Electronic Structure of Condensed Matter
Fudan University - April 2010

Lecture 2
Crystals, the Bloch Theorem, Bands
Understanding using different points of view

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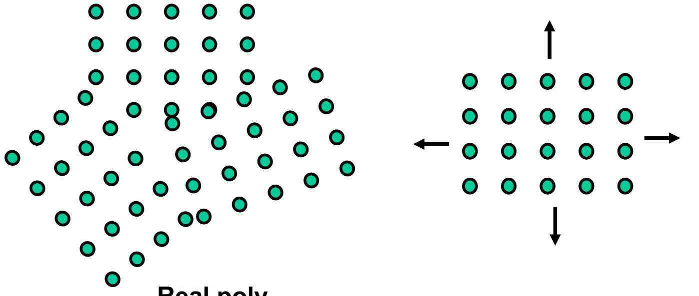
Ideal crystals are simple and relevant!



- Many solids are made of crystallites that are microscopic - but contain ~ 10^{20} atoms!

Lecture 2: Periodic Crystals

Only key ideas and figures are given here for use in class
Material is in any basic text on solid state physics.
It is also in the text, Chapter 4, which is essentially the same

OUTLINE

Crystal Structure = Lattice + Basis

Translation symmetry
Reciprocal Lattice
Brillouin Zone (BZ)
Bloch Theorem
……

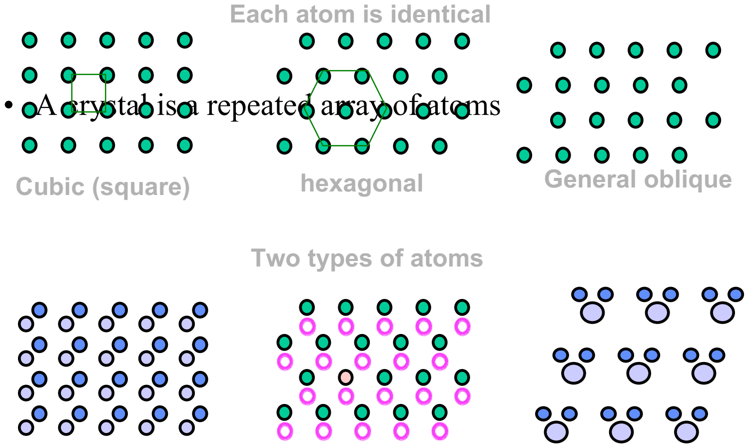
Types and Positions of atoms

Bloch Theorem for excitations in crystals
  Proof by group theory
  Proof by Fourier Expansion (later)
  Applies to any excitations - phonons, electrons, etc.

Qualitative discussion of Bloch functions. Zone center, Zone boundary

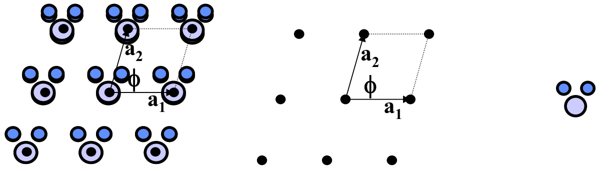
The first qualitative estimates of band widths in solids

Crystals



- A crystal is a repeated array of atoms

Two Dimensional Crystals

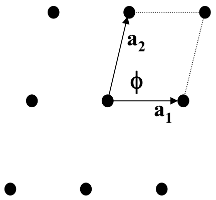


Crystal = Lattice + Basis

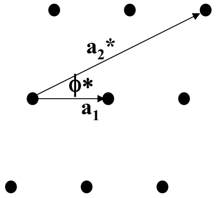
Called the Bravais Lattice

(Easier to draw in 2 dimensions – 3 dimensions later)

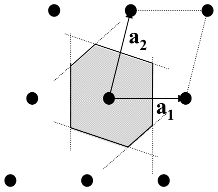
Lattices and Translations



One possible Primitive Cell



Another choice

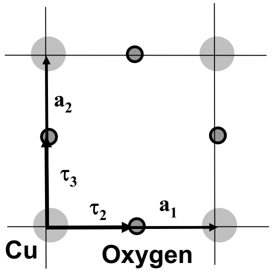


Wigner-Seitz Cell -- Unique

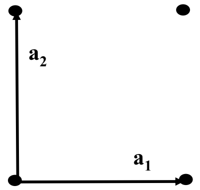
- The entire infinite lattice is specified by 2 primitive vectors a_1 and a_2 (also a_3 in 3-d)
- $T(n_1,n_2,\ldots) = n_1\ a_1 + n_2\ a_2$ (+ $n_3\ a_3$ in 3-d), where the n's are integers
- Note: the primitive vectors are not unique different vectors a_1 and a_2 can define the same lattice

- **All primitive cells have same area (volume)**
- **Wigner Seitz Cell is most compact, highest symmetry cell possible**
- **Also same rules in 3 dimensions**

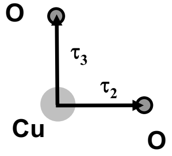
Crystalline layers with >1 atom basis



CuO$_2$ Layer



Square Lattice

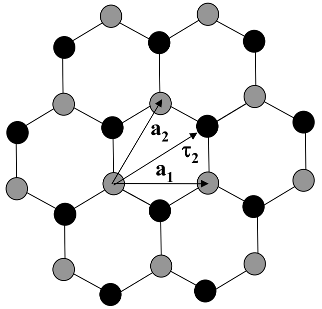


CuO$_2$ Basis

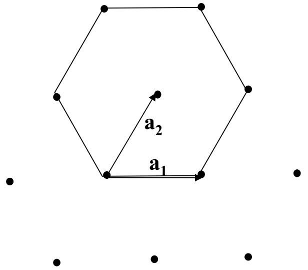
- One CuO$_2$ layer in the High Tc superconductors

- **Square lattice**
- **One basis unit on each site**

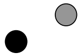
Crystalline layers with >1 atom basis



Honeycomb Lattice
(graphene or BN layer)



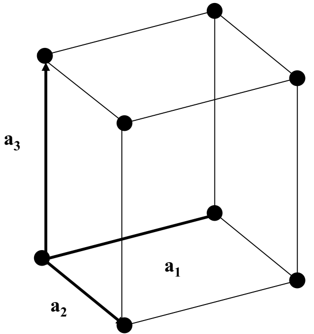
Hexagonal Lattice



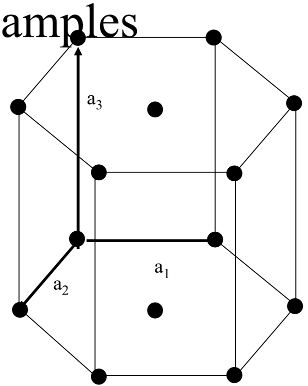
Basis
2 C atoms
or BN pair

- A single layer of graphitic carbon (graphene)
  - The two atoms in the cell are both Carbon
- A single layer of hexagonal boron nitride

Three Dimensional Lattices
Simplest examples



Simple Orthorhombic Bravais Lattice

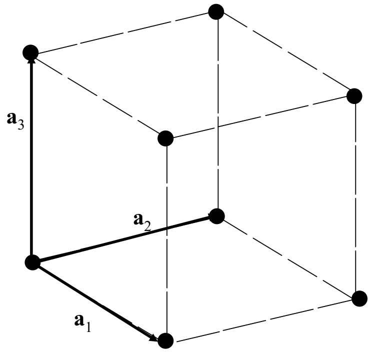


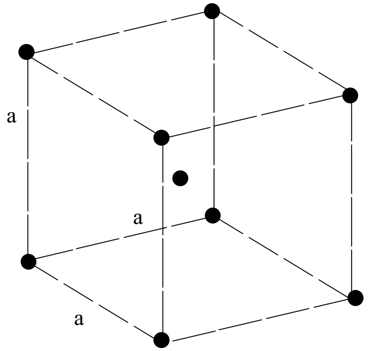
Hexagonal Bravais Lattice

- Orthorhombic: **angles 90 degrees, 3 lengths different**
  Tetragonal: **2 lengths same**
  Cubic: **3 lengths same**
- Hexagonal: **a_3 different from a_1, a_2 by symmetry**

Cubic Lattices

Length of each side - a





Simple Cubic

Primitive lattice vectors

$\mathbf{a}_1 = (1,0,0)\ a$
$\mathbf{a}_2 = (0,1,0)\ a$
$\mathbf{a}_3 = (0,0,1)\ a$

One atom per cell at position (0,0,0)

Body Centered Cubic (BCC)

Conventional Cell with 2 atoms at positions

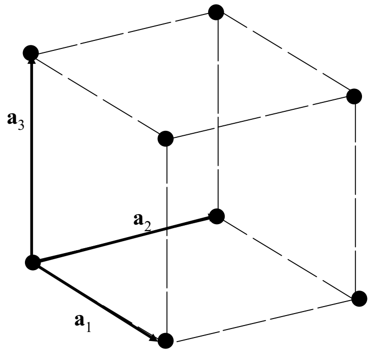
(000), (1/2,1/2,1/2) a

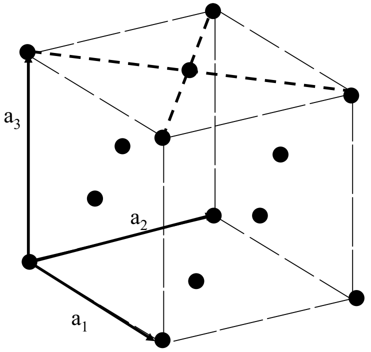
Primitive cell is one atom

8 neighbors

Cubic Lattices

Length of each side - a





Simple Cubic

Primitive lattice vectors

$\mathbf{a}_1 = (1,0,0)\ a$
$\mathbf{a}_2 = (0,1,0)\ a$
$\mathbf{a}_3 = (0,0,1)\ a$

One atom per cell at position (0,0,0)

Face Centered Cubic (FCC)

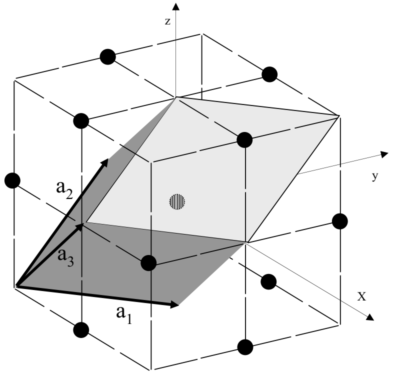
Conventional Cell with 4 atoms at positions

(000), (0,1/2,1/2), (1/2,0,1/2), (1/2,1/2,0)a

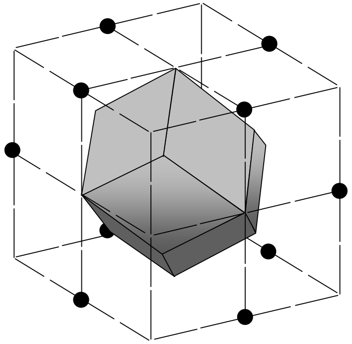
Primitive cell is one atom

12 neighbors (cubic close-packed)

Face Centered Cubic



One Primitive Cell



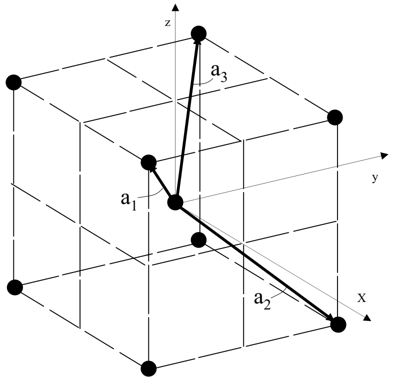
Wigner-Seitz Cell

Primitive lattice vectors

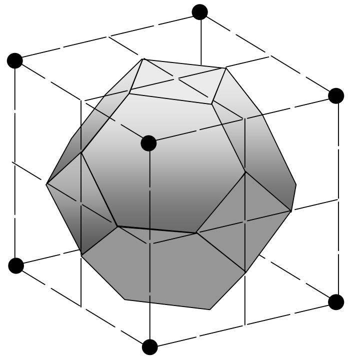
$\mathbf{a}_1 = (1/2,1/2,0)\ a$
$\mathbf{a}_2 = (1/2,0,1/2)\ a$
$\mathbf{a}_3 = (0,1/2,1/2)\ a$

One atom per cell at position (0,0,0)

Body Centered Cubic



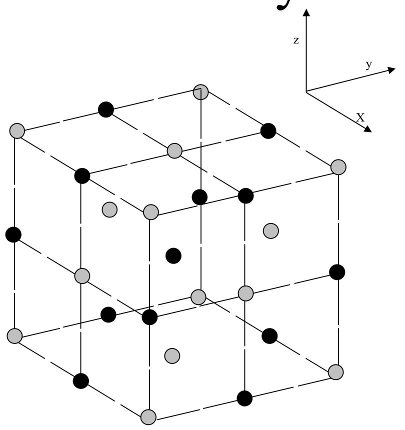
One Primitive Cell



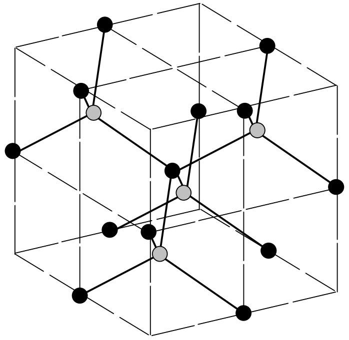
Wigner-Seitz Cell

Primitive lattice vectors
$\mathbf{a}_1 = (1/2, 1/2, -1/2)\, a$
$\mathbf{a}_2 = (1/2, -1/2, 1/2)\, a$
$\mathbf{a}_3 = (-1/2, 1/2, 1/2)\, a$
One atom per cell at position (0,0,0)

Cubic crystals with a basis

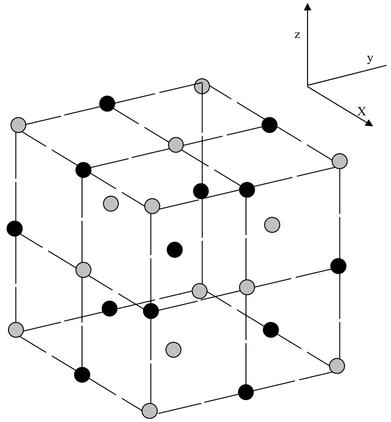


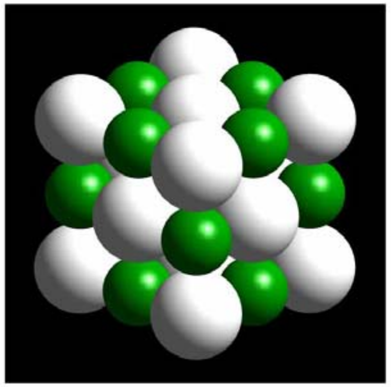
NaCl Structure with
Face Centered Cubic Bravais Lattice



ZnS Structure with
Face Centered Cubic Bravais Lattice
C, Si, Ge form diamond structure with
only one type of atom

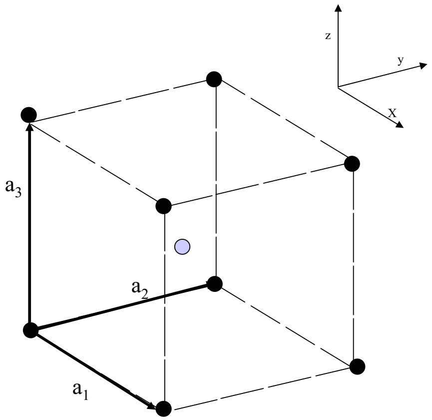
NaCl Structure



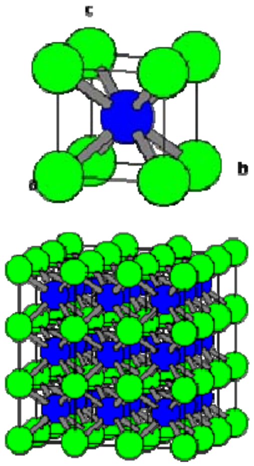


NaCl Structure with
Face Centered Cubic Bravais Lattice

CsCl Structure

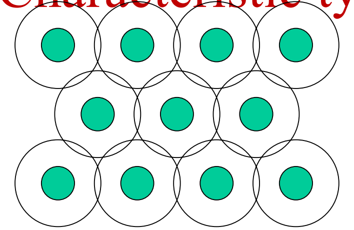


CsCl Structure
Simple Cubic Bravais Lattice

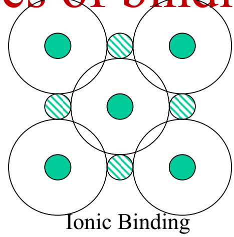


From http://www.ilpi.com/inorganic/structures/cscl/index.html

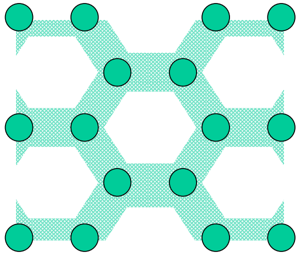
Characteristic types of binding



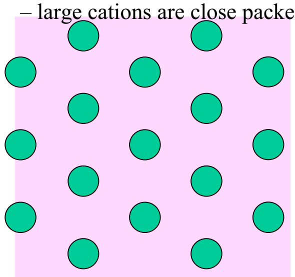
Closed-Shell Binding
Close packed



Ionic Binding
Structure depends upon radii of the two ions
– large cations are close packed



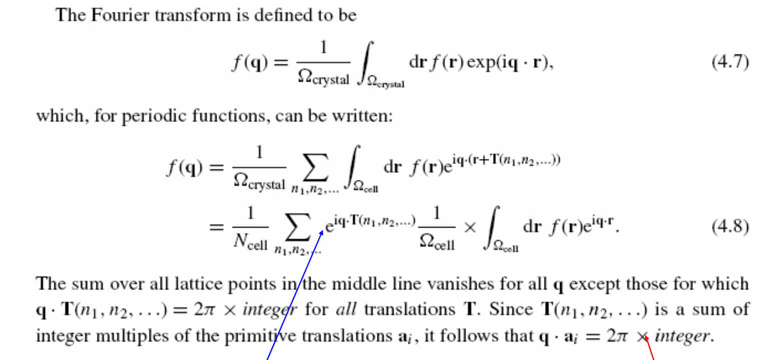
Covalent Binding
Open Structures



Metallic Binding
Close packed

Reciprocal lattice and Brillouin zone (BZ)

Fourier Components of a periodic f(r) function in a crystal



The Fourier transform is defined to be

$$f(\mathbf{q}) = \frac{1}{\Omega_{\text{crystal}}} \int_{\Omega_{\text{crystal}}} \mathrm{d}\mathbf{r}\, f(\mathbf{r}) \exp(\mathrm{i}\mathbf{q}\cdot\mathbf{r}), \tag{4.7}$$

which, for periodic functions, can be written:

$$f(\mathbf{q}) = \frac{1}{\Omega_{\text{crystal}}} \sum_{n_1,n_2,\ldots} \int_{\Omega_{\text{cell}}} \mathrm{d}\mathbf{r}\; f(\mathbf{r}) \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot(\mathbf{r}+\mathbf{T}(n_1,n_2,\ldots))}$$
$$= \frac{1}{N_{\text{cell}}} \sum_{n_1,n_2,\ldots} \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{T}(n_1,n_2,\ldots)} \frac{1}{\Omega_{\text{cell}}} \times \int_{\Omega_{\text{cell}}} \mathrm{d}\mathbf{r}\; f(\mathbf{r})\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}}. \tag{4.8}$$

The sum over all lattice points in the middle line vanishes for all $\mathbf{q}$ except those for which $\mathbf{q}\cdot\mathbf{T}(n_1, n_2, \ldots) = 2\pi \times$ *integer* for *all* translations $\mathbf{T}$. Since $\mathbf{T}(n_1, n_2, \ldots)$ is a sum of integer multiples of the primitive translations $\mathbf{a}_i$, it follows that $\mathbf{q}\cdot\mathbf{a}_i = 2\pi \times$ *integer*.

The sum vanishes unless q●T = 2π x integer for all T -- Thus q●a$_i$ = 2π x integer

This leads to the definition of the reciprocal lattice – next slide

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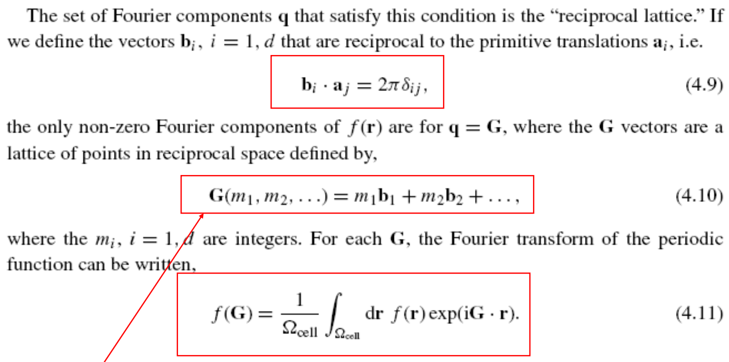
Reciprocal lattice and Brillouin zone (BZ)

The set of vectors q that satisfy the condition q ● a$_i$ = 2π x integer form a lattice



The set of Fourier components $\mathbf{q}$ that satisfy this condition is the "reciprocal lattice." If we define the vectors $\mathbf{b}_i$, $i = 1, d$ that are reciprocal to the primitive translations $\mathbf{a}_i$, i.e.

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}, \tag{4.9}$$

the only non-zero Fourier components of $f(\mathbf{r})$ are for $\mathbf{q} = \mathbf{G}$, where the $\mathbf{G}$ vectors are a lattice of points in reciprocal space defined by,

$$\mathbf{G}(m_1, m_2, \ldots) = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + \ldots, \tag{4.10}$$

where the m_i, $i = 1, d$ are integers. For each $\mathbf{G}$, the Fourier transform of the periodic function can be written,

$$f(\mathbf{G}) = \frac{1}{\Omega_{\text{cell}}} \int_{\Omega_{\text{cell}}} \mathrm{d}\mathbf{r}\; f(\mathbf{r}) \exp(\mathrm{i}\mathbf{G}\cdot\mathbf{r}). \tag{4.11}$$

This is the definition of the reciprocal lattice – examples on next slide

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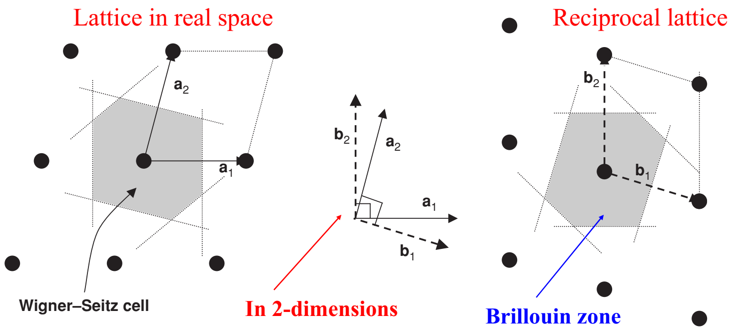
Brillouin Zone – example in 2 dimensions



In 2-dimensions
b$_1$ ● a$_1$ =2π, b$_1$ ● a$_2$ =0
b$_2$ ● a$_1$ =0, b$_2$ ● a$_2$ = 2π

Brillouin zone
Wigner-Sietz cell
of reciprocal lattice

Physical importance of BZ – For vectors k on the boundary of the BZ, k = ½ G so that |k| = |k-G|. This is the condition for Bragg scattering, which occurs only for k on the surface of the BZ.

Reciprocal lattices - examples for cubic lattices

Primitive translation vectors of lattice in real space in units of lattice constant a

	simple cubic	simple hex.	fcc	bcc
$\mathbf{a}_1 =$	$(1, 0, 0)$	$(1, 0, 0)$	$(0, \frac{1}{2}, \frac{1}{2})$	$(-\frac{1}{2}, \frac{1}{2}, \frac{1}{2}),$
$\mathbf{a}_2 =$	$(0, 1, 0)$	$\left(\frac{1}{2}, \frac{\sqrt{3}}{2}, 0\right)$	$(\frac{1}{2}, 0, \frac{1}{2})$	$(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}),$
$\mathbf{a}_3 =$	$(0, 0, 1)$	$(0, 0, \frac{c}{a})$	$(\frac{1}{2}, \frac{1}{2}, 0)$	$(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}).$

Primitive translation vectors of reciprocal lattice in units of 2π/a

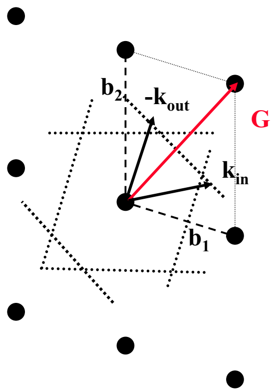
	simple cubic	simple hex.	fcc	bcc
$\mathbf{b}_1 =$	$(1, 0, 0)$	$\left(1, -\frac{1}{\sqrt{3}}, 0\right)$	$(1, 1, -1)$	$(0, 1, 1),$
$\mathbf{b}_2 =$	$(0, 1, 0)$	$\left(0, \frac{2}{\sqrt{3}}, 0\right)$	$(1, -1, 1)$	$(1, 0, 1),$
$\mathbf{b}_3 =$	$(0, 0, 1)$	$(0, 0, \frac{a}{c})$	$(-1, 1, 1)$	$(1, 1, 0).$

Rotated

Fcc, bcc are reciprocal to one another

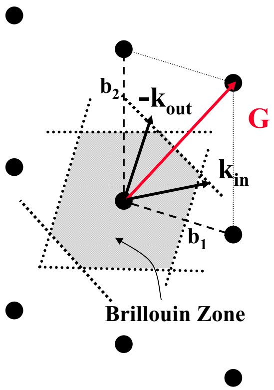
Check it your self – Do the vectors obey the conditions?

Geometric Construction of Diffraction Conditions



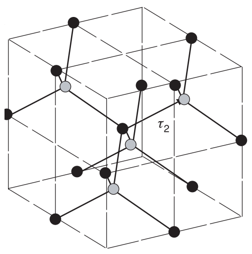
- Recall $k_{in} - k_{out} = G$ and $|k_{in}| = |k_{out}|$
- Consequence of condition $| 2\, k_{in} \cdot G | = G^2$
- The vector k_{in} (and k_{out}) lies along the per Perpindicular bisector of a G vector
- One example is shown

Diffraction and the Brillouin Zone



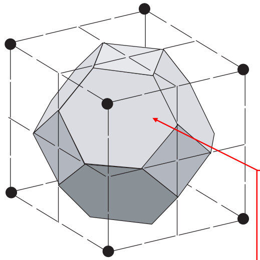
- Brillouin Zone - (BZ) - the Wigner-Seitz cell of the reciprocal lattice
- Formed by perpendicular bisectors of G vectors
- Special Role of Brillouin Zone
  - Diffraction occurs only for k on

Example of FCC



ZnS (GaAs, …)
(Diamond if the two atoms are the same element)

fcc lattice
Basis: Zn at (0,0,0)
S at (¼, ¼, ¼)



Brillouin Zone (Wigner-Seitz cell for the reciprocal lattice)

Reciprocal lattice – bcc

Conclusions

- Crystal structure = lattice + basis
  - Bravais lattice of translations – multiples of the primitive translations
  - Basis specifies the atoms that are associated with each lattice point
- Reciprocal lattice
  - Set of vectors G in reciprocal space that are the Fourier components of periodic functions
- Brillouin zone (BZ)
  - Wigner-Seitz cell of the reciprocal lattice
  - The surface of the BZ are the points where Bragg scattering occurs
  - Will be important in the understanding of electron states
- Often used examples
  - Zinc-blende (diamond) – fcc lattice - basis of 2 atoms
  - Reciprocal lattice is bcc

Electronic Structure of Condensed Matter
Fudan University - April 2010

Lecture 2
Crystals, the Bloch Theorem, Bands
Understanding using different points of view

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Schrodinger Equation

- Basic equation of Quantum Mechanics

$$[-(\hbar^2/2m)\nabla^2 + V(\underline{\mathbf{r}})]\,\Psi(\underline{\mathbf{r}}) = E\,\Psi(\underline{\mathbf{r}})$$

where

m = mass of particle
$V(\underline{\mathbf{r}})$ = potential energy at point $\underline{\mathbf{r}}$
$\nabla^2 = (d^2/dx^2 + d^2/dy^2 + d^2/dz^2)$
E = eigenvalue = energy of quantum state
$\Psi(\underline{\mathbf{r}})$ = wavefunction
$n(\underline{\mathbf{r}}) = |\Psi(\underline{\mathbf{r}})|^2$ = probability density

- Key Point for electrons in a crystal: The potential $V(\underline{\mathbf{r}})$ has the periodicity of the crystal

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Schrodinger Equation

- How can we solve the Schrodinger Eq.

$$[-(\hbar^2/2m)\nabla^2 + V(\underline{\mathbf{r}})]\,\Psi(\underline{\mathbf{r}}) = E\,\Psi(\underline{\mathbf{r}})$$

where $V(\underline{\mathbf{r}})$ has the periodicity of the crystal?

- This is the key practical computational problem for the methods used in the electronic structure school

- Here we consider simple cases as an introduction
  One dimension

Consider 1 dimensional example

- If the electrons can move freely on a line from 0 to L (with no potential),

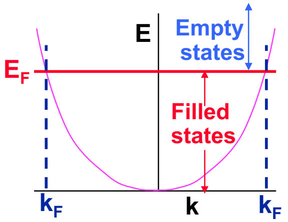
- Schrodinger Eq. In 1d with V = 0
  $-(\hbar^2/2m)\, d^2/dx^2\, \Psi(x) = E\, \Psi(x)$
- If we have periodic boundary conditions ($\Psi(0) = \Psi(L)$) then the solution is:

$\Psi(x) = L^{-1/2}\exp(ikx)$, $k = \pm m(2\pi/L)$, m = 0,1,..

$E(k) = (\hbar^2/2m)\,|k|^2$

Electrons on a line

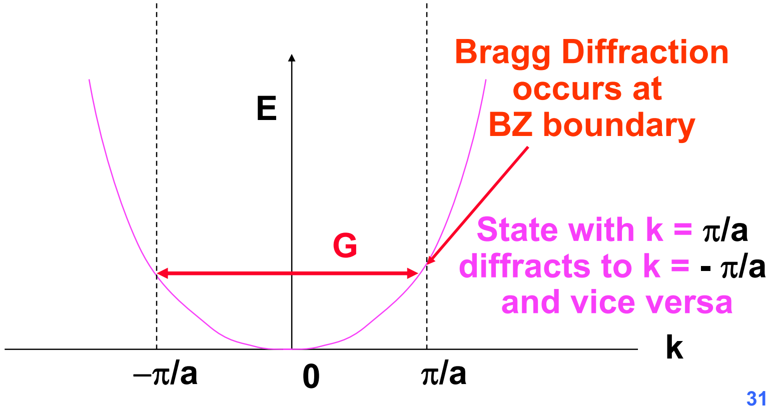
- For electrons in a box, the energy is just the kinetic energy
  $E(k) = (\hbar^2/2m)\, k^2$
- Values of k fixed by the box, $k = \pm m(2\pi/L)$, m = 0, 1, . . .



- Pauli Principle - The lowest energy state is for electrons is to fill the lowest states up to the Fermi energy E_F and Fermi momentum k_F – two electrons (spin up and down) in each state
- This is a metal – the electrons can conduct electricity

Electrons on a line with potential V(x)

- What happens if there is a potential V(x) that has the periodicity a of the crystal?
- An electron wave with wavevector k can suffer Bragg diffraction to k ± G, with G any reciprocal lattice vector



Bragg Diffraction occurs at BZ boundary

State with $k = \pi/a$ diffracts to $k = -\pi/a$ and vice versa

---

Interpretation of Standing waves at Brillouin Zone boundary

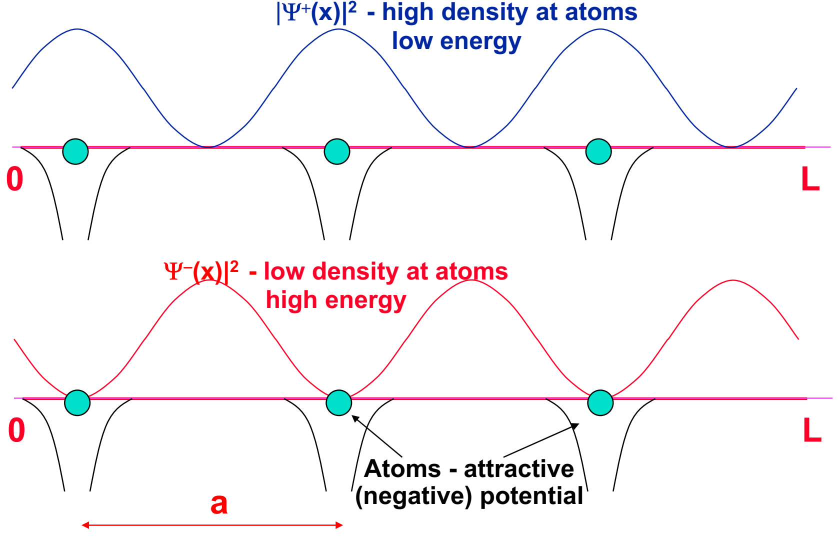
- Bragg scattering at $k = \pi/a$ leads to the two possible standing waves. Each is a combination of the right and left going waves $\exp(i\pi x/a)$ and $\exp(-i\pi x/a)$:

$$\Psi^+(x) = \exp(i\pi x/a) + \exp(-i\pi x/a) = 2\cos(\pi x/a)$$
$$\Psi^-(x) = \exp(i\pi x/a) - \exp(-i\pi x/a) = 2i\sin(\pi x/a),$$

The density of electrons for each standing wave is:

$$|\Psi^+(x)|^2 = 4\cos^2(\pi x/a)$$
$$|\Psi^-(x)|^2 = 4\sin^2(\pi x/a)$$

Interpretation of Standing waves at Brillouin Zone boundary

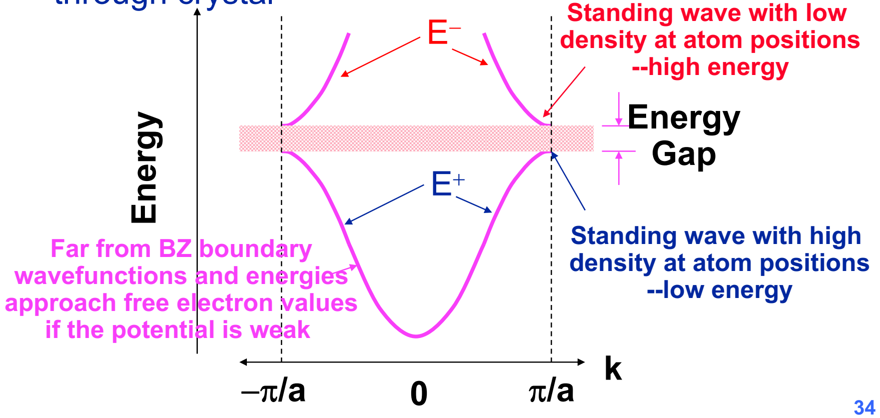

$|\Psi^+(x)|^2$ - high density at atoms
low energy

$\Psi^-(x)|^2$ - low density at atoms
high energy

Atoms - attractive (negative) potential

Electrons on a line with a periodic V(x)

- Bands changed greatly only at zone boundary
  Standing wave at zone boundary
  Energy gap -- energies at which no waves can travel through crystal


Standing wave with low density at atom positions --high energy

Standing wave with high density at atom positions --low energy

Far from BZ boundary wavefunctions and energies approach free electron values if the potential is weak

---

Independent electrons – Plane wave methods (1)

General theory -- From book –or Solid State Physics text

The independent-particle Schrodinger equation

The eigenstates of any independent particle Schrödinger-like equation in which each electron moves in an effective potential $V_{eff}(\mathbf{r})$,[1] such as the Kohn–Sham equations, satisfy the eigenvalue equation

$$\hat{H}_{eff}(\mathbf{r})\psi_i(\mathbf{r}) = \left[-\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}). \qquad (12.1)$$

Using the fact that any periodic function can be expanded in the complete set of Fourier components, an eigenfunction can be written

$$\psi_i(\mathbf{r}) = \sum_{\mathbf{q}} c_{i,\mathbf{q}} \times \frac{1}{\sqrt{\Omega}}\exp(i\mathbf{q}\cdot\mathbf{r}) \equiv \sum_{\mathbf{q}} c_{i,\mathbf{q}} \times |\mathbf{q}\rangle, \qquad (12.2)$$

where $c_{i,\mathbf{q}}$ are the expansion coefficients of the wavefunction in the basis of orthonormal plane waves $|\mathbf{q}\rangle$ satisfying

$$\langle\mathbf{q}'|\mathbf{q}\rangle \equiv \frac{1}{\Omega}\int_{\Omega} d\mathbf{r}\ \exp(-i\mathbf{q}'\cdot\mathbf{r})\exp(i\mathbf{q}\cdot\mathbf{r}) = \delta_{\mathbf{q},\mathbf{q}'}. \qquad (12.3)$$

Plane wave basis – always possible – it is Fourier analysis

Independent electrons – Plane wave methods (2)

Expression for the Schr. Eq. in a plane wave basis

Inserting (12.2) into (12.1), multiplying from the left by $\langle\mathbf{q}'|$ and integrating as in (12.3) leads to the Schrödinger equation in Fourier space

$$\sum_{\mathbf{q}}\langle\mathbf{q}'|\hat{H}_{eff}|\mathbf{q}\rangle c_{i,\mathbf{q}} = \varepsilon_i\sum_{\mathbf{q}}\langle\mathbf{q}'|\mathbf{q}\rangle c_{i,\mathbf{q}} = \varepsilon_i c_{i,\mathbf{q}'}. \qquad (12.4)$$

Kinetic energy is simple – easy to differentiate a plane wave!

The matrix element of the kinetic energy operator is simply

$$\langle\mathbf{q}'| - \frac{\hbar^2}{2m_e}\nabla^2|\mathbf{q}\rangle = \frac{\hbar^2}{2m_e}|q|^2\delta_{\mathbf{q},\mathbf{q}'} \rightarrow \frac{1}{2}|q|^2\delta_{\mathbf{q},\mathbf{q}'}, \qquad (12.5)$$

Plane wave are eigenstates of K.E. – The only thing that mixes the plane waves is the potential

Independent electrons – Plane wave methods (3)

Fourier Components of the potential in a crystal

For a crystal, the potential $V_{eff}(\mathbf{r})$ is periodic and can be expressed as a sum of Fourier components (see Eqs. (4.7) to (4.11))

$$V_{eff}(\mathbf{r}) = \sum_m V_{eff}(\mathbf{G}_m)\exp(\mathrm{i}\mathbf{G}_m \cdot \mathbf{r}), \tag{12.6}$$

where $\mathbf{G}_m$ are the reciprocal lattice vectors, and

$$V_{eff}(\mathbf{G}) = \frac{1}{\Omega_{\text{cell}}}\int_{\Omega_{\text{cell}}} V_{eff}(\mathbf{r})\exp(-\mathrm{i}\mathbf{G}\cdot\mathbf{r})\mathrm{d}\mathbf{r}, \tag{12.7}$$

with Ω_{cell} the volume of the primitive cell. Thus the matrix elements of the potential

$$\langle \mathbf{q}'|V_{eff}|\mathbf{q}\rangle = \sum_m V_{eff}(\mathbf{G}_m)\delta_{\mathbf{q}'-\mathbf{q},\mathbf{G}_m}, \tag{12.8}$$

are non-zero only if $\mathbf{q}$ and $\mathbf{q}'$ differ by some reciprocal lattice vector $\mathbf{G}_m$.

Key point: The potential only couples waves q and q' if they differ by a reciprocal lattice vector -- $q - q' = G_m$

Independent electrons – Plane wave methods (4)

The hamiltonian matrix in a plane wave basis

k is defined to be in a primitive cell of the reciprocal lattice around k =0

Finally, if we *define* $\mathbf{q} = \mathbf{k} + \mathbf{G}_m$ and $\mathbf{q}' = \mathbf{k} + \mathbf{G}_{m'}$ (which differ by a reciprocal lattice vector $\mathbf{G}_{m''} = \mathbf{G}_m - \mathbf{G}_{m'}$), then the Schrödinger equation for any given $\mathbf{k}$ can be written as the matrix equation

$$\boxed{\sum_{m'} H_{m,m'}(\mathbf{k})c_{i,m'}(\mathbf{k}) = \varepsilon_i(\mathbf{k})c_{i,m}(\mathbf{k})}, \tag{12.9}$$

Matrix eigenvalue equation

where[2]

$$H_{m,m'}(\mathbf{k}) = \langle \mathbf{k}+\mathbf{G}_m|\hat{H}_{eff}|\mathbf{k}+\mathbf{G}_{m'}\rangle = \frac{\hbar^2}{2m_e}|\mathbf{k}+\mathbf{G}_m|^2\delta_{m,m'} + V_{eff}(\mathbf{G}_m - \mathbf{G}_{m'}). \tag{12.10}$$

Note that k only appears in the kinetic energy!
(Actually V depends on k in pseudopotentials)

Key point: Each k is independent. The problem can be solved at each k-point separately

---

Bloch theorem

We have found that each eigenstate has a definite k and it is composed of Fourier components k + G where G is any reciprocal lattice vector. Therefore, ψ can always be written $\psi_k = \exp(ikr)\, u_k(r)$ where u is periodic

1. The Bloch theorem

* 1. **The Bloch theorem.** Each eigenfunction of the Schrödinger equation, (12.9), for a given $\mathbf{k}$ is given by (12.2), with the sum over $\mathbf{q}$ restricted to $\mathbf{q} = \mathbf{k} + \mathbf{G}_m$, which can be written

$$\psi_{i,\mathbf{k}}(\mathbf{r}) = \sum_m c_{i,m}(\mathbf{k}) \times \frac{1}{\sqrt{\Omega}}\exp(\mathrm{i}(\mathbf{k}+\mathbf{G}_m)\cdot\mathbf{r}) = \exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r})\frac{1}{\sqrt{N_{\text{cell}}}}u_{i,\mathbf{k}}(\mathbf{r}), \tag{12.11}$$

where $\Omega = N_{\text{cell}}\Omega_{\text{cell}}$ and

$$u_{i,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega_{\text{cell}}}}\sum_m c_{i,m}(\mathbf{k})\exp(\mathrm{i}\mathbf{G}_m\cdot\mathbf{r}), \tag{12.12}$$

which has the periodicity of the crystal. This is the Bloch theorem

* **2. The solutions form bands of eigenvalues $\varepsilon_i(k)$**

* **3. k is conserved – it is called crystal momentum which is like real momentum except that it is only defined in the BZ – the solutions are periodic in k, i.e., the same for k and k+G for any reciprocal lattice vector G**

Role of the Brillouin Zone (BZ)

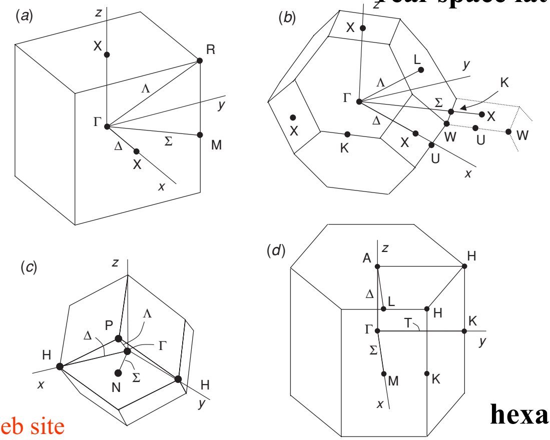
The BZ is the Wigner Seitz cell of the reciprocal lattice -- the most compact primitive cell

The BZ is unique among all primitive cells because its boundaries are the bisecting planes of the G vectors where Bragg scattering occurs (see Sec. 4.2). Inside the Brillouin zone there are no such boundaries:

the bands must be continuous and analytic inside the zone.

The boundaries are of special interest since every boundary point is a k vector for which Bragg scattering can occur; this leads to special features, such as zero group velocities due to Bragg scattering at the BZ boundary

Brillouin Zone - Examples



Simple cubic

BZ for FCC real-space lattice

BCC

hexagonal

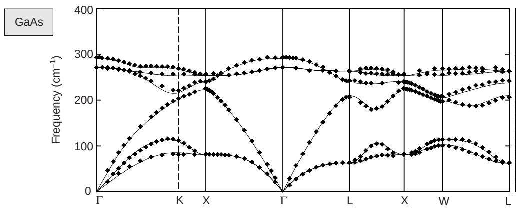
Useful Web site

BZ with labels for all 230 space groups

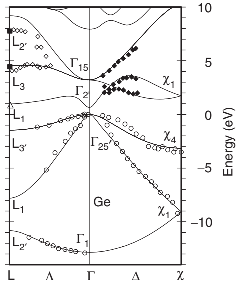
http://www.cryst.ehu.es/cryst/get_kvec.html

Examples of bands in fcc crystals
Electron bands, phonon bands in same BZ

GaAs – phonons – lattice vibrations
described by phonons with k vectors in the BZ



Germanium - electrons

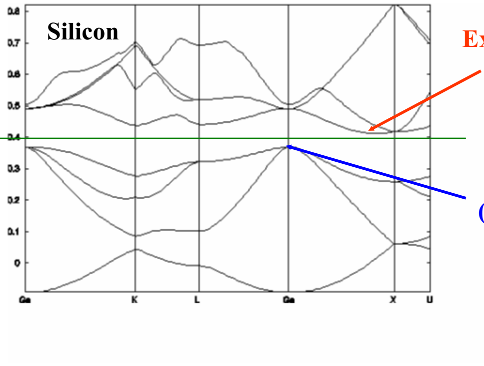


Electron Excitations - Bands

- **Understood since the 1920's - independent electron theories predict that electrons form bands of allowed eigenvalues, with forbidden gaps**

•Lowest energy state is for bands filled to the Fermi level (exclusion principle)

- **Established by experimentally for states near the Fermi energy**



Empty Bands

Gap

Filled Bands

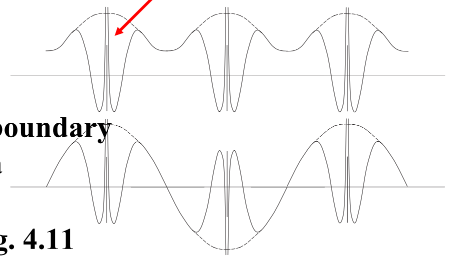
Extra added electrons go in bottom of conduction band

Missing electrons (holes) go in top of valence band

Nature of the Bloch functions

Zone center
k = 0

Atomic-like near each nucleus



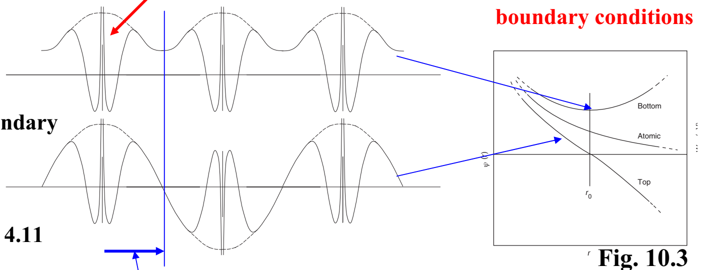
Zone boundary
k = π/a

Fig. 4.11

Just by inspection of these two figures, one can see a way to make qualitative (often quantitative!) estimates about energy bands in solids!

Can you see the idea?

Estimates of band widths in solids
-- using only information from atoms! --



Zone center
k = 0

Atomic-like near each nucleus

Calculation on atom with different boundary conditions

Zone boundary
$k = \pi/a$

Fig. 4.11

Fig. 10.3

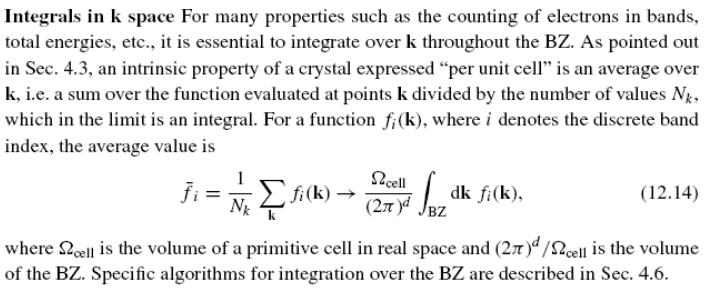
r_0 = ½ the nearest neighbor distance in the solid

The change in energy of the atomic state with boundary conditions ($\psi = 0$ at the $r = r_0$ or $d\psi/dr = 0$ at $r=r_0$) gives an estimate of the band width in the solid!

This idea is close to the original work of Wigner and Seitz in 1933 and modern KKR and LMTO work! More later in course.

Integrals over the BZ

Integrated quantities like the density and the total energy are always sums over all the occupied states. In a crystal this means a sum over bands and an integral over the BZ



Integrals in k space For many properties such as the counting of electrons in bands, total energies, etc., it is essential to integrate over **k** throughout the BZ. As pointed out in Sec. 4.3, an intrinsic property of a crystal expressed "per unit cell" is an average over **k**, i.e. a sum over the function evaluated at points **k** divided by the number of values N_k, which in the limit is an integral. For a function $f_i(\mathbf{k})$, where i denotes the discrete band index, the average value is

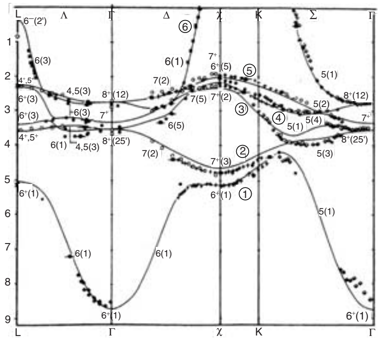
$$\bar{f}_i = \frac{1}{N_k}\sum_{\mathbf{k}} f_i(\mathbf{k}) \rightarrow \frac{\Omega_{\text{cell}}}{(2\pi)^d}\int_{\text{BZ}} d\mathbf{k}\, f_i(\mathbf{k}), \qquad (12.14)$$

where Ω_{cell} is the volume of a primitive cell in real space and $(2\pi)^d/\Omega_{\text{cell}}$ is the volume of the BZ. Specific algorithms for integration over the BZ are described in Sec. 4.6.

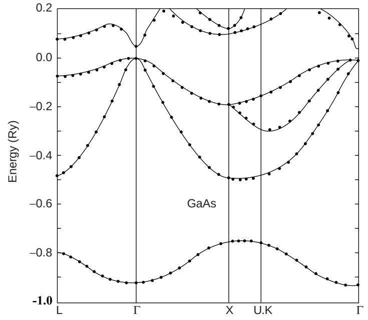
NOT in a standard `text – but needed for any total quantity- energy, density, etc. are sums over all occupied states – in Integrals over the BZ

Example of bands plotted along lines in the BZ

Two fcc crystals



Copper



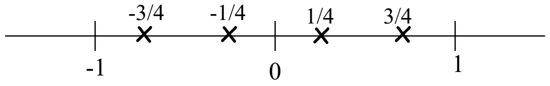
GaAs

Special k-points

"Special k-points" denotes a regular grid of point in the BZ chosen to be optimal for integrating a smooth periodic function

This is useful in crystals because the eigenvalues ε_k and eigenfunctions $\psi_k(r)$ vary smoothly in the BZ for each band. Thus special points are useful for integrals such as the sum of eigenvalues of the occupied bands and the electron density.

Examples of special points in the BZ in units of π/a

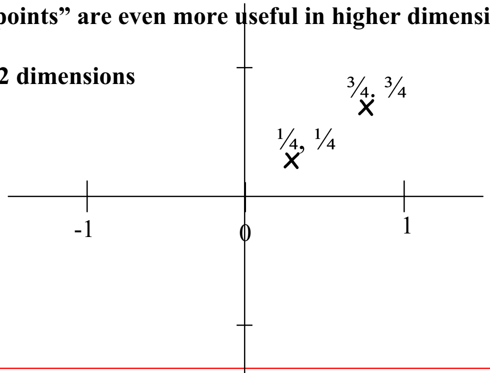


Key points: Any function g(k) that can be expended in Fourier components up to $3\pi/a$ are integrated exactly by the sum at these points.
Only two points need to be calculated since k and –k are conjugate solutions.

Special k-points

"Special k-points" are even more useful in higher dimensions

Example - 2 dimensions



Key points: Only 2 points are needed in 2 dimensions to get the same accuracy as in one dimension described before
This also works in 3-d – two points can give an accurate result for the integral!

Conclusions

- Plane waves solution for electronic states in crystals
  - **Hmiltoian matrix given simply in terms involving Fourier components of the potential**
- Bloch theorem – proved easily using plane waves
  - **$\psi_k(r) = \exp(ikr)U_k(r)$ where $u_k(r)$ is periodic**
- Electron bands
  - **Plotted along bands in the BZ**
  - **Interpretation in terms of atomic-like states (LCAO defined more carefully later)**
- Integration over the BZ to find total properties
  - **Total energy, electron density, forces, . . .**
  - **Special k points**
- These are the parts that enable actual Kohn-Sham calculations