Revised theory of the magnetic surface anisotropy of impurities in metallic mesoscopic samples

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In several experiments the magnitude of the contribution of magnetic impurities to the Kondo resistivity shows size dependence in mesoscopic samples. It was suggested ten years ago that magnetic surface anisotropy can be responsible for the size dependence in cases where there is strong spin-orbit interaction in the metallic host. The anisotropy energy has the form $\Delta E = K_d(nS)^2$ where $n$ is the vector perpendicular to the plane surface, $S$ is the spin of the magnetic impurity and $K_d > 0$ is inversely proportional to distance $d$ measured from the surface. It has been realized that in the tedious calculation an unjustified approximation was applied for the hybridizations of the host atom orbitals with the conduction electrons which depend on the position of the host atoms. Namely, the momenta of the electrons were replaced by the Fermi momentum $k_F$. That is reinvestigated considering the $k$-dependence which leads to singular energy integrals and in contrary to the previous result $K_d$ is oscillating like $\sin(2k_Fd)$ and the distance dependence goes like $1/d^2$ in the asymptotic region. As the anisotropy is oscillating, for integer spin the ground state is either a singlet or a doublet depending on distance $d$, but in the case of the doublet there is no direct electron induced transition between those two states at zero temperature. Furthermore, for half-integer ($S > 1/2$) spin it is always a doublet with direct transition only in half of the cases.

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I. INTRODUCTION

There are substantial experimental evidences that the amplitude of the Kondo effect due to magnetic impurities in metallic samples of limited size are reduced\textsuperscript{1,2} but with unchanged Kondo temperature. That indicates that not all of the impurities contribute in the same way. There were early speculations that this reduction appears where the sample size is comparable with the Kondo screening cloud. This is incorrect as the Kondo coupling is localized and the only relevant energy scale to be compared with the Kondo temperature is the level spacing of the conduction electrons which is e.g. zero for semi-infinite samples. Later it was suggested\textsuperscript{3} that a magnetic surface anisotropy can develop due to the spin-orbit interaction in the host metal, which has the form

$$H = K_d(S_z)^2$$

(1)

where the constant $K_d$ depends on the distance measured from the surface of the sample and $S_z$ is the component of the impurity spin perpendicular to the surface (see Fig. 1). In those papers\textsuperscript{2,3} it was stated that surprisingly $K_d$ for large distances is always positive and decays with the first power of the distance. That result was not questioned in Ref. [3]. Recently, one of the authors (L.Sz.) has called the attention to an unjustified approximation in the previous lengthy calculation\textsuperscript{3,4} which can be responsible for the very surprising results. That approximation was that in the hybridizations of the host atom orbitals with the conduction electrons which depend on the position of the host atoms (see Eq.(3) and (9) of Ref. [3]), the momenta of the electrons were replaced by the Fermi momentum $k_F$. That was even not the case in the derivation of the Friedel oscillation\textsuperscript{2}.

FIG. 1: The magnetic impurity at a distance $d$ from the surface in a metallic host with homogeneously dispersed spin-orbit scatterers labeled by $n$.

Meanwhile great efforts has been made to derive the surface anisotropy by using electronic structure calculations. First Szunyogh and Gyorffy calculated the anisotropy in semi-infinite Au host for Fe impurities\textsuperscript{5}. They found that $K_d$ is an oscillating function of the distance $d$ and the amplitude falls as $1/d^2$. That was a calculation of mean field type and the discrepancy between those and the analytical ones was not surprising as in the latter the diagrams calculated are beyond the mean field approximation. Recently, Szunyogh, Zaránd, Gallego, Muñoz and Gyorffy\textsuperscript{6} have developed another model, where the spin-orbit interaction was placed on the $d$-level of the impurity instead of the host. They considered the Friedel oscillation in the density of states nearby the Fermi energy due to the presence of the surface and the different $d$-orbitals of the impurity coupled differently to these oscillations and that is realized in the
oscillating anisotropy decaying as $1/d^2$. It is interesting to note that the Hartree-Fock mean field approximation and the diagram beyond that play equal role. We are also informed that very elaborate calculations by A. Szilva, L. Szunyogh, G. Zaránád, and M.C. Muñoz are in progress where the spin-orbit interaction in the host is considered.

The relative importance of the spin-orbit interactions on the $d$-level and the host material must be very specific for which impurity atom and host metal are considered and the final answer can be given only by detailed electronic structure calculations.

The present analytical calculation is focused at the oscillating behavior and the decay rate of the $K_d$ model is called the local system labeled by $n$ in first order of the spin-orbit coupling is following Ref. [4] the conduction electron Green’s function is kept i.e. $G_d(i\omega_n) = \frac{1}{i\omega_n - \omega_d}$ where $\omega_d = \epsilon_d - i\Delta$ and $\epsilon_d$ (measured from the Fermi level) and $\Delta$ are the energy and width of the $d$-level, respectively and $-2 \leq m \leq 2$ for the conduction electrons.

In Eq. (2) now

$$W_{kk'}(R_n) = \lambda 
\lambda V^2 \left( B^+(k,k')\sigma^- + B^-(k,k')\sigma^+ + B^z(k,k')\sigma^z \right)_{m'm'n} \left( \sigma \sigma \right)$$

which follows from a similar calculation like in Ref. [4] and $\lambda$ is the strength of the spin-orbit interaction. $B^+(k,k')$ and $B^z(k,k')$ are $5 \times 5$ matrices in the quantum number $m$, having the form

$$B^+(mm')(k,k') = \sqrt{(3 + m')(2 - m')}v_m(k)v_m(k')\delta_{m,m'+1},$$

$$B^−(mm')(k,k') = \sqrt{(3 - m')(2 + m')}v_m(k)v_m(k')\delta_{m,m'-1},$$

$$B^z(mm')(k,k') = mv_m(k)v_m(k')\delta_{m,m'},$$

where the $v_m(k)$ matrix elements given in Appendix A are the same as in Eq. (13) of Ref. [4]. These are combinations of oscillating functions like $\sin(kR_n)$ and $\cos(kR_n)$ combined with powers like $(kR_n)^{-m-n}$ ($n = 1, 2, \ldots$).

![FIG. 2: The self-energy diagram for the impurity spin. The double line represents the spin, the single one the conduction electrons. The solid circles stand for the exchange interaction and the $x$ labeled by $n$ for the effective spin-orbit interaction on the orbital of the host atom at $R_n$.](image)

The next step of the calculation is the rotation of the coordinate system from the $n$-local one to that one where the $z$-axis is perpendicular to the surface. The angle between the $z$-axis of the old $(\hat{z})$ and the new $(\hat{z})$ coordinate system is labeled by $\Theta_n$. The calculation of the spin factor of the self-energy diagram (see Fig. 2) giving the anisotropy for the impurity spin is also similar to the original one (see Eqs.(21)-(25) of Ref. [4]).

The average over the positions of the scattering atoms $R_n$ and $R_{n'}$ must be performed for the whole volume of the sample, separately. For the sake of simplicity the continuous limit is applied outside the impurity spin. As it was shown in the earlier works in order to get the dominant contribution one of $n$-s is near the impurity and the other one experiences the existence of the surface at large distances.
The analytical part of the self-energy diagram Fig. 2 now is, however, more complicated as \( W \)-s depend also on four different electronic momenta and the corresponding energies appear in the energy denominators of the electron Green’s functions. In this way the prefactors also depend on the momenta and that plays a crucial role in the following.

For the sake of simplicity we consider the conduction electron band with constant density of states \( \rho_0 \) in the energy interval \( -D < \varepsilon < D \) where \( \varepsilon \) is measured from the Fermi energy and we will assume linear dispersion, i.e. the corresponding \( k \)-values are \( k = k_F + \frac{\varepsilon}{v_F} \) where \( v_F \) is the Fermi velocity.

As in a noble metal host like Cu, Ag or Au the \( d \)-band is below the Fermi energy, it does not give a new singularity in the energy integrals (see Section III), thus we can replace the \( d \)-level propagator by a constant \( \varepsilon_0^{-1} \).

Calculating the contribution of the diagram in Fig. 2 we applied the Abrikosov’s pseudofermion technique\(^ \dagger \) for the spin. After performing the summation over the Matsubara-frequencies we get

\[
K = \rho_0^6 \int \frac{d^3 R_n}{D} \int \frac{d^3 R_n'}{D} \int \frac{d^3 R_n''}{D} \int \frac{d^3 R_n'''}{D} \rho_0^6 \int \frac{d\varepsilon_1}{-D} \int \frac{d\varepsilon_2}{-D} \int \frac{d\varepsilon_3}{-D} \int \frac{d\varepsilon_4}{-D} \left\{ \frac{1}{\varepsilon_1 - \varepsilon_2} \frac{1}{\varepsilon_3 + \omega - \varepsilon_1} \frac{1}{\varepsilon_3 - \varepsilon_4} \right\} \left\{ \frac{1}{\varepsilon_1 - \varepsilon_2} \frac{1}{\varepsilon_3 + \omega - \varepsilon_1} \frac{1}{\varepsilon_3 - \varepsilon_4} \right\} \times F_2(R_n, \theta_n, \theta_n', \theta_n''; k_1, k_2, k_3, k_4),
\]

where \( \omega \) is the energy of the spin after analytical continuation and the \( F_1, F_2 \) functions given in Appendix A are defined in the same way as in Ref. [4].

As that diagram contains two host atoms, averages have to be taken over \( n \) and \( n' \). According to our simple model\(^ \ddagger \), the anisotropy factor\(^ \ddagger \) follows as

\[
J_1(R_n, n'; k_1, k_2, k_3, k_4) = (2\pi)^2 \int \frac{d\theta_n}{\theta_n, \min} \sin \theta_n \int d\theta_n' \sin \theta_n' F_2(R_n, R_{n''}, \theta_n, \theta_n'; k_1, k_2, k_3, k_4),
\]

\[
J_2(R_n, n'; k_1, k_2, k_3, k_4) = (2\pi)^2 \int \frac{d\theta_n}{\theta_n, \min} \sin \theta_n \int d\theta_{n''} \sin \theta_{n''} F_2(R_n, R_{n''}, \theta_n, \theta_{n''}; k_1, k_2, k_3, k_4),
\]

where \( \theta_{n, \min} = \arccos(d/R_n) \), \( \theta_{n'', \min} = \arccos(d/R_{n''}) \).

Since according to the earlier works\(^ \ddagger \), the largest contribution comes from the first part of Eq. (7) corresponding to \( J_1 \) we will consider that.

The evaluation of the integrals with respect to \( \theta_n \) and \( \theta_n' \) gives

\[
J_1(R_n, R_n'; k_1, k_2, k_3, k_4) = \frac{4}{15} j^2 \left( 2\pi V^2 \lambda \right) d^2 \left( \frac{R_{n''}^3 - d^2}{\varepsilon_0^3} \right) \times \left[ 3v_0(k_2, R_n)v_1(k_1, R_n) + 3v_0(k_1, R_n)v_1(k_2, R_n) - 2v_1(k_1, R_n)v_1(k_2, R_n) + 2v_1(k_1, R_n)v_2(k_2, R_n) - 8v_2(k_1, R_n)v_2(k_2, R_n) \right] \times \left[ 3v_0(k_4, R_{n''})v_1(k_3, R_{n''}) + 3v_0(k_3, R_{n''})v_1(k_4, R_{n''}) + v_1(k_3, R_{n''})v_1(k_4, R_{n''}) + 2v_1(k_4, R_{n''})v_2(k_3, R_{n''}) + 2v_1(k_4, R_{n''})v_2(k_4, R_{n''}) + 4v_2(k_3, R_{n''})v_2(k_4, R_{n''}) \right].
\]

where \( a^3 \) is the size of the volume per host atom.

Changing the order of the summation over the host atoms with the energy integrals, the former can be evaluated in a similar way like in Ref. [4].
If \( k_1, k_2, k_3, k_4 \) are replaced by \( k_F \) that gives back the half of Eq. (B2) of Ref. [4].

After a straightforward calculation of the integrals with respect to \( R_n \) and \( R_{nv} \) (see Appendix B) the first part of Eq. (7) corresponding to \( J_1 \) reads

\[
\rho_0^4 \int_{-D}^D \int_{-D}^D \int_{-D}^D \int_{-D}^D \frac{1}{\varepsilon_1 - \varepsilon_2} \left( 1 - n_F(\varepsilon_1) n_F(\varepsilon_3) \right) \frac{1}{\varepsilon_3 - \varepsilon_4} + (\varepsilon_1 \leftrightarrow \varepsilon_2) + (\varepsilon_3 \leftrightarrow \varepsilon_4) + (\varepsilon_1 \leftrightarrow \varepsilon_2 \text{ and } \varepsilon_3 \leftrightarrow \varepsilon_4) \right)
\times \frac{4}{15} f^2 \left( \frac{2\pi V^2}{\lambda} \right)^2 \times \left[ C(k_1 d, k_2 d) D(k_3 d, k_4 d) + C(k_3 d, k_4 d) D(k_1 d, k_2 d) \right],
\]

where the functions \( C \) and \( D \) are given by Eqs. (B3) and (B11), respectively.

As \( C \) and \( D \) are symmetric in their variables we can change the integration variables according to the changes indicated in the energy dependent factor in the integrand of Eq. (11) resulting in a simpler form like

\[
\rho_0^4 \int_{-D}^D \int_{-D}^D \int_{-D}^D \int_{-D}^D \frac{1}{\varepsilon_1 - \varepsilon_2} \frac{1}{\varepsilon_3 + \omega - \varepsilon_1} \frac{1}{\varepsilon_3 - \varepsilon_4} \right)
\times \left[ C(k_1 d, k_2 d) D(k_3 d, k_4 d) + C(k_3 d, k_4 d) D(k_1 d, k_2 d) \right],
\]

where we have exploited the \( 1 - n_F(\varepsilon_1) \) and \( n_F(\varepsilon_3) \) factors as well.

### III. THE ENERGY INTEGRALS

In the following the asymptotic behavior for large distances \( d \) is considered, therefore, only the leading order in \( \frac{1}{d} \) is kept everywhere.

For large distances the radial electronic wave functions are fast oscillating as the energy is changed. These fast oscillations lead to essential cancellations. In order to keep track of the cancellations in the limit \( d \to \infty \), the Riemann theorem with the first asymptotic correction is applied in the following form:

\[
\int_a^b ds f(s) \cos(xs) \sim \frac{f(b) \sin(xb)}{x} - \frac{f(a) \sin(xa)}{x} \quad (13a)
\]

and

\[
\int_a^b ds f(s) \sin(xs) \sim \frac{f(a) \cos(xa)}{x} - \frac{f(b) \cos(xb)}{x} \quad (13b)
\]

which is valid in the leading order in \( 1/x \) where \( f \) must be integrable.

Let us consider the integrations with respect to the energies. In the first part of Eq. (12) the integral with respect to \( \varepsilon_2 \) is

\[
\int_{-D}^D d\varepsilon_2 \frac{C(k_1 d, k_2 d)}{\varepsilon_1 - \varepsilon_2} = \int_{-D}^D dk_2 \frac{C(k_1 d, k_2 d)}{k_1 - k_2}.
\]

Introducing a new integration variable \( \Delta k = k_2 - k_1 \) and using linear dispersion \( \varepsilon = v_F(k - k_F) \), the integral reads

\[
-\frac{k_1 + k_F + \frac{D}{v_F}}{\Delta k}
- \frac{g}{\Delta k}
= \frac{d^3}{a^1} \int_{-k_1 - k_F - \frac{D}{v_F}}^{-k_1 + k_F + \frac{D}{v_F}} d(\Delta k)
\times \left[ f_{+}(k_1 d, (k_1 + \Delta k) d) \cos[2k_1 d] \frac{\cos[\Delta k d]}{\Delta k} - \sin[2k_1 d] \frac{\sin[\Delta k d]}{\Delta k} \right]
+ f_{-}(k_1 d, (k_1 + \Delta k) d) \cos[\Delta k d] \frac{\sin[2k_1 d]}{\Delta k}
+ f_{+}(k_1 d, (k_1 + \Delta k) d) \cos[\Delta k d] \frac{\sin[2k_1 d]}{\Delta k}
+ f_{-}(k_1 d, (k_1 + \Delta k) d) \cos[\Delta k d] \frac{\sin[2k_1 d]}{\Delta k}
+ \Delta k d f_{ci}(k_1 d, (k_1 + \Delta k) d)
\times (C_i[2k_1 + \Delta k d] - C_i[\Delta k d]),
\]

where we used the symmetry property of the cosine integral function \( C_i[-x] = C_i[x] \) and trigonometrical identities.

To evaluate the terms containing the \( C_i[x] \) function we use

\[
C_i[x] = -\int_{-\infty}^{\infty} du \frac{\cos u}{u} = -\int_{1}^{\infty} dv \frac{\cos xv}{v}
\]

and change the order of the integrations with respect to \( v \) and \( \Delta k \).

Due to the cosine and sine functions in the integrand, the integral is determined by the singularity at \( \Delta k = 0 \) \((k_2 = k_1)\). Searching for that we expand the \( f \)-functions around \( k_1 d \) in their second variables and then drop the terms which are not singular at \( \Delta k = 0 \). Then the inte-
As \( \varepsilon_3 < 0 \) \( (k_3 < k_F) \) in Eq. (12) and \( \omega \approx 0 \) the integrand has no singularities in the range of the integration, thus in order to find the leading order contribution in \( 1/k_Fd \) we can apply the Riemann theorem given by Eq. (13). Then Eq. (21) is

\[
\int_{-D}^{D} \frac{d\varepsilon_1}{\varepsilon_3 + \omega - \varepsilon_1} \int_{-D}^{D} \frac{d\varepsilon_2}{\varepsilon_1 - \varepsilon_2} \approx \frac{d^3}{a^3} \frac{v_F}{\omega} \frac{225\pi}{(k_Fd)^3} \frac{1}{\varepsilon_3 + \omega} \frac{1}{\varepsilon_1 - \varepsilon_2} C(k_1d, k_2d) \approx \frac{225\pi v_F}{2} \frac{1}{(k_Fd)^3} \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_3 + \omega} \frac{c}{(k_1d)^3} \frac{1}{2} \cos[2kd] \]

in leading order in \( 1/k_Fd \), where we kept only the contribution of the lower limit, as the contribution of the upper limit of the integral in Eq. (22) is proportional to \( 1/D \), thus it is of lower order.

Now we have to evaluate the remaining integrals with respect to \( \varepsilon_3 \) and \( \varepsilon_4 \) in the first part of Eq. (12) i.e.

\[
\int_{-D}^{D} \frac{d\varepsilon_4}{\varepsilon_3 + \omega} \int_{-D}^{D} \frac{d\varepsilon_3}{\varepsilon_3 - \varepsilon_4} \approx \int_{-D}^{D} \frac{d\varepsilon_3}{\varepsilon_3 + \omega} \int_{-D}^{D} \frac{D(k_3d, k_4d)}{\varepsilon_3 - \varepsilon_4} \]

Starting with the first part of Eq. (23) corresponding to the \( g \) functions in \( D \) (see Eq. (B11)), we introduce again new integration variable \( \Delta k = k_4 - k_3 \) and use linear dispersion. Thus Eq. (23) reads

\[
\int_{-D}^{D} \frac{d\varepsilon_3}{\varepsilon_3 + \omega} \frac{1}{\varepsilon_3 - \varepsilon_4} \approx \frac{d^3}{a^3} \frac{v_F}{\omega} \frac{225\pi}{(k_Fd)^3} \frac{1}{\varepsilon_3 + \omega} \frac{1}{\varepsilon_3 - \varepsilon_4} \frac{c}{(k_3d)^3} \frac{1}{2} \cos[2kd] \]

and in the first part containing the \( g \) functions (see Eq. (B11)) we can repeat the considerations used in performing the integrals with respect to \( \varepsilon_1 \) and \( \varepsilon_2 \) giving

\[
\int_{-D}^{D} \frac{d\varepsilon_1}{\varepsilon_3 + \omega - \varepsilon_1} \int_{-D}^{D} \frac{d\varepsilon_2}{\varepsilon_1 - \varepsilon_2} \approx \frac{d^3}{a^3} \frac{v_F}{\omega} \frac{225\pi}{(k_Fd)^3} \frac{1}{\varepsilon_1 - \varepsilon_2} \frac{c}{(k_3d)^3} \frac{1}{2} \cos[2kd] \]

Since \( k_F - \frac{\omega}{v_F} > 0 \) we can again apply the Riemann theorem given by Eq. (13). The terms coming from the
lower limit of the integrals are less by $1/D$ than the terms coming from the upper limit of the integral which give
\begin{equation}
-\frac{d^3}{d^3} \frac{v_F}{v_F} \frac{\cos[2kFd]}{2d} + g_{s+}(k_Fd, k_Fd) \sin[2kFd] \approx -\frac{d^3}{d^3} \frac{v_F}{v_F} \frac{225 \cos[2kFd]}{(2kFd)^4} - 1125 \sin[2kFd] \frac{d}{2d} \approx -\frac{1}{(k_Fa)^3} \frac{225\pi}{\omega} 4(kFd)^2 \cos[2kFd],
\end{equation}
where only the leading order contribution in $1/kFd$ was kept.

Turning to the second part of Eq. (23) corresponding to the $h$ functions in $D$ (see Eq. (B11)), after using the following properties
\begin{equation}
h(k_3d, k_4d, r_0/d) = \frac{1}{(k_Fa)^3} h(k_3/k_F, k_4/k_F, k_Fr_0),
\end{equation}
for the $h_{c+/c-+/s+}$ functions (see Eq. (B13)) and
\begin{equation}(k_3 - k_4)dh_{s-}(k_3d, k_4d, r_0) = \frac{1}{(k_Fa)^3} \frac{k_4 - k_3}{k_F} h_{s-}(k_3/k_F, k_4/k_F, k_Fr_0),
\end{equation}
for the $h_{s-}$ function, and introducing the $s = k_F$ and $t = \frac{r_0}{k_F}$ new integration variables, we get
\begin{equation}\frac{1}{(k_Fa)^3} \frac{P_1(k_Fr_0, \omega)}{15\pi},
\end{equation}
where
\begin{equation}P_1(x, \omega) = 15\pi \int ds \frac{H(s, t, x)}{1 - \frac{1}{\epsilon_F}} \int dt \frac{H(s, t, x)}{s - t},
\end{equation}
and
\begin{equation}H(s, t, x) = h_{c+}(s, t, x) \cos[(s + t)x] + h_{c-}(s, t, x) \cos[(s - t)x] + h_{s+}(s, t, x) \sin[(s + t)x] + (s - t)h_{s-}(s, t, x) \sin[(s - t)x].
\end{equation}
Thus the terms corresponding to the $h$ functions give $d$-independent contribution, therefore Eq. (24) is Eq. (24) in leading order in $1/kFd$.

Combining that with Eqs. (22) and (12) we get for the first part of Eq. (12) in leading order in $1/kFd$
\begin{equation}16\epsilon_F(Jp_0)^2 \frac{\Delta^2 \lambda^2}{\epsilon_0^2} \frac{1}{(k_Fa)^6} P_1(k_Fr_0, \omega) \cdot \frac{\sin[2kFd]}{(kFd)^3},
\end{equation}
where $\Delta = \pi V^2 \rho_0$ is the width of the $d$-levels due to hybridization.10

Turning to the second part of Eq. (12), after changing the integration variables as $\epsilon_1 \leftrightarrow \epsilon_3$ and $\epsilon_2 \leftrightarrow \epsilon_4$ and performing similar calculation as before we get in leading order with respect to $1/kFd$
\begin{equation}16\epsilon_F(Jp_0)^2 \frac{\Delta^2 \lambda^2}{\epsilon_0^2} \frac{1}{(k_Fa)^6} P_2(k_Fr_0, \omega) \cdot \frac{\sin[2kFd]}{(kFd)^3},
\end{equation}
where
\begin{equation}P_2(x, \omega) = \int_1^{1+\frac{\omega}{P}} ds \frac{1}{s - 1 - \frac{\omega}{P}} \int \frac{dt}{s - t} H(s, t, x),
\end{equation}
Thus the anisotropy factor coming from the first part of Eq. (12) is $J_1$ — giving the leading contribution in leading order in $1/kFd$ is
\begin{equation}K = 16\epsilon_F(Jp_0)^2 \frac{\Delta^2 \lambda^2}{\epsilon_0^2} \frac{1}{(k_Fa)^6} P(k_Fr_0, \omega) \frac{\sin[2kFd]}{(kFd)^3},
\end{equation}
where
\begin{equation}P(x, \omega) = P_1(x, \omega) + P_2(x, \omega)
\end{equation}
which is finite for $\omega = 0$.

Evaluating $P$ by numerical integration it turns out that for $x \sim 1/kF$ the integrals with respect to $t$ and $s$ are dominated by the $t = s$ and $s = 1$ singularity, respectively. Thus
\begin{equation}P(x, \omega = 0) \approx 15\pi \int_0^2 ds H(s, s, x) \ln(s) = 15\pi H(1, 1, x) \frac{\pi^2}{2},
\end{equation}
where we used $D = \epsilon_F$. In Table I we compare the results obtained by numerical integration and by Eq. (37) for $x \sim 0.5 - 1.5$.

| $x$     | 0.5  | 0.75 | 1     | 1.25  | 1.5   |
|---------|------|------|-------|-------|-------|
| $P_{\text{num}}(x, \omega = 0.01)$ | -135.8 | -128.1 | -116.5 | -1552.9 | -2215.9 |
| $P_{\text{app}}(x, \omega = 0)$   | -138.3 | -138.4 | -952.6 | -1664.6 | -2514.1 |

TABLE I: Comparison of $P_{\text{num}}(x, \omega = 0.01)$ obtained by numerical integration and $P_{\text{app}}(x, \omega = 0)$ obtained by Eq. (37) for $x \sim 0.5 - 1.5$.

The result Eq. (35) for the anisotropy factor is essentially different from the earlier one (see Eq. (31) of Ref. [4]) obtained by an unjustified assumption which corresponds formally to the approximation $C(k_1d, k_2d) \approx C(kFd, kFd)$ and $D(k_3d, k_2d) \approx D(kFd, kFd)$ in Eq. (12). The main differences are
- it contains the oscillating factor $\sin[2kFd]$
• the asymptotic distance dependence is \( \frac{1}{r_d} \) instead of \( \frac{1}{k_FR} \), thus it is essentially weaker

• instead of the \( f(\frac{\pi}{2})P_{(2)}^{pol}(k_FR) \) factor which contains the short range cutoff \( r_0 \) and estimated to be between 50 – 950 for \( \omega \approx 0 \) and \( k_FR \approx 0.5 – 1.5 \), we have \( P_{new}^{pol}(k_FR, \omega) \) which is for \( \omega = 0 \) and \( k_FR \approx 0.5 – 1.5 \) between \(-140\) and \(-2500\),

thus in the asymptotic region using the same parameters as in Eq. (32) in Ref. 4,

\[
0.01 \frac{eV}{(d/A)^3} < |K_d| < 1.75 \frac{eV}{(d/A)^3},
\]

Finally, the question can be raised how justified is the assumption of homogeneous distribution of the spin-orbit scatterers. In order to give the answer in the following the scatterers are considered homogeneously distributed on sheets which are parallel to the surface and separated by a distance \( a \). According to the previous works, the pair of sheets in equal distances from the impurity do not contribute to the anisotropy, thus only the unpaired ones must be considered. The sheet \( n \) is in the distance \( na \) from the impurity and only sheets with \( n > d/a \) are considered. As it was discussed in Ref. [2][3][4] one of the two scatterers \( n \) and \( n' \) is nearby the impurity and the other one is far from it on one of the sheets considered. Therefore, the contribution of the sheets is additive. The contribution of sheet \( n \) can be easily obtained from the present calculation as

\[
K_n = a \frac{\partial}{\partial d} K_n|_{d=na},
\]

where the derivative gives the contribution of an infinitely narrow layer and the prefactor provides the correct normalization. Thus the final result in the asymptotic region is

\[
K = \sum_{n > \frac{d}{2}} K_n \approx \sum_{n > \frac{d}{2}} 2ak_F \frac{\cos(2k_Fna)}{(k_Fna)^3},
\]

where the omitted prefactor is the same as in Eq. 33.

Thus the separate sheets contribute by different signs and amplitude. Due to the fast decay by increasing \( n \) only sheets of restricted numbers are essential. Adding the contribution of the sheets with different signs and amplitudes (likely randomly distributed) the final amplitude of the anisotropy \( |K| \) can be larger than \( |K_d| \) thus the \( \frac{1}{\pi} \) decay rate can be somewhat reduced. The situation is different in a coherent case with \( k_Fa = p\pi \) where \( p \) is integer. For even \( p \) the contributions have the same sign and \( \sum_{n > \frac{d}{2}} \frac{1}{\pi t} \approx \frac{a}{2\pi} \) which provides a slower decay rate.

IV. CONCLUSIONS

The amplitude of the anisotropy is oscillating and weaker than the one earlier estimated. In these changes the sharp edge in the \( R \)-integral thus the existence of the surface is crucial. We used a uniform distribution of the spin-orbit scatterers in space. Considering the question how the results are changed in the case where continuum layers of the scatterers are considered, it is argued that the overall behavior is not expected to change, but only the amplitude can be influenced moderately. Furthermore, it is assumed, that the spin-orbit scattering is point like, but a finite extension \( r_d \) (it is assumed that \( k_FR_d < \pi \)) smears somewhat the \( \sin(2k_FRd) \) function in Eq. (33). The actual size of that can be estimated only by electronic structure calculations and certainly will be included in the recent work of one of the authors (L.Sz.) and his coworkers in progress.

The way how the spin is frozen by the surface anisotropy is essentially different from the previous works as \( K_d \) is not always positive (see Fig. 3) and also depends whether the spin is integer or half-integer.

\[
\begin{align*}
K_d &> 0 & K_d &< 0 \\
S_d = \pm 2 & S_d = 0 & & \\
S_d = \pm 1 & & S_d = \pm 1 & \\
S_d = 0 & S_d = \pm 2 & & \\
\text{singlet} & \text{doublet} & \text{no scattering} & \\
\text{scattering} & \text{no scattering} & & \\
\end{align*}
\]

FIG. 3: The level splitting due to the surface anisotropy for (a) integer (e.g. \( S = 2 \)) and (b) half-integer (e.g. \( S = 5/2 \)) spins. It is also indicated whether the electrons can be scattered by the degenerate ground states or not.

• Integer spin (e.g. \( S = 2 \)): the ground state is either singlet or doublet depending on the sign of \( K_d \), however, the electron cannot be scattered by transition in the doublet as the spin momentum difference is \( \Delta S = \pm 4 \) and the turning the electron spin allows only \( \Delta S = \pm 1 \). Thus the spin at low temperature can be completely frozen in.

• Half-integer spin (e.g. \( S = 5/2 \)): the ground state is always doublet, however, in one of the cases \( \Delta S = \pm 1 \) which can cause scattering in contrary to the case where \( \Delta S = \pm 5 \). Thus only half of
the impurities can cause electron spin flips at low temperature. That is different from the previously assumed \( K_d > 0 \) case.

This result shows analogies with Ref. [15] where magnetic molecules with large spins on metallic surface were considered. The spin levels are split in a similar way and electron induced transitions are allowed only between certain levels.

For comparison with experiment the presymptotic behavior is very essential which is beyond the scope of the present paper. The electronic calculations in progress must provide those information including the amplitude of the anisotropy as in the other model in Ref. [8].

The present results valid in the asymptotic region can provide a good possibility to test the numerical calculation. Detailed comparison with experiments must wait for completing the numerical calculation which is going to provide more necessary information.

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APPENDIX A

The \( v_m(k) \) (matrix elements are the same as in Eq. (13) of Ref. [4]):

\[
v_0(k, R_n) = \begin{cases} 
10 \left( \frac{\sin(kR_n)}{2kR_n} + \frac{3\cos(kR_n)}{(kR_n)^2} - \frac{12\sin(kR_n)}{(kR_n)^3} \right) \\
\quad - \frac{27\cos(kR_n)}{(kR_n)^4} + \frac{27\sin(kR_n)}{(kR_n)^5} 
\end{cases}, \quad (A1a)
\]

\[
v_1(k, R_n) = \begin{cases} 
15 \left( \frac{\cos(kR_n)}{(kR_n)^2} + \frac{5\sin(kR_n)}{(kR_n)^3} + \frac{12\cos(kR_n)}{(kR_n)^4} \right) \\
\quad - \frac{12\sin(kR_n)}{(kR_n)^5} 
\end{cases}, \quad (A1b)
\]

\[
v_2(k, R_n) = 15 \left( \frac{-\sin(kR_n)}{(kR_n)^3} - \frac{3\cos(kR_n)}{(kR_n)^4} + \frac{3\sin(kR_n)}{(kR_n)^5} \right). \quad (A1c)
\]

The \( F_1 \) and \( F_2 \) functions are defined in the same way as in Ref. [4], namely

\[
F_1(R_n, \theta_n, R_n', \theta_n'; k_1, k_2, k_3, k_4) = \frac{2J^2}{\varepsilon_0} f_{1122}, \quad (A2a)
\]

and

\[
F_2(R_n, \theta_n, R_n', \theta_n'; k_1, k_2, k_3, k_4) = \frac{2J^2}{\varepsilon_0} (f_{1111} - f_{1212} - f_{1122}), \quad (A2b)
\]

where

\[
f_{\sigma_1\sigma_2\sigma_3\sigma_4} = \sum_{m m'} W_{k_1k_2} (R_n, \theta_n) W_{k_4k_3} (R_{n'}, \theta_{n'}). \quad (A3)
\]

\( W \) gives the form of \( W \) in the rotated coordinate system (where the \( z \)-axis is perpendicular to the surface) given by

\[
W_{mm'} (R_n, \theta_n) = \delta_{m+\sigma, m'+\sigma'} \sum_{n n'} d_{nn'} (\theta_n) d^{(1/2)}_{\sigma\sigma'} (\theta_n)
\]

\[
\times W_{n'n'} (R_{n'}, \theta_{n'}) \cdot d_{nn'}^{(1/2)} (\theta_n) d^{(1/2)}_{\sigma\sigma'} (\theta_{n'}) \quad (A4)
\]

where the Wigner-formula for rotation matrices was used.

APPENDIX B

Here we perform the integrations with respect to \( R_n \) and \( R_{n'} \) in the first part of Eq. (11). Let us start with the integration with respect to \( R_n \), namely

\[
\hat{C}(k_1, k_2) := \frac{1}{a^d} \int dR_n R_n d(R_n^2 - d^2)
\]

\[
\times [3v_0(k_2, R_n)v_1(k_1, R_n) + 3v_0(k_1, R_n)v_1(k_2, R_n) - 2v_1(k_1, R_n)v_2(k_2, R_n) + 2v_1(k_1, R_n)v_2(k_2, R_n) - 8v_2(k_1, R_n)v_2(k_2, R_n)] \quad (B1)
\]

After substituting the \( v_m(k, R_n) \) matrix elements given by Eq. (A1) and introducing the dimensionless integration variable \( y = R_n/a \) and notations \( t_1 = k_1d \) and \( t_2 = k_2d \) we get

\[
\hat{C}(k_1, k_2) = C(k_1d, k_2d), \quad (B2)
\]

where

\[
C(t_1, t_2) = \frac{d^3}{a^3} \int \frac{dy}{y^2 - 1} \int dy \quad (B3)
\]

The occurring integrals with respect to \( y \) look like

\[
G_c(t, n) := \int_1^\infty \frac{y^2 - 1}{y^2} \cos[ty], \quad (B4a)
\]

and

\[
G_s(t, n) := \int_1^\infty \frac{y^2 - 1}{y^2} \sin[ty]. \quad (B4b)
\]
Evaluating the \( G_s \) and \( G_c \) functions analytically by using MATHEMATICA, we get
\[
C(t_1, t_2) = \frac{d^3}{dt^3} \left[ f_{c+}(t_1, t_2) \cos[t_1 + t_2] + f_{c-}(t_1, t_2) \sin[t_1 - t_2] + f_{s+}(t_1, t_2) \sin[t_1 + t_2] + (t_1 - t_2)^2 f_{s-}(t_1, t_2) \right] \text{Ci}[t_1 + t_2 - \text{Ci}[t_1 - t_2]],
\]
where for \( t_1 = t_2 = t \gg 1 \)
\[
f_{c+}(t, t) \approx \frac{3825}{4t^6}, \quad f_{c-}(t, t) \approx \frac{225}{2t^4}, \quad f_{s+}(t, t) \approx \frac{225}{2t^4}, \quad f_{s-}(t, t) \approx \frac{225}{2t^4}
\]
and \( \text{Ci}[t] = -\int \frac{\cos u}{u} du \) is the cosine integral function.

Let us consider now the integration with respect to \( R_n \) in the first part of Eq. (11):
\[
\tilde{D}(k_3, k_4) := \frac{1}{a^3} \int_0^d dR_n R_n^2 \times \left[ 3v_0(k_4, R_n)v_1(k_3, R_n') + 3v_3(k_3, R_n')v_1(k_4, R_n') + v_1(k_3, R_n')v_1(k_4, R_n') + 2v_1(k_3, R_n')v_2(k_4, R_n') + 2v_2(k_3, R_n')v_2(k_4, R_n') + 4v_2(k_3, R_n')v_2(k_4, R_n') \right]
\]
After substituting the \( v_m(k, R_n) \) matrix elements given by Eq. (\ref{eq:V_m}) and introducing the dimensionless integration variable \( y' = R_n/d \) and notations \( t_3 = k_3d, t_4 = k_4d \) and \( y_0 = R_0/d \) we get
\[
\tilde{D}(k_3, k_4) = D(k_3d, k_4d),
\]
where
\[
D(t_3, t_4) = \frac{d^3}{dt^3} \int_{y_0}^{1} dy' y'^2 \times \left[ D_{c+}(t_3, t_4, y') \cos[(t_3 + t_4)y'] + D_{c-}(t_3, t_4, y') \cos[(t_3 - t_4)y'] + D_{s+}(t_3, t_4, y') \sin[(t_3 + t_4)y'] + D_{s-}(t_3, t_4, y') \sin[(t_3 - t_4)y'] \right].
\]
The occurring integrals with respect to \( y' \) look like
\[
H_{c}(t, n) := \int_{y_0}^{1} dy' y'^2 \frac{\cos[(t_3 + t_4)y']}{y'^n}, \quad \text{and} \quad H_{s}(t, n) := \int_{y_0}^{1} dy' y'^2 \frac{\sin[(t_3 + t_4)y']}{y'^n}
\]
Evaluating the \( H_{s} \) and \( H_{c} \) functions analytically by using MATHEMATICA, we get
\[
D(t_3, t_4) = \frac{d^3}{dt^3} \left[ g_{c+}(t_3, t_4) \cos[t_3 + t_4] + g_{c-}(t_3, t_4) \cos[t_3 - t_4] + g_{s+}(t_3, t_4) \sin[t_3 + t_4] + g_{s-}(t_3, t_4) \sin[t_3 - t_4] + h_{c+}(t_3, t_4, y_0) \cos[(t_3 + t_4)y_0] + h_{c-}(t_3, t_4, y_0) \cos[(t_3 - t_4)y_0] + h_{s+}(t_3, t_4, y_0) \sin[(t_3 + t_4)y_0] + h_{s-}(t_3, t_4, y_0) \sin[(t_3 - t_4)y_0] \right],
\]
where for \( t_3 = t_4 = t \gg 1 \)
\[
g_{c+}(t, t) \approx \frac{225}{2t^4}, \quad g_{c-}(t, t) \approx \frac{1125}{2t^4}, \quad g_{s+}(t, t) \approx \frac{1125}{2t^4}, \quad g_{s-}(t, t) \approx \frac{1125}{2t^4}
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