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AUTOLOCALIZED STATES OF AN EXCESS ELECTRON IN AN IONIC CLUSTER

A theory of electron affinity for an ionic cluster is proposed both in a quasiclassical approach and with quantization of a polarization electric field in a nanoparticle. The critical size of a cluster as for the formation of electron's autolocalized state and dependences of the energy and the radius of a polaron on cluster's size are obtained by the variational method. It has been found that the binding energy of an electron in the cluster depends on cluster's radius, but the radius of electron's autolocalization does not and equals the polaron radius in a corresponding infinite crystal. The bound state of an electron in the cluster is possible only if cluster's radius is more than the polaron radius.

Keywords: cluster, polaron, autolocalization, phonon confinement.

1. Introduction

The bound state of an electron in a polar medium is caused by a local polarization of the medium inducted by the electron. The electron is in a potential well in states with a discrete energy, and its field supports the polarization. In terms of the self-consistent state of an electron and a polar medium (ammonium, water, protein globules), some mathematical models of an excess electron in a cluster have been built and investigated [1–3]. In the models, it is supposed that the solvated electron does not belong to a separate molecule but collectively interacts with many atoms of the polar medium. It is shown by analytical and numerical methods that a critical size of clusters composed of polar molecules exists. In a cluster with a less size than the critical size, the autolocalized state (polaron state) cannot exist.

Since the polaron effect exists in an ionic crystal, we can suppose that the effect can occur in an ionic cluster too (e.g., $Na_{14}Cl_{13}$), beginning with a some critical size. In works [7–9], the electron localization in alkali-halide clusters $M_n^+X_{n-1}^-$ and $M_n^+X_{n-2}^-$ was numerically investigated. It was supposed that the clusters contain F-center defects and electron localized near a halide ion. Obviously, the localization of an electron in a cluster takes place in this model, rather than the autolocalization, because the main contribution to the binding energy of the excess electron is a Coulomb-like interaction with the F-center. In this case, the critical size is not observed. This problem is analogous to that of the F-center model of negatively charged metal-ammonium clusters [3]. We will consider the neutral ionic cluster + excess electron system, where the electron interacts with an induced polarization only, and the process of autolocalization occurs.

The electron + polarization system can be described in the quasiclassical approach. This means that the motion of an electron is quantized; however, the specific polarization of the medium $\mathbf{P}(\mathbf{r})$ is considered as a classical variable. However, the interaction of a electron with the polarization field can be described in the quantum approach. The borders of a cluster essentially influence the quantization of optical oscillations, i.e. the optical phonon confinement [10]. The influence of a geometry on the quantization of optical oscillations and on the interaction of

an electron with them was investigated in [11–13] for quantum wells, wires, and boxes. However, it should be noted that the polaron states in the heterostructures essentially depend on a confining potential. But in a nanoparticle, the polaron effect is stipulated by the interaction with the induced polarization only. The basic difference of optical and acoustical modes in a cluster and a heterostructure from the modes in an infinite crystal is the restriction to possible wavelengths of the oscillation and the presence of interfacial phonons. These properties of phonons cause the difference of the polaron state in a nanoparticle from that in an infinite crystal.

In Section 2, we will find the energy of a polaron in a nanoparticle and the critical parameters of nanoparticles as for the formation of a polaron state within the variational method in the quasiclassical approach. The variational method, unlike numerical calculations, aoolw one to obtain analytic expressions for the connection of autolocalized state's energy and the polaron radius with parameters of a cluster. In Section 3, the field of deformations of an ionic cluster is quantized taking the boundary condition on its surface into account. The energy of a polaron state, the critical size of a nanoparticle, and the polaron radius are determined by the variational method on the basis of an electron-phonon Hamiltonian for a spatially bounded medium.

2. Quasiclassical Approach

In this section, we will consider a quasiclassical description of electrons' interaction with a polarization displacement of ions from their equilibrium positions. Let us suppose that an electron is localized in the ionic cluster of a spherical shape with radius R and is described by a wave function $\Psi(\mathbf{r})$. The electron-created field $\mathrm{div}\mathbf{D}(\mathbf{r}) = e|\Psi(\mathbf{r})|^2$ induces a polarization of the cluster. In turn, the electric field of the polarization acts on the electron. The dipole moment of cluster's unit volume $\mathbf{P}(\mathbf{r})$ is determined by a difference of static and high-frequency polarizations:

$$\mathbf{P}(\mathbf{r}) = \mathbf{P}_0(\mathbf{r}) - \mathbf{P}_\infty(\mathbf{r}) = \left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon}\right)\mathbf{D} \equiv \frac{1}{\widetilde{\varepsilon}}\mathbf{D}, \quad (1)$$

where $\mathbf{D}$ is an electric displacement, and ε and ε_∞ are static and high-frequency permittivities, respectively. For the medium surrounding the cluster (e.g., vacuum), we have $\varepsilon_\infty = \varepsilon$. Then

$$\frac{1}{\widetilde{\varepsilon}} = \frac{\varepsilon - \varepsilon_\infty}{\varepsilon\varepsilon_\infty} \quad \text{for } r < R,$$
$$\widetilde{\varepsilon} = \infty \quad \text{for } r \geq R. \quad (2)$$

The polarization of a cluster brings to the appearance of a polarization charge $\rho = -\mathrm{div}\mathbf{P}$. Let $\mathbf{E} = -\nabla\varphi$ be an electric field of the polarization, and let $\mathrm{div}\mathbf{E} = \rho/\varepsilon_0 \Longrightarrow \mathbf{D} = -\varepsilon_0\widetilde{\varepsilon}\mathbf{E}$, where ε_0 is an electric constant. Then the energy of cluster's polarization is [15]

$$U_{\text{field}} = \frac{1}{2}\int \mathbf{P}\frac{\mathbf{D}}{\varepsilon_0}dV = \frac{1}{2}\varepsilon_0\int \widetilde{\varepsilon}\mathbf{E}^2 dV. \quad (3)$$

Hence, the energy functional of the electron + + polarized cluster system has the form

$$I(\Psi,\varphi) = \frac{\hbar^2}{2m}\int |\nabla\Psi|^2 dV +$$
$$+ e\int |\Psi|^2\varphi dV + \frac{1}{2}\varepsilon_0\int \widetilde{\varepsilon}(\nabla\varphi)^2 dV, \quad (4)$$

where the first term is the kinetic energy of a localized electron in the state $\Psi(\mathbf{r})$, the second term is the interaction energy of the electron with the electric field $\varphi(\mathbf{r})$ of the induced polarization. The localized state of an electron in the cluster is energetically profitable if $I < 0$.

We note that electron's energy in vacuum is more than electron's energy on the bottom of a conduction band by the electron affinity χ. Unlike a cluster in an infinite crystal, the value of χ can be made zero, by reckoning the energy from the affinity energy. In addition, the Coulomb blockade exists: to localize an electron in the cluster, the work $e^2/2C$ must be done, where $C = 4\pi\varepsilon_0\varepsilon R$ is the capacity of the cluster. In an infinite crystal, the Coulomb blockade is absent, because $C = \infty$. The calculation of these energies can change the situation basically, because the localization (due to the affinity) and the autolocalization can exist simultaneously, or the Coulomb blockade creates a barrier for the autolocalization. However, we can control the affinity and the blockade with an applied external potential V, which changes the electron energy by $-eV$ so that

$$\frac{e^2}{2C} - \chi - eV = 0. \quad (5)$$

Then electron's energy in vacuum is equal to the energy in a cluster (without $I(\Psi,\varphi)$). This mechanism is used in a quantum-dot one-electron transistor. Hence, the interaction of an electron with the cluster is caused by the induced polarization only, and we can observe the effect of autolocalization.

Varying functional (4) in Ψ under the condition $\int|\Psi|^2dV=1$, we obtain an equation describing the movement of the electron with energy E in a potential well $e\varphi$ created by the electron itself:

$$-\frac{h^2}{2m}\Delta\Psi+e\varphi\Psi=E\Psi. \tag{6}$$

Varying functional (4) in φ with regard for (2), we obtain an equation describing the polarization field induced by the electron:

$$\left\{\begin{array}{ll}\Delta\varphi=\frac{e|\Psi|^2}{\varepsilon_0\widetilde{\varepsilon}} & r<R\\ \Delta\varphi=0 & r\geq R\end{array}\right\}. \tag{7}$$

The boundary conditions on the surface of the cluster (1) and the environment (2) take the form

$$\varphi_1=\varphi_2,\quad \widetilde{\varepsilon}_1\frac{\varphi_1}{\partial n}=\widetilde{\varepsilon}_2\frac{\varphi_2}{\partial n}, \tag{8}$$

where $\mathbf{n}$ is a normal to cluster's surface. In view of $\widetilde{\varepsilon}_2=\infty$ and Eq. (7) on the cluster boundary and out of the cluster, we can suppose

$$\varphi=0\quad\text{for}\quad r\geq R. \tag{9}$$

The boundary condition (9) $\varphi(R)=0$ is the main difference of electron's autolocalization in a cluster from the polaron state in an infinite crystal, where the electrical field of the polarization is equal to zero only at infinity: $\varphi(\infty)=0$. In addition, we have to calculate the boundary conditions for polaron's wave function at the boundary of a cluster $\Psi(r)_{r=R-0}=\Psi(R-)_{r=R+0}$ and $\frac{1}{m}\Psi'(r)_{r=R-0}=\frac{1}{m_0}\Psi'(R-)_{r=R+0}$, because electron's masses inside and outside the cluster are different: $m\neq m_0$. However, as it will be shown in Appendix 4, the boundary conditions give the insignificant contribution to system's energy I, and we can use the united wave function Ψ (which is a continuous function and has continuous derivatives) and the mass m on the assumption that the radius of a cluster is bigger than or equal to the critical radius.

To obtain the energies of polaron states and the critical size of a cluster, we will use the variational method because it allows us to find analytic expressions. Let the cluster be characterized by the values of static ε and high-frequency ε_∞ permittivities and the effective mass m of an electron in crystal's conduction band (for NaCl, $m=2.78m_0$, m_0 is electron's mass in vacuum). Obviously, these values have meaning for clusters with sizes, which are much more than interatomic distances only. However, the method proposed below can be extrapolated to small clusters. With the help of Eqs. (7) and the condition $\varphi(\infty)=0$, functional (4) can be simplified:

$$I(\Psi,\varphi)=\frac{\hbar^2}{2m}\int|\nabla\Psi|^2dV-\frac{1}{2}\varepsilon_0\int\widetilde{\varepsilon}(\nabla\varphi)^2dV. \tag{10}$$

For a region out of the cluster $r\geq R$, we suppose $\widetilde{\varepsilon}\varphi=0$. The wave function of system's (electron + + polarized cluster) ground state can be taken in the form [15]

$$\Psi=\frac{1+r/r_0}{\sqrt{7\pi r_0^3}}\exp\left(-\frac{r}{r_0}\right), \tag{11}$$

where the radius r_0 is a variational parameter, namely, the polaron radius. Substituting the wave function (11) in Eq. (7) and taking the boundary condition (9) into account, we obtain the first integral and the solution as follows:

$$\frac{\partial\varphi}{\partial r}=\frac{e}{\varepsilon_0\widetilde{\varepsilon}}\frac{1}{4\pi r^2}\left[1-\exp\left(-2\frac{r}{r_0}\right)\times\right.$$
$$\left.\times\left(1+2\frac{r}{r_0}+2\frac{r^2}{r_0^2}+\frac{8}{7}\frac{r^3}{r_0^3}+\frac{2}{7}\frac{r^4}{r_0^4}\right)\right]\ \text{for}\ r<R, \tag{12}$$

$$\varphi=\frac{e}{\varepsilon_0\widetilde{\varepsilon}}\frac{14}{56\pi r}\left[\exp\left(-2\frac{r}{r_0}\right)\times\right.$$
$$\left.\times\left(1+\frac{19}{14}\frac{r}{r_0}+\frac{10}{14}\frac{r^2}{r_0^2}+\frac{2}{14}\frac{r^3}{r_0^3}\right)-1\right]-$$
$$-\frac{e}{\varepsilon_0\widetilde{\varepsilon}}\frac{14}{56\pi R}\left[\exp\left(-2\frac{R}{r_0}\right)\times\right.$$
$$\left.\times\left(1+\frac{19}{14}\frac{R}{r_0}+\frac{10}{14}\frac{R^2}{r_0^2}+\frac{2}{14}\frac{R^3}{r_0^3}\right)-1\right]\ \text{for}\ r<R, \tag{13}$$

$$\frac{\partial\varphi}{\partial r}=0,\ \varphi=0\ \text{for}\ r\geq R. \tag{14}$$

Substituting Ψ (11) and $\frac{\partial\varphi}{\partial r}$ (12,14) in functional (10), we obtain the energy of the system as a function of the polaron radius:

$$I(r_0) = \frac{3\hbar^2}{14mr_0^2} - \frac{5373}{100352}\frac{e^2}{\varepsilon_0\widetilde{\varepsilon}\pi r_0} \times$$
$$\times\left[1 + \frac{\exp\left(-2\frac{R}{r_0}\right)}{5373r_0^6R}\left(34048r_0^6R - 25088r_0^7 + \right.\right.$$
$$\left.\left. + 17920r_0^5R^2 + 3584r_0^4R^3\right)\right] + \frac{e^2}{\varepsilon_0\widetilde{\varepsilon}\pi r_0}\frac{\exp\left(-4\frac{R}{r_0}\right)}{100352r_0^6R} \times$$
$$\times\left(12544r_0^7 + 39421r_0^6R + 57322r_0^5R^2 + 50152r_0^4R^3 + \right.$$
$$\left. + 28640r_0^3R^4 + 10720r_0^2R^5 + 2432r_0R^6 + 256R^7\right) +$$
$$+ \frac{12544}{100352}\frac{e^2}{\varepsilon_0\widetilde{\varepsilon}\pi r_0}\frac{r_0}{R}. \qquad (15)$$

The following terms give the main contribution to the energy (15) at $r_0/R > 0.5$:

$$I(r_0) \approx \frac{3\hbar^2}{14mr_0^2} - \frac{5373}{100352}\frac{e^2}{\varepsilon_0\widetilde{\varepsilon}\pi r_0}\left[1 - \frac{12544}{5373}\frac{r_0}{R}\right] \equiv$$
$$\equiv I_\infty + \frac{12544}{100352}\frac{e^2}{\varepsilon_0\widetilde{\varepsilon}\pi R}, \qquad (16)$$

where I_∞ is the energy of an infinite crystal with a localized electron. The autolocalized state of an electron in a cluster (or in a crystal) is energetically profitable if $I < 0$. From Eqs. (15), (16), we can see a limitation $I_\infty < I$. From Eq. (16), we can see that polaron's radius r_0 does not depend on cluster's radius R:

$$\frac{\partial I}{\partial r_0} = 0 \Longrightarrow r_0 = 8.00\frac{\hbar^2\varepsilon_0\widetilde{\varepsilon}\pi}{me^2}. \qquad (17)$$

Function (15) for various values of cluster's radius R is shown in Fig. 1. We can see that the bound state of an electron in a cluster consisting of molecules NaCL can exist, by beginning from $R \approx 3a$, where $a = 2.81$ Å is the interatomic distance. With increase in cluster's size, the binding energy increases and tends to a polaron energy in an infinite crystal $I_\infty \approx -0.265$ eV. The radius of electron's autolocalization r_0 in a cluster minimizes the energy I. From Fig. 1, we can see that r_0 does not depend almost on cluster's radius. For sodium chloride, the radius is

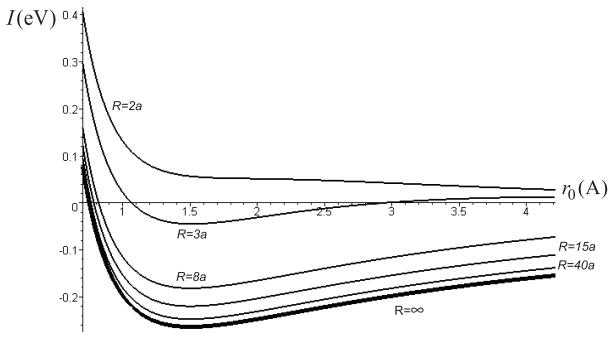

Fig. 1. Dependences of the energy of the electron + cluster system (15) on the polaron radius $I = I(r_0)$ for an ionic cluster consisting of molecules NaCL. The curves have been built for cluster's radii: $2a, 3a, 8a, 15a$, and $40a$, where $a = 2.81$ Å is the interatomic distance. The bold line is the energy of an infinite crystal with an electron

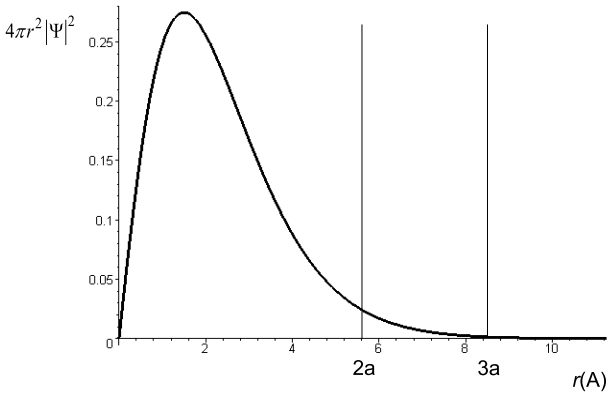

Fig. 2. Probability distribution for an electron in a cluster. The vertical lines indicate the radii of clusters, for which the energy of electron's autolocalized state was calculated (see Fig. 1). The radius $2a$ is subcritical (the bound state is absent), the radius $3a$ is somewhat bigger than the critical radius – the bound state appears

equal to $r_0 = 1.5$ Å. The dependence shown in Fig. 1 is well approximated by the simpler dependence (16).

Equations (6), (7) were solved numerically in [2] for clusters of ammonia and water. It was shown that the critical size of clusters exists. However, the analytic method discovers the next pattern. The polaron radius in a cluster does not depend on the radius of a cluster. The bound state of an electron in the cluster exists if the polaron radius is less than cluster's radius. In other words, the autolocalized electron is hidden in depth of the cluster always and has a negligibly low probability to be outside it. If the cluster

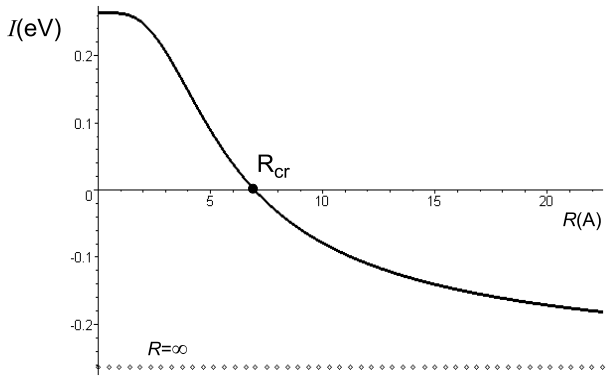

Fig. 3. Energy of the electron + cluster (consisting of NaCL) system as a function of cluster's radius $I(R)$ (solid line). The doted line is the energy of a polaron in an infinite crystal $R = \infty$. $R_{\rm cr}$ is the critical radius of a cluster

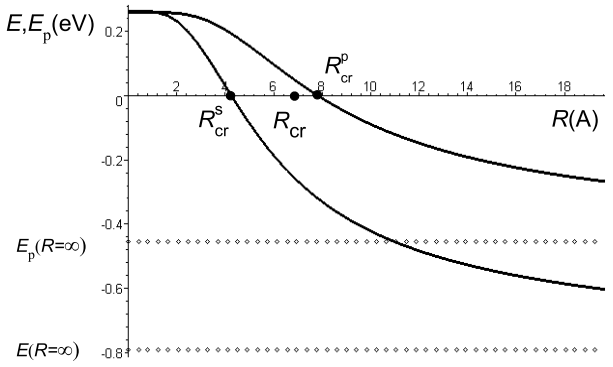

Fig. 4. Energies of electron's ground state $1s$ and the p-state in the potential well $e\varphi$ as functions of cluster's radius $E(R)$ and $E_p(R)$ (solid lines). The dotted lines show the energies of an electron in an infinite crystal $R = \infty$. $R_{\rm cr}$ is the critical radius, when the polaron state is energetically profitable (see Fig. 3), $R^{\rm s}_{\rm cr}$ and $R^{p}_{\rm cr}$ are a critical radii when, respectively, the $1s$-state and p-state of an electron in the potential well (13), (14) are energetically profitable

is enough small so that the electron can be out of the cluster, the bound state disappears. The above-mentioned particulars are illustrated in Fig. 2. Similar results were obtained in [4], but another functional $I(\Psi, \varphi)$ was considered, and the ground-state energy of an electron in a cluster and the autolocalization radius were expressed in term of the static dielectric constant only. Hence, the autolocalization effect in that model is not the polaron effect, unlike our model.

Since the polaron radius r_0 is independent of cluster's radius R, we can obtain the energy of the system as a function of cluster's radius $I(R)$, by assuming that the polaron radius in formula (15) is equal to the optimal value (17). The result is shown in Fig. 3, where we can see that the critical radius of a cluster determined by the equation $I(R_{\rm cr}) = 0$ is equal to $R_{\rm cr} = 7.0$ Å ($2 \div 3$ of the interatomic distance). With increase in cluster's radius, the energy asymptotically tends to its value in an infinite crystal $I(R \to \infty) \to I_\infty$.

The ground state of an electron in the potential well $e\varphi$ is $1\mathtt{s}$. The energy $I(\Psi, \varphi)$ (4,10) is a sum of the ground state energy of an electron in the potential well and the energy of cluster's polarization $1/2\varepsilon_0 \int \widetilde{\varepsilon}(\nabla\varphi)^2 dV > 0$. Then the ground-state energy of the electron is

$$E(R) = \frac{\hbar^2}{2m} \int |\nabla\Psi|^2 dV - \varepsilon_0 \int \widetilde{\varepsilon}(\nabla\varphi)^2 dV, \qquad (18)$$

where the wave function Ψ and the field φ are taken in the forms (11) and (12)–(14), respectively. The radius r_0 is equal to its optimal value (17). The energy $E(r)$ is the energy required to quickly transfer an electron from the localized state in a free state (e.g., by the absorption of a photon with an energy $\hbar\omega > |E|$). The plot $E(R)$ is shown in Fig. 4, where we can see that the $1s$-state is energetically profitable, by beginning from cluster's radius $R^s_{\rm cr} \approx 4$ A $< R_{\rm cr} = 7$ Å. In other words, the metastable autolocalized state of an electron in an ionic cluster is possible in the interval $R^s_{\rm cr} < R < R_{\rm cr}$.

If the potential well (13) is sufficiently deep, then other discrete energy levels are possible. As cluster's radius increases, the p-state can appear. The $s - p$ photo-transitions occur without changes of ions' positions, according to the Franck–Condon principle. The polarization field φ and the polaron radius r_0 are the same as those in the s-state: (13) and (17), respectively. However, the wave function of an electron can be chosen in the form

$$\Psi = \left(\frac{\zeta}{r_0}\right)^{3/2} \frac{r\zeta}{\pi r_0} \exp\left(-\frac{\zeta r}{r_0}\right) \cos\theta, \qquad (19)$$

where ζ is a variational parameter, θ is a polar angle. Then the energy of an electron in the p-state is

$$E_p = \frac{\hbar^2}{2m_*} \int\limits_0^\infty 2\pi r^2 dr \int\limits_0^\pi \sin\theta d\theta \left|\nabla\Psi_p(r,\theta)\right|^2 + \\ + e \int\limits_0^\infty 2\pi r^2 dr \int\limits_0^\pi \sin\theta d\theta \left|\Psi_p(r,\theta)\right|^2 \varphi(r). \qquad (20)$$

Expression (20) is a function of the variation parameter ζ. The plots of the dependence E_p on ζ for clusters' radii $R = 2a, 3a, 8a$, and ∞ are shown in Fig. 5, where we can see that the optimal value (it minimizes E_p) of parameter ζ weakly depends on cluster's radius, and it can be supposed $\zeta = 0.65$. Then we can easily find the dependence of the p-state energy on cluster's radius $E_p(R)$ (Fig. 4, where we can see that the p-state is energetically profitable, by beginning from the radius of the cluster $R^p_{\rm cr} \approx 8$ Å $> R_{\rm cr} > R^s_{\rm cr}$. With increase in cluster's radius, the energy $E_p(R)$ asymptotically tends to its value in an infinite crystal. In bigger clusters, the d, f, and higher states are possible.

The essential difference of the polaron state of an electron in a cluster from the polaron state in an infinite crystal is the localization of the electron at cluster's center as a result of the boundary condition (9). On the contrary, all points in an infinite crystal are equivalent (in the continuous representation of a substance). Therefore, the polaron can move. In this case, the polaron is characterized by an effective mass $M \gg m$.

3. Quantum Approach

The interaction of an electron with the polarization field can be described in the quantum approach. The boundaries of a cluster essentially influence the quantization of optical oscillations, which is not considered in the quasiclassical approach. The basic difference of optical and acoustic modes in a cluster from the modes in an infinite crystal is a restriction to the possible wavelengths of oscillations. In a such situation, it is necessary to quantize the field of cluster's polarization φ. In the harmonic approximation, the Hamiltonian of the electron + cluster system has the form

$$H = -\frac{\hbar^2}{2m}\Delta + \frac{1}{2}\varepsilon_0\widetilde{\varepsilon}\int\left[\frac{1}{\omega^2}(\nabla\dot{\varphi})^2 + (\nabla\varphi)^2\right]dV + \\ + e\varphi \equiv \widehat{T} + \widehat{U}_f + \widehat{V}_{\rm int}, \qquad (21)$$

where the first term $\widehat{T}$ is the operator of kinetic energy of an electron, $\widehat{U}_f$ is the operator of deformation energy of a crystal (cluster), $\widehat{V}_{\rm int}$ is the operator of interaction of the electron with the deformation field. The procedure of quantization of the deformation field is based on the fact that the electric field φ must be expressed in terms of the creation $b^\dagger$ and annihilation b operators of optical phonons, so that

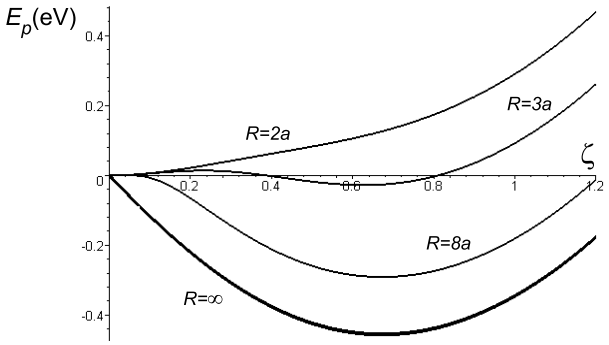

Fig. 5. Dependence of electron's energy in the p-state in a cluster on the parameter ζ for an ionic cluster consisting of NaCL. The curves are built for the radii of clusters equal to $2a, 3a$, and $8a$. The bold line is electron's energy in the p-state in an infinite crystal

$$\widehat{U}_f = \frac{1}{2}\varepsilon_0\widetilde{\varepsilon}\int\left[\frac{1}{\omega^2}(\nabla\dot{\varphi})^2 + (\nabla\varphi)^2\right]dV = \\ = \hbar\omega\sum_{\mathbf{q}}\left(b^\dagger_{\mathbf{q}}b_{\mathbf{q}} + \frac{1}{2}\right), \qquad (22)$$

where $\mathbf{q}$ is the wave vector of a phonon. For simplicity, we will suppose that the optical oscillations are dispersionless $\omega = {\rm const}$. The field φ is proportional to a displacement of atoms ξ. The displacement and the field must satisfy the periodic boundary conditions

$$\xi_{\mathbf{n}} = \xi_{\mathbf{n}+N2\mathbf{a}}, \quad \varphi_{\mathbf{n}} = \varphi_{\mathbf{n}+N2\mathbf{a}}, \qquad (23)$$

where $2a$ is the lattice constant of a two-component ionic crystal. Then the potential of interaction of an electron with the deformation field (electron-phonon interaction) can be written as

$$\widehat{V}_{\rm int} = e\widehat{\varphi} = e\sqrt{\frac{\hbar\omega}{2\varepsilon_0\widetilde{\varepsilon}V}}\sum_{\mathbf{q}}\frac{e^{i\mathbf{qr}}}{q}\left(b_{\mathbf{q}} + b^\dagger_{-\mathbf{q}}\right), \qquad (24)$$

where $\mathbf{q}$ is taken from the first Brillouin zone $-\pi/2a < q_x, q_y, q_z < \pi/2a$. The creation and annihilation operators are written in sense $b_{\mathbf{q}} \to b_{\mathbf{q}}e^{i\omega t}$, $b^\dagger_{\mathbf{q}} \to b^\dagger_{\mathbf{q}}e^{-i\omega t}$. The cyclic boundary conditions are ensured with periodic multipliers $e^{i\mathbf{qr}}$. For an infinite crystal, we can neglect the discreteness of a substance, and we can assume the period of a lattice is infinitely small, i.e., $-\infty < q_x, q_y, q_z < \infty$.

Due to the ionic-type connection between atoms, the shape of an ionic cluster is close to the cubic

one (e.g., unlike the ball shape of a metallic cluster). Computer simulations and experimental evidences [7–9] show that the alkali halide clusters $M_n^+X_m^-$, $n \approx m \gtrsim 14$ form stable cuboid structures and have a cubic microlattice. Clusters can have magic numbers of atoms, i.e., such numbers, when all shells are filled. Magic clusters are most stable, and magic ionic clusters have cuboid shape. For large clusters $R \gg a$, the shape can be arbitrary (a is the interatomic distance). Obviously, the shape of large clusters $R \gg r_0$ has no basic importance, because the excess electron has a low probability to be near the surface of the cluster. For convenience, we will consider the large cluster as cubic in this case too.

Let us have an ionic cluster (e.g., consisting of NaCL) of the cubic form with sizes $-\frac{L}{2} < x, y, z < \frac{L}{2}$. The main difference between a cluster and an infinite crystal is the condition on cluster's boundary (9) instead of the cyclic boundary condition (23), which causes the phonon confinement. For a cube, the boundary conditions read

$$\varphi\left(x = \pm\frac{L}{2}\right) = \varphi\left(y = \pm\frac{L}{2}\right) = \varphi\left(z = \pm\frac{L}{2}\right) = 0. \quad (25)$$

The field φ does not satisfy conditions (25). In [11], a method of construction of the Hamiltonian for the electron-optical phonon interaction in a dielectric slab (with the boundary conditions $\varphi\left(z = \pm\frac{L}{2}\right) = 0$) was proposed. But the method brings to a very cumbersome expression for a quantum box (cluster). We propose the following method. The boundary condition is satisfied by the operator

$$\widehat{\varphi} = \frac{A}{\sqrt{L^3}} \sum_{q_x} \sum_{q_y} \sum_{q_z} \frac{1}{q} \left(b_{\mathbf{q}} + b^{\dagger}_{-\mathbf{q}}\right) \times$$
$$\times \begin{bmatrix} \cos(q_x x), & \text{odd} & n_x \\ \sin(q_x x), & \text{even} & n_x \end{bmatrix} \begin{bmatrix} \cos(q_y y), & \text{odd} & n_y \\ \sin(q_y y), & \text{even} & n_y \end{bmatrix} \times$$
$$\times \begin{bmatrix} \cos(q_z z), & \text{odd} & n_z \\ \sin(q_z z), & \text{even} & n_z \end{bmatrix}, \quad (26)$$

where the projections of the wave vector $\mathbf{q}$ of an optical phonon are $q_{x,y,z}\frac{L}{2} = n_{x,y,z}\frac{\pi}{2}$ (such that $\cos\left(q_{x,y,z}\frac{L}{2}\right) = 0$, $\sin\left(q_{x,y,z}\frac{L}{2}\right) = 0$). The unknown constant A is found from the condition of secondary quantization of the deformation field (22): $A = \sqrt{\frac{\hbar\omega}{2\varepsilon_0\widetilde{\varepsilon}}}$. The energy of an electron is minimal, when it is situated at the center of a cluster, and the probability amplitude is symmetric about the center $\Psi(\mathbf{r}) = \Psi(-\mathbf{r})$. Then the terms with sine may be omitted, because they give no contribution to the electron-phonon interaction energy (and, hence, to the polarization): $\int_{-L/2}^{L/2} \Psi^2(x) \sin(q_x x) = 0$. This is equivalent to the boundary conditions

$$\frac{\partial\varphi}{\partial x}(x=0) = \frac{\partial\varphi}{\partial y}(y=0) = \frac{\partial\varphi}{\partial z}(z=0) = 0. \quad (27)$$

The integer number n of half-waves of phonons must be placed on a cube edge $L = na$. Moreover, a half of phonon's wavelength must not be bigger than the cube edge length and smaller than the interatomic distance a (between a cation and an anion on a cube edge): $a < \lambda/2 = \frac{\pi}{q} < L$. Hence, the possible projections of the wave vector $\mathbf{q} = (q_x, q_y, q_z)$ must take the values

$$n_x, n_y, n_z = \pm1, \pm3, \pm5..., \begin{pmatrix} \pm n, & \text{odd} & n \\ \pm(n-1), & \text{even} & n \end{pmatrix}, \quad (28)$$

$$L = na.$$

Then the Hamiltonian of the electron + cluster system can be written as

$$H = -\frac{\hbar^2}{2m}\Delta + \hbar\omega \sum_{\mathbf{q}} \left(b^{\dagger}_{\mathbf{q}} b_{\mathbf{q}} + \frac{1}{2}\right) +$$
$$+ \frac{M_0}{\sqrt{L^3}} \sum_{\mathbf{q}} \frac{\cos(q_x x)\cos(q_y y)\cos(q_z z)}{q} \left(b_{\mathbf{q}} + b^{\dagger}_{-\mathbf{q}}\right), \quad (29)$$

where

$$M_0^2 = e^2 \frac{\hbar\omega}{2\varepsilon_0\widetilde{\varepsilon}} \equiv \frac{4\pi\alpha\hbar(\hbar\omega)^{3/2}}{\sqrt{2m}},$$
$$\alpha = \frac{e^2}{4\pi\varepsilon_0\widetilde{\varepsilon}\hbar}\left(\frac{m}{2\hbar\omega}\right)^{1/2}. \quad (30)$$

Here, α plays the role of the electron-phonon coupling constant. We suppose that the optical phonons are dispersionless, and α does not depend on the sizes of a cluster. Experimental data indicate that the oscillatory spectrum $\omega(q)$ for clusters $(\text{NaCL})_N$ quickly approaches that of an infinite crystal, as N increases. $N = 4$ is enough to have the characteristics of an infinite crystal [14]. Since the cluster is situated in a nonpolarizable substance $\widetilde{\varepsilon}_2 = \infty$, the interaction with interface phonons is absent [16].

It is convenient to transit from the creation and annihilation operators to new conjugate operators:

$$Q_{\mathbf{q}} = \frac{1}{\sqrt{2}}\left(b_{\mathbf{q}} + b^{\dagger}_{-\mathbf{q}}\right), \quad P_{\mathbf{q}} = \frac{-i}{\sqrt{2}}\left(b_{\mathbf{q}} - b^{\dagger}_{-\mathbf{q}}\right). \quad (31)$$

Then the Hamiltonian takes the form

$$\widehat{H} = -\frac{\hbar^2}{2m_*}\Delta + \frac{\hbar\omega}{2}\sum_{\mathbf{q}}\left(|Q_{\mathbf{q}}|^2 + |P_{\mathbf{q}}|^2\right) +$$

$$+ M_0\sqrt{\frac{2}{L^3}}\sum_{\mathbf{q}}\frac{\cos(q_x x)\cos(q_y y)\cos(q_z z)}{q}Q_{\mathbf{q}}. \qquad (32)$$

System's wave function $\Phi(\mathbf{r}, Q_{\mathbf{q}})$ has to contain the coordinates of an electron $\mathbf{r}$ and ions' displacement $Q_{\mathbf{q}}$. Usually, it is supposeв that the wave function is a product of two parts depending only on the electron coordinates and the phonon coordinates, respectively:

$$\Phi(\mathbf{r}, Q_{\mathbf{q}}) = \Psi(\mathbf{r})\phi(Q_{\mathbf{q}} + \delta Q_{\mathbf{q}}) \qquad (33)$$

$$\Psi(\mathbf{r}) = \left(\frac{1}{\pi r_0}\right)^{3/2}\exp\left(-\frac{r^2}{2r_0^2}\right), \qquad (34)$$

where the electron wave function is chosen in the Gauss form to describe a localized electron in a cluster, and r_0 is the polaron radius playing the role of a variational parameter. The phonon wave function ϕ is the wave function of a harmonic oscillator centered on the equilibrium displacement $-\delta Q_{\mathbf{q}}$ (an electron deforms a cluster, and the ions pass into new centers of equilibrium), which must be determined. Let us average Hamiltonian (32) over electron's coordinates: $H(Q_{\mathbf{q}}) = \int \Psi\dagger(\mathbf{r})\widehat{H}\Psi(\mathbf{r})d^3r$:

$$H(Q_{\mathbf{q}}) = \frac{\hbar\omega}{2}\sum_{\mathbf{q}}\left(|Q_{\mathbf{q}}|^2 + |P_{\mathbf{q}}|^2\right) +$$

$$+\frac{3\hbar^2}{4m_* r_0^2} + \sum_{\mathbf{q}} L_{\mathbf{q}} Q_{\mathbf{q}}, \qquad (35)$$

where

$$L_{\mathbf{q}} = M_0\sqrt{\frac{2}{L^3}}\int\limits_{-L/2}^{L/2}\int\limits_{-L/2}^{L/2}\int\limits_{-L/2}^{L/2}\Psi^2(\mathbf{r})\times$$

$$\times\frac{\cos(q_x x)\cos(q_y y)\cos(q_z z)}{q}dxdydz. \qquad (36)$$

The first term in Hamiltonian (35) describes harmonic oscillations (optical phonons) about equilibrium positions $Q_{\mathbf{q}} = 0$ (zero oscillations and excited phonons if they are). The second term $3\hbar^2/4m_* r_0^2$ is the kinetic energy of an electron in the localized state. The last term is the potential energy of electron's interaction with a deformation field. Following

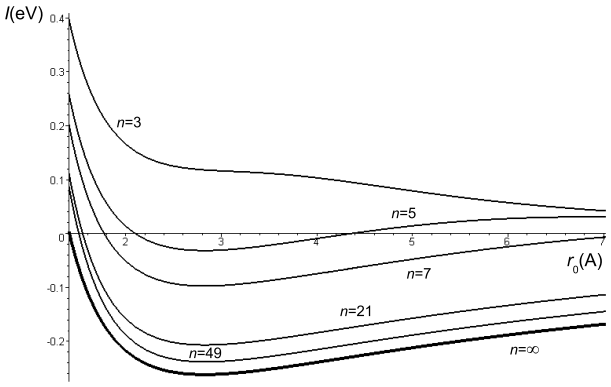

Fig. 6. Dependences of the energy of the electron + cluster system (15) on the polaron radius $I = I(r_0)$ for an ionic cluster consisting of NaCL. The curves were built for the edges of cubic clusters $3a, 5a, 7a, 21a$, and $49a$, where $a = 2.81$ Åis the interatomic distance. The bold line is the energy of an infinite crystal with an electron

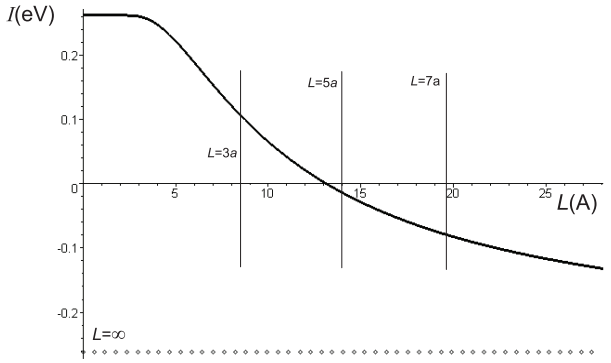

Fig. 7. Energy of the electron + cluster system (consisting of NaCl) as a function of the diameter of a cluster $I(L)$ (solid line). The energy of a polaron in an infinite crystal $L = \infty$ is shown by a dotted line. The lengths of edges (in interatomic distances a) of cubic clusters $n = 3$, $n = 5$, $n = 7$ are marked by vertical lines

[17], let us suppose that the equilibrium displacement is $\delta Q_{\mathbf{q}} = L_{\mathbf{q}}/\hbar\omega$. Then the term in electron's energy which is linear in $Q_{\mathbf{q}}$ disappears. This gives us the energy of the electron + deformation field system $I(r_0)$:

$$H(Q_{\mathbf{q}}) = \frac{\hbar\omega}{2}\sum_{\mathbf{q}}\left(|Q_{\mathbf{q}} + \delta Q_{\mathbf{q}}|^2 + |P_{\mathbf{q}}|^2\right) +$$

$$+\frac{3\hbar^2}{4mr_0^2} + \frac{1}{2\hbar\omega}\sum_{\mathbf{q}} L_{\mathbf{q}}^2 \equiv \qquad (37)$$

$$\frac{\hbar\omega}{2}\sum_{\mathbf{q}}\left(|Q_{\mathbf{q}} + \delta Q_{\mathbf{q}}|^2 + |P_{\mathbf{q}}|^2\right) + I(r_0). \qquad (38)$$

The first term in (37) describes the harmonic oscillations about new equilibrium positions $-\delta Q_{\mathbf{q}}$. The second term is the kinetic energy of an electron in the localized state. After the transition done in Hamiltonian (35), the last term is the potential energy of electron's interaction with a deformation field plus the energy of the deformation field.

The summation over $\mathbf{q}$ is equivalent to the summation over n_x, n_y, n_z in accordance with Eq. (28). Since the summation is spreading on odd n only, it is convenient to pass to new variables: $\widetilde{n}_x = (n_x - -1)/2, \widetilde{n}_y = (n_y - 1)/2, \widetilde{n}_z = (n_z - 1)/2$. In addition, the limits of integration in formula (36) can be expanded to $\pm\infty$, which simplifies the calculation without a essential error, because restriction (28) on the wave vectors of phonons does the main contribution to the effect of finite volume of a cluster. Hence, the energy can be written as follows:

$$I(r_0) = \frac{3\hbar^2}{4m_* r_0^2} + \frac{M_0^2}{2\hbar\omega}\frac{2}{L^3}\times$$
$$\times\left\{\begin{array}{ll} \displaystyle\sum_{\widetilde{n}_x=(-n+1)/2}^{(n-1)/2}\sum_{\widetilde{n}_y=(-n+1)/2}^{(n-1)/2}\sum_{\widetilde{n}_z=(-n+1)/2}^{(n-1)/2} & \text{for odd } n,\\ \displaystyle\sum_{\widetilde{n}_x=-n/2}^{(n-2)/2}\sum_{\widetilde{n}_y=-n/2}^{(n-2)/2}\sum_{\widetilde{n}_z=-n/2}^{(n-2)/2} & \text{for even } n,\end{array}\right\}\times$$
$$\times\frac{L^2}{\pi^2}\frac{\exp\left(-\frac{\pi^2}{L^2}\frac{r_0^2}{4}[(2\widetilde{n}_x+1)^2+(2\widetilde{n}_y+1)^2+(2\widetilde{n}_z+1)^2]\right)}{(2\widetilde{n}_x+1)^2+(2\widetilde{n}_y+1)^2+(2\widetilde{n}_z+1)^2}. \quad (39)$$

For an infinite crystal ($n\to\infty$), system's energy and the polaron radius are

$$\left\{\begin{array}{l} I(r_0) = \dfrac{3\hbar^2}{4mr_0^2} - \dfrac{M_0^2}{2\sqrt{2}\pi^{(3/2)}\hbar\omega}\dfrac{1}{r_0},\\ r_0 = \dfrac{3\sqrt{2}\pi^{(3/2)}\hbar^2\hbar\omega}{mM_0}.\end{array}\right\} \quad (40)$$

The results of calculation of $I(r_0)$ for various n are shown in Fig. 6. We can see that the bound state of an electron exists for clusters with edge's lengths $n > 5$. Moreover, the polaron radius does not depend almost on cluster's size and is equal to that in an infinite crystal (40), $r_0 \approx 2.8$ Å. With increase in cluster's size, the energy of a polaron tends to its energy in an infinite crystal $I_\infty = -0.26$ eV. Comparing Fig. 6 with the results in Fig. 1 obtained in the quasiclassical approach, we can see the quantization of cluster's oscillation brings to the same critical diameter of a cluster $5a$.

The bulky expression (39) containing a triple sum can be simplified by the continuous approximation. The polaron radius r_0 nearly does not depend almost on cluster's size L and is equal to its value in an infinite crystal. Then we can suppose that r_0 in expression (39) equals the optimal value (40). Hence, the energy of a cluster with an electron is a function of cluster's size only: $I = I(L)$. In a cubic cluster with edge's length L, no phonons with wave vectors $q < \pi/L$ can propagate. The upper limit of wave vectors' values, which is determined by the crystal lattice, does not influence the result essentially. Then the cluster can be supposed spherical with diameter L, and we can replace the triple sum in (39) by an integral:

$$I(L) = \frac{3\hbar^2}{4mr_0^2} + \frac{M_0^2}{2\hbar\omega\pi^2}\int\limits_{\pi/L}^{\infty}\exp\left(-\frac{q^2r_0^2}{2}\right)dq. \quad (41)$$

The result of calculations of the energy of the electron + cluster system by formula (41) is shown in Fig. 7. Comparing it with the exact result shown in Fig. 6, we can see that the critical sizes of a cluster in both methods of calculation coincide, $L_{\rm cr} = 4a \div 5a$, and the energies of the system for the corresponding sizes of a cluster are almost equal. As cluster's size increases to the infinite value, the energy of a polaron tends to its value in an infinite crystal. These facts afford ground to use the simplified expression (41) instead of formula (39).

4. Conclusion

In this article, we have calculated polaron's energy in an ionic cluster (by the example of a nanoparticle consisting of NaCl) and the critical size of a cluster in view of the formation of the autolocalized state of an additional electron. The calculation is done within both the quasiclassical method and the quantum approach (in the meaning of the quantization of a deformation field).

Like the numerical solution and computer simulations in [2], we have obtained that the bound state of an electron in clusters from polar substances can be realized, by starting with a some critical radius in agreement with the boundary conditions on cluster's surface for the polarization field potential $\varphi(R) = 0$.

The neglect of boundary conditions for electron's wave function on cluster's surface does not influence this phenomenon. With increase in cluster's size, the binding energy increases and tends to the polaron energy in an infinite crystal. The radius of electron's autolocalization in a cluster (a polaron size) is such that the energy of the electron + polarized cluster system is minimal. Within the analytic variational method, we have found that this radius does not depend almost on cluster's radius. The binding energy increases monotonically with cluster's size. Moreover, the following pattern is observed: the bound state exists, if the polaron radius is less than cluster's radius. In other wods, the autolocalized electron is hidden in depth of the cluster and has a negligibly low probability to be outside it. If the cluster is enough small so that an electron can be outside, the bound state disappears. Unlike the results of numerical simulation in [2, 5, 6], where the surface states that can be understood as excited states were found, we have found that if the polarization well is enough deep (cluster's size is enough big), then other discrete levels are possible except for the s-state of the autolocalized electron. We have calculated the energy of the p-state and obtained cluster's critical radius for this state.

The interaction of an electron with the polarization field is the interaction with longitudinal optical phonons. Due to the ionic-type coupling of atoms, the ionic clusters form stable cuboid structures and have a cubic microlattice. For clusters with a size bigger than the critical size $R \gg r_0$, an excess electron has a low probability to be near the cluster surface. Hence, the shape has no basic importance. The boundary condition on cluster's surface for the polarization field $\varphi(R) = 0$ brings to the restriction on the possible wave vectors of optical phonons $\pi/L < q < \infty$. The optical phonons are standing waves between opposite sides of a nanoparticle. We have obtained the polaron energy (39) in a cluster with regard for the restrictions on the propagation of phonons. The results for the energy and the radius of a polaron correspond to those of the quasiclussical approach: the existence of the critical size of a cluster as for the formation of the autolocalized state of an electron, asymptotic tending of the binding energy of an electron in the cluster to that in an infinite crystal, as cluster's radius increases, independence of the polaron radius on cluster's size, and infinitely low probability for an electron to be outside the cluster if the electron is in the autolocalized state. It is worth to note that the essential difference of the polaron state in a cluster from that in a crystal is the localization of an electron at the center of the cluster. On the contrary, all points in an infinite crystal are equivalent (in the continual representation of a medium); hence, the electron can move.

APPENDIX A
Boundary conditions for polaron's wave function on cluster's surface

Electron's effective masses outside, m_0, and inside, m, of a cluster are different: $m_0 \neq m$. Thus, the mass difference can influence the localization energy I and the critical size of a cluster $R_{\mathtt{cr}}$. Hence, the boundary condition on cluster's surface $\frac{1}{m}\Psi'(r)_{r=R-0} = \frac{1}{m_0}\Psi'(r)_{r=R+0}$ has to be considered, and the kinetic energy operator has to be written as $\frac{\hbar^2}{2m}\Delta$ for $r < R$, $\frac{\hbar^2}{2m_0}\Delta$ for $r \geq R$. Let us take electron's wave function in a form to be similar to function (11):

$$\Psi = \begin{Bmatrix} A\,(1 + r/r_{01})\exp\left(-\frac{r}{r_{01}}\right) & \text{for } r < R, \\ B\,(1 + r/r_{02})\exp\left(-\frac{r}{r_{02}}\right) & \text{for } r \geq R, \end{Bmatrix} \tag{A1}$$

where one of the autolocalization radii r_{01} is a variational parameter, the other constants r_{02}, A, and B are found from the normalization condition for the wave function Ψ and from the boundary conditions:

$$\Psi(r)_{r=R-0} = \Psi(r)_{r=R+0} \Rightarrow$$

$$\Rightarrow A\left(1 + \frac{R}{r_{01}}\right)\exp\left(-\frac{R}{r_{01}}\right) = B\left(1 + \frac{R}{r_{02}}\right)\exp\left(-\frac{R}{r_{02}}\right), \tag{A2}$$

$$\frac{1}{m}\Psi'(r)_{r=R-0} = \frac{1}{m_0}\Psi'(r)_{r=R+0} \Rightarrow$$

$$\Rightarrow \frac{A}{mr_{01}^2}\exp\left(-\frac{R}{r_{01}}\right) = \frac{B}{m_0 r_{02}^2}\exp\left(-\frac{R}{r_{02}}\right). \tag{A3}$$

The kinetic energy of a localized electron takes the form

$$T = \frac{\hbar^2 A^2 \pi}{2r_{01}^3 m}\left[3r_{01}^4 - \exp\left(-\frac{2R}{r_{01}}\right) \times \right.$$
$$\left. \times \left(2R^4 + 4R^3 r_{01} + 6R^2 r_{01}^2 + 6Rr_{01}^3 + 3r_{01}^4\right)\right] +$$
$$+ \frac{\hbar^2 B^2 \pi}{2r_{02}^3 m_0}\exp\left(-\frac{2R}{r_{02}}\right) \times$$
$$\times \left(2R^4 + 4R^3 r_{02} + 6R^2 r_{02}^2 + 6Rr_{02}^3 + 3r_{02}^4\right). \tag{A4}$$

The normalization condition is as follows:

$$\frac{A^2\pi}{r_{01}}\left[7r_{01}^4 - \exp\left(-\frac{2R}{r_{01}}\right)\left(14R^2 r_{01}^2 + \right.\right.$$
$$\left.\left. + 14Rr_{01}^3 + 7r_{01}^4 + 8R^3 r_{01} + 2r_{01}^4\right)\right] +$$
$$+ \frac{B^2\pi}{r_{02}}\exp\left(-\frac{2R}{r_{01}}\right)\left(14R^2 r_{02}^2 + \right.$$
$$\left. + 14Rr_{02}^3 + 7r_{02}^4 + 8R^3 r_{02} + 2r_{02}^4\right) = 1. \tag{A5}$$

Using the boundary condition (A3), we can rewrite Eqs. (A4 and A5) as

$$T = \frac{\hbar^2 A^2 \pi}{2r_{01}^3 m} 3r_{01}^4 - \frac{h^2 A^2 \pi}{2r_{01}^3 m} \exp\left(-\frac{2R}{r_{01}}\right) \times$$
$$\times \Big[\left(2R^4 + 4R^3 r_{01} + 6R^2 r_{01}^2 + 6Rr_{01}^3 + 3r_{01}^4\right) -$$
$$- \frac{m_0 r_{02}}{m r_{01}} \left(2R^4 + 4R^3 r_{02} + 6R^2 r_{02}^2 + 6Rr_{02}^3 + 3r_{02}^4\right)\Big]. \quad \text{(A6)}$$
$$1 = \frac{A^2 \pi}{r_{01}} 7r_{01}^4 - \frac{A^2 \pi}{r_{01}} \exp\left(-\frac{2R}{r_{01}}\right) \times$$
$$\times \Big[\left(14R^2 r_{01}^2 + 14Rr_{01}^3 + 7r_{01}^4 + 8R^3 r_{01} + 2r_{01}^4\right) -$$
$$- \frac{m_0^2 r_{02}^3}{m^2 r_{01}^3} \left(14R^2 r_{02}^2 + 14Rr_{02}^3 + 7r_{02}^4 + 8R^3 r_{02} + 2r_{02}^4\right)\Big]. \quad \text{(A7)}$$

We can see that the exponential function $\exp\left(-\frac{2R}{r_{01}}\right)$ suppresses the second terms in Eqs. (A6) and (A7) if the polaron radius is $r_{01} < R$ similarly to the interaction energy (15). In addition, the expressions in the square brackets compensate almost each other (the difference is not equal to zero if $m \neq m_0$ only). The energy of the electron + polarized cluster system is minimized on $r_{01} < R$ always under the condition that the energy is negative, $I < 0$. Thus, the second term with the exponential functions can be omitted, and we have the normalization constant and the kinetic energy as

$$A = \frac{1}{\sqrt{7\pi r_0^3}}, \quad T = \frac{3\hbar^2}{14 m r_0^2}. \quad \text{(A8)}$$

This means that we can use the total wave function (11) for the description of excess electron's state and consider electron's mass to be equal to its effective mass in a cluster. This approximation has a validity criterion

$$\exp\left(-\frac{2R}{r_0}\right) \frac{\left(2R^4 + 4R^3 r_0 + 6R^2 r_0^2 + 6Rr_0^3 + 3r_0^4\right)}{3r_0^4} \times$$
$$\times \left|1 - \frac{m_0}{m}\right| \ll 1,$$
$$\exp\left(-\frac{2R}{r_0}\right) \frac{\left(14R^2 r_0^2 + 14Rr_0^3 + 7r_0^4 + 8R^3 r_0 + 2r_0^4\right)}{7r_0^4} \times \quad \text{(A9)}$$
$$\times \left|1 - \frac{m_0^2}{m^2}\right| \ll 1,$$

where the polaron radius r_0 is determined by formula (17). In our case where $m = 2.78m_0, r_0 \approx 1.5$ Å $< R_{\rm cr} \approx 7$ Å, the criterium is well realized. Thus, the main contribution to the autolocalization energy is caused by the boundary conditions (9) for the polarization field, rather than the boundary conditions for electron's wave function. The independence of the radius r_0 on cluster's radius R is a result of the boundary conditions for the polarization field, rather than the consequence of the neglect of boundary conditions for electron's wave function. This approximation is not correct for the investigation of surface metastable states of an excess electron near the cluster surface.

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АВТОЛОКАЛІЗОВАНІ СТАНИ НАДЛИШКОВОГО ЕЛЕКТРОНА В ІОННОМУ КЛАСТЕРІ

Р е з ю м е

Запропоновано теорію спорідненості електрона до іонного кластера як у квазікласичному подході, так і з квантуванням електричного поля поляризації у наночастинці. Варіаційним методом отримано критичний розмір кластера відносно утворення автолокалізованого стану електрона, отримано залежність енергії та радіуса полярона як функції розміру кластера. Було знайдено, що енергія зв'язку електрона у кластері залежить від радіуса кластера, однак радіус автолокалізації електрона не залежить від розміру кластера і рівний поляронному радіусу у нескінченному кристалі. Зв'язаний стан електрона у кластері можливий, тільки якщо радіус кластера більший за поляронний радіус.