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Orbital contribution to the magnetic properties of nanowires: is the orbital polarization ansatz justified?

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Abstract. We show that considerable orbital magnetic moments and magneto-crystalline anisotropy energies are obtained for a Fe monatomic wire described in a tight-binding method with intra-atomic electronic interactions treated in a full Hartree Fock (HF) decoupling scheme. Even though the use of the orbital polarization ansatz with simplified Hamiltonians leads to fairly good results when the spin magnetization is saturated this is not the case of unsaturated systems. We conclude that the full HF scheme is necessary to investigate low dimensional systems.

PACS. 75.30.Gw Magnetic anisotropy – 75.75.+a Magnetic properties of nanostructures – 75.90.+w Other topics in magnetic properties and materials

In the bulk of ferromagnetic transition metals it is well-known that the orbital magnetic moment $\mathbf{L}$ is quenched and that the magneto-crystalline anisotropy energy (MAE) is very small as a result of crystal field and strong electron delocalization. In nano-objects the dimensionality or coordination is reduced so that the influence of intra-atomic Coulomb interactions, responsible for Hund's rules in the free atom, becomes more and more important and both the spin and orbital magnetic moments increase dramatically. This is seen in experiments on chains of Co atoms at step edges of Pt(997) [1] and Co single atoms or nanoparticles deposited on Pt(111) in which orbital moments as large as 1.1 μ_B per atom have been measured [2], associated with a considerable enhancement of the MAE.

On the theoretical side, in the Local Spin Density Approximation (LSDA) or in simplified tight-binding (TB) Hartree-Fock (HF) schemes where the intra-atomic matrix elements of the Coulomb interaction are averaged, the distribution of electrons between the orbital states of opposite magnetic quantum numbers m is poorly described, especially in low dimensional systems. As a result these approximations yield underestimated values of $\mathbf{L}$, even though these values increase when the dimensionality is lowered [3]. Eriksson et al. [4] have proposed to correct for this effect by adding a term proportional to $-\widehat{\mathbf{L}}^2/2$ in the Hamiltonian, treated in mean-field, which will be referred to as Orbital Polarization Ansatz (OPA) in the following. The effect of this term is obviously to increase $\langle\widehat{\mathbf{L}}\rangle$ [5]. A more rigorous way of obtaining both the spin and orbital moments is to solve the HF equations by taking into account all intra-atomic terms in the decoupling with all matrix elements of the Coulomb interaction $U_{\gamma_1\gamma_2\gamma_3\gamma_4} = \langle\gamma_1(\boldsymbol{r}),\gamma_2(\boldsymbol{r'})|\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r'}|}|\gamma_3(\boldsymbol{r}),\gamma_4(\boldsymbol{r'})\rangle$, where γ_i are atomic orbitals, expressed in terms of three Racah parameters A, B and C, for d electrons [6] in a system of homonuclear atoms. Starting from this Hamiltonian Solovyev et al. [7] have shown, in an elegant work, that the OPA cannot be derived analytically from the HF Hamiltonian except in some very special cases and that, even in the latter, the proportionality factor is not B as usually assumed but $3B/2$. Very recently Nicolas et al. [8] have discussed the effect of orbital polarization, using either a Stoner-like TB Hamiltonian with the OPA or an HF Hamiltonian in which the one and two orbital matrix elements of the Coulomb interaction are treated exactly in the spherical harmonics (SH) basis but three and four orbital terms are neglected. These latter terms depend both on B and C in the SH basis which results in a symmetry breaking that they claim to overcome by averaging over different orbital basis. On the opposite, a recent work by Xiangang Wan et al. [9] is based on a complete HF decoupling. However their effective intra-atomic potential (see Eq. (4) of their work) is the same as in LSDA+U while the TB part of their total Hamiltonian is not spin polarized. As a result when the approximations leading to the Stoner model are carried out in their equation (4), it does not lead to the correct Stoner parameter. Finally, Shick et al. [10] have shown that a better agreement with experiment is

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obtained for a monatomic Cobalt wire at a Pt(111) surface step edge when the rotationally invariant LSDA+U method of reference [11] is used instead of LSDA.

It is thus of fundamental importance to investigate not only the ability of the full HF scheme to predict large **L** and MAE in nano-objects, but also to check whether the OPA can account for these effects. In this paper we compare, on the simple model of a monatomic wire, the results given by the full HF decoupling and two currently used simplified Hamiltonians corrected or not by the OPA term. We use a TB model in a minimal orthogonal basis set of d valence orbitals $|i,\gamma,\sigma\rangle = |i,\gamma\rangle \otimes |\sigma\rangle$, of spin σ and orbital γ centered at site i. In the following γ will either denote cubic harmonics (CH) ($\gamma = \lambda = d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{3z^2-r^2}$) or spherical harmonics ($\gamma = m = -2,-1,0,1,2$). Our Hamiltonian H can be expressed as the sum of a standard one-body TB Hamiltonian H_0 (determined by the bare d level ε_0, and hopping integrals) and an electron-electron interaction Hamiltonian H_{int} in which only on-site electron-electron interactions are considered. The standard Hartree Fock decoupling leads to the one-electron Hamiltonian (denoted as HF1) which, in the second quantization formalism can be written

$$H_{\text{int}}^{\text{HF1}} = \sum_{\substack{i\gamma_1\gamma_2\gamma_3\gamma_4\\ \sigma\sigma'}} \Big(U_{\gamma_4\gamma_2\gamma_3\gamma_1} \langle c^{\dagger}_{i\gamma_4\sigma} c_{i\gamma_3\sigma}\rangle c^{\dagger}_{i\gamma_2\sigma'} c_{i\gamma_1\sigma'} - U_{\gamma_4\gamma_2\gamma_1\gamma_3} \langle c^{\dagger}_{i\gamma_4\sigma} c_{i\gamma_3\sigma'}\rangle c^{\dagger}_{i\gamma_2\sigma'} c_{i\gamma_1\sigma} \Big). \quad (1)$$

Note that this expression includes spin-flip terms due to spin-orbit coupling. The matrix elements $U_{\gamma_1\gamma_2\gamma_3\gamma_4}$ obviously depend on the atomic basis, but the resolution of the full Hartree-Fock Hamiltonian (namely without any approximation) must lead to the same results whatever the basis. However, the use of CH is quite attractive for discussing the OPA since in this basis the three and four orbital matrix elements of the electron-electron interaction are proportional to the Racah parameter B only [6]. Moreover in CH the different values of the two orbital matrix elements $U_{\lambda\mu\lambda\mu}$ and $U_{\lambda\mu\mu\lambda}$ ($\lambda \neq \mu$) only differ by terms proportional to B. The average values: $(1/4)\sum_{\mu,\mu\neq\lambda} U_{\lambda\mu\lambda\mu}$ and $(1/4)\sum_{\mu,\mu\neq\lambda} U_{\lambda\mu\mu\lambda}$ are independent of λ and are given by $U = A - B + C$ and $J = 5B/2 + C$ [12] while the one orbital terms $U_{\lambda\lambda\lambda\lambda}$ are all equal to $U + 2J$. This leads us to define (U, J, B) as a new set of parameters. The two orbital terms $U_{\lambda\mu\lambda\mu}$ (resp. $U_{\lambda\mu\mu\lambda}$) can then be expressed in terms of U and B (resp. J and B) while the three and four orbital terms are proportional to B only. As already stated, this is no longer true in the SH basis.

When B is neglected in the above Hamiltonian HF1, we recover the model (hereafter referred to as HF2) that has been used in our previous studies [13] ($U_{\lambda\mu\lambda\mu} = U$ and $U_{\lambda\mu\mu\lambda} = J$ for any pair of different orbitals λ and μ and no three and four orbital terms) in which spin-flip terms were omitted since the spin-orbit coupling interaction was not taken into account. Starting from this Hamiltonian, keeping only the diagonal terms and replacing each orbital population of a given spin by its average value, leads to a Stoner-like Hamiltonian (called HF3) that we have also investigated since it has widely been used in the literature [14]:

$$H_{\text{int}}^{\text{HF3}} = \sum_{i\lambda,\sigma} (U_{\text{eff}} N_i - \sigma I M_i/2) c^{\dagger}_{i\lambda\sigma} c_{i\lambda\sigma}. \quad (2)$$

In this Hamiltonian $I = (U + 6J)/5$ is the Stoner parameter while N_i and M_i are, respectively, the total charge and moment on site i. U_{eff} is equal to $(9U - 2J)/10$ if one derives HF3 from HF2 as explained above. Since here we are interested in systems with geometrically equivalent atoms (i.e., $N_i = N, M_i = M$) we can choose the energy zero in all Hamiltonians as $\varepsilon_0 + U_{\text{eff}} N$ so that the first term in equation (2) disappears from the total Hamiltonian HF3. The spin magnetism is governed by the Stoner parameter I that will be kept constant in all our calculations and determined so that it reproduces the experimental value of the spin moment in the bulk phase.

From the above discussion it is clear that HF2 differs from HF1 by terms proportional to B, this is also true for HF3 as far as this Hamiltonian is justified. Eriksson et al. [4] have proposed to introduce an OPA term to account for this difference. This term is written in meanfield $\Delta E_{\text{OP}} = -\frac{1}{2} B \sum_i \langle \boldsymbol{L}_i \rangle^2$ which reduces to $-\frac{1}{2} B \sum_i \langle L_{iz} \rangle^2$ when the spin and orbital moments have the same quantization axis z (which is strictly verified along high symmetry directions). The corresponding Hamiltonian is then:

$$H_{\text{OP}} = -B \langle L_z \rangle \sum_{i\gamma\gamma'} [L_z]_{\gamma\gamma'} c^{\dagger}_{i\gamma\sigma} c_{i\gamma'\sigma} \quad (3)$$

where $[L_z]_{\gamma\gamma'}$ are the matrix elements of the local orbital moment operator L_{iz}. $[L_z]_{\gamma\gamma'}$ is spin independent and diagonal in the SH basis when the orbital momentum quantization axis of the SH orbitals is rotated so that it coincides with the spin quantization axis. This is no longer true if the SH orbital momentum axis is along a crystallographic axis which is not parallel to the spin quantization axis, or when $[L_z]_{\gamma\gamma'}$ is expressed in the CH basis. Finally the last term of our Hamiltonian takes into account the intra-atomic spin-orbit interactions determined by the spin-orbit coupling parameter ξ.

A monatomic wire of a transition metal is a handy system to compare the results given by the various models described above. The parameters of the model are chosen to mimic Fe which is assumed to have $N = 7$ valence d electrons per atom in the bulk as well as in the wire. The hopping integrals $dd\sigma$, $dd\pi$ and $dd\delta$ are chosen proportional to (−6, 4, −1) and decrease with the interatomic distance according to a R^{-5} law. The numerical value of $dd\sigma$ is fitted to the bulk d band width of Fe ($W_d = 6$ eV) which leads to $dd\sigma = -0.749$ eV at the bulk nearest neighbor distance ($d = 4.7$ a.u.). First and second nearest neighbor hopping integrals have been taken into account. The Stoner parameter is $I = 0.67$ eV. The spin-orbit coupling parameter is taken from a previous work ($\xi = 0.06$ eV) [15]. It is well-known that the parameter U is strongly screened in metals. In particular in a recent paper Solovyev [16] has shown that this parameter is almost independent of the

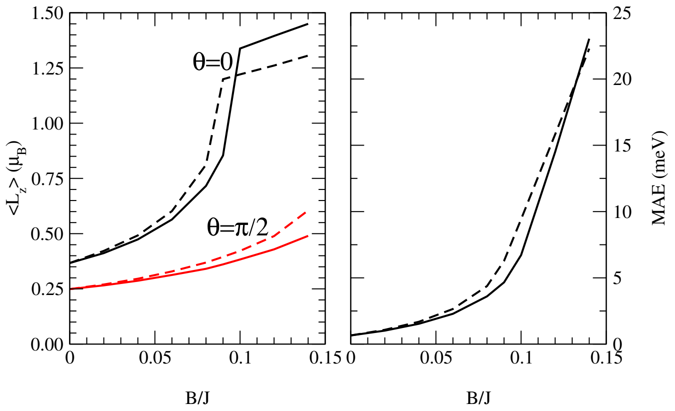

Fig. 1. $\langle L_z\rangle$ and MAE as a function of B/J from HF1 (full line) and HF2+OPA (HF3+OPA results are undistinguishable from the HF2+OPA (dashed line) ones) for a saturated magnetic Fe monatomic wire ($d = 4.7$ a.u.).

bare interaction. From Figure 1 of this reference it can be deduced that $U \simeq J$ in Fe [17]. In that case $I = 7J/5$ so that $U = J = 0.48$ eV, a numerical value in good agreement with that given by Solovyev. Finally, as in previous works [16], we have taken $B = 0.14J$ [12].

The calculations are carried out in k-space by diagonalizing the 10×10 Hamiltonian matrix using a sampling of $200k$ points and a Fermi broadening (1 meV) of the eigenvalues. We thus obtained a numerical accuracy of 0.1 meV on the total energy and 10^{-3} μ_B on the spin and orbital moments. Self-consistency is achieved by using an iterative procedure. Depending on the input density matrix several solutions sometimes exist. In the following, only the minimal energy solution is reported.

When applied to bulk Fe, the complete HF decoupling yields $\langle 2S_z\rangle = 2.12$ μ_B and $\langle L_z\rangle = 0.08$ μ_B when $B = 0$ (HF2 model), and $\langle 2S_z\rangle = 2.11$ μ_B and $\langle L_z\rangle = 0.12$ μ_B when B is taken into account (HF1 model). Then, we have compared the results derived from the five models (HF2 and HF3 with and without H_{OP}, and HF1) for the spin and orbital moments with magnetizations along the wire ($\theta = 0$) and perpendicular to it ($\theta = \pi/2$) and the corresponding MAE, i.e., $\Delta E = E_{tot}(\theta = \pi/2) - E_{tot}(\theta = 0)$ where E_{tot} is the total energy per atom of the system. Two interatomic distances have been considered: the bulk interatomic distance at which the spin magnetization is saturated and a shorter distance (4.25 a.u.) corresponding to unsaturated spin moments. The results are given in Table 1.

Let us first discuss the wire at the bulk interatomic distance. All models agree to predict saturated spin magnetization, i.e., the spin magnetic moment is 3 μ_B to less than a few 10^{-3} μ_B. As a consequence the effective atomic orbital levels with down spin are identical in HF2 and HF3 models since $U = J$. This is no longer true for the up spin orbitals for which the atomic levels are orbital dependent with HF2 and not with HF3. However the average atomic level is the same in both models. Therefore the orbital moment, which arises only from the spin down band, the spin up band being filled, is almost identical in both models similarly to the total energy (see Tab. 1). As expected the orbital moments for both magnetization orientations and the associated MAE, even though reinforced compared to the bulk ones, are largely underestimated by the HF2 and HF3 models with $B = 0$ compared to those predicted by the complete HF decoupling (HF1). When the OPA term is added to the HF2 and HF3 Hamiltonians, the results given by the latter models become in fair agreement with those obtained from HF1 for the orbital moment while the MAE is well reproduced.

Table 1. The spin ($\langle 2S_z\rangle$) and orbital ($\langle L_z\rangle$) magnetic moments (in μ_B per atom) for a monatomic Fe wire and two magnetization orientations (parallel ($\theta = 0$) and perpendicular ($\theta = \pi/2$) to the wire) and the corresponding magnetocrystalline anisotropy MAE ($E_{tot}(\pi/2) - E_{tot}(0)$) in meV per atom for two interatomic distances.

	HF1	HF2	HF2 OPA	HF3	HF3 OPA
			$d = 4.7$ a.u.		
$\langle 2S_z(0)\rangle$	3	3	3	3	3
$\langle 2S_z(\pi/2)\rangle$	3	3	3	3	3
$\langle L_z(0)\rangle$	1.45	0.37	1.31	0.37	1.31
$\langle L_z(\pi/2)\rangle$	0.49	0.25	0.61	0.25	0.60
MAE	23.4	0.7	22.3	0.6	22.3
			$d = 4.25$ a.u.		
$\langle 2S_z(0)\rangle$	1.51	1.24	1.23	0.94	0.78
$\langle 2S_z(\pi/2)\rangle$	1.51	1.23	1.24	0.93	0.94
$\langle L_z(0)\rangle$	0.33	0.19	0.39	0.24	1.07
$\langle L_z(\pi/2)\rangle$	0.21	0.10	0.18	0.08	0.15
MAE	–0.7	-0.3	1.5	0.0	6.2

The above trends completely change when the interatomic distance is shortened to 4.25 a.u.. It is first seen that the spin moment depends on the model. In this respect the HF2 model is much better than the HF3 one. Moreover, taking into account the OPA term leads to an increase of the orbital moments for both magnetization orientations which are rather close to the HF1 results for HF2 but not for HF3.

To summarize this discussion we can state that the OPA is rather good for saturated spin magnetization while for the unsaturated case it leads to results depending critically on the approximations made concerning the electron-electron interaction Hamiltonian. In order to verify that the good performance of the OPA for the saturated spin magnetization is not due to the particular value of B, we have studied the variation of $\langle L_z\rangle$ at $\theta = 0$ and $\theta = \pi/2$ and the associated MAE as a function of the ratio B/J. The results (Fig. 1) show that the OPA gives the right trends on the full domain of B/J values that we have investigated. In particular an abrupt variation of $\langle L_z\rangle$ at $\theta = 0$ occurs around a critical value of $B/J \simeq 0.09$ above which the upper δ band (the corresponding eigenfunctions

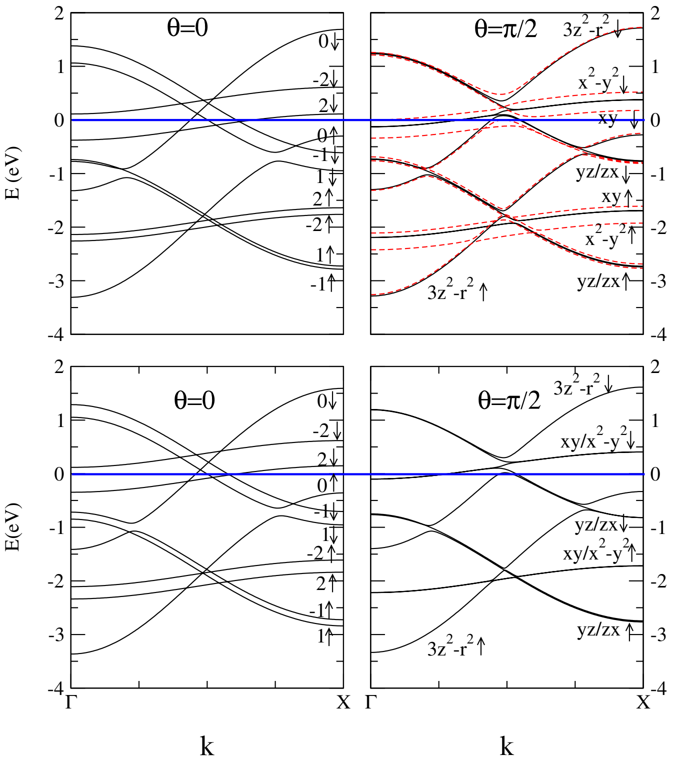

Fig. 2. HF1 (top) and HF2+OPA (bottom) band structure (referred to the Fermi level) for a magnetic Fe monatomic wire ($d = 4.7$ a.u.) with a magnetization parallel ($\theta = 0$) and perpendicular ($\theta = \pi/2$) to the wire. All results are obtained for $U/J = 1$ and $B = 0.14J$ save for the dotted band structure of the top right panel obtained for $U/J = 1.34$ and $B = 0.14J$. Each curve is labelled by the main character of its eigenfunction, i.e., denoted by the m value for $\theta = 0$ and the CH for $\theta = \pi/2$.

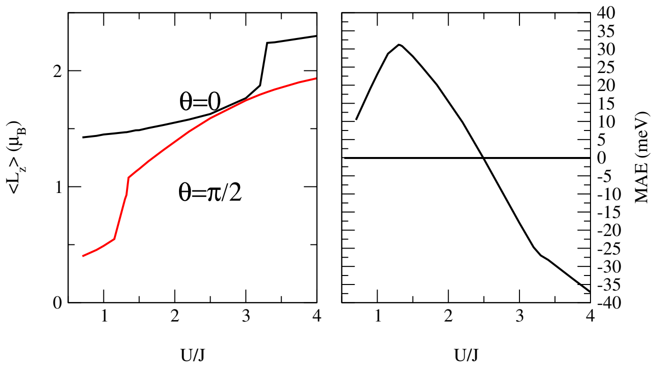

Fig. 3. $\langle L_z \rangle$ and MAE as a function of U/J from HF1 for a magnetic Fe monatomic wire ($d = 4.7$ a.u.).

being mostly linear combinations of SH with $|m| = 2$) of minority spin becomes empty.

Even if the OPA works reasonably in the saturated spin magnetization case for determining $\langle L_z \rangle$ and the MAE, this does not mean that it reproduces the band structure correctly. Let us first note that for $\theta = 0$, the eigenfunctions have a largely dominating single SH character while at $\theta = \pi/2$ they are almost pure single CH orbitals. The band structures corresponding to HF1 and HF2+OPA are drawn in Figure 2 (the band structure of HF3+OPA is close to that of HF2+OPA). At first sight they look quite similar. However a closer examination reveals some differences. Let us first comment on the majority spin bands at $\theta = 0$. While the splittings of the $|m| = 2$ (δ) and $|m| = 1$ (π) bands are respectively given by 2ξ and ξ with the HF1 model, they become $2\xi - 4B\langle L_z \rangle$ and $\xi - 2B\langle L_z \rangle$ with both the HF2 and HF3 models incuding OPA, respectively. In addition the m character of the bands is reversed, i.e., the $m = 2(1)$ band is above the $m = -2(-1)$ band in the HF1 while it is the opposite with the HF2 and HF3 models including OPA. This inversion does not occur in the minority spin bands and the splittings of the δ and π bands are not exactly the same with the HF2+OPA and HF3+OPA as with the HF1 models. At $\theta = \pi/2$ all models agree that for $U = J$ there are almost no band splittings and that the removals of degeneracy around the midpoint between Γ and X are more pronounced in the minority bands than in the majority ones.

Finally it is interesting to study the variation of $\langle L_z \rangle$ and of the MAE with the HF1 model when the ratio U/J is varied by keeping the Stoner parameter fixed. Indeed this ratio is not perfectly known. The results are shown in Figure 3. Abrupt variations of $\langle L_z \rangle$ are observed at $U/J \simeq 1.34$ when $\theta = \pi/2$ and $U/J \simeq 3.25$ when $\theta = 0$. They correspond respectively to the occurrence of a splitting of the δ bands (see Fig. 2) and to the complete filling of the lowest δ band of minority spin. These abrupt changes of $\langle L_z \rangle$ are associated with a change of sign of the variation of the MAE as a function of U/J.

In conclusion we have studied orbital polarization effects for a Fe monatomic wire with various HF Hamiltonians in a tight-binding scheme: a full HF Hamiltonian (HF1) including all the Coulomb interaction matrix elements, a simplified one (HF2) neglecting the Racah parameter B, and finally a Stoner-like Hamiltonian (HF3). OPA has then been reintroduced in HF2 and HF3 as proposed by Eriksson et al. [4]. With HF1 we find that very large values of $\mathbf{L}$ and MAE are possible in agreement with existing experiments. The same trends are obtained by adding the OPA to simplified Hamiltonians when the spin moment is saturated, however noticeable differences appear in the band structure since some splitting and band characters are wrongly reproduced. This fair agreement strongly deteriorates when dealing with an unsaturated system, especially with the Stoner-like model. It is thus of prime importance to use the HF1 model for the study of low dimensional systems with much more complex geometries (surfaces, clusters, break junctions), in a realistic s, p and d basis set, or to implement it in ab-initio codes. Indeed from our results large orbital moment and giant MAE and anisotropy of magneto-resistance in low dimensional systems such as break junctions are expected [18].

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