

Band-Edge Electroabsorption in Quantum Well Structures: The Quantum-Confined Stark Effect

D. A. B. Miller, D. S. Chemla, and T. C. Damen
AT&T Bell Laboratories, Holmdel, New Jersey 07733

and

A. C. Gossard and W. Wiegmann
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

and

T. H. Wood and C. A. Burrus
AT&T Bell Laboratories, Crawford Hill, New Jersey 07733
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We present theory and extended experimental results for the large shift in optical absorption in GaAs-AlGaAs quantum well structures with electric field perpendicular to the layers. In contrast to the Stark effect on atoms or on excitons in bulk semiconductors, the exciton resonances remain resolved even for shifts much larger than the zero-field binding energy and fields > 50 times the classical ionization field. The model explains these results as a consequence of the quantum confinement of carriers.

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When semiconductors are fabricated in very thin layers (e.g., ~ 100 Å), the optical absorption spectrum changes radically as a result of the quantum confinement of carriers in the resulting one-dimensional potential wells.¹ In such multiple quantum wells of GaAs, sandwiched between barrier layers of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ of thickness sufficient to prevent significant coupling between adjacent GaAs layers, the confinement changes the absorption spectrum from the smooth function of bulk material to a series of steps. Additionally, the confinement also increases the binding energy of excitons, resulting in exceptionally clear exciton resonances at room temperature in GaAs-AlGaAs quantum wells.²⁻⁵

When electric fields are applied to bulk semiconductors, the Franz-Keldysh effect gives primarily a broadening of the band-edge absorption.⁶ When the effect of the Coulomb correlation of electron and hole is properly included⁷ a Stark shift of the exciton resonance to lower energies is expected. However, for fields of the order of a few times the classical ionization field E_i ($= E_B/8ea$, where E_B is the zero-field binding energy and a is the Bohr radius⁷), the resonance is severely broadened because field ionization drastically reduces the exciton lifetime and the resonance shift is limited to $\sim 10\%$ of the binding energy.⁷ Similar limitations should be expected for Stark shifts in atoms.

In GaAs-AlGaAs quantum wells, we have, however, recently observed large shifts in band-edge absorption for electric fields perpendicular to the

layers.⁸ The shifts can exceed the exciton binding energy and yet the exciton resonances remain well resolved. Extended room-temperature measurements reported in this paper confirm the existence of exciton resonances up to $\sim 50E_i$ ($\sim 10^5$ V/cm). The purpose of this paper is to explain (i) the large shifts and (ii) the persistence of the exciton peaks to these large fields.

In contrast with the Franz-Keldysh effect which is independent of crystal size, the mechanism which we propose here requires the quantum confinement in the thin semiconductor layers. Large effects are to be expected with moderate fields because the particle-in-a-box envelope functions of electrons and holes and the exciton envelope functions are large (~ 100 Å), have low associated energies (~ 10 MeV), and hence are significantly perturbed by moderate fields (10 meV across 100 Å corresponds to 10^4 V/cm).⁸

The mechanism which we propose is as follows. (a) Electric fields perpendicular to the quantum well layers pull the electrons and holes towards opposite sides of the layers resulting in an overall net reduction in energy of an electron-hole pair and a corresponding Stark shift in the exciton absorption. Two separate reasons explain the persistence of the peaks. (b) The walls of the quantum well impede the electron and hole from tunneling out of the well in rapid field ionization. (c) Because the well is narrow (e.g., ~ 100 Å) compared to the three-dimensional (3D) exciton size (e.g., ~ 300 Å), the

electron-hole interaction, although slightly weakened by the separation of electron and hole, is still strong, and well defined excitonic states can still exist. Thus exciton resonances can remain to much higher fields than would be possible in the absence of this confinement, and large absorption shifts can be seen without excessive broadening. Note that, although the mechanism is discussed for the particular case of excitons, it is applicable to any hydrogenic system.

To justify this mechanism (i) we calculate the overall shifts of the resonances; (ii) we calculate the exciton binding energy (included in the overall shift) to show that it remains large; and (iii) we calculate the additional broadening of the resonances due to tunneling of the individual electrons and holes out of the well to show that it remains small.

To analyze the problem of the exciton energy in an electric field F perpendicular to the quantum well layers (i.e. in the z direction), we consider the Hamiltonian

$$H = H_{ez} + H_{hz} + H_{eh}, \quad (1)$$

where

$$\begin{aligned} H_{ez} &= \frac{-\hbar^2}{2m_{e\perp}^*} \frac{\partial^2}{\partial z_e^2} + V_e(z_e) + eFz_e, \\ H_{hz} &= \frac{-\hbar^2}{2m_{h\perp}^*} \frac{\partial^2}{\partial z_h^2} + V_h(z_h) - eFz_h, \\ H_{eh} &= \frac{-\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} - \frac{e^2}{\epsilon[(z_e - z_h)^2 + r^2]^{1/2}}. \end{aligned}$$

Here z_e (z_h) is the z coordinate of the electron (hole); $m_{e\perp}^*$ ($m_{h\perp}^*$) is the effective mass of the electron (hole) in the z direction; \vec{r} is the relative position of electron and hole in the (x,y) plane; $\mu = m_{e\parallel}^* m_{h\parallel}^* / (m_{e\parallel}^* + m_{h\parallel}^*)$ is the reduced effective mass in the plane of the layers [$m_{e\parallel}^*$ ($m_{h\parallel}^*$) is the electron (hole) effective mass in the plane]. $V_e(z_e)$ [$V_h(z_h)$] is the built-in rectangular quantum well potential for electrons (holes) due to the band discontinuity in the conduction (valence) band.

This is a complete Hamiltonian for the envelope functions of electrons and holes within the effective-mass approximation, except for the usual omission of the center-of-mass kinetic energy of electron and hole in the plane as negligible kinetic energy can be given to this motion under optical excitation.

We choose a separable wave function Φ for the exciton for simplicity, i.e., $\Phi(z_e, z_h, \vec{r}) = \Psi_e(z_e) \times \Psi_h(z_h) \phi_{eh}(\vec{r})$, where $\Psi_e(z_e)$ is the (lowest-energy) solution of $H_{ez} \Psi_e(z_e) = E_{ez} \Psi_e(z_e)$ for a given field F and $\Psi_h(z_h)$ is similarly the lowest-

energy eigenfunction of H_{hz} with energy E_{hz} . $\phi_{eh}(\vec{r})$ is a 1S-like Bohr orbital with variational parameter λ , $\phi_{eh}(\vec{r}) = (2/\pi)^{1/2} \exp(-r/\lambda)/\lambda$.

Because we have chosen the separable-wave-function approximation the resultant energy of the lowest, 1S-like exciton resonance then becomes $E_{ex} = E_{ez} + E_{hz} + E_{exb}$, where $E_{exb} = \langle \Phi | H_{eh} | \Phi \rangle$ is variationally minimized for each field F .

The sample used experimentally⁸ had 95-Å GaAs layers and 98-Å $\text{Al}_x\text{Ga}_{1-x}\text{As}$ barriers with $x = 0.32$. The parameters used throughout our calculations are $x = 0.32$; valence-band discontinuity (hole well depth), 60 meV; conduction-band discontinuity (electron well depth), 340 meV; electron effective mass, $0.0665 + 0.0835x$; heavy-hole effective mass perpendicular to the plane, $0.45 + 0.31x$; light-hole effective mass perpendicular to the plane, $0.088 + 0.049x$ (hole effective masses parallel to the plane were calculated as specified by Miller *et al.*⁹); dielectric constant, $\epsilon = 12.15$. The zero-field heavy-(light-) hole exciton peak was at a phonon energy of 1.457 (1.466) eV.

To evaluate E_{ex} , we first solve for E_{ez} , E_{hz} , Ψ_e , and Ψ_h . We use three methods, the first being a tunneling resonance technique. The actual potential of the structure in the presence of the field was modeled by a single well between two finite barriers, with the potentials of all three layers skewed as appropriate for the applied electric field [e.g., a potential $V_e(z_e) + eFz_e$ for the electrons]. We looked numerically for resonances in the tunneling current through the whole structure as the kinetic energy of particles incident on the structure was varied. The energies of the tunneling resonances at each field give the positions of the energy levels within the well (this calculation does not give Ψ_e and Ψ_h directly); these results give the solid lines of Fig. 1 (and the dashed lines of Fig. 2 when the electron shift is added to the appropriate hole shift). Second, we derived an exact solution valid for all field values for the problem of a single particle in an infinitely deep well in a uniform field. The resulting wave functions are Airy functions. The details of this solution will be discussed elsewhere. Third, we extended the variational calculations of Bastard *et al.*¹⁰ for particles in an infinite well to higher fields. We found that if we used larger effective infinite-well widths L_{eff} , chosen to give the correct E_{ez} and E_{hz} at zero field as calculated with use of the actual finite-well parameters, then all three methods of calculation gave very similar results, even up to 10^5 V/cm (see Fig. 1). The calculated energies of the first confined levels were 35.7 meV (electron), 5.7 meV (heavy hole), and

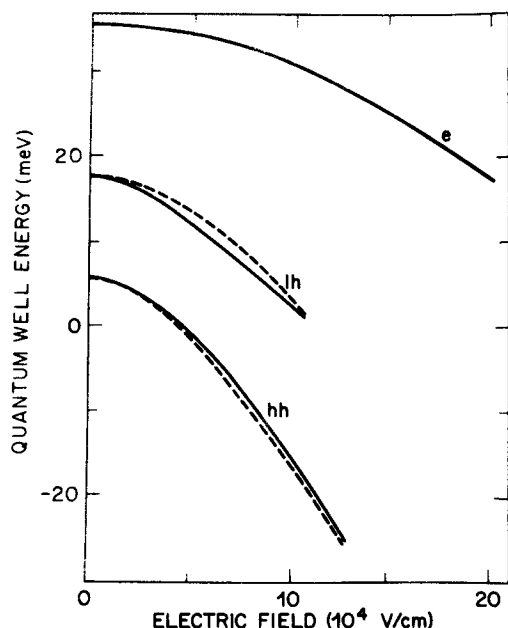


FIG. 1. Calculations of the first confined electron (e) energy E_{ez} in the conduction band and the first confined hole energy E_{hz} in the valence band for the heavy (hh) and light (lh) holes as a function of field. Solid lines, tunneling resonance calculation; broken lines, "exact" infinite-well model with effective well widths. The two models are indistinguishable for the electron at these fields. The energy zero is chosen at the bottom and center of the well in each case. The shifts of electron and hole add in computing the overall absorption shift.

17.7 meV (light hole) at zero field; the resulting effective well widths were $L_{\text{eff}} = 126, 121, \text{ and } 155 \text{ \AA}$, respectively. The larger effective widths account for wave-function penetration into the barriers. The variational and exact infinite-well models agreed within $\sim 5\%$. Consequently, we felt confident in using the analytically tractable single-particle variational wave functions¹⁰ (sinusoidal functions skewed by an exponential) for Ψ_e and Ψ_h in our exciton binding calculations.

The evaluation of the exciton binding correction, E_{exb} , is more tedious as only one variable (r) could be integrated exactly for the potential energy leaving a numerical double integral over z_e and z_h . The range of z_e and z_h is in each case $\pm L_{\text{eff}}/2$, where L_{eff} is in general different for each particle. At zero field E_{exb} is the exciton binding energy and we obtain an energy of 8.6 meV (9.3 meV) for the heavy- (light-) hole exciton with corresponding variationally minimized radius $\lambda/2$ of 64 \AA (57 \AA) in agreement with other calculations.^{9,11} With field, $|E_{\text{exb}}|$ decreases to 5.9 meV (6.7 meV) at 10^5 V/cm with a corresponding increase in radius 87 \AA (76 \AA). Note

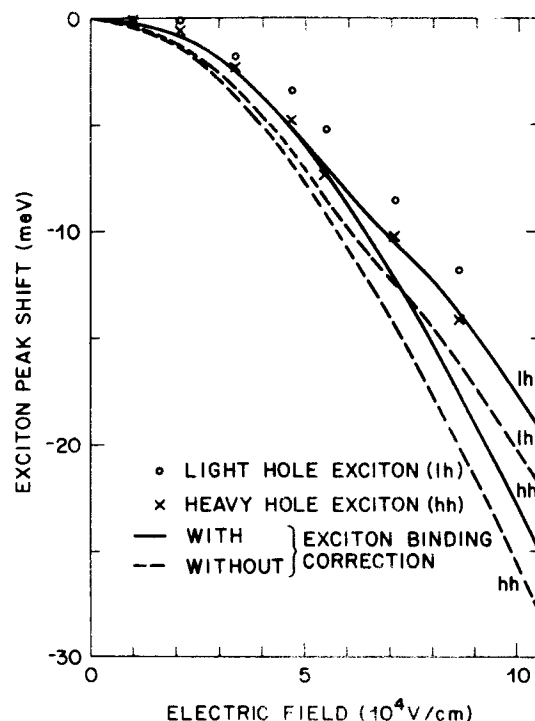


FIG. 2. Shift of the exciton peak position with applied field. The points are experimental. The lines are the theory discussed in the text with (solid) and without (dashed) the shift in exciton binding correction E_{exb} .

that E_{exb} still significantly exceeds the three-dimensional exciton binding energy ($\sim 4.2 \text{ meV}$) despite this reduction. E_{exb} at other fields may be inferred from Fig. 2; the solid lines are the sum of E_{exb} and $E_{ez} + E_{hz}$ (evaluated by the tunneling resonance method).

The experimental results in Fig. 2 are the measured shifts of the exciton optical absorption peaks at room temperature taken in an extension of previous⁸ experiments. The error in the field measurement is $\sim \pm 10^4 \text{ V/cm}$.⁸ Comparing theory and experiment in Figure 2 we find good agreement for the shift of exciton absorption with field in the multiple quantum wells, especially as there are *no fitted parameters* in the theory. The dominant contribution, at least at higher fields ($\geq 3 \times 10^4 \text{ V/cm}$) is the shift of the single-particle energies E_{ez} and E_{hz} . The dominance of the shifts of the hole subbands over the electron subband (see Fig. 1) can be attributed to the lower confinement energies of the holes and the larger overall wave functions due to penetration into the comparatively low hole barriers. It appears to be coincidental that the two hole levels move at approximately the same rate with field. The fit to the data could be improved if we

adjusted the 85%-15% split of the energy-gap discontinuity between conduction and valence bands¹² to give greater valence-band discontinuity in agreement with recent measurements.¹³

The tunneling resonance calculations also give widths in energy of the single-particle states due to the static field; these widths reflect the finite tunneling time of the particles out of the well. The half widths at half maximum are very small at 10^4 V/cm (< 0.5 μ eV for electrons and heavy holes and ~ 40 μ eV for light holes). Significant broadening starts to be apparent at 10^5 V/cm for the holes (still < 0.5 μ eV for electrons, but ~ 0.7 meV for heavy holes and ~ 6 meV for light holes). The exciton binding energies remain ≥ 6 meV at all fields and the half width due to other causes is already ~ 4 meV,^{4,5} so that the effect of this field broadening should only become strong at the highest fields used in the experiments. This agrees with the results (at 10^5 V/cm, the resonances are marginally resolvable) even although the field inhomogeneity may contribute a further apparent broadening. Adjusting the band-gap discontinuity for greater valence-band depth gives even narrower hole resonances.

In summary, the calculations show that (i) there is good agreement with the experimental shifts with no adjustable parameters; (ii) the Coulomb binding of electron and hole is still strong at high fields because the particles are confined; and (iii) the additional broadening due to the tunneling of electrons and holes out of the wells is only important at the highest fields used.

In conclusion, we have demonstrated good agreement between theory and experiment for the large shift of the excitonic optical absorption with field in multiple-quantum-well semiconductor structures. *We resolve Stark shifts up to 2.5 times the zero-field binding energy for fields ~ 50 times the classical ionization field.*¹⁴ Although demonstrated here in one specific system, similar Stark effects enhanced by

quantum confinement should be observable in other layered semiconductors or confined hydrogenic systems.

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