PHYSICAL REVIEW B VOLUME 33, NUMBER 4 15 FEBRUARY 1986

Theory of the exciton molecule bound to an isoelectronic impurity in GaP

B. Arfi, W. T. Masselink, and Yia-Chung Chang
Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign,
Urbana, Illinois 61820
(Received 3 September 1985)

We present a theoretical calculation of the fine structure of an exciton molecule bound to a nitrogen center in GaP. The conduction-band structure is properly taken into account (except for the camel's back effect) by using a combination of Wannier states and effective-mass states for the center electron. The valence-band warping is included by using *s*-like and *d*-like effective-mass states for the holes. Solving the one-exciton problem, we obtain a splitting of 0.78 meV of the $J=2$ and 1 levels due to the electron-hole exchange Coulomb interaction. Including the electron-hole exchange Coulomb interaction and the *j*-*j* coupling between holes in the exciton molecule gives a splitting of 0.20 meV for the lowest-lying states with total angular momenta $J=0$ and $J=2$. The results are in good agreement with experiment.

I. INTRODUCTION

It is well known that an isoelectronic impurity in a semiconductor may bind an exciton.[1] The mechanism for such binding is commonly described as follows: An electron is trapped in the short-range isoelectronic potential of the impurity and then binds a hole in the Coulomb field resulting from the electron.[2–4] Although such a description is useful for visualizing the problem it leads one to suppose that an exciton will remain unbound unless the electron itself may first be trapped. Actually, as has been previously pointed out,[3–7] the picture is probably much more complex and in some systems the electron by itself may not even bind.

Often studied as an example of the isoelectronic impurity problem is GaP:N. Because of the complexity of the binding mechanism, accurate first-principles calculations of the electron and exciton binding energies are not available. Semiempirical calculations of the electron binding energies in Ga-As-P alloys have proven successful[8] and are consistent with the picture that the electron by itself is bound in GaP. Lacking a detailed calculation of the binding energy of the whole system, the electron binding energy is frequently taken to be the difference between the bound-exciton energy and the free-exciton energy. Thus in GaP, the electron binding energy is taken to be ~8 meV (Refs. 5 and 6) given a total binding energy ~28 meV (Ref. 9) and a free-exciton binding energy ~20 meV.[10]

Recently, Masselink and Chang[11] have performed theoretical calculations for the electronic structure of an exciton bound to a nitrogen trap in GaP, taking into account for the first time the band structures for both particles and their mutual Coulomb interaction. They found that the bare electron is bound by only 0.6 meV instead of 8 meV as usually quoted. Furthermore, their calculation predicts the *A*-*B* splitting of the bound-exciton luminescence in good agreement with the experimental data.[12]

It was shown via photoluminescence studies[12] that an exciton molecule can become bound to the nitrogen trap in GaP. To our knowledge, no theoretical calculations on the electronic structure of excitonic molecules bound to isoelectronic traps in semiconductors have been reported.

In this paper, we report the first such theoretical calculation. We find that since the inner electron of the system is very localized near the isoelectronic trap, the single exciton bound to the trap behaves like a neutral acceptor system. Hence, the exciton molecule bound to the trap can be viewed as an acceptor—bound-exciton system (A^0X) commonly observed in semiconductors.[13–15] It is well known that the *j*-*j* coupling of the two spin-$\frac{3}{2}$ holes in A^0X leads to a fine structure described by two states with total angular momenta J_{hh} equal to 2 and 0.[16] The $J_{hh}=2$ states are further split into two states labeled by Γ_3 and Γ_5 due to the crystal field.[12–15] Such a *j*-*j* coupling scheme also applies to the exciton molecule bound to isoelectronic traps.[12] Our present calculation is able to predict the magnitude of the $J_{hh}=2$ and $J_{hh}=0$ splitting and the value obtained is 0.20 meV, in fairly good agreement with the experimental data ($\simeq$0.17 meV).[12]

This paper is organized as follows: In Sec. II, we report the details of the calculation on a single exciton bound to the nitrogen trap in GaP, previously reported by two of us (W.T.M. and Y.C.C.). In Sec. III we report the calculation on an excitonic molecule bound to the nitrogen trap in GaP. In Sec. IV we set down our concluding remarks.

II. SINGLE EXCITON BOUND TO AN ISOELECTRONIC IMPURITY

In this section, we study the electronic structure of a single exciton trapped to an isoelectronic impurity in GaP. Part of the results obtained here has been summarized previously in a letter.[11]

The Hamiltonian for a single exciton bound to an isoelectronic trap is given by

$$H_0(1)+V(1)+H_0(2)+v(1,2)\ , \qquad (1)$$

where $H_0(1)$ and $H_0(2)$ are the individual Hamiltonians for the electron and hole in the absence of each other and the nitrogen impurity, $V(1)$ is a short-range potential attractive to electrons,[2] and $v(1,2)$ is the Coulomb interaction between electron and hole. The interaction of the hole with the isoelectronic impurity is probably repulsive and is neglected in the present calculation. There also exists an exchange interaction between the electron and hole, which will be included later.

A. Hartree-Fock approximation

We shall first study the two-particle wave function in the self-consistent Hartree-Fock approximation (HFA) and then examine the effect of correlation. Within the HFA, the two-particle wave function of the system is written as

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\psi_e(\mathbf{r}_1)\psi_h^{(\mu)}(\mathbf{r}_2)\chi_e \ , \tag{2}$$

where ψ_e and $\psi_h^{(\mu)}$ are the single-particle wave functions for the electron and hole, respectively. χ_e denotes the electron spinor and μ is the column index for the fourfold hole state. In the spherical model, the hole is described by a spin-$\frac{3}{2}$ particle, and $\mu=-\frac{3}{2}$, $-\frac{1}{2}$, $\frac{1}{2}$, and $\frac{3}{2}$. Because of the complicated nature of the valence band, the hole state cannot be written as a simple product of a spatial function and a spinor.

The electron wave function ψ_e is described in terms of linear combinations of Bloch states belonging to the first conduction band, viz.,

$$\psi_e(\mathbf{r})=\sum_{\mathbf{k}}\widetilde{F}_e(\mathbf{k})\phi_{c\mathbf{k}}(\mathbf{r}) \ , \tag{3}$$

where $\phi_{c\mathbf{k}}(\mathbf{r})$ denotes the Bloch function of the conduction band of GaP and the summation over $\mathbf{k}$ is restricted in the first Brillouin zone. The possible mixing with the valence bands and higher conduction bands is neglected. It was found in a previous calculation that more than 90% of the electron charge density is derived from the conduction band.[4] The expression (3) can be transformed into the Wannier representation as

$$\psi_e(\mathbf{r})=\sum_{\mathbf{R}}F_e(\mathbf{R})W_{\mathbf{R}}(\mathbf{r}) \ , \tag{4}$$

where

$$W_{\mathbf{R}}(\mathbf{r})=\sum_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{R}}\phi_{c\mathbf{k}}(\mathbf{r}) \ ,$$

$\mathbf{R}$ denotes lattice vectors, and $F_e(\mathbf{R})$ is just the Fourier transform of $\widetilde{F}_e(\mathbf{k})$.

To take full advantage of the short-ranged nature of the isoelectronic potential and the small binding energy of the isoelectronic trap, we rewrite $\psi_e(\mathbf{r})$ in a mixed representation as

$$\psi_e(\mathbf{r})=\sum_{\mathbf{R}}G_e(\mathbf{R})\Theta(R_c-|\mathbf{R}|)W_{\mathbf{R}}(\mathbf{r}) + \sum_{\nu=1}^{m}C_\nu\sum_{\mathbf{k}}\widetilde{\beta}_\nu(\mathbf{k})\phi_{c\mathbf{k}}(\mathbf{r}) \ , \tag{5}$$

where in the first term the summation over $\mathbf{R}$ is truncated at a short distance, R_c, and in the second term the envelope functions $\widetilde{\beta}_\nu(\mathbf{k})$ are symmetric sums of three wave packets localized at the three equivalent X minima (ignoring the camel's back in the conduction-band structure of GaP). m is the number of trial basic functions ($\widetilde{\beta}_\nu$) used in the calculation. By symmetry $G_e(\mathbf{R})$ only depends on $|\mathbf{R}|$. Hence, the first term in (5) reduces to $\sum_{s=0}^{s_c}G_e(R_s)W_s(\mathbf{r})$, where s denotes the shell number ($s=0$ indicating the impurity site), s_c is the cutoff for s ($s_c=9$ in the present calculation), R_s is the shell radius, and $W_s(\mathbf{r})$ is the "shell" Wannier orbital, defined as

$$W_s(\mathbf{r})\equiv\sum_{\mathbf{R}}\delta_{R,R_s}W_{\mathbf{R}}(\mathbf{r}) \ . \tag{6}$$

The envelope functions in the second term of the expansion in (5) are chosen to be of the following form:

$$\widetilde{\beta}_\nu(\mathbf{k})=\frac{1}{\sqrt{3}}\sum_{j=x,y,z}\beta_\nu^j(\mathbf{k}) \tag{7a}$$

with

$$\beta_\nu^z(\mathbf{k})=\exp\{-[(k_x^2+k_y^2)+(k_z-k_0)^2/\mu_\nu]/4\alpha_\nu\} \ , \tag{7b}$$

where k_0 is the distance in $\mathbf{k}$ space between Γ and X, μ_ν are the anisotropy factors, and α_ν are Gaussian exponents which determine the spread of the wave packet in $\mathbf{k}$ space. For $\nu=1,\ldots,5$, we choose $\mu_\nu=1$ and $\alpha_\nu=3(\sqrt{8}^{\nu-5})$. For $\nu=6,\ldots,10$ and $\nu=11,\ldots,15$, α_ν are repeated but μ_ν are chosen to be $\sqrt{8}$ and 8, respectively. We have used the normalized units in which distance is measured in effective bohrs,

$$a_0^*=\frac{\epsilon_0 m_e}{m_e^*}(0.529\,\text{Å})\simeq 23\ \text{Å} \ .$$

Note that the maximum spread in $\mathbf{k}$ space of the wave packet used in our calculation is $\sqrt{24}$ along the [001] direction and $\sqrt{3}$ along the perpendicular directions. Within these restricted regions surrounding the three X minimum the band structure is approximately parabolic and the effective-mass approximation can be used in the evaluation of the kinetic energy. Thus, the basis wave functions

$$\beta_\nu(\mathbf{r})\equiv\sum_{\mathbf{k}}\widetilde{\beta}_\nu(\mathbf{k})\phi_{c\mathbf{k}}(\mathbf{r})$$

shall be referred to as the effective-mass orbitals. In terms of the shell Wannier orbitals and the effective-mass orbitals, the electron wave function takes the final simple form:

$$\psi_e(\mathbf{r})=\sum_{s=0}^{9}G_e(R_s)W_s(\mathbf{r})+\sum_{\nu=1}^{15}C_\nu\beta_\nu(\mathbf{r}) \ . \tag{8}$$

Here, the coefficients $G_e(R_s)$ and C_ν are variational parameters to be determined by solving the self-consistent Schrödinger equation for the electron.

The interactions between the shell Wannier orbitals, $|W_s\rangle$ due to $H_0(1)$ are given by

$$\langle W_s|H_0(1)|W_{s'}\rangle=\sum_{\mathbf{k}}E_c(\mathbf{k})\widetilde{W}_{s'}(\mathbf{k})\widetilde{W}_s(\mathbf{k}) \ , \tag{9}$$

where $\widetilde{W}_s(\mathbf{k})=\langle\phi_{c\mathbf{k}}|W_s\rangle$ and $E_c(\mathbf{k})$ is the dispersion function for the conduction band. We find that $\widetilde{W}_s(\mathbf{k})$ can be written in a closed form as

$$\tilde{W}_s(\mathbf{k})=\frac{N_s}{6}[\cos(l_s k_x a)\cos(m_s k_y a)\cos(n_s k_z a)+5\text{ terms}]\ , \tag{10}$$

where N_s is the number of atoms belonging to the sth shell, and l_s, m_s, n_s are the three principal indices for lattice vectors $\mathbf{R}$ in the sth shell. For the first ten shells, they are given by $(l_s,m_s,n_s)=(0,0,0)$, (0,1,1), (0,0,2), (1,1,2), (0,2,2,), (0,1,3), (2,2,2), (1,2,3), (0,0,4), (1,1,4), and (0,3,3). The remaining five terms in (10) are obtained by permutation of (k_x,k_y,k_z) in the first term.

The conduction-band dispersion $E_c(\mathbf{k})$ is given by

$$E_c(\mathbf{k})=\sum_{\mathbf{R}} V(R)e^{i\mathbf{k}\cdot\mathbf{R}}\ , \tag{11}$$

where $\mathbf{R}$ runs over the lattice vectors and $V(R)$ are adjustable parameters which only depend on the distance R. If we truncate the summation in (11) at the s_cth shell, then

$$E_c(\mathbf{k})=\sum_{s=0}^{s_c} V(R_s)\tilde{W}_s(\mathbf{k})\ . \tag{12}$$

The parameters $V(R)$ are determined by fitting (12) to the dispersion curve obtained by an emperical pseudopotential method.[17] However, the transverse effective mass at the X point of the band structure is fit to the experimental value.[18] The quality of the fit is demonstrated in Fig. 1, and the parameters $V(R_s)$ which give the best fit are listed in Table I. Using the expression (12), the matrix elements in (9) can be rewritten as

$$\langle W_s \,|\, H_0(1) \,|\, W_{s'}\rangle = N_s \sum_{\mathbf{R}'} V(\,|\mathbf{R}-\mathbf{R}'|\,)\delta_{R',R_{s'}}\ , \tag{13}$$

where $\mathbf{R}$ is any lattice vector belonging to the sth shell.

To calculate the matrix elements of $H_0(1)$ between the effective mass orbitals, we take $E_c(\mathbf{k})=\hbar^2/2m_t^*[k_x^2+m_t^*/m_l^*(k_z-k_0)^2]$ for the z valley where m_l^*, the longitudinal effective mass, is taken to be $8m_t^*$.[19] (This ignores the existence of the camel's back structure, but gives the correct overall curvature of the conduction band near the X points.)

The interaction between the effective-mass and Wannier orbitals is given by

$$\langle \beta_\nu \,|\, H_0(1) \,|\, W_s\rangle = \sqrt{3}\sum_{\mathbf{k}} E_c(\mathbf{k})\tilde{\beta}_\nu^z(\mathbf{k})\tilde{W}_s(\mathbf{k})\ , \tag{14}$$

which can also be performed analytically given (7) and (12). Thus, for the electron, the conduction-band structure (except for the camel's back) has been included for the Wannier orbitals exactly and for the effective-mass orbitals to the extent that the band is parabolic at its minimum.

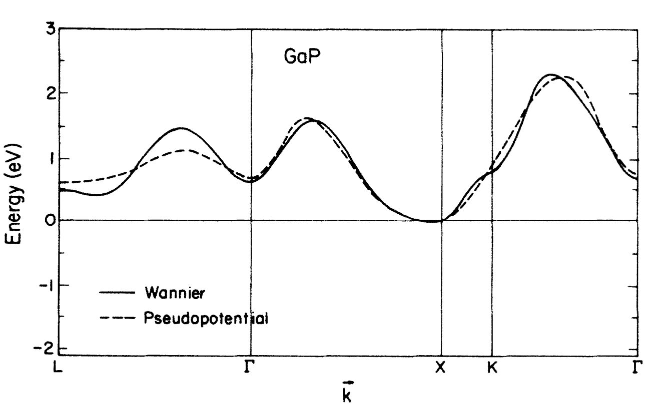

FIG. 1. GaP band structure as obtained in the Wannier representation and by a pseudopotential method.

TABLE I. Interaction parameters for fitting the conduction-band dispersion of GaP. All values of $V(R_s)$ are in eV.

Shell no.	$V(R_s)$
0	1.5377
1	0.010 48
2	−0.044 04
3	0.023 99
4	−0.099 67
5	0.004 94
6	0.009 97
7	0.013 67
8	0.000 22
9	−0.006 36
10	−0.0707

Since the impurity potential is very localized in real space, we take $V(1)=V_0\,|W_0\rangle\langle W_0|+V_1\,|W_1\rangle\langle W_1|$. In our calculation we have $V_1=0$ and adjust V_0 to bind the exciton by the observed energy. Allowing V_1 to be as large as $V_0/4$ does not alter the results except for slightly shifting some of the electronic wave function from $|W_0\rangle$ to $|W_1\rangle$. (Faulkner[3] predicted that when included properly, $V_1 \sim 0.01V_0$.)

Because the effective-mass orbitals are not orthogonal to the Wannier orbitals, the overlap between them also needs to be evaluated. We obtain

$$\langle \beta_\nu \,|\, W_s\rangle = \sqrt{3}\sum_{\mathbf{k}} \tilde{\beta}_\nu^z(\mathbf{k})\tilde{W}_s(\mathbf{k})\ . \tag{15}$$

Furthermore, for the impurity potential sandwiched between two effective-mass orbitals, we have

$$\langle \beta_\nu \,|\, V(1) \,|\, \beta_{\nu'}\rangle = \langle \beta_\nu \,|\, W_0\rangle V_0 \langle W_0 \,|\, \beta_{\nu'}\rangle + \langle \beta_\nu \,|\, W_1\rangle V_1 \langle W_1 \,|\, \beta_{\nu'}\rangle\ .$$

For the interaction between the effective mass and Wannier orbitals, we have

$$\langle \beta_\nu \,|\, V(1) \,|\, W_s\rangle = \langle \beta_\nu \,|\, W_0\rangle V_0\delta_{0s} + \langle \beta_\nu \,|\, W_1\rangle V_1\delta_{1s}\ .$$

The hole envelope wave function is described in the effective-mass approximation as a linear combination of eight s-like and eight d-like Gaussian orbitals. The d-like orbitals are included here to take into account the warping of the valence band. We write

$$\psi_h^{(\mu)}(\mathbf{r})=\sum_{\nu=1}^{8}[C_\nu^{(s)}S_\nu^{(\mu)}(\mathbf{r})+C_\nu^{(d)}D_\nu^{(\mu)}(\mathbf{r})]\ , \tag{16a}$$

where

$$S_\nu^{(\mu)}(\mathbf{r})=e^{-\alpha_\nu r^2}\phi_{v0}^{(\mu)}(\mathbf{r})Y_{00}(\Omega)\ ,$$
$$D_\nu^{(\mu)}(\mathbf{r})=r^2e^{-\alpha_\nu r^2}\sum_m C(\mu;m)Y_{2m}(\Omega)\phi_{v0}^{(\mu-m)}(\mathbf{r})\ . \tag{16b}$$

Here, $\phi_{v0}^{(\mu)}(\mathbf{r})$ is the zone-center valence-band Bloch state with spin component μ. $Y_{2m}(\Omega)$ is the second-order spherical harmonic function, and $C(\mu;m)$ is the coupling coefficient defined in Table III of Ref. 20. The eight exponents used in the calculation are $3(\sqrt{8})^{\nu-5}$, $\nu=1-8$. The matrix elements of $H_0(2)$ between the hole basis states are calculated following the method of Baldereschi and Lipari.[21]

The Coulomb interaction is given by

$$v(1,2)=\int\frac{d^3q}{(2\pi)^3}\frac{8\pi}{q^2}\frac{e^{i\mathbf{q}\cdot\mathbf{r}_{12}}}{\epsilon(q)}\equiv\frac{2}{r_{12}\epsilon(r_{12})}\ , \tag{17}$$

where the dielectric screening function takes the form[22]

$$\frac{1}{\epsilon(r)}=\sum_{\nu=1}^{4}S_\nu e^{-\sigma_\nu r}\ .$$

Because the dielectric constant ϵ_0 used here (11.02) (Ref. 23) is different from that in Ref. 22, we have readjusted the values of σ_ν such that $\epsilon(q)$ agrees with the result of Ref. 24. For ease in computation, we also fit the above expression by a four-term Gaussian function $\sum_{\nu=1}^{4}C_\nu e^{-\alpha_\nu r^2}$ with $C_\nu=(1,5.512,5.508,-1)$ and $\alpha_\nu=(0,20.66,13.02,20.41)$ Å^{-2}. The Coulomb interaction between effective mass orbitals can then be carried out analytically. The evaluation of the Coulomb interaction involving Wannier orbitals must be performed with some approximation. For simplicity, we treat the electron in a Wannier orbital centered at $\mathbf{R}$ as a point charge there. This is a good approximation, considering the localized character of a Wannier state compared with the charge distribution in the hole.

To find the self-consistent electron and hole wave functions ψ_e and ψ_h, we solve the secular equation

$$\langle\psi_e\psi_h\,|\,H\,|\,\psi_e\psi_h\rangle=E\langle\psi_e\psi_h\,|\,\psi_e\psi_h\rangle \tag{18}$$

iteratively using the Rayleigh-Ritz variational method in our basis.[8] Using this technique, we calculate both the electron and exciton binding energies as functions of V_0. The results along with the localization of the hole are shown in Fig. 2. When $V_0=-1.147$ eV, the calculated system energy coincides with the experimental binding energy of 28.0 meV. This same trap potential binds an electron by 0.6 meV. This is much shallower than the value of 8 meV, quoted in previous calculations,[3-6] but also much more reasonable. Our calculations also show that for some values of V_0 which do not bind the electron, the exciton is still bound deeper than the 20 meV of a free exciton. Conceivably there are physical systems (perhaps GaAs) in which this situation is realized.

Figure 3 depicts the electron's envelope wave function in k space [denoted $\tilde{F}_e(\mathbf{k})$], with and without the hole along the [100] direction. Also included is the result without the hole obtained by using the Green's-function method, which can be shown to be proportional to $1/E_c(\mathbf{k})-E$. Good agreement is found between our method and the Green's-function method. The Green's-function method, however, does not apply to the case with hole, due to the presence of the long-range interaction. For all cases, we find that the electron is fairly localized near X. The X-valley peaks contain approximately 80% and 95% of the total electronic charge for the cases of with and without a hole. The effect of including the hole in the calculation, then, is to further localize the electron in real space and thereby delocalize it in k space. Transforming the wave function into real space shows that with a hole present, about 16% of the electronic charge lies within the first shell surrounding the impurity site. Without the hole, about 4% lies within the first shell.

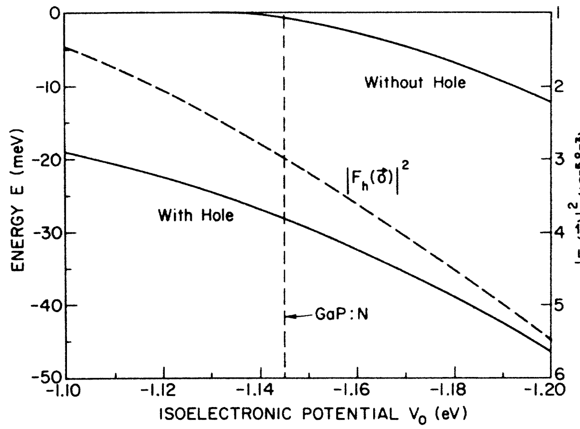

FIG. 2. Ground-state energies of an electron bound to an isoelectronic trap in GaP with and without the presence of a hole plotted as functions of potential V_0. Also plotted as a function of V_0 is the hole wave-function squared at $\mathbf{r}=0$, $|F_h(0)|^2$ (dashed). The vertical dashed line indicates the position of the observed photoluminescence data for GaP:N.

The Hamiltonian used in calculating the binding energy of the exciton [Eq. (1)] does not account for the presence of two lines in the recombination radiation of bound excitons. This splitting is apparently caused by an electron-hole exchange term which depends upon the total angular momentum J of the exciton. Since the angular momentum of the hole is $\frac{3}{2}$ and that of the electron is $\frac{1}{2}$, the exciton may have either $J=2$ or $J=1$. Because of the rela-

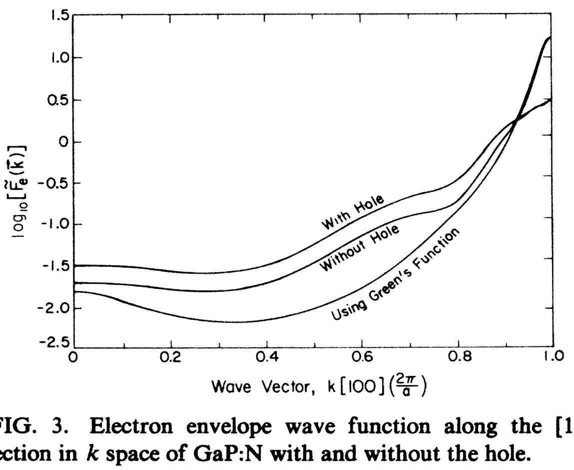

FIG. 3. Electron envelope wave function along the [100] direction in k space of GaP:N with and without the hole.

tively small size of the splitting (0.8 meV) (Ref. 12) compared to the binding energy (28 meV), the exchange interaction energy may be calculated using first-order perturbation theory.

Let ΔE be the A-B splitting due to the exchange interaction energy difference between the $J=1$ and $J=2$ bound exciton states. We find (see Appendix A for derivation)

$$\Delta E = \tfrac{4}{3} J_{\mathrm{ex}} \, | F_h(0) |^2 \, , \tag{19a}$$

where

$$J_{\mathrm{ex}} \simeq \sum_{\mathbf{k}} | \widetilde{F}_e(k) |^2 \langle \phi_{c\mathbf{k}} \phi_{v0} | v | \phi_{v0} \phi_{c\mathbf{k}} \rangle \, , \tag{19b}$$

and $F_h(0)$ is the hole envelope function evaluated at $\mathbf{r}=0$. $|\phi_{c\mathbf{k}}\rangle$ denotes the conduction-band Bloch state with wave vector $\mathbf{k}$ and $|\phi_{v0}\rangle$ the valence-band Bloch state at $\mathbf{k}=0$. Both $|\phi_{c\mathbf{k}}\rangle$ and $|\phi_{v0}\rangle$ are expanded in 137 plane waves using the empirical pseudopotential method.[9] To perform the integration over $\mathbf{k}$ we use the ten-special-point technique. From our bound-exciton calculation, we find $|F_h(0)|^2 = 3.0 \times 10^{-5}$ Å^3. Using the pseudopotential of Cohen and Bergstresser, we find that $J_{\mathrm{ex}} = 1.95 \times 10^4$ meV Å^3. (In the previous report[11] we used a different approximation for the $\mathbf{k}$ integration and obtained 1.8×10^4 meV Å^3.) Thus $\Delta E = 0.78$ meV. This is in excellent agreement with the measured value of 0.8 meV. For comparison, in a free exciton we find $\Delta E = 0.2$ meV.

B. Correlation effect

Next, we examine the correlation effect. For simplicity, we use a spherical effective-mass approximation (EMA) with constant dielectric screening. We further model the isoelectric potential by a short-range potential of the form

$$V(r_1) = -U_0 e^{-\alpha r_1^2} \, ,$$

where U_0 is an empirical constant adjusted such that the resulting total energy matches the experimental value. α controls the range of the potential, and is related to the core radius (r_c) by $\alpha = 1/r_c^2$.

The EMA Hamiltonian for the system is (in normalized units)

$$-\nabla_1^2 - \sigma \nabla_2^2 + V(r_1) - \frac{2}{r_{12}} \, , \tag{20}$$

where $\sigma \equiv m_e^*/m_h^*$ is the electron to hole effective-mass ratio; $-\nabla_1^2$ and $-\sigma\nabla_2^2$ describe the kinetic energies for the electron and hole.

The two-particle wave function of the system, $\psi(\mathbf{r}_1, \mathbf{r}_2)$, is expressed in terms of two sets of basis functions. The first set contains single-particle product functions of the Gaussian form

$$\beta_n(r_1)\beta_m(r_2) \propto e^{-b_n r_1^2} e^{-b_m r_2^2} \, .$$

The second set contains the product of an electron wave function and an exciton wave function of the form

$$\beta_n(r_1)\beta_m(r_2 - r_1) \propto e^{-b_n r_1^2} e^{-b_m r_{12}^2} \, .$$

The inclusion of this set is essential since it gives the correct limiting form for the total wave function when the electron potential becomes very shallow. The variational principle ensures that the results obtained from combining the two sets will be at least as good as from either set individually. The parameters, b_n, are taken to be 5^{n-5} where $n = 1, \ldots, 9$, to cover a large physical range. A convergence test by including more basis states indicates that the present basis set is sufficient.

The bound-exciton binding energy is calculated not only in the combined basis as described, but also in the smaller set-1 and set-2 bases separately as functions of U_0. It should be noted that using set 1 alone will yield a total energy essentially equivalent to (but slightly lower than) that obtained in a Hartree-Fock calculation.

Using the same values of U_0 and α, the related problem of an electron bound to the impurity is also solved. For this problem, $H = -\nabla_1^2 + V(r_1)$ in normalized units using the same $V(r_1)$ as before. We take $\psi_e = \sum_{n=1}^{9} C_n \beta_n(\mathbf{r}_1)$ with $\beta_n(\mathbf{r}_1)$ as defined for the exciton problem. The ground-state eigenvalues of all four calculations are graphed as functions of U_0 (see Fig. 4).

For application to GaP:N, we take $\sigma = 1.0$ (Refs. 25 and 26) and α such that the potential core radius $(r_c) \approx 2$ Å. The free-exciton binding energy ($=1$ Ry$^*/1+\sigma$) has been measured to be 20.5 meV (Ref. 10) which implies 1 Ry$^* = 41$ meV. Furthermore, since $\epsilon_0 \approx 11.02$,[23] we obtain $a_0^* \approx 15$ Å. Thus since $r_c \approx 1/\alpha$, we take $\alpha = 50$.

As expected, we see that the combined basis predicts a lower energy and is thus superior to either of the separate bases. Furthermore, we note that the set-2 basis predicts that the bound-exciton binding energy is the sum of the

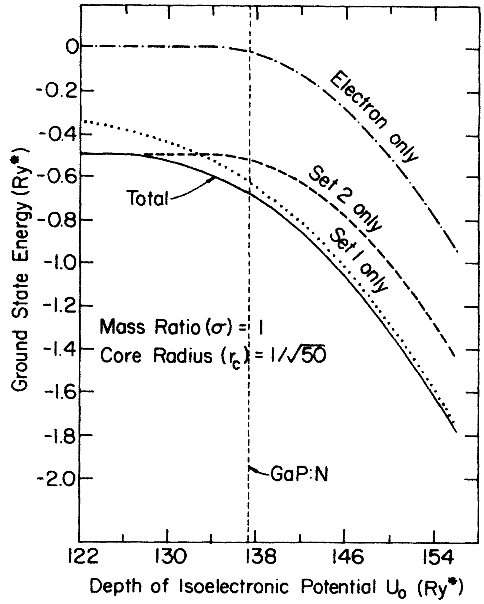

FIG. 4. Ground-state energies of an electron (dashed-dotted) and exciton bound to an isoelectronic trap calculated with set-1 basis (dotted), set-2 basis (dashed), and combined basis (solid), plotted as functions of the depth of the isoelectronic potential (U_0) for mass ratio $\sigma=1$ and core radius $(r_c) = 1/\sqrt{50}$. The vertical dashed lines indicate the positions where the observed photoluminescence datum for GaP:N is fitted. The datum is taken from Ref. 7.

electron binding energy and the free-exciton binding energy $[E_x=(1+\sigma)^{-1}]$. This, in fact can be proved rigorously when only s-like electron and exciton product functions are used.

When the potential is shallow, the combined basis solution converges to the free-exciton (or set-2) solution, but as the exciton becomes more spatially localized, the difference between the combined basis and set-2 basis solutions becomes greater. We shall refer to this energy difference as the exciton localization energy. The difference between the combined basis and set-1 basis solutions is attributed to the correlation effect. It can be seen from this figure that as long as the electron alone is bound, the correlation effect contributes to less than 6% of the total energy. A similar consideration of the electron-hole correlation effect has recently been published.[27]

III. EXCITONIC MOLECULE BOUND TO AN ISOELECTRONIC IMPURITY

In this section, we study the electronic structure of an excitonic molecule bound to an isoelectronic impurity in GaP. The Hamiltonian of the system is given by

$$H=\sum_{i=1}^{4} H_0(i)+\sum_{i=1}^{2} V(i)+\sum_{\substack{i,j\\(i<j)}}^{4} v(i,j)\ , \tag{21}$$

where $H_0(i)$ is the individual Hamiltonian for the ith particle in the absence of the three other particles and the nitrogen impurity, $V(i)$ is the short-range potential attractive to electrons, and $v(i,j)$ is the Coulomb interaction between the ith and jth particles. Here, the center electron is labeled by 1, the outer electron by 2, and the two holes by 3 and 4. The calculation is done in an "unrestricted" Hartree-Fock approximation (UHFA).[28]

The four-particle wave function of the system is written as

$$\psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4)=\psi_{ee}(\mathbf{r}_1,\mathbf{r}_2)\psi_{hh}(\mathbf{r}_3,\mathbf{r}_4)\ ,$$

where ψ_{ee} is the two-electron wave function and ψ_{hh} is the two-hole wave function. In the present calculation, we neglect the electron-hole correlation effect on the total wave function.

The total Hamiltonian of the four-particle system can be rewritten as

$$H=H_{ee}+H_{hh}+H_{eh}\ , \tag{22a}$$

where

$$H_{ee}=\sum_{i=1}^{2} H_0(i)+v(1,2)+\sum_{i=1}^{2} V(i)\ , \tag{22b}$$

$$H_{hh}=\sum_{i=3}^{4} H_0(i)+v(3,4)\ , \tag{22c}$$

and

$$H_{eh}=v(1,3)+v(1,4)+v(2,3)+v(2,4)\ , \tag{22d}$$

H_0, v, and V being defined earlier in Sec. I. The total energy E is given by

$$\langle\psi|H|\psi\rangle=\langle\psi_{ee}\psi_{hh}|H|\psi_{ee}\psi_{hh}\rangle=E\langle\psi_{ee}\psi_{hh}|\psi_{ee}\psi_{hh}\rangle \tag{23}$$

which can be rewritten as

$$\langle\psi_{hh}|\psi_{hh}\rangle\langle\psi_{ee}|H_{ee}|\psi_{ee}\rangle+\langle\psi_{hh}|H_{hh}|\psi_{hh}\rangle\langle\psi_{ee}|\psi_{ee}\rangle+\langle\psi_{ee}\psi_{hh}|H_{eh}|\psi_{ee}\psi_{hh}\rangle=E\langle\psi_{ee}|\psi_{ee}\rangle\langle\psi_{hh}|\psi_{hh}\rangle\ . \tag{24}$$

The outer-electron wave function is chosen to be of the form

$$\psi_2(\mathbf{r})=\sum_{\mathbf{k}}\widetilde{F}_2(\mathbf{k})\psi_{c\mathbf{k}}(\mathbf{r})\ , \tag{25a}$$

where $\psi_{c\mathbf{k}}(\mathbf{r})$ is the conduction-band Bloch state at $\mathbf{k}$, and $\widetilde{F}_2(\mathbf{k})$ (the envelope function) is given by

$$\widetilde{F}_2(\mathbf{k})=\frac{1}{\sqrt{3}}\sum_j\widetilde{F}_2^j(\mathbf{k})\ , \tag{25b}$$

where j labels the three equivalent minima and $\widetilde{F}_2^j(\mathbf{k})$ has the Fourier transform in real space:

$$F_2^j(\mathbf{r})=\frac{b^{3/2}}{\sqrt{\pi}}e^{-br}e^{i\mathbf{k}_j\cdot\mathbf{r}}\ , \tag{25c}$$

where $|\mathbf{k}_j|=k_0$. b is a variational parameter obtained by minimizing the total energy of the system.

The spatial part of the two-electron wave function is written as

$$\psi_{ee}(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{\sqrt{2}}\sum_\sigma D_\sigma[\gamma_\sigma(\mathbf{r}_1)\psi_2(\mathbf{r}_2)+\psi_2(\mathbf{r}_1)\gamma_\sigma(\mathbf{r}_2)] \tag{26}$$

where γ_σ denotes the basis states for the inner electron, which consist of the shell Wannier orbitals $W_s(\mathbf{r})$ and the effective-mass orbitals $\beta_\nu(\mathbf{r})$. The spin part of the two-electron state is given by

$$\chi_{12}=\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)-\alpha(2)\beta(1)]$$

(a spin singlet), where α and β are up and down spinors. We shall omit writing the spinors explicitly in the rest of the paper. The coefficients D_σ in (26) are variational parameters to be determined by solving (24) self-consistently for the four-particle system.

Using the definition of H_{ee} we can write

$$\langle\psi_{ee}|H_{ee}|\psi_{ee}\rangle=2\langle\psi_{ee}|H_0(1)+V(1)|\psi_{ee}\rangle+\langle\psi_{ee}|v(1,2)|\psi_{ee}\rangle\ , \tag{27}$$

where the symmetry of exchanging two electrons in ψ_{ee} has been used. Using the expansion (26), we see that the first term in (27) contains matrix elements like $\langle\gamma_\sigma|H_0(1)+V(1)|\gamma_\sigma\rangle$, $\langle\psi_2|H_0(1)+V(1)|\gamma_\sigma\rangle$, and $\langle\psi_2|H_0(1)+V(1)|\psi_2\rangle$. All these matrix elements can be evaluated in the same manner as discussed in Sec. I, if we also use a ten-Gaussian expansion for the exponential function in ψ_2, i.e.,

$$e^{-br}=\sum_{n=1}^{10}C_n e^{-P_n b^2 r^2}\ ,$$

where the parameters C_n and P_n can be found in Ref. 29.

The mutual Coulomb interaction $\langle\psi_{ee}|v(1,2)|\psi_{ee}\rangle$

can be written as the sum of direct and exchange terms. For the direct term, we have

$$\langle \psi_{ee} | v(1,2) | \psi_{ee} \rangle_{\text{direct}} = \int \left| \sum_{\sigma} D_\sigma \gamma_\sigma(\mathbf{r}) \right|^2 V_e(r) d^3r \;, \tag{28}$$

where

$$\begin{aligned} V_e(r_1) &\equiv \int d^3r_2 \frac{2}{|\mathbf{r}_1-\mathbf{r}_2|} |\psi_2(\mathbf{r}_2)|^2 \\ &\simeq \frac{2}{r_1}(1-e^{-2br_1}) - 2be^{-2br_1} \;, \end{aligned} \tag{29}$$

which is an effective potential for particle 1 due to the outer electron. The expression is exact, if the intervalley scattering terms are ignored (this is a very good approximation, since the envelope function of the outer electron is sharply peaked at the three equivalent minima).

The expression (28) contains the following matrix elements:

(i) $\langle W_s | V_e | W_{s'} \rangle$

$$= \begin{cases} \delta_{ss'} \left[\dfrac{2}{R_s}(1-e^{-2bR_s}) - 2be^{-2bR_s} \right], & s,s' \neq 0 \\ 2b, \; s=s'=0 \end{cases}$$

(ii) $\langle \beta_\nu | V_e | \beta_{\nu'} \rangle = \int d^3r \beta_\nu^*(\mathbf{r}) \beta_{\nu'}(\mathbf{r}) V_e(\mathbf{r}) \;,$ (30)

(iii) $\langle \beta_\nu | V_e | W_s \rangle = v_e(R_s) \langle \beta_\nu | W_s \rangle \;.$

The exchange Coulomb interactions are more complicated since we cannot use the effective potential, but still we can handle them properly by using the ten-Gaussian expansion for e^{-br} and by using the well-known formula[24]

$$\frac{1}{r} = \frac{2}{\sqrt{\pi}} \int_0^1 \exp\left[-r^2 \left[\frac{v^2}{1-v^2} \right] \right] \frac{dv}{(1-v^2)^{3/2}} \tag{31}$$

we obtain the following matrix elements:

(a) $\langle W_{\mathbf{R}} \psi_2 | v(1,2) | \psi_2 W_{\mathbf{R}'} \rangle$

$$= \begin{cases} \langle \psi_2 | W_{\mathbf{R}'} \rangle \langle W_{\mathbf{R}} | \psi_2 \rangle \dfrac{2}{|\mathbf{R}-\mathbf{R}'|} & \text{if } \mathbf{R} \neq \mathbf{R}', \\ 2b \, |\langle \psi_2 | W_{\mathbf{R}} \rangle|^2 \;\; \text{if } \mathbf{R}=\mathbf{R}' \;, \end{cases}$$

(b) $\langle \beta_\nu^z \psi_2^z | v(1,2) | \psi_2^z \beta_\nu^z \rangle$

$$\begin{aligned} &= \int d^3r_1 d^3r_2 [\beta_\nu^z(\mathbf{r}_1)]^* [\psi_2^z(\mathbf{r}_2)]^* v(\mathbf{r}_1,\mathbf{r}_2) \\ &\quad \times \beta_\nu^z(\mathbf{r}_2) \psi_2^z(\mathbf{r}_1) \end{aligned}$$

(c) $\langle W_s \psi_2^z | v(1,2) | \psi_2^z \beta_\nu^z \rangle = \langle W_s | \psi_2^z \rangle \int d^3r \beta_\nu^z(\mathbf{r}) [\psi_2^z(\mathbf{r})]^*$

$$\times \frac{2}{|\mathbf{r}-\mathbf{R}_s|} \;.$$

In all Coulomb-interaction matrix elements, we neglect the very small contributions due to intervalley scatterings. In fact, we found that the correction arising by including intervalley contributions to these matrix elements is much less than 1%.

The two-hole wave function is given by

$$\psi_{hh}^{\mu\mu'}(\mathbf{r}_3,\mathbf{r}_4) = \frac{1}{\sqrt{2}} [\psi_h^{(\mu)}(\mathbf{r}_3) \bar{\psi}_h^{(\mu')}(\mathbf{r}_4) + \bar{\psi}_h^{(\mu')}(\mathbf{r}_3) \psi_h^{(\mu)}(\mathbf{r}_4)] \;, \tag{32}$$

where $\psi_h^{(\mu)}$ and $\bar{\psi}_h^{(\mu')}$ are single-particle hole wave functions as defined in (16), with new coefficients $C_\nu^{(s)}$ $(\bar{C}_\nu^{(s)})$ and $C_\nu^{(d)}$ $(\bar{C}_\nu^{(d)})$ to be determined by solving (24) for the four-particle system self-consistently. In the absence of *j-j* coupling between the two holes, all 16 possible two-hole wave functions given by (32) will yield the same ground-state energy. The *j-j* coupling which we shall include later will give rise to a fine structure splitting between the energies of two-hole wave functions having definite total spin angular momentum, $J_{hh}=0$ and 2.

The expectation value of the two-hole Hamiltonian is given by

$$\begin{aligned} \langle \psi_{hh} | H_{hh} | \psi_{hh} \rangle &= \langle \psi_{hh} | H_0(3) + H_0(4) | \psi_{hh} \rangle \\ &\quad + \langle \psi_{hh} | v(3,4) | \psi_{hh} \rangle \;. \end{aligned} \tag{33}$$

The first term on the right-hand side of (33) contains single-particle matrix elements for the hole, which are evaluated in the same way as discussed in Sec. II. The Coulomb-interaction term $\langle \psi_{hh} | v(3,4) | \psi_{hh} \rangle$ contains the following matrix elements, $\langle ss | v | ss \rangle$, $\langle dd | v | dd \rangle$, $\langle sd | v | sd \rangle$, and $\langle ss | v | dd \rangle$. Here, s and d represent the s-like and d-like effective-mass basis orbitals $S_\nu^{(\mu)}$ and $D_\nu^{(\mu)}$, respectively, as defined in (16b). Explicit expressions of these matrix elements are given in Appendix C.

The remaining part of the total Hamiltonian H is the electron-hole Coulomb interaction H_{eh}, namely

$$H_{eh} = v(1,3) + v(1,4) + v(2,3) + v(2,4) \;.$$

The first two parts $v(1,3)$ and $v(1,4)$ are dealt with just as in the case of the one-exciton problem in Sec. II. For the last two parts $v(2,3)$ and $v(2,4)$ we use the effective potential defined earlier in this section.[29] The dielectric constant has been taken to be q independent, since including this effect only augments the accuracy of the calculation by a few percent.

The self-consistent procedure for determining the expansion coefficients D_σ in (26) and $C_\nu^{(i)}$ $(\bar{C}_\nu^{(i)})$, $i=s,d$, in (32) is briefly described below. First, the two-electron state ψ_{ee} is solved in the absence of the two holes with a trial value b for describing the outer electron. Then the two-hole state ψ_{hh} is obtained by solving

$$\langle \psi_{hh} | \tilde{H} | \psi_{hh} \rangle = E \langle \psi_{hh} | \psi_{hh} \rangle \;, \tag{34}$$

where

$$\tilde{H} \equiv \langle \psi_{ee} | H | \psi_{ee} \rangle \;.$$

To solve (34) for ψ_{hh}, we first "freeze" the single-particle wave function $\psi_h^{(\mu)}(\mathbf{r}_3)$ in (32). This input wave function is obtained by solving the three-particle (two electrons and one hole) Schrödinger equation self-consistently. Because the effect of the second electron can be incorporated via the effective potential as given in (29), the three-particle problem is no more complicated than the single-exciton problem dealt with in Sec. II. Given this input wave function $\psi_h^{(\mu)}(\mathbf{r}_3)$, Eq. (34) can be cast into a generalized eigenvalue problem with the eigenvectors being $(\overline{C}_v^{(s)},\overline{C}_v^{(d)})$. Once $\overline{\psi}_h^{(\mu')}(\mathbf{r}_4)$ is found, the previous procedure is iterated by exchanging the role of $\psi_h^{(\mu)}$ and $\overline{\psi}_h^{(\mu')}$, until self-consistency is reached. The trial value b for describing the second electron wave function is then varied to minimize the total energy of the whole four-particle system.

The total energy E as a function of the variational parameter b is plotted in Fig. 5. We find that the optimized value of b is 0.49 bohr^{-1} and the minimized total energy is $E \simeq -44.6$ meV. The radial charge densities of the two holes and the outer electron are shown in Fig. 6.

In the total Hamiltonian H written at the beginning of this section two terms have been omitted, namely, the terms accounting for the j-j coupling of the two spin-$\frac{3}{2}$ holes and the electron-hole exchange term. The electron-hole exchange term, E_{ex}, was found to be $2\langle 0 | V_r | 0\rangle$ for all low-lying states with zero two-electron total spin. A derivation is given in Appendix B. The contribution of the j-j coupling is calculated with a method similar to the one used by Pan.[30] We write the single-hole wave functions $\psi_h^{(\mu)}(\mathbf{r})$ in (32) as

$$\psi_h^{(\mu)}(\mathbf{r})=f(\mathbf{r})\phi_{v0}^{(\mu)}(\mathbf{r})Y_{00}(\Omega)+g(\mathbf{r})\sum_m C(\mu,m)Y_{2m}(\Omega)\phi_{v0}^{(\mu-m)}(\mathbf{r})\ , \qquad (35)$$

where

$$f(\mathbf{r})=\sum_\nu C_\nu^{(s)}e^{-\alpha_\nu r^2}$$

and

$$g(\mathbf{r})=r^2\sum_\nu C_\nu^{(d)}e^{-\alpha_\nu r^2}\ ,$$

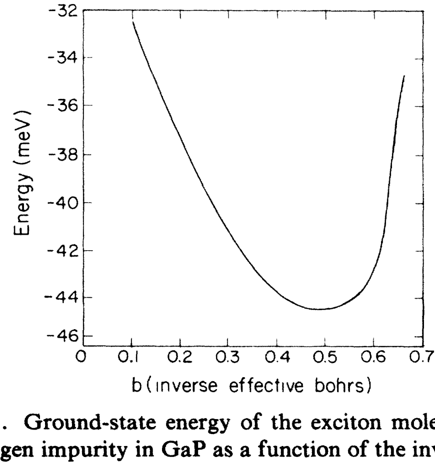

FIG. 5. Ground-state energy of the exciton molecule bound to a nitrogen impurity in GaP as a function of the inverse radius of the second electron.

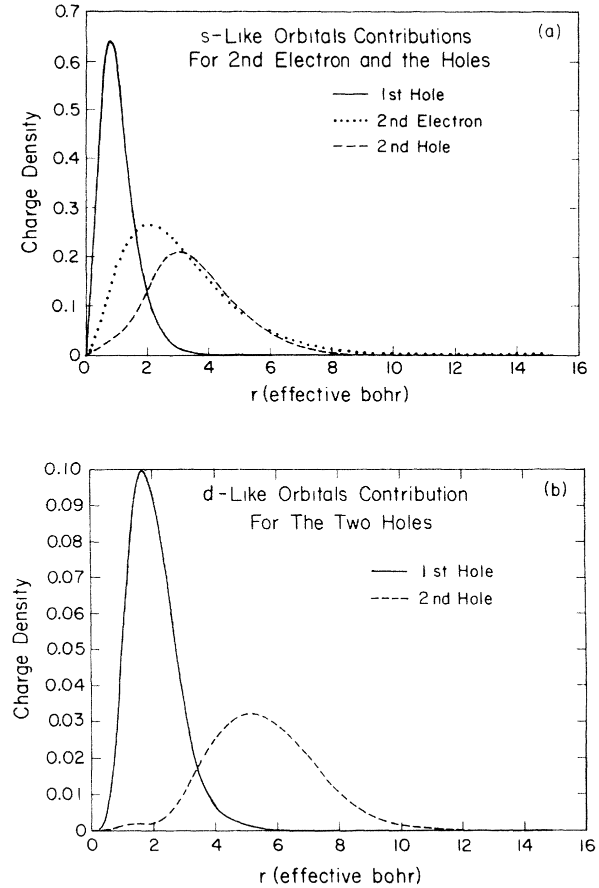

FIG. 6. Radial charge densities of the two holes and the outer electron.

$\overline{\psi}_h^{(\mu')}(\mathbf{r})$ in (32) is similarly written in terms of $\overline{f}(\mathbf{r})$ and $\overline{g}(\mathbf{r})$. Then following Pan's calculation,[30] we obtain the j-j splitting (the energy separation between the $J=0$ and $J=2$ states) as

$$\Delta E_{j\text{-}j}=\tfrac{64}{25}\int_0^\infty\int_0^\infty f(r_3)g(r_3)\frac{r_<^2}{r_>^3}\overline{f}(r_4)\overline{g}(r_4)\times r_3^2r_4^2dr_3dr_4+\cdots\ , \qquad (36)$$

where $\cdots$ represents the exchange term, $r_>=\max(r_3,r_4)$, and $r_<=\min(r_3,r_4)$. The exchange term in (36) is in the same form as the direct term except that g and $\overline{g}$ are switched. Details of the evaluation of the integrals in (36) are discussed in Appendix D.

Using the wave function ψ_{hh} obtained by solving the four-particle system self-consistently, we found a value $\Delta E_{j\text{-}j}=0.20$ meV and $E_{\text{ex}}\simeq 0.38$ meV. Experimentally, the ground state of the exciton molecule bound to a nitrogen trap is observed to split into three states labeled Γ_1, Γ_3, and Γ_5. The Γ_1 state is associated with $J=0$. The Γ_3 and Γ_5 states are associated with $J=2$. The splitting between the Γ_3 and Γ_5 states is 0.19 meV, which is due to the crystal field. In our calculation, the crystal-field effect is not included. Thus, our predicted value for $\Delta E_{j\text{-}j}$ should be compared with the energy separation between the Γ_1 state and the center of gravity of the Γ_3 and Γ_5 states, which is observed to be 0.17 meV.[12] Hence, our theoretical prediction of 0.20 meV is in reasonably good agreement with the experimental data.

IV. CONCLUDING REMARKS

We have studied the electronic structure of an exciton molecule bound to a nitrogen trap in GaP. We found that this system has an electronic structure similar to that of an acceptor—bound-exciton (A^0X), because the inner electron is very localized at the nitrogen center, forming a negatively charged center analogous to an acceptor impurity. The *j-j* coupling mechanism of A^0X in GaP was not well understood, because of the complexity caused by the comparable magnitudes of the electron-hole exchange interaction, the *j-j* splitting, and the crystal-field splitting. It turns out that the *j-j* coupling of the exciton molecule bound to the nitrogen center in GaP is less ambiguous, because of the pairing of the two electrons in the low-lying states which leads to the same electron-hole exchange interaction for both $J_{hh}=0$ and $J_{hh}=2$ states. Furthermore, because the holes are more weakly bound to the charged nitrogen center than to an acceptor impurity as in A^0X, the effective-mass approximation used to describe the hole wave functions is better justified in the present calculation than in previous calculations for A^0X. It is thus not surprising that we are able to obtain a *j-j* splitting based on the effective-mass approximation in reasonable agreement with the experimental data.

ACKNOWLEDGMENTS

We acknowledge fruitful discussions with T. N. Morgan and M. Jaros. This work was supported by the U.S. Office of Naval Research (ONR) under Contract No. N00014-81-K-0430 and the University of Illinois Materials Research Laboratory under Contract No. NSF-DMR-83-16891.

APPENDIX A: DERIVATION FOR THE *A-B* SPLITTING

The exchange energy for the exciton with total angular momentum J is given by

$$E_{\text{exch}}(J)=\langle \Phi_J(\mathbf{r}_1,\mathbf{r}_2)\,|\,V_{\text{ex}}\,|\,\Phi_J(\mathbf{r}_2,\mathbf{r}_1)\rangle \;, \tag{A1}$$

where $\Phi_J(\mathbf{r}_1,\mathbf{r}_2)$ is the total wave function for the exciton with $\mathbf{r}_1$ and $\mathbf{r}_2$ describing the positions of the electron and hole, respectively. The exchange potential V_{ex} is given by[31]

$$V_{\text{ex}}=V_{\text{spin}}V_r(r_{12}) \;, \tag{A2}$$

where $V_r(r)=e^2/\epsilon(r)r$ and

$$\begin{aligned}V_{\text{spin}}=&\,|\uparrow_h\downarrow_e\rangle\langle\uparrow_h\downarrow_e| + |\downarrow_h\uparrow_e\rangle\langle\downarrow_h\uparrow_e|\\ &-|\uparrow_h\downarrow_e\rangle\langle\downarrow_h\uparrow_e| - |\downarrow_h\uparrow_e\rangle\langle\uparrow_h\downarrow_e| \;.\end{aligned} \tag{A3}$$

The ket $|\uparrow_h\downarrow_e\rangle$, for example, denotes a state with the electron having $m_s=+\frac{1}{2}$ and the hole having $m_s=-\frac{1}{2}$.

The exciton is composed of a spin-$\frac{3}{2}$ hole and a spin-$\frac{1}{2}$ electron. Coupling angular momenta, we see the total angular momentum may be either $J=2$ or $J=1$. Consider first the case of $J=1, m_J=0$. (The $m_J=0$ states are degenerate with the $m_J=0$ state by symmetry.) From the Clebsch-Gordan coefficient tables we see that

$$\Psi_{J=1}\equiv|1,0\rangle=\sqrt{1/2}\,|\tfrac{1}{2},\downarrow_e\rangle-\sqrt{1/2}\,|-\tfrac{1}{2},\uparrow_e\rangle \;, \tag{A4}$$

where the latter kets represent $|\,m_j$ for valence-band hole, m_s for electron$\rangle$. Again from the Clebsch-Gordan coefficient tables, we see that in order to couple the $L=1$ valence band with the spin-$\frac{1}{2}$ hole to form a $j=\frac{3}{2}$ hole,

$$\begin{aligned}|\tfrac{1}{2},\downarrow_e\rangle&=\sqrt{1/3}\,|1,\downarrow_h,\downarrow_e\rangle+\sqrt{2/3}\,|0,\uparrow_h,\downarrow_e\rangle \;,\\ |-\tfrac{1}{2},\uparrow_e\rangle&=\sqrt{2/3}\,|0,\downarrow_h,\uparrow_e\rangle+\sqrt{1/3}\,|-1,\uparrow_h,\uparrow_e\rangle \;.\end{aligned} \tag{A5}$$

In this notation the ket is defined by $|\,m_l$ for the valence band, m_s for the hole, m_s for the electron$\rangle$.

Substituting Eqs. (A4) and (A5) into Eq. (A1), we obtain

$$\begin{aligned}\langle\Psi_{J=1}|V_{\text{ex}}|\Psi_{J=1}\rangle=&\,\tfrac{1}{6}\langle 1|V_r|1\rangle\langle\downarrow_h\downarrow_e|V_{\text{spin}}|\downarrow_h\downarrow_e\rangle+\tfrac{1}{3}\langle 0|V_r|0\rangle\langle\uparrow_h\downarrow_e|V_{\text{spin}}|\uparrow_h\downarrow_e\rangle\\ &-\tfrac{1}{3}\langle 0|V_r|0\rangle\langle\uparrow_h\downarrow_e|V_{\text{spin}}|\downarrow_h\uparrow_e\rangle-\tfrac{1}{3}\langle 0|V_r|0\rangle\langle\downarrow_h\uparrow_e|V_{\text{spin}}|\uparrow_h\downarrow_e\rangle\\ &+\tfrac{1}{3}\langle 0|V_r|0\rangle\langle\downarrow_h\uparrow_e|V_{\text{spin}}|\downarrow_h\uparrow_e\rangle+\tfrac{1}{6}\langle -1|V_r|-1\rangle\langle\uparrow_h\uparrow_e|V_{\text{spin}}|\downarrow_h\downarrow_e\rangle\\ =&\,\tfrac{4}{3}\langle 0|V_r|0\rangle \;.\end{aligned} \tag{A6}$$

Similarly for $J=2$ we have

$$\begin{aligned}\Phi_{J=2}=|2,0\rangle=&\,\sqrt{1/2}\,|1,\downarrow_h,\downarrow_e\rangle+\sqrt{1/3}\,|0,\uparrow_h,\downarrow_e\rangle\\ &+\sqrt{1/3}\,|0,\downarrow_h,\uparrow_e\rangle+\sqrt{1/6}\,|-1,\uparrow_h,\uparrow_e\rangle \;.\end{aligned} \tag{A7}$$

Substituting Eq. (A7) into Eq. (A1) yields

$$\langle\Phi_{J=2}|V_{\text{ex}}|\Phi_{J=2}\rangle=0 \;.$$

Therefore, the exchange splitting ΔE is obtained by

$$\begin{aligned}\Delta E&=E_{\text{exch}}(J=1)-E_{\text{exch}}(J=2)\\ &=\tfrac{4}{3}\langle 0|V_r|0\rangle \;.\end{aligned} \tag{A8}$$

Here,

$$|0\rangle=\sum_{k_e}\widetilde{F}_e(\mathbf{k}_e)\,|\phi_{c\mathbf{k}}\sum_{k_h}\widetilde{F}_h(\mathbf{k}_h)\,|\phi_{v\mathbf{k}_h}\rangle \;, \tag{A9}$$

where $|\phi_{c\mathbf{k}}\rangle$ and $|\phi_{v\mathbf{k}}\rangle$ are the Bloch functions for the conduction band and the $m_l=0$ valence band at $\mathbf{k}$. $\widetilde{F}_e(\mathbf{k}_e)$ and $\widetilde{F}_h(\mathbf{k}_h)$ are the electron and hole envelope functions in $\mathbf{k}$ space. Since the hole envelope function, $\widetilde{F}_h(\mathbf{k}_h)$ is sharply peaked at $\mathbf{k}_h=0$, we may approximate $|\phi_{v\mathbf{k}_h}\rangle$ in Eq. (A9) by $|\phi_{v0}\rangle$. Therefore

$$|0\rangle\simeq\sum_{k}\widetilde{F}_e(\mathbf{k})\,|\phi_{c\mathbf{k}}\phi_{v0}\rangle\sum_{\mathbf{k}_h}\widetilde{F}_h(\mathbf{k}_h) \;.$$

Then,

$$\langle 0|V_r|0\rangle \simeq |F_h(0)|^2 \left\langle \sum_{k_1} \tilde{F}(\mathbf{k}_1)\phi_{c\mathbf{k}_1}\phi_{v0} \middle| V_r \middle| \sum_{k_2} \tilde{F}_e(\mathbf{k}_2)\phi_{v0}\phi_{c\mathbf{k}_2} \right\rangle$$

$$= |F_h(0)|^2 \sum_{\mathbf{k}} |\tilde{F}_e(\mathbf{k})|^2 \langle \phi_{c\mathbf{k}}\phi_{v0}|V_r|\phi_{v0}\phi_{c\mathbf{k}}\rangle \;, \tag{A10}$$

where $F_h(0)$ is the hole envelope function in real space evaluated at $\mathbf{r}=0$. We finally have $\Delta E = \frac{4}{3}|F_h(0)|^2 J_{\text{ex}}$, where

$$J_{\text{ex}} \equiv \sum_{\mathbf{k}} |\tilde{F}_e(\mathbf{k})|^2 \langle \phi_{c\mathbf{k}}\phi_{v0}|V_r|\phi_{v0}\phi_{c\mathbf{k}}\rangle \;.$$

APPENDIX B: ELECTRON-HOLE EXCHANGE INTERACTION IN THE EXCITON MOLECULE

In this appendix, we show that the electron-hole exchange interactions are the same for the low-lying exciton molecule states in which the two-electron total spin (J_{ee}) is zero. The two-hole total spin angular momenta (J_{hh}) of these states are 0 and 2. The product states $|J_{ee}=0\rangle|J_{hh},m_J\rangle$ are eigenstates of the four-particle total spin angular momentum $\mathbf{J}_t=\mathbf{J}_{ee}+\mathbf{J}_{hh}$; thus, the electron-hole exchange interaction will not mix these states. Hence, we only have to evaluate the diagonal terms for $J_{hh}=0$ and 2.

By symmetry, the states of different m_J but the same J_{hh} should have the same electron-hole exchange interaction. Therefore, we only have to consider the states $|J_{hh}=0,m_J=0\rangle$ and $|J_{hh}=2,m_J=0\rangle$. We write

$$\phi_{J_{hh}} \equiv |J_{ee}=0\rangle|J_{hh};0\rangle = \frac{1}{\sqrt{2}}(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2)\sum_{m_j} C(J_{hh},0;m_j,-m_j)\,|\tfrac{3}{2},m_j\rangle\,|\tfrac{3}{2},-m_j\rangle \;, \tag{B1}$$

where $m_j=-\frac{3}{2},-\frac{1}{2},\frac{1}{2},\frac{3}{2}$ and $C(J_{hh},0;m_j,-m_j)$ are Clebsch-Gordan coefficients for the coupling $\frac{3}{2}+\frac{3}{2}=J_{hh}$. $\uparrow_1$ ($\downarrow_1$) and $\uparrow_2$ ($\downarrow_2$) denote the electron spinors for particles 1 and 2. We now evaluate the expectation values of $V_{\text{ex}}(1,3)$ in these states. We have

$$\begin{aligned}\langle \Phi_{J_{hh}}|V_{\text{ex}}(1,3)|\Phi_{J_{hh}}\rangle &= \tfrac{1}{2}\sum_{m_j,m_j'} (\langle \uparrow_1 m_j|V_{\text{ex}}|\uparrow_1 m_j\rangle + \langle \downarrow_1 m_j|V_{\text{ex}}|\uparrow_1 m_j\rangle)\delta_{m_j m_j'} \\ &\qquad \times C(J_{hh},0;m_j,-m_j)C(J_{hh},0;m_j',-m_j') \\ &= \tfrac{1}{8}\sum_{m_j} (\langle \uparrow_1 m_j|V_{\text{ex}}|\uparrow_1 m_j\rangle + \langle \downarrow_1 m_j|V_{\text{ex}}|\downarrow_1 m_j\rangle) \;,\end{aligned} \tag{B2}$$

where $\langle \uparrow_1 m_j|V_{\text{ex}}|\uparrow_1 m_j\rangle$ is the electron-hole exchange interaction in the product state $|\uparrow_1\rangle|\frac{3}{2},m_j\rangle$. In deriving (B2), we have used the fact that

$$|C(J_{hh},0;m_j,-m_j)|^2=\tfrac{1}{4}$$

for all m_j and $J_{hh}=0,2$.

Using the expansion

$$|\tfrac{3}{2},m_j\rangle = \sum_{m_l,m_s} C(\tfrac{3}{2},m_j;m_l m_s)\,|1,m_l\rangle\,|\tfrac{1}{2},m_s\rangle$$

and the definition of $V_{\text{ex}}(1,3)$ in (A2) and (A3), we obtain

$$\langle \bar{m}_s m_j|V_{\text{ex}}|\bar{m}_s m_j\rangle = G(\bar{m}_s,m_j)\langle 0|V_r|0\rangle \;, \tag{B3}$$

where $\bar{m}_s=\frac{1}{2}$ and $-\frac{1}{2}$ for $\uparrow_1$ and $\downarrow_1$, $\langle 0|V_r|0\rangle$ is defined in the same manner as in (A10), and the coefficients $G(\bar{m}_s,m_j)$ are given in Table II. In deriving (B3), we have used the relation $\langle 1|V_r|1\rangle=\langle -1|V_r|-1\rangle=\langle 0|V_r|0\rangle$. Substituting (B3) into (B2), we obtain

$$\langle \Phi_{J_{hh}}|V_{\text{ex}}(1,3)|\Phi_{J_{hh}}\rangle = \tfrac{1}{2}\langle 0|V_r|0\rangle$$

for both $J_{hh}=0$ and 2. By symmetry, one can show that

$$\begin{aligned}\langle \Phi_{J_{hh}}|V_{\text{ex}}(2,3)|\Phi_{J_{hh}}\rangle &= \langle \Phi_{J_{hh}}|V_{\text{ex}}(2,4)|\Phi_{J_{hh}}\rangle \\ &= \langle \Phi_{J_{hh}}|V_{\text{ex}}(1,4)|\Phi_{J_{hh}}\rangle \\ &= \langle \Phi_{J_{hh}}|V_{\text{ex}}(1,3)|\Phi_{J_{hh}}\rangle \;,\end{aligned}$$

and the total electron-hole exchange interaction in the low-lying states (with $J_{ee}=0$) is $2\langle 0|V_r|0\rangle$.

TABLE II. Coefficients $G(\bar{m}_s,m_j)$ for the electron-hole exchange interaction in low-lying exciton molecule states with $J_{ee}=0$.

	m_j			
$\bar{m}_s$	$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$
$-\frac{1}{2}$	1	$\frac{2}{3}$	$\frac{1}{3}$	0
$\frac{1}{2}$	0	$\frac{1}{3}$	$\frac{2}{3}$	1

APPENDIX C: COULOMB INTERACTION BETWEEN TWO HOLES

The hole-hole interaction matrix elements for Slater-type orbitals has previously been discussed in Ref. 20 (Appendix A). It was shown that the dominating contributions come from the diagonal terms ($\mu_1=\mu_1'$ and $\mu_2=\mu_2'$). These terms include $\langle ss|v|ss\rangle$, $\langle dd|v|dd\rangle$, $\langle sd|v|sd\rangle$ (or $\langle ds|v|ds\rangle$), and $\langle ss|v|dd\rangle$, where s and d denote the s-like and d-like effective-mass basis orbitals $S_\nu^{(\mu)}$ and $D_\nu^{(\mu)}$, respectively. For the first three terms ($l_1=l_1'$ and $l_2=l_2'$) it can be shown that[20]

$$\begin{aligned}\langle l_1 l_2 \,|\, v \,|\, l_1 l_2 \rangle &= \int r_1^{2l_1} e^{-(\alpha_1+\alpha_1')r_1^2} V(\mathbf{r}_1-\mathbf{r}_2) r_2^{2l_2} e^{-(\alpha_2+\alpha_2')r_2^2} d^3r_1 d^3r_2 \\ &= \int \phi_{2l_1}(\alpha_1+\alpha_1';q)\widetilde{V}(q)\phi_{2l_2}(\alpha_2+\alpha_2';q)\frac{q^2dq}{(2\pi^2)} ,\end{aligned} \tag{C1}$$

where

$$\phi_l(\alpha;q) \equiv \int r^l e^{-\alpha r^2} e^{i\mathbf{q}\cdot\mathbf{r}} d^3r$$

$$= \left[\frac{\pi}{\alpha}\right]^{3/2} \alpha^{-l} e^{-q^2/4\alpha} \times \begin{cases} 1, & l=0 \\ \dfrac{3}{2}-\dfrac{q^2}{4\alpha}, & l=2 \\ \dfrac{15}{4}-5\left[\dfrac{q^2}{4\alpha}\right]+\left[\dfrac{q^2}{4\alpha}\right]^2, & l=4 \end{cases} \tag{C2}$$

and

$$\widetilde{v}(q) \equiv \sum_{\nu=1}^{4} S_\nu \left[\frac{8\pi}{q^2+\sigma_\nu^2}\right] .$$

Note that if the q dependence in the dielectric screening is ignored, the integral in (C1) can be performed analytically. For $\langle ss \,|\, v \,|\, dd \rangle$, we have

$$\begin{aligned}\langle ss \,|\, v \,|\, dd \rangle &= \tfrac{1}{5} \int r_1^2 e^{-(\alpha_1+\alpha_1')r_1^2} V(\mathbf{r}_1-\mathbf{r}_2) r_2^2 e^{-(\alpha_2+\alpha_2')r_2^2} Y_{00}(\Omega_1)Y_{20}(\Omega_1)Y_{00}(\Omega_2)Y_{20}(\Omega_2) d^3r_1 d^3r_2 \\ &= \frac{1}{20\pi} \int \bar{\phi}_2(\alpha_1\alpha_1';q)\bar{\phi}_2(\alpha_2+\alpha_2';q)\widetilde{V}(q)\frac{q^2dq}{(2\pi)^3} ,\end{aligned} \tag{C3}$$

where

$$\bar{\phi}_2(\alpha;q) \equiv (q^2/4\alpha^2)\left[\frac{\pi}{\alpha}\right]^{3/2} e^{-q^2/4\alpha} .$$

APPENDIX D: *j-j* COUPLING OF TWO SPIN-$\frac{3}{2}$ HOLES

From (36) and using the expansion

$$\frac{1}{r_{12}} = 4\pi \sum_{l,m} \frac{1}{2l+1} \frac{r_<^l}{r_>^{l+1}} Y_{lm}^*(\Omega_1) Y_{lm}(\Omega_2) , \tag{D1}$$

we can write

$$\Delta E_{j-j} = \frac{1}{5\pi^3} \sum_{\substack{\nu_1,\nu_2 \\ \nu_1',\nu_2'}} C_{\nu_1}^{(s)} C_{\nu_1'}^{(d)} \bar{C}_{\nu_2}^{(s)} \bar{C}_{\nu_2'}^{(d)} I(\nu_1\nu_2\nu_1'\nu_2') + \cdots \tag{D2}$$

($\cdots$ represents the exchange term), where

$$I(\nu_1\nu_2\nu_1'\nu_2') \equiv \int d^3r_1 d^3r_2 r_1^2 e^{-(\alpha_{\nu_1}+\alpha_{\nu_2})r_1^2} \frac{1}{r_{12}} \times r_2^2 e^{-(\alpha_{\nu_1'}+\alpha_{\nu_2'})r_2^2} Y_{20}(\Omega_1) Y_{20}(\Omega_2) . \tag{D3}$$

The integral can be easily done if we use the transformation

$$\frac{1}{r_{12}} = \int \frac{d^3q}{(2\pi)^3} \frac{4\pi}{q^2} e^{i\mathbf{q}\cdot\mathbf{r}_{12}}$$

and

$$r^2 Y_{20}(\Omega) = \sqrt{5/16\pi}(3z^2-r^2) .$$

We arrive at the result

$$I(\nu_1\nu_2\nu_1'\nu_2') = \frac{3\pi^{5/2}}{2}[\alpha\alpha'(\alpha+\alpha')]^{-5/2} , \tag{D4}$$

where $\alpha = \alpha_{\nu_1}+\alpha_{\nu_2}$ and $\alpha' \equiv \alpha_{\nu_1'}+\alpha_{\nu_2'}$. The exchange term in (D2) is similarly obtained.

---

[1] D. G. Thomas and J. J. Hopfield, Phys. Rev. 150, 680 (1966).
[2] J. J. Hopfield, D. G. Thomas, and R. T. Lynch, Phys. Rev. Lett. 17, 312 (1966).
[3] R. A. Faulkner, Phys. Rev. 175, 991 (1968).
[4] M. Jaros, Adv. Phys. 29, 409 (1980).
[5] J. W. Allen, J. Phys. C 4, 1936 (1971).
[6] S. F. Ross and M. Jaros, J. Phys. C 7, L235 (1974).
[7] E. Cohen and M. Sturge, Phys. Rev. B 15, 1039 (1976).
[8] W. Y. Hsu, J. E. Dow, D. J. Wolford, and B. G. Streetmen, Phys. Rev. B 16, 1597 (1977).

[9] E. Cohen, M. D. Sturge, N. O. Lipari, M. Altarelli, and A. Baldereschi, Phys. Rev. Lett. **35**, 1591 (1975).

[10] R. G. Humphreys, U. Rossler, and M. Cardona, Phys. Rev. B **18**, 5590 (1978).

[11] W. T. Masselink and Y. C. Chang, Phys. Rev. Lett. **51**, 5091 (1983).

[12] J. L. Merz, R. A. Faulkner, and P. J. Dean, Phys. Rev. **188**, 1228 (1969).

[13] A. M. White, P. J. Dean, and B. Day, J. Phys. C **7**, 1450 (1974).

[14] M. Schmidt, T. N. Morgan, and W. Schairen, Phys. Rev. B **11**, 5002 (1975).

[15] K. R. Elliott, G. C. Osbourn, D. L. Smith, and T. C. McGill, Phys. Rev. B **17**, 1808 (1978).

[16] E. U. Conndon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, New York, 1963).

[17] M. L. Cohen and T. K. Bergstresser, Phys. Rev. **141**, 789 (1966).

[18] K. Suzuki and N. Miura, Solid State Commun. **18**, 233 (1976).

[19] Taking $m_l^* = 8m_t^*$ allows one to obtain the binding energy of a free exciton in GaP in good agreement with the experimental value.

[20] Y. C. Chang and T. C. McGill, Phys. Rev. B **25**, 3963 (1982).

[21] A. Baldereschi and N. O. Lipari, Phys. Rev. B **8**, 2697 (1973).

[22] J. Bernhold and S. T. Pantelides, Phys. Rev. B **15**, 4935 (1977).

[23] A. T. Vink, R. L. A. Van Der Heyden, and J. A. W. Van Der Does DeBye, J. Lumin. **8**, 105 (1973).

[24] R. K. W. Vinsome and D. Richardson, J. Phys. C **4**, 2650 (1971).

[25] The mass ratio is taken to be the ratio of the donor acceptor binding energies calculated within the EMA. The donor and acceptor binding energies are taken to be 60 meV (Ref. 26) and 56 meV (Ref. 22), respectively.

[26] Y. C. Chang and T. C. McGill, Solid State Commun. **33**, 1035 (1980).

[27] H. Gerstlinger and W. Weller, Phys. Status Solidi B **128**, 313 (1985).

[28] Y. C. Chang, in *Proceedings of the Seventeenth International Conference on the Physics of Semiconductors (San Francisco, 1984)*, edited by J. O. Chadi and W. A. Harrison (Springer, New York, 1984), p. 601.

[29] S. Huzinaga, J. Chem. Phys. **42**, 1293 (1965).

[30] D. S. Pan, Solid State Commun. **37**, 375 (1981).

[31] J. J. Forney and A. Quattropani, Il Nuovo Cimento **22**, 153 (1974).