Kinetic equations for the hopping transport and spin relaxation in random magnetic field.

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Abstract

We derive the kinetic equations for the hopping transport that take into account electron spin and the possibility of double occupation. In the Ohmic regime the equations are reduced to the generalized Miller-Abrahams resistor network. We apply these equations to the problem of the magnetic moment relaxation due to the interaction with the random hyperfine fields. It is shown that in a wide range of parameters the relaxation rate is governed by the hops with the similar rates as spin precession frequency. It is demonstrated that at the large time scale spin relaxation is non-exponential. We argue that the non-exponential relaxation of the magnetic moment is related to the spin of electrons in the slow-relaxing traps. Interestingly the traps can significantly influence the spin relaxation in the infinite conducting cluster at large times.

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I. INTRODUCTION

In recent years investigations of the spin phenomena in hopping transport have gone through a vigorous revival. In particular, the increasing interest to this problem is related to the discovery of a strong spin-valve effect in organic semiconductor devices\(^1, 2\). There is a consensus that the conductivity in these devices is determined by hopping polarons\(^3\). Such devices show a number of spin-related phenomena, including the spin-valve effect itself that are not understood. These experimental results were followed by a number of theoretical investigations of the hopping conduction \(^4, 5\) including fluctuations of conductivity \(^6, 7\) and most important the spin phenomena like magnetoresistance \(^8–12\) and the relaxation of magnetic moment\(^13–15, 18, 19\).

Most of these theoretical studies are based on semi-qualitative concepts with the lack of solid theoretical proof. Although in some cases (for example in the case of strong Coulomb interaction) the self consistent theory of hopping transport does not exist, there is a way to make theory of hopping transport self consistent. This theory is described in Ref.\(^20\). Up to now the theory includes the electron spin only in the limit of the small electron density\(^21–23\).

Here we develop the generalization of this theory to include spin and arbitrary probability of the site occupation (with possible double occupation). We argue that the self consistent theory of hopping transport is necessary in order to test the semi-qualitative concepts\(^8–10\) and to understand the electron and the spin transport in organic semiconductors.

Our starting point is the general Hamiltonian that describe a system of localized sites with the possibility of hopping due to electron-phonon interaction. Then we derive general kinetic equations that describe both the charge and the spin transport in hopping media. We argue that these equations are a useful tool to study hopping transport phenomena.

In the present paper we apply these kinetic equations to the problem of the spin relaxation due to random on-site magnetic fields in a system with the positional disorder. The understanding of the spin relaxation is clearly important for the theory of the spin-related transport phenomena like spin-valve magnetoresistance. Up to now the most studied mechanism of the spin relaxation in hopping transport is the spin-orbit interaction. The theory of this relaxation mechanism is discussed in Refs.\(^13–15\). In Ref.\(^13\) the basic understanding of spin relaxation for the hopping transport due to spin-orbit interaction was formulated.
In Ref. [14] the results of [13] were significantly expanded. It was pointed out [14] that exponentially broad distribution of hopping rates plays determinant role in the relaxation. However this distribution was considered semi-quantitatively. In Ref. [15] it was proposed that in the case of hopping conduction the spin relaxation due to the spin-orbit interaction may be significantly enhanced by the exchange interaction.

While the spin-orbit interaction is supposed to dominate the spin relaxation in non-organic semiconductors with hopping conductivity the situation in the organic materials may be different. In organic semiconductors the spin-orbit interaction is substantially suppressed [16] and another mechanisms like hyperfine interaction can govern the spin relaxation. The theoretical description of this mechanisms is different because the spin-orbit interaction does not affect the spin of a localized electron and manifest itself only in the spin rotation during the hop. On the other hand the hyperfine interaction leads to the appearance of random effective on-site magnetic fields that rotate electron spins even without hops. Note that in the organic spin-valve devices there is the another source of random fields unique to these case. The finite roughness of the contacts leads to a leakage of the magnetic field from the ferromagnetic contacts to the organic layer [17]. This fringe magnetic field can be a source of additional mechanism of the spin relaxation. In terms of theoretical description it is added to the hyperfine field and also rotate spins on the localized sites.

Recently Harmon and Flatte [18, 19] proposed an interesting approach to the spin relaxation based on the waiting time distribution. They considered both the spin-orbit and the hyperfine relaxation mechanisms. However their approach does not take into account the Pauli principle and is applicable only to the limit of the small electron concentrations. Also Refs. [18, 19] consider only the energy disorder and the positional disorder was neglected.

The derived kinetic equations allow us to describe spin relaxation with any site occupation probability. In the present work we apply them to the problem with the positional disorder and neglect the energy disorder. We show that even in this case there are several phenomena in the spin relaxation that were not discussed previously. Most important of them is perhaps the non-homogeneous character of the spin relaxation. In some cases the relaxation of spin of the electrons important for conduction is substantially different from the relaxation of the average spin of the system.

The paper is organized as follows. In section II we discuss the usual way of describing hopping conduction and its justification in terms of kinetic equations. In section III we
generalize approach \cite{20} to include electron spin and derive general form of kinetic equation. In section III B we linearize the kinetic equations and derive generalized version of Miller-Abrahams resistor network. Finally in section IV we use the kinetic equations to describe the spin relaxation in the hopping conduction regime.

II. KINETIC EQUATIONS FOR HOPPING TRANSPORT

The usual approach to the theoretical description of the hopping transport starts with the introduction of the hopping rates between pairs of sites \cite{24}. The hopping rate from site \( i \) to site \( j \) is defined as

\[
\Gamma_{ij} \propto |I_{ij}|^2 f^{(i)}(1 - f^{(j)}) P_{ph}(\Delta E_{ij}).
\] (1)

Here \( I_{ij} \propto \exp(-r_{ij}/a) \) is the overlap integral between sites \( i \) and \( j \), \( r_{ij} \) is the distance between these sites, \( a \) is the localization radius. \( f^{(i)} \) and \( f^{(j)} \) are the occupation probabilities of sites \( i \) and \( j \). \( \Delta E_{ij} \) is the difference of energies of states \( i \) and \( j \). \( P_{ph}(\Delta E_{ij}) \) is the part of hopping rate related to the number of phonons, involved in the hopping. It is equal to \( N_{ph} + 1 \) when \( \Delta E_{ij} > 0 \), i.e., when the hopping occurs with the phonon emission and to \( N_{ph} \) otherwise. Here \( N_{ph} \) is the number of phonons with energy \( |\Delta E_{ij}| \).

Then the current between sites \( i \) and \( j \) is introduced as

\[
J_{ij} = -e(\Gamma_{ij} - \Gamma_{ji}).
\] (2)

\( J_{ij} = 0 \) when the external electric field is absent. In a weak electric field the current follows the Ohm law \( J_{ij} = U_{ij}/R_{ij} \) with the resistance

\[
R_{ij} = \frac{k_B T}{e^2 \Gamma_{ij}(0)},
\] (3)

where \( \Gamma_{ij}(0) \) is the hopping rate between sites \( i \) and \( j \) without the external field, \( k_B \) is the Boltzmann constant.

As a result the real system with the hopping conductivity is replaced by a network of classical resistors. This network can be treated with percolative methods. In this case one finds the threshold resistance that allows the percolation to the macroscopic distances. In the case when the distribution of resistances \( R_{ij} \) is exponentially broad, this threshold resistance governs the conductivity of the whole system.
Without Coulomb interaction this approach can be consistently derived in terms of kinetic equations\textsuperscript{20}. It is the starting point of many theoretical studies and works quite well in many cases. However it has some problem when the hopping conductance becomes dependent on the electron spin. Naturally there is no spin in the equations\textsuperscript{11 -3} and therefore the spin should be artificially introduced in the discussed scheme.

There are two contradicting ways of introducing of the spin variables in this scheme. In the first way we look at the instantaneous orientation of the electron spins and write the expressions for the resistors and consider the percolation taking into account these orientations. The second way is to consider all possible orientations of the spin on the given site and average the expression for the resistor over these orientations and only then calculate the percolation. Every theory that considers the spin phenomena within this classical framework of hopping conductivity necessarily uses one of these two ways of the spin inclusion (or, maybe, some combination of these ways) either implicitly or explicitly.

Let us for example discuss the results of Refs.\textsuperscript{8-10}. In this theory the hopping system with the small Hubbard energy $U << k_B T$ is discussed. As a result the double occupancy of every site is possible. It was noted that an electron can hop to a site that is already occupied only when its spin is antiparallel to the spin of the electron on the destination site. When the spin relaxation is absent, the authors relate the conductivity of the system to a minimal distance the electron should travel to connect the percolation network. This minimal distance corresponds to the percolation parameter $\xi_c$ from\textsuperscript{24} when the site energies do not contribute to the resistances. This minimal distance is larger than it could be for the system where electron can tunnel to any site. It is the implicit application of the first way to include spin - the percolation was calculated with the momentary spin projections. It means that the resistances that correspond to the pairs of sites that at the given moment have electrons with the same spin direction were efficiently set to be infinite.

In the presence of the spin relaxation the authors compared the relaxation time with the time of hopping. If the relaxation is faster than the characteristic hopping time, then hops to any single occupied sites are allowed. Therefore the authors apply the first way to treat spin when spin relaxation is slow (i.e. they considered percolation for given directions of electron spins) and the second way when it is fast. The difference between the results obtained with these two approaches yielded the dependence of the system conductivity on the spin relaxation time. However, the authors of Refs.\textsuperscript{8-10} do not provide any justification
for this procedure.

To understand how to include spin into the theory of the hopping transport correctly let us consider the procedure of the consistent derivation of the approach \[^{[1]}\]. This procedure is described by Bottger and Bryksin \[^{[20]}\], however we remake it here in a slightly different way to make its generalization easier.

We start with the hopping Hamiltonian after polaron transformation, which is well known in the polaron transport theory \[^{[20]}\].

\[
H = H_0 + H_{\text{hop}}, \quad H_0 = \sum_i (\varepsilon_i - E_p) a_i^+ a_i + \sum_q \hbar \omega_q \left(b_q^+ b_q + \frac{1}{2}\right), \\
H_{\text{hop}} = \sum_{ij} t_{ij} a_i^+ a_j \Phi_{i,j}.
\]

Here \( a_i \) is the electron annihilation operator on site \( i \), \( b_q \) is the annihilation operator for a phonon with the wave-vector \( q \) and with frequency \( \omega_q \). We take into account an energy disorder therefore each site has a random energy \( \varepsilon_i \). \( t_{ij} \) are the overlap integrals between the sites. \( t_{ij} \) are much smaller than the differences in random energies \( \varepsilon_i - \varepsilon_j \). \( M_q \) is the electron-phonon interaction matrix element \( M_q = M^*_q \). \( r_i \) is the position of the site \( i \), \( E_p = \sum_q |M_q|^2/\hbar \omega_q \) is the polaron binding energy.

The conventional derivation of the kinetic equation \[^{[25]}\] starts with the full description of the system (with Liouville equations if the system is classical or with Hamiltonian if the system is quantum). Then the system is divided into the parts that interact weakly or rarely. We divide the system into the set of noninteracting sites, described by the Hamiltonian \( H_0 \), and weak interaction of different sites, described by the Hamiltonian \( H_{\text{hop}} \). In order to describe the system with the set of kinetic equation we have to assume that the eigenstates of the Hamiltonian \( H_0 \) are well defined and therefore \( H_{\text{hop}} \) is much smaller than \( H_0 \).

In zero order over \( H_{\text{hop}} \) the full density matrix of the system is diagonal in terms of electron filling numbers \( n_i \). The theory of hopping conduction near Fermi level (that we are interested in) is based on the Hartree-Fock decoupling for the density matrix \[^{[20]}\]. With this decoupling the full density matrix can be expanded as a product of the single site density matrices.

\[
\rho_{n_1,n_2,\ldots,n_N} = \rho_{n_1}^{n_1(1)} \cdot \rho_{n_2}^{n_2(2)} \cdot \ldots \cdot \rho_{n_N}^{n_N(N)}. 
\]
Here we used the basis of the filling numbers. The set of the system states that has definite filling numbers $n_i$ is the complete set of states of the system. As usual the density matrix has two indexes each of them corresponding to one of the states of the complete set. The upper indexes in round brackets correspond to a number of site.

The single site density matrix $\rho_{n_i}^{n_i(i)}$ has only two indexes $n_i = 0, 1$ that are the possible filling numbers of site $i$. Without $H_{\text{hop}}$ this matrix is defined as:

$$
\rho^{(i)} = \begin{pmatrix} f^{(i)} & 0 \\ 0 & 1 - f^{(i)} \end{pmatrix},
$$

(6)

where $f^{(i)}$ is the probability for site $i$ to have an electron.

Here we will use the interaction representation, therefore $\rho_{n_i}^{n_i(i)}$ does not depend on time without perturbation. In the first perturbation order we obtain

$$
\frac{d\rho^{(i)}}{dt} = \frac{1}{i\hbar} \sum_j \text{Tr}_j \left[ (\tilde{H}_{\text{hop}})_{ij}, \rho^{(ij)} \right], \quad \rho^{(ij)} = \rho^{(i)}\rho^{(j)} + d^{(ij)}.
$$

(7)

Here $(\tilde{H}_{\text{hop}})_{ij}$ is the part of $H_{\text{hop}}$ corresponding to the hops between sites $i$ and $j$ in the interaction representation. $\rho^{(ij)}$ is the two-site density matrix. We divide $\rho^{(ij)}$ into the product of the one-site density matrices and a small off-diagonal (in terms of electron filling numbers) correlated part $d^{(ij)} \propto H_{\text{hop}}$. The contribution of the product $\rho^{(i)}\rho^{(j)}$ corresponds to the mean-field correction to the energy $\varepsilon_i$ and is usually neglected. The time evolution of $\rho^{(i)}$ is governed by the off-diagonal part $d^{(ij)}$.

To obtain the equation for $d^{(ij)}$ one should write the equation for the two site density matrix

$$
\frac{d\rho^{(ij)}}{dt} = \frac{1}{i\hbar} \left[ (\tilde{H}_{\text{hop}})_{ij}, \rho^{(ij)} \right] + \frac{1}{i\hbar} \sum_k \text{Tr}_k \left[ (\tilde{H}_{\text{hop}})_{ik} + (\tilde{H}_{\text{hop}})_{kj}, \rho^{(ijk)} \right].
$$

(8)

Note that $d^{(ij)}$ enters equation (7) with the coefficient $\propto H_{\text{hop}}$. The right hand side of Eq.(8) also contains $H_{\text{hop}}$. Here we neglect all powers of $H_{\text{hop}}$ higher than 2. Therefore we replace all many-site density matrices by the products of the one-site density matrices in the right hand side of Eq.(8). As a result we obtain the expression for $d^{(ij)}(t)$:

$$
d^{(ij)}(t) = \frac{1}{i\hbar} \int_{-\infty}^{t} \left[ (\tilde{H}_{\text{hop}})_{ij}(t'), \rho^{(i)}(t')\rho^{(j)}(t') \right] dt'.
$$

(9)

To get the kinetic equation we assume that the correlated part $d^{(ij)}(t)$ decays much faster in comparison with the time scale on which the one-particle density matrix changes. Therefore
the one-site density matrices are out of the integral in Eq. (9). This assumption allows to get the final equation for the one-site density matrix:

$$\frac{d\rho^{(i)}}{dt} = -\frac{1}{\hbar^2} \sum_j \left\langle \text{Tr}_j \left[ (\tilde{H}_{\text{hop}})^{(i)}(t), \left[ \int_{-\infty}^t (\tilde{H}_{\text{hop}})^{(i)}(t')dt', \rho^{(i)}(t) \rho^{(j)}(t) \right] \right] \right\rangle_{ph}.$$ (10)

$H_{\text{hop}}$ contains not only electron but also phonon operators. Therefore we should average the right-hand side of this equation over phonons. Substituting Eqs. (4) and (6) into (10) we obtain the following result:

$$\frac{df^{(i)}}{dt} = \sum_j W_{ji} f^{(j)}(1 - f^{(i)}) - W_{ij} f^{(i)}(1 - f^{(j)}),$$ (11)

where the hopping rate in the limit $M_q/\hbar \omega_q \ll 1$ has the form:

$$W_{ji} = \frac{2\pi}{\hbar} \sum_q \frac{t_{ji}^2}{\hbar^2 \omega_q^2} |M_q|^2 |e^{i q r_i} - e^{i q r_j}|^2 \left[ (N_{ph} + 1) \delta(\varepsilon_i - \varepsilon_j + \hbar \omega_q) + N_{ph} \delta(\varepsilon_i - \varepsilon_j - \hbar \omega_q) \right].$$ (12)

The hoping rates in the limit of $M_q/\hbar \omega_q \geq 1$ are derived in [20].

It is the kinetic equation for the spinless electrons. In order to derive the dc current one should consider the steady state solutions of these equations $df_i/dt = 0$ and then introduce a small electric field. As a result the equation yields the standard formula for the current (2) where $\Gamma_{ij} = W_{ij} f^{(i)}(1 - f^{(j)})$.

Let us discuss the applicability conditions of the kinetic equation. First of all it relies on the smallness of the intersite correlations $d^{(ij)}$. In the discussed problem they are small if $H_{\text{hop}}/\Delta \varepsilon_i \ll 1$. Real systems, however can have other sources of these correlations. The most known of them is the Coulomb interaction. The problem of the Coulomb interaction in hopping conductivity is rather long-standing. If the Coulomb interaction between neighboring sites is comparable with the random energies, the correlations can appear even without $H_{\text{hop}}$. In that case the applicability of the kinetic equation becomes questionable even in the spinless case. The standard answer for this problem is that the kinetic equation is still applicable but the density of single electron states should be considered taking into account the Coulomb interaction. It leads to the formation of the Coulomb gap near Fermi level. Equation (11) with the Coulomb gap was successfully used in a number of studies in the past, however the other consequences of Coulomb interaction are still under discussion.

Another important simplification is neglecting of all the high-order terms of $H_{\text{hop}}/\varepsilon_i$. It is known that these higher order terms may lead to the phenomena that are important for
the hopping conductivity. One of these phenomena is the exchange interaction. Recently in Refs. [15, 26] it was argued that exchange effects may be important for the spin relaxation and the spin transport. Another example is the sub-barrier scattering that is responsible for the linear negative magnetoresistance in semiconductors with the variable-range hopping conductivity [27]. Although these phenomena are important, we believe that it is more important to understand low-order physics before consider these high-order phenomena.

III. KINETIC EQUATION WITH SPIN AND POSSIBILITY OF DOUBLE OC-

CUPATION

Up to this moment our results repeat the traditional scheme [24], at least when dc current is under consideration. The advantage of our approach is that it may be easily generalized for the case when electrons have spins and can double occupy a site.

Equation (10) does not depend on the exact structure of the one site density matrix corresponding to spinless electrons. It relies only on the kinetic equation assumptions that are valid in general case. Therefore in order to generalize our theory we have to include spin into the Hamiltonian, define the structure of one-site density matrix in general case, and perform the calculations that are analogous to the derivation of Eq.(11).

Here we consider the case when the electron spin conserves during the hopping (the under-barrier spin rotation is discussed in section III A). However we include small on-site spin Hamiltonian $H_S$ that describes rotation of the spin over the effective local magnetic field.

$$H = H_0 + H_S + H_{hop}.$$  \hspace{1cm} (13)

$$H_0 = \sum_{i,s} \varepsilon_i a_i^+ a_i s + \sum_i U a_i^+ a_i^+ a_i^+ a_i^-; \quad H_S = \sum_i H_{S,i}$$

Here $s$ is the spin index that can have two values “+” and “−”. $U$ is the Hubbard energy. $H_{S,i}$ acts only on electrons on site $i$ and conserve the filling number of this site, i.e., it can only rotate the spin on a single-occupied site.

$$H_{hop} = \sum_{ij,s} t_{ij} a_i^+ a_j s \hat{\Phi}_{i,j},$$  \hspace{1cm} (14)

where $\hat{\Phi}_{i,j}$ is defined after Eq.(4). The hopping part of the Hamiltonian (14) conserves the spin.
The one-site density matrix in the representation of filling numbers \( \rho_{i',i'} \) now contains four indexes and have 16 matrix elements. We however will use another representation in this section. The complete set of states for one site with possibility of double occupation has four states that can be selected as

\[
|0\rangle, |+\rangle, |−\rangle, |2\rangle.
\] (15)

Here \(|0\rangle\) is the empty site, \(|2\rangle\) is the double occupied site, \(|+\rangle\) and \(|−\rangle\) are the states of the site when it has one electron with spin up and down respectively. So one can write one-site density matrix with only two indexes, each of them can have any of four values described in (15).

In zeroth order over \( H_{\text{hop}} \) we have only matrix elements of the one-site density matrix that conserve the filling number. For the spinless electrons there were only two such elements. Now we have six of them.

\[
\rho_0^0, \rho_+^+, \rho_+^-, \rho_-^+, \rho_-^-, \rho_2^2.
\] (16)

Only these 6 matrix elements appear in the kinetic equation.

Along with the density matrix elements (16) it is sometimes useful to consider another set of 6 numbers, that are linear combinations of the matrix elements (16), in order to describe the state of the site. These numbers allow us to track directly the occupation number and the mean value of the magnetic moment of the site. The transition to these numbers was proposed by Bryksin (without double occupation probability)[28].

\[
f_0 = \rho_0^0, \quad f_1 = \rho_+^+ + \rho_-^-,
M_z = \rho_+^+ - \rho_-^-, \quad M_x = \rho_-^+ + \rho_+^-,
M_y = -i(\rho_+^+ - i\rho_-^-), \quad f_2 = \rho_2^2.
\] (17)

Here \( f_0, f_1 \) and \( f_2 \) are the probabilities for a site to have 0, 1 and 2 electrons respectively. \( M_\alpha \) is the mean magnetic moment of the site in the direction \( \alpha \).

The generalized equation (10) in these notations has the following form:

\[
\frac{d\rho_x^{(i)}}{dt} - S_{xy}(i)\rho_y^{(i)} = \sum_j W_{xyz}(ij)\rho_y^{(i)}\rho_z^{(j)}.
\] (18)

Here \( x, y \) and \( z \) have 6 possible values, \( \rho_x \) correspond to some filling number probabilities or mean projections of magnetic moment defined in (17). The term \( S_{xy}(i)\rho_y^{(i)} \) corresponds to
the action of the spin part of the Hamiltonian $H_S$. For the Hamiltonian $H_S$ corresponding to a local magnetic field $H^{(i)}$ we have

$$S_{M_\alpha M_\beta} = \frac{\mu_b g}{\hbar} \epsilon_{\alpha\beta\gamma} H^{(i)}_\gamma = \epsilon_{\alpha\beta\gamma} \mathcal{H}^{(i)}_\gamma.$$ 

Here $\epsilon_{\alpha\beta\gamma}$ is Levi-Civita symbol, $\mu_b$ is the Bhor magneton and $g$ is the g-factor. It correspond to the precession of the local magnetic moment $dM(i)/dt = (\mu_b g/\hbar) [M(i), H(i)]$. We also introduced here a renormalized local magnetic field measured in units of frequency $\mathcal{H}^{(i)} = (\mu_b g/\hbar)H^{(i)}$.

The important assumption related to eq. (18) is that the on-site Hamiltonian can be treated independently from $H_{hop}$. It is valid when $H_S \delta t_{Mark} / \hbar \ll 1$, where $\delta t_{Mark}$ is the characteristic decay time of the correlation $d_{ij}$. (In the opposite limit the kinetic equation becomes non-Markovian).

Let us note that time integral in (9) oscillate with frequency $\varepsilon_i - \varepsilon_j$ so the kinetic equation is of Markovian type when $H_S \ll |\varepsilon_i - \varepsilon_j|$. For larger magnetic fields the kinetic equations in the present form are valid only when the site magnetization is oriented along the local magnetic field (in that case $H_S$ does not lead to the magnetization precession). In that case the site energies in the equation should include the Zeeman energy.

The term $W_{xyz}(ij)\rho^i_x \rho^j_z$ is the “collision integral”

$$- \frac{1}{\hbar^2} \left\langle \text{Tr} \left[ (\mathcal{H}_{hop})_{ij}(t), \left[ \int_{-\infty}^t (\mathcal{H}_{hop})_{ij}(t')dt', \rho^{(i)}(t)\rho^{(j)}(t) \right] \right] \right\rangle_{ph}$$

represented in the notations (17). Each of the indexes $x, y$ and $z$ can have 6 different values, so there are $6^3$ matrix elements $W_{xyz}$ and their calculation is rather cumbersome. Using the trick described in the Appendix we derive the following set of kinetic equations:

$$\frac{df^{(i)}_0}{dt} = \sum_{j \neq i} W_{ij} f^{(i)}_1 f^{(j)}_0 + \frac{W^{-U}}{2} \left[ f^{(i)}_1 f^{(j)}_0 - M^{(i)}_\alpha M^{(j)}_\alpha \right] - W_{ji} f^{(i)}_0 f^{(j)}_1 - 2W_{ji}^{+U} f^{(i)}_0 f^{(j)}_2.$$ 

$$\frac{df^{(i)}_1}{dt} = \sum_{j \neq i} W_{ij} f^{(j)}_1 f^{(i)}_0 + 2W_{ji}^{+U} f^{(j)}_2 f^{(i)}_0 + W_{ij} f^{(i)}_2 f^{(j)}_1 + 2W_{ji}^{+U} f^{(i)}_2 f^{(j)}_0 - \frac{W^{-U}}{2} \left[ f^{(i)}_1 f^{(j)}_0 - M^{(i)}_\alpha M^{(j)}_\alpha \right] - W_{ji} f^{(i)}_0 f^{(j)}_1 - W_{ji}^{+U} f^{(i)}_0 f^{(j)}_2.$$ 

$$\frac{dM^{(i)}_\alpha}{dt} + \epsilon_{\alpha\beta\gamma} M^{(i)}_\beta \mathcal{H}^{(i)}_\gamma = \sum_{j \neq i} W_{ji} M^{(j)}_\alpha f^{(i)}_0 + W_{ij} M^{(j)}_\alpha f^{(i)}_2 +$$

$$\left(\frac{d}{dt}M^{(i)}_\alpha \right)_{\alpha \beta \gamma}. \text{We also have}$$

$$S_{M_\alpha M_\beta} = \frac{\mu_b g}{\hbar} \epsilon_{\alpha\beta\gamma} H^{(i)}_\gamma = \epsilon_{\alpha\beta\gamma} \mathcal{H}^{(i)}_\gamma.$$
Here we have introduced the hopping rates $W_{ij}^U$ and $W_{ij}^{-U}$. One can note that $W_{ij}$ defined in (12) depends on the energy difference $\varepsilon_i - \varepsilon_j$. However if one of the initial and the final state of the hop corresponds to the upper Hubbard band, the actual energy $\varepsilon_i + U_h$ or $\varepsilon_j + U_h$ should be used. Therefore $W_{ij}^+ U$ is the hopping rate $W_{ij}$ where $\varepsilon_i$ is substituted by $\varepsilon_i + U_h$ and $W_{ij}^- U$ is $W_{ij}$ with $\varepsilon_j$ substituted with $\varepsilon_j + U_h$.

\section{Spin-orbit couplings}

The kinetic equations Eqs. (20-23) were derived with the approximation that the electron spin is conserved during the hop. This approximation is not sufficient when the spin-orbit interaction is essential for the kinetics. Although we do not want to discuss the role of the spin-orbit interaction in details we briefly outline the procedure of the inclusion of the spin-orbit interaction in the kinetic equations in this section.

The possibility of inclusion of the spin-orbit interaction into kinetic equation for hopping conductivity was discussed in [21–23], where corresponding kinetic equations were derived in the limit of low occupation numbers. The spin-orbit interaction leads to a precession of the electron spin during the under-barrier motion. It is important that for a given pair of sites $i$ and $j$ the angle of precision is not random (at least when the distance between sites is greater than the localization length). Therefore the spin orbit interaction can be described with rotation matrixes $D^{ij}_{\alpha\beta}$. If the electron on site $i$ has momentum expectations $M_\alpha$ (where index $\alpha$ stands for the cartesian coordinates), then after the tunneling to site $j$ the expectation value of the magnetic moment is $\sum_\beta D^{ij}_{\alpha\beta} M_\beta$. This rotation matrix should be defined for every pair of sites $D^{ij}_{\alpha\beta} = (D^{ji}_{\alpha\beta})^{-1}$.

To include rotation matrixes into kinetic equations (20-23), one should make a substitution

\begin{equation}
M_\alpha^{(j)} \rightarrow D^{ji}_{\alpha\beta} M_\beta^{(j)}
\end{equation}
in all kinetic equations Eqs. (20-23). On the other hand projections $M^{(i)}_{\alpha}$ should be unchanged.

B. Generalized resistance network

When the linear response of a hopping system to a small applied dc voltage is considered the kinetic equations can be reduced to a resistor network. In this section we show how this network is generalized when the electron spin and the Hubbard energy are taken into account.

The reduction to the resistor network depends on the possibility to introduce quantities that change slowly in space. Note that probabilities $f_i$ and magnetic moments $M^{(i)}_{\alpha}$ differ significantly from site to site even in the equilibrium in the case of the broad distribution of random energies.

In the case when the directions of magnetizations on all the sites are the same one can introduce chemical potentials for spin up and spin down electrons $\mu_{\uparrow}$ and $\mu_{\downarrow}$. The occupation probabilities should be expressed as functions of these chemical potentials.

$$f^{(i)}_{0} = \frac{1}{Z_i}, \quad \rho_+^{(i)} = \frac{\exp{-\epsilon_i + \mu_{\uparrow}^{(i)}}}{Z_i}, \quad \rho_-^{(i)} = \frac{\exp{-\epsilon_i + \mu_{\downarrow}^{(i)}}}{Z_i}, \quad f^{(i)}_{2} = \frac{\exp{-2\epsilon_i - U_h + \mu_{\uparrow}^{(i)} + \mu_{\downarrow}^{(i)}}}{Z_i}. \quad (25)$$

where $Z_i$ is the statistical sum on site $i$

$$Z_i = 1 + \exp{-\epsilon_i + \mu_{\uparrow}^{(i)}} + \exp{-\epsilon_i + \mu_{\downarrow}^{(i)}} + \exp{-2\epsilon_i - U_h + \mu_{\uparrow}^{(i)} + \mu_{\downarrow}^{(i)}}. \quad (26)$$

Here we assume that the magnetization of all sites is directed along z axis, therefore $\rho_-^{(i)} = \rho_+^{(i)} = 0$. $f^{(i)}$ and $M_{\alpha}^{(i)}$ are expressed in terms of $\rho_+^{(i)}$ and $\rho_-^{(i)}$ according to Eq. (17).

It is easy to check by the direct substitution that when chemical potentials are the same in all sites $\mu_{\uparrow} = \mu_{\downarrow} = \mu$ the system is in the equilibrium for any on-site random energies $\epsilon_i$ and all time derivatives in the kinetic equations are zero.

It is useful to have expressions for the spin up and the spin down currents. The spin up current between sites $i$ and $j$ is given by the formula:

$$J_{ij}^{\uparrow} = -e(\Gamma_{ij}^{\uparrow} - \Gamma_{ji}^{\uparrow}), \quad (27)$$

Here $\Gamma_{ij}^{\uparrow}$ is the hopping rate for the spin up electrons from site $i$ to the site $j$.

$$\Gamma_{ij}^{\uparrow} = W_{ij}f^{(i)}_0 f^{(j)}_0 + W_{ij}^{+\downarrow} f^{(i)}_2 f^{(j)}_0 + W_{ij} f^{(i)}_2 f^{(j)}_2 + W_{ij}^{\downarrow\uparrow} f^{(i)}_0 f^{(j)}_0. \quad (28)$$
To get this expression from the kinetic equations one should consider the time derivative of the probability \( P_i^+ \) to have an electron with the spin up on site \( i \). Note that a double occupied site contains electron with spin up and thus \( P_i^+ = \rho_i^+(i) + f_2^i \). Direct calculation yields:

\[
- e \frac{dP_i^+}{dt} = \sum_j J_{ji}^+
\]

with Eq.(27) for the currents \( J_{ji}^+ \). The expression for spin down current can be obtained from (27) and (28) by replacing index + with −.

The current appears when the system is placed in the electric field or when there is a shift of the chemical potential. Expanding the kinetic equation over the small electrostatic potential \( \Delta \varphi_i \) and the small shift of the chemical potentials \( \Delta \mu_i^\pm \) we obtain:

\[
J_{ij}^+ = R_{ij}^{-1}(\Delta \varphi_{ij} - \Delta \mu_{ij}^+/e)
\]

where \( \Delta \mu_{ij}^+ = \mu_i^+ - \mu_j^+ \), \( \Delta \varphi_{ij} = \varphi_i - \varphi_j \) and \( R_{ij}^{-1} \) is the effective resistance of the pair of sites \( ij \). It contains four contributions.

\[
R_{ij} = \left[ \frac{k_B T}{e^2 \Gamma_{ij,AA}^+} + \frac{k_B T}{e^2 \Gamma_{ij,AB}^+} + \frac{k_B T}{e^2 \Gamma_{ij,BA}^+} + \frac{k_B T}{e^2 \Gamma_{ij,BB}^+} \right]^{-1}
\]

where \( \Gamma_{ij}^+ \) with additional indexes \( A \) and \( B \) are the contributions to \( \Gamma_{ij}^+ \)

\[
\Gamma_{ij,AA}^+ = W_{ij} f_i^i f_f^j, \quad \Gamma_{ij,AB}^+ = W_{ij}^{-U} f_i^i f_f^j, \quad \Gamma_{ij,BA}^+ = W_{ij}^+ f_i^i f_f^j, \quad \Gamma_{ij,BB}^+ = W_{ij} f_i^i f_f^j.
\]

The additional upper index (0) in (31) means that values \( \Gamma \) are calculated for \( \Delta \varphi_{ij} = 0 \) and \( \Delta \mu_{ij} = 0 \).

The physical meaning of different contributions to \( \Gamma \) becomes apparent when one considers large Hubbard energy \( U \gg k_B T \). Note that in order to contribute to hopping conductivity a site should have the energy level close to the chemical potential. In this case the sites that take part in conductivity are divided into two groups [30]: A-sites that have \( \varepsilon_i \sim \mu \) and B-sites with \( \varepsilon_i + U \sim \mu \). A-sites are practically never double-occupied so for these sites \( f_2 \approx 0 \). For B-sites \( f_0 \approx 0 \), these sites never have zero electrons. For this model only one contribution to \( R_{ij} \) is important for each pair of sites. For example if the site \( i \) is of type A and the site \( j \) is of type B, the resistance \( R_{ij} \) for this pair is

\[
R_{ij} \approx R_{ij,AB} = \frac{k_B T}{e^2 \Gamma_{ij,AB}^+}.
\]
When the temperature is comparable to the Hubbard energy each site plays both roles: of A-type and B-type. The corresponding resistances appear to be connected in parallel.

When magnetization is not restricted to one axis, the problem of slowly changing quantities becomes slightly more complex. In these case one can use chemical potentials $\mu_+ \text{ and } \mu_-$ where $+$ and $-$ refer to the spin projection on the local magnetization axis. They should be supplied by the angles $\varphi_m(r)$ and $\theta_m(r)$ that describe the direction of magnetization in the given point of space. The dependence of these angles on $r$ leads to the spin relaxation.

Finally let us note that although magnetization $M_i$ depends (even in the equilibrium) on random energies $\epsilon_i$, the relative magnetization $M_i = M_i / f_i$ is the function of the chemical potentials only.

$$M_i = \tanh \left( \frac{\mu^+_i - \mu^-_i}{k_B T} \right). \tag{32}$$

C. Singlet magnetoresistance

A new mechanism of singlet magnetoresistance was recently proposed in organic semiconductors\[8–10\]. This mechanism is based on the fact that two electrons with the same spin cannot occupy the same site even in the case of small Hubbard energy. In Ref.\[8–10\] it was stated that when the spin relaxation time is longer than the hopping time, in order to hop the electron should find the site which is either free or have an electron with opposite spin direction. This makes the characteristic hop longer than in the case of the fast spin relaxation. In the latter case the electron have enough of time to wait for correct spin polarizations and make a hop to any single-occupied site. These arguments lead to the strong magnetoresistance even in the weak magnetic fields where Zeeman energy is less than temperature.

The arguments used in Ref.\[8–10\] effectively correspond to the case when the percolation threshold is calculated for the instantaneous state of electrons. The model used in Ref.\[8–10\] does not include Coulomb interaction and any of the higher order terms (exchange interaction or under-barrier scattering). Therefore the kinetic equations Eqs.\[20\,23\] should be applicable to this case. We have shown that the correct procedure is to consider averaged on-site density matrix and only then calculate the parameters of percolation like the characteristic hopping length. As a result the magnetic field can affect the effective resistances only via magnetization $M_i$ (at least for the case of small dc current when resistor network
approximation is applicable). When Zeeman energy can be neglected in comparison with temperature, the on-site magnetization is absent $M_i = 0$. In this case the spin relaxation time does not contribute to the expression for the resistances and does not have any effect on the resulting conductivity.

The singlet magnetoresistance appear only when Zeeman energy becomes comparable with the temperature. In this case the stationary state have finite magnetization on each site aligned along the magnetic field. This on-site magnetization influences the resistor network in accordance with equation (31) and leads to the magnetoresistance.

However it is not a novel effect (at least for large Hubbard energy $U$). It is well known from semiconductor physics and was first reported in [29]. It is positive and a linear function of the magnetic field for $k_B T < E_Z < \xi_c k_B T$, where $\xi_c$ is the critical exponent of hopping conductivity and $E_Z = \mu_B gH$ is the Zeeman energy [30]. At higher fields $E_Z > \xi_c k_B T$ this magnetoresistance saturates. In the limit of the small magnetic fields $E_Z < k_B T$ it becomes quadratic $\propto (E_Z/k_B T)^2$ [31].

IV. SPIN RELAXATION DUE TO THE RANDOM FIELDS

In order to demonstrate that the kinetic equations Eqs. (20-23) are a useful tool to understand the physics of hopping conduction we apply them to the problem of spin relaxation in disordered semiconductors with the hopping transport.

We consider the simple case of neighbor hopping. It means that we assume the temperature to be larger than the width of the distribution of site energies $\varepsilon_i$. In this case the energy disorder can be neglected and the positional disorder define the distribution of hopping rates. We show that even in this simple case there is a number of novel effects that were not discussed previously. This effects are related to the exponentially broad distribution of the hopping rates.

Numerical studies of the hopping conduction usually consider a set of sites with random energies on a lattice. Thus the spatial disorder is totally ignored and only energy disorder is considered. It is usually believed that both types of disorder are equivalent. However this equivalence was never fully proved. Also at least one case is known when the spatial and the energy disorder lead to different results. It is the case of slow relaxation in systems with the hopping conduction and the strong Coulomb interaction [36]. It gives us additional reason
to focus on the positional disorder in the present paper.

We consider a set of identical sites that are randomly distributed in space with the hopping probability exponentially decaying with the distance between sites $r_{ij}$, $W_{ij} \propto W_0 \exp(-2r_{ij}/a)$, where $a$ is the localization radius. At each site there is a random hyperfine magnetic field $\vec{H}_i$ with the characteristic scale $\langle \mathcal{H} \rangle$. Initially the system is in the equilibrium. At $t = 0$ all sites obtain small magnetization $M_i$ aligned along $z$-axis. As far as it is small the relaxation of magnetic moments does not influence occupation probabilities $f_0, f_1, f_2$. The system is defined by two parameters: the conventional localization parameter $na^3$ and the ratio of the characteristic precession frequency in the hyperfine magnetic field to the hopping rates $\langle \mathcal{H} \rangle/W_0$. In the case of the variable range hopping conductivity (when the energy disorder is essential) one should also keep in mind the relation between the characteristic size of random energy, Hubbard energy and the temperature. These parameters however are out of the scope of our work.

Let us write the general equation for the spin relaxation

$$\frac{dM^{(i)}}{dt} + \epsilon_{\alpha\beta\gamma}M^{(i)}_\beta \mathcal{H}^{(i)}_\gamma = \sum_j \Upsilon_{ji}M^{(j)}_\alpha - \Upsilon_{ij}M^{(i)}_\alpha,$$

$$(33)$$

$$\Upsilon_{ij} = W_{ij}f_0^{(j)} + W_{ji}f_2^{(j)} + \frac{W_{ij}^U}{2}f_1^{(j)} + \frac{W_{ji}^U}{2}f_1^{(j)}.$$  

$$(34)$$

Here $\Upsilon_{ij}$ is the rate of spin transition from site $i$ to site $j$. Note that in general case $\Upsilon_{ij} \neq \Upsilon_{ji}$ even in equilibrium. It is related to the fact that different sites have different equilibrium probability $f_1$ to be single-occupied and thus different equilibrium magnetization. However in the considered problem the sites are equivalent and therefore the spin transfer rate is directly connected with the charge transfer rate

$$\Upsilon_{ij} = \Upsilon_{ji} \propto R_{ij}^{(-1)}.$$

A. Spin relaxation in a pair of sites.

The elementary source of the magnetic moment relaxation is a pair of sites with different local hyperfine magnetic fields. These sites are connected by the spin transition rate $\Upsilon$. The magnetization dynamics of these sites is described by the equations:

$$\frac{dM_1}{dt} + \vec{H}_1 \times M_1 = \Upsilon(M_2 - M_1),$$

$$(35)$$
Let us discuss the relaxation in the two limiting cases: when the precession frequency is larger than the tunneling rate $\mathcal{H}_{1,2} \gg \Upsilon$ and in the opposite limit $\mathcal{H}_{1,2} \ll \Upsilon$.

In the case of the strong magnetic field the moments precess around the local fields. The relaxation of their absolute values is governed by the tunneling rate $\Upsilon$. Let us assume that at $t = 0$, $|\mathbf{M}_1| = |\mathbf{M}_2| = M$. It is easy to show that relation $|\mathbf{M}_1| = |\mathbf{M}_2|$ holds during the relaxation. Therefore we may write only the equation for $\mathbf{M}$

\[
\frac{d\mathbf{M}}{dt} = -\Upsilon (1 - \cos(\angle \mathbf{M}_1 \mathbf{M}_2)) \mathbf{M}.
\]  

(36)

Here $\angle \mathbf{M}_1 \mathbf{M}_2$ is the angle between magnetic moments $\mathbf{M}_1$ and $\mathbf{M}_2$. In the case of fast precession it should be averaged over precession period. Assuming that $|\mathbf{H}_1| \neq |\mathbf{H}_2|$ yields:

\[
\frac{d\mathbf{M}}{dt} = -\Upsilon \left(1 - \frac{M_1|| M_2||}{M_1 M_2} \cos(\angle \mathbf{H}_1 \mathbf{H}_2)\right) \mathbf{M}.
\]  

(37)

Here $M_1|| (M_2||)$ is the component of magnetic moment $\mathbf{M}_1 (\mathbf{M}_2)$ aligned along the local field $\mathbf{H}_1 (\mathbf{H}_2)$.

The relaxation rate is zero for the case when both magnetic field and magnetic moments are aligned along the same axis and $\mathbf{M}_1 = \mathbf{M}_2$. In all other cases it is finite and proportional to $\Upsilon$.

In the opposite case $\Upsilon \gg \mathcal{H}$ in the initial relaxation phase $t \sim 1/\Upsilon$ the difference of magnetic moments $\mathbf{M}_1 - \mathbf{M}_2$ relaxes with the fast relaxation rate $\Upsilon$. After this phase of relaxation the moments are different only because of finite local fields and $\mathbf{M}_1 - \mathbf{M}_2 \propto \mathcal{H} / \Upsilon$. However the average magnetic moment $\mathbf{M}_+ = (\mathbf{M}_1 + \mathbf{M}_2) / 2$ cannot relax with the rate $\Upsilon$.

The equation for $\mathbf{M}_+$ up to the terms $\propto \mathcal{H}^2 / \Upsilon$ has the following form:

\[
\frac{d\mathbf{M}_+}{dt} + \mathbf{H}_+ \times \mathbf{M}_+ - \frac{1}{2\Upsilon} [\mathbf{H}_- \times [\mathbf{H}_- \times \mathbf{M}_+]] = 0.
\]  

(38)

Here $\mathbf{H}_\pm = (\mathbf{H}_1 \pm \mathbf{H}_2) / 2$.

The magnetic moment $\mathbf{M}_+$ precess around average magnetic field, as it can be seen from the second term of the equation. The third term gives a small alternation to this precession, but more importantly, it yields relaxation of the absolute value $M_+ = |\mathbf{M}_+|$.

\[
\frac{dM_+}{dt} = -\frac{\mathcal{H}^2}{2\Upsilon} \left(1 - \frac{(\mathbf{H}_- \cdot \mathbf{H}_+)^2 (\mathbf{H}_+ \cdot \mathbf{M}_+)^2}{\mathcal{H}_+^2 \mathcal{H}_-^2 \mathcal{H}_+^2 M_+^2}ight) M_+.
\]
The relaxation of the magnetic moment is proportional to $H^2/\Upsilon$. It is the motion suppression of relaxation well known from $[32]$, where it is related to the electron diffusion. Here we show that for considered problem the diffusion over macroscopic distances is not required for this suppression. It appears even when tunneling between two sites is considered.

### B. System without disorder

![Graph](image1.png)

**FIG. 1**: The relaxation of the magnetic moment of a hopping system without disorder. (a) The dependence of logarithm of $\langle|m|\rangle$ and $\langle m_z \rangle$ on time for different values of random magnetic field. (b) The dependence of relaxation rate on average on-site magnetic field.

A system with a large number of sites with low disorder can be characterized by some average spin transition rate $\Upsilon$. The spin relaxation in such a system is analogous to the spin relaxation in a pair of sites. For the case of fast hopping $\Upsilon \gg H$ the magnetization is aligned along the initial magnetization axis and slowly precess around average magnetic field (that tends to zero for a macroscopic system). As a results the magnetization relaxes with the rate $\propto H^2/\Upsilon$.

For a large magnetic field slow tunneling cannot keep site moments out of the precession around their local fields. Due to this precession the macroscopic moment of the system is decreased by a factor of 3, according to Kubo-Toyabe formula $[33]$. On the other hand the local magnetic moments on sites remains. The following relaxation of the magnetic moment goes with the rate $\Upsilon$ that does not depend on the magnetic field.

In Fig. 1 the results of numerical solution of Eq. (33) for the cubic lattice are shown. The considered system has the following set of parameters $\Upsilon_0 = 1$, $na^{1/3} = 0.5$ and $n = 1$. The spin transition rate between neighboring sites is $\Upsilon_{neib} = 0.018$. In the model we use
linearized kinetic equation considering the initial magnetization to be small $M_i(0) \ll 1$. In Fig. 1 we plot relative magnetizations $m_i(t) = M_i(t)/|M_i(0)|$. Naturally at the beginning of the simulation for every site $|m_i| = 1$ and all $m_i$ are aligned along $z$-axis. In the linear case $m_i$ follow the same equations as $M_i$.

We track independently averaged absolute value of the on-site magnetic moment $\langle |m| \rangle$, and averaged $z$-component of the magnetic moments (that correspond to the macroscopic magnetization of the system). It can be seen that during the first phase of the relaxation $\langle |m| \rangle$ and $\langle m_z \rangle$ become slightly different due to random precession in magnetic field. However random magnetic field does not reduce the ratio $\langle m_z \rangle / \langle |m| \rangle$ below $1/3$. The hopping makes this ratio even larger. Then the relaxation of $\langle m_z \rangle$ follows the relaxation of absolute values of the on-site moments. The relaxation has exponential form with some relaxation rate.

In Fig. (1b) we show the dependence of relaxation rate on average magnetic field. It agrees with qualitative assumptions: the dependence is quadratic for small fields and saturates when oscillation in random fields becomes much faster than the spin transition.

C. Random positions of sites

The system with the positional disorder is characterized by the parameter $na^3$ where $n$ is the site concentration and $a$ is the localization length. For large $na^3 \sim 1$ the hopping rates to the neighbors are of the same order for all sites. In this case the disorder becomes relatively unimportant. Without polaronic effects this system exhibit the metal-insulator transition and its conductivity is of the band type. Due to polaron formation the transport mechanism in a system with low disorder can still be of the hopping type but most interesting part of the physics that is usually associated with hopping conduction is absent. Therefore we expect that the system should behave similarly to the hopping systems without disorder discussed in previous section.

For the small values of $na^3$, when the characteristic distance to the nearest neighbor is larger than the localization length $r_{nn} \sim n^{-1/3} \gg a$, the hopping rates (even without energy disorder) have exponentially broad distribution. Transport in that case is usually described in terms of the percolation theory. The conduction is governed by the threshold hopping rate $\Gamma_{peck}$ that allows the percolation over the macroscopic distances. Most of the current is carried by the infinite cluster of the sites that are connected with hopping rates.
The density of the infinite cluster tends to zero for $na^3 \to 0$. This small portion of sites that form the infinite cluster plays important role in the theory of variable range hopping conductivity. However for the problem of neighbor hopping the infinite cluster density becomes small only for very small localization length $n^{1/3}a < 0.1$.

For the systems with low disorder there are two possible relation of parameters $\langle H \rangle < \Upsilon$ and $\langle H \rangle > \Upsilon$. The first relation leads to the motion suppression of the relaxation with relaxation rate $\sim \langle H \rangle^2 / \Upsilon$. The second relation leads to the relaxation rate $\sim \Upsilon$. When the distribution of the hopping rates $\Gamma_{ij}$ and the spin transfer rates $\Upsilon_{ij}$ is exponentially broad, the natural situation is that this inequality have different sign for different hops.

In this case one can assume that in terms of the spin relaxation the sites should be arranged into clusters. Inside the cluster the spin transfer rates $\Upsilon > \langle H \rangle$ and the magnetic moments in the cluster have approximately the same direction. Different clusters are connected by a relatively slow hopping rates $\Upsilon < \langle H \rangle$. Thus the relaxation will be governed by the critical transfer rates $\Upsilon_{th} \sim \langle H \rangle$. The relaxation due to the fast transfer rates $\Upsilon \gg \langle H \rangle$ is suppressed by the motion and transfer rates that are smaller than precession rate $\Upsilon \ll \langle H \rangle$ are too slow to influence the relaxation significantly. Therefore it is natural to assume that the dependence of spin relaxation on the characteristic scale of random magnetic field should be $\propto \langle H \rangle$, or may be $\propto \langle H \rangle^\alpha$, where $\alpha < 2$.

In order to study spin relaxation we perform extensive numerical calculations based on the general kinetic equation (33). We consider numerical samples with random uncorrelated positions of sites. Each site is ascribed by a random local magnetic field. The spin transition rates between sites are exponentially decaying with distance

$$\Upsilon_{ij} = \Upsilon_0 \exp(-2r_{ij}/a).$$

We use cutoff at some large distance $r_{max}$. $r_{max}$ is chosen in such way that each site is connected in average with 20 other sites. This choice of $r_{max}$ allows us to consider relatively large systems up to $10^4$ sites.

We start from the case when all the magnetic moments are aligned along $z$ axis and consider the relaxation of the relative magnetizations $m_i(t) = M_i(t)/|M_i(0)|$ in time. We consider three different values of parameter $n^{1/3}a$: 0.2, 0.5 and 1. For $n^{1/3}a = 0.2$ ($na^3 = 8 \cdot 10^{-3}$) the system is deeply in the localized regime even without formation of polarons. Percolation hopping rate $\Gamma_{perk}$ is four orders of magnitude less than $\Gamma_0$. However even for
this small $na^3$ the density of infinite cluster is rather high $\sim 0.85$, yet the amount of sites that are out of the infinite cluster is significant. For the value $n^{1/3}a = 0.5$ ($na^3 = 0.125$) the hopping distances are still larger than the localization length and exponentially broad distribution of hopping rates persist. However the density of infinite cluster is $> 0.95$ and there is only small amount of sites that are out of this cluster. Finally for $n^{1/3}a = 1$ there is no exponential distribution of neighbor hopping rates. In this case hopping transport is possible only due to formation of polarons.

For the small localization length $n^{1/3}a = 0.2$ the percolative value of the spin transition rate $\gamma_{\text{perk}} \approx 1.8 \cdot 10^{-4} \gamma_0$. We start the discussion from the case when the characteristic size of local hyperfine magnetic fields is slightly below of $\gamma_{\text{perk}}$, $\langle H \rangle = 10^{-4} \gamma_0$. The results of calculations are shown in Fig. 2. We averaged the results over 50 numerical samples with different random positions of sites (each sample contains $10^4$ sites).

![Fig. 2](image)

At the initial phase of the relaxation $t \lesssim H^{-1}$, there is little change in $\langle |m| \rangle$ while $\langle m_z \rangle$ decreases due to rotation of the magnetic moments in the hyperfine magnetic field. However, the rotation in the random magnetic field alone cannot decrease $\langle m_z \rangle$ more that to $1/3$. Therefore subsequent relaxation of $\langle m_z \rangle$ accompanies the relaxation of $\langle |m| \rangle$.

Then for a large time interval $Ht < 20$, the relaxation is exponential. However at larger time the exponential relaxation slows down. To understand this behavior we computed the distribution of absolute values of on-site magnetization at different $\gamma_0t$ (Fig. 2 (c)). This distribution becomes exponentially broad for $\gamma_0t > 20$ and the average magnetic moment
is determined by a small number of sites with the largest magnetic moment. This behavior is quite natural for a system with the exponential distribution of the hopping times.

In Ref. [35] Shklovskii has introduced a concept of "traps" that appear in the hopping systems. The typical trap is a pore with relatively large radius that can randomly appear in a random site distribution. There is one site inside the pore that act as a trap. The capture/release rate of the trap is related to the hopping rate from the site in the pore to the outside sites. In Ref. [35] this concept was applied to explain $1/f$ noise in the hopping systems. We argue that the same traps can be responsible for the spin relaxation at large times. Naturally, the spin on these traps cannot relax faster than $\Upsilon_{\text{trap}}$, where $\Upsilon_{\text{trap}}$ is the highest spin transfer rate from the trap to the surroundings. In section [IV.D] we show that the spin relaxation due to these traps is non-exponential and derive the analytical approximation for this non-exponential relaxation.

Note that the initial exponential part of the relaxation appears to be self-averaged even for one numerical sample consisting of $10^4$ sites. However for larger times it becomes more difficult to obtain averaged results. For $\Upsilon_0 t > 50 \cdot 10^4$ we observed oscillation in $\langle m_z \rangle$ that are due to the lack of disorder averaging. We believe that this slow suppression of these oscillations with averaging over disorder realizations is related to the trap-dependent relaxation. The characteristic size of the trap that governs magnetic moment at time $t$ grows with time. However the probability to find corresponding trap exponentially decreases with the trap size leading to the poor averaging of magnetic moment at large times.

FIG. 3: The relaxation of the magnetic moment for $n^{1/3}a = 0.2$ and different magnetic fields $\langle H \rangle/\Upsilon_0$ (a) and the dependence of the relaxation rate (in the exponential phase of relaxation) on the magnetic field (b).

Let us now discuss the dependence of the relaxation on the characteristic value of the magnetic field. This dependence is shown in Fig. 3. It is seen from this figure that the
final phase of the relaxation at large $t$ is essentially independent of the magnetic field. The rate of the exponential part of the relaxation depends linearly on the magnetic field, as it was predicted above on the basis of simplified arguments. The characteristic time of the transition from exponential to non-exponential relaxation decreases with increasing field. For large magnetic field the relaxation is non-exponential at any time.

We have shown that the spin relaxation in the systems with the hopping conductivity is extremely non-homogenous. Spin on different sites relaxes with different rates. Note that significance of different sites in other situations, for example for the electrical current, is also different. The current is carried by the infinite percolative cluster. Therefore it is interesting to know whether the relaxation on the sites of the infinite cluster is different from the relaxation on the sites out of this cluster. In our study we use the following formal definition of the conductive cluster (for details see [24]). First we find the percolative threshold, i.e. the critical distance $r_{th}$ that allows the percolation across the numerical sample with hops over distances $r \leq r_{th}$. Then we consider sites to be connected if the distance between them is less or equal than $r_{th} + a/2$ (it ensures that hopping rate between these sites is higher or comparable with the critical percolative rate). Finally we find the infinite cluster connected with distances $r \leq r_{th} + a/2$. We consider this cluster to be the percolative cluster responsible for conduction. The density of this cluster appears to be relatively high ($\approx 0.85$) for $n^{1/3}a = 0.2$.

![FIG. 4: (a) the relaxation of the magnetic moment inside and outside of the infinite cluster. (b) the contribution of sites out of the cluster to spin relaxation in the cluster](image)

We perform the averaging of the magnetic moments independently for the sites of the infinite cluster and for the sites outside of the infinite cluster and compare the results with the magnetic moment averaged over all the sites (Fig. 4 (a)). One can see that initially ($\gamma_0 t \leq 2.5 \cdot 10^3$) the relaxation of the whole numerical sample follows the relaxation of
the infinite cluster. It is natural because most of sites belong to this cluster. However for \( \Upsilon_0 t > 2.5 \cdot 10^3 \) these relaxations start to deviate one from another and magnetization of the whole sample appears to be larger than magnetization of the infinite cluster. In this time domain the relaxation is governed by the spin relaxation on the relatively rare sites with the slow relaxation rate that are outside of the infinite cluster. The relaxation of the average moment slows down while the relaxation of the magnetic moment on the infinite cluster is still exponential until \( \Upsilon_0 t \approx 4 \cdot 10^3 \).

Most interesting is that for larger times \( \Upsilon_0 t > 4 \cdot 10^3 \), the relaxation of sites in the infinite cluster also slows down. We believe that the reason for this slowing down of the relaxation is the spin transfer from slow relaxing traps to the infinite cluster which leads to the re-magnetization of the cluster. Actually, the traps can not lose magnetization by themselves. They slowly transfer the magnetic moment to the sites of the infinite cluster where it relaxes. To prove that we remove from the system all sites that do not belong to the infinite cluster and recalculate the relaxation. We compare the results with the average magnetic moment on the cluster when all the sites in the system are present in Fig. 4(b). For times \( \Upsilon_0 t < 4 \cdot 10^3 \) the curves are the same except for the small difference in relaxation time. However for \( \Upsilon_0 t > 4 \cdot 10^3 \) the relaxation of cluster slows down when all sites are included into the computation and remains exponential when we exclude all sites outside of the cluster. Therefore we conclude that \( \approx 15\% \) sites that are not included in the infinite cluster govern the magnetization dynamics of the infinite cluster at sufficiently large times.

![Graphs](image)

FIG. 5: (a) Spin relaxation for \( n^{1/3}a = 0.5 \) for different magnetic fields. Numbers on plots correspond to \( \langle \mathcal{H} \rangle / \Upsilon_0 \). (b) The dependence of the relaxation rate (in the exponential regime) on the characteristic scale of the random field.

Let us now consider other values of the parameter \( n^{1/3}a \). The results of computation of spin relaxation for intermediate localization length \( n^{1/3}a = 0.5 \) are shown in Fig. 5.
The qualitative picture of the relaxation is similar to the case of small localization length $n^{1/3}a = 0.2$. The relaxation is exponential for the short times and then follows universal non-exponential curve independent from the value of random field. The rate of the exponential relaxation is proportional to the magnetic field for a wide range of fields $0.01 < \langle \mathcal{H} \rangle / \Upsilon_0 < 0.2$ (Fig. 5(b)). At fields $\langle \mathcal{H} \rangle / \Upsilon_0 > 0.2$ the linear dependence starts to saturate. However for these fields exponential part of the relaxation is rather small. In this part spin decrease is less than one order of magnitude. For $\langle \mathcal{H} \rangle / \Upsilon_0 > 0.5$ it is impossible to separate the exponential part of the relaxation. The conductive cluster (with the above formal definition) consist of $\sim 98\%$ of sites making the concept of percolative cluster ill-defined. Therefore we do not discuss the difference between relaxation of sites within and outside of the percolative cluster for $n^{1/3}a = 0.5$.

Finally at fig. 6 we present the results of relaxation computation for $n^{1/3}a = 1$. They are quite similar to the relaxation for hoppnig system on the lattice. However the relaxation in the limit of strong random field is slightly non-exponential.

D. Analytical approximation for non-exponential relaxation.

We have demonstrated that even at the small magnetic fields the relaxation of the magnetic moment have slow non-exponential tails. At large values of the random magnetic fields these non-exponential regime covers most part of the relaxation. We have argued that at least for large times this non-exponential relaxation can be described in term of traps, the sites that are rather far from their neighbors. Let us discuss the physics of this
non-exponential relaxation.

Let us consider the spin on some trap. When the magnetic moment is transferred from
the trap to its neighbors it quickly relaxes due to fast hops outside of the trap. Therefore
each trap \(i\) has the relaxation rate \(\gamma_i\) that is the rate of electron hopping from this trap.

Naturally \(\gamma_i\) is proportional to the \(\exp\left(-\frac{2}{a}r_{\text{neib}}^i\right)\), where \(r_{\text{neib}}^i\) is the distance between
the trap and the nearest site. It is important that \(r_{\text{neib}}^i \gg a\). The characteristic number of
sites that are effective neighbors of the trap is \(\sim 4\pi n (r_{\text{neib}}^i)^2 a\). For large \(r_{\text{neib}}^i\) it becomes
larger than unity. In this case \(\gamma_i\) can be expressed as

\[
\gamma_i = \Upsilon_0 \int_{r_{\text{neib}}^i}^{\infty} e^{-2r/a} 4\pi r^2 ndr = \Upsilon_0 \frac{\pi n a^3}{2} \left( 2 + \frac{4r_{\text{neib}}^i}{a} + \frac{4(r_{\text{neib}}^i)^2}{a^2} \right) e^{-2r_{\text{neib}}^i/a}. \tag{39}
\]

FIG. 7: Spin relaxation for \(n^{1/3}a = 0.2\), \(\langle H \rangle / \Upsilon_0 = 2 \cdot 10^{-4}\) compared with analytical approximation \((40)\) and \((41)\).

To estimate the relaxation one should integrate the exponent \(e^{-\gamma_i t}\) with the distribution function of distances to the nearest neighbor.

\[
\langle |m(t)| \rangle = \int_0^\infty 4\pi nr^2 \exp \left( -\Upsilon_0 t e^{-2r/a} \frac{\pi n a^3}{2} \left( 2 + \frac{4r}{a} + \frac{4r^2}{a^2} \right) - \frac{4\pi n r^3}{3} \right) dr \tag{40}
\]

The integral \((40)\) can be approximated in the limit \(r_{\text{neib}}^i \gg a\),

\[
\langle |m| \rangle (t) = m_0 \exp \left( -\frac{\pi n a^3}{6} \ln^3 (\Upsilon_0 t) \right). \tag{41}
\]

Fig. [7] shows the comparison of the numerical simulations of the relaxation of the magnetic
moment for \(n^{1/3}a = 0.2\), \(\langle H \rangle / \Upsilon_0 = 2 \cdot 10^{-4}\) with the approximate formulae \((40)\) and \((41)\). The
comparison with Eq.(40) contain no free parameters, comparison with Eq.(41) contain one free parameter \( m_0 \). We conclude that there is at least semi-quantitative agreement between the simulation in the non-exponential phase of relaxation and approximate formulae.

Eq.(41) is in agreement with the expression proposed in Ref.[14] for the case of the spin-orbit mechanism of relaxation in the limit of strong spin-orbit coupling. Note that the similar expression in [14] has more free parameters. Although our theory and the theory presented in Ref.[14] deal with different relaxation mechanisms, in the limit of strong magnetic field or the limit of strong spin orbit interaction the relaxation in both cases is governed by the distribution of hopping rates. As a result different spin relaxation mechanisms lead to the similar non-exponential regimes of the spin relaxation.

V. CONCLUSION

We derived the kinetic equations for the hopping transport that take into account the electron spin and the possibility of double occupation. In the limit of low voltage they are reduced to the generalized Miller-Abrahams resistor network. We have applied the kinetic equations to the problem of spin relaxation in the positionally disordered system with neighbor hopping due to interaction with the random on-site hyperfine (or fringe) magnetic field. We show that the initial relaxation rate is governed by the critical hops with the rates comparable with the rate of the spin precession in a random field. At large times as well as in the case of the large random fields the relaxation becomes non-exponential and is related to the relaxation of the spin in the traps. The relaxation is strongly inhomogeneous: the relaxation of sites in the conduction cluster differs substantially from the relaxation of the sites outside of this cluster. However in some cases the traps can drastically affect the relaxation of the magnetic moment of the infinite cluster.

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VI. APPENDIX 1: KINETIC EQUATION COEFFICIENTS WITH DOUBLE OCCUPATION AND SPIN

Here we present the derivation of matrix elements $W_{xyz}$ in the equation (18)

$$\frac{d\rho_x^{(i)}}{dt} - S_{xy}(i)\rho_y^{(i)} = \sum_j W_{xyz}(ij)\rho_y^{(i)}\rho_z^{(j)}. \quad (42)$$

where $x$, $y$ and $z$ can correspond to one of $f_0$, $f_1$, $f_2$, $M_x$, $M_y$ or $M_z$. The straightforward calculation of matrix elements with equation (19) is rather cumbersome. The two-site density matrix is a $16 \times 16$ matrix with 256 matrix elements. Therefore we introduce a trick to find elements $W_{xyz}$.

Let us note that equation (42) should be valid for any density matrices $\rho_x(i)$ and $\rho_y(j)$. However there are some special cases when this equation is reduced to a more simple form. Consider for example tunneling from a site $i$ that is single-occupied with an electron with spin up (at some moment $t_1$) to a site $j$ that is free at this moment. It means that at $t = t_1$,

$$f_1^{(i)} = 1, \quad M_z^{(i)} = 1, \quad f_0^{(j)} = 1.$$

Other elements of $\rho(i)$ and $\rho(j)$ are equal to zero. The transition probability in this case is $W_{ij}$ described in Eq.(12). Therefore one can write:

$$\frac{df_1^{(j)}}{dt} = W_{ij}, \quad \frac{dM_z^{(j)}}{dt} = W_{ij}, \quad \frac{df_0^{(j)}}{dt} = -W_{ij}.$$
The derivatives of other elements of $\rho^{(j)}$ are equal to zero. The same situation is described with equation (18) at the moment $t_1$ as:

$$\frac{df_1^{(j)}}{dt} = W_{f_1,f_0,f}(ij) + W_{f_1,f_0,M_z}(ij), \quad \frac{dM_z^{(j)}}{dt} = W_{M_z,f_0,f_1}(ij) + W_{M_z,f_0,M_z}(ij),$$

$$\frac{df_0^{(j)}}{dt} = W_{f_0,f_0,f}(ij) + W_{f_0,f_0,M_z}(ij).$$

As a result we obtain three equations for the hopping rates $W_{xyz}(ij)$.

Considering tunneling of the electron with other spin projections from a single-occupied site to a free site we obtain a set of equations

$$W_{f_1,f_0,f}(ij) \pm W_{f_1,f_0,M_z}(ij) = W_{ij},$$
$$W_{M_z,f_0,f_1}(ij) \pm W_{M_z,f_0,M_z}(ij) = \pm \delta_{\alpha\beta} W_{ij},$$
$$W_{f_0,f_0,f_1}(ij) \pm W_{f_0,f_0,M_z}(ij) = -W_{ij}.$$

Equations (44) have the following solution:

$$W_{f_1,f_0,f_1}(ij) = W_{ij}, \quad W_{f_1,f_0,M_z} = 0;$$
$$W_{M_z,f_0,f_1} = 0, \quad W_{M_z,f_0,M_z} = W_{ij};$$
$$W_{f_0,f_0,f_1}(ij) = -W_{ij}, \quad W_{f_0,f_0,M_z} = 0.$$ (44)

This gives us 20 (from 216) elements $W_{x,y,z}$.

Similarly we can describe other “simple” cases: tunneling a form double-occupied site to a free one, tunneling from a single-occupied site to another single-occupied one and so on. Each case gives us a set of equations. As a result using these equations one can find all the hopping rates $W_{xyz}$. 

31