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Fully relativistic treatment of core states for a spin-dependent potential

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Abstract. An efficient and reliable algorithm for solving the Dirac equation for core-state wavefunctions in the presence of a spin-dependent potential is presented. The approach is applied to calculate the contributions to the hyperfine field of Fe, Co and Ni stemming from non-s core electrons.

1. Introduction

The interplay of relativistic effects (primarily spin-orbit coupling) and spin polarisation gives rise to a number of interesting effects, such as magneto-crystalline anisotropy and magneto-optical phenomena. A rigorous theoretical investigation of such effects should be based on a description of the electronic structure that takes relativistic effects as well as spin polarisation properly into account. The problem of dealing within the local spin-density formalism with the corresponding Dirac equation for a spin-dependent potential has been discussed in the past by several authors (Doniach and Sommers 1981, Feder *et al* 1983, Strange *et al* 1984). The solutions of the emerging sets of radial differential equations permit a more or less straightforward generalisation of conventional band-structure schemes. This has been shown for the KKR method (Feder *et al* 1983, Strange *et al* 1984) as well as for the LMTO method (Ebert 1988) and several corresponding relativistic spin-polarised band-structure calculations can now be found in the literature. In contrast to this situation for the conduction electrons, to our knowledge only one analogous calculation for the tightly bound core electrons has been done until now (Cortona *et al* 1985). This situation presumably arises from the problem that the corresponding core wavefunctions do not have unique spin-angular character and have to satisfy specific boundary conditions at the nuclear site and far away from it. Cortona *et al* (1985) have proposed an algorithm to deal with the corresponding complex boundary problem. In the following we present an alternative algorithm, which is very efficient, easy to implement and, we feel, clearer than the former approach. As an application of our method we calculate the contributions of non-s core electrons to the hyperfine field of Fe, which were previously ignored. Further applications of relativistic spin-polarised calculations of core wavefunctions are, for example, rigorous total energy calculations and investigations of the polarisation dependence of x-ray absorption by magnetic materials (MXD: magnetic x-ray dichroism; see, for example, Ebert *et al* 1989a).

2. Solution of the 'relativistic' core-state eigenvalue problem for a spin-dependent potential

From a technical point of view, the most important consequence of having a spin-dependent potential is that the corresponding solutions to the single-site Dirac equation do not have unique spin-angular character. This is due to the coupling of partial waves with the same quantum number μ and parity, which is introduced by the spin-dependent part of the potential. Fortunately, it is justified to neglect this coupling other than for partial waves with the same μ - and l -quantum numbers (Feder *et al* 1983, Cortona *et al* 1985). Instead of dealing with an infinite set of differential equations one is left with the coupling of the two partial waves for the angular momentum $j = l \pm \frac{1}{2}$ or, equivalently, $\kappa = +l$ and $-l - 1$. This simplification leads finally to a set of at most four radial differential equations (Strange *et al* 1984):

$$\partial P_{\Lambda i} / \partial r = -(\kappa/r)P_{\Lambda i} + [(E - V)/c^2 + 1]Q_{\Lambda i} + (B/c^2)\langle \chi_{-\Lambda} | \sigma_3 | \chi_{-\Lambda} \rangle Q_{\Lambda i} \quad (1)$$

$$\partial Q_{\Lambda i} / \partial r = (\kappa/r)Q_{\Lambda i} - (E - V)P_{\Lambda i} + B\langle \chi_{\Lambda} | \sigma_3 | \chi_{\Lambda} \rangle P_{\Lambda i} + B\langle \chi_{\Lambda} | \sigma_3 | \chi_{\bar{\Lambda}} \rangle P_{\bar{\Lambda} i} \quad (2)$$

where i labels the two possible independent solutions and the notation $P = gr$ and $Q = cfr$ has been used. $V(B)$ stands for the spin-averaged (-dependent) part of the potential $V + \beta\sigma_3 B$, and Λ , $-\Lambda$ and $\bar{\Lambda}$ represent the sets of quantum numbers (κ, μ) , $(-\kappa, \mu)$ and $(-\kappa - 1, \mu)$, respectively. All other quantities have their usual meanings (Rose 1961). The last term in (2) is responsible for the coupling of the partial waves with quantum numbers Λ and $\bar{\Lambda}$, i.e. for $P_{\bar{\Lambda} i}$ and $Q_{\bar{\Lambda} i}$ relations analogous to (1) and (2) hold with Λ and $\bar{\Lambda}$ interchanged. For $|\mu| = l + \frac{1}{2}$ no Λ - $\bar{\Lambda}$ coupling is possible and there are only the two coupled equations for P_{Λ} and Q_{Λ} with $\kappa = -l - 1$.

A bound solution to the Dirac equation, representing a core state, has to be regular at the origin, the site of the nucleus, and decays exponentially at large distances. The conventional way to solve this boundary problem is to integrate the radial Dirac equations outwards and inwards and to match the solutions at a convenient matching radius. This technique can also be used for the case of a spin-dependent potential (Cortona *et al* 1985). The corresponding outward integration starts with a series expansion:

$$P_{\Lambda i}^{\text{out}} = r^{\gamma_i} \sum_n p_{\Lambda i; n} r^n \quad (3)$$

$$Q_{\Lambda i}^{\text{out}} = r^{\gamma_i} \sum_n q_{\Lambda i; n} r^n \quad (4)$$

with $\gamma_i = \sqrt{\kappa_i^2 - (2Z/c)^2}$. The two independent solutions for the two values of i can be selected by setting $\kappa_i = \kappa$ ($\kappa_i = -\kappa - 1$) and $p_{\bar{\Lambda} i; 0} = 0$ ($p_{\Lambda i; 0} = 0$). The inward integration is started using the asymptotic form of P and Q for large r -values:

$$P_{\Lambda i}^{\text{in}} = p e^{-\mu r} \quad (5)$$

$$Q_{\Lambda i}^{\text{in}} = q e^{-\mu r} \quad (6)$$

with

$$\mu = \sqrt{-E - E^2/c^2} \quad (7)$$

and

$$p = -[(1 + E/c^2)/\mu]q. \quad (8)$$

The above-mentioned matching of the inward and outward solutions can only be

achieved if the wavefunctions are evaluated for the correct energy eigenvalue E of the boundary problem. Because the wavefunction will be normalised to 1, the matching depends on only four parameters: the relative weights of two solutions for the two values of i for outward and inward integration, A^{out} and A^{in} respectively, the relative scaling factor A of the superposed outward and inward wavefunctions and the energy E . For this reason, the matching at radius r_m (normally the classical turning point) can be expressed thus:

$$\Psi^{\text{out}}(r_m, E) = A\Psi^{\text{in}}(r_m, E) \quad (9)$$

with

$$\Psi^w(r, E) = \Psi_1^w(r, E) + A^w\Psi_2^w(r, E) \quad (10)$$

and

$$\Psi_\alpha^w(r, E) = \begin{bmatrix} g_{\lambda\alpha}^w(r)\chi_{\lambda}(\hat{r}) + g_{\bar{\lambda}\alpha}^w(r)\chi_{\bar{\lambda}}(\hat{r}) \\ if_{\lambda\alpha}^w(r)\chi_{-\lambda}(\hat{r}) + if_{\bar{\lambda}\alpha}^w(r)\chi_{-\bar{\lambda}}(\hat{r}) \end{bmatrix} \quad (11)$$

where $w = (\text{out}, \text{in})$ and $\alpha = (1, 2)$.

To find the energy eigenvalue E for which (9) can be satisfied, we adopt the Newton-Raphson algorithm. A detailed discussion of this approach to the boundary problem together with program listings can be found in Press *et al* (1986). For our purpose we define the four-component error function

$$\mathbf{F} = \begin{bmatrix} (g_{\lambda 1}^{\text{out}} + A^{\text{out}}g_{\lambda 2}^{\text{out}}) - A(g_{\lambda 1}^{\text{in}} + A^{\text{in}}g_{\lambda 2}^{\text{in}}) \\ c(f_{\lambda 1}^{\text{out}} + A^{\text{out}}f_{\lambda 2}^{\text{out}}) - cA(f_{\lambda 1}^{\text{in}} + A^{\text{in}}f_{\lambda 2}^{\text{in}}) \\ (g_{\bar{\lambda} 1}^{\text{out}} + A^{\text{out}}g_{\bar{\lambda} 2}^{\text{out}}) - A(g_{\bar{\lambda} 1}^{\text{in}} + A^{\text{in}}g_{\bar{\lambda} 2}^{\text{in}}) \\ c(f_{\bar{\lambda} 1}^{\text{out}} + A^{\text{out}}f_{\bar{\lambda} 2}^{\text{out}}) - cA(f_{\bar{\lambda} 1}^{\text{in}} + A^{\text{in}}f_{\bar{\lambda} 2}^{\text{in}}) \end{bmatrix} \quad (12)$$

with the functions g and f evaluated at $r = r_m$. Here, \mathbf{F} is obviously a function of the parameter vector

$$\mathbf{P} = \begin{bmatrix} E \\ A \\ A^{\text{out}} \\ A^{\text{in}} \end{bmatrix}. \quad (13)$$

The eigenvalue E is now simply found by seeking for the vector \mathbf{P} that gives $\mathbf{F}(\mathbf{P}) = 0$. This is done iteratively, i.e. from a parameter set \mathbf{P}_i an improved set \mathbf{P}_{i+1} is obtained by solving

$$\mathbf{0} = \mathbf{F}(\mathbf{P}_{i+1}) \simeq \mathbf{F}(\mathbf{P}_i) + \mathbf{J}\Delta\mathbf{P}_i \quad (14)$$

for $\Delta\mathbf{P}_i$. Then \mathbf{P}_{i+1} is obtained from

$$\mathbf{P}_{i+1} = \mathbf{P}_i - \Delta\mathbf{P}_i. \quad (15)$$

The Jacobian matrix $(J_{\alpha\beta})_i = (\partial F_\alpha / \partial P_\beta)_i$ can be replaced by the matrix $(\Delta F_\alpha / \Delta P_\beta)_i$. To start the iteration for \mathbf{P} a reasonable guess can be obtained from perturbational arguments. For a spin-dependent part of the potential $B(r)$ that is not too high only some $(-\kappa-1)$ character will be admixed into the wavefunction, which for a paramagnetic potential is characterised by the quantum numbers n , κ and μ . For this reason E will not

change dramatically, i.e. E can be initialised as for the paramagnetic case (Desclaux 1969). A^{out} and A^{in} can be set to some percentage value and A is fixed to $g_{k1}^{\text{out}}/g_{k1}^{\text{in}}$ to start the iteration. The step size ΔP_β ($\beta = 1, \dots, 4$) for evaluating the matrix $(J_{\alpha\beta})_i$ can be chosen to be some percentage of the corresponding parameters P_α and be decreased successively. If the starting values are not unreasonably chosen, the iteration converges very rapidly—normally within three to five iterations—to a relative change in the parameters of less than 10^{-14} .

The description of the algorithm given above assumes that there is a coupling of the partial waves, i.e. $|\mu| < l + \frac{1}{2}$. For $|\mu| = l + \frac{1}{2}$, A^{out} and A^{in} are identically zero and there are only two parameters to be determined. If there is no coupling, the conventional algorithm (Lieberman *et al* 1965) used to find the energy eigenvalue for a paramagnetic potential can of course also be used to treat the spin-dependent potential. On comparing results obtained this way with results produced by an application of the above Newton–Raphson approach, perfect agreement was found for all cases studied so far.

3. Application to Fe, Co and Ni

The above-described approach for a relativistic spin-polarised calculation of core wavefunctions has been applied in a number of different cases. Here results for the pure ferromagnetic metals Fe, Co and Ni are presented that are based on the potentials tabulated by Moruzzi *et al* (1978).

To obtain some idea of the influence of the spin-dependent part of the potential we show in figure 1 energy eigenvalues calculated by zeroth-, first- and second-order perturbation theory, compared with the *exact results*. Obviously the convergence of the

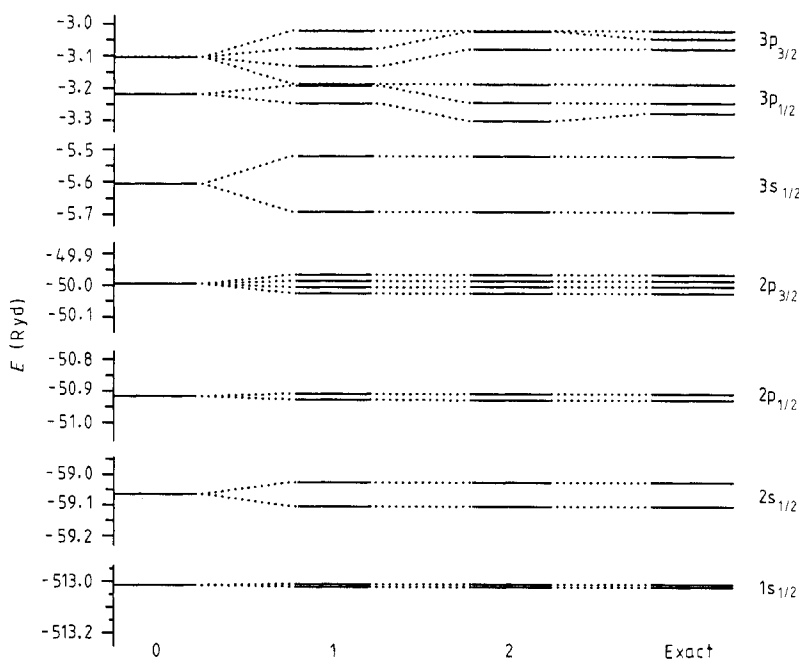


Figure 1. A core-state energy eigenvalue scheme for Fe calculated in zeroth-, first- and second-order perturbation theory with respect to $B(r)$ (marked 0, 1 and 2, respectively) compared with the exact values.

Table 1. κ - μ -resolved hyperfine fields $\langle \Phi_{\kappa', n\kappa\mu} | (\boldsymbol{\alpha} \cdot \boldsymbol{\mu}_n \times \mathbf{r}/r^3) e/\mu_n | \Phi_{\kappa', n\kappa\mu} \rangle$ for the $2p_{1/2}$ and $2p_{3/2}$ core states of Fe, with $\Phi_{n\kappa\mu} = \Phi_{\kappa, n\kappa\mu} + \Phi_{-\kappa, n\kappa\mu}$ (see (11) and (16)).

	κ	μ	$\kappa' = \kappa'' = \kappa$	$\kappa' = \kappa = -\kappa'' - 1$	$\kappa' = \kappa'' = -\kappa - 1$
$2p_{1/2}$	+1	-1/2	-83053.5	-398.3	-12.7
	+1	+1/2	83097.4	-415.4	13.8
$2p_{3/2}$	-2	-3/2	-46876.0	—	—
	-2	-1/2	-15603.0	410.3	-71.7
	-2	+1/2	15592.2	427.5	77.5
	-2	-3/2	46789.1	—	—

Table 2. Theoretical hyperfine fields for Fe, Co and Ni split into their various contributions compared with experimental data (Stearns 1987, Bonnenberg *et al* 1987).

	Fe	Co	Ni
1s	-17.7	-14.9	-6.9
2s	-515.8	-422.9	-178.6
2p	1.7	1.5	0.7
3s	301.0	263.9	115.8
3p	-0.7	-0.7	-0.4
Conduction band:			
s	-42.1	-72.0	-5.9
p	0.7	1.7	0.8
d	23.9	47.6	36.9
Sum	-249.0	-195.8	-37.6
Experiment	-339.0	-215.0	-75.0

perturbation series is normally quite rapid, but there are also exceptions. This depends, as one would expect, on the overlap of the spin-dependent part of the potential $B(r)$ and the unperturbed wavefunction.

Nearly all calculations of hyperfine fields B_{HF} for magnetic materials performed so far have been done in a non-relativistic or scalar relativistic manner. Recently, Ebert *et al* (1988) performed fully relativistic calculations for Fe, Co and Ni, which gave for the first time theoretical access to the orbital-dipolar contributions to the hyperfine fields coming from non-s conduction electrons. The contribution of non-s core electrons was, however, ignored in these calculations. Although this part of B_{HF} should be small—it is a second-order effect—in general one cannot rule out its importance because there is a strong variation of the influence of $B(r)$ for the various core states. A fully relativistic calculation of the core hyperfine fields can be based on the expression

$$B_{\text{HF}} = \frac{e}{\mu_n} \sum_{n\kappa\mu} \langle \Psi_{n\kappa\mu} | \boldsymbol{\alpha} \cdot \boldsymbol{\mu}_n \times \mathbf{r}/r^3 | \Psi_{n\kappa\mu} \rangle \quad (16)$$

(Rose 1961, Ebert *et al* 1988). Because the potential is spin-dependent the sum over μ for a given κ no longer cancels to zero as for a paramagnetic potential. The fact that $\Psi_{n\kappa\mu}$ (see (9)) does not have unique spin-angular character (κ and μ are used only to label the core states in a perturbation theoretical sense) implies that there are mixing terms between κ and $-\kappa - 1$ partial waves. For the $2p_{1/2}$ and $2p_{3/2}$ core states the corresponding decomposition is given in table 1. Obviously the $2p_{1/2}$ fields are higher than the $2p_{3/2}$ fields because of the non-vanishing amplitude of the $p_{1/2}$ wavefunctions at the nuclear site. The contributions of all core states for Fe, Co and Ni are summarised in table 2

together with the conduction band contributions (Ebert *et al* 1988). Obviously the individual p core contributions to B_{HF} are in general small compared with the s contributions. Because of the difference in sign the 2p and 3p contributions nearly cancel, giving rise to a rather small and positive p core contribution in contrast to the negative s core hyperfine field. This result has also been found in the case of 5d impurity atoms dissolved in Fe (Ebert *et al* 1989b), where the non-s contributions arising from p, d and f electrons are of greater importance.

Adding all terms in table 2, one finds that the inclusion of non-s core electrons cannot remove the discrepancy found earlier between the theoretical and experimental hyperfine fields of Fe, Co and Ni. For this reason, one has to conclude that this deviation, which is also found by other authors, points to a shortcoming of local spin-density theory in treating with sufficient accuracy the polarisation of the core wavefunction using a spin-split conduction band.

4. Summary

A fast and reliable algorithm has been presented to solve the boundary problem that occurs in relativistic calculations of core wavefunctions for a spin-dependent potential. An application to ferromagnetic Fe, Ni and Co has demonstrated that the influence of the spin-dependent potential on the various core states can vary strongly from case to case. Finally, it has been found that the neglect of non-s core-state contributions to the hyperfine fields is not responsible for the discrepancy between theory and experiment in the notoriously problematic case of Fe.

References

- Bonnenberg D, Hempel K A and Wijn H P J 1987 *Landolt-Börnstein New Series* Group III, vol 19a, ed. K-H Hellwege and O Madelung (Berlin: Springer) p 142
- Cortona P, Doniach S and Sommers C 1985 *Phys. Rev. A* **31** 2842
- Desclaux J P 1969 *Comput. Phys. Commun.* **1** 216
- Doniach S and Sommers C 1981 *Proc. Int. Conf. Valence Fluctuations of Solids* ed L M Falikov, W Hanke and M B Maple (Amsterdam: North-Holland)
- Ebert H 1988 *Phys. Rev. B* **38** 9390
- Ebert H, Drittler B, Zeller R and Schütz G 1989a *Solid State Commun.* **69** 485
- Ebert H, Strange P and Gyorffy B L 1988 *J. Phys. F: Met. Phys.* **18** L135
- Ebert H, Zeller R, Drittler B and Dederichs P H 1989b *J. Appl. Phys.* submitted
- Feder R, Rosicky F and Ackermann B 1983 *Z. Phys. B* **52** 31
- Lieberman D, Waber J T and Cromer D T 1965 *Phys. Rev.* **137** A27
- Moruzzi V L, Janak J F and Williams A R 1978 *Calculated Electronic Properties of Metals* (New York: Pergamon)
- Press W H, Flannery B P, Teukolsky S A and Vetterling W T 1986 *The Art of Scientific Computing* (London: CUP)
- Rose M E 1961 *Relativistic Electron Theory* (New York: Wiley)
- Stearns M B 1987 *Landolt-Börnstein New Series* Group III, vol 19a, ed. K-H Hellwege and O Madelung (Berlin: Springer) p 24
- Strand P, Staunton J B and Gyorffy B L 1984 *J. Phys. C: Solid State Phys.* **17** 3355