General Potentials

Let's consider a periodic potential $U(x)$ with periodicity a, such that $U(x) = U(x+a)$.
Any function invariant under a translation given by $\vec{T} = \mu\vec{a}_1 + \nu\vec{a}_2 + \lambda\vec{a}_3$, can be written in terms of a Fourier series

$$U(x) = \sum_G U_G e^{iGx}$$

The values U_G decrease rapidly as $|G| \gg 1$
For a bare Coulomb potential U_G decreases as $1/G^2$
As we want the potential to be real-valued

$$U(x) = \sum_{G>0} U_G \left(e^{iGx} + e^{-iGx}\right)$$

$$= 2\sum_{G>0} U_G \cos(Gx)$$

for convenience, we assume that $U_0 = 0$ and that $U(x)$ is symmetric around $x=0$

The Schrödinger Eq. in this case becomes

$$\left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)\right]\psi(x) = \left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + 2\sum_{G>0} U_G \cos(Gx)\right]\psi(x) = E\psi(x)$$

The WF can also be written as a Fourier series

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

k: the allowed values of the wave vector obtained the PBC method

That means that $k = \frac{2\pi n}{L}$ $n \in \mathbb{Z}$

n can be positive and negative
L is the lenght of the crystal

we cannot assume, and in general it is not true, that $\psi(x)$ has the periodicity of the $U(x)$. It has its own periodic properties dictated by Bloch theorem.

we can label the WF $\psi(x)$ which contains the wavevector k as ψ_k ⇒ but we could also label it ψ_{k+G}, because if k enters the Fourier series, so does $k+G$.

To solve Schrödinger Eq. we replace our WF:

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\sum_k c_k e^{ikx} = \frac{\hbar^2}{2m}\sum_k k^2 c_k e^{ikx}$$

$$U(x)\psi(x) = \left(\sum_G U_G e^{iGx}\right)\left(\sum_k c_k e^{ikx}\right)$$

$$= \sum_G \sum_k U_G c_k e^{i(k+G)x}$$

$$\sum_k \frac{\hbar^2 k^2}{2m} c_k e^{ikx} + \sum_k \sum_G U_G c_k e^{i(k+G)x} = \sum_k E c_k e^{ikx}$$

$$\sum_k \frac{\hbar^2 k^2}{2m} c_k e^{ikx} + \sum_k \sum_G U_G c_k e^{i(k+G)x} - \sum_k E c_k e^{ikx} = 0$$

$$\sum_k' \left[\frac{\hbar^2 k^2}{2m} C_k e^{ikx} + \sum_G' U_G C_k e^{i(k+G)x} - E C_k e^{ikx} \right] = 0$$

$k \to k - G$

$$\sum_k' \left[\left(\frac{\hbar^2 k^2}{2m} - E \right) C_k e^{ikx} + \sum_G' U_G C_{k-G} e^{ikx} \right] = 0$$

$$\sum_k' \left[\left(\frac{\hbar^2 k^2}{2m} - E \right) C_k + \sum_G' U_G C_{k-G} \right] = 0$$

we need the [ ] = 0 for each k.

$$\boxed{\left(\frac{\hbar^2 k^2}{2m} - E \right) C_k + \sum_G' U_G C_{k-G} = 0}$$

This is known as the "Central equation"

The problem here is to find the coefficients C_k

Once we determine C_k, the WF becomes

$$\psi_k(x) = \sum_G' C_{k-G} e^{i(k-G)x}$$

which can be rearranged

$$\psi_k(x) = \sum_G' C_{k-G} e^{-iGx} e^{ikx}$$

$$= \left(\sum_G C_{k-G} e^{-iGx} \right) e^{ikx}$$

$$= U_k(x) e^{ikx} \qquad \text{with } U_k(x) = \sum_G' C_{k-G} e^{-iGx}$$

Because $U_k(x)$ is a Fourier series over the reciprocal space, it is invariant under a crystal lattice translation T, which was

$$u_k(x) = u_k(x+T)$$

we can verify:

$$u_k(x+T) = \sum_G C_{k-G}\, e^{-iG(x+T)} = \sum_G C_{k-G}\, e^{-iGx}\, e^{-iGT}$$

$$= u_k(x)\, e^{-iGT} \qquad \text{by construction } \bar{G}\cdot\bar{T} = 2\pi\mu$$

$$= u_k(x)$$

This is an alternative and also exact proof of Bloch theorem.

Solution to the central equation

$$\left(\frac{\hbar^2 k^2}{2m} - E\right) C_k + \sum_G U_G\, C_{k-G} = 0$$

This is a set of equations conected through the coefficients C_{k-G}. It is a set because there are as many equations as there are coefficients.

Let there be g the shortest value that G's can take. let's assume that we have a potential

$$U(x) = U_g\, e^{igx} + U_{-g}\, e^{-igx}$$

let's also assume that $U_g = U_{-g} = U$

$$U(x) = 2U\cos(gx)$$

Let's define $\lambda_k = \dfrac{\hbar^2 k^2}{2m}$

$$(\lambda_k - E)\, C_k + \sum_G U_G\, C_{k-G} = 0$$

$$(\lambda_k - E)\, C_k + U(C_{k-g} + C_{k+g}) = 0$$

$$(\lambda_{k-g} - E)\, C_{k-g} + U(C_{k-2g} + C_k) = 0$$

$$(\lambda_{k+g} - E)\, C_{k+g} + U(C_k + C_{k+2g}) = 0$$

$$(\lambda_{k-2g} - E)\, C_{k-2g} + U(C_{k-3g} + C_{k-g}) = 0$$

$$(\lambda_{k+2g} - E)\, C_{k+2g} + U(C_{k+g} + C_{k+3g}) = 0$$

$$\vdots \qquad\qquad\qquad \vdots$$

Although the coefficients are infinte, each of them is only connected to two other coefficients. we can write a matrix with the coefficients:

$$M = \begin{pmatrix}
\ddots & U & & & & & \\
U & \lambda_{k-2g}-E & U & & 0 & & \\
 & U & \lambda_{k-g}-E & U & & & \\
 & & U & \lambda_k - E & U & & \\
 & & & U & \lambda_{k+g}-E & U & \\
 & 0 & & & U & \lambda_{k+2g}-E & U \\
 & & & & & U & \ddots
\end{pmatrix}$$

The equation that we have is $M\vec{C} = 0$

The solution to this system is obtained when $\det(M) = 0$. This yields a set of E_{nk} (are the eigenvalues of the matrix), where n: labels the energies and k: labels the coefficients C_k.