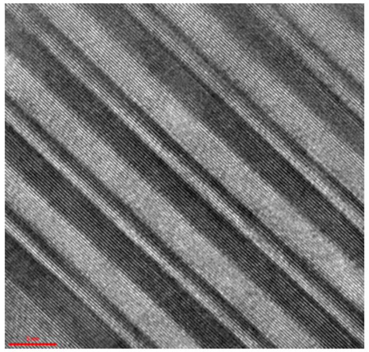
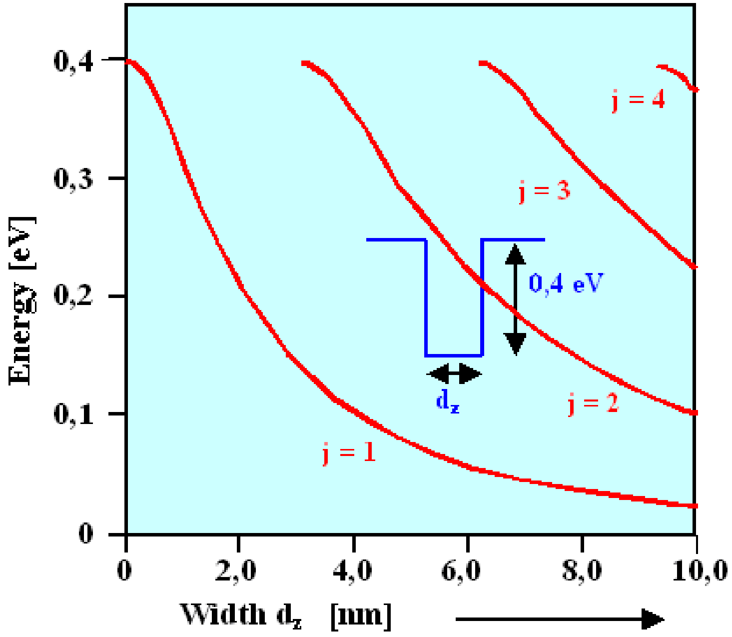
Lecture 3 – 05/03/2025

Quantum nanostructures

- Determination of quantum well energy levels
- Case of superlattices
- Excitonic features: bulk and 2D cases



Quantum well energy levels



Energy variation of quantized levels as a function of the well width

$\Rightarrow$ Confinement energy, band offset and well width will define the possible number of confined states!

Number of bound states

$$\boxed{1 + Int\left[\left(\frac{2m_A^* V_0 L^2}{\pi^2 \hbar^2}\right)^{1/2}\right]} \quad if\ m_A^* = m_B^*$$

Significant impact depending on the desired applications $\Rightarrow$ e.g., case of quantum cascade lasers (QCLs) relying on intersubband transitions!

Quantum well energy levels

Hole levels in a quantum well (tricky problem) $\Rightarrow$ cf. Lecture 3, fall semester, for bulk case

Qualitative description (case of zincblende semiconductors): successive perturbation approach[1]

(i) QW potential lifts the degeneracy of $J_z = \pm 3/2$ and $\pm 1/2$ bands (different masses)

(ii) Luttinger equation (bulk case) $k_y = k_\perp$, $k_x = k_z = 0 \Rightarrow k$ dispersion in direction $\perp z$ (quantization axis)

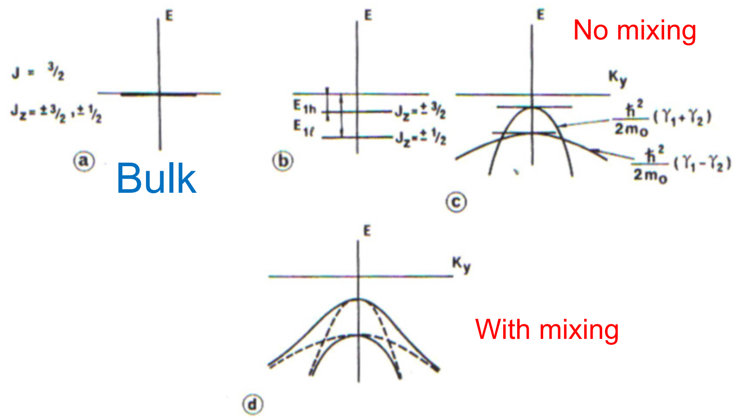
$$E = \frac{\hbar^2 k_\perp^2}{2m_0}(\gamma_1 + \gamma_2), \quad \text{for } J_z = \pm\tfrac{3}{2}$$

$$= \frac{\hbar^2 k_\perp^2}{2m_0}(\gamma_1 - \gamma_2), \quad \text{for } J_z = \pm\tfrac{1}{2}$$

$\Rightarrow$ $J_z = \pm 3/2$ (heavy-hole band along z direction) now has a light mass $m_0/(\gamma_1+\gamma_2)$ and the $J_z = \pm 1/2$ level now has a heavy mass $m_0/(\gamma_1-\gamma_2)$

γ_1, γ_2 Luttinger parameters of VB

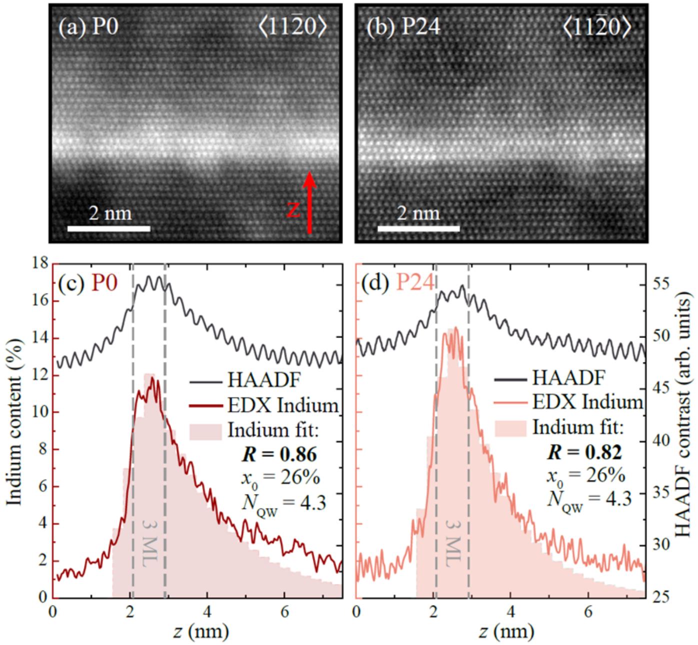
But higher-order ***k.p*** perturbation terms $\Rightarrow$ **anticrossing behavior** (increase of "heavy-hole" band mass and decrease of "light-hole" band mass)



[1]D. S. Chemla, Helv. Phys. Acta **56**, 607 (1983).

Quantum well energy levels

Example of true quantum well profiles with graded interfaces



STEM-HAADF images of **two nominally 3-monolayer (ML) thick single InGaN/GaN** QWs taken down the <11-20> axis

During the growth of one ML of InGaN, a fraction (1-*R*) of the indium atoms at the surface are incorporated into the ML while the remaining fraction *R* segregates to the new surface with *R* the degree of segregation occurring during growth.[1]

The In content in the n^{th} ML, x_n, is given by:

$$x_n = x_0(1 - R^n) \quad (1 \leq n \leq N_{QW};\ \text{well})$$

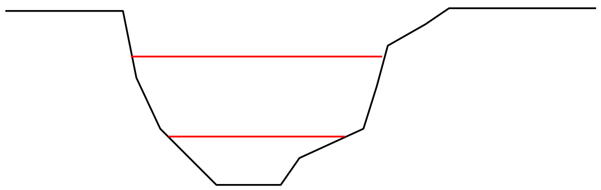
$$x_n = x_0(1 - R^{N_{QW}})R^{n-N_{QW}} \quad (n > N_{QW};\ \text{barrier})$$

where N_{QW} and x_0 are the nominal width and indium content of the QW

[1]T. F. K. Weatherley *et al.*, Nano Lett. **21**, 5217 (2021).

Quantum well energy levels

True quantum well profile (with graded interfaces)



Transfer matrix method

⇒ Discretization of the structure in N layers with a constant potential V_i (Δz << 1 ML)

General solution: $\varphi_i(z) = A_i e^{ikz} + B_i e^{-ikz}$

with $$\frac{\hbar^2 k_i^2}{2m_i} = E - V_i$$

Boundary conditions at interfaces:

$$\begin{cases} \varphi_i(z_i) = \varphi_{i+1}(z_i) \\ \frac{1}{m_i}\left(\frac{d\varphi_i}{dz}\right)_{z=z_i} = \frac{1}{m_{i+1}}\left(\frac{d\varphi_{i+1}}{dz}\right)_{z=z_i} \end{cases}$$

Quantum well energy levels

Considering that $\beta_{i,i+1} = \dfrac{m_i k_{i+1}}{m_{i+1} k_i}$

$$\begin{cases} 2e^{ik_i z_i} A_i = (1+\beta_{i,i+1}) e^{ik_{i+1} z_i} A_{i+1} + (1-\beta_{i,i+1}) e^{-ik_{i+1} z_i} B_{i+1} \\ 2e^{ik_i z_i} B_i = (1-\beta_{i,i+1}) e^{ik_{i+1} z_i} A_{i+1} + (1+\beta_{i,i+1}) e^{-ik_{i+1} z_i} B_{i+1} \end{cases}$$

These two equations can be written as $\begin{pmatrix} A_i \\ B_i \end{pmatrix} = M_{i,i+1} \begin{pmatrix} A_{i+1} \\ B_{i+1} \end{pmatrix}$

with

$$M_{i,i+1} = \begin{pmatrix} \dfrac{(1+\beta_{i,i+1})}{2} e^{-i(k_i - k_{i+1}) z_i} & \dfrac{(1-\beta_{i,i+1})}{2} e^{-i(k + k_{i+1}) z_i} \\ \dfrac{(1-\beta_{i,i+1})}{2} e^{i(k_i + k_{i+1}) z_i} & \dfrac{(1+\beta_{i,i+1})}{2} e^{i(k_i - k_{i+1}) z_i} \end{pmatrix}$$

Quantum well energy levels

In a system consisting of N layers:

$$\begin{pmatrix} A_1 \\ B_1 \end{pmatrix} = M_{1,2} \times \ldots M_{i,i+1} \times \ldots . M_{N-1,N} \begin{pmatrix} A_N \\ B_N \end{pmatrix} = M_T \begin{pmatrix} A_N \\ B_N \end{pmatrix}$$

finally

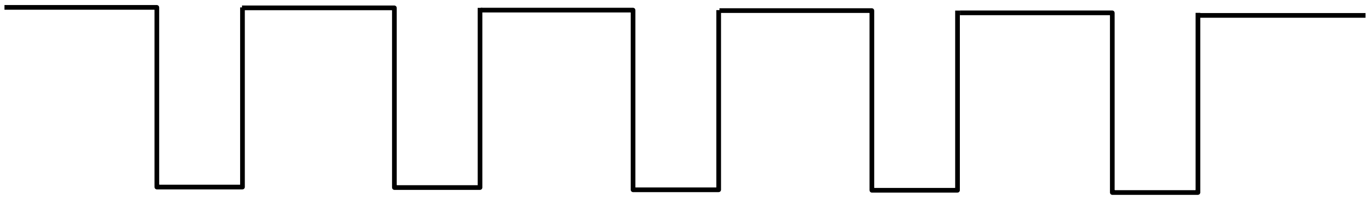
$$M_T(E) = \begin{pmatrix} m_{11}(E) & m_{12}(E) \\ m_{21}(E) & m_{22}(E) \end{pmatrix}$$

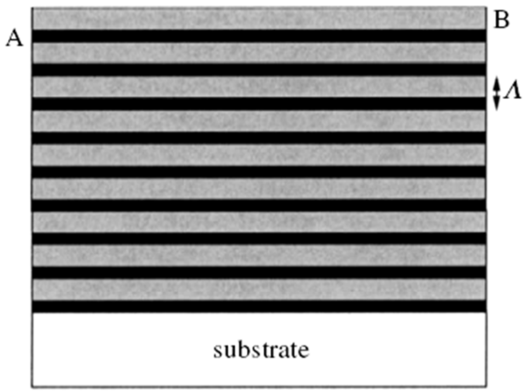
The wavefunctions are evanescent at $\pm\infty \Rightarrow A_1 = 0$ and $B_N = 0$

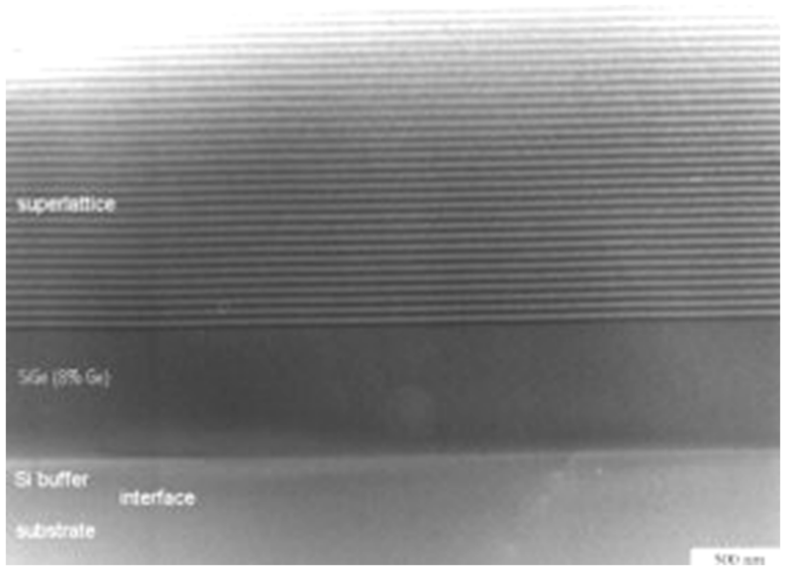
$\boxed{\text{Thus } 0 = m_{11}(E)A_N \;\Rightarrow\; m_{11}(E) = 0}$

In addition, $\int_{-\infty}^{\infty} |\psi_i(z)|^2 dz = 1$

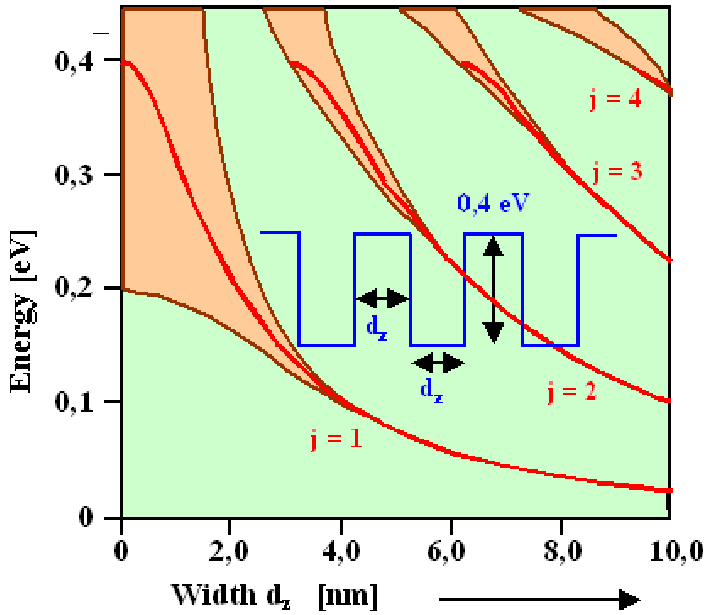
Multiple quantum wells/superlattices

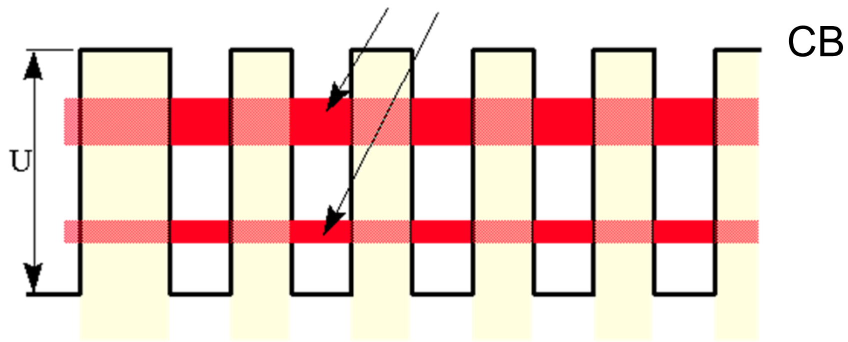






Superlattices





Miniband formation

Tunneling structures: double-well structure

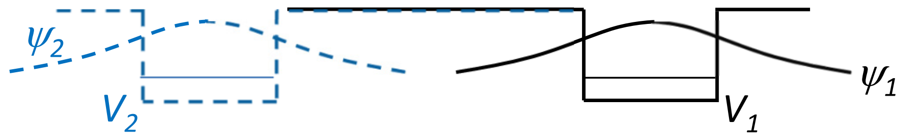
Tunneling phenomena across barriers (Kronig-Penney model,[1] multiple tunneling model,[2] perturbative tight-binding model,[3] or LCAO model[4])

The double-well structure

$$V_{12} = \langle \psi_1 | H | \psi_2 \rangle = \langle \psi_1 | V_2 | \psi_2 \rangle$$

Confining potential of well #2

Perturbation matrix element describing wavefunction overlap



ψ_1 and ψ_2 are degenerate states

Coefficients describing the linear combination of ψ_1 and ψ_2

$$\begin{pmatrix} E_1 + V_1 - \varepsilon & V_{12} \\ V_{12}^* & E_1 + V_1 - \varepsilon \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

Shift in position of the ground state, which is lowered vs single QW case due to the presence of the neighboring well
$\Rightarrow$ **increased effective well width**

$$V_1 = \langle \psi_1 | V_2(z) | \psi_1 \rangle = \langle \psi_2 | V_1(z) | \psi_2 \rangle \quad \text{and} \quad V_{12} = \langle \psi_1 | V_2(z) | \psi_2 \rangle = \langle \psi_2 | V_1(z) | \psi_1 \rangle$$

V_1 and $V_{12} < 0$

Ground state energy in the single (isolated) QW case

$$\boxed{\varepsilon = E_1 + V_1 \pm |V_{12}|}$$

Levels split by the amount $2|V_{12}|$

Symmetric and antisymmetric states

[1]L. Esaki and R. Tsu, IBM J. Dev. **14**, 61 (1970) (> 2920 citations).
[2]R. Tsu and L. Esaki, Appl. Phys. Lett. **22**, 562 (1973) (> 2080 citations).
[3]J. N. Schulman and T. C. McGill, Phys. Rev. B **19**, 6341 (1979) (> 130 citations).
[4]J. N. Schulman and Y. C. Chang, Phys. Rev. B **24**, 4445 (1981) (> 140 citations).

Tunneling structures: superlattices[1]

N wells $\Rightarrow$ N degenerate levels $\Rightarrow$ bands with 2N quantum states

Tight-binding model of N-well chain:[2]

$$\psi_q^{(j)}(z) = \frac{1}{\sqrt{N}} \sum_n e^{iqnd} \chi_{loc}^{j}(z - nd) \quad \Rightarrow$$

Bloch wavevector

j^{th} QW wavefunction centered at $z = nd$

Principal quantum number

shift transfer

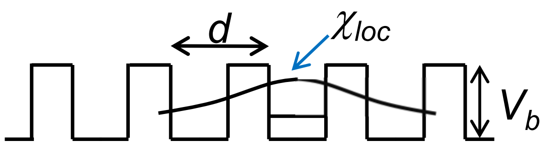
$$\varepsilon_j(q) = E_j + s_j + 2t_j \cos qd \quad \text{with}$$

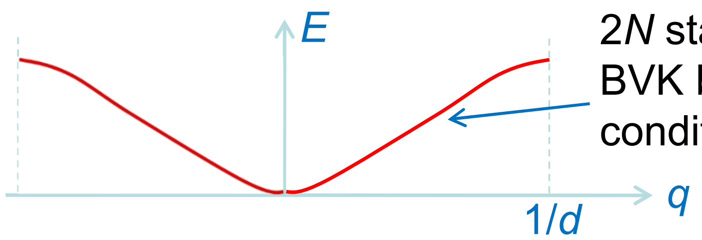
$$s_j = \int_{-\infty}^{+\infty} \chi_{loc}^{j}(z-d)\, V(z)\, \chi_{loc}^{j}(z-d)\, dz$$

$$t_j = \int_{-\infty}^{+\infty} \chi_{loc}^{j}(z)\, V(z)\, \chi_{loc}^{j}(z-d)\, dz$$

Integrals < 0

Nearest well interaction, Born-von Karman (BVK) periodic conditions, **bandwidth of 4t_j**
(*interaction with 2 neighboring wells*)





q can only take discrete values (integer multiples of $2\pi/Nd$)

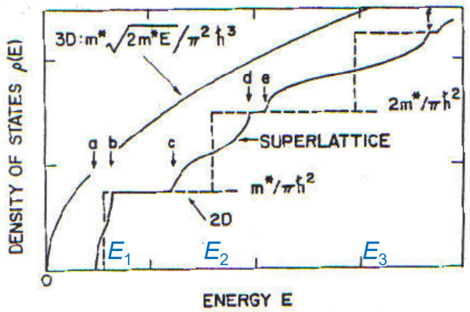
Chain length

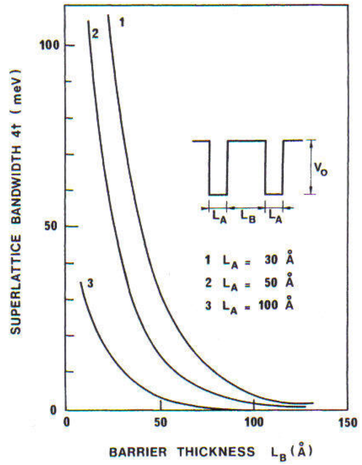
[1]R. Dingle *et al.*, Phys. Rev. Lett. **34**, 1327 (1975) (> 330 citations).
[2]G. Bastard, Acta Electron. **25**, 147 (1983); G. Bastard, Phys. Rev. B **24**, 5693 (1981) (> 1200 citations); G. Bastard, Phys. Rev. B **25**, 7584 (1982) (> 600 citations).

Tunneling structures: superlattices

Superlattice (SL) effect $\Rightarrow$ profound change in 2D-DOS since the steepness of the square density of states is destroyed

$$\boxed{\begin{aligned} \varepsilon_j(q,k_\perp) &= \varepsilon_j(q) + \frac{\hbar^2 k_\perp^2}{2m^*} \\ \rho_j(\varepsilon) &= N\frac{m^*}{\pi^2\hbar^2}\arccos\left(\frac{\varepsilon_j - E_j - s_j}{2t_j}\right) \end{aligned}}$$





For $k_\perp = 0$, in the parabolic band approximation, q values given by a simple Kronig-Penney form (implicit equations):

$$\cos qd = \cos k_A L_A \cosh \kappa_B L_B - \tfrac{1}{2}\left(1/\bar{\xi} - \bar{\xi}\right)\sin k_A L_A \sinh \kappa_B L_B \quad \text{with} \quad \bar{\xi} = m_B^* \kappa_B / m_A^* k_A$$

bound states ($-V_b \le \varepsilon_j(q) \le 0$)

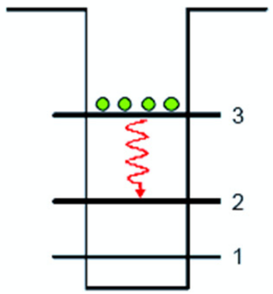
$\boxed{\text{Allowed bands given by } -1 \le \cos qd \le 1}$ Eqs. solved numerically or graphically

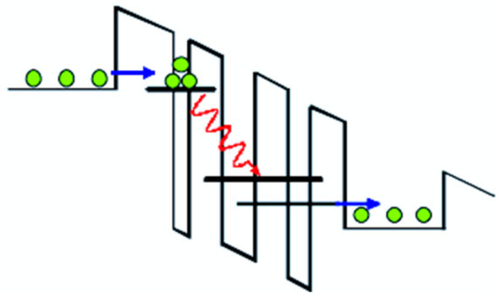
$$\cos qd = \cos k_A L_A \cos k_B L_B - \tfrac{1}{2}\left(1/\xi + \xi\right)\sin k_A L_A \sin k_B L_B \quad \text{with} \quad \xi = m_B^* k_B / m_A^* k_A$$

unbound states ($\varepsilon_j(q) \ge 0$)

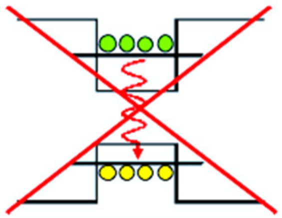
Limit of non communicating wells, i.e., isolated QWs, found for $\kappa_B L_B \to \infty$

Superlattices and quantum cascade lasers[1]



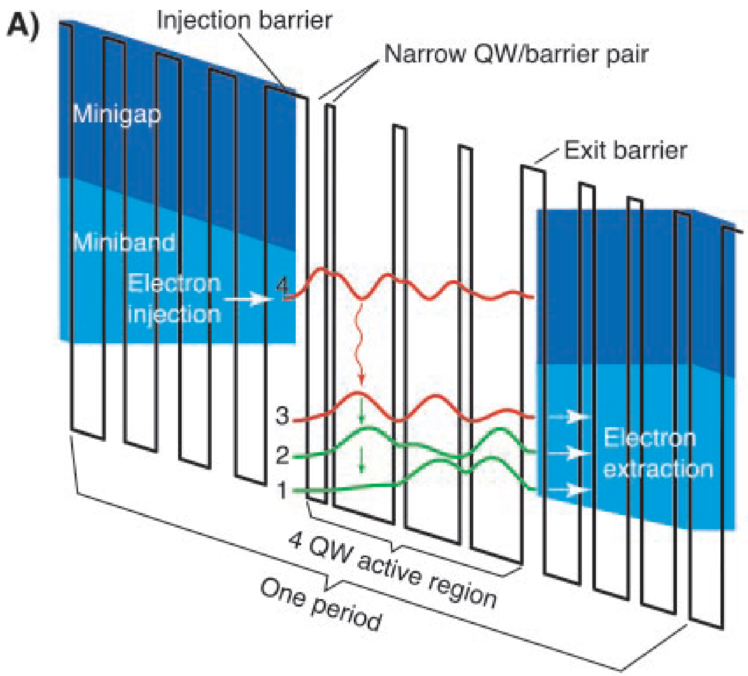


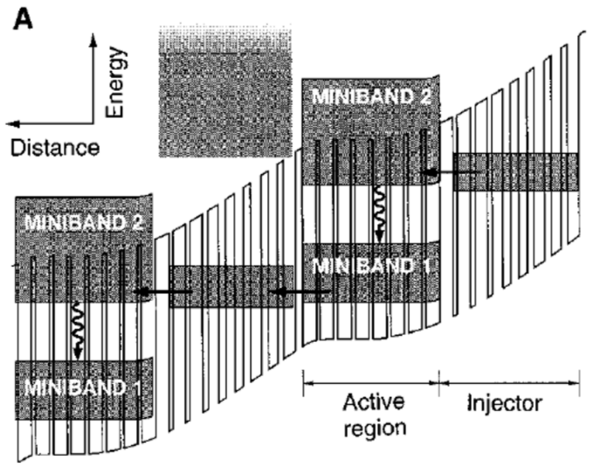
NO ELECTRON - HOLE RECOMBINATION

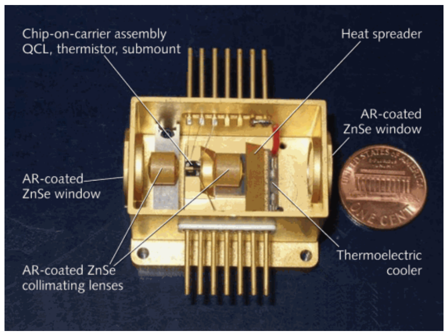


[1]J. Faist *et al.,* Science **264**, 553 (1994) (> 4300 citations).

Superlattices and quantum cascade lasers[1-2]

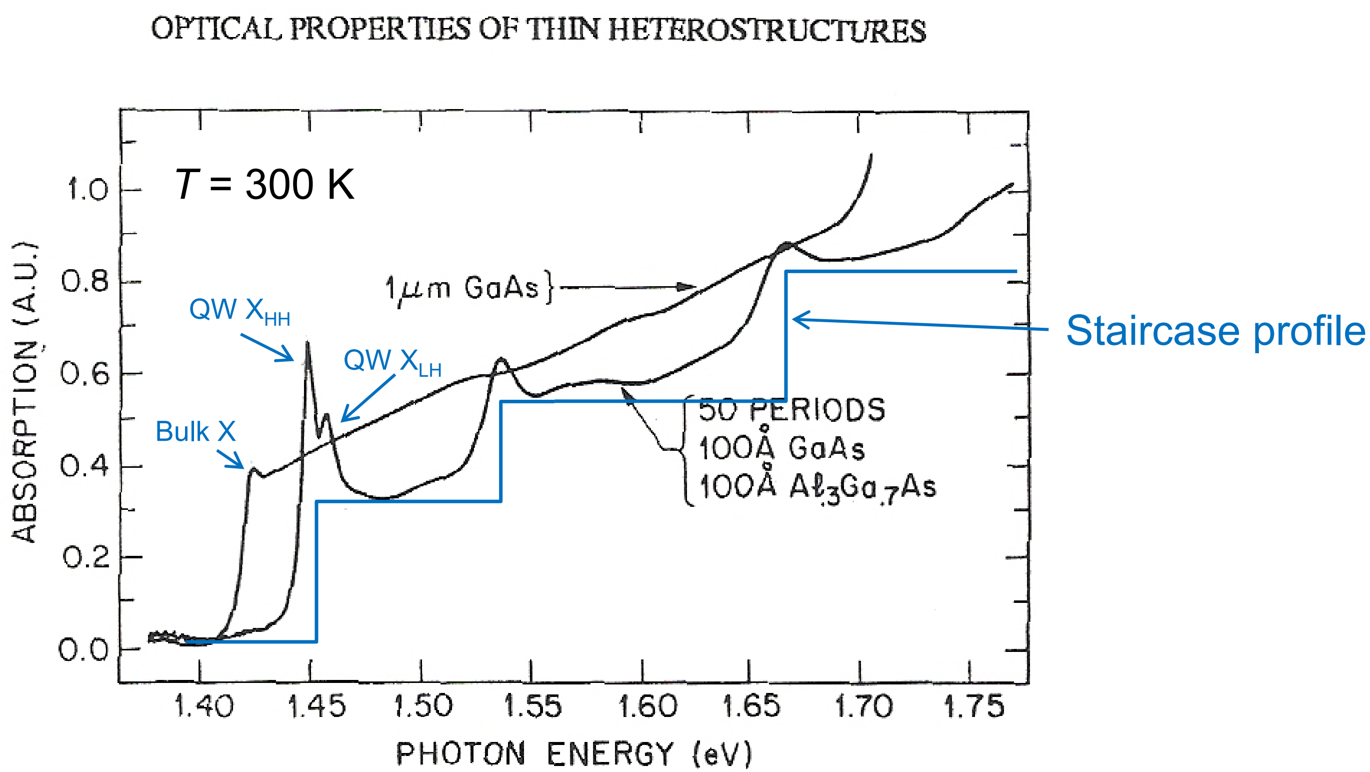






[1]G. Scamarcio *et al.,* Science **276**, 773 (1997) (> 150 citations)
[2]M. Beck *et al.,* Science **295**, 301 (2002) (> 740 citations)

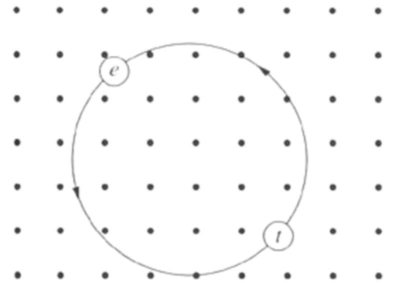
Absorption and excitons in semiconductors



Absorption in quantum wells

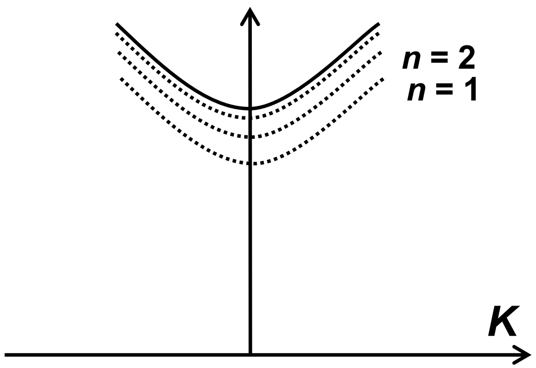
Excitons in bulk semiconductors

Exciton: electron-hole pair bound via Coulomb interaction

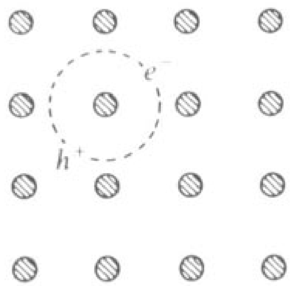


Wannier exciton

$\Rightarrow$ III-V and II-VI semiconductors (but also TMDCs)



Hydrogenic model



Frenkel exciton

$\Rightarrow$ organic semiconductors

$$E_X = E_g + \frac{\hbar^2 K^2}{2M} - \frac{Ry^*}{n^2}$$

$$Ry^* = \frac{m_r}{m_0 \varepsilon_r^2} E_{H_I} = \frac{m_r e^4}{2\hbar^2 \left(4\pi\varepsilon_0\varepsilon_r\right)^2}$$

Ry^* = 4 meV for GaAs

Ry^* = 26 meV for GaN

Ry^* = 60-70 meV for ZnO

$$a_B = \frac{m_0}{m_r}\varepsilon_r a_0 = \frac{\hbar^2 4\pi\varepsilon_0\varepsilon_r}{m_r e^2}$$ **Bohr radius**

Excitons in quantum wells

Case of an infinitely deep quantum well

Reminder: exciton characteristics in the bulk case[1]

$$Ry^* = \frac{2\mu e^4}{\hbar^2 (8\pi\varepsilon_r\varepsilon_0)^2} = \frac{\mu}{m_0}\frac{1}{\varepsilon_r^2} Ry \qquad \frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*} \qquad Ry = 13.6 \text{ eV};\ a_0 = 0.529 \text{ Å}$$

relative permittivity

$$a_B = \frac{4\pi\varepsilon_r\varepsilon_0\hbar^2}{\mu e^2} = \varepsilon_r \frac{m_0}{\mu} a_0$$

Limiting exact 2D case ($L \ll a_B$) ⇒ 1st treatment for surface inversion layer in MIS/MOS structures[2]

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\varepsilon_r\varepsilon_0 r}\right)\psi_{n,m}(r,\theta) = E\psi_{n,m}(r,\theta) \qquad \boxed{\psi_{1,0}(r,\theta) = \left(\frac{8}{\pi}\right)^{1/2} a_B^{-1}\, exp\left(-\frac{2r}{a_B}\right)}$$

$$\boxed{E_n^{2D} = -\frac{Ry^*}{\left(n - 1/2\right)^2} \Rightarrow E_1^{2D} = -4Ry^*} \qquad \boxed{a_B^{2D} = \frac{a_B}{2}}$$

Excitonic features more prominent with decreasing dimensionality!

[1] R. S. Knox, *Theory of Excitons*, Solid-State Physics Suppl. **5** (Academic Press, New York, 1963).
[2] F. Stern and W. E. Howard, Phys. Rev. **163**, 816 (1967) (> 1800 citations) ; T. Ando, A. B. Fowler, and F. Stern, Rev. Mod. Phys. **54**, 437 (1982) (> 6540 citations).

Excitons in quantum wells

Case of an infinitely deep quantum well

Excitons in finite thickness QWs[1]

Exciton binding energy calculated using a variational method
Perturbative exciton Hamiltonian assuming nondegenerate isotropic bands:

in-plane reduced mass

$$H = \frac{p_{ze}^2}{2m_e^*} + \frac{p_{zh}^2}{2m_h^*} + \frac{P_x^2 + P_y^2}{2\left(m_e^* + m_h^*\right)} + \frac{p_x^2 + p_y^2}{2\mu_\perp} - \frac{e^2}{4\pi\varepsilon_0\varepsilon_r\left[x^2 + y^2 + \left(z_e - z_h\right)^2\right]^{1/2}} + V_{conf}\left(z_e\right) + V_{conf}\left(z_h\right) + E_g$$

center-of-mass exciton momentum P, relative momentum projections p

$$(1)\ \psi_\lambda(\mathrm{r}) = N(L,\lambda)\cos\left(\pi z_e/L\right)\cos\left(\pi z_h/L\right)exp\left[-\left(\rho/\lambda\right)\right]\ or$$

separated

$$(2)\ \psi_{\lambda'}(\mathrm{r}) = N(L,\lambda')\cos\left(\pi z_e/L\right)\cos\left(\pi z_h/L\right)exp\left[-\left[\rho^2 + \left(z_e - z_h\right)^2\right]^{1/2}/\lambda'\right]$$

nonseparated

normalizing coefficients

variational parameters

$$\rho = \left(x^2 + y^2\right)^{1/2}$$

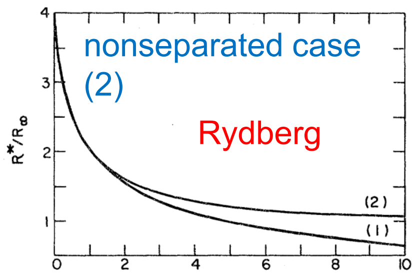
without plane-wave term

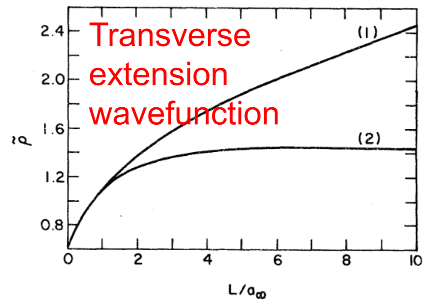
Reminiscence of Coulombic binding

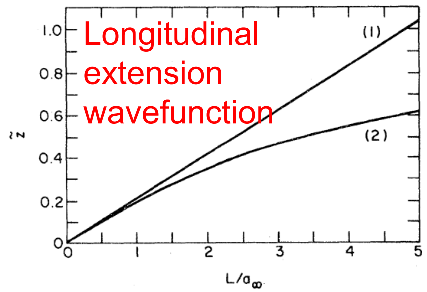
$$\boxed{\frac{Ry^{2D}}{Ry^*} = \left[E_g + \frac{\hbar^2\pi^2}{2L^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \min_i\left\langle\psi_i\middle|H\middle|\psi_i\right\rangle\right]/Ry^*,\ i = \lambda, \lambda'}$$

Infinitely deep QW
Single electron picture (no excitonic feature)

R_∞ and $a_\infty \equiv$ bulk values





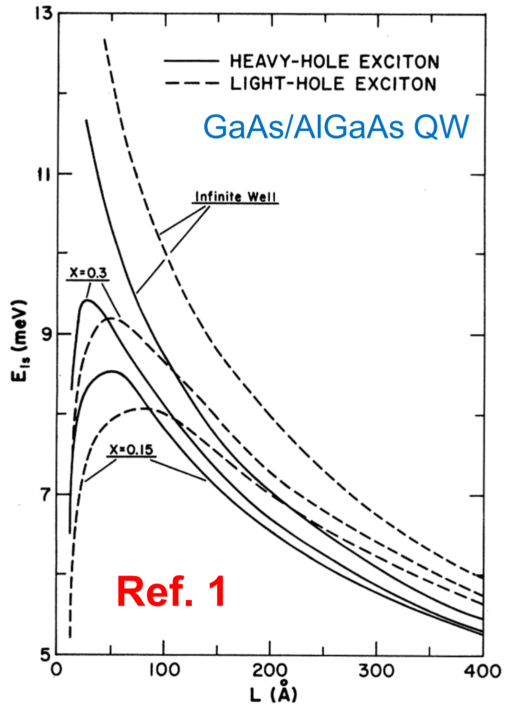


[1]G. Bastard *et al.*, Phys. Rev. B **26**, 1974 (1982) (> 800 citations).

Excitons in quantum wells

Improved accuracy for the determination of Ry^{2D} when taking into account the finite well depth (simple parabolic hole bands)[1] and valence-band mixing, dielectric mismatch, Coulomb coupling between subbands, nonparabolicity effects[2]
Introduction of a fractional-dimensional space $1 < \alpha < 3$:[3]

$$\boxed{E_n^{\alpha} = E_g - \frac{Ry^*}{\left[n + \frac{\alpha - 3}{2}\right]^2}, \quad n = 1, 2, \ldots \quad a_{B,n}^{\alpha} = \left[n + \frac{\alpha - 3}{2}\right]^2 a_B}$$



Ry^{2D} > 3D case (e.g., 4-5 meV in bulk GaAs) $\Rightarrow$ optical properties can be dominated by exciton effects even at 300 K
Features such as: optical bistability, large electro-optic coefficients

[1]R. L. Greene *et al.*, Phys. Rev. B **29**, 1807 (1984) (> 530 citations).
[2]L. C. Andreani and A. Pasquarello, Phys. Rev. B **42**, 8928 (1990) (> 360 citations).
[3]X.-F. He, Phys. Rev. B **43**, 2063 (1991) (> 270 citations); H. Mathieu *et al.*, Phys. Rev. B **46**, 4092 (1992) (> 290 citations).