Polarizability of D^+X complex in bulk semiconductors

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Abstract. The electric polarizability α of ionized-donor-bound exciton D^+X in bulk semiconductor is calculated for all values of the effective electron-to-hole mass ratio σ included in the range of stability ($\sigma<\sigma_\chi$). The calculation is performed within the variational method by using 56-term wave function. An asymptotic behavior of α in the vicinity of the critical value σ_c is deduced. We have also calculated the limiting value σ for which the polarizability equals that of D^- system.

Keywords: exciton, polarizability, wave function, variational method.

1. Introduction

The existence of ionized-donor-bound exciton in semiconductors was first predicted by Lampert [1] and confirmed later by experimental works [2-4]. For direct gap semiconductors with isotropic bands, the calculation of the ground state energy of such a complex is reduced in the effective mass approximation, to solve the Hamiltonian of three bodies system formed by one electron-hole pair (e,h) trapped by one donor centre D^+. This system is labelled D^+X. It is clear that when the energy E_{D^+X} is less than the neutral donor energy E_{D^0}, the excitonic complex forms and may affect, to some extent, the optical spectra of the host material. The stability of such a complex depends on the electron-hole mass ratio $\sigma = m_e/m_h$. Several works have been devoted to this question [5-9]. Particularly, Skettrup *et al.* [8] have shown that the D^+X complex stabilizes for all σ values lying lower than a critical point $\sigma_c = 0.426$. Recently, dos Santos *et al.* [10] have reconsidered again the question and calculated σ_c by an original adiabatic approach using hyperspherical coordinates and obtained $\sigma_c = 0.431$. In the particular case of 2D system, Stauffer and Stébé [9] have shown that the range of stability extends to $\sigma_c^{2D} = 0.88$. However, if one reviews the literature in the area, one is surprised by the insufficiency of works carrying on the effect of the electric field on D^+X complex, in particular, the calculation of polarizability. To our knowledge, the unique work dealing with this question is that of Essaoudi *et al.* [11] in which the specific case of GaAs/Ga$_{1-x}$Al$_x$As quantum well with the electric field

applied parallel to the growth direction is studied. It has been shown in this work that the D^+X complex is sensitive to the action of the field only for well widths higher than 10 nm. The numerical method used in this calculation cannot be generalized to the bulk limiting case because of the axial character of the used trial function inherent in the specific case of the 2D symmetry.

Let's recall that in a previous paper, we have calculated the polarizability of X^- and X_2^+ complexes [12, 13]. But for these systems, the range of stability covers all σ-values whereas for D^+X, the range of stability is limited. This is why we were interested in the present study. In what follows we calculate the electric polarizability of D^+X complex in the framework of the variational method by using a trial function including 56 terms which gives an accurate numerical result.

This paper is organized as follows: in section II we outline our method to determine the polarizability of D^+X, in section III we explain our numerical method using a 56 terms trial wave function. Finally, in the last section we discuss our results.

2. The model

In the effective mass approximation, the Hamiltonian of an ionized donor bound to an exciton in the presence of a constant electric field *F* directed along to the *z*-axis can be written as:

$$H = H_0 + W, \tag{1}$$

where H_0 is given by

$$H_0 = T + V. \tag{2}$$

Here, T is the kinetic energy and V is the Coulomb interaction between the particles of the system

$$T = -\frac{1}{2}\Delta_e - \frac{\sigma}{2}\Delta_h, \tag{3}$$

$$V = -\frac{1}{r_e} + \frac{1}{r_h} - \frac{1}{r_{eh}}, \tag{4}$$

and W is the electric energy operator

$$W = (z_e - z_h)F. \tag{5}$$

Note that in the previous expressions, we have used the atomic units (a.u.); $a_D = \varepsilon\hbar^2/m_e e^2$ as the unit of length, $E_D = e^2/\varepsilon a_D$ as the unit of energy and $F_0 = E_D/ea_D$ as the unit of electric field strength. ε is an appropriate dielectric constant taking into account possible polarization effects. The parameter $\sigma = m_e/m_h$ defines the electron-to-hole effective mass ratio. r_e and r_h are the distances from the ionized donor to the electron and the hole, respectively, while r_{eh} is the distance between the electron and the hole. z_e and z_h denote the coordinates of the electron and the hole along the electric field direction, respectively. Δ_e and Δ_h are the Laplacian operators with respect to the hole and electron coordinates.

In order to calculate the polarizability α of the system, we develop the wave function Ψ and the energy E of the system in power series with respect to the electric field intensity. So we have

$$\Psi = \Psi_0 + \Psi_1 F + \Psi_2 F^2 + ..., \tag{6}$$

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = E_0 + E_1 F + E_2 F^2 + ..., \tag{7}$$

where Ψ_0, Ψ_1 and Ψ_2 are F-independent functions, Ψ_0 and E_0 being the wave function and the energy of D^+X in the absence of the field. Substituting H and Ψ in equation (7) and taking into account the spherical symmetry of the ground state in absence of electric field ($F=0$), we obtain:

$$\begin{cases} E_1 = 0 \\ E_2 = -\frac{1}{2}\alpha \end{cases} \tag{8}$$

where the polarizability α is given by

$$\alpha = \frac{-2\langle \Psi_1 | H_0 | \Psi_1 \rangle + 2E_0\langle \Psi_1 | \Psi_1 \rangle - 4\langle \Psi_0 | (z_e - z_h) | \Psi_1 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} +$$

$$+ 8E_0 \frac{\langle \Psi_0 | \Psi_1 \rangle^2}{\langle \Psi_0 | \Psi_0 \rangle^2}. \tag{9}$$

One may ensure, as established in the appendix, that this entity is essentially positive for all σ values, what proves the stability of the complex for any weak electric field. Furthermore, equation (9) shows that the polarizability α depends only on E_0, Ψ_0 and Ψ_1, the terms including Ψ_2 simplify. E_0 and Ψ_0 are the well-known energy and wave function of the ground state of D^+X in absence of electric field which are determined variationally by several authors [5-9]. As we can remark, the determination of the polarizability requires the knowledge of the wave function part Ψ_1. On the other hand, since we are interested with the calculation of the polarizability, we consider that the electric field is sufficiently low, so, we can restrict the development of the energy to its quadratic form:

$$E = E_0 + E_2 F^2. \tag{10}$$

Then it is convenient to use the variational method for calculating the energy E of the ground state of the system. With account of the symmetry of the problem, the trial function Ψ is chosen in the following way [12]:

$$\Psi_1(r_e, r_h, r_{eh}, z_e, z_h) = z f(r_e, r_h, r_{eh}), \tag{11}$$

where

$$z = z_e - z_h, \tag{12}$$

f is a function that contains the variational parameters. Hence,

$$E = \min \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \tag{13}$$

Such a choice allows considerable simplifications. First, we can ensure that the integral $\langle \Psi_0 | \Psi_1 \rangle$ vanishes. In addition, we may establish the following relations whatever the choice of the function $f(r_e, r_h, r_{eh})$:

$$H_0(z_e - z_h)|f\rangle = (z_e - z_h)H_0|f\rangle +$$
$$+ (\sigma\frac{\partial}{\partial z_h} - \frac{\partial}{\partial z_e})|f\rangle = zH_0|f\rangle - (1+\sigma)\frac{\partial}{\partial z}|f\rangle, \tag{14}$$

$$\langle f | z^2 H_0 | f \rangle = \frac{1}{3}\langle f | r_{eh}^2 H_0 | f \rangle, \tag{15a}$$

$$\langle f | z\frac{\partial}{\partial z} | f \rangle = \frac{1}{3}\langle f | \vec{r}_{eh} \cdot \vec{\nabla}_{eh} | f \rangle =$$
$$= \frac{1}{3}\langle f | r_{eh}\frac{\partial}{\partial r_{eh}} | f \rangle, \tag{15b}$$

$$\langle f | z^2 | f \rangle = \frac{1}{3}\langle f | r_{eh}^2 | f \rangle, \tag{15c}$$

$$\langle \Psi_0 | z^2 | f \rangle = \frac{1}{3}\langle \Psi_0 | r_{eh}^2 | f \rangle. \tag{15d}$$

In these conditions, the expected value of E_2 is written as:

$$E = \min \frac{\langle f|G|f\rangle + 2\langle \Psi_0 | r_{eh}^2 | f\rangle}{3 \langle \Psi_0 | \Psi_0 \rangle},\qquad(16)$$

where the operator G is given by

$$G = r_{eh}^2 H_0 - E_0 r_{eh}^2 - (1+\sigma)\, r_{eh}\frac{\partial}{\partial r_{eh}}\ .\qquad(17)$$

The expression (16) shows that the calculation of E_2 involves only the distances r_e, r_h, r_{eh}.

Next we use for Ψ_0 the expression given by Stauffer and Stébé [9]:

$$\Psi_0(s,t,u) = \sum_{l,m,n} C_{lmn} k^{l+m+n} s^l u^m t^n \exp(-\frac{ks}{2})\ .\qquad(18)$$

The exponents l, m, n are positive or zero integers and the elliptical coordinates s, t, u are given by

$$s = r_e + r_{eh},\ t = r_e - r_{eh},\ u = r_h\ .\qquad(19)$$

The scaling factor k and the linear coefficients C_{lmn} are determined variationaly for each σ value in the range of stability. We choose the function f in the following form:

$$f(r_e, r_h, r_{eh}) = \sum_{l,m,n} A_{lmn} k^{l+m+n} s^l u^m t^n \exp(-\frac{ks}{2})\ ,\quad(20)$$

where A_{lmn} are the linear variational parameters. Following the Hasse variational method [15], we use the values of k and C_{lmn} that we obtain by minimizing the mean values of the Hamiltonian H_0 in the absence of electric field. The variational parameters A_{lmn} are obtained by minimising the following expression (21) obtained after substituting equations (18) and (20) into (16).

$$E_2 = \min \frac{\tilde{A}^+ \tilde{G}\tilde{A} + 2\tilde{C}^+ \tilde{R}\tilde{A}}{3k^2 \tilde{C}^+ \tilde{S}\tilde{C}}\ ,\qquad(21)$$

where $\tilde{A}(\tilde{C})$ denotes the column matrix of the coefficients $A_{lmn}(C_{lmn})$ and $\tilde{A}^+(\tilde{C}^+)$ its transposed matrix. $\tilde{G}$, $\tilde{R}$ and $\tilde{S}$ are the squared matrices of the coefficients defined by:

$$G_{lmn}^{l'm'n'} = \langle lmn|(r_{eh}^2(k^2 T + kV - E_0) -$$
$$-(1+\sigma)k^2 r_{eh}\frac{\partial}{\partial r_{eh}})|l'm'n'\rangle,\qquad(22a)$$

$$R_{lmn}^{l'm'n'} = \langle lmn|r_{eh}^2|l'm'n'\rangle\ ,\qquad(22b)$$

$$S_{lmn}^{l'm'n'} = \langle lmn|l'm'n'\rangle\ .\qquad(22c)$$

The basic functions $|lmn\rangle$ are given by

$$|lmn\rangle = s^l u^m t^n \exp(-\frac{s}{2})\ .\qquad(23)$$

Equalling to zero the derivative of the expression involved in equation (21) with respect to $\tilde{A}$, we find the following secular equation for A_{lmn},

$$\frac{1}{2}(\tilde{G}^+ + \tilde{G})\tilde{A} = -\tilde{R}\tilde{C}\ ,\qquad(24)$$

which yields

$$\alpha = \frac{-2}{3k^2}\frac{\tilde{C}^+ \tilde{R}\tilde{A}_0}{\tilde{C}^+ \tilde{S}\tilde{C}},\qquad(25)$$

where $\tilde{A}_0$ is the solution of the equation (24).

3. Numerical steps

The calculation of the scaling factor k, the coefficients C_{lmn} and the energy E_0 is derived from the solution of the generalized eigenvalue problem [9]

$$\tilde{P}\tilde{C} = k\tilde{Q}\tilde{C}\qquad(26)$$

with

$$P_{lmn}^{l'm'n'} = -\langle lmn|V|l'm'n'\rangle\quad\text{and}\quad \tilde{Q} = \tilde{T} + \beta\tilde{S}\ ,\qquad(27)$$

where

$$T_{lmn}^{l'm'n'} = \langle lmn|T|l'm'n'\rangle\quad\text{and}\quad \beta = \frac{\tilde{C}^+ \tilde{T}\tilde{C}}{\tilde{C}^+ \tilde{S}\tilde{C}}\ .\qquad(28)$$

Starting from $\beta_0 = (1 + \sigma/2)/4$ that corresponds to the asymptotic behavior, we calculate the upper eigenvalue k, and then we deduce the corresponding vector $\tilde{C}$ which gives the next value of β and so on until the desired convergence on β, k and $\tilde{C}$. Consequently, the energy E_0 is deduced from the relation $E_0 = -\beta k^2$ [9]. Let's note in passing that the solution of equation (26) requires to solve the eigenvalue problem of the real symmetric matrix $\tilde{M} = \tilde{Q}^{-1/2}\tilde{P}\tilde{Q}^{-1/2}$. This calculation is performed by using the Jacobi numerical method [14]. The system of linear equations (24) is solved numerically by using the LU-decomposition method [14]. Practically, we have limited the development of the functions Ψ_0 and Ψ_1 to 56 terms corresponding to the condition $l + m + n \leq 5$. Within this approximation, we obtain a rather good value of the critical mass ratio $\sigma_c = 0.367$.
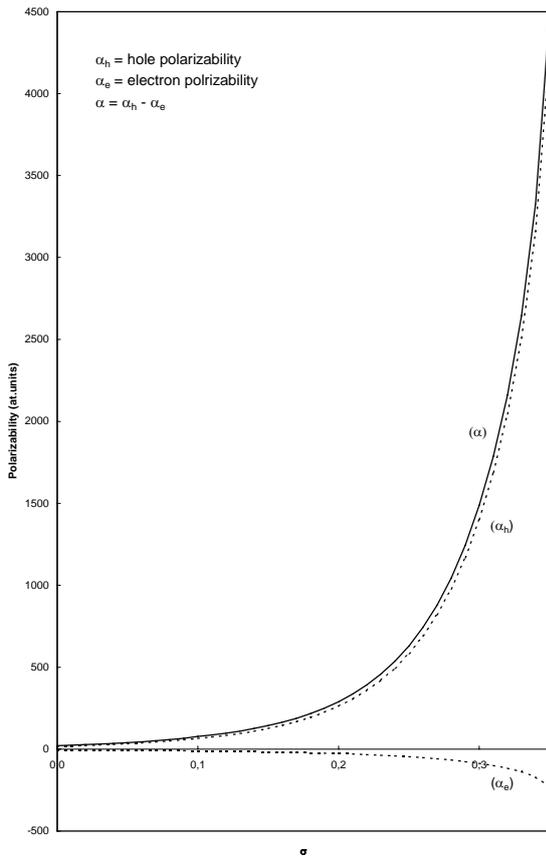
4. Results

The variations of the polarizability of D^+X versus the mass ratio σ is presented in Fig. 1 (solid line). It is seen
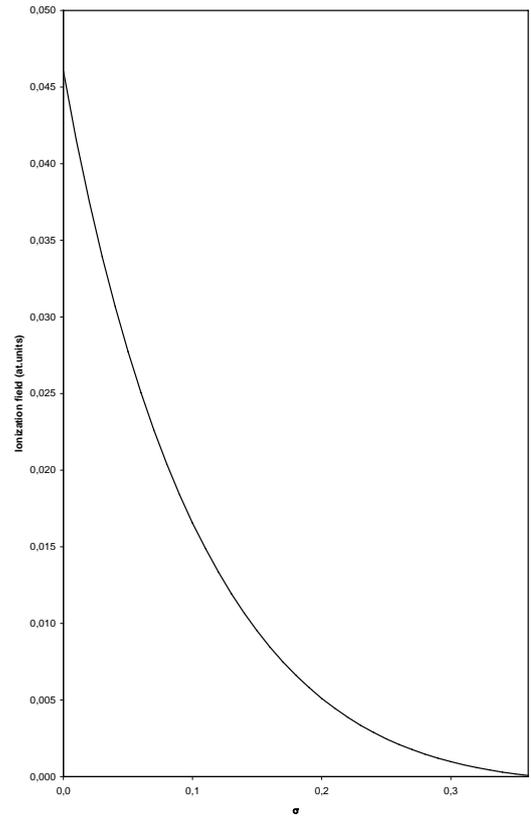
that the polarizability increases with increasing σ up to the critical value σ_c in the vicinity of which an asymptotic behaviour is observed. Such a result may be interpreted physically by the weak bonding of the hole to the neutral donor in this point. Indeed, it is well known that the binding energy of D^+X decreases with increasing σ in the absence of the electric field [8]. In the presence of a weak field, the hole is removed far from the electron along the direction of the field. This behaviour is confirmed by the variations of the electron polarizability (α_e) and the hole polarizability (α_h) defined by $\langle z_{e,h} \rangle = \alpha_{e,h}F$ for weak electric field. This result is illustrated in Fig. 1 (dashed lines). The polarizability of D^+X is then given by $\alpha = \alpha_h - \alpha_e$. This asymptotic trend attests the consistency of our method because it is compatible with physics of such systems.

After calculating the polarizability, we have deduced the binding energy of the complex in the presence of a weak electric field, which is defined as

$$W = E(D^0) - E . \tag{29}$$

Fig. 2. The variation of ionization electric field (in a.u.) versus σ.

The calculation was made in the weak field approximation: $F << F_I$, where F_I is the ionization field defined by

$$\left\langle r_{eh} \right\rangle_0 F_I = W_0 = -\frac{1}{2} - E_0 . \tag{30}$$

As an illustration, the variations of F_I versus σ are reported in Fig. 2.

In this condition, the neutral donor energy can be written as follows:

$$E(D^0) = -\frac{1}{2} - \frac{9}{4}F^2 \tag{31}$$

and in the same way:

$$E = E_0 - \frac{1}{2}\alpha F^2 . \tag{32}$$

Practically, we have restricted our calculation to the strength field value $F = 0.3F_I$ which may be considered as consistent with the quadratic approximation in calculating the binding energy. Recall that it has been shown [16] that the perturbative calculation of the binding energy of the exciton for the strength field values up to $0.5F_I$ gives good results. In Table, we report the values (in a.u.) of α, W_0, and W for the strength field value $F = 0.3F_I$ in the range of σ values between 0 and σ_c.

Fig. 1. The polarizability of D^+X complex (in a.u. $= \varepsilon a_D^3$) as a function of the electron-to-hole effective mass ratio (solid line). Electron and hole polarizabilities in D^+X (dashed lines).

Table. Listing of α, W_0, and W for the strength field value $F = 0.3F_I$, in the range of σ values between 0 and σ_c (in a.u.)

σ	α	$F = 0.3F_I$	W_0	W
0	22	0.01381	0.08378	0.08545
0.05	39	0.00832	0.05767	0.05886
0.1	77	0.00496	0.03946	0.04035
0.15	143	0.00285	0.02618	0.02674
0.2	289	0.00153	0.01645	0.01678
0.25	630	0.00074	0.00941	0.00958
0.3	1488	0.00029	0.00444	0.00450
0.35	4483	0.00005	0.00096	0.00096
σ_c	∞	0	0	0

As an indication, we have calculated the value σ_D of σ for which the polarizability equals that of D^- system. To do that, analogy of D^- with the negative hydrogen ion [17] is made and gives $\sigma_D = 0.1765$ with the corresponding polarizability $\alpha = 206$ (a.u.). That means that for this limiting value of σ, the shift of both D^- and D^+X lines in the optical spectra when a weak electric field is applied is the same. Hence, for semiconductors with $\sigma < \sigma_D$, the D^+X shift is lower than that of D^- while the situation is inverted for $\sigma > \sigma_D$.

In summary, we have presented a variational calculation of the polarizability of D^+X as well as the binding energy in the presence of a weak electric field. This study shows an asymptotic behaviour of the polarizability in the vicinity of σ_c. This behaviour is principally due to the contribution of the hole which is weakly bound to the neutral donor D^0. It has been established also that the effect of a weak electric field is more pronounced for σ values lower that $\sigma = 0.3$. As a comparison, confrontation of the polarizability of D^+X with D^- system is made and shows that it is possible to range the semiconductors in two classes following the relative shift of D^+X and D^- lines.

Appendix

We establish in what follows the effect of the stabilization of D^+X complex in the presence of weak electric field. The expansion in power series of the dipolar electric moment in terms of the electric field strength yields:

$$\frac{\langle \Psi | (z_h - z_e) | \Psi \rangle}{\langle \Psi | \Psi \rangle} = $$

$$= \frac{2\langle \Psi_0 | (z_h - z_e) | \Psi_1 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} F + ... = \alpha F + ... \quad \text{(A1)}$$

By identifying to α as given by Eq. (9), we obtain:

$$\langle \Psi_0 | (z_e - z_h) | \Psi_1 \rangle = E_0 \langle \Psi_1 | \Psi_1 \rangle -$$

$$- \langle \Psi_1 | H_0 | \Psi_1 \rangle + 4 E_0 \frac{\langle \Psi_0 | \Psi_1 \rangle^2}{\langle \Psi_0 | \Psi_0 \rangle}. \quad \text{(A2)}$$

Substituting then (A2) in (9) gives

$$\alpha = 2\frac{\langle \Psi_1 | H_0 | \Psi_1 \rangle - E_0 \langle \Psi_1 | \Psi_1 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} -$$

$$- 8 E_0 \frac{\langle \Psi_0 | \Psi_1 \rangle^2}{\langle \Psi_0 | \Psi_0 \rangle^2}. \quad \text{(A3)}$$

It is evident that the first term in (A3) is positive because of the variational principle, and regarding to the negative value of E_0, the sign of α is always positive which asserts the property of the stability of the complex as advanced above.

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