Calculating Scattering Matrices by Wave Function Matching on Cu-Co interfaces

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Abstract

In this paper the spin-dependent transmission through an ideal copper-cobalt interface is calculated using the method of wavefunction matching (WFM) implemented with a basis of muffin-tin orbitals (MTO) within the framework of density functional theory (DFT). A sketch of DFT is given and the theory of muffin-tin orbitals is explained, illustrated with examples of vanadium, copper and cobalt bands structures.

Keywords: density functional theory, muffin-tin orbitals, scattering matrix, wavefunction matching, spin transport

1   Introduction

For many modern electronic applications it is necessary to accurately describe and control electronic transport within electronic devices at nanometer scale. At this scale the effect of interfaces on electronic transport becomes very important. An interface between two infinite crystals breaks the translational Bloch symmetry that allows the electronic structure of solids to be studied theoretically using the Kohn-Shame equations of density functional theory (DFT). In this paper we will first outline the methods of DFT and linear muffin-tin orbitals (LMTO) and illustrate the latter with numerical results obtained for the band structures of vanadium, copper and cobalt.

Secondly the method of wave function matching (WFM) derived by Ando [1] and reviewed by Brocks et al. [2] will be used together with the transport code provided by the chair of Computational Material Science to calculate the transmission through a cobalt-copper interface.

2 Density Functional Theory

2.1 Hohenberg-Kohn theorems

Metals can be modeled as three dimensional lattices in which electrons are confined by the potential of the lattice ions. Such a situation can be described by the Schrödinger equation for all of the ions and electrons in the system. Because of the mass difference between the electrons and the ions, the ions can be considered to be stationary, with only the electrons able to move. This justifies the use of the so called Born-Oppenheimer approximation, which states that the behaviour of the electrons can be described a Schrödinger equation for the electrons only, by finding a wavefunction Ψ, as a function of the positions $\mathbf{r_i}$ of the electrons in the system, satisfying the eigenvalue problem

$$-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2\Psi(\mathbf{r_1},\mathbf{r_2},...\mathbf{r_N}) + V(\mathbf{r_1},\mathbf{r_2},...\mathbf{r_N})\Psi = E\Psi, \qquad (1)$$

where $\hbar$ is the reduced Planck constant, m the electron mass, V the potential of the system and E the energy of the system.

The operator ∇_i^2 is the Laplacian operator acting on the coordinates of the i-th electron.

In quantum mechanics the kinetic energy operator and the Hamiltonian operator are given by

$$\hat{T} = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2$$

$$\hat{H} = \hat{T} + V$$

The properties of an N-electron system can be described by wavefunctions Ψ, which are solutions to the Schrödinger equation. The *ground state* is the value of Ψ that minimizes the energy E. In particular from this state many transport properties can be deduced.

In (1) the potential V describes the influence of the ionic lattice on the electrons and the interaction between the electrons. Due to this electron-electron interaction the Schrödinger equation becomes a many-body problem and the hope of finding an analytical solution is lost.

To find the eigenvalues and eigenfunctions of the Schrödinger equation one quickly has to resort to numerical techniques for solving many-body problems. As the wavefunction and the potential in (1) depend on $3N$ variables, techniques for directly solving this equation become computationally intractable for large systems.

The best approach found so far to solve a many-body Schrödinger equation is by using Density Functional Theory (DFT). In this framework one does not need a wavefunction which depends on $3N$ variables. Instead observables are written as functions of the electron density $n(\mathbf{r})$, which depends on only the 3 coordinate variables. This remarkable result is stated by the Hohenberg-Kohn Theorems [3].

In this framework the Hamiltonian operator is split up into three components

$$\hat{H} = \hat{T} + V_{ext} + V_{ee},$$

where the complete potential V is the sum of V_{ee}, the interaction potential between electrons and V_{ext}, the external potential.

The first Hohenberg-Kohn theorem states that:

Theorem 1 *The ground state energy of an interacting electron system is a unique functional of the electron density. [3]*

This functional can be expressed as

$$E[n] \equiv E[n(\mathbf{r})] = \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} + F[n], \qquad (2)$$

where the integral is over all of space and the functional $F[n]$ is given by:

$$F[n] = T[n] + E_{ee}[n], \qquad (3)$$

with $T[n]$ the kinetic energy as a functional of the electron density and $E_{ee}[n]$ the electron interaction energy.

As electrons carry a charge q, classically their interaction energy is given by the Coulomb interaction energy of two charge densities:

$$E_c[n] = \frac{q^2}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \qquad (4)$$

Electrons can, however, also interact in different ways, such as through spin densities, and the energies of these interactions are bundled as the non-classical interaction energy $E_{nc}[n]$. The functional in (3) can thus be written as:

$$F[n] = T[n] + E_c[n] + E_{nc}[n] = T[n] + \frac{q^2}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{nc}[n].$$

The second Hohenberg-Kohn theorem explains how to find the ground state energy using the electron density in (2).

Theorem 2 *The electron density that minimizes the energy functional is the ground state density of the interacting electron system. [3]*

Proofs of the Hohenberg-Kohn theorems can be found in their original paper [3].

2.2 Kohn-Sham equations

According to the second Hohenberg-Kohn theorem the ground state energy can be found by minimizing (2) over the electron density, but before this can be done, one first needs to find the correct expression for (3).

Determining the correct expression for $F[n]$ is the biggest challenge in density functional theory. Especially since the form of the non-classical electron-electron energy is hard to determine. One method to determine the expression for $F[n]$ was introduced by Kohn and Sham [4].

The idea of their method is to find a system of N non-interacting electrons with the same electron density as the interacting system, $n_s(\mathbf{r}) = n(\mathbf{r})$, whose kinetic energy is given by:

$$T_s[n] = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \langle \psi_i | \nabla^2 | \psi_i \rangle^\infty. \tag{5}$$

In this expression the *bra-ket* notation is used:

The brackets $\langle |$ and $| \rangle$ represent respectively a column and a row vector.
$\langle | \rangle$ then defines an inner product and we use the expression $\langle | \rangle^\infty$ to denote that this inner product is an integral over all of space.
Lastly the notation $\langle || \rangle$ is defined by:

$$\langle A|B|C \rangle = \langle A|BC \rangle,$$

where B is an operator.

The ψ_i in (5) are the one electron wavefunctions, so called *orbitals*, of the non-interacting system.

The functional in (3) can be written in terms of the kinetic energy of the non-interacting system:

$$F[n] = T_s[n] + E_c + E_{XC}, \tag{6}$$

where E_{XC} is the *exchange-correlation energy* defined as:

$$E_{XC}(n) \equiv (T[n] - T_s[n]) + (E_{ee}[n] - E_c[n]).$$

According to the second Hohenberg-Kohn theorem the correct ground state energy and ground state electron density can then be found by minimizing the

energy in (2) over all possible electron densities:

$$0 = \frac{\partial E[n]}{\partial n(\mathbf{r})} = \frac{\partial}{\partial n(\mathbf{r})} \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} + \frac{\partial F[n]}{\partial n(\mathbf{r})}$$

$$= \frac{\partial}{\partial n(\mathbf{r})} \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} + \frac{\partial T_s[n]}{\partial n(\mathbf{r})} + \frac{\partial E_c[n]}{\partial n(\mathbf{r})} + \frac{\partial E_{XC}[n]}{\partial n(\mathbf{r})}$$

$$= \frac{\partial T_s[n]}{\partial n(\mathbf{r})} + V_{ext} + V_c + V_{XC} = \frac{\partial T_s[n]}{\partial n(\mathbf{r})} + V_s(\mathbf{r}),$$

where $V_s(\mathbf{r}) = V_{ext} + V_c + V_{XC}$ is called the effective Kohn-Sham potential, $V_c(\mathbf{r})$ is the functional derivative of classical interaction energy $E_c[n]$

$$V_c(\mathbf{r}) = \frac{q^2}{2} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}',$$

and the so called *exchange-correlation potential* $V_{xc}(\mathbf{r})$ is given by

$$V_{xc}(\mathbf{r}) = \frac{\partial E_{XC}[n]}{\partial n(\mathbf{r})}.$$

As a consequence we see that the electron density that minimizes the energy functional in Eq. (2) also minimizes the energy of a non interacting system with kinetic energy $T_s(\mathbf{r})$ and potential $V_s(\mathbf{r})$. Solving the Schrödinger equation for the full system is thus equivalent to solving the Schrödinger equation for the non-interacting system

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_s(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}), \tag{7}$$

where ε_i are called the Kohn-Sham eigenvalues.

Since the squared norm of the wavefunction $\Psi(\mathbf{r})$ is the probability amplitude for finding an electron at $\mathbf{r}$, the electron density is given by:

$$n_s(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2. \tag{8}$$

Equations (7) and (8) together are called the Kohn-Sham equations. Using these equations the problem of solving the Schrödinger equation of an N-electron interacting system is reduced to solving N non-interacting one-electron equations.

Since $V_s(\mathbf{r})$ depends on $n(\mathbf{r})$, which via $\psi_i(\mathbf{r})$ also depends on $V_s(\mathbf{r})$, the problem must be solved iteratively by first guessing an electron density $n_s(\mathbf{r})$ and then calculating the corresponding $V_s(\mathbf{r})$ and $\psi_i(\mathbf{r})$ and using these to calculate a new electron density to use in the next iteration. This procedure is then repeated until convergence is reached.

3 LMTO method

3.1 LCAO and Partial Waves

The wavefunction $\psi(\mathbf{r})$ is a one-electron wavefunction extending over the whole lattice. Working directly with this wavefunction is quite difficult. It is easier to split this wavefunction up into many single electron orbitals χ localized at different atomic sites. The wavefunction $\psi(\mathbf{r})$ can be written as a linear combination of these orbitals.

$$\psi_i(\mathbf{r}) = \sum_{\mathbf{R}n\ell m} \chi_{\mathbf{R}n\ell m}(\mathbf{r} - \mathbf{R})c_{\mathbf{R}n\ell m,i}, \tag{9}$$

where the c are expansion coefficients, $\mathbf{R}$ is a vector that runs over all the coordinates of the atomic sites and n, ℓ and m are the quantum numbers of an orbital.

This method of expansion is called the *linear combination of atomic orbitals* (LCAO) method.
For simplicity in the rest of this paper we will use the notation $L = \ell m$ and $\mathbf{r_R} = \mathbf{r} - \mathbf{R}$

In this way the first Kohn-Sham equation (7) can be written as:

$$\sum_{\mathbf{R}nL} H_{ks}\chi_{\mathbf{R}nL}(\mathbf{r_R})c_{\mathbf{R}nL,i} = \varepsilon_i \sum_{\mathbf{R}nL} \chi_{\mathbf{R}nL}(\mathbf{r_R})c_{\mathbf{R}nL,i},$$

where H_{ks} is the Kohn-Sham Hamiltonian:

$$H_{ks} = -\frac{\hbar^2}{2m}\nabla^2 + V_s(\mathbf{r}).$$

Multiplying this equation by a single basis function $\chi_{\mathbf{R}'n'L'}$ and integrating over the whole space gives

$$\sum_{\mathbf{R}nL} c_{\mathbf{R}nL,i} \int \chi_{\mathbf{R}'n'L'} H_{ks}\chi_{\mathbf{R}nL}(\mathbf{r_R})d\mathbf{r} = \varepsilon_i \sum_{\mathbf{R}nL} c_{\mathbf{R}nL,i} \int \chi_{\mathbf{R}'n'L'}\chi_{\mathbf{R}nL}d\mathbf{r},$$

which can be written as a matrix equation

$$(H - \mathcal{E}\mathcal{O}) \cdot c = 0,$$

Where the Hamiltonian matrix H is given by

$$H_{R'n'L',RnL} = \langle\chi_{\mathbf{R}'n'L'}\big| - \frac{\hbar^2}{2m}\nabla^2 + V_s\big|\chi_{\mathbf{R}nL}\rangle^\infty, \tag{10}$$

and $\mathcal{O}$ is the *overlap matrix*, given by

$$\mathcal{O}_{R'n'L',RnL} = \langle\chi_{R'n'L'}\big|\chi_{RnL}\rangle^\infty, \tag{11}$$

c is a column vector containing the different expansion coefficients, and $\mathcal{E}$ is a diagonal matrix containing the Kohn-Sham eigenvalues ε_i.

The one electron energies can be found by diagonalizing the matrix $(H - \mathcal{E}\mathcal{O})$.

A commonly used basis is the set of muffin-tin orbitals. Muffin-tin orbitals are solutions to the so called muffin-tin potential,which is an approximation to the real metallic potential. The muffin-tin potential is spherically symmetric inside spheres of radius s_R surrounding atomic sites and constant in the so called *interstitial region* between those sites. The potential is given by

$$V_{mt}(\mathbf{r}) = \sum_R \theta_R(r_R)V_R(r_R) + \theta_i(\mathbf{r})V_i,$$

where θ is one inside the corresponding region and zero outside, and V_R and V_i are respectively the potentials inside the spheres and in the interstitial regions.

This muffin-tin potential is not exactly equal to the Kohn-Sham potential. There is a part left over.

$$V_{ks} = V_{mt} + V_{nmt},$$

where we call V_{nmt} the non muffin-tin part of the potential.

Each orbital $\chi(\mathbf{r_R})$ consists of a component inside the sphere where it is centered, which we call the *head* of the orbital, and a component outside its own sphere: its *tail*.

Because the muffin-tin potential is split up into two potentials, one inside the atomic spheres and one in the interstitial region, the solution to the Kohn-Sham equation with $V_s = V_{mt}$ can be written as a linear combination of so called *partial waves* $\phi_{RL}(E, \mathbf{r_R})$ with different energies

$$\psi(E, \mathbf{r}) = \sum_{RL} \theta_R(r_R)\phi_{RL}(E, \mathbf{r_R})b_{RL}, \tag{12}$$

where the b are expansion coefficients.
Because the muffin-tin potential is spherically symmetric inside the atomic spheres the partial waves can be split up into a radial and an angular component.

$$\phi_{RL}(E, \mathbf{r_R}) = \phi_{R\ell}(E, r_R)Y_L(\hat{\mathbf{r}_R}),$$

where the Y_L are spherical harmonics, which are solutions to the angular part of the Schrödinger equation, and the radial functions $\phi_{R\ell}(E, r)$ are solutions to the radial part of the Schrödinger equation.

$$\frac{d^2}{dr^2}[r\phi_{R\ell}(E, r)] = [V_R(r) + \frac{\ell(\ell+1)}{r^2} - E]r\phi_{R\ell}(E, r).$$

7

We will now introduce the so called *logarithmic derivative*, which is defined as

$$D_{R\ell}(E) \equiv s_R \frac{d}{dr} \ln[\phi_{R\ell}(E, s_R)] = s_R \frac{\phi'_{RL}(\mathcal{E}, s_R)}{\phi_{R\ell}(\mathcal{E}, s_R)}, \tag{13}$$

and is related to the slope of the radial functions $\psi_{R\ell}$ at the sphere boundaries. We will make frequent use of the logarithmic derivative in the coming sections.
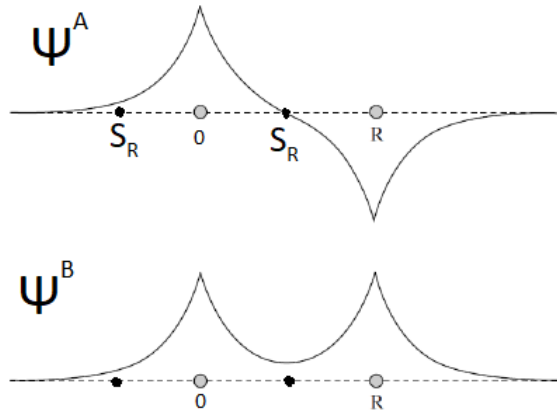
3.2 Tail augmentation

Figure 1: Bonding (Ψ^B) and anti-bonding (Ψ^A) wavefunctions of a one-dimensional two site system. The atoms are centered at 0 and R and the radius of the muffin-tin orbital around 0 is s_R.

The LCAO method and the method of partial waves both have their advantages and disadvantages. The LCAO method transforms the Kohn-Sham equation into an eigenvalue problem, which is not difficult to solve. To give accurate solutions it does, however, need a reasonably complete basis set, which requires many different basisfunctions χ.

The method of partial waves can give solutions to arbitrary accuracy, but to obtain this solution of set of equations with a non-linear energy dependence needs to be solved.

It would thus be desirable to find a method which has all the advantages of the LCAO and partial waves methods but non of the disadvantages. To explain how the LCAO method and the method of partial waves can be combined we first look at a simple one-dimensional two site example with one atom at the origin and one at position R. In this case (9) reduces to

$$\psi_A^B = \chi(r) \pm \chi(r - R), \tag{14}$$

where the constants c can be left out because they are equal by symmetry and can thus be embedded into the basis functions χ.

This system thus has two possible states. The anti-bonding state ψ^A, which corresponds to an energy A, and the bonding state ψ^B, which corresponds to an energy B.

The bonding and anti-bonding states are shown in Figure 1. Each of these states belongs to one particular energy (A or B) and can thus be described by a single energy-dependent partial wave.

In Figure 1 it can be seen that the anti-bonding wavefunction has a node at the sphere radius s_R. At that point the logarithmic derivative in (13) becomes infinite. The partial wave for this state can thus be found as:

$$\psi_A = \phi(A, r) \tag{15}$$

if the logarithmic derivative of A satisfies

$$D(A) = \infty.$$

Similarly in the bonding state the radial wave-function has zero slope at the sphere radius and the logarithmic derivative is thus zero:

$$\psi_B = \phi(B, r) \tag{16}$$

if the logarithmic derivative of B satisfies

$$D(B) = 0.$$

To combine the LCAO and the partial wave method, equations (14), (15) and (16) must all be true,and inside the sphere at the origin the orbital centered at R must satisfy

$$\chi(r - R) = [\phi(B, r) - \phi(A, r)]/2. \tag{17}$$

But $\chi(r-R)$ is a localized energy independent basis function centered at position R and we cannot expect it to everywhere match this combination of energy-dependent partial waves. We can expect only that it matches at the boundary of the sphere.

We must thus find a way to satisfy (17). This can be done by choosing the basis functions χ to be the atomic orbitals whose tails are *augmented* to fit $[\phi(B, r) - \phi(A, r)]/2$ inside other spheres.

In the general case there is a continuous set of states instead of only a bonding and anti-bonding state and the augmentation is done by using the derivative

with respect to energy of the partial waves around some energy E_ν at the center of our interest.

This method is called the *linear* muffin-tin orbitals (LMTO) method because via the Taylor series expansion the relation between partial waves of different energies can be found to linear order as

$$\phi(E, r) \approx \phi(E_\nu, r) + (E - E_\nu)\dot\phi(E_\nu, r),$$

where we us an overdot to indicate a derivative with respect to energy.

$$\dot\phi(E_\nu, r) \equiv \left.\frac{\partial\phi(E, r)}{\partial E}\right|_{E=E_\nu}.$$

We will from this point on use the notation $\phi(r) = \phi(E_\nu, r)$.

Because of this augmentation by the energy derivative the new basis functions χ cannot be written as a linear combination of only the partial waves. The energy derivative has to be included as well

$$\chi(\mathbf{r}) = \sum_{RL}[\phi_{RL}(\mathbf{r_R})\Pi_{RL} + \dot\phi_{RL}(\mathbf{r_R})\Omega_{RL}] + \chi_i(\mathbf{r}), \tag{18}$$

where χ_i is the component of the basis function in the interstitial region and for notational simplicity the θs are dropped.

To obtain a physical solution, these basis functions and their derivatives need to be continuous. The matrices Π and Ω are coefficient matrices chosen such that the basis functions satisfy this condition.

It is convenient to write (18) in matrix form.

$$|\phi\rangle\Pi + |\dot\phi\rangle\Omega + |\chi\rangle^i = |\chi\rangle^\infty, \tag{19}$$

where $|\rangle$ and $|\rangle^i$ denote functions defined in respectively an atomic sphere and the interstitial region.

3.3 Hamiltonian and Atomic Spheres Approximation

Without loss of generality the partial waves ϕ can be chosen to be normalized inside their sphere.

$$\langle\phi_{RL}|\phi_{RL}\rangle \equiv \int_0^{s_R} \phi_{R\ell}^2(E, r)r^2 dr = 1$$

By differentiating this expression with respect to the energy we see that ϕ and $\dot\phi$ must be orthogonal.

$$\langle\phi_{RL}|\dot\phi_{RL}\rangle = \int_0^{s_R} \phi_{R\ell}(E, r)\dot\phi_{R\ell}(E, r)r^2 dr = 0.$$

10

The partial waves are solutions to the Schrödinger equation with the muffin-tin potential inside the spheres.

$$[-\frac{\hbar^2}{2m}\nabla^2 + V_R(r)]\phi_{RL}(E,\mathbf{r}) = E\phi_{RL}(E,\mathbf{r}). \tag{20}$$

We are interested in the region around the energy $E = E_\nu$. Near this energy the Schrödinger equation can be written in bra-ket notation as

$$(-\frac{\hbar^2}{2m}\nabla^2 + V_R(r) - E_\nu)|\phi\rangle = 0,$$

and by differentiating (20) with respect to energy we obtain

$$(-\frac{\hbar^2}{2m}\nabla^2 + V_R(r) - E_\nu)|\dot{\phi}\rangle = |\phi\rangle.$$

Using these expressions, the orthogonality of ϕ and $\dot{\phi}$ and the expression of the basis function χ in (19), the full Hamiltonian matrix including the contribution of the interstitial region and the non-muffin-tin potential in (10) can be written as

$$\langle\chi| - \frac{\hbar^2}{2m}\nabla^2 + V_{ks}|\chi\rangle^\infty = \Pi^*\Omega + \langle\chi| - \frac{\hbar^2}{2m}\nabla^2|\chi\rangle^i + \langle\chi|V_{nmt}|\chi\rangle^\infty$$
$$= H - E_\nu\mathcal{O},$$

where the non muffin-tin potential V_{nmt} is chosen as V_{ks} in the interstitial region, and the overlap matrix can be written as

$$\mathcal{O} = \langle\chi|\chi|\rangle^\infty = \Pi^*\Pi + \Omega^*\langle\dot{\phi}^2\rangle\Omega + \langle\chi|\chi\rangle^i,$$

where $\langle\dot{\phi}^2\rangle$ is a diagonal matrix with elements

$$\langle\dot{\phi}_{RL}^2\rangle = \int_0^{s_R} \dot{\phi}_{r\ell}^2(r)r^2dr.$$

In principle the basis function is known once the matrices Π and Ω are known and the one electron energies can be found. To calculate these matrices one has to integrate over the interstitial region and the non muffin-tin part of the potential. Calculations in the interstitial region can be done with plane waves or muffin-tin orbitals. Plane waves have the disadvantage that a large basis set of 10-50 plane waves is needed to describe the potential in the interstitial region accurately. Muffin-tin orbitals allow us to work with a smaller basis set, but the energies in the interstitial region can, however, not be accurately described with this set.

A more convenient approach, especially in metals, where the atoms are densely packed, is to eliminate the interstitial region by employing the so called *atomic*

spheres approximation (ASA), which is actually a combination of two approximations. The first approximation is that in the interstitial region the kinetic energy $|E - V_i(\mathbf{r})|$ can be treated as a constant independent of the energy. We will use this approximation later.

The second approximation is that around the atomic sites the potential is spherically symmetric, and that these atomic spheres surrounding the atoms can be expanded such that they fill up all of space, with a slight overlap that can be ignored.

The ASA works very well in combination with muffin-tin orbitals, because these orbitals are the solutions to a spherical symmetric potential near the atomic sites. By eliminating the interstitial region in this ASA the muffin-tin orbitals in (19) can be replaced by a new set of basis functions; the so called theta-orbitals, which are orbitals that are augmented in other spheres by only $\dot{\phi}$ functions. These orbitals are obtained by multiplying (19) by Π^{-1} leaving out the interstitial region.

$$|\phi\rangle + |\dot{\phi}\rangle\Omega\Pi^{-1} = |\chi\rangle^\infty\Pi^{-1} = |\Theta\rangle^\infty. \tag{21}$$

In this set of basis function the Hamiltonian matrix can be represented as

$$H = \langle\Theta| - \frac{\hbar^2}{2m}\nabla^2 + V_s|\Theta\rangle^\infty = \Omega\Pi^{-1} + E_\nu\mathcal{O} = h + E_\nu\mathcal{O}, \tag{22}$$

where the matrix h is defined as

$$h = H - E_\nu\mathcal{O} = \Omega\Pi^{-1}, \tag{23}$$

and the overlap matrix is given by

$$\mathcal{O} = \langle\Theta|\Theta\rangle^\infty = 1 + h\langle\dot{\phi}^2\rangle h.$$

The second term of the overlap matrix is second order in h and the real Hamiltonian can to the second order in h be approximated by

$$\tilde{H} = H - E_\nu.$$

The only problem remaining now is finding the matrices Ω and Π in the LMTO formalism.

3.4   Logarithmic derivative

In (13) the logarithmic derivative was defined and it was shown that the bonding and anti-bonding wavefunction in a simple two atom system are related to the logarithmic derivative.
The wavefunctions were later augmented by $\dot{\phi}$ to connect the LCAO and partial

waves method, but to ensure continuity of the wavefunction after the augmentation, the combination of ϕ and $\dot\phi$,

$$\Phi(D,r) \equiv \phi(r) + \omega(D)\dot\phi(r) \tag{24}$$

should have the same logarithmic derivative as the radial function $\phi(\mathbf{r})$. This is the case if we have:

$$\omega(D) = -\frac{\phi(s_R)}{\dot\phi(s_R)}\frac{D - D\{\phi\}}{D - D\{\dot\phi\}},$$

where we use the notation

$$D\{\phi\} = s\frac{d\phi}{dr}(s)/\phi(s),$$

and

$$D\{\dot\phi\} = s_R\frac{d\dot\phi}{dr}(s_R)/\dot\phi(s_R). \tag{25}$$

The variables Φ and ω are called *potential parameters* because their values depend intrinsically on the potential. The virtue of a linear method is that these parameters depend on the potential only via the logarithmic derivative.

$$\omega = \omega(D), \tag{26}$$
$$\Phi = \Phi(D), \tag{27}$$

and according to Andersen [5] the Wronskian relation between two different logarithmic derivatives D_+ and D_- is

$$(D_+ - D_-)s_R\Phi_+\Phi_- = \omega_- - \omega_+, \tag{28}$$

where ω_+ and ω_- are $\omega(D)$ for respectively D_+ and D_-.

3.5   Structure Constants

Muffin-tin orbitals are the solutions of a spherically symmetric potential in spheres surrounding the atomic-sites and are thus angular-momentum eigenfunctions, which can be separated into a radial part and an angular part.

$$\chi_{RL}(\mathbf{r}) = \chi_{R\ell}(r)Y_L(\hat{\mathbf{r}}).$$

In the interstitial region the tail function $\chi^i_{RL}(\mathbf{r})$ is a solution to (7) for a constant potential i.e. to the Helmholtz equation.

$$\nabla^2\chi^i_{RL}(\kappa,\mathbf{r}) + \kappa^2\chi^i_{RL}(\kappa,\mathbf{r}) = 0, \tag{29}$$

where $\kappa^2 = E - V$ is a constant. Because the packing of the atomic spheres in metal is very close, especially in the ASA, κ^2 is very small and for simplicity we make the choice $E = V$, such that $\kappa^2 = 0$.

In this case (29) reduces to the Laplace equation whose solutions are proportional to $r^{-\ell-1}$ and r^ℓ.

The radial part of the tail function extends throughout the whole crystal and must thus be chosen such that it vanishes as r goes to infinity.

$$\chi^i_{R\ell}(r_R) = \left(\frac{r_R}{s}\right)^{-\ell-1},$$

where s is a scaling constant, which can be chosen arbitrarily.

In the LMTO method the tail function is augmented in all spheres. It can thus be expanded around the other sites using the multipole expansion[1].

$$\left(\frac{r_R}{s}\right)^{-\ell-1} Y_L(\hat{\mathbf{r}}_\mathbf{R}) = -\sum_{L'}\left(\frac{r_{R'}}{s}\right)^{\ell'}\frac{Y_{L'}(\hat{\mathbf{r}}_{\mathbf{R}'})}{2(2\ell'+1)}S_{R'L',RL} \tag{30}$$

where the coefficients S are called the structure constants, which are given by

$$S_{R'\ell'm',R\ell m} = (4\pi)^{\frac{1}{2}}g_{\ell'm',\ell m}\left(\frac{R-R'}{s}\right)^{-\ell'-\ell-1}Y^\star_{\ell'-\ell,m'-m}(\mathbf{R}\hat{-}\mathbf{R}'), \tag{31}$$

with

$$g_{\ell'm',\ell m} = (-1)^{\ell+m+1}\;2\left[\frac{(2\ell'+1)(2\ell+1)(\ell'+\ell+m'-m)!(\ell'+\ell-m'+m)!}{(2\ell'+2\ell+1)(\ell'+m')!(\ell'-m')!(\ell+m)!(\ell-m)!}\right]^{\frac{1}{2}}.$$

The head and tail of the LMTO must match continuously on the sphere radius s_R and we can thus define the LMTO as

$$\chi_{RL}(\mathbf{r}) = Y_L(\hat{\mathbf{r}})\begin{cases}\Phi^-_{R\ell}(-\ell-1,r) & \text{for } r \leq s_R \\[2mm] \left(\frac{r}{s_R}\right)^{-\ell-1}\Phi^-_{R\ell}(,\ell-1,s_R) & \text{for } r \geq s_R\end{cases}, \tag{32}$$

where $\Phi^-_{R\ell}$ is given by (24), where the logarithmic derivative is $D = -\ell-1$, which is the logarithmic derivative of $r^{-\ell-1}$.

Using (30) and (32) the contribution of an orbital at position R inside a sphere at position R' can be seen to be

$$\chi_{RL}(\mathbf{r}_\mathbf{R}) = -\sum_{L'}\frac{\Phi^+_{R'L'}(r'_R)}{2(2\ell'+1)\phi^+_{R'\ell'}(s'_R)}\left(\frac{s_{R'}}{s}\right)^{\ell'}S_{R'L',RL}\left(\frac{s}{s_R}\right)^{-\ell-1}\Phi^-_{R\ell}(s_R), \tag{33}$$

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[1] For a derivation see J.D. Jackson, *Classical electrodynamics*, pp 145-150.

where $\Phi_{R\ell}^+$ is given by (24) for the logarithmic derivative $D = \ell$, which is the logarithmic derivative of r^ℓ.

3.6 Π and Ω matrices

Equation (33) can be simplified by introducing two new parameters.

$$\sqrt{\Delta} \equiv \left(\frac{s}{s_R}\right)^{-\ell-1} \left(\frac{s}{2}\right)^{\frac{1}{2}} \Phi^-(-\ell-1, s_R),$$

$$\sqrt{\Gamma} \equiv 2(2\ell+1) \left(\frac{s}{s_R}\right)^{\ell} \left(\frac{s}{2}\right)^{\frac{1}{2}} \Phi^+(\ell, s_R) \equiv Q\Delta^{\frac{1}{2}},$$

where Q is called the *screening* parameter.

Using these parameters the relation from (28) can be rewritten as

$$\sqrt{\Delta}\sqrt{\Gamma} = (2\ell+1)s_R\Phi^-(-\ell-1, s_R)\Phi^+(\ell, s_R) = \omega_- - \omega_+, \tag{34}$$

where ω_+ and ω_- are $\omega(D)$ for respectively $D = \ell$ and $D = \ell - 1$.

Using the potential parameters, (33) can be written as

$$\chi_{RL}(\mathbf{r_R}) = -\sum_{L'} \Phi_{R'L'}^+(r'_R)\Gamma_{R'L'}^{-1/2} S_{R'L',RL}\Delta_{RL}^{1/2}. \tag{35}$$

Equation (32) gives the shape of the LMTO inside its own sphere and (35) gives the contribution to the LMTO inside this sphere from the LMTOs centered at other sides. Taking into account all these contributions, the complete basis functions can be written in matrix notation as

$$|\Phi^-\rangle - |\Phi^+\rangle\Gamma^{-\frac{1}{2}}S\Delta^{\frac{1}{2}} + |\chi\rangle^i = |\chi\rangle^\infty. \tag{36}$$

According to (24) the functions Φ_+ and Φ_- are given by

$$|\Phi_+\rangle = |\phi\rangle + \omega_+|\dot\phi\rangle,$$
$$|\phi_-\rangle = |\phi\rangle + \omega_-|\dot\phi\rangle,$$

and the expressions for the Π and Ω matrix are then given by

$$\Pi = 1 - \Gamma^{-\frac{1}{2}}S\Delta^{\frac{1}{2}} \tag{37}$$

and

$$\Omega = \omega_- - \omega_+\Gamma^{-\frac{1}{2}}S\Delta^{\frac{1}{2}} \tag{38}$$

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3.7   LMTO-ASA Hamiltonian

Using the atomic sphere approximation (ASA), the interstitial region is eliminated and the Hamiltonian can be written as in (22). The matrices Π^{-1} and Ω in the Hamiltonian can be obtained from (37) and (38) as

$$\Pi^{-1} = \Delta^{-\frac{1}{2}}(Q-S)^{-1}\Gamma^{\frac{1}{2}},$$

and

$$\Omega = (\omega_- + \omega_+) + \omega_+ \Gamma^{-\frac{1}{2}}(Q-S)\Delta^{\frac{1}{2}},$$

where Q is now used as a diagonal matrix with the values Q_{RL} on its diagonal.

Using these relations and (34) and (22) we obtain an expression for $h = \Omega\Pi^{-1}$.

$$h = \Gamma^{\frac{1}{2}}(Q-S)^{-1}\Gamma^{\frac{1}{2}} + \omega_+$$
$$= \Delta^{\frac{1}{2}}S(1-Q^{-1}S)^{-1}\Delta^{1/2} + \omega_-.$$

The full Hamiltonian can then be obtained as

$$\tilde{H}_{RL,R'L'} = \Delta^{\frac{1}{2}}_{R\ell}\tilde{S}_{RL,R'L'}\Delta^{\frac{1}{2}}_{R'\ell'} + \omega_- + E_{\nu R\ell} \tag{39}$$

$$= \Delta^{\frac{1}{2}}_{R\ell}\tilde{S}_{RL,R'L'}\Delta^{\frac{1}{2}}_{R'\ell'} + C_{R\ell}\delta_{RR'}\delta_{LL'}, \tag{40}$$

where the $\tilde{S}$ denote the *screened structure constants*.

$$\tilde{S} = S(1-Q^{-1}S)^{-1}.$$

This is the reason why we call Q, the screening parameter, because it relates the ordinary structure constants S to the screened structure constants $\tilde{S}$.

3.8   Canonical Bands

We start by discussing the case without screening, which is obtained by setting the screening matrix $Q^{-1} = 0$. The screened structure constants then reduce to the ordinary structure constants and the Hamiltonian can be written as

$$H = C + \sqrt{\Delta}S\sqrt{\Delta}.$$

Our goal is the find the so-called energy bands $\varepsilon(\mathbf{k})$, which describe the energies that electrons can have.

To calculate these energy bands one needs to transform the Hamiltonian from real space into the so-called *k-space*, which is essentially the Fourier transform of the real lattice. The Hamiltonian is transformed from real space to k-space by performing a Bloch summation over all the atoms in the lattice.

$$H^k_{\ell m,\ell'm'} = \sum_{\mathbf{R}\neq 0} e^{i\mathbf{k}\cdot\mathbf{R}}H_{0L,RL'} \tag{41}$$

As taking a summation over an infinite lattice is not possible, the Bloch summation must be performed only over all neighbours within a certain radius. This can be done by setting up the 3 spanning vectors such that the lattice can be generated by a linear combination of these vectors. We will do a sample calculation for vanadium, which has a bcc (body centered cubic) lattice, which is a cubic lattice with lattice points on all its vertices and one in the center of the cube. Another useful lattice is the fcc (face centered cubic) lattice, which is a cubic lattice with lattice points on all its vertices an on the center of its faces. A bcc lattice is shown in Figure (2). The corresponding lattice vectors are

$$\mathbf{a}_1 = \frac{a}{2} \begin{pmatrix} 1 \\ 1 \\ -1 \end{pmatrix}, \quad \mathbf{a}_2 = \frac{a}{2} \begin{pmatrix} 1 \\ -1 \\ 1 \end{pmatrix}, \quad \mathbf{a}_3 = \frac{a}{2} \begin{pmatrix} -1 \\ 1 \\ 1 \end{pmatrix},$$

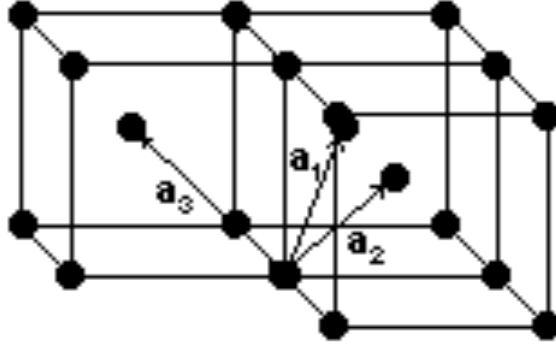where a is the lattice constant, which is the length of one edge of the cubic lattice.

Figure 2: bcc lattice spanned by the vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$.

A lattice of neighbours is then a set containing the linear combinations of these lattice vectors.

$$R_N = \{n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \mid n_1, n_2, n_3 \in \{-N, N\}\}$$

We will call R_N the set containing N shells of neighbours.

To each lattice in real space belongs a *reciprocal lattice* in k-space, spanned by the vectors $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$, which are defined as

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)}$$

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)}.$$

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As the scaling matrices Δ and Γ are independent of the shape of the lattice, the Bloch summation can be done using only the structure constants.

$$S^k_{\ell m, \ell' m'} = \sum_{\mathbf{R} \in R_N} e^{i\mathbf{k} \cdot \mathbf{R}} S_{0L, RL'}.$$

The so-called *canonical bands* can be obtained by neglecting *hybridization*, which is the influence the different bands have on each other. This can be done by separately diagonalizing the diagonal blocks $\ell = \ell'$ of the matrix $S^k_{\ell m, \ell' m'}$.

Energy bands are drawn between so called *high symmetry points*, which are points in k-space that represent the symmetry of the lattice. Some high symmetry points are listed in table 1.

The bcc canonical *d*-bands ($\ell = 2$) are shown in Figure 4.

High symmetry point	position in k-space
Γ	(0,0,0)
N	$(0,\pi/a,\pi/a)$
P	$(\pi/a, \pi/a, \pi/a)$
H	$(0,0,2\pi/a)$
X	$(0,2\pi/a,0)$
W	$(\pi/a,2\pi/a,0)$
K	$(3\pi/2a,3\pi/2a,0)$
L	$(\pi/a,\pi/a,\pi/a)$

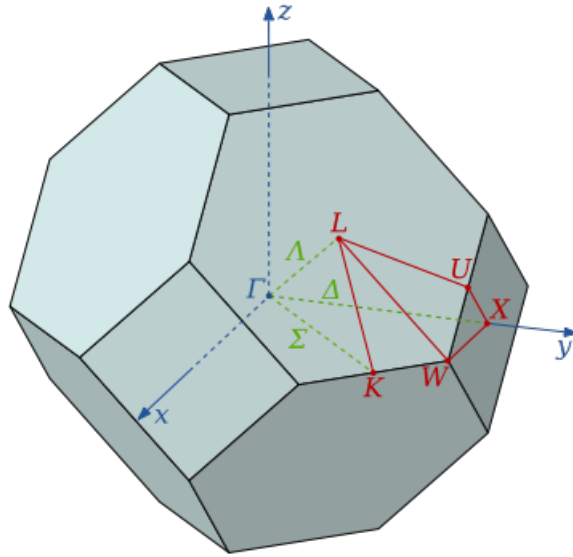Table 1: High symmetry points and their position in k-space.

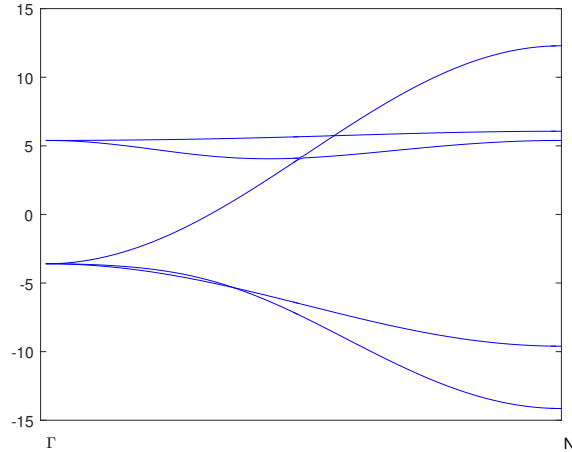Figure 3: Some high symmetry points for an fcc lattice in k-space.

Figure 4: Canonical d-bands for a bcc lattice calculated with 20 shells of neighbours. The bands are dimensionless and are shown between the two high symmetry points Γ and N. These canonical bands give a first order approximation of the real energy of bcc materials.

Energy bands represent the energy that electrons can have. Each line in a band diagram is a dispersion relation $\varepsilon(\mathbf{k})$, which matches a point in k-space to a

correspond electron energy. Because the structure constants are dimensionless quantities, the canonical bands are also dimensionless. Their dimensionless values are those for the structure constants in (31) when s is chose as the so-called Wigner-Seitz radius.

$$s = a\left(\frac{3}{8\pi}\right)^{\frac{1}{3}}$$

The convergence of the canonical bands can be made a bit more concrete by looking at the behaviour of one of the bands at the point Γ for a different number of shells of neighbours, as shown in Table 2. It can be seen from the last column of the table that the effect of taking into account more neighboring shells becomes weaker very quickly. The canonical bands obtained will thus quickly converge.

Neighbour shells	Energy at Γ	Contribution of new shells
1	-3.852	-3.852
2	-3.685	0.168
4	-3.623	0.062
8	-3.603	0.020
16	-3.598	0.005
32	-3.596	0.002

Table 2: Energy of the lowest bcc canonical bands at the high symmetry point Γ computed with various numbers of shells of neighbours.

3.9 Hybridized Bands

The canonical bands are very similar to real energy bands. They form a dimensionless template for the real energy bands, but to obtain the real bands three additional steps have to be made.

Firstly the structure constants have to be screened by the screening parameter Q.

Because both the structure constants and the screening parameter are dimensionless, the bands have to be scaled and positioned at the right energy for a specific system, which is done by the parameters Δ (or Γ) and C respectively.

All of these steps are incorporated in the Hamiltonian in (40). The corresponding Hamiltonian in k-space is given by (41) by replacing H with $\tilde{H}$.

The last step to obtain real energy bands is by applying *hybridization*. Hybridization is the influence that the different energy bands have on each other. The hybridization is applied by diagonalizing the entire k-space Hamiltonian instead of diagonalizing each diagonal block $\ell = \ell'$ at a time. The energy bands that result from this diagonalization are called the *hybridized bands*. The shape

of these bands depends on the potential parameters, such as E_ν, ω_-, Φ^- and Φ^+. These parameters are all material dependent and can be found in literature [5]. In Figure 5 the hybridized energy bands for bcc-vanadium are shown.
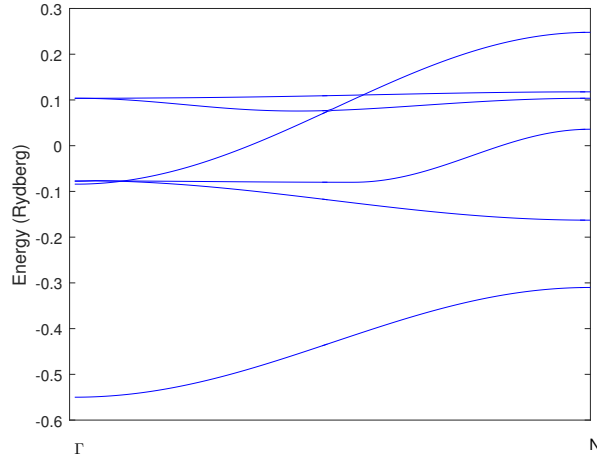

Figure 5: Hybridized energy bands for bcc vanadium calculated with two shells of nearest neighbours.

The Hybridized energy bands are real energy bands, meaning that each line represents a dispersion relation $\varepsilon(\mathbf{k})$ for an electron. All the possible energies an electron can have, can be found in such a band diagram.

The numerical convergence of the LMTO method is very good. From Table 3 it can be seen that the influence of adding a second shell of nearest neighbours on the energies is already very small and that further shells will contribute very little.

$N = 1$	$N = 2$
-0.5678	-0.5757
-0.0804	-0.0824
-0.0770	-0.0816
-0.0736	-0.0808
0.1054	0.1099
0.1055	0.1099

Table 3: Energies of the hybridized vanadium bands in Rydberg at the point Γ for a different number of neighboring shells.

Using the LMTO code written by Andersen and Jepsen, band structures can be calculated efficiently and with great accuracy. Figures (6), (7) and (8) show

the band structures of vanadium, copper and cobalt respectively. These band structures were calculated using the LMTO code.

For cobalt two band structures are shown. This is because cobalt is a magnetic material. Where in non-magnetic materials all electrons have identical band structures, in magnetic materials the spin of an electron plays an important role. Spin can be conceived as the rotational angular momentum of the electron. This is however not completely true, because electron spin can only take two values, spin up (majority spin) or spin down (minority spin). In magnetic materials electrons tend to align their spin to the magnetic field, and one spin is favoured over the other. In cobalt this has as a consequence that majority spin electrons have lower energies than minority spin electrons, resulting in two distinct band structures.
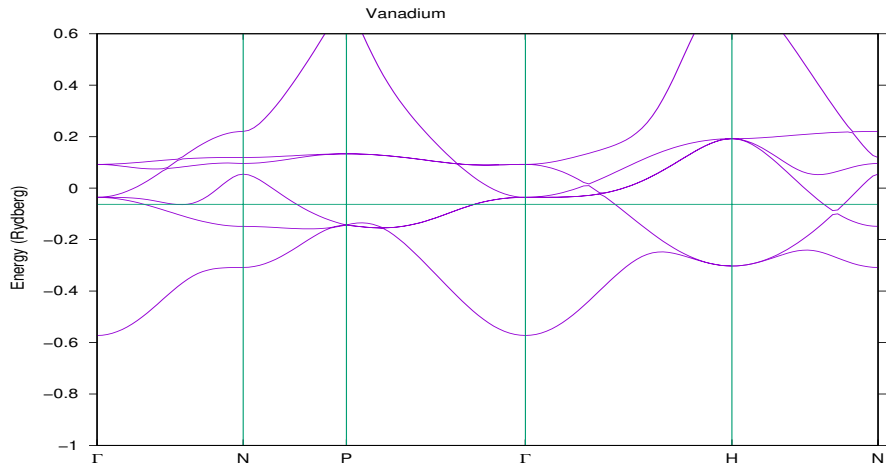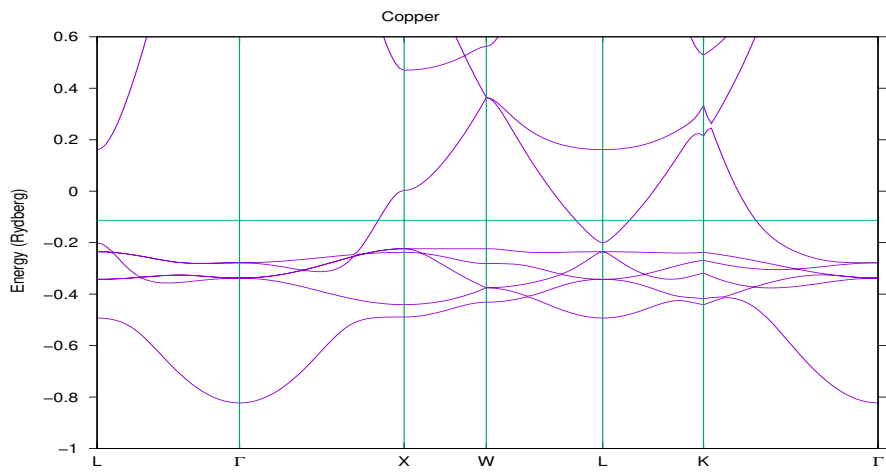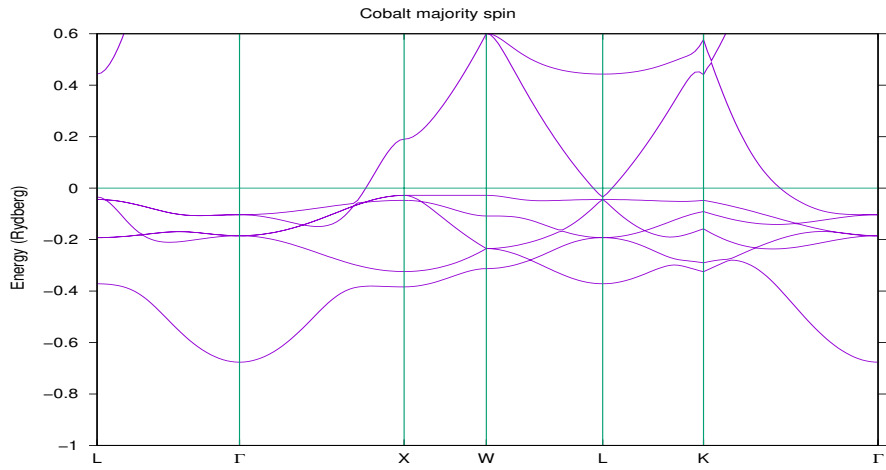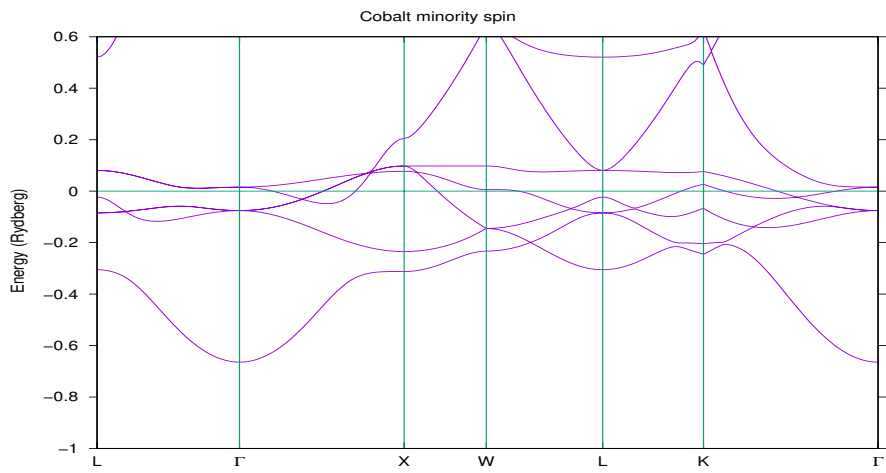
Figure 6: Vanadium energy bands.

Figure 7: Copper energy bands.

Figure 8: Energy bands for (a) majority spin cobalt and (b) minority spin cobalt electrons. Because Cobalt is magnetic the minority spin bands lie at higher energies than the majority spin bands.
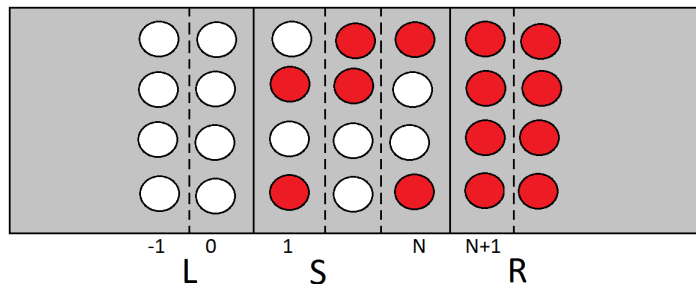
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4 Transport

4.1 Scattering Formalism

Figure 9: Schematic of the configuration used for transport calculations. A scattering region S is sandwiched by left (L) and right (R) leads. The scattering region is divided into N layers.

One of the applications of muffin-tin orbitals is the calculation of the conductance of metallic interfaces, such as the one depicted in Figure 9. Such an interface can be divided into three regions: The left and right leads, which are assumed to be ideal and periodic conductors, such that the Bloch theorem can be used, and the scattering region, which is the region sandwiched between these two ideal leads.

In electronic transport the concept of a *scattering matrix* is very important. Scattering matrices are used to relate incoming and outcome waves trough a barrier.

$$\begin{pmatrix} F \\ G \end{pmatrix} = \begin{pmatrix} t & \gamma \\ \gamma^* & t^* \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix},$$

where A and B are the amplitudes of respectively the right-going and the left-going waves in the left lead, and F and G are the amplitudes of respectively the right and left-going waves in the right lead. In the scattering matrix the coefficient t is the probability that a right going wave on the left is transmitted to a right going wave on the right.

Conductance through an interface can be described in terms of scattering matrices by the Landauer-Bütticker formula.

$$G = \frac{e^2}{h} \sum_{n,m} |t_{n,m}|^2, \tag{42}$$

where $t_{n,m}$ is the probability that a state n in the left lead scatters into a state m in right lead.

For this purpose we are concerned with only a single energy and it is desirable not to expand the wavefunction $\psi(\mathbf{r})$ in a basis of linear muffin-tin orbitals, but to expend it into energy dependent orbitals. We define the radial part of these orbitals as

$$\chi_{R\ell}(E,r) = \begin{cases} \phi(E,r) - \dfrac{D_{R\ell}(E)+\ell+1}{2\ell+1}\left(\dfrac{r}{s_R}\right)^{\ell}\phi_{R\ell}(E,s_R) & \text{for } r \leq s_R \\ \dfrac{\ell - D_{R\ell}(E)}{2\ell+1}\left(\dfrac{r}{s_R}\right)^{-\ell-1}\phi_{R\ell}(E,s_R) & \text{for } r \geq s_R. \end{cases}$$

Defined this way the MTO is continuous and differentiable everywhere, and is thus a physical basis function. The notation can be cleaned up by introducing two new quantities.

$$|r_+\rangle \equiv \left(\frac{r_R}{s_R}\right)^{\ell} \frac{Y_L(\hat{r}_R)}{2(2\ell+1)},$$

and

$$P(E) \equiv 2(2\ell+1)\frac{D(E)+\ell+1}{D(E)-\ell}, \tag{43}$$

where $P(E)$ is called the *potential function*.

We can still use (30) to expand the tails of the orbitals. The total orbital can thus be written in matrix form as

$$|\phi(E)\rangle + |r_+\rangle\big[P(E)-S\big]\chi(E,s_R) = |\chi(E)\rangle^{\infty}.$$

The wavefunction can be found as a linear combination of these MTO's centered at different sites.

$$\Psi(E,\mathbf{r}) = \sum_{RL} \chi(E,\mathbf{r_R})C_{RL}. \tag{44}$$

The wavefunction can thus be represented by the expansion coefficients.

$$\mathbf{\Psi} = \begin{pmatrix} \vdots \\ c_{i-1} \\ c_i \\ c_{i+1} \\ \vdots \end{pmatrix}.$$

From the partial wave point of view we already know that $\phi(E,r)Y_L(\hat{\mathbf{r}})$ is a solution to the Schrödinger equation. The only way that the expansion of orbitals in (44) holds is if the tails from all orbitals cancel inside each atomic sphere, i.e.

$$\sum_{R'L'} \Big[P_{RL}(E)\delta_{RR'}\delta_{LL'} - S_{RL,R'L'} \Big] C_{R'L'} = 0.$$

This is called the *tail cancellation equation.*

For performing calculations it is impractical that the MTO's have an infinite range. This can be solved in a simple way by introducing screening constants $\alpha_{R\ell}$ such that the tail-cancellation equation changes to

$$\sum_{R'L'} \Big[P_{RL}^{\alpha}(E)\delta_{RR'}\delta_{LL'} - S_{RL,R'L'}^{\alpha} \Big] C_{R'L'}^{\alpha} = 0, \tag{45}$$

Where the screened potential function matrix and the screened structure constants are given by [6]

$$P_{\ell}^{\alpha}(E) = P_{\ell}(E)\Big[1 - \alpha P_{\ell}(E) \Big]^{-1},$$

$$S_{RL,R'L'}^{\alpha} = S_{RL,R'L'}\Big[1 - \alpha S_{RL,R'L'} \Big]^{-1}.$$

Due to this screening the structure constants can have a very short range. The set of screening constants for which the range of the structure constants is minimized is denoted by $\beta_{R\ell}$.

We will take into account only the interaction between neighbouring layers. The structure constant matrix can then be written as

$$\mathbf{S} = \begin{pmatrix} \ddots & \cdots & 0 & 0 & 0 \\ \vdots & \mathbf{S}_{i-1,i-1} & \mathbf{S}_{i-1,i} & 0 & 0 \\ 0 & \mathbf{S}_{i-1,i} & \mathbf{S}_{i,i} & \mathbf{S}_{i+1,i} & 0 \\ 0 & 0 & \mathbf{S}_{i,i+1} & \mathbf{S}_{i+1,i+1} & \vdots \\ 0 & 0 & 0 & \cdots & \ddots \end{pmatrix}, \tag{46}$$

Where the structure matrix $\mathbf{S}_{i,j}$ denotes the structure interactions between sites in layer i and j.

Using (46) we can write out the tail cancellation equation in its terms to obtain the so-called *equation of motion.*

$$-\mathbf{S}_{i,i-1}^{\beta}\mathbf{C}_{i-1} + \Big(\mathbf{P}_{i,i}^{\beta}(\mathcal{E}) - \mathbf{S}_{i,i}^{\beta} \Big)\mathbf{C}_i - \mathbf{S}_{i,i+1}^{\beta}\mathbf{C}_{i+1} = 0, \tag{47}$$

where $\mathbf{C}_i$ is an M dimensional vector, where $M = (\ell_{max} + 1)^2 N$, N is the number of sites in a layer and $(\ell_{max} + 1)^2$ is the number of orbitals used per atomic site.

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4.2 Leads

In a periodic potential, such as in an ideal metal, the wavefunction should satisfy Bloch's theorem and the expansion coefficients $\mathbf{C}$ should be related by

$$\mathbf{C}_n = \lambda \mathbf{C}_{n-1}, \tag{48}$$

where λ is the Bloch phase factor.

$$\lambda = e^{i\mathbf{k}\cdot\mathbf{T}},$$

with $\mathbf{T}$ the vector connecting two equivalent sites in neighbouring layers.

Using (48) the equation of motion can be written in matrix form.

$$\begin{pmatrix} \mathbf{S}_{i,i+1}^{-1}(\mathbf{P}_{i,i} - \mathbf{S}_{i,i}) & \mathbf{S}_{i,i+1}^{-1}\mathbf{S}_{i,i-1} \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \mathbf{C}_i \\ \mathbf{C}_{i-1} \end{pmatrix} = \lambda \begin{pmatrix} \mathbf{C}_i \\ \mathbf{C}_{i-1} \end{pmatrix}$$

This eigenvalue problem has $2M$ eigenvalues and eigenvectors. The eigenvectors are divided into M right-going waves and M left-going waves.

Following the notation introduced by Ando [1], let $\mathbf{u}_1(-),\ldots,\mathbf{u}_M(-)$ be the vectors $\mathbf{C}_0$ of the left-going solutions corresponding to the eigenvalues $\lambda_1(-),\ldots,\lambda_M(-)$ and $\mathbf{u}_1(+),\ldots,\mathbf{u}_M(+)$ the vectors $\mathbf{C}_0$ of the right-going solutions corresponding to the eigenvalues $\lambda_1(+),\ldots,\lambda_M(+)$.

We then define $U(\pm)$ and $\Lambda(\pm)$ as the matrices

$$U(\pm) = (\mathbf{u}_1(\pm)\ldots\mathbf{u}_M(\pm)),$$

and

$$\Lambda(\pm) = \begin{pmatrix} \lambda_1(\pm) & & \\ & \ddots & \\ & & \lambda_M(\pm) \end{pmatrix}.$$

Any solution to the equation of motion at in the layer $\mathbf{C}_0$ can be written as a linear combination of left or right going solutions.

$$\mathbf{C}_0(\pm) = U(\pm)\mathbf{C}(\pm),$$

where $\mathbf{C}(\pm)$ is a vector of expansion coefficients.

By (48) in general any solution can be written as

$$\mathbf{C}_j(\pm) = U(\pm)\Lambda(\pm)^j\mathbf{C}(\pm).$$

Two solutions can be related as

$$\mathbf{C}_j(\pm) = F(\pm)^{j-j'}\mathbf{C}'_j(\pm), \tag{49}$$

with

$$F(\pm) = U(\pm)\Lambda(\pm)U^{-1}(\pm).$$

4.3 Scattering region

Now that the relation between two solutions is known, it can be applied to a scattering problem. We consider the scattering problem shown in Figure 9: a scattering region consisting of N layers, which has an ideal lead attached to both its left and right side.

By linearity of the wave equation the total amplitude of the wave at each cell can be written as the sum the right-going and the left-going waves at that point.

$$\mathbf{C}_j = \mathbf{C}_j(+) + \mathbf{C}_j(-).$$

We consider the case where a current is sent into the left lead. At the left end of the scattering region there are left-going and right-going solutions resulting from reflection and transmission. Using (49) the amplitude at cell -1 inside the left lead can then be related to the amplitude at cell 0.

$$\mathbf{C}_{-1} = F^{-1}(-)\mathbf{C}_0 + [F^{-1}(+) - F^{-1}(-)]\mathbf{C}_0(+).$$

The equation of motion at cell 0 can then be written as

$$-\mathbf{S}^{\beta}_{0,-1}\mathbf{C}_{-1} = (\mathbf{P}^{\beta}_{0,0} - \mathbf{S}^{\beta}_{0,0})\mathbf{C}_0 - \mathbf{S}^{\beta}_{0,1}\mathbf{C}_1 = 0,$$

which becomes:

$$(\mathbf{P}_{0,0} - \tilde{\mathbf{S}}_{0,0})\mathbf{C}_0 - \mathbf{S}_{0,1}\mathbf{C}_1 = \mathbf{S}_{0,-1}[F^{-1}(+) - F^{-1}(-)]\mathbf{C}_0(+),$$

with

$$\tilde{\mathbf{S}}_{0,0} = \mathbf{S}_{0,0} + F^{-1}(-). \tag{50}$$

This expression shows the basis principle of the *wave function matching method*. By matching the waves coming from the left lead with the waves in the scattering region, the wave amplitude in all layers in the left lead can be written in terms of the amplitude $\mathbf{C}_0$ and the whole left lead essentially turns into a single layer $\mathbf{C}_0$.

To the right of the scattering region there are only right-going waves, because the right lead,as an ideal conductor, does not reflect. Amplitudes of successive layers in this lead can thus written in terms of the previous layer.

$$\mathbf{C}_{N+2} = F(+)\mathbf{C}_{N+1}.$$

The equation of motion in layer $N + 1$ can then be written as

$$(\mathbf{P}_{N+1,N+1} - \tilde{\mathbf{S}}_{N+1,N+1})\mathbf{C}_{N+1} - \mathbf{S}_{N+1,N}\mathbf{C}_N = 0. \tag{51}$$

Equations (50) and (51) can be seen as boundary conditions on the scattering region, and the problem of finding the conductance through the interface is reduced from a problem over an infinite region to a problem over only the scattering region.

For the whole scattering region the tail cancellation matrix can be written as

$\mathbf{P} - \tilde{\mathbf{S}} =$

$$\begin{pmatrix} (P - \tilde{S})_{0,0} & -S_{0,1} & 0 & \cdots & 0 & 0 \\ -S_{1,0} & (P - S)_{1,1} & -S_{1,2} & \cdots & 0 & 0 \\ 0 & -S2,1 & (P - S)_{2,2} & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & 0 \\ 0 & 0 & \cdots & \cdots & (P - S)_{N,N} & -S_{N,N+1} \\ 0 & 0 & 0 & \cdots & -S_{N+1,N+1} & (P - \tilde{S})_{N+1,N+1} \end{pmatrix}.$$

The scattering problem can then written as a set of in-homogeneous linear equations.

$$(\mathbf{P} - \tilde{\mathbf{S}}) \begin{pmatrix} \mathbf{C}_0 \\ \mathbf{C}_1 \\ \mathbf{C}_2 \\ \vdots \\ \mathbf{C}_N \\ \mathbf{C}_{N+1} \end{pmatrix} = \begin{pmatrix} S_{0,-1}[F^{-1}(+) - F^{-1}(-)]\mathbf{C}_0(+) \\ 0 \\ 0 \\ \vdots \\ 0 \\ 0 \end{pmatrix}.$$

The solution to which is given by

$$\begin{pmatrix} \mathbf{C}_0 \\ \mathbf{C}_1 \\ \mathbf{C}_2 \\ \vdots \\ \mathbf{C}_N \\ \mathbf{C}_{N+1} \end{pmatrix} = \mathbf{g} \begin{pmatrix} S_{0,-1}[F^{-1}(+) - F^{-1}(-)]\mathbf{C}_0(+) \\ 0 \\ 0 \\ \vdots \\ 0 \\ 0 \end{pmatrix},$$

where $\mathbf{g}$ is defined as

$$\mathbf{g} = (\mathbf{P} - \tilde{\mathbf{S}})^{-1}.$$

The amplitude of the wave at the right of the scattering region $\mathbf{C}_{N+1}$ can now be related to the incoming wave amplitude $\mathbf{C}_0$.

$$\mathbf{C}_{N+1} = g_{N+1,0} S_{0,-1}[F^{-1}(+) - F^{-1}(-)]\mathbf{C}_0(+) \tag{52}$$

From this expression the transmission coefficient $t_{\mu\nu}$ for a incident wave ν with velocity v_ν and outgoing wave μ with velocity v_μ can be expressed as

$$t_{\mu\nu} = \left(\frac{v_\mu}{v_\nu}\right)^{1/2} \{U^{-1}(+)g_{N+1,0}S_{0,-1}[F^{-1}(+) - F^{-1}(-)]U(+)\}_{\mu\nu} \qquad (53)$$

Now the conductance of the interface can be calculated using the Landauer-Buttiker equation (42).
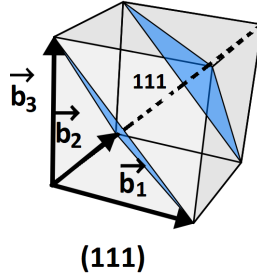
4.4 Cu-Co interface

Figure 10: Cubic crystal with (111) planes shown in blue. These planes are perpendicular to the vector $1\mathbf{b_1} + 1\mathbf{b_2} + 1\mathbf{b_3}$ indicated by the broken line.

We are now ready to commit ourselves to finding the conductance through a copper-cobalt interface.

The wavefunction matching method explain previously can be used for this situation. We are interested in transport across the (111) plan, which is the plane in a cubic crystal perpendicular to the reciprocal lattice vector $1\mathbf{b_1} + 1\mathbf{b_2} + 1\mathbf{b_3}$, as shown in Figure (10). We use the transport code developed by the chair of Computational Materials Science, in which the scattering formalism is combined with the wavefunction matching method. With this code the transmission coefficients in (53) can be calculated as a function of the Bloch-wave vector parallel to the (111) direction $\mathbf{k}_{||}$.

All the different Bloch states $\mathbf{k}_{||}$ can be visualized by a projection of the Fermi surface onto the a (111) plane, as shown in Figures 11a and 11b for copper and cobalt respectively.
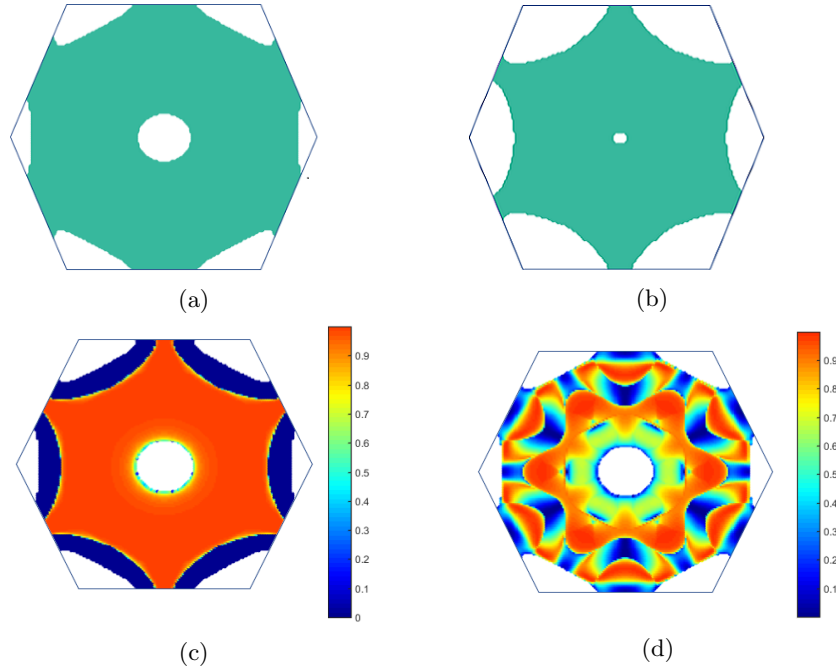
Figure 11: Top row: projection of the Fermi surfaces of copper (a) and cobalt (b) onto the (111) plane, perpendicular to the transport direction. Bottom row: Transmission probability as a function of $\mathbf{k}_{||}$, $T(\mathbf{k}_{||})$ of an ordered copper-cobalt interface for majority spin (c) and minority spin(a). The transmission probability is indicated by the color scheme, with red being complete transmission and blue being total reflection. White indicates points where there is no state.

These Fermi surface projections already give a good estimate of the Transmission probability spectrum for the interface. In ordered interfaces, which we are dealing with now, the crystal momentum parallel to the interface $\mathbf{k}_{||}$ must be conserved. There can only be transmission for a given $\mathbf{k}_{||}$ if their exists a state for it in both copper and cobalt. If there exists a state in copper, but there is no corresponding state in cobalt there will be no transmission and the electron will be totally reflected.

The transmission spectrum for the majority-spin states as shown in Figure 11c follows this intuitive picture quite nicely. It can be seen that if there is no state $\mathbf{k}_{||}$ in either copper or cobalt there is no transmission and for other states the transmission is almost everywhere unity.

The transmission spectrum for the minority-spin states, shown in Figure 11d is more complicated. The transmission is not uniform for the $\mathbf{k}_{||}$ points which exist in both copper and cobalt. This is because of the magnetic properties of cobalt. Due to cobalt's ferromagnetism its 3 minority d-bands are partially lifted

above the Fermi energy, which is the energy of the highest occupied, and are thus only partially occupied.These band can thus all contribute a state $\mathbf{k}_{||}$ for transmission. This means that an propagating state in copper with momentum $\mathbf{k}_{||}$ is transmitted into a combination of the propagating states in cobalt with the same $\mathbf{k}_{||}$.

This however still does not fully explain the minority transmission probabilities. Fur a full explanation the k-points need to be examined one by one. At each point there are different propagating states in copper and cobalt, with odd or even symmetry. Propagating from an even to an odd state and vice versa is not allowed, and at some points this results in vanishing transmission probabilities, while in other points these can become very large.

By comparing the transmission probabilities for the majority and minority spin cases, it can be seen that the total transmission of majority spin electrons is higher than that of the minority spin electrons, by about 20%. In this way ferromagnetic materials like cobalt thus act as a spin-polarizer, allowing more majority spin electrons than minority electrons. Such a polarizer is very useful in the field of *spintronics* (spin electronics), which has many applications, such as hard drives or spin-bases transistors.

5   Summary & Conclusion

In this paper we calculated the energy bands of vanadium, copper and cobalt, and the transmission probability spectrum through a copper-cobalt interface using scattering formalism and wavefunction matching, where the electronic structure was calculated using the LMTO-ASA formalism within the framework of density functional theory.

In particular, we explained how in DFT a $3N$-dimensional quantum mechanical problem is transformed to a 3-dimensional problem, making numerical solutions possible, and how this framework can be implemented using the Schrödinger-like Kohn-Sham equations to obtain solutions for metallic structures.

Furthermore, we explained the method of muffin-tin orbitals and showed that these orbitals form a flexible basis set for solving the Kohn-Sham equations. For energy intervals we showed that these orbitals can be modified to linear muffin-tin orbitals using tail augmentation and can be used to calculate band structures of metals.

We demonstrated that for a single energy the muffin-tin orbitals can be used in combination with the tail cancellation condition to give equations for a scattering problem which can be solved with wavefunction matching to obtain transmission probabilities and subsequently the conductivity of an interface.

We illustrated this method for the case of a copper-cobalt interface and calculated the transmission spectra for transport perpendicular throug the (111)

plane. Lastly we explained how the magnetic properties of cobalt lead to different transmission spectra for majority and minority spin electrons.

Furthermore we have only looked at ordered interfaces with equal lattice parameters in all layers of the scattering region. Real interfaces often have some form of disorder and the lead can have very different lattice parameters. An approach that could be able to take into account disorder and different lattice parameters is by extending the current wave function matching model by the use of *supercells* [6].

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