Mathematical justification of the stability of axially symmetric singlet large bipolaron

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Abstract**—**Using the variational method we investigated spatial symmetry of a large bipolaron in singlet state. It is shown strictly mathematically that the formation stable state of bound two polarons in the singlet state corresponds to an axially symmetric spatial formation. It was found that the inclusion step-by-step of electron correlations lead to an increase in the binding energy of the bipolaron, but does not change spatial symmetry of bipolaron. At the same time spherically symmetric two polarons formation is not stable, even after accounting for electronic correlations. There are numerous arguments that point out the fallacy of spherically symmetric model of singlet bipolaron. It is shown that the variational principle should apply subject to certain restrictions that are imposed on the wave function. We performed a comparison of experimental data with the theoretical results. Theoretical results have been obtained in the framework of an axially symmetric bipolaron. At the same time for electronic-excited triplet states we have shown that a large bipolaron is one-center formation. We give explanations of changing the spatial symmetry of a large bipolaron when changing its spin state.

Keywords**—**Axially symmetric, bipolaron, electron-electron correlations, magnetic susceptibility, optical absorption, singlet, stability, triplet, variational method

I. INTRODUCTION

RISENTLY, numerous publications have appeared on the stability of adiabatic large bipolarons and its dependence on the electron-phonon coupling constant and the dielectric parameters of polar media. The exact solution of the bipolaron problem can be reduced to finding a solution to a nonlinear integro-differential equation for the self-consistent field [1]. Since solution of this equation poses formidable difficulties, variational methods have commonly been employed to find approximations to solutions. However, care should be taken when directly applying the variational method and searching for approximations to the solution. Indeed, as the trial electronic function becomes more complicated, the search for a constrained minimum of the energy of a system can be unintentionally replaced by study of the global minimum, which has no physical meaning. In this paper, we study the relations between the variational method and the virial theorem with regard to the problem of bipolaron stability, analyze additional restrictions that optimize electronic wave functions of bipolaron problem, and discuss the physical consequences of these restrictions. Further, we will show that the axial-symmetric model of a large bipolaron can correctly interpret the known experimental results.

II. PROBLEM FORMULATION

Studies of the dependence of the Hartree-Fock approximation for a large bipolaron problem on the distance R between the centers of gravity of the polarons have shown that the bipolaron potential has a maximum as $R \to 0$ and, therefore, a spherically symmetric state of large bipolaron is unstable [2]. A minimum of the interpolaron potential appears only at intermediate equilibrium distances ($R > 0$) between polarons. Therefore, it is important to study the role played by the electron correlations in the stabilization of bipoilarons and elucidate whether the electron correlations able for change the Hartree-Fock approximation so strongly that the bipolaron passes from an axially symmetric two-center state to a spherically symmetric one-center state [3]. For this purposes we use the well-known principles of the variational method and firmly established the physical consequences due to by the influence electronic correlations on the electronic systems. Using these well-known concepts, we show mathematically strongly and at the same time very evidently, using both variational procedure and the physical principles the instability of the spherically symmetric state of Landau-Pekar large bipolaron. Moreover, we demonstrate a clear physical sense of the arguments that we use. Incorrect application of variational method leads to results that have contradictory physical meaning.

III. PROBLEM SOLUTION

Using the results from the adiabatic translationally invariant theory of a large bipolaron [4], we can replace the integro-differential equation with an equivalent variational functional for the total self-consistent electronic energy $E(R)$ of the motionless bipolaron:

$$E(R) = -\frac{\hbar^2}{4m^*}\left(\int \nabla_1^2 \rho_1(\mathbf{r}_1) d\tau_1 + \int \nabla_2^2 \rho_1(\mathbf{r}_2) d\tau_2\right) +$$

$$\frac{1}{4}\iint d\tau_1 d\tau_2 \rho_2(\mathbf{r}_1, \mathbf{r}_2) \times$$

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$$\left\{2g(\mathbf{r}_1,\mathbf{r}_2)\varepsilon_\infty^{-1}+\varepsilon^{*-1}\sum_{i=1,2}\int g(\mathbf{r}_i,\mathbf{r}_i^{'})\rho(\mathbf{r}_i^{'})d\tau_i^{'}\right\}=$$

$$=T(R)+U(R). \qquad (1)$$

Here, the dielectric medium is replaced by a continuum; m^* is the isotropic effective mass of the electron; $g(\mathbf{r}_1,\mathbf{r}_2)$ is the electron-electron interaction operator; $\rho(\mathbf{r}_1)$ and $\rho(\mathbf{r}_1,\mathbf{r}_2)$ are the one-particle and two-particle spinless electronic densities, respectively; $\varepsilon^{*-1}=\varepsilon_\infty^{-1}-\varepsilon_s^{-1}$, $\boldsymbol{\varepsilon}_\infty$ and ε_s are the high frequency and static permittivities of the polar medium. Functional (1) depends parametrically on the distance R between centers of gravity of two polarons. The quantities $T(R)$ and $U(R)$ are the average electron kinetic and potential energies. The energy is measured off from the bottom of the conduction band. Effective translational mass of the polaron is equal to $m^{**}=0.023\alpha_c^4 m^* >> m^*$. $\alpha_c=(1/2\varepsilon^*)(e^2/\hbar\omega)\times (2m^*\omega/\hbar)^{1/2}>10$ is the dimensionless constant of the electron-phonon coupling. These inequalities justify the using of "fixed" polarons approximation. Functional (1) was analyzed in the papers [2], [5]-[7] for arbitrary distances R. In the variational calculations, trial electronic wave functions are considered optimal if these quantities satisfy to the conditions of the virial theorem.

We perform a simple and mathematically very clear analysis that will demonstrate the incorrectness of the spherically symmetric model of bipolaron.

Using the scaling transformation $\mathbf{r}_i \to \lambda\mathbf{r}_i$ and $\boldsymbol{R}\to\lambda\boldsymbol{R}$ we can write a normalized trial two-electron wave function in the form $\chi(\mathbf{r}_1,\mathbf{r}_2;\boldsymbol{R})\to\lambda^{3n/2}\chi(\lambda\mathbf{r}_1,\lambda\mathbf{r}_2;\lambda\boldsymbol{R})$, where $n = 2$ is the dimensionality of the configuration space and λ is an arbitrary scaling factor. For the particles the interaction between which is inversely proportional to the distance, the total energy can be written in the following form

$$E(s)=\lambda^2 T(s)+\lambda U(s)\ , \quad s=\lambda R\,, \qquad (2)$$

Then, we find that functional (2) reaches an extremum when the following relation holds

$$\lambda=-(U+sdU/ds)(2T+sdT/ds)^{-1} \qquad (3)$$

for any distance R. Obviously, as $R\to 0$ or at the point of an extremum of the potential, the scaling factor is equal to $\lambda = -U(\lambda R)/2T(\lambda R)$. Thus, using the equation (3) the variational method allows us to determine the variational parameter. Taking into account that the energy E is a homogeneous function of the variational parameter λ and the distance R we can find the derivative of the total energy:

$$R\frac{dE(R)}{dR}=\lambda^2 s\frac{dT(s)}{ds}+\lambda s\frac{dU(s)}{ds}\ . \qquad (4)$$

Substituting (3) and (2) into (4), we obtain virial relation for the Coulomb system:

$$R\frac{dE(R)}{dR}+2T(R)+U(R)=0\ , \qquad (5)$$

Thus, when minimizing the total energy functional (1) it is necessary that equation (5) would be satisfied for the optimum wave functions at any value of R. For these variational problems the existence of a minimum of functional (1) is a necessary but is not sufficient condition. A sufficient condition is closely related to the validity (5) for any R. Obviously, not all of the functions for which functional (1) reaches the extremum satisfy (5).

Since the stability of large bipolaron at $R\to 0$ is of the greatest interest, we find the second derivative of the energy with respect to R. Taking into account that the virial relation $2T + U = 0$ is satisfied at zero distance, we obtain from (5) a relation between the total electronic energy of a large bipolaron and the kinetic energy :

$$\lim_{R\to 0} R\frac{d^2E(R)}{dR^2}=-\lim_{R\to 0}\frac{dT(R)}{dR}\,. \qquad (6)$$

Thus, the second derivative of the total energy with respect to the variable R at the origin is opposite in sign to the first derivative of the electron kinetic energy. Therefore, rather than performing complicated calculations of the bipolaron total energy $E(R)$ we can restrict ourselves to an analysis of the dependence of the average kinetic energy on R. In this case, the virial theorem is satisfied.

For an isolated bipolaron, we search zeroth-order approximation to the eigenfunction Hamiltonian using the electronic wave function in the following form:

$$\chi_0(\mathbf{r}_1,\mathbf{r}_2;R)\sim\chi_s^a(\mathbf{r}_1)\chi_s^b(\mathbf{r}_2)+\chi_s^a(\mathbf{r}_2)\chi_s^b(\mathbf{r}_1)\,. \qquad (7)$$

Approximation (7) we shall call the Hartree-Fock approximation. Here, the superscript a refers to the centre gravity of polaron at the point $\boldsymbol{R}_1$; the superscript b refers to the second polaron at the point $\boldsymbol{R}_2$; $\boldsymbol{R}=\boldsymbol{R}_1-\boldsymbol{R}_2$; $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of the first and second electrons measured from the centers of gravity of the first ($\boldsymbol{R}_1$) and second ($\boldsymbol{R}_2$) polarons, respectively. The method of separating the polaron coordinates $\boldsymbol{R}_i$ from the electronic coordinates $\mathbf{r}_i$ is described in Ref. [4]. At the distance $R\to\infty$ equation (1) gives the twin total energy of the polaron. We approximate the one-electron wave function in a central field by the one parameter function for a smoothed hydrogenic potential $\chi_s(r)\sim(1+\alpha r)\exp(-\alpha r)$ where α is a variational parameter. As is well known, the wave function in the form of Gaussian function $\left(\chi\sim\exp(-\eta r^2)\right)$ incorrectly behaves close to points $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$. Such wave functions do not have the so-called "cuspidal point", which is available for Coulomb functions.

Fundamentally important in calculations of the correlation effects is the choice of initial basic of wave functions and point of origin. It is known that when we are looking for the absolute extremum of functional then value of its maximum is obtained in large disadvantage. In this case, the success of the method is largely dependent on the correct choice point of origin and of the two-centered functions. Therefore, to avoid this error, we need to pass to one-center wave basis. Generally, in the numerical calculations using the functional (1) and two-center wave functions we are faced with the problem of the two-center integrals calculations. To overcome this difficulty, you can use, for example, method [8]. This method allows you to move from two-center integrals to one-center integrals. Using this method, we can present the radial part $R_s(r)$ of the wave function $\chi_s^b(r)$ in the coordinates of which are assigned to center a as follows:

$$R_s(r)=\frac{\pi}{\alpha^2Cr}\left[\left(A_1-A_2r+A_3r^2\right)\exp(\alpha r)-\right.$$
$$\left.\left(A_1+A_2r+A_3r^2\right)\exp(-\alpha r)\right]\exp(-C)\,,\quad r<R,$$
$$R_s(r)=\frac{\pi}{\alpha^2Cr}\left[\left(B_1-B_2r+B_3r^2\right)\exp(-\alpha r)\right],\ r>R.$$

Here

$$A_1=2\left(3+3C+C^2\right),\ A_2=2\alpha(3+2C),\ A_3=2\alpha^2\,,$$
$$A_4=2\left(3-3C+C^2\right),\ A_5=2\alpha(3-2C),\ C=\alpha R\,,$$
$$B_1=A_4\exp(C)-A_1\exp(-C)\,,$$
$$B_2=A_5\exp(C)-A_2\exp(-C)\,,$$
$$B_3=A_3(\exp(C)-\exp(-C))\,.$$

In this representation, coordinate r is measured from the center of a. Similar expansions can be obtained for other wave functions.

When we use a one-center basis set functions unlike two-center basic set we can avoid problems of wave functions redundancy. This can lead to divergences in variational calculations (see, Eg., [3]). As it is well known [9]-[11], using of two-center basic set leads to an uncontrolled overestimation of electron-electron correlations in binding energy. In addition, using of one-center conception of the wave functions allow us to control the sequential convergence of variational procedure. As established in the paper [12] using of the one-center expansion is ideal for calculating energy derivatives (or finite difference energies) on the nuclear coordinates. Since we are interested in the behavior of the total energy at distances close to $R = 0$ we expand the functions centered at the point b in a power series in R about the origin a. Then, using (7), we can write the variation in the kinetic energy $\Delta T(R) = T(R) - 2T_s$ (where T_s is the average electron kinetic energy of an isolated polaron in the ground state) associated with the formation of bipolaron as follows:

$$\Delta T(R)=2\alpha_c^2\hbar\omega\times$$
$$\left(1.324\cdot10^{-5}R+7.58\cdot10^{-4}R^2+4.07\cdot10^{-7}R^3\right).\qquad(8)$$

Here, ω is the limiting frequency of long-wavelength phonons and we assumed that $\varepsilon^*/\varepsilon_\infty$ is equal to 1.0. In equation (8), we have retained the cubic terms in the parameter R.

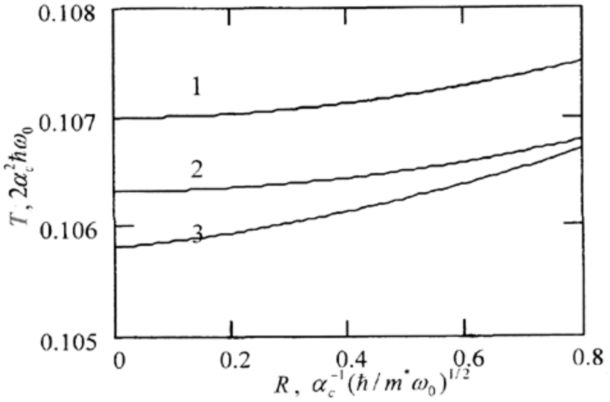

Fig. 1 Distance dependence of the electronic kinetic energy of axially symmetric large bipolaron: (1) is zeroth-order approximation; (2) wave function contains one additional configuration $2p^2$; (3) wave function contains two additional configurations $2p^2$ and $1s2p$.

It is seen from Figure 1 the average kinetic energy $T(R)$ has a minimum at $R = 0$. Therefore, the first derivative is positive and it follows from Eq. (6) that the total Hartree-Fock energy has maximum at $R = 0$; i.e., spherically symmetrical bipolaron is unstable even after taking into account electron correlations. These results (Fig.1) fully coincide with the results of variational calculations for bipolaron in the approximation of quasi-independent electrons [13] and remain valid for all values of the dielectric parameters of the polar medium admitting the existence of a bipolaron. Analysis has shown [4] that the difference $\Delta T(R)$ depends only weakly on the chosen basis of the one-electron functions $\chi_s(r)$, since the bipolaron bond energy is a composite quantity and the errors of the choice of the basic functions are compensated.

IV. STABILITY OF LARGE BIPOLARON AND ELECTRON-ELECTRON CORRELATIONS

Approximation of Hartree-Fock Hartree-Fock approximation takes into account the correlation of electrons due to antisymmetry of the wave function, but does not take into account the Coulomb electron-electron correlations.

In the variational procedure, the electron correlations can be taken into account either by including an additional function that depends explicitly on the distance r_{12} between electrons or by constructing of a two-electron function that takes into account the superposition of electronic configurations. These two approaches are alternative with proper application of the variational method [14], [15]. For the purposes of clarity and visibility of the results, we will use the second method. We add the electron configuration $2p^2$ to the initial function: $\chi_0(\mathbf{r}_1,\mathbf{r}_2;R)$.

According to Pekar [16] the 2*p* function corresponds to the lowest of the electron excited states of a large polaron. Thus, the trial electronic wave function can be written as the sum of the electron wave functions χ_0 and orthogonal complement (function χ_1):

$$\chi(\mathbf{r}_1,\mathbf{r}_2;R)\sim$$
$$\chi_0(\mathbf{r}_1,\mathbf{r}_2;R)+C_1(\chi_p^a(\mathbf{r}_1)\chi_p^b(\mathbf{r}_2)+\chi_p^a(\mathbf{r}_2)\chi_p^b(\mathbf{r}_1))$$
$$=\chi_0+C_1\chi_1\,, \qquad (9)$$

here $\chi_\mathrm{p}\sim\ z\exp(-\beta r)$ and the *z* axis coincides with bipolaron binding axis. The wave function (9) allows us to take into account the permutation degeneracy. The parameters β and C_1 are additional variational parameters. Functions χ_s and χ_p belong to the set of wave functions of the polaron Hamiltonian [16]. The representation of the wave function in the form of (9) virtually coincides with the approximation that was used in [11], [17], [18] and made it possible to obtain substantially more exact bond energies of the hydrogen molecule compared with the zeroth approximation. It was shown in Ref. [12] that the Hellman-Feynman variational theorem for optimum wave functions can be strictly satisfied only with such “floating” functions. Moreover, the new wave function must have the same qualitative properties as the initial wave function [19]. Again, we use expansion in a series the functions centered at the point *b* in (9). We easily obtain the following expression for the average kinetic energy:

$$T(R)=2\alpha_c^2\hbar\omega K(R)/N(R)\,, \qquad (10)$$

where

$$K(R)=0.107+0.038\cdot C_1^2+R$$
$$\times\left(1.324\cdot10^{-5}+1.045\cdot10^{-6}\cdot C_1+9.887\cdot10^{-4}\cdot C_1^2\right)+$$
$$R^2\left(7.58\cdot10^{-4}+5.23\cdot10^{-3}\cdot C_1-2.334\cdot10^{-4}\cdot C_1^2\right)+$$
$$R^3\left(4.07\cdot10^{-7}+2.183\cdot10^{-6}\cdot C_1-1.417\cdot10^{-5}\cdot C_1^2\right),$$
$$N(R)=1+C_1^2+C_1(2.286\cdot10^{-9}+4.573\cdot10^{-6}\cdot R$$
$$+2.287\cdot10^{-3}\cdot R^2+6.8\cdot10^{-5}\cdot R^3)\,.$$

We will test changes whether the sign of derivative $\lim\limits_{R\to0} dT/dR$ as compared to the zeroth-order approximation. To define energy (10) it is necessary to find the numerical value of the variational parameter C_1. Let us consider the difference $\Delta E(R=0)=-E(R=0)+2E_s$, which determines the effect of the interaction between polarons in ground state E_s. Omitting simple calculations we find the correlation contribution demotes the bipolaron energy, i.e., $\Delta E(R=0)>0$, if the following inequality is satisfied (for $\varepsilon^*/\varepsilon_\infty=1.00$):

$$2C_1^3V_1+2C_1^2V_3-C_1(-4V_1+4V_2)+2V_3<0\,, \qquad (11)$$

here

$$V_1=<\chi_s^2(r_1)\,|\,r_{12}^{-1}\,|\,\chi_s^2(r_2)>,\ V_2=<\chi_s^2(r_1)\,|\,r_{12}^{-1}\,|\,\chi_p^2(r_2)>,$$
$$V_3=<\chi_s(r_1)\chi_p(r_2)\,|\,r_{12}^{-1}\,|\,\chi_s(r_2)\chi_p(r_1)>.$$

Since the two-electron integrals satisfy to the relation $V_2\approx V_1/2$ inequality (11) can be rewritten in the form:

$$C_1^3V_1+C_1^2V_3+C_1V_1+V_3<0\,. \qquad (12)$$

Using the numerical values of the integrals and Eq. (12) we find that inequality (11) is satisfied if $C_1<-V_3/3V_1\approx-0.04$ ($V_3>0$, $V_1>0$). After simple mathematical manipulation we can write the second derivative in the following form

$$d^2E/dC_1^2=C_1^3V_1+3C_1^2V_3-3C_1V_1-V_3\,. \qquad (13)$$

From equation (13) it follows inequality: $C_1<-V_3/3V_1$. Hence the second derivative $d^2E/dC_1^2>0$; i.e., the electron correlation demotes the total bipolaron energy. Thus, the parameter C_1 must be negative and smaller than unity. That is, the correlation contribution to energy bipolaron is small. This contribution can not significantly alter the bond energy of bipolaron, which is obtained in the Hartree-Fock approximation. Straightforward variational calculations with simultaneous variation of the parameters α, *β*, and C_1 have given $C_1=-0.097$ for $R=0$ and for $\varepsilon^*/\varepsilon_\infty=1.00$. This value does not contradict the results obtained from conditions (12) and (13). Using the value $C_1=-0.1$, we obtain from (10) that in this case also $d^2E(R)/dR^2<0$ (line 2, Fig.1). Consequently, the spherically symmetric state of bipolaron has a maximum as $R=0$. That is, spherically symmetric bipolaron formation is unstable. This coincides with the results of Pekar and Tomacevich [16], [20].

Thus, the following important requirement of the variational method should be implemented. Not only the correction function should be close to zero approximation function, but theirs the first derivatives should be close too. Figure 2 shows that these requirements are not always met (see calculations in the paper [3]).

This result indicates the logical correctness of applying the variational procedure. That is, the bipolaron total energy reaches a maximum as $R\to0$, as well as in the case of the zeroth-order approximation. Therefore, a one-center bipolaron remains unstable. It is known [21] that, once the wave function has become close to the correct wave function, further changes in the wave function produce relatively small variations in the energy $E(R)$ rather than fundamental changes including a change in the symmetry of a large bipolaron. That is, calculations must demonstrate the convergence, and do not make radical changes in the Hartree-Fock state of the coupled system.

Let us increase the flexibility of the wave function by including one more electronic configuration $1s2p_z$:

$$\chi(\mathbf{r}_1,\mathbf{r}_2;R) \sim \chi_0(\mathbf{r}_1,\mathbf{r}_2;R) + C_1(\chi_p^a(\mathbf{r}_1)\chi_p^b(\mathbf{r}_2) + \chi_p^a(\mathbf{r}_2)\chi_p^b(\mathbf{r}_1)) + C_2\left(\chi_s^a(\mathbf{r}_1)\chi_p^b(\mathrm{r}_2) + \chi_s^a(\mathrm{r}_2)\chi_p^b(\mathbf{r}_1)\right) = \chi_0 + C_1\chi_1 + C_2\chi_2 \ . \tag{14}$$

Just simply we can show that the approximate value of the variational parameter is equal to $C_2 \approx 0.1$ as $R \to 0$. Line 3 (Fig.1) shows that a spherically symmetrical bipolaron remains unstable. Thus, no additional minimum for the energy of the bipolaron does not appear as that claimed in [3]. The variational function (14) belongs to the class of functions (7) and (9).

Additional the correctional functions χ_1 and χ_2 have a precise physical meaning. For example, the function χ_1 determines the contribution of the polarization effects to the binding energy. In accordance with theorem of Brillouin the electron excitation are determined by the wave function χ_2. The function in the form (14) proved to be very significant for diatomic molecules at any distances R [2], [22], [23].

Importantly, the correlation contributions must also take into account the spatial symmetry of the axially symmetric (two-center) bipolaron. That is, we must consider the point symmetry group, which corresponds to the Hartree-Fock spatial configuration of the bipolaron and by the irreducible representation by which must transform the electronic wave function [2], [4], [22]. The importance of considering the symmetry of a large bipolaron at the formation of the electronic wave function consists in the fact that it allows us to formulate the correct the regular principle of consistent expansion of the function flexibility and the convergence of the variational procedure. This principle is another natural restriction by using variational procedure that is imposed on the choice of the correction functions to the Hartree-Fock approximation. As is well known, the wrong choice of the basis set functions is the source of large errors (Fig.2) of the variational procedure. The use of additional conditions within the variational method is natural and abundant in other physical problems. For example, in the variational problems of the quantum collision theory are used so-called "principle of radiation" as an additional condition (requirement of the satisfiability of causal-investigatory conditions) [19].

Figure 1 shows that increasing the flexibility of the electronic wave function reduces to decrease of the correlation contributions step-by-step to the binding energy of the bipolaron as $R \to 0$, and for the bipolaron binding energy is retained maximum when $R = 0$ ($\lim_{R\to 0} d^2E/dR^2 < 0$ and $\lim_{R\to 0} dT/dR > 0$). Spherically symmetric state of a large bipolaron remains unstable, even at varying of the functional by four parameters α, β, C_1 and C_2. That is, the symmetry of zeroth-order approximation is retained. The sensitivity analysis of the equation (6) to changing of the parameters C_1 and C_2 shows that the sign of the second derivative does not change in a wide range of variation of these parameters. It is well known [21] that the method of expansion by the electronic configurations is able approximate the solution of the Schrödinger equation with any accuracy.

Smallness of the variational parameters $|C_1| << 1$ and $|C_2| << 1$ indicates that the correlation effects are the corrections to the zeroth-order approximation as it is required for coupled electronic systems. It is well known that the correction to the eigenvalue has the second order of smallness by difference $|\chi - \chi_0|$.

The same conclusions about the instability of a spherically symmetric bipolaron can be obtained by solving of the differential equation (5). This equation relates to the type of Riccati equations. Approximating the kinetic energy under condition $R \to 0$ by the function $T(R) = B + A \cdot R^2$ it is easy to find the solution of the differential equation:

$$d(RE(R))/dR + B + A \cdot R^2 = 0 .$$

The solution of this equation can be written in the following form: $E(R) = -B - A \cdot R^2 / 3$. Here A and B are positive constants. It follows inequality: $\lim_{R\to 0}(d^2E(R)/dR^2) < 0$, that is spherically symmetric bipolaron remains unstable.

As it is noted in the paper [24] the least preconceived approach to calculate of the correlation contribution in binding energy is the approach that simulates the sequence of the perturbation series. This is an important provision of the variational approach is ignored often. Hence, the calculation of variations of these authors leads to a significant overestimation of the contribution of electron-electron correlations in the bipolaron binding energy.

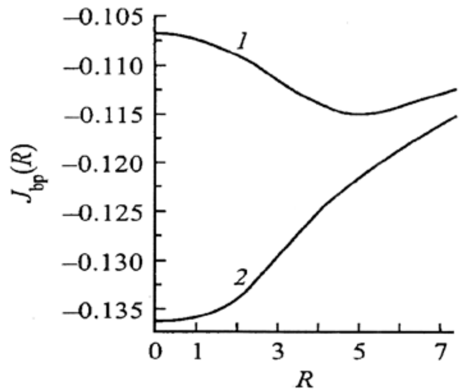

Fig. 2 Line 1 is the total energy of the bipolaron in Hartree-Fock approximation; line 2 is the total energy after accounting electron-electron correlations. Figure was taken from [3].

Large quantity of studies have firmly established [9] that zeroth-order approximation gives for diatomic molecules contribution to the total electron energy is equal to 95–99.5%, and only the remaining 0.5–5% gives the electron-electron correlations contribution. Evidently, for such ratio in the energies, the correlation contribution can't change the spatial symmetry of the coupled system corresponding to the zeroth-order approximation. Practically, from calculations of the global minimum follow that zeroth-order approximation becomes a correction to the electron-electron correlations contributions (Fig.2). This is obviously absurdly.

Thus, increase the flexibility of the trial functions and additional taking into account of electron-electron correlations does not alter fundamentally the functional dependence of the bipolaron potential on the distance between the centers of gravity of polarons. Maximum of the bipolaron potential remains valid at $R = 0$ (Fig.3). This result coincides with the known results of Pekar and Tomacevich [16], [20]. With correct application of variational method the contribution of electron-electron correlations to the binding energy is identical [14], [15] using both the method of superposition of electronic configurations and by using the explicit dependence of the wave function of the distance r_{12}.

It is known [9], [25] the contribution of electron-electron correlations to the electronic energy follows the same virial rule as for the quasi-independent electrons in zeroth-order approximation:

$$R\frac{dE_{corr}(R)}{dR} + 2T_{corr}(R) + U_{corr}(R) = 0 .$$

Therefore, the dependence of the bipolaron potential of R has the same form both for the quasi-independent electrons (zeroth-order approximation) and for the contribution of the electron-electron correlations to the binding energy. This relationship remains valid for the entire domain of bipolaron existence along the all admissible values of the parameter $\varepsilon^* / \varepsilon_\infty$.

Qualitatively, the correlation energy $E_{corr}(R)$ correlates (Fig.3) with approximation of Hartree-Fock [9]. It is well known that double excited electronic configurations make a smaller contribution to the binding energy compared with single excited configurations. Namely this argument is confirmed by the calculations, which are presented in Fig.3.

The importance of considering the bipolaron symmetry at the construction of the wave function consists that it is allows us to formulate the correct consecution of expansion of the basis set of elements that belong to the same set. If the set of functions is not invariant, then search of eigenvalue becomes uncertain. The set of functions with a given symmetry form a linear space, as well as their linear combination belongs to this space. At the same time, the combination of Gaussian functions [3] does not form a linear space.

At short distances the greatest contribution to the binding energy comes from the so-called "axial" correlation between the electrons [17], [26]. However, calculations show that even these correlative contributions can't change the bipolaron axial symmetry (Figs.3 and 4). If the spherically symmetric bipolaron is stable then the additional incorporation of the so-called "ionic" correlative terms (Weinbaum's function [27]) must result to stabilization of the bipolaron.

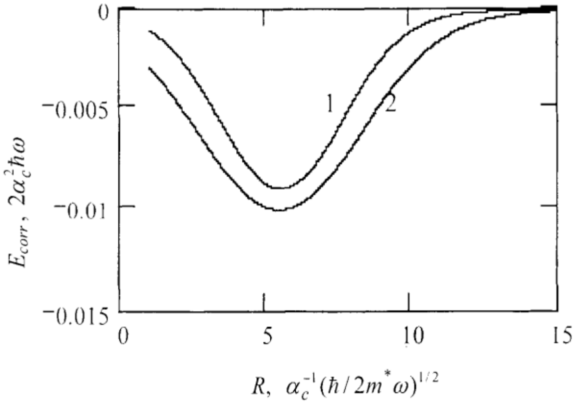

Fig. 3 Distance dependence of the correlation contributions to the axially symmetric large bipolaron binding energy ($\varepsilon^*/\varepsilon_\infty = 1.05$). (1) corresponds to the wave function (9); (2) corresponds to the wave function (14).

However, simple and physically understandable calculations demonstrated that these correlation corrections do not contribute to the binding energy of the spherically symmetric bipolaron. Indeed, in this case the electronic wave function can be written as a sum of the wave functions [27]:

$$\chi(\mathbf{r}_1,\mathbf{r}_2;R) \sim \chi_0(\mathbf{r}_1,\mathbf{r}_2;R) + \mu\left(\chi_{1s}^a(\mathbf{r}_1)\chi_{1s}^a(\mathbf{r}_2) + \chi_{1s}^b(\mathbf{r}_1)\chi_{1s}^b(\mathbf{r}_2)\right). \qquad (17)$$

Here μ is additional linear parameter and obviously $0 \le \mu \le 1$. It would seem that this term must give the contribution to the stabilization of the spherically symmetric bipolaron. The electronic energy of a bipolaron in the maximum of the bipolaron potential ($R = 0$) can be represented in the following form ($\varepsilon^* / \varepsilon_\infty = 1.00$):

$$E(\mu) = -[(0.918 + 2.982\mu + 4.016\mu^2 + 2.331\mu^3 + 0.557\mu^4)\times (2.787 + 5.019\mu + 2.791\mu^2)^{-2}]\times 2\alpha_c^2\hbar\omega \ . \qquad (18)$$

The numerical values in (18) we obtained for the case that is the most favorable for the positive manifestations of so-called "ionic" correlation contributions. Direct Coulomb repulsion between electrons is extremely weakened for the parameter of $\varepsilon^* / \varepsilon_\infty = 1.00$. The extremal properties of the functional (18) demonstrate that the variational parameter μ = 0; i.e., one-centered electron-electron correlations do not lead to stabilization of spherically symmetric bipolaron. At the same time if we use the wave function in the form of (17) then it leads to the stabilization of an axially symmetric bipolaron.

This conclusion remains valid over the entire range of acceptable values $\varepsilon^* / \varepsilon_\infty$. In this situation the contribution to the bipolaron bonding energy is due to by oscillations of electron between two potential wells [28].

In the papers [29]-[31] we are demonstrated the pair bipolaron potentials for a wide range of dielectric constants. In addition, we take into account the additional restrictions imposed by the virial interrelations, orthogonality requirements, spatial symmetry and convergence of variational procedure. Within those functions, the inequality: $dT/dR > 0$ is likewise satisfied; i.e., for spherically symmetric state of a large bipolaron remains unstable (Fig.4). Figure 4 shows the rapid convergence of the variational procedure. The problem of symmetry of the wave function by using the variational principle is discussed in the paper [19].

Thus increase the flexibility of the trial wave function leads only to increasing of the binding energy of the axially symmetric singlet bipolaron. However, the common character of the dependence of the bipolaron binding energy from the distance *R* remains the same as for quasi-independent electrons and does not depend of the dielectric properties of the polar medium (Figs. 4 and 5).

For curve 4 (Fig.4) we used a superposition of four electronic configurations: basic (see (7)), singly excited: 1*s*+2*p* and 1*s*+2*s*, and doubly excited configuration: 2*p*+2*p*. In a symbolic form the electronic wave function can be written as follows:

$$\chi \sim \chi_0(1s^2) + C_1\chi_2(2p^2) + C_2\chi_1(1s2p) + C_3\chi_3(1s2s)\,. \qquad (19)$$

Function χ_{2s} was chosen in the following form: $\sim(1-\gamma_1 r)\exp(-\gamma_2 r)$, where γ_1 and γ_2 are additional variational parameters. The sequence of the functions χ_i belongs to the range of definition of the polaron functional.

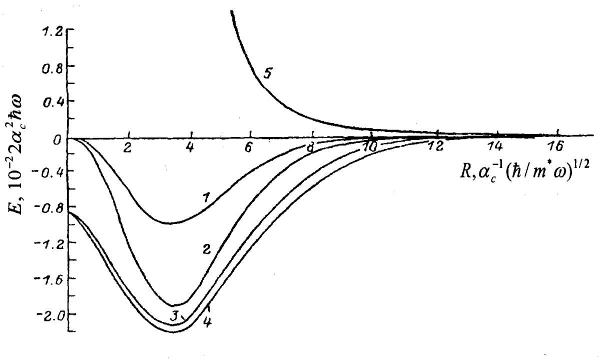

Fig. 4 The binding energy of the axially symmetric large bipolaron versus of distance *R* ($\varepsilon^* / \varepsilon_\infty = 1.00$). (1) $C_1 = C_2 = C_3 = 0$ (zeroth-order approximation); (2) $C_1 \neq 0$, $C_2 = C_3 = 0$; (3) $C_1 \neq 0$, $C_2 \neq 0$, $C_3 = 0$; (4) $C_1 \neq 0$, $C_2 \neq 0$, $C_3 \neq 0$; (5) triplet state of the bipolaron.

Number of variational parameters run up to seven, but no additional minimums does not appear (Fig.4). On the contrary there exists a smooth downtrend in bipolaron potential with increasing flexibility of trial function. At the same time is kept the qualitative dependence of the potential on the distance *R* and transition to a spherically symmetric state of bipolaron does not occur. If the variational procedure is used correctly no significant change of the bipolaron binding energy does not happen, and there no exist any change in the spatial symmetry of bipolaron. In this case the equilibrium distance $R \neq 0$ remains between the polarons for each value of $\varepsilon^* / \varepsilon_\infty$. For series of the minimizing electronic functions (7), (9) and (19) justly the following inequality: $\lim\limits_{R\to 0} dT/dR > 0$. That is, the bipolaron potential retains the shape. Spherically symmetric singlet state of bipolaron is unstable. In addition, it should be noted that we get rapid convergence of variational series (Figure 4). According to the literature it is known [9] that for the calculation of the dissociation energy of diatomic molecules sufficiently to consider only two electronic configurations. Increase the flexibility of the wave function retains the correct uniform convergence of the results, in accordance with the requirements of the variational method (compare with curve 2 of the Figure 2).

At the same time, using equation (5) and (6) it can be shown [32]-[34] that the triplet electron-excited states of a large bipolaron are one-center formations (except of the state ${}^3\Sigma_u$, which is repulsive (Fig. 5)). Studies have shown that the singlet electron-excited states of the bipolaron are axially symmetric quasimolecular formations.

Change in the equilibrium distance between polarons is due to modification of the parameter $\varepsilon^* / \varepsilon_\infty$ (Fig.5). Figure 5 shows that increasing of the ratio $\varepsilon^* / \varepsilon_\infty$ leads to monotonous decreasing of the bipolaron binding energy at that the equilibrium distance between the polarons is increased. Reducing the binding energy of the bipolaron is accompanied by increasing the effective size of large bipolaron . At the same time the spherically symmetric bipolaron is not sensitive to changes of the polar medium.

Fig. 5 The bipolaron binding energy in the ground state versus of the distance *R*. $\varepsilon^* / \varepsilon_\infty$ = 1.00 (1), 1.02 (2),1.05 (3), 1.08 (4), 1.10 (5).

Variational calculations of the paper [3] are characterized by the divergent sequence, i.e. stationary points can not be determined. Such variational calculations lead to instability of the computational algorithm. Therefore, Ritz computational procedure should be verified by requirement of procedure stability and convergence. That is, the parameters of the Ritz procedure vary significantly and the approximation to the solution very differs from the zeroth-order approximation. This makes Ritz procedure unstable and diverging. Incorrect application of the variational method leads to a significant overestimation of the electron-electron correlations contribution to the binding energy of a large bipolaron. This is due nonoptimality of two-electron wave functions, which in turn leads to unfounded changes in the spatial symmetry of bipolaron. The consequence of this is the results that have no physical meaning. In accordance with the perceptive remark of Epstein [35] such bipolaron calculations can be attributed to "pathological type."

In the paper [36] is used the density matrix formalism of Gunnarsson-Lundqvist [37] to account the electron-electron correlations. The results of this work also point to the instability of a spherically symmetric bipolaron. In the paper [38] it is shown that the bipolaron Hamiltonian has not spherically symmetric solutions for the singlet spin state in the presence of electron-electron repulsion.

Further, it will be shown that the axially symmetric bipolaron interprets correctly experimental data.

V. INTERPRETATION OF EXPERIMENTAL DATA

A. Regeneration of Hydrated Electrons

Axially symmetric large bipolaron allow us to interpret the spectroscopic experiments. It has been experimentally established [39] that on photo-excitation of a hydrogen-saturated alkali system by light in the UV region of the spectrum, hydrated electrons (e_{aq}) were formed at a concentration 10^{-6}M. As one would expect, disappearance hydrated electrons occurred according to a second order law. Subsequent irradiation of the system by pulses of red light ($\lambda_{\text{exp}} > \lambda_{\min}$ = 700nm) after disappearance of 98% of the hydrated electrons led to regeneration of trapped electrons e_{aq} (polaron type). Here we assumed that the reason of regeneration is optical excitation of the bound two electron species (bipolaron type) decaying to the reaction:

$$(e_{aq})_2 \xrightarrow[\lambda > 700\text{nm}]{} e_{aq} + e_{aq}\,.$$

Formation of molecules H_2 following after disappearance of hydrated electrons, which occurs considerably slower than the primary process is in favor of the existence of the bound two-electron species. Further experiments of flash photolysis [39] have confirmed the existence in aqueous solution of singlet $(e_{aq})_2$.

Figure 6 demonstrates that the singlet ground and excited states of large bipolaron correspond to axisymmetrical state, while the triplet states of the bipolaron are spherically symmetric formations. This result is physically obvious and understandable. For triplet bipolaron formations [40] the electrons are at different orbitals and distant from each other.

As shown in the papers [4,6,7], the transitions ${}^1\Sigma(1s^2) \to {}^1\Sigma(1s2p_z)$ and ${}^1\Sigma(1s^2) \to {}^1\Pi(1s2p_{x\pm iy})$ will be most probably (oscillator strength in dipole approximation will be following $f \geq 0.7$). Here the *z* axis coincides with the symmetry axis of the large bipolaron; the indices in parentheses of the spectroscopic symbols signify the single-electron states, arising on adiabatic propagation of hydrated electrons at the distance $R \to \infty$. Figure 6 shows the electronic terms of axially symmetric large bipolaron are given as functions of the distance *R* for $\varepsilon^* / \varepsilon_\infty = 1.02$ ($\varepsilon_s = 78.3$, $\varepsilon_\infty = 1.78$).

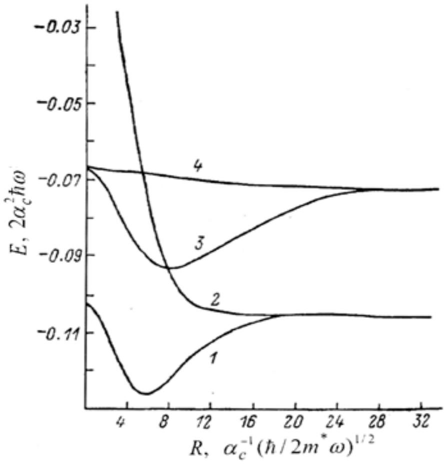

Fig. 6 The ground state and excited quasi-molecular terms of the axially symmetric bipolaron for $\varepsilon^* / \varepsilon_\infty = 1.02$. (1) ${}^1\Sigma(1s^2)$; (2) ${}^3\Sigma(1s^2)$; (3) ${}^1\Sigma(1s2p_z)$; (4) ${}^1\Pi(1s2p_{x\pm iy})$.

Let us examine the dipole-allowed electronic transition ${}^1\Sigma(1s^2) \to {}^1\Pi(1s2p_{x\pm iy})$ the frequency of which at the maximum of the absorption band in correspondence with the Frank-Condon principle we determine from the Pekar's relation [16]:

$$\hbar\Omega_1 = | E_1 - E_0 | + \frac{A_0^1}{2}\sqrt{n(1+n)}\ln\left(1+\frac{1}{n}\right),$$
$$n = \left[\exp(\hbar\omega / k_B T) - 1\right]^{-1}, \qquad (20)$$

here $E_0 = -1.26 \cdot 10^{-1} \cdot 2\alpha_c^2 \hbar\omega$, $E_1 = -6.8 \times 10^{-2} \cdot 2\alpha_c^2 \hbar\omega$ are the self-consistent total energies of the initial (0) and final (1) electronic states, respectively. The energy of reorganization of the polarization state of the polar medium as a result of the photo-transition ($0 \to 1$) is determined from the relation

$$A_0^1 = \left(\frac{2}{\hbar\omega}\right)_{\mathbf{k},\, j=1,2} \sum |\mathrm{V}_{\mathbf{k}}[\rho_{\mathrm{j}}^{(0)}(\mathbf{k}) - \rho_{\mathrm{j}}^{(1)}(\mathbf{k})]|^2 ,$$

$$\mathrm{V}_{\mathbf{k}} = \frac{e}{k}\left(\frac{4\pi\hbar\omega}{V\varepsilon^*}\right)^{1/2}, \tag{21}$$

here

$$\rho_1(\mathbf{k}) = \int |\chi(\mathbf{r}_1, \mathbf{r}_2)|^2 \exp(i\mathbf{k}\mathbf{r}_2) d\tau_1 d\tau_2 .$$

Frequency ω can be estimated from the half-width $W_{1/2}$ of the optical absorption band of polaron. In the low-temperature limit ($n < 1$)

$$W_{1/2} = 2\sqrt{A_0^1 \hbar\omega \ln 2} . \tag{22}$$

Here the energy of reorganization of the polar medium A_0^1 relates to the $1s \to 2p$ phototransition of the polaron. Taking into account the known experimental value $W_{1/2} = 0.29\text{eV}$ [39] from (22) we find $\omega = 2.2 \cdot 10^{13}\text{sec}^{-1}$. The isotropic electron effective mass is equal to $m^* = 2.52m$, which we determined by comparing the experimental and theoretical the maximums optical absorption of the hydrated electron.

Considering that the photo-transition is performed from the minimum ($R_0 = 4.32 \cdot \alpha_c^{-1}(\hbar / m^*\omega)^{1/2}$) of the ${}^1\Sigma(1s^2)$ ground term (Fig.6), i.e., we neglect the intrinsic vibrational-rotational structure of the bipolaron [31]. For the temperature conditions usual in experiment (T = 298K) from Eq. (20) we obtained: $\hbar\Omega_1 = 6.81 \cdot 10^{-2} \cdot 2\alpha_c^2 \hbar\omega = 1.41\text{eV}$. These conditions correspond to the wavelength: $\lambda = 877\text{nm} > \lambda_{\min}$. It is not difficult to see from Fig.7 the final term ${}^1\Pi(1s2p_{x\pm iy})$ (line 4, Fig.7) is repulsive in the entire interval of distances R, which finally leads to dissociation of a bipolaron. For the transition ${}^1\Sigma(1s^2) \to {}^1\Sigma(1s2p_z)$ the situation turns out to be different. We calculated the transition energy by using (20): $\hbar\Omega_2 = 1.37\text{eV}$. This corresponds to the wavelength: $\lambda = 905\text{nm} > \lambda_{\min}$. After the transition the electronic subsystem turns out to be into nonequilibrium state and during the time $\tau \approx \omega^{-1}$ relaxes to the minimum of state ${}^1\Sigma(1s2p_z)$ (line 3, Fig.6) through which the repulsive triplet term ${}^3\Sigma(1s^2)$ (line 2, Fig.6) passes. In the vicinity of the crossing point of the terms due to interactions acting on the spin variables (for example, transverse optical vibrations of a polar medium [41] generating an oscillating magnetic field) intercombinational singlet-triplet transitions ${}^1\Sigma(1s2p_z) \sim\sim> {}^3\Sigma(1s^2)$ are possible with a high probability.

With a lowering of temperature the absorption band is shifted into the long-wavelength region and for T = 80K at the maximum of the absorption band $\hbar\Omega_3 = 1.26\text{eV}$ ($\lambda_{\text{theor}} = 982\text{nm}$). The wavelength obtained very close to the experimental value $\lambda = 1000\text{nm}$ [39]. At the same time the wavelength corresponding to the energy of photo-ionization ($I = 0.178 e^4 m^* / \varepsilon^{*2} \hbar^2$) of bipolaron turns out to be considerably shifted into the short-wave region: $\hbar\Omega_1 = 0.77\text{eV}$. It is important to note that bipolaron formations is accompanied by a shift of the absorption band to longer wavelengths region with respect to the experimental absorption band of the hydrated electron ($\hbar\Omega_{\max}(e_{aq}) = 1.73\text{eV}$ [39]).

B. The Absorption Band of the Bipolaron in Ammonia

According to magnetic and optical studies, and studies of the electron mobility, reliably experimentally established [42,43] that in ammonia systems there exist highly mobile two-electron diamagnetic formations of bipolaron type. Bipolarons were found in organic compounds [44]-[46], molten salts [47], metal-ammonia systems [43]-[53], and vanadium bronzes [54]. According to Mott [55] a sequence of experimental data can be interpreted only suggesting the possibility of the existence of two-electron mobile diamagnetic formations in the polar media. This opinion is shared by Thompson [56]. Importantly, alkali metal ions in the ammonia solution have not the affinity to the solvated electron [43].

Furthermore, the optical properties of additional electrons are identical both the injected electrons and the dissolved alkali metals. That is, the electrons are not associated with cations.

It is well-known experiments that studied the conductivity of the metal-ammonia solutions. It is found that with a change of the electron concentration the electrolytic equivalent conductance of electrons varies unusual manner. With increasing of the electron concentration of 0.01 M to 0.4 M the conductivity is reduced by 20%. At the same time reduces the paramagnetic susceptibility of the solution. According to the authors [53] occurs pairing of electron spins without the participation of the metal cations. A further increase in concentration leads to the restorer of conduction.

It has been established experimentally [52], [57] that electrons in metal-ammonia systems able to form of the bipolarons with dissociation energy D = 0.15−0.2eV. For the axially symmetric bipolaron in ammonia theoretical estimates give the following value: D = 0.14−0.16eV [58]. The applicability of the polaron model to describe the properties of electrons in polar liquids has been discussed repeatedly [43], [59]-[61]. As it turned out, many of the properties of electrons in ammonia can be interpreted using the polaron theory.

Now that, using the system of electronic terms of a bipolaron (Fig.7), we will compare the experimental optical characteristics of the bipolaron in ammonia ($\varepsilon^* / \varepsilon_\infty = 1.075$) with the theoretical calculations. The optical transition ${}^1\Sigma(1s^2) \to {}^1\Sigma(1s2p_z)$ is assumed to take place from the minimum of the ground term: $R_0 = 5.1\alpha_c^{-1}(\hbar / m^*\omega)^{1/2}$. The total self-consistent energies of the initial and final states are: $E_0 = -1.158 \cdot 10^{-1} \cdot 2\alpha_c^2\hbar\omega$, $E_1 = -8.77 \cdot 10^{-2} \cdot 2\alpha_c^2\hbar\omega$, respectively; $A_0^1 = 8.68 \times 10^{-2} \cdot 2\alpha_c^2\hbar\omega$. Since the optical measurements is usually carried out at 225 K we obtain from (20) the following energy: $\hbar\Omega_1 = 0.77\text{eV}$. The transition ${}^1\Sigma(1s^2) \to {}^1\Pi(1s2p_{x\pm iy})$ is also possible. In this case, for the self-consistent final state we have: $E_1 = -6.5 \times 10^{-2} \cdot 2\alpha_c^2\hbar\omega$, $A_0^1 = 2.7 \times 10^{-2} \cdot 2\alpha_c^2\hbar\omega$, and the transition energy is equal to $\hbar\Omega_2 = 0.84\text{eV}$. Here we used the following parameters for the polaron in ammonia: $\varepsilon_\infty = 1.756$, $\varepsilon_s = 22.8$, $m^* = 1.73m$, $\omega = 5.5 \cdot 10^{13} s^{-1}$, $\alpha_c = 13.4$.

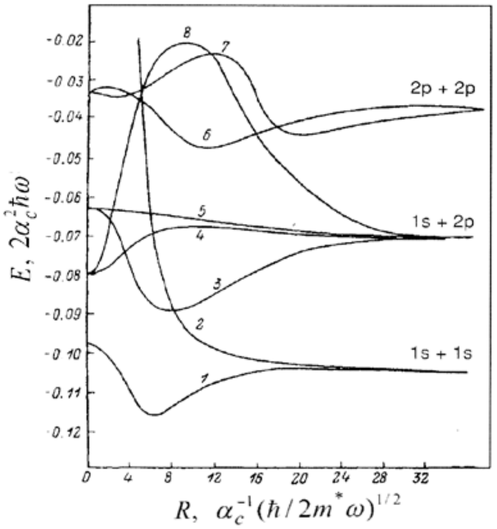

Fig. 7 The ground state and excited quasi-molecular terms of the axially symmetric bipolaron ($\varepsilon^* / \varepsilon_\infty = 1.075$). (1) – ${}^1\Sigma_g(1s^2)$; (2) – ${}^3\Sigma_u(1s^2)$; (3) – ${}^1\Sigma_g(1s2p_z)$; (4) – ${}^3\Pi_u(1s2p_{x\pm iy})$; (5) – ${}^1\Pi_g(1s2p_{x\pm iy})$; (6) – ${}^1\Sigma_g(2p_z^2)$; (7) – ${}^1\Delta_g(2p_{x\pm iy}^2)$; (8) – ${}^3\Sigma_g(1s2p_z)$.

Details of the calculations are presented in the papers [33,58]. Thus, the maximum of the bipolaron absorption band in both the first and second case is close to the experimental maximum photo-transition of polaron in the metal-ammonia system $\hbar\Omega_{\max}(1s \to 2p) = 0.885\text{eV}$. Similarly to the hydrated electron it has been experimentally established [39] that the maximum of optical absorption band for bipolaron in ammonia is shifted to longer wavelengths region. The measurement of the position of the absorption band maximum of the bipolaron, gives the value $\hbar\Omega_{\exp} = 0.81\text{eV}$ that is within the range of calculated frequencies. The theoretical maximum turns out to be precisely in the 0.81–0.82eV energy range. In which connection for a sequence of excited electronic terms of bipolaron, is kept well-known Hund's rule as $R \to 0$ (Fig.7). Axially symmetric large bipolaron allows us to interpret correctly other experimental data.

C. The Magnetic Susceptibility of Polarons in Ammonia Systems

Study of the concentration dependence of electron magnetic susceptibility of the metal-ammonia systems have shown [62], [63] that the static susceptibility depends on the concentration of dissolved alkali metal. Susceptibility is changed from a paramagnetic state to a diamagnetic state in the area of electron concentration 10^{19} - 10^{20} cm^{-3} at temperature below 200K. Additional experimental studies [64] confirmed the pairing of electron spins.

Using the results of the paper [65], we can write the diamagnetic contribution to the susceptibility in the following form:

$$\chi^{(d)} = -(e^4 / 4m^*c^2)\sum_{i=1,2}\left\langle \chi(\mathbf{r}_i) \,|\, r_i^2\delta_{\alpha\beta} - r_{i\alpha}r_{i\beta} \,|\, \chi(\mathbf{r}_i) \right\rangle$$
$$= -39.52\mu_B^2 a_0 / e^2, \quad \alpha, \beta = x, y, z. \qquad (23)$$

Here μ_B is the electronic magneton; a_0 is Bohr radius.

For axially symmetric electron systems the paramagnetic susceptibility can be approximated by the following equation [66]

$$\chi^{(p)} = 2(\chi_{xx}^{(d)} - \chi_{zz}^{(d)}) / |\, \chi_{yy}^{(d)} = 1.52\mu_B^2 a_0 / e^2. \qquad (24)$$

Electronic magnetic susceptibility can be written as follows:

$$\chi = n_p\chi_p + n_{bp}\chi_{bp}. \qquad (25)$$

Here, χ_p is the magnetic susceptibility of polarons, which also takes into account the Pauli spin paramagnetic susceptibility $\chi_{pauli} = \mu_B^2 / k_B T$; χ_{bp} is the magnetic susceptibility of a bipolaron. The total number of electrons is equal to $n_p + 2n_{bp} = n_0$. In accordance with the low of mass action, the equilibrium constant K of the reaction $n_{bp} \leftrightarrow 2n_p$ in the thermodynamic equilibrium state at temperature T is given by

$$nK = \frac{n_p^2}{n_{bp}} =$$
$$4\left(\frac{m_p^{**}k_B T}{2\pi\hbar^2}\right)^3 \left(\frac{2\pi\hbar^2}{m_{bp}^{**}k_B T}\right)^{3/2} \frac{\exp(-D_{bp} / k_B T)}{Z_{vibr}Z_{rot}}. \qquad (26)$$

Here Z_{vibr} and Z_{rot} are the vibrational and rotational partition functions of the bipolaron, and D_{bp} is its dissociation energy.

In Fig. 8 is made the comparison between the theoretical and experimental results [62], [63] for the magnetic susceptibility of metal-ammonia systems at temperatures of 198 and 239 K as a function of the degree of dilution of the solution lg(n/n_0), where $n = 2.43 \cdot 10^{22}$ cm^{-3} is the concentration of solvent atoms [59] and n_0 is alkali metal concentration. In Figure 8, we present the change of the equilibrium concentrations of polarons and bipolarons depending as a function of concentration of dissolved alkali metal Na. It can be seen that the formation of bound electron pairs is initiated at alkali metal concentrations of $\approx 5 \cdot 10^{17}$ cm^{-3}; in the range $n_0 \approx 3 \cdot 10^{18}$ to 10^{19}cm^{-3} the number of diamagnetic formations begins to exceed the number of polarons.

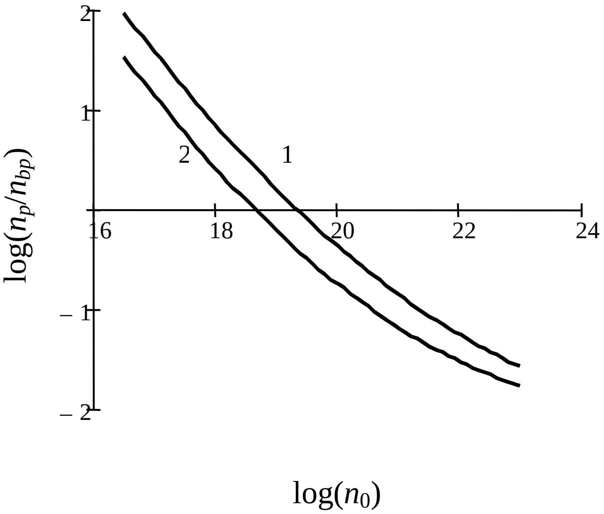

Fig. 8 The relative concentrations of polarons and bipolarons as a function of dissolved metal concentration. (1) T = 239 and (2) 198 K.

It is important to emphasize that in this region of concentrations there exist a shift of the maximum of the optical absorption band toward the long-wave region (Section V B). In this concentration range it is found that equivalent conductivity of electrons decreases on 20%. This drop of conductivity may be due to the formation of bipolarons. These findings are confirmed by measuring of the proton relaxation velocity [67]. These studies show that the formation of singlet spin pairs is initiated at concentrations $n_p \approx 5 \cdot 10^{17}$ to $3 \cdot 10^{18}$ cm^{-3}.

To compare the theoretical results of the calculation of the static magnetic susceptibility with experiment, we use the following equation

$$C_k = N_A \chi T / n_p = N_A \mu_B^2 \left[\chi_p / \chi_{Pauli} - (\chi_{bp} / \chi_{Pauli} - 2) n_{bp} / n_p \right] / k_B , \qquad (27)$$

here N_A is Avogadro number.

Figure 9 demonstrates the comparison of the theoretical and experimental [62] atomic magnetic susceptibilities as a function of concentration for two temperatures 198 and 239 K.

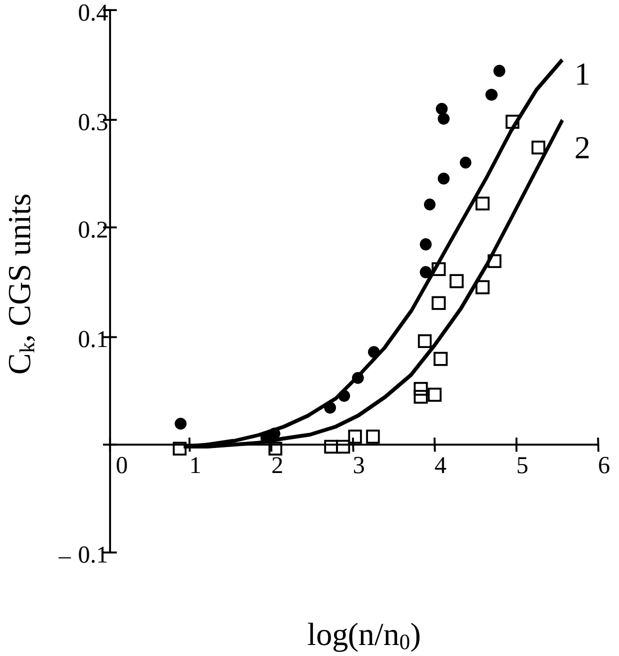

Fig. 9 Atomic magnetic susceptibility as a function of concentration. The solid curves give the theoretical results.
●, □ experimental values for T = 239 (1) and 198 K (2), respectively [62].

We proposed a theoretical model that correctly describes the dependence of the magnetic susceptibility both the concentration and the temperature. As increasing of the electron concentrations and lowering the temperature the paramagnetism of electrons decreases. Magnetic susceptibility of C_k changes sign when the electron concentration is equal to $n \approx 10^{21}$ cm^{-3}. The system of electrons in ammonia becomes diamagnetic completely ($C_k < 0$). The detailed mathematical analysis of the magnetic susceptibility dependence on the temperature and the concentration we have given in the paper [65].

VI. CONCLUSION

This shift of optical band is confirmed by theoretical calculations for the axially symmetric large bipolaron (Sections V A and V B) and it is in complete agreement with the observed change in the optical absorption band when passing from two separated ($R \to \infty$) hydrogen atoms (spherically symmetric) to a hydrogen molecule (axially symmetric) [68], i.e., at the change from a spherically symmetric object to an axially symmetric object. This rule is observed for other two-electron physical objects. For example, a similar shift in the long wavelength region of the optical spectrum was noted for quasi-molecular biexciton [69]. However, for the spherically symmetric small bipolaron which analogous to a helium atom that corresponds to bipolaron calculations [3], the expected shift of the optical absorption maximum would occur to the opposite (short-wavelength) region of the spectrum. This is confirmed by experiment [70]. We present in this article the numerous theoretical arguments which indicate that inclusion of electron-electron correlations does not lead to the stability of spherically symmetric bipolaron. Beside that the spherically symmetric model of bipolaron also come into conflict with the existing experimental data.

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