Low Temperature Physics ARTICLE scitation.org/journal/ltp

Time evolution of spin singlet in static homogeneous exchange and magnetic fields

Cite as: Fiz. Nizk. Temp. **47**, 895–902 (October 2021); doi: 10.1063/10.0006061
Submitted: 17 August 2021

S. V. Kuplevakhsky and S. V. Bengus[a)]

AFFILIATIONS

B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine, Kharkiv 61103, Ukraine

[a)]**Author to whom correspondence should be addressed:** sbengus@ilt.kharkov.ua

ABSTRACT

Within the framework of an idealized theoretical model, we study the effect of external static homogeneous exchange and magnetic field on the spin part of the singlet wave function of two electrons. We begin by revising the traditional (textbook) approach to the spin singlet. Basing our own approach solely on the property of invariance under rotations of the coordinate system and using the theory of spinor invariants, we derive a generalized representation of the spin singlet whose main feature is that the spins are in mutually time-reversed states. We show that exactly this feature predetermines the actual form of the Hamiltonian of interaction with the external field and stipulates time evolution of the singlet. Some applications of these results to the theory of superconductivity and spin chemistry are presented. In particular, it is shown that the case of ferromagnetic superconductors constitutes a good illustration of the validity of our quantum-mechanical consideration.

1. INTRODUCTION

The aim of this paper is to study theoretically the effect of external static homogeneous exchange and magnetic fields on the spin part of a singlet wave function of two electrons. For fear of possible misreading, we shall first of all formulate our exact statement of the problem. The idealized model accepted in this paper does not take into account any electromagnetic or exchange interactions between the electrons of the singlet. Moreover, to make our consideration uniform, we completely disregard orbital degrees of freedom and concentrate only on spin dynamics. Surprisingly, although the thus stated problem concerns the basics of quantum mechanics and has important applications in related sciences, it is not discussed in standard textbooks,[1–6] and we are unaware of the correct solution to it in literature. For example, if we choose the spin quantization axis to be perpendicular to the external field, we notice that the probabilities of definite spin orientations oscillate with time and that spin flips occur.[3] These intuitive conjectures about the behavior of the spin singlet in the presence of external fields will be verified, refined on and developed by means of rigorous mathematical methods in the sections of the paper that follow.

In particular, we begin Sec. 2 with an analysis of certain drawbacks of the traditional (textbook)[1–6] representation of the spin singlet. After that, based on the theory of spinor invariants,[7,8] we derive a generalized representation of the spin singlet which is free from the drawbacks of the traditional one: the generalized representation is explicitly invariant under rotations of the coordinate system. The main feature of the generalized representation is that the spins are in mutually time-reversed states. Relationship to the representation of the spin singlet as a normalized metric spinor is established.

In Sec. 3, we use the results of section Sec. 2 to study the evolution of the spin singlet. An exact time dependent spin wave function is derived. This wave function exhibits periodic conversions from the spin singlet to the zero component of the spin triplet along the external field. Periodic permutations of the spins of the singlet, caused by spin flips, are also envisaged.

In Sec. 4, we consider the application of the results of the previous section to the theory of ferromagnetic super- conductors and spin chemistry. Some mathematical details related to the results of Secs. 2–4 are relegated to Appendices A and B. In Sec. 5, key results of the paper are discussed and several conclusions are drawn.

2. THE GENERALIZED REPRESENTATION OF THE SPIN SINGLET

The correlation between the spins of the singlet clearly manifests itself in the property of invariance under rotations of the coordinate system. To explain the situation, we begin by drawing the reader's attention to some little-known mathematical aspects of the singlet wave function, not mentioned in standard textbooks (see, for example, Refs. 1–6).

Traditionally, the singlet wave function is written down as an antisymmetric linear combination of the eigenfunctions of one of the Cartesian components of the total spin $S = s_1 + s_2$, corresponding to a zero eigenvalue of the operator S^2:

$$\Psi_S(1,2) = \frac{1}{\sqrt{2}}(\Psi_{\alpha+} \otimes \Psi_{\alpha-} - \Psi_{\alpha-} \otimes \Psi_{\alpha+}). \tag{1}$$

Here, $\alpha = x, y, z$; the sign $\otimes$ denotes a direct product of two-dimensional Hilbert spaces of spin 1 (on the left) and spin 2 (on the right) $\Psi_{\alpha+}$ and $\Psi_{\alpha-}$ are the eigenfunctions of the corresponding Pauli matrices.

Using the properties of the time-reversal operator K,[9] we may obtain the following generalized representation of the singlet state:

$$\Psi_S(1,2) = \frac{1}{\sqrt{2}}(K\Psi_{\alpha-} \otimes \Psi_{\alpha-} + K\Psi_{\alpha+} \otimes \Psi_{\alpha+}), \tag{2}$$

where $K\Psi_{\alpha-} = \Psi_{\alpha+}$ and $K\Psi_{\alpha+} = -\Psi_{\alpha-}$.

We want to say that Eq. (2) are not merely a new representation of the singlet state, different from the traditional one. It emphasizes only that the singlet state is formed by two spin states that are mutually reversed in time.

3. TIME EVOLUTION OF THE SPIN SINGLET

Now we are fully prepared to return to our main problem: the evolution of the singlet state. If the spins were independent, the dynamics of both of them would be generated by the same single-particle Hamiltonian

$$\mathcal{H} = -\sigma_z J. \tag{3}$$

Note that in the case of an exchange field, which is parallel to z direction, J is just its value; in the case of a magnetic field H, $J = -g\mu_b H_z$ with μ_b is the Bohr magneton. The evolution operator for an initial state is Ψ

$$U(t) = \exp\left(-i\frac{\mathcal{H}}{\hbar}t\right). \tag{4}$$

The evolution operator for the time-reversed state $K\Psi$ is[9]

$$U_{\text{rev}}(t) = KU(-t)K^{+} = \exp\left(-i\frac{K\mathcal{H}K^{+}}{\hbar}t\right). \tag{5}$$

Thus, the evolution operator for the spin singlet (2) has the following form:

$$U_{1,2}(t) = \exp\left(-i\frac{K\mathcal{H}K^{+}}{\hbar}t\right) \otimes \exp\left(-i\frac{\mathcal{H}}{\hbar}t\right). \tag{6}$$

For the perpendicular magnetic field the corresponding time-dependent two-spin state has the form

$$\Psi(1,2;\ t) = a(t)\Psi_S(1,2) + b(t)\Psi_T(1,2), \tag{7}$$

where $\Psi_T(1,2)$ is the triplet two-spin function with z projection of total spin $S^Z = 0$

$$\Psi_T(1,2) = \frac{1}{\sqrt{2}}(\Psi_{\alpha+} \otimes \Psi_{\alpha-} + \Psi_{\alpha-} \otimes \Psi_{\alpha+}). \tag{8}$$

Among other things, relation (6) implies that the actual interaction Hamiltonian for the spin singlet is not

$$\mathcal{H} \otimes I + I \otimes \mathcal{H}, \tag{9}$$

as would be the case for two independent spins, but rather

$$\mathcal{H} \otimes I + I \otimes K\mathcal{H}\mathrm{K}^{+} \tag{10}$$

or

$$\mathrm{K}\mathcal{H}\mathrm{K}^{+} \otimes I + H \otimes I, \tag{11}$$

where I is a unit operator. Relations (10) and (11) take explicitly into account the correlation between the spins of the singlet.

Consider first the representation (2) and the evolution operator (6). Although the explicit form of the time-dependent state

$$\begin{aligned}\Psi(1,2;\ t) = U_{1,2}(t)\Psi_S(1,2) \equiv \frac{1}{\sqrt{2}}[&U(t)\Psi_{\hat{\mathbf{n}}+} \otimes U_{\text{rev}}(t)K\Psi_{\hat{\mathbf{n}}+}\\ &+U(t)\Psi_{\hat{\mathbf{n}}-} \otimes U_{\text{rev}}(t)K\Psi_{\hat{\mathbf{n}}-}]\end{aligned} \tag{12}$$

can be evaluated for an arbitrary direction of the vector $\hat{\mathbf{n}}$ in Eq. (12), from the point of view of physical interpretation, it is reasonable to take $\hat{\mathbf{n}}$ perpendicular to the direction of the field: say, $\hat{\mathbf{n}} = \hat{\mathbf{x}}$. In this way, we immediately arrive at the following set of expressions:

$$\Psi(1,2;\ t) = \begin{cases} a(t)\Psi_S(1,2) + b(t)\Psi_{T,S_z=0}(1,2), & a(t) > 0; \\ |a(t)|\Psi_S(2,1) + b(t)\Psi_{T,S_z=0}(2,1), & a(t) < 0; \end{cases} \tag{13}$$

$$\begin{aligned}\Psi_S(1,2) = -\Psi_S(2,1) &= -\frac{1}{2}\left[\begin{pmatrix}1\\1\end{pmatrix} \otimes \begin{pmatrix}1\\-1\end{pmatrix} - \begin{pmatrix}1\\-1\end{pmatrix} \otimes \begin{pmatrix}1\\1\end{pmatrix}\right]\\ &= \frac{1}{2}\left[\begin{pmatrix}1\\0\end{pmatrix} \otimes \begin{pmatrix}0\\1\end{pmatrix} - \begin{pmatrix}0\\1\end{pmatrix} \otimes \begin{pmatrix}1\\0\end{pmatrix}\right],\end{aligned} \tag{14}$$

$$\Psi_{T,S_z=0}(1,2) = \Psi_{T,S_z=0}(2,1) = \frac{1}{2}\left[\begin{pmatrix}1\\0\end{pmatrix} \otimes \begin{pmatrix}0\\1\end{pmatrix} + \begin{pmatrix}0\\1\end{pmatrix} \otimes \begin{pmatrix}1\\0\end{pmatrix}\right], \tag{15}$$

$$a(t) = \cos\left(\frac{2Jt}{\hbar}\right) \equiv 2\left[\frac{1}{2} - \sin^2\left(\frac{Jt}{\hbar}\right)\right], \tag{16}$$

$$b(t) = i\sin\left(\frac{2Jt}{\hbar}\right) \equiv i2\sin\left(\frac{Jt}{\hbar}\right)\cos\left(\frac{Jt}{\hbar}\right). \tag{17}$$

Here, $\Psi_{T,S_z=0}(1,2)$ is the component of the triplet state corresponding to $S_z = 0$; $a(t)$ and $b(t)$ are the probability amplitudes of the states Ψ_S and $\Psi_{T,0}$, respectively; $\sin^2\left(\frac{Jt}{\hbar}\right)$ is the probability of a spin flip in a perpendicular field J;[3] $\sin\left(\frac{Jt}{\hbar}\right)$ and $\cos\left(\frac{Jt}{\hbar}\right)$ are the probability amplitudes of a spin flip and of the absence of a spin flip, respectively. Furthermore, $\left|\frac{1}{2} - \sin^2\left(\frac{Jt}{\hbar}\right)\right|$ is the probability of a definite spin orientation.

In addition, we want to emphasize that time dependence of the probability amplitude $a = a(t)$ reflects the dynamics of the time-reversal operator $K = K(t)$, which is clear from the representations derived in Appendix A:

$$a(t) = \frac{1}{2}\mathrm{Sp}[K(t)K^+(0)] = \frac{1}{2}\mathrm{Sp}[K(-t)K^+(0)], \tag{18}$$

$$K(t) = \exp\left(i\frac{\mathcal{H}}{\hbar}t\right)K(0)\exp\left(i\frac{\mathcal{H}}{\hbar}t\right). \tag{19}$$

Here, the time-reversal operators are, of course, written down in the Heisenberg representation. Equal sign in the arguments of both the exponents in Eq. (19) is due to the antilinearity of K: $Ki = -iK$.

As can be seen from Eqs. (13)–(17), when an external non-time-reversible field is "switched on" at $t = 0$, the initial singlet state Ψ_S starts to decay gradually, whereas the zero component of the triplet state along the external field, $\Psi_{T,S_z=0}$, is emerging owing to spin flips induced by the field. At $t = \frac{\pi\hbar}{4J}$ a permutation of the spins 1 and 2 occurs, which is reflected in the second line of Eq. (13). At $t = \frac{3\pi\hbar}{4J}$ a new permutation of the spins occurs. Formally, the process is periodic with the period $T = \frac{\pi\hbar}{J}$.

Certainly, in view of idealized character of our model (see the Introduction) the possibility of the observation of the above-described quantum-mechanical effects in real electron systems strongly depends on concrete physical situations. For example, periodic conversions $\Psi_S \rightarrow \Psi_{T,S_z=0}$, envisaged by Eqs. (13)–(17), are prohibited in homogeneous ferromagnetic superconductors (Sec. 4.1). By contrast, such conversions are experimentally observed in some situations encountered in spin chemistry (Sec. 4.2).

If we now take the representation of (2) and the evolution operator (6), the result for the corresponding time-dependent state will be straightforward:

$$\begin{aligned}\Psi^*(1,2;\,t) &\equiv U^*_{1,2}(t)\Psi_S(1,2) = K_0U_{1,2}(t)\Psi_S(1,2)\\ &= \begin{cases} a(t)\Psi_S(1,2) + b^*(t)\Psi_{T,S_z=0}(1,2), & a(t) > 0,\\ |a(t)|\Psi_S(2,1) + b^*(t)\Psi_{T,S_z=0}(2,1), & a(t) < 0.\end{cases}\end{aligned} \tag{20}$$

Given that the function $\Psi^*(1,2;\,t)$ is the complex conjugate of the function $\Psi(1,2;\,t)$ and differs from the latter only by complex conjugation of the probability amplitude $b(t)\left[b^*(t) = -i\sin\left(\frac{2Jt}{\hbar}\right)\right]$, both $\Psi(1,2;\,t)$ and $\Psi^*(1,2;\,t)$ describe the same physical situation, as could be expected.

4. APPLICATIONS

The quantum-mechanical results of the two previous sections have immediate applications in related sciences, namely the theory of superconductivity and spin chemistry. We begin with the theory of superconductivity.

4.1. Coexistence of superconductivity and ferromagnetism

As was first observed by Anderson a long time ago[10] (see also Ref. 11), in the BCS theory of superconductivity,[12] superconducting correlations (or Cooper pairs) are formed by electron states that are mutually reversed in time, e.g., $|\mathbf{p}\uparrow\rangle$ and $|-\mathbf{p}\downarrow\rangle$ if the electron momentum $\mathbf{p}$ is a good quantum number. Unfortunately, it seems that implications of this observation for ferromagnetic superconductors have not been understood in the literature. As an explanation, we consider the linearized equation for the superconducting order parameter $\Delta = \Delta(\mathbf{r})$, valid near the transition curve between the superconducting and normal phases $T_c = T_c(J)$ (provided the transition is of second order:

$$\begin{aligned}\Delta(r) &= \int d\mathbf{r}'^3\mathcal{K}(\mathbf{r},\mathbf{r}')\Delta(\mathbf{r}'),\\ \mathcal{K}(\mathbf{r},\mathbf{r}') &= \int\frac{d\mathbf{p}^3}{(2\pi\hbar)^3}\exp\left[\frac{i\mathbf{p}}{\hbar}(\mathbf{r}\text{-}\mathbf{r}')\right]\mathcal{K}(p).\end{aligned} \tag{21}$$

As regards some details, see for example, the old reviews Refs. 13 and 14 and references therein.

A Fourier transform of Eq. (21) to the momentum space was employed in the literature[13,14] to evaluate peculiar behavior of the second-order transition curve that had a branching point designating the origin of a first-order phase transition, but we will not discuss this issue here. Neither will we ponder on the problem of existence or non-existence of the so-called FFLO phase (see the original papers Refs. 15 and 16 and the review Ref. 17): this problem is also beyond the scope of our paper. Instead, we will focus on those mathematical properties of the integral kernel $\mathcal{K}(\mathbf{r},\mathbf{r}')$ that are intimately connected with our quantum-mechanical results and not reflected in the existing literature.

The quantity $\mathcal{K}(p)$ is given in Ref. 13 in the quasi-classical approximation (when $\max\left\{\frac{T_c}{E_F},\frac{J}{E_F}\right\} \ll 1$, with E_F being the Fermi energy) for the two extreme cases, namely: the "clean" limit (no impurities) and the "dirty" limit (a chaotic distribution of non-magnetic impurities).

However, to elucidate the effect of the exchange field, we have to resort to the coordinate representation of the integral kernel that describes the propagation of superconducting correlations between the points $\mathbf{r}'$ and $\mathbf{r}$. Thus, in the "clean" limit we have:

$$\begin{aligned}\mathcal{K}(p) = \frac{2\pi N(0)|g|T_c}{pv_F}\sum_{\omega_n>0}\Bigg[&\arctan\left(\frac{pv_F-2J}{2\omega_n}\right)\\ &+\arctan\left(\frac{pv_F+2J}{2\omega_n}\right)\Bigg],\end{aligned} \tag{22}$$

$$\mathcal{K}(\mathbf{r},\,\mathbf{r}') = \frac{N(0)|g|T_c}{\hbar v_F|\mathbf{r}\text{-}\mathbf{r}'|^2}\sum_{\omega_n>0}\left[1-2\sin^2\left(\frac{|\mathbf{r}\text{-}\mathbf{r}'|J}{\hbar v_F}\right)\right] \times \exp\left(-\frac{2\omega_n|\mathbf{r}\text{-}\mathbf{r}'|}{\hbar v_F}\right), \tag{23}$$

where $N(0)=\frac{mp_F}{2\pi^2\hbar^3}$ is the density of states at the Fermi level in the normal phase, v_F is the Fermi velocity, $|g|$ is the value of the constant of effective electron-electron interaction, and $\omega_n=(2n+1)\pi T_c(n=0,\ \pm 1,\ \pm 2,\ \ldots)$. As can be easily seen, the preexponential factor in the square brackets in Eq. (23) is nothing but an image (in a rigorous mathematical sense) of the probability amplitude $a(t)$ [Eq. (18)]. Indeed, physically, the quasi-classical approximation implies that each electron of the Cooper pair is represented by a wave packet[2,4] formed by the states with the momenta

$$p \in \left(p_F - \max\left\{\frac{T_c}{v_F},\,\frac{J}{v_F}\right\},\,p_F + \max\left\{\frac{T_c}{v_F},\,\frac{J}{v_F}\right\}\right).$$

The centres of these packets move at the velocity υ_F along the classical trajectories linking the points $\mathbf{r}'$ and $\mathbf{r}$.[18–20] (As a matter of fact, there are four trajectories of equal contribution: two direct in time trajectories for opposite orientation of electron spin plus the two time-reversed trajectories. The probability of each trajectory is equal to the probability of a definite spin orientation: see Appendix B for mathematical details.) As the dynamics of the spins is purely quantum-mechanical, the ratio $\frac{|\mathbf{r}-\mathbf{r}'|}{\upsilon_F}$ in the preexponential factor of Eq. (23) should be identified with time t in Eq. (16): see Eq. (B.4).

In the opposite, "dirty" limit the kernel has the following coordinate representation:

$$\mathcal{K}(p) = 2N(0)|g|T_c\sum_{\omega_n>0}\frac{2\omega_n+\dfrac{D}{\hbar}p^2}{\left(2\omega_n+\dfrac{D}{\hbar}p^2\right)^2+4J^2}, \tag{24}$$

$$\mathcal{K}(\mathbf{r},\mathbf{r}') = \frac{N(0)|g|T_c}{\hbar|\mathbf{r}-\mathbf{r}'|D} \times \sum_{\omega_n>0}\left\{1-2\sin^2\left[\frac{|\mathbf{r}-\mathbf{r}'|}{2\sqrt{\hbar D}}\sqrt{\sqrt{\omega_n^2+J^2}-\omega_n}\right]\right\} \times \exp\left[-\frac{|\mathbf{r}-\mathbf{r}'|}{\sqrt{\hbar D}}\sqrt{\sqrt{\omega_n^2+J^2}+\omega_n}\right]. \tag{25}$$

Here, $D=\frac{v_F l}{3}$ is the diffusion coefficient. As in the "clean" limit, the preexponential factor (in the figure brackets) reflects spin-flip processes. The complexity of the argument of the spin-flip probability ($\sin^2[\ldots]$) in Eq. (25) is due to the fact that in the "dirty" limit the relevant classical trajectories of electron motion are those of a random walk process:[19,20] see Eq. (B.5).

The above Eqs. (23) and (25) do not exhibit any trace of the $\Psi_S \rightarrow \Psi_{T,S_z=0}$ conversions described in the previous section, because the BCS Hamiltonian precludes the formation of superconducting correlations between two electrons in a triplet state.[12,11] By contrast, the accompanying effects of the vanishing of the probability amplitude $a(t)$ and spin permutations within the singlet pair do take place. These effects can be interpreted as a manifestation of a new mechanism of the destruction of superconducting correlations, completely overlooked in the literature. Finally, we want to say a few words about an application of our results to spin chemistry.

4.2. Spin chemistry

Spin chemistry[21–23] is a new and rapidly developing interdisciplinary science relating chemistry, physics and biology. It is concerned with the effect of external magnetic fields (including static ones) on chemical reactions. A significant group of chemical reactions, sensitive to external static magnetic fields, involve as intermediates so-called radical pairs in the singlet state. Singlet radical pairs themselves emerge, in particular, when certain organic molecules experience photochemical reactions that are accompanied by electron transfer from one molecular complex to the other.[22,23] Although singlet radical pairs are usually short-living and tend to recombine, it has been noticed that external static magnetic fields can induce a conversion of the singlet state of radical pairs to the triplet one. Our exact solution represented by Eqs. (13)–(17) sheds new light on the nature of this latter effect.

Indeed, it is universally believed in spin chemistry[22] that the $\Psi_S \rightarrow \Psi_{T,S_z=0}$ conversion in not too small static magnetic fields should be ascribed to presumed inequality of spin Landé factors of the members of a radical pair (i.e., $\Delta g_s \equiv g_{s1} - g_{s2} \neq 0$). However, Eqs. (13)–(17) suggest that $\Psi_S \rightarrow \Psi_{T,S_z=0}$ conversions may occur under the condition of equal g_s-factors for both the members of the radical pair (i.e., no assumption of the inequality $\Delta g_s \neq 0$ is required).

Certainly, the value of the g_s-factor was calculated by methods of quantum electrodynamics for free electrons only.[24,25] The unpaired electrons of free radicals are by no means free: different small interactions within each radical may cause the g_s-factors to deviate. Nevertheless, our results must necessarily be taken into account in any considerations of the effect of singlet-triplet conversions.

5. DISCUSSION AND CONCLUSIONS

Summarizing, within the framework of a theoretical model described in the Introduction, we have studied time evolution of the spin part of the singlet wave function of two electrons in the presence of external static homogeneous magnetic and exchange fields. In order to obtain the exact solution to this quantum-mechanical problem, we have had to revise in Sec. 2 the traditional approach[2] to the spin singlet, because it does not take adequately into account the property of invariance under rotations of the coordinate system. Basing our own approach in Sec. 2 solely on this invariance property and using the theory of spinor invariants,[7,8] we have derived the generalized representation of the spin singlet [Eq. (2)] whose fundamental feature is that the spins are in mutually time-reversed states.

We think that exactly the misunderstanding of the above-mentioned fundamental feature of the spin singlet is the main reason why the problem of time evolution has not been solved in the available literature. In this regard, it would be in order to point out that, although the alternative form of the generalized representation is well-known (at least, in the theory of superconductivity[26]), any detailed analysis of the representation, analogous to ours in Appendix A, has not been undertaken. In particular, the correct form of the interaction Hamiltonian [our Eqs. (10) and (11)], which is crucial to the solution of the problem of time evolution, has not been established.

Our exact solution to the problem of time evolution [Eqs. (13)–(17)], derived by different mathematical methods in Sec. 3 and Appendix A, implies the existence of two non-trivial quantum-mechanical effects, namely: periodic singlet-triplet conversions and periodic permutations of the spins within the singlet. These effects are described in more detail in Sec. 3 itself and Sec. 4 concerned with some applications to the theory of ferromagnetic superconductors and spin chemistry.

By the way, the theory of ferromagnetic superconductors provides a very good illustration of the validity of the exact solution (13)–(17) and its consequences: the quasi-classical expressions (23) and (25), derived by quantum-mechanical methods in Appendix B, have as Fourier transforms the well-known[13] expressions (22) and (24), respectively. However, applications to the theory of ferro-magnetic superconductors by no means reduce to mere restatement of already known results: one of the implications of the exact solution (13)–(17) is a new mechanism of the destruction of superconducting correlations by the exchange field, not reported in previous publications.

As regards applications to spin chemistry,[21–23] our exact solution (13)–(17) yields a natural explanation of the experimentally observed effect of singlet-triplet conversion in radical pairs in the presence of external static magnetic fields. This explanation does not require any assumptions of inequality between the relevant spin Landé factors, which should be contrasted with typical publications on this subject:[22] see Sec. 4 for more detail. To draw the line, we think that our results may stimulate further theoretical studies of the problem of time evolution of the singlet state of two electrons on the basis of more realistic models than the one employed in our paper.

ACKNOWLEDGMENTS

The authors are grateful to A. S. Kovalev for invaluable help in discussing the content of this article. The authors thank A. I. Korobov for a fruitful discussion of relevant problems of spin chemistry.

APPENDIX A: Spin singlet as the normalized metric spinor

We begin by reminding the well-known[4] property of the metric spinor:

$$g_{ij} = g^{ij}. \tag{A.1}$$

This property means that the matrix g can be regarded both as a covariant and a contravariant spinor of rank two, which is verified directly. Moreover, the metric spinor satisfies a set of elementary relations:

$$g^{+}=g^{-1} = \tilde{g} = -g, \tag{A.2}$$

where the tilde ($\tilde{\ }$) denotes a transposition.

If we now write down explicit expressions for the direct products of the spinors on the right-hand side of (2) we immediately get:

$$\Psi_S = \frac{1}{\sqrt{2}}g,\ \ \Psi_S(i;\,j) = \frac{1}{\sqrt{2}}g^{ij} = \frac{1}{\sqrt{2}}g_{ij}. \tag{A.3}$$

(This result is just a manifestation of the fact that any antisymmetric spinor of rank two is equal to the metric spinor multiplied by a scalar.[4])

It is instructive to check the main properties of the spin singlet for expression (A.3) independently. The fulfillment of the normalization condition is evident:

$$\mathrm{Sp}(\Psi_S^{+}\Psi_S) = -\frac{1}{2}\mathrm{Sp}(g^2) = 1. \tag{A.4}$$

As is well known from the classical mechanics,[27] any rotation of the Cartesian coordinate system about the origin can be parameterized by the Euler angles and is represented by a product of three consecutive rotations about certain axes. Therefore, to verify the invariance of (A.3) under rotations, it is sufficient to consider rotations by an angle ϕ about an arbitrary axis specified by a unit vector $|\mathbf{m}|(|\mathbf{m}| = 1)$. The transformation of spinor components under such rotations are realized by the unitary transformation matrix[4]

$$D(\mathbf{m};\,\phi) = \exp\left(\frac{i}{2}\mathbf{m}\boldsymbol{\sigma}\right). \tag{A.5}$$

To avoid misunderstandings, we note that the matrix D is not a spinor; therefore, the position of the matrix indices (upper, lower or mixed) is nonessential for this matrix. Thus, we write:

$$\begin{aligned}\Psi_S(i';\,j') &= D^{i'}_{k}D^{j'}_{l}\Psi_S(k;\,l) \equiv \frac{1}{\sqrt{2}}D^{i'}_{k}\,D^{j'}_{l}\,g^{kl}\\ &= \frac{1}{\sqrt{2}}D^{i'}_{k}g^{kl}\tilde{D}^{j'}_{l} = \frac{1}{\sqrt{2}}D^{i'}_{k}[D^{-1}]^{k}_{\ l}g^{l\,j'}\\ &= \frac{1}{\sqrt{2}}g^{i'\,j'} = \Psi_S(i;\,j).\end{aligned} \tag{A.6}$$

In the above transformations we have used convention concerning the repeated indices and employed commutation relations between the Pauli matrices.

A proof of the fact that the spins of a singlet pair are in mutually time-reversed states is slightly more involved. Consider a somewhat idealized situation when these spins are separated far apart in the coordinate space, so that only one of the spins (say, the spin whose state is specified by the row index of the matrix g) is under the influence of the perturbation, whereas the second one (whose state is specified by the column index) is not. In this situation, the state of the pair is described by the time-dependent function

$$\begin{aligned}\Psi_{\text{row}} &= \frac{1}{\sqrt{2}}[U(t)]^{i}_{k}g^{kj}\\ &= \frac{1}{\sqrt{2}}g^{ik}[\tilde{U}(-t)]^{j}_{k} = \frac{1}{\sqrt{2}}[U_{\text{rev}}(t)]^{j}_{k}g^{ik}\\ &= -\frac{1}{\sqrt{2}}[U_{\text{rev}}(t)]^{j}_{k}g^{ki}, \end{aligned}\tag{A.7}$$

where the evolution operators $U(t)$ and $U_{\text{rev}}(t)$ are given by Eq. (4) and Eq. (5), respectively. In the last line of (A.7) the antisymmetric property of the spin singlet has been used.

Similarly, in the opposite situation, when the role of the spins is interchanged, we have:

$$\begin{aligned}\Psi_{\text{column}} &= \frac{1}{\sqrt{2}}[U(t)]^{j}_{k}g^{ik}\\ &= \frac{1}{\sqrt{2}}[\tilde{U}(-t)]^{i}_{k}g^{kj} = \frac{1}{\sqrt{2}}[U_{\text{rev}}(t)]^{i}_{k}g^{kj}\\ &= -\frac{1}{\sqrt{2}}[U_{\text{rev}}(t)]^{i}_{k}g^{jk}. \end{aligned}\tag{A.8}$$

A comparison between the first and the last lines of relations (A.7) and (A.8) proves our time-reversal-symmetry statement.

The above considerations allow us to conclude that in the situation, when both the spins are under the influence of the perturbation, their state is represented by either the time-dependent function

$$\begin{aligned}\Psi(t) &= \frac{1}{\sqrt{2}}[U(t)]^{i}_{k}[U_{\text{rev}}(t)]^{j}_{l}g^{kl} = \frac{1}{\sqrt{2}}[U(t)]^{i}_{k}g^{kl}[\tilde{U}_{\text{rev}}(t)]^{j}_{l}\\ &\equiv \frac{1}{\sqrt{2}}U(t)g\tilde{U}_{\text{rev}}(t), \end{aligned}\tag{A.9}$$

or by its complex conjugate

$$\begin{aligned}\Psi^{*}(t) &= \frac{1}{\sqrt{2}}[U_{\text{rev}}(t)]^{i}_{k}[U(t)]^{j}_{l}g^{kl}\\ &= \frac{1}{\sqrt{2}}[U_{\text{rev}}(t)]^{i}_{k}g^{kl}[\tilde{U}(t)]^{j}_{l}\\ &\equiv \frac{1}{\sqrt{2}}U_{\text{rev}}(t)g\tilde{U}(t). \end{aligned}\tag{A.10}$$

Explicitly, these two relations, of course, reproduce relations (13) and (20) of the main text with Ψ_S and $\Psi_{T,S_z=0}$ in the matrix form:

$$\Psi_S \equiv \frac{1}{\sqrt{2}}g, \quad \Psi_{T,S_z=0} \equiv \frac{1}{\sqrt{2}}\sigma_z. \tag{A.11}$$

The symbolic forms of the last lines of relations (A.9) and (A.10) are convenient for the determination of the probability amplitude $a(t)$:

$$\begin{aligned}a(t) &= \text{Sp}[\Psi_S^{+}\Psi(t)] = -\frac{1}{2}\text{Sp}[gU(t)g\tilde{U}_{\text{rev}}(t)]\\ &= -\frac{1}{2}\text{Sp}[gU(t)gK^{+}\tilde{U}(-t)K] = \frac{1}{2}\text{Sp}[U(t)K^{+}U(t)K]\\ &= \frac{1}{2}\text{Sp}[K^{+}(t)K(0)] = \frac{1}{2}\text{Sp}[K(-t)K^{+}(0)]\\ &= \frac{1}{2}\text{Sp}\left[\exp\left(-i\frac{2\sigma_z J}{\hbar}t\right)\right] = \cos\left(\frac{2J}{\hbar}t\right), \end{aligned}\tag{A.12}$$

$$\begin{aligned}a(t) &= \text{Sp}[\Psi_S^{+}\Psi^{*}(t)] = -\frac{1}{2}\text{Sp}[gU_{\text{rev}}(t)g\tilde{U}(t)]\\ &= -\frac{1}{2}\text{Sp}[gKU(-t)gK^{+}\tilde{U}(t)] = \frac{1}{2}\text{Sp}[KU(-t)K^{+}U(-t)]\\ &= \frac{1}{2}\text{Sp}[K(0)K^{+}(-t)] = \frac{1}{2}\text{Sp}[K(t)K^{+}(0)]\\ &= \frac{1}{2}\text{Sp}\left[\exp\left(i\frac{2\sigma_z J}{\hbar}t\right)\right] = \cos\left(\frac{2J}{\hbar}t\right). \end{aligned}\tag{A.13}$$

APPENDIX B: The superconducting integral kernel as a time laplace transform of a classical correlation function

The kernel of the integral Eq. (21) in the quasi-classical approximation can be represented in the following form:

$$\mathcal{K}(\mathbf{r},\mathbf{r}') = \frac{2\pi N(0)|g|T_c}{\hbar}\sum_{\omega_n>0}\int_{0}^{+\infty}dt\,\exp\left(-\frac{2\omega_n}{\hbar}t\right)f(\mathbf{r},\mathbf{r}';t). \tag{B.1}$$

Here, $f(\mathbf{r},\mathbf{r}';t)$ is a sum of four classical correlation functions times relevant probability factors and appropriate sign:

$$\begin{aligned}f(\mathbf{r},\mathbf{r}';t) &= \langle\delta(\mathbf{r}(t)-\mathbf{r}')\delta(\mathbf{r}(0)-\mathbf{r})\rangle_{p_1=p_F;s_{1z}=\frac{\hbar}{2}\text{sign}\,a(t)}\frac{|a(t)|}{2}\text{sign }a(t)\\ &+\langle\delta(\mathbf{r}(-t)-\mathbf{r}')\delta(\mathbf{r}(0)-\mathbf{r})\rangle_{p_2=p_F;s_{2z}=-\frac{\hbar}{2}\text{sign}\,a(t)}\frac{|a(-t)|}{2}\text{sign }a(-t)\\ &+\langle\delta(\mathbf{r}(t)-\mathbf{r}')\delta(\mathbf{r}(0)-\mathbf{r})\rangle_{p_1=p_F;s_{1z}=-\frac{\hbar}{2}\text{sign}\,a(t)}\frac{|a(t)|}{2}\text{sign }a(t)\\ &+\langle\delta(\mathbf{r}(-t)-\mathbf{r}')\delta(\mathbf{r}(0)-\mathbf{r})\rangle_{p_2=p_F;s_{2z}=\frac{\hbar}{2}\text{sign}\,a(t)}\frac{|a(-t)|}{2}\text{sign }a(-t). \end{aligned}\tag{B.2}$$

The four terms on the right-hand side of Eq. (B.2) represent kinematics of the two electrons of a Cooper pair. Thus, for the time interval $0 \le t < \frac{\pi\hbar}{4J}$, the first and the third terms correspond to classical motion of electron 1 from the point $\mathbf{r}$ to the point $\mathbf{r}'$, with $\frac{|a(t)|}{2}$ being the probability of a definite spin orientation: see the definition of $a(t)$ in Eqs. (16) and (18), and the text below Eq. (19). At $t = \frac{\pi\hbar}{4J}$, the right-hand of Eq. (B.2) goes to zero because of a permutation of spin 1 and spin 2: see the main text. This effect should be interpreted as the destruction of superconducting correlations (or Cooper pairs) by the exchange field; hence the reduction of the transition temperature analyzed, for example, in Refs. 13 and 14.

As a result of the spin permutation, the function $f(\mathbf{r},\mathbf{r}';t)$ acquires minus sign in the time interval $\frac{\pi\hbar}{4J} < t < \frac{3\pi\hbar}{4J}$. This process is periodic with the period $T = \frac{\pi\hbar}{J}$.

Given time-reversal symmetry of classical mechanics[9] and the equality $a(-t) = a(t)$, it is clear that all the four terms on the right-hand side of Eq. (B.2) yield equal contributions. Therefore, Eq. (B.2) can be rewritten in a more economical form:

$$f(\mathbf{r},\mathbf{r}';t) = 2\langle\delta(\mathbf{r}(t)-\mathbf{r}')\delta(\mathbf{r}(0)-\mathbf{r})\rangle_{p=p_F}\langle K(t)K^+(0)\rangle, \tag{B.3}$$

where

$$\langle K(t)K^+(0)\rangle \equiv \frac{1}{2}\mathrm{Sp}[K^+(t)K(0)] = a(t).$$

[By rewriting the probability amplitude in the form of a correlator $\langle KK^+\rangle$ we just want to remind that correlators of this kind were first introduced in de Gennes' formulation of the theory of superconductivity[19] to describe the effect of non-time-reversal perturbations of different types. In our case, this correlator is responsible for the preexponential factors in Eqs. (23) and (25)].

The classical correlator $\langle\delta\delta\rangle$ is well-known[19,20] for the two limiting cases discussed in our paper. Thus, in the "clean" limit, it reads:

$$\langle\delta(\mathbf{r}(t)\text{-}\mathbf{r}')\delta(\mathbf{r}(0)-\mathbf{r})\rangle_{p=p_F} = \frac{1}{4\pi}|\mathbf{r}-\mathbf{r}'|^{-2}\delta(|\mathbf{r}-\mathbf{r}'|-v_F t). \tag{B.4}$$

In the "dirty" limit,

$$\langle\delta(\mathbf{r}(t)-\mathbf{r}')\delta(\mathbf{r}(0)-\mathbf{r})\rangle_{p=p_F} = (4\pi Dt)^{-\frac{3}{2}}\exp\left[\frac{|\mathbf{r}-\mathbf{r}'|^2}{4Dt}\right]. \tag{B.5}$$

Upon the substitution of relations (B.4) and (B.5) into (B.3) and carrying out integration over time in (B.4), we arrive at relations (23) and (25) of the main text.

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