

in the figure) lie between 35 and 40 meV, while the accepted ionization energy of Zn in GaP is 62 meV.<sup>10</sup> In the absence of complete Hall data for these samples this is seen as satisfactory agreement. As a further test of this model we have performed similar measurements on GaP doped with Cd and O, and find an activation energy of about 70 meV, which is consistent with the known difference in ionization energies of the two acceptors Cd and Zn.<sup>10</sup> The green exciton in Cd+O-doped material appears at the same energy as in the Zn-doped samples.

In conclusion, we have interpreted the temperature

<sup>10</sup> P. J. Dean, J. D. Cuthbert, D. G. Thomas, and R. T. Lynch, *Phys. Rev. Letters* **18**, 122 (1967).

dependence of the efficiency of red radiation from O<sup>+</sup>+Zn<sup>-</sup>-doped GaP in terms of specific competing processes, both radiative and nonradiative, which apply in different temperature ranges. The list is not exhaustive and further work at temperatures greater than 250°K would be necessary to elucidate the nature of other nonradiative processes which become important at still higher temperatures.

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## Binding Energy of the Excitonic Molecule

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The binding energy of the excitonic molecule, a complex consisting of two electrons and two holes, has been determined as a function of  $\sigma$ , the ratio of the mass of the electron to that of the hole. We find the binding energy of the excitonic molecule in Si to be 0.63 meV, as compared with the experimental result of  $\leq 2$  meV. Our analysis also predicts that the excitonic molecules should also be observed in a wide variety of crystals for which  $\sigma$  does not lie in the range  $0.2 \leq \sigma \leq 0.4$ .

THE aim of this paper is to present theoretical evidence of the experimental observation<sup>1</sup> in Si of the excitonic molecule, a complex consisting of two electrons and two positive holes. It is the first theoretical work which gives the binding energy of the excitonic molecule for various values of  $\sigma$ , the ratio of the mass of the electron to that of the hole. For the history of such complexes, see Ref. 1. In our estimate of the binding energy of the complex, we assume a model in which the constant energy surfaces are spherical and the effective-mass approximation is valid. In order to eliminate the kinetic energy of the c.m. of the complex, a suitable transformation is applied to the Hamiltonian. We have used a five-parameter variational wave function for obtaining the ground state of the system. For the calculation of the energy matrix elements a method due to James and Coolidge<sup>2</sup> is employed. The results are displayed in Fig. 1, in which the ratio of the binding energy  $W_{em}$  of the excitonic molecule to  $E_0$  (where  $E_0 = m_e e^4 / 2\hbar^2 K^2$ ;  $m_e$  is the effective mass of the electron and  $K$  is the dielectric constant of the medium) is plotted against  $\sigma$ , for  $0 \leq \sigma \leq 1$ . The results for  $1 \leq \sigma \leq \infty$  can easily be obtained from Fig. 1 by considering that

the binding energy of the complex does not change on inverting the sign of the charges of the constituent particles and thereby reducing the problem to the case for which  $0 \leq \sigma \leq 1$ . We find the binding energy of the excitonic molecule in Si to be 0.63 meV (making use of  $m_e = 0.39$  in units of free-electron mass,  $\sigma = 0.75$  and  $K = 19.4$ ), consistent with the experimental observation<sup>1</sup> of  $\leq 2$  meV.

Since the complex is stable against dissociation when its binding energy is positive, Fig. 1 predicts that such excitonic molecules should also be observed in a wide variety of other crystals for which  $\sigma$  does not lie in the range  $0.2 \leq \sigma \leq 0.4$ . It is true that such will also be the case for  $\sigma$  not lying between the reciprocals of these limits. The latter case is not of much interest since we are dealing with semiconductors where mostly  $0 \leq \sigma \leq 1$ . Consequently, it is hoped that this work will give impetus for the discovery of excitonic molecules in crystals other than Si. It will be more gratifying if experiments are conducted which can give a definite value for the binding energy of the complex. In the following, we describe our method for estimating the binding energy of the system, namely, the excitonic molecule.

The excitonic molecule is a complex consisting of two positive holes, each of mass  $m_h$ , and two electrons, each

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<sup>1</sup> J. R. Haynes, *Phys. Rev. Letters* **17**, 860 (1966).

<sup>2</sup> H. M. James and A. S. Coolidge, *J. Chem. Phys.* **1**, 825 (1933).

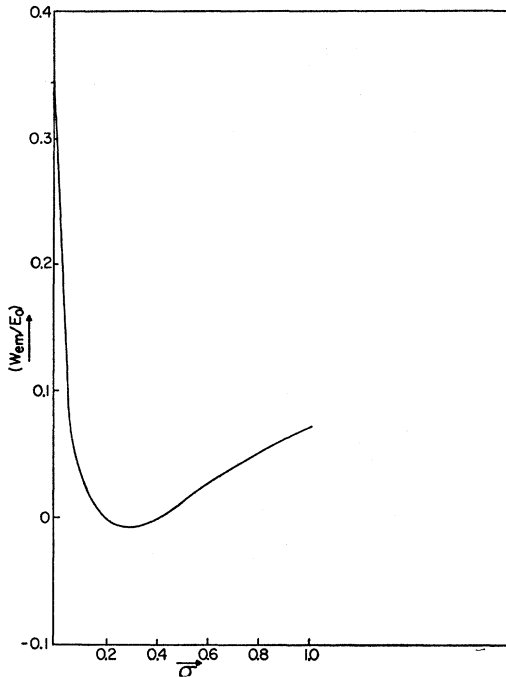


FIG. 1. Binding energy of the excitonic molecule as a function of  $\sigma$ , the ratio of the mass of the electron to that of the hole.

of mass  $m_e$ , interacting with one another through a Coulomb potential. The Hamiltonian for the system is

$$\mathcal{H} = -\frac{1}{2}\sigma(\nabla_{h_1}^2 + \nabla_{h_2}^2) - \frac{1}{2}(\nabla_{e_1}^2 + \nabla_{e_2}^2) + V_0, \quad (1)$$

with  $V_0$ , the potential of interaction, given by

$$V_0 = \frac{1}{r_{h_1 h_2}} + \frac{1}{r_{e_1 e_2}} + \frac{1}{r_{h_1 e_1}} + \frac{1}{r_{h_2 e_2}} + \frac{1}{r_{h_1 e_2}} + \frac{1}{r_{h_2 e_1}}, \quad (2)$$

where we have taken the unit of distance to be  $\hbar^2 K / m_e e^2$  and that of energy to be  $m_e e^4 / \hbar^2 K^2$ .

The first four terms in Eq. (1) are the kinetic energies of the holes and electrons with respect to a fixed origin 0 of a coordinate system. We designate the holes by  $h_1$  and  $h_2$  and the electrons by  $e_1$  and  $e_2$ . The distance between the holes  $h_1$  and  $h_2$  is denoted by  $r_{h_1 h_2}$ . Other distances carry a similar meaning.

We transform the Hamiltonian and eliminate the kinetic energy of the system since it does not contribute to its binding energy. To this end we introduce a new set of coordinates defined by

$$\begin{aligned} \mathbf{R}_{c.m.} &= [\mathbf{r}_{h_1} + \mathbf{r}_{h_2} + \sigma(\mathbf{r}_{e_1} + \mathbf{r}_{e_2})] / 2(1 + \sigma), \\ \mathbf{R} &= \mathbf{r}_{h_1} - \mathbf{r}_{h_2}, \\ \mathbf{R}_1 &= \mathbf{r}_{e_1} - \frac{1}{2}(\mathbf{r}_{h_1} + \mathbf{r}_{h_2}), \quad \mathbf{R}_2 = \mathbf{r}_{e_2} - \frac{1}{2}(\mathbf{r}_{h_1} + \mathbf{r}_{h_2}). \end{aligned} \quad (3)$$

In Eq. (3),  $\mathbf{r}_{h_1}$  and  $\mathbf{r}_{h_2}$  are the position vectors of the holes  $h_1$  and  $h_2$  with respect to the origin 0. Other vectors are defined in a similar way.  $\mathbf{R}_{c.m.}$  is the position vector of the c.m. of the system.  $\mathbf{R}$  is the distance

between the holes.  $\mathbf{R}_1$  and  $\mathbf{R}_2$  are the position vectors of the electrons 1 and 2 measured from the midpoint of the line joining the holes.

The new coordinate system (3) transforms the Hamiltonian (1) into

$$\mathcal{H} = -\sigma \nabla_{\mathbf{R}}^2 - \frac{1}{2}(\frac{1}{2}\sigma + 1)[\nabla_1^2 + \nabla_2^2] - \frac{1}{2}\sigma \nabla_1 \cdot \nabla_2 + V_0 \quad (4)$$

with  $\nabla_{\mathbf{R}} = \partial / \partial \mathbf{R}$ ,  $\nabla_1 = \partial / \partial \mathbf{R}_1$ ,  $\nabla_2 = \partial / \partial \mathbf{R}_2$ , where we have dropped the kinetic energy of the c.m. of the system since it does not contribute to the binding energy of the system.

It is worth remarking that the Hamiltonian (4) reduces to the Hamiltonian of the hydrogen molecule<sup>2</sup> if  $\sigma \rightarrow 0$  ( $m_h \gg m_e$ ) as expected.

In order to obtain the lowest eigenvalue of the Hamiltonian (4) we assume a variational wave function of the form

$$\Psi = f(\mathbf{R})g(\lambda_1, \mu_1, \lambda_2, \mu_2, \rho_{12}), \quad (5)$$

where  $\lambda_1$ ,  $\mu_1$ , etc., are the elliptical coordinates defined by

$$\begin{aligned} R\lambda_1 &= r_{h_1 e_1} + r_{h_2 e_1}, & R\lambda_2 &= r_{h_1 e_2} + r_{h_2 e_2}, \\ R\mu_1 &= r_{h_1 e_1} - r_{h_2 e_1}, & R\mu_2 &= r_{h_1 e_2} - r_{h_2 e_2}, \\ R\rho_{12} &= 2r_{e_1 e_2}. \end{aligned} \quad (6)$$

If the wave function  $\Psi$  is normalized, the eigenvalue  $W$  is

$$W = -\sigma \langle fg | \nabla_{\mathbf{R}}^2 | fg \rangle + \langle f | V(\mathbf{R}) | f \rangle, \quad (7)$$

with

$$V(\mathbf{R}) = \langle g | H | g \rangle, \quad (8)$$

where

$$H = -\frac{1}{2}(\frac{1}{2}\sigma + 1)[\nabla_1^2 + \nabla_2^2] - \frac{1}{2}\sigma \nabla_1 \cdot \nabla_2 + V_0. \quad (9)$$

Now we choose for  $g$  a variational function of the form

$$g = N^{-1/2} \sum_{m n j k p} C_{m n j k p} \Psi_{m n j k p}, \quad (10)$$

where

$$\begin{aligned} \Psi_{m n j k p} &= (2\pi)^{-1} \exp[-\delta(\lambda_1 + \lambda_2)] \\ &\times (\lambda_1^m \lambda_2^n \mu_1^j \mu_2^k \rho^{2p} + \lambda_1^n \lambda_2^m \mu_1^k \mu_2^j \rho^{2p}). \end{aligned} \quad (11)$$

The normalization constant  $N$  is determined by  $\langle g | g \rangle = 1$ . One can show that<sup>3</sup>

$$V(\mathbf{R}) = P/R^2 - B/R, \quad (12)$$

<sup>3</sup> The form of the operators  $\nabla_1^2$  and  $\nabla_2^2$  in terms of the elliptical coordinates can be obtained from H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1961), p. 367. The form of the operator  $\nabla_1 \cdot \nabla_2$  in elliptical coordinates was determined from the Cartesian form  $\nabla_1 \cdot \nabla_2 = (\partial / \partial x_1) \partial / \partial x_2 + (\partial / \partial y_1) \partial / \partial y_2 + (\partial / \partial z_1) \partial / \partial z_2$  and making use of  $(\partial / \partial x_1) = (\partial \lambda_1 / \partial x_1) \partial / \partial \lambda_1 + (\partial \mu_1 / \partial x_1) \partial / \partial \mu_1 + (\partial \rho_1 / \partial x_1) \partial / \partial \rho_1$  and the similar expressions. The partial derivatives  $\partial \lambda_1 / \partial x_1$ , etc., were derived from the relations connecting the Cartesian coordinates with the elliptical coordinates.

with

$$P = N_0^{-1} \sum_{m_a n_a j_a k_a p_a m_b n_b j_b k_b p_b} C_{m_a n_a j_a k_a p_a} C_{m_b n_b j_b k_b p_b} \times [\omega_{ab}^{(1)} + \omega_{ab}^{(2)} + \omega_{ab}^{(3)} + \omega_{ab}^{(4)}], \quad (13)$$

where

$$\omega_{ab}^{(1)} = (\frac{1}{2}\sigma + 1)u_{ab}^{(1)} + \frac{1}{2}\sigma \times [P_2 + 2P_3 + P_4 + 2(P_5 + P_6) + P_7]. \quad (14)$$

$u_{ab}^{(1)}$  in Eq. (14) is given by Eq. (15) of Ref. 4, and

$$P_2 = -\frac{1}{16} [m_b n_b \{z'(00000) + z(11110) - z(-11110) - z(1-1110) + z(-1-1110)\} \\ - n_b \delta \{z'(10000) + z(21110) - z(01110) - z(2-1110) + z(0-1110)\} \\ - m_b \delta \{z'(01000) + z(12110) - z(-12110) - z(10110) + z(-10110)\} \\ + \delta^2 \{z'(11000) + z(22110) - z(02110) - z(20110) + z(00110)\}],$$

$$P_3 = -\frac{1}{16} j_b [n_b \{-z'(00000) + z(11-110) - z(11110) - z(1-1-110) + z(1-1110)\} \\ - \delta \{-z'(01000) + z(12-110) - z(12110) - z(10-110) + z(10110)\}],$$

$$P_4 = -\frac{1}{16} j_b k_b \{z'(00000) + z(11-1-10) - z(11-110) - z(111-10) + z(11110)\},$$

$$P_5 = -\frac{1}{16} p_b [n_b \{\chi(1111-2) - \chi(1-111-2) - \chi(0200-2) + \chi(0000-2) + z'(2000-2) - z'(0020-2)\} \\ - \delta \{\chi(1211-2) - \chi(1011-2) - \chi(0300-2) + \chi(0100-2) + z'(2100-2) - z'(0120-2)\}],$$

$$P_6 = -\frac{1}{16} k_b p_b [\chi(111-1-2) - \chi(1111-2) - \chi(0000-2) + \chi(0002-2) - z'(2000-2) + z'(0020-2)],$$

and

$$P_7 = -\frac{1}{16} (p_b + 1)(p_b) [\chi(0002-2) - \chi(0200-2)].$$

The symbols  $z^r(11110)$ , etc., are the sixfold integrals defined in Ref. 2. The expression for  $\omega_{ab}^{(2)}$  is obtained from  $\omega_{ab}^{(1)}$  by the substitutions [ $m_a \leftrightarrow n_a$ ,  $j_a \leftrightarrow k_a$ ].  $\omega_{ab}^{(3)}$  is obtained from  $\omega_{ab}^{(1)}$  by making the changes [ $m_b \leftrightarrow n_b$ ,  $j_b \leftrightarrow k_b$ ] and  $\omega_{ab}^{(4)}$  by

$$[m_a \leftrightarrow n_a, j_a \leftrightarrow k_a, m_b \leftrightarrow n_b, j_b \leftrightarrow k_b].$$

The factor  $N_0$  in Eq. (13) is defined in (16) and (17) of Ref. 4. The parameter  $B$  in (12) can be obtained from Eqs. (18) and (19) of the same reference.

The normalization constant  $N$  in Eq. (10) is related to  $N_0$  by  $N = N_0 R^6$ . The variational function  $g$  is a function of  $R$  through the normalization constant  $N$  and therefore is proportional to the inverse cube of  $R$ . We choose  $f(\mathbf{R}) = R^{-2}F(R)$ , where  $F(R)$  is the eigenfunction of the operator

$$-\sigma d^2/dR^2 + P/R^2 - B/R \quad (15)$$

corresponding to its lowest eigenvalue. This completes the choice of the form of the wave function. The expect-

ation value  $W$  of  $3\mathcal{C}$  is then given by<sup>5</sup>

$$W = (-2B^2/\sigma)E_0[1 + \{1 + (4P/\sigma)\}^{1/2}]^{-2}, \quad (16)$$

where we have restored the original cgs units. The binding energy  $W_{em}$  of the excitonic molecule is the energy absorbed when the system dissociates into two excitons so that  $W_{em} = -W - 2W_e$ , where  $W_e = E_0/(1 + \sigma)$  is the binding energy of the exciton. Thus

$$W_{em} = E_0 \{ (2B^2/\sigma)[1 + \{1 + (4P/\sigma)\}^{1/2}]^{-2} - 2/(1 + \sigma) \}. \quad (17)$$

We choose five variational parameters  $C_{00000}$ ,  $C_{00020}$ ,  $C_{00110}$ ,  $C_{10000}$ , and  $C_{00001}$ . In order to obtain the maximum value of  $W_{em}$  for each value of  $\sigma$ , the coefficient  $C_{00000}$  was kept constant equal to unity while  $\delta$  and other parameters  $C_{00020}$ ,  $C_{00110}$ ,  $C_{10000}$ , and  $C_{00001}$  were varied. The values of  $W_{em}/E_0$  so obtained are displayed in Fig. 1.

The author is very thankful to Professor S. Rodriguez for useful discussions.

<sup>4</sup> R. R. Sharma and S. Rodriguez, *Phys. Rev.* **159**, 649 (1967).

<sup>5</sup> L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1958), p. 128.