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LANDAU-PEKAR BIPOLARON IN SINGLET AND TRIPLET STATES

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ABSTRACT

We give an overview of studies a bipolaron stability by variational method. For bipolaron formations, a relation is established between the variational principle and the virial theorem optimizing the electronic wave functions. We present a large number of qualitative and quantitative arguments, which indicate that the Landau-Pekar bipolaron is an axially-symmetrical formation. Much attention is paid to the analysis of the influence of the Coulomb electron-electron correlations on the stability of a large bipolaron. In detail we analyzed the criteria for determining the optimal wave functions. It is established that a step-by-step increase in the flexibility of the electronic wave function due to the electron correlations does not stabilize a one-center bipolaron. We show after into account of electron-electron correlations a singlet bipolaron retains spatial axially-symmetrical. At the same time, the electron-excited triplet states of Landau-Pekar bipolaron have spherical symmetry. The results of Kasirina and Lakhno are based on the one-center bipolaron model are incorrect. Presented evidence that the correct application of the variational method and correct account of electron-electron correlations only increase the binding energy of the bipolaron but symmetry of Hartree-Fock approximation can not change. We adduce proofs which point to methodological errors of one-center bipolaron model as well as arising from their calculations incorrect physical consequences. As illustrated in this review the axially symmetric Landau-Pekar bipolaron can correctly interpret the experimentally detected spectroscopic data.

Keywords: Large bipolaron, Electron correlations, Singlet, Stability, Triplet, Variational procedure, Virial.

Contribution/ Originality

We have established mathematically that the spatial symmetry of the singlet bipolaron Landau-Pekar is axial-symmetric. At the same time, triplet states of the bipolaron are spherically symmetric formations. Increasing the flexibility of the wave function does not change the spatial symmetry of the bipolaron. Knowledge of the bipolaron symmetry allows to correctly interpret experiment.

1. INTRODUCTION

Recently, 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 various approximate 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 conditional (local) minimum of the energy of a system can be unintentionally replaced by study of the unconditional (absolute) minimum, which has no physical meaning.

In this paper, we study the relation between the variational method and the virial theorem with regard to the problem of bipolaron stability, analyze additional restrictions which optimize variational electronic wave functions of bipolaron problem, and discuss the physical consequences of these restrictions. The complication regarding a trial electronic wave function is primarily related to the correct description of electronic correlations in two-electron systems. Pekar and Tomasevich [2] were the first to include the electron-electron correlations by introducing the functional dependence of the wave function on the distance between the electrons. They have established that the inter electron correlations do not stabilize a one-center large singlet bipolaron with respect to the dissociation into two large polarons.

Studies of the dependence of the Hartree-Fock self-consistent approximation of a large bipolaron problem on the distance R between the centers of gravity of the polarons have shown that the interpolaron potential has a maximum as $R \rightarrow 0$ and, therefore, a one-center state of large bipolaron is unstable [3-6]. A minimum of the interpolaron potential appears only at intermediate equilibrium distances ($R > 0$) between the polarons. Therefore, it is important to study the role played by the electron-electron correlations in the stabilization of a large bipolaron and elucidate whether the electron-electron correlations can indeed modify the Hartree-Fock approximation for the model of quasi-independent electrons so strongly that the bipolaron passes from an axially symmetric two-center state to a spherically symmetric one-center state as claimed, for example, in Refs. [7, 8]. For this aim we use the well-known principles of the variational method and firmly established the physical consequences due to the influence electronic correlations on the electronic systems. There are firmly established principles of the correct application of the variational method, especially important for quantum-mechanical systems. There are also firmly determined physical consequences associated with proper allowance for the effects of electron-electron correlations in electronic systems. Using these well-known concepts, we show mathematically strongly and at the same time fallacy both variational calculations and the far-fetched of the physical consequences obtained for one-center model of Landau-Pekar bipolaron. Moreover, we shall demonstrate a clear physical sense of the arguments that we use.

2. VARIATIONAL METHOD AND VIRIAL RELATIONSHIPS

Using the results from the adiabatic translationally invariant theory of a large bipolaron [6, 9, 10], we can replace the integro-differential equation with an equivalent variational functional for the total self-consistent electronic energy $E(R)$ of the singlet motionless bipolaron:

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

$$\frac{1}{4}\iint d\tau_1 d\tau_2 \rho_2(\mathbf{r}_1,\mathbf{r}_2)\left\{ 2g(\mathbf{r}_1,\mathbf{r}_2)\varepsilon_\infty^{-1} + \varepsilon^{*-1}\sum_{i=1,2}\int g(\mathbf{r}_i,\mathbf{r'_i})\rho(r'_i)d\tau'_i \right\} =$$

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

Here, the dielectric medium is replaced by a continuum; m^* is the isotropic effective mass of the Bloch 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; $\varepsilon^{*-1} = \varepsilon_\infty^{-1} - \varepsilon_s^{-1}$, ε_∞ and ε_s are the high frequency and static permittivities of the polar medium. The energy in Eq. (1) is measured from the bottom of the conduction band. Functional (1) depends parametrically on the distance R between centers of gravity of two polarons. For adiabatic a large polarons, the translational polaron effective mass is $m^{**} = 0.023\alpha_c^4 m^* >> m^*$ ($\alpha_c > 10$ is the dimensionless electron-phonon coupling constant); therefore, the Born-Oppenheimer approximation can be used for functional (1). The quantities $T(R)$ and $U(R)$ are the average electron kinetic and potential energies. Functional (1) was analyzed in [6, 9, 10] for arbitrary distances between the polarons and for electronic wave functions of different degrees of complexity. In variational calculations, trial electronic wave functions minimizing the total energy functional are considered optimal if these functions *satisfy the conditions* of the virial theorem, which, in turn, is consequence of the variational principle. The importance of the virial theorem in studying the polaron energy states has been pointed out by Pekar [11]. It is known that if a trial electronic wave function gives kinetic and potential energies that do not satisfy the virial theorem, then the total energy obtained by the variational method is far its correct value and the wave function is not optimum. Using a scaling transformation of the variables, a trial wave function can be reduced to another normalized trial function that satisfies the virial theorem [12]. In variational calculations the virial theorem is not only a necessary criterion for the optimality of the wave function but also makes it possible to clearly to demonstrate the dependence of the bipolaron total energy on the distance R without resorting to complicated and not always easily verifiable calculations of the bipolaron total energy using wave functions that take into account electron correlations.

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, whose value is determined by minimizing E with respect to parameter λ. For the particles the interaction

between which is inversely proportional to the distance, the total energy can be written in the following form

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

Then, assuming that $T(s)$ and $U(s)$ are homogeneous functions, we find that functional (2) reaches an extremum when

$$\lambda = -(U + s\, dU/ds)(2T + s\, dT/ds)^{-1} \qquad (3)$$

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

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

Substituting Eqs. (3) and (2) into Eq. (4), we obtain the well-known virial relation for the Coulomb system:

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

that is valid for an arbitrary distance R. Thus, when minimizing the total energy functional (1) with respect to the variational parameters, it is necessary that Eq. (5) be satisfied for the optimum wave functions at any value of R. It is important to note that the virial relation (5) follows from the variational principle and is a natural *additional condition* imposed on trial wave functions in variational calculations. Such problems belong to the class of isoperimetric problems. 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 of Eq. (5) for any R. Obviously, not all of the functions for which functional (1) reaches an extremum satisfy Eq. (5) for any distance R.

Since the stability of Landau-Pekar bipolaron at $R \to 0$ (spherically-symmetrical case) 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 Eq. (5) a relation between the total electronic energy of Landau-Pekar bipolaron and the kinetic energy [13]:

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

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 will be satisfied.

For an isolated bipolaron at rest, we search for the Hartree-Fock approximation to eigen electron wave function of the bipolaron Hamiltonian for the singlet ground state using the electronic wave function of quasi-independent electrons in the Heitler-London 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 zero-order approximation. Here, the superscript a refers to the centre gravity of polaron at the point $\mathbf{R}_1$; the superscript b to the second polaron at the point $\mathbf{R}_2$; $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$; and $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of the first and second electrons measured from the centers of gravity of the first ($\mathbf{R}_1$) and ($\mathbf{R}_2$) polarons, respectively. The method of separating the polaron coordinates $\mathbf{R}_1$ and $\mathbf{R}_2$ from the electronic coordinates $\mathbf{r}_i$ is described in detail in Refs. [10, 14, 15]. Functional (1) with wave function (7) gives the correct asymptotic behavior for the total two-electron energy. At distance $R \to \infty$ Eq. (1) with wave function (7) gives a doubled total energy of an isolated 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 $\left(\chi \sim \exp(-\eta r^2)\right)$ that is used by Kashirina, et al. [7], Kashirina and Lakhno [8] incorrectly behaves close to points $\mathbf{R}_1$ and $\mathbf{R}_2$. Such wave functions do not have the so-called "cuspidal point", which is available for Coulomb functions. Pekar and Tomasevich [2] used wave functions that depends explicitly on the interelectronic distance r_{12} only the single-particle functions contained simple exponential dependence (Coulomb approximation). However, from their analysis follow that even in this most favorable case, the one-center large bipolaron state remains unstable.

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 (global) 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 a 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 the method [16]. In this representation, the electron coordinate r is counted off from the center a.

When we use a one-center basis set functions unlike multicenter basic set we can avoid problems of wave functions redundancy. As it is well known [17], using of two-center basic set, as is done, for example, in the Refs. [7, 8] leads to an uncontrolled overestimation of the electron correlations for binding energy. In addition, the using of a one-center conception of the wave functions allow us to control the sequential convergence of the variational procedure. In contrast to multicenter wave functions the one-center set of functions allow us to avoid problems of the set

wave functions redundancy. As established in the Ref. [18] using of the one-center expansion is ideal for calculating energy derivatives (or finite difference energies) on the nuclear coordinates. This advantage we shall use in the subsequent text comments. Since we are interested in the behavior of the total energy at distances close to zero (stability of spherically symmetric bipolaron), we expand the functions centered at the point b in a power series in R about the origin. Then, using Eq. (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 large polaron in the ground state) associated with the formation of a bipolaron as follows:

$$\Delta T(R) = 2\alpha_c^2 \hbar \omega \left(1.324 \cdot 10^{-5} R + 7.58 \cdot 10^{-4} R^2 + 4.07 \cdot 10^{-7} R^3\right). \qquad (8)$$

Here, ω is the limiting frequency of long-wavelength longitudinal optics phonons and also we assumed $\varepsilon^*/\varepsilon_\infty = 1.00$. In Eq. (8), we retained the cubic terms in R. This dependence, corresponding to the Hartree-Fock approximation, was taken into account when deriving Eq. (8). In Figure 1, the change in kinetic energy $\Delta T(R)$ is shown as a function of the distance. It is seen from Figure 1 that 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 a maximum at $R = 0$; i.e., the bipolaron one-center state is unstable. This result (line 1, Fig.1) fully coincides with the results of variational calculations for a large bipolaron in the approximation of quasi-independent electrons (zeroth approximation) [2, 4-6] and remains valid for all values of the dielectric parameters of the medium admitting the existence of a large bipolaron. Analysis has shown [10, 14, 15] that the difference $\Delta T(R)$ depends only weakly on the chosen basis of the one-electron functions $\chi_s(r)$, since the bipolaron binding energy is a composite quantity and the errors in the choice of the basic functions are compensated [19]. For most of the quantum-mechanical problems concerned with electronic systems, the Hartree-Fock solutions automatically satisfy to the virial theorem [12, 20]. However, for solutions that take into account the electron-electron correlations, the virial theorem imposes *an additional condition* on a variational solution. In fact, the variational solution of the bipolaron problem is reduced not to finding the absolute minimum [7, 8] of the functional (1) but rather to determining *a conditional minimum* of the functional $E(R)$ in presence of nonholomic constraints (5).

3. ELECTRON CORRELATIONS AND STABILITY OF A LARGE BIPOLARON

Hartree-Fock method takes into account the correlation of the electrons due to the skew symmetrization of the wave function, but, as it is know, is not taken into account the Coulomb electron correlations. In the variational method, the electron-electron correlations can be taken into account either by including an additional function that depends explicitly on the distance r_{12} between electrons in the original two-electron wave function $\chi_0(\mathbf{r}_1, \mathbf{r}_2; R)$ or by constructing a two-electron function that takes into account the interaction of electronic configurations. It was shown in Refs. [1, 21, 22] these two approaches to the study of large bipolaron stability are alternatives under the assumption of the correct application of the variational method. For the purposes of clarity and visibility of the results, we will use the second method of accounting for

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electron-electron correlations. We add the electronic $2p^2$ electron configuration to the wave function $\chi_0(\mathbf{r}_1,\mathbf{r}_2;R)$. According to Pekar [11] the $2p$ 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 $\chi_p \sim z\exp(-\beta r)$ and the z axis coincides with the bipolaron binding axis. The wave function (9) allows us to take into account the permutation degeneracy of the system. 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. The representation of the wave function in the form (9) virtually coincides with the approximation that was used in [23-25] and made it possible to obtain substantially more exact binding energies of the hydrogen molecule compared with the zeroth approximation. It was shown in Hurley [26] that the Hellman-Feynman variational theorem for optimum wave functions can be strictly satisfied only with such "floating" functions which are not at all taken into account in the works [7, 8]. Again, we expand the functions centered at the point b in Eq. (9) for the wave function in a power series in the vicinity of $R = 0$ andweeasily obtain the following expression for the average electron kinetic energy:

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

here

$$K(R) = 0.107 + 0.038 \cdot C_1^2 + R\left(1.324 \cdot 10^{-5} + 1.045 \cdot 10^{-6} \cdot C_1 + 9.887 \cdot 10^{-4} \cdot C_1^2\right) +$$

$$+ R^2\left(7.58 \cdot 10^{-4} + 5.23 \cdot 10^{-3} \cdot C_1 - 2.334 \cdot 10^{-4} \cdot C_1^2\right) +$$

$$+ R^3\left(4.07 \cdot 10^{-7} + 2.183 \cdot 10^{-6} \cdot C_1 - 1.417 \cdot 10^{-5} \cdot C_1^2\right),$$

$$N(R) = 1 + C_1^2 + C_1(2.286 \cdot 10^{-9} + 4.573 \cdot 10^{-6} \cdot R + 2.287 \cdot 10^{-3} \cdot R^2 + 6.8 \cdot 10^{-5} \cdot R^3).$$

It is well known [27] that correlation effects are not very sensitive to variations in the Hartree-Fock wave function. Therefore, in Eq. (10), both $\beta(R)$ and $\alpha(R)$ were taken to be equal to the functional dependence obtained for a large bipolaron with quasi-independent electrons.

To define energy (10) it is necessary to find the numerical value of the variational parameter C_1. The possible values of this parameter can be established even without lengthy calculation of the bipolaron electronic energy. Indeed, for our purposes, it is important to know the value of the bipolaron energy at $R = 0$ to compare with the results [7, 8]. 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). We use the virial relation $2T + U = 0$, which is valid at $R = 0$ and relates the kinetic and potential energies both for the bipolaron and for large polaron of Pekar. Omitting

simple calculations [28, 29], we find the correlation contribution lowers the bipolaron energy, i.e., $\Delta E(R{=}0) > 0$, if the following inequality is satisfied (for $\varepsilon^*/\varepsilon_\infty = 1.00$):

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

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 the relation $V_2 \approx V_1/2$ with satisfactory accuracy, inequality (11) can be rewritten as:

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

Using the numerical values of the integrals and Eq. (12) we find that inequality (11) is satisfied if $C_1 < -V_3/3V_1 \approx -0.04$ ($V_3 > 0$, $V_1 > 0$). With that end in view we calculate the second derivative d^2E/dC_1^2. After simple mathematical manipulation involving the expression for $\Delta E(R{=}0)$ and the virial relation between the average kinetic and potential energies, the second derivative can be found to be

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

It follows from Eq. (13) that, for $C_1 < -V_3/3V_1$ the second derivative $d^2E/dC_1^2 > 0$; i.e., the inclusion of electron-electron correlations in the wave function lowers the total bipolaron electron energy. Thus, the parameter C_1 must be negative and smaller than unity. Thus is satisfied one of the important requirements of the variational method. Not only correlation functions should be close to zeroth approximation functions but also their first derivatives. Figure 2 shows that for spherically-symmetrical bipolaron this requirement is not obvious. Straightforward variational calculations [6, 13, 17] with simultaneous variation of the parameters α, β, and C_1 have given $C_1 = -0.097$ for $R = 0$ and $\varepsilon^*/\varepsilon_\infty = 1.00$. This value does not contradict the results obtained from conditions (12) and (13). Using the value $C_1 = -0.1$, we obtain from Eq. (10) that in this case also $d^2E(R)/dR^2 < 0$ (line 2; Fig.1). This result indicates the logical correctness of applying the variational method. That is, even though the bipolaron total energy at $R = 0$ is lowered due to the inclusion of electron correlations in the wave function, the bipolaron total energy reaches a maximum as $R \to 0$, as well as in the case of the zeroth approximation. Therefore, in agreement with the result of Pekar and Tomasevich [2] the one-center state of bipolaron remains unstable. It is known [30, 31] 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).

Let us increase the flexibility of the wave function by including one more electronic configuration (1s2p):

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

$$C_2\left(\chi_s^a(\mathbf{r}_1)\chi_p^b(\mathbf{r}_2) + \chi_s^a(\mathbf{r}_2)\chi_p^b(\mathbf{r}_1)\right) = \chi_0 + C_1\chi_1 + C_2\chi_2. \qquad (14)$$

Just simply without resorting to hard to reproduce and cumbersome calculations with obscure physical meaning [7, 8], we can show that the approximate value of the variational parameter is equal to $C_2 \approx 0.1$ as $R \to 0$. The detailed variational calculations gives for wave function (14) the value: $C_2 \approx 0.105$ at $R \to 0$ and $\varepsilon^*/\varepsilon_\infty = 1.00$ [9, 10, 28, 29]. Line 3 (Fig. 1) shows that a one-center large bipolaron in that case remains unstable at $R = 0$. Thus, no additional minimums do not appear for the energy of the bipolaron as it is stated in Refs. [7, 8]. Of course, if researcher does not violate the basic principles of the variational method (see Fig. 2).

Additional correction 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 determined by the wave function χ_2. As shown in Refs. [31, 32], the function of the form (14) proved to be very important for diatomic molecules at any distances between nuclei. Importantly, the correlation contributions must also take into account the spatial symmetry of the two-center formation. That is, we must consider the point group symmetry, which corresponds to the initial spatial configuration of the bipolaron and the irreducible representation which must transform the electronic wave function of the bipolaron [9, 17].The importance of considering the symmetry of a bipolaron of the construction of the electronic wave function consists in the fact that it allows us to formulate the correct regular rule of consistent expansion of the function flexibility. This rule is another natural restriction that is imposed on the choice of the correction functions. As is well known, the wrong choice of the basis set of functions is the source of large errors in the variational calculations.

In Fig. 1 we see that with increasing flexibility of the electronic wave function the general trend of the contribution to the electronic kinetic energy decreasing as $R \to 0$ is retained and the bipolaron total energy at $R = 0$ has a maximum (for $R \to 0$ $\lim d^2E/dR^2 < 0$ and $\lim dT/dR > 0$). In this case, the spherically-symmetrical bipolaron also remains unstable with respect to variations in the four parameters α, β, C_1 and C_2 just as for the bipolaron with quasi-independent electrons (zeroth approximation). An analysis of the sensitivity of Eq. (6) to variations in the parameters C_1 and C_2 showed that the sign of the second derivative of the total energy $R \to 0$ remains unchanged over a wide range of values of these parameters. It is well known [30] that the method of expansion wave function over the configurations can approximate the solution of the Schrödinger equation with arbitrary precision.

Contrary to bipolaron calculations Kashirina, et al. [7], Kashirina and Lakhno [8] smallness variational parameters $|C_1| << 1$ and $|C_2| << 1$ indicates that the correlation effects are the corrections to the zero order approximation, as it is required for coupled electronic systems. As noted in Ref. [33] the least preconceived approach to calculate of the correlation contribution is the approach that simulates the sequence of the perturbation series. Large quantity of studies have firmly established (see, for example, [17]) that Hartree-Fock 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 correlation contribution. Evidently, for such ratio for the energies,

the correlation contribution cannot change the spatial symmetry of the coupled system corresponding to the zeroth approximation. Moreover, firmly established that with decreasing distance R correlation contribution to the energy decreases. However, the calculations in [7, 8] give a result opposite to this well-known rule. According these calculations electron correlations so great that they fundamentally modify the original (zeroth approximation) spatial symmetry of singlet Landau-Pekar bipolaron (Fig. 2).Practically, from their calculations follow that zeroth approximation becomes a correction to the correlation contributions. It is well known for the variational method the correction to the eigen value has the second order of smallness in the difference $|\chi - \chi_0|$.

The conclusion that the one-center model of bipolaron is unstable can be drawn without using Eq. (6) by directly solving the differential equation (5) which is of the Riccati type. Approximating the R dependence of the kinetic expression $T(R) = A + BR^2$ near $R = 0$ (Fig. 1) we obtained the differential equation

$$d(RE(R))/dR + B + AR^2 = 0.$$ (15)

The solution to Eq. (15) can be written in the form $E(R) = -B - AR^2/3$, where A and B are positive constants. Obviously, it follows that limit of $\lim_{R \to 0}[d^2 E(R)/dR^2] < 0$. That is instability of spherically symmetric (one-center) large bipolaron remains in force. Thus, increasing the flexibility of the variational trial functions and additional accounting of electronic correlations does not alter fundamentally the functional dependence of the bipolaron potential on the distance between the centers of gravity of the polarons. Maximum of the bipolaron potential remains valid at $R = 0$ (Fig.3).At correct applying of the variational method it gives identical results [21, 22] for multiconfiguration wave function, and for function that depends on the electron-electron distance r_{12}.

When we using the variational method the applicability of the virial relationships for a bipolaron at $R = 0$ and the bipolaron stability with regard to electron correlations cannot be ensured simultaneously without contradicting the basic principles of quantum mechanics. For example, we find that the *absolute* minimum of the electron energy of the $1s$ state is higher than that of the electron $2p$ state [21, 22]. In this case, the virial theorem is also satisfied. However, the result is obviously absurd. Thus, in a direct variational method, the optimality of the wave functions with regard to electron correlations should be checked not by verifying that the virial theorem is satisfied but also by analyzing the physical meaning of the obtained solutions. In the general case, minimization of the functional $E(R)$ using a variational method is inevitably reduced to the *absolute* minimum of the system [7, 8], which can be devoid of physical meaning. It is well known that the correlation contribution to the total energy satisfies the same virial relations for zeroth approximation[20]:

$$R \frac{dE_{corr}(R)}{dR} + 2T_{corr}(R) + U_{corr}(R) = 0.$$ (16)

Therefore, the shape of the bipolaron potential remains the same for quasi-independent electrons (zeroth approximation), and for the contribution of electron correlations. That is, if the zeroth approximation corresponds to the minimum of two-centered formation, the contribution of the correlation energy also has the minimum at $R > 0$. However, as follow from Ref. [7] for $R \rightarrow 0$ the direction of change in energies $E(R)$ (Eq. (15)) and $E_{corr}(R)$ (Eq. (16)) are opposite (compare lines 1 and 2; Fig.2).Firmly established [17] that the qualitative dependence of the correlation energy $E_{corr}(R)$ on the distance R coincides with the Hartree-Fock approximation (line 1; Fig. 2). Ruedenberg K. explained the physical reason of this dependence [34]. Figure 3 shows the change in the correlation contribution of distance between center of gravity of polarons obtained for axisymmetrical Landau-Pekar bipolaron [9, 10]. This change is of a general nature, correlates with zeroth approximation, and this correlation persists in the whole region of existence of a large bipolaron for all values of the parameter $\varepsilon^* / \varepsilon_\infty$.

It is well known that double excited electronic configurations make a smaller contribution to the binding energy compared to once excited configurations. Namely this argument is confirmed by the calculations, which are presented in Figure 3. This dependence of the correlation contribution on the distance R is known to be dictated by the spatial symmetry of the system under study [30], i.e., by the point symmetry group corresponding to the original zero-order approximation of spatial configuration; the true electron wave function of the bipolaron with electron correlations should be transformed according to an irreducible representation of the symmetry group. The importance of considering the bipolaron symmetry in the construction of the electron wave function is also in that it allows us to formulate the correct scheme to systematically step-by-step expansion of the basis set of a set of elements that belong to the same set. If the set is not invariant, then search eigenvalue of the operator is undefined. Set of functions with a given symmetry form a linear space, as well as their linear combination belongs to this set. At the same time the combination of Gaussian functions do 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 [23] which is determined by wave functions like those in Eqs. (9) and (14). However, calculations show that even these correlation contributions cannot change the axially symmetric state of the bipolaron which obtained in zero-order approximation (Fig. 3). We will perform a very simple mathematical analysis, which demonstrates that the electron correlations do not lead to the stabilization of a spherically (one-center) symmetrical state of a large bipolaron and even more so they do not lead to change in the symmetry of bipolaron as it is stated in Ref. [7, 8]. If a one-center state of a large bipolaron will be stable then the additional incorporation of the so-called "ionic" terms (Weinbaum's function [35]) into the total two-electron wave function would result in stabilization of the bipolaron. However, simple and physically understandable calculations (see, for example, [9]) have show that these corrections do not contribute to the binding energy of the singlet large bipolaron in the ground state under any conditions and hence their inclusion does not play any role in the stabilization of one-center bipolaron. Indeed, in this case the two-electron wave function can be written as the sum of the wave functions [35]:

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

Here μ is additional variational parameter, and obviously $0 \leq \mu \leq 1$. The term which proportional to parameter μ determines the contribution "ionic" state in bipolaron stabilization. However, very simple calculations with a clear and understandable physical meaning showed that this additional electron configuration (17) does not contribute to the stabilization energy of the bipolaron at distances $R \rightarrow 0$. The electronic energy of a large bipolaron in the maximum ($R = 0$) of the bipolaron potential 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 parameters in Eq. (18) we obtained for the case which is the most favorable for the positive manifestations of so-called "ionic" correlation contributions. For polar mediums, for which rightly the ratio $\varepsilon^*/\varepsilon_\infty = 1.00$ direct Coulomb interaction between electrons is extremely weakened. From the extreme properties of the functional (18) we can see that the variational parameter $\mu = 0$, i.e., one-centered correlations ("ionic" term) do not make one's contribution to stabilization of a spherically symmetric large bipolaron. All the more, such an electron correlations cannot change the spatial symmetry of the bipolaron. Equality $\mu = 0$ for the so-called "ionic" of one-center correlation contribution is a cogent argument that points to the instability of a spherically symmetric state of singlet bipolaron. This conclusion is entirely consistent with Pekar's research. At the same time if we take into account correlations in the form of (17) for arbitrary distances $R > 0$ then this leads to the stabilization of the axisymmetrical bipolaron, as it should be for the two-center electronic systems [17, 35]. Contribution to the binding energy is due to electron oscillation between two potential wells [36-38]. In which connection this conclusion remains valid in the entire region of admissible dielectric permittivities $\varepsilon^*/\varepsilon_\infty$ (Fig.3). Thus, these are very simple calculations with a clear physical meaning demonstrate that singlet one-center bipolaron is unstable.

Bipolaron one-center model [7, 8] of a large bipolaron obviously also contain an internal contradiction. The zero-order approximation relative to which are constructed the successive approximations becomes the correction to contribution in the binding energy of the bipolaron, caused by the effect of correlations (see Fig.2; curve 2). This is contrary to the principle of successive approximations. In papers [28, 29, 39-41] are demonstrated the pair bipolaron potentials for a wide range of dielectric constants. Potentials were obtained by the variational method with the wave functions, which include until seven variational parameters (zero-order approximation $1s^2$ consistently is added by electron configurations: $2p^2$, $1s2p$, and $1s2s$). In addition, we take into account the *additional restrictions* imposed by all virial relations,

orthogonality requirements, spatial symmetry and convergence of variational approximation. Within those potentials, the follow inequality: $dT/dR > 0$ is likewise satisfied; i.e., for Landau-Pekar bipolaron spherically symmetrical state remains unstable (Fig. 4).

By increasing the flexibility of the trial wave function leads to increasing of the binding energy of the axisymmetrical Landau-Pekar bipolaron. However, the common character of the dependence of the bipolaron binding energy on the distance between polarons remains the same as for quasi-independent electrons (zero-order approximation) and does not depend of the dielectric properties of the polar medium (Figs.4 and 5).

Figure4 shows the rapid convergence of the variational series. According to the works [17, 30, 31] to calculate the dissociation energy of simple diatomic molecules often is enough to consider only two additional electronic configurations. Increase the flexibility of the wave function retains the right uniform convergence of the variational procedure (compare with Figure 2). For curve 4in Figure 4 is useda superposition of four electronic configurations: basic- $1s^2$ (zero-order approximation), singly excited- $1s2p$ and $1s2s$, and doubly excited configuration $2p^2$. In the symbolic form the trial electron wave function can be written as follows:

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

here χ_0, χ_1, χ_2 and χ_3 are the wave functions of two-electron configurations. Function χ_{2s} was chosen in the following analytical form: $\sim (1-\gamma_1 r)\exp(-\gamma_2 r)$, where γ_1 and γ_2 additional variational parameters. Number of variational parameters run up to seven, but no additional minimums [8] does not appear (Fig. 4).On the contrary, as it is required under correct applying of the variational method, there is a smooth downtrend in bipolaron potential with increasing flexibility of trial function. At the same time is kept the dependence of the potential on the distance R (as for zero-order approximation) and transition to a one-center bipolaron state does not occur. Moreover, in accordance with correct application of variational method, a sequential increase in the flexibility of the wave function leads to a smooth convergence of variational series (Fig. 4).If the variational method is used correctly, no significant change in the binding energy of the bipolaron does not happen, and changes in the spatial symmetry bipolaron does not occurs. In this case the equilibrium distance between polarons is kept. Change in the equilibrium distance is due to modification of the parameter $\varepsilon^*/\varepsilon_\infty$ (Fig. 5).Evidently, for one-center bipolaron computational methods [7, 8] are used at best lead to so-called unstability of the computational algorithm caused by poor choice of the coordinate functions. Such features of the method lead to significant errors in variational calculations. As is well known, it is manifested in the fact that the Ritz parameters begin to change sharply, and the approximation to the solution begins significantly to differ from the zeroth approximation. This makes the procedure of Ritz unstable.

Figure 5 shows that when the ratio of $\varepsilon^*/\varepsilon_\infty$ is increased then monotonically is decreased the binding energy of the bipolaron, and also is increased the equilibrium distance between

polarons, which is quite natural and physically logical, unlike bipolaron calculations of Kashirina, et al. [7], Kashirina and Lakhno [8]. Reducing the binding energy of the bipolaron increases the effective size of large bipolaron (Fig. 5). However, spherically symmetric pair bipolaron potential that obtained in Ref. [7] is not sensitive to changes of the polar medium. At the same time one-center bipolaron potential characterized by a sharp change in the form of bipolaron potential after accounting of electron correlations (Fig. 2). Obviously, the limitations to the variational method, which are superimposed on the approximation to the solution of the equation in theirs calculations evidently are violated.

In many available publications in which authors use alternative analytical methods for solving the bipolaron problem [42-50] it was established that a large bipolaron in the ground singlet state is an axially symmetrical two-center formation. The authors of the papers [42-44] likewise arrived at similar conclusions by analyzing the distance dependence of the bipolaron ground state using the Feynman path integral method. The authors of very interesting work [50] come to a similar conclusion. They are used approach of Feynman in their research. In Ref. [45], the electron correlations were included using the Gunnarson-Lundqvist density matrix formalism [51]. The results of that study completely confirm the results obtained by expanding the electronic wave function in terms of electronic configurations [6, 14, 15, 28]. Furthermore, incorrectness one-center bipolaron model also confirmed by studies which made in paper [52]. Without using a variational approach authors of this paper are demonstrated, that Hamiltonian for ground state of bipolaron has no spherically symmetrical solutions. Variational procedure without prior study of the operator, the underlying of equations or functional, can only lead to absolute extremals. Therefore, minimization of the functional must be performed on the class of admissible functions from which the function (19) is constructed. The sequence of functions χ_i belongs to the range of definition of the polaron functional and can there fore be called a minimizing sequence for this functional. Usually a system of linearly independent functions are selected so that it is the complete set of functions. Requirement of completeness means that you can approximate the solution with arbitrary precision by linear combinations of admissible functions, consisting of set of functions χ_i.

At the same time using Eqs. (5), and (6) it can easily be shown [14, 53, 54] that the triplet electron-excited bipolaron states are spherically-symmetric formations (with the exception of the

electron-excited $^3\Sigma_u$ state, which is repulsive for any distance R). Outlined in this paper numerous

arguments showed that the electron correlations do not lead to stabilization of the spherically symmetric bipolaron with respect to axisymmetrical Landau-Pekar bipolaron.

4. INTERPRETATION OF EXPERIMENTAL DATA

It is well established [55, 56] in experiments on magnetic and optical studies, and studies on the mobility of electrons that in ammonia systems there are two-electron formations with high mobility. Experimentally, bipolarons have been observed in organic compounds [57-59], molten salts [60] and ammonia-based system [61-69], in vanadium bronzes [70]. In accordance with

Mott N.F.[71]series of experimental results can be explained only by considering existence in a polar medium including ammonia the coupled two-electron diamagnetic formations.This opinion is shared by many researchers (see, for example, the review [65]).It should be noted that, for example, in ammonia alkali metal ions do not possess affinity for solvated electrons[56]. Moreover, the optical properties of the additional electrons are identical for both the injected electrons and dissolving the alkali metals. That is coupling of the cation with electrons missing. It is well known the experimental data on the conductivity of metal-ammonia solutions. In considering the experimental data on metal-ammonia solutions, one is stuck by the concentration dependence of equivalent conductivity and paramagnetic susceptibility. The anionic conductivity beyond 0.01 molar solutions is essential constant showing a minimum of about twenty per cent decrease at about 0.04 molar, after which the conductivity again increases with concentration. The paramagnetic susceptibility decreases much more rapidly at low concentrations and reaches a minimum at about 0.5 molar where its value is about 2.5% of that at 10^{-2} molar. It is obvious that some pairing of spins must occur [64].

Applicability polaron model for describing the properties of electrons in polar liquids has been discussed in the literature. By using the variational method it was calculated [9, 10, 27] the ground state of a large bipolaron and the lowest electronically excited singlet and triplet states. The figure 6 presents that the singlet state of Landau-Pekar bipolaron correspond to axisymmetrical state, while the triplet states of the bipolaron are spherically symmetrical formations [53, 54]. This result is physically obvious and understandable. For triplet bipolaron formations the electrons are at different orbitals and distant from each other. In which connection for a sequence of relaxation-excited electronic terms of large bipolaron, is kept well-known Hund's rule (Fig.6) for $R \rightarrow 0$. In variational calculations in Refs. [7, 8] singlet and triplet bipolarons are spherically symmetrical formations. In this case it is not obvious that the Hund's rule must be satisfied.

Axisymmetrical Landau-Pekar bipolaron allow us to interpret the spectroscopic experiments. We demonstrate this by comparing the spectral characteristics of two-center bipolaron with experimental data. It has been experimentally established [72] that on photo-excitation of a hydrogen-saturated alkali solution by light in the UV region of the spectrum, hydrated electrons were formed at a concentration of 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 ($\lambda_{\exp} > \lambda_{\min} = 700 \text{nm}$) after disappearance of 98% of the hydrated electrons led to

regeneration of hydrated electrons e_{aq} (polaron type; $\varepsilon^*/\varepsilon_\infty = 1.05$). 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 H₂ following after disappearance of e_{aq} 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 [72] have confirmed the existence in aqueous solution of $(e_{aq})_2$. As it was shown in Refs. [9, 10] the transitions $^1\Sigma(1s^2) \rightarrow {}^1\Sigma(1s2p_z)$ and $^1\Sigma(1s^2) \rightarrow {}^1\Pi(1s2p_{x\pm iy})$ will be most probably (oscillator strength in dipole approximation will be following: $f \geq 0.7$) where the z axis coincides with the symmetry axis of Landau-Pekar bipolaron; the indices in parentheses on the spectroscopic symbols signify single-electron states, arising on adiabatic propagation of e_{aq} at the distance $R \rightarrow \infty$.

In Figure 6 the electronic terms of the bound two-electron species are given as functions of the distance R. Let us examine the dipole-allowed transition: $^1\Sigma(1s^2) \rightarrow {}^1\Pi(1s2p_{x\pm iy})$, the frequency of which at the maximum of the absorption band in correspondence with the Frank-Condon principle we determine from the relation of Pekar [11]:

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

here $E_0 = -1.26\times10^{-1}\times 2\alpha_c^2\hbar\omega$, $E_1 = -6.8\times10^{-2}\times 2\alpha_c^2\hbar\omega$ are the self-consistent total energies of the initial and final electronic states, respectively. The energy of reorganization of the polarization state of the polar medium as a result of the photo-transition ($0 \rightarrow 1$) is determined from the relation

$$A_0^1 = \left(\frac{2}{\hbar\omega}\right)\sum_{\mathbf{k}, j=1,2} |V_{\mathbf{k}}[\rho_j^{(0)}(\mathbf{k}) - \rho_j^{(1)}(\mathbf{k})]|^2, \qquad V_{\mathbf{k}} = \frac{e}{k}\left(\frac{4\pi\hbar\omega}{V\varepsilon^*}\right)^{1/2}. \qquad (21)$$

Here the Fourier transformation of the electron distribution in the state with two-electron function $\chi(\mathbf{r}_1, \mathbf{r}_2)$:

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

The characteristic frequency ω of the long-wavelength longitudinal optical vibrations of the dielectric medium which are usually bound with elastic displacements of the molecular dipoles around their equilibrium positions can be estimated from the half-width $W_{1/2}$ of the optical absorption spectrum of a large polarons. In the low-temperature limit ($n < 1$)

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

Here the energy of reorganization of the polar medium A_0^1 relates to the $1s \rightarrow 2p$ photo-transition of the polaron. Taking into account experimental value $W_{1/2} = 0.29\text{eV}$ [72] from Eq.

(22) we find $\omega = 2.2 \cdot 10^{13}$ sec^{-1}. The value obtained of ω is within the limits determined from Fröchlich phenomenological dielectric model for resonance absorption in a polar liquid $\omega = 7 \cdot 10^{12}$ sec^{-1} and estimates from dispersion curves $\omega \approx 6 \cdot 10^{13}$ sec^{-1}.

Considering that the photo-transition is performed from the minimum ($R_0 = 4.32 \times \alpha_c^{-1}(\hbar/m^*\omega)^{1/2}$) of the $^1\Sigma(1s^2)$ ground term (Fig.6; curve 1), i.e., it is neglected the intrinsic vibrational − rotation structure of the bipolaron for the temperature conditions usual in experiments $T = 298$K from Eq. (20) we obtained: $\hbar\Omega_1 = 6.81 \times 10^{-2} \times 2\alpha_c^2\hbar\omega = 1.41$eV . This corresponds to the wavelength of $\lambda_{calc} = 877$nm $> \lambda_{min}$. As it is not difficult to see from Figure 6, the final term $^1\Pi(1s2p_{x\pm iy})$ (Fig. 6; curve 5) is repulsive in the entire interval of distances R, which finally leads to photo-dissociation of a large bipolaron. For the photo-transition $^1\Sigma(1s^2) \rightarrow {}^1\Sigma(1s2p_z)$ the situation turns out to be different. The energy of the electron transition we calculated by using Eq. (20) equal to $\hbar\Omega_2 = 1.37$eV . This corresponds to the wavelength of $\lambda_{calc} = 905$nm $> \lambda_{min}$. After the photo-transition the electronic subsystem turns out to be in a nonequilibrium state and during the time $\tau \approx \omega^{-1}$ is relaxes to the minimum of the term $^1\Sigma(1s2p_z)$ (Fig. 6; curve 3) through which the repulsive triplet term $^3\Sigma(1s^2)$ (Fig. 6; curve 2) 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 [73] generating an oscillating magnetic field). Intercombinatory singlet-triplet transition $^1\Sigma(1s2p_z) \sim> {}^3\Sigma(1s^2)$ are possible with a high probability.

With a lowering of temperature the absorption band is shifted into the long-wavelength region and for $T = 80$ K at the maximum of the absorption band $\hbar\Omega_3 = 1.26$eV ($\lambda_{calc} = 982$nm). Theoretical wavelength is close to the experimental value $\lambda_{exp} = 1000$nm [72]. At the same time the wavelength corresponding to the energy of photo-ionization ($I = 0.178e^4m^*/\varepsilon^{*2}\hbar^2$) of bipolaron turns out to be considerably shifted into the short-wave length region: $\lambda_{calc} = 340$nm $< \lambda_{min}$. Bipolaron formation is accompanied by a shift of the maximum of absorption band at longer wavelengths region with respect to the band of the hydrated electron ($\hbar\Omega_{max}(e_{aq}) = 1.73$eV[72]).

Now that, using the system of electronic terms of Landau-Pekar bipolaron (Fig.6), we will compare the experimental optical characteristics of the bipolaron in ammonia ($\varepsilon^*/\varepsilon_\infty = 1.075$) with the theoretical calculations. It has been experimentally established [55, 56] that the maximum of the bipolaron in ammonia optical absorption band is shifted to longer wavelengths as

compared to that of an isolated polaron. The most probable dipole-allowed optical transition will

be $^1\Sigma(1s^2)\to {}^1\Sigma(1s2p_z)$. The optical transition is assumed to take place from the minimum of the

ground term: $R_0 = 5.1 \times \alpha_c^{-1}(\hbar/m^*\omega)^{1/2}$. The total self-consistent energies of the initial and final

states are: $E_0 = -1.158\times10^{-1}\times 2\alpha_c^2\hbar\omega$, $E_1 = -8.77\times10^{-2}\times 2\alpha_c^2\hbar\omega$, respectively;

$A_0^1 = 8.68\times10^{-2}\times 2\alpha_c^2\hbar\omega$. Since the optical measurements for ammonia is usually carried out at

225 K we obtain from Eqs. (20) following energy: $\hbar\Omega_1 = 0.77\text{eV}$. Details of the calculations are

shown in the publications [54, 74].

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 $E_1 = -6.5\times10^{-2}\times 2\alpha_c^2\hbar\omega$, $A_0^1 = 2.7\times10^{-2}\times 2\alpha_c^2\hbar\omega$, and the transition energy

is $\hbar\Omega_2 = 0.84\text{eV}$. Thus, the maximum of the bipolaron absorption band in both the first and

second case is close to the photo-transition experimental maximum polaron in the ammonia

system $\hbar\Omega(1s \to 2p) = 0.885\text{eV}$ and, as expected the shift takes in the long-wavelength region.

The measurement of the position of the absorption band maximum of the bipolaron, carried out in

[55, 56] gives the value $\hbar\Omega_{\text{exp}} = 0.81\text{eV}$ which is within the range of calculated frequencies.

Since the absorption spectrum of a large bipolaron is significantly broadened the bands of the

transitions $^1\Sigma(1s^2)\to {}^1\Sigma(1s2p_z)$ and $^1\Sigma(1s^2)\to {}^1\Pi(1s2p_{x\pm iy})$ overlap appreciable and the

theoretical maximum of the resulting band turns out to be precisely in the 0.81−0.82 eV energy

range. This value is very close to the experimental value. Axially symmetric model of a large

bipolaron allows us to interpret other experimental data, such as concentration and temperature

dependence of the magnetic properties of polarons [75].

Further, it will be shown that the axial-symmetric model of Landau-Pekar bipolaron can

correctly interprets experimental data. It has been established also experimentally [61, 69] that

electrons in metal-ammonia systems tend to form bound two-electron species of bipolaron type of

fairly high dissociation energy $D = 0.15$-0.2 eV, these species being independent of the nature of

the dissolved metal and not bound to the initial cation of metal [64]. For bipolaron in ammonia

theoretical estimates [9, 28, 29, 74] give the following value: $D = 0.14$-0.16 eV.

5. CONCLUSION

This shift of optical band is confirmed by theoretical calculations for a two-center Landau-

Pekar bipolaron [54, 74] and it is in complete agreement with the observed change in the optical

absorption spectrum when passing from two separated $(R \to \infty)$ hydrogen atoms (spherically

symmetrical) to a hydrogen molecule (axisymmetrical) [76], i.e., at the change from a spherically

symmetrical object to an axisymmetrical one. This rule is observed for other quantum physical objects. For example, a similar shift in the long wavelength region of the optical spectrum was noted for quasi-molecular biexciton with respect to the spectrum of the exciton [77]. However, for the one-center small bipolaron, which analogous to a helium atom, expected shift of the optical absorption maximum would occur to the opposite (short-wavelength) region of the spectrum. This is confirmed by experiment [78].Thus, inclusion of electron-electron correlation does not change the axial symmetry of the Landau-Pekar bipolaron, which corresponds to the zero-order approximation, and one-center bipolaron remains unstable. Obviously, both theoretical considerations and experimental observations do not confirm the stability of the spherically symmetrical model of bipolaron which is proposed in the works [7, 8].

REFERENCES

[1]   V. K. Mukhomorov, "Triplet two-electron quasi-stationary states in polar medium," *Optics and Spectroscopy*, vol. 50, pp. 90-94, 1981.

[2]   S. I. Pekar and O. F. Tomasevich, "Theory of F centers," *Zh. Eksp. Teor. Fyz.*, vol. 21, pp. 1218-1222, 1951.

[3]   V. L. Vinetskii, "Thesis for a doctor's degree," Institute of Physics of the Academy of Sciences of the Ukrainian SSR, Kiev, 1969.

[4]   S. A. Moskalenko, "Adiabatic form of the perturbation theory of the problem of two particles interacting with the quantum field," *Uch. Zap., Kishinev Gos. Univ.*, vol. 17, pp. 103-114, 1955.

[5]   V. L. Vinetskii, "On bipolaron states of current carriers in ionic crystals," *Zh. Eksp. Teor. Fiz.*, vol. 40, pp. 1459-1468, 1961.

[6]   V. K. Mukhomorov, "Interelectron correlations in the two-electron self-localized formations in polar semiconductors," *Semiconductors*, vol. 16, pp. 700-701, 1982.

[7]   N. I. Kashirina, V. D. Lakhno, and V. V. Sychev, "Electron correlations and unstability of two-center bipolaron," *Fiz. Tverd. Tela.*, vol. 45, pp. 163-167, 2003.

[8]   N. I. Kashirina and V. D. Lakhno, "The spatial configuration of the bipolaron and the virial theorem," *Fiz. Tverd. Tela.*, vol. 50, pp. 11-16, 2008.

[9]   V. K. Mukhomorov, "The energy states and optical properties of bound two-electron quasi-molecular self-localized impurity centers in polar media," *Optics and Spectroscopy*, vol. 55, pp. 145-150, 1983.

[10]   V. K. Mukhomorov, "Singlet and triplet states of a continuum bipolaron for adiabatic and strong coupling," *Optics and Spectroscopy*, vol. 74, pp. 644-655, 1993.

[11]   S. I. Pekar, *Research in electron theory of crystals.* Wachington. DC: USAE C, 1963.

[12]   V. A. Fock, "New derivation of the virial theorem in quantum mechanics " *Zs. Phys.*, vol. 63, pp. 855-858, 1930.

[13]   W. L. Clinton, "Forces in molecules. 1. Applications of the virial theorem," *J. Chem. Phys.*, vol. 33, pp. 1603-1607, 1960.

[14]   V. K. Mukhomorov, "The region of existence of the three-dimensional continuum bipolaron," *Physics of the Solid State*, vol. 44, pp. 241-247, 2002.

[15]   V. K. Mukhomorov, "Eigen values of vibrational states of continual bipolaron of adiabatic and strong coupling. Method of shifted 1/N expansion," *Optics and Spectroscopy*, vol. 74, pp. 149-159, 1993.

[16]   A. B. Bolotin and V. K. Shugurov, "Transformation of the multicenter integrals to one center," *Vychisl. Mat. Mat. Fiz. (In Russian)*, vol. 3, pp. 560-564, 1963.

[17]   S. Wilson, *Electron correlations in molecules.* Oxford: Clarendon, 1984.

[18]   J. Ladik and J. Cizek, "A proposal for the calculation of the correlation energy using a one-center expansion on large molecules," *J. Chem. Phys.*, vol. 73, pp. 2357-2360, 1980.

[19]   H. F. Shaefer, D. R. McLauglin, F. H. Harris, and B. J. Alder, "Calculation of the attractive he pair potential," *Phys. Rev. Lett.*, vol. 25, pp. 988-990, 1970.

[20]   P. O. Lŏwdin, "Expansion theorems for the total wave function and extended Hartree-Fock," *Rev. Mod. Phys.*, vol. 32, pp. 328-334, 1960.

[21]   V. K. Mukhomorov, "Correlation effects in two-electron self-localized formations in polar semiconductors," *Semiconuctors*, vol. 14, pp. 940-942, 1980.

[22]   V. K. Mukhomorov, "Effect of magnetic field on the energy states of two-electron species in ammonia," *Optics and Spectroscopy*, vol. 70, pp. 706-710, 1991.

[23]   N. Rosen, "The normal state of the hydrogen molecule," *Phys. Rev.*, vol. 38, pp. 2099-2114, 1931.

[24]   E. F. Gurnee and J. L. Magee, "The energy of the hydrogen molecule," *J. Chem. Phys.*, vol. 18, pp. 142-144, 1950.

[25]   A. Bongers, "A convergence theorem for ritz approximation of eigenvalues with application to CI − calculations," *Chem. Phys. Lett.*, vol. 49, pp. 393-398, 1977.

[26]   A. C. Hurley, "The electrostatic calculation of molecular energy. II. Approximate wave functions and the electrostatic method," *Proc. Roy. Soc. (London.) A.*, vol. 226, pp. 179-192, 1954.

[27]   O. Sinanoglu, "Many-electron theory of atoms molecules and interactions," *Adv. Chem. Phys.*, vol. 6, pp. 315-412, 1964.

[28]   V. K. Mukhomorov, "Two-electron self-trapped quasi-molecular formation in ammonia," *Khim. Fizika. (Chemical Physics), (in Russian)*, vol. 2, pp. 642-651, 1983.

[29]   V. K. Mukhomorov, "Ground state of an optical bipolaron with an intermediate strength of coupling," *J. Phys.: Condens. Matter. B*, vol. 13, pp. 3633-3642, 2001.

[30]   J. C. Slater, *Electronic structure of molecules.* New-York, San-Francisco, Toronto, London: Mc Grow − Hill Book Corporation, Inc., 1963.

[31]   H. Kim and J. O. Hirschfelder, "Energy of interaction between two hydrogen atoms by the Gaussian-type function," *J. Chem. Phys.*, vol. 47, pp. 1005-1009, 1965.

[32]   S. Wilson and J. Gerratt, "Calculation of potential energy curves for the ground state of the hydrogen molecule," *Mol. Phys.*, vol. 30, pp. 777-787, 1975.

[33]   B. H. Brandov, *In: Effective interactions and operators in nuclei.* Berlin: Springer-Verlag, 1975.

[34]   K. Ruedenberg, "The physical nature of chemical bond," *Rev. Mod. Phys.*, vol. 34, pp. 326-376, 1962.

[35]   S. Weinbaum, "The normal state of the hydrogen molecule," *J. Chem. Phys.*, vol. 1, pp. 593-596, 1933.

[36] V. K. Mukhomorov, "Optical excitation of an additional electron delocalized state in a polar liquid," *Optics and Spectroscopy*, vol. 47, pp. 272-277, 1979.

[37] V. K. Mukhomorov, "Effect of magnetic field on the energy states of two-electron species in ammonia," *Optika. i Spektroskop*, vol. 73, pp. 425-436, 1992.

[38] V. K. Mukhomorov, "Quantum oscillations of a large polarons in magnetic and electric fields in the dielectric layers and bipolaron formation," *Phys. Rev. & Phys. Intern.*, vol. 3, pp. 504-521, 2013.

[39] V. K. Mukhomorov, *In: Nanotechnology. Fundamentals and applications* vol. 1. Houston: Studium Press LLC, 2013.

[40] G. Iadonisi, V. Cataudella, G. De Filippis, and V. K. Mukhomorov, "Internal vibrational structure of the three-dimensional large bipolaron," *Eur. Phys. J. (B)*, vol. 18, pp. 67-75, 2000.

[41] C. A. Perroni, G. Iadonisi, and V. K. Mukhomorov, "Formation of polaron clusters," *Eur. Phys. J. (B)*, vol. 41, pp. 163-170, 2004.

[42] T. Massumi, "A supplement improvement of the Feynman-polaron model and the possibility of bipolaron formation," *Suppl. Progr. Theor. Phys.*, pp. 22-34, 1975.

[43] M. F. Bishop and A. W. Overhauser, "Phonon-mediate electron-electron interaction in real space," *Phys. Rev. B*, vol. 23, pp. 3627-3637, 1981.

[44] H. Hiramoto and Y. Toyozawa, "Inter-polaron interaction and bipolaron formation," *J. Phys. Soc. Japan*, vol. 54, pp. 245-259, 1985.

[45] A. V. Glushkov, "Taking into account the electron correlation in the quasi-molecular self-trapped dimmers," *Zh. Fiz. Khim. (Phys. Chem.), (In Russian)*, vol. 64, pp. 1579-1581, 1990.

[46] S. Sahoo, "A variational calculation of the stability of the two-center Fröhlich bipolaron," *Phys. Lett. A.*, vol. 195, pp. 105-109, 1994.

[47] S. Sahoo, "On the formation and stability of the Fröhlich bipolaron in two − and three-dimensional systems," *Il Nuovo Cimento.D.*, vol. 18, pp. 849-853, 1996.

[48] D. Emin, *In: Polarons and bipolarons in high-Tc superconductors and related materials.* Cambridge: Univ. Press, 1995.

[49] G. De Filippis, V. Cataudella, and G. Iadonisi, "Normal state properties of an interacting large polaron gas," *Europ. Phys. J. (B)*, vol. 8, pp. 339-351, 1999.

[50] R. T. Senger, B. Kozal, A. Chatterjee, and A. Erçelebi, "Hartree −fock approximation of bipolaron state in quantum dots and wires," *Eur. Phys. J. B.*, vol. 78, pp. 525-529, 2010.

[51] O. Gunnarsson and B. Lundqvist, "Exchange and correlation in atomic, molecules, and solids by the spin-density-functional formalism," *Phys. Rev. B.*, vol. 13, pp. 4274-4298, 1976.

[52] R. L. Frank, E. H. Lieb, and R. Seiriger, "Symmetry of bipolaron bound states for small Coulomb Repulsion. arXiv:1201.3954v1 [math-ph] (19.01.2012)," 2012.

[53] V. K. Mukhomorov, "On the possibility of Landau-Pekar triplet bipolaron existence," *Amer. J. of Cond. Matt. Phys.*, vol. 2, pp. 77-82, 2012.

[54] V. K. Mukhomorov, "Singlet and triplet excited states of quasi-molecular dimmer solvated in ammonia," *Optics and Spectroscopy*, vol. 69, pp. 43-46, 1990.

[55]   N. C. R. Symons and K. Catteral, "Unstable intermediates. Part XXXIV. Solvated electrons: A model for the spin-paired species in liquid ammonia," *J. Chem. Soc. A. Inorg. Phys. Theor.*, pp. 13-16, 1966.

[56]   J. C. Thompson, *Electrons in liquid ammonia*. Oxford: Clarendon, 1976.

[57]   J. C. Scott, P. Pfluger, M. T. Kronnbi, and G. B. Street, "Electron-spin-resonance studies of pyrrole polymers: Evidence for bipolaron," *Phys. Rev. B.*, vol. 28, pp. 2140-2145, 1983.

[58]   R. R. Chance, J. L. Bredas, and R. Silbey, "Bipolaron transport in doped conjugated polymers," *Phys. Rev. B*, vol. 29, pp. 4491-4495, 1984.

[59]   K. F. Voss, C. M. Foster, and L. Smilowitz, "Substitution effects on bipolarons in alxoxy derivatives of poly (1,4-phenylen-vinylen)," *Phys. Rev. B.*, vol. 43, pp. 5109-5118, 1991.

[60]   R. Catteral, "Electron spin relaxation in solid metal-ammonia solutions. Evidence for high mobile electron pairs near the metal-nonmetal transition," *Phil. Mag.*, vol. 22, pp. 779-786, 1970.

[61]   D. E. O'Reilly, "Knight shifts and relaxation times of alkali − metal and nitrogen nuclei in metal-ammonia solutions," *J. Chem. Phys.*, vol. 41, pp. 3729-3735, 1964.

[62]   D. E. O'Reilly, "Spin densities in alkali metal-ammonia solutions," *J. Chem. Phys.*, vol. 41, pp. 3736-3742, 1964.

[63]   T. David, W. S. Glauninger, S. Zolotov, and M. J. Sienko, "Strange magnetic behavior and phase relations of metal-ammonia compounds. In: Metal-ammonia solutions," in *Proc. of Int. Conf. Eds. Lagowski J.J. & Sienko M.J.*, London, 1970, pp. 323-329.

[64]   N. R. Kestner and D. A. Copeland, "Studies of the species (e2-2)am," in *Proc. Int. Conf. Metal-Ammonia Solutions. Eds. Lagowski J., Sienko M.*, London, 1970, pp. 27-39.

[65]   J. C. Thompson, "Metal-nonmetal transition in metal-ammonia solutions," *Rev. Mod. Phys.*, vol. 40, pp. 704-710, 1968.

[66]   A. Stay, D. C. Johnson, and M. J. Sienko, "Low temperature magnetic susceptibility of the expanded metal compounds Li(NH3)4, Li(ND3)4, and Li(CH3NH2)4," *J. Chem. Phys.*, vol. 76, pp. 4248-4254, 1982.

[67]   T. R. White, S. P. Hsu, M. J. Mobley, and W. S. Glauninger, "Magnetic properties of metal-ammonia compounds," *J. Phys. Chem.*, vol. 88, pp. 3890-3895, 1984.

[68]   E. S. Fois, A. Selloni, M. Parrinello, and R. Carr, "Bipolaron in metal-metal holide solutions," *J. Phys. Chem.*, vol. 92, pp. 3268-3273, 1988.

[69]   J. B. Russel, "Free energy and the electron electrode in liquid ammonia " *J. Am. Chem. Soc.*, vol. 79, pp. 4051-4054, 1957.

[70]   B. K. Chakraverty, M. J. Sienko, and J. Bonnerot, "Low-temperature specific heat and magnetic susceptibility of nonmetallic vanadium bronzes," *Phys. Rev.*, vol. 17, pp. 3781-3789, 1978.

[71]   N. F. Mott, *Metal-insulator transitions*. London: Taylor & Francis, 1974.

[72]   E. Hart and M. Anbar, *The hydrated electron*. New York: Wiley, 1970.

[73]   V. K. Mukhomorov, "Intercombinative spontaneous transitions in two-electron quasi-atomic species solvated in ammonia," *Khim. Fiz. (Chemical Physics), (in Russian)*, vol. 8, pp. 1163-1167, 1989.

[74]   V. K. Mukhomorov, "Magnetic properties of electrons in metal-ammonia solutions," *Technical Physics. The Russian Journal of Applied Physics*, vol. 42, pp. 855-865, 1997.

[75]   V. K. Mukhomorov, *Bipolarons. Structure. Properties.* Saarbrücken, Germany: LAP Lampert Academic Publishing, (In Russian), 2011.

[76]   H. A. Bethe, *Quantum mechanics of one- and two-electron atoms.* Berlin: Springer, 1957.

[77]   S. A. Moskalenko, *Introduction to the theory of large density excitons.* Kishinev: Shteentza, (In Russian), 1983.

[78]   O. F. Schirmer and E. Salje, "Conduction bipolarons in low-temperature crystalline WO3-x," *J. Phys. C: Solid State Physics.*, vol. 13, pp. L 1067-L 1072, 1980.

Figure-1. Distance dependence of the electronic kinetic energy of two-center large bipolaron: (1) in zeroth approximation and (2,3) solutions with allowance for electron-electron orrelations: (2) an additional $2p^2$ configuration and (3) two additional electron configurations $2p^2$ and $1s2p$.
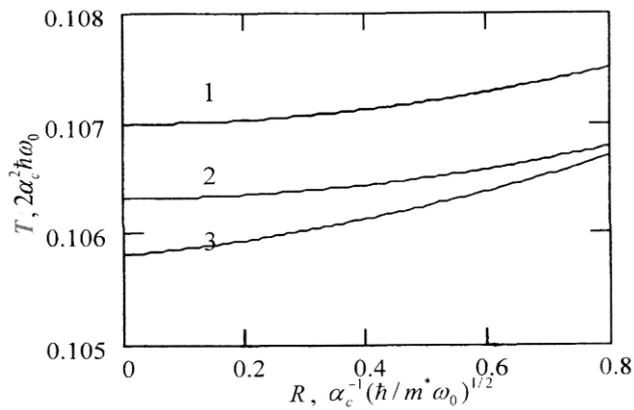
Figure-2. Line 1 is the total energy of the bipolaron in Hartree-Fock approximation (zeroth approximation); line 2 is the energy of the bipolaron after accounting for electron correlations. The figure was taken from Ref. [7].
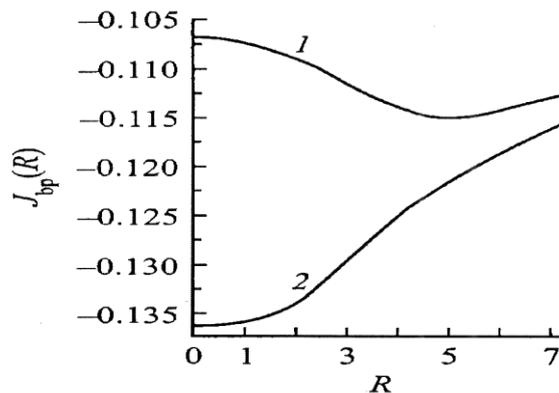
Figure 3. Distance dependence of the correlation contribution to the two-center bipolaron binding energy calculated for $\varepsilon*/\varepsilon_\infty = 1.05$ with the addition to the Hartree-Fock approximation of (1) one electronic configuration $(1s2p)$ and (2) two configurations $(1s2p)$ and $(2p^2)$.
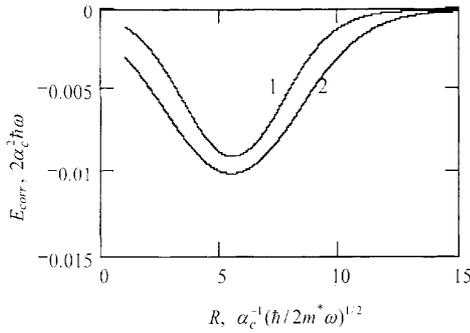
Figure-4. Binding energy of a large two-center bipolaron ($\varepsilon^*/\varepsilon_\infty = 1.00$) in the ground singlet state as a function of the interpolaron distance. Electronic wave function was chosen in the form (19). $(1) - C_1 = C_2 = C_3 = 0$ (zeroth approximation); $(2) - C_1 \neq 0, C_2 = C_3 = 0$; $(3) - C_1 \neq 0, C_2 \neq 0, C_3 = 0$; $(4) - C_1 \neq 0, C_2 \neq 0, C_3 \neq 0$; $(5) -$ triplet state of a large bipolaron.
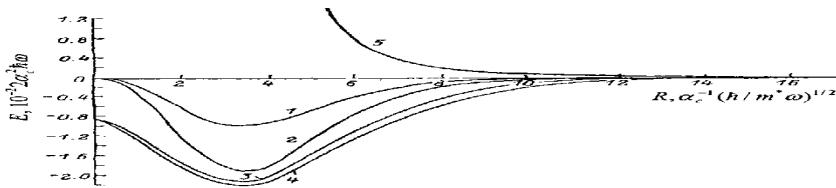
Figure-5. The binding energy of the singlet large bipolaron as a function of distance between polarons. The calculations are made taking into account the electron-electron correlations by using wave function (19). $\varepsilon^*/\varepsilon_\infty = 1.00$ (1), 1.02 (2), 1.05 (3), 1.08 (4), 1.10 (5).
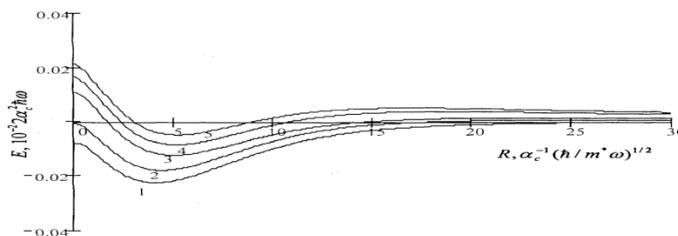
Figure-6. The ground state and relaxation-excited quasi-molecular terms of the two-center large bipolaron ($\varepsilon^*/\varepsilon_\infty = 1.075$). We took into account the electron-electron correlations by superposition of electronic configurations. $(1) - {}^1\Sigma_g(1s^2)$; $(2) - {}^3\Sigma_u(1s^2)$; $(3) - {}^1\Sigma_g(1s2p_z)$; $(4) -$

${}^3\Pi_u(1s2p_{x\pm iy})$; $(5) - {}^1\Pi_g(1s2p_{x\pm iy})$; $(6) - {}^1\Sigma_g(2p_z^2)$; $(7) - {}^1\Delta_g(2p_{x\pm iy}^2)$; $(8) - {}^3\Sigma_g(1s2p_z)$.