LOCAL STATES IN A SEMICONDUCTOR WITH A NARROW FORBIDDEN BAND

V. I. SHEKA and D. I. SHEKA

Institute of Semiconductors, Academy of Sciences, Ukrainian S.S.R.; Kiev State University

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A theory of impurity states in semiconductors with a InSb band structure is developed in a multiband approximation that takes into account the interaction between the conduction and valence bands in a straightforward manner. A general investigation of the solution of the equations of motion indicates that the behavior of the carrier near the acceptor center can be correctly described only if the upper bands are taken into account; in the vicinity of the donor it is virtually independent of them. The energy levels of large-radius local centers in InSb are calculated numerically. The obtained value of the ionization potential for a singly charged acceptor center in InSb is in agreement with the experimental value.

THE theory of large-radius local states in semiconductors is usually based on the effective-mass method, the motion of the carrier being governed by the structure of one or several bands adjacent to the edge. The local center is a donor or an acceptor, depending on the type of the chosen band. We can regard as a natural generalization of this approximation a model in which the behavior of the charged quasiparticle is described by the form of the nearest most vital bands; the latter can be separated by a forbidden band. Such a model, in particular, is the fruitful scheme proposed by Kane,[1] which considers simultaneously both the conduction band and the spin-split valence bands. In this scheme, the possibility that the quasiparticle will stay in an electron or hole band is already implicit in the equations of motion themselves, so that it becomes necessary to speak here of a single quasiparticle that is predominantly in one of the charged states. This pertains also to the behavior of the carrier near a charged center; such a multiband theory of local states was first proposed by Keldysh.[2]

In this paper we consider, within the framework of Kane's scheme, shallow local states in cubic crystals. A detailed account of the band structure has enabled us to calculate, in accord with experiment, the ionization energy of the acceptors in InSb, and also to determine the wave function of the corresponding state. The changes occurring in the analytic structure of the solutions for the local center when account is taken of the remote bands are analyzed.

1. HAMILTONIAN OF THE PROBLEM AND SEPARATION OF VARIABLES IN THE EQUATIONS OF MOTION

We use the matrix Hamiltonian (2) from [3], and retain in its off-diagonal elements the terms proportional to the interaction parameter P. The discarded terms constitute small corrections of higher order in $\hat{\mathbf{k}}$ of the effective-mass method; in a crystal with an inversion center, the symmetry always annihilates these corrections. The operator $\hat{H}$ from [3] can play at zero magnetic field the role of kinetic energy in the total Hamiltonian:

$$\hat{H} = \hat{H} + V(r) = \hat{H} - Ze^2/\varepsilon_0 r. \qquad (1)$$

The operator $\hat{H}$ describes the interaction of only the conduction band and the spin-split valence band, so that it contains the infinite mass of the heavy holes. In Kane's scheme, this defect is eliminated by taking into account the influence of the upper bands. In the lowest order in $\hat{\mathbf{k}}$, this influence can be taken into account by terms quadratic in $\hat{\mathbf{k}}$ along the diagonal and in the i, j = 3–6 block of the matrix $\hat{H}$. In order to retain the spherical symmetry of the problem, we discard terms causing the anisotropy of the band energy. The remaining off-diagonal terms $\sim\hat{k}^2$ can be compensated with the aid of a unitary transformation of the matrix $\hat{H}$, by changing the constant P by an amount equal to a fraction of the order of the ratio of the masses of the light and heavy holes. This gives rise in the Hamiltonian to negligibly small terms

that are inversely proportional to the square of the width of the forbidden band. The matrix elements of $\hat{H}$ which differ from those in [3] are

$$\begin{aligned} \hat{H}_{jj} &= a\hat{k}^2, && j = 1, 2; \\ \hat{H}_{jj} &= -E_g + b\hat{k}^2, && j = 3, 4, 5, 6; \\ \hat{H}_{jj} &= -\Delta - E_g + c\hat{k}^2, && j = 7, 8. \end{aligned} \tag{2}$$

These elements contain also terms with the vacuum mass of the electron. It is easy to verify that all three parameters a, b, and c are negative. The elements with $b\hat{k}^2$ are responsible for the finite mass of the heavy holes.

In the chosen approximation, the Hamiltonian has spherical symmetry and we can separate the variables in the corresponding Schrödinger equation. To this end we note that the operators of the rotation group are in this case matrices (of eighth order, which is the order of $\hat{H}$), and consequently, coincide with one of its representations. This representation, according to Schur's lemma,[4] is reducible, since its matrices commute with the diagonal part of $\hat{H}$ for arbitrary E_g and Δ. Consequently, in the chosen basis,[3] only the square cells of second, fourth, and second order, respectively, arranged along the principal diagonal, differ from zero in these matrices, in accord with (2). Therefore the spherical functions, which represent in this case columns of eight elements, can be written in the form

$$U_e = \begin{pmatrix} u_e \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad U_h = \begin{pmatrix} 0 \\ u_h \\ 0 \end{pmatrix}, \quad U_s = \begin{pmatrix} 0 \\ 0 \\ 0 \\ u_s \end{pmatrix}. \tag{3}$$

Here u_e and u_s are two-dimensional vectors while u_h is a four-dimensional one. The symbol 0 stands for a two-dimensional zero vector. The indices of the spherical functions relate them with each of the three bands directly accounted for in the Hamiltonian. The spinors u_e and u_s (or u_h), which transform in accordance with the irreducible representation $D_{1/2}$ (or respectively $D_{3/2}$) of the rotation group, can be written in the form of columns with a single nonzero element. We now can, using the Clebsch Gordan coefficients,[5] construct the basis functions u_e and u_s (or u_h) of the irreducible representation $D_{l-1/2}$ and $D_{l+1/2}$ (or $D_{l-3/2}, \ldots, D_{l+3/2}$) as linear combinations of the products of these spinors by the usual one-dimensional spherical functions $Y_{l,u}(\theta, \varphi)$ belonging to D_l. Since the transformation properties of the basis functions (3) from [3] differ from those customarily assumed in the Clebsch-Gordan theory, we have constructed by this method the function u_e; the others are generated by applying to it the operator $\hat{H}$.

The calculations lead to the following angle functions belonging to the total angular momentum $j = l + 1/2$ and its projections m (m assumes 2j + 1 half-integer values from −j to j):

$$u_e^{jm} = \begin{pmatrix} \sqrt{\dfrac{j+m}{2j}}\, Y_{j-1/2,\, m-1/2} \\ -\sqrt{\dfrac{j-m}{2j}}\, Y_{j-1/2,\, m+1/2} \end{pmatrix},$$

$$u_{h1}^{jm} = N_1 \begin{pmatrix} [3(j+m)(j-m+1)(j-m+2)]^{1/2} Y_{j+1/2,\, m-3/2} \\ i(j+3m)\sqrt{j-m+1}\, Y_{j+1/2,\, m-1/2} \\ (j-3m)\sqrt{j+m+1}\, Y_{j+1/2,\, m+1/2} \\ i[3(j-m)(j+m+1)(j+m+2)]^{1/2} Y_{j+1/2,\, m+3/2} \end{pmatrix},$$

$$N_1 = [2j(2j+2)(2j+3)]^{-1/2};$$

$$u_{h2}^{jm} = N_2 \begin{pmatrix} -[(j+m)(j+m-1)(j+m-2)]^{1/2} Y_{j-3/2,\, m-3/2} \\ i[3(j-m)(j+m-1)(j+m)]^{1/2} Y_{j-3/2,\, m-1/2} \\ [3(j+m)(j-m)(j-m-1)]^{1/2} Y_{j-3/2,\, m+1/2} \\ -i[(j-m)(j-m-1)(j-m-2)]^{1/2} Y_{j-3/2,\, m+3/2} \end{pmatrix},$$

$$N_2 = [2j(2j-1)(2j-2)]^{-1/2};$$

$$u_s^{jm} = \begin{pmatrix} -\left[\dfrac{j-m+1}{2(j+1)}\right]^{1/2} Y_{j+1/2,\, m-1/2} \\ -\left[\dfrac{j+m+1}{2(j+1)}\right]^{1/2} Y_{j+1/2,\, m+1/2} \end{pmatrix}. \tag{4}$$

We can similarly construct spherical functions with total momentum $j = l - 1/2$, completing the system of functions written out above. It is essential that these two subsystems have different parity for equal values of j, and therefore the angular dependence of the eigenfunction ψ of the spherically symmetrical even operator $\hat{H}$ is described by functions from only one of the subsystems. For example, for $j = l + 1/2$ we have

$$\begin{aligned} \psi^{jm}(r, \theta, \varphi) &= U_e{}^{jm} g_1(r) + U_{h1}{}^{jm} g_2(r) \\ &+ U_{h2}{}^{jm} g_3(r) + U_s{}^{jm} g_4(r). \end{aligned} \tag{5}$$

The radial functions satisfy the system of equations

$$\begin{aligned} &-\left(\alpha\Delta_L + \frac{\varkappa}{r} + \varepsilon\right) g_1 - \sqrt{\frac{L+2}{2L+1}}\left(\frac{d}{dr} + \frac{L+2}{r}\right) g_2 \\ &\quad - \sqrt{\frac{3L}{2L+1}}\left(\frac{d}{dr} - \frac{L-1}{r}\right) g_3 - \left(\frac{d}{dr} + \frac{L+2}{r}\right) g_4 = 0, \\ &\sqrt{\frac{L+2}{2L+1}}\left(\frac{d}{dr} - \frac{L}{r}\right) g_1 - \left(\beta\Delta_{L+1} + \frac{\varkappa}{r} + \varepsilon_1\right) g_2 = 0, \\ &\sqrt{\frac{3L}{2L+1}}\left(\frac{d}{dr} + \frac{L+1}{r}\right) g_1 - \left(\beta\Delta_{L-1} + \frac{\varkappa}{r} + \varepsilon_1\right) g_3 = 0, \\ &\left(\frac{d}{dr} - \frac{L}{r}\right) g_1 - \left(\gamma\Delta_{L+1} + \frac{\varkappa}{r} + \varepsilon_2\right) g_4 = 0. \end{aligned} \tag{6}$$

Here L is equal to l or $-l - 1$ respectively for

$j = l + 1/2$ and $j = l - 1/2$; the parameters α, β, γ, κ, ϵ, ϵ_1, and ϵ_2, multiplied by $P\sqrt{3}$, are equal to a, b, c, Ze^2/ϵ_0, E, E + E_g, and E + Δ + E_g; E is the eigenvalue of $\hat{H}$, and P can be regarded as positive without loss of generality;

$$\Delta_L = \frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{L(L+1)}{r^2}.$$

In accordance with symmetry requirements, the energy levels are (2j + 1)-fold degenerate in the magnetic quantum number m.

2. BEHAVIOR OF THE RADIAL FUNCTIONS

The terms quadratic in $\hat{k}$, which enter in the system (6), are relatively small: the parameter b is directly connected with the mass of the heavy holes, $b = -\hbar^2/2m_h$; a and c are of the same order. The role of these terms can be explained most clearly by going over to the single-band approximation. In this case the elimination of the interband matrix elements $\sim Pk$ generates large terms $\sim P^2k^2/E_g$, due to the small mass of the electron and of the light holes. In the electronic and the spin-split bands, these terms enter in the diagonal matrix elements and consequently mask $a\hat{k}^2$ and $c\hat{k}^2$. Thus, the value of the latter is qualitatively inessential (also quantitatively if the masses of the light and heavy holes differ greatly). The situation is different in the band of the light and heavy holes, in which the terms $\sim P^2k_ik_j$ enter only off the diagonal, and cannot cancel out the term $b\hat{k}^2$. We must therefore expect here an appreciable dependence of the spectrum on the heavy-hole mass.

The foregoing properties of the Hamiltonian $\hat{H}$ are implicit also in the system (6), although, to be sure, in a somewhat unexpected form.

We begin the investigation of this system with the limiting case when $\alpha = \beta = \gamma = 0$. In this situation it is possible to exclude from (6) the functions g_2, g_3, and g_4 and to reduce the equation for g_1 to the standard form:

$$\frac{d^2}{dr^2}g_1 + p(r)\frac{dg_1}{dr} + q(r)g_1 = 0, \tag{7}$$

where

$$p(r) = \frac{3}{r} + \frac{1}{r-r_0} - \frac{1}{r-r_1} - \frac{1}{r-r_2},$$

$$q(r) = \frac{\varepsilon\varepsilon_1\varepsilon_2}{\varepsilon_1+2\varepsilon_2} + \frac{A}{r} + \frac{B}{r-r_0} + \frac{1}{r-r_1}\frac{\varepsilon_1 L}{2\kappa} - \frac{1}{r-r_2}\frac{\varepsilon_2 L}{\kappa} - \frac{L(L+1)-\kappa^2/3}{r^2},$$

$$A = \frac{2(\varepsilon_2-\varepsilon_1)}{3\kappa}L + \frac{\kappa}{9}(2\varepsilon_1+\varepsilon_2+3\varepsilon),$$

$$B = -\frac{2\kappa}{9}\frac{(\varepsilon_1+2\varepsilon_2-3\varepsilon)(\varepsilon_1-\varepsilon_2)^2}{(\varepsilon_1+2\varepsilon_2)^2} + \frac{\varepsilon_1+2\varepsilon_2}{6\kappa}L. \tag{8}$$

The singular points r_j are

$$r_0 = -\frac{3\kappa}{\varepsilon_1+2\varepsilon_2}, \quad r_1 = -\frac{\kappa}{\varepsilon_1}, \quad r_2 = -\frac{\kappa}{\varepsilon_2}.$$

In addition to these points, Eq. (7) has singular points r equal to zero and infinity. In the vicinity of zero, $g_1(r)$ behaves like $r^{-1+\nu}$, where

$$\nu = \pm[l(l+1) + 1 - \kappa^2/3]^{1/2}, \tag{9}$$

and at infinity it behaves like $\exp(-\lambda r)$, with

$$\lambda = \pm[-\varepsilon\varepsilon_1\varepsilon_2/(\varepsilon_1+2\varepsilon_2)]^{1/2}. \tag{10}$$

We see from (10) that a discrete spectrum can appear in the forbidden band

$$-E_g < E < 0, \tag{11}$$

and also near the top of the spin-split band

$$-E_g - \Delta < E < -E_g - 2/3\Delta. \tag{12}$$

In a small x-vicinity of the points rj, the coefficients of (7) reduce to (x = r − r_j)

$$p(x) = \mathcal{P}/x + p_0 + p_1(x) + \ldots,$$
$$q(x) = Q/x + q_0 + q_1(x) + \ldots \tag{13}$$

For arbitrary values of Δ and E_g at the points r_1 and r_2, where $\mathcal{P} = -1$, the characteristic equation for the exponent η of the solution $g_1(x) \sim x^\eta$ has roots 0 and 2. If the particular solution for g_1 corresponding to a larger root is

$$w = x^2\left(1 + \sum_{n=1}^{\infty} a_n x^n\right), \tag{14}$$

then, in accordance with the theory of differential equations (see, for example, [6]), the general solution of (7) is

$$g_1(x) = C_1 w + C_2 w \int^x \frac{1}{w^2}\exp\left\{-\int^x p(x)\,dx\right\}dx. \tag{15}$$

By directly substituting w in (7) with coefficients (13) we can determine several of the first coefficients a_n, and then expand the integral of (15) in powers of x. Then

$$g_1(x) = C_1 w + C_2(-1/2 - 1/2Qx + \xi w \ln x + \ldots),$$
$$\xi = 1/4[q_0 + Q(p_0 + Q)]. \tag{16}$$

We have left out from (16) the positive powers of x, starting with x^2.

Expanding p(r) and q(r) in terms of x in the vicinity of the singular points, we can readily determine p_0 and q_0. The coefficient ξ for the point r_1 turns out to be

$$\xi = -\frac{3\varepsilon_1^2}{16\kappa^2}L(L+2). \tag{17}$$

According to (6) in the vicinity of r_1, where $Q = -L/2r_1$,

$$g_2 \sim \frac{1}{x}\sqrt{\frac{L+2}{2L+1}}\left(\frac{d}{dx}-\frac{L}{r_1}\right)g_1 \sim \frac{L}{x}\sqrt{\frac{L+2}{2L+1}} \sim \frac{\sqrt{L(L+2)}}{r-r_1},$$

$$g_3 \sim \frac{1}{x}\sqrt{\frac{L}{2L+1}}\left(\frac{d}{dx}+\frac{L+1}{r_1}\right)g_1 \sim \frac{L+2}{x}\sqrt{\frac{L}{2L+1}} \sim \frac{\sqrt{L(L+2)}}{r-r_1}. \quad (18)$$

For the point r_2 we have $Q = L/r_2$,

$$g_4 \sim \frac{1}{x}\left(\frac{d}{dx}-\frac{L}{r_2}\right)g_1 \sim \text{const}, \quad (19)$$

and $\xi = 0$; therefore all the $g_i(r)$ in the vicinity of this point are analytic.

In the singular point r_0, where $\mathcal{P} = 1$ and the characteristic equation has multiple roots $\eta = 0$, the general solution g_1 begins with the logarithmic term[6]

$$g_1 = C_2 \ln|r-r_0| + \ldots \quad (20)$$

and a pole appears also in the remaining functions of the system.

If $\kappa > 0$ and the spectrum lies within the forbidden band, corresponding to a center attracting the electrons, then the points r_0 and r_1 are negative and consequently fall in the unphysical region of values of the variable r. A similar situation arises when $\kappa < 0$ if the spectrum lies near the top of the spin-split band (12). On the other hand, if the spectrum of the acceptor center lies inside the forbidden band, then the singular points r_0, $r_1 > 0$ are in the real region of r and it is necessary to examine in this case whether g_i are finite. Thus, we must impose on the solution of the second-order differential equation (7) the following four conditions: boundedness at infinity ($\lambda > 0$), absence of singularities at $r = 0$ ($\nu > 0$) and $r = r_0$, and a definite behavior at the point $r = r_1$; this is generally speaking impossible.

In this case it is naturally necessary to resort to the terms that are quadratic in $\hat{\mathbf{k}}$. The most vital terms $\sim\beta\Delta_{L\pm1}$ are those directly connected with the mass of the heavy holes. Indeed, in the second and third equations of (6) the factor $(r - r_1)^{-1}$ of g_2 and g_3, which is characteristic of the singular point r_1, is "relegated to the background" together with them in the second and third equations of (6). This is the very factor which is responsible for the non-analyticity of the radial functions in r_1. It can be verified that now the g_i can be expanded in a Taylor series in the vicinity of any r and consequently, the non-analyticity in r_0 will also vanish. At $r = 0$ we have $g_i(r) \sim r^{\nu_i}$, where $\nu_i = \max\{L_i, -L_i, -1\}$, and L_i is the index of the Laplace operator in the i-th equation of the system (6). The condition (10), which governs the behavior of the functions at infinity, is written as follows (if α and γ likewise do not vanish)

$$\varepsilon + \alpha\lambda^2 + \frac{2\lambda^2}{\varepsilon_1+\beta\lambda^2} + \frac{\lambda^2}{\varepsilon_2+\gamma\lambda^2} = 0. \quad (21)$$

To conclude this section, let us list several models of the band structure, when a change in the system of singular points of (7) makes it possible to obtain its exact solution. In all the limiting cases considered below, (6) reduces to two equations analogous to the corresponding system for the radial functions of the relativistic hydrogen atom. The spectrum can be obtained from the well known formula (see, for example, [7]):

$$E = \frac{\bar{E}}{2}\left\{\left[1+\frac{\varkappa^2}{(n-l-1+[(l+1)^2-\varkappa^2]^{1/2})^2}\right]^{-1/2}-1\right\}. \quad (22)$$

The meanings of $\bar{E}$ and $\bar{\kappa}$ are explained below.

1. We consider a hypothetical case when the valence band split by the spin-orbit interaction is located above the bands of the light and heavy holes. We assume that the gap between the valence bands is infinitely large, i.e., $\epsilon_1 \to \infty$, but ϵ_2 is finite. In this case the singular points r_0 and r_1 go over into the point $r = 0$, where the course of the solution is altered, and (6) reduces to two equations for the functions g_1 and g_4. With this, we must put in (22) $E = E_g + \Delta$, $\bar{\kappa} = \kappa$, and $l = j - 1/2$. This variant was considered in [2].

2. If the spin-orbit splitting of the valence bands is annihilated (i.e., $\Delta = 0$ and $\epsilon_1 = \epsilon_2$), then all three singular points r_j coalesce into one. Going to the limit in p(r) and q(r) from (8), we obtain

$$p(r) = \frac{3}{r} - \frac{1}{r-r_1},$$

$$q(r) = \frac{\varepsilon\varepsilon_1}{3} + \frac{\varkappa(\varepsilon+\varepsilon_1)}{3r} - \frac{L(L+1)-\varkappa^2/3}{r^2}. \quad (23)$$

At the point r_1 we have $Q = 0$ and $\xi = -\epsilon_1^2 L(L+1)/4\kappa^2$. As seen directly from (6), when $L = l = 0$ we get $g_3 = 0$, and g_2 and g_3 differ by a numerical factor. Under the same conditions, the term with the logarithm in g_1 and the pole in the remaining functions vanish. Thus, when $\Delta = 0$ and $L = l = 0$ we have $E = E_g$ and $\bar{\kappa} = \kappa/\sqrt{3}$.

3. For $\Delta \to \infty$ and $l = 0$ or $l = 1$ (in both cases, for $j = 1/2$), an exact solution of (6) can also be obtained, $E = E_g$ and $\bar{\kappa} = \kappa/\sqrt{2}$.

3. VARIATIONAL PRINCIPLE FOR THE AVERAGE ENERGY

We now discuss a variational method for an approximate solution of the system (6). We stipulate beforehand that the high-lying levels of the system are vital in this case. For example, branches of the acceptor spectrum should be expected under the spectrum of the donor center. It is therefore necessary to seek here not the minimum of the average energy, but its stationary values.

The variational functional can be obtained on the basis of the system (6). After simple transformations

$$\overline{H} = H_1 + H_2, \tag{24}$$

where

$$H_1 = \int_0^\infty \Big\{ 2\sqrt{\frac{L+2}{2L+1}}\, g_2 \Big(\frac{d}{dr} - \frac{L}{r}\Big) g_1 + 2\sqrt{\frac{3L}{2L+1}}\, g_3 \Big(\frac{d}{dr} + \frac{L+1}{r}\Big) g_1 + 2g_4 \Big(\frac{d}{dr} - \frac{L}{r}\Big) g_1 - \frac{\varkappa}{r}\sum_{i=1}^{4} g_i^2 - \varepsilon_g (g_2^2 + g_3^2) - (\varepsilon_g + \varepsilon_\Delta) g_4^2 \Big\} r^2\, dr,$$

$$H_2 = -\int_0^\infty \{\alpha g_1 \Delta_L g_1 + \beta (g_2 \Delta_{L+1} g_2 + g_3 \Delta_{L-1} g_3) + \gamma g_4 \Delta_{L+1} g_4\}\, r^2\, dr, \tag{25}$$

under the normalization conditions

$$\sum_{i=1}^{4} \int_0^\infty g_i^2 r^2\, dr = 1. \tag{26}$$

Here

$$\varepsilon_g = \frac{\sqrt{3}}{P} E_g, \qquad \varepsilon_\Delta = \frac{\sqrt{3}}{P}\Delta.$$

The variational functional assumes a relatively simple form if we expand the radial functions in Laguerre polynomials[8]

$$g_i(r) = (2\lambda)^{(2\nu+1)/2} r^{\nu-1} e^{-\lambda r} \sum_{n=0}^{\infty} a_n{}^i \left(\frac{\Gamma(n+1)}{\Gamma(n+2\nu+1)}\right)^{1/2} L_n^{2\nu}(2\lambda r),$$

$$L_n^{2\nu}(x) = \frac{1}{n!} e^x x^{-2\nu} \frac{d^n}{dx^n}(x^{n+2\nu} e^{-x}). \tag{27}$$

These polynomials are orthogonal with weight $x^{2\nu}e^{-x}$. It is easy to find the relation

$$\int_0^\infty x^{2\nu-q} e^{-x} L_n^{2\nu+t}(x) L_m^{2\nu+s}(x)\, dx = \frac{\Gamma(m+2\nu+s+1)}{\Gamma(n+1)} \sum_k (-1)^k \times \frac{\Gamma(n+t+q-k)\Gamma(2\nu-q+k+1)}{\Gamma(m-k+1)\Gamma(k+1)\Gamma(k+2\nu+s+1)\Gamma(t+q-k)}$$

$$0 \leqslant k \leqslant t+q-1, \quad n > m-t-q, \tag{28}$$

if we represent in the integral $L_n^{2\nu+t}(x)$ in the form (27) and, using the formula

$$\frac{d}{dx} L_n^{2\nu}(x) = -L_{n-1}^{2\nu+1}(x), \tag{29}$$

simplify it by integration by parts. Equations (28) and (29) allow us to calculate all the integrals in (25) and (26). With this,

$$\int_0^\infty r^2 g_i^2\, dr = \sum_{n=0}^{\infty} (a_n{}^i)^2, \tag{30}$$

$$\int_0^\infty r g_i g_j\, dr = \frac{\lambda}{\nu} \sum_{n \geqslant m} \Big(h_{nm} - \frac{1}{2}\delta_{nm}\Big)(a_n{}^i a_m{}^j + a_m{}^i a_n{}^j),$$

$$\int_0^\infty r^2 g_i \Big(\frac{d}{dr} + \frac{1}{r}\Big) g_1\, dr = \lambda \sum_{n>m} h_{nm}(a_n{}^i a_m{}^1 - a_m{}^i a_n{}^1), \tag{31}$$

$$\int_0^\infty r^2 g_i \Delta_l g_i\, dr = 8\lambda^2 \sum_{n \geqslant m} \Big(h_{nm} - \frac{1}{2}\delta_{nm}\Big)\Big\{ -\frac{m}{2\nu+1} + \frac{(\nu+l)(\nu-l-1)}{2\nu}\Big(\frac{n+1}{2\nu-1} - \frac{m}{2\nu+1}\Big) - \frac{1}{4}(2-\delta_{nm})\Big\} a_n{}^i a_m{}^i,$$

where

$$h_{nm} = \left[\frac{\Gamma(n+1)\Gamma(m+2\nu+1)}{\Gamma(m+1)\Gamma(n+2\nu+1)}\right]^{1/2}. \tag{32}$$

In accordance with the deductions of the preceding section, ν is determined here by the positive root of (9), or else is equal to l when account is taken of the finite mass of the heavy holes.

Variation of $\overline{H}$ with respect to 4N coefficients $a_n^i (0 \leq n \leq N-1)$ subject to condition (26) enables us to reduce the problem of finding the energy levels to a determination of the eigenvalues of a matrix of order 4N.

The numerical calculations were made with an electronic computer. The eigenvalues and the eigenvectors (i.e., the 4N numbers a_n^i) of the matrix were determined for fixed l by the method of rotations[9][1)] with subsequent variation with respect to this parameter.

In InSb, where the width of the forbidden band is small, the scheme of the interacting nearest

[1)] The authors are grateful to V. S. Kvakush of the Institute of Cybernetics of the Ukrainian Academy of Science for supplying the corresponding program for diagonalizing the matrix.

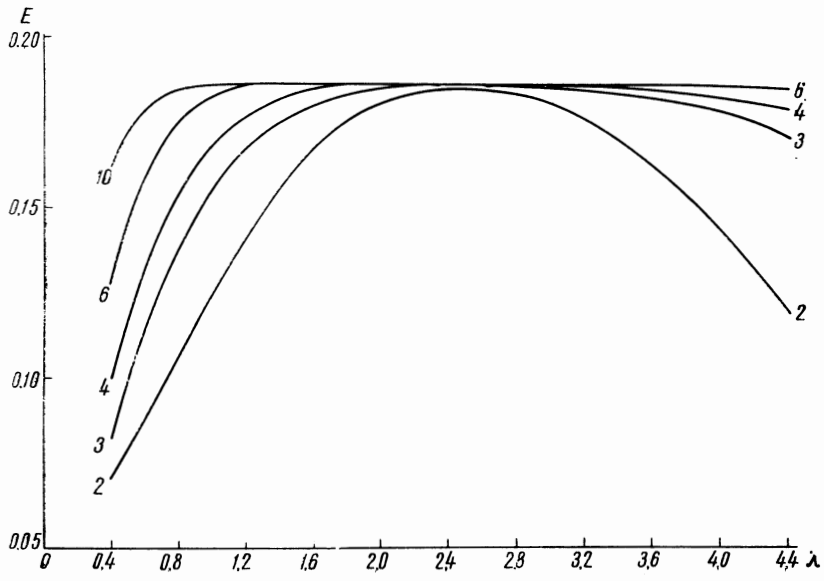

FIG. 1. Dependence of the ionization potential of the acceptor center on the variational parameter λ. The number of the curve coincides with N; the energy is plotted in units of $m_0e^4/2\hbar^2\epsilon_0^2$, and λ corresponds to the radius in units of $a_0 = 2P\epsilon_0^2\hbar^2/\sqrt{3}m_0e^4$.

bands should describe the real motion of the carriers with sufficient accuracy. In addition, the small anisotropy of the effective mass m_h of the heavy holes[10, 11] allows us to expect quantitative agreement between our present results and experiment for centers with sufficiently large radius.

This circumstance has induced us to use the following parameters of InSb: P = 0.67 at.un., E_g = 4.23 eV, Δ = 0.9 eV,[1] ϵ_0 = 17,[12] and $m_h = 0.4m_0$.[10, 11] The parameter β is assumed here equal to $-\hbar^2/2m_h$. When the masses of the light and heavy holes differ greatly (as is the case in InSb), the spectrum depends little on the values of α and γ. Since $\gamma \to \beta$ when the spin-orbit interaction vanishes, we can assume that they are equal. The constant P is determined from the effective mass of the electron,[1] and $\alpha = 0$.

As shown by the calculations, when $\kappa > 0$ (donor center attracting the electrons and repelling the holes) a discrete spectrum appears, located in the forbidden band at the bottom of the conduction band. As expected, the levels of the discrete spectrum are close to the hydrogenlike spectrum with mass equal to the effective mass of the electrons. In the case when $\kappa < 0$, which corresponds to an acceptor center, the discrete spectrum lies directly over the top of the valence band. In addition, discrete levels arise near the top of the spin-split band.

The ground state of the acceptor center corresponds to $j = {}^3/_2$ and L = 1, because it is precisely in this case that the main component of the wave function ($U_{h2}g_3$) may not have any nodes.[13] The numerical value of the energy E of the ground state of a singly-charged center, reckoned from the top of the valence band, is 0.0088 eV, which is in good agreement with the experimental value of the ionization potential.[14] It is possible to set in correspondence with the obtained level an "average effective mass" of $0.19m_0$. Figure 1 shows the dependence of E on the variational parameter λ for different value of N. As expected, with increasing number of the variational parameters, E becomes less sensitive to changes of λ.

Figure 2 shows the distribution of the charge density

$$\rho = \sum_{i=1}^{4} g_i^2(r) r^2 \qquad (33)$$

and the radial functions of the ground state. We see that the probable radius is approximately 80 Å.

As expected, the most important functions are g_2 and g_3. The smallness of the function g_1 leads

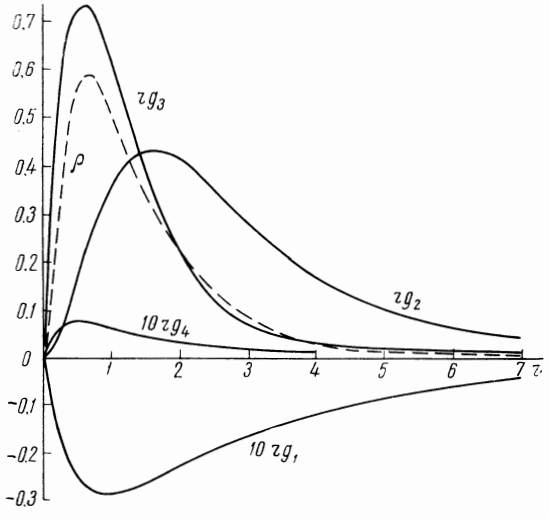

FIG. 2. Radial functions and charge density of the ground state; r is in units of a_0.

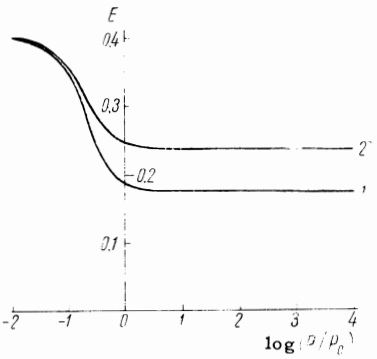

FIG. 3. Dependence of the energy of the ground state of the acceptor center on P; P_0 = 0.67 at. un., energy scale same as in Fig. 1. Curve 1 corresponds to the parameters of InSb, and curve 2 to the case $\Delta = 0$.

to the following curious circumstance: when P is large the energy ceases to depend on this parameter. In fact, in this case we can neglect the terms proportional to g_1 in the first equation of (6), after which P drops out from the solutions of the system. This is confirmed by concrete calculation (curve 1 on Fig. 3). The same figure shows an analogous dependence of E on P in the case when there is no spin-orbit splitting of the valence bands ($\Delta = 0$, b = c), considered in analytic form in [2]. Here, too, at the essential values of P the energy does not change with the increase of this parameter, thus confirming the method used in [2] for simplifying the variational functional. In this case the solution of the system (6) is equivalent to extremization of the functional, which differs from (A.8) of [2] by the sign at the term $\sqrt{l(l+1)}\,\varphi_{||}$. For the same two-parameter trial function as used in [2], the energy of the ground state ($l = 1$) is equal to

$$E = \max \bar{H} = 0.58 \frac{m_h Z^2 e^4}{2\hbar^2 \varepsilon_0^2} - E_g, \qquad (34)$$

which is in good agreement with curve 2 of Fig. 3.

The "average effective mass" $0.58\,m_h$ lies between the masses of the light and heavy holes, unlike in [2], where its value was $1.4 m_h$.

It is interesting to trace the course of the ionization potential with increasing mass of the heavy holes. Calculation shows that in this case E increases without limit and crosses the forbidden band. This result finds a simple physical explanation. Indeed, if one can speak to any extent of a separate motion of the holes in each of the valence bonds, then the band of the heavy holes should make the overwhelming contribution to the energy, the contribution increasing with increasing carrier mass.

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