THEORY OF POLARONS IN MANY-VALLEY CRYSTALS. II. STRONG INTERACTIONS BETWEEN AN ELECTRON AND THE POLARIZATION OSCILLATIONS OF THE LATTICE

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Submitted April 29, 1972

Zh. Eksp. Teor. Fiz. 63, 1455–1459 (October, 1972)

The interaction of an electron with the longitudinal optical lattice vibrations in many-valley crystals is studied in the adiabatic approximation. It is shown that the polaron is localized in one of the valleys in k-space. The constant-energy surface of the band electron near the energy minimum is assumed to be an ellipsoid of revolution. The energy and the anisotropic effective mass of the polaron are calculated. The latter quantity becomes more isotropic as the coupling force is increased.

OVER a period of many years, a theory of polarons has been developed for crystals with a simple conduction band (with the energy minimum at the point $\mathbf{k} = 0$ and a spherical constant-energy surface). It has been found, however, that in most cubic crystals the conduction band has a many-valley structure. Therefore, we must extend the theory to many-valley crystals. In the weak-coupling case, a polaron in a many-valley cubic crystal was studied in[1]. In the present paper we consider the opposite limiting case--the strong interaction of an electron with the polarization oscillations of the lattice in crystals of the same type.

It is known that, in the case of strong coupling, we can assume that the state of the electron follows adiabatically the comparatively slow oscillations of the potential of the inertial polarization of an ionic crystal. Once in a local state in a polarization potential well, the electron, by its average electrostatic field, reinforces the local polarization of the crystal, and the latter, in its turn, determines the form of the Ψ-function of the electron. Such a self-consistent state of the electron and medium was considered in detail in[2-4]. It was shown there that the Ψ-function of the electron can be determined by minimizing the functional

$$J[\Psi] = \langle \Psi | \hat{T} | \Psi \rangle + {}^1/_2 \bar{V}[\Psi], \tag{1}$$

where the first term of the right-hand side is the mean kinetic energy of the band electron, and $\hat{T}$ is the operator of the total electron energy with the nuclei fixed;

$$\bar{V}[\Psi] \equiv -e^2 c \iint \frac{|\Psi(\mathbf{r})|^2 |\Psi(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} d\tau\, d\tau', \qquad d\tau = dx\,dy\,dz. \tag{2}$$

Here $c = 1/n^2 - 1/\epsilon$, where ϵ is the isotropic dielectric permittivity and n is the refractive index. It is assumed that the effective radius of the polaron is considerably greater than the lattice constant and, therefore, we shall use a macroscopic calculation of the polarization and the effective mass method.

In a many-valley crystal, as usual,

$$\Psi = \sum_i Q_i \psi_i(\mathbf{r}), \tag{3}$$

where ψ_i is the wave function of an electron in the i-th valley, and Q_i are constants. Substituting (3) and (2) into (1), we obtain

$$J[\Psi] = \sum_i \xi_i T_i + {}^1/_2 \sum_{ij} \xi_i \xi_j V_{ij}, \tag{4}$$

where

$$\xi_i = |Q_i|^2, \quad T_i = \langle \psi_i | \hat{T} | \psi_i \rangle,$$
$$V_{ij} = -e^2 c \iint \frac{|\psi_i(\mathbf{r})|^2 |\psi_j(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} d\tau\, d\tau'. \tag{5}$$

In obtaining (4), we have discarded integrals containing products of Bloch functions $U^*_{\mathbf{K}_{0j}}(\mathbf{r})\exp(-i\mathbf{K}_{0j}\cdot\mathbf{r})$ and $U_{\mathbf{K}_{0j'}}(\mathbf{r})\exp(i\mathbf{K}_{0j'}\cdot\mathbf{r})$ referring to different valleys j and j', since these products oscillate rapidly and average to zero. But in those cases when these functions refer to the same valley ($j = j'$) the products are equal to $|U_{\mathbf{K}_{0j}}(\mathbf{r})|^2$, which can be replaced by its volume-averaged value, equal to unity. As a result, the Bloch factors disappear in the expression for V_{ij}, and ψ_i and ψ_j can be understood to be the smoothed functions of the effective-mass method.

From the normalization condition for the function (3), $\sum_i \xi_i = 1$. If we use this condition to express one of the variables in terms of the others, e.g.,

$$\xi_1 = 1 - \sum_{i>1} \xi_i,$$

then $\xi_2, \xi_3, \ldots$ will be independent variables. If we eliminate ξ_1 in this way from (4), it is easy to obtain ($i > 1$)

$$\frac{\partial^2 J}{\partial \xi_i^2} = V_{ii} + V_{11} - 2V_{i1} =$$
$$= -e^2 c \iint \frac{[|\psi_i(\mathbf{r})|^2 - |\psi_1(\mathbf{r})|^2][|\psi_i(\mathbf{r}')|^2 - |\psi_1(\mathbf{r}')|^2]}{|\mathbf{r}-\mathbf{r}'|} d\tau\, d\tau' < 0. \tag{6}$$

Consequently, within the range $0 \le \xi_i \le 1$, a minimum of J is not attained with respect to any of the variables ξ_i ($i > 1$). In this case, the lowest value of J is realized at the boundary of the range of variation of $\xi_2, \xi_3, \ldots$. This range is bounded by the set of hyperplanes $\xi_k = 0$ ($k > 1$) and by the hyperplane

$$\sum_{i>1} \xi_i = 1$$

on which $\xi_1 = 0$. Thus, the smallest value of J lies in a subspace in which one of the variables ξ_i is equal to zero. By omitting the corresponding terms in (4), we arrive at the problem of determining the smallest value of J in a space with a smaller number of coordinates ξ_i, whose range of variation is bounded by the analogous hyperplanes. Repeating these arguments, we finally reduce the space of the coordinates ξ_i to a one-dimensional space, and the last coordinate ξ should be equal to unity.

Thus, the linear combination (3) reduces to one term, i.e., the polaron wavefunction is formed from Bloch functions of one valley. Because of the equivalence of the different valleys, the polaron can be formulated equally successfully in any of them.

Below we treat a polaron in one valley, in which the constant-energy surface of the band electron is an ellipsoid of revolution and is characterized by two effective masses $\mu_\perp$ and $\mu_\parallel$. In the chosen valley (let this be the first valley), the functional (4) acquires the form

$$J[\psi_1] = T_1 + {}^1/_2 V_{11}, \tag{7}$$

where, as explained above, by ψ_1 we can understand the smoothed electron wavefunction. Then, with the appropriate choice of Cartesian coordinate axes,

$$\hat{T} = \frac{1}{2\mu_\perp}\left[\hat{p}_x^2 + \hat{p}_y^2 + \frac{1}{\chi}\hat{p}_z^2\right], \quad \chi = \frac{\mu_\parallel}{\mu_\perp}. \tag{8}$$

In the following, the index 1 will be dropped from ψ_1, T_1 and V_{11}.

The minimum of the functional (8) has been found by a direct variational method. After several trials, the following approximation for $\psi(r)$ was chosen:

$$\psi = \sum_{i=1} c_i \exp\{-\lambda^2(a_i\rho^2 + b_i z^2)\}, \quad \rho^2 = x^2 + y^2, \tag{9}$$

where c_i, a_i, b_i and λ are variational parameters. This function has continuous first and higher derivatives at the point $r = 0$, decays away at infinity, and is sufficiently flexible to reflect the specific features of the polaron potential, which is parabolic at small r and Coulomb at large r. Test calculations for the anisotropic hydrogen atom with a three-term approximation (9) gave an error in the energy of about 0.5% (the comparison was made with [5]).

We introduce the following notation:

$$\alpha_k = a_i + a_j, \ \beta_k = b_i + b_j, \qquad \alpha_k' = a_i a_j, \ \beta_k' = b_i b_j, \ \gamma_k = c_i c_j (2 - \delta_{ij}), \tag{10}$$

where

$$k = {}^1/_2(i-1)(2s-i) + j, \ j \geqslant i. \tag{11}$$

In the relation (11), there exists a unique correspondence between the value of k and the values of the pair of indices i and j. In this notation, the mean kinetic energy and the normalization factor have the form

$$T = \frac{\pi^{3/2} t}{\lambda \mu_\perp}, \quad t = \sum_{k=1}^{{}^1/_2 s(s+1)} \frac{\gamma_k}{\alpha_k \beta_k^{1/2}}\left(2\frac{\alpha_k'}{\alpha_k} + \frac{\beta_k'}{\chi \beta_k}\right), \tag{12}$$

$$N \equiv \int |\psi(r)|^2 d\tau = \frac{\pi^{3/2}}{\lambda^3} n, \quad n = \sum_{k=1}^{{}^1/_2 s(s+1)} \frac{\gamma_k}{\alpha_k \beta_k^{1/2}}. \tag{13}$$

To calculate the potential energy of the polaron, we make use of the equality

$$\iint \frac{1}{r_{12}} \exp(-\alpha_i \rho_1^2 - \beta_i z_1^2 - \alpha_j \rho_2^2 - \beta_j z_2^2)\, d\tau_1\, d\tau_2 = \frac{2\pi^{5/2} f(x_{ij})}{\alpha_i \alpha_j \sqrt{\beta_i + \beta_j}}; \tag{14}$$

$$x_{ij} = \frac{(\alpha_i + \alpha_j)\beta_i \beta_j}{(\beta_i + \beta_j)\alpha_i \alpha_j} - 1, \quad f(x) = \begin{cases} \dfrac{1}{\sqrt{x}} \operatorname{arctg} \sqrt{x}, & x \geqslant 0 \\ \dfrac{2}{\sqrt{-x}} \ln \dfrac{1+\sqrt{-x}}{1-\sqrt{-x}}, & x < 0 \end{cases} \tag{15}$$

Then,

$$V = -\frac{\pi^{5/2}}{\lambda^5} e^2 c v, \quad v = \sum_{k,l=1}^{{}^1/_2 s(s+1)} \frac{\gamma_k \gamma_l f(x_{kl})}{\alpha_k \alpha_l \sqrt{\beta_k + \beta_l}}. \tag{16}$$

Substituting (12), (13), and (16) into (7), we obtain

$$J = \frac{\lambda^2}{\mu_\perp}\frac{t}{n} - \lambda \frac{e^2 c}{\sqrt{\pi}} \frac{v}{n^2}. \tag{17}$$

After minimization with respect to λ, this functional acquires the form

$$J = -\frac{\mu_\perp e^4 c^2}{\hbar^2} J_\chi, \quad J_\chi = \frac{1}{4\pi}\frac{v^2}{t n^3}. \tag{18}$$

We emphasize that the extremal value J_χ depends only on the effective-mass anisotropy parameter χ, as the other parameters are variational.

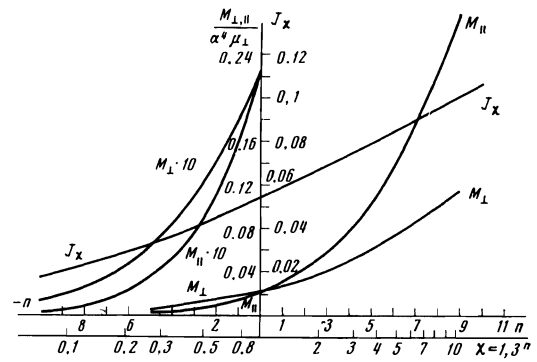
As was shown in [2,4], the minimum value of J is the total energy of the "dielectric + extra electron" system in the ground polaron state ($T^0 = 0$).

The extremal values J_χ for different χ are shown in the Figure. The energy of the system is expressed in terms of J_χ by the formula (18). The absolute minimum of J with respect to the parameters a_i, b_i, and c_i was found by a computer. The polaron energy represented in the figure was calculated with the approximation (9) with s = 3. In the one-term approximation (s = 1), the energy was found to be approximately 2% higher at all the values of χ considered. For $\chi = 1$, the value of J was calculated also with the five-term approximation (9) (s = 5), and coincided with the result of the three-term approximation to within five significant figures. This value is only 0.1% higher than the isotropic-polaron energy obtained in [2,4].

To calculate the effective masses of the polaron, the method developed in [3,4] was used. In the coordinate system defined by the principal axes of the ellipsoidal constant-energy surface of the band electron, the polaron effective masses are equal to

$$M_{\perp,\parallel} = \frac{c}{4\pi\omega^2} \int \left(\frac{\partial D}{\partial x_{\perp,\parallel}}\right)^2 d\tau, \tag{19}$$

where ω is the limiting frequency of the longitudinal



Dependence of the absolute value of the dimensionless energy J_χ and of the polaron effective masses $M_\parallel$ and $M_\perp$ on the anisotropy of the band-electron masses $\chi = \mu_\parallel/\mu_\perp$.

polarization oscillations of the ions, and $D(\mathbf{r})$ is the electrostatic induction created by the charge cloud with density $e|\psi(\mathbf{r})|^2$. In the approximation (9), we obtain

$$\left.\begin{matrix} M_\perp \\ M_\parallel \end{matrix}\right\} = \mu_\perp \alpha^4 \frac{2}{\pi^2}\frac{1}{n^2}\left(\frac{v}{tn}\right)^3 \sum_{k,l=1}^{1/2s(s+1)} \frac{\gamma_k\gamma_l\beta_k\beta_l}{\alpha_k\alpha_l(\beta_k+\beta_l)^{3/2}} \left\{\begin{matrix} -f'(x_{kl}) \\ \dfrac{1-f(x_{kl})}{x_{kl}} \end{matrix}\right. . \qquad (20)$$

Here $\alpha = (ce^2/2\hbar)(2\mu_\perp/\hbar\omega)^{1/2}$ is the dimensionless polaron coupling constant. The values of the polaron effective masses, calculated from the formula (20) ($s = 3$), are given in the figure. In the one-term approximation ($s = 1$), $M_{\perp,\parallel}$ were found to be smaller by 10--15%. For $\chi = 1$, the three-term and five-term approximations give values of M that differ by 0.01%. This value of M is 2% smaller than in[3,4].

It should be emphasized that the anisotropy $M_\parallel/M_\perp$ of the polaron masses is 2.5 to 3 times smaller than the anisotropy $\mu_\parallel/\mu_\perp$ of the band masses, with $\chi = 10$ or $\chi = 0.1$. For $\chi \to 1$, the mass anisotropies of the polaron and band electron become closer.

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Translated by P. J. Shepherd
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