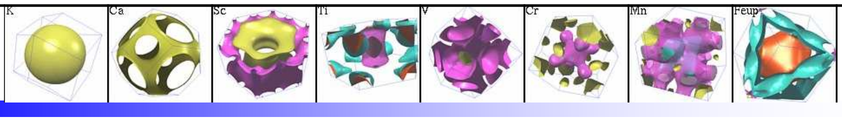


Lecture 4

Nearly Free Electron Model

4.1 Nearly Free Electron Model
    4.1.1 Brilloiun Zone
    4.1.2 Energy Gaps
4.2 Translational Symmetry – Bloch’s Theorem
4.3 Kronig-Penney Model
4.4 Tight-Binding Approximation
4.5 Examples

References:
1. Marder, Chapters 7-8
2. Kittel, Chapter 7
3. Ashcroft and Mermin, Chapter 9
4. Kaxiras, Chapter 3
5. Ibach, Chapter 7

Sommerfeld’s theory does not explain all…

Metal’s conduction electrons form highly degenerate Fermi gas

Free electron model: works only for metals
  - heat capacity, thermal and electrical conductivity, magnetic susceptibility, etc

<u>Drawbacks</u>:
predicted electron mean path is too long
increases with temperature
positive values for the Hall coefficient, magnetotransport

difference between a good conductor (10^{-10} Ohm-cm) and a good insulator (10^{-22} Ohm-cm) – 10^{32} !!!

Electron Occupancy of Allowed Energy Bands

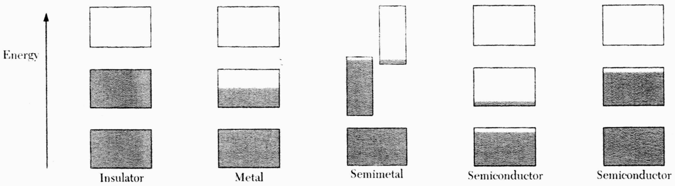


Figure 1 Schematic electron occupancy of allowed energy bands for an insulator, metal, semimetal, and semiconductor. The vertical extent of the boxes indicates the allowed energy regions; the shaded areas indicate the regions filled with electrons. In a **semimetal** (such as bismuth) one band is almost filled and another band is nearly empty at absolute zero, but a pure **semiconductor** (such as silicon) becomes an insulator at absolute zero. The left of the two semiconductors shown is at a finite temperature, with carriers excited thermally. The other semiconductor is electron-deficient because of impurities.

Adapted from Kittel

- No electrons can move in an electric field (energy band is completely filled or empty) – **insulator ;**
- One or more bands are partly filled – **conductor**

Basic Assumptions: - crystal structure is periodic
- periodicity leads to formation of **energy bands** (allowed energy levels)
- energy bands are separated by **energy gaps or band gaps** (region in energy for which no wavelike electron orbital exist)

4.1 Nearly Free Electron Model

In free electron model: all energy values from 0 to infinity are allowed

$$\boxed{\varepsilon_{\vec{k}} = \frac{\hbar^2}{2m}\vec{k}^2 = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)}$$

Wavefunctions are in the form: $\psi_{\vec{k}}(\vec{r}) = \exp(i\vec{k}\cdot\vec{r}),$

where the components of the wavevector $\vec{k}$ are: $k_x = 0; \pm\frac{2\pi}{L}; \pm\frac{4\pi}{L}; \ldots$

Nearly free electron model: weak perturbation of electrons by periodic potential of ions

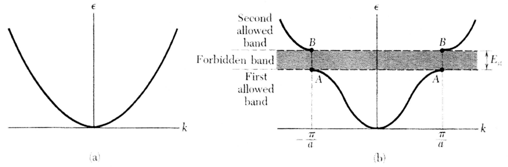


Figure 2 (a) Plot of energy ϵ versus wavevector k for a free electron. (b) Plot of energy versus wavevector for an electron in a monatomic linear lattice of lattice constant a. The energy gap E_g shown is associated with the first Bragg reflection at $k = \pm\pi/a$; other gaps are found at $\pm n\pi/a$, for integral values of n.

Nearly Free Electrons

Consider the effects due to a periodic crystal structure

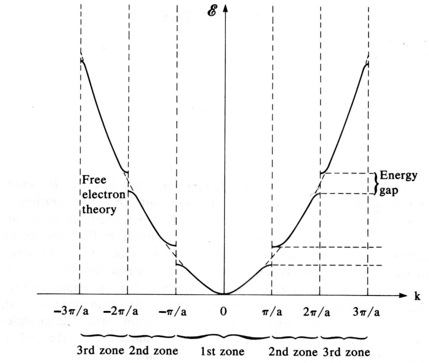


Fig. 10-1 Energy vs. wave vector for free electrons (dashed parabola) and for almost free electrons (solid lines). Gaps develop at $k = p\pi/a$ where $p = \pm 1, \pm 2$, and so forth.

Under condition $k = \pm \frac{1}{2} G = \pm \frac{n\pi}{a}$, the electron wave will undergo Bragg reflection

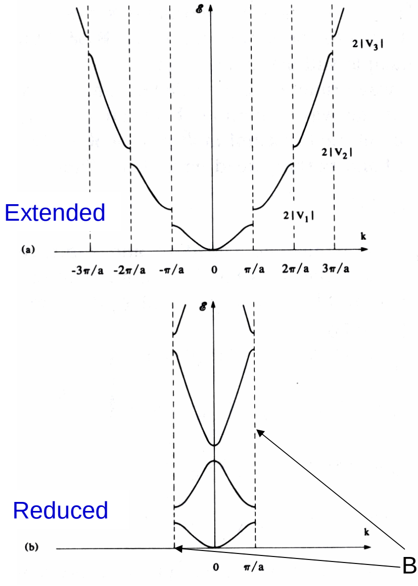
Energy gaps develop at these k due to these reflections

At $k = n\ \pi/a$ the wavefunctions are **not** the traveling wave of free electrons

The region between - π/a and π/a :

first Brillouin zone of this 1D lattice

4.1.1 Brilloiun Zone in 1D: extended, reduced and repeated



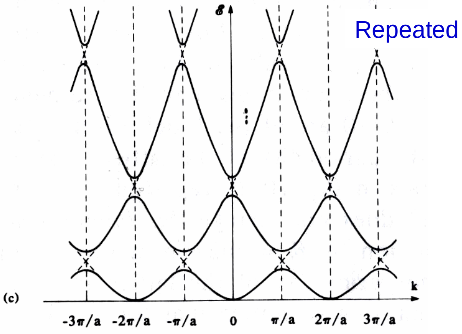


Fig. 10-5 Energy as a function of wave vector for a one-dimensional crystal, shown in the (a) extended, (b) reduced, and (c) repeated zone scheme.

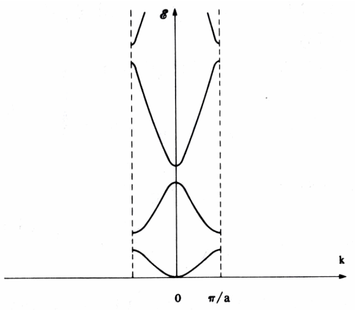
BZ boundaries

Reduction to the first Brillouin zone

This general demand of periodicity implies that the possible electron states are not restricted to a single parabola in k-space, but can be found on any parabola shifted by any G-vector:

$$\varepsilon(\vec{k}) = \varepsilon(\vec{k}+\vec{G}) = \frac{\hbar^2}{2m}\left|\vec{k}+\vec{G}\right|^2$$

For 1D case: $\vec{G} \rightarrow G = \dfrac{2\pi}{a}$



Brilloiun Zone in 3D

Brilloiun Zone in 3D: Wigner-Seitz cell of the reciprocal lattice

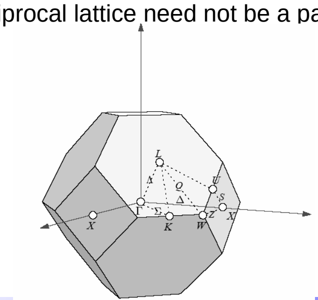
Recall: reciprocal lattice vector $\vec{G} = 2\pi\, n_1\vec{b}_1 + 2\pi\, n_2\vec{b}_2 + 2\pi\, n_3\vec{b}_3,$

where $\vec{b}_1, \vec{b}_2, \vec{b}_3$ are basic vectors such that $\vec{b}_1 = \dfrac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3};\ \vec{b}_2 = \dfrac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3};\ \vec{b}_3 = \dfrac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3};$

Some properties of reciprocal lattice:

The direct lattice is the reciprocal of its own reciprocal lattice

The unit cell of the reciprocal lattice need not be a paralellopiped, e.g., Wigner-Seitz cell



first Brilloin Zone (BZ) of the *fcc* lattice

4.1.2 Origin of the Energy Gap

Crystal Potential - U

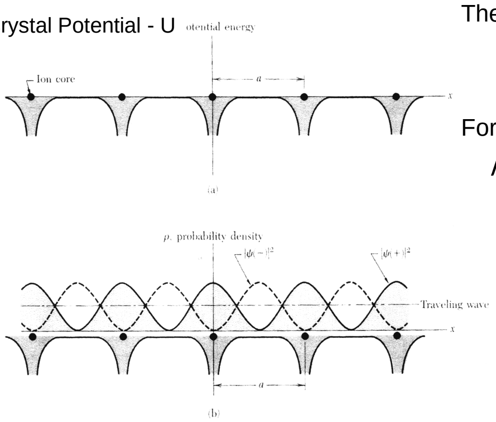


Figure 3 (a) Variation of potential energy of a conduction electron in the field of the ion cores of a linear lattice. (b) Distribution of probability density ρ in the lattice for $|\psi(-)|^2 \propto \sin^2 \pi x/a$; $|\psi(+)|^2 \propto \cos^2 \pi x/a$; and for a traveling wave. The wavefunction $\psi(+)$ piles up electronic charge on the cores of the positive ions, thereby lowering the potential energy in comparison with the average potential energy seen by a traveling wave. The wavefunction $\psi(-)$ piles up charge in the region between the ions, thereby raising the potential energy in comparison with that seen by a traveling wave. This figure is the key to understanding the origin of the energy gap.

The probability density of the particle is

$$\psi^*\psi = |\psi|^2$$

For pure traveling wave:

$$\rho = \exp(-ikx)\exp(ikx) = 1$$

For plane waves the charge density is <u>not constant</u>:

for the wave $\psi(+)$:

$$\rho(+) = |\psi(+)|^2 \propto \cos^2 \frac{\pi x}{a}$$

for the wave $\psi(-)$:

$$\rho(-) = |\psi(-)|^2 \propto \sin^2 \frac{\pi x}{a}$$

Magnitude of the Energy Gap

The potential energy due to the crystal can be approximated as:

$$U(x) = U \cos \frac{2\pi x}{a}$$

This potential has the periodicity of the lattice, $U(x) = U(x + a)$

The wavefunctions at the Brillouin zone boundary $k = \pi/a$ (normalized over unit length of line, a) are

$$\sqrt{2}\cos\frac{\pi x}{a} \text{ and } \sqrt{2}\sin\frac{\pi x}{a}$$

The difference between the two standing wave states is

$$\boxed{E_g = \int_0^1 U(x)[|\psi(+)|^2 - |\psi(-)|^2]dx = 2\int U \cos\frac{2\pi x}{a}\left(\cos^2\frac{\pi x}{a} - \sin^2\frac{\pi x}{a}\right)dx = U}$$

The <u>**gap**</u> is equal to the **Fourier component of the crystal potential**

4.2 Translational Symmetry – Bloch's Theorem

Bloch's theorem: the wave functions of the electrons in a crystal must be of a special form (the Bloch form)

$$\psi_{\vec{k}}(\vec{r}) = \exp(i\vec{k}\cdot\vec{r})u_k(\vec{r})$$
$$u_k(\vec{r}) = u_k(\vec{r}+\vec{T})$$

$u_k(r)$ – the periodicity of the lattice (depends on the wave vector!)

Note: the Bloch function can be decomposed into a sum of traveling waves

In 1D: Consider a crystal of length $L = N\,a$ (N primitive u. c. of length a on a ring)

The periodic boundary condition demans that

$C\psi(x) = \psi(x+a)$; here C - const.

Addition of the translational symmetry gives:

$\psi(x+Na) = \psi(x) = C^N\psi(x)$

$|\psi(x+na)|^2 = |\psi(x)|^2$ and $C = \exp\dfrac{i2\pi s}{N}$; s = 0, 1, 2,..., N - 1

Therefore $\psi(x) = u_k(x)\exp(\dfrac{i2\pi sx}{Na})$

Kittel, pp.179-180

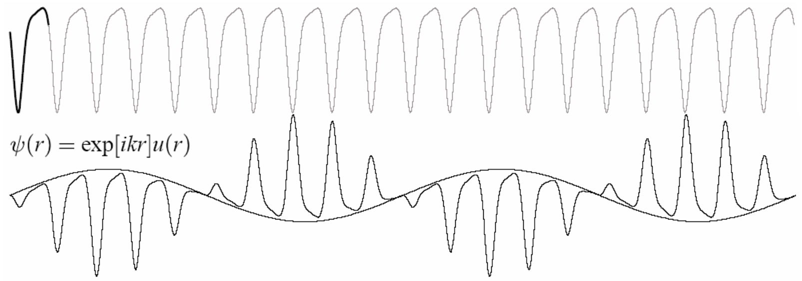
Bloch's Theorem

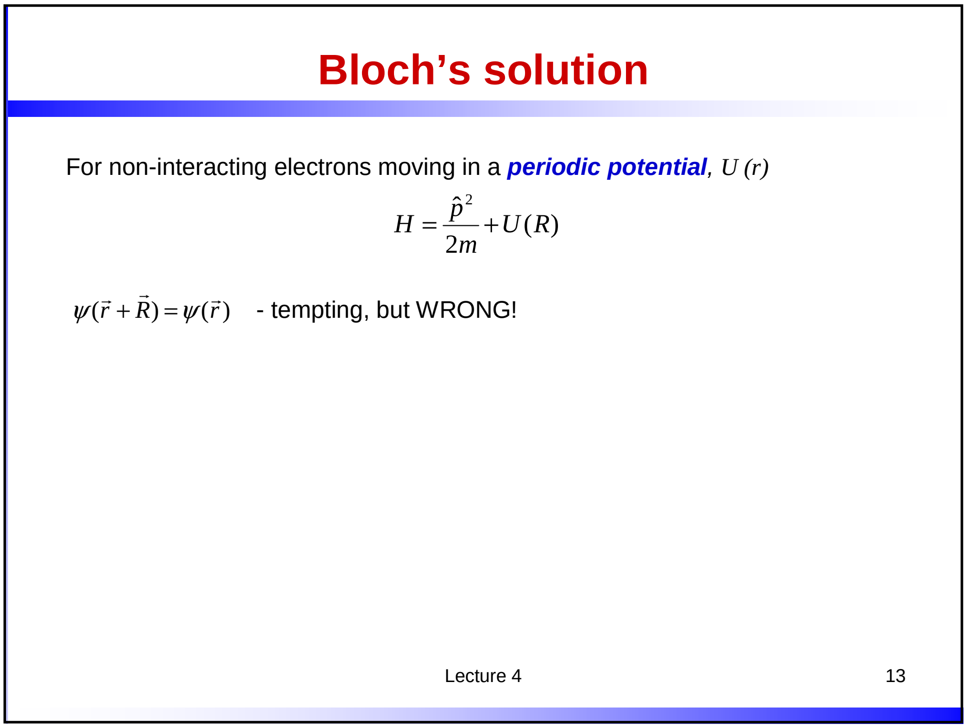
For non-interacting electrons moving in a ***periodic potential***, $U(r)$

$$U(\vec{r}+\vec{R}) = U(\vec{r})$$

Bloch wave functions are periodic functions $u(r)$ modulated by a plane wave of a longer period

Periodic function $u(r)$



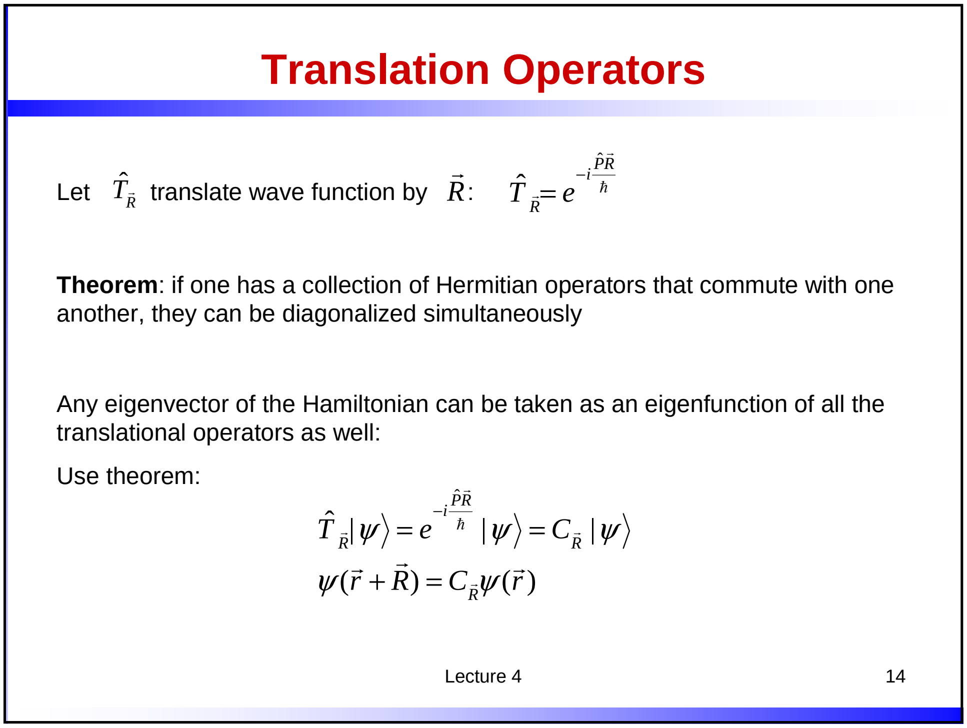


Bloch's solution

For non-interacting electrons moving in a ***periodic potential***, $U(r)$

$$H = \frac{\hat{p}^2}{2m} + U(R)$$

$\psi(\vec{r}+\vec{R}) = \psi(\vec{r})$ - tempting, but WRONG!



Translation Operators

Let $\hat{T}_{\vec{R}}$ translate wave function by $\vec{R}$: $\hat{T}_{\vec{R}} = e^{-i\frac{\hat{P}\vec{R}}{\hbar}}$

Theorem: if one has a collection of Hermitian operators that commute with one another, they can be diagonalized simultaneously

Any eigenvector of the Hamiltonian can be taken as an eigenfunction of all the translational operators as well:

Use theorem:

$$\hat{T}_{\vec{R}}|\psi\rangle = e^{-i\frac{\hat{P}\vec{R}}{\hbar}}|\psi\rangle = C_{\vec{R}}|\psi\rangle$$

$$\psi(\vec{r}+\vec{R}) = C_{\vec{R}}\psi(\vec{r})$$

Translation Operators

Operating with eigenfunction of momentum:

$$e^{i\vec{k}\vec{R}}\langle \vec{k}|\psi\rangle = C_{\vec{R}}\langle \vec{k}|\psi\rangle$$

⇒ either $C_{\vec{R}} = e^{i\vec{k}\vec{R}}$ or $\langle \vec{k}|\psi\rangle = 0$

$\vec{k}$: Bloch wave vector
$\hbar\vec{k}$: Crystal momentum
n : Band index

For a given value of Bloch wavevector, there is still the possibility of many energy eigenvalues (can be labeled by the band index *n*)

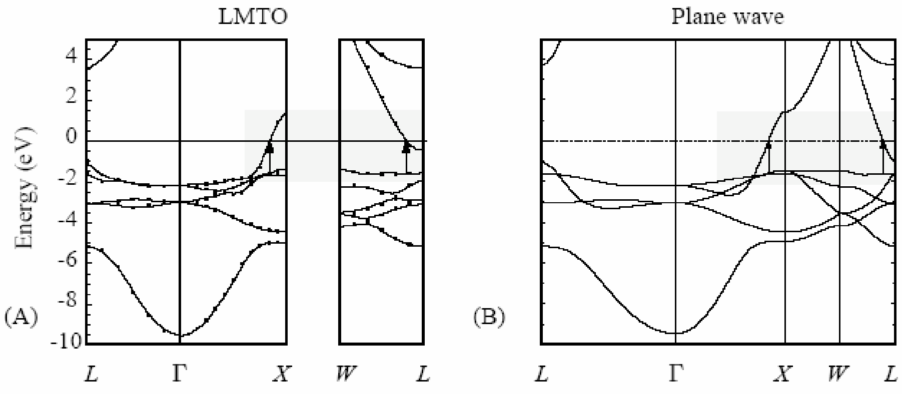
The eigenfunctions made possible by periodicity is: $\hat{H}|\psi_{n\vec{k}}\rangle = E_{n\vec{k}}|\psi_{n\vec{k}}\rangle$

$$\hat{T}_{\vec{R}}|\psi_{n\vec{k}}\rangle = e^{i\vec{k}\vec{R}}|\psi_{n\vec{k}}\rangle$$

$\psi_{n\vec{k}}(\vec{r}+\vec{R}) = e^{i\vec{k}\vec{R}}\psi_{n\vec{k}}(\vec{r})$ or
$u_{n\vec{k}}(\vec{r}) = e^{-i\vec{k}\vec{r}}\psi_{n\vec{k}}(\vec{r})$

Energy Bands

$$\hat{\mathcal{H}}_{\vec{k}}u(\vec{r}) = \frac{\hbar^2}{2m}[-\nabla^2 - 2i\vec{k}\cdot\vec{\nabla} + k^2]u(\vec{r}) + U(\vec{r})u(\vec{r}) = \mathcal{E}u(\vec{r})$$



Allowed values of k

If crystal is periodic with (macroscopic) dimensions $M_1\vec{a}_1, M_2\vec{a}_2, M_3\vec{a}_3$ then requiring $\exp[i\vec{k}\cdot\vec{r}\,]$ to be periodic constrains $\vec{k}$ to

$$\vec{k} = \sum_{l=1}^{3} \frac{m_l}{M_l}\vec{b}_l, 0 \le m_l \le M_l, \text{ where } \vec{b}_1 .. \vec{b}_3 \text{ are such that } \vec{b}_l \cdot \vec{a}_{l'} = 2\pi\delta_{ll'}$$

Periodic boundary condition place a condition on how small k can be

Demanding that $C_{\vec{R}} = e^{i\vec{k}\vec{R}}$ be unique places conditions on how big *k* can be

<u>**Number of points in crystal** equals **number of unique Bloch wave vectors**</u>

Energy Bands and Group Velocities

Velocity of electrons in the *n*th band with wave number *k* is:

$$\vec{v}_{n\vec{k}} = \frac{1}{\hbar}\nabla_{\vec{k}} E_{n\vec{k}}$$

Note: this is similar to the solution of wave equations for a group velocity: $v = \dfrac{\partial\omega}{\partial k}$

Wave packet:
$$W(\vec{r},\vec{k},t) = \int w(\vec{k}'-\vec{k})\cdot e^{i\vec{k}'\vec{r}-iE_{\vec{k}'}t/\hbar}\psi_{\vec{k}'}e^{-i\vec{k}'\vec{r}}d\vec{k}' \approx$$
$$\approx e^{i\vec{k}'\vec{r}-iE_{\vec{k}'}t/\hbar}\int w(\vec{k}'')d\vec{k}' \propto e^{i\vec{k}'\vec{r}-iE_{\vec{k}'}t/\hbar}$$

4.3 Kronig-Penney Model

The wave equation is $$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+U(x)\psi=\varepsilon\psi$$

In the region 0<x<a (U = 0), the eigenfunction is a linear combination of plane waves traveling to the right and to the left with energy $\varepsilon=\frac{\hbar^2K^2}{2m}$

$$\psi=Ae^{iKx}+Be^{-iKx}$$

In the region –b < x < 0 within the barrier the solution is

$$\psi=Ce^{Qx}+De^{-Qx},$$

$$\text{where } U_0-\varepsilon=\frac{\hbar^2Q^2}{2m}$$

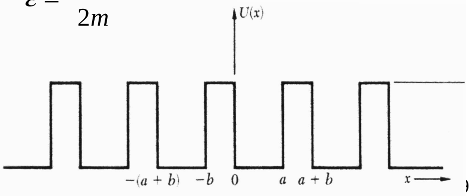


Figure 4 Square-well periodic potential as introduced by Kronig and Penney.

Kronig-Penney Model

Solution must be in the Bloch form:

$$\psi(a<x<a+b)=\psi(-b<x<0)e^{ik(a+b)}$$

The constants *A, B, C, D* are chosen so that wavefunction and its derivative are continuous at $x = 0$ and $x = a$

At $x = 0$ $\quad A + B = C + D$

$iK(A-B) = Q(C - D)$

At $x = a$ $\quad Ae^{iKa}+Be^{-iKa}=(Ce^{-Qb}+De^{Qb})e^{ik(a+b)}$

$iK(Ae^{iKa}-Be^{-iKa})=Q(Ce^{-Qb}-De^{Qb})e^{ik(a+b)}$

Solution: $\quad [(Q^2-K^2)2QK]\sinh Qb\sin Ka+\cosh Qb\cos Ka=\cos k(a+b)$

In the limit Q >> K and Qb <<1

$$\frac{P}{Ka}\sin Ka+\cos Ka=\cos ka$$

Functions and Energy for the K-P potential

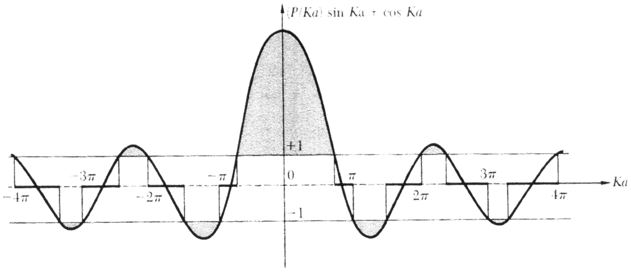


Figure 5 Plot of the function $(P/Ka)\sin Ka + \cos Ka$, for $P = 3\pi/2$. The a energy ϵ are given by those ranges of $Ka = (2m\epsilon/\hbar^2)^{1/2}a$ for which the functi For other values of the energy there are no traveling wave or Bloch-like s equation, so that forbidden gaps in the energy spectrum are formed.

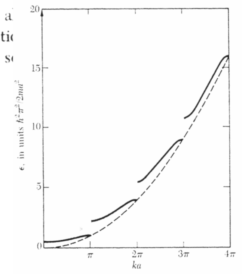
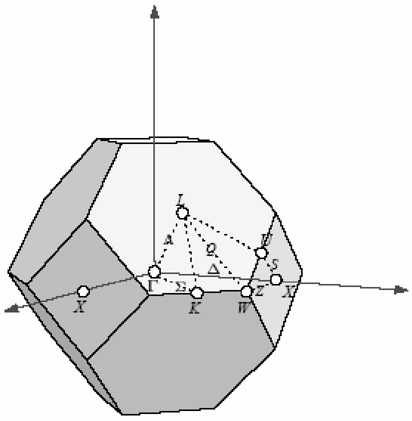


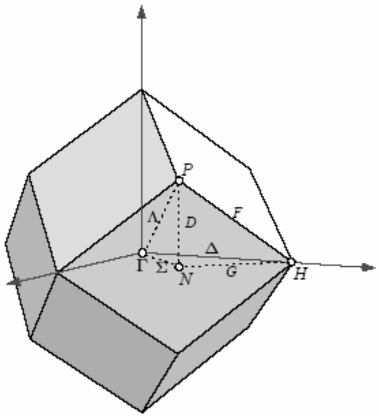
Figure 6 Plot of energy vs. wavenumber for the Kronig-Penney potential.

First Brillouin Zone for fcc lattice



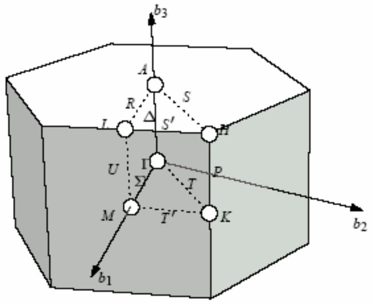
In units of $2\pi/a$, $\Gamma = (0\ 0\ 0)$, $X = (0\ 1\ 0)$, $L = (1/2\ 1/2\ 1/2)$, $W = (1/2\ 1\ 0)$, $K = (3/4\ 3/4\ 0)$, and $U = (1/4\ 1\ 1/4)$.

First Brillouin Zone for bcc lattice



In units of $\frac{4\pi}{a}$, $\Gamma = (0\;0\;0)$, $H = (0\;1\;0)$, $N = (1/2\;1/2\;0)$, and $P = (1/2\;1/2\;1/2)$.

First Brillouin Zone for hcp lattice



In units of $4\pi/a\sqrt{3}$, $4\pi/a\sqrt{3}$, and $2\pi/c$, along the three primitive vectors $\vec{b}_1$, $\vec{b}_2$, and $\vec{b}_3$; $\Gamma = (0\;0\;0)$, $A = (0\;0\;1/2)$, $M = (1/2\;0\;0)$, $K = (1/3\;1/3\;0)$, $H = (1/3\;1/3\;1/2)$, and $L = (1/2\;0\;1/2)$.

Example: Nearly Free Electron in 1D

Electrons of mass *m* are confined to one dimension. A weak periodic potential is applied:

$$V(x) = V_o + V_1 \cos\frac{2\pi x}{a} + V_2 \cos\frac{4\pi x}{a}$$

(a) Under what conditions will the nearly free-electron approximation work?

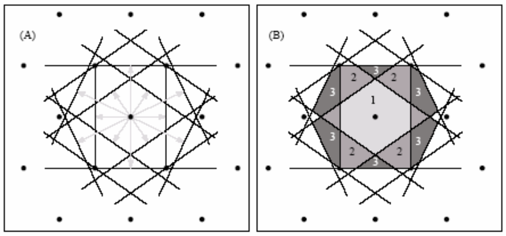
(b) Sketch the three lowest energy bands in the first Brillouin zone. Number the energy bands (starting from one at the lowest band)

(c) Calculate (to first order) the energy gap at $k = \pi/a$ (between the first and second band) and $k = 0$ (between the second and third band)

Lecture 4, continued

Nth Brillioun zone: geometrical view

$$\vec{k}\cdot\frac{\vec{K}}{K} = \frac{1}{2}K.$$

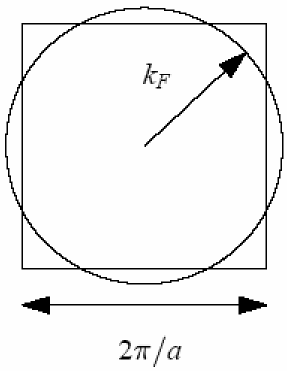


Procedure:

- perpendicular bisectors are drawn between the origin and all nearby reciprocal lattice points ⇒ zone boundaries
- the 1^{st}, 2^{nd}, and 3^{rd} BZ are shaded in different color (same volume)

- electron response to the external electric field same as for free electron till it approaches a zone boundary plane
- an electron once in the n^{th} BZ remains in the n^{th} BZ

Example in two dimensions



$$\pi k_F^2 = 4\pi^2/a^2$$

$$\Rightarrow k_F = 2\pi/\sqrt{\pi}a = 1.128\pi/a$$

Suppose 2D lattice has two conduction el. per lattice sites

The # of *k*-states in BZ = the # of lattice points

For a weak potential, shape of the energy surface ~ sphere

For lattice spacing	a
The reciprocal lattice	$2\pi/a$
The volume of 1st BZ	$4\pi^2/a^2$

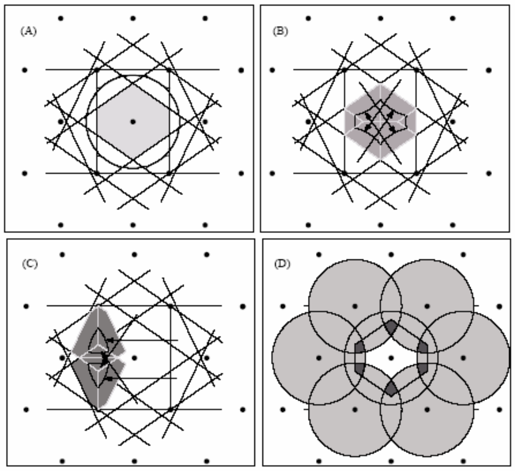
The Fermi sphere must have same volume

⇒ the Fermi surface slightly out of the 1st BZ

Example in two dimensions

- Fermi surface completely enclosing the 1st BZ
- shape of surface is modified near the zone boundary

- portion of the Fermi surface in 3rd BZ is made continuous by translation through reciprocal lattice vectors

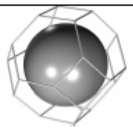


- portion of the Fermi surface in 2nd BZ is mapped back into the 1st zone

Harrison construction:

nth BZ mapped into 1st BZ

Nearly Free Electron Fermi Surface Gallery

Brillouin zone	1 electron/cell	2 electrons/cell	3 electrons/cell
First			
Second			
Third			

http://www.phys.ufl.edu/fermisurface/periodic_table.html

Symmetry Properties

Basic idea: free molecule with N-atoms ⇒ 3N degrees of freedom

⇒ $3n-6$ normal modes of vibration (or a *linear* molecule has $3n-5$ normal modes of vibration because rotation about its molecular axis cannot be observed)

What are symmetry operations of the molecule?

Operations (reflection, rotation, etc.) which leave molecule invariant

Symmetry operations:

1. Symmetry plane: σ

2. n-fold axis of symmetry $C_n \Rightarrow$ rotation by $2\pi/n$

Symmetry operations:

3. Inversion symmetry, *i*

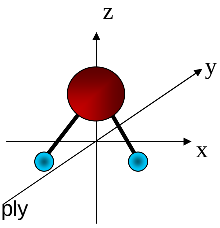
4. Identity, E

5. n-fold rotation + reflection $S_n \Rightarrow$ rotation by $2\pi/n$ + reflection through plane $\perp$ to rotational axis

Point Groups and Their Representations

Demonstrate concept by example with H_2O molecule

Consider H_2O molecule lying in xz-plane:



Which symmetry operations leave molecule unchanged?

As we shall see, these four operations form C_{2v} point group

To establish a group must consider how operations (i.e., elements) multiply

Idea: form product table

If R and R' -symmetry operation, define product R R' as consecutive application of R and R'

Group of Elements

$R \equiv$ element

Group of elements is a set of elements that satisfy:

1) E is member of set

2) Obey associative rule of multiplication: $R(R'R'') = (R\,R')\,R''$

3) Product R R' is member of set

4) R^{-1} exists

Point group $\Rightarrow$ at least one point is left unchanged under symmetry operation

Classes of conjugated elements:

R, R' are conjugate if $R = S^{-1}\,R'\,S$, where S is another element in the group

Typically associates operations such as rotations or reflections, where S takes it about another plane or axis

Matrix Representations

Matrix representation of element R of group [D_{ij} (R)]

$$C_2 \leftrightarrow \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

<u>Character of representative matrix</u>

X (R) = trace [D_{ij} (R)]

For the above representation of C_{2v} the characters are:

X (E)= X (C_2)= X (σ_{xz})= X (σ_{yz})=

Note: matrix el-ts for the representations of all 4 operators of C_{2v} are ± 1

Groups and Vibrations

General problem: how to connect representations of higher dimensions to those of lower dimensions

Define formal sum:

The 3 dimensional representation of C_{2v} that we have used can be expressed as

Groups and Vibrations

More common problem is to take high dimensional representation and reduce to sum of low dimensional representations

Proceed as guided by theorem:

1) Given any n-dimensional representation Γ_n, with matrices $D^n(R_1)$, $D^n(R_2)$, … and corresponding characters $X(D^n(R_1))$, $X(D^n(R_2))$, … where R_i is an operation of the point group.

If $D_j^0(R_1)$, $D_j^n(R_2)$, … , are the matrices and $X_j(D_j^n(R_1))$, $X_j(D_j^n(R_2))$, … the characters of the irreducible representations Γ_{oj} of the point group, then

2) The number of irreducible representations = number of classes

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Example

Let's return back to H_2O

Digression: finding the a_j’s

Extended character table

Some of the modes characterize translational and rotational degrees of freedom, remainder are vibrational