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Structure of a strongly coupled large polaron

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Contents

Abstract. We use the translationally invariant Bogolubov – Tyablikov method to propose a polaron theory. We present calculations of autolocalised electron states for different types of interaction. The structure of these states is shown to be strongly related to the structure and details of the local phonon spectrum. We calculate this spectrum in the strong-coupling limit. Applications of the large polaron model and possibilities of experimental tests are considered for the strong coupling. We generalise the Bogolubov – Tyablikov treatment to the strongly coupled bipolaron and give criteria of the stability and formation of the bipolaron states.

1. Introduction

The polaron theory is the simplest example of a quantum field theory; however, it has significant applications in condensed matter physics. The polaron problem was originally formulated as a problem of an autolocalised electron state in an ionic crystal [1]. The polaron description was assumed to correspond to the strong-coupling limit.

Since the strong-coupling criterion is not satisfied for most of the ionic crystals [2], the central problem in the polaron theory was to generalise the method to arbitrary coupling, i.e. to develop various approaches to the calculation of the dependence of the ground electron state on the electron – phonon coupling constant α [3, 4], to evaluate the effective mass for different values of α [5], to extend the treatment to finite temperatures [6], and to study the polaron transport problem [4 – 8].

However, there exist a number of physical examples for when the strong coupling is realised and the electron can be autolocalised. Among such examples are magnetically ordered crystals, where magnetic polaron states are possible [9 – 11], polar liquids, where the autolocalised states are the solvated electrons [12, 13], and other systems.

Moreover, even in ionic crystals, where polaron states are treated by the weak or intermediate coupling description, the strong coupling is realised for bipolaron states. We also note that, in the important case of the bound polaron arising in the *F*-center formation, the strong-coupling criterion is much weaker and can be satisfied for ionic crystals.

Thus, the study of the strongly coupled polaron is of interest in solid state physics, although only as a limiting case. Besides, we show in the review that the concept of the strongly coupled polaron can be successfully used for a number of related problems, such as the meson theory of nuclei interaction [14 – 16], the theory of the mobility of ions implanted into liquid helium [17], and so on.

In most works on the strongly coupled polaron, attention is focused on the study of the ground state. At the same time, the question of the possible existence of polaron states distinct from the ground state is basic to the study of processes related to electron excitation in polar media, for instance, the photoexcitation of *F*-centers and other lattice defects.

At present, the problem of the excited polaron states, apart from the fact that it is of theoretical interest, is

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gaining attention because of the problem of electron excitation transfer in a wide variety of condensed media (solutions [18], biomacromolecules [19–22], etc.).

We note that there are two types of strongly coupled polarons: the small polaron, formed when an electron is localised on one molecule of the medium [4, 23]; and the large polaron, formed when the polaron state is rather diffuse. There are a number of books and reviews devoted to the polaron problem [3–7, 24–29]. But in our opinion, there has been no unified treatment of the polaron states to date.

We will make an attempt at such a unified approach with the use of the Bogolubov–Tyablikov method developed to describe a nonrelativistic particle interacting with a quantum field. This will enable us to obtain equations asymptotically exact in the strong-coupling limit for different types of quantum fields, which play an important role in solid state theory. In cases of physical interest, the solutions of these equations give an idea of the complicated structure of autolocalised electron states.

Recently, the results have attracted attention owing to the development of a number of nonperturbation methods in the physics of elementary particles. This review is devoted to the study of the structure of a strongly coupled large polaron.

In the second part of the paper we will present the main results of the method for a nonrelativistic particle interacting strongly with a quantum field. The third part is concerned with the investigation of the electron states defined by different solutions of the nonlinear Schrodinger equation with the self-consistent potential. In the fourth part we consider the spectrum and characteristics of local phonons created by the strong electron–phonon coupling. In the fifth part we generalise the theory to the bipolaron case. Conclusions are presented at the end of the paper.

2. Theory of a strongly coupled polaron

2.1 Basic relations

The starting point in the description of motion of a nonrelativistic particle in a quantum field is the Hamiltonian [30, 31]

$$H = -\frac{\hbar^2}{2\mu}\nabla_{\tilde{r}}^2 + \frac{1}{2}\sum_k \hbar\omega_k (b_k b_k^+ + b_k^+ b_k) + \sum_k [c_k \exp(\mathrm{i}k\tilde{r})\, b_k + c_k^* \exp(-\mathrm{i}k\tilde{r})\, b_k^+] \,. \quad (1)$$

Here μ is the effective mass of the particle, $\tilde{r}$ is its coordinate, b^+ and b are the operators of annihilation and creation of the field quanta with energy $\hbar\omega_k$, c_k are the constants for the particle–field interaction defined in terms of the macroscopic state of the medium. We note that they are proportional to $\sqrt{\alpha}$, where α is the coupling constant.

Hamiltonian (1) describes the electron–phonon interaction and has been investigated actively in quantum field theory [33]. In general, in the presence of impurities, Hamiltonian (1) must contain the potential of the particle–impurity interaction.

The following study of the Hamiltonian depends on the presence of small terms in Eqn (1). If the last term of Eqn (1) is small, the problem is reduced to the weak polaron treatment [34, 35]. The other limiting case is that of strong coupling. In this case there is a small parameter $\varepsilon^2 = \omega_k/E \propto \alpha^{-2}$ (where $E \propto \alpha^2\omega$ is the characteristic electron energy).

This problem was originally investigated by Pekar in the framework of a phenomenological approach [1]. The presence of a translational invariance gives rise to additional difficulties in the problem. Consistent study of the quantum problem was carried out in Refs [30, 31] (see also Ref. [32]) with regard to the translational invariance of Eqn (1).

The first step in this method is to introduce complex lattice coordinates:

$$(\tilde{D}_k + \varepsilon\tilde{Q}_k) = \frac{1}{2}(b_k + b_{-k}^+)\,, \qquad P_k = -\mathrm{i}\,\frac{\partial}{\partial\tilde{Q}_k}\,. \quad (2)$$

Here $\tilde{D}_k$ are the equilibrium positions of the lattice coordinates, and $\tilde{Q}_k$ and P_k denote deviations from the positions and the corresponding impulses.

Then, we separate the variables related to the motion of the particle as a whole:

$$\tilde{r} = r_c + r\,, \qquad (\tilde{D}_k + \varepsilon\tilde{Q}_k) = (D_k + \varepsilon Q_k)\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_c)\,. \quad (3)$$

Here r_c is the coordinate of the rectilinear motion of the particle, and r corresponds to the fluctuating part of the motion (the trembling caused by the particle–field interaction).

Eqn (3) determines the canonical Bogolubov–Tyablikov transformation, and introduces new variables r, r_c, Q_k instead of $\tilde{r}$, $\tilde{Q}_k$, whose number has increased by 3. This generates a need for some additional restrictions,

$$\sum_k k v_k^* Q_k = 0\,, \quad (4)$$

where v_k are complex numbers satisfying the normalisation conditions

$$\sum_k k_i k_j v_k^* D_k = \delta_{ij}\,. \quad (5)$$

Eqns (3)–(5) are a closed set of equations determining the canonical transformation.

After performing the canonical transformation and separating the rectilinear motion, we use a standard perturba-tion technique over parameter ε, which enables us to obtain the corresponding wave equations for Hamiltonian (1):

$$(H_0 + \varepsilon H_1 + \varepsilon^2 H_2 + \ldots - E_0 - \varepsilon E_1 - \varepsilon^2 E_2 - \cdots)\Phi = 0\,. \quad (6)$$

Then, we present the wave function Φ of the system as

$$\Phi(r, Q_k, \ldots) = \varphi_0(r)\,\Theta(Q_k, \ldots) + \varepsilon\varphi_1(r, Q_k, \ldots)\,. \quad (7)$$

The equilibrium lattice coordinates are defined by the condition $E_1 = 0$ (which means nullifying of a form linear over displacements $\langle H_1\rangle = 0$), and have the form

$$D_{-k} = -\frac{c_k^*\omega_k}{\omega_k^2 - (v\cdot\boldsymbol{k})^2}\,\langle\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R})\rangle \equiv -\frac{c_k^*\omega_k}{\omega_k^2 - (v\cdot\boldsymbol{k})^2}\int \varphi_0^2(\boldsymbol{R})\,\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R})\,\mathrm{d}\boldsymbol{R}\,. \quad (8)$$

The canonical transformation of Eqns (3)–(5) eliminates the translational degeneracy of the initial Hamiltonian, which enables us to employ the perturbation theory. Using the standard perturbation method for the

wave function $\varphi_0(r)$, we obtain the wave equation determining the state of the quantum particle:

$$\left[-\frac{\hbar^2}{2\mu}\nabla_r^2 + U(r) - W_0\right]\varphi_0(r) = 0 ,$$

$$U(\boldsymbol{r}) = -2\sum_k \frac{c_k^2\omega_k}{\omega_k^2 - (v\cdot\boldsymbol{k})^2}\left\langle \exp\left[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')\right]\right\rangle ,$$

$$E_0 = W_0 + \frac{1}{2}\sum_k D_k D_{-k}\left[\omega_k + \frac{(v\cdot\boldsymbol{k})^2}{\omega_k}\right] . \quad (9)$$

Here E_0 and W_0 are the total and electron energies of the system in the zero approximation, and $U(r)$ is the self-consistent polaron potential.

In the slow-velocity limit we can evaluate the effective mass of the particle by expanding Eqn (9) over the velocity v:

$$M = \frac{2}{3}\sum \frac{c_k^2 k^2}{\omega_k^3}\left|\int \varphi_0^2(\boldsymbol{r})\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}\right|^2 . \quad (10)$$

Thus, in the strong-coupling limit there arises an autolocalised electron state with the energy E_0, the effective mass M, and the wave function defined by the solution of Eqn (9).

In turn, the state of the phonon subsystem in an adiabatic approximation corresponds to harmonic vibrations of the nuclei moving in a parabolic well:

$$\left(\frac{1}{2}\sum_k P_{-k}P_k - \hbar\omega_k + \sum_l \omega_k^2 \mathbf{M}_{kl} Q_k Q_l - E_2\right)\Theta_0 = 0 . \quad (11)$$

Here $\mathbf{M}_{kl}$ is the quadratic matrix defined by the electron density distribution. In the fourth part we obtain a relation to describe the matrix in terms of the states of the electron subsystem.

Eqns (8)–(11) determine completely the problem of a slow (nonrelativistic) motion of a particle in a quantum field in the strong-coupling limit. We note that the formulation of the problem implies that the medium, with which the electron interacts, is of a continuum nature (we treat the effective mass, the dependence of the coupling constant on the macroscopic medium parameters, and so on). This assumption is valid when a characteristic dimension of the electron density distribution described by Eqn (9) is much greater than the lattice constant. Otherwise it is necessary to use the small polaron treatment [23].

In the general case, the characteristic dimension of the polaron is specified by the type of the electron–medium interaction. In the case of the local short-range interaction, when $c_k \propto k^{1/2}$ and $\omega_k \propto k$, the polaron state is unstable in the strong-coupling limit [36, 37], and if we do not impose special limitations because of the discrete structure of the medium, the dimension of the polaron state will tend to zero. In the case of a long-range coulomb interaction, when $c_k \propto k^{-1}$ and $\omega \propto \omega_0$, the characteristic polaron dimension $r_\mathrm{p} \propto (\mu\omega)^{1/2}\alpha^{-1}$ can exceed greatly the lattice constant.

Thus, if the particle–field interaction can be approximated in terms of the strong coupling, Eqn (9) is fundamental in the description of the behaviour of electrons in the medium.

2.2 Polaron Hamiltonian for different types of interaction

Hamiltonian (1) encompasses many examples of the coupling of a quantum particle with a condensed medium. For instance, it describes the motion of an electron in an ionic crystal, if (see Refs [1, 34])

$$c_k = \frac{e}{|k|}\left(\frac{2\pi\hbar c\omega_k}{V}\right)^{1/2} , \quad \omega_k = \omega_0 ,$$

$$U(r) = -ce^2\int \mathrm{d}\boldsymbol{r}'\,\frac{|\phi(r')|^2}{|\boldsymbol{r}-\boldsymbol{r}'|} , \quad (12)$$

where e is the electron charge, V is the volume, and $c = \tilde{\varepsilon}^{-1} = \varepsilon_\infty^{-1} - \varepsilon^{-1}$.

The F-center model describing the interaction between an electron and an ion vacancy is practically important. In this case we must add the coulomb vacancy attraction to the interaction potential

$$U(r) = -ce^2\int \mathrm{d}\boldsymbol{r}'\,\frac{|\phi(r')|^2}{|\boldsymbol{r}-\boldsymbol{r}'|} - \frac{ze^2}{\varepsilon_0|r|} . \quad (13)$$

Here z is the charge of the vacancy.

In a piezoelectric semiconductor [38–41],

$$c_k = \frac{1}{k^{1/2}}\left(\frac{4\pi}{V}\,\frac{\hbar/\mu s}{\hbar^2\varepsilon/\mu e^2}\,\frac{\langle e_{ijk}^2\rangle}{2\varepsilon c}\right), \quad \omega_k = sk , \quad (14)$$

where s is the velocity of sound, c is the elastic constant, and $\langle e_{ijk}^2\rangle$ is the averaged square of the piezoelectric tensor. It leads to the same potential as in ionic crystals.

In a homopolar crystal [42, 43],

$$c_k = Gk\left(\frac{\hbar}{2\rho V\omega_k}\right)^{1/2} , \quad \omega_k = \left[\frac{1}{\rho}\left(K + \frac{4}{3}\tilde{\mu}\right)k\right]^{1/2} ,$$

$$U(r) = -\frac{3G^2}{3K + 4\tilde{\mu}}\,\phi(r)^2 , \quad (15)$$

where K and $\tilde{\mu}$ are the Young's and the shear moduli, respectively, and G is the constant of the deformation potential.

In the case of nuclear matter [14, 44],

$$c_k = \frac{g}{(2\omega_k V)^{1/2}} , \quad \omega_k = \left(\frac{\mu_0^2 c^4}{\hbar^2} + c^2k^2\right)^{1/2} ,$$

$$U(r) = -\frac{g^2}{4\pi}\int \mathrm{d}\boldsymbol{r}'\,\frac{|\phi(r')|^2}{|\boldsymbol{r}-\boldsymbol{r}'|}\exp\left(-\frac{\mu_0}{\hbar c}|\boldsymbol{r}-\boldsymbol{r}'|\right) , \quad (16)$$

where g is the constant of the nucleon–meson coupling, μ_0 is the meson mass, and c is the velocity of light.

In the case of the continuum exciton [29, 45],

$$c_k = \left\{\frac{2\pi\omega_p\varepsilon(k)}{V\varepsilon_0\left[\varepsilon(k) - 1\right]}\right\}^{1/2}\frac{e}{k} ,$$

$$U(r) = -\frac{e^2}{\varepsilon_0}\int \mathrm{d}\boldsymbol{r}'\,\frac{|\phi(r')|^2}{|\boldsymbol{r}-\boldsymbol{r}'|}\left[1 - \exp(-\kappa_\mathrm{D}|\boldsymbol{r}-\boldsymbol{r}'|)\right] , \quad (17)$$

where ω_p is the plasma frequency, $\varepsilon(k)$ is the dielectric constant of a doped semiconductor, and κ_D is the inverse Debye radius.

In a number of cases, Hamiltonian (1) describes the behaviour of electrons in magnetically ordered media [24, 46].

3. States of the electron subsystem

3.1 The ground state

Eqn (9) is the nonlinear Schrodinger equation. It has been investigated repeatedly for the ground electron state with various self-consistent potentials. For the polaron [Eqn (12)] and the F-center [Eqn (13)], the ground spherically symmetric state $\varphi_0(\boldsymbol{r})$ was determined in Ref. [1] by the variation method. The best numerical solution for the ground state was obtained in Ref. [47]. The results of these calculations were confirmed in Ref. [48].

The solution of the equation with the short-range potential [Eqn (15)], corresponding to the ground state, was actively investigated in nonlinear optics [49, 50], in the physics of disordered systems [51–53], in nonlinear field theory [54] either by different variation methods or by numerical iterative calculations [55]. In Ref. [42] it was investigated by the variation method as applied to the problem of an autolocalised electron state. The results were revised in Ref. [56] by the direct numerical calculation of the problem described by Eqn (15). The numerical calculations of the ground state for the self-consistent potential [Eqn (17)] are given in Refs [57, 58].

3.2 Excited states

The detailed study of the nonlinear Schrodinger equation shows that in the general case its solution is not unique; it has a discrete set of solutions, each with its own self-consistent potential. This is straightforward in the case of a F-center, where the solutions can be put into correspondence to solutions of the linear problem with the hydrogen-like potential. Here, the ground state corresponds to the $1s$-type solution, the first excited state with spherical symmetry corresponds to the $2s$-type, and the state asymmetric about the rotation corresponds to the $2p$-type, and so on.

We note that the excited states are less well understood when compared with the ground state. It was proved in Refs [59–61] that there is a countable number of solutions (modes) for the self-consistent polaron potential [Eqn (12)] and for the potential [Eqn (15)]. The spherically symmetric polaron states were numerically determined in Ref. [62], and the ones for the F-center were determined in Ref. [63]. In Refs [50, 56] the excited states were calculated for a homopolar crystal with the short-range potential [Eqn (15)].

Some of the first solutions and corresponding self-consistent potentials are shown in Fig. 1. Generally, for the $(n+1)$ spherically symmetric mode the solution intersects the x axis n times. Table 1 lists the numerical values of the radii, the effective masses, and the total energies for various spherically symmetric polaron states.

Note that in Ref. [66] the quasi-classical asymptotic behaviour (when $n \to \infty$) was found for the electron energy of the polaron, such that:

$$W_n \propto -\frac{2}{9\pi^2(0.486)^2}\,\frac{\mu e^4 c^2}{\hbar^2(n+1)^2}\,. \tag{18}$$

The data in Table 1 suggest that the radius of the state grows rapidly with the number of the solution, while the energy and the effective mass decrease.

Thus, to observe self-consistent states with the energy higher than the ground state energy, one must use the crystals with a coupling constant much greater than $\alpha = 10$ $(\alpha = e^2 c\hbar^{-1}\sqrt{\mu/2\hbar\omega})$. Typical values of the coupling constants for the majority of crystals are in the range $\alpha \approx 2-3$. So, $\alpha = 3.97$ in KCl, $\alpha = 2.0$ in AgCl, $\alpha = 1.69$ in AgBr, and $\alpha = 0.85$ in ZnO [2]. For this reason the

Table 1. Energies (in units of $e^4\mu c^2/\hbar^2$), radii (in units of $\hbar^2/\mu c e^2$) and effective masses (in units of $\alpha^4\mu$) for different self-consistent polaron states.

	n			
	0	1	2	3
E_n	−0.05426	−0.0103	−0.00416	−0.00223
R_n	9.29	48.4	120	216
M_n	0.0227	3.0×10^{-4}	2.9×10^{-5}	5.0×10^{-6}

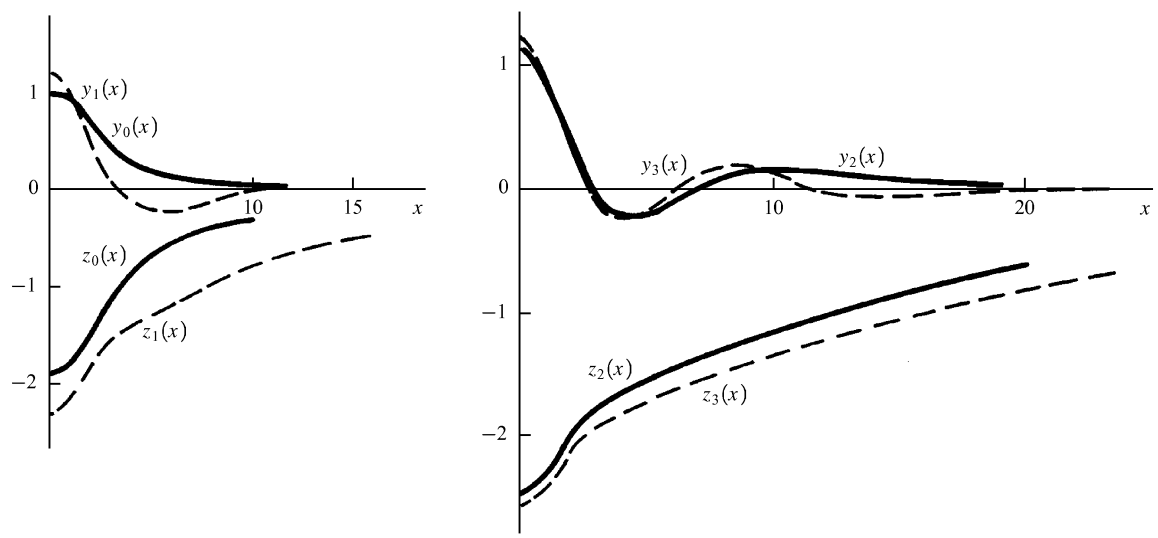

Figure 1. Wave functions $y(x) = A\phi(Bx)$ and the self-consistent potential $z(x) = |W|^{-1}U(Bx)$ for the ground $[y_0(x), z_0(x)]$, first $[y_1(x), z_1(x)]$, second $[y_2(x), z_2(x)]$, and third $[y_3(x), z_3(x)]$ excited polaron states. $A = |W|^{-1}(e\hbar)\mu^{-1/2}(2\pi c)^{1/2}$, $B = \hbar(2\mu|W|)^{-1/2}$.

calculation of self-consistent states of bound polarons is more interesting for comparison with the experimental data.

The self-consistent states have the same origin for different types of interactions considered in part 2, but their physical characteristics can be distinct for various types of interactions. For instance, the total and the electron energies are negative in the case of the polaron in an ionic crystal, so they are below the bottom of the conduction band. In the case of an electron in a homopolar crystal [Eqn (15)], the total energy of each self-consistent state is positive, while the electron energy (equal in absolute value to the total energy) is negative.

Hence, in homopolar crystals the electron energy of the excited state is lower than the energy of the ground state (nodeless state). There is also a great difference between effective masses of self-consistent states for the two cases considered. In the case of an ionic crystal, the effective mass decreases rapidly with n. On the contrary, for a homopolar crystal the effective mass increases rapidly with n.

In the case of the nonlocal screened potential (the deuteron problem), the existence of solutions to the nonlinear Schrodinger equation (16) depends on the value of the coupling constant g. The nodeless solution exists if values of g are greater than some critical value g_{cr}; moreover, the value of g_{cr} increases with n. Then, both cases are possible, i.e. the polaron case, where the total and electron energies are negative, and the case of the homopolar crystal, where the total energy is positive and the nucleon energy is negative. (In the latter case metastable states are formed [14].)

Less evidence is accumulated about the nonspherical solutions of Eqn (9). Some such solutions for self-consistent potential [Eqn (15)] were found in Ref. [64]. We do not know of any works in which the existence of nonspherical polaron-like solutions was determined. As a rule, the first step in finding such solutions is to choose the symmetry of the solutions.

For the polaron, an attempt to calculate the $2p$ state was made in Ref. [65] by the variation method. The nonspherical solutions of the $2p$- and $3p$-types, and a number of other solutions were obtained for the F-center in Ref. [67] by the direct variation method. The number and the branching conditions of the solutions were investigated in Ref. [68] in the limiting case of a very large F-center charge. A modified Galerkin method was used in Ref. [69] to calculate nonspherical solutions of the polaron problem (however, the calculations were probably numerically incorrect).

Recently, nonspherical solutions of the polaron and the F-center problem have been found numerically in Refs [70–72]. For this purpose, the nonlinear differential Eqn (9) was reduced to the infinite chain of ordinary differential equations. During the calculation, the chain was broken down into a finite number of the equations. The condition of the chain breaking was the convergence of the solution.

As a result, the numerical solutions were obtained in a series form:

$$\varphi(r) = \sum_{nl,k} c_k^{nl}\, |E|^{k/2+1} r^k\, Y_{nl}(\vartheta,\theta)\, \exp(-\tilde{a}^2 r)\ ,$$

$$\tilde{a}^2 = \frac{\mu |W_0|}{\hbar^2}\ , \tag{19}$$

where $Y_{nl}(\vartheta,\theta)$ are spherical harmonics.

Table 2. Total energies (in units of $\alpha^2\hbar\omega$) for different polaron states.

$1s$	$2s$	$3s$	$2p$
−0.1085 [47]	−0.0206 [62] −0.02048 [69] −0.0169 [67]	−0.00832 [62] −0.00804 [69]	−0.0457 [71] −0.05248 [69] −0.03829 [5] −0.0472 [67]
$3p$	$3d$	$2s-3d$	$2s+3d$
−0.0168 [71] −0.0136 [69]	−0.0207 [71] −0.0260 [69]	−0.0240 [71]	−0.030 [71]

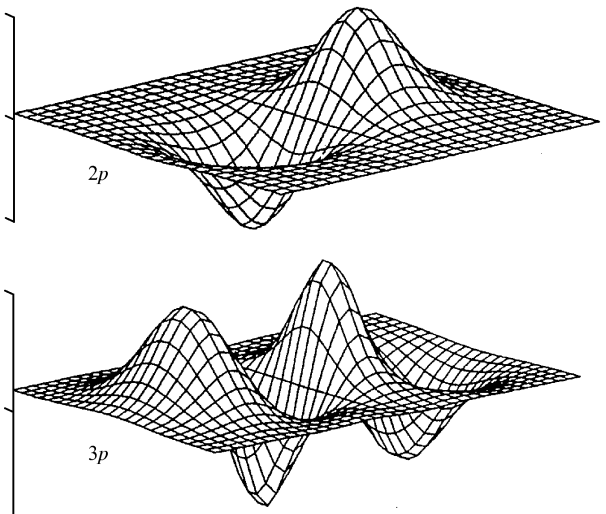

Figure 2. Polaron wave functions for the self-consistent excited states of the $2p$- and $3p$-type.

Table 2 lists the total energies of the excited polaron states obtained by some authors. Fig. 2 presents the self-consistent polaron states of the $2p$- and $3p$-type, calculated numerically in Refs [71, 72]. As is seen from Fig. 2, the electron density distribution has a 'peanut' shape typical of the p-states. Some of the solutions were tabulated in Ref. [70].

The calculations also revealed a surprising fact: that the solutions to the F-center problem branch, and there exist the excited states with mixed symmetry. (Below we will show that the formation of these states relates to phonon instability.) The new solutions may be classified in terms of s- and d-states.

Fig. 3 presents the electron density distribution for the s and d states. The sign '+' ($|\psi^2| > 10^3$) indicates regions of density condensation, and the sign '−' ($|\psi^2| < 10^3$) indicates regions with a low electron density. The hybrid states of the $(2s+3d)$- or $(2s-3d)$-type (depending on the sign of the combination) result from the combination of these two states.

These nonspherical states are similar in shape to the hybrid $(2s \pm 3d)$ states of the linear Schrodinger equation with a coulomb potential. The nonlinearity of Eqn (9) leads to the solutions, which are qualitatively different from solutions to a linear problem, especially for $r \to 0$. However, the similarity to the linear problem in terms of shape and the asymptotic behaviour for $r \to \infty$ remains, since asymptotics of linear and nonlinear problems differ only in constant.

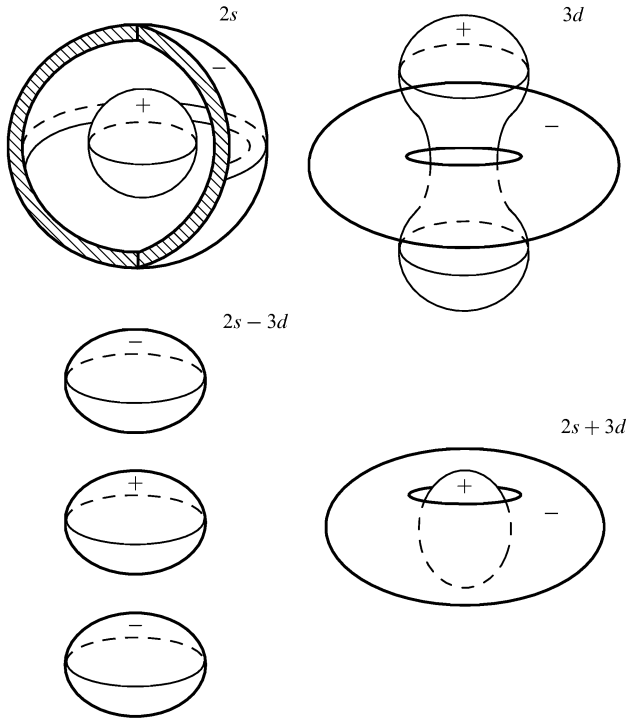

Figure 3. The electron density distribution for the self-consistent excited states with mixed symmetry $2s \pm 3d$.

3.3 Application of the large polaron model

The model of the strongly coupled polaron was the starting point in the explanation of the absorption spectrum in the *F*-center problem [1]. For a long time, the model was very attractive, as it allowed us to account for the qualitative correlation between spectrum parameters and dielectric constants of crystals. However, subsequent cyclotron-resonance experiments revealed that the measured effective masses do not agree with the strongly coupled polaron model [2].

Besides, according to the experiments on electron spin resonance [74], in the majority of ionic crystals the electron ground state has a characteristic dimension comparable with the lattice constant, and the large polaron model cannot be used in this case. As a rule, to study the electron ground state in the *F*-center, quantum-chemical calculations are used (for example, see Refs [75, 76]).

At the same time, most objections against the large polaron model disappear if we consider excited electron states in the *F*-center. The effect of the relaxed excited state on the absorption process in *F*-centers has been discussed in many reviews [73, 77 – 79].

The approximate solutions of Eqn (13), corresponding to the relaxed excited states of the $2p$-type obtained in Ref. [67], were used by Pekar [80] to describe the photo-excitation of *F*-centers, by Perlin [81] to evaluate the lifetime of excited states, and by Moskalenko [82] to describe heat excitation. The exact solutions of Eqn (13), corresponding to the extended excited $2s$-like states, were used in Ref. [83] to calculate the lifetime of photoexcited states of the *F*-center and to evaluate the photoconductivity in crystals with color centers.

The discussion of the nature of the relaxed excited state is still underway [78, 79]. This is due to the fact that in many cases experiments on photoabsorption can be described without any knowledge of the relaxation state itself. Thus, to explain the temperature dependence of the maximum of the *F*-center photoabsorption, one does not require the electron wave functions, and the data on the so-called *S*-factors, which can be used as fitting constants [84], are sufficient.

Another problem which occurs in the application of the excited states is that there are a number of absorption lines corresponding to transitions between various self-consistent states; these lines are usually wide and therefore they overlap. Each line can have a complicated shape owing to the multiphonon nature of the transition. Besides, the main contribution in the transition may be made by the local phonons (see the fourth section). It follows that the question of whether the large polaron model can be applied to the description of the relaxed excited state in the *F*-center is yet to be answered.

The large polaron can also be used to treat an autolocalised electron state in a polar liquid (solvated electron). The absorption spectrum of the solvated electron is simpler than that of the *F*-center, and consists of one or several broadened lines.

Initial attempts to consider the spectrum by means of the large polaron model [85] revealed details of the spectrum. However, subsequent experiments and calculations have shown that the model should be modified to consider short-range forces, with regard to the chemical structure of the environment (the size of the adjacent molecules, the coordination number, etc.).

At present, there are well-developed semiphenomenological methods based on the semicontinual polaron model (see Ref. [86]), which treat the effect of the cavity formation by short-range interactions and the influence of polaron tails. These models enable one to explain a lot of the experimental data on the absorption spectrum (the effects of temperature, density and pressure on the width and maximum of an absorption line, and so on).

Note that, although it is simple, the continual model of the strong coupled polaron is used to account for a number of solvated electron phenomena. The effect of salt concentrations on the absorption line has been investigated by means of this model in Ref. [87]. The generalisation of the large polaron model to disordered systems is used in Ref. [88]. This model also enables us to explain a lot of experimental data on correlations between the thermodynamic behaviour of the medium (density, pressure, and the Kirkwood effect) and the shape of the absorption spectrum.

A specific problem is the use of the large polaron model for long-range transfer. We emphasise that the large polaron model is the starting point for the theoretical study [89]. A vast amount of work has been devoted devoted to this question (see, for instance, Refs [90 – 92]). In recent years this question has taken on great significance owing to the 'superexchange' problem.

Available experimental data reveal that the rate of electron transfer is anomalously great for globular proteins and for a number of organic molecules. As assumed, electron transfer is realised by excited electron states (see Ref. [92]). The nature of these states remains to be explored [93]. In Refs [20, 22] an attempt was made to explain the high rate of electron transfer with the use of the large polaron model modified for the protein globule [19]. According to the model, results of the calculations agree with experimental data.

As a rule, the application of the polaron theory in semiconductors is limited by a weak electron–phonon coupling region ($\alpha \leqslant 1$). The experimentally observed doublet structure results from the fact that the polaron effect is accounted for in the absorption spectrum, when frequencies are in resonance with the optical vibrations of the semiconductor. The polaron effect is also very important in explaining the behaviour of charge carriers and other phenomena.

The strong coupling case can be realised in heavily doped semiconductors [29, 45]. In a heavily doped semiconductor of the hole-type, an electron is surrounded by holes; much as a polaron in an ionic crystal. Similar phenomena occur in the case of a hole in a semiconductor of the n-type. The states of this type, with the total charge equal to zero, were called continuum excitons [45].

The ground and excited states of continuum excitons have been investigated in Refs [29, 45]. Narrowing of the gap in the semiconductor results from the generation of the continuum excitons, which explains the dependence of the gap on the impurity concentration.

Usual exciton states do not exist in metals because of the strong screening of an attractive electron–hole potential. The singularities in the x-ray absorption spectrum (the so-called edge singularities) can result from the generation of continuum excitons in metals. The positron annihilation in metals can also be considered as the annihilation of continuum excitons, where the positron plays the same role as a hole.

The connection between ideas underlying many-particle theory in solid state physics and nuclear physics enable us to use the underlying methods developed in both cases [14–16]. The basic problem in nuclear physics, i.e. of a nucleon in a meson field, is similar to the polaron problem or the electron–phonon interaction. The divergence between results in the ultraviolet range when the perturbation theory is used is the principal difficulty which arises in the simplest case of an interaction between a nonrelativistic nucleon and a meson field.

A consistent treatment without any divergences is carried out in Ref. [14] for a strongly coupled nucleon in a meson field. In the case of two nucleons, the problem is shown to be similar to the bipolaron problem, where coulomb repulsion is absent, (see the details given in part 5) and is reduced to a one-particle problem [Eqn (9)]. The solution of nonlinear equation (16) gives values of the bound energy and the deuteron radius which are consistent with the experimental results.

4. Localised phonons

4.1 Spectrum of the phonon frequencies

We considered above the electron density behaviour for polaron-like states in the strong coupling limit. This distribution can be responsible for a number of important effects and this has been demonstrated in various experiments (see part 3). Equally significant is the fact that, in the case of strong interaction, the electron state is localised and the phonon subsystem state is fundamentally changed.

In terms of dynamics of the lattice, the presence of the localised density distribution of an excess electron can be considered as the presence of a special defect. As a result of the strong electron–phonon interaction, the phonon spectrum changes significantly and the bound phonon states are formed [94], as in the case of an imperfect lattice [95]. While the localisation of the latter is due to the changes in the atom mass or the lattice force constant, the localisation of the former is due to changes in the electron state itself.

In the case of translation symmetry, localised phonons form a cloud which is coupled to an electron and moves together with it. Note that bound phonon modes can also occur in the case of weak coupling, and that they were studied originally and became known as dielectric modes [96]. In Ref. [94] the earlier theoretical and experimental works on this theme are reviewed. The strong coupling case is considered in Ref. [97]. Here we present a short description of the results obtained.

As was noted in part 2, the characteristics of the phonon spectrum are described in a harmonic approximation and given by a matrix $\mathbf{M}_{kl}$. If we introduce eigenvectors Λ_{sk} and eigenvalues ω_s, such that

$$\sum_k \mathbf{M}_{kl}\Lambda_{sk} = \omega_s^2\Lambda_{sl}\,, \qquad \Lambda_{sk} = \Lambda^*_{s-k}\,,$$

$$\sum_k \Lambda_{sk}\Lambda^*_{tk} = \delta_{st}\,, \tag{20}$$

then relation (11) for the phonon subsystem takes a diagonal form:

$$\left[\sum \frac{1}{2}\left(\frac{\partial^2}{\partial\zeta_s^2} - \omega_s^2\zeta_s^2\right) + \tilde{E}_2\right]\Theta_s(\zeta_s) = 0\,, \tag{21}$$

where $\zeta_s = \sum_k \Lambda_{sk}Q_k$ are normal vibrations of the lattice.

Thus the state of the phonon subsystem in the adiabatic approximation is described as a product of wave functions $\Theta(\zeta) = \prod_s \Theta_s(\zeta_s)$ and is characterised by a set of quantum numbers $[n_1, n_2, \ldots, n_s]$ for noninteracting phonons with renormalised frequencies ω_s, whose squares are eigenvalues of the matrix $\mathbf{M}_{kl}$.

The energy $\tilde{E}_2$, which results from the second-order correction of the total energy of the system, is expressed as:

$$\tilde{E}_2 = E_2 - \frac{1}{2}\sum_k \hbar\omega_k = \frac{\hbar}{2}\sum n_s\omega_s + \frac{\hbar}{2}\sum(\omega_s - \omega_0)\,. \tag{22}$$

Thus, the state of the phonon subsystem is given by the matrix $\mathbf{M}_{kl}$ and its eigenvalues ω_s^2.

In the strong-coupling case the matrix $\mathbf{M}_{kl}$ is defined by the state of the electron subsystem. When we express the electron wave function of the first order in the form $\varphi_1(\boldsymbol{r}, \zeta) = \sum X_s(\boldsymbol{r})\,\zeta_s$, we obtain [97–99] the following relations for the eigenvectors Λ_{sk} and the eigenvalues ω_s,

$$\Lambda^*_{sk} = \frac{2}{\omega_s^2 - \omega_0^2}\left\langle \varphi_0 | h_k | X_k \right\rangle\,,$$

$$h_k = c_k \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}) + D_{-k}\,, \tag{23}$$

$$(H_0 - E_0)X_s = \frac{2\varphi_0}{\omega_0^2 - \omega_s^2}\sum_k h_k\left\langle \varphi_0 | h_k | X_s \right\rangle\,. \tag{24}$$

Eqn (24) defines the local-phonon frequency spectrum as the eigenvalue spectrum of a linear integro-differential boundary-value problem. This problem was studied for the electron ground state [99], where a set of the initial frequencies was calculated. For the polaron ground state, Eqn (24) was investigated in Ref. [100] in the variation form.

In Ref. [101] values of ω_s were found analytically for a one-dimensional problem. The influence of dispersion on

Table 3. Squares of phonon frequencies $\omega^2(n, l)$ (in units of ω_0^2) for the ground and the first excited self-consistent polaron statess

$1/n$	Ground state				First excited self-consistent polaron state			
	2	3	4	5	2	3	4	5
0	0.412	0.9254	0.9792	0.992	1.538	0.3586	0.8896	0.9574
1	0	0.8932	0.9726	0.9898	2.54	0	0.7992	0.9676
2		0.8158	0.9596	0.9864		−1.62	0.882	0.9254
3			0.9416	0.9816			0.4948	0.9362
4				0.976				0.817

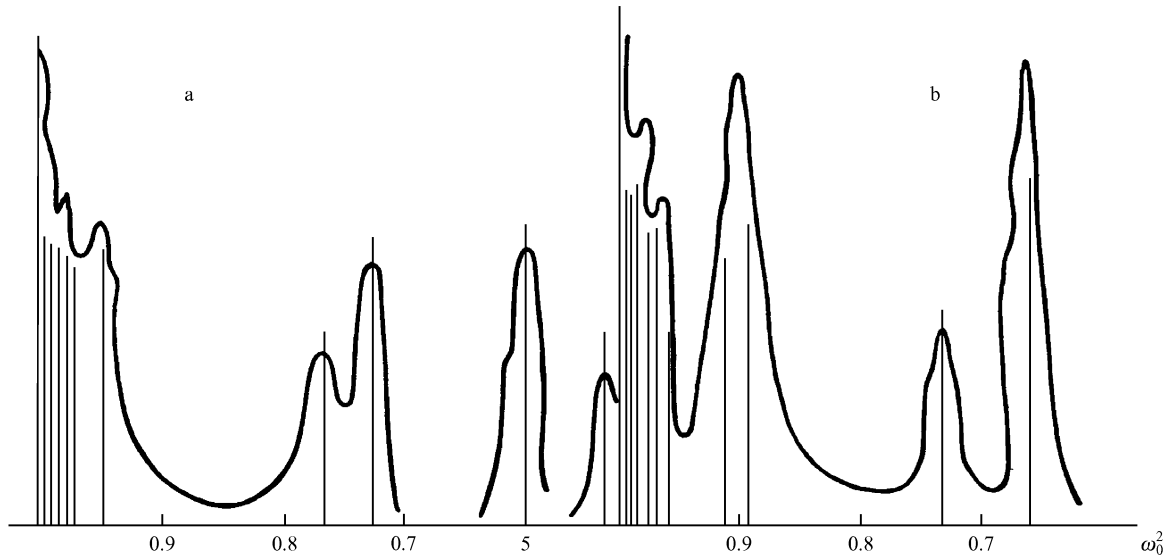

Figure 4. An approximation of the local phonon spectrum for the ground (a) and the first (b) excited states of the F-center in KCl. The half-width of each line is $\sigma = 0.0025\ \omega_0$.

the local phonon spectrum was considered in Ref. [102]. For excited spherically symmetric states of the polaron and the F-center, Eqn (24) was studied in Refs [102, 103]. Table 3 lists the dimensionless phonon frequencies for the ground and the first self-consistent polaron states. Fig. 4 shows the phonon spectrum approximation.

4.2 Phonon instability

If all the eigenvalues of the matrix $\mathbf{M}_{kl}$ are positive, then the amplitudes of the phonon oscillations are small $[\Theta(\zeta_s) \propto \exp(-\omega_s\zeta_s^2/2)]$ and the system remains stable. If any of the eigenvalues is small or negative, the amplitude in this approximation is of the order of the crystal dimension, and the system loses its stability. Thus the problem of stability, with respect to the motion of phonons, requires the study of the eigenvalues of the matrix $\mathbf{M}_{kl}$.

In Refs [102, 103] we found numerically that, for excited states of the polaron and the F-center, there are critical values of the effective F-center charge $v_{\rm cr} = Z/(\varepsilon_0 c) = 0.21$, when the square of the renormalised frequency becomes negative for one or several modes and the phonon instability of the system occurs. As shown in Ref. [98] this phonon instability is due to the branching of solutions to the nonlinear problem given by Eqn (13).

In Ref. [72] Gabdoulline found the critical values v at which the self-consistent states of the $(2s \mp 3d)$-type appear in addition to the excited self-consistent $2s$ state. Fig. 5 shows the dependences of ω_{nl}^2 for the phonon mode $n = 2$,

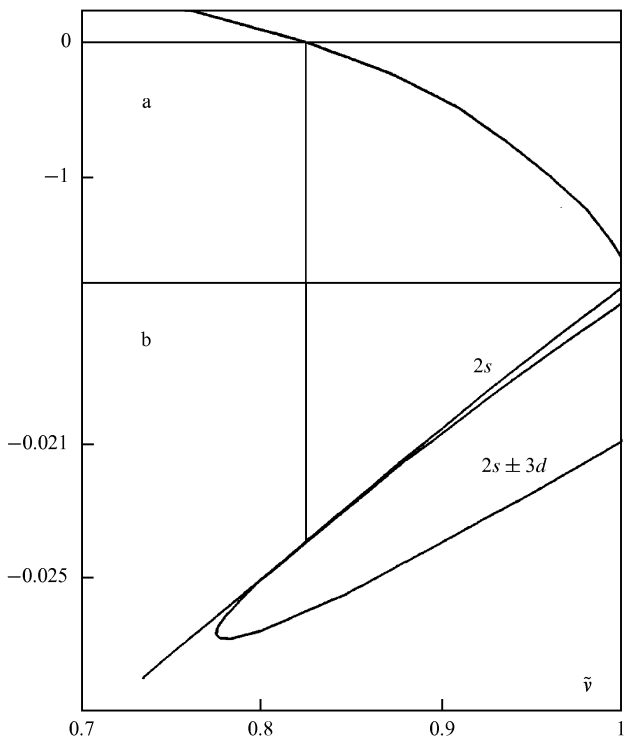

Figure 5. Dependences of the square of the local phonon frequency $\tilde{\omega}_{32}^2 = \omega_{32}^2/\omega_0$ (a) and the electron energy $\tilde{E} = W/(\alpha^2\hbar\omega_0)$ (b) on $\tilde{v} = Z/(Z + \epsilon_0 c)$.

$l = 3$, and the electron energy of self-consistent states $\tilde{E}$ on the effective F-center charge.

The occurence of the phonon instability is similar to the Jahn–Teller effect. For the polaron, in addition to self-consistent states, each corresponding to its own potential well, there is an infinite set of non-self-consistent electron levels available for each potential well. Each of these levels is characterised by its own wave function φ_n and energy E_n:

$$\left[-\nabla^2 + \int \mathrm{d}\boldsymbol{r}' \frac{|\varphi(\boldsymbol{r}')|^2}{|\boldsymbol{r}-\boldsymbol{r}'|} + \frac{v}{r} - E_n\right] \varphi_n(\boldsymbol{r}) = 0 \,, \tag{25}$$

where $\varphi(\boldsymbol{r}')$ is the self-consistent solution defined by Eqn (8).

If non-self-consistent electron levels are nondegenerate, then, according to the standard perturbation theory, the first-order correction X_s can be obtained by expanding over these functions:

$$X_s(\boldsymbol{r}) = C_s \varphi_s(\boldsymbol{r}) \,, \qquad \langle X_s(\boldsymbol{r})\, \varphi_s(\boldsymbol{r}) \rangle = 0 \,. \tag{26}$$

Substituting Eqn (26) into the frequency Eqn (24), we obtain a relation between the renormalised phonon frequencies and the spectrum of the electron states:

$$\frac{\omega_s^2}{\omega_0^2} = 1 - \frac{2e^2}{E_s - E_0} \left\langle \varphi_s \varphi_0 \left\langle \frac{\varphi_s \varphi_0}{|\boldsymbol{r}-\boldsymbol{r}'|} \right\rangle \right\rangle \,. \tag{27}$$

When $E_s - E_0 \leqslant 2\langle \varphi_s \varphi_0 \langle \varphi_s \varphi_0 e^2 |\boldsymbol{r}-\boldsymbol{r}'|^{-1} \rangle \rangle$, i.e. the electron levels are sufficiently close, the square of the frequency becomes negative; $\omega_s^2/\omega_0^2 < 0$. This entails instability, which leads to branching of the solutions. In this way the self-consistent electron state has a mixed symmetry of these two levels. Fig. 3 presents schematically the $2s$- and $3d$-states, and the resulting states of the $2s \pm 3d$-type.

The study of the phonon instability of excited polaron states makes it clear that the branching of solutions to Eqn (8) takes place at a loss of stability, which gives rise to new self-consistent states with mixed symmetry. This effect has two main causes.

The polaron state is given by nonlinear Eqn (9), which includes two types of potentials: a self-consistent polarisation potential and a coulomb one. Symmetries of these two potentials are different. As the contribution of these two interactions changes quantitatively, the symmetry of some solutions changes. This effect is characteristic not only of the F-center, but also of some other similar quasiparticles (piezopolaron, fluctuon, etc.) bounded on impurities.

Note some important consequences of this phenomenon. Unlike the problem given by Eqn (8), the stability problem [Eqn (24)] is linear. Thus it can be expected that it is easier in terms of calculations. From this standpoint it would be reasonable, first, to study the linear problem, find the symmetry of solutions and branching points; and, second, to analyse the self-consistent solutions of Eqn (8).

The described instability may be observed experimentally. It will lead to decay of excited states for time $|\omega^{-1}|$. Note that, for LiCl ($v = 0.35$), LiBr ($v = 0.29$), and fluorides of alkali-earth metals, the effective charge $v = Z/\varepsilon_0 c$ is almost equal to the critical charge $v_{\mathrm{cr}} = 0.21$. This explains the absence of luminescence [104] in experiments on photoexcitation in these crystals.

5. Strongly coupled bipolaron

5.1 History of the bipolaron problem

In the introduction we noted that bipolarons provide another example of when the strong coupling occurs. The intensive study of bipolarons in recent years is not only because of general theoretical interest in the problem, but also because of its important applications, such as in the study of high-temperature superconductivity [105, 106].

The history of bipolaron study is rather dramatic. For a long time, errors in calculation have called into question the existence of the bipolaron. The problem was first recognised by Ogg [107], who suggested the occurence of superconductivity at temperatures above the boiling point of nitrogen, when he observed abnormally high conductivity in metal–ammonia solutions (as early as forty years before the discovery of high-temperature superconductivity in metal-oxide ceramics [108]).

At present there is reliable experimental evidence that electron spin-pairing states are dominant in metal–ammonia solutions at concentrations of about 0.1 promille [109, 110]. Some authors relate this to bipolaron formation. But the mechanism of the phenomenon is still not fully understood.

In recent years, research has been conducted [111–114], which has revealed the bipolaron states at this concentration with the use of the Kohn–Sham theory and molecular dynamics methods, and where the characteristics of these states were also determined (electron density distribution, effective potential, etc.).

The bipolaron problem was first considered theoretically in 1951 [115]. In the description of the bipolaron state, the starting point is the Pekar–Frolich Hamiltonian of two electrons interacting with a phonon field:

$$\begin{aligned} H = {} & -\frac{\hbar^2}{2\mu}\nabla_{r_1}^2 - \frac{\hbar^2}{2m}\nabla_{r_2}^2 + \sum_k \hbar\omega_k b_k^+ b_k + U\big(|r_1 - r_2|\big) \\ & + \sum_k \Big\{ c_k \exp\big[\mathrm{i}k(r_1 - r_0)\big]\, b_k + c_k^* \exp\big[-\mathrm{i}k(r_1 - r_0)\big]\, b_k^+ \\ & + c_k \exp\big[\mathrm{i}k(r_2 - r_0)\big]\, b_k + c_k^* \exp\big[-\mathrm{i}k(r_2 - r_0)\big]\, b_k^+ \Big\} \,, \end{aligned} \tag{28}$$

where r_1 and r_2 are the coordinates of the first and the second electrons, respectively; r_0 is an arbitrary reference point; $U(r)$ is the electron interaction potential. It is usually assumed that $r_0 = 0$, and in this form the Hamiltonian of Eqn (28) is the initial equation in the bipolaron study.

Most authors turn to variational calculations of bipolaron wave functions. In semiclassical bipolaron theory [1] wave functions were selected in the multiplicative form. With this approximation one does not determine the presence of the bound bipolaron state. It was Vinetsky and Gitterman [116] who first obtained the bound bipolaron state in the framework of the semiclassical treatment.

The best evaluations of the bound bipolaron energy were obtained in Ref. [117], where trial wave functions were chosen with regard to the electron correlation. In particular, the condition of the bipolaron state formation was obtained ($\eta > 0.14$, where $\eta = \varepsilon_\infty/\varepsilon_0$ is the ion coupling parameter). The current state of research is presented in reviews [118, 119]. The treatment extended to the case of the presence of short-range interactions is given in Refs [120, 121].

Note that in the bipolaron theory no exact solutions have been obtained. This is in contrast with the polaron theory, where asymptotically exact solutions are known in the limits of both weak and strong coupling. Moreover, in the bipolaron case there are no solutions at all for small and intermediate values of the coupling constant α.

According to Ref. [122], a bound polaron state is possible only at sufficiently large values of the coupling ($\alpha > 5.2$). In the adiabatic limit, both the electrons are believed to move in one and the same potential well, induced by their fast oscillations. For this reason the interaction of the electrons with the polarisation $\phi(r_1, r_2)$ takes the form:

$$\phi(r_1, r_2) = F(r_1) + F(r_2) \ . \tag{29}$$

As a result, the problem is reduced to the calculation of a two-particle bipolaron wave function in a self-consistent potential. Since there are at present no methods to find asymptotically exact solutions of the problem, some additional assumptions are needed. As mentioned above, the form of the approximation of the wave function can have a significant effect on the result.

5.2 Adiabatic theory of the bipolaron

An alternative approach is exemplified by Ref. [123], where we used the Bogolubov–Tyablikov method [30, 31] to develop a consistent adiabatic translationally invariant theory. In this approximation the bipolaron motion is separated in the adiabatic limit, and the motion of the centre of the bipolaron mass is presented as a plane wave.

Relative electron coordinates describe fast oscillations in a potential well, which has the form of the electron–effective interaction:

$$\phi(r_1, r_2) = \phi(r_1 - r_2) \ . \tag{30}$$

The potential well is not fixed in space, but follows adiabatically the centre of the electron mass.

The interaction [Eqn (30)] is clearly translationally invariant unlike the usual phenomenological approach [Eqn (29)], which does not possess translational invariance with a spatially fixed potential well.

Within this approach we can treat the problem in a way similar to the treatment described in the second part of the paper. As a result, the problem becomes one-particle and is reduced to the study of a Schrodinger equation for the relative motion of the electron pair:

$$\left[-\frac{\hbar^2}{\mu}\nabla_r^2 + \Pi(r) + U(r) - W_0\right]\varphi_0(r) = 0 \ , \tag{31}$$

$$\Pi(r) = -2\sum_k \frac{\omega_k |c_k|^2}{\omega_k^2 - (v\cdot \boldsymbol{k})^2}\cos\frac{kr}{2} \times \int \mathrm{d}\boldsymbol{R}\cos\frac{kR}{2}\left|\varphi_0(R)\right|^2 \ . \tag{32}$$

Then, we can determine the bipolaron mass as in the case of Eqn (10):

$$M^* = \frac{2}{3}\sum_k \frac{c_k^2 k^2}{\omega_k^3}\left|\int \mathrm{d}\boldsymbol{R}\cos\frac{kR}{2}\,|\varphi_0(R)|^2\right|^2 \ . \tag{33}$$

5.3 Results of calculations

In Ref. [123] calculations were performed for an ion crystal ($\omega_k = \omega$, $c_k \propto k^{-1}$), and the interaction $U(r)$ between two electrons was the Coulomb repulsion screened by the high-frequency dielectric permittivity:

$$U(r_1 - r_2) = \frac{e^2}{\varepsilon_\infty |r_1 - r_2|} \ . \tag{34}$$

The solutions obtained depend on the parameter $\varkappa = 0.125(1 - \varepsilon_\infty/\varepsilon_0)$.

Fig. 6 shows particle-like solutions of the boundary problem [Eqns (31), (32)] for some $\varkappa$ values. It is evident from the figure, that the probability of the electrons being present at the same point decreases as $\varkappa$ grows, while the maximum of the electron density distribution moves to the right and goes to infinity at the critical value $\varkappa_{\mathrm{cr}} = 0.5$. This is because of the fact that, at sufficiently large values of r, the asymptote of the potential [Eqns (31), (32)] has the form:

$$r\left[e\Pi(r) - \frac{e^2}{\varepsilon_\infty r}\right] \underset{r\to\infty}{\approx} \frac{4}{\tilde{\varepsilon}} - \frac{1}{\varepsilon_\infty} \ . \tag{35}$$

The localised solution of Eqn (31) exists only when the right-hand side of Eqn (35) is positive, i.e. for $\varkappa < 0.5$. Accordingly, we have $\eta_{\mathrm{cr}} = 0.75$ for the ion-coupling parameter $\eta = \varepsilon_\infty/\varepsilon_0 = (8\varkappa - 1)/8\varkappa$, i.e. it exceeds greatly the value of this parameter obtained in phenomenological theory.

The critical value of the parameter η_{s}, at which the bipolaron is stable, is energetically advantageous to the bipolaron state with respect to its decay into two independent polaron states:

$$E \leqslant 2E_{\mathrm{pol}} \ , \tag{36}$$

where E_{pol} is the energy of a single polaron state.

Calculations show that inequality (366) is valid if $\eta < \eta_{\mathrm{s}}$, where $\eta_{\mathrm{s}} = 0.31$. Table 4 lists the values of parameters for crystals satisfying the condition $\eta < \eta_{\mathrm{s}}$, with calculated values of bipolaron energies, radii, and effective masses. When the experimental data on the effective electron mass

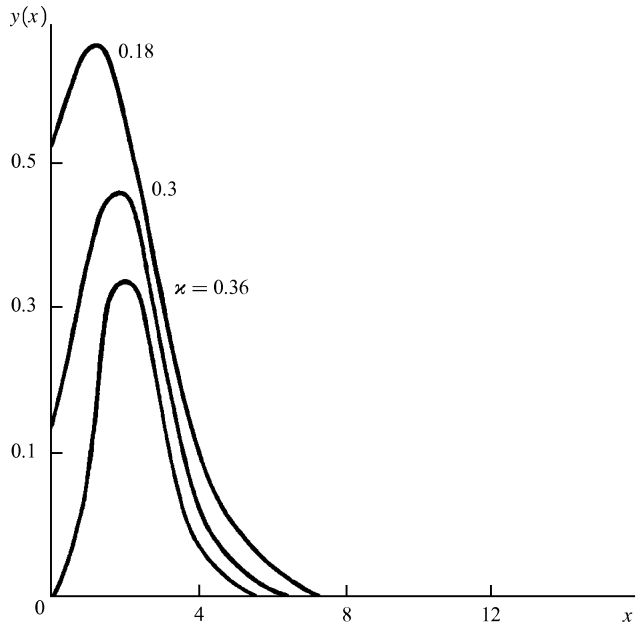

Figure 6. Quasiparticle-like solutions $y(x) = A\phi(Bx)$ of Eqn (32) for different value of $\varkappa$. $A = |W|^{-1}(e\hbar)\mu^{-1/2}(2\pi c)^{1/2}$, $B = \hbar(2\mu|W|^{-1/2}$.

Table 4. Values† of energies $\tilde{W}$, total energies $\tilde{E}$, radii $\tilde{R}$, and the effective masses of bipolarons $\tilde{M}^*$.

Crystal‡	η	$\hbar\omega$/eV	$\tilde{\alpha}$	$\tilde{W}$/eV	$\tilde{E}$/eV	$\tilde{R}$/Å	$\tilde{M}^*$
LiF	0.213	0.082	5.24	10.7	2.13	2.3	31.6§
LiCl	0.235	0.052	4.43	4.6	0.93	3.7	40.3
LiBr	0.243	0.079	5.25	3.2	0.62	4.5	71.7
LiH	0.279	0.140	1.98	2.2	0.42	5.5	1.3
TlBr	0.176	0.014	4.54	1.56	0.317	6.3	0.47
TlCl	0.202	0.020	4.46	2.15	0.45	5.3	0.61
TlI	0.315	0.012	3.4	0.54	0.1	11.3	0.6
CsF	0.269	0.030	7.13	6.3	1.2	3.3	222
RbF	0.299	0.036	7.03	7	1.25	3	186
$SrTiO_3$	0.016	0.0153	1.84	2.9	0.67	4.4	1.98

†$\alpha = \tilde{\alpha}(\mu/m_0)^{1/2}$, $W = -\tilde{W}\dot{\mu}/m_0$, $E = -\tilde{E}\dot{\mu}/m_0$, $R = \tilde{R}\dot{m}_0/\mu$, and $M^* = \tilde{M}^*(\mu/m_0)^2$ for all crystals, except LiF, TlBr, TlCl. It is assumed that $\mu \equiv m_0$. ‡Experimental values are given from Ref. [2].
§The effective mass of electron LiF is given in Ref. [124].

m are not available, we present results depending only on the ratio m/m_0, where m_0 is the free electron mass.

The condition for adiabatically strong coupling is that the frequency of the electron oscillations in the polaron well should be much greater than the frequency of lattice oscillations. It follows from Table 4 that this condition is met for reasonable values of the effective electron mass.

Thus, while a single polaron meets the condition of weak or intermediate coupling, a bipolaron follows the strong coupling condition in the case of the studied crystals. This enables us to evaluate critical values of electron–phonon coupling constants α_s, when the bound bipolaron state is possible.

It follows that the energetic requirement for the bipolaron formation is that

$$|E| > 2\alpha\hbar\omega \ . \tag{37}$$

Since $E \propto \alpha^2$, condition (37) allows us to estimate values of the critical coupling constants α_s. Table 5 lists these values.

Table 5. Critical values of electron-phonon coupling constants α_s for different values of η

η	0	0.053	0.094	0.132	0.166	0.199	0.228	0.256	0.282	0.305	0.317
α_s	1.54	1.64	1.74	1.85	1.97	2.10	2.25	2.40	2.58	2.77	2.90

Note that the critical values of coupling constants, obtained from the exact solutions of the bipolaron equations, are much smaller than those evaluated by trial variational functions. Thus, according to Ref. [124], the critical values are $\alpha_s \approx 5.4$ for $\eta = 0$, $\alpha_s \approx 7.2$ for $\eta = 0.1$, i.e. they appear to be three times as large as those obtained from the exact solution to the bipolaron problem.

Note also that in the transition from the polaron to the bipolaron state, the symmetry of the solution changes, which can lead to significant rearrangement of the local phonon spectrum near the critical value of the parameter η_s because of the phonon instability of the solution, in the same way as in polaron excited states (see part 4).

Some of the results obtained can be easily extended to the two-dimensional case. The two-dimensional bipolaron problem has attracted much interest with the discovery of high-temperature superconductivity.

The simplest model, used to describe polarons in two-dimensional space, is obtained from Eqn (12) with c_k replaced by

$$c_{k,D} = \hbar\omega\left[\frac{\alpha_D}{Vk^{D-1}}\left(\frac{\hbar}{2m\omega}\right)^{1/2}\left(2\sqrt{\pi}\right)^{D-1}\Gamma\left(\frac{D-1}{2}\right)\right]^{1/2} . \tag{38}$$

The physical parameters (frequencies, dielectric constants, effective masses) were assumed to be the same as in the three-dimensional case.

The dependence of $c_{k,D}$ on the wave vector is chosen from the requirement that the electron–polarisation interaction should be of the Coulomb form, $1/r$, in the D-dimensional case. The numerical factor in Eqn (38) is given by the condition that $c_{k,D}$ corresponds to c_k at $D = 3$.

To evaluate the energy and critical constants in the two-dimensional case, the estimates obtained in Eqn [125] with a Gauss approximation can be used. These estimates relate bipolaron energies in three- and two-dimensional cases.

As a result, in the two-dimensional case we express the bipolaron energy as

$$E_{2D,\mathrm{bipol}} = \frac{2}{3}\left(\frac{3\pi}{4}\right)^2 E_{3D,\mathrm{bipol}} \ , \tag{39}$$

where $E_{3D,\mathrm{bipol}}$ is the bipolaron energy in the three-dimensional case. Accordingly, $\varkappa_{2D} = \varkappa_{3D}$ and $\eta_{2D} = \eta_{3D}$.

The critical value of the electron–phonon coupling constant is derived similarly and in the two-dimensional case takes the form:

$$\alpha_{s,2D} = \frac{3}{4\pi}\alpha_{s,3D} \ , \tag{40}$$

where values of α_s are listed in Table 5.

The translationally invariant bipolaron theory presented above yields results qualitatively different from those obtained with the standard adiabatic method. According to Ref. [123], the situation is as follows. In bipolaron formation the electrons are localised in a deep potential well with the electron excitation energy $W \sim 1$ eV. This energy remains the same up to the critical value of the parameter $\eta_s = 0.31$, at which point the bipolaron state decays into independent polaron ones.

Up to the critical value $\eta = \eta_s$, the frequency of the electron oscillations in the bipolaron potential well greatly exceeds the frequency of the lattice oscillations, and we can

use the adiabatic approximation. The criterion of adiabaticity fails only for crystals with very small electron–phonon coupling constants, such as PbSe ($\alpha = 0.215$) and PbS ($\alpha = 0.317$), where $\eta < \eta_s$, i.e. bipolaron states are conceptually possible.

Bipolaron characteristics are best observed in crystals TlBr and TlCl. In these crystals continual approximations produce good agreement with results; the radii of the states are 20 Å and 16 Å, respectively. The adiabaticity condition is also met with a great reserve, despite a relatively small constant $\alpha \approx 2.5$.

It is significant that, in all the cases listed in Table 4, there is a great difference between the electron energy of bipolaron W and the total energy E. The modulus of the electron energy of the bipolaron is approximately 5 times as great as that of the total energy, while for a single polaron in the strong coupling limit this ratio is equal to 3. This distinction can lead to a great difference between the energies of photodissociation and thermodissociation.

In some crystals the criterion of stable bipolaron formation is at the limit of accuracy. Thus, in RbF the bipolaron is stable at room temperature ($\eta = 0.3$) and unstable at liquid helium temperature ($\eta = 0.32 > \eta_s$). Therefore, in RbF the cooling from room temperature to that of liquid helium leads to the bipolaron dissociation. This phenomenon could be observed on absorption spectra, changes in mobility and cyclotron frequency, etc.

Note also that this method for separating out the translationally invariant part of the motion and reducing a two-particle problem to a nonlinear Schrodinger equation is universal and can be applied to any other two-particle problem in the strong-coupling limit, such as excitons, electron–hole pairs, and so on.

6. Conclusions

Despite the long history of bipolaron study, the interest in the problem of the strongly coupled polaron has not diminished. This is probably because of the role which the polaron plays in the physics of particle–field interaction.

Unlike many other quasiparticles (phonons, magnons, plasmons, etc.) described by the spectrum and type of linear excitations of the system, the strongly coupled polaron is a 'nonlinear' quasiparticle formed as a result of a nonlinear self-consistent interaction. This, in turn, requires the use of nonstandard mathematics [66, 128].

In our view, the potential of modern mathematical methods has not been exploited in the polaron problem. The above example demonstrates that even the generalisation of the well-known Bogolubov–Tyablikov method to the case of two-particle self-consistent states yields new results which differ significantly from the usual variational calculations.

The above results show that a strongly coupled large polaron possesses a complicated internal structure which manifests itself in a wide variety of self-consistent states for the electron subsystem and in the local phonon spectrum. The peculiar behaviour of the local phonon spectrum is closely related to the topology of self-consistent states of the electron subsystem and is given by the symmetry of the self-consistent potential in the nonlinear Schrodinger equation.

Note that the investigation of such equations has much to do with the development of numerical methods for the solution of nonlinear boundary problems. It seems likely that new interesting results in this field can be obtained with the active use of high-performance parallel computers.

The above discussion proves that the experimental test of the possible existence of strongly coupled large polaron and bipolaron states is rather ambiguous. However, in our opinion, dramatic qualitative results of the theory (such as the availability of excited self-consistent states, or phonon instability) can be revealed in specially designed experiments.

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