

Energy Levels of Indirect Excitons in Semiconductors with Degenerate Bands*

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A method previously introduced for direct excitons is extended to investigate indirect excitons in semiconductors with degenerate bands. Even though this method can be applied in the case of a general position in k space of the conduction-band minima, the present investigation is limited to the most common directions $(1, 0, 0)$ and $(1, 1, 1)$. A splitting of the exciton levels, which is shown to be due to the anisotropy of the conduction-band minima and which is predicted by group-theoretical analysis, is quantitatively given by a simple analytical expression. The symmetry of the phonons which assist indirect optical transitions is also given. Results for the $1s$ and $2s$ exciton states in AlSb, GaP, Si, and Ge are presented. The method is very accurate and agrees well with available experimental data for the first three substances. For Ge its accuracy is not so good, because of the strong anisotropy in the conduction-band minima, but it is expected to be within 10%.

I. INTRODUCTION

All semiconductors with the diamond and zinc-blende structure have a degenerate valence-band maximum at $\vec{k}=0$. The absolute minimum of the conduction band is generally at the same point of the first Brillouin zone. In some cases, however, such a minimum is at $\vec{k}\neq 0$ and its location depends on the particular substance under consideration. For Ge,¹ the minimum is at the point $L\equiv\pi/a(1, 1, 1)$, and for Si,² it is along the axis $\Delta\equiv(k, 0, 0)$. Zinc-blende III-V compounds, such as AlP,³ AlSb,⁴ AlAs,³ and GaP,⁵ have an indirect gap, too. For these substances, theoretical band structures as well as experiments suggest that the conduction-band minimum is at the point $X\equiv 2\pi/a(1, 0, 0)$.

These differences in the band structure lead to different optical properties. For direct-gap materials, the fundamental optical edge exhibits structure due to direct exciton formation. If the conduction-band minimum is at $\vec{k}\neq 0$, additional structure due to indirect excitons appears at lower energies.

The ground-state energies of direct and indirect excitons in Si and Ge have been previously investigated by McLean and Loudon⁶ using a variational technique. We have recently presented a simple method⁷ to investigate exciton spectra in crystals with degenerate bands and arbitrary symmetry. This method has been applied in a previous paper⁸ to investigate direct excitons in semiconductors with the diamond and zinc-blende structure.

In the present paper we show that this method can be applied to investigate indirect excitons, too. Analytical expressions for the binding energies of the ground state and the first excited state are obtained.

In Sec. II, using group theory, we classify the

exciton states and determine the phonons which assist indirect optical transitions. In Sec. III, we apply our method to the energy spectra of indirect excitons. Even though the method could be applied in the case of a general position of the conduction-band minima, we shall restrict ourselves to the most common directions $(1, 0, 0)$ and $(1, 1, 1)$. In Sec. IV, we give numerical results for those crystals for which band parameters are known. The results are then compared with available experimental data. In Sec. V, we summarize the main results of the present investigation.

II. GROUP-THEORETICAL ANALYSIS

Before considering the symmetry of the electron-hole system, we briefly summarize some well-known results for the one-electron states in the diamond and zinc-blende structure.

For diamond crystals, the point group is⁹ O_h and the symmetry of the degenerate valence band at $\vec{k}=0$ is Γ_8^+ . The symmetry of the conduction-band minimum is L_1 in Ge and Δ_1 in Si, when spin is neglected. For III-V compounds, the point group is T_d , the valence-band maximum has Γ_8 symmetry, and the conduction-band minimum has X_1 symmetry.¹⁰

The exciton Hamiltonian is¹¹

$$H_{e\mathbf{x}} = H_e(\vec{p}_e) - H_h(\vec{p}_h) - e^2/\epsilon |\vec{r}_e - \vec{r}_h|, \quad (1)$$

where ϵ is the static dielectric constant, the subscripts e and h refer to the electron and the hole, respectively, H_e is the kinetic energy of the electron near the conduction-band minimum, and H_h is the well-known¹² 6×6 matrix which describes the hole kinetic energy near $\vec{k}=0$. From Hamiltonian (1) it is clear that the symmetry group for the exciton is the intersection of the symmetry group for the electron and that for the hole. For indirect excitons,

the symmetry group of the electron is a subgroup of that of the hole, so that the required intersection is just the electron symmetry group itself.

The exciton wave function can be written as¹³

$$\psi(\vec{r}_e, \vec{r}_h) = \sum_i \chi^{(i)}(\vec{r}_e - \vec{r}_h) \phi_h^{(i)}(\vec{r}_h) \phi_e(\vec{r}_e), \quad (2)$$

where ϕ_e and ϕ_h are the Bloch functions for the electron and the hole, $\chi^{(i)}$ is the envelope function which describes the relative electron-hole motion, and i runs over the degenerate valence-band states. The symmetry of the exciton wave function ψ is determined by the direct product of the representations for the envelope, hole, and electron functions. Since our analysis is limited to 1s and 2s exciton states, the envelope representation can be dropped from the direct product. The resulting symmetry of the exciton wave function is

$$\Gamma_8 \otimes X_1 = (X_6 \oplus X_7) \otimes X_1 = X_6 \oplus X_7 \quad (3)$$

for the III-V compounds,

$$\Gamma_8^+ \otimes \Delta_1 = (\Delta_6 \oplus \Delta_7) \otimes \Delta_1 = \Delta_6 \oplus \Delta_7 \quad (4)$$

for Si, and

$$\Gamma_8^+ \otimes L_1 = (L_4^+ \oplus L_5^+ \oplus L_6^+) \otimes L_1 = L_4^+ \oplus L_5^+ \oplus L_6^+ \quad (5)$$

for Ge.

The compatibility relations have been used in going from the symmetry group of the hole to that of the exciton. Furthermore, we have considered only the exciton states originating from the upper four-fold-degenerate valence band. Since the representations L_4^+ and L_5^+ , used for Ge, are degenerate for

time reversal, we see that, apart from accidental degeneracy, the exciton states always split into a doublet of twofold-degenerate levels.

Optical transitions, from the crystal ground state to the above exciton states, must be assisted by phonons in order to conserve the total momentum. Such phonons have a well-defined symmetry which can be determined from the direct product of the irreducible representations of the exciton and the phonon. Following the procedure used for one-electron indirect interband transitions¹⁴ and including the electron spin, we obtain the result that phonons with any symmetry can assist optical transitions to both exciton states for III-V compounds and Si. For Ge, only TO (L_3^+) and LA (L_2^+) phonons are allowed.

III. METHOD OF SOLUTION

The total motion of the electron-hole system is described by Hamiltonian (1). Following Dresselhaus,¹¹ we separate the relative electron-hole motion which is described by the following Hamiltonian:

$$H_{ex} = H_e(\vec{p}) - H_h(\vec{p}) - e^2/\epsilon r, \quad (6)$$

where \vec{r} and \vec{p} are the relative electron-hole coordinate and momentum, and the operators H_e and H_h are the same ones that appear in (1).

For the zinc-blende case we neglect linear terms in \vec{p} , which have been found to be extremely small.⁸ Under this assumption, the explicit expression of H_h is¹²

$$H_h = \begin{pmatrix} -P_h - Q & -L & -M & 0 & (-i/\sqrt{2})L & i\sqrt{2}M \\ -L^* & -P_h + Q & 0 & -M & i\sqrt{2}Q & (-i\sqrt{3}/\sqrt{2})L \\ -M^* & 0 & -P_h + Q & L & (i\sqrt{3}/\sqrt{2})L^* & i\sqrt{2}Q \\ 0 & -M^* & L^* & -P_h - Q & i\sqrt{2}M^* & (i/\sqrt{2})L^* \\ (i/\sqrt{2})L^* & -i\sqrt{2}Q & (-i\sqrt{3}/\sqrt{2})L & -i\sqrt{2}M & -P_h - \Delta & 0 \\ -i\sqrt{2}M^* & (i\sqrt{3}/\sqrt{2})L^* & -i\sqrt{2}Q & (-i/\sqrt{2})L & 0 & -P_h - \Delta \end{pmatrix}, \quad (7)$$

where Δ is the spin-orbit splitting of the valence band and

$$P_h = \frac{p_x^2 + p_y^2 + p_z^2}{2\mu_{0h}} \quad (s\text{-like}), \quad (8a)$$

$$Q = \frac{p_x^2 + p_y^2 - 2p_z^2}{2\mu_{1h}} \quad (d\text{-like}), \quad (8b)$$

$$L = -i \frac{(p_x - ip_y)p_z}{2\mu_{2h}} \quad (d\text{-like}), \quad (8c)$$

$$M = \sqrt{3} \frac{p_x^2 - p_y^2}{2\mu_{1h}} - i \frac{p_x p_y}{2\mu_{2h}} \quad (d\text{-like}). \quad (8d)$$

The valence-band masses μ_{0h} , μ_{1h} , and μ_{2h} are related to the Luttinger parameters¹⁵ γ_1 , γ_2 , and γ_3 and to the Dresselhaus-Kip-Kittel parameters¹⁶ A , B , and C as follows:

$$1/\mu_{0h} = \gamma_1/m_0 = -(2/\hbar^2)A, \quad (9a)$$

$$1/\mu_{1h} = \gamma_2/m_0 = -(1/\hbar^2)B, \quad (9b)$$

$$1/\mu_{2h} = 2\sqrt{3} \gamma_3/m_0 = (2/\hbar^2)(C^2 + 3B^2)^{1/2}, \quad (9c)$$

m_0 being the free-electron mass.

The explicit expression for the operator H_e depends on the position of the conduction-band minima. Since these minima generally occur on high-

symmetry directions for which the electron has cylindrical symmetry, we can write

$$H_e = \frac{p_1^2 + p_2^2}{2m_{e\perp}} + \frac{p_3^2}{2m_{e\parallel}}, \quad (10)$$

where $m_{e\perp}$ and $m_{e\parallel}$ are the transverse and longitudinal electron masses, respectively. The operator (10) is written with respect to the electron ellipsoidal axes 1, 2, and 3 which are, in general, different from the crystal cubic axes x , y , and z used for the hole. Since the operators H_e and H_h in (6) must be written in the same coordinate system, and since the expression of H_e is much simpler, we shall express the electron kinetic energy in the hole coordinate system.

We shall restrict ourselves to the cases in which the conduction-band minima lie on the most common

directions (0, 0, 1) and (1, 1, 1), and we consider the two cases separately.

A. (0,0,1) Direction

In this case the electron ellipsoidal axes are the cubic axes of the crystal and expression (10) can be written

$$H_e = \frac{p_x^2 + p_y^2 + p_z^2}{2\mu_{0e}} + \frac{p_x^2 + p_y^2 - 2p_z^2}{2\mu_{1e}}, \quad (11)$$

where

$$1/\mu_{0e} = \frac{1}{3}(2/m_{e\perp} + 1/m_{e\parallel}), \quad (12a)$$

$$1/\mu_{1e} = \frac{1}{3}(1/m_{e\perp} - 1/m_{e\parallel}). \quad (12b)$$

Using the operators (7) and (11), the exciton Hamiltonian (6) can be explicitly written as

$$H_{\text{ex}} = \begin{vmatrix} P+Q_+ & L & M & 0 & (i/\sqrt{2})L & -i\sqrt{2}M \\ L^* & P+Q_- & 0 & M & -i\sqrt{2}Q & (i\sqrt{3}/\sqrt{2})L \\ M^* & 0 & P+Q_- & -L & (-i\sqrt{3}/\sqrt{2})L^* & -i\sqrt{2}Q \\ 0 & M^* & -L^* & P+Q_+ & -i\sqrt{2}M^* & (-i/\sqrt{2})L^* \\ (-i/\sqrt{2})L^* & i\sqrt{2}Q & (i\sqrt{3}/\sqrt{2})L & i\sqrt{2}M & P+Q_e - \Delta & 0 \\ i\sqrt{2}M^* & (-i\sqrt{3}/\sqrt{2})L^* & i\sqrt{2}Q & (i/\sqrt{2})L & 0 & P+Q_e - \Delta \end{vmatrix}, \quad (13)$$

where Q , L , and M are defined by (8b) – (8d), and

$$P = \frac{p_x^2 + p_y^2 + p_z^2}{2\mu_0} - \frac{e^2}{\epsilon r} \quad (s\text{-like}), \quad (14a)$$

$$Q_{\pm} = \frac{p_x^2 + p_y^2 - 2p_z^2}{2\mu_{1\pm}} \quad (d\text{-like}), \quad (14b)$$

$$Q_e = \frac{p_x^2 + p_y^2 - 2p_z^2}{2\mu_{1e}} \quad (d\text{-like}), \quad (14c)$$

with

$$1/\mu_0 = 1/\mu_{0e} + 1/\mu_{0h}, \quad (15a)$$

$$1/\mu_{1\pm} = 1/\mu_{1e} \pm 1/\mu_{1h}. \quad (15b)$$

Hamiltonian (13) is similar to that which describes direct excitons⁸ and therefore we closely follow the procedure that we previously used in that case. Under the operations of the rotation group, the operators which appear in (13) have different symmetry properties which are indicated along with their definition. Accordingly, we write (13) as follows:

$$H_{\text{ex}} = H_s + H_d, \quad (16)$$

where H_s and H_d are 6×6 matrices which contain only s -like and d -like operators, respectively. In (16) we consider H_d as a perturbation on the unperturbed

Hamiltonian H_s .

Exact eigenfunctions and eigenvalues of H_s are easily found because the s -like operator P represents an hydrogen atom with reduced mass μ_0 and dielectric constant ϵ . Restricting ourselves to the exciton states originating from the upper fourfold-degenerate valence band, we find that the unperturbed spectrum consists of four degenerate hydrogenic series with the effective rydberg

$$R_0 = \mu_0 e^4 / 2\hbar^2 \epsilon^2. \quad (17)$$

We now include H_d as a perturbation and consider only $1s$ and $2s$ exciton states. Owing to the fourfold degeneracy of the above states, degenerate perturbation theory must be used. It turns out that the secular determinant is diagonal and, after straightforward calculations, we obtain for the perturbed energies

$$E_{1s}(X_6, \Delta_6) = -R_0 [1 + \frac{4}{5}\Phi_- S_1(0) + \frac{4}{5}\Phi_{\Delta} S_1(\bar{\Delta})], \quad (18a)$$

$$E_{1s}(X_7, \Delta_7) = -R_0 [1 + \frac{4}{5}\Phi_+ S_1(0) + \frac{4}{5}\Phi_{\Delta} S_1(\bar{\Delta})], \quad (18b)$$

$$E_{2s}(X_6, \Delta_6) = -\frac{1}{4}R_0 [1 + \frac{2}{5}\Phi_- S_2(0) + \frac{2}{5}\Phi_{\Delta} S_2(\bar{\Delta})], \quad (18c)$$

$$E_{2s}(X_7, \Delta_7) = -\frac{1}{4}R_0 [1 + \frac{2}{5}\Phi_+ S_2(0) + \frac{2}{5}\Phi_{\Delta} S_2(\bar{\Delta})], \quad (18d)$$

where the coupling parameters Φ_{\pm} and Φ_{Δ} are given by

$$\Phi_{\pm} = \left(\frac{\mu_0}{\mu_{2h}}\right)^2 + 4\left(\frac{\mu_0}{\mu_{1h}}\right)^2 + 4\left(\frac{\mu_0}{\mu_{1e}}\right)^2, \quad (19a)$$

$$\Phi_{\Delta} = 8\left(\frac{\mu_0}{\mu_{1h}}\right)^2 + \left(\frac{\mu_0}{\mu_{2h}}\right)^2. \quad (19b)$$

$\bar{\Delta}$ is the spin-orbit splitting in units of the effective rydberg R_0 , and the functions $S_1(x)$ and $S_2(x)$ have been defined and computed in Ref. 8. In the square brackets of expressions (18a)–(18d), the different contributions to the binding energies are given explicitly. The first term is the unperturbed binding energy, the second represents the interaction with excited states of the main series, and the last term is the contribution from the split-off valence states.

As shown in formulas (18), the perturbation removes the fourfold degeneracy of both the 1s and 2s exciton states and each state is split into a doublet of twofold-degenerate levels whose symmetry at X and Δ is shown on the left-hand side. This splitting, which was predicted by group theory in Sec. II, is evident from Hamiltonian (13). In fact, the diagonal terms in (13) show that heavy and light holes are bound to the electron in a different way. This is a direct consequence of the electron mass anisotropy. In effect, in the case of isotropic electron mass, as is the case for direct excitons, heavy and light holes behave identically and no splitting is obtained.

B. (1,1,1) Direction

In this case the electron ellipsoid axes 1, 2, and 3 must be rotated to coincide with the cubic axes of the crystal. After such a rotation, expression (10) becomes

$$H_e = \frac{p_x^2 + p_y^2 + p_z^2}{2\mu_{0e}} - \frac{p_x p_y}{\mu_{1e}} + \frac{(i-1)(p_x + ip_y)p_z - (i+1)(p_x - ip_y)p_z}{2\mu_{1e}}, \quad (20)$$

where μ_{0e} and μ_{1e} are still defined by (12a) and (12b). Using expressions (7) and (20), we obtain the expression for the exciton Hamiltonian which is similar to (13) and will not be given here. Following closely the procedure used for the (0, 0, 1) direction, we can still write the exciton Hamiltonian as in (16) with identical H_s and similar H_d . The main difference is that, in treating H_d with degenerate perturbation theory, the resulting secular determinant is not diagonal and, for the 1s state, is given by

$$\begin{vmatrix} A & B & C & 0 \\ B^* & A & 0 & C \\ C^* & 0 & A & -B \\ 0 & C^* & -B^* & A \end{vmatrix}, \quad (21)$$

where

$$A = -\left[\frac{32}{5}\left(\frac{\mu_0}{\mu_{1h}}\right)^2 + \frac{16}{5}\left(\frac{\mu_0}{\mu_{1e}}\right)^2 + \frac{4}{5}\left(\frac{\mu_0}{\mu_{2h}}\right)^2\right]S_1(0) - \left[\frac{32}{5}\left(\frac{\mu_0}{\mu_{1h}}\right)^2 + \frac{4}{5}\left(\frac{\mu_0}{\mu_{2h}}\right)^2\right]S_1(\bar{\Delta}), \quad (22a)$$

$$|B|^2 = \frac{512}{225}\left(\frac{\mu_0}{\mu_{1e}}\right)^2\left(\frac{\mu_0}{\mu_{2h}}\right)^2 S_1^2(0), \quad (22b)$$

$$|C|^2 = \frac{256}{225}\left(\frac{\mu_0}{\mu_{1e}}\right)^2\left(\frac{\mu_0}{\mu_{2h}}\right)^2 S_1^2(0), \quad (22c)$$

and all masses have the same definition as for the (0, 0, 1) direction. The determinant (21) can be diagonalized exactly and we obtain for the perturbed 1s energies

$$E_{1s}(L_4^+ + L_5^+) = -R_0\left[1 + \frac{4}{5}\Phi_+ S_1(0) + \frac{4}{5}\Phi_{\Delta} S_1(\bar{\Delta})\right], \quad (23a)$$

$$E_{1s}(L_6^+) = -R_0\left[1 + \frac{4}{5}\Phi_- S_1(0) + \frac{4}{5}\Phi_{\Delta} S_1(\bar{\Delta})\right], \quad (23b)$$

where

$$\Phi_{\pm} = 8\left(\frac{\mu_0}{\mu_{1h}}\right)^2 + 4\left(\frac{\mu_0}{\mu_{1e}}\right)^2 + \left(\frac{\mu_0}{\mu_{2h}}\right)^2 \pm \frac{4\sqrt{3}}{3} \frac{\mu_0^2}{\mu_{1e}\mu_{1h}} \quad (24)$$

and Φ_{Δ} is still given by expression (19b). In exactly the same way, we obtain for the perturbed 2s energies

$$E_{2s}(L_4^+ + L_5^+) = -\frac{1}{4}R_0\left[1 + \frac{2}{5}\Phi_+ S_2(0) + \frac{2}{5}\Phi_{\Delta} S_2(\bar{\Delta})\right], \quad (25a)$$

$$E_{2s}(L_6^+) = -\frac{1}{4}R_0\left[1 + \frac{2}{5}\Phi_- S_2(0) + \frac{2}{5}\Phi_{\Delta} S_2(\bar{\Delta})\right]. \quad (25b)$$

In this case, too, the numerical calculation gives the splitting predicted by group theory and which is due to the same reason as for the (0, 0, 1) case.

IV. RESULTS AND DISCUSSION

We now apply the results of Sec. III to investigate the indirect exciton spectra in diamond and zinc-blende crystals for which band parameters are available. They are the III-V compounds AlSb and GaP and the group-IV elements Si and Ge.

In Table I we give the parameters used for the calculation and in Table II the results of our investigation together with the available experimental data.

In the case of direct excitons, we obtained the result that the perturbation treatment is valid whenever the coupling parameter Φ is sufficiently small ($\Phi < 1$). In the present case this condition must be verified by the various Φ 's which describe the different couplings. This condition is generally verified for all substances shown in Table II, excluding the L_4^+ and L_5^+ exciton states in Ge. Therefore our results are expected to be generally accurate, with the exception of Ge, where, however, a good estimate of the binding energy can be obtained since the Φ values are only slightly greater than 1.

To show the validity of our perturbation treat-

TABLE I. Parameters used in the calculation: static dielectric constant ϵ_0 , longitudinal and transverse electron effective masses $m_{e\parallel}$ and $m_{e\perp}$, Dresselhaus-Kip-Kittel (Ref. 16) valence-band parameters A , B , and C^2 , and spin-orbit splitting Δ . The energy unit is meV and m_0 is the free-electron mass.

Crystal	ϵ_0	$m_{e\parallel}/m_0$	$m_{e\perp}/m_0$	A	B	C^2	Δ
AlSb	9.9 ^a	1.5 ^b	0.214 ^b	-5.38 ^c	-1.09 ^c	20.9 ^c	750 ^e
				-4.8 ^d	-4.0 ^d	-5.0 ^d	
				-5.26 ^f	-2.75 ^f	32.8 ^f	
GaP	11.1 ^g	1.7 ^h	0.191 ^h	-5.61 ^c	0.11 ^c	13.6 ^c	90 ⁱ
				-4.7 ^d	-2.6 ^d	9.0 ^d	
				-3.83 ^f	-1.72 ^f	17.6 ^f	
Si	11.4 ^j	0.9163 ^k	0.1905 ^k	-4.25 ^l	-0.7 ^l	21.72 ^l	44 ^d
				-5.2 ^d	-1.7 ^d	20.0 ^d	
				-4.23 ^f	-0.77 ^f	23.1 ^f	
Ge	15.36 ^j	1.588 ^m	0.08152 ^m	-13.38 ⁿ	-8.6 ⁿ	165.27 ⁿ	290 ^d
				-12.1 ^d	-8.0 ^d	96.0 ^d	
				-13.23 ^f	-8.54 ^f	159.3 ^f	

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ⁿFrom Ref. 21.

ment and, at the same time, to show the importance of the corrections to the unperturbed energy levels, in Table II we give the different contributions to the binding energy $E_b(1s)$ of the 1s exciton doublet. R_0 is the unperturbed binding energy; E_d represents the correction which is due to the electron anisotropy and to the interaction among the various states of the upper fourfold valence band; and E_{so} is the contribution from the split-off valence band and is always smaller than E_d because of larger energy denominators in its perturbation series. The E_d contribution is small enough to support the validity of the perturbation treatment, and it is sufficiently large to be experimentally appreciated.

From the binding energy $E_b(2s)$ of the 2s exciton doublet, which is also given in Table II, it is evident that the Rydberg law is not valid. In particular, the binding energy $E_b(2s)$ is always greater than that predicted by this law. As a consequence the exciton binding energy as obtained from the experimental data by simply multiplying the 1s-2s peak separation by $\frac{4}{3}$ is incorrect.

The indirect exciton spectrum in Si and Ge has been previously investigated by McLean and Loudon⁶ using a variational technique. To establish the accuracy of our method, we have investigated the same exciton spectra using the same parameters. For the binding energies of the 1s doublet in Si we obtain 13.3 and 12.8 meV assuming an in-

finite spin-orbit splitting. The corresponding results obtained by McLean and Loudon are 13.0 and 12.4 meV. For the same states in Ge, we obtain 3.16 and 2.84 meV, which have to be compared with the McLean-Loudon results 3.47 and 2.88 meV. From this comparison we see that for Si and for the L_6^+ level in Ge the two methods have the same accuracy. In all these cases the value of the coupling parameters Φ_{\pm} is less than 1. For the $L_4^+ + L_5^+$ level in Ge, where $\Phi_{\pm} = 1.6$, our method is less accurate and gives only a good estimate of the binding energy.

The best experimentally studied indirect exciton spectra are those in Si and Ge. Since the first observation by Macfarlane *et al.*²² and by Zwerdling *et al.*,²³ these indirect spectra have been widely investigated.²⁴ In Ge it was possible to observe the splitting of the 1s exciton state. This splitting has not yet been observed in Si, where 1s and 2s exciton states have been resolved.

For Si, Shaklee and Nahory²⁵ give a 1s-2s energy separation of 10.7 meV for TA phonon-assisted transitions and a separation of 11.0 meV for LO and TO transitions. Our investigation predicts a 1s-2s energy separation of 10.57 and 10.73 meV when Δ_7 and Δ_6 exciton states are considered, respectively. Since for this substance the spin-orbit splitting is comparable to the exciton binding energy ($\bar{\Delta} \approx 3.5$), one expects large corrections from the

interaction with the split-off valence band. From Table II we see that the corrections E_{so} , even though larger for Si than for the other substances considered, represent only a few percent of the total binding energy. This result is analogous to that found in the case of direct excitons and is due to the fact that the interaction with the split-off valence band depends not only on $\bar{\Delta}$ (the spin-orbit splitting in units of the effective rydberg R_0), but also on the coupling parameter Φ_{Δ} which is generally small. The dependence of the binding energies on $\bar{\Delta}$ is shown in Fig. 1 for the case of Si. The electron effective masses and the dielectric constant used in the calculation are those of Table I and the valence-band parameters are those given by Owner-Petersen and Samuelsen.²⁰ The figure shows a weak dependence of the binding energies on the spin-orbit splitting, and furthermore shows that, in the present approximation, the splitting of the 1s states and that of the 2s states do not depend on $\bar{\Delta}$.

For Ge the agreement between theory and experiment is not as good as in the previous case. The experimental splitting for the 1s state is²⁶ 0.8 meV, whereas our calculation gives 0.36 meV. The reason for this discrepancy is the poor accuracy of our

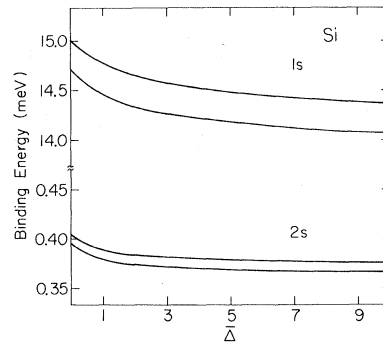


FIG. 1. Binding energies of the 1s and 2s indirect exciton states in Si versus the spin-orbit splitting in units of the effective rydberg R_0 . The valence-band parameters used in the calculation are taken from Ref. 21. The dielectric constant and the electron effective masses are those given in Table I.

results for the $L_4^+ + L_5^+$ exciton level. The poor agreement for the absolute value of the binding energy of the 1s doublet can be due to the parameters used in the calculation, but more probably is due to a not very accurate experimental determination.

A detailed investigation of indirect-gap III-V

TABLE II. Indirect exciton energy levels in group-IV elements and III-V compounds. All the quantities are defined in the text. The last column gives the reference for the valence-band parameters used in the calculation. The blanks mean lacking experimental results. The energy unit is meV.

Crystal	Symmetry	μ_0	R_0	Φ	Φ_{Δ}	E_d	E_{so}	$E_b(1s)$ theor	$E_b(1s)$ expt	$E_b(2s)$	Ref.
AlSb	$X_7(\Delta_5)$	0.115	15.92	0.370	0.353	1.06	0.08	17.06		4.41	17
		0.123	17.06	0.918	1.133	2.81	0.29	20.16		5.42	18
		0.116	16.15	0.853	0.955	2.47	0.22	18.84		5.04	19
	$X_6(\Delta_5)$	0.115	15.92	0.524	0.353	1.50	0.08	17.50		4.58	17
		0.123	17.06	1.563	1.133	4.79	0.29	22.14		6.19	18
		0.116	16.15	1.251	0.955	3.63	0.22	20.00		5.50	19
GaP	$X_7(\Delta_5)$	0.108	11.88	0.277	0.158	0.59	0.10	12.57		3.22	17
		0.119	13.17	0.516	0.609	1.22	0.44	14.83	10 ^a	3.86	18
		0.133	14.69	0.555	0.573	1.46	0.50	16.65		4.35	19
	$X_6(\Delta_5)$	0.108	11.88	0.261	0.158	0.55	0.10	12.53		3.21	17
		0.119	13.17	0.974	0.609	2.30	0.44	15.91		4.29	18
		0.133	14.69	0.932	0.573	2.46	0.50	17.65		4.74	19
Si	Δ_7	0.123	12.90	0.425	0.367	0.99	0.37	14.26		3.69	20
		0.110	11.55	0.398	0.419	0.83	0.36	12.74	14.7 ^b	3.29	18
		0.124	12.93	0.450	0.380	1.05	0.40	14.38		3.73	19
Ge	L_6^+	0.123	12.90	0.543	0.367	1.26	0.37	14.53		3.80	20
		0.110	11.55	0.628	0.419	1.30	0.36	13.21	14.7 ^b	3.48	18
		0.124	12.93	0.580	0.380	1.35	0.40	14.68		3.85	19
$L_4^+ + L_5^+$	L_6^+	0.046	2.65	0.884	1.129	0.42	0.02	3.09		0.83	21
		0.049	2.81	0.772	0.991	0.39	0.02	3.22	2.1 ^c	0.86	18
		0.046	2.67	0.877	1.121	0.42	0.02	3.11		0.83	19
	$L_4^+ + L_5^+$	0.046	2.65	1.628	1.129	0.78	0.02	3.45		0.97	21
		0.049	2.81	1.497	0.991	0.76	0.02	3.59	2.9 ^c	1.00	18
		0.046	2.67	1.623	1.121	0.78	0.02	3.47		0.97	19

^aFrom Ref. 27.

^bFrom Ref. 25.

^cFrom Ref. 26.

compounds is not possible since the present knowledge of these substances is insufficient. For AlAs and AlP,³ evidence of indirect exciton structure has been found in experimental results; in these cases, however, we cannot carry out any calculation because the necessary parameters are not yet available. Our theoretical predictions for AlSb cannot be tested because, to our knowledge, experimental results are not available. For GaP, the experimental binding energy²⁷ 10.0 meV is in fair agreement with our results.

In the present treatment we have omitted the exchange coupling between the electron and the hole, which would give rise to an additional splitting of the exciton states. The effects of this coupling have been explicitly considered by Abe²⁸ and, for the case of indirect excitons, shown to be very small in agreement with the available experimental data, which do not show any effect due to the exchange interaction.

V. CONCLUSIONS

The method previously used to investigate direct

exciton spectra in the case of degenerate bands has been shown to be generally valid for indirect excitons, too.

We have also shown that these spectra cannot be approximated by a simple Rydberg law, as is usually done in the interpretation of the experimental data. The corrections to the Rydberg law have been calculated for the 1s and 2s states taking into account the contribution of the split-off valence band. These corrections are more important than those obtained in the case of direct excitons, and should be experimentally appreciated.

The splitting of the exciton levels, which is predicted by group theory, has been numerically evaluated and shown to be due to the electron anisotropy.

The accuracy of the present method is as good as that of the variational method, for the ground state. In addition, our method can be easily applied to excited states and gives simple analytical expressions for the energy levels.

The agreement with experiment is satisfactory for those substances which have been experimentally studied.

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