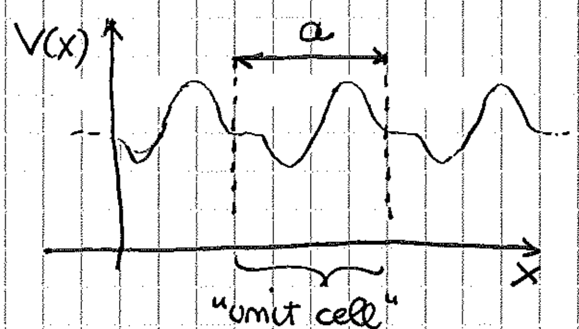
SOLIDS

We considered the case of a gas of electrons, freely moving inside a box (a 3-D quantum well), as a simplified model for a metal. Let us now add a potential due to Coulomb interaction with the ions in the lattice. This model looks more like a crystal. Let us also look at what happens in the x direction, but it is easy to generalize the math to 3 dimensions.



my crystal is periodic with period a (cell size); the potential V must have the same periodicity
a greater

A quick clarification: earlier we considered a finite box, of volume V, and size L_x, L_y, L_z in the x, y, z directions. Now, let us consider a very large (infinite ?) crystal, with a periodic potential (the size of a crystall cell).
V(x) is periodic ⟹ expandable in Fourier series:

$$V(x) = \sum_n V_n e^{iG_n x} \quad , \quad G_n = \frac{2\pi n}{a} \qquad (n = 0, \pm 1, \pm 2, \dots)$$

G's assume discrete values; we can call them "reciprocal lattice numbers".
Schroedinger's equation becomes (in 1-D, to keep things simple):

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right)\psi(x) = E\,\psi(x)$$ general solution is not plane wave

However, if V(x) is periodic, then the Hamiltonian is also periodic and commutes with the displacement operator: $Df(x) = f(x+a)$.
I can therefore choose $\psi(x)$ to be eigenstates of both H and D, since $[H,D]=0$.
How does an eigenfunction of D look like?

$$\left.\begin{array}{ll} D\psi(x) = \lambda\psi(x) & \text{definition of eigenfunction} \\ D\psi(x) = \psi(x+a) & \text{definition of displacement operator } D \\ |\psi(x)|^2 = |\psi(x+a)|^2 & \text{periodicity requires this to be true} \end{array}\right\} \Rightarrow \underline{\underline{\lambda = e^{ika}}}$$

It must therefore be that $\psi(x+a) = e^{ika}\cdot\psi(x)$. This result goes under the name of Bloch's Theorem. How can I write $\psi(x)$ that satisfies the condition above? Here:

$$\psi(x) = e^{ikx}\,\mu(x) \qquad \text{BLOCH WAVE}$$

$\mu(x)$ ↳ periodic with period a : $\mu(x) = \mu(x+a)$

Let us now move to Schroedinger's equation. Since $\mu(x)$ is periodic, I can expand it in Fourier series:

$$\mu(x) = \sum_m c_m e^{iG_m x} \qquad G_m = 2\pi m/a$$

We get:

$$-\frac{\hbar^2}{2m}\left(e^{ikx}\mu(x)\right)'' + V(x)e^{ikx}\mu(x) = E\,e^{ikx}\mu(x)$$

$$-\frac{\hbar^2}{2m}\left(\mu''(x) + 2ik\mu'(x) - k^2\mu\right)\cancel{e^{ikx}} + V(x)\cancel{e^{ikx}}\mu(x) = E\cancel{e^{ikx}}\mu(x)$$

$$-\frac{\hbar^2}{2m}\left(\frac{d}{dx} + ik\right)^2\mu(x) + V\mu(x) = E\,\mu(x) \qquad \text{Schroedinger's equation for envelope function only!}$$

now replace Fourier transform:

$$\frac{d}{dx} \longrightarrow iG_m$$

$$+\frac{\hbar}{2m}\sum_m (G_m + k)^2 c_m e^{iG_m x} + \sum_{m'} V_{m'} e^{iG_{m'}x}\sum_m c_m e^{iG_m x} = E\sum_m c_m e^{iG_m x}$$

Fourier series of $V(x)$, also periodic

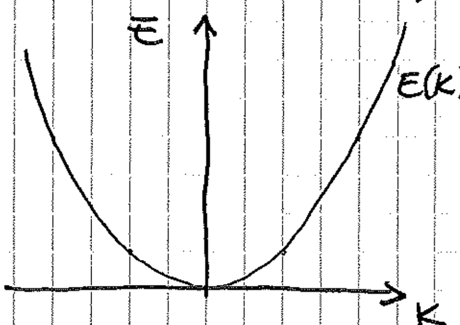
Let us now consider the case $V(x) = 0$, but still keep the imposed discrete periodicity. We obtain: $\frac{\hbar^2}{2m}\sum_m (G_m+k)^2 c_m e^{iG_m x} = E\sum_m c_m e^{iG_m x}$

Since the $e^{iG_m x}$ functions are orthonormal, we need each term in the sum to be equal, term by term. We get:

$$E = \frac{\hbar^2}{2m}\left(K+G_m\right)^2 \qquad G_m = 0, \pm\frac{2\pi}{a}, \pm\frac{4\pi}{a}, \ldots$$
$$m = 0, \pm 1, \pm 2 \ldots$$

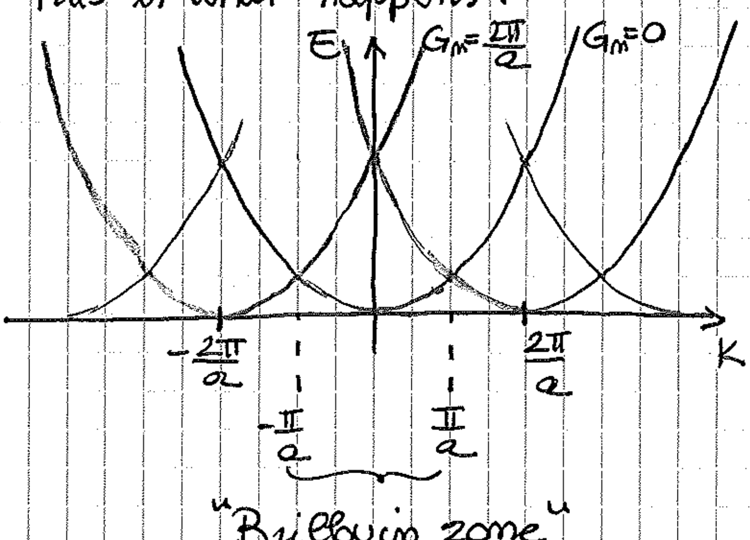
What is going on? Let us think about the free particle, $V(x)=0$, $H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$, continuous translation symmetry, i.e., free particle in free space.

Solution: $\psi(x) = e^{iKx}$, $E = \hbar^2 K^2/2m$:

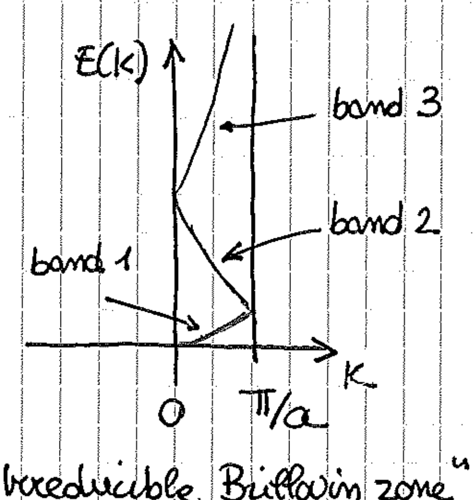


the plot is telling me that __any__ positive energy E is allowed: the wavefunction $\psi(x) = e^{iKx}$ with $K = \sqrt{2Em}/\hbar$ has energy E.

When I introduce a periodicity, with period a, in my free space ($V(x)=0$, still!), this is what happens:



folding symmetry $\Longrightarrow$



Note that this is __still__ a metal, all energies are still accessible: there always exists a Bloch wave that has energy E, for any positive value.

What happens when $V \neq 0$?

Let us go back to the $V(x)$ term in Schroedinger's equation for the Bloch wave envelope:

$$\sum_{m'} V_{m'} e^{iG_{m'}x} \sum_m C_m e^{iG_m x} = \sum_{m'}\sum_m V_{m'} C_m e^{i(G_{m'}+G_m)x} =$$

$$\underset{m''=m+m'}{=} \sum_{m''}\sum_{m'} V_{m'} C_{m''-m'} e^{iG_{m''}x} \underset{m'' \text{ just a label}}{=} \sum_m \sum_{m'} V_{m'} C_{m-m'} e^{iG_m x}$$

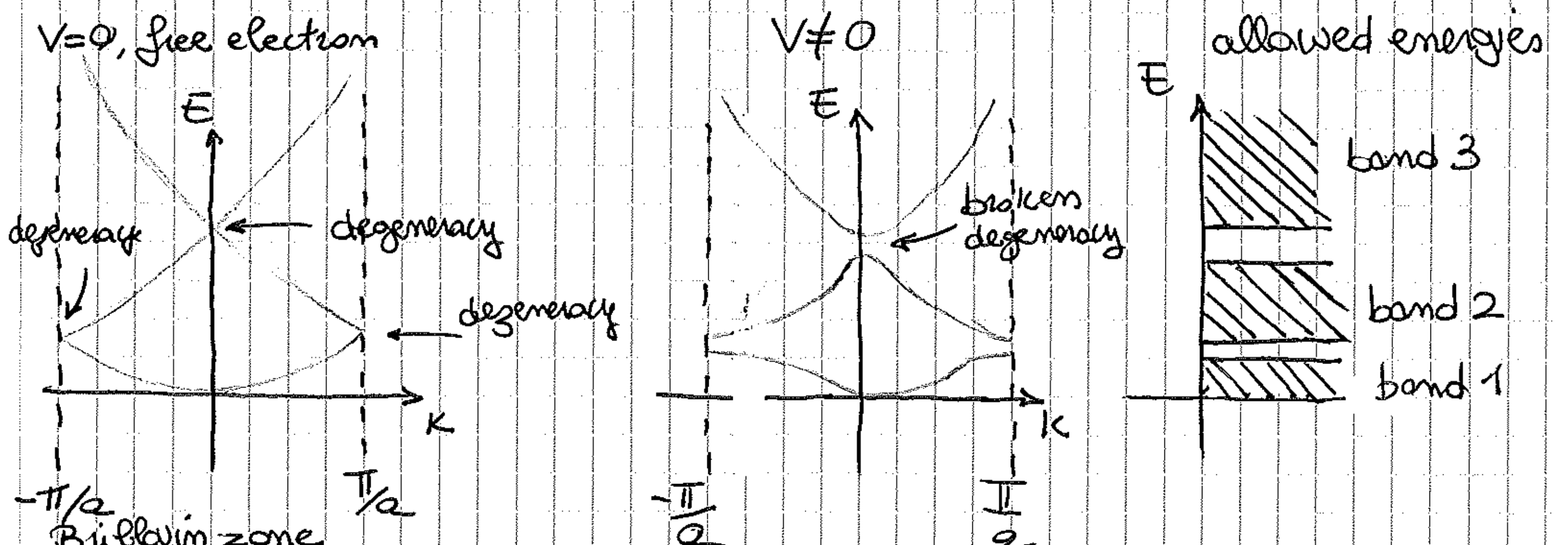
Schroedinger's equation for $u(x)$ becomes:

$$\sum_m \left(\frac{\hbar^2}{2m}(K+G_m)^2 C_m + \sum_{m'} V_{m'} C_{m-m'} \right) e^{iG_m x} = \sum_m C_m e^{iG_m x}$$

Using again orthonormality of $e^{iG_m x}$, we have term-by-term equality:

$$\frac{\hbar^2}{2m}(K+G_m)^2 C_m + \sum_{m'} V_{m'} C_{m-m'} = E\, C_m \qquad \underline{\underline{\forall m}}$$

This is an infinite set of linear equations for the coefficients C_m. Let me jump to the conclusion:



The effect of $V \neq 0$ is to create gaps in the dispersion relation $E(K)$; they correspond to energy values for which no solution to the Schroedinger's equation exists. From metals, we are now moving towards semiconductors.