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Binding energies of excitons in semiconductor quantum wells: Quantum subband interference effect

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The set of eigenequations for determining the energy levels and wave functions of Wannier excitons in a semiconductor quantum well is derived by use of Green's-function theory. These equations form a matrix labeled by the quantum-well subband index of the exciton. The coupling between excitons of different subband indices is included for the first time through the nondiagonal elements of the electron-hole Coulomb interaction. We found that this quantum interference effect represents a significant modification to calculated values of exciton binding energies.

In recent years, optical properties of semiconductor quantum wells have received considerable research interests both experimentally and theoretically. Measurements on energy levels and absorption coefficients of interband excitons in this type of novel structure showed clear evidence of multiple subbands due to the quantum confinement of electrons and holes by the band-edge discontinuities at the well interfaces.[1] It has been well established that the binding energies of excitons in quantum wells are significantly enhanced from the values in bulk materials as a result of the confined carrier motion in the direction perpendicular to the well interfaces, and depend largely on the structural parameters of the system such as the well thickness, energy band-gap discontinuity, and band offset.[2-8] In comparing with experimental observations, theoretical calculations of exciton binding energies have played an important role in determining the characteristics of such systems. In this paper, we present an improved solution to excitonic states in quantum wells by including, for the first time, the quantum-mechanical coupling between different subband energy levels.

The early theories on the binding energies[5,6] and oscillator strengths[9-11] of excitons in quantum wells are semiclassical in nature. An exciton is regarded as a pair of carriers (electron and hole), each specified by its quantum-well subband index, bound together by the electron-hole Coulomb interaction. In calculating optical transition properties of the system, excitons with different subband indices are treated separately. The whole spectrum is the simple sum of contributions from all these uncorrelated subband branches. This type of approach is equivalent to taking the diagonal approximation in the exact quantum-mechanical matrix formalism. The nondiagonal elements of the Coulomb interaction matrix give rise to couplings between different subband branches of excitons. We call this the "quantum subband interference effect" (QSIE). Recently, a number of authors studied the valence-band mixing effect in calculating the binding energies of quantum-well excitons.[12-18] Their theories take into account the mixing between the different degenerate semiconductor valence bands (the heavy-hole and light-hole bands), but still ignore the mixing between different subbands within the same valence band. In the rest of this paper, we derive a solution to QSIE within the simple two-band model using Green's-function methods and illustrate the enhancement of exciton binding energies due to this effect. We found that, for typical quantum wells, the subband interference effect gives rise to significant contributions in the calculated values of exciton binding energies.

We first introduce some definitions concerning second-quantized operators. The wave-function operator consists of two components of the conduction band and the valence band,

$$\Psi(\mathbf{r},z)=\Psi_c(\mathbf{r},z)+\Psi_v(\mathbf{r},z)\ , \tag{1a}$$

$$\Psi_c(\mathbf{r},z)=\sum_{n,\mathbf{k}} c_{n,\mathbf{k}}\frac{1}{\sqrt{A}}u_c(\mathbf{r})\phi_n^e(z)\ , \tag{1b}$$

$$\Psi_v(\mathbf{r},z)=\sum_{m,\mathbf{k}} d_{m,\mathbf{k}}\frac{1}{\sqrt{A}}u_v(\mathbf{r})\phi_m^h(z)\ , \tag{1c}$$

where $c_{n,\mathbf{k}}$ ($d_{m,\mathbf{k}}$) is the destruction of the electron (hole) with subband index n (m) and in-plane wave vector $\mathbf{k}$, $u_c(\mathbf{r})$ [$u_v(\mathbf{r})$] the periodic part of the crystal Bloch function, and $\phi_n^e(z)$ [$\phi_m^h(z)$] the subband envelope function defined as the solution to the one-dimensional quantum-well potential in the conduction (valence) band. The interband optical current operator is readily given by

$$j_\mu=w_0\sum_{n,m}S_{n,m}\sum_{\mathbf{k}}(c_{n,\mathbf{k}}d_{m,-\mathbf{k}}+d_{m,-\mathbf{k}}^\dagger c_{n,\mathbf{k}}^\dagger)\ , \tag{2}$$

where

$$w_0=\langle c|j_\mu|v\rangle \tag{3}$$

is the one-particle optical matrix element, and

$$S_{nm}=\int dz\,\phi_n^e(z)\phi_m^h(z) \tag{4}$$

is the overlap integral between subband envelope functions. The total Hamiltonian of the system can be written as

$$H=\sum_{n,\mathbf{k}}\left[E_n^e+\frac{k^2}{2m_e}\right]c_{n,\mathbf{k}}^\dagger c_{n,\mathbf{k}}+\sum_{m,\mathbf{k}}\left[E_m^h+\frac{k^2}{2m_h}\right]d_{m,\mathbf{k}}^\dagger d_{m,\mathbf{k}}+V_{e\text{-}h}\ , \tag{5}$$

where E_n^e and E_m^h are subband energy eigenvalues, m_e and m_h effective masses, and the last term in the equation is the electron-hole Coulomb interaction operator

$$V_{e\text{-}h}=\frac{1}{A}\sum_{\mathbf{q}}\sum_{n,m}\sum_{n',m'}V_{nn'}^{mm'}(\mathbf{q})\sum_{\mathbf{k},\mathbf{k}'}c_{n,\mathbf{k}+\mathbf{q}}^\dagger c_{n',\mathbf{k}}\times d_{m,\mathbf{k}'}^\dagger d_{m',\mathbf{k}'}\ , \tag{6}$$

where

$$V_{nn'}^{mm'}(\mathbf{q})=-\frac{2\pi e^2}{\epsilon q}\int dz\int dz'\,e^{-q|z-z'|}\phi_n^e(z)\phi_{n'}^e(z)\times\phi_m^h(z')\phi_{m'}^h(z')\ . \tag{7}$$

The optical-absorption rate $A(\omega)$ is related to the current-current correlation function $\Pi(i\omega)$. The expressions are

$$\Pi(i\omega)=-\frac{1}{A}\int_0^\beta d\tau\,e^{i\omega\tau}\langle T_\tau[j_\mu(\tau)j_\mu(0)]\rangle \tag{8}$$

and

$$A(\omega)=-2\,\mathrm{Im}\Pi(i\omega\to\omega+i\delta)\ , \tag{9}$$

where, in Eq. (8), $i\omega$ is the Matsubara frequency on the imaginary axis, β is the inverse temperature, and T_τ is the time ordering operator. The time-dependent current operator is related to the Hamiltonian in Eq. (5) by $j_\mu(\tau)=e^{H\tau}j_\mu e^{-H\tau}$. We evaluate Eq. (8) following similar procedures as those developed by Mahan[19] in obtaining solutions for systems of bulk semiconductors, while noting that subband indices have to be arranged correctly in the formulas for quantum-well systems. The derivation is briefly summarized in the following.

The solution to Eq. (8) can be formally expressed as

$$\Pi(i\omega)=w_0\sum_{n,m}S_{nm}\frac{1}{A}\sum_{\mathbf{k}}\frac{1}{i\omega-E_g-E_{nm}(k)}\Gamma_{nm}(\mathbf{k},i\omega)\ , \tag{10}$$

where E_g is the energy band gap of the quantum-well material,

$$E_{nm}(k)=E_n^e+E_m^h+\frac{k^2}{2\mu}\ ,$$

$$\frac{1}{\mu}=\frac{1}{m_e}+\frac{1}{m_h}\ ,$$

and the vertex function $\Gamma_{nm}(\mathbf{k},i\omega)$ introduced above satisfies the following coupled integral equation:

$$\Gamma_{nm}(\mathbf{k},i\omega)=w_0S_{nm}+\frac{1}{A}\sum_{\mathbf{k}'}\sum_{n',m'}V_{nn'}^{mm'}(\mathbf{k}-\mathbf{k}')\times\frac{1}{i\omega-E_g-E_{n'm'}(k')}\times\Gamma_{n'm'}(\mathbf{k}',i\omega)\ . \tag{11}$$

To solve Eq. (11), we define a set of auxiliary functions in the real space:

$$P_{nm}(\mathbf{r},i\omega)=\frac{1}{A}\sum_{\mathbf{k}}\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{i\omega-E_g-E_{nm}(k)}\Gamma_{nm}(\mathbf{k},i\omega)\ , \tag{12}$$

so the correlation function in Eq. (10) can be directly expressed in terms of the values of $P_{nm}(\mathbf{r},i\omega)$ at $\mathbf{r}=\mathbf{0}$:

$$\Pi(i\omega)=w_0\sum_{n,m}S_{nm}P_{nm}(\mathbf{r}=\mathbf{0},\ i\omega)\ . \tag{13}$$

It is easy to verify from Eqs. (11) and (12) that these auxiliary functions are solutions of the following coupled differential equations:

$$(i\omega-E_g-E_n^e-E_m^h+\tfrac{1}{2}\mu^{-1}\nabla^2)P_{nm}(\mathbf{r},i\omega)-\sum_{n',m'}V_{nn'}^{mm'}(\mathbf{r})P_{n'm'}(\mathbf{r},i\omega)=w_0S_{nm}\delta^2(\mathbf{r})\ , \tag{14}$$

where

$$V_{nn'}^{mm'}(\mathbf{r})=-\frac{e^2}{\epsilon}\int dz\int dz'\frac{\phi_n^e(z)\phi_{n'}^e(z)\phi_m^h(z')\phi_{m'}^h(z')}{[r^2+(z-z')^2]^{1/2}} \tag{15}$$

is just the Fourier transform of Eq. (7). Note that each pair of (n,m) should be regarded as a single index for specifying a particular branch of excitons between given electron and hole subbands. So Eqs. (11) and (14) are both matrix equations coupled by the nondiagonal elements of Coulomb interaction. From Eq. (9), the absorption rate

$$A(\omega)=w_0\sum_{n,m}S_{nm}[-2\,\mathrm{Im}P_{nm}(\mathbf{r}=\mathbf{0},\ \omega+i\delta)] \tag{16}$$

is expressed as a sum of contributions from all subband branches. However, different branches of excitons are coupled to each other and should be solved simultaneously. Clearly, the solutions we presented here are formally exact compared to the diagonal approximation used in previous theories.

The function $P_{nm}(\mathbf{r},i\omega)$ can in principle be expanded in terms of the eigenfunctions of the corresponding set of homogeneous equations:

$$-\tfrac{1}{2}\mu^{-1}\nabla^2\phi_j^{nm}(\mathbf{r})+\sum_{n',m'}V_{nn'}^{mm'}(\mathbf{r})\phi_j^{n'm'}(\mathbf{r})=-E_B^{nm}(j)\phi_j^{nm}(\mathbf{r})\ , \tag{17}$$

where the index j denotes the in-plane degrees of freedom of both bound states and continuum states. The exciton binding energy $E_B^{nm}(j)$ is given by the eigenvalue (up to a minus sign) in this equation. We investigate qualitatively the contributions from the QSIE to the binding energies by considering a specific example below.

For simplicity, we truncate the matrix equation by keeping only subband levels of $n,m \leq 2$, and solve the states with the lowest in-plane quantum number $j=0$. For quantum-well structures with inverse symmetry in the z direction, Eq. (17) reduces into two coupled equations:

$$[-\tfrac{1}{2}\mu^{-1}\nabla^2+V_{11}^{11}(\mathbf{r})]\phi^{11}(\mathbf{r})+V_{12}^{12}(\mathbf{r})\phi^{22}(\mathbf{r}) = -E_B^{11}\phi^{11}(\mathbf{r}) \, , \qquad (18)$$

$$[-\tfrac{1}{2}\mu^{-1}\nabla^2+V_{22}^{22}(\mathbf{r})]\phi^{22}(\mathbf{r})+V_{21}^{21}(\mathbf{r})\phi^{11}(\mathbf{r}) = -E_B^{22}\phi^{22}(\mathbf{r}) \, . \qquad (19)$$

In the diagonal approximation used so far, the above equations are typically solved by variational methods.[5,6] To calculate the interference correction to the first order, we use the variational wave functions for uncoupled energy levels from Ref. 6:

$$\phi^{11}(\mathbf{r})=\left[\frac{2}{\pi}\right]^{1/2}\frac{1}{\lambda_1}e^{-r/\lambda_1} \, , \qquad (20)$$

$$\phi^{22}(\mathbf{r})=\left[\frac{2}{\pi}\right]^{1/2}\frac{1}{\lambda_2}e^{-r/\lambda_2} \, , \qquad (21)$$

with λ_1 and λ_2 being variational parameters. In terms of these wave functions, the binding energies are

$$E_B^{11}=-\int d^2r\,\phi^{11}(\mathbf{r})[-\tfrac{1}{2}\mu^{-1}\nabla^2+V_{11}^{11}(\mathbf{r})]\phi^{11}(\mathbf{r}) - \int d^2r\phi^{11}(\mathbf{r})V_{12}^{12}(\mathbf{r})\phi^{22}(\mathbf{r}) \qquad (22)$$

and

$$E_B^{22}=-\int d^2r\,\phi^{22}(\mathbf{r})[-\tfrac{1}{2}\mu^{-1}\nabla^2+V_{22}^{22}(\mathbf{r})]\phi^{22}(\mathbf{r}) - \int d^2r\phi^{22}(\mathbf{r})V_{21}^{21}(\mathbf{r})\phi^{11}(\mathbf{r}) \, . \qquad (23)$$

In each of the above equations, the first term gives the binding energy in the uncoupled limit, while the second term represents the interference correction. Note that this second term gives identical enhancement to exciton binding energies in both $n=1$ and $n=2$ levels. Of course, this conclusion is based on the simplifying assumptions we made above.

As an illustration, the above approach is applied to obtain numerical solutions for a system of GaAs/Ga$_{1-x}$Al$_x$As heterostructure with Al concentration $x=25\%$. The parameters are $m_e=0.067m_0$, $m_h=0.34m_0$, background dielectric constant $\epsilon=12.5$, and quantum-well barrier heights $V_e=214$ meV and $V_h=161$ meV. The numerical results are plotted in Figs. 1 and 2, respectively. The dashed line shows the results obtained in the uncoupled limit (only the first term on the right side of the equation). In the range of $L=60-200$ Å, the interference term presents a significant correction of 20–25 %. On reducing the well thickness, the correction term becomes smaller, as a manifestation that the $n=2$ subband wave function tends to be squeezed out of the well and eventually merge into the continuum states.

Finally, we conclude by addressing the relevance of the theory presented above to experiments. The QSIE predicted in this paper is real and free from unreliable assumptions. Including this effect in the calculation should improve the agreement between theory and experiment if other effects are properly taken into account and correct values of quantum-well parameters are used. In reality, however, the comparison between theory and experiment

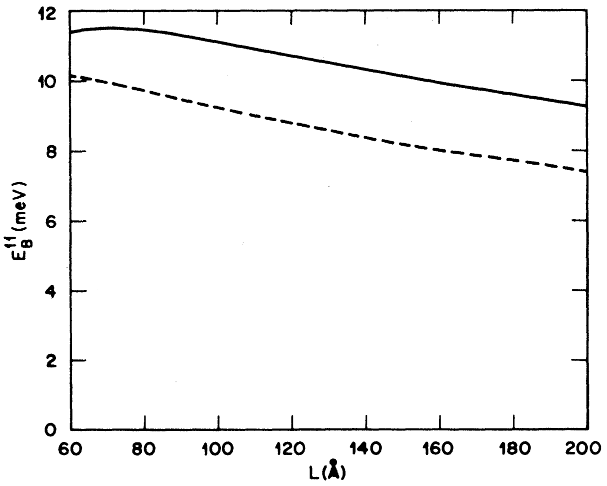

FIG. 1. The binding energy of excitons in $(n,m)=(1,1)$ subbands calculated from Eq. (22), plotted as a function of the quantum-well thickness. The dashed line indicates the results obtained using the diagonal approximation. Parameters are given in the text.

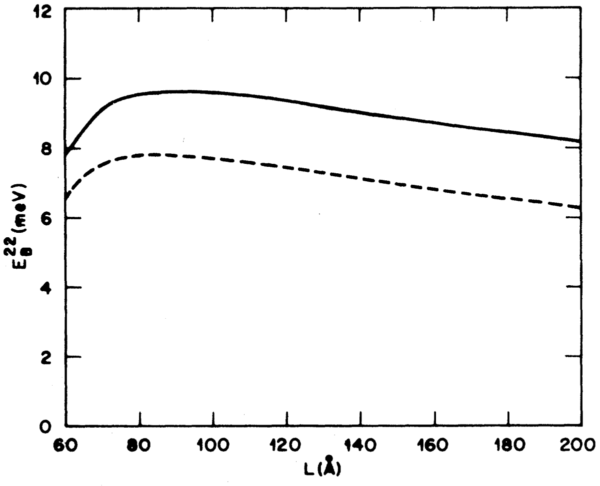

FIG. 2. The binding energy of excitons in $(n,m)=(2,2)$ subbands calculated from Eq. (23), plotted as a function of the quantum-well thickness. The dashed line indicates the result obtained using the diagonal approximation. Parameters are the same as those in Fig. 1.

is often used as a tool for determining a certain heterostructure parameter. In this regard the prediction of this long-ignored effect may modify our current knowledge about semiconductor heterostructures. For instance, reexamination of experimental data along with calculations including the QSIE on exciton binding energies in quantum wells may lead to more accurate determination of valence-band offsets in heterostructures.

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[1] See, for example, R. Dingle, in *Festkörperprobleme (Advances in Solid State Physics),* edited by H. J. Queisser (Pergamon-Vieweg, Braunschweig, 1975).

[2] B. A. Vojak, N. Holonyak, Jr., D. W. Laidig, K. Hess, J. J. Coleman, and P. D. Dapkus, Solid State Commun. **35**, 477 (1980).

[3] R. C. Miller, D. A. Kleinman, W. T. Tsang, and A. C. Gossard, Phys. Rev. B **24**, 1134 (1981).

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

[5] R. L. Greene and K. K. Bajaj, Solid State Commun. **45**, 831 (1983); R. L. Greene, K. K. Bajaj, and D. E. Phelps, Phys. Rev. B **29**, 1807 (1984).

[6] T. F. Jiang, Solid State Commun. **50**, 589 (1983).

[7] J. C. Maan, G. Belle, A. Fasolino, M. Altarelli, and K. Ploog, Phys. Rev. B **30**, 2253 (1984).

[8] S. Tarucha, H. Okamoto, Y. Iwasa, and N. Miura, Solid State Commun. **52**, 815 (1984).

[9] P. Voisin, G. Bastard, and M. Voos, Phys. Rev. B **29**, 935 (1984).

[10] Y.-C. Chang and J. N. Schulman, Appl. Phys. Lett. **43**, 536 (1983); Phys. Rev. B **31**, 2069 (1985).

[11] G. D. Sanders and Y.-C. Chang, Phys. Rev. B **31**, 6892 (1985); *ibid.* **32**, 5517 (1985).

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

[13] B. Zhu and K. Huang, Phys. Rev. B **36**, 8102 (1987).

[14] G. E. W. Bauer and T. Ando, J. Phys. (Paris) Colloq. **48**, 5-215 (1987).

[15] G. E. W. Bauer and T. Ando, Phys. Rev. B **37**, 3130 (1988).

[16] B. Zhu, Phys. Rev. B **37**, 4689 (1988).

[17] L. C. Andreani and A. Pasquarello, Europhys. Lett. **6**, 259 (1988).

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

[19] G. D. Mahan, Phys. Rev. **163**, 612 (1967); also *Many Particle Physics* (Plenum, New York, 1981), Chap. 8.