

Theory of Excitons Bound to Ionized Impurities in Semiconductors*

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The quantum-mechanical variational theorem is used to study the conditions under which an exciton can be bound to a Coulomb center in a semiconductor. The model used is that in which the electron and the hole constituting the exciton can be regarded as charged particles with effective masses m_e and m_h , respectively. It is shown that an exciton is bound to a singly ionized donor if $m_e < 0.2m_h$ and to a singly ionized acceptor if $m_e < 0.25m_h$. Estimates are given of the binding energy of the exciton-impurity complexes, and they are discussed in relation to experimental observations in semiconductors such as GaSb.

I. INTRODUCTION

EXCITONS bound to imperfections (or exciton-impurity complexes) in solids have been investigated theoretically and experimentally by several authors.¹⁻⁴ Hopfield² has considered several types of bound excitons including the case of an exciton in the presence of the Coulomb field of an ionized donor. This author treats the exciton within the framework of the effective mass approximation, i.e., as two oppositely charged particles, an electron and a hole, moving under the influence of their mutual Coulomb attraction. The electron and the hole are supposed to have spherical bands with effective masses m_e and m_h , respectively. Within this approximation a free exciton has a hydrogen-like excitation spectrum with its ground state lying at an energy $\mu e^4/2\hbar^2K^2$ below the edge of the conduction band of the semiconductor. Here $\mu = m_e m_h / (m_e + m_h)$ is the reduced mass of the exciton and K the dielectric constant of the host crystal. We shall also make use of this model in this paper.

The present work is concerned only with excitons bound to singly charged point defects in semiconductors. It is important to realize that an exciton can be effectively bound to a singly ionized donor only if the binding energy of the system composed of the exciton plus the ionized donor exceeds the binding energy E_D of the neutral donor. If this were not the case, then the exciton-donor complex would decay into a neutral donor and a free hole. In the same manner, the exciton-donor complex has a physical meaning only if its binding energy is larger than that of the free exciton E_e . We need not, however, concern ourselves with this comparison since $E_D > E_e$.

In Ref. 3, the binding energy of an exciton bound to

a singly ionized donor is computed within the approximation $m_e < m_h$ using Teller's solution⁵ for the wave functions and effective potential of the hydrogen molecular ion H_2^+ . The conclusion which follows from this analysis is that an exciton can be bound to an ionized donor if $(m_h/m_e) > 1.4$. It must be remarked, however, that the numerical value 1.4 is only an estimate of the limiting ratio m_h/m_e below which binding ceases to occur. Similarly, an exciton can be bound to a singly ionized acceptor if $(m_e/m_h) > 1.4$. In many semiconductors, particularly in those considered later on in this paper, $m_e < m_h$ so that if the condition $(m_e/m_h) > 1.4$ were the only one under which binding could occur, then one would not expect exciton-acceptor complexes to exist in these materials. However, the optical measurements of Johnson and Fan⁶ in GaSb (where $m_e/m_h = 0.23$) can be interpreted in a simple way assuming the existence of these exciton complexes. It is the purpose of the present work to investigate whether excitons can be stably bound to Coulomb centers in this and similar substances.

In Sec. II a study is given of the ground state of an exciton in the field of a singly ionized donor. The present calculation differs from that given by Hopfield in that we have constructed a variational wave function for the total system. In this way the dynamical effects associated with the finite effective mass of the hole, which were neglected in Ref. 3, are taken into account. We find that the exciton-donor complex exists if $(m_e/m_h) < 0.20$ so that in this region the present analysis yields results in considerable agreement with Hopfield's work. We can immediately state that the exciton-acceptor complex exists if $(m_h/m_e) < 0.20$. It would be incorrect, however, to infer that, because an ionized acceptor is able to bind an exciton when $m_e > 5m_h$, this is the only region in which this binding occurs. We have, in fact, demonstrated that exciton-acceptor complexes can exist if $(m_e/m_h) < 0.25$. This proof is given in Sec. III together with an estimate of the binding energy as a function of the parameter m_e/m_h . We have separated the consideration of these two cases in this fashion for convenience of presentation and to keep our ideas fixed on semiconductors having $m_e < m_h$. Of course, from

* Supported in part by the Advanced Research Projects Agency and the U. S. Army Research Office (Durham).

¹ M. A. Lampert, *Phys. Rev. Letters* **1**, 450 (1958).

² D. G. Thomas and J. J. Hopfield, *Phys. Rev.* **128**, 2135 (1962). See also C. Delbecq, P. Pringsheim, and P. Yuster, *J. Chem. Phys.* **19**, 574 (1951).

³ J. J. Hopfield, in *Proceedings of the Seventh International Conference on the Physics of Semiconductors, Paris, 1964* (Dunod Cie, Paris, 1964), p. 725.

⁴ T. C. Collins, C. W. Litton, and D. C. Reynolds, in *Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964* (Academic Press Inc., New York, 1965), p. 745. See also D. C. Reynolds, C. W. Litton, and T. C. Collins, *Phys. Status Solidi* **12**, 3 (1965).

⁵ E. Teller, *Z. Physik* **61**, 458 (1930).

⁶ E. J. Johnson and H. Y. Fan, *Phys. Rev.* **139**, A1991 (1965).

a purely formal point of view, this distinction is unnecessary. Finally Sec. IV contains a discussion of some experimental results in relation to the theoretical calculations presented in the preceding sections.

II. EXCITON BOUND TO AN IONIZED DONOR

We consider, as stated in the introduction, a simple model of an exciton formed by an electron and a hole at the edges of their respective bands. We now study the nature of the ground state of the exciton in the Coulomb field of a singly ionized donor making use of the quantum-mechanical variational theorem. The starting point is the Hamiltonian operator

$$H = -\frac{\hbar^2}{2m_h}\nabla_h^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 + \frac{e^2}{Kr_h} - \frac{e^2}{Kr_e} - \frac{e^2}{K|\mathbf{r}_e - \mathbf{r}_h|}. \quad (1)$$

In this equation, \mathbf{r}_e and \mathbf{r}_h are the position vectors of the electron and the hole, respectively, taking the origin at the nucleus of the singly ionized donor, and ∇_h^2 and ∇_e^2 are the Laplacian operators with respect to the hole and electron coordinates, respectively. The purpose of the subsequent development is to estimate the binding energy of this system, i.e., the energy required to remove the electron and the hole an infinite distance from the donor and from one another. It must be remembered, of course, that effective binding results only if this binding energy is larger than E_D .

We rewrite first Eq. (1) in the form

$$H = -(\hbar^2/2m_h)\nabla_h^2 + V(\mathbf{r}_h), \quad (2)$$

where

$$V(\mathbf{r}_h) = -\frac{\hbar^2}{2m_e}\nabla_e^2 + \frac{e^2}{Kr_h} - \frac{e^2}{Kr_e} - \frac{e^2}{K|\mathbf{r}_e - \mathbf{r}_h|}, \quad (3)$$

is just the Hamiltonian of the electron moving in the combined Coulomb field of the charged donor and of the hole assuming that the latter is fixed at position \mathbf{r}_h . The eigenvalue problem associated with $V(\mathbf{r}_h)$ is identical to that of the hydrogen molecular ion H_2^+ . We transform the coordinates $\mathbf{r}_e = (x_e, y_e, z_e)$ into the into the parabolic coordinates μ, ν, φ defined by

$$r_h\mu = r_e + |\mathbf{r}_e - \mathbf{r}_h|, \quad (4)$$

$$r_h\nu = r_e - |\mathbf{r}_e - \mathbf{r}_h|, \quad (5)$$

and φ is the angle formed by the projection of \mathbf{r}_e on a plane perpendicular to the vector \mathbf{r}_h and by an arbitrary fiducial line on this plane. The ranges of values of these coordinates are $1 \leq \mu < \infty$, $-1 \leq \nu \leq 1$, and $0 \leq \varphi < 2\pi$. Equation (3) can be rewritten as

$$V(\mathbf{r}_h) = -\frac{1}{2}\nabla_e^2 + \frac{1}{r_h} \frac{\mu^2 - \nu^2 - 4\mu}{\mu^2 - \nu^2}, \quad (6)$$

where we have taken $a^* = K\hbar^2/m_e e^2$ as the unit of length and e^2/Ka^* as the unit of energy. The Laplacian

operator in Eq. (6) is

$$\nabla_e^2 = \frac{4}{r_h^2(\mu^2 - \nu^2)} \left\{ \frac{\partial}{\partial \mu} \left[(\mu^2 - 1) \frac{\partial}{\partial \mu} \right] + \frac{\partial}{\partial \nu} \left[(1 - \nu^2) \frac{\partial}{\partial \nu} \right] + \frac{\mu^2 - \nu^2}{(\mu^2 - 1)(1 - \nu^2)} \frac{\partial^2}{\partial \varphi^2} \right\}. \quad (7)$$

A variational wave function for the Hamiltonian H will be taken of the form

$$\Psi = f(\mathbf{r}_h)g(\mu, \nu, \varphi), \quad (8)$$

where we assume f and g are normalized. Following James⁷ we take

$$g(\mu, \nu, \varphi) = N \exp(-\delta\mu)(1 + c\nu^2), \quad (9)$$

where δ and c are variational parameters and N a normalization factor. Now the expectation value of the Hamiltonian of Eq. (2) is given (in dimensionless form) by

$$W = -\frac{1}{2}\sigma \langle f | \nabla_h^2 | f \rangle + \langle fg | V(\mathbf{r}_h) | fg \rangle - \frac{1}{2}\sigma \langle fg | f \nabla_h^2 g \rangle - \sigma \langle fg | \nabla_h f \cdot \nabla_h g \rangle. \quad (10)$$

The quantity σ is the ratio m_e/m_h . The third and fourth terms arise because g is a function of r_h through the normalizing factor N . The quantity $\langle fg | V(\mathbf{r}_h) | fg \rangle$ is of the form

$$\langle fg | V(\mathbf{r}_h) | fg \rangle = \langle f | \frac{A}{r_h^2} - \frac{B}{r_h} | f \rangle, \quad (11)$$

where A and B are functions of δ and c . It turns out that⁸

$$A = N_0^2 [2\delta(1 + \frac{2}{3}c + \frac{1}{5}c^2) \{2A_1(2\delta) - \delta A_2(2\delta) + \delta A_0(2\delta)\} + (16/15)c^2 A_0(2\delta)], \quad (12)$$

and

$$B = N_0^2 [(1 + \frac{2}{3}c + \frac{1}{5}c^2) \{4A_1(2\delta) - A_2(2\delta)\} + (\frac{1}{3} + \frac{2}{5}c + \frac{1}{7}c^2) A_0(2\delta)], \quad (13)$$

with

$$N_0^{-2} = (1 + \frac{2}{3}c + \frac{1}{5}c^2) A_2(2\delta) - (\frac{1}{3} + \frac{2}{5}c + \frac{1}{7}c^2) A_0(2\delta). \quad (14)$$

The factor N_0 is related to the normalization constant N by the equation

$$N = N_0(2/\pi r_h^3)^{1/2} \exp(\delta). \quad (15)$$

The functions $A_0(x)$, $A_1(x)$, and $A_2(x)$ are given by

$$A_n(x) = \frac{n!}{x^{n+1}} \sum_{k=0}^n \frac{x^k}{k!}. \quad (16)$$

We must now choose the function $f(\mathbf{r}_h)$. We do this by requiring first that $f(\mathbf{r}_h) = f(r_h)$ be invariant under rotations about the origin. We set $f(r_h) = r_h^{1/2} F(r_h)$, and

⁷ H. M. James, J. Chem. Phys. 3, 9 (1935).

⁸ H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1961).

select F to be a solution of the differential equation

$$\left[-\frac{1}{2}\sigma \frac{d^2}{dr_h^2} + \left(\frac{A}{r_h^2} - \frac{B}{r_h} \right) \right] F = E_p F. \quad (17)$$

Here $p=0, 1, 2, \dots$ is a quantum number and E_p an eigenvalue corresponding to the linear operator on the left-hand side of Eq. (17). The eigenvalues associated with Eq. (17) are given by⁹

$$E_p = -(2B^2/\sigma)[2p+1+\{1+(8A/\sigma)\}^{1/2}]^{-2}. \quad (18)$$

Remembering that g depends on r_h only through the factor $r_h^{-3/2}$ some simple manipulations yield for W the value E_p when the function $f(r_h)$ is chosen as above.

The lowest energy state is found setting $p=0$ so that the expectation value of H in a state in which f corresponds to the quantum number $p=0$ is (in ordinary cgs units)

$$W = -(4E_D B^2/\sigma)[1+\{1+(8A/\sigma)\}^{1/2}]^{-2}. \quad (19)$$

Recalling that A and B are functions of δ and c we can now minimize W with respect to these parameters. The results obtained for the minimum value of W as a function of σ are displayed in Fig. 1. We notice from the graph in this figure that $(-W/E_D) > 1$ if $\sigma < 0.20$. Thus, exciton-donor complexes are expected to exist in semiconductors in which σ satisfies the preceding inequality. Needless to say the regions of the curve for which $(-W/E_D) < 1$ have no physical significance.

III. EXCITON BOUND TO AN IONIZED ACCEPTOR

We turn now to the study of the ground state of an exciton-acceptor complex. The Hamiltonian operator describing this system is

$$H = -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_h} \nabla_h^2 - \frac{e^2}{K|\mathbf{r}_e - \mathbf{r}_h|} - \frac{e^2}{Kr_h} + \frac{e^2}{Kr_e}, \quad (20)$$

where the symbols have meanings similar to those of the preceding section.

We first transform \mathbf{r}_e and \mathbf{r}_h into \mathbf{R} and \mathbf{r} which are the position vector of the center of mass of the exciton and relative distance of the electron from the hole, respectively [i.e., $\mathbf{R} = (m_e \mathbf{r}_e + m_h \mathbf{r}_h)/(m_e + m_h)$ and $\mathbf{r} = \mathbf{r}_e - \mathbf{r}_h$]. The Hamiltonian expressed in terms of these variables is

$$H = -\frac{\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{2\mu} \nabla_r^2 - \frac{e^2}{K|\mathbf{R} - \alpha\mathbf{r}|} + \frac{e^2}{K|\mathbf{R} + \beta\mathbf{r}|}. \quad (21)$$

Here $M = m_e + m_h$ is the total mass of the exciton, $\alpha = (m_e/M) = \sigma/(1+\sigma)$ and $\beta = (m_h/M) = (1+\sigma)^{-1}$. We now add and subtract from Eq. (21) the quantity

⁹L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), p. 128.

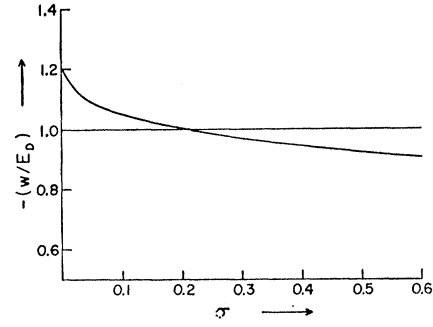


FIG. 1. Ratio of the binding energy of an exciton bound to a singly charged donor to that of the neutral donor as a function of $\sigma = m_e/m_h$.

$(1-Z)e^2/Kr$ where Z is a dimensionless parameter to be determined later. We have

$$H = -\frac{\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{2\mu} \nabla_r^2 - \frac{Ze^2}{Kr} + h_1, \quad (22)$$

where

$$h_1 = -\frac{e^2}{K|\mathbf{R} - \alpha\mathbf{r}|} + \frac{e^2}{K|\mathbf{R} + \beta\mathbf{r}|} - \frac{(1-Z)e^2}{Kr}. \quad (23)$$

We adopt now the following procedure. Consider first the part,

$$H_0 = -\frac{\hbar^2}{2\mu} \nabla_r^2 - \frac{Ze^2}{Kr}, \quad (24)$$

of the Hamiltonian H . The operator H_0 is diagonal in the representation $\Psi_{nlm}^{(0)}$, where these functions are identical to the eigenfunctions of the hydrogen atom except for appropriate scaling factors. The eigenvalues of H_0 are

$$E_n^{(0)} = -\frac{\mu Z^2 e^4}{2\hbar^2 K^2 n^2} = -\frac{\sigma Z^2 E_A}{(1+\sigma)n^2}, \quad (25)$$

where $E_A = (m_h e^4 / 2\hbar^2 K^2)$ is the binding energy of the neutral acceptor. We attempt now to find a trial wave function having the form $\Psi(\mathbf{r}, \mathbf{R}) = \Psi_{nlm}^{(0)}(\mathbf{r})\Phi(\mathbf{R})$, where we assume $\Psi_{nlm}^{(0)}$ and Φ to be normalized. The expectation value of H when the system is in the state Ψ is given by

$$W = \langle \Phi | -(\hbar^2/2M)\nabla_R^2 + E_n^{(0)} + H_{nlm}^{(1)}(\mathbf{R}) | \Phi \rangle, \quad (26)$$

where

$$H_{nlm}^{(1)} = \langle \Psi_{nlm}^{(0)} | h_1 | \Psi_{nlm}^{(0)} \rangle. \quad (27)$$

Clearly, in order to minimize W it is advantageous to choose $n=1, l=m=0$. However Φ is still at our disposal. Naturally one would like to choose Φ so that it is the ground state of a system described by the Hamiltonian $(-\hbar^2/2M)\nabla_R^2 + H_{100}^{(1)}(R)$, but this turns out to be impractical because of the difficulty encountered in the solution of the corresponding Schrödinger equation. We have then chosen Φ to be a solution of the equation

$$[-(\hbar^2/2M)\nabla_R^2 + V_M(R)]\Phi(R) = E_M\Phi(R), \quad (28)$$

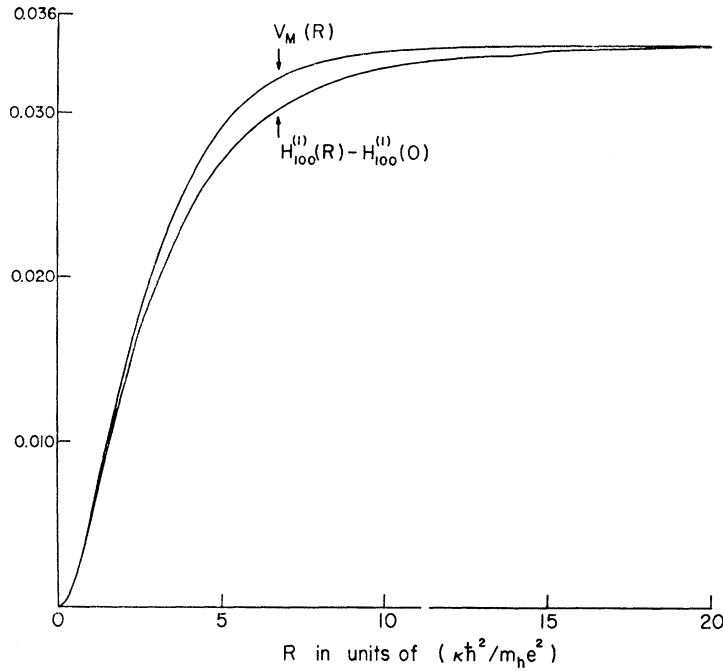


FIG. 2. Values of $V_M(R)$ and of $H_{100}^{(1)}(R) - H_{100}^{(1)}(0)$ as a function of R . The units of the ordinates are eV. This plot is drawn for the case $\sigma=0.23$ which corresponds to the mass ratio appropriate to GaSb.

where

$$V_M(R) = D[1 - \exp(-\lambda R)]^2, \quad (29)$$

is a Morse potential with the parameters D and λ chosen in such a manner so as to match the depth and curvature of the actual potential $H_{100}^{(1)}(R)$. More explicitly we require that

$$V_M(\infty) = D = H_{100}^{(1)}(\infty) - H_{100}^{(1)}(0), \quad (30)$$

and

$$\left(\frac{\partial^2 V_M(R)}{\partial R^2} \right)_{R=0} = \left(\frac{\partial^2 H_{100}^{(1)}(R)}{\partial R^2} \right)_{R=0}. \quad (31)$$

We remark that $V_M(R)$ and $H_{100}^{(1)}(R)$ are rather similar as exhibited in Fig. 2. The evaluation of $H_{100}^{(1)}(R)$ is carried out using the identity

$$\frac{1}{|\mathbf{p}|} = \frac{1}{2\pi^2} \int \frac{\exp(i\mathbf{p} \cdot \mathbf{q})}{q^2} d\mathbf{q}. \quad (32)$$

We find that

$$H_{100}^{(1)}(R) = \frac{e^2}{K} \left[\exp\left(-\frac{2RZe^2 m_h}{K\hbar^2}\right) \left(\frac{Zm_h e^2}{K\hbar^2} + \frac{1}{R}\right) - \exp\left(-\frac{2RZe^2 m_e}{K\hbar^2}\right) \left(\frac{Zm_e e^2}{K\hbar^2} + \frac{1}{R}\right) - \frac{Z(1-Z)\mu e^2}{K\hbar^2} \right]. \quad (33)$$

If we choose for Φ the eigenfunction associated with Eq. (28) corresponding to the lowest value of E_M we find

$$W = W_0 + W_1, \quad (34)$$

where

$$W_0 = E_1^{(0)} + E_M + H_{100}^{(1)}(0), \quad (35)$$

and

$$W_1 = \langle \Phi | (H_{100}^{(1)}(R) - H_{100}^{(1)}(0)) - V_M(R) | \Phi \rangle. \quad (36)$$

Remembering that both W_0 and W_1 are functions of the parameter Z which is still at our disposal, we choose this parameter to be such that W_0 is a minimum. Then we compute W for the value of Z which minimizes W_0 . According to the variational principle, W is then larger than the true ground state of the Hamiltonian H . It is interesting to notice that the contribution of the second term in Eq. (34) is rather small as compared with W_0 . Nevertheless, it has not been neglected. In Fig. 3 we show a graph of $-W/E_A$ as a function of σ calculated in the way outlined above. From this graph we see immediately that an exciton can be bound by a singly ionized acceptor if $\sigma < 0.25$.

Since, after this minimization procedure, h_1 can be regarded as small compared to the other terms in Eq. (22) we can obtain another and presumably more accurate estimate of the binding energy of the exciton-acceptor complex using perturbation theory. We take $\Psi(\mathbf{r}, \mathbf{R}) = \Psi_{nlm}(\mathbf{r})\Phi(\mathbf{R})$ where $\Psi_{nlm}(\mathbf{r})$ differs from $\Psi_{nlm}^{(0)}(\mathbf{r})$ in that we have included a first-order perturbation correction arising from h_1 . Then we can write, to second order in h_1 ,

$$W = W_0 + W_1 + W_2, \quad (37)$$

with

$$W_2 = \langle \Phi | H_{100}^{(2)}(\mathbf{R}) | \Phi \rangle, \quad (38)$$

and

$$H_{100}^{(2)}(\mathbf{R}) = \sum_{nlm \neq 100} \frac{|\langle \Psi_{nlm}^{(0)} | h_1 | \Psi_{100}^{(0)} \rangle|^2}{E_1^{(0)} - E_n^{(0)}}. \quad (39)$$

The correction W_2 has been evaluated for each σ for the value of Z which minimizes W_0 . The new value of $(-W/E_A)$ is also shown in Fig. 3. We notice that the value of σ for which $(-W/E_A)=1$ in the second-order calculation is $\sigma=0.29$ which is fairly close to the value 0.25 found to first order. Numerical applications and a comparison between theory and experiment form the object of the next section.

IV. DISCUSSION

In this section we shall be concerned with the interpretation of some experimental results that can be accounted for by exciton complexes in which the exciton can be associated with either an ionized donor or an ionized acceptor.

Exciton complexes in CdS have been identified by Thomas and Hopfield² and Collins *et al.*⁴ In this material $m_e=0.20$ in units of the free electron mass, being almost isotropic while the hole band structure is not isotropic but has $m_{h\parallel}=5$ and $m_{h\perp}=0.7$ where the subscripts \parallel and \perp denote the effective masses for directions parallel and perpendicular to the hexagonal axis, respectively. We assume that the appropriate hole mass to use in a comparison with our theory is the geometric mean of the principal effective masses, i.e., $m_h=(m_{h\parallel}m_{h\perp})^{1/2}\approx 1.4$. Thus, $\sigma=0.14$ so that an exciton can be attached to either an ionized donor or to an ionized acceptor. The experimental observations do not seem to be consistent with the second alternative. We therefore expect to find a bound exciton 0.0324 eV below the edge of the conduction band (this leads to an observed line at 2.550 eV in the absorption spectrum). If an exciton-acceptor complex existed at all, according to Fig. 3 it would occur at 2.26 eV above the valence band.

Park *et al.*¹⁰ have observed similar optical lines in ZnO. However, because the ratio σ is not known we cannot give an adequate discussion of the relation between these observations and the present theory.

Experimental studies on GaSb by Johnson and Fan⁶ can be simply interpreted if one assumes the existence of exciton-acceptor complexes. In GaSb, taking $m_e=0.052$ and $m_h=0.23$ we have $\sigma=0.23$ so that, according to our calculations an exciton in this material can

¹⁰ Y. S. Park, C. W. Litton, T. C. Collins, and D. C. Reynolds, *Phys. Rev.* **143**, 512 (1966).

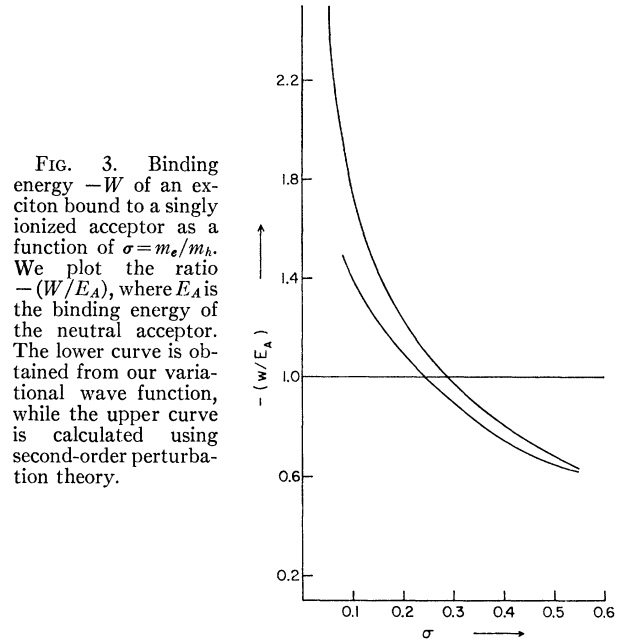


FIG. 3. Binding energy $-W$ of an exciton bound to a singly ionized acceptor as a function of $\sigma = m_e/m_h$. We plot the ratio $-(W/E_A)$, where E_A is the binding energy of the neutral acceptor. The lower curve is obtained from our variational wave function, while the upper curve is calculated using second-order perturbation theory.

only be bound to an acceptor. The binding energy of the complex (taken from Fig. 3) is $1.17E_A=0.018$ eV taking $K=14.4$ and differs from the experimental position of the γ -line in Ref. 6 by less than 5%. In ZnTe $m_e=0.09$, $m_h=0.6$ so that $\sigma=0.15$. Thus the binding energy of an exciton-acceptor complex is $1.4E_A=0.106$ eV. The corresponding binding of the exciton-donor complex, using $K=10.4$, is $1.02E_D=0.0115$ eV.

The level lying 0.0082 eV below the edge of the conduction band of GaSb cannot be regarded as being a state of the exciton-acceptor complex since its binding energy is less than that of the neutral acceptor. It could be associated with an impurity state other than the one responsible for the exciton-acceptor complex.

Finally, it is interesting to mention that in Si we do not expect any bound excitons to exist because $\sigma\approx 1$. This seems to be consistent with the observed results.¹¹

ACKNOWLEDGMENTS

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¹¹ J. R. Haynes, *Phys. Rev. Letters* **4**, 361 (1960).