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Magnetic Properties of Gold Nanoparticles: a Room Temperature Quantum Effect.

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Gold nanoparticles elicit a huge research activity in view of their applications in diagnostic^{[1][2]}, therapy^[3], drug or gene delivery^[4], sensing^[5,6,7] and imaging^[8]. Gold nanoparticles also display interesting catalytic^[9,10] and optical^[11,12,13,14] properties. This paper focuses on the least understood and so far unused property of gold: its becoming magnetic when prepared in the form of nanoparticles. All these desirable properties, bound together in one nanometric piece of matter, possibly self-organizing thanks to its ligands, make functionalized gold nanoparticles a treasurable entity for nanosciences. The *ex nihilo* magnetic properties of functionalized gold (and other diamagnetic metal such a Ag or Cu) nanoparticles, namely their ferromagnetic-like behaviour, are well documented though still poorly understood^[15]. This unexpected property currently elicits much research activity as it opens new perspectives in materials science. In particular, one may envisage applications in information storage and processing: nanometric magnetic particles with no obvious temperature limitation and possibly self-organizing are currently much sought after by the computer industry and developing a room temperature magnetic semiconductor is paramount for the realisation of spintronics technologies.

In this paper we wish to present the results of our own investigations into the magnetic properties of functionalized gold nanoparticles. We have made attempts at understanding this magnetic behavior using both traditional techniques (e.g. SQUID magnetometry) and other methods less common in this field such as zero-field ¹⁹⁷Au NMR (nuclear magnetic resonance) and SANS (small angle neutron scattering). We also directly probed the local magnetic field at the surface of gold nanoparticles using paramagnetic TEMPO radicals and ESR (electron spin resonance) spectrometry. Surprisingly, none of these experiments provided a clearer picture *in fine*. These “negative” results led us to pondering whether or not the explanation could be elsewhere. Our hypothesis is that the magnetism of gold (and possibly other metal) could very well originate in self-sustained persistent currents. We shall demonstrate hereafter that this hypothesis is indeed very plausible and would actually reconcile all of the experimental data reported to date.

Striking results are often obtained when SQUID magnetometry is performed on functionalized Au nanoparticles such as dodecanethiol-coated ones. Rather than being diamagnetic as expected, the nanoparticles can be found to be para- or ferro-magnetic at room temperature and above. When hysteresis is observed, the magnetization curve looks like that of a soft ferromagnet and exhibits a remnant magnetization M_R and a coercive field H_C , though both are rather weak. These parameters have been observed to have values that vary by orders of magnitude from sample to sample^[Erreur : source de la référence non trouvée] (see ESI 1). Very often the magnetization does not saturate. Diamagnetic samples are more diamagnetic than the bulk metal. Also, the magnetic observables show little dependence on temperature between 2K and 400K. The measurements reported so far have been performed by totally independent groups, on systems that were synthesized using known chemical procedures. Figure 1 compares the magnetization of bulk gold with that of two diamagnetic samples of gold nanoparticles. It can be seen that nanoparticles have a much larger absolute diamagnetic susceptibility than massive gold.

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Figure 1. Normalized magnetic moment vs. applied field. SQUID measurement. Bulk gold (black solid curve), 2.2±0.3nm Au particles (red dots), 3.5±0.4nm Au particles (blue triangles). The particles are coated with dodecanthiol.

Figure 2 compares two samples of gold nanoparticles, exhibiting a paramagnetic behaviour and a ferromagnetic-like one. There is a weak but clear hysteresis, and the magnetization does not really saturate even at high field values.

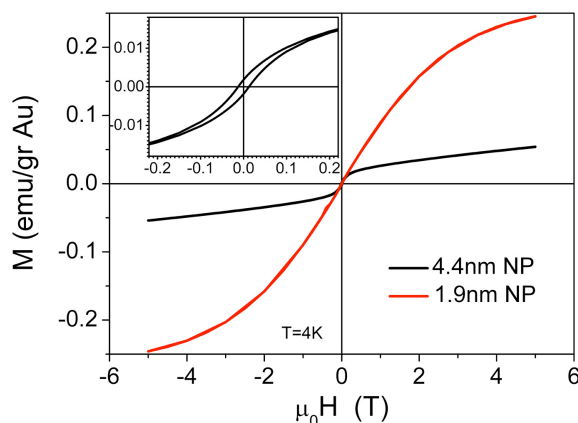


Figure 2. Normalized magnetic moment vs. applied field. SQUID measurements. Ferromagnetic-like behaviour of 4.4±1.0nm Au particles (black), paramagnetic behaviour of 1.9±0.3nm Au particles. Inset is a blow up of the low field region for the ferromagnetic-like sample. The particles are coated with dodecanthiol.

Various theories and explanations have been put forward to explain the magnetic properties of Au (and other metal) nanoparticles. The possibilities that have been suggested roughly fall into three categories^[Erreur : source de la référence non trouvée]. The magnetism could result: a) from the surface atoms of the metal cluster being more numerous than the core ones^[16]; b) the formation of covalent bonds between surface atoms and the ligands^[17,18]; c) electrons trapped in giant orbits circling around single domains of ligands (e.g. thiols)^[19] or in a shell below the surface^[20]. The model based on electrons orbiting around monodomains of ligands is favored^[21], probably because of similarities with the current theory for the magnetism of thiol-covered gold surfaces^[22]. At the date of writing, the latest theory^[Erreur : source de la référence non trouvée] hypothesizes that electrons or holes donated by the ligands or point defects populate a surface band. In this sense, this theory embeds the three mechanisms evoked hereabove: a surface effect, activated by the ligands, causing large electronic orbits. It has received some support from DFT calculations^[23,24].

We underline here an important fact: within these theories or models, all the particles are treated in the same way. This means that *any given particle* should bear a moment or, when the model is based on some magnetic polarization of the metal, that the gold atoms should be found to be magnetic by element-sensitive techniques, even if this magnetism is diluted by the diamagnetic core atoms. In the most recent model^[Erreur : source de la référence non trouvée], it is predicted that nanoparticles could bear moments larger than 100μ_B, such values should not have gone undetected. Moreover, if all particles were indeed bearing a moment (in particular a large one), collective effects should have been seen: magnetic object interacting via dipolar interactions exhibit specific and typical behaviours^[25].

We have investigated the magnetism of gold nanoparticles using element-sensitive techniques such as XMCD and ¹⁹⁷Au NMR. We could not detect any magnetic signal in the gold 5*d* band of our samples (ESI 2 and 3). More, using the XMCD data obtained by other experimenters^[26], we have been able to set an upper limit to the magnetic moment born by gold atoms: (0.004±0.004)μ_B per gold atom at the most. Even if this value is underestimated by more than one order of magnitude, which is certainly well above limits of uncertainty, it remains much lower than the reported value measured by SQUID magnetometry of 0.33μ_B per gold atom in the quoted work^[26]. Moreover, Au atoms in direct contact with a magnetic Co layer acquire a total polarization of ca. 0.03 μ_B (spin + orbital moment) only^[27]. It seems unrealistic that the sole formation of a Au-S could polarize the gold ten times more than Co. In other words, some of the Au atoms do certainly carry a magnetic moment in their 5*d* band but this moment contributes only marginally to the total magnetization that is observed. This point has been already been raised^[28]. One might consider that the magnetism could also be born by the *s* electrons, rather than -more traditionally- by the *d*-electrons, as has been observed in ZnO nanoparticle^[29]. Probing this band with XMCD is unfortunately not possible. While this text was being written, a XMCD study has revealed that bulk gold actually possess both Pauli and orbital paramagnetism, hidden below a larger diamagnetic response³⁰. A 10T field induces a moment of (1.26±0.001×10⁻⁴)μ_B per atom, which makes ~0.03μ_B for a 2nm particle counting ca. 250 Au atoms. Such a small value confirms our analysis, XMCD measurements only see the intrinsic paramagnetic reponse of gold, which is much weaker than the moment measured with SQUID magnetometry.

Since the ferromagnetism is expected to be caused by surface atoms, the two techniques above necessarily measure a value that is minored by the non-magnetic core atoms, even though 52% of the atoms are surface atoms in a 2nm diameter nanoparticle. In order to eliminate this dilution problem, we undertook a direct measurement of the surface moment born by the nanoparticles using spin probes. For this purpose, we synthesized nanoparticles bearing thiol-derivatized TEMPO radicals. Measuring the shift of the ESR signal of the radical would have given a direct measurement of the surface moment. Once again, the results obtained were negative, as if the nanoparticles did not bear any sizeable moment, contrary to what was measured with a SQUID (ESI 4). This result is actually confirmed by previous work where nanoparticles were grafted with spin-labels for studying the dynamics of the ligands. No shift or disappearance

of the ESR resonance line was reported^[31,32,33]. If all of the particles within a given batch were bearing moments as large as those predicted by some theories, a shift of the ESR line would have been quite obvious.

In spite of a borderline feasibility, given the relevant magnetic parameters, SANS experiments were also attempted, to no avail (ESI 5). With all this wealth of experimental evidence, one is forced to admit that the magnetism of gold nanoparticles is either induced by the SQUID setup, or that *it can not originate solely from the magnetic polarization of gold atoms*. Moreover, one has to consider the possibility that not all of the particles are equivalent in a given sample and that perhaps a very limited number (e.g. a few percent) of them are those who carry the magnetism.

Even though the observed magnetic properties are strikingly un-conventional, most of the theories proposed so far to explain them have been based on extensions of known principles. Even so, as mentioned before, none of these theories satisfactorily explains all the observations and in particular the obvious lack of reproducibility^[Erreur : source de la référence non trouvée]. We would like to suggest another solution which is not based on the usual recipes of magnetism.

In mesoscopic metal rings that are smaller than the electron's phase coherence length, currents can flow "forever", even if the metal is not in a superconducting state, under the condition that the ring circles around a magnetic flux^[34]. To observe these currents the temperature has to be sufficiently low to reduce the probability of inelastic scattering from phonons and other electrons, and the ring circumference must be sufficiently short such that phase coherence of the electrons is preserved around the ring. Such persistent currents are therefore usually observed in rings with a diameter smaller than 1 μ m and at temperatures lower than 1K (Figure 3).

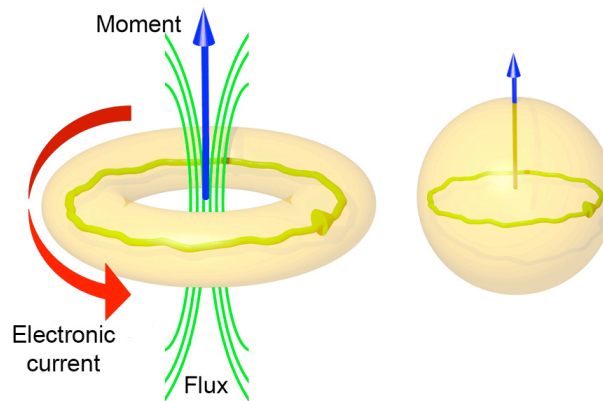


Figure 3. Schematic representation of persistent currents in a ring and in a nanoparticle.

They exist in rings that have a finite resistance and can only be revealed by the small magnetic moment that they generate since inserting a current-measuring device in the ring would kill the phase coherence of the electrons. A variability of the response from sample to sample is theoretically expected, and experimentally observed persistent currents have been found to strongly vary from sample to sample. The magnetic moment of the ring can have the same direction as the applied magnetic field (paramagnetic response), or the opposite (diamagnetic response), depending on whether the number of conduction electrons being even or odd^[35,36,37]. Statistically, in an ensemble of independent rings these fluctuations average out. However, the ensemble-averaged current is slightly paramagnetic. This shift of the average towards positive and possibly large values results from the fact that each ring has a constant number of electrons and the problem must therefore be described with the canonical ensemble^[38]. Theoretically, persistent currents cannot exceed $I_{max} \sim ev_F/2\pi r$ in the ballistic regime, with v_F the Fermi velocity and r the ring radius, in the case of a 1D ring having only one electronic channel^[39,40]. In mesoscopic rings, because of electrostatic impurities (diffusive regime), they are of the order of $e/\tau_D \sim 1$ nA, with τ_D the diffusion time of an electron around the ring, generating magnetic moments of the order of 100 μ_B per ring, in rings having a diameter of ca. 1 μ m^[41].

A dissipationless current flow in a resistive circuit looks counterintuitive but is indeed possible if this peculiar state is the ground state of the system. This is conceptually equivalent to electrons orbiting around atoms without losing energy by synchrotron radiation and generating permanent orbital magnetic moments, even in the ground state. As mentioned previously, the circuit needs not have zero resistance and furthermore, weak dissipation or "noise" does not result in the disappearance of the persistent currents^[Erreur : source de la référence non trouvée]. In any case, such currents have been observed experimentally by several groups in rings made of Cu, Au, Al or semiconductors^[Erreur : source de la référence non trouvée, 42,43].

Our proposal is that the magnetic properties of Au and possibly other metal nanoparticles are the result of persistent currents. These currents would be induced by the magnetic field which is applied in most magnetic measurements, in particular SQUID magnetometry, or even stray fields such as those from the magnetic stirrer used during the synthesis. Interestingly, the theory of persistent currents can directly be transposed to nanoparticles, without the need to develop a specific model. We show hereafter that this hypothesis is not only plausible but would also reconcile all of the experimental facts.

1) A ring structure is not mandatory for a persistent current to flow, a spherical nanoparticle could sustain such a current. Even if the conduction electrons were to be confined and diffusing in an outer shell, their mean free path would not be much different^[44].

2) Persistent currents in mesoscopic rings decrease exponentially with temperature up to the Thouless temperature,

$$T_T = \frac{\hbar\pi^2 D}{k_B (2\pi r)^2}$$

with D being the diffusion constant ($3.25 \times 10^{-2} \text{m}^2 \text{s}^{-1}$ for Au), k_B the Boltzman constant, and r the radius of the ring. The application of this formula to nanoparticles might require some adjustments, but for 2nm diameter nanoparticles the Thouless temperature is over 10^4K , which is more than enough by two orders of magnitude. Below a size of ca. 20nm, all nanoparticles can sustain persistent currents up to 300K.

In any case, gold nanoparticles (and other metals such as Cu, Ag, Ti, Cr,...) exhibit the so-called plasmon resonance which is a direct proof of the existence of the phase coherence of the conduction electrons even at room temperature, regardless of any model. Plasmon resonance is almost temperature-independent in small gold nanoparticles, the small variation observed being due to the electron density changing with the lattice expansion/contraction with temperature^[45]. These reasons would explain the temperature-independent magnetism in Au nanoparticles.

3) The great variability of the observed magnetic behaviors is actually *intrinsic*. The observation of dia- or paramagnetism would be dependent on the number of electrons within those nanoparticles which develop orbital currents, which is clearly out of control. *Vide infra* for the ferromagnetism.

4) It is generally considered that the proof of the existence of persistent currents in a ring structure is the observation of a h/e or $h/2e$ periodicity of the current when the applied magnetic field is swept^[46], the Aharonov-Bohm effect. Generating a single flux quantum^[47] $\Phi = h/e \sim 4.14 \times 10^{-15} \text{ Tm}^2$ in a 2.1nm loop would require a $\sim 1200 \text{ T}$ magnetic field, which is clearly out of reach. Whereas these oscillations can be clearly seen in lithographed 2D mesoscopic ring structures, detecting them on a sample such as ours, made of a huge number of non-identical nanoparticles, is much more challenging, if not impossible. Not only do the diameter of the electrons' orbits vary with the diameter of the nanoparticles, their average size being estimated by a gaussian function as regular and non-regular polyhedra are found, but a given particle can also accommodate several orbits of differing diameters (see ESI 6). The consequence of these two facts is a blurring of the oscillations, since they cannot all have the same period.

5) It has been theoretically predicted that persistent currents could exist even in the absence of an external field, giving rise to orbital ferromagnetism^[48,49]. The interaction of *intrinsic fields* in a 1D string of magnetically coupled rings could also give rise to strong macroscopic magnetism but this question remains theoretically open^[50]. Such self-sustained fluxes are obviously under the influence of the local organization of the nanoparticles. This would explain or at least contribute to the great variability in the magnetic behaviors that have been reported and why stirring the sample or re-solubilizing it can induce magnetic changes.

In this regard, the recent results of Kowlgi *et al.* ^[51] deserve attention. Most interestingly, they synthesized Au, Ag and Pt nanoparticles which behavior could be adjusted from diamagnetic to ferromagnetic depending on the strength of an external static magnetic field applied during the synthesis (20mT to 1.8T). The magnetic samples clearly exhibit the "usual" features: remnant magnetization and coercive field. Moreover, they form crystals with a *fcc* lattice rather than the more usual *amorphous* structure. We believe that these observations, which cannot be easily explained within the framework of the other theories, corroborate our hypothesis of an *induced* magnetism.

Along this line, we have synthesized a sample which orders into a cubic mesophase and has proven to be more magnetic than any of our other samples made from non-mesomorphous nanoparticles^[52]. A cubic lattice favors magnetic couplings, in contrast to an amorphous structure, whereas a hexagonal lattice may even generate unfavorable magnetic frustrations. Liquid crystals are known for exhibiting local order and this order survives as cybotactic groups even outside the mesomorphic temperature domain. This would enable the persistence of the magnetic coupling throughout the whole temperature range as the local cubic ordering would remain present (Figure 4). Last, on this same sample, we have observed a puzzling interplay of the mesomorphic order with the magnetic properties^[53].

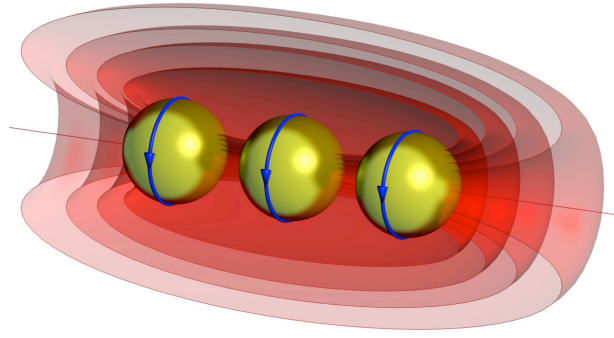


Figure 4. Schematic view of 3 nanoparticles magnetically coupled and developing a self-sustained magnetic moment resulting from persistent currents.

Under this proposed model, the magnetization of the Au nanoparticles samples would result from them experiencing a magnetic field at some time during their lifetime, *e.g.* that which is used when centering the sample in a SQUID magnetometer or during the synthesis. The moment so generated would further induce the circulation of persistent currents in the neighboring nanoparticles, as schematically depicted in Figure 4. Such a process could be at the origin of our observing time-dependent variations of the magnetic moment.

6) Magnetic moments experimentally observed on nanoparticle samples vary between 0.1 to $40\mu_B$ per particle for the saturation moment and 0.01 to $3\mu_B$ per particle for the remnant magnetization. Taking a 2nm nanoparticle, the maximum sustainable persistent current will be much larger than the maximum value $eV_F/2\pi\hbar$ given hereabove for a 1D ring since there will obviously be more than one electron channel and the transport will be ballistic. Considering a 2nm particle, and with the hypothesis that up to 10 electronic channels are open, induced currents can generate a moment of $M \sim 10^{-21}\text{Am}^2$ or $120\mu_B$. Consequently, it would be sufficient that persistent currents develop in only a small fraction of the nanoparticles to realize the bulk magnetic behavior of the sample. Nanoparticles which have a perfect geometrical shape and defectless facets are called “full shell”^[54,55]. Their structure is therefore particularly dense and metal interactions are maximized. From a purely statistical basis, in a given synthesis batch, only a small fraction of the particles can have the “magic” number of atoms required to be full shell. These full shell nanoparticles could possibly be those which boast persistent currents. This small percentage of “active” nanoparticles would then explain why it has not been possible to observe any positive results with techniques such as SANS or the spin-labeled nanoparticles. Similarly, since the origin of the magnetism is not the result of a magnetic polarization of the Au atoms, NMR and XMCD could not return any significant signal. In the case of XMCD, we have seen herabove that the magnetic polarization of the Au atoms seen by some experimenters can only contribute to a *minor part* of the total magnetic moment.

In summary, we posit that the magnetism of Au nanoparticles is of orbital origin and due to the conduction electrons being driven into persistent currents. The appearance of persistent currents under an applied magnetic field would explain the observation of both dia- and para-magnetic responses of the various samples, the high variability and the lack of thermal dependence of the magnetic properties. As the currents increase with the applied field (before eventually changing sign when a flux quantum Φ becomes enclosed in the circuit) the magnetic moment does not saturate^[66]. Occasionally, these persistent currents could even become self-sustained, giving rise to a soft ferromagnetism. The effect could be reinforced if the nanoparticles are locally arranged with the proper geometry (*e.g.* cubic lattices). However, obtaining direct proof of the existence of such persistent currents is challenging. We tentatively suggest that near field microscopy techniques could be used. One may think of attaching a gold nanoparticle to the cantilever of an AFM. When placed in a magnetic field, the vibration frequency would be sensitive to any extra force generated by the magnetic moment of the nanoparticle^[45]. If the moment is indeed field-induced and non-permanent, no extra force should be perceived in zero field. One may also consider submitting larger Au (or other metal) nanoparticles to high magnetic fields and look for Aharonov-Bohm oscillations in their magnetic response. Given the orbital nature of the magnetic moment, it is also worth trying magneto-optical experiments using circularly polarized light in order to probe the magnetoplasmons. An increase or a decrease of the magnetization might be observed upon reversal of the polarization, though the intensity of the local magnetic field may be too small^[57]. Input from theoreticians would also be most welcome. If the hypothesis developed in the present paper is proven correct, ligand-coated gold nanoparticles would provide an easily accessible physical system exhibiting quantum behavior above room temperature.

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Electronic Supplementary Information

1 - Samples preparation and characterization

Using the usual synthesis protocols such as Brust⁵⁸, inverted Brust⁵⁹ or Stucky⁶⁰, we synthesized several batches of nanoparticles. All nanoparticles used in this study were covered with dodecanethiol ligands, except when otherwise mentioned. We could never ever get twice particles having exactly the same magnetic properties, in spite of numerous efforts and a precise control of all obvious parameters such as reaction volume, temperature, agitation speed, reactants addition speed, etc. Other experimenters must have experienced the same variability though the point is barely raised. All batches were characterized by transmission electron microscopy (TEM), SQUID magnetometry, UV-vis spectrometry, plus possibly other techniques, as pointed in the text. The figure below gives the values of the coercive field H_c , saturation and remnant moments (M_S and M_R) for a few batches. The occasional purely diamagnetic samples are obviously not on the graph.

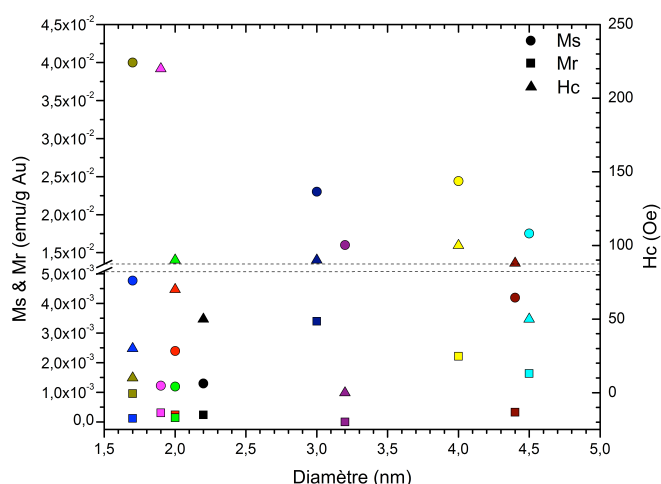


Fig. ESI-1. Values of the coercive field, saturation and remnant moments for a few batches of Au nanoparticles at 295K.

2 - X-ray magnetic circular dichroism (XMCD)

Because of its high sensitivity and chemical selectivity XMCD is a powerful tool for studying magnetic materials. Several studies have been performed on Au nanoparticles^{61,62,63}, with the largest XMCD signal being reported by Yamamoto and Hori⁶⁴, the weakest one by de la Venta *et al*⁶⁵. We could not measure any XMCD signal for our best sample ($M_S=0.006\mu_B$ per magnetic Au atom) even after averaging measurements for 48 hours, as seen in the figure below. If there is an XMCD signal, its amplitude must be less than 10^{-4} of that of the edge jump.

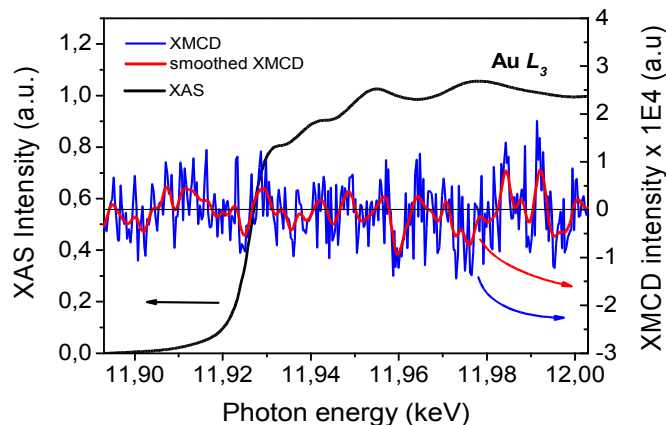


Fig. ESI-2. XAS and XMCD signals averaged over 48h for our most magnetic sample at 100K, under a field of 1T. Black line: XAS spectra, the two polarization are undistinguishable ; Blue line: XMCD signal (difference of the XAS spectra recorded for two polarizations) ; red line : smoothed XMCD signal. The right-hand scale has the same units as the lefthander one but with a magnification of 10^4 .

Indeed, the authors of reference Erreur : source de la référence non trouvée, with a much more magnetic sample ($0.3 \mu_B$ per magnetic Au atom) and under a field ten times more intense measure a XMCD signal that is $\sim 7 \times 10^{-5}$ times the height of the edge for dodecanethiol-coated Au nanoparticles. The results of reference Erreur : source de la référence non trouvée are more difficult to understand. On Au nanoparticles stabilized with polyallyl amine hydrochloride (PAAHC), bearing a smaller magnetic moment of *ca.* $0.13 \mu_B$ per magnetic Au atom, they measure a XMCD signal of $\sim 2.5 \times 10^{-4}$, which is almost one order of magnitude larger. Moreover, amine groups do not form strong covalent bonds with Au, and this reason is sometimes put forward for explaining the stronger magnetization. But the holes in the *5d* shell, which are probed by XMCD, *a priori* result from the formation of covalent bond with grafted molecules, so the XMCD signal should actually be weaker.

Since some theories relate the emergence of magnetic properties to a polarization of the metal induced by a change in the density of the electronic levels, we synthesized Rh nanoparticles coated with dodecylamine. This metal being close to being ferromagnetic, given its Stoner parameter, we expected a larger response than with gold. Rh nanoparticles were found ferromagnetic, though no more than Au, as measured with a SQUID magnetometer. We could not evidence any XMCD signal at any of the metal *M* edges, nor at the nitrogen *K* edge. Similar results were found for Ir nanoparticles.

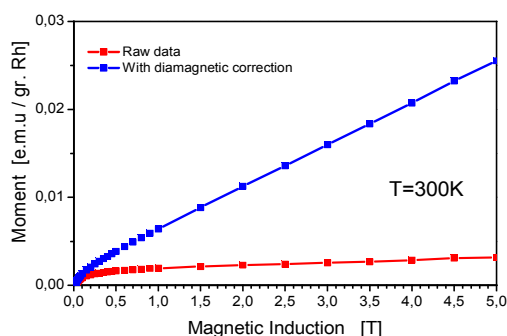


Fig. ESI-3. SQUID magnetization curves of 1.9nm Rh nanoparticles at 300K. Sample weight is 39.11mg. Coercive field is 140Oe and remnant magnetization $1 \times 10^{-3} \mu_B$ per particle

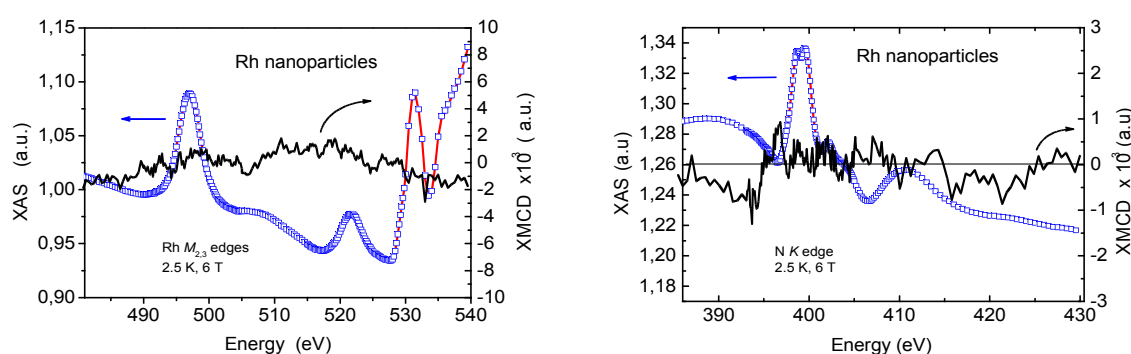


Fig. ESI-4. XAS and XMCD spectra of dodecylamine-coated Rh nanoparticles, at 2.5K and under 6T. The XAS spectra recorded with the two polarizations are undistinguishable. There is no detectable XMCD signal, neither at the rhodium $M_{2,3}$ edges (left) nor at the nitrogen K edge (right).

Going back to Au, in principle, the XMCD data can be deconvoluted using the sum rules and give the spin and orbital magnetic moments born by the metal atoms. True, these rules were established for crystalline bulk material and their extension to nanoparticles, with their peculiar electronic structure, may be adventurous. Nevertheless, even if the results are to be off by an order of magnitude, we reckon it is still an interesting piece of information. The two fundamental principles are : 1) the integrated difference between the XAS spectra of bulk gold and that of gold nanoparticles is proportional to the number of holes in the nanoparticles ; 2) the integrated dichroic signal recorded on the nanoparticles is proportional to the magnetic moment. We took the liberty of digitalizing the data of Garitaonandia *et al.* *Erreur : source de la référence non trouvée* and tried to estimate the spin moment. These authors report XMCD spectra obtained at the Au- $L_{2,3}$ edges with a magnetic field of 10T, the amplitude of the dichroic signal is about 10^{-4} of the L_3 edge. They did not attempt to estimate the S_z and L_z of $5d$ moments arguing the lack of knowledge on n_h (number of core holes) and T_z (magnetic dipole) values which are indeed needed. We

shall assume here that T_z is negligible, even if in the case of Pd and Pt particles some magnetic anisotropy was suggested⁶⁶. The main problem comes from the fact that the number of holes n_h of the $5d$ band in the Au particles is not known. Rather than using the calculated n_h value for bulk gold, we determine the change in the $5d$ hole counts between the system under study and the Au metal following the prescription given by Kuhn⁶⁷. It is possible to determine directly the isotropic cross-section per hole from the experimental data, as the intensity of the white line is directly proportional to the number of holes (first sum rule). The normalized isotropic cross-section writes:

$$\Omega_{(l)} = \frac{1}{n_h} XAS_{ISO}$$

where XAS_{ISO} is the integral of the isotropic (*i.e.* no polarization) x-ray absorption edge. According to Starace⁶⁸, the normalized isotropic cross-section $\Omega_{(l)}$ can be obtained from:

$$\Omega_{(l)} = \int_{j^+ j^-} \left[\frac{\mu_{Au\ part.}^0 - \mu_{Au\ bulk}^0}{n_h^{Au\ part.} - n_h^{Au\ bulk}} \right]$$

with μ^0 being the total isotropic absorption cross-section for Au nanoparticles or bulk gold, as indicated by the subscript, and similarly for the number of holes n_h .

When spin-orbit coupling is strong in the relevant band, as is the case with gold, the relationship between the change of hole counts relative to pure Au and the white line $A_{(3),(2)}$ is given by:

$$n_{Au\ part.}^{5d} - n_{Au\ bulk}^{5d} = \frac{1}{2C} \left[5 \frac{E_2}{E_1} A_3 - A_2 \right]$$

where:

$$A_{i=2,3} = \int_{L_{i=2,3}} [\mu_{Au\ bulk}^0(E) - \mu_{Au\ part.}^0(E)] dE$$

$C \approx 7.5 \times 10^4 \text{ eV cm}^{-1}$ is a constant proportional to $\langle 5d|r|2p \rangle$, radial matrix element energy independent over the $5d$ band and $E_{i=2,3}$ is the electron binding energy of the $2p_{1/2}$ and $2p_{3/2}$ states.

We applied this procedure to the results of Erreur : source de la référence non trouvée. The normalized Au L_3 edge XANES of the Au nanoparticles and bulk gold exhibit the same resonance pattern and a more intense resonance at the main threshold corresponding to the $2p_{3/2} \rightarrow 5d_{5/2}$ dipole transition, probing the unoccupied density of states at the Fermi level. This more intense resonance indicates an increase in the $5d$ hole population. We estimate the difference of the number of $5d$ holes between bulk gold and the nanoparticles to be about $\sum n_h = 0.17 \pm 0.05$.

After reduction of the XAS and XMCD data we therefore estimate the $5d$ -Au spin magnetic moment to be of the order of $(0.0035 \pm 0.003) \mu_B$ per gold atom, supposing $m_l=0$. The orbital moment being at the most 15% larger Erreur : source de la référence non trouvée, our upper limit of the total magnetic moment

therefore is $(0.004 \pm 0.004)\mu_B$ per gold atom. Even if our estimate of n_h was wrong by a factor of two or more, the essence of our conclusions would not be altered: SQUID results yield a magnetic moment that is two orders of magnitude smaller than the one reported in reference Erreur : source de la référence non trouvée: $0.33\mu_B$ /magnetic atom. Therefore, the observed magnetic moment cannot be ascribed to the sole $5d$ electrons. Moreover, a very recent paper reports that bulk gold actually exhibits both Pauli and orbital paramagnetism, hidden below a larger diamagnetic response⁶⁹. The total paramagnetic moment induced on one Au atom by a 10T field is $(1.26 \pm 0.001 \times 10^{-4})\mu_B$ per atom, or $0.07\mu_B$ for a 2.5nm particle counting *ca.* 560 atoms. This value confirms our analysis and proves that XMCD measurements only see the (intrinsic) paramagnetic response of Au, which is much weaker than the magnetic moment measured with SQUID magnetometry on nanoparticles.

3 - Zero-field ¹⁹⁷Au NMR

Zero field ¹⁹⁷Au NMR has been performed on the samples with an automated broadband spin echo NMR spectrometer. NMR is seldom used in ferromagnetic samples⁷⁰. A particularity of NMR, when it is applied to ferromagnets is that an external static field is not needed to lift the spin degeneracy. Indeed the magnetization of the sample is already producing a static magnetic field on the nuclei site. Therefore it is possible to perform NMR measurements in ferromagnets only by applying the radio frequency field. The NMR spectrum is usually obtained by varying the frequency of the radio-frequency field. An interesting consequence of this operating mode is that if an NMR signal can be recorded it is an unambiguous proof of the ferromagnetic property of the sample.

In the studied sample no NMR signal has been observed. While the observation of a signal would have been a proof of the ferromagnetic behavior of the sample, the absence of signal does not necessarily imply that the sample is not ferromagnetic. Several reasons might lead to absence of NMR signal:

1) Not enough NMR sensitivity: indeed Au is not the best nucleus for NMR investigation since its sensitivity is 10^4 times smaller than the one of Co that is a typical nucleus for zero field NMR investigations⁷¹. However it is 100 times larger than the one of Fe, for which NMR signal can be easily obtained on bulk samples. Therefore the lack of NMR sensitivity should not be the reason of the absence of NMR signal since the amount of sample used to perform the measurements is similar to the one used for bulk Fe containing samples.

2) Magnetic moment is too weak: as mentioned previously it is possible in ferromagnets to get an NMR signal in zero field because of the hyperfine field produced on the nuclei sites by the magnetization of the sample. However since the NMR resonance frequency is the product of the hyperfine field (atom magnetic moment) by the nucleus gyromagnetic ratio, the resonance frequency might fall outside the frequency range of the NMR spectrometer. Since the gyromagnetic ratio of Au is rather small (0.7 Mhz/T) Erreur : source de la référence non trouvée a significant hyperfine field (magnetization) is needed

to make the NMR signal arise in the frequency range of the spectrometer (20 to 700 MHz). Therefore the absence of NMR signal might be due to the smallness of the magnetic moment carried by the Au atoms.

3) Magnetic anisotropy is too high: since the samples are ferromagnetic, the radio frequency field experienced by the nuclei is mediated by the motion of the magnetization of the sample. Erreur : source de la référence non trouvée. Therefore if the magnetic anisotropy is too high it might be impossible to transfer the radiofrequency field to the nuclei and therefore it is not possible to get an NMR signal. In these samples the coercive field is quite small and therefore should make possible the observation of a zero field NMR signal.

4) Relaxation times out of the spectrometer range: NMR signal is driven by relaxation times. Spin-spin relaxation time should be long enough to allow to produce a spin echo ($>1\mu\text{s}$) while spin lattice relaxation time should be small enough to allow fast data acquisition ($<500\text{ ms}$). In such unknown materials it is difficult to guess whether or not the relaxation times will lie within the spectrometer operating windows.

4 - ESR measurements on spin-labelled NPs

Spin label molecules are routinely used for locally probing the geometrical or magnetic environment at a precise molecular locus. Being paramagnetic, such species are visible with ESR spectrometry, a very sensitive technique, enabling therefore precise measurements. In an attempt at directly measuring the surface magnetic field of Au nanoparticles through its action on the ESR lineshape, we synthesized nanometric Au nanoparticles bearing a few TEMPO derivatives in addition to the ESR-silent dodecanethiols. The TEMPO radical is routinely used in ESR studies.

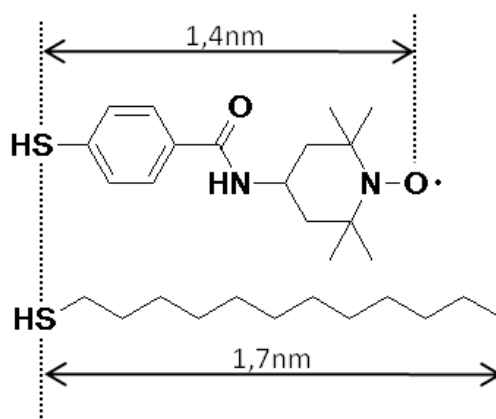


Fig. ESI-5. Molecular structure of the TEMPO thio-derivative (top) and comparison of its length with that of the dodecanethiol ligand (bottom).

The paramagnetic part of the TEMPO derivative is ca. 1.4nm away from the surface of the nanoparticle. Its grafting on the nanoparticles is ascertained by the ESR response, as seen in the figure below. The three hyperfine-split resonance lines of the grafted radical lose the symmetry they have in solution.

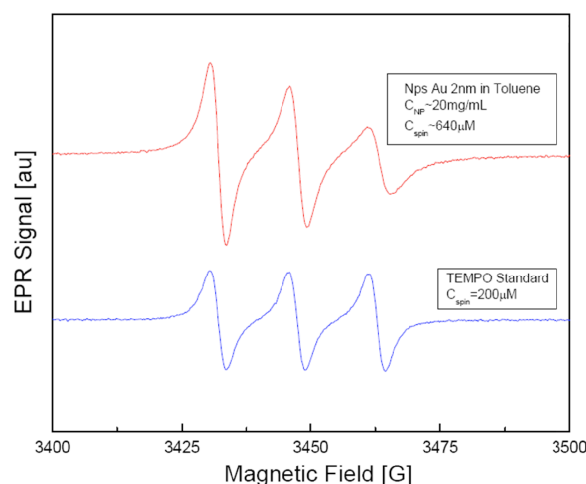


Fig. ESI-6. Comparison of the ESR lineshape of a solution of TEMPO-functionalized nanoparticles (top) with that of a free TEMPO solution (bottom).

DEER experiments (double electron-electron resonance) enable to establish that the mean distance between two TEMPO radicals is *ca.* 3.5nm (see the figure below). This means that the TEMPO radicals are not free in solution and that each particle bears on average 3 such spin labels.

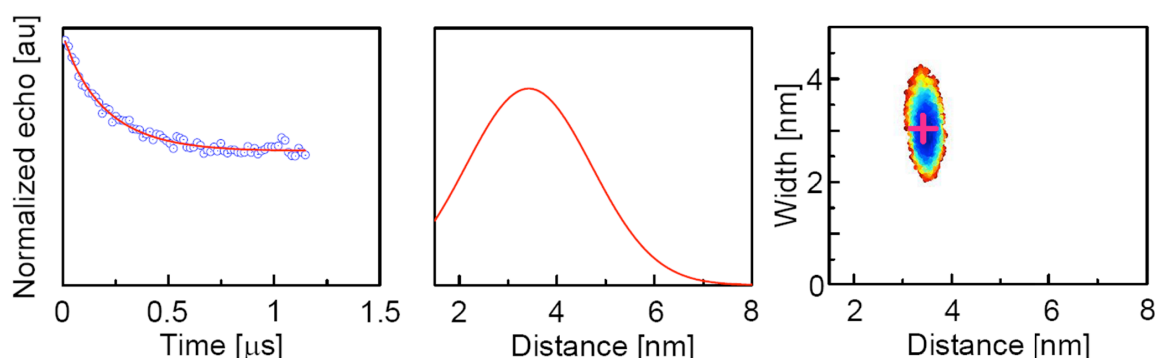


Fig. ESI-7. Measurement of the dipolar coupling with DEER spectrometry. Data recorded at 65K on a 10g/L solution of Au nanoparticles functionalized with dodecanethiol and TEMPO derivatives.

Magnetic interaction of the radicals with the local field developed by the nanoparticles should have produced a shift of the resonance lines towards low field values. No such effect has been observed, in spite of the good quality of the samples and the sensitivity of the experiments. The nanoparticles had a magnetization of $4.0 \times 10^{-3} \text{ emu/g Au}$ at 3500Oe, which should have produced a measurable effect.

5 – Small angle neutron scattering

Neutrons are sensitive to magnetic fields and commonly used for probing the magnetic properties of matter. The resolution is much better for oriented crystals than for amorphous samples, but it seems feasible to access the inner magnetic structure of nanoparticles using SANS. For many reasons detailed

hereabove, it seems logical that most of the magnetism is confined to the surface of the nanoparticles or a thin shell. We therefore assumed that 2nm spherical nanoparticles were surrounded by a 0.3nm magnetic shell for our preliminary calculations. The orientational distribution of the magnetic moment at the surface is totally unknown, but one can probably reduce the possibility to two : purely radial or partially axial.

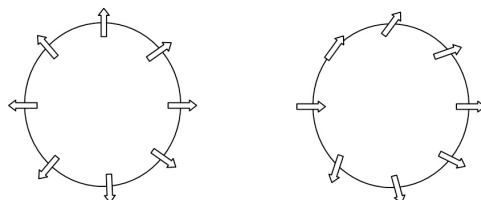


Fig. ESI-8. Distribution of the moment at the surface of the nanoparticle. Left : purely radial distribution ; right : partially axial distribution. This may be caused by the applied field.

If the distribution of the moment is purely radial, there is no magnetic scattering, as seen in the simulation below.

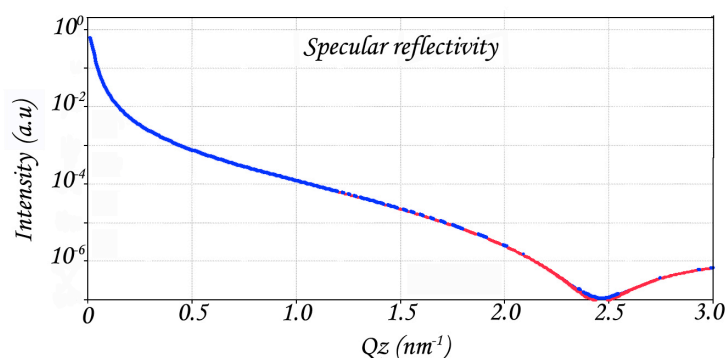
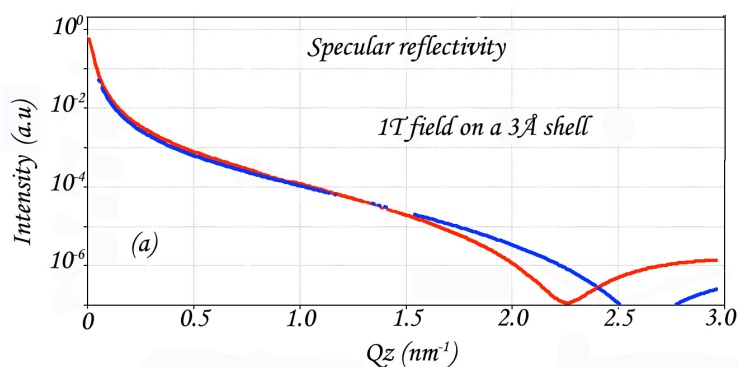


Fig. ESI-9. Specular reflectivity for two field orientations, for magnetic nanoparticles with a radial distribution. Red curve: applied field (3T) is up ; blue curve: applied field is down.

If the distribution is at least partly axial, small angle neutron scattering should become sensitive to the magnetic field, at least if the local magnetization exceeds 0.1T, as seen in the simulations below.



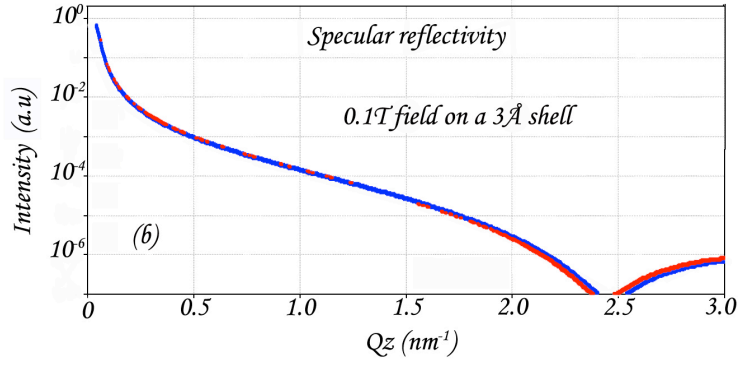


Fig. ESI-10. Specular reflectivity for two field orientations, for magnetic nanoparticles with a partly axial distribution of magnetic moments generating a surface field of 1T (top) or 0.1T (bottom). Red curves: applied field (3T) is up ; blue curves: applied field is down.

The batch of NP which was used for these experiment showed remnant magnetization, implying that the distribution of magnetic moments at the surface in the presence of an applied field was at least partly axial. Experiments were performed on a fresh NP solution in deuterated toluene. Applied magnetic field was 3T and temperature 4K. As the measurements gave no results, we must conclude that the field at the Au surface is smaller than 0.1T. Similar negative results have been reported Erreur : source de la référence non trouvée.

6 - Considerations about the electrons' mean free path in nanoparticles.

In bulk gold, electrons have a mean free path of ca. 50nm^{72,73}. Their relaxation time τ can be expressed as:

$$1/\tau = 1/\tau_{e-e} + 1/\tau_{e-ph} + 1/\tau_{e-d}$$

Where τ_{e-e} , τ_{e-ph} and τ_{e-d} are the relaxation times for the electron-electron, electron-phonon and electron-defect processes. τ_{e-d} includes scattering by impurities, grain boundaries and lattice defects. In nanoparticles this term also includes scattering by the surface, and since the mean free path becomes larger than the dimensions of the particle, this process becomes the dominant one. In 9nm Au nanoparticles $\tau_{e-e} \sim 0.5 \times 10^{-12}$ s and $\tau_{e-ph} \sim 1.6 \times 10^{-12}$ s, as reported in (⁷⁴). For a 2nm nanoparticle, τ_{e-d} can roughly be estimated as a few 10^{-15} s. Given the Fermi velocity of gold $v_F = 1.4 \times 10^6$ ms⁻¹, the mean free path of electrons is of a few nanometers. Very schematically, on may consider that the electrons have trajectories such as depicted below. Though the two geometries are not equivalent, the electron mean free path does not differ by much⁷⁵.

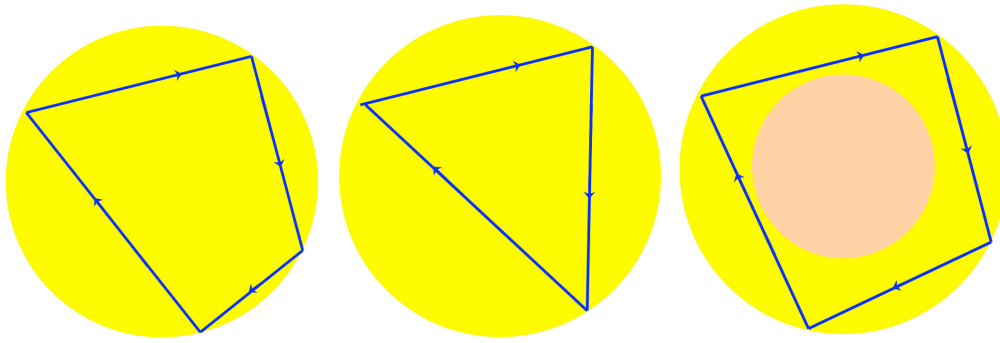


Fig. ESI-11. Schematic view of electron trajectories if the conduction takes place in the whole nanoparticle (left and center), or only in a shell (right).

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