Spin-polarized supercurrents for spintronics: a review of current progress

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Spin-polarized supercurrents for spintronics: a review of current progress

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Abstract
During the past 15 years a new field has emerged, which combines superconductivity and spintronics, with the goal to pave a way for new types of devices for applications combining the virtues of both by offering the possibility of long-range spin-polarized supercurrents. Such supercurrents constitute a fruitful basis for the study of fundamental physics as they combine macroscopic quantum coherence with microscopic exchange interactions, spin selectivity, and spin transport. This report follows recent developments in the controlled creation of long-range equal-spin triplet supercurrents in ferromagnets and its contribution to spintronics. The mutual proximity-induced modification of order in superconductor-ferromagnet hybrid structures introduces in a natural way such evasive phenomena as triplet superconductivity, odd-frequency pairing, Fulde–Ferrell–Larkin–Ovchinnikov pairing, long-range equal-spin supercurrents, $\pi$-Josephson junctions, as well as long-range magnetic proximity effects. All these effects were rather exotic before 2000, when improvements in nanofabrication and materials control allowed for a new quality of hybrid structures. Guided by pioneering theoretical studies, experimental progress evolved rapidly, and since 2010 triplet supercurrents are routinely produced and observed. We have entered a new stage of studying new phases of matter previously out of our reach, and of merging the hitherto disparate fields of superconductivity and spintronics to a new research direction: super-spintronics.

Keywords: spintronics, superconductor-ferromagnet heterostructures, proximity effect, Josephson effect

(Some figures may appear in colour only in the online journal)
1. Introduction: historical background

1.1. Superconductivity interacting with magnetism

Quantum phenomena have fascinated us and challenged our imaginations for over 100 years since the theoretical foundations of quantum physics were laid. The two prime examples for macroscopic quantum phenomena are magnetism and superconductivity. Soon after the discovery of superconductivity in 1911 in Leiden by Kamerlingh-Onnes [1, 2] it became clear that a magnetic field acts in peculiar ways on superconductors. Silsbee unified in 1927 the observations of Kamerlingh-Onnes of a critical transport current density and a critical magnetic field [3], and in 1933, following a suggestion by von Laue, Meißner and Ochsenfeld performed experiments showing that the new state of matter is a true thermodynamic phase and that it expels magnetic fields from its interior [4]. Following this pivotal discovery, Shubnikov pioneered in the 1930s the field of interplay between superconductivity and magnetic field, culminating in the discovery of what is now called the intermediate state, or the Shubnikov phase [5], where magnetic field partially penetrates the superconductor in a well defined region of the temperature-field phase diagram. After the notion of a macroscopic quantum wave function was introduced for the superconducting state by Ginzburg and Landau in 1950 [6], Abrikosov theoretically explained in the 1950s type II superconductivity, where a magnetic field penetrates the superconductor in a regular array of flux lines carrying quantized flux [7]. Abrikosov’s vortex phase exists between the upper critical field $H_{c2}$ and the lower critical field $H_{c1}$ in type II superconductors.

Soon the microscopic theories of superconductivity by Bardeen, Cooper, and Schrieffer (BCS) in 1957 [8], by Bogoliubov in 1958 [9], and by Gor’kov in 1958–59 [10] brought all previous studies on a firm ground.

Ginzburg, in an attempt to formulate a theory for ferromagnetic superconductors (he considered the possibility of superconductivity in gadolinium), concentrated in 1956 on the electromagnetic (or so-called orbital) mechanism, where a suppression of superconductivity occurs via the interaction of the Cooper pairs with the vector potential of the magnetic field due to their charge [11]. In the orbital mechanism the magnetic field leads to an additional kinetic energy of the condensate, and when this energy exceeds the condensation energy, the superconducting state is destroyed. As shown in 1966 by Werthamer, Helfand, and Hohenberg, the orbital critical field for conventional isotropic, diffusive superconductors in the presence of spin–orbit and spin paramagnetic effects is $H_{orb} \equiv H_{c2}\big|_{T=0} \approx 0.7 T_C[-dH_{c2}/dT]_{T=0}$ [12], where $T_C$ is the superconducting transition temperature.

An alternative mechanism, the exchange mechanism, was suggested in 1958 by Matthias et al [13] in order to explain the variation of $T_C$ in lanthanum with rare earth impurities and the correlation between the appearance of ferromagnetism and superconductivity in ruthenides. They observed that it is not the dipole field of the effective moments of the rare earth elements that causes decrease of superconductivity in these systems, but the spin of the solute atoms; the $T_C$ does not correlate with van Vleck’s famous curve of $\mu_{eff}$ [14], but rather with spin. In these cases an exchange interaction mediated by conduction electrons, responsible for ferromagnetism, occurs in a material that by itself is superconducting. The exchange interaction via conduction electrons tries to align spins in a ferromagnet, whereas the spins in a Cooper pair are opposite for the usual case of singlet superconductors. These antagonistic tendencies led to the so-called paramagnetic effect of pair breaking.

In 1959, Anderson and Suhl showed in a seminal paper [15] that in a system with coexisting superconductivity and...
1.2. Pair breaking by paramagnetic impurities and external fields

If one introduces paramagnetic impurities into a singlet superconductor, there is the effect of pair breaking due to scattering from paramagnetic impurities, which reduces $T_c$ with increasing impurity concentration. Following previous works by Herring [16] and by Suhl and Matthias [17] for the limit of small concentrations, Abrikosov and Gor’kov developed in 1960 a theory covering the full range of concentrations up to the critical value, when superconductivity is destroyed; the $T_c$ dependence versus concentration is described in terms of a single ‘pair breaking parameter’ $\rho$ by the Abrikosov–Gor’kov formula [18]. In particular, these authors showed that the possibility of gapless superconductivity exists in metals with paramagnetic impurities (this peculiar state was further studied in 1964 by Skalski et al [19], by Maki [20], and by de Gennes [21]). The Abrikosov–Gor’kov model, which employs the Born approximation, works well, e.g. for rare earth (except cerium) impurities. For transition metal impurities in superconductors Yu [22], Shiba [23], and Rusinov [24] discovered within the framework of a full $t$-matrix treatment of the problem that local states (now called the Yu–Shiba–Rusinov states) are present within the BCS energy gap due to multiple scattering between conduction electrons and paramagnetic impurities.

De Gennes and Tinkham noted in 1964 [25] that for a time-reversal invariant superconducting order parameter, pair breaking can be related to the asymptotic long-time behavior of the time-reversal correlation function, $\eta(t) = \lim_{t \to \infty} \langle \hat{\Theta}(0) \hat{\Theta}(t) \rangle$, with the time reversal operator $\hat{\Theta}$. An exponential decay, $\eta(t) = \exp^{-2t/T_\rho}$, with $T_\rho$ some correlation time, corresponds to pair breaking with pair breaking parameter $\rho = (2\pi T_\rho)^{-1}$. If, on the other hand, a nonzero limiting value $0 < \eta < 1$ appears, then this leads to an effective weakening of the pairing interaction.

When applying a magnetic field to a superconductor, apart from the orbital effect of the penetrating field, there is also an appreciable Zeeman coupling between the electronic spins and the magnetic field. It leads to a splitting between the electronic spin bands similarly as in a weak ferromagnet the exchange energy leads to a band splitting. This effect has been experimentally studied in the early 1970’s by Meservey and Tedrow in a series of classical papers (see [26] for a review). If the magnetic field exceeds a certain value, superconductivity becomes energetically unfavorable due to this Zeeman coupling. This limiting field is the Pauli paramagnetic limiting field or the so-called Chandrasekhar-Clogston limiting field, and was predicted independently in 1962 by Chandrasekhar [27] and by Clogston [28]. It amounts to $H_g = \sqrt{2} \Delta(T = 0)/g\mu_B$, where $\Delta$ is the excitation gap in the superconductor at zero magnetic field, $g \geq 2$ the electron $g$-factor, and $\mu_B$ the Bohr magneton. The ratio $\alpha = \sqrt{2} H_{\text{orb}}/H_g$, where $H_{\text{orb}}$ is the upper critical field in the absence of the Pauli term, was discussed in 1966 by Maki, and is known as the Maki parameter [29].

1.3. Ferromagnetic superconductors

Coexisting singlet superconductivity and ferromagnetism is rare, and can be achieved either by finding suitable crystaline materials (classical examples are the rare-earth ternary compounds ErRh$_2$B$_2$ [30] and HoMo$_6$S$_8$ [31] in a narrow temperature region below the Curie temperature), or by introducing magnetic ions in a superconducting material that order ferromagnetically. In the latter case, at high impurity concentrations, the possibility to obtain coexistence between ferromagnetism and superconductivity was theoretically predicted in 1964 by Gor’kov and Rusinov [32]. Furthermore, for the case that ferromagnetism and superconductivity coexist or an external magnetic field is applied, Fulde and Maki [33] showed that the Abrikosov–Gor’kov formula holds with a modified pair breaking parameter. For an early review on magnetic superconductors see [34].

In addition to the above cases of conventional singlet superconductors, there has been discovered a large number of unconventional superconductors, which are distinguished from the conventional ones by the fact that they break additional symmetries, e.g. the lattice symmetry of the normal state, or the spin rotational symmetry. The latter is the case for superconductors exhibiting spin-triplet pairing (see figure 1). In particular ferromagnetic superconductors are under suspicion of such a pairing state, as equal-spin triplet pairing is not sensitive to the exchange mechanism in the way singlet pairing is. This refers to some heavy fermion compounds, like UGe$_2$ [35], URhGe [36], UCoGe [37], and UIr [38], in which superconductivity can coexist with ferromagnetism, and which have been studied in the past 15 years [39].

The main problem for coexistence between superconductivity and ferromagnetism is that a strong exchange effect destroys superconductivity unless the pairing is of the triplet kind. However, not many superconductors support triplet pairing. Furthermore, such systems are typically $p$-wave superconductors [40], which are very sensitive to pair breaking by normal impurities (conventional superconductors are insensitive to scattering from normal impurities, which is the content of a theorem by Abrikosov and Gor’kov [41] and Anderson [42]). For this reason new avenues have been chosen to study such systems for $s$-wave and $d$-wave superconductors, which are much more common in nature. These avenues combine the phenomena of proximity induced superconductivity, Cooper pairs with finite center of mass momentum, and odd-frequency $s$-wave spin-triplet pairs.
The exchange field can be related to \( H_{\text{exch}} \). Thus, the system only allows
\( H_{\text{exch}} = -\mathbf{J} \cdot \mathbf{s} \).

For free electrons \( S = 0 \) and \( S = 1 \), the magnetic moment is
\( \mathbf{J} \) within a pair, \( S(S_\uparrow, S_\downarrow) \)
and
\( \mathbf{J} \) for triplet states. Thus, angular momenta can be visualized as
antiparallel for singlet pairs, whereas for triplet pairs they enclose in
average a relative angle of \( \pm 70.53^\circ \) (even for `equal spin’ pairs).

\[ S_z = \pm 1 \]
\[ S_z = 0 \]

Figure 1. Two electrons, each of which has spin \( S = \frac{1}{2} \), can
combine their spin angular momenta \( s_1 \) and \( s_2 \) to build a pair with
total spin \( S = 0 \) or a pair with total spin \( S = 1 \). In the first case, the
pair is in a spin-singlet state (shown on the left). In the second case,
the pair is in one of the three possible spin-triplet states: with spin
projection \( S_z = 0, \pm 1 \) (shown on the right). The pairs with \( S_z = \pm 1 \)
are called `equal-spin’ pairs with respect to the spin quantization
axis (here \( z \)-axis). The spin state \((S, S_z)\) is fully characterized by the
two quantum numbers \( S \) and \( S_z \). We use a spin-vector representation
to visualize pair angular momenta, where the expectation value
of the cosine of the relative angle between the two spin vectors
within a pair, \( \langle S(S_\uparrow, S_\downarrow) \rangle \), is \( -1 \) for singlet states, and
\( \frac{1}{2} \) for triplet states. Thus, angular momenta can be visualized as
antiparallel for singlet pairs, whereas for triplet pairs they enclose in
average a relative angle of \( \pm 70.53^\circ \) (even for `equal spin’ pairs).

1.4. Cooper pairs with finite center of mass momentum

When the paramagnetic limiting field is smaller than the orbital critical field, then the possibility of an inhomoge-
nous superconducting state with finite pair momentum arises
near \( H_C \). Such a state was theoretically predicted in 1964
independently by Fulde and Ferrell [43] and by Larkin and
Ovchinnikov [44]. It is known in the western literature as the
FFLO state and in the eastern as the LOFF state.

Consider superconductivity in a weakly spin-polarized
ferromagnetic material (or in an external magnetic field).
Electronic spin bands are shifted in energy with respect to each
other by an amount \( 2J \) (which in general can be anisotropic):
\( \varepsilon(\mathbf{p}) = \varepsilon(\mathbf{p}) - J(\mathbf{p}) \cdot \mathbf{s} \). The exchange field can be related to
an effective magnetic field via \( \mu B_{\text{eff}} = \mathbf{J} \) (for free electrons
the magnetic moment is \( \mu = \mu_e < 0 \)). We use the convention
that spin is quantized in direction of the exchange field. The
energy shift translates into a splitting of the Fermi surface for
the two spin species (see figure 2), which results e.g. for small
\( J \) from the relation
\[ \hbar v_F \cdot \mathbf{Q} = v_F \cdot (\mathbf{p}_{f_1} - \mathbf{p}_{f_2}) = 2J(p_{f_2}) \]

obtained by linearizing the dispersion relation around the
Fermi energy (here the Fermi velocity \( v_F \) is assumed to be
approximately equal for the two spin bands due to the small
splitting, and \( p_i = (\mathbf{p}_{f_1} + \mathbf{p}_{f_2})/2 \)). Thus, the system only allows
for opposite-spin Cooper pairs \( \mathbf{p}_{f_1}, -\mathbf{p}_{f_2} \) and \( \mathbf{p}_{f_2}, -\mathbf{p}_{f_1} \)
built from electrons at the Fermi energy if they carry a finite

\[ 2J = \frac{\hbar^2}{m} \frac{\partial^2 \varepsilon(\mathbf{p})}{\partial \mathbf{p}^2} \]

\[ \Delta_{\text{FFLO}}(\mathbf{R}) = \sum \Delta_k e^{i\mathbf{Q} \cdot \mathbf{R}}. \]

The preferred directions are chosen by the system (spontane-
ously or due to crystal anisotropy and boundary conditions).
Fulde and Ferrell suggested an order parameter characterized
by only one wavevector \( \mathbf{Q} \), leading to a spatially homogeneous
modulus and a spatially varying phase. If the order param-
eter is characterized by more than one wavevector \( \mathbf{Q} \), then
the FFLO state exhibits an inhomogeneous order showing a
periodic structure. Larkin and Ovchinnikov proposed that
the ground state may show a one-dimensional modulation
(neglecting orbital effects). However, more complex struc-
tures are possible in the general case of anisotropic metals.
In general, the pair amplitudes develop an
\( \sum \Delta_k e^{i\mathbf{Q} \cdot \mathbf{R}}. \)

The FFLO effect: due to the exchange splitting of the
energy bands (filled states are shaded blue in the picture) by \( \pm J \) the
Fermi surfaces split as well. A Cooper pair with opposite spins can be
accommodated at the Fermi surface only on the cost of a finite center of
mass momentum. Note that spin is quantized here in direction of
the exchange field \( \mathbf{J} \), entering the Hamiltonian as \( H_{\text{exch}} = -\mathbf{J} \cdot \mathbf{s} \).

\[ \mathbf{J} \] center of mass momentum \( \pm \hbar \mathbf{Q}/2 = \pm (\mathbf{p}_{f_1} - \mathbf{p}_{f_2})/2 \) (\( \hbar \mathbf{Q} \) is
the momentum of the Cooper pair). This can lead to an order
parameter characterized by a linear combination of terms with
different Cooper pair momenta

\[ \Delta_{\text{FFLO}}(\mathbf{R}) = \sum \Delta_k e^{i\mathbf{Q} \cdot \mathbf{R}}. \]

Figure 2. The FFLO effect: due to the exchange splitting of the
energy bands (filled states are shaded blue in the picture) by \( \pm J \) the
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tures are possible in the general case of anisotropic metals.
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\[ \sum \Delta_k e^{i\mathbf{Q} \cdot \mathbf{R}}. \]
quasi-two-dimensional superconductors in a magnetic field applied nearly parallel to the conducting layers. The theory for such systems was developed by Bulaevskii [48] in 1973, by Burkhardt and Rainer [49] and by Shimahara [50] in 1994, and by Buzdin and Brison [51] in 1996. For quasi-one-dimensional systems theories in terms of soliton lattice solutions were developed by Buzdin and Tugushev in 1983 [52], by Buzdin and Polonski in 1987 [53], and by Dupuis in 1995 [54]. In compounds with large spin susceptibility and high $H_{c2}$, as in heavy fermion and intermediate-valence systems, a generalized FFLO state was discussed by Tachiki and co-workers, where the order parameter is spatially modulated, and planar nodes of the order parameter are periodically aligned perpendicular to the vortices [55].

The FFLO state only appears below a certain temperature $T^*$, which determines a tri-critical point $(T^*,H^*)$ in the $(T,H)$-diagram at which the normal, BCS, and the FFLO phases meet. A generalized Ginzburg–Landau theory for the vicinity of this tri-critical point was derived by Buzdin and Kachkachi [56]. A self-consistent calculation of the field versus temperature phase diagram and order parameter structures for the FFLO states of quasi-two-dimensional $d$-wave superconductors is presented in [57]. Recently, a symmetry classification of the pairing amplitudes in FFLO states coexisting with vortices was suggested [58]. For reviews on this topic see [59–62].

The FFLO state has not been unambiguously found in bulk materials to date, although there are currently candidates under debate, as the heavy fermion material CeCoIn$_5$ [63–66], or some organic superconductors such as $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ [67–70]. However, a similar state can be realized in superconductor-ferromagnet hybrid structures, where superconducting pairs leak into a ferromagnet due to the superconducting proximity effect, as we discuss in detail further below (for earlier reviews see [71–75]).

### 1.5. Proximity effect

The pivotal role for realizing the FFLO state in such hybrid structures is played by the proximity effect between a superconducting and a normal conducting material. The theory for the proximity effect was developed largely by de Gennes [76–79], and by Werthamer [80, 81] in the 1960s. It describes the effect of penetration of Cooper pairs in a normal metal where the two conduction electrons (or holes) of the pair stay correlated with each other over a distance that depends on the amount of disorder in the normal material and on temperature. In a clean material, the penetration depth is determined by the thermal coherence length $\xi_{lc} = \hbar v_f / 2\pi k_B T$. It gives the distance, a quasiparticle with velocity $v_f$ travels during time $\hbar / 2\pi k_B T$, before thermal decoherence sets in. For ballistic motion and atomically smooth interfaces, the penetration depth depends on the angle of impact of the quasiparticles, i.e. the Fermi velocity should be replaced by the Fermi velocity component in the normal metal perpendicular to the interface, $v_{fz}$. The notion of a coherence length determined by the Fermi velocity and a characteristic superconducting energy scale was introduced by Pippard in 1953 [82].

In the presence of impurities, scattering decreases the penetration of Cooper pairs into the normal metal. If the mean free path is $\ell$, and the motion is diffusive, then the quasiparticle travels on average between two scattering events a time $\tau = \ell / v_f$. For a random walk, the variance for the $x$-component is given by $\sigma_x^2 = \frac{1}{3} \ell^2 = v_f \ell / 3$, where $\ell$ is the elapsed time. Coherence is lost when the total path traversed during the random walk is equal to $\xi_{lc}$, i.e. $v_f \tau = \xi_{lc}$. If we define the diffusive coherence length by $\xi_{lc}^2 = \sigma_x^2$, we obtain $\xi_{lc} = \xi_{lc} \sqrt{3}$. Hence, the diffusive coherence length is given by $\xi_{lc} = \sqrt{\xi_{lc} \ell / 3}$, or in other words, $\xi_{lc} = \sqrt{\hbar D / 2\pi k_B T}$ with the diffusion constant $D = v_f \ell / 3$.

The proximity amplitude is proportional to the pair potential in the superconductor, $\Delta$, and the product of the transmission amplitudes through the interface of the two particles comprising a pair. Inversely, the loss of Cooper pairs in the superconductor leads to the so-called inverse proximity effect of a weakening of the superconducting pair potential near the interface in the superconductor.

#### 1.6. Andreev reflection

A very closely related phenomenon is the so-called Andreev reflection, discovered by Andreev in 1964 [83] and by de Gennes and Saint-Jaimes in 1963/64 [84, 85] (see [86] for a review). It describes the correlations between particles and holes at the normal side of the interface due to penetration of pairs. In fact, Andreev reflection and proximity effect are two sides of one and the same coin.

Let us assume that a spin $\uparrow$ conduction electron in the normal metal with energy $\mu + e$ near the chemical potential $\mu$ moves in positive $x$-direction towards a superconductor. The excitation energy $e$ is assumed to be within the energy gap $\Delta$ of the superconductor. The electron can be transmitted into the superconductor only together with another electron with spin $\downarrow$, energy $\mu - e$, and momentum approximately opposite, to build a Cooper pair that enters the condensate at the pair chemical potential $2\mu$ (after some momentum relaxation has taken place). For $\Delta \ll \mu$ it is possible to approximate the electronic dispersion $E(p) \approx \mu = v_f \cdot (p - \mathbf{p}_f)$, with the Fermi momentum $\mathbf{p}_f$ and Fermi velocity $v_f = v(\mathbf{p}_f)$. Within this approximation, the group velocity of the incoming electron is equal to $v_f$, and its excitation energy $e = v_f \cdot (p - \mathbf{p}_f)$.

Let us consider a Landau quasiparticle with momentum $\mathbf{p}_1 = \mathbf{p}_f + \mathbf{p}_p$, spin $\uparrow$, and excitation energy $e_1 = v_f \cdot \mathbf{p}_p$. We will consider pairing with another quasiparticle with momentum $\mathbf{p}_2 = -\mathbf{p}_f + \mathbf{p}_p$, spin $\downarrow$, and excitation energy $e_2 = -v_f \cdot \mathbf{p}_p$ (see figure 3). We require that $e_2 = -e_1$. This leads to the relation $v_f \cdot (\mathbf{p}_p - \mathbf{p}_f) = 0$, which allows us to choose $\mathbf{p}_1$ such that $\mathbf{p}_f = \mathbf{p}_1 - \mathbf{p}_p$ holds. The missing electron in the spin-$\uparrow$ band is equivalent to a hole excitation characterized by energy $-e_2 = +e_1$, momentum $-\mathbf{p}_2 = \mathbf{p}_1 - \mathbf{p}_p$, group velocity

\[2\text{ In } d\text{ dimensions the factor of } 3\text{ is replaced by a factor of } d.\]

\[3\text{ Choose } \mathbf{p}_1 = \mathbf{p}_f + (\mathbf{p}_p - \mathbf{p}_f)/2, \text{ then } \mathbf{p}_1 - \mathbf{p}_f = p_2 = \mathbf{p}_p = \mathbf{p} = (\mathbf{p}_p + \mathbf{p}_f)/2. \text{ This is again (in leading order) a Fermi surface point due to } v_{f1} \cdot (\mathbf{p}_f - \mathbf{p}_1) = 0, \text{ i.e. the shift is tangential to the Fermi surface.}\]
excitations:

\[ v(\mathbf{p}_f) \approx -\mathbf{v}_F, \text{and spin } \uparrow \text{ (a missing spin )}. \]

The process can be considered as a scattering of a particle with charge \( e \), momentum \( \mathbf{p}_f + \delta \mathbf{p} \), and velocity \( \mathbf{v}_f \) into a hole with charge \( -e \), momentum \( \mathbf{p}_f - \delta \mathbf{p} \) and velocity \( -\mathbf{v}_f \). The electron-hole pair gives rise to a current density of \( e \mathbf{v}_f (+) (e \mathbf{v}_f(-)) = 2e \mathbf{v}_f \), twice the current density of the incoming particle. The incoming electron (velocity \( \mathbf{v}_f \)) is approximately ‘retro reflected’ (velocity \( \approx -\mathbf{v}_f \)) as a hole [83]. This process is called Andreev reflection, contrasting the familiar specular reflection.

A possible small angle between the reflected hole and the incoming particle is due to variation of the Fermi velocity between the momenta \( \mathbf{p}_f \) and \( \mathbf{p}_f \pm \delta \mathbf{p} \), and is of order of \( e/E_F \), with Fermi energy \( E_F \) [87]. Retroreflection is perfect for perpendicular impact if no supercurrent flows along the surface. In the Andreev particle-hole conversion process, energy and spin are conserved, however charge is not, and momentum is only approximately conserved. The charge \( 2e \) and (partially) the momentum \( h \mathbf{Q} = 2\delta \mathbf{p} \) are transferred to the superconducting condensate: two electrons with opposite spin enter the superconductor to create a Cooper pair with non-zero pair momentum, which joins the condensate, leading to a (small) supercurrent for finite excitation energies. The momentum \( h \mathbf{Q} \) is thereby partially transferred to the interface (provided a Fermi surface or Fermi velocity mismatch exists), and partially to the condensate resulting into a supercurrent consistent with total charge conservation. In equilibrium, and in the absence of a macroscopic supercurrent, this current is exactly canceled by the inverse process when a Cooper pair enters the normal metal and converts a hole into an electron.

For an atomically clean interface, if there is a macroscopic supercurrent with Cooper pair momentum \( \mathbf{p}_S \) parallel to the interface present in the superconductor, then momentum conservation requires that the created Cooper pair enters the condensate with the required Cooper pair momentum parallel to the interface, such that \( 2\delta \mathbf{p}_1 = \mathbf{p}_S \). One obtains (we assume \( v_{F_x} > 0 \)) \( 2\delta \mathbf{p}_y = (2e - \mathbf{v}_y \cdot \mathbf{p}_S)/v_{F_y} \). In particular, for \( \mathbf{p}_S = 0 \) only \( \mathbf{p}_y \) can change in the Andreev scattering process. In this case, as \( \delta \mathbf{p}_1 \) must be zero, the Cooper pair momentum is given by \( Q_c = 2e/v_{F_y} \) (see figure 3).

Figure 3. Andreev reflection: an electron at crystal momentum \( \mathbf{p}_1 \) pairs with another one at \( \mathbf{p}_2 \), under the conditions that their energies and \( \mathbf{p}_y \)-component of momentum are opposite to each other. This leads to a finite \( \mathbf{p}_y \) component and a resulting center of mass momentum \( h \mathbf{Q}/2 \) of the Cooper pair. A hole is reflected, which is drawn in this plot at the negative momentum and energy of the missing electron (in the excitation picture all excitation states inside the Fermi surface have reversed momentum and energy and are considered as hole excitation with positive excitation energy). The resulting Cooper pair transfers its momentum partially to the interface between the normal metal and the superconductor (for the case that there is a Fermi surface or Fermi velocity mismatch), and partially to the condensate in the superconductor when entering it. The amount transferred to the condensate results in a supercurrent consistent with current conservation in the scattering process.

For diffusive motion, non-magnetic scattering events conserve the time reversal symmetry, and thus scatter time-reversed states in a similar way. In particular a particle-hole pair with momenta both close to \( \mathbf{p}_f \) will scatter in a particle hole pair with a Fermi surface or Fermi velocity mismatch exists), and partially to the condensate in the superconductor when entering it. The amount transferred to the condensate results in a supercurrent consistent with current conservation in the scattering process.

During their motion in the normal metal, the phase coherence is lost due to the slight difference in momentum of the electron and the hole, given by \( 2\delta \mathbf{p}_y = 2e/v_{F_y} \). When averaged over all momentum directions, the pair correlation function decays away from the interface algebraically \( \sim \xi_c(\mathbf{Q})/x \) as function of \( x \), where we define \( \xi_c(\mathbf{Q}) = \sqrt{\hbar \nu_{\mathbf{Q}}}/(\Delta F_{\mathbf{Q}}) \). For observables in equilibrium, the decay length can be obtained by replacing \( \xi \) in the expression for the momentum \( \delta \mathbf{p}_y \) by the lowest Matsubara energy [91] \( \hbar \nu_{\mathbf{Q}}/2\pi \). This leads to an exponential decay on the length scale \( \sqrt{\hbar \nu_{\mathbf{Q}}}/2\pi \) along each ballistic trajectory, which is precisely the coherence length from the proximity effect.

For diffusive motion, non-magnetic scattering events conserve the time reversal symmetry, and thus scatter time-reversed states in a similar way. In particular a particle-hole pair with momenta both close to \( \mathbf{p}_f \) will scatter in a particle hole pair with
excitations:

Figure 4. Andreev reflection in a ferromagnet: an electron with energy $\epsilon$ and spin $\uparrow$ pairs with an electron with energy $-\epsilon$ and spin $\downarrow$, resulting into a total momentum of $\hbar(Q_x \pm Q_z)$. For sufficiently small spin band splitting a Cooper pair of the form shown to the right results, which contains singlet and triplet components with amplitudes $\cos(Q_x \chi)$ and $i \sin(Q_x \chi)$, respectively. The Cooper pair enters the condensate in the superconductor, transferring its momentum partially to the interface and partially to the singlet condensate, ensuring current conservation. The triplet component decays on the superconducting coherence length scale into the superconductor.

Momenta both close to $p_f$ (as scattering amplitude for $p_f \rightarrow p_f'$ is the same as for $-p_f' \rightarrow -p_f$ due to time reversal symmetry). Thus, scattering events change the momentum of particle and hole by the same amount, however do not destroy their coherence. This means, the deepening between the particle and hole takes place on a semiclassical trajectory as in the clean case, however the trajectory changes direction multiple times in a random way. The diffusive process away from the interface is characterized by a diffusion equation for the pair amplitude $f$, given by $\partial_t f = D \partial^2 f$. With $f = e^{i(k_{sx}x - 2\pi i t)h}$ this implies $-2i \epsilon = -\hbar D k_{sx}^2$, resulting in a complex wave vector given for decay in positive $x$ direction by $k_x = (i \pm 1)\sqrt{|\epsilon|/\hbar D}$. This gives rise to an exponential decay on the length scale $\sqrt{\hbar D/|\epsilon|}$, accompanied by an oscillation on the same length scale. For observables in equilibrium we can replace $\epsilon \rightarrow i\hbar k_{sx} T$, leading to $k_{sx}^2 = -2\pi k_{sy} T/\hbar D$ and an exponential decay on the length scale $\sqrt{\hbar D/2\pi k_{sy} T}$, again matching the length scale for the proximity effect in diffusive metals. The two phenomena, proximity effect and Andreev reflection are intertwined and cannot be discussed separately from each other. The above discussion assumes that the phase coherence is not weakened by additional effects. If phase coherence is weakened by inelastic processes, as for example magnetic scattering, this puts limitations on the proximity effect. In this case, one has to replace $\epsilon$ by $\epsilon = \epsilon + i\alpha$, with the spin-flip scattering rate $\alpha = \hbar / \tau_s$, where $\tau_s$ is the corresponding life time. This means that in the ballistic limit exponential decay of pair correlations sets in on the length scale $\hbar v_f/2\alpha = v_f \tau_s/2$ (the factor 2 takes into account that both particles and holes are affected). The corresponding coherence lengths are obtained by replacing $\pi k_{sy} T$ by $\pi k_{sy} T + \alpha_c$.

A similar mechanism works for a weakly ferromagnetic normal metal, as for example a ferromagnetic alloy (see figure 4) [90]. In this case, the electronic bands are spin-split due to the exchange interaction by an amount of $\pm J \ll E_f$. The Andreev reflection mechanism now requires that the $x$-component of the momentum of the incoming electron with spin $\uparrow$ is $p_{f_x} = p_{f_x} + (\epsilon + J)/v_f$, which pairs with an electron with momentum $p_{2x} = -p_{f_x} + (\epsilon + J)/v_f$. This leads to a Cooper pair momentum of $2(\epsilon + J)/v_f$. On the contrary, if the incoming electron has spin $\downarrow$, it pairs with a spin $\downarrow$ electron, and the sign of $J$ reverses in the above expressions, leading to a center of mass momentum of $2(\epsilon - J)/v_f$. Denoting $Q_x = 2J/\hbar v_f$ and $Q_z = 2\pi/\hbar v_f$, we see that instead of a singlet Cooper pair $(|1\uparrow - 1\downarrow\rangle + i|1\downarrow - 1\uparrow\rangle)\hbar^2/4$, as in the case of a non-magnetic normal metal, a Cooper pair of the form

\[ (|1\uparrow \rangle e^{iQ_z x} - |1\downarrow \rangle e^{-iQ_z x}) \hbar^2/4 \]

is created. This is exactly the FFLO type of pair, as it was considered in the original work. Only it is now induced as a proximity amplitude instead of a bulk phase. It can be decomposed into a spin singlet $(|1\uparrow \downarrow - 1\downarrow \uparrow\rangle)\hbar^2/4$ and a spin triplet $(|1\uparrow \downarrow + 1\downarrow \uparrow\rangle)\hbar^2/4$ (where $S$ is the total spin of the pair and $S_z$ its projection on the $z$-axis), leading to (see figure 5)

\[ [\cos(Q_x \chi)|0, 0\rangle + i \sin(Q_x \chi)|1, 0\rangle] e^{iQ_z x} \hbar^2/4. \]
link), the macroscopic wave functions of the two superconductors may overlap. Under the condition that a phase difference exists between the superconductors, a supercurrent may flow between them directly through the non-superconducting region even under zero applied voltage. This effect was discovered by Josephson in 1962 [91, 92] and first observed by Anderson and Rowell in 1963 [93]. The Josephson effect is a hallmark of macroscopic quantum coherence, proving the macroscopic character of the pair wave function as originally predicted by Ginzburg and Landau [6]. Originally, the effect described the zero resistance tunneling of Cooper pairs between two superconductors through an insulating barrier, an SIS junction. The Josephson current from superconductor 2 to superconductor 1 (i.e., electrons are flowing from 1 to 2), I, is given by the set of Josephson relations

\[ I = F(\Delta \chi), \quad F(\Delta \chi + 2\pi) = F(\Delta \chi), \]  

\[ \Delta \chi = \chi_2 - \chi_1 - \frac{q^*}{\hbar} \int_1^2 A \cdot d\mathbf{r}, \]  

\[ \frac{\partial \Delta \chi}{\partial \tau} = -\frac{q^*}{\hbar} (\Phi_2 - \Phi_1) \]  

where \( q^* = 2e = -2|e| \chi_1 \) and \( \chi_2 \) are the phases of the superconducting condensate wave function on either side of the contact, \( A \) is the electromagnetic vector potential, and \( q^*\Phi \) is the pair electrochemical potential (\( \Phi_2 - \Phi_1 = V \) is the voltage across the junction). The function \( F \) describes the current-phase relation. The critical Josephson currents in positive and negative flow directions are defined via

\[ I_+ = \max_{\Delta \chi} F(\Delta \chi), \quad I_- = -\min_{\Delta \chi} F(\Delta \chi). \]  

For non-magnetic barriers in the tunneling limit, \( I_+ = I_- = I_c \) and \( I = I_c \sin(\Delta \chi) \), where \( I_c \) is positive. The relations (5a)–(5c) are invariant against gauge transformations \( A' = A + \nabla \zeta, \Phi' = \Phi - \partial_\tau \zeta, \chi' = \chi + \frac{q^*}{\hbar} \zeta \). The function \( F(\Delta \chi) \) may not be single valued, for example for the case of a weak link multiple solutions can exist, and a hysteresis when sweeping \( \Delta \chi \) may appear. If a flux \( \Phi \) penetrates the junction, a characteristic Fraunhofer pattern appears when \( I_c \) is plotted versus the flux. A multitude of interesting effects and devices based on the Josephson relations exist, and the reader is referred to review articles, e.g. [94–98].

Here we are mainly concerned with the dc Josephson effect for the case when the non-superconducting material is an extended region of normal metal or metallic ferromagnet. With the help of the proximity effect via Andreev reflections, the Josephson effect can also occur in such devices. The current passing through the normal region is carried by the Andreev states, which build bound states below the superconducting gaps within the normal conducting region. The number and distribution of the bound states depend on details such as interface transmission, mean free path, and length of the normal metal. In general, there is a characteristic energy, the Thouless energy [99], given by \( hV/L \) for the clean limit, and by \( hD/L^2 \) for the diffusive limit. In normal metals coupled to conventional superconductors, there will be a low-energy gap in the spectrum of Andreev states, which for long junctions approximately scales with the Thouless energy and the transmission probabilities between the superconductors and the normal metal (possibly further reduced by inelastic scattering processes). This is the so-called minigap, found first by McMillan [100]. This minigap can be probed by scanning tunneling microscopy [101, 102]. When a supercurrent flows across the junction, or when an external magnetic field is applied, the minigap is reduced and eventually closes.

In the ballistic limit, each Andreev bound state with energy \( E_{bs} \) disperses as function of phase difference \( \Delta \chi \), and the current is given by \( (q^*/\hbar) dE_{bs}/d\Delta \chi \). Apart from the current carried by the Andreev bound states, there is also a contribution from continuum states above the gap.

The current-phase relation \( F(\Delta \chi) \) is in general strongly dependent on the details of the Josephson junction. Sinusoidal behavior is only observed under special circumstances, like for example in the tunneling limit. The critical Josephson current depends strongly on the length of the junction. For more details I refer the reader to the above mentioned review articles.
2. Symmetry classification of Cooper pairs in superconductors

2.1. Consequences of Pauli principle and Fermi statistics

Due to the Fermi statistics the pair correlation function, or the Gor’kov ‘anomalous Green function’ [10], fulfills fundamental symmetries following from fermionic anticommutation relations of the field operators. For fermions, the definition of the anomalous Green function [103, 104] in Matsubara representation [91] is given by

\[
-F^M_{ab}(\mathbf{r}_1, \mathbf{r}_2; \tau) = \langle T_\tau \Psi_0(\mathbf{r}_1, -\mathbf{i}\tau) \Psi_\beta(\mathbf{r}_2, 0) \rangle \
\equiv \theta(\tau) \langle \Psi_\beta(\mathbf{r}_2, 0) \Psi_\beta(\mathbf{r}_1, -\mathbf{i}\tau) \rangle
\]

(7)

where the \( \theta \)-function is defined as \( \theta(\tau) = 1 \) for \( \tau \geq 0 \) and 0 for \( \tau < 0 \), and where \(|\mathbf{r}| < h/k_B T\). The function \( F^M \) fulfills the fundamental identity

\[
-F^M_{ab}(\mathbf{r}, \mathbf{r}; \tau) = -F^M_{ba}(\mathbf{r}_2, \mathbf{r}_1; -\tau).
\]

(8)

which expresses the fermionic nature of the constituents of a pair. Going over to relative and center of mass coordinates, \( \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \), \( \mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2 \), the corresponding relation reads

\[
-F^M_{ab}(\mathbf{r}, \mathbf{R}; \tau) = F^M_{ba}(\mathbf{r}_2, \mathbf{R}; -\frac{\mathbf{r}}{2}, -\frac{\mathbf{r}}{2}, \tau; \mathbf{R}, \mathbf{R}),
\]

(9)

or after Fourier transformation in the relative coordinates \( \mathbf{r} \rightarrow \mathbf{p}, \tau \rightarrow \omega \),

\[
-F^M_{ab}(\mathbf{p}, \omega; \mathbf{R}) = F^M_{ba}(\mathbf{p}, -\omega; \mathbf{R}).
\]

(10)

Kubo–Martin–Schwinger (KMS) boundary conditions [105, 106] allow for anti-periodicity in \( \tau \) with period \( h/k_B T : F^M_{ab}(\mathbf{r}, \tau + i\hbar/k_B T; \mathbf{R}) = -F^M_{ab}(\mathbf{r}, \tau; \mathbf{R}) \). This leads to discrete Matsubara energies \( \omega_n = (2n + 1)\pi k_B T \),

\[
F^M_{ab}(\mathbf{p}, \omega_n; \mathbf{R}) = F^M_{ab}(\mathbf{p}, -\omega_n; \mathbf{R}).
\]

(11)

We consider now spin-singlet (spin-antisymmetric) and spin-triplet (spin-symmetric) components:

\[
F^M_{ab}(\mathbf{p}, \omega; \mathbf{R}) = \frac{1}{2} (F^M_{ab} \mp F^M_{ba})
\]

(12)

(suppressing the spin indices hereafter), which fulfill

\[
F^M_{s}(\mathbf{p}, \omega_n; \mathbf{R}) = -F^M_{s}(\mathbf{p}, -\omega_n; \mathbf{R})
\]

(13a)

\[
F^M_{t}(\mathbf{p}, \omega_n; \mathbf{R}) = -F^M_{t}(\mathbf{p}, -\omega_n; \mathbf{R}).
\]

(13b)

Each of these we can classify according to parity. We define even-parity and odd-parity functions

\[
F^M_{\pm}(\omega_n; \mathbf{R}) = \frac{1}{2} (F^M(\mathbf{p}, \omega_n; \mathbf{R}) \pm F^M(-\mathbf{p}, \omega_n; \mathbf{R}))
\]

(14)

(we suppress the momentum argument hereafter), and find

\[
F^M_{s}(\omega_n; \mathbf{R}) = F^M_{s}(-\omega_n; \mathbf{R})
\]

(15a)

\[
F^M_{t}(\omega_n; \mathbf{R}) = -F^M_{t}(-\omega_n; \mathbf{R})
\]

(15b)

Thus, \( F^M_{s}(\omega_n; \mathbf{R}) \) and \( F^M_{t}(\omega_n; \mathbf{R}) \) are even in Matsubara frequency, whereas \( F^M_{s}(\omega_n; \mathbf{R}) \) and \( F^M_{t}(\omega_n; \mathbf{R}) \) are odd.

After it was realized that in diffusive heterostructures with ferromagnets the type \( F^M_{t}(\omega_n; \mathbf{R}) \) appears, which is according to the above a so-called odd-frequency pair amplitude (for a review see [73]), a systematic classification according to symmetry of pairing correlations was undertaken along the lines explained above. Pair amplitudes are classified into four types according to their behavior with respect to frequency, momentum (parity), and spin (see figure 6) [107]:

Type A: spin singlet, even frequency, even parity
Type B: spin singlet, odd frequency, odd parity
Type C: spin triplet, even frequency, odd parity
Type D: spin triplet, odd frequency, even parity.

An identical classification scheme was independently proposed in [108, 109]. The four symmetry states above exhaust all possibilities compatible with Fermi statistics and the Pauli exclusion principle. The usual spin singlet, \( s \)-wave Bardeen–Cooper–Schrieffer (BCS) superconductor [8] is of type A, while the spin triplet, \( p \)-wave superfluid formed in \( ^3 \)He [110, 111] is of type C. Type D was first considered by Berezinskii [112] in connection with early research on superfluid \( ^3 \)He. Finally, type B was introduced in connection with unconventional superconductors by Balatsky, Abrahams and others [116–118].

Suggestions for realization of type B superconductivity include generalized one-dimensional \( t-J \) and Hubbard models [119, 120], two-channel Kondo models and Kondo lattices [121–124], and quantum critical points [125]. Realizations suggested for the type D state include disordered two-dimensional electron fluids in semiconductors [113–115], triangular antiferromagnets [126], composite spin and orbital triplet superconductivity in two-channel Anderson lattices [127], Hund’s coupled pairing in double orbital Hubbard models [128], strong-coupling triplet superconductivity in Holstein Hubbard models [129], and one-dimensional systems with strong charge fluctuations [130].

2.2. Odd-frequency pairing amplitudes

To date an odd-frequency superconductor has not been found in nature. However, in contrast to all cases discussed above, where the appearance of an order parameter due to spontaneous symmetry breaking (global phase symmetry in superconductors) was in the focus, in this review we are interested in the case of explicit symmetry breaking taking place locally in some spatial region, e.g. near interfaces, line defects, or inclusions. For this case an overwhelming number of experiments support the picture of the existence of proximity induced pairing states of type D. In its pure form (i.e. without additional components of different symmetry), it has been

\[ F^M_{s}(\omega_n; \mathbf{R}) = F^M_{s}(-\omega_n; \mathbf{R}) \]

(15c)

\[ F^M_{t}(\omega_n; \mathbf{R}) = F^M_{t}(-\omega_n; \mathbf{R}). \]

(15d)
first predicted theoretically for a superconductor–ferromagnet proximity structure with a spiral inhomogeneous magnetization near the interface in [131]. Previous work had predicted the appearance of similar odd-frequency triplet anomalous functions in a model of coexistence of a superconducting phase and a helical ordering of localized spins, motivated by experiments on the superconductor ErRh4B4 [132].

In fact, the Pauli principle requires odd-frequency amplitudes to be present in any inhomogeneous superconducting state, not necessarily spin-polarized [107]. For example, the case of a normal metal coupled to a superconductor involves pair amplitudes of type B. Thus, odd-frequency amplitudes appear in heterostructures naturally due to breaking of translational symmetry at interfaces (similarly as Rashba spin–orbit coupling appears at interfaces in semiconductor heterostructures). They have been present in all treatments of inhomogeneous superconductivity for a long time, however were not explicitly named as such. Similarly, pair amplitudes of type D appear as soon as spin rotational symmetry is broken, e.g. by an external magnetic field via the Zeeman effect. If both spin rotational symmetry and parity are broken, e.g. at an interface between a superconductor and a ferromagnet, all four types of pair amplitudes are generated at the interface [107, 133]. Similar conclusions have been reached in [108, 109]. The important issue in discussing odd-frequency amplitudes in [131] is not the presence of type D correlations per se, but their only presence. Thus, in diffusive structures those s-wave odd-frequency triplet pair amplitudes have a definite symmetry, and thus are of special interest for fundamental research. In regions where all amplitudes are mixed, simply all symmetries are absent, and a symmetry classification is not very useful. However, once such regions are coupled to reservoirs in which symmetries are asymptotically (far away from the spatial regions where the symmetry breaking takes place) re-established, then it is useful to discuss processes at interfaces in the light of those asymptotic symmetries.

To date it remains a great challenge to find direct experimental verification of the odd-frequency symmetry. There have been a number of proposals for indirect experimental verification via tunneling density of states studies, by inducing odd-frequency triplet superconducting correlations in a normal metal [134–136].

The odd-frequency pairing aspect in superconductor ferromagnet heterostructures was reviewed in [73]. A recent review dealing with odd-frequency pairing states and their relation to topological edge states can be found in [137]. Newer developments in finding odd-frequency order parameters include odd-frequency pairing states in multi-band superconductors [138], at the surface of topological insulators [139], and in two-particle Bose–Einstein condensates [140], as well as odd-frequency density wave states [141].

Odd-frequency symmetry requires that the equal time pair correlator vanishes, i.e. electrons in a pair avoid each other in time. It has been argued that in such a case certain particle-hole symmetries based on a Green function approach are not appropriate and a Lagrangian formalism must be used [142, 143]. In particular, these arguments were brought forward for homogeneous odd-frequency states with an odd-frequency pair potential appearing due to spontaneous symmetry breaking. However, these arguments do not take into account that symmetries following from the full many body Hamiltonian of the system are fundamental. Should they be violated in a model Lagrangian approach, for which a corresponding model Hamiltonian cannot be found, then this simply means that the model Lagrangian is not appropriate for the problem in question [144]. It has also been pointed out that spatially homogeneous odd-frequency states might be thermodynamically unstable in reality [145].

3. Magnetically active interfaces

3.1. Scattering phase delays

Let us consider the basic quantum mechanical problem of a (quasi-)particle being reflected from an insulating region (which we assume at \( x > 0 \), potential \( V \)). Let us assume the particle has energy \( 0 < E < V \) with \( E = (k^2 + k_y^2)/2m = V + (-k^2 + k_y^2)/2m \), and thus \( k(E) = [2m(V - E + k_y^2)]^{1/2} \), \( k(E) = [2mE - k_y^2]^{1/2} \). It is described by a wave function \( \Psi(x, r) = e^{ikx} \Psi(x, r) \) at \( x < 0 \) and \( \Psi(x, r) = e^{ikx} e^{-ikx} \) at \( x > 0 \). The reflection amplitude for such a process is \( r = (k - ik)/(k + ik) = e^{-2i\arctan(k/k)} \), where \( k \) is the momentum component perpendicular to the interface.
and $\kappa$ determines the exponential decay of the wave function in the insulating region. In the limit for large $\kappa$ the reflected wave is flipped by $\pi$ with respect to the incoming wave. For finite $\kappa$ there is a phase delay with respect to this, given by $\varphi(E) = \pi - 2 \arctan(\kappa / k)$. This phase delay results from the fact that the particle penetrates the insulator over a length scale $\hbar / \kappa$, and it corresponds to a time delay between the maximum of an incoming wave packet and the corresponding reflected wave packet [146] of $\tau_d = h \delta \varphi(E) = 2m \hbar / (k \kappa)$ (accompanied by a Goos–Hänchen shift along the interface of $s = 2 \hbar k / (k \kappa)$ [147]).

3.2. Spin-mixing angle and spin-dependent scattering phase shifts

We now assume that an exchange field $\mathbf{J}$ is present, leading to a contribution to the Hamiltonian given by $\mathcal{H}_{\text{exch}} = - J \cdot \mathbf{\sigma}$. This can also be written as $\mathcal{H}_{\text{exch}} = - \mu \mathbf{B}_{\text{eff}} \cdot \mathbf{\sigma}$, with $\mathbf{B}_{\text{eff}} = \mathbf{J} / \mu$, and $\mu$ is the (effective) magnetic moment of the charge carriers (negative for free electrons). Let us now consider a ferromagnetic insulating region, so that the two spin directions $\sigma$ have different reflection amplitudes $r_{\sigma} = (k - i \kappa_{\sigma}) / (k + i \kappa_{\sigma}) = e^{- 2 i \arctan(\kappa_{\sigma} / k)}$, with $\Psi_{\sigma} \sim e^{- e \sigma}$ in the ferromagnetic insulating region (see figure 7). As throughout this review, we take the spin quantization axis along the exchange field, i.e. $\sigma_{\text{exch}}(E) = [2m(V - E - \sigma J) + k]^2 / 2$, such that the majority Fermi surface is assigned spin projection $\sigma = 1^6$. The scattering phase delays now are spin dependent, $\varphi(\sigma) = \pi - 2 \arctan(\kappa_{\sigma} / k)$, and we can define a quantity $\vartheta = \varphi_1 - \varphi_0$, which is called spin-mixing angle [148] or spin dependent interface scattering phase shift [149] in the literature (it is associated with a delay time $\tau_0 = h \delta \varphi(\sigma(0)) = 2m \hbar / (\kappa_1 k) - 2m \hbar / (\kappa_0 k)$ between the two spin components). For our example we have $\kappa_1 < \kappa_0$, and consequently $\vartheta > 0$, $\tau_0 > 0$. Together with the spin-independent averaged phase $\varphi = (\varphi_1 + \varphi_0) / 2$, we write the reflection amplitude in a more general way as [148]

$$r(\varphi, \vartheta, \mathbf{n}) = - e^{i \vartheta} \cdot e^{i \varphi}$$

(16)

with respect to a spin quantization axis $\mathbf{n}$. The spin-mixing angle also describes the rotation angle of the spin components perpendicular to the axis $\mathbf{n}$ under reflection. This can be interpreted as a precession that the spins undergo around the axis $\mathbf{n}$ as a result of quantum mechanical penetration into the magnetic and insulating region.

If one considers the Cooper instability in the presence of an interface with a ferromagnetic insulator, it becomes clear that pairing near the interface will be affected by these spin-mixing angles. In particular, a spin-up electron with momentum pointing towards the interface will have a relative phase shift with respect to a spin-down electron with momentum pointing away from the interface if the Cooper pair volume overlaps with the interface region. As the Cooper pair’s size is determined by the superconducting coherence length, Cooper pairs in a layer that extends a coherence length from the interface into the bulk will feel the spin-mixing phase shifts of the interface. This is shown in figure 8 on the right. Near the interface, only a singlet-triplet mixed Cooper pair of the form

$$\left( |1^1 e^{i \vartheta} - 1^1 e^{- i \vartheta} \right) \equiv \cos(\vartheta)|0, 0\rangle + i \sin(\vartheta)|1, 0\rangle$$

(17)

can be present. According to this, we can consider the parameter $\vartheta$ also as the parameter that governs the degree of singlet-triplet mixing at a spin-active interface. As seen in figure 8, there is a certain analogy between the creation of FFLO correlations in a ferromagnetic metal and the creation of singlet-triplet mixtures
near a magnetically active interface in a superconductor. The role of the phase $Q_J$ in the former is played by the spin-mixing angle $\theta$ in the latter. As demonstrated in the middle column of figure 8, with increasing spin polarization of the ferromagnet in a superconductor-ferromagnet heterostructure, a shift from the creation of FFLO correlations in the ferromagnet to the creation of singlet-triplet mixtures in the superconductor takes place. This is because for very weak spin polarizations, the spin-mixing angle of the interface usually is of similarly small order and should be neglected in a consistent expansion in small parameters of the theory. For strong spin-polarization it is important and must be taken into account. The FFLO correlations in the ferromagnet show an inverse behavior: they are important for weak spin polarizations, however are restricted to atomically small distances from the interface for strongly spin-polarized ferromagnets.

The presence of spin-mixing angles has many consequences. For example, it leads to Andreev bound states at the interface, as predicted theoretically [151–156], and verified experimentally [157]. It also is responsible for giant thermoelectric effects in non-local setups [158, 159] and is the main ingredient for creating triplet supercurrents in strongly spin-polarized ferromagnets [133, 152]. It also crucially affects point contact spectra [155, 160–166]. Finally, it is the main cause of the inverse proximity effect and the magnetic proximity effect in strongly spin polarized hybrid structures [133, 152, 167, 169].

### 3.3. Scattering matrix and induced triplet correlations

The interface scattering matrix connects incoming Bloch waves with outgoing Bloch waves at an interface between two itinerant electron materials (metals, half metals, itinerant ferromagnets), or at a surface of such a material with an insulator. Relevant for transport are Bloch waves with energy close to the Fermi energy and momentum close to the Fermi momentum, in which case the Bloch waves are assumed to describe quasiparticle excitations. ‘Incoming’ and ‘outgoing’ refers to the projection of the quasiparticle’s Fermi velocity on the surface normal. We distinguish between electron-like and hole-like quasiparticles. For electron-like quasiparticles the projection of the group velocity on the Fermi momentum is positive, for hole-like quasiparticles it is negative. This means that electron-like and hole-like quasiparticles associated with the same Fermi momentum have opposite group velocity projections on the surface normal and consequently have different scattering matrices. For atomically ordered interfaces the crystal momentum component parallel to the interface, $\hbar \mathbf{p}$, is conserved, and then the relation between hole (h) and electron (e) like scattering matrices is

$$
\begin{bmatrix}
S_{\mathbf{h}}^1 & S_{\mathbf{h}}^2 \\
S_{\mathbf{e}}^1 & S_{\mathbf{e}}^2
\end{bmatrix} = \begin{bmatrix}
\hat{R} & \hat{T} \\
\hat{T} & -\hat{R}
\end{bmatrix}
$$

In relation to superconductivity, it is sufficient to consider the normal state scattering matrix for quasiparticles at Fermi momentum and Fermi energy. This results from a systematic classification of all terms during a perturbation expansion in the small phase space volume associated with quasiparticles, which leads to quasiclassical theory of superconductivity [185, 193]. In terms of the normal-state scattering matrix,
we can study the superconducting amplitudes induced by the presence of a singlet pair potential on either side of the interface. To simplify algebra and to gain some intuition we limit ourselves to the case of small pair amplitudes, in which case one can linearize the boundary conditions in the pair amplitudes. In our notation, \( \hat{R}_1 \) describes reflection into the superconductor, and \( \hat{R}_2 \) describes reflection into the ferromagnet. All reflection and transmission parameters in equation (18) are 2 x 2 spin matrices. We consider the ballistic case, for which the reflected and transmitted pair amplitudes \( f_{\text{out}}, f_{\text{out}}^{\text{FM}} \) are given in terms of the incoming singlet pair amplitude \( f_{\text{in}} = f_0 (i \sigma_y) \) by boundary conditions at the interface between the superconductor and the magnetic material, which in linear order read

\[
\begin{align*}
\tilde{f}_{\text{out}}^{\text{SC}} &= f_0 \hat{R}_1 (i \hat{\sigma}_y) \hat{R}_1^* \quad \text{(19)} \\
\tilde{f}_{\text{out}}^{\text{FM}} &= f_0 \hat{R}_2 (i \hat{\sigma}_y) \hat{T}_1^*.
\end{align*}
\]

The simplest case is that of total reflection from an interface with a magnetic insulator. In this case we have (choosing the quantization axis appropriately, and with a scalar phase \( \psi \))

\[
\hat{R}_1 = e^{i\psi} \begin{pmatrix} e^{\frac{\theta}{2}} & 0 \\ 0 & e^{-\frac{\theta}{2}} \end{pmatrix}.
\]

The reflected amplitudes for this case follow from equation (19) and are given by

\[
\tilde{f}_{\text{out}}^{\text{SC}} = [f_0 \cos(\theta) + i f_0 \sin(\theta) \hat{\sigma}_y] i \hat{\sigma}_y.
\]

(22)

This justifies the expression obtained by the simple arguments leading to equation (17).

Next, we consider the case of arbitrarily large pair amplitudes in a ballistic superconductor with spatially constant pair potential. This is justified for sufficiently small spin-mixing angles \( \theta \). Incoming and reflected directions are parameterized by the polar angle \( \theta_{\hat{\mathbf{r}}} \), measured from the surface normal. The cosine of this angle is called \( \mu \). Defining even parity (symmetric) and odd parity (antisymmetric) functions with respect to the propagation direction, \( f^* = [f(\mu) - f(-\mu)]/2 \) and \( f^t = [f(\mu) + f(-\mu)]/2 \), we obtain all four possible symmetry components as summarized in table 1. It can be seen that the corrections to the singlet amplitudes are \( \sim \sin^2(\theta/2) \). Thus, to linear order in \( \theta \) the pair potential stays unaffected. With increasing \( \theta \) the singlet pair potential is reduced, leading to corrections to the expressions in table 1.

For the case of an interface with a strongly spin-polarized ferromagnet, one has to consider Fermi surface geometry, due to the presence of different Fermi surfaces for the two spin projections in the ferromagnet. Various cases can occur, depending on the scattering channel (parameterized in the ballistic case by \( p_0 \), see figure 9); for example for reflection from the interface on the superconducting side, there can occur total reflection from the ferromagnet, total reflection of only one spin component from the ferromagnet (so-called half-metallic channels), or partial reflection for both spin components. Depending on the geometry of the Fermi surface in the superconductor, one, two, or all three cases may occur.

For illustrative purposes we will consider a simple model of an interface potential of width \( d \) between a superconductor and a ferromagnet, with corresponding (free) electronic dispersions \( V_{\text{Fermi}} + k^2/2m \) in the superconductor, \( V_{\text{Fermi}} - A d + k^2/2m \) in the interface region, and \( V_{\text{Fermi}} - A d + k^2/2m \) in the ferromagnet. If the magnetization in the interface region is collinear with that in the ferromagnet, there will be no transmitted pair amplitudes, as for a strongly spin-polarized ferromagnet only up and down spins are supported, which both are not generated in such a system. There is, however, an induced triplet component on the superconducting side, with spin projection zero on the spin quantization axis. It is shown in figure 10, for the case of a strongly spin polarized ferromagnet in (a), and for the case of a half-metallic ferromagnet (with only spin projection \( \sigma = 1 \) itinerant) in (b). When the barrier is absent, there is no induced triplet component for the regions connecting wave vectors that support Bloch waves for both spin projections. Only wave vectors for which maximally one spin projection in the ferromagnet supports Bloch waves contribute to the induced triplet amplitudes in the superconductor. This shows that for high-transmission contacts half-metallic ferromagnets are most effective for including triplet correlations in the superconductor. If a spin-polarized barrier is present, triplet amplitudes are created also in the barrier region, and their sign depends on the relative size of the Fermi surfaces.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Even frequency</th>
<th>Odd frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Even parity</td>
<td>Type A, singlet ([0, 0])</td>
<td>Type D, triplet ([1, 0])</td>
</tr>
<tr>
<td>( f_0^e = \frac{\pi \Omega_\text{e} \Delta (1 - \sin^2 \frac{\theta}{2})}{\Omega_\text{e}^2 -</td>
<td>\Delta</td>
<td>^2 \sin^2 \frac{\theta}{2}} )</td>
</tr>
<tr>
<td>Odd parity</td>
<td>Type C, triplet ([0, 0])</td>
<td>Type B, singlet ([0, 0])</td>
</tr>
<tr>
<td>( f_0^a = \frac{-i \pi \Omega_\text{e} \Delta \frac{1}{2} \sin \theta}{\Omega_\text{e}^2 -</td>
<td>\Delta</td>
<td>^2 \sin^2 \frac{\theta}{2}} )</td>
</tr>
</tbody>
</table>

Note: Here, \( \Omega_\text{e} = \sqrt{[\Delta]^2 + r_\text{e}^2}, \theta \equiv \theta(\mu), \) and \( \psi = \text{sign}(\mu) \) (\( \mu \) is the cosine of the impact angle). From supplementary material of [133].
in the superconductor and in the ferromagnet. In the tunneling limit, the creation of triplet correlations happens mainly in the barrier region, such that they become insensitive to the Fermi surface geometry.

In order to allow for proximity induced triplet amplitudes in the ferromagnet, one needs an inhomogeneous non-collinear magnetization in the interface region. We study a simple model where the interface barrier is magnetized in direction perpendicular to the magnetization in the ferromagnet. We again assume a spin quantization axis in direction of the exchange field in the ferromagnet, which we take as the \( z \)-axis, and a barrier exchange field pointing along the \( x \)-axis in spin space. In figure 11 we show for two values of barrier thickness all triplet amplitudes generated in the superconductor and in the ferromagnet. For each value of barrier thickness we show three representative Fermi surface geometries. In the ferromagnet the spin bands support only triplet amplitudes of the form \( f^{\text{FM}}_{\downarrow \downarrow} \) and \( f^{\text{FM}}_{\uparrow \uparrow} \), whereas in the superconductor we show all three triplet amplitudes \( f^{\text{SC}}_{\downarrow \downarrow}, f^{\text{SC}}_{\downarrow \uparrow}, f^{\text{SC}}_{\uparrow \uparrow} \) and \( f^{\text{SC}}_{\downarrow \downarrow} \) is purely imaginary.

It is interesting to note that for intermediate barrier thicknesses, also a component \( f^{\text{SC}}_{\downarrow \uparrow} \) is generated, although the magnetization always lies in the \( x-z \) plane. This is due to the fact that spins polarized in \( z \)-direction, precessing around the \( x \)-direction, develop a \( y \)-component (and similarly for spins polarized in \( x \)-direction and precessing around the \( z \)-direction). In a real gauge of the singlet pair potential, \( f^{\text{SC}}_{\downarrow \downarrow} \) and \( f^{\text{SC}}_{\downarrow \uparrow} \) are purely imaginary, and \( f^{\text{SC}}_{\uparrow \uparrow} \) is purely real. As a consequence, only the former two contribute to the magnetization in the superconductor.

Furthermore, depending on the barrier thickness, the vector of the triplet amplitudes in the superconductor changes direction rapidly as function of impact angle with respect to the surface normal. Only for tunneling barriers the direction of the triplet vector is dominated by the barrier exchange field.

---

**Figure 9.** Fermi surface geometry for a superconductor (left)-ferromagnet (right) interface. Various types of scattering events include total reflection (green), involvement of only one (blue) or of both spin bands (red). After [168], copyright (2009) by the American Physical Society.

**Figure 10.** Induced triplet components at a superconductor-ferromagnet interface with an interface barrier of width \( d \). Model free-electron dispersions are: \( V_s + k^2/2m \) (superconductor), \( V_b - \sigma J + k^2/2m \) (barrier), \( V_{\text{FM}} - \sigma J + k^2/2m \) (ferromagnet). The singlet amplitude in the superconductor is \( f_0 \), the induced triplet component is \( f_{\text{FT}} \) (and \( f_{\text{FT}}^0 \) is purely imaginary). The Fermi wavevectors for the spin bands in the ferromagnet are fixed in (a) and (b). The various curves correspond to various Fermi wavevectors in the superconductor (as illustrated in the top left diagram in each panel). Wavevectors are normalized to \( k_0 = \sqrt{2mE_F} \). For (a) \( V_b = 1.3, V_{\text{FM}} = 0.5, J = 0.2, V_s = 0 \) (black dashed-dotted), 0.5 (green full line), 0.9 (magenta dashed); for (b) \( V_b = 1.4, V_{\text{FM}} = 0.8, J = 0.3, V_s = 0 \) (black dashed-dotted), 0.5 (green full line), 0.9 (magenta dashed); energies are in units of the Fermi energy \( E_F \). (b) corresponds to a half-metallic ferromagnet, with only one spin projection itinerant (i.e. a Fermi surface exists only for \( \sigma = 1 \)).
Figure 11. Induced triplet components at a superconductor-ferromagnet interface with an interface barrier of width \( d \), spin polarized in \( x \)-direction, perpendicular to the ferromagnet’s spin polarization in \( z \)-direction. Other parameters are as in figure 10(a), with \( V_0 = 0, 0.5E_F, 0.9E_F \) for each thickness \( d \). The components shown are: in the superconductor \( f_{01}^{SC}(\vec{r}) = f_{01}^{SC}(\vec{r}) \) (black); \( f_{01}^{FM}(\vec{r}) \) (red).}

The equal-spin triplet amplitudes generated in the ferromagnet have opposite sign for the two spin projections. This reflects the fact that a triplet component with zero spin projection along the exchange field in the barrier region \((x\)-direction) decomposes into equal-spin pairs with respect to the \( z \)-direction with equal magnitude and opposite sign: \((\uparrow \downarrow + \downarrow \uparrow) = (\uparrow \downarrow + \downarrow \uparrow) \). Whereas in the tunneling limit the largest contributions to triplet amplitudes arise from near-normal impact, for thin barriers the dominating contributions arise from wavevectors that have for at least one spin projection evanescent solutions in the ferromagnet.

For a general orientation of the interface barrier exchange field we parameterize its direction by polar and azimuthal angles, \( \alpha \) and \( \varphi \), respectively, measured from the \( z \)-axis in spin space. The well-known transformation formulas for basis vectors quantized along the direction \( \alpha, \varphi \) in terms of basis vectors quantized along the \( z \)-axis read

\[
\begin{align*}
\uparrow_{\alpha, \varphi} & = \cos \frac{\alpha}{2} e^{-i \varphi} \uparrow_z + \sin \frac{\alpha}{2} e^{i \varphi} \downarrow_z \tag{23a} \\
\downarrow_{\alpha, \varphi} & = -\sin \frac{\alpha}{2} e^{-i \varphi} \uparrow_z + \cos \frac{\alpha}{2} e^{i \varphi} \downarrow_z \tag{23b}
\end{align*}
\]

and can be used to find the transformation for pair amplitudes, for example

\[
\begin{align*}
(\uparrow \downarrow - \downarrow \uparrow)_{\alpha, \varphi} & = (\uparrow \downarrow - \downarrow \uparrow) \tag{24a} \\
(\uparrow \uparrow + \downarrow \downarrow)_{\alpha, \varphi} & = -\sin \alpha \{e^{-i\varphi}(\uparrow \downarrow) - e^{i\varphi}(\downarrow \uparrow)\} + \cos \alpha (\uparrow \downarrow + \downarrow \uparrow) \tag{24b}
\end{align*}
\]

It can be seen from this that if a triplet component of the form \((24b)\) is created in the barrier region, it gives rise to \( f_{\uparrow \uparrow}^{FM} \) and \( f_{\downarrow \downarrow}^{FM} \) correlations in the ferromagnet with relative phase of \( \pi + 2\varphi \). This leads to a non-trivial current-phase relation in Josephson devices, in which two singlet superconductors are connected by the two spin bands of the ferromagnet, each with their own separate current-phase relation [168]. The azimuthal angle \( \varphi \) plays a crucial role in such devices [107, 133, 170].

For the case of a long-wavelength magnetic inhomogeneity one has to deal with the spatial variation of the pair amplitudes, which can be done within the framework of quantum transport equations, which we discuss in the next section. In general the scattering matrix should be calculated from first principles or from microscopic models, taking into account disorder, band anisotropy, and micromagnetics.

4. Theoretical tools

Theoretical treatments of superconductor-ferromagnet heterostructures can be separated into two types: microscopic treatments and quasiclassical treatments. There are two main methods, which both can be applied to the two types of theories: wave-function methods and Green function methods. Green function methods are based on an asymptotic expansion of the fundamental many-body Hamiltonian, whereas wave function methods work preferably with an effective mean-field Hamiltonian. Green function methods allow in an easier way for the treatment of disorder, and for generalization to strong coupling with bosonic excitations and to non-equilibrium situations. The resulting four theoretical frameworks with their corresponding equations of motion are shown in table 2. The Bogoliubov–de Gennes equations [9, 78] lead in quasiclassical approximation to the Andreev equations for the envelopes of the waves [83]. Alternatively, one can start from the microscopic Nambu–Gor’kov matrix Green functions obeying the Gor’kov equations [10, 171]. These lead in quasiclassical

---

In the following the scalar scattering phase \( \varphi \) will not appear any more in this review, such that no confusion with the azimuthal angle \( \varphi \) should arise.
approximation to the Eilenberger–Larkin–Ovchinnikov equations \[172, 173\], where the concepts of BCS pairing theory of superconductors \[8\] were merged with the concepts of Boltzmann transport equations within Landau’s Fermi-liquid theory \[174\]. An extension to non-equilibrium was developed by Eliashberg \[175\] and by Larkin and Ovchinnikov \[176\]. In quasiclassical approximation the Gor’kov equations result into envelope Green functions that vary on the superconducting coherence length scale and are free of irrelevant fine-scale structures on the Fermi wavelength scale. Dynamical phenomena are described in Green function methods within the Keldysh technique \[177\].

In this review we concentrate on two, which have been mostly used so far in the literature: microscopic wave function methods based on the Bogoliubov–de Gennes equations, and quasiclassical Green function methods, based on Eilenberger–Larkin–Ovchinnikov equations and their counterpart for diffusive systems, the Usadel equations. The two frameworks, not covered in this review, are formulated in terms of Andreev equations and in terms of Gor’kov equations.

### 4.1. Bogoliubov–de Gennes equations

The Hartree–Fock–Bogoliubov (HFB) mean-field Hamiltonian

\[ \mathcal{H}_{\text{HFB}} = \int d^3r \left( \sum_{n, \alpha} \left( \mathcal{H}_{\text{HF}, n, \alpha} \Psi_n^\dagger \Psi_n + \frac{1}{2} \Delta_{\text{HF}, n, \alpha} \Psi_n^\dagger \Psi_n^\dagger + \frac{1}{2} \Delta_{\text{HF}, n, \alpha} \Psi_n \Psi_n^\dagger \right) \right) \]

is the basis for the Bogoliubov–de Gennes theory. Hermiticity requires \( \mathcal{H}_{\text{HF}, n, \alpha} = \mathcal{H}_{\text{HF}, n, -\alpha} \), and Fermi statistics leads to \( \Delta_{\text{HF}, n, \alpha} = -\Delta_{\text{HF}, n, -\alpha} \). The Hamiltonian can be rewritten in a compact form using the 4×4 matrix

\[ \hat{\mathcal{H}}(\mathbf{r}, \mathbf{r}’) \equiv \begin{pmatrix} [\mathcal{H}_{\text{HF}, n, \alpha}]_{2 \times 2} & [\Delta_{\text{HF}, n, \alpha}]_{2 \times 2} \\ -[\Delta_{\text{HF}, n, \alpha}]_{2 \times 2} & [-\mathcal{H}_{\text{HF}, n, \alpha}]_{2 \times 2} \end{pmatrix} \]  

where, for example,

\[ [\mathcal{H}_{\text{HF}, n, \alpha}]_{2 \times 2} = \begin{pmatrix} H_{\text{HF}, n, \alpha} & H_{\text{HF}, n, \alpha}^\dagger \\ H_{\text{HF}, n, \alpha}^\dagger & H_{\text{HF}, n, \alpha} \end{pmatrix} \]  

With the definitions \( \hat{\Psi}^\dagger(\mathbf{r}) = (\Psi_{\alpha, \mathbf{r}}, \Psi_{\alpha, \mathbf{r}}^\dagger, \Psi_{\alpha, \mathbf{r}}, \Psi_{\alpha, \mathbf{r}}^\dagger)^\dagger \) (here T denotes a transpose) the Hartree–Fock–Bogoliubov Hamiltonian reads

\[ \mathcal{H}_{\text{HFB}} = \frac{1}{2} \int d^3r d^3r’ (\hat{\Psi}^\dagger(\mathbf{r}) \hat{\mathcal{H}}(\mathbf{r}, \mathbf{r}’) \hat{\Psi}(\mathbf{r}’)) + \text{const.} \]  

This Hamiltonian is diagonalized by a Bogoliubov–Valatin transformation \[178, 179\]. To achieve this, we introduce the notation for the Bogoliubov amplitudes \((\alpha \in \{+, -\})\)

\[ U_{\alpha \alpha}(\mathbf{r}) \equiv \begin{pmatrix} u_{\alpha, n, \alpha} & v_{\alpha, n, \alpha}^\dagger \\ v_{\alpha, n, \alpha} & u_{\alpha, n, \alpha}^\dagger \end{pmatrix}, \quad \hat{U}_{\alpha \alpha}(\mathbf{r}) \equiv \begin{pmatrix} v_{\alpha, n, \alpha} & u_{\alpha, n, \alpha}^\dagger \\ u_{\alpha, n, \alpha} & v_{\alpha, n, \alpha}^\dagger \end{pmatrix} \]

Here, the index \( \alpha \) may, e.g. refer to another spin basis, or to a helicity basis if strong spin–orbit interactions are present. The quantum numbers \( n, \alpha \) fully characterize the eigenstates of the set of Bogoliubov–de Gennes equations given by

\[ \int d^3r’ \hat{\mathcal{H}}(\mathbf{r}, \mathbf{r}’) U_{\alpha \alpha}(\mathbf{r}) = E_{\alpha \alpha} U_{\alpha \alpha}(\mathbf{r}) \]  

\[ \int d^3r’ \hat{\mathcal{H}}(\mathbf{r}, \mathbf{r}’) \hat{U}_{\alpha \alpha}(\mathbf{r}) = -E_{\alpha \alpha} \hat{U}_{\alpha \alpha}(\mathbf{r}). \]

For each eigenvalue \( E_{\alpha \alpha} > 0 \) there exists an eigenvalue \( -E_{\alpha \alpha} \), with corresponding eigenvectors obtained by the substitution \( u_{\alpha, n, \alpha} \rightarrow v_{\alpha, n, \alpha}, v_{\alpha, n, \alpha} \rightarrow u_{\alpha, n, \alpha}^\dagger \). One can divide the quantum numbers \( n \) in disjoint sets \( \mathcal{Z}, \mathcal{P} \) and \( \mathcal{N} \) (and relabel them if necessary) such that for \( n \in \mathcal{Z} \) we have \( E_{\alpha \alpha} = 0 \), for \( n \in \mathcal{P} \) we have \( E_{\alpha \alpha} > 0 \) and for \( n \in \mathcal{N} \) we have \( E_{\alpha \alpha} < 0 \). The eigenvectors can be chosen to build an orthonormal set, e.g. for \( n, n’ \) within \( \mathcal{P} \)

\[ \int d^3r \sum_{\alpha} (u_{\alpha, n, \alpha}^\dagger v_{\alpha, n’, \alpha}^* + v_{\alpha, n, \alpha} u_{\alpha, n’, \alpha}^\dagger) = \delta_{n n’} \delta_{\alpha \alpha’}. \]

\[ \int d^3r \sum_{\alpha} (u_{\alpha, n, \alpha} v_{\alpha, n’, \alpha}^* + v_{\alpha, n, \alpha} u_{\alpha, n’, \alpha}^\dagger) = 0. \]

We build for \( n \in \mathcal{P} \) a 4×4 matrix \( \hat{\mathcal{U}}_n(\mathbf{r}) \) from the four orthogonal eigenvectors \( U_{\alpha \alpha}(\mathbf{r}), U_{\alpha’ \alpha’}(\mathbf{r}), \hat{U}_{\alpha \alpha}(\mathbf{r}), \hat{U}_{\alpha’ \alpha’}(\mathbf{r}) \) (or a 4×2 matrix if only one value for \( \alpha \) belongs to \( n \)). Similarly, for \( n \in \mathcal{Z} \) we have build a 4×2 matrix \( \hat{\mathcal{U}}_n(\mathbf{r}), \hat{U}_{\alpha \alpha}(\mathbf{r}) \) (or a 4×1 matrix if only value for \( \alpha \) belongs to \( n \)). Then the completeness relation

\[ \sum_{n \in \mathcal{P}} \hat{\mathcal{U}}_n(\mathbf{r}) \hat{\mathcal{U}}_n^\dagger(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}’) \hat{1} \]

(with the 4×4 unit matrix \( \hat{1} \) and with \( \mathcal{P} = \mathcal{Z} \cup \mathcal{P} \)), which reads explicitly

\[ \sum_{n \in \mathcal{P} \setminus \mathcal{Z}} (u_{\alpha, n, \alpha}^\dagger v_{\alpha, n’, \alpha}^* + s_{\alpha} v_{\alpha, n, \alpha}^\dagger u_{\alpha, n’, \alpha}) = \delta_{\alpha \alpha'} \delta(\mathbf{r} - \mathbf{r}’). \]

\[ \sum_{n \in \mathcal{P} \setminus \mathcal{Z}} (u_{\alpha, n, \alpha} v_{\alpha, n’, \alpha}^* + s_{\alpha} u_{\alpha, n, \alpha}^\dagger v_{\alpha, n’, \alpha}) = 0. \]

\( s_{\alpha} = 0 \) for \( n \in \mathcal{Z}, s_{\alpha} = 1 \) else. With this, the Hartree–Fock–Bogoliubov Hamiltonian is diagonalized by

\[ \hat{\Psi}(\mathbf{r}) = \sum_{n \in \mathcal{P}} \hat{\mathcal{U}}_n(\mathbf{r}) \hat{\Psi}_n, \quad \hat{\Psi}_n = \int d^3r \hat{\mathcal{U}}_n^\dagger(\mathbf{r}) \hat{\Psi}(\mathbf{r}). \]
with, e.g., $\gamma_{\sigma}^{\pm} = \left( \gamma_{\sigma}^{+}, \gamma_{\sigma}^{-} \right)$ denoting the Bogoliubov quasiparticle operators and $\hat{E}_{\sigma} \equiv \text{diag}(E_{+}, E_{-}, -E_{+}, -E_{-})$ correspondence energies, leading to

$$\hat{H}(\mathbf{r}, \mathbf{r}') = \sum_{n \in P} \hat{U}_{n}(\mathbf{r}) \hat{E}_{\sigma} \hat{U}_{n}^{\dagger}(\mathbf{r}')$$  \hspace{1cm} (35)

$$\mathcal{H}_{\text{HFB}} = \frac{1}{2} \sum_{n \in P} \gamma_{\sigma}^{\pm} \hat{E}_{\sigma} \gamma_{\sigma}^{\mp}.$$  \hspace{1cm} (36)

Explicitly, equation (34) reads

$$\psi_{\sigma}(\mathbf{r}) = \sum_{n \in P} \left( u_{\sigma,n} \psi_{\sigma,n}^{+} + v_{\sigma,n} \psi_{\sigma,n} \right)$$  \hspace{1cm} (37a)

$$\gamma_{\sigma} = \int d^{3}r \sum_{\sigma} \left( u_{\sigma,n} \psi_{\sigma}^{+} + v_{\sigma,n} \psi_{\sigma} \right).$$  \hspace{1cm} (37b)

The Majorana property $\gamma_{\sigma} = \gamma_{\sigma}^{\dagger}$ holds if $\psi_{\sigma,n} = u_{\sigma,n} \psi_{\sigma,n}^{+}$ for $n \in \mathbb{Z}$ a solution of the Bogoliubov–de Gennes equations can always be chosen of this form provided this is compatible with the boundary conditions. The single-particle part $H_{\text{HFB},\sigma}$ of $H_{\text{HFB}}^{\text{even}}$ has typically the form

$$H_{\text{HFB},\sigma}^{\text{even}} = \delta(\mathbf{r} - \mathbf{r}') \varrho(\mathbf{r}) \mathcal{P} - \mu + g(\mathbf{P}) \cdot \mathbf{r} - h(\mathbf{r}) \cdot \mathbf{a}$$  \hspace{1cm} (38)

with $\varrho = -i \hbar \nabla - e A(\mathbf{r})$. Here, $\varrho(\mathbf{P})$ is even in $\mathbf{P}$ and $g(\mathbf{P})$ is odd in $\mathbf{P}$. The last two terms in equation (38) describe spin–orbit coupling and Zeeman coupling, and $\mu$ is the electrochemical potential. The order parameter is given self-consistently by

$$\Delta_{\text{HFB},\sigma}^{\text{even}} = \int d^{3}r d^{3}r' \sum_{\sigma \neq \bar{\sigma}} \mathcal{V}(\sigma, \bar{\sigma}) \varrho(\mathbf{r}, \mathbf{r}', \mathbf{n}, \mathbf{r}) \langle \psi_{\sigma}(\mathbf{r}) | \psi_{\bar{\sigma}}(\mathbf{r}) \rangle$$  \hspace{1cm} (39)

with

$$\langle \psi_{\sigma}(\mathbf{r}) | \psi_{\bar{\sigma}}(\mathbf{r}) \rangle = -\frac{1}{2} \sum_{n \in P} \left( u_{\sigma,n} \psi_{\sigma,n}^{+} \right) \varrho_{\sigma,n}^{\dagger}.$$  \hspace{1cm} (40)

The spin-dependence of these equations simplifies when the pairing interaction can be split into singlet and triplet parts,

$$\mathcal{V}(\sigma, \bar{\sigma}) = \frac{1}{2} \langle \mathbf{i} \sigma \mathbf{i} \bar{\sigma} \rangle \varrho_{\sigma,\bar{\sigma}} + \frac{1}{2} \langle \mathbf{i} \sigma \mathbf{i} \bar{\sigma} \rangle \varrho_{\sigma,n}^{\dagger} \varrho_{\bar{\sigma}},$$  \hspace{1cm} (41)

and similarly for the order parameter

$$\Delta_{\text{HFB},\sigma}^{\text{even}} = \Delta_{\text{HFB},\sigma}^{\text{odd}} + \Delta_{\text{HFB},\sigma}^{\text{odd}}.$$  \hspace{1cm} (42)

The gap equation for spin singlet and triplet ferromagnetic superconductors has been scrutinized by Powell et al. [180]. In order to study odd-frequency amplitudes one uses a Heisenberg representation

$$\psi_{\sigma}(t) = \sum_{n \in P, \sigma} \left( u_{\sigma,n} \psi_{\sigma,n}^{+} + v_{\sigma,n} \psi_{\sigma,n} \right)$$  \hspace{1cm} (43)

and evaluates the pair correlation function [181]

$$F_{\sigma}(t) = \langle \psi_{\sigma}(t) | \psi_{\sigma}(0) \rangle$$  \hspace{1cm} (44)

using $\langle \psi_{\sigma}(t) | \psi_{\sigma}(0) \rangle = f(E_{\sigma n})$, $\langle \psi_{\sigma,n}^{+} | \psi_{\sigma} \rangle = 1 - f(E_{\sigma n})$, with $f(E_{\sigma n}) = [1 - \tanh(E_{\sigma n}/2k_{B}T)]/2$ the fermionic distribution function. Concentrating on local correlation functions, one obtains [181, 182]

$$F_{\sigma}(t, t') \equiv F_{\sigma,\tau}(t) \equiv F_{\sigma,\tau}(t)$$  \hspace{1cm} (45a)

$$F_{\sigma}(t) \equiv F_{\sigma}(t) = \sum_{n \in P, \sigma} u_{\sigma,n} \psi_{\sigma,n}^{+} \psi_{\sigma,n}(t, T)$$  \hspace{1cm} (45b)

for the singlet ($F_{\sigma}$) and the three triplet ($F_{\sigma1}$, $F_{\sigma1}$, $F_{\sigma1}$) components, where

$$\xi_{\sigma}^{\sigma}(t, T) \equiv \cos \left( \frac{E_{\sigma n}}{h} \right) \tanh \left( \frac{E_{\sigma n}}{2k_{B}T} \right) - i \sin \left( \frac{E_{\sigma n}}{h} \right).$$  \hspace{1cm} (46a)

$$\xi_{\sigma}^{\sigma}(t, T) \equiv \cos \left( \frac{E_{\sigma n}}{h} \right) - 1 - i \sin \left( \frac{E_{\sigma n}}{h} \right) \tanh \left( \frac{E_{\sigma n}}{2k_{B}T} \right)$$  \hspace{1cm} (46b)

The triplet correlators show a time dependence according to $\xi_{\sigma}^{\sigma}$ and consequently vanish identically for $t = 0$, whereas the singlet correlators, governed by $\xi_{\sigma}^{\sigma}$, survive. This expresses the odd-frequency nature of the local triplet pair correlations in contrast to the even-frequency nature of the local singlet pair correlations. In particular, for $t \rightarrow -it$ with $\hbar k_{B}T > \tau > 0$, and applying KMS boundary conditions $\xi_{\sigma}^{\sigma}(-it + i\hbar k_{B}T) = -\xi_{\sigma}^{\sigma}(-it, T)$, the relations $\xi_{\sigma}^{\sigma}(it, T) = \pm \xi_{\sigma}^{\sigma}(-it, T)$ follow.

Similarly, measurable quantities like magnetization, current density, and charge density can be expressed in terms of Bogoliubov quasiparticle operators using equation (37a) and evaluated using the solutions of the Bogoliubov–de Gennes equations.

4.2. Quasiclassical theory of superconductivity

The treatment of a superconductor in the presence of a Zeeman spin splitting induced by an external magnetic field has been theoretically investigated in detail by Alexander, Orlando, Rainer, and Tedrow in 1985 [183] within quasiclassical theory of superconductivity. This theory, a generalization of previous studies for superfluid $^3$He [110, 184, 185], includes Fermi liquid effects self-consistently, as well as impurity scattering (including ballistic and diffusive limits), internal exchange fields, and spin–orbit effects. It is formulated in terms of generalized Landau parameters $A^{\pm} \left( \hat{p}_{x}, \hat{p}_{z} \right)$ as well as singlet and triplet pairing interactions $V^{\pm} \left( \hat{p}_{x}, \hat{p}_{z} \right)$, based on Leggett’s treatment for clean systems [110, 184], and combines previous theories of Fulde [186] and Buchholtz and Zwicknagl [187]. First experimental tests of these theories were performed by Tedrow and Meservey [188]. Generalized Landau parameters lead for example to anisotropic renormalizations of the quasiparticle magnetic moment by coupling to

8 The derivation in this work is more rigorous than in the later work by Demler et al. in 1997 [90].
electrons outside the phase space regions where quasiparticles live (‘high-energy electrons’).

For reviews of quasiclassical theory of superconductivity see [185, 189–198]. Quasiclassical theory is an expansion in quantities like temperature or gap divided by Fermi energy, or Fermi wavelength divided by superconducting coherence length [185, 199–202]. It predicts its own breakdown in low dimensions [203].

The central quantity in quasiclassical theory of superconductivity is the quasiclassical $4 \times 4$ matrix propagator or Green function $\tilde{g}(\hat{p}_f, R; \epsilon)$, which depends on the spatial coordinate $R$, on energy $\epsilon$, and on the momentum directions $\hat{p}_f$ on the Fermi surface (out of equilibrium there is in addition a time dependence and the formalism can be extended to $8 \times 8$ Keldysh matrices [177]). The $2 \times 2$ Nambu–Gor’kov matrix structure of $\tilde{g}$ reflects the particle-hole degree of freedom [10, 171]. Its matrix elements are $2 \times 2$ spin matrices (if the spin-splitting of the energy bands is not comparable to the energy band width, otherwise they are scalar). We will use a notation of unit matrices and Pauli matrices in spin space and particle hole space, where $(\sigma_0, \sigma_2, \sigma_2)$ refers to spin and $(\hat{t}_0, \hat{t}, \hat{z}, \hat{h})$ to particle-hole degrees of freedom. We expand the elements in Nambu–Gor’kov space into spin-scalars and spin-vectors,

$$\tilde{g} = \left( \begin{array}{cc} g_{\sigma_0} + g \cdot \sigma & (f \sigma_0 + f \cdot \sigma)\sigma_2 \\ i\sigma_2 (f \sigma_0 - f \cdot \sigma) & \sigma_2 (g \sigma_0 - g \cdot \sigma)\sigma_2 \end{array} \right)$$

(47)

with e.g. $g = (g_{-\sigma_0}, g_{-\sigma_2}, g_{-\sigma_2})$ the vector part of $\hat{g}_{1\uparrow}$, and $g$ its scalar part. Of particular interest for this review are $f, \tilde{f}$, describing spin-triplet correlations, and $g, \tilde{g}$ describing the spin magnetization and the spin current that develop as a result of the generation of triplet correlations.

4.3. Eilenberger equations

We discuss first the case when the spin splitting of the energy bands is small (comparable to the superconducting energy scales), so that it can be treated as a perturbation around the un-split Fermi surface. In this case one can integrate out the energy dependence of the Green’s functions identically for the spins $\uparrow$ and $\downarrow$ [161] and assume spin-independent Fermi velocities $v_{\uparrow}(\hat{p}_f)$. The propagator $\tilde{g}$ obeys the Eilenberger transport equation [172, 173]

$$[\epsilon_{\uparrow} - \hat{h}, \tilde{g}] + \mathrm{i}\hbar v_{\uparrow} \cdot \nabla_{\hat{p}_f} \tilde{g} = 0$$

(48)

with the normalization condition [172]

$$\tilde{g}^2 = -\pi^2 \delta_{0\uparrow}$$

(49)

where $v_{\uparrow}(\hat{p}_f)$ is the Fermi velocity for the direction $\hat{p}_f$ at the Fermi surface, and with

$$\hat{h} = \hat{v}_{\mathrm{ext}} + \delta_{\mathrm{mf}} + \delta_{\mathrm{imp}}$$

(50)

where $\hat{v}_{\mathrm{ext}}$ are external potentials, $\delta_{\mathrm{mf}}$ are Fermi liquid mean fields (both diagonal and off-diagonal), and $\delta_{\mathrm{imp}}$ is the impurity self energy. The matrix $\hat{h}(\hat{p}_f, R; \epsilon)$ entering the Eilenberger equation (48) has a similar structure as $\tilde{g}$.

$$\hat{h} = \left( \begin{array}{cc} \nu \sigma_0 + \nu \cdot \sigma & (\Delta \sigma_0 + \Delta \cdot \sigma)\sigma_2 \\ i\sigma_2 (\Delta \sigma_0 - \Delta \cdot \sigma) & \sigma_2 (\tilde{\nu} \sigma_0 - \tilde{\nu} \cdot \sigma)\sigma_2 \end{array} \right)$$

(51)

The Nambu–Gor’kov matrix structure contains some redundancy, which results into symmetries between the particle and hole elements [185]. They are expressed by the tilde operation $\hat{q}(\hat{p}_f, R; \epsilon) = q(-\hat{p}_f, R; -\epsilon)^\ast$ for $q \in \{ g, f, g, f, \nu, \Delta, \nu, \Delta \}$. Matsubara propagators are obtained by $(\epsilon \rightarrow i\epsilon_0)$ (where $\epsilon_0 = \pi k_B T (2n + 1)$ is the Matsubara energy), retarded propagators by $(\epsilon \rightarrow \epsilon + i\delta)$, and advanced propagators by $(\epsilon \rightarrow \epsilon - i\delta)$. Further fundamental symmetry relations are: $g(\epsilon^\ast) = g(\epsilon)^\ast$, $g(\epsilon^\ast) = g(\epsilon)^\ast$, $f(\epsilon^\ast) = \tilde{f}(\epsilon)^\ast$, $f(\epsilon^\ast) = -\tilde{f}(\epsilon)^\ast$ (we omitted here for brevity the other arguments).

The self-consistency equations for the impurity self energy $\delta_{\mathrm{imp}}$ for impurity types $i$ with impurity potential $\tilde{v}_i$ and impurity concentration $n_i$ is

$$\delta_{\mathrm{imp}}(\hat{p}_f, R; \epsilon) = \sum_i n_i \tilde{v}(\hat{p}_f, \hat{p}_f, R; \epsilon)$$

(52)

with the quasiclassical $T$-matrix equation

$$\tilde{v}_i(\hat{p}_f, \hat{p}_f, R; \epsilon) = \tilde{v}(\hat{p}_f, \hat{p}_f, R; \epsilon) + \langle N_i(\hat{p}_f) \tilde{v}(\hat{p}_f, \hat{p}_f, R; \epsilon) \rangle \hat{p}_f$$

(53)

$$\langle \ldots \rangle = \int d^2 \hat{p}_f / (2\pi\hbar)^2 \ldots$$ denotes a Fermi-surface integral, and $N_i(\hat{p}_f) = (2\pi\hbar |v_{\uparrow}(\hat{p}_f)|)^{-1}$ is for a fixed Fermi surface point the (one-dimensional) density of states in perpendicular direction to the Fermi surface, per spin projection, in the normal state.

The Fermi-liquid mean-field self energies $\delta_{\mathrm{mf}}$ are self-consistently determined from

$$\nu_{\mathrm{mf}}(\hat{p}_f, R) = k_B T \sum_{\epsilon_n} \left\{ N_i(\hat{p}_f) W(\hat{p}_f, \hat{p}_f) \tilde{v}(\hat{p}_f, R; \epsilon_n) \right\} \hat{p}_f$$

(54a)

$$\nu_{\mathrm{mf}}(\hat{p}_f, R) = k_B T \sum_{\epsilon_n} \left\{ N_i(\hat{p}_f) \tilde{v}(\hat{p}_f, R; \epsilon_n) \right\} \hat{p}_f$$

(54b)

$$\Delta_{\mathrm{mf}}(\hat{p}_f, R) = k_B T \sum_{\epsilon_n} \left\{ N_i(\hat{p}_f) V(\hat{p}_f, \hat{p}_f) f(\hat{p}_f, R; \epsilon_n) \right\} \hat{p}_f$$

(54c)

$$\Delta_{\mathrm{mf}}(\hat{p}_f, R) = k_B T \sum_{\epsilon_n} \left\{ N_i(\hat{p}_f) V(\hat{p}_f, \hat{p}_f) \tilde{f}(\hat{p}_f, R; \epsilon_n) \right\} \hat{p}_f$$

(54d)

Fermi-liquid interactions are parameterized by dimensionless Fermi-liquid parameters $A'(\hat{p}_f, \hat{p}_f) = N_i W(\hat{p}_f, \hat{p}_f)$ and $A'(\hat{p}_f, \hat{p}_f) = N_i W(\hat{p}_f, \hat{p}_f)$, with $N_i = \langle N_i(\hat{p}_f) \rangle \hat{p}_f$ the density of states per spin projection at the Fermi level, and the superconducting pair potentials by singlet and triplet pairing interactions $V$ and $V'$ (where $W$, $A'$, and $V'$ are in general tensors).
Finally, $\hat{\nu}_{\text{ext}}$ contains the coupling to external fields, for example the electro-magnetic coupling to a magnetic vector potential $A(R)$,

$$\nu_{\text{Electr}}(\hat{p}_{j}, R) = -e v f_{j}(\hat{p}_{j}) \cdot A(R) \hat{\sigma}$$  

(55)

$e = -|e|$, and the Pauli-coupling to the quasiparticle spin

$$\nu_{\text{Pauli}}(\hat{p}_{j}, R) = -B(R) \cdot \mu_{\text{eff}}(\hat{p}_{j}) \cdot \hat{\sigma}$$  

(56)

with the effective quasiparticle magnetic moment

$$\mu_{\text{eff}}(\hat{p}_{j}) = [\hat{1} - A^{\dagger}(\hat{p}_{j})] \mu_{e}$$  

(57)

where $A^{\dagger}(\hat{p}_{j}) = N_{f}^{-1}(N_{f}(\hat{p}_{j})A^{\dagger}(\hat{p}_{j} \hat{p}_{j})\hat{p}_{j}$, and the spin matrix in particle-hole space

$$\hat{\sigma} = \begin{pmatrix} \sigma & 0 \\ 0 & -\sigma \sigma_{2} \end{pmatrix}$$  

(58)

$\mu_{e}$ is the electron magnetic moment ($\mu_{e} = -|\mu_{e}|$). The vector potential $A$ and hence the magnetic field ($B = \nabla \times A$) are calculated from the current density as

$$\nabla \times \nabla \times A(R) = \mu_{e} j(R)$$  

(59)

with the permeability of free space $\mu_{0}$. The scalar electrochemical potential follows from local charge quasi-neutrality, and is zero in equilibrium. The charge current density is obtained from $g(\hat{p}_{j}, R; e_{a})$ via

$$j(R) = 2e k_{B} T \sum_{e_{a}} \left\{ N_{f}(\hat{p}_{j}) w_{j}(\hat{p}_{j}) g(\hat{p}_{j}, R; e_{a}) \right\} \hat{p}_{j}$$  

(60)

the spin current density for spin projection along the axis $e_{a}$ via

$$J_{s}(R) = 2e k_{B} T \sum_{e_{a}} \left\{ N_{f}(\hat{p}_{j}) w_{j}(\hat{p}_{j}) \sigma_{a} g(\hat{p}_{j}, R; e_{a}) \right\} \hat{p}_{j}$$  

(61)

and the spin magnetization via

$$M(R) = \sum_{e_{a}} B(R) + 2k_{B} T \sum_{e_{a}} \left\{ N_{f}(\hat{p}_{j}) \mu_{\text{eff}}(\hat{p}_{j}) \sigma_{a} g(\hat{p}_{j}, R; e_{a}) \right\} \hat{p}_{j}$$  

(62)

where $\mu_{\text{eff}} = 2N_{f}(1 - A_{0}^{\dagger}) \mu_{e}^{2}$ is the normal state spin susceptibility, defined in terms of the parameter $A_{0}^{\dagger} = N_{f}^{-1}(N_{f}(\hat{p}_{j})A^{\dagger}(\hat{p}_{j})\hat{p}_{j}$. The local density of states for a given spin direction $e$ is calculated at real energies as

$$N_{f}(\hat{p}_{j}, R; e_{a}) = -\frac{1}{\pi} \text{Im} \left\{ N_{f}(\hat{p}_{j}) g(\hat{p}_{j}, R; e_{a}) + e \cdot g(\hat{p}_{j}, R; e_{a})\right\} \hat{p}_{j}$$  

(63)

with $e_{a} = e + i \delta$ ($\delta > 0$ infinitesimal). The Eilenberger equation for $\hat{g}$, its normalization condition, the equations for the self energies $\hat{\sigma}$, and Maxwell’s equation for $A$, must be solved self consistently by iteration together with the appropriate boundary conditions imposed on the propagator and the vector potential [204–208]. Boundary conditions in quasiclassical theory

$^{9}$\(\hat{1}\) denotes a 3 x 3 unit tensor.

$^{10}$\(\mu_{e} = -\mu_{0}/2\) with the Bohr magneton $\mu_{0} = |e|/2m_{e}c$ and $g = 2.0$.

Figure 12. In quasiclassical approximation boundary conditions involve relations between the envelope functions of Bloch waves on the two sides of an interface. These envelope functions in general show a jump, even when the Bloch wave functions themselves are continuous.

are notoriously difficult to derive, as the quasiclassical propagators show in general jumps at interfaces (see figure 12), in contrast to microscopic propagators which are continuous.

A powerful way to implement boundary conditions and to solve Eilenberger equations is the Riccati method [209–212]. Modern versions of boundary conditions for Eilenberger equations using these techniques are presented e.g. in [151, 211–213]. Instead of applying an external field $B(R)$, a superconductor can be spin-polarized via the inverse (or magnetic) proximity effect when in contact with a ferromagnetic material. This effect already appears when the ferromagnet is insulating. A theory for the spin polarization and the associated induced exchange field in the superconductor has been developed by Tokuyasu et al in 1988 [148]. Although differing in details, the general mechanism presented there is essentially the same as for all subsequent studies of the inverse proximity effect in superconductor/ferromagnet heterostructures in the last decade: the appearance of a Cooper pair spin polarization, or of triplet pair correlations, in the superconductor creates a finite spin magnetization inside the superconducting region, extending roughly a coherence length away from the interface. This decay length is dictated by the decay of triplet pair correlations as the bulk of the singlet superconductor is approached.

4.4. Normalization condition and transport equation in spin-space

The interrelation between triplet amplitudes and induced magnetic moment can be understood within quasiclassical theory already by the normalization condition for the propagator. The normalization condition (49) encodes important information about the spin structure of the diagonal and off-diagonal propagators [214]. In equilibrium, physical solutions require the condition

$$\text{Tr}(\hat{g}) = 0, \text{ i.e. } \hat{g}_{0} = -g_{0}$$  

(64)

which also ensure local charge neutrality to leading order in the Fermi liquid expansion parameters. It is useful to introduce the notation $g_{\pm} = (g \pm \delta/2)$, $\nu_{\pm} = (\nu \pm \delta)/2$, $\nu_{\pm} = (\nu \pm \delta)/2$. The
external and internal fields are distributed according to: $v_{\text{orbital}}$ in $\nu_z$, $v_{\text{spin}}$ in $\nu_x$, which also contains the internal exchange field $J$; spin–orbit band splitting in $\nu_x$. In terms of measurable quantities, $g_z$ determines the magnetization, $g_y$ the spin current density, and $g_y$ the charge current density. One obtains from (49) and (64) for the spin components in (47) [214]

\[ g_z^2 + \pi^2 = f_f - f - g_z^2 \]

(65a)

\[ 2g_yg_z = i f \times f \]

(65b)

\[ 2g_yg_x = -\hat{f} \times \hat{f} \]

(65c)

with $g_z^2 = g_{z,x}^2 + g_{z,y}^2 + g_{z,z}^2 = g_z \cdot g_z$. It follows immediately that $g_z \cdot g_z = 0$, $f \cdot g_z = -g_z \cdot f = 0$. According to (65b), $g_z = 0$ when $f = f = 0$. Moreover, from (65b) and (65c) it follows that $g_x = g_y = 0$ when $f = f = 0$. The Eilenberger equations read

\[ \frac{1}{2} i \hbar \nu_z \cdot \nabla \tilde{\Psi} + (\nu_z - \nu_z) f = \nu_x f - g \Delta - g_x \Delta \]

(66a)

\[ \frac{1}{2} i \hbar (\nu_z \cdot \nabla \tilde{\Psi}) + (\nu_z - \nu_z) f - i \nu_z \times f = \nu_y f - g_y \Delta - g_y \Delta - ig_y \Delta, \]

(66b)

which must be solved together with (65a)–(65c). These equations have to be complemented by self-consistency equations for the self-energies. Near $T_c$ all off-diagonal quantities ($f$, $f$, $\Delta$, $\Delta$) are small, and then from (65a)–(65c) follows that $g_z$ can be neglected being second order in $f$, $\hat{f}$, and $g$ can be replaced by its normal state value ($-i\sigma_z v_{\text{spin}}(\nu)$) in Matsubara representation. If one introduces the matrices

\[ \tilde{V} = \begin{pmatrix} \nu_x & \nu_{x,x} & \nu_{x,y} & \nu_{x,z} \\ \nu_{x,x} & \nu_x & i\nu_{x,z} & -i\nu_{x,y} \\ \nu_{x,y} & -i\nu_{x,z} & \nu_y & i\nu_{x,x} \\ \nu_{x,z} & i\nu_{x,y} & -i\nu_{x,z} & \nu_z \end{pmatrix} \]

(67)

and

\[ \tilde{G} = \begin{pmatrix} g & g_{x,x} & g_{x,y} & g_{x,z} \\ g_{x,x} & g & i\nu_{y,z} & -i\nu_{y,y} \\ g_{x,y} & -i\nu_{y,z} & g_{y,y} & i\nu_{y,x} \\ g_{x,z} & i\nu_{y,y} & -i\nu_{y,x} & g \end{pmatrix} \]

(68)

as well as the vectors

\[ \mathbf{F} = \begin{pmatrix} f_x \\ f_y \\ f_z \\ f_{\Delta} \end{pmatrix}, \quad \Delta = \begin{pmatrix} \Delta_x \\ \Delta_y \\ \Delta_z \end{pmatrix}, \]

(69)

then the system (66a) and (66b) can be written compactly as

\[ (i\hbar \nu_y \cdot \nabla \mathbf{B} + 2\epsilon - 2\mathbf{V}) \mathbf{F} = 2\mathbf{G} \Delta. \]

(70)

The four eigenvalues of $2(\epsilon - \mathbf{V})/\hbar\nu_y$ determine the wavevectors in the system, and can be calculated as

\[ 2(\epsilon - \nu_z) \pm \sqrt{\nu_z^2 + \nu_z^2 + \nu_z^2 \pm \nu_z^2 + \nu_z^2 + \nu_z^2} \]

(71)

For a singlet superconductor in proximity contact with a ferromagnet with exchange field $J$, assuming for the following discussion $\nu_z = 0$, $\nu_x = 0$, $\nu_y = -J$, $\Delta = 0$, the Eilenberger equations simplify to

\[ \begin{pmatrix} \frac{1}{2} i \hbar \nu_y \cdot \nabla \mathbf{B} + f \end{pmatrix} \mathbf{F} = -J \cdot \mathbf{f} - g \Delta \]

(72a)

\[ \begin{pmatrix} \frac{1}{2} i \hbar \nu_y \cdot \nabla \mathbf{B} + f \end{pmatrix} \mathbf{F} = -J \cdot \mathbf{f} - g_x \Delta \]

(72b)

where we have introduced $\varepsilon = \epsilon + i\sigma_z$ for $\text{Im}(\epsilon) > 0$ and $\sigma = \epsilon - i\epsilon$ for $\text{Im}(\epsilon) < 0$ to account for possible spin-flip scattering with rate $\alpha_z = h/\tau_z$ and $\tau_z$ is the spin-flip scattering time. The wavevectors are then given by

\[ k_{1,2} = 2(\varepsilon \pm |J|)/\hbar\nu_y, \quad k_{3,4} = 2\varepsilon/\hbar\nu_y. \]

(73)

In a superconductor-ferromagnet hybrid structure, the superconducting order parameter vanishes in the ferromagnetic regions, $\Delta_{\text{eff}} = 0$. The proximity effect manifests itself in nonzero pair amplitudes $f, f \neq 0$ in the ferromagnet. In the superconductor, the exchange field vanishes, $J = 0$, expressing the non-coexistence of superconducting and ferromagnetic orders. Equation (73) defines the propagation and decay of Cooper pairs into the ferromagnet. If one replaces $\epsilon$ by the first Matsubara energy $i\pi\nu_y T$, then one obtains an exponential decay on the length scale $\xi_T = \hbar\nu_y/2(\pi k_B T + \alpha_z)$. In addition, two of the components oscillate on the length scale $\xi_f = \hbar\nu_y/|J|$ (with wavelength $2\pi k_T \xi_f$) along the direction $\nu_y$. After averaging over all directions, this leads to an algebraic decay $\sim L x$ in $x$-direction away from the interface, before on a larger length scale $\xi_T$ exponential decay sets in [107]. The components with wavevectors $k_{1,2}$, oscillating on the scale $\xi_f$, correspond to eigenvectors with $f = \pm|J|/|J|$ (i.e. $f \times |J| = 0$), and represent an equal weight superposition of the singlet amplitude ($S = 0$, $S_z = 0$) and the triplet amplitude with zero spin-projection to $J$ ($S = 1$, $S_z = 0$). The (degenerate) components with wavevectors $k_{3,4}$, insensitive to $J$, correspond to an eigenvector where $f = 0$, $f \times |J| = 0$, and represent equal-spin pairing amplitudes with respect to the quantization axis $J$ ($S = 1$, $S_z = 1$). For increasing exchange field, the pre-factor for the proximity amplitudes oscillating with wavelength $\xi_f$ is of order $\Delta|J|$ and thus vanishes in the limit of large exchange splitting.

4.5. Usadel equations

In the dirty (diffusive) limit, the transport equation (48) can be greatly simplified. A strong scattering by impurities averages the quasiclassical propagator over momentum directions. The Green’s function may be expanded in the small parameter $\varepsilon T_c$.
(τ is the momentum relaxation time) following the standard procedure [183, 215]
\[
\hat{g}(\hat{p}_f; R, \epsilon_n) \approx \hat{g}^{(0)}(R, \epsilon_n) + \hat{g}^{(1)}(\hat{p}_f; R, \epsilon_n)
\]
(74)
where the magnitude of \(\hat{g}^{(1)}\) is small compared to that of \(\hat{g}^{(0)}\).

The impurity self-energy is related to an (in general anisotropic) lifetime function \(\tau(\hat{p}_f, \hat{p}_j)\) [183], Substituting (74) into (48) and (49), multiplying with \(N_j(\hat{p}_j) \nu_j(\hat{p}_j) \tau(\hat{p}_j, \hat{p}_j)\), averaging over momentum directions, and considering that \(\Delta r/\hbar \ll 1\), one obtains (with the help of the normalization condition
\[
(N_j(\hat{p}_f) \nu_j(\hat{p}_f) \tau(\hat{p}_f, \hat{p}_f) N_j(\hat{p}_f) \nu_j(\hat{p}_f)) \hat{p}_f
\]
(75)

where

\[
D_{jk} = \frac{1}{N_f} \left\{ \left( N_j(\hat{p}_f) \nu_j(\hat{p}_f) \tau(\hat{p}_f, \hat{p}_f) N_j(\hat{p}_f) \nu_j(\hat{p}_f) \right) \hat{p}_f \right\}_{\hat{p}_j}
\]
is the diffusion constant tensor. The function \(\hat{g}^{(0)}\) obeys the Usadel transport equation (hereafter we omit the superscript (0) and apply the Einstein summation convention
\[
[\hat{\epsilon} \hat{h} - \hat{h}_0, \hat{g}] + \frac{\hbar D_{jk}}{\pi} \hat{V}_k(\hat{\Sigma} \hat{g}) = 0
\]
(76)
where \(\hat{h}_0 = (N_j(\hat{p}_f) \nu_j(\hat{p}_f) + \hat{\Sigma}_{\text{int}}(\hat{p}_f))/N_f\), together with the normalization condition
\[
\hat{g}^2 = -\pi \hat{h}_0
\]
(77)
The diffusion constant is a material property. It is spin-independent in agreement with the approximation of treating all exchange energy effects as perturbation. In the diffusive limit, the different components of \(g\) and \(f\) in the spin space are related through (65a)-(65c), since the Green’s function \(\hat{g}\) averaged over momentum fulfills the same normalization condition as before averaging. A vector potential enters in a gauge invariant manner by replacing the spatial derivative operators by (see e.g. [216])
\[
\nabla \hat{X} \rightarrow \hat{\partial} \hat{X} \equiv \nabla \hat{X} - i \left[ \frac{e}{\hbar} \hat{A} / \hat{\Sigma}, \hat{X} \right]
\]
(78)
The charge current density is obtained from \(\hat{g}(R; \epsilon_n)\) via
\[
j_k = \frac{2eN_fD_{kj}}{\pi} k_B T \sum_{\epsilon_n} \text{Im}[f^* \hat{\partial}_j f - f^* \hat{\partial}_j f],
\]
(79)
with \(\hat{\partial}_j = \nabla_j - \frac{2e}{\hbar} \hat{A}_j\), and the spin-vector current density in spatial \(k\)-direction
\[
j_k = \frac{2eN_fD_{kj}}{k_B T} \sum_{\epsilon_n} \text{Re}[g \times \nabla_j g + f^* \times \hat{\partial}_j f].
\]
(80)

Note that from equations (65b) and (65c) follows that \(g = |\text{Im}(f^* f) + i \text{Re}(f) \times \text{Im}(f)|/\text{Im}(\rho_g)\) at Matsubara frequencies. As for the case of Eilenberger equations, an important part of the problem is the formulation of appropriate boundary conditions [217, 218]. In quasiclassical theory this is usually a highly non-trivial task, as boundary conditions are in general non-linear. A powerful way to implement boundary conditions and to solve Usadel equations is also here the Riccati method [72, 219, 220]. Modern versions of boundary conditions for Usadel equations are found in [149] for weak spin polarization, small spin-dependent scattering phase shifts, and small transmission. A general formulation appropriate for arbitrary transmission, spin polarization, and spin-dependent phase shifts has been derived in [221]. The tunneling limit of this boundary condition has been used in [158], and was independently introduced in [355].

Near the critical temperature \(T_c\), the pair amplitudes \(f\) and \(g\) are small and the Green’s function \(\hat{g}\) deviates only slightly from its value in the normal state, so that the Usadel equations can be linearized and take the simpler form [73, 74, 223]
\[
\left( \frac{\hbar}{2i} \nabla_j D_{jk} \hat{V}_k + \epsilon \right) f = -j \cdot f + i\varepsilon \Delta
\]
(81)
and
\[
\left( \frac{\hbar}{2i} \nabla_j D_{jk} \hat{V}_k + \epsilon \right) \hat{g} = -j f,
\]
(82)
where \(\epsilon\) defined as after equation (72b). The characteristic wavevectors for isotropic systems \((D_{ij} \rightarrow D_{ii})\) are now given by (we chose the roots such that \(\text{Im}(k) > 0\))
\[
k_{1,2} = (1 + i) \sqrt{(\epsilon \pm |J|)/\hbar D}, \quad k_{3,4} = (1 + i) \sqrt{\epsilon/hD}.
\]
(83)
If we again substitute \(\epsilon \rightarrow i\kappa B q\), this leads to exponential decays for all four solutions. However, there are two long-range solutions with decay length
\[
\xi_l = \left( \frac{\hbar D}{2(\pi k_B T + \alpha_s)} \right)^{\frac{1}{2}},
\]
(84)
and two short-range solutions showing damped spatial oscillations with decay length [236]
\[
\xi_s = \left( \frac{\hbar D}{(\pi k_B T + \alpha_s)^2 + |J|^2 + (\pi k_B T + \alpha_s)} \right)^{\frac{1}{2}}
\]
(85)
and inverse oscillation wavevector
\[
\xi_2 = \left( \frac{\hbar D}{(\pi k_B T + \alpha_s)^2 + |J|^2 - (\pi k_B T + \alpha_s)} \right)^{\frac{1}{2}}.
\]
(86)
Note that \(\xi_1 < \xi_2\) except when \(T = 0\) and \(h/\tau_\epsilon = 0\), thus the oscillations are strongly damped, so that one cannot expect to observe many oscillation periods. This is in contrast to the clean case, where the oscillation wavelength is entirely decoupled from the decay length, which can become very long for low temperatures. Thus, many oscillation periods are expected to be observable in experiment. For the diffusive case, on the other hand, both length scales are temperature dependent. This allows for oscillatory behavior as a function of temperature, an effect absent in the clean limit. For \(|J| \gg k_B T, \alpha_s\), both length scales merge and approach [224]
\[
\xi_{1,2} = \left( \frac{\hbar D}{|J|} \right) \left( \frac{1 + (\pi k_B T + \alpha_s)}{2|J|} \right)
\]
(81)

11 A subsequently derived alternative boundary condition [222] has a considerably narrower range of applicability.
With increasing exchange splitting, the decay length shrinks to zero and the short-range proximity amplitudes are expected to be suppressed to unmeasurable size, unless one finds a mechanism to create new types of proximity amplitudes.

4.6. General features of the S/F proximity effect

It can be noticed from the transport equation (72b) or (82) that the triplet vector \( \mathbf{f} \) obeys in the ferromagnet an inhomogeneous differential equation, implying that \( \mathbf{f} \) is necessarily non-zero if the singlet component \( \mathbf{f} \) penetrates in the ferromagnet. For spatially constant exchange field \( \mathbf{J} \), the triplet vector aligns with \( \mathbf{J} \). The singlet component and the triplet component with the zero spin-projection on \( \mathbf{J} \) coexist always in the ferromagnet near the S/F interface. As they both involve electrons from both spin bands, both are characterized by short-range penetration lengths in the ferromagnet.

On the contrary, if the triplet vector \( \mathbf{f} \) is non-collinear with \( \mathbf{J} \), triplet components with nonzero spin-projection on \( \mathbf{J} \) are produced. Since these correspond to equal-spin pairing, they are not limited locally by the paramagnetic interaction with the local exchange field and have long-range scales in the ferromagnet. A misalignment between the triplet vector \( \mathbf{f} \) and the moment \( \mathbf{J} \) occurs in presence of sudden changes in orientation of \( \mathbf{J} \). The reason is that \( \mathbf{f} \) obeys a differential equation and its variations in orientation have thus to be relatively smooth.

The counterpart for the production of triplet components (\( \mathbf{f} \neq 0 \)) in the pair amplitudes is the presence of \( \mathbf{g} \neq 0 \) in the diagonal components of the Green function [212]. As a direct consequence, the density of states for the up and down spin projections differs (see equation (63)). This feature of the S/F proximity effect has been found numerically as early as in 1999 [225]. In the presence of long-range triplet components, the particle-hole diagonal Green function components contain also off-diagonal terms in the spin-space, a signature of a spin-flip scattering process.

As a result of the spin splitting in the density of states generated by the S/F proximity effect, a spin magnetization \( \delta \mathbf{M} \) is also induced near the S/F interface. This magnetization leakage has been investigated in [226] within a model considering a fixed exchange field. In the dirty limit the spin magnetization induced by the proximity effect is given by [148, 183]

\[
\delta \mathbf{M}(R) = 2Nf/k_B T \mu_{\text{eff}} \sum_n \text{Re}[\mathbf{g}(\mathbf{R}, \epsilon_n)],
\]

with \( \mu_{\text{eff}} = (\mathbf{I} - A_0^2)\mu_c \). Since the triplet vector \( \mathbf{f} \) is also induced in the superconductor near the S/F interface via an inverse proximity effect, the vector \( \mathbf{g} \) characterizing the magnetic correlations penetrates also in the superconductor according to the relation (65c), which for the diffusive limit reads \( \text{Im}(g_0)\text{Re}(g) = \text{Im}(g_f^* g) \) (all functions of \( \epsilon_n \)).

It is possible to convince oneself that the sum over Matsubara frequencies in the expression (87) is nonzero. Indeed, as noticed in [131, 227, 228], in the diffusive limit the triplet components are odd functions of the Matsubara frequencies \( \epsilon_n \) while the singlet amplitude \( f \) is an even function of \( \epsilon_n \). Note that in the diffusive limit

\[
g_0(-\epsilon_n) = -g_0(\epsilon_n), \quad g(-\epsilon_n) = g(\epsilon_n).
\]

For unitary pairing states, \( f \times f = 0 \), the relations (65b) and (65c) between the vectors \( \mathbf{g} \) and \( \mathbf{f} \) get simplified. In this case, it can be seen that if the gap \( \Delta \) can be chosen real (and thus the singlet amplitude \( f(\epsilon_n) \) is real), then the triplet vector \( f(\epsilon_n) \) is purely imaginary, i.e., \( f = f^* = -f \) (taking into account that \( \mathbf{g}_0 = -g_0 \), i.e. \( g_0 \) is purely imaginary). As a result, one obtains the simpler relations

\[
\mathbf{g} = \mathbf{g} \cdot g_0 \mathbf{g} = \mathbf{f}.
\]

These simplifications arise also when \( f \parallel \mathbf{J} \) [226]. Combining the relations (89) and (88), it follows that the spin-vector part \( \mathbf{g} \) is an even function of \( \epsilon_n \) in the diffusive limit, which demonstrates that the induced spin magnetization \( \delta \mathbf{M} \) is in general non-zero.

Near \( T_c \), the singlet amplitude \( f \) and the triplet vector amplitude are small so that \( \mathbf{g} \) and thus \( \delta \mathbf{M} \) appear to be second order terms (see equation (65c)). Accordingly, the induced spin magnetization \( \delta \mathbf{M} \) penetrating the superconductor, which is negligibly small near \( T_c \), increases significantly by reaching temperatures well below \( T_c \).

4.7. Strongly spin-polarized ferromagnets

In the case that the spin splitting of the spin bands in a ferromagnet is much larger than the superconducting gap in the adjacent superconductor, the above mentioned theories must be modified in various respects. First, Usadel approximation assumes that the inverse life time of quasiparticles due to impurity scattering averaged over the Fermi surface, \( h/T \), is much larger than all energy scales appearing in the Usadel equation, including the magnitude of the exchange field \( |\mathbf{J}| \). If this is not the case, the spatial variation of superconducting correlations into the ferromagnet happens on length scales comparable to or shorter than the mean free path, and Usadel theory cannot be used within the ferromagnet on the same footing as the exchange field \( |\mathbf{J}| \). One must resort to Eilenberger equations in this case. If the exchange splitting is, however, not much smaller than the Fermi energy scale, then even Eilenberger–Larkin–Ovchinnikov theory cannot accommodate the exchange field in the way described in the previous sections. A modified version of Eilenberger and Usadel equations can be used for the case that \( |\mathbf{J}| \sim E_F \). In this case, there exist two well separated fully spin-polarized Fermi surfaces in the system, and the length scale associated with \( h/|\mathbf{J}| \) is much smaller than the coherence length scale in the ferromagnet. Superconducting pairs of the type \( \uparrow \downarrow \) and \( \downarrow \uparrow \) are still long-ranged in such a system, however pairs of the type \( \uparrow \uparrow \) and \( \downarrow \downarrow \) are zero within quasi-classical approximation. Both Fermi velocity and density of states at the Fermi level are spin-dependent. The same holds for diffusion constant, and coherence length. The quasi-classical propagator is then spin-scalar for each quasiclassical trajectory in the ferromagnet,

\[
\tilde{g}_{\uparrow \downarrow} = \begin{pmatrix} g_{\uparrow \downarrow} & f_{\uparrow \downarrow} \\ f_{\uparrow \downarrow} & \tilde{g}_{\downarrow \uparrow} \end{pmatrix}, \quad \tilde{g}_{\downarrow \uparrow} = \begin{pmatrix} g_{\downarrow \uparrow} & f_{\downarrow \uparrow} \\ f_{\downarrow \uparrow} & \tilde{g}_{\uparrow \downarrow} \end{pmatrix}.
\]
and similarly has only a particle-hole discrete degree of freedom. Similarly, all mean field self energies have the same structure (spin-scalar, only $2 \times 2$ particle-hole matrices), and the Fermi liquid interactions are replaced by spin-scalar interactions, which in the simplest case do not mix the spin bands: $A^a, A^b \rightarrow A_{11}, A_{11}, V_1, V_2 \rightarrow V_{11}, V_{11}$ (in a more general case, the Fermi liquid interactions could be of the form $A_{1111}, A_{1111}$ etc.). Eilenberger equation and Usadel equation have the same form as before for each separate spin band. The spin-resolved current densities are given in the ballistic case by

$$j_{\uparrow} = e k_B T \sum_{\mu} \left( \frac{N_{11} \mu_{\text{eff}} |\mathbf{g}_{11}|}{\tilde{\rho}_{11}} \right) \tilde{\rho}_{11}^{-1}, \quad j_{\downarrow} = e k_B T \sum_{\mu} \left( \frac{N_{11} \mu_{\text{eff}} |\mathbf{g}_{11}|}{\tilde{\rho}_{11}} \right) \tilde{\rho}_{11}^{-1},$$

and the spin magnetization by

$$M_s = M_0 (B_r) + e k_B T \sum_{\mu} \left( \frac{N_{11} \mu_{\text{eff}} |\mathbf{g}_{11}|}{\tilde{\rho}_{11}} \right) \tilde{\rho}_{11}^{-1}.$$  \hfill (91)

The expressions in the diffusive limit are modified accordingly: e.g. for the spin-resolved current density one obtains

$$\dot{j}_{\uparrow} = -\frac{e}{\pi} k_B T \sum_{\mu} \text{Im} \left[ N_{11} D_{11} \tilde{f}_{\uparrow} \tilde{f}_{\uparrow}^{*} \right],$$

and analogously for spin down.

5. Pair amplitude oscillations and π-Josephson junctions

5.1. 0 – π transitions in Josephson junctions

Proximity-induced pairs in a superconductor-ferromagnet bilayer are subject to the FFLO effect, leading to spatially oscillating pair amplitudes in the ferromagnetic regions. These act back on the superconducting singlet pair potential in the superconducting region. How exactly this interaction between pair potential and FFLO amplitudes takes place depends on details of the interfaces and must be determined numerically, however for a sufficiently thin superconducting layer the oscillating nature of the FFLO amplitudes ultimately leads to oscillations in the modulus of the pair potential of the superconductor (and thus in the transition temperature) as function of the geometric dimensions of the hybrid structure. In addition, the oscillatory nature of the FFLO pairs in the ferromagnet affects the properties of superconductor-ferromagnet-superconductor Josephson devices, leading to the possibility of oscillations between junctions with a phase difference of zero and junctions with a phase difference of $\pi$ in the ground state, when a certain control parameter is changed.

The idea of Josephson junctions with a $\pi$ phase difference in its ground state when a magnetic impurity is inserted in the junction was introduced by Bulaevskii et al in 1977 [229]. Similar ideas had also been proposed by Kulik in 1965 [230]. In 1982 it was also shown in a classical paper by Buzdin et al that the pair amplitude oscillates in ferromagnets in contact with a superconductor [231]. Further early studies of this effect followed in [232–234]. One technological problem that became evident quickly was that weakly spin-polarized systems, like ferromagnetic Cu–Ni or Pd–Ni alloys, are better suited to observe $0 - \pi$ oscillations, as otherwise the proximity amplitudes become so short ranged that extremely thin layers are necessary. Typical ferromagnetic alloys that have been used are Cu$_{1-x}$Ni$_x$ (CuNi) and Pd$_{1-x}$Ni$_x$ (PdNi). The real break-through came in the beginning of the 2000s with the experimental verification of the switching between 0 and $\pi$-Josephson junctions based on the effect predicted theoretically before. Pioneering work was done by Ryazanov and co-workers who studied transitions between zero- and $\pi$-states as function of temperature [224, 235–237] and thickness of the ferromagnet layer [224, 237] in Nb/CuNi/Nb trilayers (see figure 13). Closely following were experiments by Kontos and
co-workers who studied the zero-\(\pi\) transition as function of barrier thickness in Nb/Al/Al_2O_3/PdNi/Nb junctions [238], by Blum et al [239], who use Nb/Cu/Ni/Cu/Nb junctions and vary both temperature and thickness of the Ni layer (thus employing a much stronger spin-polarized ferromagnet than the ferromagnetic alloys that were used by the other groups), and by Sellier et al studying a temperature induced \(0\) to \(\pi\) transition in Nb/CuNi/Nb (see figure 13), as well as the appearance of half-integer Shapiro steps [240, 241].

The critical Josephson current density as function of layer thickness in the limit \(J_{c,\text{limit}}\) is described in the clean limit by formula [74]

\[
I_c(d_F) = \frac{\sin \left( \frac{1}{2} J_{c,\text{limit}} (d_F - d_0) \right)}{\frac{1}{2} J_{c,\text{limit}} (d_F - d_0)}
\]

(94a)

where \(d_0\) is a fit parameter which is usually assigned to a ‘dead layer’, i.e. a layer of suppressed magnetism at the interface. In the diffusive limit the corresponding expression for long \((d_F \gg \xi_1)\) junctions is

\[
I_c(d_F) \sim e^{-d_F/\xi_1} \cos \left( \frac{d_F - d_0}{\xi_2} \right)
\]

(94b)

with the length scales \(\xi_1, \xi_2\) as in (85) and (86). A study by Pugach et al [242] bridging the two limiting cases showed that the two length scales \(\xi_1\) and \(\xi_2\) may exhibit a non-monotonic dependence on the properties of the ferromagnetic layer such as exchange field or electron mean-free path.

Further studies of strongly spin-polarized interlayers were performed, using various materials, among those Ni in [243], Co, Ni, and Py (Ni_{80}Fe_{20}) in [244], and Py (Fe_{0.75}Co_{0.25}) barriers in [245]. A detailed study, presented in [246], with Ni interlayers using the formulas (94a) and (94b) above has been done recently, indicating that these structures are in the dirty limit. The thicknesses of the Ni layers ranged between 1 and 5 nm. In figure 14 examples for \(0\) to \(\pi\) oscillations in a Nb/Co/Nb structure are shown. In order to eliminate unwanted effects due to the variation of the electromagnetic vector potential across the junction due to the intrinsic magnetic flux in the junction, a special geometry was used where two Co layers were exchange coupled by a thin Ru layer in between to align antiferromagnetically. This cancels all the unwanted effects to a high degree, and a previously wildly fluctuating critical current versus magnetic field curve turns into an excellent Fraunhofer pattern when the Ru interlayer present, as seen in figure 14(b) [247]. With this improvement high-quality \(0\) to \(\pi\) transitions are observed both as function of temperature and of ferromagnet thickness.
These results complement the results shown in figure 13, which are for ferromagnetic alloys. The main difference is a one order of magnitude smaller ferromagnet layer thickness necessary to observe the effect, which is an experimental challenge.

The effect of additional normal and/or insulating layers between the superconductor and the ferromagnet was studied theoretically in detail in [248]. It was found that even a thin additional normal conducting layer may shift the $0 - \pi$ transitions to larger or smaller values of the thickness of the ferromagnet, depending on its conducting properties, and for certain parameter ranges a $0 - \pi$ transition can even be achieved by changing only the normal layer thickness.

A promising setup are so-called double-proximity structures, in which two superconductors are connected by a weak link of a normal-metal/ferromagnet bilayer or a ferromagnet/normal-metal/ferromagnet trilayer forming a bridge between the superconducting banks. The proximity effect acts here twice: first to provide pair amplitudes from the superconducting banks into the bilayer or trilayer, and second at the interface between the normal metal and ferromagnet. Such structures have been proposed by Karminkaya and Kupriyanov [249], and experimental realization in terms of hybrid planar Al–(Cu/Fe)–Al submicron bridges is reported in [250]. The oscillation periods and damping lengths of the critical Josephson current can be much longer in such devices than in the conventional setup. Various geometries have been theoretically studied in subsequent work, including (SN)–(NF)–(SN), (SNF)–(NF)–(SNF), (SNF)–N–(SNF), and S–(NF)–S junctions, in order to optimize practical performance [251].

5.2. Phase sensitive measurements

The current-phase relation (CPR) as a function of temperature in a Nb/CuNi/Nb junction was measured by Frolov et al (see figure 15) [252]. Using an rf SQUID, the change of the current-phase relation from zero to $\pi$-junction behavior is clearly visible. This allows to observe the sign of the supercurrent. A $\pi$-junction is a Josephson junction with a negative critical current $I_c$, as its current-phase relation (CPR) is $I_c(\phi) = I_c|\sin(\phi + \pi)| = -I_c|\sin(\phi)|$. As conventional measurement of the current–voltage characteristic of a Josephson junction is not sensitive to the sign of the supercurrent, it was necessary to include the Josephson junction in a multiply connected geometry. The sign was in [252] observed in an rf SQUID configuration (see figure 15(a)) by shorting the electrodes of the junction with a superconducting loop. If that loop contains a $\pi$ junction in zero external field it will exhibit a spontaneous circulating current, generating a flux of $\Phi_0/2$ which can be detected by a SQUID magnetometer or a Hall probe. In figure 15(b) the transition between a zero and a $\pi$ state is unambiguously observed (although residual magnetic fields leading to shifts in the CPR curves did not allow to pin down if it was a $0 - \pi$ or a $\pi - 0$ transition).

Phase sensitive measurements of the ground state of ferromagnetic Josephson junctions using a single dc SQUID have been performed by Ryazanov and co-workers [253] for Nb/NbO$_x$/CuNi/Nb junctions, and by Guichard et al [254] for Nb/NbO$_x$/PdNi/Nb junctions, showing that the sign change of the Josephson coupling is observed as a shift of half of a flux
quantum $\Phi_0 = \frac{h}{2e}$ in the SQUID diffraction pattern (see figure 15). A 0–0 and a $\pi$–$\pi$ junction show identical critical current modulations with flux, whereas a 0–$\pi$ junction exhibits a pattern shifted by $\Phi_0/2$ with respect to that for 0-0 and $\pi$–$\pi$ junctions. In this experiment a single dc SQUID with two SFS junctions embedded. The ferromagnetic layer thickness $d_{f1}$ and $d_{f2}$ can then be chosen to correspond to zero or $\pi$ coupling independently, leading to the possibility of a 0–0, a $\pi$–$\pi$, a 0–$\pi$, or a $\pi$–0 SQUID. For a dc SQUID with negligible loop inductance and equal junction critical currents the modulation of the critical current with applied flux is given by [96]

$$L(\Phi_{\text{ext}}) = 2\hbar \left| \cos \left( \frac{\Phi_{\text{ext}}}{\Phi_0} + \frac{\delta_{12}}{2} \right) \right|$$

(95)

where $\delta_{12}$ is the sum of the internal phases (0 or $\pi$) in the two junctions of the SQUID. Thus, for a 0–0 and a $\pi$–$\pi$ SQUID the $L(\Phi_{\text{ext}})$ patterns are identical, whereas they are shifted by half a flux quantum if $\delta_{12} = \pi$, i.e. a 0–$\pi$ or a $\pi$–0 SQUID. This shift is shown in figure 15(d).

The presence of spontaneous magnetic moments in superconducting (Nb) loops containing a ferromagnetic (PdNi) junction was experimentally demonstrated by Bauer et al [255]. The loops were prepared on top of a micro-Hall sensor. The authors observed asymmetric switching of the loop between different magnetization states when reversing the sweep direction of the magnetic field. The presence of a spontaneous current near zero applied field was studied as function of temperature, and the magnetic moment approached half a flux quantum at low temperatures.

An rf SQUID geometry where the macroscopic ground state of a ferromagnetic (PdNi) Josephson junction shorted by a 0 weak link was experimentally investigated by Della Rocca et al and showed spontaneous half quantum vortices with random sign ($\pm \Phi_0/2$) [256]; it was found that 0–$\pi$ junctions behave as classical spins.

5.3. $\varphi$-Josephson junctions

An interesting separate development concerns a geometry where a step in the thickness of the ferromagnet is present in a superconductor-ferromagnet bilayer, coupled to another superconductor via an insulating barrier. On one side of the step one has a 0 junction, on the other side a $\pi$ junction. A half flux quantum (semifluxon) is trapped in such a structure at the step [257–259], and a supercurrent circulates in the structure, similarly as in a 0–$\pi$ SQUID [260–263]. Such structures were studied in detail by Weides, Kohlstedt, Koelle, Kleiner, Goldobin and co-workers. In particular, there exists in such structures the possibility of a $\varphi$-junction, which has neither 0 nor $\pi$ phase difference as a ground state. A method to realize a $\varphi$ Josephson junction by combining alternating 0 and $\pi$ parts with intrinsically non-sinusoidal current-phase relation was suggested in [264]. The realization of an SIFS $\varphi$-junction has been experimentally achieved in 2012 (see figure 17) [265]. Properties of zero–$\pi$ junctions which act as a Josephson junction with an equilibrium phase difference $0 < \varphi < \pi$ are discussed in [266], where the current-phase relation is calculated numerically and in certain limiting cases analytically.

In [267, 268], a planar Josephson junction with a ferromagnetic weak link located on top of a thin normal metal film is considered. It is shown that this Josephson junction is a promising candidate for the realization of a $\varphi$-junction.

6. Long-range triplet supercurrents

6.1. Length scales for superconducting correlations in ferromagnets

As detailed in the sections 4.4 and 4.5, proximity induced superconducting correlations in ferromagnets with sufficiently strong exchange splitting $|J|$ come in pairs of short-range and...
long-range amplitudes. The former ones are the singlet amplitude and the triplet pair amplitude with zero spin projection, $S_z = 0$, on the magnetization axis of the ferromagnet. These short-range amplitudes decay in ballistic structures algebraically with a reduced magnitude of order $\Delta I/I$, and in diffusive structures exponentially on the length scale $\xi_f$. The other two components, called long-range amplitudes, decay on the thermal coherence length scale $\xi_T$, given for ballistic structures by $h v_F/(2\kappa q_T + 2\alpha)$ and for diffusive structures by $\sqrt{h D/(2\kappa q_T + 2\alpha)}$. They are characterized by triplet amplitudes with a spin projection $S_z = \pm 1$ on the magnetization axis of the direction of the ferromagnet. Consequently, they are called equal-spin triplet pair correlations. Equal spin pairs do not suffer from having to populate spin-split pairs of Fermi surfaces. Both electrons of the pair are situated on the same spin component of the Fermi surface. For this reason, they behave like in a normal metal, with the coherence length determined by the Fermi surface properties of one spin component only (which in general differ for $S_z = +1$ and $S_z = -1$). The quest for such long-range pair amplitudes has a long history, and is one of the success stories of interaction between experiment and theory.

6.2. Experimental ‘pre-history’

As in the 1990s the field of spintronics, i.e. functional nanometer-size devices based on spin-dependent transport phenomena, developed rapidly [269], a strong motivation to search for a long-range proximity effect in ferromagnets was established. Such long-range amplitudes would lead to long-range supercurrents in Josephson devices, and would ultimately lead to valuable applications. The ultimate goal is to obtain completely spin-polarized supercurrents, which would necessarily have to be triplet supercurrents.

It was for this reason that in the second half of the 1990s experimental efforts intensified to study proximity effects in strongly spin-polarized ferromagnets. Petrashov, Antonov, Maksimov, and Shalkhaladov found in 1994 that the effect of superconducting islands, deposited on the surface of ferromagnetic Ni, can be still seen in the resistance of the Ni layer distances greater than 2 $\mu$m (exceeding by more than 30 times what the length $h v_F/|I|$ would suggest) away [270].

Lawrence and Giordano studied in 1996 the resistance as a function of temperature and magnetic field in structures containing a narrow (~2 $\mu$m) ferromagnetic strip connecting two superconducting films (In/Ni/In and Pb/Ni/Pb) [271]. They observed a magnetoresistance dip as function of magnetic field much too large to be accounted for by weak localization effects. In addition they found implausibly long phase coherence lengths, inconsistent with the usual superconducting proximity effect. In a later study of Sn/Ni/Sn structures, where the Ni was a narrow wire (~40 nm wide), they measured an unexpectedly long proximity length of about 50 nm (theory predicted 4 nm for these structures) when the Sn/Ni interfaces are clean, however with an oxide layer at the interfaces they observed an unexplained re-entrant behavior [272]. They also noted that their proximity length was of the order of the thermal length $\sqrt{h D/k q_T}$ which would appear in a normal metal.

Giroud and co-workers studied in 1998 Co/Al structures with a ferromagnetic Co wire in contact with superconducting Al [273]. They observed below the superconducting transition that the Co resistance exhibited a significant dependence on temperature and voltage, and the differential resistance showed that the decay length for the proximity effect was much larger than expected from the exchange field of Co.

Petrashov and co-workers found in 1999 a giant mutual proximity effect in Ni/Al structures with an proximity-induced conductance on the Ni side two orders of magnitude larger than predicted by theory [274]. Aumedato and Chandrasekhar, by performing multi-probe measurements on Ni/Al structures, re-evaluated these studies and came to the conclusion that superconducting correlations cannot extend into a ferromagnet over distances larger than the exchange length, and associated the large changes in resistance seen in the previous experiments with the superconductor/ferromagnet interface or the superconductor, which had been measured in series or in parallel with the ferromagnet [275]. The controversy lead to a vivid discussion about the existence of such long-range proximity components.
6.3. Theory of long-range proximity amplitudes

6.3.1. Spiral magnetic inhomogeneities and domain walls. The renewed interest created by the lack of understanding of long-range superconducting proximity effects in ferromagnets led in the beginning of the 2000s to new theoretical developments. Pivotal was a series of papers by Bergeret, Volkov, Efetov, and coworkers, who studied the effect of a spiral Bloch-type inhomogeneity close to an S/F interface, where the magnetization vector rotates along the junction direction. They found that an equal-spin triplet pair amplitude shows a long-range penetration into the ferromagnet \([73, 131, 219, 276, 277]\). The authors also noted that this, as an isotropic (‘s-wave’) triplet pair component, must be a realization of odd-frequency pairing. As impurities suppress all anisotropic pairing components, this odd-frequency amplitude is the only superconducting pairing amplitude present in the ferromagnet. Shortly after that, Kadirogbobov, Shekhter and Jonson found a similar effect \([278]\). A realization of these ideas motivated by experiment \([279]\) was studied in \([280]\), where the focus of study was a setup of a Ho/Co/Ho trilayer sandwiched between conventional s-wave superconducting leads. Holmium is a conical ferromagnet with an intrinsic spiral structure. In \([281]\) a bilayer consisting of an ordinary singlet superconductor and a magnet with a spiral magnetic structure of the holmium or erbium type was investigated by solving self-consistently Bogoliubov–de Gennes equations. A re-entrance behavior as function of temperature is observed for certain parameter ranges.

Another type of magnetic structure discussed in the literature is a domain structure of the Néel type, in which the magnetization vector lies parallel to the interface and rotates along a direction parallel to the interface. A setup with a chiral ferromagnet, exhibiting a homogeneous cycloidal spiral, placed between two conventional superconductors was studied in \([282]\). Depending on the spiral wave length, \(0 - \pi\) transitions can be induced. In the case of a uniformly rotating spiral, however, it was shown that only short-range components exist \([280]\). In a more general case, with magnetic domains separated by Néel walls, long-range triplet components are present and arise at the domain walls, decaying inside the domains \([283, 284]\). References \([285, 286]\) investigate diffusive SF and SFS structures with a domain wall in the F layer, using a Riccati representation of the non-linear Usadel equations \([72]\) and including spin-mixing parameters for interfaces. They study local density of states, induced magnetization, and spin-polarized Josephson currents. It is found that the spin polarization of the spin current in SFS structures is determined by the magnetization profile and that the spin current shows discontinuities at the zero-\(\pi\) transition points of the critical Josephson current. Similar as in \([168]\), a non-zero spin-current even for zero superconducting phase difference is reported. In \([287]\) the contribution of domain walls to the Josephson current through a ferromagnetic metal is examined for both ballistic and diffusive systems. It is found that in the clean limit domain walls enhance the Josephson current even for a collinear magnetic domain structure, whereas in the diffusive limit a non-collinear domain structure is necessary to enhance the effect. In \([288]\) the influence of the location of a domain wall within a Josephson junction on the ground state properties of the junction was the topic of investigation. The authors considered both the diffusive and ballistic limits. They find that the location of the domain wall determines if the junction is in a zero-state or in a \(\pi\)-state and influences the transition temperature of the junction.

A different type of system with inhomogeneous magnetic structure was studied in \([289, 290]\), where a ferromagnetic vortex in a mesoscopic ferromagnetic disc is brought in contact with a singlet superconductor. Proximity-induced long-range triplet components are generated by the ferromagnetic vortex under certain circumstances, leading to zero- or \(\pi\)-junction behavior depending on the contact geometry.

6.3.2. Multi-layer geometries. Instead of considering inhomogeneous magnetization profiles within a ferromagnetic layer as sources of long-range triplet correlations, one can also obtain the same effect in a multilayer geometry with non-collinear arrangement of the magnetizations of the various layers. In \([291]\) a diffusive SFIFS junction is investigated by self-consistently solving Usadel equations with appropriate boundary conditions. It is found that for antiparallel ferromagnet magnetizations the critical current is enhanced by the exchange energy, and for parallel magnetization the junction exhibits a transition to a \(\pi\)-state. A switching behavior between zero- and \(\pi\)-state can be observed when going from the antiparallel to the parallel alignment. In \([225, 228]\) a multilayered superconductor-ferromagnet structure with non-collinear alignment of the magnetizations of the ferromagnetic layers is considered, and the resulting long-range odd-frequency triplet condensate amplitude is calculated. It is found that this setup allows for a Josephson effect with possible zero- or \(\pi\)-junction behavior. It is also pointed out that the chirality of the magnetization profile matters for the direction of the Josephson current. In \([292]\) a fully self-consistent calculation was performed for a ferromagnet-superconductor-ferromagnet trilayer setup with non-collinear magnetization, and the induced spin magnetization in the entire structure is determined. This work includes self-consistency of the order parameter in the superconducting layer at arbitrary temperatures, arbitrary interface transparency, and any relative orientation of the exchange fields in the two ferromagnets. The long-range Josephson effect through a ferromagnetic trilayer was the topic of \([293]\), where conditions were derived under which the long-range triplet proximity effect dominates the short-range proximity effect. Both diffusive and clean limits were studied. Haltermann and Valls have investigated numerically ballistic S/F/S trilayer and S/F/S/F/S pentalayer Josephson junctions by self-consistently solving Bogoliubov–de Gennes equations, concentrating on the thermodynamic stability of zero- and \(\pi\)-junctions as function of material parameters and geometry \([294, 295]\).

Zero-\(\pi\) transitions in Josephson junctions with a diffusive pentalayer-structure of the form F/S/F/S/F with misaligned magnetizations in the three ferromagnetic layers were explored in \([296]\). The transition temperatures for zero- and \(\pi\)-junctions as function of misalignment angle were determined numerically using an effective and fast procedure, which is described in detail in this publication. In \([297]\) a diffusive S/F/FF/F/S structure is discussed, with two different
ferromagnetic materials F and F’. The middle FF double layer is considered to be parallel or antiparallel magnetized, whereas the F’ layers were allowed to be non-collinear. This setup is in particular adapted to the experiments by Khaire et al [298]. A similar study for clean or moderately diffuse materials was performed in [299].

An SF1F2S junction in the ballistic case (including moderate disorder in the ferromagnets) was considered in [300, 301], with misaligned ferromagnetic layers F₁ and F₂. It was found that the long-range spin-triplet correlations lead to a dominant second harmonic in the Josephson current-phase relation of asymmetric junctions [302], an effect also found for diffusive structures in [303]. In the latter reference this phenomenon is traced to the long-range coherent propagation of two triplet pairs of electrons, a process first pointed out and discussed in [168], and called there ‘crossed pair transmission’.

Magnetic moment manipulation by triplet Josephson currents in Josephson junctions with multilayered ferromagnetic weak links is discussed in [304]. It is reported that by tuning the Josephson current, one may control a long-range induced magnetic moment, which appears due to non-collinear magnetization of the layers. Alternatively, applying a voltage one can in such a geometry generate an oscillatory magnetic moment. The spin-switching behavior as function of rotation of the magnetization in one ferromagnetic layer in diffusive SFSSF and SFSFFS Josephson junctions was investigated in [305].

The proximity effect in clean superconductor-ferromagnet structures caused by either the spatial or momentum dependence of the exchange field was discussed in [306]. It was shown that in symmetric junctions the long-ranged proximity effect is present for any non-collinear ferromagnetic moment orientation and a dominant second harmonic appears for any asymmetric junction. The Josephson coupling between two s-wave superconductors separated by a ferromagnetic trilayer with non-collinear magnetization was reconsidered in [307], where in particular the dependence on strength of the exchange field and thickness of the interface layers was studied, and the competition between long-range and short-range components was investigated.

The appearance of a spin supercurrent in a diffusive SF1F2S Josephson junction was subject to study in [308]. It was found that a spin current with spin polarization normal to the magnetization vectors flows between the ferromagnetic domains. This spin current is even as function of superconducting phase difference, and odd as function of misalignment angle between F₁ and F₂.

A diffusive S–[(FNF)–S double proximity structure, in which an FNF trilayer with mutually misaligned ferromagnetic magnetization vectors bridges two superconducting banks, was investigated in [309]. In this case long-range equal-spin triplet correlations are generated by the misalignment of the two ferromagnetic layers in the bridge.

### 6.3.3. Singlet-triplet conversion at interfaces

The mechanisms discussed in the previous subsections employ a quasiclassical approximation, which is not valid for length scales as small as the Fermi wavelength. In fact, for the mechanism to work it is crucial that short-range components can enter the ferromagnet over a sufficiently long distance to feel the magnetic inhomogeneity, which was assumed to vary on the scale much larger than the Fermi wavelength. This poses the problem of what happens at interfaces between a superconductor and a ferromagnet with large exchange splitting, so that the length scale χ becomes comparable to the Fermi wave length.

An appropriate mechanism for structures with strong exchange splittings was proposed, and first exemplary studied for the extreme case of a half-metallic ferromagnet (where one spin band is insulating and one spin band metallic), in [107, 152, 161, 212]. The mechanism is based on spin-dependent scattering phases under reflection and transmission, which in combination with a misalignment with respect to the ferromagnetic bulk magnetization of the interface magnetic moment in an atomically thin interface layer leads to the creation of long-range triplet pairs. It was shown subsequently, that this mechanism persists for the full range from ballistic to diffusive systems [133].

The mechanism of long-range triplet pair creation at interfaces was generalized to Josephson structures involving strongly spin-polarized ferromagnets with two itinerant spin bands in [168].

### 6.3.4. Supercurrents in strongly spin-polarized itinerant ferromagnets and half metals

We discuss first the main predictions of a long-range Josephson effect in a structure involving a long half-metallic ferromagnetic region, as discussed in [107, 133, 152, 212, 221]. As shown in figure 18, which is for a fully self consistent calculation using a model barrier as in figure 10(b), all possible symmetry components shown in figure 6 are indeed generated at the interface. This simply reflects the fact that both spin rotational symmetry and inversion symmetry are broken by the interface. The calculation assumes that the effective magnetic moment of the interfaces is perpendicular to the bulk magnetization of the half-metallic ferromagnet. As a consequence, according to equation (24b), long-range amplitudes are generated, linking the two singlet superconductors (see lower panels in figure 18(a)). Thus, we have an example of an indirect Josephson coupling [152], via a long-range triplet component which is generated in the first place from the singlet component by microscopic processes in the interface region. Note also, that the thermodynamically stable configuration for identical interfaces is a π-junction (for asymmetric junctions the appearance of a φₐ-junction is predicted [107, 133]), for which the system tries to minimize the odd-frequency triplet amplitudes of type D in the structure. This is a general principle, as odd-frequency amplitudes
Figure 18. (a) All symmetry components in a ballistic S/F/S \( x \)-Josephson junction with a half-metallic ferromagnet (H) as F-layer (self-consistent calculation for model barrier as in figure 10(b), with \( V_S = 0.5, d = 0.5/k_B \)); barrier spin-polarized in \( z \)-direction; temperature \( T = 0.2T_c \); (b)–(c) Non-monotonic temperature dependence of critical Josephson current density in an S/F/S junction, normalized to its value at zero temperature; (b) for half-metallic ferromagnet, dependence on the mean free path \( l_B \) in H for a fixed junction length \( L = \xi_F \leq 2\pi/l_B \), where \( v_F \) is the Fermi velocity in H; (c) as in (b), but showing the dependence on junction length \( L \) for fixed \( l_B \) = 1.5 \( \xi_F \); (d) for a ferromagnet in the ballistic limit, with various spin polarizations \( P = (|P_{\uparrow} - P_{\downarrow}|) / (P_{\uparrow} + P_{\downarrow}) \); \( L = h v_F / 2\pi T_c \) with \( v_F \) the Fermi velocity in F. (e) \( I_R \) product and normal-state resistance \( R_n \) (in units of \( (e^2/4\pi N\lambda)^2 \) per spin at the Fermi level and the Fermi velocity in the superconductor, respectively) as function of \( P \) for \( T = 0.5T_c \), and various strengths of interface transmission. In all plots the interface misalignment angle is \( \alpha = \pi/2 \). (b) and (c) after [133], (d) and (e) from [212]. Copyright (2009) by the American Physical Society.

increase the free energy density, instead of decreasing it as even-frequency singlet amplitudes do. Only if the \( p \)-wave components (and all higher orbital components) are suppressed by impurity scattering, can the odd-frequency triplet amplitude dominate.

A prominent feature in such a structure is a non-monotonous temperature dependence of the critical Josephson current density, with a pronounced maximum at a temperature which can be linked to the Thouless energy of the ferromagnetic layer (see figure 18(c) and [133]). When the junction becomes effectively long compared with the diffusive-limit coherence length, \( L \gg \xi_d = \sqrt{\xi_F l_B / \lambda} \), the current is dramatically suppressed and the peak is shifted to a lower temperature. This maximum moves also to low temperatures in diffusive structures, as is seen in figure 18(b), which shows its dependence on the mean free path in the ferromagnet. If one replaces the half-metallic ferromagnet by a strongly spin-polarized ferromagnet with two itinerant spin bands, then the maximum remains only for sufficiently strong spin polarization, as seen in figure 18(d). If one projects the Fermi surfaces on the contact plane, then only the ‘half-metallic’ momentum directions contribute to the maximum, which are inside the Fermi sea for one spin projection and outside for the other [168]. Furthermore, there is an optimal spin polarization which maximizes the \( I_R R_n \)-product of the Josephson junction, which for the particular model interface studied in [168] is around \( P \sim 0.3 \). The green shadowed regions in figure 18(d) for small and large spin polarizations are regions beyond the validity of the theory, as other processes which are neglected become relevant.

Following the early theoretical work on triplet supercurrents in half-metallic ferromagnets [152, 161], which treats a fully developed triplet proximity effect self-consistently, numerous groups confirmed the existence of triplet supercurrents under various conditions in half-metallic ferromagnets. In [133] the work of [107, 152, 161] was generalized to include impurity disorder bridging between the two limits of ballistic and diffusive transport. In this work, the full Eilenberger equations with impurity self energy in self-consistent Born approximation was solved. In [170] a fully developed triplet proximity effect, just like in [152] for the clean limit, was treated for the diffusive limit. Further studies in the diffusive limit were performed in [221, 310, 311]. The role of magnon creation in the half-metallic ferromagnet was studied in [312], with a resulting temperature dependence of the critical current reproducing the temperature dependence found in [107, 152]. The case when the superconductor is unconventional was studied in [313–315]. In [212, 316] the problem was advanced on the analytical level assuming a constant singlet order parameter in the superconductor. Self-consistent solution of Bogoliubov–de Gennes equations in the clean limit [317] found results in agreement with [107, 152], including a strong influence of the junction behavior by subgap Andreev bound states.

Most of these theoretical studies deal with either the diffusive limit within the Usadel approximation or the clean limit. The full range of impurity scattering from clean to diffusive limit for a superconductor-half metal proximity structure was first covered in the theory of [133]. A treatment in the quantum limit was given by Béni et al [318].
In [168] a number of effects were pointed out that are absent in the half-metallic case, and which are due to the phase coherent transport of Cooper pairs in the two itinerant spin bands of a ferromagnet. These are illustrated in figure 19. As seen from equation (24b), equal-spin triplet correlations in the ferromagnet acquire an additional phase from the configuration of the magnetic moments in the interface region, \( \mathbf{m}_1 \) and \( \mathbf{m}_2 \), with respect to the bulk magnetization \( \mathbf{M} \). If the three magnetizations are non-coplanar, there is an important geometric phase involved, which is related to the projection of the interface magnetic moments of the two interfaces to the plane perpendicular to the bulk ferromagnetic magnetization [12]. The relative angle between these two projected magnetic moments defines the angle \( \Delta \varphi = \varphi_2 - \varphi_1 \), which is a gauge invariant quantity independent of the choice of the global spin quantization axis. This angle directly enters the current-phase relation for each spin band, and precisely with opposite sign for the spin-up and spin-down bands. This angle is illustrated in figure 19(b). Note that the current-phase relation fulfills the symmetry \( I(\Delta \varphi) = -I(\Delta \varphi - \Delta \varphi) \) following from the behavior of the current density under time reversal. The equilibrium configuration carries a non-zero spin current density \( I_s = 2I_{\text{eq}}(\Delta \varphi, \Delta \varphi) \neq 0 \). The presence of a Josephson current at zero superconducting phase difference \( \Delta \chi \) was confirmed in calculations using Bogoliubov–De Gennes equations in a tri-layer geometry [319]. A study of a superconductor/ferromagnetic-insulator/superconductor junction on the surface of a three-dimensional topological insulator revealed similar effects [320].

The first-order processes described by equations (96a) and (96b) compete with a second order process, where two (or an even number of) pairs are transmitted simultaneously. In analogy to the so-called crossed Andreev reflection process, we call this process crossed pair transmission (see figure 20). For transmission of all pairs in equal direction, this process involves phases which are multiples of \( (\Delta \chi + \Delta \varphi) + (\Delta \chi - \Delta \varphi) = 2\Delta \chi \), for which the dependence on \( \Delta \varphi \) drops out. Consequently, the corresponding contribution to the Josephson current, \( I_{\text{eq}} \), is independent of \( \Delta \varphi \) and \( \pi \)-periodic. More generally, a transmission process of \( m \) spin-up and \( n \) spin-down pairs involves a phase \( (m + n)\Delta \chi + (m - n)\Delta \varphi + (m + n)n \pi \). Thus, the corresponding Josephson charge current can be written as

\[
I = 2e \left[ \frac{1}{2} \sum_{mn} (m + n) (-1)^{m+n} I_{\text{eq}} \sin[(m + n)\Delta \chi + (m - n)\Delta \varphi] \right]
\]

whereas the spin current is

\[
I_s = \hbar \left[ \frac{1}{2} \sum_{mn} (m - n) (-1)^{m+n} I_{\text{eq}} \sin[(m + n)\Delta \chi + (m - n)\Delta \varphi] \right] \]

\[
I = h \sum_{mn} (m - n) (-1)^{m+n} I_{\text{eq}} \sin[(m + n)\Delta \chi + (m - n)\Delta \varphi].
\]

As \( I_{m,-n} = I_{\text{eq}} \), the factor \( \frac{1}{2} \) can be omitted if we restrict the summation to \( m \geq 0 \), and for \( m = 0 \) to positive \( n \). Note that the spin-current is even present in the case \( \Delta \chi = 0 \), provided that \( \Delta \varphi \neq 0 \). An example of such a case was discussed in [168], where one of the superconductors was replaced.
by an insulator, and a pure spin supercurrent remains, giving rise to a spin-Josephson effect. In this case only terms with \( m + n = 0 \) remain, with a pure spin supercurrents \( I_s = \frac{\hbar}{2} \sum_{m=-m}^{m=0} \sin(2m\Delta\phi) \). On the other hand, crossed pair transmission processes in equal direction have zero spin current and correspond to \( m = n \), leading to a contribution to charge current of the form \( 2e \sum_{m=0}^{\infty} \sin(2m\Delta\chi) \). For illustrative purposes we consider the example of only first order terms and leading order crossed pair transmission terms, i.e. only terms associated with \( I_{01}, I_{10}, I_{11}, \) and \( I_{-1,-1} \). Then

\[
\frac{I}{2e} = -I_{10} \sin(\Delta\chi + \Delta\phi) - I_{01} \sin(\Delta\chi - \Delta\phi) + 2I_{11} \sin(2\Delta\chi)
\]

\[
\frac{I}{\hbar} = -I_{10} \sin(\Delta\chi + \Delta\phi) + I_{10} \sin(\Delta\chi - \Delta\phi) + 2I_{11} \sin(2\Delta\phi).
\]

The last term in each of these equations corresponds to the crossed pair transmission process (in equal and opposite direction, correspondingly). The critical current density for positive and negative current bias differs for this case, similar as shown in figure 19(b). Furthermore, for sufficiently large \( I_{11} \) multiple minima of the free energy as function of \( \Delta\chi \) appear, leading to the characteristic jump at a certain value of \( \Delta\phi \) as illustrated in figure 19(c). If \( \Delta\phi \) were continuously varied, a hysteresis would occur, typical for a first order phase transition. Finally, when one of the superconductors is replaced by an insulating material then \( I = 0 \) and the spin-Josephson current is \( I_s = \frac{2\hbar I_{11}}{\Delta\phi} \).

6.4. Recent experimental observations

6.4.1. Triplet supercurrents in half-metallic ferromagnets. Half-metallic ferromagnets are especially promising for applications, as they are fully spin polarized and thus give the largest spin filtering effect possible. The recent developments and applications for half-metallic ferromagnets have been reviewed e.g. in [321–323].

First indications for an coupling of superconductors through a half-metallic ferromagnet came from experiments by Peña et al on ferromagnetic La0.7Ca0.3MnO3, coupled with the high-temperature \( d \)-wave singlet superconductor YBa2Cu3O7–\( \delta \) in trilayers and superlattices [324, 325]. These authors found a long-range proximity effect over a length scale of 100 nm.

In 2006, Keizer et al reported a triplet supercurrent in the half metal CrO2 [326]. The authors used NbTiN as superconducting electrodes and CrO2 grown on TiO2. After it had proved difficult to reproduce the effect, it was in 2010 when finally Anwar et al in the group of Aarts reported that they had found long-range supercurrents through CrO2 grown on Al2O3 (sapphire) [327]. The current was observed over a distance of 700 nm between two superconducting amorphous Mo70Ge30 electrodes. The effect was interpreted in terms of odd-frequency pairing correlations (although really the experiment only indicates equal-spin pairing correlations and does not provide experimental insight about the orbital and frequency symmetry of the pairs). However, the group was not able to find the long-range supercurrent in CrO2 grown on TiO2, the material used by Keizer et al. They noted that their CrO2 films showed a uniaxial anisotropy in contrast to the biaxial anisotropy present in the Keizer et al samples [327, 328].

There had been criticism that based on previous point contact spectroscopy experiments, CrO2 might not be fully spin-polarized. These data were summarized by Löwfander et al in 2010, and it was shown that all point contact data on CrO2 are indeed consistent with full spin polarization, if the theory is extended to take into account realistic interfaces [155].

Anwar et al have in a subsequent study extended their work [329] and find that if a Ni/Cu sandwich between the CrO2 film and the Mo70Ge30 electrodes is used, a long-range supercurrent is observed also for TiO2 substrate over a distance of almost a micrometer. The critical current density is 100 times larger in these Ni/Cu/CrO2 junctions on TiO2 substrate than if sapphire is used as a substrate, and is comparable to that observed by Keizer et al. This proves that in addition to the substrate on which CrO2 is grown, the interface characteristics between CrO2 and the superconductor play a decisive role, and spin-mixing due to misaligned spins as predicted before by theory [152] is the crucial ingredient for explaining the singlet-triplet conversion in these structures.

Further evidence for triplet supercurrents came from a report by Sprungman et al, who found a Josephson effect with ferromagnetic Cu4MnAl Heusler barriers [330]. It was observed that the critical current density versus temperature shows a pronounced peak around 4.5 K (electrodes were Nb), decreasing towards lower and higher temperatures. Such a maximum was predicted in [133, 152, 212]. However, there is some intrinsic gradient of the degree of L21-type Heusler structure ordering inside the Heusler layers, with a low degree if order at the interfaces and higher degree of order in the interior [330]. For that reason, it is too early to decide about the origin of this maximum in \( I_s(T) \) in these experiments.
Another half-metallic ferromagnet is La$_{0.7}$Ca$_{0.3}$Mn$_3$O$_7$, which has been studied in the context of YBa$_2$Cu$_3$O$_7$-La$_{0.7}$Ca$_{0.3}$Mn$_3$O$_7$ multilayers by Peña et al. in 2005. Kalcheim et al [331] performed scanning tunneling spectroscopy experiments on La$_{0.7}$Ca$_{0.3}$Mn$_3$O$_7$ film epitaxially grown on superconducting Pr$_{1.85}$Ce$_{0.15}$CuO$_4$, and find long-range penetration of superconductivity into half-metallic La$_{0.7}$Ca$_{0.3}$Mn$_3$O. Visani et al [332] find quasiparticle and electron interference effects in the conductance across a La$_{0.7}$Ca$_{0.3}$Mn$_3$O/YBa$_2$Cu$_3$O$_7$ interface that demonstrate long-range propagation of superconducting correlations across the half metal. The effect is interpreted in terms of equal-spin Andreev reflections (equal-spin Andreev reflection', or SAR). The peculiarities of Andreev reflection at a half-metal interface with a singlet superconductor are connected with the spin-active interfaces that unavoidably will be involved, and have been clarified in appendix C of [212], and in [155, 162, 164, 165].

6.4.2. Multilayer converter. Experiments utilizing a multilayer geometry, in some sense manufacturing an inhomogeneous magnetization profile by using different spectroscopy for the various layers, led to a successful generation of triplet supercurrents in a thick Co layer by the group of Birge in 2010 [298]. In these experiments two layers of ferromagnetic alloys were used to generate triplet amplitudes, which then are passed as long-range supercurrent through a strongly spin-polarized ferromagnet. The crucial role of the misalignment of the magnetizations was demonstrated. With this breakthrough a simple and reliable way was found to produce long-range triplet supercurrents. The geometry is shown in figure 21 together with the results. It makes use of the previously acquired knowledge of the group that a Co/Ru/Co trilayer instead of a single Co layer will give much better control over the junction behavior (see figure 14(b)) [247]. When the extra outer layers are present, a long-range effect persists, whereas if they are absent, there are only short-range supercurrents present [298, 333]. It was later shown experimentally that the triplet supercurrent is enhanced up to 20 times after the samples are subject to a large in-plane magnetizing field aligning the two Co layers perpendicular to the magnetizations of the two thin outer layers [334], exactly as predicted e.g. in [107, 152, 293]. In [335] a triplet supercurrent in S/F/S/F/S Josephson junctions was studied, where S was superconducting Nb, F a thin Ni layer with in-plane magnetization, and F a Ni/[Co/ Ni]$_n$ multilayer with out-of-plane magnetization. It was found that the supercurrent decays very slowly with F-layer thickness and is much larger when the F' layer are present than if not. This confirmed that the spin-triplet supercurrent is maximized by the orthogonality of the magnetizations in the F and F' layers.

Theoretical treatments of the geometry used by Khaire et al have appeared in [280, 297, 299]. It was subsequently demonstrated experimentally that the critical current scales linearly with area in magnetized junctions, confirming the homogeneity of the superconducting phase difference across the junction area [336].

6.4.3. Long-range effects in ferromagnetic nanowires. There have been also reports for a long-range proximity effect in long ferromagnetic nanowires. An early overview over studies of ferromagnetic nanowires with superconducting electrodes was given by Petrashov et al [337]. The controlled growth of nanowires has improved over the last decade, allowing to create crystalline nanowires of several hundreds nanometers length. Wang and coworkers used a single-crystalline ferromagnetic Co nanowire and reported zero resistance in wires up to 600 nm length [338]. A theory for a long-range singlet proximity effect in ferromagnetic nanowires was given by Konschelle et al [339]. So et al developed a theory of a
ferromagnetic nanowire-superconductor proximity structure based on Rashba spin–orbit coupling in the barrier that induces $p$-wave superconductivity in the ferromagnet [340].

Almog et al [341] report measurements of the dynamical conductance of a double In/Co/In device, where two Co wires are connected to superconducting In electrodes, running parallel less than a coherence length apart from each other. They find a spin polarization of the superconducting order parameters at the interfaces which depends on the relative spin polarization of the two wires. Colci et al [342] study a similar structure with two superconducting electrodes being bridged by two parallel ferromagnetic wires forming an SFFS junction. They concentrate on the phenomenon of crossed Andreev reflection. At low temperatures and excitation energies below the superconducting gap, they find that the superconducting phase-periodic conductance oscillations in ferromagnetic Ho wires in contact with conventional superconductors were measured. The distance between the interfaces was much larger than the singlet superconducting penetration depth.

A triplet supercurrent has been found by Robinson, Witt, and Blamire with a setup using a cobalt layer sandwiched between two holmium layers, constituting another breakthrough in 2010 [279]. The main results of this work are shown in figure 22. Without the Ho layers between the Nb and Co (or with the Ho replaced by Rh) the characteristic voltage $L,R_N$ shows fast oscillations and a short-range decay over six orders of magnitude on a scale of 10 nm. If additional Ho layers are inserted between Nb and Co, the characteristic voltage decays very slowly, by about an order of magnitude on a scale of 50 nm. The effect is spectacular especially for Co thicknesses above 10 nm. Theoretical treatments of this geometry have been given in [182, 345, 346].

Further reports concentrate on creating artificial non-collinear magnetic structures that can be brought in contact with superconductors. In [347] it is reported that a new structure using an exchange-spring magnet was fabricated that can be tuned from a collinear to a non-collinear state by a rotating external magnetic field in a controllable way. With this setup the authors found an increase of superconductivity in the structure (transition temperature and conductance) when an external magnetic field in a controllable way. With this setup the authors found an increase of superconductivity in the structure (transition temperature and conductance) when going to a non-collinear state.

Robinson et al studied Nb/Fe/Cr/Fe/Nb junctions where the thickness of the Cr layer determines the relative alignment of the Fe layers, and find a substantial enhancement of the critical Josephson current when a non-parallel configuration was realized [346].

Witt et al find that in structures with a conical magnetic spacer layer of Ho the critical Josephson current decays exponentially with layer thickness, corresponding to a coherence length of 4.34 nm in Ho, and without showing any oscillatory behavior [349]. Comparing this with the mean free path of 0.28–0.87 nm, they conclude that their Ho structures are in the dirty limit.

A realization of field-tunable in-plane Bloch domain walls in the rare-earth magnet gadolinium if grown between non-collinearly aligned ferromagnets was suggested in [350]. It was found that supercurrents flow through magnetic Ni/Gd/Ni nanopillars, the magnitude of which strongly depends on the domain wall state in Gd. The authors explain this result in terms of...
of the inter-conversion of triplet and singlet pairs, the efficiency of which depends on the magnetic helicity of the structure.

For a recent review by Blamire and Robinson see [351].

7. Modern developments

In the following I selectively give examples for exciting modern developments of the field, without claiming to cover the entire spectrum of activities.

7.1. Spin-valve devices and spin-filter junctions

Although currently the research still concentrates on studying fundamental questions, applications can be imagined in various ways. The most obvious application would be the development of a spin-valve device. Re-entrant phenomena are predicted not only as function of thickness of the adjacent ferromagnetic layers, but also as function of other parameters, e.g. the degree of magnetic inhomogeneity, as in ferromagnets with spiral order. A high degree of experimental control has been achieved in producing large batches of samples with gradually varying thicknesses, allowing for a tailoring of the Fulde–Ferrell–Larkin–Ovchinnikov state [352]. A controllable Josephson spin-valve has been realised recently [353].

Superconducting spin-filter tunnel junctions have been studied recently experimentally [354] and theoretically [355]. In [354], GdN barriers are used as ferromagnetic insulator barriers, and it is shown that the field and temperature dependence of the critical Josephson current is strongly modified by the ferromagnetic insulator. It is found that the strong suppression of Cooper pair tunneling by the spin filtering of the barrier can be modified by magnetic inhomogeneity in the barrier. In theoretical work [355] it was also demonstrated that the differential conductance may exhibit peaks at different values of the voltage depending on the polarization of the spin filter, and the relative angle between the exchange fields and the magnetization of the barrier.

7.2. Flux qubits and semifluxons

Superconducting electronics is undergoing a revival at present, with pressing need for cryogenic memory for flux quantum logic applications as well as new superconducting Qubit applications. Metal spintronics is already widely employed in computer hard disc technology, and superconducting spintronics may lead to energy efficient memory and logic for supercomputing applications. Superconducting digital single-flux-quantum circuits using superconductor-ferromagnet-superconductor sandwich technology to insert $\pi$-Josephson junctions into a circuit is promising due to its high operation speed and low energy consumption [356]. Such systems also solve the problem of high element densities on-chip for operating and holding magnetic flux quanta. A combination of magnetic Josephson junctions and conventional Josephson junctions can be used to form addressable memory cells, energy-efficient memory periphery circuits and programmable logic elements [357, 358].

Another interesting development is semifluxon physics in zero-$\pi$ Josephson junctions. Fluxons are traveling, solitonic waves of magnetic flux in long Josephson junctions, created by external magnetic fields. In a zero-$\pi$-junction a Josephson vortex of fractional magnetic flux is pinned at the zero-$\pi$-boundary. A memory cell based on a $\varphi$-Josephson vortex has been suggested [359], where writing is done by applying a magnetic field and reading by applying a bias current. Storage at low temperatures is passive, without any bias or magnetic field applied.

A high-frequency cryogenic generator operating at about 200 GHz, and based on flipping a semifluxon in a Josephson junction has recently been demonstrated in [362]. A $\pi$ junction is artificially created by current injection using a technique by Ustinov [360], giving rise to a semifluxon [361]. A conversion efficiency of $\sim$10% of dc input power to ac output power was achieved, including the losses on the way from the generator to the on-chip detector. This type of Josephson oscillator is comparable with those based on flux-flow, with advantages like small size and insensitivity to injection current.

Realization of a $0-\pi$ junction in an atomic bosonic quantum gas has been proposed in [363, 364]. In [364] it is suggested that two-state atoms in a double-well trap are coupled and an all-optical $0-\pi$ Josephson junction is created by the phase of a complex-valued Rabi frequency, exhibiting modes similar to semifluxons. It is suggested that pairs of semifluxons can be created by starting from a flat-phase state in long, optical $0-\pi$-0 Josephson junctions formed with internal electronic states of atomic Bose–Einstein condensates [365].

7.3. Non-equilibrium quasiparticle distribution

A particular exciting subject is the possibility to utilize non-equilibrium quasiparticle distribution in conjunction with quantum coherence in so-called Andreev interferometer geometries. These devices were introduced by Petrashev, Antonov, Delsing, and Claeson in 1994 [366]. A superconducting wire (e.g. aluminum) is attached at two points to a normal mesoscopic conductor (e.g. silver or antimony) to form a loop. The conductance of the wire then oscillates as function of the magnetic flux through the loop. The oscillations are attributed to phase transfer from the superconducting condensate to normal electrons via Andreev reflections at the NS interfaces. The so-called $\pi$-SQUID employs an idea of Volkov [367], where by applying a control voltage directly to a normal metal the electron distribution function in the normal metal is modified. This non-equilibrium distribution function is spread over the superconductor and influences the transport in a nonlocal way. This allows for a direct control of the supercurrent through the device, including switching between zero-junction and $\pi$-junction behavior. Such a device was realized experimentally by Morpurgo et al in 1998–99 [368, 369]. Corresponding effects are intrinsically connected with non-locality, Cadden-Zimansky et al [370] combined an Andreev interferometer arrangement with injection of non-equilibrium excitations into a normal wire, giving rise to a current that adds to the supercurrent in the Andreev interferometer and leads to a voltage at the contacts. Due to current conservation each current influences the other, and together they allow for tuning of the contact voltage.
by changing the flux through the Andreev interferometer that controls the supercurrent [371]. Coherent voltage oscillations as functions of external flux are the result.

The combination of non-equilibrium quasiparticle distribution with the Josephson effect seems particularly exciting, and is largely unexplored so far. Recent studies by Bobkova and Bobkov [372, 373] address the problem of spin-dependent non-equilibrium quasiparticle distribution. It is found that the interplay between the spin-dependent quasiparticle distribution and the triplet superconducting correlations induced by the proximity effect between the superconducting leads and ferromagnetic elements of the interlayer leads to the appearance of an additional contribution to the Josephson current. The interplay between short-range and long-range proximity effect is elucidated, and a long-range penetration of opposite-spin Cooper pairs under non-equilibrium conditions is proposed. An increase of the critical Josephson current by few orders of magnitude as a result of the non-equilibrium population in the ferromagnetic layer is suggested. Long-range spin and charge accumulation in mesoscopic superconductors with Zeeman splitting was recently also studied by Silaev et al [374].

A quantum interference transistor involving textured ferromagnets was suggested in [375]. It was shown that such a device acts as an ultra-sensitive magnetometer and allows for singlet-triplet switching by tuning a bias voltage. A combination of two spin injectors with an SFS Josephson junction was discussed in [376, 377].

7.4. Dynamical effects

Dynamical effects in superconductor-ferromagnet structures have moved in the focus of interest recently. In particular, it is clear that magnetization dynamics will be linked closely with Josephson dynamics, leading to potentially new effects. The geometric phases discussed in section 6.3.4, when time dependent, are expected to lead to spin accumulation effects via an imbalance between the equal-spin pair electrochemical potentials, very similar to the voltage linked to a dynamical superconducting phase in the ac Josephson effect [168].

The Josephson current in a diffusive superconductor-ferromagnet-superconductor junction with precessing bulk magnetization was calculated in [378]. It was found that when the junction is phase biased, a dc Josephson current without an ac component can still flow under this non-equilibrium condition. Long-range triplet amplitudes are induced by the precessing magnetization.

In [379, 380] non-equilibrium effects in a Josephson junction with two s-wave singlet superconducting leads coupled via a precessing spin in a quantum dot was examined. An external magnetic field leads to a Larmor precession of the spin, rendering the magnetically active interface time-dependent. The authors analyze the non-equilibrium population of Andreev sidebands and dynamical spin currents. It is found that the supercurrent is enhanced and the critical Josephson current density shows a non-monotonous behavior as function of temperature, accompanied by a corresponding change in spin-transfer torques acting on the precessing spin.

Supercurrent-induced magnetization dynamics in superconductor-ferromagnet Josephson junctions was explored in [381–385, 386]. It is found that the spin supercurrent can induce magnetization switching that is controlled by the superconducting phase difference. The authors in [384, 385] confirm the finding of [168], that the effect of chiral spin symmetry breaking of the structure leads to additional geometric phases that allow for the stabilization of a $\phi$-junction.

In [387] the dynamics of superconductor-ferromagnet-insulator-ferromagnet-superconductor (SFIIFS) junctions with a thin ferromagnetic layers investigated. The coupled dynamics of the magnetization and the Josephson phase leads to Josephson plasma waves coupled to oscillations of the magnetization, affecting the form of the current–voltage characteristics in weak magnetic fields.

7.5. Spin–orbit coupling and topological materials

Spin–orbit effects play an important role whenever the inversion symmetry is broken, either in the bulk material (when it is lacking a center of inversion), or at interfaces and surfaces [388]. A prominent example for spin–orbit effects at surfaces is the Rashba–Bychkov spin–orbit coupling [389], and in the bulk an example is the Dresselhaus coupling due to bulk-inversion asymmetry [390].

Whereas in materials with a center of inversion all band-diagonal matrix elements of the spin–orbit coupling vanish, this is not the case in non-centrosymmetric materials. Spin–orbit coupling in non-centrosymmetric materials is strongly enhanced due to band-diagonal contributions, leading to a splitting of the Fermi surface into spin–orbit bands, sometimes also called ‘helicity bands’ (although a well defined helicity is only in special cases present). The kinetic part of the Hamiltonian in a one-band model has the form

$$\mathcal{H}_{\text{kin}} = \sum_{\mathbf{k}} \sum_{\alpha \sigma} \epsilon(\mathbf{k}) g(\mathbf{k}) \cdot \sigma \sigma' \alpha_{\mathbf{k} \sigma} \sigma'_{\mathbf{k} \sigma'}$$

with the spin–orbit vector being odd in $\mathbf{k}$: $g(-\mathbf{k}) = -g(\mathbf{k})$. In figure 23 various spin–orbit vector fields compatible with the point group of the crystal are visualized on a hypothetical spherical Fermi surface. All three cases are relevant for materials: $C_{4v}$ for CePt$_3$Si [391], CeRhSi$_3$ [392] and CeIrSi$_3$ [393], $T_d$ for Y$_2$C$_3$ [394], and $O$ for Li$_2$Pd$_{1-x}$Pt$_x$B [395]. The kinetic part of the Hamiltonian can be diagonalized, leading to the above mentioned helicity bands. The spin–orbit interaction locks the orientation of the quasiparticle spin with respect to its momentum in each band.

One interesting aspect of a non-centrosymmetric ferromagnetic Josephson junction is the modification of the Josephson relation from an odd function in the superconducting phase difference to a current-phase relation where this symmetry is broken. For example, near the critical temperature the current-phase relation $I = I_0 \sin(\Delta x - \varphi_0)$ can be modified to

$$I = I_c \sin(\Delta x - \varphi_0),$$
where $\Delta \varphi$ is the superconducting phase difference, and $\varphi_0$ is a phase shift proportional to the magnetic moment perpendicular to the gradient of the asymmetric spin–orbit potential [397]. The possibility of a $\varphi_0$-junction has been already taken into account by Josephson [91], and was later considered in Josephson junctions involving unconventional superconductors [396]. Examples of Josephson junctions with half-metals and strongly spin-polarized ferromagnets were discussed in section 6.3.4. A similar effect has also been predicted for Josephson junctions with a spin-polarized quantum point contact in a two-dimensional electron gas with spin–orbit coupling in an external magnetic field [398]. The spin-dynamics with such a $\varphi_0$ Josephson junction has been discussed in [382]. The competition between a Zeeman interaction and a Rashba spin–orbit interaction has been in the center of attention since a while. In connection with one-dimensional quantum wires, an anomalous $\varphi_0$ shift was predicted in [399, 400]. In a model for a mesoscopic multilevel quantum dot the conditions for an anomalous Josephson current equation (101) were found to be a finite spin–orbit coupling, a suitably oriented Zeeman field, and the dot being a chiral conductor [401, 402]. In [319, 403] an anomalous Josephson current was predicted in junctions coupled with a two-dimensional electron gas exhibiting coexistence of spin–orbit coupling and Zeeman field.

A recent development concerns a gauge-covariant approach to establish the transport equations, treating the charge and spin degrees of freedom on equal footing. In this approach both the electromagnetic and spin interactions are described in terms of U(1) Maxwell and SU(2) Yang–Mills equations, respectively [404, 405]. The starting point is a quasiclassical expansion of the microscopic Gor’kov equations in a gauge-covariant manner [406, 407]. The idea is that one can re-write a Hamiltonian of the type

$$H_{\text{kin}} = \frac{(p_x - m v_{\text{s.o.}} \sigma_x)^2}{2m} + \frac{(p_y + m v_{\text{s.o.}} \sigma_y)^2}{2m} - \mu - m v_{\text{s.o.}}^2 + h \cdot \sigma, \quad (103)$$

which motivates to introduce $A_i = -m v_{\text{s.o.}} \sigma_i / \hbar$ and $A_y = m v_{\text{s.o.}} \sigma_y / \hbar$ as two non-abelian gauge potentials. In this approach, the covariant derivative

$$\nabla G = \partial_R G + i[A, G] \quad (104)$$

with the gauge potential $A$ is associated with the gauge field

$$F_{\mu\nu} = \partial_\mu A_\nu - \partial_\nu A_\mu + i[A_\mu, A_\nu] \quad (105)$$

which is antisymmetric in its indices, and has only one component, $F_{\rho\rho} = -2(m v_{\text{s.o.}})^2 \sigma_i / \hbar^2$. This leads in the transport equation to the modification

$$i h \nu_f \cdot \nabla_R \hat{g} \rightarrow i h \nu_f \cdot \nabla_R \hat{g} + i m v_{\text{s.o.}}^2 \partial_\rho [\sigma_i, \hat{g}] \quad (106)$$

with $\partial_\rho$ the derivative along the Fermi surface (which is assumed a circle for simplicity). Using this modified equation, the role of spin–orbit coupling as source of long-range triplet proximity effect in superconductor-ferromagnet structures has been explored in [407]. Furthermore, the connection to $\varphi_0$ Josephson junction behavior has been elucidated [408]. It should be cautioned, however, that the modification in equation (106) does not contain all terms of the same order as the additional term. A quasiclassical theory of disordered Rashba superconductors has also been proposed in [409].

One way to manipulate spin in spintronics devices is the so-called spin Hanle effect [410–412], which describes the coherent rotation of a spin in an external magnetic field. A recent theoretical study of this effect is given in [413]. It is demonstrated that superconductivity can strongly influence the coherent spin rotation, depending on the type of spin.
relaxation mechanism being dominated either by spin–orbit coupling or spin-flip scattering at impurities.

Another manifestation of coherence in systems with spin–orbit coupling is the Aharonov–Casher effect [414], leading to a phase on the Josephson current through a semiconducting ring attached to superconducting leads [415]. This effect is the charge-spin dual effect to the Aharonov–Bohm effect [416], which describes the relative phase shift between two charged particle paths enclosing a magnetic flux. Both effects are manifestations of geometric phases acquired by the quantum mechanic wave function under adiabatic changes [417, 418]. The particle’s spin acquires such a geometric phase in systems with spin–orbit interaction [419–425]. The Aharonov–Casher effect was, e.g. observed experimentally in ring structures of HgTe/HgCdTe quantum wells [426]. In superconducting Josephson rings, or closed Josephson junction arrays, such phases lead to the coherence of the Josephson current due to the Aharonov–Casher phase [415, 427–429]. The effect allows for control of the Josephson current through the control of the Aharonov–Casher phase by the gate voltage. Thus, this effect is a promising candidate for realizing new types of controllable devices in superconducting spintronics based on geometric phases.

Recently Mironov et al [430] studied double path interference during Cooper pair transport through a single nanowire with two conductive channels. It is found that multi-period magnetic oscillations appear due to quantum mechanical interference between channels affected by spin–orbit coupling and Zeeman coupling. The model is relevant to recent observations of interference phenomena in Bi nanowires [431].

A Josephson junction containing a spacer with strong spin–orbit interaction was considered in [432]. A nonlinear dynamical coupling between magnetic moment and charge current was found, and magnetic torque and charge pumping was investigated in such a system. The intricate coupling between spin and charge currents in systems with strong spin–orbit coupling is previously known from non-centrosymmetric superconductors, where spin-polarized Andreev states play a prominent role [433].

This connects to the current hot topic of topological materials, in particular topological insulators and superconductors, both systems with strong spin–orbit coupling. As an example for the extremely rich plethora of effects involving topological materials we mention here the possibility to observe chiral Majorana modes in one-dimensional channels built at a superconductor/ferromagnetic-insulator/superconductor junction on top of a topological insulator [320], where a \( \phi_0 \) junction is predicted. The effect is interpreted as tunneling process between two Majorana edge channels at the two interfaces between the superconductor and the ferromagnetic insulator. Majorana fermions have the property of being their own antiparticle, i.e. their field operators fulfill \( \gamma_x = \gamma_x^\dagger \) [434, 435]. A non-trivial superconducting phase is also obtained in proximity junctions involving semiconductors with Rashba spin–orbit coupling and a time-reversal symmetry breaking Zeeman term in the Hamiltonian [436, 437].

The combined effect of spin–orbit interaction, magnetic field, and Coulomb charging for a multilevel quantum dot tunnel contacted by two superconductors was analyzed in [438]. Majorana bound states in a double dot variant of this system are predicted to leave a clear signature in the 2\( \pi \)-periodic current-phase relation. Majoranas in spin–orbit coupled ferromagnetic Josephson junctions were investigated in [439], were it was shown that two delocalized Majorana fermions with no excitation gap appear in a \( \pi \)-junction. Josephson currents through Majorana bound states in topological insulators have been studied in [440–449]. Such Josephson junctions carry 4\( \pi \)-periodic bound states [440]. It has been shown that under certain conditions this periodicity manifests itself by an even-odd effect in Shapiro steps [442, 448]. In addition, a peak in the current noise spectrum at half the Josephson frequency has been predicted [449].

The diverse spectrum of effects and phenomena in hybrid systems between singlet superconductors and topological insulators (see e.g. [137, 450–456]) are promising examples of how the field can be brought forward, playing a prominent role in various modern developments at the forefront of international research.

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