Faculty of Physics,
University of Warsaw

Summer Semester 2014

Lecture

Modeling of Nanostructures and Materials

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Continuous Methods for Modeling Electronic Structure of Nanostructures

- Examples of nanostructures
- From atomistic to continuum methods
- k.p methods
- Effective mass approximation
- Envelope Function Theory

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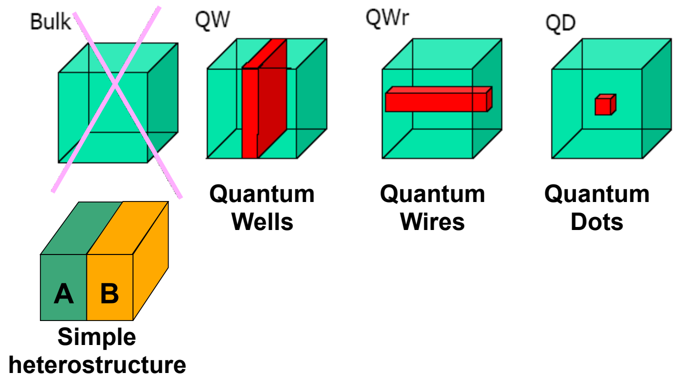
Modeling Nanostructures

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

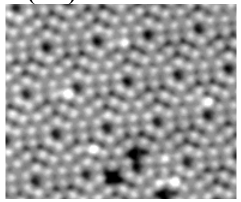
0D (quantum dots): **100K-1000 K** atoms in the unit cell

Organics

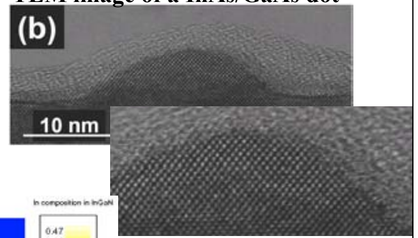
Nanotubes, DNA: **100-1000** atoms (or more)

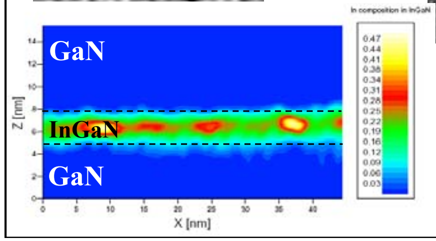
Examples of Nanostructures

Si(111)7×7 Surface



TEM image of a InAs/GaAs dot

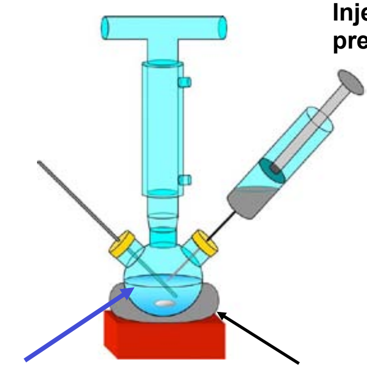


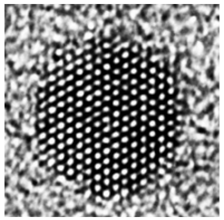


HRTEM image: segregation of Indium in GaN/InGaN Quantum Well

Synthesis of colloidal nanocrystals

Injection of organometallic precursors





Mixture of surfactants **Heating mantle**

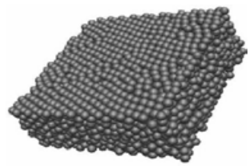
Nanostructures: colloidal crystals

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

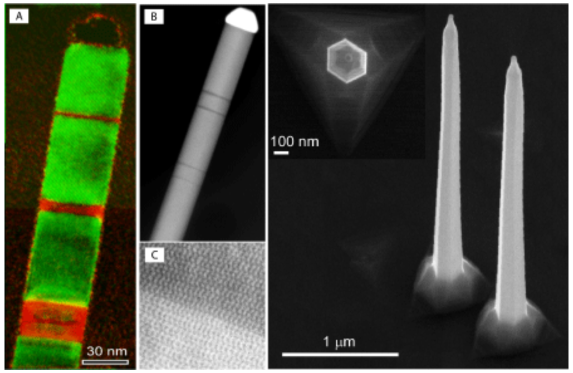
- self-assembly when spheres density high enough;

illuminated with white light →

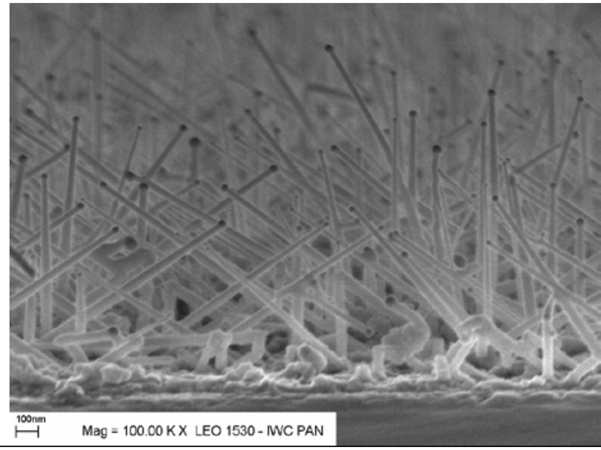
Bragg's law → different crystals → different orientation different



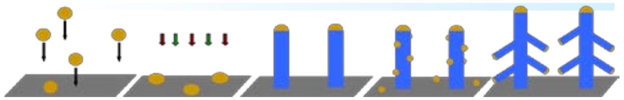
Hot topic (to come) – The curious world of nanowires



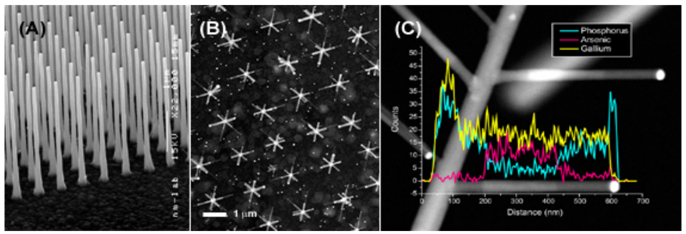
SEM of ZnTe nanowires grown by MBE on GaAs with Au nanocatalyst



Nanowire site control and branched NW structures: nanotrees and nanoforests



http://www.nano.ftf.lth.se/

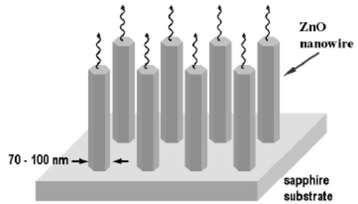


(A) Nanowires can be accurately positioned using lithographic methods such as EBL and NIL. **(B)** Subsequent seeding by aerosol deposition produces nanowire branches on an array as in panel (A). Shown here is a top view of such a 'nanoforest' where the branches grow in the <111>B crystal directions out from the stems. **(C)** Dark field STEM image and EDX line scan of an individual nanotree. **An optically active heterosegment of GaAsP in GaP has been incorporated into the branches.**

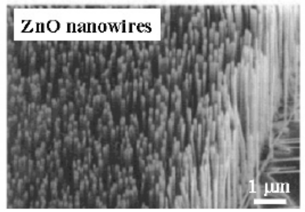
Nanowire nanolasers

Room temperature lasing action from chemically synthesized **ZnO** nanowires on sapphire substrate

Schematic illustration



A SEM image

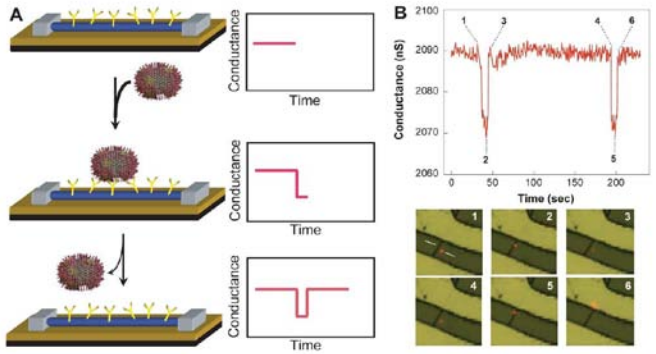


One end of the nanowire is the epitaxial interface between the sapphire and ZnO, whereas ***the other end*** is the crystalline ZnO (0001) plane **Huang, M., Mao, S.S., *et al.*, *Science* 292,**

Detection of single viruses with NW-FET

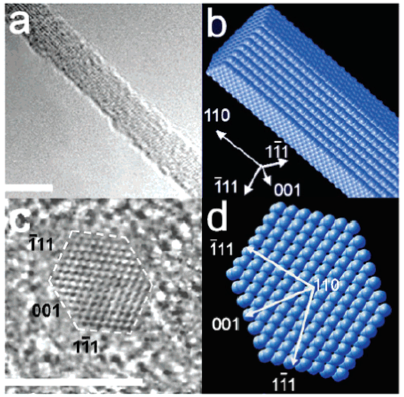
Patolsky & Lieber, Materials Today, April 2005, p. 20

*Patolsky et al., Proc. Natl. Acad. Sci. USA **101** (2004) 14017*



Simultaneous conductance and optical data recorded for a Si nanowire device after the introduction of **influenza A solution**.

Controlled Growth and Structures of Molecular-Scale Silicon Nanowires



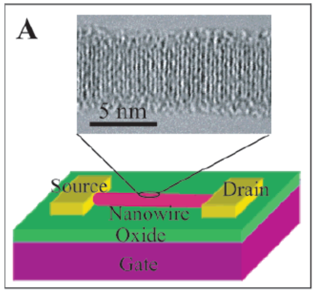
(a) TEM images of **3.8-nm** SiNWs grown along the <110> direction

(c) cross-sectional image

(b) & (d) models based on Wulff construction

Yue Wu *et al*., NANO LETTERS **4**, 433 (2004)

High Performance Silicon Nanowire Field Effect Transistors

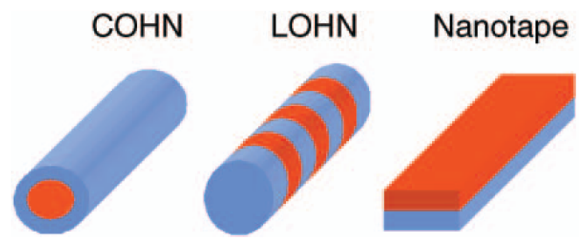


Comparison of SiNW FET transport parameters with those for state-of-the-art planar MOSFETs show that

- "SiNWs have the potential to exceed substantially conventional devices, and thus could be ideal building blocks for future nanoelectronics."

Yi Cui, *et al*. NANO LETTERS **3**, 149 (2003)

Heterostructured Nanowires



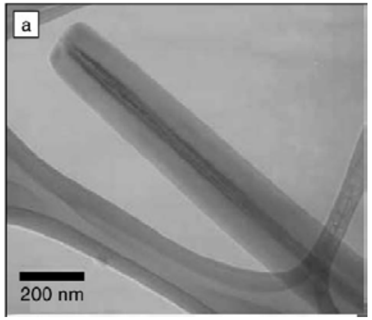
coaxial heterostructured nanowire

longitudinal heterostructured nanowire

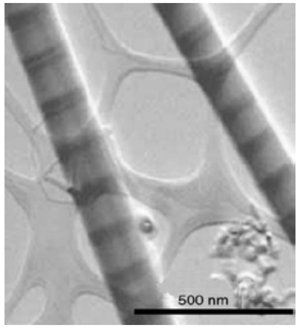
Heterostructured Nanowires

Transmission electron microscopy images of

a **GaN/AlGaN** core–sheath nanowire



two **Si/SiGe** superlattice nanowires



Methods for Nanostructure Modeling

Atomistic methods for modeling of nanostructures

- ***Ab initio* methods** (up to few hundred atoms)

Density Functional Theory (DFT)

- **One particle density determines the ground state energy of the system for arbitrary external potential**

$$E[\rho] = \int d^3\vec{r}\,\rho(\vec{r})v_{ext}(\vec{r}) + F[\rho]$$

$$\boxed{E[\rho_0] = E_0}$$

ground state energy

ground state density

Total energy functional | **Kinetic energy** | **Exchange energy** | **Correlation energy**

- $E[\rho] = \int d\vec{r}\, v_{ext}(\vec{r})\rho(\vec{r}) + T_S[\rho] + U[\rho] + E_x[\rho] + E_c[\rho]$

External energy | **Classic Coulomb energy** | **unknown!!!**

Atomistic methods for modeling of nanostructures

- *Ab initio* methods (up to few hundred atoms)
- **Semiempirical methods** (up to 1M atoms)
  - **Tight-Binding Methods**

Tight-Binding Hamiltonian

$$H = \sum_{\alpha i} \varepsilon_{i\alpha} c_{i\alpha}^{\dagger} c_{i\alpha} + \sum_{\alpha i,\beta j} t_{i\alpha,j\beta} c_{i\alpha}^{\dagger} c_{j\beta}$$

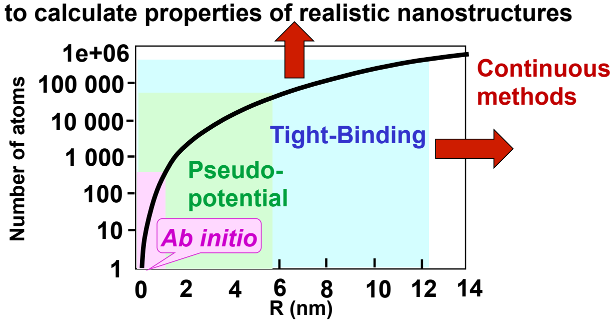
creation & anihilation operators

- ***On-site energies*** **are not atomic eigenenergies**
  They include on average the effects of neighbors

  ⇒ **Problem:** ***Transferability***
  E.g., **Si in diamond lattice (4 nearest neighbors) & in fcc lattice (12 nearest neighbors)**
- **Dependence of *the hopping energies* on the distance between atoms**

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

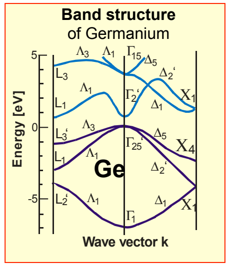
- Strongly varying on atomic scale

Non-periodic external potential

- Slowly varying on atomic scale

Band Structure

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



Electron in an external field

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

Periodic potential of crystal

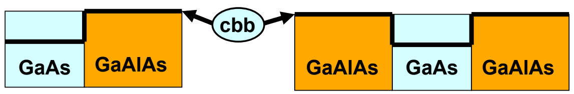
- **Strongly varying on atomic scale**

Non-periodic external potential

- **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 ?** $\left(\frac{\vec{p}^2}{2m^*}+U(\vec{r})\right)F(\vec{r})=\varepsilon F(\vec{r})$ $\quad F(\vec{r})=?$

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**

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

k.p method for bulks

k.p Method- Luttinger-Kohn basis

Bloch functions are orthogonal in the wave vector and band index

$$\int d^3\vec{r}\,\psi_l^*(\vec{k},\vec{r})\psi_n(\vec{q},\vec{r}) = \delta_{nl}\delta(\vec{k}-\vec{q})$$

$$\psi_n(\vec{k},\vec{r}) = \exp[i\vec{k}\cdot\vec{r}]u_n(\vec{r}) \qquad \int d^3\vec{r}\,u_l^*(\vec{k},\vec{r})u_n(\vec{k},\vec{r}) = \frac{\Omega}{(2\pi)^3}\delta_{nl}$$

$$\int d^3\vec{r}\,u_l^*(\vec{k},\vec{r})u_n(\vec{q},\vec{r}) \neq 0 \quad \text{for } \vec{k}\neq\vec{q}$$

Luttinger-Kohn basis

$$\chi_j(\vec{k},\vec{r}) = \exp[i(\vec{k}-\vec{k}_0)\cdot\vec{r}]\psi_j(\vec{k}_0,\vec{r}) = \exp[i\vec{k}\cdot\vec{r}]u_j(\vec{k}_0,\vec{r})$$

$$\int d^3\vec{r}\,\chi_l^*(\vec{k},\vec{r})\chi_n(\vec{q},\vec{r}) = \delta_{nl}\delta(\vec{k}-\vec{q})$$

$$\sum_n \int d^3\vec{k}\,\chi_n^*(\vec{k},\vec{r})\chi_n(\vec{k},\vec{r}\,') = \delta(\vec{r}-\vec{r}\,')$$

Luttinger-Kohn basis is orthogonal and complete

Expansion of the unknown Bloch function in terms of *known Luttinger-Kohn functions*

$$\psi_n(\vec{k},\vec{r}) = \sum_j A_{nj}(\vec{k})\chi_j(\vec{k},\vec{r})$$

k.p Method - Derivation

$$\left[\frac{\vec{p}^2}{2m}+V(\vec{r})\right]\psi_n(\vec{k},\vec{r}) = \varepsilon_n(\vec{k})\psi_n(\vec{k},\vec{r}) \qquad \psi_n(\vec{k},\vec{r}) = \sum_j A_{nj}(\vec{k})\chi_j(\vec{k},\vec{r})$$

$$\sum_j A_{nj}(\vec{k})\left[\frac{\vec{p}^2}{2m}+V(\vec{r})\right]\exp[i(\vec{k}-\vec{k}_0)\cdot\vec{r}]\psi_j(\vec{k}_0,\vec{r}) =$$

$$= \varepsilon_n(\vec{k})\exp[i(\vec{k}-\vec{k}_0)\cdot\vec{r}]\sum_{j'} A_{nj'}(\vec{k})\psi_{j'}(\vec{k}_0,\vec{r})$$

$$\vec{p} \equiv -i\hbar\nabla$$

$$\nabla\exp[i(\vec{k}-\vec{k}_0)\cdot\vec{r}]\psi_j(\vec{k}_0,\vec{r}) = \exp[i(\vec{k}-\vec{k}_0)\cdot\vec{r}]\{\nabla + i(\vec{k}-\vec{k}_0)\}\psi_j(\vec{k}_0,\vec{r})$$

$$\left[\frac{\vec{p}^2}{2m}+V(\vec{r})\right]\exp[i(\vec{k}-\vec{k}_0)\cdot\vec{r}]\psi_j(\vec{k}_0,\vec{r}) =$$

$$= \exp[i(\vec{k}-\vec{k}_0)\cdot\vec{r}]\{\frac{\hbar^2}{2m}(\vec{k}-\vec{k}_0)^2 + \frac{\hbar}{m}(\vec{k}-\vec{k}_0)\cdot\vec{p} + \varepsilon_j(\vec{k}_0)\}\psi_j(\vec{k}_0,\vec{r})$$

k.p Method - Derivation

$$\{\frac{\hbar^2}{2m}(\vec{k}-\vec{k}_0)^2 + \frac{\hbar}{m}(\vec{k}-\vec{k}_0)\cdot\vec{p} + \varepsilon_j(\vec{k}_0)\}\psi_j(\vec{k}_0,\vec{r}) =$$

$$= \{\frac{\hbar^2}{2m}\underline{(\vec{k}-\vec{k}_0)^2} + \frac{\hbar}{m}(\vec{k}-\vec{k}_0)\cdot\vec{p} + \varepsilon_j(\vec{k}_0)\}\exp[i\vec{k}_0\cdot\vec{r}]u_j(\vec{k}_0,\vec{r}) =$$

$$= \exp[i\vec{k}_0\cdot\vec{r}]\{\frac{\hbar^2}{2m}\underline{(\vec{k}^2-\vec{k}_0^2)} + \frac{\hbar}{m}(\vec{k}-\vec{k}_0)\cdot\vec{p} + \varepsilon_j(\vec{k}_0)\}u_j(\vec{k}_0,\vec{r})$$

$$\sum_j A_{nj}(\vec{k})\{\frac{\hbar^2}{2m}(\vec{k}^2-\vec{k}_0^2) + \frac{\hbar}{m}(\vec{k}-\vec{k}_0)\cdot\vec{p} + \varepsilon_j(\vec{k}_0)\}u_j(\vec{k}_0,\vec{r}) =$$

$$= \varepsilon_n(\vec{k})\sum_{j'} A_{nj'}(\vec{k})u_{j'}(\vec{k}_0,\vec{r})$$

Multiply both sides by $u_l^*(\vec{k}_0,\vec{r})$

Integrate over the unit cell $\int_\Omega d^3\vec{r}$

$$\sum_j \{[\varepsilon_j(\vec{k}_0) + \frac{\hbar^2}{2m}(\vec{k}^2-\vec{k}_0^2)]\delta_{lj} + \frac{\hbar}{m}(\vec{k}-\vec{k}_0)\cdot\vec{p}_{lj} + \}A_{nj}(\vec{k}) = \varepsilon_n(\vec{k})A_{nl}(\vec{k})$$

k dot p

$$\vec{p}_{lj} = \frac{(2\pi)^3}{\Omega}\int_\Omega d^3\vec{r}\,u_l^*(\vec{k}_0,\vec{r})\hat{\vec{p}}u_j(\vec{k}_0,\vec{r})$$

Momentum matrix elements

k.p Method – Main Equation

$$\sum_j \{[\varepsilon_j(\vec{k}_0) + \frac{\hbar^2}{2m}(\vec{k}^2 - \vec{k}_0^2)]\delta_{lj} + \frac{\hbar}{m}(\vec{k} - \vec{k}_0)\cdot \vec{p}_{lj} + \} A_{nj}(\vec{k}) = \varepsilon_n(\vec{k}) A_{nl}(\vec{k})$$

- System of homogeneous equations for expansion coefficients $A_{nj}(\vec{k})$
- This equations couple all bands $\rightarrow \varepsilon_n(\vec{k})$
- What one needs is decoupling scheme, e.g., perturbation theory

$$H = H_0 + H' \qquad H_0 |n^0\rangle = E_n^0 |n^0\rangle$$

$H|n\rangle = E_n|n\rangle$ Perturbation theory for non-degenerate states

$$E_n = E_n^0 + E_n^{(1)} + E_n^{(2)} + K$$

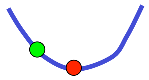
$$E_n = E_n^0 + \langle n^0 | H' | n^0\rangle + \sum_{m\neq n} \frac{|\langle m^0 | H' | n^0\rangle|^2}{E_n^0 - E_m^0} + K$$

$$|n\rangle = |n^0\rangle + \sum_{m\neq n} \frac{\langle m^0 | H' | n^0\rangle}{E_n^0 - E_m^0} |m^0\rangle + K$$

k.p Method – Non-degenerate band

Let us consider non-degenerate band and look for band energies around extremum in k_0 e.g., conduction band minimum in GaAs

$$H' = \frac{\hbar^2}{2m}(\vec{k}^2 - \vec{k}_0^2) + \frac{\hbar}{m}(\vec{k} - \vec{k}_0)\cdot \vec{p}$$



$\vec{k}_0 = 0 \equiv \Gamma$

Expansion parameter: $\vec{s} = \vec{k} - \vec{k}_0$

$$\varepsilon_n(\vec{k}) = \varepsilon_n(\vec{k}_0) + \frac{\hbar}{m}(\vec{k} - \vec{k}_0)\cdot \vec{p}_{nn} + \frac{\hbar^2}{2m}(\vec{k}^2 - \vec{k}_0^2) + \frac{\hbar^2}{m^2}\sum_{j\neq n} \frac{(\vec{s}\cdot \vec{p}_{nj})(\vec{s}\cdot \vec{p}_{jn})}{\varepsilon_n(\vec{k}_0) - \varepsilon_j(\vec{k}_0)} +$$

Energy to second order in the expansion parameter

$$u_n(\vec{k},\vec{r}) = u_n(\vec{k}_0,\vec{r}) + \frac{\hbar}{m}\vec{s}\cdot \sum_{j\neq n} \frac{\vec{p}_{jn}}{\varepsilon_n(\vec{k}_0) - \varepsilon_j(\vec{k}_0)} u_j(\vec{k}_0,\vec{r}) + \ldots$$

Periodic wave function to the first order in expansion parameter

k.p Method – Effective Mass Tensor

Taylor series

$$\varepsilon_n(\vec{k}) = \varepsilon_n(\vec{k}_0) + (\nabla\varepsilon_n(\vec{k}_0))\cdot(\vec{k} - \vec{k}_0) + \frac{1}{2}\sum_{\alpha,\beta} \frac{\partial^2 \varepsilon_n(\vec{k}_0)}{\partial k_\alpha \partial k_\beta}(\vec{k} - \vec{k}_0)_\alpha (\vec{k} - \vec{k}_0)_\beta +$$

$$\varepsilon_n(\vec{k}) = \varepsilon_n(\vec{k}_0) + \underbrace{\frac{\hbar}{m}(\vec{k} - \vec{k}_0)\cdot \vec{p}_{nn} + \frac{\hbar^2}{2m}(\vec{k}^2 - \vec{k}_0^2)}_{\frac{\hbar}{m}\vec{s}\cdot[\vec{p}_{nn} + \frac{\hbar}{2}(\vec{k} + \vec{k}_0)]} + \frac{\hbar^2}{m^2}\sum_{j\neq n} \frac{(\vec{s}\cdot \vec{p}_{nj})(\vec{s}\cdot \vec{p}_{jn})}{\varepsilon_n(\vec{k}_0) - \varepsilon_j(\vec{k}_0)} +$$

Band n has extremum in k_0

$$\left.\frac{\partial \varepsilon_n(\vec{k})}{\partial \vec{k}}\right|_{\vec{k}=\vec{k}_0} = \left.\frac{\partial \varepsilon_n(\vec{k})}{\partial \vec{s}}\right|_{\vec{s}=0} = 0 \Rightarrow \boxed{\vec{p}_{nn} + \hbar \vec{k}_0 = 0}$$

$\vec{p}_{nn} = 0 \Rightarrow \vec{k}_0 = 0$ **e.g., GaAs**

$\vec{p}_{nn} \neq 0 \Rightarrow \vec{k}_0 \neq 0$ **e.g., Si**

Let us introduce second rank tensor

Reciprocal Effective Mass Tensor

$$\left(\frac{m}{m^*}\right)_{\alpha\beta} = \left.\frac{m}{\hbar^2}\frac{\partial^2 \varepsilon_n(\vec{k})}{\partial k_\alpha \partial k_\beta}\right|_{\vec{k}=\vec{k}_0}$$

k.p Method – Effective Mass Tensor

$$\frac{\partial^2 \varepsilon_n(\vec{k}_0)}{\partial k_\alpha \partial k_\beta} = \frac{\hbar^2}{m}\delta_{\alpha\beta} + \frac{\hbar^2}{m^2}\sum_{j\neq n} \frac{p_{nj}^\alpha p_{jn}^\beta + p_{nj}^\alpha p_{jn}^\beta}{\varepsilon_n(\vec{k}_0) - \varepsilon_j(\vec{k}_0)}$$

$$\left(\frac{m}{m_n^*}\right)_{\alpha\beta} = \delta_{\alpha\beta} + \frac{1}{m}\sum_{j\neq n} \frac{p_{nj}^\alpha p_{jn}^\beta + p_{nj}^\alpha p_{jn}^\beta}{\varepsilon_n(\vec{k}_0) - \varepsilon_j(\vec{k}_0)}$$

m – free electron mass

It is always possible to diagonalize the reciprocal effective mass tensor by proper choice of the coordinate system.

- If the extremum point k_0 is a general point in the BZ, the choice of the axes depends on the details of the dynamics, that is, on the crystal potential.
- If the extremum occurs at a symmetry point or along an axis of symmetry, the axes may be partially determined by symmetry.
  In cubic crystals, for minima along [100], [110], [111], the symmetry axis must be a principal axis.
- **If k=0 is the extremum, the surface of constant energy in a cubic crystal must be spherical**

k.p Method – Effective Mass Tensor

$$\left(\frac{m}{m_n^*}\right)_{\alpha\alpha} = 1 + \frac{2}{m}\sum_{j\neq n}\frac{|p_{nj}^{\alpha}|^2}{\varepsilon_n(\vec{k}_0)-\varepsilon_j(\vec{k}_0)}$$

α -refers now to one of the principal axes

- The interaction with the lower lying levels tends to decrease an effective mass $\varepsilon_j(\vec{k}_0) < \varepsilon_n(\vec{k}_0)$
- The interaction with the higher states tends to increase an effective mass $\varepsilon_j(\vec{k}_0) > \varepsilon_n(\vec{k}_0)$
- For cubic semiconductors with minimum of the conduction band in Γ point, the band energy in the neighborhood is

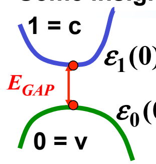
$$\varepsilon_n(\vec{k}) = \varepsilon_n(0) + \frac{\hbar^2\vec{k}^2}{2m_n^*}$$

Physical meaning of the effective mass ?

Dynamics of particles → In the presence of external fields, the crystalline electrons behave as particles with effective mass m^*.

Effective Mass - A Two-Band Model

Some insight into the nature of the results



$\varepsilon_1(0) = E_{GAP}$

$\varepsilon_0(0) = 0$

$\vec{p}_{01} = \vec{p}_{10}^* = \vec{p}$ $\quad p_\alpha = \frac{1}{\sqrt{3}}p$

$\frac{m}{m_0^*} = 1 - \frac{2p^2}{3mE_g}$ $\quad \frac{m}{m_1^*} = 1 + \frac{2p^2}{3mE_g}$

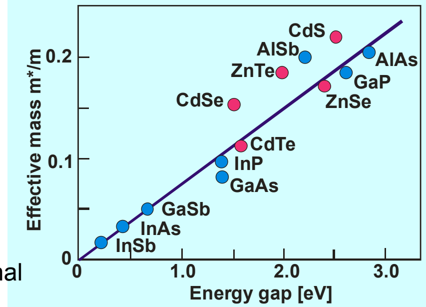
Let us assume $E_g << \frac{2p^2}{m}$

This occurs, for example, in GaSb, InAs, InSb

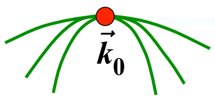
$$\frac{m}{m_1^*} \approx \frac{2p^2}{3mE_g}$$

$$\frac{m_1^*}{m} \approx \frac{3m}{2p^2}E_g$$

Effective mass proportional to the energy gap



k.P – Method – Band Degeneracies



Valence band top of cubic semiconductors

- The state of interest in $\vec{k}_0$ is degenerate
- The perturbation will remove degeneracy, at least in some directions
- Going from a point of higher symmetry the energy band split
- It is necessary to use degenerate perturbation theory

$H_0\varphi_{na}^0 = \varepsilon_n^0\varphi_{na}^0 \qquad a = 1,2,3,K, g_n$

e.g., L.I. Schiff, *Quantum Mechanics*
Schwabl, *Quantenmechanik*

$\langle a|H_0 + H'|b\rangle - E\delta_{\alpha\beta} = 0$

H_{ab}^n --- $g_n \times g_n$ --- Matrix

First order perturbation

In our case, perturbation is $H' = \frac{\hbar^2}{2m}(\vec{k}^2 - \vec{k}_0^2) + \frac{\hbar}{m}(\vec{k}-\vec{k}_0)\cdot\vec{p}$

For simplicity $\vec{k}_0 = 0$

Valence band maximum in most of semiconductors

$$H' = \frac{\hbar^2}{2m}\vec{k}^2 + \frac{\hbar}{m}\vec{k}\cdot\vec{p}$$

k.P – Method – Band Degeneracies

Löwdin perturbation theory

$$H_{ab}^n = \left(H_{ab}^n\right)^{(0)} + \left(H_{ab}^n\right)^{(1)} + \left(H_{ab}^n\right)^{(2)} =$$

$$= \varepsilon_n^0\delta_{ab} + \langle\varphi_{na}^0|H'|\varphi_{nb}^0\rangle + \sum_{m\neq n}\sum_{c=1}^{g_m}\frac{\langle\varphi_{na}^0|H'|\varphi_{mc}^0\rangle\langle\varphi_{mc}^0|H'|\varphi_{nb}^0\rangle}{\varepsilon_n^0 - \varepsilon_m^0}$$

- **The essential idea of this procedure is to separate the states considered in the perturbation calculation into two sets:**
  - **one set involves a small number of strongly coupled states whose interactions is treated exactly (g_n),**
  - **the second set, with more states, contains those states that are well removed in energy from the first set**

- **One can also treat in this way situation in which some bands, although not quite degenerate, approach each other closely. Then treatment of such bands as non-degenerate does not make sense**

k.P – Method – Band Degeneracies

$$\vec{p}_{ab}^{\,nm} = \left\langle u^0_{na} \,|\, \hat{\vec{p}} \,|\, u^0_{mb} \right\rangle$$

$$H^n_{ab} = \varepsilon_n(\vec{k}_0)\delta_{ab} + \frac{\hbar^2}{2m}\vec{k}^2\delta_{ab} + \frac{\hbar}{m}\vec{k}\cdot\vec{p}^{\,nn}_{ab} + \sum_{m\neq n}\sum_{c=1}^{g_m}\frac{(\vec{k}\cdot\vec{p}^{\,nm}_{ac})(\vec{k}\cdot\vec{p}^{\,mn}_{cb})}{\varepsilon_n(\vec{k}_0)-\varepsilon_m(\vec{k}_0)}$$

Band minimum in $\vec{k}_0 \Rightarrow \vec{p}^{\,nn}_{ab} = 0$

$$H^n_{ab} = \varepsilon_n(\vec{k}_0)\delta_{ab} + \frac{\hbar^2}{2m}\delta_{ab}\sum_{\mu=1}^{3}k_\mu^2 + \sum_{m\neq n}\sum_{c=1}^{g_m}\frac{[\sum_\mu k_\mu (p_\mu)^{nm}_{ac}][\sum_\nu k_\nu (p_\nu)^{mn}_{cb}]}{\varepsilon_n(\vec{k}_0)-\varepsilon_m(\vec{k}_0)}$$

$$H^n_{ab} = \varepsilon_n(\vec{k}_0) + \frac{\hbar^2}{2m}\delta_{ab}\sum_{\mu=1}^{3}k_\mu^2 + \sum_{\mu=1}^{3}\sum_{\nu=1}^{3}k_\mu k_\nu\sum_{m\neq n}\sum_{c=1}^{g_m}\frac{(p_\mu)^{nm}_{ac}(p_\nu)^{mn}_{cb}}{\varepsilon_n(\vec{k}_0)-\varepsilon_m(\vec{k}_0)}$$

$$H^n_{ab} = \varepsilon_n(\vec{k}_0)\delta_{ab} + \frac{\hbar^2}{2m}\sum_{\mu=1}^{3}\sum_{\nu=1}^{3}\frac{k_\mu k_\nu}{m^{ab}_{\mu\nu}}$$

$$\frac{1}{m^{ab}_{\mu\nu}} = \delta_{ab}\delta_{\mu\nu} + \frac{2}{m}\sum_{m\neq n}\sum_{c=1}^{g_m}\frac{(p_\mu)^{nm}_{ac}(p_\nu)^{mn}_{cb}}{\varepsilon_n(\vec{k}_0)-\varepsilon_m(\vec{k}_0)}$$

k.P – Method – Band Degeneracies

Special case: valence band in Γ $\quad a,b\in\{x,y,z\} \quad n\equiv v$

H^n_{ab} is 3×3 matrix $\qquad$ 3 degenerated bands: $vx,\ vy,\ vz$

$$\hat{\hat{H}} = \varepsilon_n(0) + \frac{h^2}{2m}\sum_{\mu=1}^{3}\sum_{\nu=1}^{3}k_\mu k_\nu\begin{bmatrix}(m^{xx}_{\mu\nu})^{-1} & (m^{xy}_{\mu\nu})^{-1} & (m^{xz}_{\mu\nu})^{-1}\\ (m^{yx}_{\mu\nu})^{-1} & (m^{yy}_{\mu\nu})^{-1} & (m^{yz}_{\mu\nu})^{-1}\\ (m^{zx}_{\mu\nu})^{-1} & (m^{zy}_{\mu\nu})^{-1} & (m^{zz}_{\mu\nu})^{-1}\end{bmatrix}$$

For cubic semiconductors, there are only three different matrix elements

$$L = \frac{1}{m^{xx}_{xx}} = \frac{1}{m^{yy}_{yy}} = \frac{1}{m^{zz}_{zz}} = 1 + \frac{2}{m}\sum_{m\neq n}\sum_{c=1}^{g_m}\frac{(p_z)^{vm}_{zc}(p_z)^{mv}_{cz}}{\varepsilon_n(0)-\varepsilon_m(0)}$$

$$M = \frac{1}{m^{yy}_{xx}} = \frac{1}{m^{zz}_{yy}} = \frac{1}{m^{xx}_{zz}} = \frac{1}{m^{xx}_{yy}} = \frac{1}{m^{yy}_{zz}} = \frac{1}{m^{zz}_{xx}} = 1 + \frac{2}{m}\sum_{m\neq n}\sum_{c=1}^{g_m}\frac{(p_x)^{vm}_{zc}(p_x)^{mv}_{cz}}{\varepsilon_v(0)-\varepsilon_m(0)}$$

$$N = \frac{1}{m^{xy}_{xy}} = \frac{1}{m^{yz}_{yz}} = \frac{1}{m^{zx}_{zx}} = \frac{1}{m^{yx}_{yx}} = \frac{1}{m^{zy}_{zy}} = \frac{1}{m^{xz}_{xz}} = 1 + \frac{2}{m}\sum_{m\neq n}\sum_{c=1}^{g_m}\frac{(p_x)^{vm}_{xc}(p_z)^{mv}_{cz}}{\varepsilon_n(0)-\varepsilon_m(0)}$$

L, M, N **– Dresselhaus parameters**

k.P – Method – Band Degeneracies

Degenerated Valence Band of Cubic Semiconductors

$$\hat{\hat{H}} = \hat{\hat{D}}^{\mu\nu}k_\mu k_\nu$$

$$\hat{\hat{H}} = \varepsilon_v(0)I + \frac{h^2}{2m}\begin{bmatrix}Lk_x^2 + M(k_y^2+k_z^2) & Nk_xk_y & Nk_xk_z\\ Nk_xk_y & Lk_y^2 + M(k_x^2+k_z^2) & Nk_yk_z\\ Nk_xk_z & Nk_yk_z & Lk_z^2 + M(k_x^2+k_y^2)\end{bmatrix}$$

$$\det(\hat{\hat{H}} - EI) = 0$$

These equations can be solved analytically !!
T. Manku & A. Nathan, J. Appl. Phys. 73, 1205 (1993)
J. Dijkstra, J. Appl. Phys. 81, 1259 (1997)

Pretty complicated task

SIMPLE: Find solutions along a symmetry line,
e.g., $\vec{k}\in[k_x,0,0]$ $\quad \Delta-$line

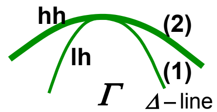
Degenerated Valence Band of Cubic Semiconductors

Dispersion relations along $\Delta-$line $\quad \vec{k}\in[k_x,0,0]$

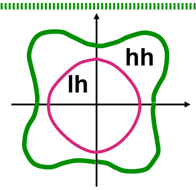
$$\hat{\hat{H}} = \begin{bmatrix}\varepsilon_v(0)+Lk_x^2 & 0 & 0\\ 0 & \varepsilon_v(0)+Mk_x^2 & 0\\ 0 & 0 & \varepsilon_v(0)+Mk_x^2\end{bmatrix}$$

$$\varepsilon_{hh} = \varepsilon_v(0) + \frac{h^2}{2m}Mk_x^2 \qquad \textbf{Heavy hole}$$

$$\varepsilon_{lh} = \varepsilon_v(0) + \frac{h^2}{2m}Lk_x^2 \qquad \textbf{Light hole}$$



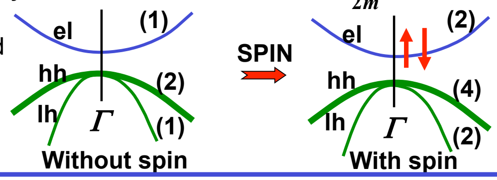
- **Generally** $\varepsilon_v(\vec{k})$ **are dependent on the direction of** k **"Warped bands"**
- ***L, M, N*** **– Dresselhaus parameters obtained from fits to experimental data**



Role of spin in the band structure

- If one includes electron spin into the band structure obtained from spin independent effective Hamiltonian the degeneracy of all bands will be doubled $\hat{H} = \frac{\hat{p}^2}{2m} + V(\vec{r})$

Bands around Γ point



- Equation of electron with spin – Dirac equation for a single particle in periodic potential

$$[-c\hat{\alpha}\cdot\hat{\vec{p}} - \hat{\beta}mc^2 + V(\vec{r})]\bar{\bar{\psi}}_n(\vec{k},\vec{r}) = E_n(\vec{k})\bar{\bar{\psi}}_n(\vec{k},\vec{r})$$

$$\hat{\alpha}_i = \begin{bmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{bmatrix} \quad \hat{\beta} = \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix}$$

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

Pauli matrices

$\bar{\bar{\psi}}_n(\vec{k},\vec{r})$ Four-component spinor

Spin-orbit coupling

- In the case of Dirac equation Bloch's theorem is still valid, since it depends only on the translational invariance of the Hamiltonian

$$\bar{\bar{\psi}}_n(\vec{k},\vec{r}) = \exp(i\vec{k}\cdot\vec{r})\bar{\bar{u}}_n(\vec{k},\vec{r})$$

$\bar{\bar{u}}_n(\vec{k},\vec{r})$ Four component Periodic spinor

Systems that require full Dirac equation - Very heavy metals, e.g., Uranium

- In semiconductors it is sufficient to consider only "large" component of the Dirac spinor

$$\bar{\bar{\psi}} \rightarrow \begin{bmatrix} \bar{\Phi} \\ 0 \end{bmatrix}$$

Two-component spinor

- Foldy-Wouthuysen-Transformation ⇒ Equation for $\bar{\Phi}$

F. Schwabl, *Advanced Quantum Mechanics*

Quantenmechanik für Fortgeschrittene

$h = c = 1$

$$\{m + \frac{\hat{\vec{p}}^2}{2m} + V(\vec{r}) - \frac{\hat{\vec{p}}^4}{8m^3} + \frac{1}{8m^2}\nabla^2 V(\vec{r}) + \frac{1}{4m^2}\hat{\vec{\sigma}}\cdot\nabla V\times\hat{\vec{p}}\}\bar{\Phi} = E\bar{\Phi}$$

Relativistic mass correction

Darwin term

Spin-orbit coupling

Spin-orbit coupling

$$\left[\frac{\hat{\vec{p}}^2}{2m} + V(\vec{r}) + \frac{\hbar}{4m^2c^2}\hat{\vec{\sigma}}\cdot(\nabla V\times\hat{\vec{p}})\right]\bar{\Phi}_n(\vec{k},\vec{r}) = \varepsilon_n(\vec{k})\bar{\Phi}_n(\vec{k},\vec{r})$$

- In the absence of the spin-orbit coupling $\bar{\Phi}_n(\vec{k},\vec{r}) = \varphi_n(\vec{k},\vec{r})\chi_\sigma$

$$\chi_+ = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad \chi_- = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

Spin functions (spinors) chosen as eigenfunctions of $\hat{\sigma}_z$

- Spin operator $\hat{\vec{\sigma}}$ commutes with the non-relativistic Hamiltonian

⇒ Spin is a good quantum numer

- Case with spin-orbit interaction $\bar{\Phi}_n(\vec{k},\vec{r}) = \begin{bmatrix} \varphi_n^{(+)}(\vec{k},\vec{r}) \\ \varphi_n^{(-)}(\vec{k},\vec{r}) \end{bmatrix}$

- Spin operator $\hat{\vec{\sigma}}$ does not commute with the Hamiltonian

⇒ Spin is not a good quantum number

State describing band n can be a mixture of spin up (+) and spin down (-) states

- Removing of some degeneracies expected

Transformation properties of spinors

- There are fundamental differences in the description of the effect of rotations on spinor, as compared to a scalar or an ordinary vector.
- Spinor transforms under rotations according to the $j=1/2$ representation of the rotational group
- Two different quantum mechanical operators exist that correspond to the same physical transformations of points in space.
- The representations of the operators, rather than physical transformations themselves, are required.
- The components of a spinor under the rotation (about axis n through an angle ϑ) transform as

$$\bar{u} = \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} \qquad \bar{u}' = \hat{R}(\vartheta,\vec{n})\bar{u}$$

$$\hat{R}(\vartheta,\vec{n}) = \cos\frac{\vartheta}{2} - i\hat{\vec{\sigma}}\cdot\vec{n}\sin\frac{\vartheta}{2}$$

$\hat{R}(\vartheta,\vec{n})$ is unitary 2x2 matrix or representation

$$\hat{R}(\vartheta+2\pi,\vec{n}) = -\hat{R}(\vartheta,\vec{n}) \equiv \check{\hat{R}}(\vartheta,\vec{n}) \qquad D^{(1/2)}(R) \equiv \hat{R}(\vartheta,\vec{n})$$

- The two rotation that are not regarded as distinct in the r-space are represented by different matrices !

Transformation properties of spinors

- Action of an operator in spinor space on spinor

$$P_R \bar{\Phi}_n(\vec{k},\vec{r}) = D^{(1/2)}(R)\begin{bmatrix} \varphi_n^{(+)}(\vec{k}, R^{-1}\vec{r}) \\ \varphi_n^{(-)}(\vec{k}, R^{-1}\vec{r}) \end{bmatrix}$$

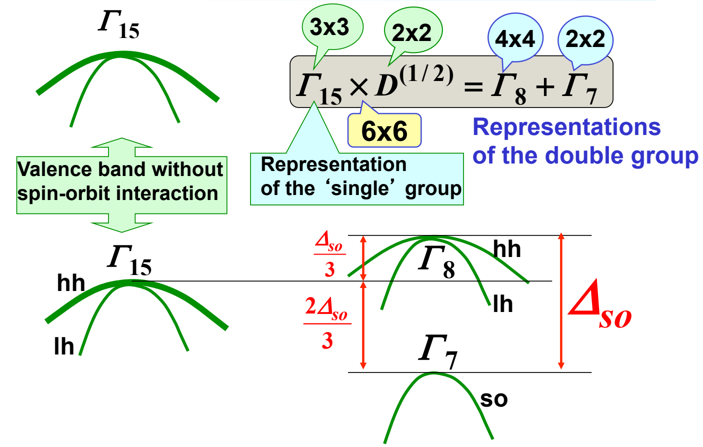
- Note there are twice so many operators P_R as Rs
- We wish to determine the behavior of an electron state that belonged to the representation $\Gamma^{(l)}$ before the spin was considered
- We form direct product $\Gamma^{(l)} \times D^{(1/2)}$
- The representations so obtained may be reducible as the representations of the group of operators in spinor space

$$\Gamma^{(l)} \times D^{(1/2)} = \sum_{\oplus i} n^{(i)} \Gamma^{(i)}$$

Irreducible representations

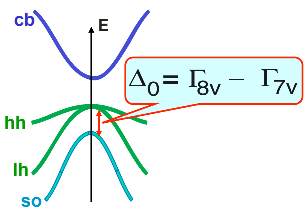
- Physical meaning: the splitting of a degenerate state l by spin-orbit coupling into states of symmetry i

Spin-splitting of the valence band of cubic semiconductors

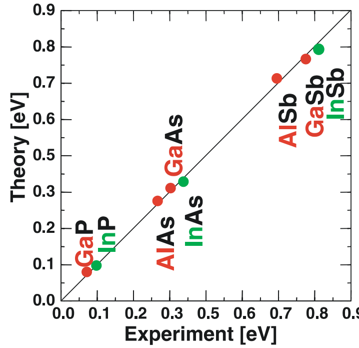


Spin-orbit splitting in semiconductors

Comparison of Theory (LDA) with Experiment

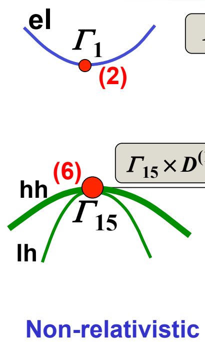


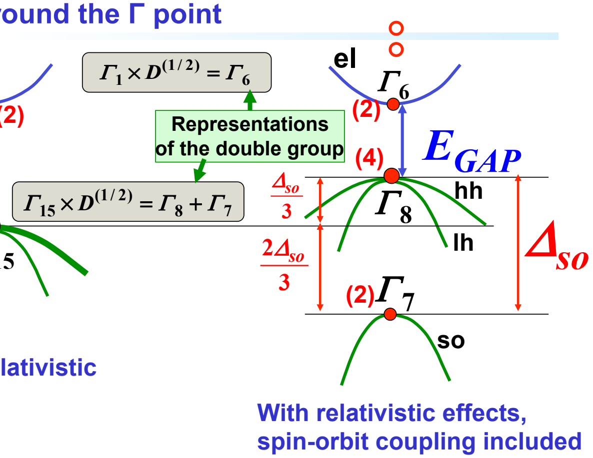
Band structure of a typical zinc-blende semiconductor



DFT gives very accurate predictions of spin-orbit splitting

Band structure of cubic semiconductors around the Γ point





k.p Method with spin-orbit coupling

$$\left[\frac{\hat{\vec{p}}^2}{2m}+V(\vec{r})+\frac{\hbar}{4m^2c^2}\hat{\vec{\sigma}}\cdot(\nabla V\times\hat{\vec{p}})\right]\vec{\Phi}_n(\vec{k},\vec{r})=\varepsilon_n(\vec{k})\vec{\Phi}_n(\vec{k},\vec{r})$$

Two-component Bloch spinor $\vec{\Phi}_n(\vec{k},\vec{r})=\exp(i\vec{k}\cdot\vec{r})\vec{u}_n(\vec{k},\vec{r})$

Periodic part

$$\left[\frac{\hat{\vec{p}}^2}{2m}+V(\vec{r})+\frac{\hbar}{4m^2c^2}\hat{\vec{\sigma}}\cdot(\nabla V\times\hat{\vec{p}})+\frac{\hbar^2k^2}{2m}+\frac{\hbar}{m}\vec{k}\cdot\hat{\vec{p}}+\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\cdot(\nabla V\times\vec{k})\right]\vec{u}_n(\vec{k},\vec{r})=\varepsilon_n(\vec{k})\vec{u}_n(\vec{k},\vec{r})$$

$$\hat{\vec{\Pi}}=\hat{\vec{p}}+\frac{\hbar}{4mc^2}(\hat{\vec{\sigma}}\times\nabla V)$$

Note
$\vec{a}\cdot(\vec{b}\times\vec{c})=\vec{c}\cdot(\vec{a}\times\vec{b})$

$$\left[\frac{\hat{\vec{p}}^2}{2m}+V(\vec{r})+\frac{\hbar}{4m^2c^2}\hat{\vec{\sigma}}\cdot(\nabla V\times\hat{\vec{p}})+\frac{\hbar^2k^2}{2m}+\frac{\hbar}{m}\vec{k}\cdot\hat{\vec{\Pi}}\right]\vec{u}_n(\vec{k},\vec{r})=\varepsilon_n(\vec{k})\vec{u}_n(\vec{k},\vec{r})$$

k.p Method with spin-orbit coupling

$$\left[\frac{\hat{\vec{p}}^2}{2m}+V(\vec{r})+\underbrace{\frac{\hbar}{4m^2c^2}\hat{\vec{\sigma}}\cdot(\nabla V\times\hat{\vec{p}})}_{\hat{H}_{SO}}+\frac{\hbar^2k^2}{2m}+\frac{\hbar}{m}\vec{k}\cdot\hat{\vec{\Pi}}\right]\vec{u}_n(\vec{k},\vec{r})=\varepsilon_n(\vec{k})\vec{u}_n(\vec{k},\vec{r})$$

Main strategy of the k.p Method
Build unknown $\vec{u}_n(\vec{k},\vec{r})$ out of known $\vec{u}_{n0}(\vec{r})$ for wave vector $\vec{k}_0=0=\Gamma$
What to do with $\hat{H}_{SO}$?

1 Include $\hat{H}_{SO}$ into unperturbed Hamiltonian

$$\hat{H}'=\frac{\hbar^2k^2}{2m}+\frac{\hbar}{m}\vec{k}\cdot\hat{\vec{\Pi}}$$

2 Include $\hat{H}_{SO}$ into perturbed Hamiltonian $\hat{H}'=\hat{H}_{SO}+\frac{\hbar^2k^2}{2m}+\frac{\hbar}{m}\vec{k}\cdot\hat{\vec{\Pi}}$

$\Rightarrow$ $\hat{H}_0\vec{u}_{n0}(\vec{r})=\varepsilon_n(0)\vec{u}_{n0}(\vec{r})$

$\hat{H}_0$ - is spin independent

Use Löwdin perturbation theory including valence and conduction band states in the group A states and the rest of states in group B

8 band k.p Method

States of group A: $\underbrace{|s+\rangle|s-\rangle}_{\text{Conduction band}}\ \underbrace{|x+\rangle|y+\rangle|z+\rangle|x-\rangle|y-\rangle|z-\rangle}_{\text{Valence band}}$ $\quad\{\vec{u}_{i0}\}$

Conduction band $\varepsilon_c(0)\equiv\varepsilon_{c0}$ — Valence band $\varepsilon_v(0)\equiv\varepsilon_{v0}$

$$\hat{\hat{H}}_{ij}=\langle i|\hat{H}_0+\hat{H}'|j\rangle+\sum_b^B\frac{\langle i|\hat{H}'|b\rangle\langle b|\hat{H}'|j\rangle}{\varepsilon_i-\varepsilon_{b0}}$$

8 x 8 Matrix $\qquad \det(\hat{\hat{H}}_{ij}-\varepsilon_i(\vec{k}))=0\quad\Rightarrow\varepsilon_i(\vec{k})$

- Commonly employed simplifications in $\hat{H}'=\hat{H}_{SO}+\frac{\hbar^2k^2}{2m}+\frac{\hbar}{m}\vec{k}\cdot\hat{\vec{\Pi}}$

$\hat{\vec{\Pi}}\approx\hat{\vec{p}}\qquad \hat{H}'=\hat{H}_{SO}+\hat{H}^{\vec{k}\cdot\vec{p}}\qquad \hat{H}^{\vec{k}\cdot\vec{p}}=\frac{\hbar^2k^2}{2m}+\frac{\hbar}{m}\vec{k}\cdot\hat{\vec{p}}$

$$\hat{\hat{H}}_{ij}=\underbrace{\langle i|\hat{H}_0+\hat{H}^{\vec{k}\cdot\vec{p}}|j\rangle+\sum_b^B\frac{\langle i|\hat{H}^{\vec{k}\cdot\vec{p}}|b\rangle\langle b|\hat{H}^{\vec{k}\cdot\vec{p}}|j\rangle}{\varepsilon_{i0}-\varepsilon_{b0}}}_{\hat{\hat{h}}_{ij}}+\underbrace{\langle i|\hat{H}_{SO}|j\rangle}_{(\hat{H}_{SO})_{ij}}$$

$\hat{\hat{h}}_{ij}$ Contains part with operators independent on spin

8 band k.p Method - Terms without spin-orbit

$$\hat{\hat{h}}_{ij}(8\times8)=\begin{bmatrix}\hat{\hat{h}}_{4\times4} & 0\\ 0 & \hat{\hat{h}}_{4\times4}\end{bmatrix}$$

$$\hat{\hat{h}}_{4\times4}=\begin{array}{c|cccc} & |s+\rangle & |x+\rangle & |y+\rangle & |z+\rangle\\ \hline |s+\rangle & \varepsilon_{c0}+\frac{h^2k^2}{2m}+A'k^2 & Bk_yk_z+iPk_x & Bk_xk_z+iPk_y & Bk_xk_y+iPk_z\\ |x+\rangle & Bk_yk_z-iPk_x & \varepsilon_{v0}+\frac{h^2k^2}{2m}+L'k_x^2+M(k_y^2+k_y^2) & N'k_xk_y & N'k_xk_z\\ |y+\rangle & Bk_xk_z-iPk_y & N'k_xk_y & \varepsilon_{v0}+\frac{h^2k^2}{2m}+L'k_y^2+M(k_x^2+k_z^2) & N'k_yk_z\\ |z+\rangle & Bk_xk_y-iPk_z & N'k_xk_z & N'k_yk_z & \varepsilon_{v0}+\frac{h^2k^2}{2m}+L'k_z^2+M(k_x^2+k_y^2)\end{array}$$

$$B=2\frac{h^2}{m^2}\sum_b\frac{\langle s|p_x|b\rangle\langle b|p_y|z\rangle}{(\varepsilon_{c0}+\varepsilon_{v0})/2-\varepsilon_{b0}}$$

$$P=-i\frac{h}{m}\langle s|p_x|x\rangle$$

8 band k.p Method – Spin-Orbit Terms

$$\left\langle s\sigma \,|\, \hat{H}_{SO} \,|\, \alpha\sigma' \right\rangle = 0 \qquad \sigma \in \{+,-\} \quad \alpha \in \{x,y,z\}$$

$$\boxed{\Delta = -i\frac{3\hbar}{4m^2c^2}\left\langle x+ \,|\, (\nabla V \times \hat{\vec{p}})_y \,|\, z- \right\rangle = -\frac{3\hbar}{4m^2c^2}\left\langle x+ \,|\, \frac{\partial V}{\partial z}\frac{\partial}{\partial x} - \frac{\partial V}{\partial x}\frac{\partial}{\partial z} \,|\, z- \right\rangle}$$

$$\begin{array}{c c} & \begin{array}{cccccc} |x+\rangle & |y+\rangle & |z+\rangle & |x-\rangle & |y-\rangle & |z-\rangle \end{array} \\ \begin{array}{c} |x+\rangle \\ |y+\rangle \\ |z+\rangle \\ |x-\rangle \\ |y-\rangle \\ |z-\rangle \end{array} & \hat{\hat{H}}_{SO} = -\dfrac{\Delta}{3}\begin{bmatrix} 0 & i & 0 & 0 & 0 & -1 \\ -i & 0 & 0 & 0 & 0 & i \\ 0 & 0 & 0 & 1 & -i & 0 \\ 0 & 0 & 1 & 0 & -i & 0 \\ 0 & 0 & i & i & 0 & 0 \\ -1 & -i & 0 & 0 & 0 & 0 \end{bmatrix} \end{array}$$

This matrix can be diagonalized easily

8 band k.p Method – Angular momentum Representation of Valence States

$\|J,m_J\rangle$		$\left\langle J,m_J \,\|\, \hat{H}_0 + \hat{H}_{SO} \,\|\, J,m_J \right\rangle$	
$\|\tfrac{3}{2},\tfrac{3}{2}\rangle$	$\frac{1}{\sqrt{2}}(\|x+\rangle + i\|y+\rangle)$	$\varepsilon_{v0} + \Delta/3$	ε_v Γ_8
$\|\tfrac{3}{2},\tfrac{1}{2}\rangle$	$-\frac{\sqrt{2}}{\sqrt{3}}(\|z+\rangle + \frac{1}{\sqrt{6}}(\|x-\rangle + i\|y-\rangle)$	$\varepsilon_{v0} + \Delta/3$	
$\|\tfrac{3}{2},-\tfrac{1}{2}\rangle$	$-\frac{\sqrt{2}}{\sqrt{3}}(\|z-\rangle - \frac{1}{\sqrt{6}}(\|x+\rangle - i\|y+\rangle)$	$\varepsilon_{v0} + \Delta/3$	
$\|\tfrac{3}{2},-\tfrac{1}{2}\rangle$	$-\frac{1}{\sqrt{2}}(\|x-\rangle - i\|y-\rangle)$	$\varepsilon_{v0} + \Delta/3$	
$\|\tfrac{1}{2},\tfrac{1}{2}\rangle$	$\frac{1}{\sqrt{3}}(\|x-\rangle + i\|y-\rangle) + \frac{1}{\sqrt{3}}(\|z+\rangle)$	$\varepsilon_{v0} - \frac{2\Delta}{3}$	$\varepsilon_v - \Delta$ Γ_7
$\|\tfrac{1}{2},-\tfrac{1}{2}\rangle$	$\frac{1}{\sqrt{3}}(\|x+\rangle - i\|y+\rangle) - \frac{1}{\sqrt{3}}(\|z-\rangle)$	$\varepsilon_{v0} - \frac{2\Delta}{3}$	

8 band k.p Method

- The most "popular" form of the k.p Method
- Hamiltonian matrices in both bases used in the calculations
- 8 x 8 matrix easily handled numerically
- For analytical purposes one must take further simplifications

  E. O. Kane, *"The k.p Method"*, Semiconductors and Semimetals, Vol. 1, eds. R. K. Willardson and A. C. Beer, (Academic Press, San Diego, 1966), p. 75.

- One author – one notation

  e.g., Luttinger parameters

$$\gamma_1 = -\frac{2m}{3h^2}(L + 2M) - 1$$

$$\gamma_2 = -\frac{m}{3h^2}(L - M)$$

$$\gamma_3 = -\frac{m}{3h^2}N$$

- Crystal potential hidden in the parameters of the k.p matrix

Envelope Function Theory – Effective Mass Equation

Electron in an external field

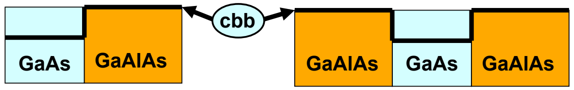
$$\left[\frac{\hat{\vec{p}}^2}{2m}+V(\vec{r})+U(\vec{r})\right]\psi(\vec{r})=\varepsilon\psi(\vec{r})$$

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 $U(\vec{r})=-\dfrac{e^2}{\kappa|\vec{r}|}$
- 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 ? $\left(\dfrac{\hat{\vec{p}}^2}{2m^*}+U(\vec{r})\right)F(\vec{r})=\varepsilon F(\vec{r})$ $\qquad F(\vec{r})=?$

Envelope Function Theory

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

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

- Ansatz: $\psi(\vec{r})=\sum_{n'}\int_{BZ}d\vec{k}'A_{n'}(\vec{k}')\chi_{n'\vec{k}'}(\vec{r})$

Integration over the Brillouin Zone

$\chi_{n\vec{k}}(\vec{r})=e^{i\vec{k}\cdot\vec{r}}u_{n0}(\vec{r})$ Luttinger – Kohn functions $\vec{k}_0=0$

- Multiply both sides of Eq. by $\chi^*_{n\vec{k}}(\vec{r})$ $\int_\Omega d^3\vec{r}$ and integrate over the crystal volume

$$[\varepsilon_{n0}+\frac{\hbar^2}{2m}\vec{k}^2]A_n(\vec{k})+\sum_{n'}\frac{\hbar}{m}\vec{k}\cdot\vec{p}_{nn'}A_{n'}(\vec{k})+$$
$$+\sum_{n'}\int_{BZ}d\vec{k}'\langle n\vec{k}|U(\vec{r})|n'\vec{k}'\rangle A_{n'}(\vec{k}')=\varepsilon A_n(\vec{k})$$

$$\langle n\vec{k}|U(\vec{r})|n'\vec{k}'\rangle=\int d\vec{r}\exp[i(\vec{k}'-\vec{k})\cdot\vec{r}]U(\vec{r})u^*_{n0}(\vec{r})u_{n'0}(\vec{r})$$

Envelope Function Theory

- When $\langle n\vec{k}|U(\vec{r})|n'\vec{k}'\rangle\cong 0$ for $n'\neq n$

then the coefficients of different bands are decoupled.

$u_{n0}(\vec{r})$ -- are periodic functions

$u^*_{n0}(\vec{r})u_{n'0}(\vec{r})=\sum_m B_m^{nn'}\exp[-i\vec{G}_m\cdot\vec{r}]$ Fourier series

Fourier coefficients

$$B_m^{nn'}=\frac{1}{\Omega_0}\int_{\Omega_0}d\vec{r}e^{i\vec{G}_m\cdot\vec{r}}u^*_{n0}(\vec{r})u_{n'0}(\vec{r}) \qquad B_0^{nn'}=\frac{1}{(2\pi)^3}\delta_{nn'}$$

$$\langle n\vec{k}|U(\vec{r})|n'\vec{k}'\rangle=\sum_m B_m^{nn'}\int d\vec{r}e^{i(\vec{k}'-\vec{k}-\vec{G}_m)\cdot\vec{r}}U(\vec{r})$$

$U(\vec{k})=\dfrac{1}{(2\pi)^3}\displaystyle\int d\vec{r}e^{-i\vec{k}\cdot\vec{r}}U(\vec{r})$ Fourier coefficients of the potential U

- $\langle n\vec{k}|U(\vec{r})|n'\vec{k}'\rangle=(2\pi)^3\sum_m B_m^{nn'}U(\vec{k}-\vec{k}'+\vec{G}_m)$

Envelope Function Theory – Condition for the external potential

$$\langle n\vec{k}|U(\vec{r})|n'\vec{k}'\rangle=(2\pi)^3\sum_m B_m^{nn'}U(\vec{k}-\vec{k}'+\vec{G}_m)$$

- For $m\neq 0$ $B_m^{nn'}\neq 0$ for $n\neq n'$
- For $m=0$ $B_m^{nn'}=0$ for $n\neq n'$

Orthogonality of periodic Bloch functions

$\langle n\vec{k}|U(\vec{r})|n'\vec{k}'\rangle\cong 0$ for $n'\neq n$ $\Longleftrightarrow U(\vec{k}-\vec{k}'+\vec{G}_m)\approx 0$ for $m\neq 0$

It means – only the first Fourier component of the potential U is of any importance !

Potential $U(\vec{r})$ should change slowly in space !

$$\frac{U(\vec{k}-\vec{k}'+\vec{G}_m)}{U(\vec{k}-\vec{k}')}\ll 1 \;\Rightarrow\; \langle n\vec{k}|U(\vec{r})|n'\vec{k}'\rangle=U(\vec{k}-\vec{k}')\delta_{nn'}$$

Envelope Function Theory – Effective Mass Equation in Momentum Space

$$[\varepsilon_{n0}+\frac{\hbar^2}{2m}\vec{k}^2]A_n(\vec{k})+\sum_{n'}\frac{\hbar}{m}\vec{k}\cdot\vec{p}_{nn'}A_{n'}(\vec{k})+\int_{BZ}d\vec{k}'U(\vec{k}-\vec{k}')A_n(\vec{k}')=\varepsilon A_n(\vec{k})$$

This equation still couples different bands

- Canonical transformation $A=e^S B \implies \hat{H}^{(new)}=e^{-S}\hat{H}e^S$

New coefficients

$$S\sim\frac{\hbar}{m}\frac{\vec{k}\cdot\vec{p}_{nn'}}{E_{GAP}}\ll 1$$

Case for non-degenerate bands

$$\left(\varepsilon_{n0}+\frac{\hbar^2\vec{k}^2}{2m}+\frac{\hbar^2}{m^2}\sum_{n''\neq n}\frac{(\vec{k}\cdot\vec{p}_{nn''})(\vec{k}\cdot\vec{p}_{n''n})}{\varepsilon_{n0}-\varepsilon_{n''0}}\right)B_n(\vec{k})+\int_{BZ}d\vec{k}'U(\vec{k}-\vec{k}')B_n(\vec{k}')=\varepsilon B_n(\vec{k})$$

$$\left[\varepsilon_{n0}+\frac{\hbar^2}{2}\sum_{\mu,\nu}^{3}\left(\frac{1}{m^*_{\mu\nu}}\right)_n k_\mu k_\nu\right]B_n(\vec{k})+\int_{BZ}d\vec{k}'U(\vec{k}-\vec{k}')B_n(\vec{k}')=\varepsilon B_n(\vec{k})$$

$$\boxed{\varepsilon_n(\vec{k})B_n(\vec{k})+\int_{BZ}d\vec{k}'U(\vec{k}-\vec{k}')B_n(\vec{k}')=\varepsilon B_n(\vec{k})}$$

Effective Mass Equation in Momentum Space

Envelope Function Theory- Transformation of the effective mass equation in momentum space into *r*-space

$$\varepsilon_n(\vec{k})B_n(\vec{k})+\int_{BZ}d\vec{k}'U(\vec{k}-\vec{k}')B_n(\vec{k}')=\varepsilon B_n(\vec{k})$$

- For isotropic effective mass $\varepsilon_n(\vec{k})=\frac{\hbar^2\vec{k}^2}{2m^*_n}$

This equation reminds the Schrödinger equation in momentum space (here $\hbar\vec{k}$ is quasi-momentum, not momentum !!)

Transformation into *r* - space

- Multiply both sides of the equation by $e^{i\vec{k}\cdot\vec{r}}$ and integrate $\int_{BZ}d\vec{k}$
- Define function $F_n(\vec{r})=\int_{BZ}d\vec{k}e^{i\vec{k}\cdot\vec{r}}B_n(\vec{k})$ **Envelope function**

ONLY BZ !!

- Write $\varepsilon_n(\vec{k})=\varepsilon_{n0}+\sum_{\mu,\nu}\alpha_{\mu\nu}k_\mu k_\nu+\ldots$

Envelope Function Theory- Transformation of the effective mass equation in momentum space into *r*-space

$$\underbrace{\varepsilon_n(\vec{k})B_n(\vec{k})}_{(a)}+\underbrace{\int_{BZ}d\vec{k}'U(\vec{k}-\vec{k}')B_n(\vec{k}')}_{(b)}=\varepsilon B_n(\vec{k})$$

$$(a)=\int_{BZ}d\vec{k}e^{i\vec{k}\cdot\vec{r}}\varepsilon_n(\vec{k})B_n(\vec{k})=\varepsilon_{n0}F_n(\vec{r})+\sum_{\mu,\nu}\alpha_{\mu\nu}\int_{BZ}d\vec{k}k_\mu k_\nu e^{i\vec{k}\cdot\vec{r}}B_n(\vec{k})=$$

$$=\varepsilon_{n0}F_n(\vec{r})+\sum_{\mu,\nu}\alpha_{\mu\nu}\left(\frac{1}{i}\frac{\partial}{\partial x_\mu}\right)\left(\frac{1}{i}\frac{\partial}{\partial x_\nu}\right)\int_{BZ}d\vec{k}e^{i\vec{k}\cdot\vec{r}}B_n(\vec{k})=$$

$$=\varepsilon_{n0}F_n(\vec{r})+\sum_{\mu,\nu}\alpha_{\mu\nu}\left(\frac{1}{i}\frac{\partial}{\partial x_\mu}\right)\left(\frac{1}{i}\frac{\partial}{\partial x_\nu}\right)F_n(\vec{r})=$$

$$=\left[\varepsilon_{n0}+\sum_{\mu,\nu}\alpha_{\mu\nu}\left(\frac{1}{i}\frac{\partial}{\partial x_\mu}\right)\left(\frac{1}{i}\frac{\partial}{\partial x_\nu}\right)\right]F_n(\vec{r})$$

$$\boxed{(a)=\varepsilon_n(\frac{1}{i}\vec{\nabla})F_n(\vec{r})}\qquad k_\mu\rightarrow\frac{1}{i}\frac{\partial}{\partial x_\mu}$$

Envelope Function Theory- Transformation of the effective mass equation in momentum space into *r*-space

$$(b)=\iint_{BZ}d\vec{k}'d\vec{k}U(\vec{k}-\vec{k}')e^{i\vec{k}\cdot\vec{r}}B_n(\vec{k}')=$$

$$=\frac{1}{(2\pi)^3}\iint_{BZ}d\vec{k}'d\vec{k}\int d\vec{r}'U(\vec{r}')e^{i(\vec{k}'-\vec{k})\cdot\vec{r}'}e^{i\vec{k}\cdot\vec{r}}B_n(\vec{k}')=$$

$$=\int d\vec{r}'U(\vec{r}')\underbrace{\left(\int_{BZ}d\vec{k}'e^{i\vec{k}'\cdot\vec{r}'}B_n(\vec{k}')\right)}_{F_n(\vec{r}')}\underbrace{\left(\frac{1}{(2\pi)^3}\int_{BZ}d\vec{k}e^{i\vec{k}\cdot(\vec{r}-\vec{r}')}\right)}_{\Delta(\vec{r}-\vec{r}')}$$

$$\Delta(\vec{r}-\vec{r}')=\frac{1}{(2\pi)^3}\int_{BZ}d\vec{k}e^{i\vec{k}\cdot(\vec{r}-\vec{r}')}$$

- In the full k-space $\Delta(\vec{r}-\vec{r}')=\delta(\vec{r}-\vec{r}')$
- $\int\Delta(\vec{r})d^3\vec{r}=1$
- $\int\Delta(\vec{r}-\vec{r}')f(\vec{r}')d^3\vec{r}'\approx f(\vec{r})$ If $f(\vec{r})$ is smooth

$$\boxed{(b)=\int d\vec{r}'U(\vec{r}')F_n(\vec{r}')\Delta(\vec{r}-\vec{r}')\cong U(\vec{r})F_n(\vec{r})}$$

Envelope Function Theory- Effective Mass Equation

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

$$A_n(\vec{k}) \approx B_n(\vec{k}) \qquad \psi(\vec{r})=\sum_n \int_{BZ} d\vec{k}B_n(\vec{k})e^{i\vec{k}\cdot\vec{r}}u_{n0}(\vec{r})=\sum_n F_n(\vec{r})u_{n0}(\vec{r})$$

EME does not couple different bands

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

"True" wavefunction

Envelope Function

Periodic Bloch Function

- Special case of constant (or zero) external potential

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

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

Envelope Function Theory- Degenerate Bands

- Matrices obtained from k.p method, e.g., 8 band k.p method

$$\hat{\hat{H}}_{ab}=D_{ab}^{(0)}+\sum_{\mu=1}^{3}D_{ab}^{(1)\mu}k_\mu+\sum_{\mu=1}^{3}\sum_{\nu=1}^{3}D_{ab}^{(2)\mu\nu}k_\mu k_\nu$$

  Periodic potential hidden in the parameters of the Hamiltonian matrix

- The effect of non-periodic external potential can be described by a system of differential equations for the envelope functions

$$\sum_{b=1}^{s}[\sum_{\mu=1}^{3}\sum_{\nu=1}^{3}D_{ab}^{(2)\mu\nu}(-i\nabla_\mu)(-i\nabla_\nu)+ \\ +\sum_{\mu=1}^{3}D_{ab}^{(1)\mu}(-i\nabla_\mu)+D_{ab}^{(0)}+U(\vec{r})\delta_{ab}]F_b(\vec{r})=\varepsilon F_b(\vec{r})$$

- Wave function $\psi(\vec{r})=\sum_{b=1}^{s}F_b(\vec{r})u_{b0}(\vec{r})$
- Basis theory for studies of low dimensional systems

Envelope Function Theory - Applications

a) Magnetic field

- Minimal coupling principle for full Hamiltonian $\hat{\vec{p}} \to \hat{\vec{p}}-\frac{e}{c}\vec{A}(\vec{r})$
- In effective Hamiltonian $k_\mu \to -i\nabla_\mu-\frac{e}{c}A_\mu(\vec{r})$
- Non-degenerate case - conduction band electrons

  $[\varepsilon(-i\vec{\nabla}-\frac{e}{c}\vec{A}(\vec{r}))-\varepsilon]F_n(\vec{r})=0 \Longrightarrow$ Landau levels
- Degenerate case of valence band

$$\sum_{b=1}^{s}[D_{ab}^{\mu\nu}(-i\nabla_\mu-\frac{e}{c}A_\mu(\vec{r}))(-i\nabla_\nu-\frac{e}{c}A_\nu(\vec{r}))]F_b(\vec{r})=\varepsilon F_b(\vec{r})$$

$$\left.\begin{array}{l}\text{b) Donors in semiconductors}\\[1em]\text{c) Low dimensional semiconductor structures}\end{array}\right\}\ \text{NEXT LECTURE}$$

Thank you !