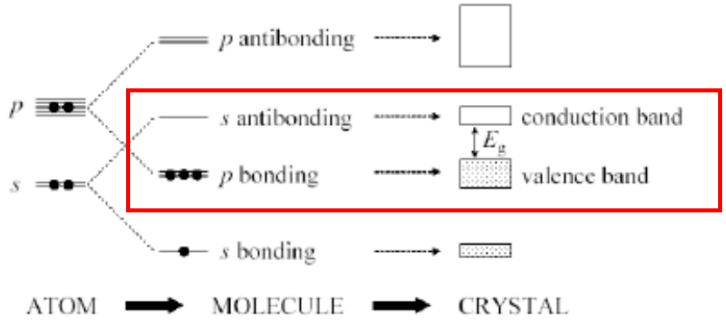
sp^3 Semiconductor



- Four valence electrons per atom: Group IV (C, Si, Ge)
- III-V compounds (GaAs, InAs, InSb, GaN ….)
- II-VI compounds (ZnS, ZnSe, CdSe, HgTe, ….)
- V.B. → C.B. is $p \rightarrow s$, hence allowed dipole transition

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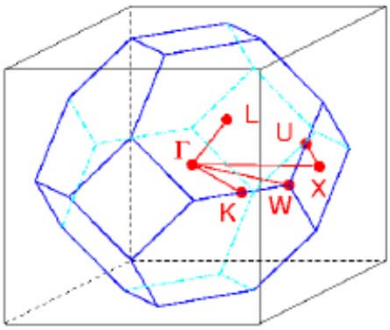
The first Brillouin zone



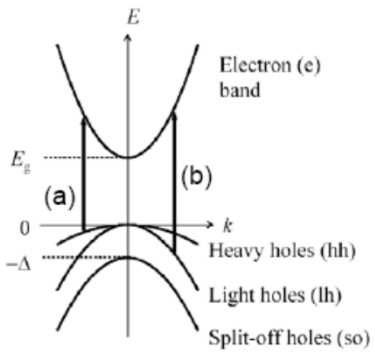
$4\pi/a_0$

High symmetry points and directions

$\Gamma = 2\pi/a_0[0, 0, 0]$
$X = 2\pi/a_0[1, 0, 0]$
$L = 2\pi/a_0[½, ½, ½]$
$U = 2\pi/a_0[1, ¼, ¼]$
$W = 2\pi/a_0[1, ½, 0]$
$K = 2\pi/a_0[¾, ¾, 0]$

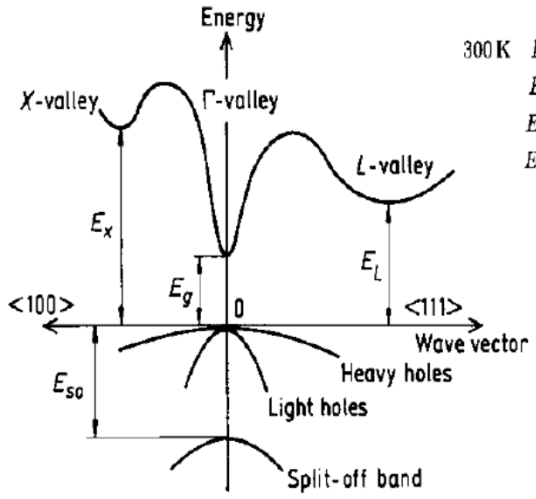
$\Delta = 2\pi/a_0[\zeta, 0, 0]$,	$0 \le \zeta \le 1$
$\Lambda = 2\pi/a_0[\zeta, \zeta, \zeta]$,	$0 \le \zeta \le ½$
$\Sigma = 2\pi/a_0[\zeta, \zeta, 0]$,	$0 \le \zeta \le ¾$
$Z = 2\pi/a_0[1, \zeta, 0]$,	$0 \le \zeta \le ½$
$Q = 2\pi/a_0[1-\zeta, ½, \zeta]$,	$0 \le \zeta \le ½$
$S = 2\pi/a_0[1, \zeta, \zeta]$,	$0 \le \zeta \le ¼$

Four-band Model (Parabolic Approximation)



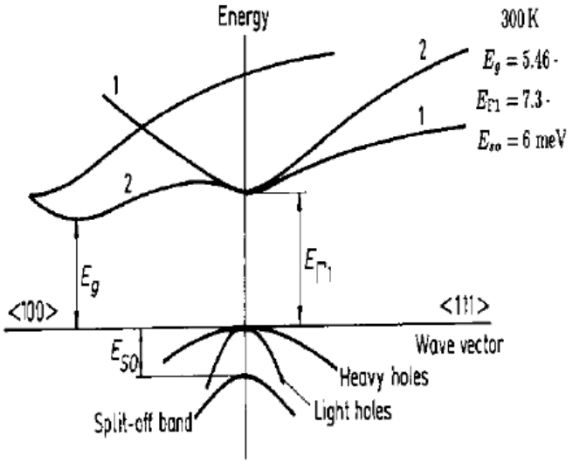
- Simplified band structure first proposed by Kane (1957)
  single *s*-like conduction band
  three *p*-like valence bands
- effective mass:
  $\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{\partial E^2}{\partial k^2}$
- valid near **k** = 0
  (a) Heavy hole transition
  (b) Light hole transition
- Split-off hole transitions also possible

GaAs



300 K $E_g = 1.42$ eV
$E_L = 1.71$ eV
$E_X = 1.90$ eV
$E_{so} = 0.34$ eV

Diamond



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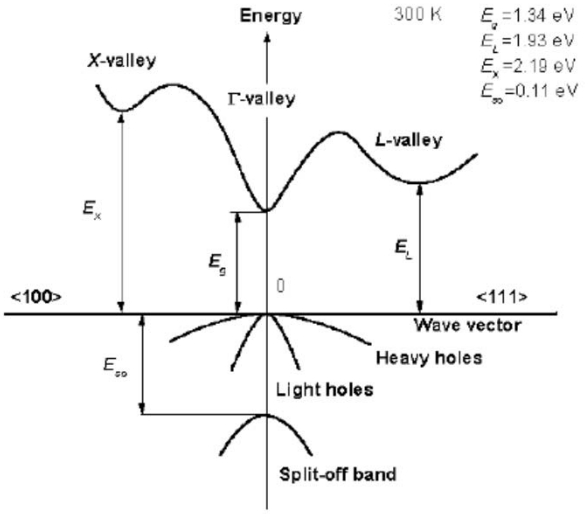
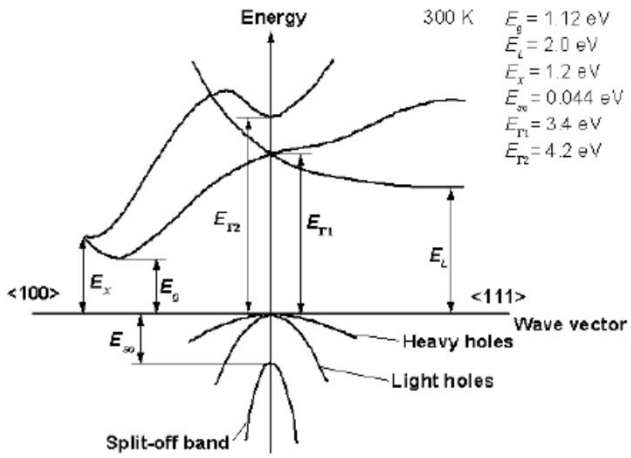
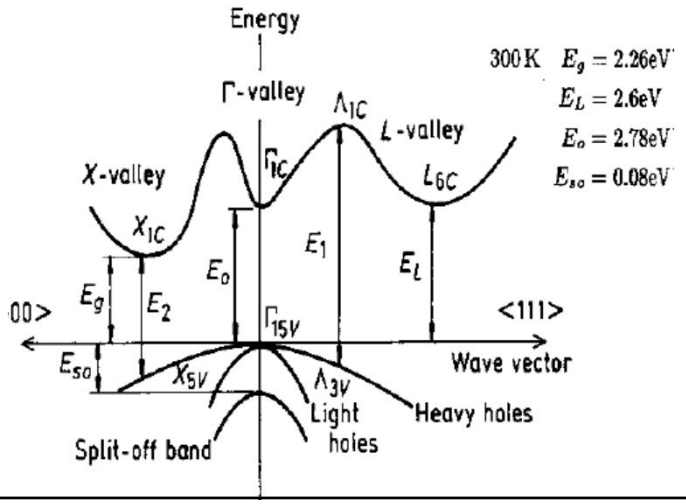
InP



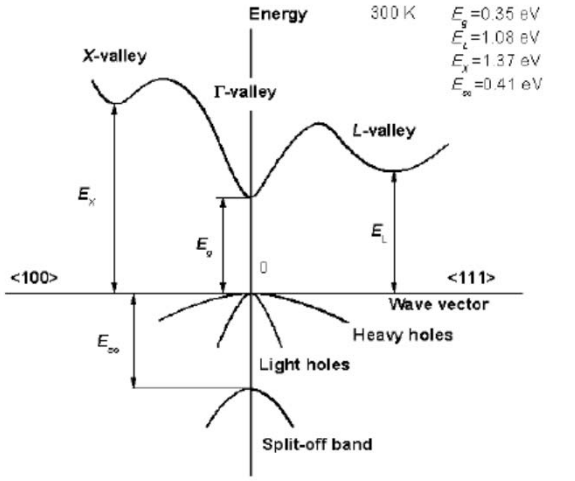
Si


Energy
300 K
E_g = 1.12 eV
E_L = 2.0 eV
E_X = 1.2 eV
E_{so} = 0.044 eV
$E_{\Gamma1}$ = 3.4 eV
$E_{\Gamma2}$ = 4.2 eV
$E_{\Gamma2}$
$E_{\Gamma1}$
E_L
E_X
E_g
<100>
<111>
Wave vector
E_{so}
Heavy holes
Light holes
Split-off band

GaP


Energy
300 K E_g = 2.26eV
E_L = 2.6eV
E_o = 2.78eV
E_{so} = 0.08eV
Γ-valley
Λ_{1C}
L-valley
X-valley
Γ_{1C}
L_{6C}
X_{1C}
E_1
E_o
E_L
E_g
E_2
00>
Γ_{15V}
<111>
E_{so}
X_{5V}
Λ_{3V}
Wave vector
Light holes
Heavy holes
Split-off band

InAs



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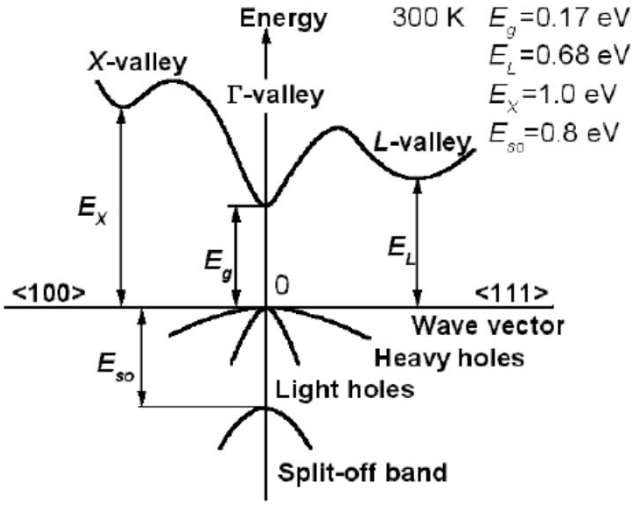
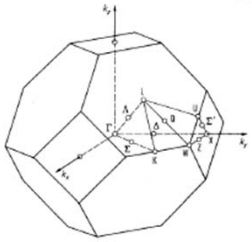
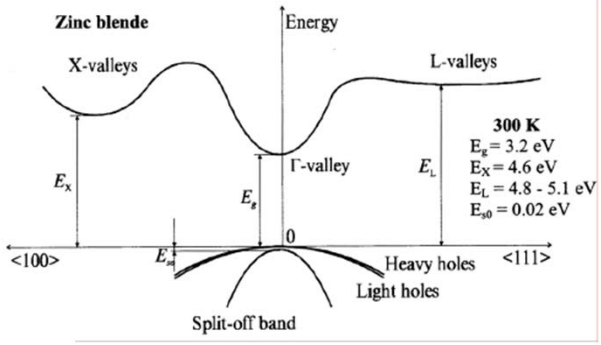
InSb



GaN (Zinc Blende)





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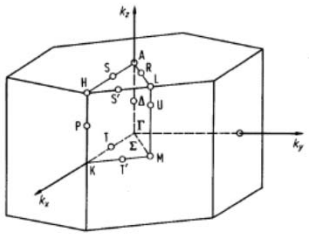
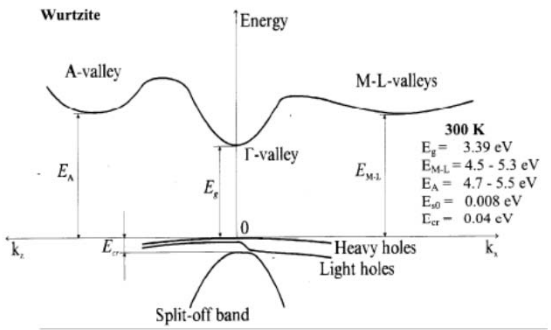
GaN (Wurtzite)





Bulk semiconductor:

$$\psi = Ae^{i(k_x x + k_y y + k_z z)}$$

$$E = \frac{\hbar^2}{2m_e^*}(k_x^{\,2} + k_y^{\,2} + k_z^{\,2})$$

$$D(E) = \frac{dN}{dE} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

$$k_F = (3\pi^2 n)^{1/3}$$

Simple metals

Electrons are considered as "**electron gas**" (Drude model), i.e. the application of an electric field accelerates them in the field direction.

Basic assumptions

no interaction between electrons; **Independent Electrons**

constant potential background, **no periodic potential** of the lattice;

electrons in a box have only kinetic energy, i.e. $E = \frac{1}{2} mv^2$

Schrödinger equation $\hat{H}\psi = E\psi$

E: eigenvalue of $\hat{H}$

$\hat{H}$: Hamilton operator

$\hat{H} = -\hbar^2/(2m)\,\nabla^2 + V$

$\hbar = h/(2\pi)$; h: Planck's constant

m: electron mass

∇^2: nabla^2 = $\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$

V: potential energy [here: V = 0]

ψ: wavefunction,

contains information of movement of the electron (e^-) and its position

E: energy

Free Electron Approximation

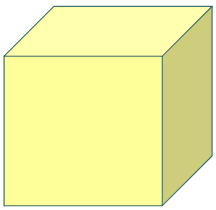
Solutions for ψ?

Simple metals: Quantum Theory

Boundary conditions

The electron is confined to the solid (a box of length L):

$\psi(0) = 0$ and $\psi(L) = 0$



$\hat{H}\psi = E\psi = -\hbar^2/(2m)\, d^2\psi/dx^2 + V$

with V = 0:

$0 = h^2/(8\pi^2 m)\, d^2\psi/dx^2 + E\psi$

$0 = d^2\psi/dx^2 + 8\pi^2 m/h^2\, E\psi$

We define for simplification

$k^2 = 8\pi^2 mE/h^2$, which gives:

$d^2\psi/dx^2 + k^2\psi = 0$

Thus, ψ is a function that is proportional to its second derivative:

$\psi \propto d^2\psi/dx^2$

Possible solution: $\psi = \exp(-ikx)$, or, if real:

$\psi = \sin(kx)$ => $d\psi/dx = k\cos(kx)$ => $d^2\psi/dx^2 = -k^2\sin(kx)$

General solution includes a constant A: $\psi = A\sin(kx)$

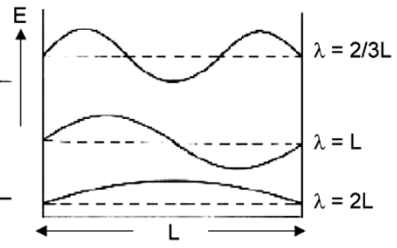
Simple metals: Quantum Theory

Are the boundary conditions [$\psi(0) = 0$ and $\psi(L) = 0$] fulfilled?

$\psi = \sin(kx)$

$\psi(0) = \sin(k0) = 0$

$\psi(L) = \sin(kL)$ is 0 if $kL = n\pi$



What are k and E?

With the definition $k^2 = 8\pi^2 mE/h^2$, and $kL = n\pi$:

$k^2 = n^2\pi^2/L^2 = 8\pi^2 mE/h^2$

=> $E = n^2h^2/(8mL^2)$

We also know $E = \frac{1}{2} mv^2$ and $p = mv$,

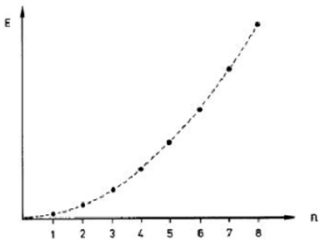
and considering the particle-wave dualism:

de Broglie: $p = h\nu = h/\lambda$ => $p/h = 1/\lambda$

=> $k^2 = 8\pi^2 mE/h^2 = 8\pi^2 m/h^2\ \frac{1}{2} mv^2 = 4\pi^2/h^2\ p^2 = 4\pi^2/\lambda^2$

$k = 2\pi/\lambda$ **wavevector** $\psi = \sin(kx) = \sin(2\pi/\lambda\, x)$

Bulk semiconductor:



Allowed electron energies in a 1D box

For each allowed energy state

$\Rightarrow$ 2 electrons

In a typical metal (L $\approx$1cm $\Leftrightarrow$ 10^8 unit cells)

ΔE between individual levels is very small,

i.e. energies are quasi-continuous.

$$\psi = Ae^{i(k_x x + k_y y + k_z z)}$$

$$E = \frac{\hbar^2}{2m_e^*}(k_x^{\,2} + k_y^{\,2} + k_z^{\,2}) \qquad E(k) = \frac{\hbar^2}{2m}[(\frac{n_x\pi}{L_x})^2 + (\frac{n_y\pi}{L_y})^2 + (\frac{n_z\pi}{L_z})^2]$$

$$D(E) = \frac{dN}{dE} = \frac{V}{2\pi^2}(\frac{2m}{\hbar^2})^{3/2} E^{1/2} \qquad k_F = (3\pi^2 n)^{1/3}$$

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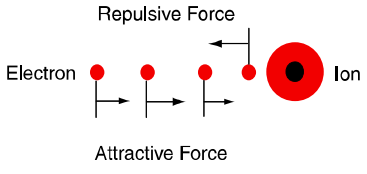
Periodic Potentials and Bloch's Theorem



$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_L\right]\phi = E\phi$$

$V_L(r) = V(r + \vec{R})$

$\vec{R}$ Lattice vector

Bloch's theorem: the eigenstates of the Hamiltonian above can be chosen to have the form of a plane wave times a function with the periodicity of the Bravais Lattice.

Bloch Wavefunction: $\phi(r) = \frac{e^{ik\cdot r}}{\sqrt{V}}u(r)$

$u(r) = u(r + \vec{R})$ periodic part of Bloch function

Quantum well, 1D confinement, 2D electronic system

$$\psi = A\sin k_z z \cdot e^{i(k_x x + k_y y)}$$

$$E = \frac{h^2 n_z^2}{8m_e^* L_z^2} + \frac{\hbar^2}{2m_e^*}(k_x^2 + k_y^2)$$

$$D(E) = \frac{m^*}{\pi\hbar^2 L_z}$$

$$k_F = \sqrt{2\pi n_{2d}}$$

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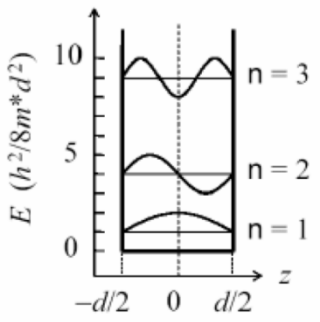
Quantum well, 1D confinement, 2D electronic system

$$-\frac{\hbar}{2m^*}\frac{d^2\varphi(z)}{dz^2} = E\varphi(z)$$

$$\varphi_n = \sqrt{\frac{2}{d}}\sin(k_n z + \frac{n\pi}{2})$$

$$k_n = n\pi / d$$

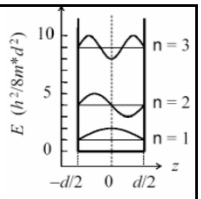
$$E_n = \frac{\hbar^2 k_n^2}{2m^*} = \frac{\hbar^2}{2m^*}(\frac{n\pi}{d})^2$$



Exp: m* = 0.1 m_0, d = 10 nm
E_1 = 38 meV
E_2 = 150 meV

Infinite Potential Well

Quantum well, 1D confinement, 2D electronic system



- Separation of the variables:
  $\Psi(x,y,z) = \Psi(x,y)\varphi(z)$
- Free in x-y plane, confined in z.

E(n,k)=E_n + E(k)

- Free motion in the x-y plane
  - (plane wave solution)

$$\Psi(x,y) = \frac{1}{\sqrt{A}} e^{ikr}$$

$$E(k)=\frac{\hbar^2 k^2}{2m^*}$$

Total Energy:

$$E(n,k)=E_n+\frac{\hbar^2 k^2}{2m^*}$$

Infinite Potential Well

$$-\frac{\hbar}{2m^*}\frac{d^2\varphi(z)}{dz^2} = E\varphi(z)$$

$$\varphi_n = \sqrt{\frac{2}{d}}\sin(k_n z + \frac{n\pi}{2})$$

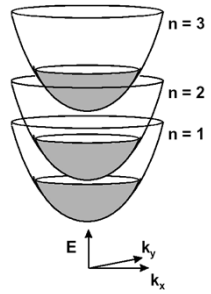
$$k_n = n\pi / d$$

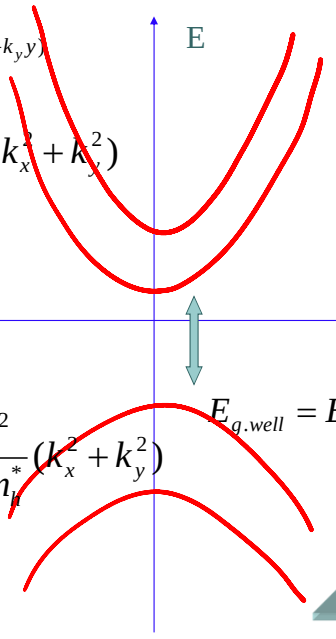
$$E_n = \frac{\hbar^2 k_n^2}{2m^*} = \frac{\hbar^2}{2m^*}(\frac{n\pi}{d})^2$$

$$\psi = A\sin k_n z \cdot e^{i(k_x x + k_y y)}$$

$$E_c = \frac{h^2 n^2}{8m_e^* L_z^2} + \frac{\hbar^2}{2m_e^*}(k_x^2 + k_y^2)$$

Quantum No.
Integer No.





$$E_v = -\frac{h^2 n^2}{8m_h^* L_z^2} - \frac{\hbar^2}{2m_h^*}(k_x^2 + k_y^2)$$

$$E_{g.well} = E_{g.o} + \frac{h^2}{8L_z^2}(\frac{1}{m_e^*} + \frac{1}{m_h^*})$$

d=Lz

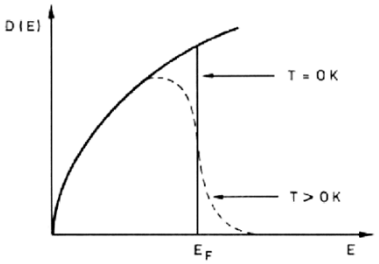
Density of States

The number of orbitals/states per unit energy range

$$D(E) = \frac{dN}{dE}$$

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

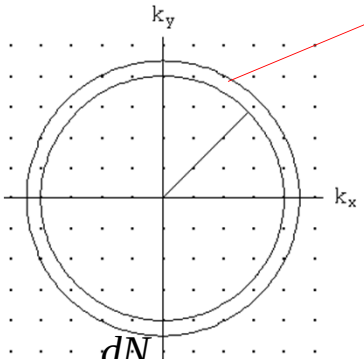
$$N = \frac{V}{3\pi^2}\left(\frac{2\pi E}{\hbar^2}\right)^{3/2}$$



$$D(E) = \frac{dN}{dE} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

2D density of states:

$$E(k) = \frac{\hbar^2 k^2}{2m} \qquad V_{2D} = \left(\frac{2\pi}{L}\right)^2$$



$$\frac{2\pi|k|dk}{\left(\frac{2\pi}{L}\right)^2}\frac{1}{L_z L^2} \times 2 = \frac{|k|dk}{\pi L_z}$$

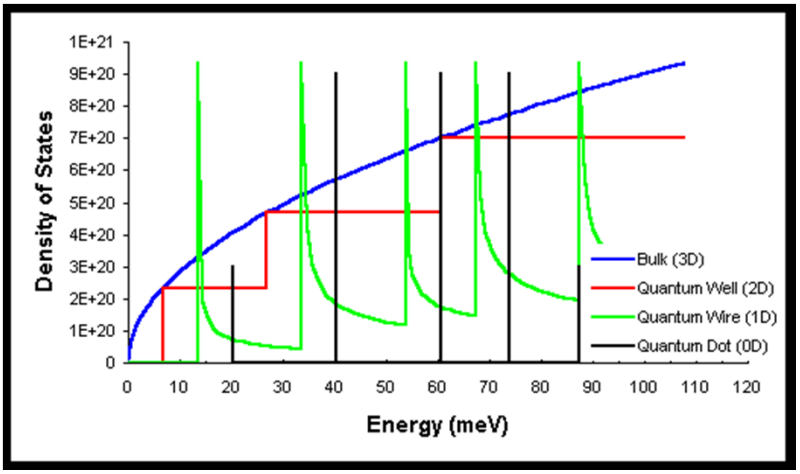
For each subband, in term of energy states per unit volume

$$\frac{|k|dk}{\pi L_z} = \sqrt{\frac{2mE}{\hbar^2}}\left(\frac{2mE}{\hbar^2}\right)^{-1/2}\frac{m}{\hbar^2}\frac{dE}{\pi L_z}$$

$$D(E) = \frac{m^*}{\pi\hbar^2 L_z}$$

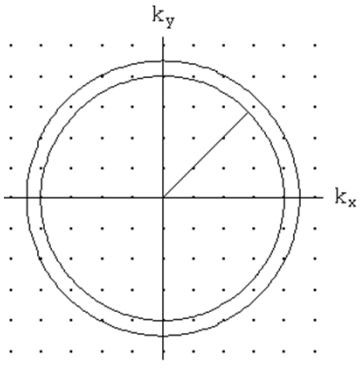
$$D(E) = \frac{dN}{dE}$$

Quantum Confinement and Dimensionality



2D density of states:

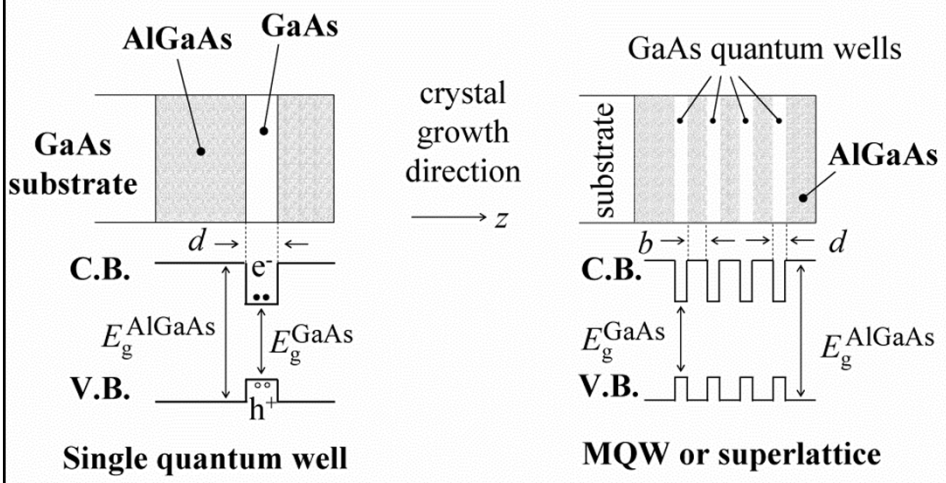
$$V_{2D} = (\frac{2\pi}{L})^2$$



$$\pi k_F^{\ 2} \frac{1}{(\frac{2\pi}{L})^2} \times 2 = N$$

$$k_F^{\ 2} = \frac{2\pi N}{L^2} = 2\pi n_{2d}$$

Semiconductor quantum wells



growth methods
- Molecular beam epitaxy (MBE)
- Metal-organic chemical vapour deposition (MOCVD)

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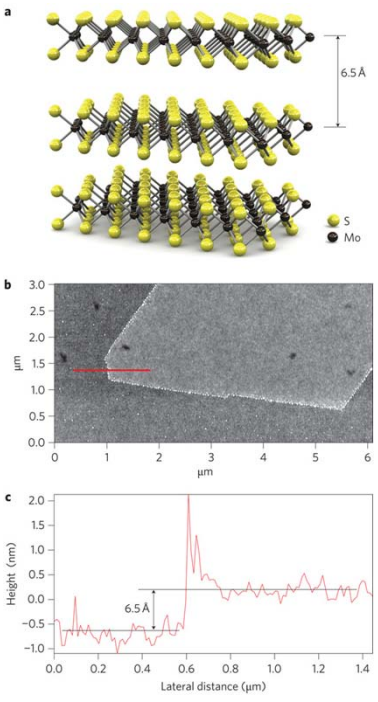
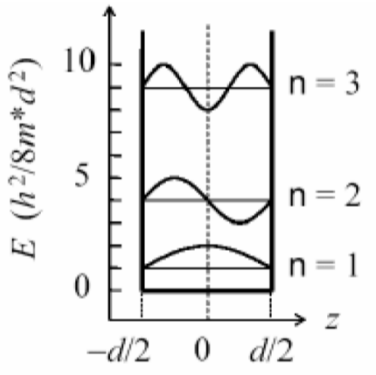
- **Single-sheet**
- **Single layer**
- **Few-layers**

- **MoS_2, C, BN, TMS_2**



Infinite Potential Well



$$-\frac{\hbar}{2m^*}\frac{d^2\varphi(z)}{dz^2} = E\varphi(z)$$

$$\varphi_n = \sqrt{\frac{2}{d}}\sin(k_n z + \frac{n\pi}{2})$$

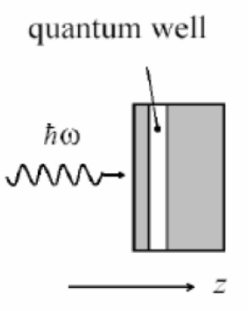
$$k_n = n\pi / d$$

$$E_n = \frac{\hbar^2 k_n^2}{2m^*} = \frac{\hbar^2}{2m^*}(\frac{n\pi}{d})^2$$

Definite parity for each state

Optical Transition: quantum well

Light polarized in x-y plane for normal incidence



Considering a general transition from the nth hole state to the n'th electron state, we can write the initial and final quantum well wave functions in Bloch function form:

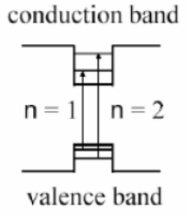
$$M = \langle f|x|i\rangle$$

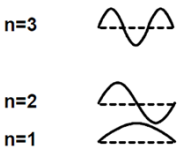
$$\langle f|x|i\rangle = \langle f|y|i\rangle \neq \langle f|z|i\rangle$$

$$|i\rangle = \frac{1}{\sqrt{V}}u_v(r)\varphi_{hn}(z)e^{ik_{xy}\cdot r_{xy}}$$

$$|f\rangle = \frac{1}{\sqrt{V}}u_c(r)\varphi_{en'}(z)e^{ik'_{xy}\cdot r_{xy}}$$

Selection Rule: Quantum well





Momentum conservation: $k_{xy}=k_{xy}'$

$$M = M_{cv} M_{nn'}$$

$$M_{cv} = \langle u_c | x | u_v \rangle \neq 0$$ Dipole allowed

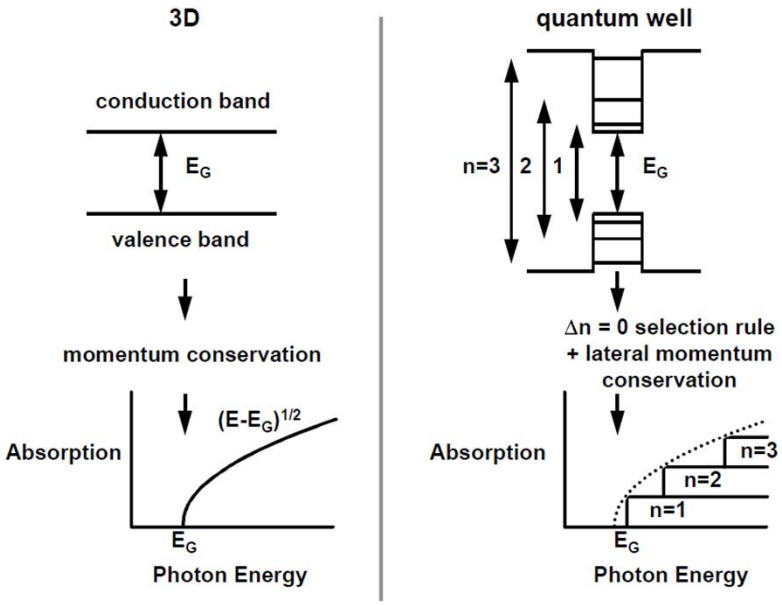
$$M_{nn'} = \langle en'hn \rangle = \int_{-\infty}^{\infty} \varphi^*_{en'}(z)\varphi_{hn}(z)dz$$

M_{CV} is the valence- conduction band dipole momentum;
$M_{nn'}$ is the electron-hole overlap.

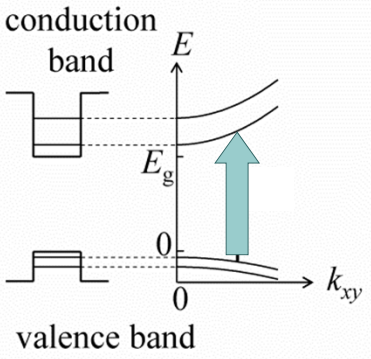
Infinite well: $$M_{nn'} = \frac{d}{2}\int_{-d/2}^{d/2} \sin(\frac{n\pi z}{d}) \sin(\frac{n'\pi z}{d}) dz$$

$M_{nn'}$ = 1 if n = n', $M_{nn'}$ = 0 otherwise.

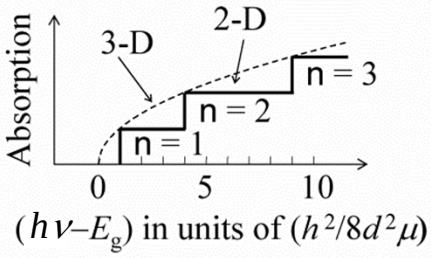
Selection rules for infinite quantum well:
$\Delta n = 0$



2-D absorption



$$E_{g.well} = E_{g.o} + \frac{h^2}{8d^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)$$

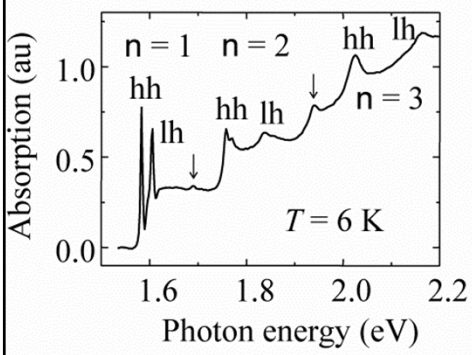


$(h\nu - E_g)$ in units of $(h^2/8d^2\mu)$

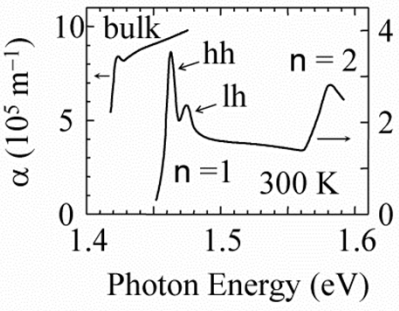
- Absorption ∝ density of states
- Density of states constant in 2-D: $g_{2D}(E) = m / \pi\hbar^2 d$
- Thresholds whenever $h\nu$ exceeds $(E_g + E_{en} + E_{hn})$
- Band edge shifts to $(E_g + E_{e1} + E_{hh1})$

GaAs quantum wells

GaAs/AlAs MQW, d = 7.6 nm



GaAs/AlGaAs MQW
d = 10 nm



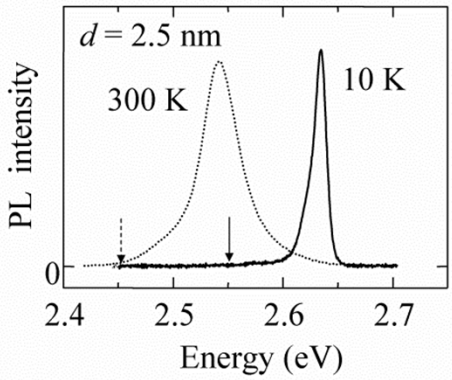
- Excitonic effects enhanced in quantum wells: strong at room temp
- Pure 2-D: $R_X^{2D} = 4 \times R_X^{3D}$
- Typical GaAs quantum well: R_X ~ 10 meV ~ 2.5 × R_X (bulk GaAs)
- Splitting of heavy and light hole transitions

Exciton: 12nm

$$E_{g.well} = E_{g.o} + \frac{h^2}{8d^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)$$

Emission spectrum

$Zn_{0.8}Cd_{0.2}Se/ZnSe$ quantum well



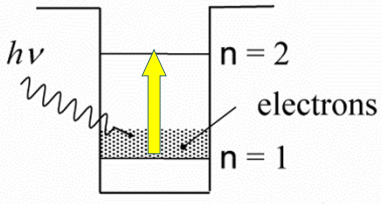
$E_g = 2.55eV$ (10K)

$E_g = 2.45eV$ (300K)

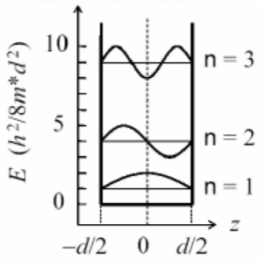
- Emission energy shifted from E_g to $(E_g + E_{e1} + E_{hh1})$
- Tune λ by changing d
- Brighter than bulk due to improved electron-hole overlap
- Used in laser diodes and LEDs

Intersubband transitions

n-type quantum well



- Need z polarized light
- Parity selection rule: Δn = odd number



$$-\frac{\hbar}{2m^*}\frac{d^2\varphi(z)}{dz^2} = E\varphi(z)$$

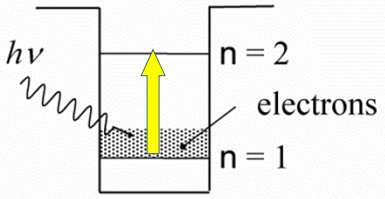
$$\varphi_n = \sqrt{\frac{2}{d}}\sin\left(k_n z + \frac{n\pi}{2}\right)$$

$$k_n = n\pi / d$$

$$E_n = \frac{\hbar^2 k_n^2}{2m^*} = \frac{\hbar^2}{2m^*}\left(\frac{n\pi}{d}\right)^2$$

Intersubband transitions

n-type quantum well



- Need *z* polarized light
- Parity selection rule:
  Δn = odd number

- Transition energy ~ 0.1 eV (~ 10 μm, infrared)
- Absorption used for infrared detectors
- Emission used for infrared lasers (Quantum cascade lasers)