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Formation of Cooper Pairs as a Consequence of Exchange Interaction

Abstract: The singlet state of two conduction electrons and the full overlap of their wave functions in the real space may minimize the energy of the electrons. This can be shown analyzing the energy of each conduction electron in the field of every particle of a crystal by use of exchange terms. It is possible that the exchange energy of two conduction electrons in the crystal is negative and, thus, the singlet state is favorable. Thus the Pauli Exclusion Principle and the exchange interaction cause a bond between two conduction electrons. The superconductivity in a metallic crystal occurs only if conduction electrons before the pairing are put closely on the Fermi surface in the momentum space. The motion of conduction electrons in the crystal may prevent the formation of Cooper pairs, because the kinetic energy of the motion is usually much larger than the binding energy in the pair. The conduction electrons as standing waves have a zero momentum, hence their momenta are synchronous; therefore the formation of Cooper pairs is more probable than in case of nonzero momenta. The approach of standing waves explains the inverse isotope effect, behavior at high pressures and many other facts about superconductors.

Keywords: Cooper pair; exchange interaction; Pauli Exclusion Principle; antiparallel spins; singlet state; superconductivity; standing wave; superconducting energy gap

1. Introduction and motivation.

The knowledge of a root cause of the superconductivity would help to explain many mysterious facts about all kinds of superconductors. It seems reasonable that the superconductivity should have one key cause, but the unified explanation remains still an open question, the current theories are not universal and explain many effects ambiguously [1]. The mainstream theories assume that the superconductivity is a result of the electron pairing at a mean field approximation, the spin ordering plays a part for the pair formation [2], [3], [4]. Every spin ordering is related with the exchange interaction, which influences the total energy of the electrons interacting with every particle of the crystal. Moreover the exchange interaction may in itself cause binding states in quantum systems at a many-body approach [5], [6]. Therefore the many-body approach seems to be more appropriate to define the electron states and the role of the exchange interaction seems to be crucially important for the pair formation. In the work is shown that the Pauli Exclusion Principle and its associated exchange interaction may in principle lead to a binding singlet state of two conduction electrons, which under certain conditions become superconducting.

2. Formation of Cooper pairs as a consequence of exchange interaction.

Normally the spins of conduction electrons in a crystal are unordered because the thermal fluctuations and own motion of electrons destroy the spin ordering. Thus the spin orientation of every conduction electron e_1 is random to spins of all other electrons. This state of e_1 is **unpaired** or **single**. If the spin of e_1 is antiparallel to the spin of electron e_2 in their overlap area in the real space, then the state of e_1 is **paired** or **singlet**.

We assume that every unpaired conduction electron has its **accurate** spatial wave function, which describes the position of the electron in the crystal. Using the accurate wave functions of the unpaired electrons e_1, e_2 we can compare the energy of singlet states with the energy of unpaired states. If two electrons e_1, e_2 are paired with antiparallel spins then their overall position-space wave function is symmetric and their overall energy is related to the sum of direct and exchange terms *D+J*, where *D* and *J* are applied to the overall energy of e_1, e_2. The exchange term takes into account the modification of the initially unpaired wave functions resulting from the pairing. Since the wave function modification influences the total energy of e_1, e_2, we must use the overall position-space wave function to find the total energy of the singlet electrons (including the kinetic energy, repulsion of e_1, e_2 from **every** conduction electron and attraction of e_1, e_2 to **every** ion). The singlet of e_1, e_2 is favorable if $J<0$ [7]. If two electrons have parallel spins, then their overall position-space wave function is antisymmetric and the exchange term changes the sign [8] (it is a property of the antisymmetric position-space wave function), hence the overall energy of e_1, e_2 is *D-J*. The parallel spin state of

e_1, e_2 is favorable if *J>0*. If the exchange interaction is weak and the exchange term is negligible, then the spins of electrons remain unpaired and fully random, in this case the energy of the unpaired electrons contains only the direct term (as it should be for the accurate wave functions of the unpaired electrons).

The exchange term *J* is related to the energy increment resulting from the pairing. If the accurate wave functions of the unpaired electrons e_1, e_2 in the crystal are known, then we can compute for each electron its energy in the unpaired state and in the paired state; hence we can compute the sign of the energy increment resulting from the pairing. The energy of the unpaired e_1 is the sum of direct terms applied to its potential and kinetic energy. The energy of the paired e_1 is the sum of direct and exchange terms, where the exchange terms take into account the modification of the initially unpaired wave functions resulting from the pairing. Since the wave function modification influences the total energy of e_1, we must apply the exchange terms for the total energy of the electron e_1 (including the kinetic energy of e_1, repulsion of e_1 from every conduction electron and attraction of e_1 to every ion).

The symmetric overall position-space wave function of e_1, e_2 is $\Phi(\vec{r}_1,\vec{r}_2) = \Psi_1(\vec{r}_1)\Psi_2(\vec{r}_2)/\sqrt{2} + \Psi_1(\vec{r}_2)\Psi_2(\vec{r}_1)/\sqrt{2}$, where $\Psi_1(\vec{r}_1)$, $\Psi_2(\vec{r}_2)$ are accurate wave functions of unpaired e_1, e_2; $\vec{r}_1, \vec{r}_2$ are radius-vectors of e_1, e_2.

The sum of the direct and exchange terms of an energy operator $\hat{O}(\vec{r}_1,\vec{r}_2)$ we find as

$$D(\hat{O}) + J(\hat{O}) = \left\langle \Phi(\vec{r}_1,\vec{r}_2) \middle| \hat{O} \middle| \Phi(\vec{r}_1,\vec{r}_2) \right\rangle \qquad (2.0)$$

We assume that $\Psi_1(\vec{r}_1)$, $\Psi_2(\vec{r}_2)$ have an overlap in the real space and contain similar atom orbitals (for sample s-waves); momenta of e_1, e_2 along the crystal are equal or zero. In this case $\Psi_1(\vec{r}\,)$, $\Psi_2(\vec{r}\,)$ are **not orthogonal** as orbitals of the ground state in H_2-molecule or in Helium atom; hence the overlap integral $\left\langle \Psi_1(\vec{r}) \middle| \Psi_2(\vec{r}) \right\rangle$ appearing in Eq. (2.0) is not zero [9].

The potential energy of repulsion of two initially **unpaired** electrons $\left\langle P\,(e_1,e_2)\right\rangle$ contains only the direct term:

$$\left\langle P\,(e_1,e_2)\right\rangle = \iint\limits_{\pm\infty} e^2 \,\frac{\left|\Psi_1(\vec{r}_1)\right|^2 \cdot \left|\Psi_2(\vec{r}_2)\right|^2 \cdot d^3r_1 \cdot d^3r_2}{\left|\vec{r}_1 - \vec{r}_2\right|} \qquad (2.1)$$

From Eq. (2.0) we find the potential energy of repulsion between two **paired** electrons with a symmetric overall position-space wave function and with antiparallel spins $\left\langle P_s(e_1,e_2)\right\rangle$ as a sum of the direct integral (2.1) and of an exchange integral, which takes into account that the average distance between two paired electrons decreases [10], [11]:

$$\left\langle P_s(e_1,e_2)\right\rangle = \iint\limits_{\pm\infty} e^2 \,\frac{\left|\Psi_1(\vec{r}_1)\right|^2 \cdot \left|\Psi_2(\vec{r}_2)\right|^2 \cdot d^3r_1 \cdot d^3r_2}{\left|\vec{r}_1 - \vec{r}_2\right|} + \iint\limits_{\pm\infty} e^2 \,\frac{\Psi_2^*(\vec{r}_1)\cdot\Psi_1(\vec{r}_1)\cdot\Psi_1^*(\vec{r}_2)\cdot\Psi_2(\vec{r}_2)\cdot d^3r_1 \cdot d^3r_2}{\left|\vec{r}_1 - \vec{r}_2\right|} \qquad (2.2)$$

In conducting crystals the wave functions of electrons of the upper shell fade out slowly with the distance and can cover many points of lattice, thus the wave functions of many electrons may overlap in a shared area in the real space, so we consider at first the limiting case that the densities $\left|\Psi_1(\vec{r}\,)\right|^2$ and $\left|\Psi_2(\vec{r}\,)\right|^2$ almost coincide in real space, i.e. $\left|\Psi_1(\vec{r}\,)\right|^2 \approx \left|\Psi_2(\vec{r}\,)\right|^2$, hence:

$$\Psi_1(\vec{r}\,) \approx \pm\Psi_2(\vec{r}\,) \quad or \quad \Psi_1(\vec{r}\,) \approx \pm i \cdot \Psi_2(\vec{r}\,) \qquad (2.3)$$

Below we show that the assumption $\left|\Psi_1(\vec{r}\,)\right|^2 \approx \left|\Psi_2(\vec{r}\,)\right|^2$ is true because a maximal overlap in the real space of two paired wave functions is energetically favorable in comparison to the unpaired state or to a partial overlap.

Substituting Eq. (2.3) into (2.2) and comparing the result with Eq. (2.1) we find:

$$\left\langle P_s(e_1,e_2)\right\rangle = 2 \cdot \left\langle P\,(e_1,e_2)\right\rangle \qquad (2.4)$$

Thus the repulsion of two paired electrons is twice as much as the repulsion of two unpaired electrons.

If all other kinds of the collective spin ordering are weak, then the spin of e_1 is antiparallel only with e_2 and is unordered with spins of other conduction electrons. In other words e_1 cannot have the antiparallel spin with all other conduction electrons at the same time. Consequently the total repulsion of the **paired** e_1 from all conduction electrons is not larger than the double value of the total repulsion of the **unpaired** e_1 from all conduction electrons, i.e.: $\sum_{k=2}^{n} \left\langle P_s(e_1,e_k)\right\rangle \le 2\cdot\sum_{k=2}^{n} \left\langle P\,(e_1,e_k)\right\rangle$, where n is the number of all conduction electrons in the crystal.

We designate: $\sum_{k=2}^{n} \left\langle P_s(e_1,e_k)\right\rangle$ as $\left\langle P_s(e_1,e)\right\rangle$; $\sum_{k=2}^{n} \left\langle P\,(e_1,e_k)\right\rangle$ as $\left\langle P\,(e_1,e)\right\rangle$. Thus one can write:

$$\left\langle P_s(e_1,e\;)\right\rangle = a\cdot\left\langle P\,(e_1,e\;)\right\rangle \qquad 1<a\le 2 \qquad (2.5)$$

The attraction energy of the unpaired electron e_1 to one-valent ions $\left\langle P\,(e_1,I)\right\rangle$ does not contain the exchange term:

$$\left\langle P\,(e_1,I)\right\rangle = -\sum_{k=1}^{n}\int_{\pm\infty} e^2\,\frac{\left|\Psi_1(\vec r_1)\right|^2\cdot d^3r_1}{\left|\vec r_1-\vec r_k\right|} \approx \left\langle P\,(e_2,I)\right\rangle = -\sum_{k=1}^{n}\int_{\pm\infty} e^2\,\frac{\left|\Psi_2(\vec r_2)\right|^2\cdot d^3r_2}{\left|\vec r_2-\vec r_k\right|} \qquad (2.6)$$

Where: n number of ions in the crystal; $\vec r_k$ radius-vectors of the ions (ions assumed motionless).

The total attraction energy to ions of two paired electrons e_1, e_2 with a symmetric overall position-space wave function and with antiparallel spins is a sum of the direct integral and of an exchange integral, which takes into account the modification of the initially unpaired wave functions resulting from the pairing:

$$\left\langle P_s(e_1e_2,I)\right\rangle = -\sum_{k=1}^{n}\iint_{\pm\infty}\left(\frac{e^2}{\left|\vec r_1-\vec r_k\right|}+\frac{e^2}{\left|\vec r_2-\vec r_k\right|}\right)\cdot\left|\Psi_1(\vec r_1)\right|^2\cdot\left|\Psi_2(\vec r_2)\right|^2\cdot d^3r_1\cdot d^3r_2 -$$

$$-\sum_{k=1}^{n}\iint_{\pm\infty}\left(\frac{e^2}{\left|\vec r_1-\vec r_k\right|}+\frac{e^2}{\left|\vec r_2-\vec r_k\right|}\right)\cdot\Psi_2^*(\vec r_1)\cdot\Psi_1(\vec r_1)\cdot\Psi_1^*(\vec r_2)\cdot\Psi_2(\vec r_2)\cdot d^3r_1\cdot d^3r_2 \qquad (2.7)$$

Equations (2.7) and (2.2) are derived from Eq. (2.0); in Eq. (2.2) we handle the operator of the overall repulsion of e_1, e_2; in Eq. (2.7) we handle the operator of the overall attraction of e_1, e_2 to ions.

The exchange term in Eq. (2.7) has a clear physical meaning. Consider a small area around one of ions in the overlap area of e_1, e_2 in the real space**;** due to the Exclusion Principle two singlet electrons are located in this small area with a probability higher than two electrons with parallel spins, because the electrons with parallel spins avoid each other and cannot be put into a small area (i.e. the probability that $\vec r_1 \approx \vec r_2$ is little). If two electrons are unpaired, then their spins are equiprobably parallel or antiparallel, hence the electrons avoid each other, but do it weaker than the electrons with parallel spins. Thus the probability to observe in this small area two unpaired electrons is larger than this probability for two electrons with parallel spins and smaller than this probability for a singlet. Therefore the singlet is in average closer to the ion than two unpaired electrons. The exchange term in Eq. (2.7) takes it into account.

Substituting Eq. (2.3) into (2.7), using the normalization to 1 for $\left|\Psi_1(\vec r_1)\right|^2$ and $\left|\Psi_2(\vec r_2)\right|^2$ [12] and comparing the result with Eq. (2.6) we find:

$$\left\langle P_s(e_1e_2,I)\right\rangle = 2\left\langle P\,(e_1,I)\right\rangle + 2\left\langle P\,(e_2,I)\right\rangle \qquad (2.8)$$

Thus the attraction to ions of each paired electron is twice as much as the attraction of the unpaired electron:

$$\left\langle P_s(e_1,I)\right\rangle = 2\cdot\left\langle P\,(e_1,I)\right\rangle \qquad (2.9)$$

The result has sense because the average distance between two paired electrons decreases, therefore the electron density may converge to ions since the ions are located somewhere between electrons.

Consider that the overlap area of e_1, e_2 is negligible, then the exchange term in Eq. (2.7) is negligible and we obtain:

$\left\langle P_s(e_1 e_2, I)\right\rangle = \left\langle P\,(e_1, I)\right\rangle + \left\langle P\,(e_2, I)\right\rangle$, what is physically correct since the electrons are separated in real space. In this case $\left\langle P_s(e_1, I)\right\rangle = \left\langle P\,(e_1, I)\right\rangle$ and there is no advantage of the singlet state.

Using Eq. (2.5) and (2.9) we express the potential energy of the paired electron $\left\langle P_s(e_1)\right\rangle = \left\langle P_s(e_1, I)\right\rangle + \left\langle P_s(e_1, e)\right\rangle$ through the potential energy of the unpaired electron $\left\langle P(e_1)\right\rangle = \left\langle P\,(e_1, I)\right\rangle + \left\langle P\,(e_1, e)\right\rangle$:

$$\left\langle P_s(e_1)\right\rangle = \left\langle P_s(e_1, I)\right\rangle + \left\langle P_s(e_1, e)\right\rangle = 2\cdot\left\langle P\,(e_1, I)\right\rangle + a\cdot\left\langle P\,(e_1, e\;)\right\rangle \qquad 1 < a \le 2 \qquad (\,2.10\,)$$

The potential energy advantage of the pairing for one electron can be expressed from Eq. (2.10):

$$\Delta_p = \left\langle P_s(e_1)\right\rangle - \left\langle P(e_1)\right\rangle = \left\langle P\,(e_1, I)\right\rangle + (a-1)\cdot\left\langle P\,(e_1, e\;)\right\rangle \qquad 1 < a \le 2 \qquad (\,2.11\,)$$

Equation (2.11) indicates: $\Delta_p < 0$ and the singlet state is favorable if the potential energy of the initially unpaired electron $\left\langle P(e_1)\right\rangle = \left\langle P\,(e_1, I)\right\rangle + \left\langle P\,(e_1, e)\right\rangle$ is negative. Since the crystal is usually a potential well for conduction electrons, $\left\langle P(e_1)\right\rangle$ is negative and the singlet state is favorable.

The kinetic energies of the unpaired electrons e_1 and e_2 are:

$$\left\langle K(e_1)\right\rangle = \left\langle \Psi_1(\vec{r}_1)\left| -\frac{\hbar^2}{2m}\nabla_1^2 \right| \Psi_1(\vec{r}_1)\right\rangle \approx \left\langle K(e_2)\right\rangle = \left\langle \Psi_2(\vec{r}_2)\left| -\frac{\hbar^2}{2m}\nabla_2^2 \right| \Psi_2(\vec{r}_2)\right\rangle \qquad (\,2.12\,)$$

The total kinetic energy $\left\langle K_s(e_1, e_2)\right\rangle$ of two paired electrons with a symmetric overall position-space wave function contains a direct term and an exchange term, which takes into account the modification of the initially unpaired wave functions resulting from the pairing:

$$\left\langle K_s(e_1, e_2)\right\rangle = \left\langle \Psi_1(\vec{r}_1)\Psi_2(\vec{r}_2)\left| -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2)\right| \Psi_1(\vec{r}_1)\Psi_2(\vec{r}_2)\right\rangle + \left\langle \Psi_2(\vec{r}_1)\Psi_1(\vec{r}_2)\left| -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2)\right| \Psi_1(\vec{r}_1)\Psi_2(\vec{r}_2)\right\rangle \quad (2.13)$$

Equations (2.13), (2.7), (2.2) are derived from Eq. (2.0), but each equation handles its own energy operator.

Substituting Eq. (2.3) into (2.13), using the normalization to 1 for $\left|\Psi_1(\vec{r}_1)\right|^2$ and $\left|\Psi_2(\vec{r}_2)\right|^2$ and comparing the result with (2.12) we find:

$$\left\langle K_s(e_1, e_2)\right\rangle = 2\cdot\left\langle K(e_1)\right\rangle + 2\cdot\left\langle K(e_2)\right\rangle \qquad (\,2.14\,)$$

Equation (2.14) means that the kinetic energy of a paired electron is twice as much as of an unpaired electron:

$$\left\langle K_s(e_1)\right\rangle = 2\cdot\left\langle K(e_1)\right\rangle \qquad (\,2.15\,)$$

A crystal is usually a potential well for all electrons. We define that the kinetic and potential energies are zero outside of the crystal. Then $\left\langle P(e_1)\right\rangle$ is negative. The value $\left\langle K(e_1)\right\rangle$ is not larger than the absolute value $\left|\left\langle P(e_1)\right\rangle\right|$ because during a transition into the potential well the kinetic energy of e_1 turns partially into radiation. So one can write:

$$\left\langle K(e_1)\right\rangle = -b\cdot\left\langle P(e_1)\right\rangle = -b\cdot\left\langle P(e_1, I)\right\rangle - b\cdot\left\langle P(e_1, e)\right\rangle \qquad 0 < b \le 1 \qquad (2.16)$$

Using Eq. (2.10), (2.15), (2.16) we can find the total energy advantage Δ of the pairing for one electron:

$$\Delta = \left\langle K_s(e_1)\right\rangle + \left\langle P_s(e_1)\right\rangle - \left\langle K(e_1)\right\rangle - \left\langle P(e_1)\right\rangle = \left\langle P(e_1, I)\right\rangle\cdot(1-b) + \left\langle P(e_1, e)\right\rangle\cdot(a-1-b) \qquad (\,2.17\,)$$

It is easy to show that the value Δ in Eq. (2.17) is not positive. If $1<a\leq 2$ and $0<b\leq 1$ and the potential energy of the unpaired electron $\langle P(e_1)\rangle = \langle P\,(e_1,I)\rangle + \langle P\,(e_1,e)\rangle$ is negative, then $\partial\Delta/\partial a$ and $\partial\Delta/\partial b$ both are positive, consequently Δ is maximal when *a* and *b* are maximal; a_{max} = 2, b_{max} = 1, hence $\Delta_{\max}=0$. Thus $\Delta\leq 0$.

We can prove that the energy increment Δ is equal to the exchange term $J\,(e_1)$ for the electron e_1. The energy of the paired e_1 from Eq. (2.17) is: $E_s(e_1)=\langle K_s(e_1)\rangle+\langle P_s(e_1)\rangle=\Delta+\langle K(e_1)\rangle+\langle P(e_1)\rangle$. The energy of the unpaired e_1 is the sum of the direct integrals applied to the kinetic and potential energy of e_1 by use of the accurate wave function $\Psi_1(\vec{r}_1)$; thus $\langle K(e_1)\rangle+\langle P(e_1)\rangle$ is the direct term $D(e_1)$ for e_1. Hence $E_s(e_1)=\Delta+D(e_1)$. On the other hand $E_s(e_1)=J(e_1)+D(e_1)$, consequently $\Delta=J(e_1)$.

The overall exchange term J for both electrons e_1,e_2 can be found knowing the values Δ_1,Δ_2 of both electrons:

$$J=\Delta_1+\Delta_2-\langle P(e_1,e_2)\rangle\approx 2\Delta-\langle P(e_1,e_2)\rangle \qquad (2.18)$$

The term $-\langle P(e_1,e_2)\rangle$ occurs because for the second electron we must correct double counting the repulsion between e_1,e_2. As one would expect the energy increment Δ and the overall exchange term J are related. The Eq. (2.18) indicates: since $\Delta\leq 0$, the value $J<0$, the singlet (e_1,e_2) is favorable in comparison with the unpaired state.

If the overlap area of e_1,e_2 in the real space is small (i.e. integral $\langle\Psi_1(\vec{r})|\Psi_2(\vec{r})\rangle$ is small), then all exchange terms are small, Δ is small but negative. Thus the larger the overlap, the greater the energy advantage of the pairing. Consequently two paired wave functions tend to a full coincidence in the real space and remain together in equilibrium. Thus the assumption $|\Psi_1(\vec{r}\,)|^2\approx|\Psi_2(\vec{r}\,)|^2$ for Eq. (2.3) is justified. Finally two electron densities stay together because the singlet state with a full overlap in the real space increases their attraction to ions.

Substituting two equal Bloch wave functions $\Psi_{\vec{k}}(\vec{r},t)=u(\vec{r})\cdot\exp(-i\omega t-i\vec{k}\,\vec{r})$ [13] into Eq. (2.0)–(2.18) we find that all conclusions are valid for the electrons as running waves. However it is a rare event that the momenta $\vec{k}$ of running waves are equal.

All conclusions from Eq. (2.0)–(2.18) are valid if before pairing each electron is a **standing wave**, which is a sum of two equiprobable Bloch waves propagating in opposite directions:

$$\Psi_{st}(\vec{r},t)=\frac{1}{\sqrt{2}}u(\vec{r})\cdot\exp(-i\omega t-i\vec{k}\,\vec{r})+\frac{1}{\sqrt{2}}u(\vec{r})\cdot\exp(-i\omega t+i\vec{k}\,\vec{r})=\sqrt{2}\cdot u(\vec{r})e^{-i\omega t}\cos(\vec{k}\,\vec{r}) \qquad (2.19)$$

The momentum of an electron as standing wave is zero [14], hence the total momentum of the pair is also zero; thus the kinetic energy of electrons (which is usually much larger than the energy gap of superconductor) cannot split the pair.

The pairing energy Δ in Eq. (2.17) is a part of $\langle P(e_1)\rangle$; hence Δ is not arbitrarily small since the potential well $\langle P(e_1)\rangle$ is not arbitrarily small. Thus the unpaired (normal) state of e_1 is **instable**. However the paired state of e_1,e_2 is permanent in time only if external energies (temperature, radiation, magnetic field) are weaker than Δ.

The electron wave density in the crystal has usually a translational symmetry with a period equal to the lattice constant *R*. Hence $|\Psi_1(\vec{r}_1)|^2$ may be shifted in the real space away from $|\Psi_2(\vec{r}_2)|^2$ at a distance $l_n=n\cdot R$, where *n* is integer. The exchange energy of e_1,e_2 is related with their degree of overlap in real space, hence the minimal shift $l_1=R$ raises the exchange energy at a finite (not arbitrarily small) value, which can be considered as the excitation energy of the pair.

Hence the excitation energy of the pair is also not arbitrarily small. If all external influences are weaker than this excitation energy, then the paired wave functions coincide in the real space permanently, therefore the spins are permanently coupled only with each other (as in Helium atom). Thus the pair cannot form/lose any bonds in the crystal, so the pair doesn't absorb/radiate any energy; as a result the total energy and momentum of all pairs don't dissipate. Thus the pairs fluctuate without resistance despite the fact that the electrons were standing waves before pairing.

In an external magnetic field *H* the crystal obtains an additional energy density $w = 0{,}5 \cdot \mu_0 \mu H^2$; the energy of the singlet electrons splits. If the energy split $(2 \cdot \mu_B \mu_0 \mu H)$ is smaller than the excitation energy of the pair then the pair fluctuates in the field *H* as a free particle with a charge *-2e* and zero spin. Consequently there are no obstacles to redistribute the non-dissipative fluctuations of the pairs into non-dissipative currents compensating the additional magnetic energy w (Meissner effect).

If the wave functions of two conduction electrons in the crystal (for sample two s-electrons) coincide in the real space and form a singlet, then the electrons are similar to the electrons in the ground state in Helium. The difference is that in the crystal the wave functions cover many ions and the pair can move in an external potential, since all crystal areas are equipotential for the pair. In the ground state of Helium the singlet state is favorable despite the fact that the repulsion of electrons is maximal; the increase in attraction of the singlet s-electrons to the Helium nucleus exceeds the increase in repulsion and in kinetic energy. The Cooper pair is stable as a valence bond in multi-atom molecules.

If the value $|\Delta|$ in Eq. (2.17) is significantly larger than the insulating band gap of the crystal, then electrons can leave the valence band at the temperature $T \le T_c$, hence the electrons may form the pairs despite the band gap. A doping in the crystal may reduce the band gap and, thus, give rise to superconductivity. This doping effect is observable in cuprates [15], in iron-based superconductors [16], in semiconductors [17].

In Eqs (2.0)-(2.18) we investigated the crystal energy terms which contain the paired electrons. The other, remaining unpaired, electrons don't change their states and wave functions; hence all other crystal energy terms (containing only the unpaired electrons and/or ions) remain unchanged; i.e. unchanged remain the kinetic energies of single electrons, interactions between single electrons, between ions and between single electrons and ions. This is easy to show taking the many-body crystal Hamiltonian $H(\vec{r}_1 ... \vec{r}_n)$ and the total crystal wave function as a product of **normalized** accurate wave functions of every single and paired electron:

$$\langle E(crystal) \rangle = \langle \Psi_{s1}(\vec{r}_1) \cdot \Psi_{s2}(\vec{r}_2) ... \Psi_3(\vec{r}_3) ... \Psi_m(\vec{r}_m) | H(\vec{r}_1 ... \vec{r}_n) | \Psi_{s1}(\vec{r}_1) \cdot \Psi_{s2}(\vec{r}_2) ... \Psi_3(\vec{r}_3) ... \Psi_m(\vec{r}_m) \rangle \qquad (2.20)$$

Where: $\Psi_{s1}(\vec{r}_1), \Psi_{s2}(\vec{r}_2) ...$ normalized accurate wave functions of every **paired** electron; $\Psi_3(\vec{r}_3) ... \Psi_m(\vec{r}_m)$ normalized accurate wave functions of every **unpaired** electron; $\vec{r}_1 ... \vec{r}_n$ radius-vectors of all electrons and ions.

Thus if the pairing of some conduction electrons doesn't modify the overall crystal structure, then the energy lowering of the paired electrons inevitably leads to the energy lowering of the whole crystal, the crystal radiates; the macroscopic state can exist.

A necessary condition for the superconductivity in a metallic crystal is that the electrons before pairing are put closely on the Fermi surface in the momentum space. To show this we assume that the pairing occurs when the energy of the single electron has a value E^*. If the thermal energy doesn't exceed the energy $|\Delta|$ in Eq. (2.17), then the concentration of the pairs is not zero and in the energy spectrum of single electrons occurs a gap around the value E^*. If E^* is significantly less than the Fermi level ($E^* < E_F$) then there are single electrons with the energy larger than E^*. These single electrons may drop to the level E^* due to energy fluctuations and may, thus, form new pairs. The momentum of every paired electron as standing wave is zero, so the concentration of the paired electrons is limited by the Exclusion Principle; therefore the new pairs replace the already paired electrons, which lose the paired state. Thus each electron is **not permanently** paired, but it becomes periodically unpaired. During every switching of states the electron absorbs/loses energy, in the unpaired state it has an electrical resistance, therefore the momentum of the electron and of the pair dissipates. Thus the macroscopic state with $E^* < E_F$ cannot be superconducting, despite the fact that the pairing is possible. If $E^* \approx E_F$ then every pair may exist **permanently in time**, because below a certain temperature the single electrons cannot overcome the superconducting gap and cannot reach the pairing level $E^* \approx E_F$; as a result the new pairs don't arise and don't replace the existing pairs. Hence the switching of states doesn't occur and the total momentum of the pairs doesn't dissipate. Thus the superconducting pairing occurs only for single electrons in a thin energy gap with E_F **as the upper limit**. Only such permanent pairs are superconducting.

3. **Pairing of standing waves.**

We found that the binding energy in the pair e_1, e_2 is maximal if the overlap integral $\langle \Psi_1(\vec{r}) | \Psi_2(\vec{r}) \rangle$ is maximal, i.e. maximal is the degree of the spatial overlap of the wave functions of two conduction electrons. The energy gap of superconductors has order of magnitude 10^{-3} eV, the Fermi level has order of magnitude a few eV. Consequently the kinetic energy can split the pair. The energy of very slow electrons is usually much lower than the Fermi level; hence these electrons cannot form superconducting pairs. Two electrons can form a pair if their momenta are synchronous before pairing, but it is a rare event for running waves. The electrons **as standing waves** form the pair much easier than as running waves, because the momentum of each standing wave is zero, hence the momenta are synchronous. As shown in Eqs (2.0)–(2.19) the pairing of electrons as standing waves is possible due to the exchange interaction.

A standing wave occurs as a result of reflections of a running wave from the periodic potential. The condition of the standing wave in a crystal is the Bragg condition [18]:

$$n\lambda = 2 \cdot R \qquad (3.1)$$

Where: *n* integer; λ length of the Bloch wave $\Psi_{\vec{k}}(\vec{r},t) = u(\vec{r}) \cdot \exp(-i\omega t - i\vec{k}\vec{r})$; R lattice constant.

Under Bragg condition the electron becomes a set of standing waves with a zero total momentum [19].

At *n=1* in Eq. (3.1) the length of the standing wave is maximal: $\lambda_1 = 2 \cdot R$. A crystal has some values *R* (depending on the crystal axis) and, thus, some values λ_1. Each value $\lambda_1 = 2 \cdot R$ is linked to the energy $E_{\lambda=2R}$:

$$E_{\lambda=2R} = \frac{(h/\lambda_1)^2}{2 \cdot m} = \frac{h^2}{R^2 \cdot 8 \cdot m} \qquad (3.2)$$

Where *m* is the inertial mass of electron.

Not all materials have conduction electrons with the value $\lambda = 2 \cdot R$ and with its associated $E_{\lambda=2R}$. If the Fermi level of a crystal is too low, then its λ values are larger than $2 \cdot R$ and its energies are lower than $E_{\lambda=2R}$. The standing waves don't occur in this crystal. In some metals the value $E_{\lambda=2R}$ is close to E_F (it is equivalent that $\lambda_F \approx 2 \cdot R$).

If the value $\lambda = 2 \cdot R$ is in a filled conduction band and if the exchange interaction makes the pairing with antiparallel spins energetically favorable, then the formation of pairs is possible. Probably in some crystals the formation of pairs is also possible at *n* larger than 1 in Eq. (3.1). For sample at *n=2* the length of standing waves is $\lambda_2 = R$.

A **paired** electron is not identical with a **single** electron with $\lambda = 2 \cdot R$, because the kinetic energy of electrons in Eq. (2.15) increases after the pairing. Thus the paired electrons form new states, they can overlap in the real space with single electrons and may be excluded from the energy spectrum of single electrons; hence two single states with $\lambda = 2 \cdot R$ in this spectrum become vacant and may be occupied by two next single electrons, which may form a new pair. Thus the single electrons with $\lambda \approx 2 \cdot R$ form the pairs and the spectrum of single electrons obtains a gap around the value $E_{\lambda=2R}$. The gap is not negligible if the pairing is favorable (i.e. Δ in Eq. (2.17) is negative and not small) and if the thermal energy is insufficient to destroy the pairs. With other things being equal the greater the energy advantage of the pairing, the greater the energy gap $(E_2 - E_1)$ in the spectrum of single electrons (E_1, E_2 are limits of the gap).

As shown above a necessary condition for the superconductivity is that E_F is the upper limit of the gap: $E_F = E_2$.

The superconducting gap is $(E_F - E_1)$, where E_1 should be below $E_{\lambda=2R}$ (otherwise new pairs arise and replace the existing ones, energy dissipates). The concentration of the superconducting electrons N_s is limited by the energy gap:

$$N_s = \int_{E_1}^{E_F} S(E_\lambda)\, dE_\lambda \qquad (3.3)$$

Where $S(E_\lambda)$ is the density of states of single conduction electrons in the crystal.

Thus the energies and states of single electrons below the gap $(E_F - E_1)$ stay unchanged as assumed for Eq. (2.20).

The electrons (before superconducting pairing) must be close to the Fermi surface, i.e. the value $E_{\lambda=2R}$ must be close to E_F (i.e. $\lambda_F \approx 2 \cdot R$). Really, the energy gap is much less than E_F; therefore if $E_{\lambda=2R}$ is significantly less than E_F, then the upper gap limit E_2 is also less than E_F; as shown above this case is not superconducting because the pairs are not permanent in time. For this reason Au, Ag, Cu (where $E_{\lambda=2R} < E_F$ significantly [20]) are not superconductors. If $E_{\lambda=2R}$ is significantly larger than E_F, then there are no electrons with $\lambda = 2 \cdot R$ and the gap doesn't occur. For this reason in some structures with a low E_F a doping may raise the carrier concentration and its associated E_F up to the level $E_{\lambda=2R}$ (which is constant, if R and $\lambda = 2 \cdot R$ don't change). Thus the doping may lead to superconductivity, T_c increases. If the crystal is overdoped, then E_F is too large; $E_{\lambda=2R} < E_F$ and T_c vanishes. This doping effect explains the **dome form** of phase diagrams of superconductors [21], [22]. A double dome form is possible due to the fact that the crystal has two (and more) lattice constants depending on the crystal axis. Thus the large value $|E_F - E_{\lambda=2R}|$ reduces T_c. If $E_{\lambda=2R} \approx E_F$ then T_c is maximal and corresponds to Δ in Eq. (2.17). So we know about the T_c tuning:

$$C k_B T_c = 0 \qquad if \ |\Delta| < |E_F - E_{\lambda=2R}| \qquad (3.4)$$

$$C k_B T_c \le |\Delta| \qquad if \ |\Delta| > |E_F - E_{\lambda=2R}| \qquad (3.5)$$

Where C is a material specific constant; k_B is the Boltzmann constant.

In the above consideration we would have to investigate how the value Δ depends on the doping. But we know that $|\Delta| << E_F$ and the increment of E_F has order of magnitude of E_F. So one can assume that the increment of E_F is much larger than the increment of $|\Delta|$; hence T_c depends mainly on the E_F modification.

The isotope substitution is another way to tune T_c by tuning E_F to $E_{\lambda=2R}$ based on the fact that E_F depends on the effective mass of electrons [23], whereas $E_{\lambda=2R}$ in Eq. (3.2) depends only on the lattice constant. The isotope effect is a consequence that the energy of phonons is proportional to $M^{-0,5}$ (M - mass of ion) [24]. The decrease in M raises the energy of phonons; therefore the electron-ion interaction and its associated reflection of electrons may intensify. This intensification is equivalent to the increase in the effective mass m^* and, thus, to the decrease in E_F (since E_F is proportional to $1/m^*$), whereas $\lambda = 2 \cdot R$ is almost unchanged. If the initial value E_F is larger than $E_{\lambda=2R}$ (it is usual for metals), then the decrease in M pulls E_F down to $E_{\lambda=2R}$; hence T_c grows (the isotope coefficient $\alpha>0$). If the initial value E_F is less than $E_{\lambda=2R}$, then the decrease in M pulls E_F down away from $E_{\lambda=2R}$; hence T_c may vanish ($\alpha<0$). One can conclude that in case $E_F \approx E_{\lambda=2R}$ the isotope effect may be weak ($|\alpha|<0,5$). Thus the different values and sign of α [25] are a result of the different initial positions E_F to $E_{\lambda=2R}$.

Other ways to tune T_c by tuning E_F to $E_{\lambda=2R}$ are the high pressure [26], [27]; electric field [28] since E_F depends on the electron concentration; film thickness [29], [30], [31] since E_F depends on the number of atom layers [32].

A further sample of the E_F tuning is the alkali metals (Li, Na, K, Rb, Cs, Fr). Only Lithium is superconductor at ambient pressure [33] and only Lithium has $E_{\lambda=2R}$=3,09 eV (calculated by Eq. (3.2), R=3,49 Å) relatively close to $E_F \approx$3,2 eV [34] at ambient temperature. The next candidate in superconductors after Lithium is Cesium: $E_{\lambda=2R}$=1,33 eV $(R = 6{,}14 \cdot \sqrt{3}/2 = 5{,}32 \ \text{Å})$ in bcc-structure, $E_F \approx$1,54 eV [35]; Cesium is really superconductor under high pressure [36]. Probably the high pressure leads to the increase in the density of ions, so m^* rises and E_F drops to $E_{\lambda=2R}$; therefore T_c grows both in Li and in Cs. We note that E_F and $E_{\lambda=2R}$ are equally proportional to R^{-2}, hence without the modification of m^* an isotropic R-reduction equally influences E_F and $E_{\lambda=2R}$. The other alkali metals are not superconductors and their values E_F are larger than $E_{\lambda=2R}$ more significantly than in Li and in Cs.

The described approach explains the combined isotope and high pressure effect in lithium [37]. In lithium 6 the high pressure and light isotope pull E_F below the level $E_{\lambda=2R}$, so T_c starts to diminish at a certain pressure p_0. In lithium 7 E_F remains above $E_{\lambda=2R}$ at p_0, hence the pressure continues to pull E_F down to $E_{\lambda=2R}$, T_c continues to grow.

A perfect conductor cannot form the Cooper pairs, because its electrons pass through the lattice without reflection, the standing waves don't occur in the crystal (i.e. the wave packets are unlimited in real space); T_c tends to zero.

Thus the binding energy Δ in a pair should be related with the strength of the electron reflection via the electron-ion attraction $\left\langle P\,(e_1, I)\right\rangle$ in Eq. (2.17). A deeper $\left\langle P\,(e_1, I)\right\rangle$ leads to a deeper Δ in Eq. (2.17) and, thus, to a stronger bond in the pair. On the other hand a deeper $\left\langle P\,(e_1, I)\right\rangle$ means a deeper potential on each ion; this deeper ion potential interacts/reflects conduction electrons more strongly. So the binding energy $|\Delta|$ is larger if the reflection of the unpaired electrons is stronger; hence T_c may also be larger but under the condition that $E_F = E_{\lambda=2R}$ is kept.

The described approach is consistent with the fact that the high temperature superconductors are layered structures and poor conductors in the normal state. In some layered structures is possible to combine two poorly compatible things: a large effective mass m^* (related to the strong electron-ion interaction/reflection) and a large E_F (up to the value $E_{\lambda=2R}$). This is because E_F in thin films is larger than in bulk [38], whereas the electron reflection and m^* in plane remain almost unchanged. In a 3-dimensional structure is difficult to combine a large m^* ($> 5\cdot m$) and $E_F \approx E_{\lambda=2R}$ (a few eV). Thus T_c in quasi 2-dimensional systems can be higher.

4. Results and discussion.

The above argumentation shows that the exchange interaction may in itself cause the formation of Cooper pairs in a crystal. Finally the superconductivity is a result of the Pauli Exclusion Principle.

If the momenta of e_1, e_2 are not equal (i.e. $\vec{k}_1 \neq \vec{k}_2$), then $\Psi_1(\vec{r}_1)$, $\Psi_2(\vec{r}_2)$ are **orthogonal,** $\left\langle \Psi_1(\vec{r}) \middle| \Psi_2(\vec{r}) \right\rangle = 0$ and we obtain from Eqs (2.0)-(2.18) that the exchange energy J is always positive; hence the singlet state is impossible.

The approach of the exchange energy is clearly applicable when the waves $\Psi_1(\vec{r}_1)$, $\Psi_2(\vec{r}_2)$ contain s-orbitals, because the s-waves envelop each ion and the singlet pairing leads to the convergence of electrons to the ions. In case of p-, d-, f-orbitals the described approach works if the orbitals envelop **nearest neighbor** ions. In this case the singlet pairing depends on the orbital orientation and on factors influencing the distance between ions (pressure, doping etc.)

The approach of standing waves is related with the Bragg-reflection, which may form diffraction patterns in the crystal. This explains why the charge density order pre-exists the superconductivity in cuprates [39], [40], [41].

The approach of standing waves is not applicable to the systems with heavy fermions, where E_F is much smaller than the energy $E_{\lambda=2R}$. But in this case the kinetic energy of electrons on the Fermi surface may be smaller than the binding energy in the pair; therefore the pair may arise and exist permanently in time what leads to the superconductivity.

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