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
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

TEM image of a InAs/GaAs dot

Si(111)7×7 Surface

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

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TEM image of a InAs/GaAs dot

Si(111)7×7 Surface

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Synthesis of colloidal nanocrystals

Injection of organometallic precursors

Mixture of surfactants Heating mantle

Nanostructures: colloidal crystals

- Crystal from sub-μm spheres of PMMA (perplex) 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

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

(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\> 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.

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

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.”


Heterostructured Nanowires

coaxial heterostructured nanowire
longitudinal heterostructured nanowire
Heterostructured Nanowires

Transmission electron microscopy images of a GaN/AlGaN core–sheath nanowire and 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

\[
E[\rho] = \int d^3\vec{r} \rho(\vec{r}) \nu_{\text{ext}}(\vec{r}) + F[\rho]
\]

\[
E[\rho_0] = E_0
\]

Ground state density

Total energy functional

<table>
<thead>
<tr>
<th>Kinetic energy</th>
<th>Exchange energy</th>
<th>Correlation energy</th>
</tr>
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<tbody>
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<td>$E[\rho] = \int d^3\vec{r} \nu_{\text{ext}}(\vec{r}) \rho(\vec{r}) + T_s[\rho] + U[\rho] + E_x[\rho] + E_c[\rho]$</td>
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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

\[ H = \sum_{\alpha i} e_{\alpha i} c_{\alpha i}^\dagger c_{\alpha i} + \sum_{\alpha i, \beta j} t_{\alpha i, \beta j} c_{\alpha i}^\dagger c_{\beta j} \]

- **Creation & annihilation 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

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

Periodic potential of crystal
Non-periodic external potential

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

Band Structure

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

Envelope Function Theory – Effective Mass Equation


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

EME does not couple different bands

- Special case of constant (or zero) external potential
  \[ U(\vec{r}) = 0 \Rightarrow F_n(\vec{r}) = \exp(ik \cdot \vec{r}) \Rightarrow \psi(\vec{r}) \] Bloch function
- \[ U(z) \Rightarrow F_n(\vec{r}) = \exp[i(k_x x + k_y y)] \]

Which external fields?
- Shallow impurities, e.g., donors
- Magnetic field \( B, \vec{B} = \text{curl} \vec{A} = \nabla \times \vec{A} \)
- Heterostructures, Quantum Wells, Quantum wires, Q. Dots

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

\( F(\vec{r}) = ? \)
**k.p method for bulks**

### k.p Method - Derivation

\[
\frac{\hbar^2}{2m} \mathbf{p}^2 + V(\mathbf{r}) \psi_{n}(\mathbf{k} \cdot \mathbf{r}) = \epsilon_n(\mathbf{k}) \psi_{n}(\mathbf{k} \cdot \mathbf{r}) = \sum_j A_{nj}(k) \chi_j(\mathbf{k} \cdot \mathbf{r})
\]

\[
\sum_j A_{nj}(k) \left[ \frac{\hbar^2}{2m} \mathbf{p}^2 + V(\mathbf{r}) \right] \chi_j(\mathbf{k} \cdot \mathbf{r}) = \epsilon_n(\mathbf{k}) \chi_j(\mathbf{k} \cdot \mathbf{r})
\]

\[
\mathbf{p} = -i \hbar \nabla
\]

\[
\nabla \left[ \frac{\hbar^2}{2m} \mathbf{p}^2 + V(\mathbf{r}) \right] \chi_j(\mathbf{k} \cdot \mathbf{r}) = \epsilon_n(\mathbf{k}) \chi_j(\mathbf{k} \cdot \mathbf{r})
\]

\[
\left[ \frac{\hbar^2}{2m} \mathbf{p}^2 + V(\mathbf{r}) \right] \chi_j(\mathbf{k} \cdot \mathbf{r}) = \epsilon_n(\mathbf{k}) \chi_j(\mathbf{k} \cdot \mathbf{r})
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\]

\[
\chi_j(\mathbf{k} \cdot \mathbf{r}) = \mathbf{k} \cdot \mathbf{r}^j
\]

**k.p Method - Luttinger-Kohn basis**

Bloch functions are orthogonal in the wave vector and band index

\[
\left| \mathbf{v}_n(\mathbf{k} \cdot \mathbf{r}) \right|^2 = \delta_{nn} \delta(\mathbf{k} \cdot \mathbf{q} - \mathbf{k} \cdot \mathbf{p} - \mathbf{p} \cdot \mathbf{p})
\]

\[
\mathbf{v}_n(\mathbf{k} \cdot \mathbf{r}) = \exp[i \mathbf{k} \cdot \mathbf{r}] u_n(\mathbf{r})
\]

\[
\left| \mathbf{u}_n(\mathbf{r}) \right|^2 = \delta_{nn} \delta(\mathbf{k} \cdot \mathbf{q} - \mathbf{k} \cdot \mathbf{p} - \mathbf{p} \cdot \mathbf{p})
\]

Luttinger-Kohn basis

\[
\chi_j(\mathbf{k} \cdot \mathbf{r}) = \exp[i \mathbf{k} \cdot \mathbf{r}] \psi_j(\mathbf{k} \cdot \mathbf{r}) = \exp[i \mathbf{k} \cdot \mathbf{r}] u_j(\mathbf{k} \cdot \mathbf{r})
\]

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

\[
\psi_n(\mathbf{k} \cdot \mathbf{r}) = \sum_j A_{nj}(k) \chi_j(\mathbf{k} \cdot \mathbf{r})
\]

\[
\frac{\hbar^2}{2m} \mathbf{p}^2 + V(\mathbf{r}) \psi_n(\mathbf{k} \cdot \mathbf{r}) = \epsilon_n(\mathbf{k}) \psi_n(\mathbf{k} \cdot \mathbf{r})
\]

\[
\sum_j A_{nj}(k) \psi_n(\mathbf{k} \cdot \mathbf{r}) = \epsilon_n(\mathbf{k}) \psi_n(\mathbf{k} \cdot \mathbf{r})
\]

Multiply both sides by \( \psi_j(\mathbf{k} \cdot \mathbf{r}) \)

Integrate over the unit cell

\[
\sum_j \left[ \left( \epsilon_j(\mathbf{k}) + \frac{\hbar^2}{2m} \mathbf{k}^2 \right) u_j(\mathbf{k} \cdot \mathbf{r}) + \frac{\hbar}{m} \mathbf{k} \cdot \mathbf{p} + \epsilon_j(\mathbf{k}) \right] A_{nj}(k) = \epsilon_n(\mathbf{k}) A_{nj}(k)
\]

\[
\mathbf{p} = \frac{(2\pi)^3}{V} \int d^3\mathbf{r} \mathbf{u}_n(\mathbf{k} \cdot \mathbf{r}) \mathbf{p} \psi_j(\mathbf{k} \cdot \mathbf{r})
\]

**k dot p**

Momentum matrix elements
Perturbation theory for non-degenerate states

- e.g., GaAs
- e.g., Si

Taylor series

\[ E_n = E_n^0 + \langle \Delta E_n \rangle + \sum_{\alpha=1}^{2d} \frac{\delta^2 E_n}{\delta k_\alpha^2} (k^2 - k_0^2)_\alpha (k^2 - k_0^2)_\beta + \]

\[ e_n(k) = E_n(k_0) + \frac{h^2}{2m}(k^2 - k_0^2) + \sum_{\alpha=1}^{2d} \frac{\delta^2 e_n}{\delta k_\alpha^2} (k^2 - k_0^2)_\alpha + \]

\[ \frac{h^2}{2m} \hat{p} \cdot \hat{p} = \frac{h^2}{2m} (k^2 - k_0^2) + \sum_{\alpha=1}^{2d} \frac{\delta^2 e_n}{\delta k_\alpha^2} (k^2 - k_0^2)_\alpha \]

- Band \( n \) has extremum in \( k_0 \)

\[ \frac{\partial e_n}{\partial k} \bigg|_{k=k_0} = 0 \]

\[ \hat{p} \cdot \hat{p} = \frac{h^2}{2m} (k^2 - k_0^2) = 0 \]

Let us introduce second rank tensor

Reciprocal Effective Mass Tensor

\[ \frac{1}{m_n} = \frac{\hbar^2}{2m} \frac{\partial^2 e_n}{\partial k_\alpha \partial k_\beta} (k^2 - k_0^2)_\alpha (k^2 - k_0^2)_\beta \]

\[ m - \text{free electron mass} \]

**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

\[ H' = \frac{\hbar^2}{2m} (k^2 - k_0^2) + \frac{h^2}{m}(k - k_0) \cdot \hat{p} \]

**k.p Method – Main Equation**

System of homogeneous equations for expansion coefficients \( A_n(k) \)

This equations couple all bands

What one needs is decoupling scheme, e.g., perturbation theory

\[ H = H_0 + H' \]

\[ H_0 |n\rangle = E_n^0 |n\rangle \]

Perturbation theory for non-degenerate states

\[ E_n = E_n^0 + E_n^{(1)} + E_n^{(2)} + K \]

\[ E_n = E_n^0 + \langle \Delta E_n \rangle + \sum_{\alpha=1}^{2d} \frac{\delta^2 E_n}{\delta k_\alpha^2} (k^2 - k_0^2)_\alpha + \]

\[ \frac{h^2}{2m} \hat{p} \cdot \hat{p} = \frac{h^2}{2m} (k^2 - k_0^2) + \sum_{\alpha=1}^{2d} \frac{\delta^2 e_n}{\delta k_\alpha^2} (k^2 - k_0^2)_\alpha \]

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**k.p Method – Effective Mass Tensor**

**k.p Method – Effective Mass Tensor**

Energy to second order in the expansion parameter

\[ u_n(k, \tilde{r}) = u_n(k_0, \tilde{r}) + \frac{h}{m} \sum_{j \neq n} \frac{\delta^2 e_j}{\delta k^2} (k_0 - k_0) - e_j(k_0) \]

Periodic wave function to the first order in expansion parameter

**k.p Method – Non-degenerate state**

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

\[ H' = \frac{\hbar^2}{2m} (k^2 - k_0^2) + \frac{h^2}{m}(k - k_0) \cdot \hat{p} \]

Expansion parameter: \( s = k - k_0 \)

\[ e_n(k) = e_n(k_0) + \frac{\hbar^2}{2m}(k - k_0) \cdot \hat{p} + \frac{\h^2}{2m}(k_0^2 - k^2) + \frac{\h^2}{2m} \sum_{j \neq n} (\hat{S} \cdot \hat{p}_j) (k - k_0) \cdot \hat{S} \cdot \hat{p}_j + \]

Energy to second order in the expansion parameter

\[ u_n(k, \tilde{r}) = u_n(k_0, \tilde{r}) + \frac{h}{m} \sum_{j \neq n} \frac{\delta^2 e_j}{\delta k^2} (k_0 - k_0) - e_j(k_0) \]

**k.p Method – Effective Mass Tensor**

**k.p Method – Effective Mass Tensor**

\[ \frac{\partial^2 e_n}{\partial k_\alpha \partial k_\beta} = \frac{\hbar^2}{m} \delta_{\alpha \beta} + \frac{\h^2}{m} \sum_{j \neq n} \frac{\partial^2 e_j}{\partial k_\alpha \partial k_\beta} - e_j(k_0) \]

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**

\[ \frac{m}{m_{\text{eff}}} = 1 + \frac{2}{m} \sum_{j=1}^{n} \epsilon_{j}(\mathbf{k}) - \epsilon_{j}(\mathbf{k}_{0}) \]

\( \alpha \) -refers now to one of the principal axes

- The interaction with the lower lying levels tends to decrease an effective mass \( \epsilon_{j}(\mathbf{k}) < \epsilon_{j}(\mathbf{k}_{0}) \)
- The interaction with the higher states tends to increase an effective mass \( \epsilon_{j}(\mathbf{k}) > \epsilon_{j}(\mathbf{k}_{0}) \)
- For cubic semiconductors with minimum of the conduction band in \( \mathbf{k} \) point, the band energy in the neighborhood is

\[ \epsilon_{n}(\mathbf{k}) = \epsilon_{n}(0) + \frac{\hbar^{2} k^{2}}{2 m_{n}} \]

**Physical meaning of the effective mass ?**

**Dynamics of particles**

In the presence of external fields, the crystalline electrons behave as particles with effective mass \( m^{*} \).

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**Effective Mass - A Two-Band Model**

Some insight into the nature of the results

\[ E_{1}(0) = E_{\text{GAP}} \]

\[ E_{0}(0) = 0 \]

Let us assume \( E_{k} \ll \frac{2}{3} m \)

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

\[ m \quad m \]

\[ m \quad m \]

\[ m \quad m \]

\[ m \quad m \]

\[ m \quad m \]

Effective mass proportional to the energy gap

---

**k.P – Method – Band Degeneracies**

- The state of interest in \( \mathbf{k}_{0} \) 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

\[ H_{\text{eff}} \psi_{m} = \epsilon_{m} \psi_{m} \quad a = 1,2,3, \quad \epsilon_{m} \]

\[ \langle a | H_{0} + H' | b \rangle - \epsilon_{\text{eff}} = 0 \]

**First order perturbation**

\[ H' = \frac{\hbar^{2}}{2 m_{1}} (\mathbf{k}^{2} - \mathbf{k}_{0}^{2}) + \frac{\hbar}{m} (\mathbf{k} - \mathbf{k}_{0}) \cdot \mathbf{p} \]

In our case, perturbation is

\[ H' = \frac{\hbar^{2}}{2 m_{1}} (\mathbf{k}^{2} - \mathbf{k}_{0}^{2}) + \frac{\hbar}{m} (\mathbf{k} - \mathbf{k}_{0}) \cdot \mathbf{p} \]

**Löwdin perturbation theory**

\[ H'_{\text{eff}} = \left( H'_{\text{eff}}^{(0)} + \left( H'_{\text{eff}}^{(1)} \right)^{(1)} + \left( H'_{\text{eff}} \right)^{(2)} \right) \]

\[ = \epsilon_{m} \delta_{ab} + \langle \phi_{m} | H' | \phi_{b} \rangle + \sum_{a' \neq a} \left( \langle \phi_{m} | H' | \phi_{a'} \rangle \langle \phi_{a'} | H' | \phi_{b} \rangle \right) / \epsilon_{m}^{2} - \epsilon_{b}^{2} \]

- 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 (\( \epsilon_{a} \)),
  - 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

\[ \tilde{p}^{nm}_{\alpha \beta} = \left( \frac{e}{m} \right) \left[ \hat{p}^0_{\alpha \beta} + \hat{p}^0_{\alpha \beta} \right] \]

\[ H^{a \beta}_{\alpha \gamma} = e_n(k_0) \delta_{a \beta} + \frac{\hbar^2}{2m} \hat{k}^2 \delta_{a \beta} + \frac{\hbar}{m} \hat{k} \cdot \tilde{p}^{nm}_{\alpha \beta} + \sum_{m,w=1}^3 \frac{\epsilon}{m} \left( \hat{k} \cdot \tilde{p}^{nm}_{\alpha \beta} \right) \delta_{a \beta} - \epsilon_m(k_0) \]

Band minimum in \( \tilde{k}_0 = \tilde{p}^{nm}_{\alpha \beta} = 0 \)

\[ H^n = e_n(k_0) \delta_{a \beta} + \frac{\hbar^2}{2m} \delta_{a \beta} + \frac{\hbar}{m} \hat{k} \cdot \tilde{p}^{nm}_{\alpha \beta} + \sum_{m,w=1}^3 \frac{\epsilon}{m} \left( \hat{k} \cdot \tilde{p}^{nm}_{\alpha \beta} \right) \delta_{a \beta} - \epsilon_m(k_0) \]

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\[ \frac{1}{m^{nm}_{\alpha \beta}} = \delta_{a \beta} + 2 \sum_{m,w=1}^3 \frac{\epsilon}{m} \left( \hat{k} \cdot \tilde{p}^{nm}_{\alpha \beta} \right) \delta_{a \beta} - \epsilon_m(k_0) \]

k.P – Method – Band Degeneracies

Degenerated Valence Band of Cubic Semiconductors

\[ \hat{\tilde{v}} = e_n(0) \hat{I} + \frac{\hbar^2}{2m} \left[ \begin{array}{ccc} \hat{k}^2 + M(k_x^2 + k_y^2) & N_x & N_y \\ N_x & \hat{k}^2 + M(k_x^2 + k_y^2) & N_y \\ N_y & N_x & \hat{k}^2 + M(k_x^2 + k_y^2) \end{array} \right] \]

\[ \text{det}(\hat{\tilde{v}} - EI) = 0 \]

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

Pretty complicated task

SIMPLE: Find solutions along a symmetry line, e.g., \( \tilde{k} \in \{k_x, 0, 0\} \)

k.P – Method – Band Degeneracies

Degenerated Valence Band of Cubic Semiconductors

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Pretty complicated task

SIMPLE: Find solutions along a symmetry line, e.g., \( \tilde{k} \in \{k_x, 0, 0\} \)
**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.
- Bands around \( \Gamma \) point
  - Without spin
  - With spin

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

\[
\begin{align*}
- \frac{\hbar^2}{2m} + V(\mathbf{r}) + \beta \cdot \mathbf{p} + c^2 \frac{\beta \cdot (\nabla V \times \mathbf{p})}{4m^2 c^2} \mathbf{\alpha} \cdot \mathbf{\sigma} \\
\end{align*}
\]

\[\psi^e_n(\mathbf{k}, \mathbf{r}) = E_n^e(\mathbf{k}) \psi_n^e(\mathbf{k}, \mathbf{r})\]

- Four-component spinor \( \psi_n^e(\mathbf{k}, \mathbf{r})\)
- Equation for \( \phi \)

**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.
- 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
- Foldy-Wouthuysen-Transformation

\[
\psi \rightarrow \begin{pmatrix} \phi^+ \\ 0 \end{pmatrix}
\]

**Two-component spinor**

**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 \( \phi \) through an angle \( \theta \) ) transform as

\[
\begin{align*}
\Phi(\theta, \hat{\mathbf{n}}) &= \cos \frac{\theta}{2} \mathbf{n} \cdot \mathbf{\sigma} + i \sin \frac{\theta}{2} \\
\end{align*}
\]

- \( \hat{\Phi}(\theta, \hat{\mathbf{n}}) \) is unitary 2x2 matrix or representation

**Spin-orbit coupling**

- 

**Four component Periodic spinor**

**Equation for Periodic spinor**

\[
\begin{align*}
\psi^e_n(\mathbf{k}, \mathbf{r}) = \exp(\mathbf{i} \mathbf{k} \cdot \mathbf{r}) \psi_n^e(\mathbf{k}, \mathbf{r}) \\
\end{align*}
\]

- Role of spin in the band structure
- Removing of some degeneracies expected

**Pauli matrices**

- Spin operator \( \mathbf{\sigma} \) 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
- The two rotations that are not regarded as distinct in the \( \mathbf{r} \)-space are represented by different matrices!
Transformation properties of spinors

- Action of an operator in spinor space on spinor
  \[ P_R \overrightarrow{\Phi}_\mu(k, R^-) = D^{(1/2)}(R) \left( \overrightarrow{\Phi}_\mu(k, R^-)^{+} \right) \]

- Note there are twice so many operators \( P_R \) as \( R \)

- We wish to determine the behavior of an electron state that belonged to the representation \( R^{(l)} \) before the spin was considered.
- We form direct product \( R^{(l)} \otimes D^{(1/2)} \)
- The representations so obtained may be reducible as the representations of the group of operators in spinor space.
  \[ \Gamma^{(l)} \times D^{(1/2)} = \sum_{\Phi} n(\Phi) R^{(l)} \]

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

### Spin-splitting of the valence band

- **Valence band without spin-orbit interaction**
- **Representation of the ‘single’ group**
  \[ \Gamma_15 \]
- **Representation of the double group**
  \[ \Gamma_8 + \Gamma_7 \]

Spin-splitting of the valence band of cubic semiconductors

Comparison of Theory (LDA) with Experiment

- **Band structure of cubic semiconductors around the \( \Gamma \) point**
  \[ \Gamma \times D^{(1/2)} = \Gamma_8 \]

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 \( \Gamma \) point

- **Non-relativistic**
- **With relativistic effects, spin-orbit effects included**
**8 band k.p Method**

**States of group A:** \[ \{ \pm \} \]

**Conduction band**
\[ \varepsilon_x(0) = \varepsilon_{c0} \]

**Valence band**
\[ \varepsilon_y(0) = \varepsilon_{v0} \]

**8 x 8 Matrix**
\[
\begin{bmatrix}
\beta_{h4} & 0 \\
0 & \beta_{h4}
\end{bmatrix}
\]

\[ \beta_{h4}(8 \times 8) = \beta_{h4} \]

- **Commonly employed simplifications**: \[ \hat{H} = \hat{H}_{SO} + \frac{\hbar^2 k^2}{2m} + \frac{\hbar k \cdot \hat{\Pi}}{m} \]

\[ \hat{\Pi} = \hat{p} \quad \hat{H} = \frac{\hbar^2 k^2}{2m} + \frac{\hbar k \cdot \hat{\Pi}}{m} \]

\[ \hat{H} = \{ \hat{H}_{SO} + \frac{\hbar^2 k^2}{2m} + \frac{\hbar k \cdot \hat{\Pi}}{m} \} \]

- **Contains part with operators independent on spin**: \( (\hat{H}_{SO})_{ij} \)

**Main strategy of the k.p Method**

**Build unknown** \( \hat{H}_{SO}(\hat{k}, \hat{r}) \) **out of known** \( \hat{H}_{SO}(\hat{r}) \) **for wave vector**

**What to do with** \( \hat{H}_{SO} \) ?

1. **Include** \( \hat{H}_{SO} \) **into unperturbed Hamiltonian**

2. **Include** \( \hat{H}_{SO} \) **into perturbed Hamiltonian**

**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 – Spin-Orbit Terms

\[ \langle \sigma | \hat{H}_{SO} | \sigma' \rangle = 0 \quad \sigma \in \{+, -\} \quad \sigma' \in \{x, y, z\} \]

\[ \Delta = -\frac{3\hbar}{4m^2c^2} \begin{pmatrix} 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} \nabla V \times \hat{p} \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \end{pmatrix} \]

\[ \hat{H}_{SO} = -\frac{\Delta}{3} \begin{bmatrix} 0 & i & 0 & 0 & -1 & 0 & 0 & 0 \\ -i & 0 & 0 & 0 & i & 0 & 0 & 0 \\ 0 & 0 & 1 & -i & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & -i & 0 & 0 & 0 \\ 0 & 0 & i & i & 0 & 0 & 0 & 0 \\ -1 & -i & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \]

This matrix can be diagonalized easily.

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

\[ \langle J, m_J | \hat{H}_\text{SO} + \hat{H}_H | J, m_J \rangle \]

\[ \begin{align*}
\left| \frac{1}{2}, \frac{1}{2} \right> & : \frac{1}{\sqrt{2}} | x+ \rangle + i | y+ \rangle & : e_a + \frac{2\Delta}{3} \\
\left| \frac{1}{2}, -\frac{1}{2} \right> & : -\frac{1}{\sqrt{2}} | x- \rangle - i | y- \rangle & : e_a + \frac{2\Delta}{3} \\
\left| \frac{3}{2}, \frac{3}{2} \right> & : \frac{1}{\sqrt{3}} | x+ \rangle + \frac{1}{\sqrt{3}} | y+ \rangle + i | z+ \rangle & : e_a - \frac{2\Delta}{3} \\
\left| \frac{3}{2}, -\frac{1}{2} \right> & : \frac{1}{\sqrt{3}} | x+ \rangle + \frac{1}{\sqrt{3}} | y+ \rangle - i | z+ \rangle & : e_a - \frac{2\Delta}{3} \\
\left| \frac{3}{2}, \frac{1}{2} \right> & : \frac{1}{\sqrt{3}} | x+ \rangle + \frac{1}{\sqrt{3}} | y+ \rangle - i | z+ \rangle & : e_a - \frac{2\Delta}{3} \\
\left| \frac{3}{2}, -\frac{3}{2} \right> & : \frac{1}{\sqrt{3}} | x+ \rangle + \frac{1}{\sqrt{3}} | y+ \rangle + i | z+ \rangle & : e_a - \frac{2\Delta}{3} \\
\end{align*} \]

Envelope Function Theory – Effective Mass Equation

\[ \gamma_1 = -\frac{2m}{3\hbar^2}(L + 2M) - 1 \]

\[ \gamma_2 = -\frac{m}{3\hbar^2}(L - M) \]

\[ \gamma_3 = -\frac{m}{3\hbar^2}N \]

- Crystal potential hidden in the parameters of the k.p matrix
Fourier series
- Are periodic functions

\[ \psi(\vec{r}) = \sum_{n} \psi_n(\vec{r}) e^{i n \cdot \vec{k}} \]

Which external fields?
- Shallow impurities, e.g., donors
- Magnetic field \( B, \vec{B} = \text{curl} A = \vec{\nabla} \times \vec{A} \)
- Heterostructures, Quantum Wells, Quantum wires, Q. Dots

- Does equation that involves the effective mass and a slowly varying function exist?
  \[ \frac{\hat{p}^2}{2m^*} + U(\vec{r}) \Rightarrow \hat{F}(\vec{r}) = \epsilon F(\vec{r}) \]

**Envelope Function Theory**
- When \( \langle \vec{k} | U(\vec{r}) | n' \vec{k}' \rangle = 0 \) for \( n \neq n' \)
  \( u_n(\vec{r}) \) = decoupled functions
  \[ u_n(\vec{r}) \propto \sum_m B_{nm} e^{i n \cdot \vec{k}^*} \]
  Fourier series

\[ B_{nm} = \frac{1}{\Omega_k} \int d\vec{r} e^{i n \cdot \vec{k}^*} u_n(\vec{r}) u_{n'}(\vec{r}) \]

\[ \langle \vec{k} | U(\vec{r}) | n' \vec{k}' \rangle = \sum_m B_{nm} \int d\vec{r} e^{i n \cdot \vec{k}^* - i n' \cdot \vec{k}'^*} U(\vec{r}) \]

\[ U(\vec{k}) = \frac{1}{(2\pi)^3} \int d\vec{r} e^{-i \vec{k} \cdot \vec{r}} U(\vec{r}) \]

\[ \langle \vec{k} | U(\vec{r}) | n' \vec{k}' \rangle = (2\pi)^3 \sum_m B_{nm} U(\vec{k} - \vec{k}' + \vec{G}_m) \]

\[ B_{nm} = \frac{1}{\Omega_k} \int d\vec{r} e^{i n \cdot \vec{k}^*} u_n(\vec{r}) u_{n'}(\vec{r}) \]

**Envelope Function Theory – Condition for the external potential**
- For \( m \neq 0 \) \( B_{nm} = 0 \) for \( n \neq n' \)
- For \( m = 0 \) \( B_{nm} = 0 \) for \( n \neq n' \)

Orthogonality of periodic Bloch functions

\[ \langle \vec{k} | U(\vec{r}) | n' \vec{k}' \rangle = 0 \] for \( n \neq n' \)

\[ \langle \vec{k} | U(\vec{r}) | n' \vec{k}' \rangle \neq 0 \] for \( m \neq 0 \)

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

\[ \frac{U(\vec{k} - \vec{k}' + \vec{G}_m)}{U(\vec{k} - \vec{k}')} \ll 1 \Rightarrow \langle \vec{k} | U(\vec{r}) | n' \vec{k}' \rangle = U(\vec{k} - \vec{k}') \delta_{nm} \]
Envelope Function Theory – Effective Mass Equation in Momentum Space

\[ \epsilon_n(k) B_n(k) + \int_{\text{BZ}} d\tilde{k}' U(\tilde{k}' - \tilde{k}) B_n(\tilde{k}') = \epsilon B_n(\tilde{k}) \]

- Canonical transformation \( A = e^{S} B \)
- New coefficients
- Case for non-degenerate bands

\[ \epsilon_n(k) = \frac{\hbar^2}{2m} \frac{k^2}{m^2} \left( \epsilon_{n-1} + \sum_{\vec{p}, \vec{p}'} \frac{k \cdot \vec{p}_{\mu} k \cdot \vec{p}'_{\mu}}{m} B_n(k) \right) + \int_{\text{BZ}} d\tilde{k}' U(\tilde{k}' - \tilde{k}) B_n(\tilde{k}') = \epsilon B_n(\tilde{k}) \]

Effective Mass Equation in Momentum Space

Envelope Function Theory – Transformation of the effective mass equation in momentum space into \( r \)-space

\[ \epsilon_n(k) B_n(k) + \int_{\text{BZ}} d\tilde{k}' U(\tilde{k}' - \tilde{k}) B_n(\tilde{k}') = \epsilon B_n(\tilde{k}) \]

(a) \[ \int_{\text{BZ}} d\tilde{k}' \epsilon_n(\tilde{k}') B_n(\tilde{k}') = \epsilon_n f_n(\tilde{r}) + \sum_{\mu, \nu} \frac{1}{i \hbar} \frac{\partial}{\partial \mu} \left( \frac{1}{i \hbar} \frac{\partial}{\partial \nu} \right) \int_{\text{BZ}} d\tilde{k}' B_n(\tilde{k}') = \]

(b) \[ \int_{\text{BZ}} d\tilde{k}' \epsilon_n(\tilde{k}') B_n(\tilde{k}') = \int_{\text{BZ}} d\tilde{k}' U(\tilde{k}' - \tilde{k}) B_n(\tilde{k}') \]

\[ \Delta(\tilde{r} - \tilde{r}') = \frac{1}{(2\pi)^3} \int_{\text{BZ}} d\tilde{k}' \epsilon_n(\tilde{k}') B_n(\tilde{k}') \]

In the full \( k \)-space

\[ \Delta(\tilde{r} - \tilde{r}') = \delta(\tilde{r} - \tilde{r}') \]

If \( \epsilon_n(\tilde{k}) \) is smooth

\[ \int_{\text{BZ}} d\tilde{k}' \Delta(\tilde{r} - \tilde{r}') f(\tilde{r}) d\tilde{r}' = f(\tilde{r}) \]

(b) \[ \int_{\text{BZ}} d\tilde{r}' U(\tilde{r}') F_n(\tilde{r}') \Delta(\tilde{r} - \tilde{r}') = U(\tilde{r}) F_n(\tilde{r}) \]
Envelope Function Theory - Effective Mass Equation

\[ \varepsilon(-i\vec{V}) + U(\vec{r}) - \varepsilon F_n(\vec{r}) = 0 \]  

(EME)

\[ A_n(\vec{k}) = B_n(\vec{k}) \quad \psi(\vec{r}) = \sum_n \int d\vec{k} B_n(\vec{k}) e^{i\vec{k} \cdot \vec{r}} u_n(\vec{r}) = \sum_n F_n(\vec{r}) u_n(\vec{r}) \]

EME does not couple different bands

\[ \psi(\vec{r}) = F_n(\vec{r}) u_n(\vec{r}) \]

"True" wavefunction

Envelope Function

Periodic Bloch Function

- Special case of constant (or zero) external potential
  \[ U(\vec{r}) = 0 \Rightarrow F_n(\vec{r}) = \exp(\vec{i} \vec{k} \cdot \vec{r}) \Rightarrow \psi(\vec{r}) \quad \text{Bloch function} \]
- \[ U(z) \Rightarrow F_n(\vec{r}) = \exp[i(k_x x + k_y y)]F_n(z) \]

Envelope Function Theory - Effective Mass Equation

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

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

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

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

Envelop Function Theory - Applications

- **a)** Magnetic field
  - Minimal coupling principle for full Hamiltonian \( \hat{\mathbf{p}} \rightarrow \hat{\mathbf{p}} - \frac{e}{c} \mathbf{A}(\vec{r}) \)
  - In effective Hamiltonian \( \hat{\mathbf{p}} \rightarrow -i\nabla - \frac{e}{c} \mathbf{A}(\vec{r}) \)
  - Non-degenerate case - conduction band electrons
    \[ [\varepsilon(-i\nabla - \frac{e}{c} \mathbf{A}(\vec{r})) - \varepsilon] F_n(\vec{r}) = 0 \quad \text{Landau levels} \]
  - Degenerate case of valence band
    \[ \sum_{b=1}^{s} [D_{ab}^{(2)} (-i\nabla_{\mu} - \frac{e}{c} \mathbf{A}_{\mu}(\vec{r})) (-i\nabla_{\nu} - \frac{e}{c} \mathbf{A}_{\nu}(\vec{r}))] F_b(\vec{r}) = \varepsilon F_a(\vec{r}) \]

- **b)** Donors in semiconductors
- **c)** Low dimensional semiconductor structures

Thank you!