As $2a \to 0$ $\quad \sinh^2(K_2 2a) \simeq K_2^2 (2a)^2 = \frac{2m}{\hbar^2}(V-E)(2a)^2$

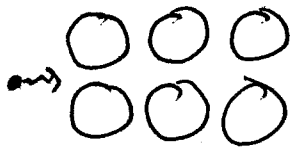
$$\Rightarrow \quad \frac{1}{T} = 1 + \frac{V^2}{4E}\frac{2m}{\hbar^2}(2a)^2$$

$$= 1 + \frac{1}{2E}\frac{\hbar^2}{m}\Delta^2 = 1 + \frac{\Delta^2}{K^2}$$

(which does agree with $\frac{1}{T} = 1 + \alpha^2$.)

Periodic Potential

One of the great triumphs of quantum mechanics is the theory of electrons in metals, semiconductors and insulators... How do electrons manage to move through a crystal? The atoms are packed tight... there isn't much room to squeeze through the spaces in between.



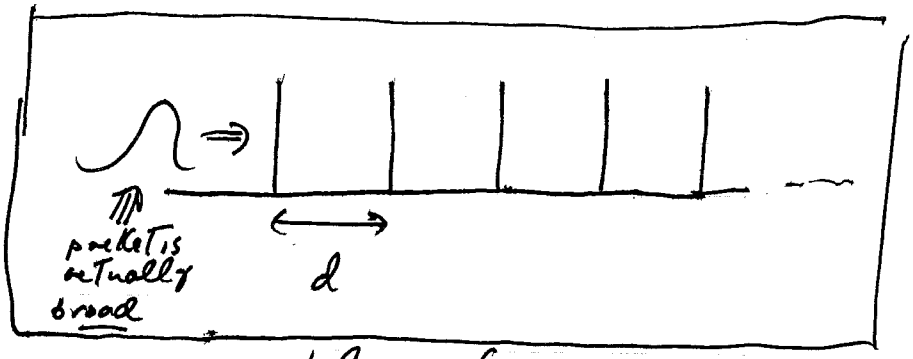
Yet somehow, in a conductor, the electrons manage to drift through... how do they do it?

The electrons don't actually squeeze through the atoms, they tunnel through. How can they tunnel through a macroscopic crystal?

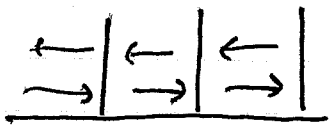
For the electrons to perform this miracle, it is crucially important that the atoms

are periodically spaced. In fact in a perfect crystal at zero temperature electrons (in a conductor) would propagate without resistance. Real conductors have nonzero resistivity because (1) there are impurities (or defects) — departures from perfect periodicity, and (2) at finite temperature the atoms shake.

To understand how this works, we'll study the problem of transmission through a periodic potential — we'll choose the periodic δ-function -- δ-functions spaced a distance d apart, because we can solve it explicitly. (This is a limiting case of the problem treated in Liboff — the periodic rectangular barrier.)

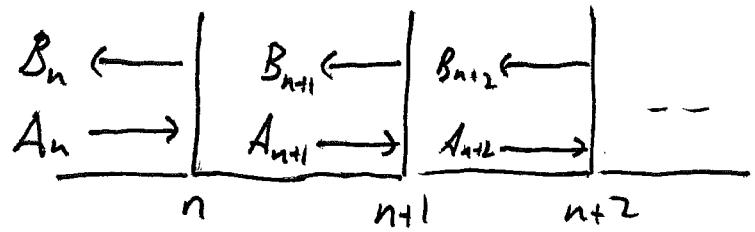


It might seem at first that each time the particle encounters a potential spike, it will be partially reflected, so that when it reaches the other end of the crystal, the wave is exponentially attenuated. But this way of thinking about the problem is not self-consistent. The wave that is transmitted through the first barrier is partially reflected by the second barrier, so we need



to include a wave incoming from the right to analyze the transmission through the first barrier. If we take this into account, it might be possible for the right-moving wave to arrive at the second barrier without any attenuation.

To solve the problem self-consistently, we use our matrix formulation:



$$\begin{pmatrix} A_{n+1} \\ B_{n+1} \end{pmatrix} = \begin{pmatrix} e^{ikd} & 0 \\ 0 & e^{-ikd} \end{pmatrix} \begin{pmatrix} 1+i\alpha & i\alpha \\ -i\alpha & 1-i\alpha \end{pmatrix} \begin{pmatrix} A_n \\ B_n \end{pmatrix}$$

this is the effect of propagating to the next barrier

transfer matrix computed earlier

or $$\begin{pmatrix} A_{n+1} \\ B_{n+1} \end{pmatrix} = M \begin{pmatrix} A_n \\ B_n \end{pmatrix}; \quad M = \begin{pmatrix} (1+i\alpha)e^{ikd} & i\alpha e^{ikd} \\ -i\alpha e^{-ikd} & (1-i\alpha)e^{-ikd} \end{pmatrix}$$

To find the effect of N periodically spaced barriers, we apply the matrix M all together N times

$$\begin{pmatrix} A_N \\ B_N \end{pmatrix} = M^N \begin{pmatrix} A_0 \\ B_0 \end{pmatrix}$$

– This is the solution to the problem of transmission through a periodic potential barrier

How does the matrix M^N behave? The answer depends on the nature of the eigenvalues of M.

Since $\det M = 1$ $\quad Tr\,M = 2\cos kd - 2\alpha \sin kd$ the characteristic eqn for the eigenvalues is

$$0 = \lambda^2 - 2C\lambda + 1$$

where $\quad C = \frac{1}{2} Tr\,M = \cos kd - \alpha \sin kd$

the solutions are

$$\lambda_\pm = \frac{1}{2}\left(2C \pm \sqrt{4C^2-4}\right) = C \pm \sqrt{C^2-1}$$

we distinguish two cases:

① $|C| > 1$ In this case the eigenvalues are real

$$\lambda_+ > 1 \qquad (\text{or } \lambda_+ < -1)$$

$$\lambda_- = 1/\lambda_+ < 1$$

Thus M^N (N large) has eigenvalues

$$\lambda_+^N >> 1$$

$$\lambda_-^N << 1$$

This means that there is an exponentially growing and an exponentially decaying solution

The physical solution is the exponentially decaying one (if a wave packet is incoming

from the left). So the wave that reaches the other end of the crystal is exponentially attenuated in this case, and the wave packet is totally reflected in the limit $N \to \infty$. There is no "conduction."

But now consider:

(2) $|C| < 1$ In this case $\lambda_\pm = C \pm i\sqrt{1-C^2}$

The eigenvalues are a complex conjugate pair with modulus 1; we may write them as

$$\lambda_\pm = e^{\pm i K_B d} \qquad (B \text{ for "Bloch"})$$

In this case M^N also has eigenvalues of modulus 1, which means that electrons can propagate through the crystal without any attenuation.

[Note: I have used a different notation here than Liboff uses:
He uses K to denote what I call K_B
K_1 to denote what I call K]

An eigenstate of M means that

$$\begin{pmatrix} A_{n+1} \\ B_{n+1} \end{pmatrix} = e^{i K_B d} \begin{pmatrix} A_n \\ B_n \end{pmatrix},$$

or $$\varphi(x+d) = e^{i K_B d} \varphi(x)$$

Wave functions in a periodic potential with this property are called Bloch states.

That we have found eigenstates of this form should not be a surprise. The periodic potential is invariant under a symmetry, a discrete translation

Now we assume either
1) $N \to \infty$, or
2) P.B.C.
$\Rightarrow K_B = \frac{2\pi}{Nd}$ int

$$\hat{D}_d : f(x) \to f(x+d) \quad (\text{where } d \text{ is the period})$$

Since this operation commutes with $\hat{H}$, we can simultaneously diagonalize $\hat{H}$ and $\hat{D}_d$. The Bloch state is an eigenstate of $\hat{D}_d$ with eigenvalue $e^{iK_B d}$. An alternative way to describe the Bloch state is

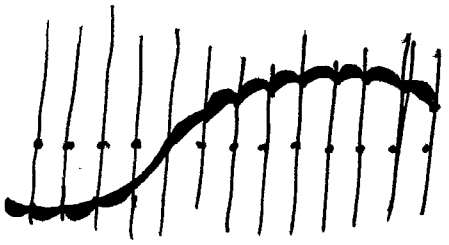
$$\ell(x) = e^{iK_B x} u(x)$$

where $u(x)$ is a periodic function

$$u(x+d) = u(x)$$

we see that K_B for the periodic potential problem is closely analogous to K for the free particle. (The free particle has a continuous translation symmetry $f(x) \to f(x+a)$, and the solution $\ell = e^{iKx}$ is an eigenstate with eigenvalue e^{iKa}

For long wavelengths $\frac{2\pi}{K_B} >> d$ — the (real part of) the solution looks like $e^{iK_B x}$ — but with some



"small scale structure" superposed on top (if a is small). Thus, if we want to build localized wave packet states that describe particles propagating through the crystal, we superpose Bloch states in much the way we superpose plane waves to construct free-particle wave packets.

In this and other ways, K_B is very analogous to the wave number for a free particle, and $\hbar K_B$ is analogous to the momentum of a free particle. We call $\hbar K_B$ the Bloch momentum, or quasimomentum of the particle.

Let's return now to the condition that must be satisfied by the M eigenstates:
(In the case $|C| < 1$, where propagation is not attenuated)

$$\cos Kd - \alpha \sin Kd = \tfrac{1}{2} \mathrm{tr} M = \cos K_B d = \tfrac{1}{2}(\lambda_+ + \lambda_-)$$

This equation implicitly determines K as a (multivalued) function of the quasi-momentum K_B. Since $E = \frac{\hbar^2 K^2}{2m}$, this is a relation $E = E(K_B)$ that generalizes the free particle relation.

This equation is unchanged if $K_B d \to K_B d \pm 2\pi$ so K and E will evidently be a periodic function of $K_B d$ with period 2π. Of course, that makes sense, since the eigenvalue of $\mathcal{D}_d$ depends only on $K_B d$ modulo 2π.

We can glimpse the qualitative properties of $E(K_B)$ if we consider solving for K graphically. We plot

$$\cos K_B d = \cos Kd - \alpha \sin Kd \qquad (\alpha = \frac{\Delta}{K})$$

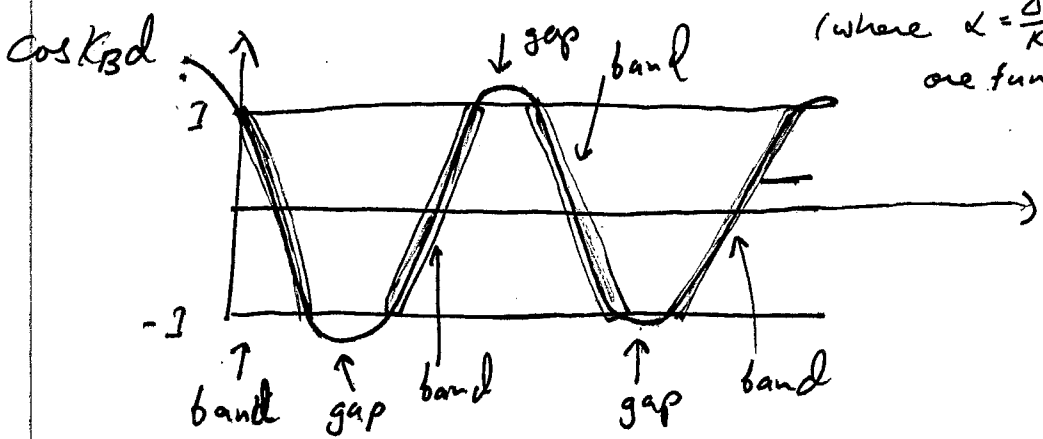
We recall that

$$B\cos(Kd+\varphi) = B[\cos\varphi\cos Kd - \sin\varphi \sin Kd]$$

So taking $B\cos\varphi = 1$, $B\sin\varphi = \alpha$ $\Rightarrow$ $\tan\varphi = \alpha$, $B^2 = 1+\alpha^2$,

we have

$$\cos(K_B d) = \sqrt{1+\alpha^2}\cos(Kd+\varphi)$$



(where $\alpha = \frac{\Delta}{K}$ and $\varphi(\alpha)$ are functions of K).

Note: α gets smaller as K increases

We see that there are bands in Kd where propagation through the crystal, separated by gaps where the particle is totally reflected -- there is no solution because $|RHS| > 1$.

Why should there be gaps?

Note that the edge of a gap occurs for

$$\cos K_B d = \pm 1 = \cos Kd - \alpha \sin Kd$$

one solution is $\cos Kd = \pm 1$ (since then $\sin Kd = 0$ — except in the case $K = 0$, since then $\frac{\Delta}{K}\sin Kd$ does not vanish).

For $\alpha = \frac{\Delta}{K} \ll 1$, the other edge is nearby

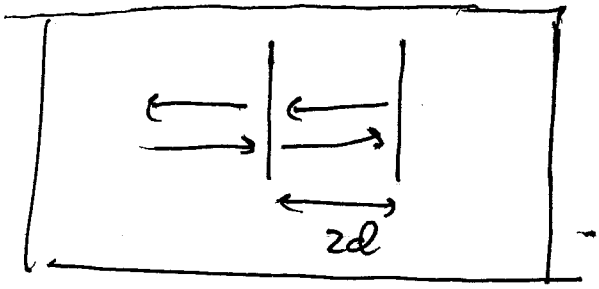
$$\pm 1 = \pm 1 \mp \tfrac{1}{2}(\Delta Kd)^2 \mp \alpha(\Delta Kd)$$

$$\Rightarrow (\Delta Kd) = -2\alpha$$

For transmitted wave, there are two $\frac{1}{2}$ phase shifts due to 2 reflections $\Rightarrow$ phase shift of π (which is obvious from the graphical solution!)

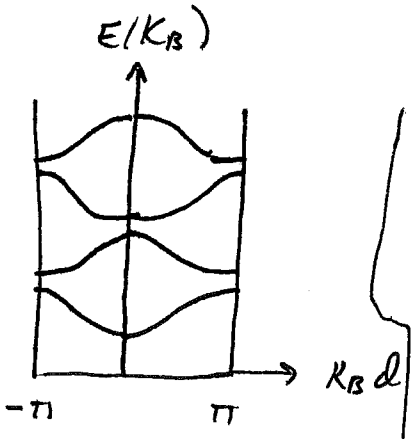
The gaps occur for $Kd = \pi \cdot$ integer, or

$$2d = \frac{2\pi}{K} \cdot \text{integer}$$



this is just the condition for the reflected waves off two successive barriers to interfere constructively — Bragg scattering condition — so there is no transmission

Since E is a periodic function of $K_B d$ with period 2π, we can represent the "band structure" as a plot of $E(K_B)$ as a function of $K_B d$ in the range $(-\pi, \pi)$ — the "reduced zone" or "Brillouin zone."



We note that:

- E(K_B) is an even function
  - $e^{\pm iK_B d}$ are degenerate eigenvalues of M.
- Periodicity ⇒ slope vanishes at $K_B d = \pm\pi$

- The bands alternate between energy min at $\cos K_B d = \pm 1$

Since we construct localized wave packets, by superposing Bloch states, for a long wavelength packet we have a group velocity

$$v(K_B) = \frac{\partial \omega(K_B)}{\partial K_B} = \frac{\partial E(K_B)}{\partial p_B} \qquad K_B d \ll 1$$

(p_B: quasi-momentum)

For the odd bands, the sign is different, so $K_B > 0$ actually describes a particle moving to the left.

For $K_B d$ small we can expand in a power series

$$E(K_B) = E_0 + \frac{1}{2} K_B^2 \left.\frac{\partial^2 E}{\partial K_B^2}\right|_{K_B=0} = \frac{\hbar^2}{2m^*} K_B^2$$

- which is just a free particle dispersion relation, but with an effective mass

$$m^* = \hbar^2 / \left(\partial^2 E / \partial K_B^2\right)$$

"Band curvature"

or we have $E \simeq \frac{1}{2m_*} p_B^2$

- just as for a free particle, but with Bloch momentum p_B and <u>effective</u> mass m_*,

$$p_B = m_* v_{group}.$$

In the case of the periodic δ-function

$$\cos k_B d \simeq 1 - \tfrac{1}{2}(k_B d)^2 = 1 - \tfrac{1}{2}[(\Delta K)d]^2 - \alpha(\Delta K d) \quad (\alpha = \tfrac{\Delta}{K})$$

$$\Rightarrow \quad \Delta K \simeq \frac{1}{\alpha d}\tfrac{1}{2}(k_B d)^2 = \tfrac{1}{2}\frac{Kd}{\Delta}k_B^2$$

$$E \sim \frac{1}{2m}(K_0+\Delta K)^2 \sim E_0 + \frac{K_0 \Delta K}{m} + \cdots$$

$$\sim E_0 + \frac{1}{2m}\left(K_0 \frac{Kd}{\Delta}\right) k_B^2$$

$$\text{or} \quad m_* = \left(\frac{K_0 \Delta}{Kd}\right) m$$

The one exception is the lowest band:

$$1 - \tfrac{1}{2}(k_B d)^2 = 1 - \tfrac{1}{2}(Kd)^2 - \frac{\Delta}{K} Kd$$

$$\Rightarrow \tfrac{1}{2}(Kd)^2 = \tfrac{1}{2}(k_B d)^2 - \Delta d$$

$$E = \frac{\hbar^2 K^2}{2m} = \frac{\hbar^2 k_B^2}{2m} - \frac{\hbar^2}{m}\frac{1}{d}$$

$\Uparrow_{m_* = m}$

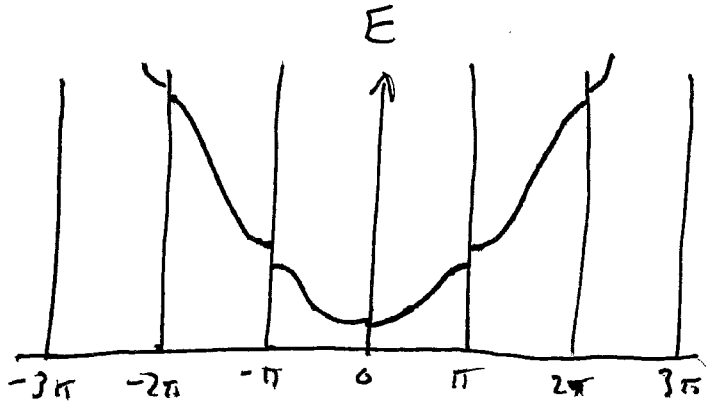
what is the interpretation of the "zero point energy"

Recall

$$V(2a) = -\frac{\hbar^2}{m}\Delta \quad \text{in the } \delta\text{-function limit}$$

So this is $V_0 \left(\begin{matrix}\text{well width} \\ \text{per unit distance}\end{matrix}\right)$

we should be able to see that we recover free-particle behavior as $\alpha = \Delta/K \to 0$. To see this, plot the energy differently — as a single valued function — by expanding the reduced zone



As $\alpha \to 0$, this approaches the free particle parabola (and the gaps disappear)

The "Band Edge"

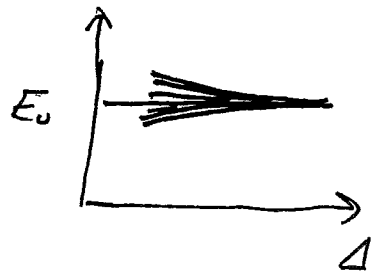
Note that we can also find the eigenfunctions for each K_B, by constructing the eigenstates of the matrix M. Consider, in particular, how the eigenstates behave as we approach the "band edge" where $\cos(K_B d) = \pm 1$

Recall that generically M has two eigenvalues $e^{\pm i K_B d}$ -- but these coalesce and become a single eigenvalue at the band edge

E.g. $e^{ikd} = 1 \Rightarrow$

$$M = \begin{pmatrix} 1+i\alpha & i\alpha \\ -i\alpha & 1-i\alpha \end{pmatrix} = \mathbb{1} + i\alpha \begin{pmatrix} 1 & 1 \\ -1 & -1 \end{pmatrix}$$

- this matrix has only one eigenstate $\sim \begin{pmatrix} 1 \\ -1 \end{pmatrix}$



As Δd decreases, tunneling is more frequent, and the degeneracy is split more — the band broadens. For $\Delta d \sim 1$, tunneling is unsuppressed, the band is quite broad, and wavepackets propagate with an effective mass m^* comparable to m.

Band Theory of Solids

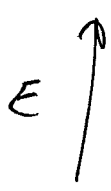
So far, we have discussed only one-dimensional potentials, and have considered in detail only the periodic δ-function. But our main qualitative conclusion — that the allowed energies form bands separated by gaps — is true for other periodic potentials, in one or three dimensions.

Just from this observation, we can understand a lot about the behavior of electrons in solids. But to do so we need to consider not a single electron in the potential, but many electrons (of the order of the number of ions or wells).

Although this is far from obvious, it turns out to be a remarkably good approximation to ignore the interactions between the electrons.

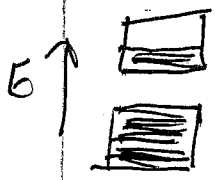
This sounds surprising, because electrons are electrically charged, and should feel a Coulomb interaction (repulsion), but for subtle reasons it is qualitatively correct to ignore this for the purpose of studying long wavelength electron wavepackets propagating in the crystal. (Landau's "Fermi liquid.")

The other important thing to know about electrons is that (like all fermions) they obey the Pauli exclusion principle — only one electron can occupy each quantum state. So if we can ignore the interactions among the electrons, we can easily understand the energy eigenstates of the many-electron system in terms of the solution to the one-electron problem. We construct an eigenstate by occupying each energy level with either one or zero electrons. If there are N electrons, we construct the ground state by occupying the N lowest energy levels and leaving the rest unoccupied. (We fill all energy levels up to a maximum E_F called the Fermi energy.) In the ground state (the state occupied at $0^\circ K$), no current flows (there are as many electrons in right-moving states as in left-moving states)



Three types of solids with qualitatively distinct properties:

① Metal

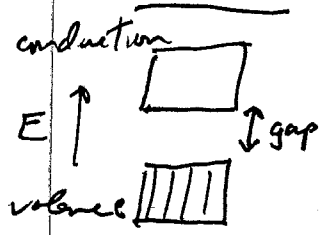


At zero Temperature, the highest band is partially filled ("conduction band")

Thus electrons are easily excited. We can construct very low energy broad wave packets from the accessible excited states, so the electrons are highly mobile

- The metal conducts heat and electricity well
- It absorbs and emits (visible photons) — metals are opaque and shiny

② Insulator



The highest band is completely filled, and there is a large gap between this band and the next (conduction) band.

E.g. in diamond gap ≈ 6eV

cf $\sim \frac{1}{40}$ eV $= kT_{room}$. It is very difficult to excite the electron across the finite gap, so the state is very unresponsive to external perturbations

- Insulator: will not conduct heat or electricity
- Won't absorb a photon (no place for the energy to go) — it is transparent

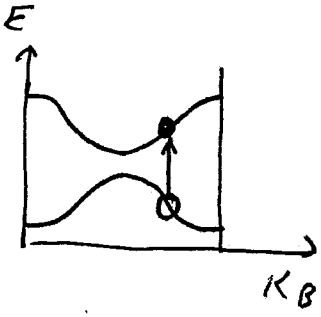
③ Semiconductor

The valence band is full — but the gap is not so large

eg. 1.11 eV in Silicon
.72 eV in Germanium

At $T \neq 0$, there are some conduction electrons — and the number is very sensitive to T and other external conditions

(Another reason that Si and Ge are interesting is that it is possible to grow very pure crystals, so that the electrons that are in the conduction band have exceptionally good mobility — don't scatter off impurities) — And can dope — see below



Exciting an electron across the gap actually creates two charge carriers — an electron in the conduction band and a hole (missing electron) in the valence band. The hole, like the electron, can propagate through the crystal, and so contributes to the conductivity. (The process shown conserves the block momentum — the electron and the hole have group velocities of opposite sign.)

Note: we can control the density of electrons or holes by doping — substituting nearby elements in the periodic table that serve as either electron donors or acceptors.