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# Acceptorlike bound excitons in semiconductors

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An effective-mass equation for the hole binding energy of an acceptorlike bound exciton in semiconductors is developed. The motion of the electron is represented by an effective charge which modifies the Coulomb interaction. An expression for the oscillator strength of the bound exciton is given in terms of the wave function of the bound-exciton state. The theory is applied to the GaP:N system, which gives hole binding energies for excitons bound to nitrogen pairs in good agreement with experiment, and predicts that the electron binding energy for an isolated-nitrogen-bound exciton is about 6 meV.

## I. INTRODUCTION

The hole binding energies of the acceptorlike bound excitons in semiconductor GaP are all found to be close to but smaller than the acceptor binding energy in the effective mass (EM) approximation, $E_A = 45.3$ meV.[1] For deep nitrogen pair bound excitons ($i \leq 5$),[2] the nearest-neighbor (Zn,O) or (Cd,O) complex bound exciton,[3] and the neutral oxygen bound exciton,[4] hole binding energies are around 40 meV. There are two possible mechanisms which might explain the deviation of the hole binding energies of these bound excitons from the acceptor binding energy. One is the core correction due to the repulsive core to the hole. The other is the charge distribution of the bound electron. According to Faulkner's estimate,[5] the core correction should not be important for a short-range potential. Thus, the most distinguishing difference for the bound exciton from an ideal EM acceptor is that the bound electron is not localized at the impurity site but moves around the impurity. In this work, we are going to concentrate on the effect of the electron charge distribution on the hole binding energy. It is to be expected that the deeper, and therefore more localized, the electron bound state, the larger the hole binding energy will be. The hole binding energy will converge to $E_A$ for a "real" deep impurity center.

The acceptorlike bound exciton is treated in a way similar to the standard treatment of the free exciton in a semiconductor.[6] A Schrödinger equation is developed for the hole in which everything is the same as for an EM acceptor except for the potential, in which the simple Coulomb interaction is modified by a factor $d(r)$, the normalized effective charge. Also, an expression for the oscillator strength of the bound exciton is obtained, which is more general than the one usually used.

The calculation for the hole binding energies is applied to nitrogen pair bound excitons in GaP. Quite good agreement is found for these pairs $NN_i$, $i \leq 7$ for which experimental values are available. The observed binding energy of the exciton bound to isolated nitrogen is only consistent with the calculation if the electron is bound by about 6 meV. This disagrees with previous theoretical calculations[7-9] in which the electron binding energies were found to be near zero.

## II. THE HOLE BINDING ENERGY OF AN ACCEPTORLIKE BOUND EXCITON

In the Hartree-Fock one-electron approximation, the ground state of a semiconductor can be described by a Slater determinant

$$\Psi_0 = \mathcal{A}\{\Psi_{v\mathbf{k}1}(\mathbf{r}_1)\alpha(1)\Psi_{v\mathbf{k}1}(\mathbf{r}_2)\beta(2)\cdots\Psi_{v\mathbf{k}h,sh}(\mathbf{r}_m)\cdots\Psi_{v\mathbf{k}N}(\mathbf{r}_{2N})\beta(2N)\}\ , \tag{1}$$

where $\mathcal{A}$ indicates the antisymmetrization operator, $\Psi_{v\mathbf{k}}$ is a one-electron wave function in the valence band, and $\alpha$ and $\beta$ indicate the two spin eigenfunctions. We can also use $\Psi_0$ as the ground state for the impurity problem, as long as we assume that in the ground state the impurity atom is essentially the same as the host atom so that the coupling between valence-band state and conduction-band state due to the impurity potential is very weak. This is the case for isoelectronic impurities in semiconductors.

The bound-exciton state is an excited state of the system. The basic assumption made here is that of the so-called HTL (Hopfield-Thomas-Lynch) model.[10] In this model, for the case of the acceptorlike bound exciton, firstly the electron is bound to a short-range attractive impurity potential, giving a negative center, like an ionized acceptor, and then a hole is bound to the negative center via the long-range Coulomb attraction, forming a bound exciton. The bare electron bound state can be written as

$$\Psi_{ie}=\sum_{n,\mathbf{k}} a_{n\mathbf{k}}\Psi_{n\mathbf{k}} , \tag{2}$$

where $\Psi_{n\mathbf{k}}$ are the conduction-band states. $\Psi_{ie}$ gives a true description for the ionized state of the bound exciton, equivalent to the conduction-band state in the free-exciton problem.

A trial function for the excited states of the system (i.e., bound-exciton states) is given by

$$\Phi_{ie,se;v\mathbf{k}h,sh}=\mathcal{A}\{\Psi_{v\mathbf{k}1}(\mathbf{r}_1)\alpha(1)\Psi_{v\mathbf{k}1}(\mathbf{r}_2)\beta(2)\cdots\Psi_{ie,se}(\mathbf{r}_m)\cdots\Psi_{v\mathbf{k}N}(\mathbf{r}_{2N})\beta(2N)\} \tag{3}$$

in which the impurity state $\Psi_{ie,se}$ replaces the valence-band state $\Psi_{v\mathbf{k}h,sh}$ in $\Psi_0$. The state $\Phi_{ie,se;v\mathbf{k}h,sh}$ has one electron in the electron bound state $\Psi_{ie,se}$ and one hole in the valence-band state $\Psi_{v\mathbf{k}h,sh}$.

If the total Hamiltonian of the system is taken to be spin independent, it is convenient to consider trial states $\Phi^{(M)}_{ie,v\mathbf{k}h}$ with a definite spin multiplicity. They are

$$(1/\sqrt{2})(\Phi_{ie,\alpha;v\mathbf{k}h,\alpha}+\Phi_{ie,\beta;v\mathbf{k}h,\beta}) \tag{4}$$

for singlet states (total spin=0), and

$$\begin{aligned}&\Phi_{ie,\alpha;v\mathbf{k}h,\beta} ,\\ &(1/\sqrt{2})(\Phi_{ie,\alpha;v\mathbf{k}h,\beta}-\Phi_{ie,\beta;v\mathbf{k}h,\beta}) ,\\ &\Phi_{ie,\beta;v\mathbf{k}h,\alpha} ,\end{aligned} \tag{5}$$

for triplet states (total spin is equal to 1).

Now $\Phi^{(M)}_{ie,v\mathbf{k}h}$ are used as trial states with definite spin multiplicity. A bound-exciton state of multiplicity $M$ can be expanded in the form

$$\Psi^{(M)}_{\text{ex}}=\sum_{\mathbf{k},h} A(\mathbf{k}_h)\Phi^{(M)}_{ie,v\mathbf{k}h} . \tag{6}$$

The total Hamiltonian of the system is written as

$$H_e=\sum_i H_i+\tfrac{1}{2}\sum_{i,j} e^2/|\mathbf{r}_i-\mathbf{r}_j| \tag{7}$$

with

$$H_i=-\hbar^2/2m\nabla^2-\sum_l V(\mathbf{R}_l-\mathbf{r}_i) .$$

$H_i$ includes the impurity potential.

The eigenvalue equation is

$$H_e\Psi^{(M)}_{\text{ex}}=E_{\text{ex}}\Psi^{(M)}_{\text{ex}} . \tag{8}$$

Multiply by $\Phi^{(M)}_{ie,v\mathbf{k}h}$ and integrate both sides, and use the following results:

$$\begin{aligned}&\langle\Phi_{ie,v\mathbf{k}h}|\Psi^{(M)}_{\text{ex}}\rangle=A(\mathbf{k}_h) ,\\ &\langle\Phi^{(M)}_{ie,v\mathbf{k}h}|H_e|\Phi^{(M)}_{ie,v\mathbf{k}h'}\rangle=[E_{ie}-E_v(\mathbf{k}_h)]\delta_{\mathbf{k}h,\mathbf{k}h'}\\ &\qquad-\langle\Psi_{ie}(\mathbf{r}_1)\Psi_{v\mathbf{k}h'}(\mathbf{r}_2)|(e^2/r_{12})|\Psi_{ie}(\mathbf{r}_1)\Psi_{v\mathbf{k}h}(\mathbf{r}_2)\rangle\ \text{(Coulomb term)}\\ &\qquad+2\delta M\langle\Psi_{ie}(\mathbf{r}_1)\Psi_{v\mathbf{k}h'}(\mathbf{r}_2)|(e^2/r_{12)|}\Psi_{v\mathbf{k}h}(\mathbf{r}_1)\Psi_{ie}(\mathbf{r}_2)\rangle\ \text{(exchange term)} .\end{aligned}$$

Here, $\delta M=0$ for single states and $\delta M=1$ for triplet states. $\langle\Psi_0|H_e|\Psi_0\rangle$ is taken as the zero of energy. Also, it is assumed that the contribution from the valence band to the bound electron wave function $\Psi_{ie}$ is negligible. This would not be a good approximation if one was attempting to calculate the electron binding energy $E_e$ from first principles, but it should not introduce significant error here, where $E_e$ is treated as an empirical parameter. Thus, Eq. (8) becomes

$$[E_{ie}-E_v(\mathbf{k}_h)-E_{\text{ex}}]A(\mathbf{k}_h)+\sum_{\mathbf{k}h'} A(\mathbf{k}'_h)[-\langle\Psi_{ie}\Psi_{v\mathbf{k}h'}|(e^2/r_{12})|\Psi_{ie}\Psi_{v\mathbf{k}h}\rangle+2\delta M\langle\Psi_{ie}\Psi_{v\mathbf{k}h'}|(e^2/r_{12})|\Psi_{v\mathbf{k}h}\Psi_{ie}\rangle]=0 . \tag{9}$$

First, let us examine the Coulomb term:

$$-\langle\Psi_{ie}\Psi_{v\mathbf{k}h'}|(e^2/r_{12})|\Psi_{ie}\Psi_{v\mathbf{k}h}\rangle=-\sum_{\mathbf{k}e,\mathbf{k}e'} a^*_{\mathbf{k}e}a_{\mathbf{k}e'}\langle\Psi_{\mathbf{k}e}\Psi_{v\mathbf{k}h'}|(e^2/r_{12})|\Psi_{ke'}\Psi_{v\mathbf{k}h}\rangle .$$

The only nonzero matrix elements in the sum on the right-hand side have $\mathbf{k}_e-\mathbf{k}_h=\mathbf{k}'_e-\mathbf{k}'_h$, in which the approximation $u^*_{c\mathbf{k}e}u_{c\mathbf{k}e}u^*_{v\mathbf{k}h'}u_{v\mathbf{k}h}\approx 1/V^2$ can be used. Here $u_{n\mathbf{k}}$ are the periodic part of the Bloch functions and $V$ is the volume of the crystal. The range within the Brillouin zone where the states $\Phi^{(M)}_{ie,v\mathbf{k}h}$ have appreciable coefficients in the expansion of the bound-exciton state is assumed to be small enough to justify this approximation. This approximation is usually used for free-exciton states, acceptor, and donor states to get an envelope-function equation. Since the hole binding energies of acceptorlike bound excitons are usually smaller than those of acceptor states, although larger than the free-exciton binding energy, this approximation is as reasonable for the bound-exciton problem as it is for the related acceptor problem. Then the Coulomb terms are

$$-\sum_{\mathbf{k}h'} A(\mathbf{k}h')\langle \Psi_{ie}\Psi_{v\mathbf{k}h'}|(e^2/r_{12})|\Psi_{ie}\Psi_{v\mathbf{k}h}\rangle = -\sum_{\mathbf{k}'} A(\mathbf{k}-\mathbf{k}')f(\mathbf{k}')s(\mathbf{k}') \ ,$$

where $f(\mathbf{k})$ is the Fourier transform of $e^2/r_{12}$, $f(\mathbf{k})=4\pi e^2/k^2$, and $s(\mathbf{k})$ reflects the charge distribution due to the delocalization of the bound electron:

$$s(\mathbf{k})=\sum_{\mathbf{k}e} a^*_{\mathbf{k}e}a_{\mathbf{k}e-\mathbf{k}} \ . \tag{10}$$

Now let us turn to the exchange term:

$$\begin{aligned}2\delta M\langle \Psi_{ie}\Psi_{v\mathbf{k}h'}|(e^2/r_{12})|\Psi_{v\mathbf{k}h}\Psi_{ie}\rangle &= 2\delta M \sum_{\mathbf{k}e,\mathbf{k}e'} a^*_{\mathbf{k}e}a_{\mathbf{k}e'}\langle \Psi_{c\mathbf{k}e}\Psi_{v\mathbf{k}h'}|(e^2/r_{12})|\Psi_{v\mathbf{k}h}\Psi_{c\mathbf{k}e'}\rangle \\ &\cong 2\delta M \sum_{\mathbf{k}e} a^*_{\mathbf{k}e}a_{\mathbf{k}e-\mathbf{k}h+\mathbf{k}h'}J_{cv} \ ,\end{aligned}$$

where $J_{cv}$ are matrix elements for exchange interaction,

$$J_{cv}=2\langle \Psi_{c\mathbf{k}e}\Psi_{v\mathbf{k}h'}|(e^2/r_{12})|\Psi_{v\mathbf{k}h}\Psi_{c\mathbf{k}e-\mathbf{k}h+\mathbf{k}h'}\rangle \ .$$

$J_{cv}$ can be approximated by a constant $J_{cv}=2\langle \Psi_{c0}\Psi_{v0}|(e^2/r_{12})|\Psi_{v0}\Psi_{c0}\rangle$ since we expect that $A(\mathbf{k})$ is appreciable only in a small range of $\mathbf{k}$. Finally, we have the eigenvalue equation in $\mathbf{k}$ space:

$$\begin{aligned}&[E_{ie}-E_v(\mathbf{k})-E_{\text{ex}}]A(\mathbf{k}) \\ &\quad +\sum_{\mathbf{k}'} A(\mathbf{k}-\mathbf{k}')s(\mathbf{k}')[-f(\mathbf{k}')+\delta M J_{cv}]=0 \ .\end{aligned} \tag{11}$$

Now we have to transform this equation to real space. Multiplying by $\exp(i\mathbf{k}\cdot\mathbf{r})$ to both sides and summing over $\mathbf{k}$, we will get the equation for the envelope function $F(\mathbf{r})$. $F(\mathbf{r})$ is defined as

$$F(\mathbf{r})=(1/\sqrt{V})\sum_{\mathbf{k}} A(\mathbf{k})\exp(i\mathbf{k}\cdot\mathbf{r}) \tag{12}$$

and the equation is

$$[E_v(-i\nabla)+d(\mathbf{r})e^2/\epsilon r-\delta M\, J_{cv}\rho(\mathbf{r})]F(\mathbf{r})=E_hF(\mathbf{r}) \ . \tag{13}$$

This is an effective-mass equation, in which $E_h=E_{ie}-E_{\text{ex}}$ is the hole binding energy of an acceptorlike bound exciton, and $E_v(-i\nabla)$ is the kinetic-energy operator for the valence-band states. The most important difference from the equation for an ideal EM acceptor is a factor $d(\mathbf{r})$, which is the result of delocalization of the bound electron:

$$d(\mathbf{r})=\frac{\sum_{\mathbf{k}} \exp(i\mathbf{k}\cdot\mathbf{r})f(\mathbf{k})s(\mathbf{k})}{\sum_{\mathbf{k}} \exp(i\mathbf{k}\cdot\mathbf{r})f(\mathbf{k})} \ . \tag{14}$$

$d(r)$ can be understood as a normalized effective charge experienced by the hole at position $\mathbf{r}$. The denominator is just the Coulomb potential; in the numerator each Fourier component of the Coulomb potential is weighted by a factor $s(\mathbf{k})$. For the singlet state, there is an additional short-range, repulsive potential $J_{cv}\rho(\mathbf{r})$ for the hole, here

$$\rho(\mathbf{r})=\sum_{\mathbf{k}} \exp(i\mathbf{k}\cdot\mathbf{r})s(\mathbf{k}) \ , \tag{15}$$

which is approximately the probability distribution of the bound electron, because in the effective-mass approximation $s(\mathbf{k})$ is the Fourier transform of the $|\Psi_{ie}|^2$. This repulsive potential will contribute to the core correction. It is assumed that the contribution from this potential is negligible for an extended hole bound state, because the exchange splitting is smaller than 1 meV for nitrogen bound excitons.[11] Thus, the equation becomes the same for singlet and triplet bound-exciton states, the only difference from the equation for the EM acceptor being the reduction factor $d(r)$. Under the parabolic band approximation, it becomes

$$[(\hbar^2/2m_h^*)\nabla^2+d(\mathbf{r})e^2/\epsilon r]F(\mathbf{r})=E_hF(\mathbf{r}) \ . \tag{16}$$

It is obvious that $E_h$ will always be smaller than $E_A$ (the acceptor binding energy in the EM approximation) due to the charge distribution effect. The direct reason for this effect is that $s(\mathbf{k})<1$ except for $\mathbf{k}=0$. $s(\mathbf{k})<1$ means that the contribution from each $\mathbf{k}$ component to the electron bound state is not uniform. This is always true for real semiconductors, since the conduction band is never flat. Only when the impurity potential is very localized (for example, in the sense of the Koster-Slater one-site approximation[5]) and the conduction band is flat as viewed by the impurity state can we say it is a "real" deep impurity. For a weakly bound electron, $E_h$ can be much smaller than $E_A$.

Since we started from the Hartree-Fock approximation, screening is not included in this approximation. But, as in the case of treating free-exciton or acceptor and donor problems, we can add a static dielectric constant $\epsilon$ to the Coulomb interaction in the last step as long as the bound hole is not very localized.

The factor $d(\mathbf{r})$ is determined by the electron bound state. The Koster-Slater one-band one-site approximation[5] is used to get the electron wave function $\Psi_{ie}$. In this approximation, $d(\mathbf{r})$, and thus the hole binding energy, is uniquely determined by the electron binding energy $E_e$. In calculating $s(\mathbf{k})$, the summation over the Brillouin zone has been done by using Kleiman's method,[12] in which the Brillouin is divided to $X$, $L$, and $\Gamma$ valleys. The numerical results for the charge distribution $d(\mathbf{r})$ are shown in Fig. 1 for different electron binding energies. It is clear that when $E_e$ is large, $d(r)$ deviates from 1 only in a small range of $r$; when it is small, $d(r)$ is less than 1 in a large range of $r$. For an ideal acceptor $d(r)$ should equal 1 everywhere.

Equation (16) has been solved variationally for nitrogen bound excitons in GaP. Since the spin-orbit coupling is not taken into account in our derivation, but was included in calculating the acceptor binding energy,[1] to simplify the problem a parabolic valence band is assumed with an equivalent effective mass which gives the correct EM acceptor binding energy $E_A$ when $d(r)=1$. For the ground state, a hydrogenlike 1$S$ function is chosen as the variational function

$$F(r)=(\lambda^3/\pi)^{1/2}\exp(-\lambda r) , \tag{17}$$

where $\lambda$ is the variational parameter. The calculated hole binding energy $E_h$ is shown as a function of $E_e$ in Fig. 2.

In this calculation, pair states are treated as single centers with different electron binding energies, so the interference effect[5] in the bound electron wave function is neglected. If the orbit of the hole is much larger than the pair separation, the single center approximation is reasonable as far as the hole is concerned.

The hole binding energies for deep bound centers $NN_1$ and $NN_2$ are very close to the experimental result of Ref. 2, which suggests that the core correction is not important for nitrogen bound excitons. The deviations for $NN_3$ through $NN_7$ are 3–4 meV, probably because the single center approximation is not good enough for those wider spaced pairs.

For the isolated center, it is expected that the theory should work better since there is no interference effect in this case. It is found that when electron binding energy is 5.8 meV (which corresponds to the potential constant[5] $J=1.799$ eV), the corresponding hole binding energy is 27.2 meV, which gives a total binding energy 33 meV in agreement with the experiment.[13] Figure 3 shows the probability distributions of the electron bound state and the hole in the isolated center.

It can be concluded that the deviation of the hole binding energy from the EM acceptor is to be mostly attributed to the charge distribution of the bound electron, and this model predicts that an electron should bind to isolated $N$ with $E_e \approx 6$ meV. It is important to emphasize that there is no adjustable parameter in this calculation.

## III. OPTICAL TRANSITION RATE OF AN ACCEPTORLIKE BOUND EXCITON

The optical transition rate from a ground $\Psi_0$ to an excited state $\Psi_{\mathrm{ex}}$ is[6]

$$P=(2\pi/\hbar)(eA_0/mc)^2|\langle\Psi_{\mathrm{ex}}|\mathbf{e}\cdot\sum_i \mathbf{p}_i|\Psi_0\rangle|^2 \times\delta(E_{\mathrm{ex}}-E_0-\hbar\omega) . \tag{18}$$

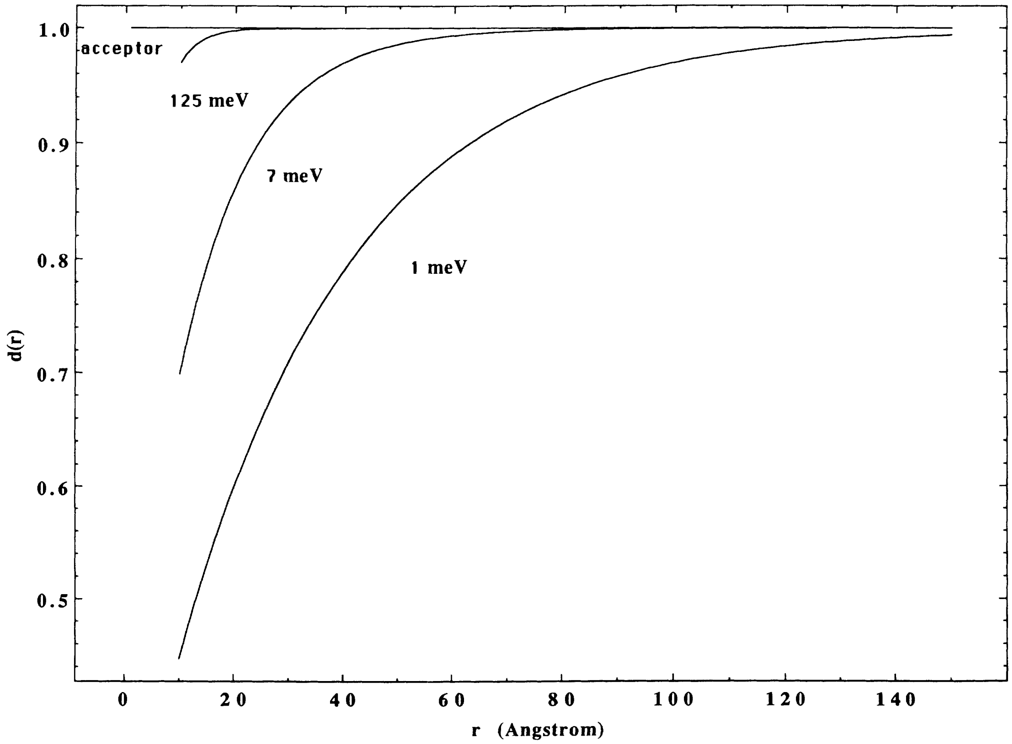

FIG. 1. The effective charge for different electron binding energies.

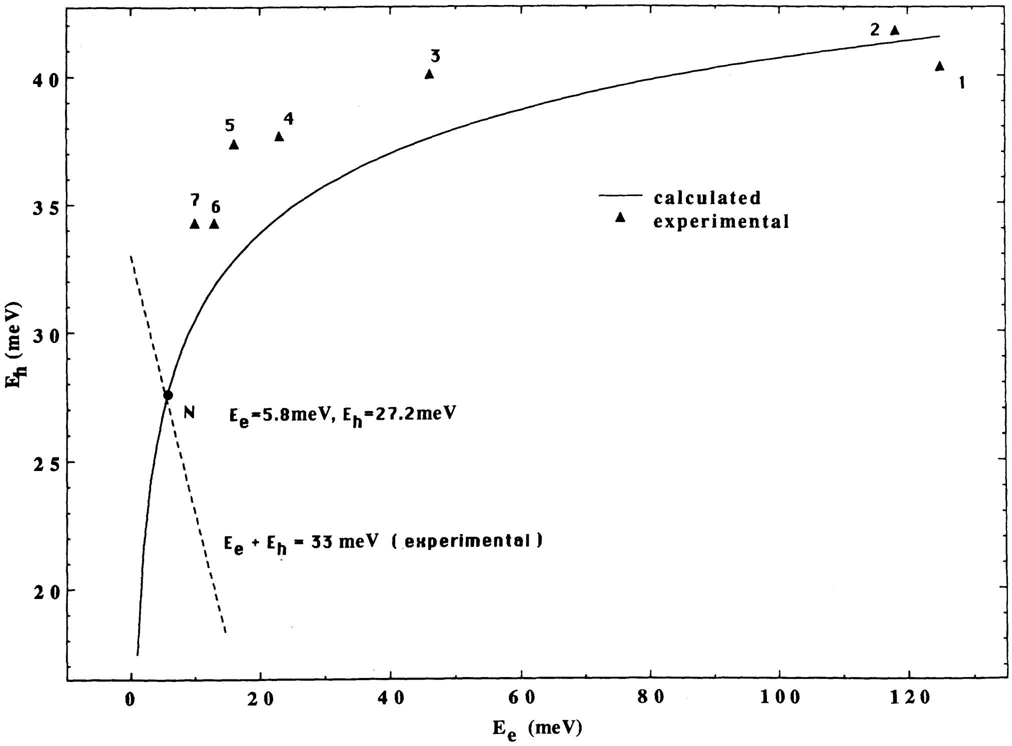

FIG. 2. The hole binding energy $E_h$ as a function of the electron binding energy $E_e$.

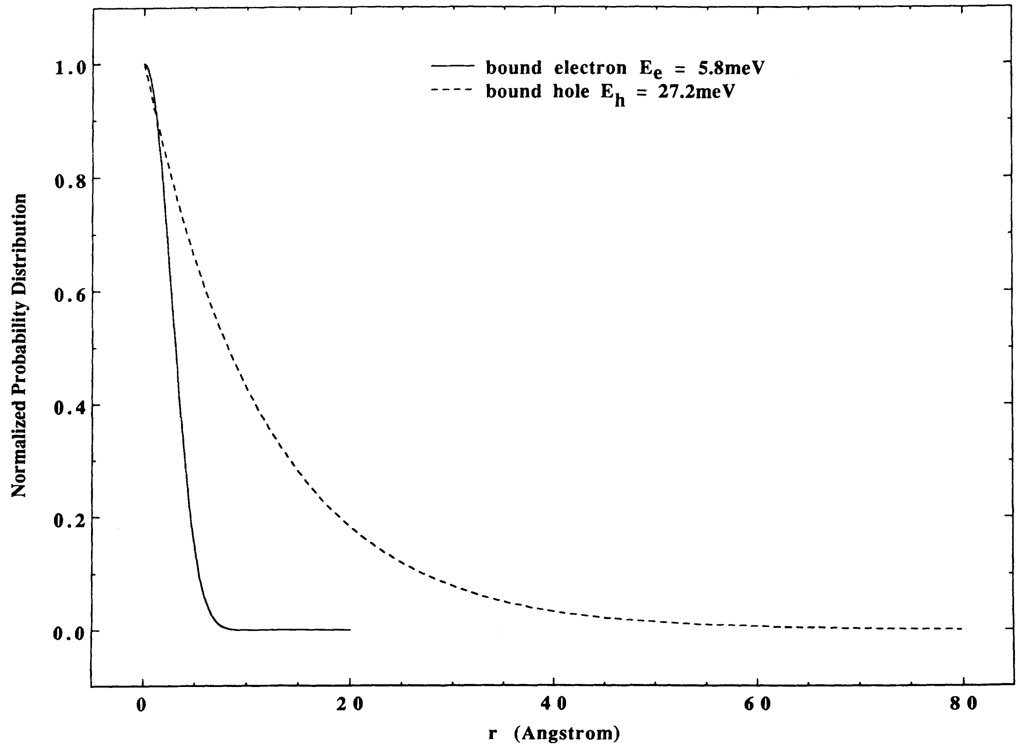

FIG. 3. The probability distributions of the electron and the hole in an isolated-nitrogen-bound exciton.

The matrix element

$$\begin{aligned}\left\langle \Psi_{\text{ex}} \left| \mathbf{e}\cdot \sum_i \mathbf{p}_i \right| \Psi_0 \right\rangle &= \sum_{\mathbf{k}} A^*(\mathbf{k}) \langle \Psi_{ie,v\mathbf{k}} | \mathbf{e}\cdot \sum_i \mathbf{p}_i | \Psi_0 \rangle \\ &= \sum_{\mathbf{k}} A^*(\mathbf{k}) \langle \Psi_{ie} | \mathbf{e}\cdot \mathbf{p}_i | \Psi_{v\mathbf{k}} \rangle \\ &= \sum_{\mathbf{k}} A^*(\mathbf{k}) a_{\mathbf{k}}^* \langle \Psi_{c\mathbf{k}} | \mathbf{e}\cdot \mathbf{p}_i | \Psi_{v\mathbf{k}} \rangle \\ &= \sum_{\mathbf{k}} A^*(\mathbf{k}) a_{\mathbf{k}}^* M_{cv}(\mathbf{k}) \ ,\end{aligned}$$

where $M_{cv}(\mathbf{k}) = \langle \Psi_{c\mathbf{k}} | \mathbf{e}\cdot \mathbf{p}_i | \Psi_{v\mathbf{k}} \rangle$. If the $\mathbf{k}$ dependence of $M_{cv}(\mathbf{k})$ is negligible, then the optical transition rate for an acceptorlike bound exciton is

$$P = (2\pi/\hbar)(eA_0/mc)^2 |M_{cv}|^2 \left| \sum_{\mathbf{k}} A(\mathbf{k}) a_{\mathbf{k}} \right|^2 . \tag{19}$$

The transition rate given by (19) is somewhat more general that normally used in some references:[5,8]

$$P = (2\pi/h)(eA_0/mc)^2 |M_{cv}|^2 V |a_0|^2 |F(0)|^2 . \tag{20}$$

This is only valid when $a_{\mathbf{k}}$ is very smooth in the vicinity of $\Gamma$ point, when one can write

$$\begin{aligned}\left| \sum_{\mathbf{k}} A(\mathbf{k}) a_{\mathbf{k}} \right|^2 &\cong |a_0|^2 \left| \sum_{\mathbf{k}} A(\mathbf{k}) \right|^2 \\ &= V |a_0|^2 |F(0)|^2 .\end{aligned}$$

By introducing a factor $\eta$:

$$\eta = \left| \sum_{\mathbf{k}} A(\mathbf{k}) a_{\mathbf{k}} \right|^2 \Bigg/ \left[ |a_0|^2 \left| \sum_{\mathbf{k}} A(\mathbf{k}) \right|^2 \right] \tag{21}$$

the transition rate can be rewritten as

$$P = (2\pi/h)(eA_0/mc)^2 \eta |M_{cv}|^2 V |a_0|^2 |F(0)|^2 . \tag{22}$$

The oscillator strength for the bound excitons can be defined as[14]

$$f = [2/(3m\hbar\omega)] \left| \left\langle \Psi_{\text{ex}} \left| \sum_i \mathbf{p}_i \right| \Psi_0 \right\rangle \right|^2 , \tag{23}$$

which is given explicitly as

$$f = 3\eta V |a_0|^2 |F(0)|^2 f_{cv}(E_g/\hbar\omega) , \tag{24}$$

where $f_{cv} = E_p/(3E_g)$,[15] $E_g$ is the direct band gap, and $E_p = 2|\langle X|p_x|S\rangle|^2/m$. For GaP, $f_{cv} = 2.58$. For the isolated-nitrogen-bound exciton, $|F(0)|^2 = 2.5\times10^{-5}$ Å$^{-3}$, $V|a_0|^2 = 72$ Å$^3$, and $\eta = 0.56$. The factor 3 in (24) comes from the degeneracy. The, $f = 0.01$. This is an order of magnitude smaller than the experimental value of 0.1 derived from the radiative lifetime[16] or the absorption cross section[17] of the $A$ line. Although the local field effect,[14] neglected in Refs. 16 and 17, could explain part of this discrepancy, the main source is presumably the inaccuracy of the one-band–one-site model used in this calculation. As has been pointed out previously,[7,18] a multiband model should be used for impurity states localized by short-range potentials. The existing multiband calculations[7] give a ratio $|a_0|^2/|a_X|^2 \sim 0.1$ compared to $\sim 1\times10^{-4}$ in the present one-band calculation, so that the predicted $f$ is about two orders of magnitude too large, rather than one order of magnitude too small. The contribution from different bands must clearly be included to give an accurate bound electron wave function close to the impurity, and if the electron binding energy is to be calculated from first principles. Even though $a_k$ in the $\Gamma$ valley are relatively small, they are sensitive to the detail of the potential near the impurity site which determines the behavior of the bound electron wave function near the center. However, far from the impurity, the contribution from the first conduction-band minima (i.e., the $X$ valley) is dominant. The extent of the wave function is a function only of the binding energy (which is an empirical parameter in this calculation). In general, while most properties of the bound-exciton state depend on the detailed behavior of the bound electron wave function, such as the oscillator strength, binding energy, and its pressure coefficient, which depend on $a_k$ in the $\Gamma$ valley or $a_k$ in whole BZ, the hole binding energy and the electron–LO-phonon coupling for polar interaction should not, since they are mainly determined by the long-range behavior of the electron wave function. In this calculation, the correlation inside the exciton is neglected. The correlation correction was calculated to be small for the isolated-nitrogen-bound exciton,[8] and it will be even less important for the pair centers since the wave functions for the electron and the hole will be more different for the nitrogen pair bound excitons.[9]

Finally, a few words about the generality of this theory are in order. First, it has been assumed that there is no contribution to the electron wave function $\Psi_{ie}$ from the highest valence band, in order to satisfy the orthogonality relation between the ground state and the trial states. Since the highest valence band in zinc-blende crystal is $p$-like and the relevant contribution to the bound electron wave function exhibits a node in the region where the impurity potential is strong, there is no significant contribution from this band.[18] Thus, the orthogonality relation holds even in a multiband model, as long as it is safe to say that the hole bound state has contributions only from the highest valence band. In the multiband model, the only change to be made is that $s(\mathbf{k})$ is generalized to

$$s(\mathbf{k}) = \sum_{n,n',\mathbf{k}e} a_{n\mathbf{k}e}^* a_{n'\mathbf{k}e-\mathbf{k}} . \tag{25}$$

Second, the spin-orbit effect can be taken into account from the starting point: the ground state $\Psi_0$. If this is done, Eq. (16) will become a $4\times4$ or $6\times6$ set of second-order differential equations, as in the EM acceptor problem.[1] This would need a lot more work than what has been done here. Third, this theory is generally applicable to acceptorlike bound excitons in semiconductors as long as the approximations made in the first section are satisfied. It is expected that this approach should be good for the systems like ZnTe:O,[19] in which the isoelectronic impurity oxygen binds an exciton in a very similar way to nitrogen in GaP. Also it is possibly applicable to the deep neutral donor bound excitons like oxygen in GaP where the electron is very tightly bound to the neutral oxygen.

## IV. SUMMARY

An effective-mass equation has been set up for the hole binding energy of an acceptorlike bound exciton. The effective potential for describing the motion of the hole is determined by the bound electron wave function. When the attractive potential to the electron is a short-range one, the hole binding energy is determined only by the electron binding energy. An expression for the oscillator strength of the bound exciton is given in terms of the wave function of the bound-exciton state.

The theory has been applied to nitrogen bound excitons in GaP:N. Good agreement is obtained between the theoretical and experimental results for the hole binding energies of excitons bound to nitrogen pairs. The spread in the charge distribution of the bound electron is found to be the main mechanism for the deviation of the hole binding energy from that of the EM acceptor. The electron binding energy of the isolated nitrogen bound exciton is predicted to be about 6 meV.

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[1] A. Baldereschi and N. O. Lipari, Phys. Rev. B **9**, 1525 (1974); A. A. Kopylov and A. N. Pikhtin, Solid State Commun. **26**, 735 (1978).

[2] E. Cohen and M. D. Sturge, Phys. Rev. B **15**, 1039 (1975).

[3] C. H. Henry, P. J. Dean, and J. D. Cuthbert, Phys. Rev. **166**, 754 (1968).

[4] P. J. Dean, in *Proceedings of the International Conference on the Physics of Semiconductors, Montpellier, 1982*, edited by M. Averous [Physica B+C **117-118B**, 140 (1983)].

[5] R. A. Faulkner, Phys. Rev. **175**, 991 (1968).

[6] F. Bassani and G. P. Parravicini, *Electronic States and Optical Transitions in Solids* (Permagon, New York, 1975).

[7] S. Brand and M. Jaros, J. Phys. C **12**, 2789 (1979).

[8] W. T. Masselink and Ya-Chung Chang, Phys. Rev. Lett. **51**, 509 (1983).

[9] C. Benoit a la Guillaume, Physica B+C **117-118B**, 105 (1983).

[10] J. J. Hopfield, D. G. Thomas, and R. T. Lynch, Phys. Rev. Lett. **17**, 312 (1966).

[11] D. G. Thomas and J. J. Hopfield, Phys. Rev. **150**, 680 (1966).

[12] G. G. Kleiman, Phys. Rev. B **19**, 3198 (1979).

[13] M. D. Sturge, A. T. Vink, and F. P. J. Kuijpers, Appl. Phys. Lett. **32**, 49 (1978).

[14] D. L. Dexter, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. 6, p. 361.

[15] P. Lawaetz, Phys. Rev. B **4**, 3460 (1971).

[16] J. D. Cuthbert and D. G. Thomas, Phys. Rev. **154**, 763 (1967).

[17] M. D. Sturge, E. Cohen, and K. F. Rodgers, Phys. Rev. B **15**, 3169 (1977).

[18] M. Jaros and S. Brand, Phys. Rev. B **14**, 4494 (1976); M. Jaros, *Deep Levels in Semiconductors* (Adam Hilger, Ltd., Bristol, 1982), p. 103.

[19] P. J. Dean and D. C. Herbert, in *Bound Excitons in Semiconductors,* edited by K. Cho, Topics in Current Physics: Excitons 14 (Springer-Verlag, Berlin, 1979), p. 55.