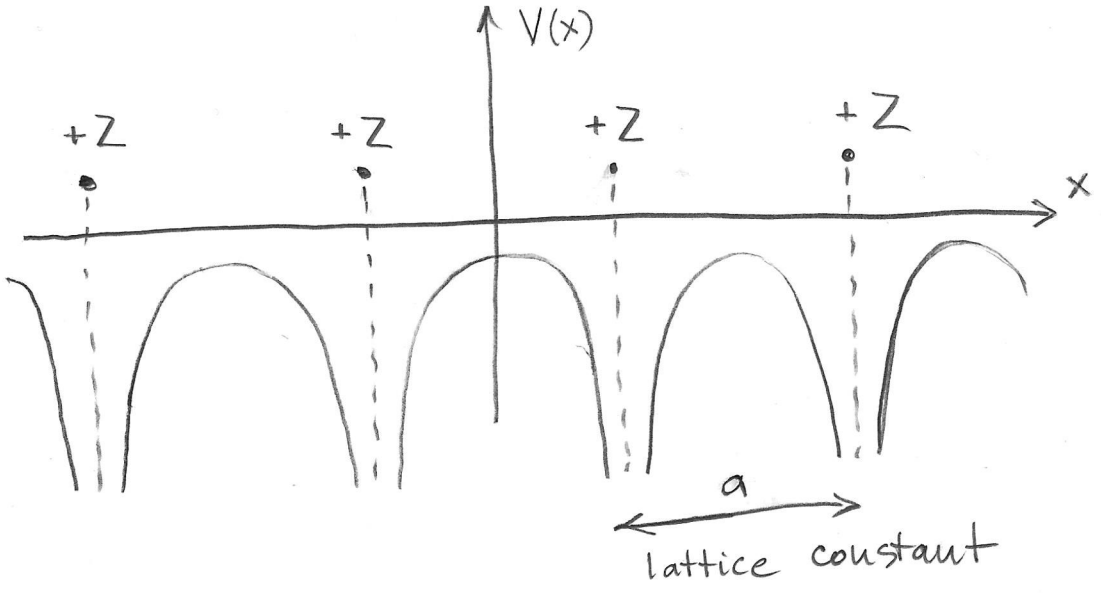
Periodic potential and band structure

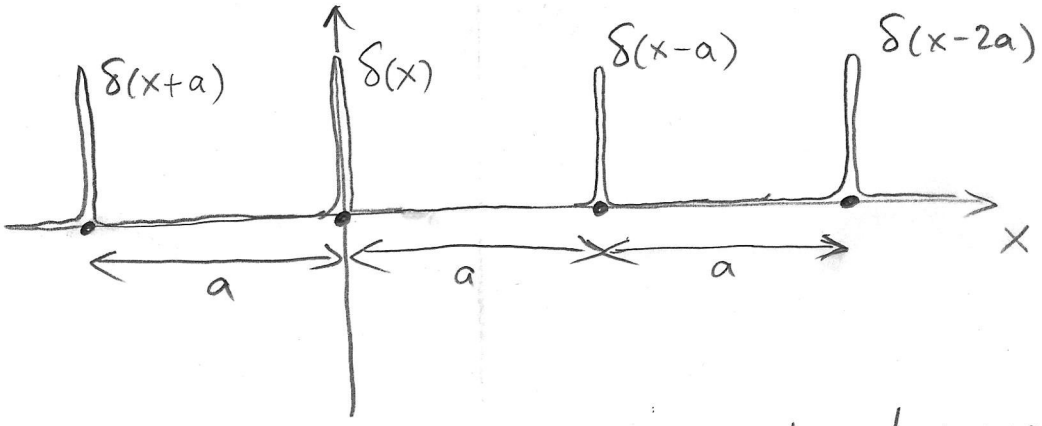
So far we have investigated the solutions of the Schrödinger equation where the potential (if nonzero) was localized in certain region of space. An electron that moves in the field of a much heavier proton (i.e. hydrogen atom) or a particle in a parabolic potentia (quantum harmonic oscillator) are examples of this. However, in many important applications of quantum mechanics we encounter a different situation, where a particle moves in a potential that is periodic (i.e. repeats itself in space). An immediate example of this is a crystall lattice, such as the one shown below:



Let us investigate what happens to the energies and wave functions in such cases. To simplify things, we will consider a 1D motion in the so called Dirac comb – a potential made of evenly separated (from $-\infty$ to $+\infty$) delta-spikes,

$$V(x) = \alpha \sum_j{}' \delta(x - ja)$$

Again, for simplicity we will assume that $\alpha > 0$ (positive spikes):



This assumption of positive α, however, will not cause any qualitative difference in the behavior of the solution. The above potential is periodic with a period a:

$$V(x+a) = V(x)$$

In order to find eigenfunctions of the Hamiltonian $\hat{H} = \frac{p^2}{2m} + V(x)$ with such a periodic potential we will employ the translation operator $\hat{T}_a$:

$$\hat{T}_a f(x) = f(x+a)$$

which translates the function it acts on by exactly a. If the potential has a period a then $\hat{T}_a$ commutes with the Hamiltonian

$$[\hat{T}_a, \hat{H}] = 0$$

This is easy to see: because $\hat{T}_a$ does not change $\hat{H}$ when it acts on it, the order in which these two operators act can be swapped.

Since $\hat{T}_a$ commutes with $\hat{H}$, they have a common system of eigenfunctions. Therefore,

the eigenfunctions of $\hat{T}_a$ are also eigenfunctions of $\hat{H}$. The eigenfunctions of $\hat{T}_a$ are

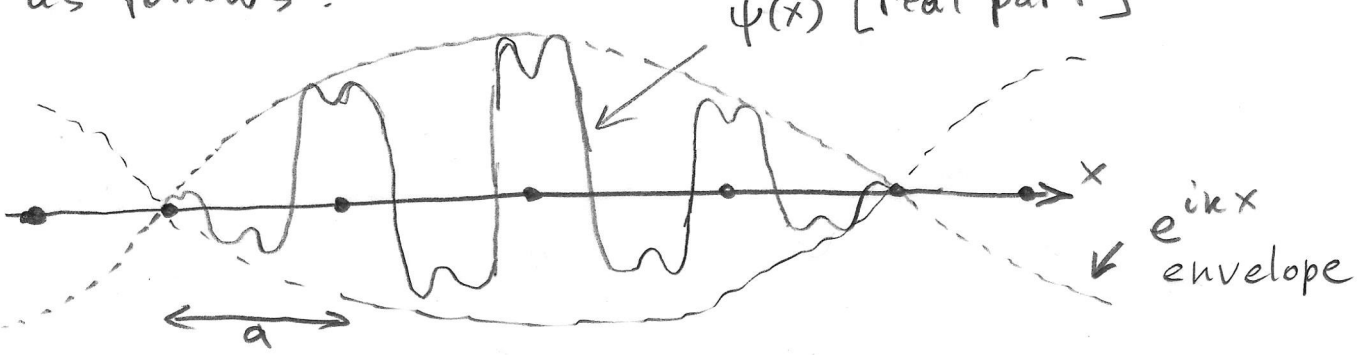
$$\psi(x) = e^{ikx} u(x) \qquad (*)$$

where function $u(x)$ has the same periodicity as the lattice (i.e. period a) and k is a constant (independent on x but may depend on energy) called crystal wave vector. $\hbar k = p$ is often called the crystal momentum or quasimomentum. Function $\psi(x)$ in $(*)$ is called the Bloch wave. The Bloch theorem states that Bloch wave functions are energy eigenstates and can be written in form $(*)$. Note that the eigenvalue of $\hat{T}_a$ corresponding to $\psi(x)$ is e^{ika}. Indeed,

$$\hat{T}_a \psi(x) = \hat{T}_a e^{ikx} u(x) = e^{ik(x+a)} u(x+a) = e^{ika} e^{ikx} u(x)$$

$$= e^{ika} \psi(x)$$

Also note that although both factors in $\psi(x)$ are periodic (u has a period a, e^{ikx} has a period $\frac{2\pi}{k}$) $\psi(x)$ itself, in general, is not periodic. $\psi(x)$ becomes periodic only if both periods commensurate, i.e. only when $na = \frac{2\pi}{k}\ell$, where n and ℓ are integers. A schematic form of $\psi(x)$ looks as follows:



We have obtained functions $\psi(x)$ using the translation operator $\hat{T}_a$. But we could also use the argument that the probability density for a particle in the crystall lattice should be periodic. In other words,

$$|\psi(x)|^2 = |\psi(x+a)|^2$$

This admits the solution $\psi(x) = e^{i\gamma(x)} u(x)$, where, again, $u(x)$ is a periodic function with period a and $\gamma(x)$ is a real function independent of a. Now if we take the limit $a \to \infty$, $V = \text{const}$ we essentially have a free particle wave function e^{ikx} with arbitrary (but real) k. Because $\gamma(x)$ is independent of a we must conclude that

$\gamma(x) = kx$, i.e.

$$\psi(x) = e^{ikx} u(x)$$

which reproduces the Bloch theorem we had previosly.

The form of function $\psi(x)$ suggests how the lattice structure influences the wave function of a particle in this lattice. The structure of the lattice is primarily contained in $u(x)$ (which depends on a). $u(x)$ also modulates the free-particle wave, e^{ikx}.

We can also rewrite the Bloch theorem (*) in another way:

$$\psi(x+a) = e^{ika}\psi(x) \quad \text{or} \quad \psi(x) = e^{ika}\psi(x-a)$$

Indeed, $\psi(x+a) = e^{ik(x+a)}u(x+a) = e^{ika}e^{ikx}u(x) = e^{ika}\psi(x)$

If the eigenstate $\psi(x)$ is known over the interval $[0, a]$ corresponding to a single lattice cell, the above relations allow to generate $\psi(x)$ in all other cells.

Any real crystal is finite. At its edges $V(x)$ is no longer periodic and the Bloch theorem is no longer applicable. However, it is reasonable to expect that for a cryslal lattice with a large (10^{23}) number of lattice sites the edge effects will not have any significant influence on the particle deep inside. This allows us to impose a formal boundary condition:

$$\psi(x + Na) = \psi(x)$$

It follows then from the Bloch theorem that

$$e^{iNka}\psi(x) = \psi(x) \quad \text{and} \quad e^{iNka} = 1$$

which yields

$$k = \frac{2\pi n}{Na} \qquad n = 0, \pm 1, \pm 2, \ldots$$

Now going back to the Dirac comb we note that in the region $0 < x < a$ (i.e. $x \neq 0$, $x \neq a$) the potential is zero, so the Schrödinger equation reads as

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \quad \text{or} \quad \psi'' + \varkappa^2\psi = 0 \quad \text{with} \quad \varkappa = \frac{\sqrt{2mE}}{\hbar}$$

The general solution is

$$\psi(x) = A \sin \varkappa x + B \cos \varkappa x \qquad (0 < x < a)$$

According to the Bloch theorem

$$\psi(x) = e^{-ika}\psi(x+a) = e^{-ika}\left[A\sin\alpha(x+a) + B\cos\alpha(x+a)\right]$$

$(-a < x < 0)$

At $x = 0$ must be continuous, so

$$B = e^{-ika}\left[A\sin\alpha a + B\cos\alpha a\right] \quad (**)$$

The first derivative of ψ has a discontinuity proportional to the strenght of the delta function, which, as we can recall it, follows from integrating the Schrödinger equation over an infinitely narrow interval $[-\epsilon, \epsilon]$:

$$-\frac{\hbar^2}{2m}\int_{-\epsilon}^{+\epsilon}\frac{d^2\psi}{dx^2}dx + \int_{-\epsilon}^{+\epsilon}V(x)\psi(x)dx = \underbrace{E\int_{-\epsilon}^{+\epsilon}\psi(x)dx}_{0} \qquad \epsilon \to 0$$

$$\psi'(+\epsilon) - \psi'(-\epsilon) = \frac{2m}{\hbar^2}\int_{-\epsilon}^{+\epsilon}V(x)\psi(x)dx$$

or

$$\psi'(+\epsilon) - \psi'(-\epsilon) = \frac{2m\alpha}{\hbar^2}\psi(0)$$

In our case we have $\psi' = \alpha\left[A\cos\alpha x - B\sin\alpha x\right]$

$(0 < x < a)$

and so

$$\alpha A - e^{-ika}\alpha\left[A\cos\alpha a - B\sin\alpha a\right] = \frac{2m\alpha}{\hbar^2}B$$

Now, if we solve $(**)$ for $A\sin\alpha a$ (which yields $A\sin\alpha a = \left[e^{ika} - \cos\alpha a\right]B$) and substitute that into the last equation, then after cancelling αB we obtain

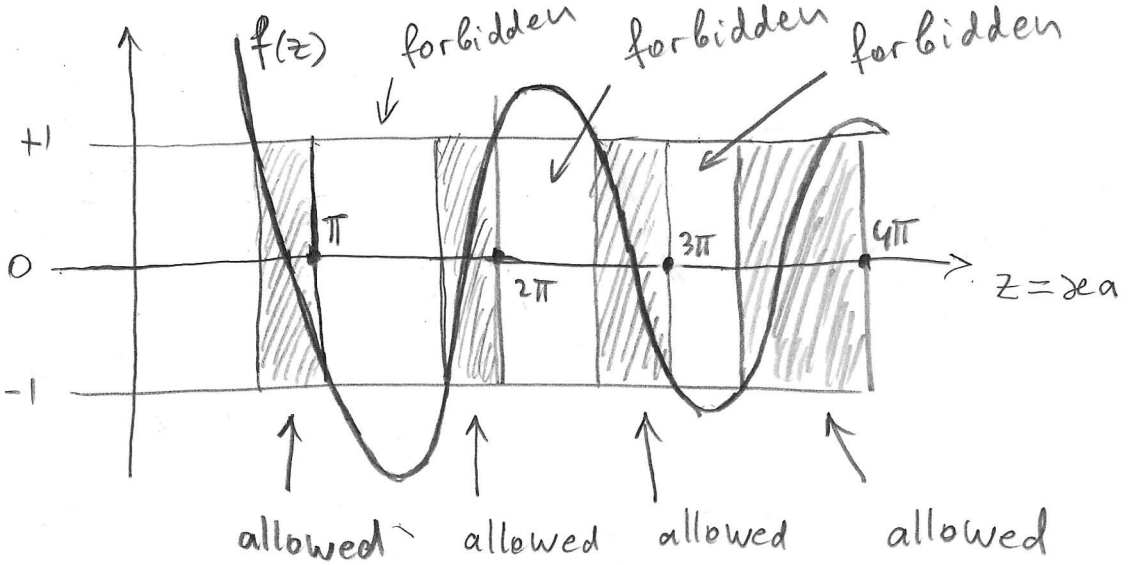
$$\left[e^{ika} - \cos\alpha a\right]\left[1 - e^{-ika}\cos\alpha a\right] + e^{-ika}\sin^2\alpha a = \frac{2m\alpha}{\hbar^2 k}\sin\alpha a$$

The latter equation can be simplified to

$$\cos ka = \cos \varkappa a + \frac{m\alpha}{\hbar^2 \varkappa} \sin \varkappa a$$

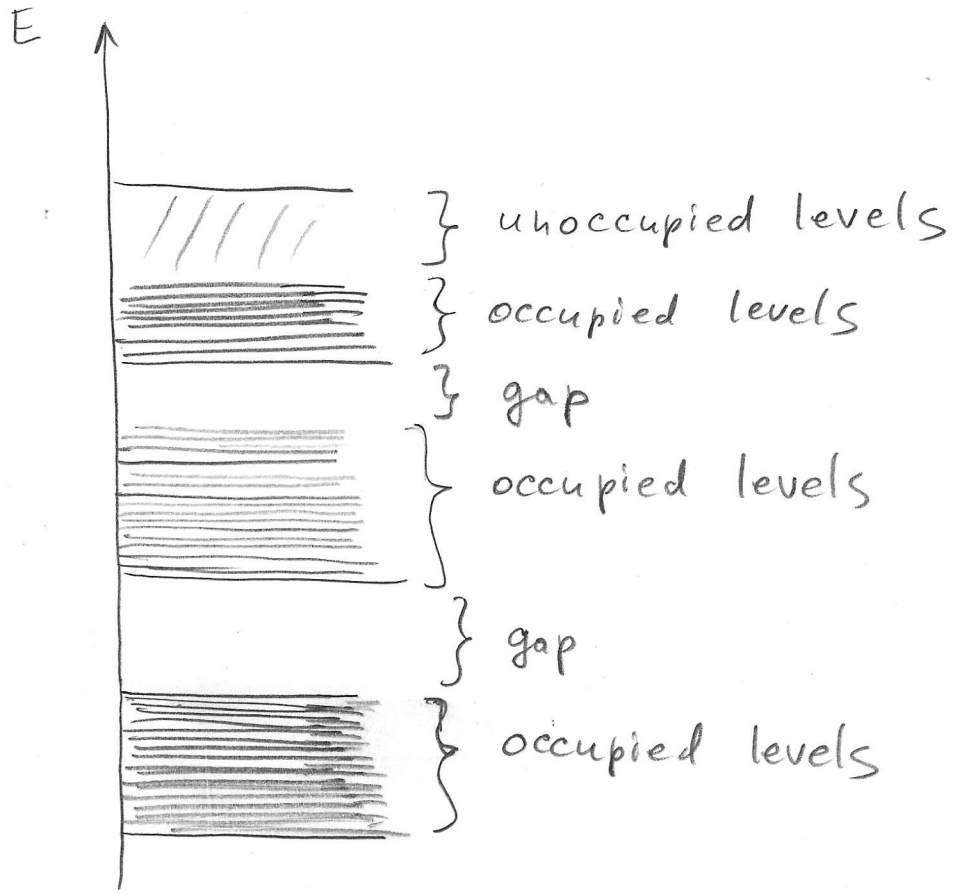
The above formula defines possible values of $\varkappa$ (and, thus, allowed energies). Let us introduce some notations: $z \equiv \varkappa a$ $\beta \equiv \frac{m\alpha a}{\hbar^2}$ $f(z) \equiv \cos z + \beta \frac{\sin z}{z}$

For those z values where $f(z)$ stays outside of interval $[-1, +1]$ the solutions do not exist



Thus the corresponding $z = \varkappa a$ range is forbidden. The intervals of z for which $f(z)$ stays within $[-1, +1]$ range represent allowed energies

Within a given allowed band essentially any energy value is possible because $ka = \frac{2\pi n}{N}$ and $N \approx 10^{23}$, while $\cos ka$ runs over nearly continuous range. If we now imagine that we have $N \approx 10^{23}$ non-interacting particles (electrons) in our lattice, then they will fill those closely spaced energy levels up to a certain point between the valence and conduction bands



This picture corresponds to a conductor because the top-shown band is partially filled.