

EC(MS)574A1 Physics of Semiconductor Materials

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Figure Sources

- C. Kittel - Introduction to Solid State - 8th Edition.
Charts 11, 13, 15, 16
- J. Callaway - Quantum Theory of the Solid State - 2nd Edition.
Charts 38
- B.H. Bradson and C.J. Joachain - Quantum Mechanics - 2th Edition.
Charts 48, 49

Electronic Structure Crystalline Materials

- We intend to study the electrical, optical and thermal properties of semiconductor materials (crystalline solids) that are relevant for electronics and optoelectronic devices (Nano-or-Not).
- We will use the quantum mechanics tool-box to understand the properties of the solids (semiconductors) of interest.
- Electrical Properties: electrons and holes response to and external force, electric or magnetic field, thermal gradient.
- Optical Properties: electrons and holes response and/or ionic response to and external optical excitation.
- Thermal Properties: change of the carrier and ionic response as a function of the temperature.

Types of Solids: General Classification - II

- **Crystalline Solids:** they are characterized by a periodic (ordered) arrangement of the constituent atoms.
- **Non-Crystalline/Amorphous Solids:** They have no structural order other than almost constant nearest-neighbor distance. Amorphous solids may sometimes incorporate grains of crystalline material.
- **Things to remember:**
 - Crystal are held together by Coulomb interactions.
 - The particular (ordered) configuration of the atoms in the crystal depends on how the solid minimizes the total energy.
 - **Cohesive Energy** \triangleq Energy required to disassemble the solid into neutral atoms at r_e (kJ/mole or eV/atom). Note that the equilibrium configuration also maximizes the cohesive energy.

Types of Solids: General Classification - II

- **Melting point:** Crystal with strong cohesive energies are characterized by high melting point.
- **Compressibility** $\triangleq -\frac{\partial V}{\partial p}/V$: Crystal with strong cohesive energies are characterized by low compressibility.

Example

- Silicon-carbide has many possible crystalline configurations (polytypes): 3C (Cubic), 2H (wurtzite), 4H and 6H (Hexagonal with 8 and 12 basis)
- Those that occur naturally or that can be grown more easily (4H and 6H) have the lowest energy.

Classification of Crystals

1 – **Molecular Crystals:** composed by neutral atoms (with complete shells electronic configurations) held together by small perturbation in their charge distribution. Typically Van der Waals interaction.

- They are characterized by low cohesive energy and are in general insulators.

2 – **Ionic Crystals:** composed by ions held together by strong Coulomb interaction. For example NaCl, where Na has an extra electron in the outermost shell (3s1) and the Chlorine has one missing electrons (3s2-3p5).

- They are characterized by large cohesive energy and are in general insulators.

Classification of Crystals - II

3 – **Covalent Crystals:** Neighboring atoms are joined by covalent bonds consisting of 2-electrons contributed one by each atom. In this case the outermost shell has four electrons, for example Silicon ($2s^2-2p^2$).

- They are characterized by large cohesive energy and are in general insulators or semiconductors.
- Note that many semiconductors are both type 1 and 3. For example GaAs and GaN are partly covalent and partly ionic. This is due to the difference in electron affinity between the two atoms (larger for Arsenic and Nitrogen).

4 – **Metals:** Ions held together by a *glue* of electrons, for example Copper.

- They are characterized by an intermediate cohesive energy and are in general good conductors because of the presence of conduction electrons and for the same reason are also malleable and good thermal conductors.

Characteristics of Crystals

Periodic Structure

- The environment around an atom repeats itself periodically in space.
- We can build the entire crystal starting from a basic building block and, by suitable operations, repeat it in space.
- The dimension of such a building block can change and depends on the particular crystal.

There are two important concepts necessary to understand crystals:

Lattice. The *lattice*, it is a set of points that form a perfect periodic structure. Each point sees exactly the same environment around itself.

Basis. The second concept is the *basis*, that is a set of atoms attached to each lattice points, so that the crystal is produced.

The combination of lattice and basis yield the crystal.

Primitive cell. Volume that fills all space when translated through all translation vectors.

Space Lattice, Basis and Crystals

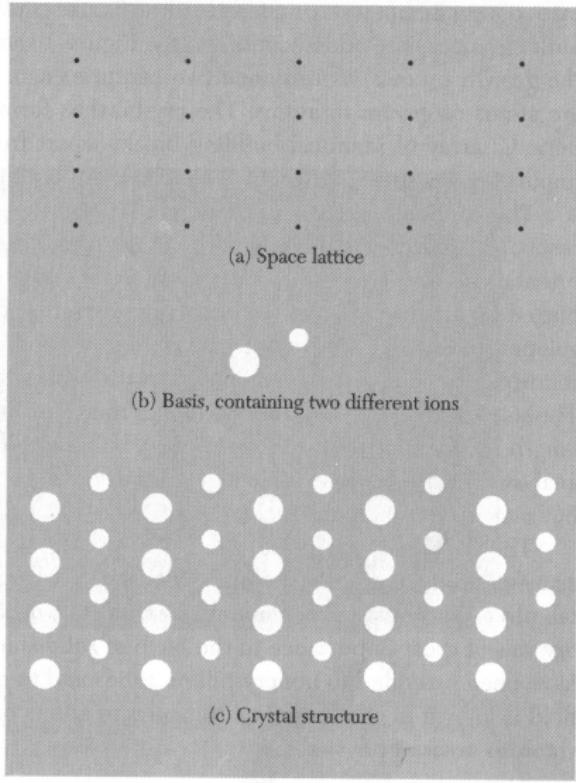


Figure 2 The crystal structure is formed by the addition of the basis (b) to every lattice point of the space lattice (a). By looking at (c), one can recognize the basis and then one can abstract the space lattice. It does not matter where the basis is put in relation to a lattice point.

The Direct Lattice

- The lattice, because of its periodicity, can be described mathematically by three vectors $\vec{a_1}, \vec{a_2}, \vec{a_3}$, so that any lattice point can be reached from any other by a suitable combination of such three vectors,

$$\vec{R}' = \vec{R} + n_1 \vec{a_1} + n_2 \vec{a_2} + n_3 \vec{a_3} \quad (1)$$

where the n_i are three integers. \vec{R} is a **direct lattice vector**.

- The translation vectors $\vec{a_1}, \vec{a_2}, \vec{a_3}$ have the following properties:
 - $\vec{a_1}$ is the shortest period of lattice,
 - $\vec{a_2}$ is the shortest period of lattice non parallel to $\vec{a_1}$,
 - $\vec{a_3}$ is the shortest period of lattice non coplanar to $\vec{a_1}$ and $\vec{a_2}$.
- The set of primitive vectors is not unique, it depends on the convenience of use, and the volume enclosed is the *primitive unit cell*.

Two- and Three-dimensional Space Lattices

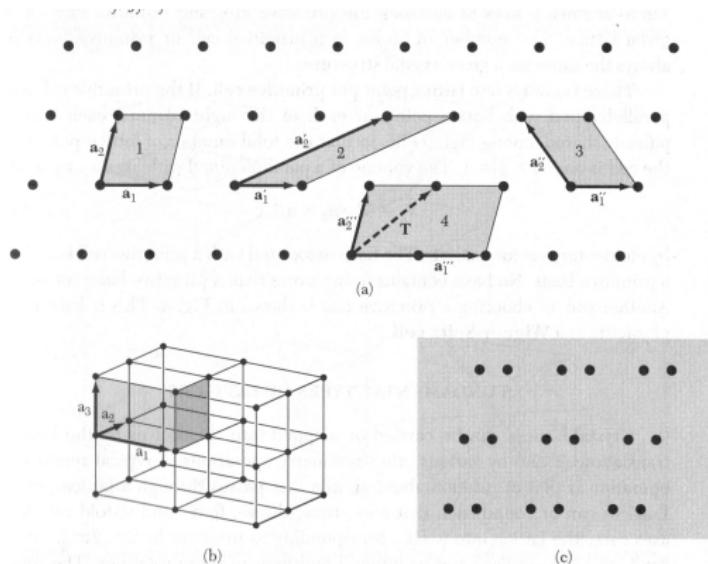


Figure 3a Lattice points of a space lattice in two dimensions. All pairs of vectors \mathbf{a}_1 , \mathbf{a}_2 are translation vectors of the lattice. But \mathbf{a}_1''' , \mathbf{a}_2''' are not primitive translation vectors because we cannot form the lattice translation \mathbf{T} from integral combinations of \mathbf{a}_1''' and \mathbf{a}_2''' . The other pairs shown of \mathbf{a}_1 and \mathbf{a}_2 may be taken as the primitive translation vectors of the lattice. The parallelograms 1, 2, 3 are equal in area and any of them could be taken as the primitive cell. The parallelogram 4 has twice the area of a primitive cell.

Figure 3b Primitive cell of a space lattice in three dimensions.

Figure 3c Suppose these points are identical atoms: Sketch in on the figure a set of lattice points,

Lattice Properties

- **Coordination Number** \triangleq Number of nearest neighbors at each lattice point.
- **Primitive cell**. Cell of minimum volume that fills all space when translated through **all** translation vectors.
 - NOTE Any primitive cell contains exactly one lattice point or fractions of a lattice point adding up to one.
 - NOTE Any **non-primitive** cell contains more than one lattice point.
 - **Wigner-Seitz Cell** \triangleq Region closer to a given lattice point than any other.

To construct it:

- 1 Choose a lattice point.
- 2 Draw lines connecting it to its surrounding points.
- 3 Draw planes bisecting each lines.
- 4 WSC is the smallest volume bounded by these planes containing the chosen point.

2D and 3D Lattices

- Based on a set of space group symmetry operations (operations that take - transform the lattice into itself) we can identify 5 types of two-dimensional lattices and 14 types of three-dimensional lattices.

Table 1 The 14 lattice types in three dimensions

System	Number of lattices	Restrictions on conventional cell axes and angles
Triclinic	1	$a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2	$a_1 \neq a_2 \neq a_3$ $\alpha = \gamma = 90^\circ \neq \beta$
Orthorhombic	4	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$
Tetragonal	2	$a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$
Cubic	3	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90^\circ$
Trigonal	1	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma < 120^\circ, \neq 90^\circ$
Hexagonal	1	$a_1 = a_2 \neq a_3$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$

Figure: Three-dimensional space lattices

- These are called **Bravais Lattices**

Cubic Lattices

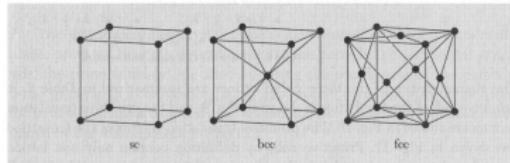


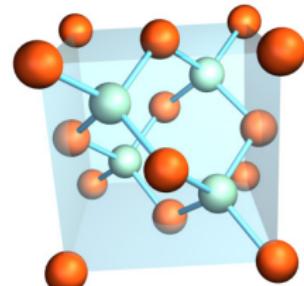
Figure 8 The cubic space lattices. The cells shown are the conventional cells.

- Simple Cubic (SC).
- Body-centered Cubic (BCC).
- Face-centered Cubic (FCC).
- NOTE: the majority of semiconductors of technological relevance are FCC, in particular Silicon and the III-Vs.
- The FCC bravais lattice with the Si atom basis is called **diamond**.
- The FCC bravais lattice with the III-V atom basis is called **zincblend**.

Table 2 Characteristics of cubic lattices^a

	Simple	Body-centered	Face-centered
Volume, conventional cell	a^3	a^3	a^3
Lattice points per cell	1	2	4
Volume, primitive cell	a^3	$\frac{1}{8}a^3$	$\frac{1}{8}a^3$
Lattice points per unit volume	$1/a^3$	$2/a^3$	$4/a^3$
Number of nearest neighbors	6	8	12
Nearest-neighbor distance	a	$\sqrt[3]{a/2} = 0.866a$	$a/2^{1/2} = 0.707a$
Number of second neighbors	12	6	6
Second neighbor distance	$2^{1/2}a$	a	a
Packing fraction ^a	$\frac{1}{6}\pi$ = 0.524	$\frac{1}{8}\pi\sqrt{3}$ = 0.680	$\frac{1}{8}\pi\sqrt{2}$ = 0.740

^aThe packing fraction is the maximum proportion of the available volume that can be filled with hard spheres.



Hexagonal Lattices

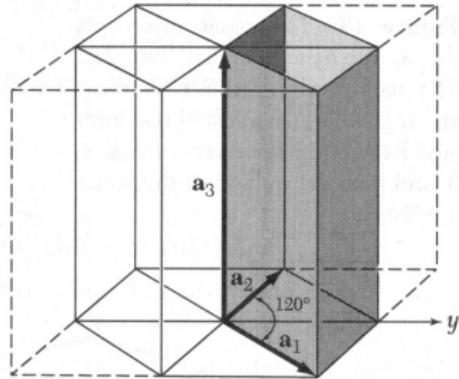
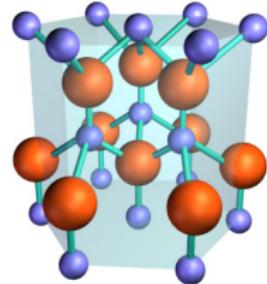


Figure 12 Relation of the primitive cell in the hexagonal system (heavy lines) to a prism of hexagonal symmetry. Here $a_1 = a_2 \neq a_3$.

- Simple Hexagonal (SH).



- NOTE: new technologically relevant semiconductors such as the III-Nitrides have an exaggerated hexagonal crystal structure.
- The hexagonal bravais lattice with the four III-V atom basis is called **Wurtzite**.

Cubic, Wurtzite, 4H and 6H Crystals

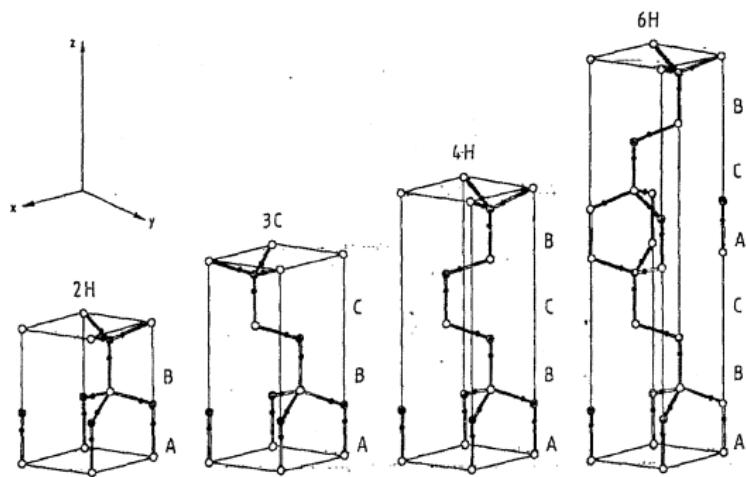
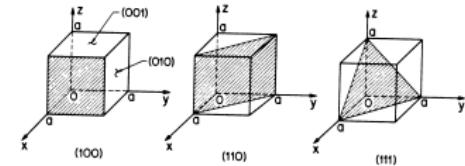


FIG. 2. Unit cells of the hexagonal SiC polytypes 2H, 4H, and 6H. For completeness the 3C structure is also drawn in a hexagonal cell. Furthermore, the stacking sequences AB, ABC, ABCB, and ABCACB are indicated. Si atoms are denoted by open circles, C atoms by hatched circles, and bond charges by dots.

Index System

- To specify a particular plane or direction in a crystal structure a set of indeces is normally used -
- Miller Indices.** They are obtained as follows:

- Define a set of crystal axes $\vec{a}_1, \vec{a}_2, \vec{a}_3$ (\vec{a}_4 for hexagonal lattice).
- Find the intercept point between plane with axes $x_1 \vec{a}_1, x_2 \vec{a}_2, x_3 \vec{a}_3$ ($x_4 \vec{a}_4$).
- Miller indices of the plane are the smallest set of integers (h, k, l) : $h = C/x_1, k = C/x_2, l = C/x_3$ ($m = C/x_4$)
- NOTE: $(h, \bar{k}, l) = (h, -k, l)$
- NOTE: $\{h, k, l\}$ define all the planes equivalent to (h, k, l) by symmetry.



- To specify a particular direction:
- Define a set of crystal axes $\vec{a}_1, \vec{a}_2, \vec{a}_3$ (\vec{a}_4).
- Find the components of \vec{U} along the axes $\vec{U} = x_1 \vec{a}_1 + x_2 \vec{a}_2 + x_3 \vec{a}_3 (+ x_4 \vec{a}_4)$.
- Miller indices: smallest set of integers $[h, k, l]$: $h = Cx_1, k = Cx_2, l = Cx_3, (m = Cx_4)$
- NOTE: $\langle h, k, l \rangle$ all the directions equivalent to $[h, k, l]$ by symmetry.

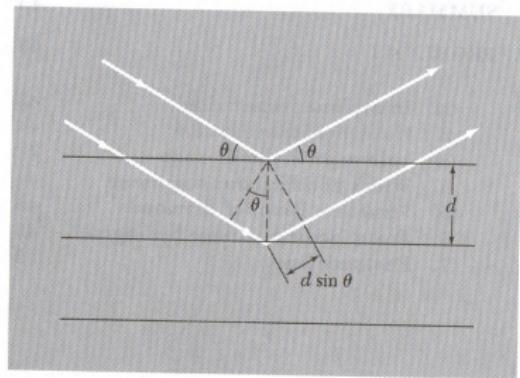
Some Important Crystals

- **Sodium-Chloride NaCl** - Lattice FCC - Two basis atom displaced by $a/2(\vec{a_1}, \vec{a_2}, \vec{a_3})$ - Coordination number 4 - It is an ionic crystal.
- **Zincblende Crystal** - Lattice FCC - Two different atom basis displaced by $a/4(\vec{a_1}, \vec{a_2}, \vec{a_3})$ - Coordination number 2 - It is an ionic/covalent crystal. Note that there is no symmetry of inversion along $\hat{x} + \hat{y} + \hat{z}$.
- **Diamond Crystal** - Lattice FCC - Two similar atom basis displaced by $a/4(\vec{a_1}, \vec{a_2}, \vec{a_3})$ - Coordination number 2 - It is a covalent crystal. Note that there is symmetry of inversion along $\hat{x} + \hat{y} + \hat{z}$.
- **Hexagonal Closed-Packed (hcp)** - Lattice SH - Two similar atom basis displaced by $1/3\vec{a_1} + 1/3\vec{a_2} + 1/2\vec{a_3}$ - A possible way of packing rigid spheres as close as possible if $c/a = \sqrt{8/3}$ or FCC - Metals and Molecular Crystals.
- **Wurtzite** - Lattice SH - Four atom (two types) basis. Two HCP structures with different atoms displaced by $8/3 c \hat{z}$ - coordination number 4 - ionic/covalent bonding - III-N and II-VI semiconductors - no inversion symmetry along \hat{z} .

Crystals Diffraction

- The study of the light diffraction patterns from crystal is an important tool to study their properties. We will look at Bragg's and Laue's formulations and define the reciprocal lattice and Brillouin Zone.

Bragg Formulation



- Bragg Diffraction geometry

- Assumes that the diffraction occurs from parallel planes spaced at a distance d .
- We have diffraction peaks when constructive interference is present.

$$\frac{2\pi}{\lambda} (\overline{AB} + \overline{BC}) = 2m\pi \quad (2)$$

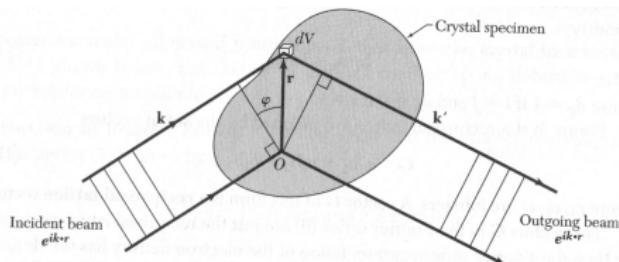
where m is an integer number and λ the radiation wavelength.

$\lambda = \sin\theta 2d \leq 2d$, the radiation wavelength has to be smaller than the distance between planes. Since the atomic planes distance is typically less than a few Angstroms X-ray radiation is needed.

NOTE – The diffraction condition is only dependent on the crystal geometry and not on its composition.

NOTE – Changing the incidence angle θ different sets of planes (hkl) can be probed.

Laue Formulation



- Laue Diffraction geometry: assumes that the diffraction occurs from each lattice point in all the directions.

– If $\vec{r} = \vec{T} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$ is a Lattice Translation Vector or Direct Lattice Vector, then:

$$\frac{2\pi}{\lambda} (\overline{AB} + \overline{BC}) = 2m\pi \quad (3)$$

and

$$\overline{AB} = T \cos\theta = \vec{T} \cdot \vec{k} \quad (4)$$

$$(\vec{k} - \vec{k}') \cdot \vec{T} = \vec{G} \cdot \vec{T} = 2m\lambda \quad (6)$$

- We obtain a diffraction peak in correspondence of each translation vector \vec{T} for a given vector $\vec{G} = \vec{k} - \vec{k}'$. Such a vector is called Reciprocal Lattice vector.

– Reciprocal Lattice Vectors

Because of the periodicity of the crystal, physical quantities, for example the electronic charge, have the same symmetry. In this case if $n(\vec{r})$ is the charge distribution in the crystal then $n(\vec{r} + \vec{T}) = n(\vec{r})$

- Since $n(\vec{r})$ is a periodic function then it can be represented as a (3D) fourier series, or:

$$n(\vec{r}) = \sum_{\vec{G}} n_{\vec{G}} e^{i\vec{G} \cdot \vec{r}} \quad (7)$$

NOTE – The quantities $n_{\vec{G}}$ are the X-ray scattered amplitude and the vectors \vec{G} have to be determined so that $n(\vec{r})$ is invariant for all the translation $n(\vec{T})$. To this end we will first define the primitive vectors of the Reciprocal Lattice.

The Bloch's Theorem

- Let us consider a generic crystal that is specified by three noncoplanar vector $\{\vec{a}_1, \vec{a}_2, \vec{a}_3\}$, such that any lattice vector \vec{R}_i can be expressed as,

$$\vec{R}_i = n_{i,1}\vec{a}_1 + n_{i,2}\vec{a}_2 + n_{i,3}\vec{a}_3$$

the integers $n_{i,j}$ define the lattice.

- If the crystal has only one atom in the unit cell, then \vec{R}_i defines the positions of all the atoms.
- If there is more than one atom we need a set of basis vectors \vec{d}_j , and j spans all the atoms in the unit cell.
- Then the positions of all the atoms in the unit cell id given by:

$$\vec{X}_{i,j} = \vec{R}_i + \vec{d}_j$$

- If we now consider the potential $\vec{V}(\vec{r})$ the periodicity requires that

$$\vec{V}(\vec{r} + \vec{R}_i) = \vec{V}(\vec{r})$$

The Bloch's Theorem - II

What can we say about the solution of the Schrödinger equation?

- Consider the solution $\Psi(\vec{r})$ of:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \Psi(\vec{r}) = E \Psi(\vec{r}) \quad (8)$$

- If we consider the physical interpretation of the wavefunction, that is the charge density $\rho(\vec{r}) = q|\Psi(\vec{r})|^2$, then clearly has to be:

$$\rho(\vec{r}) = q|\Psi(\vec{r})|^2 = q|\Psi(\vec{r} + \vec{R}_i)|^2$$

- Since the charge density does not depend on the position where we set our reference system. Although this poses a requirement on the absolute square value of the wavefunction we still have to understand how the wavefunction itself transforms.

Translation Operator

- Let us consider now a set of operators $\mathcal{T}(\vec{R}_i)$, such that given a function $f(\vec{r})$, translate this function by a certain vector \vec{R}_i . The translation operator acts on $f(\vec{r})$ so that:

$$\mathcal{T}\vec{R}_i f(\vec{r}) = f(\vec{r} + \vec{R}_i)$$

- One can verify that the translation operator and the Hamiltonian commute,

$$[\mathcal{T}(\vec{R}_i), H] = 0 \tag{9}$$

Consequently, the Hamiltonian and the operator \mathcal{T} have a set of common wavefunctions.

- Note that if $\vec{R}_I = \vec{R}_i + \vec{R}_j$ then:

$$\mathcal{T}(\vec{R}_I) = \mathcal{T}(\vec{R}_i + \vec{R}_j) = \mathcal{T}(\vec{R}_i)\mathcal{T}(\vec{R}_j)$$

Translation Operator - II

- Due to Eq.9, the solutions of Eq. 8 are also solutions of the eigenvalues equation for the translation operator:

$$\mathcal{T}(\vec{R}_i)\Psi(\vec{r}) = \lambda(\vec{R}_i)\Psi(\vec{r})$$

where $\lambda(\vec{R}_i)$ is the eigenvalue.

- Now following the definition of translation operator we can write:

$$\mathcal{T}(\vec{R}_i)\Psi(\vec{r}) = \Psi(\vec{r} + \vec{R}_i) = \lambda(\vec{R}_i)\Psi(\vec{r}) \quad (10)$$

- Since $|\Psi(\vec{r})|^2 = |\Psi(\vec{r} + \vec{R}_i)|^2$ It follows that the eigenvalue of Eq.10 needs to be of the form:

$$|\lambda(\vec{R}_i)|^2 = 1$$

or

$$\lambda(\vec{R}_i) = e^{i\theta(\vec{R}_i)} = e^{i\vec{k}\cdot\vec{R}_i}$$

For the wavefunctions follows that:

The Bloch's Theorem - III

Bloch's Therorem

$$\Psi(\vec{r} + \vec{R}_i) = e^{i(\vec{k} \cdot \vec{R}_i)} \Psi(\vec{r})$$

The solution of the Schrödinger equation has the same periodicity of the potential. \vec{k} is a characteristic of a given wavefunction and determines the eigenvalues for all translations R_i

Note

If the potential is no longer periodic as a result of an external perturbation, then Bloch's theorem is no longer applicable.

Note

As opposed to the charge density $\rho(\vec{r}) = q|\Psi(\vec{r})|^2$ in the crystal that is periodic, the wavefucntions are not and they are multiplied by a *phase factor*: $e^{i(\vec{k} \cdot \vec{R}_i)}$

Bloch's Wavefunctions

Bloch's Wavefunctions

In general terms we can write the *Bloch wavefunction* as the product of a plane wave and a function $u(\vec{k}, \vec{r})$ that has the periodicity of the crystal:

$$\Psi(\vec{k}, \vec{r}) = e^{i\vec{k} \cdot \vec{r}} u(\vec{k}, \vec{r})$$

and

$$\Psi(\vec{k}, \vec{r} + \vec{R}_i) = e^{i\vec{k} \cdot \vec{R}_i} u(\vec{k}, \vec{r}) = e^{i\vec{k} \cdot (\vec{r} + \vec{R}_i)} u(\vec{k}, \vec{r} + \vec{R}_i)$$

then

$$u(\vec{k}, \vec{r}) = u(\vec{k}, \vec{r} + \vec{R}_i)$$

Envelope Wavefunctions

The function $u(\vec{k}, \vec{r})$ has the same periodicity of the crystal.

Wavevector \vec{k} and Periodic Boundary Conditions

- The wavevector \vec{k} defines the Bloch wavefunction and determines the eigenvalues.
- How do we specify \vec{k} ? → **Impose periodic boundary conditions on the solution.**
- We consider an infinitely extending crystal and a set of three integers $\{N_1, N_2, N_3\}$. We will consider first the N_j finite and then will take the limit to infinity.
- The entire crystal repeats itself in all directions defined by the translation vectors:

$$\vec{R}_1 = (2N_1 + 1)\vec{a}_1; \quad \vec{R}_2 = (2N_2 + 1)\vec{a}_2; \quad \vec{R}_3 = (2N_3 + 1)\vec{a}_3$$

due to the Bloch's Theorem these vectors need to satisfy to conditions:

$$e^{\vec{k} \cdot (2N_1 + 1)\vec{a}_1} = e^{\vec{k} \cdot (2N_2 + 1)\vec{a}_2} = e^{\vec{k} \cdot (2N_3 + 1)\vec{a}_3} = 1 \quad (11)$$

Reciprocal Space and Reciprocal Lattice Vectors

– To find the condition on \vec{k} to satisfy Eq.11, we introduce three vectors \vec{b}_1 , \vec{b}_2 , and \vec{b}_3 that satisfy the condition:

$$\vec{b}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$$

and are defined as:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}; \quad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}; \quad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$

Reciprocal Lattice

\vec{b}_1 , \vec{b}_2 , and \vec{b}_3 define a periodic in wavevector space: *Reciprocal Lattice*.

Reciprocal Lattice Vectors

$\vec{G}_j = g_{j,1}\vec{b}_1 + g_{j,2}\vec{b}_2 + g_{j,3}\vec{b}_3$ are reciprocal lattice vectors that span the entire *Reciprocal Lattice*, and $g_{j,1}$ are integers.

Reciprocal Space and Reciprocal Lattice Vectors - II

Reciprocal Lattice Vectors

The *reciprocal lattice vectors* defines all the n points in the *Reciprocal Lattice*, and satisfy the condition:

$$\vec{G}_i \cdot \vec{R}_j = 2\pi n_{i,j} \quad (12)$$

with $n_{i,j}$ an integer.

Equivalent \vec{k}

Consider the vector

$$\vec{k}' = \vec{G}_j + \vec{k} \quad (13)$$

\vec{k}' and \vec{k} are said to be equivalent since:

$$e^{i\vec{k}' \cdot \vec{R}_j} = e^{i(\vec{k} + \vec{G}_j) \cdot \vec{R}_j} = e^{i\vec{k} \cdot \vec{R}_j} \quad (14)$$

for all lattice vectors \vec{R}_j

Equivalent \vec{k} : Eigenvalues and Eigenfunctions

- Due to the definition of equivalent \vec{k} , $\Psi(\vec{k}, \vec{r})$ and $\Psi(\vec{k}', \vec{r})$ have the same eigenvalue $\lambda(\vec{R}_j)$ for each translation \vec{R}_j .
- This also means that $\Psi(\vec{k}, \vec{r})$ and $\Psi(\vec{k}', \vec{r})$ satisfy the same boundary conditions.

Brillouin Zone

As a result of Eq.12 there is a region in \vec{k} -space in which no two \vec{k} and \vec{k}' are equivalent: *Brillouin Zone*.

Brillouin Zone Eigenvalues and Eigenfunctions

For \vec{k} in the *Brillouin Zone* we define the Bloch wavefunctions such that:

$$\Psi_n(\vec{k}, \vec{r}) = \Psi_n(\vec{k} + \vec{G}_j, \vec{r}) \quad (15)$$

$$H\Psi_n(\vec{k}, \vec{r}) = E_n(\vec{k})\Psi_n(\vec{k}, \vec{r}) \quad (16)$$

$$E_n(\vec{k}) = E_n(\vec{k} + \vec{G}_j) \quad (17)$$

(This is for \vec{k} in the FBZ and \vec{k}' outside)

Reciprocal Lattice and Brillouin Zone Summary

We define the primitive vectors of the reciprocal lattice as:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$

It can be verified that

$$\vec{b}_i \cdot \vec{a}_j = 2\pi \delta_{ij}$$

In the same way we defined the direct lattice vectors we can define reciprocal lattice vectors:

$$\vec{G}_j = m_{j,1} \vec{b}_1 + m_{j,2} \vec{b}_2 + m_{j,3} \vec{b}_3$$

Where $m_{j,i}$ are integers. It can be verified that

$$e^{\vec{G}_j \cdot \vec{R}_i} = 1 \quad (18)$$

Consequently we have:

$$\begin{aligned} n(\vec{r} + \vec{R}_i) &= \sum_{\vec{G}_j} n_{\vec{G}_j} e^{i\vec{G}_j \cdot \vec{r}} e^{i\vec{G}_j \cdot \vec{R}_i} \\ &= \sum_{\vec{G}_j} n_{\vec{G}_j} e^{i\vec{G}_j \cdot \vec{r}} = n(\vec{r}) \end{aligned}$$

Because of equation (18).

Reciprocal Lattice and Brillouin Zone Summary - II

Reciprocal Lattice

Reciprocal Lattice \triangleq Set of all the points with vector position
 $\vec{G}_j = m_{j,1}\vec{b}_1 + m_{j,2}\vec{b}_2 + m_{j,3}\vec{b}_3$, where $m_{j,i}$ are integers, and satisfy equation (18).

Brillouin Zone

Brillouin Zone \triangleq Is defined as a Wigner-Seitz primitive cell in the reciprocal lattice. (Using the same construction of the one in the direct lattice)

First Brillouin Zone

First Brillouin Zone \triangleq Is defined as the smallest volume entirely enclosed by planes that are perpendicular bisectors of the reciprocal lattice vectors drawn from the origin.

Reciprocal Lattice and Brillouin Zone Summary - III

SC Lattice

The simple cubic (SC) crystal with lattice constant a is associated with a simple cubic (SC) reciprocal lattice of size $2\pi/a$.

BCC Lattice

The BCC crystal with lattice constant a is associated with a FCC reciprocal lattice of size $4\pi/a$

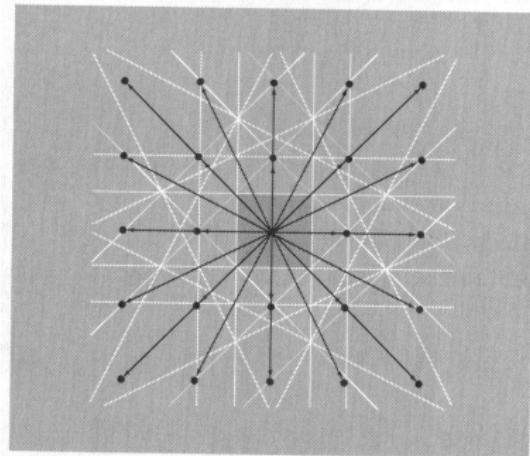
FCC Lattice

The FCC crystal with lattice constant a is associated with a BCC reciprocal lattice of size $4\pi/a$

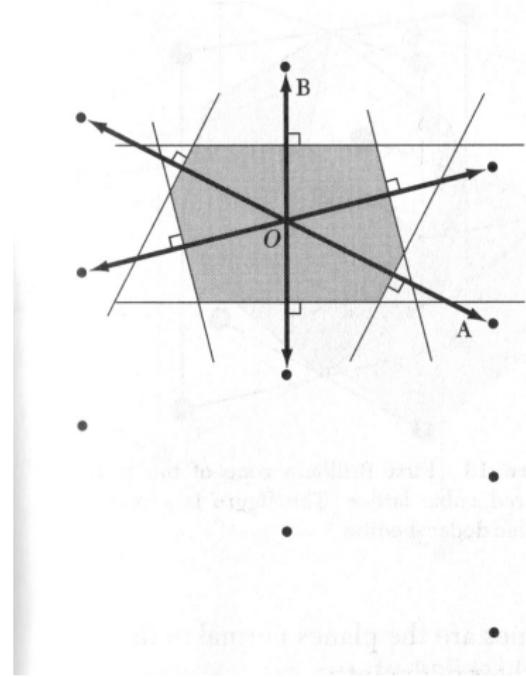
Hexagonal Lattice

The simple hexagonal crystal with lattice constants a and c is associated with a simple hexagonal reciprocal lattice of size $4\pi/\sqrt{3}a$ and $2\pi/c$, and rotated 30° about the c-axis relative to the direct lattice.

First Brillouin Zone (FBZ) Construction

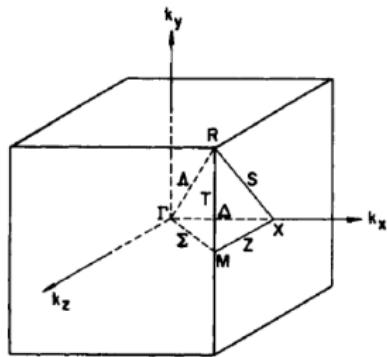


Construction of the FBZ for a square lattice.

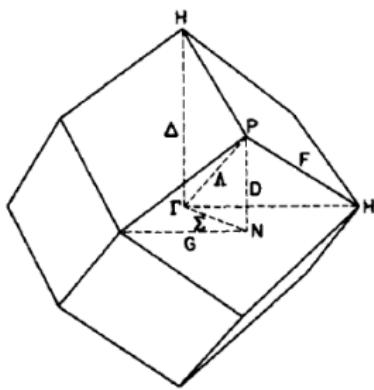


FBZ for a square lattice for an oblique lattice in two dimensions

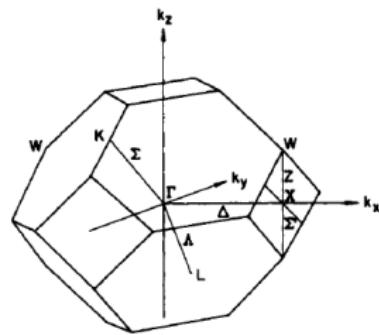
First Brillouin Zones



FBZ of the simple cubic (SC) lattice.

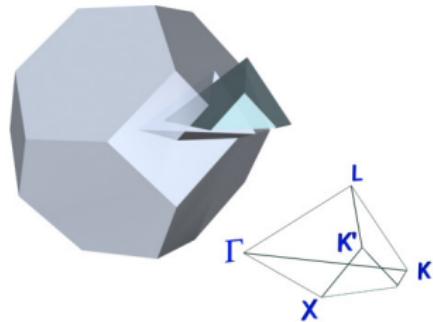


FBZ of the body centered cubic (BCC) lattice.

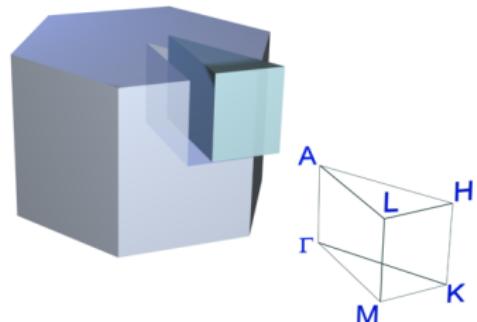


FBZ of the face centered cubic (FCC) lattice.

First Brillouin Zone: FCC and SH



- The FBZ of a FCC lattice is a truncated octahedron.
- Most of the conventional III-V semiconductors with Zincblende (two interpenetrated FCC) structure have this first BZ.



- The FBZ of a SH lattice is still a SH.
- The new III-N semiconductors with Wurtzite (two interpenetrated SH) structure have this first BZ.

Crystal Momentum

- The Bloch wavefunction for the electron in a periodic potential is:

$$\Psi(\vec{k}, \vec{r}) = e^{i\vec{k} \cdot \vec{r}} u(\vec{k}, \vec{r})$$

and

$$u(\vec{k}, \vec{r}) = u(\vec{k}, \vec{r} + \vec{R}_i)$$

if we apply the momentum operator we have:

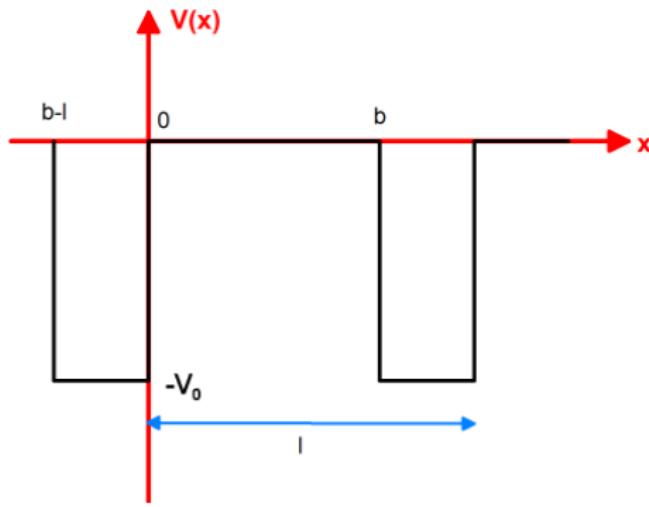
$$-i\hbar \nabla \Psi(\vec{k}, \vec{r}) = \hbar \vec{k} e^{i\vec{k} \cdot \vec{r}} u(\vec{k}, \vec{r}) - i\hbar e^{i\vec{k} \cdot \vec{r}} \nabla u(\vec{k}, \vec{r})$$

$$-i\hbar \nabla \Psi(\vec{k}, \vec{r}) = \hbar \vec{k} \Psi(\vec{k}, \vec{r}) - i\hbar e^{i\vec{k} \cdot \vec{r}} \nabla u(\vec{k}, \vec{r})$$

- \vec{k} is not proportional to the electrons' momentum since the hamiltonian does not full translational invariance (the potential is periodic but not constant).
- Although $\hbar \vec{k}$ is not the true electron momentum nevertheless it is normally described (in analogy with the free particle) as the crystal momentum.

Periodic Potential: The Kronig-Penney Model

- Consider a simple 1D periodic potential as illustrated in the figure below:



- The potential repeats itself after a period of length l and it is confining between $b-l$ and b .
- This can be realized using a multiple semiconductor quantum well (MQW) or due to the presence of an ion core at each confining region.

The Kronig-Penney Model: Confining Region $-V_0 < E < 0$

- We solve the Schrödinger equation within the wells and in the barriers between two wells.
- For $b - l < x < 0$ we have:

$$\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x) + \alpha^2 \Psi(x) = 0; \quad \alpha = \left[\frac{2m}{\hbar^2} (V_0 + E) \right]^{\frac{1}{2}}$$

- For $0 < x < b$ we have:

$$\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x) - \beta^2 \Psi(x) = 0; \quad \beta = \left[-\frac{2m}{\hbar^2} E \right]^{\frac{1}{2}}$$

- The two solutions are:

$$\Psi(x) = A e^{i\alpha x} + B e^{-i\alpha x}; \quad b - l \leq x \leq 0 \quad (19)$$

$$\Psi(x) = C e^{\beta x} + D e^{-\beta x}; \quad 0 \leq x \leq b \quad (20)$$

The Kronig-Penney Model: Boundary Conditions I

- We have two kinds of boundary conditions that we need to impose to determine the four coefficients A, B, C, and D.
- 1 – Since the potential is periodic, the solution has to be of the form:

$$\Psi(\vec{k}, \vec{r}) = e^{i\vec{k} \cdot \vec{r}} u(\vec{k}, \vec{r}); \quad u(\vec{k}, \vec{r}) = e^{-i\vec{k} \cdot \vec{r}} \Psi(\vec{k}, \vec{r})$$

Substituting the expression for the wavefunctions (Eq.23 and 22) in the Bloch wavefunction and collecting the exponential we have:

$$u(k, x) = A e^{i(\alpha - k)x} + B e^{-i(\alpha + k)x}; \quad b - l \leq x \leq 0 \quad (21)$$

$$u(k, x) = C e^{(\beta - ik)x} + D e^{-(\beta + ik)x}; \quad 0 \leq x \leq b \quad (22)$$

Additionally $u(k, x)$ need to have the same periodicity of $V(x)$, that is:

$$u(k, x) = A e^{i(\alpha - k)(x - l)} + B e^{-i(\alpha + k)(x - l)}; \quad b \leq x \leq l \quad (23)$$

The Kronig-Penney Model: Boundary Conditions II

– 2 – We need to impose the continuity of the wavefunction and conservation of the probability current density within each period. We can set this at $x = 0$ and $x = b$, furthermore due to the Bloch wavefunctions this will hold for all the other periods.

$$u(k, 0^-) = u(k, 0^+); \quad \left. \frac{\partial u(k, x)}{\partial x} \right|_{x=0^-} = \left. \frac{\partial u(k, x)}{\partial x} \right|_{x=0^+}$$

That results in two conditions:

$$A + B = C + D$$

$$\imath(\alpha - k)A - \imath(\alpha + k)B = (\beta - \imath k)C - (\beta + \imath k)D$$

The Kronig-Penney Model: Boundary Conditions III

At $x = b$ we have:

$$u(k, b^-) = u(k, b^+); \quad \left. \frac{\partial u(k, x)}{\partial x} \right|_{x=b^-} = \left. \frac{\partial u(k, x)}{\partial x} \right|_{x=b^+}$$

That results in two conditions:

$$Ae^{-\imath(\alpha-k)(l-b)} + Be^{\imath(\alpha+k)(l-b)} = Ce^{(\beta-\imath k)b} + De^{-(\beta+\imath k)b}$$

and

$$\begin{aligned} & \imath(\alpha - k)Ae^{-\imath(\alpha-k)(l-b)} - \imath(\alpha + k)Be^{\imath(\alpha+k)(l-b)} \\ &= (\beta - \imath k)Ce^{(\beta-\imath k)b} - (\beta + \imath k)De^{-(\beta+\imath k)b} \end{aligned}$$

The two sets of two equations for $x = 0$ and $x = b$, provide a system of four equations in the four unknowns: A, B, C, and D.

The non trivial solution occurs when the determinant of the 2x2 coefficient matrix is zero.

The Kronig-Penney Model: Energy Eigenvalues

The secular equation is given by:

$$\cos[\alpha(l - b)]\cosh(\beta b) - \frac{\alpha^2 - \beta^2}{2\alpha\beta}\sin[\alpha(l - b)]\sinh(\beta b) = \cos kl \quad (24)$$

This is a transcendental (non-linear) equation in the energy E that is in the expressions of α and β .

$$\alpha = \left[\frac{2m}{\hbar^2} (V_0 + E) \right]^{\frac{1}{2}}; \quad \beta = \left[-\frac{2m}{\hbar^2} E \right]^{\frac{1}{2}}$$

Given a value of the energy E , the corresponding values of α and β are computed and the LHS of Eq.25 is evaluated.

The only acceptable values of E are those for which:

$$-1 \leq \cos[\alpha(l - b)]\cosh(\beta b) - \frac{\alpha^2 - \beta^2}{2\alpha\beta}\sin[\alpha(l - b)]\sinh(\beta b) \leq 1 \quad (25)$$

The Kronig-Penney Model: Unbound States $E > 0$

- For $b - l < x < 0$ we have:

$$\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x) + \alpha^2 \Psi(x) = 0; \quad \alpha = \left[\frac{2m}{\hbar^2} (V_0 + E) \right]^{\frac{1}{2}}$$

- For $0 < x < b$ we have:

$$\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x) + \beta^2 \Psi(x) = 0; \quad \beta = \imath \bar{k} = \imath \left[\frac{2m}{\hbar^2} E \right]^{\frac{1}{2}}$$

- The two solutions are:

$$\Psi(x) = A e^{\imath \alpha x} + B e^{-\imath \alpha x}; \quad b - l \leq x \leq 0$$

$$\Psi(x) = C e^{\imath \beta x} + D e^{-\imath \beta x}; \quad 0 \leq x \leq b$$

The Kronig-Penney Model: Energy Dispersion

Using the same boundary conditions for $x = 0$ and $x = b$, the secular equation is given by:

$$\cos[\alpha(l - b)]\cos(\bar{k}b) - \frac{\alpha^2 + \bar{k}^2}{2\alpha\bar{k}}\sin[\alpha(l - b)]\sin(\bar{k}b) = \cos kl \quad (26)$$

Note that the value \bar{k} is determined once the energy value E is chosen.

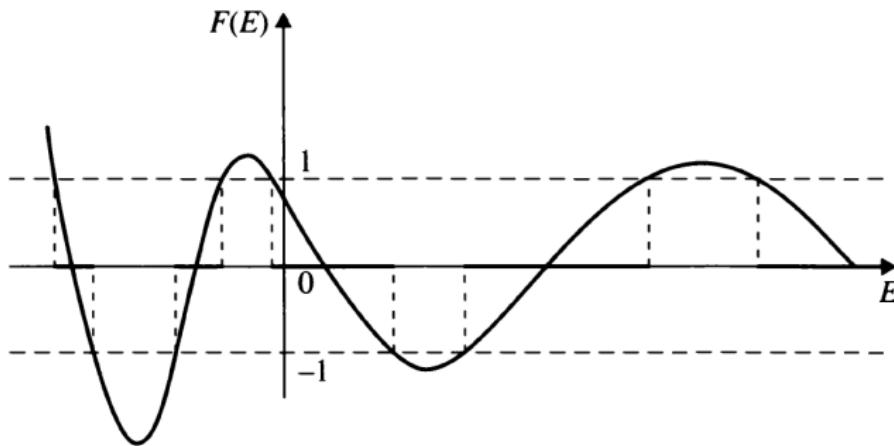
Energy Dispersion

The two equations Eq.25 and Eq.26 have the same value at $E=0$. As a result we can express these two equations as:

$$F(E) = \cos kl \quad (27)$$

The only possible states for the particle are the ones for which the energy satisfies Eq.27.

The Kronig-Penney Model: Energy Dispersion II

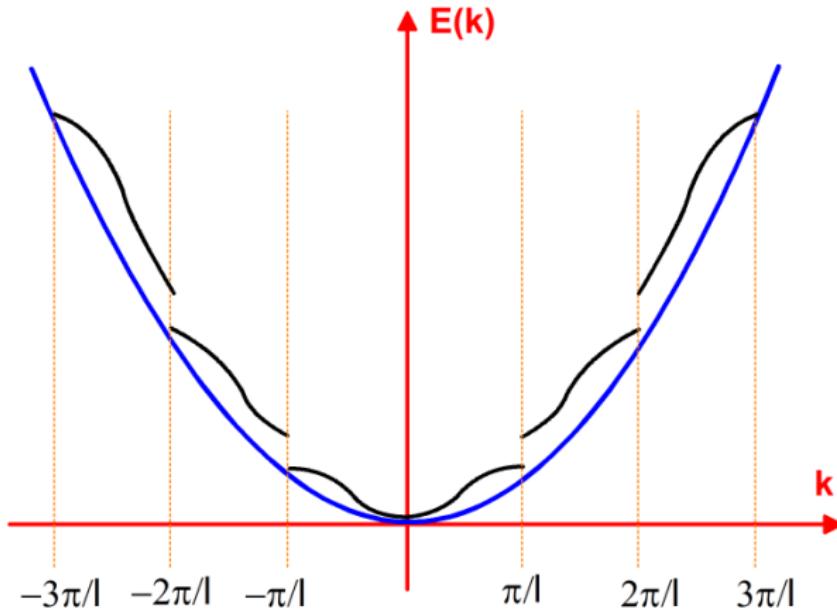


Energy Bands

For $E > 0$ the condition $-1 < \cos kl < 1$ is satisfied only in specific intervals of the energy spectrum: **Energy Bands**.

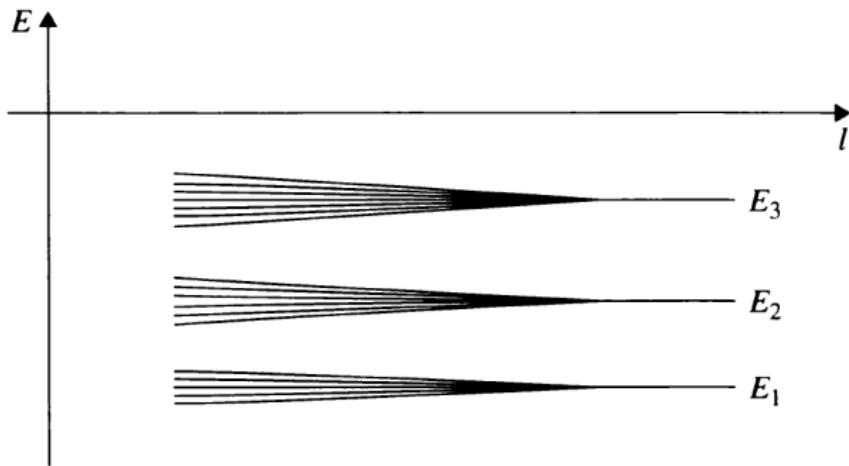
For $E < 0$ the condition $-1 < \cos kl < 1$ is satisfied for energy values for which particles tunnel from one well to another: **Extended States** or **Minibands**.

The Kronig-Penney Model: Energy Dispersion III



For a given values of $E > 0$ the solution of Eq.27 provides value of k . If we plot $E(k)$ we obtain the figure above, along with the free particle dispersion $k = \sqrt{2mE/\hbar^2}$.

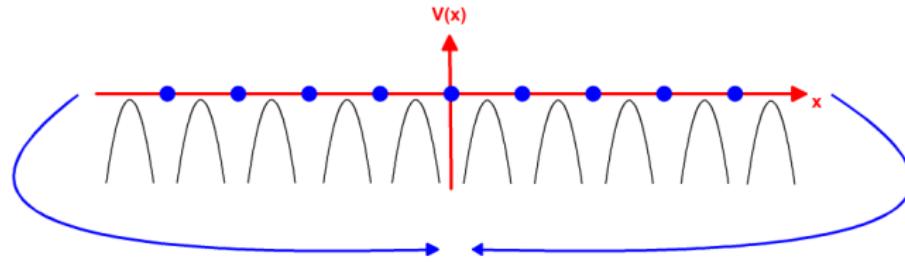
The Kronig-Penney Model: Extended States - Minibands



- In the case $-V_0 < E < 0$ if we keep the width of the well constant and increase l , the width of the minibands (extended states) in the confined regions decreases to a single energy value.
- In this case the wells are separated by increasingly wide barriers and they become isolated from one another. There are no extended states but independent quantum wells.

Kronig-Penney Model: Periodic Boundary Conditions

- The Bloch Theorem specifies the conditions that the wavefunction (solution of the Schrödinger equation) must satisfy at the boundary of each crystal *unit cell*.
- The crystal itself is finite and at the surfaces one can reasonably impose that $\Psi(\vec{k}, \vec{r}) = 0$.



- Since the crystal contains a large number N of unit cells ($N \approx 10^{23}$) one can disregard the effect of the surfaces, assume that the system is infinite in dimension and use boundary conditions.

Kronig-Penney Model: Periodic Boundary Conditions I

- If N (with $N \rightarrow \infty$) is the number of unit cells, of size l , in the crystal, then the periodic boundary conditions are written as:

$$\Psi(k, x) = \Psi(k, x + Nl) \quad (28)$$

- Since from the Bloch theorem we have:

$$\Psi(k, x + nl) = e^{i n k l} \Psi(k, x) \quad (29)$$

- Then we have:

$$e^{i N k l} = 1 \Rightarrow k = \frac{2\pi n}{Nl}, \quad n = 0, \pm 1, \pm 2, \dots \quad (30)$$

- Because of the definition of the equivalent k vectors, the energy E is unchanged if we transform k into $k + 2\pi/l$. As a result:

$$-\frac{\pi}{l} \leq k \leq \frac{\pi}{l} \quad (31)$$

From the previous discussion we have that:

Energy Bands

- There are N allowed k states in each band.
- To each k state correspond an energy eigenvalue.
- There are N energy eigenvalues in each band.
- As $I \rightarrow \infty$ the N eigenvalues collapse in to an N -fold degenerate energy state.

Energy Band Theory of Crystals

The determination of the energy bands for a crystal require addressing two main questions:

- How does one determine the periodic potential $V(\vec{r})$?
- If $V(\vec{r})$ is known, how does one solve the Schrödinger equation with appropriate boundary conditions?
- We consider a simplified picture in which each atom in the crystal is divided in a core with full electron shells and valence electrons contribution to the bonds (covalent/ionic crystal) or delocalized (metals).

$$\text{Periodic Potential } V(\vec{r}) = V_{ion}(\vec{r}) + V_H(\vec{r}) + V_{exc-corr}(\vec{r})$$

- Ionic potential $V_{ion}(\vec{r})$.
- Valence electron (Hartree) potential $V_H(\vec{r})$.
- Exchange-Correlation potential $V_{exc-corr}(\vec{r})$.
- Several (approximate) methods are available to determine $V(\vec{r})$.

Solid as a System of Non-Interacting Particles

- In a solid we need to consider a large number of interacting particles: ions and electrons.
- If they are not interacting we can always break up the Hamiltonian operator in the contribution of the single particle Hamiltonians and find the single particle wavefunction for each one of them:

$$H = \sum_i H_i \quad (32)$$

$$\left[-\frac{\hbar^2}{2m_i} \nabla_i^2 + V(\vec{r}_i) \right] \Psi(\vec{r}_n^i) = E_n \Psi(\vec{r}_n^i) \quad (33)$$

- The solution of each *single-particle* is similar to what we have already seen.
- If the particles are interacting, then the *single-particle* solution is no longer possible and a different wavefunction formulation and Hamiltonian are needed.

Solid as a System of Interacting Particles

- In a solid body we encounter a situation where we have interaction among many bodies.
- A solid is composed of an array of atoms in a crystal lattice, each one is characterized by a positive charge and a electrons surrounding it.

$$\begin{aligned} H = & \sum_i -\frac{\hbar^2 \nabla_i^2}{2M_i} + \frac{1}{2} \sum_{i,j} \frac{Z^2 e^2}{|\vec{R}_i - \vec{R}_j|} \\ & + \sum_k -\frac{\hbar^2 \nabla_k^2}{2m_k} + \frac{1}{2} \sum_{k,l} \frac{e^2}{|\vec{r}_k - \vec{r}_l|} - \frac{1}{2} \sum_{k,i} \frac{Z^2 e^2}{|\vec{r}_k - \vec{R}_i|} \end{aligned} \quad (34)$$

- The first and second terms are respectively the kinetic energy and the ion-ion interaction, \tilde{R}_j , \tilde{R}_i are the nuclear coordinate, and Z the atomic number.
- The third and fourth terms are respectively the kinetic energy and the electron-electron interaction, \tilde{r}_k , \tilde{r}_l the electron coordinates.
- The last term is the electron-ion interaction.

Solid as a System of Interacting Particles - I

- Since ions are much heavier than the electrons their velocity is much lower and the response time to an external perturbation is much longer than the one of electrons. The first two terms of Eq. 34 can be considered irrelevant as far as the electronic motion is concerned.

Adiabatic Approximation

- This assumption is the *adiabatic approximation*, and the dynamics of the electron gas is studied with the core frozen at their equilibrium positions.

Core and Valence Electrons

- Of all the electrons, those belonging to the outermost atomic shells, are the ones important in determining the properties of the solid.
- The atom can then be considered as a *core*, made up of the ionic part plus all electrons in the inner shells.
- The core is surrounded by the valence electrons. The contribution of the core electrons is then moved from the electron-electron interaction term to the ion-ion interaction part.

Solid as a System of Interacting Particles - II

- Within the *adiabatic approximation* the hamiltonian of the solid is given by:

$$H = T + V_{e,e} + V(\vec{r}) \quad (35)$$

- Where the first term is the kinetic energy
- The second the electron-electron interaction
- The third the potential due to the electronic charge of the cores.

$$H = \sum_k -\frac{\hbar^2 \nabla_k^2}{2m_k} - \frac{1}{2} \sum_{k,i} \frac{Z^2 e^2}{|\vec{r}_k - \vec{R}_i|} + \frac{1}{2} \sum_{k,l} \frac{e^2}{|\vec{r}_k - \vec{r}_l|} \quad (36)$$

- One needs to determine the solution of the Schrödinger equation with the hamiltonian of Eq. 36 for different atomic species and configurations.

The Hartree Approximation

- In the case of interacting electrons Eq. 36 indicated that the potential acts on an electron depends on all the other electrons.
- If one finds a way of making the interaction in Eq. 36 dependent only on the position of the single electron, it would be possible to separate the total hamiltonian in the single particle contributions.
- Assume that the interaction term for a single electron arises from the other electrons in fixed positions.
- In this case we can approximate the electron-electron term in Eq. 35 as:

$$V_{e,e}(\vec{r}_1 \cdots \vec{r}_N) = \frac{1}{2} \sum_{k,l} \frac{e^2}{|\vec{r}_k - \vec{r}_l|} \quad (37)$$

with:

$$\tilde{V}_{e,e}(\vec{r}_1 \cdots \vec{r}_N) = \sum_k V_k(\vec{r}_k) \quad (38)$$

The Hartree Approximation - I

- In this way the many-body Eq. 36 can be separated to obtain the single particle equation:

$$[H_0(\vec{r}_k) + V_k(\vec{r}_k)]\Psi(\vec{r}_k) = E_k \Psi(\vec{r}_k) \quad (39)$$

- Where $H_0(\vec{r}_k)$ contains the part of the hamiltonian which is separable, and $V_k(\vec{r}_k)$ the kinetic energy and the electron-ion interaction.
- In terms of electronic wavefunctions, we can write the interaction potential as a function of single particle wavefunctions:

$$V_{H,k}(\vec{r}_k) = \sum_I \int \frac{e^2 |\Psi_I(\vec{r}_I)|^2}{|\vec{r}_k - \vec{r}_I|} d\vec{r}_I \quad (40)$$

- We can start computing the interaction potential with a given set of single particle wavefunctions and, as the system develops we can compute a new set of wavefunctions and reach iteratively the solution.

The Hartree Approximation - II

Hartree Approximation

- In the *Hartree approximation* we express the many-body wavefunction as a product of single particle wavefunctions and the interaction potentials seen by one electron is the sum of all the potential from the others in a fixed position

The Hartree form of the many-body Schrödinger equation is then given by:

$$[E - \sum_{k=1}^N (H_0(\vec{r}_k) + V_k(\vec{r}_k))] \Psi(\vec{r}_1 \cdots \vec{r}_N) = 0 \quad (41)$$

and the total wavefunction is given by:

$$\Psi(\vec{r}_1 \cdots \vec{r}_N) = \Psi(\vec{r}_1)\Psi(\vec{r}_2) \cdots \Psi(\vec{r}_N) \quad (42)$$

And we have to solve N single particle equations:

$$[H_0(\vec{r}_k) + V_k(\vec{r}_k)] \Psi(\vec{r}_k) = E_k \Psi(\vec{r}_k) \quad (43)$$

The Hartree-Fock Approximation

- To improve the model provided by the Hartree approximation we need to include the the *Pauli exclusion principle* and start with an initial guess that provides the correct symmetry.
- An antisymmetric form (in spatial and spin coordinates) of the wavefunction can be written using the Slater determinant:

$$\Psi(\vec{r}_1 \cdots \vec{r}_N) = \frac{1}{\sqrt{N}} (-1)^P P \{ \Psi_\alpha(\vec{r}_1), \Psi_\beta(\vec{r}_2) \cdots \Psi_\eta(\vec{r}_N) \} \quad (44)$$

where P is a permutation operator which exchanges the labels $\alpha, \beta, \eta, \dots$

- For a two particle system we have:

$$\Psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} [\Psi_\alpha(\vec{r}_1)\Psi_\beta(\vec{r}_2) - \Psi_\beta(\vec{r}_1)\Psi_\alpha(\vec{r}_2)] \quad (45)$$

The Hartree-Fock Approximation - I

- For a N particle system the antisymmetric wavefunction can be obtained from a Slater type determinant:

$$\Psi(\vec{r}_1 \cdots \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_\alpha(\vec{r}_1) & \Psi_\alpha(\vec{r}_1) & \cdots & \Psi_\alpha(\vec{r}_N) \\ \Psi_\beta(\vec{r}_1) & \Psi_\beta(\vec{r}_1) & \cdots & \Psi_\beta(\vec{r}_N) \\ \vdots & \vdots & \vdots & \vdots \\ \Psi_\eta(\vec{r}_1) & \Psi_\eta(\vec{r}_1) & \cdots & \Psi_\eta(\vec{r}_N) \end{vmatrix}$$

- The new wavefunction is still composed of single particle wavefunction, except that now the recipe to generate to global one has changed.
- If now express the Hartree potential in the same way as before (Eq.40) and we write the single particle system of equations we have:

$$[H_0(\vec{r}) + V_{H\alpha}(\vec{r}) - E_\alpha] \Psi_\alpha(\vec{r}) + \int V_{\text{exch}}(\vec{r}, \vec{r}') \Psi_\alpha(\vec{r}') d\vec{r}' = 0 \quad (46)$$

The Hartree-Fock Approximation - II

- In addition to the Hartree potential $V_{H\alpha}(\vec{r})$ As a result of the total wavefunction symmetry properties an *exchange potential* is also needed.
- The exchange potential has the form:

$$V_{exch}(\vec{r}, \vec{r}') = \frac{-e^2}{|\vec{r} - \vec{r}'|} \sum_{\beta, \alpha \neq \beta} \Psi_\beta(\vec{r}) \Psi_\beta^*(\vec{r}')$$
 (47)

Exchange Potential

- The exchange potential is non-local, that is, it depends on two variables and it appears under the sign of integral as in (Eq. 46).
- The single particle equation – is an integro-differential equation.
- Because now the effect of the spin has been taken into account, particles of the same spin are not allowed to be in close proximity, as opposed if they had opposite spin. In this case the system experiences a *lack of charge* or *hole* and this changes the electrostatic contribution (Hartree).
- The exchange potential is a measure of the effect of the *hole state* on the single particle state.

Planewaves, Pseudopotentials and Tight Binding Method

- The Tight Binding Method (TBM) relies on the choice of a particular set of basis function to diagonalize the Hamiltonian and determine the electronic structure. The basis function chosen for the task were atomic orbitals. In this framework the valence electrons, responsible for the chemical bond where thought as loosely bound to the core. The total electronic wavefunction was computed as superposition of atomic orbitals. In this picture, although the valence electrons are still linked to some extent to the core, they are shared in the crystal.
- The opposite situation can be studied if we consider the electrons as delocalized in the whole crystal. In this case, rather than a description based on atomic orbitals, plane waves should be used and in this model electrons are considered as *nearly free* (NFE). The difference between the TBM and the NFE is that now valence electrons are no longer described as if they were localized on a particular atom, but are treated as belonging to the crystal system.

Plane Wave Expansion Method

Energy Band Theory - Expansion Methods

The unknown crystal wavefunction $\Psi(\vec{k}, \vec{r})$ is expanded in series of a CON set of known wavefunctions:

- Plane Waves - superposition of free electron states.
- Atomic Wavefunctions - superposition of localized states.
- Consider a CON set of plane waves with k-vectors equal to the reciprocal vectors $\{\vec{G}_i\}$.
- These plane waves satisfy the condition:

$$e^{i\vec{G}_i \cdot \vec{r}} = e^{i\vec{G}_i \cdot (\vec{r} + \vec{R}_j)}$$

since \vec{G} and \vec{R} are respectively a reciprocal and direct lattice vectors.

- Notice that they also satisfy Bloch Theorem:

$$e^{i(\vec{k} + \vec{G}_i) \cdot (\vec{r} + \vec{R}_j)} = e^{i\vec{k} \cdot \vec{R}_j} e^{i(\vec{k} + \vec{G}_i) \cdot \vec{r}}$$

Plane Wave Expansion Method - I

- We can expand the periodic part of the Bloch wavefunction as:

$$u(\vec{k}, \vec{r}) = \sum_{\vec{G}_i} a_{\vec{G}_i} e^{i\vec{G}_i \cdot \vec{r}}$$

- As a result the Bloch Wavefunction is expanded as:

$$\begin{aligned}\Psi(\vec{k}, \vec{r}) &= \frac{1}{\sqrt{N\Omega}} e^{i\vec{k} \cdot \vec{r}} u(\vec{k}, \vec{r}) = \frac{1}{\sqrt{N\Omega}} e^{i\vec{k} \cdot \vec{r}} \sum_{\vec{G}_i} a_{\vec{G}_i} e^{i\vec{G}_i \cdot \vec{r}} \\ &= \frac{1}{\sqrt{N\Omega}} \sum_{\vec{G}_i} a_{\vec{G}_i} e^{i(\vec{k} + \vec{G}_i) \cdot \vec{r}}\end{aligned}\quad (48)$$

Where N is the number of the elementary cells we are considering and Ω the volume of the unit cell of the crystal.

- The goal is to determine the expansion coefficients $a_{\vec{G}_i}$

Plane Wave Expansion Method - II

Let us know consider the Schrödinger equation for the crystal:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi_n(\vec{r}, \vec{k}) = E_n \psi_n(\vec{r}, \vec{k})$$

and as usual $V(\vec{r}) = V(\vec{r} + \vec{R})$. We substitute expression 48 in equation 49. We have:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \frac{1}{\sqrt{N\Omega}} \sum_{\vec{G}_i} a_{n,\vec{G}_i} e^{i(\vec{G}_i + \vec{k}) \cdot \vec{r}} = E_n \frac{1}{\sqrt{N\Omega}} \sum_{\vec{G}_i} a_{n,\vec{G}_i} e^{i(\vec{G}_i + \vec{k}) \cdot \vec{r}}$$

- Note that there is a different set of expansion coefficients a_{n,\vec{G}_i} for each eigenstate $\psi_n(\vec{r}, \vec{k})$ corresponding to a energy band eigencvalue E_n .

Plane Wave Expansion Method - III

Expanding the LHS we obtain:

$$\begin{aligned} \frac{\hbar^2}{2m} \left| \vec{G}_i + \vec{k} \right|^2 \frac{1}{\sqrt{N\Omega}} \sum_{\vec{G}_i} a_{n,\vec{G}_i} e^{i(\vec{G}_i + \vec{k}) \cdot \vec{r}} + V(\vec{r}) \frac{1}{\sqrt{N\Omega}} \sum_{\vec{G}_i} a_{n,\vec{G}_i} e^{i(\vec{G}_i + \vec{k}) \cdot \vec{r}} \\ = E_n \frac{1}{\sqrt{N\Omega}} \sum_{\vec{G}_i} a_{n,\vec{G}_i} e^{i(\vec{G}_i + \vec{k}) \cdot \vec{r}} \end{aligned} \quad (49)$$

Now we can multiply by:

$$\frac{1}{\sqrt{N\Omega}} e^{-i(\vec{G}_j + \vec{k}) \cdot \vec{r}}$$

and integrate over the entire volume of the crystal.

Plane Wave Expansion Method - IV

$$\begin{aligned} & \frac{\hbar^2}{2m} \left| \vec{G}_i + \vec{k} \right|^2 \sum_{\vec{G}_i} a_{n,\vec{G}_i} \frac{1}{N\Omega} \int e^{i(\vec{G}_i - \vec{G}_j) \cdot \vec{r}} d\vec{r} \\ & + \sum_{\vec{G}_i} a_{n,\vec{G}_i} \frac{1}{N\Omega} \int V(\vec{r}) e^{i(\vec{G}_i - \vec{G}_j) \cdot \vec{r}} d\vec{r} \\ & = E_n \sum_{\vec{G}_i} a_{n,\vec{G}_i} \frac{1}{N\Omega} \int e^{i(\vec{G}_i - \vec{G}_j) \cdot \vec{r}} d\vec{r} \end{aligned} \quad (50)$$

taking into account that,

$$\frac{1}{N\Omega} \int e^{i(\vec{G}_i - \vec{G}_j) \cdot \vec{r}} d\vec{r} = \int_{\Omega} e^{i(\vec{G}_i - \vec{G}_j) \cdot \vec{r}} d\vec{r} = \delta_{i,j}$$

it follows

Plane Wave Expansion Method - V

$$\sum_{\vec{G}_i} \left[\frac{\hbar^2}{2m} \left| \vec{G}_i + \vec{k} \right|^2 \delta_{i,j} + V(\vec{G}_i - \vec{G}_j) \right] a_{n,\vec{G}_i} = E_n \sum_{\vec{G}_i} a_{n,\vec{G}_i} \delta_{i,j}$$

where:

$$V(\vec{G}_i - \vec{G}_j) = \frac{1}{\Omega} \int_{\Omega} V(\vec{r}) e^{i(\vec{G}_i - \vec{G}_j) \cdot \vec{r}} d\vec{r}$$

is the Fourier transform of the periodic potential that has to be determined.

Secular Equation

$$\sum_{\vec{G}_i} \left[\left(\frac{\hbar^2}{2m} \left| \vec{G}_i + \vec{k} \right|^2 - E_n \right) \delta_{i,j} + V(\vec{G}_i - \vec{G}_j) \right] a_{n,\vec{G}_i} = 0 \quad (51)$$

- The secular equation Eq. 51 is a complex eigenvalue problem of infinite order.

- Once the expression of the potential is known, then the eigenvalue problem can be solved and the electronic structure computed.

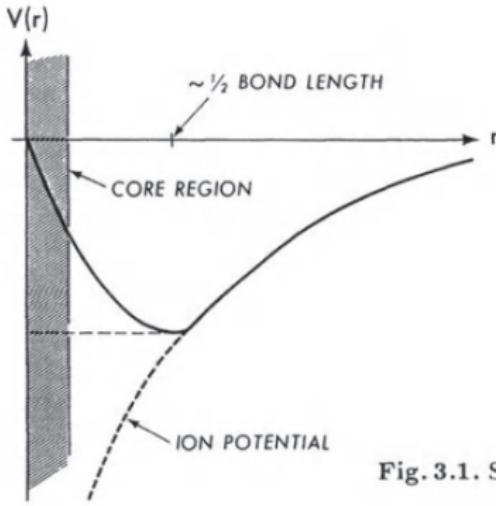


Fig. 3.1. Sch

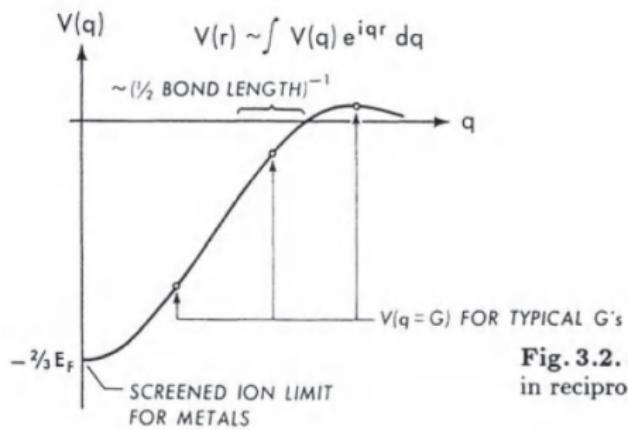


Fig. 3.2. S
in reciproc

Real space pseudopotential.

Reciprocal space (Fourier transform) pseudo potential.

- An expression for the Fourier transform of the potential can be determined from the knowledge of the particular crystal being investigated.
 - Equation 51 is the basic tool that it is used to study electronic structures every time a plane wave expansion is employed.

Secular Equation Solution Near a Bragg Plane

- Consider Eq. 51 and assume that the expansion coefficients a_{n,\vec{G}_i} are non-zero only for the first two reciprocal lattice vectors \vec{G}_0 and \vec{G}_1 .
- Eq. 51 then becomes:

$$\begin{cases} \left[(\lambda_{\vec{k}+\vec{G}_0} - E_0) + V(\vec{G}_1 - \vec{G}_0) \right] a_{\vec{G}_0} = 0 \\ \left[(\lambda_{\vec{k}+\vec{G}_0} - E_1) + V(\vec{G}_0 - \vec{G}_1) \right] a_{\vec{G}_1} = 0 \end{cases}$$

- This system of equations has non-zero solutions when the determinant is zero:

$$\begin{vmatrix} (\lambda_{\vec{k}+\vec{G}_0} - E_0) & V(\vec{G}_1 - \vec{G}_0) \\ V(\vec{G}_0 - \vec{G}_1) & (\lambda_{\vec{k}+\vec{G}_1} - E_1) \end{vmatrix} = 0$$

Secular Equation Solution Near a Bragg Plane - I

- If we assume $\vec{G}_0 = 0$ and $\vec{G}_1 \neq 0$ the boundary of the First Brillouin Zone is at $\vec{k} = \pm \frac{1}{2}\vec{G}_1$.
- The general solution of Eq. 74 is:

$$E_{\pm}(\vec{k}) = \frac{\lambda_{\vec{k}+\vec{G}_0} - \lambda_{\vec{k}+\vec{G}_1}}{2} \pm \sqrt{\left(\frac{\lambda_{\vec{k}+\vec{G}_0} - \lambda_{\vec{k}+\vec{G}_1}}{2}\right)^2 + V^2(\vec{G}_1)} \quad (52)$$

evaluated at $\vec{k} = \pm \frac{1}{2}\vec{G}_1$ we have:

$$E_{\pm} \left(\frac{1}{2}\vec{G}_1 \right) = \frac{\lambda_{\vec{G}_1/2}}{2} \pm |V(\vec{G}_1)| \quad (53)$$

with

$$\lambda_{\vec{k}+\vec{G}_1} = \lambda_{+\vec{G}_1/2} = \lambda_{-\vec{G}_1/2} = \frac{\hbar^2}{2m} \left| \frac{\vec{G}_1}{2} \right|^2 \quad (54)$$

Secular Equation Solution Near a Bragg Plane - II

- And eigenvectors:

$$\frac{a_{\vec{G}_0}}{a_{\vec{G}_1}} = \pm \frac{V(\vec{G}_1)}{|V(\vec{G}_1)|} \quad (55)$$

- The wavefunctions are of the type:

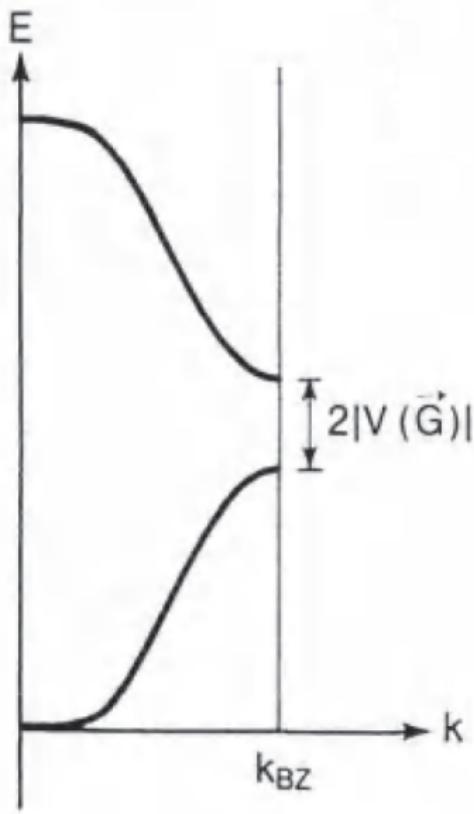
$$\psi(\vec{r}) = a_{\vec{G}_1} \left(e^{\frac{\vec{G}_1}{2} \cdot \vec{r}} \pm e^{\frac{-\vec{G}_1}{2} \cdot \vec{r}} \right) \quad (56)$$

or

$$\psi(\vec{r}) = 2a_{\vec{G}_1} \cos \left(\frac{\vec{G}_1}{2} \cdot \vec{r} \right) \quad (57)$$

$$\psi(\vec{r}) = 2\imath a_{\vec{G}_1} \sin \left(\frac{\vec{G}_1}{2} \cdot \vec{r} \right) \quad (58)$$

Secular Equation Solution Near a Bragg Plane - III



- At the edge of the FBZ the energy dispersion has an energy gap.
- At the edge of the FBZ the wavefunctions Eq. 57 and Eq. 58 are non-propagating wavefunctions: standing-waves.
- The derivate of the energy dispersion at the FBZ edge is zero.

$$v_g = \left. \frac{\partial E_{\pm}}{\partial k} \right|_{k=\frac{G_1}{2}} = 0 \quad (59)$$

Since at the FBZ edge there is no wavefunction propagation.

Energy Band Theory - Tight Binding Method

The **Tight Binding Method (TBM)** relies on the choice of a particular set of basis function to diagonalize the Hamiltonian and determine the electronic structure.

- The basis function chosen for the task are atomic orbitals.
- The valence electrons, responsible for the chemical bond are thought as loosely bound to the core.
- The total electronic wavefunction is computed as superposition of atomic orbitals.
- In this picture, although the valence electrons are still linked to some extent to the core, they are shared in the crystal.
- NOTE! As it has already been discussed, the valence electrons in the outmost shells are those more important in the formation of the chemical bond. It is then useful to divide the atom in core and valence electrons.

Energy Band Theory - Tight Binding Method

For the most important semiconductors we have valence electrons of type s and p.

Material	core	valence
C	$1s^2$	$2s^22p^2$
N	$1s^2$	$2s^22p^3$
Si	$1s^22s^62p^6$	$3s^23p^2$
Ge	$1s^22s^22p^63s^23p^63d^{10}$	$4s^24p^2$
Ga	$1s^22s^22p^63s^23p^63d^{10}$	$4s^24p^1$
As	$1s^22s^22p^63s^23p^63d^{10}$	$4s^24p^3$

In case of heavier elements like Ga or In the presence of d-orbitals, that we consider part of the core may be a problem. Such orbitals have a bonding energy similar to the 2s level in the Nitrogen atom and play a significant role in the chemical bond. In this situation it is necessary to include the effect of the d-orbitals in the valence states.

Tight Binding Method

- In the same line of thinking of the LCAO we select atomic orbitals as basis functions.
- Such functions satisfy the Schrödinger equation for the isolated atom:

$$H_A \phi_l^A = E_l^A \phi_l^A \quad (60)$$

where E_l is the energy level for the orbital ϕ_l^A of type l in the isolated atom.

- The ϕ_l^A are a C.O.N. set accordingly to the lattice site \vec{R}_i where the atoms is. For the same atomic site:

$$\int \phi_l^{A*}(\vec{r}) \phi_q^A(\vec{r}) d\vec{r} = \delta_{l,q} \quad (61)$$

or equivalently:

$$\int \phi_l^{A*}(\vec{r}) \phi_q(\vec{r} - \vec{R}_i) d\vec{r} \neq \delta_{l,q} \text{ for } \vec{R}_i \neq 0 \quad (62)$$

where \vec{R}_i is a direct lattice vector.

Tight Binding Method - II

- We can construct a Bloch function using a linear combination of $\phi_s^A(\vec{r})$.
- If \vec{R}_i are all the lattice sites in the crystal we can write a Bloch wavefunction:

LCAO Bloch Wavefunction

$$\varphi_{i,l}(\vec{k}, \vec{r}) = \frac{1}{\sqrt{N}} \sum_n e^{i(\vec{k} \cdot \vec{R}_n)} \phi_{i,l}(\vec{r} - \vec{R}_n - \vec{b}_i) \quad (63)$$

- i is the index of the atom in the basis located at \vec{b}_i in the unit cell.
- l is the index of the orbital type.
- n is the index of the lattice site we are considering.
- We expand the solution of the Schrödinger equation for the crystal using the $\varphi_{i,l}(\vec{k}, \vec{r})$.

Tight Binding Method - III

- The expansion can be written as:

$$\Psi(\vec{k}, \vec{r}) = \sum_i \sum_I c_{i,I,\vec{k}} \varphi_{i,I}(\vec{k}, \vec{r}) \quad (64)$$

where $c_{i,I,\vec{k}}$ are expansion coefficients to be determined. or as follows:

$$\Psi(\vec{k}, \vec{r}) = \sum_i \sum_I c_{i,I,\vec{k}} \frac{1}{\sqrt{N}} \sum_n e^{i(\vec{k} \cdot \vec{R}_n)} \phi_{i,I}(\vec{r} - \vec{R}_n - \vec{b}_i) \quad (65)$$

- The wavefunction $\Psi(\vec{k}, \vec{r})$ must satisfy the Schrödinger equation for the crystal:

$$H_{CR} \Psi_n(\vec{k}, \vec{r}) = E_n(\vec{k}) \Psi_n(\vec{k}, \vec{r}) \quad (66)$$

- To determine completely $\Psi(\vec{k}, \vec{r})$ we need to compute the expansion coefficients $c_{i,I,\vec{k}}$.

Tight Binding Method - IV

- As usual we multiply for $\varphi_{j,p}^*(\vec{k}, \vec{r})$ and integrate. We have:

$$\int \varphi_{j,p}^*(\vec{k}, \vec{r}) H_{CR} \Psi_n(\vec{k}, \vec{r}) d\vec{r} = E_n(\vec{k}) \int \varphi_{j,p}^*(\vec{k}, \vec{r}) \Psi_n(\vec{k}, \vec{r}) d\vec{r} \quad (67)$$

- On the RHS: substituting the expression for the basis function (Eq.63):

$$RHS = E(\vec{k}) \sum_n e^{i(\vec{k} \cdot \vec{R}_n)} \sum_i \sum_l c_{i,l}(\vec{k}) \int \phi_{j,p}^*(\vec{r} - \vec{b}_j) \phi_{i,l}(\vec{r} - \vec{R}_n - \vec{b}_i) d\vec{r} \quad (68)$$

- This can be written in a simplified way introducing the overlap matrix elements:

$$S_{j,p}^{i,l} = \sum_n e^{i(\vec{k} \cdot \vec{R}_n)} \int \phi_{j,p}^*(\vec{r} - \vec{b}_j) \phi_{i,l}(\vec{r} - \vec{R}_n - \vec{b}_i) d\vec{r} \quad (69)$$

and the RHS can be written as

$$RHS = \sum_i \sum_l c_{i,l} S_{j,p}^{i,l} \quad (70)$$

Tight Binding Method - Site Integrals

- We can distinguish some important cases:

On-Site Integral

If $\vec{R}_n = 0$ then we have:

$$\int \phi_{j,p}^*(\vec{r} - \vec{b}_j) \phi_{i,l}(\vec{r} - \vec{b}_i) d\vec{r} = \delta_{p,l} \quad (71)$$

if $i = j$ and we have an *on site integral*,

Two-Center Integral

If $\vec{R}_n \neq 0$ we can write

$$S_{j,p}^{i,l}(\vec{u}) = \int \phi_{j,p}^*(\vec{r} - \vec{b}_j) \phi_{i,l}(\vec{r} - \vec{R}_n - \vec{b}_i) d\vec{r} \quad (72)$$

where \vec{u} is the difference between the two atomic positions where the *two-center integral* is evaluated.

Tight Binding Method - V

- Then the RHS of Eq.67 can be decomposed in a diagonal matrix coming from the on site integrals and off diagonal elements coming from two-center integrals.
- On the LHS: the matrix elements of the hamiltonian are a sum of the contribution from the atomic hamiltonian H_{CR} and the contribution of the periodic potential $V(\vec{r})$

$$H_{CR} = H_A + V(\vec{r}) \quad (73)$$

- As usual we multiplying for $\varphi_{j,p}^*(\vec{k}, \vec{r})$ and integrating. For H_A we have:

$$\int \varphi_{j,p}^*(\vec{k}, \vec{r}) H_A \Psi(\vec{k}, \vec{r}) d\vec{r} = \quad (74)$$

$$\sum_n e^{i(\vec{k} \cdot \vec{R}_n)} \sum_i \sum_l c_{i,l,\vec{k}} \int \phi_{j,p}^*(\vec{r} - \vec{b}_j) H_A \phi_{i,l}(\vec{r} - \vec{R}_n - \vec{b}_i) d\vec{r} \quad (75)$$

Tight Binding Method - VI

- Using Eq.60 and the translation properties of the hamiltonian, we can write

$$\cdots = \sum_n e^{i(\vec{k} \cdot \vec{R}_n)} \sum_i \sum_I E_I^A c_{i,I\vec{k}} \int \phi_{j,p}^*(\vec{r} - \vec{b}_j) \phi_{i,I}(\vec{r} - \vec{R}_n - \vec{b}_i) d\vec{r} \quad (76)$$

- This is clearly again of the a type similar to $S_{j,p}^{i,I}$ and we can include the **On-Site Integral** and **Two-Center Integral** for the atomic hamiltonian in the RHS of Eq.67
- The last term to be evaluated is the crystal potential $V(\vec{r} - \vec{R}_m - \vec{b}_i)$.

Three-Center Integral

$$V_{j,p}^{i,I}(\vec{u}) = \int \phi_{j,p}^*(\vec{r} - \vec{b}_j) V(\vec{r} - \vec{R}_m - \vec{b}_z) \phi_{i,I}(\vec{r} - \vec{R}_n - \vec{b}_i) d\vec{r} \quad (77)$$

with $\vec{u} = \vec{r} - \vec{R}_n - \vec{b}_i$.

Tight Binding Method - VII

- In this situation we can have four different cases since the two wavefunctions and the atomic potential can belong to different point in space.
- All the three components are on the same atom ($i = j = z$ and $R_m = R_n = 0$), and this is an **On-Site Integral**.
- The location of the potential is the same of the location of one of the wavefunction and the other wavefunction is on a separate location ($i \neq j = z$ and $R_m = 0$). In this case we have a **Two-Center Integral**
- The two wavefunctions and the potentials are all in different locations. In this case we have a **Three-Center Integral**.
- The two wavefunctions come from the same site but the potential comes from another ($i = j \neq z$ and $R_n = 0$), This integral is a mixed case between **Two-Center Integral** and a **Three-Center Integral**. This introduces only small local corrections and it is usually neglected.

Tight Binding Method - VIII

Putting all the terms together we have:

Tight Binding Model: Secular Equation

$$\sum_i \sum_l \left[V_{j,p}^{i,l}(\vec{u}) - E_n(\vec{k}) S_{j,p}^{i,l} \right] c_{i,l\vec{k}} = 0 \quad (78)$$

- The secular equation we have to solve is a **generalized eigenvalue problem**. The matrix $S_{j,p}^{i,l}$ is not diagonal.
- For each \vec{k} we need to solve the **generalized eigenvalue problem** to obtain the eigenvalues $E_n(\vec{k})$ and the expansion coefficients $c_{i,l\vec{k}}$.
- Note that evaluating $V_{j,p}^{i,l}(\vec{u})$ and $S_{j,p}^{i,l}$ involves a summation over all the atoms in the crystal.
- Possible simplifications involve: limit range of the sum and number of orbitals

Tight Binding Method: s-orbital Expansion

- Let us suppose we want to determine our band structure using a single s-type orbital. In this case $l=1$ and $p=1$.
- We define as $\vec{R} = \vec{R}_m - \vec{b}_z$, and suppress the indexes i and j.
- The generalized eigenvalue system of Eq.78 reduces to a single equation, that can be solved for $E_n(\vec{k})$ to give:

$$E(\vec{k}) = E_s^A - \beta_s - \sum_n \gamma(\vec{R}_n) e^{i(\vec{k} \cdot \vec{R}_n)} \quad (79)$$

where, E_s^A is the value of the matrix element from the atomic hamiltonian.

- The **On-Site Integral** are:

$$\beta_s = - \int \phi_s^*(\vec{r}) V(\vec{r}) \phi_s(\vec{r}) d\vec{r} \quad (80)$$

- The **Two-Center Integral** are:

$$\gamma_s = - \int \phi_s^*(\vec{r}) V(\vec{r}) \phi_s(\vec{r} - \vec{R}_n) d\vec{r} \quad (81)$$

Tight Binding Method: s-orbital Expansion for FCC

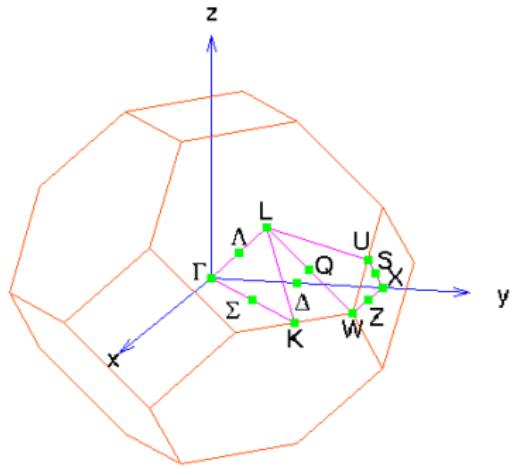
- The three-center and the two-center overlap integral have been supposed to be small compared to the two-center integrals and neglected.
- At this point we need to specify the position of the atoms.
- Consider a simple FCC crystal, assume that only the first nearest neighbors give a contribution
- we have to sum over 12 \vec{R}_n vectors:

$$\begin{aligned} & \frac{a}{2}(\pm 1, \pm 1, 0) \\ & \frac{a}{2}(\pm 1, 0, \pm 1) \\ & \frac{a}{2}(0, \pm 1, \pm 1) \end{aligned} \tag{82}$$

where $a/2$ is the lattice constant. Using these vectors we obtain:

$$E(\vec{k}) = E_s - \beta_s - \gamma \left(\cos \frac{k_x a}{2} \cos \frac{k_y a}{2} + \cos \frac{k_y a}{2} \cos \frac{k_z a}{2} + \cos \frac{k_z a}{2} \cos \frac{k_x a}{2} \right) \tag{83}$$

Tight Binding Method: s-orbital Expansion for FCC



– FBZ of the FCC crystal with principal crystallographic directions.

$$\Gamma - X: \langle 0, 0, 0 \rangle \rightarrow \langle 1, 0, 0 \rangle$$

$$\Gamma - L: \langle 0, 0, 0 \rangle \rightarrow \langle 1, 1, 1 \rangle$$

$$\Gamma - K: \langle 0, 0, 0 \rangle \rightarrow \langle 1, 1, 0 \rangle$$

For the principal directions above we have (see figure of the FCC FBZ) the following expressions:

$$\Gamma - X \quad E(\vec{k}) = E_s - \beta_s - \gamma(1 + 2 \cos \pi l)$$

$$\Gamma - L \quad E(\vec{k}) = E_s - \beta_s - 12\gamma \cos^2 \pi l$$

$$\Gamma - K \quad E(\vec{k}) = E_s - \beta_s - 4\gamma(\cos^2 \pi l + 2 \cos \pi l)$$

Empirical Tight Binding Method

- One of the simplest way of determining the matrix elements is to use them as disposable constant and determine their values by fitting the results of the solution of Eq.78 to the experimental values of the band structure.
- In the simplest approach the **Three-Center Integral** are considered small compared to the two-center ones and neglected (as Slater and Koster proposed) and the wavefunction are considered tightly bounded to the atoms, so that off-site overlaps are negligible.
- In this case only the Hamiltonian matrix elements are non zero and the problem reduces to a standard eigenvalue problem.

Empirical Tight Binding Method for Zincblende

- A typical approach for zincblende type materials is to use three orbitals: or sp^3 (s,px,py,pz), and a second nearest neighbor approximation.
- In this case we have eight basis functions, four for each atom and the hamiltonian matrix to be diagonalize has rank 8. In case the spin is included the rank doubles.
- In the second neighbor approximation, chosen the cation as the reference, the first neighbor is going to be a anion, and a the second neighbor a cation again.

Empirical Tight Binding Method - Zincblende Crystals - I

In this case the hamiltonian determinant becomes of the type:

$$H = \begin{bmatrix} H(0,0) & H(0,1) \\ H(1,0) & H(1,1) \end{bmatrix}$$

- $H(0,0)$ includes the matrix elements for cations centers self interactions and between cations second neighbors.
- $H(0,1)$ includes the interaction between anion centers and cation first neighbors.
- In the same way, $H(1,0)$ includes the interaction between cation centers and anion first neighbors.
- $H(1,1)$ includes the matrix elements for anions centers self interactions and between anions second neighbors.

- For example a representative matrix element can be written:

$$\langle s^0 | H | p_x^1 \rangle = e^{i(\vec{k} \cdot \vec{R}_1)} \langle s^0(\vec{R}_1) | H | p_x^1 \rangle + e^{i(\vec{k} \cdot \vec{R}_2)} \langle s^0(\vec{R}_2) | H | p_x^1 \rangle + \\ e^{i(\vec{k} \cdot \vec{R}_3)} \langle s^0(\vec{R}_3) | H | p_x^1 \rangle + e^{i(\vec{k} \cdot \vec{R}_4)} \langle s^0(\vec{R}_4) | H | p_x^1 \rangle$$

- The matrix elements in the previous equation are all related by symmetry operations.
- Instead of using directly explicitly the components along the three cartesian axis, it is possible to give only one value for the interaction, for example: along the segment connecting to atoms and project it using the directional cosines.
- In this way it is possible to collect the matrix elements in a standard set of parameters as reported in the following table:

Empirical Tight Binding Method - Zincblende Crystals - III

Self Int. En.	First neighbors	Second neighbors
E_{s0}	ss_{σ}^{01}	ss_{σ}^{00}
E_{p0}	sp_{σ}^{01}	sp_{σ}^{00}
E_{s1}	ss_{σ}^1	pp_{σ}^{00}
E_{p1}	pp_{σ}^{01} pp_{π}^{01}	pp_{π}^{00} ss_{σ}^{11} sp_{σ}^{11} pp_{σ}^{11} pp_{π}^{11}

- The generic matrix element at the position \vec{r} is given by

$$\langle s^{\vec{k}} | H | p_x^1 \rangle = \cos(\theta) sp_{\sigma}^{01} \quad (84)$$

where θ is the angle between \vec{r} and the x axis.

Empirical Tight Binding Method - Zincblende Crystals - IV

More in general we have

$$\begin{aligned}\langle s|H|s \rangle &= ss_\sigma \\ \langle s|H|p_x \rangle &= lsp_\sigma \\ \langle p_x|H|p_x \rangle &= l^2 pp_\sigma + (1 - l^2) pp_\pi \\ \langle p_x|H|p_y \rangle &= lmpp_\sigma + lmpp_\pi\end{aligned}$$

where l,m,n are the cosines between \vec{r} and the three principal axes.

Hellmann–Feynman Theorem

Consider the solution of the Schrödinger equation where the Hamiltonian \hat{H}_λ depends on a parameter λ :

$$\hat{H}_\lambda |\psi_{n,\lambda}\rangle = E_{n,\lambda} |\psi_{n,\lambda}\rangle \quad (85)$$

The eigenfunctions ψ_λ depend implicitly on the parameter λ as well. If the eigenfunctions are normalized we have:

$$\langle \psi_{n,\lambda} | \psi_{n,\lambda} \rangle = 1, \quad \langle \psi_{n,\lambda} | \psi_{m,\lambda} \rangle = 0, \quad \frac{d}{d\lambda} \langle \psi_{n,\lambda} | \psi_{n,\lambda} \rangle = 0 \quad (86)$$

The Hellmann–Feynman theorem relates the derivative of the total energy with respect to a parameter to the expectation value of the derivative of the Hamiltonian with respect to that same parameter.

$$\frac{dE_\lambda}{d\lambda} = \left\langle \psi_\lambda \left| \frac{d\hat{H}_\lambda}{d\lambda} \right| \psi_\lambda \right\rangle \quad (87)$$

Carrier Transport Models - Semiclassical Model

Consider a charged particle, the force on the particle due to an external electric $\vec{\mathcal{E}}$ and/or magnetic $\vec{\mathcal{B}}$ field is given by:

$$\vec{F}(\vec{r}) = -q \left[\vec{\mathcal{E}}(\vec{r}) + \vec{v} \times \vec{\mathcal{B}}(\vec{r}) \right] \quad (88)$$

The particle in the crystal will be characterized by a Bloch wavefunction corresponding to a wavevector \vec{k} and band n.

$$\Psi_n(\vec{k}, \vec{r}, t) = u_n(\vec{k}, \vec{r}) e^{i\vec{k} \cdot \vec{r}} e^{-i \frac{E_n(\vec{r})}{\hbar} t} \quad (89)$$

$$u_n(\vec{k}, \vec{r}) = u_n(\vec{k}, \vec{r} + \vec{R}_i)$$

If an electric field $\vec{\mathcal{E}}$ is applied, how does the state of the particle evolves?

- How does the velocity change?
- What is the acceleration as a result of the electric field?

Carrier Transport Models: Carrier Velocity

We start with the First Ehrerferst Theorem, and assume we are in one dimension:

$$\langle v_x \rangle = \frac{d}{dt} \langle x \rangle = \frac{1}{m} \langle p_x \rangle \quad (90)$$

$$\langle v_x \rangle = \frac{1}{m} \int \Psi_n^*(k, x) \left(-i\hbar \frac{d}{dx} \right) \Psi_n(k, x) dx \quad (91)$$

Using the expression of the Bloch wavefunction (Eq.89) we have:

$$\langle v_x \rangle = \frac{1}{m} \int u_n^*(k, x) \left(-i\hbar \frac{d}{dx} + \hbar k \right) u_n(k, x) dx \quad (92)$$

One can show that $u_n(k, x)$ is the solution of:

$$H(k) u_n(k, x) = E_n(k) u_n(k, x) \quad (93)$$

and

$$\int u_n^*(k', x) u_n(k, x) dx = \delta_{k', k} \quad (94)$$

Carrier Transport Models: Carrier Velocity - I

Where the Hamiltonian operator is give by:

$$H(k) = \frac{1}{2m} \left(-i\hbar \frac{d}{dx} + \hbar k \right)^2 + V(x) \quad (95)$$

The Hamiltonian operator in Eq. 95 can be seen as a parameter (that is: k) dependent operator:

$$H(\lambda) \phi(\lambda) = E_n(\lambda) \phi(\lambda) \quad (96)$$

We perturb the Hamiltonian changing the parameter: $\lambda \rightarrow \lambda + d\lambda$, and the hamiltonian will change as:

$$\frac{\partial H(\lambda)}{\partial \lambda} d\lambda \quad (97)$$

The corresponding change in energy eigenvalue can be determine from first order perturbation. Since $d\lambda$ is infinitesimal, this is exact.

Carrier Transport Models: Carrier Velocity - II

$$E_n(\lambda) = \int \phi^*(\lambda) H(\lambda) \phi(\lambda) dx \quad (98)$$

and, using first order perturbation:

$$\frac{\partial E_n(\lambda)}{\partial \lambda} d\lambda = \int \phi^*(\lambda) \frac{\partial H(\lambda)}{\partial \lambda} d\lambda \phi(\lambda) dx \quad (99)$$

or

$$\frac{\partial E_n(\lambda)}{\partial \lambda} = \int \phi^*(\lambda) \frac{\partial H(\lambda)}{\partial \lambda} \phi(\lambda) dx \quad (100)$$

- This is the Hellman-Feynman theorem applied to the Hamiltonian operator, with the parameter λ .
- Since $V(x)$ in Eq.95 does not depend on the parameter k , we have that:

$$\frac{\partial H(k)}{\partial k} = \frac{\hbar}{m} \left(-i\hbar \frac{d}{dx} + \hbar k \right) \quad (101)$$

Carrier Transport Models: Carrier Velocity - III

Consequently from Eq.92:

$$\frac{\hbar}{m} \int u_n^*(k, x) \left(-i\hbar \frac{d}{dx} + \hbar k \right) u_n(k, x) dx = \frac{\partial E_n(k)}{\partial k} \quad (102)$$

as a result:

Carrier Velocity

$$\langle v_x \rangle = \frac{1}{\hbar} \frac{\partial E_n(k)}{\partial k} \quad (103)$$

or

$$\langle \vec{v} \rangle = \frac{1}{\hbar} \nabla_{\vec{k}} E_n(\vec{k}) \quad (104)$$

Carrier Transport Models: Applied Electric Field

- Consider an electric field \mathcal{E} applied to the crystal. We assume that the field magnitude varies slowly on the scale of the lattice constant.
- The energy (classical) the particle gains from the field, it is given:

$$W(x) = q\mathcal{E}x$$

The rate of change of the energy of the particle's energy due to the field is:

$$\frac{\partial E(k)}{\partial t} = -\frac{\partial W(x)}{\partial t} = q\mathcal{E}\frac{\partial x}{\partial t} = q\mathcal{E}v$$

Since

$$\frac{\partial E(k)}{\partial t} = \frac{\partial E(k)}{\partial k} \frac{\partial k}{\partial t} = \hbar v \frac{\partial k}{\partial t}$$

- Combining the last two equations:

Carrier Velocity

$$\hbar \frac{dk}{dt} = -e\mathcal{E} \quad (105)$$

Carrier Transport Models: Acceleration and Effective Mass

- The acceleration is given by:

$$a = \frac{dv}{dt} = \frac{d}{dt} \left[\frac{1}{\hbar} \frac{dE_n(k)}{dk} \right] = \frac{1}{\hbar} \left[\frac{d^2 E_n(k')}{dk'^2} \right] \Bigg|_{k'=k} \frac{dk}{dt}$$
$$a = \frac{1}{\hbar^2} \left[\frac{d^2 E_n(k')}{dk'^2} \right] (-q\mathcal{E}) = \frac{1}{m^*} \mathcal{F}$$

Effective Mass

$$m^* = \hbar^2 \left[\frac{d^2 E_n(k')}{dk'^2} \right]^{-1} \Bigg|_{k'=k} \quad (106)$$

- The particle responds to the application of a force (electric field) with an acceleration that is proportional through a wavector dependent mass.

Next Chart