**SPIN-ORBIT COUPLING:
A RECURSION METHOD APPROACH**

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Abstract

Relativistic effects play a significant role in alloys of the heavier elements. The majority of earlier works on alloys had included the scalar relativistic corrections. We present here a methodology to take into account the spin-orbit coupling using the recursion method. The basis used for the representation of the Hamiltonian is the TB-LMTO [1], since its sparseness is an essential requirement for recursion. The recursion technique [2, 3] can then be extended to augmented space to deal with disordered alloys or rough surfaces.

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1. Introduction

Inclusion of relativistic corrections to standard electronic structure calculations are often essential for the discussion of stability properties of alloys involving the heavier elements. Singh [4] and Paudyal *et al* [5] have argued that unless we include at least the scalar relativistic corrections for NiPt, we cannot predict the observed low temperature ordering in the 25% , 50% and 75% composition alloys. Scalar relativistic corrections are now routinely incorporated in most electronic structure calculations for both ordered compounds as well as disordered alloys. The inclusion of the spin-orbit coupling has been less common. In this communication we describe a method for including the spin-orbit term in a calculation of the electronic energy spectrum using the recursion method [2].

It is conventional to estimate the spin-orbit effects in many-electron systems using the Hamiltonian [6]

$$H_{SO} = \frac{1}{c^2} \frac{1}{r} \frac{dV(r)}{dr} \vec{L} \cdot \vec{S} = v(r) \vec{L} \cdot \vec{S} \quad (1)$$

As in earlier calculations [7] we shall use the self-consistently computed LSDA potential in an atomic sphere for the potential $V(r)$. We shall use the spherically averaged form, as in standard LMTO approaches, although this restriction may be relaxed. We shall also use inflated atomic spheres and neglect contributions from the interstitial regions. The use of the LSDA potential in H_{SO} has really no formal justification. Stiles *et al* [8] have argued that a more systematic approach should incorporate, within the Hamiltonian, two-body terms of the kind introduced by Breit [9]. This would require corrections to the Hartree energy of the form:

$$E_{SO} = \frac{\alpha^2 E_h a_0^3}{4} \int d^3\vec{r} \int d^3\vec{r}' \left\{ n(\vec{r}') \vec{d}(\vec{r}) \cdot \frac{\vec{r} - \vec{r}'}{|\vec{r} - \vec{r}'|^3} - 2 \vec{j}(\vec{r}) \cdot \vec{m}(\vec{r}') \times \frac{\vec{r} - \vec{r}'}{|\vec{r} - \vec{r}'|^3} \right\} \quad (2)$$

where, $\alpha \simeq 1/137$, $E_h \simeq 27.21$ eV and $a_0 \simeq 0.529$ nm and,

$$\begin{aligned} n(\vec{r}) &= \sum_{i \in occ, \sigma} \psi_{i\sigma}^*(\vec{r}) \psi_{i\sigma}(\vec{r}) \\ \vec{j}(\vec{r}) &= -i \sum_{i \in occ, \sigma} \psi_{i\sigma}^*(\vec{r}) \vec{\nabla} \psi_{i\sigma}(\vec{r}) \\ \vec{m}(\vec{r}) &= \sum_{i \in occ, \sigma} \psi_{i\sigma}^*(\vec{r}) \hat{\sigma} \psi_{i\sigma}(\vec{r}) \\ \vec{d}(\vec{r}) &= -i \sum_{i \in occ, \sigma} \psi_{i\sigma}^*(\vec{r}) \hat{\sigma} \times \vec{\nabla} \psi_{i\sigma}(\vec{r}) \end{aligned}$$

The variational derivative of the above equation (2) with respect to the wave function would yield the effective spin-orbit term that enters the Kohn-Sham equations as H_{SO} . The first term yields the standard spin-orbit term shown by us earlier. The second term yields the so-called “spin-other-orbit” Hamiltonian, which we have neglected in this work.

2. Methodology

2.1. A real space recursion approach using a $\{LL_z S_z\}$ type muffin-tin orbital basis

We shall use as our basis set for the representation of the Hamiltonian, the muffin-tin orbitals built out of the solutions of the Schrödinger equation with scalar relativistic terms but *without* the spin-orbit correction. We are free to choose our basis set, provided they are linearly independent. The appropriateness or otherwise of the basis will become clear from the systems under study. Approximations, if any, will be made subsequently. In this basis the representation of the Hamiltonian is:

$$\underline{\underline{H}} = \underline{\underline{E}}_\nu + \underline{\underline{h}}^\beta - \underline{\underline{h}}^\beta \underline{\underline{0}} \underline{\underline{h}}^\beta + \underline{\underline{H}}_{SO}$$

where,

$$h_{RL,R'L'}^\beta = \left[C_{RL}^\beta - E_{\nu\ell} + \Delta_{RL}^{\beta\ 1/2} S_{RL,RL}^\beta \Delta_{RL}^{\beta\ 1/2} \right] \delta_{R,R'} \delta_{L,L'} + \dots$$

$$\dots + \left[\Delta_{RL}^{\beta\ 1/2} S_{RL,R'L'}^\beta \Delta_{R'L'}^{\beta\ 1/2} \right] (1 - \delta_{RR'})$$
(3)

Here L denotes the composite index $\{\ell, m, m_s\}$ including the spin-index. The representation of the spin-orbit part of the hamiltonian in this basis is:

The part diagonal in real space:

$$\langle \chi_{RL} | H_{SO}(\vec{r}) | \chi_{RL'} \rangle = \left\{ \langle \phi_{RL} | + h_{RL,RL}^\gamma \langle \dot{\phi}_{RL}^\gamma | \right\} H_{SO}(\vec{r}) \left\{ | \phi_{RL'} \rangle + | \dot{\phi}_{RL'}^\gamma \rangle h_{RL',RL'}^\gamma \right\}.$$

The part off-diagonal in real space:

$$\langle \chi_{RL} | H_{SO}(\vec{r}) | \chi_{R'L'} \rangle = \sum_{L''} h_{RL,R'L''}^\gamma \langle \dot{\phi}_{R'L''}^\gamma | H_{SO}(\vec{r}) | \phi_{R'L'} \rangle$$

$$+ \sum_{L''} \langle \phi_{RL} | H_{SO}(\vec{r}) | \dot{\phi}_{RL''}^\gamma \rangle h_{RL'',R'L'}^\gamma$$

$$+ \sum_{R''} \sum_{L''L'''} h_{RL,R''L''}^\gamma \langle \dot{\phi}_{R''L''}^\gamma | H_{SO}(\vec{r}) | \dot{\phi}_{R''L'''}^\gamma \rangle h_{R''L''',R'L'}^\gamma$$

We now need to calculate the following matrix elements:

$$\mathcal{A}_{R,LL'} = \langle \phi_{RL} | H_{SO}(\vec{r}) | \phi_{RL'} \rangle = \langle \phi_{\ell s} | v(r) | \phi_{\ell' s'} \rangle \cdot \langle \ell m s | \vec{L} \cdot \vec{S} | \ell' m' s' \rangle$$

$$\mathcal{B}_{R,LL'} = \langle \dot{\phi}_{RL}^\gamma | H_{SO}(\vec{r}) | \phi_{RL'} \rangle = \langle \dot{\phi}_{\ell s}^\gamma | v(r) | \phi_{\ell' s'} \rangle \cdot \langle \ell m s | \vec{L} \cdot \vec{S} | \ell' m' s' \rangle$$

$$\mathcal{C}_{R,LL'} = \langle \dot{\phi}_{RL}^\gamma | H_{SO}(\vec{r}) | \dot{\phi}_{RL'}^\gamma \rangle = \langle \dot{\phi}_{\ell s}^\gamma | v(r) | \dot{\phi}_{\ell' s'}^\gamma \rangle \cdot \langle \ell m s | \vec{L} \cdot \vec{S} | \ell' m' s' \rangle$$

The angular part of the integrals are readily obtained. Since,

$$\vec{L} \cdot \vec{S} = \frac{1}{2} \left[L^+ S^- + L^- S^+ \right] + L_z S_z$$

$$\mathcal{L}(L, L') = \langle L | \vec{L} \cdot \vec{S} | L' \rangle$$

$$= \delta_{\ell, \ell'} \left[N_{L'}^+ \delta_{m, m'+1} \delta_{s, s'-1} + N_{L'}^- \delta_{m, m'-1} \delta_{s, s'+1} + N_{L'}^0 \delta_{m, m'} \delta_{s, s'} \right]$$
(4)

where,

$$N_L^+ = \frac{1}{2} \sqrt{(\ell - m)(\ell + m + 1)} \left(\frac{1}{2} + s \right) \left(\frac{3}{2} - s \right)$$

$$N_L^- = \frac{1}{2} \sqrt{(\ell + m)(\ell - m + 1)} \left(\frac{1}{2} - s \right) \left(\frac{3}{2} + s \right)$$

$$N_L^0 = m s$$

The four matrix elements are:

$$\begin{aligned}
\mathcal{A}_{R,L,L'} &= \mathcal{L}(L, L') \cdot \int_0^{r_0} dr \, r^2 \, v(r) \, \phi_{\ell s}(r) \, \phi_{\ell' s'}(r) = \mathcal{L}(L, L') \cdot \mathbf{A}_{R,L,L'} \\
\mathcal{B}_{R,L,L'} &= \mathcal{L}(L, L') \cdot \int_0^{r_0} dr \, r^2 \, v(r) \, \dot{\phi}_{\ell s}^\gamma(r) \, \phi_{\ell' s'}(r) = \mathcal{L}(L, L') \cdot \mathbf{B}_{R,L,L'} \\
\hat{\mathcal{B}}_{R,L,L'} &= \mathcal{L}(L, L') \cdot \int_0^{r_0} dr \, r^2 \, v(r) \, \phi_{\ell s}(r) \, \dot{\phi}_{\ell' s'}^\gamma(r) = \mathcal{L}(L, L') \cdot \hat{\mathbf{B}}_{R,L,L'} \\
\mathcal{C}_{R,L,L'} &= \mathcal{L}(L, L') \cdot \int_0^{r_0} dr \, r^2 \, v(r) \, \dot{\phi}_{\ell s}^\gamma(r) \, \dot{\phi}_{\ell' s'}^\gamma(r) = \mathcal{L}(L, L') \cdot \mathbf{C}_{R,L,L'}
\end{aligned}$$

Finally, the matrix elements of the spin-orbit term are:

$$\begin{aligned}
H_{RL,RL'}^{SO} &= \mathcal{A}_{R,L,L'} + h_{RL,RL}^\gamma \mathcal{B}_{R,L,L'} + \hat{\mathcal{B}}_{R,L,L'} h_{RL',RL}^\gamma + \dots \\
&+ h_{RL,RL}^\gamma \mathcal{C}_{R,L,L'} h_{RL',RL'}^\gamma + \sum_{R' \neq R} \sum_{L_1 L_2} h_{RL,R'L_1}^\gamma \mathcal{C}_{R'L_1,L_2} h_{R'L_2,RL}^\gamma
\end{aligned} \tag{5}$$

$$\begin{aligned}
H_{RL,R'L'}^{SO} &= \sum_{L'} \left\{ h_{RL,R'L'}^\gamma \mathcal{B}_{R',L',L'} + \hat{\mathcal{B}}_{R',L,L'} h_{RL',R'L'}^\gamma \right\} + \dots \\
&+ \sum_{R' \neq R} \sum_{L_1 L_2} h_{RL,R'L_1}^\gamma \mathcal{C}_{R'L_1,L_2} h_{R'L_2,R'L'}^\gamma
\end{aligned} \tag{6}$$

Equations (3), (5) and (6) give a representation of the entire Hamiltonian. For most lattices the most tight-binding matrix $\underline{h}^\beta$ is short ranged and upto nearest neighbours only. The second order Hamiltonian in (3) then extends upto the second nearest neighbours. A simple and consistent approximation would replace $\underline{h}^\gamma$ in (5)-(6) by $\underline{h}^\beta$. The spin-orbit part also extends upto the second nearest neighbours.

At this stage, if the $L - S$ coupling is considered to be small, many authors have calculated the correction to the spectrum (band-structure) in solids using a second order perturbation theory. However, since we have obtained a sparse representation of the Hamiltonian in a suitable basis, we can approach the determination of the spectrum through the recursion method of Haydock *et al* [2]. For this, first we shall rewrite an operator form of the Hamiltonian in our basis :

$$\begin{aligned}
\mathbf{H} &= \mathbf{H}' - (\mathbf{H}' - \mathbf{E}) \circ (\mathbf{H}' - \mathbf{E}) + \mathbf{H}_{SO} \\
\mathbf{H}' &= \sum_R \left[\left\{ C_{RL}^\beta + \Delta_{RL}^{\beta \, 1/2} S_{RL,RL}^\beta \Delta_{RL}^{\beta \, 1/2} \right\} \delta_{LL'} \right] \mathbf{P}_R + \dots \\
&\dots + \sum_{R \neq R'} \left[\Delta_{RL}^{\beta \, 1/2} S_{RL,R'L'}^\beta \Delta_{R'L'}^{\beta \, 1/2} \right] \mathbf{T}_{RR'} \\
\mathbf{H}_{SO} &= \sum_R H_{RL,RL'}^{SO} \mathbf{P}_R + \sum_{R \neq R'} H_{RL,R'L'}^{SO} \mathbf{T}_{RR'} \\
\mathbf{E} &= \sum_R E_{\nu L} \delta_{LL'} \mathbf{P}_R \quad \circ = \sum_R o_{RL} \delta_{LL'} \mathbf{P}_R
\end{aligned} \tag{7}$$

$\mathbf{P}_R$ and $\mathbf{T}_{RR'}$ are projection and transfer operators in the Hilbert space spanned by the tight-binding LMTO basis.

The recursion method then carries out a change of basis starting from a chosen state in the Hilbert space, repeatedly operating on by the Hamiltonian and subtracting projection on the earlier members through a three term recurrence relation [2]. The calculations yield the Green function as a continued fraction :

$$\begin{aligned}
G_{RL,RL}(E) &= \langle R, L | (EI - \mathbf{H})^{-1} | R, L \rangle \\
&= \frac{1}{E - \alpha_1 - \frac{\beta_1^2}{E - \alpha_2 - \frac{\beta_2^2}{\ddots \frac{\beta_{N-1}^2}{E - \alpha_N - T(E)}}}}
\end{aligned} \tag{8}$$

$T(E)$ is the appropriate *terminator* obtained from the initial part of the continued fraction. The terminator preserves the herglotz analytic properties of the approximated Green function. We have used the terminator of Luchini and Nex [10]. To obtain the magnetic moment, we first obtain the spheridized local charge density within an atomic sphere centered at R :

$$\begin{aligned}
\rho_\sigma^{(i)}(r_R) &= \frac{1}{4\pi} \sum_\ell \left[m_{R\ell}^{(0)} \varphi_{\ell\sigma}(r_R)^2 + 2m_{R\ell}^{(1)} \varphi_{\ell\sigma}(r_R) \dot{\varphi}_{\ell\sigma}(r_R) + \dots \right. \\
&\quad \left. + m_{R\ell}^{(2)} \{ \dot{\varphi}_{\ell\sigma}(r_R)^2 + \varphi_{\ell\sigma}(r_R) \ddot{\varphi}_{\ell\sigma}(r_R) \} \right]
\end{aligned} \tag{9}$$

where the energy moments are

$$m_{R\ell}^{(n)} = -\frac{1}{\pi} \Im m \int_\infty^{E_F} dE G_{RL,RL}(E) (E - E_{\nu,R\ell})^n$$

The magnetization density within that sphere is :

$$M^{(i)}(r_R) = \rho_\uparrow^{(i)}(r_R) - \rho_\downarrow^{(i)}(r_R)$$

The charge and magnetization densities are then inputs into the self-consistency iterations using the LSDA. If we wish to carry out a fully self-consistent solution then the charge and magnetization densities are input into an expression of the total energy which should include a Breit like term as in eqn (2). However, because of the smallness of the spin-orbit correction, one usually carries out fully self-consistent electronic structure calculation without the correction, and then carries out one calculation with it after convergence. In this work we have followed this procedure and left the study of the effect of full self-consistency for a later work.

The magnetic moment per atom is given by :

$$M_R^{(i)} = \int_0^{s_R} M^{(i)}(r_R) r_R^2 dr_R$$

2.2. Generalization to disordered alloys : the augmented space recursion

The above procedure may be generalized for application to disordered alloys through the augmented space technique [11]. The methodology has been described in great detail in earlier papers and the readers are referred to the review [12] for details. Operationally the augmented space theorem [12] states that : if we can represent the hamiltonian in a countable (*site* labelled) basis where the disorder appears in the *single site* terms, we may *augment* the hamiltonian by replacing the random elements by operators whose

spectral densities are their probability densities. This *augmented* Hamiltonian is an operator in a space which is the product of the space spanned by the countable basis and that spanned by the configurations of the random variables. The configurational averages are then matrix elements of a particular configuration state, which, in analogy with many-body scattering theory we call the *vacuum* state. The configuration averaged Green function may then be obtained through the recursion method on the full *augmented* space.

First we rewrite the hamiltonian as follows :

$$\begin{aligned} \mathbf{H} &= \Delta^{1/2} \left[\tilde{\mathbf{C}} + \mathbf{S} - (\mathbf{C}' + \mathbf{S}) \mathbf{o}' (\mathbf{C}' + \mathbf{S}) + \dots \right. \\ &\quad \left. \dots + \mathbf{A}' + (\mathbf{C}' + \mathbf{S}) \mathbf{B}' + \hat{\mathbf{B}}' (\mathbf{C}' + \mathbf{S}) + \mathbf{C}' \mathbf{C}' \mathbf{C}' + \mathbf{S} \mathbf{C}' \mathbf{S} \right] \Delta^{1/2} \\ &= \Delta^{1/2} \left[\tilde{\mathbf{C}} + \mathbf{S} - \mathbf{H}' \right] \Delta^{1/2} \end{aligned} \quad (10)$$

where we have :

$$\begin{aligned} \mathbf{o}' &= \mathbf{o} \Delta & \tilde{\mathbf{C}} &= \frac{\mathbf{C}}{\Delta} & \mathbf{C}' &= \frac{\mathbf{C} - \mathbf{E}}{\Delta} \\ \mathbf{C}' &= \Delta^{1/2} \mathbf{C} \Delta^{1/2} & \mathbf{B}' &= \Delta^{1/2} \mathbf{B} \Delta^{-1/2} & \mathbf{B}' &= \Delta^{-1/2} \mathbf{B} \Delta^{1/2} \\ \mathbf{A}' &= \Delta^{-1/2} \mathbf{A} \Delta^{-1/2} \end{aligned} \quad (11)$$

For a substitutional binary random alloy, the site labelled potential parameters have a binary distribution: taking values appropriate for the A and B constituents with probabilities proportional to their concentrations: x_A and x_B . The corresponding configuration space is isomorphic to that for an Ising model and the operator whose spectrum is the probability density is :

$$\mathbf{M}^R = x_A \mathbf{P}_\uparrow + x_B \mathbf{P}_\downarrow + \sqrt{x_A x_B} (\mathbf{T}_{\uparrow\downarrow}^R + \mathbf{T}_{\downarrow\uparrow}^R)$$

From equation (10) we get:

$$\begin{aligned} \mathbf{G}(z) &= \left(z \mathbf{I} - \Delta^{1/2} \left[\tilde{\mathbf{C}} + \mathbf{S} - \mathbf{H}' \right] \Delta^{1/2} \right)^{-1} \\ &= \Delta^{-1/2} \left(z \Delta^{-1} - \tilde{\mathbf{C}} - \mathbf{S} + \mathbf{H}' \right)^{-1} \Delta^{-1/2} \end{aligned} \quad (12)$$

We shall now apply the augmented space theorem to obtain the following : for any single site labelled random hamiltonian element $\mathbf{K} \in \mathcal{H}$, using the augmentation transformation we obtain

$$\begin{aligned} \hat{\mathbf{K}} &= \sum_R \left\{ \frac{A(K_R)}{A(\Delta_R^{-1/2})^2} \mathbf{P}_R \otimes \mathbf{I} + \frac{B(K_R)}{A(\Delta_R^{-1/2})^2} \mathbf{P}_R \otimes \mathbf{P}_\downarrow^R + \dots \right. \\ &\quad \left. \dots + \frac{F(K_R)}{A(\Delta_R^{-1/2})^2} \mathbf{P}_R \otimes (\mathbf{T}_{\uparrow\downarrow}^R + \mathbf{T}_{\downarrow\uparrow}^R) \right\} \end{aligned}$$

For terms which are not random we have, for example,

$$\hat{\mathbf{S}} = \sum_R \sum_{R' \neq R} S_{RR'} \mathbf{T}_{RR'} \otimes \mathbf{I}$$

where, K_R and $S_{RR'}$ are matrices $K_{R,LL'}$ and $S_{RL,R'L'}$ in angular momentum-spin indices and,

$$\begin{aligned}
A(K_R) &= x_A K_A + x_B K_B \\
B(K_R) &= (x_B - x_A) (K_B - K_A) \\
F(K_R) &= \sqrt{x_A x_B} (K_B - K_A)
\end{aligned}$$

The configuration averaged Green function matrix element is :

$$\ll G_{RR}(z) \gg = \ll 1 | (z\hat{\mathbf{I}} - \hat{\mathbf{H}}_{eff})^{-1} | 1 \gg$$

where,

$$|1 \gg = |R \otimes \{\emptyset\}\rangle + \frac{F(\Delta_R^{-1/2})}{A(\Delta_R^{-1/2})} |R \otimes \{R\}\rangle$$

and,

$$\begin{aligned}
\hat{\mathbf{H}}_{eff} &= \left[z (\hat{\mathbf{I}} - \hat{\Delta}^{-1}) + \hat{\mathbf{C}} + \hat{\mathbf{S}} - (\hat{\mathbf{C}}' + \hat{\mathbf{S}}) \hat{\sigma}' (\hat{\mathbf{C}}' + \hat{\mathbf{S}}) + \dots \right. \\
&\quad \left. \dots + \hat{\mathbf{A}}' + (\hat{\mathbf{C}}' + \hat{\mathbf{S}}) \hat{\mathbf{B}}' + \hat{\mathbf{B}}' (\hat{\mathbf{C}}' + \hat{\mathbf{S}}) + \hat{\mathbf{C}}' \hat{\mathbf{C}}' \hat{\mathbf{C}}' + \hat{\mathbf{S}} \hat{\mathbf{C}}' \hat{\mathbf{S}} \right]
\end{aligned} \tag{13}$$

States in the configuration space are uniquely labelled by the *cardinality sequence* $\{R_1, R_2 \dots\}$ which denotes the sites at which we have a configuration fluctuation (denoted by a $\downarrow$) from the *averaged state* (denoted by an $\uparrow$). The configuration averaged Green function is then obtained directly by recursion in the augmented space with $|1 \gg$ as the starting state. The averaged density of states and both the local and averaged magnetic moments may then be obtained from the averaged Green functions,

2.3. Recursion formulation for surfaces

The real space formalism using the recursion method is ideally suited for application to surfaces. Haydock *et al* [2] originally introduced the recursion method to study Cu surfaces. The Hamiltonian [13] is modified somewhat :

$$\begin{aligned}
\mathbf{H}' &= \sum_{s=-1}^S \sum_{R_s} \left[\left\{ C_{R_s L}^\beta + \Delta_{R_s L}^{\beta 1/2} S_{R_s L, R_s L}^\beta \Delta_{R_s L}^{\beta 1/2} \right\} \delta_{LL'} \right] \mathbf{P}_{R_s} + \dots \\
&\quad \dots + \sum_{s=-1}^S \sum_{s'=-1}^S \sum_{R_s \neq R_{s'}} \left[\Delta_{R_s L}^{\beta 1/2} S_{R_s L, R_{s'} L'}^\beta \Delta_{R_{s'} L'}^{\beta 1/2} \right] \mathbf{T}_{R_s R_{s'}}, \\
\mathbf{H}_{SO} &= \sum_s \sum_{R_s} H_{R_s L, R_s L'}^{SO} \mathbf{P}_{R_s} + \sum_{ss'} \sum_{R \neq R'} H_{R_s L, R_{s'} L'}^{SO} \mathbf{T}_{R_s R_{s'}}, \\
\mathbf{E} &= \sum_s \sum_{R_s} E_{\nu s L} \delta_{LL'} \mathbf{P}_{R_s}, \quad \mathbf{o} = \sum_s \sum_{R_s} o_{R_s L} \delta_{LL'} \mathbf{P}_{R_s},
\end{aligned} \tag{14}$$

We have labelled planes parallel to the free surface by s . $s = 0$ labels the free surface and $s = n$ the n th plane parallel to the free surface and below it into the bulk. Usually by $s = 4$ we reach bulk behavior [13, 14], R_s refers to the position of an ion-core on the surface labelled by s . The potential parameters depend upon the surface label. This is because the charge densities, being dependent on the local environment, depend upon s and in the LSDA, the charge densities uniquely determine the

Metal/Alloy	Structure	equilibrium lattice parameter in amstrong unit [5]
NiPt ₃	L1 ₂	6.758
NiPt	L1 ₀	7.127
Ni ₃ Pt	L1 ₂	7.196

Table 1. The basic structure and equilibrium lattice parameters for the Ni/Pt based alloys.

potential and hence the potential parameters. The structure matrix between sites on the same surface label s are similar, but that between two adjacent surfaces may be different because of surface dilatation to minimize the energy.

$$\rho_{\sigma}^{(s)}(r_{R_s}) = \frac{1}{4\pi} \sum_{\ell} \left[m_{R_s\ell}^{(0)} \varphi_{\ell\sigma}(r_{R_s})^2 + 2m_{R_s\ell}^{(1)} \varphi_{\ell\sigma}(r_{R_s}) \dot{\varphi}_{\ell\sigma}(r_{R_s}) + \dots + m_{R_s\ell}^{(2)} \{ \dot{\varphi}_{\ell\sigma}(r_{R_s})^2 + \varphi_{\ell\sigma}(r_{R_s}) \ddot{\varphi}_{\ell\sigma}(r_{R_s}) \} \right] \quad (15)$$

where the energy moments are

$$m_{R_s\ell}^{(n)} = -\frac{1}{\pi} \Im m \int_{\infty}^{E_F} dE G_{R_sL,R_sL}^{(s)}(E) (E - E_{\nu,R_s\ell})^n$$

We have to remember that the total energy per atom, which is minimized in LSDA calculations should contain the Madelung terms due to the surface dipole layer formed by charges leaking out of the surface [15]. In order to take care of the charge leakage, we have added a layer of *empty spheres* carrying charge but no ion-cores in the layer labelled $s = -1$.

$$E_{TOT} = \frac{1}{S} \sum_{s=-1}^S \sum_L \int_{-\infty}^{E_F} dE E n_L^{(s)}(E) + \sum_{\substack{R_s R'_s \\ s=-1}} \sum_{LL'} M_{LL'}(R_s - R'_s) Q_{R_sL} Q_{R'_sL'} \dots - \frac{1}{\sqrt{4\pi}} \sum_s \int_0^{r_0} dr r^2 \rho^{(s)}(r) \left\{ \frac{2Z}{r} - \epsilon_{xc}[\rho^{(s)}(r)] \right\} + E_{core}$$

The Q are the multipole moments of the charges in the empty spheres and M the Madelung matrices defined by Skriver and Rosengaard [15].

3. RESULTS

3.1. Application to Bulk Solids

We shall first apply our recursion method to a series of alloys : Ni₃Pt, NiPt, NiPt₃ . The basic structural information on these alloys is given in Table 1.

Initially we carried out a self-consistent calculation of the electronic structure of the alloys with scalar relativistic correction terms alone. For the calculation of the spin-resolved local density of states by recursion of the above, we have used a real-space cluster of 24739 atoms which remain within the 20-th nearest neighbour shells from the starting atom. In case of fcc lattices, each shell around a site consists of 12 nearest neighbours on the lattice. In case of the L1₀ structure for $A_{50}B_{50}$ type alloys, of the 12 neighbours of A, 8 are occupied by B and 4 by A. In case of L1₂ structure for $A_{75}B_{25}$ type alloys, each B atom has 12 nearest neighbours which are A, whereas each A atom has 8 nearest neighbours which are B and 4 nearest neighbours which are A. In all cases, we generate 25 pairs of recursion coefficients accurately and the continued fraction is terminated by the terminator proposed by Luchini and Nex [10].

In order to check that our estimate of the spin-orbit terms are indeed OK, we have compared our calculations with the parameter estimated by Daalderop *et al* [16], which is our A_{dd} . The results are shown in table 2:

Material	Our calculations		Daalderop <i>et al</i> calculation		
	$A_{ll} \uparrow$	$A_{ll} \downarrow$	Solid $\uparrow$	Solid $\downarrow$	Atomic
Ni	6.31	6.06	6.98	6.91	6.47
Ni in Ni ₃ Pt	6.28	6.08			
Pt in Ni ₃ Pt	14.16	13.84			
Ni in NiPt	6.15	6.15			
Pt in NiPt	14.04	14.04			
Ni in NiPt ₃	6.19	5.96			
Pt in NiPt ₃	14.11	13.99			
Pt	13.97	13.97			

Table 2. The value of d-state spin-orbit parameters for different metals and alloys in mRyd.

Our estimates for Ni are in good agreement with the results quoted by Daalderop *et al* [16]. It should be noted that the parameter quoted by Daalderop *et al* is only a part of the contribution of the spin-orbit term to the hamiltonian, although it is the most dominant one. Other contributions come from the off-diagonal elements of $A_{LL'}$ as well as from $B_{LL'}$ and $C_{LL'}$.

We carry out the recursion calculations with the spin-orbit part of the Hamiltonian included. Note that we now have to calculate the majority and minority spins simultaneously because the presence of spin-orbit coupling leads to off-diagonal term in the Hamiltonian between the spin states.

Figure 1 displays the density of states of Ni₃Pt, NiPt and NiPt₃ with spin-orbit coupling. In all these cases the fermi energy of the density of states are shifted to zero. Figure 2 displays the fractional change in the spin-resolved density of states of Ni₃Pt, NiPt and NiPt₃. It is clear from the figure 2 that

Figure 1. Density of states for (top) Ni₃Pt, (middle) NiPt and (bottom) NiPt₃ with LS-coupling included.

Figure 2. Fractional Change in the spin-resolvent density of States for (top) Ni_3Pt , (middle) NiPt and (bottom) NiPt_3 due to LS coupling.

the spin-orbit coupling produces a minor change in the density of states across the band.

Table. 3 presents the band energies and magnetic moments per atom per cell for the above mentioned metals and alloys. In case of pure materials $\text{Fe}(Z=26)$, $\text{Ni}(Z=28)$ and $\text{Pt}(Z=78)$, the change in band energies increases with the proton numbers of the constituents. Also we observe that for Ni and Pt bases alloys, the change is increasing with the increase of heavier atom (Pt) in the alloys. So it is evident from here that in case of presence of heavier atom, inclusion of spin-orbit coupling term is necessary. In case of magnetic moment calculation of pure materials, the magnetic moment of Fe is increased by 10 mBohr-magneton/atom, whereas the change in Ni is only 6 mBohr Magneton/Atom-Cell. However, paramagnetic Pt possess a magnetic moment of 37 mBohr-magneton/atom because of spin-orbit coupling, which gives rise to non-collinearity in Pt.

In case of Ni and Pt based alloys, the magnetic moment/atom-cell of Ni_3Pt changed from 0.413 bohr-magneton/atom (0.472 for Ni and 0.234 for Pt) to 0.422 (0.485 for Ni and 0.231 for Pt). Similarly the magnetic moment of NiPt_3 changed from 0.190 (0.518 for Ni and 0.081 for Pt) to 0.203 (0.532 for Ni and 0.0931 for Pt). On the other hand, the paramagnetic NiPt possesses a slight magnetic moment of 0.005, which again is a case of non-collinearity in NiPt .

Examined property	Fe	Ni	Ni_3Pt	NiPt	NiPt_3	Pt
Band Energy(a)	3.297	3.772	4.276	4.682	4.931	5.437
Band Energy(b)	3.307	3.792	4.411	4.717	5.032	5.652
Diff.(b-a)	0.010	0.014	0.070	0.092	0.130	0.201
Magnetic Moment(a)	2.262	0.521	0.413	0.000	0.190	0.00
Magnetic Moment(b)	2.272	0.527	0.422	0.005	0.203	0.037
Diff(b-a)	0.010	0.006	0.009	0.005	0.013	0.037

Table 3. Band Energy(Ryd),Magnetic Moment(Bohr-Magneton/atom-cell) and Density of States at Fermi Energy for Fe, Ni, NiPt_3 , NiPt , Ni_3Pt and Pt (a) Real Space Recursion without LS coupling (b) Real Spcae Rucursion with LS coupling.

3.2. Application in Fe surfaces

In an earlier communication [13], we used a supercell calculation and a layer resolved real space recursion calculation to study the variation of magnetic moments at different layers. In this communication we tried to find out the effect of spin-orbit coupling on different layers. For this purpose we used a layer dependent real space recursion with and without the spin-orbit coupling term and found the differences in magnetic moment.

For the spin-resolved local density of states calculation of bcc Fe, we used a real space cluster of about 29679 atoms which remain within 20th shell from the starting atom, each shell around a site in this case consists of 8 nearest neighbours and 6 next nearest neighbours. For the recursion calculation we have carried out the recursive calculations upto 25 steps on a real space cluster consisting of 18 nearest neighbour shells around the starting site. In this part of numerical calculation, we used the methodology mentioned in Sec 2.3. We found that the spin-orbit coupling parameter terms are layer dependent and the diagonal d-state coupling parameter terms (A_{dd}) are shown in Table 4.

Parameter	S	S-1	S-2	B
$A_{LL}\uparrow$	4.5691	4.4286	4.5014	4.4797
$A_{LL}\downarrow$	3.7495	3.3589	3.5677	3.3607
$B_{LL}\uparrow$	4.4564	4.4023	4.4496	4.4736
$B_{LL}\downarrow$	3.7321	3.3581	3.3559	3.5974
$C_{LL}\uparrow$	4.4597	4.4545	4.45289	4.5120
$C_{LL}\downarrow$	3.7586	3.6070	3.5862	3.6305

Table 4. The value of d-state spin-orbit parameters for different layers of Fe(001) surface in mRyd.

Table. 5 represents the magnetic moments with and without spin-orbit coupling term in various layers of the bcc Fe[001] surface. The difference in the magnetic moments are presented in mBohr Magneton. It is clear the change in magnetic moment increases as we go from the bulk to the surface. We observe a Freidel-like oscillation as we go from the surface into the bulk, the spin-orbit correction to the magnetic moment does the same.

Method	S	S-1	S-2	B
(a)	2.992	2.173	2.400	2.263
(b)	3.007	2.184	2.412	2.272
Diff(in mBohr Magneton)	15.04	10.79	11.59	9.94

Table 5. Local magnetic moments in Bohr-magneton/atom. (a) Real space recursion (b) Real space recursion+LS coupling

In our earlier work [13], we studied magnetism on a rough surface. The rough surface is obtained by a pair of coupled continuum equation proposed by Sanyal *et al* [17], which were later modified by Huda *et al* [18]. We have used the same rough surface to study the effect of spin-orbit correction to the local magnetic moment on it.

For the calculation of the spin-resolved density of states by recursion, we have used a real-space cluster of 6402-11011 atoms (depending on the position of the starting site on the surface of dimension 11×11 atoms), which remain within 16 th shell from the starting atom. Each shell around a site consists of the eight nearest and six next nearest neighbours on the BCC lattice. We generated 25 pairs of recursion coefficient accurately and continued fraction was terminated by the Luchini-Nex terminator. As the surface is rough, we take all the 121 points on the rough surface as our starting point.

Figure 3 shows the scatter diagram relating the change in local magnetic moment due to spin-orbit coupling to the local curvature, together with the regression line. The negative slope of the regression line indicates that the maximum change occurs for large negative curvatures, that is on sharp mound and the minimum change occurs for large positive curvatures, that is in deep grooves. Since the local environmental effect leads to large local magnetization on sharp mounds and low magnetization in deep grooves and consequently a roughness in magnetization [13], our results indicate that spin-orbit coupling reinforces the environmental effects and leads to an enhancement of magnetic roughness.

Figure 3. Fractional Change in magnetic moment(δm) on a rough surface as a function of local curvature(C). The figure shows the linear regression curve $\delta m = 0.0107 - 0.00137 C$

4. Conclusion

In this work, we present a methodology to include spin-orbit coupling term in recursion method. We observe from numerical calculation that the spin-orbit coupling term is important in alloys having heavier elements and the effect is more prominent in surfaces than in the bulk. The spin-orbit coupling has been found to be important for calculating the non-collinearity of magnetic moment and also for calculating anisotropic magneto-crystalline energy. We intend to carry forward our calculations in these directions.

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