Chair of Condensed Matter Physics
Institute of Theoretical Physics
Faculty of Physics, Universityof Warsaw

Semester Zimowy 2012/2013

Wykład

Modelowanie Nanostruktur

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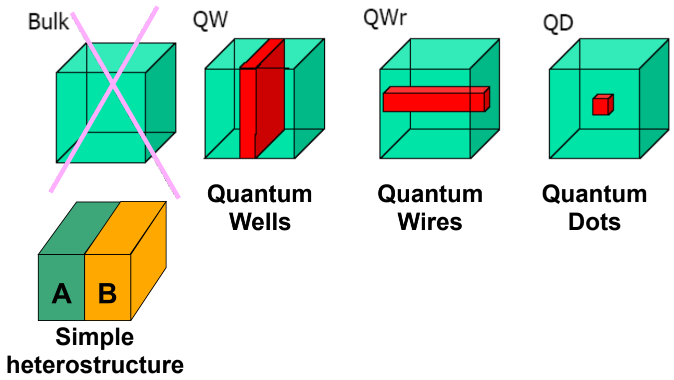
Modelowanie Nanostruktur, 2012/2013
Jacek A. Majewski

Wykład 3 – *9 X 2012*

Metody ciągłe w modelowaniu nanostruktur

Metoda masy efektywnej dla studni kwantowej

Nanotechnology – Low Dimensional Structures



What about realistic nanostructures ?

Inorganics

3D (bulks) : **1-10** atoms in the unit cell

2D (quantum wells): **10-100** atoms in the unit cell

1D (quantum wires): **1 K-10 K** atoms in the unit cell

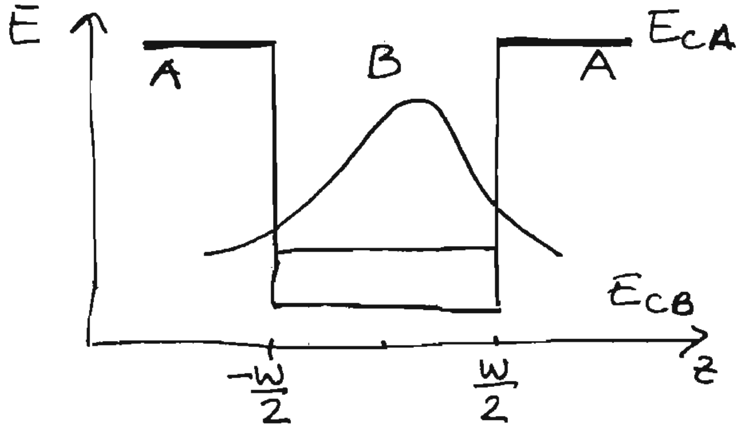
0D (quantum dots): **100K-1000 K** atoms in the unit cell

Organics

Nanotubes, DNA: **100-1000** atoms (or more)

WYKŁAD 2, 9.10.2012 CZĘŚĆ II

STANY ZWIĄZANE W STUDNI KWANTOWEJ



$m_A^* \neq m_B^*$

$E_{CA} \neq E_{CB}$

$$-\frac{\hbar^2}{2m_A^*}\nabla^2 F(\vec{r}) = (E - E_{CA})F(\vec{r}) \quad \text{dla } |z| > \frac{W}{2} \qquad (1)$$

$$-\frac{\hbar^2}{2m_B^*}\nabla^2 F(\vec{r}) = (E - E_{CB})F(\vec{r}) \quad \text{dla } |z| < \frac{W}{2}$$

Warunki brzegowe na granicy materiałów A i B

$$\begin{cases} F^{(A)}(\vec{r}) = F^{(B)}(\vec{r}) \\ \frac{1}{m_A^*}\nabla F^{(A)}(\vec{r}) = \frac{1}{m_B^*}\nabla F^{(B)}(\vec{r}) \end{cases}$$

Skąd drugi warunek ⇐ równość prądów $j^{(A)}(\vec{r}) = j^{(B)}(\vec{r})$

$$j^{(A)}(\vec{r}) = \frac{i\hbar}{2m_A^*}\left(F_c^{(A)}(\vec{r})\nabla F^{(A)*} - c.c.\right) =$$
$$= \frac{i\hbar}{2m_B^*}\left(F^{(B)}(\vec{r})\nabla F^{(B)*} - c.c\right) = j^{(B)}(\vec{r})$$

- W kierunku x, y ~~pole~~ układ jest jednorodny (stały potencjał)
- Potencjał zmienia się tylko w kierunku z

Funkcja obwiedni F może być przedstawiona w postaci

$$F(\vec{r}) = e^{ik_x x} e^{ik_y y} \chi(z)$$

Wstawiając do równań (1) mamy:

$$\frac{\hbar^2}{2m^*_A}\left[-\frac{d^2}{dz^2}+k_{\parallel}^2\right]\chi(z) = (E-E^{\varepsilon}_{CA})\chi(z) \quad \text{dla } |z| > W/2$$

$$\frac{\hbar^2}{2m^*_B}\left[-\frac{d^2}{dz^2}+k_{\parallel}^2\right]\chi(z) = (E-E_{CB})\chi(z) \quad \text{dla } |z| < W/2$$

gdzie $k_{\parallel}^2 = k_x^2 + k_y^2$

Jesteśmy zainteresowani stanami związanymi czyli $E_{CA} > E > E_{CB}$

Problem jest symetryczny względem $z=0$

$$\chi(z) = B\begin{cases}\sin(k_z z)\\ \cos(k_z z)\end{cases} \quad \text{dla } |z| < W/2$$

$$\chi(z) = A e^{-\varkappa z} \quad \text{dla } |z| > W/2$$

gdzie
$$k_z := \sqrt{\frac{2m_B^*(E-E_{CB})}{\hbar^2} - k_{\parallel}^2}$$

$$\varkappa := \sqrt{\frac{2m_A^*(E_{CA}-E)}{\hbar^2} + k_{\parallel}^2}$$

Warunki brzegowe prowadzą do równań

$$A e^{+\varkappa W/2} = B\begin{cases}-\sin(k_z \frac{W}{2})\\ \cos(k_z \frac{W}{2})\end{cases}$$

$$\frac{A\varkappa}{m_A^*} e^{+\varkappa W/2} = \frac{B k_z}{m_B^*}\begin{cases}\cos(k_z \frac{W}{2})\\ \sin(k_z \frac{W}{2})\end{cases}$$

i dalej do równań transcendalnych na energię E

$$\begin{Bmatrix}-\mathrm{tg}(k_z \frac{W}{2})\\ \mathrm{ctg}(k_z \frac{W}{2})\end{Bmatrix} = \frac{m_A^*}{m_B^*}\frac{k_z}{\varkappa}$$

Te równania można rozwiązać numerycznie
Wartości własne przyjmują postać

$$E = E_n(k_{\parallel}) + \frac{\hbar^2 k_{\parallel}^2}{2m_B^*}$$

kurs mechaniki kwantowej

$m_A^* = m_B^* = m_0$; $k_{\parallel} = 0$; $E_{CA} - E_{CB} = V_0$

STANY ZWIĄZANE W STUDNI KWANTOWEJ

zasada wariacyjna (Ritza)

$$E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_0$$

równość wtedy i tylko wtedy, gdy ψ jest stanem podstawowym o energii własnej E_0, czyli ψ_0

INACZEJ SFORMUŁOWANA ZASADA WARIACYJNA

ZASADA WARIACYJNA z warunkiem pobocznym dodatkowym

$$F[\psi] = \langle \psi | H | \psi \rangle$$

$$\Phi[\psi] = \langle \psi | \psi \rangle - 1 \qquad \Phi(\psi_0) = 0$$ warunek dodatkowy

$$\tilde{F}[\psi] := F[\psi] + \lambda \Phi[\psi]$$

λ - dowolna liczba rzeczywista, mnożnik Lagrange'a

Jeżeli F ma w ψ_0 wartość ekstremalną z warunkiem dodatkowym $\Phi[\psi_0] = 0$ to muszą być spełnione równania

$$\text{(a)} \quad \frac{\delta \tilde{F}}{\delta \psi}\Big|_{\psi_0} = \frac{\delta F}{\delta \psi}\Big|_{\psi_0} + \lambda \frac{\delta \Phi}{\delta \psi}\Big|_{\psi_0}$$

$$\text{(b)} \quad \frac{\partial \tilde{F}}{\partial \lambda}\Big|_{\psi_0} = \Phi[\psi_0] = 0$$

$$\Rightarrow \psi_0, \lambda$$

Jeżeli znaleźliśmy stan podstawowy ψ_0, E_0 to stosując zasadę wariacyjną możemy znaleźć pierwszy wzbudzony

$$E_1 = \min \langle \psi_1 | H | \psi_1 \rangle$$ z warunkami dodatkowym

$$\langle \psi_1 | \psi_1 \rangle = 1 \quad \text{oraz} \quad \langle \psi_1 | \psi_0 \rangle = 0.$$

itd..

Bardzo ważny przykład: szukamy ψ w postaci

$$\psi = \sum_{i=1}^{N} c_i \varphi_i$$

$\{\varphi_i\}$ - zbiór znanych funkcji

chcemy znaleźć równanie na współczynniki c_i (odpowiadające funkcjom własnym) oraz energie własne

$$J := \langle\psi|H|\psi\rangle = \sum_i^N \sum_j^N c_i^* c_j \langle\varphi_i|H|\varphi_j\rangle = \sum_i \sum_j c_i^* c_j \underbrace{H_{ij}}_{\text{el. macierowe}}$$ (2-4)

$$I := \langle\psi|\psi\rangle = \sum_{i=1}^N \sum_{j=1}^N c_i^* c_j S_{ij}$$

gdzie $S_{ij} := \langle\varphi_i|\varphi_j\rangle$

$S_{ij} = \delta_{ij}$ gdy $\{\varphi_i\}$ ortonormalny układ funkcji

$$\left.\begin{aligned} &\frac{\partial}{\partial c_k^*}(J + \lambda(I-1)) \quad k=1\ldots N \\ &\sum_{i,j=1}^N c_i^* c_j S_{ij} - 1 = 0 \end{aligned}\right\} \Rightarrow \boxed{\begin{aligned} &\sum_{j=1}^N H_{kj} c_j + \lambda \sum_{j=1}^N S_{kj} c_j = 0 \\ &\text{oraz} \sum_{i,j=1}^N c_i^* c_j S_{ij} = 1 \end{aligned}}$$

$$\lambda = -E$$

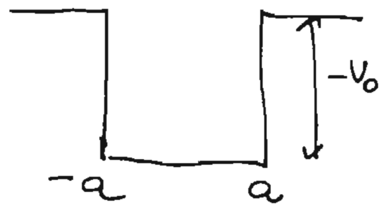
$$\begin{bmatrix} H_{11} & H_{12} & \ldots & H_{1N} \\ \vdots & & & \\ H_{N1} & H_{N2} & \ldots & H_{NN} \end{bmatrix} \begin{bmatrix} c_1 \\ \vdots \\ c_N \end{bmatrix} = E \begin{bmatrix} S_{11} & S_{12} \ldots S_{1N} \\ S_{N1} & S_{N2} \quad S_{NN} \end{bmatrix} \begin{bmatrix} c_1 \\ \vdots \\ c_2 \end{bmatrix}$$

Uogólnione zagadnienie własne

- Procedura znajdowania stanów związanych dla układu fizycznego o Hamiltonianie H
  (1) wybrać układ funkcji bazy $\{\varphi_i\}$ najlepiej ortonormalny
  (2) Policzyć elementy macierzowe Hamiltonianu $H_{ij} := \langle\varphi_i|H|\varphi_j\rangle$
  (3) Przeprowadzić diagonalizację macierzy H_{ij} $\hat{H}\vec{c} = E\vec{c}$, która da stany własne (energie i wektory własne)

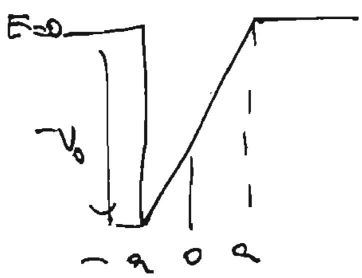
Problem policzyć stany związane w studniach kwantowych o następujących kształtach

① prostokątna studnia kwantowa



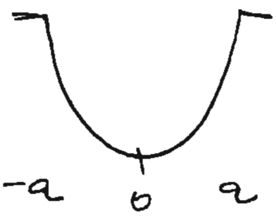
$$V(z)=\begin{cases}0 & |z|>a\\ -V_0 & |z|\leq a\end{cases}\qquad V_0\geqslant 0$$

② trójkątna studnia kwantowa



$$V(z)=\begin{cases}0 & |z|>a\\ \frac{V_0}{2}\left(\frac{z}{a}-1\right) & |z|\leq a\end{cases}$$

③ paraboliczna studnia kwantowa

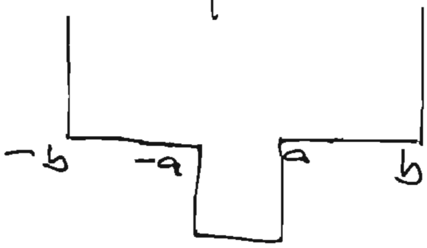


$$V(z)=\begin{cases}0 & |z|>a\\ \frac{V_0}{a^2}z^2-V_0 & |z|\leq a\end{cases}$$

Jakie funkcje wziąć za funkcje bazy? $\{\varphi_n\}$

Jako φ_i bierzemy funkcje własne nieskończonej studni potencjału o szerokości $2b$

$b>a$



$$\phi_n^{(+)}(z)=\frac{1}{\sqrt{b}}\cos\left(n-\frac{1}{2}\right)z\frac{\pi}{b}\qquad E_n^{(+)}=\frac{\hbar^2}{2m^*}\frac{\pi^2}{b^2}\left(n-\frac{1}{2}\right)^2$$

$$\phi_n^{(-)}(z)=\frac{1}{\sqrt{b}}\sin\frac{n\pi}{b}z\qquad E_n^{(-)}=\frac{\hbar^2}{2m^*}\frac{\pi^2}{b^2}n^2$$

$$\boxed{H=-\frac{\hbar^2}{2m^*}\frac{d^2}{dz^2}+V(z)}$$

m^* – nie zależy od z

$n=1,2,3,\ldots$

$\sigma\in\{+,-\}$

$H\psi=E\psi$ gdzie $\psi(z)=\sum_{\sigma n}c_{n\sigma}\phi_n^{(\sigma)}(z)$

Parzyste i nieparzyste stany.

$$\int_{-b}^{b} [\phi_n^{(\sigma)}(z)]^* \phi_{n'}^{(\sigma')}(z)\, dz = \delta_{nn'}\delta_{\sigma\sigma'}$$

Musimy policzyć elementy macierzowe

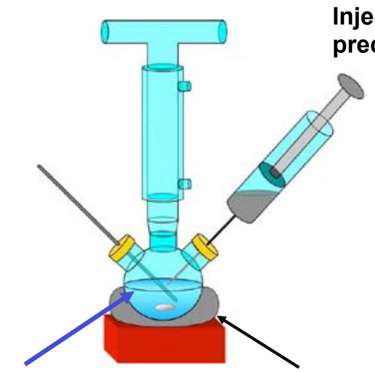
$$\langle \phi_n^{\sigma} | \hat{H} | \phi_m^{\sigma'} \rangle = H_{n\sigma, m\sigma'} = T_{n\sigma,m\sigma'} + V_{n\sigma, m\sigma'}$$

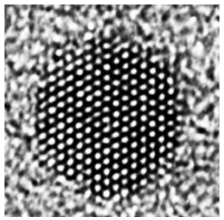
gdzie

$$T_{n\sigma,n'\sigma'} := \langle \varphi_n^{(\sigma)} | -\frac{\hbar^2}{2m^*}\frac{d^2}{dz^2} | \varphi_{n'}^{(\sigma')} \rangle$$

$$V_{n\sigma,n'\sigma'} := \langle \varphi_n^{(\sigma)} | V(z) | \varphi_{n'}^{(\sigma')} \rangle$$

Synthesis of colloidal nanocrystals

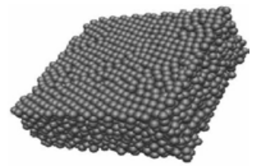




Nanostructures: colloidal crystals

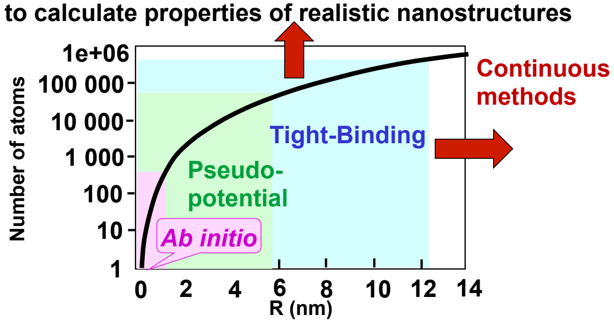
-Crystal from sub-μm spheres of PMMA (perpex) suspended in organic solvent;

- self-assembly when spheres density high enough;



Atomistic vs. Continuous Methods

- Microscopic approaches can be applied to calculate properties of realistic nanostructures



Number of atoms in a spherical Si nanocrystal as a function of its radius R.
Current limits of the main techniques for calculating electronic structure.
Nanostructures commonly studied experimentally
lie in the size range 2-15 nm.

Atomistic methods for modeling of nanostructures

- ***Ab initio* methods** (up to few hundred atoms)
- **Semiempirical methods** (up to 1M atoms)
  - (Empirical Pseudopotential)
  - **Tight-Binding Methods**
- **Continuum Methods**
  (e.g., effective mass approximation)

Continuum theory-
Envelope Function Theory

Electron in an external field

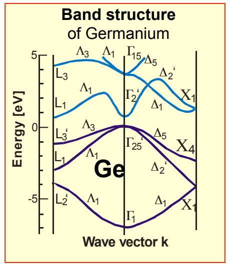
$$\left[\frac{\hat{\vec{p}}^2}{2m} + V(\vec{r}) + U(\vec{r})\right]\psi(\vec{r}) = \varepsilon\psi(\vec{r})$$

Periodic potential of crystal — Non-periodic external potential

- Strongly varying on atomic scale
- Slowly varying on atomic scale

Band Structure

$U(\vec{r}) = 0 \Rightarrow \varepsilon_n(\vec{k}) \Rightarrow$



Electron in an external field

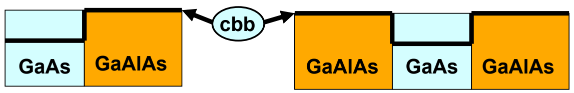
$$\left[\frac{\hat{\vec{p}}^2}{2m} + V(\vec{r}) + U(\vec{r})\right]\psi(\vec{r}) = \varepsilon\psi(\vec{r})$$

Periodic potential of crystal — **Non-periodic external potential**

- **Strongly varying on atomic scale**
- **Slowly varying on atomic scale**

Which external fields ?

- **Shallow impurities, e.g., donors** $U(\vec{r}) = -\frac{e^2}{\kappa|\vec{r}|}$
- **Magnetic field** B, $\vec{B} = curl\vec{A} = \vec{\nabla}\times\vec{A}$
- **Heterostructures, Quantum Wells, Quantum wires, Q. Dots**



- **Does equation that involves the effective mass and a slowly varying function exist ?** $\left(\frac{\hat{\vec{p}}^2}{2m^*} + U(\vec{r})\right)F(\vec{r}) = \varepsilon F(\vec{r})$ $\quad F(\vec{r}) = ?$

Envelope Function Theory –
Effective Mass Equation

J. M. Luttinger & W. Kohn, Phys. Rev. B **97**, 869 (1955).

$$[\varepsilon(-i\vec{\nabla}) + U(\vec{r}) - \varepsilon]F_n(\vec{r}) = 0 \qquad \textbf{(EME)}$$

EME does not couple different bands

$$\psi(\vec{r}) = F_n(\vec{r})u_{n0}(\vec{r})$$

"True" wavefunction — **Envelope Function** — Periodic Bloch Function

- Special case of constant (or zero) external potential

$U(\vec{r}) = 0 \Rightarrow F_n(\vec{r}) = \exp(i\vec{k}\cdot\vec{r}) \Rightarrow \psi(\vec{r})$ **Bloch function**

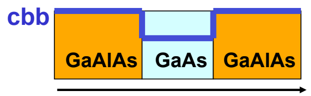
- $U(z) \Rightarrow F_n(\vec{r}) = \exp[i(k_x x + k_y y)]F_n(z)$

Electronic states in Quantum Wells

Envelope Function Theory- Electrons in Quantum Wells

Effect of Quantum Confinement on Electrons

- Let us consider an electron in the conduction band near Γ point



Growth direction (z – direction)

Potential $U(\vec{r})$?

$$U(\vec{r}) = U(z) = \begin{cases} \varepsilon_{c0} & z \in \text{GaAs} \\ \varepsilon_{c0} + \Delta E_c & z \in \text{GaAlAs} \end{cases}$$

$$\varepsilon_c(\vec{k}) = \varepsilon_{c0} + \frac{\hbar^2}{2m^*}\vec{k}^2$$

$U(\vec{r})$ is constant in the xy plane

Effective Mass Equation for the Envelope Function F

$$-\frac{\hbar^2}{2m^*}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)F(x,y,z)+U(z)F(x,y,z)=EF(x,y,z)$$

Separation Ansatz $\quad F(x,y,z) = F_x(x)F_y(y)F_z(z)$

$$-\frac{\hbar^2}{2m^*}\left(\frac{\partial^2 F_x}{\partial x^2}F_yF_z+\frac{\partial^2 F_y}{\partial y^2}F_xF_z+\frac{\partial^2 F_z}{\partial z^2}F_xF_y\right)+U(z)F_xF_yF_z = EF_xF_yF_z$$

Effective Mass Equation of an Electron in a Quantum Well

$$-\frac{\hbar^2}{2m^*}\left(\frac{\partial^2 F_x}{\partial x^2}F_yF_z+\frac{\partial^2 F_y}{\partial y^2}F_xF_z+\frac{\partial^2 F_z}{\partial z^2}F_xF_y\right)+U(z)F_xF_yF_z = EF_xF_yF_z$$

$$E = E_x + E_y + E_z$$

$$-\frac{\hbar^2}{2m^*}\frac{\partial^2 F_x}{\partial x^2}F_yF_z = E_xF_xF_yF_z \qquad -\frac{\hbar^2}{2m^*}\frac{\partial^2 F_y}{\partial y^2}F_xF_z = E_yF_xF_yF_z$$

$$-\frac{\hbar^2}{2m^*}\frac{\partial^2 F_z}{\partial z^2}F_xF_y + U(z)F_xF_yF_z = E_zF_xF_yF_z$$

$$-\frac{\hbar^2}{2m^*}\frac{\partial^2 F_x}{\partial x^2} = E_xF_x \quad \Rightarrow F_x \sim e^{ik_x x}, \quad E_x = \frac{\hbar^2}{2m^*}k_x^2$$

$$-\frac{\hbar^2}{2m^*}\frac{\partial^2 F_y}{\partial y^2} = E_yF_y \quad \Rightarrow F_y \sim e^{ik_y y}, \quad E_y = \frac{\hbar^2}{2m^*}k_y^2$$

$$-\frac{\hbar^2}{2m^*}\frac{\partial^2 F_{zn}}{\partial z^2} + U(z)F_{zn} = E_{zn}F_{zn}$$

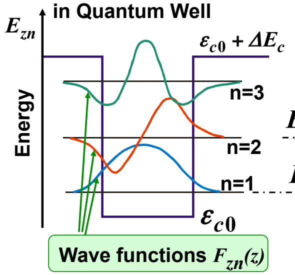
Conduction band states of a Quantum Well

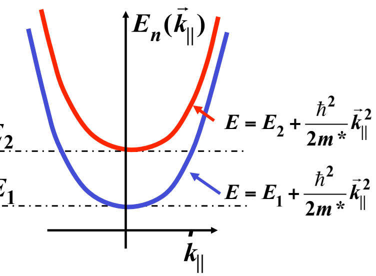
$$F_{\vec{k}_\parallel}(\vec{r}_\parallel) = \frac{1}{A}\exp[i(k_x x + k_y y)] = \frac{1}{A}\exp(i\vec{k}_\parallel\cdot\vec{r}_\parallel)$$

$$F_{n,\vec{k}_\parallel}(\vec{r}) = F_{\vec{k}_\parallel}(\vec{r}_\parallel)F_{zn}(z) = \frac{1}{A}\exp(i\vec{k}_\parallel\cdot\vec{r}_\parallel)F_{zn}(z) \quad \leftarrow F_{zn}(z)$$

$$E_n(\vec{k}_\parallel) = \frac{\hbar^2}{2m^*}\vec{k}_\parallel^2 + E_{zn} \quad \leftarrow E_{zn} \quad -\frac{\hbar^2}{2m^*}\frac{\partial^2 F_{zn}}{\partial z^2} + U(z)F_{zn} = E_{zn}F_{zn}$$

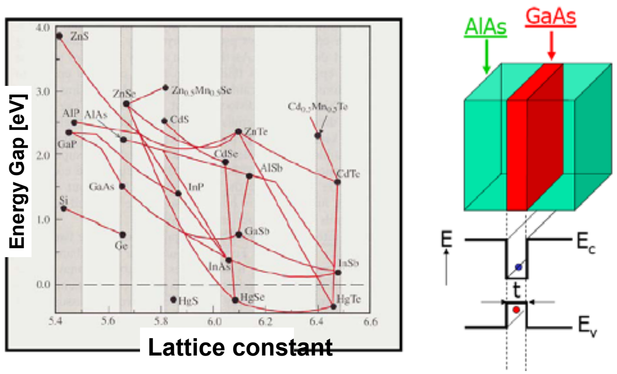
Energies of bound states in Quantum Well





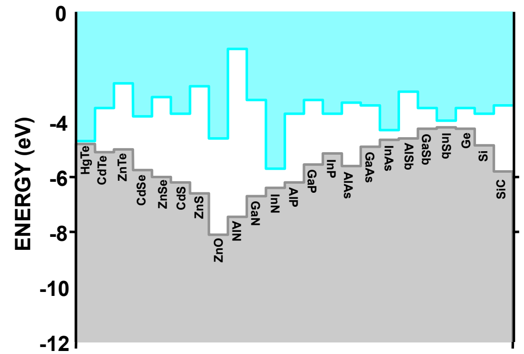
Band structure Engineering

Semiconductor Multilayers → Heterostructures



The major goal of the fabrication of heterostructures is the controllable modification of the energy bands of carriers

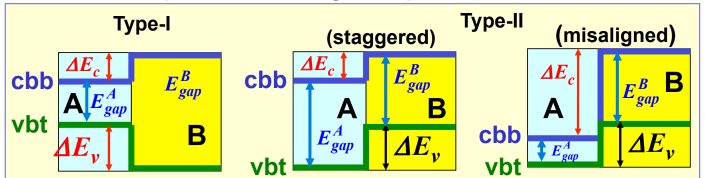
Band lineups in semiconductors



Band edges compile by: *Van de Walle (UCSB) Neugebauer (Padeborn), Nature'04*

Envelope Function Theory- Electrons in Quantum Structures

Various possible band-edge lineups in heterostructures

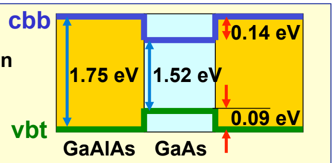


e.g., GaAs/GaAlAs GaN/SiC InAs/GaSb

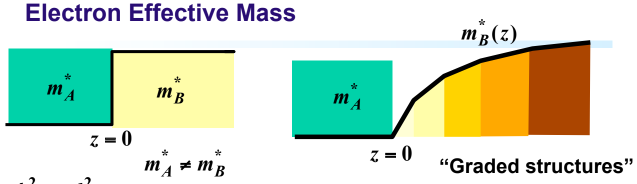
ΔE_v - Valence Band Offset (VBO) ΔE_c - Conduction band offset

VBO's can be only obtained either from experiment or ab-initio calculatio

Band lineup in GaAs / GaAlAs Quantum Well with Al mole fraction equal 20%



Effective Mass Theory with Position Dependent Electron Effective Mass



$-\frac{\hbar^2}{2m^*(z)}\frac{d^2}{dz^2}$ IS NOT HERMITIAN !!

→ Symetrization of the kinetic energy operator $-\frac{\hbar^2}{2}\frac{d}{dz}\frac{1}{m^*(z)}\frac{d}{dz}$ IS HERMITIAN !

$$-\frac{\hbar^2}{2}\frac{d}{dz}\left[\frac{1}{m^*(z)}\frac{d}{dz}\right]F(z)+U(z)F(z)=EF(z)$$

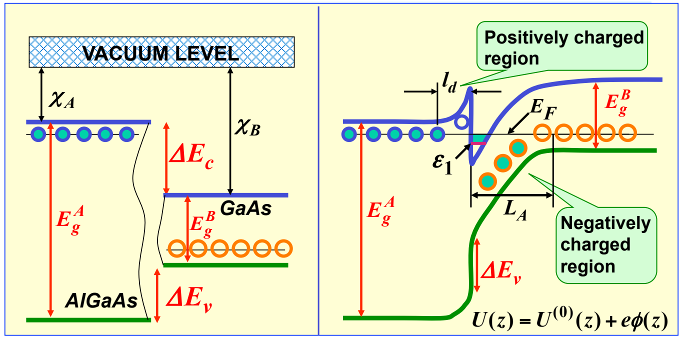
$F(z)$ and $\frac{1}{m^*(z)}\frac{dF(z)}{dz}$ ARE CONTINOUOS !

General form of the kinetic energy operator

$T=[m^*(z)]^{\alpha}\hat{p}_z[m^*(z)]^{\beta}\hat{p}_z[m^*(z)]^{\alpha}$ with $2\alpha+\beta=-1$

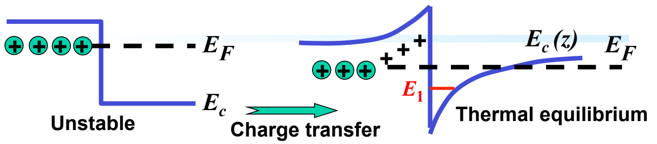
Doping in Semiconductor Low Dimensional Structures

Energy band diagram of a selectively doped AlGAAs/GaAs Heterostructure before (left) and after (right) charge transfer



- χ_A and χ_B - The electron affinities of material A & B
- The Fermi level in the *GaAlAs* material is supposed to be pinned on the donor level.
- The narrow bandgap material GaAs is slightly p doped.

Effects of Doping on Electron States in Heterostructures



Resulting electrostatic potential

Fermi distribution function

$$\nabla^2\Phi(\vec{r}) = \frac{4\pi e}{\varepsilon}\left[\sum_{(acc)}\delta(\vec{r}-\vec{R}_A) - \sum_{(don)}\delta(\vec{r}-\vec{R}_D) - \sum_{\nu} f_\nu |\psi_\nu(\vec{r})|^2\right]$$

should be taken into account in the Effective Mass Equation

$$\left[-\frac{\hbar^2}{2m^*}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right) + U(x,y,z) - e\Phi(\vec{r})\right]\psi_\nu(\vec{r}) = E_\nu\psi_\nu(\vec{r})$$

Electrostatic potential can be obtained from the averaged acceptor and donor concentrations

$$\nabla^2\Phi(\vec{r}) = \frac{4\pi e}{\varepsilon}\left[N_A(\vec{r}) - N_D(\vec{r}) - \sum_{\nu} f_\nu |\psi_\nu(\vec{r})|^2\right]$$

- The self-consistent problem, so-called **"Schrödinger-Poisson" problem**

To be continued!