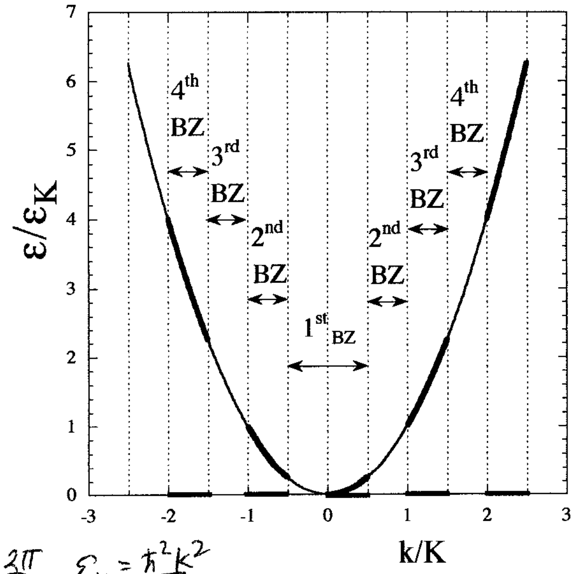
Band structure and ground state in weak potential approximation

Free electron energy spectrum is $\varepsilon_k^0 = \frac{\hbar^2 k^2}{2m}$

To represent the free electron energy spectrum in the "reduced zone" scheme, for each wavevector $\vec{k}$ we write

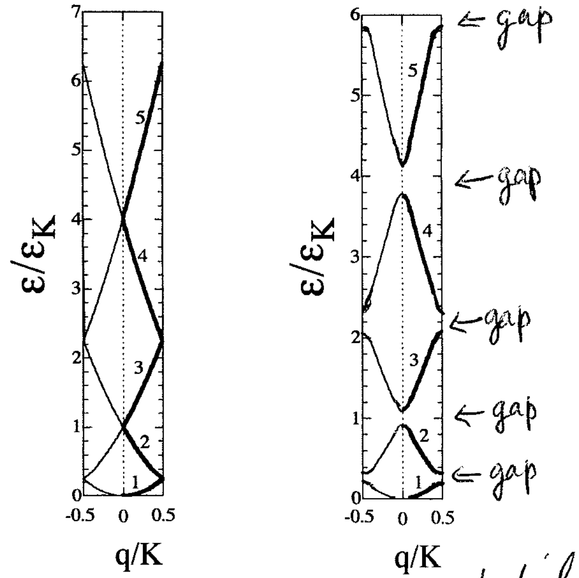
$$\vec{k} = \vec{q} + \vec{K}$$

where $\vec{q}$ is in the 1st BZ and $\vec{K}$ is in R.L. This decomposition is unique. We then plot $\varepsilon_k^0 = \hbar^2(\vec{q}+\vec{K})^2/2m$ as a function of $\vec{q}$ in 1st BZ. This gives a separate curve for each RL vector $\vec{K}$, and thus gives ε_k^0 represented as separate bands in the reduced zone scheme. When a weak potential is turned on, energy gaps are introduced wherever the free ~~electron~~ electron bands have a degeneracy (the degeneracies will occur when $\vec{q}+\vec{K}$ lies on a Bragg plane). In one dimension, the result looks like below:



$K \equiv \frac{2\pi}{a}$, $\varepsilon_K \equiv \frac{\hbar^2 K^2}{2m}$

extended zone



free electrons

weak potential

reduced zone

heavy lines are for $q+K$ with $0 \leq q \leq \frac{K}{2}$ – positive half 1st BZ

light lines are for $q+K$ with $-\frac{K}{2} \leq q \leq 0$ – negative half 1st BZ

In reduced zone plots, the numbers label the BZ that the band came from in the extended zone plot.

In 1-D the bands do not overlap ie

$$\max_{q} \mathcal{E}_n(q) < \min_{q} \mathcal{E}_{n+1}(q) \qquad n \text{ is band index}$$

When $\max \mathcal{E}_n(\vec{q})$ and $\min \mathcal{E}_{n+1}(\vec{q})$ occur at the same value of $\vec{q}$, we say there is a direct gap. When they occur at different $\vec{q}$, we say there is an indirect gap.

Ground State in 1-D weak potential

To construct the ground state one fills up the lowest energy single electron eigenstates to get the lowest total energy many electron state consistent with the Pauli exclusion principal.

From Born-van Karman boundary conditions we know that in a BL with N sites, there are N allowed $\vec{k}$ vectors in any primitive cell of the R.L. ⇒ N allowed $\vec{q}$ vectors in the 1st BZ and hence 2N allowed electron states in each energy band (factor of 2 from spin ↑ or spin ↓ for each $\vec{q}$)

⇒ each energy band can hold 2 electrons per Bravais Lattice site

Assume for simplicity we have a crystal structure with one ion at each BL site, with valence Z. ie each BL site contributes Z conduction electrons

In 1-D, since energy bands do not overlap:

① If $Z = 2m$ is <u>even</u>, then we completely fill up the lowest m bands and all other bands are completely empty

② If $Z = 2m+1$ is <u>odd</u>, then we completely fill up the lowest m bands, and the $(m+1)^{st}$ band is 1/2 filled. All higher bands are completely empty.

<u>case ① Z even</u> : material is an <u>insulator</u>

At low T in equilibrium, bands are completely filled or completely empty ⇒ there is an energy gap ε_g between the most energetic electron and the lowest unoccupied electron state (ie the first excited state)

$$\varepsilon_g = \min_q \varepsilon_{n+1}(q) - \max_q \varepsilon_n(q)$$

⇒ Unless electrons somehow receive an energy $\gtrsim \varepsilon_g$, they cannot scatter - no empty states nearby in energy to scatter to! We will soon see that a filled band can carry no current ⇒ material is an insulator provided $k_B T \lesssim \varepsilon_g$ and $eEl \lesssim \varepsilon_g$ where l is the mean free path

When $k_B T \gtrsim \varepsilon_g$, the equilibrium state will have some electrons, with density $\sim e^{-\varepsilon_g/k_B T}$, excited over the gap ε_g from the top of the $m = Z/2$ band into the bottom of the $m+1$

band. Now these electrons at bottom of m+1 band at at top of m band will have nearly empty states they can scatter into. Applying an $\vec{E}$ field will scatter electrons and create a non equilibrium distribution that carries a finite current.

$$\Rightarrow \begin{cases} k_BT \ll \mathcal{E}_g & \Rightarrow \text{insulator} \\ k_BT \gtrsim \mathcal{E}_g & \Rightarrow \underline{\text{semiconductor}} \text{ - carrier density} \sim e^{-\mathcal{E}_g/k_BT} \end{cases}$$

case ② Z odd : Material is a metal

The highest band containing electrons is partially (half) filled at $T=0$.

$\Rightarrow$ at any T there are empty states nearby in energy ~~to scatter into [illegible] gap~~ to the most energetic electrons at $\mathcal{E}_F$. There is no energy gap. When apply electric field $\vec{E}$ one will set up a non-equilibrium distribution carry a current

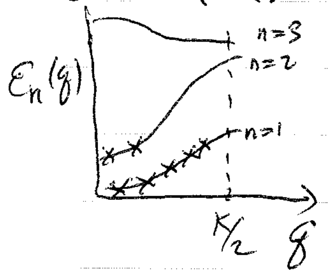
So for 1-D weak potential, Z odd $\Rightarrow$ metal
Z even $\Rightarrow$ insulator

This was a consequence of the non-overlaping bands.

But in 2-D or 3-D (or even perhaps 1-D when potential is NOT weak) bands <u>can</u> coverlap, ie we may have the case that

$$\max_q \mathcal{E}_n(q) > \min_q \mathcal{E}_{n+1}(q)$$

In such a case, as one constructs the ground state, one will start to fill up the $n+1$ band before one has completely filled the n band.
Thus Z even <u>need not be</u> an insulator - we might have more than one partially filled band containing the most energetic electrons at ε_F
$\Rightarrow$ metal.



{when bands overlap, can have several partially filled bands before completely filling a given band

However, we still <u>would expect</u> that if a material <u>is</u> an insulator, it must have only completely filled bands and completely empty bands (so no scattering possible). Since each filled band holds 2 electrons per Bravais lattice site, we would still expect Z must be <u>even</u>.

Thus we would expect that Z even is a necessary but not sufficient condition to have an insulator.

But it turns out that even this is not always true. While most insulators do have Z even, it was known in 1940's that some transition metal oxides, such as NiO and CoO, have Z odd but are still insulators!

Such materials, where Z is odd but material is an insulator, are called Mott insulators. It is believed that in these cases strong electron-electron interactions are responsible for the effect, invalidating the conclusions of the independent electron approximation that is the basis of band theory. To study such problems the simple Hubbard model is often used (the Hubbard model is simple to state, but very difficult to solve!)

2D weak potential band structure - single square BL

R.L. is square with $\vec{K} = K(n\hat{x}+m\hat{y})$ n, m integers

$K = 2\pi/a$

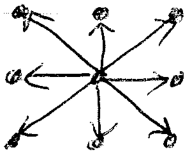
The smallest R.L. vectors are

a = lattice constant BL

$\vec{K}_0 = 0$

$\{\vec{K}_1\} = \{K\hat{x}, -K\hat{x}, K\hat{y}, -K\hat{y}\}$

$\{\vec{K}_2\} = \{K(\hat{x}+\hat{y}), K(\hat{x}-\hat{y}), K(-\hat{x}+\hat{y}), K(-\hat{x}-\hat{y})\}$



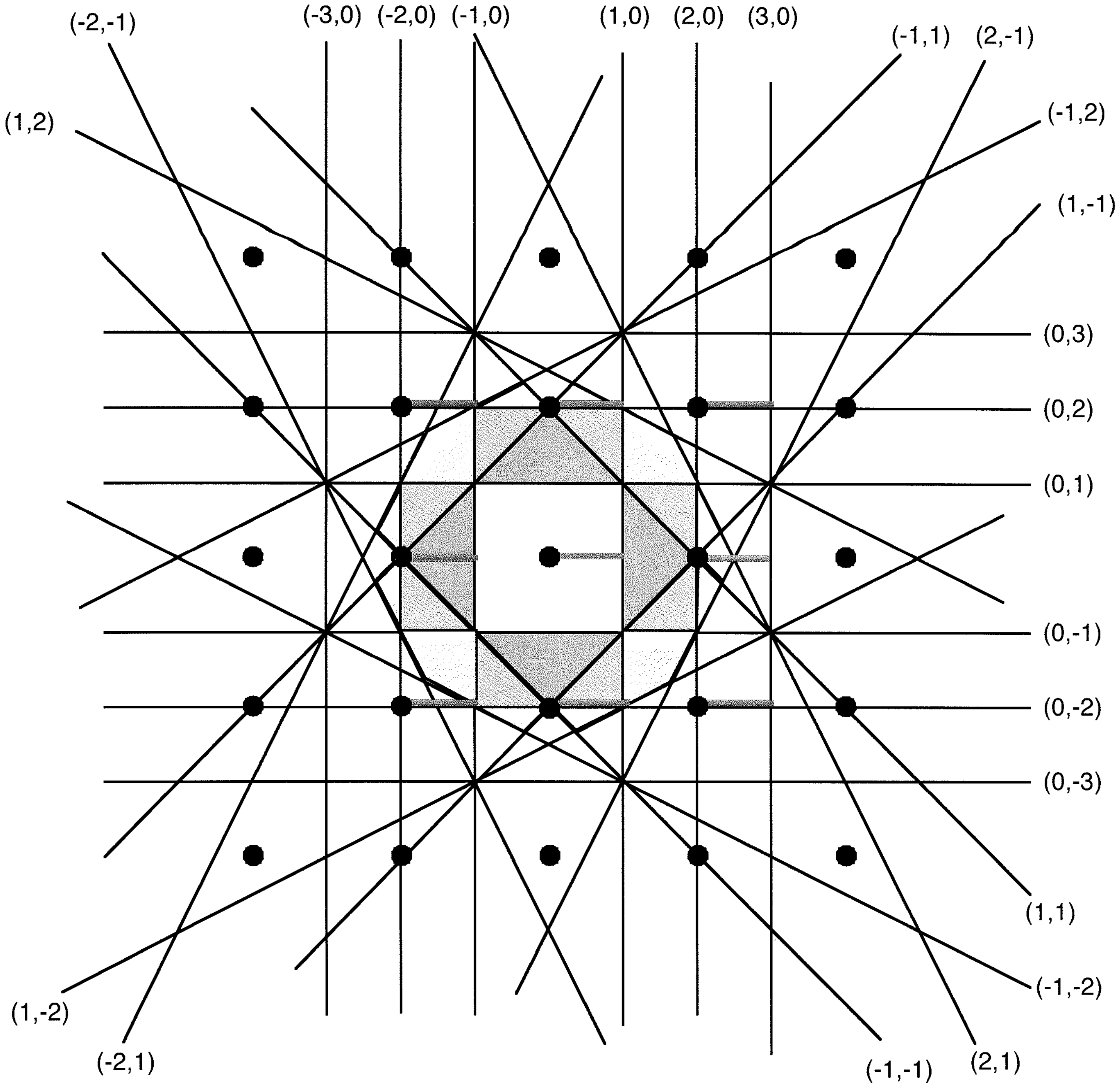
For $\vec{q} = q\hat{x}$ in 1st BZ, ie $0 \le q \le \frac{K}{2}$, we will plot the band structure, in the reduced zone scheme, for all bands corresponding the above 8 R.L. vectors.

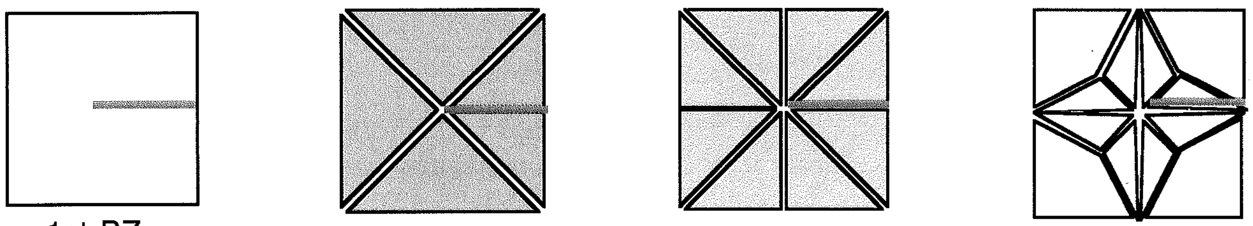
$\varepsilon_i(\vec{q}) = \frac{\hbar^2}{2m}(\vec{q}+\vec{K}_i)^2$ measure energy in units of $\varepsilon_X = \frac{\hbar^2}{2m}\left(\frac{K}{2}\right)^2$

	R.L. vector	energy		degeneracy	
	$\vec{K}_0 = 0$	$\varepsilon = \frac{\hbar^2 q^2}{2m}$	$\varepsilon/\varepsilon_X = 4(q/K)^2$	1	(a)
$\{\vec{K}_1\}$	$-K\hat{x}$	$\varepsilon = \frac{\hbar^2}{2m}(q-K)^2$	$\varepsilon/\varepsilon_X = 4(\frac{q}{K}-1)^2$	1	(b)
	$+K\hat{x}$	$\varepsilon = \frac{\hbar^2}{2m}(q+K)^2$	$\varepsilon/\varepsilon_X = 4(\frac{q}{K}+1)^2$	1	(c)
	$\pm K\hat{y}$	$\varepsilon = \frac{\hbar^2}{2m}(q^2+K^2)$	$\varepsilon/\varepsilon_X = 4((\frac{q}{K})^2+1)$	2	(d)
$\{\vec{K}_2\}$	$K(-\hat{x}\pm\hat{y})$	$\varepsilon = \frac{\hbar^2}{2m}[(q-K)^2+K^2]$	$\varepsilon/\varepsilon_X = 4[(\frac{q}{K}-1)^2+1]$	2	(e)
	$K(+\hat{x}\pm\hat{y})$	$\varepsilon = \frac{\hbar^2}{2m}[(q+K)^2+K^2]$	$\varepsilon/\varepsilon_X = 4[(\frac{q}{K}+1)^2+1]$	2	(f)

we plot the above curves of $\varepsilon/\varepsilon_X$ vs q/K in reduced zone scheme

Reciprocal Lattice and k-space for a two-dimensional square Bravais Lattice of lattice constant *a*. Bragg planes are labeled by the reciprocal lattice vector that they bisect, $\mathbf{K} = (2\pi/a)(n, m)$.





1st BZ

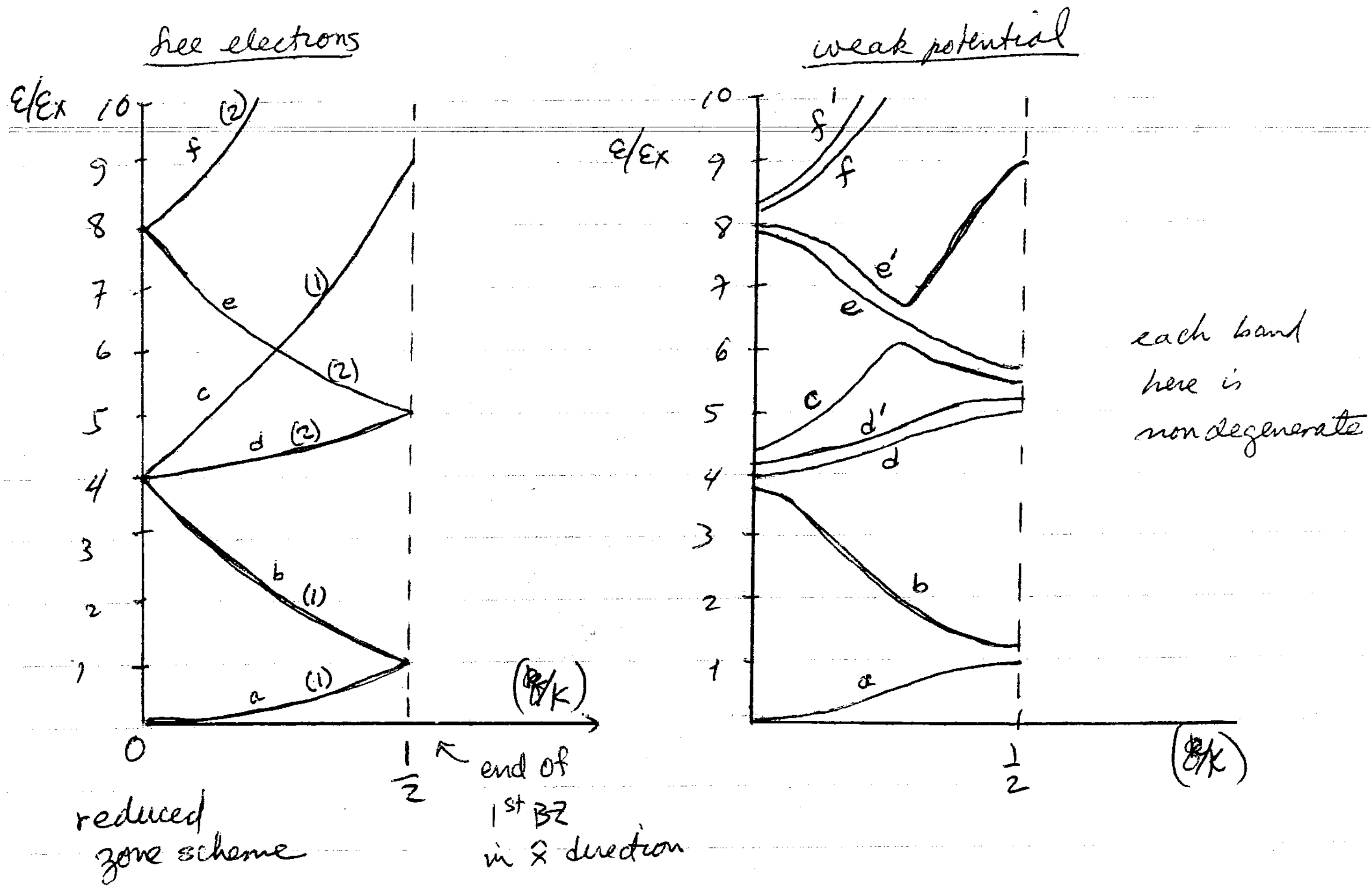
2nd BZ

3rd BZ

4th BZ

Pieces of the nth Brillouin Zone translated back into the 1st BZ

Red lines indicate values of $\vec{k}$ for free electron states giving rise to the band structure plotted in reduced ~~sol~~ zone scheme on preceeding page.



a) 1st BZ

b) 2nd BZ

d) 3rd + 4th BZs

c) 5th + 7th BZs

e) 5th, 6th + 7th BZs

f) 8th + 9th BZ + higher

a) 1st BZ

b) 2nd BZ

d) 3rd BZ

d') 4th BZ

c) 5th BZ

e) 6th BZ

e') 7th BZ

f) 8th BZ

f') 9th BZ

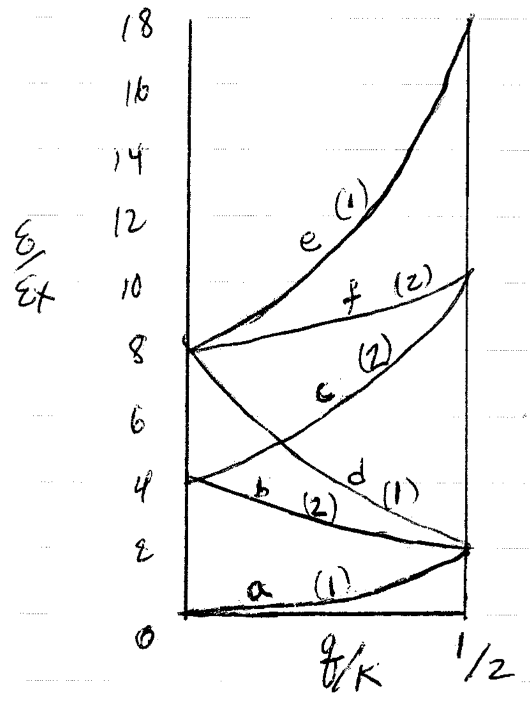
Weak potential splits degeneracies

More complicated band structure than in 1 dimension

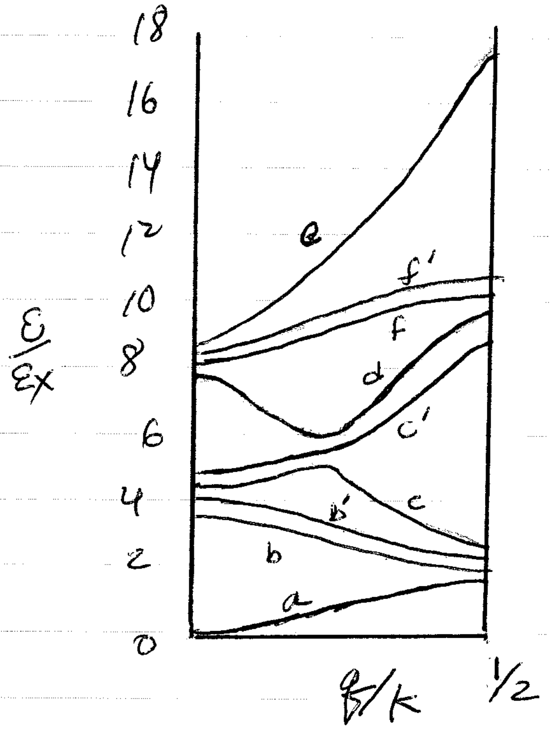
Not necessarily true that $\max[\varepsilon_n(\vec{k})] \leq \min[\varepsilon_{n+1}(\vec{k})]$

We can do the same thing for wave vectors along the diagonal of the 1st BZ, ie $\vec{q} = q(\hat{x} + \hat{y})$, $0 \le q \le K/2$

	R.L.	energy		degeneracy
	$\vec{K}_0 = 0$	$\mathcal{E} = \frac{\hbar^2 q^2}{2m}(2)$	$\mathcal{E}/\mathcal{E}_X = 8(q/K)^2$	1 (a)
$\{\vec{K}_1\}$	$-K\hat{x}, -K\hat{y}$	$\mathcal{E} = \frac{\hbar^2}{2m}\left[(q-K)^2 + q^2\right]$	$\mathcal{E}/\mathcal{E}_X = 4\left[\left(\frac{q}{K}-1\right)^2 + \left(\frac{q}{K}\right)^2\right]$	2 (b)
	$+K\hat{x}, +K\hat{y}$	$\mathcal{E} = \frac{\hbar^2}{2m}\left[(q+K)^2 + q^2\right]$	$\mathcal{E}/\mathcal{E}_X = 4\left[\left(\frac{q}{K}+1\right)^2 + \left(\frac{q}{K}\right)^2\right]$	2 (c)
$\{\vec{K}_2\}$	$-K\hat{x} - K\hat{y}$	$\mathcal{E} = \frac{\hbar^2}{2m}\left[2(q-K)^2\right]$	$\mathcal{E}/\mathcal{E}_X = 8\left[\frac{q}{K}-1\right]^2$	1 (d)
	$+K\hat{x} + K\hat{y}$	$\mathcal{E} = \frac{\hbar^2}{2m}\left[2(q+K)^2\right]$	$\mathcal{E}/\mathcal{E}_X = 8\left[\frac{q}{K}+1\right]^2$	1 (e)
	$-K\hat{x} + K\hat{y}$ $K\hat{x} - K\hat{y}$	$\mathcal{E} = \frac{\hbar^2}{2m}\left[(q+K)^2 + (q-K)^2\right]$	$\mathcal{E}/\mathcal{E}_X = 4\left[\left(\frac{q}{K}+1\right)^2 + \left(\frac{q}{K}-1\right)^2\right]$	2 (f)



free electrons



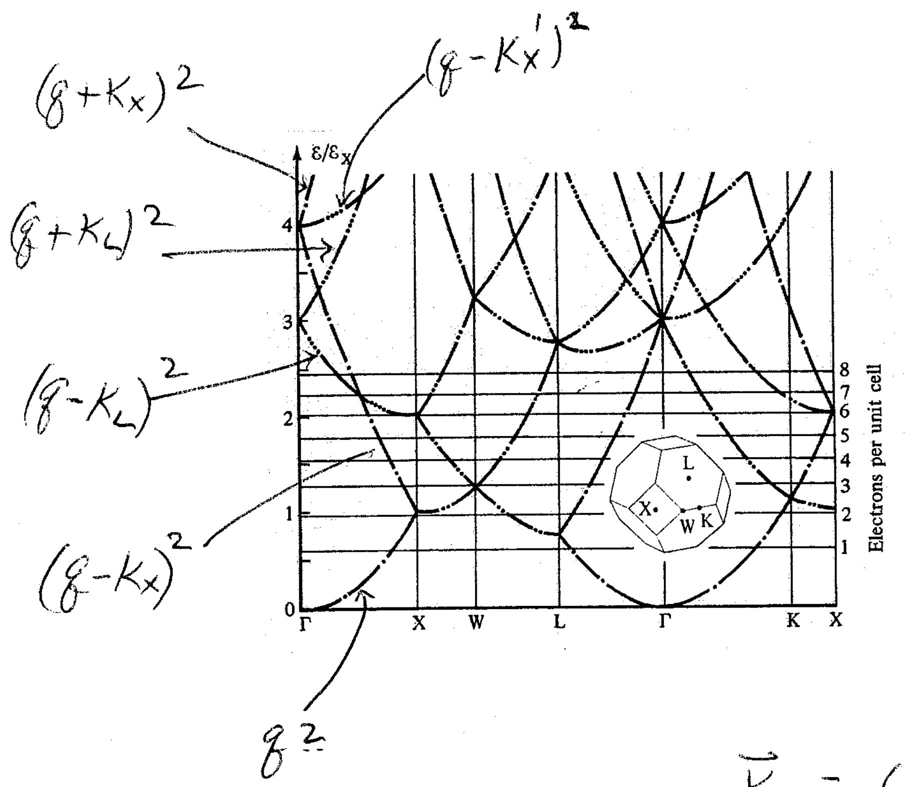
weak potential

gaps open up where free electron states are degenerate

weak potential "lifts" degeneracies

[To represent band structure in 2D or 3D one picks $\vec{q}$ in certain symmetry directions, and plots $\mathcal{E}_n(\vec{q})$ vs $|\vec{q}|$ along these directions, as done above.]

3 Dimensional free electron band structure

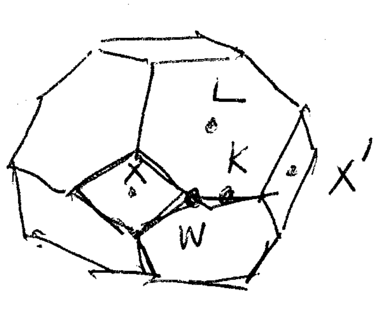


A+M

Figure 9.5
Free electron energy levels for an fcc Bravais lattice. The energies are plotted along lines in the first Brillouin zone joining the points $\Gamma(\mathbf{k}=\mathbf{0})$, K, L, W, and X. $\mathcal{E}_x$ is the energy at point X ($[\hbar^2/2m][2\pi/a]^2$). The horizontal lines give Fermi energies for the indicated numbers of electrons per primitive cell. The number of dots on a curve specifies the number of degenerate free electron levels represented by the curve. (From F. Herman, in *An Atomistic Approach to the Nature and Properties of Materials*, J. A. Pask, ed., Wiley, New York, 1967.)

plot $\mathcal{E}^0_{q-K}$ for $\vec{q}$ in special directions for all $\vec{K}$ in R-L.

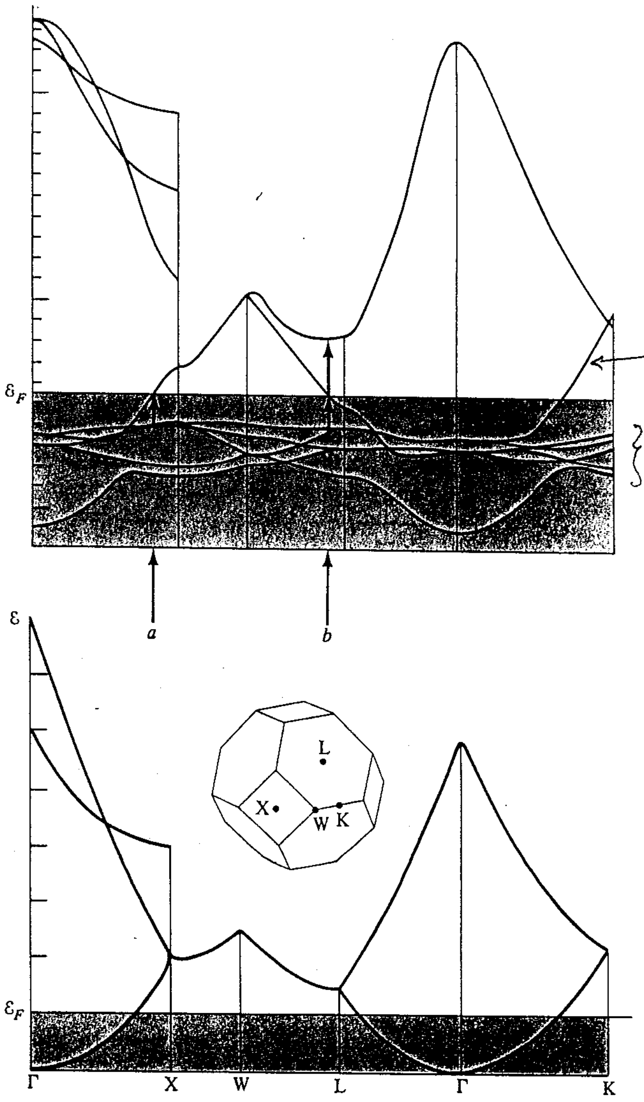
$\vec{K}_X = (1,0,0)$
$\vec{K}_L = (\frac{1}{2},\frac{1}{2},\frac{1}{2})$
$\vec{q}_X = (\frac{1}{2},0,0)$



← 1st BZ of fcc

A+M

Figure 15.11
Burdick's calculated bands for copper, illustrating that the absorption threshold for transitions up from the conduction band is about 4 eV, while the threshold for transitions from the *d*-band to the conduction band is only about 2 eV. (The energy scale is in tenths of a rydberg (0.1 Ry = 1.36 eV).) Note the resemblance of the bands other than the *d*-bands to the free electron bands plotted below.



s band - free electron like

} d bands - tight binding like

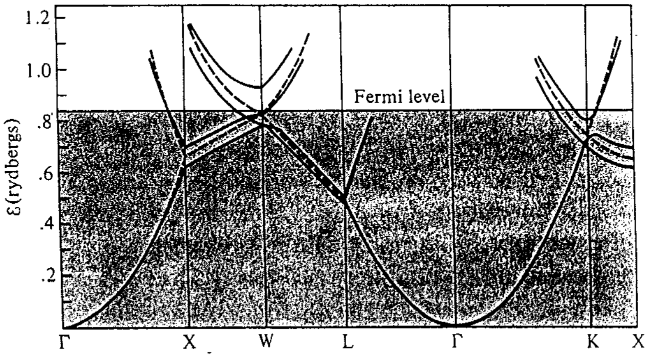
$Cu = [Ar]\,3d^{10}4s^{1}$

~~[illegible]~~

free electron bands →

A+M

Figure 11.9
Calculated valence bands for aluminum (three electrons outside of a closed-shell neon configuration) compared with *free* electron bands (dashed lines). The bands are computed by the KKR method. (B. Segall, *Phys. Rev.* **124**, 1797 (1961).)



$AL = [Ne]\,3s^{2}3p^{1}$

$Z = 3$

Bravais Lattice with a basis

Suppose we have a monatomic BL with a basis (all atoms identical). If $\phi(\vec{r}-\vec{r}_0)$ is the potential from the ion centered at $\vec{r}_0$, then the periodic ion potential is

$$u(\vec{r}) = \sum_i \sum_j \phi(\vec{r}-\vec{R}_i-\vec{d}_j)$$

since ions are located at positions $\vec{R}_i+\vec{d}_j$

Fourier transform is:

$$u_K = \frac{1}{v} \int_{\substack{\text{primitive}\\\text{cell}}} d^3r \, e^{-i\vec{K}\cdot\vec{r}} \sum_{ij} \phi(\vec{r}-\vec{R}_i-\vec{d}_j)$$

$$= \frac{1}{V} \int_{\substack{\text{all}\\\text{space}}} d^3r \, e^{-i\vec{K}\cdot\vec{r}} \sum_{ij} \phi(\vec{r}-\vec{R}_i-\vec{d}_j)$$

$$= \sum_i \frac{1}{V} \int_{\substack{\text{all}\\\text{space}}} d^3r \, e^{-i\vec{K}\cdot\vec{r}} \sum_j \phi(\vec{r}-\vec{R}_i-\vec{d}_j)$$

let $\vec{r}\,' = \vec{r}-\vec{R}_i$ and do change of integration variable

$$u_K = \sum_i \frac{1}{V} \int_{\substack{\text{all}\\\text{space}}} d^3r' \, e^{-i\vec{K}\cdot(\vec{r}\,'+\vec{R}_i)} \sum_j \phi(\vec{r}\,'-\vec{d}_j)$$

$$= \sum_i \frac{1}{V} \int_{\substack{\text{all}\\\text{space}}} d^3r' \, e^{-i\vec{K}\cdot\vec{r}\,'} \sum_j \phi(\vec{r}\,'-\vec{d}_j)$$

since $\vec{K}\cdot\vec{R}_i = 2\pi$

$$= \frac{N}{V} \int_{\substack{\text{all}\\\text{space}}} d^3r' \, e^{-i\vec{K}\cdot\vec{r}\,'} \sum_j \phi(\vec{r}\,'-\vec{d}_j)$$

Since all the terms in the $\sum_i$ are now identical

$$U_K = \frac{1}{v}\int_{\substack{\text{all}\\\text{space}}} d^3r \; e^{-i\vec{K}\cdot\vec{r}} \sum_j \phi(\vec{r}-\vec{d}_j) \qquad \text{as } v \equiv \frac{V}{N}$$

substitute in F.T. of $\phi(\vec{r})$

$$\phi(\vec{r}-\vec{d}_j) = \int \frac{d^3k'}{(2\pi)^3} e^{i\vec{k}'\cdot(\vec{r}-\vec{d}_j)} \phi_{k'}$$

So

$$U_K = \frac{1}{v}\int d^3k' \, \phi_{k'} \underbrace{\int_{\substack{\text{all}\\\text{space}}} \frac{d^3r}{(2\pi)^3} e^{i(\vec{k}'-\vec{K})\cdot\vec{r}}}_{\delta(\vec{k}'-\vec{K})} \sum_j e^{-i\vec{k}'\cdot\vec{d}_j}$$

$$= \frac{1}{v}\phi_K \sum_j e^{-i\vec{K}\cdot\vec{d}_j}$$

$$U_K = \frac{1}{v}\phi_K S_K$$ proportional to geometric structure factor S_K

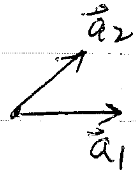
If S_K vanishes - we saw that there will be no diffraction peak in X-ray scattering at $\vec{K}$.

Now we see the analogous result, when $S_K = 0$ then $U_K = 0$, and there will be <u>no energy gap</u> opening up for electron states with $\vec{k}$ that lie on the Bragg plane bisecting $\vec{K}$.

An important case where this happens is for hcp crystals

For hcp $\vec{a}_1 = a\hat{x}$, $\vec{a}_2 = \frac{a}{2}\hat{x} + \frac{\sqrt{3}a}{2}\hat{y}$, $\vec{a}_3 = c\hat{z}$

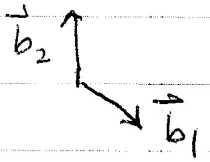
two point basis $\vec{d}_1 = 0$, $\vec{d}_2 = \frac{1}{3}(\vec{a}_1 + \vec{a}_2) + \frac{1}{2}\vec{a}_3$



lies in center of cells of triangular lattice in xy plane, and halfway between the two triangular layers

R.L.

$$\vec{K} = n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3 \qquad \begin{cases} \vec{b}_1 = \frac{4\pi}{\sqrt{3}a}\left(\frac{1}{2}\hat{x} - \frac{\sqrt{3}}{2}\hat{y}\right) \\ \vec{b}_2 = \frac{4\pi}{\sqrt{3}a}\hat{y} \\ \vec{b}_3 = \frac{2\pi}{c}\hat{z} \end{cases}$$



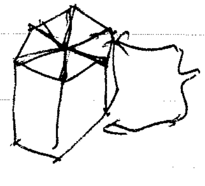
Then $S_K = e^{-i\vec{K}\cdot\vec{d}_1} + e^{-i\vec{K}\cdot\vec{d}_2}$

$$= 1 + e^{-i(n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3)\cdot\left(\frac{\vec{a}_1}{3} + \frac{\vec{a}_2}{3} + \frac{\vec{a}_3}{2}\right)}$$

$$S_K = 1 + e^{-2\pi i\left(\frac{n_1}{3} + \frac{n_2}{3} + \frac{n_3}{2}\right)}$$

If, for example, $n_1 = n_2 = 0$, $n_3 = \pm 1$, then $S_K = 0$. So no gap opens on the Bragg plane that bisects $\vec{K} = \pm\frac{2\pi}{c}\hat{z}$ – ie the top and bottom surfaces of the 1st BZ.

1st BZ



no gap on these Bragg planes!