XIIth-IIC-EMTCCM

European Master in Theoretical Chemistry and Computational Modelling

Lecture 1

Periodicity and Spatial Confinement

Crystal structure
Translational symmetry
Energy bands
k·p theory and effective mass
Heterostructures

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SUMMARY (keywords)

Lattice → Wigner-Seitz unit cell

Periodicity → Translation group → wave-function in Block form

Reciprocal lattice → k-labels within the 1rst Brillouin zone

Schrodinger equation → BCs depending on k; bands E(k); gaps

Gaps → metal, isolators and semiconductors

Heterostructures: EFA

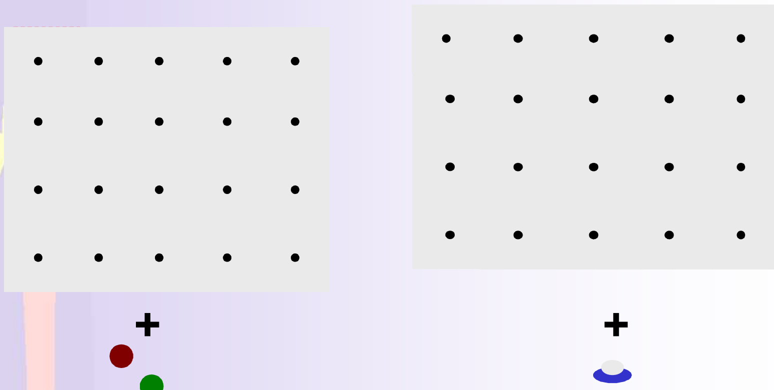
$k \rightarrow \hat{p} = -i\nabla$

$confinement \rightarrow V_c = band\ \ offset$

QWell QWire QDot

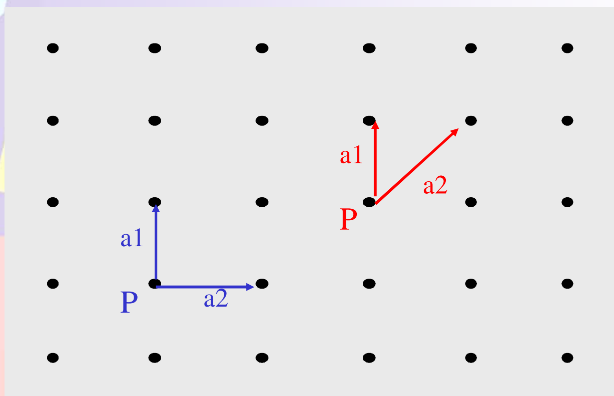
Crystal structure

A crystal is a solid material whose constituent atoms, molecules or ions are arranged in an orderly repeating pattern



Crystal = lattice + basis

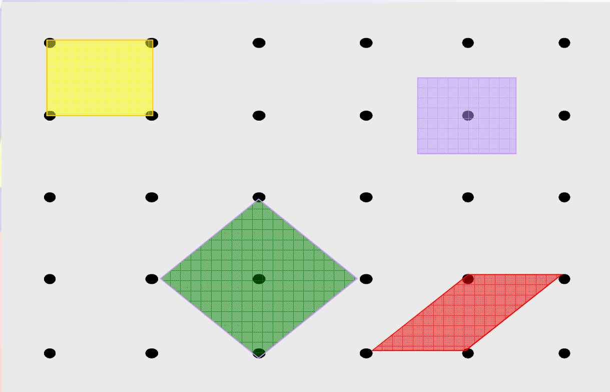
Bravais lattice: the lattice looks the same when seen from *any* point



$$P' = P + (m,n,p) * (a1,a2,a3)$$

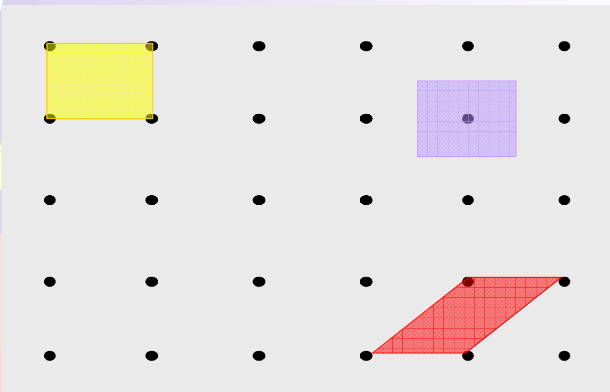
integers

Unit cell: a region of the space that fills the entire crystal by translation



Primitive: smallest unit cells (1 point)

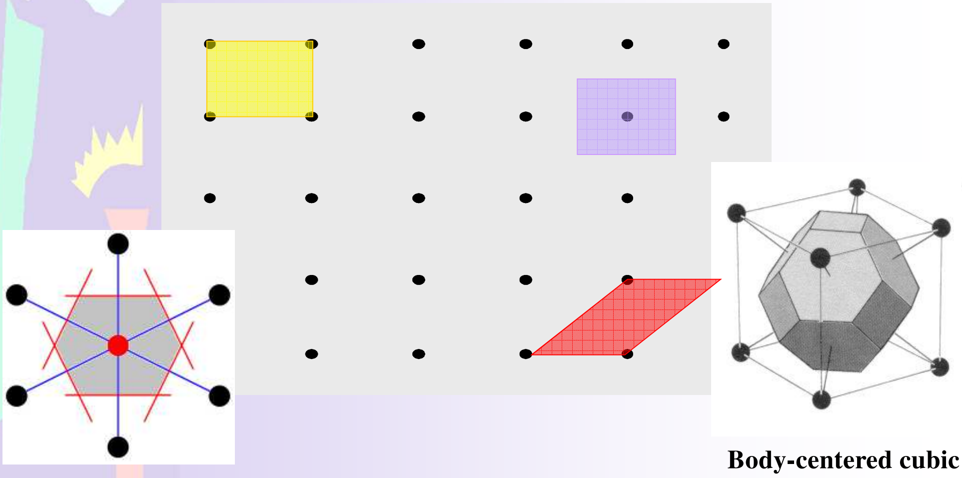
Unit cell: a region of the space that fills the entire crystal by translation



Primitive: smallest unit cells (1 point)

Wigner-Seitz unit cell: primitive and captures the point symmetry

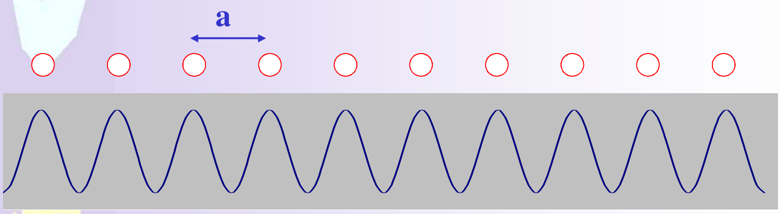
Centered in one point. It is the region which is closer to that point than to any other.



Body-centered cubic

Translational symmetry

We have a periodic system.
Is there a simple function to approximate its properties?



$$\rho(x) = \rho(x+na) \Leftrightarrow |f(x)|^2 = |f(x+na)|^2 \Rightarrow f(x+na) = e^{i\phi} f(x)$$

$$T_n f(x) = f(x+na) \rightarrow \quad \{T_n\} \rightarrow Translation\ \ Group$$

$$[T_n, T_m] = 0 \rightarrow Abelian\ Group$$

$$T_n = e^{i\,a\,n\,\hat{p}} = \sum_q \frac{(i\,a\,n)^q}{q!}\hat{p}^q \qquad T_n f(x) = e^{ian\hat{p}} f(x) = \sum_q \frac{(ian)^q}{q!}(-i)^q \frac{d^q f}{dx^q} = f(x+an)$$

Eigenfunctions of the linear momentum (Also Bloch Functions) are basis of translation group irreps

linear momentum $T_n e^{ikx} = e^{ian\hat{p}} e^{ikx} = e^{iank} e^{ikx}$

Bloch functions $\Psi_k(x) = e^{ik\cdot x} u(x); \quad u(x+a) = u(x)$

$$T_n \Psi_k(x) = T_n e^{ikx} u(x) = e^{ian\hat{p}} e^{ikx} u(x) = e^{iank} \Psi_k(x)$$

	E	$\cdots$	T_n	$\cdots$	
$\vdots$	$\vdots$	$\cdots$	$\vdots$	$\cdots$	$\vdots$
k	1	$\cdots$	e^{ikna}	$\cdots$	e^{ikx}
$\vdots$	$\vdots$	$\cdots$	$\vdots$	$\cdots$	$\vdots$

Range of k and 3D extension

$k \sim k' = k + \frac{2\pi}{a} m, \quad m \in Z$ **same character:** $e^{i[k+\frac{2\pi}{a}m]na} = e^{ikna}$

$k \in [-\frac{\pi}{a}, \frac{\pi}{a}]; \quad \mathrm{k} = 0$ labels the fully symmetric A_1 irrep

3D extension $\begin{cases} \mathrm{x} \to \boldsymbol{r} \\ k \to \boldsymbol{k} \end{cases}$ $\Psi_{\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u(\boldsymbol{r}); \quad u(\boldsymbol{r}+\boldsymbol{a}) = u(\boldsymbol{r})$

$$T_{\boldsymbol{a}} \Psi_{\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot(\boldsymbol{r}+\boldsymbol{a})} u(\boldsymbol{r}+\boldsymbol{a}) = \underbrace{e^{i\boldsymbol{k}\cdot\boldsymbol{a}}}_{character} \; e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u(\boldsymbol{r})$$

Reciprocal Lattice

$$1D: \quad k \sim k' \to k'-k = K = \frac{2\pi}{a}: \quad e^{iKa} = 1$$

$$3D: \quad \boldsymbol{k} \sim \boldsymbol{k'} \to \boldsymbol{k'}-\boldsymbol{k} = \boldsymbol{K}: \quad e^{i\boldsymbol{K}\cdot\boldsymbol{a}_i} = 1, \quad \boldsymbol{a}_i = \boldsymbol{a},\boldsymbol{b},\boldsymbol{c} \ \ (\textit{lattice vectors})$$

$\boldsymbol{K}$? $\quad \boldsymbol{K} = \mathrm{p}_1\boldsymbol{k}_1 + \mathrm{p}_2\boldsymbol{k}_2 + \mathrm{p}_3\boldsymbol{k}_3, \quad \boldsymbol{k}_\mathrm{i} = 2\pi\frac{(\boldsymbol{a}_\mathrm{j}\times\boldsymbol{a}_\mathrm{k})}{(\boldsymbol{a}_\mathrm{j}\times\boldsymbol{a}_\mathrm{k})\boldsymbol{a}_\mathrm{i}}, \quad \mathrm{p}_\mathrm{i} \in Z$

$\boldsymbol{K}\cdot\boldsymbol{a}_\mathrm{i} = 2\pi\, p_i \qquad \{\boldsymbol{k}_1,\boldsymbol{k}_2,\boldsymbol{k}_3\} \to$ *reciprocal lattice*

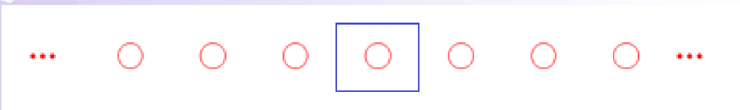
$$\Gamma: \ \boldsymbol{k} = 0, \qquad \boldsymbol{k} = \mathrm{x}\boldsymbol{k}_1 + \mathrm{y}\boldsymbol{k}_2 + \mathrm{z}\boldsymbol{k}_3, \qquad \mathrm{x},\mathrm{y},\mathrm{z} \in (-1/2, 1/2)$$

First Brillouin zone: Wigner-Seitz cell of the reciprocal lattice

Solving Schrödinger equation: Von-Karman BCs

Crystals are infinite... How are we supposed to deal with that?

We use periodic boundary conditions



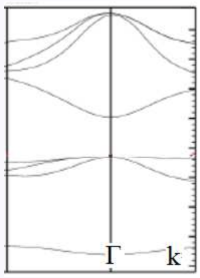
Group of translations:

$T_a\Psi_k(\boldsymbol{r}) = e^{i\,k\cdot a}\,\Psi_k(\boldsymbol{r})$

$\Psi_k(-a/2) = e^{i\,\phi}\Psi_k(a/2), \quad \phi \in [-\pi,\pi]$

k is a quantum number due to translational symmetry

1rst Brillouin zone



We solve the Schrödinger equation ***for each k value****:*

The plot $E_n(k)$ represents an ***energy band***

How does the wave function look like?

$[\hat{T},\hat{H}]=0$ Hamiltonian eigenfunctions are basis of the T_n group irreps

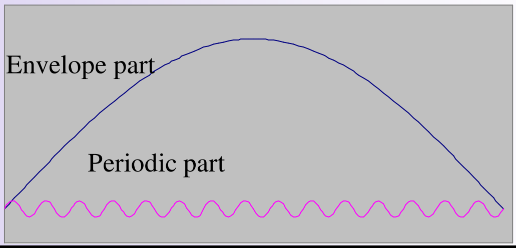
We require $\hat{T}\,\Psi = e^{i\vec{k}\vec{t}}\,\Psi$

$$\Psi_k(\vec{r}) = e^{i\vec{k}\vec{r}}\,u_k(\vec{r})$$ **Bloch function**

Envelope part

Periodic (unit cell) part

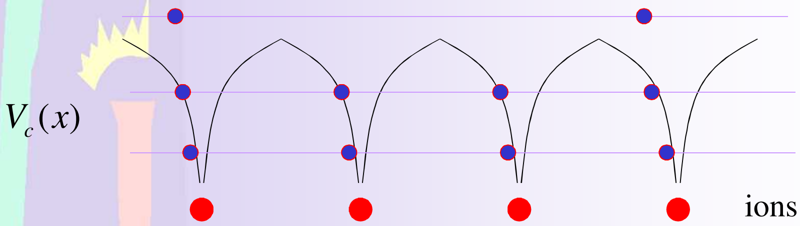
$u_k(\vec{r}+\vec{t})=u_k(\vec{r})$



Energy bands

How do electrons behave in crystals?

quasi-free electrons



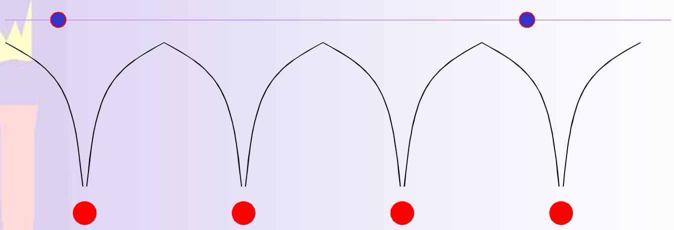
$$\left(\frac{p^2}{2m} + V_c(x)\right)\Psi_k(x) = \varepsilon_k\,\Psi_k(x)$$

$BC: \Psi_k(x+a) = e^{ika}\,\Psi_k(x)$ $\quad \varepsilon_k >> V_c(x)$ $\quad$ Empty lattice

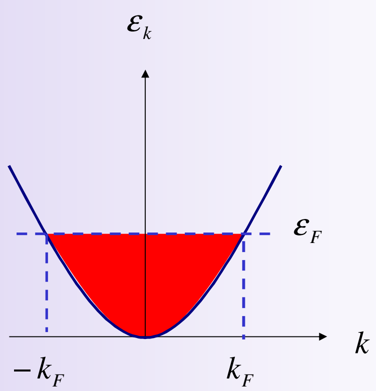
$$\Psi_k(x) = N\,e^{ikx} \qquad k = \frac{2\pi\,p}{a}$$

Plane wave

$V_c(x)$



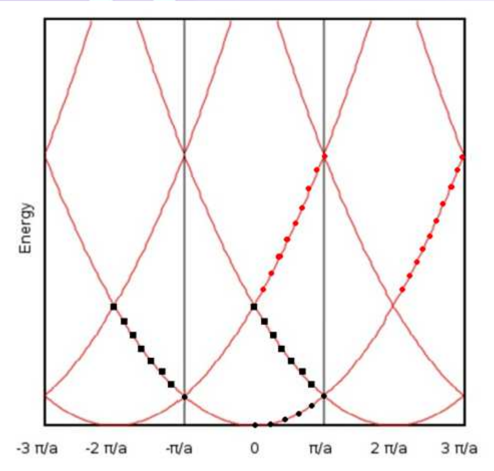
$$\hat{p}\,\Psi_k(x) = \hbar\,k\,\Psi_k(x) \qquad \varepsilon_k = \frac{\hbar^2 k^2}{2m}$$



T=0 K
Fermi energy

$$\varepsilon_k = \frac{\hbar^2 k^2}{2m}$$

Band folded into the first Brillouin zone



$$\varepsilon_k = \frac{\hbar^2 k^2}{2m}$$

$\varepsilon(k)$: **single parabola**

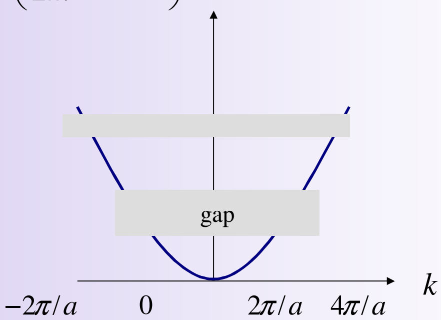
$$BC: \Psi_k(x+a) = e^{ika}\,\Psi_k(x)$$

$$k \sim k' \rightarrow k' - k = K = \frac{2\pi}{a}: \;\; e^{iKa} = 1$$

folded parabola

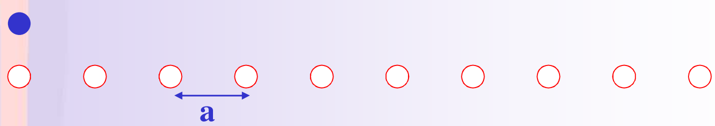
Bragg difraction

$$\left(\frac{p^2}{2m} + V_c(x)\right)\Psi_k(x) = \varepsilon_k\,\Psi_k(x)$$

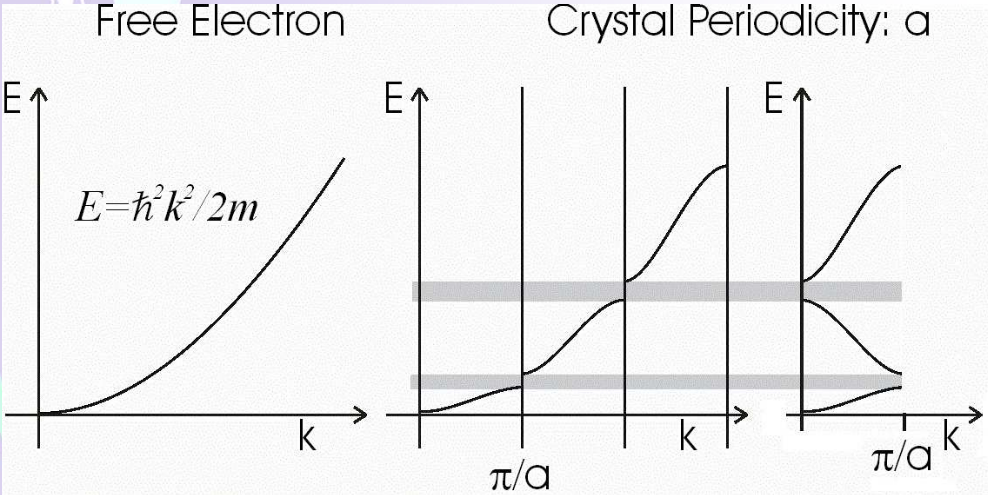


Bragg diffraction

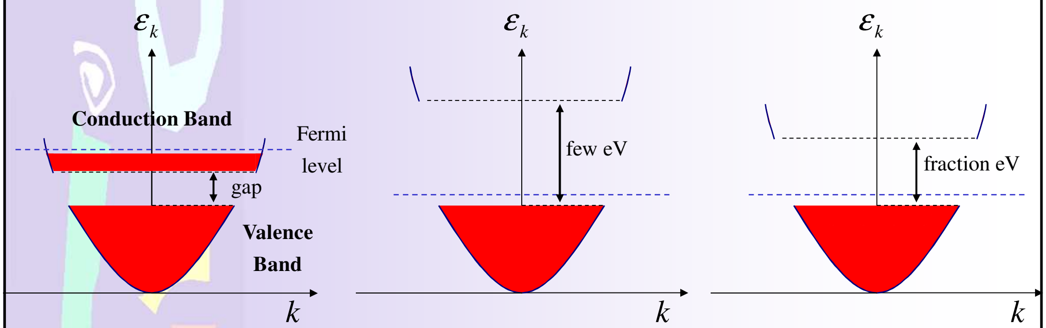
$a\,k = 2\pi\,n, \quad n \in Z$



$$\left(\frac{p^2}{2m} + V_c(x)\right)\Psi_k(x) = \varepsilon_k\,\Psi_k(x)$$



Types of crystals



Metal	Insulator	Semiconductor
• Empty orbitals available at low-energy: high conductivity	• Low conductivity	• Switches from conducting to insulating at will

k·p Theory

How do we calculate realistic band diagrams?

- Tight-binding
- Pseudopotentials
- k·p theory

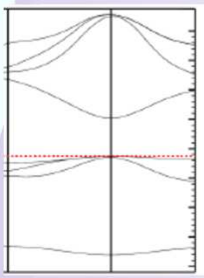
$$\hat{H} = \left(\frac{\vec{p}^2}{2m} + V_c(\vec{r}) \right) \qquad \Psi_k(\vec{r}) = e^{i\vec{k}\vec{r}} u_k(\vec{r})$$

$$e^{-i\vec{k}\vec{r}} \, \hat{H} \, \Psi_k(\vec{r}) = \varepsilon_k \, e^{-i\vec{k}\vec{r}} \, \Psi_k(\vec{r})$$

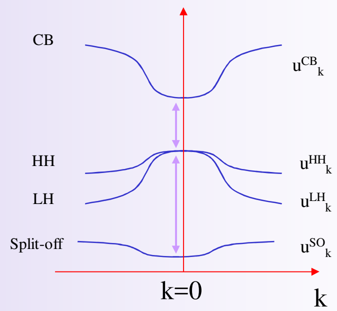
$$\left(\frac{\vec{p}^2}{2m} + V_c(\vec{r}) + \frac{\hbar^2 k^2}{2m} + \hbar \frac{\vec{k}\cdot\vec{p}}{m} \right) u_k(\vec{r}) = \varepsilon_k \, u_k(\vec{r})$$

The k·p Hamiltonian

MgO



k=Γ

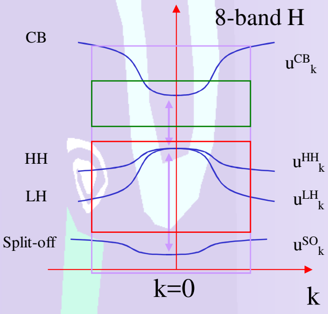


1. Solving H_{kp} at Γ point (k=0) $\longrightarrow$ $\{\varepsilon_0^n, u_0^n\}$
2. Expanding H_{kp} in this basis $\quad u_k^n(\vec{r}) = \sum_n^{\infty} c_{nk} \, u_0^n(\vec{r})$

gap

$$\left\langle u_0^n \middle| \hat{H}_{kp} \middle| u_0^{n'} \right\rangle = \left(\varepsilon_0^n + \frac{\hbar^2 |\vec{k}|^2}{2m} \right) \delta_{n,n'} + \hbar \frac{\vec{k}}{m} \left\langle u_0^n \middle| \vec{p} \middle| u_0^{n'} \right\rangle$$

Kane parameter



1-band H

4-band H

1-band H

	$\lvert s\uparrow\rangle$	$\lvert s\downarrow\rangle$
$\lvert s\uparrow\rangle$	$\frac{k^2}{2m}$	0
$\lvert s\downarrow\rangle$	0	$\frac{k^2}{2m}$

8-band H

	$\lvert s\uparrow\rangle$	$\lvert s\downarrow\rangle$	$\lvert\frac{3}{2},\frac{3}{2}\rangle$	$\lvert\frac{3}{2},\frac{1}{2}\rangle$	$\lvert\frac{3}{2},\frac{-1}{2}\rangle$	$\lvert\frac{3}{2},\frac{-3}{2}\rangle$	$\lvert\frac{1}{2},\frac{1}{2}\rangle$	$\lvert\frac{1}{2},\frac{-1}{2}\rangle$
$\langle s\uparrow\rvert$	$\frac{k^2}{2m}$	0	Pk_+	$-\sqrt{\frac{2}{3}}Pk_z$	$-\sqrt{\frac{1}{3}}Pk_-$	0	$\sqrt{\frac{1}{3}}Pk_z$	$-\sqrt{\frac{2}{3}}Pk_-$
$\langle s\downarrow\rvert$	0	$\frac{k^2}{2m}$	0	$\sqrt{\frac{1}{3}}Pk_-$	$-\sqrt{\frac{2}{3}}Pk_z$	Pk_-	$\sqrt{\frac{2}{3}}Pk_-$	$\sqrt{\frac{1}{3}}Pk_z$
$\langle\frac{3}{2},\frac{3}{2}\rvert$	Pk_+	0	$-\varepsilon_0+\frac{k^2}{2m}$	0	0	0	0	0
$\langle\frac{3}{2},\frac{1}{2}\rvert$	$-\sqrt{\frac{2}{3}}Pk_z$	$\sqrt{\frac{1}{3}}Pk_-$	0	$-\varepsilon_0+\frac{k^2}{2m}$	0	0	0	0
$\langle\frac{3}{2},\frac{-1}{2}\rvert$	$-\sqrt{\frac{1}{3}}Pk_-$	$-\sqrt{\frac{2}{3}}Pk_z$	0	0	$-\varepsilon_0+\frac{k^2}{2m}$	0	0	0
$\langle\frac{3}{2},\frac{-3}{2}\rvert$	0	Pk_-	0	0	0	$-\varepsilon_0+\frac{k^2}{2m}$	0	0
$\langle\frac{1}{2},\frac{1}{2}\rvert$	$\sqrt{\frac{1}{3}}Pk_z$	$\sqrt{\frac{2}{3}}Pk_-$	0	0	0	0	$-\varepsilon_0-\Delta+\frac{k^2}{2m}$	0
$\langle\frac{1}{2},\frac{-1}{2}\rvert$	$-\sqrt{\frac{2}{3}}Pk_-$	$\sqrt{\frac{1}{3}}Pk_z$	0	0	0	0	0	$-\varepsilon_0-\Delta+\frac{k^2}{2m}$

Influence of the romote bands: one-band Hamiltonian for conduction

$$\left\langle u_0^n \middle| \hat{H}_{kp} \middle| u_0^{n'} \right\rangle = \left(\varepsilon_0^n + \frac{\hbar^2 |\vec{k}|^2}{2m} \right) \delta_{n,n'} + \hbar \frac{\vec{k}}{m} \left\langle u_0^n \middle| \vec{p} \middle| u_0^{n'} \right\rangle$$

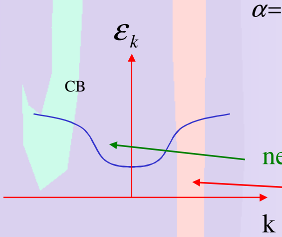
$$\varepsilon_k^{cb} = \varepsilon_0^{cb} + \frac{\hbar^2 |\vec{k}|^2}{2m}$$

This is a crude approximation... Let's include remote bands perturbationally

$$\varepsilon_k^{cb} = \varepsilon_0^{cb} + \sum_{\alpha=x,y,z} \frac{\hbar^2 |k_\alpha|^2}{2m} + \frac{\hbar^2}{m^2} |k_\alpha|^2 \sum_{n \neq cb} \frac{\left| \left\langle u_0^{cb} \middle| p_\alpha \middle| u_0^n \right\rangle \right|^2}{\varepsilon_0^{cb} - \varepsilon_0^n}$$

1/m*

Effective mass



negative mass?

Free electron

m=1 a.u.

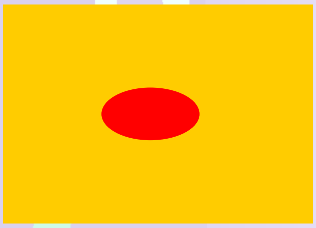
InAs

m*=0.025 a.u.

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial \varepsilon_k^{cb}}{\partial k^2}$$

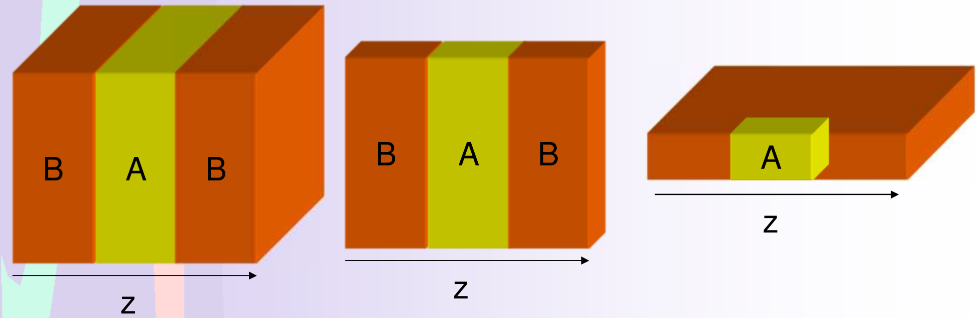
$$\varepsilon_k^{cb} = \varepsilon_0^{cb} + \frac{\hbar^2 k_\alpha^2}{2m_\alpha^*}$$

Heterostructures



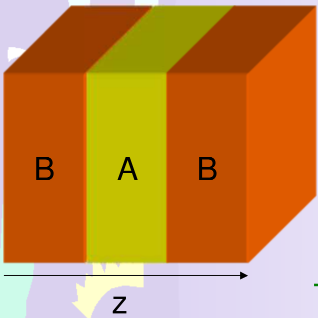
Brocken translational symmetry

How do we study this?



quantum well quantum wire quantum dot

Heterostructures



How do we study this?

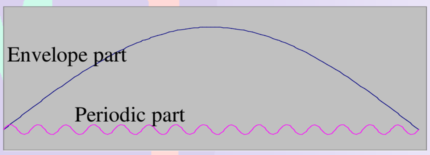
If A and B have:
- the same crystal structure
- similar lattice constants
- no interface defects

...we use the "envelope function approach"

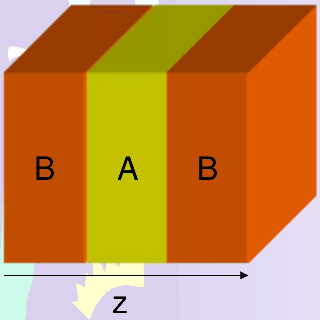
$$\sout{\Psi_k(\vec{r}) = e^{i\vec{k}\vec{r}}\, u_k(\vec{r})} \rightarrow \Psi_k(\vec{r}) = e^{i\vec{k}_\perp \vec{r}_\perp}\, \chi(z)\, u_k(\vec{r})$$

Project H_{kp} onto $\{\Psi_{nk}\}$, considering that:

$$\int_\Omega f(r)\, u_{nk}(r)\, dr \approx \frac{1}{\Omega} \int_{unit\,cell} u_{nk}(r)\, dr \cdot \int_\Omega f(r)\, dr \cdot$$

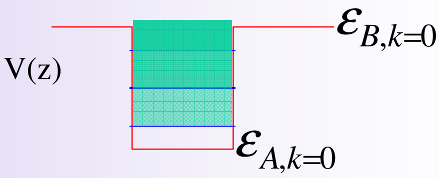


Heterostructures



In a one-band model we finally obtain:

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dz^2}+V(z)+\frac{\hbar^2 k_\perp^2}{2m}\right)\chi(z)=\varepsilon\,\chi(z)$$



1D potential well: particle-in-the-box problem

Quantum well

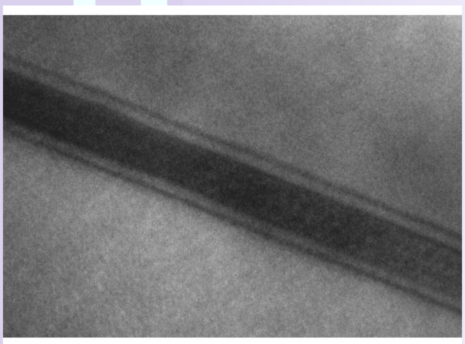


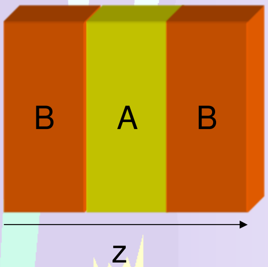
Image: CNRS France

Most prominent applications:

- Laser diodes
- LEDs
- Infrared photodetectors

Image: C. Humphrey, Cambridge

Quantum well



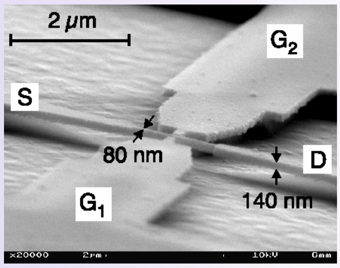
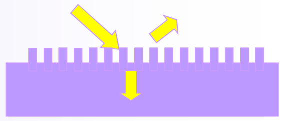
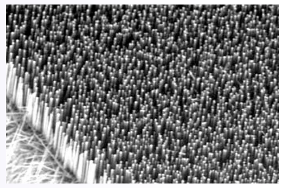


Image: U. Muenchen

$$\left(-\frac{\hbar^2}{2m}(\nabla_y^2+\nabla_z^2)+V(y,z)+\frac{\hbar^2 k_x^2}{2m}\right)\chi(y,z)=\varepsilon\,\chi(y,z)$$

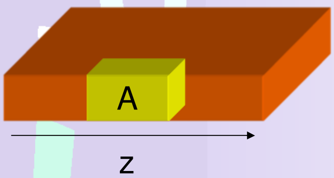


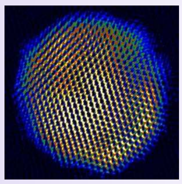


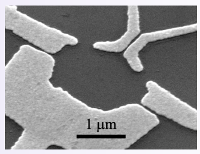
Most prominent applications:

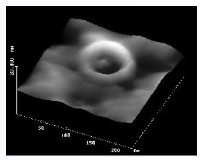
- Transport
- Photovoltaic devices

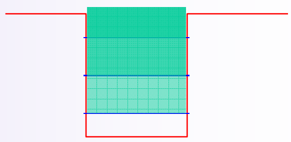
Quantum wire











$$\left(-\frac{\hbar^2}{2m}\nabla^2+V(x,y,z)\right)\chi(x,y,z)=\varepsilon\,\chi(x,y,z)$$

Most prominent applications:

- Single electron transistor
- In-vivo imaging
- Photovoltaics
- LEDs
- Cancer therapy
- Memory devices
- Qubits?

Quantum dot