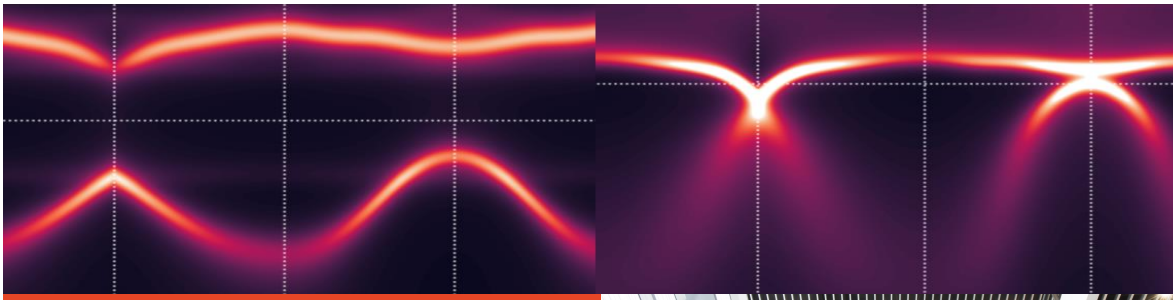

CMP Lecture 10

School of Physics
The University of Sydney

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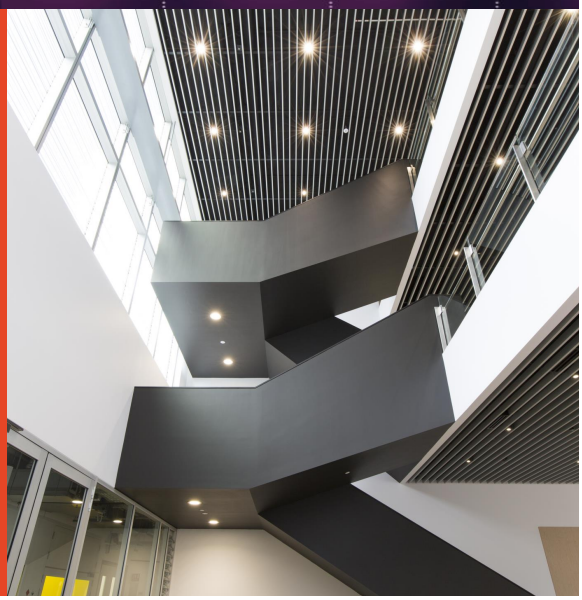
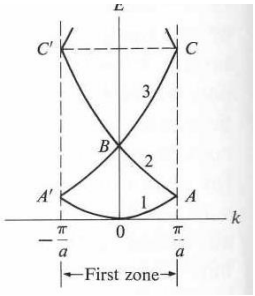
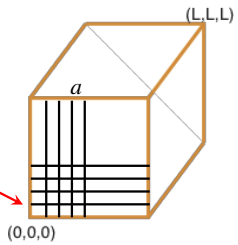




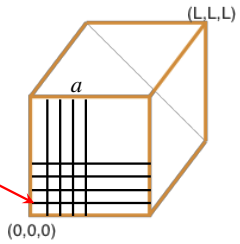
From Bloch's theorem

N unit cells
lattice constant a



- The number of states in a band within the first Brillouin zone is equal to the number of unit cells N in the crystal. Consider a one-dimensional case: the allowed $\mathbf{k}$ values form a uniform mesh with spacing $2\pi/L$. The number of states inside the first zone, whose length is $2\pi/a$, is then
$(2\pi/a)/(2\pi/L) = L/a = N$
- Since each state can accommodate at most two electrons, of opposite spins, it follows that the maximum number of electrons that may occupy a single band is 2*N*.

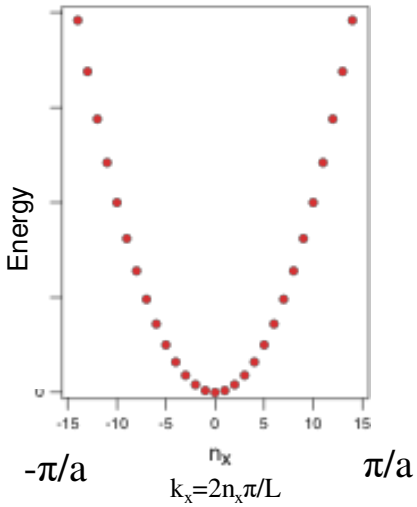
Nearly free electron model



N unit cells
lattice constant a

So number of states/k-point values in a band is

$$(2\pi/a)/(2\pi/L) = L/a = N$$



Here, we will consider electrons as free-electron waves that are only very weakly perturbed by the periodic potential from the atoms in the solid.

Nearly free electron model
Very weak potential

Ch. 15 Oxford Basics
Ch. 9 Ashcroft & Mermin

Now turn on weak potential

$$H = H_0 + V(\mathbf{r})$$
$$H_0|k\rangle = \epsilon_0|k\rangle\,, \epsilon_0 = \frac{\hbar^2 k^2}{2m}$$
$$V(\mathbf{r}) = V(\mathbf{r}+\mathbf{R})$$

Model is a good approximation to the valence bands in the simple metals such as Na, K, Al etc. They are even called "*nearly free Electron metals*"

The matrix elements of this potential are the Fourier components

$$\langle \mathbf{k}'|V|\mathbf{k}\rangle = \frac{1}{L^3}\int \mathbf{dr}\, e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}\, V(\mathbf{r}) \equiv V_{\mathbf{k}'-\mathbf{k}}$$

which is zero unless **k**'-**k** is a reciprocal lattice vector

Oxford Basics
- *Eq. 14.1 and*
- *Sec. 13.1.3*

i.e. $V(\boldsymbol{r}) = \sum_{\boldsymbol{G}} V_{\boldsymbol{G}} e^{i\,\boldsymbol{G}.\boldsymbol{r}}$

That is, any plane-wave state **k** can scatter into another plane-wave state **k**' only if these two plane waves are separated by a reciprocal lattice vector.

Very weak potential

Apply perturbation theory

At first order in the perturbation *V*, we have:

$$\epsilon(\mathbf{k}) = \epsilon_0(\mathbf{k}) + \langle \mathbf{k}|V|\mathbf{k}\rangle = \epsilon_0(\mathbf{k}) + V_0$$

V_0 just a constant energy shift, set to zero

At second order we have:

dash means G not equal to 0

$$\epsilon(\mathbf{k}) = \epsilon_0(\mathbf{k}) + V_0 + {\sum_{\mathbf{k}'=\mathbf{k}+\mathbf{G}}}' \frac{|\langle \mathbf{k}'|V|\mathbf{k}\rangle|^2}{\epsilon_0(\mathbf{k}) - \epsilon_0(\mathbf{k}')}$$

Possible that $\epsilon_0(\mathbf{k})$ is close to or equal to $\epsilon_0(\mathbf{k}')$ then the sum diverges and the perturbation expansion makes no sense.
For this degenerate situation; use degenerate perturbation theory.
The degeneracy will occur when:

$$\begin{aligned} \epsilon_0(\mathbf{k}) &= \epsilon_0(\mathbf{k}') \\ \mathbf{k}' &= \mathbf{k} + \mathbf{G} \end{aligned}$$

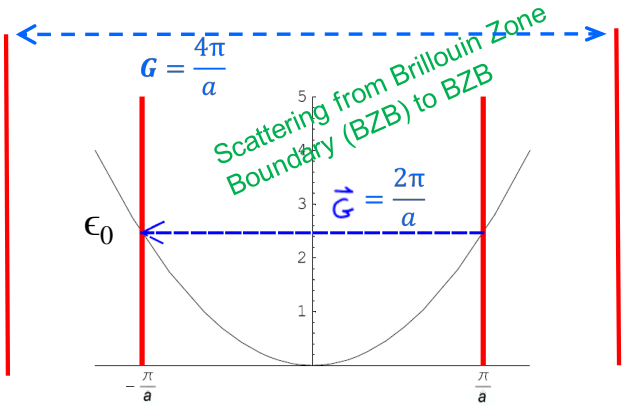
Working

Very weak potential

- In one-dimension, divergence in 2nd order perturbation theory will occur when

$$k' = -k = \pi n/a$$

- This means that k must lie on the Brillouin zone boundary (i.e. on a Bragg plane determined by reciprocal lattice **G**)



The states at the two zone boundaries are separated by a reciprocal lattice vector **G** and have the same energy.

$$\epsilon_0(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$$

Very weak potential

Ch. 15 Oxford Basics

Degenerate perturbation theory

Here we diagonalize the Hamiltonian within the degenerate space first; that is, we take states of the same energy that are connected by the matrix element and treat their mixing exactly

Consider two plane wave states $|\mathbf{k}\rangle$ and $|\mathbf{k}'\rangle = |\mathbf{k}+\mathbf{G}\rangle$ that are approximately of the same energy and close to the zone boundaries,

We had from earlier,

$$\langle \mathbf{k}'|V|\mathbf{k}\rangle = \frac{1}{L^3}\int \mathrm{d}\mathbf{r}\, e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}\, V(\mathbf{r}) \equiv V_{\mathbf{k}'-\mathbf{k}}$$

diagonal elements:

$$\langle \mathbf{k}|\ H\ |\mathbf{k}\rangle = \epsilon_0(\mathbf{k})$$
$$\langle \mathbf{k}'|\ H\ |\mathbf{k}'\rangle = \epsilon_0(\mathbf{k}') = \epsilon_0(\mathbf{k}+\mathbf{G})$$

off diagonal elements:

$$\langle \mathbf{k}|\ H\ |\mathbf{k}'\rangle = V_{\mathbf{k}-\mathbf{k}'} = V^*_{\mathbf{G}}$$
$$\langle \mathbf{k}'|\ H\ |\mathbf{k}\rangle = V_{\mathbf{k}'-\mathbf{k}} = V_{\mathbf{G}}$$

In this 2D space, can write any wave function as:

$$|\Psi\rangle = \alpha|\mathbf{k}\rangle + \beta|\mathbf{k}'\rangle = \alpha|\mathbf{k}\rangle + \beta|\mathbf{k}+\mathbf{G}\rangle$$

Solving the effective SE to find the best linear combination of these two kets to give the lowest energy state:

$$\begin{pmatrix} \epsilon_0(\mathbf{k}) & V^*_{\mathbf{G}} \\ V_{\mathbf{G}} & \epsilon_0(\mathbf{k}+\mathbf{G}) \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

$V_{-\mathbf{G}} = V^*_{\mathbf{G}}$ since potential real

Working

Working

Very weak potential

Degenerate perturbation theory

Secular equation determining *E* is:

$$\Big(\epsilon_0(\mathbf{k}) - E\Big)\Big(\epsilon_0(\mathbf{k}+\mathbf{G}) - E\Big) - |V_\mathbf{G}|^2 = 0$$

And if exactly on the zone boundary where it reduces to:

$$\begin{aligned}\epsilon_0(\mathbf{k}) &= \epsilon_0(\mathbf{k}')\\ \mathbf{k}' &= \mathbf{k}+\mathbf{G}\end{aligned}$$

$$\Big(\epsilon_0(\mathbf{k}) - E\Big)^2 = |V_\mathbf{G}|^2$$

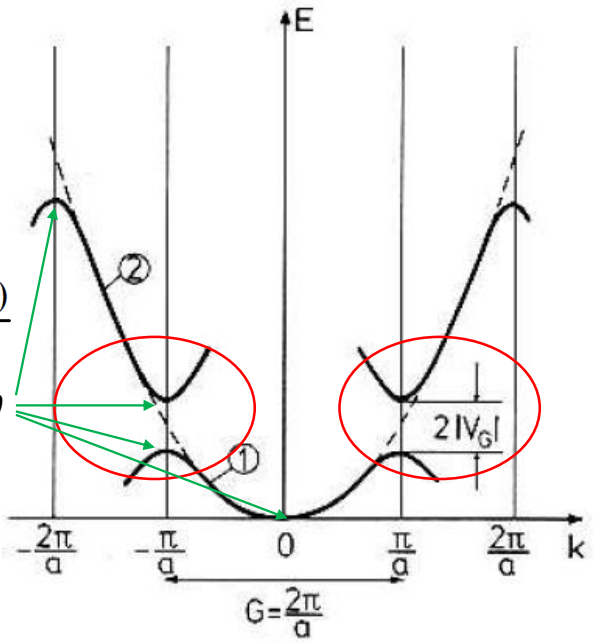
$$E_\pm = \epsilon_0(\mathbf{k}) \pm |V_\mathbf{G}|$$

That is, a gap opens up at the zone boundary! - due to scattering by a reciprocal lattice vector

Very weak potential

$$\mathbf{v}_n(\mathbf{k}) = \frac{dE_n(\mathbf{k})}{\hbar d\mathbf{k}}$$

group velocity = 0



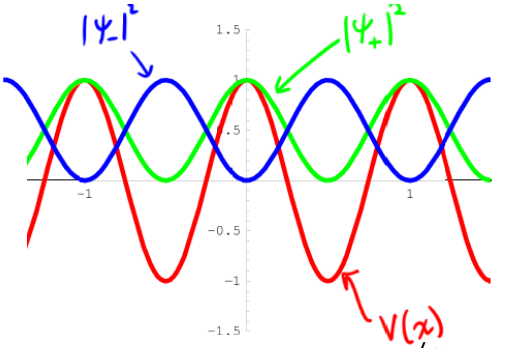
Very weak potential

One dimension with $V(x) = \tilde{V}\cos(2\pi x/a)$ with $\tilde{V} > 0$

At zone boundary, we have: $\epsilon_0(k) = \epsilon_0(k')$ $\begin{pmatrix} \epsilon_0(\mathbf{k}) & V_{\mathbf{G}}^* \\ V_{\mathbf{G}} & \epsilon_0(\mathbf{k}+\mathbf{G}) \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$

leads to: $\alpha = \pm\beta$

$$|\psi_\pm\rangle = \frac{1}{\sqrt{2}}\left(|k\rangle \pm |k'\rangle\right)$$



$$|k\rangle \rightarrow e^{ikx} = e^{ix\pi/a}$$
$$|k'\rangle \rightarrow e^{-ik'x} = e^{-ix\pi/a}$$

$$\psi_+ \sim e^{ix\pi/a} + e^{-ix\pi/a} \propto \cos(x\pi/a)\,, E_+ = \epsilon_0^{\pi/a} + \tilde{V}$$
$$\psi_- \sim e^{ix\pi/a} - e^{-ix\pi/a} \propto \sin(x\pi/a)\,, E_+ = \epsilon_0^{\pi/a} - \tilde{V}$$

At zone boundary have two plane waves propagating in opposite directions, combine to form standing waves; i.e. reflection of incident wave at zone boundary.

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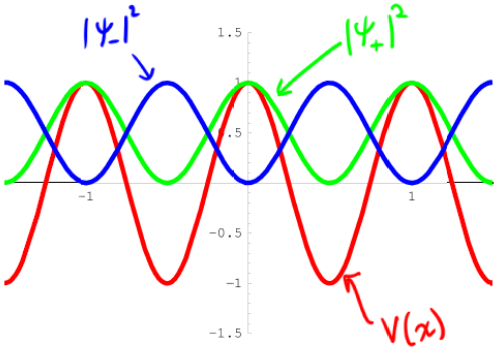
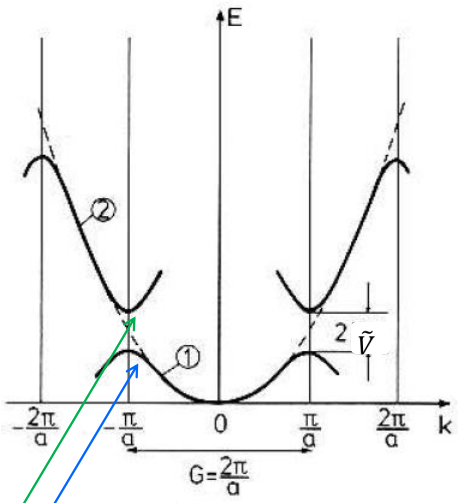
Very weak potential





Probability density along the x-axis

$|\psi_+|^2$ sees mostly +ve $V(x)$ →pushed up in energy by $\tilde{V}$

$|\psi_-|^2$ sees mostly -ve $V(x)$ →pushed down in energy by $\tilde{V}$

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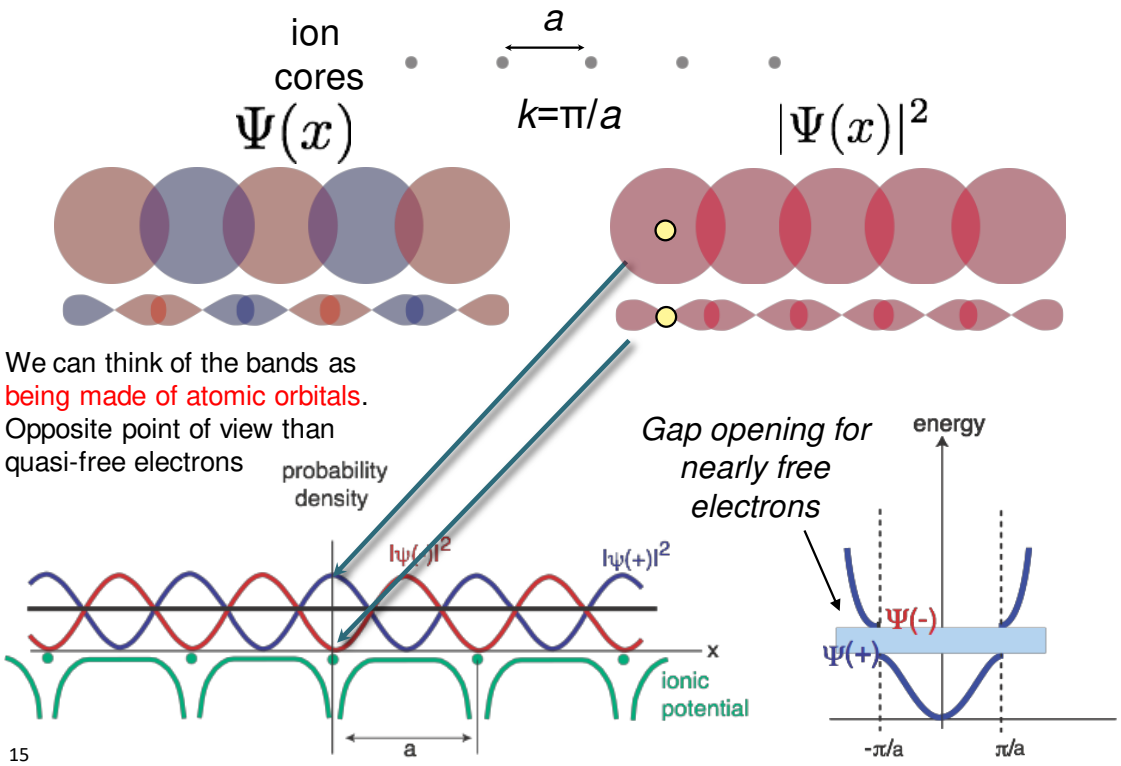
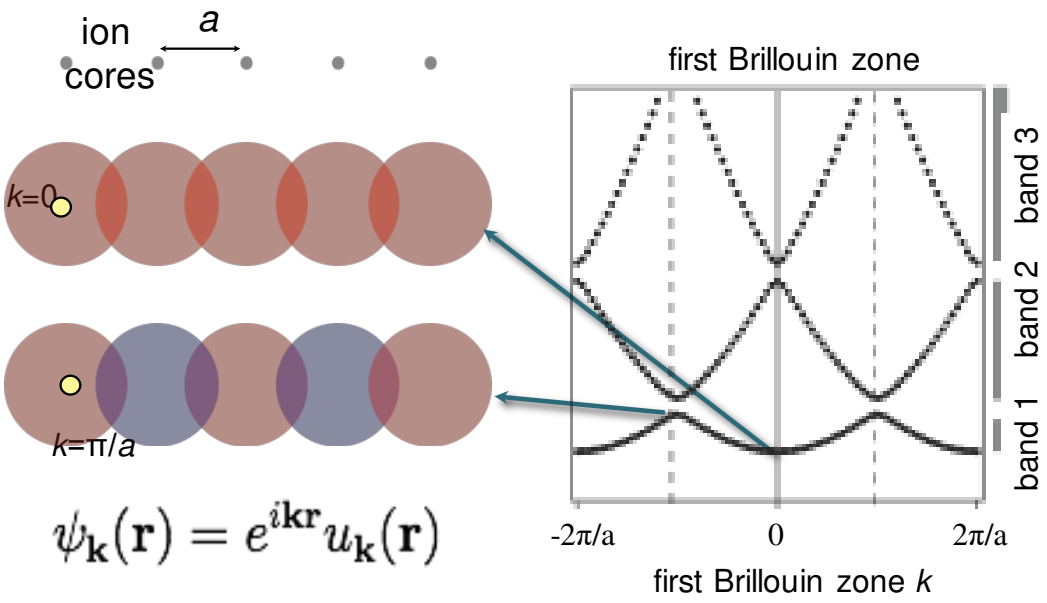
...another point of view

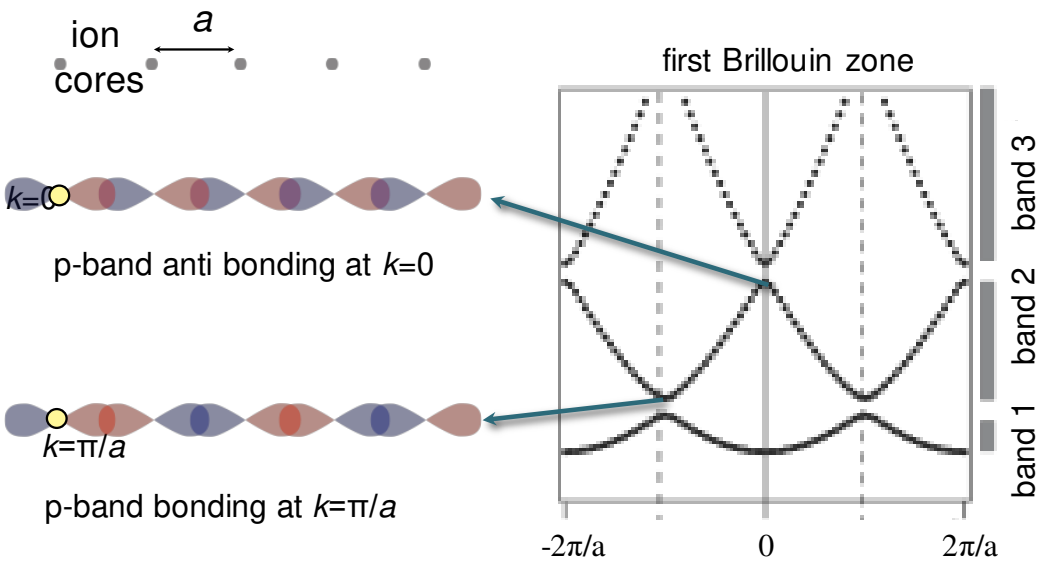


...another point of view



Completely different point of view: instead of free electrons perturbed by the lattice, we think of atomic orbitals on the lattice. We can think of the bands as being made of atomic orbitals. Opposite point of view than quasi-free electrons
s-band bonding at *k*=0, anti-bonding at *k*=pi/*a*

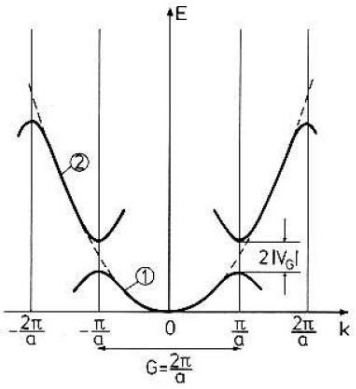
...yet another point of view



$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$$

Very weak potential

Oxford Basics, Ch. 15



But how do we understand the parabolic nature at the zone boundaries?

Consider not quite on zone boundary

$$k = n\pi/a + \delta \qquad k' = -n\pi/a + \delta$$

$$\epsilon_0(n\pi/a + \delta) = \frac{\hbar^2}{2m}\left[(n\pi/a)^2 + 2n\pi\delta/a + \delta^2\right]$$

$$\epsilon_0(-n\pi/a + \delta) = \frac{\hbar^2}{2m}\left[(n\pi/a)^2 - 2n\pi\delta/a + \delta^2\right]$$

It can be shown that

$$E_\pm = \frac{\hbar^2(n\pi/a)^2}{2m} \pm |V_G| + \frac{\hbar^2\delta^2}{2m}\left[1 \pm \frac{\hbar^2(n\pi/a)^2}{m}\frac{1}{|V_G|}\right]$$

Working

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The characteristic equation

$$\left(\frac{\hbar^2}{2m}\left[(n\pi/a)^2+\delta^2\right]-E+\frac{\hbar^2}{2m}2n\pi\delta/a\right)$$
$$\times\left(\frac{\hbar^2}{2m}\left[(n\pi/a)^2+\delta^2\right]-E-\frac{\hbar^2}{2m}2n\pi\delta/a\right)-|V_G|^2=0$$

which simplifies to

$$\left(\frac{\hbar^2}{2m}\left[(n\pi/a)^2+\delta^2\right]-E\right)^2=\left(\frac{\hbar^2}{2m}2n\pi\delta/a\right)^2+|V_G|^2$$

or

$$E_\pm=\frac{\hbar^2}{2m}\left[(n\pi/a)^2+\delta^2\right]\pm\sqrt{\left(\frac{\hbar^2}{2m}2n\pi\delta/a\right)^2+|V_G|^2}\ . \qquad (15.11)$$

Expanding the square root for small δ we obtain

$$E_\pm=\frac{\hbar^2(n\pi/a)^2}{2m}\pm|V_G|+\frac{\hbar^2\delta^2}{2m}\left[1\pm\frac{\hbar^2(n\pi/a)^2}{m}\frac{1}{|V_G|}\right]. \qquad (15.12)$$

Working from Ch. 15, p. 167, Oxford Basics

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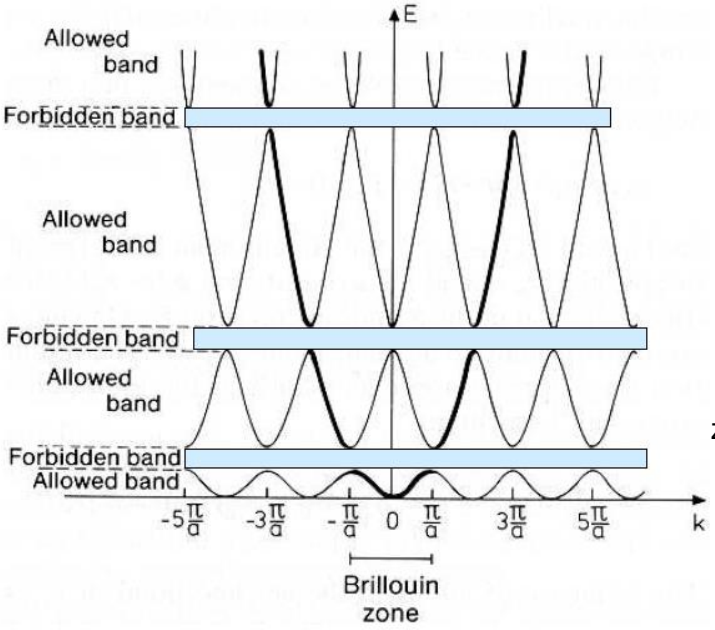
Nearly free electron model

The dispersion is quadratic in δ near the band gap

$$E_{\pm} = \frac{\hbar^2(n\pi/a)^2}{2m} \pm |V_G| + \frac{\hbar^2\delta^2}{2m}\left[1 \pm \frac{\hbar^2(n\pi/a)^2}{m}\frac{1}{|V_G|}\right]$$



Dispersion of a Nearly Free Electron Model plotted in repeated zone scheme

Small gaps open up at the Brillouin zone boundaries in what is otherwise a parabolic spectrum.

Nearly free electron model

Can rewrite below,

$$E_{\pm} = \frac{\hbar^2(n\pi/a)^2}{2m} \pm |V_G| + \frac{\hbar^2\delta^2}{2m}\left[1 \pm \frac{\hbar^2(n\pi/a)^2}{m}\frac{1}{|V_G|}\right]$$

as:

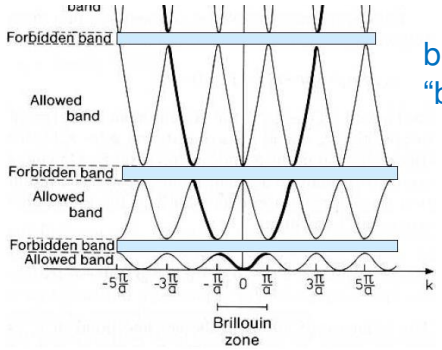
$$E_+(G+\delta) = C_+ + \frac{\hbar^2\delta^2}{2m_+^*}$$

$$E_-(G+\delta) = C_- - \frac{\hbar^2\delta^2}{2m_-^*}$$

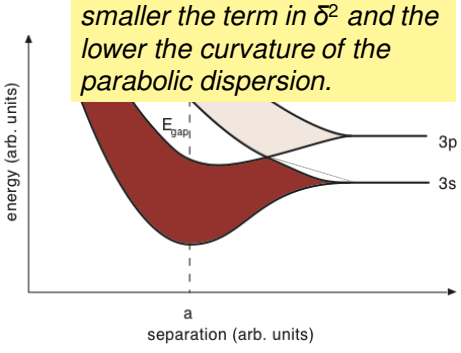
At every Brillouin zone boundary, the dispersion is parabolic. m is called the effective mass. – for now think of as a way to describe the parabolic dispersion at zone Boundaries – will define more precisely later.*

$$m_{\pm}^* = \frac{m}{\left|1 \pm \frac{\hbar^2(n\pi/a)^2}{m}\frac{1}{|V_G|}\right|}$$

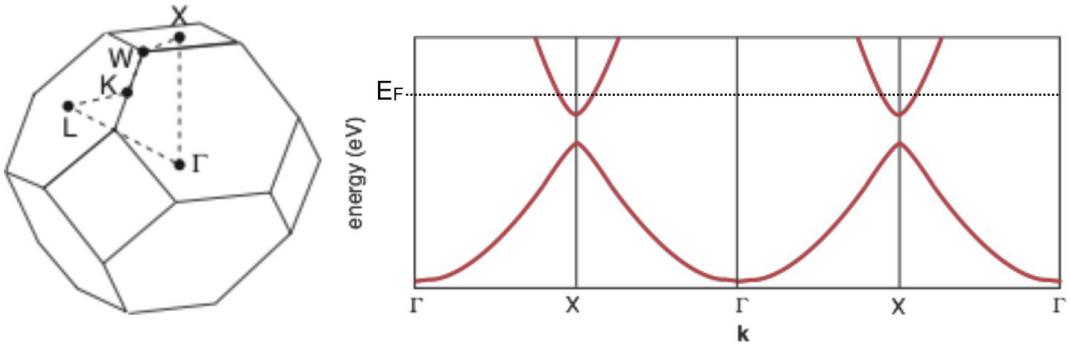
Can see, the greater m, the smaller the term in δ^2 and the lower the curvature of the parabolic dispersion.*



both exhibit "band gaps"

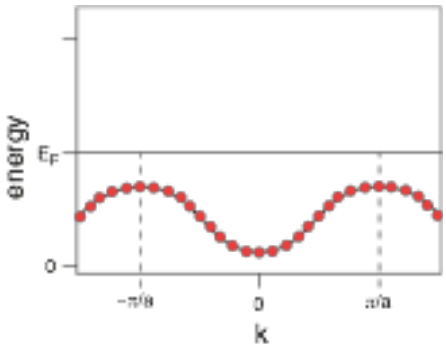


Metal or semiconductor?



Since the Fermi level cuts an occupied band, the material is a metal.
If the Fermi level would be between the bands, we could have a semiconductor (just by filling in a smaller amount of electrons).

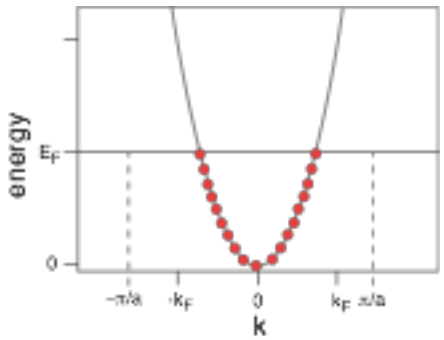
Filling the bands - electron counting



N unit cells -> N possible (different) k values

$$k = \frac{2\pi}{aN} n$$

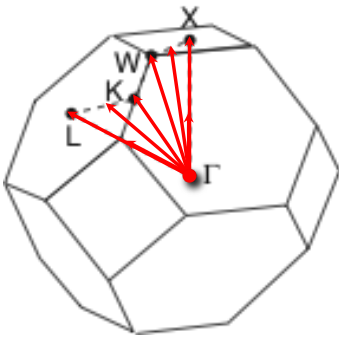
2N possible states per band (because of spin)

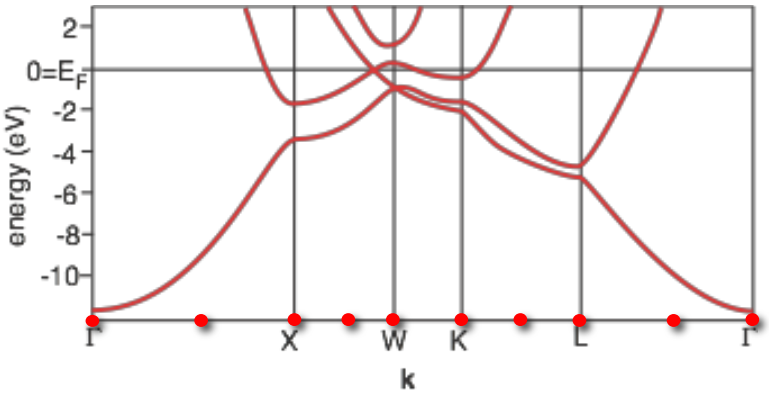


2 valence electrons per unit cell fill one band

An odd number of valence electrons per unit cell results in a metal

Band structures of real materials: Al

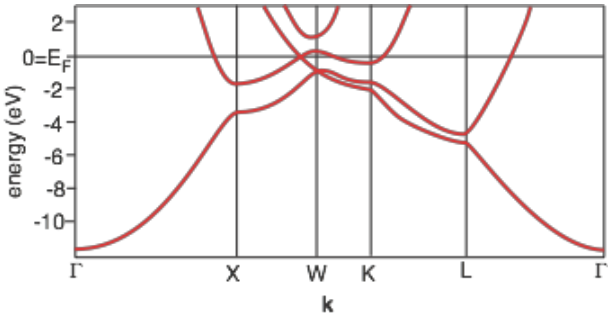




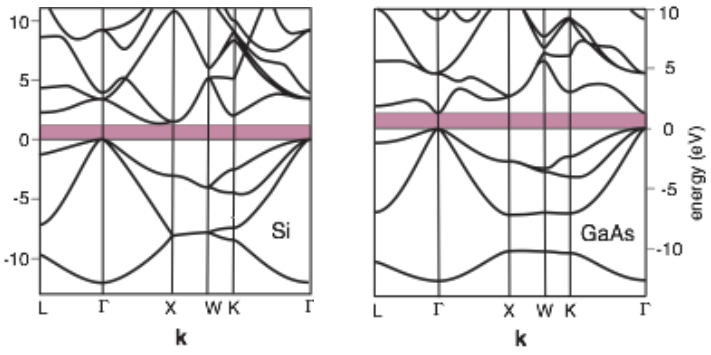
Electron counting: examples

N unit cells -> N possible (different) k values in band in 1st BZ
2N possible states per band

Al: fcc,
1 atom per unit cell,
3 electrons per atom
need states for 3N electrons – fill one and half bands - **metal**



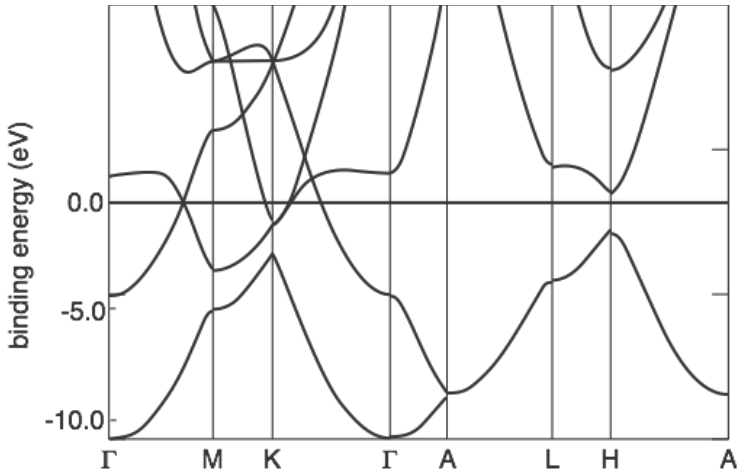
Si: fcc,
2 atoms per unit cell,
4 electrons per atom
8 electrons per cell – need states for 8N electrons –fill four bands - **semiconductor**



8=4+4

8=3+5

Electron counting



- Example 3: Be, hcp structure, 2 atoms per unit cell, 2 electrons per atom, 4 valence electrons per unit cell, METAL.

An even number of electrons per unit cell is necessary for an insulator - not sufficient!

Effective mass of electron

We have defined the effective masses above in analogy with that of free electrons, by looking at the curvature of the dispersion.
An equivalent definition is to define the effective mass m* as being the quantity that satisfies Newton's second law, $F = m^* a$

Consider applying a force to an electron in the system and then equate the work done on the electron to its change in energy.
Take the electron in momentum state **k**. Its group velocity is $\mathbf{v} = \frac{\nabla_{\mathbf{k}} E}{\hbar}$
Applying a force, the work done per unit time is,

$$dW/dt = \mathbf{F} \cdot \mathbf{v} = \mathbf{F} \cdot \nabla_k E(\mathbf{k})/\hbar$$

The change in energy per unit is,

$$dE/dt = d\mathbf{k}/dt \cdot \nabla_k E(\mathbf{k}) \qquad \left(chain\ rule\ \frac{dE}{dt} = \frac{dE}{dk}\frac{dk}{dt} \right)$$

Equating the above two expressions, we obtain Newtons 2nd law,

$$\mathbf{F} = \hbar \frac{d\mathbf{k}}{dt} = \frac{d\mathbf{p}}{dt} \quad \text{using} \quad \mathbf{p} = \hbar\mathbf{k}$$

Effective mass of electron

Consider electrons near the bottom of a band, we can write,

$$\mathbf{F} = m^* \frac{d\mathbf{v}}{dt}$$

It is then sometimes convenient to define the effective mass of an electron as a function of momentum. This can be found to be (in one dimension),

$$\frac{\hbar^2}{m^*(k)} = \frac{\partial^2 E}{\partial k^2}$$

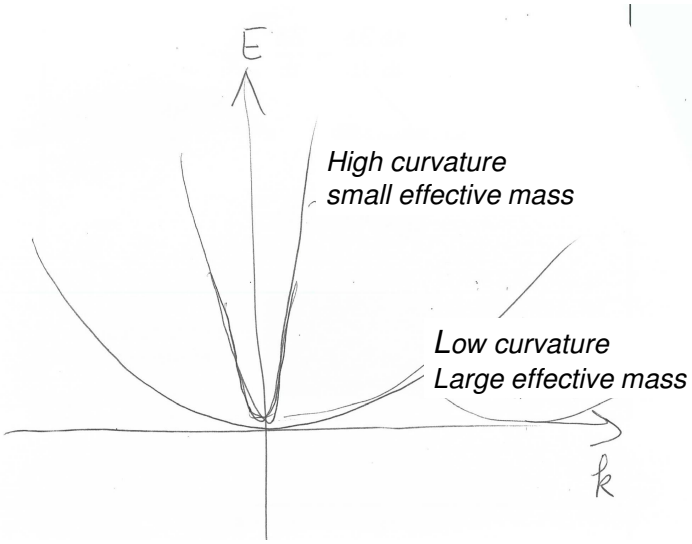
This is obtained by substituting the group velocity $\mathbf{v} = \frac{\nabla_{\mathbf{k}} E}{\hbar}$ into the expression for force above (with some manipulation), and using $\boldsymbol{F} = \frac{d\boldsymbol{p}}{dt}$.

Finally, we can equivalently write:

$$m^* = \frac{\hbar^2}{\partial^2 E / \partial k^2}$$

Effective mass example

It is like classical motion, only that the electrons have a different ("effective") mass now!
Seems artificial but is really ingenious. Treat electrons as classical particle. All the lattice effect is in m*.
This can be dramatic. m* can be a thousand times bigger or smaller than the free electron mass. It can also be negative (!).



Effective mass examples

Nanomaterial	m_{eff}
Si [16]	1.08 m_e
TiO_2 [17]	6 m_e
ZnO [18]	0.24 m_e
CTN [19]	0.5 m_e
GaAs [20-22]	0.067 m_e

m_e: mass of the electron

End