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Relativistic calculation of conduction-electron g-factors in noble metals

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Abstract. An *ab initio* fully relativistic approach to the calculation of conduction-electron g-factors in metals is presented. The electron magnetic moment tensor is determined by evaluating the matrix elements of the relativistic magnetic moment operator with the wave functions of the fully relativistic linear muffin-tin orbital LMTO method. Calculations of the g-factors for cyclotron orbits in noble metals using this new approach resolve a long-standing problem in the interpretation of the experimental data.

1. Introduction

The electronic g-factor is a quantity of fundamental importance for describing the response of a non-magnetic metal to an external magnetic field. Recent advances in experimental techniques for studying the de Haas–van Alphen (DHVA) quantum oscillations in metals have made it possible to obtain reliable values for the cyclotron-orbit-averaged g_c-factors (for a review, see [1]).

The spin–orbit interaction is responsible for deviations of the g-factors in metals from the free electron value ($g_s = 2.0023$ including quantum-electrodynamical corrections). Even though quasiparticle states in a magnetic field are Landau levels rather then states with well-defined k, their splitting in the framework of Fermi liquid theory [2]

$$\Delta E_n(k_z) = \pm\tfrac{1}{2} g_n(k_z)\mu_B H \tag{1}$$

is an average of the electron magnetic moment tensor $g_n(k)$ over a cyclotron orbit on the nth band at the Fermi surface, renormalized by quasiparticle interactions.

Previous theoretical calculations of the g_c-factors in noble [3, 4] and transition [5] metals were unable to account for the experimentally observed anisotropy. These calculations employed a scalar-relativistic band-structure model using an effective LMTO Hamiltonian based on the Pauli equation. Recently, Hjelm and Calais [6] attempted to improve this calculational scheme by including the perturbation from the magnetic field in a self-consistent cycle. This shifted the calculated values of the g_c factors without significantly affecting their anisotropy.

The scalar-relativistic LMTO Hamiltonian for an electron in a uniform magnetic field $\boldsymbol{H}$ is usually taken in the form

$$\mathcal{H} = \mathcal{H}_{\mathrm{LMTO}} + \mathcal{H}_{\mathrm{so}} + \mathcal{H}_{\mathrm{Z}} \tag{2}$$

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where the spin–orbit term is

$$\mathcal{H}_{so} = \xi L \cdot \sigma \tag{3}$$

(ξ is a parameter of the spin–orbit interaction) and the external field is introduced to first order through the Zeeman term

$$\mathcal{H}_Z = \mu_B (L + \sigma) \cdot H. \tag{4}$$

Other relativistic terms and terms quadratic in H are neglected.

In the absence of spin–orbit interaction, the electron in the magnetic field has an isotropic magnetic moment due to spin with the free-electron value of $g_s \mu_B$. The effects of spin–orbit interaction are to induce an orbital magnetic moment and to modify the value of g_s.

In a scalar-relativistic treatment, the Kramers-conjugate states are represented by a product of orbital and spin functions. Matrix elements of the orbital part of the Zeeman operator in (4) between such orbitally non-degenerate states are identically equal to zero, so the g-shift calculated from scalar-relativistic band models [3, 4, 5, 6] arises entirely from the orbital moment induced by the spin–orbit term (3). It contains no contribution from the spin–orbit-induced correction to the free-electron value of g_s.

This spin-only g-shift is given to a leading order of perturbation theory by

$$\frac{g_n^{\hat{\alpha}}(k)^2}{4} = 1 + \xi \sum_{m \neq n} \frac{\left| \hat{\alpha} \cdot \langle \psi_m(k) | L | \psi_n(k) \rangle \right|^2}{E_n(k) - E_m(k)} \tag{5}$$

where $\hat{\alpha}$ is a unit vector specifying the direction of the magnetic field, and $(E_n - E_m)$ is the difference in energy between the given state n and a state m with appropriate symmetry [7]. It can be neglected whenever the spin–orbit interaction is sufficiently small that Bloch states for any given direction of spin quantization are almost pure spin states.

MacDonald [8] has analysed the trends in the g-factor variation among transition metals in the tight-binding approximation, using canonical d-bandwidths and spin–orbit parameters ξ_d, so that his calculations set a lower bound on the spin-only g-shift. A comparison between his results and the results of scalar-relativistic band calculations [5] demonstrates that even at moderate spin–orbit interactions the shift due to the orbital moment and the spin-only shift are of comparable magnitude. Neither the band nor the tight-binding approach alone yields a complete description of the g-shift.

An additional complication arises from the fact that the expectation value of the Zeeman operator is not gauge-invariant. According to Moore [9], its gauge invariance can be retained by adding further terms to the Hamiltonian as it was done, for example, in the work of Singh *et al* [10] on the g-factors of ferromagnetic metals. They estimated the correction due to lack of gauge invariance as typically being about 5% of the spin-only shift.

This paper presents a new method for the calculation of g-factors in metals. Such a calculation must involve a proper treatment of the spin–orbit interaction and the interaction of spin with the field, as well as including the external magnetic field in a gauge-invariant manner. These requirements are met by carrying out a relativistic calculation based on the Dirac equation.

2. Theory

In a fully relativistic treatment, spin is not a good quantum number and the eigenstates can not be expressed as product states. Because of spin–orbit interaction, the magnetic moment of the electron acquires a tensor character [2]. If the magnetic moment operator is defined from the Dirac equation, the requirement of gauge invariance is automatically satisfied. The Hamiltonian for a Dirac electron in an external magnetic field with vector potential $\boldsymbol{A}$ is [11]

$$\mathcal{H} = \mathcal{H}_{\mathrm{D}} - e\boldsymbol{\alpha} \cdot \boldsymbol{A} \tag{6}$$

where $\mathcal{H}_{\mathrm{D}}$ is the Dirac Hamiltonian in the absence of external field and $\boldsymbol{\alpha}$ are the Dirac matrices in the standard representation in terms of the Pauli matrices $\boldsymbol{\sigma}$. In this relativistic formulation there are no explicit terms quadratic in magnetic field. Therefore it includes, among other effects, the influence of the A^2-term neglected in a scalar-relativistic treatment. Using the symmetric gauge for the homogeneous field, the relativistic magnetic moment operator can be written (in the atomic Rydberg system such that $\hbar = 2m_0 = 1$) as

$$-(\partial\mathcal{H}/\partial H) = \tfrac{1}{2}\mu_{\mathrm{B}} c r \tag{7}$$

The eigenvalues of the relativistic magnetic moment operator $g_n(\boldsymbol{k})$ were evaluated using Dirac wave functions of the relativistic linear muffin-tin orbital (RLMTO) method [12] in the atomic-sphere approximation (ASA). Self-consistent charge densities were obtained using the relativistic Dirac–Hartee–Fock–Slater atomic program to construct the initial charge densities. The exchange–correlation part of the potential was included in the local-density approximation using von Barth–Hedin parametrization [13].

By analogy with its non-relativistic counterpart [14], the orthonormalized wave function of the Bloch electron is given in the form of a one-centre expansion

$$\Psi_{n\sigma}(\boldsymbol{k}, \boldsymbol{r}) = \sum_{\kappa,\kappa'} \sum_{\mu,\mu'} [\Phi_{\kappa\mu}(\boldsymbol{r}) \Pi_{\kappa\mu,\kappa'\mu'}(\boldsymbol{k}) + \dot{\Phi}_{\kappa\mu}(\boldsymbol{r}) \Omega_{\kappa\mu,\kappa'\mu'}(\boldsymbol{k})] C^{\sigma}_{\kappa'\mu'}(E_n, \boldsymbol{k}) \tag{8}$$

in terms of the basis functions

$$\Phi_{\kappa\mu}(\boldsymbol{r}) = \mathrm{i}^l \begin{pmatrix} g_\kappa(r) \chi^{\mu}_{\kappa}(\hat{\boldsymbol{r}}) \\ \mathrm{i} f_\kappa(r) \chi^{\mu}_{-\kappa}(\hat{\boldsymbol{r}}) \end{pmatrix}. \tag{9}$$

κ is the relativistic quantum number, $g_\kappa(r)$ and $f_\kappa(r)$ are the large and small component solutions of the coupled system of radial Dirac equations at some appropriately chosen energy E_ν, the dot denotes their energy derivatives at E_ν, E_n are the eigenvalues and $C^{\sigma}_{\kappa\mu}(E_n, \boldsymbol{k})$ are the eigenvectors of the RLMTO generalized eigenvalue problem, and $\Pi_{\kappa\mu,\kappa'\mu'}(\boldsymbol{k})$, $\Omega_{\kappa\mu,\kappa'\mu'}(\boldsymbol{k})$ are the matrices of expansion coefficients. The relativistic Dirac spinors include mixed angular and spin functions

$$\chi^{\mu}_{\kappa}(\hat{\boldsymbol{r}}) = \sum_{s=\pm\frac{1}{2}} C(l\, \tfrac{1}{2}\, j; \mu - s, s) Y_{l,\mu-s}(\hat{\boldsymbol{r}}) \chi(s) \tag{10}$$

that are the eigenfunctions of the spin–orbit interaction operator [11].

The matrix elements of the relativistic magnetic moment operator (7) on these wave functions can be written as

$$g_n^{\sigma\sigma'}(k) = \langle \Psi_{n\sigma}(k,r) \,|\, c\, r \times \alpha \,|\, \Psi_{n\sigma'}(k,r) \rangle$$
$$= \sum_{\kappa,\kappa'} i^{l'-l+1} \sum_{\alpha,\beta=1}^{2} R_{\kappa\kappa'}^{\alpha\beta} \sum_{\mu,\mu'} Q_{n\kappa\mu}^{\sigma\alpha *}(k) A_{\kappa\mu,\kappa'\mu'} Q_{n\kappa'\mu'}^{\sigma'\beta}(k) \tag{11}$$

in terms of the radial integrals

$$R_{\kappa\kappa'}^{\alpha\beta} = c \int_0^{S_{WS}} dr\, r^3 \left(g_\kappa^\alpha f_{\kappa'}^\beta + f_\kappa^\alpha g_{\kappa'}^\beta \right) \tag{12}$$

where S_{WS} is the Wigner–Seitz radius, $g_\kappa^1 \equiv g_\kappa$, $g_\kappa^2 \equiv \dot{g}_\kappa$, etc; the angular integrals

$$A_{\kappa\mu,\kappa'\mu'} = \int d\Omega\, \chi_\kappa^{\mu\dagger} \hat{r} \times \sigma \chi_{-\kappa'}^{\mu'} \tag{13}$$

and the complex coefficients

$$Q_{n\kappa\mu}^{\sigma 1}(k) = \sum_{\kappa',\mu'} \Pi_{\kappa\mu,\kappa'\mu'}(k) C_{\kappa'\mu'}^{\sigma}(E_n, k) \tag{14}$$

and

$$Q_{n\kappa\mu}^{\sigma 2}(k) = \sum_{\kappa',\mu'} \Omega_{\kappa\mu,\kappa'\mu'}(k) C_{\kappa'\mu'}^{\sigma}(E_n, k). \tag{15}$$

The angular integrals involving spin-angular functions can be easily evaluated using the Racah algebra of irreducible tensor operators [15]. A complete derivation of expressions for matrix elements, selection rules and tests of convergence and accuracy will be presented elsewhere.

To find the eigenvalues $g_n(k)$ of the relativistic magnetic moment operator for any band state, the operator must be diagonalized for the pair of Kramers-degenerate eigenstates (σ, σ') (no additional degeneracies are supposed). The solutions of the eigenvalue equation for each component $g_n(k)$ are simply

$$g_n(k) = \pm \left(|g_n^{\sigma\sigma}(k)|^2 + |g_n^{\sigma\sigma'}(k)|^2 \right)^{1/2} \tag{16}$$

since due to Hermicity of the operator (7) its matrix elements on Kramers-conjugate states have the symmetry properties

$$g^{\sigma\sigma'}(k) = g^{\sigma'\sigma}(k) \qquad g^{\sigma\sigma}(k) = -g^{\sigma'\sigma'}(k). \tag{17}$$

The g-factor for a cyclotron orbit in a given band g_c^{band} is calculated by taking the time-weighted average of g-factors $g_n^{\hat{\alpha}}(k) = \hat{\alpha} \cdot g_n(k)$ around the orbit

$$g_c^{\text{band}} = \oint_c dk\, g_n^{\hat{\alpha}}(k) v_\perp^{-1}(k) \Big/ \oint_c dk\, v_\perp^{-1}(k) \tag{18}$$

where $\hat{\alpha}$ is a direction of the magnetic field perpendicular to the plane of the orbit, and $v_\perp$ is the component of the electron velocity in that plane. The value that is directly comparable with experimental data is the g_c-factor renormalized by many-body effects

$$g_c^* = \frac{S_{xc} g_c^{\text{band}}}{1 + \lambda_c^{ep}} \tag{19}$$

where S_{xc} is the exchange–correlation (Stoner) enhancement factor and $1 + \lambda_c^{ep}$ is the electron–phonon enhancement factor [3].

3. Results

Table 1 compares present and previous theoretical values for the g_c-factors for principal orbits on the Fermi surfaces of noble metals with experimental values deduced from DHVA data. The noble metals copper, silver and gold have topologically identical Fermi surfaces. Even though the anisotropy of the g_c-factors should be larger in gold due to the stronger spin–orbit interaction, similar relative values are expected on corresponding orbits in the different metals.

Table 1. Band theoretical and experimental values of g_c-factors for principal orbits in noble metals. After correcting for the mass enhancement from cyclotron mass data, the ratio yields the Stoner enhancement S_{xc}.

	Orbit	g_c ([3])	Δg_c (equation (5))	g_c^{band} (present work)	$1+\lambda_c^{ep}$ ([3])	g_c^{expt} ([3])	S_{xc}
Cu	$B\langle 100\rangle$	2.13		2.16	1.052	2.24(5)	1.09(3)
	$R\langle 100\rangle$	2.05		2.05	1.071	2.08(5)	1.09(2)
	$D\langle 110\rangle$	2.09		2.08	1.091	2.11(2)	1.10(1)
	$B\langle 111\rangle$	2.12		2.10	1.034	2.12(2)	1.04(1)
	$N\langle 111\rangle$	2.04	−0.02	2.04	1.198	1.90(4)	1.12(2)
Ag	$B\langle 100\rangle$	2.09		2.10	1.057	2.14(20)	1.07(10)
	$R\langle 100\rangle$	2.04		2.04	1.109		
	$D\langle 110\rangle$	2.07		2.05	1.122	2.24(10)	1.22(5)
	$B\langle 111\rangle$	2.10		2.08	1.041	2.43(15)	1.21(7)
	$N\langle 111\rangle$	2.01	−0.02	2.00	1.264	1.92(5)	1.21(3)
Au	$B\langle 100\rangle$	2.40		2.35	1.111	2.29(4)	1.08(2)
	$R\langle 100\rangle$	2.13		2.11	1.103	2.26(10)	1.18(5)
	$D\langle 110\rangle$	2.19		2.12	1.167	2.03(20)	1.11(10)
	$B\langle 111\rangle$	2.43		2.28	1.051	2.42(13)	1.11(7)
	$N\langle 111\rangle$	2.20	−0.17	2.05	1.98[a]	1.15(5)	1.11[a]

[a] Best estimate, see text.

However, two independent scalar-relativistic calculations [3,4] both yield g_c-factors on the neck orbit in gold that are larger than those on the rosette and dogsbone, whereas in the other noble metals the g_c values on the rosette and dogsbone are intermediate between the belly and the neck. Eriksson *et al* [4] have attributed this discrepancy to the incomplete treatment of spin–orbit interaction within the scalar-relativistic band model.

The calculation of the spin-only correction to g_c requires the evaluation of the perturbation theory expression (5) for all $\boldsymbol{k}$-points around the extremal cyclotron orbit. However, it can be assumed to be constant for all points on the neck orbits in the noble metals due to the relatively small area of the orbits. It is therefore easy to estimate the value of the spin-only shift using the spin–orbit splitting and band gap calculated at the centre of the orbit, which is the symmetry point L (see table 1). The scalar-relativistic band calculations yield a positive g-shift due to the orbital moment, $\Delta g_c = 0.20$, on the neck orbit in gold, while a perturbation theory calculation yields a negative spin-only shift $\Delta g_c \approx -0.17$, resulting in the value $g_c \approx 2.03$.

The results of the present fully relativistic calculations of orbital g_c-factors for gold are consistent with those for the other noble metals. Our calculated value of $g_c = 2.05$ on the neck is in good agreement with results of scalar-relativistic calculations combined with the perturbation theory estimate of the spin-only g shift.

By comparing the experimental orbital g-factor with a reliable band value, the orbital average of the Stoner factor S_{xc} can be deduced. In order to extract S_{xc} from the data in table 1, we have adopted electron–phonon enhancement factors obtained [3] by fitting a KKR band model to experimental Fermi-surface data.

In gold, the data for the belly, rosette, and dogsbone orbits yield no evidence for significant anisotropy in S_{xc}, whereas the data for the neck orbit yield a value less than unity, which is unphysical. The best estimate of S_{xc} deduced from the other orbits, $S_{xc} = 1.11 \pm 0.02$, is in reasonable agreement with the result of the first-principles calculation by MacDonald *et al* [16] of the average enhancement $S_{xc} = 1.06$. If this estimate is supposed to apply also to the neck, then the data imply that $1 + \lambda_c^{ep} = 1.98 \pm 0.02$. Independent evidence that the band calculation seriously underestimates $1 + \lambda_c^{ep}$ in gold comes from the interpretation of acoustic attenuation data, on the basis of which it has been found that $1 + \lambda_c^{ep} \approx 1.90$ [3].

In conclusion, a new fully relativistic method for calculating conduction-electron g-factors in metals has been presented. Our approach, which is based on the Dirac equation, offers a natural framework for the calculation of g-factors, automatically providing a proper treatment of the modification of the electron magnetic moment by spin–orbit interaction and satisfying the requirement of gauge invariance. It is shown that all previous calculations of band g-factors neglected contributions that are significant on the neck orbit of gold.

By comparing band g-factors with experimental g-factors (which are renormalized by many-body effects) it is possible to extract valuable information about many-body interactions at the Fermi surface. The present calculations yield a consistent interpretation of the gold data, in which the Stoner enhancement is isotropic and in which the many-body enhancement of the cyclotron mass on the neck orbit is much larger than previously deduced from cyclotron mass data, but in line with the results of acoustic attenuation studies.

The present approach is being extended to transition metals, where a complex configuration of energy bands and strong spin–orbit interaction are expected to make fully relativistic g-factor calculations especially effective.

References

[1] Shoenberg D 1984 *Magnetic Oscillations in Metals* (London: Cambridge University Press) ch IX
[2] Lifshitz E M and Pitaevski L P 1980 *Statistical Physics. Part 2: Theory of Condensed Matter* 3rd edn (Oxford: Pergamon) ch VI
[3] Grechnev G E, Savchenko N V, Svechkarev IV, Lee M J G and Perz J M 1989 *Phys. Rev.* B **39** 9865
[4] Eriksson O, Ohlsén H and Calais J-L 1989 *Phys. Rev.* B **40** 5961
[5] Ohlsén H and Calais J-L 1987 *Phys. Rev.* B **35** 7914
[6] Hjelm A and Calais J-L 1991 *Phys. Rev. Lett.* **67** 2064
[7] Koelling D D and MacDonald A H 1981 *Relativistic Effects in Atoms, Molecules, and Solids (NATO ASI Series B: Physics)* vol 87, ed G L Malli (New York: Plenum) p 227
[8] MacDonald A H 1982 *J. Phys. F: Met. Phys.* **12** 2579
[9] Moore R A 1975 *J. Phys. F: Met. Phys.* **5** 459
[10] Singh M, Callaway J and Wang C S 1976 *Phys. Rev.* B **14** 1214
[11] Rose M E 1960 *Relativistic Electron Theory* (New York: Wiley) ch V
[12] Godreche G 1982 *J. Magn. Magn. Mater.* **29** 262
[13] von Barth U and Hedin L 1972 *J. Phys. C: Solid State Phys.* **5** 1629
[14] Andersen O K 1975 *Phys. Rev.* B **12** 3060
[15] Varshalovich D A, Moskalev A N and Khersonski V K 1988 *Quantum Theory of Angular Momentum* (Singapore: World Scientific) ch XIII
[16] MacDonald A H, Daams J M, Vosko S H and Koelling D D 1982 *Phys. Rev.* B **25** 713