Effective mass of the Pekar polaron

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(Submitted 3 April 1987)
Zh. Eksp. Teor. Fiz. **94**, 177–181 (February 1988)

It is shown that polaron motion in the Pekar model is possible only in ionic crystals with a positive dispersion $\Omega^2(\mathbf{k}) = \Omega_0^2 + V_0^2\mathbf{k}^2$ and a velocity $V \leqslant V_0$. An expression for the polaron effective mass accurate to order V_0^2 is obtained.

INTRODUCTION

Pekar polarons[1,2] in ionic crystals are self-localized structures arising due to nonlinear interaction of the field of an excess electron with the field of the inertial polarization of the crystal. Such structures are related to the class of two-component solitons. Their motion is possible only with a speed less than the lowest of the group velocities allowed in each field. The group velocity V_g of an excess electron is proportional to the conduction band width; it is comparatively large. The group velocity V_0 of a displacement in the polarization field is determined by the three-dimensional dispersion of the optical phonons. In ionic crystals $V_0 < V_g$ holds; therefore the limiting velocity for polarons is V_0. In the absence of a positive three-dimensional dispersion, the optical phonon field is stationary, and thus the polarons arising in such a medium are also immobile (i.e., stationary self-localized states). Electron motion is also decoupled from displacement of the polarization field for negative dispersion.

In this article we investigate the Pekar[2] model of the polaron, in which we include for the first time inertia and the three-dimensional dispersion of the optical phonons of the polarization field.

1. GENERALIZATION OF THE ADIABATIC THEORY OF PEKAR POLARONS

We assume that in the continuum approximation the polarization field of an ionic crystal is characterized by a dispersion relation

$$\Omega^2(\mathbf{k}) = \Omega_0^2 + V_0^2\mathbf{k}^2, \quad V_0^2 > 0. \tag{1.1}$$

Here the speed V_0 corresponds to the maximum group velocity in the phonon subsystem.

An excess electron (quasiparticle) in an isotropic ionic crystal near the conduction band edge (energy $\mathscr{E}_0$) is characterized by a charge e and an effective mass m^*. The inertial polarization field of the crystal is characterized by an effective dielectric constant $\tilde{\varepsilon}$ (Ref. 2).

The state of an electron (quasiparticle) interacting with the polarization field is described by a functional, subject to the normalization condition

$$\int |\Psi(\mathbf{r}, t)|^2 d^3\mathbf{r} = 1 \tag{1.2}$$

of the wave function $\Psi(\mathbf{r},t)$ of the excess electron and the polarization vector $\mathbf{P}(\mathbf{r},t)$:

$$H = \int d^3\mathbf{r}\left\{\Psi^*\left[\mathscr{E}_0 - \frac{\hbar^2}{2m^*}\nabla_{\mathbf{r}}^2\right]\Psi + \frac{2\pi\tilde{\varepsilon}}{\Omega_0^2}\left[\Omega_0^2\mathbf{P}^2 + \left(\frac{\partial\mathbf{P}}{\partial t}\right)^2 - V_0^2\mathbf{P}\nabla_{\mathbf{r}}^2\mathbf{P}\right] - \mathbf{PD}\right\}. \tag{1.3}$$

The vector

$$\mathbf{D} = -e\nabla_{\mathbf{r}}\int |\Psi(\mathbf{r}', t)|^2 \frac{d^3\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} \tag{1.4}$$

determines the induction of the electric field of the electron.

From (1.3) there follow the equations:

$$\left[i\hbar\frac{\partial}{\partial t} - \mathscr{E}_0 + \frac{\hbar^2}{2m^*}\nabla_{\mathbf{r}}^2 - e\varphi\right]\Psi = 0, \tag{1.5}$$

$$\left[\frac{\partial^2}{\partial t^2} + \Omega_0^2 - V_0^2\nabla_{\mathbf{r}}^2\right]\varphi = -\frac{e\Omega_0^2}{\tilde{\varepsilon}}\int |\Psi(\mathbf{r}', t)|^2 \frac{d^3\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}, \tag{1.6}$$

where $\varphi(\mathbf{r},t)$ is the potential of the polarization vector

$$\nabla_{\mathbf{r}}\varphi = 4\pi\mathbf{P}. \tag{1.7}$$

We determine the polaronic state of constant speed V as the soliton solution of Eqs. (1.5), (1.6). Since such solitons form as a result of the interaction of two fields, they can be called two-component solitons. We will search for a soliton solution of Eqs. (1.5), (1.6) of the form

$$\varphi(\mathbf{r}, t) = \varphi(\boldsymbol{\rho}), \quad \Psi(\mathbf{r}, t) = a^{-3/2}\Phi(\boldsymbol{\rho})e^{i(\mathbf{kr}-\omega t)}, \tag{1.8}$$

where $\varphi(\boldsymbol{\rho})$ and $\Phi(\boldsymbol{\rho})$ are smooth, real functions of the dimensionless vector $\rho = (x/a, y/a\ (z - z_0 - Vt)/a)$, rapidly decaying in the limit $\boldsymbol{\rho} = (\xi,\eta,\zeta) \to \infty$. In (1.8) a is the lattice constant, $|\mathbf{k}| = m^*V/\hbar$, and $\hbar\omega$ is the system energy. The Green's function $G(\boldsymbol{\rho})$ for Eq. (1.6) is given by the expression

$$G(\boldsymbol{\rho}) = \frac{1}{(2\pi)^3}\int \frac{\exp(i\mathbf{q}\boldsymbol{\rho})\, d^3\mathbf{q}}{1 - \sigma^2 q_z^2 + \sigma_0^2\mathbf{q}^2}, \tag{1.9}$$

in which we have taken

$$\sigma_0^2 \equiv V_0^2/a^2\Omega_0^2, \quad \sigma^2 \equiv V^2/a^2\Omega_0^2. \tag{1.10}$$

The Green's function (1.9) takes into account the nonlocal nature of the interaction between the electron and the polarization field, due to the phonon dispersion ($\sigma_0 \neq 0$) and the time resulting from electron motion ($\sigma \neq 0$). When the condition

$$0 \leqslant s^2 = \sigma^2/\sigma_0^2 \leqslant 1 \tag{1.11}$$

is fulfilled, the Green's function (1.9) takes the form

$$G_1(\boldsymbol{\rho}) = \frac{\exp\{-[\zeta^2 + (1-s^2)(\xi^2+\eta^2)]^{1/2}/\sigma_0(1-s^2)^{1/2}\}}{4\pi\sigma_0[\zeta^2 + (1-s^2)(\xi^2+\eta^2)]^{1/2}}, \quad s^2 \leqslant 1. \tag{1.12}$$

For $s^2 > 1$ it has the value

 0038-5646/88/020313-03$04.00

$$G_2(\rho)=\frac{\cos\{[\xi^2-(s^2-1)(\xi^2+\eta^2)]^{1/2}/\sigma_0(s^2-1)^{1/2}\}}{2\pi\sigma_0[\xi^2-(s^2-1)(\xi^2+\eta^2)]^{1/2}},$$

$$s^2>1, \tag{1.13}$$

if the inequality

$$\zeta<0, \quad \xi^2>(s^2-1)(\xi^2+\eta^2) \tag{1.13a}$$

holds, and is equal to zero otherwise.

The solutions of Eq. (1.6) obtained by using $G_2(\rho)$ determine a potential $\varphi(\rho)$ which oscillates with constant amplitude as $\rho\to\infty$. Therefore the solutions satisfying the normalization condition (1.2) can only be expressed in terms of $G_1(\rho)$. In other words, spatially localized solutions are possible only for speeds less than or equal to V_0. In the absence of dispersion in the optical phonons ($V_0=0$) the excitation does not move. With the help of the Green's function (1.12) we can write the solution of Eq. (1.6), using (1.8) in the form

$$\varphi(\rho)=-\frac{e}{\tilde{\varepsilon}a}\int\frac{G_1(\rho-\rho_2)\Phi^2(\rho_1)\,d^3\rho_1\,d^3\rho_2}{|\rho_2-\rho_1|}. \tag{1.14}$$

Substituting this into (1.5), we get an integrodifferential equation for the envelope function $\Phi(\rho)$ of (1.8):

$$\left\{\frac{\hbar^2}{2m^*a^2}\nabla_\rho^2+\Lambda+\frac{e^2}{a\tilde{\varepsilon}}\int\frac{G_1(\rho-\rho_2)\Phi^2(\rho_1)\,d^3\rho_1\,d^3\rho_2}{|\rho_2-\rho_1|}\right\}\Phi(\rho)=0, \tag{1.15}$$

where Λ is the electronic energy relative to the conduction band edge in the potential well $\varphi(\rho)$ which is moving with velocity V. The function $\Phi(\rho)$ in Eq. (1.15) can be calculated by the variational method, minimizing the functional

$$J(\Phi)=-\frac{\hbar^2}{2m^*a^2}\int d^3\rho\,\Phi(\rho)\cdot\left[\nabla_\rho^2\Phi(\rho)+\gamma\Phi(\rho)\int\frac{G_1(\rho-\rho_1)\Phi^2(\rho_1)\,d^3\rho_1\,d^3\rho_2}{|\rho_1-\rho_2|}\right], \tag{1.16}$$

where

$$\nabla_\rho^2\equiv\frac{\partial^2}{\partial\xi^2}+\frac{\partial^2}{\partial\eta^2}+\frac{\partial^2}{\partial\zeta^2}, \quad \gamma\equiv\frac{e}{a\tilde{\varepsilon}}\frac{m^*a^2}{\hbar^2}. \tag{1.16a}$$

In the absence of dispersion and for a stationary polaron ($\sigma_0=\sigma=0$) the Green's function $G(\rho-\rho_1)$ reduces to a delta function $\delta(\rho-\rho_1)$. In this case the functional (1.16) transforms into the Pekar functional[2] and the zeroth-order approximation functional in the work of Bogoliubov and Tyablikov.[3-5]

Minimization of the functional (1.16) can be carried out by a straightforward variational procedure. Since for a moving electron the accompanying polarization has cylindrical symmetry, we may use as the trial function the normalized function

$$\Phi(\rho)=(2/\pi)^{3/4}\alpha^{1/2}\beta\exp\{-\alpha\zeta^2-\beta(\xi^2+\eta^2)\}, \tag{1.17}$$

which has two variational parameters α and β. Evaluation of this function was carried out by the authors in Ref. 6.

2. ENERGY AND WAVE FUNCTION OF A SLOWLY MOVING POLARON

The application of the continuum approximation means that the present theory can only be used to investigate excitations with a localization region significantly exceeding a lattice constant. In this case the optical phonon dispersion is small and satisfies the inequality

$$\sigma_0^2\ll 1. \tag{2.1}$$

Since spatially localized two-component solitons (polarons) can arise in an ionic crystal only at speeds V less than V_0, the inequality

$$\sigma^2\leqslant\sigma_0^2\ll 1 \tag{2.2}$$

is always satisfied. For typical ionic crystals we have $a\Omega_0\approx 2.5\times10^4$ cm/s. Consequently the inequality (2.2) is well satisfied. Thus in calculating the function (1.17) with the aid of the functional (1.16) we can use the approximate Green's function

$$G_1(\rho)=\left[1+\sigma_0^2\left(\frac{\partial^2}{\partial\xi^2}+\frac{\partial^2}{\partial\eta^2}\right)-\sigma^2\frac{\partial^2}{\partial\zeta^2}\right]\delta(\rho). \tag{2.3}$$

In Ref. 6 the present authors show that in this case the square of the wave function $\Phi(\rho)$, which characterizes the spatial distribution of the quasiparticle, is given by the expression

$$\Phi^2(\rho)=(2/\pi)^{3/4}\alpha\beta^2\exp\{-2\beta^2(\rho^2+{}^{12}/_{7}\alpha_0\sigma^2\zeta^2)\} \tag{2.4}$$

with the values

$$\beta=\alpha_0+6\alpha_0^3({}^2/_7\sigma^2-\sigma_0^2), \quad \alpha=\beta[1+{}^{12}/_{7}\alpha_0\sigma^2]^{1/2}, \quad \alpha_0=\gamma/3\sqrt{\pi}.$$

Therefore, for the case of a stationary polaron ($\sigma=0$) the spatial probability distribution of the quasiparticle has spherical symmetry. An increase in polaron velocity is accompanied by stronger localization. An increase in the dispersion σ_0 decreases the range of the localization. For nonzero polaron velocities, constant values of $\Phi^2(\rho)$ are distributed over a surface having the shape of an oblate ellipsoid of revolution, with the axis directed along the polaron velocity vector.

Using (1.4), we can now calculate the induction vector $\mathbf{D}(\rho)$ of the polarization field, in terms of which the basic quantities characterizing the slowly-moving polaron are expressed. Thus, for example, the soliton energy $E(V)$ is determined by the expression

$$E(V)=E(0)+{}^1/_2M_{eff}V^2, \tag{2.5}$$

in which the energy $E(0)$ of the polaron at rest has the value

$$E(0)=\mathscr{E}_0-\frac{a^3}{8\pi\tilde{\varepsilon}}\int[\mathbf{D}^2(\rho)+\sigma_0^2(\nabla_\rho\mathbf{D})^2]\,d^3\rho \approx\mathscr{E}_0-0.053E_a(m^*/m\tilde{\varepsilon})(1-0.142\gamma^2\sigma_0^2), \tag{2.6}$$

and its effective mass is

$$M_{eff}=m^*+\frac{a}{4\pi\tilde{\varepsilon}\Omega_0^2}\int d^3\rho\left[\left(\frac{\partial\mathbf{D}}{\partial\zeta}\right)^2-2\sigma_0^2\left(\frac{\partial}{\partial\zeta}\nabla_\rho\mathbf{D}\right)^2+3\sigma^2\left(\frac{\partial^2\mathbf{D}}{\partial\zeta^2}\right)^2\right]=m^*+\frac{4e^2\gamma^2}{9\pi^2a^2\Omega_0^2}\left(1+\frac{\gamma^2}{5\pi}\left(\frac{187}{21}\sigma^2-18\sigma_0^2\right)\right), \tag{2.7}$$

where m is the free-electron mass and $E_a=me^4/\hbar^2$ is the atomic unit of energy. We note that in the absence of dispersion and for vanishingly small speeds ($\sigma\to0$) the expression (2.7) coincides with the expression obtained in a very heuristic way by Landau and Pekar.[7]

The vector of the polarization field, $\mathbf{P}(\rho)$, accompanying the polaron motion can also be expressed in terms of the induction vector:

$$\mathbf{P}(\rho)=(4\pi a^2\tilde{\varepsilon})^{-1}\mathbf{D}(\rho)-\left\{\frac{\sigma^2\partial^2}{\partial\xi^2}-\sigma_0{}^2\left(\frac{\partial^2}{\partial\xi^2}+\frac{\partial^2}{\partial\eta^2}\right)\right\}\mathbf{D}(\rho). \tag{2.8}$$

For polaron velocities V equal to V_0, the radial dependence of the potential energy of interaction of the electron with the polarization field is determined by the expression

$$e\varphi_0(\rho)=-e^2W(\alpha\rho\sqrt{2})/\alpha\rho\tilde{\varepsilon}, \tag{2.9}$$

where

$$W(x)=\frac{2}{\sqrt{\pi}}\int_0^x\exp(-t^2)\,dt$$

is the probability integral. The potential well has a depth $-e^2\alpha 2\sqrt{2}/a\tilde{\varepsilon}\sqrt{\pi}$ and displays spherical symmetry.

CONCLUSIONS

Thus, localized two-component solitons (polarons) in ionic crystals can move only in the presence of positive dispersion, with speeds less than or equal to V_0. In the subsequent calculation of the effective mass of the polaron even in the limit of very low velocities it is necessary to take into account the small dispersion. In the opposite case the polaron is immobile.

For quasiparticle motion with speeds $V>V_0$ spatially localized solutions of the form (1.8) do not exist. With the aid of the variational method in Ref. 6, solutions oscillatory to infinity were found. Consequently, for these speeds localization is only possible on short time scales, as the electron breaks away from the polarization field by its own motion.

Analogous conclusions can be reached in looking at the motion of an excess electron in a one-dimensional molecular chain, self-localizing due to short-range interaction with optic phonons. The present authors investigated this problem in Ref. 8. We note that the results obtained there for speeds $V>V_0$ describe unstable self-localized states, existing on short time scales. Similar results were obtained by numerical methods in recently completed work.[9]

For speeds $V>V_0$ nonlocalized stationary states, described by plane waves, are possible in a crystal. In this case the function $\Phi(\rho)$ and the polarization field do not depend on ρ and are uniformly distributed throughout the crystal with a negligibly small density. Electron motion in such states is described by spreading wave packets. It is accompanied by a small "coat" of virtual phonons, continuously exchanging with each other.

The authors are indebted to I. V. Simenog for discussion and critical comment.

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Translated by I. A. Howard