Electronic structure of free carriers in quantum wells calculated by density-functional theory

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(Received 27 January 1986)

Density-functional calculations of the electronic structure of GaAs-$Ga_{1-x}Al_xAs$ quantum wells in the presence of free carriers are reported. We investigate the effect of p-type modulation doping, electric fields, and electron-hole plasmas on the band gap. The results are compared with published photoluminescence experiments. The electron-hole drop is found to be unstable with respect to dissociation into excitons.

I. INTRODUCTION

Local density-functional theory is an established tool for the calculation of the properties of the inhomogeneous electron gas.[1] Its application to the calculation of the electronic structure of quasi-two-dimensional systems as inversion layers[2] and quantum wells[3] has been very successful.

In previous work[4,5] we have found excellent agreement of the results of local density-functional theory with experiments for the photoluminescence frequency, i.e., the band gap,[4,5] of n-type modulation-doped GaAs-$Ga_{1-x}Al_xAs$ quantum wells. Here we extend the calculations to different situations of physical interest.

It is straightforward to apply the method employed in Refs. 4 and 5 to p-type modulation-doped systems. Our results are presented and compared with those of Ref. 6 in Sec. II. Electric fields modify the band gap and emission frequency as shown in Sec. III. The results are of relevance for the interpretation of the luminescence of asymmetrically doped quantum wells.[7] A third problem concerns the effects caused by high photoexcitation of the system, i.e., the effect of an electron-hole plasma, which is treated in Sec. IV.

II. p-TYPE MODULATION DOPING

In a p-type modulation-doped quantum well the holes in the valence band are spatially confined to the well by the potential discontinuity at the interface. For not too narrow wells the holes may be treated approximately as positively charged fermions with an effective isotropic mass m_h. The Kohn-Sham equations for the hole system have been solved self-consistently in the local-density approximation, using the Gunnarson-Lundqvist potential[8] and a numerical method described in Ref. 3.

In a luminescence experiment a small number of electrons are excited into the conduction band. The electron band structure can also be calculated by density-functional theory, using the exchange-correlation potential determined in Ref. 5. The difference of the effective masses should be taken properly into account (last entry of Table I of Ref. 5).

We have carried out calculations for a quantum well for which experimental and theoretical results have been reported recently:[6] The sample has a width of $d=115$ Å an alloy parameter $x=0.44$, and a hole density of $N_s^h=0.53\times10^{11}$ cm^{-2}. Other parameters used here and later are $m_h=0.4$, $m_e=0.068$, dielectric constant $\kappa_s=12.9$, and total band-gap discontinuity $\Delta E_g=1230x$ meV. We consider band-gap offsets for the valence band and conduction band of both $0.15\Delta E_g$ and $0.85\Delta E_g$, respectively (Dingle's rule), and $0.40\Delta E_g$ and $0.6\Delta E_g$, respectively. Our results for the confinement energy (sum of electron and hole energies in the Hartree approximation), electron renormalization, hole renormalization, and total band-gap shift relative to bulk GaAs are, respectively, 34.3, −5.8, −3.5, and 25.0 meV, determined using Dingle's rule, and 33.3, −6.0, −3.4, and 23.9 meV for the 0.4 and 0.6 band-gap offsets. The agreement with the experimental result[6] for the gap shift of 24 meV is excellent. The theoretical results of Ref. 6 are 35.9, −6.0, −6.0, and 23.9 meV assuming a 0.43 and 0.57 band-gap offset and a transverse hole mass of 0.1. Electron and hole renormalization have been assumed to be identical in Ref. 6, which is found here to be a crude approximation. The agreement of the gap shifts is accidental and caused by the larger confinement energies calculated by Ref. 6 due to the small hole mass.

III. ELECTRIC FIELD

The optical properties of quantum wells vary as a function of electric field, which may be applied externally or created in the sample by asymmetrical doping. We only have to add a linear term to the confinement potentials to calculate electric field effects.[9] Electron and hole wave functions get spatially separated, which results in a reduction of the transition probabilities. If modifications of the vertex part are neglected luminescence intensities are simply proportional to the squared overlap matrix elements of electron and hole envelope wave functions.

We have calculated the band-gap shift and overlap matrix elements for an n-type symmetrically doped quantum well with $d=150$ Å, $x=0.35$, and $N_s=4\times10^{11}$ cm^{-2} as a function of an applied field. The field F is measured in units of 56 kV/cm such that $F=1$ corresponds to an asymmetrically doped well, i.e., a flat potential at one side of the GaAs layer. Results are displayed in Figs. 1 and 2.

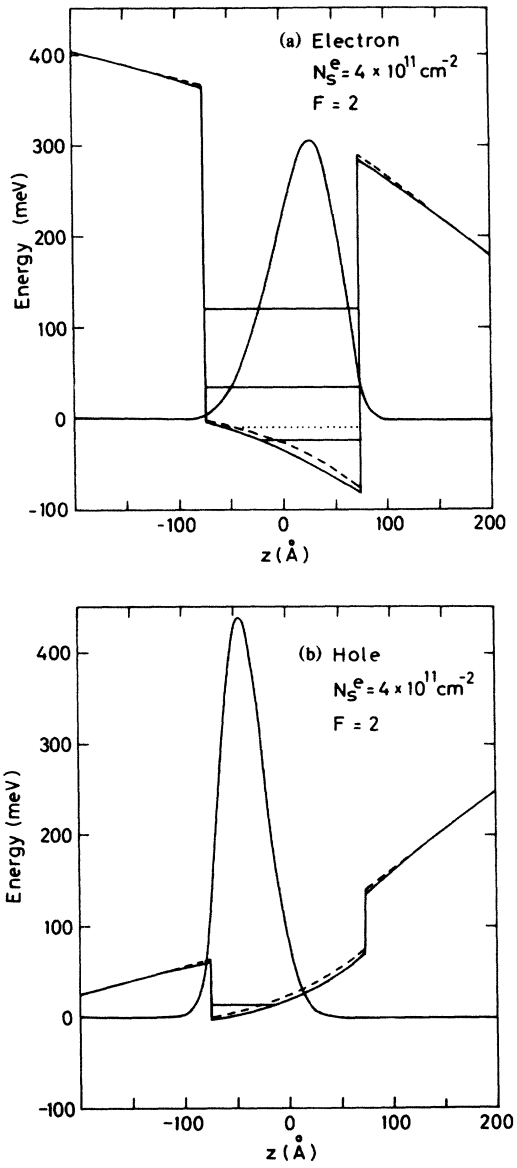

FIG. 1. Electronic structure of a modulation-doped GaAs-$Ga_{1-x}Al_xAs$ quantum well in the presence of an electric field of 112 kV/cm: (a) electrons, (b) holes. Indicated are the potential profiles (dashed line: Hartree approximation), charge-density distributions (arbitrary units), some subband energies (full horizontal lines), and the electronic Fermi energy (dotted horizontal line).

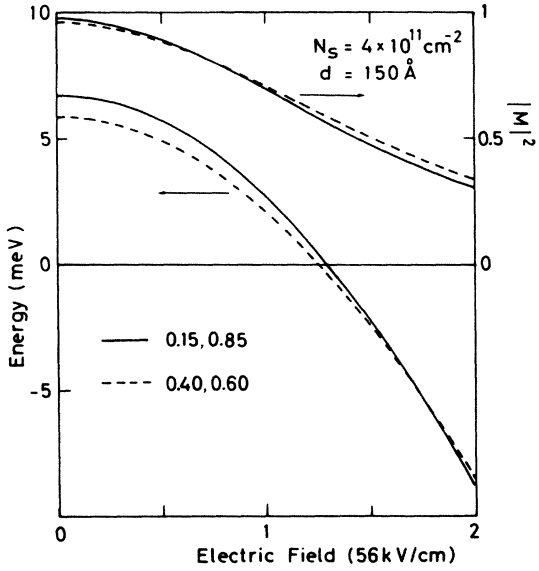

FIG. 2. Band gap relative to GaAs and squared overlap matrix element of electron and hole envelope functions $|M|^2$ as a function of the electric field (see also Fig. 1). The full (dashed) lines correspond to 0.15 and 0.85 (0.4 and 0.6) band-gap offsets.

An experimental photoluminescence study of an asymmetrically doped quantum well has been reported recently.[10] The experimental emission frequency (-4 meV relative to the GaAs band gap) does not compare favorably with the present results for the nominal situation $F=1$ (2.7 meV). Agreement with experiment is reached for $F=1.6$, however. This result points to the existence of additional internal fields of 34 kV/cm due to residual doping or electrostatic charging of the sample.

At high excitation intensity it is obvious from the strong emission originating from the narrow quantum wells which provide for the substrate of the well[10] that free carriers are available everywhere in the sample which screen the internal fields. The well potential thus will become approximately symmetrical in this limit. On illumination of the asymmetric quantum well an increase of the band gap is reported[10] which saturates at 7 meV relative to GaAs at high excitation intensities. This result indeed agrees well with the calculation for the symmetric well ($F=0$) of 6.7 meV. On the other hand, our results do not support the interpretation that the blue shift of the emission is largely caused by a reduction of the electron density by recombination with photoexcited holes: The theoretical band-gap shift for a symmetrical well with an electron density reduced by, e.g., a factor of 10 is about 10 meV larger than the experimental value. This could indicate that the photoexcited holes are relatively immobile and only a small fraction is actually collected by the quantum well. The electron density will then not decrease significantly by electron-hole recombination. We thus believe that the observed blue shift does not so much reflect an electron correlation effect but mainly the symmetrization of the well potential.

Indicated in Fig. 2 is the squared overlap matrix element of the envelope functions which decreases as a function of the electric field because electron and holes become spatially separated (Fig. 1). Note that these results only represent an upper bound for the expected decrease of the emission intensity, because the reduction of the excitonic enhancement by the field has not been calculated.

IV. ELECTRON-HOLE PLAMSA

Under photoexcitation of a semiconductor a neutral electron-hole plasma is formed which displays intricate but well-studied many-body effects.[10,11] Density-functional theory may be applied meaningfully to the electron-hole

plasma in undoped quantum wells if the charge densities are sufficiently high. We calculate the electronic structure using the following convenient approximation for the exchange-correlation energy functional (per unit area):[11]

$$E_{xc}[\rho_h,\rho_e] = \int dz \, \tfrac{1}{2}[\rho_e(z)\varepsilon_{xc}(\rho_e(z)) + \rho_h(z)\varepsilon_{xc}(\rho_h(z))] \, . \quad (1)$$

ε_{xc} is the exchange-correlation energy of the homogeneous electron-hole plasma per electron-hole pair as parametrized in Ref. 11. This approximation is valid as long as the electron and hole densities ρ_e and ρ_h are sufficiently similar. Electron and hole band structures and the total energy of the plasma have been computed by solving the coupled Kohn-Sham equations for electrons and holes self-consistently. If the total plasma energy per e-h pair has a minimum (or is equal to the chemical potential) as a function of the plasma density and if this energy is lower than the energy of the exciton (or excitonic molecule), electron-hole drops may be formed.

In actual calculations ρ_e and ρ_h turn out to be very similar so that the approximation in Eq. (1) is valid. The Hartree potential is very small. Since the exchange-correlation potentials depend only relatively weakly on the densities, the confining potentials are approximately rigidly shifted in the presence of carriers. The subband spacings are therefore very insensitive with respect to the carrier density, which explains the results of light scattering experiments.[12]

The energy position and the bandwidth of the luminescence as calculated for $x = 0.3$ and a well width of 41 Å is displayed in Fig. 3 together with a recent experiment.[13] The well is very narrow so that the results are rather sensitive to the band-offset parameter. The agreement of experiment and theory is rather moderate, but one should keep in mind that the plasma density has been determined experimentally[13] by line-shape fitting. Note that a variation of the well thickness by one half of the lattice constant shifts the band gap also by 10 meV. We thus expect a significant intrinsic broadening such that the parameter fit might not be very reliable.

The luminescence band is spanned by the band gap and the chemical potential of the electron-hole plasma. It is displayed as a function of the density for a quantum well of a width of 145 Å (0.15 and 0.85 band offsets) in Fig. 4 together with the total energy. At a density of 1.23×10^{11} cm^{-2} a maximum binding energy of 8.0 meV is observed. We have also carried out a variational calculation of the exciton binding energy in the present model system. For a transverse-hole mass parameter of 0.1 and a dielectric constant of 12.5 our result for the exciton binding energy (7.4 meV) agrees well with that of Ref. 14. For the parameters used in the density-functional calculations we obtain a binding energy of 8.8 meV which is significantly larger than that of the electron-hole plasma. In agreement with a study of strictly two-dimensional systems[15] the electron-hole drop in a GaAs quantum well is found to be unstable with respect to dissociation into excitons. We thus conclude that the density-independent luminescence peak observed recently in a GaAs quantum well under low excitation intensities[16] cannot be simply explained by the formation of an electron-hole drop. Even if against our expectations the electron-hole drop would be stable, the observed line shape would be difficult to explain. The experimental emission peaks at the lower energy edge of the calculated

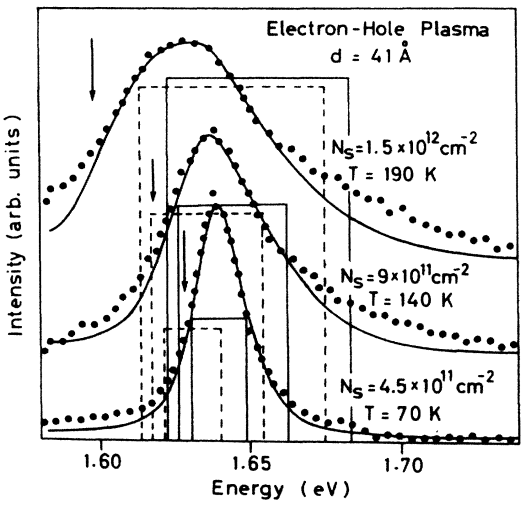

FIG. 3. Photoluminescence bands of a GaAs-$Ga_{1-x}Al_xAs$ quantum well (width 41 Å) for different plasma densities. The experimental results (dots) and the line fits including the band-gap estimations (arrows) have been taken from Ref. 13. The boxes indicate the theoretical luminescence bands defined by the band gap (low-energy edge) and the chemical potential (high-energy edge). The full (dashed) lines correspond to 0.15 and 0.85 (0.4 and 0.6) band-gap offsets. (The unit and the origin of the ordinate is arbitrary and different for different curves.)

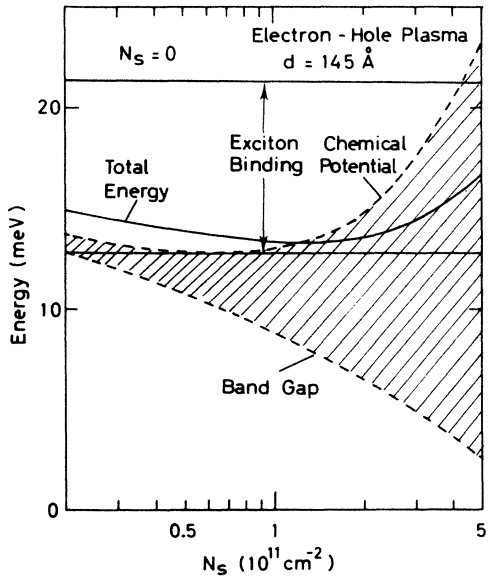

FIG. 4. Total energy (full line) and luminescence band (shaded area) of the electron-hole plasma in a quantum well as a function of the density of electron-hole pairs. 0.15 and 0.85 band-gap offsets have been used. (For 0.4 and 0.6 offsets the curves are shifted by −0.7 meV.) Also indicated is the band gap of the well in the absence of carriers and the calculated exciton binding energy.

luminescence band. The electron-hole Coulomb interaction enhances the line shape at the high-energy edge, however.[17] An impurity scattering effect as calculated in the self-consistent Born approximation (cf. Ref. 18) can be responsible for a weak maximum at lower energies, but it does not bare resemblence with the sharp experimental line shape.

V. CONCLUDING REMARKS

Here (and in Refs. 4 and 5) we have employed density-functional theory to calculate optical properties of quantum wells. By comparison with experiments carried out under well-defined conditions, as, for example, in Sec. II, we have gathered evidence by now that the method is quantitatively reliable. We are therefore optimistic that it may be used fruitfully as an interpretation aid for experiments where not all parameters are known well. A good example is the discussion of the photoluminescence properties of the asymmetrically doped quantum well in Sec. III, where the combined evidence from calculations and experiment lead to different conclusions than was obvious from the experimental data alone.

Note added in proof. After submission of our manuscript, an article appeared [D. A. Kleinman, Phys. Rev. B **33**, 2540 (1986)] with model calculations of the electron-hole liquid in quantum wells. The binding energy of the electron-hole drop is reported to be larger than that of the exciton for well widths $d > 80$ Å and larger even than that of the biexciton for $d > 220$ Å. We find, however, that the electron-hole drop is less bound than the exciton at least up to $d > 250$ Å, also when using Kleinman's parameters. In the three-dimensional limit the electron hole drop in a direct-gap semiconductor is not or only marginally stable.[11]

ACKNOWLEDGMENTS

We are grateful to Professor S. Katayama for helpful discussions. This work has been supported in part by Grants-in-Aid for Fundamental Scientific Research and Special Distinguished Research from the Ministry of Education of Japan. One of us (G.B.) acknowledges the support of the Japan Society for the Promotion of Science and the Lynen Program of the Alexander-von-Humboldt Stiftung.

[1]For example, *Theory of the Inhomogeneous Electron Gas,* edited by S. Lundqvist and N. H. March (Plenum, New York, 1983).

[2]T. Ando, Surf. Sci. **68**, 128 (1976); Phys. Rev. B **13**, 3468 (1976).

[3]T. Ando and S. Mori, J. Phys. Soc. Jpn. **47**, 1518 (1979).

[4]G. E. W. Bauer and T. Ando, Phys. Rev. B **31**, 8321 (1985).

[5]G. E. W. Bauer and T. Ando, J. Phys. C **19**, 1537 (1986).

[6]D. A. Kleinman and R. C. Miller, Phys. Rev. B **32**, 2266 (1985).

[7]A. S. Chaves, A. F. S. Penna, J. M. Worlock, G. Weimann, and W. Schlapp, Surf. Sci. **170**, 618 (1986).

[8]O. Gunnarson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[9]K. Inone, H. Sakaki, J. Yoshino, and T. Hotta, J. Appl. Phys. **58**, 4277 (1985).

[10]H. Haug and S. Schmitt-Rink, Prog. Quantum Electron. **9**, 3 (1984).

[11]P. Vashishta, R. K. Kalia, and K. S. Singwi, in *Electron-Hole Droplets in Semiconductors,* edited by C. D. Jeffries and L. V. Keldysh (North-Holland, Amsterdam, 1983).

[12]A. Pinczuk, J. Shah, A. C. Gossard, and W. Wiegmann, Phys. Rev. Lett. **28**, 1341 (1981).

[13]G. Tränkle, H. Leier, A. Forchel, and G. Weimann, Surf. Sci. (to be published).

[14]A. L. Greene, K. K. Bajaj, and D. E. Phelps, Phys. Rev. B **28**, 1807 (1984).

[15]Y. Kuramoto and H. Kamimura, J. Phys. Soc. Jpn. **37**, 716 (1974).

[16]H. Q. Le, B. Lax, B. A. Vojak, and A. R. Calawa, Phys. Rev. B **32**, 1419 (1985).

[17]S. Schmitt-Rink, C. Ell, and H. Haug, Phys. Rev. B **33**, 1183 (1986).

[18]G. E. W. Bauer and T. Ando, J. Phys. C **19**, 1553 (1986).