g-Factors of Discrete Levels in Nanoparticles

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Spin-orbit scattering suppresses Zeeman splitting of individual energy levels in small metal particles. This suppression becomes significant when the spin-orbit scattering rate τ_{so}^{-1} is comparable to the quantum level spacing δ. At small $\delta\tau_{so}$ the g-factor exhibits strong mesoscopic fluctuations. We find the shape of their distribution function using the random matrix theory, and express its parameters in terms of physical characteristics: τ_{so}, δ, the electron mean free path l, and the particle size L. At $\delta\tau_{so} \to 0$ the average g-factor levels off at a small value $g \sim (l/L)^{1/2}$. However, in 2D quantum dots the g-factor is strongly enhanced by spin-orbit coupling.

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In bulk metals the spin-orbit interaction is known to result in relatively weak corrections to the g-factors of electrons [1]. For instance, in aluminum the g-factor is indistinguishable from the nominal value of 2, and in bulk gold $g = 2.1$. However, recent experiments with nanoparticles found much smaller values of g. Measurements of the level splitting induced by magnetic field in Al grains [2] yielded $g \approx 1.7$. Adding to these grains of only 4% of Au resulted in the drop of g down to ~ 0.7. In Au nanoparticles the value $g \approx 0.3$ was observed [3]. The lowest-order perturbation theory [1,4] in the strength of spin-orbit scattering enables one to analyze [2] small deviations of the g-factor in a nanoparticle from the nominal value $g = 2$. In this paper we develop a theory of the g-factor in the regime when it is strongly affected by spin-orbit scattering, which was the case in experiments [2,3].

In bulk materials the g-factor is conventionally determined from the electron spin resonance (ESR) data. ESR involves transitions between states of the electron continuum. However, the experiments with nanoparticles [2,3] study the Zeeman splitting of individual electron levels ϵ_i:

$$\epsilon_{i\sigma}(H) = \epsilon_i \pm \tfrac{1}{2} g_i \mu_B H . \tag{1}$$

Here H is the magnetic field, $\mu_B = e\hbar/2mc$ is Bohr magneton, and m is the free electron mass. The splitting (1) is linear in H as long as it is small compared to the quantum level spacing δ. The g-factor determined by Eq. (1), in general, varies from level to level. In the absence of spin-orbit interaction, $g_i = 2$. Evidently [2,3] the spin-orbit scattering affects the values of g_i.

Unlike its bulk value, the g-factor defined by Eq. (1) is very sensitive to even weak spin-orbit interaction. The reason is that the magnitude of the correction to $g = 2$ value, measured by ESR in the bulk, is determined by the comparison of spin-orbit interaction to the typical electron bandwidth, whereas the relevant energy scale for g-factors of individual levels is the quantum level spacing δ. Indeed, the spin-orbit interaction is usually described by the mean time of spin-orbit scattering τ_{so}. The scattering time should be compared with the time $\sim 1/\delta$ that an electron travels along a closed trajectory corresponding to a quantum level. At $\delta\tau_{so} \gg 1$ the electron spin flips very infrequently, and the effect of the spin-orbit scattering is weak. However, at $\delta\tau_{so} \ll 1$ the spin flips the average of $N = 1/\delta\tau_{so}$ times during the electron motion along the closed trajectory. Thus the average spin in such a quantum state is significantly less than $1/2$, and the response (1) to the magnetic field is strongly suppressed. The g-factor of this level can be estimated by assuming that electron spin-flips occur at random moments in time. The root-mean-square value of the spin is then $1/\sqrt{N}$, resulting in $g_i \sim g_0\sqrt{\delta\tau_{so}}$. Here g_0 is the bulk value of the g-factor, determined by the band structure of the material; $g_0 = 2$ for free electrons.

The above estimate accounts only for the spin contribution to the g-factor. In fact, the level splitting in a magnetic field is determined by the total magnetic moment of the state

$$\langle M\rangle_i = \langle M_z^{\rm orb}\rangle_i + \langle M_z^{\rm sp}\rangle_i . \tag{2}$$

Here $\mathbf{M}^{\rm orb} = (e/2c)[\mathbf{r} \times \mathbf{v}]$ and $\mathbf{M}^{\rm sp} = g_0\mu_B\mathbf{s}$ are the orbital and spin magnetic moments; $\mathbf{r}$, $\mathbf{v}$, and $\mathbf{s}$ are the operators of position, velocity, and spin of the electron, respectively. The brackets $\langle\cdots\rangle_i$ denote the expectation value in the ith eigenstate of an electron confined to a nanoparticle in an infinitesimal magnetic field in z direction. In a nanoparticle of a generic shape, the orbital levels are not degenerate. Then in the absence of the spin-orbit interaction the time reversal symmetry dictates $\langle[\mathbf{r} \times \mathbf{v}]_z\rangle_i = 0$ at $H \to 0$, although the variance $\langle[\mathbf{r} \times \mathbf{v}]_z^2\rangle_i \neq 0$. It is important to note that in the presence of spin-orbit interaction $\langle[\mathbf{r} \times \mathbf{v}]_z\rangle_i \neq 0$, and the orbital motion contributes to the splitting of levels by the magnetic field [5].

In the presence of strong spin-orbit coupling, $\delta\tau_{so} \ll 1$, one can estimate $\langle[\mathbf{r} \times \mathbf{v}]_z\rangle_i$ as the root-mean-square value $\sqrt{\langle[\mathbf{r} \times \mathbf{v}]_z^2\rangle_i} \sim |A|\delta$ calculated without accounting for that coupling; here A is the (directed) area covered by a trajectory corresponding to level i. To find A we

notice that during time $1/E_T$ the electron travels across the grain and, therefore, covers the area $\sim L^2$. (Here $E_T = D/L^2$ is the Thouless energy, L is the grain size, and D is the diffusion constant for electrons in the grain.) During the period of motion $1/\delta$ the electron bounces off the boundaries $\sim E_T/\delta$ times. Since the direction of motion after each bounce is random, the total directed area is $|A| \sim L^2\sqrt{E_T/\delta}$. Consequently, the orbital magnetic moment of a given state can be estimated as

$$\langle M_z^{\rm orb}\rangle_i \sim \frac{e\hbar}{c} L\sqrt{D\delta} \sim \frac{e\hbar}{cm^*} \times \begin{cases} \sqrt{l/L}, & \text{3D}, \\ \sqrt{k_F l}, & \text{2D}. \end{cases} \quad (3)$$

Here l is the transport mean free path of electrons, k_F is their Fermi wave vector, and m^* is of the order of the effective mass derived from the density of states of a bulk material.

One can also see from Eq. (3) that in a three-dimensional (3D) nanoparticle the orbital contribution to the g-factor is small, $g_i^{\rm orb} \sim \sqrt{l/L} \ll 1$. However, in the case of strong spin-orbit scattering, $\delta\tau_{\rm so} \ll 1$, the above estimated spin contribution is also small, $g_i^{\rm sp}/g_0 \sim \sqrt{\delta\tau_{\rm so}} \ll 1$. Therefore in this regime both contributions may have to be taken into account.

We will now show that at $\delta\tau_{\rm so} \ll 1$ the g-factor of a level is a random quantity with the distribution function

$$P(g) = 3\sqrt{\frac{6}{\pi}} \frac{g^2}{\langle\langle g^2\rangle\rangle^{3/2}} \exp\left(-\frac{3g^2}{2\langle\langle g^2\rangle\rangle}\right), \quad (4)$$

where the averaging $\langle\langle\cdots\rangle\rangle$ is performed either over an ensemble of 3D nanoparticles or over different levels in a single nanoparticle. Furthermore, we express $\langle\langle g^2\rangle\rangle$ in terms of two quantities, $\tau_{\rm so}$ and l, which can be measured independently:

$$\langle\langle g^2\rangle\rangle = \frac{3g_0^2}{2\pi\hbar}\,\delta\tau_{\rm so} + \alpha\,\frac{l}{L}. \quad (5)$$

Here the dimensionless constant α is determined by the geometry of the nanoparticle; its exact value will be discussed later. Equations (4) and (5) are the main result of this paper.

We begin the study of the g-factors of individual levels by finding a relation between g_i and the matrix elements of the operator of magnetic moment M. Because of the time reversal symmetry, the levels in the nanoparticle are degenerate, with the wave functions $|\psi_i\rangle$ and $|T\psi_i\rangle$, where T stands for the time reversal operator. In a weak magnetic field H the levels are split by the perturbation MH. By using the standard method of degenerate perturbation theory, one can easily find the splitting in the form (1) with the g-factor

$$g_i = 2\frac{|\vec{\mu}|}{\mu_B}, \quad (6)$$

where the real vector $\vec{\mu}$ is defined as

$$\mu_x + i\mu_y = \langle T\psi_i|M|\psi_i\rangle, \qquad \mu_z = \langle\psi_i|M|\psi_i\rangle. \quad (7)$$

The distribution function $p(\vec{\mu})$ is, by definition,

$$p(\vec{\mu}) = \int \frac{d^3\lambda}{(2\pi)^3} e^{i\vec{\lambda}\cdot\vec{\mu}} \langle\langle \exp(-i\lambda_x {\rm Re}\langle T\psi_i|M|\psi_i\rangle - i\lambda_y {\rm Im}\langle T\psi_i|M|\psi_i\rangle - i\lambda_z\langle\psi_i|M|\psi_i\rangle)\rangle\rangle. \quad (8)$$

To perform the averaging in Eq. (8), we use the random matrix theory (RMT) approach [6]. Instead of the ensemble of nanoparticles with strong spin-orbit scattering we will consider an ensemble of symplectic matrices of size $2N \times 2N$ with $N \gg 1$. Then the eigenfunctions $\langle\psi|$ and $\langle T\psi|$ of the Hamiltonian are N-component spinors:

$$\langle\psi| = (\{\phi_k^*, \chi_k^*\}), \qquad \langle T\psi| = (\{-\chi_k, \phi_k\}). \quad (9)$$

The operator of magnetic moment M is a Hermitian matrix, which due to its time reversal properties can be diagonalized to the form ${\rm diag}\{M_1, -M_1, \ldots, M_k, -M_k, \ldots, M_N, -M_N\}$. In the basis of the eigenfunctions of M the matrix elements (7) take the form

$$\langle\psi|M|\psi\rangle = \sum_{k=1}^{N} M_k(|\phi_k|^2 - |\chi_k|^2), \quad (10)$$

$$\langle T\psi|M|\psi\rangle = -2\sum_{k=1}^{N} M_k\phi_k\chi_k. \quad (11)$$

The advantage of the RMT approach is that the ensemble averaging in Eq. (8) is easily performed using the Porter-Thomas distribution [6] of the matrix elements:

$$\langle\langle\cdots\rangle\rangle = \int \prod_{k=1}^{N} \frac{d^2\phi_k d^2\chi_k}{(\pi/2N)^2} e^{-2N(|\phi_k|^2+|\chi_k|^2)}\cdots. \quad (12)$$

The averaging in Eq. (8) with the help of (10)–(12) reduces to the calculation of N identical quadruple Gaussian integrals. The result has the form

$$p(\vec{\mu}) = \int \frac{d^3\lambda}{(2\pi)^3} e^{i\vec{\lambda}\cdot\vec{\mu}} \prod_{k=1}^{N}\left(1 + \frac{|\vec{\lambda}|^2 M_k^2}{(2N)^2}\right)^{-1}. \quad (13)$$

In the limit of large $N \gg 1$, this integral becomes Gaussian also, and we find

$$p(\vec{\mu}) = \left(\frac{2N^2}{\pi {\rm Tr}M^2}\right)^{3/2} \exp\left(-\frac{2N^2}{{\rm Tr}M^2}|\vec{\mu}|^2\right). \quad (14)$$

Taking into account the relation (6), we now immediately find the distribution function of the g-factor in the form (4) with the mean square g defined as

$$\langle\langle g^2\rangle\rangle = \frac{3}{\mu_B^2}\frac{{\rm Tr}M^2}{N^2}. \quad (15)$$

As a phenomenological theory, RMT enabled us to find the functional form of the distribution function; however, the width of the distribution (15) is now expressed in terms of a phenomenological parameter ${\rm Tr}M^2/N^2$. The relation between this parameter and the microscopic properties of the system cannot be established within the RMT. To do this, one has to find an observable quantity Q which can

be evaluated within both the phenomenological RMT and a microscopic theory.

We choose Q to be the energy absorbed in unit time from a weak external ac magnetic field $H(t) = H_0 \cos\omega t$. Such a field induces transitions between quantum levels in the grain, leading to the absorption of the energy in the grain. Within the RMT, the absorption can be found with the help of the Fermi golden rule as

$$Q = \left\langle\left\langle 2\pi \sum_{k\le k_f<p} \left| \frac{1}{2} H_0 \langle\psi_k|M|\psi_p\rangle \right|^2 \delta(\omega + \epsilon_k - \epsilon_p)\right\rangle\right\rangle \omega . \tag{16}$$

The expression inside $\langle\langle\cdots\rangle\rangle$ is the rate of absorption of quanta of radiation interacting with the system. The absorption occurs due to the transitions from occupied states with $k \le k_f$ to the empty states, $p > k_f$, and are induced by the term $\frac{1}{2} H_0 M e^{-i\omega t}$ in the corresponding coupling Hamiltonian.

In RMT the energy levels and the eigenfunctions are uncorrelated, i.e., the averaging over the energy levels and matrix elements in Eq. (16) can be performed independently. Also, at $\omega \gg \delta$, one can neglect the correlations of the densities of states at energies separated by ω, and we find

$$Q = \frac{\pi\omega^2 H_0^2}{2\delta^2} \langle\langle |M_{kp}|^2\rangle\rangle . \tag{17}$$

It is important to note that contrary to the above calculation of the g-factors of individual levels [Eqs. (6) and (7)], here the matrix elements M_{kp} are between eigenstates with different energies. Upon averaging over the ensemble, $\langle\langle |M_{kp}|^2\rangle\rangle$ becomes independent of k and p. Its magnitude can be found by presenting the invariant $\mathrm{Tr}M^2$ as a sum of $\langle\langle |M_{kp}|^2\rangle\rangle$ over all $2N$ values of k and p. Since the number of diagonal matrix elements $2N$ is small compared to the number of the off-diagonal ones, $4N^2 - 2N$, we conclude that $\langle\langle |M_{kp}|^2\rangle\rangle = \mathrm{Tr}M^2/4N^2$ at $N \gg 1$. By combining this relation with Eqs. (17) and (15), we find

$$\langle\langle g^2\rangle\rangle = \frac{24\delta^2}{\pi\hbar\omega^2(\mu_B H_0)^2} Q . \tag{18}$$

It is noteworthy that this result, obtained within the RMT, contains no phenomenological parameters. It establishes a relationship between the property of a single level, the g-factor, and a macroscopic quantity Q insensitive to the effects of discreteness of levels.

To evaluate the absorption rate Q for a given nanoparticle, it is convenient to express it as $Q = \frac{1}{2}\omega A'' H_0^2$ in terms of the imaginary part A'' of the zz component of the tensor of magnetic polarizability of the sample A_{ik}, defined as $M_i = A_{ik} H_k$, (Ref. [7]). Then the result for the mean square g-factor takes the form

$$\langle\langle g^2\rangle\rangle = \frac{12\delta^2}{\pi\hbar\mu_B^2} \frac{A''(\omega)}{\omega} . \tag{19}$$

It is well known [7] that at $\omega \to 0$ the imaginary part of the polarizability vanishes as $A''(\omega) \propto \omega$.

Since $M = M_z^{\mathrm{orb}} + M_z^{\mathrm{sp}}$, one can distinguish between the orbital and spin contributions to the magnetic polarizability of the nanoparticle. The spin contribution has the form

$$A_s(\omega) = \frac{\mu_B^2 g_0^2}{4\delta} \frac{1}{1 - i\omega\tau_{\mathrm{so}}/2} . \tag{20}$$

Here the first factor is the usual static Pauli susceptibility of the electron gas of the nanoparticle, and the second one accounts for the fact that spin correlations decay exponentially with the time constant $\tau_{\mathrm{so}}/2$. Substituting the imaginary part of the polarizability (20) into (19), we reproduce the first term of our main result (5).

The orbital contribution to the magnetic polarizability is due to the magnetic moment of the eddy currents generated in the sample by the ac magnetic field. For a particle of a shape symmetrical with respect to the rotations around the z axis, one can easily find

$$A'' = \frac{\omega\sigma}{4c^2} \overline{\rho_\perp^2} V, \qquad \omega \to 0 . \tag{21}$$

Here σ is the conductivity of the metal, V is the volume of the nanoparticle, and $\overline{\rho_\perp^2}$ is the "moment of inertia" of the grain, assuming unit density. For a spherical nanoparticle of radius L the combination of Eqs. (19) and (21) reproduces the second term in Eq. (5) with $\alpha = (6/5)(m/m^*)^2$.

For the thin ring geometry, Eqs. (19) and (21) result in $\langle\langle g^2\rangle\rangle = 3m^2L^2D\delta/\pi^3\hbar^3$, where L stands for the circumference of the ring. In the context of the persistent current problem the orbital effect of magnetic field on the splitting of the energy levels was studied earlier by Kravtsov and Zirnbauer [5]. They used the nonlinear σ-model techniques [8] to solve the general problem of crossover from the symplectic ensemble to the unitary one. A special limiting case of that solution gave rise to a distribution function of level splittings, which reassuringly coincides with our result for the thin ring geometry. Phenomenologically the crossover problem was solved within RMT by Mehta and Pandey [9]. Our approach enables one to express their phenomenological crossover parameter to physical observables without resorting to σ-model calculations.

In the case of weak spin-orbit interaction, $\delta\tau_{\mathrm{so}} \gg 1$, the correction to the average g-factor is small and can be found by perturbation theory. In the lowest-order perturbation theory in spin-orbit coupling, one finds [1]

$$g_i/g_0 = 1 - \frac{\hbar\delta}{\pi\tau_{\mathrm{so}}} \sum_{j\ne i} \frac{1}{(\epsilon_i - \epsilon_j)^2} . \tag{22}$$

Assuming that the energy levels ϵ_j are equidistant, the sum (22) was evaluated by Kawabata [4]. However, in a disordered system the Wigner-Dyson statistics of the energy levels is a more realistic assumption. In this case one of

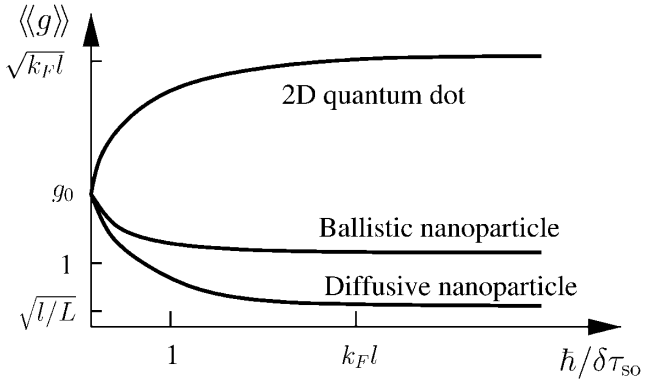

FIG. 1. Sketch of the dependence of the average g-factor on the strength of spin-orbit scattering (see text). We assumed $m^*/m \simeq 1$ in this plot.

the levels j can be close to level i, resulting in a particularly large correction to the g-factor. Taking into consideration the fact that the level repulsion in the orthogonal ensemble suppresses the probability p_o of two levels being very close, $p_o(\epsilon_i - \epsilon_j) = \pi^2|\epsilon_i - \epsilon_j|/6\delta^2$ [6], we find that the average value of the sum in Eq. (22) is logarithmically large:

$$\langle\langle g\rangle\rangle = g_0 - \frac{\pi g_0}{12}\,\frac{\hbar}{\delta\tau_{so}}\,\ln\frac{\delta\tau_{so}}{\hbar}\,. \qquad (23)$$

The logarithmic divergence in Eq. (23) was cut off at the energy scale $|\epsilon_i - \epsilon_j| \sim \sqrt{\delta/\tau_{so}}$, because of the additional level repulsion caused by the weak spin-orbit coupling.

Our results are summarized in Fig. 1. The lower curve shows the dependence of the average g-factor on the strength of the spin-orbit scattering in the case of a diffusive nanoparticle. In the regime of $1/\delta\tau_{so} \ll 1$ the behavior is described by Eq. (23), and at $1/\delta\tau_{so} \gg 1$ the average g-factor drops, in agreement with Eq. (5). In the latter regime, $\langle\langle g\rangle\rangle = (8/3\pi)^{1/2}\langle\langle g^2\rangle\rangle^{1/2}$, as one can easily see from the distribution function (4).

The middle curve in Fig. 1 shows schematically the behavior of a ballistic nanoparticle, where all of the scattering of electrons is due to the reflection from the boundaries only. One can conduct a quantitative study in a simple model of a spherical ballistic nanoparticle of radius L with totally diffusive scattering off the boundaries. The result amounts to replacing $l \to 5L/8$ in Eq. (5) and keeping α the same as in the case of a diffusive sphere. Taking into consideration the rapid decrease of the distribution function (4) of the g-factor at $g^2 \ll \langle\langle g^2\rangle\rangle$, one should conclude that the nanoparticles showing the values of g^2 well below the ballistic value $\langle\langle g^2\rangle\rangle = (3/4)\,(m/m^*)^2$ are most likely in the diffusive regime. This is apparently the case in the experiment [3]: as it follows from Eq. (5), the measured $g = 0.3$ value yields the boundaries $l/L \lesssim 0.1$ and $\tau_{so}\delta/\hbar \lesssim 0.05$ for the mean free path and spin-orbit scattering rate, respectively.

The top curve in Fig. 1 shows the behavior of the g-factor in the case of a 2D quantum dot in a perpendicular magnetic field. In accordance with Eq. (3), in the strong spin-orbit scattering case, $1/\delta\tau_{so} \gg 1$, the orbital moment $\langle l_z\rangle$ reaches a very large value $\sim\sqrt{k_F l}$. In experiments with quantum dots in GaAs heterostructures the orbital effect should be further enhanced due to a small effective mass $m^* \approx 0.067m$ of electrons, so one can expect to find an independent of g_0 value, $\langle\langle g\rangle\rangle \sim (m/m^*)\sqrt{k_F l}$. At weaker spin-orbit scattering, $1/\delta\tau_{so} \lesssim 1$, the orbital enhancement of the g-factor is reduced.

Our discussion of the effects of spin-orbit scattering on the g-factors of individual levels neglected electron-electron interactions. In the mean-field approximation we do not expect the interactions to affect our results. In particular, the well-known exchange enhancement of the g-factor occurs in the thermodynamic limit, and should not affect the g-factors of individual quantum levels defined by Eq. (1). On the other hand, in general the electron-electron correlations scramble the picture of single-electron levels used in this paper. However, for a few lowest energy levels usually observed in the experiment the single-electron picture is still valid [10], provided the conductance of the grain is large compared to $e^2/\hbar$.

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