PHYSICAL REVIEW B VOLUME 42, NUMBER 18 15 DECEMBER 1990-II

Simple method for calculating exciton binding energies in quantum-confined semiconductor structures

R. P. Leavitt
U.S. Army Laboratory Command, Harry Diamond Laboratories, 2800 Powder Mill Road, Adelphi, Maryland 20783-1197

J. W. Little
Martin Marietta Laboratories, 1450 South Rolling Road, Baltimore, Maryland 21227

(Received 6 November 1989; revised manuscript received 7 June 1990)

We present a simple, general method for calculating the binding energies of excitons in quantum-confined structures. The binding energy is given by an integral (over the electron and hole coordinates perpendicular to the confining layers) of a prescribed function weighted by the squares of the electron and hole subband envelope functions. As a test of the method, we calculate the binding energies for heavy- and light-hole excitons in a rectangular GaAs/$Al_{0.3}Ga_{0.7}As$ quantum well as functions of the well width. Very good agreement with previous results is obtained over a wide range of quantum-well widths. Also, we determine the binding energies for heavy-hole excitons as functions of electric field in a GaAs/$Al_{0.35}Ga_{0.65}As$ asymmetric coupled-quantum-well structure. Our results compare favorably with those obtained in a treatment in which coupling of the electron subbands via the electron-hole Coulomb interaction is considered. Our method should be applicable to a variety of complex quantum-confined semiconductor structures for which more rigorous approaches require extensive numerical calculations.

I. INTRODUCTION

For the past several years there has been considerable interest in the electronic structure and optical properties of quantum wells and superlattices. Much of the interest has centered around the properties of quantum-confined states, i.e., states that have a limited spatial extent along a particular crystal direction. Because of the close proximity of electrons and holes that occupy such states, excitons have considerably larger bindings energies in these quantum-confined structures than in bulk semiconductors and can, for example, be easily observed in room-temperature absorption spectra.[1] Consequently, excitons have large effects on optical phenomena observed in these structures, and elucidation of their properties has become an important topic in the physics of multilayered semiconductor systems.

Much of the theoretical work in this area has concentrated on excitons in rectangular quantum wells grown along a [001] direction. Several authors[1-3] have calculated binding energies for excitons in wells with infinite barriers. Greene, Bajaj, and Phelps[4] calculated the binding energies for excitons in $GaAs/Al_xGa_{1-x}As$ quantum wells with finite barriers for various values of the Al mole fraction x using a variation approach, in which coupling of the light- and heavy-hole bands was neglected, and each of the bands was assumed to have a parabolic dispersion relation. Priester, Allan, and Lannoo[5] extended the results of Greene, Bajaj, and Phelps, by allowing for effective-mass mismatch between the well and barrier materials. Both sets of authors obtained results that are qualitatively in accord with experiment. Sanders and Chang[6] allowed for valence-band mixing and showed that the coupling of light and heavy holes away from $\mathbf{k}_{\parallel}=0$ resulted in highly distorted subband dispersion relations (particularly for the light hole) and, consequently, increases in the exciton binding energies on the order of 1 meV for heavy holes and 2 meV for light holes. Many other binding-energy calculations for rectangular quantum wells have been performed as well.[7-11]

The main feature of all these calculations is that they are variational; the accuracy of the results depends to a large degree on physical intuition used in choosing the form of the exciton wave function. Consequently, generalization to more complex systems has been difficult, and few results on systems other than rectangular wells have been published. (Exciton binding-energy calculations have been performed for parabolic wells and wells with linearly graded band gaps.[12])

In this work, we present a simple method for calculating exciton binding energies in quantum-confined structures. We were motivated to develop this method by the increasing interest in two particular semiconductor systems: coupled quantum wells[13,14] and Stark-localized states in superlattices.[15] In an accompanying paper,[16] we include the method as part of a theoretical description of the electronic and optical properties of small-period superlattices in an electric field, and we defer discussion of these structures until then. Here, we will treat excitons in the coupled-well system as an example of the applicability of the method.

The main result obtained in this paper is an expression for the exciton binding energy as the integral (over the coordinates of the electron and hole perpendicular to the confining layers) of a prescribed function multiplied by the squares of the electron and hole subband envelope functions. For simplicity, we neglect both band nonparabolicity[17] (arising from coupling between valence and conduction bands) and valence-band mixing (described by off-diagonal terms in the Kohn-Luttinger Hamiltonian[18]). We also assume that each exciton supported by the system can be associated with a specific pair of electron and hole subbands. Normally, the latter assumption would imply that the exciton binding energy is small compared with the differences between successive subband-edge energies. However, in our approach the exciton envelope function naturally manifests correlated electron-hole motion along the quantization direction. Consequently, a single term for the envelope function is sufficient to give reasonably accurate exciton binding energies for a wide range of quantum-well widths, as opposed to previous approaches.[8–10] Because of this, and because details of the structure enter only through the subband envelope functions, our method can be applied to a wide variety of structures in which the electron and hole states are localized.

In Sec. II we derive our results for the exciton binding energy. The binding energy for an exciton in which both electron and hole motions are confined to spatially separated planes is of central importance in evaluating the quantum-confined binding energies, and we treat the solution of this problem in Sec. III. In Sec. IV we compare results obtained with our method for rectangular GaAs/$\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ quantum wells with corresponding results obtained by Greene, Bajaj, and Phelps,[4] and by Priester, Allan, and Lannoo.[5] In Sec. V we apply the formalism to the coupled-quantum-well system, and we show that it gives results that compare well with a more complete treatment that includes coupling of electron subbands by the electron-hole Coulomb interaction.

II. EXCITON BINDING ENERGY

We consider a general multilayer semiconductor system. Although valence-band coupling has been shown[6–9] to contribute to some extent to exciton binding energies in quantum wells, we will, for simplicity, assume that this coupling can be neglected. We also neglect coupling of the valence and conduction bands. Therefore, both conduction and valence bands are assumed to have parabolic dispersion relations. The valence-band anisotropy is described by using different hole masses in different directions. The hole mass along the quantization direction (i.e., perpendicular to the layers comprising the structure) is $m_{\text{hh(lh)}\perp}$, and the hole mass in directions orthogonal to the quantization direction (i.e., parallel to the layers) is $m_{\text{hh(lh)}\parallel}$, where hh(lh) stands for heavy (light) holes. Generally, the perpendicular and parallel hole effective masses are distinct. If the quantization direction is parallel to a [001] axis, then we obtain $m_{\text{hh(lh)}\perp}=m_0/(\gamma_1\mp 2\gamma_2)$ and $m_{\text{hh(lh)}\parallel}=m_0/(\gamma_1\pm\gamma_2)$, where γ_1 and γ_2 are the Luttinger parameters.[18] We assume that the average dielectric constant for the structure is ϵ, and we neglect image-charge effects in our treatment of the electron-hole Coulomb interaction. The electron and the hole are subject to confining potentials V_e and V_h respectively, which can represent the effects of heterojunctions, doping, and external electric fields. In what follows, we allow for the possibility that the effective masses depend on position, although we do not express the position dependence explicitly.

Within the approximations given above, the Hamiltonian for an electron-hole pair (with zero center-of-mass momentum) can be written as

$$H=-\frac{\hbar^2}{2}\frac{\partial}{\partial z_e}\left[\frac{1}{m_e}\frac{\partial}{\partial z_e}\right]-\frac{\hbar^2}{2}\frac{\partial}{\partial z_h}\left[\frac{1}{m_{h\perp}}\frac{\partial}{\partial z_h}\right]+V_e(z_e)+V_h(z_h)-\frac{\hbar^2}{2\mu_\parallel}\nabla_\parallel^2-\frac{e^2}{\epsilon|\mathbf{r}_e-\mathbf{r}_h|}\ , \tag{1}$$

where $\mu_\parallel=m_e m_{h\parallel}/(m_e+m_{h\parallel})$, m_e is the conduction-band effective mass, $m_{h\perp}$ and $m_{h\parallel}$ are the valence-band effective masses perpendicular and parallel to the layers, respectively, $\mathbf{r}_e$ and $\mathbf{r}_h$ are the electron and hole position vectors, z_e and z_h are their z components (perpendicular to the layers), and $\nabla_\parallel$ is the component of the gradient (with respect to the relative coordinate $\rho=\mathbf{r}_{e\parallel}-\mathbf{r}_{h\parallel}$) parallel to the layers.

We choose the following form for the wave function of an electron-hole pair:

$$\psi_n(\mathbf{r}_e,\mathbf{r}_h)=\phi(z_e,z_h)g_n(\rho;z_e-z_h)\ , \tag{2}$$

where $n=1,2,\ldots$ labels the eigenstates in order of increasing energy (i.e., $n=1$ is the excitonic ground state), and where g_n is an eigenfunction of a two-dimensional Hamiltonian, representing an exciton in which the electron is confined to the plane $z=z_e$, and the hole is confined to the plane $z=z_h$. This quantity is obtained by solving the radial Schrödinger equation:

$$-\frac{\hbar^2}{2\mu_\parallel}\frac{1}{\rho}\frac{d}{d\rho}\left[\rho\frac{dg_n(\rho;Z)}{d\rho}\right]-\frac{e^2}{\epsilon(\rho^2+Z^2)^{1/2}}g_n(\rho;Z)=-E_n^{(2\text{D})}(Z)g_n(\rho;Z)\ , \tag{3}$$

where $Z=z_e-z_h$, subject to the boundary conditions that $g_n(\rho;Z)\to 0$ as $\rho\to\infty$ and $g_n(0;Z)$ is bounded, where $-E_n^{(2\text{D})}(Z)$ is the corresponding eigenvalue. The function g_n is normalized as follows:

$$\int_0^\infty \rho\,d\rho|g_n(\rho;Z)|^2=1\ . \tag{4}$$

Both $E_n^{(2\text{D})}(Z)$ and $g_n(\rho;Z)$ depend parametrically on the z coordinates through the Coulomb potential.

The form of Eq. (2) is similar to that used in the Born-Oppenheimer separation[19,20] of electronic and nuclear coordinates. Following Messiah,[19] we derive an effective Hamiltonian that acts on ϕ only. Consider the expectation value of the Hamiltonian, Eq. (1), using the trial wave function given by Eq. (2). We have

$$\langle H\rangle=\int_{-\infty}^{\infty}dz_e dz_h\left\{\int_0^{\infty}\rho\, d\rho\left[-\frac{\hbar^2}{2m_e}\left[\frac{\partial}{\partial z_e}\phi g_n\right]^2-\frac{\hbar^2}{2m_{h\perp}}\left[\frac{\partial}{\partial z_h}\phi g_n\right]^2\right]\right.$$
$$\left.+[V_e(z_e)+V_h(z_h)-E_n^{(2\mathrm{D})}(z_e-z_h)]\phi^2\right\}\Big/\int_{-\infty}^{\infty}dz_e dz_h\phi^2\,, \tag{5}$$

where we have used Eq. (3). This expression may be recast into the form of

$$\langle H\rangle=\int_{-\infty}^{\infty}dz_e dz_h\left[-\frac{\hbar^2}{2m_e}\left[\frac{\partial\phi}{\partial z_e}\right]^2-\frac{\hbar^2}{2m_{h\perp}}\left[\frac{\partial\phi}{\partial z_h}\right]^2\right.$$
$$\left.+[V_e(z_e)+V_h(z_h)-E_n^{(2\mathrm{D})}(z_e-z_h)+W_n^c(z_e-z_h)]\phi^2\right]\Big/\int_{-\infty}^{\infty}dz_e dz_h\phi^2\,, \tag{6}$$

where

$$W_n^c(Z)=\frac{\hbar^2}{2\mu_\perp}\int_0^{\infty}\left|\frac{\partial g_n(\rho;Z)}{\partial Z}\right|^2\rho\, d\rho\,. \tag{7}$$

If we require that Eq. (6) be stationary with respect to small changes in ϕ, we obtain the following effective Hamiltonian for state n of the electron-hole pair:

$$H_n^{\mathrm{eff}}=-\frac{\hbar^2}{2}\frac{\partial}{\partial z_e}\left[\frac{1}{m_e}\frac{\partial}{\partial z_e}\right]-\frac{\hbar^2}{2}\frac{\partial}{\partial z_h}\left[\frac{1}{m_{h\perp}}\frac{\partial}{\partial z_h}\right]+V_e(z_e)+V_h(z_h)-E_n^{(2\mathrm{D})}(z_e-z_h)+W_n^c(z_e-z_h)\,. \tag{8}$$

In the standard treatment of the electronic structure of molecules and solids, the adiabatic approximation[19] is used to separate the electronic and nuclear degrees of freedom. Born and Oppenheimer[20] introduce a small parameter $\chi=(m/M)^{1/4}$, where m and M are the electron and nuclear masses, respectively; in their treatment, the quantity analogous to $W_n^c(Z)$ is of order χ^4 and is therefore negligible compared with the other terms. In the excitonic problem, there is no corresponding small parameter, and dropping the $W_n^c(Z)$ term at this stage is not justified. Nevertheless, as we shall see below, this term contributes negligibly to the exciton binding energy.

In the semiconductor structures of interest, it is assumed that a number of discrete subbands exist in both the valence and conduction bands. The subband-edge energies (i.e., the energies for which $\mathbf{k}_\parallel=0$) are labeled $E_i^{(e)}$ and $E_j^{(h)}$ for the electron and hole bands, respectively, where $(i,j)=1,2,3,\ldots$ label the states in order of increasing energies. The states are described by single-band envelope functions $f_i^{(e)}$ and $f_j^{(h)}$, satisfying

$$\left[-\frac{\hbar^2}{2}\frac{d}{dz_e}\left[\frac{1}{m_e}\frac{d}{dz_e}\right]+V_e(z_e)\right]f_i^{(e)}=E_i^{(e)}f_i^{(e)}(z_e)\,, \tag{9a}$$

and

$$\left[-\frac{\hbar^2}{2}\frac{d}{dz_h}\left[\frac{1}{m_{h\perp}}\frac{d}{dz_h}\right]+V_h(z_h)\right]f_j^{(h)}=E_j^{(h)}f_j^{(h)}(z_h)\,. \tag{9b}$$

We now assume that the binding energies of the excitons supported by the system are small compared with the differences between successive subband-edge energies; consequently, each exciton can be associated with a pair (i,j) of electron and hole subbands. (This assumption is generally valid for quantum wells less than about 200 Å in thickness. The coupled-quantum-well system is an exception, since, in that case, an electric field can tune two electron subbands into resonance. We shall see in what follows that our formalism gives an adequate description of these systems well beyond the range in which this assumption is strictly valid.) Hence, we can treat the quantities $E_n^{(2\mathrm{D})}(Z)$ and $W_n^c(Z)$ in Eq. (8) as perturbations. Consequently, we can evaluate the expectation value of Eq. (8) using the unperturbed wave function:

$$\phi(z_e,z_h)=f_i^{(e)}(z_e)f_j^{(h)}(z_h)\,. \tag{10}$$

The result is

$$\langle H_n^{\mathrm{eff}}\rangle=E_i^{(e)}+E_j^{(h)}-E_{n,ij}^{(2\mathrm{D})}+W_{n,ij}^c\,, \tag{11}$$

where $E_{n,ij}^{(2\mathrm{D})}$ and $W_{n,ij}^c$ are matrix elements of $E_n^{(2\mathrm{D})}(Z)$ and $W_n^c(Z)$ calculated using the unperturbed wave function, Eq. (10).

The binding energy is defined as the difference in energy between the bottom of the electron-hole-pair continuum and the lowest excitonic bound state. In terms of the quantities defined above, we obtain the binding energy as

$$E_{ij}^B=E_{1,ij}^{(2\mathrm{D})}-W_{1,ij}^c-\lim_{n\to\infty}(E_{n,ij}^{(2\mathrm{D})}-W_{n,ij}^c)\,. \tag{12}$$

Equation (12) may be simplified further as follows. Note first that $\lim_{n\to\infty}E_n^{(2\mathrm{D})}(Z)=0$ for all Z. [Continuum solution to Eq. (3) first appear at zero energy.] Also, although the functions $W_n^c(Z)$ are comparable to the two-dimensional binding energies $E_n^{(2D)}(Z)$, our numerical calculations show that the *difference* between $W_1^c(Z)$ and $W_n^c(Z)$ for $n>1$ is significantly different from zero only for arguments whose magnitudes are on the order of 0.01 times the exciton Bohr radius or smaller. This result suggests that the W^c terms in Eq. (12) can be neglected. To estimate the error arising from neglecting these terms, the functions $W_n^c(Z)$ were calculated numerically using a 25-parameter variational wave function (similar to that described in Sec. III below) for g_n. While the results obtained are not very accurate (and depend to some degree on the choice of basis), they can be used to establish a rough upper bound on the contribution of the W^c terms to the binding energy. For systems such as those considered below, where the spatial extents of the electron and hole subband envelope functions are not considerably smaller than the exciton Bohr radius, we obtain an upper bound on the W^c contributions of about 0.5 meV for heavy holes and 0.9 meV for light holes for excitons in GaAs/Al$_x$Ga$_{1-x}$As quantum wells. Therefore we can safely neglect these terms in the remainder of this paper, and we obtain the following simple result for the exciton binding energy:

$$E_{ij}^B=\int_{-\infty}^{\infty} dz_e dz_h |f_i^{(e)}(z_e)|^2 |f_j^{(h)}(z_h)|^2 E_1^{(2D)}(z_e-z_h) \; . \tag{13}$$

Equation (13) represents the binding energy for a two-dimensional exciton, with the electron confined to $z=z_e$, and the hole confined to $z=z_h$, weighted by the probability of finding an electron at z_e and a hole at z_h, and averaged over the (z_e,z_h) configuration space.

III. SOLUTION TO THE TWO-DIMENSIONAL EXCITON PROBLEM

All that remains to complete the model is to obtain an expression for the two-dimensional exciton binding energy, $E_1^{(2D)}(Z)$, that occurs in Eq. (13). Here, we obtain three approximate forms for this quantity. In addition, we obtain a 15-parameter variational solution which, for the purpose of the present work, can be considered exact. The value of the approximate forms is that they can be easily implemented by others to calculate exciton binding energies without the need of repeating the calculations described below.

It is convenient to case Eq. (3) into dimensionless form. If we define $u=\rho/a_0$, $v=Z/a_0$, $E_1^{(2D)}(Z)=E_0 w(v)$, and $G(u;v)=a_0 g(\rho;Z)$, where $a_0=\epsilon\hbar^2/\mu_\parallel e^2$, and $E_0=\mu_\parallel e^4/2\epsilon^2\hbar^2$, we obtain the differential equation

$$\frac{1}{u}\frac{d}{du}\left[u\frac{dG}{du}\right]+\frac{2}{(u^2+v^2)^{1/2}}G-w(v)G=0 \; . \tag{14}$$

If $v=0$, Eq. (14) reduces to the differential equation for the two-dimensional hydrogen atom, whose ground-state solution is

$$G(u;0)=4e^{-2u} \; , \tag{15}$$

and we obtain $w(0)=4$. On the other hand, if $v\gg 1$, the potential energy term can be expanded as $2/(u^2+v^2)^{1/2}\sim 2/v-u^2/v^3$; thus Eq. (14) reduces to the two-dimensional harmonic oscillator equation, and hence

$$G(u,v\gg 1)=\frac{\sqrt{2}}{v^{3/4}}\exp(-u^2/v^{3/2}) \; , \tag{16}$$

with $w(v\gg 1)=2/v-2/v^{3/2}$. Therefore, exact results can be obtained in both limits.

A reasonably accurate variational wave function can be chosen that gives correct results for both $v\rightarrow 0$ and $v\gg 1$. We choose

$$G(u,v)=N\exp\{-\lambda[(u^2+v^2)^{1/2}-v]\} \; , \tag{17}$$

where $\lambda\rightarrow 2$ as $v\rightarrow 0$, and $\lambda\rightarrow v^{-1/2}$ as $v\rightarrow\infty$. The expectation value of the binding energy can be obtained as

$$\langle w(v)\rangle=-\lambda^2+\frac{4\lambda+4\lambda^4 v^2 E_1(2\lambda v)\exp(2\lambda v)}{1+2\lambda v} \; , \tag{18}$$

where $E_1(x)$ is the exponential integral.[21] Treating λ as a variational parameter, we choose the value that maximizes $\langle w(v)\rangle$ (i.e., minimizes the total energy). This variational approach is referred to below as approximation 1:

$$w(v)=\max_\lambda\langle w(v)\rangle \; . \tag{19}$$

Since the limiting values of λ are known for both $v\rightarrow 0$ and $v\gg 1$, it seems reasonable to evaluate $\langle w(v)\rangle$ with a simple functional form for $\lambda(v)$ that describes both limits correctly. A good choice is

$$\lambda_0(v)=2/(1+2\sqrt{v}) \; . \tag{20}$$

This approach has the desirable feature that Eq. (18) can be evaluated directly without finding its minimum. We refer to this result below as approximation 2:

$$w(v)=\langle w(v)\rangle_{\lambda=\lambda_0(v)} \; . \tag{21}$$

For comparison, we solved the eigenvalue equation, Eq. (14), using a 15-parameter variational wave function. For the purpose of this work, this 15-term variational solution can be considered exact. We developed also an expression for the binding energy as a ratio of two polynomials by fitting to the 15-parameter result over the range $0<v<1000$. The result is approximation 3:

$$w(v)=\frac{4+c_1 v+c_2 v^2}{1+d_1 v+d_2 v^2+d_3 v^3} \; , \tag{22}$$

with

$$\begin{aligned} c_1&=12.97 \; , \\ c_2&=0.7180 \; , \\ d_1&=9.65 \; , \\ d_2&=9.24 \; , \\ d_3&=0.3706 \; . \end{aligned} \tag{23}$$

In Fig. 1 we compare our approximation 1, the one-parameter variational result (dashed curve), with the 15-parameter "exact" result (solid curve). Agreement is excellent everywhere; the maximum deviation in w is 0.014,

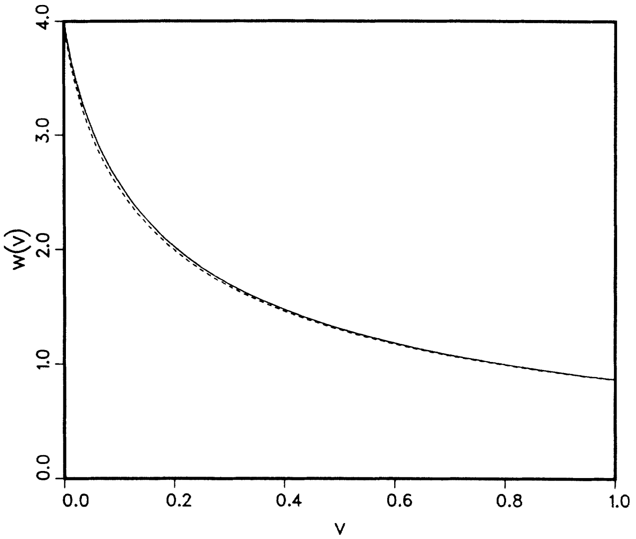

FIG. 1. Exciton binding energy $w(v)$ (normalized to the bulk binding energy E_0) for a two-dimensional system in which the electrons and holes are confined to planes separated by $z_e - z_h = a_0 v$. The solid curve corresponds to the full 15-parameter variational calculation; the dashed curve is the one-parameter variational result (approximation 1; see text).

which occurs at $v \sim 0.1$. To further compare our approximations, we show in Fig. 2 the relative errors $\Delta w / w$, where Δw is the difference between the exact result and an approximate result, plotted as functions of v on a logarithmic scale. Since approximations 1 and 2 are variational lower bounds, the corresponding relative errors are always positive. The error in approximation 3, on the other hand, oscillates in sign. The maximum absolute value of the errors for approximations 2 and 3 are $|\Delta w| = 0.063$ and 0.039, respectively. For GaAs quantum wells, the corresponding maximum error in the calculated exciton binding energy is on the order of 0.2 meV for approximation 2, and much less than this for the other approximations. This error is considerably less than the error in measuring the binding energy and on the order of the errors expected in the approximations made in developing Eq. (13).

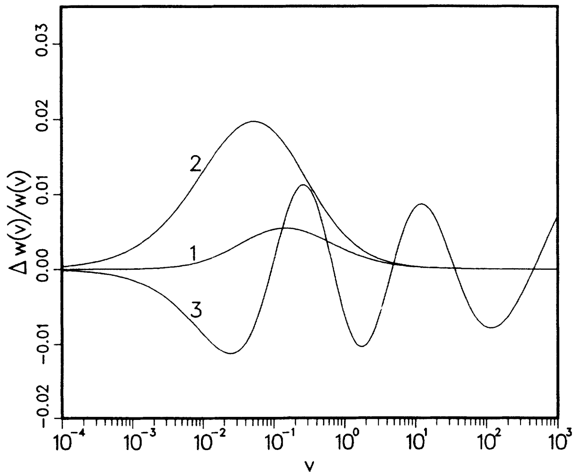

FIG. 2. Relative errors $\Delta w(v)/w(v)$ in the exciton binding energy for a two-dimensional system, in which the electrons and holes are confined to planes separated by $z_e - z_h = a_0 v$. Curves labeled 1, 2, and 3 correspond to approximations 1, 2, and 3, respectively (see text).

In terms of the dimensionless quantities discussed above, Eq. (13) may be rewritten as

$$E_{ij}^{B} = \int_{-\infty}^{\infty} dz_e dz_h E_0 |f_i^{(e)}|^2 |f_j^{(h)}|^2 w[(z_e - z_h)/a_0] \,, \tag{24}$$

where we have included the factor E_0 under the integral sign since it depends on the position-dependent effective masses.

IV. EXCITONS IN RECTANGULAR GaAs QUANTUM WELLS

As a simple check on the validity and accuracy of our method, we have calculated the binding energy of the ground-state heavy- and light-hole excitons in GaAs/$\mathrm{Al_{0.3}Ga_{0.7}As}$ quantum wells as functions of the well width, where the quantization direction is taken as (001). Since we compare these results with the results of Greene, Bajaj, and Phelps[4] and Priester, Allan, and Lannoo,[5] we use the same effective-mass parameters. They are as follows: For GaAs, $m_e = 0.067$, $m_{\mathrm{lh}\perp} = 0.08$, and $m_{\mathrm{hh}\perp} = 0.45$; for $\mathrm{Al_{0.3}Ga_{0.7}As}$, $m_e = 0.092$, $m_{\mathrm{lh}\perp} = 0.102$, and $m_{\mathrm{hh}\perp} = 0.51$. The conduction- and valence-band energy discontinuities are $\Delta_c = 322.8$ meV, and $\Delta_v = 57.0$ meV, respectively. The dielectric constant ϵ is 12.5. Our calculations of the exciton binding energies via Eq. (24) are made using the density-of-states reduced mass,[5] given by

$$\langle \mu_{\parallel}^{-1} \rangle = \int_{-\infty}^{\infty} dz_e |f_i^{(e)}(z_e)|^2 / m_e + \int_{-\infty}^{\infty} dz_h |f_j^{(h)}(z_h)|^2 / m_{h\parallel} \,, \tag{25}$$

in place of the z-dependent reduced masses.

In Fig. 3(a) we show the results for the ground-state heavy-hole exciton binding energies. Our results (solid line) are in very good agreement with the results of Ref. 4 (dot-dashed line) for wide wells, and with those of Ref. 5 (dashed line) for narrow wells. These results can be understood simply in terms of the approximations made by these authors. In the Greene-Bajaj-Phelps calculation, a flexible form (with several variational parameters) is chosen for the exciton envelope function. This function contains some dependence on the difference in electron and hole z coordinates, and therefore allows for correlated electron and hole motion along the quantization direction. This correlation is expected to be important for wide wells, in which the exciton retains some three-dimensional character. The fact that our formalism gives good results for wide wells implies that the assumption made following Eq. (9) is not as restrictive as it might appear.

As the well width decreases, both electron and hole envelope functions become compressed, and the Coulomb attraction between the electron and the hole results in an increase in the binding energy. However, for very narrow wells, the envelope functions "spill" over into the barrier, and their spatial extents actually begin to increase as the well width is decreased further. There is a maximum in the calculated binding energy corresponding to the onset of this spreading. Because Greene, Bajaj, and Phelps have neglected the effective-mass mismatch between the well and barrier materials, the well width at which their binding energy is a maximum is larger than what would result if the mismatch were included, as it is in our results and in those of Priester, Allan, and Lannoo.

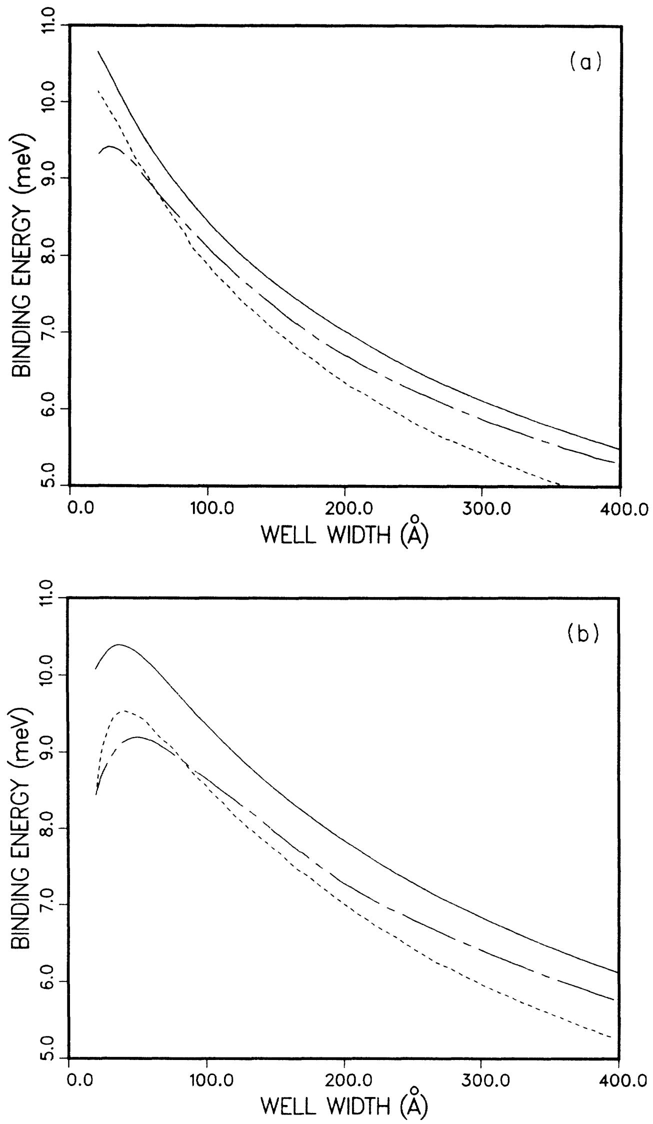

FIG. 3. Binding energies for (a) heavy-hole and (b) light-hole excitons in rectangular GaAs/$Al_{0.3}Ga_{0.7}As$ quantum wells as functions of the well width. Parameter values used in the calculation are given in the text. The solid curves were calculated using Eq. (24); the dot-dashed curves are from Greene, Bajaj, and Phelps (Ref. 4), and the dashed curves are from Priester, Allan, and Lannoo (Ref. 5).

On the other hand, the exciton envelope function chosen by Priester, Allan, and Lannoo is a simple exponential function of the radial coordinate; correlated electron-hole motion along z is neglected, and as a result they obtain less accurate results for wider wells. Since our results account for the effective-mass mismatch and also contain some z-correlation effects [through the dependence of the envelope function $g(\rho;Z)$ on the z coordinates], they reproduce accurately the expected behavior of the exciton binding energy throughout a wide range of quantum-well widths.

Figure 3(b) gives corresponding results for the ground-state light-hole exciton. The well width for which the binding energy is a maximum is about the same in our results as in those of Priester, Allan, and Lannoo. For wider wells, our calculated binding energies are closer to those obtained by Greene, Bajaj, and Phelps, although the agreement is not as favorable as for the heavy-hole exciton. Generally, the difference between our results and the results obtained elsewhere is between 0.2 and 0.5 meV for the heavy-hole exciton, and between 0.4 and 1 meV for the light-hole exciton, in accord with the error estimates made at the end of Sec. II.

V. EXCITONS IN ASYMMETRIC COUPLED QUANTUM WELLS

Structures containing coupled quantum wells are of increasing interest because of new electroabsorption and electrorefraction phenomena that occur in these structures.[13,14,22] Here, we use a system of asymmetric, coupled quantum wells as a test of our method by comparing calculated exciton binding energies with those determined from a treatment (see the Appendix) in which coupling of the two electron subbands by the electron-hole Coulomb interaction is included. In particular, this comparison provides a measure of the effects of violating the assumption [made following Eq. (9)] that the separations of electron and hole subband energies are large compared with the exciton binding energy.

Consider the coupled-well configuration shown in Fig. 4. Figure 4(a) shows an energy-level diagram for the configuration at zero field. If an external field is applied that points to the left, the energies of the lowest-energy electron states associated with each of the wells approach one another, whereas the lowest-energy hole state associated with the wide well remains well isolated in energy from other hole states for all field magnitudes. In Fig. 4(b), the field magnitude is equal to the resonance field F_r, for which these two electron states are in resonance, leading to a minimum splitting of the two states' energies. In each state, the electron is delocalized, i.e., has a significant probability of being in either of the wells. Beyond resonance, as in Fig. 4(c), electrons once again become localized in the individual wells.

We take the two GaAs quantum wells as having widths of 100 and 50 Å, respectively, bounded by $Al_{0.35}Ga_{0.65}As$, and with a 25-Å $Al_{0.35}Ga_{0.65}As$ potential barrier between the wells. Energy gaps and effective masses used in the calculations were taken from Refs. 23 and 24 (with linear interpolation of the effective-mass parameters for

$Al_{0.35}Ga_{0.65}As$). They are as follows: For GaAs, $m_e=0.067$, $m_{\text{lh}\perp}=0.08$, and $m_{\text{hh}\perp}=0.353$; for $Al_{0.35}Ga_{0.65}As$, $m_e=0.1206$, $m_{\text{lh}\perp}=0.0993$, and $m_{\text{hh}\perp}=0.370$. The conduction- and valence-band energy discontinuities are $\Delta_c=306$ meV, and $\Delta_v=131$ meV, respectively. The dielectric constant ϵ is 13.1. The heavy-hole–to–electron transitions, shown in Fig. 4, are the lowest energy electron-hole transitions supported by the coupled-well system when the external field points from the narrow to the wide well, and they are well isolated from other optical transitions. For the well and barrier parameters given above, the avoided crossing between the two electron energies occur at a field F_r of about 47 kV/cm; the splitting between electron subbands at this field is 6.6 meV.

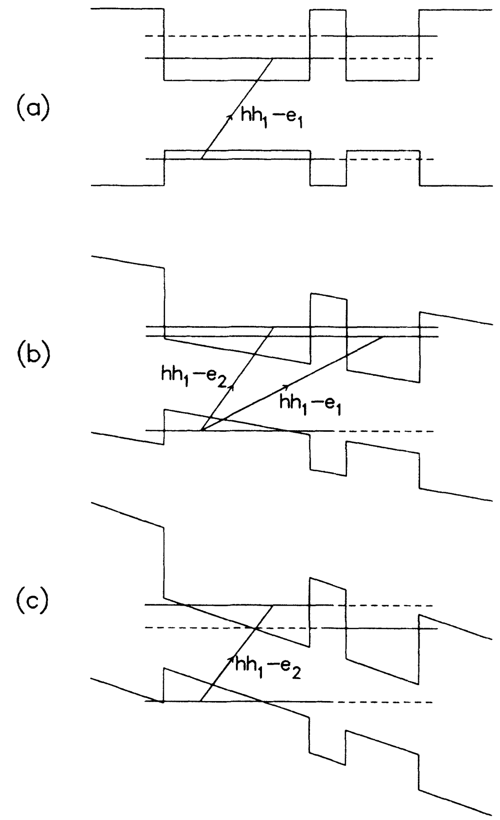

FIG. 4. Energy-band diagram for a $GaAs/Al_{0.35}Ga_{0.65}As$ asymmetric coupled-quantum-well system for three values of the applied field: (a) zero field, (b) resonance field, and (c) a field beyond the resonance field. The lowest-energy pair of electron levels (e_1,e_2) and the lowest-energy heavy-hole level (hh_1) are shown; solid lines indicate regions where the wave functions are large and dashed lines where the wave functions are small. The hh_1 state remains localized in the wide well for all electric fields. Arrows show allowed electron-hole transitions. The well widths are 100 and 50 Å, and the barrier width is 25 Å.

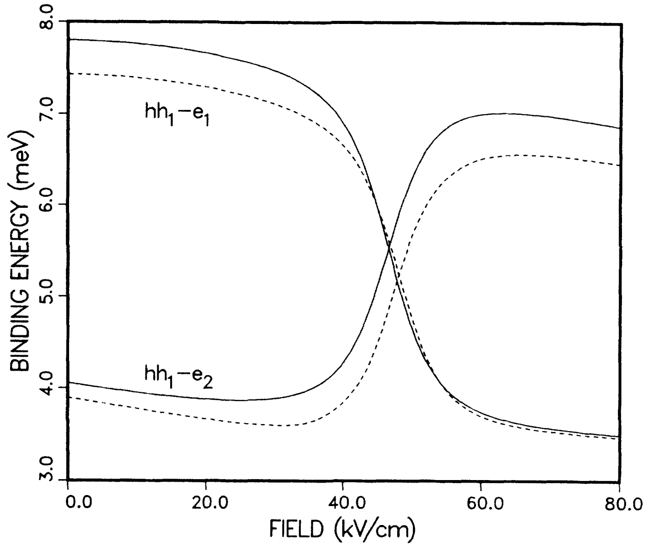

FIG. 5. Exciton binding energies vs electric field for the asymmetric coupled-quantum-well structure shown in Fig. 4. As the field is tuned through resonance, e_1 becomes localized in the narrow well and e_2 in the wide well, with a corresponding reversal in the exciton binding energies. The solid lines result from Eq. (24), and the dashed lines were obtained by using the coupled-subband treatment (with two electron subbands and one hole subband retained).

Electron and hole subband-edge energies and envelope functions were calculated by using the scattering phase-shift method in conjunction with the exact Airy-function solutions[25] of the effective-mass Schrödinger equations. In Fig. 5 we show the binding energies of the excitons associated with the two heavy-hole transitions depicted in Fig. 4, as functions of the external field. Solid and dashed lines in this figure correspond to results obtained with Eq. (24), our result, and Eq. (A2), the coupled-subband treatment, respectively. The hh_1-e_1 exciton has the electron in the wide well for fields well below F_r, and in the narrow well for fields well above F_r. For the hh_1-e_2 exciton, the situation is reversed. For all fields away from resonance, the exciton having both electron and hole in the same (i.e., wide) well has the highest binding energy and is the one observed optically. Near resonance, electrons associated with both excitons are likely to be found in either well; thus the binding energies for the two states are comparable. From the figure it is apparent that our approach gives a good description of these phenomena; the difference between binding energies calculated with Eq. (24) and with the coupled-subband method is less than 0.5 meV over the entire range of electric fields considered, in agreement with the error estimates given above.

Although the binding energies of the two excitons cross near the resonance field, the net electron-hole transition energies do not. In Fig. 6 we show these transitions energies plotted as functions of electric field with (solid lines) and without (dashed lines) the exciton binding energies. It is apparent from the figure that inclusion of the field-dependent exciton binding energies changes the apparent resonance field, i.e., the field of closest approach of the two transition energies. Thus it follows that the exciton binding energies should be included in order to obtain an accurate interpretation of experimental data in these structures.

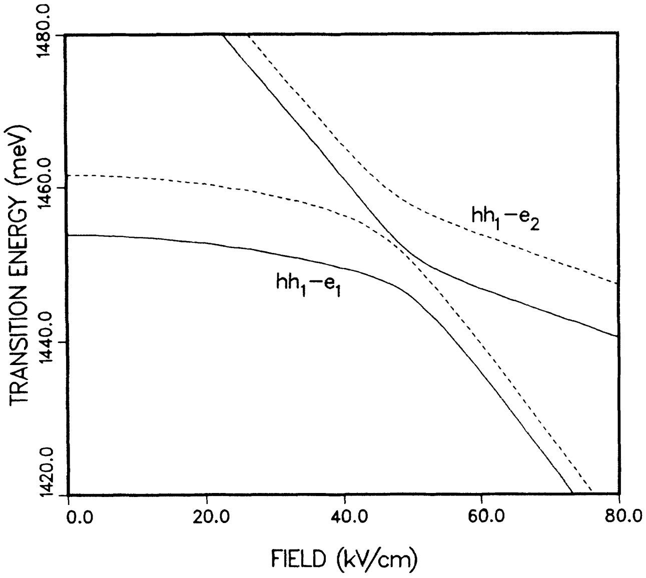

FIG. 6. Electron-hole transition energies for the structure of Fig. 4 with (solid lines) and without (dashed lines) the exciton binding-energy correction. The effect of subtracting the binding energies is to push the apparent crossing to higher electric fields.

VI. DISCUSSION AND CONCLUSIONS

We have presented a simple, general method for calculating exciton binding energies in quantum-confined semiconductor structures. Our main result is an expression for the binding energy as the integral of a prescribed function (the exciton binding energy for a system in which electrons and holes are confined to spatially separated planes) weighted by the squares of the electron and hole subband envelope functions. This result was obtained by choosing a form for the wave function similar to that used in the Born-Oppenheimer separation of electron and nuclear coordinates. Although in the latter case it is necessary to assume the existence of a small parameter (the ratio of electron to nuclear mass), such an assumption is not required in our treatment of the exciton problem because of a near cancellation of the terms $W_n^c(Z)$ in the expression for the exciton binding energy, Eq. (12). As a consequence, the simple result, Eq. (13) [or, equivalently, Eq. (24)], gives accurate results when applied to a variety of physical systems.

As examples of the applicability of the method, we calculated the binding energies for light- and heavy-hole excitons in rectangular GaAs/$Al_{0.3}Ga_{0.7}As$ quantum wells as functions of the well width. The results compare favorably with the corresponding results of Refs. 4 and 5. We also calculated the binding energies of excitons in a GaAs/$Al_{0.35}Ga_{0.65}As$ asymmetric coupled-quantum-well system. Very good agreement is obtained in comparison with results calculated using a coupled-subband approach. Both of these calculations have shown that the validity of our method extends well into a regime in which one of our assumption (that subband separations are large compared with exciton binding energies) is not strictly valid. Hence we feel that this assumption is not overly restrictive, and that the model, because of its generality, will be extremely useful for calculating binding energies in complex quantum-confined structures, such as superlattices, which we consider in the following paper.[16]

The main advantage of our approach is its computational simplicity. The result, Eq. (24), is very easy to incorporate into a computer code that calculates the electron and hole subband energies and envelope functions. Three different approximations (all quite accurate) for the prescribed function $w(v)$ have been given that allow rapid computation of this function. No additional differential equations need to be solved, nor variational minimizations performed. As an example of the computational advantage, the calculation reported in Sec. V for the asymmetric coupled-well system, using the coupled-subband approach, took well in excess of 1000 times the computer time needed to obtain the corresponding results using Eq. (24). Thus the method should prove extremely useful for parametric studies, in which well and barrier thicknesses and compositions, as well as external parameters, such as electric fields, are varied to optimize some desired effect, such as electroabsorption.

Generally speaking, other methods for calculating exciton binding energies fall into two categories. In the first, typified by Bastard *et al.*,[2] a specific form for the wave function is chosen, and the binding energy is calculated variationally. This method has the disadvantage that it is not general; the form of the wave function must be altered if the structure is changed. In the second category (typified by the coupled-subband treatment of the coupled-well system given in the Appendix), one integrates out the z coordinates to obtain an equation (or set of equations) for the radial component of the exciton envelope function. This approach is more general than the first, but it suffers from the disadvantage that one must solve a relatively complicated eigenvalue problem to obtain each binding energy. Also, in this approach, the exciton envelope function does not contain any dependence on z other than that contained in the subband envelope functions. As a result, correlated motion of the electron and hole along the quantization direction is neglected, and the partially three-dimensional nature of the exciton in wider wells is not properly characterized. Our method overcomes these deficiences in that it (a) is general, i.e., the result for the binding energy depends on the details of the structure only through the subband envelope functions, and (b) includes correlated electron-hole motion along the quantization direction in a natural manner.

In a study of the effects of strain on quantum-well optical spectra, Lee *et al.*[11] determined the binding energy via an equation similar to Eq. (A2) (with a single term), in which the effective radial potential $U_{ij}^{ij}(\rho)$ was replaced by $-e^2/\epsilon[\rho^2+\langle(z_e-z_h)^2\rangle]^{1/2}$, where $\langle(z_e-z_h)^2\rangle$ is averaged over the z coordinates. They then proceeded to solve the resulting second-order differential equation, formally identical to Eq. (14), using a variational wave function similar to Eq. (17). Their approach is similar to ours, in that the binding energy can be simply evaluated as an integral of some quantity over the z coordinates and is therefore computationally simple. However, there is no stated justification for replacing the effective radial potential (which depends on the details of the structure, electric fields, strain, etc.) by the simple form used. Also, Lee *et al.* do not give separately the results for the binding energies, nor do they compare these results with those obtained using other methods. Therefore it is difficult to assess the accuracy of their method. (This method also does not account for correlated electron-hole motion along z.)

Our study of the asymmetric quantum-well structure has provided a stringent test that extends the applicability of our method to a more complex system than the rectangular quantum well. It has revealed interesting excitonic phenomena that occur in these types of structures. As the field is tuned through the electron-subband resonance, the electron states become increasingly delocalized (until at resonance a given state's charge density is equally distributed between both wells) and then localized again, but with their roles reversed. Beyond resonance, the lowest-energy electron state is localized again, but with their roles reversed. Beyond resonance, the lowest-energy electron state is localized to the narrow well, and the next-lowest-energy state is in the wide well. Binding energies of excitons formed from the lowest-energy hole state (always in the wide well) and this pair of electron states show very strong field dependences as the system passes through resonance. The method presented in this paper reproduces the results of the more sophisticated coupled-subband treatment very well, although the latter treatment is necessary to quantitatively describe certain aspects of this system (such as the electric field at which the binding energies of the two excitons become equal). These results are of general significance since they show that our method is accurate for systems in which the electron and hole are spatially separated.

The main drawback in the present treatment is that valence-band coupling by off-diagonal terms in the Kohn-Luttinger Hamiltonian is not included. It has been shown[6–9] that including valence-band coupling adds about 1–2 meV to the binding energies of excitons in isolated, rectangular wells grown along a [001] direction. We feel that the lack of this correction is the dominant error in our calculations. The correction could be added perturbatively to the model in a manner analogous to the treatment of Ekenberg and Altarelli.[7] Even without it, we feel that our model, because of its generality, is a useful tool for examining the dependences of exciton binding energies on system parameters (such as well widths and electric fields) in complex quantum-confined structures.

ACKNOWLEDGMENTS

We thank John D. Bruno of Harry Diamond Laboratories for a careful and critical reading of the manuscript. A portion of this work was supported by Rome Air Development Center (RADC/ESOC), under Contract No. F19628-86-C-0059.

APPENDIX: COUPLED-SUBBAND TREATMENT OF EXCITON BINDING ENERGIES

The coupled-subband treatment of excitons in quantum wells is similar to that described in Refs. 8–10, where it is applied to coupling of subbands by the electron-hole Coulomb interaction in rectangular wells. We assume an excitonic wave function of the form:

$$\psi(\mathbf{r}_e,\mathbf{r}_h)=\sum_{i,j} f_i^{(e)}(z_e) f_j^{(h)}(z_h)\xi_{ij}(\rho) \ . \tag{A1}$$

The radial functions $\xi_{ij}(\rho)$ are to be determined, and the sum in Eq. (A1) is over all subbands that couple significantly with the subbands of interest.

By calculating the expectation value of Eq. (1) and requiring that the set of ξ_{ij} give a variational lower bound to the energy, we obtain the following set of effective radial equations:

$$\sum_{i',j'}\left[-\frac{\hbar^2}{2\mu^{ij}_{i'j'}}\nabla^2_{\parallel}+U^{ij}_{i'j'}(\rho)+(E_i^{(e)}+E_j^{(h)})\delta_{ii'}\delta_{jj'}\right]\xi_{i'j'}(\rho)=E\xi_{ij}(\rho) \ , \tag{A2}$$

where $(\mu^{ij}_{i'j'})^{-1}$ and $U^{ij}_{i'j'}(\rho)$ are integrals over z_e and z_h of the inverse parallel reduced mass and the electron-hole Coulomb interaction multiplied by the appropriate sets of electron and hole envelope functions, i.e.,

$$(\mu^{ij}_{i'j'})^{-1}=\int_{-\infty}^{\infty} dz_e f_{i'}^{(e)}(z_e) f_i^{(e)}(z_e)/m_e+\int_{-\infty}^{\infty} dz_h f_{j'}^{(h)}(z_h) f_j^{(h)}(z_h)/m_{h\parallel} \ , \tag{A3}$$

and

$$U^{ij}_{i'j'}=-\frac{e^2}{\epsilon}\int_{-\infty}^{\infty} dz_e dz_h f_{i'}^{(e)}(z_e) f_i^{(e)}(z_e) f_{j'}^{(h)}(z_h) f_j^{(h)}(z_h)/[\rho^2+(z_e-z_h)^2]^{1/2} \ . \tag{A4}$$

For the coupled-well system, we considered two terms in Eq. (A1) (i.e., the two electron states of interest and a single-hole state localized in the wide well). Properties of the ground-state exciton were calculated both by numerically integrating the set of Eqs. (A2) and searching for a bound state, and also, as a check, by using a variational set of wave functions, consisting of superpositions of exponential functions. In all cases, the calculated ground-state energies agreed to within a tenth of a percent. For the specific problem considered here, the exciton associated with the higher of the two electron subbands is "buried" in the continuum absorption associated with the lowest electron subband. Continuum solutions to Eqs. (A2) are obtained by numerical integration, and the exciton feature appears naturally as a Fano resonance[8] in the continuum absorption; the exciton energy was chosen as the energy for which the calculated absorption was a maximum.

---

[1] D. A. B. Miller, D. S. Chemla, T. C. Damen, A. C. Gossard, W. Wiegmann, T. Wood, and C. A. Burrus, Phys. Rev. B **32**, 1043 (1985).

[2] G. Bastard, E. E. Mendez, L. L. Chang, and L. Esaki, Phys. Rev. B **26**, 1974 (1982).

[3] S. Nojima, Phys. Rev. B **37**, 9087 (1988).

[4] R. L. Greene, K. K. Bajaj, and D. E. Phelps, Phys. Rev. B **29**, 1807 (1984).

[5] C. Priester, G. Allan, and M. Lannoo, Phys. Rev. B **30**, 7302 (1984).

[6] G. D. Sanders and Y.-C. Chang, Phys. Rev. B **32**, 5517 (1985).

[7] U. Ekenberg and M. Altarelli, Phys. Rev. B **35**, 7585 (1987).

[8] D. A. Broido and L. J. Sham, Phys. Rev. B **34**, 3917 (1986).

[9] G. E. W. Bauer and T. Ando, Phys. Rev. B **38**, 6015 (1988).

[10] J.-W. Wu, Phys. Rev. B **39**, 12 944 (1989).

[11] J. Lee, M. O. Vassell, E. S. Koteles, C. Jagannath, K. T. Hsu, G. J. Jan, C. P. Liu, and I. F. Chang, Phys. Rev. B **40**, 1703 (1989).

[12] J.-L. Zhu, D.-H. Tang, and J.-J. Xiong, Phys. Rev. B **39**, 8609 (1989); T. Hiroshima and K. Nishi, J. Appl. Phys. **62**, 3360 (1987); G. D. Sanders and K. K. Bajaj, J. Vac. Sci. Technol. B **5**, 1295 (1989).

[13] J. W. Little and R. P. Leavitt, Phys. Rev. B **39**, 1365 (1989).

[14] R. P. Leavitt, J. W. Little, and S. C. Horst, Phys. Rev. B **40**, 4183 (1989).

[15] E. E. Mendez, F. Agulló-Rueda, and J. M. Hong, Phys. Rev. Lett. **60**, 2426 (1988).

[16] R. P. Leavitt and J. W. Little, following paper, Phys. Rev. B **42**, 11 784 (1990).

[17] K. H. Yoo, L. R. Ram-Mohan, and D. F. Nelson, Phys. Rev. B **39**, 12 808 (1989). These authors have shown that inclusion of nonparabolicity via an eight-band $\mathbf{k}\cdot\mathbf{p}$ model has little effect on the ground-state energies of electrons and holes in quantum wells.

[18] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).

[19] A. Messiah, *Quantum Mechanics* (Wiley, New York, 1963), Vol. II, pp. 781-793.

[20] M. Born and J. R. Oppenheimer, Ann. Phys. (Leipzig) **84**, 457 (1927).

[21] W. Gautschi and W. F. Cahill, in *Handbook of Mathematical Functions,* Natl. Bur. Stand. Appl. Math. Ser. No. 55, edited by M. Abramowitz and I. Stegun (U.S. GPO, Washington, D.C., 1964), p. 228.

[22] K. W. Steijn, R. P. Leavitt, and J. W. Little, Appl. Phys. Lett. **55**, 383 (1989).

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

[24] H. C. Casey and M. B. Panish, *Heterostructure Lasers, Part B: Materials and Operating Characteristics* (Academic, New York, 1978).

[25] E. J. Austin and M. Jaros, Phys. Rev. B **31**, 5569 (1985).