We found that the electronic eigen-energies for a weak periodic potential in the case of non-degenerate energies is

$$\varepsilon = \varepsilon^0_{k-K_1} + \sum_{K} \frac{|U_{K-K_1}|^2}{\varepsilon^0_{k-K_1} - \varepsilon^0_{k-K}} + O(U^3) \Bigg\} \text{ non degenerate}$$

Now, we consider the degenerate case

Case 2: degenerate

Consider fixed $\vec{k}$ but a set of reciprocal lattice vectors $K_1, K_2, \ldots K_m$ (m such vectors) in which the free-electron energies are close (to within U) of each other

$$\varepsilon^0_{k-K_1} \simeq \varepsilon^0_{k-K_2} \simeq \varepsilon^0_{k-K_3} \simeq \ldots \simeq \varepsilon^0_{k-K_m}$$

(within U of each other)

and

$\{\varepsilon^0_{k-K_i}\}$ are far away from other ε^0_{k-K} (compared to U)

$$\Rightarrow \quad \left|\varepsilon^0_{k-K} - \varepsilon^0_{k-K_i}\right| \gg U \quad , \quad i = 1, \ldots, m$$

$\Rightarrow$ treat separately the eigen equations for ε's and c's when K is set equal to $K_1, \ldots K_m$

→ Separate out terms involving coefficients C_{k-K_j}, $j = 1, \ldots, m$

Eigenequation

$$\left(\mathcal{E}^{\circ}_{k-K} - \mathcal{E}\right) C_{k-K} + \sum_{K'} U_{K'-K} C_{k-K'} = 0$$

so for each K_i, $i = 1, \ldots, m$

$$\Rightarrow \underbrace{\left(\mathcal{E} - \mathcal{E}^{\circ}_{k-K_i}\right) C_{k-K_i}}_{\substack{\text{LHS for the} \\ i^{th}\ K = K_i \\ \text{(m such equations)}}} = \underbrace{\overbrace{\sum_{j=1}^{m} U_{K_j - K_i} C_{k-K_j}}^{\text{this term was 0 in the non-degenerate case !}}}_{\substack{\text{terms involving} \\ \text{eigenvectors} \\ K_1, \ldots, K_m}} + \underbrace{\sum_{K \neq K_1 \ldots K_m} U_{K-K_i} C_{k-K}}_{\substack{\text{all other} \\ \text{terms} \\ \text{(using K for} \\ \text{sum variable)}}}$$

Next, find general expression for C_{k-K}

→ just take the above equation, letting $K_i = K$

$$\Rightarrow \quad C_{k-K} = \frac{1}{\left(\mathcal{E} - \mathcal{E}^{\circ}_{k-K}\right)} \left[\sum_{j=1}^{m} U_{K_j - K} C_{k-K_j} + \sum_{K' \neq K_1 \ldots K_m} U_{K'-K} C_{k-K'} \right]$$

(using K' for sum variable)

substitute this into above equation

$$\Rightarrow \left(\mathcal{E} - \mathcal{E}^{\circ}_{k-K_i}\right) C_{k-K_i} = \left.\sum_{j=1}^{m} U_{K_j - K_i} C_{k-K_j} \right\} \text{order of } U = O(U)$$

$$+ \underbrace{\sum_{j=1}^{m} \left(\sum_{K \neq K_1 \ldots K_m} \frac{U_{K-K_i} U_{K_j - K}}{\left(\mathcal{E} - \mathcal{E}^{\circ}_{k-K}\right)} \right) C_{k-K_j}}_{O(U^2)} + O(U^3)$$

(this term did not exist for non-degen case)

To leading order then, we get:

$$\underbrace{\left(\mathcal{E} - \mathcal{E}^{\circ}_{k-K_i}\right) c_{k-K_i} = \sum_{j=1}^{m} U_{K_j - K_i} c_{k-K_j}}_{\uparrow} \quad , \quad i = 1 \dots m$$

set of m coupled equations for

and $c_{k-K_1}, \dots \dots c_{k-K_m}$ & $\mathcal{E}$

we have m equations and $m+1$ unknowns

$\Rightarrow$ 2 possible solutions (we will find them)

Take now the simplest (and most important) example of 2 degenerate levels

$$\left| \mathcal{E}^{\circ}_{k-K_1} - \mathcal{E}^{\circ}_{k-K_2} \right| < U$$

but $\left| \mathcal{E}^{\circ}_{k-K_i} - \mathcal{E}^{\circ}_{k-K} \right| \gg U \qquad i = 1, 2 \;, \; K \neq K_1, K_2$

$\Rightarrow$ 2 equations:

$$\left(\mathcal{E} - \mathcal{E}^{\circ}_{k-K_1}\right) c_{k-K_1} = U_{K_1-K_1} c_{k-K_1} + U_{K_2-K_1} c_{k-K_2}$$

$$\left(\mathcal{E} - \mathcal{E}^{\circ}_{k-K_2}\right) c_{k-K_2} = U_{K_1-K_2} c_{k-K_1} + U_{K_2-K_2} c_{k-K_2}$$

but $U_{K_1-K_1} = U_{K_2-K_2} = U_0 = 0$

$$\Rightarrow \left[\begin{array}{l} (\varepsilon - \varepsilon^0_{h-K_1})\, C_{h-K_1} = U_{K_2-K_1}\, C_{k-K_2} \\ (\varepsilon - \varepsilon^0_{h-K_2})\, C_{h-K_2} = U_{K_1-K_2}\, C_{k-K_1} \end{array}\right]$$

2 coupled equations

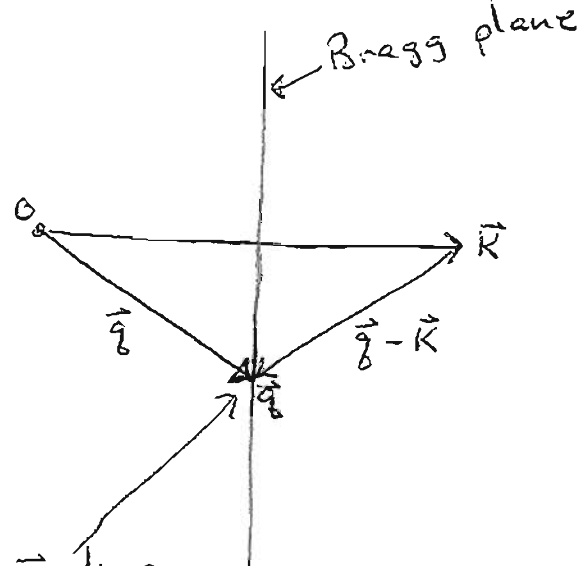
some simplification by setting

$$q = h - K_1 \qquad q - K = h - K_2$$
$$K = K_2 - K_1$$

$$\Rightarrow \left[\begin{array}{l} (\varepsilon - \varepsilon^0_q)\, C_q = U_K\, C_{q-K} \\ (\varepsilon - \varepsilon^0_{q-K})\, C_{q-K} = U_{-K}\, C_q = U_K^*\, C_q \end{array}\right]$$

since $\varepsilon_q \approx \varepsilon_{q-K}$

$$\Rightarrow |q| = |q - K|$$



point $\vec{q}$ lies
on the Bragg plane determined by $\vec{K}$

$\Rightarrow$ condition of 2 degenerate levels applies to an electron whose wave vector satisfies condition for Bragg scattering

$\Rightarrow$ Conclusion: a weak periodic potential has its major effects on only those free electron levels whose wave vectors are close to ones at which Bragg reflections can occur

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system of equations is:

$$(\mathcal{E} - \mathcal{E}^{\circ}_{q})\, C_q + (-U_K)\, C_{q-K} = 0$$

$$(-U^{*}_{K})\, C_q + (\mathcal{E} - \mathcal{E}^{\circ}_{q-K})\, C_{q-K} = 0$$

$\Rightarrow$ solution when determinant $= 0$

$$\begin{vmatrix} \mathcal{E} - \mathcal{E}^{\circ}_{q} & -U_K \\ -U^{*}_{K} & \mathcal{E} - \mathcal{E}^{\circ}_{q-K} \end{vmatrix} = 0$$

$$\Rightarrow \quad (\mathcal{E} - \mathcal{E}^{\circ}_{q})(\mathcal{E} - \mathcal{E}^{\circ}_{q-K}) = |U_K|^2$$

This equation has $\underline{2}$ roots:

$$\mathcal{E} = \tfrac{1}{2}\left(\mathcal{E}^{\circ}_{q} + \mathcal{E}^{\circ}_{q-K}\right) \mp \left[\left(\frac{\mathcal{E}^{\circ}_{q} - \mathcal{E}^{\circ}_{q-K}}{2}\right)^2 + |U_K|^2\right]$$

Consider now $\varepsilon^0_q \simeq \varepsilon^0_{q-K}$

$$\Rightarrow \quad \varepsilon = \varepsilon^0_q \pm |U_K| \quad , \ \vec{q} \text{ on a single Bragg plane}$$

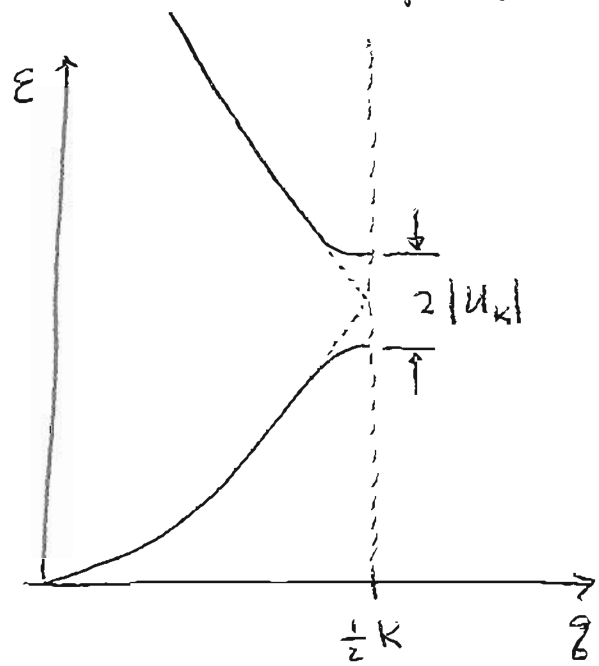
also, can show that:

$$\frac{\partial \varepsilon}{\partial q} = \frac{\hbar^2}{m}\left(\vec{q} - \tfrac{1}{2}\vec{K}\right)$$

which is parallel to the Bragg plane

$\Rightarrow$ $\vec{\nabla}_q \varepsilon_n(\vec{k})$ in Bragg plane

$\Rightarrow$ constant-energy surface is $\perp$ to Bragg plane



Next, find relationship between the c's by plugging back into the 2 equations (either one will do)

$$\varepsilon = \varepsilon^0_q \pm |U_K|$$

$$\Rightarrow \quad \pm |U_K| \, c_q = U_K \, c_{q-K} \quad \Rightarrow \quad c_q = \pm \frac{U_K}{|U_K|} c_{q-K}$$

$$\text{and} \quad \pm |U_K| \, c_{q-K} = U_K \, c_q \quad \Rightarrow \quad c_q = \pm \frac{|U_K|}{U_K} c_{q-K}$$

or $\boxed{c_q = \pm \, \mathrm{sgn}(U_K) \, c_{q-K}}$

With this, we can now look at the wavefunction solutions

$$\psi_k(r) = \sum_K C_{k-K}\, e^{i(k-K)\cdot r} \qquad q = k - K_1$$

$$q - K = k - K_2$$

$$C_q = \pm\, \mathrm{sgn}(U_K)\, C_{q-K}$$

$$\psi_k(\vec r) = C_q e^{iq\cdot r} + C_{q-K} e^{i(q-K)\cdot r}$$

(+) case (and $U_K > 0$) $\rightarrow \left(C_q = C_{q-K} \right)$

$$\Rightarrow \quad \psi_k(\vec r) = C_q e^{iq\cdot r} + C_q e^{i(q-K)\cdot r}$$

$$|\psi(\vec r)|^2 = \psi\psi^* = \left(C_q e^{iq\cdot r} + C_q e^{i(q-K)\cdot r} \right)\left(C_q e^{-iq\cdot r} + C_q e^{-i(q-K)\cdot r} \right)$$

$$= C_q^2 \left[1 + 1 + e^{iK\cdot r} + e^{-iK\cdot r} \right]$$

$$= C_q^2 \left[1 + 1 + 2\cos K\cdot r \right]$$

$$= 2C_q^2 \left[1 + \cos K\cdot r \right]$$

$$\left(\text{but } \cos\frac{u}{2} = \pm\sqrt{\frac{1+\cos u}{2}} \right)$$

$$\Rightarrow \quad |\psi(\vec r)|^2 = 4C_q^2\left[\frac{1+\cos K\cdot r}{2}\right]$$

$$\boxed{|\psi(\vec r)|^2 = 4C_q^2\cos^2\frac{K\cdot r}{2}} \qquad \mathcal{E} = \mathcal{E}_q^0 + |U_K|$$

"s-like"

"piles up at the ions"

$(C_q = -C_{q-K})$

<u>(−) case (and $U_K > 0$)</u>

$$\psi_k(\vec r) = C_q e^{iq\cdot r} - C_q e^{i(q-K)\cdot r}$$

$$|\psi_k(\vec r)|^2 = \psi\psi^* = C_q^2\left[1 + 1 - e^{+iK\cdot r} - e^{-iK\cdot r}\right]$$

$$= C_q^2\left[2 - 2\cos K\cdot r\right]$$

$$= 4C_q^2\left[\frac{1-\cos K\cdot r}{2}\right]$$

$$\boxed{|\psi_k(\vec r)|^2 = 4C_q^2\sin^2\frac{K\cdot r}{2}} \qquad \mathcal{E} = \mathcal{E}_q^0 - |U_K|$$

"p-like"

"piles up between the ions"