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New method for the calculation of the binding energy of exciton complexes: The exciton–ionized-donor complex

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The Callan method for the helium atom has been developed for complicated exciton complexes. This method has been applied to the exciton–ionized-donor complex in CdS. With a mass ratio $\sigma = m_e^*/m_h^* = 0.182$, where m_e^* and m_h^* are the electron and hole effective masses, very good agreement with experiment has been obtained for the binding energies of the neutral donor, of the exciton, and of the complex itself. The value 1.7×10^4 for the relative oscillator strength obtained by this method can be compared with the best value 3.6×10^4 calculated by Suffczynsiki using a more complicated wave function. The simplification of this method and the good agreement with experiment for the exciton–ionized-donor complex indicate a substantial advance in the solution of complicated exciton complexes having more than three particles whatever the value of σ.

I. INTRODUCTION

The Pekeris[1,2] and Pluvinage[3–5] methods that were used for helium atoms have been developed extensively in previous papers[6–8] to apply to exciton complexes having three particles. Using these methods,[6–8] the binding energies for excitons bound to ionized donors have been calculated for several real systems of semiconductors. Good agreement with experiment has been obtained. Due to the limitations of the use of the perimetric coordinates,[9–12] the Pekeris method cannot be developed for systems having more than three particles. For such systems the Pluvinage method gives rise to quite complicated integrals which are difficult to solve without making some approximations. For exciton complexes of four particles various authors[13–16] have used the Born-Oppenheimer approximation in their calculations. This approximation is usually valid for a small mass ratio $\sigma = m_e^*/m_h^*$, where m_e^* and m_h^* are, respectively, the effective masses of the electron and the hole. On the other hand, complicated exciton complexes having five, six, eight, ..., etc., particles have been observed[17–19] recently. For this reason, it is of considerable interest to develop a method that can be applied to systems of any number of particles and that is valid for any value of σ. As the number of particles of the system increases, the integrals that one has to deal with become more complicated. Using the usual methods for systems of five particles, it is almost impossible to solve the problem. Any new method has to contain from the beginning an appropriate physical assumption to avoid such complicated integrals. In the case of systems of four particles the exchange integrals can be solved analytically instead of being computed numerically as in the other methods. The basic idea of the Callan[20,21] method for the helium atom could be considered as an appropriate physical assumption in solving such complicated exciton complexes. The Callan method truncates the interelectron Coulomb potential at a minimum distance R which is related to the energy available to the electrons, and uses a constant potential for smaller interelectronic distances. In this article, this method has been developed to apply, for example, to three-particle systems. Other advantages of the method presented in this paper are that one can calculate not only the binding energy of the complex E_c, but also the binding energies of the neutral donor E_D and the free exciton E_x, as well as the dielectric constants corresponding to the neutral donor K_D and the free exciton K_x. In the case of CdS, good agreement with experiment has been obtained for the quantities E_c, E_D, E_x, K_D, and K_x. Owing to the success of this method for such exciton–ionized-donor systems, its application to exciton–neutral-donor and neutral acceptor systems as well as the excitonic molecule are in progress. In these calculations, the effect of the polarizability has been considered and Haken's exciton potential[22] has been adopted. It should be noted that a somewhat similar approach to that of Callan[20,21] was taken by Clementi[23] with the deletion of a ring in the integrals to account for what is called in atomic physics the Coulomb hole.

II. FORM OF POTENTIAL

In solid-state physics the effective mass m^* and the dielectric constant K are used to reproduce the effects of the surroundings. The distances r_{ij} between any two particles i and j are screened by the dielectric constant K. This reduces the N-body problem to that of one particle. The exciton–ionized-donar complex can then be represented by three isolated particles, as shown in Fig. 1. Let r_{12}, r_{13}, and r_{23} be, respectively, the distances between the donor and the electron, the donor and the hole, and the two particles of the exciton. Tak-

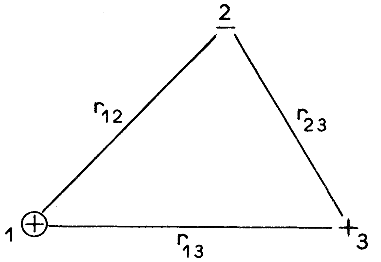

FIG. 1. Exciton–ionized-donor complex.

ing into account the effect of the polarizability of the lattice,[22] the dielectric constant between the hole and the electron of a delocalized exciton is a function of the distance r_{23}, of their effective masses, of the longitudinal vibrational frequency ω of the lattice, and of the optical (K_o) and the static (K_s) dielectric constants. Due to the effect of the polarizability of the lattice, the dielectric constants along the coordinates r_{12}, r_{23}, and r_{13} are no longer the same. The distances r_{12}, r_{23}, and r_{13} are then screened by the different dielectric constants $K(r_{12})$, $K(r_{23})$, and $K(r_{13})$, respectively. The Coulomb potentials along these coordinates are $-Z_1Z_2e^2/r_{12}K(r_{12})$, $-Z_2Z_3e^2/r_{23}K(r_{23})$, and $Z_1Z_3e^2/r_{13}K(r_{13})$, where e is the electron charge and Z_1, Z_2, and Z_3 are, respectively, the absolute values of the charge units on the fixed donor, the electron, and the hole.

Since atomic units in terms of a certain effective dielectric constant $K_{\rm eff}$ are usually adopted, the generalized[7] Haken's potential for any two particles i and j of effective masses m_i^* and m_j^* in a crystal can be written in the following form:

$$1/K(r_{ij}) = (1/K_{\rm eff})\{(Z_iZ_j)[(K_{\rm eff}/K_s)(1-\tfrac{1}{2}\zeta_{ij}) + (K_{\rm eff}/K_0)\tfrac{1}{2}\zeta_{ij}]\}\ , \qquad (1)$$

with

$$\zeta_{ij} = e^{-\kappa_i r_{ij}} + e^{-\kappa_j r_{ij}}\ , \qquad (2a)$$

$$\kappa_i = (2m_i^*\,\omega/\hbar)^{1/2}\ , \qquad (2b)$$

$$\kappa_j = (2m_j^*\,\omega/\hbar)^{1/2}\ . \qquad (2c)$$

For the exciton–ionized-donor complex shown in Fig. 1, the potential energy of the system is

$$V(r_{12},\ r_{13},\ r_{23}) = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\frac{e^2\lambda_{ij}}{K_{\rm eff}\,r_{ij}}\ , \qquad (3)$$

where λ_{12}, λ_{13}, and λ_{23} are the coefficients of the terms r_{12}, r_{13}, and r_{23}, respectively, and are given by the terms in brackets in Eq. (1).

Owing to the difficulty that may occur in solving the problem using the general potential of Eqs. (1)–(3), mean values of λ_{ij}'s should be used. Knowing an approximate wave function Φ for the system, one can write

$$\bar{\lambda}_{ij} = Z_iZ_j\left[\frac{K_{\rm eff}}{K_s} + \frac{1}{2}K_{\rm eff}\left(\frac{1}{K_o}-\frac{1}{K_s}\right)\left(\frac{\int\Phi\zeta_{ij}\Phi\,d\tau}{\int\Phi\Phi\,d\tau}\right)\right]. \qquad (4)$$

The mean values $\bar{\lambda}_{12}$, $\bar{\lambda}_{13}$, and $\bar{\lambda}_{23}$ are denoted by λ, μ, and ν, respectively. The values λ, μ, and ν depend on the fundamental constants m_e^*, m_h^*, K_o, K_s, and ω.

The binding energy of the complex shown in Fig. 1 can be calculated in terms of the neutral-donor binding energy E_D,

$$E_D = -m_e^*e^4/2\hbar^2K_D^2\ . \qquad (5)$$

The dielectric constant $K_D = K(r_{12}) = K_{\rm eff}$ is evaluated using $\lambda = 1$. In this case the atomic units $\hbar^2K_{\rm eff}/m_e^*e^2$ and $m_e^*e^4/\hbar^2K_{\rm eff}^2$ will be adopted for length and energy, respectively, and the units $m_e^* = \hbar = 1$ and $e^2/K_{\rm eff} = 1$ will be used. The binding energy E_D is simply then equal to $\frac{1}{2}$ a.u. and the mass ratio $\sigma = 1/m_h^*$ a.u. In these atomic units, the attractive potentials between the particles 1-2 and 2-3 are, respectively, $-\lambda/r_{12}$ and $-\nu/r_{23}$, while the repulsive potential is μ/r_{13}.

An atomic system such as He or H^- could be considered as a particular case of Fig. 1. Such an atomic system can be obtained simply by replacing the positive hole (particle 3) of Fig. 1 by an electron of negative charge (Fig. 2). Neglecting the effect of the polarizability and using the same atomic units with $K_{\rm eff} = 1$, which is the case in atomic physics, the attractive potentials between the particles 1-2 and 1-3 of Fig. 2 having the same charge units $Z = Z_1Z_2 = Z_1Z_3$ are, respectively, $-Z/r_{12}$ and $-Z/r_{13}$. To pass from Fig. 1 to Fig. 2, one has simply to change the sign of μ and ν and to consider the particular case $\sigma = 1$. The coefficients λ and μ of Fig. 1 then correspond to what is denoted by Z in Fig. 2. In this case the absolute values of λ and μ are equal (polarizability neglected) and correspond to the same value of Z.

III. METHOD OF SOLUTION

In these atomic units with $E_D = \frac{1}{2}$ a.u. and using the classical treatment of Hylleraas, the Schrödinger equation for the system shown in Fig. 1 can be written in the form

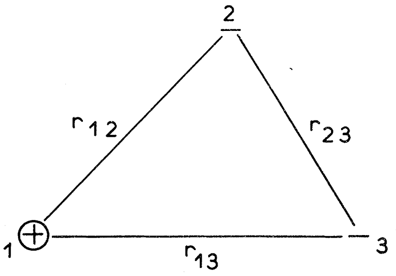

FIG. 2. Three-particle atomic system, for example, He or H^-.

$$\frac{1}{2}\left[\frac{\partial^2\psi}{\partial r_{12}^2}+\frac{2}{r_{12}}\left(\frac{\partial\psi}{\partial r_{12}}\right)\right]+\frac{\sigma}{2}\left[\frac{\partial^2\psi}{\partial r_{13}^2}+\frac{2}{r_{13}}\left(\frac{\partial\psi}{\partial r_{13}}\right)\right]+\frac{1}{2}\,(1+\sigma)\left[\frac{\partial^2\psi}{\partial r_{23}^2}+\frac{2}{r_{23}}\left(\frac{\partial\psi}{\partial r_{23}}\right)\right]+\frac{1}{2}\left(\frac{\partial^2\psi}{\partial r_{12}\,\partial r_{23}}\right)\frac{1}{r_{12}r_{23}}$$

$$\times(r_{12}^2+r_{23}^2-r_{13}^2)+\frac{\sigma}{2}\left(\frac{\partial^2\psi}{\partial r_{13}\,\partial r_{23}}\right)\frac{1}{r_{13}r_{23}}\,(r_{13}^2+r_{23}^2-r_{12}^2)+\left(E+\frac{\lambda}{r_{12}}-\frac{\mu}{r_{13}}+\frac{\nu}{r_{23}}\right)\psi=0\,. \qquad (6)$$

The effects of the polarizability between the three particles of Fig. 1 are expressed in terms of λ/Z_1Z_2, μ/Z_1Z_3, and ν/Z_2Z_3. These quantities play an important role[6,8] in the solid state and are usually neglected in atomic systems such as He and H^- of Fig. 2. Again mathematically the coefficients λ and $-\mu$ of Eq. (6) correspond to the charge unit Z for He and H^-. The screening of the distances r_{ij} by the dielectric constants and the effect of the polarizability in the solid state then transform the mathematical treatment of exciton complexes into a general three-particle atomic-physics problem given in Eq. (6). The values of λ, μ, ν, and σ of Eq. (6) always take either integer or noninteger values. The integer numbers for these quantities correspond to particular cases that represent the atomic systems. The exciton complexes usually belong to the noninteger number category. Equation (6) then no longer concerns only a problem of the solid state, but is a general form for any three-particle system in atomic physics. For instance, the particular cases with $\sigma=1$, the He atom[6,24] and H^- ion,[24] correspond, respectively, to the two sets of values $\lambda=2$, $\mu=-2$, $\nu=-1$, and $\lambda=1$, $\mu=\nu=-1$. Thus all the possible methods used in atomic physics by Pekeris,[1] Pluvinage,[3,4] and Callan,[20,21] or any variational calculations which take into account the charge screening[25–27] (effective charge) for helium, can be applied successfully in solving Eq. (6) for the exciton–ionized-donor complex. The only difference between exciton complexes and atomic systems comes in at the end when one tries to convert, for instance, the length and energy into Å and eV. In this case, for atomic systems $K_{\text{eff}}=1$ and $m_e^*=m_0$, where m_0 is the free-electron mass.

The one big difficulty met by the different authors in trying to solve completely the three- and four-particle systems is the singularity that occurs in the exchange integral from 0 to ∞. Also the correlation effect[1,3,4,6,8] incorporated into the wave function itself that contains the repulsive-potential coordinates r_{23} (Fig. 1) or r_{13} (Fig. 2) complicates the calculations. To avoid this singularity and meantime include the correlation effect, Callan's idea[20,21] to consider only this integral from $\int_R^\infty$ instead of $\int_0^\infty$ tremendously simplifies the different calculations and can even be helpful in solving systems having more than four particles. In this case the wave function does not include the coordinate r_{23} (Fig. 2). The results[20] obtained for helium are quite comparable to those given by Pekeris[1] method, which is one of the most complicated treatments.

There are, of course, some differences between the exciton–ionized-donor complex of Fig. 1 and that of helium. For example, in exciton complexes, it is preferable to use the terminology of interparticle coordinates or interparticle distances rather than the corresponding interelectron quantities in the usual atomic systems. This is due to the fact that in exciton complexes the particles are not only of one type, as in atomic systems, but are of two kinds, namely, electrons and holes of different effective masses. Meanwhile, Eq. (6) is valid for an exciton complex as well as for any atomic system of three particles. In this case, there exists a new criterion that one does not find in atomic systems. With $\sigma=0$, for instance, in an exciton–ionized-donor complex, the system turns out to be the H_2^+ ion. The solution for such a complex has to take into consideration such a criterion. Also for exciton complexes the polarizability[6–8,28] plays an important role that has to be taken into account. The value of R that represents the lower limit of the integral μ/r_{13} can then be chosen such that for $\lambda=\mu=\nu=1$ (polarizability neglected) one has to get the well-known value (0.6 a.u.) for the binding energy of H_2^+ that corresponds to $\sigma=0$.

In Callan's method[20,21] the total wave function is given simply by the product of bound-state hydrogenic wave functions, which correspond to attractive Coulomb potentials, for the nuclear coordinates. In this wave function the interacting charge $Z=2$, which is the same for the attractive potentials along the coordinates r_{12} and r_{13}, has been screened as usual[25–27] by the variational parameter β determined from the minimization of energy. The approximate wave function for He corresponding to the totally uncorrelated hydrogenic-type atoms treated by Kellner[29] has been written in the form

$$\Phi_1=e^{-(Z-\beta)(r_{12}+r_{13})}\,. \qquad (7)$$

For the exciton–ionized-donor complex the attractive potentials corresponding to bound hydrogenic states are along the coordinates r_{12} and r_{23} (Fig. 1). In Eq. (6) the coefficients λ and ν of these two potentials are not the same as in the case of He along r_{12} and r_{13} (Fig. 2). They are different due to the polarizability effect. To follow the same technique as in atomic physics, the screening procedure for both λ and ν leads to the use of two different variational parameters σ_1 and σ_3, instead of only

TABLE I. Fundamental constants for CdS.

	m_e^*	$m_{h\perp}^*$	$m_{h\parallel}^*$	σ	$K_{s\perp}$	$K_{s\parallel}$	K_s	K_o	ω
CdS I	0.18[a,b]			0.182					
CdS II	0.171[c,d]	0.7[e] (Ref. 26)	5[e]	0.173	9.35 (Ref. 29)	10.33 (Ref. 29)	9.8278	5.24 (Ref. 29)	306
CdS III	0.205[e]			0.207					

[a] D. C. Reynolds, C. W. Litton, and T. C. Collins, Phys. Rev. 174, 845 (1968).

[b] D. C. Reynolds and T. C. Collins, Z. Naturforsch. 249, 1311 (1969).

[c] K. Kobayashi, in *International Conference on II–VI Semiconducting Compounds*, *Providence*, *Rhode Island*, 1967, edited by D. G. Thomas (Benjamin, New York, 1968), p. 735.

[d] W. S. Baer and R. N. Dexter, Phys. Rev. 135, A1388 (1964); K. Sawamoto, J. Phys. Soc. Jpn. 19, 318 (1964); M. Suffczynski, W. Gorzkowski, and R. Kowalczyk, Phys. Lett. 24A, 453 (1967).

[e] J. J. Hopfield and D. G. Thomas, Phys. Rev. 122, 35 (1961); J. O. Dimmock, in Ref. c, p. 2; B. Segall, *ibid.*, p. 327.

one for Z in the case of He [Eq. (7)]. Following Callan's method and applying this screening technique as in atomic physics[20,21,25–27] to Eq. (6), the approximate totally uncorrelated wave function Φ can be expressed as the product of the two bound hydrogenic wave functions. The solution can be written in the form

$$\Phi = e^{-\lambda_1 r_{12}} e^{-\nu_1/(1+\sigma) r_{23}} , \tag{8}$$

with

$$\lambda_1 = \lambda - \sigma_1 \quad \nu_1 = \nu - \sigma_3 , \tag{9}$$

where σ_1 and σ_3 are positive variational parameters determined from the minimization of the energy of the system. Another alternative solution of Eq. (6) is to consider the approximate wave function (8) with λ_1 and ν_1 themselves as the variational parameters, instead of σ_1 and σ_3 of Eq. (9). The calculated values of λ_1 and ν_1 will certainly be different from those of λ and ν. The differences between them can be interpreted as being due to the charge screening. Since the technique given in Eqs. (8) and (9) is quite similar to that of Eq. (7) commonly used for He, it is quite logical to apply a procedure such as that of Eq. (9). It is also worth mentioning that the screening procedure of Eqs. (8) and (9) has already been quite successful[8] in treating the same complex by the Pluvinage method,[3,4] and an excellent agreement with experiment has been obtained[8] in CdSe.

In Callan's method the value of R has been determined by the minimization of energy. The purpose of the present work is to develop a method for solving complexes having a large number of particles which already exist experimentally. Consequently, one expects to deal with a large number of variational parameters, which usually requires a great deal of computer time. Thus the determination of R—not as a variational parameter but such that the correct binding energy is obtained for the corresponding $\sigma = 0$ system—is justified. Another strong justification for the determination of R in this manner is the excellent agreement with experiment reported in this paper for the exciton and neutral-donor dielectric constants K_x and K_D as well as for the binding energies of the neutral donor E_D, of the free exciton E_x, and of the complex itself $(E - E_D)$. This agreement obtained simultaneously for these quantities has never been found by any other, even a sophisticated, theoretical treatment.

With the wave function given in Eq. (8), the total energy is

$$E = -\frac{\lambda_1^2}{2} + (\lambda_1 - \lambda)\frac{I_1}{N} - \frac{\nu_1^2}{2(1+\sigma)} + (\nu_1 - \nu)\frac{I_2}{N} + \frac{I_3}{N} + I_4, \tag{10}$$

where N is the normalization constant

$$N = \int \Phi\Phi \, d\tau = \frac{2}{ab}\left(\frac{1}{a^2} - \frac{1}{b^2}\right)\left(\frac{1}{d^2} - \frac{1}{c^2}\right) + 2\left[\frac{1}{a}\left(\frac{1}{d^3} - \frac{1}{c^3}\right) + \frac{1}{b}\left(\frac{1}{d^3} + \frac{1}{c^3}\right)\right], \tag{11}$$

$$I_1 = \int \frac{\Phi\Phi}{r_{12}} d\tau = \frac{2}{ab}\left[\left(\frac{1}{a} - \frac{1}{b}\right)\left(\frac{1}{d^2} - \frac{1}{c^2}\right) + \frac{4}{d^3}\right], \tag{12}$$

$$I_2 = \int \frac{\Phi\Phi}{r_{23}} d\tau = \frac{2}{ab}\left[\left(\frac{1}{a} + \frac{1}{b}\right)\left(\frac{1}{d^2} - \frac{1}{c^2}\right) - \frac{4}{c^3}\right], \tag{13}$$

$$\begin{aligned} I_3 = \int \frac{\Phi\Phi}{r_{13}} d\tau = \frac{2}{ab}\bigg[&\frac{1}{d}\left(\frac{1}{a^2} - \frac{1}{b^2}\right) e^{-dR} + \left(\frac{1}{a} + \frac{1}{b}\right) \\ &\times \left(\frac{1}{d}\right) e^{-dR}\left(R + \frac{1}{d}\right) - \frac{1}{c}\left(\frac{1}{a^2} - \frac{1}{b^2}\right) e^{-cR} \\ &- \left(\frac{1}{a} - \frac{1}{b}\right) e^{-cR}\frac{1}{c}\left(R + \frac{1}{c}\right)\bigg], \end{aligned} \tag{14}$$

$$\begin{aligned} I_4 &= -\frac{1}{2N}\int (r_{12}^2 + r_{23}^2 - r_{13}^2)\left(\frac{1}{r_{12} r_{23}}\right)\left(\frac{\partial^2 \Phi}{\partial r_{12}\,\partial r_{23}}\right)\Phi \, d\tau \\ &= -\frac{\lambda_1 \nu_1}{1+\sigma} + \frac{2}{b}\left(\frac{\lambda_1 \nu_1}{1+\sigma}\right)\left(\frac{1}{c} + \frac{1}{d}\right)\left[2\left(\frac{1}{c^2} - \frac{1}{cd} + \frac{1}{d^2}\right) + \frac{1}{b}\left(\frac{1}{c} - \frac{1}{d}\right)\right]\Big/\frac{ab}{2} N, \end{aligned} \tag{15}$$

with

$$a=\lambda_1+\nu_1/(1+\sigma),\quad b=\lambda_1-\nu_1/(1+\sigma),\quad c=a+b=2\lambda_1,\quad d=a-b=2\nu_1/(1+\sigma). \tag{16}$$

Using the approximate wave function Φ of Eq. (8), the mean values λ, μ, and ν are given by

$$\lambda=K_D/K_s+\tfrac{1}{2}K_D\left(\frac{1}{K_o}-\frac{1}{K_s}\right)\frac{2}{Na'b'}\left\{\left(\frac{1}{a'^2}-\frac{1}{b'^2}\right)\left(\frac{1}{d'^2}-\frac{1}{c'^2}\right)+2\left[\frac{1}{a'}\left(\frac{1}{d^3}-\frac{1}{c'^3}\right)+\frac{1}{b'}\left(\frac{1}{d^3}+\frac{1}{c'^3}\right)\right]\right\}, \tag{17}$$

$$\begin{aligned}\mu=\frac{K_D}{K_s}+\tfrac{1}{2}K_D\left(\frac{1}{K_o}-\frac{1}{K_s}\right)\frac{2}{abN}\Bigg(&\left(\frac{1}{a^2}-\frac{1}{b^2}\right)\left[\left(\frac{R}{d'''}+\frac{1}{d'''^2}\right)e^{-d'''R}-\left(\frac{R}{c_4}+\frac{1}{c_4^2}\right)e^{-c_4R}\right]\\&+R^2\left[\frac{1}{a}\left(\frac{1}{d'''}e^{-d'''R}-\frac{1}{c^4}e^{-c_4R}\right)+\frac{1}{b}\left(\frac{1}{d'''}e^{-d'''R}+\frac{1}{c_4}e^{-c_4R}\right)\right]\\&+\frac{2}{\alpha}\left[\frac{1}{d'''^2}\left(R+\frac{1}{d'''}\right)e^{-d'''R}-\frac{1}{c_4^2}\left(R+\frac{1}{c_4}\right)e^{-c_4R}\right]+\frac{2}{b}\left[\frac{1}{d'''^2}\left(R+\frac{1}{d'''}\right)e^{-d'''R}+\frac{1}{c_4^2}\left(R+\frac{1}{c_4}\right)e^{-c_4R}\right]\Bigg),\end{aligned} \tag{18}$$

$$\begin{aligned}\nu=\frac{K_D}{K_s}+K_D\left(\frac{1}{K_o}-\frac{1}{K_s}\right)\left(\frac{1}{N}\right)\Bigg(&\left(\frac{1}{a'b''}\right)\left\{\left(\frac{1}{a'^2}-\frac{1}{b''^2}\right)\left(\frac{1}{d''^2}-\frac{1}{c^2}\right)+2\left[\frac{1}{a}\left(\frac{1}{d''^3}-\frac{1}{c^3}\right)+\frac{1}{b''}\left(\frac{1}{d''^3}\right.\right.\right.\\&\left.\left.\left.+\frac{1}{c^3}\right)\right]\right\}+\frac{1}{a''b'''}\left\{\left(\frac{1}{a''^2}-\frac{1}{b'''^2}\right)\left(\frac{1}{d'''^2}-\frac{1}{c^2}\right)+2\left[\frac{1}{a''}\left(\frac{1}{d'''^3}-\frac{1}{c^3}\right)+\frac{1}{b'''}\left(\frac{1}{d'''^3}+\frac{1}{c^3}\right)\right]\right\}\Bigg),\end{aligned} \tag{19}$$

$$\begin{aligned}&a'=\lambda_1+\tfrac{1}{2}\kappa_e+\nu_1/(1+\sigma),\\&b'=\lambda_1+\tfrac{1}{2}\kappa_e-\nu_1/(1+\sigma),\\&c'=a'+b',\quad d'=a'-b',\\&b''=\lambda_1-\tfrac{1}{2}\kappa_e-\nu_1/(1+\sigma),\quad d''=a'-b'',\\&a''=\lambda_1+\tfrac{1}{2}\kappa_h+\nu_1/(1+\sigma),\\&b'''=\lambda_1-\tfrac{1}{2}\kappa_h-\nu_1/(1+\sigma),\\&c_4=a+b+\kappa_h,\quad d'''=a-b+\kappa_h,\\&\kappa_e=(2m_e^*\omega/\hbar)^{1/2},\quad \kappa_h=(2m_h^*\omega/\hbar)^{1/2}.\end{aligned} \tag{20}$$

To compute the oscillator strength f_3 of the exciton–ionized-donor complex, the formula given by Glauberman *et al.*[30,31] is used:

$$f_3=f_x(\pi a_x^3/\Omega)\,F(m_e^*/m_h^*), \tag{21}$$

$$F(m_e^*/m_h^*)=\left|\int_{r_{12}=r_{13}}\Phi(r_{12},r_{13})\,d^3r_{12}\right|^2\Big/N. \tag{22}$$

In these equations f_x and a_x are, respectively, the oscillator strength and the radius of the free exciton, Ω is the volume of the elementary cell, and N is the normalization factor expressed by Eq. (11).

IV. COMPUTATIONS AND COMPARISON WITH EXPERIMENT

The experimental values for $(E-E_D)/E_D$, E_D, E_x and K_x corresponding to exciton–ionized-donor complex in CdS are known quantitatively.[32–36] Furthermore, for this semiconductor the values of $(E-E_D)/E_D$ calculated either by Suffczynski *et al.*[31,37] or by the sophisticated method developed previously by the author[6] are still in poor agreement with experiment. For instance, the best calculated value[6] for this quantity is 3.5×10^{-2}, which is compared to 2.5×10^{-2} obtained from experiment.[31,32] This semiconductor can then be considered as a test for the method described in this paper. The calculations are carried out for the different available values of the electron effective masses. The program SIMPLEX[38] written in double precision for a UNIVAC 1108 computer has been used to calculate the minimum of the energy E in Eqs. (10)–(20). This minimum corresponds to certain values of R, σ_1, and σ_3. For $\sigma=0$ and $\lambda=\mu=\nu=1$, the value of R has been chosen such that the binding energy of the system corresponds exactly to the value known for H_2^+. Using this value of $R=1.1091$ a.u. the value of K_D has been chosen such that

TABLE II. Calculated values of λ, μ, ν, σ_1, σ_3, K_x, and K_D in CdS.

	λ	μ	ν	σ_1	σ_3	K_x	K_D
CdS I	1.000 00	0.984 003	1.031 19	0.2	0.6	8.757 8	9.031
CdS II	1.000 00	0.987 902	1.035 31	0.205 25	0.601 25	8.754 1	9.063 2
CdS III	1.000 00	0.977 768	1.028 05	0.203	0.588	8.723 3	8.968

TABLE III. Experimental and calculated values for K_x, E_x, E_D, and $(E-E_D)/E_D$ in CdS.

	K_x	E_x (meV)		E_D (meV)		$10^2\ (E-E_D)/E_D$	
	Expt.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
CdS I	8.67 (Ref. 31)	28 (Refs. 27 and 28)	27.1995	32.8 (Refs. 27 and 28)	30.234	2.5	2.435
CdS II			26.06		28.519		2.673
CdS III			30.627		34.919		2.115

$\lambda = 1$, and the calculations have been carried out in a self-consistent manner to obtain reasonable agreement with experiment, at least for the binding energy E_D of the neutral donor. The justification for this procedure of the determination of R is discussed in Sec. III. The values of σ_1 and σ_3 corresponding to the minimum energy of the system can be determined. In Table I the different values of the fundamental constants m_e^*, m_h^*, K_s, K_o, and ω for CdS I, CdS II, and CdS III are given. In Table II the calculated values of λ, μ, ν, σ_1, σ_3, K_x, and K_D are reported for this semiconductor. The experimental values of K_x, E_x, E_D, and $(E-E_D)/E_D$ as well as the calculated values of E_x, E_D, and $(E-E_D)/E_D$ are compared in Table III for the three different types of CdS considered. From Tables II and III one can see that the electron effective mass $m_e^* = 0.18$ corresponding to CdS I gives the best agreement with experiment. From Table III one can notice that the value $(E-E_D)/E_D = 2.435 \times 10^{-2}$ calculated from the method developed in this paper is in better agreement with experiment than 3.5×10^{-2}, reported previously[6] using the sophisticated Pekeris method. Table II shows that for all the three types of CdS the values of σ_3 are generally greater than those of σ_1. This result is quite appropriate to the physical picture in which the screening between the exciton particles is greater than that between the electron and the fixed hole (Fig. 1). The values of μ calculated in Table II are slightly different from unity,[39] which is the value of λ. In this case the dielectric constant between the hole of the exciton and the fixed hole of the neutral donor is different from K_D, which is in turn different from K_s. With the three different available values of the effective mass m_e^* corresponding to CdS I, CdS II, and CdS III the static dielectric constant K_s does not correspond to the experimental value of E_D. In the aspect of the hydrogenic formula of Eq. (5), once the calculated value of E_D is in agreement with experiment, the dielectric constant K_D also has to be in agreement with a corresponding experimental value. In this problem one can conclude that there are five different types of dielectric constants: the optical dielectric constant K_o, the static dielectric constant K_s, the dielectric constant K_D of the neutral donor, the dielectric constant K_x of the exciton, and finally the dielectric constant between the hole of the exciton and the fixed hole of the neutral donor.

With the wave function Φ of Eq. (8) and $\Omega = 49.4 \times 10^{-24}$, the value $f_3/f_x = 1.7 \times 10^4$ is obtained from Eqs. (21) and (22) for the relative oscillator strength corresponding to CdS I. This value is one order of magnitude smaller than that given in Ref. 30. On the other hand, it can be compared to those obtained by Rashba[40] (5×10^4) using a phenomenological theory and those obtained by Suffczynski[37] (3.6×10^4), whose wave function is more complicated than that of Eq. (8). The agreement between the method presented in this paper and other theories for the relative oscillator strength is another strong argument for the validity of such a method.

The simplification of this method and the agreement with experiment for the exciton–ionized-donor complex in CdS indicate a substantial advance in the solution of the complicated exciton complexes. The truncation of the Coulomb repulsive potential at a distance R seems to be quite appropriate physically. This is also adequate due to the fact that two like charges cannot get closer than a certain distance from each other. The development of this method as applied to the exciton–neutral-donor or neutral acceptor complex, as well as to the excitonic molecule, is in progress.

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