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Binding energies of the exciton—ionized-donor complex and the exciton line $n=1$ in PbI_2

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The exciton binding energy of the line $n=1$ in PbI_2 presented a dilemma since the calculated energy using different methods is much greater than that obtained experimentally. In the present work, with the use of the methods developed and applied previously with success for different semiconductors by Elkomoss for the exciton—ionized-donor complex and in which the polarizability of the lattice has been taken into account, the binding energy of the complex has been calculated in PbI_2. This complex turns out to be stable. The exciton binding energy for the line $n=1$ has also been determined. For the first time quite good agreement between the calculated value and the experiments of Nikitine *et al.* and Harbeke *et al.* for this line $n=1$ has been obtained. The oscillator strength f_3/f_x for the complex has also been calculated.

I. INTRODUCTION

The absorption spectra in PbI_2 have been explained in terms of a Wannier exciton series of up to four lines with the Rydberg constants $R_x=142$ meV (Refs. 1—5) and $R_x=127$ meV (Refs. 4—7) for the 4*H* and 2*H* polytypes, respectively. It was a surprising result that the positions of the $n=1$ line for the 4*H* and 2*H* polytypes were, respectively, 82 meV (Refs. 1—3,5,8) and 72 meV (Refs. 5 and 8) higher than predicted from the Wannier series. In an attempt to resolve the difficulty, the line $n=1$ has been represented by a different Wannier series.[2] Since then the anomaly of the line $n=1$ in PbI_2 has been the subject of particular interest over the years. Different authors have tried unsuccessfully to explain this anomaly theoretically.[9,10] In an excellent review[5] of this problem Harbeke and Tosatti[5] have shown recently that the lines $n=1,2,3,\ldots$ all belong to one and the same Wannier series. These authors[5] have treated the problem using a perturbing central-cell potential. In such a case for the 4*H* polytype, the $n=1$ anomaly from the Wannier isotropic value is resolved, but the agreement with the observed $n=2,3,\ldots$ lines and isotropic energies has been spoiled.[5]

In recent work, Levy *et al.*[11,12] have observed a new line that they have interpreted as the line $n=3$. Based on this finding and on the positions of what are generally accepted to be the $n=1$ and 2 lines, these authors[11,12] have proposed a new assignment of the exciton spectrum in terms of a normal, isotropic Wannier series with a binding energy $R_x=30$ meV. Harbeke and Tosatti[4] have given different arguments that are not in favor of such a finding.[11,12] The conclusion of these authors[4] is that the exciton line $n=3$ observed by Levy *et al.*[11,12] must be just a coincidence, and no such line is expected to be there. It is then of interest to consider a different theoretical treatment in order to solve the anomaly of the $n=1$ line and to obtain good agreement between the calculated and the experimental values for the energy of this line.

In preceding papers given in Refs. 13 and 14, respectively, the Pekeris[15] and Callan[16,17] methods for helium have been developed for the exciton—ionized-donor complex given in Fig. 1. Haken's exciton potential,[18] in which the effect of polarizability is included, has been generalized for such a system.[13,14,19–22] These methods,[13,14] applied with success for different semiconductors have also been used to calculate the exciton binding energy E_x in TlCl, TlBr,[13,19] and CdS.[14] The calculated values of E_x in CdS (Ref. 14) for the different available values of $\sigma=m_e^*/m_h^*$, where m_e^* and m_h^* are, respectively, the electron and the hole effective masses, are in quite good agreement with experiment. For TlCl and TlBr the calculated values[13,19] of E_x are in better agreement with experiment[23] than those obtained from the simple hydrogenic formula with the static dielectric constant.[23] The theoretical values[13,19] are also in better agreement with experiment than those obtained in Ref. 23 by Bachrach and Brown using Haken's potential[18] for the exciton with a simple wave function. This has been interpreted as being due to the defect of the wave function used in Ref. 23, particularly for small distances.

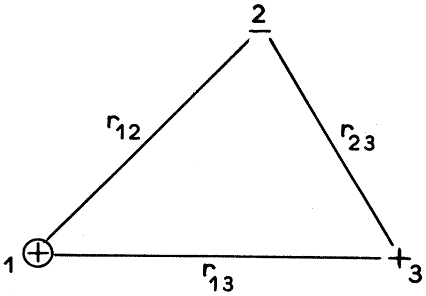

FIG. 1. Exciton—ionized-donor complex.

In the present work, the methods given in Refs. 13 and 14 have been applied to calculate the binding energy of the exciton—ionized-donor complex as well as that for the exciton line $n=1$ in PbI_2. In our calculations we tried to consider the least favorable values in obtaining the results. Thus, the electron m_e^* and the hole m_h^* effective masses determined from the series $n=2,3,4,\ldots$ have been considered. The self-consisent calculations lead to an excellent agreement with experiment for the binding energy of the exciton line $n=1$. The exciton—ionized-donor complex in PbI_2 is quite stable. The relative oscillator strength f_3/f_x has also been calculated for this material, where f_3 and f_x are the oscillator strengths of the complex and the exciton, respectively.

II. FORM OF THE POTENTIAL

As described by Haken,[18] the dielectric constant $K(r_{23})$ between the hole and the electron of a delocalized exciton is a function of the distance r_{23} separating the two particles, of their effective masses, of the optical and static dielectric constants K_0 and K_s, respectively, and of the longitudinal vibrational frequency ω of the lattice. As atomic units in terms of a certain effective dielectric constant K_{eff} are usually adopted, the generalized[13,22] Haken 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:

$$\frac{1}{K(r_{ij})}=\frac{1}{K_{\text{eff}}}\left[\frac{K_{\text{eff}}}{K_s}\left[1-\frac{\zeta_{ij}}{2}\right]+\frac{K_{\text{eff}}}{K_o}\frac{\zeta_{ij}}{2}\right], \tag{1}$$

with

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

$$\kappa_i=(4\pi m_i^*\omega/h)^{1/2}, \tag{2b}$$

$$\kappa_j=(4\pi m_j^*\omega/h)^{1/2}, \tag{2c}$$

where h is Planck's constant. For the exciton—ionized-donor complex of Fig. 1, the potential energy of the system[22] is

$$V(r_{12},r_{13},r_{23})=\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j\,(\neq i)}^{N}e^2\lambda_{ij}/K_{\text{eff}}r_{ij}, \tag{3}$$

where λ_{12}, λ_{13}, and λ_{23} are the coefficients of the terms $1/r_{12}$, $1/r_{13}$, and $1/r_{23}$, respectively, and which are given in the large square brackets of Eq. (1). Owing to the difficulties that may occur in solving the problems of exciton complexes using the general potential of Eqs. (1)—(3), mean values of λ_{ij}'s are considered. By knowing the wave function Ψ of the system, one can write

$$\bar{\lambda}_{ij}=\frac{K_{\text{eff}}}{K_s}+(1/2)K_{\text{eff}}\left[\frac{1}{K_o}-\frac{1}{K_s}\right]\left[\frac{\int\Psi^*\zeta_{ij}\Psi\,d\tau}{\int\Psi^*\Psi\,d\tau}\right]. \tag{4}$$

The mean values $\bar{\lambda}_{ij}$ 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_o, K_s, and ω.

III. METHOD OF SOLUTION

In Refs. 13 and 14, the binding energy of 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

$$\tfrac{1}{2}\nabla_e^2\Psi+\tfrac{1}{2}\sigma\nabla_h^2\Psi+(E-V)\Psi=0, \tag{5}$$

where ∇_e^2 is the Laplacian for the electron, ∇_h^2 is that for the hole, $\sigma=1/m_h^*$ is the mass ratio given in the atomic units used, and V is the potential energy of the system given in Eqs. (1)—(4). With the classical method of Hylleraas,[24] Eq. (5) for Fig. 1 can be written in the form

$$\frac{\partial^2\Psi}{\partial r_{12}^2}+\frac{2}{r_{12}}\frac{\partial\Psi}{\partial r_{12}}+\sigma\left[\frac{\partial^2\Psi}{\partial r_{13}^2}+\frac{2}{r_{13}}\frac{\partial\Psi}{\partial r_{13}}\right]+(1+\sigma)\frac{\partial^2\Psi}{\partial r_{23}^2}+\frac{2}{r_{23}}(1+\sigma)\frac{\partial\Psi}{\partial r_{23}}$$
$$+\frac{\partial^2\Psi}{\partial r_{12}\partial r_{23}}(r_{12}^2+r_{23}^2-r_{13}^2)\frac{1}{r_{12}r_{23}}+\sigma\frac{\partial^2\Psi}{\partial r_{13}\partial r_{23}}(r_{13}^2+r_{23}^2-r_{12}^2)\frac{1}{r_{12}r_{23}}+2\left[E+\left[\frac{\lambda}{r_{12}}-\frac{\mu}{r_{13}}+\frac{\nu}{r_{23}}\right]\right]\Psi=0. \tag{6}$$

IV. PEKERIS METHOD

In Ref. 13 the Pekeris method[15] for helium has been developed for the exciton—ionized-donor complex. We introduce[13] the parametric coordinates u, v, and w given by

$$u=\alpha\epsilon(-r_{12}+r_{13}+r_{23}),\quad v=\beta\epsilon(r_{12}-r_{13}+r_{23}),$$
$$w=\gamma\epsilon(r_{12}+r_{13}-r_{23}), \tag{7}$$

where α, β, and γ are variational parameters. From Eq. (7), the distances r_{12}, r_{13}, and r_{23} between the particles can be written in terms of u, v, and w. If this energy E is given in terms of ϵ,

$$E=-(\kappa+\sigma X)\epsilon^2, \tag{8}$$

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

$$\kappa=\tfrac{1}{8}(\alpha^2+3\beta^2+\gamma^2-2\alpha\gamma)\,, \tag{9}$$

$$\chi=\tfrac{1}{8}(3\alpha^2+\beta^2+\gamma^2-2\beta\gamma)\,. \tag{10}$$

Let

$$\Psi=e^{-(1/2)(u+v+w)}F(u,v,w)\,, \tag{11}$$

with

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

where L_l, L_m, and L_n denote, respectively, the normalized Laguerre polynomials of order l, m, and n. After different transformations and using the relations between the Laguerre polynomials of Eq. (12) and their derivatives, Eq. (6) gives[13] a considerably long, 57-term recursion relation between the coefficients $A(l,m,n)$ of Eq. (12). This recursion relation takes the form of the eigenvalue problem,

$$H+\epsilon(P+\sigma Q)=0\,. \tag{13}$$

The solution of the recursion relation (13) obtained using the wave function of Eqs. (11) and (12) gives the energy ratio E/E_D as a function of $\sigma=1/m_h^*$ for different values of λ, μ, and ν. 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 given by Eq. (4). The exponential part of the wave function (11) can be written in terms of r_{12}, r_{13}, and r_{23} as

$$\Psi=e^{-\epsilon(ar_{12}-br_{13}+cr_{23})}F(u,v,w)\,, \tag{14}$$

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

$$\begin{aligned} a&=\tfrac{1}{2}(-\alpha+\beta+\gamma)\,,\\ b&=\tfrac{1}{2}(\alpha-\beta+\gamma)\,,\\ c&=\tfrac{1}{2}(\alpha+\beta-\gamma)\,. \end{aligned} \tag{15}$$

For a specific semiconductor, the corresponding mean values λ, μ, and ν of Eq. (4) must be calculated. For these computations one needs to know the wave function Ψ of Eqs. (11) and (12). The calculations concerning this wave function are quite complicated. As a simplification, only the exponential part of Eq. (14) has been used to evaluate the integrals of Eq. (4) and, consequently, to calculate the values of λ, μ, and ν. In this case the values of λ, μ, and ν for a particular semiconductor are obtained by Eq. (36) given in Ref. 13. In Eq. (36) of Ref. 13, the values of λ, μ, and ν depend not only on the fundamental constants, but also on a function of α, β, and γ of Eq. (15) and of the energy ϵ of the complex. This energy minimum corresponding to particular values of α, β, and γ has been calculated using the determinant of Eq. (13) for some values of λ, μ, and ν. In this case, the computations have to be self-consistent as described in detail in Ref. 13. This means that the values of λ, μ, and ν considered in the determination of the energy of Eqs. (8)—(10) and (13) must be the same as those calculated from Eq. (36) of Ref. 13 for the same value of ϵ.

V. CALLAN METHOD

In Ref. 14 the Callan method[16,17] for helium has been developed for the exciton—ionized-donor complex. In this method, the approximate wave function Φ corresponding to the solution of Eq. (6) has been written in the form

$$\Phi=e^{-\lambda_1 r_{12}}e^{-[\nu_1/(1+\sigma)]r_{23}}\,, \tag{16}$$

with

$$\lambda_1=\lambda-\sigma_1,\ \ \nu_1=\nu-\sigma_3\,, \tag{17}$$

where σ_1 and σ_3 are positive variational parameters determined from the minimization of the energy of the system. Following this method, the correlation effect has been considered such that the repulsive potential along the direction r_{13} is truncated at a minimum distance R. This distance $R=1.1091$ a.u. is determined such that for $\lambda=\mu=\nu=1$ (polarizability neglected) one must obtain the well-known value (0.6 a.u.) for the binding energy of $H_2{}^+$ which corresponds to $\sigma=0$.

With the wave function given in Eqs. (16) and (17) the total energy E is

$$E=-\frac{\lambda_1^2}{2}+(\lambda_1-\lambda)\frac{I_1}{N}-\frac{\nu_1^2}{2(1+\sigma)}+(\nu_1-\nu)\frac{I_2}{N}+\frac{I_3}{N}+I_4\,, \tag{18}$$

where N is the normalization constant,

$$N=\int\Phi^*\Phi\,d\tau=\frac{2}{ab}\left\{\left[\frac{1}{a^2}-\frac{1}{b^2}\right]\left[\frac{1}{d^2}-\frac{1}{c^2}\right]+2\left[\frac{1}{a}\left[\frac{1}{d^3}-\frac{1}{c^3}\right]+\frac{1}{b}\left[\frac{1}{d^3}+\frac{1}{c^3}\right]\right]\right\}, \tag{19}$$

with

$$\begin{aligned} &a=\lambda_1+\frac{\nu_1}{1+\sigma},\ \ b=\nu_1-\frac{\nu_1}{1+\sigma}\,,\\ &c=a+b=2\lambda_1,\ \ d=a-b=\frac{2\nu_1}{1+\sigma}\,. \end{aligned} \tag{20}$$

The integrals I_1, I_2, I_3, and I_4 are given by Eqs. (11)—(15) of Ref. 14. In this case the theoretical expressions for λ, μ, and ν of Eq. (4) are given explicitly in Eqs. (17)—(20) of Ref. 14. Again, the computations must be self-consistent as explained in detail in this reference. The values of λ, μ, and ν considered in the determination of the energy of Eq. (18) must be the same as those calculated theoretically from Eqs. (17)—(20) of Ref. 14. This method is simpler and needs considerably less computer time than the previous method of Pekeris. Moreover, using this method[14] one can calculate the oscillator strength[14] f_3 of the exciton–ionized-donor complex as follows:

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

$$F(m_e^*/m_h^*)=N^{-1}\left|\int_{r_{12}=r_{13}}\Phi(r_{12},r_{13})d^3r_{12}\right|^2\ , \tag{22}$$

where Ω is the volume of the elementary cell, and a_x and f_x are, respectively, the radius and the oscillator strength of the free exciton.

In both the Pekeris and Callan methods not only the binding energy or the exciton–ionized-donor complex is determined, but also the donor dielectric constant $K_D=K(r_{12})=K_{\text{eff}}$, the exciton dielectric constant K_x, the exciton radius a_x, the neutral donor E_D, and the exciton E_x binding energies. For instance, once ν is determined the exciton binding energy in both methods is given by

$$E_x=-\frac{Me^4\nu^2}{2\hbar^2K_{\text{eff}}^2}\ , \tag{23}$$

where M is the exciton reduced mass. In this case

$$K_x=\frac{K_{\text{eff}}}{\nu} \tag{24}$$

can be determined.

VI. COMPUTATIONS AND RESULTS

The problem of anisotropy for the dielectric constant is eliminated by taking mean values with the use of the formula of Hopfield and Thomas[25]

$$K_s=(K_{s\perp}K_{s\|})^{1/2}\ , \tag{25}$$

$$K_o=(K_{o\perp}K_{o\|})^{1/2}\ . \tag{26}$$

The effective masses m_e^* and m_h^* can be determined from the following two relations:

$$\frac{1}{M}=\frac{1}{m_e^*}+\frac{1}{m_h^*}\ , \tag{27}$$

$$g^*=\frac{2E_{\text{s.o.}}}{3E_g+2E_{\text{s.o.}}}\left[\frac{1}{m_e^*}-\frac{1}{m_h^*}\right]\ , \tag{28}$$

where s.o. denotes spin orbit and where the notations of Eq. (28) are those given by Baldini and Franchi.[8] Different cases corresponding to the various values of the fundamental constants have been considered. In Table I the values of the fundamental constants m_e^*, m_h^*, σ, $K_{s\perp}$, $K_{s\|}$, K_s, $K_{o\perp}$, $K_{0\|}$, K_o and ω which are used in the calculations are given for the polytypes $4H$ and $2H$ of PbI_2 (I)—PbI_2 (VIII). The least favorable conditions for obtaining good agreement between the calculated and experimental values for the $n=1$ binding energies have been considered. This corresponds to the use of the optical dielectric constant K_o and the consideration of the R_x value for $n=2,3,4,\ldots$. The values of $M=0.3701$ and 0.3881 for PbI_2 (I) and PbI_2 (II) (Table I) have been determined from the series $n=2,3,4,\ldots$ having $R_x=142$

TABLE I. Fundamental constants for PbI_2.

	m_e^*	m_h^*	M	σ	$K_{s\perp}$	$K_{s\|}$	K_s	$K_{o\perp}$	$K_{o\|}$	K_o	ω
$4H$-PbI_2 (I)	0.5194	1.2877	0.3701	0.4033	9.3[a,b]	26.8	15.7873	6.1[a]	5.9[a]	6	121[a]
$4H$-PbI_2 (II)	0.5369	1.4001	0.3881	0.3835	9.5	26.4[a,b]	15.8367			6.1	110[c]
$2H$-PbI_2 (III)	0.4964	1.1542	0.3471	0.4279	9.5	26.4	15.8367			6.1	110
$2H$-PbI_2 (IV)	0.46[d]	1.1012[d]	0.3245	0.4177	9.5	26.4	15.8367			6.1	110
$4H$-PbI_2 (V)	0.5737	1.6576	0.4262	0.3461	9.5	26.4	15.8367			6.1	110
$4H$-PbI_2 (VI)	0.5737	1.6576	0.4262	0.3461	9.5	26.4	15.8367			6.25[e]	110[c]
$4H$-PbI_2 (VII)	0.5737	1.6576	0.4262	0.3461	9.5	26.4	15.8367			6.25	121[a]
$4H$-PbI_2 (VIII)	0.5737	1.6576	0.4262	0.3461	9.5	26.4	15.8367	7.3[f]	5.55[f]	6.365	121[a]

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TABLE II. Calculated values of λ, μ, ν, K_x, K_{eff}, E_x, and $(E-E_D)/E_D$ obtained by the Callan method in PbI_2. In the last column the experimental values $(E_x)_{\text{expt}}$ for the 4H and 2H polytypes of this material are also given.

	λ	μ	ν	K_x	K_{eff}	E_x (meV)	$(E-E_D)/E_D$	$(E_x)_{\text{expt}}$ (meV)
PbI_2 (I)	1.0000	0.9798	1.2600	10.0714	12.69	49.69	0.2305	60[a,b]
PbI_2 (II)	1.0000	0.9875	1.2947	9.6365	12.4764	56.899	0.2797	60
PbI_2 (III)	1.0000	0.9722	1.2574	9.9979	12.5714	47.2763	0.2182	55[b]
PbI_2 (IV)	1.0000	0.9745	1.2541	10.1158	12.6862	43.1679	0.2172	55
PbI_2 (V)	1.0000	0.9960	1.3044	9.4666	12.3483	64.7469	0.2986	60[a,b]
PbI_2 (VI)	1.0000	0.9941	1.2842	9.7183	12.4802	61.4376	0.2667	60
PbI_2 (VII)	1.0000	0.9923	1.2690	9.9434	12.6182	58.6867	0.2434	60
PbI_2 (VIII)	1.0000	0.9910	1.2546	10.1328	12.7126	56.5137	0.2216	60

[a] References 1–3.

[b] References 5 and 8.

meV.$^{1-5}$ These values of M correspond, respectively, to the dielectric constants $K_0=6$ and 6.1 (Table I). As a matter of fact, according to Haken,[18] the dielectric constant corresponding to the lines of high quantum numbers should approach that of the static K_s. In such a case, the use of the values of $M=0.3701$ and 0.3881 for PbI_2 (I) and PbI_2 (II) (Table I) in the calculations for the line $n=1$ could be the least favorable for obtaining good results. For the 2H polytype, the value $R_x=127$ meV (Refs. 4—7) for $n=2,3,4,\ldots$ has been used. For PbI_2 (I)—PbI_2 (III), by knowing the values of M, Eqs. (27) and (28) can be used to determine the corresponding values of m_e^* and m_h^*. In Eq. (28) the values[8] $g^*=0.2$, $E_{\text{s.o.}}=0.81$ eV, and $E_g=2.56$ eV have been used. The value of m_e^* given in Table I for 2H-PbI_2 (IV) is that published by Bloch *et al.*[26] obtained from the cyclotron resonance measurements. Considering the values of $m_{h\parallel}^*=1.67$ and $m_{h\parallel}^*/m_{h\perp}^*=2.3$ reported in Ref. 26, one can find $m_{h\perp}^*=0.726$. Assuming an effective-mass relationship similar to that of Eq. (25), the value of $m_h^*=1.1012$ given in Table I for 2H-PbI_2 (IV) is easily obtained. For PbI_2 (V)—PbI_2 (VIII) the calculations have been carried out for the different available values of $K_{o\perp}$, $K_{o\parallel}$, and ω with the same values of m_e^* and m_h^*. These values of m_e^* and m_h^* have been chosen such that excellent agreement with the $n=1$ experimental $(E_x)_{\text{expt}}$ value$^{1-5}$ is obtained (Table II).

In the Pekeris method, assuming the trial values 1.0, 0.975, and 1.445 for λ, μ, and ν, respectively, and using the constants of Table I for PbI_2 (I), the values of $\epsilon=1.0011$ as well as $(E-E_D)/E_D=0.5239$ have been obtained from the recursion relation (13). This value of $(E-E_D)/E_D$ shows that the exciton—ionized-donor complex is stable. Taking $\epsilon=1.0011$, the calculated values of $\lambda=0.9999$, $\mu=0.9769$, and $\nu=1.4600$ correspnding to $K_{\text{eff}}=14.3758$ have been obtained using Eq. (36) of Ref. 13. The very small differences between the initial and the calculated values of μ and ν are 0.2% and 1%, respectively. In view of the long computations these differences are quite satisfactory. With $\nu=1.445$ and using Eqs. (23) and (24), one can find $E_x=50.91$ meV and $K_x=9.949$. Taking the calculated value $\nu=1.46$, one finds $E_x=51.97$ meV, which is 2% higher than that obtained with the initial value $\nu=1.445$.

On the other hand, using the constants of Table I, for PbI_2 (I)—PbI_2 (VIII) the corresponding results of λ, μ, ν, K_x, K_{eff}, and E_x obtained by the Callan method are reported in Table II. In this table the experimental values $(E_x)_{\text{expt}}$ for the 4H and 2H polytypes are also given. From Table II, the values of $E_x=49.67$ meV and $K_x=10.0714$ for 4H-PbI_2 (I) are in quite good agreement with the corresponding values obtained above in the rigorous Pekeris method. The computations in the Callan method need much less computer time than those carried out in the Pekeris method. For this reason the different results obtained in Table II are carried out in Callan's method for the various cases PbI_2 (I)—PbI_2 (VIII) of Table I. It is surprising that the values of $K_x=9.949$ and 10.0714 obtained for PbI_2 (I), respectively, in the Pekeris and Callan methods, are in good agreement with $K_o=9$ considered by Nikitine *et al.*[2] assuming a different exciton rydberg series, $R_x=506\ \text{cm}^{-1}$, for the line $n=1$. The values of $E_x=49.67$ (Table II), 50.91 or 51.97 meV (Pekeris method) obtained in this paper for 4H-PbI_2 (I) are also in good agreement with the corresponding experimental value $(E_x)_{\text{expt}}=60$ meV (Table II) for the same polytype.$^{1-3,5,8}$ From Table II one can notice that the calculated values of E_x for PbI_2 (II) and PbI_2 (V)—PbI_2 (VIII) of the 4H polytypes are in excellent agreement with the same experimental values of $(E_x)_{\text{expt}}$ of 60 meV.$^{1-3,5,8}$ On the other hand, the values of $E_x=47.2763$ and 43.1679 meV calculated, respectively, in Table II for PbI_2 (III) and PbI_2 (IV) of the 2H polytypes, are in good agreement with the experimental value $(E_x)_{\text{expt}}=55$ meV (Refs. 5,8) reported by different authors for the same polytype and which is also given in Table II. In Table II the calculated values of $(E-E_D)/E_D$ for the different cases PbI_2 (I)—PbI_2 (VIII) are also reported. These values calculated using the Callan method and which are greater than 0 show that the exciton—ionized-donor complex in PbI_2 is stable.

As is noticeable, the value of $R_x=127$ meV (Refs. 4—7) for the 2H polytypes is smaller than that of $R_x=142$ meV (Refs. 1—5) for the 4H polytypes. That is why the experimental value of $(E_x)_{\text{expt}}$ for the 2H polytypes is smaller than that of the 4H polytypes (Table II). Again the calculated values of E_x given in Table II for the different cases of the 2H and the 4H polytypes are in agreement with this experimental result. It is obvious that the degree of agreement between the calculated and the experimental values of E_x depends on the different values of the fundamental constants given in Table I. If the degree of agreement with experiment for most of the cases of the 4*H* polytypes [PbI_2 (II), PbI_2 (V)—PbI_2 (VIII)] studied in Table II happen to be better than that corresponding to the 2*H* polytypes, it is simply that the fundamental constants given in Table I for these 4*H* polytypes fit the experiment better than those considered for the 2*H* polytypes which are also given in Table I.

For PbI_2 (I), considering the results given in Table II and the value of the elementary unit-cell volume[2] $\Omega = 125$ Å^3, the relative oscillator strength $f_3/f_x = 0.573\times 10^3$ has been obtained from Eqs. (16)—(22). This value of f_3/f_x corresponds to a calculated value of the exciton radius $a_x = 14.37$ Å. With the value $a_x = 19$ Å given by Nikitine *et al.*[1,2,5] the ratio $f_3/f_x = 1.324\times 10^3$ has been obtained. These values of f_3/f_x in PbI_2 are at least 1 order of magnitude smaller than those previously[14] calculated for CdS. This is due to the fact that a_x for CdS is greater than that in PbI_2, Ω in CdS is smaller than that in PbI_2, and the results given in Table II concerning μ and ν are different from those already calculated in Table II of Ref. 14 for CdS. Taking $f_x = 1.8\times 10^{-2}$ given by Nikitine *et al.*[2] the values of f_3 corresponding to $a_x = 14.37$ and 19 Å are, respectively, 6.875 and 15.892. For $f_x = 3.75\times 10^{-2}$ given by Biellmann *et al.*,[27] the values of f_3 corresponding to $a_x = 14.37$ Å and 19 Å are, respectively, 14.323 and 33.108. It must be mentioned that Gähwiller and Harbeke[6] give a value of $f_x = 6.02\times 10^{-2}$ for the 2*H* polytype of PbI_2.

VII. CONCLUSIONS

In PbI_2 the existence of an anomaly between two rydberg series, one belonging to the $n=1$ line and the other corresponding to the lines $n=2,3,4,\ldots,$ has been reported by different authors.[1–7] In this paper, using the fundamental constants obtained from the exciton Wannier series for $n=2,3,4,\ldots,$ we resolve the anomaly for the binding energy of the $n=1$ line reported by these authors.[1–7] Thus, good agreement between the calculated and experimental values for the energy of the $n=1$ line has been obtained. Such a result has not been achieved before. This was done by using the Haken potential, taking into account the effect of the polarizability of the lattice; the choice of the wave function is also quite important. The calculations show that the exciton—ionized-donor complex in PbI_2 is stable. This result has not yet been observed and, consequently, the oscillator strength f_3 calculated in this paper for this complex cannot yet be compared with experiment.

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