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Orbital magnetism in transition-metal systems: The role of local correlation effects

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Abstract. - The influence of correlation effects on the orbital moments for transition metals and their alloys is studied by first-principle relativistic Density Functional Theory in combination with the Dynamical Mean-Field Theory. In contrast to the previous studies based on the orbital polarization corrections we obtain an improved description of the orbital moments for wide range of studied systems as bulk Fe, Co and Ni, Fe-Co disordered alloys and 3d impurities in Au. The proposed scheme can give simultaneously a correct dynamical description of the spectral function as well as static magnetic properties of correlated disordered metals.

The growing interest in magnetic materials, their surfaces and nanostructures requires improved theoretical first-principle methods for their description, in particular, when a complex behavior of magnetic properties is observed as in low dimensional systems as, e.g. magnetic clusters, multilayers, thin films and magnetic impurities [1–3]. Their magnetic anisotropies, magneto-optical spectra, magnetic dichroism and other important properties are caused by spin-orbit coupling. While the spin magnetic moments for 3d-transition metals (3d-TM), their alloys and impurities in non-magnetic host are described rather accurately by density functional theory in the local spin-density approximation (LSDA), the orbital moments are systematically underestimated. The reason for this is well-known: the functional variables of the LSDA potential (the charge and spin density) are defined as averages over occupied orbitals. It is natural that such an approximation gives a good description only for the quantities which are slightly dependent on the deviations of orbital occupation numbers from their average, as e.g. spin magnetic moments.

An often used approach to improve the description of orbital magnetism is the so-called orbital polarization correction (OP) scheme introduced by Brooks *et al.* [4–6] in a form of an additional *ad hoc* term to the Hamiltonian. As it was shown by Ebert and Battocletti [7] the OP enhancement of the orbital moment partially could be realized by utilizing the more general current density functional theory. Analyzing the CDFT Eschrig *et al.* [8] have derived a systematic expression for the OP correction (for an overview and results of this approach see Ref. [9]). However, despite of a quite accurate description of the orbital moments in pure 3d-TMs and their alloys [10, 11], the LSDA+OP calculations noticeably overestimate

the unquenched orbital moments of the $3d$ -TM impurities in noble metal hosts [9, 12, 13]. In the case of clusters deposited on metal surfaces Gambardella *et al.* [2] have noticed that the Racah parameter has to be reduced by about 50% in order to describe the experimental orbital moments correctly. However, in this case the calculated magnetic anisotropy is still much too high [2, 14].

An alternative approach is based on the explicit account for the local (on-site) many-body correlations. In particular, Solovyev *et al.* [15, 16] have shown on the basis of calculations within the random-phase approximation that the OP picture is one of the limits of the more general LSDA+U concept [17] and the later can provide a better agreement with experiment for pure Fe, Co and Ni.

On the other hand, the LSDA+U approach fails to give a proper description for the spectral properties of the $3d$ -TMs having problems with the bandwidth, spin splitting and satellite in Ni, absence of quasiparticle damping, etc. [18, 19].

A state of the art way to treat the local correlation (Hubbard) effects is based on the Dynamical Mean-Field Theory (for review see [20]) which takes into account dynamical correlation effects, in particular spin-flip processes induced by fluctuations. Combined with the LSDA this scheme (LSDA+DMFT) provides a very reliable basis explaining a wide range of both static and spectral properties of $3d$ -TM materials (magneto-optics, photoemission, total energy, etc.) [18, 19, 21–23]. In contrast to all the previous approaches this method allows to study systematically the temperature dependence of the electronic structure and gives an adequate description of magnetic properties of Fe and Ni in a broad temperature range [18].

The well-known complication of combining the LSDA with the DMFT is the uncertainty in separating of the Hubbard Hamiltonian from the LSDA one, the so-called double-counting problem. As it was indicated by numerous DMFT studies, the static many-body effects which can be overcounted in the LSDA+DMFT combination are relatively small in $3d$ -TMs. Accordingly, for the description of spectral properties the established procedure is to leave only the dynamical part of the self-energy by setting it to zero at the Fermi level [18, 19, 24]. However, as it was recently shown by Braun *et al.* [23], that this approximation is not sufficient for a precise description of the angular-resolved photoemission spectra of Ni and an additional static orbital polarization should be included.

In this letter we demonstrate that accounting for the orbital polarization in the static part of the LSDA+DMFT provides a proper description not only for the spectral properties but also for the spin and orbital magnetic moments for a wide range of $3d$ -TM systems (bcc Fe, hcp Co and fcc Ni, bcc $\text{Fe}_x\text{Co}_{1-x}$ disordered alloys as well as $3d$ -impurities in the Au host).

The calculations were done within the relativistic full potential Green's function (SPR-KKR) method [25]. As a DMFT-solver the relativistic version of the so-called Spin-Polarized T-Matrix Plus Fluctuation Exchange (SPTF) approximation [24, 26] was used. According to this scheme the local Green's function is obtained by the corresponding site projection of the full KKR Green's function. The local Green's function is needed to obtain the bath Green's function for the Anderson impurity model via the saddle-point equation. The bath Green's function is used as an input for the SPTF scheme to calculate the local self-energy. The latter is added as an additional energy-dependent potential in the radial Dirac equation which is solved to calculate the new full KKR Green's function. This procedure is repeated until the self-consistency in both the self-energy and the charge density is achieved. The scheme has already been successfully applied for the description of magneto-optics [27] and photoemission [22, 23] in $3d$ -TMs including corresponding matrix element effects.

In the present work we concentrate on a more accurate account for the orbital polarization when calculating the self-energy. This is achieved by treating the static part of the self-energy on a Hartree-Fock level (first-order contribution in terms of the Coulomb interaction) described in a local approximation to the self-energy by the LSDA+U method. The static double-counting is subtracted from the self-energy in the so-called “around mean-field

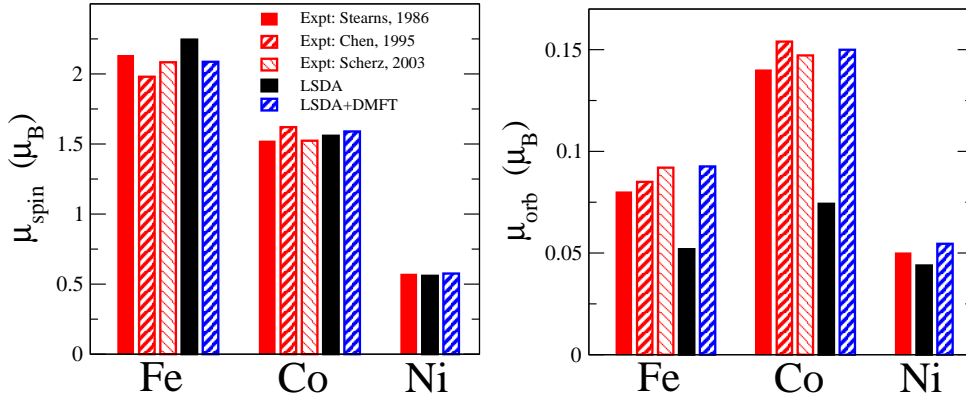


Fig. 1: (color online) Spin (left panel) and orbital (right panel) magnetic moments in bcc Fe, hcp Co and fcc Ni calculated using LSDA+DMFT (hatched blue bars) compared with plain LSDA calculations (black filled bars) and experimental data (red bars) taken from Refs. [29–31]. The corresponding DMFT parameters are $U_{\text{Fe}} = 2$ eV, $U_{\text{Co}} = U_{\text{Ni}} = 3$ eV and $J_{\text{Fe}} = J_{\text{Co}} = J_{\text{Ni}} = 0.9$ eV.

limit” (AMF) of LSDA+U as given by Czyzyk and Sawatsky [28]:

$$V_{m\sigma}^{\text{LSDA+U}}(\vec{r}) - V_{m\sigma}^{\text{LSDA}}(\vec{r}) \approx \sum_{m'} U_{mm'} (n_{m'-\sigma} - n_{-\sigma}^0) + \sum_{m' \neq m} (U_{mm'} - J_{mm'}) (n_{m'\sigma} - n_{\sigma}^0), \quad (1)$$

where $n_{m\sigma}$ are the occupation numbers of the localized d -orbitals and n_{σ}^0 stands for the sum $\frac{1}{2l+1} \sum_m n_{m\sigma}$.

The self-energy within the DMFT can be calculated in terms of two parameters: averaged screened Coulomb interaction U and exchange interaction J . For the latter the screening is usually not crucial; the value of J can be calculated directly from LSDA and is approximately equal to 0.9 eV for all $3d$ elements. This value has been adopted for all calculations presented here. Different methods of calculating the screened Coulomb interaction U for $3d$ -TMs lead to estimates in the range between 2-3 eV which have been used here (see discussion below).

A comparison to experiment for the spin and orbital magnetic moments calculated within LSDA+DMFT for bcc Fe, hcp Co and fcc Ni using the experimental values for the lattice parameters is shown in Fig. 1. The self-energy was parameterized using the values $U = 3$ eV for Co and Ni, and $U = 2$ eV for Fe. As expected, the LSDA+DMFT approach gives results similar to the OP correction: the small orbital splittings imposed by the LSDA+DMFT around the Fermi level have almost no effect on the spin moment, but enhance the orbital moment in an appreciable way.

By construction the dynamical part of the self-energy Σ in the vicinity of the Fermi level behaves like that of a Fermi liquid. Thus it cannot noticeably affect integral quantities as spin and orbital magnetic moments. On the other hand, the applied AMF static double counting which splits the orbitals only slightly at the Fermi level, has no impact on the renormalization of the density of states. As it follows from Fig. 2, the total DOS curves calculated within LSDA and LSDA+U as well as within LSDA+ Σ (e.g. only dynamical part of self energy is used) and LSDA+DMFT are nearly indistinguishable.

As the energy shifts of the $(-m, -m)$ and (m, m) matrix elements of the Green’s function occur in opposite directions, the total DOS shift for a given spin character appears to be small. As a result, the most affected quantity is the orbital magnetic moment while the change of the spin moment is negligible. At the same time the renormalization of the spectrum is controlled by the dynamical part of the self-energy.

It follows from the various DMFT studies as well as from the DMFT+GW-based calculation [32] that realistic values of U for $3d$ -TMs are found between 2-3 eV. As it is shown in Fig. 1 this range of U parameters brings both spin and orbital moments into very close

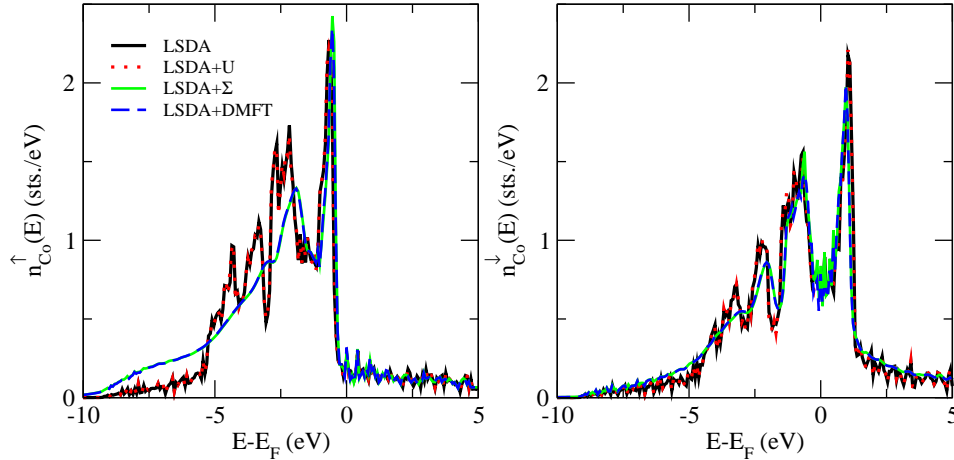


Fig. 2: (color online) Spin-resolved total DOS for hcp Co calculated via different approaches: black solid curve corresponds to plain LSDA, dotted (red) curve - accounts for local static correlations only (LSDA+U), light (green) solid line - only dynamical part of the self-energy (LSDA+ Σ) is used, dashed (blue) - both static and dynamic correlations are taken into account (LSDA+DMFT). The corresponding DMFT parameters are $U_{\text{Co}} = 3$ eV and $J_{\text{Co}} = 0.9$ eV.

agreement with experiment. In the case of Fe the deviation of the orbital moment for U above 2 eV are found to be rather big (see Fig. 3), so that the optimal values of U are confined within 1.5-2 eV. On the other hand, it was already proposed [18] that the local approximation (DMFT) works much better for Ni and Co than for Fe due to relative softness of magnons in the latter case. Recently, the essential non-locality of correlation effects in Fe was also demonstrated experimentally by angle-resolved photoemission [33].

It is worth to mention that some of the experimental results (Refs. [30,31]) are obtained from the measurements of the x-ray magnetic circular dichroism (XMCD) at the $L_{2,3}$ -edges. The sum rules used to derive the spin and orbital magnetic moments from XMCD spectra provide only the d -shell contributions to the total spin and orbital moments. In Fig. 1 these values are compared to the calculated total spin and orbital moments. However, as it follows from the calculations, the s - and p -contributions to the total spin moments constitute at

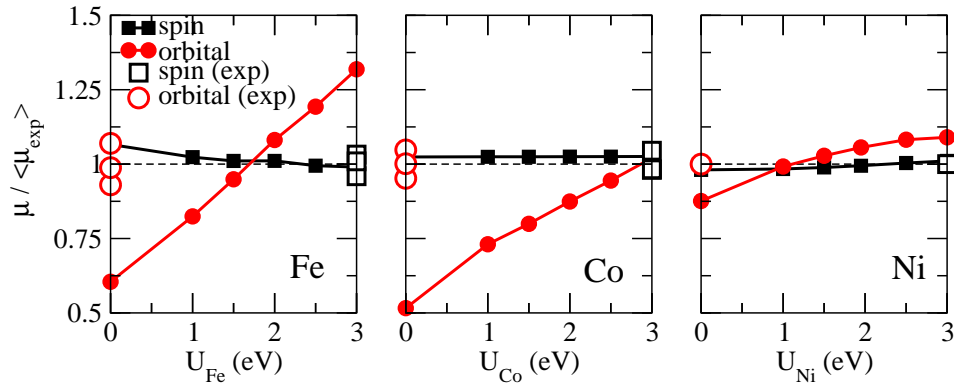


Fig. 3: (color online) Dependence of spin (black squares) and orbital (red circles) magnetic moments on U parameter. Magnetic moments are given in units of ratios of $\langle \mu_{\text{exp}} \rangle$ which is the average over the experimental moments (taken from Refs. [29–31]). Experimental values are marked with open squares (spin) and circles (orbital). The case $U = 0$ corresponds to the plain LSDA calculations. For all $U \neq 0$ the J parameter is fixed to 0.9 eV.

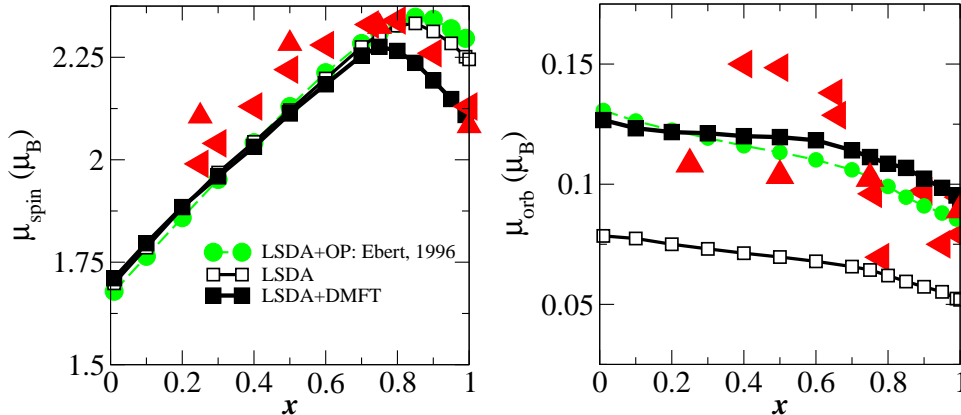


Fig. 4: (color online) Spin (left panel) and orbital (right panel) total magnetic moments of disordered bcc $\text{Fe}_x\text{Co}_{1-x}$ alloys calculated as a function of Fe concentration x via LSDA+DMFT (black line, filled squares), compared to present plain LSDA (black line, open squares), LSDA+OP calculations [11] (green line, filled circles), and experimental data (red triangles) taken from Refs. [29]. The corresponding DMFT parameters are $U_{\text{Fe}} = 2$ eV, $U_{\text{Co}} = 3$ eV and $J_{\text{Fe}} = J_{\text{Co}} = 0.9$ eV. In nature the bcc structure exists only for $x > 0.25$.

most 5%. The corresponding contributions to the total orbital moments are found even smaller and thus could be neglected.

Among other advantages, the SPR-KKR method utilized in the present work can straightforwardly combine the Coherent Potential Approximation (CPA) theory describing disordered alloys with the DMFT scheme. The latter is illustrated for the bcc $\text{Fe}_x\text{Co}_{1-x}$ disordered alloys. As one can see from Fig. 4, while the spin magnetic moments for all approaches agree rather well, LSDA+DMFT considerably improves the orbital moments in comparison to plain LSDA calculations in a way similar to the result obtained by Ebert and Battocletti using the LSDA+OP combined with the CPA [11]. Also in contrast to both the LSDA and LSDA+OP calculations, a more pronounced agreement with experimental spin magnetic moments is achieved by LSDA+DMFT within the Fe-rich area of concentrations.

As a further example we consider the unquenching of the orbital moment of $3d$ -TM impurities embedded in Au. Tab. 1 illustrates the results of LSDA+DMFT calculations compared to the experimental orbital to spin moment ratios. For the case of a Co impurity we have reached a drastic improvement when comparing to previous OP studies [9, 12, 13]; the latter gives a ratio of orbital to spin magnetic moments of about 0.7 whereas the ratio calculated in the present work is very close to the experimental value 0.35. For the case of Fe the agreement with experiment is not perfect but still reasonable.

Here we want to mention that no relaxation of the lattice near the impurity was considered. As reported in Ref. [34] for the case of an Co impurity in Au the additional lattice relaxation (about 2%) leads to a about 5% decrease for the spin and 28% decrease for the

Table 1: Orbital to spin ratios of total magnetic moments of diluted Fe and Co impurities embedded in fcc Au host calculated via LSDA+DMFT compared with present plain LSDA and experimental data [12]. The corresponding DMFT parameters are $U_{\text{Fe}} = 2$ eV, $U_{\text{Co}} = 3$ eV and $J_{\text{Fe}} = J_{\text{Co}} = 0.9$ eV.

	LSDA	LSDA+DMFT	LSDA+OP [12]	Exp.
$\text{Fe}_{0.008}\text{Au}_{0.992}$	0.007	0.018	0.098	0.034
$\text{Co}_{0.015}\text{Au}_{0.985}$	0.109	0.345	0.7	0.336

orbital magnetic moment of the impurity atom, leading to a 25% reduction for the orbital to spin moment ratio. Assuming corresponding changes for our results gives good agreement with experiment. Thus, although the lattice relaxation around the impurity site might be an important factor a complete description of the magnetic properties of impurities require first of all a satisfying treatment of correlation effects.

Summarizing the results, we emphasize that the presented LSDA+DMFT scheme which has proven already its efficiency in the description of the spectral properties of 3d-TMs has also greatly improved the description of the orbital magnetic moments for pure transition metals, their alloys and impurities in noble metal host.

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