Born - von Karmen boundary conditions
and Fourier transforms for a Bravais lattice

We generalize the idea of periodic (or Born-von Karmen) boundary conditions to electron states on a Bravais lattice.

B.L. vectors $\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$

n_1, n_2, n_3 integers.

For a BL of finite size we have $0 \leq n_i < N_i$

$N = N_1 N_2 N_3$ is total number of points in the BL.

Total volume of this finite BL is

$$V = \underbrace{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}_{\text{volume of primitive cell}} N$$

We want our electron wave functions to be periodic on such a finite BL

$$\psi(\vec{r} + N_i \vec{a}_i) = \psi(\vec{r})$$

As we saw earlier for free electrons, this imposes a constraint on the wave vectors $\vec{k}$ that can appear in the Fourier transform of $\psi(\vec{r})$.

Write $\psi(\vec{r})$ in terms of its ~~Fourier~~ transform

$$\psi(\vec{r}) = \sum_{k} e^{i \vec{k} \cdot \vec{r}} c_{\vec{k}}$$

↑ Fourier coefficients for $\psi(\vec{r})$

Then

$$\psi(\vec{r} + N_i \vec{a}_i) = \sum_k e^{i\vec{k}\cdot(\vec{r}+N_i\vec{a}_i)} c_k$$

$$= \sum_k e^{i\vec{k}\cdot\vec{r}} \left[e^{i\vec{k}\cdot N_i \vec{a}_i} c_k \right]$$

$$= \psi(\vec{r}) = \sum_k e^{i\vec{k}\cdot\vec{r}} c_k$$

$$\Rightarrow e^{i\vec{k}\cdot N_i \vec{a}_i} c_k = c_k \quad \text{for all } \vec{k} \text{ that appear}$$

in the Fourier transform of $\psi(\vec{r})$

$$\Rightarrow e^{i\vec{k}\cdot N_i \vec{a}_i} = 1 \quad \text{for all } \vec{k}$$

Write $\vec{k}$ in terms of the primitive vectors of the RL

$$\vec{k} = x_1 \vec{b}_1 + x_2 \vec{b}_2 + x_3 \vec{b}_3 \qquad x_i \text{ are not in general integers}$$

Then

$$e^{i N_i \vec{k}\cdot\vec{a}_i} = e^{i N_i 2\pi x_i} = 1$$

$$\text{since } \vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}$$

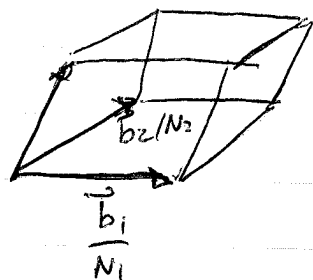$$\Rightarrow x_i N_i = m_i \quad \text{integer}$$

$$x_i = \frac{m_i}{N_i}$$

So the allowed wavevectors are

$$\boxed{\vec{k} = \frac{m_1}{N_1}\vec{b}_1 + \frac{m_2}{N_2}\vec{b}_2 + \frac{m_3}{N_3}\vec{b}_3}$$

where m_1, m_2, m_3 are integers.

This is the Born – von Karman boundary conditions

volume per allowed wavevector in $\vec{k}$-space is the volume of the parallelepiped formed by the vectors $\dfrac{\vec{b}_i}{N_i}$

$$= \frac{\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)}{N_1 N_2 N_3} = \frac{(2\pi)^3}{N\,(\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3))}$$

$$= \frac{(2\pi)^3}{v\,N} = \frac{(2\pi)^3}{V} \qquad\qquad V = v\,N \\ = \text{total volume BL}$$

where $v = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$ is the volume of the primitive cell of the B.L. and $\dfrac{(2\pi)^3}{v}$ is the volume of the primitive cell of the R.L.

Note: volume per allowed wavevector $\dfrac{(2\pi)^3}{V}$ is same as we had for free electrons.

Number of allowed $\vec{k}$ values in any primitive cell of the R.L. is

$$\frac{\left[\dfrac{(2\pi)^3}{v}\right]}{\left[\dfrac{(2\pi)^3}{v\,N}\right]} = N \quad \text{number of ions in BL}$$

Number of allowed $\vec{k}$ values in any primitive cell of the R.L., for example the 1st BZ, is N

$\Rightarrow$ # electron states in 1st BZ is $2N$ (2 from spin $= \pm 1$)
$\Rightarrow$ when valence $Z = 1$, ground state occupies half the states of 1st BZ

We now define the Fourier transform and its inverse that is consistent with the allowed wavevectors $\vec{k}$ of the Born - von Karman boundary conditions

IF
$$\psi(\vec{r}) \equiv \sum_{k} e^{i\vec{k}\cdot\vec{r}} c_k$$

$\uparrow$ sum over all $\vec{k}$ that obey
Born - von Karman boundary conditions

Then the inverse Fourier transform is

$$c_k = \frac{1}{V} \int_V d^3r \, e^{-i\vec{k}\cdot\vec{r}} \psi(\vec{r})$$

Proof:
$$\frac{1}{V} \int_V d^3r \, e^{-i\vec{k}\cdot\vec{r}} \psi(\vec{r}) = \sum_{k'} c_{k'} \frac{1}{V} \int d^3r \, e^{i(\vec{k}'-\vec{k})\cdot\vec{r}}$$

since both $\vec{k}$ and $\vec{k}'$ satisfy Born - von Karman boundary conditions, we can write

$$\vec{k}' - \vec{k} = \frac{m_1}{N_1} \vec{b}_1 + \frac{m_2}{N_2} \vec{b}_2 + \frac{m_3}{N_3} \vec{b}_3$$

with m_1, m_2, m_3 integers,

Also we can write

$$\vec{r} = x_1 \vec{a}_1 + x_2 \vec{a}_2 + x_3 \vec{a}_3 \qquad 0 \leq x_i \leq N_i$$

since $\vec{r}$ is not in general a BL vector, the x_i are any real values (not necessarily integers)

Now

$$\int_V d^3r = v \int_0^{N_1} dx_1 \int_0^{N_2} dx_2 \int_0^{N_3} dx_3 \qquad \text{since } V = vN$$
$$v = \text{vol primitive cell}$$

and

$$(\vec{k}' - \vec{k}) \cdot \vec{r} = 2\pi \left(\frac{m_1}{N_1} x_1 + \frac{m_2}{N_2} x_2 + \frac{m_3}{N_3} x_3 \right)$$

So

$$\frac{1}{V} \int d^3r \, e^{i(\vec{k}' - \vec{k}) \cdot \vec{r}} = \frac{v}{V} \prod_{i=1}^{3} \left[\int_0^{N_i} dx_i \, e^{2\pi i \frac{m_i}{N_i} x_i} \right]$$

do for example the x_1 integral

$$\int_0^{N_1} dx_1 \, e^{2\pi i \frac{m_1 x_1}{N_1}} = \frac{e^{2\pi i m_1} - 1}{\frac{2\pi i m_1}{N_1}}$$

$$= \begin{cases} 0 & m_1 \neq 0 \quad \text{since } m_1 \text{ integer} \\[2mm] N_1 & m_1 = 0 \quad (\text{take limit } m_1 \to 0) \end{cases}$$

So

$$\frac{1}{V} \int d^3r \, e^{i(\vec{k}' - \vec{k}) \cdot \vec{r}} = \frac{v N_1 N_2 N_3}{V} \, \delta_{k', k}$$
$$= \delta_{k', k} \qquad \underset{\substack{\text{zero unless} \\ \vec{k} = \vec{k}'}}{\uparrow}$$

So $\displaystyle \sum_{k'} C_{k'} \frac{1}{V} \int d^3r \, e^{i(\vec{k}' - \vec{k}) \cdot \vec{r}} = \sum_{k'} C_{k'} \, \delta_{k', k} = C_k$

Bloch's Theorem

Now we prove Bloch's theorem by substituting the Fourier transform in the Schrodinger Equ.

$$-\frac{\hbar^2}{2m}\nabla^2\psi + U(\vec{r})\psi = \varepsilon\psi$$

where $U(\vec{r})$ is the ionic potential
and ε is the eigenvalue = electron energy

Substitute in the Fourier transforms

$$\psi(\vec{r}) = \sum_k e^{i\vec{k}\cdot\vec{r}} c_k$$

$$U(\vec{r}) = \sum_{k'} e^{i\vec{k}'\cdot\vec{r}} U_{k'}$$

to get

$$\sum_k e^{i\vec{k}\cdot\vec{r}} \frac{\hbar^2 k^2}{2m} c_k + \sum_{k''}\sum_{k'} e^{i(\vec{k}''+\vec{k}')\cdot\vec{r}} U_{k'} c_{k''}$$

$$= \varepsilon\sum_k e^{i\vec{k}\cdot\vec{r}} c_k$$

Now ~~sta~~ transform summation variable in the 2nd term to $\vec{k} = \vec{k}'' + \vec{k}'$ so $\vec{k}'' = \vec{k} - \vec{k}'$

$$\Rightarrow \sum_k e^{i\vec{k}\cdot\vec{r}}\left[\left(\frac{\hbar^2 k^2}{2m} - \varepsilon\right)c_k + \sum_{k'} U_{k'} c_{k-k'}\right] = 0$$

write $\varepsilon_k^0 \equiv \frac{\hbar^2 k^2}{2m}$

$$\Rightarrow \quad \varepsilon_k^0 \, c_k + \sum_{k'} U_{h'} \, c_{k-k'} = \varepsilon \, c_k$$

Now the ionic potential $U(\vec{r})$ is periodic on the Bravais lattice, ie

$$U(\vec{r} + \vec{R}) = U(\vec{r}) \quad \text{for all } \vec{R} \text{ in BL}$$

$\Rightarrow$ the only wave vectors $\vec{k}$ that appear in its Fourier transform are the wavevectors $\{\vec{K}\}$ of the reciprocal lattice.

$$U(\vec{r} + \vec{R}) = \sum_k e^{i k \cdot (\vec{r} + \vec{R})} U_k = \sum_k e^{i \vec{k} \cdot \vec{r}} \, e^{i \vec{k} \cdot \vec{R}} U_k$$

$$U(\vec{r}) = \sum_k e^{i \vec{k} \cdot \vec{r}} U_k$$

these can be equal only if $e^{i \vec{k} \cdot \vec{R}} = 1$ for any $\vec{R}$ in BL
$\Rightarrow \vec{k}$ must be a $\vec{K}$ in the R.L.

So the sum on $\vec{k}'$ in above becomes a sum on $\vec{K}$

$$\Rightarrow \boxed{\varepsilon_k^0 \, c_k + \sum_K U_K \, c_{k-K} = \varepsilon \, c_k}$$

note: $U_K = \dfrac{1}{V} \displaystyle\int_V d^3r \; e^{-i \vec{K} \cdot \vec{r}} \, U(\vec{r})$

$$= \dfrac{1}{v} \int_C d^3r \; e^{-i \vec{K} \cdot \vec{r}} \, U(\vec{r})$$

where C is any primitive cell of the B.L. This follows from fact that $U(\vec{r})$ is periodic on the BL

$$\varepsilon_k^0 \, c_k + \sum_{K'} U_{K'} \, c_{k-K'} = \varepsilon \, c_k$$

apply the above to the wave-vector $\vec{k} - \vec{K}$

$$\varepsilon_{k-K}^0 \, c_{k-K} + \sum_{K'} U_{K'} \, c_{k-K-K'} = \varepsilon \, c_{k-K}$$

or relabeling the summation vector in the 2nd term
$$\vec{K} + \vec{K}' \to \vec{K}'$$

$$\boxed{\varepsilon_{k-K}^0 \, c_{k-K} + \sum_{K'} U_{K'-K} \, c_{k-K'} = \varepsilon \, c_{k-K}}$$

As $\vec{K}$ in the above varies through the wavevectors in the R.L. we get a set of linear equations for the Fourier coefficients $\{ c_{k-K} \}$, $\vec{K}$ in RL.

Above can be viewed as a matrix eigenvalue problem for the eigen-vector $\{ c_{k-K} \}$ (viewing $\vec{K}$ as the index of the vector, and ε as the eigenvalue.

Solution gives

$$\psi_k(\vec{r}) = \sum_K e^{i(\vec{k}-\vec{K})\cdot\vec{r}} \, c_{k-K} = e^{i\vec{k}\cdot\vec{r}} \sum_K e^{-i\vec{K}\cdot\vec{r}} \, c_{k-K}$$

Define $\quad u_k(\vec{r}) \equiv \sum_K e^{i\vec{K}\cdot\vec{r}} \, c_{k-K}$

then eigenstates have the form

$$\psi_k(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \, u_k(\vec{r})$$

where $\boxed{u_k(\vec{r}+R) = u_k(\vec{r})}$ ie $U(\vec{r})$ is periodic on the B.L.

This is __Bloch's theorem__

If we label the R.L. wavevectors as $\vec{K}_i$, the Schrödinger Eqn takes the matrix form

$$\begin{pmatrix} \mathcal{E}_k^0 & U_{K_1} & U_{K_2} & U_{K_3} & \cdots \\ U_{-K_1} & \mathcal{E}_{k-K_1}^0 & U_{K_2-K_1} & U_{K_3-K_1} & \\ U_{-K_2} & U_{K_1-K_2} & \mathcal{E}_{k-K_2}^0 & U_{K_3-K_2} & \\ U_{-K_3} & U_{K_1-K_3} & U_{K_2-K_3} & \mathcal{E}_{k-K_3}^0 & \\ \vdots & & & & \ddots \end{pmatrix} \begin{pmatrix} c_k \\ c_{k-K_1} \\ c_{k-K_2} \\ c_{k-K_3} \\ \vdots \end{pmatrix} = \mathcal{E} \begin{pmatrix} c_k \\ c_{k-K_1} \\ c_{k-K_2} \\ c_{k-K_3} \\ \vdots \end{pmatrix}$$

Note: Since $U(\vec{r})$ is a real function,

$$U_{\vec{K}}^* = \frac{1}{V} \int_V d^3r \, e^{i\vec{K}\cdot\vec{r}} \, U(\vec{r}) = U_{-K}$$

Hence the above matrix is __Hermitian__ as it should be to guarantee it is diagonalizable with real eigenvalues

Also: If the ~~crystal~~ crystal has inversion symmetry, ie $U(\vec{r}) = U(-\vec{r})$

then $U_K = \frac{1}{V} \int_V d^3r \, e^{-i\vec{K}\cdot\vec{r}} \, U(\vec{r}) = \frac{1}{V} \int d^3r \, e^{-i\vec{K}\cdot\vec{r}} \, U(-\vec{r})$

$$= \frac{1}{V} \int d^3r \, e^{i\vec{K}\cdot\vec{r}} \, U(\vec{r}) = U_{-K} = U_K^* \text{ is real}$$

Also, we can assume $U_{K=0} = 0$ due to charge neutrality, since

$$U(\vec{r}) = \int d^3r' \frac{\rho(r')}{|\vec{r} - \vec{r}'|}$$

$\rho(\vec{r})$ is total charge density from all ions and electrons

$$U_{K=0} = \frac{1}{V} \int d^3r' \, \rho(r') \underbrace{\int d^3r \frac{1}{|\vec{r} - \vec{r}'|}}$$

independent of $\vec{r}'$ if using periodic boundary conditions

$$\propto \int d^3r' \rho(\vec{r}') = 0 \qquad \text{if charge neutral}$$

Thus we see that the periodic ionic potential $U(\vec{r})$ only couples wavevectors $\vec{k}$ to the wave vectors $\vec{k}' = \vec{k} - \vec{K}$, with $\vec{K}$ in the RL. These $\vec{k}'$ are just the wave vectors one gets from scattering of the electron off the Bragg planes.

Note: If we let $\vec{k} \rightarrow \vec{k} + \vec{K}_0$ in the above matrix equation, the only result is a permutation of the rows and columns since the set
$$\{\vec{k} + \vec{K}\} = \{\vec{k} + \vec{K}_0 + \vec{K}\}$$
since $\vec{K}_0 + \vec{K}$ is vector in the R.L. if both $\vec{K}_0$ and $\vec{K}$ are.

Hence the eigenvectors and eigenvalues are periodic functions of wavevector with periodicity given by the R.L. That is, if

$$\psi_{k,n}(\vec{r}) = \sum_K e^{i(\vec{k} - \vec{K}) \cdot \vec{r}} \, c_{k-K} \quad \text{with eigenvalue } \varepsilon_n(\vec{k})$$

is the nth eigenvector and eigenvalue of the matrix then ~~then~~

$$\psi_{k+K,n}(\vec{r}) = \psi_{k,n}(\vec{r}) \left. \right\} \text{periodic in}$$
$$\varepsilon_n(\vec{k} + \vec{K}) = \varepsilon_n(\vec{k}) \left. \right\} \begin{array}{l} \vec{k} \rightarrow \vec{k} + \vec{K} \\ \text{for any } \vec{K} \text{ in R.L.} \end{array}$$

Therefore the unique states are specified by a wave vector $\vec{q}$ in the 1st BZ (called the "crystal momentum") and the discrete "band index" n that labels the different eigenvalues of the above matrix for a given value of $\vec{q}$.

(all other $\vec{k}$ values can always be written as $\vec{k} = \vec{q} + \vec{K}$ where $\vec{q}$ is in 1st BZ and $\vec{K}$ is in R.L.)