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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 λ is e-p

coupling strength and ω 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 hight-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 μ^* 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 became 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 antiferomagnetic 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 $0.05 \leq x < 0.27$ 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 $CaCuO_2$ (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 K (or 34 K for electron doping) at about 0.15 charge carriers per 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 α 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 α (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 (~ 60 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 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 $k_B T_c = \hbar\omega\lambda^{1/2}/2\pi$. However, in reality there is problem with correct estimation of Coulomb pseudopotential μ^* and with unrealistically large values of λ that would match high experimental T_c of novel superconductors. It has to be stressed, however, that strong coupling regime $\lambda > 1$ violates adiabatic condition $\omega/E_F \ll 1$ 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 $\omega/E_F < 1$ [47], in contrast to elementary metals, where adiabatic condition $\omega/E_F \ll 1$ 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 λ and perturbative in $\lambda\omega_D/E_F$, 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 quasiadiabatic state $\omega/E_F \leq 1$ is able to simulate different properties of high-T_c superconductors, including high-value of T_c, already at relatively moderate value of 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 $\omega/E_F \leq 1$, or $\lambda \geq 1$, and for $\omega/E_F \geq 1$ at whatever small value $\lambda \ll 1$, the nonadiabatic polaron theory has been shown to be basically exact [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 σ 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^σ of σ band electrons (chemical potential μ) is relatively small, ≈ 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 $\omega/E_F \approx 0.15$ 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 σ band at Γ point crosses Fermi level (FL) at vibration displacement ≈ 0.016 A°/B-atom, that is, with amplitude ≈ 0.032 A°, which is smaller than root- mean square (rms) displacement (≈ 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^σ of σ band electrons (chemical potential μ) close to Γ 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, $E_F \to 0$. Moreover, shift of the ACP substantially increases density of states (DOS) at FL,

$n_\sigma(E_F) = (\partial\varepsilon^0_\sigma/\partial k)^{-1}_{E_F}$, and induces corresponding decrease of effective electron velocity $(\partial\varepsilon^0_\sigma/\partial k)_{E_F}$ of fluctuating band in this region of k-space. From the physical stand point, 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, $\omega/\mathrm{E} \ll 1$. 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 "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, $E_{\mathrm{corr}} = E_{\mathrm{exact}} - E_{\mathrm{HF}}$

($E_{\text{exact}} < E_{\text{HF}}$), 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 antiparalel 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)

$$\hat{H}\Psi(r,R) = E^{TS}\Psi(r,R) \tag{1}$$

with the Hamiltonian

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{ee}(r) + \hat{V}_{eN}(r,R) + E_{NN}(R), \tag{2}$$

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

$$\Psi(r,R) = \sum_m \chi_m(R)\Phi_m(r,R), \tag{3}$$

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

$$\hat{H}_e\Phi_m(r,R) = E_m^e\Phi_m(r,R), \tag{4}$$

with the electronic Hamiltonian:

$$\hat{H}_e = \hat{T}_e + \hat{V}_{ee}(r) + \hat{V}_{eN}(r,[R]), \tag{5}$$

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 $\{E_m^e(R)\}$ of nuclear motion.

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

$$\left\{\hat{T}_N + E_n^{te}(R) - E^{TS}(R)\right\}\chi_n(R) = \sum_m \hat{\Lambda}_{nm}(R)\chi_m(R) \tag{6}$$

with the term $\hat{\Lambda}_{nm}(R)$, which couples electronic and nuclear motions, on the right-hand side (rhs):

$$\begin{aligned}\hat{\Lambda}_{nm}(R) &= \hat{A}_{nm}(R) - B_{nm}(R) \\ &= \sum_j \frac{\hbar^2}{M_j} \int \Phi_n^*\left(r, R_j\right) \frac{\partial}{\partial R_j} \Phi_m\left(r, R_j\right) dr \cdot \frac{\partial}{\partial R_j} \\ &\quad - \int \Phi_n^*(r,R) \hat{T}_N(R) \Phi_m(r,R) dr.\end{aligned} \tag{7}$$

The term E_n^{te} in (6):

$$E_n^{te}(R) = \left(E_n^e(R) + E_{NN}(R)\right) \tag{8}$$

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), $\hat{\Lambda}_{nm}(R)$, which represents possibility of transitions between different adiabatic electronic states, $\Phi_n(r,R) \leftrightarrow \Phi_m(r,R)$, 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:

$$\left\{\hat{T}_N + \left(E_n^{te}(R) + B_{nn}(R)\right) - E_{n,\nu}^{TS}(R)\right\}\chi_{n,\nu}(R) = 0, \tag{9}$$

where B_{nn} is the only a nonzero diagonal contribution of the Λ term

$$\begin{aligned}B_{nn}(R) &= \int \Phi_n^*(r,R) \hat{T}_N(R) \Phi_n(r,R) dr \\ &= \sum_n^N -\frac{\hbar^2}{2M_n} \int \Phi_n^*(r,R) \nabla_n^2 \Phi_n(r,R) dr \\ &= \sum_{n\alpha} \frac{\hbar^2}{2M_n} \int \left(\frac{\partial \Phi_n\left(r, \vec{R}\right)}{\partial R_{n\alpha}}\right)^* \left(\frac{\partial \Phi_n\left(r, \vec{R}\right)}{\partial R_{n\alpha}}\right) dr|_{[R]}.\end{aligned} \tag{10}$$

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 $E_n^{te}(R)$. However, (9) is then the equation of motion of nuclei and it has the form of Schrödinger equation with Hamiltonian:

$$\hat{H}_N(R) = \hat{T}_N + V_{NN}^{\text{eff}}(R). \tag{11}$$

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

$$V_{NN}^{\text{eff}}(R) = E_n^{te}(R) + B_{nn}(R) \tag{12}$$

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 $E_n^e(R)$, 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:

$$\hat{H}(R) = \hat{H}^0(R) + H'(R) \tag{13}$$

is studied, where

$$\hat{H}^0(R) = \hat{H}_{te}(R) + H_N(R) = \{(5) + E_{NN}(R)\} + (11) \tag{14}$$

is unperturbed part, and

$$H'(R) = \hat{\Lambda}_{mn}(R); \quad \left(H'_{mn}(R) = \int \chi_{m\mu}^*(R) \hat{\Lambda}_{mn}(R) \chi_{n\nu}(R) dR\right); \quad m \neq n \tag{15}$$

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:

$$\Psi_0(r,R) = \chi_{0,\nu}(R) \Phi_0(r,R). \tag{16}$$

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

$$\Psi_0(r,R) = \chi_{0,\nu}(R) \Phi_0\left(r, R_{\text{eq}}\right). \tag{17}$$

Contributions of the off-diagonal terms $\hat{\Lambda}_{0m}(R)$ 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, $E_0^{TS}(R)$, which are small providing that

$$\left|\int \chi_{0,\nu}^*(R) \hat{\Lambda}_{0m}(R) \chi_{m,\mu}(R) dR\right| \ll \left|E_{0,\nu}^{TS}(R) - E_{n,\mu}^{TS}(R)\right|. \tag{18}$$

It can be derived (see, e.g., [72]), based on the expansion of the effective nuclear potential ($V_{NN}^{\text{eff}}(R) = E_0^{te}(R)$) at equilibrium nuclear geometry R_{eq} (where the total electronic ground-state energy reaches its absolute minimum) at least up to the quadratic term in a displacement ΔR:

$$\begin{aligned} E_0^{te}(R) &= E_0^{te}\left(R_{\text{eq}}\right) + \frac{1}{2}\frac{\partial^2 E_0^{te}(\Delta R)}{\partial \Delta R^2}\cdot \Delta R^2 + \cdots \\ &= E_0^{te}\left(R_{\text{eq}}\right) + \frac{\hbar}{2}\sum_s \omega_s \xi_s^2 + \cdots . \end{aligned} \tag{19}$$

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

$$\left| E_0^{te}\left(R_{\text{eq}}\right) - E_n^{te}\left(R_{\text{eq}}\right) \right| \gg \hbar\omega_s \tag{20}$$

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_{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, $\hat{H} = \hat{H}^0 + \hat{H}_{ep}$, with

$$\hat{H}^0 = \sum_{k\sigma} \varepsilon_k^0 a_{k\sigma}^+ a_{k\sigma} + \sum_q \hbar\omega_q \left(b_{-q}^+ b_q + \frac{1}{2} \right). \tag{21}$$

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

$$\hat{H}_{ep} = \sum_{k,q,\sigma} u^q \left(b_q + b_{-q}^+ \right) a_{k+q,\sigma}^+ a_{k,\sigma}. \tag{22}$$

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_{ep}, it is immediately seen from the form of (16) and (22) that the first-order correction, that is, diagonal perturbation term, equals zero: $\langle \Phi_0 | \hat{H}_{ep} | \Phi_0 \rangle = 0$. 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 $\langle \Phi_0 | \hat{H}_{ep} | \Phi_n \rangle \langle \Phi_n | \hat{H}_{ep} | \Phi_0 \rangle / (E_0^{te} - E_n^{te})$.

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_{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

$$\hat{H}(R) = \hat{H}^e(R) + H'(R) \tag{23}$$

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_{eq} but also for displaced geometry ($R_{\text{eq}} + \Delta R$). Displacement ΔR has to be as large as to cover full configuration space $\{R\}$ experienced by nuclei in the vibration (phonon) modes of system. At 0 K temperature, ΔR has to be greater than (or at least equal to) root-mean square displacement $\overline{x}_{0(\nu)}$ of vibration (phonon) mode (ν) at zero-point energy:

$$|\Delta R| \geq \overline{x}_{0(\nu)}, \qquad \overline{x}_{0(\nu)} = \left| \left\langle x_{0(\nu)}^2 \right\rangle \right|^{1/2}. \tag{24}$$

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

$$\left| E_0^{te}\left(R_{\text{eq}} + \overline{x}_{0(\nu)}\right) - E_n^{te}\left(R_{\text{eq}} + \overline{x}_{0(\nu)}\right) \right| \gg \hbar\omega_\nu. \tag{25}$$

In this context, the adiabatic electronic energies of the ground and excited electronic states $\{E_0^{te}, (E_n^{te})\}$, at fixed nuclear geometry $[R]$, 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:

$$\begin{aligned} &\Phi_0(r, [R]) \\ &\quad = \left| \varphi_1(1)\overline{\varphi}_1(2)\varphi_2(3)\overline{\varphi}_2(4)\cdots\varphi_{n_e}(2n_e-1)\overline{\varphi}_{n_e}(2n_e) \right|, \end{aligned} \tag{26}$$

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 α spin, φ_n, and once with β spin, $\overline{\varphi}_n$. 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 $[R] = R_0$:

$$\begin{aligned} E_0^{te}(R_0) &= E_{NN}^0(R_0) + E_{SCF}^0(R_0) \\ &= E_{NN}^0(R_0) + \left(2\sum_I^{occ} h_{II}^0 + \sum_{IJ}^{occ}\left(2v_{IJIJ}^0 - v_{IJJI}^0\right)\right) \\ &= E_{NN}^0(R_0) + \left(2\sum_I^{occ} h_{II}^0 + \sum_{IJ}^{occ}(2J_{IJ} - K_{IJ})\right) \\ &= E_{NN}^0(R_0) + \sum_I^{occ}\left(\varepsilon_I^0 + h_{II}^0\right). \end{aligned} \tag{27}$$

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

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

$$\varepsilon_P^0 = h_{PP}^0 + \sum_Q\left(2v_{PQPQ}^0 - v_{PQQP}^0\right) \tag{28}$$

of the Fock operator $F(R_0) = h^0(R_0) + \sum_Q(2J_Q - K_Q)$:

$$F(R)\varphi_P(r, R_0) = \sum_Q \varepsilon_{PQ}^0\varphi_Q(r, R_0) \tag{29}$$

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 J_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 $\{E_{n(\neq 0)}^e(R)\}$, 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 $\{\varphi_n(R)\}$ and corresponding eigenenergies $\{\varepsilon_n^0(R)\}$, but only n_e lowest-lying spatial orbitals $\{\varphi_I(R)\}_{(n_e)}$ are occupied and remaining $(n - n_e)$ are virtual—unoccupied orbitals $\{\varphi_A(R)\}_{(n-n_e)}$. 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 $\{\Phi_{I\to A}\}$ 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 ${}^3\Phi_{A(I\to A)}$, and singly excited singlet state ${}^1\Phi_{A(I\to A)}$. 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 triplet state,

$${}^3E_{A(I\to A)}^e(R) - E_0^e(R) = \varepsilon_A^0(R) - \varepsilon_I^0(R) - J_{IA}; \tag{30}$$

(i) for singly excited singlet state,

$${}^1E_{A(I\to A)}^e(R) - E_0^e(R) = \varepsilon_A^0(R) - \varepsilon_I^0(R) - J_{IA} + 2K_{IA}. \tag{31}$$

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:

$$E_{A(I\to A)}^e(R) - E_0^e(R) = \varepsilon_A^0(R) - \varepsilon_I^0(R). \tag{32}$$

Multiple electronic excitations can be calculated in a similar way, by generation of Slater determinants of p-particle, $h(\equiv p)$-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 (φ_I) and unoccupied-virtual (φ_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},

$$\left|\varepsilon_I^0\left(R_{\text{eq}}\right) - \varepsilon_A^0\left(R_{\text{eq}}\right)\right| \gg \hbar\omega_\nu \tag{33}$$

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;

(i) more over,

$$\left|\varepsilon_I^0\left(R_{\text{eq}} + \overline{x}_{0(\nu)}\right) - \varepsilon_A^0\left(R_{\text{eq}} + \overline{x}_{0(\nu)}\right)\right| \gg \hbar\omega_\nu \tag{34}$$

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

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

$$\left|\varepsilon_S^0(k_c) - \varepsilon_F^0\right|_{R_{\text{eq}}} \gg \hbar\omega_r \tag{35}$$

for equilibrium nuclear geometry, and

$$\left|\varepsilon_S^0(k_c) - \varepsilon_F^0\right|_{R_{\mathrm{eq}}+\vec{x}_{0(r)}} \gg \hbar\omega_r \tag{36}$$

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 $\{\varepsilon_S^0(k_c)\}$ 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 ε_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 $E_0^{te}(R)$) 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 $\Delta E_0^{te}(R_{\mathrm{eq}}+\Delta R)$ as to ensure at least harmonic approximation) even if displacement ΔR yields significant changes in the one-electron spectrum (orbital energies) of the ground state

$$\left\{\varepsilon_Q^0\right\}_{R_{\mathrm{eq}}} \neq \left\{\varepsilon_Q^0\right\}_{R_{\mathrm{eq}}+\bar{x}_0}, \tag{37}$$

provided that these changes are well balanced by changes Δh_{II} and ΔE_{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}, $\{\varepsilon_Q^0\}_{R_{\mathrm{eq}}}$, can be significantly different from the one-electron spectrum $\{\varepsilon_Q^0\}_{R_{\mathrm{eq}}+\bar{x}_0}$ at displaced nuclear configuration $(R_{\mathrm{eq}} + \bar{x}_{0,\nu})$ for some phonon mode ν.

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

$$\left|\varepsilon_S^0(k_c) - \varepsilon_F^0\right|_{R_{\mathrm{eq}}+\bar{x}_{0(\nu)}} \leq \hbar\omega_\nu \tag{38}$$

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 (Δh_{IJ}) and/or two-electron Coulomb repulsion and exchange integrals (ΔJ_{IJ}, ΔK_{IJ}). Which of these are dominant (hopping terms, onsite/intersite 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 $(\partial|\varepsilon_{0,a}(k)|/\partial k)_{k_c}$, in particular band close to analytic critical point k_c at the Fermi level $\varepsilon_{0,F}$. Or, what is equivalent, the effective mass of electrons have been increased in this region. In any case, however, it means that at displaced nuclear geometry $(R_{\mathrm{eq}} + \bar{x}_{0,(\nu)})$, 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 adiabaticaly. The motion of electrons and nuclei is now strongly correlated. The new situation occurs, the adiabatic BOA is not valid for nuclear geometry $(R_{\mathrm{eq}}+\bar{x}_{0,(\nu)})$, and wave function cannot be factorized in the form (16) and (3), that is,

$$\Psi_0\left(r, R_{\mathrm{eq}} + \bar{x}_{0(\nu)}\right) \neq \chi_{0,\nu}\left(R_{\mathrm{eq}} + \bar{x}_{0(\nu)}\right)\Phi_0\left(r, R_{\mathrm{eq}} + \bar{x}_{0(\nu)}\right), \tag{39}$$

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-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

$$\begin{aligned} H = {} & T_N(P) + E_{NN}(Q) + \sum_{PQ} h_{PQ}(Q)a_P^+ a_Q \\ & + \frac{1}{2}\sum_{PQRS} v_{PQRS}^0 a_P^+ a_Q^+ a_S a_R. \end{aligned} \tag{40}$$

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_r 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

nuclear momenta operators P_r. For nuclear coordinate and momentum operators hold:

$$Q_r = (b_r + b_{\check{r}}^+), \quad Q_{\check{r}} = (b_{\check{r}} + b_r^+), \quad Q_r^+ = (b_r^+ + b_{\check{r}}) = Q_{\check{r}},$$
$$P_r = (b_r - b_{\check{r}}^+), \quad P_{\check{r}} = (b_{\check{r}} - b_r^+), \quad P_r^+ = (b_r^+ - b_{\check{r}}) = -P_{\check{r}}. \tag{41}$$

The (a, a^+), (b, b^+) are standard fermion and boson annihilation and creation operators, respectively.

The Q-dependence of terms $E_{NN}(Q)$ and $h_{PQ}(Q)$ in (40) can be expressed through the Taylor's expansion at fixed nuclear configuration R_0:

$$E_{NN}(Q) = E_{NN}^0(R_0) + \sum_{j=1}^{\infty} E_{NN}^{(j)}(Q),$$
$$h_{PQ}(Q) = h_{PQ}^0(R_0) + \sum_{i=1}^{\infty} u_{PQ}^{(i)}(Q). \tag{42}$$

The term $E_{NN}^0(R_0)$ represents potential energy of bare nuclei at fixed nuclear configuration R_0, $h_{PQ}^0(R_0)$ is one-electron core term (electron kinetic energy plus electron-nuclear coulomb attraction term) at fixed nuclear configuration R_0 and terms $\{u_{PQ}^{(i)}(Q)\}$ are related to matrix elements of electron-vibration (phonon) coupling ($u_{PQ}^{(i)}$), that is,

$$u_{PQ}^r(Q) = \frac{\partial h_{PQ}(Q)}{\partial Q_r} Q_r = u_{PQ}^r Q_r;$$
$$u_{PQ}^{r\cdots s}(Q) = \frac{\partial h_{PQ}(Q)}{\partial Q_r \cdots \partial Q_s} Q_r \cdots Q_s = u_{PQ}^{r\cdots s} Q_r \cdots Q_s. \tag{43}$$

Two-electron terms v_{PQRS}^0 (electron-electron coulomb repulsion and exchange integrals) do not depend explicitly on the nuclear operators.

2.2.1. Crude-Adiabatic Approximation: Clamped Nuclei Solution. Since the crude-adiabatic approximation is the reference level for study the effect of nuclear dynamics on electronic structure, some details should be introduced.

With respect to sequence of transformations, which will be presented in the following parts, let as distinguish particular representation; that is, dependence of electronic states on nuclear operator Q only by double-bar over particular operator symbol (e.g., $\overline{\overline{a}}$,$\overline{\overline{b}}$), dependence on both Q and P will be without bar (a, b) and for fixed basis (independent on Q and QP, resp.) the operators will be with a single-bar $(\overline{a}, \overline{b})$ over the particular symbol. In this sense, the operators in crude-adiabatic approximation are written as single-bar operators, that is, $(\overline{a}, \overline{b}, \overline{Q}, \overline{P})$.

Provided that phonon and electronic energy spectrum are well separated and (20) holds for relevant configuration space R near to R_{eq}, crude-adiabatic (clamped nuclei) treatment is justified. Electronic Hamiltonian is now only parametrically dependent on nuclear configuration, that is, nuclear geometry is fixed at nuclear configuration R_0:

$$H_e(R_0) = E_{NN}^0(R_0) + \sum_{PQ} h_{PQ}^0(R_0) \overline{a}_P^+ \overline{a}_Q + \frac{1}{2} \sum_{PQRS} v_{PQRS}^0 \overline{a}_P^+ \overline{a}_Q^+ \overline{a}_S \overline{a}_R. \tag{44}$$

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:

$$\sum_{PQ} h_{PQ}^0 \overline{a}_P^+ \overline{a}_Q = \sum_{PQ} h_{PQ}^0 N[\overline{a}_P^+ \overline{a}_Q] + \sum_{I}^{occ} h_{II}^0, \tag{45}$$

$$\sum_{PQRS} v_{PQRS}^0 \overline{a}_P^+ \overline{a}_Q^+ \overline{a}_S \overline{a}_R = \sum_{PQRS} v_{PQRS}^0 N\left[\overline{a}_P^+ \overline{a}_Q^+ \overline{a}_S \overline{a}_R\right] + \sum_{PQ} \left(\sum_{I}^{occ} \left(v_{PIQI}^0 + v_{IPIQ}^0 - v_{PIIQ}^0 - v_{IPQI}^0 \right) \right) N[\overline{a}_P^+ \overline{a}_Q] + \sum_{IJ}^{occ} \left(v_{IJIJ}^0 - v_{IJJI}^0 \right). \tag{46}$$

Application of Wick's theorem introduces renormalized Fermi vacuum, that is, the total set of orthonormal base orbitals $(\varphi_{P'}, \varphi_Q, \ldots)$ is divided on two distinct groups; the set of occupied $(\varphi_I, \varphi_J, \ldots)$ spinorbitals which form a Fermi see (FS) and set of unoccupied-virtual $(\varphi_A, \varphi_B, \ldots)$ 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:

$$H_e(R_0) = H_{(0)}(R_0) + H_{(1)}(R_0) + H_{(2)}(R_0). \tag{47}$$

(I) *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

$$H_{(0)}(R_0) = \langle \Phi_0 | H_e | \Phi_0 \rangle = \sum_{I}^{occ} h_{II}^0 + \frac{1}{2} \sum_{IJ}^{occ} \left(v_{IJIJ}^0 - v_{IJJI}^0 \right) = E_{SCF}^0(R_0). \tag{48}$$

This term represents ground-state electronic energy calculated by unrestricted Hartree-Fock SCF (HF-SCF) procedure at fixed nuclear configuration R_0. It is obvious that addition of nuclear repulsion $E_{NN}(R_0)$ to this term yields total electronic energy $E_0^{te}(R_0)$. Electronic ground state is represented by renormalized Fermi vacuum Φ_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 $\{\varphi_P\}$:

$$\Phi_0(r, R_0) = |\varphi_1 \cdots \varphi_I| \tag{49}$$

(II) *Electronic energy spectrum.*

The one-particle term $H_{(1)}(R_0) = H'_{(cad)}(R_0)$ of the electronic Hamiltonian (47) has the form,

$$H_{(1)}(R_0) = \sum_{PQ} F_{PQ} N[\overline{a}_P^+ \overline{a}_Q]. \tag{50}$$

The elements F_{PQ} are calculated as matrix elements of Hartree-Fock one-particle operator:

$$F(R_0) = h^0(R_0) + \sum_Q (J_Q - K_Q). \tag{51a}$$

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

$$F(R_0)\varphi_P(r, R_0) = \sum_Q \varepsilon_{PQ}\varphi_Q(r, R_0) \tag{51b}$$

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

$$\varepsilon_P^0 = h_{PP}^0 + \sum_Q \left(\nu_{PQPQ}^0 - \nu_{PQQP}^0\right), \tag{51c}$$

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,

$$H_{(1)}(R_0) = \sum_P \varepsilon_P^0 N[\overline{a}_P^+ \overline{a}_P], \tag{51d}$$

$$H_{(1)}(R_0)|\Phi_0\rangle = 0 \tag{51e}$$

for excited states hold:

$$H_{(1)}(R_0)|\Phi_{I\to A}\rangle = \left(\varepsilon_A^0 - \varepsilon_I^0\right)|\Phi_{I\to A}\rangle \quad \text{for } I \in FS,\ A \notin FS. \tag{51f}$$

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 $\Phi_{h_n p_n}$ 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 (h_n) and particles (p_n) 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, $E_0^{te}(R_0)$ holds:

$$\begin{aligned} E_0^{te}(R_0) &= E_{NN}^0(R_0) + E_{SCF}^0(R_0) \\ &= E_{NN}^0(R_0) + \left(\sum_I^{occ} h_{II}^0 + \frac{1}{2}\sum_{IJ}^{occ}\left(\nu_{IJIJ}^0 - \nu_{IJJI}^0\right)\right) \\ &= E_{NN}^0(R_0) + \frac{1}{2}\sum_I^{occ}\left(\varepsilon_I^0 + h_{II}^0\right). \end{aligned} \tag{52}$$

For closed-shell electronic systems, within restricted HF approximation (doubly occupied spatial orbitals with α and β spins, (27) holds. Total electronic ground-state energy of the system reaches the minimum at some equilibrium nuclear configuration $R_0 = R_{\text{eq}}$. 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

$$H_{(2)}(R_0) = H''_{(cad)}(R_0) = \frac{1}{2}\sum_{PQRS} \nu_{PQRS}^0 N\left[\overline{a}_P^+ \overline{a}_Q^+ \overline{a}_S \overline{a}_R\right]. \tag{53}$$

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 $\{\varepsilon_P^0\}$ 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

$$E_{\text{corr}}(R_0) = H_{(h_1 h_2 p_1 p_2)}(R_0) = \sum_{IJ}^{occ}\sum_{AB}^{unocc} \frac{\left(2\nu_{IJAB}^0 - \nu_{IJBA}^0\right)}{\left(\varepsilon_I^0 + \varepsilon_J^0 - \varepsilon_A^0 - \varepsilon_B^0\right)}. \tag{54}$$

Related to energy of the Fermi level, energies of unoccupied states are $\{\varepsilon_A^0\} > 0$ and energies of occupied states are $\{\varepsilon_I^0\} < 0$. It means that E_{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

$$H_N = T_N + V_{NN}^{\text{eff}}(R) = \sum_r \hbar\omega_r \left(\overline{b}_r^+ \overline{b}_r + \frac{1}{2}\right). \tag{55}$$

For different, but fixed nuclear configurations $[R]$ at $R_0 = R_{\text{eq}}$, $E_0^{te}(R)$ is calculated and effective potential for nuclear motion is derived $V_{NN}^{\text{eff}}(R)$. It has to be stressed that contributions of DBOC—$B_{00}(R)$, that is, (10), to $V_{NN}^{\text{eff}}(R)$ are in this case neglected.

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

$$E_0^{TS}(R_0) = E_0^{te}\left(R_{\text{eq}}\right) + \sum_r \hbar\omega_r (n_r + 1/2), \tag{56}$$

$$\begin{aligned} &\Psi_0(r,R) = \chi_0(R)\Phi_0\left(r, R_{\text{eq}}\right), \\ &\text{or in terms of } Q: \Psi_0\left(r,Q\right) = \chi_0\left(Q\right)\Phi_0(r,0). \end{aligned} \tag{57}$$

Nuclear wave function is

$$\chi_0(R) = \prod_r \chi_{0r,n}(R) = \prod_r \frac{1}{\sqrt{n_r!}}\left(\overline{b}_r^+\right)^{n_r}|0\rangle. \tag{58a}$$

2.2.2. Base Transformation-Introduction of New Dynamical Variables. Each eigenfunction φ_J in Slater determinant (49) can be expressed as a linear combination of atomic orbital (AO) basis functions $\{\mu\}$, $\varphi_P = \sum_\mu c_{\mu_P}|\mu\rangle$, which are fixed at the positions of the particular nuclei in clamped nuclei configuration R_0. It represents fixed basis set $\{\mu(x,0) \equiv \mu(x,\overline{Q})\}$.

In second quantization, with single-bar $\overline{a}^+$ 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

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

and

$$\begin{aligned} \varphi_P(x,0) &= \sum_\mu c_{\mu P}\,|\mu(x,0)\rangle \\ &= \sum_\mu c_{\mu P}\overline{a}_\mu^+(x,0)|0\rangle \\ &= \overline{a}_P^+(x,0)|0\rangle. \end{aligned} \tag{60a}$$

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

$$\mu(k,x,0) = \frac{1}{\sqrt{N}}\sum_{tR}^{N} e^{ik\cdot tR}\mu(x - tR). \tag{60b}$$

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 φ_P is then crystal orbital CO-φ_P (band φ_P), which is a linear combination of the Bloch-periodic basis functions $\{\mu(k,x,0)\}$.

In a second quantization, it has the form

$$\mu(k,x,0) = \frac{1}{\sqrt{N}}\sum_{tR}^{N} e^{ik\cdot tR}\overline{a}_\mu^+(x,0)|0\rangle, \tag{60c}$$

$$\begin{aligned} \varphi_P(k,x,0) &= \sum_\mu c_{\mu P}^{(k)}\,|\mu(k,x,0)\rangle \\ &= \sum_\mu c_{\mu P}^{(k)}\frac{1}{\sqrt{N}}\sum_{tR}^{N} e^{ik.tR}\overline{a}_\mu^+(x,0)|0\rangle \\ &= \frac{1}{\sqrt{N}}\sum_{tR}^{N} e^{ik\cdot tR}\overline{a}_{Pk}^+(k,x,0)|0\rangle. \end{aligned} \tag{60d}$$

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 $\varepsilon_P^0(k)$ with respect to the energy of Fermi level ε_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:

$$\left\{\overline{a}_P, \overline{a}_Q\right\} = 0, \quad \left\{\overline{a}_P, \overline{a}_Q^+\right\} = \delta_{PQ}, \tag{61a}$$

$$\left[\overline{b}_r, \overline{b}_s\right] = 0, \quad \left[\overline{b}_r, \overline{b}_s^+\right] = \delta_{rs}. \tag{61b}$$

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:

$$\left[\overline{a}_P, \overline{b}_r\right] = 0, \quad \left[\overline{a}_P, \overline{b}_r^+\right] = 0. \tag{61c}$$

(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,

$$\begin{aligned} &\Psi_0(r,R) = \chi_{0,\nu}(R)\Phi_0(r,R), \\ &\text{or} \quad \Psi_0\left(r,\overline{\overline{Q}}\right) = \chi_{0,\nu}(R)\Phi_0\left(r,\overline{\overline{Q}}\right). \end{aligned} \tag{62}$$

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

$$\begin{aligned}\left\langle \varphi_R\left(x,\overline{\overline{Q}}\right)\middle|\,\varphi_S\left(x,\overline{\overline{Q}}\right)\right\rangle &= \delta_{RS},\\ \sum_R\left|\,\varphi_R\left(x,\overline{\overline{Q}}\right)\right\rangle\left\langle\varphi_R\left(x,\overline{\overline{Q}}\right)\right| &= 1.\end{aligned} \tag{63}$$

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

$$\overline{\overline{Q}}_r = \left(\overline{\overline{b}}_r^+ + \overline{\overline{b}}_{\breve{r}}\right), \qquad \overline{\overline{P}}_r = \left(\overline{\overline{b}}_r - \overline{\overline{b}}_{\breve{r}}^+\right). \tag{64}$$

Then,

$$\begin{aligned}\overline{\overline{a}}_R^+\left(x,\overline{\overline{Q}}\right)|0\rangle &= \left|\,\varphi_R\left(x,\overline{\overline{Q}}\right)\right\rangle,\\ \overline{\overline{a}}_R\left(x,\overline{\overline{Q}}\right)\left|\,\varphi_R\left(x,\overline{\overline{Q}}\right)\right\rangle &= 0.\end{aligned} \tag{65}$$

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

$$\left\{\overline{\overline{a}}_R,\overline{\overline{a}}_S^+\right\} = \delta_{RS}, \qquad \{\overline{\overline{a}}_R,\overline{\overline{a}}_S\} = 0. \tag{66}$$

Shorthand notation, $\overline{\overline{a}}_R \equiv \overline{\overline{a}}_R(x,\overline{\overline{Q}})$, $\overline{\overline{a}}_R^+ \equiv \overline{\overline{a}}_R^+(x,\overline{\overline{Q}})$ 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

$$\begin{aligned}\langle\varphi_R(x,0)\,|\,\varphi_S(x,0)\rangle &= \delta_{RS},\\ \sum_R|\,\varphi_R(x,0)\rangle\langle\varphi_R(x,0)\,| &= 1.\end{aligned} \tag{67}$$

Crude-adiabatic fermion creation and annihilation operators that correspond to the fixed basis set are written as single-bar operators $(\overline{a}^+,\overline{a})$, that is,

$$\begin{aligned}&\overline{a}_R^+(x,0)|0\rangle = |\,\varphi_R(x,0)\rangle, \quad \overline{a}_R(x,0)\,|\,\varphi_R(x,0)\rangle = |0\rangle,\\ &\text{or in short-hand notation}\\ &\overline{a}_R^+|0\rangle = |\,\varphi_R(x,0)\rangle, \quad \overline{a}_R\,|\,\varphi_R(x,0)\rangle = |0\rangle.\end{aligned} \tag{68}$$

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:

$$\begin{aligned}|\,\varphi_R(x,0)\rangle &= \sum_S\left|\,\varphi_S\left(x,\overline{\overline{Q}}\right)\right\rangle\left\langle\varphi_S\left(x,\overline{\overline{Q}}\right)\middle|\,\varphi_R(x,0)\right\rangle\\ &= \sum_S\left(c_{RS}\left(\overline{\overline{Q}}\right)\right)^+\left|\,\varphi_S\left(x,\overline{\overline{Q}}\right)\right\rangle.\end{aligned} \tag{69}$$

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

$$\overline{a}_R = \sum_S c_{RS}\left(\overline{\overline{Q}}\right)\overline{a}_S, \qquad \overline{a}_R^+ = \sum_S\left(c_{RS}\left(\overline{\overline{Q}}\right)\right)^+\overline{a}_S^+. \tag{70}$$

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

$$c_{RS}\left(\overline{\overline{Q}}\right) = \left\langle\varphi_R(x,0)\middle|\,\varphi_S\left(x,\overline{\overline{Q}}\right)\right\rangle. \tag{71}$$

Since

$$c_{RS}^*\left(\overline{\overline{Q}}\right) = \left\langle\,\varphi_S\left(x,\overline{\overline{Q}}\right)\middle|\,\varphi_R(x,0)\right\rangle, \tag{72}$$

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:

$$\begin{aligned}\sum_T c_{RT}c_{ST}^* &= \delta_{RS} = \sum_T c_{TR}^*c_{TS},\\ C^+ &= \left(C^T\right)^* = C^{-1}.\end{aligned} \tag{73}$$

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

$$\begin{aligned}&\overline{a}_R = U^+\overline{a}_RU, \quad \overline{a}_R^+ = U^+\overline{a}_R^+,\\ &\longrightarrow \overline{a}_R = \sum_S\left(e^{y_{RS}\left(\overline{Q}\right)}\right)\overline{a}_S, \quad \overline{a}_R^+ = \sum_S\left(e^{y_{RS}\left(\overline{Q}\right)}\right)^+\overline{a}_S^+.\end{aligned} \tag{74}$$

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,

$$c_{PQ}\left(\overline{\overline{Q}}\right) = \sum_{k=0}^{\infty}\frac{1}{k!}\sum_{r_1\cdots r_k}c_{PQ}^{r_1\cdots r_k}\overline{\overline{Q}}_{r_1}\cdots\overline{\overline{Q}}_{r_k}. \tag{75}$$

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:

$$\begin{aligned}\{\overline{\overline{a}}_P,\overline{\overline{a}}_Q\} &= 0, \qquad \left\{\overline{\overline{a}}_P,\overline{\overline{a}}_Q^+\right\} = \delta_{PQ},\\ \left[\overline{\overline{b}}_r,\overline{\overline{b}}_s\right] &= 0, \qquad \left[\overline{\overline{b}}_r,\overline{\overline{b}}_s^+\right] = \delta_{rs},\end{aligned} \tag{76}$$

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:

$$\left[\overline{\overline{a}}_P,\overline{\overline{b}}_r\right] = 0, \qquad \left[\overline{\overline{a}}_P,\overline{\overline{b}}_r^+\right] = 0. \tag{77}$$

With respect to the fermion transformation relations (70), the form of transformation relations for boson operators is expressed as

$$\begin{aligned}\overline{b}_r &= \overline{\overline{b_r}} + \sum_{PQ} d_{rPQ}\left(\overline{\overline{Q}}\right)\overline{\overline{a_P^+}}\,\overline{\overline{a_Q}},\\ \overline{b}_r^+ &= \overline{\overline{b_r^+}} + \sum_{PQ}\left(d_{rPQ}\left(\overline{\overline{Q}}\right)\right)^+\overline{\overline{a_P^+}}\,\overline{\overline{a_Q}}.\end{aligned} \tag{78}$$

Also for matrix elements $d(\overline{\overline{Q}})$ of transformation matrix $D(\overline{\overline{Q}})$, the Taylor' expansion is defined as

$$d_{rPQ}\left(\overline{\overline{Q}}\right) = \sum_{k=0}^{\infty}\frac{1}{k!}\sum_{s_1\cdots s_k} d_{rPQ}^{s_1\cdots s_k}\overline{\overline{Q}}_{s_1}\cdots\overline{\overline{Q}}_{s_k}. \tag{79}$$

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 $d(\overline{\overline{Q}})_{RS}$ through coefficients $c(\overline{\overline{Q}})_{RS}$ (see [66]—Appendix A). It will be shown that c_{PR}^r 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 $\Delta E_{(ad)}^0$.

The adiabatic transformation preserves total number of electrons, and nuclear coordinate operator is invariant under the transformation, that is,

$$\begin{aligned}\overline{\overline{\mathrm{N}_\mathrm{e}}} &= \sum_P \overline{\overline{a_P^+}}\,\overline{\overline{a_P}} = \sum_P \overline{a}_P^+\overline{a}_P = \overline{\mathrm{N}}_\mathrm{e},\\ \overline{\overline{Q}}_r &= \left(\overline{\overline{b}}_r^+ + \overline{\overline{b}}_{\check{r}}\right) = \left(\overline{b}_r^+ + \overline{b}_{\check{r}}\right) = \overline{Q}_r.\end{aligned} \tag{80}$$

Up to the first order of Taylor's expansion, the crude-adiabatic momentum operator $\overline{P}_r = (\overline{b}_r - \overline{b}_{\check{r}}^+)$ is transformed as

$$\overline{P}_r = \left(\overline{\overline{b}}_r - \overline{\overline{b}}_{\check{r}}^+\right) + 2\sum_{PQ} c_{PQ}^{\check{r}}\overline{\overline{a}}_P^+\,\overline{\overline{a}}_Q = \overline{\overline{P}}_r + 2\sum_{PQ} c_{PQ}^{\check{r}}\overline{\overline{a}}_P^+\,\overline{\overline{a}}_Q. \tag{81}$$

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

For adiabatic Q-dependent spinorbitals $|\varphi_P(x,\overline{\overline{Q}})\rangle$, 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:

$$\begin{aligned}\left|\varphi_P\left(x,\overline{\overline{Q}}\right)\right\rangle &= \overline{\overline{a}}_P^+\left(x,\overline{\overline{Q}}\right)|0\rangle\\ &= \left(\overline{a}_P^+ - \sum_{rR} c_{PR}^r\overline{\overline{Q}}_r\overline{a}_R^+ + O\left(\overline{\overline{Q}}^2\right)\right)|0\rangle\\ &= |\varphi_P(x,0)\rangle - \sum_{rR} c_{PR}^r\overline{\overline{Q}}_r\,|\varphi_R(x,0)\rangle + \cdots\\ &= |\varphi_P(x,0)\rangle - \sum_{rR} c_{PR}^r\overline{Q}_r\,|\varphi_R(x,0)\rangle + \cdots.\end{aligned} \tag{82}$$

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

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 $\Psi_0(r,R) = \chi_{0,\nu}(R)\Phi_0(r,R)$. 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 Λ terms on the rhs of equation (6). The off-diagonal Λ terms are absent and from the diagonal Λ terms, the only non-zero element is B_{00}. It is the DBOC, $\Lambda_{00}(\overline{\overline{Q}}) \equiv B_{00}(\overline{\overline{Q}}) = \langle\Phi_0(r,\overline{\overline{Q}})|T_N|\Phi_0(r,\overline{\overline{Q}})\rangle$, 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:

$$\Psi(r,Q,P) = \sum_m \chi_m(Q,P)\Phi_m(r,Q,P). \tag{83}$$

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

$$\Psi_0(r,Q,P) = \chi_0(Q,P)\Phi_0(r,Q,P). \tag{84}$$

It means that effect of nuclear momenta will be covered only in the form of QP-dependent diagonal correction $\Lambda_{00}(Q,P) = \langle\Phi_0(r,Q,P)|\widetilde{T}_N|\Phi_0(r,Q,P)\rangle$, 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, $\Lambda_{00}(\overline{\overline{Q}}) = \langle\Phi_0(r,\overline{\overline{Q}})|T_N|\Phi_0(r,\overline{\overline{Q}})\rangle$.

Solution of this problem is similar to the transition from crude-adiabatic to adiabatic level as presented above. Now, however, 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:

$$\begin{aligned}&\langle \varphi_R(x,Q,P)\,|\,\varphi_S(x,Q,P)\,\rangle = \delta_{RS},\\ &\sum_R |\,\varphi_R(x,Q,P)\rangle\langle\varphi_R(x,Q,P)\,|\,| = 1.\end{aligned} \tag{85}$$

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, $Q_r = (b_r^+ + b_{\breve{r}})$ and $P_r = (b_r - b_{\breve{r}}^+)$. Then,

$$\begin{aligned}&a_R^+(x,Q,P)|0\rangle = |\,\varphi_R(x,Q,P)\rangle,\\ &a_R(x,Q,P)\,|\,\varphi_R(x,Q,P)\rangle = |0\rangle.\end{aligned} \tag{86}$$

Since nonadiabatic electrons remain fermions, the operators obey standard fermion anticommutation relations (it follows from canonical transformation, see (91)):

$$\{a_R, a_S^+\} = \delta_{RS}, \qquad \{a_R, a_S\} = 0. \tag{87}$$

In (87), shorthand notation is used, that is, $a_R \equiv a_R(x,Q,P)$ and $a_R^+ \equiv a_R^+(x,Q,P)$.

Since adiabatic Q-dependent moving base derived by adiabatic transformation is complete and orthonormal (63), then due to (85), the base transformation to nonadiabatic (QP)-dependent moving base can be established over the base transformation relation:

$$\begin{aligned}\left|\,\varphi_R\left(x,\overline{\overline{Q}}\right)\right\rangle &= \sum_S |\,\varphi_S(x,Q,P)\rangle\langle\varphi_S(x,Q,P)\,|\,\varphi_R\left(x,\overline{\overline{Q}}\right)\rangle\\ &= \sum_S \left(\hat{c}_{RS}(P)\right)^+ |\,\varphi_S(x,Q,P)\,\rangle.\end{aligned} \tag{88}$$

For fermion operators of second quantization, it follows that

$$\overline{\overline{a}}_R = \sum_S \hat{c}_{RS}(P)a_S, \qquad \overline{\overline{a}}_R^+ = \sum_S \left(\hat{c}_{RS}(P)\right)^+ a_S^+ \tag{89}$$

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

$$\begin{aligned}\hat{c}_{RS}(P) &= \left\langle \varphi_R\left(x,\overline{\overline{Q}}\right)\,\middle|\,\varphi_S(x,Q,P)\right\rangle,\\ c_{RS}^*(P) &= \left\langle \varphi_S(x,Q,P)\,\middle|\,\varphi_R\left(x,\overline{\overline{Q}}\right)\right\rangle.\end{aligned} \tag{90}$$

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

$$\begin{aligned}&\sum_T \hat{c}_{RT}\hat{c}_{ST}^* = \delta_{RS} = \sum_T \hat{c}_{TR}^*\hat{c}_{TS},\\ &\hat{C}^+ = \left(\hat{C}^T\right)^* = \hat{C}^{-1}.\end{aligned} \tag{91}$$

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). Also 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,

$$\begin{aligned}&\{a_P, a_Q\} = 0, \quad \left\{a_P, a_Q^+\right\} = \delta_{PQ},\\ &[b_r, b_s] = 0, \quad [b_r, b_s^+] = \delta_{rs},\end{aligned} \tag{92}$$

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:

$$[a_P, b_r] = 0, \qquad [a_P, b_r^+] = 0. \tag{93}$$

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

$$\begin{aligned}\overline{\overline{b}}_r &= b_r + \sum_{PQ} \hat{d}_{rPQ}(P)a_P^+a_Q,\\ \overline{\overline{b}}_r^+ &= b_r^+ + \sum_{PQ} \left(\hat{d}_{rPQ}(P)\right)^+ a_P^+a_Q.\end{aligned} \tag{94}$$

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 $\hat{d}_{RS}$ trough coefficients $\hat{c}_{RS}$, see [66]—Appendix B.

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

$$\mathrm{N_e} = \sum_P a_P^+a_P = \overline{\overline{\mathrm{N_e}}} = \sum_P \overline{\overline{a}}_P^+\overline{\overline{a}}_P = \sum_P \overline{a}_P^+\overline{a}_P = \overline{\mathrm{N}}_\mathrm{e}. \tag{95}$$

Invariant of transformation is now momentum operator:

$$\begin{aligned}P_r = (b_r - b_{\breve{r}}^+) &= \overline{\overline{P}}_r = \left(\overline{\overline{b}}_r - \overline{\overline{b}}_{\breve{r}}^+\right)\\ &\neq \overline{P} = \left(\overline{b}_r - \overline{b}_{\breve{r}}^+\right), \quad P_r = \overline{\overline{P}}_r \neq \overline{P}_r.\end{aligned} \tag{96}$$

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

$$\begin{aligned}Q_r &= (b_r + b_{\breve{r}}^+)\\ &= \left(\overline{\overline{b}}_r + \overline{\overline{b}}_{\breve{r}}^+\right) - 2\sum_{PQ} \hat{c}_{PQ}^{\breve{r}}(P)a_P^+a_Q\\ &= \overline{\overline{Q}}_r - 2\sum_{PQ} \hat{c}_{PQ}^{\breve{r}}(P)a_P^+a_Q\\ &= \overline{Q}_r - 2\sum_{PQ} \hat{c}_{PQ}^{\breve{r}}(P)a_P^+a_Q,\end{aligned} \tag{97}$$

that is,

$$\overline{Q}_r = \overline{\overline{Q}}_r \neq Q_r. \tag{98}$$

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:

$$\begin{aligned}
|\varphi_P(x,Q,P)\rangle &= a_P^+(x,Q,P)|0\rangle \\
&= \left(\overline{a}_P^+ - \sum_{rR} c_{PR}^r \overline{Q}_r \overline{a}_R^+ \right. \\
&\quad \left. - \sum_{\check{r}R} \hat{c}_{PR}^r P_{\check{r}} \overline{a}_R^+ + O\left(\overline{Q}^2, \overline{Q}P, P^2\right)\right)|0\rangle \\
&= |\varphi_P(x,0,0)\rangle - \sum_{rR} c_{PR}^r \overline{Q}_r |\varphi_R(x,0,0)\rangle \\
&\quad - \sum_{\check{r}R} \hat{c}_{PR}^r \overline{P}_{\check{r}} |\varphi_R(x,0,0)\rangle + \cdots .
\end{aligned} \tag{99}$$

Nonadiabatic wave function (99) in contrast to adiabatic wave function (82) is modulated not only by the instantaneous nuclear coordinates $\{\overline{Q}_r\}$of particular vibration (phonon) modes $\{r\}$ but modulation is also over corresponding instantaneous nuclear momenta $\{P_{\check{r}}\}$. The weight of momentum modulation is proportional to the P-dependent transformation coefficients $\hat{c}_{PR}^r$. It represents first derivative of $\hat{c}_{PR}$ matrix element with respect to nuclear momentum P_r, $\hat{c}_{PR}^r = \partial \hat{c}_{PR}(P)/\partial P_r$, 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 $|\varepsilon_I^0(R) - \varepsilon_A^0(R)| < \hbar\omega_r$, 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:

$$\begin{aligned}
H &= T_N\left(\overline{P}\right) + E_{NN}\left(\overline{Q}\right) \\
&\quad + \sum_{PQ} h_{PQ}\left(\overline{Q}\right)\overline{a}_P^+ \overline{a}_Q + \frac{1}{2}\sum_{PQRS} v_{PQRS}^0 \overline{a}_P^+ \overline{a}_Q^+ \overline{a}_S \overline{a}_R
\end{aligned} \tag{100}$$

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

$$H_N \rightarrow H_B = \sum_r^{\text{mod}} \hbar\omega_r\left(\overline{b}_{\check{r}}^+ \overline{b}_r + 1/2\right). \tag{101}$$

In general, this part can be written as the sum of nuclear kinetic and nuclear potential energy:

$$H_B = E_{kin}\left(\overline{P}\right) + E_{pot}\left(\overline{Q}\right), \tag{102}$$

whereas

$$E_{pot}\left(\overline{Q}\right) = E_{NN}^{(2)}\left(\overline{Q}\right) + V_N^{(2)}\left(\overline{Q}\right). \tag{103a}$$

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 $\overline{\overline{Q}}$-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,

$$E_{kin}\left(\overline{P}\right) = T_N\left(\overline{P}\right) + W_N^{(2)}\left(\overline{P}\right). \tag{103b}$$

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, $|E_0^{te}(R) - E_n^{te}(R_{\text{eq}})| \leq \hbar\omega_\nu$, 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

$$\begin{aligned}
H_A &= E_{NN}\left(\overline{Q}\right) - E_{NN}^{(2)}\left(\overline{Q}\right) - V_N^{(2)}\left(\overline{Q}\right) \\
&\quad - W_N^{(2)}\left(\overline{P}\right) + \sum_{PQ} h_{PQ}\left(\overline{Q}\right)\overline{a}_P^+ \overline{a}_Q \\
&\quad + \frac{1}{2}\sum_{PQRS} v_{PQRS}^0 \overline{a}_P^+ \overline{a}_Q^+ \overline{a}_S \overline{a}_R.
\end{aligned} \tag{104}$$

It is evident that the division on the two parts is only formal

$$H = H_A + H_B = (100). \tag{105}$$

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,

$$T : H\left(A_\mu\right) \equiv \widetilde{H}\left(A_\mu\right) = H\left(\widetilde{A}_\mu\right) = H\left(U^+(A_\nu)A_\mu U(A_\nu)\right), \tag{106}$$

$$\widetilde{A}_\mu = U^+(A_\nu)A_\mu U(A_\nu) = f(A_\nu), \tag{107a}$$

is applied in order to get diagonal, or "more diagonal", final form at least up to first order of commutation expansion, $[H_0, S] + H_{\text{int}} = 0$. 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 $(\overline{a}, \overline{a}^+, \overline{b}, \overline{b}^+)$, new adiabatic $(\overline{\overline{a}}, \overline{\overline{a}}^+, \overline{\overline{b}}, \overline{\overline{b}}^+)$, and nonadiabatic (a, a^+, b, b^+) quasiparticles are introduced. At these circumstances, canonical transformation of Hamiltonian means introduction of new dynamical variables

$$A_\mu \equiv A_\mu(A'_\nu) = U^+(A'_\nu)A'_\nu U(A'_\nu). \tag{108}$$

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

$$H\left(A_\mu\right) \equiv H\left(U^+(A'_\nu)A'_\nu U(A'_\nu)\right). \tag{109a}$$

The Hamiltonian written in new variables is

$$H\left(A_\mu(A'_\nu)\right) \equiv \widetilde{H}(A'_\nu). \tag{109b}$$

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 $H_{A\overline{\overline{i(j,k)}}}$ and $H_{B\overline{\overline{i(j,k)}}}$ whereas i, j, k in subscript $\overline{\overline{i(j,k)}}$ stand now for the ith order of Taylor' series expansion in adiabatic representation, the jth order of the coordinate operator $\overline{\overline{Q}}$, and the kth order of momentum operator $\overline{\overline{P}}$ within the given order i of Taylor's expansion; that is, $i = (j + k)$.

Up to the second-order expansion in $\overline{\overline{Q}}$, $\overline{\overline{P}}$ and in second-order expansion of the operators of quasiparticle transformation $(\overline{c}_{PQ}, \overline{d}_{rPQ})$, the H_A and H_B parts are transformed in the following way:

$$H_{A\overline{0}(0,0)} \longrightarrow H_{\overline{\overline{A0(0,0)}}} + H_{\overline{\overline{A1(1,0)}}} + H_{\overline{\overline{A2(2,0)}}}, \tag{110a}$$

$$H_{A\overline{1}(1,0)} \longrightarrow H_{\overline{\overline{A1(1,0)}}} + H_{\overline{\overline{A2(2,0)}}}, \tag{110b}$$

$$H_{A\overline{2}(2,0)} \longrightarrow H_{\overline{\overline{A2(2,0)}}}, \tag{110c}$$

$$H_{A\overline{2}(0,2)} \longrightarrow H_{\overline{\overline{A2(0,2)}}}, \tag{110d}$$

$$H_B = H_{B\overline{0}(0,0)} \longrightarrow H_{\overline{\overline{B0(0,0)}}} + H_{\overline{\overline{B1(0,1)}}} + H_{\overline{\overline{B2(1,1)}}} + H_{\overline{\overline{B2(0,0)}}}. \tag{110e}$$

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):

$$H_{\overline{\overline{A0(0,0)}}} \longrightarrow H_{A0(0,0)} + H_{A1(0,1)} + H_{A2(0,2)}, \tag{111a}$$

$$H_{\overline{\overline{A1(1,0)}}} \longrightarrow H_{A1(1,0)} + H_{A2(1,1)} + H_{A2(0,0)}, \tag{111b}$$

$$H_{\overline{\overline{A2(2,0)}}} \longrightarrow H_{A2(2,0)}, \tag{111c}$$

$$H_{\overline{\overline{A2(0,2)}}} \longrightarrow H_{A2(0,2)}, \tag{111d}$$

$$H_{\overline{\overline{B0(0,0)}}} \longrightarrow H_{B0(0,0)} + H_{B1(1,0)} + H_{B2(1,1)} + H_{B2(0,0)}, \tag{111e}$$

$$H_{\overline{\overline{B1(0,1)}}} \longrightarrow H_{B1(0,1)} + H_{B2(0,2)}, \tag{111f}$$

$$H_{\overline{\overline{B2(1,1)}}} \longrightarrow H_{B2(1,1)}, \tag{111g}$$

$$H_{\overline{\overline{B2(0,0)}}} \longrightarrow H_{B2(0,0).} \tag{111h}$$

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 $H_{(0)}(R)$ 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:

$$E^{0,te}(R) = [\langle\Phi_0(R)|H_e(r,R)|\Phi_0(R)\rangle + E_{NN}(R)] + \Delta E^0(R). \tag{112}$$

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

$$\Delta E^0(R) = \sum_{rAI} \hbar\omega_r \left(|\, c^r_{AI}\,|^2 - |\,\hat{c}^r_{AI}\,|^2 \right), \tag{113}$$

$\{I\}$-occupied orbitals, $\{A\}$-unoccupied orbitals

In (113),

$$c^r_{PR} = \frac{\partial c_{PR}(Q)}{\partial Q_r}, \qquad \hat{c}^r_{PR} = \frac{\partial \hat{c}_{PR}(P)}{\partial P_r} \tag{114}$$

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:

$$c^r_{PQ} = u^r_{PQ} \frac{\left(\varepsilon^0_P - \varepsilon^0_Q\right)}{(\hbar\omega_r)^2 - \left(\varepsilon^0_P - \varepsilon^0_Q\right)^2}; \quad P \neq Q,\ \varepsilon^0_S \equiv \varepsilon^0_S(R), \tag{115}$$

$$\hat{c}^r_{PQ} = u^r_{PQ} \frac{\hbar\omega_r}{(\hbar\omega_r)^2 - \left(\varepsilon^0_P - \varepsilon^0_Q\right)^2}; \quad P \neq Q,\ \varepsilon^0_S \equiv \varepsilon^0_S(R). \tag{116}$$

The final form of the correction is

$$\begin{aligned} \Delta E^0(R) &= \sum_{rAI} \hbar\omega_r \left(|\, c^r_{AI}\,|^2 - |\,\hat{c}^r_{AI}\,|^2 \right) \\ &= \sum_{A}^{unocc} \sum_{I}^{occ} \sum_{r} |\, u^r_{AI}\,|^2 \frac{\hbar\omega_r}{\left(\varepsilon^0_A - \varepsilon^0_I\right)^2 - (\hbar\omega_r)^2} \\ &= \sum_{A}^{unocc} \sum_{I}^{occ} \Omega_{AI}. \end{aligned} \tag{117}$$

The Ω matrix is a symmetric matrix of the form

$$\begin{aligned} \Omega_{PQ} &= \sum_{r} \hbar\omega_r \left(\left|\, c^r_{PQ}\,\right|^2 - \left|\,\hat{c}^r_{PQ}\,\right|^2 \right) \\ &= \sum_{r} \left|\, u^r_{PQ}\,\right|^2 \frac{\hbar\omega_r}{\left(\varepsilon^0_P - \varepsilon^0_Q\right)^2 - (\hbar\omega_r)^2}. \end{aligned} \tag{118}$$

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

(i) True nonadiabatic or antiadiabatic state, $(\varepsilon^0_A - \varepsilon^0_I) < \hbar\omega_r$.

In this case the correction is negative, $\Delta E^0_{(nad)} < 0$, 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 $\hat{c}^r_{AI}$ 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, $\hbar\omega_r/|\varepsilon^0_P - \varepsilon^0_Q| \to \infty$. However, the contribution in this case does not represent the largest possible negative value and it is equal to $\Delta E^0_{(sna)} = -\sum_{rAI} \hbar\omega_r(|\hat{c}^r_{AI}|^2) = -\sum_{rAI} |u^r_{AI}|^2/\hbar\omega_r$.

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

$$\Delta E^0_{(ad)} = \sum_{rAI} \hbar\omega_r \left(|\, c^r_{AI}\,|^2 \right). \tag{119}$$

In case of strong adiabaticity, $(\varepsilon^0_A - \varepsilon^0_I) \gg \hbar\omega_r$, which is standard condition for the BOA we have

$$\Delta E^0_{(sad)} = \sum_{rAI} \hbar\omega_r \left(|\, c^r_{AI}\,|^2 \right) = \sum_{rAI} |\, u^r_{AI}\,|^2 \frac{\hbar\omega_r}{\left(\varepsilon^0_A - \varepsilon^0_I\right)^2} \longrightarrow \approx 0. \tag{120}$$

In contrast to nonadiabatic level when the correction is negative, $\Delta E^0_{(nad)} < 0$, 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, $\overline{\overline{Q}}$-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:

$$\begin{aligned} B_{00}(R) &= \int \Phi^*_0(r,R)\hat{T}_N(R)\Phi_0(r,R)dr \\ &= \sum_{n}^{N_n} -\frac{\hbar^2}{2M_n} \int \Phi^*_0(r,R)\nabla^2_n\Phi_0(r,R)dr \\ &= \sum_{n\alpha} \frac{\hbar^2}{2M_n} \int \left(\frac{\partial\Phi_0\left(r,\vec{R}\right)}{\partial R_{n\alpha}} \right)^* \left(\frac{\partial\Phi_0\left(r,\vec{R}\right)}{\partial R_{n\alpha}} \right) dr|_{[R]}. \end{aligned} \tag{121}$$

We have shown [73] that (121) is the same as the adiabatic correction (119) to the electronic energy of the ground state

Φ_0, calculated through the expansion coefficients $c_{PQ}(\overline{\overline{Q}})$ of $\overline{\overline{Q}}$-dependent transformation, that is,

$$\begin{aligned}\Delta E^0_{(ad)}(R) &= B_{00}(R)\\ &= \left\langle \Phi_0\left(r,\vec{R}\right)\,\middle|\, T_N \,\middle|\, \Phi_0\left(r,\vec{R}\right)\right\rangle_{\hat{\mathrm{R}}}\\ &= \sum_{rAI}\hbar\omega_r\,|\,c^r_{AI}\,|^2.\end{aligned} \tag{122}$$

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

$$\sum_Q |\,\varphi_Q(r,R)\rangle\langle\varphi_Q(r,R)\,| = 1. \tag{123}$$

It means that both subsets, that is, occupied $\{\varphi_I(r,R)\}$ and unoccupied $\{\varphi_A(r,R)\}$ 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 $\{\varphi_I(r,R)\}$ and unoccupied orbitals $\{\varphi_A(r,R)\}$ at nuclear vibration motion. It should be stressed that at these virtual transitions the system remains in its electronic ground state $\Phi_0(r,R_{\mathrm{eq}})$. In this respect, even $\Delta E^0_{(\mathrm{ad})}$ 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 $\Phi_0(r,R_{\mathrm{eq}})$ 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:

$$\begin{aligned}\Delta\omega_r &= -2(\hbar\omega_r)^2\sum_{AI}\frac{1}{\left(\varepsilon^0_A-\varepsilon^0_I\right)}\left(c^r_{AI}\right)^2\\ &= -2(\hbar\omega_r)^2\sum_{AI}|\,u^r_{AI}\,|^2\frac{\left(\varepsilon^0_A-\varepsilon^0_I\right)}{\left[\left(\varepsilon^0_A-\varepsilon^0_I\right)^2-(\hbar\omega_r)^2\right]^2}.\end{aligned} \tag{124}$$

The final effect is softening of normal mode vibration frequency:

$$\hbar\omega_{r(ad)} = \hbar\omega_r - 2(\hbar\omega_r)^2\sum_{AI}\frac{1}{\left(\varepsilon^0_A-\varepsilon^0_I\right)}\left(c^r_{AI}\right)^2. \tag{125}$$

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,

$$\Delta\omega_r = -2(\hbar\omega_r)^2\sum_{AI}|\,u^r_{AI}\,|^2\frac{\left(\varepsilon^0_A-\varepsilon^0_I\right)}{\left[\left(\varepsilon^0_A-\varepsilon^0_I\right)^2-(\hbar\omega_r)^2\right]^2}. \tag{126}$$

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 $\langle\varphi_I|\hat{H}_{ep}|\varphi_A\rangle\langle\varphi_A|\hat{H}_{ep}|\varphi_I\rangle/(\varepsilon^0_I-\varepsilon^0_A)$.

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:

$$\begin{aligned}\Delta E^0_{(na)} = 2\Bigg(\sum_{R(k),S(k')}\Bigg(\sum_{k<k_F,k'>k_F}\left|u^{k'-k}\right|^2 f_k(1-f_{k'})\\ \times\frac{\hbar\omega_{k'-k}}{\left(\varepsilon^0_{k'}-\varepsilon^0_k\right)^2-(\hbar\omega_{k'-k})^2}\Bigg)\Bigg),\\ \varphi_{Rk}\neq\varphi_{Sk'}.\end{aligned} \tag{127}$$

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

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

$$\Delta E^0_{(na)} = 2\left(\sum_{R(k),S(k')}\left(\sum_{kk'}\left|u^{k'-k}\right|^2\frac{\hbar\omega_{k'-k}}{\left(\varepsilon^0_{k'}-\varepsilon^0_k\right)^2-(\hbar\omega_{k'-k})^2}\right)\right). \tag{128}$$

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 $H_{(1)}(R)$ of (47).

The one-particle correction has been derived in the form

$$\begin{aligned}\Delta H'_{ep} = \sum_{rPQ}\hbar\omega_r\Bigg(\sum_A\left(c^r_{PA}c^{r*}_{QA}-\hat{c}^r_{PA}\hat{c}^{r*}_{QA}\right)\\ -\sum_I\left(c^r_{PI}c^{r*}_{QI}-\hat{c}^r_{PI}\hat{c}^{r*}_{QI}\right)\Bigg)N[a^+_Pa_Q]\\ +\sum_{rPR}\left(\left(\varepsilon^0_P-\varepsilon^0_R\right)\left(|\,c^r_{PR}\,|^2+|\,\hat{c}^r_{PR}\,|^2\right)\right.\\ \left.-2\hbar\omega_r\,\mathrm{Re}(\hat{c}^r_{PR}c^{r*}_{PR})\right)N[a^+_Pa_P].\end{aligned} \tag{129}$$

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., $(\nu^0_{PRPA} - \nu^0_{PRAP})(c^r_{IR}c^{r*}_{IA} + \hat{c}^r_{IR}\hat{c}^{r*}_{IA})$) 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

$$\Delta H'_{ep}(dg) = \sum_{rP}\hbar\omega_r\left(\sum_A\left(|c^r_{PA}|^2 - |\hat{c}^r_{PA}|^2\right) - \sum_I\left(|c^r_{PI}|^2 - |\hat{c}^r_{PI}|^2\right)\right)N[a^+_P a_P] + \sum_{rPR}\left(\left(\varepsilon^0_P - \varepsilon^0_R\right)\left(|c^r_{PR}|^2 + |\hat{c}^r_{PR}|^2\right) - 2\hbar\omega_r\,\mathrm{Re}\left(\hat{c}^r_{PR}c^{r*}_{PR}\right)\right)N[a^+_P a_P]. \tag{130a}$$

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

$$\Delta H'_{ep}(dg) = \sum_{rPR(P\neq R)}|u^r_{PR}|^2\frac{1}{\left(\varepsilon^0_P - \varepsilon^0_R\right) - \hbar\omega_r}N[a^+_P a_P] - 2\sum_{rPI(P\neq I)}|u^r_{PI}|^2\frac{\hbar\omega_r}{\left(\varepsilon^0_P - \varepsilon^0_I\right)^2 - (\hbar\omega_r)^2}N[a^+_P a_P]. \tag{130b}$$

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

$$\Delta H'_{ep}(dg) = \sum_{Pk,Rk-q}\left(\sum_{qk\sigma}|u^q|^2\frac{1}{\left(\varepsilon^0_k - \varepsilon^0_{k-q}\right) - \hbar\omega_q}N\left[a^+_{k,\sigma}a_{k,\sigma}\right]\right) - 2\sum_{Pk,Sk-q}\left(\sum_{qk\sigma}|u^q|^2 f_{k-q}\frac{\hbar\omega_q}{\left(\varepsilon^0_k - \varepsilon^0_{k-q}\right)^2 - \left(\hbar\omega_q\right)^2}\times N\left[a^+_{k,\sigma}a_{k,\sigma}\right]\right). \tag{130c}$$

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 $(\varepsilon^0_P - \varepsilon^0_R)$, 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 $\Delta\varepsilon_P$ of general state ε^0_P, from the first term in (130a), it follows that

$$\Delta\varepsilon_P = \sum_r\hbar\omega_r\left(\sum_A\left(|c^r_{PA}|^2 - |\hat{c}^r_{PA}|^2\right) - \sum_I\left(|c^r_{PI}|^2 - |\hat{c}^r_{PI}|^2\right)\right) = \left(\sum_A^{unocc}\Omega_{PA} - \sum_I^{occ}\Omega_{PI}\right). \tag{131}$$

Finally, corrected orbital energy is

$$\varepsilon_P = \varepsilon^0_P + \Delta\varepsilon_P. \tag{132a}$$

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

$$\Delta\varepsilon_A = \left(\varepsilon_A - \varepsilon^0_A\right) = -\Omega_{AI} > 0, \quad \Delta\varepsilon_I = \Omega_{IA} = \Omega_{IA} < 0, \quad \Delta\varepsilon_I = -\Delta\varepsilon_A. \tag{132b}$$

It means that orbital energy of unoccupied state has been increased, $\varepsilon_A > \varepsilon^0_A$, and orbital energy of the occupied state has been decreased, $\varepsilon_I < \varepsilon^0_I$. It can be generalized for a set of quasidegenerate occupied $\{J\}$ and unoccupied $\{B\}$ 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:

$$\Delta\varepsilon_B = \sum_{A}^{unocc}\Omega_{BA} - \sum_{I}^{occ}\Omega_{BI} \geq 0,$$
$$\Delta\varepsilon_J = \sum_{A}^{unocc}\Omega_{JA} - \sum_{I}^{occ}\Omega_{JI} \leq 0. \tag{133}$$

In particular,

$$\Delta\varepsilon_B = \sum_{r}\sum_{A}^{unocc}|u^r_{BA}|^2\frac{\hbar\omega_r}{\left(\varepsilon^0_B-\varepsilon^0_A\right)^2-(\hbar\omega_r)^2} - \sum_{r}\sum_{I}^{occ}|u^r_{BI}|^2\frac{\hbar\omega_r}{\left(\varepsilon^0_B-\varepsilon^0_I\right)^2-(\hbar\omega_r)^2}, \tag{134a}$$

$$\Delta\varepsilon_J = \sum_{r}\sum_{A}^{unocc}\left|u^r_{JA}\right|^2\frac{\hbar\omega_r}{\left(\varepsilon^0_J-\varepsilon^0_A\right)^2-(\hbar\omega_r)^2} - \sum_{r}\sum_{I}^{occ}\left|u^r_{JI}\right|^2\frac{\hbar\omega_r}{\left(\varepsilon^0_J-\varepsilon^0_I\right)^2-(\hbar\omega_r)^2}. \tag{134b}$$

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

$$\Delta\varepsilon_P(T) = \sum_{Q}\Omega_{PQ}(1-2f_Q), \tag{135}$$

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

The occupation factor f_Q obeys the Fermi-Dirac statistics:

$$f_Q = \left(\exp\left(\frac{\varepsilon_Q-\mu}{k_BT}\right)+1\right)^{-1}, \quad \varepsilon_Q = \varepsilon^0_Q + \Delta\varepsilon_Q. \tag{136}$$

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

$$\Delta(T) = \Delta(0)tgh\left(\frac{\Delta(T)}{4k_BT}\right). \tag{137}$$

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

$$\Delta(0) = \left(\varepsilon_{B(LUMO)} + \left|\varepsilon_{J(HOMO)}\right|\right). \tag{138}$$

Factor 4 in the denominator of the argument of *tgh* in (137) follows from the assumption that at Fermi level density of quasidegenerate occupied $\{\varepsilon^0_J\}$ and unoccupied $\{\varepsilon^0_B\}$ states of the band with gap opening is the same and consequently $\varepsilon_{B(LUMO)} = |\varepsilon_{J(HOMO)}|$. 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 $(\varepsilon^0_A - \varepsilon^0_I) \gg \omega$.

(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]

$$\Delta H''_{ep} = \sum_{rPQRS}\hbar\omega_r\left(c^r_{PR}c^{r*}_{SQ} - \hat{c}^r_{PR}\hat{c}^{r*}_{SQ}\right)N\left[a^+_Pa^+_Qa_Sa_R\right]. \tag{139}$$

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

$$\Delta H''_{ep} = \sum_{rPQRS(P\neq R,Q\neq S)}u^r_{PR}u^{r*}_{SQ} \times\frac{\hbar\omega_r\left(\left(\varepsilon^0_P-\varepsilon^0_R\right)\left(\varepsilon^0_S-\varepsilon^0_Q\right)-(\hbar\omega_r)^2\right)}{\left(\left(\varepsilon^0_P-\varepsilon^0_R\right)^2-(\hbar\omega_r)^2\right)\left(\left(\varepsilon^0_S-\varepsilon^0_Q\right)^2-(\hbar\omega_r)^2\right)} \times N\left[a^+_Pa^+_Qa_Sa_R\right]. \tag{140}$$

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

$$\Delta H''_{ep} = \sum_{R(k)S(k')}\sum_{kk'q\sigma\sigma'(q\neq 0)}|u^q|^2 \times\frac{\hbar\omega_q\left(\left(\varepsilon^0_{k+q}-\varepsilon^0_k\right)\left(\varepsilon^0_{k'+q}-\varepsilon^0_{k'}\right)-\left(\hbar\omega_q\right)^2\right)}{\left(\left(\varepsilon^0_{k+q}-\varepsilon^0_k\right)^2-\left(\hbar\omega_q\right)^2\right)\left(\left(\varepsilon^0_{k'+q}-\varepsilon^0_{k'}\right)^2-\left(\hbar\omega_q\right)^2\right)} \times N\left[a^+_{k+q,\sigma}a^+_{k',\sigma'}a_{k'+q,\sigma'}a_{k,\sigma}\right]. \tag{141}$$

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, *P6mmm*, #191; $AlB_2\omega$-type) coupling to the E_{2g} phonon mode (in-plane stretching vibration of B-B) results in splitting of σ bands (p_x, p_y electrons of B atoms in a-b plane) in Γ point of the first Brillouin zone (BZ)—Figure 1(b). Related to band topology, the analytic critical point (ACP, maximum) of σ bands is located at Γ point and, for the displacement $\approx 0.016\,A^\circ$/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, *Pm3m*, #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 $\approx 0.017\,A^\circ$/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 $YBa_2Cu_3O_7$ (oP14, *Pmmm*, #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 $\approx 0.031\,A^\circ$ of apical O(4) in the A_g mode and $\approx 0.022\,A^\circ$ of O(2) and O(3) in the B_{2g}, B_{3g} modes, the ACP (saddle point) of one of the Cu-O plane (d-pσ) 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 $\pm\Delta f_b$, that is, by change of the fractional coordinates; (1/3,2/3-Δf_b,1/4), (2/3,1/3+Δf_b,3/4) in hexagonal lattice (hP2, $P6_3$/mmc, #194; Mg type). At relatively small displacements, $\pm$ (0.0105–0.0157) A°/Zn atom, top of the σ band in Γ 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 μ) of the particular band-electrons close to the point where ACP crosses FL is smaller than the vibration energy of corresponding phonon mode, $E_F < \omega_{2g}$. 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, $n_\sigma(E_F) = (\partial\varepsilon^0_\sigma/\partial k)^{-1}_{E_F}$, and induces the corresponding decrease in the effective electron velocity $(\partial\varepsilon^0_\sigma/\partial k)_{E_F}$ 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, $E_F \ll \omega_{2g}$, 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, $YBa_2Cu_3O_6$, and Mg. Even in the case of the XB_2, coupling to the E_{2g} mode induces splitting of σ bands in the Γ point, the systems remain stable in the adiabatic state. For these systems, the ACP of σ 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 σ bands splitting and nearly the same value of the e-p interaction strength (the calculated mean value is $\overline{u} \approx 1.01$ eV/u.cell) as that of MgB_2 ($\overline{u} \approx 0.98$ 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 ($\mu_{ad} > \hbar\omega$) 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, $YBa_2Cu_3O_6$, in contrast to the superconducting $YBa_2Cu_3O_7$, 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 $YBa_2Cu_3O_7$, the ACP (saddle point) at Y point fluctuates across FL (see Figures 1(e) and 1(f)), which yields substantial reduction of chemical potential $\rightarrow \mu_{antiad} < \hbar\omega$. For $YBa_2Cu_3O_6$ the ACP does not fluctuate across FL and chemical potential remains larger than the phonon energy spectrum, $\mu_{ad} > \hbar\omega$, 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 $E^{te}_0(R_{eq})$ has minimum at R_{eq}, $(dE^{te}_0/dR)_{R_{eq}} = 0$, and within the HF-SCF approximation it is equal to (27).

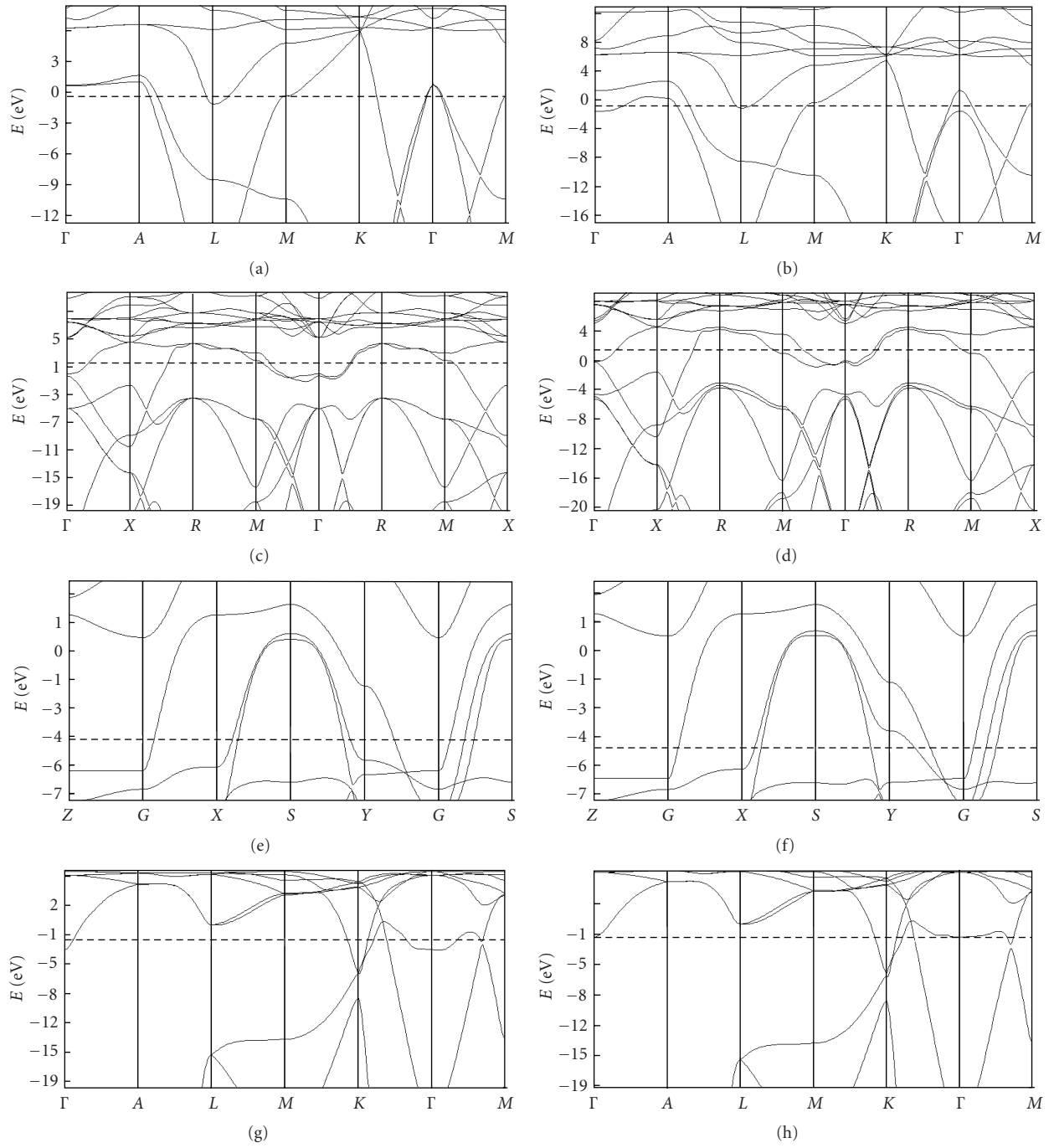

FIGURE 1: Band structures of MgB_2 (a, b), YB_6 (c, d), $YBa_2Cu_3O_7$ (e, f) and Zn (g, h). Pictures on the left (a, c, e, g) correspond to equilibrium high-symmetry structures. On the right are the band structures (b, d, f, h) of distorted geometry with atom displacements in the respective phonon modes.

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}:

$$E^{te}_{0\text{corr}}\left(R_{\text{eq}}\right) = E^{te}_{0}\left(R_{\text{eq}}\right) - |E_{\text{corr}}|_{R_{\text{eq}}},$$
$$\left(dE^{te}_{0\text{corr}}/dR\right)_{R_{\text{eq}}} = 0. \tag{142}$$

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:

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

Since two-electron coulomb interactions $\{v^0_{PQRS}\}$ do not depend explicitly on nuclear variables it can be expected

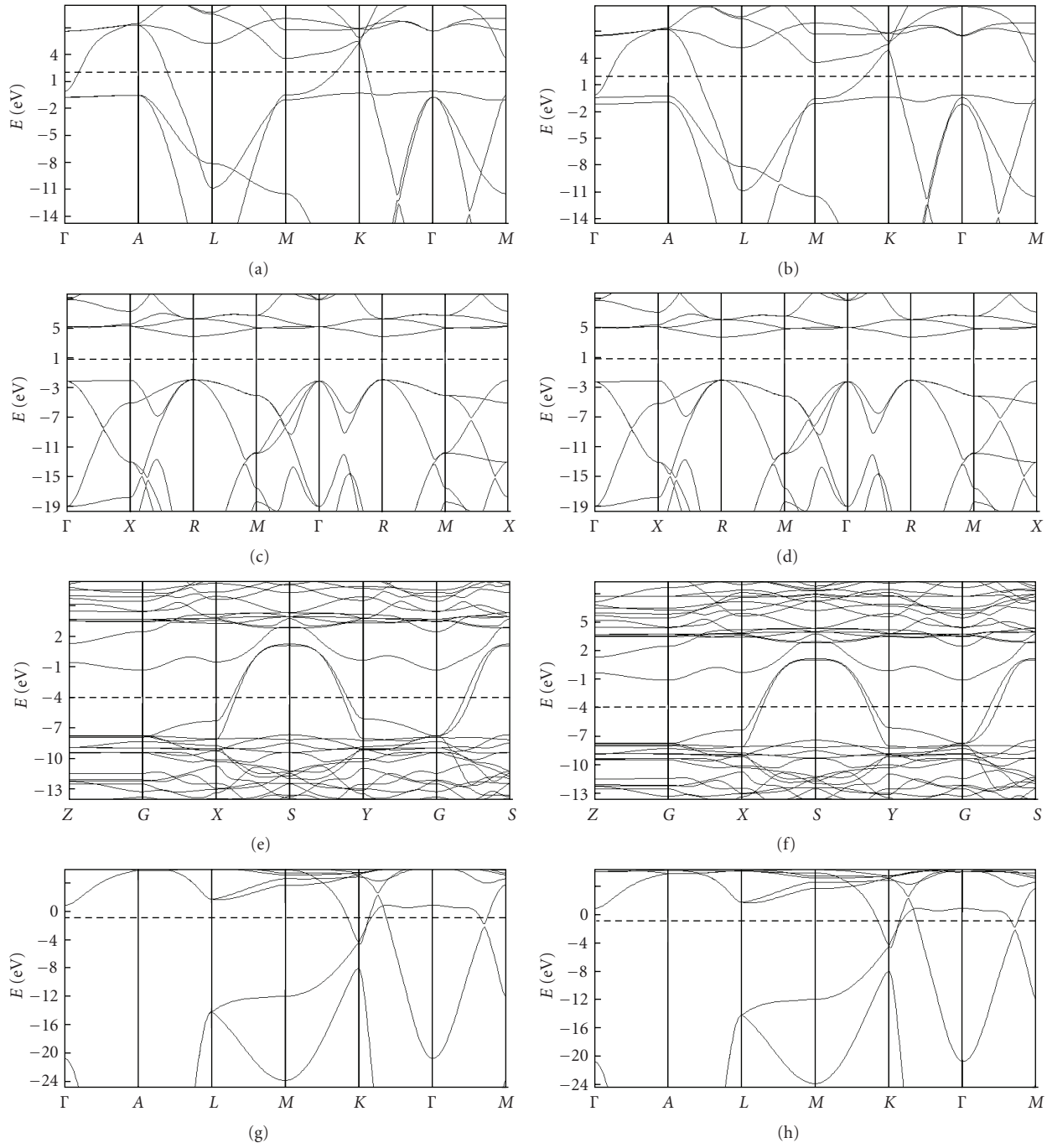

Figure 2: Band structure of AlB_2, CaB_6, $YBa_2Cu_3O_6$, and Mg at equilibrium geometry (a, c, e, g) and at distorted geometry (b, d, f, h).

that electron correlation energy at vibration displacement R_d has not been changed significantly, that is, $(E_{\text{corr}})_{R_{\text{eq}}} \approx (E_{\text{corr}})_{R_d}$. On crude-adiabatic level, for an increase of the total electronic energy ΔE_d due to nuclear displacement R_d then holds:

$$\Delta E_d(R_d) = E_0^{te}(R_d) - E_0^{te}\left(R_{\text{eq}}\right) > 0. \tag{144}$$

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).

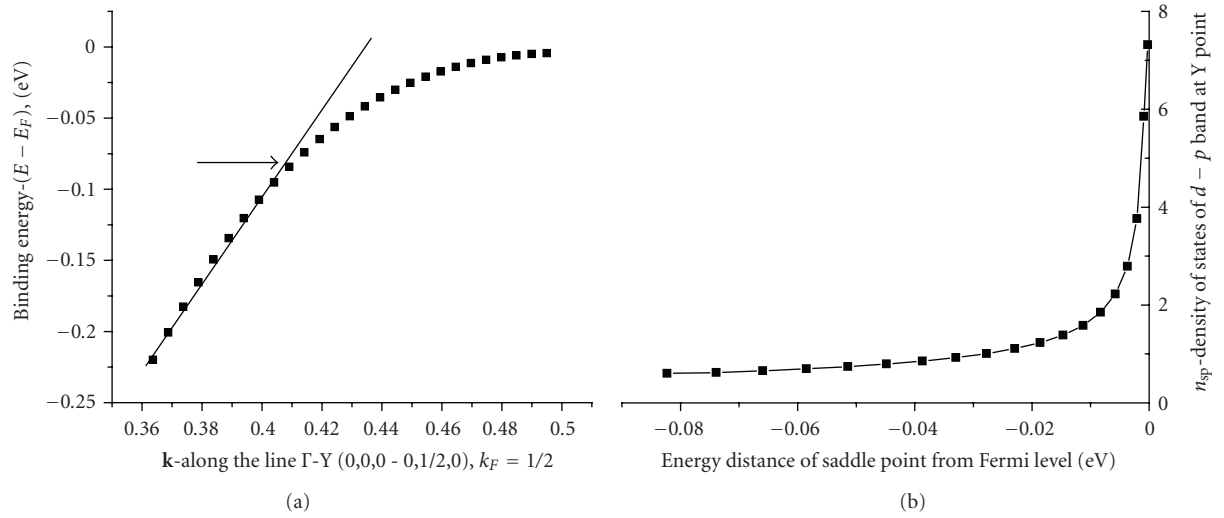

FIGURE 3: Calculated dispersion of CuO_2 layer ($d_{x^2-y^2} - p\sigma$) band in the ΓY direction with the kink formation indicated by the arrow (a) and increase in the ($d_{x^2-y^2} - p\sigma$) band DOS when ACP approaches the FL (b) for $YBa_2Cu_3O_7$ at e-p coupling (see text). In both figures, the energy of Fermi level is rescaled to 0 eV.

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

$$\left|\Delta E^0_{(na)}(R_d)\right| > \Delta E_d(R_d) \tag{145}$$

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 $\widehat{c}^r_{AI}$ 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

$$E^0_{cond} = \Delta E_d(R_d) - \left|\Delta E^0_{(na)}(R_d)\right|. \tag{146}$$

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

$$\Delta E^0_{(na)} = 2\sum_{\varphi_{Rk}}\sum_{\varphi_{Sk'}}\int_0^{\varepsilon_{k',\max}} n_{\varepsilon_{k'}}\left(1 - f_{\varepsilon^0 k'}\right)d\varepsilon^0_{k'} \times \int_{\varepsilon_{k,\min}}^{\varepsilon_{k,\max}} f_{\varepsilon^0 k}\left|u^r_{k-k'}\right|^2 n_{\varepsilon_k}\frac{\hbar\omega_r}{\left(\varepsilon^0_k - \varepsilon^0_{k'}\right)^2 - (\hbar\omega_r)^2}d\varepsilon^0_k, \quad \varphi_{Rk} \neq \varphi_{Sk'}. \tag{147}$$

In general, all bands of 1st BZ of a multiband system are covered, including intraband terms, that is, $\varphi_{Rk}, \varphi_{Rk'}$, $k \neq k'$, while $\varepsilon^0_k < \varepsilon_F$; $\varepsilon^0_{k'} > \varepsilon_F$. Fermi-Dirac populations $f_{\varepsilon^0 k}$, $f_{\varepsilon^0 k'}$ make correction (147) temperature-dependent. Term $u^r_{k-k'}$ stands for matrix element of e-p coupling and $n_{\varepsilon k}, n_{\varepsilon k'}$ are DOS of interacting bands at $\varepsilon^0_{k'}$ and ε^0_k. 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 $u^r_{k-k'}$ and $n_{\varepsilon k}, n_{\varepsilon k'}$ 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, $n_\sigma(E_F) = \left(\partial\varepsilon^0_\sigma/\partial k\right)^{-1}_{E_F}$, 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, $\Delta E^0_{(na)}$ 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), $E^0_{cond} \approx -34$ meV/unit cell, has been calculated [76] for $YBa_2Cu_3O_7$. In the case of MgB_2, $E^0_{cond} \approx -13$ meV/unit cell has been obtained. For YB_6, and Zn the values of E^0_{cond} 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 ACP when it approaches FL (see Figure 3(a), which presents calculated results for $YBa_2Cu_3O_7$). The crucial influence on the final value of the correction $\Delta E^0_{(na)}(R_d)$ is related to an increase of the DOS ($n_{\varepsilon k}, n_{\varepsilon k'}$ in (147)) connected to the ACP when it approaches ($\pm\omega$) FL at transition into antiadiabatic state. Situation for $YBa_2Cu_3O_7$ is presented in Figure 3(b). In the ARPES spectra of $YBa_2Cu_3O_7$ 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 antiadiabatic state should be stressed. Due to translation symmetry of the lattice, the created antiadiabatic electronic ground state is geometrically degenerate in distorted geometry ($R_{d,cr}$) 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_{cr} at FL crossing, without the energy dissipation.

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

$$\begin{aligned}\Delta\varepsilon(Pk') = &\sum_{Rk'_{1>k_F}} \left| u^{k'-k'_1} \right|^2 \left(1 - f_{\varepsilon^0 k'_1}\right) \\ &\times \frac{\hbar\omega_{k'-k'_1}}{\left(\varepsilon^0_{k'} - \varepsilon^0_{k'_1}\right)^2 - \left(\hbar\omega_{k'-k'_1}\right)^2} \\ &- \sum_{Sk<k_F} \left| u^{k-k'} \right|^2 f_{\varepsilon^0 k} \\ &\times \frac{\hbar\omega_{k-k'}}{\left(\varepsilon^0_{k'} - \varepsilon^0_{k}\right)^2 - \left(\hbar\omega_{k-k'}\right)^2}\end{aligned} \tag{148a}$$

for $k' > k_F$, and

$$\begin{aligned}\Delta\varepsilon(Pk) = &\sum_{Rk'_{1>k_F}} \left| u^{k-k'_1} \right|^2 \\ &\times \left(1 - f_{\varepsilon^0 k'_1}\right) \frac{\hbar\omega_{k-k'_1}}{\left(\varepsilon^0_{k} - \varepsilon^0_{k'_1}\right)^2 - \left(\hbar\omega_{k-k'_1}\right)^2} \\ &- \sum_{Sk_1<k_F} \left| u^{k-k_1} \right|^2 f_{\varepsilon^0 k} \\ &\times \frac{\hbar\omega_{k-k_1}}{\left(\varepsilon^0_{k} - \varepsilon^0_{k_1 1}\right)^2 - \left(\hbar\omega_{k-k_1}\right)^2}\end{aligned} \tag{148b}$$

for $k \le k_F$.

Replacement of discrete summation by integration, $\sum_k \cdots \rightarrow \int n(\varepsilon_k)$, 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 $\Delta\varepsilon_k$ of orbital energies, the following relation can be derived:

$$n(\varepsilon_k) = \left| 1 + \left(\partial(\Delta\varepsilon_k)/\partial\varepsilon^0_k\right) \right|^{-1} n^0\left(\varepsilon^0_k\right). \tag{149}$$

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

$$n^0\left(\varepsilon^0_k\right) = \left| \left(\partial\varepsilon^0_k/\partial k\right) \right|^{-1}. \tag{150}$$

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, $YBa_2Cu_3O_7$ exhibits an asymmetric gap in two directions: for Cu-O1 chain-derived (d-$p\sigma$) band the gap in one-particle spectrum is $\Delta_b(0) \approx 35.7$ meV in the Γ-Y direction (4a) and $\Delta_a(0) \approx 24.2$ meV in the Γ-X direction (4b), respectively. The calculated asymmetry, that is, the ratio $(\Delta_a(0)/\Delta_b(0))_{\text{theor}} \approx 0.68$, or $(\Delta_b(0)/\Delta_a(0))_{\text{theor}} \approx 1.47$ is very close to the experimental values, ($\Delta_a/\Delta_b \approx 0.66$ and $\Delta_b/\Delta_a \approx 1.5$) which have been recorded [79, 80] for untwined $YBa_2Cu_3O_7$. 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(b) and Γ-X (a) 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 $\Delta_{\Gamma-S} \le \Delta_{a(\Gamma-X)}$, that is, top of the dispersion should appear ≤ 15 meV below FS. One can expect opening of very small gap for this band also in Γ-T(U) direction [76]. However, due to relatively large distance of CuO_2 layers (≈ 8.3 A°), 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): $\Delta_\sigma(0)/2 \approx 7.6$ meV and $\Delta_\pi(0)/2 \approx 2.2$ 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 YB_6 (4d): $\Delta_{pd}(0)/2 \approx 2.2$ 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 K disappears, $\Delta(T_c) = 0$ (continuum of states is established at

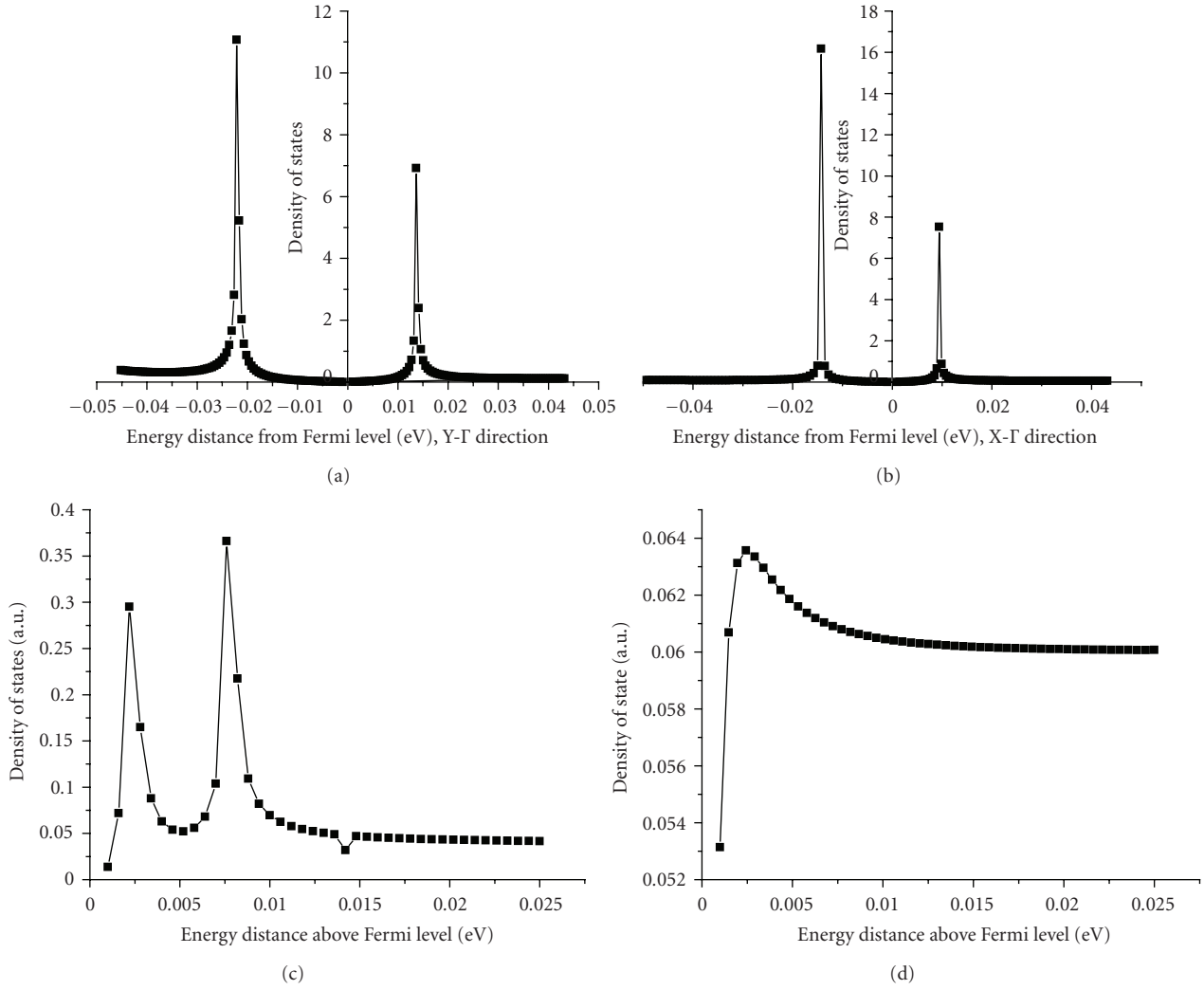

FIGURE 4: Corrected DOS and gap formation near **k** point where particular bands intersect FL, 0 K. Gap of $YBa_2Cu_3O_7$ in Γ-Y(4a) and Γ-X(4b) direction. Half-gap in MgB_2 (Figure 4(c)) and half-gap in YB_6 (Figure 4(d)).

FL), while $|\Delta E^0_{(na)}(T_c)| \leq \Delta E_{d,cr}$ and the system undergoes transition from the antiadiabatic into adiabatic state, which is stable for equilibrium high-symmetry structure above T_c. With respect to $\Delta(0)$, from (137) a simple approximate relation follows for critical temperature T_c of the adiabatic ↔ antiadiabatic state transition:

$$T_c = \Delta(0)/4k_B. \tag{151}$$

The calculated values of T_c for presented compounds are $YBa_2Cu_3O_7, T_c \approx 92.8$ K, MgB_2, $T_c \approx 39.5$ K, and $YB_6, T_c \approx 11$ K. It is in a good agreement with the experimental values of T_c for superconducting state transition of these compounds [4, 60, 83].

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 $\Delta R = |R_{\text{eq}} - R_{d,cr}|$. 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

$$\Delta H'_{\langle e-p0\rangle}(dg) = \sum_{rPR}\Big(\left(\varepsilon_P^0 - \varepsilon_R^0\right)\left(|\,c_{PR}^r\,|^2 + |\,\hat{c}_{PR}^r\,|^2\right) - 2\hbar\omega_r\,\mathrm{Re}\left(\hat{c}_{PR}^r c_{PR}^{r*}\right)\Big)N[a_P^+ a_P]. \tag{152}$$

After substitution for transformation coefficients $c_{PR}^r, \hat{c}_{PR}^r$ (115), (116) and algebraic manipulation, the quasimomentum form of this term is

$$\Delta H'_{\langle e-p0\rangle}(dg) = \sum_{k,q}|u^q|^2\left\{\frac{\left(\varepsilon_k^0 - \varepsilon_{k-q}^0\right)}{\left[\left(\varepsilon_k^0 - \varepsilon_{k-q}^0\right)^2 - \left(\hbar\omega_q\right)^2\right]}\right\} \times N\left[a_k^+ a_k\right]. \tag{153a}$$

For extreme nonadiabatic limit $\hbar\omega_q/|\varepsilon_k^0 - \varepsilon_{k-q}^0| \to \infty$, from (153a), it follows that

$$\Delta H'_{\langle e-p0\rangle}(dg)_{na} \longrightarrow 0. \tag{153b}$$

It means that for electrons that satisfy condition of extreme nonadiabaticity with respect to interacting phonon mode r in particular direction of reciprocal lattice where the gap in one-electron spectrum has been opened, the electron (nonadiabatic polaron)-renormalized phonon interaction energy equals zero. Expressed explicitly, in the presence of external electric potential, dissipation-less motion of relevant valence band electrons (holes) on the lattice scale can be induced 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), $|\Delta E_{(na)}^0(R_d)| \leq \Delta E_d(R_d)$ 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 $\hbar\omega_q/|\varepsilon_k^0 - \varepsilon_{k-q}^0| \to 0$, from (153a) for electron-phonon interaction energy in this case it follows that

$$\Delta H'_{\langle e-p0\rangle}(dg)_{ad} \longrightarrow \sum_{qk}|u^q|^2\frac{1}{\left(\varepsilon_k^0 - \varepsilon_{k-q}^0\right)}. \tag{153c}$$

Expression (153c) represents basically energy of standard adiabatic polarons (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,

$$C_{V,el}(T) = \frac{d\Delta E_{(na)}^0}{dT} = T\frac{dS}{dT} \tag{154}$$

can be derived:

$$C_{V,el}(T) = -\frac{\overline{n}(\varepsilon_{k_F})}{2}\frac{\Delta(T)}{\Delta(0)}\left(\frac{\Delta(T)}{dT}\right). \tag{155}$$

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:

$$S = -k_B\sum_k[f_k\ln f_k + (1-f_k)\ln(1-f_k)]. \tag{156}$$

In (156), f_k is the Fermi-Dirac occupation factor of state $\varepsilon_k = \varepsilon_k^0 + \Delta\varepsilon_k$. Then for entropy related to formation of antiadiabatic state can be derived:

$$S = k_B\ \ln\ 2 - \overline{n}(\varepsilon_{k_F})\frac{(\Delta(T))^2}{2T\Delta(0)} + 2k_B\overline{n}(\varepsilon_{k_F})\ln\left(\cosh\frac{\Delta(T)}{4k_BT}\right). \tag{157a}$$

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

$$\frac{dS}{dT} = -\frac{\overline{n}(\varepsilon_{k_F})}{2T}\frac{\Delta(T)}{\Delta(0)}\frac{d\Delta(T)}{dT}. \tag{157b}$$

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

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

$$\lim\left(C_{V,el}(T)\right)_{T\to 0} \approx \exp\left(-\frac{\Delta(0)}{2k_BT}\right). \tag{158}$$

The density of states at Fermi level $\overline{n}(\varepsilon_{k_F})$ 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 $(\pm\omega/2)$ Fermi level (antiadiabatic 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 $\rho \neq 0$ 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, $T \geq T_c$, critical magnetic field has to be zero, $H_c(T \geq T_c) = 0$.

It can be shown that antiadiabatic state exhibits this property.

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

$$\frac{H_c^2}{8\pi} = F_{(ad)} - F_{(na)}. \tag{159}$$

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

$$F_{(ad)} - F_{(na)} = \Delta E^0_{(na)} - TS. \tag{160a}$$

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

$$\begin{aligned}\Delta E^0_{(na)}(T) &= \Delta E^0_{(na)}(0) + \int_0^T C_{V(el)}(T)dT \\ &= \Delta E^0_{(na)}(0) - \frac{\overline{n}(\varepsilon_{k_F})}{4\Delta(0)}\left((\Delta(T))^2 - (\Delta(0))^2\right) \\ &= -\frac{\overline{n}(\varepsilon_{k_F})}{4}\Delta(0) - \frac{\overline{n}(\varepsilon_{k_F})}{4\Delta(0)}\left((\Delta(T))^2 - (\Delta(0))^2\right).\end{aligned} \tag{160b}$$

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

$$\begin{aligned}\frac{(H_c(T))^2}{8\pi} &= -\frac{\overline{n}(\varepsilon_{k_F})}{4}\Delta(0) - \frac{\overline{n}(\varepsilon_{k_F})}{4\Delta(0)}\left((\Delta(T))^2 - (\Delta(0))^2\right) \\ &\quad + \frac{\overline{n}(\varepsilon_{k_F})}{2}\frac{(\Delta(T))^2}{\Delta(0)} \\ &\quad - 2k_B\overline{n}(\varepsilon_{k_F})T\ln\left(\frac{\Delta(0)}{\left((\Delta(0))^2 - (\Delta(T))^2\right)^{1/2}}\right).\end{aligned} \tag{160c}$$

At temperature 0 K, for critical magnetic field results,

$$(H_c(0))^2 = 2\pi\Delta(0)\overline{n}(\varepsilon_{k_F}). \tag{160d}$$

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

$$\begin{aligned}&\left(\frac{H_c(T)}{H_c(0)}\right)^2 \\ &= \left[\left(\frac{\Delta(T)}{\Delta(0)}\right)^2 - \frac{8k_BT}{\Delta(0)}\ln\left(\frac{\Delta(0)}{\left((\Delta(0))^2 - (\Delta(T))^2\right)^{1/2}}\right)\right].\end{aligned} \tag{161}$$

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, $H_c(T \geq T_c) = 0$. Since there is no gap in one-electron spectrum in metal-like adiabatic state, $\Delta(T \geq T_c) = 0$, then zero value of critical magnetic field follows directly from (160c), (161). Derived equations show that system in the antiadiabatic state, beside zero value of electric resistance $\rho = 0$ (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 $\Delta H''_{ep}$ 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 $H_{(0)}(R_0) = E^0_{SCF}(R_0)$-, (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 unbalanced 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), $E_{\text{corr}}(R_0)$.

Let us see if the correction to correlation energy due to e-p coupling $\Delta H''_{ep}$ represents stabilization or destabilization contribution [66, 67]. For antiadiabatic system $|\varepsilon^0_{k'} - \varepsilon^0_k| < \hbar\omega_{k'-k}$, 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 $(\varepsilon^0_{k+q} - \varepsilon^0_k) = -(\varepsilon^0_{k'+q} - \varepsilon^0_{k'})$. Since $q \neq 0$, it can be reached if $q = -k - k'$. At these circumstances for reduced form which maximizes e-e attraction, it can be derived that

$$\begin{aligned}\Delta H''_{ep}(\text{red})_{na} &= -2\sum_{k>k_F, k'<k_F}\left|u^{k'-k}\right|^2 \\ &\quad \times \frac{\hbar\omega_{k'-k}\left(\left(\varepsilon^0_{k'} - \varepsilon^0_k\right)^2 + (\hbar\omega_{k'-k})^2\right)}{\left(\left(\varepsilon^0_{k'} - \varepsilon^0_k\right)^2 - (\hbar\omega_{k'-k})^2\right)^2} \\ &\quad \times N\left[a^+_{k'\uparrow}a^+_{-k'\downarrow}a_{-k\downarrow}a_{k\uparrow}\right].\end{aligned} \tag{162}$$

In this expression, summation over bands is not explicitly indicated, but it should be understand implicitly. This correction is due to pairs of electrons with opposite quasi-momentum and antiparallel spins ($k\uparrow, -k\downarrow$). It should be noticed that it is the contribution of biexcited configurations $\{\Phi_{(k',-k')\to(k,-k)}\}$ (i.e., two-particle ($k\uparrow, -k\downarrow$), two-hole ($k'\uparrow, -k'\downarrow$) excited singlet states) to the electronic ground state, that is, represented by renormalized Fermi vacuum Φ_0. Expressed explicitly, first nonzero contributions are from the matrix elements of the type $\langle\Phi_0|\Delta H''_{ep}|\Phi_{(k',-k')\to(k,-k)}\rangle^2$, that is, contributions in the second order of perturbation theory. Now, $\{\varepsilon_k\}$ represent particle states that are occupied above Fermi level and $\{\varepsilon_{k'}\}$ 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 $|\varepsilon^0_{k'} - \varepsilon^0_k| < \hbar\omega_{k'-k}$, that is, for system which is in antiadiabatic state.

In case of strong antiadiabatic regime $|\varepsilon^0_{k'} - \varepsilon^0_k|/\hbar\omega_{k'-k} \to 0$, for correction to electron correlation energy, it follows that

$$\Delta H''_{ep}(\mathrm{red})_{\mathrm{sna}} = -2\sum_{kk'} \frac{\left|u^{k'-k}\right|^2}{\hbar\omega_{k'-k}} N\left[a^+_{k'\uparrow}a^+_{-k'\downarrow}a_{-k\downarrow}a_{k\uparrow}\right]. \tag{163a}$$

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

$$\Delta H''_{ep}(\mathrm{red})_{\mathrm{sad}} = -2\sum_{kk'} \left|u^{k'-k}\right|^2 \frac{\hbar\omega_{k'-k}}{\left(\varepsilon_{k'} - \varepsilon_k\right)^2} \times N\left[a^+_{k'\uparrow}a^+_{-k'\downarrow}a_{-k\downarrow}a_{k\uparrow}\right] \longrightarrow 0. \tag{163b}$$

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

$$\Delta H''_{ep(ad)} = \sum_{kk'q\sigma\sigma'} |u^q|^2 \frac{\hbar\omega_q}{\left(\varepsilon^0_{k+q} - \varepsilon^0_k\right)\left(\varepsilon^0_{k'+q} - \varepsilon^0_{k'}\right)} \times N\left[a^+_{k+q,\sigma}a^+_{k',\sigma'}a_{k'+q,\sigma'}a_{k,\sigma}\right]. \tag{164}$$

The reduced form is

$$\Delta H''_{ep}(\mathrm{red})_{\mathrm{ad}} = -2\sum_{kk'} \left|u^{k'-k}\right|^2 \frac{\hbar\omega_{k'-k}}{\left(\varepsilon^0_{k'} - \varepsilon^0_k\right)^2} \times N\left[a^+_{k'\uparrow}a^+_{-k'\downarrow}a_{-k\downarrow}a_{k\uparrow}\right]. \tag{165}$$

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 $R_{d,cr}$. 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: $\sum_{kk'}\cdots \to \sum_{kk'} \mathrm{f_k}(1 - \mathrm{f_{k'}}),\ldots$. With increasing temperature from 0 K, the value of the correction (162) which is characteristic for antiadiabatic state decreases and at $T = T_c$ when system undergoes sudden transition from antiadiabatic state at distorted geometry $R_{d,cr}$ into adiabatic state at undistorted geometry $R_0 = R_{\mathrm{eq}}$ and above this temperature, for correction to electron correlation energy holds corresponding temperature-dependent adiabatic form (165). Above T_c, this correction along with crude-adiabatic correlation energy (54) stabilizes adiabatic ground state of system at undistorted-adiabatic equilibrium geometry $R_0 = R_{\mathrm{eq}}$.

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

$$H''_{\mathrm{eff}}(\mathrm{Fr}) = \sum_{kk'q\sigma\sigma'} |u^q|^2 \frac{\hbar\omega_q}{\left(\varepsilon^0_{k+q} - \varepsilon^0_k\right)^2 - \left(\hbar\omega_q\right)^2} \times a^+_{k+q,\sigma}a^+_{k',\sigma'}a_{k'+q,\sigma'}a_{k,\sigma}. \tag{166}$$

The reduced for of this Hamiltonian is

$$H''_{\mathrm{red}}(\mathrm{Fr}) = 2\sum_{kk'} \left|u^{k'-k}\right|^2 \frac{\hbar\omega_{k'-k}}{\left(\varepsilon^0_{k'} - \varepsilon^0_k\right)^2 - (\hbar\omega_{k'-k})^2} \times a^+_{k'\uparrow}a^+_{-k'\downarrow}a_{-k\downarrow}a_{k\uparrow}. \tag{167}$$

This interaction term is either attractive or repulsive depending on the sign of denominator. For antiadiabatic conditions $|\varepsilon^0_{k'} - \varepsilon^0_k| < \hbar\omega_{k'-k}$, 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 $|\varepsilon^0_P - \varepsilon^0_Q|/\hbar\omega_r \to 0$, the form of the Fröhlich two-particle effective Hamiltonian

(166) and the correction to electron correlation energy (141) are identical and equal to

$$\lim\left(\Delta H''_{ep}\right)_{\Delta\varepsilon/\hbar\omega\to 0} = \lim\left(H''_{\text{eff}}(\text{Fr})\right)_{\Delta\varepsilon/\hbar\omega\to 0} = -\sum_{kk'q\sigma\sigma'}\frac{|u^q|^2}{\hbar\omega_q}a^+_{k+q,\sigma}a^+_{k',\sigma'}a_{k'+q,\sigma'}a_{k,\sigma}. \tag{168}$$

On the adiabatic level $|\varepsilon^0_{k'} - \varepsilon^0_k| \gg \hbar\omega_{k'-k}$, 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 $|\varepsilon^0_{k'} - \varepsilon^0_k| \gg \hbar\omega_{k'-k}$ of the Fröhlich form results in

$$H''_{\text{eff}}(\text{Fr})_{\text{ad}} = \sum_{kk'q\sigma\sigma'}|u^q|^2\frac{\hbar\omega_q}{\left(\varepsilon^0_{k+q} - \varepsilon^0_k\right)^2} \times a^+_{k+q,\sigma}a^+_{k',\sigma'}a_{k'+q,\sigma'}a_{k,\sigma}. \tag{169}$$

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 e-e 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 $|\varepsilon^0_{k'} - \varepsilon^0_k| \gg \hbar\omega_{k'-k}$. 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) $\varphi_{R(k)}$ relation (99) holds, that is,

$$\begin{aligned}
&|\varphi_P(x,Q,P)\rangle \\
&\quad = a^+_P(x,Q,P)|0\rangle \\
&\quad = \left(\overline{a}^+_P - \sum_{rR}c^r_{PR}\overline{Q}_r\overline{a}^+_R - \sum_{\check{r}R}\hat{c}^r_{PR}P_{\check{r}}\overline{a}^+_R + O\left(\overline{Q}^2, \overline{Q}P, P^2\right)\right)|0\rangle \\
&\quad = |\varphi_P(x,0,0)\rangle - \sum_{rR}c^r_{PR}\overline{Q}_r|\varphi_R(x,0,0)\rangle \\
&\qquad - \sum_{\check{r}R}\hat{c}^r_{PR}\overline{P}_{\check{r}}|\varphi_R(x,0,0)\rangle + \cdots.
\end{aligned} \tag{170}$$

At transition into antiadiabatic state $|\varepsilon^0_S(k_c) - \varepsilon^0_F|_{R_{\text{eq}}\pm Q} \ll \hbar\omega_r$, coefficients c^r_{RS} of Q-dependent transformation matrix become negligibly small and absolutely dominant for modulation of crude-adiabatic wave function are in this case coefficients $\hat{c}^r_{RS}$ 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 YB_6, 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 $\varphi^0_k(x,0,0)$ is changed in the following way:

$$\varphi_k(x,Q,P) \propto \left(1 + \sum_q u^{|q|}\frac{\hbar\omega_q}{\left(\hbar\omega_q\right)^2 - \left(\varepsilon^0_k - \varepsilon^0_{k+q}\right)^2} \times\left(P_1 e^{iq\cdot[x-(m_1-d_1)]} + P_2 e^{iq\cdot[x-(m_2+d_2)]}\right)\right) \times \varphi^0_k(x,0,0). \tag{171}$$

In (171), site approximation for momentum has been used, that is, $P_q \propto (\text{sign}\cdot q)\sum_m P_m e^{iq\cdot m}$.

In antiadiabatic state, for particular k and proper q values, nonadiabatic prefactors under summation symbol in (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-symetry 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

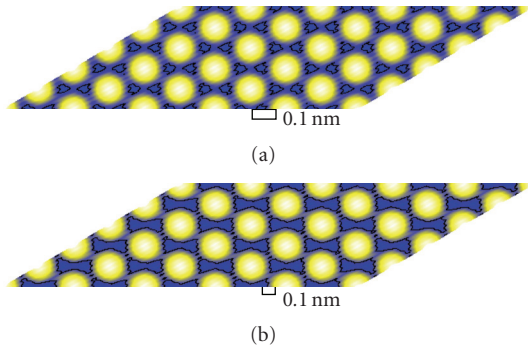

Figure 5: Iso-density line of highest electron density at equilibrium nuclear geometry R_{eq} of MgB_2 (a) and at the distorted geometry of B atoms in E_{2g} phonon mode $R_{d,cr}$ when nonadiabatic e-p interactions trigger transition into antiadiabatic state and intersites polarization is induced (b).

theory can account for, mainly if theory is formulated on microscopic level and some unnecessary approximations and assumptions are usually incorporated. On the other hand, interpretation of many experimental results is based on particular theoretical model. This is also the case of ARPES experiments at reconstruction of Fermi surface for electronic structure determination of high-T_c cuprates. Interpretation of experimental results is based on band structure calculated for particular compound. Methods of band structure calculations are always approximate, with different level of sophistication. Calculated band structure, mainly its topology at FL, is a kind of reference frame for assignment of particular dispersion of energy distribution curve (EDC) or momentum distribution curve (MDC) to particular band of studied compound at interpretation of ARPES. This is in direct relation with theoretical understanding of crucial aspects of SC-state transition and with mechanism of superconductivity in general.

In case of high-T_c cuprates, the crucial is considered to be the order parameter, that is, 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 ≈ 60 meV) in off-nodal direction has been observed. The gap is opened in off-nodal (Γ-X and Γ-Y) directions with top of the dispersion at ≈ 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 Γ-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 Γ-X nor in Γ-Y direction, but the bands intersect FL in nodal Γ-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 (Γ-X and Γ-Y) directions and also in nodal Γ-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, Γ-Y and Γ-S directions, the BS [85] yields for Cu-O chain band intersections with FL in Γ-X, Γ-Y and Γ-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 annihilation radiation (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 Γ-X, Γ-Y directions, prediction has also been for FL intersection in Γ-T, Γ-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 (Γ-X, Γ-Y) and nodal (Γ-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 Cu-O_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 ligh-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-Γ 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 ($\mu_{ad} \gg \mu_{antiad} < \hbar\omega$), 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 $R_{d,cr}$ 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 Γ-X and Γ-Y ($k_{\Gamma Y} \approx 0.053\,A^{-1}$, $k_{\Gamma X} \approx 0.016\,A^{-1}$) and also in nodal Γ-S direction. The half-gaps in the off-nodal directions are $\Delta_{\Gamma Y}/2, \approx 22$ meV, $\Delta_{\Gamma X}/2, \approx 15$ meV and gap in the nodal direction is expected to be $\Delta_{\Gamma S}/2 \leq 15$ 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 ($\Delta_{\Gamma T/U} \approx 5$ meV) has been predicted [76] to be opened also in Γ-T/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 hight-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 μ_{ad} is substantially reduced to $\mu_{antiad}(\mu_{ad} \gg \mu_{antiad} < \hbar\omega)$. 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 moveover 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

[1] K. Onnes, *Communications from the Physical Laboratory of the University of Leiden*, vol. 124c, 1911.

[2] R. Simon and A. Smith, *Superconductors*, Plenum Press, New York, NY, USA, 1988.

[3] J. G. Bednorz and K. A. Muller, "Possible high T_c superconductivity in the Ba-La-Cu-O system," *Zeitschrift für Physik B*, vol. 64, no. 2, pp. 189–193, 1986.

[4] P. H. Hor, R. L. Meng, Y. Q. Wang, et al., "Superconductivity above 90 K in the square-planar compound system ABa2Cu3O6+x with A = Y,La,Nd,Sm,Eu,Gd,Ho,Er and Lu," *Physical Review Letters*, vol. 58, no. 18, pp. 1891–1894, 1987.

[5] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, "Theory of superconductivity," *Physical Review*, vol. 108, no. 5, pp. 1175–1204, 1957.

[6] H. Fröhlich, "Theory of the superconducting state. I. The ground state at the absolute zero of temperature," *Physical Review*, vol. 79, no. 5, pp. 845–856, 1950.

[7] H. Fröhlich, "Interaction of electrons with lattice vibrations," *Proceedings of the Royal Society A*, vol. 215, no. 1122, pp. 291–298, 1952.

[8] A. B. Migdal, "Interaction between electrons and lattice vibrations in a normal metal," *Zh. Eksp. Teor. Fiz*, vol. 34, pp. 1438–1446, 1958, English translation in *Journal of Experimental and Theoretical Physics*, vol. 7, p. 996, 1958.

[9] G. M. Eliashberg, *Zh. Eksp. Teor. Fiz*, vol. 38, p. 996, 1960, English translation in *Journal of Experimental and Theoretical Physics*, vol. 11, p. 696, 1960.

[10] G. M. Eliashberg, *Zh. Eksp. Teor. Fiz*, vol. 39, p. 1437, 1960, English translation in *Journal of Experimental and Theoretical Physics*, vol. 12, p. 1000, 1960.

[11] E. Dagotto, "Correlated electrons in high-temperature superconductors," *Reviews of Modern Physics*, vol. 66, no. 3, pp. 763–840, 1994.

[12] P. W. Anderson, *The Theory of Superconductivity in High-T_c Cuprates*, Princeton University Press, Princeton, NJ, USA, 1997.

[13] M. L. Kulic, "Interplay of electron phonon interaction and strong correlations: the possible way to high-temperature superconductivity," *Physics Reports*, vol. 338, no. 1-2, pp. 1–264, 2000.

[14] W. J. McMillan, "Transition temperature of strong-coupled superconductors," *Physical Review B*, vol. 167, no. 2, pp. 331–344, 1968.

[15] Th. Maier, M. Jarrell, T. Pruschke, and J. Keller, "*d*-wave superconductivity in the Hubbard model," *Physical Review Letters*, vol. 85, no. 7, pp. 1524–1527, 2000.

[16] S. Sorella, G. B. Martins, F. Becca, et al., "Superconductivity in the two-dimensional t-*J* model," *Physical Review Letters*, vol. 88, no. 11, Article ID 117002, 4 pages, 2001.

[17] S. R. White and D. Scalapino, "Density matrix renormalization group study of the striped phase in the 2D t-*J* model," *Physical Review Letters*, vol. 80, no. 6, pp. 1272–1275, 1998.

[18] S. R. White and D. Scalapino, "Competition between stripes and pairing in t-t′-J model,," *Physical Review B*, vol. 60, no. 2, pp. R753–R756, 1999.

[19] A. Paramekanti, M. Randeria, and N. Trivedi, "High- T_c superconductors: a variational theory of the superconducting state," *Physical Review B*, vol. 70, no. 5, Article ID 054504, 21 pages, 2004.

[20] A. Mourachkin, *High-Temperature Superconductivity in Cuprates*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2002.

[21] A. Fukuoka, A. Tokima-Yamamoto, M. Itoh, R. Usami, S. Adachi, and S. Tamato, "Dependence of T_c and transport properties on the Cu valence in $HgBa_2Ca_{n-1}Cu_nO_{2(n+1)+\delta}$(n = 2, 3) superconductors," *Physical Review B*, vol. 55, no. 10, pp. 6612–6620, 1997.

[22] J. Frank, "Experimental studies of the isotope effect in high T_c superconductors," *Physica C*, vol. 282–287, pp. 198–201, 1997.

[23] D. J. Pringle, G. V. M. Williams, and J. L. Tallon, "Effect of doping and impurities on the oxygen isotope effect in high-temperature superconducting cuprates," *Physical Review B*, vol. 62, no. 18, pp. 12527–12533, 2000.

[24] A. Lanzara, P. V. Bogdanov, X. J. Zhou, et al., "Evidence for ubiquitous strong electron phonon coupling in high-temperature superconductors," *Nature*, vol. 412, pp. 510–514, 2001.

[25] X. J. Zhou, T. Yoshida, A. Lanzara, et al., "High-temperature superconductors: universal nodal Fermi velocity," *Nature*, vol. 423, p. 398, 2003.

[26] A. D. Gromko, A. V. Ferdorov, Y. D. Chuang, et al., "Mass-renormalized electronic excitations at $(\pi, 0)$ in the superconducting state of $Bi_2Sr_2CaCu_2O_{8+\delta}$," *Physical Review B*, vol. 68, no. 17, Article ID 174520, 7 pages, 2003.

[27] T. Cuk, F. Baumberger, D. H. Lu, et al., "Coupling of the B_{1g} phonon to the antinodal electronic states of $Bi_2Sr_2Ca_{0.92}Y_{0.08}Cu_2O_{8+\delta}$," *Physical Review Letters*, vol. 93, no. 11, Article ID 117003, 4 pages, 2004.

[28] T. Takahashi, T. Sato, H. Matsui, and K. Terashima, "High-resolution ARPES study of quasi-particles in high-T_c superconductors," *New Journal of Physics*, vol. 7, p. 105, 2005.

[29] X. J. Zhou, T. Cuk, T. P. Devereaux, N. Nagaosa, and Z.-X. Shen, "Angle-resolved photoemission spectroscopy on electronic structure and iectron—phonon coupling in cuprate superconductors ," in *Handbook of High-Temperature Superconductivity*, J. R. Schrieffer and J. S. Brooks, Eds., pp. 87–138, Springer Science and Business Media LLS, New York, NY, USA, 2007.

[30] M. Okawa, K. Ishizaka, M. Uchiyama, et al., "Superconducting electronic state in optimally doped $YBa_2Cu_3O_{7-\delta}$ observed with laser-excited angle-resolved photoemission spectroscopy," *Physical Review B*, vol. 79, no. 14, Article ID 144528, 9 pages, 2009.

[31] J. H. Chung, T. Egami, R. J. McQuinney, et al., "In-plane anisotropy and temperature dependence of oxygen phonon modes in $YBa_2Cu_3O_{6.95}$," *Physical Review B*, vol. 67, no. 1, Article ID 014517, 9 pages, 2003.

[32] L. Pintschovius, D. Reznik, W. Reichardt, et al., "Oxygen phonon branches in $YBa_2Cu_3O_7$," *Physical Review B*, vol. 69, no. 21, Article ID 214506, 11 pages, 2004.

[33] L. Pietronero, "Superconductivity mechanisms in doped C_{60}," *Europhysics Letters*, vol. 17, pp. 365–371, 1992.

[34] L. Pietronero and S. Strassler, "Theory of nonadiabatic superconductivity," *Europhysics Letters*, vol. 18, pp. 627–633, 1992.

[35] L. Pietronero, S. Strassler, and C. Grimaldi, "Nonadiabatic superconductivity. I. Vertex corrections for the electron-phonon interactions," *Physical Review B*, vol. 52, no. 14, pp. 10516–10529, 1995.

[36] L. Proville and S. Aubry, "Small bipolarons in the 2-dimensional Holstein-Hubbard model. I. The adiabatic limit," *The European Physical Journal B*, vol. 11, no. 1, pp. 41–58, 1999.

[37] J. Bonca, S. A. Trugman, and I. Batistic, "Holstein polaron," *Physical Review B*, vol. 60, no. 3, pp. 1633–1642, 1999.

[38] P. Benedetti and R. Zeyher, "Holstein model in infinite dimensions at half-filling," *Physical Review B*, vol. 58, no. 21, pp. 14320–14334, 1998.

[39] H. Fehske, J. Loos, and G. Wellein, "Spectral properties of the 2D Holstein polaron," *Zeitschrift für Physik B*, vol. 104, no. 4, pp. 619–627, 1997.

[40] A. R. Bishop and M. Salkola, in *Polarons and Bipolarons in High-T_c Superconductors and Related Materials*, E. K. H. Salje, Ed., Cambridge University Press, Cambridge, UK, 1995.

[41] A. S. Alexandrov and P. E. Kornilovitch, "Incorporating novel magnetism," *The Journal of Superconductivity*, vol. 15, no. 5, pp. 403–408, 2002.

[42] A. S. Alexandrov and J. Runninger, "Theory of bipolarons and bipolaronic bands," *Physical Review B*, vol. 23, no. 4, pp. 1796–1801, 1981.

[43] A. S. Alexandrov and J. Runninger, "Bipolaronic superconductivity," *Physical Review B*, vol. 24, no. 3, pp. 1164–1169, 1981.

[44] A. S. Alexandrov, *Zh.Fiz.Chim*, vol. 57, p. 273, 1983, English translation in *Russian Journal of Physical Chemistry*, vol. 57, p. 167, 1983.

[45] D. J. Scalapino, "Random magnetism, high temperature superconductivity," in *Superconductivity*, R. D. Parks, Ed., vol. 1, p. 449, Marcel Dekker, New York, NY, USA, 1969.

[46] P. B. Allen and R. C. Dynes, "Transition temperature of strong-coupled superconductors reanalyzed," *Physical Review B*, vol. 12, no. 3, pp. 905–922, 1975.

[47] A. S. Alexandrov, "Nonadiabatic polaronic superconductivity in MgB_2 and cuprates," *Physica C*, vol. 363, no. 4, pp. 231–236, 2001.

[48] G. Grimaldi, L. Pietronero, and S. Strassler, "Nonadiabatic superconductivity. II. Generalized Eliashberg equations beyond Migdal's theorem," *Physical Review B*, vol. 52, no. 14, pp. 10530–10546, 1995.

[49] G. Grimaldi, L. Pietronero, and S. Strassler, "Nonadiabatic superconductivity: electron-phonon interaction beyond Migdal's theorem," *Physical Review Letters*, vol. 75, no. 6, pp. 1158–1161, 1995.

[50] G. Grimaldi, E. Cappelluti, and L. Pietronero, "Isotope effect on m^* in high-T_c materials due to the breakdown of Migdal's theorem," *Europhysics Letters*, vol. 42, pp. 667–672, 1998.

[51] G. Grimaldi, L. Pietronero, and M. Scottani, "The physical origin of the electron-phonon vertex correction," *The European Physical Journal B*, vol. 10, no. 2, pp. 247–255, 1999.

[52] E. Cappelluti, G. Grimaldi, and L. Pietronero, "Nonadiabatic pauli susceptibility in fullerene compounds," *Physical Review B*, vol. 64, no. 12, Article ID 125104, 8 pages, 2001.

[53] M. Botti, E. Cappelluti, G. Grimaldi, and L. Pietronero, "Nonadiabatic theory of the superconducting state," *Physical Review B*, vol. 66, no. 5, Article ID 054532, 10 pages, 2002.

[54] E. Cappelluti, S. Ciuchi, G. Grimaldi, and L. Pietronero, "Band-filling effects on electron-phonon properties of normal and superconducting states," *Physical Review B*, vol. 68, no. 17, Article ID 174509, 10 pages, 2003.

[55] A. S. Alexandrov, *Theory of Superconductivity: From Weak to Strong Coupling*, IoP, Bristol, Pa, USA, 2003.

[56] A. S. Alexandrov, "Strong coupling theory of high temperature superconductivity," in *Studies of High Temperature Superconductors, Golden Jubilee Volume*, A. Narlikar, Ed., pp. 1–69, Nova Science, New York, NY, USA, 2006.

[57] A. S. Alexandrov and P. P. Edwards, "High-T_c cuprates: a new electronic state of matter?" *Physica C*, vol. 331, no. 2, pp. 97–112, 2000.

[58] A. S. Alexandrov, "Many-body effects in the normal-state polaron system," *Physical Review B*, vol. 23, no. 5, pp. 2838–2844, 1992.

[59] J. P. Hague, P. E. Kornilovich, J. H. Samson, and A. S. Alexandrov, "Superlight small bipolarons," *Journal of Physics: Condensed Matter*, vol. 19, Article ID 255214, 26 pages, 2007.

[60] J. Nagamatsu, N. Nakagava, T. Muranaka, Y. Zenitani, and J. A. kimitsu, "Superconductivity at 39 K in magnesium diboride," *Nature*, vol. 410, pp. 63–64, 2001.

[61] J. M. An and W. E. Picket, "Superconductivity of MgB_2: covalent bonds driven metallic," *Physical Review Letters*, vol. 86, no. 19, pp. 4366–4369, 2001.

[62] T. Yilderim, O. Gulseren, J. W. Lynn, et al., "Giant anharmonicity and nonlinear electron-phonon coupling in MgB_2: a combined first-principles calculation and neutron scattering study," *Physical Review Letters*, vol. 87, Article ID 037001, 4 pages, 2001.

[63] J. Kortus, I. I. Mazin, K. D. Belashchenko, V. P. Antropov, and L. L. Boyer, "Superconductivity of metallic Boron in MgB_2," *Physical Review Letters*, vol. 86, no. 20, pp. 4656–4659, 2001.

[64] P. Baňacký, "Nonadiabatic sudden increase of the cooperative kinetic effect at lattice energy stabilization—microscopic mechanism of superconducting state transition: model study of MgB_2," *International Journal of Quantum Chemistry*, vol. 101, no. 2, pp. 131–152, 2005.

[65] L. Boeri, E. Cappelluti, and L. Pietronero, "Small Fermi energy, zero-point fluctuations, and nonadiabaticity in MgB_2," *Physical Review B*, vol. 71, no. 1, Article ID 012501, 4 pages, 2005.

[66] P. Baňacký, "*Ab initio* theory of complex electronic ground state of superconductors: I. Nonadiabatic modification of the Born—oppenheimer approximation ," *Journal of Physics and Chemistry of Solids*, vol. 69, no. 11, pp. 2728–2747, 2008.

[67] M. Svrček, P. Baňacký, and A. Zajac, "Nonadiabatic theory of electron-vibrational coupling: new basis for microscopic interpretation of superconductivity," *International Journal of Quantum Chemistry*, vol. 43, no. 3, pp. 393–414, 1992.

[68] P. Baňacký, "*Ab initio* theory of complex electronic ground state of superconductors: II. Antiadiabatic state-ground state of superconductors," *Journal of Physics and Chemistry of Solids*, vol. 69, no. 11, pp. 2696–2712, 2008.

[69] M. Born and J. R. Oppenheimer, *Annals of Physics*, vol. 84, p. 457, 1927.

[70] M. Born and M. Göttinger, *Nachrichten der Akademie der Wissenschaften Mathematisch Physikalische Klasse*, p. 1, 1951.

[71] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, Oxford University Press, London, UK, 1956.

[72] A. S. Davydov, *Quantum Mechanics*, Addison-Wesley, New York, NY, USA, 1965.

[73] M. Svrček, P. Baňacký, S. Biskupič, J. Noga, P. Pelikán, and A. Zajac, "Adiabatic correction to the energy of molecular systems: the CPHF equivalent of the Born-handy formula," *Chemical Physics Letters*, vol. 299, no. 2, pp. 151–157, 1999.

[74] T. D. Lee, F. Low, and D. Pines, "The motion of slow electrons in a polar crystal," *Physical Review*, vol. 90, no. 2, pp. 297–302, 1953.

[75] P. Baňacký, "Aspects of electronic structure instability in search for new superconductors: superconducting boride at liquid nitrogen temperature?" *Collection of Czechoslovak Chemical Communications*, vol. 73, pp. 795–810, 2008.

[76] P. Baňacký, "Theoretical study of YBa2Cu3O7 beyond the Born-Oppenheimer approximation and Migdal theorem: Antiadiabatic ground state induced by phonones modes coupling," in *Superconducting Cuprates*, K. N. Courtland, Ed., chapter 6, pp. 187–212, Nova Science, New York, NY, USA, 2009.

[77] J. Labbe and J. Bok, "Superconductivity in alcaline-earth-substituted La_2CuO_4: a theoretical model," *Europhysics Letters*, vol. 3, pp. 1225–1230, 1987.

[78] J. Bok and J. Bouvier, "Van Hove scenario for high T_c superconductors," *Physica C*, vol. 460, pp. 1010–1012, 2007.

[79] D. H. Lu, D. L. Feng, N. P. Armitage, et al., "Superconducting gap and strong in-plane anisotropy in untwinned $YBa_2Cu_3O_{7-\delta}$," *Physical Review Letters*, vol. 86, no. 19, pp. 4370–4373, 2001.

[80] H. J. M. Smilde, A. A. Golubov, A. G. Rijnders, et al., "Admixtures to d-wave gap symmetry in untwinned $YBa_2Cu_3O_7$ superconducting films measured by angle-resolved electron tunneling," *Physical Review Letters*, vol. 95, no. 25, Article ID 257001, 4 pages, 2005.

[81] P. Martinez-Samper, J. G. Rodrigo, G. Rubio-Bollinger, et al., "Scanning tunneling spectroscopy in MgB_2," *Physica C*, vol. 385, no. 1-2, pp. 233–243, 2003.

[82] P. Szabo, P. Samuely, J. Kacmarek, et al., "Evidence for two superconducting energy gaps in MgB_2 by point-contact spectroscopy," *Physical Review Letters*, vol. 87, no. 13, Article ID 137005, 4 pages, 2001.

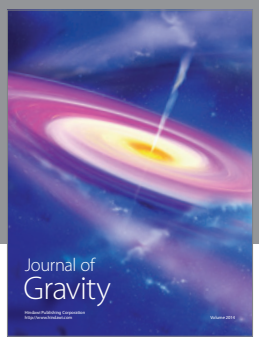
[83] B. T. Matthias, T. M. Gebale, and K. Andres, "Superconductivity and antiferromagnetism in boron-rich lattices," *Science*, vol. 159, no. 3814, p. 530, 1968.

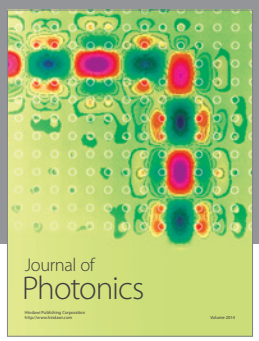
[84] O. K. Andersen, A. I. Lichtenstein, O. Jepsen, and F. Paulsen, "LDA energy bands, low-energy hamiltonians, t', t'', $t_\perp(k)$, and $J_\perp$," *Journal of Physics and Chemistry of Solids*, vol. 56, no. 12, pp. 1573–1591, 1995.

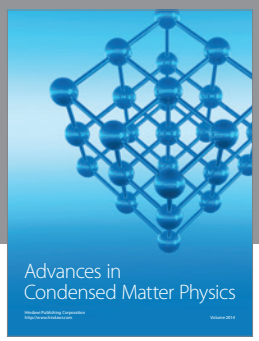
[85] R. Kouba, C. Ambrosch-Draxl, and B. Zangger, "Structure optimization of $YBa_2Cu_3O_7$ and its influence on phonons and Fermi surface," *Physical Review B*, vol. 60, no. 13, pp. 9321–9324, 1999.

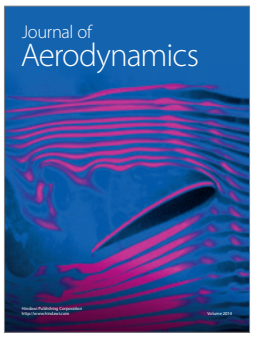
[86] H. Haghighi, J. H. Kaiser, S. Raynar, et al., "Direct observation of Fermi surface in $YBa_2Cu_3O_{7-\delta}$," *Physical Review Letters*, vol. 67, no. 3, pp. 382–385, 1991.

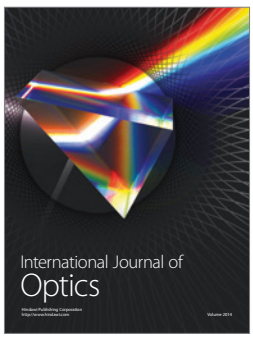
[87] D. Singh, W. E. Pickett, E. C. van Stetten, and S. Berko, "Theoretical electron-positron zone-reduced momentum density for $YBa_2Cu_3O_7$: Fermi surface and wave-function effects ," *Physical Review B*, vol. 42, no. 4, pp. 2696–2699, 1990.

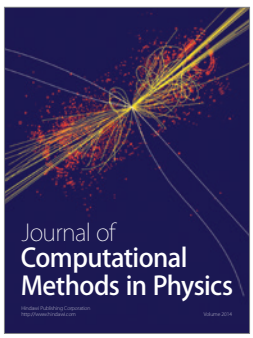


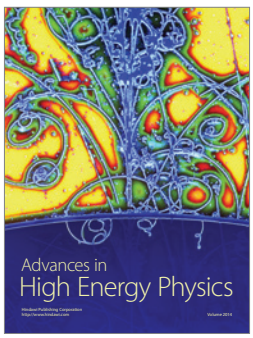


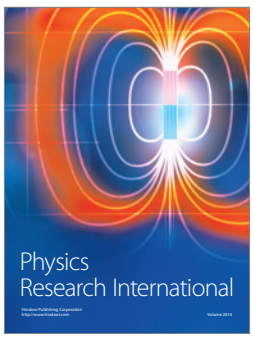


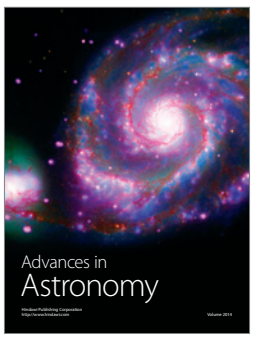


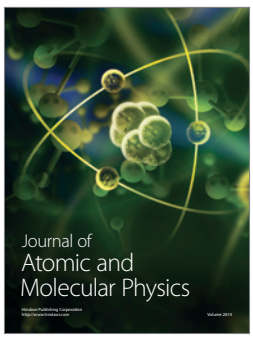












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