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***Ab initio* THEORY OF COMPLEX ELECTRONIC GROUND STATE OF SUPERCONDUCTORS: II. Antiadiabatic state - ground state of superconductors**

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Abstract

Based on Q,P -dependent modification of the Born-Oppenheimer approximation (BOA), the *ab initio* theory of complex electronic ground state of superconductors is presented. As an illustrative example, application of the theory to superconductors of different character and to corresponding nonsuperconducting analogues is presented. It is shown, that due to electron-phonon (EP) interactions, which drive system from adiabatic into antiadiabatic state, adiabatic translation symmetry is broken and system is stabilized in antiadiabatic state at distorted geometry with respect to adiabatic equilibrium high symmetry structure. Stabilization effect in the antiadiabatic state is due to strong dependence of the electronic motion on the instantaneous nuclear kinetic energy, i.e. on the effect which is neglected on the adiabatic level within the BOA. At distorted geometry, antiadiabatic ground state is geometrically degenerate with fluxional nuclear configurations in the phonon modes that drive system into this state. It has been shown that until system remains in antiadiabatic state, nonadiabatic polaron – renormalized phonon interactions are zero in well-defined k region of reciprocal lattice. This, along with geometric degeneracy of the antiadiabatic state, enables formation of mobile bipolarons that can move over lattice as supercarriers without dissipation. More over, it has been shown that due to EP interactions at transition into antiadiabatic state, k -dependent gap in one-electron spectrum has been opened. Gap opening is associated with shift of the original adiabatic Hartree-Fock orbital energies and with the k -dependent change in density of states of particular band(s) at Fermi level. Corrected one-particle spectrum enables to derive thermodynamic properties in full agreement with corresponding thermodynamic properties of superconductors.

Based on the complex *ab initio* theory, it has been shown that Fröhlich's effective attractive electron-electron interaction term represents correction to electron correlation energy at transition from adiabatic into antiadiabatic state due to EP interactions. It has been shown that increased electron correlation is consequence of stabilization of the system in superconducting electronic ground state, but not the reason of its formation.

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Keywords: A. superconductors; C. ab initio calculations; D. electronic structure; lattice dynamics

I. Introduction

In the precedent paper - part I [1], theoretical background of the nonadiabatic P -dependent modification of the adiabatic Born-Oppenheimer approximation (BOA) has been presented along with corresponding sequence of canonical transformations of general nonrelativistic form of system Hamiltonian (molecular or solid state system). In the present paper – part II, consistent *ab initio* theory of complex electronic ground state of superconductors beyond the adiabatic BOA is formulated. Based on the equations presented in part I [1], transition from adiabatic into antiadiabatic state is analyzed. It is shown, that due to electron-phonon (EP) interactions, which drive system from adiabatic into antiadiabatic state, adiabatic symmetry is broken and system is stabilized in antiadiabatic state at distorted geometry with respect to adiabatic equilibrium high symmetry structure. Stabilization effect in the antiadiabatic state is due to strong dependence of the electronic motion on the instantaneous nuclear kinetic energy, i.e. on the effect which is neglected on the adiabatic level within the BOA. Antiadiabatic ground state is geometrically degenerate at distorted geometry, with fluxional nuclear configurations in the phonon modes that drive system into this state. It has been shown that until system remains in antiadiabatic state, nonadiabatic polaron – renormalized phonon interactions are zero in well defined k -region of reciprocal lattice. Along with geometric degeneracy of the antiadiabatic state it enables formation of mobile bipolarons that can move over lattice as supercarriers without dissipation (coherent dynamics). Due to EP interactions at transition into antiadiabatic state, k -dependent gap in one-electron spectrum has been opened. Gap opening is related to the shift of the original adiabatic Hartree-Fock orbital energies and to the k -dependent change in density of states (DOS) of particular band(s) at Fermi level. The shift of orbital energies determines in a unique way one-particle spectrum and thermodynamic properties of system. It has been shown that resulting one-particle spectrum yields all thermodynamic properties, which are characteristic for system in superconducting state, i.e. temperature dependence of the gap, specific heat, entropy, free energy and critical magnetic field. The k -dependent change in DOS near to Fermi level at transition from adiabatic (nonsuperconducting) into the antiadiabatic state (superconducting) can be experimentally verified by ARPES or tunneling spectroscopy as spectral weight transfer at cooling superconductor from temperatures above T_c down to temperatures below T_c .

As an illustrative example, application of the theory to superconductors of different character (MgB_2 , $\text{YBa}_2\text{Cu}_3\text{O}_7$) and to corresponding nonsuperconducting analogs (AlB_2 , $\text{YBa}_2\text{Cu}_3\text{O}_6$) is presented. While MgB_2 is interpreted usually as strong EP coupling-based BCS superconductor, see e.g. [2], for transition to superconducting state in the $\text{YBa}_2\text{Cu}_3\text{O}_7$ and high- T_c cuprates in general, the mechanism of strong electron correlation is advocated as the crucial driving force [see e.g. 3, 4]. In the present work it has been shown that the same physical effect is active at transition into superconducting state in different classes of superconductors. In particular, it is the EP interaction driven transition into antiadiabatic state that exhibits all thermodynamic properties of superconducting state.

In relation to the *ab initio* theory of complex electronic ground state of superconductors, the BCS theory and the Fröhlich effective attractive electron-electron interaction Hamiltonian are discussed. It has been shown that, with respect to contemporary experimental and theoretical knowledge, the BCS theory (including concept of Cooper pairs formation) with its remarkable interpretative ability of superconducting state properties is simplified model description of superconducting ground state. The main points are specified in this paper. It has also been shown, that BCS Hamiltonian as a generic form with attractive electron-electron interaction term, e.g. for models of strongly correlated electrons at description of superconducting ground state does not cover the physical origin of the effect. The reason is

related to the fact that the Fröhlich effective attractive electron-electron interaction term represents correction to electron correlation energy that arises as a consequence of EP interactions. In this respect, strong electron correlation that is advocated mainly for cuprates is very realistic assumption but it is not the primary reason of superconducting state stabilization. Results of the *ab initio* theory of complex electronic ground state of superconductors show that increased electron correlation is a consequence of EP interactions that drive system into antiadiabatic state and stabilize it at distorted nuclear geometry. Expressed in the other way, strong electron correlation is a consequence of stabilization of the system in superconducting electronic ground state, but not the primary reason of its formation.

Antiadiabatic state, i.e. ground electronic state of superconductors is analyzed in section II and derivation of corresponding thermodynamic quantities is presented in section III. Correction to electron correlation energy due to dependence of electronic motion on nuclear coordinates and momenta is specified in section IV. Effective attractive electron-electron interaction is analyzed in section V with respect to the *ab initio* theory and to the original Fröhlich's and the BCS treatment. In this connection, formation of mobile bipolarons is discussed based on the Q, P -dependent form of the wave function pertaining to system in antiadiabatic state. There is supplementary part, Appendix A and B, that presents details to the particular parts in the main text.

II. Antiadiabatic state - ground electronic state of superconductors

II. 1. Clamped nuclear (crude-adiabatic) structure

Band structure of superconductors, no matter if high- T_c cuprates, MgB_2 , simple metals or metal alloys, calculated at equilibrium geometry with unit cell atom positions corresponding to particular symmetry group, are of metal-like character with at least one band continually crossing Fermi level in some direction of reciprocal lattice. Fermi energy (chemical potential μ) is always greater than corresponding frequencies of pertaining phonon modes. It indicates that for equilibrium structures the adiabatic BOA can be applied. For distorted structures with atom displacements characteristic for vibration motion in some phonon modes, the band structure topology of superconductors undergoes significant change. Of particular importance is fluctuation of analytic critical point (ACP - maximum, minimum or saddle point) of some band across the Fermi level. It indicates significant reduction of Fermi energy (chemical potential μ) that is associated with formation of antiadiabatic state, $|\varepsilon_S^0(k_c) - \varepsilon_F^0|_{R_{eq} \pm Q} < \hbar\omega_r$, at vibration motion. It means that standard adiabatic Q -dependent BOA is not adequate starting point for theoretical study of electronic structure of superconductors. Modified, Q, P -dependent BOA accounts for adiabatic as well for antiadiabatic state and can be suitable approximation at theoretical study of superconductors.

Let us see superconductors at equilibrium geometry R_{eq} when adiabatic approximation is valid. As an illustrative example, the two well known superconductors of different character are presented; $YBa_2Cu_3O_7$ and MgB_2 with critical temperature $T_c \approx 92 - 94$ K [5] and $T_c \approx 39$ K [6], respectively.

The study starts with the LCAO-based HF-SCF calculation of the electronic band structure for clamped nuclear configuration (crude-adiabatic level) at high-symmetry equilibrium geometry. The band structure calculations have been performed by computer code SOLID 2000 [7]. The code is based on the method of cyclic cluster [8] with quasi-relativistic INDO Hamiltonian [9]. Based on the results of atomic Dirac-Fock calculations [10], the INDO version used in the SOLID package is parameterized for nearly all elements of the Periodic chart. Within the INDO calculation scheme, the one-electron off-diagonal inter-site matrix elements $h_{\mu_A \nu_B}$ (β integrals – hopping terms) are not restricted only to nearest-neighbour or

next nearest-neighbour terms but all terms among involved atoms and AOs are included. Two-electron coulomb repulsion is calculated for one and two-center terms (three and four center terms are neglected) in the form $(\mu\mu|\nu\nu)$ through the Slater-Condon parameters. For two-electron one-center terms, also exchange repulsion in the form $(\mu\nu|\mu\nu)$ is involved in calculations. In general, the INDO Hamiltonian yields good results for electronic properties related to frontier orbitals and for calculation of equilibrium geometries but overestimates total band-width (bonding character) due to approximation of β integrals.

The experimental lattice parameters [11] of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (orthorhombic structure, space group Pmmm, oP14), with the fractional coordinates of unit cell atoms: Cu(1) = (0,0,0); Cu(2) = (0,0, ± 0.355); Y = (1/2,1/2,1/2), Ba = (1/2,1/2, ± 0.186), O(1) = (0,1/2,0), O(2) = (1/2,0, ± 0.380), O(3) = (0,1/2, ± 0.376), O(4) = (0,0, ± 0.156) and lattice constants $a = 3.817 \text{ \AA}$, $b = 3.882 \text{ \AA}$, $c = 11.671 \text{ \AA}$ have been used. The unit cell has 13 atoms as it corresponds to the formula unit with the chain oxygen O(1) in **b**-direction and vacancy in **a** direction. The MgB_2 is characteristic of hexagonal structure (hP3, P6mmm, #191- AlB_2 type) with 3 atoms per unit cell. The fractional coordinates are: Mg = (0,0,0); B1 = (1/3,2/3,1/2); B2 = (2/3,1/3,1/2) and lattice constants $a = b = 3.0823$; $c = 3.5146 \text{ \AA}$ [12]. For $\text{YBa}_2\text{Cu}_3\text{O}_7$, the basic cluster of the dimension $5 \times 5 \times 5$ has been generated by the corresponding translations of the unit cell in the directions of crystallographic axes, **a** (5), **b** (5), **c** (5). The cluster of this size (1625 atoms) generates a grid of 125 points in k-space. In case of MgB_2 , the basic cluster of the dimension $9 \times 9 \times 7$ with 1701 atoms (567 points in k-space) has been used. The Pyykko-Loehr quasi-relativistic basis set of the valence electron atomic orbitals (s,p-AO for Ba, O, and s,p,d-AO for Cu and Y) has been used, i.e., 72 AO/unit cell and the total number of STO type functions in the basic cluster has been 9,000 in case of $\text{YBa}_2\text{Cu}_3\text{O}_7$. Valence electron atomic orbitals s,p has also been used for Mg and B atoms in case of MgB_2 , i.e. 6,804 STO type function for basic cluster. The HF-SCF procedure is performed for each k-point with the INDO Hamiltonian matrix elements that obey the boundary (Born-Karman) conditions of the cyclic - infinite cluster [8].

In Fig.1, the band structures of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (1a) and MgB_2 (1b) at respective equilibrium geometries are presented. The band structures of corresponding non superconducting analogues, $\text{YBa}_2\text{Cu}_3\text{O}_6$ and AlB_2 , are shown in Fig.2.

The band structures of the presented compounds are of adiabatic, metal-like character. Even in case of MgB_2 , the Fermi energy (chemical potential μ of σ -bands electrons) is relatively small, $E_F \approx 0.5 \text{ eV}$, it is still much larger than highest frequency ($\omega_{E2g} \approx 0.066 - 0.07 \text{ eV}$) of pertaining optical phonons.

Fig.1. Band structures of (a) $\text{YBa}_2\text{Cu}_3\text{O}_7$ and (b) MgB_2 (b) at equilibrium geometries.

Fig.2. Band structures of nonsuperconducting analogues; (a) $\text{YBa}_2\text{Cu}_3\text{O}_6$ at equilibrium geometry of $\text{YBa}_2\text{Cu}_3\text{O}_7$ without the chain oxygen O(1) and (b) AlB_2 at equilibrium geometry.

On crude-adiabatic level, total ground state electronic energy $E_0^{te}(R_{eq})$ has minimum at R_{eq} , $(dE_0^{te}/dR)_{R_{eq}} = 0$, and within the HF-SCF approximation it is equal to (30 - part I).

The only correction to this energy is electron correlation energy (32a- part I), which is negative and contributes to stabilization of the ground state at equilibrium geometry R_{eq}

$$E_{0corr}^{te}(R_{eq}) = E_0^{te}(R_{eq}) - |E_{corr}|_{R_{eq}}, \quad (dE_{0corr}^{te}/dR)_{R_{eq}} = 0 \quad (1)$$

Related to any phonon mode, nuclear displacements at vibration motion increase total electronic energy (potential energy of nuclear motion in particular phonon mode). For displaced geometry R_d on crude-adiabatic level holds,

$$E_{0corr}^{te}(R_d) = E_0^{te}(R_d) - |E_{corr}|_{R_d} \quad (2)$$

Since two-electron coulomb interactions $\{V_{PQRS}^0\}$ do not depend explicitly on nuclear displacements it can be expected that electron correlation energy at vibration motion has not been changed significantly, i.e. $(E_{corr})_{R_{eq}} \approx (E_{corr})_{R_d}$. On crude-adiabatic level, for an increase of the total electronic energy ΔE_d due to nuclear displacement R_d then holds

$$\Delta E_d(R_d) = E_0^{te}(R_d) - E_0^{te}(R_{eq}) > 0 \quad (3)$$

In principle, two situations can occur; nuclear displacements related to some phonon mode(s) induce formation of antiadiabatic state, or system remains in adiabatic state with respect to vibration motion in all phonon modes.

In Fig. 3, the band structures of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (3a) and MgB_2 (3b) at distorted geometries are presented.

Fig.3. Band structures of (a) $\text{YBa}_2\text{Cu}_3\text{O}_7$ and (b) MgB_2 at distorted geometries. Distortions are related to vibration of O(4), O(2), O(3) atoms in the A_g , B_{2g} and B_{3g} modes of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and vibration of B atoms in the E_{2g} mode of MgB_2 – for details see text below.

Distortion is related to nuclear motion in respective phonon modes. In case of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (3a), it is combination of displacements of O4, O2, O3 atoms in the A_g , B_{2g} and B_{3g} modes (for notation see e.g. [13-15]). For the c-direction displacement $\Delta f_c = -0.0027$ ($-0.03151 \text{ \AA}^0$) of the apical O4, i.e. change of the inner coordinate $0.156 \rightarrow 0.1533$ and **a**, **b** - direction displacements of O2 and O3 atoms by $\Delta f_a = 0.0057$ ($0.02175 \text{ \AA}^0$) for O2 and $\Delta f_b = -0.0057$ ($-0.02213 \text{ \AA}^0$) for O3, the ground state energy with respect to undistorted structure has been increased - destabilized by $\Delta E_d(R_{dcr}) \approx +170 \text{ meV/unit cell}$. What is crucial, however, is the fact that the band structure for this distortion (Fig.3a) has changed significantly the topology with respect to the equilibrium structure – Fig.1a. The change is characteristic by the shift of the analytic critical point (ACP, in this case the saddle point) of d-p σ band at Y point of 1st BZ from the bonding region across the Femi level (FL) to antibonding region. At vibration motion it represents periodic fluctuation of the ACP across FL. At the moment when the ACP approaches FL and touches it, the chemical potential of dp- σ band electrons in CuO plane is reduced to negligibly small value – $\mu_{d-p\sigma} \rightarrow 0 \text{ eV}$. It is related to antiadiabatic state formation with violation of the adiabatic BOA.

Similar effect can be identified in MgB_2 . Displacement of B atoms in the E_{2g} phonon mode (B-B stretching vibration in **a-b** plane) by $\Delta f = 0.005$ ($0.016 \text{ \AA}^0/\text{atom}$) out-of equilibrium positions induces splitting of σ -bands in Γ point and shift of the ACP (in this case it is maximum) of the σ_1 -band from the antibonding region across FL to bonding region (cf. Fig. 1b and 3b). The ground state energy at this displacement, with respect to undistorted structure, has been increased - destabilized by $\Delta E_d(R_{dcr}) \approx +12 \text{ meV/unit cell}$. At vibration motion it represents periodic fluctuation of the ACP across FL. It is associated with reduction of chemical potential of σ -band electrons in B-plane to negligibly small value – $\mu_\sigma \rightarrow 0 \text{ eV}$ when the ACP approaches FL and consequently, transition into antiadiabatic state is induced.

II. 2. Nonadiabatic corrections

II. 2.1. Ground state energy correction

In the case when at displaced geometry R_d , related to vibration motion in phonon mode r , the antiadiabatic state $|\varepsilon_s^0(k_c) - \varepsilon_F|_{R_d(R_{eq} \pm Q)} < \hbar\omega_r$ is formed, the crude-adiabatic total electronic energy is corrected by Q, P -dependent zero-particle term correction $\Delta E_{(na)}^0(R_d)$. The correction (94a – part I) can be written as,

$$\Delta E_{(na)}^0 = 2 \sum_{\varphi_{Rk}} \sum_{\varphi_{Sk'}} \int_0^{\varepsilon_k^0, \max} n_{\varepsilon_k^0} (1 - f_{\varepsilon_k^0}) d\varepsilon_k^0 \int_{\varepsilon_k^0, \min}^{\varepsilon_k^0, \max} f_{\varepsilon_k^0} |u_{k-k'}^r|^2 n_{\varepsilon_k} \frac{\hbar\omega_r}{(\varepsilon_k^0 - \varepsilon_{k'}^0)^2 - (\hbar\omega_r)^2} d\varepsilon_k^0, \quad \varphi_{Rk} \neq \varphi_{Sk'} \quad (4)$$

In general, all bands of 1st BZ of multiband system are covered, including intraband terms, i.e. $\varphi_{Rk}, \varphi_{Rk'}, k \neq k'$ and $\varepsilon_k^0 < \varepsilon_F$, $\varepsilon_{k'}^0 > \varepsilon_F$. Fermi-Dirac populations $f_{\varepsilon_k^0}, f_{\varepsilon_{k'}^0}$, make correction (4) temperature dependent. Term $u_{k-k'}^r$ stands for matrix element of EP coupling and $n_{\varepsilon_k}, n_{\varepsilon_{k'}}$ are DOS of interacting bands at ε_k^0 and $\varepsilon_{k'}^0$. For adiabatic systems, e.g. metals ($\mu > \omega$), this correction is positive and negligibly small (i.e. adiabatic DBOC). Only for systems in antiadiabatic state ($\mu < \omega$) the correction is negative and absolute value depends on the magnitudes of $u_{k-k'}^r$ and $n_{\varepsilon_k}, n_{\varepsilon_{k'}}$ at the displacement for FL crossing. At the moment when ACP approach FL, system not only undergoes transition into antiadiabatic state but DOS of fluctuating band is considerably increased at FL – see Fig.4.

Fig.4. Density of states (DOS) of fluctuating band as a function of energy - situation when the ACP touches Fermi level. The DOS of d-p σ at Y point of YBa₂Cu₃O₇ (a) and DOS of σ_1 band at Γ of MgB₂ (b).

The nonadiabatic corrections are calculated as post-SCF procedures based on the quantities derived from clamped-nuclear crude adiabatic results. In particular, clamped-nuclear density of states (DOS) of involved bands at FL is calculated from respective band dispersions; $n^0(\varepsilon_k^0) = \left| \left(\partial \varepsilon_k^0 / \partial k \right)^{-1} \right|_{FL}$. For fluctuating band, the mean value $\bar{n}^0$ is used. It corresponds to density of states in situation when fluctuating ACP is $\pm \omega/2$ from FL. In case of YBa₂Cu₃O₇, calculated value is $\bar{n}_{d-p\sigma}^0 \approx 2$ states/eV ($\pm \omega_{Bg}/2 \approx 0.036$ eV) close to Y point in Y- Γ (S) direction. For equilibrium structure, DOS of this band at FL is small, $n_{d-p\sigma}^0 \approx 0.04$ states/eV. In the case of MgB₂, the DOS of fluctuating σ_1 band at FL for equilibrium structure is $n_{\sigma}^0 \approx 0.03$ states/eV. Coupling to vibration motion of B atoms in the E_{2g} phonon mode induces fluctuation of σ band that considerably changes σ band DOS at FL – Fig. 4b. The mean value of σ_1 -DOS for the ACP position $\pm \omega_{E2g}/2 \approx 0.033$ eV from the FL is $\bar{n}_{\sigma}^0 \approx 0.2$ states/eV. Also in this case, the increase of DOS at FL is significant.

From the SCF-HF calculation, at displacement of vibrating atoms related to Fermi level crossing, the overall value of EP interactions can be extracted, i.e. change of one-electron core term $\Delta h(Q_{cross \sin g}) = u^{(1)}(Q_{cross \sin g}) \equiv \bar{u}$. In what follows, this value represents maximal value $\bar{u}$ of EP interaction at transition from adiabatic into antiadiabatic state. At calculation of nonadiabatic corrections, dependence of EP coupling on the difference of orbital energies is approximated by functional form,

$$(u_z)^2 = (\bar{u})^2 (0.99 + 0.12.z - 0.31.z^2), \text{ for } \Delta \varepsilon_{kk'} \leq 2\hbar\omega;$$

$$u_z = 0 \text{ for } \Delta \varepsilon_{kk'} > 2\hbar\omega \text{ and } z = \Delta \varepsilon_{kk'} / \hbar\omega.$$

The SCF-HF calculations yield $\bar{u} = 2.5$ eV for YBa₂Cu₃O₇ and $\bar{u} = 0.95$ eV for MgB₂. Calculated nonadiabatic correction to the ground state energy (4) for studied systems in antiadiabatic state is: $\Delta E_{(na)}^0(R_d) \approx -204$ meV/u.c. for YBa₂Cu₃O₇ and $\Delta E_{(na)}^0(R_d) \approx -25$ meV/u.c. for MgB₂.

For total electronic energy at displaced geometry R_d then holds,

$$E_{0,na}^{te}(R_d) = E_{0,eq}^{te}(R_{eq}) + \Delta E_d(R_d) + \Delta E_{(na)}^0(R_d) \quad (5)$$

Since for antiadiabatic state this correction is negative, $\Delta E_{(na)}^0(R_d) < 0$, then if the inequality

$$|\Delta E_{(na)}^0(R_d)| > \Delta E_d(R_d) \quad (6)$$

holds, the electronic state of the system is stabilized at distorted geometry R_d . The reason of it is significant participation of the nuclear kinetic energy term expressed through contribution of the coefficients $\hat{c}_{At}^r$ of P -dependent transformation - see (93-part I), which stabilize fermionic ground state energy in antiadiabatic state with distorted nuclear structure.

Stabilization (condensation) energy at transition from adiabatic into antiadiabatic state is,

$$E_{cond}^0 = \Delta E_d(R_d) - |\Delta E_{(na)}^0(R_d)| \quad (7)$$

In case of $\text{YBa}_2\text{Cu}_3\text{O}_7$ it is $E_{cond}^0 = 170 - 204 = -34 \text{ meV/u.c.}$ and for MgB_2 calculated value is $E_{cond}^0 = 12 - 25 = -13 \text{ meV/u.c.}$

At temperature 0 K, distorted geometry represents true equilibrium geometry R_{teq} of the system ($R_d \equiv R_{teq}$) and corresponding total electronic energy represents electronic ground state energy of the system,

$$\left(\frac{dE_{0,na}^{te}(R)}{dR} \right)_{R_{ed}} = 0, \quad E_{0,na}^{te}(R_d) < E_0^{te}(R_{eq}) \quad (8)$$

It can be shown that due to translation symmetry of the lattice, antiadiabatic ground state is geometrically degenerate. In case of $\text{YBa}_2\text{Cu}_3\text{O}_7$, there is infinite number of in-plane displacements of the O2, O3 atoms, i.e. different nuclear configurations, with the same ground state energy. Energetically equivalent positions are on perimeters of the circles with radii equal to the displacements for FL crossing $\Delta f_a, \Delta f_b \approx 0.0057$. The circles are centred at the high-symmetry equilibrium positions of the O2 and O3. In case of MgB_2 circles are with the radii $\Delta f_a, \Delta f_b \approx 0.005$, centred at B1, B2 equilibrium positions. As an illustrative example, situation for MgB_2 is schematically visualized in Fig.5

Fig.5. Fluxional nuclear configurations of B atoms at distorted geometry of MgB_2 . In antiadiabatic state, the electronic ground state energy is geometrically degenerate – there is infinite number of energetically equivalent nuclear configurations of B1-B2 atoms on perimeters of the flux-circles (see text).

On the lattice scale, geometric degeneracy of the fermionic ground state energy for distorted structure, i.e. existence of an infinite number of involved atoms displacements (fluxional structure of $\text{Cu}_2\text{-O}_2\text{O}_3$ plane, or B1-B2 plane, respectively), enables cooperative and dissipationless motion of displaced O2, O3 and B1, B2 atoms along the perimeters of specified circles (keeping motion of the displacement vectors in out-of phase position). Antiadiabatic ground state with fluxional geometric degeneracy is a new, coherent macroscopic quantum state.

The electronic structure instability is absent in respective non-superconducting analogues, e.g. $\text{YBa}_2\text{Cu}_3\text{O}_6$ and XB_2 ($\text{X} \equiv \text{Al, Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, ...}$). In spite of the fact that in case of XB_2 , coupling to the E_{2g} mode induces σ bands splitting in Γ point, the systems remain stable in adiabatic state – the ACP of σ band does not fluctuate across FL. In Fig.6 are band structures of $\text{YBa}_2\text{Cu}_3\text{O}_6$ and AlB_2 at distorted geometries with the same O4, O2, O3 atom displacements in the A_g , B_{2g} and B_{3g} modes or B-atom displacements in the E_{2g} phonon mode as in the case of $\text{YBa}_2\text{Cu}_3\text{O}_7$ or MgB_2 in transition to superconducting state.

Fig.6. Band structure of (a) $\text{YBa}_2\text{Cu}_3\text{O}_6$ and (b) AlB_2 at the same distorted geometries as it corresponds to nuclear displacements in superconducting compounds $\text{YBa}_2\text{Cu}_3\text{O}_7$ and MgB_2 , respectively.

In the case of deoxygenated YBCO – $\text{YBa}_2\text{Cu}_3\text{O}_6$, in contrast to superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$, combination of couplings to the A_g , B_{2g} and B_{3g} phonon modes leaves band structure without substantial change (cf. Fig.2a and 6a). The EP coupling is smaller ($\bar{u} \approx 1.0$ eV) than corresponding value for $\text{YBa}_2\text{Cu}_3\text{O}_7$ ($\bar{u} \approx 2.5$ eV). The ACP at Y point, in case of $\text{YBa}_2\text{Cu}_3\text{O}_7$ fluctuates across FL and yields substantial reduction of chemical potential $\rightarrow \mu_{\text{antad}} < \hbar\omega$. In the case of $\text{YBa}_2\text{Cu}_3\text{O}_6$, the SP does not fluctuate across FL and chemical potential remains larger than phonon energy spectrum ($\mu_{\text{ad}} > \hbar\omega$) and system remains in adiabatic state.

In this respect, the effect is similar also for diborides. In spite of σ bands splitting (cf. Fig.2b and 6b) and nearly the same value of EP interaction strength (calculated value for AlB_2 is $\bar{u} \approx 1.01$ eV/u.c) as that of MgB_2 ($\bar{u} \approx 0.98$ eV/u.c), the AlB_2 remains at EP coupling in adiabatic state as a non-superconducting compound. In this case, band structure fluctuation (bands splitting at EP coupling) does not decrease chemical potential and it remains at EP coupling still larger than vibration energy ($\mu_{\text{ad}} \gg \hbar\omega$) and consequently, there is no driving force for transition into antiadiabatic state.

II. 2.2. Nonadiabatic correction to orbital energies – gap opening in one-particle spectrum

For geometry $R_d = R_{\text{teq}}$, the one-particle spectrum with quasi-continuum of states at Fermi level is significantly changed. It concerns not only topology of the fluctuating band but also “immobile” bands, which through phonon mode r interact with the fluctuating band. Quasi-momentum counterpart of the corrections to one-particle spectrum (98b,c-part I, the shift of orbital energies), i.e. change in dispersion of band $\varphi_p(k)$ has the form,

$$\Delta\mathcal{E}(Pk') = \sum_{Rk'_1 > k_F} |u^{k-k'_1}|^2 (1 - f_{k'_1}) \frac{\hbar\omega_{k-k'_1}}{(\varepsilon_k^0 - \varepsilon_{k'_1}^0)^2 - (\hbar\omega_{k-k'_1})^2} - \sum_{Sk < k_F} |u^{k-k'}|^2 f_k \frac{\hbar\omega_{k-k'}}{(\varepsilon_k^0 - \varepsilon_k^0)^2 - (\hbar\omega_{k-k'})^2} \quad (9a)$$

for $k' > k_F$, and

$$\Delta\mathcal{E}(Pk) = \sum_{Rk'_1 > k_F} |u^{k-k'_1}|^2 (1 - f_{k'_1}) \frac{\hbar\omega_{k-k'_1}}{(\varepsilon_k^0 - \varepsilon_{k'_1}^0)^2 - (\hbar\omega_{k-k'_1})^2} - \sum_{Sk_1 < k_F} |u^{k-k_1}|^2 f_k \frac{\hbar\omega_{k-k_1}}{(\varepsilon_k^0 - \varepsilon_{k_1}^0)^2 - (\hbar\omega_{k-k_1})^2} \quad (9b)$$

for $k \leq k_F$

Replacement of discrete summation by integration introduces into derived relations density of states $n(\varepsilon_k)$, $\sum_k \dots \rightarrow \int n(\varepsilon_k) \dots$. It is of crucial importance in relation to the fluctuating band

since at the moment when ACP of the band approaches Fermi level, density of states at Fermi level is considerably increased, Fig.4. This effect could be related to possibility of van Hove singularity formation at Fermi level as it has been proposed in [16].

As the consequence of the shift of orbital energies (9a,b), the gap is opened (100 - part I) in one-particle spectrum at Fermi level. It is close to the k point, in which immobile band on the crude-adiabatic level intersects Fermi level. The gap has character of indirect gap as it follows from relations (9a,b). This fact can be observed by ARPES (occupied states below Fermi level) and inverse ARPES spectra (unoccupied states above Fermi level) or tunneling spectroscopy in the form of peaks that appear below and above Fermi level (spectral weight - density transfer) at decreasing temperature from above to below T_c . Since for corrected orbital energy holds, $\varepsilon_k = \varepsilon_k^0 + \Delta\varepsilon_k$, then for corrected DOS $n(\varepsilon_k)$ due to orbital energy shifts $\Delta\varepsilon_k$, the following relation can be derived straightforwardly,

$$n(\varepsilon_k) = \frac{1}{|1 + \partial(\Delta\varepsilon_k)/\partial\varepsilon_k^0|} n^0(\varepsilon_k^0) \quad (10)$$

The quantity $n^0(\varepsilon_k^0)$ in relation (10) stands for uncorrected DOS of particular band (density of states on crude-adiabatic level),

$$n^0(\varepsilon_k^0) = \left| \left(\partial\varepsilon_k^0 / \partial k \right)^{-1} \right| \quad (10a)$$

From (9a,b, 10a,b), it can be seen that dominant changes in DOS (regions with increased and decreased densities) can be expected within the energy distance up to $\pm \hbar\omega_r$ at the Fermi level, near to the k point where the band intersects Fermi level. The gap $\Delta(0)$, which is opened in one-particle spectrum, equals to the energy distance of the peaks that appear in corrected DOS of occupied and unoccupied states at the Fermi level.

Inspection of Fig.1a and 3a indicates that for basal-**a,b** plain, the dominant part of nonadiabatic corrections in the case of $\text{YBa}_2\text{Cu}_3\text{O}_7$ can be expected from EP interactions of occupied states ε_k of the fluctuating d- $p\sigma$ band with unoccupied states ε_k^* of the Cu1O1-derived $p\sigma$ band (and vice-versa) in Γ -Y and Γ -X directions. Interaction of the two d- $p\sigma$ bands that correspond to different Cu2-O2O3 layers, which are separated nearly by $8.3 \text{ \AA}^0$, can be expected to be negligibly small.

The DOS of Cu1O1- $p\sigma$ band in Γ -Y direction (**b**) at FL is $\bar{n}_{p\sigma-b}^0 \approx 0.04 \text{ states/eV}$ and $\bar{n}_{p\sigma-a}^0 \approx 0.03 \text{ states/eV}$ in Γ -X direction (**a**). The mean values of DOS for fluctuating d- $p\sigma$ band $\bar{n}_{d-p\sigma}^0$ in antiadiabatic state at FL and mean value of EP coupling $\bar{u}$ has been estimated above; $\bar{n}_{d-p\sigma}^0 \approx 2 \text{ states/eV}$ and $\bar{u} = 2.5 \text{ eV}$. The final DOS of Cu1O1- $p\sigma$ band in antiadiabatic state, calculated according to Eq. (10, 9a,b) is shown in Fig. 7. Energy distance between the peaks in DOS of Cu1O1- derived $p\sigma$ band, which arise on bonding and antibonding sites of energy spectrum, i.e. the gap that is opened in one-particle spectrum at 0 K is $\Delta_b(0) = 35.7 \text{ meV}$ in Γ -Y **b**-direction (Fig.7a) and $\Delta_a(0) = 24.2 \text{ meV}$ in Γ -X **a**-direction (Fig.7b). Calculated corrected DOS simulates **a/b** asymmetry of the ARPES spectra for $\text{YBa}_2\text{Cu}_3\text{O}_7$. The asymmetry for calculated gaps, i.e. the ratio $(\Delta_a(0)/\Delta_b(0))_{\text{theor}} \approx 0.68$ is very close to the experimental value (≈ 0.66) that has been recorded [17] for untwined $\text{YBa}_2\text{Cu}_3\text{O}_7$.

Fig.7. Corrected DOS of (a) the Cu1O1- derived $p\sigma$ band of $\text{YBa}_2\text{Cu}_3\text{O}_7$ in Γ -Y **b**- direction and (b) in Γ -X **a**-direction at the k point where the band intersects Fermi level.

If there is a phonon coupling with two different bands, which intersect Fermi level in a given direction of reciprocal lattice at points k_1 and k_2 , then two gaps are opened in one-particle spectrum near to these points. It is characteristic for MgB_2 with σ_2 and π -band gaps that are opened along Γ -K direction due to $\sigma_1 - \sigma_2$ and $\sigma_1 - \pi$ coupling mediated by the E_{2g} phonon mode. The Fig. 8 presents final DOS in Γ -K direction on antibonding site of the energy spectrum, calculated according to (10, 9a).

Fig.8. Corrected DOS of π band (peak at 2.2 meV) and of the σ_2 band (peak at 7.6 meV) of MgB_2 on antibonding site of the energy spectrum at the k points where the bands intersect Fermi level.

The mean value of DOS for fluctuating σ_1 band in antiadiabatic state $\bar{n}_{\sigma_1}^0 = 0.2$ states/eV has been used at the calculations. The uncorrected DOS of “immobile” σ_2 band at FL is $n_{\sigma_2}^0 \approx 0.02$ states/eV and basically the same DOS $n_{\pi}^0 \approx 0.02$ states/eV is for π band at FL. The overall EP coupling $\bar{u} = 0.95$ eV has been divided on two components, $\bar{u}_{\sigma-\sigma} = 0.7$ eV for σ_1 - σ_2 coupling and $\bar{u}_{\sigma-\pi} = 0.25$ eV for σ_1 - π coupling. As it can be seen from Fig. 8, two gaps are formed in **a-b** plane of MgB_2 . The larger half-gap $\Delta_{\sigma}(0)/2 \approx 7.6$ meV is opened in σ_2 band and smaller half-gap $\Delta_{\pi}(0)/2 \approx 2.2$ meV is opened in π band. The result simulates tunneling spectra at positive bias voltage and calculated half-gaps are in a good agreement with experimental high-precision measurements [18, 19].

Increase of the total electronic energy $\Delta E_d(R_d)$ related to nuclear displacement out-of-equilibrium on the crude-adiabatic level (3), is the only temperature independent correction to the total electronic energy. All the other corrections related to nuclear motion are temperature dependent. Due to thermal excitations, at some critical temperature T_c the nonadiabatic correction to electronic ground state energy (4), $\Delta E_{(na)}^0(R_d)$, becomes in absolute value smaller than $\Delta E_d(R_d)$,

$$|\Delta E_{(na)}^0(R_d)|_{T_c} \leq \Delta E_d(R_d) \quad (11)$$

Consequently, for $T > T_c$, system is stabilized at adiabatic equilibrium geometry R_{eq} , which is identical to the R_{eq} that correspond to high-symmetry structure on crude-adiabatic level. System is now in adiabatic state. It means that over T_c , band structure at Fermi level has to be represented by quasi-continuum of occupied and unoccupied states without the gap in one-electron spectrum that has been opened at 0 K. Temperature dependence of the gap (100-part I) in one-electron spectrum is represented by the equation,

$$\Delta(T) = \Delta(0) \tanh(\Delta(T)/4k_B T) \quad (12)$$

In the limit $\Delta(T) \rightarrow 0$, from (12) for critical temperature follows,

$$T_c = \Delta(0)/4k_B \quad (12a)$$

Based on Eq. (12a), for critical temperature of the adiabatic-antiadiabatic state transition follows; $T_c = 92.8$ K for $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $T_c = 39.5$ K for MgB_2 . Calculated critical temperatures are in a good agreement with the experimental critical temperatures of superconducting state transition recorded for $\text{YBa}_2\text{Cu}_3\text{O}_7$ [5] and MgB_2 [6].

III. Thermodynamic properties of antiadiabatic state

For temperatures $T < T_c$ when nonadiabatic correction to electronic energy (4,6) stabilizes ground state at distorted geometry $R_d = R_{req}$, system is in the antiadiabatic state and exhibits some remarkable properties.

1/ in the antiadiabatic state, ground state total electronic energy of system is geometrically degenerate. Distorted nuclear structure, related to couple of nuclei in the phonon mode r that induces transition into antiadiabatic state, has fluxional character. There exist an infinite number of different - distorted configurations of this couple of nuclei in the phonon mode r and all these configurations, due to translation symmetry of the lattice, have the same ground state energy. Position of the involved displaced couple of nuclei is on the perimeter of circles with the centers at R_{eq} (equilibrium on crude-adiabatic level) and with radii equal to $\Delta R = |R_{eq} - R_{d,cr}|$.

2/ the second property of the ground state of system in the antiadiabatic state is even more striking. The effective EP interaction that covers the Q , P -dependence has the form that is for boson vacuum represented by the second term in (96 – part I), i.e.

$$\Delta H'_{\langle e-p0 \rangle}(dg) = \sum_{rPR} \left((\varepsilon_P^0 - \varepsilon_R^0) \left(|c_{PR}^r|^2 + |\hat{c}_{PR}^r|^2 \right) - 2\hbar\omega_r \text{Re}(\hat{c}_{PR}^r c_{PR}^{r*}) \right) N[a_P^+ a_P] \quad (13)$$

After substitution for transformation coefficients $c_{PR}^r, \hat{c}_{PR}^r$ (Appendix C2a, C2b – part I) and algebraic manipulation, the quasi-momentum form of this term is,

$$\Delta H'_{\langle e-p0 \rangle}(dg) = \sum_{k,q} |u^q|^2 \left\{ (\varepsilon_k^0 - \varepsilon_{k-q}^0) / \left[(\varepsilon_k^0 - \varepsilon_{k-q}^0)^2 - (\hbar\omega_q)^2 \right] \right\} N[a_k^+ a_k] \quad (13a)$$

For extreme nonadiabatic limit $\hbar\omega_q / |\varepsilon_k^0 - \varepsilon_{k-q}^0| \rightarrow \infty$, from (13a) follows;

$$\Delta H'_{\langle e-p0 \rangle}(dg)_{na} \rightarrow 0 \quad (13b)$$

It means that for electrons that satisfy condition of extreme nonadiabaticity with respect to interacting phonon mode r in particular direction of reciprocal lattice where the gap in one-electron spectrum has been opened, the electron (nonadiabatic polaron)-renormalized phonon interaction energy equals zero. Expressed explicitly, in the presence of external electric potential, dissipation-less motion of relevant valence band electrons (holes) on the lattice scale can be induced in the respective direction of reciprocal lattice at the Fermi level, while motion of nuclei remains bound to fluxional revolution over distorted, energetically equivalent, configurations. The electrons move in a form of bipolarons, i.e. as a polarized cloud of intersite charge density distribution (see section V of this paper). Due to temperature increase, thermal excitations of valence band electrons to conduction band induce sudden transition from the antiadiabatic state into adiabatic state (11) at $T = T_c$.

In the adiabatic state, properties of the electrons are in sharp contrast with the properties of electrons in antiadiabatic state. The electrons in this case, are in a valence band more or less, tightly bound to respective nuclei at adiabatic equilibrium positions and their motion in conducting band is restricted by scattering with interacting phonon modes. It corresponds to situation at $T > T_c$. For extreme adiabatic limit $\hbar\omega_q / |\varepsilon_k^0 - \varepsilon_{k-q}^0| \rightarrow 0$, from (13a) for electron-phonon interaction energy in this case follows,

$$\Delta H'_{\langle e-p0 \rangle} (dg)_{ad} \rightarrow \sum_{qk} |u^q|^2 \frac{1}{(\varepsilon_k^0 - \varepsilon_{k-q}^0)} \quad (13c)$$

Expression (13c) represents basically energy of standard adiabatic polarons that contribute to the total energy of system.

3/ as it has been shown, at formation of the antiadiabatic ground state, electronic energy is decreased and for involved band(s) the gap in one-particle spectrum has been opened (shift of orbital energies). This fact has to be reflected by change of related thermodynamic properties. In particular, for electronic specific heat

$$C_{V,el}(T) = \frac{d\Delta E_{(na)}^0}{dT} = T \frac{dS}{dT} \quad (14)$$

can be derived

$$C_{V,el}(T) = -\frac{\bar{n}(\varepsilon_{k_F})}{2} \frac{\Delta(T)}{\Delta(0)} \left(\frac{\Delta(T)}{dT} \right) \quad (14a)$$

At derivation of (14a) it has been assumed that for the band with gap opening, uncorrected density of quasi-continuum of occupied and unoccupied states at Fermi level is the same. Expression (14a) can be derived from the ground state energy correction (94-part I, or Eq.4 in this part), or from the basic statistical relation for entropy

$$S = -k_B \sum_k [f_k \ln f_k + (1 - f_k) \ln(1 - f_k)] \quad (14b)$$

In (14b), f_k is the Fermi-Dirac occupation factor of state $\varepsilon_k = \varepsilon_k^0 + \Delta\varepsilon_k$. Then for entropy related to formation of antiadiabatic state can be derived,

$$S = k_B \ln 2 - \bar{n}(\varepsilon_{k_F}) \frac{(\Delta(T))^2}{2T\Delta(0)} + 2k_B \bar{n}(\varepsilon_{k_F}) \ln \left(\cosh \frac{\Delta(T)}{4k_B T} \right) \quad (14c)$$

For temperature derivative of entropy holds,

$$\frac{dS}{dT} = -\frac{\bar{n}(\varepsilon_{k_F})}{2T} \frac{\Delta(T)}{\Delta(0)} \frac{d\Delta(T)}{dT} \quad (14d)$$

Electronic specific heat of system in antiadiabatic state (14a) obeys temperature dependence of electronic specific heat of superconductors and for the limit $T \rightarrow 0$ K, characteristic exponential behavior can be seen,

$$\lim(C_{V,el}(T))_{T \rightarrow 0} \approx \exp\left(-\frac{\Delta(0)}{2k_B T}\right) \quad (14e)$$

The density of states at Fermi level $\bar{n}(\varepsilon_{k_F})$ in (14a-d) represents mean value of corrected density of states close to the k -point where the peak in density of states has been formed. From practical reasons it can be approximated by mean value of density of states of the fluctuating band in ACP at the moment when it approaches Fermi level (antiadiabatic state) and density of occupied (unoccupied) quasi-continuum of states of the band that intersects Fermi level and interacts with fluctuating band through phonon mode r , $\bar{n}(\varepsilon_{k_F}) = \frac{1}{2}[n(\varepsilon_{k_c}^0)_{fb} + n(\varepsilon_{k_F \pm \Delta k}^0)]$. In the antiadiabatic state, density of states at Fermi level is

considerably increased since density of states of fluctuating band at ACP is usually high (possibility of van Hove singularity formation at Fermi level as it has been proposed in [16]).

4/ magnetic properties of system in the antiadiabatic state, in particular existence of the Meissner effect, do not follow automatically from the fact that motion of electrons in this state is dissipation-less (13b), i.e. with zero electric resistance $\rho = 0$ at finite-nonzero density of electric current j . According to Maxwell equations, it only indicates that time derivative of magnetic induction B is zero - $\frac{dB}{dt} = 0$. It means that $B = const$, but in general it does not mean that value of the constant is zero. On the other hand, system in antiadiabatic state can exhibits absolute diamagnetism and Meissner effect only if $B = 0$. In this case, there has to exists some critical value of external magnetic field H_c which destroy antiadiabatic state and induces transition of the system into adiabatic state (characteristic by finite-nonzero value of electric resistance $\rho \neq 0$ at finite-nonzero density of electric current j) like it occurs in the case of temperature increase above T_c . It also means that at critical temperature and above it, $T \geq T_c$, critical magnetic field has to be zero, $H_c(T \geq T_c) = 0$. It can be shown that antiadiabatic state exhibits this property.

From thermodynamics for critical magnetic field in this case follows,

$$\frac{H_c^2}{8\pi} = F_{(ad)} - F_{(na)} \quad (15)$$

In (15), $F_{(ad)}$ and $F_{(na)}$ stand for free energies of the system in adiabatic and nonadiabatic (antiadiabatic) state. Then,

$$F_{(ad)} - F_{(na)} = \Delta E_{(na)}^0 - TS \quad (15a)$$

From (14, 14a) follows,

$$\begin{aligned} \Delta E_{(na)}^0(T) &= \Delta E_{(na)}^0(0) + \int_0^T C_{V(el)}(T) dT = \Delta E_{(na)}^0(0) - \frac{\bar{n}(\varepsilon_{k_F})}{4\Delta(0)} ((\Delta(T))^2 - (\Delta(0))^2) = \\ &= -\frac{\bar{n}(\varepsilon_{k_F})}{4} \Delta(0) - \frac{\bar{n}(\varepsilon_{k_F})}{4\Delta(0)} ((\Delta(T))^2 - (\Delta(0))^2) \end{aligned} \quad (15b)$$

After substitution of (15b), (14c) into (15a) and algebraic rearrangements, for critical magnetic field at finite temperature T follows,

$$\begin{aligned} \frac{(H_c(T))^2}{8\pi} &= -\frac{\bar{n}(\varepsilon_{k_F})}{4} \Delta(0) - \frac{\bar{n}(\varepsilon_{k_F})}{4\Delta(0)} ((\Delta(T))^2 - (\Delta(0))^2) + \frac{\bar{n}(\varepsilon_{k_F})}{2} \frac{(\Delta(T))^2}{\Delta(0)} - \\ &- 2k_B \bar{n}(\varepsilon_{k_F}) T \ln \left(\frac{\Delta(0)}{((\Delta(0))^2 - (\Delta(T))^2)^{\frac{1}{2}}} \right) \end{aligned} \quad (15c)$$

At temperature 0 K, for critical magnetic field results,

$$(H_c(0))^2 = 2\pi\Delta(0)\bar{n}(\varepsilon_{k_F}) \quad (15d)$$

From (15c,d) the relation between critical magnetic fields at finite and zero temperature can be derived,

$$\left(\frac{H_c(T)}{H_c(0)}\right)^2 = \left[\left(\frac{\Delta(T)}{\Delta(0)}\right)^2 - \frac{8k_B T}{\Delta(0)} \ln \left(\frac{\Delta(0)}{((\Delta(0))^2 - (\Delta(T))^2)^{1/2}} \right) \right] \quad (16)$$

At critical temperature T_c , when due to thermal excitations the antiadiabatic state is suddenly changed into adiabatic state and above this temperature, critical magnetic field has to be zero, $H_c(T \geq T_c) = 0$. Since there is no gap in one-electron spectrum in metal-like adiabatic state, $\Delta(T \geq T_c) = 0$, then zero value of critical magnetic field follows directly from (15c,16). Derived equations show that system in the antiadiabatic state, beside zero value of electric resistance $\rho = 0$, has also specific property that is necessary for occurrence of the Meissner effect.

IV. Correction to electron correlation energy

The electron correlation energy (32a–part I) is the only correction, which stabilizes electronic ground state on crude-adiabatic level. As it has been shown, EP interactions give rise to additional corrections to electronic energy terms when system is in the antiadiabatic state. In particular, electronic ground state is stabilized at distorted nuclear configuration $R_d = R_{teq}$ and gap in one-electron spectrum is opened. The question remains, what is the influence of EP interactions on electron correlation energy. This effect is represented by two-particle correction, i.e. by correction to electron correlation energy (101b–part I), i.e.

$$\Delta H_{ep}'' = \sum_{R(k)S(k')} \sum_{kk'q\sigma\sigma'(q \neq 0)} |u^q|^2 \frac{\hbar\omega_q ((\varepsilon_{k+q}^0 - \varepsilon_k^0)(\varepsilon_{k'+q}^0 - \varepsilon_{k'}^0) - (\hbar\omega_q)^2)}{((\varepsilon_{k+q}^0 - \varepsilon_k^0)^2 - (\hbar\omega_q)^2)((\varepsilon_{k'+q}^0 - \varepsilon_{k'}^0)^2 - (\hbar\omega_q)^2)} N[a_{k+q,\sigma}^+ a_{k',\sigma'}^+ a_{k'+q,\sigma'} a_{k,\sigma}] \quad (17)$$

Without loss of generality, in what follows summation over bands is not explicitly indicated, but it should be kept in mind that k, k' can belong to the same as well as to different bands.

It is not immediately clear from the general form (17) if correction to electron correlation energy is negative or positive. For antiadiabatic system $|\varepsilon_{k'}^0 - \varepsilon_k^0| < \hbar\omega_{k'-k}$, denominators in (17) are positive and negative value of the matrix elements of this two-particle correction is reached for a reduced form if nominators are negative, i.e. if $(\varepsilon_{k+q}^0 - \varepsilon_k^0) = -(\varepsilon_{k'+q}^0 - \varepsilon_{k'}^0)$. Since $q \neq 0$, it can be reached if

$$q = -k - k' \quad (18)$$

Substitution of (18) into (17) and subsequent interchange $-k' \rightarrow k'$ ($\varepsilon_{-k'} = \varepsilon_{k'}$) results in the following reduced form of the correction to electron correlation energy,

$$\Delta H_{ep}''(red)_{na} = -2 \sum_{k > k_F, k' < k_F} |u^{k'-k}|^2 \frac{\hbar\omega_{k'-k} ((\varepsilon_{k'}^0 - \varepsilon_k^0)^2 + (\hbar\omega_{k'-k})^2)}{((\varepsilon_{k'}^0 - \varepsilon_k^0)^2 - (\hbar\omega_{k'-k})^2)} N[a_{k'\uparrow}^+ a_{-k'\downarrow}^+ a_{-k\downarrow} a_{k\uparrow}] \quad (19)$$

Expression (19) shows that due to EP interactions on the Q, P -dependent nonadiabatic level, this correction increases electron correlation energy (32 – part I) in the electronic ground state. This correction is due to pairs of electrons with opposite quasi-momentum and antiparallel spins ($k \uparrow, -k \downarrow$). It has to be noticed that it is the contribution of bi-excited

configurations $\{\Phi_{(k',-k') \rightarrow (k,-k)}\}$ (i.e. two-particle $(k \uparrow, -k \downarrow)$, two-hole $(k' \uparrow, -k' \downarrow)$ excited singlet states) to the electronic ground state that is represented by renormalized Fermi vacuum Φ_0 . Expressed explicitly, first nonzero contributions are from the matrix elements of the type $\langle \Phi_0 | \Delta H_{ep}'' | \Phi_{(k',-k') \rightarrow (k,-k)} \rangle$, i.e. contributions in the second order of perturbation theory. Now, $\{\varepsilon_k\}$ represent particle states that are occupied above Fermi level and $\{\varepsilon_{k'}\}$ are empty – hole states below Fermi level due to excitations. From the denominator of (19) it is clear that the largest contribution to the correlation energy correction is for pair of electrons at Fermi level when $|\varepsilon_{k'}^0 - \varepsilon_k^0| < \hbar\omega_{k'-k}$, i.e. for system that is in antiadiabatic state.

For the extreme antiadiabatic regime $|\varepsilon_{k'}^0 - \varepsilon_k^0| / \hbar\omega_{k'-k} \rightarrow 0$, from (19) for correction to electron correlation energy follows,

$$\Delta H_{ep}''(red)_{sna} = -2 \sum_{kk'} \frac{|u^{k'-k}|^2}{\hbar\omega_{k'-k}} N[a_{k'\uparrow}^+ a_{-k'\downarrow}^+ a_{-k\downarrow} a_{k\uparrow}] \quad (20)$$

The second extreme case is for strong adiabatic regime $\hbar\omega_{k'-k} / |\varepsilon_{k'}^0 - \varepsilon_k^0| \rightarrow 0$. At these circumstances, correction to electron correlation energy approaches zero value,

$$\Delta H_{ep}''(red)_{sad} = -2 \sum_{kk'} |u^{k'-k}|^2 \frac{\hbar\omega_{k'-k}}{(\varepsilon_{k'}^0 - \varepsilon_k^0)^2} N[a_{k'\uparrow}^+ a_{-k'\downarrow}^+ a_{-k\downarrow} a_{k\uparrow}] \rightarrow 0 \quad (21)$$

For an intermediate adiabatic regime (i.e. Q -dependent adiabatic level $|\varepsilon_{k'}^0 - \varepsilon_k^0| > \hbar\omega_{k'-k}$), for correction to electron correlation energy directly from the adiabatic form of this correction (second term in A32 – part I), or from (101 – part I) in the limit $\hat{c} = 0$ can be derived,

$$\Delta H_{ep}'' = \sum_{kk'q\sigma\sigma'} |u^q|^2 \frac{\hbar\omega_q}{(\varepsilon_{k+q}^0 - \varepsilon_k^0)(\varepsilon_{k'+q}^0 - \varepsilon_{k'}^0)} N[a_{k+q,\sigma}^+ a_{k',\sigma'}^+ a_{k'+q,\sigma'} a_{k,\sigma}] \quad (22)$$

The reduced form is,

$$\Delta H_{ep}''(red)_{ad} = -2 \sum_{kk'} |u^{k'-k}|^2 \frac{\hbar\omega_{k'-k}}{(\varepsilon_{k'}^0 - \varepsilon_k^0)^2} N[a_{k'\uparrow}^+ a_{-k'\downarrow}^+ a_{-k\downarrow} a_{k\uparrow}] \quad (22a)$$

Like for nonadiabatic Q, P -dependent case also for adiabatic Q -dependent level, correction to electron correlation energy is negative. By comparing (19) with (22a) it can be seen that nonadiabatic correction to electron correlation energy is in absolute value larger than corresponding adiabatic correction. More over for antiadiabatic state, when system is close to singular point in (19), nonadiabatic correction can be significant.

It means that along with crude-adiabatic correlation energy (32a–part I) also the correction to electron correlation energy (19) contributes to stabilization of antiadiabatic state - the ground state of the system at distorted nuclear geometry $R_d = R_{teq}$. It should be reminded, however, that even without account for the correction to electron correlation energy (that represents contributions of second and higher orders of perturbation theory), system is already stabilized in antiadiabatic state at distorted geometry due to correction to the ground state electronic energy (4), which represents zero-order correction in terms of perturbation theory. In this respect, increased electron correlation is the consequence of EP interactions that have induced transition of the system from adiabatic into antiadiabatic state.

At finite temperature, the product of Fermi-Dirac occupation factors has to be introduced into derived equations, $\sum_{kk'} \dots \rightarrow \sum_{kk'} f_k (1 - f_{k'}) \dots$. With increasing temperature from 0 K, the value of the correction (19) that is characteristic for antiadiabatic state decreases and at $T = T_c$ when system undergoes sudden transition from antiadiabatic state at distorted geometry $R_d = R_{teq}$ into

adiabatic state at undistorted geometry $R_0=R_{eq}$ and above this temperature, for correction to electron correlation energy holds corresponding T-dependent adiabatic form (22a). Above T_c , this correction along with crude-adiabatic correlation energy (32a–part I) stabilizes adiabatic ground state of system at undistorted - adiabatic equilibrium geometry $R_0=R_{eq}$.

V. Effective attractive electron-electron interactions, Cooper's pairs and bipolarons

From a formal stand-point, the expressions for correction to electron correlation energy (19) appear to be a kind of effective attractive electron-electron interactions. It can be compared to the Fröhlich effective Hamiltonian of electron – electron interactions [20],

$$H_{eff}''(Fr) = \sum_{kk'q\sigma\sigma'} |u^q|^2 \frac{\hbar\omega_q}{(\varepsilon_{k+q}^0 - \varepsilon_k^0)^2 - (\hbar\omega_q)^2} a_{k+q,\sigma}^+ a_{k',\sigma'}^+ a_{k'+q,\sigma'} a_{k,\sigma} \quad (23)$$

or to its reduced form that maximizes attractive contribution of electron – electron interactions,

$$H_{red}''(Fr) = 2 \sum_{kk'} |u^{k'-k}|^2 \frac{\hbar\omega_{k'-k}}{(\varepsilon_{k'}^0 - \varepsilon_k^0)^2 - (\hbar\omega_{k'-k})^2} a_{k'\uparrow}^+ a_{-k'\downarrow}^+ a_{-k\downarrow} a_{k\uparrow} \quad (23a)$$

This interaction term is either attractive or repulsive depending on the sign of denominator. For antiadiabatic conditions it represents effective attractive electron-electron interactions. In the limit of extreme antiadiabaticity $|\varepsilon_p^0 - \varepsilon_q^0|/\hbar\omega_r \rightarrow 0$, the form of the Fröhlich two-particle effective Hamiltonian (23) and the correction to electron correlation energy (17) are identical and equal to,

$$\lim_{\Delta\varepsilon/\hbar\omega \rightarrow 0} (\Delta H_{ep}'') = \lim_{\Delta\varepsilon/\hbar\omega \rightarrow 0} (H_{eff}''(Fr)) = - \sum_{kk'q\sigma\sigma'} \frac{|u^q|^2}{\hbar\omega_q} a_{k+q,\sigma}^+ a_{k',\sigma'}^+ a_{k'+q,\sigma'} a_{k,\sigma} \quad (23b)$$

Correction to electron correlation energy (17) has been derived in the explicit assumption of the dependence of electronic motion on nuclear coordinates and momenta, i.e. at the derivation very general Q,P -dependent form of the electronic Hamiltonian (see Appendix B – part I) has been used. On the other hand, at derivation of (23), starting form has been simple model Hamiltonian (39 - part I). However, instead of the simplest form of the EP interaction term (39b - part I), Fröhlich used more general form that can be written as (see [21]),

$$H_{ep} = \sum_{k,q,\sigma} [g_q^* b_q^+ a_k^+ a_{k+q} + h.c.] , \quad g_q^* = -g_q \quad (24)$$

This form explicitly introduces the EP interactions to be dependent not only on nuclear coordinates Q_q (like term 39b - part I) but also on nuclear momenta P_q ($b_q^+ = \frac{1}{2}(Q_q - P_q)$). In

this respect, correction to correlation energy (17) derived from general form of system Hamiltonian and term of the effective electron-electron interaction (23) derived by Fröhlich from model Hamiltonian (and corresponding reduced forms 19 and 23a) represents the same physical effect. The difference in the final forms (17 and 23) is due to different kind of canonical transformations used – see Appendix A.

Fröhlich's treatment of effective electron-electron interaction Hamiltonian with respect to development of theory of superconductivity is well known [22]. Within the free particle approximation, zero order contribution of the effective interaction Hamiltonian (23) yields correction to ground state electronic energy that is formally identical with $\Delta E_{(na)}^0$ as it has been derived in the present work (4, or 94 – part I), i.e.

$$\Delta E = \langle \Phi_0 | H_{red}''(Fr) | \Phi_0 \rangle = 2 \sum_{kk'} |u^{k'-k}|^2 f_k (1 - f_{k'}) \frac{\hbar \omega_{k'-k}}{(\varepsilon_{k'} - \varepsilon_k)^2 - (\hbar \omega_{k'-k})^2}, k < k_F, k' > k_F \quad (25)$$

It was derived by Fröhlich also directly, without canonical transformation, in the form of correction to ground state electronic energy in second order of perturbation theory (E_2 term for boson vacuum in [22]). Search for electronic distribution $f_k, f_{k'}$, over the original adiabatic (metal-like) one-electron spectrum resulted in energy minimalization (extreme negative value of E_2) of electronic ground state that was supposed to be superconducting state. Similar results were obtained also by Bardeen [23] based on a variational approach. Results, even correctly describe isotope effect, have never been accepted as relevant for superconductivity. The reason is related to the fact that on this level of approximation a phase with superconducting properties, including gap formation, can not be identified and energy difference between electronic state that was supposed to correspond to superconducting state and normal ground electronic state (condensation energy) has been found too large. In this connection, it was concluded by Fröhlich [20] that free particle approximation cannot be expected to be applicable to study details of the energy spectrum, specific heat and magnetic properties.

Different treatment of this problem has been elaborated within the BCS theory [24]. This theory and its modifications are well known and in spite of serious problems with high- T_c superconductors, it remains the basic framework of microscopic mechanism of superconductivity until present. It is not the aim to analyze the BCS theory, but with respect to the results presented in this paper some key points underlying the BCS theory should be reminded. The best platform for it offers general derivation based on the Bogoljubov - Valatin canonical transformations of the BCS model Hamiltonian - see Appendix B.

Let us first point-out relevant results derived within antiadiabatic theory as presented in this paper. Ground state of superconductors and resulting thermodynamics (superconducting properties) are directly related to the antiadiabatic state that arises in system with complex electronic structure as a consequence of band structure fluctuation due to EP interactions for this class of solids. Transition into antiadiabatic state is connected to considerable decrease of Fermi energy (chemical potential μ) with respect to Fermi energy of normal-adiabatic state, $\mu_{s(antad)} < \hbar \omega_r < \mu_{n(ad)}$. The EP interactions that drive the adiabatic $\rightarrow$ antiadiabatic state transition decrease electronic energy and stabilize system (4) at a new equilibrium - distorted nuclear configuration in relevant phonon mode(s). In order to study antiadiabatic state it is necessary to introduce dependence of electronic motion on instantaneous nuclear positions Q as well as on instantaneous nuclear momenta P . In antiadiabatic state not only electronic energy of the ground state is stabilized and chemical potential μ is reduced, but also the original adiabatic HF one-particle spectrum $H_{(1)ad} = \sum_k (\varepsilon_k^0)_{R_0} N[\bar{a}_k^+ \bar{a}_k]$ is changed;

$$H_{(1)nad} = \sum_k (\varepsilon_k^0 + \Delta \varepsilon_k)_{R_d} N[a_k^+ a_k] \quad (26)$$

One-particle spectrum (26) corrected by the correction term $\Delta \varepsilon_k$ (9a,b), that incorporates the effect of EP interactions on electronic structure in antiadiabatic state, is crucial quantity that in full extend determines thermodynamic properties (gap in one-particle spectrum, specific heat, entropy, internal energy, free energy and critical magnetic field), i.e. superconducting state of the system.

As it follows from the Bogoljubov-Valatin canonical transformations (Appendix B), the crucial point underlying formulation of the BCS theory is directly associated with possibility to derive one-particle spectrum in the form of (B17). Also in this case, the original adiabatic HF one-particle spectrum is corrected (B16c). The correction Δ_k (B16b) reflects the effect of effective attractive electron-electron interactions on single-particle excitation spectrum, which determines superconducting properties of the system. This solution can be derived, however,

only if it is correct to assume that ensemble of Cooper's pairs lying in thick layer ($\approx \hbar\omega$) at Fermi level can be separated-out as a subsystem that is independent of the rest of complex electronic structure of the system and at the same time to assume that chemical potential of the system in normal (adiabatic) metal state is the same as chemical potential of the system in superconducting state, i.e. $\mu_s = \mu_n$, (B22a). Independence of the subsystem of Cooper's pairs is expressed by condition (B20), which introduces electron-electron interactions to be zero outside the relevant interval and constant attractive ($-V$) inside it. However, from the standpoint of complex electronic structure of metals, system is adiabatic and in the limit of strong adiabaticity ($\hbar\omega/|\Delta\epsilon_{kk'}| \rightarrow 0$) the Fröhlich effective electron-electron interactions term (23), which is valid for complex structure, goes to zero. On the other hand, correction to electron correlation energy, as derived in this paper, expresses more precisely the influence of nuclear motion on electron correlations than the Fröhlich effective electron-electron interaction term. It has been shown above (and also derived by Wagner in the adiabatic Q -dependent representation [25]) that for intermediate adiabatic regime this correction (even small) is always negative (22a), in contrast to the Fröhlich term which is in this regime positive. But, as it follows from (22a), in spite that the main attractive contribution is due to couple of states $|\Delta\epsilon_{kk'}| \approx \hbar\omega$, there are still nonzero attractive contributions of couple of states outside this region. Within the BCS solution, condition (B20) with constant attractive value inside and zero outside is crucial, however. It can be seen from the derivation of distribution function (B16a), i.e. u_k^2, v_k^2 coefficients that determine distribution of the Cooper's pairs in superconducting ground state. In order to derive this distribution, which decreases ground state energy, the external constrain (B14) has to be fulfilled. It means that the Hamiltonian (B11) of two-particle excited states (pair-excitations) has to be zero. Since pair-excited states, $\gamma_{k\uparrow}^+ \gamma_{-k\downarrow}^+ |\Theta\rangle$, like single-particle excited states, are "good" excited states (orthogonal to the ground state $|\Theta\rangle$), there is no physical reason to exclude these states from excitation processes. Then, constrain (B14) means that pair-excitation energies in (B11) are zero over the relevant energy interval $\hbar\omega_D < |\xi_k|$, i.e. $E_k^{(2)} = 0$. It holds only in the assumption that all Cooper's pairs in this energy interval are stabilized by the same value of interaction energy, i.e. $V = \text{const}$, (B20). Any other assumption does not yield superconducting solution. It can be shown straightforwardly that e.g. assumption of the same excitation spectrum for single-particle and two-particle excitations, i.e. $E_k = E_k^{(2)} \neq 0$ in (B10, B11), yields distribution coefficients u_k^2, v_k^2 in the form substantially different from the BCS solution (B16a). In relation to the assumption of $V = \text{const}$ (B20), also introduction of the cutoff energy $\hbar\omega_D$ as the upper integration limit at solution of integral form of the gap equation (B18) has nontrivial physical meaning. Basically it means isolation of the subsystem of Cooper's pairs in the antiadiabatic state (i.e. introduction of separate chemical potential μ for the subsystem), independently of the complex system that itself is in the adiabatic state. Since existence of Cooper's pairs fully determine superconducting state of the system, then this assumption contradicts the other crucial requirement of the BCS theory, i.e. the assumption (B22a) of the equality of chemical potentials in normal (adiabatic) and superconducting state, $\mu_N = \mu_S$. Within the BCS solution only if these assumptions hold, system can be stabilized in superconducting state (B23) at 0 K. Solution for finite temperatures is then straightforward. Excited states are realized by thermal population of corrected Hartree-Fock one-particle states by single (free) electrons. However, Cooper's pairs excitations are possible only in the indirect way, as the destruction of pairs and formation of two independent electrons in excited single-particle states, k' and $-k'$. Excited particles obey standard Fermi-Dirac statistics, (B24).

This is also the result of the original derivation [24]. The possibility of pair excitations has been formally considered there, but minimization of the free energy has resulted in the statistics of excited quasi-particles that corresponds to the standard fermions (see, eq.3.25 in [24]). Corrected Hartree-Fock one-particle states along with Fermi-Dirac statistics determine directly thermodynamics (i.e. specific heat, entropy, free energy and existence of critical magnetic field) in the way that is formally identical with the derivation of thermodynamic properties of antiadiabatic state presented in section V of this paper.

Recent experimental results of high T_c cuprates, in particular the high-resolved ARPES [26-28] and theoretical studies of band structure fluctuation of MgB_2 [29-33] and $YBa_2Cu_3O_7$ [34] indicate that validity of the key assumptions at derivation of the BCS theory and BCS-like theories is violated. It is related mainly to the crucial assumption of constant chemical potentials in normal and superconducting state ($\mu_N = \mu_S$) at derivation of the BCS solution. Not only results of ARPES and band structure fluctuation are indicative, but more over from the standpoint of thermodynamics a phase transition can be realized only if chemical potentials of considered phases are different. In this particular case it means that transition from normal to superconducting state can be realized only if $\mu_N > \mu_S$. In contrast to the BCS theory, this condition is in a natural way incorporated in the *ab initio* theory of complex electronic ground state of superconductors at transition from adiabatic into antiadiabatic state, $\mu_{ad} > \mu_{antad}$.

In this context, stabilized antiadiabatic ground state at distorted geometry indicates a need to reconsider applicability of the idea of Cooper's pairs for development of microscopic theory of superconductivity. The Q, P -modified theory of EP interactions that consider in a consistent way complex electronic structure of studied system, yields for antiadiabatic ground state formally similar equations as derived in the BCS theory for superconducting state. As it follows from the results presented in sections II-IV of this paper, the underlying physics is substantially different, however. Instead of the Cooper's pairs, the supercarriers appear to be rather mobile valence band bipolarons that are situated in tin layer ($< \hbar\omega$) below the Fermi level. The bipolaron theory of superconductivity has been proposed already before discovery of high- T_c superconductors [35a-c] and it is advocated by Alexandrov mainly for strong EP coupling regime in relation to superconductivity of high- T_c cuprates [36, 37 and referencies therein].

Results of Q, P -modified *ab initio* theory of complex electronic ground state of superconductors indicate that formation of mobile bipolarons is not restricted for high- T_c cuprates only, but it is rather an inherent property of a system in the antiadiabatic electronic ground state. The bipolarons arise as polarized intersite charge density distribution that can move over lattice without dissipation due to geometric degeneracy (fluxional structure) of the antiadiabatic ground state at distorted nuclear configurations. Formation of polarized intersite charge density distribution at transition from adiabatic into antiadiabatic state is reflected by corresponding change of the wave function. For spinorbital (band) $\varphi_{R(k)}$ holds relation (92 – part I), i.e.

$$\begin{aligned} |\varphi_p(x, Q, P)\rangle &= a_p^+(x, Q, P)|0\rangle = \left(\bar{a}_p^+ - \sum_{rR} c_{pR}^r \bar{Q}_r \bar{a}_R^+ - \sum_{\bar{r}R} \bar{c}_{pR}^r P_r \bar{a}_R^+ + O(\bar{Q}^2, \bar{Q}P, P^2) \right) |0\rangle = \\ &= |\varphi_p(x, 0, 0)\rangle - \sum_{rR} c_{pR}^r \bar{Q}_r |\varphi_R(x, 0, 0)\rangle - \sum_{\bar{r}R} \bar{c}_{pR}^r P_r |\varphi_R(x, 0, 0)\rangle + \dots \end{aligned} \quad (27)$$

At transition into antiadiabatic state $|\mathcal{E}_S^0(k_c) - \mathcal{E}_F^0|_{R_{eq} \pm Q} \ll \hbar\omega_r$, coefficients c_{RS}^r of Q -dependent transformation matrix become negligibly small and absolutely dominant for modulation of (crude)adiabatic wave function are in this case coefficients $\hat{c}_{RS}^r$ of P -dependent transformation matrix (Appendix C– part I). For simplicity, let to consider that transition into antiadiabatic state is driven by coupling to a phonon mode r with stretching vibration of two atoms (e.g. B-

B in E_{2g} mode of MgB_2 , or vibration motion of O2, O3 in Cu-O planes - B_{2g} , B_{3g} modes of YBCO). Let m_1 and m_2 are equilibrium site positions of involved nuclei on (crude)adiabatic level and d_1 and d_2 are nuclear displacements at which crossing into antiadiabatic state occurs. At these circumstances, the original crude-adiabatic wave function $\varphi_k^0(x,0,0)$ is changed in a following way,

$$\varphi_k(x, Q, P) \propto \left(1 + \sum_q u^{[q]} \frac{\hbar \omega_q}{(\hbar \omega_q)^2 - (\varepsilon_k^0 - \varepsilon_{k+q}^0)^2} (P_1 e^{iq \cdot [x - (m_1 - d_1)]} + P_2 e^{iq \cdot [x - (m_2 + d_2)]}) \right) \varphi_k^0(x, 0, 0) \quad (27a)$$

In (27a), site approximation for momentum has been used, i.e. $P_q \propto (sign.q) \sum_m P_m e^{iq \cdot m}$.

In antiadiabatic state, for particular k and proper q values, nonadiabatic prefactors under summation symbol in (27a) can be large. The prefactors, i.e. coefficients of P -dependent transformation matrix, reflect influence of nuclear kinetic energy on electronic structure (Appendix B,C- part I). At the dominance of these contributions (antiadiabatic state), strong increase in localization of charge density appears at distorted site-positions for x equal to $(m_1 - d_1)$ and $(m_2 + d_2)$. It induces (or increases) intersite polarization of charge density distribution. Intersite charge density polarization at different nuclear configurations on perimeters of flux-circles (see Fig. 5) in case of MgB_2 is shown in Fig.9.

Fig.9. Valence electron iso-density lines of MgB_2 in **a,b**-plane calculated for (a) adiabatic equilibrium structure and (b-d) for different B-B atoms configurations on perimeters of flux-circles. Fig.9e represents larger lattice segment at the distortion (d). White regions correspond to lowest electron density.

As it has been mentioned in section II and III, there is infinite number of energetically equivalent displacements d_1 , d_2 of involved couple of nuclei (fluxional structure). Energetically equivalent geometrical positions of the involved displaced couple of nuclei is on the perimeter of circles centered at m_1 and m_2 with radii d_1 and d_2 , respectively. It enables, due to translation symmetry of the lattice, dissipation-less motion of increased polarized intersite charge density (while motion of involved nuclei remains bound to revolution over perimeters of the respective circles) until system remains in antiadiabatic state - i.e. for temperatures $T < T_c$.

Increase of temperature above T_c induces transition from the antiadiabatic state into adiabatic state. At these circumstances coefficients of P -dependent transformation matrix equal zero. System is stabilized at adiabatic equilibrium geometry with nuclear site-positions m_1 and m_2 . The modulation of the wave function is now possible only through coefficients c_{RS}^r of Q -dependent transformation matrix. These are very small also in adiabatic state (see Appendix C

–part I) and cannot induce significant change in localization of charge distribution. More over, even if polarized intersite charge density exists already on crude adiabatic level (this is determined by the inner structure of wave function $\varphi_k^0(x,0,0)$), this polarization is immobile and localized between sites m_1 and m_2 . Modulation through coefficients c'_{RS} does not increase polarization of intersite charge density distribution and does not change at all the character of its immobility.

VI. Discussion and conclusion

From a formal standpoint there is no restriction on application of the McMillan's formula, which is very good approximation for T_c of elementary metals and their alloys [38], also for calculation of critical temperature of high- T_c superconductors within the BCS-generic framework. It has been shown [39] that in strong-coupling regime $\lambda \gg 1$, T_c can be as large as $k_B T_c = \hbar \omega \lambda^{1/2} / 2\pi$. However, in reality there is problem with correct estimation of Coulomb pseudopotential μ^* and with unrealistically large values of λ that would match high experimental T_c of novel superconductors. More over, new class of superconductors, e.g. cuprates, fullerides and MgB_2 are systems that are rather pseudo-adiabatic with sizeable adiabatic ratio $\omega/E_F < 1$, in contrast to elementary metals where adiabatic condition $\omega/E_F \ll 1$ is perfectly fulfilled. This situation indicates importance of nonadiabatic contributions at calculation of EP interactions within the BOA, an effect that is beyond the standard Migdal approach. Formulation of the nonadiabatic theory of superconductivity by Pietronero and coworkers [40a-e], which accounts for vertex corrections and cross phonon scattering (beyond Migdal approximation), has solved this nontrivial problem by generalization of Eliashberg equations. The theory, which is nonperturbative in λ and perturbative in $\lambda \omega_d / E_F$, has been applied at simulation and interpretation of different aspects of high- T_c superconductivity [41a-e]. Basically, it can be concluded that accounts for nonadiabatic effects in quasi-adiabatic state $\omega/E_F \leq 1$ is able to simulate different properties of high- T_c superconductors, including high-value of T_c , already at relatively moderate value of EP coupling, $\lambda \approx 1$. More over, it has also been shown that increased electron correlation is important factor that makes corrections to vertex function positive, which is in this context crucial for increasing T_c .

Nonetheless, an elegant treatment of high- T_c superconductivity within the nonadiabatic theory faces serious problem related to possibility of polaron collaps of the band and bipolaron formation. According to bipolaron theory of Alexandrov [35-37,42], polaron collaps occurs already at $\lambda \approx 0.5$ for uncorrelated polarons and even at smaller value for a bare EP coupling in strongly correlated systems. For $\omega/E_F \leq 1$, or $\lambda \geq 1$ and for $\omega/E_F \geq 1$ at whatever small value $\lambda \ll 1$, the nonadiabatic polaron theory has been shown to be basically exact [42]. Bipolarons can be simulataneously small and light in suitable range of Coulomb repulsion and EP interaction [43]. These results have important physical consequences. There are arguments that effect of polaron collaps cannot be covered through calculation of vertex corrections due to translation symmetry breaking and mainly, polaron collaps changes possible mechanism of pair formation, i.e. instead of BCS scenario with Cooper pair formation, the BEC with mobile bipolarons (charged bosons) becomes operative.

Experimental ARPES study of high- T_c cuprates [e.g. 26-28] and theoretical results of low-Fermi energy band structure fluctuation [e.g.32-34,44] for different groups of superconductors indicate that electron coupling to pertinent phonon modes drive system from adiabatic into

antiadiabatic state $\omega/E_F \geq 1$. At these circumstances, not only ME approximation is not valid, but basic adiabatic BOA does not hold. It implicates that current microscopic theories build on effective model Hamiltonians that tacitly assume validity of the BOA, including BCS theory and models of strongly correlated electrons, are inadequate for correct description of the ground electronic state of superconductors.

The EP interactions driven transition from adiabatic into antiadiabatic state indicates that in some region of k -space, nuclear motion dynamics becomes crucial for electronic state. At these circumstances, electronic motion has to be studied as explicitly dependent on instantaneous nuclear coordinates as well as on instantaneous nuclear momenta. It enables nonadiabatic Q, P -dependent modification of the BOA as presented in this paper. Based on this modification, the *ab initio* theory of complex electronic ground state of superconductors has been presented.

It has been shown that due to EP interactions, which drive system from adiabatic into antiadiabatic state, adiabatic symmetry is broken and system is stabilized in the antiadiabatic state at distorted geometry with respect to the adiabatic equilibrium high symmetry structure. Stabilization effect is due to participation of nuclear kinetic energy term, which is expressed through the coefficients $\hat{c}_{AI}^r$ of P -dependent transformation matrix. The antiadiabatic ground state at distorted geometry is geometrically degenerate with fluxional nuclear configuration in the phonon modes that drive system into this state. It has been shown that while system remains in antiadiabatic state, nonadiabatic polaron – renormalized phonon interactions are zero in well defined k -region of reciprocal lattice. Along with geometric degeneracy of the antiadiabatic state it enables formation of mobile bipolarons (in a form of polarized intersite charge density distribution) that can move over lattice in external electric potential as supercarriers without dissipation. More over, it has been shown that due to EP interactions at transition into antiadiabatic state, k -dependent gap in one-electron spectrum has been opened. Gap opening is related to the shift of the original adiabatic Hartree-Fock orbital energies and to the k -dependent change of density of states of particular band(s) at the Fermi level. The shift of orbital energies determines in a unique way one-particle spectrum and thermodynamic properties of a system. It has been shown that resulting one-particle spectrum yields all thermodynamic properties that are characteristic for system in superconducting state, i.e. temperature dependence of the gap, specific heat, entropy, free energy and critical magnetic field. The k -dependent change of the density of states at the Fermi level in transition from adiabatic (nonsuperconducting) into antiadiabatic state (superconducting) can be experimentally verified by ARPES or tunneling spectroscopy as spectral weight transfer at cooling superconductor from temperatures above T_c down to temperatures below T_c .

Results of the *ab initio* theory of antiadiabatic state have shown that the Fröhlich's effective attractive electron-electron interaction term represents correction to electron correlation energy in transition from adiabatic into antiadiabatic state due to EP interactions. Analysis of this term has shown that increased electron correlation is a consequence of stabilization of the system in superconducting electronic ground state, but not the reason of its formation.

The question remains if transition into antiadiabatic state is a general property valid for high, as well as for low- T_c superconductors. So far, the EP interactions-based band structure fluctuation that induces formation of antiadiabatic state $\omega/E_F \geq 1$ is well documented only for MgB_2 [29-33, 44]. For cuprates, as it is described in the present work, this effect has been identified for YBCO [34]. Unpublished results show that transition into antiadiabatic state related to EP interactions-based band structure fluctuation can also be identified in low- T_c superconductors, e.g. YB_6 [45] and Nb. Confirmation of these findings requires independent study of EP interactions-based band structure fluctuation for a wider group of superconductors, however.

There is also some controversy at interpretation of ARPES and tunneling spectra of novel class of superconductors. The point is, if single-particle spectral function seen by ARPES (and by differential conductance of tunneling spectroscopy) can be compatible with picture of (bi)polarons. There are the results, however, which show that single-particle spectral function derived for pure bipolaronic system describes all essential features of tunneling and ARPES spectra of cuprates [46, see also 37 and discussion therein].

Also the results of one-particle spectra calculation for $\text{YBa}_2\text{Cu}_3\text{O}_7$ and MgB_2 in the antiadiabatic state (Eq. 9 and 10 and Figs. 7, 8 of the present work), are compatible with bipolaronic picture of superconducting ground state. Appearance of narrow peak in corrected DOS at Fermi level of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and asymmetry in **a**, **b** directions are compatible with the experimental ARPES spectra [17]. One can argue, however, that the position of “superconducting” (SC) peak in the Γ -X **a**-direction (25-28 meV) and Γ -Y **b**-direction (~ 44 meV) of the experimental spectra (Fig.3 in [17]) is not the same as the position of peaks calculated for corrected DOS in the present work (24.2 meV- Fig.7b and 35.7 meV-Fig.7a). In this connection, it has to be realized that experimental spectra [17] are superposition of at least two spectral functions, that of SC state and very intensive surface state (SS) near to Fermi level. It is obvious that numerical fit of the overall spectral feature, without knowledge of exact half-width of spectral lines, mutual intensities and peak positions of contributing components, is not unambiguous. It means that SC peak position in the overall spectra need not correspond to the DOS maximum of “bare” SC state, i.e. if sample would be without surface state. In this respect, also appearance of peak-dip-hump feature of the spectrum in Γ -X **a**-direction after subtracting SS state contribution (Fig.3b in [17]) can as well be the result of numerical fit. It is hard to compare this fit to intrinsic peculiar peak-dip-hump spectral feature of Bi2212 that is “pure” - without presence of any surface state. The fact that Bi2212 is without CuO chains but with CuO_2 planes, does not mean that eventual peak-dip-hump spectral appearance in case of $\text{YBa}_2\text{Cu}_3\text{O}_7$ must be of CuO_2 planes origin. It should be stressed that the couple of $\text{Cu}(2)\text{O}(2)\text{O}(3)$ planes-derived ($d_{x^2-y^2} - p\sigma$) bands in the case of $\text{YBa}_2\text{Cu}_3\text{O}_7$ intersects Fermi level in the S-X and S-Y directions (see.e.g.[47] and Fig.1a in the present work). The EP coupling induces fluctuation of the ACP in one of these band across Fermi level in the Y point (Fig. 1a $\leftrightarrow$ 3a). In the X- Γ **a**-direction (and Y- Γ **b**-direction), there is only chain oxygen $\text{Cu}(1)\text{O}(1)$ -derived $p\sigma$ band that intersects Fermi level. Peak formation (and gap opening) in chain oxygen $\text{Cu}(1)\text{O}(1)$ -derived $p\sigma$ band near Fermi level at transition into superconducting state in the X- Γ **a**-direction (Y- Γ **b**-direction) has been calculated in the present work (Fig. 7b, a). It is in agreement with the original assignment of the intense peak at Fermi level to the CuO chain oxygen band at interpretation of polarized ARPES data recorded for untwined $\text{YBa}_2\text{Cu}_3\text{O}_7$ [48]. It should be stressed, however, that it does not mean that in $\text{YBa}_2\text{Cu}_3\text{O}_7$ the CuO chains are superconducting. As it has been discussed on the other place of this work, supercarrier motion is bound to CuO_2 plains in the form of mobile cloud of intersite charge density polarization (bipolarons).

In the case of MgB_2 , the DOS of σ and π band in antiadiabatic state are corrected due to σ_1 - σ_2 and σ_1 - π EP interactions. It results in formation of 2 peaks, at 2.2 meV for corrected π band DOS and at 7.6 meV for corrected σ_2 band DOS – Fig.8. This result is fully compatible with the high-precision tunneling spectra at positive bias voltage recorded for MgB_2 [18, 19]. Experimental position of the peaks for differential conductance is in the range of 1.9-2.8 meV for π band and 7-7.5 meV for σ band.

Although the present work does not deal with theory of ARPES or tunneling spectra of superconductors, the legitimate question is if emerging single-particle spectrum at transition into antiadiabatic state (corrected DOS, eqs. 9, 10) is able, in principle, to cover such peculiar spectral feature as e.g. peak-dip-hump character and pseudogap in spectra of Bi2212. The form of corrected DOS (9, 10) offers positive answer. The peak-dip-hump feature of spectrum

below Fermi level can emerge from (9b) if both terms contribute to the correction, while contribution of the first term is dominant and contribution of the second term is not negligibly small. Dominance of the first term at transition into antiadiabatic state is mainly due to increased DOS of fluctuating band at the Fermi level (ACP approaches Fermi level). In case when contribution of the second term is negligibly small, only single intensive peak appears in corrected DOS. Presence of pseudogap in experimental spectra of Bi2212, seems to be related to intrinsic complex electronic structure of this material in quasi-adiabatic state that is covered in the term $n^0(\varepsilon_k^0)$ of (10). Temperature-dependant spectral simulation [49], based on the Eq.(9b,10) with Lorentzian line-shape form, has shown that antiadiabatic theory is able to reproduce the basic ARPES spectral character of Bi2212, including peak-dip-hump feature and pseudogap.

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Appendix A: The Fröhlich effective Hamiltonian of electron – electron interactions

The Fröhlich transformation is of the following standard type,

$$T : U^\dagger H(A_\mu) U \equiv \tilde{H}(A_\mu) = H(U^\dagger(A_\nu) A_\mu U(A_\nu)) .$$

The model Hamiltonian (39 – part I) is transformed in an effort to remove interaction term H_{ep} , i.e. $[H_0, S] + H_{ep} = 0$ (see [21]). Generator S of canonical transformation

$$U = \exp S = \exp \left(\sum_{k,k+q} \Lambda_{k,k+q} \right) \text{ has been used in the form [21],}$$

$$S = - \sum_{k,k+q} \left[\frac{g^*(-q)}{(\varepsilon_k^0 - \varepsilon_{k+q}^0) + \hbar\omega_{k+q}} b_q^+ a_k^+ a_{k+q} - h.c. \right], \quad g(q) = g(|q|) = -g^*(|q|), \quad q = k' - k \quad (A1)$$

The elements of Λ matrix are ,

$$\Lambda_{k,k+q} = g(q) \frac{(\varepsilon_k^0 - \varepsilon_{k+q}^0)}{(\varepsilon_{k+q}^0 - \varepsilon_k^0)^2 - (\hbar\omega_{-q})^2} \left[\sqrt{\frac{\hbar\omega_{-q}}{2}} Q_{-q} - \frac{i}{\sqrt{2\hbar\omega_{-q}}} P_q \right] \quad (A2)$$

This is a single-step Q, P -dependent transformation of the original Hamiltonian, and since Q and P do not commute, the general form of final results of the Fröhlich transformation and sequence of base transformations (introduction of new dynamical variables) used in this paper are different. While in the extreme antiadiabatic case $|\varepsilon_p^0 - \varepsilon_q^0| / \hbar\omega_r \rightarrow 0$, the results for two-particle term are identical and equal to (23b), on the adiabatic level $|\varepsilon_{k'}^0 - \varepsilon_k^0| \gg \hbar\omega_{k'-k}$ the results are substantially different. Adiabatic correction to correlation energy has the form (22, 22a) that is always attractive. On the other hand, adiabatic limit $|\varepsilon_{k'}^0 - \varepsilon_k^0| \gg \hbar\omega_{k'-k}$ of the Fröhlich form (23) results in,

$$H_{eff}''(Fr)_{ad} = \sum_{kk'q\sigma\sigma'} |u^q|^2 \frac{\hbar\omega_q}{(\varepsilon_{k+q}^0 - \varepsilon_k^0)^2} a_{k+q,\sigma}^+ a_{k',\sigma'}^+ a_{k'+q,\sigma'} a_{k,\sigma} \quad (A3)$$

It is immediately seen that this interaction, in contrast to (22a) is always repulsive. More over, expression (A3) as well as the general form of the Fröhlich effective Hamiltonian (23) has

incorrect k, k' symmetry. It can be shown, however, that strict adiabatic canonical transformation (generator S of the transformation is only Q -dependent – see [21,25]) of the model Hamiltonian with the Fröhlich form of H_{ep} (24), yields effective electron-electron interaction Hamiltonian in the form that is identical to the correction to electron correlation energy on adiabatic level as presented in this paper (22). The same result is obtained for H_{ep} of the form (39b – part I). This interaction is always attractive and the resulting form of Hamiltonian has correct k, k' symmetry (see 22).

Appendix B: Superconducting ground state and excitation spectrum of BCS theory

In its original form the Fröhlich model Hamiltonian with effective electron-electron interaction when related to normal ground state of metals (i.e. at 0 K all states below Fermi level are occupied and all states above Fermi level are empty) failed at description of superconducting phase [20,22]. Instead of this form, within the BCS theory [24] formally similar model Hamiltonian is introduced but with the different philosophy based on the idea of Cooper's pairs. According to it, electrons situated in a tin layer (up to $\hbar\omega$) above Fermi level can form a stable pairs at the presence of whatever weak but attractive interactions between electrons. Most stable pairs are formed for electrons with opposite quasimomentum and antiparallel spins ($k \uparrow, -k \downarrow$). Hamiltonian with only attractive part of effective electron-electron interaction $H_{eff}''(Fr)$, i.e. valid for electrons fulfilling condition $|\varepsilon_k - \varepsilon_{k+q}| < \hbar\omega$, has than the following (reduced) BCS form

$$H_{BCS} = \sum_k \varepsilon_k a_k^+ a_k + \sum_{kk'} W_{kk'} c_k^+ c_k = 2 \sum_k \varepsilon_k c_k^+ c_k + \sum_{kk'} W_{kk'} c_k^+ c_k \quad (B1)$$

In (B1), c_k^+, c_k are creation and annihilation operators of singlet electron pairs $c_k^+ = a_{k\uparrow}^+ a_{-k\downarrow}^+$, $c_k = a_{-k\downarrow} a_{k\uparrow}$. These particles obey different anticommutation and commutation relations than those valid for standard electrons and bosons. The matrix element $W_{kk'}$ is the sum of standard coulomb electron-electron repulsion and attractive Fröhlich electron-electron interaction $H_{red}''(Fr)$ that must be negative ($W_{kk'} < 0$). Superconducting ground state has been derived [24] by variation principle considering specific form of ground state wave function,

$$|BCS\rangle = \prod_k (u_k + v_k c_k^+) |0\rangle = \prod_k (u_k |0\rangle + v_k |k \uparrow, -k \downarrow\rangle) \quad (B1a)$$

It is a product of infinite number of liner combinations of two functions, vacuum state with probability of occurrence u_k^2 , and two-particle state with probability factor v_k^2 . The normalization condition is obvious, $u_k^2 + v_k^2 = 1$. As it can be seen, this wave function mixes together two Fock's subspaces of different dimensions, vacuum state and two-particle (bi-excited) states, i.e. it does not correspond to definite number of particles. The $|BCS\rangle$ wave function is reduced to normal ground state wave function of metals if $(u_k = 0; v_k = 1)$ for $k < k_F$ and $(u_k = 1; v_k = 0)$ for $k > k_F$.

Instead of the original formulation, let to see the underlying physics of the BCS theory as it follows from general derivation based on Bogoliubov – Valatin canonical transformation (see e.g. derivation presented in [50]).

Since pairing of electrons in states $(k \uparrow)$ and $(-k \downarrow)$ with attractive electron-electron interaction plays a special role, the following canonical transformation is introduced,

$$\gamma_{k\uparrow} = u_k a_{k\uparrow} - v_k a_{-k\downarrow}^+, \gamma_{-k\downarrow} = u_k a_{-k\downarrow} + v_k a_{k\uparrow}^+, \gamma_{k\uparrow}^+ = u_k a_{k\uparrow}^+ - v_k a_{-k\downarrow}, \gamma_{-k\downarrow}^+ = u_k a_{-k\downarrow}^+ + v_k a_{k\uparrow} \quad (B2)$$

The c-number coefficients u_k and v_k are real and depends only on $|k|$. Transformation is canonical if standard anticommutation relations for fermions hold also for new quasi-particles, i.e.

$$\{\gamma_{k\uparrow}, \gamma_{k'\uparrow}^+\} = \{\gamma_{-k\downarrow}, \gamma_{-k'\downarrow}^+\} = \delta_{kk'}, \text{ and all other anticommutators} = 0 \quad (\text{B3})$$

Since standard anticommutation relations $\{a_{k\sigma}, a_{k'\sigma'}^+\} = \delta_{kk'}\delta_{\sigma\sigma'}$ holds for original electrons, then with respect to (B3), for u_k, v_k follows,

$$u_k^2 + v_k^2 = 1 \quad (\text{B4})$$

For original operators then hold,

$$a_{k\uparrow} = u_k \gamma_{k\uparrow} + v_k \gamma_{-k\downarrow}^+, a_{-k\downarrow} = u_k \gamma_{-k\downarrow} - v_k \gamma_{k\uparrow}^+, a_{k\uparrow}^+ = u_k \gamma_{k\uparrow}^+ + v_k \gamma_{-k\downarrow}, a_{-k\downarrow}^+ = u_k \gamma_{-k\downarrow}^+ - v_k \gamma_{k\uparrow} \quad (\text{B5})$$

In order to treat indefinite number of particles N , system is studied as grand canonical ensemble with thermodynamic potential,

$$\hat{K} = \hat{H} - \mu \hat{N} = \sum_{k\sigma} a_{k\sigma}^+ a_{k\sigma} (\varepsilon_k^0 - \mu) - \frac{1}{2} \sum_{k_1+k_2=k_3+k_4, \sigma_1\sigma_2\sigma_3\sigma_4} \langle k_1\sigma_1 k_2\sigma_2 | V | k_3\sigma_3 k_4\sigma_4 \rangle a_{k_1\sigma_1}^+ a_{k_2\sigma_2}^+ a_{k_4\sigma_4} a_{k_3\sigma_3} \quad (\text{B6})$$

In the end, chemical potential μ (Fermi energy E_F) is chosen as to ensure $\langle \hat{N} \rangle = N$.

Interaction potential V is assumed to be attractive ($V > 0$ with respect to minus sign at second sum of B6) as it corresponds to attractive part of the Fröhlich effective electron-electron interaction (23a). The Wick's theorem is applied to one and two-electron terms in thermodynamic potential (B6). Then, if a new - renormalized Fermi vacuum $|\Theta\rangle$ is introduced with respect to (γ) operators,

$$\gamma_{k\uparrow} |\Theta\rangle = \gamma_{-k\downarrow} |\Theta\rangle = 0, \quad (\text{B7})$$

the corresponding contractions of operators and terms with single-particle and two-particle N -products can be derived (for details see [38]). It enables to write thermodynamic potential (B6) as a function of (γ) operators in the form,

$$\hat{K} = U + \hat{H}_1 + \hat{H}_2 + N[\hat{V}] \quad (\text{B8})$$

Particular terms in (B8) are:

a/ scalar quantity, i.e. zero-particle term U is,

$$U = 2 \sum_k \xi_k v_k^2 + \sum_{kk'} v_k^2 v_{k'}^2 \langle kk' | \bar{V} | kk' \rangle - \sum_k u_k v_k \Delta_k \quad (\text{B9})$$

In (B9), ξ_k is new single-particle Hartree-Fock energy measured with respect to chemical potential,

$$\xi_k = \varepsilon_k - \mu, \quad \varepsilon_k = \varepsilon_k^0 - \sum_{k'} \langle kk' | \bar{V} | kk' \rangle v_{k'}^2 \quad (\text{B9a})$$

Term $\langle kk' | \bar{V} | kk' \rangle$ is abbreviation for,

$$\langle kk' | \bar{V} | kk' \rangle \equiv \langle kk' | V | kk' \rangle - \langle kk' | V | k'k \rangle + \langle k-k' | \bar{V} | k-k' \rangle \quad (\text{B9b})$$

Quantity Δ_k stands for,

$$\Delta_k \equiv \sum_{k'} \langle k-k' | V | k'-k' \rangle u_{k'} v_{k'}. \quad (\text{B9c})$$

b/ one-particle Hamiltonian term $\hat{H}_1$ that corresponds to single-particle excited states has diagonal form,

$$\hat{H}_1 = \sum_k (\gamma_{k\uparrow}^+ \gamma_{k\uparrow} + \gamma_{-k\downarrow}^+ \gamma_{-k\downarrow}) [(u_k^2 - v_k^2) \xi_k + 2u_k v_k \Delta_k] = \sum_k E_k (\gamma_{k\uparrow}^+ \gamma_{k\uparrow} + \gamma_{-k\downarrow}^+ \gamma_{-k\downarrow}) \quad (\text{B10})$$

c/ two- particle Hamiltonian term $\hat{H}_2$ corresponds to pair-excited states and has the form,

$$\hat{H}_2 = \sum_k (\gamma_{k\uparrow}^+ \gamma_{-k\downarrow}^+ + \gamma_{-k\downarrow} \gamma_{k\uparrow}) [2u_k v_k \xi_k - (u_k^2 - v_k^2) \Delta_k] = \sum_k E_k^{(2)} (\gamma_{k\uparrow}^+ \gamma_{-k\downarrow}^+ + \gamma_{-k\downarrow} \gamma_{k\uparrow}) \quad (\text{B11})$$

d/ the last term in (B8), $N[\hat{V}]$, is sum of two terms with normal products of four creation and annihilation operators (multi-excited states),

$$N[\hat{V}] = -\frac{1}{2} \sum_{kk'q} \langle kk' | V | k+q, k'-q \rangle N [a_{k\uparrow}^+ a_{k'\uparrow}^+ a_{k'-q\uparrow} a_{k+q\uparrow} + a_{-k\downarrow}^+ a_{-k'\downarrow}^+ a_{-k'+q\downarrow} a_{-k-q\downarrow}] - \sum_{kk'q} \langle k-k' | V | k+q, -k'-q \rangle N [a_{k\uparrow}^+ a_{-k'\downarrow}^+ a_{-k'-q\downarrow} a_{k+q\uparrow}] \quad (\text{B12})$$

After replacement of (a) operators by (γ) operators according to (B5), it can be shown that with respect to renormalized ground state $|\Theta\rangle$ contribution of this term is zero,

$$\langle \Theta | N[\hat{V}] | \Theta \rangle = 0 \quad (\text{B13})$$

Nonzero contributions are in higher orders of perturbation theory and represent nonadiabatic corrections..

Up to this point, with respect to the form of model Hamiltonian in (B6), derivation of quasi-particle form of thermodynamic potential (B8), has been without any other approximations. Condition (B4) that is valid for coefficients (u, v) is exact and follows from canonical character of transformation (B2).

Derivation of superconducting solution (BCS) is based on some crucial external constrains. The first one is restriction imposed on coefficients (u, v) . It is required the following condition to hold,

$$2\xi_k u_k v_k = \Delta_k (u_k^2 - v_k^2) \quad (\text{B14})$$

At these circumstances, the term $\hat{H}_2$ in (B8) equals zero and quasi-particle form of thermodynamic potential reads,

$$\hat{K}_0 = U + \hat{H}_1 \quad (\text{B15})$$

Then from canonical condition (B4) and external constrain (B14) can be derived straightforwardly,

$$\Delta_k (\Delta_k^2 + \xi_k^2)^{-\frac{1}{2}} = 2u_k v_k, \quad \xi_k (\Delta_k^2 + \xi_k^2)^{-\frac{1}{2}} = u_k^2 - v_k^2 \quad (\text{B16})$$

and

$$u_k^2 = \frac{1}{2} \left[1 + \xi_k (\Delta_k^2 + \xi_k^2)^{-\frac{1}{2}} \right], \quad v_k^2 = \frac{1}{2} \left[1 - \xi_k (\Delta_k^2 + \xi_k^2)^{-\frac{1}{2}} \right] \quad (\text{B16a})$$

$$\Delta_k \equiv \frac{1}{2} \sum_{k'} \langle k-k' | V | k'-k' \rangle \Delta_{k'} (\Delta_{k'}^2 + \xi_{k'}^2)^{-\frac{1}{2}} \quad (\text{B16b})$$

If abbreviate notation is introduced,

$$E_k = (\xi_k^2 + \Delta_k^2)^{\frac{1}{2}} \quad (\text{B16c})$$

then $\hat{H}_1$ can be written in a compact quasi-particle form,

$$\hat{H}_1 = \sum_k E_k (\gamma_{k\uparrow}^+ \gamma_{k\uparrow} + \gamma_{-k\downarrow}^+ \gamma_{-k\downarrow}) \quad (\text{B17})$$

This form represents single-(quasi-)particle excitation spectrum. From (B17) and (B16c) follows that lowest laying excited state with energy E_k (represented by two independent, free

quasi-particles $(k \uparrow)$ and $(-k \downarrow)$ that are created by destruction of Cooper's pair $(k \uparrow, -k \downarrow)$ is separated from the ground state $|\Theta\rangle$ by a finite energy gap. For k -state close to Fermi level, $\xi_k \rightarrow 0$, the gap is $2\Delta_k$. In this sense, equation (B16b) written in a compact form

$$\Delta_k \equiv \frac{1}{2} \sum_{k'} \langle k-k | V | k'-k' \rangle \Delta_{k'} E_{k'}^{-1} \quad (\text{B18})$$

is gap equation as it has been derived for the first time in [24] by variation principle with the BCS wave function (B1) that represents new Fermi vacuum, i.e. $|\Theta\rangle = |BCS\rangle$.

Homogeneous, nonlinear integral gap equation (B18) has two solutions. The trivial solution is for $\Delta_k = 0$ (valid for all k). Now,

$$E_k = |\xi_k|, \quad u_k v_k = 0, \quad u_k^2 = \frac{1}{2} \left(1 + \frac{\xi_k}{|\xi_k|} \right) = \theta(\varepsilon_k - \mu), \quad v_k^2 = \frac{1}{2} \left(1 - \frac{\xi_k}{|\xi_k|} \right) = \theta(\mu - \varepsilon_k) \quad (\text{B19})$$

with step function $\theta(x)$. In this case the problem is reduced to standard Hartree-Fock description of electrons interacting through coulomb potential.

Non-trivial solution of the gap equation, so called superconducting solution, has been derived assuming constant value of electron-electron interaction ($V_{kk'} = \text{const.}$) over relevant energy interval $|\xi_k| < \hbar\omega_D$ at Fermi level and $V_{kk'} = 0$ outside this interval. In particular,

$$\langle k-k | V | k'-k' \rangle = g V^{-1} \theta(\hbar\omega_D - |\xi_k|) \theta(\hbar\omega_D - |\xi_{k'}|) \quad (\text{B20})$$

where cutoff energy $\hbar\omega_D$ (mean phonon energy) has been introduced to render the integral convergence.

At these circumstances, gap function Δ_k (B9c) is reduced to k -independent form,

$$\Delta_k = \Delta \theta(\hbar\omega_D - |\xi_k|) \quad (\text{B20a})$$

Solution of integral form of gap equation (B18) then yields,

$$\Delta = 2\hbar\omega_D \exp \left[- \frac{1}{gN(0)} \right] \quad (\text{B21})$$

In (B21) $N(0)$ is density of one-particle states at Fermi level.

Important physical meaning has condensation energy E_c that is represented by difference of ground state energy of system in superconducting and normal state at fixed number of particles N ,

$$E_c = E_s - E_n = U_s(\mu_s) - U_n(\mu_n) + (\mu_s - \mu_n)N \quad (\text{B22})$$

Assuming that chemical potential in superconducting and normal metal state is the same,

$$\mu_s = \mu_n \quad (\text{B22a})$$

for condensation energy can be derived,

$$E_c = E_s - E_n = -2N(0)(\hbar\omega_D)^2 \left[\exp \left(\frac{2}{VN(0)} \right) - 1 \right]^{-1} = -\frac{1}{2} VN(0) \Delta^2 \quad (\text{B23})$$

It is understood as energy of number $VN(0)\Delta$ electrons in pairs virtually excited above Fermi level with gain of energy $(-\Delta)$ per each pair.

It should be stressed that assumption (B22a) is crucial. It enables to derive condensation energy in the form (B23) and what is more important, only at these circumstances (fixed μ) mean number of particles in superconducting and normal state remain the same, $N_s = N_n$.

With respect to development of superconductivity theory (BCS), the key result is derivation of one-particle excitation spectrum (B17) which incorporates effect of effective attractive electron-electron interactions in one-particle energy term E_k (B16c). At finite T , excited states

ply crucial role. Then, if f_k is probability that state k (or $-k$) is occupied by single (quasi)particle, probability that couple of states $(k, -k)$ is available for pair formation $|k - k\rangle$ is equal to $(1-2f_k)$. Since single (quasi)particle is fermion, then f_k is occupation factor obeying Fermi-Dirac statistic,

$$f_Q = \left(\exp\left(\frac{E_k - \mu}{k_B T}\right) + 1 \right)^{-1} \quad (\text{B24})$$

and energy term E_k is equal to (B16c).

The gap equation (B18) can now be written in T-dependent form,

$$\Delta_k \equiv \frac{1}{2} \sum_{k'} \langle k - k' | V | k' - k \rangle \Delta_{k'} E_{k'}^{-1} (1 - 2f_{k'}) \quad (\text{B25})$$

At the assumptions (B20, 20a), from (B25) results the BCS temperature-dependent gap equation,

$$1 = VN(0) \int_0^{\hbar} \frac{\text{tgh}\left[\left(\varepsilon^2 + \Delta^2\right)^{\frac{1}{2}} / k_B T\right]}{\left[\varepsilon^2 + \Delta^2\right]^{\frac{1}{2}}} d\varepsilon \quad (\text{B26})$$

It can be rearranged into more compact form,

$$\Delta(T) = \Delta(0) \cdot \text{tgh}\left(\frac{\Delta(T)}{3.52 k_B T}\right) \quad (\text{B26a})$$

Existence of one-particle excitation spectrum (B17), obeying Fermi-Dirac statistic (B24), determines also all thermodynamic properties. For entropy holds standard expression of statistical thermodynamics with distribution (B24),

$$S_s = -k_B \sum_k [f_k \ln f_k + (1 - f_k) \ln(1 - f_k)] \quad (\text{B27})$$

It enables to derive free energy of system in superconducting states,

$$F_s = U_s - TS_s \quad (\text{B28})$$

From the free energy, electronic specific heat and critical magnetic field (Meissner effect) is then derived in a straightforward way, like it has been derived in the present work at transition from adiabatic into antiadiabatic state (14, 15).

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