# Energy of a strong-coupling hole polaron in the case of degenerate bands

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An approach is developed which represents generalization of the Feynman variational method in the theory of polarons and which can be used to determine the energy of the ground state of a polaron in the case of valence bands with a point of degeneracy. In the limit of a strong electron-phonon coupling when the spin-orbit interaction is ignored this energy is identical with that given in the literature and calculated allowing for spontaneous breaking of symmetry.

## 1. INTRODUCTION

Very detailed investigations have been made of the states of a large-radius polaron in a simple energy band. However, in the case of a hole polaron in a cubic crystal, when the band degeneracy at $k = 0$ is important, the ground state[1,2] and the characteristics of the spectrum near the threshold of emission of an optical phonon[3] have been studied only in the limit of small values of the electron-phonon coupling constant. The case of a strong coupling is more appropriate to a hole polaron than to an electron polaron because the electron-phonon interaction constant is proportional to the square root of the mass of a band carrier and because a hole is relatively heavy compared with an electron. Very recently the energy of the ground state of such a hole polaron has been determined by a variational method using the adiabatic approximation[4] and it has been concluded that spontaneous symmetry breaking occurs. An allowance for the resultant lowering of symmetry complicates greatly the calculations. We shall develop a method which is a generalization, to the case of degenerate bands, of the Feynman method in the theory of polarons,[5–7] which in principle should yield the ground-state energy for a polaron characterized by an arbitrary electron-phonon coupling. This generalization makes it possible to derive an approximate effective Hamiltonian with a spherical symmetry in the case when the Jahn-Teller symmetry lowering is important. The spectrum of this Hamiltonian considered in the self-consistent scheme can be found using functions with a fixed angular momentum, which greatly simplifies the calculations. The values of the energy obtained for a hole polaron in the limit of strong coupling but without allowance for the spin-orbit interaction are practically identical with those found in Ref. 4.

## 2. CALCULATION OF THE GROUND-STATE ENERGY OF A POLARON BY THE METHOD OF PATH INTEGRALS

We shall take the initial Hamiltonian in the form of the energy operator for a free electron which is subject to a periodic potential $W(\mathbf{r})$ and which interacts with longitudinal optical phonons of frequency $\omega_{\mathbf{q}}$:

$$H=\frac{\mathbf{p}^2}{2m}+W(\mathbf{r})+\sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}a_{\mathbf{q}}^{+}a_{\mathbf{q}}+\sum_{\mathbf{q}}V_{\mathbf{q}}(a_{\mathbf{q}}e^{i\mathbf{qr}}+a_{\mathbf{q}}^{+}e^{-i\mathbf{qr}}),$$
$$V^2=\frac{e^2}{q^2}\frac{2\pi\hbar\omega_{\mathbf{q}}c}{V},\quad c=\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon_0}, \tag{1}$$

where $m$ and $e$ are the electron mass and charge; $\varepsilon_0$ and $\varepsilon_\infty$ are the values of the permittivity at low and high frequencies; $V$ is the volume of the crystal.

In the method of path integrals[5,6] or in the equivalent trace method[7] the problem under discussion reduces to calculation of the partition function

$$Z=\mathrm{Sp}\,e^{-\lambda H}, \tag{2}$$

where $\lambda$ is the reciprocal of temperature.

We shall be interested in the ground-state energy, i.e., in the value of $Z$ corresponding to the limit $\lambda\to\infty$. Bearing this in mind, we can modify Eq. (2) by replacing calculation of the trace for all the phonons with averaging of phonons over their vacuum states. Consequently, we obtain the following inequality for $Z$:

$$Z\geqslant\mathrm{Sp}_{\mathbf{r}}\exp\left[-\int_0^\lambda H_{\mathbf{r}}(\lambda_1)\,d\lambda_1+\sum_{\mathbf{q}}V_q^2G_{\mathbf{q}}(\mathbf{r})\right],$$
$$H_{\mathbf{r}}=\mathbf{p}^2/2m+W(\mathbf{r}), \tag{3}$$

where $\lambda_1$ is an ordering index and the trace is assumed to be calculated for the electron coordinates. The form of the operator $G_{\mathbf{q}}(\mathbf{r})$ is given in Ref. 7 and it is unimportant in the present context. The only significant feature is that it is independent of $V_q$.

Using the variational principle,[6,7] we shall introduce a trial potential $v(\mathbf{r})$ and then, enhancing the inequality (3), we obtain

$$\begin{aligned}Z&\geqslant\mathrm{Sp}_{\mathbf{r}}\exp\left\{-\int_0^\lambda[H_{\mathbf{r}}(\lambda_1)+v(\mathbf{r},\lambda_1)]\,d\lambda_1\right.\\&\left.+\int_0^\lambda v(\mathbf{r},\lambda_1)\,d\lambda_1+\sum_{\mathbf{q}}V_q^2G_q(\mathbf{r})\right\}\\&\geqslant\mathrm{Sp}_{\mathbf{r}}\exp[-\lambda(H_r+v(\mathbf{r}))]\\&\times\exp\left[(\lambda v)_{\mathrm{av}}+\sum_{\mathbf{q}}(V_q^2G_{\mathbf{q}}(\mathbf{r}))_{\mathrm{av}}\right],\end{aligned} \tag{4}$$

where the average is calculated using the operator functions

$$H'=H_{\mathbf{r}}+v \tag{5}$$

with an arbitrary potential $v = v(\mathbf{r})$.

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The operator $V_q^2 G_q(\mathbf{r})$ is small, because $V_q^2 \propto V^{-1}$ and, therefore, its average can be calculated by the methods of perturbation theory,[7] in which the second order gives the exact value. We shall not give the steps in detail, but only the final result for the ground-state energy of a polaron (more exactly, for the upper limit to this energy):

$$E_m = \mathscr{E}_m - v_{mm} - \sum_{\mathbf{q},n} V_q^2 \frac{(e^{i\mathbf{qr}})_{mn}(e^{-i\mathbf{qr}})_{nm}}{\mathscr{E}_n - \mathscr{E}_m + \hbar\omega_q}, \tag{6}$$

where $m$ labels the various functions of the ground state (if it is degenerate) of the Hamiltonian $H'$; $\mathscr{E}_m$ and $\mathscr{E}_n$ are the eigenfunctions of this operator; the summation with respect to $n$ is carried out over all the states of $H'$. In this formula the trial potential is arbitrary: it should be selected from the condition for minimum of the energy $E_m$. An expression similar to Eq. (6) for the nondegenerate case has been used implicitly for a polaron in Ref. 7 and for a Wannier-Mott exciton in Ref. 8.

We shall now employ the effective mass method. It would have been undesirable to employ this approximate method in the earlier stages of our calculations because the representation of the partition function as a path integral is standard for systems described by a classical Lagrangian[5,6] (the case of a carrier in a periodic potential in the absence of the spin--orbit interaction reduces to this Lagrangian) and for systems with double spin degeneracy[9,10] (when a carrier is considered in a periodic potential subject to the spin-orbit interaction). However, in the effective mass approximation the degeneracy multiplicity for a hole in a cubic crystal is higher (it amounts to three or four), which complicates introduction of a path integral. Equation (6) is not affected if smoothed-out functions of the effective mass method are used to calculate the matrix elements. This approach is justified subject to the standard restrictions on the smoothness of the electron-phonon interaction operator, which are satisfied as demonstrated by the nature of the interaction costant $V_q$ in Eq. (1); the restrictions applicable to the trial potential will be formulated below.

It follows that the "Feynman" approach provides an opportunity for calculating the energy of a polaron with an arbitrary electron-phonon coupling in a system with degenerate energy bands.

## 3. STRONG-COUPLING LIMIT

In the case of a strong electron-phonon interaction the expression (6) for the energy simplifies greatly because the separation between the various energy levels of the trial Hamiltonian $H'$ is large (for an ordinary polaron it is proportional to the square of the coupling constant) and, therefore, we can limit Eq. (6) to just terms with such values of $n$ for which we have $\mathscr{E}_n = \mathscr{E}_m$. This approximation again increases the upper limit for the ground state. Since Eq. (6) contains now only the wave functions of the lowest level of the Hamiltonian $H'$, we can replace the explicit form of the trial potential $v(\mathbf{r})$ with trial wave functions. Equation (6) then becomes

$$E_m = \langle \psi_m | T(\hat{\mathbf{k}}) | \psi_m \rangle - \sum_{\mathbf{q},m'} \frac{V_q^2}{\hbar\omega_q} (e^{i\mathbf{qr}})_{mm'} (e^{-i\mathbf{qr}})_{m'm}$$

$$\equiv T_{mm} + V_{mm}^{\text{int}}, \tag{7}$$

where $\hat{\mathbf{k}} = -i\nabla$; $T(\hat{\mathbf{k}})$ is the Hamiltonian of a free hole; $m$ and $m'$ label the orthogonal trial wave functions for the lowest degenerate state.

The kinetic energy operator of a hole considered in the spherical approximation can be written in the form[11]

$$T(\hat{\mathbf{k}}) = a[\hat{\mathbf{k}}^2 I + \mu B(\hat{\mathbf{k}})], \tag{8}$$

where in the absence of the spin-orbit interaction (intrinsic momentum of a hole is $j = 1$) using a basis of functions transforming as $x$, $y$, and $z$ (which is convenient for our calculations), we find that

$$B_{mm'}(\mathbf{k}) = k_m k_{m'} - {}^1/_3 k^2 \delta_{mm'}; \quad m, m' = x, y, z. \tag{9}$$

It should be pointed out that

$$B^2(\mathbf{k}) = {}^2/_9 k^4 I + {}^1/_3 k^2 B(\mathbf{k}). \tag{10}$$

In the case of an extremely strong spin-orbit interaction ($j = 3/2$) the Hamiltonian of Eq. (3) should be supplemented by a term describing this interaction (it should be pointed out that a rigorous justification of the variational principle in the method of path integration has been provided so far only for the Hamiltonian with $j = 1$). Then, we find that

$$B(\mathbf{k}) = (\mathbf{Lk})^2 - {}^1/_4 I \operatorname{Sp} (\mathbf{Lk})^2, \tag{11}$$

where

$$B^2(\mathbf{k}) = Ik^4, \tag{12}$$

$I$ is a unit matrix and $\mathbf{L}$ are the matrices of the momentum for $j = 3/2$. The parameters $a$ and $\mu$ are related to the masses of the light $m_l$ and heavy $m_h$ holes by

$$a = \frac{\hbar^2}{2m_h} \frac{\chi+\delta}{1+\delta}, \quad \mu = \frac{\chi-1}{\chi+\delta}(2\delta-1);$$

$$\chi = \frac{m_h}{m_l}, \quad \delta = 1 + \delta_{j1}. \tag{13}$$

The wave functions $\psi_m$ of the ground state of a polaron are selected in the form of combinations of spherical functions which are eigenfunctions of the operator $T(\hat{k})$. Since in the case of wave functions of the ground state the total momentum of a hole is the same as its intrinsic momentum, it is found that, after allowance for the parity,

$$\psi_m = f_0(r) e_m + B(\hat{\mathbf{k}}) f_2(r) e_m, \; m = 1, 2, \ldots, 2j+1, \tag{14}$$

where $e_m$ is a column consisting of $2j + 1$ elements in which the $p$th element is $\delta_{pm}$.

It should be noted that the functional (7) for an optical polaron ($\omega_{\mathbf{q}} = \omega$) can be represented in the form

$$E_m = \int \psi_m^*(\mathbf{r})\, T(\hat{\mathbf{k}})\, \psi_m(\mathbf{r})\, d\mathbf{r} - e^2 c \int \psi_m^*(\mathbf{r})\, V[\psi_m]\, d\mathbf{r}, \qquad (15)$$

where

$$V[\psi_m] = \sum_{m'} \int \psi_{m'}(\mathbf{r}) \langle \psi_{m'}^*(\mathbf{r}')\, \psi_m(\mathbf{r}') \rangle |\mathbf{r}-\mathbf{r}'|^{-1}\, d\mathbf{r}'; \qquad (16)$$

here, $\langle\rangle$ denotes convolution of the spinors $\psi$. If we use Eqs. (10) and (12) and apply the theorem of addition of spherical functions,[12] we can show that when the wave functions are selected in the form given by Eq. (14), then

$$V[\psi_m] = [IF(r) + B(\mathbf{r})\, G(r)]\, e_m, \qquad (17)$$

where $F$ and $G$ are functions dependent only on the modulus of $\mathbf{r}$.

We thus find that $V[\psi_m]$ has the same symmetry as $T\psi_m$ and not lower, contrary to the adiabatic approximation (see Ref. 4 and also Sec. 4 in the present paper). Therefore, in the adopted approach all the calculations may be carried out in a self-consistent manner using the basis of the spherical functions described by Eq. (14).

We must bear in mind that, although the calculations are being carried out using trial wave functions, we are assuming the existence of a trial Hamiltonian $H'$ which in the effective mass approximation is

$$H' = T(\hat{\mathbf{k}}) + V_{eff}(\mathbf{r}). \qquad (18)$$

Since the wave functions (14) contain two independent radial components $f_0(r)$ and $f_2(r)$, it follows that a matrix Schrödinger equation corresponding to $H'$ can be satisfied by arbitrary functions $f_0(r)$ and $f_2(r)$ only if $V_{\text{eff}}$ has a structure similar to that of $T(\mathbf{k})$, i.e., if

$$V_{eff} = V_0(r) + B(\mathbf{r})\, V_2(r). \qquad (19)$$

The first term of $V_0(r)$ appears when we adopt the effective mass approximation for the smooth part of the trial potential; the second term $V_2(r)$ exists if the trial potential $v(\mathbf{r})$ in Eq. (5) includes Fourier harmonics with the wave vector of the order of the reciprocal lattice vector [Eq. (2.19) from Ref. 13]. It should be noted that this requirement differs from that adopted usually in the theory of local large-radius centers where only the smooth part of the potential is retained in order to simplify the calculations.

Before considering the calculations, we must point out that the normalization of the functions (14) and the average kinetic energy are given by

$$N = (\psi_m, \psi_m) = \langle f_0 | f_0 \rangle + \gamma \langle f_2 | \hat{k}^4 | f_2 \rangle,$$
$$T \equiv T_{mm} = a\{\langle f_0 | \hat{k}^2 | f_0 \rangle + \gamma (1 + {}^1/_3 \mu \delta_{j1}) \langle f_2 | \hat{k}^6 | f_2 \rangle + 2\gamma\mu \langle f_0 | \hat{k}^4 | f_2 \rangle\}, \qquad (20)$$

where

$$\gamma = {}^2/_9 \text{ for } j = 1, \quad \gamma = 1 \text{ for } j = {}^3/_2. \qquad (21)$$

The matrix elements occuring in $V_{\text{int}}$ have the structure

$$(e^{i\mathbf{qr}})_{mm'} = F(q)\, \delta_{mm'} + B_{mm'}(\mathbf{q})\, G(q), \qquad (22)$$

whereas the interaction energy itself is

$$V_{\text{int}} = -\frac{e^2 c}{\pi} \int_0^\infty [F^2(q) + q^4 G^2(q)]\, dq. \qquad (23)$$

It should be noted that in the case described by Eq. (7) the virial theorem is valid so that the ground-state energy of a hole polaron can be expressed in the form

$$E_m = -\frac{e^4 c^2}{2\pi^2} \frac{V_{\text{int}}^2}{TN^3}. \qquad (24)$$

## 4. GROUND-STATE ENERGY OF A POLARON IN THE ADIABATIC APPROXIMATION

In the limit of strong coupling we can use the adiabatic approximation and the values of the energy calculated using this approximation in the principal order with respect to the coupling constant should in principle be identical with those obtained by the Feynman method. In the case of a nondegenerate band the adiabatic method is self-consistent in the class of spherically symmetric functions. However, in the case of a degenerate band, self-consistency is attained only if an allowance is made for the lowering of symmetry.[4] The calculation given below is carried out in the adiabatic approximation using spherical functions (14) which in this variant are not self-consistent. Nevertheless, a comparison with the $j = 1$ case considered in Ref. 4 shows that the energy differences are only 3%.

It is convenient to begin directly from the effective mass Hamiltonian by replacing the first two terms in Eq. (1) with the operator $T(\hat{\mathbf{k}})$ and assuming that the phonon operators $a_{\mathbf{q}}$ and $a_{\mathbf{q}}^+$ are $c$ numbers, which corresponds to a polarization static relative to the instantaneous position of a hole. The variational functional corresponding to this Hamiltonian has the form (7) after minimalization with respect to phonons, but now this equation consists of just one term with $m' = m$ and it is identical with the result obtained in Ref. 14; hence, it is clear that in the case of a degenerate Hamiltonian and an extremely strong coupling the Feynman method gives lower values of the energy than those deduced in the spherical nonself-consistent approximation.

The trial wave function of a hole is selected in the form

$$\psi = \sum_{m=1}^{2j+1} C_m \psi_m, \qquad (25)$$

where $\psi_m$ are defined by Eq. (14). The difference from the preceding case is manifested only in the interaction energy, which is now

$$V_{\text{int}} = -\sum_{\mathbf{q}} \frac{V_q^2}{\hbar\omega} [F^2(q)\, (\mathbf{C}, \mathbf{C})^2 + (\mathbf{C}, B(\mathbf{q})\, \mathbf{C})^2 G^2(q)]. \qquad (26)$$

When the kinetic energy of a hole is selected in the form of Eqs. (8) and (9), it can be shown that the minimum of $E_m$ for a polaron with $j = 1$ is obtained for real values of $C_m$. Then, $E_m$ depends only on the invariant combination $(\mathbf{C}, \mathbf{C})$

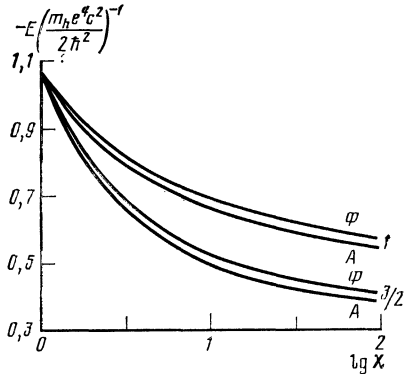


FIG. 1. Dependence of the polaron energy on the ratio of the masses of heavy and light holes $\chi$ ($n = 2$; F is the Feynman approach and A is the spherical adiabatic approximation; the numbers outside the curves are the values of the angular momentum $j$).

equal to unity. For a polaron with $j = 3/2$ it is found that $E_m$ depends only on (**C**, **C**) for any value of **C**. Therefore, the main term of a hole polaron does not become split when spherical functions are used.

The final expression for the interaction energy obtained in the adiabatic approximation is

$$V_{\text{int}} = -\frac{e^2 c}{\pi}\int_0^\infty \left[ F^2(q) + \frac{\delta\gamma}{5} q^4 G^2(q) \right] dq; \qquad (27)$$

the total energy is still given in terms of $V_{\text{int}}$ and Eq. (24).

## 5. RESULTS OF CALCULATIONS

Two variants of trial radial functions $f_0$ and $f_2$ from Eq. (14) were used: I) polynomials multiplied by $\exp(-\alpha r)$; II) functions defined by

$$f_l = \sum_{i=1}^{n} A_{il} \exp(-\alpha_{il} r^2), \qquad l = 0.2, \qquad (28)$$

where $A_{il}$ and $\alpha_{il}$ are the variational parameters. The number of terms in the above sum was selected in accordance with the required precision. The second set of functions gave lower values of the energy for the same number of parameters: the results are presented in Fig. 1.

The form of Eq. (28) for the radial functions with $n = 3$ and $\mu = 0$ (nondegenerate polaron) gives the energy $-0.108512$ (the energy will be given in units of $m_h e^2 c^2/2\hbar^2$), identical with the value found in Ref. 15. This is the lowest energy among those given in the literature. Calculations based on Eqs. (23), (24), and (27) with $n = 3$ give for the $\chi = 10$ case the following values of the energy calculated in the Feynman (adiabatic) approximation: $E_1 = -0.06887$ ($-0.06632$), $E_{3/2} = -0.05188$ ($-0.04921$). In the self-consistent adiabatic approximation with $j = 1$ it is found[4] that $E_1^c = -0.06844$, which is practically identical with $E_1$ in the Feynman approximation; if $j = 3/2$, the value of the energy[1)] obtained in Ref. 16 is higher and amounts to $E_{3/2}^c = -0.047$.

## 6. CONCLUSIONS

The method based on the continued integration makes it possible to calculate the energy of a hole polaron with an arbitrary electron-phonon coupling and still remain within the framework of the spherically symmetric model, which simplifies greatly the calculations and provides a realistic opportunity of finding not only the energy but also other parameters of a polaron (such as the structure of the polaron band). It is very remarkable that exact exclusion of phonons in the initial stage of calculations carried out in the path integration model has the effect that the spherically symmetric approximation is applicable to systems in which spontaneous lowering of symmetry is possible. In contrast to Ref. 4, the Jahn-Teller effect does not appear directly. The numerical agreement between the energies obtained for $j = 1$, in spite of the difference between the basis functions, shows that both approaches are valid.

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[1)]The results are given in Refs. 4 and 16 in the form of curves. We are grateful to F. V. Kusmartsev for kindly supplying us with the numerical data.

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