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†Present address: Raytheon Research Division, Waltham, Mass. 02154.

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Excitons Bound to Ionized Impurities: Calculation of the Binding Energies of Exciton—Ionized-Donor Complexes*

S. G. Elkomoss

Laboratoire de Spectroscopie et d'Optique du Corps Solide, † *Institut de Physique, Strasbourg, France*

The method given by Pekeris for the helium atom and generalized recently by Frost for the three-particle system has been developed extensively to apply to complexes of excitons bound to ionized impurities in semiconductors. Haken's exciton potential is generalized for the complex, and the dielectric constant between the different particles is a function of the interparticle distances. This potential is different from that given by Schroder and Birman, where the ionic polarizability has been neglected. An elaborate general recursion relation is obtained. The application of this relation to the case of ionized donors shows the importance of the corrections introduced due to the polarizability of the potential between the particles. The calculations also show that the critical mass ratio below which the system is stable depends not only on the wave function, but also on the distances between the particles as well as on the fundamental constants: the optical and static dielectric constants, the effective masses of the electron and the hole, and the longitudinal vibrational frequency of the lattice. The results for exciton—ionized-donor complexes in CdS, CdTe, ZnSe, ZnTe, and ZnO give better agreement with experiment than those reported by the previous authors where the polarizibility has been neglected. The calculations also confirm the existence of such a complex for 6H SiC. The exciton binding energies calculated for TlCl and TlBr are in better agreement with experiment than those given previously.

I. INTRODUCTION

In semiconductors, experimental evidence[1-34] has shown the existence of excitons bound to ionized donors and acceptors. Using the variational-principle technique, different authors have calculated the binding energies of these complexes.[35-42] These binding energies are a function of the variable $\sigma = m_e^* / m_h^*$, where m_e^* and m_h^* are, respectively, the effective masses of the electron and the hole. A critical value σ_c is usually found below which the system is stable. Unfortunately, the theoretical results in Refs. 35–42 do not agree with each other, and different values of σ_c have been reported. Thus, it is of interest to carry out some exact calculations for these complexes. The method given by Pekeris[43] for the helium atom and generalized recently by Frost[44-46] for the three-particle system

has been developed further. This method has the advantage of avoiding all the elaborate integrals that occur in the variational technique. The effect of polarizability given by Haken's potential[47] is used to some extent in the present calculations. The complexes bound to donors of single, double, and triple degree of ionization are treated, and comparison is made with experiment for some real systems.

II. FORM OF THE POTENTIAL

As described by Haken,[47] the dielectric constant $K(r_{12})$ between the hole and the electron of a delocalized exciton is a function of the distance r_{12} separating the two particles, of their effective masses, of the optical (K_0) and the static (K_s) dielectric constants, and of the longitudinal frequency ω of the lattice. This dielectric constant $K(r_{12})$ is given by the following expression:

$$\frac{1}{K(r_{12})} = \frac{1}{K_0} + \left(\frac{1}{K_s} - \frac{1}{K_0} \right) \left[1 - \tfrac{1}{2}(e^{-\kappa_e r_{12}} + e^{-\kappa_h r_{12}}) \right] ,$$

$$(1)$$

with

$$\kappa_e = (4\pi m_e^* \omega/h)^{1/2} , \quad \kappa_h = (4\pi m_h^* \omega/h)^{1/2} ,$$

$$(2)$$

where h is Planck's constant. If

$$\zeta = e^{-\kappa_e r_{12}} + e^{-\kappa_h r_{12}} ,$$

$$(3)$$

then Eq. (1) can be written in the form

$$\frac{1}{K(r_{12})} = (1 - \tfrac{1}{2}\zeta) \frac{1}{K_s} + \tfrac{1}{2}\zeta \frac{1}{K_0} .$$

$$(4)$$

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 electron, the fixed donor, and the hole.

Recently Schroder and Birman[48] have derived a potential form similar to that given in Eq. (10). In this potential, the electronic polarizability only has been considered. This assumption is usually valid for localized excitons. However these authors[48] did not apply their potential in further computations.

The binding energy E_D of the neutral donor, which is usually slightly greater in absolute value than that of E_x, is generally given by

$$E_D = -m_e^* e^4/2K^2 \hbar^2 ,$$

$$(11)$$

The exciton lines in different semiconductors generally follow a Rydberg series with a certain dielectric constant K. The binding energy E_x of the line $n = 1$ is given by the approximate hydrogenic formula

$$E_x = -Me^4/2K^2\hbar^2 ,$$

$$(5)$$

with $\hbar = h/2\pi$, M, the exciton reduced mass, and K, simply equal to $K(r_{12})$ given by Eq. (4). As atomic units in terms of a certain effective dielectric constant will be adopted in this article, Eq. (4) is rewritten in the following form:

$$\frac{1}{K(r_{12})} = \frac{1}{K_{eff}} \left((1 - \tfrac{1}{2}\zeta) \frac{K_{eff}}{K_s} + \tfrac{1}{2}\zeta \frac{K_{eff}}{K_0} \right) .$$

$$(6)$$

Consider the case of an exciton bound to an ionized donor, where the donor is supposed to be of infinite mass. For the interactions between the electron and the hole with the fixed donor, the two similar expressions of the dielectric constants $K(r_1)$ and $K(r_2)$ are

$$\frac{1}{K(r_1)} = \frac{1}{K_{eff}} \left((1 - \tfrac{1}{2}\xi) \frac{K_{eff}}{K_s} + \tfrac{1}{2}\xi \frac{K_{eff}}{K_0} \right) ,$$

$$(7)$$

$$\frac{1}{K(r_2)} = \frac{1}{K_{eff}} \left((1 - \tfrac{1}{2}\eta) \frac{K_{eff}}{K_s} + \tfrac{1}{2}\eta \frac{K_{eff}}{K_0} \right) ,$$

$$(8)$$

where

$$\xi = e^{-\kappa_e r_1}, \quad \eta = e^{-\kappa_h r_2} ,$$

$$(9)$$

r_1 is the distance between the electron and the fixed donor, and r_2 is that between the donor and the hole. From Eqs. (6)–(8) the potential energy of the system is

$$V(r_1, r_2, r_{12}) = - \frac{e^2}{K_{eff}} \left[\frac{Z_1 Z_2}{r_1} \left(\frac{K_{eff}}{K_s}(1 - \tfrac{1}{2}\xi) + \tfrac{1}{2}\xi \frac{K_{eff}}{K_0} \right) \right.$$

$$\left. - \frac{Z_2 Z_3}{r_2} \left(\frac{K_{eff}}{K_s} (1 - \tfrac{1}{2}\eta) + \tfrac{1}{2}\eta \frac{K_{eff}}{K_0} \right) + \frac{Z_1 Z_3}{r_{12}} \left(\frac{K_{eff}}{K_s} (1 - \tfrac{1}{2}\zeta) + \tfrac{1}{2}\zeta \frac{K_{eff}}{K_0} \right) \right] , \quad (10)$$

where K in this equation is that given by Eq. (7). The atomic units $K_{eff} \hbar^2/e^2 m_e^*$ and $m_e^* e^4/K_{eff}^2 \hbar^2$ will be adopted for length and energy, respectively, and the units $m_e^* = \hbar = 1$ and $e^2/K_{eff} = 1$ will be used. In this case, the energy E_D of Eq. (11) is simply $\tfrac{1}{2}$ a.u. and K_{eff} in the expressions (6)–(8) is equal to $K(r_1)$. Consequently, the term between brackets on the right-hand side of Eq. (7) is equal to unity.[49] In these units the energy E of the complex can be given in terms of E_D.

In atomic units, the nonrelativistic Schrödinger equation written for the system is

$$\tfrac{1}{2}\nabla_e^2 \Psi + \tfrac{1}{2}\sigma\nabla_h^2\Psi + \left[E + \left(\frac{\lambda_1}{r_1} - \frac{\mu_2}{r_2} + \frac{\nu_{12}}{r_{12}} \right) \right] \Psi = 0 , \quad (12)$$

where ∇_e^2 is the Laplacian for the electron, ∇_h^2 is

that for the hole, and λ_1, μ_2, and ν_{12} are, respectively, the coefficients in atomic units of the terms $1/r_1$, $1/r_2$, and $1/r_{12}$ of the potential (10). These coefficients, again in a.u., are given by the following expressions:

$$\lambda_1 = Z_1 Z_2 [(K_{eff}/K_s)(1 - \tfrac{1}{2}\xi) + \tfrac{1}{2}\xi (K_{eff}/K_o)] , \quad (13)$$

$$\mu_2 = Z_2 Z_3 [(K_{eff}/K_s)(1 - \tfrac{1}{2}\eta) + \tfrac{1}{2}\eta(K_{eff}/K_o)] , \quad (14)$$

$$\nu_{12} = Z_1 Z_3 [(K_{eff}/K_s)(1 - \tfrac{1}{2}\zeta) + \tfrac{1}{2}\zeta(K_{eff}/K_o)] , \quad (15)$$

with

$$\xi = e^{-\kappa_e r_1} = \exp[-(2\omega)^{1/2} r_1] , \quad (16)$$

$$\eta = e^{-\kappa_h r_2} = \exp\{-[(2/\sigma)\omega]^{1/2} r_2\} , \quad (17)$$

$$\zeta = e^{-\kappa_e r_{12}} + e^{-\kappa_h r_{12}} = \exp[-(2\omega)^{1/2} r_{12}]$$
$$+ \exp\{-[(2/\sigma)\omega]^{1/2} r_{12}\} . \quad (18)$$

In these calculations the values of Z_1 and Z_3 are always taken as unity, while $Z_2 = 1, 2$, and 3 correspond, respectively, to singly, doubly, and triply ionized donors.

The solution of Eq. (12) using the general potential (10) is difficult. For simplification the mean values of λ_1, μ_2, and ν_{12} have been considered. In this case one needs to know the wave function and the self-consistent procedure has to be applied throughout the different computations. The mean values of λ_1, μ_2, and ν_{12} are denoted by λ, μ, and ν, respectively. The values of λ, μ, and ν depend on the fundamental constants m_e^*, m_h^*, K_s, K_o, and ω. For a particular semiconductor there corresponds a set of values of λ, μ, and ν. To show the effect of polarizability and the variation of the dielectric constant between the different particles, some interesting cases corresponding to specific values of λ, μ, and ν are treated. The case $\lambda = \mu = \nu = 1$ corresponds to an effective dielectric constant supposed to be the same for the three particles. This is usually the case considered by other authors, with the exception that they have been concerned with the static K_s instead of an effective dielectric constant K_{eff}. The case $\lambda = \nu = 1$ and $\mu = 0.95$ corresponds to an effective dielectric con-

stant between the electron and the hole equal to that between the electron and the donor with a different dielectric constant between the hole and the donor. For comparison with experiment, computations for real systems such as CdS, CdTe, ZnSe, ZnTe, ZnO, SiC 6H, TlCl, and TlBr have been carried out.

III. METHOD OF SOLUTION

With the classical method of Hylleraas,[50] Eq. (12) can be written in the following form:

$$\frac{\partial^2 \Psi}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial \Psi}{\partial r_1} + \sigma\left(\frac{\partial^2 \Psi}{\partial r_2^2} + \frac{2}{r_2}\frac{\partial \Psi}{\partial r_2}\right) + (1+\sigma)\frac{\partial^2 \Psi}{\partial r_{12}^2}$$

$$+ \frac{2}{r_{12}}(1+\sigma)\frac{\partial \Psi}{\partial r_{12}} + \frac{\partial^2 \Psi}{\partial r_1 \partial r_{12}}(r_1^2 + r_{12}^2 - r_2^2)$$

$$\times \frac{1}{r_1 r_{12}} + \sigma\frac{\partial^2 \Psi}{\partial r_2 \partial r_{12}}\frac{1}{r_2 r_{12}}(r_2^2 + r_{12}^2 - r_1^2)$$

$$+ 2\left[E + \left(\frac{\lambda}{r_1} - \frac{\mu}{r_2} + \frac{\nu}{r_{12}}\right)\right]\Psi = 0 . \quad (19)$$

Introduce the perimetric coordinates[43, 45, 51] u, v, and w given by

$$u = \alpha\epsilon(-r_1 + r_2 + r_{12}), \quad v = \beta\epsilon(r_1 - r_2 + r_{12}) ,$$
$$w = \gamma\epsilon(r_1 + r_2 - r_{12}) , \quad (20)$$

where α, β, and γ are variational parameters. If the energy E is given in terms of ϵ,

$$E = -(\kappa + \sigma\chi)\epsilon^2 , \quad (21)$$

where κ and χ are determined from the approximation at infinity, then one obtains

$$\kappa = \tfrac{1}{8}(\alpha^2 + 3\beta^2 + \gamma^2 - 2\alpha\gamma) , \quad (22)$$

$$\chi = \tfrac{1}{8}(3\alpha^2 + \beta^2 + \gamma^2 - 2\beta\gamma) . \quad (23)$$

Put

$$\Psi = e^{-(1/2)(u+v+w)} F(u, v, w) . \quad (24)$$

Substituting Eqs. (20), (21), and (24) into (19) one gets

$$\epsilon\left(\frac{\partial^2 F}{\partial u^2}\left[\alpha^2\left(\frac{4u^2 w}{\alpha^2 \gamma} + \frac{4uw^2}{\alpha\gamma^2}\right) + \sigma\alpha^2\left(\frac{4u^2 v}{\alpha^2 \beta} + \frac{4uv^2}{\alpha\beta^2} + \frac{8uvw}{\alpha\beta\gamma} + \frac{4u^2 w}{\alpha^2 \gamma} + \frac{4uw^2}{\alpha\gamma^2}\right)\right]\right.$$

$$+ \frac{\partial^2 F}{\partial v^2}\left[\beta^2\left(\frac{4u^2 v}{\alpha^2 \beta} + \frac{4uv^2}{\alpha\beta^2} + \frac{8uvw}{\alpha\beta\gamma} + \frac{4v^2 w}{\beta^2 \gamma} + \frac{4vw^2}{\beta\gamma^2}\right) + \sigma\beta^2\left(\frac{4v^2 w}{\beta^2 \gamma} + \frac{4vw^2}{\beta\gamma^2}\right)\right]$$

$$+ \frac{\partial^2 F}{\partial w^2}\left[\gamma^2\left(\frac{4u^2 w}{\alpha^2 \gamma} + \frac{4uw^2}{\alpha\gamma^2}\right) + \sigma\gamma^2\left(\frac{4v^2 w}{\beta^2 \gamma} + \frac{4vw^2}{\beta\gamma^2}\right)\right] + \frac{\partial^2 F}{\partial u \partial w}\left[-4\left(\frac{2u^2 w}{\alpha} + \frac{2uw^2}{\gamma}\right)\right]$$

$$+ \frac{\partial^2 F}{\partial v \partial w}\left[-4\sigma\left(\frac{2v^2 w}{\beta} + \frac{2vw^2}{\gamma}\right)\right] + \frac{\partial F}{\partial u}\left\{4\alpha\left(\frac{w^2}{\gamma^2} - \frac{u^2}{\alpha^2}\right) + (\alpha\gamma - \alpha^2)\left(\frac{4u^2 w}{\alpha^2 \gamma} + \frac{4uw^2}{\alpha\gamma^2}\right)\right.$$

$$+\sigma\left[4\alpha\left(\frac{2uv}{\alpha\beta}+\frac{2uw}{\alpha\gamma}+\frac{2vw}{\beta\gamma}+\frac{w^2}{\gamma^2}+\frac{v^2}{\beta^2}\right)-\alpha^2\left(\frac{4u^2v}{\alpha^2\beta}+\frac{4uv^2}{\alpha\beta^2}+\frac{8uvw}{\alpha\beta\gamma}+\frac{4u^2\omega}{\alpha^2\gamma}+\frac{4uw^2}{\alpha\gamma^2}\right)\right]\Bigg\}$$

$$+\frac{\partial F}{\partial v}\Bigg\{4\beta\left(\frac{u^2}{\alpha^2}+\frac{2uv}{\alpha\beta}+\frac{2uw}{\alpha\gamma}+\frac{2vw}{\beta\gamma}+\frac{w^2}{\gamma^2}\right)-\beta^2\left(\frac{4u^2v}{\alpha^2\beta}+\frac{4uv^2}{\alpha\beta^2}+\frac{8uvw}{\alpha\beta\gamma}+\frac{4v^2w}{\beta^2\gamma}+\frac{4vw^2}{\beta\gamma^2}\right)$$

$$+\sigma\left[4\beta\left(\frac{w^2}{\gamma^2}-\frac{v^2}{\beta^2}\right)+(\beta\gamma-\beta^2)\left(\frac{4v^2w}{\beta^2\gamma}+\frac{4vw^2}{\beta\gamma^2}\right)\right]\Bigg\}$$

$$+\frac{\partial F}{\partial w}\Bigg\{(-\gamma^2+\alpha\gamma)\left(\frac{4u^2w}{\alpha^2\gamma}+\frac{4uw^2}{\alpha\gamma^2}\right)+4\gamma\left(\frac{u^2}{\alpha^2}-\frac{w^2}{\gamma^2}\right)+\sigma\left[4\gamma\left(\frac{v^2}{\beta^2}-\frac{w^2}{\gamma^2}\right)-(\gamma^2-\beta\gamma)\left(\frac{4v^2w}{\beta^2\gamma}+\frac{4vw^2}{\beta\gamma^2}\right)\right]\Bigg\}$$

$$+F\Bigg\{2(\alpha-\gamma-\beta)\frac{u^2}{\alpha^2}-2(\alpha-\gamma+\beta)\frac{w^2}{\gamma^2}-2\beta\left(\frac{2uv}{\alpha\beta}+\frac{2uw}{\alpha\gamma}+\frac{2vw}{\beta\gamma}\right)$$

$$+(\alpha^2+\gamma^2-2\alpha\gamma-2\kappa)\left(\frac{u^2w}{\alpha^2\gamma}+\frac{uw^2}{\alpha\gamma^2}\right)+(\beta^2-2\kappa)\left(\frac{u^2v}{\alpha^2\beta}+\frac{uv^2}{\alpha\beta^2}+\frac{2uvw}{\alpha\beta\gamma}+\frac{v^2w}{\beta^2\gamma}+\frac{vw^2}{\beta\gamma^2}\right)$$

$$+\sigma\left[2(\gamma-\beta-\alpha)\frac{w^2}{\gamma^2}-2(\gamma-\beta+\alpha)\frac{v^2}{\beta^2}-2\alpha\left(\frac{2uv}{\alpha\beta}+\frac{2uw}{\alpha\gamma}+\frac{2vw}{\beta\gamma}\right)$$

$$+\tfrac{1}{4}\alpha^2\left(\frac{4u^2v}{\alpha^2\beta}+\frac{4uv^2}{\alpha\beta^2}+\frac{8uvw}{\alpha\beta\gamma}+\frac{4u^2w}{\alpha^2\gamma}+\frac{4uw^2}{\alpha\gamma^2}\right)$$

$$+\tfrac{1}{4}(\beta^2+\gamma^2-2\beta\gamma)\left(\frac{4v^2w}{\beta^2\gamma}+\frac{4vw^2}{\beta\gamma^2}\right)-2\chi\left(\frac{u^2v}{\alpha^2\beta}+\frac{uv^2}{\alpha\beta^2}+\frac{2uvw}{\alpha\beta\gamma}+\frac{v^2w}{\beta^2\gamma}+\frac{u^2w}{\alpha^2\gamma}+\frac{uw^2}{\alpha\gamma^2}+\frac{vw^2}{\beta\gamma^2}\right)\right]\Bigg\}$$

$$+4\left[\lambda\left(\frac{u^2}{\alpha^2}+\frac{uv}{\alpha\beta}+\frac{uw}{\alpha\gamma}+\frac{vw}{\beta\gamma}\right)-\mu\left(\frac{uv}{\alpha\beta}+\frac{uw}{\alpha\gamma}+\frac{v^2}{\beta^2}+\frac{vw}{\beta\gamma}\right)+\nu\left(\frac{uv}{\alpha\beta}+\frac{uw}{\alpha\gamma}+\frac{vw}{\beta\gamma}+\frac{w^2}{\gamma^2}\right)\right]F=0\quad . \quad (25)$$

Assume the expansion

$$F=\sum_{l,m,n=0}^{\infty}A(l,m,n)L_l(u)L_m(v)L_n(w)\ , \qquad (26)$$

where L_l, L_m, and L_n denote, respectively, the normalized Laguerre polynomials of order l, m, and n. Using the different relations between these polynomials and its derivatives, one obtains a considerably long 57-terms recursion relation between the coefficients $A(l,m,n)$. Owing to the length of this recursion relation, it will not be given here.[52] For $\sigma=1$ the recursion relation reduces to a relation of 33 terms, which corresponds to the case of helium derived by Pekeris with $\lambda=1$, $\mu=-1$, and $\nu=-1$. For the helium atom Pekeris[43] considered the case corresponding to $\alpha=\beta=1$, and $\gamma=2$.

IV. COMPUTATIONS

Assign to each triplet of indices (l,m,n) an index k given by the relation

$$k(l,m,n)=\tfrac{1}{24}\overline{\omega}(\overline{\omega}+2)(2\overline{\omega}+5)+\tfrac{1}{16}[1-(-1)^{\overline{\omega}}]+\tfrac{1}{4}(l+m)^2$$

$$+\tfrac{1}{8}[1-(-1)^{l+m}]+l+1+\tfrac{1}{2}(l+m)\ , \qquad (27)$$

$$\overline{\omega}=l+m+n\ . \qquad (28)$$

The recursion relation takes the form of the eigenvalue problem

$$H+(P+\sigma Q)\epsilon=0\ . \qquad (29)$$

A special program in double precision has been written for IBM 360 to evaluate the different coefficients of $A(l,m,n)$ in the recursion relation for different values of l, m, and n (Prog A). These coefficients permit the evaluation of the matrices P, Q, and H for different values of α, β, and γ. With the partitioning technique developed by Lowdin,[53] a program is written in double precision for IBM 360 to calculate the largest positive value of ϵ in Eq. (29) for different values of σ (Prog B).

To calculate the energy E of the system, Prog A is used first to evaluate the values of κ and χ following Eqs. (22) and (23) as well as the matrices P, Q, and H corresponding to specific values of α, β, and γ. These matrices are then used as input data in Prog B to obtain the largest positive value of ϵ for a particular value of σ. Equation (21) is then applied to calculate the energy E of the system that corresponds to these specific values of α, β, γ, and σ. This procedure is referred to as Proc I. To get the minimum energy of the
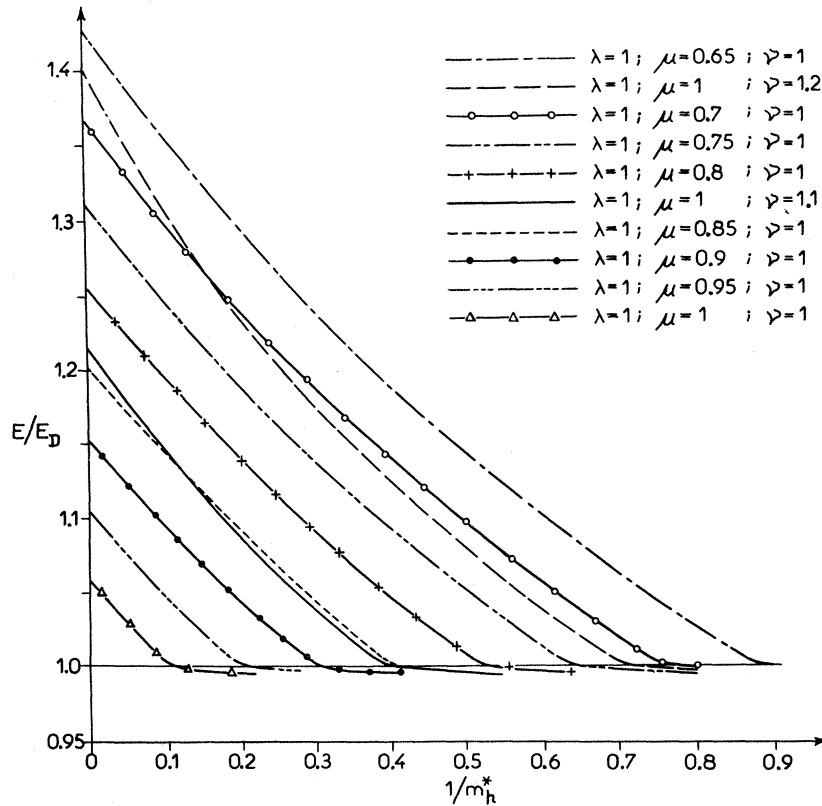
FIG. 1. Plots of E/E_D vs $1/m_h^*$ for the cases $\lambda = \mu = \nu = 1$; $\lambda = \nu = 1$, $\mu = 0.95$; $\lambda = \nu = 1$, $\mu = 0.9$; $\lambda = \nu = 1$, $\mu = 0.85$; $\lambda = \mu = 1$, $\nu = 1.1$; $\lambda = \nu = 1$, $\mu = 0.8$; $\lambda = \nu = 1$, $\mu = 0.75$; $\lambda = \nu = 1$, $\mu = 0.7$; $\lambda = \mu = 1$, $\nu = 1.2$; and $\lambda = \nu = 1$, $\mu = 0.65$ with $\kappa = 0.847\,3625$ and $\chi = 0.307\,2125$.

system for particular value of σ, several runs are carried out following Proc I for different values of α, β, and γ.

Another procedure followed by Frost to get the minimum energy is to consider $\chi = 0$ and to vary the values of α, β, γ, and κ simultaneously. In this case the energy is given by the following form:

$$E = -\kappa\epsilon^2 . \tag{30}$$

This procedure needs many more computations than Proc I. To save computer time, one can take the specific values of α, β, and γ corresponding to the minimum energy in Proc I and vary κ until convergence is attained. This method is called Proc II. In this case, Prog A has to be used first to evaluate the matrices Q and P that correspond, respectively, to $\chi = 0$ and to the different values of κ, for which convergence was attained. To study the convergence, the values of ϵ corresponding to specific set of α, β, γ, and σ are calculated for the different determinants (29) of order $N = 10$, 11, 12, ..., 50. The final results given in this paper correspond to the determinants of order 50 that converge to four decimals.

The different calculations for the minimum energy were carried out following both Procs I and II. Computations were performed for different

cases with the following values of λ, μ, and ν:

λ	μ	ν	λ	μ	ν
1	1	1	1	0.95	1
1	0.9	1	1	0.85	1
1	0.8	1	1	0.75	1
1	0.7	1	1	0.65	1
1.05	1	1	1.1	1	1
1.15	1	1	1	1	1.05
1	1	1.1	1	1	1.2
1.05	1	1.1	1.05	0.95	1.1
1.05	1.05	1.1	2	2	1
2	1.9	1	3	3	1

The last three cases correspond to doubly and triply ionized donors. For these three cases the solutions of the determinants (29) of order 50 converge to three decimals. Since $\lambda = \mu = \nu = 1$ is considered to be the standard case, it is preferable to assign for this case the symbols λ', μ', and ν' to λ, μ, and ν, respectively.

V. RESULTS

Figures 1 and 2 represent the values of E/E_D as a function of the mass ratio $\sigma = 1/m_h^*$ in a.u. with E the energy of the complex given by Eqs. (21)–(23). The cases considered in these figures are
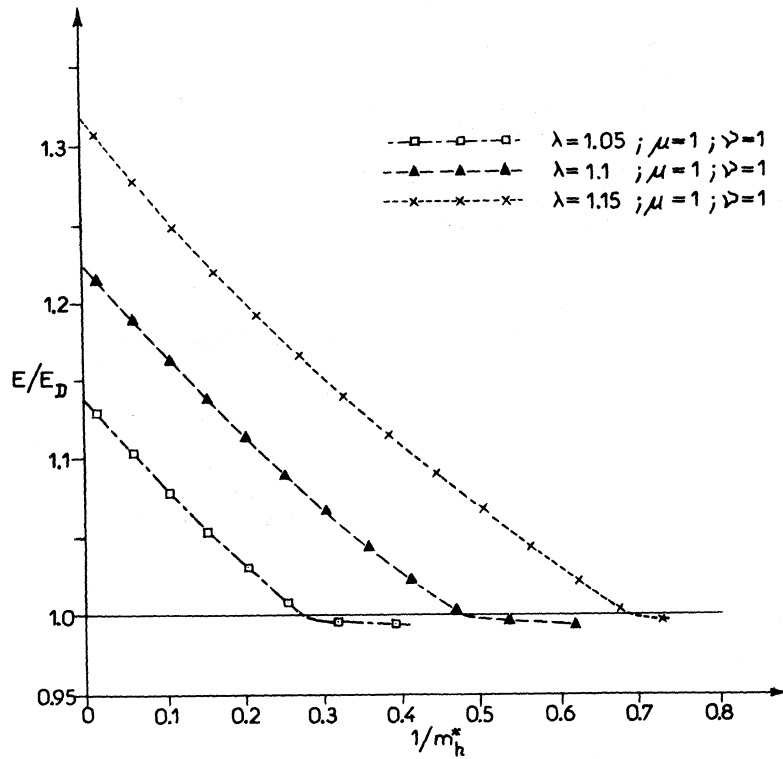
FIG. 2. Plots of E/E_D vs $1/m_h^*$ for the cases $\lambda = 1.15$, $\mu = \nu = 1$; $\lambda = 1.1$, $\mu = \nu = 1$; and $\lambda = 1.05$, $\mu = \nu = 1$ with $\kappa = 0.847\,3625$ and $\chi = 0.307\,2125$.
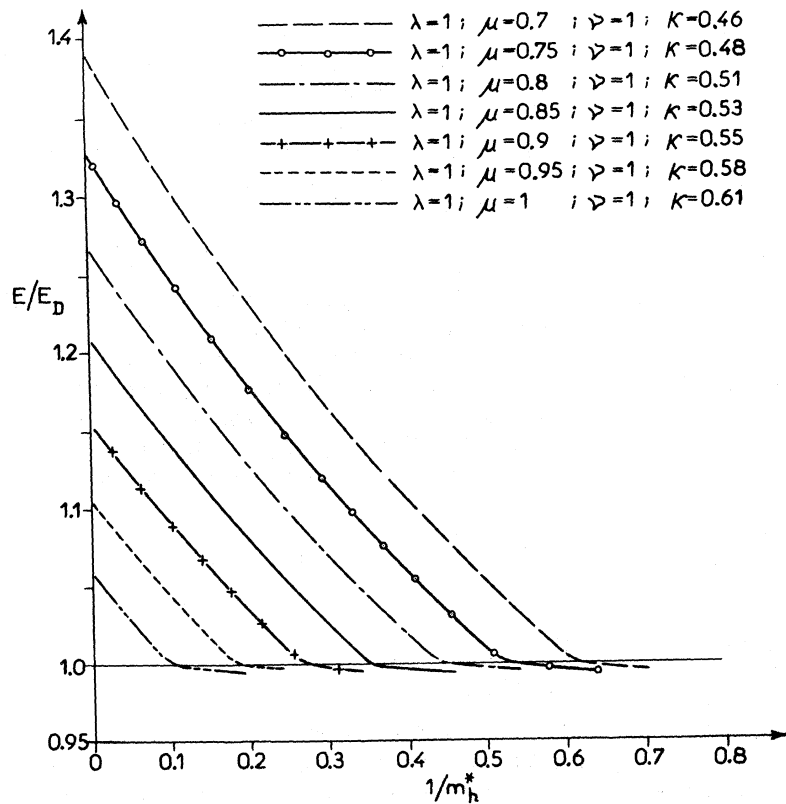
FIG. 3. Plots of E/E_D vs $1/m_h^*$ for the cases $\lambda = \mu = \nu = 1$: $\lambda = \nu = 1$, $\mu = 0.95$; $\lambda = \nu = 1$, $\mu = 0.9$; $\lambda = \nu = 1$, $\mu = 0.85$; $\lambda = \nu = 1$, $\mu = 0.8$; $\lambda = \nu = 1$, $\mu = 0.75$; and $\lambda = \nu = 1$, $\mu = 0.7$ with $\kappa = 0.61$, 0.58, 0.55, 0.53, 0.51, 0.48, and 0.46, respectively.
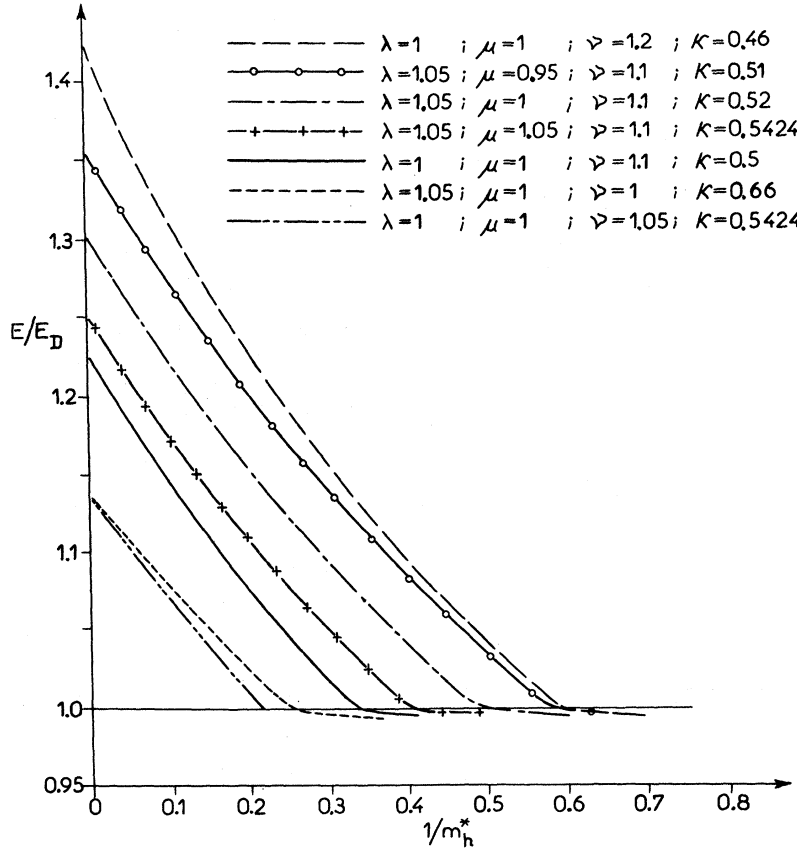
FIG. 4. Plots of E/E_D vs $1/m_h^*$ for the cases $\lambda = \mu = 1$, $\nu = 1.05$; $\lambda = 1.05$, $\mu = \nu = 1$; $\lambda = \mu = 1$, $\nu = 1.1$; $\lambda = \mu = 1.05$, $\nu = 1.1$; $\lambda = 1.05$, $\mu = 1$, $\nu = 1.1$; $\lambda = 1.05$, $\mu = 0.95$, $\nu = 1.1$; and $\lambda = \mu = 1$, $\nu = 1.2$ with $\kappa = 0.5424$, 0.66, 0.5, 0.5424, 0.52, 0.51, and 0.46, respectively.

λ'	μ'	ν'	λ	μ	ν
1	1	1	1	0.95	1
			1	0.85	1
λ	μ	ν	1	0.8	1
1	0.9	1	1	0.7	1
1	1	1.1	1	0.65	1
1	0.75	1	1.1	1	1
1	1	1.2			
1.05	1	1			
1.15	1	1			

For these cases the calculations are carried out following Proc I. With $\lambda' = \mu' = \nu' = 1$, the values of α, β, and γ that minimize the energy for all values of σ are 0.72, 1.5, and 0.55, respectively. These values are obtained after carrying out a tremendous number of computations. For this reason, it would have been very difficult to determine the corresponding values of α, β, and γ that minimize the energy for each set of λ, μ, and ν. The values $\alpha = 0.72$, $\beta = 1.5$, and $\gamma = 0.55$ are thus used for all cases. For all the curves in Figs. 1 and 2, the values of κ and χ calculated from Eqs. (22) and (23) are 0.847 3625 and 0.307 2125, respectively.

The results are strongly dependent on the values of λ, μ, and ν. This means that the variation in the dielectric constant due to the polarizability between the three particles makes an important contribution. The intersections between the curves $E/E_D = f(\sigma)$ and $E/E_D = 1$ give critical values σ_c for the mass ratios. The systems are stable for $\sigma \leqslant \sigma_c$ and unstable otherwise. From Figs. 1 and 2 one can notice that the values of σ_c are also a function of λ, μ, and ν. In Fig. 1 the value $\sigma_c = 0.11$ corresponds to the case $\lambda' = \mu' = \nu' = 1$, while for $\lambda = \nu = 1$, $\mu = 0.65$ the value of σ_c is 0.9. From Figs. 1 and 2, knowing the value of σ_c that corresponds to the case $\lambda' = \mu' = \nu' = 1$, for instance, it is easy to write a simple empirical formula that determines the approximate value of σ_c for any set of λ, μ, and ν:

$$\sigma_c(\lambda, \mu, \nu) \simeq \sigma_c(\lambda' = \mu' = \nu') + [3.67(\lambda - \lambda')$$
$$- 2(\mu - \mu') + 3(\nu - \nu')] , \quad (31)$$

with

$$\sigma_c(\lambda' = \mu' = \nu' = 1) = 0.11 .$$

Figures 3 and 4 represent the values of E/E_D as a function of σ following Proc II. The energy E of the complex is obtained using Eq. (30). The
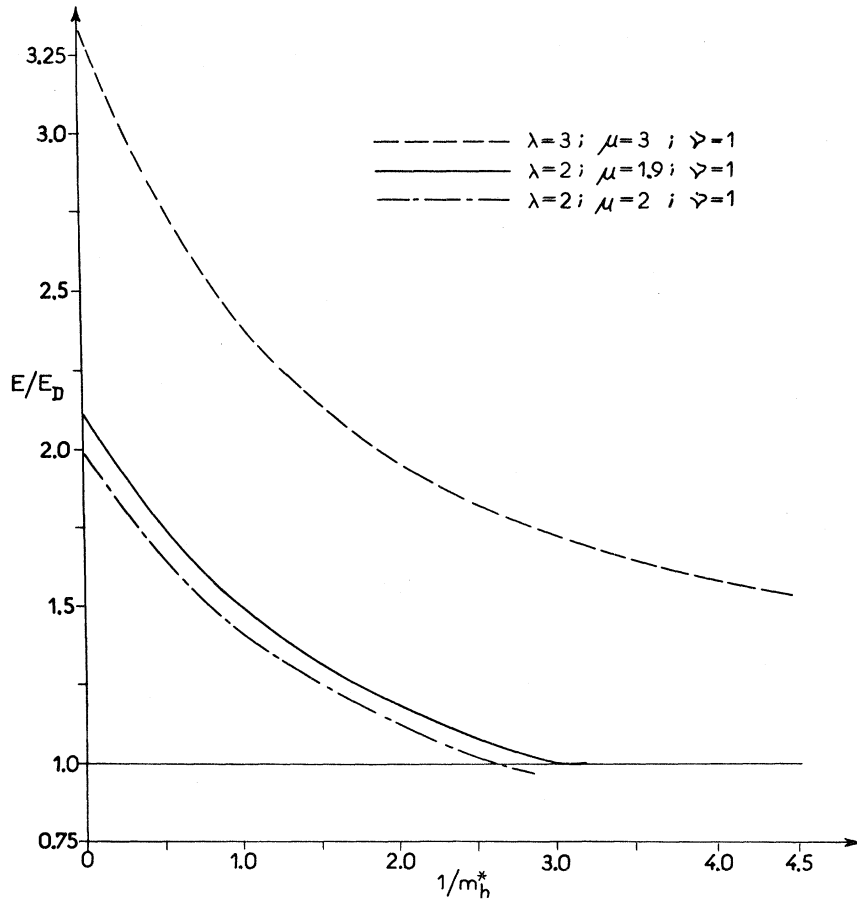
FIG. 5. Plots of E/E_D vs $1/m_h^*$ for the cases $\lambda = \mu = 2$, $\nu = 1$; $\lambda = 2$, $\mu = 1.9$, $\nu = 1$; and $\lambda = \mu = 3$, $\nu = 1$ with $\kappa = 0.847\,3625$ and $\chi = 0.307\,2125$.

cases considered in these figures are

λ'	μ'	ν'	λ	μ	ν
1	1	1	1	0.95	1
			1	0.85	1
λ	μ	ν	1	0.75	1
1	0.9	1	1	1	1.05
1	0.8	1	1	1	1.1
1	0.7	1	1.05	1	1.1
1.05	1	1	1	1	1.2
1.05	1.05	1.1			
1.05	0.95	1.1			

The values of κ for which energy convergence is attained and which correspond to the different sets of λ, μ, and ν are indicated in these figures. Since the values of λ, μ, and ν are different, the variations in σ_c are also strongly dependent on the dielectric constants between the three particles. Comparing these curves with those in Figs. 1 and 2 that correspond to the same values of λ, μ, and ν, one can notice that for small mass ratios $\sigma = 1/m_h^*$ the values of E/E_D are higher in Figs. 3 and 4 than in Figs. 1 and 2. For greater mass ratios the values of E/E_D in Figs. 3 and 4 are

smaller than those in Figs. 1 and 2, and consequently, smaller values of σ_c are obtained.
In Fig. 3, the value of σ_c for the case $\lambda' = \mu' = \nu' = 1$ is 0.1 which is slightly smaller than that in Fig. 1. For the cases in Figs. 3 and 4, a simple empirical formula can also be found to determine the value of σ_c for any set of λ, μ, and ν:

$$\sigma_c(\lambda, \mu, \nu) = \sigma_c(\lambda' = \mu' = \nu' = 1) + [3.2(\lambda - \lambda')$$
$$- 1.7(\mu - \mu') + 2.4(\nu - \nu')] . \quad (32)$$

Figures 1–4 all correspond to the case of singly ionized donor. The solutions of the determinants (29) of order 50 used in these calculations are correct to the fourth decimal. In Fig. 5 the cases

λ	μ	ν	λ	μ	ν
2	2	1	2	1.9	1
3	3	1			

that correspond to doubly and triply ionized donors are calculated following Proc I. The values of α, β, and γ are also the same as those for $\lambda' = \mu' = \nu' = 1$, that is, 0.72, 1.5, and 0.55, respectively. The values of κ and χ given from Eqs. (22) and (23) are also 0.847 3625 and 0.307 2125, respectively.

The solutions of the determinants (29) of order 50 used in these calculations are correct to the third decimal. For these complexes of excitons bound to doubly and triply ionized donors, a simple relation similar to that of Eq. (31) can also be found for σ_c for any set of λ, μ, and ν.

In Eqs. (31) and (32), the coefficients of $(\lambda - \lambda')$ terms are greater than those for $(\nu - \nu')$, terms which are in turn greater than the ones for $(\mu - \mu')$ terms. This means that the effect along the r_1 direction is stronger than that along r_{12} while the repulsion between the hole and the donor has the smallest effect. Also, the higher the values of λ and ν and the smaller those of μ the more stability of the system one can obtain. That is why one expects that the higher the degree of ionization of the donor the greater the stability of the system. As a matter of fact, if the effect of the repulsion along the direction r_2 were the strongest, the system would be completely unstable.

Using Eq. (20), the exponential part of the wave function (24) can be written in terms of r_1, r_2, and r_{12} as follows:

$$\Psi = e^{-\epsilon(ar_1 - br_2 + cr_{12})} F(u, v, w) , \qquad (33)$$

where a, b, and c are given by the following expressions:

$$a = \tfrac{1}{2}(-\alpha + \beta + \gamma) ,$$
$$b = \tfrac{1}{2}(\alpha - \beta + \gamma) , \qquad (34)$$
$$c = \tfrac{1}{2}(\alpha + \beta - \gamma) .$$

Taking $\alpha = 0.72$, $\beta = 1.5$, and $\gamma = 0.55$, the corresponding values of a, b, and c are 0.665, 0.115, and 0.835, respectively, all positive numbers. These values of $a, b,$ and c show that the repulsion between the hole and the donor has a smaller effect than the attractions along the directions of r_1 and r_{12}. Another important feature that did not appear in the other variational calculations treated by the previous authors is the positive sign of the r_2 term in the exponential of Eq. (33). This sign has a significant physical meaning in that it explains the repulsive forces between the hole of the exciton and the donor. The two negative signs of r_1 and r_{-2} in the exponential represent, of course, the attractive forces between the electron and the donor, as well as between the two exciton particles, respectively. The wave function (33) still converges since the value of b is much smaller than that of a or c. This has been demonstrated by studying the integrals of Eqs. (35) used for calculating the values of λ, μ, and ν which are necessary for comparing experiment and theory.

VI. COMPARISON WITH EXPERIMENT

The values of λ, μ, and ν depend on the fundamental constants m_e^*, m_h^*, K_o, K_s, and ω. For a particular semiconductor there corresponds one set of values for λ, μ, and ν. To carry out the comparison between theory and experiment for a specific semiconductor, the corresponding mean values λ, μ, and ν given in Eqs. (35) have to be calculated:

$$\lambda = \frac{K_{eff}}{K_s} + \tfrac{1}{2}K_{eff}\left(\frac{1}{K_o} - \frac{1}{K_s}\right)\frac{\int \Psi \xi \Psi \, d\tau}{\int \Psi \Psi \, d\tau} , \qquad (35a)$$

$$\mu = \frac{K_{eff}}{K_s} + \tfrac{1}{2}K_{eff}\left(\frac{1}{K_o} - \frac{1}{K_s}\right)\frac{\int \Psi \eta \Psi \, d\tau}{\int \Psi \Psi \, d\tau} , \qquad (35b)$$

$$\nu = \frac{K_{eff}}{K_s} + \tfrac{1}{2}K_{eff}\left(\frac{1}{K_o} - \frac{1}{K_s}\right)\frac{\int \Psi \zeta \Psi \, d\tau}{\int \Psi \Psi \, d\tau} . \qquad (35c)$$

For these computations one needs to know the wave functions Ψ. The calculations concerning the wave functions (33) are quite elaborate. For simplifications only the exponential part[54] of Eq. (33) has been used to evaluate the integrals of Eqs. (35) and consequently to calculate the values of λ, μ, and ν. Using elliptical coordinates for integration, the values of λ, μ, and ν for a given semiconductor are given by the following expressions:

$$\lambda = \frac{K_{eff}}{K_s} + \tfrac{1}{2}K_{eff}\left(\frac{1}{K_o} - \frac{1}{K_s}\right)\left(\frac{SF}{R(c + a_1)^3(c - a_1)^3}\right) ,$$

$$\mu = \frac{K_{eff}}{K_s}\left(\frac{1}{K_o} - \frac{1}{K_s}\right)\frac{T}{R} ,$$

$$\nu = \frac{K_{eff}}{K_s} + \tfrac{1}{2}K_{eff}\left(\frac{1}{K_o} - \frac{1}{K_s}\right)\left(\frac{(U+V)F}{R(c_1 + a)^3(c_1 - a)^3}\right) ,$$

where

$$a_1 = a + \frac{\kappa_e}{2\epsilon} , \quad a_2 = a + \frac{\kappa_h}{2\epsilon} , \quad c_1 = c + \frac{\kappa_e}{2\epsilon} ,$$

$$c_2 = c + \frac{\kappa_h}{2\epsilon} , \quad G_1 = (c_1 - b)^3 , \quad G_2 = (c_2 - b)^3 ,$$

$$F = (c_2 - a^2)^3 , \quad G = (a - b)^3 , \quad J = (c - b)^3 ,$$

$$R = c(c^2 - 3a^2 + 2ab)/G + a(3c^2 - a^2 - 2cb)/J ,$$

$$S = [c(c^2 - 3a_1^2 + 2ba_1)]/(a_1 - b)^3$$
$$+ [ac^2 - aa_1^2 + 2ca_1(c - b)]/J ,$$

$$T = c(c^2 - 3a^2 + 2ab_2)/(a_2 - b)^3$$
$$+ a(3c^2 - a^2 - 2cb_2)/(c_2 - b)^3 , \qquad (36)$$

$$U = c_1[c^2 + (c\kappa_e/2\epsilon) - 3a^2 + (\kappa_e/2\epsilon)^2 + 2ab]/G$$
$$+ a[3c^2 + 3(c\kappa_e/2\epsilon) - a^2 + 3(\kappa_e/2\epsilon)^2$$
$$- 2cb - b(\kappa_e/\epsilon)]/G_1 ,$$

$$V = [c^2 + (c\kappa_h/\epsilon) - 3a^2 + (\kappa_h/2\epsilon)^2 + 2ab]/G$$
$$+ a[3c^2 + 3(c\kappa_h/\epsilon) - a^2 + 3(\kappa_h/2\epsilon)^2$$

$$-2cb - (b\kappa_h/\epsilon)]/G_2 ,$$

with κ_e and κ_h given by Eq. (2). The values of λ, μ, and ν depend not only on the fundamental constants but are also a function of the energy ϵ of the complex. This energy has been calculated following Proc I and using the determinant (29). In this case the computations have to be self-consistent. The two matrices P and Q of Eq. (29) which correspond to the minimum energy for the case $\lambda' = \mu' = \nu' = 1$ are considered the same for the different semiconductors. On the other hand the matrix H of this equation varies from one semiconductor to another for its explicit dependence on the values of λ, μ, and ν. Simple IBM 360 programs are used to compute the values of λ, μ, and ν of Eqs. (36) for each specific semiconductor. The values $a = 0.665$, $b = 0.115$, and $c = 0.835$ considered in these computations are invariant for the different semiconductors. These values correspond to the minimum energy for the case $\lambda' = \mu' = \nu' = 1$.

The self-consistent calculations for a particular semiconductor are carried out as follows: The values of λ are computed as a function of the energy ϵ with $\Delta\epsilon = 10^{-4}$. For the different semiconductors studied, the values of ϵ lie between 0.7 and 0.84. The value of K_{eff} is chosen such that for an initial value of ϵ, say ϵ_i, the value of λ is 1. With this value of K_{eff}, the values of μ and ν of Eqs. (36) are calculated for the energy ϵ_i. Prog A is then used to compute the matrix H that corresponds to these values of λ, μ and ν. Prog B is used to calculate the final value of ϵ_f of the energy for this specific semiconductor. If ϵ_f computed using Prog B is the same to four decimals as ϵ_i chosen at the beginning, the computation process stops and the energy E of the system is calculated using Eq. (21). On the other hand, if $\epsilon_f \neq \epsilon_i$ another value of ϵ_i is chosen and the whole process is repeated. The computations are carried out until the condition $|\epsilon_f - \epsilon_i| < 10^{-4}$ is reached.

For a particular semiconductor, different values of effective masses and dielectric constants are available in the literature. The computations corresponding to a particular semiconductor are carried out for these different effective masses and dielectric constants. In Table I, the fundamental constants and the computed values of $(E - E_D)/E_D$ for CdS, ZnO, ZnSe, ZnTe, CdTe, SiC 6H, TlCl, and TlBr are given. The problem of anisotropy for the effective masses and the dielectric constants is eliminated by taking mean values for these constants using the formulas of Hopfield and Thomas[55]:

$$1/m_h^* = \tfrac{1}{3}[(2/m_{h\perp}^*) + (1/m_{h\parallel}^*)(K_{s\perp}/K_{s\parallel})] ,$$

$$1/m_e^* = \tfrac{1}{3}[(2/m_{e\perp}^*) + (1/m_{e\parallel}^*)(K_{s\perp}/K_{s\parallel})] , \qquad (37)$$

$$K_s = (K_{s\perp}K_{s\parallel})^{1/2} .$$

The stability of the exciton–ionized-donor complex calculated in Table I for these materials agrees with observations.[2-22, 24-31, 33, 34] Due to the complexity[27] of SiC 6H, this material will be studied in more detail in a subsequent article. For TlCl and TlBr, the calculations predict the existence of such complex. No experimental evidence is yet available to confirm this prediction for such materials. The computed values of $(E - E_D)/E_D$ for the materials CdS and ZnO given in Table I are in better agreement with experiment than any other values reported by previous authors where the effect of the polarizability has been neglected. The value $(E - E_D)/E_D = 3.524 \ 10^{-2}$ computed for CdS IV in Table I and which corresponds to $K_s = 9.2$ is in better agreement with experiment[5, 30] (2.5×10^{-2}) than the best previous value (4.04×10^{-2}), calculated recently by Suffczynski et al.[41, 42] using Rutenberg and Stein's[40] wave function. The value $K_s = 9.2$ taken for CdS IV gives better agreement with experiment than the mean value 9.8278 that corresponds to $K_{s\perp} = 9.35$ and $K_{s\parallel} = 10.33$. One can also notice that the value $m_e^* = 0.205$ gives better agreement with experiment than the values 0.18 and 0.171 that correspond to CdS II and CdS III, respectively. The discrepancy between the value 3.767×10^{-2} calculated for CdS I in Table I and the observed one, 2.5×10^{-2}, may be due to the high measured m_h^* value. With $m_h^* = 0.854$ the computed value of $(E - E_D)/E_D$ for CdS V is 2.464×10^{-2}, which is in excellent agreement with experiment. With $K_s = 9.2$, $m_e^* = 0.205$, and $m_h^* = 0.854$, the value of $(E - E_D)/E_D$ would be slightly smaller than 2.464×10^{-2} and will still be in excellent agreement with experiment. For ZnO II and ZnO III the computed values 5.91×10^{-2} and 6.4×10^{-2} are again in better agreement with experiment[20, 30] (9.61×10^{-2}) than the previous best value 5.085×10^{-2} calculated recently by Suffczynski et al.[42] using Rutenberg and Stein's wave function.[40] It is the value 6.4×10^{-2} that has to be compared with the value 5.085×10^{-2} given in Ref. 42 since they correspond to the same fundamental constants. For ZnO IV and ZnO V the values 9.328×10^{-2} and 9.68×10^{-2} are in excellent agreement with experiment. For these two, as well as for ZnO VI and ZnO VII, the dielectric constant $K_0 = 4$ is used. From Table I one can see that the calculated exciton binding energy E_x for ZnO IV, ZnO V, ZnO VI, and ZnO VII is greater in absolute value than that of the neutral donor E_D. Although the case $|E_x| > |E_D|$ is not very common in most of semiconductors, it has been reported in some experiments[20, 28, 56, 57] concerning ZnO. One cannot then say which of the two values $K_0 = 4.59$ or $K_0 = 4$ is the more reasonable for this material.

For the materials ZnSe, ZnTe, and CdTe, in spite of the observation of such a complex and which is confirmed by the calculations given in Table I

TABLE I. Fundamental constants and the computed values of $(E - E_D)/E_D$ for exciton–ionized-donor complex in CdS, ZnO, ZnSe, ZnTe, CdTe, SiC 6H, TlCl, and TlBr.

	$m^*_{e\perp}$	$m^*_{e\parallel}$	$m^*_{h\perp}$	$m^*_{h\parallel}$	$K_{s\perp}$	$K_{s\parallel}$	K_0	σ	ω	$(E-E_D)/E_D$ $\times 10^2$
CdS I	0.205[a]	0.7[a,b]	5[a]		9.35[c]	10.33	5.24[c]	0.207	306	3.767
					$\lambda=1,\ \mu=1.0017,\ \nu=1.06753$					
CdS II	0.18[d]	0.7	5		9.35	10.33	5.24	0.182		4.18
					$\lambda=1,\ \mu=1.00128,\ \nu=1.0612$					
CdS III	0.171[e]	0.7	5		9.35	10.33	5.24	0.173		4.258
					$\lambda=1,\ \mu=1.00109,\ \nu=1.05832$					
CdS IV	0.205	0.7	5		9.2[f]		5.24	0.207		3.524
					$\lambda=1,\ \mu=1.0017,\ \nu=1.06568$					
CdS V	0.205			0.854	9.35	10.33	5.24	0.24		2.464
					$\lambda=1,\ \mu=1.00215,\ \nu=1.06975$					
ZnO I	0.38[c]			1.8[c]	8.5[c]		4.59[c]	0.21	580	5.686
					$\lambda=1,\ \mu=1.00229,\ \nu=1.0834$					
ZnO II	0.24[g]			1.8	8.5		4.59	0.1333		5.911
					$\lambda=1,\ \mu=1.0007,\ \nu=1.05527$					
ZnO III	0.29[h]			1.8	8.5[h]	11	4.59	0.1611		6.4
					$\lambda=1,\ \mu=1.0012,\ \nu=1.0697$					
ZnO IV	0.38			1.8	8.15[c]		4[c]	0.21		9.328
					$\lambda=1,\ \mu=1.0031,\ \nu=1.11063$					
ZnO V	0.38			1.8	8.5		4	0.21		9.68
					$\lambda=1,\ \mu=1.00322,\ \nu=1.1133$					
ZnO VI	0.24			1.8	8.5		4	0.1333		8.58
					$\lambda=1,\ \mu=1.00094,\ \nu=1.07447$					
ZnO VII	0.24			1.8	8.15		4	0.1333		8.413
					$\lambda=1,\ \mu=1.00091,\ \nu=1.0733$					
ZnSe I	0.1[c]			0.6[c]	9.2[i]		6.1	0.167	253	0.5
					$\lambda=1,\ \mu=1.00048,\ \nu=1.02733$					
ZnSe II	0.1			0.6	9.2		5.75[j]	0.167		1.158
					$\lambda=1,\ \mu=1.00057,\ \nu=1.03242$					
ZnSe III	0.1			0.6	9.1[k]		5.75	0.167		0.848
					$\lambda=1,\ \mu=1.0005,\ \nu=1.03$					
ZnTe I	0.096[l]			0.6[m]	10.38[n]		6.7[o]	0.16	206	0.875
					$\lambda=1,\ \mu=1.00044,\ \nu=1.02763$					
ZnTe II	0.096			0.6	10.1[c]		6.7	0.16		0.76
					$\lambda=1,\ \mu=1.00042,\ \nu=1.02673$					
CdTe	0.096[c,p]			0.68	10.6[q]		7.13[q]	0.1412	168	1.827
					$\lambda=1,\ \mu=1.00038,\ \nu=1.02792$					
SiC 6H	0.25[r]	1.5[r]	3.5[r]		9.66[s]	10.03[s]	6.7[s]	0.1	967[s]	3.007
					$\lambda=1,\ \mu=1.00017,\ \nu=1.021$					
TlCl	0.53[t]			2.72[t]	37.6[t]		5.1[t]	0.1915	174[t]	25.446
					$\lambda=1,\ \mu=1.00338,\ \nu=1.21155$					

TABLE I   (*Continued*).

	$m_{e\perp}^*$	$m_{e\parallel}^*$	$m_{h\perp}^*$	$m_{h\parallel}^*$	$K_{s\perp}$	$K_{s\parallel}$	K_0	σ	ω	$(E-E_D)/E_D$ $\times 10^2$
TlBr	0.28^t		0.72^t		35.1^t		5.4^t	0.3889	116^t	6.73

$$\lambda = 1, \quad \mu = 1.0051, \quad \nu = 1.15727$$

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[n] S. Narita, H. Harada, and K. Nagasaka, J. Phys. Soc. Japan **22**, 1176 (1967).

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[s] L. Patrick and W. J. Choyke, Westinghouse Scientific Paper No. 70-9J3-OPGAP-P1, 1970 (unpublished).

[t] See Ref. 58.

for these semiconductors, the corresponding experimental values of $(E - E_D)/E_D$ are not well determined. Taking $\nu = 1.21155$ and $\nu = 1.15727$ given, respectively, for TlCl and TlBr in Table I, the corresponding exciton binding energies for these materials are 6.312 and 2.95 meV. These energies are in very good agreement with the experimental values (11 ± 2) and (6 ± 1) meV given by Bachrach and Brown[58] for TlCl and TlBr, respectively. One can also notice that the greater the value of K_s/K_o the greater the probability of existence of such a complex.

VII. DISCUSSION

The modifications in the potential due to the variation of the dielectric constant with the distance between the particles of the exciton bound to an ionized donor have been shown to make considerable contributions to the binding energies of these complexes. These corrections are expressed in terms of λ, μ, and ν. Even slight variations in these quantities lead to considerable changes in the curves for $E/E_D = f(\sigma)$. The use of a single curve corresponding to the special case $\lambda' = \mu' = \nu' = 1$ from which one calculates the binding energies of this complex in all semiconductors certainly leads to inaccurate results. From my calculations it appears that

semiconductors are characterized not by a single value of σ_c but by many, each of which corresponds to a specific semiconductor and consequently to a particular set of λ, μ, and ν.

Considering that the values of α, β, and γ obtained by the variational principle for the case $\lambda' = \mu' = \nu' = 1$ are the same as those that could have been calculated for any set of λ, μ, and ν may not be quite correct. This assumption has been adopted due to the tremendous number of computations involved in the minimization of the energy. On the other hand the integrals of Eqs. (35) evaluated for the mean values λ, μ, and ν are not strong functions of α, β, and γ. As a result the binding energies and consequently the values of σ_c given in these calculations may be slightly smaller than the corresponding real minimum energies for the different sets of λ, μ, and ν. For the materials studied in Table I, the values of μ are close to 1, while those of ν vary between 1 and 1.21. To carry out more accurate computations, one could calculate the values of a, b, and c that correspond to the minimum energies for the cases $\lambda = 1$, $\mu = 1$ and $\nu = 1.03$, 1.05, 1.08, 1.1, 1.15, and 1.2. This would probably give better agreement with experiment for the semiconductors under consideration but would need of course several more hours of

computer time.

To calculate the mean values λ, μ, and ν, only the exponential part of Eq. (33) has been considered. This is, of course, not consistent with the rest of the calculations. This approximation has been adopted to simplify the calculations which otherwise become much more tedious and require several more hours of computer time. As a matter of fact, eliminating this approximation together with the one mentioned in the preceding paragraph would be quite impractical unless one were to possess his own high speed computer.

In spite of the complexity of the calculations described in this paper, the consideration of the two approximations mentioned above, and the strong dependence of the computations on the fundamental constants K_o, K_s, m_e^*, m_h^*, and ω, satisfactory agreement has been obtained with experiment for the semiconductors studied in Table I. This agreement is better than obtained by previous authors where the effect of the polarizability has been neglected. An interesting result that appeared in using this method of the generalized three-particle problem is the positive and negative signs of the coefficients in the exponential term of the wave function (33) obtained by the variational principle. These signs correspond, respectively, to the attraction and repulsion between the three particles.

In carrying out the comparison with experiment for a certain semiconductor, the first thing one has to look for is the experimental value of E_x or preferably that of E_D. If E_x is the value that one is obliged to consider, then $K(r_{12})$ is set equal to K_{eff} and the term between brackets on the right-hand side of Eq. (4) is equal to unity. In this case the values of E/E_x are obtained by multiplying those of E calculated for the specific semiconductors, by the factor $2(1+\sigma)$. Working with E_x instead of E_D has the disadvantage that one may be dealing with the case $|E_x| < |E| < |E_D|$. In this case the system is stable with respect to the exciton and unstable with respect to the neutral donor. To determine if $|E|$ is smaller than or greater than $|E_D|$ for a given semiconductor, one has to compare the value of σ_c obtained from the curve $E/E_D = f(\sigma)$ in which $K(r_1) = K_{eff}$, that is $\lambda = 1$, with the mass ratio σ of that semiconductor. For $\sigma < \sigma_c$, the system for which $|E_x| < |E|$ is certainly stable. If $\sigma > \sigma_c$, the system is unstable with respect to the neutral donor. On the other hand, if the value of E_D is available, then $K(r_1)$ is set equal to K_{eff} and the term between brackets on the right-hand side of Eq. (6) is simply unity. The comparison with experiment can be carried out correctly for semiconductors having available values of E_D.

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†Research Group associated with the Centre Nationale de la Recherche Scientifique (CNRS), France.

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