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RESEARCH ARTICLE

Relativistic LMTO method for systems of light elements

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The paper reviews theoretical backgrounds of an approximate treatment of relativistic effects within the tight-binding (TB) linear muffin-tin orbital (LMTO) method for *ab initio* electronic structure calculations of solids. The formalism employs two-component spinors and an orbital basis set of the scalar-relativistic approximation. The developed theory is applied to selected metallic systems and its results are compared to those of a fully relativistic TB-LMTO method.

Keywords: electronic structure calculations; density functional theory; relativistic effects; spin-orbit interaction; random alloys; itinerant magnetism

1. Introduction

It is well known that the role of relativistic effects in electronic properties of solids is pronounced especially for systems with heavy elements (*5d* transition metals, actinides). In magnetic solids, however, this role becomes non-negligible even for systems consisting of light elements. In particular, the spin-orbit (SO) interaction in *3d* transition metals and their alloys is responsible for a number of important properties of itinerant magnets, such as magnetocrystalline anisotropy, galvanomagnetic phenomena [1], or imperfect spin polarization of carriers in halfmetallic ferromagnets [2].

Existing *ab initio* approaches to an accurate treatment of the relativistic effects employ inevitably four-component wave functions within the Kohn-Sham-Dirac (KSD) theory [see 3, 4, and references therein]. This leads—even in cases with weak SO interaction—to profound changes of the whole formalism in comparison to usual non-relativistic or scalar-relativistic descriptions. The purpose of this paper is twofold. First, we sketch briefly (Section 2) an easy modification of the scalar-relativistic tight-binding (TB) linear muffin-tin orbital (LMTO) method [3, 5] that takes into account the SO interaction but retains a number of features of the original formalism. Second, we check reliability of the developed technique (Section 3) by performing selfconsistent calculations for several non-magnetic and spin-polarized bulk systems and by comparing their results to those of the fully relativistic TB-LMTO method [3, chap. 6].

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2. Theory

2.1. Kohn-Sham-Dirac Hamiltonian and its approximations

A relativistic density functional theory neglecting diamagnetic effects [6] leads to the KSD equation for a one-electron four-component wave function $\Psi(\mathbf{r})$ describing non-interacting electrons in an effective spin-dependent potential

$$H_{\text{KSD}}\Psi = E\Psi, \quad H_{\text{KSD}} = c\boldsymbol{\alpha} \cdot \mathbf{p} + (\beta - I_4)mc^2 + V_0(\mathbf{r})I_4 + \mathbf{B}_{\text{xc}}(\mathbf{r}) \cdot \boldsymbol{\Sigma}\beta, \quad (1)$$

where the 4×4 matrices $\boldsymbol{\alpha}$, β , I_4 and $\boldsymbol{\Sigma}$ are defined (in a 2×2 block-wise notation and with the Pauli spin matrices $\boldsymbol{\sigma}$) as

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad I_4 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \boldsymbol{\Sigma} = \begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix}. \quad (2)$$

The $V_0(\mathbf{r})$ and $\mathbf{B}_{\text{xc}}(\mathbf{r})$ denote the spin-independent part of the potential and the exchange-correlation magnetic field, respectively [3, chap. 6]. After separating the large (Φ) and the small (Υ) components of the bispinor Ψ ,

$$\Psi = \begin{pmatrix} \Phi \\ \Upsilon \end{pmatrix}, \quad (3)$$

and after exclusion of the small component, the resulting equation $H_{\text{eff}}(E)\Phi = E\Phi$ is obtained for the large component with an effective energy-dependent Hamiltonian

$$H_{\text{eff}}(E) = \mathbf{p} \cdot \boldsymbol{\sigma} \frac{c^2}{2mc^2 + E - V_0(\mathbf{r}) + \mathbf{B}_{\text{xc}}(\mathbf{r}) \cdot \boldsymbol{\sigma}} \mathbf{p} \cdot \boldsymbol{\sigma} + V_0(\mathbf{r}) + \mathbf{B}_{\text{xc}}(\mathbf{r}) \cdot \boldsymbol{\sigma}. \quad (4)$$

In atomic Rydberg units (used in the rest of the paper): $2m = 1$, $\hbar = 1$, $e^2/(4\pi\epsilon_0) = 2$, hence $c \approx 2 \times 137$.

For valence electrons of a typical solid, one can neglect their energy range (~ 1 Ry) and the exchange splitting B_{xc} (~ 0.1 Ry) against $2mc^2 \approx 75$ kRy in the denominator in equation (4). This yields an approximate equation for the two-component spinor Φ with an energy-independent Hamiltonian of the form

$$H\Phi = E\Phi, \quad H = \mathbf{p} \cdot \boldsymbol{\sigma} \omega^{-1}(\mathbf{r}) \mathbf{p} \cdot \boldsymbol{\sigma} + V_0(\mathbf{r}) + \mathbf{B}_{\text{xc}}(\mathbf{r}) \cdot \boldsymbol{\sigma}, \\ \omega(\mathbf{r}) = 1 + c^{-2}[E_0 - V_0(\mathbf{r})], \quad (5)$$

where E_0 is an energy inside the valence band and $\omega(\mathbf{r})$ denotes the relativistic mass enhancement factor. The use of the energy-independent Hamiltonian H (5) for the large component Φ is compatible with the neglect of the small-component contribution to the electron density which is justified only for valence states of not too heavy atoms.

In the scalar-relativistic approximation (SRA) [7], equation (5) is replaced by

$$H_{\text{SRA}}\Phi = E\Phi, \quad H_{\text{SRA}} = \mathbf{p} \cdot \omega^{-1}(\mathbf{r})\mathbf{p} + V_0(\mathbf{r}) + \mathbf{B}_{\text{xc}}(\mathbf{r}) \cdot \boldsymbol{\sigma}. \quad (6)$$

Note that for magnetic fields \mathbf{B}_{xc} of a constant direction along the z axis, the spin operator σ_z commutes with the H_{SRA} and the two components of Φ are not mixed in equation (6). The H_{SRA} follows from the H (5) by omitting the second term in a well-known relation of the Pauli-matrix algebra $\sigma_\mu\sigma_\nu = \delta_{\mu\nu} + i\sum_\lambda \varepsilon_{\mu\nu\lambda}\sigma_\lambda$,

where $\mu, \nu, \lambda \in \{x, y, z\}$. The SO interaction is then defined as the difference of Hamiltonians H (5) and H_{SRA} (6), i.e.,

$$H_{\text{SO}} = H - H_{\text{SRA}} = \{[\nabla\omega^{-1}(\mathbf{r})] \times \mathbf{p}\} \cdot \boldsymbol{\sigma}. \quad (7)$$

The effect of the H_{SO} can be included as a correction to the H_{SRA} [8]. Nevertheless, this procedure takes properly into account the singular behavior of the mass enhancement factor $\omega(\mathbf{r})$ (5) for points close to the atomic nuclei which is the main origin of SO splittings.

2.2. Orbitals and Hamiltonians in the LMTO method

Here we derive a matrix representation of the Hamiltonians H_{SRA} , H_{SO} and H of Section 2.1 in the framework of the LMTO method and within the atomic sphere approximation (ASA) [3, 8]. We assume a spin-polarized system with a collinear spin structure and with the spin polarization along the z axis.

The LMTO orbitals $|\chi_{\mathbf{R}Ls}\rangle$ derived from the H_{SRA} have the form

$$\begin{aligned} |\chi_{\mathbf{R}'L's'}\rangle = & - \sum_{\mathbf{R}Ls} |\phi_{\mathbf{R}Ls}\rangle \left(\dot{K} - JS^0 \right)_{\mathbf{R}Ls, \mathbf{R}'L's'} \\ & + \sum_{\mathbf{R}Ls} |\dot{\phi}_{\mathbf{R}Ls}\rangle (K - JS^0)_{\mathbf{R}Ls, \mathbf{R}'L's'}, \end{aligned} \quad (8)$$

where \mathbf{R} is the site index, $L = (\ell, m)$ is the orbital index, $s = \uparrow, \downarrow$ is the spin index, and $|\phi_{\mathbf{R}Ls}\rangle$ and $|\dot{\phi}_{\mathbf{R}Ls}\rangle$ denote the phi and phi-dot orbitals (non-zero only inside the \mathbf{R} -th atomic sphere). The symbol S^0 denotes the matrix of canonical LMTO structure constants with matrix elements $S^0_{\mathbf{R}Ls, \mathbf{R}'L's'} = \delta_{ss'} S^0_{\mathbf{R}L, \mathbf{R}'L'}$ and the symbols J, K, \dot{J}, \dot{K} abbreviate diagonal matrices with elements given by Wronskians,

$$J_{\mathbf{R}Ls, \mathbf{R}'L's'} = \delta_{\mathbf{R}Ls, \mathbf{R}'L's'} \{J, \phi\}_{\mathbf{R}Ls}, \quad \dot{K}_{\mathbf{R}Ls, \mathbf{R}'L's'} = \delta_{\mathbf{R}Ls, \mathbf{R}'L's'} \{K, \dot{\phi}\}_{\mathbf{R}Ls},$$

etc. [3, chap. 2]. Note that the matrices $(K - JS^0)$ and $(\dot{K} - JS^0)$ are diagonal in the spin index and the orbitals $|\chi_{\mathbf{R}Ls}\rangle$, $|\phi_{\mathbf{R}Ls}\rangle$ and $|\dot{\phi}_{\mathbf{R}Ls}\rangle$ have to be understood as spin-orbitals (two-component non-relativistic spinors) with a trivial dependence on the spin variable:

$$\begin{aligned} \langle \mathbf{r}\bar{s} | \phi_{\mathbf{R}Ls} \rangle &= \delta_{\bar{s}s} \langle \mathbf{r} | \phi_{\mathbf{R}Ls} \rangle, & \langle \mathbf{r}\bar{s} | \dot{\phi}_{\mathbf{R}Ls} \rangle &= \delta_{\bar{s}s} \langle \mathbf{r} | \dot{\phi}_{\mathbf{R}Ls} \rangle, \\ \langle \mathbf{r}\bar{s} | \chi_{\mathbf{R}Ls} \rangle &= \delta_{\bar{s}s} \langle \mathbf{r} | \chi_{\mathbf{R}Ls} \rangle. \end{aligned} \quad (9)$$

The angular dependence of the orbitals $\langle \mathbf{r} | \phi_{\mathbf{R}Ls} \rangle$ and $\langle \mathbf{r} | \dot{\phi}_{\mathbf{R}Ls} \rangle$ is given by real spherical harmonics $Y_L(\hat{\mathbf{r}})$ while their radial amplitudes will be denoted as $g_{\mathbf{R}Ls}(r)$ and $\dot{g}_{\mathbf{R}Ls}(r)$, respectively.

The overlap matrix O and the matrix representing the SRA Hamiltonian in the basis of the LMTO orbitals $|\chi_{\mathbf{R}Ls}\rangle$ (8) are given by

$$\begin{aligned} O &= \left(\dot{K} - S^0 J \right) \left(\dot{K} - JS^0 \right), \\ H_{\text{SRA}} &= \left(\dot{K} - S^0 J \right) E_\nu \left(\dot{K} - JS^0 \right) - \left(\dot{K} - S^0 J \right) \left(K - JS^0 \right), \end{aligned} \quad (10)$$

where E_ν denotes a diagonal matrix of the energies $E_{\nu, \mathbf{R}Ls}$ used for the linearization and where terms containing the small parameters $p_{\mathbf{R}Ls}$ of the LMTO theory were

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omitted [3, chap. 2]. In deriving these results, normalization and orthogonality of the spin-orbitals $|\phi_{\mathbf{R}Ls}\rangle$ and $|\dot{\phi}_{\mathbf{R}Ls}\rangle$ were used:

$$\langle \phi_{\mathbf{R}Ls} | \phi_{\mathbf{R}'L's'} \rangle = \delta_{\mathbf{R}\mathbf{R}'} \delta_{LL'} \delta_{ss'}, \quad \langle \dot{\phi}_{\mathbf{R}Ls} | \phi_{\mathbf{R}'L's'} \rangle = 0. \quad (11)$$

The factorized form of the overlap matrix (10) leads to an explicit definition of the basis of orthonormal LMTO orbitals $|\chi_{\mathbf{R}Ls}^{\text{orth}}\rangle$:

$$\begin{aligned} |\chi_{\mathbf{R}'L's'}^{\text{orth}}\rangle &= |\phi_{\mathbf{R}'L's'}\rangle + \sum_{\mathbf{R}Ls} |\dot{\phi}_{\mathbf{R}Ls}\rangle h_{\mathbf{R}Ls, \mathbf{R}'L's'}, \\ h &= -(K - JS^0) (\dot{K} - jS^0)^{-1}. \end{aligned} \quad (12)$$

The SRA Hamiltonian is then represented in the orthonormal LMTO basis by

$$H_{\text{SRA}}^{\text{orth}} = E_\nu + h = C + \sqrt{\Delta} S^0 (1 - \gamma S^0)^{-1} \sqrt{\Delta}, \quad (13)$$

where C , Δ and γ denote diagonal matrices of the standard LMTO potential parameters $C_{\mathbf{R}Ls}$, $\Delta_{\mathbf{R}Ls}$ and $\gamma_{\mathbf{R}Ls}$.

Let us evaluate matrix elements of the H_{SO} (7) between two orbitals $|\phi_{\mathbf{R}Ls}\rangle$ and $|\phi_{\mathbf{R}'L's'}\rangle$ where $\langle \mathbf{r} | \phi_{\mathbf{R}Ls} \rangle = g_{\mathbf{R}Ls}(r) Y_{\ell m}(\hat{\mathbf{r}})$. We assume a spherically symmetric potential $V_0(\mathbf{r}) = V_{\mathbf{R}}(r)$ inside the \mathbf{R} -th atomic sphere; the matrix elements are:

$$\begin{aligned} \langle \phi_{\mathbf{R}'L's'} | H_{\text{SO}} | \phi_{\mathbf{R}Ls} \rangle &= \\ &= \sum_{\mu\nu\lambda} \varepsilon_{\mu\nu\lambda} \langle s' | \sigma_\lambda | s \rangle \int g_{\mathbf{R}'L's'}(r) Y_{\ell' m'}(\hat{\mathbf{r}}) \frac{r_\mu}{r} [\omega_{\mathbf{R}}^{-1}(r)]' p_\nu g_{\mathbf{R}Ls}(r) Y_{\ell m}(\hat{\mathbf{r}}) d^3\mathbf{r} \\ &= \sum_{\lambda} \langle s' | \sigma_\lambda | s \rangle \int Y_{\ell' m'}(\hat{\mathbf{r}}) L_\lambda Y_{\ell m}(\hat{\mathbf{r}}) d^2\hat{\mathbf{r}} \int r g_{\mathbf{R}'L's'}(r) g_{\mathbf{R}Ls}(r) [\omega_{\mathbf{R}}^{-1}(r)]' dr, \end{aligned}$$

where $Y_{\ell m}(\hat{\mathbf{r}})$ are real spherical harmonics, the prime denotes radial derivative, and the components L_λ of the angular orbital momentum operator $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ were used. Note that the matrix elements vanish for $\ell \neq \ell'$. The final expression for matrix elements between all phi orbitals can be written as [7]

$$\langle \phi_{\mathbf{R}'L's'} | H_{\text{SO}} | \phi_{\mathbf{R}Ls} \rangle = \delta_{\mathbf{R}'\mathbf{R}} \delta_{\ell'\ell} \xi_{\mathbf{R}L, s's} \langle L's' | \mathbf{L} \cdot \mathbf{S} | Ls \rangle, \quad (14)$$

where we introduced the spin operator $\mathbf{S} = \boldsymbol{\sigma}/2$ and the SO parameters $\xi_{\mathbf{R}L, s's}$ defined by

$$\xi_{\mathbf{R}L, s's} = 2 \int_0^{s_{\mathbf{R}}} r g_{\mathbf{R}'L's'}(r) g_{\mathbf{R}Ls}(r) [\omega_{\mathbf{R}}^{-1}(r)]' dr, \quad (15)$$

where $s_{\mathbf{R}}$ denotes the \mathbf{R} -th atomic sphere (Wigner-Seitz) radius. The resulting SO matrix elements (14) bear a form originating apparently from a simple $\xi \mathbf{L} \cdot \mathbf{S}$ term; they are, however, more general for magnetic systems due to the spin dependence of the SO parameters (15).

The matrix representations of the H_{SO} in the original (8) and the orthogonal (12) LMTO bases can respectively be written as

$$H_{\text{SO}} = (\dot{K} - S^0 j) \xi (\dot{K} - jS^0), \quad H_{\text{SO}}^{\text{orth}} = \xi, \quad (16)$$

where ξ denotes a site-diagonal matrix of the SO parameters $\xi_{\mathbf{R}\ell,s's}$ according to equation (14). In deriving relations (16), matrix elements of the H_{SO} between the orbitals $|\phi_{\mathbf{R}\ell s}\rangle$ and $|\phi_{\mathbf{R}\ell' s'}\rangle$ (and also between $|\dot{\phi}_{\mathbf{R}\ell s}\rangle$ and $|\dot{\phi}_{\mathbf{R}\ell' s'}\rangle$) were omitted which corresponds to a neglect of varying SO-coupling strength for energies inside the valence band [8]. The form of the omitted matrix elements is similar to equations (14) and (15) but their inclusion spoils many simple relations of the TB-LMTO theory.

Matrix elements of the full Hamiltonian $H = H_{\text{SRA}} + H_{\text{SO}}$ in the orthonormal LMTO basis follow from equations (13) and (16); they are finally given by

$$\begin{aligned} H^{\text{orth}} &= \underline{E}_\nu + h = \underline{C} + \sqrt{\Delta} S^0 (1 - \gamma S^0)^{-1} \sqrt{\Delta}, \\ \underline{E}_\nu &= E_\nu + \xi, \quad \underline{C} = C + \xi, \end{aligned} \quad (17)$$

so that the only effect of the SO interaction is a trivial change of two potential parameter matrices: the $\mathbf{R}\ell s$ -diagonal matrices E_ν and C of the SRA are replaced by the $\mathbf{R}\ell$ -diagonal matrices \underline{E}_ν and \underline{C} with intermixed indices of the magnetic (m) and spin (s) quantum numbers.

2.3. Screening transformations and Green's functions

The formulation of the TB-LMTO method rests on two points [5]. First, the site-diagonal potential function matrix $P^\alpha(z)$ in a general screened LMTO representation (superscript α) is introduced, which in the present case acquires the form

$$P^\alpha(z) = \left[\sqrt{\Delta} (z - \underline{C})^{-1} \sqrt{\Delta} + \gamma - \alpha \right]^{-1}. \quad (18)$$

Here z is a complex energy and the α on the r.h.s. denotes a diagonal matrix of m - and s -independent screening constants $\alpha_{\mathbf{R}\ell}$. Second, the matrix of screened structure constants S^α is defined by means of the original (canonical) structure constants S^0 . The relation of both screened quantities $[P^\alpha(z), S^\alpha]$ to their unscreened counterparts $[P^0(z), S^0]$ – corresponding to all $\alpha_{\mathbf{R}\ell} = 0$ is given by

$$P^\alpha(z) = P^0(z) [1 - \alpha P^0(z)]^{-1}, \quad S^\alpha = S^0 (1 - \alpha S^0)^{-1}. \quad (19)$$

Detailed discussion of the screening transformations can be found in [3, chap. 3].

The TB-LMTO Green's functions (GF) include the resolvent $G(z)$ of the Hamiltonian H^{orth} (17) and an auxiliary GF matrix $g^\alpha(z)$:

$$G(z) = (z - H^{\text{orth}})^{-1}, \quad g^\alpha(z) = [P^\alpha(z) - S^\alpha]^{-1}. \quad (20)$$

These definitions lead to an important expression for the resolvent [3, chap. 3]:

$$G(z) = \lambda^\alpha(z) + \mu^\alpha(z) g^\alpha(z) \tilde{\mu}^\alpha(z), \quad (21)$$

where the quantities $\lambda^\alpha(z)$, $\mu^\alpha(z)$ and $\tilde{\mu}^\alpha(z)$ denote $\mathbf{R}\ell$ -diagonal matrices

$$\begin{aligned} \mu^\alpha(z) &= \frac{1}{\sqrt{\Delta}} [1 + (\alpha - \gamma) P^\alpha(z)], & \lambda^\alpha(z) &= \mu^\alpha(z) \frac{\gamma - \alpha}{\sqrt{\Delta}}, \\ \tilde{\mu}^\alpha(z) &= [1 + P^\alpha(z)(\alpha - \gamma)] \frac{1}{\sqrt{\Delta}}. \end{aligned} \quad (22)$$

All these relations are essentially identical with their SRA counterparts; the only difference is due to the non-diagonal nature of the matrices \underline{C} , $P^\alpha(z)$, $\lambda^\alpha(z)$, $\mu^\alpha(z)$ and $\tilde{\mu}^\alpha(z)$. However, these matrices remain diagonal in the site index \mathbf{R} . Consequently, all basic GF techniques developed within the SRA can easily be modified for the present case with SO interaction. This refers, e.g., to the coherent potential approximation (CPA) for disordered alloys [3, 9].

2.4. Physical one-particle quantities

Quantum-mechanical averages of one-particle operators for a many-electron non-interacting system in thermodynamic equilibrium can be expressed by means of the one-particle density matrix $\rho_{ss'}(\mathbf{r}, \mathbf{r}')$. Its definition employs the orthonormal basis (12) and the spectral density matrix of the Hamiltonian H^{orth} (17):

$$\mathcal{D}(E) = \delta(E - H^{\text{orth}}) = \frac{i}{2\pi} [G(E + i0) - G(E - i0)]. \quad (23)$$

The valence contribution to the one-particle density matrix at zero temperature is then equal to

$$\begin{aligned} \rho_{s_1 s_2}(\mathbf{r}_1, \mathbf{r}_2) = & \sum_{\mathbf{R}'L's'} \sum_{\mathbf{R}''L''s''} \langle \mathbf{r}_1 s_1 | \chi_{\mathbf{R}'L's'}^{\text{orth}} \rangle \langle \chi_{\mathbf{R}''L''s''}^{\text{orth}} | \mathbf{r}_2 s_2 \rangle \\ & \times \int_{E_B}^{E_F} \mathcal{D}_{\mathbf{R}'L's', \mathbf{R}''L''s''}(E) dE, \end{aligned} \quad (24)$$

where the energy integration is performed between the bottom of the valence band E_B and the Fermi energy E_F .

Let us now evaluate the $\rho_{s_1 s_2}(\mathbf{r}_1, \mathbf{r}_2)$ by means of the phi and phi-dot orbitals up to terms linear in the phi-dot orbitals, i.e., in accuracy consistent with equation (10). The procedure starts by substitution of equation (12) into (24). The next step employs the identity $(E - H^{\text{orth}})\mathcal{D}(E) = 0$ and equation (17) to express $h\mathcal{D}(E) = (E - \underline{E}_\nu)\mathcal{D}(E)$ [and similarly for $\mathcal{D}(E)h$]. In displaying the final formula we assume that the vectors \mathbf{r}_1 and \mathbf{r}_2 lie inside the atomic spheres \mathbf{R}_1 and \mathbf{R}_2 , respectively, and we employ the trivial spin-dependence of the phi and phi-dot orbitals (9):

$$\begin{aligned} \rho_{\mathbf{R}_1 s_1, \mathbf{R}_2 s_2}(\mathbf{r}_1, \mathbf{r}_2) = & \\ = & \sum_{L'L''} \langle \mathbf{r}_1 | \phi_{\mathbf{R}_1 L' s_1} \rangle \langle \phi_{\mathbf{R}_2 L'' s_2} | \mathbf{r}_2 \rangle \int_{E_B}^{E_F} \mathcal{D}_{\mathbf{R}_1 L' s_1, \mathbf{R}_2 L'' s_2}(E) dE \\ & + \sum_{L'L''} \langle \mathbf{r}_1 | \dot{\phi}_{\mathbf{R}_1 L' s_1} \rangle \langle \phi_{\mathbf{R}_2 L'' s_2} | \mathbf{r}_2 \rangle \int_{E_B}^{E_F} [(E - \underline{E}_\nu)\mathcal{D}(E)]_{\mathbf{R}_1 L' s_1, \mathbf{R}_2 L'' s_2} dE \\ & + \sum_{L'L''} \langle \mathbf{r}_1 | \phi_{\mathbf{R}_1 L' s_1} \rangle \langle \dot{\phi}_{\mathbf{R}_2 L'' s_2} | \mathbf{r}_2 \rangle \int_{E_B}^{E_F} [\mathcal{D}(E)(E - \underline{E}_\nu)]_{\mathbf{R}_1 L' s_1, \mathbf{R}_2 L'' s_2} dE. \end{aligned} \quad (25)$$

Since the matrix \underline{E}_ν is site-diagonal, evaluation of quantum-mechanical averages of operators local in the real space requires only site-diagonal elements of the resolvent or the spectral density matrix, i.e., $G_{\mathbf{R}Ls, \mathbf{R}L's'}(z)$ or $\mathcal{D}_{\mathbf{R}Ls, \mathbf{R}L's'}(E)$.

This can be illustrated, e.g., by the local $\mathbf{R}Ls$ -resolved densities of states (DOS)

$n_{\mathbf{R}Ls}(E)$ that are equal to

$$n_{\mathbf{R}Ls}(E) = \mathcal{D}_{\mathbf{R}Ls, \mathbf{R}Ls}(E) = -\frac{1}{\pi} \Im G_{\mathbf{R}Ls, \mathbf{R}Ls}(E + i0). \quad (26)$$

Another application of equation (25) concerns the valence spin-resolved electron density $\varrho_{\mathbf{R}s}(\mathbf{r}) = \rho_{\mathbf{R}s, \mathbf{R}s}(\mathbf{r}, \mathbf{r})$ for vectors \mathbf{r} inside the \mathbf{R} -th atomic sphere:

$$\begin{aligned} \varrho_{\mathbf{R}s}(\mathbf{r}) &= \sum_{L'L''} \langle \mathbf{r} | \phi_{\mathbf{R}L's} \rangle \langle \phi_{\mathbf{R}L''s} | \mathbf{r} \rangle \int_{E_B}^{E_F} \mathcal{D}_{\mathbf{R}L's, \mathbf{R}L''s}(E) dE \\ &+ \sum_{L'L''} \langle \mathbf{r} | \dot{\phi}_{\mathbf{R}L's} \rangle \langle \dot{\phi}_{\mathbf{R}L''s} | \mathbf{r} \rangle \int_{E_B}^{E_F} [(E - \underline{E}_\nu) \mathcal{D}(E)]_{\mathbf{R}L's, \mathbf{R}L''s} dE \\ &+ \sum_{L'L''} \langle \mathbf{r} | \phi_{\mathbf{R}L's} \rangle \langle \dot{\phi}_{\mathbf{R}L''s} | \mathbf{r} \rangle \int_{E_B}^{E_F} [\mathcal{D}(E)(E - \underline{E}_\nu)]_{\mathbf{R}L's, \mathbf{R}L''s} dE. \end{aligned} \quad (27)$$

The Ls -resolved valence charges inside the \mathbf{R} -th sphere are obtained by integration of equation (27) over the sphere volume:

$$Q_{\mathbf{R}Ls} = \int_{E_B}^{E_F} \mathcal{D}_{\mathbf{R}Ls, \mathbf{R}Ls}(E) dE = \frac{1}{2\pi i} \oint_C G_{\mathbf{R}Ls, \mathbf{R}Ls}(z) dz, \quad (28)$$

where C denotes the usual closed complex contour around the occupied part of the valence band [3, chap. 10]. The z -component of the local spin magnetic moment (in units of the Bohr magneton μ_B) is equal to $M_{\mathbf{R}}^{\text{spin}, z} = \sum_L (Q_{\mathbf{R}L\uparrow} - Q_{\mathbf{R}L\downarrow})$, while the z -component of the local orbital magnetic moment (in μ_B) is given by

$$\begin{aligned} M_{\mathbf{R}}^{\text{orb}, z} &= \int_{E_B}^{E_F} \sum_{LL's} \langle L' | L_z | L \rangle \mathcal{D}_{\mathbf{R}Ls, \mathbf{R}L's}(E) dE \\ &= \frac{1}{2\pi i} \oint_C \sum_{LL's} \langle L' | L_z | L \rangle G_{\mathbf{R}Ls, \mathbf{R}L's}(z) dz. \end{aligned} \quad (29)$$

The sums in equation (29) contain terms with $\ell = \ell'$ and $m \neq m'$ due to the use of real spherical harmonics, see text below equation (9).

The charge and spin selfconsistency within the ASA is based on the spherically symmetric part $\tilde{\varrho}_{\mathbf{R}s}(r)$ of the valence spin-resolved electron density $\varrho_{\mathbf{R}s}(\mathbf{r})$ (27). In full analogy to the SRA [3, chap. 5], the final form of $\tilde{\varrho}_{\mathbf{R}s}(r)$ involves radial amplitudes $g_{\mathbf{R}\ell s}(r)$ and $\dot{g}_{\mathbf{R}\ell s}(r)$ of the orbitals $|\phi_{\mathbf{R}Ls}\rangle$ and $|\dot{\phi}_{\mathbf{R}Ls}\rangle$:

$$\tilde{\varrho}_{\mathbf{R}s}(r) = \frac{1}{4\pi} \sum_{\ell} \left[m_{\mathbf{R}\ell s}^{(0)} g_{\mathbf{R}\ell s}^2(r) + m_{\mathbf{R}\ell s}^{(1)} g_{\mathbf{R}\ell s}(r) \dot{g}_{\mathbf{R}\ell s}(r) \right]. \quad (30)$$

Here the energy moments $m_{\mathbf{R}\ell s}^{(0)}$ and $m_{\mathbf{R}\ell s}^{(1)}$ can be formulated as real or complex energy integrals, namely,

$$m_{\mathbf{R}\ell s}^{(0)} = \int_{E_B}^{E_F} \sum_{m=-\ell}^{\ell} \mathcal{D}_{\mathbf{R}Ls, \mathbf{R}Ls}(E) dE = \frac{1}{2\pi i} \oint_C \sum_{m=-\ell}^{\ell} G_{\mathbf{R}Ls, \mathbf{R}Ls}(z) dz, \quad (31)$$

and

$$\begin{aligned}
 m_{\mathbf{R}Ls}^{(1)} &= \int_{E_B}^{E_F} \sum_{m=-\ell}^{\ell} [(E - \underline{E}_\nu)\mathcal{D}(E) + \mathcal{D}(E)(E - \underline{E}_\nu)]_{\mathbf{R}Ls, \mathbf{R}Ls} dE \\
 &= \frac{1}{2\pi i} \oint_C \sum_{m=-\ell}^{\ell} [(z - \underline{E}_\nu)G(z) + G(z)(z - \underline{E}_\nu)]_{\mathbf{R}Ls, \mathbf{R}Ls} dz. \quad (32)
 \end{aligned}$$

The core contribution to the electron density is constructed from all components of the bispinor $\Psi(\mathbf{r})$ and it is based on a numerical solution of coupled radial Dirac equations [see 3, 4, and references therein].

3. Applications

3.1. Numerical implementation

Numerical implementation of the above formalism is similar to the original SRA technique [3, chap. 10] as well as to the TB-LMTO techniques appropriate for the KSD Hamiltonian in the non-magnetic [10] and magnetic [11] cases. The local spin-dependent exchange-correlation potential was parametrized according to Ref. [12], the valence basis set comprised *spd*-orbitals for transition-metal systems while *spdf*-orbitals were included in the case of plutonium. The energy E_0 in the $\omega(\mathbf{r})$ (5) was kept in the middle of the occupied valence spectrum and energy integrals were performed using 14 nodes along a semicircle complex contour. The Brillouin-zone (BZ) integrals were calculated by means of a homogeneous \mathbf{k} -mesh corresponding to more than 5×10^4 sampling points in the full BZ.

3.2. Non-magnetic systems

Results of various approaches are compared in Fig. 1 for species-resolved DOS of a random face-centered cubic (fcc) $\text{Cu}_{0.75}\text{Au}_{0.25}$ alloy treated in the CPA. One can see that the Cu DOS is very little influenced by the SO interaction in contrast to the Au DOS which exhibits a single broad peak at energy about 0.45 Ry below the E_F in the SRA (top panel of Fig. 1a) that becomes strongly modified by the SO coupling. The SO-split Au DOS is practically identical in the simple theory based on equation (17) (bottom panel of Fig. 1a) and in the full KSD theory (Fig. 1b) [3, chap. 7]. Similar degree of agreement of both approaches (not shown here) was obtained for the Bloch spectral functions of the random $\text{Cu}_{0.75}\text{Au}_{0.25}$ alloy as well as for the band structure of pure fcc Au.

3.3. Spin-polarized systems

The calculated spin and orbital magnetic moments in ferromagnetic 3d transition metals (Fe, Co, Ni) and their two random alloys ($\text{Co}_{0.5}\text{Ni}_{0.5}$, $\text{Co}_{0.5}\text{Pt}_{0.5}$) are summarized in Table 1. The values obtained by the present approach agree reasonably well with those of the fully relativistic TB-LMTO method [11]; minor differences are seen for the orbital moments in the Co-Pt case, most probably due to a heavy element (Pt) in the alloy. However, the profiles of spin-polarized DOS calculated by both approaches exhibit very good agreement with each other, as follows from comparison of Fig. 2a and [11, fig. 3 and 4].

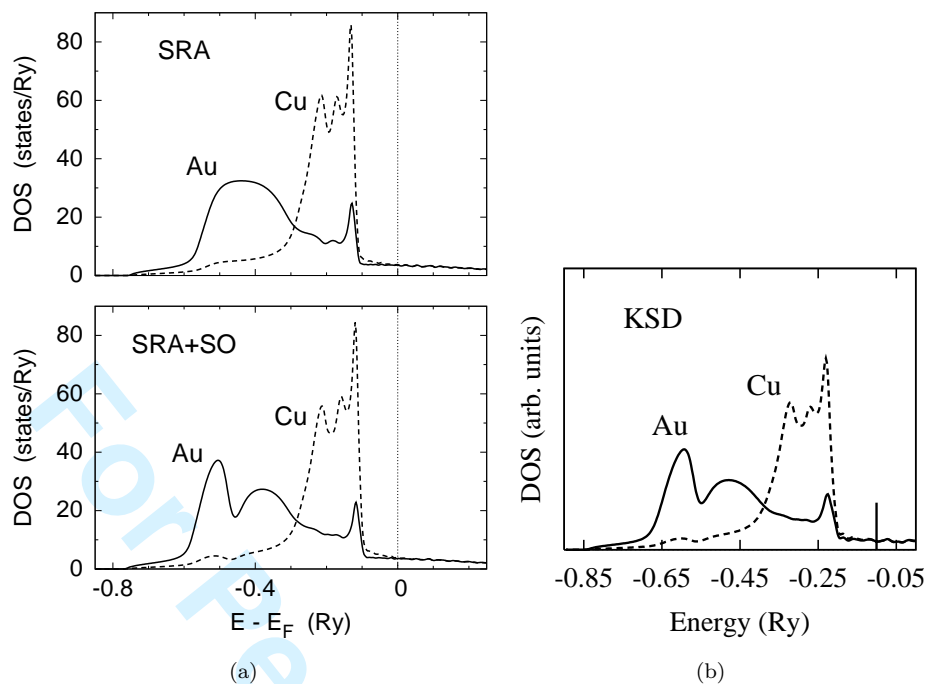


Figure 1. Calculated local DOS in a random fcc $\text{Cu}_{0.75}\text{Au}_{0.25}$ alloy: (a) in the SRA (13) (top) and in the SRA with inclusion of SO interaction (17) (bottom); (b) based on the KSD Hamiltonian.

Table 1. Calculated local spin and orbital magnetic moments in selected itinerant ferromagnets.

system	element	$M^{\text{spin},z} (\mu_B)$	$M^{\text{orb},z} (\mu_B)$
bcc Fe	Fe	2.23 ^a , 2.23 ^b	0.036 ^a , 0.043 ^b
fcc Co	Co	1.65 ^a , 1.63 ^b	0.067 ^a , 0.069 ^b
fcc Ni	Ni	0.65 ^a , 0.64 ^b	0.047 ^a , 0.049 ^b
fcc $\text{Co}_{0.5}\text{Ni}_{0.5}$	Co	1.66 ^a , 1.63 ^b	0.067 ^a , 0.066 ^b
fcc $\text{Co}_{0.5}\text{Ni}_{0.5}$	Ni	0.67 ^a , 0.65 ^b	0.043 ^a , 0.045 ^b
fcc $\text{Co}_{0.5}\text{Pt}_{0.5}$	Co	1.88 ^a , 1.86 ^b	0.080 ^a , 0.052 ^b
fcc $\text{Co}_{0.5}\text{Pt}_{0.5}$	Pt	0.32 ^a , 0.34 ^b	0.058 ^a , 0.080 ^b
fcc Pu	Pu	4.51 ^a , 4.5 ^c	-2.23 ^a , -2.4 ^c

^aPresent work, the SRA+SO Hamiltonian (17).

^bRef. [11], the KSD Hamiltonian.

^cRef. [13], the KSD Hamiltonian.

The most stringent test of reliability of the developed approximate scheme requires a system with strong exchange and SO splittings. For this reason we have chosen fcc plutonium (δ Pu) in its experimental equilibrium volume and in a hypothetical ferromagnetic state, and treated it using the standard local spin-density approximation as done in Ref. [13]. Comparison of the resulting magnetic moments (Table 1) and of the spin-polarized DOS (Fig. 2b and [13, fig. 8]) indicates that the simple LMTO Hamiltonian (17) describes successfully a substantial part of the combined effect of spin polarization and SO coupling in this actinide system.

4. Conclusions

The developed approach represents a conceptually easy way of treating the spin-orbit interaction within an existing formalism of the all-electron scalar-relativistic TB-LMTO method. More tests are desirable in order to assess limits of its validity;

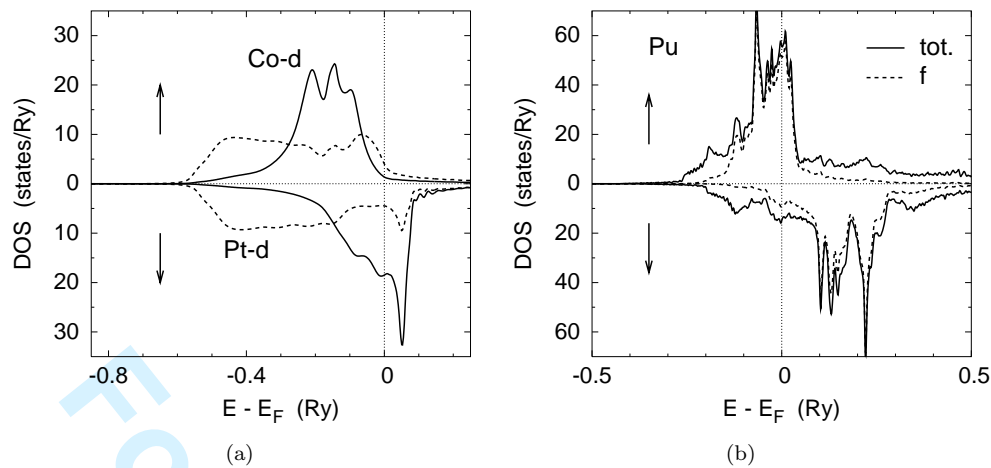


Figure 2. Calculated spin-polarized DOS in the SRA with inclusion of SO interaction (17): (a) local d -orbital DOS in a random fcc $\text{Co}_{0.5}\text{Pt}_{0.5}$ alloy; (b) total and f -orbital DOS in fcc Pu.

the first results reported here show that the range of reliability includes (but need not be confined to) $3d$ transition-metal based non-magnetic and magnetic materials. One can thus expect that the described technique will be useful especially in cases with weak or moderate spin-orbit coupling as encountered, e.g., in systems with potential applicability in spintronics [2].

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References

- [1] J. Banhart and H. Ebert, *Europhys. Lett.* 32 (1995), p. 517.
- [2] P. Mavropoulos et al., *Phys. Rev. B* 69 (2004), p. 054424.
- [3] I. Turek et al. *Electronic Structure of Disordered Alloys, Surfaces and Interfaces*, Kluwer, Boston, 1997.
- [4] J. Zabloudil et al. *Electron Scattering in Solid Matter*, Springer, Berlin, 2005.
- [5] O.K. Andersen and O. Jepsen, *Phys. Rev. Lett.* 53 (1984), p. 2571.
- [6] A.H. MacDonald and S.H. Vosko, *J. Phys. C: Solid State Phys.* 12 (1979), p. 2977.
- [7] D.D. Koelling and B.N. Harmon, *J. Phys. C: Solid State Phys.* 10 (1977), p. 3107.
- [8] O.K. Andersen, *Phys. Rev. B* 12 (1975), p. 3060.
- [9] I. Turek, J. Kudrnovský, and V. Drchal, in *Electronic Structure and Physical Properties of Solids*, H. Dreyssé ed., Vol. 535 of *Lecture Notes in Physics*, Springer, Berlin, 2000, p. 349.
- [10] V. Drchal, J. Kudrnovský, and P. Weinberger, *Phys. Rev. B* 50 (1994), p. 7903.
- [11] A.B. Shick et al., *Phys. Rev. B* 54 (1996), p. 1610.
- [12] S.H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* 58 (1980), p. 1200.
- [13] I.V. Solovyev et al., *Phys. Rev. B* 43 (1991), p. 14414.