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Binding energy for some atomic and exciton complex systems

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The general recursion relation developed previously for the exciton–ionized-donor complex has been applied to different atomic and exciton complex systems. The calculated values of the energies in the helium atom and the hydrogen negative ion are in good agreement with those obtained by Pekeris. The binding energy for the excitonic-molecule positive ion has been calculated as a function of the mass ratio $\sigma = m_e^*/m_h^*$. The system is stable for all values of σ. For the exciton negative ion the calculations are carried out in terms of $\delta = m_h^*/m_e^*$. The existence of such a complex is highly improbable in the known semiconductors. The stability of the excited states for the exciton–ionized-donor complex has been studied qualitatively in CdS, CuCl, and CuBr. Reasonable agreement with experiment has been found for CdS.

I. INTRODUCTION

In a preceding paper[1] referred to as I, the Pekeris method[2] for helium has been developed for the exciton–ionized-donor complex (Fig. 1). Haken's exciton potential[3] in which the effect of the polarizability is included has been generalized for such a system.[1,4] The effect of the polarizability between pairs of the three particles of the complex of Fig. 1 is expressed in terms of λ, μ, and ν which in this case have positive values. A considerably long general recursion relation of 57 terms has been obtained. An important advantage of this general recursion relation is that by varying the values of λ, μ, and ν and by taking some precautions, which will be discussed in Sec. VIII, one can calculate the binding energy of any three-particle system, either atomic or exciton complex. In this paper the energies for atomic systems such as the helium atom He and hydrogen negative ion H^- (Fig. 2) are calculated and compared to those obtained by Pekeris[2,5] in atomic physics. The stability for the excitonic-molecule positive ion (Fig. 3) and the exciton negative ion (Fig. 4) has been, respectively, studied as function of $\sigma = m_e^*/m_h^*$ and $\delta = m_h^*/m_e^*$ where m_e^* and m_h^* are the electron and the hole effective masses. The existence of the excited state 2S for the exciton–ionized-donor complex (Fig. 1) in CdS has also been discussed.

II. METHOD OF SOLUTION

In I the binding energy for the complex of Fig. 1 has been calculated in terms of the binding energy E_D of the neutral donor. The atomic units $K_{\text{eff}}\hbar^2/m_e^* e^2$ and $m_e^* e^4/K_{\text{eff}}^2\hbar^2$ have been adopted for length and energy, respectively, and the units $m_e^* = \hbar = e^2/K_{\text{eff}} = 1$ have been used. The effective dielectric constant $K_{\text{eff}} = K(r_{12})$ has been chosen such that $\lambda = 1$. In this case the neutral-donor binding energy $E_D = -m_e^* e^4/2K_{\text{eff}}^2\hbar^2$ is simply $\frac{1}{2}$ a.u. In these atomic units, the nonrelativistic Schrödinger equation written for the system of Fig. 1 is

$$\tfrac{1}{2}\nabla_e^2\Psi + \tfrac{1}{2}\sigma\nabla_h^2\Psi + \left[E + \left(\frac{\lambda_{12}}{r_{12}} - \frac{\mu_{13}}{r_{13}} + \frac{\nu_{23}}{r_{23}}\right)\right]\Psi = 0, \qquad (1)$$

where ∇_e^2 is the Laplacian for the electron; ∇_h^2 is that for the hole; and λ_{12}, μ_{13}, and ν_{23} are the inverse of the dielectric constants[1] between the different particles 1-2, 1-3, and 2-3, respectively, written in the form of Haken's exciton potential where the effect of the polarizability has been included. The quantities λ_{12}, μ_{13}, and ν_{23} are functions of the longitudinal vibrational frequency ω of the lattice, of the effective masses m_e^* and m_h^*, of the optical K_0 and static K_s dielectric constants as well as of the distances r_{12}, r_{13}, and r_{23} between the different particles. Due to the difficulty of solving Eq. (1) with λ_{12}, μ_{13}, and ν_{23} being functions of the distances between the particles, mean values λ, μ, and ν for these quantities have been considered. The values λ, μ, and ν correspond, respectively, to the average of λ_{12}, μ_{13}, and ν_{23} over the wave function Ψ of the system. With the classical method of Hylleraas, Eq. (1) for Fig. 1 can be written in the form

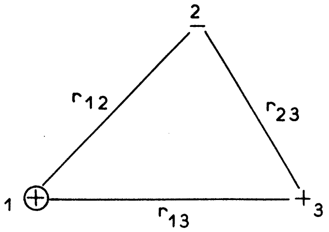

FIG. 1. Exciton–ionized-donor complex.

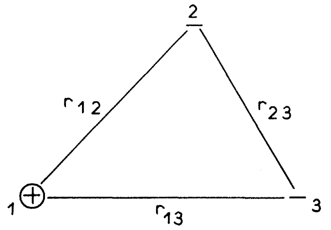

FIG. 2. Three-particle atomic systems such as He and H⁻.

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

Following the Pekeris[2] method for helium, we introduce the perimetric coordinates u, v, and w given by

$$u=\alpha\epsilon(-r_{12}+r_{13}+r_{23})\,,$$
$$v=\beta\epsilon(r_{12}-r_{13}+r_{23})\,, \tag{3}$$
$$w=\gamma\epsilon(r_{12}+r_{13}-r_{23})\,,$$

where α, β, and γ are variational parameters. From Eq. (3) the distances r_{12}, r_{13}, and r_{23} between the particles can be written in terms of u, v, and w,

$$r_{12}=(1/2\epsilon)(v/\beta+w/\gamma)\,,$$
$$r_{13}=(1/2\epsilon)(u/\alpha+w/\gamma)\,, \tag{4}$$
$$r_{23}=(1/2\epsilon)(u/\alpha+v/\beta)\,.$$

If the energy E is given in terms of ϵ,

$$E=-(\kappa+\sigma\chi)\epsilon^2\,, \tag{5}$$

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

$$\kappa=\tfrac{1}{8}(\alpha^2+3\beta^2+\gamma^2-2\alpha\gamma)\,, \tag{6}$$
$$\chi=\tfrac{1}{8}(3\alpha^2+\beta^2+\gamma^2-2\beta\gamma)\,. \tag{7}$$

With

$$\Psi=e^{-(1/2)(u+v+w)}F(u,v,w) \tag{8}$$

and substituting Eqs. (3), (5), and (8) into (2), one gets Eq. (25) of I, part of which seems useful to give here

$$\Bigg[\epsilon\Bigg(\frac{\partial^2F}{\partial u^2}\left[\alpha^2\left(\frac{4u^2w}{\alpha^2\gamma}+\frac{4uw^2}{\alpha\gamma^2}\right)+\sigma\alpha^2\left(\frac{4u^2v}{\alpha^2\beta}+\frac{4uv^2}{\alpha\beta^2}+\frac{8uvw}{\alpha\beta\gamma}+\frac{4u^2w}{\alpha^2\gamma}+\frac{4uw^2}{\alpha\gamma^2}\right)\right]+\frac{\partial^2F}{\partial v^2}\left[\beta^2\left(\frac{4u^2v}{\alpha^2\beta}+\frac{4uv^2}{\alpha\beta^2}+\frac{8uvw}{\alpha\beta\gamma}+\frac{4v^2w}{\beta^2\gamma}+\frac{4vw^2}{\beta\gamma^2}\right)\right.$$
$$\left.+\sigma\beta^2\left(\frac{4v^2w}{\beta^2\gamma}+\frac{4vw^2}{\beta\gamma^2}\right)\right]+\frac{\partial^2F}{\partial w^2}\left[\gamma^2\left(\frac{4u^2w}{\alpha^2\gamma}+\frac{4uw^2}{\alpha\gamma^2}\right)+\sigma\gamma^2\left(\frac{4v^2w}{\beta^2\gamma}+\frac{4vw^2}{\beta\gamma^2}\right)\right]+\frac{\partial^2F}{\partial u\partial w}\left[-4\left(\frac{2u^2w}{\alpha}+\frac{2uw^2}{\gamma}\right)\right]$$
$$+\frac{\partial^2F}{\partial v\partial w}\left[-4\sigma\left(\frac{2v^2w}{\beta}+\frac{2vw^2}{\gamma}\right)\right]+\frac{\partial F}{\partial u}\Bigg\{4\alpha\left(\frac{w^2}{\gamma^2}-\frac{u^2}{\alpha^2}\right)+(\alpha\gamma-\alpha^2)\left(\frac{4u^2w}{\alpha^2\gamma}+\frac{4uw^2}{\alpha\gamma^2}\right)+\sigma\Bigg[4\alpha\left(\frac{2uv}{\alpha\beta}+\frac{2uw}{\alpha\gamma}+\frac{2vw}{\beta\gamma}+\frac{w^2}{\gamma^2}+\frac{v^2}{\beta^2}\right)$$
$$-\alpha^2\left(\frac{4u^2v}{\alpha^2\beta}+\frac{4uv^2}{\alpha\beta^2}+\frac{8uvw}{\alpha\beta\gamma}+\frac{4u^2w}{\alpha^2\gamma}+\frac{4uw^2}{\alpha\gamma^2}\right)\Bigg]\Bigg\}+\frac{\partial F}{\partial v}\Bigg\{4\beta\left(\frac{u^2}{\alpha^2}+\frac{2uv}{\alpha\beta}+\frac{2uw}{\alpha\gamma}+\frac{2vw}{\beta\gamma}+\frac{w^2}{\gamma^2}\right)-\beta^2\left(\frac{4u^2v}{\alpha^2\beta}+\frac{4uv^2}{\beta^2\alpha}\right.$$
$$\left.+\frac{8uvw}{\alpha\beta\gamma}+\frac{4v^2w}{\beta^2\gamma}+\frac{4v^2w}{\beta\gamma^2}\right)+\sigma\left[4\beta\left(\frac{w^2}{\gamma^2}-\frac{v^2}{\beta^2}\right)+(\beta\gamma-\beta^2)\left(\frac{4v^2w}{\beta^2\gamma}+\frac{4vw^2}{\beta\gamma^2}\right)\right]\Bigg\}+\frac{\partial F}{\partial w}\Bigg\{(-\gamma^2+\alpha\gamma)\left(\frac{4u^2w}{\alpha^2\gamma}+\frac{4uw^2}{\alpha\gamma^2}\right)$$
$$+4\gamma\left(\frac{u^2}{\alpha^2}-\frac{w^2}{\gamma^2}\right)+\sigma\left[4\gamma\left(\frac{v^2}{\beta^2}-\frac{w^2}{\gamma^2}\right)-(\gamma^2-\beta\gamma)\left(\frac{4v^2w}{\beta^2\gamma}+\frac{4vw^2}{\beta\gamma^2}\right)\right]\Bigg\}+\cdots\Bigg)+\cdots\Bigg]=0. \tag{9}$$

With Eq. (3), the exponential part of the wave function can be written in terms of r_{12}, r_{13}, and r_{23},

$$\Psi=e^{-\epsilon(ar_{12}+br_{13}+cr_{23})}F(u,v,w)\,, \tag{10}$$

where

$$a=\tfrac{1}{2}(-\alpha+\beta+\gamma)\,,$$
$$b=\tfrac{1}{2}(\alpha-\beta+\gamma)\,, \tag{11}$$
$$c=\tfrac{1}{2}(\alpha+\beta-\gamma)\,.$$

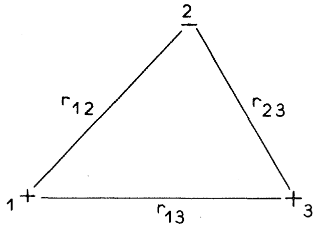

FIG. 3. Excitonic-molecule positive-ion complex.

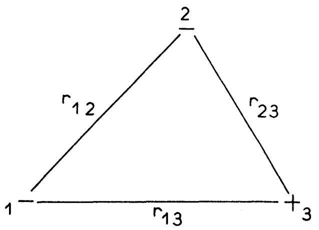

FIG. 4. Exciton negative-ion complex.

Assume the expression

$$F=\sum_{l,m,n=0}^{\infty} A(l,m,n)L_l(u)L_m(v)L_n(w), \qquad (12)$$

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 term general recursion relation between the coefficients $A(l; m; n)$. The recursion relation takes the form of the eigenvalue problem

$$H+(P+\sigma Q)\epsilon=0. \qquad (13)$$

The H, P, and Q are 50×50 matrices and are functions of the three variational parameters α, β, and γ which are determined from the minimization of the energy E. The matrix H is also a function of λ, μ, and ν.

The solution of Eq. (13) following the procedure in which ϵ and E are related by Eqs. (5)–(7) is referred to as "Proc I." Another procedure followed by Frost[6] to get the minimum energy is to consider $\chi=0$ and to vary α, β, γ, and κ simultaneously. In this case the energy is given by the following equation:

$$E=-\kappa\epsilon^2. \qquad (14)$$

This procedure requires much more computation than Proc I. To save computer time, one can take the specific values of α, β, and ν corresponding to the minimum energy in Proc I and vary κ until convergence is attained. This method is called "Proc II." The method of computation according to each of the two procedures is given in detail in I.

III. HYDROGEN NEGATIVE ION H⁻

The system is represented in Fig. 2. This ion is a particular case of Fig. 1. It results from replacing the positive hole of the exciton (particle 3) of Fig. 1 by an electron of negative charge and effective mass m_e^*. In this case $\lambda=1$, $\mu=\nu=-1$, and $\sigma=1$. For this system the recursion relation (13) reduces to the 33 term equation obtained by Pekeris[2,5] for H^-. The computations have been carried out following both Proc I and Proc II. With Proc I the minimum energy $E=-0.5224$ a.u. is obtained for $\alpha=0.508$, $\beta=0.514$, and $\gamma=1.522$. As has been pointed out in I, it is seen that the coefficients a and b of r_{12} and r_{13}, respectively, in the exponential term of the wave function (10) have positive values while the coefficient c of r_{23} is negative. This corresponds physically to an attractive potential between particles 1-2 and 1-3 and a repulsive potential between particles 2-3. This value of the minimum energy E is in good agreement with the value -0.52775 a.u. obtained by Pekeris.[5] Using Proc II and the values for $\alpha=\beta=1$ and $\gamma=2$, the minimum energy $E=-0.5217$ a.u. is obtained with $\kappa=1.9$. The value of E obtained in Proc I is in better agreement with that of Pekeris[5] than the value given in Proc II. The effect of the variation in λ, μ, and ν has also been studied in Proc I. For $\lambda=1$, $\mu=-1$, and $\nu=-0.95$, one expects to get a greater binding energy since the repulsive potential expressed in terms of the absolute value of ν between the pair of particles 2-3 is decreased. This energy $E=-0.53966$ a.u. corresponds to $\alpha=0.517$, $\beta=0.528$, and $\gamma=1.513$. For $\lambda=0.95$ and $\mu=\nu=-1$, one should get an energy less negative since the value of λ representing an attractive potential between the pair of particles 1-2 is decreased. This energy $E=-0.49286$ a.u. corresponds to $\alpha=0.58$, $\beta=0.394$, and $\gamma=1.49$. Considering $\lambda=0.95$ and $\mu=\nu=-0.95$, the minimum energy becomes less negative for a decrease in both attractive potentials between the particles 1-2 and 1-3 expressed in terms of λ and the absolute value of μ, although the repulsive potential in terms of the absolute value of ν is also decreased. In this case $E=-0.47646$ a.u. when calculated with $\alpha=0.468$, $\beta=0.476$, and $\gamma=1.402$. In all these cases one notes that the coefficients a, b, and c of r_{12}, r_{13}, and r_{23} in the wave function (10) correspond to the physical situation. This means that the coefficients a and b corresponding to attractive potentials have positive values while the coefficient c which corresponds to a repulsive potential has a negative value.

Finally, one may think that the consideration $\lambda=\mu=-1$, $\nu=1$, and the immobility of the positive hole (particle 3) of Fig. 4 with $\sigma=0$, would lead to the same results obtained above for H^- from Fig. 2 with $\lambda=1$, $\mu=\nu=-1$, and $\sigma=1$. This is not correct, at least in this treatment, since the interparticle distances r_{12} and r_{23} of Eq. (4) would be interchanged which means interchange between l and n of Eq. (12). As a matter of fact the interparticle distances cannot be interchanged. Otherwise the recursion relation (13) is not the same and the matrices P, Q, and H are different. This question will be discussed in detail in Sec. VIII.

IV. HELIUM ATOM He

This atom is represented by Fig. 2 with $\sigma=1$, $\lambda=2$, $\mu=-2$, and $\nu=-1$. In this case the recursion relation (13) reduces to 33 terms as that derived by Pekeris[2] for helium. For the helium atom Pekeris[2] considered the case $\alpha=\beta=1$ and $\gamma=2$. For this atom Proc II has been used. With the values for α, β, and γ adopted by Pekeris, the minimum energy $E=-5.8038$ Ry is obtained with $\kappa=2.6$. This value for E is in better agreement with -5.8074 Ry obtained by Pekeris[2] for $\kappa=2$ than the -5.80214 Ry calculated by Whitten and Sims.[7] One should note that in Pekeris treatment for helium with $\sigma=\alpha=\beta=1$ and $\gamma=2$, the value of $\kappa=2$ is determined from the approximation at infinity of Proc I in the present treatment. In Proc II (Frost procedure) κ is a variational parameter obtained from the minimization of the energy. In Pekeris treatment, the matrix P is then different from that obtained by Proc II since it corresponds to different values of κ. As a matter of fact what is denoted by κ in Pekeris calculations for the helium atom is $\kappa+\chi$ in the present treatment for the same atom. Considering $\sigma=\alpha=\beta=1$ and $\gamma=2$ and taking the Ry for unit of energy as Pekeris did, instead of a.u., one gets from Eqs. (6) and (7) the value of $\kappa+\chi=2$ which is the same as the $\kappa=2$ obtained by Pekeris.

The agreement between the general recursion relation (13) and the results obtained independently by Pekeris for H$^-$ and He to three decimals gives one confidence in this general relation (13). It should be pointed out that relation (13) was developed for three-particle exciton complexes. In these systems observations are not made with as much accuracy as in atomic physics. As a matter of fact the accuracy with which relation (13) is solved is quite enough for the purpose for which it was derived. The numerical solution to this relation was carried out in double precision with a limitation to 50×50 matrices due to the capacity of the UNIVAC 1108 computer used. One has to mention that it is the partitioning technique of Löwdin[8] that has been used in solving the eigenvalue problem of Eq. (13). This method is different from that used by Pekeris[2] or by Frost.[6,9,10] It has to be mentioned also that for the atomic systems H$^-$ and He, the quantities $K_{\mathrm{eff}}=K(r_{ij})=1$ and $m_e^*=m_0$, where m_0 is the free-electron mass.

V. EXCITONIC-MOLECULE POSITIVE ION

This molecule is represented by Fig. 3 in which the fixed hole (particle 1) of Fig. 1 becomes mobile. In this case one has simply to add[6] to Eq. (1) the Laplacian for this hole. In the case that the atomic units are the same as those considered for Figs. 1 and 2, the term would by simply $\frac{1}{2}\sigma\nabla_{h1}^2\Psi$. In other words the terms to be added to Eq. (2) to represent Fig. 3 are

$$\sigma\left(\frac{\partial^2\Psi}{\partial r_{12}^2}+\frac{2}{r_{12}}\frac{\partial\Psi}{\partial r_{12}}+\frac{\partial^2\Psi}{\partial r_{13}^2}+\frac{2}{r_{13}}\frac{\partial\Psi}{\partial r_{13}}+\frac{1}{r_{12}r_{13}}(r_{12}^2+r_{13}^2-r_{23}^2)\frac{\partial^2\Psi}{\partial r_{12}\partial r_{13}}\right). \tag{15}$$

The terms to be added to Eq. (9) are

$$\begin{aligned}\sigma\epsilon\Bigg\{&\left(\alpha^2\frac{\partial^2F}{\partial u^2}+\beta^2\frac{\partial^2F}{\partial v^2}-2\alpha\beta\frac{\partial^2F}{\partial u\partial v}\right)\left(\frac{4u^2v}{\alpha^2\beta}+\frac{4uv^2}{\alpha\beta^2}\right)+\gamma^2\frac{\partial^2F}{\partial w^2}\left(\frac{8uvw}{\alpha\beta\gamma}+\frac{4v^2w}{\beta^2\gamma}+\frac{4vw^2}{\beta\gamma^2}+\frac{4u^2w}{\alpha^2\gamma}+\frac{4uw^2}{\alpha\gamma^2}\right)\\ &+\frac{\partial F}{\partial u}\left[(\alpha\beta-\alpha^2)\left(\frac{4u^2v}{\alpha^2\beta}+\frac{4uv^2}{\alpha\beta^2}\right)+4\alpha\left(\frac{v^2}{\beta^2}-\frac{u^2}{\alpha^2}\right)\right]+\frac{\partial F}{\partial v}\left[(\alpha\beta-\beta^2)\left(\frac{4u^2v}{\alpha^2\beta}+\frac{4uv^2}{\alpha\beta^2}\right)-4\beta\left(\frac{v^2}{\beta^2}-\frac{u^2}{\alpha^2}\right)\right]\\ &+\frac{\partial F}{\partial w}\left[-\gamma^2\left(\frac{8uvw}{\alpha\beta\gamma}+\frac{4v^2w}{\beta^2\gamma}+\frac{4vw^2}{\beta\gamma^2}+\frac{4u^2w}{\alpha^2\gamma}+\frac{4uw^2}{\alpha\gamma^2}\right)+4\gamma\left(\frac{u^2}{\alpha^2}+\frac{v^2}{\beta^2}+\frac{2uv}{\alpha\beta}+\frac{2uw}{\alpha\gamma}+\frac{2vw}{\beta\gamma}\right)\right]+F\Bigg[\left(\frac{u^2v}{\alpha^2\beta}+\frac{uv^2}{\beta^2\alpha}\right)(\alpha^2+\beta^2-2\alpha\beta)\\ &+\gamma^2\left(\frac{2uvw}{\alpha\beta\gamma}+\frac{v^2w}{\beta^2\gamma}+\frac{vw^2}{\beta\gamma^2}+\frac{u^2w}{\alpha^2\gamma}+\frac{uw^2}{\alpha\gamma^2}\right)+\frac{2v^2}{\beta^2}(-\alpha+\beta-\gamma)+2\frac{u^2}{\alpha^2}(\alpha-\beta-\gamma)-2\gamma\left(\frac{2uv}{\alpha\beta}+\frac{2uw}{\alpha\gamma}+\frac{2vw}{\beta\gamma}\right)\Bigg]\Bigg\}.\end{aligned} \tag{16}$$

For the excitonic-molecule positive ion of Fig. 3 the eigenvalue problem of Eq. (13) becomes

$$H+[P+\sigma(Q+Q_1)]\epsilon=0. \tag{17}$$

The term Q_1 contains the matrix coefficients of the additional terms of Eq. (16). The computational procedure is carried out according to Proc I. In this case Eq. (5) is replaced by

$$E=-(\kappa+\sigma\chi_1)\epsilon^2, \tag{18}$$

with κ the same expression given by Eq. (6) and with

$$\chi_1=\tfrac{1}{4}[2(\alpha^2+\gamma^2)+\beta(\beta-\alpha-\gamma)]. \tag{19}$$

The expressions for κ and χ_1 are determined as before from the approximation at infinity. With the same atomic units of Figs. 1 and 2 in which the binding energy E_D is simply $\frac{1}{2}$a.u., the minimum energy E given by $E/E_D=1.058$ when $\lambda=\mu=\nu=1$, $\alpha=0.659$, $\beta=1.514$, $\gamma=0.482$, and $\sigma=0$ are used. To save computer time, the values of α, β, and γ are considered constant for all values of σ. One

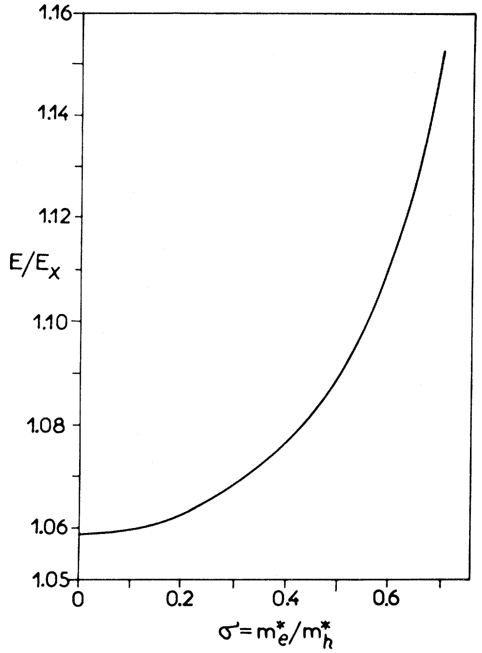

FIG. 5. Plot of E/E_x vs m_e^*/m_h^* for the excitonic-molecule positive-ion complex.

can note that the values of E/E_D, α, β, and γ are practically the same[1] as those obtained for Fig. 1 for the same value of $\sigma = 0$. This is quite logical. One can also see that the coefficients a and c of the exponential term in Eq. (10) have positive values representing the attractive potential between the particles 1-2 and 2-3 while b, corresponding to a repulsive potential of the particles 1-3, has a negative value.

The stability of the excitonic molecule positive ion has to be studied in terms of the exciton binding energy E_x and not in terms of E_D. In this case the atomic units $K_{\text{eff}}\hbar^2/e^2M$ and $Me^4/K_{\text{eff}}^2\hbar^2$ have to be adopted, respectively, for length and energy and the units $M=\hbar=e^2/K_{\text{eff}}=1$ have to be used with M being the exciton reduced mass. In these units the exciton binding energy $E_x = -Me^4/2\hbar^2K_{\text{eff}}^2$ is simply $\frac{1}{2}$ a.u. Since $\lambda=\nu=1$, the dielectric constant K_{eff} is the same for E_x and E_D. The results in terms of E_D can be easily obtained in terms of E_x. Since

$$E/E_x = (E/E_D)E_D/E_x = (E/E_D)m_e^*/M = (E/E_D)(1+\sigma)\,, \tag{20}$$

the results in terms of E_x are those obtained in terms of E_D times the factor $(1+\sigma)$. This conclusion can also be obtained[4] by writing the Schrödinger equation in the beginning in both systems of atomic units. The plot of E/E_x as a function of σ for the excitonic-molecule positive ion is given in Fig. 5. This curve that starts with the value 1.058 for $\sigma=0$ and increases as σ increases shows the stability and the existence of such a molecule for all values of σ. No experimental evidence has yet been established for such a complex. On the other hand the values of E/E_D decrease as σ increases and consequently there is a critical mass ratio $\sigma_c \ll 1$ below which the system is stable; for $\sigma > \sigma_c$ the system is unstable. The molecule of Fig. 3 corresponds in atomic physics to a positron bound to a hydrogen atom. The theoretical study of a bound state in such a system has been carried out by different authors.[6,11,12] The calculations of these authors are given in terms of E_D and that is why such a bound state has not been found for $\sigma = 1$. This result is then in agreement with the present calculations.

VI. EXCITON NEGATIVE ION

In a preceding paper[13] referred to as II, the exciton–ionized-acceptor complex represented in Fig. 6 has been studied. The stability of such a complex has to be studied in terms of the neutral acceptor binding energy $E_A = -e^4m_h^*/2\hbar^2K_{\text{eff}}^2$ and not in terms of E_D as has been the case for Fig. 1. In the present case the atomic units $K_{\text{eff}}\hbar^2/e^2m_h^*$ and $e^4m_h^*/\hbar^2K_{\text{eff}}^2$ have been adopted, respectively, for length and energy and the units $m_h^*=\hbar=e^2/K_{\text{eff}}=1$ have been used. In such units the binding energy E_A is simply $\frac{1}{2}$ a.u. The Schrödinger equation for Fig. 6 is

$$\tfrac{1}{2}\delta\nabla_e^2\Psi + \tfrac{1}{2}\nabla_h^2\Psi + [E + (\lambda/r_{12} - \mu/r_{13} + \nu/r_{23})]\Psi = 0\,, \tag{21}$$

with λ and μ having negative values and $\delta = m_h^*/m_e^*$. The eigenvalue problem similar to that of Eq. (13) is

$$H' + (\delta P + Q)\epsilon = 0\,. \tag{22}$$

The results of E/E_A obtained from the solution of Eq. (22) are given as a function of δ and not as a function of σ was the case for Fig. 1. These calculations lead to the conclusion that it is highly improbable for Fig. 6 to exist in the known semiconductors which have particularly big values of δ.

A complex in a more general form than that of Fig. 6 can be obtained by having the electron 1 of this figure mobile instead of being fixed. This gives Fig. 4 that represents the exciton negative ion. Figure 6 is then a particular case of Fig. 4 as Fig.

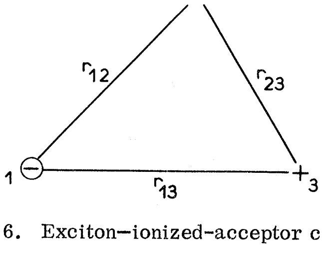

FIG. 6. Exciton–ionized-acceptor complex.

1 is a particular case of Fig. 3. The stability of such a complex (Fig. 4) has been studied recently[14] as a function of σ. For both complexes of Figs. 4 and 6 with $\delta = 0$, one should get the same results for E/E_A when the same values of λ, μ, and ν are used. Since $\delta = 0$ and not $\sigma = 0$ is the limiting case for the study of the stability of the complex of Fig. 4, it is a strong argument to carry out the calculations for such a complex as a function of δ. This point will be discussed in detail in Sec. VIII.

For Fig. 4 one simply has to add the term $\frac{1}{2}\delta\nabla^2_{e1}\Psi$ to those of Eq. (21). This term corresponds to that given by Eqs. (15) and (16) except that the factor σ should be replaced by the factor δ. In this case the corresponding eigenvalue problem for Fig. 4 is

$$H + [\delta(P + P_1) + Q]\epsilon = 0 . \tag{23}$$

The same computational procedure can be carried out following Proc I. In this case Eq. (5) is replaced by

$$E = -(\delta\kappa_1 + \chi)\epsilon^2 , \tag{24}$$

with χ the same as in Eq. (7) and

$$\kappa_1 = \tfrac{1}{4}[\alpha^2 + 2(\beta^2 + \gamma^2) - \alpha(\beta + \gamma)]. \tag{25}$$

The expressions for χ and κ_1 are determined from the approximation at infinity.

The stability of the exciton negative ion has to be studied in terms of the exciton binding energy E_x and not in terms of E_A. The atomic units adopted in Sec. V for the excitonic molecule positive ion in which E_x is simply $\frac{1}{2}$ a.u. have to be used. As with Eq. (20) and assuming that ν and μ have the same absolute values, one can show

$$E/E_x = (E/E_A)(1 + \delta) . \tag{26}$$

This would mean that for Fig. 4 the results E/E_x as function of δ can be obtained by multiplying the values of E/E_A by the factor $(1+\delta)$. The computations for all of these systems would normally need an enormous number of computer hours. It happens that for the exciton negative ion, one can use some of the informations already given in this paper to make some kind of analysis and consequently to reach a reasonable conclusion without going through the detailed computations. The binding energies corresponding to $\delta = 0$ for both the exciton negative ion and exciton-ionized-acceptor complexes of Figs. 4 and 6, respectively, have the same value $E/E_x = 1.15$. This is quite similar to the result obtained in Sec. V, where the binding energies of the exciton–ionized-donor complex (Fig. 1) and the excitonic molecule positive ion (Fig. 3) have the same value for $\sigma = 0$. Also one can consider the value $E/E_x = 1.048$ obtained independently by Frost[6] and Kolos *et al.*[15] for the trielectron or positronium ion with $\sigma = m_e^*/m_h^* = 1$ to be the same for the exciton negative ion for the same value of $\delta = m_h^*/m_e^* = 1$. The value $E/E_x = 1.0448$ has been obtained in Ref. 7 for the system $e^-e^+e^-$. One can see that for Fig. 4 the values of E/E_x decrease as δ increases. For the known semiconductors δ is greater than 3. It seems then that it is highly improbable that the exciton negative ion can exist in semiconductors, which is also the case of the exciton–ionized-acceptor complex of Fig. 6 that has been treated in full detail in II, unless the effect of the polarizability plays a very important role. Note that all the discussion given in this section concerns the case $\lambda = \mu = -1$ and $\nu = 1$ in which the polarizability has been neglected.

VII. EXCITED STATES OF THE EXCITON-IONIZED-DONOR COMPLEX

In CdS excited states of the exciton[16] and exciton–ionized-donor complex[17] have been observed. For the A-band exciton the binding energy[16] of the 2S state is 8 meV. For the excited state of the exciton–ionized-donor complex the observed binding energy[17] relative to that of the 2S excited state of the exciton is 9.1 meV. The stability and existence of the complex excited state has to be studied in terms of the corresponding excited state and not in terms of the ground state of the exciton. In spite of the fact that these experiments do not specify to what quantum number this complex excited state corresponds, these results still show the stability of the excited state of the exciton–ionized-donor complex in CdS. The calculations have been carried out in terms of the exciton ground state. To have some correspondence between theory and experiment it is good to give some experimental ratios concerning the energies of the complex and the ground-state exciton binding energy. The experimental ratio between the ground state energy of the complex and the A-band exciton is 1.171; that between the excited state of the complex and the A-band exciton ground state is 0.61. The value 0.71 corresponds to the ratio between the excited state of the complex and the ground state of the exciton B band. One has to mention that the experimental[16] binding energies of the exciton A and B bands are 28 and 24 meV, respectively. The recursion relation (13) has been solved in a self-consistent manner in the atomic unit system corresponding to $E_x = \frac{1}{2}$ a.u. With $\sigma = 0.207$, $\omega = 306$, $K_{s\perp} = 9.35$, $K_{s\parallel} = 10.33$, and $K_0 = 5.24$ the minimization of the energy of the complex ground state has been obtained for $\lambda = 0.988$, $\mu = 0.98$, $\nu = 1$, $\alpha = 0.373$, $\beta = 1.474$, and $\gamma = 0.588$. The first root of Eq. (13) corresponds naturally to the complex ground state. The second, third, fourth, etc., should correspond to the complex $n\,^1S$ excited states. The calculated value 1.191 of the complex ground-state energy in terms of E_x is in very good agreement with the experimental ratio[18,19] 1.171 mentioned above. The values of the second, third, and fourth roots of Eq. (13) in terms of E_x are, respectively, 0.8472, 0.7367, and 0.5948. The third root is in agreement with the experimental ratio 0.71 while the fourth root agrees with the value 0.61 which is given above. Although these results for the complex excited states may not be in quantitative agreement with experiment, still they show the existence and stability of such states in agreement with observations on CdS.

For CuCl with $\sigma = 0.03846$, the first, second, and third roots of Eq. (13) in terms of E_x are, respectively, 1.149, 0.918, and 0.8537. With $\sigma = 0.0207$ corresponding to CuBr these roots are 1.154, 0.905, and 0.845. Unfortunately the complex excited states in CuCl and CuBr have not yet been observed. The comparison with experiment for the complex ground state in these two materials has been already discussed in II.

To study carefully the complex excited states, one has to calculate the lower bounds of the different energies.[5] This requires the determination of the corresponding wave functions of Eqs. (8) and (12). This would be an elaborate task which would take a great deal of computer time.

VIII. SOME REMARKS CONCERNING THE RECURSION RELATION

As has been mentioned before in Sec. III, one may think that with $\sigma = 0$, Fig. 4 corresponds to the hydrogen negative ion H^-. This would mean that Fig. 4 with $\sigma = 0$ give the same results as Fig. 2 with $\sigma = 1$. For Fig. 2 with $\sigma = 1$, Eq. (2) becomes

$$\left(\frac{\partial^2\Psi}{\partial r_{12}^2} + \frac{2}{r_{12}}\frac{\partial\Psi}{\partial r_{12}}\right) + \left(\frac{\partial^2\Psi}{\partial r_{13}^2} + \frac{2}{r_{13}}\frac{\partial\Psi}{\partial r_{13}}\right) + 2\left(\frac{\partial^2\Psi}{\partial r_{23}^2} + \frac{2}{r_{23}}\frac{\partial\Psi}{\partial r_{23}}\right) + \frac{1}{r_{12}r_{23}}(r_{12}^2 + r_{23}^2 - r_{13}^2)\frac{\partial^2\Psi}{\partial r_{12}\partial r_{23}}$$
$$+ \frac{1}{r_{13}r_{23}}(r_{13}^2 + r_{23}^2 - r_{12}^2)\frac{\partial^2\Psi}{\partial r_{13}\partial r_{23}} + 2\left[E + \left(\frac{\lambda}{r_{13}} - \frac{\mu}{r_{13}} + \frac{\nu}{r_{23}}\right)\right]\Psi = 0. \tag{27}$$

In this equation μ and ν take negative values.

Writing the corresponding equation for Fig. 4 with $\sigma = 0$, one gets

$$\left(\frac{\partial^2\Psi}{\partial r_{23}^2} + \frac{2}{r_{23}}\frac{\partial\Psi}{\partial r_{23}}\right) + \left(\frac{\partial^2\Psi}{\partial r_{13}^2} + \frac{2}{r_{13}}\frac{\partial\Psi}{\partial r_{13}}\right) + 2\left(\frac{\partial^2\Psi}{\partial r_{12}^2} + \frac{2}{r_{12}}\frac{\partial\Psi}{\partial r_{12}}\right) + \frac{1}{r_{12}r_{23}}(r_{12}^2 + r_{23}^2 - r_{13}^2)\frac{\partial^2\Psi}{\partial r_{12}\partial r_{23}}$$
$$+ \frac{1}{r_{12}r_{13}}(r_{12}^2 + r_{13}^2 - r_{23}^2)\frac{\partial^2\Psi}{\partial r_{12}\partial r_{13}} + 2\left[E + \left(\frac{\lambda}{r_{12}} - \frac{\mu}{r_{13}} + \frac{\nu}{r_{23}}\right)\right]\Psi = 0, \tag{28}$$

with λ and μ taking negative values.

By interchanging r_{12} and r_{23}, Eqs. (27) and (28) lead to the same equation. This would mean that if one succeeds in obtaining the same recursion relation for both Figs. 2 and 4, corresponding, respectively, to $\sigma = 1$ and $\sigma = 0$, by simply interchanging r_{12} and r_{23}, one should expect to get the same results for H^-. From Eq. (4), the interchange of r_{12} and r_{23} means the interchange of α and γ as well as the interchange of u and w. This would mean that the interchange of $\partial^2F/\partial u^2$, $\partial^2F/\partial w^2$, $\partial F/\partial u$, $\partial F/\partial w$, $\partial^2F/\partial v\partial w$, $\partial^2F/\partial u\partial v$, u, and w should lead to the same coefficients in Eq. (9) for both figures which is not the case. The general recursion relation (13) derived for Fig. 1 and adopted for Fig. 2 by simply changing the signs of λ and ν and putting $\sigma = 1$ cannot be the same recursion relation for Fig. 4 with $\sigma = 0$ in which the coordinates r_{12} and r_{23} have been interchanged. As one can see, the interchange of r_{12} and r_{23} changes completely the recursion relation. Dealing with Fig. 4 such that it corresponds to H^- with $\sigma = 0$, one has to start from the beginning to derive a new recursion relation. This would again be a tremendous task. The only figure corresponding to H^- and for which the recursion relation (13) is applicable is then Fig. 2.

In applying the general recursion relation (13) to a particular case similar to any of these represented in Figs. 2–4 and 6, one has to be very careful not to introduce any change except in the constants as for instance in the signs and values of λ, μ, and ν and the interchange between σ and δ. The coordinates r_{12}, r_{13}, and r_{23} are not to be interchanged. Any interchange between these coordinates is capable of leading to a completely different recursion relation that would render inapplicable the general recursion relation (13).

The Fig. 4 with $\sigma = 0$ does not then correspond to the recursion relation (13). On the other hand, Fig. 6 that represents the exciton-ionized-acceptor complex for which the atomic units correspond to $E_A = \frac{1}{2}$ a.u. is a particular case of Fig. 4. The limiting case for Fig. 4 is then $\delta = 0$ and not $\sigma = 0$. In this case one has to carry out the calculations for Fig. 4 as a function of δ and not as a function of σ. The Eqs. (2) and (15) would have exactly the same form for both Figs. 3 and 4 except that the matrices P and Q are interchanged as can be seen from Eqs. (17) and (23). The matrices P, P_1, Q, and Q_1 for both Figs. 3 and 4 have exactly the same forms. For Fig. 3, the matrix $Q+Q_1$ is multiplied by the factor σ and P is not while for Fig. 4, the matrix $P+P_1$ is multiplied by the factor δ and Q is no longer multiplied by σ. These arguments show why the calculations for Fig. 4 have been carried out in terms of δ and not in terms of σ.

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