EFFECTIVE MASS APPROXIMATION FOR ACCEPTOR STATES IN InSb, GaAs, GaSb

By D. Thanh

Institute of Theoretical Physics, Warsaw University*

(Received July 9, 1971)

The acceptor levels in InSb have been computed from the effective mass equations with and without the terms linear in the wave vector. The results calculated with the terms linear in wave vector are in better agreement with the experimental results than those obtained without the terms linear in the wave vector. The acceptor levels in GaAs and GaSb have been computed without the terms linear in the wave vector. The agreement between the energy of the ground state and experimentally determined energy is very good for GaAs.

1. Introduction

The theoretical investigation of shallow acceptor states in germanium and silicon is usually based on the effective mass approximation [1–3]. This paper presents a treatment of the effective mass equations. The energies are calculated by a variational method for the ground state and all types of excited states for InSb, GaAs and GaSb. Some results were communicated shortly in Phys. Status Solidi [4, 5].

In the effective mass theory one considers a single hole moving in the periodic potential of the pure crystal plus the perturbing potential produced by the acceptor ion. One then expresses the wave function of the hole in the form:

$$\Psi(\vec{r}) = \sum_j F_j(\vec{r})\varphi_j(\vec{r}) \tag{1.1}$$

where $\varphi_j(\vec{r})$ are the Bloch functions at the valence band edge in the unperturbed crystal and $F_j(\vec{r})$ are the modulating or "envelope" functions.

Let us start with a brief review of the valence band structure in compounds $A^{III}B^{V}$. Owing to the lack of inversion symmetry in these compounds, in principle, the spin-orbit interaction may shift the maximum of the valence band away from the point Γ ($\vec{k} = 0$). This shift is very small and is determined experimentally only in InSb [6]. Therefore InSb has the valence band structure which is shown in Fig. 1. There are various attempts to detect the terms linear in $\vec{k}$ *e. g.* by their effects in magnetoabsorption [7] and

* Address: Instytut Fizyki Teoretycznej, Uniwersytet Warszawski, Warszawa, Hoża 69, Poland.

uniaxial stress [8]. For other compounds $A^{III}B^{V}$, *i. e.* for GaAs and GaSb we neglect the terms linear in $\vec{k}$ and assume the valence band structure to be identical with that of Ge and Si (see Fig. 2). Since the valence band is degenerate in the vicinity of the band maximum, the acceptor states are composed of states from various valence bands. In $A^{III}B^{V}$ compounds the spin-orbit splitting is considerably larger than the acceptor energies. Consequently, one expects that only wave functions from the upper four valence bands will

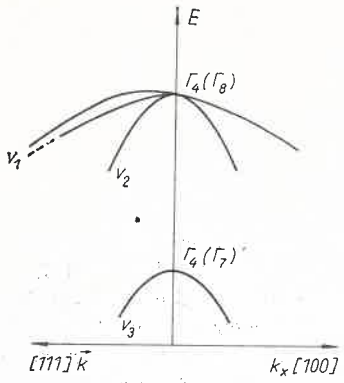

Fig. 1

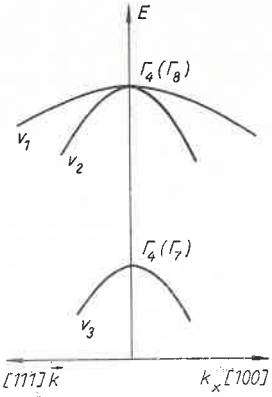

Fig. 2

Fig. 1. Schematic picture of the valence band structure near the band maximum including spin-orbit splitting for InSb

Fig. 2. Schematic picture of the valence band structure near the band maximum including spin-orbit splitting for GaAs and GaSb

occur in the acceptor states with appreciable amplitude. The Bloch functions of these bands at $\vec{k} = 0$ transform like atomic $p^{3/2}$ functions under the operations of the full "double" tetrahedral group and belong to the Γ_8 representations:

$$\varphi_{3/2}^{(3/2)} = \frac{1}{\sqrt{2}}(X+iY)|\alpha\rangle$$

$$\varphi_{1/2}^{(3/2)} = \frac{i}{\sqrt{6}}[(X+iY)|\beta\rangle - 2Z|\alpha\rangle]$$

$$\varphi_{-1/2}^{(3/2)} = \frac{1}{\sqrt{6}}[(X-iY)|\alpha\rangle + 2Z|\beta\rangle]$$

$$\varphi_{-3/2}^{(3/2)} = \frac{i}{\sqrt{2}}(X-iY)|\beta\rangle \tag{1.2}$$

where α and β are the spin functions corresponding to spin "up" and "down" respectively.

Shallow impurity states with larger orbits should be well described by the effective mass equations:

$$HF(\vec{r}) = EF(\vec{r}) \tag{1.3}$$

where H is the effective mass Hamiltonian matrix, $F(\vec{r})$ are column matrices having as elements the functions $F_j(\vec{r})$. The potential of the acceptor is assumed coulombic $-e^2/\kappa r$ with κ the static dielectric constant of the crystal.

In the units:
of energy $E_0 = e^4/4\kappa^2|A|$,
and length $L_0 = 2\kappa|A|/e^2$,
the effective mass Hamiltonian H can be expressed in the form:

$$H = H_0 + H_1 \tag{1.4}$$

where H_0 is the 4×4 matrix given by Schechter [1]:

$$H_0 = \begin{vmatrix} \frac{1}{2}P - \frac{2}{r} & L & M & 0 \\ L^* & \frac{1}{6}P + \frac{2}{3}Q - \frac{2}{r} & 0 & M \\ M^* & 0 & \frac{1}{6}P + \frac{2}{3}Q - \frac{2}{r} & -L \\ 0 & M^* & -L^* & \frac{1}{2}P - \frac{2}{r} \end{vmatrix}$$

with

$$P = -2\nabla^2 + 2\bar{D}\left[\frac{\partial^2}{\partial z^2} - \frac{1}{2}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\right],$$

$$Q = -\nabla^2 - 2\bar{D}\left[\frac{\partial^2}{\partial z^2} - \frac{1}{2}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\right],$$

$$L = \frac{i\bar{C}}{\sqrt{3}}\left(\frac{\partial}{\partial x} - i\frac{\partial}{\partial y}\right)\frac{\partial}{\partial z},$$

$$M = -\frac{1}{\sqrt{12}}\left[3\bar{D}\left(\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2}\right) - 2i\bar{C}\frac{\partial^2}{\partial x \partial y}\right], \tag{1.6}$$

and H_1 is deduced from [10] with functional basis (1.2):

$$H_1 = \bar{K}\begin{vmatrix} 0 & -\left(\frac{\partial}{\partial x} + i\frac{\partial}{\partial y}\right) & 2i\frac{\partial}{\partial z} & \sqrt{3}\left(\frac{\partial}{\partial x} - i\frac{\partial}{\partial y}\right) \\ \left(\frac{\partial}{\partial x} - i\frac{\partial}{\partial y}\right) & 0 & \sqrt{3}\left(\frac{\partial}{\partial x} + i\frac{\partial}{\partial y}\right) & -2i\frac{\partial}{\partial z} \\ 2i\frac{\partial}{\partial z} & -\sqrt{3}\left(\frac{\partial}{\partial x} - i\frac{\partial}{\partial y}\right) & 0 & -\left(\frac{\partial}{\partial x} + i\frac{\partial}{\partial y}\right) \\ -\sqrt{3}\left(\frac{\partial}{\partial x} + i\frac{\partial}{\partial y}\right) & -2i\frac{\partial}{\partial z} & \left(\frac{\partial}{\partial x} - i\frac{\partial}{\partial y}\right) & 0 \end{vmatrix} \tag{1.7}$$

The matrix operator H_1 following from the inversion asymmetry in Zinc-Blende type structure is responsible for the shift of the maximum of the valence band from the Γ point. The constants in (1.6) and (1.7) are:

$$\bar{C} = C/A, \bar{D} = B/A, \bar{K} = 2\kappa K/e^2, \tag{1.8}$$

where constants A, B, C are determined by the cyclotron resonance experiments, and K is the constant introduced by Kane [10]. The values of the parameters used in our calculations are presented in Table I.

TABLE I

Values of parameters used in calculations

	k	K	A B C	$\bar{C}$	$\bar{D}$	$\bar{K}$	E_0 (meV)	$L_0(10^{-8}\text{cm})$
InSb	15.9 [15]	4.210^{-10}eV.cm [9]	−25.0 −21 16 [11, 12]	2.75	0.84	0.096	2.15	210
GaAs	11.5 [16]	0	−7.2 −5.0 0 [13]	2.083	0.694	0	14.27	43.8
GaSb	14.8 [16]	0	−11.0 −6.0 11.0 [14]	2.382	0.545	0	5.64	86.15

2. *Trial functions*

To set up variational trial functions, we expanded the envelope functions in spherical harmonics:

$$F_j(\vec{r}) = \sum_l \sum_k c_{lk} A_j^{(lk)}(\theta, \varphi) r^l e^{-r/r_l} \tag{2.1}$$

where the angular functions $A_j^{(lk)}(\theta, \varphi)$ are linear combinations of spherical harmonics of order l. Schechter [1] has shown how to determine appropriate linear combination of the symmetry properties of the problem. The symmetry group of the acceptor Hamiltonian is the full tetrahedral group T_d^2. The wave functions corresponding to different energy levels of the acceptor form a basis for the Γ_6, Γ_7, or Γ_8 irreducible representations of this group.

Because of the presence of the term H_1 the Hamiltonian (1.4) for InSb is not invariant under inversion, since the envelope functions of acceptor states do not have, in general, a definite parity. On the other hand, for GaAs and GaSb the coefficient $K = 0$, Hamiltonian (1.4) is invariant under inversion, thus the envelope functions have a definite parity as in the case of Ge and Si.

1. Case of $K \neq 0$

The trial functions used in this calculations are shown below. For the Γ_8 states the general form of the trial function up to f-like terms ($l = 3$) is

$$F = C_0 \begin{vmatrix} 1 \\ 0 \\ 0 \\ 0 \end{vmatrix} e^{-r/r_0} + C_{11} \begin{vmatrix} 0 \\ \frac{1}{\sqrt{3}}(x-iy) \\ \frac{2i}{\sqrt{3}} z \\ -(x+iy) \end{vmatrix} e^{-r/r_1} +$$

$$+C_{12} \begin{vmatrix} 0 \\ (x-iy) \\ -iz \\ 0 \end{vmatrix} e^{-r/r_1} + C_{21} \begin{vmatrix} z^2 - \frac{1}{2}(x^2+y^2) \\ 0 \\ -\frac{\sqrt{3}}{2}(x^2-y^2) \\ 0 \end{vmatrix} e^{-r/r_2} +$$

$$+C_{22} \begin{vmatrix} 0 \\ iz(x+iy) \\ ixy \\ 0 \end{vmatrix} e^{-r/r_2} + C_{23} \begin{vmatrix} 0 \\ iz(x+iy) \\ -2ixy \\ \sqrt{3}\, iz(x-iy) \end{vmatrix} e^{-r/r_2} +$$

$$+C_{31} \begin{vmatrix} \frac{\sqrt{3}}{4}[5z(x-iy)^2 - z(x+iy)^2] \\ 0 \\ 0 \\ -i\frac{\sqrt{3}}{4}\left[5\left(z^2 - \frac{r^2}{5}\right)(x+iy) + (x-iy)^3\right] \end{vmatrix} e^{-r/r_3} +$$

$$+C_{32} \begin{vmatrix} \frac{\sqrt{3}}{2}[z(x+iy)^2 + z(x-iy)^2] \\ \frac{3i}{4}\left[\left(z^2 - \frac{r^2}{5}\right)(x-iy) + (x+iy)^3\right] \\ -3z\left(z^2 - \frac{3r^2}{5}\right) \\ \frac{i\sqrt{3}}{4}\left[7\left(z^2 - \frac{r^2}{5}\right)(x+iy) - (x-iy)^3\right] \end{vmatrix} e^{-r/r_3} +$$

$$+C_{33}\begin{vmatrix} \frac{3\sqrt{3}}{2}\left[z(x+iy)^2+z(x-iy)^2\right] \\ \frac{i}{2}\left[15\left(z^2-\frac{r^2}{5}\right)(x-iy)+(x+iy)^3\right] \\ 5z\left(z^2-\frac{3r^2}{5}\right) \\ i\sqrt{3}\,(x-iy)^3 \end{vmatrix} e^{-r/r_3}+$$

$$+C_{34}\begin{vmatrix} -\frac{\sqrt{3}}{14}\left[9z(x+iy)^2-3z(x-iy)^2\right] \\ \frac{3i}{4}\left[3\left(z^2-\frac{r^2}{5}\right)(x-iy)-(x+iy)^3\right] \\ -3z\left(z^2-\frac{3r^2}{5}\right) \\ \frac{i3\sqrt{3}}{28}\left[5\left(z^2-\frac{r^2}{5}\right)(x+iy)+(x-iy)^3\right] \end{vmatrix} e^{-r/r_3}. \qquad (2.2)$$

This function depends on ten linear and four nonlinear variational parameters.

In our computation of Γ_8 state we do not use, in fact, this general trial function but we make some further approximations. The approximations are different for the lowest Γ_8-type state which appeared to be the ground state and for the excited states. We discuss them in the next chapter. The numerical results are tabulated in Tables II, III.

For the Γ_7 states the trial function is:

$$F = C_1\begin{vmatrix} (x+iy) \\ 0 \\ -\sqrt{3}\,(x-iy) \\ 2iz \end{vmatrix} e^{-r/r_1}+C_{21}\begin{vmatrix} 0 \\ z^2-\frac{1}{2}(x^2+y^2) \\ 0 \\ -\frac{\sqrt{3}}{2}(x^2-y^2) \end{vmatrix} e^{-r/r_2}+$$

$$+C_{22}\begin{vmatrix} iz(x-iy) \\ 0 \\ i\sqrt{3}\,z(x+iy) \\ 2ixy \end{vmatrix} e^{-r/r_2}+C_3\begin{vmatrix} -\frac{3}{4}\left[(x-iy)^3+(x+iy)\left(z^2-\frac{r^2}{5}\right)\right] \\ \frac{i\sqrt{3}}{2}\left[z(x+iy)^2+z(x-iy)^2\right] \\ -\frac{\sqrt{3}}{4}\left[7(x-iy)\left(z^2-\frac{r^2}{5}\right)-(x+iy)^3\right] \\ -3iz\left(z^2-\frac{3r^2}{5}\right) \end{vmatrix} e^{-r/r_3}. \qquad (2.3)$$

TABLE II

Variational results of E (meV), $r_I(10^{-8}\text{cm})$, C_0 ($\text{cm}^{-3/2}$), C_{1i} ($\text{cm}^{-5/2}$), C_{2i} ($\text{cm}^{-7/2}$) for the ground state $\Gamma_8(\Gamma_8^+)$

$K \neq 0$		$K = 0$	
InSb Γ_8	InSb Γ_8^+	GaAs Γ_8^+	GaSb Γ_8^+
Theory $E = 9.3$ Experimental 9.7 [17]	$E = 7.8$	Theory $E = 25$ Experimental 24 [19] 26 [18]	Theory E = 10 Experimental 34 [20]
$r_0 = 39.17$, $r_1 = 46.6$, $r_2 = 32.07$,	$r_0 = 46.9$, $r_2 = 38.2$	$r_0 = 22.18$, $r_2 = 16.88$	$r_0 = 42.37$, $r_2 = 32.35$
$C_0 = 1.8075\times10^9$, $C_{11} = 2.6863\times10^{14}$,	$C_0 = 1.4412\times10^9$, $C_{21} = -1.8620\times10^{21}$	$C_0 = 4.8320\times10^9$,	$C_0 = 1.8233\times10^9$,
$C_{12} = 0.9362\times10^{14}$, $C_{21} = -3.1731\times10^{21}$,	$C_{22} = 3.5550\times10^{21}$, $C_{23} = 0.$	$C_{21} = -2.7016\times10^{22}$	$C_{21} = -2.1784\times10^{21}$,
$C_{21} = 6.9364\times10^{21}$, $C_{23} = -1.1750\times10^{21}$.		$C_{22} = 4.6820\times10^{22}$, $C_{23} = 0.$	$C_{22} = 0.5496\times10^{22}$, $C_{23} = 0.$

TABLE III

Variational results of E (meV), r_1 (10^{-8} cm), C_{1i} ($cm^{-7/2}$), C_{3i} ($cm^{-9/2}$) for the excited states Γ_8^-

	InSb	GaAs	GaSb
$\Gamma_{8.1}^-$	$E = 4.4$ $r_1 = 51.1,\ r_3 = 28.3,$ $C_{11} = 0.6347\times10^{15},\ C_{12} = 1.3655\times10^{15}$ $C_{31} = -1.7381\times10^{26},\ C_{32} = -1.2211\times10^{27}$ $C_{33} = -1.4439\times10^{26},\ C_{34} = -1.1274\times10^{27}$	$E = 10.8$ $r_1 = 29.01,\ r_3 = 16.05$ $C_{11} = 3.1782\times10^{15},\ C_{12} = 5.5932\times10^{15},$ $C_{31} = -5.7707\times10^{27},\ C_{32} = -1.1568\times10^{28},$ $C_{33} = -2.8830\times10^{28},\ C_{34} = -1.3474\times10^{28},$	$E = 4.5$ $r_1 = 54.31,\ r_3 = 30.04$ $C_{11} = 0.4486\times10^{15},\ C_{12} = 1.2215\times10^{15}$ $C_{31} = -1.2024\times10^{26},\ C_{32} = -1.0568\times10^{27}$ $C_{33} = -0.3552\times10^{26},\ C_{34} = -0.6365\times10^{27}$
$\Gamma_{8.2}^-$	$E = 2.5$ $r_1 = 86.88,\ r_3 = 47.54,$ $C_{11} = 0.3763\times10^{15},\ C_{12} = -1.2425\times10^{14},$ $C_{31} = -0.4924\times10^{27},\ C_{32} = 1.5398\times10^{26},$ $C_{33} = -0.8743\times10^{26},\ C_{34} = 0.8795\times10^{26},$	$E = 6.7$ $r_1 = 45.76,\ r_3 = 25.17,$ $C_{11} = 1.8401\times10^{15},\ C_{12} = -7.9646\times10^{14},$ $C_{31} = -7.3963\times10^{27},\ C_{32} = 2.5414\times10^{27},$ $C_{33} = -1.3861\times10^{27},\ C_{34} = 1.6168\times10^{27},$	$E = 2.9$ $r_1 = 80.81,\ r_3 = 41.51,$ $C_{11} = 0.4782\times10^{15},\ C_{12} = -1.2448\times10^{14}$ $C_{31} = -0.6084\times10^{27},\ C_{32} = 1.5632\times10^{26}$ $C_{33} = -0.8556\times10^{26},\ C_{34} = 0.5533\times10^{26}.$

TABLE IV

Variational results of E (meV), r_1 (10^{-8} cm), C_1 ($cm^{-5/2}$), C_{2i} ($cm^{-7/2}$), C_3 ($cm^{-9/2}$) for the excited states Γ_7

	$K \neq 0$		$K = 0$		
	InSb		InSb	GaAs	GaSb
$\Gamma_{7.1}$	$E = 1.48$ $r_1 = 148.7,\ r_2 = 86.7,\ r_3 = 82.2$ $C_1 = 0.5050\times10^{14},\ C_{21} = -0.3468\times10^{19}$ $C_{22} = -0.3615\times10^{19},\ C_3 = -0.4187\times10^{26}$	Γ_7^-	$E = 1.48$ $r_1 = 149{,}5,\ r_3 = 82.56$ $C_1 = 0.5042\times10^{14}$ $C_3 = -0.4182\times10^{26}$	$E = 5.8$ $r_1 = 53.13,\ r_3 = 29.18$ $C_1 = 7.0406\times10^{14}$ $C_3 = -3.8001\times10^{27}$	$E = 1.94$ $r_1 = 122.63,\ r_3 = 67.18$ $C_1 = 0.8559\times10^{14}$ $C_3 = -0.9456\times10^{26}$
$\Gamma_{7.2}$	$E = 0.2$ $r_1 = 399.2,\ r_2 = 774,\ r_3 = 911$ $C_1 = 4.0303\times10^{12},\ C_{21} = 4.0450\times10^{17}$ $C_{22} = 2.2603\times10^{17},\ C_3 = 5.3939\times10^{21}$	Γ_7^+	$E = 0.2$ $r_2 = 774.4$ $C_{21} = 1.1427\times10^{17}$ $C_{22} = 0.6396\times10^{17}$	$E = 1.3$ $r_2 = 157.48$ $C_{21} = 2.9759\times10^{19}$ $C_{22} = 1.718\times10^{19}$	$E = 0.57$ $r_2 = 287.13$ $C_{21} = 0.3807\times10^{19}$ $C_{22} = 1.9423\times10^{18}$

The numerical results are tabulated in Table IV.

For the Γ_6 states the trial function is:

$$F = C_1 \begin{vmatrix} \sqrt{3}\,(x-iy) \\ 2iz \\ (x+iy) \\ 0 \end{vmatrix} e^{-r/r_1} + C_{21} \begin{vmatrix} z^2 - \frac{1}{2}(x^2+y^2) \\ 0 \\ \frac{\sqrt{3}}{2}(x^2-y^2) \\ 0 \end{vmatrix} e^{-r/r_2} +$$

$$+ C_{22} \begin{vmatrix} 0 \\ iz(x+iy) \\ -2ixy \\ -\sqrt{3}\,iz(x-iy) \end{vmatrix} e^{-r/r_2} + C_3 \begin{vmatrix} -\frac{\sqrt{3}}{4}\left[7\left(z^2-\frac{r^2}{5}\right)(x-iy)-(x+iy)^3\right] \\ 3iz\left(z^2-\frac{3r^2}{5}\right) \\ \frac{3}{4}\left[(x-iy)^3+(x+iy)\left(z^2-\frac{r^2}{5}\right)\right] \\ \frac{i\sqrt{3}}{2}\left[z(x+iy)^2+z(x-iy)^2\right] \end{vmatrix} e^{-r/r_3}. \quad (2.4)$$

The numerical results are tabulated in Table V.

TABLE V

Variational results of E (meV), r_1 (10^{-8} cm), C_1 ($\text{cm}^{-5/2}$), C_{2i}($\text{cm}^{-7/2}$), C_3 ($\text{cm}^{-9/2}$) for excited states Γ^6

	InSb	GaAs	GaSb
$\Gamma_{6.1}(\Gamma_6^+)$	$E = 0.7$ $r_2 = 227.4$ $C_{21} = 0.9374\times10^{19}$ $C_{22} = -0.3250\times10^{19}$	$E = 3.2$ $r_2 = 64.15$ $C_{21} = 8.0437\times10^{20}$ $C_{22} = -2.6998\times10^{20}$	$E = 1.16$ $r_2 = 140.23$ $C_{21} = 0.5105\times10^{20}$ $C_{22} = -1.8973\times10^{19}$
$\Gamma_{6.2}(\Gamma_6^-)$	$E = 0.3$ $r_1 = 787.8$ $r_3 = 407.2$ $C_1 = 0.9175\times10^{12}$ $C_3 = 0.7331\times10^{22}$	$E = 1.27$ $r_1 = 64.96$ $r_3 = 123.12$ $C_1 = 2.7565\times10^{10}$ $C_3 = 1.2741\times10^{25}$	$E = 0.86$ $r_1 = 282.4$ $r_3 = 149$ $C_1 = 1.868\times10^{13}$ $C_3 = 1.1880\times10^{24}$

2. Case of $K=0$

The trial functions used in this calculations are shown below. For the Γ_8^+ states the trial function is:

$$F = C_0 \begin{vmatrix} 1 \\ 0 \\ 0 \\ 0 \end{vmatrix} e^{-r/r_0} + C_{21} \begin{vmatrix} z^2 - \frac{1}{2}(x^2+y^2) \\ 0 \\ -\frac{\sqrt{3}}{2}(x^2-y^2) \\ 0 \end{vmatrix} e^{-r/r_2} +$$

$$+ C_{22} \begin{vmatrix} 0 \\ iz(x+iy) \\ ixy \\ 0 \end{vmatrix} e^{-r/r_2} + C_{23} \begin{vmatrix} 0 \\ iz(x+iy) \\ -2ixy \\ \sqrt{3}\, iz(x-iy) \end{vmatrix} e^{-r/r_2}. \qquad (2.5)$$

The numerical results are tabulated in Table II.

For the Γ_8^- states the trial function is:

$$F = C_{11} \begin{vmatrix} 0 \\ \frac{1}{\sqrt{3}}(x-iy) \\ \frac{2i}{\sqrt{3}} z \\ -(x+iy) \end{vmatrix} e^{-r/r_1} + C_{12} \begin{vmatrix} 0 \\ (x-iy) \\ -iz \\ 0 \end{vmatrix} e^{-r/r_1} +$$

$$+ C_{31} \begin{vmatrix} \frac{\sqrt{3}}{4}[5z(x-iy)^2 - z(x+iy)^2] \\ 0 \\ 0 \\ -i\frac{\sqrt{3}}{4}\left[5\left(z^2 - \frac{r^2}{5}\right)(x+iy) + (x-iy)^3\right] \end{vmatrix} e^{-r/r_3} +$$

$$+C_{32}\begin{vmatrix} \frac{\sqrt{3}}{2}\left[z(x+iy)^2+z(x-iy)^2\right] \\ \frac{3i}{4}\left[\left(z^2-\frac{r^2}{5}\right)(x-iy)+(x+iy)^3\right] \\ -3z\left(z^2-\frac{3r^2}{5}\right) \\ \frac{i\sqrt{3}}{4}\left[7\left(z^2-\frac{r^2}{5}\right)(x+iy)-(x-iy)^3\right] \end{vmatrix} e^{-r/r_3}+$$

$$+C_{33}\begin{vmatrix} \frac{3\sqrt{3}}{2}\left[z(x+iy)^2+z(x-iy)^2\right] \\ \frac{i}{2}\left[15\left(z^2-\frac{r^2}{5}\right)(x-iy)+(x+iy)^3\right] \\ 5z\left(z^2-\frac{3r^2}{5}\right) \\ i\sqrt{3}\,(x-iy)^3 \end{vmatrix} e^{-r/r_3}+$$

$$+C_{34}\begin{vmatrix} -\frac{\sqrt{3}}{14}\left[9z(x+iy)^2-3z(x-iy)^2\right] \\ \frac{3i}{4}\left[3\left(z^2-\frac{r^2}{5}\right)(x-iy)-(x+iy)^3\right] \\ -3z\left(z^2-\frac{3r^2}{5}\right) \\ \frac{i3\sqrt{3}}{28}\left[5\left(z^2-\frac{r^2}{5}\right)(x+iy)+(x-iy)^3\right] \end{vmatrix} e^{-r/r_3}. \qquad (2.6)$$

The numerical results are tabulated in Table III.

For the Γ_7^+ states the trial function is:

$$F = C_{21}\begin{vmatrix} 0 \\ z^2-\frac{1}{2}(x^2+y^2) \\ 0 \\ -\frac{\sqrt{3}}{2}(x^2-y^2) \end{vmatrix} e^{-r/r_2}+C_{22}\begin{vmatrix} iz(x-iy) \\ 0 \\ i\sqrt{3}\,z(x+iy) \\ 2ixy \end{vmatrix} e^{-r/r_2}. \qquad (2.7)$$

The numerical results are tabulated in Table IV.

For the Γ_7^- states the trial function is:

$$F = C_1 \begin{vmatrix} (x+iy) \\ 0 \\ -\sqrt{3}\,(x-iy) \\ 2iz \end{vmatrix} e^{-r/r_1} +$$

$$+C_3 \begin{vmatrix} -\frac{3}{4}\left[(x-iy)^3+(x+iy)\left(z^2-\frac{r^2}{5}\right)\right] \\ \frac{i\sqrt{3}}{2}\left[z(x+iy)^2+z(x-iy)^2\right] \\ -\frac{\sqrt{3}}{4}\left[7(x-iy)\left(z^2-\frac{r^2}{5}\right)-(x+iy)^3\right] \\ -3iz\left(z^2-\frac{3r^2}{5}\right) \end{vmatrix} e^{-r/r_3} \qquad (2.8)$$

The numerical results are tabulated in Table IV.

For the Γ_6^+ states the trial function is:

$$F = C_{21} \begin{vmatrix} z^2-\frac{1}{2}(x^2+y^2) \\ 0 \\ \frac{\sqrt{3}}{2}(x^2-y^2) \\ 0 \end{vmatrix} e^{-r/r_2} + C_{22} \begin{vmatrix} 0 \\ iz(x+iy) \\ -2ixy \\ -\sqrt{3}\,iz(x-iy) \end{vmatrix} e^{-r/r_2} \qquad (2.9)$$

The numerical results are tabulated in Table V.

For the Γ_6^- states the trial function is:

$$F = C_1 \begin{vmatrix} \sqrt{3}\,(x-iy) \\ 2iz \\ (x+iy) \\ 0 \end{vmatrix} e^{-r/r_1} +$$

$$+C_3\begin{vmatrix} -\frac{\sqrt{3}}{4}\left[7\left(z^2-\frac{r^2}{5}\right)(x-iy)-(x+iy)^3\right] \\ 3iz\left(z^2-\frac{3r^2}{5}\right) \\ \frac{3}{4}\left[(x-iy)^3+(x+iy)\left(z^2-\frac{r^2}{5}\right)\right] \\ \frac{i\sqrt{3}}{2}\left[z(x+iy)^2+z(x-iy)^2\right] \end{vmatrix} e^{-r/r_3}. \tag{2.10}$$

The numerical results are tabulated in Table V.

3. *Results and discussion*

InSb:

In order to visualize the role of the H_1 Hamiltonian we performed the calculations twice, first for purely symmetric and purely antisymmetric trial wavefunctions Γ_8^+, Γ_8^-, Γ_7^+, Γ_7^-, Γ_6^+, Γ_6^-, and then for more general trial functions Γ_8, Γ_7, Γ_6, which consist of both symmetrical and antisymmetrical terms. The first calculation is equivalent to the omission of the Hamiltonian H_1.

The results obtained for Γ_6 and Γ_7 type functions are almost the same as for Γ_6^+, Γ_6^-, and Γ_7^+, Γ_7^- type functions. (See Tables II–V). The calculations for Γ_8 type function of the form (2.2.) would be rather elaborate, because of four nonlinear parameters. It can be expected that the admixture of *f*-like terms should not play an essential role for the ground state function which in the case $K = 0$ has Γ_8^+ symmetry. Thus in the calculation of the ground state energy Γ_8 we restricted the number of spherical harmonics in the trial function omiting *f*-like $l = 3$ terms.

The energies of excited levels calculated with the function consisting of *s*, *p*, *d* terms ($E = 1.8$ meV [4]) turned out to be almost the same as for purely *p*-type function ($E = 1.85$ meV [4]) and were higher than energies for excited Γ_8^- levels for the case $K = 0$, see Table III. The functions Γ_8^-, consist of *p* and *f*-like terms and are nearly orthogonal

TABLE VI

Excitation theoretical and experimental energies for InSb

Theory				Experimental [21]	
$K = 0.096$		$K = 0$		Ge	Zn
$\Gamma_8 \to \Gamma_{8,1}$	4.9	$\Gamma_8 \to \Gamma_{8,1}^-$	3.4	6.87	6.72
$\Gamma_8 \to \Gamma_{8,2}$	6.8	$\Gamma_8 \to \Gamma_{8,2}^-$	5.3	7.24	7.09
$\Gamma_8 \to \Gamma_{7,1}$	7.82	$\Gamma_8 \to \Gamma_7^-$	6.32	7.82	7.67
$\Gamma_8 \to \Gamma_{6,1}$	8.60	$\Gamma_8 \to \Gamma_6^+$	7.1	8.23	8.08

to the ground state wave function consisting of *s*, *p*, and *d*-like terms. We can orthogonalize them exactly to the ground state function. One can show that the orthogonalization procedure does not change the mean value of the Hamiltonian by more than 1% [22]. The functions Γ_8^- can be treated as a better approximation for excited levels $\Gamma_{8.1}$ and $\Gamma_{8.2}$ than those consisting of *s*, *p*, and *d* like terms. Comparison of the resulting ground and excitation energies of acceptors with the experimentally determined energies [17, 21] is given in Tables II and VI. It seems that the values calculated for $K \neq 0$ are in better agreement with the experimental results than those obtained for $K = 0$. At present there is still an uncertainty in the assignment of the observed lines to the possible transitions [4].

GaAs and GaSb:

The variational calculations were performed for six acceptor levels with different types of symmetry $\Gamma_8^+, \Gamma_{8.1}^-, \Gamma_{8.2}^-, \Gamma_7^+, \Gamma_7^-, \Gamma_6^+, \Gamma_6^-$ as for InSb $K = 0$. The only experimental data for comparison are the ionization energies of acceptors in GaAs [18, 19] and GaSb [20]. No experimental data about the excited states are available at present. One can see from Table II that the agreement is very good for acceptor ionization energy in GaAs, whereas for GaSb there is a significant discrepancy between the calculated and experimental results.

The author wishes to express his gratitude to Professor M. Suffczyński for suggesting this work and for many valuable discussions and remarks and to Dr J. Blinowski for valuable discussions and suggestions.

REFERENCES

[1] D. Schechter, *J. Phys. Chem. Solids*, **23**, 237 (1962); Ph. D. Thesis Carnegie Institute of Technology 1958.
[2] K. Mendelson, H. M. James, *J. Phys. Chem. Solids*, **25**, 729 (1964).
[3] K. Mendelson, D. R. Schultz, *Phys. Status Solidi*, **31**, 59 (1969).
[4] D. Thanh, *Phys. Status Solidi*, **42**, K65 (1970).
[5] D. Thanh, *Phys. Status Solidi*, **42**, K61 (1970).
[6] M. L. Robinson, *Phys. Rev. Letters*, **17**, 963 (1966).
[7] R. L. Bell, K. T. Rogers, *Phys. Rev.*, **152**, 746 (1966).
[8] J. Blinowski, M. Grynberg, *Phys. Rev.*, **168**, 882 (1968).
[9] C. R. Pidgeon, S. H. Groves, *Proc. Internat. Conf. Phys. Semiconductors*, Moscow 1968, p. 307.
[10] E. O. Kane, *J. Phys. Chem. Solids*, **1**, 249 (1957).
[11] D. M. S. Bagguley, M. L. A. Robinson, R. A. Stradling, *Phys. Letters*, **6**, 143 (1963).
[12] C. R. Pidgeon, R. N. Brown, *Phys. Rev.*, **146**, 575 (1966).
[13] Q. H. F. Vrehen, *J. Phys. Chem. Solids*, **29**, 129 (1968).
[14] R. A. Stradling, *Phys. Letters*, **20**, 217 (1966).
[15] P. S. Kireev, *Fizika Poluprovodnikov*, Izd. Vissa Skola, Moscow 1969, p. 131. (in Russian).
[16] G. Picus, E. Burstein, B. W. Henvis, M. Hass, *J. Phys. Chem. Solids*, **8**, 282 (1959).
[17] R. Sharan, E. L. Heasell, *J. Phys. Chem. Solids*, **31**, 541 (1970).
[18] M. A. Gilleo, P. T. Bailey, D. E. Hill, *Phys. Rev.*, **174**, 898 (1968).
[19] S. M. Sze, J. C. Irvin, *Solid State Electronics*, **11**, 599 (1968).
[20] E. J. Johnson, H. Y. Fan, *Phys. Rev.*, **139**, A 1991 (1965).
[21] V. N. Murzin, A. I. Demeshina, L. M. Umarov, *Fiz. Tekh. Poluprov.*, **3**, 434 (1969).
[22] D. Thanh, Ph. D. Thesis, Warsaw University 1971.