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

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Outline

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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.

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Introduction to noncollinear magnetism and spin-orbit
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]:

\[ i\hbar \frac{\partial \psi(r, t)}{\partial t} = \left( c\alpha \cdot p + \beta mc^2 \right) \psi(r, t), \]

where \( c \) is the speed of light, \( m \) is the electron mass and \( \alpha \) and \( \beta \) are \( 4 \times 4 \) matrices. The form of \( \alpha \) and \( \beta \) 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:

\[
\alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},
\]
The Dirac equation - II

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

\[
\psi(r, t) = \begin{pmatrix}
\psi_1(r, t) \\
\psi_2(r, t) \\
\psi_3(r, t) \\
\psi_4(r, t)
\end{pmatrix} = \begin{pmatrix}
\psi_A(r, t) \\
\psi_B(r, t)
\end{pmatrix},
\]

where \(\psi_A(r, t)\) and \(\psi_B(r, t)\) 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:

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

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

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

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

\[
\begin{align*}
    c\sigma \cdot \pi \psi_B(r) + \left( mc^2 + q\phi(r) - E \right) \psi_A(r) &= 0 \\
    c\sigma \cdot \pi \psi_A(r) - \left( E + mc^2 - q\phi(r) \right) \psi_B(r) &= 0.
\end{align*}
\]
Small v/c limit of the Dirac equation - I

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

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

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

$$
\left[ \frac{1}{2m} (\sigma \cdot \pi)(\sigma \cdot \pi) + q\phi(r) - E' \right] \psi_A(r) = 0.
$$
Small v/c limit of the Dirac equation - II

Using the relationship:

\[(\sigma \cdot \pi)(\sigma \cdot \pi) = \pi^2 - \hbar q \sigma \cdot \nabla \times A(r),\]

we can rewrite the Pauli equation as:

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

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 \(\mu_B \sigma\) 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]:

\[
H = H_{\text{Pauli}} - \frac{p^4}{8m^3c^2} \quad \text{mass} - \text{velocity}
\]

\[
+ \frac{\hbar^2q}{8m^2c^2} \nabla \cdot \nabla \phi(r) \quad \text{Darwin}
\]

\[
- \frac{\hbar q}{4m^2c^2} \sigma \cdot \left[ \pi \times \nabla \phi(r) \right] \quad \text{spin} - \text{orbit}
\]
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:

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

One can show that:

\[ [H, L] \neq 0 \quad [H, S] \neq 0 \]

\[ [H, J] = 0 \quad J = L + S, \]

where \( L \) is the orbital angular momentum, \( S \) is the spin angular momentum and \( J \) is the total angular momentum.
The spin-angle functions

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

\[ J^2 Y^{j,m_j}_{\ell,1/2}(\Omega, \sigma) = \hbar^2 j(j + 1) Y^{j,m_j}_{\ell,1/2}(\Omega, \sigma), \]

\[ J_z Y^{j,m_j}_{\ell,1/2}(\Omega, \sigma) = \hbar m_j Y^{j,m_j}_{\ell,1/2}(\Omega, \sigma). \]

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

\[ \psi(r) = \frac{1}{r} \left( \begin{array}{c} P(r) Y^{j,m_j}_{\ell,1/2}(\Omega, \sigma) \\ iQ(r) Y^{j,m_j}_{\ell',1/2}(\Omega, \sigma) \end{array} \right). \]
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]:

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

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

\[ V_{\text{ext}}^{\sigma,\sigma'}(r) = \left( q\phi(r) - \mu_B B_z(r), -\mu_B (B_x(r) - iB_y(r)) \right) \times \left( q\phi(r) + \mu_B B_z(r), -\mu_B (B_x(r) + iB_y(r)) \right). \]

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:

\[ n(r, \sigma, \sigma') = N \sum_{\sigma_2, \sigma_3, \cdots, \sigma_N} \int d^3r_2 \cdots d^3r_N \psi^*(r, \sigma, r_2, \sigma_2, \cdots, r_N, \sigma_N) \times \psi(r, \sigma', r_2, \sigma_2, \cdots, r_N, \sigma_N). \]

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

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

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

\[ n(r) = \sum_{i, \sigma} \psi_i^*(r, \sigma) \psi_i(r, \sigma) = \sum_{\sigma} n(r, \sigma, \sigma). \]

\[ E_H = \frac{1}{2} \int d^3 r \ \frac{n(r)n(r')}{|r - r'|}. \]
The total energy - III

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

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

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 \( E_{\text{xc}} \ [n, |m|] \). The noncollinear magnetization density of the non-interacting electron gas can be written as:

\[
m(r) = \mu_B \sum_{i, \sigma_1, \sigma_2} \Psi_i^*(r, \sigma_1) \sigma^{\sigma_1, \sigma_2} \Psi_i(r, \sigma_2) = \mu_B \sum_{\sigma_1, \sigma_2} \sigma^{\sigma_1, \sigma_2} n(r, \sigma_1, \sigma_2)\]
The magnetization density

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

\[ m_x(r) = \mu_B \sum_i \left[ \psi_i^*(r, \uparrow)\psi_i(r, \downarrow) + \psi_i^*(r, \downarrow)\psi_i(r, \uparrow) \right] \]

\[ m_y(r) = -i\mu_B \sum_i \left[ \psi_i^*(r, \uparrow)\psi_i(r, \downarrow) - \psi_i^*(r, \downarrow)\psi_i(r, \uparrow) \right] \]

\[ m_z(r) = \mu_B \sum_i \left[ |\psi_i(r, \uparrow)|^2 - |\psi_i(r, \downarrow)|^2 \right] \]
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:

\[ \frac{\partial E_{\text{tot}}}{\partial \psi_i^*(r, \sigma)} = \varepsilon_i \psi_i(r, \sigma), \]

or:

\[ - \frac{1}{2} \nabla^2 \psi_i(r, \sigma) + \sum_{\sigma'} V^\sigma_{\text{ext}}(r) \psi_i(r, \sigma') + V_H(r) \psi_i(r, \sigma) + \frac{\partial E_{\text{xc}}}{\partial n} \psi_i(r, \sigma) + \mu_B \sum_{\alpha, \sigma'} \frac{\partial E_{\text{xc}}}{\partial m_\alpha} \sigma_\alpha^\sigma,\sigma' \psi_i(r, \sigma') = \varepsilon_i \psi_i(r, \sigma). \]
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

\[
V_{xc}(r) = \frac{\partial E_{xc}}{\partial n} \quad \text{and} \quad B_{xc,\alpha}(r) = -\frac{\partial E_{xc}}{\partial m_{\alpha}} = -\frac{\partial E_{xc}}{\partial |m|} \frac{m_{\alpha}}{|m|},
\]

and define a spin dependent self-consistent local potential

\[
V_{\sigma,\sigma'}^{\text{LOC}}(r) = V_{\text{ext}}^{\sigma,\sigma'}(r) + [V_H(r) + V_{xc}(r)] \delta_{\sigma,\sigma'} - \mu_B \sum_{\alpha} B_{xc,\alpha}(r) \sigma_{\alpha}^{\sigma,\sigma'},
\]

obtaining the equation:

\[
\sum_{\sigma'} \left[ -\frac{1}{2} \nabla^2 \delta_{\sigma,\sigma'} + V_{\text{LOC}}^{\sigma,\sigma'}(r) \right] \psi_i(r, \sigma') = \varepsilon_i \psi_i(r, \sigma).
\]
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:

\[
\psi_i(r) = \left( \begin{array}{c} \psi_i(r, \uparrow) \\ 0 \end{array} \right), \quad \psi_j(r) = \left( \begin{array}{c} 0 \\ \psi_j(r, \downarrow) \end{array} \right).
\]

Computing the magnetization density, we find \( m_x = m_y = 0 \), and

\[
m_z(r) = \mu_B \left[ \sum_{i}^{N_\uparrow} |\psi_i(r, \uparrow)|^2 - \sum_{i}^{N_\downarrow} |\psi_i(r, \downarrow)|^2 \right],
\]

where \( N_\uparrow \) and \( N_\downarrow \) are the number of electrons with spin up and spin down, respectively. From the definition of \( B_{xc} \) we find also \( B_{xc,x} = 0, B_{xc,y} = 0 \).
The LSDA approximation revisited - II

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

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

for electrons with spin up and the equation:

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

for electrons with spin down.
The LSDA approximation revisited - III

Within LSDA:

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

or, equivalently:

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

Therefore we have:

\[ V_{xc}(r) - \mu_B B_{xc,z}(r) = \frac{\partial E_{xc}}{\partial n_{\uparrow}}, \quad V_{xc}(r) + \mu_B B_{xc,z}(r) = \frac{\partial E_{xc}}{\partial n_{\downarrow}}, \]

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 $V^{\sigma,\sigma'}_{\text{ext}}$ is diagonal in the spin indexes. One applies to both spin components a pseudo-potential which has a local part $V_{\text{loc}}(\mathbf{r})$ and a nonlocal part. The nonlocal part can be written by introducing projectors on the orbital angular momentum channels about each atom:

$$V_{\text{NL}} = \sum_{I} \sum_{\ell,m_{\ell}} E_{\ell}^{I} |\beta_{\ell}^{I} Y_{\ell,m_{\ell}}^{I} \rangle \langle \beta_{\ell}^{I} Y_{\ell,m_{\ell}}^{I}|$$

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 \( \ell \) 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 \( 2 \times 2 \) 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:

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

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

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 \( \alpha_{\sigma,\ell,j}^{m_j} \), a unitary matrix \( U_{m_j,m'}^{\sigma,\ell,j} \) which selects the appropriate spherical harmonic and to summarize the above relationships by:

\[
Y_{\ell,1/2}^{j,m_j,\sigma} = \alpha_{\sigma,\ell,j}^{m_j} \sum_{m'=-\ell}^\ell U_{m_j,m'}^{\sigma,\ell,j} Y_{\ell,m'},
\]
Real materials with spin-orbit coupling - III

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

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

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

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

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