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Properties of Excitons Bound to Ionized Donors

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Binding energies, interparticle distances, oscillator strengths, and exchange corrections are calculated for the three-particle complex corresponding to an exciton bound to an ionized donor. The results are given as functions of the mass ratio of the electron and hole. Binding of the complex is obtained for mass ratios up to 0.426. The interparticle distances are up to 50 times larger than the corresponding exciton radius. The oscillator strengths are about 10^4 times greater than those of free excitons, while the exchange corrections for the complex are comparable to those of free excitons. The results are applied to CdS and ZnO and compared with experimental results on these.

I. INTRODUCTION

The three-particle complex consisting of an electron and a hole bound to an ionized donor is the simplest possible bound-exciton complex. Hopfield¹ has estimated the binding energies of bound-exciton complexes by extrapolations of molecular binding energies. More accurate calculations of binding energies for the three-particle complex were carried out by means of variational methods by Sharma and Rodriguez² and Suffczynski *et al.*³

Here we compute binding energies of the three-particle complex for a practically important interval of electron-hole mass ratios m_e/m_h by adding a long-range tail to the variational function. The wave functions obtained in this variational procedure are then, furthermore, used for computing other characteristic quantities of the center, such as interparticle distances, oscillator strengths, and exchange corrections as a function of m_e/m_h .

II. GROUND-STATE ENERGY

The ground-state energy of the three-particle complex was calculated by variational means in the effective-mass approximation. The effective-mass Hamiltonian H for the complex is conveniently scaled as follows:

$$H^1 = H/2E_a$$

$$= -\frac{1}{2} (m_h/m_e) \Delta'_e - \frac{1}{2} \Delta'_h + 1/R'_h + 1/R'_e - 1/R'_{eh}. \quad (1)$$

Here R_h and R_e are the distances from the ionized donor to the hole and the electron, respectively, while R_{eh} is the distance between the electron and hole. Further,

$$E_a = \frac{e^4 m_h}{2\hbar^2 (4\pi\epsilon_0\epsilon)^2} = \frac{\hbar^2}{2m_h a_h^2} = \frac{e^2}{2(4\pi\epsilon_0)\epsilon a_h} \quad (2)$$

and

$$a_h = 4\pi\epsilon_0\epsilon\hbar^2/e^2 m_h \quad (3)$$

are energy and radius for the hydrogenlike acceptor in the semiconductor. The e is the electronic charge, m_e and m_h are electron and hole masses, respectively, ϵ_0 is the permittivity vacuum, while ϵ is the low-frequency value of the dielectric constant of the material. The primed coordinates are then measured in units of a_h . They are thus scaled with the dielectric constant and the hole mass. It is seen that the scaled Hamiltonian depends on only one parameter, the mass ratio m_e/m_h . In case of anisotropic masses or dielectric constants a transformation⁴ to the isotropic case can be applied. Hence, only the isotropic solutions will be considered here.

The trial function was of the form,

$$f(\vec{R}_e, \vec{R}_h) = R'_h{}^p \sum_{i=1}^N X_i \exp[-(A_i R'_e + B_i R'_{eh} + C_i R'_h)]$$

$$+ X_{N+1} e^{-A_0 R'_e} \frac{e^{-C_0 R'_h} - e^{-C R'_h}}{R'_h}, \quad (4)$$

where the variational parameters are X_i , A_i , B_i , C_i , C_0 , and C , whereas $1/A_0$ is the radius of the donor. p and N were usually 2 and 4, respectively. Previous calculations³ of the ground-state energy were performed only with the first part of this trial function. The inclusion of the last term which is similar to that used by Rotenberg and Stein⁵ is particularly useful when m_e/m_h is close to the value where this complex ceases to be bound. Near this limit the center is characterized, approximately, by an electron in the donor level and a loosely bound hole as described by the last term in the trial function.

By means of (4) the variational estimate of the ground-state energy was obtained as a function of

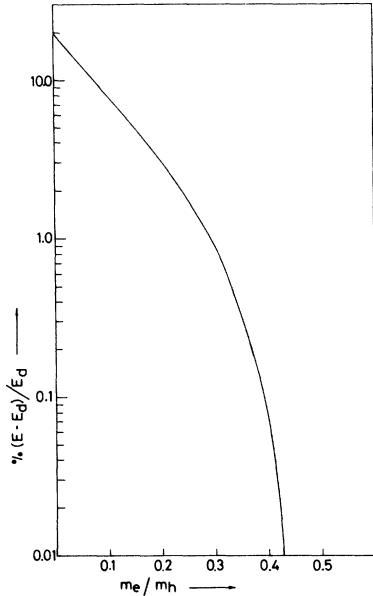


FIG. 1. Binding energy E for the three-particle center relative to the donor energy E_d as a function of the mass ratio. $m_e/m_h=0$ corresponds to the H_2^+ molecule. The binding energy of an exciton to an ionized donor may be found from Eq. (5).

m_e/m_h . The results are given in Fig. 1. The ratio of the ground-state energy E to the donor energy E_d varies monotonically with the mass ratio.⁶ We obtain binding of the complex up to $m_e/m_h = 0.426$ where we found $(E - E_d)/E_d = (1.8 \times 10^{-4})\%$. The binding energy given in Fig. 1 is that of a hole bound to a neutral donor. The complex may equally well be visualized as an ionized donor binding an exciton with a binding energy

$$E - E_{ex} = \left[\left(1 + \frac{m_e}{m_h} \right) \frac{E - E_d}{E_d} + \frac{m_e}{m_h} \right] E_{ex}, \quad (5)$$

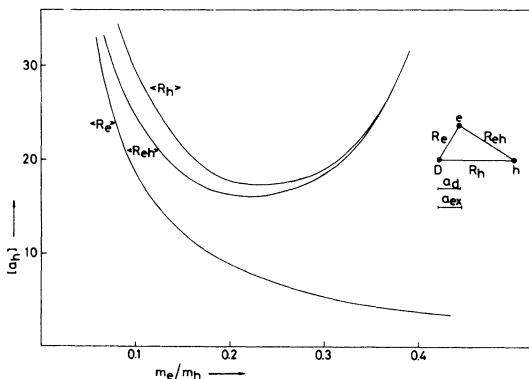


FIG. 2. Expectation values of the interparticle distances in the three-particle complex in units of the effective Bohr radius of the hole a_h ($a_h = 4\pi\epsilon_0\epsilon\hbar^2/e^2m_h$). The case of $m_e/m_h = 0.20$ is explicitly shown (in scale 1:2).

where E_{ex} is the binding energy of the free exciton.

III. INTERPARTICLE DISTANCES

It is important to know approximately the distances between the particles in the complex since the validity of the effective-mass equation (1) breaks down when these distances are too small. It is, furthermore, of interest to calculate these distances because they yield the extension of the center and hence the largest possible concentration of bound excitons before their envelopes substantially overlap. The expectation values of the distances are computed by means of the trial functions which gave lowest ground-state energy. The results are shown in Figs. 2 and 3. It is seen that all the distances are greater than the donor radius. The use of the effective-mass equation is therefore justified. In the limit $m_e/m_h \rightarrow 0$, $\langle R_e \rangle \rightarrow \langle R_{eh} \rangle \rightarrow 0.69 \times \langle R_h \rangle$ as for the H_2^+ complex. In the limit where the complex becomes ionized $\langle R_{eh} \rangle$ and $\langle R_h \rangle$ are large, and $\langle R_e \rangle$ is slightly larger than the donor radius a_d .

We have also computed the average interaction energies between the particles which we define as $\langle e^2/8\pi\epsilon_0\epsilon R \rangle$, where R is the distance between the particles in question. These energies are two times smaller than the expectation values of the corresponding potential energies. The results are given in Fig. 4. It is seen that the binding energy of the complex appears as the sum of the interaction energies between the particles. It is interesting to note that there exists an upper limit of R_h (and R_{eh}) since curves (a) and (b) cross at $m_e/m_h = 0.426$. Here, the repulsive potential energy of the hole equals the attractive potential energy, and the hole ceases to be bound. At this point R_h and R_{eh} are about 50 times greater than a_d , the donor radius, corresponding to the largest possible extension of the wave function in the direct space is consistent with the observation of Reynolds *et al.*⁷ that the phonon side bands for three-particle complexes are sharper than for four-particle complexes. This indicates a more localized wave function in k space for three-particle complexes.

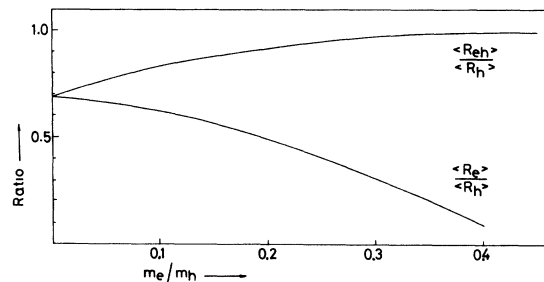


FIG. 3. Ratios of the expectation values of the interparticle distances in the three-particle complex.

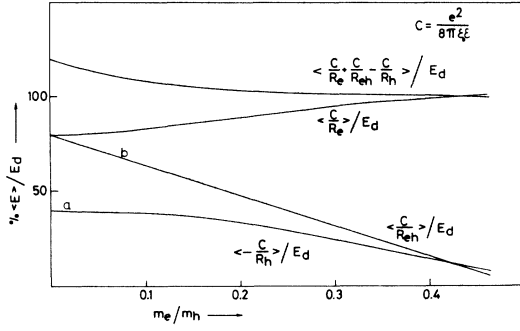


FIG. 4. Expectation values of the interaction energies, defined as half the potential energies. It is seen that above the limit mass ratio the repulsive energy for the hole is larger than the attractive energy, and the complex cannot exist.

IV. OSCILLATOR STRENGTHS

The oscillator strength f_c of the complex may be obtained by computing the momentum matrix element $\langle p \rangle$ between the crystal ground state and the excited state corresponding to the three-particle complex. From the definition of the oscillator strength, one then finds⁸

$$f_c = \frac{2|\langle p \rangle|^2}{3m\hbar\omega_0} = \left(\frac{2|p_{cv}|^2}{3m} \right) \frac{1}{\hbar\omega_0} \left| \sum_{\vec{R}} f(\vec{R}, \vec{R}) \right|^2$$

$$= \frac{P^2}{\hbar\omega_0} \left| \sum_{\vec{R}} f(\vec{R}, \vec{R}) \right|^2, \quad (6)$$

where m is the free-electron mass, ω_0 is the frequency of the transition, and $f(\vec{R}_e, \vec{R}_h)$ is the envelope function for the three-particle complex in Eq. (4). The $f(\vec{R}_e, \vec{R}_h)$ should be normalized such that

$$\sum_{\vec{R}_e, \vec{R}_h} |f(\vec{R}_e, \vec{R}_h)|^2 = 1. \quad (7)$$

The p_{cv} is the usual one-electron p -matrix element between valence and conduction band, and P^2 is the value of the terms in the brackets. Cardona⁹ reports that the value of P^2 is remarkably constant within the different groups of materials. For II-VI compounds he finds $P^2 \approx 21$ eV, and for III-V and IV-IV materials, $P^2 \approx 23$ eV. The modifying factor $|\sum f(R, R)|^2$, which multiplies the pure band-to-band strength in (6), is not just the probability that the electron and hole are in the same unit cell, as is usually assumed in optical transitions. The factor is the square of the sum of the amplitude probabilities that the electron and hole are in same unit cell or, if Fourier transformed, that the electron and hole have opposite k vectors.

Introducing the oscillator strength f_{ex} per unit cell Ω of the free excitons, one obtains^{8,10}

$$f_c = f_{ex} \frac{\omega_{ex}}{\omega_0} \frac{\pi a_{ex}^3}{\Omega} \left| \sum_{\vec{R}} f(\vec{R}, \vec{R}) \right|^2, \quad (8)$$

where ω_{ex} and a_{ex} , respectively, are the resonance frequency and the radius of the free excitons. By computing $|\sum f(R, R)|^2$, the ratio f_c/f_{ex} may be obtained. Rashba and Gurgenshvil¹¹ and Henry and Nassau⁸ have done this with a wave function for a short-range potential representing very loosely bound-exciton complexes. Here we compute $|\sum f(R, R)|^2$ for excitons bound to ionized centers by means of the wave function Eq. (4) obtained in the variational procedure.

The computed values of $|\sum f(\vec{R}, \vec{R})|^2$ for the three-particle complex are given in Fig. 5 vs m_e/m_h . It is seen that these values are of the order of 10 which means that the strengths of these complexes are of the order 10^4 times greater than the strengths of free excitons.

It is interesting to know the limiting value of the oscillator strength when the center ceases to be bound. To calculate this we use Eq. (6). Now, the complex consists of an electron in the donor level and a free hole in the valence band. For this complex we have

$$f_{\vec{k}}(R_e, \vec{R}_h) = \left(\frac{\Omega}{N\pi a_d^3} \right)^{1/2} e^{-R_e/a_d} e^{i\vec{k} \cdot \vec{R}_h}, \quad (9)$$

where N is the number of unit cells of volume Ω in the crystal, a_d is the donor radius, and \vec{k} is the wave vector of the hole. Then,

$$\left| \sum_{\vec{R}} f(R, R) \right|^2 = \sum_{\vec{k}} \left| \sum_{\vec{R}} f_{\vec{k}}(R, R) \right|^2$$

$$= \frac{N\Omega}{(2\pi)^3} \int_{\vec{k}} \frac{1}{N\Omega\pi a_d^3} \frac{64\pi^2 a_d^6}{(1+a_d^2|\vec{k}|^2)^4} d^3k$$

$$= 1, \quad (10)$$

where the contribution from each k vector has been

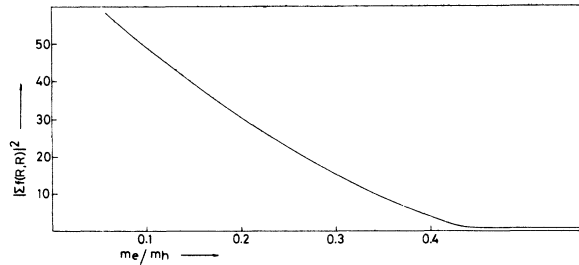


FIG. 5. Enhancement factor for the oscillator strength of the three-particle complex. The strength may be obtained from Eq. (6) or (8). Above the limit mass ratio, the enhancement factor is 1, corresponding to the integrated strength of the recombination of a free hole and a bound electron.

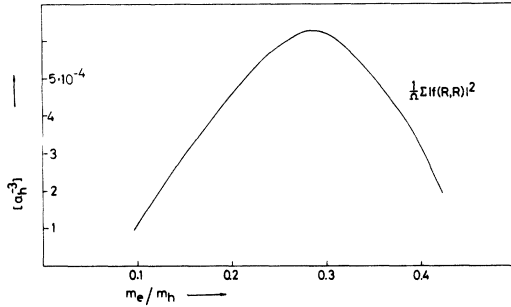


FIG. 6. Factor determining the exchange correction for the three-particle complex. Ω is the volume of one molecule in the solid in units of the effective Bohr radius of the hole a_h . Since $\sum |f(R, R)|^2$ is proportional to Ω , the factor shown in this figure is the proportionality constant $\sum |f(R, R)|^2/\Omega$. The exchange splitting may be obtained from Eq. (13).

taken into account. The oscillator strength for the recombination of a free hole and a bound electron therefore is

$$f = P^2/\hbar\omega_0. \quad (11)$$

Note that this strength is independent of the mass ratio and the donor radius.

V. EXCHANGE CORRECTION

The levels corresponding to parallel and antiparallel orientations of the electron and hole spins are split by the exchange interaction. Only the state with antiparallel spins is optically allowed. Thomas and Hopfield¹² mentioned that the exchange splitting is proportional to the probability that the electron and hole are in the same unit cell, i. e., $\sum_{\vec{R}} |f(R, R)|^2$. Henry *et al.*¹³ applied this result to weakly bound excitons. Here, we compute the exchange splitting of the three-particle complex by means of the wave functions of Eq. (4).

The exchange splitting may be computed from first-order perturbation theory. This has been done for free excitons.¹⁴ We modify these results to apply to the case of the three-particle complex. Eq. (19) in Ref. 14 then becomes

$$\Delta_0 = J_0 \sum_{\vec{R}} |f(\vec{R}, \vec{R})|^2, \quad (12)$$

where J_0 is the exchange integral of the conduction- and valence-band Wannier functions for the same unit cell. Equation (12) represents only the short-range part of the exchange interaction. The long-range part [Eq. (11) in Ref. 14] vanishes for a single isotropic center. If, however, all three-particle complexes in the crystal are taken into account, a long-range exchange splitting is found. The optically active excitations of this system of centers have different energies, depending on its transverse or longitudinal character. This splitting between longitudinal and transverse states of the

whole system of centers is due to the long-range exchange interaction. It may be computed in the same way as for free excitons.¹⁴ From Eqs. (14) and (15) in Ref. 14 one then obtains for the total exchange correction of the three-particle complex

$$\Delta_T = J_0 \sum_{\vec{R}} |f(\vec{R}, \vec{R})|^2 - \frac{1}{3} (\mu_x^2 N_c / \epsilon_0 \epsilon') |\sum_{\vec{R}} f(\vec{R}, \vec{R})|^2 \quad (\vec{k} \perp \vec{\mu}), \quad (13)$$

$$\Delta_L = J_0 \sum_{\vec{R}} |f(\vec{R}, \vec{R})|^2 + \frac{2}{3} (\mu_x^2 N_c / \epsilon_0 \epsilon') |\sum_{\vec{R}} f(\vec{R}, \vec{R})|^2 \quad (\vec{k} \parallel \vec{\mu}). \quad (14)$$

Here Δ_T is the exchange energy of the transverse states (optically active), Δ_L is that of the longitudinal states, μ_x is the magnitude of the dipole moment associated with a valence-conduction-band transition, ϵ_0 is the permittivity of vacuum, whereas ϵ' is the background dielectric constant at the transition frequency, and N_c is the concentration of centers. A detailed calculation, based on the assumption that the random distribution of centers may be replaced by an ordered distribution, shows that $|\sum f(R, R)|^2$ appears as the factor due to the centers in the long-range terms and not $\sum |f(R, R)|^2$ which only is present in the short-range terms.

Note that the long-range exchange splitting between transverse and longitudinal states depends on the concentration of complexes in the crystal, and that it is proportional to the oscillator strength (6) of the complex. It should be noticed that there are three relevant energy states for the complex: The state with parallel spin which is not affected by exchange, and the states with antiparallel spins for which the transverse and longitudinal states are split.

The $\sum |f(\vec{R}, \vec{R})|^2$ is given in Fig. 6 for the three-particle complex. It is of the order of 10^{-3} which is the same order as for free excitons. Hence, the short-range exchange correction for free and bound excitons should be comparable. The long-range exchange correction Δ_{LR} for the bound excitons may be expressed in terms of the long-range exchange correction Δ_{free} for free excitons and the oscillator strength ratio (8) as follows:

$$\Delta_{LR} = \Delta_{free} N_c \Omega f_c / f_{ex}. \quad (15)$$

Since f_c/f_{ex} is of the order 10^4 , N_c should be of the order 10^{18} cm^{-3} to get Δ_{LR} comparable with Δ_{free} ($\Delta_{free} = -\frac{1}{3} E_{LT}$, where E_{LT} is the splitting between transverse and longitudinal free excitons¹⁴). This high content of impurities will, however, because of the large oscillator strengths of bound excitons, give rise to a bound-exciton absorption comparable to the free-exciton absorption. This results in a broad absorption edge below the band gap without any structure. For most measurements on bound-

TABLE I. Results computed for CdS and ZnO compared with experimental results. Only the three experimental values of m_e/m_h , m_e , and E_{ex} are used in the calculations.

	CdS	ZnO	
Parameters			
$\sigma = m_e/m_h$	0.20 ^a	0.21 ^b	
m_e	0.20 ^a	0.24 ^c	
E_{ex} (meV)	27 ^a	59 ^d	
Computed results			
$(E - E_d)/E_d$ (%)	3.1	2.7	
$E - E_d$ (meV)	1.0	1.9	$[(E - E_d)/E_d \times E_{ex}(1 + \sigma)]$
$E - E_{ex}$ [Eq. (5)] (meV)	6.4	13.4	
$ \sum f(R, R) ^2$	31	29	
f_c [Eq. (6)]	255	180	
f_c/f_{exA}^e	1.0×10^5	0.69×10^5	
$\sum f(R, R) ^2/\Omega$ [a_h^{-3}]	0.45×10^{-3}	0.49×10^{-3}	
$\sum f(R, R) ^{2f}$	0.195×10^{-3}	0.375×10^{-3}	
Δ_0^g [Eq. (12)] (meV)	0.49	0.83	
Δ_{LR} [Eq. (15)] (meV)	-0.044	-0.061	(for 10^{16} centers/cm ³)
Δ_{exch} (meV)	0.45	0.77	
Experimental values			
Γ_{6-free} (eV)	2.55266 ^h	3.3758 ^d	
$(E - E_{ex})_{Expt}$ (meV)	4.66 - 7.10 ^h	11.3, 17.0, 20.9 ⁱ	
$(\Delta_{exch})_{Expt}$ (meV)	0.31 ^j	0.9 ^k	

^aReference 4.

^bReference 15.

^cW. Baer, Phys. Rev. **154**, 785 (1967).

^dD. G. Thomas, J. Phys. Chem. Solids **15**, 86 (1960).

^eD. G. Thomas and J. J. Hopfield, Phys. Rev. **116**, 573 (1959); Ref. 14.

^f $\Omega_{CdS} = 49.4 \text{ \AA}^3$, $\Omega_{ZnO} = 23.7 \text{ \AA}^3$ (per molecule), a_h is found from $a_h = 0.53 \text{ \AA} [13.6 \text{ eV} \times \sigma^2 / E_{ex}(1 + \sigma)m_e]^{1/2}$.

^g $J_0 = 2.2 \text{ eV}$ (ZnO, Ref. 14). For CdS, J_0 is found from $J_0 = \frac{1}{3}(\Delta_L + 2\Delta_T)\pi a_{ex}^3/\Omega$, where $\Delta_L = A_L - A_F$ and $\Delta_T = A - A_F$

from Ref. 4, and a_{ex} is the exciton radius [see also Eq. (28) in Ref. 14]. Result: $J_0 = 2.5 \text{ eV}$ for CdS.

^hReference 17.

ⁱI. Filinski and T. Skettrup, *Proceedings of the Ninth International Conference on the Physics of Semiconductors*, edited by S. M. Ryvkin (Nauka, Leningrad, 1968), p. 216.

^jReference 12.

^kReference 16.

exciton levels one is therefore restricted to use samples with $N_c < 10^{18} \text{ cm}^{-3}$ so that $\Delta_{LR} < \Delta_{free} \approx \Delta_0$. Hence, Δ_{LR} is usually only a minor correction to Δ_0 .

VI. COMPARISON WITH EXPERIMENT

The properties of the three-particle centers in CdS and ZnO have been computed by means of the results obtained in the previous sections. The values are given in Table I and compared with experimental results on these materials. The parameters used in the calculations are m_e/m_h , m_e , and E_{ex} . The values for m_e and m_h determined from experiments vary somewhat. We have chosen $m_e/m_h = 0.20$ for⁴ CdS and $m_e/m_h = 0.21$ for¹⁵ ZnO both of these being obtained from measurements on excitons. Thus, there are no adjustable parameters in

the calculation. The experimental energy separations which should be compared with the computed ones are those between the optically inactive states, because only these are insensitive to exchange.

The optically inactive free exciton ($\Gamma_{6,free}$) has been observed for both materials. The optically inactive bound exciton ($\Gamma_{6,bound}$) is found from the observed $\Gamma_{5,bound}$ line by subtracting the experimental exchange splittings.^{12,16} The binding energies quoted in Table I are the energy separations between the $\Gamma_{6,free}$ and the $\Gamma_{6,bound}$ exciton lines.

The observed values vary somewhat because the binding energies depend on the type of donor which bind the exciton.¹⁷ These effects of central-cell corrections for the different kinds of donors are not included in our calculations of the binding energies.

For CdS we compute a binding energy of 6.4 meV

whereas the experimental values vary from 4.6 to 7.1 meV. For ZnO we obtain 13.4 meV and experimental numbers range from 11.3 to 20.9 meV. Thus, for both materials we obtain a good agreement, since central-cell corrections are not considered here. Also the computed exchange splitting agree well with the observed values. The oscillator strengths are predicted to be 255 for CdS and 180 for ZnO. The oscillator strengths have not yet been measured. The computed values are 10–100 times greater than those reported for excitons bound to neutral centers.⁶ However, the fact that the three-particle centers are actually observed at helium temperature where only a few donors are ionized indicates that the strengths must be quite large.

VII. SUMMARY

Properties of the three-particle complex, consisting of an electron and a hole bound to an ionized donor have been computed as a function of m_e/m_h .

The ground-state energy was calculated in the effective-mass approximation by the variational method. The energy depends only on the mass ratio m_e/m_h and varies monotonically with this. The wave functions derived from the variational procedure were used for computing interparticle distances and oscillator strengths of the complex. The exchange splitting between states with parallel and antiparallel electron and hole spins was also computed, and it was found that long-range effects may be important when the concentration of centers is large. Finally the properties of the three-particle complexes in CdS and ZnO were calculated. By comparing with experimental values, good agreement was obtained.

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