



# QUANTUM STATES AND OPTICAL TRANSITIONS OF ELECTRON IN A POLARON AND AT A COLOR CENTER OF A CRYSTAL

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We have considered the polarons, i.e., electrons self-localized in an ideal ionic crystal [1, 2], and color centers of a crystal (in alkali-halide crystals), whose model was developed by one of the authors in the previous work [3]. The energy levels, electron  $\psi$ -functions, and oscillator strengths of optical transitions are calculated.

## 1. Introduction

We present the quantitative consideration of electron quantum states both in a polaron and at a color center of the crystal. The term “polaron” means the local quantum state of an electron in the ideal ionic crystal [1] created by the following way: the electron being in the local state polarizes dielectrically the crystal due to the own electric field, while the crystal polarized in this manner represents some potential well for the electron, so that the well keeps stationarily the electron in its local state. The study of properties of a polaron is of high interest, because, according to preliminary Pekar’s investigations, the polaron in an electric field should move like a negative charge and is, apparently, the main current carrier on the electron conduction of ionic crystals [4].

The term “color center” means the electron which self-localized in the crystal near a lattice periodicity distortion and causes the commonly known phenomenon of “alkali-halide crystal coloration” well experimentally studied by Pohl, Gudden *et al.*, Tartakovsky and his co-workers, *etc.*

The analysis of vast experimental data and theoretical conceptions performed by Pekar [3] enabled him to draw the conclusion that the color center is represented by an electron localized in the alkali-halide crystal near a site where the halide ion position is empty. The same conclusion was drawn by Seitz [5] as well. On the basis of such a model of color centers, on the one

hand, and the notion of polaron, on the other hand, the detailed theory of colored crystals was developed [3] in good agreement with experimental data. There were no detailed quantitative estimations in some places of work [3]; so they are given here.

As was shown in works [1–3], the  $\psi$ -function of a localized electron and the inertial part of the specific polarization of the crystal  $\mathbf{P}(x, y, z)$  are determined from the condition of minimum for the functional of the total energy of the system.

$$F[\psi, \mathbf{P}] = (\hbar^2/2\mu) \int |\nabla\psi|^2 d\tau + \int V |\psi|^2 d\tau - \int (\mathbf{P}, D[\psi, \mathbf{r}]) d\tau + (2\pi/c) \int P^2 d\tau, \quad (1)$$

$$c = (1/n^2) - (1/\varepsilon),$$

with the additional condition

$$\int |\psi|^2 d\tau = 1. \quad (2)$$

Here,  $\mu$  is the electron effective mass in the crystal, whose introduction allows one to ignore the periodical potential of the crystal [6],  $\varepsilon$  the dielectric constant,  $n$  the refraction index of light characterizing the inertialess part of the crystal polarization,  $V(\mathbf{r})$  a change of the crystal potential caused by a defect (for example, the absence of a halide ion), and  $D[\psi, \mathbf{r}]$  the mean electrostatic induction caused by the “cloud of the localized electron”:

$$D[\psi, \mathbf{r}] = e \int |\psi(\mathbf{r}_1)|^2 [(\mathbf{r} - \mathbf{r}_1)/|\mathbf{r} - \mathbf{r}_1|^3] d\tau_1. \quad (3)$$

## 2. Quantum States of an Electron in a Polaron

In the case of a polaron, the crystal is assumed to be ideal, so that  $V = 0$ . The ground state of the polaron

(the state with the lowest energy) has been already considered by one of the authors [2] in detail. The minimum of functional (1) was found using the Ritz method. In this case, the  $\psi$ -function was approximated with the expression

$$\psi_{1s} = A(1 + \alpha r + \gamma \alpha^2 r^2) e^{-\alpha r}, \quad (4)$$

where  $A$ ,  $\alpha$ , and  $\gamma$  are the approximation parameters. As a result, the  $\psi$ -function of the ground state has the following form:

$$\begin{aligned} \psi_{1s} &= 0.1229 \alpha^{3/2} (1 + \alpha r + 0.4516 \alpha^2 r^2) e^{-\alpha r}, \\ \alpha &= 0.6585 (\mu e^2 / \hbar^2) c. \end{aligned} \quad (5)$$

The corresponding Schrödinger energy term for the electron in a polarization potential well reads

$$E_{1s} = -0.164 (\mu e^4 / \hbar^2) c^2. \quad (6)$$

The total energy of the system  $F[\psi_{1s}, \mathbf{P}_{1s}]$  exceeds the value of  $E_{1s}$  by the crystal polarization energy [the last term in formula (1)]. As a result of calculations, it happened that

$$F_{1s} = E_{1s}/3. \quad (7)$$

The quantity  $\mathbf{P}_{1s}$  is the inertial part of the specific polarization of the crystal created by the field of an electron being in the state  $\psi_{1s}$ :

$$P_{1s} = (c/4\pi) D[\psi_{1s}, \mathbf{r}]. \quad (8)$$

In this sense, the ground state can be named “self-consistent.”

When considering the optical transitions on the basis of the Franck–Condon principle, one should assume that, during a short time of the phototransition, heavy ions cannot be noticeably shifted, so that the polarization of the crystal  $\mathbf{P}$  remains fixed. Therefore, while considering the phototransitions, the upper states should be calculated in the assumption that the potential well for the electron is set and corresponds to the polarization  $\mathbf{P}_{1s}$ . This polarization well possesses the spherical symmetry, consequently, transitions from the  $1s$  state are allowed only to the  $np$  states.

In accordance with the above consideration and with regard for the known asymptotic course of  $\psi$  for small and large  $r$ , the  $2p$  state was approximated with the function

$$\psi_{2p} = CY_1(\vartheta, \varphi) 2\alpha r e^{-2\alpha\beta r}, \quad (9)$$

where  $C$  and  $\beta$  are the approximation parameters. The minimum of functional (1) was found by using the Ritz method. In this case,  $\mathbf{P}$  was not varied and was set to be equal to  $P_{1s}$ . As a result, we obtained

$$2\beta = 0.5146, \quad C^2 = (2\alpha)^3 (2\beta)^5 / 4!, \quad (10)$$

$$E_{2p} = -0.0935 (\mu e^4 / \hbar^2) c^2. \quad (11)$$

At large distances  $r$ , the polarization potential well looks like the Coulomb term:  $-e^2 c/r$ . Therefore, in the case of excited states with a large effective radius (high quantum numbers), the energy can be calculated by using the formula for a hydrogen-like atom with the effective charge of the nucleus  $ec$ .

Using  $\psi$ -functions (5) and (9), we calculated the oscillator strength for the transition  $1s \rightarrow 2p$ ; it turned out to be

$$f_{21} = 0.93. \quad (12)$$

This extremely high value of oscillator strength for the transition  $1s \rightarrow 2p$  means that all the rest transitions both to discrete levels and to the continuous spectrum have a comparatively low probability.

### 3. Quantum States of an Electron in the Color Center

As was mentioned above, the authors consider an electron localized near a vacant site of the crystal lattice as a model of color centers. The energy levels and the  $\psi$ -functions of an electron in the color center can be determined, using the way described in the previous section, from the condition for functional (1) to be minimum [1, 3]. However, the essential difference lies in the fact that we considered the ideal crystal (the case where  $V = 0$ ) in Section 1, while now we will consider a crystal, where a halide ion is absent in its regular position. A change of the potential caused by this defect at distances exceeding the radius of this ion has the Coulomb form

$$V = -ze^2/\varepsilon r \quad (13)$$

(ion charge  $z$  is introduced for generality; in the case of alkaline ions,  $z = 1$ ). At distances less than the ion radius, the potential  $V(\mathbf{r})$  has more complicated form, but the behavior of the potential within this region is not significant, because the  $\psi$ -cloud radius for the localized electron considerably exceeds the ion radius.

The minimum of functional (1) was determined, by using the Ritz method. Moreover, for the ground state,

the  $\psi$ -functions were approximated with expressions of the following three forms:

$$1) \psi = A(1 + \alpha r)e^{-\alpha r}, \quad (14)$$

$$2) \psi = Ae^{-\alpha r}, \quad (15)$$

$$3) \psi = Ae^{-\alpha r^2} \quad (16)$$

( $A$  and  $\alpha$  are parameters).

As a result of three approximations, we obtain, respectively, the following values for the Schrödinger energy levels and total energies:

$$1) E_{1s} = -\frac{\mu e^4}{\hbar^2} \frac{27}{56} \left( \frac{z^2}{\varepsilon^2} + \frac{4}{3} \frac{zc}{\varepsilon} + \frac{c^2}{3} \right),$$

$$F_{1s} = -\frac{\mu e^4}{\hbar^2} \frac{27}{56} \left( \frac{z}{\varepsilon} + \frac{c}{3} \right)^2,$$

$$\alpha = (\mu e^2 / 2\hbar^2) (3z\varepsilon^{-1} + c), \quad A = \alpha^{3/2} / (7\pi)^{1/2}; \quad (17)$$

$$2) E_{1s} = -\frac{\mu e^4}{2\hbar^2} \left( \frac{z^2}{\varepsilon^2} + \frac{5}{4} \frac{zc}{\varepsilon} + \frac{75}{256} c^2 \right),$$

$$F_{1s} = -\frac{\mu e^4}{2\hbar^2} \left( \frac{z}{\varepsilon} + \frac{5}{16} c \right)^2,$$

$$\alpha = (\mu e^2 / 2\hbar^2) (2z/\varepsilon + 5c/8), \quad A = \alpha^{3/2} / \pi^{3/2}; \quad (18)$$

$$3) E_{1s} = -\frac{\mu e^4}{2\hbar^2} \left( \frac{8}{3\pi} \frac{z^2}{\varepsilon^2} + \frac{8\sqrt{2}}{3\pi} \frac{zc}{\varepsilon} + \frac{1}{\pi} c^2 \right),$$

$$F_{1s} = -\frac{\mu e^4}{2\hbar^2} \left( \frac{2^{3/2} z}{\sqrt{3\pi\varepsilon}} + \frac{c}{\sqrt{3\pi}} \right)^2,$$

$$\alpha = (\mu^2 e^4 / 9\pi\hbar^4) (2^{3/2} z\varepsilon^{-1} + c)^2, \quad A = (2\alpha/\pi)^{3/4}. \quad (19)$$

In all these three cases, the accuracy of results was estimated by comparison of the obtained value for the energy term with its known values in two limiting cases: hydrogen-like atom ( $c \rightarrow 0$ ) and polaron ( $z \rightarrow 0$ ). Approximation (14) turned out most successful. Using it, the error of calculations of the energy term does not exceed 3% in the whole interval of possible values of  $c$  and  $z$ . In what follows, we use just this approximation.

It is expedient to pay attention to the result somewhat rounded to the side of the lowering of the term:

$$E_{1s} = -\frac{\mu e^4}{2\hbar^2} \left( \frac{z^2}{\varepsilon^2} + \frac{4}{3} \frac{zc}{\varepsilon} + \frac{c^2}{3} \right),$$

$$F_{1s} = -\frac{\mu e^4}{2\hbar^2} \left( \frac{z}{\varepsilon} + \frac{c}{3} \right)^2. \quad (20)$$

As was explained in Section 1, to consider electron optical transitions, one should calculate the excited electron states in the assumption that the crystal polarization remains fixed and corresponds to the  $1s$  state (it is determined by formulae (8) and (3), in which the formula for  $\psi_{1s}$  is substituted).

To calculate the electron  $2p$  state, we use, as in Section 1, the following approximation:

$$\psi_{2p} = CY_1(\vartheta, \varphi) 2\alpha r e^{-2\alpha\beta r}. \quad (21)$$

Here,  $\alpha$  is determined by formula (17), and  $C$  and  $\beta$  are the approximation parameters. We obtain the following expression for the energy:

$$E_{2p} = \frac{\mu e^4}{2\hbar^2} c \left( \frac{3z}{\varepsilon} + c \right) \left\{ \left( \frac{3z}{\varepsilon c} + 1 \right) \beta^2 - \beta + \frac{(2\beta)^5}{14(2\beta+1)^7} [7(2\beta+1)^3 + 19(2\beta+1)^2 + 25(2\beta+1) + 15] - \frac{\beta}{\varepsilon c} \right\}. \quad (22)$$

The condition for the minimum of functional (1) results in the following equation to determine  $\beta$ :

$$\frac{1}{6\beta-1} \left\{ 1 - 2\beta - \frac{1}{7} \left( \frac{2\beta}{2\beta+1} \right)^4 \left[ 7 + \frac{28}{2\beta+1} + \frac{70}{(2\beta+1)^2} + \frac{120}{(2\beta+1)^3} + \frac{105}{(2\beta+1)^4} \right] \right\} = \frac{z}{(\varepsilon/n^2) - 1}. \quad (23)$$

This equation was solved in the case where  $z = 1$ . The values of  $\beta$  for various values of  $\varepsilon/n^2$  are summarized in the Table.

The normalization of the  $\psi$ -function yields

$$C^2 = (2\alpha)^3 (2\beta)^5 (2\beta)^5 / 4!. \quad (24)$$

$\varepsilon/n^2$	$\beta$	$\varepsilon/n^2$	$\beta$	$\varepsilon/n^2$	$\beta$
1.00	0.1666	2.4096	0.2430	2.8290	0.2540
1.2766	0.1900	2.4267	0.2435	2.8696	0.2550
1.4144	0.2000	2.4433	0.2440	2.9871	0.2575
1.5926	0.2100	2.4606	0.2445	3.1097	0.2600
1.7909	0.22	2.4780	0.2450	3.2374	0.2625
2.0264	0.23	2.5136	0.2460	3.3779	0.2650
2.1622	0.235	2.5496	0.2470	3.5286	0.2675
2.3118	0.240	2.5866	0.2480	3.6897	0.2700
2.3436	0.241	2.6249	0.2490	3.8822	0.2725
2.3760	0.242	2.6639	0.2500	4.0522	0.2750
2.3929	0.2425	2.7438	0.2520	$\infty$	0.3361

Like the case of a polaron, the excited states with large effective radii (great quantum numbers  $n$ ) can be approximately calculated with the use of the formulae for a hydrogen-like atom with the nucleus charge  $e(z\varepsilon^{-1} + c)$ . This allowed one of the authors (M.F. Deigen) to successfully calculate the excited states by using perturbation theory and taking the solution of the task for a hydrogen-like atom as the zero approximation. It is of interest that, already for the electron  $2p$  state, the correction to the energy in the first approximation is equal only about 5% of the zero-approximation energy, while this correction for the  $3p$  state is about 1.5%. It is obvious that, for all the above-positioned  $np$  levels, one can safely use the formulae for a hydrogen-like atom. For the sake of control, we compared the  $2p$  energy level calculated with the use of the Ritz method [formula (22)] with that calculated by perturbation theory. The former turned out by 6% higher than the latter.

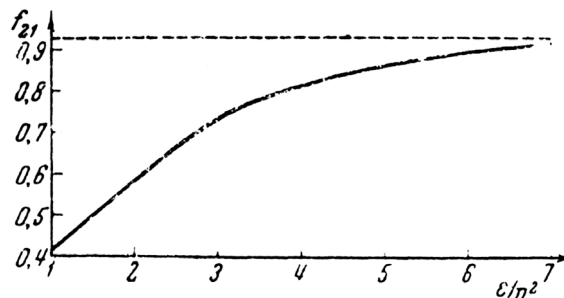
Using formulae (14), (17), (21), and (22), we calculated the oscillator strength for the transition  $1s \rightarrow 2p$ . The results are depicted in the Figure.

In most cases, the ratio  $\varepsilon/n^2$  is sufficiently high for the transition  $1s \rightarrow 2p$  to be more probable than any other of the transitions.

#### 4. Conclusions

Both in a polaron and a color center, the ground state of the electron is "self-consistent" in the sense that the dielectric polarization of the crystal by the localized electron is determined by the shape of the electron  $m$ -cloud; the latter is determined, in its turn, by the crystal polarization. Since the polarization of ionic crystals is inertial, the electron phototransitions should be considered, according to the Franck-Condon principle, for the fixed invariable crystal polarization. In this case, the excited electron states turn out nonself-consistent: immediately after the phototransition, the polarization begins to change, and the electron state adiabatically follows it.

Since, during the short time of the phototransition, the spherical symmetry of the potential well is conserved, the corresponding selection rules are valid: the transitions from the ground state  $1s$  to the  $np$  states are allowed.



In the present work, we have calculated the energy spectrum, electron  $\psi$ -functions and oscillator strengths for these transitions. Both for a polaron and a color center, the energy spectrum asymptotically approaches the hydrogen-like atom spectrum with increase in the quantum number  $n$ .

Under illumination, the electron transition  $1s \rightarrow 2p$  is much more probable than all the other ones.

Finally, it is a great pleasure for us to express our gratitude to B.I. Livshits who helped us in calculations.

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S.I. Pekar was born in Kyiv. He was graduated from Kyiv State University in 1938. At the age of 24, he was conferred the Doctor degree for his candidate thesis "Studies on the Theory of Semiconductors". From 1941 up to his death, S.I. Pekar was working at the Academy of Sciences of UkrSSR as the Head of the Department of Theoretical Physics (1941-1960 – Institute of Physics, 1960-1985 – Institute of Semiconductors). Since 1946, he was Professor. S.I. Pekar headed the Chair of Theoretical Physics at Kyiv State University in 1944-1949 and in 1953-1962. There, he founded the specialization "physicist-theorist" for students and postgraduates. In 1961, S.I. Pekar was elected Academician of the Academy of Sciences of UkrSSR without intermediate grade "Corresponding member". He is the author of several important discoveries in solid-state physics. Two of them are commonly recognized peaks of the world science: the theory of autolocalized states of electrons named polarons by him (1946) and the discovery of additional light waves in crystals (1957) plus a new theory of crystalloptics (the phenomenon was officially registered as a discovery).

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Mykhailo Fedorovych Deigen was born at the settlement of Proskuriv (now the town of Khmelnytskyi) of the Kam'yanets-Podilsk region. Doctor of Phys.-Math. Sci. (1959), Professor (1962), Corresponding member of the Acad. of Sci. of UkrSSR (1968). He graduated from Taras Shevchenko Kyiv State University in 1940. M.F. Deigen worked at the Institute of Physics of the Acad. of Sci. of UkrSSR (1947–1960) and Institute of Semiconductors of the Acad.

of Sci. of UkrSSR (1960–1977): since 1961 – he is Head of a department. He is the founder of the Kyiv school of radiospectroscopists. In 1963–1965, he lectured at Kyiv State University. His scientific publications deal with different aspects of the theory of solids and radiospectroscopy, in particular, the theory of the electron processes in metal-ammonia solutions, the theory of electron and double electron-nuclear resonances of paramagnetic centers in crystals, radiospectroscopy of semiconductors and ferroelectrics, electronic effects in radiospectroscopy, paraelectric resonance, and spin relaxation of electron centers.