Revisiting magnetism of capped Au and ZnO nanoparticles: Surface band structure and atomic orbital with giant magnetic moment

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In this article we review the exotic magnetism of nanoparticles (NPs) formed by substances that are not magnetic in bulk as described with generality in Section 1. In particular, the intrinsic character of the magnetism observed on capped Au and ZnO NPs is analysed. X-ray magnetic circular dichroism (XMCD) analysis has shown that the magnetic moments are intrinsic and lie in the Au and Zn atoms, respectively, as analysed in Section 2, where the general theoretical ideas are also revisited. Since impurity atoms bonded to the surface act as donor or acceptor of electrons that occupy the surface states, the anomalous magnetic response is analysed in terms of the surface band in Section 3. Finally, Section 4 summarizes our last theoretical proposal.

1 Influence of size on magnetic properties

As is known, the nanoscale alters the properties of bulk ferromagnetic materials that in form of NPs show different coercivity, remanence, relaxation time, etc. However, this is not the only effect of nanoscale on the magnetic properties of the materials. Recent experimental results showed that the nanoscale can also induce ferromagnetic behaviour in materials that are non ferromagnetic in bulk state.

1.1 Surface to volume number of atoms. Magnetism of Pd and Pt NPs

In particular, it has been demonstrated that small Pd NPs show ferromagnetic behaviour [1]. Pd is an fcc metal exhibiting enhanced Pauli paramagnetism.

An important characteristic of NPs is the enormous surface to volume number of atoms. There are two important consequences related to this ratio. For an ideal solid the surface can be thought of as a defect. The breaking of translational symmetry gives rise to different local physical properties. The electronic states change to surface states, the magnetic anisotropy is modified to surface anisotropy and the crystalline short range order undergoes a sharp discontinuity as the surface is approached from the internal volume. Thereby, all the physical properties sensitive to short range order exhibit surface behaviour different to that observed in the volume. The solid properties can be roughly envisaged as an average of the surface and volume properties, the relative weights being the surface and volume atoms number fraction. The number fraction of surface atoms, \( n_s \), for a solid with dimension \( L \) and average interatomic distance \( a \) is given by \( \beta a/L \), where \( \beta \) is a sample geometry dependent parameter (\( \beta = 6 \) for a cubic shape). The number fraction of volume atoms, \( n_v \), is then given by \( 1 - \beta a/L \). For bulk samples \( n_v \) is much greater than \( n_s \) and the macroscopic
properties are those corresponding to volume atoms slightly modulated by surface contribution. For instance, for a cube shaped particle with \(a = 1.5 \text{Å} \) and \(L = 1 \text{mm}, n_s \) is about \(10^{-6}\). However, for \(L = 1.5 \text{nm}, n_s \) is about 0.9 and the average sample properties are expected to be those corresponding to the surface. As a consequence of these considerations about the overwhelming influence of surface on physics of NPs, it is interesting to remember that high resolution electron diffraction microscopy has shown that metallic NPs often exhibit different crystalline symmetry than bulk samples of the same metal. These observations consist in a direct evidence that the leader role of surface in NPs is strong enough to modify even the crystalline structure. For instance fcc bulk palladium evolves towards other structures different form the fcc-cube octahedron, such as icosahedra \([2]\) when dimensions fall into the nanoscale realm. It is the high surface energy of fcc high energy facets that forces the crystalline structure. For instance fcc bulk palladium evolves towards other structures different from the fcc-cube octahedron, such as icosahedra \([2]\) when dimensions fall into the nanoscale realm. It is the high surface energy of fcc high energy facets that forces the crystalline order of NPs breaking the typical bulk symmetry to avoid these characteristic fcc high energy facets.

Although Pd has a large density of states at the Fermi level, \((N(E_F) = 1.23 \text{eV}^{-1} \cdot \text{spin}^{-1} \cdot \text{atom}^{-1})\) it is not enough to satisfy the Stoner criterion for ferromagnetism in its bulk state (for \(Pd J = 0.71 \text{eV} \) and therefore \(N(E_F) \cdot J = 0.87 < 1\)). Surprisingly, as shown in Fig. 1(b), in the ferromagnetic Pd NPs the magnetic behaviour results almost independent of \(T\) in the range 5–300 K, without superparamagnetic effects, as it happens for NPs of bulk ferromagnetic materials. The detailed analysis performed by TEM on these NPs \([1]\) showed that most of these NPs exhibit twin boundaries in order to reduce their energy: fcc metals present a highly anisotropic surface energy. In a spherical NP, all the possible surface orientations are present. However, the presence of twin boundaries allows to avoid the most energetic orientations, therefore reducing the surface energy.

The twin boundary formation energy for fcc metals is quite low, and thus, in the energy balance, these twin boundaries reduce the total (surface plus volume) energy. In this situation, the NPs exhibit a large fraction of atoms without cubic symmetry: those at the surface (representing a significant percentage of the total) and those close to the twin boundaries. The lack of cubic symmetry prevents the splitting of d band into the \(t_{2g}\) and \(e_g\) sublevels and therefore, it yields to narrowing of the band. Hence, in the vicinity of those atoms there is a higher density of states that could be enough to satisfy the Stoner criterion.

Magnetic response has also been observed in Pt NPs \([3]\).

1.2 Influence of the capping molecules: Magnetism of capped Au and ZnO NPs

The second consequence of the governing role of surface is the enormous influence that atoms at the environment exert on the NPs physical properties. In the case of NPs the solid is formed almost only by the surface itself. Therefore, the sample as a whole is dramatically sensitive to the atoms coating the particle in several possible different forms. This influence has been experimentally found to be as important as the previously discussed one, as for instance through the effect of capping on the magnetic properties. In bulk solids the dependence of physical properties on the chemical environment can be defined as weak when compared to that exerted on NPs. Recent experimental studies have shown that physical properties of NPs can be tuned by suitable coating. It seems to be obvious that covalent bond, for instance, of surface atoms of NPs are going to affect drastically their electronic and, consequently, the optical and magnetic properties. In other words, the electronic structure extremely sensitive to the nanoscale will also be deeply modified by the chemical bonding of the atoms. Note that coating of NPs by covalent bond to other type of atoms gives rise to a singular type of chemical compounds very different to those we are familiar with in bulk scale. For instance a Au NP coated with thiol bonding is not expected to behave as gold sulphide, even though a large number of covalent Au–S bonds seems identical in both type of sample\[4]\.

Recently, anomalous magnetism has been observed and reported in different types of nanoparticles (NPs) either uncapped or capped with some organic molecules \([5–9]\). We will focus along this review only on both of them, capped Au \([5]\) and ZnO \([9]\) NPs for which X-ray circular magnetic dichroism, XCMD, has neatly shown that the magnetic moments lie indeed in the Au and Zn atoms. It is important to remark that the possible influence of small concentration (few ppm) magnetic impurities can distort the measurement of the macroscopic magnetization leading to dramatic errors in the interpretation of the experimental results. This effect has been carefully analysed \([10, 11]\).

The more common characteristics of the observed anomalous magnetic behaviour can be summarized as follows: (i) in all cases the saturation magnetization is very low, typically in the range of \(10^{-1}\) or \(10^{-2}\) Bohr magnetons per atom, and is reached at moderate applied fields (0.5 T) and (ii) the magnetization values are weakly dependent of temperature in the range from 4 K up to room temperature. The magnetism observed in NPs of substances that are not magnetic in bulk raises two main questions: (i) What is the

![Figure 1](online color at: www.pss-b.com) Hysteresis of Pd NPs (a) and its thermal dependence of the magnetization (b). From Ref. [1](Copyright 2003, American Physical Society, http://prl.aps.org/abstract/PRL/v91/i23/e237203).
source of the magnetic moment? and (ii) Why the low saturating field at room temperature?

2 XCMD analysis in Au and ZnO NPs X-ray circular magnetic dichroism (XCMD) is a magnetometric technique that results particularly interesting for the analysis of NP [12, 13]. As stated above, usually NP are embedded in a medium or deposited onto a substrate in which they only represent a small percentage of the total mass. Thus, the presence of impurities in the surrounding media can lead to large mistakes in the measurement of their magnetic properties.

The XCMD is based on the fact that the absorption of light by the matter may depend on the relative light polarization and the spin orientation of the atomic magnetic moments. Thus, when an electron has a certain polarization of the spin, the absorption of light at a certain edge will be different for light right-handed polarized or left-handed polarized. Actually, measuring the absorption of both light polarization it is possible to calculate the magnetic moment of the electron by means of the so-called summation rules. Furthermore, the technique allows us to separate the spin and orbital contribution to the magnetic moment.

As the measurements are carried out at the absorption edge of a certain element, we only observe the contribution of this particular element. This feature results particularly interesting when dealing with alloys NPs, as it also allows us to measure separately the contribution of each element to the total magnetization. For instance, contribution of Fe and Pt to magnetization of FePT nanostructures has been interesting when dealing with alloys NPs, as it also allows to measure separately the contribution of each element to the total magnetization. For instance, contribution of Fe and Pt to magnetization of FePT nanostructures has been recently measured separately showing that surprisingly, the presence of Pt increase the magnetization of Fe [14].

2.1 Thiol capped Au NPs Garitaonanindia et al. [15] used two element specific techniques to show the intrinsic magnetism of thiol capped gold NPs: XCMD and Mössbauer effect.

It was astonishing to the discovery that Au NPs also exhibit ferromagnetic behaviour up to room temperature [5]. Differently to the case of Pd, Au is diamagnetic with a very low density of states at the Fermi level \( N(E_F) = 0.3 \text{ eV}^{-1} \cdot \text{spin}^{-1} \cdot \text{atom}^{-1} \). For Au NPs the presence of ferromagnetic behaviour was associated with selective capping of the NP with certain molecules. Au NPs capped with weak interacting tetraalkylammonium that merely passivate the particle and avoid further growing (named Au-NR) show diamagnetic behaviour as bulk Au does. On the contrary, Au NPs capped with strongly interacting thiols (named Au-SR), exhibits ferromagnetism up to room temperature as shown. In this case the presence of ferromagnetic behaviour was associated with the covalent bond between Au atoms at the NP surface and the S atoms at the end of the thiol chain. It was proposed that this bond gives rise to a charge transfer from the Au to the S, therefore, modifying the electronic configuration of both atoms and, consequently, the value of their magnetic moments.

However, two main questions were hidden behind the experimental observation of macroscopic magnetization: is the origin of the magnetism located on the Au atoms? If it is the case, are there more elements susceptible to induce magnetism on them?

It was observed that X-ray absorption structure (XAS) of the Au atoms of thiol capped Au NPs present and increase in the intensity of the resonance at the threshold (whiteline) associated with \( 2p_{3/2} \rightarrow 5d_{3/2} \) dipole transition with respect to the bare Au metal. That probes the existence of unoccupied d states in the Au atoms at the Fermi level. Garitaonanindia et al. measured the difference between the absorptions of the sample to the right and left circularly polarized X-ray, (XMCD), under an applied magnetic field.

Two different XCMD signals with an order of magnitude of \( 10^{-5} \) of the XAS step height were clearly observed at both L2 and L3 edges. One of the signals was centred at 11.92 keV(L3) and at 13.74 keV(L2), and its sign changes when the applied field was reversed so verifying the magnetic origin of the contribution. By considering the XCMD signal proportional to the magnetization Garitaonanindia et al. also measured the amplitude of the signal at L3 as a function of the external magnetic field and found a clear hysteretic behaviour, similar to that obtained by macroscopic magnetization measurements.

Mössbauer spectroscopy is a well-known element selective technique based on γ-energy recoilless nuclear resonance. The Au spectra showed two components. The main one centred at \(-0.26 \text{ mm/s}\), comes from the core fcc Au atoms and is not magnetic. The isomer shift is in the range of the values found for Au atoms in clusters [16]. The second one is a split component that stems from the surface Au atoms. The quadrupolar splitting reflects the loss of symmetry respect to the inner atoms and the presence of chemical bonds. The splitting showed eight different transitions with well-known intensities. The experimental spectra were fitted resulting in a isomer shift of 3.55 mm/s, a quadrupolar splitting of \(-4.3 \text{ mm/s}\) a hyperfine field of 9.0 T, and a width of 2.0 mm/s.

Therefore, from the results reported in Ref. [15], the magnetism of thiol capped Au NPs can be ascribed to the electronic structure modification induced at the NPs surface by the chemical bonding to the capping molecules. The magnetic moment lie in the Au atoms of thiol capped Au NPs present and increase in the measured magnetism is intrinsic and not due to ferromagnetic impurities.

It is worth noting that De la Ventra et al. [17] were also able to detect clearly a similar XCMD spectra on thiol capped Au NPs embedded in a polyethylene matrix. A signal \( 0.8 \times 10^{-4} \) was found at the Au L3-edge.

Different reports on the exotic magnetic behaviour of Au and Ag NPs have appeared in the last years [18–25]. Most of the articles invoke the charge transfer between the surface Au atoms and the capping molecule as the origin of the unexpected magnetization. However, the details of the bonding are far of being well understood. Theory and experiments have been shown that the coverage of the

magic gold clusters by thiols with well-defined compositions [26–28] is rather complicated. Additionally, alkenethiols with longer chains on Au surfaces have been the focus of detailed theoretical studies [29] and the presence of several different metastable states are known. In these cases the sulphur atoms in the gold layers becomes arranged in a bridge configuration for the ground state.

Recent ab initio calculations carried out by Ayuela et al. [30] show that the S-Au bond is such that an electron is transferred to the Au cluster.

### 2.2 Capped ZnO NPs

The ferromagnetic like behaviour of ZnO NPs capped with different organic molecules, without introducing any transition element [9] pointed out that ZnO can exhibit magnetization independently of its possible induction through the dilution of ferromagnetic impurities. This finding represented a breakthrough with the commonly accepted point of view that the 3d band played an important role in the magnetism of semiconductor oxides.

Chaboy et al. [31] thoroughly studied the XAS and XMCD spectra of ZnO capped by organic molecules through N (amina) atoms. The formation of a well-defined interface between ZnO and the capping molecule was observed. Therefore, two different Zn atoms can be distinguished, the core and unbound Zn atoms and those surface Zn atoms bonded to N. XAS and XMCD Zn L₂,₃-edge spectra clearly indicate that the magnetism is not induced in the 3d band of Zn as in the measured energy region no XMCD signal could be observed, as indicated in Fig. 2(a). By contrast a neat XMCD signal is found at the Zn K edge as illustrated by Fig. 2(b). This result indicated that the magnetization is intrinsic or not associated with impurities and, furthermore, that it relays on the 4sp Zn conduction band. Note that the 4sp conduction band is completely empty for pure, non-doped and free of defects, ZnO. Therefore, the electrons occupying partially this band should reasonably be donated by the capping molecules.

Anderson and Nichols, Botello-Méndez et al. [32] had found that the effect of the complex bonding of carbon monoxide to Zn atoms on a ZnO surface can be summarized as the donation of one electron from the molecule to the 4sp surface orbitals of Zn that are initially empty. The 4sp magnetism observed by XMCD in capped ZnO NPs should be that of the electrons donated by the capping molecule. It is reasonable to assume that the bonding of surface Zn atoms to N atoms might also result in the donation of one electron by the capping molecule. Moreover, as Chaboy et al. observations suggest, these electrons should be confined in a thin Zn-N inter-phase extended on the surface of the NPs, thereby forming a system similar to a two-dimensional electron gas.

### 2.3 Magnetism in other type NPs formed by materials that are not magnetic in bulk, its universal character

Apart of the cases of capped Au and ZnO NPs in which selective techniques as XMCD and Mössbauer spectra have shown its intrinsic magnetism, many other reports based on macroscopic magnetization measurements invoke the appearance of ferromagnetism in NPs formed by substances that are not magnetic in bulk. For instance there exists a tremendous interest in semiconductor NPs. It was anticipated that transition metal-doped semiconductors will be good candidates for spintronic applications [33, 34]. NPs should also exhibit quantum confinement effects, consequently promising applications in optoelectronic as band gap tuning and band edge luminescence were predicted [35, 36]. NPs of Au were of special interest for biomedical applications as hyperthermia and drug delivery due to biocompatibility.

Sundaresan et al. [37] reported in 2006 the ferromagnetic character of CeO₂, Al₂O₃, ZnO, In₂O₃, and SnO₂ at room temperature. Sing et al. [38] observed room temperature ferromagnetism in thiol-capped CdSe and CdSe:Cu NPs. Note that CdSe becomes ferromagnetic, even being doped with a non-magnetic transition element as Cu. NPs of nitrides as GaN exhibits room temperature ferromagnetism [39].

Cu NPs were also reported to be ferromagnetic at room temperature when capped with dodecanethiol [15]. It is to be remarked that there appears a large dispersion in the reported values of the saturation magnetization in different articles. The influence of the capping coverage
factor, the nature of the capping molecule and the size of the NPs might explain these differences. However, the contribution of magnetic atoms diluted as non-detectable impurities together with the low values of the intrinsic magnetization must also be considered as a tremendous drawback for the accuracy of the magnetization measurements.

From this overview of the experimental results it can be concluded that, independently of the effects that have been customarily used to account for ferromagnetism in metals and dilute magnetic semiconductors [40–42] there should be a characteristic effect of surface physics underlying the surface magnetization of NPs. A component of the magnetization of the NPs seems to be universally induced at its surface. As experimentally found, by using XMCD, modification in the surface electronic structure yields modifications of the surface magnetic properties. In ferromagnetic NPs the surface component of the magnetization is masked by the core contribution. A characteristics of this surface component is that is almost independent of temperature up to room temperature and that saturates at relatively small field around 0.5 T. It is also obvious that the relative importance of this surface component should decrease with increasing the NP size. Therefore, independently of the effects that have been customarily used to account for ferromagnetism in metals and dilute magnetic semiconductors, there should be a characteristic effect of surface physics underlying the surface magnetization of NPs.

In an interesting article Sundaresan and Rao [43] have invoked the universality of the ferromagnetism in inorganic NPs. They propose that the observed ferromagnetism is a surface effect due to the presence of defects. As is known, point defects in insulators can create localized electronic states within the band gap with different electron occupancies and different electric charge and magnetic moment. A short range ferromagnetic interaction with correlation length of four neighbours have been shown to allow ferromagnetic percolation for 4.9% vacancies in CaO [44]. Consequently, the surface component of the magnetization in NPs should then be originated by short range exchange interactions acting among the magnetic moments induced at surface point defects.

Coye et al. [45] have revisited the magnetism of oxide NPs and focused on TiO$_2$ (rutile). They proposed a new theory that corrected its first impurity band model that included effective Heisenberg exchange interaction between 3d local moments within magnetic polarons [46]. In this new theory they invoke inhomogeneous Stoner-type ferromagnetism associated with percolating defect structures. Charge transfer to or from a charge reservoir into a narrow band, associated with defects, can induce inhomogeneous Stoner-type wandering axis magnetism.

Sánchez et al. [47] have reported that at the polar (0001) oriented surfaces of ZnO (wurtzite), even in the absence of magnetic ions, it is promoted the formation of a p-derived extended magnetic state that has not counterpart in bulk. This result, obtained from $ab\initio$ calculations, reinforces the importance of the surface on the magnetism of nanostructures.

Recently, Hernando et al. [48, 49] based on the study of the two-dimensional electron gas on a spherical surface carried out by Tempere et al. [50] have proposed a simple framework to account for the origin of the surface component of NPs. This idea is outlined below.

3 Surface states and wave functions We have seen that the effect of the complex bonding of different atoms to the surface of NPs is to introduce a modification in the electronic structure of the surface band of the NPs. In principle the bonding, as other point defects, can provide either electrons or holes to the surface of the NPs. It has been also indicated that theoretical calculations have shown that for both ZnO [32] and Au [30] electrons are donated by the capping organic molecules.

Let us analyse those electrons that form the surface band of the NPs that have been donated by the capping molecules. Let us assume that the surface band was initially empty, as it happens for instance for ZnO NPs for which the surface s-p band is empty before capping. We will focus on ZnO, even though the analysis could be applied to any substance with surface point defects, and unfilled surface band. It is also assumed the electrons at the surface are confined by a Dirac δ potential to jump between surface atomic sites thus forming a spherical two-dimensional (2DEG) where the quasi-free electrons are characterized by its effective mass, $m$.

Electrons forming a two-dimensional gas on a spherical surface of nanometric radius behave in a way that is intermediate between atoms and solids. It is shown that depending on their radius the NPs can behave as quasi atomic systems when the radius is below a critical one.

Functions that form a complete set of eigenstates of the kinetic energy and take definite complex values at any point of a spherical surface are the spherical harmonics $Y_{lm}(\theta,\phi)$. The spherical symmetry gives rise to free electron wave functions characterized by a quantum number $l$ that determines the angular momentum [50, 51].

The kinetic energy eigenvalues have been shown to depend on the angular quantum number $l$ as

$$e_l = \frac{l(l+1)\hbar^2}{2mr^2} = \frac{l(l+1)}{2}e_1,$$  \hspace{1cm} (1)

where $r$ is the radius of the NPs and the effective mass can be written as $m = (\hbar^2/2a^2b)$ [52]; $b$ being the hopping amplitude proportional to the surface band width ($\approx 4b$) and $a$ the average inter-atomic distance at the surface. Notice that $e_l = (\hbar^2/2mr)$. Let $N$ be the number of surface atoms available to supply an electron through bond to the capping molecule and suppose that each bonding supplies an extra electron. There are actually $N_b = aN$ (<$N$) electrons, where the coverage factor $a < 1$. If we proceed by filling successively the levels of increasing energy given by Eq. (1) up to $N_b$ and after taking into account that the
maximum number of electrons that can occupy any level is given by \(2(2l + 1)\) it can be seen that the Fermi level, \(l_F\), is implicitly defined through the following relationship [47]:

\[
N_b = \alpha 4\pi \left( \frac{r}{a} \right)^2 = 2(l_F + 1)^2. \tag{2}
\]

Figure 3 shows \(l_F\) as a function of \((r/a)\) for different \(\alpha\), according to Eq. (2). From Eqs. (1) and (2), \(\Delta\), the distance in energy between the Fermi level and the level immediately above can be expressed as

\[
\Delta = 2\hbar \sqrt{2\pi \alpha \frac{a}{r}}. \tag{3}
\]

The experimentally measured width, \(4b\), of surface bands varies between 0.5 and 1.0 eV [53]. Therefore, for \(b = 0.25\) eV and \(\alpha = 1\), \(\Delta\) is given approximately by \((a/r)\) eV. Consequently for \((a/r) > 0.025\) the distance \(\Delta\) should be larger than the thermal energy at room temperature and the transition induced by scattering to upper energy levels (upper \(l\) values) may be disregarded. Figure 4 illustrates the range of NP radius for which \(\Delta\) remains larger than the thermal energy at room temperature for different values of \(\alpha\). (Note that \(a\) is about 0.2 or 0.25 nm) For \(\Delta > 0.3\) eV the excitation of electrons to levels above the Fermi level induced by either exchange interactions or an applied magnetic field should then be negligible.

According to Fig. 4, \(\Delta\) remains larger than the thermal energy for sufficiently small size of the NPs. As the size of the NPs increase the distance between adjacent levels decreases and the surface band energy spectrum approach to a continuum. The Figure also indicates that for a given NPs size the discreteness of the spectrum increase with the hopping term \(b\), as is obviously expected since the increase of the hopping implies an increase of the band width keeping constant the number of levels, and the coverage factor. In fact the discreteness of the spectrum as predicted by Eq. (3) is roughly given by the band width times the Fermi quantum number \(l_F\).

Figure 4 is very important since it defines for any NPs the size \((r/a)\) and the number of point defects \((\alpha N)\) required to present a permanent orbital magnetic moment at room temperature as we analyse below.

4 Magnetic moment of an NP with an unfilled orbital at the Fermi level In general the Fermi level will not be completely filled. Let \(n^*\) be the number of electrons that occupy an NPs Fermi level. It is useful to classify the NPs into two types, diamagnetic NPs for which \(n^* = 2 (2l_F + 1)\) and paramagnetic NPs for which \(n^* < 2 (2l_F + 1)\). Associated with the \(n^*\) electrons occupying the unfilled Fermi level there exists magnetic moment. However, even if \(n^*\) is known the estimation of the moment requires also to know the way in which these individual moments are coupled to create the collective moment of the surface state. We need something akin Hund’s rules for the spherical 2DEG.

Besides the kinetic energy the surface electrons are subject to electron–electron interactions [50] as well as to surface spin–orbit coupling. The relative strength of these Hamiltonian terms would determine, as it happens in atomic physics, the order in which the perturbation terms should be introduced in the Hamiltonian to approximate the wave function.

When the kinetic energy is assumed to be the main contributing term to the total Hamiltonian, two limiting cases for the coupling of the angular momentum could be considered by analogy with atomic physics. For the case of electron–electron interaction larger than the spin–orbit coupling [53], the angular moments couple to each other according to the Hund rules, trying to reach the maximum
spin. Independently of the type of coupling the possible values of the total angular momentum quantum number, J, are the same in both cases even though the corresponding energies can differ in magnitude. As we are here only concerned with the magnetic moment the calculation we assume that progressive filling of the Fermi level proceeds according to the Hund rules, i.e., maximum S and maximum allowed L. This assumption is similar to that leading to the enhanced Pauli’s paramagnetism and is based on the general rule establishing that the minimum energy for electron–electron interaction corresponds to the state of maximum spin. If the Fermi level is not completely filled there is not any obstacle, different to the Pauli exclusion principle, to reach the state of maximum spin, since in this case the density of states at the Fermi level diverges.

The values of L and S are symmetric with respect to \( n^* = (2l_F + 1) \). Therefore, the following relationship holds for L and S, \( L(n^*) = L(2l_F + 1 - n^*) \); \( n^* \) can then be restricted for calculation to the condition \( 0 < n^* < (2l_F + 1) \).

Then, if the ground spectral term is that with quantum numbers \( L(n^*) \) and \( S(n^*) \) the value of \( J(n^*) \) corresponding the ground state is either \( J = L + S \) or \( J = L - S \) for negative or positive sign of spin–orbit coupling, respectively. According to the Hund’s rules the orbital moment obtained by considering \( n^* \) electrons in the \( l_F \) level is that given by \( L(n^*) = (2l_F - (n^* - 1))(n^*/2) \).

Therefore, for negative spin–orbit coupling the value of \( J(n^*) \) becomes

\[
J(l_F, n^*) = \left( l_F - 1 - \frac{n^*}{2} \right) n^*,
\]

whereas for positive spin–orbit coupling, \( J(l_F, n^*) \) can be written as

\[
J(l_F, n^*) = \left( l_F - \frac{n^*}{2} \right) n^*.
\]

In general the spin–orbit coupling is negative for orbital level occupied below one-half of the total occupation and positive for higher occupation numbers.

### 4.1 Magnetic moment

By analogy with atomic physics for an NP with total momentum quantum number \( J \) the magnetic moment can be written as

\[
\mu_J = \mu_B g_J J(l_F, n^*),
\]

where \( g_J \) is the Landé factor for the particular \( 2J + 1 \) subspace corresponding to the quantum number \( J \).

\[
g_J = 1 + \frac{J(J + 1) - L(L + 1) + S(S + 1)}{2J(J + 1)}.
\]

In an assembly of NPs both \( (r/a) \) and \( \alpha \) will present fluctuations with respect to their average values \( \langle r/a \rangle \) and \( \langle \alpha \rangle \) that will give rise, according to Eq. (3), to fluctuations in \( I_F \) and \( n^* \). For a given value of \( I_F \) and a uniform distribution of \( n^* \) the average value of the quantum magnetic moment is

\[
\langle \mu \rangle_{I_F} = \mu_B g_J \langle J(l_F, n^*) \rangle.
\]

The order of magnitude of the average \( < \mu >_{I_F} \) when \( n^* \) varies between 1 and \( 2(2l_F + 1) \) can be estimated from Eqs. (4) or (5), after approximating, for the sake of simplicity, \( g_J = 1 \). For \( n^* \) larger than \( 2(l_F + 1) \), negative spin–orbit coupling, (4) yields

\[
\langle \mu \rangle_{I_F} = \frac{1}{3} \left( I_F^2 + 2l_F + 1 \right) \mu_B.
\]

Whereas, for \( n^* \) smaller than \( 2(l_F + 1) \), positive spin–orbit coupling, (5) yields

\[
\langle \mu \rangle_{I_F} = \frac{1}{3} \left( I_F^2 - \frac{1}{2} l_F + \frac{1}{2} \right) \mu_B.
\]

Consequently for large \( I_F \), i.e., \( I_F > 10 \), the order of magnitude of the average magnetic moment at \( I_F \) is \( \mu_B I_F^2 \).

Expression (10) provides the order of magnitude of the magnetic moment of an assembly of NPs with a well-defined Fermi level and with the same probability for any occupation number ranging from \( I \) to \( 2(2l_F + 1) \).

The order of magnitude of the average saturation magnetic moment per atom for the assembly of NPs and for constant \( I_F \) can be easily found to be approximately

\[
\mu_{at} = \frac{3\langle \mu \rangle_{I_F} a^2}{4\pi r^3} \approx \frac{g_J \mu_B a^2}{r}.
\]

As shown in Fig. 5, this is in agreement with the experimental values, \( 10^{-1} \) or \( 10^{-2} \mu_B \) per atom, reported in the literature ([42] and references therein).

It is remarkable that the nanometric scale reflected in the \( (a/r) \) ratio governs, (i) the importance of the kinetic energy as it enhances \( \Delta \) in (3) and (ii) the value of the average magnetic moment per atom in (11) that originates exclusively at the surface of the NPs and is macroscopically negligible when the ratio \( (a/r) \) is of the order of the sensitivity and precision of the magnetometer.

### 4.2 Giant paramagnetism

When a magnetic field is applied along the polar or \( z \)-axis, as thoroughly analysed in Ref. [48], the spectrum of the kinetic energy splits the degenerate ground state into its \( 2J + 1 \) components and induces a diamagnetic moment, \( m_d \), given by

\[
m_d = -N_0 \frac{e^2 B r^2}{4m}.
\]

The diamagnetic component is much larger than that usually observed for atoms as a consequence of the mesoscopic diameter of the orbits [54], but it remains almost
close to saturation, the Brillouin curve describing the paramagnetism of the NPs is negligibly small.

However, the paramagnetism is expected to outweigh the diamagnetism, since with surface collective magnetic moments of the order of $g\mu_B^2 R$, (8), an applied magnetic field of 1 T would induce a maximum Zeeman splitting of $2\mu_B^2 R^2$ that is larger than the thermal energy at room temperature for any $l_B > 10$. It can be concluded that the Langevin or Brillouin curve describing the paramagnetism of the NPs is close to saturation, i.e., the condition $\mu_B^2 R^2 > 3k_B T$, holds for $B = 1.5$ T and $T = 300$ K if $l_B$ is larger than 10.

5 Conclusions It has been generally accepted in the literature cited in this article that the origin of the ferromagnetic like behaviour observed in NPs formed by non-magnetic substances is originated from point defects located at the surface of the NPs. The main difficulty arises to account for the type of exchange interaction between the localized magnetic moments. The XMCD and XAS experiments reported in Refs. [15, 16] and [31], reviewed above in Section 2, confirm that the modification induced in the electronic structure of the surface by the bonding to organic molecules is associated with modifications in the magnetic properties. In Sections 3 and 4 we have described in detail our proposal to account for the origin of this macroscopic magnetization. Giant orbital moments are generated at the Fermi level that carry associated giant orbital magnetic moment, up to that temperature for which KT becomes of the order of the distance in energy between the Fermi level and the immediately upper one. It has been shown how NPs with radius below 10 nm, even if they are made of diamagnetic substances, can exhibit giant paramagnetism when capped with molecules that act as donors or receptor of surface electrons. It is the, generally unfilled, Fermi level that generates large magnetic moment of mainly orbital character that reproduces the experimental values. The magnetic saturation, typically of 0.1 to 0.01 Bohr magnetons per atom, is reached under moderate fields at room temperature. The large value of the collective magnetic moment of the NPs, generally larger than 100 Bohr magnetons should be responsible for the low saturation field. With generality, it has been shown that two-dimensional confinement of electrons (or holes) introduced by capping molecules (or impurities) in previously empty surface states may be the source of that magnetic moments observed in many type of NPs. In summary it has been shown that similarly to the intrinsic ferromagnetism of atoms promoted by the Hund rule in an unfilled orbital there exist an intrinsic ferromagnetism at the surface of NPs with unfilled Fermi level in its surface band.

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References


