Electron-phonon bound states in a one-dimensional system

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An exact solution to the problem of the bound states of a self-localized electron (or exciton) with phonons in a one-dimensional system is obtained in the strong-coupling limit. The phonons are assumed to be nondispersive, while the interaction is assumed to be of the contact type. The bound state energies differ from the energy of the free phonon by universal numerical factors. The oscillator strengths of the optical transitions are computed.

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When an electron or an exciton interacts sufficiently strongly with the vibrations of the lattice, there arise self-localized states of these quasiparticles. The type of self-localized state is determined not only by the interaction strength, but also by the interaction law, the particle-dispersion law, and the dimensionality of the space.

It was shown by Pekar[1] that, when an electron interacts with polarization vibrations in a three-dimensional crystal, a self-localized state (the polaron) is realized even in the macroscopic limit. In the case of a deformation interaction in a three-dimensional crystal there is a potential barrier for the transition into the self-localized state, the minimum of the energy being attained outside the region of applicability of the macroscopic approximation.[2]

In one-dimensional systems, on the other hand, the self-localized states can, as has been shown by Rashba[3] and Holstein,[4] possess macroscopic dimensions even in the case of the deformation interaction. Of late there has been a significant rise in interest in the properties of one-dimensional systems. Apparently, this should explain the publication of papers in which the laws of dispersion of one-dimensional self-localized states are computed.[5,6]

It is interesting in the case of self-localization under conditions of strong coupling of the particle to the lattice to elucidate the nature of the energy spectrum in the vicinity of the ground state. It has been shown[7] that in the case of the polaron the lowest excited levels are the phonon-polaron bound states, the free-phonon energy being a point of accumulation of the spectrum of these bound states. But it was not possible to solve the problem completely, since the variational functional contained the polaron ground-state wave function, for which an analytic expression is not known.

In contrast, in the one-dimensional case the ground-state wave function is known in the strong-coupling limit, and has a simple form.[3,4] This allows us to solve completely the problem of the bound states of a phonon and an electron (or exciton), and find the oscillator strengths of the optical transitions. Below we shall, for brevity, speak of the electron, but the obtained results (except the oscillator-strength values) apply equally well to the exciton.

Let us write down the Hamiltonian for the electron and phonons, the contact interaction of which is characterized by the constant α:

$$H=\hbar\omega_0\left\{\frac{p^2}{2}+(2^{3/2}\alpha)^{1/2}\sum_k Q_k e^{ikx}+\frac{1}{2}\sum_k (P_k P_{-k}+Q_k Q_{-k})\right\}, \tag{1}$$

The dimensionless length is expressed in units of $(\hbar/m\omega_0)^{1/2}$. The constant α has been introduced in such a way that the first correction to the energy of the stationary electron from the interaction with the phonons is equal to $-\alpha\hbar\omega_0$.

Averaging the Hamiltonian (1), in which the phonon kinetic energy has been omitted, over the electron ground-state wave function Ψ_0, and minimizing the obtained expression over Q_k, we obtain

$$H_0=\hbar\omega_0\left\{\frac{1}{2}\int\left(\frac{d\Psi_0}{dx}\right)^2 dx-2^{1/2}\alpha\int\Psi_0^4\,dx\right\}. \tag{2}$$

To eliminate α, we make the substitution

$$x=\xi/2^{1/2}\alpha,\quad \Psi_0(x)=(2^{1/2}\alpha)^{1/2}\psi_0(\xi). \tag{3}$$

Varying the functional H_0 with respect to ψ_0, we obtain an equation for the determination of the self-consistent ground-state function ψ and the excited-state functions ψ_s $(s>0)$ in the same potential

$$\left[-\frac{d^2}{d\xi^2}-4\psi_0^2\right]\psi_s=\varepsilon_s\psi_s. \tag{4}$$

For ψ_0 and ε_0 we obtain

$$\psi_0=1/2^{1/2}\operatorname{ch} z,\quad \varepsilon_0=-1. \tag{5}$$

With allowance for this, the ground-state energy is equal to

$$H_0=-\alpha^2\hbar\omega_0/3. \tag{6}$$

The mass of the self-localized electron is expressible, as before,[1,8] in terms of the equilibrium phonon coordinates

$$\bar{Q}_k=(2^{3/2}\alpha)^{1/2}\int e^{ikx}\,\Psi_0(x)\,dx \tag{7}$$

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in the ground state, to wit

$$M=m\int\frac{dk}{2\pi}k^2\overline{Q}_k\overline{Q}_{-k}=\frac{32}{15}\alpha^4 m. \tag{8}$$

It follows from the relation (6) that the criterion for strong coupling in the one-dimensional case, $|H_0| \gg \hbar\omega_0$ (where $H_0 \approx -0.1\,\alpha^2\hbar\omega_0$), is less rigid than in the three-dimensional case.

The interaction of an electron with phonons and an attracting center leads to the formation of a bound state. We shall assume the potential of the interaction of the electron with the center to be of short range:

$$V(x)=-\gamma\delta(x). \tag{9}$$

If this potential is sufficiently weak, then the dimension of the bound state, determined by the mass (8) and the magnitude, γ, of the potential, and equal to $\hbar^2(\alpha^4\gamma m)^{-1}$, exceeds the dimension, $\hbar^{1/2}/\alpha(m\omega_0)^{1/2}$, of the self-localized state. In this case the reduction in the ground state energy on account of the coupling to the center is quadratic in γ, so that

$$H_0(\gamma)=-\frac{\alpha^2\hbar\omega_0}{3}-\frac{16\alpha^4\gamma^2 m}{15\hbar^2},\qquad \gamma\ll\frac{\hbar^{3/2}}{\alpha^3}\left(\frac{\omega_0}{m}\right)^{1/2}. \tag{10}$$

The interaction of the electron with a stronger potential should be included in the nonlinear functional (2). In this case

$$H_0(\gamma)=-\frac{\alpha^2\hbar\omega_0}{3}-\alpha\gamma\left(\frac{m\omega_0}{2\hbar}\right)^{1/2}-\frac{\gamma^2 m}{2\hbar^2},\qquad \gamma\gg\frac{\hbar^{3/2}}{\alpha^3}\left(\frac{\omega_0}{m}\right)^{1/2}. \tag{11}$$

The coupled states of a phonon and a self-localized electron arise owing to the quadratic—in Q_k—term in the energy, a term which appears in second-order perturbation theory with respect to the electron-phonon interaction near the ground state ψ_0.[5,8] With allowance for this term, we obtain, after making the substitution $Q(x)=(2^{1/2}\alpha)^{1/2}q(\xi)$, the following expression for the phonon potential energy:

$$U=\hbar\omega_0\left\{\frac{1}{2}\int q^2(\xi)\,d\xi+4\sum_{s>0}\frac{\left[\int\psi_0(\xi)q(\xi)\psi_s(\xi)\,d\xi\right]^2}{\varepsilon_0-\varepsilon_s}\right\}. \tag{12}$$

This expression does not contain the coupling constant α; therefore, the bound-state energies differ from the free-phonon energy $\hbar\omega_0$ by universal numerical factors.

Let us show that there exists such a function, $q(\xi)$, which transforms the expression (12) into zero. For this purpose let us write down the following identical relation between the eigenfunctions, the eigenvalues, and the potential of the Schrödinger equation:

$$\frac{1}{2}\int\psi_0\frac{d^2V}{d\xi^2}\psi_0\,d\xi+\sum_{s>0}\frac{\left[\int\psi_0(dV/d\xi)\psi_s\,d\xi\right]^2}{\varepsilon_0-\varepsilon_s}\equiv 0. \tag{13}$$

To derive this relation, we should shift the potential $V(\xi)$ from the coordinate origin, expand the ground-state energy up to terms quadratic in the shift, and take into account the fact that the energy does not depend on the position of the potential. The substitution into (13) of the potential $-4\psi_0^2(\xi)$ from (4) yields, after integration by parts, an expression that differs only by a numerical factor from the result of the substitution into the potential energy (12) of the function $q(\xi)\sim d\psi_0^2/d\xi$. The vanishing of the potential energy in the case of a definite form of the phonon function corresponds to the vanishing of the frequency of that localized vibration which corresponds to a small shift of the self-localized electron from the state of neutral equilibrium. The vanishing of the frequencies of three vibration modes for the case of the polaron was demonstrated by Pekar.[1]

For the determination of the frequencies, $\tilde{\omega}_n=\nu_n\omega_0$, of the bound phonons, we use the equation

$$\nu^2 q(\xi)=q(\xi)+8\sum_{s>0}\frac{\psi_0(\xi)\psi_s(\xi)\int\psi_s(\xi')q(\xi')\psi_0(\xi')\,d\xi'}{\varepsilon_0-\varepsilon_s}, \tag{14}$$

the right-hand side of which was obtained by means of the variation of the functional (12). Dividing (14) by $\psi_0(\xi)$ and letting the operator standing in the square brackets in Eq. (4) act from the left, we obtain after obvious transformations the final equation

$$\left[-\frac{d^2}{d\xi^2}-2\left(1+\frac{2}{1-\nu^2}\right)\frac{1}{\operatorname{ch}^2\xi}+1\right]\frac{q(\xi)}{\psi_0(\xi)}=-\frac{8\psi_0(\xi)}{1-\nu^2}\int q(\xi')\psi_0^2(\xi')\,d\xi'. \tag{15}$$

The eigenfunctions of the operator standing on the left-hand side of (15) are the associated Legendre polynomials $P^1_{n+2}(\operatorname{th}\xi)$ $(n\geqslant 0)$. Since $\psi_0(\xi)\sim P_1'(\operatorname{th}\xi)$, and polynomials with different lower indices are mutually orthogonal, the right-hand side of (15) is equal to zero for all the eigenfunctions of the left-hand side. Therefore,

$$q_n(\xi)=A_nP^1_{n+2}(\operatorname{th}\xi)/\operatorname{ch}\xi,\qquad \tilde{\omega}_n=\omega_0\left(\frac{n^2+5n}{n^2+5n+4}\right)^{1/2},\qquad n\geqslant 0. \tag{16}$$

It is clear that the minimum frequency $\tilde{\omega}_0$ is equal to zero, in accordance with the foregoing.

For the determination of the normalization constant A_n, it is sufficient to equate the potential energy (12) computed with the eigenfunction $q_n(\xi)$ to $\hbar\tilde{\omega}_n/4$. Using Eq. (15) to transform the second term in (12), we obtain the normalization condition in the form

$$\int_{-\infty}^{\infty}q_n^2(\xi)\,d\xi=\frac{1}{2\nu_n}. \tag{17}$$

Knowledge of the bound-phonon frequencies allows us to find the ground-state energy of the self-localized electron, including the coupling-constant-independent term. For this purpose, it is sufficient to determine the change in the energy of the zero-point vibrations:

$$H_0=-\frac{\alpha^2\hbar\omega_0}{3}-\frac{\hbar\omega_0}{2}\sum_{n=0}^{\infty}(1-\nu_n)\approx-\frac{\alpha^2\hbar\omega_0}{3}-0.88\hbar\omega_0. \tag{18}$$

Notice that the use of the variational principle proposed by Feynman[9] leads to an expression that differs from the exact expression (18) by the replacement of the number 3 by π in the first term and of 0.88 by 0.94 in the second term.

To determine the optical characteristics of the phonon bound states, it is necessary to find the matrix element of the dipole moment for the excitation of these states. Let us write in the respresentation of the functions ψ_s the Hamiltonian (1) without the third term, but with allowance for the interaction of the electron with an external field:

$$H_{ss'}=\hbar\omega_0\left\{\alpha^2\varepsilon_s\delta_{ss'}+4\alpha\langle\psi_s|q(\xi)|\psi_{s'}\rangle+\frac{eE}{\alpha\hbar\omega_0}\left(\frac{\hbar}{2m\omega_0}\right)^{1/2}\langle\psi_s|\xi|\psi_{s'}\rangle\right\}. \tag{19}$$

We are interested in the Hamiltonian's matrix element which is diagonal in the ground-state index $s=0$ and which contains the product of the field E and the phonon coordinate q_n. It is obtained from (19) in second-order perturbation theory, and is given in the representation of the phonon creation and annihilation operators by the expression

$$eE\sum_{n=1}^{\infty}d_n(a_n^+ + a_n), \tag{20}$$

where d_n is the matrix element of the dipole moment:

$$d_n=\frac{2e}{\alpha^2}\left(\frac{2\hbar}{m\omega_0}\right)^{1/2}\sum_{s>0}\frac{\langle\psi_0|q_n(\xi)|\psi_s\rangle\langle\psi_s|\xi|\psi_0\rangle}{\varepsilon-\varepsilon}. \tag{21}$$

In this expression the sum over s can be evaluated if $q_n(\xi)\,\psi_0(\xi)$ is represented in the form

$$q_n(\xi)\psi_0(\xi)=\frac{1-\nu_n^2}{8}\left[-\frac{d^2}{d\xi^2}-\frac{2}{\mathrm{ch}^2\xi}+1\right]\frac{q_n(\xi)}{\psi_0(\xi)}, \tag{22}$$

which follows from (15). The operator in the square brackets in (22), acting on $\psi_s(\xi)$, yields $(\varepsilon_s-\varepsilon_0)\,\psi_s(\xi)$, as a result of which the energy denominator gets canceled out. After this the sum over s gives a delta-function, the function $\psi_0(\xi)$ gets canceled out, and we finally obtain

$$d_n=-\frac{e(1-\nu_n^2)}{\alpha^2 2^{3/2}}\left(\frac{\hbar}{m\omega_0}\right)^{1/2}\int_{-\infty}^{\infty}q_n(\xi)\,\xi\,d\xi. \tag{23}$$

It can be seen from a comparison of (23) and (16) that the electric field excites transitions only into states with even n. The first of these states has a zero frequency. The frequencies $\tilde{\omega}_n$ and the oscillator strengths f_n for the transitions into the next two states are:

$$\tilde{\omega}_2=0.88\omega_0,\ f_2=0.024/\alpha^4,\ \tilde{\omega}_4=0.95\omega_0,\ f_4=0.0046/\alpha^4. \tag{24}$$

As has been shown by Rashba,[10] the intensity of Raman scattering with excitation of the phonon bound states is high only in the case of polarization interaction. In the case considered by us the Raman-scattering intensity referred to one electron is small compared to the lattice-Raman-scattering intensity computed for one unit cell in terms of the parameter $(\hbar/m\omega_0)^{3/2}/\alpha^3\lambda^2 d$, where λ is the wavelength of the light and d is the lattice constant.

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[1] S. I. Pekar, Issledovaniya po élektronnoĭ teorii kristallov (Research in Electron Theory of Crystals), Gostekhizdat, 1951 (Eng. Transl., AEC, Division of Technical Information, Washington, D.C., 1963; translation series No. AEC-tr-5575 Physics).

[2] M. F. Deĭgen and S. I. Pekar, Zh. Eksp. Teor. Fiz. **21**, 803 (1951).

[3] É. I. Rashba, Opt. Spektrosk. **2**, 75, 88 (1957).

[4] T. Holstein, Adv. Phys. **8**, 325 (1959).

[5] A. S. Davydov and N. I. Kislukha, Zh. Eksp. Teor. Fiz. **71**, 1090 (1976).

[6] G. Whitfield and P. B. Shaw, Phys. Rev. **B14**, 3346 (1976).

[7] V. I. Mel'nikov and É. I. Rashba, Pis'ma Zh. Eksp. Teor. Fiz. **10**, 95, 359 (1969) [JETP Lett. **10**, 60, 228 (1969)].

[8] V. I. Mel'nikov and G. E. Volovik, Zh. Eksp. Teor. Fiz. **65**, 1637 (1973) [Sov. Phys. JETP **38**, 819 (1974)].

[9] R. Feynman and A. Hibbs, Quantum Mechanics and Path Integrals, McGraw-Hill, New York, 1965 (Russ. Transl., Mir, 1968).

[10] É. I. Rashba, Zh. Eksp. Teor. Fiz. **71**, 319 (1976) [Sov. Phys. JETP **44**, 166 (1976)].

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