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Binding energy of biexcitons and bound excitons in quantum wells

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The binding energy of excitons in a semiconductor (e.g., GaAs) quantum well to each other and to neutral donors is calculated variationally using the six-parameter wave function of Brinkman, Rice, and Bell. The biexciton results for wells of various thicknesses agree closely with some of the data previously assigned to the biexciton. The biexciton binding relative to the exciton binding in the two-dimensional limit is about 3—4 times larger than in the three-dimensional case, but otherwise varies in a similar way with the mass ratio. It is found that the biexciton and bound exciton closely obey Haynes's rule.

I. INTRODUCTION

Quantum wells for holes and electrons are formed in semiconductor heterostructures when a thin layer ($l \sim 20$—500 Å) of semiconductor (e.g., GaAs) is bounded on both sides by a semiconductor of larger gap (e.g., $Ga_{1-x}Al_xAs$). The excitation and luminescence spectra of quantum wells are dominated by peaks due to two-dimensional (2D) excitons, which have much greater oscillator strength and binding energy than the three-dimensional (3D) exciton in the same semiconductor. It has not been possible to determine directly by examination of the spectra the binding energy B_{1S} of the exciton ground state (1S) because the exciton continuum limit is not recognizable as a feature in the spectra. Nevertheless, a reliable indirect determination of B_{1S} as a function of l (42—145 Å) has been reported[1] based on the observation of the exciton excited state (2S) in the excitation spectra of a number of samples, giving a direct determination of the term value B_{1S}-B_{2S}. It was shown[1] that theory can account quantitatively for both the term value and the integrated strength of the main (1S) peak, strongly suggesting that the calculated values of B_{1S} are accurate. A particularly interesting feature of this work is the observation that the heavy-hole (hh) exciton has slightly smaller B_{1S} than the light-hole (1h) exciton, the difference being quantitatively in accord with theory. The theory is simple for quantum wells because the confinement splits the degenerate hole band of the semiconductor allowing separate uncoupled heavy and light holes.

The photoluminescence spectra of quantum wells are dominated by the hh 1S exciton. Recently, a splitting of this peak into two peaks has been observed[2] in a number of samples ($l \sim 50$—1000 Å) in which the dependence of the lower-energy peak on polarization, temperature, and excitation intensity is consistent with the 2D biexciton. If this assignment is correct, the binding energy B of the 2D biexciton is $B \sim 1$ meV, which is surprisingly high compared to the value (0.13 meV) calculated[3,4] for the 3D biexciton in bulk GaAs. As far as we know, no experimental determination has been reported for bulk GaAs, but the experimental value 1.46 ± 0.9 meV has been reported for bulk silicon[5] which is much higher than the calculated value[3,5] (0.24 meV). It must be mentioned, however, that in other cases (CuBr,CuCl,Cu_2O) the calculated[3] and observed values for the 3D biexciton are in good agreement. A preliminary calculation has been presented[2] for the 2D biexciton which predicts values of B about half of those observed (if the assignment is correct), but, nevertheless, of the correct order of magnitude to account for B being much larger in the 2D case than the 3D case. As far as we know, this is the only published theoretical treatment of the 2D biexciton.

Formally, if the conduction and valence bands can be assumed to be nondegenerate, spherical, and parabolic, the 3D biexciton is equivalent to the positronium molecule. The first treatment of this problem to predict a stable molecule was that of Hylleraas and Ore[6] on the basis of the wave function

$$\psi(\beta;r)=\exp[-(s_1+s_2)/2]\cosh[\beta(t_1-t_2)/2]\ ,$$
$$s_1=r_{1a}+r_{1b},\quad s_2=r_{2a}+r_{2b}\ , \tag{1}$$
$$t_1=r_{1a}-r_{1b},\quad t_2=r_{2a}-r_{2b}\ ,$$

where 1,2 denote electrons and a,b denote positrons (or holes). The two-parameter variational wave function $\psi(\beta;kr)$, where k is a scaling parameter, provides probably the simplest description capable of giving a binding energy. This is the function used in the 2D calculation of Ref. 2. It is not possible with this function to calculate the dependence of B on the mass ratio σ of the electron and hole. It was conjectured in Ref. 2 that an increase of about 70% in the calculated B might be expected from the six-parameter variational function employed by Brinkman, Rice, and Bell[3] $\Phi(kr)$ with

$$\Phi(r)=\psi(\beta;r)\chi(\nu,\rho,\lambda,\tau;r_{ab})\ , \tag{2}$$

where

$$\chi(\nu,\rho,\lambda,\tau;v)=v^{\nu}\exp(-\rho v)+\lambda\exp(-\tau v)\ , \tag{3}$$

and β, ν, ρ, λ, τ, and k are variational parameters ($\nu=1,2,\ldots,$ runs over integer values). With this function they[3] calculated a B about 70% larger than that given by ψ alone for the 3D case. In 3D, B is just a single value, whereas in 2D it is necessary to calculate the function $B(l)$.

In the present work we have applied (2) to the 2D case and have obtained the expected increase in B. The results are in excellent agreement with the experimental values[2] for the three thinnest samples ($l=81,102,145$ Å). For the thicker samples ($l=222,327,520$ Å), the calculated $B(l)$ falls off smoothly with l while the measured values[2] increase to about twice the calculated value before falling off at $l=1000$ Å to about the value expected in bulk GaAs. It was not possible in Ref. 2 to give more than a sketchy description of the computation. Here we give complete information on the essential formulas and special problems of the computations.

A problem closely related to the biexciton is that of the bound exciton, an exciton (X) bound to a neutral donor (D^0) or acceptor (A^0) center. For simple bands this is equivalent in 3D to the positronium hydride molecule which has been extensively studied theoretically.[7,8] As far as we know, no theoretical treatment of the 2D bound exciton has previously been published, so there may be some interest in the binding energies predicted by (2) for 2D bound excitons. We believe the theory is on firm ground for X-D^0, although clearly not as accurate as it is for the biexciton. The only difficulty in this case is that Φ allows for only one scale parameter, which prevents a correct description of the separated exciton and donor center. However, an interesting result of these as well as the biexciton calculations is the confirmation for the 2D case of "Haynes's rule"[9]

$$B=f_H B_0 \;, \tag{4}$$

where B_0 is the binding energy of the neutral center (D^0, A^0, or X) and the "Haynes factor" $f_H \sim 0.1$ depends only slightly on the particular center. By scaling our result to the correct value of B_0+B_x, we obtain in a simple way a correction to B which we believe overcomes the difficulty mentioned above. Unfortunately, no data are available as yet on X-D^0. To treat X-A^0, for which data has recently been reported,[10] we would have to give up our absolute theory containing no adjustable parameters (other than variational parameters completely determined by the requirement of maximizing B) and introduce a model energy band for the holes determined perhaps by requiring that it give the correct B_0 for A^0. The separated system then involves a hypothetical model exciton with the wrong hole mass. A more fundamental difficulty is that the factorization implied in (2) of the wave function into Φ and other factors [not shown in (2)] representing the confinement of the particles in the quantum well is not valid for such a deep level as A^0. In view of the uncertainties involved in making the necessary corrections, we do not attempt to treat X-A^0 in this paper. However, it is interesting to note that X-A^0 obeys[10] Haynes's rule (4) with $f_H=0.13$.

Although the Φ we obtain is variational, we believe it is the best wave function available at present to describe biexcitons and X-D^0. It can be used to calculate quantities of physical interest including radiative and nonradiative (Auger) recombination. Here we do not go into these calculations but we give all the parameters specifying Φ at each l for a series of l out to 520 Å. We cannot treat larger l because our wave function does not go over to the correct form in the bulk limit $l \to \infty$. A model treatment based on an isotropic hole mass recently described by Bastard and co-workers[11,12] can cover the whole range of l, but has the disadvantage of not correctly involving the hh mass in the limit $l \to 0$.

II. THEORETICAL FORMULATION FOR THE EXCITON AND BIEXCITON

If the well width l is sufficiently small the heavy and light holes moving along the layer normal (001) direction $\hat{z}$ (masses m_h, m_l, respectively) are uncoupled. The Hamiltonian for one electron and one hole can then be written

$$H_t=H_e+H_h+H_x \;, \tag{5}$$

where H_e and H_h describe the $\hat{z}$ motion of the electron and hole including the quantum-well potential, and

$$H_x=\frac{P^2}{2M_\pm}+\frac{p^2}{2\mu_\pm}-\left[\frac{e^2}{\epsilon}\right]\frac{1}{(r^2+z^2)^{1/2}} \tag{6}$$

describes the 2D exciton with total 2D mass $M_\pm$ and reduced 2D mass $\mu_\pm$, relative coordinates $\bar{r}=\bar{r}_e-\bar{r}_h$ and $z=z_e-z_n$, total 2D momentum $\bar{P}=\bar{p}_e+\bar{p}_h$, and relative 2D momentum $\bar{p}$ conjugate to $\bar{r}$. The 2D masses pertaining to motion in the (x,y) plane of the heavy $(+)$ and light $(-)$ hole are given by

$$\begin{aligned} m_\pm^{-1}&=(1\mp\tfrac{1}{2})(2m_h)^{-1}+(1\pm\tfrac{1}{2})(2m_l)^{-1} \;, \\ M_\pm&=m_e+m_\pm \;, \\ \mu_\pm^{-1}&=m_e^{-1}+m_\pm^{-1} \;. \end{aligned} \tag{7}$$

Note that the heavy hole is light and the light hole is heavy for the x,y motion, but the isotropic mass m_i defined by

$$m_i^{-1}=\tfrac{1}{2}(m_h^{-1}+m_l^{-1})=\tfrac{1}{2}(m_+^{-1}+m_-^{-1}) \tag{8}$$

is the same in the z and x,y directions.

Strictly speaking, one should include in H_x a contribution from image charges due to the discontinuity in the dielectric constant ϵ at the well interfaces. However, the discontinuity is typically only $\sim 15\%$, so image charges can be satisfactorily taken into account simply by using an effective $\epsilon=(\epsilon_w\epsilon_b)^{1/2}$, where ϵ_w,ϵ_b are the well and barrier dielectric constants, respectively. This form specifically comes from the equivalent dielectric continuum corresponding to thin wells and barriers of equal width.

If the quantum well is sufficiently deep, H is dominated by H_e+H_h, allowing the wave function to be written in factored form

$$\Psi=\phi(r,z)w_e(z_e)w_h(z_h) \;, \tag{9}$$

where the well states w_e,w_h are eigenfunctions of H_e,H_h, respectively, and $\phi(r,z)$ describes the 2D exciton of zero total momentum, $\bar{P}=0$. It is assumed that $\phi(\bar{r},z)$ is normalized over $\bar{r}$,

$$\int [\phi(r,z)]^2 d\bar{r}=1 \;, \tag{10}$$

independent of z.

The binding energy B_x corresponding to Ψ is

$$B_x=-\int\int\int \Psi(H_t-W_e-W_h)\Psi d\bar{r}\,dz_e dz_h \;, \tag{11}$$

where W_e,W_h are the eigenvalues of H_e,H_h corresponding to the well states w_e,w_h. If $\phi(\bar{r},z)$ is taken to be a function only of r, (11) reduces to the simpler form

$$B_x=-\int\int\int \phi(r)\langle H_x\rangle\phi(r)d\bar{r} \;, \tag{12}$$

where $\langle H_x\rangle$ is H_x averaged over z_e,z_h,

$$\langle H_x \rangle = p^2/2\mu + V(r) , \tag{13}$$

$$V(r) = -\left[\frac{e^2}{\epsilon}\right] \int \int dz_e dz_h \frac{w_e(z_e)^2 w_h(z_h)^2}{(r^2+z^2)^{1/2}} . \tag{14}$$

Here $V(r)$ is the effective 2D Coulomb interaction which depends both on l and the particular well states of the electron and hole. Here, however, we are only concerned with the lowest states. If there is significant penetration of the barrier, μ^{-1} should be approximately averaged over the well and barrier effective masses. As pointed out in Ref. 1, the function

$$\phi_{1S}(r,z) = \left[\frac{2}{\pi b^2}\right]^{1/2} \frac{\exp(|z|/b)}{(1+2|z|/b)^{1/2}} \times \left[\frac{-(r^2+z^2)^{1/2}}{b}\right] , \tag{15}$$

with b a variational parameter, gives better results than the simpler function $\phi_{1S}(r) = \phi_{1S}(r,0)$. It is clear that (11) must give values of B_x larger than the bulk binding energy; $\phi_{1S}(r,z)$ meets this requirement out to $l \sim 500$ Å, whereas $\phi_{1S}(r)$ fails around $l \sim 300$ Å for GaAs.

For the biexciton we use the wave function

$$\Psi = \Phi(kr) w_e(z_1) w_e(z_2) w_h(z_a) w_h(z_b) , \tag{16}$$

where k is a scaling parameter, Φ is the function (2), and r stands for the set of interparticle distances r_{1a}, r_{1b}, r_{2a}, r_{2b}, r_{12}, and r_{ab}. The form Φ is expected to be most accurate when $\sigma \ll 1$, but we shall apply it over the whole range $0 \leq \sigma \leq 1$ as in Ref. 3. To simplify the calculation we have not included an explicit z dependence in Φ. The Hamiltonian of interest is then just $\langle H_x \rangle$, which we write in dimensionless form

$$H = -\frac{\sigma}{1+\sigma}(\nabla_a^2 + \nabla_b^2) - \frac{1}{1+\sigma}(\nabla_1^2 + \nabla_2^2) - 2(U_{1a} + U_{1b} + U_{2a} + U_{2b} - U_{ab} - U_{12}) , \tag{17}$$

where $\sigma = m_e/m_+$ is the mass ratio, 1,2 are electrons and a,b are holes, the units of energy and distance are the hh Rydberg and Bohr radius, respectively,

$$\mathcal{R} = e^2/2\epsilon a_B, \quad a_B = \epsilon\hbar^2/e^2\mu_+ , \tag{18}$$

and $U_{ij} = U(r_{ij})$, which comes from the effective Coulomb interaction (14), is defined by

$$U(r) = \int \int dz_e dz_h \frac{w(z_e)^2 w(z_h)^2}{(r^2+z^2)^{1/2}} , \tag{19}$$

which we take the same for all particles. The total binding energy is

$$B_{2e,2h} = -\frac{\int d\Omega\, \Phi(kr) H \Phi(kr)}{\int d\Omega\, \Phi(kr)^2} , \tag{20}$$

where $d\Omega = d\bar{r}_1 d\bar{r}_2 d\bar{r}_a d\bar{r}_b$ is the total volume element. When $B_{2e,2h}$ is maximized by varying $k,\beta,\nu,\rho,\lambda,\tau$, the biexciton binding energy is

$$B_{xx} = B_{2e,2h} - 2B_x . \tag{21}$$

Following Hylleraas and Ore[6] we eliminate the scale parameter k at the outset. Assume that (19) can be replaced by the simple model function

$$U(r) = (1 - e^{-\gamma r})/r , \tag{22}$$

where γ^{-1} is a measure of the well width l/a_B. Then define the following integrals with $k=1$ in Φ:

$$\begin{aligned} N &= \int \Phi^2 d\Omega , \\ M &= \frac{\sigma}{1+\sigma} \int [(\nabla_a \Phi)^2 + (\nabla_b \Phi)^2] d\Omega \\ &\quad + \frac{1}{1+\sigma} \int [(\nabla_1 \Phi)^2 + (\nabla_2 \Phi)^2] d\Omega , \\ L(\gamma) &= \int \Phi^2 (U_{1a} + \cdots - U_{ab} - U_{12}) d\Omega , \\ D &= \frac{\partial L}{\partial \gamma}, \quad \Phi = \Phi(r) . \end{aligned} \tag{23}$$

Now (20) can be written

$$B_{2e,2h} = [2kL(\gamma/k) - k^2 M]/N . \tag{24}$$

Optimizing with respect to k gives the two relations

$$\gamma = p[L(p) - pD(p)]/M , \tag{25}$$

$$B_{2e,2h} = [L(p)^2 - p^2 D(p)^2]/MN , \tag{26}$$

for γ and $B_{2e,2h}$ as function of $p = \gamma/k$. To find $B_{2e,2h}$ for a fixed γ, (25) must be numerically solved for p. Any common factor in N,M,L,D cancels out of (25) and (26).

Since (22) is just a model potential, the parameter γ must be calibrated by requiring that (22) gives the correct B_x for a single exciton. It is easy to show that for a single exciton the relations corresponding to (25) and (26) are

$$\begin{aligned} \gamma &= p^3/[2(1+p/2)^2] , \\ B_x &= [2\gamma/(1+p/2)] - \gamma^2/p^2 . \end{aligned} \tag{27}$$

By requiring that (27) gives the B_x obtained using (15) as reported in Ref. 1, we obtain the calibration $\gamma(l)$ shown in Fig. 1. This calibration makes it possible to use the form (16) out to large values of $l \sim 500$ Å even though $\Phi(kr)$

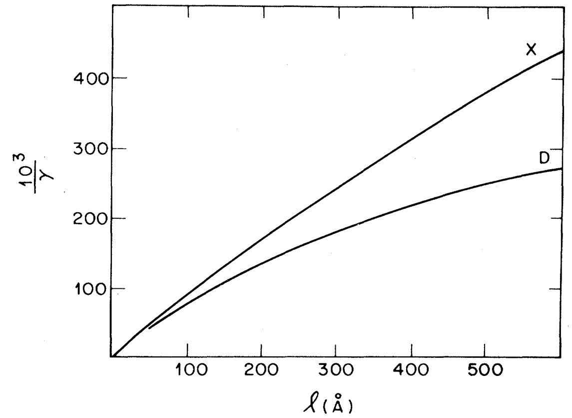

FIG. 1. Calibration of the parameter γ in the model potential (22) to the exciton calculations of Ref. 2 (curve X) and the donor calculations of Ref. 11 (curve D) for GaAs quantum wells of thickness l (Å).

contains no z dependence. The limit $\nu=0$, $\rho=0$, $\lambda=0$, $\tau=0$, $\beta\to 1$ corresponds to two separated excitons, and therefore

$$B_{2e,2h} \underset{\beta\to 1}{\longrightarrow} 2B_x, \quad \nu=\rho=\lambda=\tau=0 \tag{28}$$

must hold for any value of γ, providing a check on the computations.

III. EVALUATION OF INTEGRALS

Because Φ is invariant to any rigid translation or rotation of the molecule, the eightfold integrations in (23) can be reduced to fivefold integrations with volume element $d\Omega$ and limits,

$$\begin{gathered} d\Omega = v\,dv\,d\bar{r}_1\,d\bar{r}_2 = (v\,dv)(J_1 ds_1 dt_1)(J_2 ds_2 dt_2)\ , \\ J = [(s^2-t^2)/4][(s^2-v^2)(v^2-t^2)]^{-1/2}\ , \\ 0 \le v < \infty,\quad v \le s < \infty,\quad -v < t < v \end{gathered} \tag{29}$$

where $v = r_{ab}$ and the elliptic coordinates $s_1, \ldots, t_2$ are defined in (1). The integration over s,t covers only half the $\bar{r}$ space, the other half being a reflection in the line ab. In all the integrals except those containing r_{12}, this is fixed by supplying a factor of 2. We write the integrals (23) in the form

$$\left.\begin{matrix} N \\ M \\ L \\ D \end{matrix}\right\} = \int_0^\infty v\chi(v)^2 dv \times \left\{\begin{matrix} n(v) \\ m(v) \\ q(v) \\ d(v) \end{matrix}\right. \tag{30}$$

and further resolve $q(v)$ and $d(v)$ into separate parts in the form

$$q(v) = (q_{1a}+q_{1b}+q_{2a}+q_{2b}) - q_{ab} - q_{12}\ . \tag{31}$$

As a result of the convenient form chosen for $U(r)$ in (22), all integrals over $\bar{r}_1, \bar{r}_2$ except q_{12} and d_{12} can be obtained in exact closed form by use of the integrals

$$\int_v^\infty \frac{ds}{(s^2-v^2)^{1/2}} \times \left\{\begin{matrix} 1 \\ s \\ s^2 \end{matrix}\right\} \times \exp(-\mu s) = \left\{\begin{matrix} K_0(\mu v) \\ vK_1(\mu v) \\ v^2[K_0(\mu v)+K_1(\mu v)/\mu v]\ , \end{matrix}\right. \tag{32}$$

$$\int_{-v}^{v} \frac{dt}{(v^2-t^2)^{1/2}} \times \left\{\begin{matrix} 1 \\ t \\ t^2 \end{matrix}\right\} \times \exp(-\mu t) = \left\{\begin{matrix} I_0(\mu v) \\ -vI_1(\mu v) \\ v^2[I_0(\mu v)-I_1(\mu v)/\mu v]\ , \end{matrix}\right.$$

where K_n, I_n are the modified Bessel functions. It is not possible to do any of the final integrals over v analytically.

To express the integrals more conveniently we define the following quantities:

$$\begin{gathered} T_1 = 2K_1 - \beta^2 v K_0,\quad T_2 = K_1 + vK_0/2\ , \\ T_3 = K_1 I_0 + \beta K_0 I_1,\quad T_4 = K_1 I_0 + K_0 I_1/\beta\ , \\ T_5 = K_1 I_0 - K_0 I_1/\beta,\quad T_6 = K_1 - vK_0/2\ , \\ T_7 = (\beta^{-1}-\beta)K_1 I_1,\quad T_8 = vK_1/2\ , \\ T_9 = I_0^{(-)} + I_0^{(+)},\quad T_{10} = I_1^{(-)} - I_1^{(+)}\ , \\ T_{11} = K_1^{(+)} I_0^0 + K_0^{(+)} I_1^0\ , \\ T_{12} = I_1^{(+)}/(\beta+p/2) + I_1^{(-)}/(\beta-p/2)\ , \\ T_{13} = K_0^{(+)} I_1^0/(p/2) + K_1^{(+)} I_0^0/(1+p/2)\ , \end{gathered} \tag{33}$$

with the notation

$$\begin{gathered} K_n = K_n(v),\quad K_n^{(+)} = K_n(v+pv/2)\ , \\ I_n = I_n(\beta v),\quad I_n^{(+-)} = I_n(\beta v \pm pv/2)\ , \\ I_n^0 = I_n(pv/2)\ . \end{gathered} \tag{34}$$

The results are as follows (dropping a factor $\pi^2/8$) for the integrals which can be done exactly:

$$n(v) = v^2(T_2^2+T_4^2)\ , \tag{35}$$

$$q_{ab}(v) = \{[1-\exp(-pv)]/v\}n(v)\ , \tag{36}$$

$$d_{ab}(v) = \exp(-pv)n(v)\ , \tag{37}$$

$$\begin{aligned} m(v) = v^2(T_1T_2+2T_3T_4) + v^2[\sigma/(1+\sigma)] \\ \times[(T_2^2+T_4^2)(\chi'/\chi)^2 - 4(T_2T_8+T_4T_7)(\chi'/\chi) + (1+\beta^2)(T_8^2-T_2T_6) + T_7^2 \\ -(1-\beta^2)T_4T_5]_1\ , \end{aligned} \tag{38}$$

$$q_{1a}+q_{1b}+q_{2a}+q_{2b} = 2v^2[4K_1(T_2+I_0T_4) - 2T_4(K_1^{(+)}T_9 - K_0^{(+)}T_{10}) - 4T_2T_{11}]\ , \tag{39}$$

$$d_{1a}+d_{1b}+d_{2a}+d_{2b} = 2v^2\{T_4[K_0^{(+)}T_{12} + K_1^{(+)}T_9/(1+p/2)] + 2T_2T_{13}\}\ . \tag{40}$$

The quantity in square brackets with subscript 1 will be referred to again in (59) and (60). When $\chi=$const, symmetry requires $q_{12}=q_{ab}, d_{12}=d_{ab}$. Also, when $\chi=$const, it can be shown that the term in $m(v)$ containing σ contributes nothing when integrated over v, providing a valuable check on the computations.

We define

$$\begin{aligned} q_{12}(v) &= g(v)-h(v) , \\ g(v) &= \int d\bar{r}_1 d\bar{r}_2 \psi^2 u^{-1} , \\ h(v) &= \int d\bar{r}_1 d\bar{r}_2 \psi^2 \exp(-pu) u^{-1} , \end{aligned} \tag{41}$$

where $u=r_{12}$. The most serious problem in the whole calculation is obtaining a satisfactory approximation for $g(v)$. We define the function

$$g(u,v)=g(v,u)=2\int d\theta\, ds_a J\, dt_a \psi^2 , \tag{42}$$

so that

$$g(v)=\int_0^\infty g(u,v)du . \tag{43}$$

We shall approximate $g(v)$ by smoothly joining two expansions. The small $v \ll r_{1a}, r_{2a}$ expansion is (dropping $\pi^2/8$)

$$\begin{aligned} g(u,v) \underset{v\to 0}{\longrightarrow} 4u^2[&(1+\beta^2 v^2/2)K_0(2u) \\ &+(1-v^2)K_1(2u)/u] . \end{aligned} \tag{44}$$

It now follows that the expansion of $g(v)$ in powers of v is

$$g(v)=(3\pi/4)[1-2v^2(1-\beta^2/4)/3+\cdots] . \tag{45}$$

As a check, the corresponding expansion of $n(v)$ given by (35) can be obtained in two ways, either directly from (35) or from

$$n(v)=\int_0^\infty g(u,v)u\,du=2[1-(1-\beta^2)v^2/2+\cdots] .$$

The quantity which we wish to join smoothly between its large- and small-v expansions is

$$g(v)/n(v)=(3\pi/8)[1-(1+\beta^2/2)v^2/6+\cdots] . \tag{46}$$

The large-v expansion has already been given by Brinkman, Rice, and Bell[3] (Appendix B) in terms of certain integrals $I_1, \ldots, I_5$. Their result can be written

$$\frac{g(v)}{n(v)}=\frac{1}{v}\left[1-\frac{2I_2}{I_1 v}+\frac{(1-\beta)(I_1 I_3-I_2 I_4)-I_1 I_5+2I_2^2}{I_1^2 v^2}\right] . \tag{47}$$

For the 2D case, the integrals are

$$\begin{aligned} I_1 &= \int_0^\infty du\, u e^{-Gu} \int_0^{2\pi} d\theta\, e^{-Fu\cos\theta} , \\ I_2 &= \int_0^\infty du\, u^2 e^{-Gu} \int_0^{2\pi} d\theta\, e^{-Fu\cos\theta}\cos\theta , \\ I_3 &= \int_0^\infty du\, u^4 e^{-Gu} \int_0^{2\pi} d\theta\, e^{-Fu\cos\theta}\sin^2\theta\cos\theta , \\ I_4 &= \int_0^\infty du\, u^3 e^{-Gu} \int_0^{2\pi} d\theta\, e^{-Fu\cos\theta}\sin^2\theta , \\ I_5 &= \int_0^\infty du\, u^3 e^{-Gu} \int_0^{2\pi} d\theta\, e^{-Fu\cos\theta}(1-3\cos^2\theta) . \end{aligned} \tag{48}$$

Evaluation of these integrals gives the large-v expansion

$$\frac{g(v)}{n(v)}=\frac{1}{v}\left[1+\frac{3(1-\beta)}{2\beta v}+\frac{3(7-12\beta+7\beta^2)}{8\beta^2 v^2}+\cdots\right] . \tag{49}$$

Note that this expansion is not valid as $\beta\to 0$, but this causes no problem in our calculation as the optimum is always $\beta\sim 0.5$.

We write the function to be interpolated between (46) and (49) as

$$f(v)=g(v)/n(v) \underset{v\to 0}{\longrightarrow} a-bv^2 \underset{v\to\infty}{\longrightarrow} v^{-1}(1+c/v+d/v^2) . \tag{50}$$

We augment the first form with two more terms,

$$f_i(v) \underset{v\to 0}{\longrightarrow} a-bv^2+sv^3+tv^4 , \tag{51}$$

where s,t are determined by requiring that at some value $v=v_0$, $f_i(v)$ in (50) joins smoothly (continuous f and f') to the second ($v\to\infty$) form in (50). Then the function $f(v)$ is taken to be

$$f(v_0,v)=\begin{cases} f_i(v), & 0\le v\le v_0 \\ v^{-1}(1+c/v+d/v^2), & v\ge v_0 . \end{cases} \tag{52}$$

The parameter $v_0(\beta)$ is determined numerically from the exact condition

$$\int_0^\infty f(v)n(v)v\,dv=\int_0^\infty n(v)dv , \tag{53}$$

which follows from the symmetry of $g(u,v)$. There is always a unique v_0 satisfying (53). Finally $g(v)$ is taken to be $n(v)f(v_0,v)$.

The functions

$$d_{12}(v)=\int d\bar{r}_1 d\bar{r}_2 \psi^2 \exp(-pu) \tag{54}$$

and $h(v)$ given in (41) are treated by considering an expansion for small $u \ll v$ which is analogous to the small-v expansion leading to (43). Without repeating any details we can write the result by interchanging u,v in (43),

$$\begin{aligned} g(u,v) \underset{u\to 0}{\longrightarrow} 4v^2[&(1+\beta^2 u^2/2)K_0(2v) \\ &+(1-u^2)K_1(2v)/v] . \end{aligned} \tag{55}$$

It follows that for sufficiently large p we can write

$$\begin{aligned} d_{12}(v) &= \int_0^\infty du\, u e^{-pu} g(u,v) \\ &= 4C_d v^2[(K_0+K_1/v)/p^2+6(\beta^2 K_0/2-K_1/v)/p^4] , \end{aligned} \tag{56}$$

$$\begin{aligned} h(v) &= \int_0^\infty du\, e^{-pu} g(u,v) \\ &= 4C_h v^2[(K_0+K_1/v)/p+2(\beta^2 K_0/2-K_1/v)/p^3] , \end{aligned} \tag{57}$$

where $K=K(2v)$ and C_d, C_h are correction factors close to unity. We determine C_d, C_h by requiring that $d_{12}(v), h(v)$ satisfy the exact conditions required by symmetry

$$\begin{aligned} \int_0^\infty v d_{12}(v)dv &= \int_0^\infty v n(v) e^{-pv} dv , \\ \int_0^\infty v h(v)dv &= \int_0^\infty n(v) e^{-pv} dv . \end{aligned} \tag{58}$$

For the range of interest $p > 2.5$, the required values of C_d, C_h are found to be close to unity justifying (56) and (57).

The case $\sigma = 0$ requires special treatment. In this case the form (3) for $\chi(v)$ is inappropriate and no optimization of ν, ρ, λ, τ can be found. It is found that as σ decreases below 0.1, larger and larger values of ν and ρ are required corresponding to a distribution in the hole-hole distance v that is more and more localized around an optimum value $\bar{v}$. To treat this case we drop the integration over v in (30), set $v = \bar{v}$, and then optimize $B_{2e,2h}$ with respect to $\beta, \bar{v}$. Numerical quadratures are still required to find the parameters v_0 in (53) and C_d, C_h in (58). Note that the actual hole-hole separation is $\bar{v}/k$, where k is the scale parameter.

IV. MODIFICATIONS FOR THE BOUND EXCITON

To treat the bound exciton two modifications in the formulation are required: (a) in M [see (23)] one of the kinetic energy terms must be dropped, e.g., $(\nabla_b \Phi)^2$ for X-D^0 or $(\nabla_2 \Phi)^2$ for X-A^0; (b) in L it is necessary to use different model potentials characterized by different γ for interaction between particles and between a particle and the center. We continue to use the same units (18). It is straightforward to obtain the modified forms of (38),

$$(X\text{-}D^0) m(v) = \frac{1+\sigma/2}{1+\sigma} v^2 (T_1 T_2 + 2T_3 T_4) + \frac{\sigma/2}{1+\sigma} v^2 [\mathscr{T}]_1 \,, \tag{59}$$

$$(X\text{-}A^0) m(v) = \frac{\sigma + \frac{1}{2}}{1+\sigma} v^2 (T_1 T_2 + 2T_3 T_4) + \frac{\sigma}{1+\sigma} v^2 [\mathscr{T}]_1 \,, \tag{60}$$

where $[\mathscr{T}]_1$ is the same quantity in square brackets identified in (38). Actually, we do not consider X-A^0 here, but (60) is useful for treating X-D^0 when $m_+ < m_e$ and σ is redefined as $\sigma = m_+/m_e$.

For generality, suppose that each interaction U_{ij} in L has a separate parameter γ_{ij} when written in the form (22). We still have only one scale parameter k. $B_{2e,2h}$ still has the form (24) except that L is a function of more parameters,

$$\begin{aligned} L &= L_{1a}(p_{1a}) + \cdots - L_{ab}(p_{ab}) - L_{12}(p_{12}) \\ &= \sum_i L_i(p_i), \quad p_i = \gamma_i / k \,. \end{aligned} \tag{61}$$

We assume that the ratios of the p_i

$$R_i = p_i / p = \gamma_i / \gamma \quad (\gamma = \gamma_{12}, p = p_{12}) \tag{62}$$

are known given any value of p. Now if D is defined by

$$\begin{aligned} D(p) &= \sum_i R_i D_i(p_i) \,, \\ D_i(p_i) &= \frac{\partial L_i}{\partial p_i} \,, \end{aligned} \tag{63}$$

γ and the total binding energy $B_{2e,hD}$ are given by (25) and (26).

For X-D^0, with the center at a, we have

$$\begin{aligned} &\gamma_{1b} = \gamma_{2b} = \gamma_{12} = \gamma \,, \\ &\gamma_{1a} = \gamma_{2a} = \gamma_{ab} = R\gamma \,, \\ &D = (D_{1b} + D_{2b} - D_{12})_p + R(D_{1a} + D_{2a} - P_{ab})_{Rp} \,, \\ &L = (L_{1b} + L_{2b} - L_{12})_p + (L_{1a} + L_{2a} - L_{ab})_{Rp} \,. \end{aligned} \tag{64}$$

It is possible to determine a $\gamma_D(l)$ for the donor in the same way as $\gamma(l)$ was determined for the exciton [see (27)] taking care to describe the donor in the same units (18) (even though these are not the most natural units for the donor). We have calibrated $\gamma_D(l)$ to the recent calculations of Bastard[11] for a donor in the center of the well. The result for GaAs is shown along with $\gamma_{(l)}$ in Fig. 1. This calculation determines

$$R(l) = \gamma_D(l) / \gamma(l) \,. \tag{65}$$

We do not consider the case X-A^0 here because the acceptor level is too deep to be treated as a hh state, yet the binding energy is relative to the separated system in which one of the holes must be treated as the heavy hole. At present we do not have a satisfactory and simple way of constructing the wave function so as to properly describe both situations, so X-A^0 is beyond the scope of the present treatment. Nevertheless, we have given (60) for its possible future interest and for its usefulness in the X-D^0 problem with electrons and holes interchanged.

For X-D^0, values can be calculated, using the modifications described above, for the total binding energy $B_{2e,hD}$, the bound exciton binding energy B_{xD}, and the binding energy B_∞ of the separated system

$$\begin{aligned} &B_\infty = \lim_{\substack{\nu=\rho=\lambda=\tau=0}} \beta \to 1 \; B_{2e,hD} \,, \\ &B_{xD} = B_{2e,hD} - B_\infty \,. \end{aligned} \tag{66}$$

However, B_∞ is not equal to $B_D + B_x$ because our wave function with only one scale parameter cannot describe the

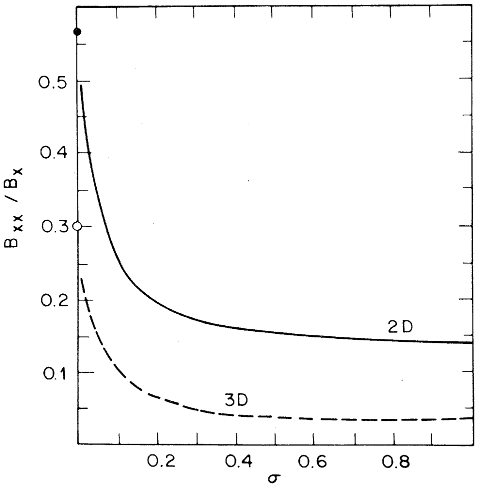

FIG. 2. 2D biexciton binding energy relative to the exciton binding energy as a function of the mass ratio $\sigma = m_e/m_+$ for the case $l = 0$. Also shown (dashed) is the 3D result of Ref. 3. Intercepts at $\sigma = 0$ are indicated by points.

TABLE I. Summary of the optimized results for the 2D biexciton. Values given for l assume GaAs. The Haynes factor f_H is defined in (4). Here $\nu=1$ and $\sigma=0.68$.

l (Å)	γ	k	β	ρ	λ	τ	B_{xx}	f_H
0	∞	2.51	0.66	0.43	0.42	0.28	0.585	0.15
52	20	1.94	0.61	0.39	0.37	2.4	0.376	0.13
81	12.5	1.74	0.60	0.38	0.37	2.9	0.314	0.12
102	10.0	1.64	0.60	0.38	0.40	3.0	0.285	0.12
145	7.75	1.52	0.59	0.37	0.40	3.1	0.252	0.11
171	6.76	1.46	0.59	0.36	0.41	3.1	0.235	0.11
222	5.41	1.35	0.59	0.36	0.43	3.2	0.207	0.11
272	4.50	1.27	0.58	0.35	0.43	3.3	0.186	0.11
327	3.85	1.20	0.56	0.34	0.43	3.3	0.169	0.10
415	3.10	1.10	0.55	0.33	0.43	3.4	0.148	0.10
520	2.54	1.04	0.55	0.25	0.46	3.4	0.130	0.10

different sizes of the donor and exciton states when separated. The simplest way of correcting for this is to take

$$\bar{B}_{2e,hD}=[(B_D+B_x)/B_\infty]B_{2e,hD} \tag{67}$$

as the corrected total binding energy, and

$$\bar{B}_{XD}=\bar{B}_{2e,hD}-B_D-B_x \tag{68}$$

as the corrected binding energy of X-D^0. The correct value of B_D is easily obtained from (27) or (28) using $\gamma=\gamma_D$,

$$B_D=(1+\sigma)B_x(\gamma_D)\ . \tag{69}$$

The validity of (67) is closely connected with Haynes's rule to be discussed later.

V. NUMERICAL INTEGRATIONS

The final integrations over v in (30) were all done using the Gauss-Laguerre numerical quadrature formula[13]

$$\int_0^\infty f(x)dx=\sum_1^N W_n f(X_n)\ , \tag{70}$$

where W_n, X_n are the weights and abscissas for the quadrature of order N. In practice, it is necessary to condition the integral with a scaling function $s(x)$,

$$\begin{aligned}\int_0^\infty f(v)dv&=\int_0^\infty f(s(x))s'(x)dx\\&=\sum_1^N W_n f(s(X_n))s'(X_n)\ ,\end{aligned} \tag{71}$$

chosen so as to ensure that the set $X_1,\ldots,X_N$ adequately covers the most significant region of the integrand.

Consider the integrals $(m=0,1,2)$

$$\begin{aligned}S_m&=\int_0^\infty dv\, ve^{-\kappa v}\chi(\nu,\rho,\lambda,\tau;v)^2v^m\\&=\frac{(2\nu+m+1)!}{(2\rho+\kappa)^{2\nu+m+2}}+\frac{\lambda^2(m+1)!}{(2\tau+\kappa)^{m+2}}\\&\quad+\frac{2\lambda(\nu+m+1)!}{(\rho+\tau+\kappa)^{\nu+m+2}}\ ,\end{aligned} \tag{72}$$

with χ given by (3), which are closely related to the integrals required in (30), and from the values of S_0,S_1,S_2 we determine the quantities

$$\begin{aligned}&\langle v\rangle=S_1/S_0,\quad \langle v^2\rangle=S_2/S_0\ ,\\&\Delta v=(\langle v^2\rangle-\langle v\rangle^2)^{1/2}\ .\end{aligned} \tag{73}$$

The region of v which contributes most to the integrals (30) is approximately $\langle v\rangle<v<(\langle v\rangle+\Delta v)$; the scaling function should place a number of points $v_n=s(X_n)$ in this region, and also provide that at the last point $v_N=s(X_N)$ the integrand is very small. We have used $N=20$ and the function

$$\begin{aligned}s(x)&=ax+\tfrac{1}{2}(b-a)x+\tfrac{1}{2}(c-b)x\\&\quad+\frac{\epsilon(b-a)}{2}\ln\left[\frac{\cosh[(x-X_{10})/\epsilon]}{\cosh[(X_{10}/\epsilon)]}\right]\\&\quad+\frac{\epsilon(c-b)}{2}\ln\left[\frac{\cosh[(x-X_{14})/\epsilon]}{\cosh[(X_{14}/\epsilon)]}\right]\ ,\\&a=\langle v\rangle/X_{10},\quad b=\Delta v/(X_{14}-X_{10}),\quad \epsilon=2\ .\end{aligned} \tag{74}$$

The parameter c is determined to satisfy the condition $f_{20}s'_{20}<10^{-6}f_{14}s'_{14}$. The parameter ϵ, which is arbitrary,

TABLE 2. Summary of the optimized results for the 2D bound exciton X-D^0 in GaAs. The values listed for B_{XD} are the uncorrected values (66). Here $\sigma=0.68$.

l (Å)	R	k	β	ν	ρ	λ	τ	B_{XD}
81	1.10	2.04	0.60	1	0.54	0.26	5.0	0.414
171	1.25	1.74	0.56	1	0.49	0.29	5.0	0.319
222	1.30	1.63	0.55	1	0.48	0.30	5.1	0.287
327	1.37	1.49	0.45	2	0.89	0.21	2.5	0.242
520	1.53	1.35	0.46	2	0.74	0.19	2.9	0.214

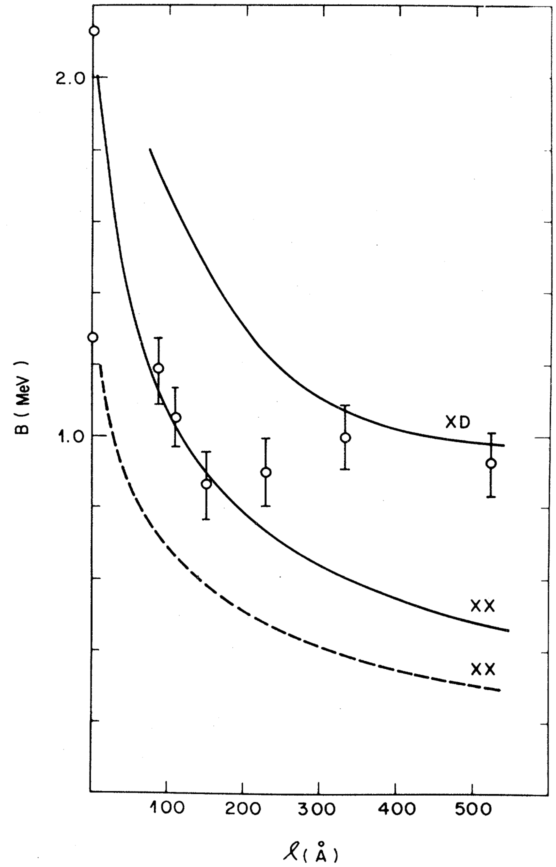

FIG. 3. Binding energy B_{xx} (meV) of the biexciton and $\bar{B}_{XD}$ of the bound exciton X-D^0 as a function of well thickness l (Å) of GaAs. The dashed curve is the previous result of Ref. 2 and the experimental points are from Ref. 2, attributed tentatively to the biexciton. Points indicate the XX intercepts at $l=0$.

determines the rounding of $s(x)$ as it passes X_{10} and X_{14} into a new regime. We have found $\epsilon=2$ to be the best value. The accuracy of (71) with (74) can be studied on the integrals S_m; these studies show that our error is consistently less than 1 in 10^6. Binding energies B_{xx} and B_{XD} are obtained with computational error less than 1 in 10^4; however, optimization of parameters was carried out only to an accuracy in B_{xx},B_{XD} of about 1 in 10^3.

VI. DISCUSSION OF RESULTS

Our results for B_{xx}/B_x as a function of σ for the case $l=0$ are plotted in Fig. 2 as the solid curve labeled 2D; also shown by the dashed curve 3D are the results of Brinkman, Rice, and Bell.[3] At $\sigma=0$ we obtain $B_{xx}/B_x=0.564$, $\beta=0.54$, $\bar{v}=0.94$, $k=2.59$, corresponding to an optimum hole-hole separation $\bar{v}/k=0.36$. The quantity plotted is the Haynes factor f_H in Haynes's rule[9] (4). We see that qualitatively the 3D and 2D cases behave similarly; a kind of Haynes's rule (with an anomalous f_H) holds approximately over a considerable range in σ but finally breaks down as $\sigma\rightarrow 0$. The results shown in Fig. 2 are independent of material parameters and the model-potential assumption (22).

Our complete results for the 2D biexciton as a function of well thickness are listed in Table I for 11 well thicknesses. The listed values of l are for GaAs, as is the chosen value $\sigma=0.68$, and most of the values of γ were chosen to give the l for measured samples. Nevertheless, the dependence of all computed quantities on γ is material independent. The Haynes factor f_H in the last column has the customary value (~ 0.1) except for the $l=0$ case. Figure 3 shows B_{xx} (meV) against l (Å) for GaAs along with the curve (dashed) obtained previously[2] and the experimental data published previously.[2] We see that the present calculations are about a 70% improvement on Ref. 2 as speculated. The calculated B_{xx} fits the experimental points very well for $l=81$ 102 145 Å. The other three points deviate to higher values as l increases, a very anomalous behavior from the theoretical standpoint.

The complete results for the 2D bound exciton X-D^0 in GaAs as a function of l are given in Tables II and III. Table II gives the calculated quantities optimized in the same way as the biexciton calculations. In this case the results are not material independent because of the parameter $R(l)$ in (65). The B_{XD} values are the uncorrected values (66) produced by optimization. The information necessary to get the corrected values $\bar{B}_{XD}$ [see (68)] is listed in Table III along with the Haynes factor. It is seen that $f_H(XD)$ has the expected value and is very nearly constant over the range of l studied. Figure 3 shows $\bar{B}_{XD}$ (meV) plotted against l. It is tempting to note that the curve is close to the points at $l=327$ and 520 Å.

For the samples $l=81-520$ Å, the constancy and magnitude of f_H remarkably confirm Haynes's rule[9] (4) first put forward for the 3D case. In view of this, we believe that the scaling procedure used in (68) to correct the computed B_{XD} is justified. Recently, B_{XA} has been observed[10] in p-doped GaAs quantum wells and found to obey Haynes's rule with $f_H=0.13$. It should be noted that Haynes's rule has in the past been attributed[14] to central-cell corrections to the effective-mass Hamiltonian. In the present calculations, binding arises from correlation (represented principally by the parameter β) and there are no central-cell corrections.

TABLE III. Summary of the quantities needed to obtain the corrected X-D^0 binding energies according to (68).

l (Å)	B_x	B_D	B_∞	B_{XD}	$\bar{B}_{XD}$	f_H
81	2.62	4.52	6.20	0.414	0.476	0.11
171	2.11	3.86	5.04	0.319	0.377	0.10
222	1.92	3.60	4.62	0.287	0.343	0.095
327	1.64	3.19	3.98	0.242	0.295	0.092
520	1.32	2.78	3.29	0.214	0.266	0.096

We have used the same physical constants for GaAs as in Ref. 1 (see references there),

$$m_e=0.067m_0,\quad m_h=0.35m_0,\quad m_l=0.08m_0\ ,$$

$$\epsilon_w=13.1,\quad \epsilon_b=11.4\ ,$$

$$\mathscr{R}=3.7,\quad a_B=160\ ,$$

the latter terms measured in meV and Å, respectively. Note that both m_h, m_l are required to compute the transverse hh mass $m_+=0.099m_0$ required for $\sigma=m_e/m_+=0.68$, and the units $\mathscr{R}$, a_B in (18). The value of m_e/m_0 is experimentally well established, but a wide range of values[15] has been reported for m_h/m_0. The first detailed analysis[16] of quantum-well spectra used the value 0.45 determined from interband magnetoabsorption.[17] The most precise determination is probably 0.475 by cyclotron resonance.[18] However, we have observed from detailed examination of a number of quantum-well spectra (including Fig. 12 of Ref. 16) that somewhat better agreement is obtained using the smaller value 0.35. This value also agrees with the band parameters γ_1,γ_2 given by Lawaetz[19] [$\gamma_1=7.65$, $\gamma_2=2.41$, $m_h/m_0=(\gamma_1-2\gamma_2)^{-1}=0.35$ for (001) motion].

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