ij} a^+_{mi\sigma} a^+_{mj\sigma'} a_{mi\sigma'} a_{mj\sigma}),$$
$$(1)$$

where five equivalent 3d orbitals (i, j) at each atom m (n) are assumed. The corresponding local densities of states (DOS's) may be either assumed or taken from band structure calculations as the canonical DOS's for bcc and fcc structure [18], respectively. In both cases they depend only on one free parameter, the bandwidth W. The orbital energies ε_{mi} may differ due to crystal field splitting and due to different local configurations around the atoms. U_{ij} and J_{ij} stand for local Coulomb and exchange interaction, respectively. They may be expressed by the Coulomb element U, the exchange constant J and the anisotropy ΔJ [16]. We

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fixed two of these parameters assuming $\Delta J = 0.15\ J$ and $J = 0.2\ U$ [9] which leaves only one free parameter U.

Electron correlations are treated within the LA in which the correlated ground state $|\psi_0\rangle$ is obtained from the corresponding Hartree-Fock (HF) state $|\phi_0\rangle$ as follows [12-17]

$$|\psi_0\rangle = \exp\left[-\sum_n \eta_n O_n\right] |\phi_0\rangle. \qquad (2)$$

This method is thus a natural generalization of the Gutzwiller *ansatz* [19] to a multiorbital problem. The variational parameters η_n are found by the minimization of the ground state energy $E_{LA} = \langle\psi_0|H|\psi_0\rangle / \langle\psi_0|\psi_0\rangle$. For the local operators O_n we use $n_{mi\uparrow}n_{mi\downarrow}$ and $n_{mi}n_{mj}$ to reduce charge fluctuations within orbital i and between two orbitals i and j, respectively, while the operators $s_{mi}s_{mj}$ introduce spin-spin correlations which express the Hund's rule coupling which leading to the formation of local moments. In this way a spin-dependent correlation hole around each electron is generated. We calculate the ground state energy E_{LA} by performing a variational second order expansion in powers of η_n. The respective quantities $\langle O_n H\rangle$ and $\langle O_n H O_{n'}\rangle$, where $\langle\cdots\rangle$ stands for $\langle\phi_0|\cdots|\phi_0\rangle$, are evaluated by making use of the so-called $R = 0$ approximation [10] in which only the leading local terms are preserved. The calculation is then significantly simplified since the correlation energy is found only by using the DOS's and the corresponding energy densities. The estimated error of this procedure does not exceed 5 % for transition metals [14]. More details may be found in reference [16].

3. Magnetic order and correlations in transition metals

The cohesive energy E_{coh} exhibits a spectacular dependence along a transition metal series with a minimum originating from the exchange interaction and reproduced already in HF approximation [9, 15]. E_{coh} decreases with increasing electron interaction energy in HF approximation and changes its sign already at moderate values of Coulomb interaction $U/W \approx 0.5$, practically independently of the details of DOS [15, 2]. The latter energy contribution is proportional to the local charge fluctuations (CF)

$$\sigma^2(n_m) = \langle\psi_0|n_m^2|\psi_0\rangle - \langle\psi_0|n_m|\psi_0\rangle^2, \qquad (3)$$

where $n_m = \sum_i n_{mi}$. They may be reduced in the HF approximation only by the breaking of magnetic symmetry. Electron correlations decrease $\sigma^2(n_m)$ and thus stabilize NM states [5, 12]. Simultaneously local moments with enhanced spin fluctuations (SF), $\sigma^2(S_m)$, defined in a similar way to (3), are developed (see

Fig. 1). In the presence of magnetic order (e.g. antiferromagnetic (AF) of Fig. 1), CF are reduced already in the HF state $|\phi_0\rangle$ and the SF are blocked to a large extent.
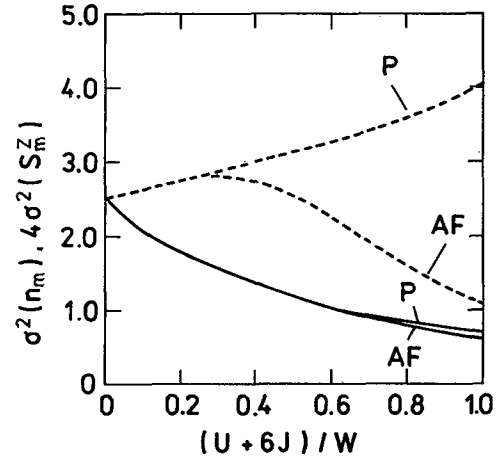

Fig. 1. – Reduction of $\sigma^2(n_m)$ (solid) and enhancement of $\sigma^2(S_m)$ (dashed) with increasing U in P and AF states for the degenerate orbital model at $n_d = 5$ [15].

It is now of interest to ask how the criterion for the occurrence of magnetic order is changed in the presence of correlations. In the HF approximation one finds for two different subbands e_g and t_{2g} with DOS's $N_e(\varepsilon_F)$ and $N_t(\varepsilon_F)$ at the Fermi energy ε_F, respectively, the following condition of ferromagnetic (F) instability [16]

$$3\left(U + J + \frac{19}{2}\Delta J\right) N_t^2(\varepsilon_F)$$

$$+2\left(U + J + \frac{7}{2}\Delta J\right) N_e^2(\varepsilon_F)$$

$$+\left(J - \frac{3}{2}\Delta J\right) N^2(\varepsilon_F) = N(\varepsilon_F). \qquad (4)$$

Here $N(\varepsilon_F) = 3N_t(\varepsilon_F) + 2N_e(\varepsilon_F)$ is the total DOS. The critical values of $U(n_d)$ which follow from (4) are nonuniformly enhanced by correlations, as shown in figure 2a for fcc structure. Figure 2b shows the regions of stable saturated ferromagnetism. F states with nonsaturated moment are present between the F instability and the saturated phase. One observes here a particular tendency to saturated ferromagnetism for $7 < n_d < 9.6$, where $n_d = \langle n_m\rangle$. The corrections due to spin-spin correlations are in this case typically smaller than for the F instability.

There are two principal complications in the treatment of correlations in antiferromagnetic (AF) states: (i) the possibility of different types of AF order and (ii) the nontrivial dependence of the Bloch states on
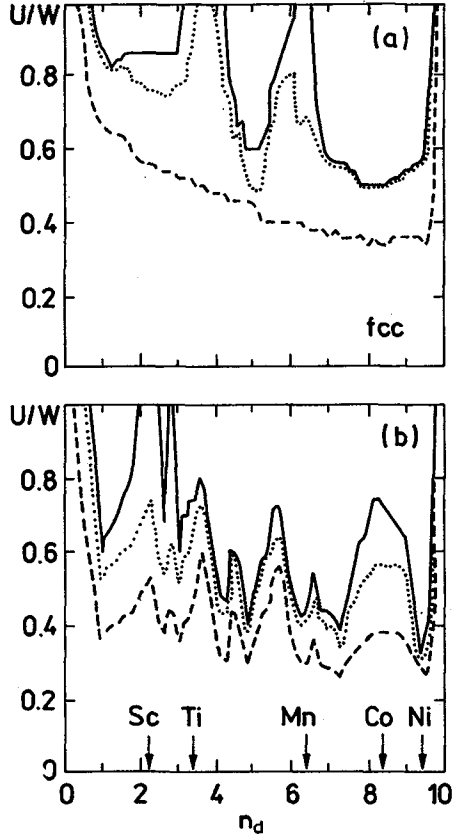
Fig. 2. – Ferromagnetic instabilities for a fcc structure: (a) onset of ferromagnetic order and (b) regions of saturated order in HF (dashed) and within LA without (dotted) and with (full lines) spin-spin correlations [16].

the magnetic order. A qualitative picture may be obtained with a degenerate orbital model with a rectangular DOS $N_i(\omega) = 1/W$ and assuming two interpenetrating AF sublattices [15]. In HF approximation the AF phase is stable for $U + 6J > -W/\log|1 - n_d/5|$, while F state is stable if $U + 6J > W$ (see (4)), as shown in figure 3. As expected, the regions of AF and F states are reduced by correlations. The Coulomb (U) and exchange (J) interactions play thereby different roles. While the density correlations, related to U, suppress magnetic order, the presence of local moments $\langle S_m^2 \rangle$ which develop for finite J, favours it [15]. The preference of AF over F order is expected also for more realistic DOS's for $n_d \approx 5$.

4. Ground states of Fe, Co and Ni

Below we analyse in more detail the ground states of Fe (bcc) and Co and Ni (both fcc). The electron densities are n_d= 7.4, 8.4 and 9.4, the bandwidths W = 5.43, 4.84 and 4.35 eV, respectively [18]. The Coulomb interaction U is chosen to reproduce the ex-
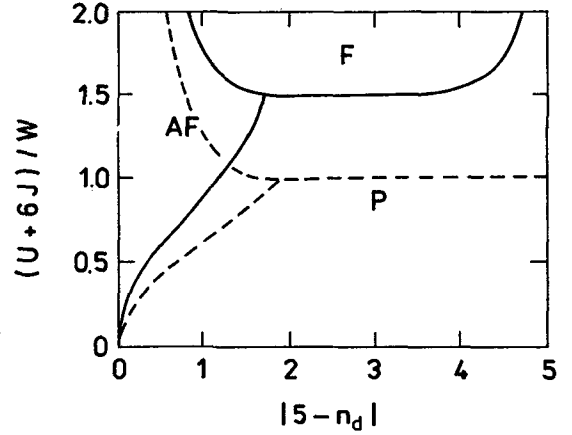

Fig. 3. – Phase diagram of the degenerate orbital model in HF (dashed) and within LA (full lines) [15].

perimental magnetic moment for each substance, being M_0 = 2.12, 1.6 and 0.6 μ_B. In this way we find $U = 2.4$ eV for Fe and $U \geq 2.6$ eV and $U \geq 3.1$ eV for Co and Ni. Looking at the energy difference between the P and F states, we have chosen $U = 3.1$ eV and $U = 3.3$ eV for Co and Ni. Thus, $U/W = 0.44$, 0.64 and 0.75, respectively. The energy gain due to magnetic order is drastically reduced from its HF value by the density correlations (Tab. I). The spin correlations reduce ΔE_{dc} 33 and 30 % for Fe and Co, respectively. This energy gain is only $\sim$ 10 % for Ni due to the reduced probability of finding two d holes at one atomic site.

Table I. – *Energy gains due to F order in the HF approximation (ΔE_{HF}) and found when density correlations (ΔE_{dc}) as well as spin correlations (ΔE_c) are included, exchange splittings (S_e and S_t), the Stoner parameters found when density and spin correlations (I_1), density correlations (I_2) and only correlations due to U_{ij} (I_3) are included and average exchange splittings $S = I_1 M_0$. All quantities in eV.*

	Fe	Co	Ni
ΔE_{HF}	0.564	0.430	0.115
ΔE_{dc}	0.224	0.161	0.039
ΔE_c	0.150	0.113	0.035
S_e	1.74	1.28	0.15
S_t	1.30	1.06	0.57
I_1	0.66	0.72	0.68
I_2	0.75	0.88	0.77
I_3	0.85	1.07	1.11
S	1.40	1.15	0.41

The ES presented in table I are found from the condition that the partial occupation numbers n_e and

n_t agree with those minimizing the full Hamiltonian (1). They are determined under assumption that the canonical DOS for each spin subband does not change with increasing magnetic moment. While S_e and S_t for Fe and Co are rather similar, one finds a considerable anisotropy in the ES for Ni (holes are located in t_{2g} orbitals, see Fig. 4), coming partially from ΔJ (if $\Delta J = 0$, $S_e = 0.27$ eV and $S_t = 0.50$ eV). It agrees reasonably well with the experimental data and with the results of other calculations [2] and gives the upper limit for the anisotropy which is likely to decrease when the hybridization effects are explicitly taken into account.
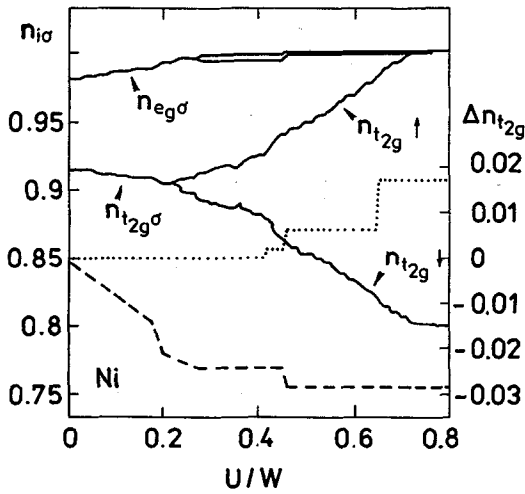

Fig. 4. – Electron fillings $n_{i\sigma}$ (full lines) for Ni(fcc). The dotted and dashed line show the change of electron density per one t_{2g} orbital with respect to the ground state at $U = 0$ in the Stoner model and in the present calculation, respectively [16].

Even stronger anisotropy than in bulk Ni was found by our calculations at the surface Ni(001) [17]. Thereby the results of the accurate LSDA calculations [7] were simulated by simplified analytic DOS's. If we replace the isotropic exchange which simulates the LSDA calculations by the true nonlocal one, the partial occupancies change from 0.16, 0.15, 0.13 and 0.08 to about 0.21, 0, 0.22 and 0 for xy, $x^2 - y^2$, xz (yz) and $3z^2 - r^2$ orbitals, respectively. As a consequence, the ES of e_g orbitals are again by more than a factor of 3 lower than those of t_{2g} ones.

The magnetic energy is conventionally quantified by the Stoner parameter I [8]. In our calculation the total energy is

$$E_c(M_0) = E_c(0)$$
$$+ \frac{1}{4} \int_0^{M_0^2} D(M^2) \, dM^2 - \frac{1}{4} \int_0^{M_0^2} I(M^2) \, dM^2, \quad (5)$$

where the second and third term stand for the loss of kinetic energy and for the gain of interaction and correlation energy due to magnetic order, respectively. $I(0)$ is the Stoner parameter I. It is reduced by electron correlations from its HF value and has a rather complex dependence on the electron density n_d [20]. We have used three successive approximations to evaluate the effects of different correlations on $I(M)$ [21], getting: $I_1(M)$ from the complete LA (2), $I_2(M)$ by neglecting the spin correlations and $I_3(M)$ by neglecting all correlation effects due to J_{ij}. The spin correlations are not included in the LSDA scheme at all, while other nonlocal correlations due to exchange interaction J_{ij} are treated rather poorly. Thus, $I_2(M)$ and $I_3(M)$ form a lower and upper limit for the inaccuracy of LSDA calculations. $I(M)$ has an explicit dependence on M and is strongly reduced by correlations for $M \approx 0$ (see Tab. I and Fig. 5). Our results suggest that the error in the Stoner parameter found in LSDA calculations amounts to 12-22 % , 18-33 % and 12-39 % for Fe, Co and Ni, respectively. This means that the predicted values of the transition temperature [8] should be reduced accordingly. The same applies to the average ES S which may be found from the relation $S = I_1 M_0$.
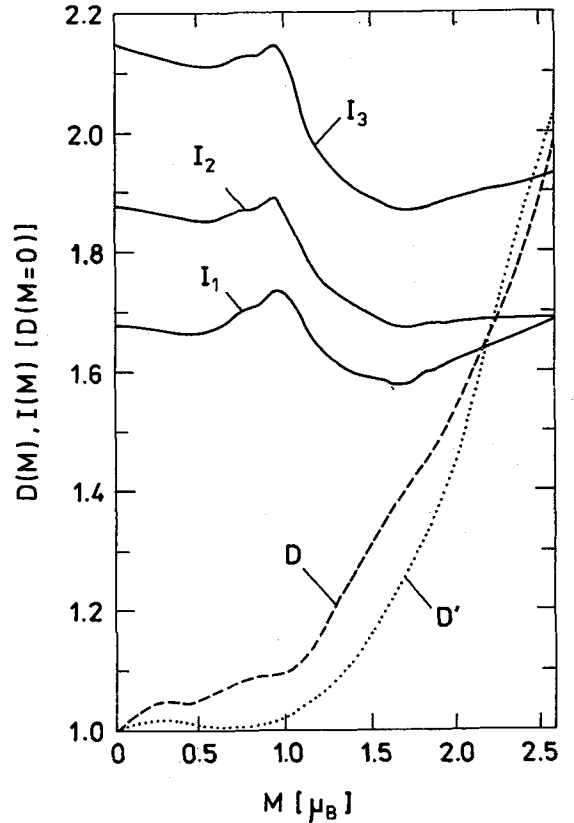

Fig. 5. – Stoner parameter $I(M)$ and the loss of kinetic energy $D(M)$ for Fe as obtained from the canonical bcc band (dashed) and within LSDA (dotted) [21].

The values of S presented in table I agree very well with the averages over S_e and S_t. On the other hand, the ground state magnetic moment M_0 of Fe changes only by 4 % (15 %) when I_1 is replaced by $I_2(I_3)$ (Fig. 5). This effect is even smaller when the DOS obtained from the LSDA calculations is used ($D'(M)$ in Fig. 5). We recall that M_0 found within the LSDA scheme is indeed by ~ 5 % too large.

The lattice constants calculated within the LSDA are different for NM and F states. Since no appreciable difference is observed, it suggests that magnetic moments exist in the P phase and are almost as large as in the ordered ground state [22]. According to the LSDA, the magnetovolume effect (MVE) is given by two contributions: the difference in kinetic energy $\Delta E_{kin}^{(0)}$ of noninteracting electrons in two states and the difference ΔE_{xc} in the local exchange-correlation potential. The second term includes small correlation corrections only. Our model Hamiltonian (1) does not depend explicitly on volume and we have to investigate its dependence on W. Due to correlations we found a reduction of the kinetic energy difference. For instance, in Fe $\Delta E_{kin}^{(0)} = 0.099\ W$ is reduced to $\Delta E_{kin} = 0.071\ W$. This large (almost 30 %) reduction of the MVE is apparently missing within the LSDA. Together with the second term ΔE_{xc} the MVE in Fe is thus reduced by ~ 50 %. For Co and Ni the correlation corrections to $\Delta E_{kin}^{(0)}$ are only about 50 % of what they are for Fe. It is likely that the missing reduction of the MVE in 3d metals could be explained by the volume dependence of the exchange and correlation energy, not fully described within the LSDA and reflected in a rather strong volume dependence of the Stoner parameter I [23]. In fact, we found $\partial \ln I / \partial \ln V \approx -0.7$ for $n_d = 9.5$ in fcc lattice [23], while the LSDA gives a much weaker dependence, not exceeding -0.2 in the case of Pd. This has a strong effect on the value of the magnetic pressure which is proportional to the derivative $\partial \ln (IN) / \partial \ln V$ [23] which is reduced to about 60 % by electron correlations. This agrees very well with the trends found experimentally for Pd and Ni alloys [23].

5. Correlations in the excited states and final remarks

Correlation effects were observed in the photoemission spectroscopy. The presence and positions of satellites, narrowing of DOS as well as the experimentally determined dispersions of d bands can be explained only after correcting the results of the LSDA calculations by the correlation effects [2]. The simplest way to include them is by SOP formula making use of the $R = 0$ approximation [24]. The fit to the observed band structure gives then the values of $U = 1$, 1.5 and 2 eV for Fe, Co and Ni, respectively. More ad-

vanced calculations in the t-matrix approach gave the ES $S_e = 0.21$ eV and $S_t = 0.37$ eV for Ni [25] which agree better with the experimental values of 0.2 eV and 0.33 eV than our numbers extracted from canonical fcc band. It would be of interest to investigate the explicit role of s-p hybridization and to consider the excited states beyond the low-density limit by a proper extension of LA.

The flexibility of the LA allows to investigate as well nearest-neighbour correlations. One finds a decrease of AF correlations except for $3.5 < n_d < 6.5$, where these correlations are enhanced [26], in agreement with the phase diagram of figure 3. Surprisingly, the energy gain connected with the spin-spin correlations for the neighbouring atoms is lower than 100 K per atom [26]. It is much smaller than the Curie temperature and indicates that the magnetic order in P phase may exist only within domains exceeding certain critical size. The stability and the role of such domains in neutron scattering have to be investigated further.

Summarizing, we have reviewed the most important results obtained for correlation effects in 3d metals by making use of the LA. This method contributes significantly to our present understanding of local correlations in transition metals and provides a systematic method to correct the results of LSDA calculations by a proper inclusion of nonlocal effects. It was also generalized to finite temperatures in which case it improves the static appoximation in the functional integral method [27].

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