# Theory of the Exciton Bound to an Isoelectronic Trap in GaP

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A theoretical calculation for the electronic structure of an exciton bound to a nitrogen trap in GaP is presented. For the first time, the band-structure effect for both the electron and hole and their mutual Coulomb interaction are included simultaneously. It is found that the bare electron is bound by only 0.6 meV instead of 8 meV as usually quoted. Furthermore, this calculation predicts the $A$-$B$ splitting and the oscillator strength of the bound-exciton luminescence in good agreement with the experimental data.

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Luminescence and absorption spectra indicate, as 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 a hole is bound in the Coulomb field resulting from the electron.[2-4] Because of the degeneracy of the valence-band structure, the lowest-lying configuration of the bound-exciton system consists of two closely spaced energy levels associated with different total angular momenta. The difference between these energies is experimentally seen as the $A$-$B$ line splitting. GaP:N is often studied as an example of the isoelectronic impurity problem. Because of the complexity of the binding mechanism, accurate first-principles calculations of the electron and exciton binding energies are not available.[5] Because of the lack of a detailed calculation of the binding energy of the whole system, the electron binding energy is frequently taken to be 8 meV.[3,4,6-9]

In this paper we study the binding of excitons to isoelectronically substituted nitrogen in GaP. For the first time, the Coulomb interaction between the electron and hole is correctly included. By comparing the total binding energy with the experimental data, we can extract the correct value for the electron binding energy of an isoelectronic trap. We show that although the electron is bound in GaP:N, it is much shallower than supposed. We further show that it is possible for an exciton to bind to an impurity which will not bind either an electron or a hole individually. Finally, we present the first calculation of the $A$-$B$ splitting in GaP:N and compare it with experimental data.

The Hamiltonian for a bound exciton is

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

where $H_0(1)$ and $H_0(2)$ are the individual Hamiltonians for the electron and hole in the absence of each other and of 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 two-particle wave function of the system is assumed separable, i.e., $\Psi(\vec{r}_1,\vec{r}_2)=\psi_e(\vec{r}_1)\times\psi_h(\vec{r}_2)$, so that each particle's wave function may be considered individually. A simpler calculation[10] (spherical effective-mass approximation) shows that the correlation correction which results from not separating the wave function is only about 6%.

We describe the electron in a combined basis as follows: Wannier states localized in real space near the impurity and effective-mass-approximation–type (EMA) states localized in $k$ space near the $X$ minima. This choice of basis for the electron allows a correct description of both the short-range behavior and the tail of the electron and is flexible enough to allow the electron to assume almost whatever shape minimizes the energy. Each Wannier basis state $|W_s\rangle$ is chosen as a symmetrized linear combination of conduction-band Wannier orbitals associated with a given ($s$th) shell ($s=0$ being on the impurity site). Our basis includes ten such $A_1$-symmetry Wannier states and fifteen EMA states. This basis is large enough that including more states does not appreciably lower the energies. The possible mixing with the valence bands and higher conduction bands is neglected. This was justified in a previous calculation[4] and is fairly obvious given the shallow binding of the electron.

The EMA basis states, $\beta_{ij}$, are chosen as linear combinations of conduction-band Bloch states localized at the three equivalent $X$ valleys, with envelope function in each valley described by an anisotropic Gaussian function; e.g., for the $z$ valley

$$\beta_{ij}{}^z(\vec{k})=\exp[-(k_x{}^2+k_y{}^2)/4\alpha_i-(k_z-k_0)^2/4\alpha_j],$$

where $k_0$ is the distance in $k$ space between $\Gamma$ and $X$. We use different exponents $\alpha_i$ and $\alpha_j$ for the longitudinal and transverse directions to take into account the anisotropy of the conduction band at the $X$ points. We further restrict $\alpha_j \geq \alpha_i$ because the longitudinal effective mass is greater than the transverse effective mass.

The interactions between the Wannier basis states $|W_s\rangle$ due to $H_0(1)$ are given by

$$\langle W_s|H_0(1)|W_{s'}\rangle = \sum_{\vec{k}} E_c(\vec{k})\tilde{W}_s(\vec{k})\tilde{W}_{s'}(\vec{k}), \quad (2)$$

where $\tilde{W}_s(\vec{k}) = \langle c,\vec{k}|W_s\rangle$ and $E_c(\vec{k})$ is the dispersion function for the conduction band. We describe $E_c(\vec{k})$ by the tight-binding expression

$$E_c(\vec{k}) = \sum_{\vec{R}} V(R) e^{i\vec{k}\cdot\vec{R}}, \quad (3)$$

where $\vec{R}$ runs over the lattice vectors and $V(R)$ are adjustable parameters which only depend on the distance $R$. The summation is truncated at the tenth shell. The parameters $V(R)$ are determined by fitting (3) to the dispersion curve obtained by an empirical pseudopotential method.[11] However, the transverse effective mass at the $X$ point of the band structure is fitted to the experimental value.[12] With use of the expression (3), the matrix elements in (2) can be calculated analytically. To calculate the matrix elements of $H_0(1)$ between the EMA states, we take

$$E_c(\vec{k}) = \frac{\hbar^2}{2m_t^*}\left[k_x^2 + k_y^2 + \frac{m_t^*}{m_l^*}(k_z - k_0)^2\right]$$

for the $z$ valley where $m_l^*$, the longitudinal effective mass, is taken to be $8m_t^*$.[13] (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 EMA and Wannier states is given by

$$\langle\beta_{ij}|H_0(1)|W_s\rangle = \sqrt{3}\sum_{\vec{k}} E_c(\vec{k})\beta_{ij}^z(\vec{k})\tilde{W}_s(\vec{k})$$

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

Since the impurity potential is very localized in real space, we take $V(1) = V_0|W_0\rangle\langle W_0| + V_1|W_1\rangle \times\langle W_1|$.[5] 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 $V_0$ 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] predicts that when included properly, $V_1 \sim 0.01V_0$.)

We describe the hole envelope wave function entirely in the EMA basis as a linear combination of nine $s$-like and nine $d$-like Gaussian orbitals. The $d$-like orbitals are included here to take into account the warping of the valence band. The matrix elements of $H_0(2)$ between the hole basis states are calculated following the method of Baldereschi and Lipari.[14]

The Coulomb interaction is

$$v(1,2) = \int \frac{d^3q}{(2m)^3}\frac{4\pi e^2}{q^2}\frac{e^{i\vec{q}\cdot\vec{r}_{12}}}{\epsilon(q)} \equiv \frac{e^2}{r_{12}\epsilon(r_{12})};$$

the dielectric screening, $1/\epsilon(r)$, is expressed as a sum of four Gaussian functions least-squares fitted to the empirical expression given by Bernholc and Pantelides.[15] In evaluating the Coulomb interaction involving Wannier states, we treat the electron in a Wannier orbital centered at $\vec{R}$ as a point charge there. This is a very good approximation, considering the localized character of a Wannier state compared with the charge distribution in the hole.

We solve the secular equation

$$\langle\psi_e\psi_h|H|\psi_e\psi_h\rangle = E\langle\psi_e\psi_h|\psi_e\psi_h\rangle \quad (4)$$

iteratively using the Rayleigh-Ritz variational method in our basis. 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. 1. When $V_0 = -1.145$ eV, the calculated system en-

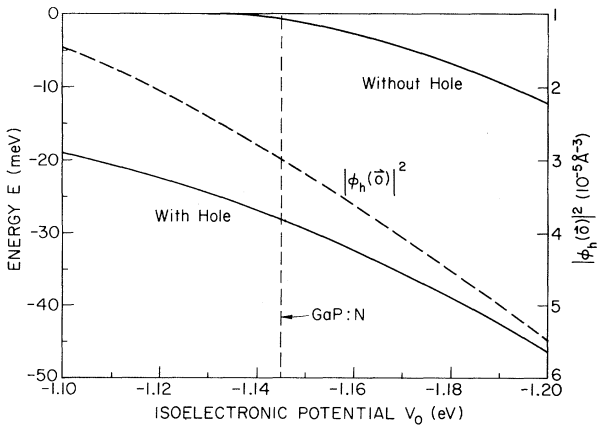


FIG. 1. Ground state energies of an electron bound to an isoelectronic trap in GaP with and without the presence of a hole plotted as functions of potential $V_0$. Also plotted as a function of $V_0$ is the hole wave function squared at $\vec{r} = 0$, $|\varphi_h(0)|^2$ (dashed). The vertical dashed line indicates the position of the observed photoluminescence data for GaP:N.

ergy 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 frequently quoted 8 meV, but is also much more reasonable. These calculations also show that for some values of $V_0$ which do not bind the electron, the exciton is still bound more deeply than the 20 meV of a free exciton. Conceivably there are physical systems (perhaps GaAs) in which this situation is realized.

Figure 2 depicts the electron's envelope wave function in $k$ space [denoted $\tilde{\varphi}_e(\vec{k})$], with and without the hole along the [100] direction. We see that in both cases the electron is very localized near $X$. The $X$-valley peaks contain approximately 80% and 95% of the total electronic charge for the cases with and without a hole, respectively. 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 nearest-neighbor distance from the impurity site. Without the hole, about 4% lies within the nearest-neighbor distance.

The values of the electron wave function at $\Gamma$ with and without the hole are 3.5 and 2.2 $\text{Å}^{3/2}$, respectively. The resulting $\Gamma/X$ ratios can be fitted with a simple Koster-Slater (KS) calculation using binding energies of 1 meV for the bare electron and 8 meV for the actual electron. We see, then, that our calculation involving only the electron is consistent with a KS calculation. The fact

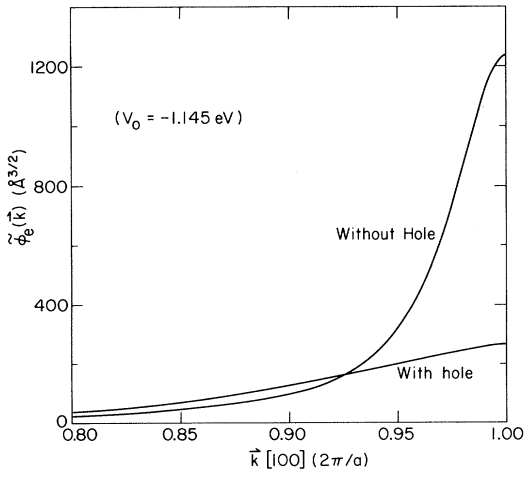


FIG. 2. The electron envelope wave function along the [100] direction in $k$ space of GaP:N with and without the hole.

that the electronic charge density of the electron when treated correctly with the hole is essentially that of a bare electron bound by 8 meV under the KS method and with the hole ignored is probably only a coincidence.

We find that the self-consistent hole envelope wave function is approximately 80% $s$ like and 20% $d$ like and the wave function squared evaluated at the origin is $|\varphi_n(0)|^2 = 3.0\times 10^{-5}\ \text{Å}^{-3}$. For comparison, the corresponding values for the free exciton and the acceptor are $1.0\times 10^{-5}$ and $60\times 10^{-5}\ \text{Å}^{-3}$, respectively.

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 relatively small size of the splitting (0.8 meV)[16] compared to the binding energy (28 meV), the exchange interaction energy may be calculated by means of perturbation theory.

Let $\Delta E$ be the $A$-$B$ splitting due to the exchange-interaction energy difference between the $J=1$ and $J=2$ bound exciton states. We find[10] $\Delta E = \frac{4}{3} J_{\text{ex}} |\varphi_h(0)|^2$, where

$$J_{\text{ex}} \simeq \sum_{\vec{k}} |\tilde{\varphi}_e(\vec{k})|^2 \langle \psi_{c\vec{k}}\, \psi_{v\vec{0}} | v | \psi_{v\vec{0}}\, \psi_{c\vec{k}} \rangle$$

and $\varphi_h(0)$ is the hole envelope function evaluated at $\vec{r}=0$. $|\psi_{c\vec{k}}\rangle$ denotes the conduction band Bloch state with wave vector $\vec{k}$ and $|\psi_{v\vec{0}}\rangle$ the valence band Bloch state at $\vec{k}=0$. Both $|\psi_{c\vec{k}}\rangle$ and $|\psi_{v\vec{0}}\rangle$ are expanded in 137 plane waves by means of the empirical pseudopotential method.[11] To simplify the integration over $\vec{k}$ we assume that 80% of the electron envelope wave function is localized at $X$ and 20% is uniformly spread in $k$ space. Using the pseudopotential of Cohen and Bergstresser, we find that $J_{\text{ex}} = 1.8\times 10^4$ meV Å$^3$. Thus $\Delta E = 0.72$ meV. This is in very good agreement with the measured value of 0.8 meV. For comparison, in a free exciton we find $\Delta E = 0.2$ meV.

The oscillator strength is easy to calculate since we already know the electron and hole wave functions. The oscillator strength is given by[17]

$$f = \frac{2}{\hbar\omega m_e} \frac{\Gamma}{g} \sum_{\alpha=1}^{g} |\langle G|\, \vec{P}\, |\psi_\alpha\rangle|^2, \tag{5}$$

where $|\psi_\alpha\rangle$, $\alpha = 1, \ldots, g$, denote the degenerate initial states and $|G\rangle$ is the ground state of the crystal. We derive $f \cong \frac{4}{3}(E_p/\hbar\omega)|\psi_h(0)|^2|\tilde{\varphi}_e(0)|^2$

for the dipole-allowed $A$ ($J=1$) state where $E_p = 22.2$ eV,[18] $\tilde{\varphi}_e(0)$ is the electron envelope wave function evaluated at $\vec{k}=0$, and $\varphi_h(0)$ is the hole envelope wave function evaluated at $\vec{r}=0$. The factor 4 comes from the summation on the spin-angle coupling coefficients in (5). We find $f = 0.005$. This agrees reasonably well with the experimental result of 0.01. (The total oscillator strength for the $A$ line is 0.1; the zero-phonon contribution was measured to be 10% of the total.[7])

To summarize, we have investigated the binding of an exciton to N in GaP including the band-structure effect for both the electron and the hole. Using a realistic Hamiltonian and flexible bases, we find that when the exciton is bound by 28 meV, the bare electron binds by 0.6 meV. This value is substantially smaller than the previously assumed value of 8 meV. By treating the hole with the electron, we were able to calculate the $A$-$B$ splitting of the bound-exciton recombination radiation. Our calculated energy difference of 0.72 meV compares well with the measured 0.8 meV. Finally, our calculated oscillator strength agrees reasonably well with the experimental value. The ability to correctly calculate both the exchange interaction energy and the oscillator strength further confirms the validity of the method employed here and therefore substantiates the entire calculation.

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