Spin-polarised relativistic electronic structure calculations

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Abstract. A fully relativistic first-principles electronic structure calculation method is presented for magnetic materials. The method is based on the local spin moment density concept for relativistic Hamiltonians. In order to obtain manageable Kohn–Sham–Dirac equations including magnetic fields, the orbital contribution to the four-current density is omitted. The starting point is Takeda's relativistic generalisation of the augmented spherical wave method for non-magnetic crystals (RASW). In its basic form, the proposed method for magnetic crystals is only slightly more involved as RASW, and still takes all relativistic and spin polarisation effects into account, from first principles (including the $\Delta l = 2$ coupling). The treatment of relativistic and spin polarisation effects can be called 'on equal footing'. In both relevant limits the method is exact (within the mentioned framework). Furthermore, a more elaborate scheme is suggested, which is a systematic improvement of the basic scheme. A comparison is made with other recently published methods. Finally, results of self-consistent calculations for ferromagnetic Ni and Gd, performed with the basic scheme, are compared with previous calculations and experimental data from the literature. For Ni, the results are in good agreement both with previous calculations and with experiment. For Gd interesting new results have been obtained concerning the spectroscopic splitting factor g. The influence of the choice for an explicit exchange and correlation functional is studied as well as the influence of the coupling between l and $l + 2$ levels.

1. Introduction

Considerable progress has recently been made in developing tools for the calculation of the electronic structure of crystalline solids in which both magnetic and relativistic effects play an important role. The interplay of these effects is responsible for a number of interesting physical properties such as magnetic anisotropy, but the mere coexistence of both effects already presents a challenge to electronic structure calculations.

First of all there is the need of a four-current version of local density functional theory (DFT). Furthermore, it is still an open question whether such a DFT can give reliable groundstate properties for systems that often contain very localised electrons. Up to now there is only one manageable four-current DFT. It omits orbital contributions to the four-current and is equivalent to local spin density (LSD) theory in the non-relativistic limit. This DFT leads to Kohn–Sham–Dirac equations including magnetic fields. In a spherically symmetric potential all the resulting radial equations for different orbital momentum number l are coupled through two semi-infinite series of odd and even l.

Recently a number of ways have been proposed to deal with these radial equations. The goal of this paper is to make a contribution to this final step by the presentation

(in §§3 and 4) of two calculation schemes based on the existing relativistic augmented spherical wave (RASW) method, which is explained in §2. The scheme of §3 has actually been implemented on a computer and applied to the elemental ferromagnets nickel and gadolinium. The results can be found in §5 and conclusions are drawn in §6.

2. The RASW method

The RASW method of Takeda [1] can be seen as a natural extension for relativistic electrons of the ASW method introduced by Williams *et al* [2]. Since we would like to discuss newly developed spin-polarised versions in §§3 and 4, we reformulate the basic ideas of RASW.

In the RASW method the potential is approximated as in ASW, where the crystal is divided into spheres centered at atomic positions and the remaining interstitial space. Inside the spheres the potential is spherically averaged, while it is taken as constant (V_{MT}) and equal to the (weighted) average of the potential at the sphere boundaries in the interstitial space. Depending on the choice of the sphere radii, this is called the muffin-tin approximation (MTA) or the atomic sphere approximation (ASA). The RASW basis functions are given by an analytical prescription in the interstitial region. For spherical symmetrical potentials $V(r)$ the solutions to the Dirac equation can be written as

$$\psi_\kappa^\mu(r) = \begin{pmatrix} (g_\kappa(r)/r)\chi_\kappa^\mu \\ +(\mathrm{i}f_\kappa(r)/r)\chi_{-\kappa}^\mu \end{pmatrix} \tag{1}$$

where the radial functions $g_\kappa(r)$ and $f_\kappa(r)$ obey the radial equations [3]:

$$\frac{\mathrm{d}g_\kappa}{\mathrm{d}r} + \frac{\kappa}{r} g_\kappa = [2/\alpha + \alpha(E - V)]f_\kappa$$

$$\frac{\mathrm{d}f_\kappa}{\mathrm{d}r} - \frac{\kappa}{r} f_\kappa = \alpha(V - E)g_\kappa. \tag{2}$$

The Pauli spinors χ_κ^μ are eigenstates of $(1 + \boldsymbol{\sigma} \cdot \boldsymbol{L})$ and $J_z = L_z + S_z$ with eigenvalues $-\kappa$ and μ respectively. The equations are given in atomic units with $e = \hbar = m_e = 1$ and $c = 1/\alpha$, where $\alpha \simeq (137)^{-1}$ is the fine structure constant.

In the interstitial region, where V is constant, the large component g_κ satisfies the Helmholtz equation

$$\frac{\mathrm{d}^2 g_\kappa}{\mathrm{d}r^2} - \frac{\kappa(\kappa + 1)}{r^2} g_\kappa = -\alpha\epsilon(2/\alpha + \alpha\epsilon)g_\kappa \tag{3}$$

where we have defined $\epsilon \equiv E - V_{MT}$. As in the ASW, we choose outgoing Hankel functions, $h_l^+(r)$, for $g_\kappa(r)/r$. (The $h_l^+(r)$ are related to the Hankel functions $H_l^{(+)}$ in [4] by $h_l^+(r) = (\mathrm{i}k_\epsilon)^{l+1}H_l^{(+)}(\mathrm{i}k_\epsilon r)$.)

Since $\kappa(\kappa + 1) = l(l + 1)$ both for $\kappa = l$ and $\kappa = -l - 1$ it is natural to take $g_l = g_{-l-1}$ for the interstitial region, indicating the absence of spin–orbit splitting for constant potential. Therefore we define

$$g_\kappa(r) = rh_l^+(r). \tag{4}$$

The Hankel function $h_l^+(r)$ satisfies for some $k_\epsilon < 0$

$$-\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2}\right) r h_l^+(r) = -k_\epsilon^2 r h_l^+(r). \tag{5}$$

The kinetic energy parameter k_ϵ is fixed at some small negative value and not used as a variational parameter. Therefore, the k_ϵ is suppressed notationally. The small radial component $f_\kappa(r)$ is found from (4) and (2) and is different for $\kappa = l$ and $\kappa = -l - 1$. This difference is not important because (especially for the ASA) the contribution of the small components to the interstitial charge is very small and can be neglected. The energy E of the interstitial RASW functions can be found from (3) and (5) to satisfy

$$\epsilon = E - V_{MT} = \frac{-1 + \sqrt{1 - k_\epsilon^2 \alpha^2}}{\alpha^2} \simeq -\tfrac{1}{2} k_\epsilon^2 < 0. \tag{6}$$

Inside the spheres the interstitial prescription is augmented by a numerical solution of the radial equations (2) for an energy such that both g_κ and f_κ (thus ψ_κ^μ) are continuous at $r = R$, the sphere radius, in order to have a Hermitian variational problem. The boundary conditions become

$$g_\kappa(R) = R h_l^+(R)$$

$$\tag{7}$$

$$(f_\kappa / g_\kappa)(R) = \left(\frac{1}{2/\alpha + \alpha\epsilon}\right)\left[\left(\frac{dh_l^+}{dr}\frac{1}{h_l^+}\right)(R) + \left(\frac{\kappa + 1}{R}\right)\right].$$

The number of nodes within the sphere is chosen independently for each l and is taken equal to the number of nodes of the atomic functions that are expected to form the valence bands. If one is interested in excited states as well, one may include more than one principle quantum number n per l-value [5]. For the moment we will assume only one and suppress the n notationally.

Unlike Takeda, we will now make a transformation from basis functions that have an angular dependence χ_κ^μ for their large component, to functions that have a large component with a pure spin character in the interstitial region as done before in APW [6]. This transformation is made for reasons that will become clear in the discussion of the spin-polarised versions in §§3 and 4. Such a transformation is possible since g_l and g_{-l-1} are chosen to be equal in the interstitial region, which was a natural consequence of the potential approximation. The (unitary) transformation is [3]:

$$\phi(lm \uparrow) = \sqrt{\frac{l + m + 1}{2l + 1}} \, \psi_{-l-1}^{m+1/2} - \sqrt{\frac{l - m}{2l + 1}} \, \psi_l^{m+1/2}$$

$$\tag{8}$$

$$\phi(lm \downarrow) = \sqrt{\frac{l - m + 1}{2l + 1}} \, \psi_{-l-1}^{m-1/2} + \sqrt{\frac{l + m}{2l + 1}} \, \psi_l^{m-1/2}.$$

For the interstitial region this means

$$\phi(lm \uparrow) = \left(\begin{array}{c} (g_l(r)/r) \, Y_l^m(\hat{r}) \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ * \end{array} \right)$$

$$\tag{9}$$

$$\phi(lm \downarrow) = \left(\begin{array}{c} (g_l(r)/r) \, Y_l^m(\hat{r}) \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ * \end{array} \right)$$

where Y_l^m are the spherical harmonics and the asterisks (*) represent the rather complicated small components. The charge density contribution from the small components can be shown to be approximately a factor $\alpha^2/4$ smaller than the contribution from the large component in this region. Inside the sphere the functions $\phi(lm\sigma)$ of course do not represent pure spin states even for the large component. However, in the non-relativistic limit we have $g_l \simeq g_{-l-1}$ and $f_l \simeq f_{-l-1} \simeq 0$ inside the sphere and our wavefunctions, consisting then only of a large component, approach the ASW atomic functions with pure spin-up and spin-down character.

The construction of the RASW basis functions as Bloch sums over the functions $\phi(lm\sigma)$ and the evaluation of overlap and Hamiltonian matrix elements can be done by straightforward application of the methods presented in the original ASW paper by Williams et al [2], and will not be repeated here.

3. The spin-polarised case: basic scheme

For magnetic relativistic electron systems a consistent version of local four-current density functional theory (DFT) has been derived by Eschrig et al [7]. Since there are no explicit functionals for this theory available, it is usual practice to use a local spin moment DFT which is equivalent to the normal local spin DFT in the non-relativistic limit [7, 8]. It can be found from the four-current DFT by omission of the orbital contribution to the four-current in a Gordon decomposition [9].

The Kohn–Sham–Dirac equations of such a DFT have an interaction term of the form [10]:

$$H_m = b(r)[\pi(\uparrow) - \pi(\downarrow)] \tag{10}$$

$$b(r) = \frac{\alpha}{2}h_z(r) + \left(\frac{\delta E_{xc}[n, m_z]}{\delta m_z}\right)(r) \tag{11}$$

where we have defined the spin projection operators $\pi(\sigma)$ as

$$\pi(\sigma) = \frac{1}{2}\begin{pmatrix} 1 + (\text{sgn}\sigma)\sigma_z & 0 \\ 0 & 1 + (\text{sgn}\sigma)\sigma_z \end{pmatrix}. \tag{12}$$

The external magnetic field along the z axis, $h_z(r)$, is used in the first iteration only to break the symmetry. The energy functional for exchange and correlation, $E_{xc}[n, m_z]$, is today probably best approximated by the relativistic expressions for exchange given by McDonald [11] and Xu et al [12] and the correlation parametrisation of Perdew and Zunger [13], using Monte Carlo results of Ceperley and Alder [14]. The polarisation $m_z(r)$ is to be evaluated from the eigenstates $\psi_i(r)$ of the previous iteration by the spherical average:

$$m_z(r) = \sum_{i\ \text{occup}} \int \psi_i^+(r)[\pi(\uparrow) - \pi(\downarrow)]\psi_i(r)\,\mathrm{d}\Omega. \tag{13}$$

As outlined in §2, the RASW functions $\phi(lm\sigma)$ have pure spin character in the non-relativistic limit. Therefore, in this limit, it is obvious that the total effect of magnetism can be included in the basis functions as follows: Because the projection operators $\pi(\sigma)$ are block diagonal in $\{\phi(lm\sigma)\}$ with respect to σ in the non-relativistic limit, the term

H_m can be included in the original Hamiltonian. The new basis functions $\tilde{\phi}(lm\sigma)$ have the same analytical prescription in the interstitial region, but the numerical parts in the spheres are solutions of the radial equations with potentials $V(r) + \text{sgn}(\sigma)b(r)$. For this modification both parts of $\tilde{\phi}(lm\sigma)$, the functions ψ_l^μ and ψ_{-l-1}^μ, have to be evaluated in each potential and will be written $\tilde{\psi}_l^\mu(\sigma)$ and $\tilde{\psi}_{-l-1}^\mu(\sigma)$, respectively. This procedure for the non-relativistic limit is equivalent to a spin-polarised ASW calculation.

Now we will propose a similar method for the relativistic regime. The terms of the relativistic Hamiltonian that are not included in the non-relativistic procedure described above, will be taken into account using so called pseudo-perturbation theory. For this procedure it is essential that we made the transformation to basis functions with a large component of pure spin character in the interstitial region as defined in §2.

In the relativistic regime the spin–orbit coupling removes the pure spin character of the basis functions $\tilde{\phi}(lm\sigma)$. Therefore the non-relativistic approach is not correct any more. However, it remains a good starting point since the basis functions will have almost pure spin character for their large component at least in the neighbourhood of the sphere boundaries and in the interstitial region. The term of the Hamiltonian H_m, representing the coupling between spin–orbit interaction and spin polarisation, which we will call $\tilde{H}_m$, is not included in this non-relativistic approach and will now be included in the band matrix. This term is given by the difference between the polarisation terms (10) of the full Hamiltonian and the polarisation terms included in the Hamiltonian for the construction of the basis functions:

$$\tilde{H}_m = \{[\pi(\uparrow) - \pi(\downarrow)] - [P(\uparrow) - P(\downarrow)]\}b(r) \tag{14}$$

where the projection operators $P(\sigma)$ are defined by

$$P(\sigma)\tilde{\phi}(lm\sigma') \equiv \delta_{\sigma\sigma'}\,\tilde{\phi}(lm\sigma). \tag{15}$$

The matrix elements $\langle\tilde{\phi}(lm\sigma)|\tilde{H}_m|\tilde{\phi}(l'm'\sigma')\rangle$, needed to build the band matrix, can be evaluated using definition (15) for the operators $P(\sigma)$. For the terms with $\pi(\sigma)$, we use the definitions of $\tilde{\phi}(lm\sigma)$ and $\tilde{\psi}_\kappa^\mu(\sigma)$ from the appropriate modification of equations (8) and (1), the equalities

$$\langle\tilde{\psi}_\kappa^\mu(\sigma)|b(r)[\pi(\uparrow) - \pi(\downarrow)]|\tilde{\psi}_{\kappa'}^{\mu'}(\sigma')\rangle$$

$$= \int_0^R dr(\tilde{g}_\kappa^\mu(\sigma,r))^* b(r)\tilde{g}_{\kappa'}^{\mu'}(\sigma',r)\langle\chi_\kappa^\mu|\sigma_z|\chi_{\kappa'}^{\mu'}\rangle_\Omega$$

$$+ \int_0^R dr(\tilde{f}_\kappa^\mu(\sigma,r))^* b(r)\tilde{f}_{\kappa'}^{\mu'}(\sigma',r)\langle\chi_{-\kappa}^\mu|\sigma_z|\chi_{-\kappa'}^{\mu'}\rangle_\Omega \tag{16}$$

with

$$\langle\chi_l^\mu|\sigma_z|\chi_{l'}^{\mu'}\rangle_\Omega = \left(\frac{-2\mu}{2l+1}\right)\delta_{ll'}\delta_{\mu\mu'}$$

$$\langle\chi_{-l-1}^\mu|\sigma_z|\chi_{-l'-1}^{\mu'}\rangle_\Omega = \left(\frac{2\mu}{2l+1}\right)\delta_{ll'}\delta_{\mu\mu'} \tag{17}$$

$$\langle\chi_l^\mu|\sigma_z|\chi_{-l'-1}^{\mu'}\rangle_\Omega = \left(\frac{-2\sqrt{(l+1/2)^2 - \mu^2}}{2l+1}\right)\delta_{ll'}\delta_{\mu\mu'}$$

and the orthonormality relations

$$\langle \chi_\kappa^\mu | \chi_{\kappa'}^{\mu'} \rangle_\Omega = \delta_{\kappa\kappa'} \delta_{\mu\mu'}. \tag{18}$$

If this procedure is followed, we have a single formalism that has two exact limits: the non-magnetic relativistic limit and the magnetic non-relativistic limit. Between these limits, the coupling between spin–orbit interaction and spin polarisation is included in the band matrix. For this coupling our procedure is comparable to the pseudo-perturbation treatment of spin–orbit coupling in a scalar relativistic approach as suggested by Andersen [15] and Koelling and Harmon [16], but we have the advantage that we are working with an explicitly Hermitian variational problem.

There are several other methods available today that are comparable with our basic scheme as far as their complexity and time consumption is concerned. First there are the scalar relativistic methods treating $L \cdot S$ as a pseudo-perturbation but including spin polarisation in the basis functions [17]. Fritsche *et al* introduced a version of the linear rigorous cell (LRC) method that includes both spin–orbit coupling and spin polarisation as a pseudo-perturbation [18]. Ebert proposed an RLMTO method including magnetic effects as a pseudo-perturbation including spin–orbit coupling in the basis functions [19]. These methods lack, however, either or both of the exact limits mentioned above.

We believe the basic scheme of this section will be adequate in most cases. Since this scheme treats relativistic and magnetic effects on an equal footing it is a simple and efficient alternative to the more involved SPRLMTO method of Ebert *et al* [20] and to the multiple scattering approach (SPRKKR) of Strange *et al* [21]. (A similar approach was given in [22]. Non-self-consistent applications can be found in [23]. The tools for self-consistent calculations with this method were developed (but not yet applied) in [24].) The more elaborate scheme of the next section applies approximations comparable to those complex methods used by Ebert and Strange.

4. Beyond the basic scheme

We shall now show how the basic scheme of §3 can be systematically improved. If both relativistic and magnetic effects are equally important and if one is interested in the details of the spin as a function of the position inside the spheres (magnetic form factors), one may partially include the coupling between spin–orbit interaction and spin polarisation, $\tilde{H}_m$, in the Hamiltonian used to construct the basis functions, in order to increase the variational freedom. The idea of such a calculation procedure was inspired by the ionic calculations of Cortona *et al* [10].

The matrix elements of $\tilde{H}_m$ on $\{\tilde{\phi}(lm\sigma)\}$ are seen, in §3, to be diagonal in l and μ. This means $\tilde{H}_m$ couples (to order α^2) the states $\kappa = l$ and $\kappa = -l - 1$ and $\kappa = l$ and $\kappa = l + 2$. We will include the coupling between $\kappa = l$ and $\kappa = -l - 1$ in the basis functions because, for sufficiently slowly varying magnetic field, this coupling is the more important, as shown from a Foldy–Wouthuysen transformation by Feder *et al* [25]. The analytic prescription of the basis functions remains unaltered. Also the definition of $\phi(lm\sigma)$ in equations (8) and the boundary conditions in equations (7) will not be changed. We return to the full Hamiltonian and substitute the definition of $\phi(lm\sigma)$ in the Kohn–Sham–Dirac equation

$$\left[\frac{1}{\alpha} \begin{pmatrix} 0 & \sigma \cdot p \\ \sigma \cdot p & 0 \end{pmatrix} + \frac{1}{\alpha^2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + V(r) + b(r) \begin{pmatrix} \sigma_z & 0 \\ 0 & \sigma_z \end{pmatrix} \right] \psi(r)$$
$$= \left(E + \frac{1}{\alpha^2} \right) \psi(r). \tag{19}$$

The usual manipulations lead to the following set of radial equations (the $\kappa = l - 1$ to $\kappa = l + 1$ coupling is neglected implicitly since we use $\phi(lm\sigma)$):

$$\frac{\mathrm{d}g_l^\mu(\sigma)}{\mathrm{d}r} + \left(\frac{l}{r}\right) g_l^\mu(\sigma) = [2/\alpha + \alpha(E - V(r))]f_l^\mu(\sigma) - \alpha b(r) \left(\frac{2\mu}{2l-1}\right) f_l^\mu(\sigma)$$

$$\frac{\mathrm{d}f_l^\mu(\sigma)}{\mathrm{d}r} - \left(\frac{l}{r}\right) f_l^\mu(\sigma) = \alpha[V(r) - E]g_l^\mu(\sigma) + \alpha b(r) \left[\left(\frac{-2\mu}{2l+1}\right) g_l^\mu(\sigma)\right.$$

$$\left. + \left(\frac{-2\sqrt{(l+1/2)^2 - \mu^2}}{2l+1}\right) \gamma(l\mu\sigma)g_{-l-1}^\mu(\sigma)\right]$$

$$\frac{\mathrm{d}g_{-l-1}^\mu(\sigma)}{\mathrm{d}r} + \left(\frac{-l-1}{r}\right) g_{-l-1}^\mu(\sigma) = [2/\alpha + \alpha(E - V(r))]f_{-l-1}^\mu(\sigma) - \alpha b(r) \left(\frac{-2\mu}{2l+3}\right) f_{-l-1}^\mu(\sigma)$$

$$\frac{\mathrm{d}f_{-l-1}^\mu(\sigma)}{\mathrm{d}r} - \left(\frac{-l-1}{r}\right) f_{-l-1}^\mu(\sigma) = \alpha[V(r) - E]g_{-l-1}^\mu(\sigma) + \alpha b(r) \left[\left(\frac{2\mu}{2l+1}\right) g_{-l-1}^\mu(\sigma)\right.$$

$$\left. + \left(\frac{-2\sqrt{(l+1/2)^2 - \mu^2}}{2l+1}\right) \gamma^{-1}(l\mu\sigma)g_l^\mu(\sigma)\right] \tag{20}$$

where the relative coefficients $\gamma(l\mu\sigma)$ are given by

$$\gamma(l\mu\sigma) = -(\mathrm{sgn}\sigma) \left(\frac{l + \mu + 1/2}{l - \mu + 1/2}\right)^{(\mathrm{sgn}\sigma)/2} \tag{21}$$

The radial components g and f now depend on μ as well as σ. For each l the equations (20) have to be solved $4l + 2$ times: for $\mu = -l - 1/2$ to $l + 1/2$ for $\sigma = \uparrow$ and for $\mu = -l + 1/2$ to $l - 1/2$ for $\sigma = \downarrow$. The equations for $\sigma = \downarrow$ can be found from those for $\sigma = \uparrow$ by making use of the operation $z \to -z$ with $l \to -l-1$; $\mu \to -\mu$ and $b(r) \to -b(r)$.

The radial equations proposed by Cortona *et al* are the equations (20) with $\gamma(l\mu\sigma) = 1$, since they hold for solutions that are the trivial linear combination of ψ_l^μ and ψ_{-l-1}^μ. Cortona *et al* show how to solve their equations and find for all (l, μ) both a symmetric and an anti-symmetric solution. For core electrons this method can be applied unchanged. But since the valence electron states $\phi(lm\sigma)$ are linear combinations of ψ_l^μ and ψ_{-l-1}^μ with definite symmetry, the equations (20) will have only *one* solution for each spin direction.

Finally we include the remainder coupling $\tilde{\tilde{H}}_\mathrm{m}$ between spin–orbit interaction and spin polarisation by analogy with the basic scheme into the band matrix. These terms are given by

$$\tilde{\tilde{H}}_\mathrm{m} = b(r) \left([\pi(\uparrow) - \pi(\downarrow)] - \sum_l (\tilde{P}(l))^+ [\pi(\uparrow) - \pi(\downarrow)]\tilde{P}(l)\right) \tag{22}$$

while the orbital projection operators $\tilde{P}(l)$ are defined as

$$\tilde{P}(l) \, \tilde{\tilde{\phi}} \, (l'm\sigma) = \delta_{ll'} \, \tilde{\tilde{\phi}} \, (lm\sigma). \tag{23}$$

The functions $\tilde{\tilde{\phi}} \, (lm\sigma)$ are the new basis functions with radial parts obeying equations (20).

This procedure represents a pseudo-perturbation approach with more variational freedom than the basic scheme of §3. The two exact limits of the basic scheme are exact for this procedure also. In practice this scheme represents the limit (because the number of coupled radial equations grows enormously if the above scheme has to be improved) of the local moment density approximation within the RASW formalism, as far as relativistic and (collinear) magnetic effects are concerned. (In our approach there remains the problem of non-collinear magnetism. Recently an ASW-based method for different (but constant) magnetisation directions in different atomic spheres was presented in [26]. See also [27].) The price to be paid for the accuracy of this improved scheme is the numerical solution of a large number (for all μ) of four coupled radial equations. The SPRLMTO method mentioned above, can be considered almost equivalent to this improved scheme apart from the fact that the former method does not include the $\Delta l = 2$ coupling.

In fact, we expect that the accuracy obtained by the basic scheme of §3 will be sufficient in most cases. Such a basic scheme can only be applied in a linear method like RASW. If non-linearised methods are used, one can only apply more elaborate schemes as presented in this section. Even then, it seems not practicable to take care of the terms $\tilde{\tilde{H}}_{\mathrm{m}}$.

5. Calculations with the basic scheme

The basic scheme of §3 has been implemented and tested extensively on non-magnetic crystals such as the noble metals, PbTe and $AuTe_2$—this work will be reported elsewhere. In this section we present results for ferromagnetic nickel and gadolinium. The lattice constants used are $a = 6.550$ au for FCC nickel and $a = 6.858$ au, $c = 10.952$ au for HCP gadolinium. The Wigner–Seitz radii are (atomic sphere approximation) chosen to be $R_{\mathrm{Ni}} = 2.560$ and $R_{\mathrm{Gd}} = 3.764$ au. In both cases the magnetisation direction was taken parallel to the c axis and corrections for interstitial charge were accounted for in the standard way, through the calculation of the energy derivative of the structure constants. Several different exchange and correlation functionals were used.

Hedin–Lundqvist, von Barth–Hedin (XC1)

In the expressions found in von Barth and Hedin's paper [28] for the interpolation between the ferromagnetic and paramagnetic electron gas, we take the original values of Hedin and Lundqvist [29] for the parameters of the paramagnetic gas ($c_{\mathrm{P}} = 0.045$ and $r_{\mathrm{P}} = 21.0$ au) and find the ferromagnetic values by the application of the scaling laws of the random phase approximation [28]: $c_{\mathrm{F}} = \frac{1}{2}c_{\mathrm{P}}$ and $r_{\mathrm{F}} = 2^{4/3}r_{\mathrm{P}}$.

Gunnarsson–Lundqvist (XC2)

Gunnarsson and Lundqvist found the following set of parameters for the same interpolation formula [31]: $c_{\mathrm{P}} = 0.0666$, $r_{\mathrm{P}} = 11.4$ au and $c_{\mathrm{F}} = 0.0406$, $r_{\mathrm{F}} = 15.9$ au.

Perdew–Zunger, Ceperley–Alder (XC3)

Perdew and Zunger [13] fitted their formulae to Monte Carlo results of Ceperley and Alder [14].

Perdew–Zunger, Ceperley–Alder, McDonald–Xu (XC4)

Parametrisation XC3 is modified with relativistic corrections to the exchange part given by McDonald [11] and Xu [12].

5.1. Results for nickel

For nickel the ground state expectation values of $\langle J_z \rangle = \langle L_z + \frac{1}{2}\sigma_z \rangle$ and $\langle \sigma_z \rangle$ are given in table 1, as well as orbital and spin contributions to the magnetic moment and the inferred value for the g-factor:

$$g = (\mu_{\text{total}}/\mu_{\text{spin}})g_e$$

where g_e ($\simeq 2.0023$) is the electronic gyromagnetic ratio. In the table we have included the contributions with different l-values for both wavefunctions of the inner product of equation (13), in the row with the lowest l-value. Therefore we used the $\simeq$ sign to indicate the l-value.

Table 1. Occupation numbers and magnetic moments μ (in units of μ_B) for ferromagnetic FCC nickel with the magnetisation direction parallel to a fourfold rotation axis.

Reference	Calculations							Experiment
	This work		[30]	[19]	[19]	[18]	[32]	[34]
Method	SPRASW	SPRASW	SPRKKR	SPRLMTO	RLMTO	LRC	LMTO	
XC	XC4	XC1	XC1	XC1	XC1	XC2	XC2	
No k-vectors	1997	1997				1575	505	
Self-consistent	yes	yes	no	no	no	yes	yes	
$\langle \sigma_z \rangle$								
$l \simeq 0$	−0.004	−0.004	−0.002	−0.005	−0.006			
$l \simeq 1$	−0.021	−0.021	−0.022	−0.027	−0.027			
$l \simeq 2$	0.603	0.621	0.622	0.604	0.601			
$l \simeq 3$	−0.001	−0.001						
$\langle J_z \rangle$								
$l \simeq 0$	−0.002	−0.002	−0.001	−0.003	−0.003			
$l \simeq 1$	−0.010	−0.010	−0.011	−0.013	−0.013			
$l \simeq 2$	0.345	0.355	0.357	0.350	0.348			
$l \simeq 3$	−0.001	−0.001						
μ_{spin}	0.578	0.596	0.598	0.572	0.568	0.52	0.60	0.57
μ_{orbital}	0.043	0.042	0.046	0.049	0.048	0.045		0.050
μ_{total}	0.620	0.639	0.644	0.621	0.616	0.565	0.60	0.62
g	2.15	2.15	2.16	2.17	2.17	2.18	2	2.18

Also included in table 1 are the results of Jarlborg and Peter [32] with the non-relativistic LMTO method [38], the results of Fritsche, Noffke and Eckhardt [18] obtained from the LRC method including scalar-relativistic corrections in the basis functions and spin–orbit coupling as well as spin polarisation in pseudo-perturbation and the results of Ebert, Strange and Gyorffy [30] using a spin-polarised relativistic multiple scattering method (SPRKKR) which is non-linear and treats all interactions exact (within the limitations of the KKR framework, of course) except for the $\Delta l = 2$ coupling that is omitted entirely. However, the results of the latter method are not self-consistent, but make use of the non-relativistic self-consistent potentials of Moruzzi

et al [33]. Furthermore table 1 contains SPRLMTO and RLMTO (see §§4 and 3) results from another paper of Ebert [19] based on the same non-relativistic potential. The experimental values are taken from [34].

From a test of the accuracy of the numerical Brillouin zone integration we deduce that our values for the moments are converged to within a few thousands of μ_B. The agreement with experiment especially for the XC4 exchange and correlation is satisfying. It can be concluded that the differences between the calculated values are small, as they should be for a system with a relatively light atom such as Ni and that the overall agreement with experiment is very good.
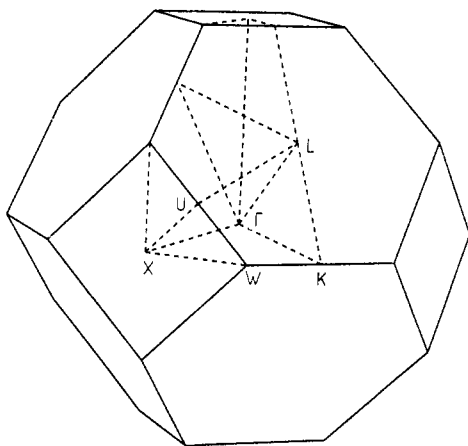

Figure 1. The Brillouin zone for FCC Ni with the magnetisation parallel to [001]. The irreducible wedge is marked by the broken lines.
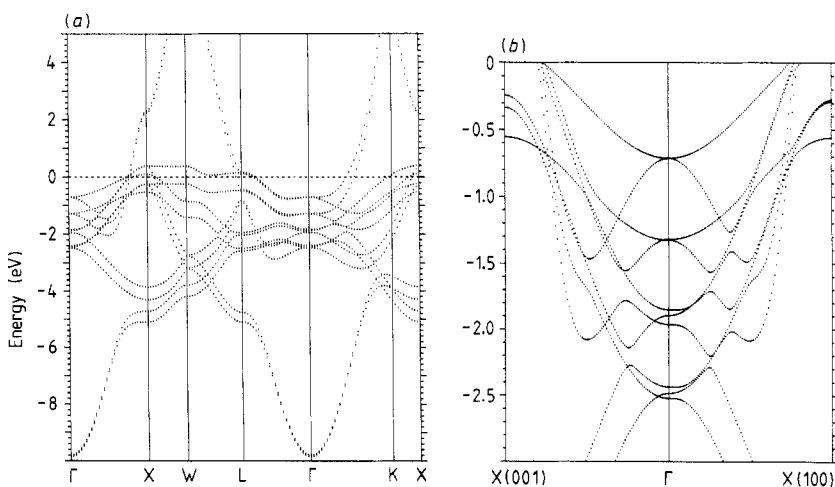

Figure 2. The energy bands for FCC Ni with the magnetisation parallel to [001], following the symmetry lines of figure 1 along (units $2\pi/a$): (*a*) $\Gamma(0,0,0)$–X$(1,0,0)$–W$(1,0,\frac{1}{2})$–L$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$–$\Gamma$–K$(\frac{3}{4},\frac{3}{4},0)$–X$(1,1,0)$; (*b*) X$(0,0,1)$–$\Gamma$–X$(1,0,0)$. Both have the Fermi level at $E = 0$.

Figure 2 shows the energy bands of Ni along the symmetry directions of the Brillouin zone indicated in figure 1. The anisotropy of the bands along Γ–X[001] and Γ–X[100], which are equivalent in a non-relativistic calculation, is stressed in figure 2(*b*). These bands are in good agreement with those of Ebert [19] and Ebert *et al* [20]. The total density of states (DOS, figure 3) was calculated with the linear analytic tetrahedron method for 9216 simplices in the irreducible wedge and a resolution of 0.02 eV.
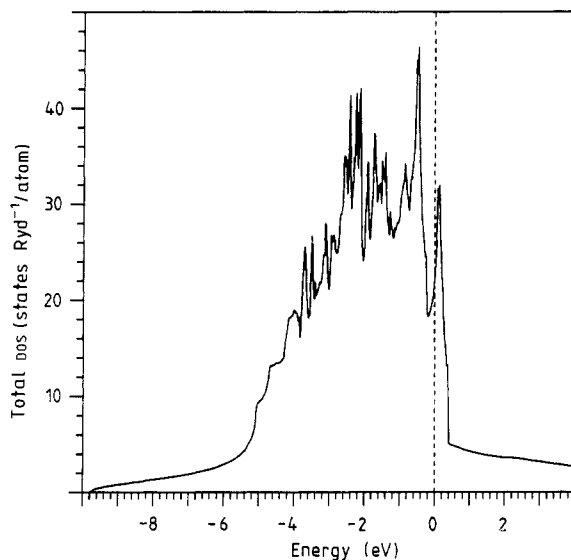

Figure 3. The total DOS for FCC Ni with the magnetisation parallel to [001]. The broken line indicates the Fermi level.

5.2. Results for gadolinium

Gadolinium is the heaviest elemental ferromagnet. It contains seven unpaired 4f electrons. After some initial doubts [35] it is now accepted that Gd can be treated in a band calculation (including the f electrons) giving reasonable ground state properties even in local spin density [17]. The results of the basic scheme for Gd, results of Sticht and Kübler [17] and experimental values for the different contributions to the magnetisation are collected in table 2. The SPRASW magnetisations are converged to within $0.01\mu_{\rm B}$. The radial mesh contained 2500 points to get a secular problem which is Hermitian with an accuracy of 10^{-7} Hartree.

For the same exchange and correlation functional XC2 we find almost the same $\mu_{\rm total}$ as Sticht and Kübler. Their results were found with a scalar relativistic ASW program including $L \cdot S$ coupling as a pseudo-perturbation in the band matrix, within the self-consistent cycle (without adjustable parameters). The SPRASW calculations with XC3 and XC4 show that the total moment is quite sensitive to the explicit form of the XC functional. Therefore the suggested accuracy from a comparison of XC2 results with the Roeland experiment [37] only, should be considered too optimistic. The g-factor calculated by Sticht and Kübler [17] is 2.068 and deviates appreciably from the value 2 expected in an atomic picture for a half-filled f shell. The only measured value we are aware of, $g = 2.00 \pm 0.02$, seems to have been performed on a less pure sample

Table 2. Occupation numbers and magnetic moments μ (in units of μ_B) for ferromagnetic HCP gadolinium with the magnetisation direction parallel to a threefold rotation axis.

	Calculations					Experiment		
Reference	This work				[17]	[37]	[36]	
Method	SPRASW	SPRASW	SPRASW	SPRASW	ASW			
XC	XC4	XC3	XC1	XC2	XC2			
No k-vectors	233	233	233	233				
Self-consistent	yes	yes	yes	yes	yes			
$\langle \sigma_z \rangle$								
$l \simeq 0$	0.021	0.022	0.027	0.026	}0.16			
$l \simeq 1$	0.128	0.137	0.167	0.158				
$l \simeq 2$	0.416	0.437	0.537	0.513	0.47			
$l \simeq 3$	6.762	6.784	6.814	6.789	6.76			
$\langle J_z \rangle$								
$l \simeq 0$	0.008	0.008	0.011	0.010	}0.07			
$l \simeq 1$	0.060	0.065	0.079	0.074				
$l \simeq 2$	0.176	0.185	0.229	0.218	0.20			
$l \simeq 3$	3.598	3.572	3.555	3.584	3.59			
μ_{spin}	7.34	7.39	7.55	7.50	7.39			
$\mu_{orbital}$	0.163	0.123	0.084	0.127	0.25			
μ_{total}	7.50	7.51	7.64	7.62	7.64	7.63 ± 0.01	7.50	
g	2.047	2.036	2.025	2.036	2.068		2.00 ± 0.02	

than the ones available today ($\mu_{total} = 7.50\mu_B$ [36] while a more recent experiment [37] gives $\mu_{total} = 7.63 \pm 0.01\mu_B$). The deviation of g from 2 is almost twice as small in our calculation. It seems as if the quenching of orbital momentum in our calculation is more effective and it could be supposed to result from the larger variational freedom included in our method. The results of the calculation with XC1 are almost in agreement with the measured 2.00 ± 0.02 for g. As can be seen from the table, the relativistic corrections to the exchange part of McDonald and Xu decrease the spin moment in favour of the orbital moment, while the total moment changes only slightly.
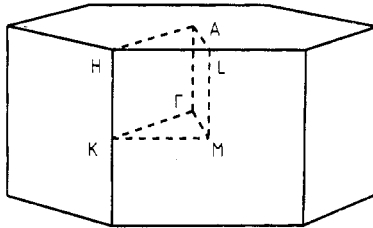
Figure 4. The Brillouin zone for HCP Gd with the magnetisation parallel to [001]. The irreducible wedge is marked by the broken lines.

Finally we tried to get an idea about the importance of the $\Delta l = 2$ coupling. For this purpose the calculation with XC4 was repeated with the change that in the second part of $\tilde{H}_m$ in equation (14) the $\Delta l = 2$ terms were omitted. The result is that the orbital moment remains almost unchanged, while the spin moment decreases by $2 \times 10^{-3} \ \mu_B$.
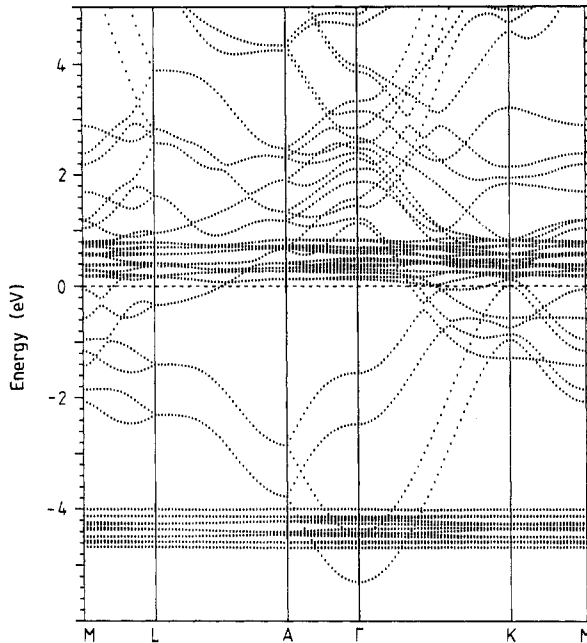
Figure 5. The energy bands for HCP Gd with the magnetisation parallel to [001], following the symmetry lines of figure 4. The broken line indicates the Fermi level.

It can be concluded that the $\Delta l = 2$ coupling can safely be omitted for the calculation of the occupation numbers studied in the materials under consideration.

The Gd energy bands along symmetry directions (figure 4) are shown in figure 5 and the total DOS in figure 6, calculated with 2048 simplices in the irreducible part of the Brillouin zone with a resolution of 0.02 eV.

The value for the DOS at the Fermi level is $N(E_F) = 2.7$ (eV atom)$^{-1}$ which is about 20% lower than the ASW result of Sticht and Kübler. This is still too high to make the free electron contribution to the specific heat γ coincide with the experimental γ, which cannot be considered surprising for an excited state property of a system containing f electrons. The bandwidth of 0.7 eV is in agreement both with experiment and the ASW result [39, 17], but the 4f binding energy inferred from the DOS is too small with respect to the experimental value which is also not surprising.

6. Conclusion

We introduced LSD methods based on RASW for magnetic systems. The first (§3) is as simple as a first-principles LSD method including all relativistic and spin polarisation effects can be. It has two exact limits, the non-relativistic magnetic and the relativistic non-magnetic limit, and treats relativistic and magnetic effects on equal footing. The second, (§4) improved scheme is more involved, especially as far as the solution of the radial Kohn–Sham–Dirac equations is concerned. It represents, in practice, the limit of the local moment DFT in an ASW framework as far as relativistic and magnetic interactions are concerned.
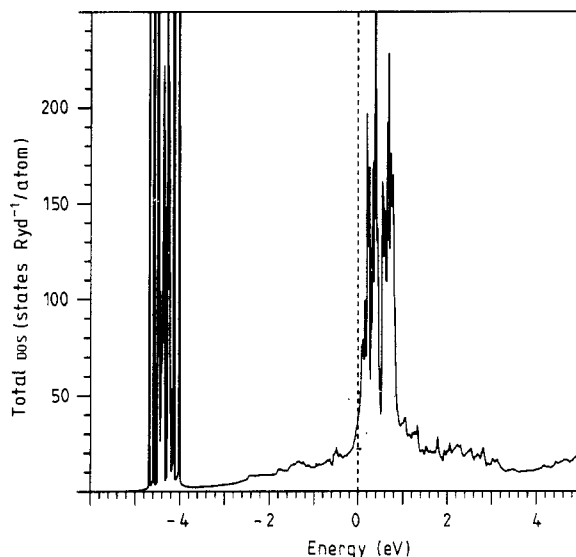
Figure 6. The total DOS for HCP Gd with the magnetisation parallel to [001]. The broken line indicates the Fermi level.

The first, basic scheme was applied to ferromagnetic Ni and Gd. For both materials these calculations yield the first self-consistent results based on the solution of radial Kohn–Sham–Dirac equations. The calculated ground state properties of nickel agree very well with experiment and the differences between the results obtained by our and other, different methods are small. The gadolinium case is much more complicated, because of the seven 4f electrons. However, we find good agreement with experiment for the ground state occupation numbers. The spectroscopic splitting factor *g* is significantly smaller in our calculation than in an ASW calculation, where it comes out too large, compared to the only experimental value known (to us). In order to judge the merits of the basic scheme, more and better experimental determinations of *g* would be very welcome. Also further calculations (for example on ferromagnetic actinide compounds) would be instructive, not least because they provide possibilities to explore the limits of local spin moment DFT for ground state properties of systems with localised electrons.

Acknowledgments

References

[1] Takeda T 1979 *J. Phys. F: Metal Phys.* **9** 815
     Takeda T 1980 *J. Phys. F: Metal Phys.* **10** 1135
[2] Williams A R, Kübler J and Gelatt C D Jr 1979 *Phys. Rev.* B **19** 6094
[3] Rose M E 1961 *Relativistic Electron Theory* (New York: Wiley)
[4] Messiah A 1961 *Quantum Mechanics, Vol I* (Amsterdam: North-Holland)
[5] Czyżyk M T, de Groot R A, Dalba G, Fornasini P, Kisiel A, Rocca F and Burattini E 1989 *Phys. Rev.* B **40** at press

[6] McDonald A, Pickett W and Koelling D 1980 *J. Phys. C: Solid State Phys.* **13** 2675
[7] Eschrig H *et al* 1985 *Solid State Commun.* **56** 777
[8] Rajagopal A 1978 *J. Phys. C: Solid State Phys.* **11** L943
      Ramana M and Rajagopal A 1979 *J. Phys. C: Solid State Phys.* **12** L845
      McDonald A and Vosko S 1979 *J. Phys. C: Solid State Phys.* **12** 2977
[9] Gordon W 1928 *Z. Phys.* **50** 630
[10] Cortona P, Doniach S and Sommers C 1985 *Phys. Rev.* A **31** 2842
[11] McDonald A and Vosko S 1979 *J. Phys. C: Solid State Phys.* **12** 2977
[12] Xu Bu Xing, Rajagopal A and Ramana M 1984 *J. Phys. C: Solid State Phys.* **17** 1339
[13] Perdew J and Zunger A 1981 *Phys. Rev.* B **23** 5048
[14] Ceperley D and Alder B 1980 *Phys. Rev. Lett.* **45** 566
[15] Andersen O K 1975 *Phys. Rev.* B **12** 3060
[16] Koelling D D and Harmon B N 1977 *J. Phys. C: Solid State Phys.* **10** 3107
[17] Sticht J and Kübler J 1985 *Solid State Commun.* **53** 529
[18] Fritsche L, Noffke J and Eckhardt H 1987 *J. Phys. F: Metal Phys.* **17** 943
[19] Ebert H 1988 *Phys. Rev.* B **38** 9390
[20] Ebert H, Strange P and Gyorffy B 1988 *J. Appl. Phys.* **63** 3052
[21] Strange P, Staunton J and Gyorffy B 1984 *J. Phys. C: Solid State Phys.* **17** 3355
[22] Feder R, Rosicky R and Ackermann B 1983 *Z. Phys.* B **52** 31
[23] Ackermann B, Feder R and Tamura E 1984 *J. Phys. F: Met. Phys.* **14** L173
      Tamura E, Ackermann B and Feder R 1984 *J. Phys. C: Solid State Phys.* **17** 5455
      Thörner G and Borstel G 1984 *Phys. Status Solidi* b **126** 617
      Ackermann B and Feder R 1985 *J. Phys. C: Solid State Phys.* **18** 1093
      Schadler G, Weinberger P, Boring A and Albers R 1986 *Phys. Rev.* B **34** 713
[24] Schadler G, Albers R, Boring A and Weinberger P 1987 *Phys. Rev.* B **35** 4324
[25] Feder R, Rosicky R and Ackermann B 1983 *Z. Phys.* B **52** 31
[26] Kübler J, Hök K H, Sticht J and Williams A R 1988 *J. Phys. F: Metal Phys.* **18** 469
[27] Sandratskii L and Guletskii P 1985 *J. Phys. F* **16** L43
[28] von Barth U and Hedin L 1972 *J. Phys. C: Solid State Phys.* **5** 1629
[29] Hedin L and Lundqvist B 1971 *J. Phys. C: Solid State Phys.* **4** 2064
[30] Ebert H, Strange P and Gyorffy B 1988 *J. Phys. F: Met. Phys.* **18** L135
[31] Gunnarsson O 1976 *Phys. Rev.* B **13** 4274
[32] Jarlborg T and Peter M 1984 *J. Magn. Magn. Mater.* **42** 89
[33] Moruzzi V L, Janak J F and Williams A R 1978 *Calculated Electronic Properties of Metals* (New York: Pergamon)
[34] *Landolt-Börnstein, New Series* 1987 Group III, Vol 19a (Berlin: Springer)
[35] Harmon B and Freeman A 1974 *Phys. Rev.* B **10** 1979
[36] Rodbell D and Moore T 1964 *Magnetism Proceedings of the International Conference* (London: IOP) p 427
[37] Roeland L, Cock G, Muller F, Moleman A, McEwen K, Jordan R and Jones D 1975 *J. Phys. F: Metal Phys.* **5** L233
[38] Skriver H L 1984 *The LMTO Method* (Berlin: Springer)
[39] Campagna M, Wertheim G K and Bear Y 1979 *Photoemission in Solids II* ed. L Ley and M Cardona (Berlin: Springer)