Ph.D THESIS

Theoretical study of magnetic impurities in low-dimensional systems

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1 Introduction

1.1 Motivation

Thin films and nanoparticles are new devices of high-density magnetic recording and spintronics. Because of challenging quantum phenomena these systems are also preferred subjects of modern solid state research. Important features of the electronic and magnetic structure of nanosystems are often determined/modulated by relativistic spin-orbit (SO) interaction that gives rise, e.g., to the magnetic anisotropy, the anisotropic magnetoresistance, the Kerr and Faraday effects, the Rashba effect, and the anomalous and spin Hall effects. The study of spin-orbit (SO) induced effects in reduced dimension was the main motivation of my Ph.D work.

Impurities in metals cause the so-called residual resistance at $T = 0$ which depends on the concentrations of the impurities (Ref. [1], Sec: 24.4.1). In presence of magnetic impurities, for instance in case of dilute Au(Fe), Cu(Cr), Cu(Fe) alloys, there is a minimum of the resistance at temperatures as low as few Kelvins. The first theoretical explanation of this minimum was given by J. Kondo [2]. The conduction electrons of a nonmagnetic host such as Al, Cu, Ag, Au are scattered on magnetic impurities. The spin of the conduction electrons and of the magnetic impurities can change, but the total spin of the system remains unchanged (Ref. [1], Sec: 24.4.3). The interaction between the conduction electrons and the magnetic impurity is described by an effective $H_{s-d}$ Hamiltonian which contains a coupling constant $J$. Near the Kondo-temperature, $T_K$, in third order to the coupling constant, $J$, the spin-dependent scattering appears as an extra term in the resistance formula,

$$\Delta \rho = -B \ln \left( \frac{T}{T_K} \right),$$  \hspace{1cm} (1)

where the parameter $B$ depends on the host metal and on the impurity. The impurity spin is screened by the conduction electrons with a characteristic coherence length $\xi \sim h v_F/k_B T_K$, where $v_F$ is the Fermi-velocity: in case of Au(Fe) $\xi = 10^5 \text{ Å}$. If the size of the system in any direction is comparable to or less than $\xi$ then we speak about a reduced dimensional system.

The size dependent Kondo-resistance was observed by G. Chen and N. Giordano in the early 90’s in a lot of experiments in thin films (< 2000 Å) of dilute magnetic alloys [3, 4, 5, 6]. The experimental result for Au(Fe) is shown in Fig. 1, displaying the strong thickness-dependence of the parameter $B$.

A few years later, Újsághy et al. [7, 8, 9] proposed an explanation of the experimental observations based on a SO induced magnetic anisotropy in the vicinity of the surface: SO coupling (SOC) gives rise to a level splitting of the impurity spin, thus, blocks the spin-flip
processes responsible for the Kondo effect. It can be supposed that the energy level of the impurity spin splits near the surface and if the energy splitting, $\Delta E(d)$, where $d$ denotes the distance of the impurity from the surface, is larger than $k_B T_K$ the dynamical spin-flip process is suppressed. Clearly, $\Delta E(d)$ should decrease if the impurity is moved away from the surface (at least on average), because by symmetry there is no splitting in the bulk. The so-called 'dead layers' are defined by $\Delta E(d) > k_B T_K$. Notice that for Au(Fe) $T_K = 0.3$ $K \sim 0.03$ $meV$. If the thickness of the dead layers is denoted by $t_c$, see Fig. 2, the resistance $\rho_K(t)$ of the film ($t >> t_c$), can be related to the corresponding bulk value, $\rho_K^{bulk}(t)$ as [7]

$$\rho_K(t) \simeq \left(1 - \frac{2t_c}{t}\right) \rho_K^{bulk}(t) . \quad (2)$$

Indeed, experiments seem to be in agreement with this simple scenario and confirm the predictions that follow from it [10]. Fitting the experimental data for the Au(Fe) film, Űjsághy et al. [7] estimated the width of the dead layer as $t_c \simeq 180$ $\AA$.

To explain the unexpectedly large width of the dead layer, Űjsághy et al. [7] also proposed a model to describe surface magnetic anisotropy, which we shall refer to as the host spin-orbit (HSO) model. In this model an impurity with a half-filled $d$ shell and spin $S = \frac{5}{2}$ is immersed in a host metal, where conduction electrons experience spin-orbit scattering through hybridizing with low-lying $d$ orbitals of the host material [7, 8, 9]. These calculations have been revised recently in Ref. [11]. Reassuringly, the HSO mechanism does not lead to
the splitting of the degenerate spin state of the impurity when placed in a bulk host with cubic or continuous rotational symmetry. However, the presence of the surface induces an anisotropy term,

$$H_{anis}^{HSO} = K^H(d) \left( \vec{n} \vec{S} \right)^2,$$

where $\vec{n}$ is the normal vector of the surface, $\vec{S}$ is the spin operator, and $K^H(d)$ is called the magnetic anisotropy constant (MA) at a distance $d$ from the surface. The anisotropy constant was estimated within a simple free-electron model by treating the spin-orbit coupling and the exchange coupling $J$ perturbatively. This calculation leads to the asymptotic form [11]:

$$K^H(d) = A(k_F) J^2 \xi^2 \frac{\sin(2k_Fd)}{(k_Fd)^3},$$

where $k_F$ is the Fermi wave number. Unfortunately, the constant $A(k_F)$ contains some cutoff parameters, which makes the above formula less predictive for the experiments. It should be noted that Eq. (4) refers to a homogeneous distribution of host atoms, while for the case of a layered geometry and phase coherence, $k_F a = p \pi$, with $a$ and $p$ being the interlayer distance and a positive integer, respectively, a slower decay $K(d) \sim 1/d^2$ has been predicted [11].

Based on density functional theory, L. Szunyogh and B. Győrffy performed ab initio calculations of the MA constant of a Fe impurity in the vicinity of Au surface [12]. They used the so-called Screened Korringa-Kohn-Rostoker (SKKR) method which treats the semi-infinite geometry and the host band structure properly and takes into account SOC nonperturbatively. The calculation resulted in $K(d) \sim 1/d^2$, but also in a magnitude for the MA energy much smaller than $k_B T_K = 0.03 \text{ meV}$, so the authors concluded that the HSO mechanism is too weak to explain the experimental findings.

Later on a rather different mechanism has been proposed by L. Szunyogh and G. Zaránđ to produce MA in the vicinity of a surface [13]. This mechanism, which we shall refer to as the local spin-orbit (LSO) mechanism, assumes strong local SOC on the impurity’s $d$ level.
The basic observation leading to this mechanism is that, for partially (but not half) filled $d$ shells, spin states have also a large orbital content. Therefore, spin states couple very strongly to Friedel oscillations in the vicinity of a surface. Electrons on the deep $d$ levels can lower their energy by hybridizing with the conduction electrons through virtual fluctuations. The magnetic anisotropy appears already to first order in the exchange coupling $J$ and decays as $1/d^2$. In the specific case of an impurity with a $d^1$ configuration, the corresponding $J_{3/2}$ ground-state multiplet is split by the presence of the surface as [13],

$$H_{LSO}^{\text{anis}} = K^L(d) \left( \bar{n} \cdot \mathcal{J} \right)^2,$$

where $\mathcal{J}$ stands for the total angular-momentum operators and $K(d) \sim J \sin (Q_F d) / d^2$, with $Q_F$ being the length of an extremal vector of the Fermi surface ($FS$). As shown in Ref. [13] the anisotropy constant can be of the desired magnitude of about a few tenths of $meV$ even beyond $100 \, \text{Å}$ from the surface.

Consequently, it is natural to suppose that the LSO mechanism is a dominant source of the magnetic anisotropy of random impurities in mesoscopic (noble metal) particles. Theoretical [14, 15] and experimental [16] works examined the fluctuating spin $g$-tensor in small metal mesoscopic grains. With the advance of nanoparticle technology, it has become possible to resolve individual energy levels $\varepsilon_\mu$ for electrons in ultrasmall metal grains. Application of an external magnetic field $\vec{B} = (0, 0, B_z)$ implies Zeemann-splitting. The splitting of a level $\varepsilon_\mu$ is described by a $g$-factor,

$$\delta \varepsilon_\mu = \pm \frac{1}{2} \mu_B g B_z,$$

where $\mu_B$ is the Bohr magneton. A free electron has $g = 2$, but in small metal grains the effective $g$-factor may be reduced as a result of spin-orbit scattering [14]. In order to study this reduction, Salinas et al. [17] have doped Al grains (which do not have significant spin-orbit scattering) with Au (which has). For small concentrations of Au, the effective $g$-factor was seen to drop from 2 to around 0.7. Even lower values ($\sim 0.3$) were reported in experiments on Au grains [18]. For disordered systems with spin-orbit scattering, the splitting of a level $\varepsilon_\mu$ does not depend only on the magnitude of the magnetic field $\vec{B}$, but also on its direction. The Zeeman field splits the Kramers’ doublet according to

$$\delta \varepsilon_\mu^2 = \frac{\mu_B^2}{4} \vec{B} \cdot G_\mu \vec{B},$$

where $G_\mu$ is a $3 \times 3$ tensor. $G_\mu$ will be anisotropic only in presence of SOC in the host. $G_\mu$ then becomes a fluctuating quantity, and the authors of Ref. [14] published analytical and numerical results of the statistical distribution of the principle components of the $G_\mu$ tensor using the methods of random matrix theory (RMT). The above works motivated us to investigate the level splitting distribution caused by the LSO mechanism in disordered Au particles.
The Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction in bulk materials is known for a long time [19] and has become a textbook knowledge. In the bulk, the magnitude of the RKKY interaction decays as \(1/R^3\), where \(R\) is the distance between the impurities, and the frequency of the oscillations is determined by the extremal vectors of the Fermi surface. It is well known that the (111) surface of noble metals contains Schockley type surface states [20, 21, 22, 23], which behaves as a two dimensional electron gas (2DEG). Despite of some theoretical studies it has not been fully explored in the literature what is the role of these type of states in the RKKY interaction and, in general, what is the form of the interaction near a surface? A part of my research activity has been devoted to answer these questions.

One of the most intriguing manifestation of SOC at surfaces is the splitting of these above mentioned surface states, known as Bychkov-Rashba (BR) splitting [24, 25]. Such BR splitting was observed via photoemission by LaShell et al. [20] for the \(L\)-gap surface state at Au(111) and explained theoretically in terms of a tight-binding model [22] and \textit{ab initio} calculations [23, 26]. Several studies of the Rashba splitting were recently published on Bi(111) and Bi/Ag(111) [27, 28, 29], as well as on Bi,Pb\(_{1-x}\)/Ag(111), where atomic Bi \(p\)-orbitals lead to a more pronounced spin-orbit splitting [30, 31, 32, 33]. In these systems and in others [34] it turned out that the standard isotropic Rashba model is insufficient to describe the splitting of the dispersion curves. It became necessary to work out theoretically and test numerically the anisotropic Rashba effect.

### 1.2 Structure of the thesis

In most parts of this thesis I deal with the properties of magnetic impurities embedded into a nonmagnetic host, namely, with the MA energy of an impurity and also with the exchange interaction of two impurities. Simple models of magnetic impurities, together with details of the HSO and LSO models and the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction are introduced in Section 2.

Although the LSO mechanism is expected to explain the Kondo-resistance in reduced dimension, in Ref. [13] only a toy model, namely, a single-band metal on a simple-cubic lattice has been considered. For a quantitative comparison of the HSO and LSO models more realistic band structures should be used. For this purpose an fcc lattice and a realistic tight-binding (TB) surface Green’s function method [35] is chosen to describe the conduction and valence electrons of the host material. This method allows for a numerically exact treatment of the semi-infinite geometry of the surface and also incorporates the SOC non-perturbatively. Motivated by [14], I also investigated the magnetic anisotropy of randomly distributed impurities in mesoscopic metallic (Au) nanoballs of 100 – 400 gold atoms cut out from an ordered fcc lattice. The spectral statistics of the Hamiltonian of the (non-symmetric
or disordered) particles has been analyzed using random matrix theory. The description of the surface and statistical features of the spectrum of disordered nanograins can be found in Section 3.

I shall then study the surface-induced HSO anisotropy and derive explicit expressions for the anisotropy constants in terms of the local spectral functions around the magnetic impurity. The results for the surface induced magnetic anisotropy in case of the HSO model is presented in Section 4.

The analytical derivation of the structure of the general LSO anisotropy matrix, the Friedel-oscillations-induced surface magnetic anisotropy and the symmetry analysis of the the calculated LSO-MA in ordered nanoparticles by using group theoretical methods can be found in Section 5. It should be noted that our results on the LSO magnetic anisotropy in gold nanograins have not yet been published.

In Refs. [36, 37], we presented ab initio (SKKR) calculations for the (100), (110) and (111) surfaces of Cu and Au in order to investigate the exchange interactions between Co atoms placed on these surfaces. Calculation of the RKKY interaction in terms of TB method helped to understand the ab initio results and highlighted the influence of the SOC for bulk RKKY interaction. I shall briefly summarize the ab initio calculations [36] and present my relativistic and nonrelativistic TB results for Cu and Au bulk in Section 6.

The results for the anisotropic Bychkov-Rashba splitting of Au(111) and Au(110) surfaces can be found in Section 7. The effective Rashba Hamiltonian $H_R(\vec{k})$ as derived originally by Szabolcs Vajna [38] using group theoretical methods is introduced in case of $C_{3v}$ and $C_{2v}$ symmetries and compared with my numerical results in terms of TB calculations.
2 Models of magnetic impurities

2.1 Simple models

Here we summarize the simple models of the magnetic impurities well-known from textbooks [1], [39]. For sake of simplicity we will forget about the degeneracy of the $d$ shell of the transition metal and assume just a single nondegenerate level of energy $\varepsilon_d$. This level can be at most doubly occupied. Because of the Coulomb repulsion, the energy of the doubly occupied state is $2\varepsilon_d + U$. Moreover, since the wavefunction of the $d$ level is not orthogonal to the states of the conduction band, they may be hybridized. P. W. Anderson [40] proposed the Hamiltonian,

$$ H_A = \sum_{k,\sigma} \varepsilon_{\tilde{k}} s_{k,\sigma}^+ s_{k,\sigma} + \sum_\sigma \varepsilon_d d_{\sigma}^\dagger d_\sigma + Un_{d\uparrow}n_{d\downarrow} + \frac{1}{\sqrt{V}} \sum_{k,\sigma} \left( V_{d\tilde{k}} s_{k,\sigma}^+ d_\sigma + V_{d\tilde{k}}^* d_{\sigma}^\dagger s_{k,\sigma} \right), $$

(8)

which describes the system of conduction electrons interacting with a single impurity. This is the nondegenerate single-impurity Anderson model. $s_{k,\sigma}^+$ creates a conduction electron with wavenumber $\tilde{k}$, energy $\varepsilon_{\tilde{k}}$ and spin $\sigma$; $d_\sigma^\dagger$ is the creation operator of the impurity $d$ state, $n_{d\sigma} = d_{\sigma}^\dagger d_\sigma$, $V$ denotes the volume of the sample and $V_{d\tilde{k}}$ are the $s-d$ hybridization matrix elements.

Let’s consider first a free ion. It has four possible states. The $d$ level is empty in state $|d^0\rangle$, it is occupied by an electron with spin $\sigma$ in state $|d_{\sigma}\rangle$, and it is doubly occupied by electrons with opposite spins in state $|d^2\rangle$. The energies of these states are $\varepsilon(d^0) = 0$, $\varepsilon(d_{\sigma}) = \varepsilon_d$ and $\varepsilon(d^2) = 2\varepsilon_d + U$. The ground state of the ion has a magnetic moment if the magnetic doublet is the lowest in energy, that is if $\varepsilon(d^2) > \varepsilon(d_{\sigma})$ and $\varepsilon(d^0) > \varepsilon(d_{\sigma})$, i.e. if $-\frac{1}{2}U < \varepsilon_d + \frac{1}{2}U < \frac{1}{2}U$. When $U$ is large, no double occupancy happens and the spin fluctuates. If the hybridization does not destroy the magnetic moment then the conduction electrons have an extra scattering channel. If $U$ is large and the singly occupied site is energetically more favorable than the empty or doubly occupied site, the $d$ electron can hop into the conduction band or a conduction electron can hop onto a singly occupied site for a short period. Although the impurity is singly occupied in most of the time, the spin may fluctuate with a characteristic time $\tau$ via these hopping processes. This time defines a characteristic temperature by the relation (Ref. [1], Sections: 35.2),

$$ k_B T_K = \frac{\hbar}{\tau}. $$

(9)

Schrieffer and Wolff derived an effective model from $H_A$ using a canonical transformation (Ref. [1], Sec: 35.2.4), and they got the Hamiltonian of the so-called $s-d$ exchange model,

$$ H_{s-d} = \sum_{\tilde{k},\sigma} \varepsilon_{\tilde{k}} s_{\tilde{k},\sigma}^+ s_{\tilde{k},\sigma} - \frac{1}{V} \sum_{\tilde{k}k'\sigma\sigma'} J_{\tilde{k}k'} \overrightarrow{S}_\sigma \overrightarrow{\sigma'} s_{\tilde{k},\sigma}^+ s_{k',\sigma'}^+ s_{\tilde{k},\sigma}. $$

(10)
where
\[ J_{\vec{k}\vec{k}'} = -\frac{1}{2} V_{\vec{k}d} V_{\vec{k}d'} \left[ \frac{1}{\varepsilon_d + U - \varepsilon_{\vec{k}}} + \frac{1}{\varepsilon_d + U - \varepsilon_{\vec{k}'} - \varepsilon_d} + \frac{1}{\varepsilon_{\vec{k}' - \varepsilon_d} - \varepsilon_d} \right], \quad (11) \]
\( \vec{S} \) denotes the impurity spin, \( \vec{\sigma} \) is a vector of Pauli matrices (Refs. [41] and [1], Sec: 35.2.4).

If the \( |\varepsilon_{\vec{k}' - \varepsilon_d}| \ll |\varepsilon_d| \) and \( |\varepsilon_{\vec{k}' - \varepsilon_d}| \ll |\varepsilon_d + U| \) and an antiferromagnetic \( \vec{k} \)-independent coupling is considered, i.e. \( J_{\vec{k}\vec{k}'} = -J \ll 0 \), one gets the well-known Kondo Hamiltonian [2],
\[ H_K = J \sum_{\vec{k}\vec{k}'} \left[ S_{\vec{k}'}^+ s_{\vec{k}'}^+ s_{\vec{k}}^+ s_{\vec{k}} + S_{\vec{k}'}^- s_{\vec{k}'}^- s_{\vec{k}} + S_{\vec{k}}^z \left( s_{\vec{k}'}^+ s_{\vec{k}}^+ s_{\vec{k}}^+ s_{\vec{k}}^+ - s_{\vec{k}'}^- s_{\vec{k}'}^- s_{\vec{k}}^+ s_{\vec{k}}^+ \right) \] \quad (12)

The Anderson or Kondo model successfully describes the magnetic impurities in a simple metal, if there is no interaction between the impurities. In case of higher concentration of the impurities, but still in case low to form an ordered magnetic structure, the interaction of spin \( \vec{S}_1 \) and \( \vec{S}_2 \) (at site \( \vec{R}_1 \) and \( \vec{R}_2 \)) mediated via conduction electrons is described by the following \( s - d \) Hamiltonian (Ref. [1], Sec: L.3.1),
\[ H = -J \sum_{l=1}^{2} \sum_{\vec{k}\vec{k}'} \exp \left( i(\vec{k} - \vec{k}') \vec{R}_l \right) \left\{ S_{\vec{k}'}^+ s_{\vec{k}'}^+ s_{\vec{k}}^+ s_{\vec{k}} + S_{\vec{k}'}^- s_{\vec{k}'}^- s_{\vec{k}}^+ s_{\vec{k}}^+ + S_{\vec{k}}^z \left( s_{\vec{k}'}^+ s_{\vec{k}'}^+ s_{\vec{k}} - s_{\vec{k}'}^- s_{\vec{k}'}^- s_{\vec{k}}^+ s_{\vec{k}}^+ \right) \right\} , \quad (13) \]
where \( J \) is the same exchange constant as in Eq. (12). Clearly, the total spin remains constant of motion, but spin can be transferred between conduction electrons and impurities: the first term in the curly parentheses on the right-hand side of Eq. (13) increases, the second term decreases and the third one leaves intact the \( z \) component of the impurities’ spins. Applying a canonical transformation, an effective Hamiltonian can be constructed that leaves the spin of the conduction electrons unchanged, but the impurity spins can be changed. In fact, the impurities’ spins will interchange simultaneously via interacting with conduction electrons. This new canonical transformation results in the effective Hamiltonian, see Ref. [1], Sec: L.3.1),
\[ H_{RKKY} = -2J(r) \vec{S}_1 \vec{S}_2 , \quad (14) \]
where \( r = |\vec{R}_1 - \vec{R}_2| \) is the distance of two spins, and the effective exchange constant depends on \( r \),
\[ J(r) = \frac{m_e J^2 k_F^4}{\hbar^2 \pi^3} F(2k_Fr) , \quad (15) \]
where \( k_F \) is the Fermi-wavelength, and
\[ F(x) = \frac{x \cos (x) - \sin (x)}{x^4} . \quad (16) \]
Eq. (14) is the Hamiltonian of the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, which e.g. describes spin glasses (Ref. [1], Sec. L.3.1 and [19]).
The so called ionic model is a possible generalization of the Anderson model, Eq. (8), [42]. The Hamiltonian contains three terms as usual: the impurity, the conduction electron, and the hybridization terms. If the multiplet of the impurity ion is denoted by \( |n, m_n\rangle \), where \( n \) indicates the number of electrons in the shell and \( \{m_n\} \) the set of quantum numbers characterizing the multiplet, and the corresponding energy is denoted by \( E_{n,m_n} \), then the impurity term can be written as

\[
H_{\text{imp}} = \sum_{n,m_n} E_{n,m_n} |n, m_n\rangle \langle n, m_n| .
\] (17)

If the impurity has only a single nondegenerate \( d \) level and the Coulomb interaction \( U \) is that large, that the doubly occupied configuration is on high energy, \( n = 0 \) or \( n = 1 \) and the Hamiltonian of the ionic model can be approximated as:

\[
H_{\text{ionic}} = E_0 |0, 0\rangle \langle 0, 0| + \sum_m E_{1,m} |1, m\rangle \langle 1, m| + \sum_{k,m} \varepsilon_k s_{k,m}^\dagger s_{k,m}^+ + \\
+ \sum_{k,m} \left( V_k |0, 0\rangle \langle 0, 0| s_{k,m}^\dagger s_{k,m} + V_{k,m} s_{k,m}^\dagger |0, 0\rangle \langle 1, m| \right) ,
\] (18)

where \( m \) runs over \( 2j + 1 \) values, for instance in case of Ti \( j = \frac{3}{2} \) or in case of Yb \( j = \frac{7}{2} \). In case of \( j = \frac{1}{2} \) the \( U = \infty \) Anderson model is recovered (Ref. [39], Sec: 1.9).

### 2.2 The local spin-orbit model of a magnetic impurity

As in Ref. [13] let us now consider a magnetic impurity in a \( |d_{5/2}\rangle \) configuration such as a \( V^{4+} \) or \( Ti^{3+} \) ion. If there is one electron in a spherically symmetric environment then the spin and orbital degrees of freedom transform under the rotation group as representation of \( SO(3) \), following the Clebsch-Gordon decomposition,

\[
D^2 \times D^{1/2} = D^{5/2} + D^{3/2} .
\] (19)

According to Hund’s third rule, a strong local spin-orbit coupling will lead to a six-dimensional \( D^{5/2} \) multiplet separated from a four-dimensional \( D^{3/2} \) multiplet typically by an energy of the order of \( 1 \) eV. In a cubic crystal field, the \( D^{3/2} \) ground state multiplet remains degenerate (\( \Gamma_8 \) double representation, see Eq. (232)), but the \( D^{5/2} \) multiplet splits into a two and a four dimensional multiplet (\( \Gamma_8, \Gamma_7 \)). Detailed explanation of crystal double groups can be found in Appendix 1: Eq. (232) shows the splitting of levels with different angular momentum, implying that only the \( j = \frac{1}{2} \) and \( j = \frac{3}{2} \) multiplets remain unsplit in a cubic field. The crystal field splitting and shifting are supposed to be much smaller than the local spin-orbit induced \( D^{5/2} - D^{3/2} \) separation, so we shall just consider the \( j = \frac{3}{2} \) (\( D^{3/2} \)) multiplet supposed to be lower in energy. The standard \( j = \frac{3}{2} \) representation of the generators of the Lie-algebra
\( \text{su}(2) \), see Appendix 1, can be expressed as

\[
J_x = \hbar \begin{pmatrix}
0 & \frac{\sqrt{3}}{2} & 0 & 0 \\
\frac{\sqrt{3}}{2} & 0 & 1 & 0 \\
0 & 1 & 0 & \frac{\sqrt{3}}{2} \\
0 & 0 & \frac{\sqrt{3}}{2} & 0
\end{pmatrix},
\]

\[
J_y = \hbar \begin{pmatrix}
0 & \frac{-\sqrt{3}}{2}i & 0 & 0 \\
\frac{-\sqrt{3}}{2}i & 0 & -i & 0 \\
0 & i & 0 & \frac{-\sqrt{3}}{2}i \\
0 & 0 & \frac{-\sqrt{3}}{2}i & 0
\end{pmatrix},
\]

\[
J_z = \hbar \begin{pmatrix}
\frac{3}{2} & 0 & 0 & 0 \\
0 & \frac{1}{2} & 0 & 0 \\
0 & 0 & -\frac{1}{2} & 0 \\
0 & 0 & 0 & -\frac{3}{2}
\end{pmatrix}.
\]

(20)

The matrix

\[
U_j (\vec{n}, \phi) = \exp \left( i\phi \vec{n} \cdot \vec{J} / \hbar \right)
\]

represents an element of the \( SO(3) \) group on the Hilbert space of physical states, namely, a rotation with an angle \( \phi \) around unit vector \( \vec{n} \), while \( j \) denotes the representation. If the cubic double character table in Appendix 1 is considered, one can see that the \( D^{3/2} \) multiplet is indeed represented by the \( \Gamma_8 \), which is the only four-dimensional representation in the cubic double group, \( O' \), see Appendix 1.

Next, using the character table of \( O' \) we build \( \Gamma_8 \) from the tensor-product of spin and orbital parts. The half spin is represented by \( \Gamma_6 \) and \( \Gamma_3 \) corresponds to the two-dimensional (\( d \)-type) irreducible representation (irrep) \( E \) in the simple cubic group. Using then the character table of \( O' \) we have,

\[
\Gamma_3 \times \Gamma_6 = \Gamma_8,
\]

(22)

where \( \times \) denotes the tensor-product. Equation (22) corresponds to the \( D^{3/2} \) multiplet. This implies that no level spacing appears for the magnetic impurity in a cubic bulk.

The desired effective Hamiltonian, which describes the interaction of the magnetic impurity and the host (conduction) electrons should be invariant under the cubic group symmetry. In spirit of the Anderson model we consider only \( s \)-type host electrons (that have dominant component near the Fermi-energy). Using a real-space tight-binding representation for the valence states we consider \( s \) orbitals at the nearest neighbor sites of the impurity. The symmetry invariance of the effective Hamiltonian implies the use of \( \Gamma_8 \) symmetry adapted combinations of these orbitals. In the following these functions will be referred to as \( d \)-type combinations.
The gold or copper host atoms form an fcc lattice: an impurity has 12 nearest neighbor host atoms. The operators

\[ s_{xy}^e, s_{xy}^\dagger, s_{xy}^\dagger, s_{xy}^\dagger, s_{x^2}^e, s_{x^2}^\dagger, s_{y^2}^e, s_{y^2}^\dagger, s_{g^2}^e, s_{g^2}^\dagger \] (23)

create the appropriate \( s \)-electrons at the nearest neighbor sites with either spin \( \sigma \). The subscript of the creation operators refer to the nearest neighbor sites. For instance if the impurity takes place at site \((0, 0, 0)\) then index \( xy \) denotes the coordinate of the site \((\frac{1}{2}, \frac{1}{2}, 0)\).

Using the following combinations from (23),

\[ s_{xy}^e = \frac{1}{\sqrt{2}} (s_{xy}^\dagger + s_{xy}^\dagger), \ s_{xy}^\dagger = \frac{1}{\sqrt{2}} (s_{xy}^\dagger + s_{xy}^\dagger), \]
\[ s_{xz}^e = \frac{1}{\sqrt{2}} (s_{xz}^\dagger + s_{xz}^\dagger), \ s_{xz}^\dagger = \frac{1}{\sqrt{2}} (s_{xz}^\dagger + s_{xz}^\dagger), \]
\[ s_{yz}^e = \frac{1}{\sqrt{2}} (s_{yz}^\dagger + s_{yz}^\dagger), \ s_{yz}^\dagger = \frac{1}{\sqrt{2}} (s_{yz}^\dagger + s_{yz}^\dagger), \] (24)

and

\[ S_{x^2} = \frac{1}{\sqrt{2}} (s_{y^2}^e + s_{y^2}^\dagger), \ S_{y^2} = \frac{1}{\sqrt{2}} (s_{x^2}^e + s_{x^2}^\dagger), \ S_{z^2} = \frac{1}{\sqrt{2}} (s_{xy}^e + s_{xy}^\dagger) \] (25)

the symmetry adapted \( d \)-like combinations, \( D_\sigma \), can be expressed as

\[ D_{xz} = \frac{1}{\sqrt{2}} (s_{xz}^e - s_{xz}^\dagger), \ D_{yz} = \frac{1}{\sqrt{2}} (s_{yz}^e - s_{yz}^\dagger), \ D_{xy} = \frac{1}{\sqrt{2}} (s_{xy}^e - s_{xy}^\dagger), \]
\[ D_{x^2-y^2} = \frac{1}{\sqrt{6}} (2S_{x^2} - S_{x^2} - S_{y^2}). \] (26)

Including spin variables this means ten \( D_\sigma |\sigma\rangle \) combinations. The combinations \( D_{xz}, D_{yz}, D_{xy} \) transform as \( \Gamma_5 \), while \( D_{x^2-y^2} \) and \( D_{2z^2-x^2-y^2} \) transform as \( \Gamma_3 \). According to (22), the \( \Gamma_3 \) combinations are relevant for the construction of the LSO effective Hamiltonian.

Next, we should find the relation between standard \( \Gamma_8 \) basis

\[ \begin{pmatrix} |s_{3/2}\rangle \\ |s_{1/2}\rangle \\ |s_{-1/2}\rangle \\ |s_{-3/2}\rangle \end{pmatrix} \] (27)

and the tensor-product basis,

\[ D_{x^2-y^2} |\uparrow\rangle = \frac{1}{2} (s_{y^2,z^2}^e + s_{y^2,z^2}^\dagger - s_{x^2,z^2}^e - s_{x^2,z^2}^\dagger) \],
\[ D_{x^2-y^2} |\downarrow\rangle = \frac{1}{2} (s_{y^2,z^2}^e + s_{y^2,z^2}^\dagger - s_{x^2,z^2}^e - s_{x^2,z^2}^\dagger) \],
\[ D_{2z^2-x^2-y^2} |\uparrow\rangle = \frac{1}{\sqrt{12}} (2s_{xy,z^2}^e + 2s_{xy,z^2}^\dagger - s_{y^2,z^2}^e - s_{y^2,z^2}^\dagger - s_{x^2,z^2}^e - s_{x^2,z^2}^\dagger) \],
\[ D_{2z^2-x^2-y^2} |\downarrow\rangle = \frac{1}{\sqrt{12}} (2s_{xy,z^2}^e + 2s_{xy,z^2}^\dagger - s_{y^2,z^2}^e - s_{y^2,z^2}^\dagger - s_{x^2,z^2}^e - s_{x^2,z^2}^\dagger) \]. (28)
Let $Q$ denote the matrix of the transformation, i.e.,

$$\{|s_m\} = Q \{|D_\delta|\sigma\} ,$$

(29)

where $\delta = x^2 - y^2$ or $2z^2 - x^2 - y^2$ and $\sigma = \uparrow, \downarrow$.

To do this we compare the action of a rotation around the $z$ axis by angle $\frac{\pi}{2}$ in both basis. In case of (27),

$$U_{\pi} \left( z, \frac{\pi}{2} \right) = \begin{pmatrix}
\exp \left( i \frac{3\pi}{4} \right) & 0 & 0 & 0 \\
0 & \exp \left( i \frac{\pi}{4} \right) & 0 & 0 \\
0 & 0 & \exp \left( -i \frac{\pi}{4} \right) & 0 \\
0 & 0 & 0 & \exp \left( -i \frac{3\pi}{4} \right)
\end{pmatrix} .$$

(30)

The same transformation is denoted by $W_{\pi} \left( z, \frac{\pi}{2} \right)$ in basis (28). If $Z \left( z, \frac{\pi}{2} \right)$ rotates the orbitals and $U_{\pi} \left( z, \frac{\pi}{2} \right)$ rotates the spin part, i.e.,

$$Z \left( z, \frac{\pi}{2} \right) \left( \begin{array}{c} D_{x^2 - y^2} \\
D_{2z^2 - x^2 - y^2} \end{array} \right) = \left( \begin{array}{cc}
-1 & 0 \\
0 & 1
\end{array} \right) \left( \begin{array}{c} D_{x^2 - y^2} \\
D_{2z^2 - x^2 - y^2} \end{array} \right)$$

then

$$U_{\pi} \left( z, \frac{\pi}{2} \right) = \begin{pmatrix}
\exp \left( i \frac{\pi}{4} \right) & 0 \\
0 & \exp \left( -i \frac{\pi}{4} \right)
\end{pmatrix} ,$$

(31)

and

$$W \left( z, \frac{\pi}{2} \right) = Z \left( z, \frac{\pi}{2} \right) \otimes U_{\pi} \left( z, \frac{\pi}{2} \right) .$$

(32)

The result of the above procedure can be written as,

$$D_{x^2 - y^2}|\uparrow\rangle \Rightarrow \exp \left( -i \frac{3\pi}{4} \right) D_{x^2 - y^2}|\uparrow\rangle ,$$

$$D_{x^2 - y^2}|\downarrow\rangle \Rightarrow \exp \left( i \frac{3\pi}{4} \right) D_{x^2 - y^2}|\downarrow\rangle ,$$

$$D_{2z^2 - x^2 - y^2}|\uparrow\rangle \Rightarrow \exp \left( i \frac{\pi}{4} \right) D_{2z^2 - x^2 - y^2}|\uparrow\rangle ,$$

$$D_{2z^2 - x^2 - y^2}|\downarrow\rangle \Rightarrow \exp \left( -i \frac{\pi}{4} \right) D_{2z^2 - x^2 - y^2}|\downarrow\rangle .$$

(33)

The rotation around the $z$ axis yields diagonal matrices in both bases, so we can easily determine a transformation matrix,

$$Q = \begin{pmatrix}
0 & e^{i\alpha} & 0 & 0 \\
0 & 0 & e^{i\beta} & 0 \\
0 & 0 & 0 & e^{i\gamma} \\
1 & 0 & 0 & 0
\end{pmatrix} ,$$

(34)

where $\alpha$, $\beta$ and $\gamma$ are unknown phases. The equation

$$W \left( \vec{n}', \phi \right) = Q^\dagger U_{\pi} \left( \vec{n}', \phi \right) Q ,$$

(35)
should be satisfied in case of each cubic group element. Fortunately, if we repeat the \( \frac{\pi}{2} \) rotation around the axis \( x \), the unknown phases will be fully determined:

\[
W(x, \phi) = Z(x, \phi) \otimes U_\frac{\pi}{2}(x, \phi),
\]

(36)

specifically,

\[
W(x, \frac{\pi}{2}) = \frac{1}{2} \begin{pmatrix}
1 & 1 & -\sqrt{3} & -\sqrt{3}i \\
1 & -\sqrt{3} & -1 & -\sqrt{3}i \\
-\sqrt{3} & -\sqrt{3}i & -1 & -i \\
-\sqrt{3}i & -i & -1 & -1
\end{pmatrix},
\]

(37)

i.e.

\[
W(x, \frac{\pi}{2}) = \frac{1}{2\sqrt{2}} \begin{pmatrix}
1 & i & -\sqrt{3} & -\sqrt{3}i \\
i & 1 & -\sqrt{3}i & -\sqrt{3}i \\
-\sqrt{3} & -\sqrt{3}i & -1 & -i \\
-\sqrt{3}i & -i & -1 & -1
\end{pmatrix}.
\]

(38)

Next, we derive the \( U_\frac{\pi}{2}(x, \frac{\pi}{2}) \) using the eigenvectors of \( U_\frac{\pi}{2}(\vec{z}, \frac{\pi}{2}) \) in the standard basis:

\[
U_\frac{\pi}{2}(x, \frac{\pi}{2}) = VU_\frac{\pi}{2}(\vec{z}, \frac{\pi}{2}) V^\dagger,
\]

(39)

where

\[
V = \begin{pmatrix}
\frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\
\frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\
\frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\
\frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}}
\end{pmatrix},
\]

(40)

so we get the unitary matrix

\[
U_\frac{\pi}{2}(x, \frac{\pi}{2}) = \frac{1}{2\sqrt{2}} \begin{pmatrix}
1 & i\sqrt{3} & -\sqrt{3} & -i \\
i\sqrt{3} & -1 & i & -\sqrt{3} \\
-\sqrt{3} & i & -1 & i\sqrt{3} \\
-i & -\sqrt{3} & i\sqrt{3} & 1
\end{pmatrix}.
\]

(41)

Using the Eqs. (34) and (41) we can write

\[
Q^\dagger U_\frac{\pi}{2}(x, \frac{\pi}{2}) Q = \begin{pmatrix}
1 & -ie^{i\alpha} & -\sqrt{3}e^{i\beta} & -i\sqrt{3}e^{i\gamma} \\
-ie^{-i\alpha} & e^{-i\alpha}e^{i\alpha} & i\sqrt{3}e^{-i\alpha}e^{i\beta} & -\sqrt{3}e^{-i\alpha}e^{i\gamma} \\
-\sqrt{3}e^{-i\beta} & i\sqrt{3}e^{i\alpha}e^{-i\beta} & -e^{-i\beta}e^{i\beta} & -i\sqrt{3}e^{-i\alpha}e^{i\gamma} \\
i\sqrt{3}e^{-i\gamma} & -\sqrt{3}e^{i\alpha}e^{-i\gamma} & ie^{i\beta}e^{-i\gamma} & -e^{-i\gamma}e^{i\gamma}
\end{pmatrix}.
\]

(42)

Comparing Eqs. (38) and (42) one obviously concludes that \( e^{i\alpha} = -1, e^{i\beta} = 1 \) and \( e^{i\gamma} = -1 \), i.e.

\[
Q = \begin{pmatrix}
0 & -1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & -1 \\
1 & 0 & 0 & 0
\end{pmatrix},
\]

(43)

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implying,
\[
\begin{align*}
\left| s_{3/2} \right\rangle &= -D_{x^2-y^2} \left| \downarrow \right\rangle, \\
\left| s_{1/2} \right\rangle &= D_{2x^2-x^2-y^2} \left| \uparrow \right\rangle, \\
\left| s_{-1/2} \right\rangle &= -D_{2x^2-x^2-y^2} \left| \downarrow \right\rangle, \\
\left| s_{-3/2} \right\rangle &= D_{x^2-y^2} \left| \uparrow \right\rangle. 
\end{align*}
\]
By probing for the rest of the generating point group elements of the cubic point-group it can easily be shown that this basis forms indeed a \( \Gamma_8 \) representation of the cubic double point-group.

The ionic Hamiltonian, Eq. (18), without kinetic energy of the host (conduction) electrons reduces to
\[
H_{LSO} = E_d \sum_m \langle m | m \rangle + V \sum_m \left( \langle m | \langle 0 | s_m \right) + s_m^\dagger \langle 0 | m \rangle \right) ,
\]
where \( V \) is the hybridization parameter, and we choose \( E_0 = 0 \) and \( E_{1,m} = E_d \) for each \( m \). Using a Coqblin-Schrieffer canonical transformation (Refs. [43] and [39], Sec: 1.10) for (45) Hamiltonian,
\[
H_{LSO} = J \sum_{m,m'} s_m^\dagger s_m | m' \rangle \langle m |,
\]
can be obtained. This procedure is a natural generalization of the derivation of the \( s-d \) model by Schrieffer and Wolff for case of \( j = \frac{1}{2} \). The so-called \( \{ | m \rangle \} \) Hubbard operators refer to the states \( \{ \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2} \} \) of the impurity, and \( s_m^\dagger \) create appropriate host electrons, while \( J \) denotes the exchange constant,
\[
J = \frac{V^2}{|E_d|} \approx 1 \, eV .
\]

2.3 The host spin-orbit model of a magnetic impurity

As in Refs. [7, 8, 9] and [11] let us consider a spin \( S = \frac{1}{2} \) impurity with a half-filled \( d \) shell. In this case, we can neglect the spin-orbit interaction on the magnetic ion and the bulk SO interaction is the primary source of the surface-induced anisotropy. Note that within this model SOC affects directly the low-lying filled \( d \)-orbitals of the host. As described in Refs. [7, 8, 9], \( s \)-like conduction electrons experience this SOC in terms of virtual fluctuations mediated via \( s-d \) hybridization. In case of noble metals, the \( d \)-band lies well below the Fermi level, suggesting that this mechanism for the magnetic anisotropy should be rather weak. To construct the effective interaction between the host electrons and the magnetic impurity, one can safely assume that the deep \( d \)-levels of the magnetic impurity hybridize only with the \( s \)-orbitals of the neighboring host atoms. However, by symmetry considerations, the deep
$d$-levels of magnetic impurity can hybridize only with the five linear combinations of these $s$-orbitals $D_s$, see Eq. (26), which have $d$-wave character. Using these five spin-degenerate states, see Ref. [8], a Schrieffer-Wolf transformation leads to the following Kondo-type Hamiltonian,

$$H_{HSO} = H_{J,s,s'} = \sum_{i=x,y,z} \sum_{s,s'} J_{s,s'} \sum_{\sigma \sigma'} c_{s \sigma}^\dagger \sigma \sigma' c_{s \sigma'} S_{s,s'}^i ,$$

where $s, s' = -\frac{5}{2}, ..., \frac{5}{2}$, $S^i$ are the components of the impurity spin and $\sigma^i$ denote the Pauli matrices. The operator $c_{s \sigma}^\dagger$ creates a conduction electron in state $D_s |\sigma\rangle$. In the bulk, only two of the exchange constants $J$ are independent, since by symmetry we have $J_{xy} = J_{xz} = J_{yz}$ and $J_{x^2-y^2} = J_{2z^2-x^2-y^2}$. In the following, for the sake of simplicity, we shall set all these coupling constants equal and assume

$$J_{s,s} = J \simeq 1 \text{ eV} .$$

This value refers to a rough estimate based on experimental Kondo temperatures, $T_K \sim 0.01 - 1 \text{ K}$. 
3 Description of the nonmagnetic host

3.1 Hamiltonian of the host

In order to describe the electronic structure of surfaces of Au and Cu, as well as of Au nanograins, we used a tight binding model with spd canonical orbitals and treated SOC of the host atoms non-perturbatively.

In case of the surface calculations the host system has two-dimensional translational symmetry. If \( \vec{T}_n \) is the translation vector of the two-dimensional lattice and \( \vec{C}_p \) denotes the position vector of an arbitrary site in layer \( p \), then the corresponding position vector is given by

\[
\vec{R}_{pn} = \vec{C}_p + \vec{T}_n , \quad \begin{cases} 
  p > N & \text{vacuum layers} \\
  1 \leq p \leq N & \text{surface layers} \\
  p \leq 0 & \text{bulk layers}
\end{cases}
\]

where \( N \) surface layers are considered on top of a semi-infinite bulk region, see Fig. 3.

![Figure 3: Sketch of the layer structure of the host. The surface layer is labeled by \( N \).](image)

The tight-binding model uses (nearly) orthonormal basis functions which are localized at sites, \( \vec{R}_{pn} \),

\[
\langle \vec{r} \mid pn; \alpha \sigma \rangle = \langle \vec{r} - \vec{R}_{pn} \mid \alpha \sigma \rangle = \psi_{\alpha}(\vec{r} - \vec{R}_{pn})\phi_{\sigma} ,
\]

where the index \( \alpha \) denotes the so called canonical basis (real spherical harmonics),

\[
\begin{align*}
\alpha &= s & \ell &= 0 \\
\alpha &= p_x, p_y, p_z, & \ell &= 1 \\
\alpha &= d_{xy}, d_{xz}, d_{yz}, d_{x2-y^2}, d_{3z^2-1} & \ell &= 2
\end{align*}
\]

\( \psi_{\alpha} \) depends only on the azimuthal quantum number \( \ell \) and the spin quantum number is labeled by \( \sigma = \pm \frac{1}{2} \). The Hamiltonian of the noble metal host is written as

\[
H_{surf} = \{ H_{pn, p' n'} \} = \{ H_{\alpha \sigma, \alpha' \sigma'} \} ,
\]
\[ H_{\alpha\sigma,\alpha'^{\prime}\sigma'^{\prime}}^{\rho\rho'} = (\varepsilon_{\alpha}^{\rho} \delta_{\alpha\alpha'} \delta_{\sigma\sigma'} + \xi_{\xi}^{\rho} H_{\alpha\sigma,\alpha'^{\prime}\sigma'^{\prime}}^{LS}) \delta_{\rho\rho'} \delta_{\sigma\sigma'} + V_{\alpha,\alpha'}^{\rho\rho'} \delta_{\sigma\sigma'}, \]  

(54)

where \( \varepsilon_{\alpha}^{\rho} \) is the so-called on-site energy parameter,  
\[ H_{\alpha\sigma,\alpha'^{\prime}\sigma'^{\prime}}^{LS} = \langle \alpha\sigma | \vec{L} \vec{S} | \alpha'^{\prime}\sigma'^{\prime} \rangle, \]  

(55)

\( \xi_{\xi}^{\rho} \) are the SOC parameters and \( V_{\alpha,\alpha'}^{\rho\rho'} \) are the hybridization matrixelements (or hopping integrals) between the different orbitals. Translation symmetry then implies  
\[ \varepsilon_{\alpha}^{\rho} = \varepsilon_{\alpha}^{\rho} \ (\forall n) \]  

(56)

\[ \xi_{\xi}^{\rho} = \xi_{\xi}^{\rho} \ (\forall n) \]  

(57)

\[ V_{\alpha,\alpha'}^{\rho\rho'}(n+m) = V_{\alpha,\alpha'}^{\rho\rho'}(n) \ (\forall n, m) . \]  

(58)

The matrixelements of the SOC can easily be calculated with the help of following identity,  
\[ \vec{L} \vec{S} = \frac{1}{2}(L_+ S_- + L_- S_+) + L_z S_z . \]  

(59)

As a simple approximation, in case of \( p > N \), i.e., in the vacuum region, the on-site energies are taken to be infinity, \( \varepsilon_{\alpha}^{\rho} \to \infty \), so we have to deal with a semi-infinite system. (This sharp cut does not cause a problem, if we examine for instance the magnetic anisotropy far away from the surface, i.e., in the so-called asymptotic region, see later.) The hopping integrals are considered to first- and second nearest neighbors, and their layer dependence is also neglected. The hybridization matrixelements then depend only on the relative positions of the sites,  
\[ V_{\alpha,\alpha'}^{\rho\rho'}(\vec{n}) = V_{\alpha,\alpha'}(\vec{n}) \text{ where } \vec{n} = \vec{R}_{\rho\rho'} - \vec{R}_{\rho m} . \]  

(60)

The calculation of \( V_{\alpha,\alpha'}(\vec{n}) \) matrices is described in Appendix 2. Similary, we use the approach \( \xi_{\xi}^{\rho} = \xi_{\xi} \).

Two-dimensional lattice-Fourier transformation, following,  
\[ H_{\alpha\sigma,\alpha'^{\prime}\sigma'^{\prime}}^{pp'}(\vec{k}) = \sum_{\vec{n}} H_{\alpha\sigma,\alpha'^{\prime}\sigma'^{\prime}}^{00,\rho\rho'} e^{i\vec{k}\vec{n}}, \]  

(61)

applied to Eq. (54) leads to  
\[ H_{\alpha\sigma,\alpha'^{\prime}\sigma'^{\prime}}^{pp'}(\vec{k}) = \delta_{\rho\rho'} (\varepsilon_{\alpha}^{\rho} \delta_{\alpha\alpha'} \delta_{\sigma\sigma'} + \xi_{\xi}^{\rho} H_{\alpha\sigma,\alpha'^{\prime}\sigma'^{\prime}}^{LS}) + \delta_{\sigma\sigma'} \sum_{\vec{n}} V_{\alpha,\alpha'}^{\rho\rho'}(\vec{n}) e^{i\vec{k}\vec{n}}, \]  

(62)

for \( p, p' \leq N \). Using second nearest neighbor approach, layer \( p \) couples only with \( p' = p \pm 1 \) and \( p' = p \pm 2 \), the other elements of \( H_{\alpha\sigma,\alpha'^{\prime}\sigma'^{\prime}}^{pp'}(\vec{k}) \) are zero. The Hamiltonian in reciprocal space is then built up from five different blocks,  
\[ H_{\alpha\sigma,\alpha'^{\prime}\sigma'^{\prime}}^{00}(\vec{k}) \equiv H_{\alpha\sigma,\alpha'^{\prime}\sigma'^{\prime}}^{pp}(\vec{k}) \text{ for } p \leq N, \]  

(63)

\[ H_{\alpha\sigma,\alpha'^{\prime}\sigma'^{\prime}}^{01}(\vec{k}) \equiv H_{\alpha\sigma,\alpha'^{\prime}\sigma'^{\prime}}^{p,p+1}(\vec{k}) \text{ for } p \leq N - 1, \]  

(64)

\[ H_{\alpha\sigma,\alpha'^{\prime}\sigma'^{\prime}}^{10}(\vec{k}) \equiv H_{\alpha\sigma,\alpha'^{\prime}\sigma'^{\prime}}^{p+1,p}(\vec{k}) \text{ for } p \leq N - 1, \]  

(65)

\[ H_{\alpha\sigma,\alpha'^{\prime}\sigma'^{\prime}}^{02}(\vec{k}) \equiv H_{\alpha\sigma,\alpha'^{\prime}\sigma'^{\prime}}^{p,p+2}(\vec{k}) \text{ for } p \leq N - 2, \]  

(66)

\[ H_{\alpha\sigma,\alpha'^{\prime}\sigma'^{\prime}}^{20}(\vec{k}) \equiv H_{\alpha\sigma,\alpha'^{\prime}\sigma'^{\prime}}^{p+2,p}(\vec{k}) \text{ for } p \leq N - 2. \]  

(67)
In addition, Hermiticity implies

\begin{align}
\tilde{H}^{00}(\vec{k}) &= H^{00}(\vec{k})^+, \\
\tilde{H}^{01}(\vec{k}) &= H^{10}(\vec{k})^+, \\
\tilde{H}^{02}(\vec{k}) &= H^{20}(\vec{k})^+.
\end{align}

The so-called principal layer construction (Ref. [44], Sec. 17.2) will be very useful for the calculation of the Green’s function. The atomic layers can be organized into bigger (principal) units such that there is only first neighbor interaction between these units,

<table>
<thead>
<tr>
<th>Atomic layer</th>
<th>Principal layer</th>
<th>Position in given principle layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N)</td>
<td>(\tilde{N})</td>
<td>2</td>
</tr>
<tr>
<td>(N - 1)</td>
<td>(\tilde{N})</td>
<td>1</td>
</tr>
<tr>
<td>(N - 2)</td>
<td>(\tilde{N} - 1)</td>
<td>2</td>
</tr>
<tr>
<td>(N - 3)</td>
<td>(\tilde{N} - 1)</td>
<td>1</td>
</tr>
<tr>
<td>(\vdots)</td>
<td>(\vdots)</td>
<td>(\vdots)</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(\vdots)</td>
<td>(\vdots)</td>
<td>(\vdots)</td>
</tr>
</tbody>
</table>

where \(\tilde{N} = N/2\). This construction works only with even \(N\), but this is not an essential restriction. Note that, considering the semi-infinite bulk region, the number of the layers and of the principal layers goes to \(-\infty\), see Eq. (50). The matrices (63)-(67) can be ordered into the following blocks,

\begin{align}
\tilde{H}^{00}(\vec{k}) &= \begin{pmatrix} H^{00}(\vec{k}) & H^{01}(\vec{k}) \\ H^{10}(\vec{k}) & H^{00}(\vec{k}) \end{pmatrix}, \\
\tilde{H}^{01}(\vec{k}) &= \begin{pmatrix} H^{02}(\vec{k}) & 0 \\ H^{01}(\vec{k}) & H^{02}(\vec{k}) \end{pmatrix}, \\
\tilde{H}^{10}(\vec{k}) &= \begin{pmatrix} H^{20}(\vec{k}) & H^{10}(\vec{k}) \\ 0 & H^{20}(\vec{k}) \end{pmatrix},
\end{align}

thus, the two-dimensional Fourier-transformed Hamiltonian of the surface system is described by a semi-infinite tridiagonal matrix,
\[ H(\tilde{k}) = \begin{pmatrix} \tilde{N} & \tilde{N} - 1 & \tilde{N} - 2 & \tilde{N} - 3 & \tilde{N} - 4 & \cdots \\
\tilde{H}^{00}(\tilde{k}) & \tilde{H}^{01}(\tilde{k}) & & & & \\
\tilde{H}^{10}(\tilde{k}) & \tilde{H}^{00}(\tilde{k}) & \tilde{H}^{01}(\tilde{k}) & & & \\
\tilde{H}^{10}(\tilde{k}) & \tilde{H}^{00}(\tilde{k}) & \tilde{H}^{01}(\tilde{k}) & \tilde{H}^{00}(\tilde{k}) & \tilde{H}^{01}(\tilde{k}) & \cdots \\
\tilde{H}^{10}(\tilde{k}) & \tilde{H}^{00}(\tilde{k}) & \tilde{H}^{01}(\tilde{k}) & \tilde{H}^{00}(\tilde{k}) & \tilde{H}^{01}(\tilde{k}) & \cdots \\
\end{pmatrix} \]

In case of nanoparticles, we use a similar Hamiltonian in real space,

\[ H_{\text{grain}} = \left\{ H_{\alpha \alpha', \sigma \sigma'}^{n,n'} \right\} = (\varepsilon_\alpha \delta_{\alpha \alpha'} \delta_{\sigma \sigma'} + \xi H_{\alpha \sigma \alpha', \sigma'}^{LS}) \delta_{nn'} + V_{\alpha, \alpha', \delta \sigma'}^{n,n'}, \]

where the dimension of the matrix is \( 18 \times N \), with \( N \) being the number of sites in the nanograin.

### 3.2 Green’s function of the host

As we shall see later Green’s functions will be very useful, in particular, for the surface systems. The Green’s function (or resolvent) matrix of the semi-infinite system in the reciprocal space is defined as,

\[ G_{\text{surf}}(z, \tilde{k}) = \left(z - H_{\text{surf}}(\tilde{k})\right)^{-1}, \]

where \( z \) denotes an arbitrary complex number (energy). The most expensive numerical step of our calculation is the matrix inversion in (77).

The inversion of the semi-infinite matrix (75) has been exactly treated using the so-called Surface Green Function technique which is detailed in Refs. [44] and [45]. After this step one has to invert a matrix of \( \tilde{N} \times \tilde{N} \) blocks. The tridiagonal structure of this matrix reduces the computing time from \( O(N^3) \) to \( O(N) \) (Refs. [46] and [47], Sec: 3.7.1).

The Green’s function can be rewritten into atomic layer-blocks,

\[ G_{\text{surf}}(z, \tilde{k}) = \left\{ G_{p,p'}^{pp'}(z, \tilde{k}) \right\}_{p,p'=1,\ldots,N}, \]

and in terms of inverse Fourier transformation the real-space Green’s function can be obtained,

\[ G_{\text{surf}}(z) = G_{p,m,p',m'}^{pp'}(z) = \frac{1}{\Omega_{BZ}} \int_{BZ} d^2 k \tilde{G}_{pp'}^{pp'}(z, \tilde{k}) e^{-i \tilde{k} (\tilde{T}_{m'} - \tilde{T}_m)}, \]
where $BZ$ is the two dimensional Brillouin-zone with volume $\Omega_{BZ}$. Considering the $C_{4v}$ symmetry of an fcc(001) surface, the integration volume can be reduced to only the irreducible segment of the $BZ$, which in this case is $1/8$ part of the full $BZ$. In general, about $10^4$ $k$-points were sufficient to calculate all quantities with a relative accuracy of 1%.

The Green’s function or resolvent operator of a nanoparticle is defined as

$$G_{\text{grain}}(z) = G_{\alpha\sigma, \alpha'\sigma'}^{\nu, \nu'}(z) = (z - H_{\text{grain}})^{-1}. \quad (80)$$

In this case, one can calculate the eigenvalues $\{\varepsilon_i\}$ and eigenvectors $\{|v_i\rangle\}$ of the Hamiltonian (76), $i = 1...M$, where $M = 18 \times N$, for $N$ sites in a given cluster. The spectral representation of the resolvent operator,

$$G_{\text{grain}}(z) = \sum_i \frac{|v_i\rangle\langle v_i|}{z - \varepsilon_i}. \quad (81)$$

can then be used.

The host Hamiltonian in case of surface (54) or cluster (76) system must be modified in the presence of a magnetic impurity. In this case, the hopping of the conduction electrons to the impurity’s $d$ orbitals should be excluded since this process is incorporated in the effective exchange interactions, Eqs. (46) and (48). The simplest way to account for this constraint is to shift the on-site $d$-state energies of the impurity $\varepsilon^i_\sigma$ far below the valence band and add the following term to the Hamiltonian,

$$\Delta H_{\text{surf}} = \Delta H_{\alpha\sigma, \alpha'\sigma'}^{(q)p_n,p'_{n'}} = \left(\varepsilon^i_\alpha - \varepsilon^i_\sigma\right) \delta_{pq} \delta_{\mu\mu'} \delta_{n0} \delta_{n'0} \delta_{\alpha\sigma} \delta_{\alpha'\sigma'}, \quad (82)$$

where the impurity is at site $n = 0$ of layer $q$. The Hamiltonian (82) destroys the two dimensional translation invariance of the surface host. This influences qualitatively the structure of the host (local) spectral density matrix and the symmetry adapted density matrices in the LSO and the HSO models. In case of an impurity at site $n = 0$ of a nanograin, one has to modify Eq. (76) as in the surface case,

$$\Delta H_{\text{grain}} = \Delta H_{\alpha\sigma, \alpha'\sigma'}^{n,n'} = \left(\varepsilon^i_\alpha - \varepsilon^i_\sigma\right) \delta_{n0} \delta_{n'0} \delta_{\alpha\sigma} \delta_{\alpha'\sigma'}. \quad (83)$$

According to the effective impurity models introduced in Section 2, we need the Green’s function only for a small cluster of sites, $C$, consisting of nearest neighbor atoms around the impurity and of the impurity itself. The corresponding Green’s function matrix can be evaluated as

$$g(z) = g'(z) (I - \Delta H g'(z))^{-1}, \quad (84)$$

where $I$ is a unit matrix and $g'(z) = \{G(z)\}_C$. Finally, the spectral function matrix on cluster $C$ is defined as

$$\rho_{\text{local}}(\varepsilon) = \frac{1}{2\pi i} \lim_{\delta \to 0} \left( g(\varepsilon + i\delta) - g(\varepsilon - i\delta) \right) = \frac{1}{2\pi i} \lim_{\delta \to 0} \left( g(\varepsilon + i\delta) - g(\varepsilon + i\delta)^+ \right). \quad (85)$$
The dimension of the matrices (84) and (85) is (13 × 9 × 2), because the number of sites, orbital and spin-indexes are 13, 9 and 12, respectively. Our impurity models are restricted to the hybridization between the impurity and the $s$-type conduction electrons. Therefore, from the $s$-components of the $\rho_{\text{local}}(\varepsilon)$ matrix we define the following projected matrix,
\[ \rho_{s-\text{local},\sigma\sigma'}^{nn'}(\varepsilon) = \rho_{\text{local},s\sigma\sigma'}^{nn'}(\varepsilon), \]
where $n, n' \in C$ and $\rho_{s-\text{local}}$ is a $26 \times 26$ matrix.

### 3.3 Electronic structure of the bulk host

For a realistic description of the host’s valance and conduction bands I used the on-site energies,
\[ \varepsilon_s(Au) = 7.64 \text{ eV}, \quad \varepsilon_s(Cu) = 10.812 \text{ eV}, \]
\[ \varepsilon_p(Au) = 17.39 \text{ eV}, \quad \varepsilon_p(Cu) = 18.4156 \text{ eV}, \]
\[ \varepsilon_{d-E_g}(Au) = 3.55 \text{ eV}, \quad \varepsilon_{d-E_g}(Cu) = 5.0759 \text{ eV}, \]
\[ \varepsilon_{d-T_{2g}}(Au) = 3.44 \text{ eV}, \quad \varepsilon_{d-T_{2g}}(Cu) = 5.0586 \text{ eV}, \]
the first and second nearest neighbor hopping parameters as given in a table of Appendix 2, and set the cubic lattice constants to their experimental values, $a_{Cu} = 3.615 \text{ Å}$ and $a_{Au} = 4.078 \text{ Å}$ [48]. The spin-orbit coupling parameter $\xi$ has been determined from the difference of the $SO$-split $d$-resonance energies
\[ \Delta E_d = E_{j=5/2} - E_{j=3/2}, \]
as derived from self-consistent relativistic (SKKR) first-principles calculations [49]. This splitting is related to the SOC strength as
\[ \Delta E_d \simeq \frac{5}{2} \xi. \]
For Au we obtained $\xi = 0.64 \text{ eV}$, while $\xi = 0.1 \text{ eV}$ for Cu.

The real space Green’s function $G_{\text{surf}}(z)$, was introduced in the previous section in case of a semi-infinite system. In a similar way it is also possible to determine the Green’s function of the bulk $G_{\text{bulk}}(z)$ using appropriate constraints. The imaginary part of $G_{\text{bulk}}(z)$ defines the bulk spectral density matrix,
\[ \rho_{\text{bulk}}(\varepsilon) = -\frac{1}{2\pi i} \lim_{\delta \to 0} (G_{\text{bulk}}(\varepsilon + i\delta) - G_{\text{bulk}}(\varepsilon - i\delta)), \]
and the trace of the $\rho_{\text{bulk}}(\varepsilon)$ gives the bulk density of states, $n_{\text{bulk}}(\varepsilon)$. As shown in Fig. 4, the dispersion of the 3$d$-band of Cu is about 4 eV, while the 5$d$-band of Au is much broader.
Figure 4: Calculated valence band densities of states for Cu and Au bulk without SO interaction (dots) and with SO interaction (solid line). For the latter case, the Fermi energies, $\varepsilon_F^{Cu} = 8.3$ eV and $\varepsilon_F^{Au} = 7.4$ eV, are indicated by vertical lines.

($\sim 7eV$). Reassuringly, the positions and the heights of the characteristic peaks of the DOS compare well with those obtained from self-consistent first principles calculations [49, 50]. Clearly, in copper, the small SOC, causes merely a slight modification of the DOS in the vicinity of the $d$-like on-site energy $\sim 5.07$ eV. In the case of Au the SOC is large enough to influence the whole $d$-band. It gives rise to strong splittings of the dispersion peaks and it also increases slightly the bandwidth. As indicated by the vertical lines in Fig. 4, the Fermi energies $\varepsilon_F^{Cu} = 8.3$ eV and $\varepsilon_F^{Au} = 7.4$ eV lie well above the $d$ band for both metals.

From the so-called asymptotic analysis, we shall see that the extremal vectors of the Fermi surface play a crucial role in determining the oscillations of the magnetic anisotropy constants. Therefore, we next investigate the plane cuts of the Fermi surface perpendicular to the (1,-1,0) direction of the FS of Cu and Au. If the energy $\varepsilon$ is fixed, the poles of the
Figure 5: Calculated plane cuts perpendicular to the (1-1 0) direction of the FS of Cu and Au. The arrows along the (001) direction denote the extremal vectors of lengths, $Q_{\text{Cu}}^{\text{min}} = 0.505 \, \text{Å}^{-1}$, $Q_{\text{Cu}}^{\text{max}} = 1.208 \, \text{Å}^{-1}$ and $Q_{\text{Au}}^{\text{min}} = 0.298 \, \text{Å}^{-1}$, $Q_{\text{Au}}^{\text{max}} = 1.228 \, \text{Å}^{-1}$. The horizontal vectors $Q_{110}^\text{Au} = 2.017 \, \text{Å}^{-1}$ and $Q_{110}^\text{Cu} = 2.200 \, \text{Å}^{-1}$ will appear in the RKKY interaction, see Section 5.

Bloch-spectral function,

$$n(\varepsilon, \vec{k}) = -\frac{1}{2\pi i} Tr \left[ \lim_{\delta \to 0} \left( G \left( \varepsilon + i\delta, \vec{k} \right) - G \left( \varepsilon - i\delta, \vec{k} \right) \right) \right],$$

have to be looked for. Note that the Bloch-spectral function is related to the DOS by,

$$n(\varepsilon) = \frac{1}{\Omega_{\text{BZ}}} \int d^3 k \, n(\varepsilon, \vec{k}).$$

The poles of the Bloch-spectral function take place at the eigenvalues $\varepsilon(\vec{k})$. If the calculation is extended to complex energies $z = \varepsilon + i\delta$, the dispersion relation is determined by the center positions of the Lorentzian-peaks. One can easily read off the length of the (001) extremal vectors from the cuts depicted in Fig. 5. The absolute minimum of the width of the Fermi surface $Q_{\text{min}}$ can be found at $\vec{k} = 0$ of the (001) surface Brillouin zone,
while the maximum width of the corresponding cut, $Q_{\text{max}}$, is related to saddle points of the Fermi surface. In the case of a $Cu$ host the values obtained from our tight-binding analysis, $Q_{\text{min}}^{Cu} = 0.505 \AA^{-1}$ and $Q_{\text{max}}^{Cu} = 1.208 \AA^{-1}$, agree fairly well with the results of Lathiotakis [51] and Bruno and Chappert [52]. It should be noted, however, that the shape of the FS depends very sensitively on the position of the Fermi energy.

### 3.4 Electronic structure of the grain

Eq. (76) defines the Hamiltonian of a nanograin. The features of a mesoscopic non-magnetic particle are quite different from those of the semi-infinite system. The spectral statistics of the Hamiltonian of the disordered sample has been analyzed using Random Matrix Theory.

<table>
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<th>Shell</th>
<th>$N_{sh}$</th>
<th>$N$</th>
<th>$N_c$</th>
<th>Shell</th>
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Table 1: The shell structure of fcc clusters. Label, $a$ and $b$ denote shells at the same distance, but inequivalent by symmetry. $N_{sh}$ denotes the number of sites in a given shell, $N_c$ is the number of core sites in case of cluster containing $N$ atoms.

First, we consider a center atom and its first, second, third etc. neighbor sites taken from a perfect fcc lattice. The atoms, at the same distance from the center atom define a shell in a nanoparticle. We model disordered grains having an outmost shell with missing atoms.
Figure 6: The spd-DOS components of an ordered nanograin ($N=393$)

Figure 7: The integrated DOS of $n_{\text{samp}} = 20$ disordered nanograin. There are two linear ranges ($E_d$ and $E_s$) marked by thick lines.
The inner shells are always completely filled with gold atoms and the ordered (or symmetric) cluster has only completely filled shells. For instance an ordered grain with $N = 43$ is built from 4 occupied shells: 1 center atom, 12 first-, 6 second- and 24 fourth-neighbors. Defined with more care the sites in a nanograin belong to same shell if they transform into each other under $O_h$ transformations. So, for instance the site $(0, 1.5, 1.5)$ belongs to shell 9NNa, while the site $(0.5, 0.5, 2)$ is on shell 9NNb, though they are at the same distance from the origin (center atom). The so-called core atoms in a given grain are those that have all the first neighbors: the core region is away from the surface of the cluster. $N_c$ denotes the number of core atoms in a given grain. Table 1 shows the $N_c$ values in case of $N$ gold atoms. If in a disordered grain there are 12 atoms in the outmost shell instead of 24, one has $\binom{24}{12}$ configurations with the same $N$. In practice, we choose randomly only $n_{\text{samp}}$ grains from the big configuration space. We examined the statistical features of grain-Hamiltonians with and without host SOC. In case of $\xi = 0$ we speak on nonrelativistic grains, and $\xi = 0.64$ eV defines the relativistic grains.

![Graph](image)

**Figure 8:** The level spacing distribution of $n_{\text{samp}} = 19$ nonrelativistic disordered nanograins in the d-band ($N=237$).

The Hamiltonian (76) is an $M \times M$ matrix, where $M = 18 \times N$ which has at most $M/2$ different eigenvalues $\{\varepsilon_i\}$ because of Kramers-degeneracy. The level spacings $\{s_i\}$ are defined as

$$s_i = \varepsilon_{i+1} - \varepsilon_i,$$

(93)
Figure 9: The level spacing distribution of 10 nonrelativistic disordered nanograins near the Fermi-surface ($N=393$).

and $\varepsilon_1 \leq \varepsilon_2 \leq \ldots \leq \varepsilon_{M/2}$. In case of disordered nanograins the eigenvalues are strictly doubly degenerate, so we always deal with $M/2$ different eigenvalues and $M/2 - 1$ level spacing values $\{s_i\}$. In a given sample there are $n_{s_{amp}} \times M/2$ eigenvalues and $n_{s_{amp}} \times (M/2 - 1)$ level spacings. We briefly summarized the derivation of the $n(\varepsilon)$ and $p(s)$ distribution functions of $\{\varepsilon_i\}$ and $\{s_i\}$ using Random Matrix Theory in Appendix 3, respectively. The universal $p(s)$ function can be written as

$$p_\beta (x) = a_\beta x^\beta \exp \left(-b_\beta x^2\right),$$

where the parameter $\beta$ denotes the appropriate Gaussian Ensemble, where $x = s/\Delta$ and $\Delta$ is the expected value of the level spacings.

The calculated density of states $n(\varepsilon)$ in case of a nanograin containing $N = 393$ gold atoms can be seen in Fig. 6. One can see large DOS arising form the 'd-band' near 3 $eV$ similar to bulk cases in Fig. 4. The highest occupied energy (Fermi energy) is also on the same value as in bulk case, $\varepsilon_F = 7.4$ $eV$. The integration of $n(\varepsilon)$ from the bottom of the band to a given energy defines the integrated density of states $N(\varepsilon)$. The Fig. 7 shows the calculated value $N(\varepsilon)$. The corresponding sample contains $n_{s_{amp}} = 20$ different random particles with $N = 393$ atoms. We can see, that there are two energy ranges, $\varepsilon_d$ and $\varepsilon_s$, where the integrated DOS is a nearly linear function and it can be supposed, that $n(\varepsilon)$ is constant in these ranges, at least on averages. The average level spacing can then be defined
as,

\[ \Delta_i = \frac{1}{(M/2)n(E_i)}; \quad (i = d, s). \]  

(95)

In case of \( d \)-band between 3 and 4.5 \( eV \) \( (E_d) \) a good statistical analysis can be done because of the large values of \( n(E_d) \). The other energy range, \( E_s \) is chosen from 6 to 14 \( eV \), where the dominant component of the DOS is the \( s \)-type states. The value of \( \rho(E_s) \) is smaller than \( \rho(E_d) \), therefore we cannot do a satisfactory statistical analysis, but the range \( E_s \) contains the Fermi energy.

Kubo-relation says that the expected value of the level spacings is inverse proportional to \( L^d \), where \( L \) is the linear size of a \( d \) dimensional system. It follows that

\[ \Delta_{N,i} \sim \frac{1}{N}; \quad (i = d, s). \]  

(96)

Reassuringly, the ratios of \( \Delta_{393,d} = 2.337 \ meV \) and \( \Delta_{273,d} = 3.667 \ meV \ agree with the value of \( \frac{237}{393} \) within an accuracy of 10\% in case of nonrelativistic particles and the ratio of \( \Delta_{237,d} = 3.983 \ meV \) \( \approx \Delta_{165,d} = 5.469 \ meV \ agree with \( \frac{165}{237} \) within an accuracy of 5\% in the presence of host SOC.

The distribution of the level spacings is shown in Fig. 8, in case of \( n_{samp} = 19 \) nonrelativistic disordered nanograins with \( N = 237 \) atoms in the range \( E_d \). The level spacing values
are measured in units of $x = \frac{\Delta}{x}$. The dominant part of the data is between $x = 0$ and $x = 3$. The values of the parameters $a_1 = 1.66$ and $b_1 = 0.86$ agree with $\frac{\pi}{2}$ and $\frac{\pi}{4}$, see Eq. (254) within an accuracy of 6 and 8 %, respectively, so the level spacing statistics is described very well by the GOE, see Appendix 3. The fitting of the data is not so satisfactory in the energy range $E_s$, see Fig. 9, but the linear level repulsion is obvious in case of small $x$. Furthermore, the distribution has a fat tail, which is damped in the case of bigger particles and larger samples. The relativistic result ($\xi = 0.64 \text{ eV}$) is plotted in Fig. 10 for the case of $n_{\text{sam}} = 10$ disordered particles containing $N = 165$ atoms. The fitted parameters $a_4 = 11.25$ and $b_4 = 2.36$ agree again with Eq. (254) within an accuracy of 3 and 4 %, respectively. The SOC on the gold atoms, thus, induces a spectral statistics that should be described by a Gaussian Symplectic Ensemble ($GSE$, $\beta = 4$).
4 The HSO mechanism

4.1 Evaluation of the magnetic anisotropy constant

The interaction of conduction electrons with the impurity spin is described by the HSO-Hamiltonian defined in Eq. (48). As in Ref. [7] the zero-temperature first- and second-order contributions to the static ($\omega = 0$) self-energy of the impurity spin can be expressed in terms of the local spectral function matrix $\varepsilon_{\sigma,\delta',\sigma}'^H \equiv \rho^H(\varepsilon)$ as [13],

$$\Sigma_{s,s'}^H(\omega = 0) = \Sigma_{s,s'}^{H(1)} + \Sigma_{s,s'}^{H(2)},$$

(97)

where

$$\Sigma_{s,s'}^{H(1)} = \int_{-\infty}^{\varepsilon_F} d\varepsilon \text{Tr} \left\{ \rho^H(\varepsilon) H_{s,s'} \right\} = J \sum_i \int_{-\infty}^{\varepsilon_F} d\varepsilon \text{Tr} \left\{ \rho^H(\varepsilon) \sigma^i \right\} S_{s,s'}^i,$$

(98)

and

$$\Sigma_{s,s'}^{H(2)} = \int_{-\infty}^{\varepsilon_F} \int_{-\varepsilon}^{\varepsilon_F} d\varepsilon d\varepsilon' \sum_{i,j} \text{Tr} \left\{ \rho^H(\varepsilon) H_{i,s} \rho^H(\varepsilon') H_{j,s'} \right\}$$

$$= J^2 \sum_{i,j} \int_{-\infty}^{\varepsilon_F} \int_{-\varepsilon}^{\varepsilon_F} d\varepsilon d\varepsilon' \text{Tr} \left\{ \rho^H(\varepsilon) \sigma^i \rho^H(\varepsilon') \sigma^j \right\} \int_{-\varepsilon}^{\varepsilon_F} S_{s,s'}^{i,j},$$

(99)

with $\text{Tr}\{\ldots\}$ denoting the trace in the ten-dimensional subspace of the conduction electrons ($D_s|\sigma\rangle$) and $\varepsilon_F$ is the Fermi energy. The spectral function $\rho^H_{\delta,\sigma,\delta',\sigma}'$ can easily be obtained from the restricted real-space local spectral function matrix elements that are defined in Eq. (86), by using a transformation to the combinations, Eqs. (26), that produce the $d$-type functions from the $s$-states.

Exploiting the $C_{4v}$ symmetry of an $fcc$ (001) surface system and time-reversal invariance, one finds that the $10 \times 10$ matrix $\rho^H_{\delta,\sigma,\delta',\sigma}'$, has the following structure,

$$\rho^H(\varepsilon) = 
\begin{pmatrix}
\varrho_1 I_2 & i\varrho_5 \sigma_z & i\varrho_6 \sigma_x & i\varrho_7 \sigma_y & -i\varrho_8 \sigma_y \\
-i\varrho_5 \sigma_z & \varrho_1 I_2 & -i\varrho_6 \sigma_x & i\varrho_7 \sigma_y & i\varrho_8 \sigma_x \\
-i\varrho_6 \sigma_x & i\varrho_6 \sigma_y & \varrho_2 I_2 & i\varrho_9 \sigma_z & 0 \\
-i\varrho_7 \sigma_y & i\varrho_7 \sigma_x & -i\varrho_9 \sigma_z & \varrho_3 I_2 & 0 \\
i\varrho_8 \sigma_y & -i\varrho_8 \sigma_x & 0 & 0 & \varrho_4 I_2
\end{pmatrix},$$

(100)

where $\forall \varrho_i \in \mathbb{R}$ and we dropped the energy argument of the spectral functions. The above form is fully confirmed by our numerical calculations. Inserting Eq. (100) into Eq. (98) yields $\Sigma_{s,s'}^{H(1)} = 0$. This is in full agreement with Ref. [7].

Furthermore, $\text{Tr}\{\ldots\}$ in Eq. (99) can be evaluated as follows,

$$\text{Tr} \left\{ \rho^H(\varepsilon) \sigma^i \rho^H(\varepsilon') \sigma^j \right\} = [2\varrho_1(\varepsilon) \varrho_1(\varepsilon') + \varrho_2(\varepsilon) \varrho_2(\varepsilon') + \varrho_3(\varepsilon) \varrho_3(\varepsilon') + \varrho_4(\varepsilon) \varrho_4(\varepsilon')] \text{tr} (\sigma^i \sigma^j)$$

$$+ \varrho_5(\varepsilon) \varrho_5(\varepsilon') |\text{tr} (\sigma^i \sigma^j) | + \varrho_6(\varepsilon) \varrho_6(\varepsilon') |\text{tr} (\sigma^i \sigma^j) | + \varrho_7(\varepsilon) \varrho_7(\varepsilon') |\text{tr} (\sigma^i \sigma^j) | + \varrho_8(\varepsilon) \varrho_8(\varepsilon') |\text{tr} (\sigma^i \sigma^j) |,$$

(101)
which by using the algebra of Pauli-matrices implies

\[ \text{Tr} \left\{ \rho^H(\varepsilon) \sigma^i \rho^H(\varepsilon') \sigma^j \right\} = \]
\[ 2\delta_{ij} [2\varrho_1(\varepsilon)\varrho_1(\varepsilon') + \varrho_2(\varepsilon)\varrho_2(\varepsilon') + \varrho_3(\varepsilon)\varrho_3(\varepsilon') + \varrho_4(\varepsilon)\varrho_4(\varepsilon') - \varrho_9(\varepsilon)\varrho_9(\varepsilon') - \varrho_5(\varepsilon)\varrho_5(\varepsilon')] \]
\[ - 4\delta_{ij}\delta_{z_1} [\varrho_6(\varepsilon)\varrho_6(\varepsilon') + \varrho_7(\varepsilon)\varrho_7(\varepsilon') + \varrho_8(\varepsilon)\varrho_8(\varepsilon') - \varrho_9(\varepsilon)\varrho_9(\varepsilon') - \varrho_5(\varepsilon)\varrho_5(\varepsilon')] \]  

(102)

The self-energy can be written in a spin-matrix form,

\[ \Sigma^H \approx \Sigma^{H(2)} = C^H \left( S^2 \right) + \bar{K}^H \left( \bar{S}^2 \right) \]  

(103)

where the anisotropy constant \( \bar{K}^H \) arises from the off-diagonal elements of \( \rho^H(\varepsilon) \) and it can be expressed as

\[ \bar{K}^H = K_6^H + K_7^H + K_8^H - K_5^H - K_9^H \]  

(104)

with

\[ K_i^H = -4J^2 \int_{-\infty}^{\varepsilon_F} d\varepsilon \int_{\varepsilon_F}^{\infty} d\varepsilon' \frac{\varrho_i(\varepsilon)\varrho_i(\varepsilon')}{\varepsilon' - \varepsilon} \quad (i = 5 \ldots 9) \]  

(105)

It should be noted that the off-diagonal elements of \( \rho^H(\varepsilon) \) vanish in the absence of SOC, thus, \( \bar{K}^H = 0 \) if \( \xi = 0 \). Furthermore, when the impurity is placed in the bulk, cubic symmetry implies,

\[ \varrho_i^0(\varepsilon) = \varrho_i^0(\varepsilon) \]  

\[ \varrho_6^0(\varepsilon) = -\varrho_5^0(\varepsilon) \]  

\[ \varrho_8^0(\varepsilon) = \sqrt{3}\varrho_7^0(\varepsilon) \]  

\[ \varrho_9^0(\varepsilon) = -2\varrho_7^0(\varepsilon) \]  

(106)

where the subscript 0 refers to the bulk and again \( \bar{K}^H = 0 \) is obtained. Thus, the anisotropy is indeed generated by the surface, which breaks the cubic symmetry of the crystal.

### 4.2 Asymptotic form of \( \bar{K}^H(d) \)

The presence of the surface induces Friedel oscillations in the local spectral functions [53]. For long distances \( d \) from the surface, an asymptotic analysis can be performed based on the rapid oscillations of the electronic wave function, \( \sim \exp(ikzd) \). When the constant energy surface in the three-dimensional Brillouin zone of the bulk system is formed by a single band, such as in the case of noble metals, the following asymptotic expression for the spectral functions in Eq. (100) applies,

\[ \varrho_i(\varepsilon, d) \simeq \varrho_i^0(\varepsilon) + \frac{2}{d} \sum_{\nu} g_i^\nu(\varepsilon) \cos [Q_i^\nu(\varepsilon) d + \theta_i^\nu(\varepsilon)] \]  

(107)

where \( \varrho_i^0(\varepsilon) \) is the spectral function in the bulk, the \( Q_i^\nu(\varepsilon) \) denote the lengths of extremal vectors of the constant energy surface normal to the geometrical surface, the \( g_i^\nu(\varepsilon) \) stand for the amplitudes of the oscillations and \( \theta_i^\nu(\varepsilon) \) are phases. The Eq. (107) are based on Ref.
[55]. As discussed in the previous section, in case of fcc (001) geometry there are two different extremal vectors, $Q_{\text{min}}$ and $Q_{\text{max}}$. Furthermore, it turns out that each of the spectral function matrix elements has a non-negligible contribution related to only $Q_{\text{max}}$, therefore, as what follows, the extremal vectors in Eq. (107) will be labeled by the index of the matrix elements $i$. By substituting expression (107) into Eq. (105), we obtain,

$$K_i^H = 2 \Re \left( \tilde{K}_i^{H1} + \tilde{K}_i^{H2} \right),$$  

where in leading order of $1/d$,

$$\tilde{K}_i^{H1} = -\frac{4J^2}{d} \int_{-\infty}^{\infty} \frac{d\varepsilon'}{\varepsilon'} \int_{-\infty}^{\varepsilon'} \frac{d\varepsilon}{\varepsilon - \varepsilon'} g_i(\varepsilon) e^{i(Q_i(\varepsilon)d + \theta_i(\varepsilon))},$$  

$$\tilde{K}_i^{H2} = -\frac{4J^2}{d} \int_{-\infty}^{\infty} \frac{d\varepsilon'}{\varepsilon'} \int_{-\infty}^{\varepsilon'} \frac{d\varepsilon}{\varepsilon - \varepsilon'} g_i(\varepsilon) e^{i(Q_i(\varepsilon)d + \theta_i(\varepsilon'))}.$$  

Introducing a new integration variable,

$$\varepsilon'' = \varepsilon' - \varepsilon, \quad 0 < \varepsilon'' < \infty,$$

we get

$$\tilde{K}_i^{H1} = -\frac{4J^2}{d} \int_{0}^{\infty} \frac{d\varepsilon''}{\varepsilon''} \int_{\varepsilon''}^{\infty} \frac{d\varepsilon}{\varepsilon + \varepsilon''} g_i(\varepsilon) e^{i(Q_i(\varepsilon)d + \theta_i(\varepsilon))},$$  

$$\tilde{K}_i^{H2} = -\frac{4J^2}{d} \int_{0}^{\infty} \frac{d\varepsilon''}{\varepsilon''} \int_{\varepsilon''}^{\infty} \frac{d\varepsilon}{\varepsilon + \varepsilon''} g_i(\varepsilon) e^{i(Q_i(\varepsilon)d + \theta_i(\varepsilon'))}.$$  

Assuming that $\rho_0(\varepsilon), Q_i(\varepsilon), g_i(\varepsilon),$ and $\theta_i(\varepsilon)$ are slowly varying functions of $\varepsilon,$ whereas for large $e^{iQ_i(\varepsilon)d}$ is rapidly oscillating, the inner integrals in Eqs. (112) and (113) give sizable contributions only for small values of $\varepsilon''$, and therefore we can expand $Q_i(\varepsilon)$ around $\varepsilon_F$,

$$Q_i(\varepsilon) \simeq Q_i(\varepsilon_F) + Q_i'(\varepsilon_F)(\varepsilon - \varepsilon_F),$$  

and replace all the other functions by their values at $\varepsilon_F$,

$$\tilde{K}_i^{H1} \simeq -\frac{4J^2}{d} g_i(\varepsilon_F) g_i(\varepsilon_F) e^{i(Q_i(\varepsilon_F)d + \theta_i(\varepsilon_F))} \int_{0}^{\infty} \frac{d\varepsilon''}{\varepsilon''} \int_{\varepsilon''}^{\infty} \frac{d\varepsilon}{\varepsilon + \varepsilon''} e^{iQ_i'(\varepsilon_F)(\varepsilon - \varepsilon_F)d},$$  

$$\tilde{K}_i^{H2} \simeq -\frac{4J^2}{d} g_i(\varepsilon_F) g_i(\varepsilon_F) e^{i(Q_i(\varepsilon_F)d + \theta_i(\varepsilon_F))} \int_{0}^{\infty} \frac{d\varepsilon''}{\varepsilon''} \int_{\varepsilon''}^{\infty} \frac{d\varepsilon}{\varepsilon + \varepsilon''} \left[ 1 - e^{-iQ_i'(\varepsilon_F)d} \right],$$  

and, similarly,

$$\tilde{K}_i^{H2} \simeq -\frac{4J^2}{d} g_i(\varepsilon_F) g_i(\varepsilon_F) e^{i(Q_i(\varepsilon_F)d + \theta_i(\varepsilon_F))} \int_{0}^{\infty} \frac{d\varepsilon''}{\varepsilon''} \int_{\varepsilon''}^{\infty} \frac{d\varepsilon}{\varepsilon + \varepsilon''} \left[ e^{iQ_i'(\varepsilon_F)d} - 1 \right].$$  

Substituting Eqs. (116) and (117) into (108) yields,

$$K_i^H(d) \simeq -\frac{8\pi J^2 g_i^0(\varepsilon_F) g_i(\varepsilon_F) \cos(Q_i(\varepsilon_F)d + \theta_i(\varepsilon_F))}{|Q_i'(\varepsilon_F)|} \frac{d^2}{d^2}.$$  

For free electrons, $Q(\varepsilon_F) = 2k_F$, and the above result resembles that of Üjsághy et al. [11], however with a $\sim 1/d^2$ rather than a $\sim 1/d^3$ decay. This difference is a consequence of the assumption made in Ref. [11] that the scatterers in the host are distributed homogeneously.
4.3 Numerical results for $K^H(d)$

We performed calculations for the matrix elements of $\rho^H(\varepsilon)$, Eq. (100) for up to 50 monolayers (ML) below the surface, corresponding to a separation of $d \simeq 90$ and $\simeq 100$ Å for Cu and Au, respectively. As a convincing check of our numerical procedure we verified that the $d$-dependence of the calculated matrix elements agreed with that derived analytically from symmetry principles.

![Graph showing off-diagonal spectral function matrix elements at the Fermi energy as a function of the distance, d, from the (001) surface of a Au host.](image)

Figure 11: Calculated off-diagonal spectral function matrix elements at the Fermi energy as a function of the distance, $d$, from the (001) surface of a Au host.

In the case of a Au host, in Fig. 11 the calculated off-diagonal matrix elements $\varrho_5(\varepsilon_F)$, $\ldots$, $\varrho_9(\varepsilon_F)$ are plotted as functions of the distance $d$ from the surface. As expected, large oscillations are seen for all the spectral functions near the surface ($d > 20$ Å). These oscillations, however, survive for large distances $d$, only for $\varrho_6(\varepsilon_F)$, while they are strongly
damped in all the other cases. The limiting values of \( g_i \) correspond to the bulk case and, as we checked, satisfy the conditions (106) within 1% relative numerical accuracy.

![Graph](image)

**Figure 12:** Asymptotic fit to the function (107) (solid line) of the calculated values of the \( g_0(\varepsilon_F) \) spectral function (triangles) as a function of the distance from a Au(001) surface. The dashed line denotes the bulk value of \( g_0(\varepsilon_F) \).

In Fig. 12 the spectral function \( g_0(\varepsilon_F) \) is displayed on an enlarged scale, together with a fitting function of the form Eq. (107). Quite surprisingly, the asymptotic function applies already in the range of \( d > 20 \, \text{Å} \) and, therefore, there is no need to perform a “preasymptotic” analysis as suggested in [11]. The fitted parameters of Eq. (107) are: \( g_0^0(\varepsilon_F) = -3.99 \pm 0.01 \times 10^{-4} \, eV^{-1} \), \( g_0(\varepsilon_F) = -7.42 \pm 0.04 \times 10^{-4} \, eV^{-1} \), \( Q_0(\varepsilon_F) = 1.2228 \pm 0.0001 \, \text{Å}^{-1} \), and \( \theta_0(\varepsilon_F) = 1.324 \pm 0.006 \, \text{rad} \). It is particularly noteworthy that the fitted wave number agrees with an accuracy of 0.5% with the length of the extremal vector \( Q_{max} \) derived from the Au Fermi surface.

Performing the double energy integral in Eq. (105) is a quite demanding numerical procedure. Therefore, we used the asymptotic form (118) to compute the magnetic anisotropy \( K_i^H \). It was possible to fit all other off-diagonal spectral function components entering the expression of \( K^H \) with a similar fit with exactly the same wave number. However, the amplitude of these other components was by at least two orders of magnitude smaller than \( g_0(\varepsilon_F) \).

Our calculations thus indicate that the long-wavelength oscillation corresponding to \( Q_{min} \) of the Fermi surface either enters with a negligibly small amplitude or does not enter at all in
Figure 13: Upper panel: $K^H_6$ contribution to the magnetic anisotropy constant within the host spin-orbit coupling model for a Au host as calculated from the asymptotic expression, Eq. (118). Lower panel: The $K^H_6$ contribution to the magnetic anisotropy constant in the case of a Cu host. In both cases an exchange interaction parameter $J = 1$ eV was used.

the asymptotic form of the off-diagonal spectral function matrix elements. This can easily be understood by noticing that the asymptotic contributions to the real-space spectral function matrix elements $\mathcal{Q}_{\sigma \sigma', \delta \delta'}^{(q+p)n, (q+p')n'}(\varepsilon) (p, p' = 0, \pm 1, d = q^2_2)$ related to $Q_{\min}$ are of the following form:

$$
\mathcal{Q}_{\sigma \sigma', \delta \delta'}^{(q+p)n, (q+p')n'}(\varepsilon) \approx \mathcal{Q}_{\sigma \sigma', \delta \delta'}^{(0)n, n'}(\varepsilon) + \frac{g_{\sigma \sigma', \delta \delta'}^{p, p'}(\varepsilon)}{d} \cos (Q_{\min}(\varepsilon) + \theta(\varepsilon)) ,
$$

where $\mathcal{Q}_{\sigma \sigma', \delta \delta'}^{(0)n, n'}(\varepsilon)$ refer to the corresponding bulk matrix elements. Eq. (119) implies that the oscillating part does not depend on the in-plane positions $n$ and $n'$, which is the consequence of the minimal extremal vector being at the $\vec{k} = 0$ point of the 2D Brillouin zone. The matrixelements $\rho_{\delta \sigma, \delta' \sigma'}^H$ in Eq. (100) are linear combinations of the above real-space matrixelements according to the states in Eq. (26), $D_\delta |\sigma\rangle$, where $\delta = xz, yz, xy, x^2 - y^2$ are constructed as antisymmetric combinations of neighboring s orbitals in the same plane $q + p$ or as a sum of such antisymmetric combinations, tush, in their matrixelements the
asymptotic oscillatory part corresponding to $Q_{\text{min}}$ necessarily cancels. As a consequence, only the spectral function $\varrho_4 = \langle 2z^2 - x^2 - y^2 | \rho | 2z^2 - x^2 - y^2 \rangle$ has asymptotic oscillations with wave number $Q_{\text{min}}$, which, however, does not give a contribution to $K^H(d)$.

The energy derivative of the magnitude of the extremal vector $Q'(\varepsilon_F)$ was determined by fitting the spectral functions at two energy values close below and above $\varepsilon_F$. For Au(001) we obtained $Q'(\varepsilon_F) = 0.235 \, (\text{ÅeV})^{-1}$. Thus, in case of a Au host we get the following asymptotic function for $K^H_6(d)$ and displayed in the upper panel of Fig. 13,

$$K^H_6(d) = \frac{31.66}{d^2} \cos(1.2228d + 1.324) \, \mu\text{eV},$$

(120)

where $d$ is measured in Å. Notice the surprisingly small magnitude of $K^H_6$. Even at a distance of about $d = 20$ Å the amplitude of the above oscillating function is about $0.079 \, \mu\text{eV}$.

We performed similar calculations for a Cu host. In Cu, the spectral functions show asymptotic oscillations with $Q(\varepsilon_F) = 1.205 \, \text{Å}^{-1}$ that agrees within 0.3 % with the length of the extremal vector $Q_{\text{max}}$ of the Cu Fermi surface. In Cu, the $K^H_6(d)$ contribution shown in the lower panel of Fig. 13 dominates the magnetic anisotropy. This is in the range of $0.01 \, neV = 10^{-11} \, \text{eV}$, i.e., it is at least by three orders of magnitude smaller than the one found in case of a Au host. This decrease is mostly due to the smaller SO interaction in Cu than in Au. As we checked by varying $\xi$ for Au, the spectral functions in Eq. (100) scale linearly with $\xi$, therefore, by Eq. (105) $K^H$ scales as $\sim \xi^2$. This result clearly justifies the approach of Újsághy et al., [7, 8, 9, 11] who treated the SO interaction perturbatively.

In summary, we can conclude, that within HSO model, the $K^H$ remains well below the Kondo temperature $T_K$, therefore, this mechanism can not explain the anomaly of the Kondo resistance in reduced dimension.
5 The LSO mechanism

5.1 The structure of the LSO spectral density matrix

Within the LSO model, the spectral density matrix \( \rho^L(\varepsilon) \) is constructed from the restricted host spectral matrix \( \rho_{s-local} \), Eq. (86). The symmetry analysis of the \( j = 3/2 \) multiplet implies that we need only the states \( \delta = x^2 - y^2 \) and \( 2z^2 - x^2 - y^2 \), see Eq. (28), implying that the dimension of the Hilbert space is now four. We have to change for the appropriate basis corresponding to the representation \( \Gamma_8 \), i.e., transform the spectral density matrix,

\[
\bar{\rho}(\varepsilon) = \begin{pmatrix}
\Theta_{x^2,x^2,\uparrow\uparrow} & \Theta_{x^2,x^2,\uparrow\downarrow} & \Theta_{x^2,x^2,\downarrow\uparrow} & \Theta_{x^2,x^2,\downarrow\downarrow} \\
\Theta_{x^2,x^2,\downarrow\uparrow} & \Theta_{x^2,x^2,\downarrow\downarrow} & \Theta_{x^2,x^2,\uparrow\uparrow} & \Theta_{x^2,x^2,\uparrow\downarrow} \\
\Theta_{x^2,x^2,\downarrow\downarrow} & \Theta_{x^2,x^2,\uparrow\uparrow} & \Theta_{x^2,x^2,\downarrow\uparrow} & \Theta_{x^2,x^2,\downarrow\downarrow} \\
\Theta_{x^2,x^2,\uparrow\downarrow} & \Theta_{x^2,x^2,\downarrow\uparrow} & \Theta_{x^2,x^2,\downarrow\downarrow} & \Theta_{x^2,x^2,\uparrow\uparrow}
\end{pmatrix}, \tag{121}
\]

where subscript \( x^2 \) refers to \( \delta = x^2 - y^2 \) and \( z^2 \) stands for \( \delta = 2z^2 - x^2 - y^2 \) in terms of the unitary matrix \( Q \), Eq. (43),

\[
\rho^L(\varepsilon) = Q \bar{\rho}(\varepsilon) Q^\dagger, \tag{122}
\]

leading to

\[
\{ \ell_{mm'}^L(\varepsilon) \} = \begin{pmatrix}
\Theta_{x^2,x^2,\uparrow\uparrow} & -\Theta_{x^2,x^2,\uparrow\downarrow} & -\Theta_{x^2,x^2,\downarrow\uparrow} & \Theta_{x^2,x^2,\downarrow\downarrow} \\
-\Theta_{x^2,x^2,\downarrow\uparrow} & \Theta_{x^2,x^2,\downarrow\downarrow} & \Theta_{x^2,x^2,\uparrow\uparrow} & -\Theta_{x^2,x^2,\uparrow\downarrow} \\
-\Theta_{x^2,x^2,\downarrow\downarrow} & \Theta_{x^2,x^2,\uparrow\uparrow} & -\Theta_{x^2,x^2,\downarrow\uparrow} & \Theta_{x^2,x^2,\downarrow\downarrow} \\
\Theta_{x^2,x^2,\uparrow\downarrow} & -\Theta_{x^2,x^2,\downarrow\uparrow} & \Theta_{x^2,x^2,\downarrow\downarrow} & -\Theta_{x^2,x^2,\uparrow\uparrow}
\end{pmatrix}, \tag{123}
\]

with \( m, m' = \{ \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2} \} \) as in Eq. (44). We will analyze the density matrix \( \rho^L(\varepsilon) \) in case of different symmetries.

In case of a nanograin there is no global spatial symmetry, we can make use the time reversal symmetry only. The density matrix, Eq. (121) is built up from the following orbital-blocks,

\[
R_{11}(\varepsilon) = \begin{pmatrix}
\Theta_{x^2,x^2,\uparrow\uparrow} & \Theta_{x^2,x^2,\uparrow\downarrow} \\
\Theta_{x^2,x^2,\downarrow\uparrow} & \Theta_{x^2,x^2,\downarrow\downarrow}
\end{pmatrix}
R_{12}(\varepsilon) = \begin{pmatrix}
\Theta_{x^2,x^2,\uparrow\uparrow} & \Theta_{x^2,x^2,\uparrow\downarrow} \\
\Theta_{x^2,x^2,\downarrow\uparrow} & \Theta_{x^2,x^2,\downarrow\downarrow}
\end{pmatrix},
\]

\[
R_{21}(\varepsilon) = \begin{pmatrix}
\Theta_{x^2,x^2,\uparrow\uparrow} & \Theta_{x^2,x^2,\uparrow\downarrow} \\
\Theta_{x^2,x^2,\downarrow\uparrow} & \Theta_{x^2,x^2,\downarrow\downarrow}
\end{pmatrix}
R_{22}(\varepsilon) = \begin{pmatrix}
\Theta_{x^2,x^2,\uparrow\uparrow} & \Theta_{x^2,x^2,\uparrow\downarrow} \\
\Theta_{x^2,x^2,\downarrow\uparrow} & \Theta_{x^2,x^2,\down\downarrow}
\end{pmatrix}. \tag{124}
\]

Let’s investigate the action of time reversal for these,

\[
R_{ij}(\varepsilon) = \Theta^{-1} R_{ij}(\varepsilon) \Theta, \tag{125}
\]

where the antiunitary operator \( \Theta \) is the product of unitary operator \( u = i\sigma_y \) and the conjugation \( C \), i.e.

\[
\Theta = i\sigma_y C. \tag{126}
\]
One can then write

\[ R_{ij}(\varepsilon) = C^{-1} u^{-1} R_{ij}(\varepsilon) u C = (u^{-1} R_{ij}(\varepsilon) u)^* , \]  

where we used \( C^{-1} = C \). Written out in details,

\[
\begin{pmatrix}
    x & y \\
    z & r
\end{pmatrix}
= \Theta^{-1}
\begin{pmatrix}
    x & y \\
    z & r
\end{pmatrix}
\Theta
= \begin{pmatrix}
    r^* & -z^* \\
    -y^* & x^*
\end{pmatrix}.
\]  

Furthermore, \( \tilde{\rho}(\varepsilon) \) is Hermitean, i.e.,

\[
\tilde{\rho}_{kk'}(\varepsilon) = \tilde{\rho}^{*}_{k'k}(\varepsilon),
\]

which together with Eq. (128) implies the following structure of \( \tilde{\rho} \),

\[
\tilde{\rho}_{kk'}(\varepsilon) = \begin{pmatrix}
    \rho_1(\varepsilon) & 0 & \rho_4(\varepsilon) - \rho_5(\varepsilon)i & -\rho_3(\varepsilon) - \rho_6(\varepsilon)i \\
    0 & \rho_1(\varepsilon) & \rho_3(\varepsilon) + \rho_6(\varepsilon)i & \rho_2(\varepsilon) \\
    \rho_4(\varepsilon) + \rho_5(\varepsilon)i & \rho_3(\varepsilon) + \rho_6(\varepsilon)i & \rho_2(\varepsilon) & 0 \\
    -\rho_3(\varepsilon) + \rho_6(\varepsilon)i & \rho_4(\varepsilon) - \rho_5(\varepsilon)i & 0 & \rho_2(\varepsilon)
\end{pmatrix},
\]

where \( \forall \rho_i(\varepsilon) \in \mathbb{R} \). The LSO density matrix contains, therefore, only six real parameters.

The matrix of (121) can also be reordered into spin-blocks,

\[
\begin{pmatrix}
    \rho_{\uparrow\downarrow} & \rho_{\uparrow\uparrow} \\
    \rho_{\downarrow\uparrow} & \rho_{\downarrow\downarrow}
\end{pmatrix},
\]

with

\[
\rho_{\uparrow\downarrow} = \begin{pmatrix}
    \rho_{x^2,x^2,\downarrow\uparrow} & \rho_{x^2,x^2,\downarrow\downarrow} \\
    \rho_{x^2,x^2,\uparrow\uparrow} & \rho_{x^2,x^2,\uparrow\downarrow}
\end{pmatrix},
\]

\[
\rho_{\uparrow\uparrow} = \begin{pmatrix}
    \rho_{x^2,x^2,\uparrow\uparrow} & \rho_{x^2,x^2,\uparrow\downarrow} \\
    \rho_{x^2,x^2,\downarrow\uparrow} & \rho_{x^2,x^2,\downarrow\downarrow}
\end{pmatrix},
\]

\[
\rho_{\downarrow\uparrow} = \begin{pmatrix}
    \rho_{x^2,x^2,\downarrow\uparrow} & \rho_{x^2,x^2,\downarrow\downarrow} \\
    \rho_{x^2,x^2,\uparrow\uparrow} & \rho_{x^2,x^2,\uparrow\downarrow}
\end{pmatrix},
\]

\[
\rho_{\downarrow\downarrow} = \begin{pmatrix}
    \rho_{x^2,x^2,\downarrow\uparrow} & \rho_{x^2,x^2,\downarrow\downarrow} \\
    \rho_{x^2,x^2,\uparrow\uparrow} & \rho_{x^2,x^2,\uparrow\downarrow}
\end{pmatrix},
\]

and we also used Eq. (130). In absence of SOC \( \tilde{\rho} \) must commute with \( \sigma_z \). The up (\( \uparrow \)) and down (\( \downarrow \)) spin channels do not mix, so Eq. (131) has no offdiagonal elements and \( \rho_{\uparrow\downarrow} = \rho_{\downarrow\uparrow} \). Thus, in case of nonrelativistic nanograins there are only three nonvanishing elements: \( \rho_1(\varepsilon), \rho_2(\varepsilon) \) and \( \rho_4(\varepsilon) \), i.e.,

\[
\tilde{\rho}_{kk'}(\varepsilon) = \begin{pmatrix}
    \rho_1(\varepsilon) & 0 & 0 & 0 \\
    0 & \rho_1(\varepsilon) & 0 & 0 \\
    0 & 0 & \rho_2(\varepsilon) & 0 \\
    0 & 0 & 0 & \rho_2(\varepsilon)
\end{pmatrix}.
\]
Finally, $\rho^L(\varepsilon)$ is expressed from (130) by using the transformation (122),

$$
\varrho_{m'm'}^L(\varepsilon) = \begin{pmatrix}
\varrho_1(\varepsilon) & -\varrho_3(\varepsilon) + \varrho_6(\varepsilon)i & \varrho_4(\varepsilon) + \varrho_5(\varepsilon)i & 0 \\
-\varrho_3(\varepsilon) + \varrho_6(\varepsilon)i & \varrho_2(\varepsilon) & 0 & \varrho_4(\varepsilon) + \varrho_5(\varepsilon)i \\
\varrho_4(\varepsilon) - \varrho_5(\varepsilon)i & 0 & \varrho_3(\varepsilon) + \varrho_6(\varepsilon)i & \varrho_1(\varepsilon) \\
0 & \varrho_4(\varepsilon) - \varrho_5(\varepsilon)i & \varrho_3(\varepsilon) + \varrho_6(\varepsilon)i & \varrho_1(\varepsilon)
\end{pmatrix}, \quad (137)
$$

and, specifically, in nonrelativistic case, $\varrho^L(\varepsilon) = \tilde{\varrho}(\varepsilon)$, Eq. (136). The above structure of $\varrho^L(\varepsilon)$ is fully confirmed by our numerical calculations. Recalling also Eq. (123) it can be easily see, that $\varrho^L(\varepsilon)$ has no offdiagonal elements in case of cubic (bulk) symmetry or in case of tetragonal symmetry of a surface. The diagonal elements $\varrho_1(\varepsilon)$ and $\varrho_2(\varepsilon)$ are equal in the bulk case, however, they are different for tetragonal symmetry.

5.2 Numerical calculation and multipole decomposition of the LSO-anisotropy matrix

Again perturbation calculation technique is used to compute the self-energy of the impurity [13]. Using the up to second order in $J$, the diagrams are shown in Fig. 14, and the self energy at $T = 0$ temperature is given by [13],

$$
\Sigma^L_{m m'}(\omega = 0) = \Sigma^L_{m m'}^{(1)} + \Sigma^L_{m m'}^{(2)},
$$

$$
\Sigma^L_{m m'}^{(1)} = J \int_{-\infty}^{\varepsilon_F} d\varepsilon \varrho^L_{m m'}(\varepsilon),
$$

$$
\Sigma^L_{m m'}^{(2)} = J^2 \int_{-\infty}^{\varepsilon_F} d\varepsilon \int_{-\infty}^{\varepsilon_F} d\varepsilon' \frac{1}{\varepsilon' - \varepsilon} \varrho^L_{m m'}(\varepsilon) \sum_{m''} \varrho^L_{m'' m'''}(\varepsilon') \varrho^L_{m''' m'''}(\varepsilon').
$$

Interestingly, already the first-order contribution to the self-energy gives a nonvanishing anisotropy in the vicinity of a surface or at a site of a nanograin. Therefore, as what follows we consider this term only.

![Figure 14: First and second ordered self energy diagrams of the impurity spin. The dashed and continuous lines denote the propagators of the spin and the conduction electrons, respectively.](image)

a.  
b.
Eqs. (139) and (137) imply that the first order LSO anisotropy matrix is given by

$$
\Sigma_{mm'}^{L(1)} = J \int_{-\infty}^{E_F} d\varepsilon g_{mm'}^{L}(\varepsilon) = \begin{pmatrix}
  K_1^L & -K_3^L + K_6^L i & K_4^L + K_5^L i & 0 \\
  -K_3^L - K_6^L i & K_2^L & 0 & K_4^L + K_5^L i \\
  K_4^L - K_5^L i & 0 & K_2^L & K_3^L - K_5^L i \\
  0 & K_4^L - K_5^L i & K_3^L + K_6^L i & K_1^L 
\end{pmatrix},
$$

(141)

with

$$
K_i^L = J \int_{-\infty}^{E_F} d\varepsilon q_i(\varepsilon) \in \mathbb{R}.
$$

(142)

Actually, the local host Green’s function $g(z)$, as defined in Eq. (84), is integrated to obtain

$$
\int_{-\infty}^{E_F} d\varepsilon \rho_{s-local}(\varepsilon) = -\frac{1}{2\pi i} \left\{ \int_{-\infty}^{E_F} d\varepsilon \left[ g(\varepsilon + i0) - \left( \int_{-\infty}^{E_F} d\varepsilon \, g(\varepsilon + i0) \right) \right] \right\}.
$$

(143)

Recall that $g(z)$ is calculated from the projection of $G(z)$ to a given site and its first nearest neighbors. For a semi-infinite system $G(z)$ is defined in Eq. (79), while there are two options in case of nanograins: (i) direct inversion for each different complex energies $z$, Eq. (80), or (ii) the previously computed eigenvectors of the host-Hamiltonian are used in Eq. (81). These two methods produce the same results with in an accuracy of ten digits.

In case of a semi-infinite system a similar procedure as in model HSO is used to calculate the anisotropy constant in the asymptotic regime. However, now, it is also possible to compute the anisotropy matrixelements directly from Eq. (142) and to compare with the asymptotic calculation. Considering that the (local) Green’s function $g(z)$ is analytic on the upper complex semi-plane, one can choose an appropriate path of integration,

$$
\int_{E_b}^{E_F} d\varepsilon \, g(\varepsilon + i0) = \int_{\sim} d\varepsilon \, g(z),
$$

(144)

where $E_b$ denotes the bottom of the energy band and $\sim$ is a semicircular contour, from $E_b$ to $E_F$. Moreover, a Gaussian-quadrature is used for the numerical integration,

$$
\int_{\sim} d\varepsilon \, g(z) = \sum_{i=1}^{N} w_i g(z_i),
$$

(145)

where $z_i$ denote the complex energy values on the contour and $w_i$ are weighting factors. The contour integration is a very robust method, because the poles of the Green’s function on the real axis are avoided, so $10 - 16$ points along the contour are sufficient for a very precise numerical integration.

After diagonalizing the anisotropy matrix (141), the following eigenvalues are obtained,

$$
\lambda_1^L = \frac{K_1^L + K_2^L}{2} + \sqrt{\frac{(K_1^L - K_2^L)^2}{2} + (K_4^L)^2 + (K_5^L)^2 + (K_6^L)^2 + (K_0^L)^2},
$$

(146)
\[ \lambda_2^L = \frac{K_1^L + K_2^L}{2} - \sqrt{\left(\frac{K_1^L - K_2^L}{2}\right)^2 + (K_3^L)^2 + (K_4^L)^2 + (K_5^L)^2 + (K_6^L)^2}. \] (147)

It is worth to define the anisotropy constant from the level splitting,
\[ K^L = \frac{\lambda_2^L - \lambda_2^L}{2}. \] (148)

A general $4 \times 4$ Hermitian matrix contains 16 independent real parameters, so one can express this matrix using a multipolar basis consisting, specifically, of one monopole, three dipole, five quadrupole and seven octopole matrices (operators). Time reversal implies vanishing dipole and octopole contributions. The remaining six real parameters of the anisotropy (self-energy) matrix (141) can be expressed by the monopole (unit) operator and the five quadrupole operators. The quadrupole operators can be defined with the help of $J_x, J_y, J_z$, as given in Eqs. (20),

\[ Q_2 = \frac{1}{\mathcal{H}^2} (2J_z^2 - J_x^2 - J_y^2) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \] (149)

\[ Q_3 = \frac{\sqrt{3}}{\mathcal{H}^2} (J_x J_z + J_z J_x) = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{pmatrix}, \] (150)

\[ Q_4 = \frac{\sqrt{3}}{\mathcal{H}^2} (J_x^2 - J_y^2) = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \] (151)

\[ Q_5 = \frac{\sqrt{3}}{\mathcal{H}^2} (J_x J_y + J_y J_x) = \begin{pmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{pmatrix}, \] (152)

\[ Q_6 = \frac{\sqrt{3}}{\mathcal{H}^2} (J_y J_z + J_z J_y) = \begin{pmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & i \\ 0 & 0 & -i & 0 \end{pmatrix}. \] (153)

It is easy to check that $Tr(Q_i) = 0$, $Tr(Q_i Q_j) = 4\delta_{ij}$, and $Q_i Q_j + Q_j Q_i = 2I_4$. The $Q_i$’s, thus, form a legitimate basis for the multipole expression. $J_i$’s transform as the components of an axial vector: they can change sign under time reversal and remain invariant under space inversion, i.e., they transform as the gerade irrep $T_{1g}$ of $O_h$. The construction of quadrupoles follows from the direct product
\[ T_{1g} \times T_{1g} = A_{1g} + E_g + T_{2g} + T_{1g}, \] (154)
where the term $T_{1g}$ change sign under time reversal and $A_{1g}$ is proportional to the unit matrix. \{Q_2, Q_4\} form a basis for $E_g$ and \{Q_3, Q_5, Q_6\} basis for $T_{2g}$. Comparing with Eq. (141), the anisotropy matrix can be expressed on the basis \{Q_1, I_4\} as

$$\Sigma_{m'm}^{L(1)} = \frac{K_1^L + K_2^L}{2} I_4 + \frac{K_1^L - K_2^L}{2} Q_2 + K_4^L Q_4 - K_3^L Q_3 - K_5^L Q_5 - K_6^L Q_6 .$$  \hspace{1cm} (155)

It should be noted, that as follow from Eq. (136), without host SOC the only remaining coefficients are those of the quadrupoles \{Q_2, Q_4\}, i.e. \(\frac{K_1^L - K_2^L}{2}\) and \(K_4^L\).

### 5.3 Symmetry of the anisotropy parameters for ordered nanograins

Here, I present the symmetry analysis of the anisotropy matrices (141) in case of ordered nanograins. Let us consider an ordered nanocluster with \(N = 153\) atoms, which has only nine occupied shells, see Table 1. The number of core atoms is \(N_c = 55\), that contains the center atom and the four innermost shells, Fig. 15 shows the geometric structure of a cluster of \(N_c = 55\) core atoms.

![Figure 15: The geometric structure of the core of an ordered nanograin containing \(N_c = 55\) atoms. The shell structure is explained in Table 1. Color coding: center-black, first shell-red, second shell-green, third shell-blue, fourth shell-cyan.](image-url)
The anisotropy matrices are different for the different sites even in the same shell, but symmetry relations can be found between their elements. Let us enumerate the core sites by index $i = 1\ldots55$. We shall label the anisotropy matrices $\Sigma^{L(1)}_{mm'}$, see Eq. (141), by a site index $i$ and suppress the matrix index $m$ and $m'$, i.e., we introduce the matrices $\Sigma^{L(1)}_i$. Each matrix can be described by six parameters, so these parameters will have a site index $i$ and a parameter index $\alpha = 1\ldots6, K^L_{\alpha,i}$. Let $i$ and $j$ be two sites in the same shell and let the two sites be connected by the group element $g \in O_h$, i.e., $g\vec{R}_i = \vec{R}_j$. So the transformation rule for the matrices $\Sigma^{L(1)}_i$ and $\Sigma^{L(1)}_j$ can be written as

$$\Sigma^{L(1)}_j = U^{L}_2(g)\Sigma^{L(1)}_i U^{L}_2(g)^\dagger,$$

where $U^{L}_2(g)$ is defined in Eq. (230) of Appendix 1, whereas $g$ corresponds to the rotation around axis $\vec{n}$ with angle $\phi$. From Eq. (156) we can derive relations between the anisotropy matrix elements of the different sites.

Motivated by the quadrupole-decomposition of the anisotropy matrices, it seems reasonable to calculate the transformation rules for the coefficients in Eq. (155). The quadrupolar

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Figure 16: The anisotropy parameters in the $\frac{K_{1}^{L}-K_{2}^{L}}{2}$-$K_{1}^{L}$ plane in case of an ordered relativistic grain built up from 153 atoms (55 core atoms). Color coding: center-black, first shell-red, second shell-green, third shell-blue, fourth shell-cyan.
operators form the basis of a real six-dimensional vector space (parameter space), and the transformation matrices between the parameter sets of the different sites $i$ and $j$ are defined as,

$$
\begin{align*}
\begin{bmatrix}
\frac{K_{i,j}^L + K_{i,j}^L}{2} & \frac{K_{i,j}^L - K_{i,j}^L}{2} & K_{i,j}^L & -K_{3,j}^L & -K_{5,j}^L & -K_{6,j}^L
\end{bmatrix}
&= \Gamma^{(i-j)}(g)
\end{align*}
\begin{align*}
\begin{bmatrix}
\frac{K_{i,j}^L + K_{i,j}^L}{2} & \frac{K_{i,j}^L - K_{i,j}^L}{2} & K_{i,j}^L & -K_{3,j}^L & -K_{5,j}^L & -K_{6,j}^L
\end{bmatrix}
\end{align*}
\tag{157}
$$

The transformation matrices $\Gamma^{(i-j)}(g)$ have a very special structure, namely they are block-diagonal with three blocks. These blocks correspond to irreps of $O_h$, $A_{1g}^{(i-j)}(g)$, $E_g^{(i-j)}(g)$ and $T_{2g}^{(i-j)}(g)$ in order. As a conclusion the six-dimensional parameter space is decomposed into three subspaces with dimension one, two and three, respectively. In the following we handle these subspaces separately.

$A_{1g}^{(i-j)}(g)$ is the totally symmetric irrep, and the corresponding parameter $\frac{K_{i,j}^L + K_{i,j}^L}{2}$ is the quarter of the trace of the anisotropy matrix, that is equal for all sites. This parameter can of course be different for different shells. The Eq. (156) leaves the eigenvalues, Eqs. (146) and (147), of the anisotropy matrices invariant, so the values of $\frac{K_{i,j}^L + K_{i,j}^L}{2}$ and the LSO

Figure 17: The magnetic anisotropy parameters in the $K_3^L - K_5^L - K_6^L$ space in case of ordered relativistic sample which is built up from 153 atoms (55 core atoms). Color coding: center-black, first shell-red, second shell-green, third shell-blue, fourth shell-cyan.
Figure 18: Calculated $K^L$ values in case of relativistic ordered and disordered nanoball. The number of all sites is $N = 153$ and the number of core sites is $N_c = 55$ in the ordered case. An extra atom to the outmost shell is put in case of disordered cluster. The solid line corresponds to the values of $K^L$ for the ordered case.

magnetic anisotropy constants $K^L$, see Eq. (148), are equal for sites in the same shell. The anisotropy matrices and the anisotropy constant $K^L$ were calculated for all core sites of a nanograin numerically in case of $N_c = 55$,

$$K^L_{\text{center}} = 0 \text{ meV} , \quad (158)$$
$$K^L_{\text{shell}_1} = -5.300 \text{ meV} , \quad (159)$$
$$K^L_{\text{shell}_2} = -6.304 \text{ meV} , \quad (160)$$
$$K^L_{\text{shell}_3} = -3.089 \text{ meV} , \quad (161)$$
$$K^L_{\text{shell}_4} = -22.97 \text{ meV} , \quad (162)$$

i.e., the numerical results confirmed the equality of these values in a given shell.

The parameters $K^L_{i,1}-K^L_{i,2}/2$ and $K^L_{4,i}$ define a two-dimensional parameter plane and the numerically calculated values are plotted in case of each core site of the nanograin in Fig. 16. The parameters in a given shell are cast into the vertices of an equilateral triangle. The second column of Table 5 in Appendix 4 shows the site indeces and the column fifth contains the corresponding parameter values on the parameter plane. For instance, in case of the first shell, which is denoted by red color in Fig. 16, $i = 2, 5, 9, 12$, $i = 4, 7, 8, 10$ and $i = 3, 6, 11, 13$
collapse into common points. The reason behind this observation is that the representation matrices of the irrep $E_g^{(i-j)}(g)$ are the symmetry transformations of an equilateral triangle centered at the origin.

The parameters $K_{3, i}^L, K_{5, i}^L$ and $K_{6, i}^L$ span a three-dimensional parameter space, see Fig. 17. We can identify the tetrahedral ordering patterns of the parameters which can be explained by the $T_{2g}^{(i-j)}(g)$ transformation matrices. The sixth column of Table 5 in Appendix 4 contains the coordinates of the appropriate points in the three dimensional parameter space. The symmetry analysis of the ordered grains completed in the same sense, and it was applied to the first six shells as can be seen in Table 5. Larger ordered nanograins can be handled by the same methods with obvious modifications. As a conclusion, a symmetry analysis in both the two-dimensional parameter plane and the three-dimensional parameter space explains perfectly the numerical results.

It should be noted, that the magnetic anisotropy values are mostly governed by $\frac{K_{1, i}^L - K_{2, i}^L}{2}$ and $K_{4, i}^L$. The parameters $K_{3, i}^L, K_{5, i}^L$ and $K_{6, i}^L$ appear only in the presence of host SOC and they are smaller by about one order in magnitude than the parameters $\frac{K_{1, i}^L - K_{2, i}^L}{2}$ and $K_{4, i}^L$. The sixth shell is a bit special. It has eight sites which take place at the corners of a cube, with the coordinates $(\pm 1, \pm 1 \pm 1)$. They cannot be cast into equilateral triangles, so it can be shown that $\frac{K_{1, i}^L - K_{2, i}^L}{2} = K_{4, i}^L = 0$ in this special case. If there is no host SOC then $K_{3, i}^L, K_{5, i}^L$ and $K_{6, i}^L$ are zero too, it then follows that the $K^L$ is zero as in case of the center atom, see the last four rows of the sixth column in Table of Appendix 4. Surprisingly, therefore, the source of the LSO-anisotropy is $SOC$ in the host at sites $(\pm 1, \pm 1 \pm 1), (\pm 2, \pm 2 \pm 2), (\pm 3, \pm 3 \pm 3)$ etc.

Next, if an extra atom is put to the outmost shell, for which we found a GSE-type distribution of the level spacings of the eigenenergies. The calculated magnetic anisotropy constants, $K^L$, are shown in Fig. 18. It can be seen that the ‘shell-degeneracy’ is lifted by the disorder. The effect of disorder manifested in the parameter spaces is the subject of current investigations.

5.4 Results for the surface induced LSO anisotropy

The Eq. (137) shows the general structure of the $\rho^L(\varepsilon)$. It can be seen, that $\rho^L(\varepsilon)$ has only diagonal elements if the magnetic impurity is in the vicinity of a noble metal surface, because the $x^2z^2$ and $z^2x^2$-type elements of the matrix (123) vanish in case of $C_{4v}$ symmetry. Obviously, the LSO anisotropy matrix, see Eq. (141), has also only diagonal elements, $K_{1, i}^L$ and $K_{2, i}^L$. The LSO magnetic anisotropy constant defined in Eq. (148) reduces, tush,

$$K^L = \frac{K_{1, i}^L - K_{2, i}^L}{2}. \quad (163)$$
It should be noted, that in case of cubic symmetries \( K_1^L = K_2^L \), i.e., the LSO anisotropy is zero for an impurity in the bulk. We can write,

\[
K^L(d) = \frac{J}{2} \int_{-\infty}^{\infty} d\varepsilon \Delta \varrho(\varepsilon, d),
\]

where \( \Delta \varrho(\varepsilon, d) = \varrho_1(\varepsilon, d) - \varrho_2(\varepsilon, d) \). \( K^L \) can be calculated in terms of contour integration as explained in the previous section, see Eq. (145), or a similar asymptotic analysis can be performed as for \( K^H \). Based on Eq. (107) the difference of the diagonal elements is approximated by

\[
\Delta \varrho(\varepsilon) \simeq \frac{2}{d} \Delta g(\varepsilon) \cos (Q(\varepsilon) d + \theta(\varepsilon)),
\]

i.e.,

\[
\Delta \varrho(\varepsilon) = \frac{1}{d} \left[ \Delta g(\varepsilon) e^{i(Q(\varepsilon)d + \theta(\varepsilon))} + \Delta g(\varepsilon) e^{-i(Q(\varepsilon)d + \theta(\varepsilon))} \right],
\]

where \( \Delta g(\varepsilon) \) is the amplitude, \( \theta(\varepsilon) \) is the phase and \( Q(\varepsilon) \) is the wavelength of the oscillation.

In Appendix 5 it is proved that

\[
I^L(d, T) = \int_{-\infty}^{\infty} \Delta g(\varepsilon) e^{i(Q(\varepsilon)d + \theta(\varepsilon))} d\varepsilon \simeq \Delta g(\varepsilon_F) \frac{e^{i(Q(\varepsilon_F)d + \theta(\varepsilon_F))}}{i Q'(\varepsilon_F)} \frac{1}{d}.
\]

Using Eqs. (164), (165) and (167) we arrive at

\[
K^L(d) = \frac{J \Delta g(\varepsilon_F)}{d^2 |Q'(\varepsilon_F)|} \sin (Q(\varepsilon_F) d + \theta(\varepsilon)).
\]

Interestingly, the asymptotic dependence of the magnetic anisotropy is described by similar functions within the HSO and LSO models, only the coefficients and the prefactors are different.

As pointed out in Ref. [13], of the local SO mechanism can give rise to a level splitting that is orders of magnitude larger than the host-induced anisotropy. To demonstrate this idea, in Ref. [13] the authors studied a quite unrealistic case of a single-band metal on a simple cubic lattice. Here the calculations of Ref. [13] are extended to realistic host metals (Cu and Au). Our calculations clearly showed that the \( d \)-dependent Friedel oscillations of \( \varrho_1(\varepsilon, d) \) are several orders of magnitude smaller than those of \( \varrho_2(\varepsilon, d) \). This can be understood by noticing that, due to the different spatial character of these two states \( (\delta = x^2 - y^2 \text{ and } \delta = 2z^2 - x^2 - y^2) \), \( \varrho_1 \) comprises an average of spectral weights in layers \( q - 1 \) and \( q + 1 \), see Eqs. (23-26), while \( \varrho_2 \) takes the difference of spectral weights in layer \( q \) with respect to those in layers \( q - 1 \) and \( q + 1 \), with \( q \) denoting the layer of the impurity’s position. Recalling, furthermore, that for a cubic bulk \( \varrho_1^0 = \varrho_2^0 \), i.e., the four diagonal elements are the same, in the asymptotic region \( K^L(d) \) becomes proportional to the integral of the function,

\[
\Delta \varrho_2(\varepsilon, d) \equiv \varrho_2(\varepsilon, d) - \varrho_2^0(\varepsilon).
\]
This function is displayed in Fig. 19 for both the Au and the Cu hosts. Remarkably, the amplitude of the Friedel oscillations is about one order larger than those of the off-diagonal spectral functions in the matrix $\rho^H(\varepsilon, d)$ (compare with Fig. 13 for the case of Au).

![Graph](image_url)

Figure 19: Calculated values of $\Delta \rho_2(\varepsilon_F) \equiv \rho_2(\varepsilon_F) - \rho_2^0(\varepsilon_F)$ (squares) with corresponding asymptotic fits, Eq. (165), (solid line) as a function of the distance from the (001) surface of Au and Cu.

The LSO oscillations seen in Fig. 19 have larger periods as compared to the off-diagonal spectral functions, being relevant to the HSO model. A fit to the asymptotic function (165) shown also in Fig. 19 resulted in the values, $Q^{\text{Au}} = 0.292 \ \text{Å}^{-1}$ and $Q^{\text{Cu}} = 0.505 \ \text{Å}^{-1}$, which are in very good agreement with the length of the small extremal vector $Q_{\text{min}}$ of the corresponding Fermi surfaces. Interestingly, the amplitude of the oscillations is more than three times larger for Cu than for Au. From the fits we obtained $\Delta g_2(\varepsilon_F) = 5.8 \times 10^{-3}$ and $\Delta g_2(\varepsilon_F) = 1.77 \times 10^{-2} \text{ÅeV}^{-1}$ for the case of Au and Cu, respectively. It should, however, be again emphasized that the SO coupling in the host has a negligible influence to the surface induced LSO mechanism. The origin of the oscillations of $\rho_2(\varepsilon, d)$ is crystal-field splitting acting directly on the charge distribution.
Figure 20: Magnetic anisotropy constants within the local spin-orbit coupling model calculated by using the asymptotic formula, Eq. (168), as a function of the distance $d$ from the (001) surface of a Au (dashes) and a Cu host (solid line). In case of Au the squares stand for the magnetic anisotropy constants calculated directly from Eq. (164).

Figure 20 shows the magnetic anisotropy constants obtained using Eq. (168) with the parameters extracted from the fit of $\Delta \phi_2(\varepsilon_F, d)$. The parameter $Q'(\varepsilon_F)$ was computed for the diagonal spectral functions and took a value of 0.245 (ÅeV)$^{-1}$ for Au and 0.238 (ÅeV)$^{-1}$ for Cu with the value of $J$ chosen to be 1 eV we obtained for the amplitudes of the oscillations of $K^L(s)$, $A(d) = 0.0237/d^2$ and 0.0742/$d^2$ eV ($d$ measured in Å) in Au and Cu, respectively. In particular, for Cu this gives an amplitude of 0.03 meV at $d = 50$ Å or 0.007 meV at $d = 100$ Å, which is in the range of Kondo-temperature $T_K$ for typical dilute magnetic alloys such as Cu(Mn) and Cu(Cr).

In Fig. 20, the anisotropy constants obtained from the asymptotic analysis are compared with the values calculated in terms of the contour integration, Eq. (164). Apparently, already for $d > 35$ Å, these values lie almost perfectly on the asymptotic curve. This nice agreement proves the validity of the asymptotic formula (168), as well as the accuracy of our numerical procedure to compute the magnetic anisotropy constant.
6 Exchange interaction between magnetic impurities

The effective Hamiltonian (14) describes the indirect interaction between two magnetic impurity spins via conduction electrons. The magnitude of the interaction decays as $1/R^3$ in the bulk, where $R$ is the distance between the impurities and the frequency of the oscillation is $2k_F$ where $k_F$ is the Fermi-wave number. In case of realistic metals the extremal vectors of the Fermi surface determine the frequency of the oscillatory interaction. Here we briefly sketch this result.

We consider the Hamiltonian $H_{surf}$, Eq. (54), which describes a metal semi-infinite host. The presence of the impurities is modeled by perturbations,

$$\Delta H_{1,e\sigma,E\sigma'}^{m,n,m'} = (\varepsilon_{\sigma}^{imp} - \varepsilon_{\epsilon}) \delta_{pr} \delta_{\rho',r} \delta_{n,0} \delta_{n',0} \delta_{\ell_2} \delta_{\ell',2},$$

and

$$\Delta H_{2,e\sigma,E\sigma'}^{m,n,m'} = (\varepsilon_{\sigma}^{imp} - \varepsilon_{\epsilon}) \delta_{pr} \delta_{\rho',r} \delta_{nm} \delta_{n',m} \delta_{\ell_2} \delta_{\ell',2},$$

where the impurities take place at sites 0 and m sites in layer r, respectively, and we consider spin-dependent on-site energy shifts for the d-orbitals. Let $G_0(z)$ refer to the nonperturbed Green’s function, see Eq. (77), and introduce the following matrices,

$$T_i(z) = \Delta H_i + \Delta H_i G_0(z) \Delta H_i + \Delta H_i G_0(z) \Delta H_i G_0(z) \Delta H_i + ... \quad (i = 1, 2).$$

We can also write

$$T_i(z) = \Delta H_i + T_i(z) G_0(z) \Delta H_i \quad (i = 1, 2).$$

The DOS and the integrated DOS of the unperturbed and perturbed systems are denoted by $n_0(\varepsilon)$, $n(\varepsilon)$, $N_0(\varepsilon)$ and $N(\varepsilon)$, respectively. The integrated DOS of perturbed system can be obtain form the Lloyd-formula, see Ref. [54]. In case of the presence of only one impurity, the Lloyd-formula reads,

$$N_i(\varepsilon) = N_0(\varepsilon) + \frac{1}{\pi} \text{Im} Tr \ln T_i^+(\varepsilon),$$

where

$$T_i^+(\varepsilon) = \lim_{\delta \to 0} T_i(\varepsilon + i\delta).$$

It is well known from statistical physics that the grand potential $\Omega$ of a noninteracting system can be obtained from the integrated DOS,

$$\Omega = -\int_{-\infty}^{\infty} N(\varepsilon) f(\varepsilon) = \Omega_0 + \Delta \Omega_1 + \Delta \Omega_2 + \Omega_{12},$$

where $f(\varepsilon)$ is the one-particle (Fermi-Dirac) distribution function,

$$\Omega_0 = -\int_{-\infty}^{\infty} N_0(\varepsilon) f(\varepsilon),$$

53
while $\Delta \Omega_i$’s represent the effect of single impurities,

$$\Delta \Omega_i = -\frac{1}{\pi} \Im \int_{-\infty}^{\infty} d\varepsilon f(\varepsilon) \text{Tr} \ln \left( T_i^+ \right),$$  \hspace{1cm} (178)

and $\Omega_{12}$ denotes the interacting energy term,

$$\Omega_{12} = -\frac{1}{\pi} \Im \int_{-\infty}^{\infty} d\varepsilon f(\varepsilon) \text{Tr} \ln \left( I - G_0^+ T_1^+ G_0^+ T_2^+ \right).$$  \hspace{1cm} (179)

If the distance of the impurities is large (asymptotic regime) then Eq. (179) can be reduced to

$$\Omega_{12} = -\frac{1}{\pi} \Im \int_{-\infty}^{\infty} d\varepsilon \text{Tr} \left( G_0^+ T_1^+ G_0^+ T_2^+ \right),$$  \hspace{1cm} (180)

where we considered zero temperature. An asymptotic analysis in similar that in the previous sections results

$$\Omega_{12} \sim \frac{1}{R^2} \sum_n \Re \left( f_n(\varepsilon_F) \exp(iQ^n(\varepsilon_F)R) \right),$$  \hspace{1cm} (181)

for the bulk, where $Q^n(\varepsilon_F)$ denote the appropriate extremal vectors of the Fermi surface, $f_n(\varepsilon_F)$ is an irrelevant function and $R$ is the distance between impurities. This above expression are based on Ref. [55].

![Figure 21: Calculated exchange energy between impurity spins in Cu bulk host. Black triangles refer to the nonrelativistic calculation and the red squares denote the exchange energy in the presence of host SOC.](image)

In my calculations I have investigated impurities embedded in Cu and Au bulk. In case of Cu we chose the parameters $\varepsilon_{\uparrow}^{\text{imp}} = 3\,\text{eV}$ and $\varepsilon_{\downarrow}^{\text{imp}} = 1\,\text{eV}$, while in case of Au host, $\varepsilon_{\uparrow}^{\text{imp}} = 4$
Figure 22: Calculated exchange energy between impurity spins in Au bulk host. Black triangles refer to the nonrelativistic calculation and the red squares denote the exchange energy in the presence of host SOC.

eV and $\xi_1^{imp} = 2 \text{ eV}$. The definition of the exchange energy is the following,

$$E_{\text{exch}} = \Omega^{\uparrow\downarrow} + \Omega^{\downarrow\uparrow} - \Omega^{\uparrow\uparrow} - \Omega^{\downarrow\downarrow},$$

which by using Eq. (180) can be calculated as,

$$E_{\text{exch}} = \frac{1}{\pi} \text{Im} \int_{-\infty}^{\infty} d\varepsilon \, Tr \left[ G_0^+ (T_{1,1}^+ - T_{1,1}^+) G_0^+ (T_{2,1}^+ - T_{2,1}^+) \right].$$

Figs. 21 and 22 show the calculated exchange energies in case of Cu and Au, respectively. The impurities are placed along the (110) direction, i.e., the nearest neighbor direction, their distance is measured in units of the two-dimensional lattice constant $a_{2D}$, where $a_{2D} = \sqrt{2}a_{3D}$. It is clear that the influence of the SOC is much stronger in case of Au host. This result can be explained as follows: in case of Cu, $\xi_{cu} = 0.1 \text{ eV}$, the spin-channels are well defined, but in case of Au, $\xi_{Au} = 0.64$, the SOC mixes the spin-channels, thus, reduces the energy difference between the relative spin-orientations of the two impurities.

The magnitude of the oscillations decays as $1/R^3$ in all cases. The fitted frequency parameters are $Q_{110}^{Au} = 0.152 \text{ \AA}^{-1}$ and $Q_{110}^{Cu} = 0.262 \text{ \AA}^{-1}$ which correspond to the complementary of the extremal vectors $Q_{110}$ in Fig. 5 ($Q_{110}^{Au} = 2.017 \text{ \AA}^{-1}$ and $Q_{110}^{Cu} = 2.200 \text{ \AA}^{-1}$). Indeed,

$$2\pi a_{2D}^{-1} - Q_{110}^{Au} = 0.159 \text{ \AA}^{-1}$$

(184)
and

\[ 2\pi a_{2D}^{-1} - Q_{110}^{Cu} = 0.258 \text{ Å}^{-1}, \]

which agrees with \( Q^{Au} \) and \( Q^{Cu} \) within an accuracy of 1%.

On the other hand, when the impurities are placed along (001) direction, i.e., the next nearest neighbor direction, the frequencies of the oscillation are \( Q_{min}^{Au} = 0.321 \text{ Å}^{-1} \) and \( Q_{min}^{Cu} = 0.536 \text{ Å}^{-1} \) which correspond to the extremal vectors \( Q_{min}^{Au} = 0.298 \text{ Å}^{-1} \) and \( Q_{min}^{Cu} = 0.505 \text{ Å}^{-1} \) in Fig. 5. The tight-binding calculations confirmed the the asymptotic formula (181).

Figure 23: Calculated exchange interactions as a function of the distance between Co adatoms on top of the vicinal surfaces of Cu and Au along the directions specified in the text. Symbols refer to the calculated data, solid lines to the fitted curves.

In the rest of this Section I briefly summarize the results of Refs. [36] and [37]. The exchange interactions between Co atoms placed on (111), (110) and (100) surface of Cu and Au were calculated using the Screened Korringa-Kohn-Rostoker (KKR) method [57, 44] combined with the embedding technique [58]. The exchange interactions, \( J(R) \), between two
Co adatoms for distances up to $R \simeq 100 - 150 \text{Å}$, can be considered safely as the asymptotic region. The calculated results are shown in Fig. 23 (Ref. [36]) as a function of the distance between the adatoms. In case of the (100) and the (111) surfaces, the two Co atoms were placed along the (110), i.e., the nearest neighbor direction, while in case of the (110) surface along the (001), i.e., the next nearest neighbor direction.

For the (111) surface of Cu, see left-top panel of Fig. 23, $J(R)$ shows clear oscillations with a period of $L = 18.5 \text{Å}$, corresponding to a Fermi wavelength of the surface states, $k_F = \pi/L = 0.17 \text{Å}^{-1}$. In agreement with theoretical predictions [59, 61, 60, 62, 63, 64], the numerical fit of the SKKR results also confirmed that the amplitude of the oscillations decays as $1/R^2$,

$$E_{\text{exch}}^\text{surf} = J(R) \sim \frac{1}{R^2} \sum_n \text{Re} \left( f_n(\varepsilon_F) \exp \left( iQ^n(\varepsilon_F)R \right) \right). \quad (186)$$

The asymptotic curve of $J(R)$ displays a more complicated behavior for Au(111), see right-top panel of Fig. 23, since this curve could be fitted as the sum of two oscillations with the Fermi wavelengths, $k_{F_1}^1 = 0.104 \text{Å}^{-1}$ and $k_{F_2}^2 = 0.142 \text{Å}^{-1}$. The appearance of the two oscillation periods is due to the famous Bychkov-Rashba splitting [56] (see next section) of the Au(111) surface states experiencing the strong spin-orbit interaction of Au. This splitting of the surface states gives rise to two distinct spherical Fermi-cuts, thus, to two distinct asymptotic oscillations for the exchange interaction between magnetic adatoms.

In obvious contrast to all previous cases, in case of the (100) surfaces (lower panels of Fig. 23) the exchange interactions show no oscillations in the asymptotic regime. For Cu(100), $J(R)$ is well described by an exponential decay. For Au(100), it also rapidly decreases with $R$, though, $J(R)$ changes sign at $R \simeq 30 \text{Å}$. This result can be attributed to the fact that on the (100) surfaces there are no Schockley-type surface states, that can mediate RKKY interactions between magnetic impurities.
7 Anisotropic Bychkov-Rashba splitting of surface states

Metallic surfaces often exhibit Shockley-type surface states, 2DEG, located in a relative band gap of the bulk band structure, and forming a two-dimensional electron gas. One of the most intriguing manifestation of SOC at surfaces is the splitting of these surface states, known as Bychkov-Rashba splitting. The simplest way to understand the origin of this effect is to take nearly free electrons, confined by a crystal potential, \( V(z) \), and having a plane-wave function,

\[ \psi_{s, \vec{k}} = \chi_s \exp(i\vec{k}\vec{r}) , \]  

with \( \chi_s \) denoting spinor eigenfunctions and \( \vec{k} \) the momentum parallel to the surface. The crystal potential \( V(z) \) obviously produces an electric field, \( \vec{E} \), perpendicular to the surface, which, in the presence of spin-orbit interaction leads to the following effective Hamiltonian,

\[ H_R(\vec{k}) = \gamma (k_x \sigma_x - k_y \sigma_y) , \]  

called Rashba-Hamiltonian, where

\[ \gamma = \frac{\hbar^2}{4m^2c^2} \int d^3r \frac{\partial V(z)}{\partial z} , \]  

is the Rashba-parameter. If the effective mass of the electrons on the surface is \( m^* \), then the Hamiltonian of the 2DEG can be written as

\[ H(k) = E_0 + \frac{\hbar^2 k^2}{2m^*} + H_R(k) , \]  

where \( k = |\vec{k}| \). The eigenvalue problem, \( H \psi_{\vec{k}} = E \psi_{\vec{k}} \), can then easily be solved, resulting in a splitting of the spin-degeneracy of the surface states,

\[ E_{\vec{k}}^\pm = E_0 + \frac{\hbar^2 k^2}{2m^*} \pm \gamma |\vec{k}| , \]  

with the eigenfunctions

\[ \psi_{\vec{k}}^\pm(\vec{r}) = \frac{1}{\sqrt{2}} \left( \begin{array}{c} 1 \\ i \exp(i\alpha) \end{array} \right) \exp(i\vec{k}\vec{r}) , \]  

where \( \tan \alpha = k_y/k_x \). Clearly, the above dispersion is isotropic in \( \vec{k} \)-space, hence we term it as isotropic Rashba splitting. In case of Au(111) surface 2DEG is fairly well described by the Eqs. (188) and (190).

Some metal surfaces show, however, anisotropic splitting in the \( \vec{k} \)-space, for instance Au(110) Refs. [65, 67, 66], Bi/Ag(111) Ref. [29], Bi/BaTiO\(_3\) (001) Ref. [34], hence, we refer this phenomenon to anisotropic Bychkov-Rashba effect. We have to construct more general effective Hamiltonian’s according to the symmetry of the surface. Oguchi and Shishidu
determined the effective Hamiltonian of anisotropic Bychkov-Rashba splitting in first order in $\vec{k}$ using group theoretical methods Ref. [68]. This effective Hamiltonian describes well the surface states on Au(110) which has $C_{2v}$ symmetry. The 2DEG on the Au(111) is the typical case of the isotropic Rahsa splitting, but an anisotropic splitting can also be derived in case of $C_{3v}$ symmetry, though, in higher, at least, third order in $\vec{k}$.

![Figure 24: Sketch of the fcc(110) Surface Brillouin zone. The dark area denotes the projection of the relative gap of bulk Au.](image)

Here, I present how to derive Rashba-Hamiltonians, in principle, in any order of $\vec{k}$. Because of two-dimensional discrete translation invariance, we use the Bloch-theorem,

$$
\psi_{\vec{k}}(\vec{r} + \vec{T}) = \exp \left( i \vec{k} \vec{T} \right) \psi_{\vec{k}}(\vec{r}) ,
$$

(193)

where $\vec{T}$ is two-dimensional lattice vector. Let $\vec{Q}$ denote a high symmetry point of the two-dimensional Brillouin-zone, where the surface states are degenerate in the presence of SOC. Fig. 24 shows the high symmetry point, $\bar{Y}$, in case of Au(110). We will expand the Bloch-functions near this $\vec{Q}$ point, i.e.,

$$
\psi_{\vec{k} + \vec{Q}}(\vec{r}) = \exp \left( i \vec{k} \vec{r} \right) \phi_{\vec{Q}, \vec{k}}(\vec{r}) ,
$$

(194)

with the condition,

$$
\phi_{\vec{Q}, \vec{k}}(\vec{r} + \vec{T}) = \exp \left( i \vec{Q} \vec{T} \right) \phi_{\vec{Q}, \vec{k}}(\vec{r}) .
$$

(195)

Time reversal implies the transformation $\vec{k} \rightarrow -\vec{k}$, thus, to ensure double degeneracy at $\vec{Q}$, we require

$$
-\vec{Q} = \left\{ \begin{array}{c}
\vec{Q} \\
\vec{Q} + \vec{G}
\end{array} \right\} ,
$$

(196)
where $\vec{G}$ is a reciprocal lattice vector. We consider the little group of $\vec{Q}$,

$$g\vec{Q} = \begin{cases} 
\vec{Q} \\
\vec{Q} + \vec{G} 
\end{cases} \quad (g \in G) . \quad (197)$$

In case of $\bar{C}_{2v}$ and $\bar{C}_{3v}$ double groups there are two-dimensional irreps only, therefore, we should find a $2 \times 2$ effective Hamiltonian. The most general form is as follows,

$$H_R(\vec{k}) = \gamma_0(\vec{k})I_2 + \vec{\gamma}(\vec{k})\vec{\sigma}, \quad (198)$$

and we will determine $\gamma_0(\vec{k})$ and $\vec{\gamma}(\vec{k})$ for both symmetry groups.

In Eq. (126) we introduced the time-reversal operator $\Theta$. It can be shown that

$$H_R(\vec{k}) = \Theta^{-1} H_R(-\vec{k})\Theta = -\sigma_y CH_R(-\vec{k})\gamma_0(\vec{k})\sigma_y C , \quad (199)$$

which implies that

$$\gamma_0(-\vec{k}) = \gamma_0(\vec{k}) , \quad (200)$$

$$\vec{\gamma}(-\vec{k}) = -\vec{\gamma}(\vec{k}) , \quad (201)$$

where we used the relations $\Theta \vec{\sigma} \Theta^{-1} = -\vec{\sigma}$.

If $D(g)$ is a $2 \times 2$ unitary representation matrix of a group element $g$ then we can write

$$H_R(g\vec{k}) = D(g)H(\vec{k})D(g)^\dagger , \quad (202)$$

so $H(\vec{k})$ can be expressed as

$$H_R(\vec{k}) = \gamma_0(g\vec{k})I_2 + \vec{\gamma}(g\vec{k})D(g)^\dagger \vec{\sigma}D(g) . \quad (203)$$

The vector $\vec{\sigma}$ transforms as an axial vector, i.e.,

$$D(g)^\dagger \vec{\sigma}D(g) = \det(g)g\vec{\sigma} , \quad (204)$$

where for proper rotations $\det(g) = 1$, while for improper rotations $\det(g) = -1$. Therefore

$$H_R(\vec{k}) = \gamma_0(g\vec{k})I_2 + \vec{\gamma}(g\vec{k})\det(g)g\vec{\sigma} = \gamma_0(g\vec{k})I_2 + \det(g)g^{-1}\vec{\gamma}(g\vec{k})\vec{\sigma} . \quad (205)$$

Eqs. (198) and (205) imply that

$$\gamma_0(g\vec{k}) = \gamma_0(\vec{k}) , \quad (206)$$

$$\vec{\gamma}(g\vec{k}) = \det(g)g\vec{\gamma}(\vec{k}) . \quad (207)$$
Figure 25: Dispersion relation of the Au(110) surface states in two different directions.

Using the consequences of the time-reversal, Eqs. (200) (201), and relations (206) and (207), in case of $\tilde{C}_{2v}$, the following effective Hamiltonian can be obtained up to second order in $\vec{k}$,

$$H_R (\vec{k}) = \gamma_0(\vec{k}) I_2 + \begin{pmatrix} -\gamma_y k_y & \gamma_x k_x \\ \gamma_x k_x & 0 \end{pmatrix} \vec{\sigma} + \begin{pmatrix} C_{11} k_x^2 k_y + C_{12} k_y^3 \\ C_{21} k_y^3 + C_{22} k_x k_y^2 \end{pmatrix} \vec{\sigma}$$

with

$$\gamma_0(k_x, k_y) = A + B_x k_x^2 + B_y k_y^2.$$  

The eigenvalues of the Hamiltonian (208) can be written as

$$E_{\pm} (k_x, k_y) = A + B_x k_x^2 + B_y k_y^2 \pm \sqrt{\gamma_x^2 k_x^2 + \gamma_y^2 k_y^2}.$$  

The coefficients of $k_i^2$ can be expressed by the appropriate effective masses, specifically, $B_x = \frac{\hbar^2}{2m_x^*}$ and $B_y = \frac{\hbar^2}{2m_y^*}$. We should emphasize, that the $C_{2v}$ point-group symmetry of the system not only implies the asymmetry of the effective mass, $m_x^* \neq m_y^*$ but, in leading order in $\vec{k}$, the representation theory also predicts different $\gamma_x$ and $\gamma_y$ Rashba parameters. In case of $\tilde{C}_{4v}$ symmetry the parameters are reduced, specifically $m_{xx}^* = m_{yy}^* = m^*$ and $\gamma_x = \gamma_y = \gamma$, i.e., the Hamiltonian (190) is recovered.
In case of \( \tilde{C}_3 \), the effective Hamiltonian can be expressed up to third order in \( \tilde{k} \) as,

\[
H_R\left(\tilde{k}\right) = \gamma_0(\tilde{k})I_2 + \gamma \left( \begin{array}{c} -k_y \\ k_x \end{array} \right) \begin{array}{c} \sigma_x \\ \sigma_y \end{array} + \left( \begin{array}{c} Ck_x^2k_y + Ck_y^3 \\ -Ck_x^3 + Ck_xk_y^2 \\ Dk_x^2 - 3Dk_xk_y^2 \end{array} \right) \begin{array}{c} \sigma_x \\ \sigma_y \end{array}, \tag{210} \]

with

\[
\gamma_0(k_x, k_y) = A + Bk_x^2 + Bk_y^2,
\]

implying a dispersion relation,

\[
E_{\pm}(k_x, k_y) = A + Bk^2 \pm \sqrt{\gamma^2k^2 - 2\gamma Ck^4 + [C^2 + D^2 \cos^2 \alpha (4 \cos^2 \alpha - 3)]k^6}. \tag{211} \]

Clearly, the parameter \( D \) is the only source of the anisotropy third order in \( \tilde{k} \).

The dispersion relations on Au(110) and Au(111) 2DEG’s were determined by using the Bloch-spectral functions (91) in terms of TB calculation. The surface state was modeled by choosing on-site energies of \( \sim 9 \) eV in the first four (vacuum) layers. In particular, the fourth layer defines the layer just above the surface, where I determined the dispersion relation using the peaks of the Bloch-spectral function. It should be noted, that these states appear only in the relative bulk gap, i.e. if there are no bulk electron states in the given energy range along the considered \( \tilde{k} \) direction.

Fig. 25 shows the numerical results of my TB calculation in case of Au(110) in two different directions: The \( \alpha = 0 \) corresponds to the \( \overline{\Gamma\Sigma} \) direction and \( \alpha = \pi/2 \) to the \( \overline{\Gamma\Sigma} \) line in Fig. 24. We fitted two functions from Eq. (209),

\[
F(k) \equiv \frac{E_+ + E_-}{2} = A + B_xk_x^2 + B_yk_y^2, \tag{212} \]

and

\[
G(k) \equiv \left( \frac{E_+ - E_-}{2} \right)^2 = \gamma_y^2k_y^2 + \gamma_x^2k_x^2. \tag{213} \]

Using the Ordinary Least Squares method the fitted parameters are as follows,

\[
A = 7.59095 \pm 1.4 \times 10^{-6} \text{ eV}, \tag{214} \]

\[
B_x = 0.87045 \pm 1.7 \times 10^{-4} \text{ eV}a_{3D}^2, \tag{215} \]

\[
B_y = 0.56453 \pm 1.7 \times 10^{-4} \text{ eV}a_{3D}^2, \tag{216} \]

and

\[
\gamma_x = 0.0426 \text{ eV}a_{3D}, \tag{217} \]

\[
\gamma_y = 0.0289 \text{ eV}a_{3D}. \tag{218} \]

It should be noticed, that previous \textit{ab initio} calculations [65, 67] did find a Rashba splitting of the Au(110) surface state, they focused only on the dispersion along the \( \overline{\Gamma\Sigma} \) direction,
and therefore the anisotropy of the Rashba term remained unnoticed. We also perform ab initio calculations of the Rashba-split surface state of an unreconstructed Au(110) surface, see Ref. [66], and confirm with a high numerical accuracy that there is a large anisotropy in \( k \)-space, \( \gamma_x \sim 5\gamma_y \), which is larger considerably than the ratio of the TB Rashba-parameters, (217) and (218). The predicted anisotropic Rashba splittings turned out to be in range of experimental accuracy.

![Graph showing dispersion relation](image)

Figure 26: Dispersion relation of the Au(111) surface state in four different directions. The degeneracy of the dispersion relations caused by symmetry.

As we mentioned, the parameter \( D \) of the Hamiltonian (210) describes the anisotropy up to third order in \( \vec{k} \) for the case of \( C_{3v} \) symmetry. For Au(111) it was necessary to determine the dispersion relation with an accuracy of 6 – 8 digit to achieve successful fitting. The calculated dispersion relations are shown in Fig. 26 in four different directions, the degeneracy is caused by symmetry. The points in the \( \vec{k} \) space were chosen in two ranges: in case of small wave number \( k = 0 \ldots 0.17 \frac{1}{a_{3D}} \) and in case of larger values of, specifically \( k = 0.4 \ldots 0.8 \frac{1}{a_{3D}} \). The parameters \( A \) and \( B \) are obtained from fitting \( F(k) \) at small \( k \)-points, 

\[
F(k) \equiv \frac{E_+ + E_-}{2} = A + Bk^2 , \tag{219}
\]

and we got, \( A = 7.9215 \text{ eV} \) and \( B = 0.37\pm 5 \times 10^{-5} \text{ eV} a_{3D}^2 \) which is also satisfactory fit in case
of larger values of $k$. The parameters $\gamma$, $C$ and $D$ can determined from a two-dimensional fit of the function,

$$G(\alpha, k) \equiv \left( \frac{E_+ - E_\alpha}{2} \right)^2 = \gamma^2 k^2 - 2\gamma Ck^4 + [C^2 + D^2 \cos^2 \alpha (4 \cos^2 \alpha - 3)]k^6,$$  \hspace{1cm} (220)

and resulted in the values,

\begin{align*}
\gamma &= (4.7401 \pm 0.0007) \times 10^{-2} \text{ eV}a_{3D}, \\
C &= (8.999 \pm 0.015) \times 10^{-3} \text{ eV}a_{3D}^3, \\
D &= (1.710 \pm 0.320) \times 10^{-3} \text{ eV}a_{3D}^3. \\
\end{align*}  \hspace{1cm} (221, 222, 223)

Using the formula (220) we can define the functions $G_1(k)$ and $G_2(k)$ as

$$G(\alpha, k) = G_1(k) + G_2(k) \cos(6\alpha),$$  \hspace{1cm} (224)

in particular, with

$$G_2(k) = \frac{D^2}{2}k^6.$$  \hspace{1cm} (225)

Fig. 27 shows the angle dependence of the function $G(\alpha, k)$ in case of $k = 1.8 \frac{1}{a_{3D}}$. Specifically, we can write for $\alpha = 0$ and $\alpha = \pi/6,$

$$G(0, k) - G\left(\frac{\pi}{6}, k\right) = 2G_2(k) = D^2k^6,$$  \hspace{1cm} (226)

providing an alternative way to determine the parameter $D$. I fitted the function

$$G_2(k) = \frac{D^2}{2}k^6.$$  \hspace{1cm} (227)
for the range, \( k = 0.4 - 0.8 \frac{1}{a_{3D}} \), see Fig. 28. The result of the fitting procedure was

\[
D = 1.76 \times 10^{-3} \text{ eV} a_{3D}^3 , \tag{228}
\]

\[
x = 5.63 \pm 0.02 V . \tag{229}
\]

This means some deviation \( x \) form the theoretical value of 6, that can be attributed to insufficient determination of the dispersion relation, however, we can see that value of \( D \) is in nice agreement with the one obtained from our previous fit (223). As a conclusion, the TB calculations satisfactory justified the Rasba-Hamiltonian (210) derived by group-theoretical arguments.
8 Conclusion and thesis statements

The main objective of my Ph.D work was to study spin-orbit induced effects on magnetic impurities placed, in particular, in low-dimensional systems. In order to access the problems mentioned above it was necessary to work out a link between the quantum-impurity models and realistic bandstructure calculations of the valence and conduction electrons, for both surfaces and nanoparticles. For this purpose I employed a tight-binding Green's function technique, which allowed for a perfect treatment of the semi-infinite geometry of a surface and made also possible a nonperturbative treatment of the SO interaction.

By using the TB Green’s function method, a quantitative comparison of the HSO and LSO models has become possible for the realistic cases of Cu and Au host surfaces. In this way I made reliable predictions in favor of one of these mechanisms for the surface-induced anisotropy proposed originally by Ujsaghy et al. to explain the Kondo effect in reduced dimension.

Motivated by previous theoretical studies on the spin g-factor distribution [14, 15, 16], I analyzed the statistical features of the level spacing of disordered nanograins in terms of random matrix theory and I studied the magnetic anisotropy of a magnetic impurity in ordered Au nanoclusters in terms of the LSO model and real-space TB calculations.

The TB Green’s function method provided also possibility to calculate the exchange interaction between two impurities in bulk and at surfaces. I examined in my thesis how the SO coupling in the host influences the RKKY interaction. In relation to this phenomenon, I also investigated the Bychkov-Rashba effect in two-dimensional electron states at Au(111) and Au(110) surfaces, with emphasis to the anisotropic BR splitting.

Thesis statements

1. I derived analytical expression of the HSO and LSO magnetic anisotropy constants, $K(d)$, and performed an asymptotic analysis for large distances $d$ from the surfaces. As a result of this analysis the period of the oscillations could be identified as the length of an extremal vector of the Fermi surface of the bulk host and the amplitude decayed as $1/d^2$ in both models. The results are published in Refs: [69] and [70].

2. In terms of the TB-GF method, I performed calculations of the anisotropy constant of impurities near the (001) surface of copper and gold. The numerical results confirmed the analytical expressions for $K(d)$. In case of the HSO model the magnitude of $K(d)$ remained well below the Kondo temperature, while within the LSO model it turned to be in the desired energy range up to $d$ 100Å. I, therefore, concluded that the LSO mechanism can explain
the suppression of the Kondo resistance observed in thin films. The results are published in Refs: [69] and [70].

3. Using Random Matrix Theory, I performed an analysis of the spectral statistics of the Hamiltonian of disordered gold nanoparticles. I showed that, within satisfactory numerical accuracy, the distribution of eigenenergy spacings follows a universal behavior: without SOC the distribution refers to a Gaussian Orthogonal Ensemble (GOE), while SO coupling on the gold atoms implies a Gaussian Symplectic Ensemble (GSE) for the level-spacing distribution. These results are not published yet.

4. I showed that, within the LSO mechanism, the magnetic anisotropy can, in general, be described by a $4 \times 4$ self-adjoint matrix containing six real parameters. I explored the structure of this matrix and defined magnetic anisotropy terms related to a quadrupole operator basis. In the case of ordered nanograins, I numerically found symmetry constraints in the six-dimensional parameter space. Using representation theory of double groups I fully explained the observed symmetry relations of the anisotropy parameters. These results are not published yet.

5. By using a T-matrix technique combined with the TB method, I examined the RKKY interaction between impurities embedded in Cu and Au bulk host. My numerical calculations confirmed within a relative accuracy of 1% that magnitude of the oscillations of the exchange interaction decays as $1/R^3$, $R$ being the distance of the impurities, and that the period is related to the length of an appropriate extremal vector of the Fermi surface. I pointed out that strong SO coupling in Au drastically reduced the magnitude of the exchange energy. The underlying physics is attributed to the spin-mixing induced by SO coupling, see Refs: [37] and [36].

6. I performed detailed calculations for the dispersion relations of the Shockley-type surface states of Au(110) and on Au(111) surfaces. In agreement with analytical $k \cdot p$ perturbation theory and first principles calculations, I confirmed that the Bychkov- Rashba splitting is anisotropic for Au(110) that can be described with a Hamiltonian in first order of $k$. Furthermore, my calculations evidenced that for Au(111) surface (case of $C_{3v}$ symmetry) an anisotropy of the BR splitting arises according to an effective Hamiltonian in third order of $k$, see Ref. [66].
Acknowledgments

This thesis is dedicated to my parents.

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9 Appendix

9.1 Appendix - Cubic double group

The 3 components of the angular momentum operator \( \vec{J} = (J_x, J_y, J_z) \) generate the \( \mathfrak{su}(2) \) Lie-algebra, \([J_i, J_j] = i\hbar\epsilon_{ijk}J_k\). \( \mathfrak{su}(2) \) is the Lie-algebra of the group \( SU(2) \) and \( SO(3) \). The unitary matrix

\[
U_j(\vec{n}, \phi) = \exp \left( i\phi \vec{n} \cdot \vec{J} / \hbar \right)
\]

represents an element of the group on the Hilbert space of physical states, \( U_j \) refer to a rotation with an angle \( \phi \) around unit vector \( \vec{n} \), \( j \) denotes the representation. The character of a rotation around an arbitrary axis with angle \( \phi \) is:

\[
\chi_j(\phi) = \frac{\sin \left( (j + \frac{1}{2})\phi \right)}{\sin (\phi/2)},
\]

where \( j \) is an integer or half integer number, \( 2j + 1 \) is the dimension of the representation. Note, that \( \chi_j(\phi + 2\pi) = (-1)^{2j}\chi_j(\phi) \), while \( \chi_j(\phi \pm 4\pi) = \chi_j(\phi) \), so \( 4\pi \) should be considered as identity (for half integer spins). For integer spins (odd dimensional representations) a \( 2\pi \) rotation is the identity. The half integer representations are the irreps of \( SU(2) \), but they are projective or double-valued irreps of \( SO(3) \). So there is a new group element \( R \) introduced which represents a rotation by \( 2\pi \) and has the property \( R \neq E \) but \( R^2 = E \) and \( E \) corresponds to rotation by \( 4\pi \).

As an example, I introduce the octahedral double group \( O' \). This consists of 48 elements: each of the 24 in \( O \) together with the 24 new elements obtained by combining each of them with \( R \). The double group has more classes (and irreps) than the original, but not necessary twice as many, since \( \chi_j(RC_2) = \chi_j(C_2) = 0 \), making it possible that \( RC_2 \) is in the same class as \( C_2 \). In addition to the five classes of \( O \), I have the classes \( R, RC_3 \) and \( RC_4 \). In Bethe’s notation the \( \Gamma_1...\Gamma_5 \) corresponds to the original single-valued representations and \( \Gamma_6...\Gamma_8 \) are the double valued representation. The character table Table 2 summarizes the results.

The representations \( \Gamma_6 \) and \( \Gamma_7 \) are two dimensional, while \( \Gamma_8 \) is four dimensional. The
Table 2: Character table for cubic double group

<table>
<thead>
<tr>
<th>$O'$</th>
<th>$E$</th>
<th>$R$</th>
<th>$8C_3$</th>
<th>$8RC_3$</th>
<th>$3C_2 + 3RC_2$</th>
<th>$6C_2 + 6RC_2$</th>
<th>$6C_4$</th>
<th>$6RC_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_1$ ($A_1$)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_2$ ($A_2$)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$\Gamma_3$ ($E$)</td>
<td>2</td>
<td>2</td>
<td>-1</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\Gamma_4$ ($T_1$)</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_5$ ($T_2$)</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$\Gamma_6$</td>
<td>2</td>
<td>-2</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>$\sqrt{2}$</td>
<td>$-\sqrt{2}$</td>
</tr>
<tr>
<td>$\Gamma_7$</td>
<td>2</td>
<td>-2</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>$-\sqrt{2}$</td>
<td>$\sqrt{2}$</td>
</tr>
<tr>
<td>$\Gamma_8$</td>
<td>4</td>
<td>-4</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

cubic representations that correspond to the given angular momenta are the following:

\[
\begin{align*}
  j &= \frac{1}{2} \rightarrow \Gamma_6, \\
  j &= \frac{3}{2} \rightarrow \Gamma_8, \\
  j &= \frac{5}{2} \rightarrow \Gamma_7 + \Gamma_8, \\
  j &= \frac{7}{2} \rightarrow \Gamma_6 + \Gamma_7 + \Gamma_8, \\
  j &= \frac{9}{2} \rightarrow \Gamma_6 + 2\Gamma_8, \\
  \ldots
\end{align*}
\]

Thus levels with $j = \frac{1}{2}$ or $j = \frac{3}{2}$ are unsplit in cubic field; $j = \frac{5}{2}$ level splits into a doublet and a quartet, and so on. This Appendix based on Ref. [71].
9.2 Appendix - Hybridization matrix

The matrix elements $V_{\alpha,\alpha'}(\vec{n})$ are defined in the following way:

$$V_{\alpha,\alpha'}(\vec{n}) := \int d^3 r R_\alpha(|\vec{r}|)K_\alpha(\vec{r})V(\vec{r})R_{\alpha'}(|\vec{r} - \vec{n}|)K_{\alpha'}(\vec{r} - \vec{n}) ,$$  
(233)

where $R_i$ denotes the radial part of the wave function, and $K_\alpha$ is a real spherical function.

The orthogonal Wannier functions are replaced by atomic wave functions in the TB model. That means

$$V(\vec{r}) = U(\vec{r}) - v_{pn}(\vec{r}) ,$$  
(234)

where $U(\vec{r})$ is the periodical crystal potential and $v_{pn}(\vec{r} - \vec{R}_{pn})$ denotes the potential function of an atom which sits on the site $\vec{R}_{pn}$, see Ref. [68], Sec. 18.2.

The $V(\vec{r})$ is also lattice periodical, $V(\vec{r} + \vec{n}) = V(\vec{r})$, that means $V_{\alpha,\alpha'}(\vec{n}) = V_{\alpha',\alpha}(-\vec{n})$, indeed

$$V_{\alpha,\alpha'}(\vec{n}) = \int d^3 r R_\alpha(|\vec{r}|)K_\alpha(\vec{r})V(\vec{r})R_{\alpha'}(|\vec{r} - \vec{n}|)K_{\alpha'}(\vec{r} - \vec{n}) = \int d^3 r R_\alpha(|\vec{r}|)K_\alpha(\vec{r})V(\vec{r} - \vec{n})R_{\alpha'}(|\vec{r} - \vec{n}|)K_{\alpha'}(\vec{r} - \vec{n}) = \int d^3 r R_\alpha(|\vec{r} + \vec{n}|)K_\alpha(\vec{r} + \vec{n})V(\vec{r})R_{\alpha'}(|\vec{r}|)K_{\alpha'}(\vec{r}) = V_{\alpha',\alpha}(-\vec{n}) .$$  
(235)

If $g$ is a point group transformation of the system, $V(g\vec{r}) = V(\vec{r})$ and

$$V_{\alpha,\alpha'}(\vec{n}) = \int d^3 r R_t(|g\vec{r}|)K_\alpha(g^{-1}\vec{r})V(g\vec{r})R_{\alpha'}(|\vec{r} - \vec{n}|)K_{\alpha'}(\vec{r} - \vec{n}) = \int d^3 r R_t(|g\vec{r}|)K_\alpha(g^{-1}\vec{r})V(\vec{r})R_{\alpha'}(|g\vec{r} - g\vec{n}|)K_{\alpha'}(g^{-1}\vec{r} - \vec{n}) = \int d^3 r R_t(|g\vec{r}|)K_\alpha(g^{-1}\vec{r})V(\vec{r})R_{\alpha'}(|\vec{r} - g\vec{n}|)K_{\alpha'}(g^{-1}\vec{r} - g\vec{n}) .$$  
(236)

$D(g)$ is a representation of the $g$ symmetry transformation,

$$g \circ K_\alpha(\vec{r}) := K_\alpha(g^{-1}\vec{r}) = \sum_\beta D_{\alpha\beta}(g)K_\beta(\vec{r}) = \sum_\beta K_\beta(\vec{r})D_{\beta\alpha}^t(g) ,$$  
(238)

where $D_{\beta\alpha}^t(g)$ is the transpose matrix. We get from (236) then

$$g \circ V(\vec{n}) := V(g^{-1}\vec{n}) = D(g)V(\vec{n})D_{\alpha\beta}^t(g) .$$  
(239)

It can be supposed that there is an atom 'over' site $n$, distance $|\vec{Z}|$ in $z$ direction. First we determine the hybridization matrix $V_{\alpha,\alpha'}(\vec{Z})$. $g$ is an element of $C_{3v}$, what is to say $g\vec{Z} = \vec{Z}$.
Table 3: Table of first (1NN) and second (2NN) neighbor hopping parameters in case of Au [72] and Cu [73] host in units eV

<table>
<thead>
<tr>
<th></th>
<th>1NN(Au)</th>
<th>2NN(Au)</th>
<th>1NN(Cu)</th>
<th>2NN(Cu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{s,s}$</td>
<td>-0.908480</td>
<td>0.037672</td>
<td>-1.0229</td>
<td>-0.0125</td>
</tr>
<tr>
<td>$V_{s,p}$</td>
<td>1.322056</td>
<td>0.035496</td>
<td>1.5743</td>
<td>0.1661</td>
</tr>
<tr>
<td>$V_{s,d}$</td>
<td>-0.642190</td>
<td>-0.106620</td>
<td>-0.4227</td>
<td>-0.1159</td>
</tr>
<tr>
<td>$V_{p,p,\sigma}$</td>
<td>2.429776</td>
<td>0.504152</td>
<td>2.6761</td>
<td>0.7332</td>
</tr>
<tr>
<td>$V_{p,p,\pi}$</td>
<td>-0.223720</td>
<td>-0.139400</td>
<td>0.2640</td>
<td>0.1151</td>
</tr>
<tr>
<td>$V_{d,p,\sigma}$</td>
<td>-0.870260</td>
<td>-0.103630</td>
<td>-0.4475</td>
<td>-0.0729</td>
</tr>
<tr>
<td>$V_{d,p,\pi}$</td>
<td>0.257856</td>
<td>0.063920</td>
<td>0.2385</td>
<td>0.0437</td>
</tr>
<tr>
<td>$V_{d,d,\sigma}$</td>
<td>-0.676060</td>
<td>-0.041480</td>
<td>-0.3491</td>
<td>-0.0614</td>
</tr>
<tr>
<td>$V_{d,d,\pi}$</td>
<td>0.356864</td>
<td>0.032640</td>
<td>0.2449</td>
<td>0.0328</td>
</tr>
<tr>
<td>$V_{d,d,d}$</td>
<td>-0.062150</td>
<td>-0.007750</td>
<td>-0.0555</td>
<td>-0.0039</td>
</tr>
</tbody>
</table>

The representation matrices of $C_{4v}^x$ in orbital space are

\[
E : \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, C_4^+ : \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}, C_4^- : \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}, C_2 : \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix},
\]

\[
\sigma_{v1} : \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \sigma_{v2} : \begin{pmatrix} 0 & 1 \\ 0 & -1 \end{pmatrix}, \sigma_{d1} : \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}, \sigma_{d2} : \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix},
\]

(240)

and in the spin space are

\[
D_{1/2}(E) : \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, D_{1/2}(C_4^+) : \begin{pmatrix} \epsilon^* & 0 \\ 0 & \epsilon \end{pmatrix}, D_{1/2}(C_4^-) : \begin{pmatrix} \epsilon & 0 \\ 0 & \epsilon^* \end{pmatrix}, D_{1/2}(C_2) : \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix},
\]

\[
D_{1/2}(\sigma_{v1}) : \begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}, D_{1/2}(\sigma_{v2}) : \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}, D_{1/2}(\sigma_{d1}) : \begin{pmatrix} 0 & -\epsilon \\ \epsilon & 0 \end{pmatrix}, D_{1/2}(\sigma_{d2}) : \begin{pmatrix} 0 & -\epsilon^* \\ \epsilon^* & 0 \end{pmatrix},
\]

(241)

where $\epsilon = e^{i\pi/4}$. If $V_{\alpha,\alpha'}(\mathbf{Z}) = -V_{\alpha,\alpha'}(\mathbf{Z})$ then $V_{\alpha,\alpha'}(\mathbf{Z}) = 0$ and the inversion symmetry implies

\[
V_{\alpha,\alpha'}(\mathbf{n}) = (-1)^{\ell + \ell'} V_{\alpha',\alpha}(\mathbf{n}).
\]

(242)

The potential has spherical symmetry, so $V_{d_{xy}} = V_{d_{x^2-y^2}}$ from $\pi/4$ rotations. After the
calculation we obtain

\[
\mathbf{V}(\overrightarrow{Z}) = \begin{pmatrix}
V_{s,s} & 0 & 0 & V_{s,p} & 0 & 0 & 0 & 0 & V_{s,d} \\
0 & V_{p,p,\pi} & 0 & V_{d,p,\pi} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & V_{p,p,\pi} & 0 & 0 & 0 & V_{d,p,\pi} & 0 & 0 \\
-V_{s,p} & 0 & 0 & V_{p,p,\sigma} & 0 & 0 & 0 & 0 & V_{d,p,\sigma} \\
0 & 0 & 0 & 0 & V_{d,d,\pi} & 0 & 0 & 0 & 0 \\
0 & -V_{d,p,\pi} & 0 & 0 & V_{d,d,\sigma} & 0 & 0 & 0 & 0 \\
0 & 0 & -V_{d,p,\pi} & 0 & 0 & 0 & 0 & V_{d,d,\pi} & 0 \\
V_{s,d} & 0 & 0 & -V_{d,p,\sigma} & 0 & 0 & 0 & 0 & V_{d,d,d} \\
\end{pmatrix}
\] (243)

and the other matrices \( V_{\alpha,\alpha'}(\overrightarrow{n}) \) come from \( \mathbf{V}(\overrightarrow{Z}) \) with the appropriate \( g \) transformation. The Table 3 contains the numerical values of the hybridization parameters.
9.3 Appendix - Random Matrix Theory

As we mentioned, the Hamiltonian (76) is an $M \times M$ matrix, where $M = 18 \times N$ and it has at most $M/2$ different eigenvalues $\{\varepsilon_i\}$ because of Kramers-degeneracy. The level spacings $\{s_i\}$ are defined as

$$s_i = \varepsilon_{i+1} - \varepsilon_i \, ,$$

and $\varepsilon_1 \leq \varepsilon_2 \leq ... \leq \varepsilon_{M/2}$.

In case of general integrable systems the eigenvalues follow a Poisson-distribution, so the level spacings are described by the exponential distribution,

$$p(s) = \frac{1}{\Delta} \exp \left( -\frac{s}{\Delta} \right) \, ,$$

where $\Delta$ denotes the expected value of the level spacings.

In case of disordered nanograins the eigenvalues are only doubly degenerate, so we always deal with $M/2$ different eigenvalues and $M/2 - 1$ level spacing values $\{s_i\}$. In a given sample there are $n_{samp} \times M/2$ eigenvalues and $n_{samp} \times (M/2 - 1)$ level spacings. The Hamiltonian is a random matrix and we try to find $P(H)d\mu(H)$, where $d\mu(H)$ is a probability measure on the space of $M \times M$ self-adjoint matrices. Actually, we try to determine the $n(\varepsilon)$ and $p(s)$ distribution functions of $\{\varepsilon_i\}$ and $\{s_i\}$, respectively.

If there are no external magnetic fields and no host SOC then $H$ is a real symmetric matrix so it can be diagonalized by an appropriate orthogonal matrix. Obviously, the $P(H)d\mu(H)$ does not depend on the basis, where $d\mu(H)$ is a probability measure on the space of real symmetric matrices, but $P(H)$ and $d\mu(H)$ should be basis-independent according that the eigenvalues of $H$ do not depend on the basis. A real symmetric matrix is described by $\frac{M(M+1)}{2}$ parameters $\{q_i\}$, and I choose the measure $d\mu$ that it does not depend on the set $\{q_i\}$ and should be invariant under the orthogonal transformations, i.e. should leave the $\frac{M(M+1)}{2}$ dimensional volume invariant. After the fixing of the measure $d\mu(H)$ we can determine the quantity $P(H)$. It can be supposed that

$$P(H) = P(Tr(H), Tr(H^2), ..., Tr(H^N)) \, .$$

Using the maximum entropy principle, i.e.

$$S = -\int d\mu(H) P(H) \ln (P(H))$$

should be minimized with the following constrains:

$$\int d\mu(H) P(H) = 1 \, ,$$

$$\int d\mu(H) Tr(H) P(H) = 0 \, ,$$

$$\int d\mu(H) Tr(H^2) P(H) = const \, .$$

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The Eq. (246) says that the expected value of the energy can be chosen to be zero, and the Eq. (247) fixes an energy scale. Finally, we get

\[ P\left( H \right) = c \exp \left( -\lambda Tr(H^2) \right) , \tag{248} \]

where \( c \) and \( \lambda \) are constants. Eq. (248) describes the so-called Gaussian Ensembles. In that case an orthogonal matrix can diagonalize the real symmetric random \( H \), so we speak on Gaussian Orthogonal Ensemble (GOE). It can be written,

\[ d\mu(H)P(H) = C \left( \prod_{i \geq j} dH_{ij} \right) \exp \left( -\lambda Tr(H^2) \right) . \tag{249} \]

We should determine the distributions \( P(\{\varepsilon_i\}) \prod_i d\varepsilon_i \) and \( P(\{s_i\}) \prod_i ds_i \), after the calculation it can be obtain, that

\[ P(\{\varepsilon_i\}) \prod_i d\varepsilon_i = c' \left( \prod_{i \geq j} (\varepsilon_i - \varepsilon_j) \right) \exp \left( -\lambda \sum_i \varepsilon_i^2 \right) \prod_i d\varepsilon_i \]

for GOE.

The general formula can be written as

\[ P_\beta(\{\varepsilon_i\}) \prod_i d\varepsilon_i = c_\beta \prod_{i \geq j} |\varepsilon_i - \varepsilon_j|^{\beta} \exp \left( -\lambda \sum_i \varepsilon_i^2 \right) \prod_i d\varepsilon_i , \tag{250} \]

or

\[ P_\beta(\{\varepsilon_i\}) \prod_i d\varepsilon_i \sim \exp \left( -\lambda \sum_{i=1}^N \varepsilon_i^2 + \beta \sum_{i<j} \ln (|\varepsilon_i - \varepsilon_j|) \right) \prod_i d\varepsilon_i , \tag{251} \]

where \( \beta \) labels the type of the Ensemble, the \( \beta = 1, 2 \) and 4 corresponds to GOE, GUE and GSE, respectively. The distribution of the level spacings is a universal feature of the random matrices,

\[ p_\beta(x) = a_\beta x^\beta \exp \left( -b_\beta x^2 \right) , \tag{252} \]

where \( x = s/\Delta \). The constraints,

\[ \int_0^\infty p_\beta(x)dx = 1 \quad \text{and} \quad \int_0^\infty xp_\beta(x)dx = \frac{1}{\Delta} \]

imply

\[ a_\beta = 2 \frac{\Gamma^{\beta+1}(\beta + 1/2)}{\Gamma^{\beta+1}(\beta + 1/2)} \quad \text{and} \quad b_\beta = \frac{\Gamma^2((\beta + 2)/2)}{\Gamma^2((\beta + 1)/2)} . \tag{253} \]

Eq. (94) shows that the \( p(s) \) function is very different from the distribution function of integrable systems. The logarithmic repulsive interaction in Eq. (251) implies level repulsion, hence \( p(s) \) goes as \( s^\beta \) near \( s = 0 \) and the tail of the distribution goes as \( \exp \left( -\left( \frac{s}{\Delta} \right)^2 \right) \). The
Parameter $\beta$ has a crucial role in classification of the different universal cases. $\beta = 1$ corresponds to the GOE, $\beta = 2$ is the Gaussian Unitary Ensemble GUE and $\beta = 4$ is the Gaussian Symplectic Ensemble (GSE). If time reversal of a system is broken (e.g. there is an external magnetic field), then $\beta = 2$ and GUE is the correct ensemble. The GOE is the appropriate ensemble in the presence of time reversal symmetry in case of particles with integer spins, and an orthogonal matrix diagonalizes the Hamiltonian. Without host SO interaction the distribution of the level spacings is described by GOE. In case of particles with half integer spins GSE applies in the presence of the host SOC. The numerical values of the parameters in Eq. (253) are as follows:

$$a_1 = \frac{\pi}{2} \approx 1.571, \quad b_1 = \frac{\pi}{4} \approx 0.785 \text{ (GOE)} ,$$

$$a_2 = \frac{32}{\pi^2} \approx 3.242, \quad b_2 = \frac{4}{\pi} \approx 1.273 \text{ (GUE)} ,$$

$$a_4 = \frac{262144}{729\pi^3} \approx 11.597, \quad b_4 = \frac{64}{9\pi} \approx 2.264 \text{ (GSE)} .$$

This Appendix is largely based on the course [74].
9.4 Appendix - Site ordering in LSO-anisotropy parameter space

Table 5 of this appendix contains information about the anisotropy parameters $K_{\alpha,i}^L$ of the different sites of the symmetric nanograin consisting of $N_C = 87$ core sites ($N = 225$ sites all). The structure of the table is the following. The first column refers to the shells (defined in Sec. 3.4). The second column refers to the sites whose anisotropy parameters are given in columns 4-6. The third column gives the site symmetry group of the sites (i.e. the subgroup of $O_h$ that leaves the appropriate points invariant). The notation of the symmetry elements of these subgroups is the following: $E$ refers to the identity element, $I$ refers the inversion operator, $C_{n\alpha}$ means an $n$-fold rotation around axis $\alpha = x, y, z, a, b, c, d, e, f$, where the axes are graphically explained in Fig. 29, overbear means the generatum of the element under the bar, and the superscript $\pm$ refers to the direction of the corresponding rotation following the right-hand rule. Columns 4-6 give the anisotropy parameters of the corresponding sites. Note that in the fourth the rather irrelevant parameters are all denoted by the same letter $k_1$ although these values are only the same for points belonging to the same shell; the different shells have different values of this parameter.

![Symmetry elements of the cubic group O][75].

Every six parameters for all the core sites were calculated numerically. Surprisingly symmetric objects were found in the six-dimensional parameter space, equilateral triangles in $\frac{K_1^L - K_2^L}{2} - K_4^L$ plane in Fig. 16. The relations between the numerical values of the parameters were confirmed up to ten decimals, for instance the edge lengths of the triangles were the same up to this accuracy. The careful group theoretical analysis of the spatial symmetries of the ordered nanograin confirmed these numerical investigations. All the numerically relations found in parameter space have been exactly confirmed. These relations between
Table 4: Table of numerical value of the anisotropy parameters in case of $N_c = 87$ core atoms in units meV

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2d_1$</td>
<td>$-6.4811130$</td>
</tr>
<tr>
<td>$2d_4$</td>
<td>$-12.1119220$</td>
</tr>
<tr>
<td>$b_1$</td>
<td>$0.3414470$</td>
</tr>
<tr>
<td>$b_4$</td>
<td>$0.0913560$</td>
</tr>
<tr>
<td>$2d_2$</td>
<td>$7.2868220$</td>
</tr>
<tr>
<td>$2d_3$</td>
<td>$7.2208940$</td>
</tr>
</tbody>
</table>

The parameters are quite general, i.e. Table 5 is valid for the first six shells for even larger nanograins, only the numerical values of the parameters, seem Table 4, have to be changed appropriately.
| Shell   | Sites $(i)$ | Site symmetry of site $i$ | $|C^L|$ | $\{(K^L_{1} - K^L_{2})/2, K^L_{1}\}$ | $-\{K^L_{1}, K^L_{2}, K^L_{3}\}$ |
|---------|-------------|--------------------------|-------|----------------------------------|----------------------------------|
| Shell$_0$ | (2 - 5), (44 - 45) | $\{E, C_{2x}, C_{2y}, I\}$ | $\{k_1\}$ | $\{0, 0\}$ | $\{0, 0, 0\}$ |
| Shell$_1$ | (9 - 12), (48 - 53) | $\{E, C_{2x}, C_{2y}, C_{2z}I\}$ | $\{k_1\}$ | $\{2d_1, 0\}, \{2d_4, 0\}$ | $\{0, b_1, 0\}, \{0, b_4, 0\}$ |
| Shell$_1$ | (4 - 10), (49 - 52) | $\{E, C_{2x}, C_{2y}, C_{2x}I\}$ | $\{k_1\}$ | $\{-d_1, \sqrt{3}d_1\}, \{-d_4, \sqrt{3}d_4\}$ | $\{0, 0, b_1\}, \{0, 0, b_4\}$ |
| Shell$_1$ | (7 - 8), (50 - 51) | $\{E, C_{2x}, C_{2y}, C_{2z}I\}$ | $\{k_1\}$ | $\{-d_1, \sqrt{3}d_1\}, \{-d_4, \sqrt{3}d_4\}$ | $\{0, 0, -b_1\}, \{0, 0, -b_4\}$ |
| Shell$_1$ | (3 - 13), (46 - 55) | $\{E, C_{2x}, C_{2y}, C_{2z}I\}$ | $\{k_1\}$ | $\{-d_1, -\sqrt{3}d_1\}, \{-d_4, -\sqrt{3}d_4\}$ | $\{b_1, 0, 0\}, \{b_4, 0, 0\}$ |
| Shell$_1$ | (6 - 11), (47 - 54) | $\{E, C_{2x}, C_{2y}, C_{2x}I\}$ | $\{k_1\}$ | $\{-d_1, -\sqrt{3}d_1\}, \{-d_4, -\sqrt{3}d_4\}$ | $\{-b_1, 0, 0\}, \{-b_4, 0, 0\}$ |
| Shell$_2$ | (17 - 18) | $\{C^L_{n}\}, \{C_{2x}, C_{2y}, C_{2z}I\}$ | $\{k_1\}$ | $\{2d_2, 0\}$ | $\{0, 0, 0\}$ |
| Shell$_2$ | (14 - 15) | $\{C^L_{n}\}, \{C_{2x}, C_{2y}, C_{2z}I\}$ | $\{k_1\}$ | $\{-d_2, \sqrt{3}d_2\}$ | $\{0, 0, 0\}$ |
| Shell$_2$ | (16 - 19) | $\{C^L_{n}\}, \{C_{2x}, C_{2y}, C_{2z}I\}$ | $\{k_1\}$ | $\{-d_2, -\sqrt{3}d_2\}$ | $\{0, 0, 0\}$ |
| Shell$_3$ | (31 - 33), (26 - 40) | $\{E, C_{2y}I\}$ | $\{k_1\}$ | $\{-d_3, -\sqrt{3}d_3\}$ | $\{-l, k, -k\}, \{-l, -k, k\}$ |
| Shell$_3$ | (24 - 36), (43 - 21) | $\{E, C_{2y}I\}$ | $\{k_1\}$ | $\{-d_3, \sqrt{3}d_3\}$ | $\{k, k, l\}, \{-k, -k, l\}$ |
| Shell$_3$ | (32 - 35), (29 - 29) | $\{E, C_{2y}I\}$ | $\{k_1\}$ | $\{d_3, 0\}$ | $\{k, -l, -k\}, \{-k, -l, k\}$ |
| Shell$_3$ | (20 - 27), (28 - 29) | $\{E, C_{2y}I\}$ | $\{k_1\}$ | $\{d_3, 0\}$ | $\{-k, l, -k\}, \{k, l, k\}$ |
| Shell$_3$ | (42 - 25), (34 - 30) | $\{E, C_{2y}I\}$ | $\{k_1\}$ | $\{-d_3, -\sqrt{3}d_3\}$ | $\{l, -k, k\}, \{l, k, k\}$ |
| Shell$_3$ | (22 - 41), (37 - 23) | $\{E, C_{2y}I\}$ | $\{k_1\}$ | $\{-d_3, \sqrt{3}d_3\}$ | $\{k, -k, -l\}, \{-k, -k, l\}$ |
| Shell$_5$ | (65 - 69) | $\{E, C_{2y}I\}$ | $\{k_1\}$ | $\{d_5, -e_5\}$ | $\{0, 0, -b_5\}$ |
| Shell$_5$ | (68 - 67) | $\{E, C_{2y}I\}$ | $\{k_1\}$ | $\{d_5, -e_5\}$ | $\{0, 0, b_5\}$ |
| Shell$_5$ | (64 - 75) | $\{E, C_{2y}I\}$ | $\{k_1\}$ | $\{d_5, e_5\}$ | $\{-b_5, 0, 0\}$ |
| Shell$_5$ | (74 - 66) | $\{E, C_{2y}I\}$ | $\{k_1\}$ | $\{d_5, e_5\}$ | $\{b_5, 0, 0\}$ |
| Shell$_5$ | (79 - 57) | $\{E, C_{2y}I\}$ | $\{k_1\}$ | $\{-d_5 + \sqrt{3}e_5\}, \{-d_5 + \sqrt{3}e_5\}$ | $\{-b_5, 0, 0\}$ |
| Shell$_5$ | (56 - 58) | $\{E, C_{2y}I\}$ | $\{k_1\}$ | $\{-d_5 + \sqrt{3}e_5\}, \{\sqrt{3}d_5 - e_5\}$ | $\{b_5, 0, 0\}$ |
| Shell$_5$ | (60 - 78) | $\{E, C_{2y}I\}$ | $\{k_1\}$ | $\{-d_5 + \sqrt{3}e_5\}, \{\sqrt{3}d_5 + e_5\}$ | $\{0, -b_5, 0\}$ |
| Shell$_5$ | (76 - 62) | $\{E, C_{2y}I\}$ | $\{k_1\}$ | $\{-d_5 + \sqrt{3}e_5\}, \{-d_5 + \sqrt{3}e_5\}$ | $\{0, 0, -b_5\}$ |
| Shell$_5$ | (71 - 73) | $\{E, C_{2y}I\}$ | $\{k_1\}$ | $\{d_5 + \sqrt{3}e_5\}, \{-d_5 + \sqrt{3}e_5\}$ | $\{0, b_5, 0\}$ |
| Shell$_5$ | (72 - 61) | $\{E, C_{2y}I\}$ | $\{k_1\}$ | $\{-d_5 + \sqrt{3}e_5\}, \{d_5 + \sqrt{3}e_5\}$ | $\{0, 0, -b_5\}$ |
| Shell$_5$ | (70 - 63) | $\{E, C_{2y}I\}$ | $\{k_1\}$ | $\{-d_5 + \sqrt{3}e_5\}, \{-d_5 + \sqrt{3}e_5\}$ | $\{0, 0, b_5\}$ |
| Shell$_6$ | (81 - 80) | $\{C_{3y}\}, \{C_{2x}, C_{2y}, C_{2z}I\}$ | $\{k_1\}$ | $\{0, 0\}$ | $\{a_6, a_6, a_6\}$ |
| Shell$_6$ | (85 - 84) | $\{C_{3y}\}, \{C_{2x}, C_{2y}, C_{2z}I\}$ | $\{k_1\}$ | $\{0, 0\}$ | $\{-a_6, -a_6, a_6\}$ |
| Shell$_6$ | (87 - 82) | $\{C_{3y}\}, \{C_{2x}, C_{2y}, C_{2z}I\}$ | $\{k_1\}$ | $\{0, 0\}$ | $\{-a_6, a_6, -a_6\}$ |
| Shell$_6$ | (83 - 86) | $\{C_{3y}\}, \{C_{2x}, C_{2y}, C_{2z}I\}$ | $\{k_1\}$ | $\{0, 0\}$ | $\{a_6, -a_6, -a_6\}$ |

Table 5: Symbolical anisotropy parameter values for the first six shells. Numerical values for a nanograin consisting of $N_C = 87$ core sites are enumerated in Table 4. $C^L = \frac{K^L_{1} + K^L_{2}}{2}$. 
9.5 Appendix - Single energy integration

In this Appendix we will prove that

\[
I^L (d, T) = \int_{-\infty}^{\varepsilon_F} \Delta g (\varepsilon) e^{i(Q(\varepsilon)d+\theta(\varepsilon))} d\varepsilon \simeq \Delta g (\varepsilon_F) \frac{e^{i(Q(\varepsilon_F)d+\theta(\varepsilon))}}{iQ' (\varepsilon_F)} \frac{d}{d}. \tag{255}
\]

Proof:

\[
\int_{-\infty}^{\infty} f (\varepsilon, T) n (\varepsilon) d\varepsilon = \int_{-\infty}^{\infty} d\varepsilon \left( - \frac{df (\varepsilon, T)}{d\varepsilon} \right) N (\varepsilon), \tag{256}
\]

where

\[
N (\varepsilon) = \int_{-\infty}^{\varepsilon} n (\varepsilon') d\varepsilon', \tag{257}
\]

and

\[
f (\varepsilon, T) = \frac{1}{e^{(\varepsilon-\mu)/k_B T}+1}.	ag{258}\]

Since

\[
\frac{df (\varepsilon, T)}{d\varepsilon} = - \frac{1}{k_B T} \frac{e^{(\varepsilon-\mu)/k_B T}}{(e^{(\varepsilon-\mu)/k_B T}+1)^2} = - \frac{1}{4k_B T \cosh^2 \left( \frac{\varepsilon-\mu}{2k_B T} \right)}, \tag{259}
\]

\[
\int_{-\infty}^{\infty} f (\varepsilon, T) n (\varepsilon) d\varepsilon = \frac{1}{4k_B T} \int_{-\infty}^{\infty} d\varepsilon \frac{N (\varepsilon)}{\cosh^2 \left( \frac{\varepsilon-\mu}{2k_B T} \right)}
\]

\[
= \frac{1}{2} \int_{-\infty}^{\infty} \frac{N (\mu + 2k_B T x)}{\cosh^2 x} dx. \tag{260}
\]

Let us now deal with the integral,

\[
I^L (d, T) = \int_{-\infty}^{\infty} f (\varepsilon, T) \left[ \Delta g (\varepsilon) e^{i(Q(\varepsilon)d+\theta(\varepsilon))} \right] d\varepsilon \quad (d \to \infty). \tag{261}
\]

Since the function \( e^{iQ(\varepsilon)d} \) oscillates rapidly and \( \Delta g (\varepsilon) \) and \( Q (\varepsilon) \) are slowly varying function \( \Delta g (\varepsilon) \) because of the Fermi-function \( f (\varepsilon, T) \), only the vicinity of \( \mu \) contributes to the above integral. In that region the also slowly varying phase \( Q (\varepsilon) \) can be approximated by

\[
Q (\varepsilon) = Q (\mu) + (\varepsilon - \mu) Q' (\mu), \tag{262}
\]

and we take \( \Delta g (\varepsilon) \simeq \Delta g (\mu) \), such that

\[
I^L (d, T) \simeq e^{i(Q(\mu)d+\theta(\mu))} \Delta g (\mu) \int_{-\infty}^{\infty} f (\varepsilon, T) e^{i(\varepsilon-\mu)Q'(\mu)d} d\varepsilon' \tag{263}
\]

\[
= \frac{e^{i\delta'(\mu)d} \Delta g (\mu)}{2i\delta' (\mu) d} \int_{-\infty}^{\infty} \frac{e^{i2k_B TQ'(\mu)x d}}{\cosh^2 x} dx, \tag{264}
\]

and

\[
I^L (d, T) = \frac{e^{i(Q(\mu)d+\theta(\mu))} \Delta g (\mu)}{2iQ'(\mu) d} \int_{-\infty}^{\infty} \frac{e^{i2k_B TQ'(\mu)x d}}{\cosh^2 x} dx. \tag{265}
\]

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and using the relation
\[
\int_{0}^{\infty} \frac{\cos ax}{\cosh^2 \beta x} dx = \frac{a\pi}{2\beta^2 \sinh \left(\frac{a\pi}{2\beta}\right)},
\]
we arrive at,
\[
I^L(d, T) = \frac{e^{i(Q(\mu)d+\theta(\mu))} \Delta g(\mu)}{iQ'(\mu) d} \frac{k_B T Q'(\mu) d\pi}{\sinh (k_B T Q'(\mu) d\pi)}.
\]
Specifically, for \( T = 0 \),
\[
I^L(d, T = 0) = \frac{e^{i(Q(\mu)d+\theta(\mu))} \Delta g(\mu)}{iQ'(\mu) d}.
\]

This Appendix is largely based on the course [55].
References


[34] H. Mirhosseini, I. V. Maznichenko, Samir Abdelouahed, S. Ostanin, A. Ernst, I. Mertig, and J. Henk,


[55] L. Szunyogh, Electronic Structure Calculations, graduate course, BME


[74] G. Zaránd, Physics of Mesoscopic Systems, graduate course, BME