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Superconductivity: From Fröhlich to Nonadiabatic Theory

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A new insight on superconductivity stemming from the nonadiabatic molecular vibration-electronic theory is presented. An elegant synthesis of apparently quite controversial ideas, contained in Fröhlich's three famous papers is made leading to one-particle theory of superconductivity. The critical comment on two-particle theories (such as BCS theory) is added. In our theory the elementary excitations are identical with selfconsistent polarons. The condition for creation of a superconductive state is equivalent to that of creation of an insulator with several equienergetical groundstates rising due to the crystal symmetry lowering. The essence of superconductivity is bound to the existence of microflows (tunneling) of atomic nuclei below T_c. The carriers of current are charge density waves connected to the motion of the couples of electrons forming the resonant valence bonds. In addition to the known properties of superconductors recent experiments concerning the density of electron states near the Fermi surface are explained.

I. Introduction

After discovery of high-temperature superconductivity the explosion of a diverse spectrum or theoretical works has emerged. Most of the works is built on the two-particle mechanism of Cooper pair creation, which became famous due to its explanation of low-temperature superconductivity within the framework of the BCS theory [4]. On the other hand the majority of works contains an attempt to explain the superconductivity mechanism via diverse range of interactions except for the electron-phonon one. The most likely reason is the absence of isotope effect (or its smallness). The evolution of understanding of low-T_c superconductivity can be shortly described in two phases: In the first phase the primary concept of the electron-phonon interaction has been built into the theory, inspired by the appearance of the isotope effect. In the second phase, on the basis of the

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aforementioned primary concept, the second one, namely the idea of Cooper pairs has been developed. In contrast to the evolution of the ideas regarding the low-T_c superconductivity, in high-T_c superconductivity the tendency to maintain the secondary Cooper-pair concept acquires primary importance while the electron-phonon interaction mechanism is loosing its original key role. Now we can ask an important question: Could it be the other way around? And moreover, the second question: Could a unifying theory of both low-T_c and high-T_c superconductivity be constructed? And finally and foremost, the third question: Do we understand the low-T_c superconductivity correctly (is the BCS explanation the only possible)?

In such a critical point where the contemporary development of the theory of superconductivity appears to be, one is forced to focuse the attention on the very beginning when the first serious microscopic ideas about superconductivity have arisen. Let us mention one useful example from history of the origin of the theory of relativity. After the crisis of classical mechanics had occurred, Mach has turned his attention to the very early time of Newton, rediscovered his antimetaphysical requirements and made the decision that the further development of classical physics was very declined from the original Newton's requirements. As a result of this retrospectives the principle of relativity has arisen, firstly pronounced by Mach.

Nowadays a crisis of theories of superconductivity is indicated after the appearance of high-T_c effects. Therefore we will follow the Mach's approach and turn back into the pioneer time of Fröhlich. He was the first who has performed the serious and important attempts to explain superconductivity microscopically from the first principles. We mention now his — according to our opinion — three famous papers.

The first one, entitled "Theory of the superconducting state. I. The ground state at the absolute zero of temperature" [1], deals with the derivation of the ground state energy lowering in superconductors by means of the second-order perturbation theory. From furher discussions it will be seen that this formula is really fundamental for understanding of superconductivity. Unfortunately, the further theoretical development has ignored this important result. Fröhlich's conception was criticized on basis of the fact that except of isotopic effect and ground state energy decrease it is unable to explain the fundamental physical properties of superconductors, such as the existence of the gap, excitation spectrum, specific heat etc. It has been believed that the reason of failure lies in the use of the perturbative method.

Fröhlich, being aware of this fact, created a new Hamiltonian by means of the canonical transformation, i.e. by a nonperturbative way, published in his second famous paper (Interaction of electrons with lattice vibrations [2]). The main result is the derivation of effective two-electron interaction term. On the basis of this theory Fröhlich tested the result of ground state energy lowering contained in the previous paper. Both formulae were the same but Fröhlich was not satisfied with

just pure verification that could not give any new result. He wrote that the theoretical treatment of the superconductivity effects had to wait for development of new methods to deal with effective two-electron interaction term. This prophetic statement was really fulfilled several years later in the BCS theory. As will be discussed later in this paper, we have proved that BCS theory is controversial in nature in spite of the fact that it is commonly accepted. Nevertheless, we show that the effective two-electron term has a fundamental meaning for superconductivity and, in addition, how to fulfill the above mentioned prophetic statement in a correct way.

In the third famous paper (On the theory of superconductivity: the one-dimensional case [3]) Fröhlich pointed out that the theoretical methods usually employed in field theory are unsatisfactory. In order to explain some properties of superconductors he proposed somewhat unrealistic one-dimensional model which is based on the principle of lattice displacement due to the interaction of one critical vibrational mode $2k_F$ with electrons. According to our opinion two results are fundamental here: the lattice symmetry reduction and the nature of the gap formation which is of one-particle origin. Fröhlich was aware of limited applicability of this one-dimensional model. His last wish brought out at the end of this third paper was to overcome the complementarity of the two aspects of electron-phonon interaction: The first aspect, contained in the first and the second paper, points to the importance of the dynamic part of the interaction and indicates the isotope effect. The second aspect, contained in the third paper, is based on the interaction between electrons arising due to lattice displacement which leads to the cooperative behaviour. Our theory of superconductivity presented in this paper follows this Fröhlich's testament.

II. Quantum chemical Hamiltonian

The most fundamental role in the microscopic understanding of superconductivity is played by the Hamiltonian and the way of it is handled. Before we introduce our approach we mention the first misleading concept in treating the superconductivity problem. It is the paradigm of Bloch states which was introduced in theoretical conception of superconductivity by Fröhlich [1] and was then automatically accepted by Bardeen, Cooper and Schrieffer [4] and by all their successors. This paradigm was taken over from quantum field theory and was built on a simple model: two sets of free independent particles and the interaction between them leading to energy renormalization (selfenergy) of quasiparticles (particles surrounded by a cloud of particles belonging to the other set). This paradigm is very successful in calculation of scattering processes, and in its Bloch's version also in solids in calculation of conduction effects. It was, in our opinion, a historical misunderstanding to treat superconductivity as a limiting case of infinite conductivity and to describe superconductive current in quasimomentum space with

prevailing values in some chosen direction **k**. It is worthwhile to note that we do not speak about the problem Bloch versus Wannier (delocalized versus localized) states. We only assert that the quantum field description represented by Bloch states is inadequate to the strong selfconsistent effect of condensation of a matter in superconducting state. This means that the Hamiltonian most often used in books and papers dealing with theory of solids:

$$H = H_0 + H' \tag{2.1}$$

where

$$H_0 = \sum_{\mathbf{k},\sigma} \varepsilon_{\mathbf{k}} a^+_{\mathbf{k},\sigma} a_{\mathbf{k},\sigma} + \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}} \left(b^+_{\mathbf{q}} b_{\mathbf{q}} + \tfrac{1}{2}\right) \tag{2.2}$$

$$H' = \sum_{\mathbf{k},\mathbf{q},\sigma} u^{\mathbf{q}} \left(b_{\mathbf{q}} + b^+_{-\mathbf{q}}\right) a^+_{\mathbf{k}+\mathbf{q},\sigma} a_{\mathbf{k},\sigma} \tag{2.3}$$

can never explain the true origin of superconductivity. Two independent unperturbed electron and phonon fields are represented by spectral values $\varepsilon_{\mathbf{k}}$ and $\hbar\omega_{\mathbf{q}}$ here. Values of $\varepsilon_{\mathbf{k}}$ represent continuous spectrum in metals. We shall try to elucidate in the following sections that no treatment of Hamiltonian (2.1) is able to produce necessary renormalizations and/or corrections to unperturbed values $\varepsilon_{\mathbf{k}}$ in order to get superconducting state. The above mentioned strong selfconsistent effect get us to change the values of unperturbed energies $\varepsilon_{\mathbf{k}}$ as it will be seen later. As far as the frequencies $\omega_{\mathbf{q}}$ are concerned, they usually remain unchanged in contemporary superconductivity theories, including BCS. On the contrary, Fröhlich in his second above mentioned paper [2] pointed out the necessity of introduction of renormalization for $\omega_{\mathbf{q}}$ and consequently also for matrix elements of electron-phonon interaction $u^{\mathbf{q}}$. It is a very nice idea but it is, due to the strong selfconsistent effect, not sufficient as seen in the case of $\varepsilon_{\mathbf{k}}$. It will be necessary to construct quite new selfconsistent values of frequencies $\omega_{\mathbf{q}}$. The selfconsistent solution of the total Hamiltonian has to be found as a simultaneous optimization of the electronic as well as the nuclear parts of the Hamiltonian. The model Hamiltonian (2.1) corresponds only to the simplest (adiabatic) separation of the total Hamiltonian and is fully unsatisfactory for the description of superconducting state.

In order to overcome the difficulties connected with the quantum field Hamiltonian (2.1-3) we are forced to go back to the ab-initio formulation of interaction of the systems of nuclei and electrons, i.e. to the quantum chemical Hamiltonian [5–8, 13]. We will use the spinorbital notation for electron operators $\bar{a}_P$, $\bar{a}^+_P$, for coordinate and momentum harmonic oscillator operators the notation $\bar{B}_r = \bar{b}_r + \bar{b}^+_{\check{r}}$ and $\bar{\bar{B}}_r = \bar{b}_r - \bar{b}^+_{\check{r}}$ will be used [9]. We assume that for any vibrational mode r there exists corresponding mode $\check{r}$ fulfilling the identity $\omega_r = \omega_{\check{r}}$. The operators marked with the bar are operators of "original" quasiparticles (electrons and phonons) in the crude representation, i.e. the representation of fixed nuclear positions [7, 8]. Comparing this notation with the usual solid state notation the simple transition $P \to \mathbf{k}, \sigma, r \to \mathbf{q}, \check{r} \to -\mathbf{q}$, is supposed [9].

General form of nonrelativistic electron-vibrational Hamiltonian for any molecular system can be written in the form

$$H = T_N(\bar{B}) + E_{NN}(\bar{B}) + \sum_{P,Q} h_{PQ}(\bar{B})\, \bar{a}_P^+ \bar{a}_Q + \frac{1}{2} \sum_{P,Q,R,S} v^0_{PQRS} \bar{a}_P^+ \bar{a}_Q^+ \bar{a}_S \bar{a}_R \qquad (2.4)$$

where T_N stands for kinetic energy of nuclei and E_{NN} for the potential energy of nuclei interactions. One-electron matrix elements $h_{PQ}(\bar{B})$ comprise electron kinetic energy and electron-nuclear interaction. The term v^0_{PQRS} represents two-electron interaction matrix elements. The terms E_{NN} and h_{PQ} are defined through their Taylor expansion

$$E_{NN}(\bar{B}) = \sum_{i=0}^{\infty} E^{(i)}_{NN}(\bar{B}) \qquad (2.5)$$

$$h_{PQ}(\bar{B}) = h^0_{PQ} + \sum_{i=1}^{\infty} u^{(i)}_{PQ}(\bar{B}) \qquad (2.6)$$

where h^0_{PQ} is one-electron term for fixed (equilibrium) nuclear coordinates and

$$u_{PQ}(\bar{B}) = \left\langle P \left| \sum_j \frac{-Z_j e^2}{|\mathbf{r} - \mathbf{R}_j|} \right| Q \right\rangle \qquad (2.7)$$

in terms of the second quantization represents the matrix elements of electron-phonon interaction. We assume in (2.5-6) that the sums are convergent.

In order to understand the origin of superconductivity we will treat the Hamiltonian (2.4) up to the second order of Taylor boson expansion, i.e. we will use only the harmonic level. Anharmonicities of the third and higher orders will be disregarded.

III. The break-down of Born-Oppenheimer approximation

Let us consider solid state matter as a giant molecule. Molecules with energy difference between lowest unoccupied and highest occupied orbitals smaller than $\hbar\omega$ are calculated as a special class of molecules where the Jahn-Teller effect [14–16, 8] occurs. It is a case of break-down of Born-Oppenheimer approximation [17]. Conductors are characterized by the continuous strongly degenerate spectrum in partially occupied band. Here we find a motivation to treat a transition from the conducting to superconducting state as a Jahn-Teller process of removing the degeneration and creation of an energy gap.

Let us introduce the vibrational part of Hamiltonian in the crude representation

$$H_B = \sum_r \hbar\omega_r (\bar{b}_r^+ \bar{b}_r + \tfrac{1}{2}) \qquad (3.1)$$

which can be divided onto kinetic and potential parts

$$H_B = E_{kin}(\bar{\bar{B}}) + E_{pot}(\bar{B}). \tag{3.2}$$

Potential energy is defined through the quadratic part of internuclear potential plus some additive term representing the selfconsistent influence of electron-nuclear potential

$$E_{pot} = E^{(2)}_{NN}(\bar{B}) + V^{(2)}_N(\bar{B}). \tag{3.3}$$

In the adiabatic limit the values of $V^{(2)}_N$ can be evaluated simply through the coupled perturbed Hartree-Fock method [18, 19, 6] and the kinetic energy E_{kin} is identical with the kinetic energy of nuclei T_N. Now the crucial step is coming: At the case when the adiabatic approximation is not valid it is necessary to incorporate the new additive kinetic term originating from the kinetic energy of electrons. The resulting kinetic energy of vibrational system has the form [8, 9]

$$E_{kin} = T_N(\bar{\bar{B}}) + W^{(2)}_N(\bar{\bar{B}}). \tag{3.4}$$

On the contrary to the Fröhlich conception of frequency renormalization [2] we attempt to construct directly the final vibrational frequencies in a maximal selfconsistent way. The resulting Hamiltonian (2.4) has than the form

$$H = H_A + H_B \tag{3.5}$$

where

$$H_A = E_{NN}(\bar{B}) - E^{(2)}_{NN}(\bar{B}) - V^{(2)}_N(\bar{B}) - W^{(2)}_N(\bar{\bar{B}}) + \sum_{\mathrm{P,Q}} h_{\mathrm{PQ}}(\bar{B})\, \bar{a}^+_P \bar{a}_Q \tag{3.6}$$
$$+ \frac{1}{2} \sum_{\mathrm{P,Q,R,S}} v^0_{\mathrm{PQRS}} \bar{a}^+_P \bar{a}^+_Q \bar{a}_S \bar{a}_R$$

Further we will follow the Fröhlich's conception of unitary transformation with $S(Q, P)$ given in [2]

$$H' = \mathrm{e}^{-S(Q,P)}\, H\, \mathrm{e}^{S(Q,P)} \tag{3.7}$$

Since the operators Q, P do not commute some complications arise [20]. In order to remove them we will use instead (3.7) the alternative form

$$H' = \mathrm{e}^{-S_2(P)}\, \mathrm{e}^{-S_1(Q)} H\, \mathrm{e}^{S_1(Q)}\, \mathrm{e}^{S_2(P)} \tag{3.8}$$

The first transformation with generator S_1 is equivalent to the adiabatic quasiparticle transformation from the crude into the adiabatic representation, defined through new quasiparticles in adiabatic representation with double bar

$$\bar{a}_P = \sum_Q c_{PQ}(\bar{\bar{B}})\, \bar{\bar{a}}_Q \tag{3.9}$$

$$\bar{b}_r = \bar{\bar{b}}_r + \sum_{P,Q} d_{rPQ}(\bar{\bar{B}})\, \bar{\bar{a}}^+_P \bar{\bar{a}}_Q \tag{3.10}$$

where the operators $c_{PQ}(\bar{\bar{B}})$ and $d_{rPQ}(\bar{\bar{B}})$ are defined trough their Taylor expansions and are limited through the unitarity condition

$$\sum_R c_{PR} c_{QR}^+ = \delta_{PQ} \tag{3.11}$$

$$d_{rPQ} = \sum_R c_{RP}^+ [\bar{b}_r, c_{RQ}] \tag{3.12}$$

The second transformation with generator S_2 is equivalent to the nonadiabatic transformation from the adiabatic representation into the final one which we shall call "diabatic" [15, 8]. This representation is defined through new quasiparticles denoted simply without bar

$$\bar{\bar{a}}_P = \sum_Q \tilde{c}_{PQ}(\tilde{B})\, a_Q \tag{3.13}$$

$$\bar{b}_r = b_r + \sum_{P,Q} \tilde{d}_{rPQ}(\tilde{B})\, a_P^+ a_Q \tag{3.14}$$

where the operators $\tilde{c}_{PQ}(\tilde{B})$ and $\tilde{d}_{rPQ}(\tilde{B})$ are defined through their Taylor expansions and are limited through the unitarity condition

$$\sum_R \tilde{c}_{PR} \tilde{c}_{QR}^+ = \delta_{PQ} \tag{3.15}$$

$$\tilde{d}_{rPQ} = \sum_R \tilde{c}_{RP}^+ [b_r, \tilde{c}_{RQ}] \tag{3.16}$$

The form of the transformed Hamiltonian is very complex and we omit it here. The detailed derivations and results are described in our previous papers [8, 9]. We demonstrate now only the main steps of treatment of the transformed Hamiltonian in the diabatic representation.

At the first stage we will apply the Wick's theorem as it is standardly defined in quantum chemistry [21] i.e. with respect to Fermi vacuum. We have used the notation P, Q, R. S, ... for arbitrary spinorbitals and now we introduce the notation A, B, C, D for virtual spinorbitals and I, J, K, L for occupied spinorbitals. For one-fermion terms the Wick's theorem results in

$$\sum_{P,Q} \lambda_{PQ} a_P^+ a_Q = \sum_{P,Q} \lambda_{PQ} N[a_P^+ a_Q] + \sum_I \lambda_{II} \tag{3.17}$$

and for two-fermion terms

$$\sum_{P,Q,R,S} \mu_{PQRS} a_P^+ a_Q^+ a_S a_R = \sum_{P,Q,R,S} \mu_{PQRS} N[a_P^+ a_Q^+ a_S a_R] \tag{3.18}$$

$$+ \sum_{P,Q,I} (\mu_{PIQI} + \mu_{IPIQ} - \mu_{PIIQ} - \mu_{IPQI})\, N[a_P^+ a_Q] + \sum_{I,J} (\mu_{IJIJ} - \mu_{IJJI}) .$$

Analogical relations hold for three-fermion terms which also occur in the transformed Hamiltonian. After complex application of the Wick's theorem on all fermion operators we get the normal form of the Hamiltonian in the diabatic representation.

At the second stage we perform the very well known Moller-Plesset splitting [22] of the diabatic Hamiltonian, i.e. the diagonalization of one-fermion terms in the normal form according to the formula [8, 9]

$$\sum_{P,Q} \lambda_{PQ} N[a_P^+ a_Q] \to \sum_P \Lambda_P N[a_P^+ a_P] . \tag{3.19}$$

It is enough to perform the diagonalization (3.19) in the zeroth and first orders of boson Taylor expansion. The result of the zeroth order diagonalization is the one-particle fermion spectrum. The general analytical diagonalization of diabatic Hamiltonian is very complex and therefore we limit ourselves to the diagonalization of some part of the diabatic Hamiltonian which is identical with the Hamiltonian in the crude representation. As it will be seen later, the fermionic part of the diabatic Hamiltonian is expressed as a sum of the fermionic part of the crude Hamiltonian and some other additive terms. The partial diagonalization is justified through the translational symmetry that in solid crystals holds, i.e. it implies the complete diagonalization automatically. This partial diagonalization is equivalent to Hartree-Fock diagonalization of the crude Hamiltonian

$$f_{PQ}^0 = h_{PQ}^0 + \sum_I (v_{PIQI}^0 - v_{PIIQ}^0) = \varepsilon_P^0 \delta_{PQ} . \tag{3.20}$$

Diagonalization of the terms which contain boson operators in the first order gives us equations for the first order coefficients of the unknown operators c and $\tilde{c}$ of quasiparticle transformations (3.9) and (3.13)

$$u_{PQ}^r + (\varepsilon_P^0 - \varepsilon_Q^0) c_{PQ}^r + \sum_{A,I} [(v_{PIQA}^0 - v_{PIAQ}^0) c_{AI}^r - (v_{PAQI}^0 - v_{PAIQ}^0) c_{IA}^r] - \hbar\omega_r \tilde{c}_{PQ}^r = \varepsilon_P^r \delta_{PQ} \tag{3.21}$$

$$(\varepsilon_P^0 - \varepsilon_Q^0) \tilde{c}_{PQ}^r + \sum_{A,I} [(v_{PIQA}^0 - v_{PIAQ}^0) \tilde{c}_{AI}^r - (v_{PAQI}^0 - v_{PAIQ}^0) \tilde{c}_{IA}^r] - \hbar\omega_r c_{PQ}^r = \tilde{\varepsilon}_P^r \delta_{PQ} . \tag{3.22}$$

At the third stage all bosonic terms up to the second order of the Taylor expansion not containing any fermion operator are set equal to zero [8, 9]. In the first order we get the equations for equilibrium nuclear positions. Their exact derivation in the diabatic representation would require some information about the third order (anharmonicities) and is very complex. In what follows it is omitted here because the analytical result will not be important for our further considerations. The set of equations in the second order of the Taylor expansion results in the ab-initio selfconsistent equations for vibrational frequencies ω_r, namely for unknown potential and kinetic matrix elements (3.3) and (3.4)

$$V_N^{rs} = \sum_I u_{II}^{rs} + \sum_{A,I} [(u_{IA}^r + \hbar\omega_r \tilde{c}_{IA}^r) c_{AI}^s + (u_{IA}^s + \hbar\omega_s \tilde{c}_{IA}^s) c_{AI}^r] \tag{3.23}$$

$$W_N^{rs} = 2\hbar\omega_r \sum_{A,I} c_{AI}^r \tilde{c}_{IA}^s \tag{3.24}$$

We can look at equations (3.21 – 24) as the generalization of the CPHF (coupled perturbed Hartree-Fock) equations for the case of nonadiabatic representation, i.e. the case of break-down of the Born-Oppenheimer approximation [8].

Comparison of our preceding consideration and of the standard ideal prevailing in the description of superconductors leads to the first historical critical point: The frequencies ω and one-particle energies ε are not understood in our approach as independent phonon and electron fields of metallic conductive phase with continuous spectra where the mutual interaction causes the phase change into the superconducting state (as it was drafted by Fröhlich's and BCS papers). Our formulation supposes the derivation of strictly selfconsistent frequencies ω under special conditions when the Born-Oppenheimer approximation does not hold and therefore the vibrational kinetic energy has to contain new additive kinetic energy term (3.24) together with the kinetic nuclear one. A similar treatment as applied in the calculation of the selfconsistent values of frequencies ω has to be applied also in the calculation of one-particle energies ε. Although the Hartree-Fock diagonalization procedure (3.20) was performed from strategical reasons (in order to get a reasonable analytical solution) only for unperturbed energies ε^0, it is not a case of standard perturbation and/or renormalization procedure. The energies ε^0 are "unperturbed" in a very special way since the diagonalization (3.20) is performed simultaneously with the optimization of equilibrium nuclear positions which are dependent on nonadiabatic one-particle energy corrections Δε. As will be seen later, the nonadiabatic corrections Δε will have feed-back influence on ε^0 to high extend so that energies ε^0 will not represent the continuous metallic band spectrum. It will lead to new qualitative understanding of superconductivity.

IV. Fermion Hamiltonian in diabatic representation

The resulting fermionic part of diabatic Hamiltonian can be written in the form

$$H_F = H_{F(crude)} + \Delta H_F \tag{4.1}$$

where $H_{F(crude)}$ stands for the fermionic part of Hamiltonian in the crude representation and ΔH_F denotes the terms arising after switching on the electron-phonon interaction. For calculation details, see our precedent paper [9].

The Hamiltonian $H_{F(crude)}$ consists of three parts

$$H_{F(crude)} = H^0_{F(crude)} + H'_{F(crude)} + H''_{F(crude)} \tag{4.2}$$

where

$$H^0_{F(crude)} = E^0_{NN} + E^0_{SCF} = E^0_{NN} + \sum_I h^0_{II} + \frac{1}{2}\sum_{I,J}(v^0_{IJIJ} - v^0_{IJJI}) \tag{4.3}$$

is the SCF energy of "crude" electronic system,

$$H'_{F(crude)} = \sum_P \varepsilon_P^0 N[a_P^+ a_P] \tag{4.4}$$

is one-electron spectrum as a result of diagonalization (3.20) and

$$H''_{F(crude)} = \frac{1}{2} \sum_{P,Q,R,S} v_{PQRS}^0 N[a_P^+ a_Q^+ a_S a_R] \tag{4.5}$$

is a residual two-electron Coulomb interaction in a normal product form.

The most interesting is the Hamiltonian ΔH_F consisting of four parts. Because the three-fermion terms arising in the diabatic Hamiltonian are irrelevant for the mechanism of superconductivity we limit the study only to the three important parts:

$$\Delta H_F = \Delta H_F^0 + \Delta H'_F + \Delta H''_F \tag{4.6}$$

where in the notation of quasiparticle transformation coefficients c and $\tilde{c}$

$$\Delta H_F^0 = \sum_{A,I,r} \hbar\omega_r \left(|c_{AI}^r|^2 - |\tilde{c}_{AI}^r|^2 \right) \tag{4.7}$$

is the correction to the ground state energy. After neglecting of Coulomb interaction in equations (3.21, 22) (the procedure usually used in solids) we get the analytical expressions for the first order coefficients c and $\tilde{c}$

$$c_{PQ}^r = u_{PQ}^r \frac{\varepsilon_P^0 - \varepsilon_Q^0}{(\hbar\omega_r)^2 - (\varepsilon_P^0 - \varepsilon_Q^0)^2} \tag{4.8}$$

$$\tilde{c}_{PQ}^r = u_{PQ}^r \frac{\hbar\omega_r}{(\hbar\omega_r)^2 - (\varepsilon_P^0 - \varepsilon_Q^0)^2} \tag{4.9}$$

Substituting (4.8, 9) into (4.7) we have

$$\Delta H_F^0 = \sum_{A,I,r} |u_{AI}^r|^2 \frac{\hbar\omega_r}{(\varepsilon_A^0 - \varepsilon_I^0)^2 - (\hbar\omega_r)^2} \tag{4.10}$$

or equivalently rewritten in solid state notation ($r \to \mathbf{q}$; $I \to \mathbf{k}$, σ with occupation factor $f_\mathbf{k}$; A $\to \mathbf{k}'$, σ' with occupation factor $1 - f_{\mathbf{k}'}$; $\varepsilon_I^0 \to \varepsilon_\mathbf{k}$; $\varepsilon_A^0 \to \varepsilon_{\mathbf{k}'}$; $u_{AI}^r \to u_{\mathbf{k}'\mathbf{k}}^\mathbf{q} = u^{\mathbf{k}'-\mathbf{k}} = u^\mathbf{q}$)

$$\Delta H_F^0 = 2 \sum_{\mathbf{k},\mathbf{k}'} |u^{\mathbf{k}-\mathbf{k}'}|^2 f_\mathbf{k}(1 - f_{\mathbf{k}'}) \frac{\hbar\omega_{\mathbf{k}'-\mathbf{k}}}{(\varepsilon_{\mathbf{k}'} - \varepsilon_\mathbf{k})^2 - (\hbar\omega_{\mathbf{k}'-\mathbf{k}})^2} \tag{4.11}$$

This formula was derived by Fröhlich by means of the second order perturbation theory [1] and rederived by means of the unitary transformation [2].

The correction $\Delta H'_F$, in (4.6) is more complex and therefore we select only that terms which are decisive for superconductivity [9]

$$\Delta H'_F = \sum_{P,r} \hbar\omega_r \Big[\sum_A \big(|c^r_{PA}|^2 - |\tilde{c}^r_{PA}|^2 \big) - \sum_I \big(|c^r_{PI}|^2 - |\tilde{c}^r_{PI}|^2 \big) \Big] N\big[a^+_P a_P\big] \quad (4.12a)$$

$$+ \sum_{P,R,r} \big[(\varepsilon^0_P - \varepsilon^0_R) \big(|c^r_{PR}|^2 + |\tilde{c}^r_{PR}|^2 \big) - 2\hbar\omega_r \, \mathrm{Re}(\tilde{c}^r_{PR} c^r_{PR}{}^*) \big] N\big[a^+_P a_P\big] \quad (4.12b)$$

The first part (4.12a) is of a pure one-fermion origin but in the complete derivation [9] has a nondiagonal form. The use of the diagonal form in (4.12a) is justified only in solids where the translational symmetry holds. The second part (4.12b) is automatically diagonal but is not of a pure one-fermion origin. It is a vacuum value of type $\langle 0 | B_r B_s | 0 \rangle$ and/or $\langle 0 | \tilde{B}_r \tilde{B}_s | 0 \rangle$ of the mixed fermion-boson terms, where the bosonic part is of the quadratic form of coordinate and/or momentum operators. The substitution for c and $\tilde{c}$ in (4.12a) and (4.12b) gives us

$$\Delta H'_F = \sum_{P,r} \hbar\omega_r \left(\sum_A \frac{|u^r_{PA}|^2}{(\varepsilon^0_P - \varepsilon^0_A)^2 - (\hbar\omega_r)^2} - \sum_I \frac{|u^r_{PI}|^2}{(\varepsilon^0_P - \varepsilon^0_I)^2 - (\hbar\omega_r)^2} \right) N\big[a^+_P a_P\big] \quad (4.13a)$$

$$+ \sum_{P,R,r} |u^r_{PR}|^2 \frac{\varepsilon^0_P - \varepsilon^0_R}{(\varepsilon^0_P - \varepsilon^0_R)^2 - (\hbar\omega_r)^2} N\big[a^+_P a_P\big] \quad (4.13b)$$

$$= \sum_{P,r} \left(\sum_A \frac{|u^r_{PA}|^2}{\varepsilon^0_P - \varepsilon^0_A - \hbar\omega_r} + \sum_I \frac{|u^r_{PI}|^2}{\varepsilon^0_P - \varepsilon^0_I + \hbar\omega_r} \right) N\big[a^+_P a_P\big] \quad (4.13)$$

and in the solid state notation (another redistribution (4.14a) is not identical with (4.13a))

$$\Delta H'_F = \sum_{\mathbf{k},\mathbf{q},\sigma} |u^{\mathbf{q}}|^2 \frac{1}{\varepsilon^0_{\mathbf{k}} - \varepsilon^0_{\mathbf{k}-\mathbf{q}} - \hbar\omega_{\mathbf{q}}} N\big[a^+_{\mathbf{k},\sigma} a_{\mathbf{k},\sigma}\big] \quad (4.14a)$$

$$-2 \sum_{\mathbf{k},\mathbf{q},\sigma} |u^{\mathbf{q}}|^2 f_{\mathbf{k}-\mathbf{q}} \frac{\hbar\omega_{\mathbf{q}}}{(\varepsilon^0_{\mathbf{k}} - \varepsilon^0_{\mathbf{k}-\mathbf{q}})^2 - (\hbar\omega_{\mathbf{q}})^2} N\big[a^+_{\mathbf{k},\sigma} a_{\mathbf{k},\sigma}\big] \quad (4.14b)$$

The corrections (4.14a) to the electron energies $\varepsilon_{\mathbf{k}}$ represent the well-known quasiparticles — polarons which were originally derived on the basis of Lee-Low-Pines transformation [23]. Now it is clear how the polarons can be directly derived from the diabatic representation. Whereas the term (4.14a) concerns only individual polarons, the diabatic representation yields also the correction (4.14b) which must be added to the polaron energies. Put differently, every polaron "feels" an effective field of other polarons, ergo, dressed polarons are created.

From the correction $\Delta H''_F$ in (4.6) we select only the dominant term

$$\Delta H''_F = \sum_{P,Q,R,S,r} \hbar\omega_r (c^r_{PR} c^r_{SQ}{}^* - \tilde{c}^r_{PR} \tilde{c}^r_{SQ}{}^*) \, N\big[a^+_P a^+_Q a_S a_R\big] \quad (4.15)$$

In solid state notation this term reads

$$\Delta H''_F = \sum_{\mathbf{k},\mathbf{k}',\mathbf{q},\sigma,\sigma'} \frac{|u^{\mathbf{q}}|^2 \hbar\omega_{\mathbf{q}}\left[(\varepsilon_{\mathbf{k}+\mathbf{q}}-\varepsilon_{\mathbf{k}})(\varepsilon_{\mathbf{k}'+\mathbf{q}}-\varepsilon_{\mathbf{k}'})-(\hbar\omega_{\mathbf{q}})^2\right]}{\left[(\varepsilon_{\mathbf{k}+\mathbf{q}}-\varepsilon_{\mathbf{k}})^2-(\hbar\omega_{\mathbf{q}})^2\right]\left[(\varepsilon_{\mathbf{k}'+\mathbf{q}}-\varepsilon_{\mathbf{k}'})^2-(\hbar\omega_{\mathbf{q}})^2\right]} N\left[a^+_{\mathbf{k}+\mathbf{q},\sigma}a^+_{\mathbf{k}',\sigma'}a_{\mathbf{k}'+\mathbf{q},\sigma}a_{\mathbf{k},\sigma}\right] \tag{4.16}$$

If we compare (4.16) with the Fröhlich result [2] for effective two-electron interaction

$$\Delta H''_{F(Fr)} = \sum_{\mathbf{k},\mathbf{k}',\mathbf{q},\sigma,\sigma'} |u^{\mathbf{q}}|^2 \frac{\hbar\omega_{\mathbf{q}}}{(\varepsilon_{\mathbf{k}+\mathbf{q}}-\varepsilon_{\mathbf{k}})^2-(\hbar\omega_{\mathbf{q}})^2} a^+_{\mathbf{k}+\mathbf{q},\sigma}a^+_{\mathbf{k}',\sigma'}a_{\mathbf{k}'+\mathbf{q},\sigma'}a_{\mathbf{k},\sigma} \tag{4.17}$$

we see the little difference caused by application of various transformations (3.7) and (3.8). The first remarkable consequence of this fact is the symmetrical relation between indices $\mathbf{k}$ and $\mathbf{k}'$ in (4.16) that is not fulfilled in the expression (4.17). Wagner was the first who pointed out this problem in the Fröhlich's expression and therefore proposed the effective two-electron interaction gained on the basis of pure adiabatic transformation with the generator $S_I(Q)$ [20]. He also derived the reduced form of the effective Hamiltonian and the result was the fully attractive expression for all Cooper pairs in the whole region of electron spectrum. The Fröhlich's reduced form of the Hamiltonian

$$\Delta H_{red(Fr)} = 2\sum_{\mathbf{k},\mathbf{k}'} |u^{\mathbf{k}'-\mathbf{k}}|^2 \frac{\hbar\omega_{\mathbf{k}'-\mathbf{k}}}{(\varepsilon_{\mathbf{k}'}-\varepsilon_{\mathbf{k}})^2-(\hbar\omega_{\mathbf{k}'-\mathbf{k}})^2} a^+_{\mathbf{k}\uparrow}a^+_{-\mathbf{k}'\downarrow}a_{-\mathbf{k}\downarrow}a_{\mathbf{k}\uparrow} \tag{4.18}$$

has both attractive and repulsive parts but the reduced form of our diabatic Hamiltonian (4.16)

$$\Delta H_{red(diab)} = -2\sum_{\mathbf{k},\mathbf{k}'} |u^{\mathbf{k}'-\mathbf{k}}|^2 \frac{\hbar\omega_{\mathbf{k}'-\mathbf{k}}\left[(\varepsilon_{\mathbf{k}'}-\varepsilon_{\mathbf{k}})^2+(\hbar\omega_{\mathbf{k}'-\mathbf{k}})^2\right]}{\left[(\varepsilon_{\mathbf{k}'}-\varepsilon_{\mathbf{k}})^2-(\hbar\omega_{\mathbf{k}'-\mathbf{k}})^2\right]^2} a^+_{\mathbf{k}\uparrow}a^+_{-\mathbf{k}'\downarrow}a_{-\mathbf{k}\downarrow}a_{\mathbf{k}\uparrow} \tag{4.19}$$

is fully attractive similarly as Wagner's expression. The advantage of our diabatic Hamiltonian $\Delta H''_F$ (4.16) lies in the fact that in the adiabatic limit $\left(\frac{\hbar\omega}{\Delta\varepsilon} \to 0\right)$ it coincides with the Wagner's adiabatic Hamiltonian and differs from Fröhlich's Hamiltonian (4.17). On the contrary, in the opposite limit $\left(\frac{\Delta\varepsilon}{\hbar\omega} \to 0\right)$ where the Wagner's adiabatic conception can no longer be applied, it coincides with the Fröhlich's Hamiltonian.

Now we proceed to the second historical critical point: The most important result of this section is the derivation of total energy decrease ΔH^0_F (4.10) after inclusion of electron-phonon interaction. This formula is identical with (4.11) derived by Fröhlich by means of the second order perturbation theory [1] and rederived on the basis of the canonical transformation [2]. The expression ΔH^0_F is really fundamental for true understanding of superconductivity although it was, in the further historical development of the theory of superconductivity, forgotten altogether. The question: Why this could have happened? naturally comes to our mind. If we will watch the following Fröhlich's treatment of the expression ΔH^0_F (4.11) we will see that he tried to find the minimum of ΔH^0_F by the variational

methods where the occupation factors $f_{\mathbf{k}}$ and $f_{\mathbf{k}'}$ were the variable parameters. He got the minimum for certain values of $f_{\mathbf{k}}$ and $f_{\mathbf{k}'}$ but this treatment is not able to give the experimentally detected gap and, consequently, the majority of physical properties of superconductors. Therefore this first Fröhlich's approach was criticized and the mistake was attributed to the use of the perturbation theory. According to the BCS theory the gap has to depend on the interaction V through the expression $e^{-1/V}$ which can not be expanded into the Taylor expansion and therefore the theory of superconductivity has to be constructed in a non-perturbative way. It is a misleading argument. Fröhlich rederived his formula by canonical transformation, i.e. by a formally non-perturbative way. The historical mistake, in our opinion, lies in variational treatment! The function of variable parameters $f_{\mathbf{k}}$ and $f_{\mathbf{k}'}$ can have the minimum not only in the points where the first order derivatives equal zero but also in the boundary points. Fröhlich, unfortunately, did not consider this alternatives but, as argued bellow, it turns out to be the key to the secret of mechanism of superconductivity. We have new kind of equations where the parameters $f_{\mathbf{k}}$, $f_{\mathbf{k}'}$ have discrete values 0 or 1. In our quantum chemical notation we have to solve the problem of how to devide the general spinorbitals (P) into the occupied ones (I) and virtual ones (A) what resembles the problem of Diophantic equations (equations with the integer variable parameters). This is the consequence of the breakdown of the Born-Oppenheimer approximation where we have to take into account the redefinition of Fermi vacuum at the transition from metallic to superconducting state. The redefinition of the Fermi vacuum is immediately connected with the redistribution of occupied and unoccupied states near the Fermi surface.

V. Is superconductivity based on one-particle or two-particle mechanism?

Let us continue in the preceding considerations of the division of spinorbitals near the Fermi surface into the occupied and virtual ones. In order to get the required maximum ground state energy lowering according to the formula (4.10) such division of states is necessary that for the majority of pairs of occupied and virtual states I and A the inequality $|\varepsilon_A^0 - \varepsilon_I^0| < \hbar\omega_r$ is fulfilled. We can reformulate this requirement in a stronger form in the two following statements: Let F be the set of states near the Fermi surface.

1. For any occupied state $I \in F$ the majority of states $P \in F$ fulfilling the inequality $|\varepsilon_P^0 - \varepsilon_I^0| < \hbar\omega_r$ are virtual.
2. For any virtual state $A \in F$ the majority of states $P \in F$ fulfilling the inequality $|\varepsilon_A^0 - \varepsilon_P^0| < \hbar\omega_r$ are occupied.

Two questions now arise. The first question: Does such a rearrangement of states causing the ground state energy lowering really exist and what is the algorithm of this rearrangement? The second question: May this rearrangement create an energy

gap? The first question will be answered in the following section VI. The second question we try to illuminate now.

Let us focus the attention at the similarity of the expressions for the ground state correction (4.7) and the first part of the one-particle expression (4.12a). If we define the symmetric matrix Ω_{PQ} as

$$\Omega_{PQ} = \Omega_{QP} = \sum_r \hbar\omega_r(|c^r_{PQ}|^2 - |\bar{c}^r_{PQ}|^2) = \sum_r \hbar\omega_r \frac{|u^r_{PQ}|^2}{(\varepsilon^0_P - \varepsilon^0_Q)^2 - (\hbar\omega_r)^2} \tag{5.1}$$

we get the very simple notation for ΔH^0_F and the first part of $\Delta H'_F$ (denoted as $\Delta H'_{F_1}$)

$$\Delta H^0_F = \sum_{A,I} \Omega_{AI} \tag{5.2}$$

$$\Delta H'_{F_1} = \sum_P \Delta\varepsilon_P N[a^+_P a_P] = \sum_P \left(\sum_A \Omega_{PA} - \sum_I \Omega_{PI}\right) N[a^+_P a_P] \tag{5.3}$$

The first above mentioned requirement implies the inequality

$$\sum_A \Omega_{IA} < \sum_J \Omega_{IJ} \tag{5.4}$$

for all occupied states $I \in F$ and the second above mentioned requirement implies the inequality

$$\sum_I \Omega_{AI} < \sum_B \Omega_{AB} \tag{5.5}$$

for all virtual states $A \in F$.

If the one-particle term $\Delta H'_F$ (4.12) is able to create the energy gap then just the first term $\Delta H'_{F_1}$ (4.12a) plays the crucial role. The second term (4.12b) can be omitted because it does not yield the qualitative change of the electronic structure at finite temperature since it does not distinguish occupied and unoccupied states. Moreover, at finite temperature its contribution will depend on boson (vibrational) excitations (multiples of (4.12b)).

For the one-particle corrections $\Delta\varepsilon_P$ defined through (5.3), using the inequalities (5.4, 5) we have the following inequalities:

$$\Delta\varepsilon_A > 0 \tag{5.6}$$

for all virtual states near the Fermi surface and

$$\Delta\varepsilon_I < 0 \tag{5.7}$$

for all occupied states near the Fermi surface. It means that the occupied states have the tendency to decrease their energies and the virtual ones to increase their energies. This implies there is a possibility of an energy gap creation between the highest occupied and the lowest unocuppied orbitals provided the required rearrangement of states near the Fermi surface exists.

Let us study the dependence of the energy gap on the temperature. Fermions in the diabatic representation naturally obey the Fermi-Dirac statistics and therefore the occupation probability for the state Q is given by the well-known expression

$$f_Q = \frac{1}{e^{(\varepsilon_Q - \mu)\, kT} + 1} \tag{5.8}$$

where ε_Q is the energy of the fermion state Q (i.e. $\varepsilon_Q^0 + \Delta\varepsilon_Q$). The expression (5.3) for $\Delta\varepsilon_P$ can be extrapolated for any nonzero temperature

$$\Delta\varepsilon_P(T) = \sum_Q \Omega_{PQ}(1 - 2f_Q) = \sum_Q \Omega_{PQ} \operatorname{tgh} \frac{\varepsilon_Q - \mu}{2kT} \tag{5.9}$$

In order to simplify the calculation let us adopt a simplified model where for any virtual state near the Fermi surface:

$$\varepsilon_A - \mu = \Delta\varepsilon(T) \tag{5.10}$$

and for any occupied state near the Fermi surface:

$$\varepsilon_I - \mu = -\Delta\varepsilon(T) \tag{5.11}$$

Then (5.9) has the form

$$\Delta\varepsilon_P(T) = \Delta\varepsilon_P(0) \operatorname{tgh} \frac{\Delta\varepsilon(T)}{2kT} \tag{5.12}$$

Further we omit the index P according to the simplifying conditions (5.10, 11) and will search for the critical temperature T_c at which the energy gap vanishes. Because the energy gap Δ_0 at the zero temperature is given as:

$$\Delta_0 = 2\,\Delta\varepsilon(0) \tag{5.13}$$

we finally get the ratio between the energy gap and the critical temperature

$$\frac{\Delta_0}{kT_c} = 4 \tag{5.14}$$

For comparison, in the BCS theory this ratio is 3,52. In relative values both the BCS and our dependence of the energy gap on the temperature are exactly the same (i.e. the dependences of $\frac{\Delta(T)}{\Delta_0}$ on $\frac{T}{T_c}$). The study of other physical properties, such as specific heat, are published in our previous paper [10].

The above mentioned results represent the one-particle mechanism of gap opening, i.e. the one-particle theory of superconductivity. The metallic spectrum is degenerate. After transition into superconducting state the degeneracy is removed. In order to remove the degeneracy of quantum mechanical systems we usually proceed in the following way: In the first step we try to remove the degeneracy on the one-particle (onedeterminantal) level. If this is not successful, we try to do it on the two-particle (multideterminantal) level. However, we have demonstrated

possibility of the one-particle mechanism at the removing of the metal degeneracy. If one-particle mechanism works then the two-particle Fröhlich interaction (4.15) will not have any qualitative influence on the gap formation, it will play the role of a correlation energy. If we realize that the energy gap in superconductors is comparable with $\hbar\omega$ and that the range of interaction of the two-particle term $\Delta H_F''$ is also limited by the value of $\hbar\omega$, then the correlation effect of $\Delta H_F''$ will not change qualitatively the picture, assuming that the one-particle mechanism exists.

On the other hand, let us suppose that the one-particle mechanism of removing the degeneracy does not exist. This will be connected to the fact that there is not possible required redistribution of states near the Fermi surface with occupation factors 0 or 1. We have only the initial metallic degenerate continuum. Then the last possibility how to remove the degeneracy would be the configuration interaction method with interaction term $\Delta H_F''$. It was just the idea of BCS [4] that the attractive two-particle interaction $\Delta H_F''$, acting among states near the Fermi surface can decrease the total energy and open an energy gap.

We have studied the influence of two-particle interaction on the removing the degeneracy in continuous spectrum [12] and our results are alarming: This degeneracy can never be removed by a two-particle mechanism. The two-particle mechanism can only decrease the total energy but does not open any gap. It represents only the correlation energy. The detailed analysis was performed in our previous paper [12] and here we are going to deal only with the principal arguments against the two-particle theories (as e.g. the BCS one).

1. We agree with the Cooper's argument that the two-particle interaction is most attractive for pairs of electrons with quasimomentum $\mathbf{k}$, $-\mathbf{k}$ (Cooper pairs). The wavefunction can be then written in the restricted multiconfigurational form

$$\psi = \sum_{M_i} c_{M_i} \prod_{\mathbf{k}\in M_i} a^+_{\mathbf{k}\uparrow} a^+_{-\mathbf{k}\downarrow} |0\rangle = \sum_{M_i} c_{M_i} D_{M_i} \tag{5.15}$$

representing the linear combination of the Slater determinants D_{M_i} where each of the determinants corresponds to some n-fold Cooper's biexcited state. However, the correct procedure, i.e. the configuration interaction method with respect to the form of the wave function (5.15), would result in a characteristic equation of infinite dimensionality since in the solid state we deal with quasicontinuum of an infinitely large number of electronic states that are characterized by the quasimomentum $\mathbf{k}$. The impossibility of the analytic as well as the numerical solution of the infinite secular problem was probably the reason why Bardeen at al. replaced the realistic wavefunction (5.15) by the trial wave function of the form

$$\psi_{BCS} = \prod_{\mathbf{k}} (u_{\mathbf{k}} + v_{\mathbf{k}} a^+_{\mathbf{k}\uparrow} a^+_{-\mathbf{k}\downarrow} |0\rangle \tag{5.16}$$

Although the BCS theory with the trial function (5.16) was very successful in calculation and interpretation of many properties of superconductors, this theory

violates the particle conservation law and is therefore of a grandcanonical character. Our first objection is: The microscopical description of superconductors can not differ from the description of other solids and has to be formulated also in the framework of microcanonical ansamble (or of the canonical one in the case of finite temperatures).

2. There are very serious discrepancies in the wave functions of excited states. The operators of elementary excitations

$$\gamma^{+}_{\mathbf{k}\uparrow} = u_{\mathbf{k}} a^{+}_{\mathbf{k}\uparrow} - v_{\mathbf{k}} a_{-\mathbf{k}\downarrow}; \qquad \gamma^{+}_{-\mathbf{k}\downarrow} = u_{\mathbf{k}} a^{+}_{-\mathbf{k}\downarrow} + v_{\mathbf{k}} a_{\mathbf{k}\uparrow} \tag{5.17}$$

yield orthogonal states to the BCS ground state, particularly for each Cooper pair $(u_{\mathbf{k}} + v_{\mathbf{k}} a^{+}_{\mathbf{k}\uparrow} a^{+}_{-\mathbf{k}\downarrow})$, two monoexcited states $a^{+}_{\mathbf{k}\uparrow}$ and $a^{+}_{-\mathbf{k}\downarrow}$ which are interpreted as free electron states, are created. Successive application of $\gamma^{+}_{\mathbf{k}\uparrow}$ and $\gamma^{+}_{-\mathbf{k}\downarrow}$ on the BCS ground state (5.16) yields also one biexcited state $(v_{\mathbf{k}} - u_{\mathbf{k}} a^{+}_{\mathbf{k}\uparrow} a^{+}_{-\mathbf{k}\downarrow})$. It is interesting to point out the difference of the BCS approach to mono- and bi-excited states. While for the study of the gap formation only the excitation of bi-excited states has been taken into account, in performing the calculation of specific heat the monoexcited states are also included to the partition sum. Let us focus our attention, however, on the following fact: any of the above mentioned excited states which results from the BCS ground state (5.16), characterizes exclusively the change of only one particular Cooper pair $(\mathbf{k}, -\mathbf{k})$. It means some kind of effective decoupling or independence of this particular Cooper pair from any other which remain unchanged after the excitation. The numerical results of CI calculations with the wave function (5.15) are, in this respect, absolutely different [12]. From the expansion coefficients of the wave function (5.15) for the ground state $\{{}^{0}c_{M_i}\}$ and for the first excited states $\{{}^{1}c_{M_i}\}$ one can see that the excitation process is a collective property which concerns all Cooper pairs, and hence, our second objection is: The statement that each excitation is accompanied by the decay of just one Cooper pair into two conducting electrons seems to be incorrect.

3. If the multiconfigurational wave function (5.15) is more "realistic" in comparison with the "artificial" BCS function (5.16), the BCS results should be rederived by means of the configuration interaction (CI) method. We have studied this problem on a finite space, i.e. we have taken into account the various but finite numbers of Cooper pairs, and then estimated the infinite limit by inductive method [12]. The results are very interesting: The possibility of obtaining an energy gap with the required dependency on the temperature is very strongly dependent on the shape of two-particle interaction (e.g. the Fröhlich type (4.18), diabatic type (4.19) or a constant type of interaction) and on the ratio of the range of this interaction and the interval of energetic scale near the Fermi surface which is included into the multiconfigurational treatment, while on the other hand the results should not be dependent on the chosen magnitude of this interval. The only reasonable results were obtained with the constant interaction of a range identical with calculated energy interval, i.e. with the same simplification as made in the BCS theory.

Moreover, also in this "ideal" case we had difficulties with the sequence of degrees of degeneracy of excited states.

Our third objection is: All the theories based on the trial function of the BCS type (5.16), no matter as sophisticated they may be and whatever surprising result they may produce, have to be investigated using a multiconfigurational wave function which obey the quantum mechanical rules. These tests indicate that for realistic types of two-particle interaction (as e.g. Fröhlich or diabatic one) it can be hardly obtained the experimentally detected temperature dependence of the gap.

4. The restricted multiconfigurational function (5.15) allows only partial multiconfigurational treatment, particularly on a subspace with the total quasimomentum equal zero. This procedure can be justified based on the argument that every subspace with a certain value of quasimomentum represents an irreducible block. It is commonly believed that after the Hamiltonian is transformed in the Fröhlich's form there is not an interaction mechanism which would cause the transition from one irreducible block to the another one. As a consequence of this fact, it is argued that the supercurrent may flow without any dissipation. According to our opinion the problem is not so simple. Let us consider three states: the first is represented by Cooper pairs $(\mathbf{k}_1, -\mathbf{k}_1), (\mathbf{k}_2, -\mathbf{k}_2), \ldots (\mathbf{k}_n, -\mathbf{k}_n)$, the second $(\mathbf{k}_1 + \delta\mathbf{k}, -\mathbf{k}_1), (\mathbf{k}_2, -\mathbf{k}_2), \ldots (\mathbf{k}_n, -\mathbf{k}_n)$ and the third $(\mathbf{k}_1, -\mathbf{k}_1 - \delta\mathbf{k}), (\mathbf{k}_2, -\mathbf{k}_2), \ldots (\mathbf{k}_n, -\mathbf{k}_n)$ where $\delta\mathbf{k}$ is some infinitesimal shift of quasimomentum. At any finite temperature the occupation of the second and third state with the same probability represents the macroscopic state with the mean total quasimomentum equal zero. Let us suppose that the Cooper pairs $(\mathbf{k}_i, -\mathbf{k}_i)$ and $(\mathbf{k}'_i, -\mathbf{k}'_i)$ are bound by the two-particle interaction $V(\mathbf{k}_i, \mathbf{k}'_i)$. Then the Cooper pairs $(\mathbf{k}_1 + \delta\mathbf{k}, -\mathbf{k}_1)$, resp. $(\mathbf{k}_1, -\mathbf{k}_1 - \delta\mathbf{k})$ are coupled with another Cooper pairs $(\mathbf{k}'_1 + \delta\mathbf{k}, -\mathbf{k}'_1)$, resp. $(\mathbf{k}'_1, -\mathbf{k}'_1 - \delta\mathbf{k})$ by a new interaction. This interaction, due to the fact that the interaction V is a countinuous function of the matrix elements of electron-phonon interaction, one-electron and vibrational energies which, again, are continuous function of quasimomentum, can be expressed in the form $V(\mathbf{k}_1, \mathbf{k}'_1) + V(\mathbf{k}_1, \mathbf{k}'_1, \delta\mathbf{k})$. It means that the local energetic minima of the irreducible blocks with quasimomentum $\delta\mathbf{k}$ and $-\delta\mathbf{k}$ are shifted above the absolute energetic minimum by some value δE. Remember that both these blocks, represented by the above mentioned second and third Cooper pairs, contribute in the case of thermodynamical equilibrium at finite temperatures, to the macroscopic state with the zero total quasimomentum. This fact gives rise to our fourth objection: Even if at finite temperatures the excitations within particular irreducible block may indicate opening of an energy gap, there exists an "escape channel" through another irreducible representations, what results in the continuous spectrum of excitations and therefore, in fact, all the theories based on two-particle interaction mechanism can never yield the required energy gap in superconductors. The two-particle interaction represents only the correlation energy which decreases the ground as well as excited state energies but can not change the conductive character of metals, and with respect to superconductivity is irrelevant.

Now we proceed to the third historical critical point: Fröhlich decleared in the last sentence of his second famous paper [2] that the theoretical treatment of superconductivity effects has to wait for the development of new methods for dealing with two-particle effective interaction. He was indeed true. Our method of dealing with the two-particle interaction is based on the use of the Wick's theorem which enable to derive the total energy correction, the one-particle corrections, and consequently to construct the one-particle theory of superconductivity where the elementary excitations are identical with selfconsistent (dressed) polarons. Fröhlich rederived only the total energy correction (this was the main result of his first famous paper [1], calculated by means of second order perturbation theory) but he did not perform the contraction leading to one-particle terms. The historical development of new methods was unfortunately directed in a quite different way. The two-particle interaction was directly incorporated in a multiconfigurational treatment and the BCS model [4] arose on the conception of Cooper pairs mutually bound by this two-particle interaction term.

There are three fundamental differences between our one-particle theory and the commonly accepted two-particle theories:

a) *The one-particle description of the superconducting state is microcanonical (or canonical at finite temperatures) similarly as the description of any other solids whereas the two-particle description based on the BCS trial function is grand-canonical.*
b) *The one-particle theory operates with one-determinantal wave functions whereas the two-particle theory is multiconfigurational in principle.*
c) *The one-particle theory leads to the conception of the fully occupied valence band and of the empty conducting band at zero temperature i.e. to the description characteristic for semiconductors or insulators, and the excitations from the valence band into the conducting one are represented by excitations of single selfconsistent polarons, whereas the two-particle theory leads to the conception of Cooper pairs Bose condensation where the excitation process is connected with the decay of Cooper pairs in the form of free electrons in a conduction band.*

We have shown that the Cooper pairs conception based on the two-particle mechanism can represent only the calculation of correlation energy of conductors and this is irrelevant for transition to superconducting state.

VI. Transition in superconducting state

We will try to answer the first question from the preceding section which concerns the algorithm of rearrangement of states near the Fermi surface producing the ground state energy lowering and an energy gap. We consider the solid as a giant molecule. The degeneracy of molecular orbitals leads to the Jahn-Teller

effect [14] which is characterized by molecular symmetry lowering and the degeneracy removal. We are of the opinion that the same Jahn-Teller effect is the cause of transition from the metallic into the superconducting state. It means that the energy gap of superconductors is a consequence of the Jahn-Teller degeneracy removal of continuous spectra of metals. Moreover, the transition from the metallic into the superconducting state has to be connected with the Jahn-Teller change of equilibrium position of nuclei and the lowering of crystalline symmetry [11].

The initial position is illustrated on Figure 1. It represents the symmetric lattice of metal where, in the tight bond approximation, the highest valence orbitals occupied by one electron are transformed into the half-filled conducting band. The total energy of the system is denoted as E_1.

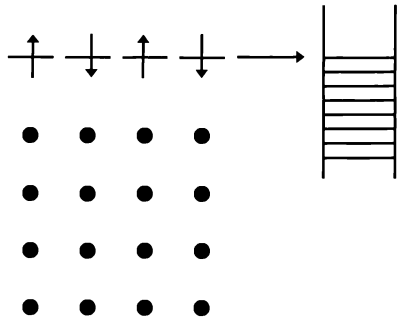

Fig. 1
The initial conducting band and the symmetric lattice of metal.

The first intermediate state is illustrated on Figure 2. It represents the symmetry lowering of the initial lattice. It is reasonable to suppose that the Jahn-Teller effect is manifested through the principle of minimal possible symmetry lowering, i.e. that from initial lattice two sublattices arise. This symmetry lowering is characterized by only one parameter — the displacement between two sublattices. As a first consequence the half-filled metal band splits into two overlapping bands. Let us underline that this intermediate state is calculated on the level of crude representation, i.e. in the representation of some fixed (even though displaced) position of nuclei without inclusion of electron-phonon interaction. The total energy of this state E_2 is greater than the energy of initial state E_1. The second consequence, each acoustic phonon branch is divided into two branches: one acoustical and one optical. In order to enable the transition into superconducting state, as it will be seen later, the magnitude of the band overlap has to be smaller than the maximum vibrational energy $\hbar\omega_{max}$. The symmetry lowering, hovewer, does not automatically lead to the fulfillment of this condition. Therefore there must be a mechanism which will "press" each of the new arisen two bands. This mechanism may have the origin — as argued bellow — in a new type of

alternating bonds which we call "nonadiabatic". The pairs of nuclei (ions) will be coupled by this bond formed by two valence electrons. In the tight bond approximation the valence orbitals occupied by two electrons binding two ions together will, in terms of the solid state language, become "the residents" of the first band and the first excited unoccupied orbitals will end up in the second band. Because these bands overlap to some extend the first one is partially unoccupied and the second one is partially occupied.

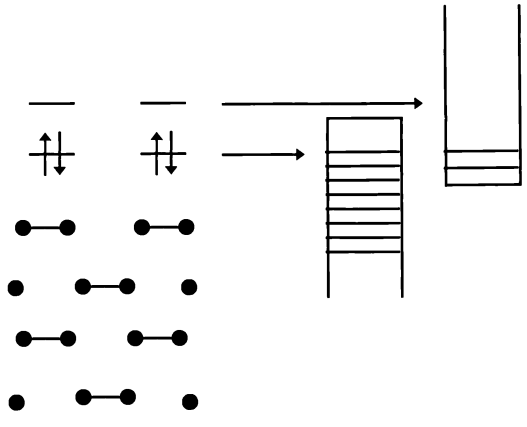

Fig. 2
The first intermediate state: Creation of two bands after the symmetry lowering of the lattice in the crude representation. Pairing of the neighboring atoms by the "nonadiabatic" chemical bond.

The second intermediate state is illustrated in Figure 3, where the redefinition of Fermi vacuum is shown. The first (valence) band is entirely filled and the second (conducting) band is completely evacuated. This second intermediate state determines the final distribution of "unperturbed" electronic states which are either

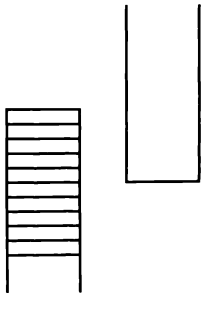

Fig. 3
The second intermediate state: Redefinition of Fermi vacuum.

occupied (I) or virtual (A). It is apparent now, as it was mentioned at the end of the section III, that the spectrum of "unperturbed" electronic energies ε_P^0 is not continuous any more in contrast to the continuous spectrum of conducting bands of metals. The total energy of this intermediate state is E_3 which is, of course, greater than the energy E_2 of the first intermediate one.

The transition in the final superconducting state is illustrated in Figure 4. After inclusion of electron-phonon interaction, i.e. after introduction of the diabatic representation, both bands are splitted and the energy gap is created. The final superconducting state is stable provided its total energy E_4 is smaller than the energy E_1 of the initial conducting state. The process of the gap formation is illustrated on the example of four representative states $J_1 - J_4$ belonging to the valence band. Using the relations (5.1) for the matrix Ω and (5.3) for the one-particle corrections $\Delta\varepsilon_P$ we find for the state J_1 lying on the top of the valence band:

$$\sum_I \Omega_{J_1 I} = \sum_{A;\varepsilon_A^0 > \varepsilon_{J_1}^0} \Omega_{J_1 A} = 0 \tag{6.1a}$$

$$\sum_{A;\varepsilon_A^0 < \varepsilon_{J_1}^0} \Omega_{J_1 A} < 0 \tag{6.1b}$$

It means that the correction $\Delta\varepsilon_{J_1}$ will be negative and the energy of the state J_1 will be lowered. For the state J_2 lying in the middle of the overlap it holds:

$$\sum_{I;\varepsilon_I^0 < \varepsilon_{J_2}^0} \Omega_{J_2 I} = \sum_{A;\varepsilon_A^0 > \varepsilon_{J_2}^0} \Omega_{J_2 A} = 0 \tag{6.2a}$$

$$\sum_{A;\varepsilon_A^0 < \varepsilon_{J_2}^0} \Omega_{J_2 A} < \sum_{I;\varepsilon_I^0 > \varepsilon_{J_2}^0} \Omega_{J_2 I} < 0 \tag{6.2b}$$

The first inequality in (6.2b) is caused by an important fact, in particular, of interband vibrational frequencies being greater than the innerband ones. It is a consequence of splitting of acoustical branches and creation of optical ones which have higher frequencies in dependence on the strength of nonadiabatic bond between the pairs of nuclei. The exact calculations of the vibrational frequencies have to be based on the solution of ab-initio equations (3.23, 24). Therefore the resulting correction $\Delta\varepsilon_{J_2}$ is negative but in absolute value is not as big as $\Delta\varepsilon_{J_1}$. For the state J_3 lying in the same position as the bottom of the conducting band it holds:

$$\sum_{I;\varepsilon_I^0 < \varepsilon_{J_3}^0} \Omega_{J_3 I} = \sum_A \Omega_{J_3 A} = 0 \tag{6.3a}$$

$$\sum_{I;\varepsilon_I^0 > \varepsilon_{J_3}^0} \Omega_{J_3 I} < 0 \tag{6.3b}$$

The correction $\Delta\varepsilon_{J_3}$ is positive, but in absolute value it is smaller than the correction $\Delta\varepsilon_{J_1}$ because the expression (6.3b) contains innerband frequencies which

are smaller than the frequencies entering into the expression (6.1b). Finally, for the state J_4 lying far bellow the Fermi surface it holds:

$$\sum_I \Omega_{J_4 I} = \sum_A \Omega_{J_4 A} = 0 \tag{6.4}$$

It means that the correction $\Delta\varepsilon_{J_4}$ equals zero. Fully analogous procedure as the one shown for the valence band holds also for the conducting band.

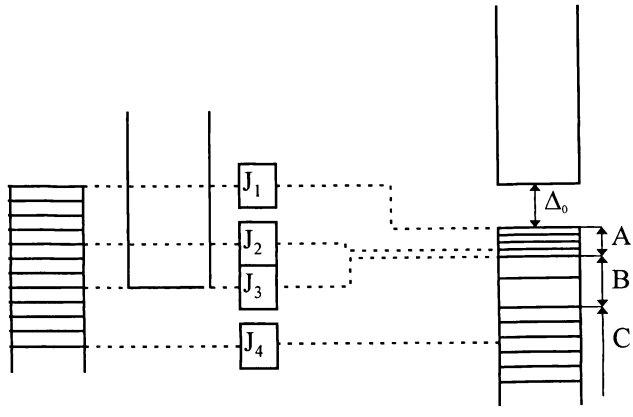

Fig. 4
Transition in the superconducting state.

Summarizing the above described process of the gap formation, we emphasize two fundamental conditions for the transition into superconducting state:

I. Lowering the symmetry of crystalline lattice and splitting the original conducting band onto two bands a nonadiabatic alternating bonds of adequate strength between the pairs of atoms have to be created in order the overlap of these two bands in the crude representation to be smaller than $\hbar\omega_{\max}$.

II. Including the electron-phonon interaction in the diabatic representation the resulting energy have to be smaller than the energy of the initial conducting state.

?We will mention two decisive recent experiments which support our theory. The first one concerns the photoemission spectra of the high-T_c superconductors in the normal and superconducting states [24–26]. The existence of the dip and the peak bellow the Fermi surface (see Figure 5) can not be understood using any microscopic theory of the BCS type. We have performed calculations based on the BCS theory and on our theory [27] and the results are remarkable. While a peak formation can be interpreted by the BCS theory, the dip formation is unexpected and the BCS theory fails at the description of the photoemission spectra. Even the most sophisticated versions of the BCS theory fail in their attempts. The recent analysis of this problem based on the Nambu-Eliashberg formalism [28] indicates serious contradictions between the standard accepted theoretical ideas and experimental results [27].

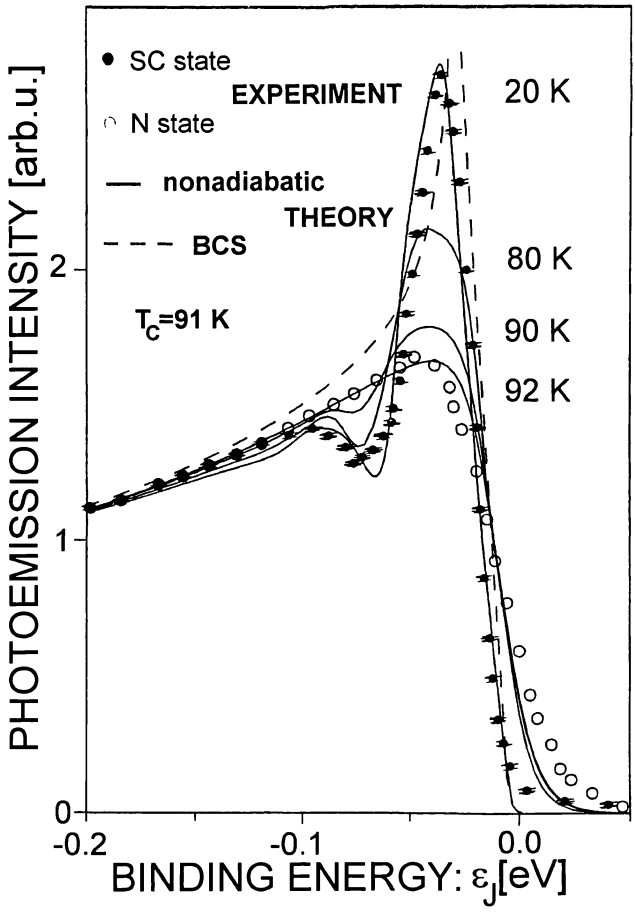

Fig. 5
Simulation of the photoemission spectra of $Bi_2Sr_2CaCu_2O_{8+\delta}$, and comparison with the experiment [26] and the BCS theory.

Comparing Figures 4 and 5 very interesting connections can be observed. The peak is caused by the high concentration of states near the top of the valence band. This region is denoted by *A*. On the contrary, the dip is caused by the low density of states in the region *B*. A standard form of the spectral line at higher binding energies in the superconducting state is then identical with a spectral line form corresponding to the normal state. This is, obviously, due to unchanged density of states in the region *C* which remains unchanged after the transition into the superconducting state. Let us stress that the fact of the highest density of states in a small region *A* justifies the simplifications (5.10, 11) used in the calculations of thermodynamical properties of superconductors in order to get the simple analytical relation for the temperature dependence of the gap.

The second important experiment concerns the measurements of relevant lifetimes of correlated states close to the critical temperature T_c [29]. According to the theories based on the mean field Cooper pair conception (e.g. BCS theory), after the break-down of the last Cooper pair no correlated state can exist at all above the T_c [30]. On the contrary, in our theory the reaching of the critical temperature where the gap is zero need not imply the immediate annihilation of the Jahn-Teller like distorted state consisting of two sublattices that is responsible for the existence of correlated states above T_c. The transition in the normal geometrical rearrangement may pass at some temperature greater than T_c.

Now we proceed to the fourth historical critical point: We have introduced in this section the parameter of lattice displacement leading to the symmetry lowering. This is an idea similar to the old one of Fröhlich, outlined in his third famous paper [3]. And moreover, we fully agree with Fröhlich who was deeply convinced that this idea is closely connected with the cooperative behaviour of superconductors, whereas the supporters of two-particle theories of the BCS type see the origin of cooperative behaviour in the off-diagonal long-range order of the Yang type [31]. On the other hand, our conception is different from the Fröhlich's one in several aspects.

a) *Fröhlich derived the theory which is limited only on one space dimension (so called one-dimensional Fröhlich superconductivity) because he was inspired by the Peierls' solution of one-dimensional instabilities [32]. Our derivation is three-dimensional.*

b) *As concerns as the description of the lattice displacement Fröhlich identified two quite diverse concepts: the parameter of displacement and the vibrational coordinate. The first consequence of this false duality is the limitation of the solution only on the one-dimensional case. The second consequence is the fact that into the diagonalization process of electron-phonon terms enters only the mentioned one vibrational mode which represents the set of zero measure in a broad quasicontinuum of vibrational modes. On the contrary to it our theory operates with a diagonalization process which concerns of all vibrational modes because for the creation of superconducting gap all modes are necessary. For example the BCS theory which gives good quantitative results with many experiments is constructed on the base of Fröhlich canonical transformation contained in his second famous paper [2] where all modes are incorporated in the diagonalization process.*

c) *Fröhlich's diagonalization in his third paper [3] is equivalent to the adiabatic canonical transformation (see Wagner's comment to one-dimensional Fröhlich's superconductivity [20]). It supposes the anharmonic adiabatic potential with the minimum different from the initial equilibrium symmetrical position. Our theory of superconductivity is nonadiabatic in nature, our transformation consists of the adiabatic and nonadiabatic transformations with generators $S_1(Q)$ and $S_2(P)$ (3.8) which resembles Fröhlich's canonical transformation with*

the generator $S(Q, P)$ (3.7) contained in his second paper [2]. Our theory explains the fundamental properties of superconductors on the harmonic level and anharmonicities are not necessary.

d) *Fröhlich's quantization of vibrational field has its center in the initial symetrical point but our quantization has its center in the new asymmetrical point after the lattice symmetry lowering. It is very important difference. Due to this fact we are able in the crude representation to gain from one original band two overlapping bands and the continuum of "unperturbed" electronic energies ε^0 is disturbed by such a way. Further we are able to gain from original set of acoustical phonon branches the double set of acoustical and optical branches. Finally we apply the quasiparticle transformations and diagonalization procedure with respect to this new asymmetrical center as initial of coordinates.*

The four above mentioned arguments are the key for unification of contents of first and second Fröhlich's papers [1, 2] with the content of his third paper [3]. Now we can see why he could not perform this unification but, nevertheless we can admire his genial intuition that in the unification of on the first sight so controversial attitudes he felt the way to the derivation of all main properties of superconductors.

Because our theory is three-dimensional, naturally a question arises if the displacement of two sublattices is determined unambiguously. The answer is negative. We can have so many realizations of displaced sublattices how many "nonadiabatic" chemical bonds is ever atom capable to create with neighboring atoms. Therefore we can define superconductor as an insulator with several equivalent ground states that correspond to different nuclear positions — Jahn-Teller equivalent configurations [11].

VII. Phenomenon of superconductivity

We shall distinguish two fundamental attributes of superconductivity — the state of superconductivity and the phenomenon of superconductivity — which lead to two complementary descriptions of superconductors. On one side the state of superconductivity is characterized by the state of a conducting material which, after the Jahn-Teller condensation, becomes an insulator with several equivalent ground states. The state of superconductivity determines all statical properties of superconductors: energy gap, its temperature dependence, specific heat, density of states near the Fermi surface etc. On the other side the phenomenon of superconductivity determines all dynamical properties of superconductors: supercurrent, Meissner effect, quantization of magnetic flux, etc. We shall devote in this section just to the problem of phenomenon of superconductivity.

The fact that the superconductor can not be defined unambiguously on the microscopical level, i.e. that it is characterized by the occurrence of several

equivalent groundstates, implies the possibility of spontaneous transition from one ground state into another. This process represents a new degree of freedom of the whole system which is orthogonal to other degrees of freedom and also independent on them. It means that this new degree of freedom is quite nondissipative. The transition process has a cooperative long range order property, i.e. the sublattices can not be deformed (otherwise the conception of two bands would be disturbed) and can only move one with respect to the other. Because the transition from one state into another is conditioned by the overcoming of the potential barrier between two neighboring ground states we shall speak about the tunneling process. In this respect we can find a quantum chemical analogy — molecules with two ground states (right torque and left torque). There is also a spontaneous tunneling transition from one configuration to the other one.

The phenomenon of superconductivity is therefore caused by nuclear microflows through equivalent ground states. There is a question if this nuclear motion and the lattice symmetry lowering can be detectable. Because all the equivalent ground states are symmetrically localized around the symmetrical central point (i.e. the point corresponding to the ground state of material above T_c) there are the same probabilities of the occurrence of the system in each of these states. The resulting effect is therefore symmetrical. The experimentally measured nuclear formfactors indicate the rotational ellipsoids originating from the vibrational degrees of freedom. There is a possibility that this new nondissipative "rotational" degree of freedom is hidden in the above mentioned rotational ellipsoids. According to our theory the rotational ellipsoids would be enhanced at the phase transition below T_c. And indeed, the recent investigation of structure and superconducting properties of Nb_3Sn (T_c = 18,5 K) by X-ray diffraction [36] fully confirms the theory presented here. On the studied low-T_c compound Nb_3Sn, where the Jahn-Teller effect at the transition from the normal to superconducting state has not been assumed before, a discontinuous increase of the isotopic Debye temperature factors of niobium and tin has been observed in the temperature dependence at cooling near to T_c. Maybe the finer experiments show in future some changes in formfactor values of further low- and high-T_c superconductors near the critical temperature.

The microflow of nuclei is followed by the motion of electronic charge distribution. This electronic motion is identical with the replacement of nonadiabatic chemical bonds by the tunneling process. There are two theoretical possibilities of electronic motion. According to the first one the bond is splitted and one electron will follow the first nucleus and one electron the second nucleus. It is a "symmetrical" solution of the tunneling problem but in the framework of this conception only the Meissner effect can be interpreted. The electronic charge is fixed to the local region around the nuclei and no supercurrent can flow. The intermediate states arising during the tunneling process and corresponding to this "symmetrical" solution are characterized by the splitting of "nonadiabatic" bonds. It implies the intermediate creation of open shell states, similarly as a conductor

in a tight bond approach can be regarded as an open shell state. The second possibility of electronic motion concerns the preservation of the "nonadiabatic" bond. It means that both electrons occupy the same orbital (with opposite spin directions) which, of course, varies during the tunneling process. All intermediate states are then of closed shell type. Moreover, the superconductor has fully occupied valence band and empty conducting band at zero temperature not only in all its equivalent ground states but also in all intermediate states by the transition from one ground state into the another one. This second "asymmetrical" solution is energetically more convenient and therefore realizable.

The Meissner effect is illustrated in Figure 6. After the magnetic field is switched on, the random fluctuations of nuclei are arranged in regular circulation in the plane orthogonal to the direction of the field. Since the radius of electronic "orbitals" is larger than that of nuclei, resulting micro-circuit will be dominated by electronic charge distribution circulation (nuclei will be "pulled" by electronic revolution) until the fully compensation of external magnetic field.

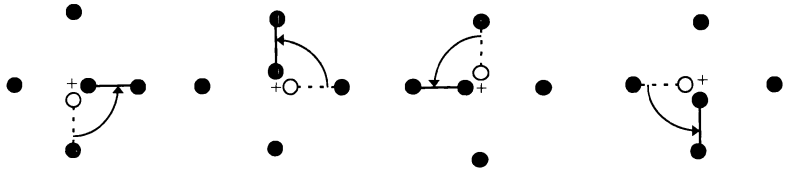

Fig. 6
Meissner effect: Four phases of circulation of nuclei and electronic charge distribution.

The principle of supercurrent is illustrated on the Figure 7. When we take into account the second above mentioned "asymmetrical" solution concerning the tunneling movement of the binding orbital occupied by two electrons as a whole, this binding orbital can follow either the first or the second nucleus. And just the arising ambiguity of the binding orbital motion enables the binding electrons to escape from the range of initial nucleus and to tunnel without dissipation through the lattice. The motion of the charge distribution keeps velocity and direction obtained from external source at initial moment. Moreover, the movement of double occupied binding orbital explains the elementary charge $2e$ measured through the quantized magnetic flux.

In this respect superconductivity resembles to the archetype of classical simple machine: the wheel. It is the motion without friction where the role of the wheel play two sublattices.

Now we proceed to the fifth historical critical point: It is a problem of correspondence between macrostates and microstates. It is commonly believed that any macrostate of superconductor with a certain value of supercurrent corresponds to one appropriate microstate described by a certain value of charge carrier quasimomentum. According to our theory the macrostate with zero supercurrent

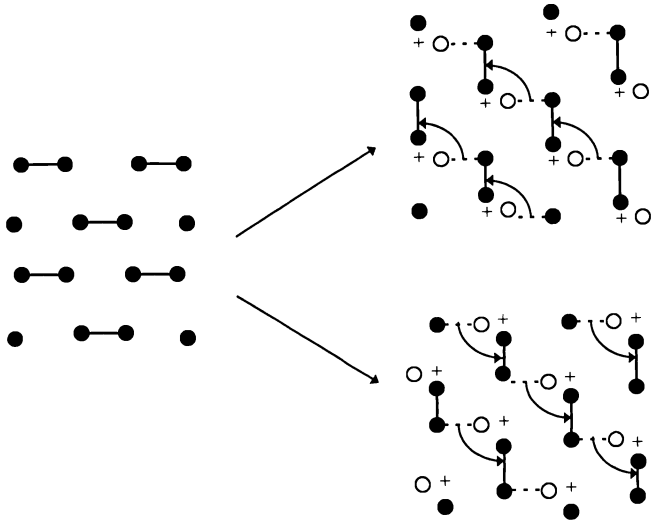

Fig. 7
Supercurrent: Ambiguity of the motion of the double occupied binding orbital leads to the possibility of nondissipative transport of electronic charge distribution of the minimal value $2e$ through the lattice.

corresponds to several microstates i.e. microscopical configurations representing equivalent ground states and any other macrostate with nonzero supercurrent corresponds to a certain transition process between these microscopical configurations.

Further we mention the conception of two phases: superconducting and conducting. This conception originates from the phenomenological idea of parallel coexistence of two phase components — superconducting (x) *and conducting* $(1 - x)$*. It is motivated by the classical thermodynamics where in a similar way e.g. the coexistence of liquid and gaseous phases of the same matter is described. This macroscopical phenomenological conception was later incorporated in microscopical theories. So the Cooper-paired electrons representing the superconducting phase coexist with free nonpaired electrons representing the conducting phase in a parallel way. On the contrary to this our theory considers these two phases to be not parallel but orthogonal in the ontological sense. What does this important difference mean?*

In the two-particle theories based on the Cooper pair idea two different entities are identified: the entity responsible for the condensation and excitation mechanism leading to the gap formation and the entity responsible for the transfer of supercurrent. Cooper pairs are the Bose condensation which decay into free conducting electrons through the excitation mechanism and simultaneously they are carriers of superconducting current.

In our theory we sharply distinguish these two entities. The former one correspond to selfconsistent polarons. The condensation process represents the creation of the multigroundstate insulator with full occupied valence band and empty conducting band. The excitation mechanism is one-particle in principle. Conducting phase of superconductor in this sense resembles the conductance of thermally excited insulator (semiconductor). The condensation and excitation mechanism is a subject of investigation of the state of superconductivity.

The latter entity corresponds to the tunneling double occupied binding orbitals producing the charge density waves which are the carriers of supercurrent. By this process one set of paired nuclei decays and another one arises. The tunneling process is two-particle in principle, is connected with the new nondissipative "rotational" degree of freedom and is orthogonal with respect to the electron-phonon interaction mechanism which is responsible for the one-particle gap formation. The carriers of supercurrent are subject of investigation of the phenomenon of superconductivity. The substance of this phenomenon is of a local character, it lies in the region of the elementary cell where the "nonadiabatic" chemical bond causes pairing of neighboring nuclei (atoms) and is of long range cooperative behaviour. It contradicts the Cooper-pair theories which are described in quasimomentum space and are nonlocal in the description of conducting as well as of superconducting phases.

VIII. Have the low-T_c and high-T_c superconductivity the same theoretical background?

In the foregoing sections we have not specified if the developed theoretical apparatus has concerned the low-T_c or the high-T_c superconductivity. The polemic with Fröhlich's and BCS papers has been related to the low-T_c superconductivity whereas the supporting experiments for our theory has been mostly related to the high-T_c one. In this section we try to specify the differences and the common background of both kinds of superconductivity.

The aim of theoretical physics is to find unified description of diverse natural phenomena which can be sometimes seemingly without mutual relation. To derive the common equations with two solutions — one for low-T_c and one for high-T_c superconductivity — it would be an ideal case.

The equations for the ground state energy lowering, the energy gap and its dependence on the temperature, contained in the section V, were derived from the general quantum mechanical principles without any limitation or specification of the character of the material. The explanation of the phenomenon of superconductivity, contained in the section VII, has its archetypal pattern in the classical physics in the movement without friction by means of the wheel as a simple machine. We are of the opinion that the both above mentioned topics constitute

a common platform for the description of the low-T_c as well as the high-T_c superconductivity.

Section VI remains questionable as concerns as the unambiguity of the algorithm of rearrangement of states near the Fermi surface. The initial conducting state was represented by one half-filled conducting band, as it is illustrated on the Figure 1. This is the conducting state of low-T_c superconductors. On the other hand, there exists another algorithm of the selection of the initial stage. The conducting state of superconductor may consist of two overlapping conducting bands. The symmetry lowering of the initial lattice and the creation of two sublattices, as it is illustrated on the Figure 2, concerns neither the band splitting (because we have two bands at the beginning) nor the splitting of phonon branches (because we have innerband acoustical branches and interband optical ones at the beginning). The transition in the first intermediate state (Figure 2) accompanied by the rising of nuclear pairing and "nonadiabatic" chemical bond evokes in this case only the deformation of two conducting bands in order their overlap to be smaller than $\hbar\omega_{max}$. The displacement of nuclei can be infinitesimally small as in the case of low-T_c superconductors or it can be comparable with the lattice internuclear distance in order to reach the optimal band overlap. The latter case really exists and is experimentally detected on some kinds of high-T_c superconductors. In the second intermediate state (Figure 3) representing the redefinition of the Fermi vacuum the lower conducting band becomes the fully occupied valence band and the higher conducting band becomes the empty conducting band. Further this process continues in analogy with that one described in the section VI.

The question is, why the high-T_c superconductivity is identified with the second alternative algorithm of two overlapping conducting bands in the initial stage. Let us note that the critical temperature is proportional to the magnitude of the gap, the latter is proportional to the magnitude of the band overlap (Figure 2) which is limited by $\hbar\omega_{max}$ where ω_{max} is the maximal interband frequency. Therefore we can state that the high critical temperatures are achieved by the great maximal interband optical frequencies. If we use the simple formula for harmonical frequency

$$\omega = \sqrt{\frac{k}{m}} \tag{8.1}$$

where k is the strength of the spring and m is the relative mass

$$m = \frac{m_1 m_2}{m_1 + m_2} \tag{8.2}$$

of two vibrating nuclei with masses m_1 and m_2, the great ω can be achieved either by the great k or by the small m. The great k can be achieved if the "nonadiabatic" chemical bond has a covalent background. It is the case of the bond between metallic and nonmetallic elements. The small m can be achieved if one of the

elements with masses m_1 and m_2 has a small mass. Combining of these two requirements we can conclude that the highest critical temperatures may be achieved if one sublattice is of metallic character and the second one is composed of light non-metallic elements with the strong covalent activity. In all known high-T_c superconductors the non-metallic element is oxygen and in majority of them the metallic element bound to oxygen is copper. The critical temperature can be also enhanced if the interband matrix elements of electron-phonon interaction are greater than the innerband ones, as follows from the relation (4.13a), or if there is a great density of states near the Fermi surface (then the summation in (4.13a) comprises the greater number of terms).

We mention now three experimentally motivated examples of differences between the low-T_c and high-T_c superconductivity which are in accordance with our theory.

1. The coherence length. The sublattices in low-T_c superconductivity are composed from the same metallic elements. The metallic bond in sublattices causes the long range stability of both of them and therefore the coherence length is great. In the high-T_c superconductivity one sublattice is of metallic character and the second one is composed purely of oxygen atoms. The oxygen sublattice may have no long range stability and therefore the coherence length may be small.
2. The anisotropy of supercurrent. Let us imagine a simple cubic lattice of low-T_c superconductor. Both sublattices are also of cubic form and may mutually perform the tunneling movement through six equivalent ground states symmetrically located in space. The supercurrent has an isotropical property. On the other hand, let us imagine the high-T_c superconductor where the oxygen atom is placed in the midst of four copper atoms. The oxygen sublattice is able to tunnel only through four equivalent ground states lying in the Cu-0 plane. The supercurrent displays anisotropy and flows in the Cu-0 plane.
3. The isotopic effect. We perform the estimation of the isotopic effect on the basis of relation (4.13a), (5.3), (5.13, 14)

$$T_c \sim \Delta_0 \sim \Delta\varepsilon \sim \sum_{\Delta\varepsilon^0} \frac{u^2\hbar\omega}{(\Delta\varepsilon^0)^2 - (\hbar\omega)^2} \tag{8.3}$$

Supposing the standard dependence on the isotopic mass M we have

$$u \sim M^{-\frac{1}{4}} \tag{8.4}$$

$$\omega \sim M^{-\frac{1}{2}} \tag{8.5}$$

The isotopic dependence of the sum over the differences of unpeturbed energies that occurs in (8.3) is questionable. It depends on the fact how the band overlap (Figure 2) will follow the isotopic change of $\hbar\omega_{\max}$. There are two extreme cases. In the first case the overlap will increase to the same extend as $\hbar\omega_{\max}$. It will have a direct proportional influence on the number of states in the summation in (8.3). Therefore the following proportionality takes place

$$\sum_{\Delta\varepsilon^0} \sim \omega \sim M^{-\frac{1}{2}} \tag{8.6}$$

In the second case the overlap will be constant after the isotopic change of $\hbar\omega_{\max}$. It implies the simple proportionality

$$\sum_{\Delta\varepsilon^0} \sim M^0 \tag{8.7}$$

The theoretical estimation of the isotopic effect is therefore ambiguous, it is only related to the interval with two limiting extremal values, namely in the first case (8.6)

$$T_c \sim M^{-\frac{1}{2}} \tag{8.8}$$

and in the second case (8.7)

$$T_c \sim M^0 \tag{8.9}$$

The experimental results indicate that the first case (8.8) concerns the low-T_c superconductors and the second case (8.9) the high-T_c ones. The explanation of this fact might lie in the magnitude of maximal interband frequency $\omega_{\max}$ which differs in both types of superconductors in the order. At the relative small values of $\omega_{\max}$ of low-T_c superconductors it is expected that the magnitude of the band overlap $\Delta\varepsilon^0_{\max}$ will be comparable with $\hbar\omega_{\max}$, i.e. $\Delta\varepsilon^0_{\max} \approx \hbar\omega_{\max}$, and will follow it by the isotopical change. On the other hand, at relative high values of $\omega_{\max}$ of high-T_c superconductors the values $\Delta\varepsilon^0_{\max}$ can be limited by some requirements relating to the geometrical configuration of nuclei, the energetical stability of the system or to the density of states near the Fermi surface, so that $\Delta\varepsilon^0_{\max} < \hbar\omega_{\max}$, and consequently, the overlap remains constant and independent on the isotopical change. The argument that the absence of isotopical effect in the case of high-T_c superconductors implies the another principle of the gap formation than the electron-phonon one, is according to our theory not justified.

IX. Conclusion

The presented theory of superconductivity is not conceived as ready, closed, and exhaustive theory. It is rather conceived as a new theory in development, open for furher ideas and discussions. We are aware of the fact that many statements and conceptions contained in this paper are nontraditional, going beyond the common acceptable language of solid state physics. Moreover, the mathematical formalism was undertaken from quantum chemistry, whereas the subject of consideration concerns the solid state physics. Nevertheless, we hope that this paper may open a new kind of cooperation between quantum chemists and theoretical physicists in this field because our theory signalizes superconductivity as lying on the boundary of these two scientifical branches.

We are also aware of the fact that the two-particle Cooper-pair theories have a very strong position among the scientific community. We bring out the often occuring objections of defenders of two-particle theories against the conception of one-particle mechanism:

The first objection: The two-particle theories offer very good numerical results in accordance with experiments. — Remember that our theory as well as the BCS one starts from the same effective electron-electron interaction term. The BCS theory consists in the multiconfigurational treatment of this term in its two-particle form whereas our theory uses the contraction on the bases of the Wick's theorem in order to convert this term in the one-particle form. Nevertheless, the resulting matrix elements are very similar, and that is the reason of an illusory numerical coincidence.

The second objection: The two-particle theories are confirmed by the off-diagonal long range order. The off-diagonal long range order of the Yang type [31] was derived without a detailed examination of the actual interaction mechanism. Recently it has been shown that one may even arrive at ODLRO solely via repulsive Coulombic interaction [33], or even via one-particle interaction [30]. In our theory we define the superconductor as an insulator with several equivalent ground states, having the fully occupied valence band and empty conducting band at zero temperature. The excitation process is one-particle, the excitation particles are selfconsistent polarons. The condensation into the state of superconductivity is caused by the Jahn-Teller splitting of half-filled conducting band (low-T_c SC) or by the Jahn-Teller separation of two overlapping conducting bands (high-T_c SC). The original lattice is splitted into two sublattices. The displacement of these two sublattices is of the cooperative character. In our one-particle theory the co-operative behaviour is a consequence of the geometrical structure of the system, not of the ODLRO of Cooper pairs.

The third objection: The experimentally detected elementary charge $2e$ *witnesses in favour of two-particle theories.* — This elementary charge $2e$ has no connection to the condensation and excitation process. We strictly distinguish the entities responsible for the condensation and excitation one-particle process — self-consistent polarons, and the entities responsible for the transport of supercurrent — double occupied binding orbitals which tunnel through the equivalent ground states. During the tunneling process the system remains in the closed-shell form. Therefore the tunneling elementary charge is $2e$. The former entities are subject of investigation of physics, whereas the latter ones are rather a subject of investigation of chemistry.

The fourth objection: The one-particle theory will be discussed if such experiments appear that will be unexplainable by the two-particle theories but explainable by one-particle one. — The newest very fine experiments, as e.g. the measurements of cooperative behaviour of the system over the critical temperature [29] are in a contradiction with the mean field BCS theory. In addition to that, the

measurements of photoemission intensity indicating very peculiar behaviour of density of states near the Fermi surface [24–26], are really unexplainable within the framework of all the existing two-particle theories. Our theory enables their explanation. We believe that further new experiments occur in future which enable the one-particle theory again and better to testify.

The nut of our theory – the derivation of one-particle energy gap – we discovered by a lucky hit when we tried to study the Jahn-Teller effect in molecules by means of canonical transformations. We noticed the similarity of these transformations and those used by Fröhlich. Formerly we investigated molecular systems with quasi-degenerate orbital levels by means of quasidegenerate perturbation theories. After many theoretical attempts, how to find an optimal version of quasidegenerate perturbation theory [34], and practical attempts, how this theory can be utilized in calculation of dissociation processes [35], we concluded – in spite of very good numerical results – that the removing of degeneracy (quasidegeneracy) of states by means of perturbation and/or multiconfigurational treatment is not fully all right from the ontological point of view. And just the Jahn-Teller effect is an excellent example that nature has another and more ingenious means how to remove the (quasi)-degeneracy. Therefore we could not accept the theories of superconductivity based on the Cooper-pair conception because they had the origin in the multiconfigurational way of degeneracy removement. We tried to find further arguments against the Cooper-pair two-particle theories and have mentioned them in this paper.

That is the reason why we came back in the pioneer times of Fröhlich's papers, before the two-particle theories begun to be developed. Let us note that Fröhlich was in all his life firmly convinced of incorrectness of the Cooper-pair theories and believed that sometime a complete one-particle description of superconductors illuminating all their main physical properties has to appear. Our paper is drafted as an attempt for rehabilitation of – according to our opinion – underestimated Fröhlich's merit. Even though he was not fully successful he came nearest to the correct resolution of the superconductivity problem. This resolution consists in the unification of his on the first sight contradictory three papers. We hope that we have fulfilled the Fröhlich's wish of such a unification.

As we were said, after the death of Fröhlich, he was one of the referee of our four preceeding papers [9–12] written on this subject. We are sorry to say, they were the last papers he had read before he died. Unfortunately, he did not manage to write the report. What his opinion was we can only guess. Anyway, we should like to thank him in this way for his lifetime endeavour.

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