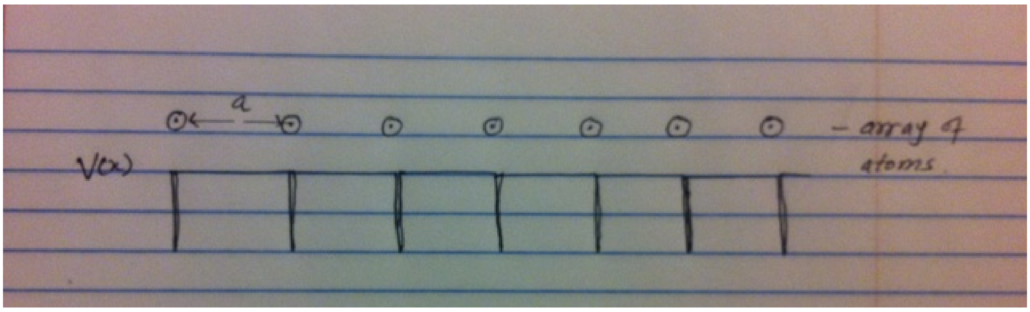
One Dimensional Solid (Crystal)

Lecture Notes 2/5/2013

Consider N atoms in a row.To make life easier we make following approximation:

a)some electrons are bound to the nucleus and some are free. In particular, say we have q electrons per atom are free, i. e, in total qN free electrons are present.
b)Bound electrons of one atom do not interact with bound electrons of another atom.
c)Potential is periodic and approximated as delta function which allows one bound state.
It looks as in figure below:



$$V(x) = -\alpha \sum_{j=0}^{N} \delta(x - ja)$$

Now, we want to solve Schrodinger equation for the above system. Before doing so, lets first define an operator $\hat{D}$.

$$\hat{D}\psi(x) = \psi(x + a)$$

$\hat{D}$is called displacement operator.
For a periodic potential [V(x)=V(x+a)],
$\hat{D}$ commutes with hamiltonian $\hat{H}$.

$$[\hat{D}, \hat{H}] = 0$$

It means we can find joint eigen function for them. Moreover, $\hat{D}$ is not hermitian, so its eigenvalue may not be real.

We have,

$$\hat{D}\psi(x) = \psi(x+a)$$
$$= \gamma\psi(x)$$

Assume:

$$\psi(0) = \psi(Na)$$

then

$$\psi(0) = (\hat{D})^N\psi(0)$$
$$= \gamma^N\psi(0)$$

Looking at this equation we can see that that γ can have following form:

$$\gamma = e^{i(\frac{2\pi}{N})}$$

or even, $\gamma = e^{i(\frac{2\pi}{N})n}$,$n$ is an integer.

Then we have

$$\hat{D}\psi(0) = e^{in\phi}\psi(x)$$

where $\frac{2\pi}{N} = \phi$

$$\psi(x-a) = e^{-in\phi}\psi(x)$$

We will now solve Schrodinger equation in the interval $ja-\epsilon \leq x \leq (j+1)a-\epsilon$ since we can recover the full solution simply by applying translations by a.

Introduce $y = x - ja; y = -\epsilon ... a - \epsilon$,then

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(y)}{\partial y^2} + V(y)\psi(y) = E\psi(y).....(1)$$

For $y > \epsilon$ potential is zero, so we have free hamiltonian,thus we can write the solution as,

$$\psi(y) = Ae^{iky} + Be^{-iky}$$

where,$k = \sqrt{\frac{2mE}{\hbar}}$
Now, we apply boundary condition:

In region $0 < y < a$ and $\epsilon > 0$ but very small,we can write

$$\psi(-\epsilon) = \psi(a-\epsilon)e^{-in\phi}$$
$$= e^{-in\phi}(Ae^{ik(a-\epsilon)} + Be^{-ik(a-\epsilon)})$$

when $\epsilon \to 0$,

$$A + B = e^{-in\phi}(Ae^{ika} + Be^{-ika})$$
$$A\left(1 - e^{ika}e^{-in\phi}\right) = B\left(e^{-in\phi}e^{-ika} - 1\right)$$
$$A = \left(\frac{e^{-ika} - e^{in\phi}}{e^{in\phi} - e^{ika}}\right)B$$

Integrating eqn(1) in [-ϵ,ϵ], we get

$$\int_{-\epsilon}^{\epsilon} \frac{-\hbar^2}{2m}\frac{\partial^2\psi(y)}{\partial y^2}dy + \int_{-\epsilon}^{\epsilon} V(y)\psi(y)dy = E\int_{-\epsilon}^{\epsilon}\psi(y)dy$$
$$\frac{-\hbar^2}{2m}\left[\frac{\partial\psi(y)}{\partial y}|_{+\epsilon} - \frac{\partial\psi(y)}{\partial y}|_{-\epsilon}\right] - \alpha\int_{-\epsilon}^{+\epsilon}\delta(y)\psi(y)dy = 0$$
$$\frac{\hbar^2}{2m}\left[-ik(A-B) + ike^{-in\phi}(Ae^{ika} - B^{-ika}\right] = \alpha(A+B)$$
$$\frac{ik\hbar^2}{2m}\left[A(e^{ika}e^{-in\phi} - 1) + B(1 - e^{-ika}e^{-in\phi})\right] = \frac{ik\hbar^2}{2m}\left[2B(1 - e^{-ika}e^{-in\phi})\right] = \alpha(A{+}B)$$
$$1 - e^{-ika}e^{-in\phi} = \frac{2m\alpha}{k\hbar^2}\frac{1}{2i}\left[\frac{e^{-ika} - e^{in\phi}}{e^{in\phi} - e^{ika}} + 1\right]$$
$$\left(e^{ika} - e^{in\phi} - e^{-in\phi} + e^{-ika}\right] = \frac{2m\alpha}{k\hbar^2}sin(ka)$$
$$cos(ka) - cos(n\phi) = \frac{ma\alpha}{\hbar^2}\frac{sin(ka)}{ka}$$

calling $ka = z$,we get

$$cos(z) - \left(\frac{ma\alpha}{\hbar^2}\right)\frac{sin(z)}{z} = cos(n\phi)$$

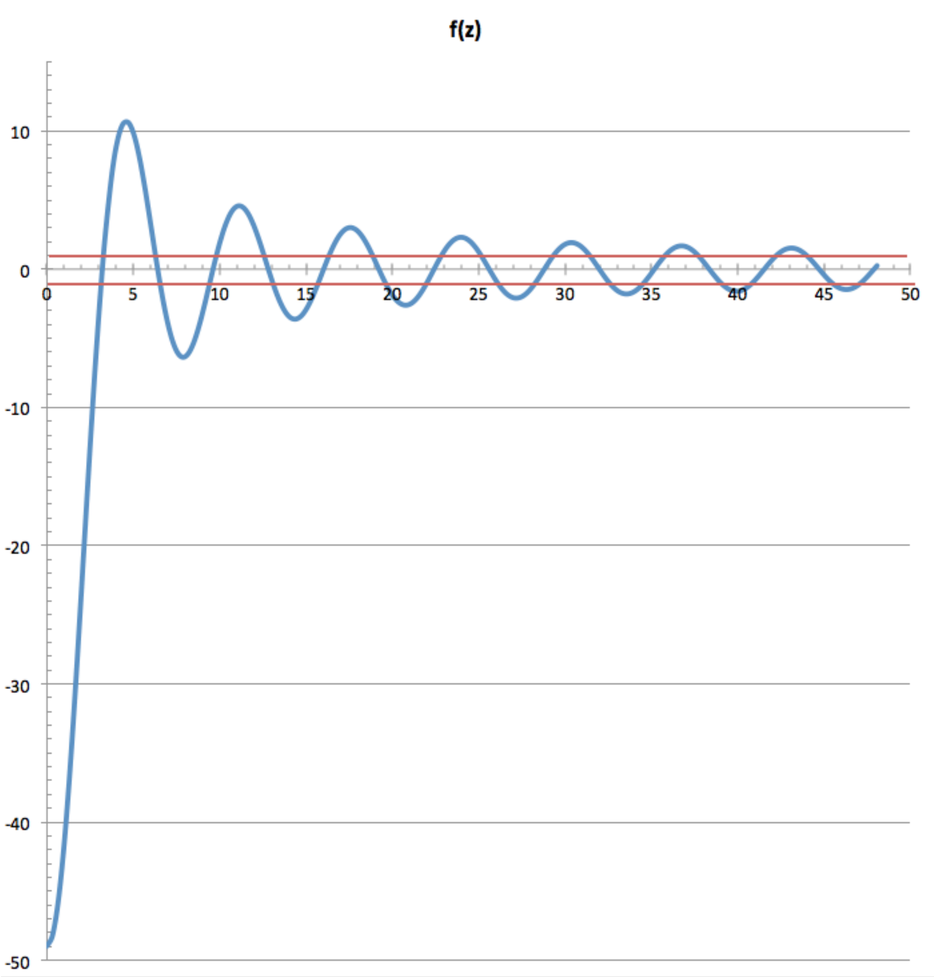


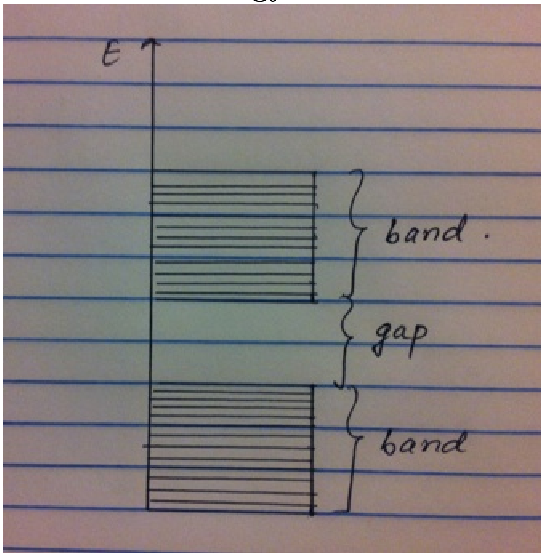
Figure 1: **PLOT of f(z) vs Z**

We can find the sequence of solutions for z by observing that the r.h.s. has exactly $N/2$ unique values between -1 and 1, after which the cos repeats itself. Therefore, from the lowest z where the function $f(z)$ crosses into the ±1 band up, there are $N/2$ unique solutions, followed by another $N/2$ for the second crossing etc.

Since $k = \frac{z}{a}$ we can find the energy eigenvalues as

$$E = \frac{z^2\hbar^2}{2ma^2}$$

Plot for energy bands



Consequences:
Each of the allowed eigenstates can be filled by (at most) 2 electrons (one spin up, one spin down), so the first band can accommodate N electrons, as well as the 2nd band and so on. The crystal behaves as an insulator if the allowed energy bands are either filled or empty.The crystal behaves as a conductor if one or more bands are partly filled.The crystal is a semiconductor if one or two bands are slightly filled or slightly empty ("doped") or if the separation between the full and the empty band is small.