Review Article

Antiadiabatic Theory of Superconducting State Transition: Phonons and Strong Electron Correlations—The Old Physics and New Aspects

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Complex electronic ground state of molecular and solid state system is analyzed on the ab initio level beyond the adiabatic Born-Oppenheimer approximation (BOA). The attention is focused on the band structure fluctuation (BSF) at Fermi level, which is induced by electron-phonon coupling in superconductors, and which is absent in the non-superconducting analogues. The BSF in superconductors results in breakdown of the adiabatic BOA. At these circumstances, chemical potential is substantially reduced and system is stabilized (effect of nuclear dynamics) in the antiadiabatic state at broken symmetry with a gap(s) in one-particle spectrum. Distorted nuclear structure has fluxional character and geometric degeneracy of the antiadiabatic ground state enables formation of mobile bipolarons in real space. It has been shown that an effective attractive e-e interaction (Cooper-pair formation) is in fact correction to electron correlation energy at transition from adiabatic into antiadiabatic ground electronic state. In this respect, Cooper-pair formation is not the primary reason for transition into superconducting state, but it is a consequence of antiadiabatic state formation. It has been shown that thermodynamic properties of system in antiadiabatic state correspond to thermodynamics of superconducting state. Illustrative application of the theory for different types of superconductors is presented.

1. Introduction

Superconductivity, an amazing physical phenomenon discovered nearly 100 years ago by Kamerlingh Onnes [1] and his assistant Gilles Holst whose name has been basically forgotten by history (see, e.g., [2]), has been one of the most important research fields of solid-state physics of last century and it remains until the present days. What is extremely irritating is the fact that microscopic mechanism of superconducting state transition, in spite of enormous attention which has been paid to this effect, remains still unclear and represents an open challenge for theory.

Until the discovery of high-temperature superconductivity of cuprates by Bednorz and Muller in 1986 [3] and synthesis of first 90 K superconductor [4] in 1987, understanding of microscopic mechanism of superconducting (SC) state transition formulated within the BCS theory in 1957 [5] was generally accepted as a firm theoretical basis behind the physics of this phenomenon. Here, the basic physics is the idea of Cooper-pairs formation, that is, formation of boson-like particles in momentum space, which are stable in thin layer above the Fermi level and drive system into more stable-superconducting state. Sufficient condition of pair formation is whatever weak, but attractive, interaction between electrons. Real possibility of effective attractive electron-electron interactions was well known. Some years, ago it was derived by Fröhlich [6, 7] as a consequence of electron-phonon (e-p) interactions.

The range of validity of the BCS theory with respect to e-p interactions has been specified by Migdal [8] and Eliashberg [9, 10]. It can be interpreted as Migdal’s theorem and Eliashberg’s restriction (ME approximation). The first is related to validity of the condition \( \omega \lambda / E_F \ll 1 \) and the second one restricts the validity only for \( \lambda \leq 1 \), where \( \lambda \) is e-p
coupling strength and $\omega$ and $E_F$ are characteristic phonon and electron energy scales, respectively. Expressed explicitly, BCS-like theories are valid only for adiabatic systems that obey the adiabatic Born-Oppenheimer approximation (BOA): $\omega/E_F \ll 1$.

While for conventional (low-temperature) superconductors, the BCS theory within the ME approximation (i.e., weak coupling regime) is an excellent extension of standard theory of metals, for high-temperature cuprates in order to interpret high critical temperature and ensure the pairs condensation, beside (or instead of) the e-p interactions the important role of other interaction mechanisms has been advocated (see e.g., [11–13]). Since the copper, a transition metal with incompletely filled d-shell when chemically bounded, is a central atom of high-$T_c$ cuprates, it is quite natural that the attention has been focused on strong electron correlations (in a sense of standard Coulomb-repulsive e-e interactions), magnetic interactions, and/or spin fluctuation effects. At the present, the effect of Coulomb repulsion is usually incorporated via Coulomb pseudopotential $\mu^*$ and critical temperature is calculated according to McMillan formula [14].

The e-p interactions, which have been accepted to be responsible for electron pairing that drive transition into superconducting state for classical low-$T_c$ superconductors, have become nearly abandoned and considered to be rather harmful for superconductivity in high-$T_c$ cuprates (see, e.g., [12]). Some aspects of d-wave superconductivity can be described within the models of strongly correlated electrons, for example, Hubbard-like or t-J models (e.g., [11, 15–19]), even without explicit account for e-p interactions. The underlying leitmotiv behind the electron correlation treatments has been to understand the phase diagram of high-$T_c$ cuprates, that is, the doping process. Introduction of charge carriers (holes or electrons) into the parent antiferromagnetic insulator that causes transition to superconductor (or metal) has been generally accepted to be a universal feature of high-$T_c$ cuprates and believed to be a matter intimately related to microscopic mechanism of superconductivity.

Bell-like-shaped dependence of $T_c$ on hole doping in the doping range $0.05 \leq x \leq 0.27$ for family of high-$T_c$ cuprates is well known (see, e.g., [20] and references therein). With the exception of YBCO ($x = 0.05$), the optimal hole doping with maximal $T_c$ is $x \approx 0.16$. The electron doping is usually less favorable, but basically either hole or electron doping can induce superconductivity. It is, for instance, the case of infinite-layer compound $\text{CaCuO}_2$ (itself is an insulator) where by hole or electron doping in field-induced transistor configuration superconductivity can be induced with $T_c$ up to $89 \text{ K}$ (or $34 \text{ K}$ for electron doping) at about 0.15 charge carriers per $\text{CuO}_2$.

Without any doubts, charge doping has no-negligible impact on e-e interactions and influences, to some extent, also more subtle spin interactions. Question remains if these are the key effects behind the physics which causes superconducting state transition upon doping?

In this respect, one has to realize that like $T_c$, the lattice parameters and, what is very important, the lattice dynamics is strongly influenced by doping. For instance, dependence of $T_c$ on lattice parameter $a$ in case of Hg-based cuprates follows similar dependence as it does $T_c$ on hole doping [21]. In spite that isotope effect coefficient $\alpha$ for optimally doped cuprates is very small ($\alpha \approx 0.05$, exception is YBCO—$\alpha \approx 0.8$), doping in underdoped as well in overdoped region for O-isotope effect (all-over the cuprates family), results in a huge changes of isotope effect coefficient $\alpha$ (see, e.g., [22, 23]. It is important experimental evidence that doping induces very strong changes in lattice dynamics, in particular in dynamics of CuO$_2$ layers. From theoretical stand point, it means that mechanism of superconducting state transition is a complex matter of electron and nuclear degrees of freedom.

The results of high-resolution ARPES study [24, 25] of wide family of different high-$T_c$ cuprates have brought the other experimental evidence indicating that beside doping, an abrupt change (decrease) of electron velocity near Fermi level, at about 50–80 meV in nodal direction, is the other feature common to high-$T_c$ cuprates. The kink in nodal direction is temperature independent. More important, from the stand point of microscopic theory of superconductivity, seems to be formation of temperature-dependent kink on momentum distribution curve (dispersion renormalization) close to Fermi level ($\sim 60 \text{ meV}$) in off-nodal direction at transition to superconducting state. It has been reported for Bi2212 [26–29]. Recently, presence of the kink in off-nodal direction has been observed at VUV ARPES study with sub-meV resolution of optimally doped untwinned YBCO in superconducting state [30].

Formation of the off-nodal kink (dispersion renormalization) has been attributed by the authors [26] to the coupling of electrons to a bosonic excitations, preferably they consider a magnetic resonance mode such as observed in some inelastic neutron scattering experiments. The inconsistency in this interpretation has been pointed out by the authors of [27, 29]. The main points are described in [29] as follows: (a) magnetic resonance has not yet been observed by neutron scattering in such a heavily doped cuprates, and (b) magnetic resonance has little spectral weight and may be too weak to cause the effect seen by ARPES. They agree, however, with the opinion of the authors [26] that the renormalization effect seen by ARPES in cuprates may indeed be related directly to the microscopic mechanism of superconductivity. The authors of [27, 29] instead of magnetic resonance mode, attribute the dispersion renormalization to coupling with phonon mode, in particular, with $\text{B}_{1g}$-buckling mode of CuO$_2$ plane. The temperature dependence of dispersion renormalization they attribute to the DOS enhancement due to SC-gap opening and to the thermal broadening of the phonon self-energy in normal state.

These results along with the results of neutron scattering [31, 32] indicate that also for high-$T_c$ cuprates the e-p coupling has to be considered as a crucial element of microscopic mechanism of SC state transition. Expressed explicitly, also in case of cuprates the role of phonons at superconducting state transition must not be overlooked. As soon as low-Fermi energy situation occurs ($\omega \leq E_F$), one can expect important contribution of nonadiabatic vertex corrections at SC state transition. It is beyond the standard ME approximation and this problem has been
studied within the nonadiabatic theory of superconductivity [33–35]. On the other hand, as the ARPES results indicate, electron kinetic energy is decreased and importance of proper treatment of electron-electron Coulomb interactions is increased. The competition between Coulomb and e-p interactions has been intensively studied within the Holstein-Hubbard models [36–40] with both interactions of short-range character. The obtained results are not satisfactory since heavy-mass polarons are formed that yield low values of $T_c$. It has been improved within the Frohlich-Coulomb model [41] that introduces long-range repulsion between charge-carriers and also long-range e-p interactions. The results show that there is a narrow window of parameters of Coulomb repulsion $V_c$ and e-p interactions $E_P$ ($V_c / E_P$) resulting in the light-mass bipolarons formation. In this case, according to bipolaron theory of superconductivity [42–44], coherent motion of bipolarons represents the supercarrier motion and high $T_c$ can be reached.

The McMillan formula, which is very good approximation for $T_c$ of elementary metals and their alloys [45], is often used also for calculation of critical temperature of high-$T_c$ superconductors within the BCS-generic framework. It has been shown [46] that in strong-coupling regime $\lambda \gg 1$, $T_c$ can be as large as $k_B T_c = \hbar \omega_c \lambda^{3/2}/2\pi$. However, in reality there is problem with correct estimation of Coulomb pseudopotential $\mu^*$ and with unrealistically large values of $\lambda$ that would match high experimental $T_c$ of novel superconductors. It has to be stressed, however, that strong coupling regime $\lambda \gg 1$ violates adiabatic condition $\omega_c / E_F \ll 1$ of the ME approximation, which is behind the derivation of the McMillan formula.

More over, new class of superconductors, for example, cuprates, fullerides, and MgB$_2$ are systems that are rather pseudoadiabatic with sizeable adiabatic ratio $\omega_c / E_F \ll 1$ [47], in contrast to elementary metals, where adiabatic condition $\omega_c / E_F \ll 1$ is perfectly fulfilled. This situation indicates the importance of nonadiabatic contributions at calculation of e-p interactions within the BOA, an effect which is beyond the standard ME approach. As mentioned above, formulation of the nonadiabatic theory of superconductivity by Pietronero et al. [33–35, 48, 49], which accounts for vertex corrections and cross phonon scattering (beyond ME approximation), has solved this nontrivial problem by generalization of Eliashberg equations. The theory, which is nonperturbative in $\lambda$ and perturbative in $\lambda \omega_c / E_F$, has been applied at simulation and interpretation of different aspects of high-$T_c$ superconductivity [50–54]. Basically, it can be concluded that accounts for nonadiabatic effects in quasidiabatic state $\omega_c / E_F \ll 1$ is able to simulate different properties of high-$T_c$ superconductors, including high-value of $T_c$, already at relatively moderate value of e-p coupling, $\lambda \approx 1$. Moreover, 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, sophisticated treatment of high-$T_c$ superconductivity within the nonadiabatic theory faces serious problem related to possibility of polaron collapse of the band and bipolaron formation. According to bipolaron theory of Alexandrov [42–44, 47, 55–58], polaron collapse occurs already at $\lambda \approx 0.5$ for uncorrelated polarons and even at smaller value for a bare e-p coupling in strongly correlated systems. For $\omega_c / E_F \ll 1$, or $\lambda \geq 1$, and for $\omega_c / E_F \approx 1$ at whatever small value $\lambda \ll 1$, the nonadiabatic polaron theory has been shown to be basically exact [58]. Bipolarons can be simultaneously small and light in suitable range of Coulomb repulsion and e-p interaction [59]. These results have important physical consequences. There are serious arguments that effect of polaron collapse cannot be covered through calculation of vertex corrections due to translation symmetry breaking and mainly, polaron collapse changes possible mechanism of pair formation, that is, instead of BCS scenario with Cooper pair formation in momentum space, the BEC with mobile bipolarons (charged bosons) in real space becomes operative.

Discovery of superconductivity in a simple compound MgB$_2$ at 40 K [60] has been very surprising and has started a new revitalization of superconductivity research. Beside the many interesting aspects, discovery of the MgB$_2$ superconductivity is, in my opinion, crucial for general theoretical understanding of SC state transition on microscopic level. It is related to band structure (BS) fluctuation and dramatic changes of BS topology at e-p coupling.

The $\sigma$ bands splitting at coupling to $E_{2g}$ mode in MgB$_2$ has been reported [61] already in 2001 but, with exception of possible impact of anharmonicity [62], no special attention has been paid to this effect. Superconductivity in MgB$_2$ has been straightforwardly interpreted [63] shortly after the discovery as a standard BCS-like, even of intermediate-strong coupling character. For clumped nuclear equilibrium geometry, the BS is of adiabatic metal-like character. The $E_F^\sigma$ of $\sigma$ band electrons (chemical potential $\mu$) is relatively small, $\approx 0.4$ eV, but still great enough comparing to vibration energy of $E_{2g}$ phonon mode, $\omega_{2g} \approx 0.07$ eV. Thought the adiabatic ratio $\omega_c / E_F \approx 0.15$ is sizable, it is small enough in order to interpret superconductivity within the BCS-generic framework. It is supposed that nonadiabatic effects, anharmonic contributions and/or Coulomb interactions within generalized Eliashberg approach should be important in this case. On the other hand, the value of e-p coupling, $\lambda \approx 0.7$ indicates that polaron collapse can be expected and superconductivity should be of nonadiabatic bipolaron character rather than the BCS-like.

Nevertheless, the matter is even more complicated. It has been shown [64, 65] that analytic critical point (ACP—maximum, minimum, or saddle point of dispersion, in case of MgB$_2$ it is maximum) of $\sigma$ band at $\Gamma$ point crosses Fermi level (FL) at vibration displacement $\approx 0.016$ A$/\text{B-atom}$, that is, with amplitude $\approx 0.032$ A, which is smaller than root- mean square (rms) displacement ($\approx 0.036$ A) for zero-point vibration energy in $E_{2g}$ mode. It means, however, that in vibration when ACP approaches FL on the distance less than $\pm \omega$, the adiabatic Born-Oppenheimer approximation (BOA) is not valid. In this case, Fermi energy $E_F^\sigma$ of $\sigma$ band electrons (chemical potential $\mu$) close to $\Gamma$ point is smaller than $E_{2g}$ mode vibration energy $E_F^\sigma < \omega_{2g}$ and at the moment when the ACP of the band touches Fermi level, the Fermi energy is reduced to zero, $E_F \rightarrow 0$. Moreover, shift of the ACP substantially increases density of states (DOS) at FL,
\( n_n(E_F) = (\frac{\partial \sigma_n}{\partial k})_{E_F}^{-1} \), and induces corresponding decrease of effective electron velocity \( \frac{\partial \sigma_n}{\partial k} \) of fluctuating band in this region of \( k \)-space. From the physical standpoint, it represents transition of the system from adiabatic \( \omega \leq E_F \) into true nonadiabatic \( \omega > E_F \), or even into strong antiadiabatic state with \( \omega \gg E_F \). This effect has crucial theoretical impact. At these circumstances, not only ME approximation is not valid (including impossibility to calculate nonadiabatic vertex corrections which represent off-diagonal corrections to adiabatic ground state) but adiabatic BOA itself does not hold as well.

The BOA is crucial approximation of theoretical molecular as well as of solid-state physics. It enables to solve many-body problem via separation of electronic and nuclear motion and to study electronic problem in a field which is created by fixed nuclei.

On the level of the BOA, the motion of the electrons is a function of the instantaneous nuclear coordinates \( Q \), but is not dependent on the instantaneous nuclear momenta \( P \). Usually, and in solid state physics basically always, only parametric dependence is considered, that is, nuclear coordinates are only parameters in solution of electronic problem within the clamped nuclei Hamiltonian treatment. Nuclear coordinate-dependence, when explicitly treated, modifies nuclear potential energy by so-called diagonal BO correction (DBOC) that reflects an influence of small nuclear displacements out of the equilibrium positions and corrects the electronic energy of clamped nuclear structure. The DBOC enters directly into the potential energy term of nuclear motion (but leaves unchanged the nuclear kinetic energy) and in this way modifies vibration frequencies. The off-diagonal terms of the nuclear part of system Hamiltonian that mix electronic and nuclear motion through the nuclear kinetic energy operator term are neglected and it enables independent diagonalization of electronic and nuclear motion (adiabatic approximation). Neglecting the off-diagonal terms is justified only if these are very small, that is, if the energy scales of electron and nuclear motion are very different and when adiabatic condition holds, that is, \( \omega/E \ll 1 \). If necessary, small contribution of the off-diagonal terms can be calculated by perturbation methods as so-called nonadiabatic correction to the adiabatic ground state.

Situation for superconductors seems to be substantially different, at least in case of the MgB\(_2\). There is considerable reduction of electron kinetic energy, which for antiadiabatic state results even in dominance of nuclear dynamics (\( \omega \gg E_F \)) in some region of \( k \)-space. In this case, it is necessary to study electronic motion as explicitly dependent on the operators of instantaneous nuclear coordinates \( Q \) as well as on the operators of instantaneous nuclear momenta \( P \). It is a new aspect for many-body theory.

The electronic theory of solids has been developed with the assumption of validity of the adiabatic BOA. In this respect, it is natural that different theoretical-microscopic treatments of superconductivity based on model Hamiltonians which stress importance of one or the other type of interaction mechanism, implicitly assume validity of the BOA, and it is very seldom that possibility of the BOA breakdown at transition to SC state is risen. The notion of “nonadiabatic” effects in relation to electronic structure is commonly used for contributions of the off-diagonal matrix elements of interaction Hamiltonian (e.g., e-p coupling, e-e correlations, etc.) to the adiabatic ground state electronic energy calculated in second and higher orders of perturbation theory and does not account for true nonadiabatic-antiadiabatic situation, \( \omega > E_F \).

In this connection, a lot of important questions arise, as the following examples.

(i) How to treat antiadiabatic state?
(ii) Can be system stable in antiadiabatic state?
(iii) Are the physical properties of the system in antiadiabatic state different from the corresponding properties in adiabatic state?
(iv) What is the driving force for adiabatic ↔ antiadiabatic state transition, that is, which type of interaction mechanism and at which circumstances trigger this type of transition?
(v) How relevant is adiabatic ↔ antiadiabatic state transition for SC state transition in MgB\(_2\)?
(vi) Is the adiabatic ↔ antiadiabatic state transition an accidental effect at SC state transition which is present only in MgB\(_2\), or this state transition is an inherent physical mechanism which is proper also for other superconductors?
(vii) Can be adiabatic ↔ antiadiabatic state transition relevant for high, as well as for low-temperature superconductors?
(viii) Phonons or strong electron correlations?
(ix) What is the character of condensate-Cooper pairs or bipolarons?
(x) Is there any relation of the adiabatic ↔ antiadiabatic state transition to Cooper pairs formation?
(xi) Cooper pairs or correction to electron correlation energy?

Theoretical aspects related to the above problems have been elaborated and discussed in details within “Ab initio theory of complex electronic ground state of superconductors”, which has been published in the papers, [66–68]. The main theoretical point is generalization of the BOA by sequence of canonical-base functions transformations. The final electronic wave function is explicitly dependent on nuclear coordinates \( Q \) and nuclear momenta \( P \), or alternatively, emerging new quasiparticles-nonadiabatic fermions are explicitly dependent on nuclear dynamics. As a result, the effect of nuclear dynamics can be calculated in a form of corrections to the clamped nuclei ground state electronic energy, to the one-particle spectrum and to the two-particle term, that is, to the electron correlation energy.

Note. To avoid confusion, it should be stressed that the notion electron correlation energy as used in this paper stands for improvement of e-e interaction term contribution beyond the Hartree-Fock (HF) level, \( E_{\text{exact}} = E_{HF} \)
\( E_{\text{exact}} < E_{\text{HF}} \), as it can be calculated, for example, by \((1/r)\)-perturbation theory in the second and the higher orders, or by configurations interaction method. In condensed matter physics, electron correlation usually stands for an account for Coulomb e-e interaction at least on Hartree or HF level. On the HF level not only repulsive e-e term is present, like on Hartree level where spin is not considered at all, but also exchange term, fermion Coulomb-hole only for electrons with parallel spins. Correlation energy improves an account for unbalanced treatment of e-e interaction for electrons with parallel and antiparallel spins on HF level.

It has been shown that due to e-p 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, that is, it is the effect of nuclear dynamics (dependence on \( P \)) which is absent in the adiabatic state on the level of the BOA. 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. Moreover, it has been shown that due to e-p 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 system. It has been shown that resulting one-particle spectrum yields all thermodynamic properties that are characteristic for system in superconducting state, that is, 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 Fröhlich's effective attractive electron-electron interaction term represents correction to electron correlation energy in transition from adiabatic into antiadiabatic state due to e-p 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.

In the present article, the key points of the theory are recapitulated and the adiabatic -- antiadiabatic state transition is shown to be operative for different types of superconductors.

## 2. Electronic Ground State Beyond the Born-Oppenheimer Approximation

### 2.1. Preliminary Remarks.
Development of the theory of molecules and solids has been enabled due to fundamental approximation, the Born-Oppenheimer approximation (BOA). With respect to electronic structure of superconductors and transition to superconducting state, some aspects of this approximation should be outlined at the beginning.

Solution of the Schrödinger equation of many-body system composed of \( N_e \) electrons and \( N_n \) nuclei (total system)

\[
\hat{H}\Psi(r, R) = E_{TS}\Psi(r, R)
\]

with the Hamiltonian

\[
\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{ee}(r) + \hat{V}_{CN}(r, R) + E_{NN}(R),
\]

and wave function \( \Psi(r, R) \), which is a general function of the sets of electron \( \{ r \} \) and nuclear \( \{ R \} \) Cartesian coordinates, is possible at the assumption of validity of the Born-Oppenheimer approximation (BOA). The BOA, originally formulated in the work in [69] by power expansion of potential surface for nuclear motion at equilibrium geometry with respect to displacement and electron/nuclear mass ratio \((m_e/M_n)^{1/4}\), has been reformulated later by Born [70, 71] in a more practical form. According to it, the wave function of the total system (1) can be expressed in the factorized form

\[
\Psi(r, R) = \sum_m \chi_m(R)\Phi_m(r, R),
\]

as a linear combination of known adiabatic electronic wave functions \( \{ \Phi_m(r, R) \} \) that are the eigenfunctions of clumped nuclei electronic Schrödinger equation

\[
\hat{H}_e\Phi_m(r, R) = E_{nm}\Phi_m(r, R),
\]

with the electronic Hamiltonian:

\[
\hat{H}_e = \hat{T}_e + \hat{V}_{ee}(r) + \hat{V}_{CN}(r, [R]),
\]

at fixed nuclear configuration \([R]\). Expansion coefficients \( \{ \chi_m(R) \} \) in (3), regarded as unknown, are nuclear wave functions for nuclear configuration \( R \) with the electronic subsystem in particular adiabatic electronic state \( \Phi_m(r, R) \).

The \( R \)-dependence in (5) is only parametric and in general it should be calculated over the full configuration space \( \{ R \} \) in order to calculate the adiabatic potential hypersurface \( \{ E_{nm}(R) \} \) of nuclear motion.

With respect to (3) and (4), the Schrödinger equation of the total system (1) for electronic state \( \Phi_m(r, R) \) can be written in the form

\[
\left\{ \hat{T}_N + E_{nm}(R) - E_{TS}(R) \right\}\chi_m(R) = \sum_m \Lambda_{nm}(R)\chi_m(R)
\]
with the term $\lambda_{nm}(R)$, which couples electronic and nuclear motions, on the right-hand side (rhs):

$$\hat{\lambda}_{nm}(R) = \hat{\lambda}_{nm}(R) - B_{nm}(R)$$

$$= \sum_j \frac{\hbar^2}{M_j} \int \Phi^*_n(r, R_j) \frac{\partial}{\partial R_j} \Phi_m(r, R_j) dr \cdot \frac{\partial}{\partial R_j}$$

$$- \int \Phi^*_n(r, R) \hat{T}_N(R) \Phi_m(r, R) dr.$$  

(7)

The term $E_{et}^N$ in (6):

$$E_{et}^N(R) = (E_{et}^N + E_{NN}(R))$$  

(8)

is total adiabatic electronic energy, that is, adiabatic electronic energy plus nuclear Coulomb repulsion at nuclear configuration $R$.

Until the Born approach (3) is valid, (6) is exact and it still describes coupled motion of electrons and nuclei over the term (7), $\lambda_{nm}(R)$, which represents possibility of transitions between different adiabatic electronic states, $\Phi_n(r, R) \rightarrow \Phi_m(r, R)$, due to nuclear motion ($R$-dependence). If such transitions are forbidden from the symmetry reasons, or if there is physically reasonably justified assumption that contributions of such transitions are negligibly small, then one can omit the rhs term, and (6) can be written in the diagonal form:

$$\{ \hat{T}_N + (E_{et}^N(R) + B_{nm}(R)) - E_{et}^N(R) \} \chi_{nm}(R) = 0,$$  

(9)

where $B_{nm}$ is the only nonzero diagonal contribution of the $\lambda$ term

$$B_{nm}(R) = \int \Phi^*_n(r, R) \hat{T}_N(R) \Phi_m(r, R) dr$$

$$= \sum_n \frac{\hbar^2}{2M_n} \int \Phi^*_n(r, R) \nabla^2 \Phi_n(r, R) dr$$

$$= \sum_{nm} \frac{\hbar^2}{2M_n} \left( \frac{\partial \Phi_n(r, \bar{R})}{\partial R_{aa}} \right) \left( \frac{\partial \Phi_n(r, \bar{R})}{\partial R_{aa}} \right) dr|_{R_{\bar{R}}}.$$  

(10)

The term (10) is the mean-value of the nuclear kinetic energy for adiabatic electronic state $\Phi_n(r, R)$ at nuclear configuration $\{ R \}$ and represents so-called adiabatic diagonal Born-Oppenheimer (DBOC) correction to the total adiabatic electronic energy $E_{et}^N(R)$. However, (9) is then the equation of motion of nuclei and it has the form of Schrödinger equation with Hamiltonian:

$$\hat{H}_N(R) = \hat{T}_N + V_{et}^{NN}(R).$$  

(11)

The effective-adiabatic potential for nuclear motion $V_{et}^{NN}(R)$:

$$V_{et}^{NN}(R) = E_{et}^N(R) + B_{nm}(R)$$  

(12)

is represented by the total electronic energy (8), that is, Coulomb potential energy of the bare nuclei repulsion $E_{NN}(R)$ and adiabatic electronic energy $E_{et}^N(R)$, which is corrected by mean-value of the nuclear kinetic energy (DBOC) for the particular adiabatic electronic state $\Phi_n(r, R)$ (10). Contribution of the adiabatic DBOC is usually neglected as very small quantity, mean value of kinetic energy of slowly moving heavy nuclei in contrast to fast motion of light adiabatic electrons.

At these circumstances, the motion of electrons and nuclei is effectively decoupled, that is, it is possible to realize an independent diagonalization of the electronic Schrödinger equation (4) and nuclear Schrödinger equation (9), electrons and nuclei of the system behave like two statistically independent sets. Assumed small contribution of the rhs term of (6) can be calculated by some approximate way, usually by perturbation theory. Then, problem with the Hamiltonian:

$$\hat{H}(R) = \hat{H}^0(R) + H'(R)$$  

(13)

is studied, where

$$\hat{H}^0(R) = \hat{H}_{et}(R) + H_N(R) = \{ (5) + E_{NN}(R) \} + (11)$$  

(14)

is unperturbed part, and

$$H'(R) = \hat{\lambda}_{mn}(R); \quad \{ H_{mn}(R) = \int \chi^*_m(R) \hat{\lambda}_{mn}(R) \chi_n(R) dr \}$$

$$m \neq n$$  

(15)

is a small perturbation.

In practice, physical and/or chemical properties of a many-body system in its ground electronic state $\Phi_0(r, R)$ are of the prime interest. In this case, the Born approach (3) is usually restricted to the single term and the total wave function of system is a simple product of the adiabatic electronic wave function $\Phi_0(r, R)$ and corresponding nuclear wave function:

$$\Psi_0(r, R) = \chi_0(r, R) \Phi_0(r, R).$$  

(16)

The Born approach in the form (16) is the adiabatic approximation. In a common sense, what is usually called the Born-Oppenheimer approximation (BOA, or clamped nuclei-crude adiabatic BOA) is the adiabatic approximation where the contribution of the DBOC (i.e., $B_{00}(R)$ term in (12)) is also neglected and wave function (16) has the form

$$\Psi_0(r, R) = \chi_0(r, R) \Phi_0(r, R_{eq}).$$  

(17)

Contributions of the off-diagonal terms $\lambda_{nm}(R)$ in (15) which are calculated as a small perturbation to the Hamiltonian (14) represent a nonadiabatic correction to the unperturbed adiabatic ground state. The conditions at which the nonadiabatic correction can be expected to be small, and the BOA (16, and in general 3) is valid, can be estimated by analysis of the second-order contributions to the energy of the total system, $E_{et}^{TS}(R)$, which are small providing that

$$\int \chi^*_m(r) \hat{\lambda}_{0m}(R) \chi_{n\nu}(R) dr \ll \left| E_{et}^{TS}(R) - E_{et}^{TS}(R) \right|.$$  

(18)
It can be derived (see, e.g., [72]), based on the expansion of the effective nuclear potential \( V_{\text{eff}}^{n}(R) = E^{n}_{0}(R) \) at equilibrium nuclear geometry \( R_{\text{eq}} \) (where the total electronic ground-state energy reaches its absolute minimum) at least up to the quadratic term in a displacement \( \Delta R \):

\[
E^{n}_{0}(R) = E^{n}_{0}(R_{\text{eq}}) + \frac{1}{2} \sum_{s} \frac{\partial^{2} E^{n}_{0}(R)}{\partial \Delta R^{2}} \cdot \Delta R^{2} + \cdots
\]

(19)

\[
E^{n}_{0}(R_{\text{eq}}) = \frac{\hbar}{2} \sum_{s} \omega_{s} x_{s}^{2} + \cdots.
\]

The result is that (18) holds and the BOA (16), (3) is valid, if inequality

\[
\left| E^{n}_{0}(R_{\text{eq}}) - E^{n}_{n}(R_{\text{eq}}) \right| \gg \hbar \omega_{s}
\]

(20)

is fulfilled for electronic and vibration (phonon) energy spectrum of a system. The meaning of (20) is clear, the electronic spectrum, that is, the differences between the total electronic energies of the excited electronic states and the ground-state energy has to be much greater than vibration (phonon) energy spectrum of system.

The long-time experience of theoretical molecular and solid-state physics has shown that for a ground electronic state of vast majority of molecular systems and solids at equilibrium geometry \( R_{\text{eq}} \), the BOA is absolutely good approximation. In case of solids, it has enabled to derive (Bloch’s assumption of small perturbation of the periodic lattice potential for small nuclear displacement out of equilibrium) the field theory Hamiltonian of total system (13) in a well-known form, \( \hat{H} = \hat{H}^{0} + \hat{H}_{\text{ep}}, \) with

\[
\hat{H}^{0} = \sum_{k\sigma} \epsilon_{k} a_{k\sigma}^{\dagger} a_{k\sigma} + \sum_{q} \hbar \omega_{q} \left( b_{q}^{\dagger} b_{q} + \frac{1}{2} \right).
\]

(21)

The perturbation Hamiltonian \( \hat{H}_{\text{ep}} \) represents now, instead of nuclear kinetic energy \( \Lambda \)-perturbation term (15), an electron-phonon (e-p) interaction term:

\[
\hat{H}_{\text{ep}} = \sum_{k,q,\sigma} \mathcal{U}^{q} \left( b_{q} + b_{q}^{\dagger} \right) a_{k+q,\sigma}^{\dagger} a_{k,\sigma}.
\]

(22)

In this case, no special attention has been paid to the diagonal correction (10) to the total electronic ground-state energy, and at derivation of (21) and (22), this correction has been omitted as negligibly small quantity. Moreover, since perturbation \( H' \) is now introduced as an e-p interaction \( H_{\text{ep}}, \) it is immediately seen from the form of (16) and (22) that the first-order correction, that is, diagonal perturbation term, equals zero: \( \langle \Phi_{0} | \hat{H}_{\text{ep}} | \Phi_{0} \rangle = 0 \). All interesting physics is then related to higher-order contributions with participation of excited electronic states, that is, the first possible nonzero contributions are in the second order of perturbation theory, that is, terms of the form \( \langle \Phi_{0} | \hat{H}_{\text{ep}} | \Phi_{n} \rangle \langle \Phi_{n} | \hat{H}_{\text{ep}} | \Phi_{0} \rangle / (E_{0}^{n} - E_{n}^{ef}), \) (26)

Hamiltonian (21), (22) has been the starting point for theoretical study of the effects connected to e-p interactions in solids. By means of the famous unitary transformation of this Hamiltonian, Fröhlich has derived [6, 7] an effective electron-electron interaction term which is a crucial element at formulation of the BCS [5] or Migdal-Eliashberg (ME) theory of superconductivity [8–10]. The extension of the ME theory, that is, inclusion of higher-order contributions of e-p interactions by means of Feynman-Dyson perturbation expansion of \( H_{\text{ep}} \) (vertex corrections) is the basis for so called "nonadiabatic" theory of superconductivity, as it has been developed by Pietronero et al. [33–35, 48, 49]. It should be pointed-out that not only the above-mentioned standard and "nonadiabatic" theories of superconductivity but also other theoretical models of superconductivity which do not consider explicitly e-p interactions assume tacitly validity of the BOA as soon as the model Hamiltonian is written in the form

\[
\hat{H}(R) = \hat{H}(R) + H'(R)
\]

(23)

no matter what perturbation \( H' \) represents.

The reason for short sketch of the BOA in the introductory part is to attract an attention toward some aspects, which at study of solids, in particular of superconductors, are tacitly assumed to hold implicitly and seemingly there are no indications raising doubts that this class of solids should be an exception.

The main aspect is the \( R \)-dependence of the BOA. Whatever trivial it seems to be, it has to be stressed that the study of many-body system by means of the clumped nuclei Hamiltonian (21)–(23) requires validity of the Born ansatz (16), (3), that is, fulfillment of (20) to hold not only for equilibrium nuclear geometry \( R_{\text{eq}} \) but also for displaced geometry \( R_{\text{eq}} + \Delta R \). Displacement \( \Delta R \) has to be as large as to cover full configuration space \( | R \rangle \) experienced by nuclei in the vibration (phonon) modes of system. At 0 K temperature, \( \Delta R \) has to be greater than (or at least equal to) root-mean square displacement \( \bar{x}_{0(v)} \) of vibration (phonon) mode \( \nu \) at zero-point energy:

\[
\bar{x}_{0(v)} = \left\langle \phi_{0(v)}^{2} \right\rangle \right\rangle^{\frac{1}{2}}.
\]

(24)

It means that for validity of the BOA, the inequality for the energy spectrum which, along with (20), has to be also fulfilled is

\[
\left| E_{0}^{n}(R_{\text{eq}} + \bar{x}_{0(v)}) - E_{0}^{n}(R_{\text{eq}} + \bar{x}_{0(v)}) \right| \gg \hbar \omega_{v}.
\]

(25)

In this context, the adiabatic electronic energies of the ground and excited electronic states \( \{ E_{0}^{n}, E_{n}^{ef} \} \) at fixed nuclear geometry \( | R \rangle \), need also some comment. Without the loss of generality, the Hartree-Fock (HF) calculation scheme in direct-real space orbital representation can be assumed. The adiabatic wave function of the electronic ground state is represented by the Slater determinant that satisfies requirement of antisymmetry:

\[
\Phi_{0}(r, | R \rangle) = \prod_{n} \tilde{\varphi}_{n}(r_{n}) = \prod_{n} \phi_{n}(r_{n})_{n} / \sqrt{N_{n}}.
\]

(26)
where for simplicity a closed-shell, \( N_e = 2n_e \) electron system, is considered. In (26), lowest laying \( n_e \) spatial orbitals are occupied, each being occupied twice, once by an electron with a spin, \( \varphi_n \), and once with \( \beta \) spin, \( \varphi_n' \). Adiabatic total electronic energy of the ground state is then the sum of adiabatic electronic energy and Coulomb repulsion \( E_{NN}(R_0) \) of bare nuclei at fixed geometry \([R] = R_0\):

\[
E^\nu_{\nu}(R_0) = E^\nu_{NN}(R_0) + E^\nu_{SCF}(R_0)
\]

\[
= E^\nu_{NN}(R_0) + \left( 2 \sum_{I} h^0_{II} + \sum_{IJ} (2\nu_{IJ} - \nu^2_{II}) \right)
= E^\nu_{NN}(R_0) + \sum_{I} \left( \epsilon^0_I + h^0_{II} \right).
\]

Summation indices \( \{I,J\} \) in (27) run over the occupied states \( \{\varphi_I, \varphi_J\} \).

Set of \( \{\epsilon^0_I\} \) in (27), is one-electron spectrum of the adiabatic electronic ground state (26), that is, orbital energies \( \{\epsilon^0_I\} \) are eigenvalues:

\[
\epsilon^0_p = h^0_{pp} + \sum_{Q} (2\nu^2_{QP} - \nu^2_{QPP})
\]

of the Fock operator \( F(R_0) = h^0_{pp}(R_0) + \sum_{Q} (2I_Q - K_Q) \):

\[
F(R)\varphi_p(r, R_0) = \sum_{Q} \epsilon^0_{pQ}\varphi_Q(r, R_0)
\]

and \( \{\varphi_Q\} \) is the set of corresponding eigenfunctions (orthonormal set of optimized orbitals). In (28), \( h_{pp} \) is diagonal element of one-electron core Hamiltonian \( h_{core} \) (integrals of electronic kinetic energy term plus electron-nuclear Coulomb attraction term), and \( I_Q, K_Q \) are 2-electron (1,2,3, or 4 nuclear center) Coulomb repulsion and exchange integrals.

In the next step, instead of independent calculation of electronic excited states energies \( \{\epsilon_{n}(\varphi_0(R))\} \), which would require new optimization of excited state wave functions \( \Phi_{m}(r, R) \) (it should be extremely complicated since excited state wave functions have to be orthogonal to the ground state wave function), in practice a fairly good approach is used which is based on the orbitals \( \{\varphi_Q\} \) already optimized for the ground-state wave function \( \Phi_{0}(r, R_0) \). Optimization is always performed within a basis set with some finite number \( n \) of basis set functions \( |\mu_{n}\rangle \), while \( n > N_e \). Diagonalization of (29) then yields \( n \) eigenfunctions \( \{\epsilon_{n}(R)\} \) and corresponding eigenenergies \( \{\epsilon_{n}(R)\} \), but only \( n_e \) lowest-lying spatial orbitals \( \{\varphi_I(R)\} \) are occupied and remaining \( (n - n_e) \) are virtual—unoccupied orbitals \( \{\varphi_A(R)\} \). By promotion of electron(s) from occupied orbital(s) \( \{I,J,\ldots\} \) to virtual—unoccupied orbital(s) \( \{A,B,\ldots\} \), excited state(s) configuration(s) \( \{\Phi_A\} \) as a linear combination of corresponding Slater determinants \( \{\varphi_I - \varphi_A\} \) can be constructed. It can be shown that, for example, single-electron excitations yield two excited state electronic configurations—lowest lying excited state, that is, singly excited triplet state \( ^3\Phi_{A(I - A)} \) and singly excited singlet state \( ^1\Phi_{A(I - A)} \). Differences in the electronic energies of these excited state configurations with respect to the electronic energy of the ground state are as follows:

(i) for singly excited singlet,

\[
E^{\nu_{\nu}}_{A(I - A)}(R) - E^{\nu_{\nu}}_{0}(R) = \epsilon^0_{A}(R) - \epsilon^0_{\nu}(R) - J_{IA};
\]

(ii) for singly excited triplet state,

\[
E^{\nu_{\nu}}_{A(I - A)}(R) - E^{\nu_{\nu}}_{0}(R) = \epsilon^0_{A}(R) - \epsilon^0_{\nu}(R) - J_{IA} + 2K_{IA}.
\]

From (30), (31), it is clear that for approximations which do not consider explicitly for two-electron terms, the differences in energies of singly excited triplet and singlet states with respect to the ground-state energy are the same:

\[
E^{\nu_{\nu}}_{A(I - A)}(R) - E^{\nu_{\nu}}_{0}(R) = \epsilon^0_{A}(R) - \epsilon^0_{\nu}(R).
\]

Multiple electronic excitations can be calculated in a similar way, by generation of Slater determinants of \( p \) (equiv. \( p \))-hole states in the language of particle-hole formalism.

The important point is that clumped nuclei electronic ground-state energy calculation provides approximate information about electronic excited states over the one-electron spectrum which corresponds to the electronic ground state. In particular, over the optimized set of occupied \( \{\varphi_I\} \) and unoccupied-virtual (\( \varphi_A \)) spinorbitals.

In the simplest form, with respect to (32), the inequalities (20), (25) which have to be valid for save application of the BOA, are in the terms of the optimized ground state orbital energies expressed as follows:

(i) for system at equilibrium geometry \( R_{eq} \),

\[
|\epsilon^0_{\nu}(R_{eq}) - \epsilon^0_{A}(R_{eq})| \gg \hbar\omega_{\nu}
\]

has to hold for the couple of frontier orbitals, that is, for highest occupied \( \varphi_I \) \( \equiv \varphi_{HOMO} \) and lowest unoccupied \( \varphi_A \) \( \equiv \varphi_{LUMO} \) orbitals;

(ii) more over,

\[
|\epsilon^0_{\nu}(R_{eq} + \varpi_{\nu}(\varphi)) - \epsilon^0_{A}(R_{eq} + \varpi_{\nu}(\varphi))| \gg \hbar\omega_{\nu}
\]

has to hold for the same system at displaced nuclear configuration with respect to particular vibration(phonon) mode \( \nu \).

In case of solids with quasicontinuum of states, in momentum \( k \)-space representation, these inequalities can be rewritten in the form

\[
|\epsilon^0_{\nu}(k_c) - \epsilon^0_{A}(k_c)| \gg \hbar\omega_{\nu}
\]
for equilibrium nuclear geometry, and

$$\left| \varepsilon_0^2(k_e) - \varepsilon_F^0 \right|_{R_{eq} + \bar{x}_{0(\nu)}} \gg \hbar \omega_\nu,$$  \hspace{1cm} (36)

for the same system at displaced nuclear configuration in particular phonon mode \(r\).

These inequalities have to be valid in a multiband system for each band \(S\) and energies \(\{\varepsilon_0^S(k_e)\}\) of analytic critical points (ACP—i.e., absolute and local minima and maxima or inflex points) located on the particular band-dispersion curve of the first BZ with respect to the energy of the Fermi level \(\varepsilon_F^0\).

An important aspect should be reminded at this place. Inequalities (33)–(36) have been derived on the basis of the expansion (19) of the effective nuclear potential (i.e., total electronic energy \(E^0_{en}(R)\)) at \(R_{eq}\). With respect to the inner structure of the total electronic energy (27), it is clear that in principle, the expansion (19) can be performed (i.e., smallness in energy change \(\Delta E^0_{en}(R_{eq}+\Delta R)\) as to ensure at least harmonic approximation) even if displacement \(\Delta R\) yields significant changes in the one-electron spectrum (orbital energies) of the ground state

$$\{\varepsilon_0^0\}_{R_{eq}} \not\equiv \{\varepsilon_0^0\}_{R_{eq}+\bar{x}_{0(\nu)}},$$  \hspace{1cm} (37)

provided that these changes are well balanced by changes \(\Delta h_{II}\) and \(\Delta E_{NN}\), eventually also by changes \(\Delta J_{ij}, K_{ij}\) if two-electron terms are explicitly included. The main point is that for the electronic ground state, the one-electron spectrum at \(R_{eq}\) \(\{\varepsilon_0^0\}_{R_{eq}}\), can be significantly different from the one-electron spectrum \(\{\varepsilon_0^0\}_{R_{eq}+\bar{x}_{\nu}}\) at displaced nuclear configuration \(R_{eq}+\bar{x}_{\nu}\) for some phonon mode \(\nu\).

In respect of it, possibility that displacement \(\bar{x}_{0(\nu)}\) yields for some band situation when

$$\left| \varepsilon_0^2(k_e) - \varepsilon_F^0 \right|_{R_{eq} + \bar{x}_{0(\nu)}} \leq \hbar \omega_\nu,$$  \hspace{1cm} (38)

even if for the equilibrium geometry \(R_{eq}\) (35) holds, is not excluded at all.

The reason of possibility for such substantial changes of the electronic (band) structure is hidden in the chemical composition and structure of particular system. With respect to (27)–(31), it is connected to the changes of one-electron core part \(\Delta h_{II}\) and/or two-electron Coulomb repulsion and exchange integrals \(\Delta J_{ij}, K_{ij}\). Which of these are dominant (hopping terms, onsite/inter-site repulsion, electron correlations, dynamic screening, etc.) can hardly be determined on the basis of model Hamiltonians without invoking for complete chemical composition and structure of the particular system.

Occurrence of such a situation means that nuclear motion (nuclear vibration, in particular, phonon mode) has induced sudden decrease of effective electron velocity \((\partial \varepsilon_0^a(k))/(\partial k)_{k_e}\) in particular band close to analytic critical point \(k_e\) at the Fermi level \(\varepsilon_0F\). Or, what is equivalent, the effective mass of electrons has been increased in this region. In any case, however, it means that at displaced nuclear geometry \(R_{eq}+\bar{x}_{0(\nu)}\), electrons, and nuclei of the system do not move as independent particles, that is, in this region, electrons are not able to follow nuclear motion adiabatically. The motion of electrons and nuclei is now strongly correlated. The new situation occurs, the adiabatic BOA is not valid for nuclear geometry \((R_{eq}+\bar{x}_{0(\nu)})\), and wave function cannot be factorized in the form (16) and (3), that is,

$$\Psi_0 \left( r, R_{eq} + \bar{x}_{0(\nu)} \right) \not\equiv \chi_{0(\nu)} \left( R_{eq} + \bar{x}_{0(\nu)} \right) \Phi_0 \left( r, R_{eq} + \bar{x}_{0(\nu)} \right),$$  \hspace{1cm} (39)

and standard adiabatic form of the Hamiltonian (21)–(23) cannot be applied to study an electron-phonon problem. What is crucial, however, is the fact that the nonadiabatic effect cannot be calculated as a perturbation, that is, as a nonadiabatic correction to the adiabatic ground state at \(R_{eq}\). In this case, system is in true nonadiabatic or antiadiabatic state.

2.2. Generalization of the BOA Beyond Adiabatic Regime. In order to solve the problems which are sketched above, one needs to study electronic motion as explicitly dependent on nuclear dynamics, that is, dependent on instantaneous nuclear coordinates \(Q\) and nuclear momenta \(P\). It means that electronic state has to be explicitly dependent on nuclear operators \(Q\) and \(P\). Approximate solution of this problem can be found in [66]. It is based on the sequence of basis functions transformations, starting with fixed basis set \((Q, P\text{-independent})\) over-\(Q\)-dependent base up to \(QP\)-dependent basis set. A base function transformation is canonical transformation and it ensures that each transformation step preserves corresponding statistics. Moreover, since we start from fixed basis set (clamped nuclei situation) which enables factorization of total system wave function, this property is required to be preserved at each transformation step up to quadratic terms in \(Q\) and \(P\). Consequently, it makes the solution of \(Q, P\)-dependence tractable. It should be stressed that base functions transformation is equivalent to the quasiparticle transformation which we have formulated in 1992 [67].

Main aspects and the results of this treatment are presented below.

General nonrelativistic form of system Hamiltonian (2) can be written in second quantization formalism as

$$H = T_N(P) + E_{NN}(Q) + \sum_{PQ} h_{PQ}(Q)a_P^+a_Q^- + \frac{1}{2} \sum_{PQRS} v_{PQRS}a_P^+a_Q^+a_R^+a_S^-$$  \hspace{1cm} (40)

Nuclear potential energy \(E_{NN}\) and one-electron core term \(h_{PQ}\) (electron kinetic energy plus electron-nuclear coulomb attraction term) are functions of the nuclear coordinate \(Q\) operators (normal modes \((r\)) nuclear displacements out of fixed nuclear geometry \(R_0\) and nuclear kinetic energy \(T_N\) is a quadratic function of the corresponding
parametrically dependent on nuclear configuration, that is, nuclear geometry is fixed at nuclear configuration \( R_0 \):

\[
H_e(R_0) = E_{NN}^0(R_0) + \sum_{PQ} h_{PQ}^0(R_0) \overline{n}_P \overline{n}_Q + \frac{1}{2} \sum_{PQRS} v_{PQRS} \overline{n}_P \overline{n}_Q \overline{n}_R \overline{n}_S.
\]

(44)

Application of Wick’s theorem to the product of creation and annihilation operators yields for particular terms the normal product form (N-product) with corresponding contractions:

\[
\sum_{PQ} h_{PQ}^0 \overline{n}_P \overline{n}_Q = \sum_{PQ} h_{PQ}^0 N[\overline{n}_P \overline{n}_Q] + \sum_{T} \overline{h}_{TT}^0,
\]

(45)

\[
\sum_{PQRS} v_{PQRS} \overline{n}_P \overline{n}_Q \overline{n}_R \overline{n}_S
\]

\[
= \sum_{PQRS} v_{PQRS} N[\overline{n}_P \overline{n}_Q \overline{n}_R \overline{n}_S] + \sum_{I,I,J} \left( v_{IJIJ}^0 + v_{I,I,J}^0 - v_{I,J,IJ}^0 - v_{I,J,J}^0 \right) N[\overline{n}_P \overline{n}_Q \overline{n}_R ]
\]

(46)

Application of Wick’s theorem introduces renormalized Fermi vacuum, that is, the total set of orthonormal base orbitals \( \{ \phi_F, \phi_Q, \ldots \} \) is divided on two distinct groups; the set of occupied \( \{ \phi_F, \phi_Q, \ldots \} \) spinorbitals which form a Fermi see (FS) and set of unoccupied-virtual \( \{ \phi_A, \phi_B, \ldots \} \) spinorbitals which are above the FS.

The electronic Hamiltonian (44) can now be written in a quasiparticle form as a sum of zero, one- and two-particle terms:

\[
H_e(R_0) = H_{(0)}(R_0) + H_{(1)}(R_0) + H_{(2)}(R_0).
\]

(47)

(1) Electronic ground state energy.

The scalar quantity in this Hamiltonian, that is, zero-particle term \( H_{(0)}(R_0) \), is the result of the operators contractions and has the form

\[
H_{(0)}(R_0) = \langle \Phi_0 | H_e | \Phi_0 \rangle
\]

\[
= \sum_{I,J} \overline{h}_{IJ}^0 + \frac{1}{2} \sum_{I,J} \left( v_{IJIJ}^0 + v_{I,J,IJ}^0 - v_{I,J,J}^0 - v_{I,J,J}^0 \right)
\]

(48)

\[
= E_{SCF}^0(R_0).
\]

This term represents ground-state electronic energy calculated by unrestricted Hartee-Fock SCF (HF-SCF) procedure at fixed nuclear configuration \( R_0 \). It is obvious that addition of nuclear repulsion \( E_{NN}^0(R_0) \) to this term yields total electronic energy \( E_{el}^0(R_0) \). Electronic ground state is represented by renormalized Fermi vacuum \( \Phi_0 \). It is an antisymmetric electronic wave function, that is, expressed in
the form of single Slater determinant constituted by lowest laying occupied spinorbitals \( \{ \varphi_I \} \) of complete orthonormal base \( \{ \varphi_p \} \):

\[
\Phi_0(r, R_0) = | \varphi_1 \cdots \varphi_I | 
\]

(49)

\( \Phi_0(r, R_0) \) holds:

(II) **Electronic energy spectrum.**

The one-particle term \( H^{(1)}(R_0) = H_{\text{cad}}^{(1)}(R_0) \) of the electronic Hamiltonian (47) has the form,

\[
H^{(1)}(R_0) = \sum_{PQ} F_{PQ} N[\pi^+ P \pi_Q].
\]

Diagonalization of (50), \( F_{PQ} = \epsilon^0_P \delta_{PQ} \), that is, solution of electronic Hartree-Fock equations by HF-SCF procedure:

\[
F(R_0) \varphi_0(r, R_0) = \sum_Q \epsilon^0_Q \varphi_Q(r, R_0)
\]

yields set of eigenvalues, that is, HF-orbital energies:

\[
\epsilon^0_p = h^0_{pp} + \sum_Q \left( \epsilon^0_Q \delta_{PQP} - \epsilon^0_P \delta_{QPP} \right),
\]

(51c)

and corresponding set of eigenfunctions \( \{ \varphi_p \} \), the orthonormal set of optimized spinorbitals.

It means that one-particle term (50) can always be written in diagonal form and represents a set of unperturbed eigenenergies of system at fixed nuclear geometry \( R_0 \), that is,

\[
H^{(1)}(R_0) = \sum_P \epsilon^0_P N[\pi^+_P \pi_P],
\]

(51d)

\[
H^{(1)}(R_0) | \Phi_0 \rangle = 0
\]

(51e)

for excited states hold:

\[
H^{(1)}(R_0) | \Phi_{I-A} \rangle = (\epsilon^0_A - \epsilon^0_I) | \Phi_{I-A} \rangle \quad \text{for } I \in \text{FS, A} \notin \text{FS},
\]

(51f)

In an approximate way, the one-particle Hamiltonian \( H^{(1)}(R_0) \) represents complete electronic spectrum expressed over occupied and unoccupied-virtual spinorbitals calculated for electronic ground state \( \Phi_0(r, R_0) \) by HF-SCF procedure. In particular, \( n \)-electron excited state wave function \( \Phi_{I-A} \) can be constructed, as it has already been mentioned, by promotion of \( n \) electrons from \( n \) occupied spinorbitals to \( n \) unoccupied spinorbitals (i.e., the same number \( n \) of holes \( \langle h_n \rangle \) and particles \( \langle p_n \rangle \) are created). Electronic energy of such excited state can be calculated through HF-eigenenergies that correspond to optimized spinorbitals of the ground state. It should be pointed that it is only an approximate way for description of true electronic excited states.

In terms of orbital energies (51c), for total electronic ground state energy, \( E^0_{\text{corr}}(R_0) \) holds:

\[
E^0_{\text{corr}}(R_0) = E_{NN}^0(R_0) + E_{\text{SCF}}^0(R_0)
\]

\[
= E_{NN}^0(R_0) + \left( \sum_{IJ} H_{J}^I + 1/2 \sum_{IJ} (\epsilon^0_{IJ} - \epsilon^0_{IJ}) \right)
\]

(52)

For closed-shell electronic systems, within restricted HF approximation (doubly occupied spatial orbitals with \( \alpha \) and \( \beta \) spins), (27) holds. Total electronic ground-state energy of the system reaches the minimum at some equilibrium nuclear configuration \( R_0 = R_0 \). Corresponding Slater determinant (49) represents wave function of the electronic ground state at equilibrium nuclear configuration.

(III) **Electron correlation energy.** (see Note in Section 1).

The third term of the electronic Hamiltonian (47), that is, the two-particle term has the form

\[
H^{(2)}(R_0) = H_{\text{cad}}^{(2)}(R_0) = \frac{1}{2} \sum_{PQRS} \epsilon^0_{PQRS} N[\pi^+_P \pi^+_Q \pi^-_R \pi^-_S].
\]

(53)

Formally it looks like standard coulomb electron-electron interaction term in (44). With respect to the fact that after application of Wick’s theorem (45) the renormalized Fermi vacuum has been introduced and zero-particle (scalar) quantity (48) represents electronic energy of the ground state that accounts also for coulomb electron-electron interactions (48) and one-particle term is diagonal (51d) and represents unperturbed HF-orbital energies \( \{ \epsilon^0_p \} \) of the system (one-electron energy spectrum), then two-particle term (53) represents perturbation part of the electronic Hamiltonian (47). Since perturbation (53) contains only electron-electron interaction term, contributions of this term represent electron correlation energy of the system in its ground electronic state. In this respect, electron correlation energy is treated as a perturbation. Calculation of the electron correlation energy up to higher order of perturbation theory is usually done by diagrammatic many-body perturbation theory. For correlation energy in second order of perturbation theory, analytic expression for closed-shell system can be derived in a simple form

\[
E_{\text{corr}}(R_0) = H_{(h_i h_p p_i)}(R_0) = \sum_{I \neq J} \sum_{AB} \frac{2\epsilon^0_{IAB} - \epsilon^0_{IAB}}{\epsilon^0_{I} + \epsilon^0_{J} - \epsilon^0_{A} - \epsilon^0_{B}}.
\]

(54)

Related to energy of the Fermi level, energies of unoccupied states are \( \{ \epsilon^0_A \} > 0 \) and energies of occupied states are \( \{ \epsilon^0_I \} < 0 \). It means that \( E_{\text{corr}} \) is negative, that is, it decreases electronic energy of the ground state (this contribution corrects and stabilizes total electronic energy of the system (27), (52)). This holds for arbitrary nuclear geometry \( R_0 \) until system remains in a bound state.
Solution of nuclear problem (9) on crude-adiabatic level is now straightforward.

Nuclear part of Hamiltonian is

$$H_N = T_N + V_{\text{eff}}(R) = \sum R \hbar \omega \left( P^+ R \frac{1}{2} \right). \tag{55}$$

For different, but fixed nuclear configurations $[R]$ at $R_0 = R_{\text{eq}}, E^{\text{eff}}_{\text{N}}(R)$ is calculated and effective potential for nuclear motion is derived $V^{\text{eff}}_{N}(R)$. It has to be stressed that contributions of DBOC—$B_{K0}(R)$, that is, (10), to $V^{\text{eff}}_{N}(R)$ are in this case neglected.

Energy and wave function of the total system in the ground electronic state are

$$E^{TS}_{0} (R_{0}) = E^{te}_{0} (R_{\text{eq}}) + \sum R \hbar \omega (n_{r} + 1/2), \tag{56}$$

$$\Psi_{0}(r, R) = \chi_{0}(R) \Phi_{0}(r, R_{\text{eq}}), \tag{57}$$

or in terms of $Q : \Psi_{0}(r, Q) = \chi_{0}(Q) \Phi_{0}(r, 0)$.

Nuclear wave function is

$$\chi_{0}(R) = \prod_{r} \chi_{0,r}(R) = \prod_{r} \frac{1}{\sqrt{N_{r}}} \left( P_{r}^{+} \right)_{0} |0\rangle. \tag{58a}$$

### 2.2.2. Base Transformation—Introduction of New Dynamical Variables.

Each eigenfunction $\phi_{f}$ in Slater determinant (49) can be expressed as a linear combination of atomic orbital (AO) basis functions $\{ \mu \}$, $\phi_{f} = \sum_{\mu} c_{\mu f} | \mu \rangle$, which are fixed at the positions of the particular nuclei in clamped nuclei configuration $R_0$. It represents fixed basis set $\{ \mu(x, 0) \equiv \mu(x, 0) \}$.

In second quantization, with single-bar $\pi^{+}$ being creation operator of the crude-adiabatic electron (clamped nuclei approximation, independent on $Q$ and $QP$), base function $\mu(x, 0)$ can be written with respect to “absolute” Fermi vacuum $|0\rangle$ as

$$\mu(x, 0) = \pi^{+}_{\mu}(x, 0) |0\rangle \tag{59}$$

and

$$\phi_{f}(x, 0) = \sum_{\mu} c_{\mu f} | \mu(x, 0) \rangle \tag{60a}$$

$$= \sum_{\mu} c_{\mu f} \pi^{+}_{\mu}(x, 0) |0\rangle$$

$$= \pi^{+}_{\mu}(x, 0) |0\rangle.$$

For solids, in electronic quasimomentum $k$-space, the basis functions are Bloch-periodic orbitals $\{ \mu(k, x, 0) \}$:

$$\mu(k, x, 0) = \frac{1}{\sqrt{N}} \sum R e^{i k R} \mu(x - t R). \tag{60b}$$

In (60b), $tR$ is translation vector and $\mu(x - tR) = \mu(x)$. The set of $\{ \mu(x) \}$ is fixed basis set $\{ \mu(x, 0) \}$ at frozen nuclear configuration $R_0(Q = 0)$. An eigenfunction $\phi_{f}$ is then crystal orbital $\text{CO-}\phi_{f}$ (band $\phi_{f}$), which is a linear combination of the Bloch-periodic basis functions $\{ \mu(k, x, 0) \}$.

In a second quantization, it has the form

$$\mu(k, x, 0) = \frac{1}{\sqrt{N}} \sum_{t R} e^{i k t R} \pi^{+}_{\mu}(x, 0) |0\rangle, \tag{60c}$$

$$\phi_{f}(k, x, 0) = \sum_{\mu} c_{\mu f} | \mu(k, x, 0) \rangle \tag{60d}$$

$$= \sum_{\mu} c_{\mu f} \frac{1}{\sqrt{N}} \sum_{t R} e^{i k t R} \pi^{+}_{\mu}(x, 0) |0\rangle$$

$$= \frac{1}{\sqrt{N}} \sum_{t R} e^{i k t R} \pi^{+}_{\mu}(k, x, 0) |0\rangle.$$

In this case, occupancy of the band is not distinguished by the index (subscript) of the band, but it is determined by the value of $k$-vector of particular band dispersion $\epsilon_{f}^{0}(k)$ with respect to the energy of Fermi level $\epsilon_{f}^{0}$. It is obvious that Hamiltonian of system (40), (44) is now Hamiltonian which corresponds to the composition of unit cell and total electronic energy calculation results in corresponding band structure.

For fermion and boson creation and annihilation operators, the standard anticommutation, and commutation relations hold:

$$[\pi_{\mu}, \pi_{Q}^{\dagger}] = 0, \quad [\pi_{\mu}, \pi_{Q}] = \delta_{\mu Q}, \tag{61a}$$

$$[\bar{\pi}_{r}, \bar{\pi}_{Q}] = 0, \quad [\bar{\pi}_{r}, \bar{\pi}_{Q}^{\dagger}] = \delta_{rs}. \tag{61b}$$

Simultaneous diagonalization of electronic and nuclear part of system Hamiltonian, that is, factorized form of system wave function (57) within adiabatic BOA implies also validity of the following commutation relations:

$$[\pi_{\mu}, \bar{\pi}_{r}] = 0, \quad [\pi_{\mu}, \bar{\pi}_{r}^{\dagger}] = 0. \tag{61c}$$

(1) Q-Dependent Adiabatic Transformation.

In case of crude-adiabatic approximation, the electrons “see” the nuclei at theirs instantaneous positions at rest and nuclei do not “feel” internal dynamics of electrons. Within the spirit of the BOA, it would be correct if the electrons follow nuclear motion instantaneously, that is, electronic state has to dependent explicitly on instantaneous nuclear positions. In this case, the wave function of the system, instead of the form (57) with Q-independent electronic part should be replaced by Q-dependent form, that is,

$$\Psi_{0}(r, R) = \chi_{0}(R) \Phi_{0}(r, R), \tag{62}$$

or

$$\Psi_{0}(r, \overline{Q}) = \chi_{0}(Q) \Phi_{0}(r, \overline{Q}).$$
Adiabatic, nuclear displacement Q-dependent electronic wave function $\Phi_0(r, \overline{Q})$ in (62) assumes existence of complete orthonormal basis set $\{\varphi_R(x, \overline{Q})\}$, that is, validity of the following relations:

$$\langle \varphi_R(x, \overline{Q}) | \varphi_S(x, \overline{Q}) \rangle = \delta_{RS},$$

$$\sum_R \left| \varphi_R(x, \overline{Q}) \right\rangle \left\langle \varphi_R(x, \overline{Q}) \right| = 1.$$

(63)

Now, electron creation and annihilation operators which correspond to the Q-dependent moving base are denoted as double-bar operators ($\overline{\pi}^\dagger, \overline{\pi}$). Also, the boson operators related to the Q-dependent moving base are written as double-bar operators:

$$\overline{Q}_r = \left( \overline{b}^+_r + \overline{b}_r \right), \quad \overline{\pi}_r = \left( \overline{b}^+_r - \overline{b}^+_r \right).$$

(64)

Then,

$$\overline{\pi}^\dagger_r(x, \overline{Q}) | 0 \rangle = | \varphi_R(x, \overline{Q}) \rangle,$n

(65)

$$\overline{\pi}_r(x, \overline{Q}) | \varphi_S(x, \overline{Q}) \rangle = 0.$$

Since adiabatic electrons remain fermions, the operators have to obey standard fermion anticommutation relations:

$$\left\{ \overline{\pi}_R, \overline{\pi}^\dagger_S \right\} = \delta_{RS}, \quad \left\{ \overline{\pi}_R, \overline{\pi}_S \right\} = 0.$$n

(66)

Shorthand notation, $\overline{\pi}_R = \overline{\pi}_R(x, \overline{Q})$, $\overline{\pi}^\dagger_R = \overline{\pi}^\dagger_R(x, \overline{Q})$ has been used in (66).

Crude-adiabatic electronic wave function $\Phi_0(r, 0)$ which does not depend on the nuclear displacements Q is expanded over fixed basis set with spinorbitals $\{\varphi_R(x, 0)\}$ that are eigenfunctions of clamped nuclear electronic Hartree-Fock equations (30). This is complete and orthonormal basis set

$$\langle \varphi_R(x, 0) | \varphi_S(x, 0) \rangle = \delta_{RS},$$

$$\sum_R \left| \varphi_R(x, 0) \right\rangle \left\langle \varphi_R(x, 0) \right| = 1.$$n

(67)

Crude-adiabatic fermion creation and annihilation operators that correspond to the fixed basis set are written as single-bar operators ($\pi^\dagger, \pi$), that is,

$$\overline{\pi}^\dagger_R(x, 0) | 0 \rangle = | \varphi_R(x, 0) \rangle, \quad \overline{\pi}_R(x, 0) | \varphi_R(x, 0) \rangle = | 0 \rangle,$$

or in short-hand notation

$$\overline{\pi}^\dagger_R | 0 \rangle = | \varphi_R(x, 0) \rangle, \quad \overline{\pi}_R | \varphi_R(x, 0) \rangle = | 0 \rangle.$$n

(68)

These operators pertain to ordinary (crude-adiabatic) electrons and the standard anticommutation relations (61a) hold.

Due to properties (63), (67), the two bases are interconnected by the base transformation of the following form:

$$| \varphi_R(x, 0) \rangle = \sum_R \left| \varphi_S(x, \overline{Q}) \right\rangle \left\langle \varphi_S(x, \overline{Q}) \right| \varphi_R(x, 0) \rangle$$

$$= \sum_S \left( c_{RS}(\overline{Q}) \right)^\dagger \left| \varphi_S(x, \overline{Q}) \right\rangle.$$

(69)

Now, for fermion operators in Q-dependent moving base one can write

$$\overline{\pi}_R = \sum_S c_{RS}(\overline{Q}) \overline{\pi}_S, \quad \overline{\pi}^\dagger_R = \sum_S (c_{RS}(\overline{Q}))^\dagger \overline{\pi}^\dagger_S.$$n

(70)

Elements $c(Q)$ of the Q-dependent transformation matrix $C(Q)$ in (69), (70) are

$$c_{RS}(\overline{Q}) = \langle \varphi_R(x, 0) | \varphi_S(x, \overline{Q}) \rangle.$$n

(71)

Since

$$c^*_{RS}(\overline{Q}) = \langle \varphi_S(x, \overline{Q}) | \varphi_R(x, 0) \rangle,$$

(72)

then due to closure property and orthonormality (63), (67) of the bases, it can be derived that base transformation matrix $C(Q)$ is an unitary matrix:

$$\sum_T c_{ETS}(\overline{Q}) = \delta_{RS} = \sum_T c^*_{TRCTS},$$n

(73)

$$C^* = \left(C^T\right)^* = C^{-1}.$$n

(74)

It can be shown [66] that the base transformation is identical with canonical transformation of operators (see (70) and (74))

$$\overline{\pi}_R = U^+ \overline{\pi}_R U, \quad \overline{\pi}^\dagger_R = U^+ \overline{\pi}^\dagger_R U,$$

(75)

$$\sum_r \left( C_{ETS}(\overline{Q}) \right) \overline{\pi}_S, \quad \overline{\pi}^\dagger_R = \sum_S \left( C^*_{ETS}(\overline{Q}) \right)^\dagger \overline{\pi}^\dagger_S.$$n

(76)

It ensures preservation of statistics, that is, validity of the anticommutation relations (66) for new, Q-dependent, adiabatic electrons. The exponential form of canonical transformation (74) legitimates Taylor’s expansion of the matrix elements (71) and (72) of base transformation matrix, that is,

$$c_{PQ}(\overline{Q}) = \sum_{k=0}^\infty \frac{1}{k!} \sum_r c_{r,0}^{PQ} \overline{Q}_n \cdot \overline{Q}_n.$$n

(77)

The form of transformation relations for boson operators of system Hamiltonian has to respect the factorized form of the total system wave function (62). It implies possibility of simultaneous, independent diagonalization of electron and boson subsystems. It means that transformed fermion and transformed boson operators obey not only standard anticommutation and commutation relations within the individual subsystems:

$$\left\{ \overline{\pi}_P, \overline{\pi}_Q \right\} = 0, \quad \left\{ \overline{\pi}_P, \overline{\pi}^\dagger_Q \right\} = \delta_{PQ},$$n

(78)

$$\left[ \overline{b}_r, \overline{b}_s \right] = 0, \quad \left[ \overline{b}_r, \overline{b}^+_s \right] = \delta_{rs},$$n

(79)

but also transformed operators of both subsystems have to commute mutually like the original operators, that is, also the following commutation relations are required to hold:

$$\left[ \overline{\pi}_P, \overline{b}_r \right] = 0, \quad \left[ \overline{\pi}^\dagger_P, \overline{b}^+_r \right] = 0.$$n

(80)
With respect to the fermion transformation relations (70), the form of transformation relations for boson operators is expressed as
\[
\begin{align*}
\bar{b}_r &= \bar{b}_r + \sum_{PQ} d_{rPQ}(\bar{Q}) \bar{a}_P \bar{a}_Q, \\
\bar{b}^+_r &= \bar{b}^+_r + \sum_{PQ} (d_{rPQ}(-\bar{Q}))^+ \bar{a}_P \bar{a}_Q.
\end{align*}
\] (78)

Also for matrix elements \(d(\bar{Q})\) of transformation matrix \(D(\bar{Q})\), the Taylor’s expansion is defined as
\[
d_{rPQ}(\bar{Q}) = \sum_{k=0}^{\infty} \frac{1}{k!} \sum_{h_1 \cdots h_k} \partial^k \bar{Q}_{h_1} \cdots \bar{Q}_{h_k}. 
\] (79)

In order to ensure possibility of practical solution, in what follows, important restriction is imposed. The commutation relation (77) is required to hold up to quadratic terms in Taylor’s expansions. It enables to express transformation coefficients \(d(\bar{Q})_{RS}\) through coefficients \(c(\bar{Q})_{RS}\) (see [66]—Appendix A). It will be shown that \(c_{PR}\) covers the strength of electron-vibration (phonon) coupling up to the first order of Taylor’s expansion and determine also adiabatic correction to the electronic energy of the ground state \(\Delta E_{0(\text{ad})}\).

The adiabatic transformation preserves total number of electrons, and nuclear coordinate operator is invariant under the transformation, that is,
\[
\bar{N}_e = \sum_p \bar{a}_p \bar{a}_p = \sum_p \bar{a}_p \bar{a}_p = N_e, \\
\bar{Q}_r = (\bar{b}_r^+ - \bar{b}_r) = (\bar{Q}_r^+ + \bar{Q}_r) = \bar{Q}_r.
\] (80)

Up to the first order of Taylor’s expansion, the crude-adiabatic momentum operator \(\bar{P}_r = (\bar{b}_r - \bar{b}_r^+)\) is transformed as
\[
\bar{P}_r = \left(\bar{b}_r - \bar{b}_r^+\right) + 2 \sum_{PQ} \bar{c}_{PQ} \bar{a}_P \bar{a}_Q = \bar{P}_r + 2 \sum_{PQ} \bar{c}_{PQ} \bar{a}_P \bar{a}_Q. 
\] (81)

The term \(\bar{P}_r = (\bar{b}_r - \bar{b}_r^+)\) in (81) is nuclear momentum operator on adiabatic level.

For adiabatic Q-dependent spin orbitals \(|\varphi_p(x, \bar{Q})\rangle\), which are the basis functions of the adiabatic Q-dependent electronic wave function of the ground state \(\Phi_0(r, Q)\), expressed over crude-adiabatic orbitals can be derived:
\[
\begin{align*}
|\varphi_p(x, \bar{Q})\rangle &= \bar{a}_p^+(x, \bar{Q}) |0\rangle \\
&= \left(\bar{a}_p^+ - \sum_{rR} \bar{c}_{pR} \bar{Q}_r \bar{a}_R^+ + O(\bar{Q}^2)\right) |0\rangle \\
&= |\varphi_p(x, 0)\rangle - \sum_{rR} \bar{c}_{pR} \bar{Q}_r |\varphi_R(x, 0)\rangle + \cdots \\
&= |\varphi_p(x, 0)\rangle - \sum_{rR} \bar{c}_{pR} \bar{Q}_r |\varphi_R(x, 0)\rangle + \cdots. 
\end{align*}
\] (82)

As it is seen from (82), adiabatic wave function is modulated by the instantaneous nuclear coordinates \{\bar{Q}_r\} of particular vibration (phonon) modes \{r\} with the weight proportional to transformation coefficients \(\bar{c}_{pR}\) (coefficients of transformation matrix in the first order of Taylor’s expansion—\(\bar{c}_{pR} = \partial c_{pR}(\bar{Q})/\partial \bar{Q}_r\)).

At solution of the problem on adiabatic (Q-dependent) level, we have restricted ourselves to study total system in its electronic ground state with (62) representing wave function \(\Psi_0(r, R) = \chi_0, r(\bar{R})|\Phi_0(r, R)\rangle\). The Schrödinger equation of the total system (6) for electronic ground state \(\Phi_0(r, R)\) is then of the diagonal form (9). Seemingly we have lost the effect of electron-nuclear coupling through nuclear kinetic energy operator which is covered by \(\Lambda\) terms on the rhs of equation (6). The off-diagonal \(\Lambda\) terms are absent and from the diagonal \(\Lambda\) terms, the only non-zero element is \(\Lambda_{00}\). It is the DBOC, \(\Lambda_{00}(\bar{Q}) = B_{00}(\bar{Q}) = (\Phi_0(r, \bar{Q})|TN|\Phi_0(r, \bar{Q}))\), the mean value of nuclear kinetic energy in the electronic ground state which is expected to be negligibly small for systems in adiabatic state. Nonetheless, it will be shown that this term \((B_{00})\) covers the same effect of e-p coupling as it is routinely calculated in solid-state physics by perturbation theory with e-p coupling Hamiltonian (22) when electronic excited states are approximated by promotion of electrons to virtual orbitals of the electronic ground state.

(2) QP-Dependent Nonadiabatic Transformation.

As it has been mentioned in Section 1, study of band structure of superconductors indicates that e-p coupling induces fluctuation of some band through Fermi level. At the moment when ACP of such a band approaches Fermi level, there is considerable reduction of electron kinetic energy, which for antiadiabatic state results even for dominance of nuclear dynamics \(\omega \gg E_F\) in some region of \(k\)-space. Electrons at these circumstances are not able to follow nuclear motion adiabatically. It means that electronic wave function, in order to respect this fact, should be dependent not only on instantaneous nuclear coordinates \(Q\) but it should also be an explicit function of the instantaneous nuclear momenta \(P\), that is, \(\Phi_0 \equiv \Phi_0(r, Q, P)\).

Let us assume that wave function of total system can be found in the following factorized form:
\[
\Psi(r, Q, P) = \sum_m \chi_m(Q, P)\Phi_m(r, Q, P). 
\] (83)

The form of the wave function (83) is basically \(P\)-dependent modification of the original Q-dependent BOA (3).

Like in adiabatic case, solution of the problem will be restricted to electronic ground state, that is, for total system, we have
\[
\Psi_0(r, Q, P) = \chi_0(Q, P)\Phi_0(r, Q, P). 
\] (84)

It means that effect of nuclear momenta will be covered only in the form of QP-dependent diagonal correction \(\Lambda_{00}(Q, P) = (\Phi_0(r, Q, P)|TN|\Phi_0(r, Q, P))\), that is, in a similar way as it has been covered the effect of instantaneous nuclear coordinates \(Q\) on the adiabatic level, that is, Q-dependent adiabatic DBOC, \(\Lambda_{00}(\bar{Q}) = (\Phi_0(r, \bar{Q})|TN|\Phi_0(r, \bar{Q}))\).
Solution of this problem is similar to the transition from crude-adiabatic to adiabatic level as presented above. Now, the transition from adiabatic to antiadiabatic level is established.

Nonadiabatic, nuclear displacements, and momenta \((QP)\)-dependent electronic wave function \(\Phi_0(r, Q, P)\) in (84) assume existence of complete orthonormal basis set \(\{\varphi_R(x, Q, P)\}\), that is, validity of the following relations:

\[
\langle \varphi_R(x, Q, P) | \varphi_S(x, Q, P) \rangle = \delta_{RS},
\]

\[
\sum_R | \varphi_R(x, Q, P) \rangle \langle \varphi_R(x, Q, P) | = 1. \tag{85}
\]

Electron creation and annihilation operators that correspond to the \((QP)\)-dependent moving base are written as bar-less operators \((a^*, a)\). Boson operators related to the \((QP)\)-dependent moving base are denoted also as bar-less operators \(\hat{a}^*\) and \(\hat{a}\).

Elements of the \(P\)-dependent transformation matrix \(\hat{C}(P)\) are

\[
\hat{c}_{RS}(P) = \langle \varphi_R(x, \overline{Q}) | \varphi_S(x, Q, P) \rangle,
\]

\[
c^*_{RS}(P) = \langle \varphi_S(x, Q, P) | \varphi_R(x, \overline{Q}) \rangle. \tag{90}
\]

The \(P\)-dependent transformation matrix \(\hat{C}(P)\) is also unitary, that is, the relations hold:

\[
\sum_T \hat{c}_{RT} c^*_{ST} = \delta_{RS} = \sum_T \hat{c}^*_{TR} \hat{c}_{TS},
\]

\[
\hat{C}^* = (\hat{C}^T)^* = \hat{C}^{-1}. \tag{91}
\]

The form of transformation relations for boson operators of system Hamiltonian has to respect again the factorized form of the total system wave function (84). In this case, it expresses possibility of simultaneous, independent diagonalization of electron and boson subsystems. It means that transformed-nonadiabatic fermion and transformed nonadiabatic boson operators obey not only standard anticommutation and commutation relations within the individual subsystems,

\[
\{a_P, a_Q\} = 0, \quad \{a_P, a_Q^*\} = \delta_{PQ}, \tag{92}
\]

but also, like the original and adiabatic operators, transformed nonadiabatic operators of both subsystems have to commute mutually, that is, also commutation relations have to hold:

\[
[a_P, b_Q] = 0, \quad [a_P, b_Q^*] = 0. \tag{93}
\]

With respect to the fermion transformation relations (89), the form of transformation relations for boson operators that fully respects conditions (92) is

\[
\overline{b}_P = b_P + \sum_{PQ} \hat{d}_{PQ}(P) a_P^* a_Q,
\]

\[
\overline{b}_P^* = b_P^* + \sum_{PQ} (\hat{d}_{PQ}(P))^* a_P^* a_Q. \tag{94}
\]

Again, in order to enable practical solution, the commutation relation (93) is required to hold up to quadratic terms in Taylor’s expansions. This restriction enables to express transformation coefficients \(\hat{d}_{RS}\) through coefficients \(\hat{c}_{RS}\), see [66]—Appendix B.

It can be shown that also this transformation preserves the total number of particles, that is,

\[
N_e = \sum_P a_P^* a_P = \overline{N}_e = \sum_P \overline{a}_P^* \overline{a}_P = \overline{N}_e. \tag{95}
\]

Invariant of transformation is now momentum operator:

\[
P_r = (b_P - b_P^*) = \overline{P}_r = \overline{(b_P - b_P^*)}, \quad P_r = \overline{P}_r \neq \overline{P}_r. \tag{96}
\]

However, coordinate operator is transformed up to first order of Taylor’s expansion, as

\[
Q_r = (b_P + b_P^*)
\]

\[
= \overline{(b_P + b_P^*)} - 2 \sum_{PQ} \hat{c}_{PQ}(P) a_P^* a_Q
\]

\[
= \overline{Q}_r - 2 \sum_{PQ} \hat{c}_{PQ}(P) a_P^* a_Q. \tag{97}
\]
that is,
\[ \overline{Q}_r = \overline{Q}_r \neq Q_r. \] (98)

For nonadiabatic \((QP)\)-dependent spinorbitals \(|\varphi_P(x, Q, P)\rangle\) which are the basis functions of the nonadiabatic \((QP)\)-dependent electronic wave function of the ground state \(\Phi_0(r, Q, P)\), expressed over crude-adiabatic orbitals can be derived:
\[ |\varphi_P(x, Q, P)\rangle = a_P^\dagger(x, Q, P)|0\rangle \]
\[ = \left( a_P^\dagger - \sum_{rR} c_{PR} \overline{Q}_r a_R \right. \]
\[ - \left. \sum_{rR} \hat{c}_{PR} P_r a_R^\dagger + O(\overline{Q}, \overline{Q}P, P^2) \right)|0\rangle \]
\[ = |\varphi_P(x, 0, 0)\rangle - \sum_{rR} c_{PR} \overline{Q}_r |\varphi_R(x, 0, 0)\rangle \]
\[ - \sum_{rR} \hat{c}_{PR} P_r |\varphi_R(x, 0, 0)\rangle + \cdots. \] (99)

Nonadiabatic wave function (99) in contrast to adiabatic wave function (82) is modulated not only by the instantaneous nuclear coordinates \(|\overline{Q}_r\rangle\) of particular vibration (phonon) modes \(\{r\}\) but modulation is also over corresponding instantaneous nuclear momenta \(|P_r\rangle\). The weight of momentum modulation is proportional to the \(P\)-dependent transformation coefficients \(\hat{c}_{PR}\). It represents first derivative of \(\hat{c}_{PR}\) matrix element with respect to nuclear momentum \(P_r\), \(\hat{c}_{PR} = \partial \hat{c}_{PR}(P)/\partial P_r\), that is, coefficient of transformation matrix in the first order of Taylor’s expansion. It will be shown that these coefficients reflect not only the strength of e-p coupling but mainly the magnitude of nonadiabaticity. For true nonadiabatic situation, that is, for antiadiabatic state \(|\varphi_P^0(R) - \varphi_R^0(R)\rangle < \hbar \omega_r\), the weight of such \(P\)-modulated state can be significant.

2.2.3. Solution of Nonadiabatic Problem: Corrections to Energy Terms

(1) Transformations of System Hamiltonian

Base functions transformations have incorporated dependence of electronic states on operators of nuclear motion and vice versa. It implies, before the system Hamiltonian transformations, necessity to rearrange starting crude-adiabatic Hamiltonian:
\[ H = T_N(\overline{P}) + E_{NN}(\overline{Q}) \]
\[ + \sum_{PQ} h_{PQ}(\overline{Q}) P^a_P Q^a_Q + \frac{1}{2} \sum_{PQRS} v_{PQRS}^0 P^a_P Q^a_Q R^a_R \] (100)

into more convenient form.

Let us formally divide this Hamiltonian on two parts, \(H_A\) and \(H_B\).

(A) The nuclear part \(H_N\), as we already know, is quantized on crude-adiabatic level as
\[ H_N \rightarrow H_B = \sum_r \hbar \omega_r (\overline{Q}_r \overline{Q}_r + 1/2). \] (101)

In general, this part can be written as the sum of nuclear kinetic and nuclear potential energy:
\[ H_B = E_{kin}(\overline{P}) + E_{pot}(\overline{Q}), \] (102)

whereas
\[ E_{pot}(\overline{Q}) = E_{NN}^{(2)}(\overline{Q}) + V_N^{(2)}(\overline{Q}). \] (103a)

The standard, usually harmonic-quadratic part of the nuclear potential energy, \(E_{NN}^{(2)}(\overline{Q})\) is corrected now by some, yet unknown, potential energy term \(V_N^{(2)}(\overline{Q})\), that is, supposed to be also quadratic function of nuclear coordinate operators. Evidently, the \(V_N^{(2)}(\overline{Q})\) term is absent on crude-adiabatic level. This correction originates from the interaction of vibrating nuclei with electrons on adiabatic \(\overline{Q}\)-dependent level. In general, kinetic energy of vibration motion can also be corrected by some, yet unknown quadratic function of nuclear momenta operators-\(W_N^{(2)}(\overline{P})\), that is,
\[ E_{kin}(\overline{P}) = T_N(\overline{P}) + W_N^{(2)}(\overline{P}). \] (103b)

On the adiabatic \(Q\)-dependent level kinetic energy correction is negligibly small and it is neglected. It becomes important only when the BOA is broken, \(|E(P)(R) - E(R)| < \hbar \omega_r\), that is, in the case when electrons due to increased effective mass are not able to follow nuclear motion adiabatically and electronic states are \(QP\)-dependent. It should be stressed that both corrections are absent on crude-adiabatic level, they have been introduced just with respect to subsequent adiabatic and nonadiabatic transformation of system Hamiltonian.

(B) The second part of divided Hamiltonian is
\[ H_A = E_{NN}(\overline{Q}) - E_{NN}^{(2)}(\overline{Q}) - V_N^{(2)}(\overline{Q}) \]
\[ - W_N^{(2)}(\overline{P}) + \sum_{PQ} h_{PQ}(\overline{Q}) a_P^a a_Q + \frac{1}{2} \sum_{PQRS} v_{PQRS}^0 a_P^a a_Q a_R^a a_R. \] (104)

It is evident that the division on the two parts is only formal
\[ H = H_A + H_B = (100). \] (105)
The reason of it is mainly pragmatic with respect to transformations and final solution. In this way the total system Hamiltonian is divided on quasi-bosonic (nuclear part $H_B$) and quasifermionic (electronic $H_A$) Hamiltonians.

The system Hamiltonian (in the form (105)) is now prepared for canonical transformations. The frequently used form of canonical transformation,

$$ T : H \left( A_\mu \right) \equiv \tilde{H} \left( \tilde{A}_\mu \right) = H \left( \tilde{A}_\mu \right) = H \left( U^+ (A_\nu) A_\sigma U (A_\nu) \right), $$

(106)

$$ \tilde{A}_\mu = U^+ (A_\nu) A_\sigma U (A_\nu) = f (A_\nu), $$

(107a)

is applied in order to get diagonal, or “more diagonal”, final form at least up to first order of commutation expansion, $[H_0, S] + H_{int} = 0$. This kind of transformation changes the form of the Hamiltonian, but leaves unchanged the system variables.

Base functions transformations, as presented in preceding parts, introduce new dynamical variables; starting from crude-adiabatic $(a, a^\dagger, b, b^\dagger)$, new adiabatic $(\tilde{a}, \tilde{a}^\dagger, \tilde{b}, \tilde{b}^\dagger)$, and nonadiabatic $(a, a^\dagger, b, b^\dagger)$ quasiparticles are introduced. At these circumstances, canonical transformation of Hamiltonian means introduction of new dynamical variables

$$ A_\mu \equiv A_\mu (A'_\nu) = U^+ (A'_\nu) A'_\sigma U (A'_\nu). $$

(108)

Unlike to (106), now the Hamiltonian is not transformed itself, it remains of the original form, but its variables $(A_\nu)$ are replaced by new variables $(A'_\nu)$:

$$ H \left( A_\mu \right) \equiv H \left( U^+ (A'_\nu) A'_\sigma U (A'_\nu) \right). $$

(109a)

The Hamiltonian written in new variables is

$$ H \left( A_\mu (A'_\nu) \right) \equiv \tilde{H} \left( A'_\nu \right). $$

(109b)

Since at this transformation, there is no any requirement for fulfillment of condition like at (106), the transformation does not make Hamiltonian “more” diagonal. Usually it is more complex, but very often it discloses physical aspects of the problem that are not obvious from nontransformed form with the original variables of system Hamiltonian.

The system Hamiltonian (105) is now subjected to this type of transformation.

In the first step, transformation from crude-adiabatic to adiabatic quasiparticles is realized.

The adiabatic quasi-particle transformations, up to the second order of Taylor’s expansion, generate terms $H_{\mu \nu 1,2}$ and $H_{\mu \nu,1,2}$ whereas $i, j, k$ in subscript $(i, j, k)$ stand now for the $i$th order of Taylor’ series expansion in adiabatic representation, the $j$th order of the coordinate operator $\vec{Q}$, and the $k$th order of momentum operator $\vec{P}$ within the given order $i$ of Taylor’s expansion; that is, $i = (j + k)$.

Up to the second-order expansion in $\vec{Q}, \vec{P}$ and in second-order expansion of the operators of quasiparticle transformation $(\tau_P, \delta_P)$, the $H_A$ and $H_B$ parts are transformed in the following way:

$$ H_{A(0,0)} \to H_{A(0,0)} + H_{A1(1,0)} + H_{A2(2,0)}, $$

(110a)

$$ H_{A1(1,0)} \to H_{A1(1,0)} + H_{A2(2,0)}, $$

(110b)

$$ H_{A2(2,0)} \to H_{A2(2,0)}, $$

(110c)

$$ H_{A7(0,2)} \to H_{A2(0,2)}, $$

(110d)

$$ H_B = H_{B(0,0)} \to H_{B(0,0)} + H_{B1(1,0)} + H_{B2(2,0)}, $$

(110e)

The particular form of the terms (110a)–(110e) and details of adiabatic transformation are in [66, Appendix A], [67].

In the next step, the adiabatic form (terms (110a)–(110e)) is transformed to nonadiabatic form, nonadiabatic quasiparticles are introduced (up to the 2nd order of Taylor’ series expansion):

$$ H_{A(0,0)} \to H_{A(0,0)} + H_{A1(1,0)} + H_{A2(2,0)}, $$

(111a)

$$ H_{A1(1,0)} \to H_{A1(1,0)} + H_{A2(2,0)}, $$

(111b)

$$ H_{A2(2,0)} \to H_{A2(2,0)}, $$

(111c)

$$ H_{A2(0,2)} \to H_{A2(0,2)}, $$

(111d)

$$ H_{B(0,0)} \to H_{B(0,0)} + H_{B1(1,0)} + H_{B2(2,0)}, $$

(111e)

$$ H_{B1(1,0)} \to H_{B1(1,0)} + H_{B2(2,0)}, $$

(111f)

$$ H_{B2(1,1)} \to H_{B2(1,1)}, $$

(111g)

$$ H_{B2(0,2)} \to H_{B2(0,2)}, $$

(111h)

The particular form of the terms (111a)–(111h) and details of nonadiabatic transformation are in [66, Appendix B], [67].

(2) Nonadiabatic Solution-Corrections to the Crude-Adiabatic Energy Terms

Like in case of the Hamiltonian transformations, also details of nonadiabatic solution are published in [66, 67].

The main results of the solution can be written in the form of corrections to particular crude-adiabatic terms:
(A) Correction to the ground state electronic energy: correction to $H_{0q}(R)$ of (47) it is correction to zero-particle term of system Hamiltonian, that is, correction to the ground state electronic energy (48) calculated in clamped-nuclei approximation at fixed nuclear configuration $[R]$ due to the effect of nuclear dynamics (QP-dependence). For total electronic energy then holds:

$$E_{0e}(R) = [(\Phi_0(R)|H_e(r,R)|\Phi_0(R)) + E_{NN}(R)] + \Delta E^0(R).$$  

(112)

The correction $\Delta E^0(R)$ is

$$\Delta E^0(R) = \sum_{r \in \Omega} \hbar \omega_r \left( |c_{r\Omega}^0|^2 - |\tilde{c}_{r\Omega}|^2 \right),$$

(113)

{\Omega}-occupied orbitals, \{A\}-unoccupied orbitals

In (113),

$$c_{PR}^0 = \frac{\partial c_{PR}(Q)}{\partial Q_r}, \quad \tilde{c}_{PR} = \frac{\partial \tilde{c}_{PR}(P)}{\partial P_r},$$

(114)

are coefficients of adiabatic transformation (70) and nonadiabatic transformation (89) in first order of Taylor’s expansion in Q or P, respectively.

Approximate solution (see [66, Appendix C],[67]) yields for these terms:

$$c_{PQ}^0 = u_{PQ} \frac{(\epsilon_p^0 - \epsilon_Q^0)}{(\hbar \omega_r)^2 - (\epsilon_p^0 - \epsilon_Q^0)^2}; \quad P \neq Q, \quad \epsilon_S^0 = \epsilon_S^0(R),$$

(115)

$$\tilde{c}_{PQ} = u_{PQ} \frac{\hbar \omega_r}{(\hbar \omega_r)^2 - (\epsilon_p^0 - \epsilon_Q^0)^2}; \quad P \neq Q, \quad \epsilon_S^0 = \epsilon_S^0(R).$$

(116)

The final form of the correction is

$$\Delta E^0(R) = \sum_{r \in \Omega} \hbar \omega_r \left( |c_{r\Omega}^0|^2 - |\tilde{c}_{r\Omega}|^2 \right)$$

$$= \sum_{A} \sum_{l} \sum_{r} |u_{rP}^0|^2 \frac{\hbar \omega_r}{(\epsilon_p^0 - \epsilon_{Q}^0)^2 - (\hbar \omega_r)^2}$$

(117)

$$= \sum_{A} \sum_{l} |\Omega_{AI}|.$$  

The $\Omega$ matrix is a symmetric matrix of the form

$$\Omega_{PQ} = \sum_{r} \hbar \omega_r \left( |c_{PQ}^0|^2 - |\tilde{c}_{PQ}|^2 \right)$$

$$= \sum_{r} |u_{PQ}^0|^2 \frac{\hbar \omega_r}{(\epsilon_p^0 - \epsilon_Q^0)^2 - (\hbar \omega_r)^2}.$$  

(118)

From the final form of the correction (117), the two limiting situations can be extracted.

(i) True nonadiabatic or antiadiabatic state, $(\epsilon_p^0 - \epsilon_Q^0) < h\omega_r$.

In this case the correction is negative, $\Delta E_{(nad)}^0 < 0$, and represents stabilization contribution to the electronic ground state energy. It is evident from (117) that the ground-state energy stabilization is exclusively the effect of nuclear dynamics, which is expressed through the coefficients $\tilde{c}_{r\Omega}$ of P-dependent transformation. This contribution can be considerably large and reach the extreme negative value for left-hand side limit toward singular point in (117). Singular point itself is excluded [66, Appendix C]. The correction is always negative for the extreme case of strong nonadiabatic limit, $h\omega_r/|\epsilon_p^0 - \epsilon_Q^0| \to \infty$. However, the contribution in this case does not represent the largest possible negative value and it is equal to $\Delta E_{(nad)}^0 = -\sum_{r\in\Omega} h\omega_r (|\tilde{c}_{r\Omega}|^2) = -\sum_{r\in\Omega} |u_{r\Omega}^0|^2/h\omega_r$.

(ii) The second limit corresponds to adiabatic level, when electronic state is only Q-dependent. In this case the coefficients $\tilde{c}_{r\Omega}$ of P-dependent transformation are absent in (118) and for the correction holds:

$$\Delta E_{(adi)}^0 = \sum_{r \in \Omega} \hbar \omega_r \left( |c_{r\Omega}^0|^2 \right).$$

(119)

In case of strong adiabaticity, $(\epsilon_p^0 - \epsilon_Q^0) \gg h\omega_r$, which is standard condition for the BOA we have

$$\Delta E_{(adi)}^0 = \sum_{r \in \Omega} \hbar \omega_r \left( |c_{r\Omega}^0|^2 \right) = \sum_{r \in \Omega} |u_{r\Omega}^0|^2 \frac{h\omega_r}{(\epsilon_p^0 - \epsilon_Q^0)^2} \to \approx 0.$$  

(120)

In contrast to nonadiabatic level when the correction is negative, $\Delta E_{(nad)}^0 < 0$, on the adiabatic level the correction is whatever small, but always positive (119).

An important aspect has to be mentioned in relation to adiabatic level. Introduction of adiabatic quasiparticles, that is, $\tilde{c}_{r\Omega}$-dependent transformation, in solution of total system problem has to reproduce the basic results of standard treatment of solid state physics (or molecular physics) at solution of electron-phonon interactions by means of perturbation theory (see, e.g., (21), (22)). It can be shown that the base transformation is in this respect equivalent to standard treatment.

The exact adiabatic correction to the electronic ground state is, according to (9), the term $B_{00}$, that is, DBOC—the mean-value of nuclear kinetic energy in adiabatic electronic ground state:

$$B_{00}(R) = \int \Phi_0^*(r,R) \tilde{T}_N(R) \Phi_0(r,R) dr$$

$$= \sum_{n} \frac{\hbar^2}{2M_n} \int \Phi_0^*(r,R) \nabla_n^2 \Phi_0(r,R) dr$$

$$= \sum_{na} \frac{\hbar^2}{2M_n} \int \left( \frac{\partial \Phi_0(r,R)}{\partial R_{na}} \right)^* \frac{\partial \Phi_0(r,R)}{\partial R_{na}} dr |_{R_{na}}.$$  

(121)

We have shown [73] that (121) is the same as the adiabatic correction (119) to the electronic energy of the ground state.
\( \Phi_0 \) calculated through the expansion coefficients \( c_{PQ}(Q) \) of \( \overline{Q} \)-dependent transformation, that is,

\[
\Delta E^0_{\text{ad}}(R) = B_{00}(R) = \left( \Phi_0(r, \overline{R}) \left| T_N \right| \Phi_0(r, \overline{R}) \right)_R
\]

(122)

\[
= \sum_{rAI} \hbar \omega_r | c^*_A |^2 .
\]

Within the single Slater determinant representation of the ground electronic state, this relation is exact since the eigenfunctions—spinorbitals \( \{ \phi_Q(R) \} \) of the Hartree-Fock equations (29) are orthonormal and form complete basis set, that is, closure property holds

\[
\sum_Q | \phi_Q(r, R) \rangle \langle \phi_Q(r, R) | = 1.
\]

(123)

It means that both subsets, that is, occupied \( \{ \phi_I(r, R) \} \) and unoccupied \( \{ \phi_A(r, R) \} \) orbitals are included at calculation of (119), (121). As it is seen from (119), (122), electronic ground state energy correction is due to virtual transitions between occupied \( \{ \phi_I(r, R) \} \) and unoccupied orbitals \( \{ \phi_A(r, R) \} \) at nuclear vibration motion. It should be stressed that at these virtual transitions the system remains in its electronic ground state \( \Phi_0(r, R_{eq}) \). In this respect, even \( \Delta E^0_{\text{ad}} \) represents exactly the DBOC, it covers basically “nonadiabatic” (off-diagonal) corrections in the sense as these are calculated in a second order of perturbation theory when excited electronic states are approximated through virtual orbitals optimized for electronic ground-state \( \Phi_0(r, R_{eq}) \) and perturbation is an electron-vibration coupling \( H_{ep} \), as it has been discussed at the beginning. It can be seen very clearly from the derived expression for correction to frequency of normal modes:

\[
\Delta \omega_r = -2(\hbar \omega_r)^2 \sum_{AI} \frac{1}{(\epsilon^0_A - \epsilon^0_I)} | c^*_A |^2 
\]

\[
= -2(\hbar \omega_r)^2 \sum_{AI} | u^0_{AI}|^2 \left( \frac{(\epsilon^0_A - \epsilon^0_I)}{(\epsilon^0_A - \epsilon^0_I)^2 - (\hbar \omega_r)^2} \right)^2.
\]

(124)

The final effect is softening of normal mode vibration frequency:

\[
\hbar \omega_{r(ad)} = \hbar \omega_r - 2(\hbar \omega_r)^2 \sum_{AI} \frac{1}{(\epsilon^0_A - \epsilon^0_I)} | c^*_A |^2.
\]

(125)

The normal mode energy correction (124) is identical to the normal mode energy correction which can be derived as nonadiabatic correction in second order of perturbation theory assuming single boson excitation processes, that is,\n
\[
\Delta \omega_r = -2(\hbar \omega_r)^2 \sum_{AI} | u^0_{AI}|^2 \left( \frac{(\epsilon^0_A - \epsilon^0_I)}{(\epsilon^0_A - \epsilon^0_I)^2 - (\hbar \omega_r)^2} \right)^2.
\]

(126)

The term nonadiabatic is related to the fact that within the perturbation treatment contributions to the correction arise due to virtual transitions between occupied \( \{ I \} \) and unoccupied \( \{ A \} \) states, that is, correction is calculated through off-diagonal elements of the form \( \langle \phi_I | H_{ep} | \phi_A \rangle \langle \phi_A | H_{ep} | \phi_I \rangle / (\epsilon^0_I - \epsilon^0_A) \).

For quasimomentum \( k, q \)-space representation of multiband solids, with respect to \( (k; -k) \) symmetry, the temperature-dependent form of the equation for correction to electronic ground-state energy (117) can be expressed in the following form:

\[
\Delta E^0_{\text{na}} = 2 \left( \sum_{R(k), S(k')} \sum_{k < k', k > k'} | u^{k'} - k |^2 f_k (1 - f_{k'}) \right)
\]

\[
\times \frac{\hbar \omega_{k'} - \hbar \omega_k}{(\epsilon^0_{k'} - \epsilon^0_k)^2 - (\hbar \omega_{k'} - \hbar \omega_k)^2},
\]

(127)

\( \varphi_{Rk} \neq \varphi_{Sk} \).

Summations in (127) are over all bands \( \{ \varphi_R, \varphi_S \} \) and \( k \) points of the first BZ of multiband system, while \( \epsilon^0_k > \epsilon_f \), \( \epsilon^0_{k'} > \epsilon_f \).

For \( T = 0 \) K, relation (127) is reduced to

\[
\Delta E^0_{\text{na}} = 2 \left( \sum_{R(k), S(k')} \sum_{k < k', k > k'} | u^{k'} - k |^2 \hbar \omega_{k'} - \hbar \omega_k \right)
\]

\[
\times \frac{1}{(\epsilon^0_{k'} - \epsilon^0_k)^2 - (\hbar \omega_{k'} - \hbar \omega_k)^2},
\]

(128)

In (128), the wave vector \( k \) corresponds to states fully occupied below Fermi level \( f_k = 1 \), and wave vector \( k' \) corresponds to empty-virtual states above the Fermi-level \( f_{k'} = 0 \). It should be noticed that \( u^{k' - k} \) is matrix element of e-p coupling (43).

(B) Correction to one-particle term: correction to \( H_{11}(R) \) of (47).

The one-particle correction has been derived in the form

\[
\Delta H_{1p}^\prime = \sum_{rPQ} \hbar \omega_r \left( \sum_A (c^*_P e^r A c^*_Q A - c^*_P e^r A c^*_Q A) \right)
\]

\[
- \sum_I \left( c^*_P e^r I c^*_Q A - c^*_P e^r I c^*_Q A \right) N[a_p^I a_Q]
\]

\[
+ \sum_{rPR} \left( (\epsilon^0_{P} - \epsilon^0_{R}) \left( | c^*_P e^r P |^2 + | c^*_P e^r R |^2 \right) \right)
\]

\[
- 2 \hbar \omega_r \left( c^*_P e^r P [c^*_P e^r P] \right) N[a_p^I a_P].
\]

(129)

It should be noticed that the second contribution in (129) originates from boson excitation dependent terms of nonadiabatic Hamiltonian and expression in the second line of (129) is for boson vacuum. The first term in (129) originates from those terms of nonadiabatic Hamiltonian which are not dependent on boson operators (pure fermionic terms). At derivation of (129), restriction has been to the first order
of e-p coupling and the terms that are the products of e-p coupling and coulomb two-electron interactions (e.g., \( \langle \psi_R^{\text{RPA}} - \psi_R^{\text{RPA}} \rangle (\hat{c}_{\ell R}^\dagger \hat{c} + \hat{c}_{\ell R}^\dagger \hat{c}) \)) have been expected to be negligibly small comparing to pure e-p coupling terms and were neglected. Details of derivation can be found in [66, 67].

(i) Nonadiabatic polarons

The diagonal form of the one-particle correction (129) is

\[
\Delta H'_{ep}(dg) = \sum_{rP} \hbar \omega_r \left( \sum_A \left( |\hat{c}_{PA}^\dagger|^2 - |\hat{c}_{PA}|^2 \right) \right)
- \sum_I \left( |\hat{c}_{PI}^\dagger|^2 - |\hat{c}_{PI}|^2 \right) N[a_P^\dagger a_P] 
+ \sum_{rPR} \left( (\epsilon_0^0 - \epsilon_R^0) \left( |\hat{c}_{PR}^\dagger|^2 + |\hat{c}_{PR}|^2 \right) \right) 
- 2\hbar \omega_r \text{Re}(\hat{c}_{PR} \epsilon_{PR}^\dagger) N[a_P^\dagger a_P].
\] (130a)

Substitution for transformation coefficients (115), (116) and rearrangement of the expression yields for e-p interaction part of the Hamiltonian:

\[
\Delta H'_{ep}(dg) = \sum_{rPR} \left( |u_{PR}^\dagger|^2 \frac{1}{(\epsilon_0^0 - \epsilon_R^0) - \hbar \omega_r} N[a_P^\dagger a_P] \right) 
- 2 \sum_{rPR} \left( |u_{PR}^\dagger|^2 \frac{\hbar \omega_r}{(\epsilon_0^0 - \epsilon_R^0)^2 - (\hbar \omega_r)^2} N[a_P^\dagger a_P] \right). 
\] (130b)

Transcription of (130b) to quasimomentum \( k,q \)-space of multiband solids has the form

\[
\Delta H'_{ep}(dg) = \sum_{pk,qk} \left( \sum_{\sigma} |u_k^\dagger|^2 \frac{1}{(\epsilon_k^0 - \epsilon_{k,q}^0) - \hbar \omega_q} N[a_{k,\sigma}^\dagger a_{k,\sigma}] \right) 
- 2 \sum_{pk,qk} \left( \sum_{\sigma} |u_k^\dagger|^2 f_{k,q} \frac{\hbar \omega_q}{(\epsilon_k^0 - \epsilon_{k,q}^0)^2 - (\hbar \omega_q)^2} \right) 
\times N[a_{k,\sigma}^\dagger a_{k,\sigma}] 
\] (130c)

Expression (130c) represents total one-electron energy correction on the general Q, P-dependent level due to e-p interactions. The first term of (130c) is standard adiabatic (Q-dependent) polaron as it can be derived from Fröhlich Hamiltonian by the Lee-Low-Pines transformation [74]. The second term of (130c) is the correction to polaron energy that arises due to dependence of electronic motion not only on nuclear coordinates but also on the nuclear momenta \( P \) (nonadiabatic modification of the BOA). This term can be interpreted as a correction to the energy of individual polaron by an effective field created by all other polarons of the system.

(ii) Correction to orbital energies: gap opening in one-particle spectrum of quasidegenerate states at Fermi level.

For quasicontinuum of states at Fermi level, which is characteristic for metal-like band structures, contribution of second term in (130a) can be expected to be negligibly small. Summation in this term runs over all states, occupied and unoccupied. Since the term is odd function of \((\epsilon_0^0 - \epsilon_R^0)\), contributions from occupied and unoccupied states will tend to cancel mutually. On the other hand, character of one-particle spectrum can be changed at the e-p coupling through contribution of the first term in (130a) since summations in this term run separately over occupied and unoccupied states. Moreover, magnitude of the change in orbital positions is temperature dependent through the temperature dependence of the population of states.

At these circumstances, for investigation of possible changes in the character of one-electron spectrum of system due to e-p interactions on Q, P-dependent level, the first term of (130a) is crucial. For correction to orbital energy \( \Delta \epsilon_P \) of general state \( \epsilon_P^0 \), from the first term in (130a), it follows that

\[
\Delta \epsilon_P = \sum_r \hbar \omega_r \left( \sum_A \left( |\hat{c}_{PA}^\dagger|^2 - |\hat{c}_{PA}|^2 \right) \right) 
- \sum_I \left( |\hat{c}_{PI}^\dagger|^2 - |\hat{c}_{PI}|^2 \right) \right) \right) 
\] (131)

\[
= \left( \sum_{\text{occ}} \right) \left( \sum_{\text{oc}} \Omega_{PA} - \sum_I \right) \Omega_{PI}. \right.
\]

Finally, corrected orbital energy is

\[
\epsilon_P = \epsilon_P^0 + \Delta \epsilon_P. \] (132a)

Let us consider only the couple of quasidegenerate states at Fermi level, occupied state \( \epsilon_j^0 \), and unoccupied state \( \epsilon_A^0 \) a situation that can characterize couple of states in antiadiabatic state, \( |\epsilon_A^0(R) - \epsilon_j^0(R)| \ll \hbar \omega_r \). From (131) and from the structure of \( \Omega \) matrix, (118) follows directly:

\[
\Delta \epsilon_A = \left( \epsilon_A - \epsilon_A^0 \right) = -\Omega_{AI} > 0, \quad \Delta \epsilon_A = \Omega_{IA} = \Omega_{AI} < 0, \quad \Delta \epsilon_A = -\Omega_{AI}. \] (132b)

It means that orbital energy of unoccupied state has been increased, \( \epsilon_A > \epsilon_A^0 \), and orbital energy of the occupied state has been decreased, \( \epsilon_j < \epsilon_j^0 \). It can be generalized for a set of quasidegenerate occupied \( \{j\} \) and unoccupied \( \{A\} \) states (quasicontinuum of states) at Fermi level. Then, with respect to the fact that for antiadiabatic state correction to
the ground electronic state (117) is negative $\sum_{AI} \Omega_{AI} < 0$, the following relations can be derived:

$$
\Delta \epsilon_B = \sum_A \sum_{\text{unocc}} \Omega_{BA} - \sum_I \Omega_{BI} \geq 0,
$$

$$
\Delta \epsilon_J = \sum_A \sum_{\text{unocc}} \Omega_{JA} - \sum_I \Omega_{JI} \leq 0.
$$

In particular,

$$
\Delta \epsilon_B = \sum_r \sum_A |u_r^A|^2 \frac{\hbar \omega_r}{\left( \epsilon_r^B - \epsilon_{A}^0 \right)^2 - (\hbar \omega_r)^2}
$$

$$
- \sum_r \sum_I |u_{rI}|^2 \frac{\hbar \omega_r}{\left( \epsilon_r^B - \epsilon_{I}^0 \right)^2 - (\hbar \omega_r)^2},
$$

$$
\Delta \epsilon_J = \sum_r \sum_A |u_r^A|^2 \frac{\hbar \omega_r}{\left( \epsilon_r^J - \epsilon_{A}^0 \right)^2 - (\hbar \omega_r)^2}
$$

$$
- \sum_r \sum_I |u_{rI}|^2 \frac{\hbar \omega_r}{\left( \epsilon_r^J - \epsilon_{I}^0 \right)^2 - (\hbar \omega_r)^2}.
$$

At finite temperature T, for a correction $\Delta \epsilon_p$ to an arbitrary state $\epsilon_p^0$, from the set of quasidegenerate occupied and unoccupied states of band at Fermi level can be written:

$$
\Delta \epsilon_p(T) = \sum_Q \Omega_{PQ} (1 - 2 f_Q),
$$

(135)

$\{Q\}$-set of quasidegenerate states at Fermi level.

The occupation factor $f_Q$ obeys the Fermi-Dirac statistics:

$$
f_Q = \left( \exp \left( \frac{\epsilon_Q - \mu}{k_B T} \right) + 1 \right)^{-1}, \quad \epsilon_Q = \epsilon_Q^0 + \Delta \epsilon_J.
$$

(136)

It is evident that for temperature 0 K, (135) is reduced to (131).

From (135), temperature dependence of energy gap which is open in one-particle spectrum at Fermi level can be derived in the form

$$
\Delta(T) = \Delta(0) \mathrm{tgh} \left( \frac{\Delta(T)}{4k_B T} \right).
$$

(137)

The gap is defined as the energy difference of lowest lying corrected unoccupied state $\epsilon_{\text{B(LUMO)}}$ and highest lying corrected occupied state $\epsilon_{\text{J(HOMO)}}$, that is, as an energy gap in one-particle spectrum. At temperature 0 K holds:

$$
\Delta(0) = (\epsilon_{\text{B(LUMO)}} + |\epsilon_{\text{J(HOMO)}}|).
$$

(138)

Factor 4 in the denominator of the argument of $\mathrm{tgh}$ in (137) follows from the assumption that at Fermi level density of quasidegenerate occupied $\{\epsilon_r^0\}$ and unoccupied $\{\epsilon_r^B\}$ states of the band with gap opening is the same and consequently $\epsilon_{\text{B(LUMO)}} = |\epsilon_{\text{J(HOMO)}}|$. This factor can be larger or smaller than 4, depending on the actual difference in the density of states of occupied and unoccupied states of band at FL.

It is trivial to show that the corrections to orbital energies are negligibly small (basically zero) for a system in adiabatic state when $(\epsilon_r^0 - \epsilon_J^0) \gg \omega$.

(C) Correction to two-particle term - correction to $H_2(R)$ of (47).

Correction to $H_2(R)$ represents correction to electron correlation energy (see Note in Section 1) due to e-p interactions, in particular, it is dependence of electronic motion on nuclear vibration displacements $Q$ and momenta $P$. It has been derived in the form [66, 67]

$$
\Delta H''_{ep} = \sum_{rPQRS} \hbar \omega_r \left( \epsilon_{PQ}^0 - \epsilon_{SR}^0 \right) N \left[ a_{p+}^* a_{q+}^* a_{s} a_{r} \right].
$$

(139)

Substituting for transformation coefficients (115), (116) yields

$$
\Delta H''_{ep} = \sum_{rPQRS} u_{PQ}^* u_{RS}^0 \hbar \omega_r \left( \epsilon_{PQ}^0 - \epsilon_{SR}^0 \right) N \left[ a_{p+}^* a_{q+}^* a_{s} a_{r} \right].
$$

(140)

Transcription of (140) to quasimomentum $k,q$-space representation of multiband solids has the form

$$
\Delta H''_{ep} = \sum_{R,k} \sum_{k',q} \left| u_{k,q}^0 \right|^2 \hbar \omega_q \left( \epsilon_{k+q}^0 - \epsilon_k^0 \right) \left( \epsilon_{k'+q}^0 - \epsilon_{k'}^0 \right)
$$

$$
\times \left( \epsilon_{k+q}^0 - \epsilon_k^0 \right)^2 - (\hbar \omega_q)^2 \right)^2 \left( \epsilon_{k'+q}^0 - \epsilon_{k'}^0 \right)^2 - (\hbar \omega_q)^2 \right)^2 \right)^2 \times N \left[ a_{k+q+}^0 a_{k'} a_{q}^+ a_{k'+q} \right].
$$

(141)

3. Adiabatic ↔ Antiadiabatic State Transition: Relevance for SC State Transition

3.1. The Effect of e-p Coupling on Band Structure of Superconductors and Nonsuperconducting Analogues. In Figures 1(a), 1(c), 1(e), 1(g), (the pictures on the left), there are band structures (BS) of four superconducting compounds of different types and crystal structures at optimized equilibrium geometries. The details of calculation are published elsewhere [64, 75, 76].
As it can be seen from Figure 1, all the band structures are of adiabatic metal-like character with a relatively low density of states at the FL (indicated by a dashed line). Coupling to the respective phonon mode(s) in particular compounds seemingly does not change the metal-like character of BS. In all cases, however, e-p coupling induces BS fluctuation (see the pictures on the right), which is characteristic by fluctuation of the analytic critical point (ACP) of some band across the FL (cf. a-b, c-d, e-f, g-h).

In particular, for MgB$_2$ (hP3, P6mm, #191; AlB$_2$-type) coupling to the E$_{2g}$ phonon mode (in-plane stretching vibration of B-B) results in splitting of $\sigma$ bands ($p_z$, $p_y$ electrons of B atoms in a-b plane) in $\Gamma$ point of the first Brillouin zone (BZ)—Figure 1(b). Related to band topology, the analytic critical point (ACP, maximum) of $\sigma$ bands is located at $\Gamma$ point and, for the displacement $\approx 0.016$ Å/B-atom out of equilibrium position, the ACP crosses FL. This means periodic fluctuation of the BS between topologies 1a $\leftrightarrow$ 1b in coupling to vibration in the E$_{2g}$ mode.

The situation is similar for YB$_6$ (cP7, Pn3m, #221; CaB$_6$ type). In this case, BS fluctuation is related to the T$_{2g}$ mode (valence vibration of B atoms in basal a-b plane of B-octahedron). At the displacement $\approx 0.017$ Å/B-atom out of equilibrium position, the ACP (saddle point) of the band with dominance of B-p and Y-d electrons crosses FL in the M point and the BS fluctuates between topologies 1c $\leftrightarrow$ 1d.

In the case of YBa$_2$Cu$_3$O$_y$ (oP14, Pnmm, #47, with chain oxygen in b-direction and vacancy in a-direction), the BS fluctuation is associated with coupling to three modes, A$_g$, B$_{2g}$, B$_{3g}$, with the apical O(4) and CuO-plane O(2), O(3) atom displacements. At displacements $\approx 0.031$ Å of apical O(4) in the A$_g$ mode and $\approx 0.022$ Å of O(2) and O(3) in the B$_{2g}$, B$_{3g}$ modes, the ACP (saddle point) of one of the CuO plane (d-p$_z$) band in Y point crosses FL and undergoes periodic fluctuation between topologies 1e $\leftrightarrow$ 1f.

An optical phonon mode is simulated by displacements of Zn atoms in the opposite directions $\pm \Delta h_b$, that is, by change of the fractional coordinates: (1/3,2/3-$\Delta h_b$,1/4), (2/3,1/3+$\Delta h_b$,3/4) in hexagonal lattice (hP2, P6$_3$/mmc, #194; Mg type). At relatively small displacements, $\pm (0.0105$–$0.0157)$ Å/Zn atom, top of the $\sigma$ band in $\Gamma$ point approaches the Fermi level (Figure 2(h)), and continues to a position above it.

As it can be seen from Figure 1 in all cases a particular ACP of the band crosses FL at a displacement which is smaller than root-mean square (rms) displacement for zero-point vibration energy in respective phonon mode. This means, however, that in vibration where ACP approaches FL at the distance less than $\pm \omega$, the Fermi energy $E_F$ (chemical potential $\mu$) of the particular band-electrons close to the point where ACP crosses FL is smaller than the vibration energy of corresponding phonon mode, $E_F < \omega$. At these circumstances the adiabatic BOA is not valid and standard adiabatic theories cannot be applied. Moreover, shift of the ACP increases substantially the density of states (DOS) at FL, $n_{\sigma}(E_F) = (\partial \varepsilon_{\sigma}^0/\partial k)^{-1}_{\partial k}$, and induces the corresponding decrease in the effective electron velocity $(\partial \varepsilon_{\sigma}^0/\partial k)_{E_F}$ of fluctuating band in this region of k-space. Under these circumstances, the system is in the intrinsic nonadiabatic state, or even in the antiadiabatic state, $E_F < \omega$, and electronic motion depends not only on nuclear coordinates $Q$ but is strongly influenced by nuclear dynamics-momenta $P$. The main part of the effect of nuclear kinetic energy on electronic motion can be derived as diagonal correction by sequential $Q$, $P$-dependent base transformations as it has been presented in preceding parts.

Instability of the electronic structure at e-p coupling is absent in respective non-superconducting analogues, such as Xb$_2$ (X=Al, Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, etc.), CaB$_6$, YBa$_2$Cu$_3$O$_6$, and Mg. Even in the case of the XB$_2$, coupling to the E$_{2g}$ mode induces splitting of $\sigma$ bands in the $\Gamma$ point, the systems remain stable in the adiabatic state. For these systems, the ACP of $\sigma$ band does not fluctuate across FL. As an illustration, in Figure 2 are band structures of corresponding nonsuperconducting analogues at equilibrium high-symmetry structure (Figures 2(a), 2(c), 2(e), and 2(g)) and at distorted geometry (Figures 2(b), 2(d), 2(f), and 2(h)) with the same displacements in respective phonon modes as those in the case of corresponding superconductors at the transition to the antiadiabatic state.

In the case of AlB$_2$, in spite of $\sigma$ bands splitting and nearly the same value of the e-p interaction strength (the calculated mean value is $\overline{\mu} \approx 1.01$ eV/u.cell) as that of MgB$_2$ ($\overline{\mu} \approx 0.98$ eV/u.cell), AlB$_2$ remains in e-p coupling in the adiabatic state as a nonsuperconducting compound. In this case, BS fluctuation (bands splitting in EP coupling) does not decrease chemical potential, it remains in e-p coupling still larger than the vibration energy ($\mu_{\text{ad}} > \hbar \omega$) and, consequently, there is no driving force for transition to the antiadiabatic state.

The CaB$_6$ is an insulator, and coupling to the T$_{2g}$ mode (valence vibration of B atoms in basal a-b plane of B-octahedron) does change the character of the BS (Figures 2(c) and 2(d)).

In the case of deoxygenated YBCO, YBa$_2$Cu$_3$O$_y$, in contrast to the superconducting YBa$_2$Cu$_3$O$_7$, a combination of electron coupling to A$_g$, B$_{2g}$, and B$_{3g}$ phonon modes leaves band structure without substantial change (Figures 2(e) and 2(f)). In the case of YBa$_2$Cu$_3$O$_7$, the ACP (saddle point) at Y point fluctuates across FL (see Figures 1(e) and 1(f)), which yields substantial reduction of chemical potential $\rightarrow \mu_{\text{antiad}} < \hbar \omega$. For YBa$_2$Cu$_3$O$_6$ the ACP does not fluctuate across FL and chemical potential remains larger than the phonon energy spectrum, $\mu_{\text{ad}} > \hbar \omega$, and the system remains in the adiabatic state.

Also the band structure of Mg remains without changes at e-p coupling (Figures 2(g) and 2(h)).

3.2. Nonadiabatic e-p Coupling Effects in the Antiadiabatic State

3.2.1. Formation of Antiadiabatic Ground State and Gap Opening. On crude-adiabatic level, total ground state electronic energy $E_{\text{gg}}^0(R_0)$ has minimum at $R_0$, $(dE_{\text{gg}}^0/dR)|_{R_0} = 0$, and within the HF-SCF approximation it is equal to (27).
Figure 1: Band structures of MgB\textsubscript{2} (a, b), YB\textsubscript{6} (c, d), YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7} (e, f) and Zn (g, h). Pictures on the left (a, c, e, g) correspond to equilibrium high-symmetry structures. On the right are the band structures (b, d, f, h) of distorted geometry with atom displacements in the respective phonon modes.

The only correction to this energy is electron correlation energy (53), or (54) in second order of PT, which is negative and contributes to stabilization of the ground state at equilibrium geometry $R_{eq}$:

$$E_{0corr}^{te}(R_{eq}) = E_{0}^{te}(R_{eq}) - |E_{corr}|_{R_{eq}},$$

$$\left(\frac{dE_{0corr}^{te}}{dR}\right)_{R_{eq}} = 0.$$ (142)

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:

$$E_{0corr}^{te}(R_d) = E_{0}^{te}(R_d) - |E_{corr}|_{R_d}.$$ (143)

Since two-electron coulomb interactions $\{\gamma^{0}_{PQRS}\}$ do not depend explicitly on nuclear variables it can be expected
that electron correlation energy at vibration displacement \( R_d \) has not been changed significantly, that is, \((E_{\text{corr}})_{R_d} \approx (E_{\text{corr}})_{R_e}\). On crude-adiabatic level, for an increase of the total electronic energy \( \Delta E_d \) due to nuclear displacement \( R_d \) then holds:

\[
\Delta E_d(R_d) = E^{\text{te}}_0(R_d) - E^{\text{te}}_0(R_{eq}) > 0.
\]  

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.

The band structures in Figure 1 indicate possibility of antiadiabatic state formation for superconductors. The question if antiadiabatic state can be a stable state, that is, to be a ground electronic state of system at distorted nuclear configuration \( R_d \), depends on the value of the ground state energy correction \( \Delta E^0(R_d) \) (117).
Since for antiadiabatic state this correction is negative, $\Delta E_{\text{0}(\text{na})}^{0}(R_{d}) < 0$, then if the inequality
\begin{equation}
\left| \Delta E_{\text{0}(\text{na})}^{0}(R_{d}) \right| > \Delta E_{d}(R_{d})
\end{equation}
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 $C_{A}^{\ell}$ of $P$-dependent transformation (see structure of (113)), which stabilizes fermionic ground state energy in antiadiabatic state at distorted nuclear configuration $R_{d}$.

Stabilization (condensation) energy at transition from adiabatic into antiadiabatic state is
\begin{equation}
E_{\text{cond}}^{0} = \Delta E_{d}(R_{d}) - \left| \Delta E_{\text{0}(\text{na})}^{0}(R_{d}) \right| .
\end{equation}
Correction (127) to the electronic ground-state energy in the k-space representation due to interaction of pair of states mediated by the phonon mode $r$ can be rewritten as
\begin{align}
\Delta E_{\text{0}(\text{na})}^{0} &= 2 \sum_{\varphi_{bk}, \varphi_{sk}'} \sum_{\varphi_{bk}'} \int_{0}^{\varepsilon_{\varphi_{bk}}'} \int_{\varepsilon_{\varphi_{sk}}'}^{\varepsilon_{\varphi_{sk}}'} n_{\varepsilon_{k}} (1 - f_{\varepsilon_{k}^{'}}) d\varepsilon_{k}^{'}
\times \int_{\varepsilon_{\min}}^{\varepsilon_{\max}} \frac{\hbar \omega_{r}}{2} \frac{n_{\varepsilon_{k}} (\varepsilon_{k}^{0} - \varepsilon_{k}^{0})}{(\varepsilon_{k}^{0} - \varepsilon_{k}^{0})^{2} - (\hbar \omega_{r})^{2}} d\varepsilon_{k}^{0},
\end{align}
$\varphi_{bk} \neq \varphi_{sk}$.\hspace{1cm} (147)

In general, all bands of 1st BZ of a multiband system are covered, including intraband terms, that is, $\varphi_{bk}, \varphi_{bk}', k \neq k'$, while $\varepsilon_{k}^{0} < \varepsilon_{k}^{0} < \varepsilon_{k}$, Fermi-Dirac populations $f_{\varepsilon_{k}^{0}}$, $f_{\varepsilon_{k}^{0}}$, make correction (147) temperature-dependent. Term $u_{\varepsilon_{k}^{0}, \varepsilon_{k}^{0}}$ stands for matrix element of e-p coupling and $n_{\varepsilon_{k}}, n_{\varepsilon_{k}^{0}}$ are DOS of interacting bands at $\varepsilon_{k}^{0}$ and $\varepsilon_{k}^{0}$. For adiabatic systems, such as metals, this correction is positive and negligibly small (DBOC). As it has been mentioned, only for systems in the antiadiabatic state the correction is negative and its absolute value depends on the magnitudes of $u_{\varepsilon_{k}^{0}, \varepsilon_{k}^{0}}$ and $n_{\varepsilon_{k}}, n_{\varepsilon_{k}^{0}}$ at displacement for FL crossing. At the moment when ACP approach FL, the system not only undergoes transition to the antiadiabatic state but also DOS, $n_{\varepsilon}(E_{F}) = (\partial \epsilon_{\varepsilon}/\partial \varepsilon_{\varepsilon})^{-1}$, of the fluctuating band is considerably increased at FL. It is a situation invoking possibility of van Hove singularity formation. Important role of van Hove singularity formation for high-$T_c$ superconductors has been proposed by Bok and his collaborators [77, 78].

For all the presented systems at 0 K, $\Delta E_{\text{0}(\text{na})}^{0}$ which covers the effect of nuclear momenta prevails in absolute value the electronic energy increase $\Delta E_{d}(R_{dcr})$, that is, (145) is fulfilled at nuclear displacements $d_{cr}$ when ACP crosses FL as calculated for clumped nuclear adiabatic structures.

The highest value of the “condensation energy” (146), $E_{\text{cond}}^{0} \approx -34$ meV/unit cell, has been calculated [76] for YBa$_2$Cu$_3$O$_7$. In the case of MgB$_2$, $E_{\text{cond}}^{0} \approx -13$ meV/unit cell has been obtained. For YB$_6$, and Zn the values of $E_{\text{cond}}^{0}$ are smaller but in both cases are also negative.

Under these circumstances, each of the studied systems is stabilized in the antiadiabatic electronic ground state at broken symmetry with respect to the adiabatic equilibrium high-symmetry structure. In my opinion, it can be identified experimentally by ARPES as a kink on momentum distribution curve at FL in form of the band curvature at the saddle point, as shown in Figure 3(a), which presents calculated results for YBa$_2$Cu$_3$O$_7$. The crucial influence on the final value of the correction $\Delta E_{\text{0}(\text{na})}^{0}(R_{d})$ is related to an increase of the DOS $n_{\varepsilon_{k}}, n_{\varepsilon_{k}^{0}}$ in (147) connected to the ACP when it approaches FL at transition into antiadiabatic state. Situation for YBa$_2$Cu$_3$O$_7$ is presented in Figure 3(b). In the ARPES spectra of YBa$_2$Cu$_3$O$_7$ a kink on momentum distribution curve in off-nodal direction (Γ-Y line, near
to Y point) should appear in low-energy region at FL for temperatures below \( T_c \) and it will be shifted away from FL, or will disappear above \( T_c \). It is related to fluctuation of the ACP (inflex point) of one of CuO\(_2\) layer (\( d_{x^2−y^2} − p\sigma \)) band when it approaches FL at coupling to mentioned phonon modes. In my opinion, it is an effect of dispersion renormalization as it has been discussed in Section 1.

Nontrivial and very important property of system which is stabilized in the adiabatic state should be stressed. Due to translation symmetry of the lattice, the created adiabatic electronic ground state is geometrically degenerate in distorted geometry (\( R_{d,c} \)) with fluxional nuclear configuration in particular phonon mode(s) (see, e.g., \[68, Figure 5\] for case of MgB\(_2\)). It means that the ground-state energy is the same for different positions of the involved atoms (in phonon modes which drive the system into this state). Expressed in the other way, the involved atoms can circulate over perimeters of the circles with the radii equal to displacements \( d_{c,r} \) at FL crossing, without the energy dissipation.

In transition to the adiabatic state, \( k \)-dependent gap \( \Delta_k(T) \) in quasicontinuum of adiabatic one-electron spectrum is opened. The gap opening is related to shift \( \Delta E_{P_k} \) of the original adiabatic orbital energies \( \varepsilon_{P_k}^0, \varepsilon_{P_k} = \varepsilon_{P_k}^0 + \Delta E_{P_k} \), and to the \( k \)-dependent change of DOS of particular band(s) at Fermi level. Shift of orbital energies in band \( \varphi \nu(k) \) has the form (134a), (134b). In quasimomentum \( k \)-space of multiband solids, these equations are

\[
\Delta \varepsilon(P'k') = \sum_{R\varepsilon_{k',k}} \left| u^{k'−k} \right|^2 (1 − f_{\varepsilon_{k'}}) \times \frac{\hbar \omega_{k'−k'}}{\left( \varepsilon_{k'}^0 − \varepsilon_{k}^0 \right)^2 − (\hbar \omega_{k'−k'})^2} − \sum_{\delta \varepsilon_{k',k}} \left| u^{k'−k} \right|^2 f_{\varepsilon_{k'}} \times \frac{\hbar \omega_{k−k'}}{\left( \varepsilon_{k'}^0 − \varepsilon_{k}^0 \right)^2 − (\hbar \omega_{k−k'})^2},
\]

(148a)

for \( k' > k_F \), and

\[
\Delta \varepsilon(Pk) = \sum_{R\varepsilon_{k,k'}} \left| u^{k−k'} \right|^2 \times \left( 1 − f_{\varepsilon_{k'}} \right) \frac{\hbar \omega_{k−k'}}{\left( \varepsilon_{k'}^0 − \varepsilon_{k}^0 \right)^2 − (\hbar \omega_{k−k'})^2} − \sum_{\delta \varepsilon_{k,k'}} \left| u^{k−k'} \right|^2 f_{\varepsilon_{k'}} \times \frac{\hbar \omega_{k−k'}}{\left( \varepsilon_{k'}^0 − \varepsilon_{k}^0 \right)^2 − (\hbar \omega_{k−k'})^2},
\]

(148b)

for \( k ≤ k_F \).

Replacement of discrete summation by integration, \( \sum_{k} \rightarrow \int n(\varepsilon_k) \), introduces DOS \( n(\varepsilon_k) \) into (148a), (148b). It is of crucial importance in relation to fluctuating band (see Figure 3(b)). For corrected DOS \( n(\varepsilon_k) \), which is the consequence of shift \( \Delta \varepsilon \) of orbital energies, the following relation can be derived:

\[
n(\varepsilon_k) = \left| 1 + \left( \frac{\partial(\Delta \varepsilon_k) / \partial \varepsilon_k^0}{\left( \partial \varepsilon_k^0 / \partial k \right) } \right) \right|^{-1} n^0(\varepsilon_k^0).
\]

(149)

The term \( n^0(\varepsilon_k^0) \) stands for uncorrected DOS of the original adiabatic states of particular band:

\[
n^0(\varepsilon_k^0) = \left| \left( \frac{\partial \varepsilon_k^0}{\partial k} \right) \right|^{-1}.
\]

(150)

Close to the \( k \)-point where the original band which interacts with fluctuating band intersects FL, the occupied states near FL are shifted downward below FL and unoccupied states are shifted upward, above FL. The gap is identified as the energy distance between created peaks in corrected DOS above FL (half-gap) and below FL. The formation of peaks is related to the spectral weight transfer, that is, observed by ARPES or tunneling spectroscopy in cooling below \( T_c \).

For some of the studied compounds, the calculated corrected DOS (149) of particular band(s) with gap opening are in Figure 4.

In particular, YBa\(_2\)Cu\(_3\)O\(_7\) exhibits an asymmetric gap in two directions: for Cu-O\(_1\) chain-derived (\( d-p\sigma \)) band the gap in one-particle spectrum is \( \Delta_0(0) \approx 35.7 \text{meV} \) in the \( Γ-Y \) direction (4a) and \( \Delta_0(0) \approx 24.2 \text{meV} \) in the \( Γ-X \) direction (4b), respectively. The calculated asymmetry, that is, the ratio \( (\Delta_0(0)/\Delta_0(0))_{\text{theor}} \approx 0.68 \), or \( (\Delta_0(0)/\Delta_0(0))_{\text{theor}} \approx 1.47 \) is very close to the experimental values, \( \Delta_0/\Delta_0 \approx 0.66 \) and \( \Delta_0/\Delta_0 \approx 1.5 \) which have been recorded [79, 80] for untwined YBa\(_2\)Cu\(_3\)O\(_7\). Inspection of the topology (Figures 1(e)–1(f) of the Cu-O\(_1\) chain-derived (\( d-p\sigma \)) band suggests that one can expect gap opening in one-particle spectrum of this band not only in \( Γ-Y \) and \( Γ-X \) direction, but it can be expected to be opened also in nodal, that is, \( Γ \)-\( S \) direction. Based on \( k \)-dependence of DOS of this band in particular directions at FS, it can be expected that \( Δ_{Γ−S} ≤ Δ_{Γ−X} \), that is, top of the dispersion should appear \( ≤ \text{15 meV} \) below FS. One can expect opening of very small gap for this band also in \( Γ-U \) direction [76]. However, due to relatively large distance of CuO\(_2\) layers (\( ≈ 8.3 \text{Å} \)), e-p coupling which mediates interactions between electrons of these layers is small, which suggests that gap in one-particle spectrum of CuO\(_2\) layer-based (\( d_{x^2−y^2} − p\sigma \)) bands is not expected to be opened.

Two gaps, in \( σ \) and \( π \) band, are opened in \( Γ-K(M) \) directions of MgB\(_2\) (4c); \( Δ_{σ}(0)/2 \approx 7.6 \text{meV} \) and \( Δ_{σ}(0)/2 \approx 2.2 \text{meV} \). The result simulates tunneling spectra at positive bias voltage and calculated half-gaps are in a very good agreement with experimental high-precision measurements [81, 82].

A small gap opens on pd-band in the \( Γ-X \) direction of YBa\(_2\) (4d); \( Δ_{pd}(0)/2 \approx 2.2 \text{meV} \).

The corrections to orbital energies (148a), (148b) and to the ground state energy (147) are temperature-dependent and decrease with increasing \( T \). At a critical value \( T_c \), the gap in one-particle spectrum (137) which is formed at \( 0 \text{K} \) disappears, \( Δ(T_c) = 0 \) (continuum of states is established at
Figure 4: Corrected DOS and gap formation near \( k \) point where particular bands intersect FL, 0 K. Gap of YBa\(_2\)Cu\(_3\)O\(_7\) in \( \Gamma \)-Y(4a) and \( \Gamma \)-X(4b) direction. Half-gap in MgB\(_2\) (Figure 4(c)) and half-gap in YB\(_6\) (Figure 4(d)).

3.3. Thermodynamic Properties of System in the Antiadiabatic State

Presented results naturally provoke the question if the antiadiabatic state is related in some way to superconducting state. Crucial in this respect are thermodynamic properties of antiadiabatic state, that is, at temperatures \( T < T_c \).

(I) Character of condensation in antiadiabatic state

As it has already been mentioned, 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 \( \Delta R = |R_{eq} - R_{d,cr}| \). The \( R_{d,cr} \) is distorted geometry at which ACP approaches FL and system undergoes transition from adiabatic into antiadiabatic state.

Due to the geometric degeneracy of the ground state energy, the involved atoms can circulate over perimeters of the circles without the energy dissipation.
The dissipation-less motion of the couple of nuclei implies, however, that e-p coupling of involved phonon mode and electrons of corresponding band has to be zero.

Let as shown that in the antiadiabatic state this aspect is fulfilled.

The effective e-p interactions which cover the Q. P.-dependence has the form that is for boson vacuum represented by the second term in (130a) is

\[
\Delta H'_{(e-p)}(dg) = \sum_{\nu \varphi} \left( \epsilon^\nu_{\nu} - \epsilon^0_{\nu} \right) \left( |\epsilon^\nu_{\nu}|^2 + |\tilde{c}^\nu_{\nu}|^2 \right)
-2\hbar \omega_{\nu} \text{Re} \left( \tilde{c}^\nu_{\nu} \tilde{c}^\nu_{\nu}^\dagger \right) N[a^\nu_{\nu} a^\nu_{\nu}].
\]

(152)

After substitution for transformation coefficients \( c^\nu_{\nu}, \tilde{c}^\nu_{\nu} \) (115), (116) and algebraic manipulation, the quasimomentum form of this term is

\[
\Delta H'_{(e-p)}(dg) = \sum_{k \varphi} |u^0_k|^2 \left\{ \frac{\left( \epsilon^0_k - \epsilon^0_{k-q} \right)}{\left( \epsilon^0_k - \epsilon^0_{k-q} \right)^2 - \left( \hbar \omega_{\nu} \right)^2} \right\}
\times N[a^\nu_{\nu} a^\nu_{\nu}].
\]

(153a)

For extreme nonadiabatic limit \( \hbar \omega_{\nu}/|\epsilon^0_k - \epsilon^0_{k-q}| \to \infty \), from (153a), it follows that

\[
\Delta H'_{(e-p)}(dg)_{na} \to 0.
\]

(153b)

It means that for electrons that satisfy condition of extreme nonadiabaticity with respect to interacting phonon mode \( \nu \) 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 at the Fermi level (electric resistance \( \rho = 0 \)), while motion of nuclei remains bound to fluxional revolution over distorted, energetically equivalent, configurations. The electrons move in a form of itinerant bipolarons, that is, as a polarized cloud of intersite charge density distribution (see Figure 5). Due to temperature increase, thermal excitations of valence band electrons to conduction band induce sudden transition from the antiadiabatic state into adiabatic state at \( T = T_c \), that is, (145) does hold. For temperatures \( T \geq T_c \), instead of (145), \( \Delta E_{(na)}(R_\varphi) \leq \Delta E_d(R_\varphi) \) holds and the system becomes stable at equilibrium \( R_{eq} \) as it is characteristic for adiabatic structure.

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 theirs motion in conducting band is restricted by scattering with interacting phonon modes. It corresponds to situation at \( T > T_c \).

For extreme adiabatic limit \( \hbar \omega_{\nu}/|\epsilon^0_k - \epsilon^0_{k-q}| \to 0 \), from (153a) for electron-phonon interaction energy in this case it follows that

\[
\Delta H'_{(e-p)}(dg)_{ad} \to \sum_{qk} |u^0_k|^2 \frac{1}{\left( \epsilon^0_k - \epsilon^0_{k-q} \right)}. \quad (153c)
\]

Expression (153c) represents basically energy of standard adiabatic polaron (small, self-trapped) that contributes to the total energy of system.

II. Electronic specific heat and entropy in antiadiabatic state.

It has been shown that 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,

\[
C_{V,el}(T) = \frac{d\Delta E_{(na)}(\omega)}{dT} = T \frac{dS}{dT}
\]

can be derived:

\[
C_{V,el}(T) = -\frac{\pi(\epsilon_{k_F})}{2} \frac{\Delta(T)}{\Delta(0)} \left( \frac{\Delta(T)}{2T} \right).
\]

(155)

At derivation of (155), it has been assumed that for the band with gap opening, uncorrected density of quasicontinuum of occupied and unoccupied states at Fermi level is the same. Expression (155) can be derived either from the ground-state energy correction (127), (147), or from the basic statistical relation for entropy:

\[
S = -k_B \sum_{\nu} [f_{\nu} \ln f_{\nu} + (1 - f_{\nu}) \ln (1 - f_{\nu})].
\]

(156)

In (156), \( f_{\nu} \) is the Fermi-Dirac occupation factor of state \( \epsilon_{\nu} = \epsilon^0_{\nu} + \Delta_{\nu} \). Then for entropy related to formation of antiadiabatic state can be derived:

\[
S = k_B \ln 2 - \pi(\epsilon_{k_F}) \frac{\Delta(T)^2}{2T\Delta(0)} + 2k_B\pi(\epsilon_{k_F}) \ln \left( \cosh \frac{\Delta(T)}{4k_BT} \right).
\]

(157a)

For temperature derivative of entropy (157a), it follows that

\[
\frac{dS}{dT} = -\frac{\pi(\epsilon_{k_F})}{2T} \frac{\Delta(T)}{\Delta(0)} \frac{d\Delta(T)}{dT}.
\]

(157b)

It yields directly to final expression (155) for \( C_{V,el}(T) \).

From the (155), in the limit \( T \to 0 \), the exponential behavior characteristic for superconductors can be derived:

\[
\lim (C_{V,el}(T))_{T \to 0} \approx \exp \left( -\frac{\Delta(0)}{2k_BT} \right).
\]

(158)

The density of states at Fermi level \( \pi(\epsilon_{k_F}) \) in the above equations 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 the mean value of density of states of the fluctuating band in ACP at the moment when it approaches \((±ω/2)\) Fermi level (adiabatic state). 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).

III. Magnetic properties of system in the antiadiabatic state-critical magnetic field

System in superconducting state can exhibit absolute diamagnetism and Meissner effect only if inside the system \(B = 0\). In this case, there has to exist some critical value of external magnetic field \(H_c\) which destroys superconducting state and induces transition of the system into normal state (characteristic by finite-nonzero value of electric resistance \(ρ \neq 0\) at finite-nonzero density of electric current \(j\), like it occurs in case of temperature increase above \(T_c\). It also means that at critical temperature and above it, \(T ≥ T_c\), critical magnetic field has to be zero, \(H_c(T ≥ T_c) = 0\).

It can be shown that antiadiabatic state exhibits this property.

From thermodynamics for critical magnetic field in this case, it follows that

\[
\frac{H_c^2}{8\pi} = F_{(ad)} - F_{(na)}.
\]

In (159), \(F_{(ad)}\) and \(F_{(na)}\) stand for free energies of the system in adiabatic and nonadiabatic (antiadiabatic) state. Then,

\[
F_{(ad)} - F_{(na)} = ΔE_{(na)} - TS.
\]

(160a)

From (154), (155), it follows that

\[
ΔE_{(na)}(T) = ΔE_{(na)}(0) + \int_0^T C_V(T) dT
\]

\[
= ΔE_{(na)}(0) - \frac{π(ε_{kF})}{4Δ(0)} ((Δ(T))^2 - (Δ(0))^2)
\]

\[
= -\frac{π(ε_{kF})}{4}Δ(0) - \frac{π(ε_{kF})}{4Δ(0)} ((Δ(T))^2 - (Δ(0))^2).
\]

(160b)

After substitution of (160b), (157a) into (160a) and algebraic rearrangements, for critical magnetic field at finite temperature \(T\), it follows that

\[
\frac{(H_c(T))^2}{8π} = -\frac{π(ε_{kF})}{4}Δ(0) - \frac{π(ε_{kF})}{4Δ(0)} ((Δ(T))^2 - (Δ(0))^2)
\]

\[
+ \frac{π(ε_{kF})}{2} (Δ(T))^2 Δ(0)
\]

\[
- 2k_BT\ln(\frac{Δ(0)}{(Δ(T))^2 - (Δ(0))^2})^{1/2}.
\]

(160c)

At temperature 0 K, for critical magnetic field results,

\[
(H_c(0))^2 = 2πΔ(0)π(ε_{kF}).
\]

(160d)

The relation between critical magnetic fields at finite and zero temperature follows from (160c), (160d):

\[
\frac{(H_c(T))^2}{H_c(0)^2} = \left[\frac{(Δ(T))^2 - 8k_BT}{Δ(0)}\ln\left(\frac{Δ(0)}{(Δ(T))^2 - (Δ(0))^2}^{1/2}\right)\right].
\]

(161)

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, \(H_c(T ≥ T_c) = 0\). Since there is no gap in one-electron spectrum in metal-like adiabatic state, \(Δ(T ≥ T_c) = 0\), then zero value of critical magnetic field follows directly from (160c), (161). Derived equations show that system in the antiadiabatic state, beside zero value of electric resistance \(ρ = 0\) (dissipation-less motion of bipolarons), has also specific property that is, necessary for occurrence of the Meissner effect.

4. Electron Correlation, Cooper’s Pairs and Bipolarons

Correction \(ΔH_{ep}'\) to the two-particle term \(H_{(2)}(R)\) represents correction to the electron correlation (see Note in Section 1) energy due to e-p coupling on QP-dependent nonadiabatic level and has the form (141). The electron correlation energy on crude-adiabatic level \(H_{(2)}(R)\) is a perturbation contribution to the electronic ground-state energy \(H_{(0)}(R_0) = E_{SCF}(R_0)\), (48). It is an improvement of e-e interaction contribution beyond the level of HF method which treats electrons with \(α\) and \(β\) spins in an balanced way. The electron correlation energy is negative (see Note in Section 1) and contributes to stabilization of ground state electronic energy as a perturbation contribution, which in the second order of perturbation theory has the form (54), \(E_{corr}(R_0)\).

Let us see if the correction to correlation energy due to e-p coupling \(ΔH_{ep}'\) represents stabilization or destabilization contribution [66, 67]. For antiadiabatic system \(|ε_{k'} - ε_{k}| < \hbarω_{k' - k}\), denominators in (141) are positive and negative value of the matrix elements of this two-particle correction is reached for a reduced form if nominators are negative, that is, if \((ε_{k+q}^0 - ε_k^0) = -(ε_{k'+q}^0 - ε_{k'}^0)\). Since \(q ≠ 0\), it can be reached if \(q = −k - k'\). At these circumstances for reduced form which maximizes e-e attraction, it can be derived that

\[
ΔH_{ep}'(red)_{na} = -2\sum_{k, k' < k < k'} |a_{k' - k}|^2
\]

\[
\times \left[\hbarω_{k' - k}(ε_{k'}^0 - ε_k^0) + (\hbarω_{k' - k})^2\right]
\]

\[
× N\left[a_{k'}^2, a_{k'}^2, a_{-k'}^2, a_{-k}^2\right].
\]

(162)
In this expression, summation over bands is not explicitly indicated, but it should be understood implicitly. This correction is due to pairs of electrons with opposite quasi-momentum and antiparallel spins \((k, -k)\). It should be noticed that it is the contribution of biexcited configurations \(\{|\Phi_{k,-k}, -\sigma\rangle\} \) (i.e., two-particle \((k, -k)\), two-hole \((k', -k')\)) excited singlet states) to the electronic ground state, that is, represented by renormalized Fermi vacuum \(\Phi_0\). Expressed explicitly, first nonzero contributions are from the matrix elements of the type \(|\Phi_0| \Delta H_{ep}''(\Phi_{k,-k}(-\sigma))|^2\), that is, contributions in the second order of perturbation theory. Now, \(\{\epsilon_k\}\) represent particle states that are occupied above Fermi level and \(\{\epsilon_k\}\) are, due to excitations, empty-hole states below Fermi level.

From (162), it follows that due to e-p interactions on the \(Q, P\)-dependent nonadiabatic level, the electron correlation energy (54) of the electronic ground state is increased by contribution of this correction. Inspection of (162) indicates that the largest contribution to the correlation energy correction is for pair of electrons at Fermi level which satisfy the condition \(|\epsilon_k^0 - \epsilon_k^0| < \hbar \omega_{k,-k}\), that is, for system which is in antiadiabatic state.

In case of strong antiadiabatic regime \(|\epsilon_k^0 - \epsilon_k^0| < \hbar \omega_{k,-k} \rightarrow 0\), for correction to electron correlation energy, it follows that

\[
\Delta H_{ep}''(\text{red})_{\text{sym}} = -2 \sum_{kk'} \left| u_{k,-k}^0 \right|^2 N \left[ a_{k,-k}^0 a_{k,-k}^0 a_{k,-k} a_{k,-k} \right].
\]

(163a)

The second extreme case is for strong adiabatic regime \(\hbar \omega_{k,-k} > \epsilon_k^0\) \(\rightarrow 0\). At these circumstances, correction to electron correlation energy approaches zero value:

\[
\Delta H_{ep}''(\text{red})_{\text{rad}} = -2 \sum_{kk'} \left| u_{k,-k}^0 \right|^2 \frac{\hbar \omega_{k,-k}}{(\epsilon_k^0 - \epsilon_k^0)^2} \times N \left[ a_{k,-k}^0 a_{k,-k}^0 a_{k,-k} a_{k,-k} \right] \rightarrow 0.
\]

(163b)

General adiabatic expression on \(Q\)-dependent adiabatic level \(|\epsilon_k^0 - \epsilon_k^0| > \hbar \omega_{k,-k}\), that is, the adiabatic form of this correction can be derived directly from (139) in the limit \(\tilde{c} = 0\),

\[
\Delta H_{ep}''(\text{ad}) = \sum_{kk',qq'} \left| u_{kk',qq'}^0 \right|^2 \frac{\hbar \omega_{k,-k}}{(\epsilon_{k+q}^0 - \epsilon_k^0)^2} \times N \left[ a_{k+q,-k}^0 a_{k,-k}^0 a_{k+q,-k} a_{k,-k} \right].
\]

(164)

The reduced form is

\[
\Delta H_{ep}''(\text{red})_{\text{ad}} = -2 \sum_{kk'} \left| u_{k,-k}^0 \right|^2 \frac{\hbar \omega_{k,-k}}{(\epsilon_k^0 - \epsilon_k^0)^2} \times N \left[ a_{k,-k}^0 a_{k,-k}^0 a_{k,-k} a_{k,-k} \right].
\]

(165)

Like for nonadiabatic \(Q, P\)-dependent case also for adiabatic \(Q\)-dependent level, the correction to electron correlation energy is negative. By comparing (162) with (163a) it can be seen that nonadiabatic correction to electron correlation energy is in absolute value larger than corresponding adiabatic correction. Moreover, for antiadiabatic state, when the system is close to singular point in (162), the nonadiabatic correction can be significant.

Along with crude-adiabatic correlation energy (54), also the correction to electron correlation energy (162) contributes to stabilization of system in antiadiabatic state, which is the ground state of the system at distorted nuclear geometry \(R_{ad,cr}\). It should be reminded, however, that regardless of the correction to electron correlation energy (which represents contributions of biexcited configurations in second and higher orders of perturbation theory), the system has already been stabilized in antiadiabatic state at distorted geometry due to correction to the ground state electronic energy (128) which represents zero-order correction in terms of perturbation theory. In this respect, increased electron correlation is the consequence of e-p interactions which have induced transition of the system from adiabatic into antiadiabatic state and stabilized it in this state no matter if correction to electron correlation energy is accounted for or not.

At finite temperature, the product of Fermi-Dirac occupation factors has to be introduced into derived equations: \(\sum_{kk'} \cdots \rightarrow \sum_{kk'} \tilde{b} \cdots (1 - \tilde{c}) \cdots\). With increasing temperature from 0 K, the value of the correction (162) which is characteristic for antiadiabatic state decreases and at \(T = T_0\) when system undergoes sudden transition from antiadiabatic state at distorted geometry \(R_{ad,cr}\) into adiabatic state at undistorted geometry \(R_0 = R_{eq}\) and above this temperature, for correction to electron correlation energy holds corresponding temperature-dependent adiabatic form (165). Above \(T_0\), this correction along with crude-adiabatic correlation energy (54) stabilizes adiabatic ground state of system at undistorted-adiabatic equilibrium geometry \(R_0 = R_{eq}\).

Let us turn attention to the Fröhlich effective Hamiltonian of e-e interactions [7]:

\[
H_{ep}''(\text{Fr}) = \sum_{kk',qq'} \left| u_{kk',qq'}^0 \right|^2 \frac{\hbar \omega_q}{(\epsilon_{k+q}^0 - \epsilon_k^0)^2 - (\hbar \omega_q)^2} \times a_{k+q,-k}^0 a_{k,-k}^0 a_{k+q,-k} a_{k,-k}.
\]

(166)

The reduced for of this Hamiltonian is

\[
H_{ep}''(\text{red})_{\text{Fr}} = 2 \sum_{kk'} \left| u_{k,-k}^0 \right|^2 \frac{\hbar \omega_{k,-k}}{(\epsilon_k^0 - \epsilon_k^0)^2 - (\hbar \omega_{k,-k})^2} \times a_{k,-k}^0 a_{k,-k}^0 a_{k,-k} a_{k,-k}.
\]

(167)

This interaction term is either attractive or repulsive depending on the sign of denominator. For antiadiabatic conditions \(|\epsilon_k^0 - \epsilon_k^0| < \hbar \omega_{k,-k}\), it represents effective attractive electron-electron interactions. It should be reminded that effective attractive e-e interactions are the crucial condition of Cooper’s pair formation and the basis of the BCS theory.

In the limit of extreme antiadiabaticity \(|\epsilon_k^0 - \epsilon_k^0| / \hbar \omega_r \rightarrow 0\), the form of the Fröhlich two-particle effective Hamiltonian
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and the correction to electron correlation energy (141) are identical and equal to

$$\lim \left( \Delta H_{\text{eff}}^\prime \right)_{\Delta E/\hbar \omega} = \lim \left( H_{\text{eff}}^\prime (\text{Fr}) \right)_{\Delta E/\hbar \omega} = - \sum_{kk',q,\sigma} \frac{|u|^2}{\hbar \omega_q} a_{k+q,\sigma}^\dagger a_{k,\sigma}^\dagger a_{k',q,\sigma} a_{k',\sigma} \epsilon_{k,\sigma} \epsilon_{k',\sigma} \epsilon_{k,\sigma}.$$

(168)

On the adiabatic level $|E^0_k - E^0_k| \gg \hbar \omega_{k' - k}$, the results are substantially different. Adiabatic correction to correlation energy has the form (164), (165), which is always attractive. On the other hand, adiabatic limit $|E^0_k - E^0_k| \gg h\omega_{k' - k}$ of the Fröhlich form results in

$$H_{\text{eff}}^\prime (\text{Fr})_{\text{ad}} = \sum_{kk',q,\sigma} \frac{|u|^2}{\hbar \omega_q} \left( \epsilon^0_k - \epsilon^0_{k+q} \right)^2 \epsilon_{k',\sigma} \epsilon_{k,\sigma} \epsilon_{k',\sigma} \epsilon_{k,\sigma}.$$

(169)

It is immediately seen that this interaction, in contrast to (165), is always repulsive and $(k, k')$ symmetry is disturbed.

With respect to the fact that effective attractive electron-electron interaction is a pure correction to electron correlation energy, the Cooper’s pair idea within the BCS treatment is without any doubts formally correct, nevertheless, it is rather a model treatment how to solve the instability problem with severe restriction to fixed nuclear framework, that is, within the crude-adiabatic BOA which requires for total system validity of the adiabatic condition $|E^0_k - E^0_k| \gg \hbar \omega_{k' - k}$. Discussion of these and related aspects, the BCS treatment of superconducting state transition and theory of antiadiabatic state formation have been analyzed in [68].

From the theory of the antiadiabatic ground state, instead of Cooper’s pairs, formation of mobile bipolarons results in a natural way as a consequence of translation symmetry breakdown on antiadiabatic level. 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) $\varphi_R(x)$ relation (99) holds, that is,

$$|\varphi_P(x, Q, P)\rangle = a^\dagger_P(x, Q, P)|0\rangle$$

$$= \left( - \sum_{rR} c^\dagger_{rR} \tilde{Q}_r \tilde{P}_r - \sum_{rR} c^\dagger_{rR} c_{rR} \tilde{P}_r \tilde{Q}_r + O(\tilde{Q}^2, \tilde{Q}^2, \tilde{P}^2) \right) |0\rangle$$

$$= |\varphi_P(x, 0, 0)\rangle - \sum_{rR} c^\dagger_{rR} \tilde{Q}_r |\varphi_P(x, 0, 0)\rangle$$

$$- \sum_{rR} c^\dagger_{rR} \tilde{P}_r |\varphi_P(x, 0, 0)\rangle + \cdots.$$  

(170)

At transition into antiadiabatic state $|E^0_k(k) - E^0_k| R_{\text{eq}+Q} \ll \hbar \omega_\epsilon$, coefficients $c_{rR}$ of $Q$-dependent transformation matrix become negligibly small and absolutely dominant for modulation of crude-adiabatic wave function are in this case coefficients $c^\dagger_{rR}$ of $P$-dependent transformation matrix. For simplicity, 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$_2$, valence $T_{2g}$ mode vibration of B-B atoms in basal a-b plane of B-octahedron in YBa$_2$, 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 $\varphi_0^0(x, 0, 0)$ is changed in the following way:

$$\varphi_k(x, Q, P) \propto \left( 1 + \sum_{q} \frac{|u|^2}{\hbar \omega_q} \left( \epsilon^0_k - \epsilon^0_{k+q} \right)^2 \right)$$

$$\times \left( P_1 e^{i \epsilon_{x-m} q} |x-(m_1-d_1)| + P_2 e^{i \epsilon_{x-m} q} |x-(m_2+d_2)| \right)$$

$$\times \varphi_0^0(x, 0, 0).$$

(171)

In (171), site approximation for momentum has been used, that is, $P_q = (\text{sign} \cdot q) \sum_{m} P_m e^{i \epsilon_{m-q} m}$. In antiadiabatic state, for particular $k$ and proper $q$ values, nonadiabatic prefactors under summation symbol in (171) can be large. The prefactors, that is, coefficients of $P$-dependent transformation matrix, reflect influence of nuclear kinetic energy on electronic structure. 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. As an example, calculated iso-density line for highest electron density in MgB$_2$ is presented in Figure 5. For equilibrium high-symmetry structure ($R_{eq}$), the highest electron density is localized at equilibrium position of B atoms (Figure 5(a)). For distorted nuclear geometry ($R_{d,cr}$) in the $E_{2g}$ mode, electron density is polarized and the highest value is shifted into the intersite positions, bipolarons are formed (Figure 5(b)). This kind of intersites polarization persists, and on a lattice scale, it has itinerant character at nuclear revolution over perimeters of the fluxional circles with the radius $R_{d,cr}$, until the system remains in the antiadiabatic state.

5. Discussion and Conclusion

Experimental results are always crucial for any theory which aims to formulate basic physics behind observed phenomenon or property. However, an experiment always cover much wider variety of different influences which have impact on results of experimental observation than any
Theoretical studies of high-temperature superconductors, such as cuprates, require a deep understanding of the electronic structure and band topology. This is achieved through experimental techniques like angle-resolved photoemission spectroscopy (ARPES), which provides insights into the Fermi surface and band structure of these materials. The E2g phonon mode relevant to CuO2 planes is critical for understanding the interaction between electronic and phononic degrees of freedom, which can trigger transitions into antiadiabatic states and intersite polarization.

The superconducting transition in cuprates is often associated with the formation of a gap in the electronic excitation spectrum, which is typically opened at the Fermi level (FL). The order parameter of the superconducting state, which determines the symmetry of the gap, is a key parameter in understanding the mechanism of superconductivity. For example, the symmetry of the order parameter in the CuO2 plane is often characterized by the $d_{x^2-y^2}$ orbital, which is a key feature of the BCS pairing model.

Recent studies have suggested that the high-temperature superconductivity in cuprates may be associated with a nodal gap, which is thought to be crucial for achieving high $T_c$. The presence of a nodal gap is often inferred from ARPES experiments, where the dispersion of the Fermi surface is probed. However, the interpretation of ARPES data requires careful considerations of band structure calculations, which are often approximations.

Figure 5: Iso-density line of highest electron density at equilibrium nuclear geometry $R_{eq}$ of MgB$_2$ (a) and at the distorted geometry of B atoms in $E_{2g}$ phonon mode $R_{eq}$, when nonadiabatic e-p interactions trigger transition into antiadiabatic state and intersites polarization is induced (b).

In the context of high-$T_c$ cuprates, the crucial is considered to be the order parameter, that is, the symmetry of superconducting gap which should be of $(d_{x^2−y^2})$ symmetry. Within a simple orbital model consideration of CuO$_2$ plane in square lattice configuration, this type of symmetry is generally accepted to simulate a-b plane superconductivity of cuprates in a best way.

In this sense, unexpected results have been published recently [30]. The high-resolved (sub-meV) ARPES with VUV laser as a light source for optimally doped untwined YBCO reveals that in superconducting state, gap is opened in one-particle spectrum. The momentum dependence is very interesting, however. Like for other cuprates, strong band renormalization (kink formation at $\approx 60$ meV) in off-nodal direction has been observed. The gap is opened in off-nodal $\Gamma$-X and $\Gamma$-Y directions with top of the dispersion at $\approx 20$ meV below FL. In contrast to [79, 80], the results of [30] do not indicate presence of a/b asymmetry. What is surprising, however, is the finding that gap remains finite also in nodal $\Gamma$-S direction, with top of dispersion at $\approx 12$ meV below FL. Presence of finite “nodeless” gap (i.e., in nodal direction) sharply contradicts to commonly accepted idea of cuprates as superconductors of $(d_{x^2−y^2})$ symmetry. In normal state (100 K), the gap is closed in both, off-nodal and nodal directions.

The order parameter of $(d_{x^2−y^2})$ symmetry assumes gap opening in a band with dominant contribution of Cu-based $(d_{x^2−y^2})$ orbital. In layered cuprates, it corresponds to $(d_{x^2−y^2}−p\sigma)$ bands of CuO$_2$ planes. Respected band structure calculation for YBCO is the DFT-based LDA published by Andersen et al. [84] to which the authors [30] refer. Inspection of BS in [84] reveals, however, that Cu2-O2O3 planes bands do not intersect FL in off-nodal $\Gamma$-X nor in $\Gamma$-Y direction, but the bands intersect FL in nodal $\Gamma$-S direction and in S-Y and S-X directions. It is an indication that experimentally detected gap [30], which is opened in off-nodal ($\Gamma$-X and $\Gamma$-Y) directions and also in nodal $\Gamma$-S direction, does not correspond probably to bands of CuO$_2$ planes.

In spite that there is a general agreement among different DFT-based band structure calculations in overall character of band structure for particular cuprate, there are small, but important differences in details concerning topology of some bands at FL. In particular, for YBCO, DFT-based all-electron band structure calculation [85] using the FLAPW method yields important differences in topology of Cu-O chain-derived $(d−p\sigma)$ band. In contrast to band structure [84], where the band intersects FL in S-X, $\Gamma$-Y and $\Gamma$-S directions, the BS [85] yields for Cu-O chain band intersections with FL in $\Gamma$-X, $\Gamma$-Y and $\Gamma$-S directions, respectively. Calculated Cu-O chain band topology [85] is in an excellent agreement with experimental electron-positron momentum density in optimally doped untwined YBCO detected [86] by 2D-angular correlation of electron-positron annihilations (ACAR) technique. It should be stressed that ACAR is particularly sensitive for study of Cu-O chain Fermi sheets in YBCO. The character of ACAR, as experimentally detected, was predicted theoretically [87], and beside intersection of FL in $\Gamma$-X, $\Gamma$-Y directions, prediction has also been for FL intersection in $\Gamma$-T, $\Gamma$-U directions by Cu-O chain band.

With respect to topology of Cu-O chain band, as discussed above, this band should be the best candidate to be considered for gap opening in both, off-nodal ($\Gamma$-X, $\Gamma$-Y) and nodal ($\Gamma$-S) directions as seen in the ARPES results for YBCO [30]. One should stress, however, that also in case of gap opening in Cu-O chain band, expected $(d_{x^2−y^2})$ symmetry is lost. Moreover, the authors in [30] attribute the effects seen in the ARPES to bands of CuO$_2$ planes and declare that in the spectra dispersion of Cu-O chain band is not present. There are a lot of experimental peculiarities of ARPES experiments with YBCO (twinning/untwining, surface states, CuO-chain problems, spectral dependence on high-source energy, etc.), so it is difficult for me to make any comment about assignment of particular EDC/MDC to CuO$_2$ plane or Cu-O chain bands as it has been done by the authors [30].

Nonetheless, an interpretation of the effects seen in the discussed ARPES from the stand-point of antiadiabatic theory should be of interest. The basic aspects concerning YBCO have been predicted [76] and shortly mentioned also in the Section 3.2.1. One should start with topology of the band.
structure (Figures 1(e)-1(f)), in particular with dispersion of Cu-O chain band at FL. It should be stressed that HF-SCF method with semiempirical INDO Hamiltonian used at band structure calculation (see reference 12 in [76]), overestimates bonding character and consequently bandwidth, which means that high-energy effects can hardly be studied, but for low-energy physics (like gap opening, kink formation, etc.) the method is reliable enough at least in a qualitative way. It can be seen that dispersion of this band at FL corresponds qualitatively to Cu-O chain band dispersion as it has been calculated by FLAPW method [85] and to its experimental character as seen at FL by ACAR method [86].

Coupling to $A_g, B_{2g}, B_{3g}$ phonon modes induces fluctuation (Figures 1(e)-1(f)) of the ACP (inflex) of Cu-O$_2$ plane $(d_{x^2-y^2} - p\sigma)$ band at Y point across the FL. In the moment when the ACP approaches FL from the bonding side, strong renormalization of dispersion of this band (kink formation) could be seen by ARPES in off-nodal Y-$\Gamma$ direction (Figure 3(a), this paper) at about $k \approx 0.41/3.82 \approx 0.1$ A$^{-1}$ (cf. [28, Figure 2a(c)]). At this situation, there is dramatic decrease of effective electron velocity and chemical potential ($\mu_{ad} \gg \mu_{antiad} < \hbar \omega_c$), while DOS is increased (Figure 3(b), this paper) at FL and system undergoes transition into antiadiabatic state. Influence of nuclear dynamics on electronic structure is now significant, antiadiabatic theory of e-p coupling as presented in this paper. System is stabilized in antiadiabatic state at distorted nuclear configuration $R_{d_{xy}}$, and gap is opened in one-particle spectrum. The gap (Section 3.2.1, Figures 4(a) and 4(b)) is opened only in the Cu-O chain $(d-p\sigma)$ band, in off-nodal directions $\Gamma-X$ and $\Gamma-Y$ ($k_{T_{\gamma}} \approx 0.053$ A$^{-1}$, $k_{T_{\chi}} \approx 0.016$ A$^{-1}$) and also in nodal $\Gamma-S$ direction. The half-gaps in the off-nodal directions are $\Delta_{T_{\gamma}}/2 \approx 22$ meV, $\Delta_{T_{\chi}}/2 \approx 15$ meV and gap in the nodal direction is expected to be $\Delta_{T_S}/2 \approx 15$ meV (cf. [28, Figures 1, 7, 8]). In contrast to [30], antiadiabatic theory yields $a/b$-gap asymmetry, which is in good agreement with other experimental results [79, 80]. At temperatures $> T_c$, the gap extinct. It should be manifested by disappearing of peaks on EDC (MDC) at FL in the ARPES spectra (see [30, Figure 8(e)]). In this situation, the adiabatic DOS, which is of constant value at FL, is established and system is in adiabatic-nonsuperconducting state.

It should be mentioned that considerably smaller gap ($\Delta_{T_{\gamma U}} \approx 5$ meV) has been predicted [76] to be opened also in $\Gamma-U$ directions. The prediction is related to the topology of the Cu-O chain $(d-p\sigma)$ band in these directions ([76, Figures 10, 11]). Theoretical calculation of the electron-positron momentum density [87] confirms this character of Cu-O chain topology. It is obvious that symmetry of the Cu-O chain band gap is not of $(d_{x^2-y^2})$ character. Symmetry of the gap is, in my opinion, the matter of band structure topology at FL, which is far more complicated than the one emerging from simple model of CuO$_2$ plane confined in a square lattice. It is a complex mater of crystal structure and chemical composition of particular cuprate. It should be reminded that YBCO is the only high-$T_c$ cuprate with Cu-O chain in its structure. The gap opening in Cu-O chain band does not mean, however, that superconductivity in YBCO is realized in Cu-O chains. Superconductivity is realized by bipolaron mechanism in Cu-O$_2$ planes, no matter if gap symmetry is $(d_{x^2-y^2})$ or any other (antiadiabatic theory, see also [76]).

In conclusion, it can be summarized that based on the ab initio theory of complex electronic ground state of superconductors, it can be concluded that e-p coupling in superconductors induces the temperature-dependent electronic structure instability related to fluctuation of analytic critical point (ACP—maximum, minimum, or saddle point of dispersion) of some band across FL, which results in breakdown of the adiabatic BOA. When ACP approaches FL, chemical potential $\mu_{ad}$ is substantially reduced to $\mu_{antiad}(\mu_{ad} \gg \mu_{antiad} < \hbar \omega_c)$. Under these circumstances, the system is stabilized due to the effect of nuclear dynamics, in the antiadiabatic state at broken symmetry with a gap in one-particle spectrum. Distorted nuclear structure, which is related to couple of nuclei in the phonon mode $r$ that induces transition into antiadiabatic state, has fluxional character. 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 ground state it enables formation of mobile bipolarons (in a form of polarized intersite charge density distribution in real space) that can moverover lattice in external electric potential as supercarriers without dissipation. With increasing $T$, the stabilization effect of nuclear kinetic energy to the electronic ground-state energy decreases and at critical temperature $T_c$ the gap(s) extinct and system is stabilized in the adiabatic metal-like state with a continuum of states at FL, which is characteristic by high-symmetry structure.

An analysis of e-p interaction Hamiltonian has shown that an effective attractive e-e interaction, which is, the basis of Cooper’s pair formation, is in fact the correction to electron correlation energy at transition from adiabatic into antiadiabatic ground electronic state. In this respect, increased electron correlation is not the primary reason for transition into superconducting state, but it is a consequence of antiadiabatic state formation which is stabilized by nonadiabatic e-p interactions at broken translation symmetry. It has been shown that thermodynamic properties of system in the antiadiabatic state correspond to thermodynamics of superconducting state.

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**References**

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