

Introduction to noncollinear magnetism and spin-orbit coupling in QUANTUM-ESPRESSO

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Relativity: quantitative effects

The relevance of relativistic effects on the electronic structure, can be estimated by the following argument [1]. The mass m_v of an electron with velocity v is:

$$m_v = \frac{m}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}$$

where m is the rest mass. Hence the Bohr radius $a_0 = \frac{\hbar^2}{m_v e^2}$ is reduced. In a.u., the electron velocity in an hydrogenic atom is $v = Z$. Since $c = 137$, taking for instance $Z = 80$, $v/c = 0.58$ and a_0 is 23% shorter. As a consequence, s and p orbitals shrink while d and f orbitals expand due to the better screening of the nuclear charge by the electrons in the s and p orbitals.

Relativity: qualitative effects

- A) Electronic states are spinors. The symmetry of the electronic states is described by the double group.
- B) Spin-orbit coupling usually split states that are degenerate in a nonrelativistic description.
- C) In magnetic systems, the electronic states and the energy depend on the direction of the magnetization with respect to the ionic positions.

The Dirac equation - I

The starting point for the relativistic description of a one-electron system is the Dirac equation [2]:

$$i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = \left(c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2 \right) \Psi(\mathbf{r}, t),$$

where c is the speed of light, m is the electron mass and $\boldsymbol{\alpha}$ and β are 4×4 matrices. The form of $\boldsymbol{\alpha}$ and β is not unique. In terms of the Pauli matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

they can be written as:

$$\alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} \mathbf{1} & 0 \\ 0 & -\mathbf{1} \end{pmatrix},$$

The Dirac equation - II

The solutions of the Dirac equation are four-component spinors:

$$\Psi(\mathbf{r}, t) = \begin{pmatrix} \Psi_1(\mathbf{r}, t) \\ \Psi_2(\mathbf{r}, t) \\ \Psi_3(\mathbf{r}, t) \\ \Psi_4(\mathbf{r}, t) \end{pmatrix} = \begin{pmatrix} \Psi_A(\mathbf{r}, t) \\ \Psi_B(\mathbf{r}, t) \end{pmatrix},$$

where $\Psi_A(\mathbf{r}, t)$ and $\Psi_B(\mathbf{r}, t)$ are two-component spinors.

The Dirac equation - III

The interaction of the electron with an electromagnetic field, described by the scalar and vector potentials $\phi(\mathbf{r})$ and $\mathbf{A}(\mathbf{r})$, can be accounted for by the usual substitution $\mathbf{p} \rightarrow \mathbf{p} - q\mathbf{A}(\mathbf{r})$ and $E \rightarrow E - q\phi(\mathbf{r})$. In terms of two-component spinors $\psi_A(\mathbf{r})$ and $\psi_B(\mathbf{r})$ we have:

$$i\hbar \frac{\partial \Psi_A(\mathbf{r}, t)}{\partial t} = c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \Psi_B(\mathbf{r}, t) + \left(mc^2 + q\phi(\mathbf{r}) \right) \Psi_A(\mathbf{r}, t),$$
$$i\hbar \frac{\partial \Psi_B(\mathbf{r}, t)}{\partial t} = c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \Psi_A(\mathbf{r}, t) - \left(mc^2 - q\phi(\mathbf{r}) \right) \Psi_B(\mathbf{r}, t),$$

where $\boldsymbol{\pi} = \mathbf{p} - q\mathbf{A}(\mathbf{r})$, and q is the electron charge (a negative number).

The time independent Dirac equation

When $\phi(\mathbf{r})$ and $\mathbf{A}(\mathbf{r})$ are time independent we can search the solution in the form $\Psi(\mathbf{r}, t) = e^{-\frac{iEt}{\hbar}} \Psi(\mathbf{r})$ and we get:

$$c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \Psi_B(\mathbf{r}) + \left(mc^2 + q\phi(\mathbf{r}) - E \right) \Psi_A(\mathbf{r}) = 0$$
$$c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \Psi_A(\mathbf{r}) - \left(E + mc^2 - q\phi(\mathbf{r}) \right) \Psi_B(\mathbf{r}) = 0.$$

Small v/c limit of the Dirac equation - I

By setting $E' = E - mc^2$, we can write the second equation in the form:

$$\Psi_B(\mathbf{r}) = \frac{c\boldsymbol{\sigma} \cdot \boldsymbol{\pi}\Psi_A(\mathbf{r})}{E' + 2mc^2 - q\phi(\mathbf{r})} \approx \frac{1}{2mc} \boldsymbol{\sigma} \cdot \boldsymbol{\pi}\Psi_A(\mathbf{r}),$$

where we expanded the denominator in a Taylor series of $\frac{E' - q\phi(\mathbf{r})}{2mc^2}$ and neglected the terms of order $(v/c)^2$. $\Psi_B(\mathbf{r})$ is of order v/c $\Psi_A(\mathbf{r})$. The latter is called the large component while the former is called the small component. Inserting this expression of $\Psi_B(\mathbf{r})$ in the equation for $\Psi_A(\mathbf{r})$, we obtain the Pauli equation $[H_{Pauli} - E']\psi_A(\mathbf{r}) = 0$:

$$\left[\frac{1}{2m} (\boldsymbol{\sigma} \cdot \boldsymbol{\pi})(\boldsymbol{\sigma} \cdot \boldsymbol{\pi}) + q\phi(\mathbf{r}) - E' \right] \Psi_A(\mathbf{r}) = 0.$$

Small v/c limit of the Dirac equation - II

Using the relationship:

$$(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})(\boldsymbol{\sigma} \cdot \boldsymbol{\pi}) = \pi^2 - \hbar q \boldsymbol{\sigma} \cdot \nabla \times \mathbf{A}(\mathbf{r}),$$

we can rewrite the Pauli equation as:

$$\left[\frac{\pi^2}{2m} - \frac{\hbar q}{2m} \boldsymbol{\sigma} \cdot \mathbf{B}(\mathbf{r}) + q\phi(\mathbf{r}) - E' \right] \Psi_A(\mathbf{r}) = 0.$$

This equation shows that the electron, in addition to the magnetic moment due to its orbital motion, has a magnetic moment due to its spin angular momentum equal to $\mu_B \boldsymbol{\sigma}$ where $\mu_B = \frac{\hbar q}{2m}$ is the Bohr magneton.

Small v/c limit of the Dirac equation - III

Keeping the terms up to order $(v/c)^2$ in the Taylor series, we obtain the equation $H\tilde{\Psi} = E\tilde{\Psi}$ for a two-component spinor $\tilde{\Psi}$, where the Hamiltonian is [3]:

$$\begin{aligned} H &= H_{Pauli} \\ &- \frac{p^4}{8m^3c^2} && \text{mass - velocity} \\ &+ \frac{\hbar^2 \mathbf{q}}{8m^2c^2} \nabla \cdot \nabla \phi(\mathbf{r}) && \text{Darwin} \\ &- \frac{\hbar \mathbf{q}}{4m^2c^2} \boldsymbol{\sigma} \cdot [\boldsymbol{\pi} \times \nabla \phi(\mathbf{r})] && \text{spin - orbit} \end{aligned}$$

Dirac equation for a spherically symmetric potential

We need also the following result. Let's consider the Dirac equation for an electron in a spherically symmetric potential:

$$H\Psi = \left[c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2 + q\phi(|\mathbf{r}|) \right] \Psi(\mathbf{r}) = E\Psi(\mathbf{r}).$$

One can show that:

$$[H, \mathbf{L}] \neq 0 \quad [H, \mathbf{S}] \neq 0$$

$$[H, \mathbf{J}] = 0 \quad \mathbf{J} = \mathbf{L} + \mathbf{S},$$

where \mathbf{L} is the orbital angular momentum, \mathbf{S} is the spin angular momentum and \mathbf{J} is the total angular momentum.

The spin-angle functions

The spin-angle functions are two-component spinors eigenstates of the total angular momentum:

$$J^2 Y_{\ell,1/2}^{j,m_j}(\Omega, \sigma) = \hbar^2 j(j+1) Y_{\ell,1/2}^{j,m_j}(\Omega, \sigma),$$

$$J_z Y_{\ell,1/2}^{j,m_j}(\Omega, \sigma) = \hbar m_j Y_{\ell,1/2}^{j,m_j}(\Omega, \sigma).$$

The solutions of the Dirac equation with a spherically symmetric potential can be written in terms of spin-angle functions:

$$\Psi(\mathbf{r}) = \frac{1}{r} \begin{pmatrix} P(r) Y_{\ell,1/2}^{j,m_j}(\Omega, \sigma) \\ iQ(r) Y_{\ell',1/2}^{j,m_j}(\Omega, \sigma) \end{pmatrix}.$$

Many-body Hamiltonian for electrons with spin

An approximate Hamiltonian for a system of interacting electrons with spin in an electromagnetic field can be written as [4]:

$$H = \sum_i \left[\frac{\pi_i^2}{2m} - \mu_B \boldsymbol{\sigma}_i \cdot \mathbf{B}(\mathbf{r}_i) + q\phi(\mathbf{r}_i) \right] + \frac{1}{2} \sum_{ij} \frac{q^2}{|\mathbf{r}_i - \mathbf{r}_j|}.$$

Before formulating density functional theory starting from this Hamiltonian, we make a further simplification. We set $\pi_i = \mathbf{p}_i$ neglecting the coupling of the electron orbital momentum with the magnetic field. Note that this Hamiltonian can be written by introducing a 2×2 matrix as an external one-body potential:

The spin-density as a basic variable

$$V_{ext}^{\sigma,\sigma'}(\mathbf{r}) = \begin{pmatrix} q\phi(\mathbf{r}) - \mu_B B_z(\mathbf{r}), & -\mu_B (B_x(\mathbf{r}) - iB_y(\mathbf{r})) \\ -\mu_B (B_x(\mathbf{r}) + iB_y(\mathbf{r})), & q\phi(\mathbf{r}) + \mu_B B_z(\mathbf{r}) \end{pmatrix}.$$

The basic variable is the spin-density and one can show that the ground state energy of the many-body Hamiltonian is a functional of the spin-density:

$$n(\mathbf{r}, \sigma, \sigma') = N \sum_{\sigma_2, \sigma_3, \dots, \sigma_N} \int d^3r_2 \cdots d^3r_N \Psi^*(\mathbf{r}, \sigma, \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_N, \sigma_N) \\ \times \Psi(\mathbf{r}, \sigma', \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_N, \sigma_N).$$

Unfortunately, in this case $V_{ext}^{\sigma,\sigma'}(\mathbf{r})$ is not uniquely determined by the spin-density.

The total energy - I

As in the standard Kohn and Sham formulation, one can introduce an auxiliary system: a gas of non interacting electrons with spin that has the same spin-density of the many-body system. The wavefunctions of this system are Slater determinants of two-component spinors ($\Psi_i(\mathbf{r}, \sigma)$) one-electron wavefunctions. The spin-density of this system is:

$$n(\mathbf{r}, \sigma, \sigma') = \sum_i \Psi_i^*(\mathbf{r}, \sigma) \Psi_i(\mathbf{r}, \sigma').$$

The kinetic energy (using from now on atomic units) is:

$$T_0 = \sum_{i,\sigma} \langle \Psi_{i,\sigma} | -\frac{1}{2} \nabla^2 | \Psi_{i,\sigma} \rangle.$$

The total energy - II

The energy due to the interaction between the electrons and the external potential is:

$$E_{ext} = \sum_{\sigma, \sigma'} \int d^3r V_{ext}^{\sigma, \sigma'}(\mathbf{r}) n(\mathbf{r}, \sigma, \sigma').$$

The Coulomb energy can be written in terms of the charge density:

$$n(\mathbf{r}) = \sum_{i, \sigma} \Psi_i^*(\mathbf{r}, \sigma) \Psi_i(\mathbf{r}, \sigma) = \sum_{\sigma} n(\mathbf{r}, \sigma, \sigma).$$

$$E_H = \frac{1}{2} \int d^3r \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.$$

The total energy - III

The unknown part of the total energy functional is the exchange and correlation energy:

$$E_{tot} = T_0 + E_{ext} + E_H + E_{xc} [n(\mathbf{r}, \sigma, \sigma')].$$

In the local spin density approximation the exchange and correlation energy depends on the density and on the modulus of the magnetization density. We use here the same functional $E_{xc} [n, |m|]$. The noncollinear magnetization density of the non-interacting electron gas can be written as:

$$\mathbf{m}(\mathbf{r}) = \mu_B \sum_{i, \sigma_1, \sigma_2} \Psi_i^*(\mathbf{r}, \sigma_1) \boldsymbol{\sigma}^{\sigma_1, \sigma_2} \Psi_i(\mathbf{r}, \sigma_2) = \mu_B \sum_{\sigma_1, \sigma_2} \boldsymbol{\sigma}^{\sigma_1, \sigma_2} n(\mathbf{r}, \sigma_1, \sigma_2)$$

The magnetization density

It is useful to write explicitly the three components of the magnetization density:

$$\mathbf{m}_x(\mathbf{r}) = \mu_B \sum_i \left[\Psi_i^*(\mathbf{r}, \uparrow) \Psi_i(\mathbf{r}, \downarrow) + \Psi_i^*(\mathbf{r}, \downarrow) \Psi_i(\mathbf{r}, \uparrow) \right]$$

$$\mathbf{m}_y(\mathbf{r}) = -i\mu_B \sum_i \left[\Psi_i^*(\mathbf{r}, \uparrow) \Psi_i(\mathbf{r}, \downarrow) - \Psi_i^*(\mathbf{r}, \downarrow) \Psi_i(\mathbf{r}, \uparrow) \right]$$

$$\mathbf{m}_z(\mathbf{r}) = \mu_B \sum_i \left[|\Psi_i(\mathbf{r}, \uparrow)|^2 - |\Psi_i(\mathbf{r}, \downarrow)|^2 \right]$$

The Kohn and Sham equations - I

Minimizing the total energy functional, keeping into account the orthogonality constraint of the one-electron wavefunctions:

$$\sum_{\sigma} \langle \Psi_{i,\sigma} | \Psi_{j,\sigma} \rangle = \delta_{ij},$$

we obtain the equation:

$$\frac{\partial E_{tot}}{\partial \Psi_i^*(\mathbf{r}, \sigma)} = \varepsilon_i \Psi_i(\mathbf{r}, \sigma),$$

or:

$$\begin{aligned} & - \frac{1}{2} \nabla^2 \Psi_i(\mathbf{r}, \sigma) + \sum_{\sigma'} V_{ext}^{\sigma, \sigma'}(\mathbf{r}) \Psi_i(\mathbf{r}, \sigma') + V_H(\mathbf{r}) \Psi_i(\mathbf{r}, \sigma) \\ & + \frac{\partial E_{xc}}{\partial n} \Psi_i(\mathbf{r}, \sigma) + \mu_B \sum_{\alpha, \sigma'} \frac{\partial E_{xc}}{\partial m_{\alpha}} \sigma_{\alpha}^{\sigma, \sigma'} \Psi_i(\mathbf{r}, \sigma') = \varepsilon_i \Psi_i(\mathbf{r}, \sigma). \end{aligned}$$

The Kohn and Sham equations - II

In order to shorten the notation, we can define the exchange and correlation potential (V_{XC}) and magnetic field (B_{XC}) as

$$V_{XC}(\mathbf{r}) = \frac{\partial E_{XC}}{\partial n} \quad \text{and} \quad B_{XC,\alpha}(\mathbf{r}) = -\frac{\partial E_{XC}}{\partial m_\alpha} = -\frac{\partial E_{XC}}{\partial |m|} \frac{m_\alpha}{|m|},$$

and define a spin dependent self-consistent local potential

$$V_{LOC}^{\sigma,\sigma'}(\mathbf{r}) = V_{ext}^{\sigma,\sigma'}(\mathbf{r}) + [V_H(\mathbf{r}) + V_{XC}(\mathbf{r})] \delta^{\sigma,\sigma'} - \mu_B \sum_{\alpha} B_{XC,\alpha}(\mathbf{r}) \sigma_{\alpha}^{\sigma,\sigma'},$$

obtaining the equation:

$$\sum_{\sigma'} \left[-\frac{1}{2} \nabla^2 \delta^{\sigma,\sigma'} + V_{LOC}^{\sigma,\sigma'}(\mathbf{r}) \right] \Psi_i(\mathbf{r}, \sigma') = \varepsilon_i \Psi_i(\mathbf{r}, \sigma).$$

The LSDA approximation revisited - I

In the LSDA, the orientation of the spin of each electron is along a fixed direction taken as the z axis. We have electrons with spin up and electrons with spin down. Their spinors are:

$$\psi_i(\mathbf{r}) = \begin{pmatrix} \Psi_i(\mathbf{r}, \uparrow) \\ 0 \end{pmatrix}, \quad \psi_j(\mathbf{r}) = \begin{pmatrix} 0 \\ \Psi_j(\mathbf{r}, \downarrow) \end{pmatrix}.$$

Computing the magnetization density, we find $m_x = m_y = 0$, and

$$m_z(\mathbf{r}) = \mu_B \left[\sum_i^{N_\uparrow} |\Psi_i(\mathbf{r}, \uparrow)|^2 - \sum_i^{N_\downarrow} |\Psi_i(\mathbf{r}, \downarrow)|^2 \right],$$

where N_\uparrow and N_\downarrow are the number of electrons with spin up and spin down, respectively. From the definition of \mathbf{B}_{xc} we find also $B_{xc,x} = 0$, $B_{xc,y} = 0$.

The LSDA approximation revisited - II

Note that now $\Psi_i(\mathbf{r}, \uparrow)$ and $\Psi_i(\mathbf{r}, \downarrow)$ are two different wave functions, not the two components of the same spinor. Calling them $\psi_{i,\uparrow}(\mathbf{r})$ and $\psi_{i,\downarrow}(\mathbf{r})$, we have the equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) - \mu_B B_{xc,z}(\mathbf{r}) \right] \psi_{i,\uparrow}(\mathbf{r}) = \varepsilon_{i,\uparrow} \psi_{i,\uparrow}(\mathbf{r})$$

for electrons with spin up and the equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) + \mu_B B_{xc,z}(\mathbf{r}) \right] \psi_{i,\downarrow}(\mathbf{r}) = \varepsilon_{i,\downarrow} \psi_{i,\downarrow}(\mathbf{r})$$

for electrons with spin down.

The LSDA approximation revisited - III

Within LSDA:

$$n(\mathbf{r}) = n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r}), \quad m_z(\mathbf{r}) = \mu_B (n_{\uparrow}(\mathbf{r}) - n_{\downarrow}(\mathbf{r}))$$

or, equivalently:

$$n_{\uparrow}(\mathbf{r}) = \frac{1}{2} \left(n(\mathbf{r}) + \frac{m_z(\mathbf{r})}{\mu_B} \right), \quad n_{\downarrow}(\mathbf{r}) = \frac{1}{2} \left(n(\mathbf{r}) - \frac{m_z(\mathbf{r})}{\mu_B} \right).$$

Therefore we have:

$$V_{xc}(\mathbf{r}) - \mu_B \mathbf{B}_{xc,z}(\mathbf{r}) = \frac{\partial E_{xc}}{\partial n_{\uparrow}}, \quad V_{xc}(\mathbf{r}) + \mu_B \mathbf{B}_{xc,z}(\mathbf{r}) = \frac{\partial E_{xc}}{\partial n_{\downarrow}},$$

and the two previous equations coincide with those of LSDA.

Towards real materials

In order to apply the above formalism to a real material we use, as external potential, a pseudo-potential. Usually, no external magnetic field is applied and $V_{ext}^{\sigma,\sigma'}$ is diagonal in the spin indexes. One applies to both spin components a pseudo-potential which has a local part $V_{loc}(\mathbf{r})$ and a nonlocal part. The nonlocal part can be written by introducing projectors on the orbital angular momentum channels about each atom:

$$V_{NL} = \sum_I \sum_{\ell, m_\ell} E'_\ell |\beta'_\ell Y'_{\ell, m_\ell}\rangle \langle \beta'_\ell Y'_{\ell, m_\ell}|$$

This pseudopotential can be constructed keeping into account scalar relativistic effects, but not the spin-orbit coupling.

Real materials with spin-orbit coupling - I

If the pseudopotential is generated starting from the large components of the solutions of the Dirac equation, we obtain projectors ($\beta_{\ell,j}$) and pseudopotential coefficients $E_{\ell,j}$ for each value of ℓ and j , the orbital and the total angular momentum. To project into states of well defined total angular momentum, we need the spin-angle functions:

$$V_{NL} = \sum_l \sum_{\ell,j,m_j} E_{\ell,j}^l |\beta_{\ell,j}^l Y_{\ell,1/2}^{l,j,m_j}\rangle \langle \beta_{\ell,j}^l Y_{\ell,1/2}^{l,j,m_j}|.$$

Therefore V_{NL} is a 2×2 matrix in the spin indexes. This pseudopotential includes both scalar relativistic and spin-orbit coupling effects. (Note that it is correct at order $1/c^2$ not only at order $(v/c)^2$ as the Taylor expansion seen before).

Real materials with spin-orbit coupling - II

The spin angle functions are:

$$Y_{\ell,1/2}^{j,m_j} = \begin{pmatrix} \left(\frac{\ell+m+1}{2\ell+1}\right)^{1/2} Y_{\ell,m} \\ \left(\frac{\ell-m}{2\ell+1}\right)^{1/2} Y_{\ell,m+1} \end{pmatrix}, \quad Y_{\ell,1/2}^{j,m_j} = \begin{pmatrix} \left(\frac{\ell-m+1}{2\ell+1}\right)^{1/2} Y_{\ell,m-1} \\ -\left(\frac{\ell+m}{2\ell+1}\right)^{1/2} Y_{\ell,m} \end{pmatrix},$$

for $j = \ell + 1/2$ and $j = \ell - 1/2$ respectively. In the first case $m = m_j - 1/2$ while, in the second, $m = m_j + 1/2$. We can introduce the Clebsch-Gordan coefficients $\alpha_{m_j}^{\sigma,\ell,j}$, a unitary matrix $U_{m_j,m'}^{\sigma,\ell,j}$ which selects the appropriate spherical harmonic and to summarize the above relationships by:

$$Y_{\ell,1/2}^{j,m_j,\sigma} = \alpha_{m_j}^{\sigma,\ell,j} \sum_{m'=-\ell}^{\ell} U_{m_j,m'}^{\sigma,\ell,j} Y_{\ell,m'},$$

Real materials with spin-orbit coupling - III

Inserting the above relationship in the nonlocal pseudopotential we find [5]:

$$V_{NL}^{\sigma,\sigma'} = \sum_l \sum_{\ell,j,m,m'} E_{\ell,j,m,m'}^{l,\sigma,\sigma'} |\beta_{\ell,j}^l Y_{\ell,m}^l\rangle \langle \beta_{\ell,j}^l Y_{\ell,m'}^l|$$

where both $-\ell < m < \ell$ and $-\ell < m' < \ell$. The coefficients of the nonlocal pseudopotential becomes spin-dependent:

$$E_{\ell,j,m,m'}^{l,\sigma,\sigma'} = E_{\ell,j}^l \sum_{m_j=-j}^j \alpha_{m_j}^{\sigma,\ell,j} U_{m_j,m}^{\sigma,\ell,j} \alpha_{m_j}^{\sigma',\ell,j} U_{m_j,m'}^{*\sigma',\ell,j}$$

but the projectors are written in terms of spherical harmonics as in the scalar relativistic pseudopotential.

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