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A simplified method of *ab initio* calculation of electron states in relativistic magnetics: I. Ferromagnets

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Abstract. A variant of the technique of electron state calculation in a ferromagnet, based on derivation of the Dirac equation by the relativistic Korringa–Kohn–Rostoker method, is presented. Using the $(l\mu)$ representation allows one to retain the same structure of the dispersive matrix as in the absence of spin polarisation.

1. Introduction

The majority of works in which the electron structure of magnetics is calculated within the framework of the single-electron approximation are based on the non-relativistic Schrödinger equation (see e.g. [1]). With such an approach the exchange–correlation interaction in magnetics leads to the appearance of two different potentials for electrons with opposite spin orientation: V_+ and V_-. Denoting

$$V = \tfrac{1}{2}(V_+ + V_-) \qquad \Delta V = \tfrac{1}{2}(V_+ - V_-) \tag{1}$$

and choosing the z axis along the spin direction, one can write the initial quantum-mechanical equation as follows:

$$[\Delta + (E - V) + \Delta V \sigma_z]\psi = 0 \tag{2}$$

(σ_z is the Pauli matrix). The spin projection in this case remains a 'good' quantum number, system (2) is separated into two ordinary Schrödinger equations and the problem is reduced to the standard one.

At the same time it is well known that the presence of even a slight spin–orbit interaction in materials with spin order leads to observable physical anomalies [2]. However, earlier, in all cases the spin–orbit interaction was taken into account according to perturbation theory either as an additional scattering mechanism or as a perturbation changing the selection rules. It would be desirable to construct a consequent theoretical scheme of calculation of the electron states in magnetics based on the Dirac equation. In recent years rather a great number of papers have been devoted to this problem; we refer to three of them [3–5], allowing one to appreciate the possibilities of the commonly used technique of calculating the energy bands based on the multiple scattering formalism. A number of recent papers [6–8] containing further development of this approach should be mentioned as well.

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In the present work a variant of the technique of calculating the electron states in a relativistic ferromagnet based on the use of the Green function for an empty lattice is suggested. Our approach is most similar to the Korringa–Kohn–Rostoker (KKR) scheme [9–11] and its relativistic variant [12, 13].

2. Problem recognition

Consider the following equation

$$(\hat{H}_0 + \Delta V\hat{\Sigma})\Psi = \varepsilon\Psi \tag{3}$$

where $\hat{H}_0$ is the ordinary Dirac operator

$$\hat{H}_0 = c\hat{\boldsymbol{\alpha}}\hat{\boldsymbol{p}} + mc^2\hat{\beta} + V\hat{I} \tag{4}$$

and the term $\Delta V\hat{\Sigma}$ provides the spin polarisation. Here

$$\hat{\boldsymbol{\alpha}} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix} \qquad \hat{\beta} = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \qquad \hat{\Sigma} = \begin{pmatrix} \sigma_z & 0 \\ 0 & \sigma_z \end{pmatrix} \tag{5}$$

σ_x, σ_y, σ_z are the Pauli matrices and I is the unit matrix. Atomic units with energy in Ryd are used, so that $m = \frac{1}{2}$ and $c = 274.072\ldots$.

As usual, we assume V and ΔV to have the muffin-tin (MT) form, which permits one to find the solution as a product of functions dependent on the modulus of r and angular-dependent ones.

It is known that at $\Delta V = 0$ the solution of equation (3) inside the MT sphere Ψ_I can be presented as an expansion in solutions of the same equation in a central-symmetric field with variational coefficients $C_{\kappa\mu}$ [14]:

$$\Psi_I = \sum_{\kappa,\mu} i^l C_{\kappa\mu} \begin{pmatrix} g_{\kappa\mu} & \varphi_{\kappa\mu} \\ -if_{\kappa\mu} & \varphi_{\bar{\kappa}\mu} \end{pmatrix}. \tag{6}$$

Here κ is a quantum number such that $\kappa = l$ if $\kappa > 0$ and $\kappa = -(l+1)$ if $\kappa < 0$; $\varphi_{\kappa\mu}$ are two-component spinors. Certainly, in the spherical-symmetric case the radial functions g and f do not depend on μ, but we shall retain this index for our subsequent work.

Let now $\Delta V \neq 0$. Then the symmetry of the problem changes: the moment-of-momentum projection on the z axis remains a preserved value (i.e. μ is, as before, the quantum number) but the operator corresponding to κ will no longer be the motion integral. Nevertheless, we shall find the solution of (3) inside the MT sphere again in the form of expansion (6).

Let us substitute the sum (6) into (3), having replaced κ by κ', perform the left multiplication of the expression obtained by the spinor $(\varphi^+_{\kappa\mu}, \varphi^+_{\bar{\kappa}\mu})$ and integrate over the angles. This gives

$$\left(cf'_{\kappa\mu} + \frac{1-\kappa}{r}cf_{\kappa\mu} + (E-V)g_{\kappa\mu}\right)C_{\kappa\mu}$$
$$= \Delta V(C_{\kappa\mu}\langle\varphi^+_{\kappa\mu}|\sigma_z|\varphi_{\kappa\mu}\rangle g_{\kappa\mu} + C_{\bar{\kappa}-1,\mu}\langle\varphi^+_{\kappa\mu}|\sigma_z|\varphi_{\bar{\kappa}-1,\mu}\rangle g_{\bar{\kappa}-1,\mu}) \tag{7a}$$

and

$$\left[g'_{\kappa\mu} + \frac{1+\kappa}{r}g_{\kappa\mu} - \left(1 + \frac{E-V}{c^2}\right)cf_{\kappa\mu}\right]C_{\kappa\mu}$$
$$= \frac{-\Delta V}{c^2}(C_{\kappa\mu}\langle\varphi^+_{\bar{\kappa}\mu}|\sigma_z|\varphi_{\bar{\kappa}\mu}\rangle cf_{\kappa\mu} + C_{\bar{\kappa}+1,\mu}\langle\varphi^+_{\bar{\kappa}\mu}|\sigma_z|\varphi_{\kappa-1,\mu}\rangle cf_{\bar{\kappa}+1,\mu}) \tag{7b}$$

where $E = \varepsilon - mc^2$. One can see that the first equation relates the indices κ and $-\kappa - 1$, which correspond to one and the same l; the second equation connects the indices κ and $-\kappa + 1$ corresponding to l and $l \pm 2$ respectively. The last term in (7*b*) makes the system infinite and the task is substantially simplified if this term is neglected [4]. Note that following [4] in all the papers using the multiple scattering formalism this term has been neglected. Omitting it in (7*a*) and (7*b*) and putting $C_{\kappa\mu} = C_{\bar{\kappa}-1,\mu} = C_{l\mu}$ we obviously obtain the same system of radial equations as in [4, 5, 8].

We shall omit the whole right-hand side of (7*b*), which seems to be of more consequence, because the ratio $|\overline{\Delta V}|/c^2$ where the averaging is performed through the MT sphere is a natural parameter of smallness. Indeed, ΔV represents the difference between the exchange–correlation potentials, which in the $X\alpha$ approximation, for example, is proportional to the difference $\rho_+^{1/3} - \rho_-^{1/3}$ ($\rho_\pm^{1/3}$ is the density of electrons with a given spin): hence, $|\overline{\Delta V}|/c^2 \ll 1$.

In the majority of papers, starting with [4], further consideration has been given to the $(\kappa\mu)$ representation, which is traditional for relativistic problems, except for a recent paper [7], where a transition is made to the (lms) representation in the $\tau(E)$ matrix. Comparing tables 1 and 2, 3 and 4 in [7] one can see that at this stage such a transition gives no practical advantages. Our consideration will be performed in the lms $(l\mu)$ representation right from the start.

Before proceeding to the discussion proper, it seems necessary to mention that the list of references does not include many works on calculations of the electronic structure of ferromagnets in the relativistic case. Papers [3–5] are referred to as the fundamental ones being close to the scheme suggested by us. Papers [6, 7] are devoted to further development of the theory and its applications. In [6] a technique of calculating the density of states is proposed, while in [7] is proposed a method of magnetic anisotropy calculation. An almost complete list of references along with necessary comments are available in [8].

3. General formalism

Let us write an arbitrary four-component spinor as

$$\Psi = \begin{pmatrix} \psi \\ -\mathrm{i}\tilde{\psi} \end{pmatrix} \tag{8}$$

and substitute it into (3). This results in the following system of equations:

$$\begin{aligned} &(\boldsymbol{\sigma}\boldsymbol{\nabla})(c\tilde{\psi}) + [E - (V + \Delta V\sigma_z)]\psi = 0 \\ &(\boldsymbol{\sigma}\boldsymbol{\nabla})\psi - \left(1 + \frac{E - V}{c^2} - \frac{\Delta V\sigma_z}{c^2}\right)(c\tilde{\psi}) = 0. \end{aligned} \tag{9}$$

Excluding the small component of $\tilde{\psi}$ and neglecting $\Delta V/c^2$ yields the equation for the large component:

$$\Delta\psi + W[E - (V + \Delta V\sigma_z)]\psi - (W'/W)(\boldsymbol{\sigma}\hat{\boldsymbol{r}})(\boldsymbol{\sigma}\boldsymbol{\nabla})\psi = 0. \tag{10}$$

Here $\hat{\boldsymbol{r}}$ is the unit vector and

$$W = 1 + (E - V)/c^2. \tag{11}$$

Let us further present the two-component spinor ψ as a product of radial functions $g_{l\mu\pm}$ and spherical harmonics Y_{lm} defined according to [15]:

$$\psi = \begin{pmatrix} g_{l\mu+} & Y_{lm} \\ g_{l\mu-} & Y_{lm'} \end{pmatrix} \qquad m = \mu - \tfrac{1}{2}, m' = \mu + \tfrac{1}{2} \tag{12}$$

and substitute it into (10). After standard transformations with spherical functions one can make sure that the presentation (12) provides the partition of variables and results in the following system of equations for the radial factors:

$$\begin{aligned} g''_{l\mu+} + \frac{2}{r} g'_{l\mu+} + \left(W(E - V_+) - \frac{l(l+1)}{r^2} \right) g_{l\mu+} \\ = \frac{W'}{W} \left[\left(g'_{l\mu+} - \frac{\mu - \frac{1}{2}}{r} g_{l\mu+} \right) + s_\mu [(l + \mu + \tfrac{1}{2})(l - \mu + \tfrac{1}{2})]^{1/2} \frac{g_{l\mu-}}{r} \right] \\ g''_{l\mu-} + \frac{2}{r} g'_{l\mu-} + \left(W(E - V_-) - \frac{l(l+1)}{r^2} \right) g_{l\mu-} \\ = \frac{W'}{W} \left[\left(g_{l\mu-} + \frac{\mu + \frac{1}{2}}{r} g_{l\mu-} \right) + s_\mu [(l + \mu + \tfrac{1}{2})(l - \mu + \tfrac{1}{2})]^{1/2} \frac{g_{l\mu+}}{r} \right] \end{aligned} \tag{13}$$

where $s_\mu = \mu/|\mu|$. This system has two linearly independent solutions regular at zero:

$$g_{l\mu,1+}, g_{l\mu,1-} \qquad \text{and} \qquad g_{l\mu,2+}, g_{l\mu,2-}. \tag{14}$$

Thus the general solution of (10) inside the MT sphere can be presented as the expansion

$$\psi_{\mathrm{I}} = \sum_{\substack{l,\mu \\ \nu=1,2}} \mathrm{i}^l C_{l\mu,\nu} \begin{pmatrix} g_{l\mu,\nu+} Y_{lm} \\ g_{l\mu,\nu-} Y_{lm'} \end{pmatrix} \tag{15}$$

with arbitrary coefficients $C_{l\mu,\nu}$.

The standard variational procedure usually used in spectral problems is not effective in this case, the operator in (10) being similar to a Hamiltonian only in appearance. That is why we have realised the alternative possibility of finding the general solution of (10) outside the MT sphere and joining it smoothly to the solution ψ_{I} through the MT sphere.

Let us now write equation (10) for an empty lattice ($V = \Delta V = 0$), which corresponds to the crystalline cell region outside the MT sphere:

$$\Delta\psi + E'\psi = 0 \tag{16}$$

where $E' = E(1 + E/c^2)$. The Green function corresponding to (16) is obviously presented with a two-dimensional scalar matrix, its diagonal containing the Green function of the empty lattice [11]

$$G(\boldsymbol{k}, E', \boldsymbol{r}, \boldsymbol{r}') = -\frac{1}{\Omega} \sum_q \frac{\exp[(\boldsymbol{k} + \boldsymbol{K}_q)(\boldsymbol{r} - \boldsymbol{r}')]}{(\boldsymbol{k} + \boldsymbol{K}_q)^2 - E'}. \tag{17}$$

Here Ω is the crystalline cell volume, $\boldsymbol{k}$ is a reduced wavevector and $\boldsymbol{K}_q$ are vectors of the reciprocal lattice. One can be convinced by direct substitution that the two-component vector function

$$\psi_{\mathrm{II}}(\boldsymbol{r}) = \int_{\Omega_{\mathrm{MT}}} G(\boldsymbol{k}, E', \boldsymbol{r}, \boldsymbol{r}') \begin{pmatrix} \Phi_+(\boldsymbol{r}') \\ \Phi_-(\boldsymbol{r}') \end{pmatrix} \mathrm{d}\boldsymbol{r}' \tag{18}$$

where $\Phi_\pm$ are arbitrary functions, is the solution of (16), i.e. it represents the large

component of the solution outside the MT sphere. (It is appropriate to mention here that the Bloch conditions at the cell boundary are satisfied automatically due to (17).)

Let us now use the known expansion of the Green function (17) in spherical harmonics [11], substitute it into (18) and perform the integration. Then for ψ_{II} we have

$$\psi_{II} = \sum_{\substack{l,m,\\ l',m'}} i^{l}[A_{lm,l'm'} j_l(\eta r) + \delta_{lm,l'm'} n_l(\eta r)] Y_{lm}(\hat{r}) \begin{cases} b^{+}_{l'm'} \\ b^{-}_{l'm'} \end{cases} \tag{19}$$

where $\eta = \sqrt{E'}$, the constants $b^{\pm}_{lm}$ being represented by the integrals

$$b^{\pm}_{lm} = \int_{\Omega_{MT}} j_l(\eta r') Y_{lm}(\hat{r}') \Phi_{\pm}(r')\, dr' \tag{20}$$

and owing to the arbitrariness of $\Phi_{\pm}$ they are arbitrary as well. Further, it is necessary to provide a smooth joining of solutions inside (15) and outside (19) the MT sphere on its surface, i.e. the following equalities should be satisfied:

$$\begin{aligned} &\psi_I(r) = \psi_{II}(r) \\ &\frac{\partial \psi_I(r)}{\partial r} = \frac{\partial \psi_{II}(r)}{\partial r} \qquad |r| = r_s \end{aligned} \tag{21}$$

r_s is the MT sphere radius. Tedious algebraic computations are carried over to appendix 1. The resulting dispersive equation is written as follows:

$$\begin{vmatrix} A + W^{++} & W^{+-} \\ W^{-+} & A + W^{--} \end{vmatrix} = 0 \tag{22}$$

where $A = A_{lm,l'm'}(k, E')$ is the structure constant matrix, and $W^{ss'} = W^{ss'}_{lm,l'm'}(E)$ are the matrices of scattering cotangents. The blocks W^{++} and W^{--} represent the diagonal matrices:

$$\begin{aligned} W^{++}_{lm,l'm'} &= \eta \frac{[n_l g_{l\mu,1+}][j_l g_{l\mu,2-}] - [n_l g_{l\mu,2+}][j_l g_{l\mu,1-}]}{\Delta_{l\mu}} \delta_{ll'} \delta_{mm'} \\ W^{--}_{lm,l'm'} &= \eta \frac{[j_l g_{l\mu,1+}][n_l g_{l\mu,2-}] - [j_l g_{l\mu,2+}][n_l g_{l\mu,1-}]}{\Delta_{l\mu}} \delta_{ll'} \delta_{mm'}. \end{aligned} \tag{23}$$

The only elements different from zero those which belong to the diagonal lying over and under the main diagonal for W^{+-} and W^{-+}, respectively:

$$\begin{aligned} W^{+-}_{lm,l'm'} &= \frac{1}{r^2} \frac{[g_{l\mu,1+} g_{l\mu,2+}]}{\Delta_{l\mu}} \delta_{ll'} \delta_{mm'} \\ W^{-+}_{lm,l'm'} &= -\frac{1}{r^2} \frac{[g_{l\mu,1-} g_{l\mu,2-}]}{\Delta_{l\mu}} \delta_{ll'} \delta_{mm'}. \end{aligned} \tag{24}$$

In (23) and (24)

$$\Delta_{l\mu} = [j_l g_{l\mu,1+}][j_l g_{l\mu,2-}] - [j_l g_{l\mu,2+}][j_l g_{l\mu,1-}] \tag{25}$$

and the following designation is introduced:

$$[h_1 h_2] = h_1 h_2' - h_1' h_2. \tag{26}$$

The non-hermiticity of the dispersive equation matrix (22) due to (24) is imaginary (see appendix 2).

So we see that the structure of the dispersive equation matrix (22) remains the same as in the absence of the spin polarisation [16]. The changes consist of: (i) the necessity of solving the system of two second-order equations (13) instead of one radial equation, (ii) the appearance of the μ dependence of the solutions and (iii) the complication due to the form of the scattering terms.

4. Limiting cases

Before discussing the limiting cases that occur in the absence of spin polarisation ($\Delta V \to 0$) or with neglect of relativistic effects ($W'/W \to 0$) we should analyse system (13). Since the potential affecting the electron near the nucleus always has a Coulomb singularity, the following asymptotic equalities hold:

$$\begin{aligned} &V_+ = V_- = -2Z/r \\ &W = 2Z/c^2 r \qquad W'/W = -1/r \end{aligned} \tag{27}$$

(Z is the nuclear charge). The asymptotic expressions for the radial functions at zero are given by

$$g_{l\mu,+} = ar^{\gamma-1} \qquad g_{l\mu,-} = br^{\gamma-1} \tag{28}$$

where γ, a and b are arbitrary constants. Substituting (28) and (27) into (13) and grouping the terms with the minimum degree of r, we get a homogeneous system of algebraic equations in a and b. The condition for its solvability yields a characteristic equation for γ having two positive roots:

$$\begin{aligned} \gamma_1 &= [(l+1)^2 - (2Z/c)^2]^{1/2} \\ \gamma_2 &= [l^2 - (2Z/c)^2]^{1/2}. \end{aligned} \tag{29}$$

(Negative values are impossible, as otherwise the requirement of the solutions $g_{l\mu,\pm}$ being regular at zero is not fulfilled.) The solutions of the algebraic system corresponding to (29) can be chosen in the form

$$\begin{aligned} a_1 &= s_\mu[l+\mu+\tfrac{1}{2}]^{1/2} \qquad & b_1 &= -[l-\mu+\tfrac{1}{2}]^{1/2} \\ a_2 &= s_\mu[l-\mu+\tfrac{1}{2}]^{1/2} \qquad & b_2 &= [l+\mu+\tfrac{1}{2}]^{1/2}. \end{aligned} \tag{30}$$

According to (30) it is convenient to introduce new radial functions $G_{\nu\pm}$ ($\nu = 1, 2$, the indices l, μ being omitted for the sake of brevity)

$$g_{l\mu,\nu\pm} = \left.\begin{matrix} a_\nu \\ b_\nu \end{matrix}\right\}(2l+1)^{-1/2} G_{\nu\pm}. \tag{31}$$

In this notation the coordinate functions (12), in which the expansion has been performed, will differ from the solutions of the ordinary relativistic problem in the central field only by the indices $\pm$ of the radial factors (see, for example, [17]). The

systems of radial equations for $G_{\nu\pm}$ are easily obtained from (13) by direct substitution. So for $G_{1\pm}$ we have

$$\begin{aligned} G''_{1+} + \frac{2}{r}G'_{1+} + \left(W(E - V_+) - \frac{l(l+1)}{r^2}\right)G_{1+} \\ = \frac{W'}{W}\left[\left(G'_{1+} - \frac{l}{r}G_{1+}\right) + (l - \mu + \tfrac{1}{2})\frac{1}{r}(G_{1+} - G_{1-})\right] \\ G''_{1-} + \frac{2}{r}G'_{1-} + \left(W(E - V_-) - \frac{l(l+1)}{r^2}\right)G_{1-} \\ = \frac{W'}{W}\left[\left(G'_{1-} - \frac{l}{r}G_{1-}\right) - (l + \mu + \tfrac{1}{2})\frac{1}{r}(G_{1+} - G_{1-})\right]. \end{aligned} \tag{32}$$

A similar system for $G_{2\pm}$ can be obtained from (32) by substituting $(-l-1)$ for l.

If we now put $\Delta V = 0$, i.e. $V_+ = V_-$, the systems considered will have solutions independent of the spin

$$\begin{aligned} G_{1+} &= G_{1-} = G_1 \\ G_{2+} &= G_{2-} = G_2. \end{aligned} \tag{33}$$

With the velocity of light tending to infinity ($c \to \infty$) one can set $W = 1$ and $W'/W = 0$; therefore, $G_{1\pm}$ and $G_{2\pm}$ could differ only by a constant factor

$$G_{2\pm} = \text{const}\, G_{1\pm}. \tag{34}$$

Let us now express the values $W^{ss'}_{lm,l'm'}$ in (23) and (24) through $G_{\nu\pm}$ and sum up. The substitution of $G_{\nu\pm}$ into (23) yields

$$\begin{aligned} W^{++}_{lm,lm} &= \frac{\eta}{\Delta_{l\mu}}\{(l + \mu + \tfrac{1}{2})[n_l G_{1+}][j_l G_{2-}] + (l - \mu + \tfrac{1}{2})[n_l G_{2+}][j_l G_{1-}]\} \\ W^{--}_{lm,lm} &= \frac{\eta}{\Delta_{l\mu}}\{(l + \mu + \tfrac{1}{2})[j_l G_{1+}][n_l G_{2-}] + (l - \mu + \tfrac{1}{2})[j_l G_{2+}][n_l G_{1-}]\}. \end{aligned} \tag{35}$$

It is more convenient to use instead of (24) the non-transformed expressions obtained from formulae (A1.5) and (A1.6) of appendix 1:

$$W^{\pm\mp}_{lm;l,m+1} = \frac{\eta}{\Delta_{l\mu}}[(l + \mu + \tfrac{1}{2})(l - \mu + \tfrac{1}{2})]^{1/2}\{[j_l G_{1\mp}][n_l G_{2\mp}] - [n_l G_{1\mp}][j_l G_{2\mp}]\} \tag{36}$$

where

$$\Delta_{l\mu} = (l + \mu + \tfrac{1}{2})[j_l G_{1+}][n_l G_{2-}] + (l - \mu + \tfrac{1}{2})[j_l G_{2+}][n_l G_{1-}]. \tag{37}$$

In the absence of spin polarisation ($\Delta V = 0$) we make use of relations (33), which results in

$$W^{\pm\pm}_{lm;lm} = \frac{\eta}{2l+1}\left((l+1)\frac{[n_lG_1]}{[j_lG_1]} + l\frac{[n_lG_2]}{[j_lG_2]}\right) \pm \frac{m}{2l+1}\left(\frac{[n_lG_1]}{[j_lG_1]} - \frac{[n_lG_2]}{[j_lG_2]}\right)$$
$$W^{\pm\mp}_{lm;l,m\pm1} = -\frac{\eta}{2l+1}[(l \pm m + 1)(l \mp m)]^{1/2}\left(\frac{[n_lG_1]}{[j_lG_1]} - \frac{[n_lG_2]}{[j_lG_2]}\right). \tag{38}$$

One can proceed to the non-relativistic case ($c \to \infty$), without any difficulties. Substituting (34) into (35) and (36), we get

$$W^{\pm\pm}_{lm;lm} = \eta\frac{[n_lG_+]}{[j_lG_-]} \qquad W^{\pm\mp}_{lm;l,m\pm1} = 0. \tag{39}$$

Thus the dispersive equation (22) obtained in this paper includes as limiting cases both the dispersive equation of the standard relativistic Green function method (RKKR) [16, 18] and the two dispersive equations of the non-relativistic spin-polarised technique. This is, so far, the main argument for the approximation made.

5. Conclusions

To conclude we shall make some remarks.

The derivation of the main dispersive equation by means of continuous prolongation of the solutions through the MT sphere into the outer part of the Wigner–Seitz cell can be performed in the $(\kappa\mu)$ representation using the relativistic Green function. Following such a procedure the ordinary relativistic structure constants are included in the elements of the dispersive equation matrix, the form of the diagonal scattering terms getting complicated and the non-diagonal scattering terms appearing at the same positions as in the t-matrix of [5]. Unfortunately, we failed to compare the corresponding expressions analytically, and the numerical values of $t_{\kappa\mu,\kappa'\mu}$ are not presented in [5]. Besides, a comparison of numerical values would make sense only with absolutely identical potentials.

Since the presence of spin polarisation makes the scattering matrix in the $(\kappa\mu)$ representation non-diagonal, the $(\kappa\mu)$ and (lms) representations are equivalent in this case. Moreover, using the (lms) representation allows one to retain the same structure of the dispersive matrix as in the absence of spin polarisation.

Both forms of the dispersive equation are interconnected in the same way as without the spin polarisation [10] through the Clebsch–Gordan coefficients.

The form of radial equations (13) and dispersive equation (22) permits a rather simple development of the perturbation theory for the eigenvalues of matrix (22) with respect to both the spin polarisation parameter ΔV and the ratio W'/W responsible for relativistic effects. This, in turn, allows one to estimate the variation of the electron energy eigenvalues for small ΔV and W'/W. We shall probably consider this point in a following paper.

Appendix 1

Let us substitute expansions (15) and (19) into (21) and make use of the orthogonality of spherical harmonics. For each $(l\mu)$ this will result in two pairs of algebraic equations in coefficients $C_{l\mu,\nu}$ (hereafter the indices $(l\mu)$ of C and g will be omitted):

$$\begin{aligned} C_1 g_{1+} + C_2 g_{2+} &= \sum_{l'',m''} [A_{lm,l''m''} j_l + \eta \delta_{lm,l''m''} n_l] b^{+}_{l''m''} \\ C_1 g'_{1+} + C_2 g'_{2+} &= \sum_{l'',m''} [A_{lm,l''m''} j'_l + \eta \delta_{lm,l''m''} n'_l] b^{+}_{l''m''} \end{aligned} \tag{A1.1a}$$

and

$$\begin{aligned} C_1 g_{1-} + C_2 g_{2-} &= \sum_{l'',m''} [A_{lm',l''m''} j_l + \eta \delta_{lm',l''m''} n_l] b^{-}_{l''m''} \\ C_1 g'_{1-} + C_2 g'_{2-} &= \sum_{l'',m''} [A_{lm',l''m''} j_l + \eta \delta_{lm',l''m''} n_l] b^{-}_{l''m''} \end{aligned} \tag{A1.1b}$$

with $m = \mu - \frac{1}{2}$ and $m' = \mu + \frac{1}{2}$. Now expressing C_ν from each pair of equations and equating appropriate expressions, we obtain the infinite homogeneous system of algebraic equations in coefficients $b^{\pm}_{lm}$:

$$\begin{aligned} &\sum_{l'',m''} \{A_{lm,l''m''}[j_l g_{1+}] + \eta \delta_{lm,l''m''}[n_l g_{1+}]\} b^{+}_{l''m''} \\ &\quad + \sum_{l'',m''} \{A_{lm',l''m''}[j_l g_{1-}] + \eta \delta_{lm',l''m''}[n_l g_{1-}]\} b^{-}_{l''m''} = 0 \\ &\sum_{l'',m''} \{A_{lm,l''m''}[j_l g_{2+}] + \eta \delta_{lm,l''m''}[n_l g_{2+}]\} b^{+}_{l''m''} \\ &\quad + \sum_{l'',m''} \{A_{lm',l''m''}[j_l g_{2-}] + \eta \delta_{lm',l''m''}[n_l g_{2-}]\} b^{-}_{l''m''} = 0 \end{aligned} \tag{A1.2}$$

where the designation

$$[h_1 h_2] = h_1 h'_2 - h'_1 h_2 \tag{A1.3}$$

is introduced and the equation

$$[g_{1+} g_{2+}] = -[g_{1-} g_{2-}] \tag{A1.4}$$

is used. (The latter is proved in appendix 2.)

In order to exclude the structure constants $A_{lm',l''m''}$ from (A1.2) we multiply the first equation by $[j_l g_{2-}]$, the second one by $[j_l g_{1-}]$ and subtract the second from the first. This yields:

$$\begin{aligned} &\sum_{l'',m''} [\![\{A_{lm,l''m''}([j_l g_{1+}][j_l g_{2-}] - [j_l g_{1-}][j_l g_{2+}]) \\ &\quad + \eta \delta_{lm,l''m''}([n_l g_{1+}][j_l g_{2-}] - [j_l g_{1-}][n_l g_{2+}])\} b^{+}_{l''m''} \\ &\quad + \eta \delta_{l,m+1;l''m''}([j_l g_{1-}][n_l g_{2-}] - [n_l g_{1-}][j_l g_{2-}]) b^{-}_{l''m''}]\!] = 0 \end{aligned} \tag{A1.5}$$

(m' is replaced by $m+1$). Similarly, excluding $A_{lm,l''m''}$, substituting m for $m'-1$ and redenoting m' by m, we have

$$\sum_{l'',m''} [\{A_{lm,l''m''}([j_l g_{1+}][j_l g_{2-}] - [j_l g_{1-}][j_l g_{2+}]) + \eta\delta_{lm,l''m''}([j_l g_{1+}][n_l g_{2-}] - [n_l g_{1-}][j_l g_{2+}])b^{-}_{l''m''} + \eta\delta_{l,m-1;l''m''}([j_l g_{1+}][n_l g_{2+}] - [n_l g_{1+}][j_l g_{2+}])b^{+}_{l''m''}] = 0. \tag{A1.6}$$

The condition for the solvability of system (A1.5) and (A1.6) results in the dispersive equation (22).

Appendix 2

The coincidence of the matrix elements $W^{+-}_{lm;l,m+1}$ and $W^{-+}_{lm;l,m-1}$ can be demonstrated straightforwardly. Indeed,

$$[n_l g_{1-}][j_l g_{2-}] - [j_l g_{1-}][n_l g_{2-}] = n_l j_k' g_{1-} g_{2-}' - n_l' j_l g_{1-} g_{2-}' + j_l n_l' g_{1-} g_{2-} - j_l' n_l g_{1-}' g_{2-} = [n_l j_l][g_{1-} g_{2-}]. \tag{A2.1}$$

Similarly,

$$[j_l g_{1+}][n_l g_{2+}] - [n_l g_{1+}][j_l g_{2+}] = -[n_l j_l][g_{1+} g_{2+}]. \tag{A2.2}$$

The coincidence of the right-hand sides of (A2.1) and (A2.2) can be proved using the radial equations (13). Since g_{1+} and g_{2+} are the solutions of the first of them, the following equations are satisfied:

$$g_{1+}'' + \frac{2}{r} g_{1+}' + \left(W(E - V_+) - \frac{l(l+1)}{r^2}\right) g_{1+} = \frac{W'}{W}\left[\left(g_{1+}' - \frac{\mu - \frac{1}{2}}{r} g_{1+}\right) + s_\mu[(l+\mu+\tfrac{1}{2})(l-\mu+\tfrac{1}{2})]^{1/2} \frac{1}{r} g_{1-}\right]$$
$$g_{2+}'' + \frac{2}{r} g_{2+}' + \left(W(E - V_+) - \frac{l(l+1)}{r^2}\right) g_{2+} = \frac{W'}{W}\left[\left(g_{2+}' - \frac{\mu - \frac{1}{2}}{r} g_{2+}\right) + s_\mu[(l+\mu+\tfrac{1}{2})(l-\mu+\tfrac{1}{2})]^{1/2} \frac{1}{r} g_{2-}\right]. \tag{A2.3}$$

Multiplying the first equation by g_{2+}, the second one by g_{1+} and subtracting the first from the second yields

$$(g_{1+} g_{2+}'' - g_{1+}'' g_{2+}) + \frac{2}{r}(g_{1+} g_{2+}' - g_{1+}' g_{2+}) - \frac{W'}{W}(g_{1+} g_{2+}' - g_{1+}' g_{2+}) = \frac{1}{r} s_\mu[(l+\mu+\tfrac{1}{2})(l-\mu+\tfrac{1}{2})]^{1/2}(g_{1+} g_{2-} - g_{1-} g_{2+}). \tag{A2.4}$$

Hence,

$$g_{1+} g_{2+}' - g_{1+}' g_{2+} = s_\mu[(l+\mu+\tfrac{1}{2})(l-\mu+\tfrac{1}{2})]^{1/2} \frac{W}{r^2} \int_0^r \frac{1}{W}(g_{1+} g_{2-} - g_{1-} g_{2+}) r \, dr. \tag{A2.5}$$

And, similarly,

$$g_{1-}g'_{2-} - g'_{1-}g_{2-}$$
$$= -s_\mu[(l+\mu+\tfrac{1}{2})(l-\mu+\tfrac{1}{2})]^{1/2}\frac{W}{r^2}\int_0^r \frac{1}{W}(g_{1+}g_{2-} \qquad \text{(A2.6)}$$
$$- g_{1-}g_{2+})r\,\mathrm{d}r.$$

It is from the last two expressions that the equality of the right-hand sides of (A2.1) and (A2.2) as well as the validity of (A1.4) follow.

References

[1] Slater J C 1974 *The Self-Consistent Field for Molecules and Solids* (New York: McGraw-Hill)
[2] Wonsovskij S V 1971 *Magnetism* (Moscow: Nauka)
[3] Feder R, Rosicky F and Ackermann B 1983 *Z. Phys.* B **52** 31
[4] Strange P, Staunton J B and Gyorffy B L 1984 *J. Phys. C: Solid State Phys.* **17** 3355
[5] Schadler G, Weinberger P, Boring A M and Albers R C 1986 *Phys. Rev.* B **34** 713
[6] Strange P, Ebert H, Staunton J B and Gyorffy B L 1989 *J. Phys.: Condens. Matter* **1** 2959
[7] Strange P, Ebert H, Staunton J B and Gyorffy B L 1989 *J. Phys.: Condens. Matter* **1** 3947
[8] Krutzen B C H and Springelkamp F 1989 *J. Phys.: Condens. Matter* **1** 8369
[9] Korringa J 1947 *Physica* **13** 392
[10] Kohn W and Rostoker N 1954 *Phys. Rev.* **94** 1111
[11] Segall B and Ham F S 1968 *Methods of Computational Physics* vol 8 (New York: Academic), p 251
[12] Takada S 1966 *Prog. Theor. Phys.* **36** 224
[13] Onodera J and Okazaki M 1966 *J. Phys. Soc. Japan* **21** 1273
[14] Loucks T L 1967 *Augmented Plane Wave Method* (New York: Benjamin)
[15] Korn G and Korn T 1968 *Mathematical Handbook* (New York: McGraw-Hill)
[16] Neto A A and Ferreira L G 1976 *Phys. Rev.* B **14** 4390
[17] Bethe H A and Salpeter E E 1957 *Quantum Mechanics of One- and Two-Electron Atoms* (Berlin: Springer)
[18] Topolskij V G and Shirokovskij V P 1980 *Metallofizika* **2** 32