PHYSICAL REVIEW B VOLUME 21, NUMBER 2 15 JANUARY 1980

Radiative recombination of donor-acceptor pairs in polar semiconductors

E. Kartheuser and R. Evrard
Institut de Physique, Université de Liège, Belgium

F. Williams
Physics Department, University of Delaware, Newark, Delaware 19711

(Received 20 August 1979)

A variational treatment of effective-mass electronic states is made for donor-acceptor (D-A) pairs, including the effects of electron-phonon interaction within the static approximation. The effective Hamiltonian is based on the Fröhlich continuum model. Expressions for the energy levels are obtained analytically and in terms of integrals involving trigonometric functions. The variational parameters for the orbital radii and for the p-state admixtures are determined, all as a function of D-A distance R. Both pairs with equal and those with unequal radii are investigated. The electron-phonon interaction is found to decrease at small R, and the departure from spherical symmetry increases at small R. The theory is applied to the zero-phonon spectra of D-A pairs in GaP and in ZnSe, using a procedure for obtaining the static dielectric constant ϵ_0 from distant-pair spectra and then focusing attention on the deviations from the ideal $1/R$ law for nearer-pair spectra. Comparisons are made with previous theoretical work.

I. INTRODUCTION

The radiative recombination of electrons and holes bound to donor-acceptor (D-A) pairs in semiconductors has been extensively investigated for more than 20 years.[1-3] However, it is only recently that the effects of the interaction with phonons on the binding energy of the electron-hole pairs have been considered[4-8] in some detail.

The semiconductors of practical interest in this field, such as GaP and ZnSe, are polar materials. Therefore, the interaction with the longitudinal-optical (L-O) phonons through the ionic polarization of the lattice is probably dominant in these materials.

As pointed out by Mehrkam and Williams,[9] the charge distribution and therefore the state of polarization are different before and after recombination. This results in a modification of the lattice-deformation energy and of the polarization self-energy of the electron and hole during the transition. Thus the transition energy is affected by the interaction of the electronic particles with the lattice distortion (virtual phonons). As the charge distribution for the excited-pair state (electron and hole bound to the donor and acceptor centers) depends on the donor-acceptor distance R, the contribution to the transition energy due to the lattice polarization depends also on R. Thus the electron- (or hole-) phonon interaction contributes to the deviation from the ideal $1/R$ dependence of the zero-phonon transition energy.

The effect of the electron-phonon interaction on the energy of the excited pair has been studied by several authors.[4-7,10] Inglis and Williams[10] started from an effective Hamiltonian developed for isolated impurities[11-14] and added the Coulomb interactions between the donor and the acceptor. They neglect departure from spherical symmetry in the electronic charge distributions in determining the self-consistent potential and they take as the zero-phonon transition energy the average between Condon-type emission and absorption energies. Stébé and Munschy[4] have used Haken's potential to describe all the Coulomb interactions modified by the lattice polarization. Their method is a variational method with s-like hydrogen wave functions as trial wave functions, which do not properly account for departure from sphericity at small pair distances. Kiefer and Schröder[6,7] have also used Haken's potential, but in the electron-hole interaction term only. These authors used trial wave functions with mixed s and p characters as introduced for the first time by Mehrkam and Williams.[15]

The use of Haken's potential for pairs in GaP or ZnSe is questionable, since the orbital time is shorter than the period of the phonon and, therefore, the effective Bohr radius is smaller than the polaron radius. In fact the opposite condition is required for Haken's potential to be valid.

Moreover, in all these studies, the electron-phonon and hole-phonon interactions were explicitly introduced only in the screening of the Coulomb potentials, changing them into effective potentials. The deformation energy due to the lattice distortion was not included except in the ionization energies of the isolated impurities. When the distance R is small enough for electron and hole orbitals to overlap, the charge compensation leads to a decrease of the lattice distortion. Therefore, the lattice-deformation energy depends on the acceptor-donor distance R, and it is essential to include it in the calculations. In a previous paper[5] (hereafter referred to as I), we have shown how to take this effect into account and to what effective Hamiltonian one is then led.

The goal of the present work is to determine the importance of the effects of the electron-phonon interaction on the recombination energy in the different cases usually found in the literature, i.e., the cases of symmetrical (same orbital radius for the acceptor and the donor) or unsymmetrical pairs, with or without s-p mixing in the wave function. The method developed in I is used for this purpose. It is based upon the description of the electron-phonon interaction by means of a static approximation.[16] This approximation is usually called "adiabatic approximation" in the theory of Fröhlich's polarons. In this approach the source of the ionic polarization is the static charge distribution of the electron and hole, i.e., the square of their wave function multiplied by their charge. This approximation is valid for orbits with a radius large compared to the lattice parameters and an orbital time far smaller than the period of the lattice vibrations, i.e., binding energies far larger than the L-O phonon energy. For the semiconductors studied in practice, this latter condition is not completely fulfilled,[9] so that the static model is valid only as a first approximation.

The static approximation used here leads to a self-consistent effective potential, the particles interacting with the ionic polarization produced by the static charge distribution due to the particles themselves. Moreover, the total energy includes the lattice-distortion energy, as it should.

Sections II and III of the present paper are devoted to the calculation and the discussion of the importance of the effects of the electron-phonon interaction on the recombination energy. The departure from sphericity is also obtained as a function of the pair distance. In Sec. IV we compare our results with experiment in the case of GaP and ZnSe.

II. EFFECTIVE HAMILTONIAN AND TRIAL WAVE FUNCTION IN ADIABATIC APPROXIMATION

Using the effective-mass approximation, the Hamiltonian of the donor-acceptor complex is written as (see I)

$$H=-\frac{\hbar^2}{2m_e}\nabla_e^2-\frac{\hbar^2}{2m_h}\nabla_h^2+\frac{e^2}{\epsilon_\infty}\left(\frac{1}{|\vec{r}_e-\vec{R}|}+\frac{1}{r_h}-\frac{1}{r_e}-\frac{1}{|\vec{r}_h-\vec{R}|}-\frac{1}{|\vec{r}_e-\vec{r}_h|}-\frac{1}{R}\right)$$
$$+\sum_{\vec{k}}\hbar\omega a_{\vec{k}}^\dagger a_{\vec{k}}+\sum_{\vec{k}}\left[V_k a_{\vec{k}}\left(e^{i\vec{k}\cdot\vec{R}}-1+e^{i\vec{k}\cdot\vec{r}_e}-e^{i\vec{k}\cdot\vec{r}_h}\right)+\text{H.c.}\right], \tag{1}$$

where $\vec{R}$, $\vec{r}_e$, and $\vec{r}_h$ denote the positions of the acceptor center, the electron, and the hole, respectively. The position of the donor impurity is taken as origin or the coordinate axes (see Fig. 1). The Laplacian ∇_e^2 and ∇_h^2 involve derivatives with respect to the coordinates of the electron and the hole, respectively. The electron charge is denoted by e, and ϵ_∞ is the high-frequency dielectric constant due to the electronic polarizability of the ions of the crystal. The masses m_e and m_h are the band masses of the electron and hole.

The interaction between the charged particles (the donor D^+, the acceptor A^-, the electron e, and the hole h) and the phonons is described by the usual Fröhlich model of polarons.[17] This assumes that, as pointed out in the Introduction, the dominant contribution to the electron-phonon or hole-phonon interaction (from now on called e-ph interaction) is the polar interaction with the long-wavelength L-O phonons. These phonons are almost dispersionless, so that their frequency ω can be taken as independent of their wave vector $\vec{k}$. The operators $a_{\vec{k}}$ and $a_{\vec{k}}^\dagger$ are annihilation and creation operators for phonons with wave vector $\vec{k}$. Following Fröhlich,[17] the interaction coefficient V_k is taken as

$$V_k=-\frac{ie}{k}\left(\frac{2\pi h\omega}{v}\right)^{1/2}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)^{1/2}. \tag{2}$$

This shows that the interaction strength depends on the difference between the static dielectric constant ϵ_0 and that measured at high frequency (ϵ_∞). In a sense, the difference $\epsilon_\infty^{-1}-\epsilon_0^{-1}$ is a measure of the ionicity of the crystal. In Eq. (2), v denotes the volume of the crystal.

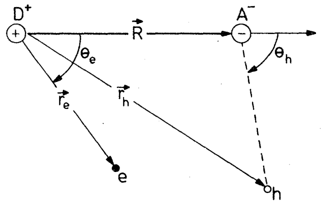

FIG. 1. Effective-mass model of the donor-acceptor pair: the coordinates of the electron e, the positive hole h, and the acceptor A^- are chosen with reference to the donor D^+.

As mentioned in the Introduction, the present work is devoted to centers which exhibit electronic orbital times small as compared to the lattice period $1/\omega$, so that the static approximation can be used. In this approximation, the source of the lattice polarization is the charge distribution in the D-A complex and the only effect of the e-ph interaction is to displace the equilibrium position of the ions. This effect is taken into account in the theory by means of the following canonical transformation:

$$\mathcal{H} = S^{-1} H S \tag{3}$$

with

$$S = \exp\left(\sum_{\vec{k}} \frac{V_k}{\hbar\omega} (\rho_{\vec{k}} - 1 + e^{i\vec{k}\cdot\vec{R}}) a_{\vec{k}} - \text{c.c.} \right) . \tag{4}$$

This transformation performs the two successive displacements of the operators $a_{\vec{k}}$ and $a_{\vec{k}}^{\dagger}$ described in I. The effect of these displacements on the lattice polarization is twofold. First, they eliminate the contribution arising from the D^+ and A^- cores[18] and then they treat the part arising from the electron and the hole in the static approximation. In the expression (4) of the unitary transformation, $\rho_{\vec{k}}$ denotes the Fourier transform of the charge distribution (except for a factor e, the charge of the electron), so that

$$\rho_{\vec{k}} = \int d\vec{r}_e \int d\vec{r}_h |F_R(\vec{r}_e, \vec{r}_h)|^2 (e^{i\vec{k}\cdot\vec{r}_e} - e^{i\vec{k}\cdot\vec{r}_h}) , \tag{5a}$$

or, as written in I,

$$\rho_{\vec{k}} = \langle F_R(\vec{r}_e, \vec{r}_h) | e^{i\vec{k}\cdot\vec{r}_e} - e^{i\vec{k}\cdot\vec{r}_h} | F_R(\vec{r}_e, \vec{r}_h) \rangle , \tag{5b}$$

where $F_R(\vec{r}_e, \vec{r}_h)$ is the electronic part of the wave function for a pair with D-A distance equal to R. This transformation being performed and the static approximation being now used, the wave function $|\Psi\rangle$ of the ground state is given by the following "Produktansatz"

$$|\Psi\rangle = F_R(\vec{r}_e, \vec{r}_h) |0\rangle , \tag{6}$$

where $F_R(\vec{r}_e, \vec{r}_h)$ is the two-particle effective-mass function introduced above for the electron and the hole and $|0\rangle$ is the vacuum state for the phonon field in the occupation number representation.

As shown in detail in I, minimizing the expectation value of the total Hamiltonian (3) with respect to the electron-hole wave function leads to the following, Schrödinger-type equation

$$H'' F_R(\vec{r}_e, \vec{r}_h) = \xi F_R(\vec{r}_e, \vec{r}_h) , \tag{7}$$

where the effective Hamiltonian H'' is given by

$$H'' = H_0 + H_1 , \tag{8}$$

with

$$H_0 = -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_h} \nabla_h^2 + \frac{e^2}{\epsilon_0} \left(\frac{1}{|\vec{r}_e - \vec{R}|} + \frac{1}{r_h} - \frac{1}{r_e} - \frac{1}{|\vec{r}_h - \vec{R}|} - \frac{1}{R} \right) \tag{9}$$

and

$$H_1 = -\frac{1}{\epsilon_\infty |\vec{r}_e - \vec{r}_h|} - \sum_{\vec{k}} \frac{|V_k|^2}{\hbar\omega} [\rho_{\vec{k}}^* (e^{i\vec{k}\cdot\vec{r}_e} - e^{i\vec{k}\cdot\vec{r}_h}) + \text{H.c.}] . \tag{10}$$

The total energy of the ground state E, has two contributions—the expectation value of this effective Hamiltonian and the lattice-distortion energy, so that

$$E = \langle F_R(\vec{r}_e, \vec{r}_h) | H'' | (F_R(\vec{r}_e, \vec{r}_h) \rangle + \sum_{\vec{k}} \frac{|V_k|^2 |\rho_k|^2}{\hbar\omega} . \tag{11}$$

Notice that, through relation (5), the Schrödinger equation (7) is in fact an integro-differential equation. This expresses that the value of the functions $\rho_{\vec{k}}$ appearing as parameters in the effective Hamiltonian H'' should be consistent with their definition [Eq. (7)]. Therefore, it seems hopeless to solve Eq. (7) exactly and approximations on the wave function $F_R(\vec{r}_e, \vec{r}_h)$ are needed.

Neglecting electron-hole correlation effects, a product of one-particle functions is used. This leads to

$$F_R(\vec{r}_e, \vec{r}_h) = \varphi_e(\vec{r}_e) \varphi_h(\vec{r}_h) . \tag{12a}$$

Owing to the Coulomb interactions, the wave functions are not perfectly spherical, especially for close D-A pairs. To take this into account we use the following forms[19,20]:

$$\varphi_e(\vec{r}_e) = \frac{a^{-3/2}}{\pi^{1/2}(1+s^2)^{1/2}} e^{-r_e/a} \left(1 + s \frac{r_e}{a} \cos\theta_e \right) , \tag{12b}$$

$$\varphi_h(\vec{r}_h) = \frac{\alpha^{-3/2}}{\pi^{1/2}(1+\sigma^2)^{1/2}} e^{-|\vec{r}_h - \vec{R}|/\alpha} \times \left(1 + \sigma \frac{|\vec{r}_h - \vec{R}|}{\alpha} \cos\theta_h \right) , \tag{12c}$$

where θ_e and θ_h are the angles defined in Fig. 1, a and α are parameters giving the size of the orbitals, whereas s and σ determine the admixture of p orbitals to the ground state. These parameters a, α, s, and σ are to be determined variationally. Using the trial functions (12) in expression (5) for the electron-hole charge distribution leads to

$$\rho_{\vec{k}} = \rho_{\vec{k}}^e - \rho_{\vec{k}}^h , \tag{13a}$$

with

$$\rho^e_{\vec{k}}=\frac{1}{(1+s^2)\,|\,1+(a/2)^2k^2\,|^2}\left[1+\frac{2is\,ak\cos\theta_e}{|\,1+(a/2)^2k^2\,|}+\frac{s^2}{|\,1+(a/2)^2k^2\,|}\times\left(1-\frac{3}{2}\,\frac{a^2k^2\cos\theta_e}{|\,1+(a/2)^2k^2\,|}\right)\right] \tag{13b}$$

and

$$\rho^h_{\vec{k}}=\frac{e^{i\vec{k}\cdot\vec{R}}}{(1+\sigma^2)\,|\,1+(a/2)^2k^2\,|^2}\left[1+\frac{2i\sigma\alpha k\cos\theta_h}{|\,1+(a/2)^2k^2\,|}+\frac{\sigma^2}{|\,1+(\alpha/2)^2k^2\,|}\times\left(1-\frac{3}{2}\,\frac{\alpha^2k^2\cos^2\theta_h}{|\,1+(\alpha/2)^2k^2\,|}\right)\right]\,. \tag{13c}$$

III. VARIATIONAL DETERMINATION OF ENERGY

For the sake of completeness, detailed expressions for the different contributions to the total energy $E(R)$ as functions of the variational parameters a, α, s, and σ are given in the Appendix.

Different approximations can now be made. One can use wave functions with equal radii ($a=\alpha$); the pair will then be called symmetrical. On the contrary one can keep different radii for the acceptor and the donor (unsymmetrical pair). On the other hand, the p admixture to the individual wave functions can be neglected or retained. This leads to the following four cases.

A. Symmetrical pairs

Without p admixture the total energy is given by

$$E(a,R)=\frac{\hbar^2}{2m_ea^2}+\frac{\hbar^2}{2m_ha^2}-\left(\frac{11}{8\epsilon_0}+\frac{5}{8\epsilon_\infty}\right)\frac{e^2}{a}-\frac{e^2}{\epsilon_0R}\left[1+\frac{5}{8}\,\frac{R}{a}-\frac{3}{4}\left(\frac{R}{a}\right)^2-\frac{1}{6}\left(\frac{R}{a}\right)^3\right]e^{-2R/a}\,, \tag{14}$$

while in the presence of p-orbital admixture we obtain (note that $\sigma=-s$, since the pair is assumed to be symmetrical)

$$E(a,s,R)=\frac{\hbar^2}{2m_ea^2}+\frac{\hbar^2}{2m_ha^2}-\frac{2(1+s^2/2)}{1+s^2}\,\frac{e^2}{\epsilon_0a}+\frac{2}{1+s^2}\left[1-g_0(a,R)+2sg_1(a,R)+s^2g_2(a,R)\right]\frac{e^2}{\epsilon_0R}-\frac{e^2}{\epsilon_0R}-2\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\gamma(s)\frac{e^2}{a}-\frac{e^2}{(1+s^2)^2\epsilon_0R}\,(G_0+G_1s+G_2s^2+G_3s^3+G_4s^4)\,, \tag{15}$$

with

$$g_0(a,R)=\left(1+\frac{R}{a}\right)e^{-2R/a}\,, \tag{16a}$$

$$g_1(a,R)=\frac{a}{R}-\left[\left(\frac{R}{a}\right)^2+\frac{2R}{a}+2+\frac{a}{R}\right]e^{-2R/a}\,, \tag{16b}$$

$$g_2(a,R)=1+3\left(\frac{a}{R}\right)^2-\left[\left(\frac{R}{a}\right)^3+3\left(\frac{R}{a}\right)^2+\frac{11}{2}\,\frac{R}{a}+7+6\,\frac{a}{R}+3\left(\frac{a}{R}\right)^2\right]e^{-2R/a}\,, \tag{16c}$$

$$\gamma(s)=\frac{1}{(1+s^2)^2}\left(\frac{5}{16}+\frac{7}{12}s^2+\frac{501}{2560}s^4\right)\,. \tag{16d}$$

Here it is convenient to express the G functions in terms of the following integrals:

$$S(n,p)=\frac{2}{\pi}\int_0^\infty\frac{dk\,k^n\sin(kR)}{[1+(a/2)^2k^2]^p}\,, \tag{17a}$$

$$C(n,p)=\frac{2}{\pi}\int_0^\infty\frac{dk\,k^n\cos(kR)}{[1+(a/2)^2k^2]^p}\,. \tag{17b}$$

This yields

$$G_0=S(-1,4)\,, \tag{18a}$$

$$G_1=-4a\left(C(0,5)-\frac{S(-1,5)}{R}\right)\,, \tag{18b}$$

$$G_2=2S(-1,5)-7a^2\left(S(1,6)+\frac{2}{R}\,C(0,6)-\frac{2}{R^2}\,S(-1,6)\right)\,, \tag{18c}$$

$$G_3=C(0,6)-\frac{1}{R}\,S(-1,6)-\frac{3a^2}{2}\left(C(2,7)-\frac{3}{R}\,S(1,7)-\frac{6}{R^2}\,C(0,7)+\frac{6}{R^3}\,S(-1,7)\right)\,, \tag{18d}$$

$$G_4=S(-1,6)-3a^2\left(S(1,7)+\frac{2}{R}\,C(0,7)-\frac{2}{R^2}\,S(-1,7)\right)+\frac{9a^4}{4}\left(S(3,8)+\frac{4}{R}\,C(2,8)-\frac{12}{R^2}\,S(1,8)-\frac{24}{R^3}\,C(0,8)+\frac{24}{R^4}\,S(-1,8)\right)\,. \tag{18e}$$

TABLE I. Variational results for the orbital radius a and the energy E in the case of symmetrical D-A pairs and spherical orbits for different pair separations R. The values of m_e, m_h, ϵ_∞, and ϵ_0 are those of GaP given in Sec. III; the columns 2 and 3 show the results for $\epsilon_\infty \neq \epsilon_0$ and $\Delta E_{\rm ep}$ is the contribution due to the e-ph interaction; columns 4 and 5 show similar results for $\epsilon_\infty = \epsilon_0$.

		$\epsilon_\infty \neq \epsilon_0$		$\epsilon_\infty = \epsilon_0$	
R (Å)	a (Å)	E (eV)	$\Delta E_{\rm ep}$ (eV)	a (Å)	E (eV)
5	28.935	−0.2779	−0.0060	35.694	−0.2724
10	19.830	−0.1525	−0.0087	25.491	−0.1447
15	13.210	−0.1238	−0.0131	15.159	−0.1115
20	11.748	−0.1194	−0.0148	12.777	−0.1052
25	11.410	−0.1195	−0.0152	12.229	−0.1048
30	11.350	−0.1202	−0.0153	12.103	−0.1054
35	11.365	−0.1207	−0.0153	12.100	−0.1059

All the integrals appearing in relations (18a)–(18e) can be performed analytically. The results are given in the Appendix [Eqs. (A21)–(A25)]. The integrals have also been evaluated numerically for different values of R, a, and s. The results are in complete agreement with the values given by their analytic expressions. This is very useful in order to control the numerical analysis involved in the case of unsymmetrical pairs. These analytical expressions verify most of the results from Roothaan's paper,[21] except for small differences in the coefficients of the R^4 and R^5 terms in G_3.

To compare with the previous theoretical calculations by Mehrkam and Williams,[15] we take $m_e = m_h$ and $\epsilon_\infty = \epsilon_0$. Then, the analytical form obtained in using Eqs. (16) and the results of the Appendix in the expression (15) for the D-A pair energy, coincides with that of Mehrkam and Williams, except for minor differences in a few coefficients.

The expectation values (14) and (15) of the energy are now minimized with respect to the variational parameters. The values of the parameters and of the energy at the minimum are given in Table I for the case of spherical wave functions and in Table II when s-p mixing is allowed. The values chosen for the different physical parameters $m_e = 0.365$ (Ref. 22), $m_h = 0.67$ (Ref. 23), $\epsilon_\infty = 9.09$ (Ref. 24), and $\epsilon_0 = 11.02$ (Ref. 25) are those of a typical III-V compound, GaP, and the range for the D-A separation is that where experimental results are available.

To determine the contribution $\Delta E_{\rm ep}$ to the pair energy due to the interaction with the phonons, we have separately evaluated the terms coming from the ionic polarization of the lattice, i.e., the terms containing $\epsilon_\infty^{-1} - \epsilon_0^{-1}$ as a factor. In this latter calculation, the values of the parameters obtained previously by minimizing the total energy were used. This correction $\Delta E_{\rm ep}$ is given in Tables I and II, depending whether the s-p mixing is included or not. It amounts to about 10% except for very close impurity centers.

To compare with results of previous theoretical work[15] in which the effects of e-ph interaction were neglected, we have also minimized the expectation value of the Hamiltonian in which we put $\epsilon_\infty = \epsilon_0$. The results are also given in Tables I and II.

B. Unsymmetrical pairs

Without p-orbital admixture the total energy becomes

$$E(a, \alpha) = \frac{\hbar^2}{2ma^2} + \frac{\hbar^2}{2m_h\alpha^2} - \frac{1}{16}\left(\frac{11}{\epsilon_0} + \frac{5}{\epsilon_\infty}\right)\left(\frac{e^2}{a} + \frac{e^2}{\alpha}\right) - \frac{e^2}{\epsilon_0 R}\left[g_0(a) + g_0(\alpha) + g(a, \alpha) - g(\alpha, a)\right], \tag{19a}$$

where g_0 has been defined in Eq. (16b) and

TABLE II. Variational results for the orbital radius a, the admixture parameter s, and the energy E in the case of symmetrical D-A pairs with s-p mixing as a function of the pair separation R. The values of m_e, m_h, ϵ_∞, and ϵ_0 are those of GaP (see Sec. III); the columns 2–5 show the results for $\epsilon_\infty \neq \epsilon_0$ and $\Delta E_{\rm ep}$ is the contribution of the e-ph interaction; columns 6–8 show similar results for $\epsilon_\infty = \epsilon_0$.

		$\epsilon_\infty \neq \epsilon_0$			$\epsilon_\infty = \epsilon_0$		
R (Å)	a (Å)	s	E (eV)	$\Delta E_{\rm ep}$ (eV)	a (Å)	s	E (eV)
5	22.152	−0.0634	−0.2906	−0.0078	25.527	−0.0560	−0.2833
10	21.180	−0.1068	−0.1561	−0.0096	17.960	−0.1137	−0.1650
12.5	15.468	−0.1197	−0.1435	−0.0112	18.149	−0.1190	−0.1331
15	13.754	−0.1147	−0.1323	−0.0126	15.661	−0.1182	−0.1204
20	12.226	−0.0938	−0.1235	−0.0142	13.398	−0.1005	−0.1099
25	11.699	−0.0765	−0.1213	−0.0148	12.624	−0.0784	−0.1070
30	11.509	−0.0500	−0.1209	−0.0151	12.333	−0.0578	−0.1064
35	11.444	−0.0335	−0.1210	−0.0152	12.224	−0.0405	−0.1063

$$g(a,\alpha)=\left[\frac{\dfrac{R}{a}}{\left[1-\left(\dfrac{\alpha}{a}\right)^2\right]^2}-\frac{2\left(\dfrac{\alpha}{a}\right)^2}{\left[1-\left(\dfrac{\alpha}{a}\right)^2\right]^3}+\frac{1}{\left[1-\left(\dfrac{\alpha}{a}\right)^2\right]^2}\right]e^{-2R/a}\,. \tag{19b}$$

Finally the general case of unsymmetrical pairs with p-orbital

$$\begin{aligned}E(a,\alpha,s,\sigma)=&\frac{\hbar^2}{2m_e a^2}+\frac{\hbar^2}{2m_h\alpha^2}-\frac{(1+s^2/2)}{1+s^2}\frac{e^2}{\epsilon_0 a}-\frac{(1+\sigma^2/2)}{1+\sigma^2}\frac{e^2}{\epsilon_0\alpha}\\&+\frac{e^2}{\epsilon_0 R}\left[1-g_0(a)+2sg_1(a)+s^2g_2(a)-g_0(\alpha)-2\sigma g_1(\alpha)+\sigma^2 g_2(\alpha)\right]\\&-\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\left(\gamma(s)\frac{e^2}{a}+\gamma(\sigma)\frac{e^2}{\alpha}\right)-\frac{G}{(1+s^2)(1+\sigma^2)}\frac{e^2}{\epsilon_0 R}\,,\end{aligned} \tag{20}$$

where the g and γ functions are defined in Eqs. (16), and G is given in the Appendix.

The variational results are given in Tables III and IV, for the cases without and with s-p mixing, respectively. Again the example of GaP has been selected. The results confirm that the contribution of the e-ph interaction to the energy of the D-A pair is about 10%.

Table V gives the same results in the unsymmetrical case without and with s-p mixing for ZnSe. Here the physical parameters used are: $m_e=0.16$ (Ref. 26), $m_h=0.52$ (Ref. 27), $\epsilon_\infty=6.10$ (Ref. 28), and the value $\epsilon_0=9.42$ is determined in a way described in Sec. IV.

IV. COMPARISON WITH EXPERIMENT

The application of the theory to experiment is based on computed eigenvalues, such as reported in Tables I-IV for GaP and Table V for ZnSe. As explained in Sec. III, the known experimental values of m_e, m_h, and ϵ_∞ were used and a, α, s, and σ were variational parameters.

As for ϵ_0, the electron-hole recombination spectra of the D-A pairs seem to give the most precise experimental values. Indeed, the recombination energy can be obtained in the following way. The energy of the excited D-A pair (i.e., before recombination) with respect to an empty conduction band and a filled valence band is $E_g+E(R)$, where E_g is the energy of the band gap and $E(R)$ is the pair energy calculated in Sec. III. The ground-state energy (i.e., after recombination) is simply the energy $-e^2/\epsilon_0 R$ due to the Coulomb interaction between the ionized donor and acceptor impurity centers. The self-energies of the cores of the impurity centers remaining unchanged during the transition, cancel in the evaluation of the transition energy and thus are not introduced explicitly in the calculation of the transition energy. Therefore, the energy of the emitted photon for a zero-phonon transition is

$$h\nu=E_g+E(R)+\frac{e^2}{\epsilon_0 R}\,. \tag{21}$$

As both centers are neutral in the excited state, their interaction vanishes faster than $1/R$ at large D-A separation. Therefore, the asymptotic be-

TABLE III. Variational results for the orbital radii a, α, and the energy E in the case of unsymmetrical D-A pairs and spherical orbits as a function of the pair separation R. The values of m_e, m_h, ϵ_∞, and ϵ_0 correspond to GaP, given in Sec. III; the columns 2–5 show the results for $\epsilon_\infty\neq\epsilon_0$ and $\Delta E_{\rm ep}$ is the contribution due to e-ph interaction; columns 6–8 show similar results for $\epsilon_\infty=\epsilon_0$.

	$\epsilon_\infty\neq\epsilon_0$				$\epsilon_\infty=\epsilon_0$		
R (Å)	a (Å)	α (Å)	E (eV)	$\Delta E_{\rm ep}$ (eV)	a (Å)	α (Å)	E (eV)
5	30.487	24.074	−0.2784	−0.0064	36.253	29.706	−0.2725
10	21.000	13.364	−0.1554	−0.0106	26.254	18.365	−0.1460
15	16.293	8.777	−0.1330	−0.0152	18.022	9.793	−0.1186
20	15.177	8.176	−0.1305	−0.0163	16.417	8.800	−0.1148
25	14.807	8.080	−0.1309	−0.0166	15.877	8.624	−0.1149
30	14.697	8.087	−0.1315	−0.0166	15.694	8.610	−0.1154
35	14.683	8.110	−0.1319	−0.0166	15.650	8.633	−0.1158

TABLE IV. Variational results for the electron and hole orbital radii (a and α), the electron and hole s-p mixing parameters (s and σ), and energy E in the case of unsymmetrical D-A pairs as a function of the pair separation R: The parameters used for m_e, m_h, ϵ_0, and ϵ_∞ correspond to GaP (see Sec. III); columns 2–7 show the results for $\epsilon_\infty \neq \epsilon_0$ and ΔE_{ep} is the contribution of the e-ph interaction; columns 8–12 give similar results for $\epsilon_\infty = \epsilon_0$.

	$\epsilon_\infty \neq \epsilon_0$						$\epsilon_\infty = \epsilon_0$				
R (Å)	a (Å)	α (Å)	s	σ	E (eV)	ΔE_{ep} (eV)	a (Å)	α (Å)	s	σ	E (eV)
5	24.707	19.427	−0.0605	0.0563	−0.2907	−0.0078	28.172	22.872	−0.0548	0.0501	−0.2833
10	20.223	12.558	−0.1053	0.0451	−0.1655	−0.0112	23.754	16.060	−0.1007	0.0435	−0.1553
12.5	18.178	9.900	−0.1099	0.0400	−0.1473	−0.0135	20.431	11.679	−0.1156	0.0334	−0.1346
15	17.089	8.881	−0.1064	0.0351	−0.1390	−0.0148	18.864	9.905	−0.1134	0.0310	−0.1250
20	15.856	8.267	−0.0914	0.0253	−0.1334	−0.0159	17.277	8.914	−0.0999	0.0232	−0.1181
25	15.238	8.138	−0.0709	0.0198	−0.1322	−0.0163	16.458	8.699	−0.0794	0.0188	−0.1164
30	14.944	8.119	−0.0522	0.0157	−0.1321	−0.0165	16.044	8.655	−0.0598	0.0158	−0.1161
35	14.815	8.127	−0.0372	0.0120	−0.1321	−0.0165	15.848	8.658	−0.0437	0.0129	−0.1161

havior of the quantum of emitted radiation for large R is, as first given by Hopfield *et al.*[29] for zero-phonon pair spectra:

$$h\nu = E_g - (E_A + E_D) + \frac{e^2}{\epsilon_0 R}, \tag{22}$$

where E_A and E_D are the absolute values of the ionization energies of, respectively, the acceptor and the donor centers. This shows that the relation between $h\nu$ and $1/R$ should asymptotically become a linear function with a slope equal to e^2/ϵ_0. For this reason, we have plotted the experimental values for $h\nu$ vs $1/R$. The results are shown in Fig. 2 for GaP (doped with Sn and Zn) and Fig. 3 for ZnSe (doped with In and Li), respectively. These figures clearly show that the asymptotic behavior for $1/R$ going to zero is actually linear. In the case of GaP, the straight line corresponding to the value $\epsilon_0 = 11.02$ proposed by Vink *et al.*[25] seems to have the right slope. Due to the uncertainty of the experimental values, it does not seem possible to improve on this result. In the case of ZnSe, however, very precise measurements are available.[30] This allows the determination of the slope by means of a linear-regression technique. The application of this method to the measurements carried out at pair distances R larger than 30 Å, leads to $\epsilon_0 = 9.42$ and $E_g - (E_A + E_D) = 2.6823$ eV. The value obtained in this way for ϵ_0 is different from that determined by other means.[27,31,32]

Comparison between our theoretical predictions and the experimental results[33] are shown in Fig. 2 for GaP. The improvement obtained in allowing p admixture is evident from this figure. The uncertainty in the experimental D-A pair spectra of GaP does not justify more detailed application of the theory in this case.

The situation is different for ZnSe: In, Li[30] as shown in Figs. 3 and 4. A more detailed application of the theory to the experimental spectra of ZnSe: In, Li is thus justified. An interesting aspect is the study of the deviation at short distance from the asymptotic law given above. This leads to consider the transition energy from which the Coulombic term $e^2/\epsilon_0 R$ has been subtracted. This quantity denoted ΔE is plotted versus R in Fig. 4,

TABLE V. Variational results for unsymmetrical D-A pairs. The values used for m_e, m_h, ϵ_∞, and ϵ_0 are those of ZnSe (Secs. III and IV); columns 2–4 show the results for the electron and hole orbital radii (a, α), the energy E, and the e-ph interaction energy ΔE_{ep} in the case of spherical orbits; columns 5–10 give the results for the electron and hole orbital radii (a, α), the electron and hole p admixture (s, σ), the pair energy E and the e-ph contribution to the pair energy in the case of p-orbital admixture.

	without p admixture				with p admixture					
R (Å)	a (Å)	α (Å)	E (eV)	ΔE_{ep} (eV)	a (Å)	α (Å)	s	σ	E (eV)	ΔE_{ep} (eV)
5	42.127	24.991	−0.3264	−0.0166	34.884	21.045	−0.0485	0.0512	−0.3383	−0.0198
10	34.987	15.328	−0.1798	−0.0244	32.184	13.767	−0.0826	0.0597	−0.1904	−0.0269
15	29.538	9.251	−0.1483	−0.0369	29.918	9.192	−0.1010	0.0471	−0.1567	−0.0369
20	28.151	8.390	−0.1426	−0.0402	29.404	8.423	−0.1140	0.0269	−0.1482	−0.0397
25	27.446	8.193	−0.1417	−0.0412	28.969	8.227	−0.1157	0.0147	−0.1453	−0.0406
30	27.034	8.148	−0.1418	−0.0415	28.484	8.175	−0.1089	0.0082	−0.1440	−0.0409
35	26.795	8.146	−0.1420	−0.0416	28.004	8.165	−0.0972	0.0050	−0.1434	−0.0411

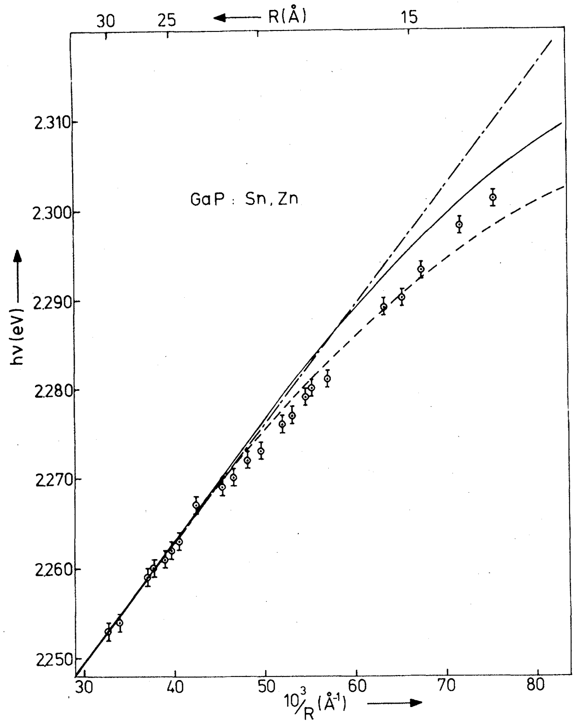

FIG. 2. Pair-transition energies [Eq. (21)] for GaP: Zn, Sn plotted against the reciprocal of the pair separation $1/R$, Φ, experimental values (Ref. 33); — - — -, asymptotic law [Eq. (22)]; ———, present theory without s-p mixing; -----, present theory with s-p mixing.

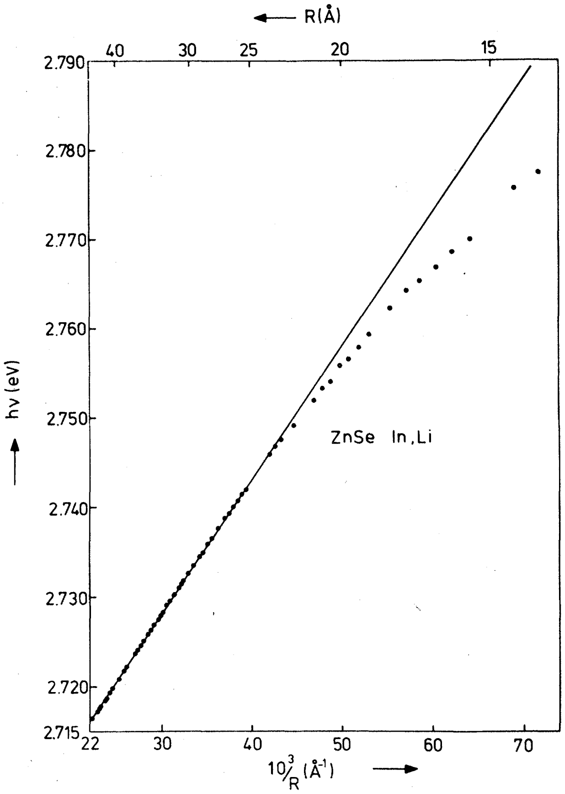

FIG. 3. Pair-transition energies $h\nu$ for ZnSe: In, Li plotted against the reciprocal of the pair separation $1/R$; the points are the experimental values (Ref. 30); the full line shows the asymptotic behavior of $h\nu$ [Eq. (22)] obtained by linear regression, with $\epsilon_0 = 9.42$ and $E_g - (E_D + E_A) = 2.6823$ eV.

where it is compared to its experimental counterpart. The value used for $E_g - (E_A + E_D)$ is that obtained by linear regression, as explained above. This focuses attention on the R dependence of the non-Coulombic terms. Again the importance of p-state admixture is evident from comparison of the theoretical curves obtained with and without this admixture.

V. DISCUSSION

The present analysis and its application to experimental spectra are distinguished from previous work on D-A pairs as follows: (1) the variation of the parameters of the electronic wave function is accomplished including electron-phonon interaction; (2) the variational analysis involves four parameters allowing independent variations in the radii and p-state admixtures for the electron and positive hole effective mass functions; (3) the comparison of experimental and theoretical spectra is made by a systematic procedure, proceeding from distant pairs to nearer pairs; (4) the principal application is to shallow dopants in ZnSe, for

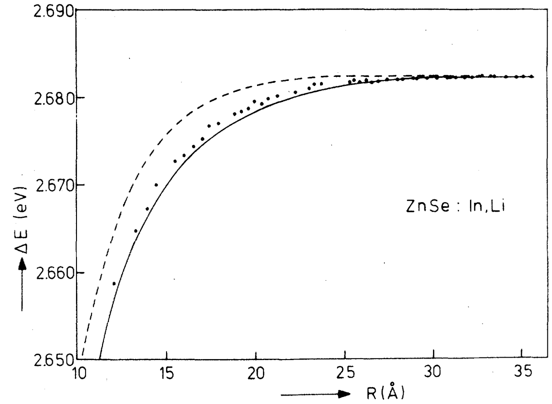

FIG. 4. Deviation ΔE of the pair energy from the asymptotic law ($\Delta E = h\nu - e^2/\epsilon_0 R$) at the case of ZnSe: In, Li; the points correspond to the experimental data (Ref. 30) with $\epsilon_0 = 9.42$; the dotted and full curve show the theoretical results without and with p-orbital admixture, respectively.

which more accurate tabulated experimental spectra have been published and which constitute a better test of effective mass theories of D-A pairs than appears to be the case for the extensively studied GaP.

Although the essential features of the zero-phonon D-A pair spectra from shallow dopants in GaP and in ZnSe are accounted for by the theory, there are several small quantitative discrepancies which may arise from effects not included in the present theory. The main discrepancy between theory and experiment is that the theoretical curve with s-p mixing on Fig. 4 lies slightly ($\sim 10^{-3}$ eV) below the experimental points for pairs with R between 15 and 25 Å. At first sight, this is unexpected for a variational treatment. Correlation in the electron and hole wave functions, which is not included in the present theory, cannot explain this discrepancy because it would yield an even lower theoretical curve at small R. A possible contribution to this discrepancy is that the adiabatic approximation is of limited validity for these dopants. If the precision of our theoretical results is weaker at large pair distance, choosing the zero of energy to obtain the correct asymptotic value (large R) for ΔE would bring the theoretical curve below the experimental points for shorter pair distances.

Another possible contribution to the discrepancy between the present theory and experiment is the central-cell effect, particularly R-dependent effects of the central cell. The central-cell effect is small for ZnSe: In, Li; larger for GaP: Sn, Zn. As is evident from the tables the effective Bohr radii for electron and hole increase markedly at small R. Continuity of the wave function into the central cell will thus reduce amplitude within the central cell, thus decreasing the E_D and E_A for those pairs with small R. Therefore, the inclusion of the R-dependent central-cell effect will raise the theoretical curve at small R. This should be more important for pairs in GaP than for those in ZnSe.

VI. CONCLUSIONS

In the present paper we have studied the importance of several effects on the electron-hole recombination energy as a function of the D-A separation for GaP and ZnSe.

The contribution due to the e-ph interaction varies from about 9 to 15 meV for GaP and from 25 to 42 meV for ZnSe. These contributions are far from being negligible since the total energy $E(R)$ is on the order of 130 to 150 meV and 140 to 190 meV for GaP and ZnSe, respectively.

Allowing different radii for the donor and acceptor orbitals introduces a correction of about 10% for GaP (compare Tables I and III and Tables II and IV). In ZnSe, the difference in hole and electron mass is much more pronounced than for GaP. Therefore treating the donor and acceptor in a symmetrical way (equal radii) would be meaningless.

Mixing a p contribution to the s-like individual wave functions of the donor and acceptor leads to a correction of almost 10% for close pairs (compare Tables I and II and Tables III and IV for GaP; see columns 4 and 10 of Table V for ZnSe).

Therefore all the effects considered in the present paper are of the same order of magnitude. However, their behavior versus the D-A separation is different. The orbital radii that measure the delocalization of the electron and the hole as well as the p-state admixture increase, whereas electron-photon interaction decreases, for the nearer pairs characterized by small R. The decrease of the e-ph interaction energy is due to an increase in the overlap of the electron and hole wave functions that is responsible for a partial compensation in the total static charge.

The published experimental spectra for shallow dopants is found to be more precise, and to provide a more critical test of effective-mass theories of D-A pairs, for ZnSe than for GaP. The application of the present theory to the spectra of ZnSe: In, Li reveals that ϵ_0 for ZnSe is larger than previous values,[27,31,32] most probably 9.42. The ϵ_0 for GaP of 11.02 is confirmed.

The small remaining discrepancies between theory and experiment are tentatively attributed to R dependence in the departure from adiabaticity and R dependence in the central-cell perturbation. Effects of correlation may be appreciable; however, their inclusion will not improve the agreement with experiment.

ACKNOWLEDGMENT

This work was performed in part in the framework of the joint E. S. I. S. (electronic structure in solids) project of the University of Antwerp and the University of Liège, and supported in part by a grant from the U. S. Army Research Office-Durham to the University of Delaware.

APPENDIX

In this Appendix we give explicit expressions for the different contributions in the expectation value of the total energy (11) in the general cases (unsymmetrical and symmetrical pairs with s-p mixing).

By straightforward integrations, one obtains

$$\left\langle F_R(\vec{r}_e,\vec{r}_h)\left|-\frac{\hbar^2\nabla_e^2}{2m_e}\right|F_R(\vec{r}_e,\vec{r}_h)\right\rangle=\frac{\hbar^2}{2m_e a^2}, \tag{A1}$$

$$\left\langle F_R(\vec{r}_e,\vec{r}_h)\left|-\frac{\hbar^2\nabla_h^2}{2m_h}\right|F_R(\vec{r}_e,\vec{r}_h)\right\rangle=\frac{\hbar^2}{2m_h\alpha^2}, \tag{A2}$$

$$\left\langle F_R(\vec{r}_e,\vec{r}_h)\left|\frac{e^2}{\epsilon_0 r_e}\right|F_R(\vec{r}_e,\vec{r}_h)\right\rangle=\frac{(1+s^2/2)}{1+s^2}\,\frac{e^2}{\epsilon_0 a}, \tag{A3}$$

$$\left\langle F_R(\vec{r}_e,\vec{r}_h)\left|\frac{e^2}{\epsilon_0|\vec{r}_h-\vec{R}|}\right|F_R(\vec{r}_e,\vec{r}_h)\right\rangle=\frac{(1+\sigma^2/2)}{1+\sigma^2}\,\frac{e^2}{\epsilon_0\alpha}, \tag{A4}$$

$$\left\langle F_R(\vec{r}_e,\vec{r}_h)\left|\frac{e^2}{\epsilon_0|\vec{r}_e-\vec{R}|}\right|F_R(\vec{r}_e,\vec{r}_h)\right\rangle$$
$$=\frac{1}{1+s^2}[1-g_0(a,R)+2sg_1(a,R)+s^2g_2(a,R)]\frac{e^2}{\epsilon_0 R}, \tag{A5}$$

$$\left\langle F_R(\vec{r}_e,\vec{r}_h)\left|\frac{e^2}{\epsilon_0|\vec{r}_h-\vec{R}|}\right|F_R(\vec{r}_e,\vec{r}_h)\right\rangle$$
$$=\frac{1}{1+\sigma^2}[1-g_0(\alpha,R)-2\sigma g_1(\alpha,R)$$
$$+\sigma^2 g_2(\alpha,R)]\frac{e^2}{\epsilon_0 R}, \tag{A6}$$

where the functions g_0, g_1, and g_2 are defined in Sec. III, Eqs. (16a)–(16c). Extensive use has been made of the Fourier transform of $1/|r|$. This allows us to write also

$$\left\langle F_R(\vec{r}_e,\vec{r}_h)\left|\frac{e^2}{\epsilon_\infty|\vec{r}_e-\vec{r}_h|}\right|F_R(\vec{r}_e,\vec{r}_h)\right\rangle$$
$$+\sum_k\frac{|V_k|^2}{\hbar\omega}|\rho(\vec{k})|^2=I_1+I_2, \tag{A7}$$

with

$$I_2=\frac{e^2}{4\pi^2}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\int\frac{d\vec{k}}{k^2}[|\rho_e(\vec{k})|^2+|\rho_h(\vec{k})|^2]$$
$$=\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\left(\gamma(s)\frac{e^2}{a}+\gamma(\sigma)\frac{e^2}{\alpha}\right) \tag{A8}$$

and

$$I_1=\frac{e^2}{2\pi^2}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\int\frac{d\vec{k}}{k^2}\rho_e(\vec{k})\rho_h^*(\vec{k})$$
$$=\frac{G}{(1+s^2)(1+\sigma^2)}\frac{e^2}{\epsilon_0 R}, \tag{A9}$$

where γ is given in Eq. (16d) and

$$G=G_0+G_{10}s+G_{01}\sigma+G_{11}s+G_{20}s^2$$
$$+G_{02}\sigma^2+G_{21}\sigma s^2+G_{12}s\sigma^2+G_{22}\sigma^2s^2. \tag{A10}$$

The coefficients in this development are expressed in terms of the integrals

$$S(n,p,q)=\frac{2}{\pi}\int_0^\infty\frac{dk\,k^n\sin(kR)}{[1+(a/2)^2k^2]^p[1+(\alpha/2)^2k^2]^q}, \tag{A11}$$

$$C(n,p,q)=\frac{2}{\pi}\int_0^\infty\frac{dk\,k^n\cos(kR)}{[1+(a/2)^2k^2]^p[1+(\alpha/2)^2k^2]^q}, \tag{A12}$$

as follows:

$$G_0=S(1,2,2), \tag{A13}$$

$$G_s(a)=2a\left(\frac{S(-1,3,2)}{R}-C(0,3,2)\right), \tag{A14}$$

$$G_\sigma(\alpha)=-G_s(a), \tag{A15}$$

$$G_{s^2}(a,\alpha)=G_{\sigma^2}(\alpha,a)=S(-1,3,2)$$
$$-\frac{3}{2}a^2\left(S(1,4,2)+\frac{2}{R}C(0,4,2)\right.$$
$$\left.-\frac{2}{R^2}S(-1,4,2)\right), \tag{A16}$$

$$G_{\sigma s}=4a\alpha\left(S(1,3,3)+\frac{2}{R}C(0,3,3)-\frac{2}{R^2}S(-1,3,3)\right), \tag{A17}$$

$$G_{\sigma s^2}(a,\alpha)=-G_{s\sigma^2}(\alpha,a)$$
$$=2\alpha\left[C(0,3,3)-\frac{1}{R}S(-1,3,3)\right.$$
$$-\frac{3}{2}a^2\left(C(2,4,3)-\frac{3}{R}S(1,4,3)\right.$$
$$\left.\left.-\frac{6}{R^2}C(0,4,3)+\frac{6}{R^3}S(-1,4,3)\right)\right], \tag{A18}$$

and

$$G_{s^2\sigma^2}=S(-1,3,3)-\frac{3}{2}\alpha^2\left(S(1,3,4)+\frac{2}{R}C(0,3,4)-\frac{2}{R^2}S(-1,3,4)\right)$$
$$-\frac{3}{2}a^2\left(S(1,3,4)+\frac{2}{R}C(0,4,3)-\frac{2}{R^2}S(-1,4,3)\right)$$
$$+\frac{9}{4}a^2\alpha^2\left(S(3,4,4)+\frac{4}{R}C(2,4,4)-\frac{12}{R^2}S(1,4,4)+\frac{24}{R^4}S(-1,4,4)-\frac{24}{R^3}C'(0,4,4)\right). \tag{A19}$$

In the symmetrical case ($a=\alpha$; $\sigma=-s$) the expressions (A14)–(A19) reduce to Eqs. (18a)–(18e) and finally after performing the integration over k, we obtain

$$G_0=1-\left[\frac{1}{6}\left(\frac{R}{a}\right)^3+\frac{3}{4}\left(\frac{R}{a}\right)^2+\frac{11}{8}\frac{R}{a}+1\right]e^{-2R/a}, \tag{A20}$$

$$G_1=4\frac{a}{R}-\left[8+4\frac{a}{R}+8\frac{R}{a}+\frac{59}{12}\left(\frac{R}{a}\right)^2+\frac{11}{6}\left(\frac{R}{a}\right)^3+\frac{1}{3}\left(\frac{R}{a}\right)^4\right]e^{-2R/a}, \tag{A21}$$

$$G_2=2+14\left(\frac{a}{R}\right)^2-\left[14\left(\frac{a}{R}\right)^2+28\frac{a}{R}+30+\frac{265}{12}\frac{R}{a}+\frac{73}{6}\left(\frac{R}{a}\right)^2+\frac{203}{40}\left(\frac{R}{a}\right)^3+\frac{89}{60}\left(\frac{R}{a}\right)^4+\frac{7}{30}\left(\frac{R}{a}\right)^5\right]e^{-2R/a}, \tag{A22}$$

$$\begin{aligned}G_3=4\frac{a}{R}+36\left(\frac{a}{R}\right)^3-\Bigg[&36\left(\frac{a}{R}\right)^3+72\left(\frac{a}{R}\right)^2+76\frac{a}{R}+56+32\frac{R}{a}+\frac{3577}{240}\left(\frac{R}{a}\right)^2+\frac{697}{120}\left(\frac{R}{a}\right)^3+\frac{113}{60}\left(\frac{R}{a}\right)^4\\&+\frac{7}{15}\left(\frac{R}{a}\right)^5+\frac{1}{15}\left(\frac{R}{a}\right)^6\Bigg]e^{-2R/a},\end{aligned} \tag{A23}$$

$$\begin{aligned}G_4=1+6\left(\frac{a}{R}\right)^2+54\left(\frac{a}{R}\right)^4-\Bigg[&54\left(\frac{a}{R}\right)^4+108\left(\frac{a}{R}\right)^3+114\left(\frac{a}{R}\right)^2+84\frac{a}{R}+49+\frac{30731}{1280}\frac{R}{a}+\frac{6411}{640}\left(\frac{R}{a}\right)^2\\&+\frac{23809}{6720}\left(\frac{R}{a}\right)^3+\frac{893}{840}\left(\frac{R}{a}\right)^4+\frac{19}{70}\left(\frac{R}{a}\right)^5+\frac{47}{840}\left(\frac{R}{a}\right)^6+\frac{1}{140}\left(\frac{R}{a}\right)^7\Bigg]e^{-2R/a}.\end{aligned} \tag{A24}$$

---

[1] F. Williams, Phys. Status Solidi 25, 493 (1968).

[2] P. J. Dean, *Progress in Solid State Chemistry* (Pergamon, New York, 1973), Vol. 8, p. 1.

[3] A. E. Yunovich, Forschr. Phys. 23, 317 (1973).

[4] B. Stébé and G. Munschy, Phys. Status Solidi B 60, 133 (1973).

[5] R. Evrard, E. Kartheuser, and F. Williams, J. Lumin. 14, 81 (1976). *Proceedings of the XIII International Conference of the Physics of Semiconductors, Rome, 1976*, edited by F. G. Fumi (Tipografia Marres, Rome, 1976), p. 1053.

[6] E. Kiefer and U. Schröder, J. Lumin. 14, 235 (1976).

[7] E. Kiefer, thesis, Universität Regensburg, 1977 (unpublished).

[8] T. Kottke, R. Morillo Soto, and F. Williams, J. Lumin. 18/19, 816 (1979).

[9] L. Mehrkam and F. Williams, *Optical Properties of Ions in Solids*, edited by B. DiBartolo (Plenum, New York, 1975), p. 459.

[10] G. B. Inglis and F. Williams, J. Lumin. 12/13, 525 (1976).

[11] J. H. Simpson, Proc. R. Soc. London A197, 269 (1949); A231, 308 (1955).

[12] R. Kubo, J. Phys. Soc. Jpn. 3, 254 (1948); 4, 322 (1949); 4, 326 (1949).

[13] K. Lehovec, Phys. Rev. 92, 253 (1953).

[14] D. Curie, C. R. Acad. Sci. (France) 238, 579 (1954).

[15] L. Mehrkam and F. Williams, Phys. Rev. B 6, 3753 (1972).

[16] A detailed discussion of the static approximation for associates of impurities centers can be found in R. Evrard and F. Williams, *Luminescence of Inorganic Solids*, edited by B. DiBartolo (Plenum, New York, 1978), p. 419.

[17] H. Fröhlich, H. Pelzer, and S. Zienan, Philos. Mag. 41, 221 (1950); see also *Polarons in Ionic Crystals and Polar Semiconductors*, edited by J. T. Devreese (North-Holland, Amsterdam, 1972).

[18] P. M. Platzman, Phys. Rev. 125, 1961 (1962).

[19] S. C. Wang, Phys. Rev. 31, 579 (1928).

[20] N. Rosen, Phys. Rev. 38, 2099 (1931).

[21] C. C. J. Roothaan, J. Chem. Phys. 19, 1445 (1951).

[22] A. Onton and R. C. Taylor, Phys. Rev. B 1, 2587 (1970).

[23] C. F. Schwerdtfeger, Solid State Commun. 11, 779 (1972).

[24] A. S. Barker, Jr., Phys. Rev. 165, 917 (1968).

[25] A. T. Vink, R. L. A. Van der Heyden, and J. A. W. Van der Heyden, and J. A. W. Van Der Does De Bye, J. Lumin. 8, 105 (1973).

[26] J. L. Merz, H. Kukimoto, K. Nassau, and J. W. Shiever, Phys. Rev. B 6, 546 (1972).

[27] M. Aven, D. T. F. Marple, and B. Segall, J. Appl. Phys. S32, 261 (1961).

[28] S. S. Mitra, J. Phys. Soc. Jpn. 21, Suppl. 61 (1966).

[29] J. J. Hopfield, D. G. Thomas, and M. Gershenzon, Phys. Rev. Lett. 10, 162 (1963).

[30] J. L. Merz, Phys. Rev. B 9, 4593 (1974).

[31] A. Manabe, A. Mitsuishi, and H. Yoshinaga, Jpn. J. Appl. Phys. 6, 593 (1967).

[32] G. E. Hite, D. T. F. Marple, M. Aven, and B. Segall, Phys. Rev. 156, 850 (1967).

[33] P. J. Dean, R. A. Faulkner, and S. Kimura, Phys. Rev. B 2, 4062 (1970).