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Wannier excitons in semiconductor quantum wells with small valence-band offsets: A generalized variational approach

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(Received 11 June 1987; revised manuscript received 18 January 1988)

The ground-state and binding energy of a Wannier exciton in a quantum well with a small valence-band offset are calculated by generalizing the variational approach normally used to study excitons in $GaAs/Al_xGa_{1-x}As$ quantum wells. The central issue is to properly include the additional confinement of the hole caused by the electron-hole Coulomb interaction in the direction perpendicular to the quantum-well interface. In addition to the relative motion part of the exciton wave function, the envelope function of the hole in that direction is also determined variationally. The application of this method to II-VI–compound semiconductor quantum wells studied in recent experiments is discussed.

There is strong experimental evidence from recent optical spectroscopy that among II-VI–compound semiconductor heterostructures the band-gap discontinuity in a $CdTe/Cd_{1-x}Mn_xTe$, $ZnSe/Zn_{1-x}Mn_xSe$, or CdTe/ZnTe superlattice is accommodated in such a way that the valence-band offset is rather small.[1–5] In terms of excitonic properties, which may be a source of optical device applications, this is an intriguing situation as it implies the presence of a quasi-two-dimensional (2D) electron interacting with a quasi-three-dimensional (3D) hole. From a fundamental point of view, study of such excitons can provide useful characterization of the electronic states if sufficiently reliable theoretical insight is available. However, most of the existing variational theories on excitons in $GaAs/Al_xGa_{1-x}As$ quantum wells in the envelope function approximation[6–8] have been constructed on the basis that the entire exciton is strongly confined by the band-gap discontinuities, i.e., the barrier heights in both conduction band (V_e^0) and the valence band (V_h^0) should be large compared with the exciton binding energy, the latter given by the effective Rydberg. In the wide-gap II-VI–compound semiconductor heterostructures mentioned above, V_h^0 is typically comparable to, or even smaller than, the excitation binding energy [in $CdTe/Cd_{1-x}Mn_xTe$ for example, the large Zeeman effects which can be induced in a dilute magnetic semiconductor may even reduce the effective barrier height to zero or slightly below zero (type II) in an external magnetic field[9,10]] so that the applicability of the usual theory to these structures is questionable. In this paper we extend the variational approach in a particular way to derive accurate solutions for excitons in this type of quantum well where one quasiparticle is weakly bound.

Within the effective-mass approximation, the exciton Hamiltonian in a single quantum well of width L can be written as (after subtracting the constant energy gap of the well material)

$$H=\sum_{i=e,h}[p_{zi}^2/2m_i+V_i^0\Theta(|z_i|-L/2)]+p_\perp^2/2\mu - e^2/\epsilon[r_\perp^2+(z_e-z_h)^2]^{1/2}$$
$$\equiv h_e(z_e)+h_h(z_h)+p_\perp^2/2\mu-e^2/\epsilon[r_\perp^2+(z_e-z_h)^2]^{1/2}\ , \tag{1}$$

where m_e and m_h are the electron and the hole effective masses in the z direction (superlattice growth axis), μ and $\mathbf{r}_\perp$ are the reduced mass and the relative coordinate in the xy plane, and ϵ is the background dielectric constant. With appropriate numerical values assigned to these parameters, Eq. (1) is valid for describing rectangular well heterostructures of any material composition. We employ a notation in this paper where the exciton binding energy E_B as a result of the electron-hole Coulomb in-

teraction is defined by writing the energy eigenvalue of Eq. (1) as

$$E_{ex}=E_e^0+E_h^0-E_B\ , \tag{2}$$

where E_e^0 and E_h^0 are eigenvalues of $h_e(z_e)$ and $h_h(z_h)$, respectively, and E_{ex} is the total exciton energy (less the band gap of the well material). An exact solution to Eq. (1) is not possible. The common practice of finding approximate solutions is a variational approach in the envelope function approximation by using separable trial wave functions of the form[6-8]

$$\Psi(r_\perp,z_e,z_h)=\psi(z_e)\psi(z_h)\phi_{e\text{-}h}(r_\perp,z_e-z_h)\ . \tag{3}$$

As is easily seen from this expression, the one-particle function ψ_e (ψ_h) describes the motion of the electron (hole) in the z direction with respect to the quantum well, while the relative motion between the electron and the hole is contained in $\phi_{e\text{-}h}$. So far, in applying the theory to type-I heterostructures of GaAs/Al_xGa_{1-x}As and other III-V–compound quantum wells, both ψ_e and ψ_h are taken to be the one-dimensional solutions of $h_e(z_e)$ and $h_h(z_h)$, respectively. However, this approach loses validity in the case of those II-VI quantum wells where the valence-band offsets are demonstrably small and exciton binding energies relatively large.[1,2] In these systems, the electron is tightly confined inside the well in a quasi-two-dimensional form so that the Coulomb potential induced by its presence is actually significantly enhanced in the z direction, i.e., the confinement of the hole to the well has a large Coulomb contribution. In other words, if the "bare" quantum well in the valence band is shallow, ψ_h should be much more tightly bound than the simple solution of $h_h(z_h)$ predicts, and therefore should be determined with Coulomb interaction properly taken into account.

The relative part of the wave function $\phi_{e\text{-}h}$ can be chosen to be of the form of the solution to the hydrogen-atom problem in either three[7] or two dimensions.[8] The former is generally more accurate especially for systems deviating from the quasi-two-dimensional limit. To be specific, we follow Ref. 7 and use the expression

$$\phi_{e\text{-}h}(r_\perp,z)^{1/2}=c\ \exp[-(r_\perp^2+z^2)^{1/2}/\lambda] \tag{4}$$

to present results in this paper, although the following discussions are applicable to both types of choice of a relative function. Some results from a similar calculation are briefly summarized in Ref. 10 where the additional complexity of effective-mass anisotropy was also taken into account.

In performing the variational calculation for excitons in GaAs/Al_xGa_{1-x}As quantum wells, $\phi_{e\text{-}h}$ is the only part containing variational parameters [such as λ in Eq. (4)]. As already noted in the case of a small valence- or conduction-band offset ψ_h (or ψ_e) needs to be determined more accurately if strong excitonic effects are present.

We generalize the above variational approach by starting with an exciton trial wave function of the same form as in Eq. (3), but then determine *both* $\psi_h(z_h)$ and $\phi_{e\text{-}h}$ variationally. The influence of the Coulomb interaction on the motion of the hole in the z direction is included by assuming $\psi_h(z_h)$ to be the solution to an "effective quantum well" (EQW) of the same width L and an effective barrier V_h, which represents the combined effective confinement for the hole arising from its bare quantum well (V_h^0) and the electron-hole potential. The quantity V_h is used as an additional variational parameter. For simplicity, $\psi_e(z_e)$ is still taken to be the solution of $h_e(z_e)$ without losing appreciable accuracy when the condition $V_e^0 \gg E_B$ is satisfied.

Before detailing our results, we note that proper choice of both the general form of the hole envelope function ψ_h and the degree of variational freedom is the key in achieving meaningfully accurate results. For example, as shown below, our choice of the variational function consistently yields better results (lower exciton interband energy) than the traditional approach to GaAs/Al_xGa_{1-x}As quantum wells (Ref. 7). Furthermore, the method compares favorably also with other choices of $\psi_h(z_h)$ with a simple analytical form. As an illustration, we found that results obtained by taking $\psi_h(z_h)$ as a Gaussian wave packet with an adjustable size [i.e., $\psi_h(z)\propto\exp(-\alpha^2z^2)$ with α being a variational parameter] is generally even worse than those from using the "fixed" $\psi_h(z_h)$ of Ref. 7.

The total exciton interband energy (less the band gap of the well material) as the eigenvalue to the Hamiltonian in Eq. (1) is, making the variational parameters explicit,

$$\begin{aligned}E_{ex}(V_h,\lambda)&=\int dz_e\int dz_h\int d^2r_\perp\Psi^*(\mathbf{r}_\perp,z_e,z_h)H_{ex}\Psi(\mathbf{r}_\perp,z_e,z_h)\\&\equiv E_e^0+E_h^0-E_B(V_h,\lambda)\ ,\end{aligned} \tag{5}$$

where the exciton wave function is normalized through the choice of the constant c in Eq. (4). Note that, in employing Eq. (5), the variational parameter V_h will be included only in defining the trial function ψ_h, while the operator h_h always takes on its form defined by the valence-band "natural quantum well" (V_h^0) in Eq. (1).

After some algebraic manipulations, Eq. (5) can be written explicitly as

$$\begin{aligned}E_{ex}=E_e^0+E_h+(\hbar^2/2\mu\lambda^2)(I_1-I_2+I_1^e+I_1^h)/I_2\\-(e^2/\epsilon\lambda)I_1/I_2\ ,\end{aligned} \tag{6}$$

where the second term is defined by

$$\begin{aligned}E_h=\int dz_e\,|\psi(z_e)|^2\int dz_h[\psi(z_h)h_h(z_h)\psi(z_h)]\\\times\int d^2r_\perp\,|\phi_{e\text{-}h}(r_\perp,z_e-z_h)|^2\end{aligned} \tag{7}$$

which, in our refined calculation, is in general different from the eigenvalue E_h^0 of $h_h(z_h)$. Other quantities in Eq. (6) are defined by

$$\begin{aligned}I_n=(\lambda/\pi)\int_{-\infty}^{\infty}dQ[1+(Q\lambda/2)^2]^{-n}\\\times\int dz_e\exp(iQz_e)\,|\psi_e(z_e)|^2\\\times m\int dz_h\exp(-iQz_h)\,|\psi_h(z_h)|^2\ ,\end{aligned} \tag{8}$$

for I_1 and I_2, and

$$I_1^e=(\lambda/\pi)\int dQ[1+(Q\lambda/2)^2]^{-1} \times\int dz_e\, Qz_e \sin(Qz_e)\,|\psi_e(z_e)|^2 \times\int dz_h \exp(-iQz_h)\,|\psi_h(z_h)|^2 , \quad (9)$$

and

$$I_1^h=(\lambda/\pi)\int dQ[1+(Q\lambda/2)^2]^{-1} \times\int dz_e \exp(iQz_e)\,|\psi_e(z_e)|^2 \times\int dz_h\, Qz_h \sin(Qz_h)\,|\psi_h(z_h)|^2 . \quad (10)$$

With the specific forms of ψ_e and ψ_h in our calculation, the integrals over z_e and z_h inside Eqs. (8)–(10) can all be expressed as elementary functions. By rewriting Eq. (7) as

$$E_h=\frac{\lambda}{\pi}\int dQ[1+(Q\lambda/2)^2]^{-1} \times\int dz_e\,|\psi_e(z_e)|^2\exp(iQz_e) \times\int dz_h \exp(-iQz_h) \times[\psi_h(z_h)h_h(z_h)\psi_h(z_h)]I_2 ,$$

Eqs. (7)–(10) can be evaluated by numerical integration of the remaining variable Q. This procedure may reduce the computing expenditure of calculating E_{ex} substantially and should be very useful when more degrees of variational freedom are introduced for improving the calculation.

We now illustrate some numerical results of this refined variational approach by examining the range of valence-band offsets where substantial improvements by our approach are in evidence. We use material parameters which are roughly representative of II-VI heterostructures such as $CdTe/Cd_{1-x}Mn_xTe$ with $x=0.20$–0.30;[3,10,11] $m_e=0.1m_0$, $m_h=0.5m_0$, $\epsilon=9$, and $V_e^0+V_h^0=E_g(x)-E_g(0)=400$ meV. The exciton binding energy in a bulk material for these parameters is $E_B^{3D}=14$ meV. Complications arising from the finite lattice mismatch, such as corrections to band energies by the hydrostatic and uniaxial strain, and mass anisotropies, are not included since they can be readily taken into account in this particular case. The well width is taken to be $L=50$ Å which is somewhat smaller than the exciton Bohr radius of the bulk material.

Figure 1 shows the calculated total exciton variational ground-state energy (interband energy less the band gap of well material) in the range of valence-band offset $0\le V_h^0\le 60$ meV (i.e., including the type-I–type-II cross over limit). A direct comparison is made with the result obtained from a calculation along the lines of Ref. 7 where the fixed value $V_h=V_h^0$ has been used (dashed line).

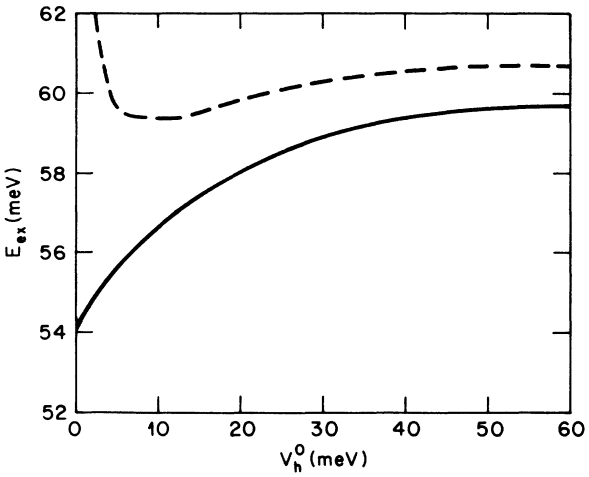

FIG. 1. The exciton interband energy E_{ex} evaluated from Eq. (6) as a function of the valence-band barrier V_h^0. The dashed line indicates the result following the approach in Ref. 7. Parameters are given in the text.

The distinct difference shows clearly how the electron-hole Coulomb interaction influences the valence-band confinement; indeed, the conventional approach breaks down as $V_h^0\to 0$.

The influence of varying valence-band offset on the exciton binding energy is shown in Fig. 2 for the same set of parameters. Even at $V_h^0=0$, our calculation predicts a significant enhancement reflecting the influence of the quasi-2D electron. Comparison with the conventional calculation (dashed line) again shows pronounced differences. On increasing V_h^0, E_B saturates to a value which is roughly twice that of E_B^{3D} as a consequence of the finite well width L in our calculation. These physical considerations, and direct application of these calculations to recent experimental results obtained by photoluminescence excitation spectroscopy in the

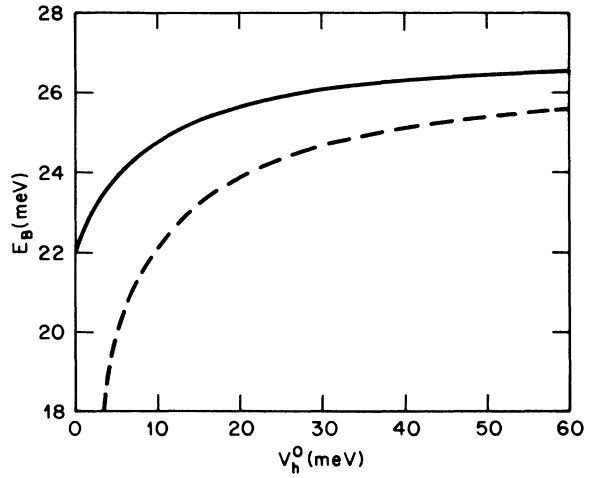

FIG. 2. The exciton binding energy E_B as defined in Eq. (2), calculated as a function of V_h^0. The result following Ref. 7 is plotted as a dashed line. Parameters are the same as in Fig. 1.

$CdTe/Cd_{1-x}Mn_xTe$ system, suggest that in characterizing such quantum wells with excitons and small valence-band offsets, our calculation may have similar accuracy as those for $GaAs/Al_xGa_{1-x}As$ quantum wells (few meV). Finally, we note that within these limits our model should also be useful for weakly type-II structures.

This work is supported by the Chester Davis Foundation (Indiana University), the National Science Foundation Grant No. DMR-8704210 (University of Tennessee), and the National Science Foundation Grant No. ECS-86-11106 (Brown University).

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