Relativistic framework for microscopic theories of superconductivity. II. The Pauli equation for superconductors

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It is shown that the interplay between relativity and coherence, found in superconductors with heavy elements, leads to a number of interesting and previously unknown effects. In particular, several types of spin-orbit coupling are shown to exist only in superconductors. Explicit expressions describing these effects are derived using a covariant formulation of the theory of superconductivity. It is demonstrated that relativistic effects can become relevant, e.g., in high-temperature and heavy-fermion superconductors, superconducting heterostructures, and rotating superconductors. [S0163-1829(99)11205-0]

I. INTRODUCTION

This is the second in a series of two papers devoted to an investigation of the effects of relativity in superconductors. In the preceding paper,[1] henceforth referred to as paper I, we studied the Dirac equation for superconductors. It was shown there that the order parameters (OP's) describing superconductivity can be represented in terms of 4×4 matrices entering the Dirac Hamiltonian on the same footing as the conventional $\hat{\gamma}$ matrices of the Dirac theory. By performing a symmetry analysis with respect to the Lorentz group it was found that only five different types of OP's, with a total of 16 components, are consistent with the requirement of covariance. (This is to be contrasted with the nonrelativistic case where one has two types of OP's, namely those for singlet and triplet superconductivity, with a total of four components). The five relativistic OP's transform as a scalar, a pseudoscalar, a four vector, an axial four vector and an antisymmetric tensor of rank two, respectively. These OP's include the relativistic generalization of the BCS (singlet) and the Balian-Werthamer (triplet) OP, among others.

Our study is motivated by the fact that relativity influences many properties of superconductors, such as, e.g., the Knight shift, the upper critical field, the order-parameter symmetry, the Meissner effect, the band structure, the magneto-optical response, etc. However, in most of these situations relativity constitutes a small perturbation acting on an unperturbed, essentially nonrelativistic, superconductor. It is, therefore, not always necessary to employ the full Dirac equation. Considerable simplification is achieved by making the transition to the weakly relativistic limit, i.e., by expanding to order $(v/c)^2$. Not only does this simplify the equations, it also yields further insight into the subtle interplay between relativistic symmetry breaking and superconducting coherence. The present paper therefore deals mainly with the derivation of weakly relativistic corrections to the conventional theory of superconductivity.

The simplest possible case, that of a local order parameter, treated within the conventional Pauli approximation to the Dirac equation, was already studied in our earlier paper, Ref. 2. In the present paper we go in three respects beyond the treatment of that work. Firstly, we use reduction methods which are both more reliable in higher orders and more convenient for numerical calculations than the conventional Pauli approximation. Secondly, we apply these methods to a more general relativistic Hamiltonian containing a nonlocal pair potential instead of a local one. This allows us to investigate the effects of relativity not only on the center-of-mass motion but also on the *internal* degrees of freedom of the Cooper pair. Thirdly, we study the weakly relativistic limit of several types of relativistic order parameters not studied in Ref. 2, but contained in the general formalism of paper I.

The present paper is organized as follows: Sec. II introduces the Dirac–Bogolubov–de Gennes equation. In Sec. III we discuss a variety of methods which can be used to reduce the Dirac equation to the form of a Schrödinger equation plus correction terms. These methods are generalized to superconducters and used to obtain zeroth-, first-, and second-order approximations. In zeroth order we recover the Bogolubov–de Gennes equations, in first order appears the interaction with magnetic fields and in second order we find, among others, several spin-orbit-type terms. Finally, Sec. IV is devoted to a first analysis of these terms and their effect on realistic superconductors.

II. THE DIRAC–BOGOLUBOV–DE GENNES EQUATIONS

The conventional 4×4 Dirac-Hamiltonian (-density), $\hat{h}_d$, is defined by[3,4]

$$\hat{h}_d\Phi := \hat{\gamma}_0[c\,\hat{\boldsymbol{\gamma}}\boldsymbol{p}+mc^2(1-\hat{\gamma}_0)+q\,\hat{\gamma}^\mu A_\mu]\Phi = E\Phi, \quad (1)$$

where E is the energy measured relative to mc^2, $A_\mu = (V/q,-\mathbf{A})$ is the four potential[5] and $\hat{\gamma}^\mu$ stands for the usual $\hat{\gamma}$ matrices.[3,4] Here and in the following a summation over repeated upper and lower greek indices, such as in $\hat{\gamma}^\mu A_\mu$, is implied.

The conventional Bogolubov–de Gennes equation, which is the basic equation of the microscopic theory of inhomogeneous superconductors, reads[6,7]

$$\begin{pmatrix} \hat{h}_s & \hat{d} \\ \hat{d}^\dagger & -\hat{h}_s^* \end{pmatrix}\begin{pmatrix} u_k(\mathbf{r}) \\ v_k(\mathbf{r}) \end{pmatrix} = E_k \begin{pmatrix} u_k(\mathbf{r}) \\ v_k(\mathbf{r}) \end{pmatrix}, \quad (2)$$

where $u_k(\mathbf{r})$ and $v_k(\mathbf{r})$ are particle- and hole amplitudes, respectively. $\hat{h}_s$ is the Schrödinger Hamiltonian

$$\hat{h}_s = \frac{p^2}{2m} + V(\mathbf{r}). \tag{3}$$

The integral operator

$$\hat{d} = \int d^3r' \ldots \Delta(\mathbf{r},\mathbf{r}') \tag{4}$$

contains the pair potential as kernel. For the case of a local pair potential it reduces to the multiplicative operator $\Delta(\mathbf{R})$, where $\mathbf{R}$ is the center-of-mass coordinate of the Cooper pairs.

In our earlier paper[2] and in paper I of this series we have shown that the proper relativistic generalization of the Bogolubov–de Gennes equation is given by the 8×8 equation

$$\begin{pmatrix} \hat{h}_d & \mathcal{D} \\ \mathcal{D}^\dagger & -\hat{h}_d^* \end{pmatrix} \begin{pmatrix} u_{jk}(\mathbf{r}) \\ v_{jk}(\mathbf{r}) \end{pmatrix} = E_{jk} \begin{pmatrix} u_{jk}(\mathbf{r}) \\ v_{jk}(\mathbf{r}) \end{pmatrix}, \tag{5}$$

which we called the Dirac–Bogolubov–de Gennes equation (DBdGE). Here h_d is the Dirac Hamiltonian, as defined in Eq. (1) and $\mathcal{D}$ is the integral operator

$$\mathcal{D} := \hat{d}\,\hat{\eta} = \int d^3r' \ldots \Delta(\mathbf{r},\mathbf{r}')\,\hat{\eta} \tag{6}$$

with the 4×4 matrix

$$\hat{\eta} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix} = \begin{pmatrix} i\hat{\sigma}_y & 0 \\ 0 & i\hat{\sigma}_y \end{pmatrix}. \tag{7}$$

The particle and hole amplitudes u_{jk} and v_{jk} are four-component (Dirac) spinors with components u_{ijk} and v_{ijk}.

In the terminology of I, the matrix $\hat{\eta}$ leads to the scalar OP of the generalized BCS type, defined as

$$\chi(\mathbf{r},\mathbf{r}') := \Psi^T(\mathbf{r})\,\hat{\eta}\,\Psi(\mathbf{r}'). \tag{8}$$

It is this OP which is the direct relativistic generalization of the BCS singlet OP. In I we derived 15 further OP's which describe more complicated pairing states of the superconductor. In the present paper we are mainly concerned with BCS-type pairing and therefore focus on the $\hat{\eta}$-OP. We return to the other 15 OP's in Sec. IV D.

III. WEAKLY RELATIVISTIC APPROXIMATION

A. Conventional Pauli method

In order to identify weakly relativistic corrections to the conventional theory of superconductivity one needs to reduce the Dirac-type equation (5) to the form of a Schrödinger-type equation plus correction terms of various orders in v/c. To this end we first briefly discuss the methods available for this purpose in the case of the conventional Dirac Hamiltonian. Introducing the vector of the Pauli matrices $\boldsymbol{\sigma}$ and writing the four-component spinor Φ in terms of two two-component spinors, ϕ and χ, as

$$\Phi(\mathbf{r}) = \begin{pmatrix} \phi(\mathbf{r}) \\ \chi(\mathbf{r}) \end{pmatrix}, \tag{9}$$

Eq. (1) can be written in terms of two 2×2 equations as

$$V\phi + c\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\chi = E\phi,$$

$$c\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\phi + (V - 2mc^2)\chi = E\chi. \tag{10}$$

Here $\boldsymbol{\pi}$ stands for $[\mathbf{p} - (q/c)\mathbf{A}]$.

For this Hamiltonian there exists a large variety of methods which can be used to generate weakly relativistic approximations. All of them are based on the observation that in the weakly relativistic limit the two components of the spinor χ, denoted the small components, are by a factor v/c smaller than those of ϕ, which are consequently termed the large components. The small components can therefore be approximately eliminated from the equation, reducing the 4×4 Dirac equation to a 2×2 equation of the Schrödinger type. The elimination can be performed in orders of, e.g., v/c, where each order contributes relativistic corrections to the zero order, i.e., Schrödinger, case.

This program is implemented directly in the conventional Pauli method (CPM) in which one solves the second equation of Eq. (10) for χ and substitutes the result into the first. This yields an equation for the large components ϕ only:

$$\left[V + c\boldsymbol{\sigma}\cdot\boldsymbol{\pi} \frac{1}{E - (V - 2mc^2)} c\boldsymbol{\sigma}\cdot\boldsymbol{\pi} \right] \phi = E\phi. \tag{11}$$

Expanding to second order in v/c and evaluating the derivatives leads to the well-known Darwin-, spin-orbit- and mass-velocity corrections.[3,8–11]

The counterpart of Eq. (11) in the superconducting case is immediately found from Eq. (5) to be

$$\left[\begin{pmatrix} V & i\hat{\sigma}_y\hat{d} \\ -i\hat{\sigma}_y\hat{d}^* & -V \end{pmatrix} + \begin{pmatrix} c\boldsymbol{\sigma\pi} & 0 \\ 0 & -c(\boldsymbol{\sigma\pi})^* \end{pmatrix} \times \begin{pmatrix} E - (V - 2mc^2) & -i\hat{\sigma}_y\hat{d} \\ i\hat{\sigma}_y\hat{d}^* & E + (V - 2mc^2) \end{pmatrix}^{-1} \times \begin{pmatrix} c\boldsymbol{\sigma\pi} & 0 \\ 0 & -c(\boldsymbol{\sigma\pi})^* \end{pmatrix} \right] \begin{pmatrix} u_L \\ v_L \end{pmatrix} = E \begin{pmatrix} u_L \\ v_L \end{pmatrix}, \tag{12}$$

which can be rewritten as

$$\Bigg[\begin{pmatrix} V & i\hat{\sigma}_y\hat{d} \\ -i\hat{\sigma}_y\hat{d}^* & -V \end{pmatrix} - \frac{1}{2m}\begin{pmatrix} \boldsymbol{\sigma\pi} & 0 \\ 0 & -(\boldsymbol{\sigma\pi})^* \end{pmatrix} \times \begin{pmatrix} \frac{V-E}{2mc^2}-1 & \frac{i\hat{\sigma}_y\hat{d}}{2mc^2} \\ -\frac{i\hat{\sigma}_y\hat{d}^*}{2mc^2} & -\frac{V+E}{2mc^2}+1 \end{pmatrix}^{-1} \begin{pmatrix} \boldsymbol{\sigma\pi} & 0 \\ 0 & -(\boldsymbol{\sigma\pi})^* \end{pmatrix}\Bigg] \times \begin{pmatrix} u_L \\ v_L \end{pmatrix} = E\begin{pmatrix} u_L \\ v_L \end{pmatrix}. \quad (13)$$

In these equations u_L and v_L are the large components of the DBdGE (the indices jk are suppressed for notational clarity). Each is itself a two-component spinor. Equation (13) is still exactly equivalent to the original DBdGE (5). According to the prescription of the CPM one now proceeds to expand in orders of

$$\frac{V-E}{2mc^2}, \quad \frac{V+E}{2mc^2} \quad \text{and} \quad \frac{\hat{d}}{2mc^2}, \quad (14)$$

and analytically performs the inversion in every order.

Although the CPM is a standard method, it suffers from several drawbacks:[12,13] (i) Already in second order of v/c, the effective Hamiltonian obtained after elimination of the small components, contains the energy to be calculated and thus does not have the form of an eigenvalue problem any more. (ii) The large components of the Dirac Hamiltonian alone are not normalized, only the full (four-component) solutions are. It is, however, these large components which become eigenfunctions of the Pauli Hamiltonian. (iii) The Darwin term, as obtained by the CPM, is not Hermitian. (iv) Detailed evaluation of the three correction terms mentioned above shows that they lead, in the presence of a Coulomb potential, to variationally unstable Hamiltonians. The reason for this lies in the bad convergence properties of the expansions used in the CPM (cf. Sec. III D below).

Similar problems show up in the Foldy-Wouthuysen transformation (FWT). While this used to be a standard method for obtaining weakly relativistic approximations to Dirac-type equations,[3] recent research has shown that in the presence of Coulomb potentials the method amounts to constructing wave functions which are extremely singular and not normalizable.[9] Recent studies and reviews thus generally advise against employing the FWT.[9,10,13–15]

In order to avoid the problems of the CPM and the FWT in the superconducting case, we turn to more sophisticated modifications of the CPM. The first of these, the modified Pauli method (MPM),[12,16] is mathematically very similar to the CPM and solves problems (i)–(iii). We employ this method in Sec. III C of the present work. In Sec. III D we generalize to superconductors a reduction method which was designed specifically to solve problem (iv), namely the regular approximation of Baerends and co-workers.[13,14,17]

As an additional complication the inversion itself is not trivial any more because in the superconducting case the matrix to be inverted contains the nonlocal integral operator $\hat{d}$. This complication was not present in our previous work,[2] because we then assumed the pair potential to be local, so that $\hat{d}$ became the multiplicative operator $\Delta(\mathbf{R})$. In Sec. III C we describe a way to perform the required inversion analytically to any required order in v/c.

B. First order in v/c: The spin–Bogolubov–de Gennes equation

Determining the first- and zero-order approximation to Eq. (13) is straightforward, because (a) all four above-mentioned problems of the CPM manifest themselves only in higher than first order and (b) the terms containing the inverse of the integral operator $\hat{d}$, too, contribute only to the second and higher orders. Setting

$$\frac{V-E}{2mc^2} \equiv \frac{V+E}{2mc^2} \equiv \frac{\hat{d}}{2mc^2} \equiv 0 \quad (15)$$

the matrix inversion becomes trivial. After straightforward algebra, which is essentially the same as in the nonsuperconducting case[3,8,12] one finds, to first order, the following 4×4 equation:

$$\begin{pmatrix} h & i\hat{\sigma}_y\hat{d} \\ -i\hat{\sigma}_y\hat{d}^* & -h^* \end{pmatrix}\begin{pmatrix} u_L \\ v_L \end{pmatrix} = E\begin{pmatrix} u_L \\ v_L \end{pmatrix}, \quad (16)$$

where

$$\hat{h} = \frac{\boldsymbol{\pi}^2}{2m} + V - \mu_0\boldsymbol{\sigma}\mathbf{B} \quad (17)$$

is the generalization of Eq. (3) in the presence of magnetic fields and $\mu_0 = \hbar q/2mc$ is the Bohr magneton. Equation (16) is the spin–Bogolubov–de Gennes equation[6,18] for the case of a nonlocal pair potential $\Delta(\mathbf{r},\mathbf{r}')$. The large components of the Dirac spinors become Pauli spinors with entries for spin-up and spin-down

$$u_L(\mathbf{r}) = \begin{pmatrix} u_{\uparrow\sigma k}(\mathbf{r}) \\ u_{\downarrow\sigma k}(\mathbf{r}) \end{pmatrix} \quad (18)$$

and correspondingly for v_L. Here σ and τ are spin-quantum numbers. Written out as a 4×4 equation, Eq. (16) thus becomes

$$\begin{pmatrix} h_{\uparrow\uparrow} & h_{\uparrow\downarrow} & 0 & \hat{d} \\ h_{\downarrow\uparrow} & h_{\downarrow\downarrow} & -\hat{d} & 0 \\ 0 & -\hat{d}^\dagger & -h^*_{\uparrow\uparrow} & -h^*_{\uparrow\downarrow} \\ \hat{d}^\dagger & 0 & -h^*_{\downarrow\uparrow} & -h^*_{\downarrow\downarrow} \end{pmatrix}\begin{pmatrix} u_{\uparrow\sigma k}(\mathbf{r}) \\ u_{\downarrow\sigma k}(\mathbf{r}) \\ v_{\uparrow\sigma k}(\mathbf{r}) \\ v_{\downarrow\sigma k}(\mathbf{r}) \end{pmatrix} = E_{k\sigma}\begin{pmatrix} u_{\uparrow\sigma k}(\mathbf{r}) \\ u_{\downarrow\sigma k}(\mathbf{r}) \\ v_{\uparrow\sigma k}(\mathbf{r}) \\ v_{\downarrow\sigma k}(\mathbf{r}) \end{pmatrix}, \quad (19)$$

where

$$h_{\tau\tau'}=\left[\frac{1}{2m}\left(-i\hbar\nabla+\frac{e}{c}\mathbf{A}(\mathbf{r})\right)^2+V(\mathbf{r})\right]\delta_{\tau\tau'}-\mu_0[\boldsymbol{\sigma}B(\mathbf{r})]_{\tau\tau'}. \tag{20}$$

We note in passing that the same equation is also found in a completely nonrelativistic calculation from the spin-dependent Bogolubov-Valatin transformation.[6,18,19]

$$\Psi_\tau(\mathbf{r})=\sum_{\sigma k}[u_{\tau\sigma k}(\mathbf{r})a_{\sigma k}+v^*_{\tau\sigma k}(\mathbf{r})a^\dagger_{\sigma k}]. \tag{21}$$

The zero-order approximation is obtained from Eq. (19) by setting $\mathbf{A}\equiv\mathbf{B}\equiv 0$. In this case the 4×4 equation (19) reduces to the conventional 2×2 Bogolubov–de Gennes equation of the theory of inhomogeneous superconductors.[6] We have thus verified that our theory has the correct nonrelativistic limit.

Note that while there are first-order corrections from the electromagnetic potentials, namely the Zeeman term $(\hbar q/2mc)\boldsymbol{\sigma}\mathbf{B}$ and the vector-potential term in $\boldsymbol{\pi}=[\mathbf{p}-(q/c)\mathbf{A}]$, there are no such terms arising from the pair potential. This is a consequence of the form of the matrix $\hat{\eta}$ which characterizes the relativistic generalization of the BCS-OP. In Sec. IV D we discuss the circumstances which can lead to first-order corrections containing the pair potential.

C. Second order in v/c: the modified Pauli approximation

Using the CPM in higher than first order leads to the four difficulties discussed in Sec. III A. The first three of these are solved by a modification of the CPM.[12,16] In the following we briefly outline this modification for the nonsuperconducting case before generalizing it to superconductors. The starting point is Eq. (11), which is written as

$$\hat{M}(E)\phi(\mathbf{r})=E\phi(\mathbf{r}), \tag{22}$$

where $\hat{M}(E)$ is the operator on the left-hand side of Eq. (11). Note that $\hat{M}(E)$ is not a standard Hamiltonian because it contains the ''eigenvalue'' E. Since the four-component wave function $\Phi(\mathbf{r})$ was properly normalized, the large components alone are not. The difference

$$1-\int d^3r\,\phi(\mathbf{r})^*\phi(\mathbf{r})=\int d^3r\,\chi(\mathbf{r})^*\chi(\mathbf{r}) \tag{23}$$

is of second order in v/c and can thus not be neglected beyond first order.

The first step of the MPM consists in rewriting Eq. (11) as[12,16]

$$\underbrace{\Omega\hat{M}(E)\Omega^{-1}}_{:=\hat{M}'(E)}\underbrace{\Omega\phi(\mathbf{r})}_{:=\phi'(\mathbf{r})}=E\underbrace{\Omega\phi(\mathbf{r})}_{=\phi'(\mathbf{r})}. \tag{24}$$

Choosing

$$\Omega=\left(1-\frac{\hbar^2\nabla^2}{8m^2c^2}\right) \tag{25}$$

leads to a properly normalized $\phi'(\mathbf{r})$. It is this function which becomes the nonrelativistic Pauli spinor, not the original $\phi(\mathbf{r})$. Equation (24) is still not an eigenvalue equation. However, operating with

$$\Omega^{-2}=\left(1+\frac{\hbar^2\nabla^2}{4m^2c^2}\right)+O(v/c)^4 \tag{26}$$

on

$$\hat{M}'(E)\phi'(\mathbf{r})=E\phi'(\mathbf{r}) \tag{27}$$

leads to

$$\Omega^{-2}\hat{M}'(E)\phi'(\mathbf{r})=E\phi'(\mathbf{r})+E\frac{\hbar^2\nabla^2}{4m^2c^2}\phi'(\mathbf{r})+O(v/c)^4. \tag{28}$$

The second term on the right-hand side in Eq. (28) now cancels, to order $(v/c)^2$, the energy-dependent term on the left-hand side. After expansion of $M(E)$ to first order in

$$\frac{V-E}{2mc^2}\propto\frac{v^2}{c^2}, \tag{29}$$

one finds from Eq. (28)

$$\left(1+\frac{\hbar^2\nabla^2}{8m^2c^2}\right)\left[V(\mathbf{r})+\frac{1}{2m}\boldsymbol{\sigma\pi}\left(1+\frac{V(\mathbf{r})}{2mc^2}\right)\boldsymbol{\sigma\pi}\right]\times\left(1+\frac{\hbar^2\nabla^2}{8m^2c^2}\right)\phi'(\mathbf{r})=E\phi'(\mathbf{r}). \tag{30}$$

Evidently, the first two above-mentioned problems of the CPM are now taken care of. It turns out that the third, the nonhermiticity of the Darwin term, does not require any further treatment. Unlike Eq. (22), Eq. (30) already yields the correct, Hermitian, Darwin term.[20] Evaluating Eq. (30) up to second order in v/c leads, after straightforward algebraic manipulations,[12] to

$$\left\{\frac{\boldsymbol{\pi}^2}{2m}+V(\mathbf{r})-\mu_0\boldsymbol{\sigma}\mathbf{B}(\mathbf{r})+\frac{1}{4m^2c^2}\left[\frac{\hbar^2}{2}\nabla^2V(\mathbf{r})+\hbar\,\boldsymbol{\sigma}(\nabla V)\times\mathbf{p}-\frac{\mathbf{p}^4}{2m}\right]\right\}\phi'(\mathbf{r})=E\phi'(\mathbf{r}). \tag{31}$$

The first line is just the first-order Hamiltonian (17), while the second line contains the usual Darwin-, spin-orbit coupling (SOC), and mass-velocity corrections.

In the superconducting case one can employ essentially the same method to generate relativistic corrections. The operator Ω is generalized to be a 2×2 matrix acting on the particle- and hole components of the DBdGE eigenfunctions. The manipulations of Eq. (11) described above have to be repeated, now starting with Eq. (12). However, this equation requires the inversion of

$$\hat{W}:=\begin{pmatrix} E-(V-2mc^2) & -i\hat{\sigma}_y\hat{d} \\ i\hat{\sigma}_y\hat{d}^* & E+(V-2mc^2) \end{pmatrix} \tag{32}$$

rather than $E-(V-2mc^2)$, as required in Eq. (11). We thus have to invert $\hat{W}$ and, in particular, the integral operator $\hat{d}$, before we can employ the machinery of the MPM. To this end we make use of the following relation for operators A and B:

$$(A+B)^{-1}=A^{-1}-A^{-1}BA^{-1}+A^{-1}BA^{-1}BA^{-1}-\cdots, \tag{33}$$

which allows us to replace the inversion of $A+B$ by an infinite series[21] in which each term requires the inversion of A only. We now decompose $\hat{W}$ according to

$$\hat{W}=\underbrace{2mc^2\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}}_{:=A}+\underbrace{\begin{pmatrix} E-V & -i\sigma_y\hat{d} \\ i\sigma_y\hat{d}^* & E+V \end{pmatrix}}_{:=B}. \tag{34}$$

In this way we achieve a decomposition where, loosely speaking, A contains the information about relativity, while B contains that about superconductivity. The matrix A can be trivially inverted. Furthermore, it contains all factors of mc^2, so that each term in the series (33) contributes as many factors of $1/c^2$ as it contains factors of A^{-1}. The matrix B, containing the integral operator $\hat{d}$, need not be inverted at all. To obtain the second-order approximation to Eq. (13) we have to go to order $1/c^4$ in Eq. (33). It is readily found from Eqs. (33) and (34) that to this order

$$\hat{W}^{-1}=\frac{1}{2mc^2}\begin{pmatrix} 1-\dfrac{E-V}{2mc^2} & -i\sigma_y\dfrac{\hat{d}}{2mc^2} \\ i\sigma_y\dfrac{\hat{d}^*}{2mc^2} & -\left(1+\dfrac{E+V}{2mc^2}\right) \end{pmatrix}+O(1/c^6). \tag{35}$$

Inserting this result in Eq. (12) we can proceed with the MPM, as above. We first define properly normalized Bogolubov spinors by

$$\begin{pmatrix} u_L' \\ v_L' \end{pmatrix}:=\begin{pmatrix} \Omega & 0 \\ 0 & \Omega \end{pmatrix}\begin{pmatrix} u_L \\ v_L \end{pmatrix} \tag{36}$$

and then eliminate the energy-dependent term on the left-hand side of Eq. (12). The counterpart of Eq. (30) is found to be

$$\left(1+\frac{\hbar^2\nabla^2}{8m^2c^2}\right)\left[\begin{pmatrix} V & i\hat{\sigma}_y\hat{d} \\ -i\hat{\sigma}_y\hat{d}^* & -V \end{pmatrix}+\frac{1}{2m}\begin{pmatrix} \boldsymbol{\sigma\pi}\left(1+\dfrac{V}{2mc^2}\right)\boldsymbol{\sigma\pi} & \boldsymbol{\sigma\pi}\dfrac{i\hat{\sigma}_y\hat{d}}{2mc^2}(\boldsymbol{\sigma\pi})^* \\ -(\boldsymbol{\sigma\pi})^*\dfrac{i\hat{\sigma}_y\hat{d}^*}{2mc^2}\boldsymbol{\sigma\pi} & -(\boldsymbol{\sigma\pi})^*\left(1+\dfrac{V}{2mc^2}\right)(\boldsymbol{\sigma\pi})^* \end{pmatrix}\right]\left(1+\frac{\hbar^2\nabla^2}{8m^2c^2}\right)\begin{pmatrix} u_L' \\ v_L' \end{pmatrix}$$
$$=E\begin{pmatrix} u_L' \\ v_L' \end{pmatrix}, \tag{37}$$

which is a proper eigenvalue equation and has the structure of a Bogolubov–de Gennes-type equation for the particle and hole amplitudes u_L' and v_L'. Note that, as is always the case for Bogolubov–de Gennes-type equations, the upper left corner of the matrix equation (37) corresponds to the nonsuperconducting result (30). By going through the same algebra as in the nonsuperconducting case, we can evaluate the various derivatives and matrix products in (37). Keeping only terms of second order in $1/c$ we finally obtain

$$\left[\begin{pmatrix} h & i\hat{\sigma}_y\hat{d} \\ -i\hat{\sigma}_y\hat{d}^* & -h^* \end{pmatrix}+\frac{1}{4m^2c^2}\begin{pmatrix} \hat{h}_2 & \hat{d}_2 \\ \hat{d}_2^\dagger & -\hat{h}_2^* \end{pmatrix}\right]\begin{pmatrix} u_L' \\ v_L' \end{pmatrix}$$
$$=E\begin{pmatrix} u_L' \\ v_L' \end{pmatrix}, \tag{38}$$

where

$$\hat{h}_2=\frac{\hbar^2}{2}\nabla^2V(\mathbf{r})+\hbar\,\boldsymbol{\sigma}(\nabla V)\times\mathbf{p}-\frac{\mathbf{p}^4}{2m} \tag{39}$$

and

$$\hat{d}_2=\int d^3r'\,\boldsymbol{\sigma p}\Delta(\mathbf{r},\mathbf{r}')\boldsymbol{\sigma p}'\ldots(i\sigma_y)$$
$$-\frac{1}{2}\int d^3r'[\mathbf{p}^2\Delta(\mathbf{r},\mathbf{r}')+\Delta(\mathbf{r},\mathbf{r}')\mathbf{p}'^2]\ldots(i\sigma_y). \tag{40}$$

Here the prime in $\mathbf{p}'$ stands for a derivative with respect to $\mathbf{r}'$. In analogy to the Dirac–Bogolubov–de Gennes equation (5) we call Eq. (38) the Pauli-Bogolubov–de Gennes equation (PBdGE).

The relativistic correction terms of $\hat{h}_2$ and $\hat{d}_2$ are the main result of the present paper. By comparison with Eq. (31) the terms of $\hat{h}_2$ are seen to be the conventional relativistic corrections in this order. In the superconducting case they appear twice, once through $\hat{h}_2$ and once through $-\hat{h}_2^*$. The terms of $\hat{d}_2$, on the other hand, are relativistic corrections of the *same* order in $1/c$ existing in superconductors only. Section IV is devoted to a first analysis of the properties and consequences of these weakly relativistic corrections.

Note that the decomposition (34) is not the only one leading to the final result (38). Choosing

$$A=\begin{pmatrix} E-(V_0-2mc^2) & -i\hat{\sigma}_y\hat{d}_0 \\ i\hat{\sigma}_y\hat{d}_0^* & E+(V_0-2mc^2) \end{pmatrix}, \tag{41}$$

where V_0 is the spatially constant part of $V(\mathbf{r})$ and $\hat{d}_0$ is the integral operator

$$\hat{d}_0=\int d^3r' \ldots |\Delta(\mathbf{r},\mathbf{r}')| \tag{42}$$

containing the modulus of the pair potential as kernel, and defining $B=W-A$, another suitable decomposition is obtained. After a lengthy calculation the matrix A can be inverted analytically up to second order in v/c. Its inverse is, to this order, of the form (35), however with V_0 and $\hat{d}_0$ substituted for V and $\hat{d}$. The second term in the series (33) then contains the contributions of the spatially dependent part of $V(\mathbf{r})$ and the phase of the pair potential. Evaluating this term to second order in v/c as well, leads to the same final expression as the simpler decomposition (34), namely to Eq. (38).

D. The regular approximation

Before we proceed to a discussion of $\hat{h}_2$ and $\hat{d}_2$, we have to return to the problems of the Pauli elimination method. As demonstrated explicitly, the MPM solves problems (i)–(iii) of the CPM, for both the superconducting and the nonsuperconducting case. Problem (iv), the variational instability of the resulting Hamiltonian, still needs to be addressed. The source of this problem is the expansion in

$$\frac{V-E}{2mc^2}\propto\frac{v^2}{c^2}, \tag{43}$$

which is small when v/c is small, but large close to the nucleus. This leads to convergence problems and related unphysical behavior of the Pauli Hamiltonian. Similarly, keeping only the first two terms in the expansion (33) is not justified, unless

$$\|B\|\ll\|A\|, \tag{44}$$

where $\|\cdot\|$ is the operator norm.[22] However, this condition is not satisfied if $E-V$ is of the same order as $2mc^2$. Very close to the nucleus, $E-V$ can even get larger than $2mc^2$ and neither the conventional, nor the modified Pauli method converge. These difficulties are avoided, e.g., in the so-called regular approximation.[13,14,17] In this method one rewrites the fraction in Eq. (11) according to

$$\frac{1}{E-(V-2mc^2)}\equiv\frac{1}{2mc^2}\left(1+\frac{E-V}{2mc^2}\right)^{-1} \equiv\frac{1}{2mc^2-V}\left(1+\frac{E}{2mc^2-V}\right)^{-1} \tag{45}$$

and proceeds to expand in

$$\frac{E}{2mc^2-V(\mathbf{r})}. \tag{46}$$

Evidently, this term is small not only in the nonrelativistic domain, where $mc^2\gg V(\mathbf{r})$, but also close to the nucleus, where $V(\mathbf{r})$ is large. It thus constitutes a much better expansion parameter as the more conventional choice, Eq. (43).[13,14,17]

The regular approximation is readily generalized to superconductors. First, the matrix to be inverted in Eq. (12) is rewritten according to

$$\begin{pmatrix} E-(V-2mc^2) & -i\hat{\sigma}_y\hat{d} \\ i\hat{\sigma}_y\hat{d}^* & E+(V-2mc^2) \end{pmatrix}^{-1} =\frac{1}{2mc^2-V}\begin{pmatrix} \frac{E}{2mc^2-V}+1 & -\frac{-\hat{\sigma}_y\hat{d}}{2mc^2-V} \\ \frac{-\hat{\sigma}_y\hat{d}^*}{2mc^2-V} & \frac{E}{2mc^2-V}-1 \end{pmatrix}^{-1}. \tag{47}$$

The inversion itself proceeds along the same lines as in the case of the MPM. The expansion, finally, is in powers of $E/(2mc^2-V)$ and $\hat{d}/(2mc^2-V)$. In the nonsuperconducting case, one often limits oneself to the zero-order term in this expansion, leading to the zero-order regular approximation (ZORA). A conceptually new feature of the regular approximation is that it no longer is an expansion in orders of v/c. As a consequence, the ZORA Hamiltonian already contains relativistic corrections to arbitrary high order in $1/c$. The same is true for the superconducting generalization of the ZORA. One finds, from Eqs. (47) and (12),

$$\begin{pmatrix} \hat{h}_z+V & i\hat{\sigma}_y\hat{d} \\ -i\hat{\sigma}_y\hat{d}^* & -\hat{h}_z^*-V \end{pmatrix}\begin{pmatrix} u_L \\ v_L \end{pmatrix}=E\begin{pmatrix} u_L \\ v_L \end{pmatrix}, \tag{48}$$

where

$$\hat{h}_z=\boldsymbol{\sigma\pi}\frac{mc^2}{2mc^2-V}\boldsymbol{\sigma\pi}. \tag{49}$$

Equation (48) is denoted the ZORA-Bogolubov–de Gennes equation (ZBdGE). Clearly, there are zero-order corrections arising from the lattice potential, $V(\mathbf{r})$, (which do not have the form of the conventional spin-orbit terms, etc.) but none from the pair potential $\Delta(\mathbf{r},\mathbf{r}')$. In higher orders, there appear also corrections containing $\Delta(\mathbf{r},\mathbf{r}')$.

On physical grounds, we expect that in most solid-state situations only the (modified) Pauli method, and hence Eqs. (38)–(40), are needed. In solids, the core electrons screen the Coulomb potential of the nuclei, so that for the conduction electrons (which are involved in superconductivity) Pauli-type expansions are sufficient. In materials with very heavy elements in the lattice, problem (iv) can also become relevant in solid-state applications. In this case, the ZBdGE (48) provides a viable alternative to Pauli-type procedures.

IV. ANALYSIS OF THE PAULI–BOGOLUBOV–DE GENNES EQUATIONS

A. Interpretation of the correction terms

The weakly relativistic correction terms in the PBdGE containing the pair potential, as given in Eq. (40), can be rewritten in a more transparent way. First, we specialize to finite systems, so that one can perform partial integrations without occurrence of surface terms. It is then readily found that

$$\hat{d}_2 = \int d^3r'\, i\boldsymbol{\sigma}[\mathbf{p}\Delta(\mathbf{r},\mathbf{r}')]\times\mathbf{p}' \ldots i\hat{\sigma}_y - \frac{1}{2}\int d^3r'[(\mathbf{p}+\mathbf{p}')^2\Delta(\mathbf{r},\mathbf{r}')] \ldots i\hat{\sigma}_y. \tag{50}$$

Here the momentum operators act only on the directly following quantities, as indicated explicitly by the brackets. Similar terms are also found in the Pauli approximation to the relativistic Breit equation for two-electron atoms.[23] In the present context we deal with single-particle equations, but the nonlocality of the pair potential reflects the two-particle aspects of the Cooper pair. We now introduce relative and center-of-mass coordinates, **s** and **R**, according to

$$\mathbf{s}(\mathbf{r},\mathbf{r}') := \mathbf{r}-\mathbf{r}' \tag{51}$$

and

$$\mathbf{R}(\mathbf{r},\mathbf{r}') := \frac{\mathbf{r}+\mathbf{r}'}{2}. \tag{52}$$

We use the same symbol for the pair potential expressed in the coordinates of the individual particles, $\Delta(\mathbf{r},\mathbf{r}')$, and expressed in center-of-mass and relative coordinates, $\Delta(\mathbf{s},\mathbf{R})$. Equation (50) then becomes

$$\hat{d}_2 = \int d^3r'[\hat{d}_2^{(1)}(\mathbf{s},\mathbf{R}) + \hat{d}_2^{(2)}(\mathbf{s},\mathbf{R}) + \hat{d}_2^{(3)}(\mathbf{s},\mathbf{R})] \ldots i\hat{\sigma}_y, \tag{53}$$

where the integration is still over $\mathbf{r}'$. The three terms in the kernel of Eq. (53) can now be interpreted physically:

$$\hat{d}_2^{(1)}(\mathbf{s},\mathbf{R}) := \hbar\,\boldsymbol{\sigma}\cdot[\nabla_R\Delta(\mathbf{s},\mathbf{R})]\times\mathbf{p}' \tag{54}$$

is a spin-orbit type term with respect to the orbital motion of the center-of-mass coordinate. It will in the following be denoted as the anomalous[24] spin-orbit coupling term (ASOC) for the center-of-mass degrees of freedom (C-ASOC).

$$\hat{d}_2^{(2)}(\mathbf{s},\mathbf{R}) := \frac{\hbar}{2}\boldsymbol{\sigma}\cdot[\nabla_s\Delta(\mathbf{s},\mathbf{R})]\times\mathbf{p}', \tag{55}$$

on the other hand, is a spin-orbit type term with respect to the *relative motion* of the two electrons in the Cooper pair. This term will be referred to as the anomalous spin-orbit coupling term for the relative degrees of freedom (R-ASOC).

Having classified the ASOC terms with respect to the orbital motion, we now turn to the spin degrees of freedom. There exist at least three spinlike quantum numbers which are of relevance for superconductors. The first is the total spin of the Cooper pair. As we discuss only singlet pairs in the present paper, this is always zero. The second is the spin of the individual electrons in the pair. Finally, there is the spinlike label for the Bogolons, the quasiparticles created by breaking Cooper pairs. [In Eqs. (18)–(21) the latter two quantum numbers are denoted τ and σ, respectively.] The spin involved in both C-ASOC and R-ASOC is the electron spin. It is coupled to the orbital motion of the individual electrons in the presence of the pair potential $\Delta(\mathbf{s},\mathbf{R})$. The effect described by these terms is the additional spin-orbit coupling which originates from the *coherent* motion of the two electrons in the Cooper pair. In the absence of coherence $\Delta(\mathbf{s},\mathbf{R})\equiv 0$ and only the conventional SOC, arising from the lattice potential, $v(\mathbf{r})$, remains.

In many situations the modulus of the pair potential is spatially constant and its phase depends only on the center-of-mass coordinate, so that the full pair potential can be written as

$$\Delta(\mathbf{s},\mathbf{R}) = \bar{\Delta}e^{i\phi(\mathbf{R})}, \tag{56}$$

where $\bar{\Delta}$ is a real-valued constant. Such a pair potential describes, e.g., supercurrents in thin films.[6] For a pair potential of the form (56) and sufficiently close to the critical temperature, the supercurrents are proportional to the gradient of the phase of the order parameter, viz.,

$$\mathbf{j}_s(\mathbf{R}) \propto |\bar{\Delta}|^2\nabla_R\phi(\mathbf{R}). \tag{57}$$

Therefore,

$$\hat{d}_2^{(1)}(\mathbf{s},\mathbf{R}) \propto \boldsymbol{\sigma}\cdot[\mathbf{j}_s\times\mathbf{p}'], \tag{58}$$

which shows that the C-ASOC term can alternatively be interpreted as a coupling of the spin to the supercurrents.

Due to the term $\mathbf{j}_s\times\mathbf{p}'$, the expectation value of Eq. (58) is roughly proportional to the ratio $v_s v/c^2$, where v_s is the velocity associated with the supercurrents (the phase of the condensate) and v is that of the quasiparticle excitations (the Bogolons). This is to be contrasted with the ratio v^2/c^2, which appears in the expectation value of the conventional relativistic corrections contained in $\hat{h}_2$. The MPM for superconductors generates the leading terms in an expansion in both of these parameters.

The R-ASOC term can, along similar lines, be interpreted as a coupling of the spin to the internal currents due to the coherent relative motion of the electrons in the Cooper pair.

The third term in Eq. (53) contains second derivatives with respect to the center-of-mass coordinate and is given by

$$\hat{d}_2^{(3)}(\mathbf{s},\mathbf{R}) := \frac{\hbar^2}{2}\nabla_R^2\Delta(\mathbf{s},\mathbf{R}). \tag{59}$$

Being the counterpart to the conventional Darwin term, this term is referred to as the anomalous Darwin term (ADT).

Note that two types of relativistic corrections one might have expected are not present. First, there is no anomalous Darwin term containing second derivatives with respect to the relative coordinate. Thus, in contrast to the ASOC terms, R-ASOC and C-ASOC, there is no "R-ADT," but only a "C-ADT" term. This is consistent with the requirement of the correct local limit, to be discussed in Sec. IV C. Furthermore, there is no superconducting counterpart to the mass-velocity correction. This is physically reasonable because the mass-velocity correction is entirely of kinematic origin and thus independent of the presence or absence of external potentials.

B. Discussion of consequences of the relativistic corrections

The various relativistic corrections can be classified according to whether they lead to the breaking of symmetries or not. The mass-velocity correction, the conventional and the anomalous Darwin terms do not break any symmetries as compared to a nonrelativistic superconductor. Retaining only these terms in the equations constitutes the superconducting analog to the familiar ''scalar relativistic'' approximation often applied in relativistic electronic structure calculations. It is generally found that the relativistic effect on the kinetic energy, i.e., the mass-velocity correction, is far more important than the Darwin term. As they do not break any symmetries, the main effect of these terms is of a quantitative nature. Examples are the relativistic mass correction for the Cooper pair, which was already measured experimentally[25–28] and the relativistic shift in the energy spectrum of a superconductor, predicted in Ref. 2.

In Refs. 25–28 the experimental data for the mass enhancement of the Cooper pair, obtained using a technique based on rotating superconductors, were interpreted on the basis of *ad hoc* substitution of relativistic mass corrections into the BCS equations. It turned out that this procedure is very delicate and is likely to miss corrections arising from the internal dynamics of the Cooper pair. Indeed, a quantitative explanation of the experimental data could not be achieved in this way.[25–28] Note that our equation (39) predicts that such a mass enhancement takes place *and* allows to evaluate it on the same footing with the effects of the internal Cooper pair dynamics and superconducting coherence.

The spin-orbit terms, on the other hand, couple the spin to the orbital degrees of freedom and, therefore, break the rotational invariance in spin space. This symmetry breaking has a large number of important consequences, such as the hybridization of singlet and triplet states, the lifting of degeneracies, the orientation of the macroscopic magnetization relative to the lattice in ferromagnetic solids and the introduction of the total angular-momentum quantum number, j, instead of the individual quantum numbers l and s.

The effect of these consequences of the conventional SOC on various properties of superconductors has been worked out in detail by many authors. From these investigations it is known that, e.g., SOC can lead to a finite Knight shift at $T=0$, which is in striking contrast to the BCS prediction of zero Knight shift at $T=0$.[29–31] The conditions for coexistence of magnetism and superconductivity are also strongly influenced by SOC.[32,33] Furthermore, SOC can induce Josephson currents in situations where none would be present nonrelativistically.[34–37] The value of the upper critical field, in particular the influence of Pauli paramagnetic limiting, is known to be significantly affected by SOC.[38,39] Moreover, the magneto-optical response of both normal and superconductors is changed in the presence of SOC. In particular, the absorption of light with left-handed polarization differs from that of light with right-handed polarization. This phenomenon, termed dichroism, is mainly due to SOC.[40–43]

With the exception of dichroism, all these effects were, as yet, analyzed on the basis of the conventional SOC only. In each case the ASOC terms provide an additional source of spin-orbit coupling which has a very different temperature behavior as compared to the conventional SOC. For the case of the absorption of polarized light we have meanwhile investigated the effects of SOC and ASOC in detail[41–43] and found that ASOC indeed constitutes an additional, potentially observable, source of dichroism, which is distinguished by its temperature dependence and unique coherence factors.

Finally, the symmetry of the order parameter is strongly influenced by SOC.[34,44–48] The ASOC terms, containing the pair potential itself, can obviously have a similar effect. In particular, the spin-orbit coupling with respect to the relative coordinate of the two electrons in the Cooper pair, R-ASOC, suggests that a classification according to the total angular momentum of the pair j, instead of its orbital component l, may be more important than previously thought. The common classification into s-wave and d-wave superconductivity refers to the internal symmetry of the Copper pair, i.e., to the relative coordinate. In order to discuss the symmetry properties of the OP one usually decomposes it in contributions which transform according to the irreducible representations of the point group of the crystal.[47,48] Specializing momentarily to the case of a homogeneous system, such a decomposition is achieved by Fourier transforming $\Delta(\mathbf{s})$ with respect to the relative coordinate $\mathbf{s}$ and expanding $\Delta(\mathbf{k})$ according to

$$\Delta(\mathbf{k})=\sum_{lm} c_{lm}(|\mathbf{k}|)Y_m^l(\hat{\mathbf{k}}), \tag{60}$$

where Y_m^l denotes the spherical harmonics and $\hat{\mathbf{k}}$ is a unit vector in the direction of $\mathbf{k}$. The approximation

$$c_{lm}(|\mathbf{k}|)\rightarrow c_m(k_F)\,\delta_{l,2}, \tag{61}$$

which restricts attention to the Fermi surface and retains only the $l=2$ spherical harmonic, then leads to the much discussed case of d-wave superconductivity. The point group of the crystal is taken into account by replacing the spherical harmonics by symmetry adapted basis functions of the point group.[47] It is tempting to speculate that the difficulties encountered in uniquely assigning the OP in the high-temperature superconductors and the heavy-fermion compounds a value of l (Refs. 34,44,48) may be partially due to the fact that, as a consequence of R-ASOC, the internal degrees of freedom actually have to be classified according to j. Whether or not this classification is mandatory depends, of course, on the actual magnitude of the various SOC terms. We, therefore, now turn to a brief discussion of the circumstances under which SOC and ASOC can be relevant for realistic superconductors.

The energy contribution due to SOC, as described by the second term in Eq. (39), is known to rise approximately as $Z_{\rm eff}^4$, where the effective nuclear charge is given by $Z_{\rm eff}=Z-z$. The shielding correction z takes into account that the core electrons screen the nuclear Coulomb potential. Normal-state calculations show that for elements with $Z>40$ inclusion of the SOC is essential. Every high-temperature superconductor and all heavy-fermion systems contain such elements.

To assess the importance of the ASOC terms we replace the gradients of the pair potential by suitable averages, according to

$$\nabla_R \Delta(\mathbf{s},\mathbf{R}) \rightarrow \frac{\langle \Delta \rangle}{\xi}, \tag{62}$$

where $\langle \Delta \rangle$ is the average energy gap and ξ is the coherence length. For a superconductor with a coherence length which is, e.g., 100 times smaller and an energy gap which is 100 times larger than for typical BCS-type superconductors, ASOC becomes 10^4 times more important. These numerical values are typical of the high-temperature superconductors.

The fact that the magnitude of ASOC hence does not depend primarily on the presence of heavy atoms (i.e., high Z), but also on typical superconducting properties such as ξ, implies that ASOC can be relevant even when SOC alone is not. Relativity might therefore be important for a larger class of materials than previously thought. Such a situation is realized, e.g., in the vortex state of a superconductor containing light atoms. Here SOC is small, since Z is small, while C-ASOC is large because $\nabla_R \Delta(\mathbf{s},\mathbf{R})$ is large in the vortices. Similar considerations apply to superconducting heterostructures where $[\nabla_R \Delta(\mathbf{s},\mathbf{R})]/\Delta(\mathbf{s},\mathbf{R})$ becomes large at the interfaces.

R-ASOC, on the other hand, can be expected to be important for an OP with a complicated internal structure, such as the OP describing anisotropic superconductivity, the Fulde-Ferrel state, coexistence of superconductivity and magnetism, etc., because in these cases $\nabla_s \Delta(\mathbf{s},\mathbf{R})$ is enhanced, as compared to homogeneous s-wave order parameters.

It should finally be stressed that, although the absolute magnitude of SOC and ASOC is small in most materials, the effects produced by them can be quite large. The SOC-induced splitting of bands can, e.g., lead to band gaps of the order of 0.1 eV or more,[49] which is due to the symmetry-breaking effect of the conventional SOC. A similar effect might occur also for the ASOC terms. Further situations in which SOC and ASOC can play a role are mentioned in Sec. V.

C. Relation to the previous formulation of the relativistic theory of superconductivity

In a previous paper[2] we presented a relativistic theory of superconductivity for superconductors with a *local* pair potential. A local formulation is, of course, not able to handle the internal degrees of freedom of the Cooper pair, but it is adequate to treat macroscopic inhomogeneities, such as surfaces, vortices, etc.

The corresponding OP was expressed in terms of the matrix $\hat{\eta}$, as given in Eq. (7) of the present paper, according to

$$\chi(\mathbf{r}) = \Psi(\mathbf{r})^T \eta \Psi(\mathbf{r}), \tag{63}$$

where $\Psi(\mathbf{r})$ is a four component solution to the Dirac equation. This is the local version of the BCS-type OP defined in Eq. (8).

In the present paper we are mainly concerned with the nonlocal case, for which we used the MPM to generate weakly relativistic corrections. In Ref. 2, on the other hand, we used the CPM for a *local* pair potential and, being faced with the above-mentioned problems of the CPM, employed perturbation theory to construct an energy-independent and Hermitian Hamiltonian.

The local limit of the first term in Eq. (40) is obtained from the replacement

$$\Delta(\mathbf{r},\mathbf{r}') \rightarrow \Delta(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}') \tag{64}$$

and yields

$$\begin{aligned}(\boldsymbol{\sigma p})[\Delta(\mathbf{r})(\boldsymbol{\sigma p})]\varphi(\mathbf{r})(i\sigma_y) &= (\mathbf{p}\Delta(\mathbf{r}))(\mathbf{p}\varphi(\mathbf{r}))(i\sigma_y) + \Delta(\mathbf{r})\mathbf{p}^2\varphi(\mathbf{r})(i\sigma_y)\\ &\quad + i\boldsymbol{\sigma}(\mathbf{p}\Delta(\mathbf{r}))\times(\mathbf{p}\varphi(\mathbf{r}))(i\sigma_y),\end{aligned} \tag{65}$$

where $\varphi(\mathbf{r})$ is an arbitrary test function and the right-hand side follows from the properties of the Pauli matrices. The corresponding limit of the second term in Eq. (40) is

$$\begin{aligned}-\frac{1}{2}[\mathbf{p}^2(\Delta(\mathbf{r})\varphi(\mathbf{r})) + \Delta(\mathbf{r})\mathbf{p}^2\varphi(\mathbf{r})](i\sigma_y) &= -\frac{1}{2}(\mathbf{p}^2\Delta(\mathbf{r}))\varphi(i\sigma_y) - \Delta(\mathbf{r})\mathbf{p}^2\varphi(\mathbf{r})(i\sigma_y)\\ &\quad - (\mathbf{p}\Delta(\mathbf{r}))(\mathbf{p}\varphi(\mathbf{r}))(i\sigma_y).\end{aligned} \tag{66}$$

The sum of both is thus

$$\left[i\boldsymbol{\sigma}(\mathbf{p}\Delta(\mathbf{r}))\times\mathbf{p} - \frac{1}{2}(\mathbf{p}^2\Delta(\mathbf{r}))\right]\varphi(\mathbf{r})(i\sigma_y), \tag{67}$$

which is the relativistic correction for a local pair potential as derived in Ref. 2. In view of the different methods used in both approaches this agreement constitutes a useful consistency test.

Note that the correct local limit is obtained from the R-ASOC, C-ASOC, and ADT contributions, as described in Sec. IV A. The presence of a further ADT containing derivatives with respect to the *relative* coordinate would be impossible to reconcile with the requirement of the correct local limit. Indeed, *postulating* the appearance of an anomalous Darwin term of the form

$$\hat{d}_2^{(4)}(\mathbf{s},\mathbf{R}) := \alpha \frac{\hbar^2}{2} \nabla_{\mathbf{s}}^2 \Delta(\mathbf{s},\mathbf{R}) \tag{68}$$

in Eq. (53) and determining the factor α from the requirement of the correct local limit, it is found that the only solution is $\alpha \equiv 0$. Our treatment of the nonlocal pair potential with the MPM automatically yields the corrrect ADT.

Concluding this section we point out that while Ref. 2 was the first to provide a microscopic derivation of a spin-orbit term containing the pair potential, Ueda and Rice[50] previously suggested such a term on group-theoretical grounds. However, their result is limited to p-wave superconductivity in a cubic crystal and contains phenomenological coefficients.

D. Inclusion of the second OP of the generalized BCS-type

In I we discussed in detail which types of OP and pair potentials can be included in a relativistic theory of superconductivity without violating covariance. It turned out that only two of the 16 OP components are consistent with the requirement of BCS-type pairing. The first, transforming as a scalar under Lorentz transformations, is $\chi(\mathbf{r},\mathbf{r}')$, as defined in Eq. (8).

The other, transforming as the zeroth component of a four vector, is

$$\chi_V^0(\mathbf{r},\mathbf{r}') := \Psi^T(\mathbf{r})\,\hat{\eta}_V^0 \Psi(\mathbf{r}'), \tag{69}$$

where $\hat{\eta}_V^0$ is defined as

$$\hat{\eta}_V^0 = \begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix} = \begin{pmatrix} i\hat{\sigma}_y & 0 \\ 0 & -i\hat{\sigma}_y \end{pmatrix}. \tag{70}$$

The associated pair potential is $\Delta_{V0}(\mathbf{r},\mathbf{r}')$ [cf. Eqs. (74) and (75) of paper I]. Although retaining only the zeroth component of the four vector is not Lorentz invariant,[51] it is interesting to investigate the weakly relativistic corrections due to the second OP of the generalized BCS type. We can include this OP in the DBdGE simply by replacing $\mathcal{D}$, as defined in Eq. (6), by

$$\mathcal{D}' = \int d^3r' \ldots [\Delta(\mathbf{r},\mathbf{r}')\,\hat{\eta} + \Delta_{V0}(\mathbf{r},\mathbf{r}')\,\hat{\eta}_V^0]. \tag{71}$$

Defining

$$\Delta_\pm(\mathbf{r},\mathbf{r}') := \Delta(\mathbf{r},\mathbf{r}') \pm \Delta_{V0}(\mathbf{r},\mathbf{r}') \tag{72}$$

and repeating the steps of the MPM, we find a slightly different form of the weakly relativistic corrections.

In zeroth and first order the only change is that $\Delta(\mathbf{r},\mathbf{r}')$ is replaced everywhere by $\Delta_+(\mathbf{r},\mathbf{r}')$. This merely amounts to a redefinition of the pair potential, without changing the structure of the equations. In second order, however, the structure does change. Namely, in all correction terms $\Delta(\mathbf{r},\mathbf{r}')$ is replaced by $\Delta_-(\mathbf{r},\mathbf{r}')$, so that now two *different* pair potentials appear in the PBdGE.

In the same way the other 14 OP's derived in I can be included as well. All OP matrices which are of the form

$$\begin{pmatrix} X & 0 \\ 0 & Y \end{pmatrix}, \tag{73}$$

where X and Y are 2×2 matrices, lead to increasingly complex combinations of pair potentials and 2×2 matrices in the weakly relativistic correction terms. The OP's of this form were shown in I to describe the relativistic generalization of singlet and triplet pairs, formed from two positive- or two negative-energy solutions of the Dirac equation.

OP's containing off-diagonal entries in Eq. (73), on the other hand, describe pairs composed of a positive and a negative-energy state. While it is unlikely that such pairs exist in solid-state situations, their existence is not forbidden by relativity. Such OP's lead to off-diagonal entries in the matrices

$$\begin{pmatrix} c\boldsymbol{\sigma\pi} & 0 \\ 0 & -c(\boldsymbol{\sigma\pi})^* \end{pmatrix} \tag{74}$$

appearing in the course of the CPM or the MPM [cf. Eq. (12)] and thus to relativistic corrections of *first order* in v/c, i.e., of the same order as the Zeeman term and the vector-potential term.

Note that the pairing interaction would have to bridge the energy gap of $2mc^2$ to yield pairs consisting of an $E>0$ and an $E<0$ solution of the Dirac equation. If such an interaction exists, the leading corrections will be of first order. However, the order parameters describing pairs composed of a positive and a negative-energy solution of the Dirac equation are matrix elements between states differing in energy by, typically, $2mc^2$ and thus expected to be very small.

Normally any given interaction leading to superconductivity will lead to only one type of OP. If several distinct OP's are present in one system this will result in a complicated phase diagram, with more than one superconducting phase. It follows from the above that the effect of relativity then depends on the phase under consideration. This might be relevant for the heavy-fermion compounds UPt_3 and $U_{1-x}Th_xBe_{13}$ which do indeed contain extremely heavy atoms and display several distinct superconducting phases.[34]

V. CONCLUSION AND OUTLOOK

The main result of this paper is the derivation of weakly relativistic correction terms to the ordinary theory of superconductivity, as given in Eqs. (39), (40), and (53). The existence of such terms is a necessary consequence of formulating the underlying theory of pairing in a Lorentz invariant fashion.

The conventional (nonrelativistic) theory of superconductivity was shown to be the nonrelativistic limit of our theory. This identification allowed us to employ various reduction procedures which generate weakly relativistic corrections from the Dirac equation, in order to derive such corrections for superconductors. Three reduction procedures, the conventional Pauli approximation, the modified Pauli approximation, and the regular approximation were generalized to superconductors and compared with each other.

The resulting weakly relativistic corrections are of two types. First, one finds the usual spin-orbit, Darwin-, and mass-velocity corrections, which are well known from the normal state. Second, there appear counterparts to these corrections containing the pair potential in place of the lattice potential. The latter type of corrections exists only in superconductors and was previously unknown.

We interpret the corrections in terms of the influence of relativity on the coherent motion of the electrons in the Cooper pair. A first analysis of the significance of the terms indicates that they may be relevant for high-temperature superconductors, heavy-fermion compounds, and superconducting heterostructures.

In all of the above we neither had to specify the precise nature of the interaction leading to pairing, nor the type of the particles involved. Therefore, just as is the case for paper I, the application of our results is not limited to proper superconductors, but extends to any situation in which pairing takes place. Apart from BCS-type and unconventional superconductivity this also includes, e.g., superfluidity in helium 3.[19,52] Other circumstances in which pairing and relativity may play a role simultaneously are the BCS model of nuclear matter,[53] and astrophysical situations, such as pairing of neutrons and protons in neutron stars.[54,55]

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[21] The question of convergence of this series is dealt with in the next section.

[22] If the operators A and B are replaced by numbers, a and b, the expansion (33) is seen to reduce to the geometrical series

$$\frac{1}{a+b} = \frac{1}{a}\frac{1}{1-(-b/a)} = \frac{1}{a}\sum_n (-1)^n \left(\frac{b}{a}\right)^n,$$

which converges only if $|b/a| < 1$.

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