1. Basic characteristics of semiconductors

Key ideas	General Properties
A *semiconductor* is neither a good insulator nor a very good conductor of electric current.	1.1 Qualitative properties
The *electrical resistivity* of semiconductor generally decreases strongly with increasing temperature, whereas the resistivity of a metal generally increases weakly with increasing temperature.	
A semiconductor can be an *element*, such as Si or Ge, or a *compound*, such as GaAs or InSb.	1.2 Composition of semiconductors
Solid semiconductors can exist in the *crystalline* or *amorphous* form.	1.3 Structure of solids
A *lattice* is a periodic array of points in space.	
A *basis* is a set of atoms associated with each *lattice point*.	
Semiconductors can crystallize in the *diamond, zincblende, wurtzite*, or other *structures*.	
The *bonding* between atoms in a semiconductor can be *covalent, ionic*, or *mixed*.	1.4 Chemical bonding in semiconductors
Layered semiconductors can *intercalate* foreign atoms or molecules.	
Very pure semiconductors can be produced by the *zone refining method*.	1.5 Growth of pure semiconductor crystals

Something about the history:

    1833 M. Faraday: For AgS decreasing ρ with increasing T

    1873 W. Smith: Photoconductivity of Se

    1874 F. Braun: Rectifying properties of PbS

    1948 Bardeen & Brattain: Bipolar transistor

1.1. Qualitative properties

Bands:
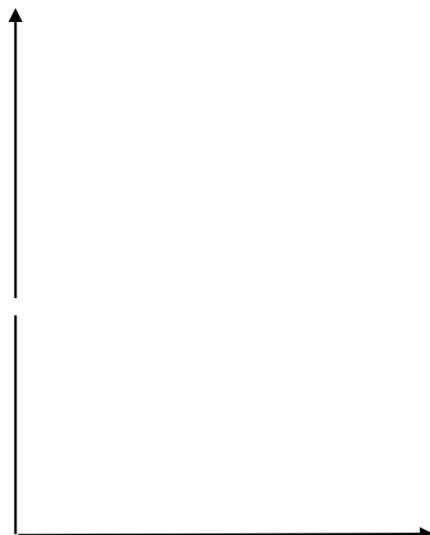
1.2. Composition of semiconductors

The most usual semiconductors are the elemental ones, Si and Ge (and diamond C). They are tetrahedrally bonded, and thus, four-fold coordinated with sp^3-hybridization.

Semiconductors are typically:
- stoichiometric:
    elemental, binary, tertiary, quaternary, ...
- crystalline
- small band gap materials
            $\Rightarrow$ semiconducting
- covalently bonded (mainly)

There are also semiconducting organic, magnetic and ferroelectric materials. Some high–T_c superconductors are semiconducting in N-state.

Periodic Table of "Semiconductor-Forming" Elements

- Elements which crystallize as Semiconductors
- Elements forming Binary III-V Semiconductors
- Elements forming Binary III-VI Semiconductors
- Elements forming Binary II-VI Semiconductors
- Elements forming Binary I-VII Semiconductors
- Elements forming Binary IV-VI Semiconductors
- Elements forming I-III-VI$_2$ Chalcopyrite Semiconductors
- Elements forming II-VI-V$_2$ Chalcopyrite Semiconductors

1.3. Structure of solids

1.3.1. Crystalline and amorphous forms

Classification by internal structure and order
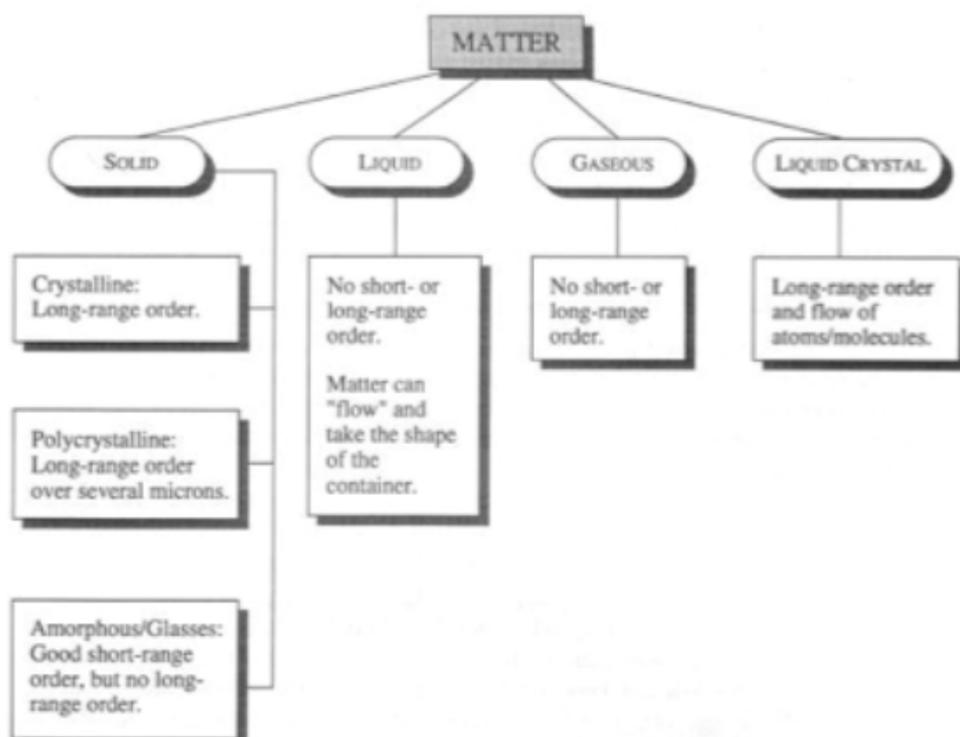
1.3.2. Lattice and basis

The lattice points are

$$\mathbf{R}(l_1, l_2, l_3) = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3 \qquad (1.1)$$

where $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ are the *primitive (translation or lattice) vectors,* and l_1, l_2 and l_3 take all integer values. Thus, In 3D we have three *primitive lattice vectors* (alkeistranslaatiovektori eli perusvektori), which *span* (virittää) the *lattice* (hila). For the specific lattice (set of points in space) the choice of primitive lattice vectors is not unique.

r = 0a + 2b + 1c
[021]

Real space
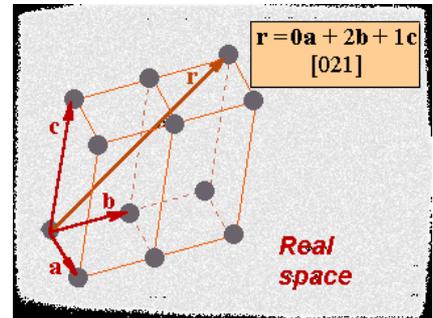
The *crystal structure* (kiderakenne) is formed by adding an atom or an identical set of atoms, the *basis* (kanta), to each lattice point.

• Lattice and basis   -->   *crystal structure*

The *coordination polyhedron* (koordi-naatiokoppi) is defined or confined around a lattice point by planes perpendicularly bisecting the nearest neighbor distances. This polyhedron is called the *Wigner–Seitz cell.*

rhombic dodecahedron   truncated octahedron
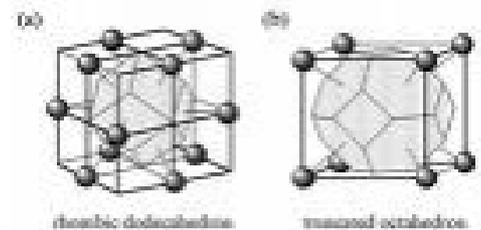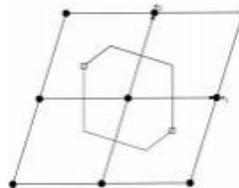
1.3.3. Bravais lattices

There are 14 possible lattices in the three dimensional space. These are called *Bravais lattices.*

The Bravais lattices can be grouped to 7 *crystal systems* (kidejärjestelmä), which is the most fundamental classification of crystal structures.

In the cubic system, the cube spanned by vectors $(a, 0, 0)$, $(0, a, 0)$ and $(0, 0, a)$ is called the crystallographic *unit cell* (yksikkökoppi) and a is the *lattice constant* (hilava-kio).

CUBIC
$a = b = c$
$\alpha = \beta = \gamma = 90°$

TETRAGONAL
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$

ORTHORHOMBIC
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$

HEXAGONAL
$a = b \neq c$
$\alpha = \beta = 90°$
$\gamma = 120°$

TRIGONAL
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$

MONOCLINIC
$a \neq b \neq c$
$\alpha = \gamma = 90°$
$\beta \neq 120°$

TRICLINIC
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$

4 Types of Unit Cell
P = Primitive
I = Body-Centred
F = Face-Centred
C = Side-Centred

7 Crystal Classes
→ **14 Bravais Lattices**

1.3.4. Crystallographic terminology

• Directions
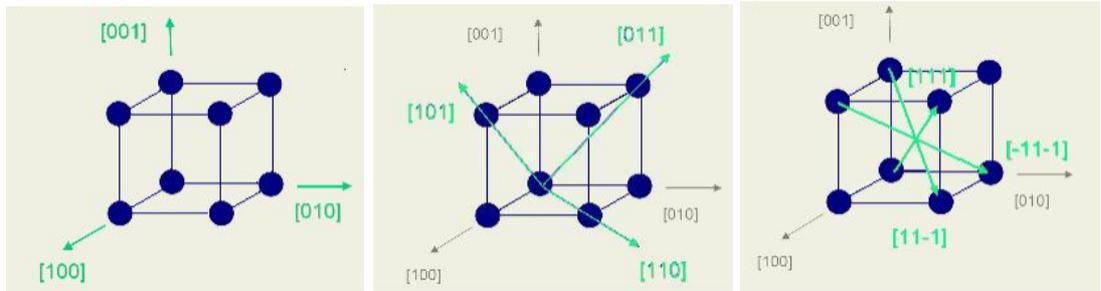
• Planes
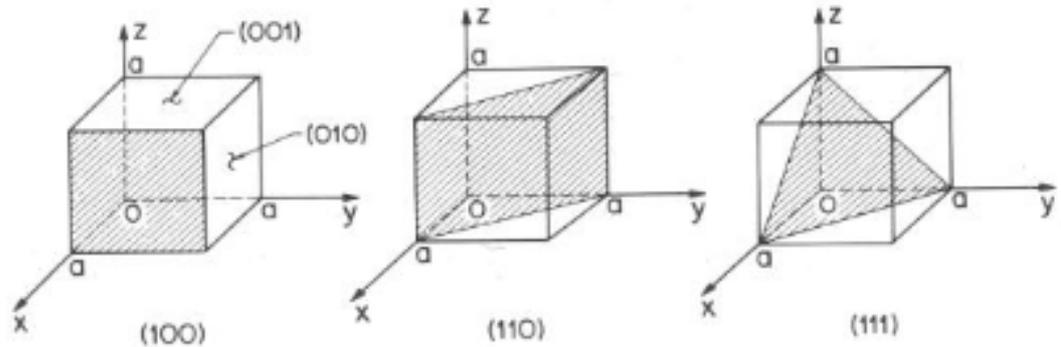
1.3.5. Structures of semiconductors

The *face-centered cubic* (fcc, pintakeskinen kuutiol-linen, pkk) lattice is spanned by primitive vectors

$$\mathbf{a}_1 = (0, a/2, a/2)$$
$$\mathbf{a}_2 = (a/2, 0, a/2)$$
$$\mathbf{a}_3 = (a/2, a/2, 0).$$

See the "periodic table" on p. 3 above.

• Elemental compounds:
The *diamond structure* (timanttirakenne) of carbon, silicon and germanium is obtained from fcc with a basis of two atoms at $(0, 0, 0)$ and $(a/4, a/4, a/4)$. Thus, the diamond structure consists of two interpenetrating fcc structures with equal nearest neighbor distances. It has eight atoms per unit cell, whereas fcc has four, see figure 2.2.

• III–V compounds:
The *zinc-blende structure* or *wurtzite structure.*
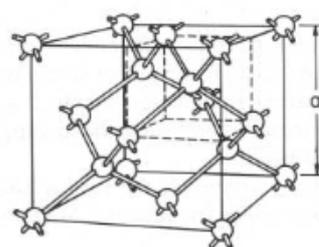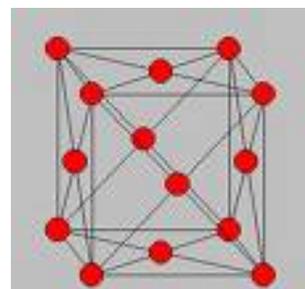
DIAMOND
(C, Ge, Si, etc)
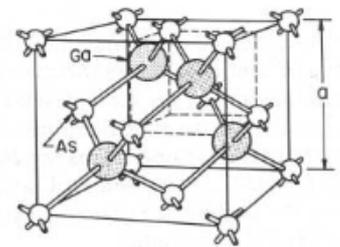
ZINCBLENDE
(GaAs, GaP, etc)
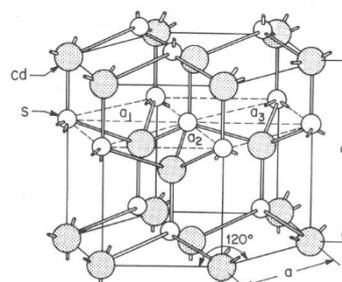
• III–V compounds:

The *zinc-blende structure* (sinkkivälke- eli sfaleriittirakenne) of the most of III–V compound semiconductors occupies the same sites as the diamond structure, but with two atoms of different elements (i.e. 2 x FCC), e.g. Ga and As.

or

     wurzite structure: ionicity in bonding ⇒ increase of band gap

• II–VI compounds:
  - zinc blende structure:
    or
    wurzite structure:
  - strong ionicity in bonding ⇒ large band gap (> 1 eV)

• I–VII compounds, e.g.,

• IV–VI compounds, e.g., PbS, PbSe and PbTe appear in rock salt structure
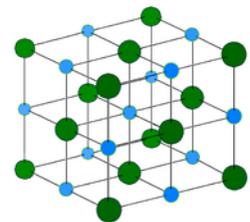
Tertiary compounds from mixing the binaries ...

• Oxides:

Oxide semiconductors are, e.g., CuO, Cu_2O and some high–T_c superconductors in N-state. Band gap of La_2CuO_4, for example, is about 2 eV. Complex crystal structures.

1.4. Chemical bonding in semiconductors

1.4.1. Diamond structure semiconductors

The electronic configuration of Si atom is $1s^2\,2s^2\,2p^6\,3s^2\,3p^2$. In solid crystal the core electrons are atomic-like but the valence electrons hybridize to

$h_1 = s + p_x + p_y + p_z,$

$h_2 = s + p_x - p_y - p_z,$

$h_3 = s - p_x + p_y - p_z,$

$h_4 = s - p_x - p_y + p_z$
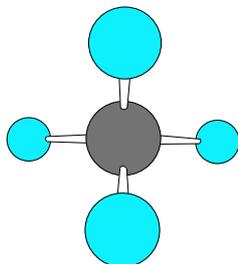
to form tetrahedrally oriented bonding. The bond angles are $\arccos(-1/3) \approx 109.47°$. This transforms the configuration $3s^2\,3p^2$ to $3s\,3p^3$. This is called sp³ *hybridization.*

Methane molecule CH_4 has the same tetra-hedrally oriented bonding as the diamond and zinc-blende structures.

120   **s–p bonding—a case study in silicon**
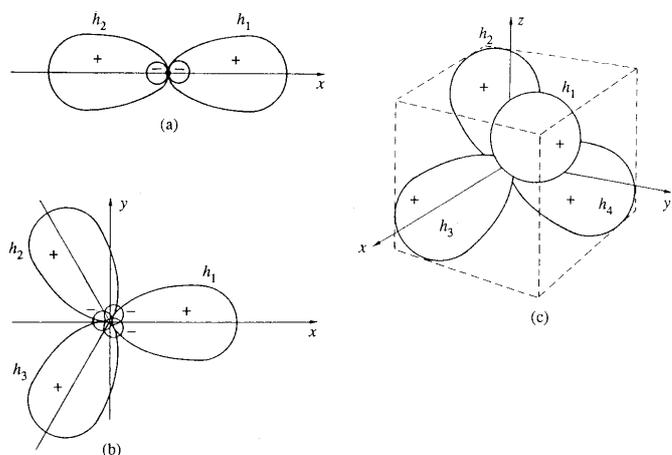
Fig. 6.7 Principal types of s–p hybridization: (a) sp hybrids pointing in opposite directions along the same axis, (b) sp² hybrids at 120° to each other in a plane, (c) sp³ hybrids at $\cos^{-1}(1/3) \approx 109°$ to each other, pointing towards the corners of a tetrahedron. From McWeeny (1979).

Relative spacing of atoms ⟶

Relative energy of electrons ⟶

4N States
0 Electrons

6N States
2N Electrons

6N States
2N Electrons

Band gap $= E_g$

4N States
4N Electrons

2N States
2N Electrons

Actual spacing

2N States
2N Electrons

8N States
4N Electrons

s	m	l	n	
$\pm(\tfrac{1}{2})$	+2			
$\pm(\tfrac{1}{2})$	+1			
$\pm(\tfrac{1}{2})$	0	2		
$\pm(\tfrac{1}{2})$	−1			
$\pm(\tfrac{1}{2})$	−2			
$\pm(\tfrac{1}{2})$	+1			
$\pm(\tfrac{1}{2})$	0	1	3	Outer shell
$\pm(\tfrac{1}{2})$	−1			
$\pm(\tfrac{1}{2})$	0	0		
$\pm(\tfrac{1}{2})$	+1			
$\pm(\tfrac{1}{2})$	0	1	2	
$\pm(\tfrac{1}{2})$	−1			
$\pm(\tfrac{1}{2})$	0	0		Middle shell
$\pm(\tfrac{1}{2})$	0	0	1	Inner shell
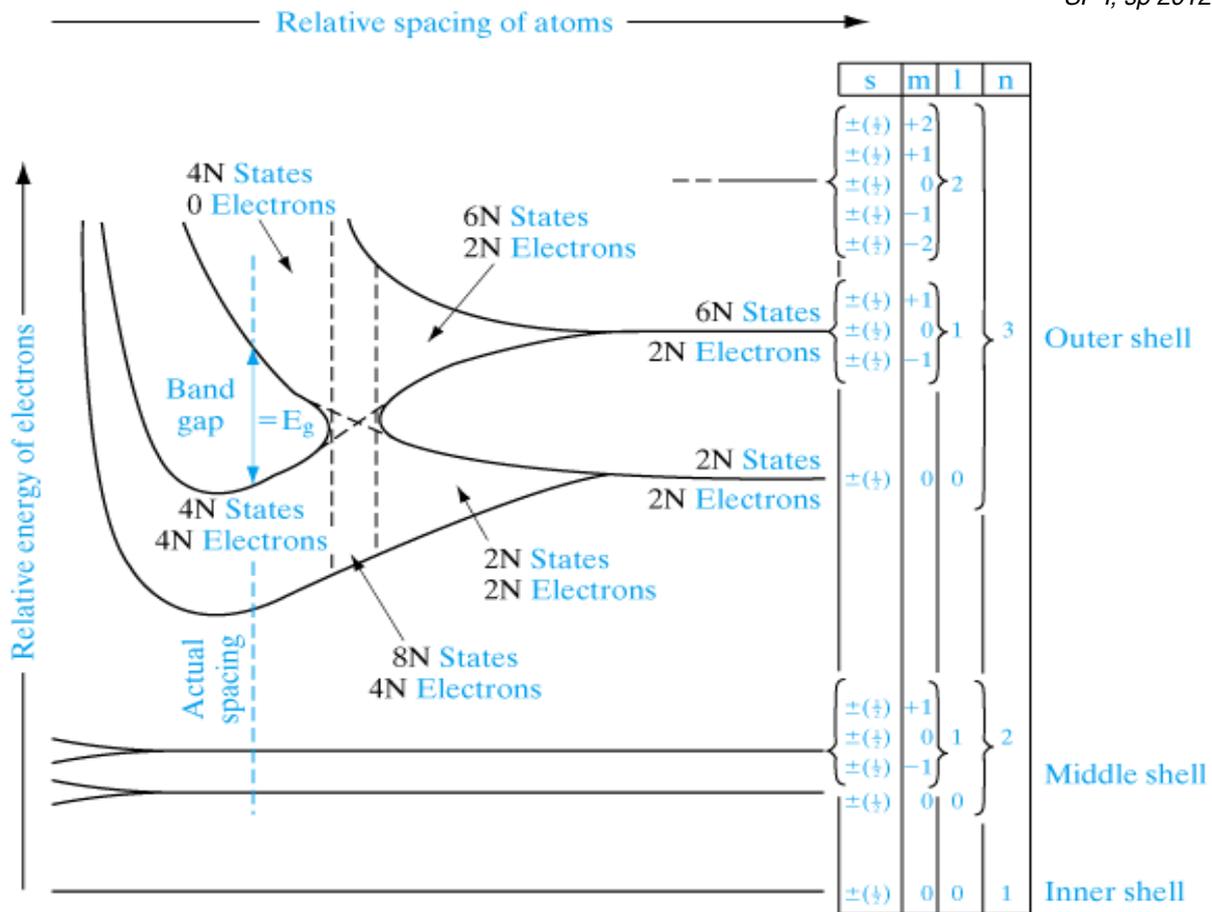
1.4.2. Zincblende structure semiconductors

Bonding in zincblende structure is basically covalent like in diamond structure, but due to difference in number of participating valence electrons, zincblende structure always includes some ionic nature;

e.g. Ga: $[Ar]3d^{10}4s^24p$ and As: $[Ar]3d^{10}4s^24p^3$ hybridize to

Ga: $[Ar]3d^{10}h_1h_2h_3h_4$ and As: $[Ar]3d^{10}h_1h_2h_3h_4$ in bonding to GaAs.

In more details, one particular "molecular orbital" can be written in "valence bond" formalism as

$$\psi = \varphi_A + \lambda\,\varphi_B = h_A + \lambda\,h_B, \tag{1.9}$$

where A and B refer to the atoms and λ is a parameter describing the charge transfer. Now, as two electrons occupy the orbital, the total wavefunction (without normalization) is

$$\Psi = \psi(1)\,\psi(2) = \tag{1.10–11}$$

For a compound semiconductor $B^{8-N}A^N$ the effective charge(transfer) can be written as

$$Q_A = e \, [(N \lambda^2 - (8-N))] / [1+\lambda^2] = -Q_B, \tag{1.12}$$

where e is the electron charge.

Table 1.6. Effective charges and ionicity parameters

Q/e	λ		
0	1		(IV, $N=4$)
0.43–0.49	0.68	BA, where B = Ga, Al, In; A = As, Sb, P	(III-V, $N=5$)
0.45–0.49	0.48–0.49	BA, where B = Zn, Cd; A = S, Se, Te	(II-VI, $N=6$)

1.4.3. Layered semiconductors

In layered III–VI compounds like InSe, each In atom is bonded to three nearest neighbor Se atoms in the same layer and to one In atom perpendicular to the layer.

PbI_2 and MoS_2, for example, form layered semiconductors, whose bonding within layers is covalent, but between layers origins from the van der Waals forces. This implies 2D charge carrier structures.

1.4.4. Wurtzite structure semiconductors

Many II-VI compounds like ZnS occur in both the wurtzite and zincblende structures. CdS takes primarily the wurtzite structure.

1.4.5. Other semiconductors

Organic semiconductors
Semiconductor like properties are also found in "organic compounds" like polydiacetylene $(CH_2)_n$ with conjugate carbon chains, fullerenes, nanotubes, BN nanotubes, etc. Organic molecules can easily be tailored at the molecular level and "tuned" for applications.

However, these are not used too much, yet, but they seem promising materials for nonlinear optics (NLO), for example.

Magnetic Semiconductors
Strong magnetooptical effect allows the material to be used in optical modulators. Their *Faraday rotation* can be up to six orders of magnitude higher than that of nonmagnetic semi-conductors. Magnetic field can also be used to cause the *metal to semiconductor transition,* a phenomenon also called *colossal magnetoresistance.*

Other ...
• ferroelectric
• complex inorganic materials ... for NLO
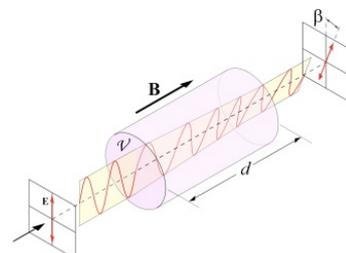
1.5. Growth of pure semiconductor crystals

Semiconductors can be grown as single crystals with high quality (dislocation densities as low as 1000 cm^{-3}) and high purity (impurity concentrations less than 1:10^{12}).

Czochralski Method
Czochralski method is for growing bulk single crystal (erilliskide) ingots (tanko). Typical growth speed is a few mm/min.

Liquid-Encapsulated Czochralski (LEC) method is used for volatile compounds.

Silicon is usually grown in [100] direction.

Bridgman Method
Bridgman method involves use of the controled temperature gradient in Czochralski growth.

The ingots (of diameter up to 30 cm) grown by the above methods are then mechanically sliced to wafers (kiekko) of submillimeter thickness. These wafers are then the substrates for the high quality epitaxial growth.

Homoepitaxy, e.g.

Heteroepitaxy, e.g.

(a)
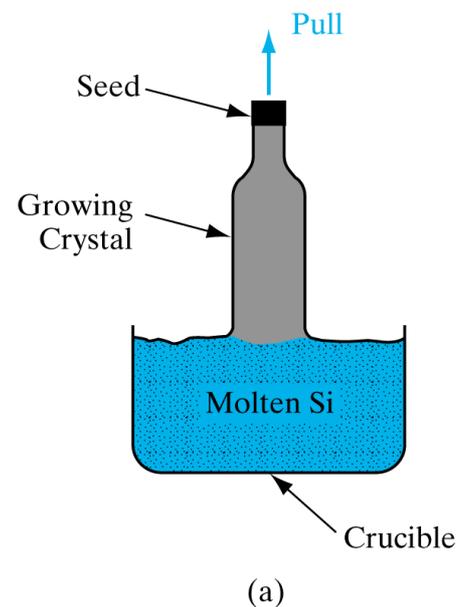
Epitaxy:

The two basic techniques are Molecular Beam Epitaxy (MBE) and Metallo-Organic Chemical Vapor Deposition (MOCVD). These allow a monolayer by monolayer growth, and thus, design and fabrication of atomic level artificial structures, such as, superlattices (superhila) and quantum wells (QW, kvanttikaivo).

Strain-induced self-organization may also be used to grow nanostructures.
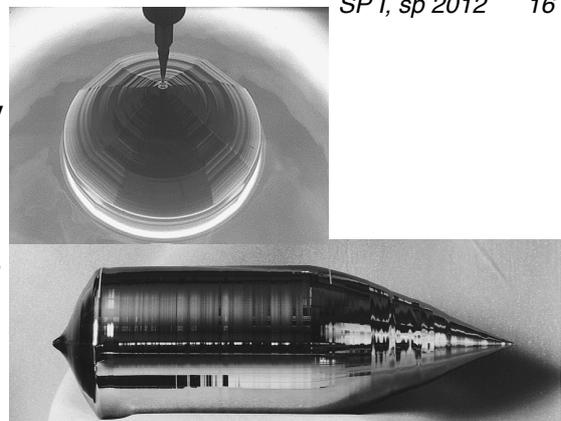
Chemical Vapor Deposition (CVD)

A suitable chemical reaction is used to deposit solid semiconductor onto the substrate.

For Si, e.g.: $SiH_4 \rightarrow Si + 2 H_2$
and dopands:
from phosphine $2 PH_3 \rightarrow 2 P + 3 H_3$
from arsine $2 AsH_3 \rightarrow 2 As + 3 H_3$

For GaAs: $Ga(CH_3)_3 + AsH_3 \rightarrow GaAs + 3CH_4$
at about 700 °C. This is MOCVD.
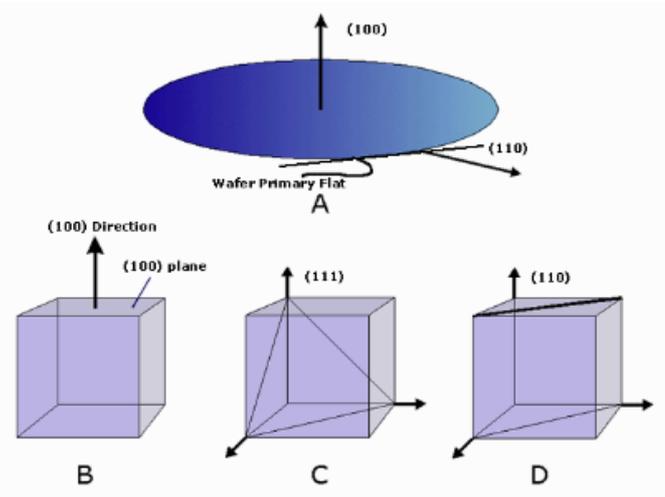
Molecular Beam Epitaxy (MBE)

MBE is accopmlished in Ultra High Vacuum (UHV, $< 10^{-11}$ torr $\approx 10^{-14}$ Pa) with ballistic molecular beams from effusion (or Knudsen) cells. This is the epitaxial technique used at the Optoelectronics Research Centre (ORC) at Tampere Univ. of Tech.

Reflection High-Energy Electron Diffraction (RHEED) is used to monitor the growth "online".
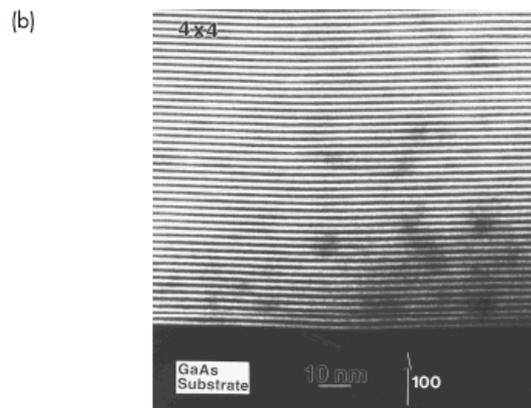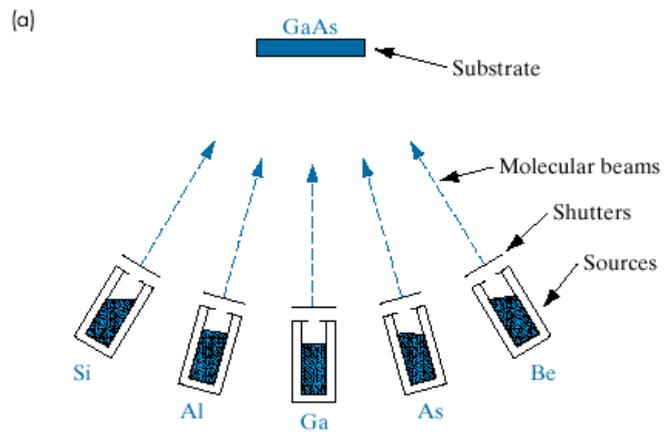
Liquid Phase Epitaxy (LPE)

LPE is an inexpensive technique for lower quality growth.

Growth of Self-Organized Quantum Dots

The three basic growth modes are:

  (1) monolayer or 2D growth

  (2) Volmer–Weber mode

  (3) Stranski–Krastanov mode

One important factor controling the growth mode is the *lattice match* (hilasovitus) or *lattice mismatch.*

Lattice mismatch causes misfit dislocations in layers thicker than the critical thickness (kriittinen paksuus) in otherwise possibly pseudomorphic growth.
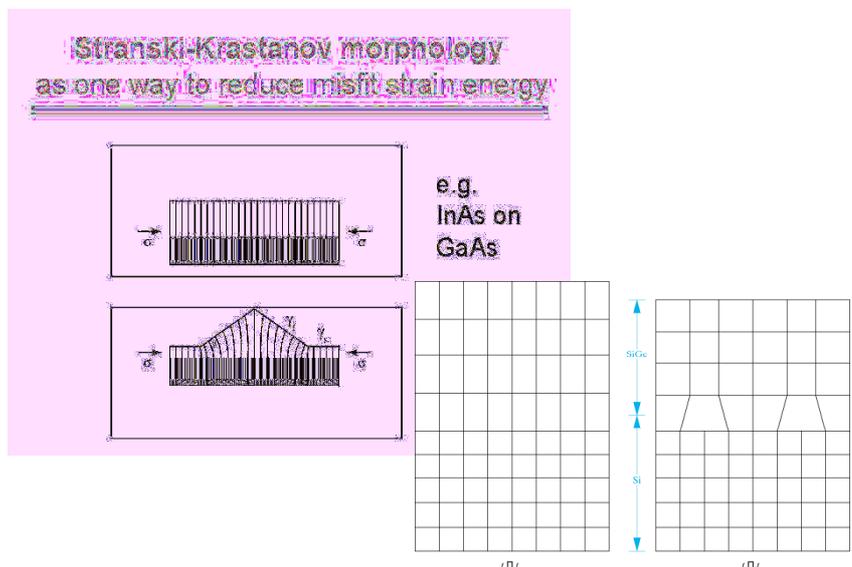
2. Electronic energy bands: basic theory

Key ideas

The eigenstates of an electron moving in the periodic potential of a crystal are *Bloch states* whose energy eigenvalues can only take certain allowed values lying in *energy bands*.

Electrons move as if the ions are instantaneously at rest.

The Fourier expansion of a *periodic potential* involves sums over wave vectors called *reciprocal lattice vectors*.

The electronic eigenstates are determined by solving the *Schrödinger equation* for a periodic potential.

The *density of electronic states* in k-space for crystal volume Ω is

$$g(k) = \frac{\Omega}{(2\pi)^3}.$$

Each eigenfunction of an electron moving in a periodic potential consists of a *plane wave factor* and a *periodic function factor*.

A weak periodic potential perturbation leads to strong scattering of electrons with wave vectors k satisfying the *Bragg condition* $k \cdot \left|\frac{G}{2}\right| = \left|\frac{G}{2}\right|^2$ where G is a reciprocal lattice vector.

The planes which bisect the reciprocal lattice vectors G, the Bragg planes, enclose spaces called *Brillouin zones*.

Bands and gaps

2.1 Schrödinger equation

2.2 Electrons in a periodic potential

2.3 Schrödinger equation for a periodic potential

2.4 Expansion of the eigenfunction in plane waves

2.5 Bloch's theorem

2.6 Electrons in a weak periodic potential

2.7 Brillouin zones

The degeneracy of the zero order states $|k\rangle$ and $|k - G\rangle$ at the Brillouin zone boundary is lifted in degenerate perturbation theory. The perturbed energies E_k are split at the Brillouin zone boundary by an amount $2|V_G|$, leading to a discontinuity or *gap* in E_k which separates two *energy bands*. In the *reduced zone scheme*, all of the energy bands can be represented within the range of wave vectors in the first Brillouin zone.

When the electron–ion interaction is strong, the *tight binding* or *LCAO method* provides the electron wave functions as series of functions localized about the nuclei. The localized functions can be represented by *Wannier functions* or by *atomic orbitals*.

2.8 Energy bands and energy band gaps

2.9 Tight binding method

The concept of *electronic structure* (elektronirakenne) of material (or a specified object) covers all aspects of the quantum state of the many-electron system: distribution of electrons in space wrt crystal lattice and atoms, distribution of electrons in energy *(density-of-states),* possible spin-density and all other related quantities.

The most complete description is given by the many-electron wavefunction, of course, which is however, not directly obtainable for the almost infinite number of electrons of a crystal. For solids the *one-electron picture* (yksi-elektronikuva) is invoked, and for periodic crystals the most important concept is the *electronic band structure,* BS (elektronien kaistarakenne eli vyörakenne).

The band structure is a classification of the one-electron energies by their symmetry, i.e. the *wave vector* (aaltovektori) k of the reciprocal space, and band index. The tool to work rigorously with translational, rotational and other symmetries is *group theory* (ryhmäteoria). It gives the rules and algorithms to calculate and label the electronic states. Here, however, we do not go to such details.

It is worth of emphasizing that the electronic structure of matter provides all the information for evaluation (at least in principle) of all the essential properties of matter (except for mass density). Thus, mechanical, thermal, electric, magnetic and optical properties relate mostly or exclusively to the states and dynamics of electrons.

Except for a few cases the electrons have to be dealt with by using *quantum mechanics,* QM, i.e. they should be solved fom the *Schrödinger equation,* S-eq. This is true for the stationary states, in particular. Approaches starting from and using only nuclear charges, QM and *Pauli principle* are called *ab initio* or first-principles methods. Those approaches who simplify the formalism by using empirical knowledge of experimental data to fit some properties to the observed ones are called *semiempirical methods.*

2.1. Schrödinger equation

The Schrödinger equation for n electrons and N ions of a crystal, omitting spin–orbit interaction and other relativistic effects, is written as

$$\left[-\sum_{i=1}^{n} \frac{\hbar^2}{2m} \nabla_i^2 - \sum_{k=1}^{N} \frac{\hbar^2}{2M_k} \nabla_k^2 + \frac{1}{4\pi\varepsilon_0} \sum_{i<j=1}^{n} \frac{e^2}{r_{ij}} + V_{ii}(\mathbf{R}) + V_{ei}(\mathbf{r},\mathbf{R}) \right] \Psi(\mathbf{r},\mathbf{R}) = E\Psi(\mathbf{r},\mathbf{R}), \qquad (2.1)$$

where Ψ is the total wavefunction, $\mathbf{R} = \{\mathbf{R}_1,...,\mathbf{R}_N\}$, $\mathbf{r} = \{\mathbf{r}_1,...,\mathbf{r}_n\}$ and the potentials are

$$V_{ii}(\mathbf{R}) = \frac{1}{4\pi\varepsilon_0} \sum_{k<l=1}^{N} \frac{Z_k Z_l e^2}{R_{kl}} \qquad \text{and} \qquad V_{ei}(\mathbf{r},\mathbf{R}) = -\frac{1}{4\pi\varepsilon_0} \sum_{i,k=1}^{n,N} \frac{Z_k e^2}{r_{ik}}$$

Other notations should be obvious.

Heading for the *adiabatic approximation* or *Born–Oppenheimer approximation* we approximate the total wavefunction as

$$\Psi(\mathbf{r},\mathbf{R}) = \psi(\mathbf{r},\mathbf{R}) \, \varphi(\mathbf{R}), \qquad (2.2)$$

where $\psi(\mathbf{r},\mathbf{R})$ is the *electronic eigenfunction* and $\varphi(\mathbf{R})$ stands for that of the nuclei.

We first consider the electronic eigenfunction $\psi(\mathbf{r},\mathbf{R})$ by assuming the nuclear coordinates $\mathbf{R} = \{\mathbf{R}_1,...,\mathbf{R}_N\}$ as parameters describing the positions of "classical mass points". This is the Born–Oppenheimer approximation.

Thus, we write the *electronic Schrödinger equation*

$$\left[-\sum_{i=1}^{n} \frac{\hbar^2}{2m}\nabla_i^2 + \frac{1}{4\pi\varepsilon_0}\sum_{i<j=1}^{n}\frac{e^2}{r_{ij}} + V_{ei}(\mathbf{r},\mathbf{R}) \right]\psi(\mathbf{r},\mathbf{R}) = E_e(\mathbf{R})\psi(\mathbf{r},\mathbf{R}), \tag{2.3}$$

where the electronic energy $E(\mathbf{R})$ is a function of nuclear coordinates.

The equation for nuclei is

$$\left[-\sum_{k=1}^{N}\frac{h^2}{2M_k}\nabla_k^2 + \Phi(\mathbf{R}) \right]\varphi(\mathbf{R}) = E\varphi(\mathbf{R}), \tag{2.4}$$

where $\Phi(\mathbf{R}) = E_e(\mathbf{R}) + V_{ii}(\mathbf{R})$ is the effective potential for nuclei. Often, it is called the *potential energy hypersurface* (PES) of atoms.

Finally, we can find the neglected terms. By substitution of (2.2) to (2.1) we obtain the Eqs. (2.3) and (2.4), and see that we have omitted terms called the *nonadiabatic coupling* of electron–ion dynamics

$$-\sum_{k=1}^{N}\frac{h^2}{2M_k}\left[\varphi(\mathbf{R})\nabla_k^2\psi(\mathbf{r},\mathbf{R}) - \nabla_k\varphi(\mathbf{R})\cdot\nabla_k\psi(\mathbf{r},\mathbf{R}) \right].$$

Next we consider the electronic Eq. (2.3) assuming the potential $V_{ei}(\mathbf{r},\mathbf{R}_0)$ to be strictly periodic and give the electrons the conventional crystal environment to dwell.

2.2. Electrons in a periodic potential

Let $\mathbf{R}_0 = \{\mathbf{R}_{01},...,\mathbf{R}_{0N}\}$ be the strictly periodic crystal lattice and denote

$$V(\mathbf{r}) = V(\mathbf{r}+\mathbf{R}(l)) = V_{ei}(\mathbf{r},\mathbf{R}_0) \tag{2.5}$$

where $\mathbf{R}(l) = \mathbf{R}(l_1,l_2,l_3)$ is any lattice vector in Eq. (1.1). Thus, $V(\mathbf{r})$ is periodic and can be expanded in a Fourier series

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \tag{2.6}$$

where $\mathbf{G}$ runs through the reciprocal lattice vectors:

Thus, the reciprocal lattice vectors are

$$\mathbf{G} \ = \ n_1 \, \mathbf{b}_1 + \ n_2 \, \mathbf{b}_2 + \ n_3 \, \mathbf{b}_3, \tag{2.12}$$

where

$$\mathbf{b}_i = \frac{2\pi}{\Omega_0} \mathbf{a}_j \times \mathbf{a}_k \tag{2.13}$$

i, j, k are permutations of $1, 2, 3$; and Ω_0 is the volume of the primitive cell given by the Eq. (1.2).

The vectors $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$ are the primitive translation vectors of the *reciprocal space.*

Finally, we note that

$$\mathbf{a}_i \cdot \mathbf{b}_j \ = 2\pi \, \delta_{ij} \ ; \quad i,j = 1, 2, 3, \tag{2.14}$$

and

$$V_{\mathbf{G}} = \frac{1}{\Omega_0} \int_{cell} V(\mathbf{r}) e^{i\mathbf{G} \cdot \mathbf{r}} d^3 r \tag{2.15}$$

and

$$\Omega_r = \frac{(2\pi)^3}{\Omega_0} \ .$$

2.3. Starting from free electrons ...

The quantum nature of electrons in a crystal can immediately be seen from their *de Broglie wavelength* $\lambda = h/p$, which thus relates to the energy as

$$E \ = \ p^2 / 2m \ = h^2 / 2m\lambda^2. \tag{2.16}$$

Now, with typical (conduction)electron energies, a few eV, the wavelength is the order of lattice constant or interatomic spacing leading to the interference phenomena.

To go to quantum description of electrons, $p \longmapsto -i\hbar\nabla$, and Eq. (2.3) above results. For free electrons with the constant potential

$$H \ \longmapsto \ H_0 \ = \ -\hbar^2 \nabla^2 / 2m \tag{2.19}$$

and solutions are planewaves

$$\psi(\mathbf{r}) \ \longmapsto \ \chi(\mathbf{r}) \ = \ e^{i\mathbf{k} \cdot \mathbf{r}}, \tag{2.21}$$

and energy is the "square parabola"

$$E_0(k) \ = \ \hbar^2 k^2 / 2m. \tag{2.16}$$

The planewaves serve as a good basis set for solutions in the periodic potential.

2.4. ... and with periodic potential: plane wave expansion

Let us use the trial expansion (plane waves) $\psi(\mathbf{r}) \ = \ \Sigma_{\mathbf{k}} \, C(\mathbf{k}) \, e^{i\mathbf{k}\cdot\mathbf{r}}$ (2.31)

and $H = H_0 + V$

$$= -\frac{\hbar^2}{2m}\nabla^2 + \sum_G V_G \, e^{iG\cdot r}$$

Now, substitute to $H\psi = E\psi$.

$$\frac{\hbar^2 k^2}{2m} C(\mathbf{k}) + \sum_G V_G C(\mathbf{k} - \mathbf{G}) - E \, C(\mathbf{k}) = 0 \qquad (2.35)$$

2.5. Bloch's theorem

The secular equations (2.35) couple the $\mathbf{k}$ vector to the others of the form $\mathbf{k} - \mathbf{G}$, only. Thus, these are the only $\mathbf{k}$ vectors we have for a certain wavefunction. The coefficients for other, say $\mathbf{k}'$, are independent. Therefore, we can now rewrite the Eq. (2.31) $\psi(\mathbf{r}) \ = \ \Sigma_{\mathbf{k}} \, C(\mathbf{k}) \, e^{i\mathbf{k}\cdot\mathbf{r}}$ in form

$$\psi_{\mathbf{k}}(\mathbf{r}) \ = \ \Sigma_{\mathbf{G}} \, C(\mathbf{k}{-}\mathbf{G}) \, e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}}. \qquad (2.36a)$$

This means that we have the one-electron eigenstates, wavefunctions and energies for each $\mathbf{k}$, independently.

Furthermore, we can write the above as

$$\psi_{\mathbf{k}}(\mathbf{r}) \ = \ [\, \Sigma_{\mathbf{G}} \, C(\mathbf{k}{-}\mathbf{G}) \, e^{-i\mathbf{G}\cdot\mathbf{r}} \,] \ e^{i\mathbf{k}\cdot\mathbf{r}} \qquad (2.36b)$$

and

$$\psi_{\mathbf{k}}(\mathbf{r}) \ = \ u_{\mathbf{k}}(\mathbf{r}) \, e^{i\mathbf{k}\cdot\mathbf{r}}. \qquad (2.37{-}2.38)$$

Note, that $u_{\mathbf{k}}(\mathbf{r})$ is periodic with the periodicity of the lattice. Thus, the $\mathbf{k}$ vectors label one-electron wavefunctions and the Bloch's theorem states that the form of the one-electron wavefunction is a plane wave modulated by the periodic prefactor $u_{\mathbf{k}}(\mathbf{r})$.

2.6. Electrons in a weak periodic potential

Let us treat the potential as weak perturbation using perturbtion theory. As 0th order solution we have the free electrons from (2.16) and (2.21)

$$|\mathbf{k}\rangle = e^{i\mathbf{k}\cdot\mathbf{r}} \qquad (2.39)$$

$$E_0(k) = \hbar^2 k^2 / 2m \qquad (2.40)$$

For the second order we get

$$E_k = E_k^{(0)} + \langle \mathbf{k}|V|\mathbf{k}\rangle + \sum_{k'} \frac{\langle \mathbf{k}|V|\mathbf{k'}\rangle\langle \mathbf{k'}|V|\mathbf{k}\rangle}{E_k^{(0)} - E_{k'}^{(0)}} \qquad (2.41)$$

$$(2.47)$$

$$E_k = E_k^{(0)} + V_0 + \sum_G \frac{|V_G|^2}{E_k^{(0)} - E_{k-G}^{(0)}}$$

Similarly,

$$\psi_k(\mathbf{r}) = \frac{1}{\sqrt{\Omega}}\left\{1 + \sum_G \frac{V_G *}{E_k^{(0)} - E_{k-G}^{(0)}} e^{i\mathbf{G}\cdot\mathbf{r}}\right\} e^{i\mathbf{k}\cdot\mathbf{r}} \qquad (2.49)$$

$$(2.50)$$

2.7. Brillouin zones

As a consequence of the above secs. 2.4–2.6, the wave vector $\mathbf{k}$ can be used as a quantum number of the one-electron state. Note, that $k = 2\pi/\lambda$ and $p = \hbar k$ or $\mathbf{p} = \hbar\mathbf{k}$ in 3D. A plot of energy eigenvalues $E_\mathbf{k}$ of (2.47) as a function of $\mathbf{k}$ is the *electronic band structure* (BS, vyörakenne eli kaistarakenne). The *band index* $n = 1, 2, 3, ...$; labels the consequent higher energy bands at the same $\mathbf{k}$-point in the *reciprocal space* (käänteisavaruus).

The reciprocal lattice of fcc is *body-centered cubic* (bcc, tilakeskinen kuutiollinen, tkk) and *vice versa*.

Fig. (a) Diamond and zinc-blende structures. (b) Fcc structure: unit cell and primitive cell. (c) Bcc structure of the reciprocal space of fcc. The first Brillouin zone is shown with its high-symmetry points and lines.
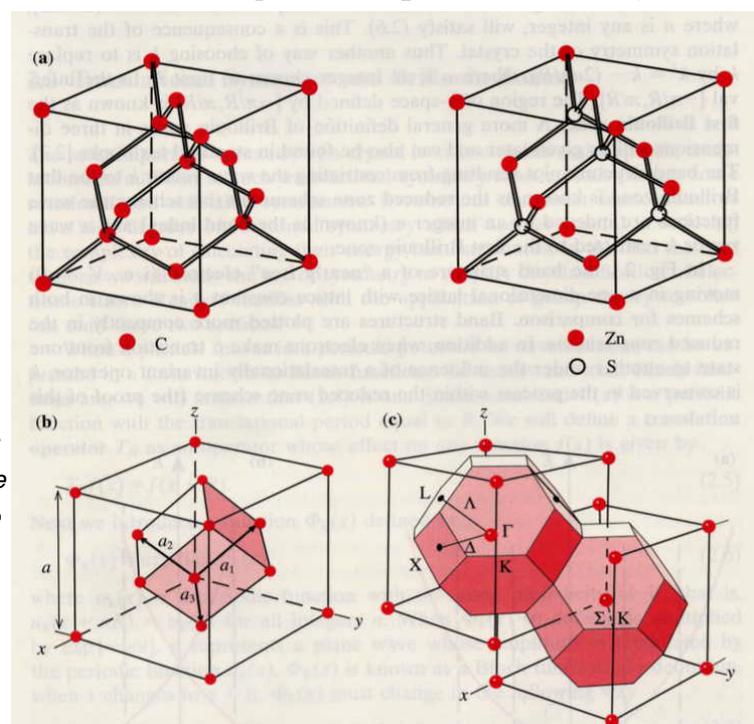
The *Wigner–Seitz primitive unit cell*, see sec. 1.3.2 on p. 5, of the reciprocal space is the *first Brillouin zone.*
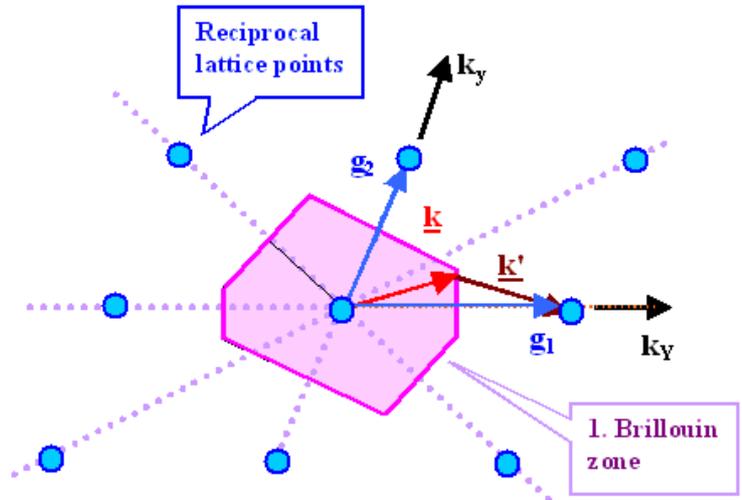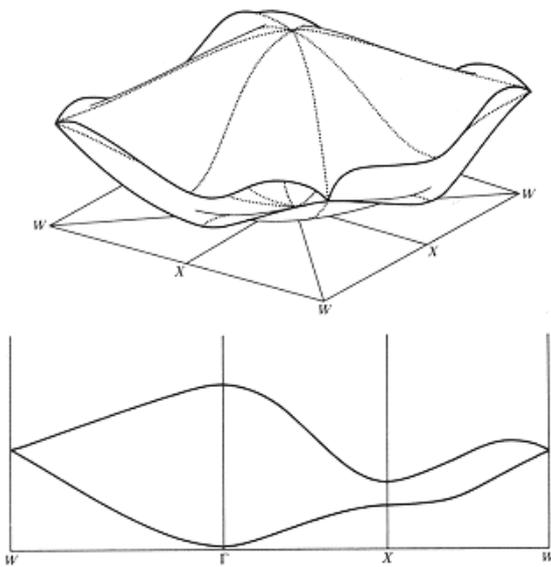
Figs: (Above) 2D reciprocal space and the 1st Brillouin zone. (Left) Bands in 2D case. (Right) 3D reciprocal space and the 1st Brillouin zone of FCC real space lattice.
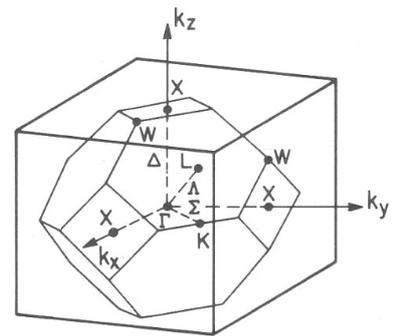
2.8. Energy bands and energy band gaps

Due to the periodicity of the reciprocal space the (free-electron) bands overlap or cross the others in the neighboring Brillouin zones. At the zone boundary, in paricular, the bands become degenerate, see the figure.
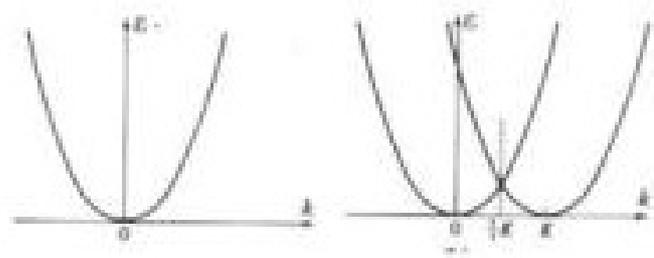
Consider now the eq. (2.35) on p. 27

$$E_{\mathbf{k}}^{(0)}C(\mathbf{k}) + \sum_{G} V_{\mathbf{G}}C(\mathbf{k} - \mathbf{G}) - E_{\mathbf{k}}C(\mathbf{k}) = 0$$

where

$$E_{\mathbf{k}}^{(0)} = \frac{\hbar^2 k^2}{2m}$$ for the degenerate states $\mathbf{k}$ and $\mathbf{k} - \mathbf{G}_0$, while neglecting all others.

Then, from Eq. (2.35) we obtain a pair of equations

$$E_{\mathbf{k}}^{(0)}C(\mathbf{k}) + V_0 C(\mathbf{k}) + V_{\mathbf{G}_0}C(\mathbf{k} - \mathbf{G}_0) - E_{\mathbf{k}}C(\mathbf{k}) = 0$$

$$E_{\mathbf{k}-\mathbf{G}_0}^{(0)}C(\mathbf{k} - \mathbf{G}_0) + V_0 C(\mathbf{k} - \mathbf{G}_0) + V_{\mathbf{G}_0}C(\mathbf{k}) - E_{\mathbf{k}}(\mathbf{k} - \mathbf{G}_0) = 0$$

and further

$$(E_{\mathbf{k}}^{(0)} + V_0 - E_{\mathbf{k}})C(\mathbf{k}) \; + \; V_{\mathbf{G}_0}C(\mathbf{k} - \mathbf{G}_0) = 0$$

$$V_{\mathbf{G}_0}^* C(\mathbf{k}) \; + \; (E_{\mathbf{k}-\mathbf{G}_0}^{(0)} + V_0 + E_{\mathbf{k}})(\mathbf{k} - \mathbf{G}_0) = 0$$

Thus, the secular equation for the nontrivial solutions $E_{\mathbf{k}}$ becomes

$$ \tag{2.54} $$

and the solution

$$ \tag{2.55} $$

At the zone boundary $\mathbf{k} = \mathbf{G}_0/2$, where due to degeneracy $E^{(0)}_{\mathbf{k}} = E^{(0)}_{\mathbf{k}-\mathbf{G}_0}$, we obtain
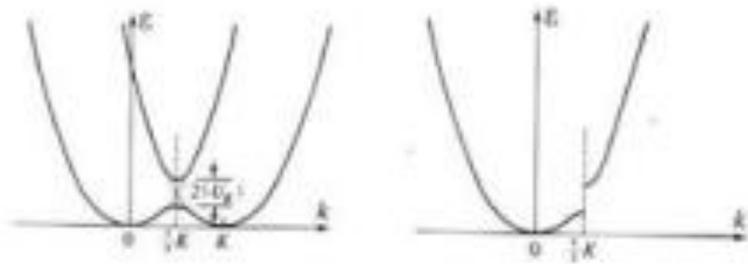
Due to the periodicity of the reciprocal space the bands can be represented in the *extended zone scheme,* the *periodic zone scheme* or the *reduced zone scheme.* The reduced zone scheme presents all the information in the first Brillouin zone and it is the most used in literature.
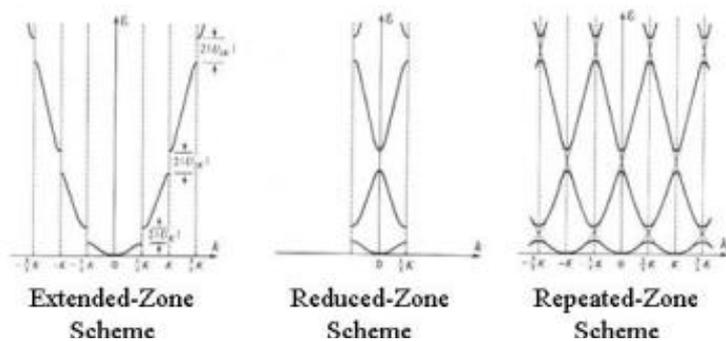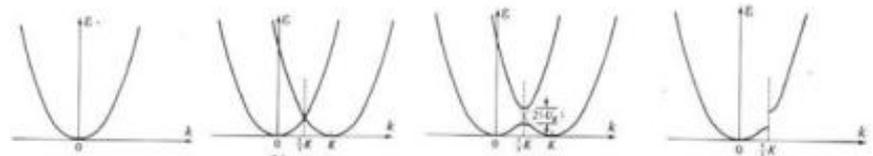
Figs: (Above) The zone schemes. (Below) Free-electron bands with a periodic potential with zero strength resulting from the periodicity of the reciprocal space,only.

Extended-Zone Scheme

Reduced-Zone Scheme

Repeated-Zone Scheme

The Kronig–Penney model includes a very week periodic potential in 1D, see the text book and exercises.
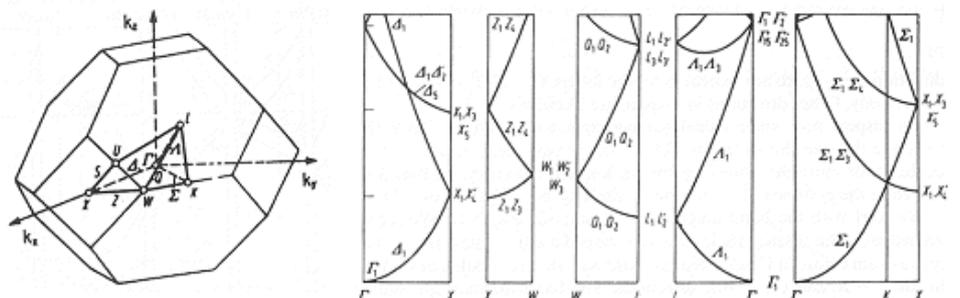
2.9. Tight binding method

The Bloch states expansion in terms of plane waves converges well in case of week electron–ion interaction. In the "opposite" case, strong electron–ion interaction, better starting point is localized atomic orbitals as a basis to form the bonding (and antibonding) states of shared electrons. This is the tight-binding (TB) or linear-combination-of-atomic-orbitals (LCAO) approach.

It should be noted that the conduction band states tend to be delocalized free-electron like (and antibonding), whereas the valence band states are more localized molecular orbital like and bonding.

2.9.1. Wannier functions

One choice of a localized basis set is sc. *Wannier functions* $w_n(\mathbf{r} - \mathbf{R}(\ell))$, Fourier transforms of fully delocalized Bloch functions $\psi_{n\mathbf{k}}(\mathbf{r})$. These two relate as

$$w_n(\mathbf{r} - \mathbf{R}(\ell)) = N^{-1/2} \Sigma_\mathbf{k} \exp(-i\mathbf{k}\cdot\mathbf{R}(\ell))\, \psi_{n\mathbf{k}}(\mathbf{r}) \tag{2.69a}$$

$$\psi_{n\mathbf{k}}(\mathbf{r}) = N^{-1/2} \Sigma_l \exp(i\mathbf{k}\cdot\mathbf{R}(\ell))\, w_n(\mathbf{r} - \mathbf{R}(\ell)), \tag{2.69b}$$

where $\mathbf{R}(\ell)$ are lattice vectors, n is band index, $\mathbf{k}$ the wave vector in the reduced zone scheme and N the number of unit cells in the crystal. Thus, the Bloch functions are indexed by the wave vectors ($\mathbf{k}$-points) in the reciprocal space and the Wannier functions by the lattice vectors (or primitive cells) in real space.

While Bloch functions are more convenient for representing extended or delocalized states in ideal crystals, the Wannier functions are more appropriate for localized electrons of defects. However, though Wannier functions form a complete basis set (as do the Bloch functions), they are of limited use in practice, because the Bloch functions are needed in Eq. (2.69a).

2.9.2. LCAO method

Following the idea of Wannier and Bloch functions in Eqs. (2.69) let us write the *tight binding Bloch function* as

$$\psi_{\mathbf{k}\kappa i}(\mathbf{r}) = N^{-1/2} \Sigma_l \exp(i\mathbf{k}\cdot\mathbf{R}(l\,\kappa))\, \varphi_{\kappa i}(\mathbf{r} - \mathbf{R}(l\,\kappa)), \tag{2.74}$$

where κ and i label the atoms and orbitals, respectively, and the atomic orbitals are solutions of the one-electron equation of the free atom

$$h_\kappa(\mathbf{r})\, \varphi_{\kappa i}(\mathbf{r}) = \varepsilon_{\kappa i}\, \varphi_{\kappa i}(\mathbf{r}).$$

Thus, $\psi_{\mathbf{k}\kappa i}(\mathbf{r})$ in (2.74) is the eigenfunction of "non-interacting atoms" of the crystal

$$H_0 = \Sigma_{l\,i}\, h_{l\,\kappa i}(\mathbf{r} - \mathbf{R}(l\,\kappa)).$$

Now, turning on the interactions between atoms will mix the functions (2.74) and the eigenfunctions of the interacting hamiltonian H can be expanded at any $\mathbf{k}$ as a linear combination

$$\Psi_\mathbf{k}(\mathbf{r}) = \Sigma_i\, C_i(\mathbf{k})\, \psi_{\mathbf{k}\kappa i}(\mathbf{r}).$$

The bands and the Bloch functions can be evaluated from

$$| \mathbf{H} - E_\mathbf{k} \mathbf{S} | = 0, \qquad (2.75)$$

where $\mathbf{H}$ and $\mathbf{S}$ are the hamiltonian and overlap matrices. Using the notation for atomic orbitals in atoms at sites j as

$$\varphi_{\kappa j}(\mathbf{r}) = \{| j\, n \rangle\} = \{| s_j \rangle, | p_{xj} \rangle, | p_{yj} \rangle, | p_{zj} \rangle\}$$

(a typical basis set) allows us to write the matrix elements of hamiltonian and overlap matrices as $\langle i\, n | H | j\, m \rangle$ and $\langle i\, n | j\, m \rangle$.

Consider the molecular orbitals of the hydrogen molecule as an example. We find graphically the bonding and antibonding nature of the two possible linear combinations:

See also the schema of bonding and antibonding bands on page 11.
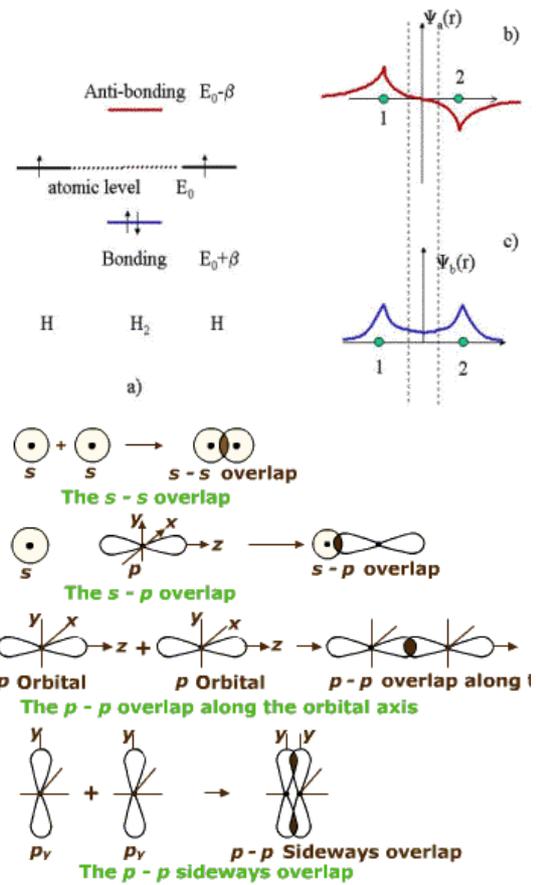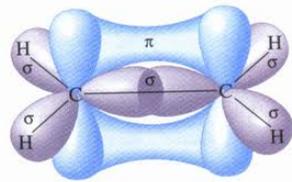
Extension to include p-orbitals:

Now, consider the matrix elements of the basis $\varphi_{\kappa j n}(\mathbf{r}) = \{|\,j\,n\,\rangle\} = \{|\,s_j\,\rangle, |\,p_{xj}\,\rangle, |\,p_{yj}\,\rangle, |\,p_{zj}\,\rangle\}$.

1) The "on-site" matrix elements (i = j) within an atom are trivial

$$\langle\, j\,n\,|\,H\,|\,j\,m\,\rangle = E_n\,\delta_{nm}$$

and $\langle\, j\,n\,|\,j\,m\,\rangle = \delta_{nm}$.

2) The matrix elements between orbitals in different (neighboring) atoms (i ≠ j) may vanish due to the symmetry. As the hamiltonian has the full symmetry, the hamilton and overlap matrix elements have the same "selection rules", which can be easily found by simple graphical inspection:

Thus, in case of basis $\{|\,s_j\,\rangle, |\,p_{xj}\,\rangle, |\,p_{yj}\,\rangle, |\,p_{zj}\,\rangle\}$ there are four independent non-zero matrix elements, in both hamiltonian and overlap matrices.

If the atoms do not lie on the z-axis, the matrix elements are linear combinations of those above.

$$\langle s\,|H|\,p_y\rangle = V_{sp\sigma}\cos\Theta + 0\sin\Theta$$

$$\langle p_y\,|H|\,p_y\rangle = V_{pp\sigma}\cos^2\Theta + V_{pp\pi}\sin^2\Theta$$
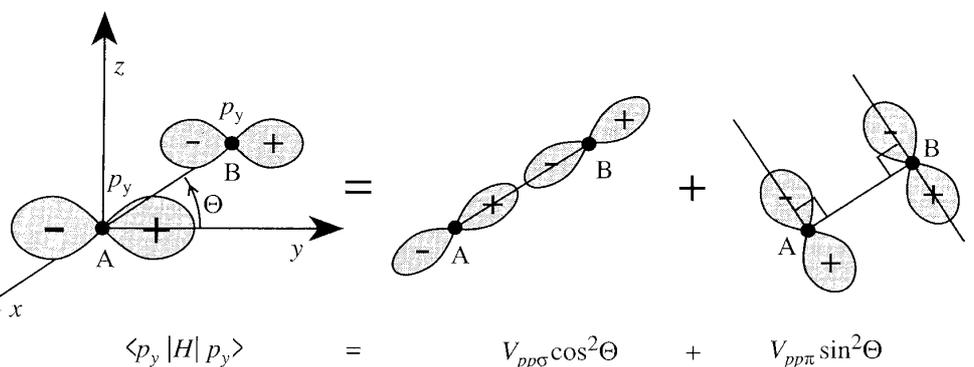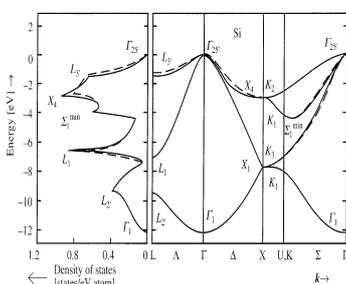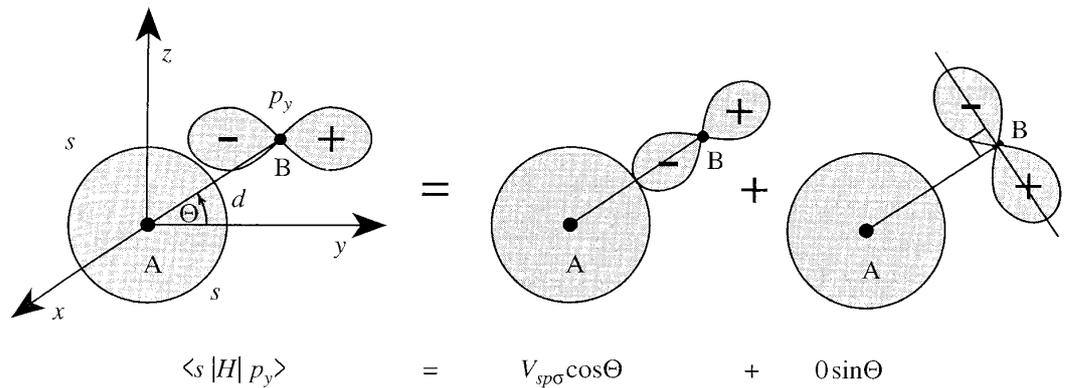
3. Electronic energy bands: semiconductors

Key ideas

A perfect semiconductor at 0 K has its *valence bands* completely full of electrons and its *conduction bands* completely empty. Between these bands is the *fundamental band gap*.

Orbital and *spin angular momenta* of electrons interact to modify their energy levels.

The effective electron–ion potential can be represented by a *pseudopotential* consisting of attractive and repulsive parts.

Electrons interact with one another through the *Coulomb interaction*. In the *Hartree–Fock method* the Pauli exclusion principle leads to the *exchange interaction* between electrons. In the *density functional method* the energy of interacting electrons is a functional of the electron density $n(r)$.

Excited state energies can be calculated with the aid of the *electron self-energy operator* that combines the effects of exchange and correlation.

The $k \cdot p$ *method* provides the energy E_{nk} as a function of wave vector k near a *band extremum* without calculating the entire band structure.

Energy bands in semiconductors

3.1 Spin–orbit interaction

3.2 Electron–ion interaction and pseudopotentials

3.3 Electron–electron interaction

3.4 The $k \cdot p$ method

A *nondegenerate band* with extremum at $k = 0$ in a cubic crystal has an *isotropic effective mass*. A *degenerate band* with extremum at $k = 0$ in a cubic crystal exhibits *warping* of the constant energy surfaces. A band with extremum at $k \neq 0$ in a cubic crystal has an *anisotropic effective mass*.

Silicon and germanium have *indirect gaps* with extrema of valence and conduction bands at different k values. The majority of III–V, II–VI, and IV–VI semiconductors have *direct gaps* with extrema of valence and conduction bands at $k = 0$.

Energy band gaps can be modified by changing the *temperature*, by applying *pressure* or *stress*, or by forming an *alloy*.

Disorder in the atomic arrangement produces an *amorphous semiconductor*.

3.5 Energy band structures for specific semiconductors

3.6 Modification of energy band gaps

3.7 Amorphous semiconductors

For the crystal properties the *core electrons* do not play an essential role and they are usually replaced together with the nuclei by some simplified description of *ion core* (atomisydän). The usual replacement is the *frozen-core* or the *pseudopotential*. If the core electrons are included explicitly in the calculation, the method is said to be an *all-electron approach.*

The valence electrons are responsible for the crystal structure and most properties, whereas the core electron wavefunctions remain relatively intact. Thus, only the *valence electrons* (valenssielektronit) are treated explicitly and solved from the relevant S-eq.

3.1. Spin–orbit interaction

The atomic p-electrons have orbital angular momentum ℓ, which couples to the spin angular momentum $\mathbf{s}$. This is called the *spin–orbit interaction* (spin–rata-vuorovaikutus). It is a relativistic effect, and thus, most important for the heavier elements, such as Ge, Ga, As and Sb of our interest.

In case of semiconductor crystals the p-electrons are often mostly responsible of the electronic structure at the valence band maximum (VBM). See hybridization discussions above and the schema on page 11. Therefore, the spin–orbit interaction is responsible of one of the main features of the VBM structure.

The effect in the (spherically symmetric) atoms serves as a good approximate model for bulk semiconductors, too. So, we will consider the atomic p-orbitals $\{|\,p_x\,\rangle,|\,p_y\,\rangle,|\,p_z\,\rangle\} = \{|x\rangle, |y\rangle, |z\rangle\}$, who relate to the angular momentum eigenfunctions as

In spherical symmetry the spin–orbit hamiltonian (energy of the spin orientation in the magnetic field of orbital motion: $-\mathbf{m}\cdot\mathbf{B} = -\mathbf{s}\cdot\mathbf{B} \propto \mathbf{s}\cdot(\mathbf{E}\times\mathbf{v}) \propto \mathbf{s}\cdot(dV/dr\,\mathbf{r}\times\mathbf{v}) \propto \mathbf{s}\cdot\boldsymbol{\ell}$) can be written in terms of orbital and spin angular momenta, $\mathbf{s}$ and $\boldsymbol{\ell}$, as

$$H_{so} = \xi(r)\,\boldsymbol{\ell}\cdot\mathbf{s}, \tag{3.1}$$

where the *coupling parameter* is

$$\tag{3.2}$$

The eigenfunctions of H_{so} turn out to be those of s.c. **jj**-*coupling,* $|j\,m_j\rangle$, which relate to coupling $\boldsymbol{\ell}$ and $\mathbf{s}$ of an electron first as $\mathbf{j} = \boldsymbol{\ell} + \mathbf{s}$, and then the electrons $\mathbf{J} = \Sigma\,\mathbf{j}$.

For a p-electron:

Compare LS- and jj-coupling:

Let us find the eigenvalues of the operator $\boldsymbol{\ell} \cdot \mathbf{s}$ for $|j\, m_j\rangle$, with $j = 3/2$ and $1/2$

The s–o splitting of VBM increases as $\Delta_0 \propto Z^4$.

<u>Table</u>

compound	C	Si	Ge	GaAs	GaP	InP	GaSb	InSb	InAs
Z	6	14	32	31–33	31–15	49–15	31–51	49–51	49–33
Δ_{so} / eV	0.013	0.044	0.295	0.341	0.08	0.11	0.75	0.81	0.38

compound	ZnTe	CdTe
Z	30–52	48–52
Δ_{so} / eV	0.93	0.92

3.2. Electron–ion interaction and pseudopotentials

The rapidly oscillating core wavefunctions are laborious to solve together with the valence electrons, and in particular, to keep them all mutually orthogonal. Furthermore, the core is well localized, whereas the valence electrons are essentially delocalized like planewaves.

3.2.1. Orthogonalized plane wave method

Let us assume we have the mutually orthogonal set of core electron states $\{|c\rangle\}_c$ and we denote the planevawes by $|\mathbf{k}\rangle = \exp(i\mathbf{k}\cdot\mathbf{r})$. Then, the orthogonalized planewaves are written as

$$|\mathbf{k}\rangle_{OPW} = |\mathbf{k}\rangle - \Sigma_c \langle c|\mathbf{k}\rangle |c\rangle, \tag{3.4}$$

where the summation is over all core states. It is easy to see that $|\mathbf{k}\rangle_{OPW}$ are orthogonal to any core state $|c'\rangle$:

$$\tag{3.5}$$

Now, following from the Bloch theorem (2.36–38), the delocalized electron states can be expanded in terms of $|\mathbf{k}\rangle_{OPW}$ as

$$|\phi_\mathbf{k}^{OPW}\rangle = \Sigma_\mathbf{G} C(\mathbf{k}-\mathbf{G}) |\mathbf{k}-\mathbf{G}\rangle_{OPW}. \tag{3.6}$$

Now, substituting this into the Schrödinger equation $H\phi_\mathbf{k} = E_\mathbf{k}\phi_\mathbf{k}$, where $H = H_0 + V$, $H_0 = -\hbar^2\nabla^2/2m$, V is the potential energy and $|\mathbf{k}\rangle_{OPW} = |\mathbf{k}\rangle - \Sigma_c \langle c|\mathbf{k}\rangle |c\rangle$ (3.4), we find

$$\Sigma_\mathbf{G} C(\mathbf{k}-\mathbf{G}) \{ [H_0 + V] |\mathbf{k}-\mathbf{G}\rangle - \Sigma_c \langle c|\mathbf{k}-\mathbf{G}\rangle [H_0 + V]|c\rangle \} =$$

$$= \Sigma_\mathbf{G} C(\mathbf{k}-\mathbf{G}) \{ E_\mathbf{k} |\mathbf{k}-\mathbf{G}\rangle - \Sigma_c \langle c|\mathbf{k}-\mathbf{G}\rangle E_\mathbf{k} |c\rangle \} \tag{3.7}$$

$$\Sigma_\mathbf{G} C(\mathbf{k}-\mathbf{G}) \{ \langle \mathbf{k}-\mathbf{G}'| H_0 |\mathbf{k}-\mathbf{G}\rangle + \langle \mathbf{k}-\mathbf{G}'| V |\mathbf{k}-\mathbf{G}\rangle - \Sigma_c \varepsilon_c \langle c|\mathbf{k}-\mathbf{G}\rangle \langle \mathbf{k}-\mathbf{G}'|c\rangle \} =$$

$$= \Sigma_\mathbf{G} E_\mathbf{k} C(\mathbf{k}-\mathbf{G}) \{ \delta_{\mathbf{G}\mathbf{G}'} - \Sigma_c \langle c|\mathbf{k}-\mathbf{G}\rangle \langle \mathbf{k}-\mathbf{G}'|c\rangle \} \tag{3.9}$$

We obtain

$$[\hbar^2(\mathbf{k}-\mathbf{G})^2/2m]\, C(\mathbf{k}-\mathbf{G}) + \sum_{\mathbf{G}} \langle \mathbf{k}-\mathbf{G'}| \{ V + \sum_c (E_{\mathbf{k}}-\varepsilon_c)\, |c\rangle\langle c|\} |\mathbf{k}-\mathbf{G}\rangle\, C(\mathbf{k}-\mathbf{G}) = E_{\mathbf{k}}\, C(\mathbf{k}-\mathbf{G'}) \quad (3.10)$$

Thus, we have found an effective potential $V + V_R$ for the continuum electron states, where

$$V_R = \sum_c (E - \varepsilon_c)\, |c\rangle\langle c|, \quad (3.11)$$

or
$$V_R(\mathbf{r},\mathbf{r'}) = \sum_c (E - \varepsilon_c)\, \varphi_c{}^*(\mathbf{r})\, \varphi_c(\mathbf{r'}).$$

This effective potential conveys the effect of core electrons in the nonlocal potential operator V_R. Therefore, this potential is repulsive and leads us to the concept of pseudopotential.

3.2.2. Pseudopotential method

We call the above found effective potential as pseudopotential

$$V_{ps} = V + V_R, \quad (3.12)$$

which lets us write the Eq. (3.10) as

$$\sum_{\mathbf{G'}} H_{\mathbf{G},\mathbf{G'}}(\mathbf{k})\, C(\mathbf{k}-\mathbf{G'}) = E\, C(\mathbf{k}-\mathbf{G}), \quad (3.13)$$

where

$$H_{\mathbf{G},\mathbf{G'}}(\mathbf{k}) = [\hbar^2(\mathbf{k}-\mathbf{G})^2/2m]\, \delta_{\mathbf{G}\mathbf{G'}} + \langle \mathbf{k}-\mathbf{G}|\, V_{ps}\, |\mathbf{k}-\mathbf{G'}\rangle \quad (3.14)$$

Now, defining the function

$$\chi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C(\mathbf{k}-\mathbf{G})\, |\mathbf{k}-\mathbf{G}\rangle \quad (3.15)$$

we can write

$$|\phi_{\mathbf{k}}{}^{OPW}\rangle = |\chi_{\mathbf{k}}\rangle - \sum_c \langle c|\chi_{\mathbf{k}}\rangle\, |c\rangle. \quad (3.16)$$

Using this as a trial solution to the Schrödinger equation

$$H\, |\phi_{\mathbf{k}}{}^{OPW}\rangle = E_{\mathbf{k}}\, |\phi_{\mathbf{k}}{}^{OPW}\rangle$$

gives

$$H\, |\chi_{\mathbf{k}}\rangle - \sum_c \langle c|\chi_{\mathbf{k}}\rangle\, H|c\rangle = E\, (|\chi_{\mathbf{k}}\rangle - \sum_c \langle c|\chi_{\mathbf{k}}\rangle\, |c\rangle) \quad (3.17)$$

and further

$$\{ H - \sum_c (E - \varepsilon_c)\, |c\rangle\langle c| \}\, |\chi_{\mathbf{k}}\rangle = E\, |\chi_{\mathbf{k}}\rangle. \quad (3.18)$$

Finally, we have

$$[H_0 + V_{ps}]\, |\chi_{\mathbf{k}}\rangle = E\, |\chi_{\mathbf{k}}\rangle. \quad (3.19)$$

3.2.2.1. Empirical pseudopotential method

3.2.2.2. Nonlocal pseudopotential method

The fitting procedure is the following:

Si

Ge

GaAs

ZnSe
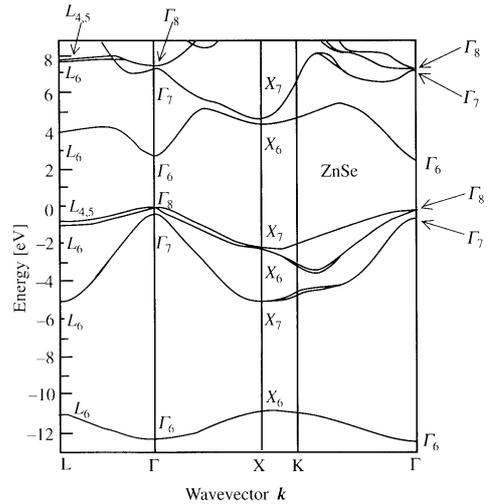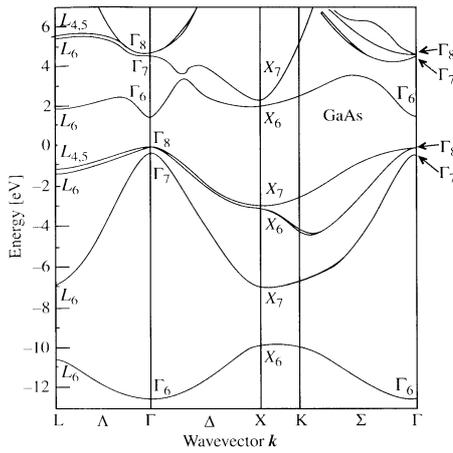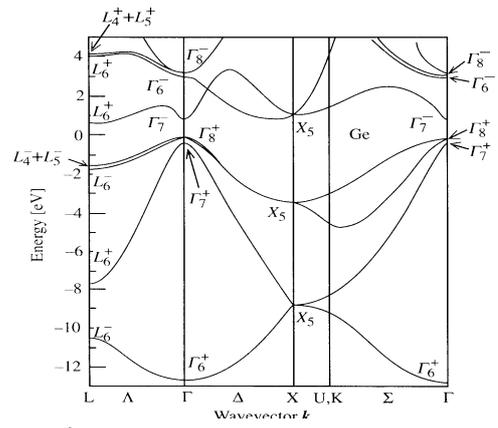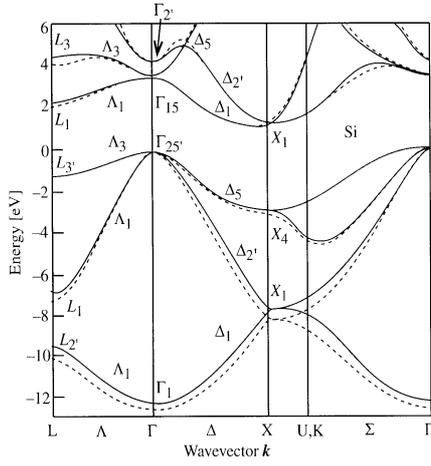
3.2.2.3. Ab initio pseudopotentials

This is what is being used today, together with planewave basis set, in particular.

Usually fitted with atomic calculations, sometimes including relativistic effects.
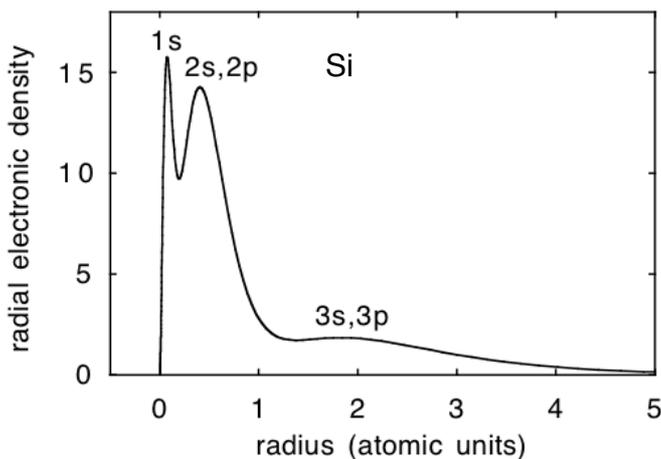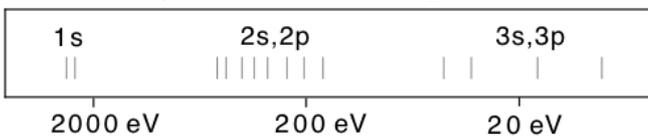
B   s states, $\ell = 0$ p states, $\ell = 1$
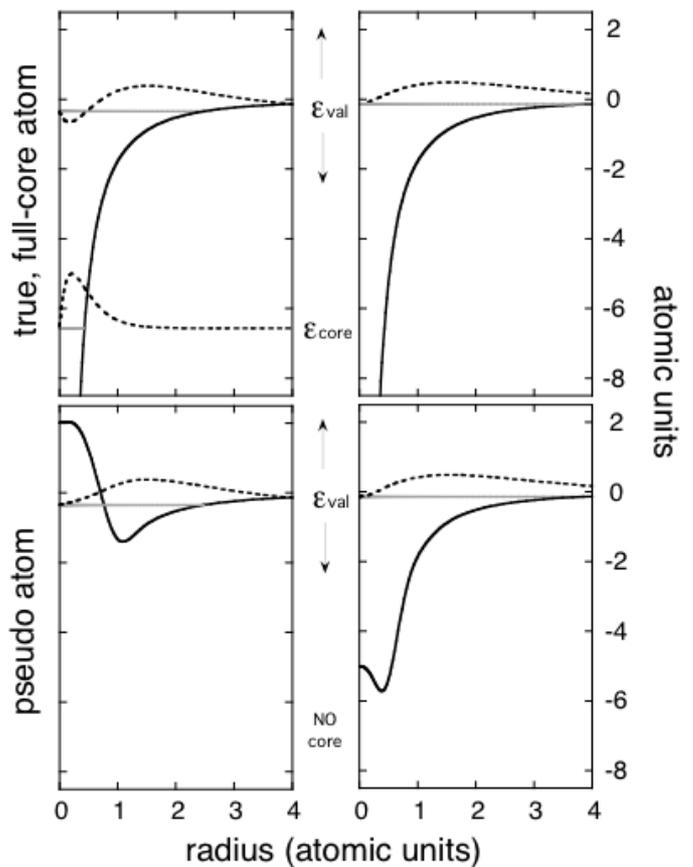
3.3. Electron–electron interaction

The full hamiltonian of the electronic structure, only, is

$$H = -\frac{\hbar^2}{2m}\sum_i^N \nabla_i^2 - \sum_i^N \sum_I^M \frac{Z_I}{4\pi\varepsilon_0}\frac{e^2}{r_{Ii}} + \tfrac{1}{2}\sum_{ij}^N \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_{ij}},$$ (3.40)

and the consequent Schrödinger equation is Eq. (2.3) on p. 23. Here the last term, electron–electron interaction, makes the one-electron problem much more complex many-body problem. There are several approaches to find approximate solutions to this and in the following we will look at some, which are introduced in more details in the lectures of *Quantum theory of molecules and nanostructures.*

3.3.1. Hartree method

In the one-electron picture we may expand the wave function as

$$\psi_N(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n) = \varphi_1(\mathbf{r}_1)\,\varphi_2(\mathbf{r}_2)\,...\,\varphi_n(\mathbf{r}_n),$$ (3.41)

neglecting the Pauli principle for the antisymmetry of total electronic wavefunction. With the hamiltonian for the electron/orbital i

$$H_i(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2 + V_{PS}(\mathbf{r},\mathbf{R}) + \frac{e^2}{4\pi\varepsilon_0}\int \frac{\rho_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'$$

we obtain the Hartree equation

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V_{PS}(\mathbf{r},\mathbf{R}) + \sum_{\substack{j=1 \\ j\neq i}}^n \frac{e^2}{4\pi\varepsilon_0}\int \frac{|\varphi_j(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\right\}\varphi_i(\mathbf{r}) = E_i\varphi_i(\mathbf{r})$$ (3.42)

for each occupied one-electron state φ_i.

3.3.2. Hartree–Fock method

With the proper antisymmetric wavefunction

$$\psi_N(\mathbf{r}_1,s_1,\mathbf{r}_2,s_2,\cdots\mathbf{r}_N,s_N)=\frac{1}{\sqrt{N!}}\begin{vmatrix} \varphi_1(\mathbf{r}_1)\sigma_1(s_1) & \varphi_1(\mathbf{r}_2)\sigma_1(s_2) & \cdots & \varphi_1(\mathbf{r}_N)\sigma_1(s_N) \\ \varphi_2(\mathbf{r}_1)\sigma_2(s_1) & \ddots & & \\ \vdots & & \ddots & \\ \varphi_N(\mathbf{r}_1)\sigma_N(s_1) & & & \varphi_N(\mathbf{r}_N)\sigma_N(s_N) \end{vmatrix}$$ (3.43)

variation of the total energy expression with respect to the one-electron orbitals φ_i yields the *Hartree–Fock equations*

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V_{PS}(\mathbf{r},\mathbf{R}) + \sum_{j=1}^N \frac{e^2}{4\pi\varepsilon_0}\int \frac{\varphi_j^*(\mathbf{r}')\varphi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\right\}\varphi_i(\mathbf{r}) +$$

$$-\sum_{j=1}^N \frac{e^2}{4\pi\varepsilon_0}\int \frac{\varphi_j^*(\mathbf{r}')\varphi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\,\varphi_j(\mathbf{r}) = E_i\varphi_i(\mathbf{r})$$ (3.44)

The exchange term can be written

$$-\sum_{j=1}^{N}\frac{e^2}{4\pi\varepsilon_0}\int\frac{\varphi_j*(\mathbf{r}')\varphi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\,\varphi_j(\mathbf{r})=\int V_x(\mathbf{r},\mathbf{r}')\varphi_i(\mathbf{r}')d\mathbf{r}' \tag{3.45}$$

in terms of the *exchange operator*

$$V_x(\mathbf{r},\mathbf{r}')=-\sum_{j=1}^{N}\frac{e^2}{4\pi\varepsilon_0}\int\frac{\varphi_j*(\mathbf{r}')\varphi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}', \tag{3.46}$$

which thus, turns out to be nonlocal and nonlinear.

The exchange interaction between the same spin electrons results in the *Fermi-hole* or *exchange hole* described by the pair correlation function. Correspondingly, the *Fermi heap* emerges in the pair correlation function of opposite spin electrons.

The many-body effects in the system of electrons are called correlations. In finite and small systems the many-electron wavefunction can be written as an expansion of ground and excited state Slater determinants

$$\Psi=C_0\psi_0+\Sigma_{a,p}C_{ap}\psi_{ap}+\Sigma_{a<b,p<q}C_{abpq}\psi_{abpq}+\Sigma_{a<b<c,p<q<r}C_{abcpqr}\psi_{abcpqr}+...$$

3.3.3. Density functional theory (DFT)

The solids with essentially an infinite number of electrons can be best treated with another approach. It can be shown that the ground state properties of the many-electron system has one-to-one correspondence with its one-electron density.

Thus, by writing the ground state energy as

$$E[\rho] \; = \; -\frac{\hbar^2}{2m} \sum_i^n \int \psi_i^*(\mathbf{r}) \, \nabla_i^2 \, \psi_i^*(\mathbf{r}) \, d\mathbf{r} \; - \; \sum_I^N \int \frac{Z_I \, e^2}{4\pi\varepsilon_0 \, r_I} \, \rho(\mathbf{r}) \, d\mathbf{r}$$

$$+ \; \frac{1}{2} \int \int \frac{e^2 \, \rho(\mathbf{r}_i) \, \rho(\mathbf{r}_j)}{4\pi\varepsilon_0 \, r_{ij}} \, d\mathbf{r}_i \, d\mathbf{r}_j \; + \; E_{xc}[\rho] \; ,$$

and requiring its variation to be stationary with respect to the density

$$\rho(\mathbf{r}) \; = \; \Sigma_i \, |\psi_i(\mathbf{r})|^2, \tag{3.47}$$

Hartree–Fock like one-electron equations, sc. Kohn–Sham equations result as

$$\left\{ -\frac{\hbar^2}{2m} \nabla_i^2 + V_{e-I}(\mathbf{r}, \mathbf{R}) + \frac{e^2}{4\pi\varepsilon_0} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \mu_{xc}[\rho(\mathbf{r})] \right\} \varphi_i(\mathbf{r}) = E_i \varphi_i(\mathbf{r}) \tag{3.48}$$

Local-Density Approximation (LDA)

is based on the HEG data for

$\varepsilon_x(\rho)$, $\varepsilon_c(\rho)$, $\mu_x(\rho)$ and $\mu_c(\rho)$.

The exchange terms are known analytically

and the correlation can be taken from the Quantum Monte Carlo simulations of Ceperley and Alder

Geometry and SCF Cycles

start geometry   start density

R_α

$q(\mathbf{r}) = \rho(\mathbf{r}) + Z(\mathbf{R}_\alpha)$ charge distribution

$H\psi_i = \varepsilon_i\psi_i$ Kohn-Sham equations

$\nabla^2 V_C(\mathbf{r}) = -4\pi\, q(\mathbf{r})$ Poisson's equation - Coulomb potential

$\mu_{xc}(\mathbf{r}) = \mu_{xc}[\rho(\mathbf{r})]$ exchange-correlation potential

Geometry optimization or dynamics

$$H_{ij} = \int \phi_i^*(\mathbf{r})\,[-\tfrac{1}{2}\nabla^2 + V_C(\mathbf{r}) + \mu_{xc}(\mathbf{r})]\,\phi_j(\mathbf{r})\,d\mathbf{r}$$

$$S_{ij} = \int \phi_i^*(\mathbf{r})\,\phi_j(\mathbf{r})\,d\mathbf{r}$$

matrix elements

Self-consistent-field (SCF) cycle

$\left(\mathbf{H} - \varepsilon\,\mathbf{S} \right)$ diagonalization

$\{\varepsilon_i\}, \{c_{ij}\}$ eigenvalues and eigenvectors

$\psi_i = \sum_j c_{ij}\phi_j$ synthesis of wave functions

$\rho(\mathbf{r}) = \sum_{i,occ} |\psi_i(\mathbf{r})|^2$ synthesis of charge density

$E[\rho(\mathbf{r}), \mathbf{R}_\alpha],\ \ \mathbf{F}_x = -\dfrac{\partial E}{\partial \mathbf{x}}$ **Calculation of properties**

total energy and forces

3.3.4. Excited electronic states

Properties and dynamics of excited electronic states are reflected in

3.4. The **k·p** method

One semiempirical approach to band structure calculations is the **k·p** method, which can use optical data, in particular, to fit its parameters. The band gaps or (transition energies) and intensities are most useful. The entire band structure can be interpolated from high symmetry points or even extrapolated from the zone center data. Also, analytic expressions for band dispersion, and thus, the charge carrier effective masses are conveniently obtained.

3.4.1. Nondegenerate bands

An electron in the constant potential is the planewave (2.21)

$$\psi(\mathbf{r}) \ = \ e^{i\mathbf{k}\cdot\mathbf{r}}$$

with the energy from the "square parabola" (2.16)

$$E_0(k) \ = \ \hbar^2 k^2 / 2m. \qquad (3.54)$$

The effective mass m^* is

$$(3.55)$$

$$(3.56)$$

Now, let us start with a Bloch function

$$\psi_{n\mathbf{k}}(\mathbf{r}) \ = \ u_{n\mathbf{k}}(\mathbf{r}) \ e^{i\mathbf{k}\cdot\mathbf{r}} \qquad (3.57)$$

and substitute into the Schrödinger equation

$$\left(\frac{p^2}{2m} + V(\mathbf{r}) \right) \psi_{n\mathbf{k}}(\mathbf{r}) = E \ \psi_{n\mathbf{k}}(\mathbf{r}) \qquad (3.58)$$

where $\mathbf{p} = -i\hbar\nabla$.

$$\left(\frac{p^2}{2m} + \frac{h\,\mathbf{k}\cdot\mathbf{p}}{m} + \frac{h^2k^2}{2m} + V(\mathbf{r}) \right) u_{n\mathbf{k}}(\mathbf{r}) \; = \; E_{n\mathbf{k}}\, u_{n\mathbf{k}}(\mathbf{r}). \tag{3.59}$$

For $\mathbf{k} = \mathbf{k}_0 = 0$ (Γ-point)

$$\left(\frac{p^2}{2m} + V(\mathbf{r}) \right) u_{n0}(\mathbf{r}) \; = \; E_{n0}\, u_{n0}(\mathbf{r}).$$

If the functions u_{n0} are known or can be solved, they can be used as a basis for the solutions of (2.35), i.e. in the perturbation expansion of $u_{n\mathbf{k}}$. The larger basis set is used, the further from the $\mathbf{k}_0$ the expansion is valid.

This is called the $\mathbf{k}\cdot\mathbf{p}$ method.

From the first order perturbation theory for nondegenerate states we obtain for the wavefunction

$$u_{n\mathbf{k}} \; = \; u_{n0} + \frac{h}{m} \sum_{n' \neq n} \frac{\langle u_{n0} \mid \mathbf{k}\cdot\mathbf{p} \mid u_{n'0}\rangle}{E_{n0} - E_{n'0}}\, u_{n'0} \,,$$

but the corresponding energy correction vanishes, as $\mathbf{k}_0$ is an extremum point of the band. The second order expansion for the energy becomes as

$$E_{n\mathbf{k}} \; = \; E_{n0} + \frac{h^2k^2}{2m} + \frac{h^2}{m^2} \sum_{n' \neq n} \frac{|\langle u_{n0} \mid \mathbf{k}\cdot\mathbf{p} \mid u_{n'0}\rangle|^2}{E_{n0} - E_{n'0}} \,. \tag{3.60}$$

By definition of the *effective mass*

$$E_{n\mathbf{k}} \; = \; E_{n0} + \frac{h^2k^2}{2m^*} \,.$$

Thus, comparison with (3.60) gives now

$$\frac{1}{m^*} \; = \; \frac{1}{m} + \frac{2}{m^2k^2} \sum_{n' \neq n} \frac{|\langle u_{n0} \mid \mathbf{k}\cdot\mathbf{p} \mid u_{n'0}\rangle|^2}{E_{n0} - E_{n'0}} \,. \tag{3.63}$$

This shows the origin of $m^* \neq m$. It is in the wave nature of electrons and the consequent coupling of different bands via $\mathbf{k}\cdot\mathbf{p}$ operator.

Let us consider the bands of the zinc blende structure at Γ-point, next. The conduction band minimum (CBM) is usually of s-type (and belongs to Γ_1 symmetry) and the valence band maximum (VBM) is of p-type (and belongs to Γ_4 symmetry), GaAs as an example.

A small (in absolute value) denominator $\Delta E = E_{n0} - E_{n'0}$ makes the coupling stronger, i.e. for $\Delta E > 0$ ($\Delta E < 0$) the inverse effective mass $1/m^*$ will increase (decrease). Thus, the bands below (above) decrease (increase) the effective mass itself m^* from its reference value free electron mass of the noninteracting band.

Let us consider next the coupling of CBM (Γ_1) to the VBM (Γ_4), which is much stronger than to the higher and further above Γ_4 bands due to the smaller $|\Delta E|$. If ignoring other couplings (3.63) gives for the conduction band inverse effective mass

$$\frac{1}{m^*} = \frac{1}{m} + \frac{2}{m^2 k^2} \frac{|\langle \Gamma_{1c} | \mathbf{k} \cdot \mathbf{p} | \Gamma_{4v}\rangle|^2}{E_0} ,$$

where E_0 is the direct band gap.

Denote the three degenerate VBM (Γ_4) wavefunctions as $|X\rangle$, $|Y\rangle$ and $|Z\rangle$. Then,

$$\langle \Gamma_1 | \mathbf{p} | X\rangle = \langle \Gamma_1 | p_x | X\rangle \hat{\mathbf{i}} + \langle \Gamma_1 | p_y | X\rangle \hat{\mathbf{j}} + \langle \Gamma_1 | p_z | X\rangle \hat{\mathbf{k}}$$

and we denote the nonzero matrix elements by

$$\langle \Gamma_{1c} | p_x | X\rangle = \langle \Gamma_{1c} | p_y | Y\rangle = \langle \Gamma_{1c} | p_z | Z\rangle = iP$$

where P is a real constant (assuming that the wavefunctions are real). Now, from (3.63) this gives

$$\frac{m}{m_c^*} = 1 + \frac{2 P^2}{m E_0} . \tag{3.65}$$

It turns out that for most of the group-IV, III–V and II–VI semiconductors the nearly free electron value $P = h/a_0$ is a good approximation, which leads to an estimate

$$2P^2/m \approx 20 \text{ eV},$$

and a further approximation

$$\frac{m}{m_c^*} \approx \frac{2 P^2}{m E_0} \approx \frac{20 \text{ eV}}{E_0} .$$

Comparison:

Table 2.22. Γ_1 conduction band effective masses

Element/compound		Ge	GaAs	GaN
E_0 / eV		0.81	1.43	3.44
m_c^*/m	Eq., above	0.041	0.072	0.17
	Observed	0.041	0.067	0.17

3.4.2. Valence bands

The $j = 3/2$ Γ_{4v} band splits to two, sc. *heavy-hole band*

$$E_{hh}(\mathbf{k}) \ = \ -A\,k^2 - \sqrt{B^2 k^4 + C^2\,[k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2]}$$

and *light-hole band*

$$E_{lh}(\mathbf{k}) \ = \ -A\,k^2 + \sqrt{B^2 k^4 + C^2\,[k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2]}$$

which are not spherical but "warped" and parabolic in directions [100] and [111], only.

The *spin–orbit split–off band* ($j = 1/2$) near Γ is spherical with parabolic dispersion

$$E_{so}(k) \ = \ -\Delta_0 + \frac{\hbar^2 k^2}{2 m_{so}} \ ,$$

where the effective mass m_{so} comes from

$$\frac{m}{m_{so}} \ = \ 1 - \frac{2}{3}\left(\frac{P^2}{m(E_0 - \Delta_0)} + \frac{2Q^2}{m(E'_0 - \Delta_0)} \right).$$

3.4.3. Conduction bands

3.4.4. Zincblende structure semiconductors

3.5. Energy band structures for specific semiconductors

3.6. Modification of energy band gaps