

## Formation of Cooper Pairs as a Consequence of Exchange Interaction

**Abstract:** Analyzing the exchange energy of two conduction electrons in a crystal at many-body approach we find that the exchange energy may be negative and, thus, the singlet state may be favorable. A full overlap in the real space of the wave functions of two conduction electrons leads to a deeper exchange energy. Thus the exchange interaction causes a bond between two conduction electrons in the real space. The singlet bond is possible because the singlet electrons are in average closer to positive ions than single electrons. If conduction electrons, before the pairing, are put on the Fermi surface in the momentum space, then every pair may exist permanently in time. The motion of conduction electrons in the crystal may prevent the formation of Cooper pairs, because the kinetic energy of the motion is usually larger than the binding energy in the pair. Conduction electrons as standing waves have zero momenta, hence their momenta are synchronous; therefore the formation of Cooper pairs is more probable than in case of non-zero momenta. The approach of standing waves explains the inverse isotope effect and many other facts about superconductors. Considering the electronic pairs as bosons we find that a further necessary condition for superconductivity is a non-zero temperature of the Bose-Einstein-Condensation.

**Keywords:** Cooper pair; exchange interaction; Pauli Exclusion Principle; singlet state; superconductivity; standing wave; Bose-Einstein-Condensation.

### 1. Introduction and motivation.

The knowledge of root causes of superconductivity (SC) would explain many mysterious facts about all classes of superconductors. However, a unified solution remains still an open question, current theories are not universal and explain many effects ambiguously [1]. The mainstream theories assume that SC 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 is more appropriate to define the electron states than the mean-field approximation, 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 binding states of conduction electrons, which under certain conditions become superconducting.

### 2. Formation of superconducting pairs.

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 of every conduction electron  $e_1$  is random to spins of all other electrons. This state of electron  $e_1$  is designated as **unpaired** or **singlet**. If the spins of electrons  $e_1, e_2$  form a **singlet** in their overlap area in the real space, then the state of the electrons is designated as **paired**.

Every unpaired conduction electron has its **accurate** spatial wave function describing the position of the electron in the crystal. Knowing the accurate wave functions of unpaired electrons  $e_1, e_2$  we can compute their exchange energy.

If two electrons  $e_1, e_2$  form a singlet, then their overall position-space wave function  $\Phi(\vec{r}_1, \vec{r}_2)$  is symmetric:

$$\Phi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \Psi_1(\vec{r}_1)\Psi_2(\vec{r}_2) + \frac{1}{\sqrt{2}} \Psi_1(\vec{r}_2)\Psi_2(\vec{r}_1) \quad (2.1)$$

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 energies ( $D+J$ ) we find substituting  $\Phi(\vec{r}_1, \vec{r}_2)$  from Eq. (2.1) into the integral with an overall energy operator  $\hat{O}(\vec{r}_1, \vec{r}_2)$ :

$$\begin{aligned} D+J &= \left\langle \Phi(\vec{r}_1, \vec{r}_2) \left| \hat{O}(\vec{r}_1, \vec{r}_2) \right| \Phi(\vec{r}_1, \vec{r}_2) \right\rangle = \\ &= \left\langle \Psi_1(\vec{r}_1)\Psi_2(\vec{r}_2) \left| \hat{O}(\vec{r}_1, \vec{r}_2) \right| \Psi_1(\vec{r}_1)\Psi_2(\vec{r}_2) \right\rangle + \left\langle \Psi_1(\vec{r}_1)\Psi_2(\vec{r}_2) \left| \hat{O}(\vec{r}_1, \vec{r}_2) \right| \Psi_1(\vec{r}_2)\Psi_2(\vec{r}_1) \right\rangle \quad (2.2) \end{aligned}$$

If the exchange interaction of electrons  $e_1, e_2$  is very weak, then their spins remain unpaired and fully random. In this case the exchange energy is negligible and the overall energy of the unpaired electrons is equal to the direct term  $D$  as it should be for the unpaired electrons with accurate wave functions  $\Psi_1(\vec{r}_1), \Psi_2(\vec{r}_2)$ :

$$\langle E(\vec{r}_1, \vec{r}_2) \rangle = D = \left\langle \Psi_1(\vec{r}_1)\Psi_2(\vec{r}_2) \left| \hat{O}(\vec{r}_1, \vec{r}_2) \right| \Psi_1(\vec{r}_1)\Psi_2(\vec{r}_2) \right\rangle \quad (2.3)$$

The exchange energy  $J$  from Eq. (2.2) is

$$J = \left\langle \Psi_1(\vec{r}_1)\Psi_2(\vec{r}_2) \left| \hat{O}(\vec{r}_1, \vec{r}_2) \right| \Psi_1(\vec{r}_2)\Psi_2(\vec{r}_1) \right\rangle \quad (2.4)$$

If the exchange interaction of electrons  $e_1, e_2$  is not negligible, then their exchange term  $J$  is not zero. A singlet state of  $e_1, e_2$  is favorable, if their exchange energy  $J$  is negative [7].  $J$  takes into account the modification of the initially unpaired wave functions resulting from the pairing. This wave function modification influences all interactions of  $e_1, e_2$  in the crystal; hence we must compute the exchange energy  $J$  for  $\hat{O}(\vec{r}_1, \vec{r}_2)$  as a sum of all interactions of  $e_1, e_2$  including their kinetic energy, repulsion of  $e_1, e_2$  from **every** conduction electron and attraction of  $e_1, e_2$  to **every** ion. If two electrons form a triplet, then their overall position-space wave function is antisymmetric. The triplet state of  $e_1, e_2$  is favorable, if their exchange energy  $J$  is positive.

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-orbitals); 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<sub>2</sub>-molecule or in Helium atom; hence the overlap integral  $\langle \Psi_1(\vec{r}) | \Psi_2(\vec{r}) \rangle$  appearing in Eq. (2.4) is not zero:

$$\langle \Psi_1(\vec{r}) | \Psi_2(\vec{r}) \rangle \neq 0 \quad (2.5)$$

The wave functions of conduction electrons 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 real space, so we consider at first the limiting case that  $\Psi_1(\vec{r}), \Psi_2(\vec{r})$  almost coincide in the real space, i.e.:

$$\Psi_1(\vec{r}) \approx \Psi_2(\vec{r}) \quad (2.6)$$

Below we will see that this assumption is true because a maximal overlap in the real space of two paired wave functions is energetically favorable in comparison to a partial overlap.

Using Eq. (2.6) and non-orthogonality of  $\Psi_1(\vec{r}), \Psi_2(\vec{r})$  in Eq. (2.5) we can use for Eq. (2.4):

$$\Psi_1(\vec{r}_2) = \Psi_2(\vec{r}_2), \quad \Psi_2(\vec{r}_1) = \Psi_1(\vec{r}_1) \quad (2.7)$$

Substituting Eq. (2.7) into (2.4) we obtain:

$$J = \left\langle \Psi_1(\vec{r}_1)\Psi_2(\vec{r}_2) \left| \hat{O}(\vec{r}_1, \vec{r}_2) \right| \Psi_1(\vec{r}_1)\Psi_2(\vec{r}_2) \right\rangle \quad (2.8)$$

We see that Eq. (2.8) is equal to Eq. (2.3), i.e. in the case of the full overlap of non-orthogonal wave functions  $\Psi_1(\vec{r}), \Psi_2(\vec{r})$  the exchange energy of two singlet electrons is equal to the overall energy of two initially unpaired electrons:

$$J = \langle E(\vec{r}_1, \vec{r}_2) \rangle \quad (2.9)$$

We may define that the electron energy outside of the crystal is zero. Then the electron energy  $\langle E(\vec{r}_1, \vec{r}_2) \rangle$  inside the crystal should be negative, otherwise the states of single electrons in the crystal are instable. Thus the exchange energy  $J$  of  $e_1, e_2$  is also negative and the paired state is favorable in comparison to the unpaired state.

This conclusion has a clear physical meaning. The exchange term takes into account that the average distance between two singlet electrons decreases [8], [9], what increases the repulsion between electrons. 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 electrons are in average closer to the ion than two unpaired electrons. In simple words two singlet electrons are

closer to each other, the ions are located somewhere between electrons, therefore the singlet electrons are unavoidably closer to ions. The exchange term takes into account this decrease in distance between electrons and ions.

Consider that the overlap area of  $e_1, e_2$  in the real space is negligible (i.e. integral  $\langle \Psi_1(\vec{r}) | \Psi_2(\vec{r}) \rangle$  is small), then the exchange energy in Eq. (2.4) is negligible. In this case there is no advantage of the singlet state, since the electrons are separated in the real space. 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 in Eq. (2.6) is justified. Finally two electron waves stay together because the singlet state with a full overlap in the real space reduces their total energy.

It is possible to show that the singlet pairing of some conduction electrons is favorable for the whole crystal. We define all parts of the overall energy of two unpaired conduction electrons  $\langle E(\vec{r}_1, \vec{r}_2) \rangle$ :

1. The kinetic energies of electrons  $e_1$  and  $e_2$ ,  $\langle K(e_1) \rangle, \langle K(e_2) \rangle$ ;
2. The potential energy of repulsion of electron  $e_1$  from all conduction electrons in the crystal,  $\langle P(e_1, e) \rangle$ ;
3. The potential energy of repulsion of electron  $e_2$  from all conduction electrons in the crystal,  $\langle P(e_2, e) \rangle$ ;
4. We must correct double counting the repulsion between  $e_1, e_2$ , so we subtract the potential energy of repulsion between electrons  $e_1, e_2$ ,  $-\langle P(e_1, e_2) \rangle$ ;
5. The potential energy of attraction of electron  $e_1$  to all ions in the crystal,  $\langle P(e_1, I) \rangle$ ;
6. The potential energy of attraction of electron  $e_2$  to all ions in the crystal,  $\langle P(e_2, I) \rangle$ .

The exchange energy of  $e_1, e_2$  in Eq. (2.9) is a sum of the points 1-6:

$$J = \langle E(\vec{r}_1, \vec{r}_2) \rangle = \langle K(e_1) \rangle + \langle K(e_2) \rangle + \langle P(e_1, e) \rangle + \langle P(e_2, e) \rangle - \langle P(e_1, e_2) \rangle + \langle P(e_1, I) \rangle + \langle P(e_2, I) \rangle \quad (2.10)$$

The points 1-6 are a list of the crystal energy terms, which contain the paired electrons  $e_1, e_2$ . If the crystal has many singlet pairs, then the energy of each pair  $(e_{i-1}, e_i)$  contains the points 1-6 (however, we must again correct double counting the repulsion between electrons of different pairs).

The total energy of the many-body crystal contains additional energy terms:

7. The kinetic energies of single conduction electrons;
8. The potential energy of repulsion between single conduction electrons;
9. The potential energy of attraction of single conduction electrons to ions;
10. The potential energy of repulsion between ions.

The points 1-10 are a full list of all crystal energy terms.

The single, remaining unpaired, electrons don't change their states; hence the crystal energy terms in the points 7-10 remain unchanged. In the points 1-6 the overall energy of every singlet pair  $(e_{i-1}, e_i)$  is lower than the energy of two unpaired electrons  $e_{i-1}, e_i$  due to the negative exchange energy  $J$ . Thus the singlet pairing of some conduction electrons inevitably leads to the energy lowering of the whole crystal, the macroscopic state can exist.

One can obtain the same result by exploring the many-body crystal Hamiltonian  $H(\vec{r}_1 \dots \vec{r}_n)$  and the total crystal wave function as a product of **normalized** accurate wave functions of every single [10] and paired electron:

$$\langle E_{crystal} \rangle = \langle \dots \varphi_{i-1}(\vec{r}_{i-1}) \cdot \varphi_i(\vec{r}_i) \dots \Psi_{m-1}(\vec{r}_{m-1}) \cdot \Psi_m(\vec{r}_m) \dots | H(\vec{r}_1 \dots \vec{r}_n) | \dots \varphi_{i-1}(\vec{r}_{i-1}) \cdot \varphi_i(\vec{r}_i) \dots \Psi_{m-1}(\vec{r}_{m-1}) \cdot \Psi_m(\vec{r}_m) \dots \rangle \quad (2.11)$$

Where:  $\varphi_{i-1}(\vec{r}_{i-1}), \varphi_i(\vec{r}_i)$  normalized accurate wave functions of **paired** electrons;  $\Psi_{m-1}(\vec{r}_{m-1}), \Psi_m(\vec{r}_m)$  normalized accurate wave functions of **unpaired** electrons;  $\vec{r}_1 \dots \vec{r}_n$  radius-vectors of all electrons and ions.

The Hamiltonian  $H(\vec{r}_1 \dots \vec{r}_n)$  is a sum of operators for energies:

1. The kinetic energies of paired and single conduction electrons;
2. The potential energy of repulsion between all conduction electrons (paired and single);
3. The potential energy of attraction to ions of all conduction electrons (paired and single);
4. The potential energy of repulsion between ions.

All conclusions from Eqs (2.1)-(2.10) are valid if the electrons  $e_1, e_2$  are two equal running Bloch waves [11]:

$$\Psi_1(\vec{r}, t) = \Psi_2(\vec{r}, t) = u(\vec{r}) \cdot \exp(-i\omega t - i\vec{k} \vec{r}) \quad (2.12)$$

However, it is a rare event that the momenta  $\vec{k}$  of two running waves are equal permanently in time.

The momenta of electrons may be permanently equal if before pairing each electron is a **standing wave**, which is a sum of two equiprobable Bloch waves propagating in opposite directions:

$$\Psi_1(\vec{r}, t) = \Psi_2(\vec{r}, t) = \frac{1}{\sqrt{2}} u(\vec{r}) \cdot \exp(-i\omega t - i\vec{k} \vec{r}) + \frac{1}{\sqrt{2}} u(\vec{r}) \cdot \exp(-i\omega t + i\vec{k} \vec{r}) \quad (2.13)$$

The total momentum of each electron as standing wave is zero, hence the momenta of electrons are synchronous, so the pairing is possible despite the fact that the kinetic energy of electrons may be larger than their pairing energy.

The overall energy of two unpaired electrons  $\langle E(\vec{r}_1, \vec{r}_2) \rangle$  is usually not arbitrarily small; consequently the exchange energy  $J$  in Eq. (2.9) is also not arbitrarily small. The sign of the exchange term  $J$  is related with the sign of the energy increment resulting from the pairing. This energy increment is related with wave function modifications and is not necessarily negligible if  $J$  is not negligible; therefore the binding energy  $2\Delta$  in the singlet pair is also not negligible:

$$2\Delta = \langle \varphi_1(\vec{r}_1) \varphi_2(\vec{r}_2) | \hat{O}(\vec{r}_1, \vec{r}_2) | \varphi_1(\vec{r}_1) \varphi_2(\vec{r}_2) \rangle - \langle \Psi_1(\vec{r}_1) \Psi_2(\vec{r}_2) | \hat{O}(\vec{r}_1, \vec{r}_2) | \Psi_1(\vec{r}_1) \Psi_2(\vec{r}_2) \rangle = A \cdot J \quad (2.14)$$

Where  $\varphi_1(\vec{r}_1), \varphi_2(\vec{r}_2)$  are normalized accurate wave functions of  $e_1, e_2$  after pairing;  $A$  is a positive material constant.

Since the binding (pairing) energy  $2\Delta$  is not arbitrarily weak, the unpaired (normal) state of  $e_1, e_2$  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  $2\Delta$ . The binding energy  $2\Delta$  is roughly related to a **pairing temperature**  $T^*$ :  $2|\Delta| \approx k_B T^*$ .

If the wave functions of two conduction electrons in the crystal (for sample two s-electrons) permanently coincide in the real space and form a permanent singlet, then the electrons are similar to the electrons in the ground state of 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 electronic pair is stable like a valence bond in multi-atom systems, so the pair doesn't form/lose any bonds in the crystal and doesn't absorb/radiate any chemical energy.

Every standing wave is limited in the real space, therefore a stable singlet of two standing waves can be considered as a zero-spin **boson**. Bosons can form the Bose-Einstein-Condensate (BEC) below a certain temperature  $T_{\text{BEC}}$ . If all electronic pairs are in the BEC ground state, then the excitation energy of every pair is roughly related to  $k_B T_{\text{BEC}}$ , which is not zero if the bosonic density is not zero. If all external influences are weaker than  $k_B T_{\text{BEC}}$ , then the pairs remain in the BEC ground state and cannot absorb/radiate any energy in the crystal; as a result the total energy and momentum of all pairs don't dissipate, the pairs fluctuate without resistance despite the fact that the single electrons were standing waves before pairing. Thus the pairing of conduction electrons and BEC of the pairs lead to the zero resistivity (likewise works the superfluidity in Helium-4; the pairing energy of electrons  $k_B T^*$  in Helium-4 is huge, whereas  $k_B T_{\text{BEC}}$  is small).

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 magnetic energy split ( $2 \cdot \mu_B \mu_0 \mu H$ ) is weaker than the binding energy  $2|\Delta| \approx k_B T^*$  and excitation energy  $\approx k_B T_{\text{BEC}}$ , 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 binding energy  $|\Delta|$  per one electron in Eq. (2.14) is larger than the insulating band gap  $E_g$  of the crystal, then electrons can leave the valence band at a temperature  $T < T^*$ , hence the electrons may pair up despite the band gap. A doping in the crystal may reduce the band gap and, thus, give rise to SC. This doping effect is observable in cuprates [12], in iron-based superconductors [13], in semiconductors [14].

A necessary condition for SC in metals is that the electrons, before pairing, are close to the Fermi surface in the momentum space. We show this assuming that the pairing occurs when the energy of the single electron has a certain value  $E_\lambda$ . If the thermal energy doesn't exceed the binding energy  $|\Delta|$  in Eq. (2.14), then the concentration of the pairs is not zero and in the energy spectrum of single electrons occurs a gap around the value  $E_\lambda$ . The gap is thin, since  $|\Delta|$  is usually small and the density of electrons with close energies is limited by the Exclusion Principle. If  $E_\lambda$  is notably less than the Fermi level  $E_F$ , then there are single electrons with the energy larger than  $E_\lambda$ . These single electrons may drop to the level  $E_\lambda$  due to energy fluctuations and may, thus, form new pairs. The concentration of the paired electrons is limited by the thin gap around  $E_\lambda$ ; therefore the new pairs replace the already existing pairs, 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 the electron is resistive, therefore the momentum of the electron and of the pair dissipates. Thus the state with  $E_\lambda < E_F$  cannot keep a supercurrent, despite the fact that the pairing is possible. If  $E_\lambda = E_F$  then every pair may exist **permanently in time**, because below a temperature  $T_c$  the

single electrons cannot overcome the energy gap and cannot reach the pairing level  $E_\lambda = E_F$ ; 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 an energy gap with  $E_F$  **as the upper limit**. Only such permanent pairs are superconducting. At a temperature above  $T_c$  the thermal energy is sufficient to scatter single electrons through the energy gap to the pairing level  $E_\lambda$ , therefore new pairs may arise and replace the existing ones, the state becomes dissipative.

### 3. Pairing of standing waves.

We found that the binding energy in the singlet 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. the wave functions coincide in the real space. The energy gap of superconductors has order of magnitude  $10^{-3}$  eV, the Fermi level has order of magnitude a few eV. Consequently the electron motion can split the pair in the real space. The energy of very slow electrons is usually much lower than the Fermi level; hence the slow electrons cannot form superconducting pairs. Two electrons can form a pair if their momenta are synchronous, but it is a rare event for running waves. The electrons as **standing waves** have zero-momenta, hence their momenta may be synchronous and the pairing is possible despite a large kinetic energy.

A standing wave occurs as a result of reflections of a running wave from a periodic potential. The condition of the standing wave in a crystal is the Bragg condition [15]:

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

Where:  $n$  integer;  $\lambda$  length of the Bloch wave in Eq. (2.12);  $R$  one of lattice parameters.

Under Bragg condition the electron becomes a set of standing waves with a zero total momentum [16].

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  $R$  ( $R_{100}, R_{110}, R_{210}$  etc. depending on the crystal axis) and, thus, some values  $\lambda_1$ . Each value  $\lambda_1 = 2 \cdot R$  is linked to the energy  $E_{\lambda=2R}$ :

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

Where  $m$  is the inertial mass of free electron.

Not all materials have conduction electrons with short values  $\lambda=2R$  and with its associated  $E_{\lambda=2R}$ . If the Fermi level of a crystal is low, then  $\lambda$  values are larger than short values  $2R$  and electron energies are lower than corresponding  $E_{\lambda=2R}$ ; so the states with short  $\lambda=2R$  are empty and short standing waves don't occur. In some metals  $E_{\lambda=2R}$  is close to  $E_F$  (it is equivalent that  $\lambda_F=2R$ ). Probably in some crystals the formation of pairs is possible at  $n$  larger than 1 in Eq. (3.1). For sample at  $n=2$  the length of standing waves is  $\lambda_2=R$ .

Every act of the pairing is energetically favorable; hence the energy  $2|\Delta|$  is emitted. Thus the momentum of each pair increases from zero to a value  $p \leq (2|\Delta| \cdot 2 \cdot 2m)^{0.5}$ . This momentum  $p$  should be added to the momenta of paired electrons in the momentum space. Therefore the kinetic energies of electrons from different pairs are not equal, but distributed into a spectrum with the width  $\approx |\Delta|$ . For instance, if the kinetic energy of normal electrons was  $E_F$  before pairing, then after the pairing the kinetic energy becomes  $\approx E_F + |\Delta|$ . So the spectrum of paired electrons is **above** the spectrum of single electrons in the momentum space. Note: the same conclusion follows from the exchange energy: the exchange term for kinetic energy is positive, i.e. the kinetic energy grows by pairing, whereas the total energy falls (the same relation is valid for all singlet bonds in chemistry). Thus the paired electrons can overlap with normal electrons in the real space. The density of paired electrons is  $\approx S(E_F) \cdot |\Delta|$ , where  $S(E_F)$  is the density of states of conduction electrons. The spectrum of normal electrons obtains a corresponding gap  $(E_2 - E_1) \approx |\Delta|$  around the value  $E_{\lambda=2R}$  ( $E_1, E_2$  are limits of the gap). The gap is not negligible if the thermal energy is insufficient to destroy the pairs. As shown above a necessary condition for SC is that  $E_F$  is the upper limit of the gap:  $E_F = E_2$ .

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

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

Thus the energies and states of single electrons below the gap  $(E_F - E_1)$  stay unchanged as assumed for Eq. (2.11).

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 [17]) 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 density and its associated  $E_F$  up to the level  $E_{\lambda=2R}$  (which is constant, if  $R$  doesn't change). Thus the doping may lead to SC,  $T_c$  increases. If the crystal is overdoped, then  $E_F$  is too large;  $E_{\lambda=2R} < E_F$ ,  $T_c$  vanishes. This doping effect explains the **dome form** of phase diagrams of superconductors [18]. A double dome form is possible due to the fact that the crystal has some lattice parameters depending on the crystal structure. Thus a large value  $|E_F - E_{\lambda=2R}|$  suppresses  $T_c$ . If  $E_{\lambda=2R} = E_F$ , then  $T_c$  corresponds to the pairing energy  $\Delta$  in Eq. (2.14); however, the doping influences on both  $E_F$  and  $\Delta$ , so the  $T_c$  - maximum is not always pinned exactly to  $E_{\lambda=2R} = E_F$ .

We can specify the energy  $Ck_B T_c$  ( $C$  is a material specific constant) as a minimum thermal energy, which is necessary to scatter single electrons from the bottom of the superconducting gap to the pairing level  $E_{\lambda=2R}$ , where new pairs arise and replace the old ones. So we know about the  $T_c$  tuning:

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

$$Ck_B T_c \leq |\Delta| \quad \text{if } |\Delta| > |E_F - E_{\lambda=2R}| \text{ and } E_{\lambda=2R} \geq E_F \quad (3.5)$$

$$Ck_B T_c \leq |\Delta| - |E_F - E_{\lambda=2R}| \quad \text{if } |\Delta| > |E_F - E_{\lambda=2R}| \text{ and } E_{\lambda=2R} < E_F \quad (3.6)$$

Thus  $Ck_B T_c$  is an energy area between the SC - gap bottom and  $E_{\lambda=2R}$ . A growing  $T$  closes continuously the area  $Ck_B T_c$  by putting there single (normal) electrons. At  $T=T_c$  the area  $Ck_B T_c$  is covered by single electrons. Knowing the density of single states  $S(E_\lambda)$  around the SC-gap, we can calculate  $T_c$  and  $C$  - parameter in  $Ck_B T_c$ .

The pairing energy  $\Delta$  in Eq. (2.14) is to find by investigating the wave function modifications resulting from the singlet pairing and leading consistently to experimental  $\Delta$ -values. The SC - gap bottom  $E_1$  is to find from Eqs (3.5), (3.6):

$$E_1 = E_{\lambda=2R} - Ck_B T_c = E_{\lambda=2R} - |\Delta| \quad \text{if } E_{\lambda=2R} \geq E_F \quad (3.7)$$

$$E_1 = E_{\lambda=2R} - Ck_B T_c = E_F - |\Delta| \quad \text{if } E_{\lambda=2R} < E_F \quad (3.8)$$

The single-electron-distribution on the SC-gap bottom  $E_1$  is the Fermi-Dirac function  $f(E_\lambda, T)$ . The single-electron-concentration  $N(T_c)$  at  $T$  just below  $T_c$  is:

$$N(T_c) = \int_0^{E_{\lambda=2R}} S(E_\lambda) \cdot f(E_\lambda, T_c) dE_\lambda = \int_0^{E_{\lambda=2R}} S(E_\lambda) \cdot \frac{1}{\exp\left(\frac{E_\lambda - E_1}{k_B T_c}\right) + 1} dE_\lambda \quad (3.9)$$

At  $T=0$  the single-electron-concentration  $N(0)$  is:

$$N(0) = \int_0^{E_1} S(E_\lambda) dE_\lambda \quad (3.10)$$

New pairs don't arise at  $T \leq T_c$ , so  $N$  is independent of  $T$ . Hence  $N(0)=N(T_c)$  and Eq. (3.9) is equal to Eq. (3.10):

$$\int_0^{E_1} S(E_\lambda) dE_\lambda = \int_0^{E_{\lambda=2R}} S(E_\lambda) \cdot \frac{1}{\exp\left(\frac{E_\lambda - E_1}{k_B T_c}\right) + 1} dE_\lambda \quad (3.11)$$

$E_1$  is calculable from Eqs (3.7) or (3.8),  $E_{\lambda=2R}$  is known from crystal structure; hence, knowing  $S(E_\lambda)$ , we can calculate  $T_c$  from Eq. (3.11).

$C$  parameter in  $Ck_B T_c$  we find from  $T_c$  and using  $Ck_B T_c = (E_{\lambda=2R} - E_1)$ . Calculations with Eq. (3.11) show:

- A.** For Fermi liquids  $S(E_\lambda)$  is proportional to  $E_\lambda^{0.5}$ , then  $C$  depends slightly on the level  $E_1$  and  $T_c$ . Substituting the ranges  $E_1=(0.25 - 3)$  eV and  $T_c=(0.1 - 50)$  K into Eq. (3.11) we find  $E_{\lambda=2R}$  and the range  $C \approx (4.5 - 10)$  units;
- B.**  $C$  depends on the  $S(E_\lambda)$ -slope around the level  $E_1$ : the larger  $dS/dE_\lambda$ , the smaller  $C$ . On the zone edge ( $\lambda=2R$ )  $dS/dE_\lambda$  may be larger than the  $E_\lambda^{0.5}$ -slope, therefore  $C$  may be smaller than (4.5 - 10) by a few units, i.e.  $C \approx (3 - 7)$ . These  $C$  - values are consistent with experiments.

The isotope substitution is a 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 electron  $m^*$  and electron density  $N$  [19], whereas  $E_{\lambda=2R}$  in Eq. (3.2) depends only on the lattice parameter  $R$ .

$$E_F = \frac{\hbar^2}{8m^*} \left( \frac{3N}{\pi} \right)^{2/3} \quad (3.12)$$

The isotope effect is a consequence that the energy of phonons is proportional to  $M^{-0.5}$  ( $M$  - mass of ion). The decrease in  $M$  raises the energy of phonons; therefore the electron-ion interaction and its associated reflection of electrons from ions may intensify. This intensification is equivalent to the increase in the effective mass  $m^*$  and, thus, to the decrease in  $E_F$ , whereas  $R$  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 closer 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  $\alpha$  [20] 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: electric field [21] since  $E_F$  depends on the electronic density; film thickness [22], [23], [24], [25] since the mutual  $E_F$  of layered structures depends on layer thicknesses; the high pressure [26], [27], [28] since  $E_F$  depends on the distance between atoms.

A further sample of the  $E_F$  tuning is the alkali metals (Li, Na, K, Rb, Cs). Only Lithium is superconductor at ambient pressure [29] and only Lithium has  $E_{\lambda=2R}=3,09$  eV (calculated by Eq. (3.2) in bcc-structure,  $R_{100}=3,49$  Å) relatively close to  $E_F \approx 3,2$  eV [30] at ambient temperature. The next candidate in superconductors after Lithium is Cesium:  $E_{\lambda=2R}=1,33$  eV (calculated by Eq. (3.2) in bcc-structure,  $R_{111} = 6,14 \cdot \sqrt{3}/2 = 5,32$  Å),  $E_F \approx 1,54$  eV calculated by Eq. (3.12); Cesium is really superconductor under high pressure [31]. The high pressure increases 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. 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 (table 1). 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 increases both  $E_F$  and  $E_{\lambda=2R}$ .

**Table 1.** Comparison of energies  $E_F$  and  $E_{\lambda=2R}$  for alkali metals.  $E_{\lambda=2R}$  are calculated by Eq. (3.2) for lattice parameters  $R_{100}$  and  $R_{111}$  in bcc crystals. Larger  $R$ -values are not considered, since they correspond to smaller  $E_{\lambda=2R}$  values. For Li is used the experimental value  $E_F$  at ambient temperature; for other alkali metals are used  $E_F$  values calculated by Eq. (3.12) corresponding roughly to the experimental values.

	$E_F$		$E_{\lambda=2R}$	$E_F - E_{\lambda=2R}$		$E_{\lambda=2R}$	$E_F - E_{\lambda=2R}$
			for $R_{100}$	for $R_{100}$		for $R_{111}$	for $R_{111}$
	eV		eV	eV		eV	eV
<b>Li</b>	3.2		3.09	<b>0.11</b>		4.12	-0.92
<b>Na</b>	3.16		2.05	1.11		2.73	0.43
<b>K</b>	2.04		1.32	0.72		1.76	0.28
<b>Rb</b>	1.78		1.15	0.63		1.54	0.24
<b>Cs</b>	1.54		1.0	0.54		1.33	<b>0.21</b>

The described approach explains the combined isotope and high pressure effect in lithium [32]. 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 heavy lithium-7  $E_F$  remains above  $E_{\lambda=2R}$  at  $p_0$ , hence the increasing pressure continues to pull  $E_F$  down toward  $E_{\lambda=2R}$ ;  $T_c$  continues to grow. As a result the sign of  $dT_c/dp$  above the pressure  $p_0$  is different for  ${}^6\text{Li}$  and  ${}^7\text{Li}$ .

A perfect conductor cannot form the Cooper pairs, because the electrons pass through the lattice without reflection, the standing waves don't arise, the electronic wave packets are unlimited in the real space, hence a correlation of wave functions in accordance with Eq. (2.1) is impossible because of a finite speed of electron-electron interaction; so the exchange energy and  $T_c$  tends to zero. Thus the exchange energy and the associated pairing energy should be related with the strength of the electron-ion reflection via the potential energy of electrons in Eq. (2.10). A deeper potential energy of electrons leads to a deeper  $J$  in Eq. (2.10) and, thus, to a stronger pairing energy in Eq. (2.14). On the other hand, a deeper potential energy means a deeper potential on each ion, which interacts/reflects conduction electrons more strongly. So the singlet bond is stronger 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 [33], whereas the electron reflection and  $m^*$  in-plane may 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.

The pairing energy in the proposed model is related rather to the lattice potential than to the carrier density. This enables SC at relatively low carrier densities. A sample is superconducting bismuth at ambient pressure, a semimetal with a low

carrier density,  $N \approx 3 \cdot 10^{17} / \text{cm}^3$  [34].  $E_F$  of bismuth is  $\approx 25$  meV, hence corresponding  $\lambda_F = h \cdot (E_F 2m)^{-0.5} \approx 0.78 \cdot 10^{-8}$  m. Thus in bismuth are working the long values of  $R = 0.5 \lambda_F \approx 0.39 \cdot 10^{-8}$  m (i.e.  $R_{810}$ ,  $R_{910}$  and similar). These long standing waves exist only due to the high crystal purity, where the electronic mean free path is much larger than  $\lambda_F$ . Thus SC-pairs emerge from the long standing waves on the Fermi level. Since the electron's waves are long range, the mean distance between electrons in one pair may be larger than the electron's wave length  $\lambda_F \approx 10^{-8}$  m, so the pairing is possible at a carrier density less than  $(\lambda_F)^{-3} \approx 10^{18} / \text{cm}^3$ .

For Fermi metals we can estimate the relation between BEC-temperature and pairing temperature,  $T_{\text{BEC}}/T^*$ . Assuming  $N_s \approx S(E_F) \cdot |\Delta|$  and  $3.5 \cdot k_B T^* \approx |\Delta|$ , using the well-known equations  $S(E_F) = 2^{1/2} m^{3/2} E_F^{1/2} / (\pi^2 \hbar^3)$  for Fermi liquid and  $T_{\text{BEC}}(N_s) \approx 3.3125 \cdot \hbar^2 (N_s / 2)^{2/3} / (2m k_B)$  for bosonic gas we obtain:

$$\frac{T_{\text{BEC}}}{T^*} \approx \left( \frac{E_F}{|\Delta|} \right)^{1/3} \quad (3.13)$$

For Fermi metals usually  $E_F \gg |\Delta|$ , hence  $T_{\text{BEC}} > T^*$  and SC depends rather on  $T^*$  than on  $T_{\text{BEC}}$ , i.e.  $T_c = T^* < T_{\text{BEC}}$ . For strongly correlated systems  $E_F$  may be order of magnitude  $|\Delta|$ , so BEC may define SC, i.e.  $T_c = T_{\text{BEC}} < T^*$ .

If the pairing temperature  $T^*$  is larger than  $T_{\text{BEC}}$  (i.e.  $T^* > T_{\text{BEC}}$ ), then at  $T$  above  $T_{\text{BEC}}$  the electronic pairs may be permanent but non-superconducting. The non-superconducting pairs are observed in [35].

Consider  $E_F$  is close to the SC-gap bottom  $E_1$  and notable below  $E_{\lambda=2R}$  (that is possible, for example, in underdoped cuprates). Then the gap ( $E_F - E_1$ ) in Eq. (3.3) is small and the singlet density  $N_s$  is also small. Hence the corresponding  $T_{\text{BEC}}$  may be lower than the pairing temperature  $T^*$ , because  $T^*$  depends rather on the lattice potential than on  $N_s$ . If the BEC is a necessary condition for SC and  $T_{\text{BEC}} < T^*$ , then  $T_c = T_{\text{BEC}}$ ; so  $T_c$  is also lower than  $T^*$ . Thus at  $T$  between  $T_c$  and  $T^*$  there are permanent pairs without SC. This may be related with the pseudogap in some superconductors.

#### 4. Conclusion and discussion.

The above argumentation shows that the exchange interaction may in itself cause the electronic pairing in a crystal. Thus the non-zero pairing (binding) energy is a result of the Pauli Exclusion Principle.

Further necessary conditions for SC: the permanency in time of every electronic pair (provided with pairing of standing waves on the Fermi surface); the non-zero temperature of the BEC ground state of the electronic pairs.

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-orbitals envelop each ion and the singlet pairing leads to a convergence of electrons to 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 [36], [37], [38].

Following the proposed approach we can define main ways to a higher  $T_c$  in new superconductors:

- The value  $E_F$  should be tunable close to  $E_{\lambda=2R}$  (i.e.  $\lambda_F$  is tunable to short  $2R$ ). The tuning is possible by doping, pressure, film thickness, electric field etc.
- The material should have a large value  $m^*$ , since  $m^*$  is related to deeper lattice potentials in Eq. (2.10) causing a deeper exchange energy. However, the condition  $E_F = E_{\lambda=2R}$  should be kept. A possible way to combine large values  $E_F$  and  $m^*$  is the low dimensionality;
- The material should be homogeneous microscopically, because impurities/defects suppress  $T_c$  by scattering the regular standing waves and values  $|E_F - E_{\lambda=2R}|$  and  $\Delta$ .

The approach of standing waves is not applicable to systems with heavy fermions, where  $E_F$  is much smaller than  $E_{\lambda=2R}$ . But in this case the kinetic energy of electrons on the Fermi surface may be smaller than the binding energy in the pair; hence the pair may arise and exist permanently in time causing SC. One can write roughly for narrow band systems:

$$C k_B T_c \leq |\Delta| - E_F \quad (4.1)$$

Therefore a tuning of  $E_F$  down may cause a higher  $T_c$  in systems with heavy fermions (observed in [39]).

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