Density of states

$g(\varepsilon)$ = # single electron states per unit energy, per unit volume, at energy ε

$g_n(\varepsilon)$ is density of states in band n

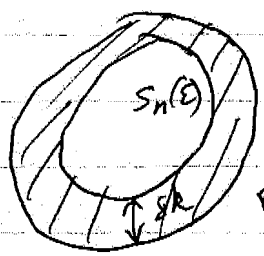
$$g(\varepsilon) = \sum_n g_n(\varepsilon)$$

$$g_n(\varepsilon) = \int_{\vec{k} \text{ in } 1^{st} BZ} \frac{d^3k}{4\pi^3}\, \delta(\varepsilon_n(\vec{k}) - \varepsilon)$$ ← includes factor of 2 for spin

Alternatively

$$g_n(\varepsilon)\, d\varepsilon = \int \frac{d^3k}{4\pi^3} \times \begin{cases} 1 & \text{if } \varepsilon \le \varepsilon_n(\vec{k}) \le \varepsilon + d\varepsilon \\ 0 & \text{otherwise} \end{cases}$$

Let $S_n(\varepsilon)$ be the surface in $\vec{k}$-space of constant energy ε, and let $\delta k(\vec{k})$ be the perpendicular distance between $S_n(\varepsilon)$ and $S_n(\varepsilon + d\varepsilon)$



← integral computes the shaded volume

$$g_n(\varepsilon)\, d\varepsilon = \int_{S_n(\varepsilon)} \frac{dS}{4\pi^3}\, \delta k(\vec{k})$$

surface area × width = volume

But we have

$$\varepsilon + d\varepsilon = \varepsilon + |\vec{\nabla}_k \varepsilon_n| \, \delta k(\vec{k})$$

since $\vec{\nabla}_k \varepsilon_n$ is normal to surface $S_n(\varepsilon)$

$$\Rightarrow d\varepsilon = |\vec{\nabla}_k \varepsilon_n| \, \delta k(\vec{k})$$

$$\Rightarrow \delta k(\vec{k}) = \frac{d\varepsilon}{|\vec{\nabla}_k \varepsilon_n|}$$

$$\boxed{g_n(\varepsilon) = \int_{S_n(\varepsilon)} \frac{dS}{4\pi^3} \frac{1}{|\vec{\nabla}_k \varepsilon_n(\vec{k})|}}$$

Since the band energies $\varepsilon_n(\vec{k})$ are periodic in $\vec{k}$ on the RL they are bounded above and below. Hence there are $\vec{k}_0$ where $\varepsilon_n(\vec{k}_0)$ is a local max or min. At such values $\vec{\nabla}_k \varepsilon_n(\vec{k})$ vanishes and the integrand in g_n diverges. One can show that these divergences are integrable in 3D, hence $g_n(\varepsilon)$ stays finite, but $\frac{dg_n}{d\varepsilon}$ will have a divergence. Such singularities are called van Hove singularities

If there is a van Hove singularity on the Fermi surface (ie at a $\vec{k}_0$ such that $\varepsilon_n(\vec{k}_0) = \varepsilon_F$) this can cause some anomalous looking behavior in quantities that depend on $\frac{dg}{d\varepsilon}$.

Energy gaps in the Weak Potential Approximation

Assume U is a weak perturbation

Consider the effect of the periodic potential U on the free electron state with wavevector $\vec{k}$ and energy ε_k^0. The potential will mix in plane waves with wavevectors $\vec{k}-\vec{K}$, for $\vec{K}$ in the R.L., and it will shift the energy eigenvalue from ε_k^0 to a new ε. For weak $U(\vec{r})$, ε is close to ε_k^0.

Schrodinger's equation for the Fourier coefficients c_k of the electron eigenstate is

$$(*) \qquad (\varepsilon - \varepsilon^0_{k-K})\, c_{k-K} = \sum_{K' \neq K} U_{K'-K}\, c_{k-K'}$$

The right hand side can be no bigger than $O(U)$ (since by normalization we will assume all $|c_{k-K}| \leq 1$).

$\Rightarrow$ The left hand side can be no bigger than $O(U)$

(1) Suppose $\vec{k}$ is <u>not</u> near any Bragg plane on an energy scale of $O(U)$, i.e. $|\varepsilon_k^0 - \varepsilon^0_{k-K}| \gg U$ for all $\vec{K}$ in the R.L.
Then it is only $(\varepsilon - \varepsilon_k^0)$ that can be small; $(\varepsilon - \varepsilon^0_{k-K})$ must be bigger than $O(U)$ for all $\vec{K} \neq 0$.

$\Rightarrow$ we must have $c_{k-K} \sim O(U)$ for all $\vec{K} \neq 0$

since we start with the free electron state at $\vec{k}$, then $c_k \sim O(1)$.

From (*) setting $\vec{K}=0$ we have

$$(\mathcal{E} - \mathcal{E}_k^0)\, c_k = \sum_{K' \neq 0} U_{K'}\, c_{k-K'}$$

but since $U_{K'} \sim O(U)$, and $c_{k-K'} \sim O(U)$, the right hand side is $O(U^2)$.

Since $c_k \sim O(1)$ we must then have

$$(\mathcal{E} - \mathcal{E}_k^0) \sim O(U^2)$$

So when $\vec{k}$ is <u>not</u> near any Bragg plane, the scattered waves mix in an amount $c_{k-K} \sim O(U)$ and the energy shifts

$$(\mathcal{E} - \mathcal{E}_k^0) \sim O(U^2)$$

The periodic potential has relatively little effect on the free electron state if U small.

(2) Now suppose that $\vec{k}$ is near the Bragg plane that bisects the R.L. vector $\vec{K}_0$, but not near any other Bragg planes, i.e.

$$|\varepsilon_k^0 - \varepsilon_{k-K_0}^0| \leq U \quad \text{but} \quad |\varepsilon_k^0 - \varepsilon_{k-K}^0| \gg U$$
$$\text{for all } \vec{K} \neq 0, \vec{K}_0$$

From (*) we can write

$\vec{K}=0$ (1) $$(\varepsilon - \varepsilon_k^0)\, c_k = U_{K_0} c_{k-K_0} + \sum_{K' \neq 0, K_0} U_{K'} c_{k-K'}$$

$\vec{K}=\vec{K}_0$ (2) $$(\varepsilon - \varepsilon_{k-K_0}^0)\, c_{k-K_0} = U_{-K_0} c_k + \sum_{K' \neq 0, K_0} U_{K'-K_0} c_{k-K'}$$

$\vec{K} \neq 0, \vec{K}_0$ (3) $$(\varepsilon - \varepsilon_{k-K}^0)\, c_{k-K} = U_{-K_0} c_k + U_{K_0-K} c_{k-K_0} + \sum_{K' \neq 0, K_0} U_{K'-K} c_{k-K'}$$

Now we can say that $(\varepsilon - \varepsilon_{k-K}^0)$ must be greater than $O(U)$ for $\vec{K} \neq 0, \vec{K}_0$ since $(\varepsilon^0 - \varepsilon_{k-K}^0)$ is greater than $O(U)$. So eqn (3) $\Rightarrow$ c_{k-K} must be no bigger than $O(U)$. So the last term on the right in all three equations above is no bigger than $O(U^2)$. Next, $c_k \sim O(1)$ since we start with a free electron of wavevector $\vec{k}$. So from (2) we must conclude that $(\varepsilon - \varepsilon_{k-K_0}^0)\, c_{k-K_0} \sim O(U)$

But $(\varepsilon - \varepsilon^{\circ}_{k-K_0})$ cannot be bigger than $O(U)$ (since the difference is due to the potential U) and c_{k-K} cannot be bigger than $O(1)$.

$\Rightarrow$ only possibility is $c_{k-K_0} \sim O(1)$ and $(\varepsilon - \varepsilon^{\circ}_{k-K_0}) \sim O(U) \Rightarrow (\varepsilon - \varepsilon^{\circ}_{k}) \sim O(U)$ also.

So when $\vec{k}$ is near the Bragg plane bisecting $\vec{K}_0$ (and not near any other Bragg planes) we have

$$c_k \sim c_{k-K_0} \sim O(1)$$
$$c_{k-K} \sim O(U) \quad \text{for all } \vec{K} \neq 0, \vec{K}_0$$
$$(\varepsilon - \varepsilon^{\circ}_{k}) \sim (\varepsilon - \varepsilon^{\circ}_{k-K_0}) \sim O(U)$$

so the energy shift is now $O(U)$ and the scattered wave c_{k-K_0} mixes equally with the original c_k.

This is quite different from case (1) where $\vec{k}$ was not near <u>any</u> Bragg plane and the energy shift was $O(U^2)$

we must ~~could~~ conclude that $(\varepsilon - \varepsilon^0_{k-K_0})\, c_{k-K_0} \sim O(U)$

But $(\varepsilon - \varepsilon^0_{k-K_0})$ should not be bigger than $O(U)$ (since the difference is due to the potential U) and c_{k-K_0} ~~should not~~ cannot be bigger than $O(1)$.

$\Rightarrow$ only possibility is $c_{k-K_0} \sim O(1)$ and $(\varepsilon - \varepsilon^0_{k-K_0}) \sim O(U)$. $\Rightarrow (\varepsilon - \varepsilon^0_k) \sim O(U)$ also.

(2) So the above three equations imply

$c_{k-K} \sim O(U)$ for $\bar{K} \neq 0, K_0$

$c_{k-K_0} \sim c_k \sim O(1)$

$(\varepsilon - \varepsilon^0_{k-K}) \sim$ large when $\bar{K} \neq 0, \bar{K}_0$

$(\varepsilon - \varepsilon^0_k), (\varepsilon - \varepsilon^0_{k-K_0}) \sim O(U)$ $\leftarrow$ compare to previous case when not near any Bragg plane – then the energy shift was $O(U^2)$.

To leading order, the above three equations reduce to two equations for c_k and c_{k-K_0}

$$\begin{cases} (\varepsilon - \varepsilon^0_k)\, c_k = U_{K_0}\, c_{k-K_0} \\ (\varepsilon - \varepsilon^0_{k-K_0})\, c_{k-K_0} = U_{-K_0}\, c_k \end{cases}$$

If $\vec{k}$ is near n Bragg planes, we wind up with $n+1$ equations for c_k, c_{k+K_1}, c_{k+K_2}, ---, c_{k+K_n}.

To leading order, the above equations (1), (2), and (3) reduce to a set of two linear equations for c_k and c_{k-K_0}

$$(\varepsilon - \varepsilon_k^0)\, c_k = U_{K_0}\, c_{k-K_0}$$

$$(\varepsilon - \varepsilon_{k-K_0}^0)\, c_{k-K_0} = U_{-K_0}\, c_k$$

[If $\vec{k}$ is near n Bragg planes - that bisect R.L. vectors $\vec{K}_1, \vec{K}_2, \ldots, \vec{K}_n$, we would wind up with $n+1$ equations for $c_k, c_{k-K_1}, c_{k-K_2}, \ldots, c_{k-K_n}$]

We can write the above pair of equations in matrix form:

$$\begin{pmatrix} \varepsilon - \varepsilon_k^0 & -U_{K_0} \\ -U_{-K_0} & \varepsilon - \varepsilon_{k-K_0}^0 \end{pmatrix} \begin{pmatrix} c_k \\ c_{k-K_0} \end{pmatrix} = 0$$

We will have a non trivial solution only when the determinant of the matrix vanishes. This condition determines the two energy eigenvalues $\varepsilon_+, \varepsilon_-$.

Note $U_{-K_0} = U_{K_0}^*$ so above matrix is Hermitian, as it must be.

$$\Rightarrow \quad (\mathcal{E} - \mathcal{E}_k^0)(\mathcal{E} - \mathcal{E}_{k-K_0}^0) = |U_{K_0}|^2$$

$$\mathcal{E}^2 - \mathcal{E}(\mathcal{E}_k^0 + \mathcal{E}_{k-K_0}^0) + \mathcal{E}_k^0 \mathcal{E}_{k-K_0}^0 - |U_{K_0}|^2 = 0$$

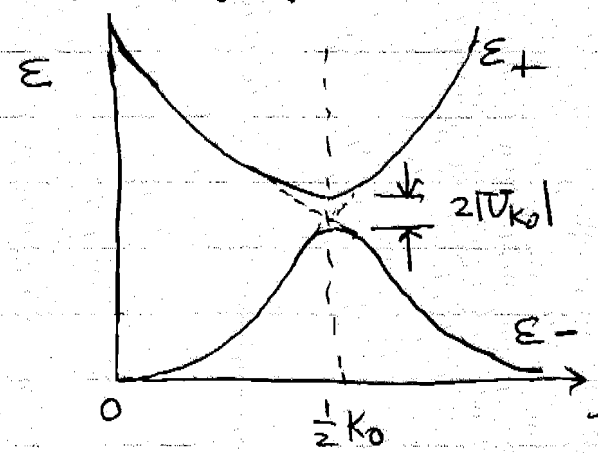
$$\mathcal{E}_\pm = \frac{\mathcal{E}_k^0 + \mathcal{E}_{k-K_0}^0}{2} \pm \sqrt{\frac{(\mathcal{E}_k^0 + \mathcal{E}_{k-K_0}^0)^2}{4} - \mathcal{E}_k^0 \mathcal{E}_{k-K_0}^0 + |U_{K_0}|^2}$$

$$(*) \quad \mathcal{E}_\pm = \frac{\mathcal{E}_k^0 + \mathcal{E}_{k-K_0}^0}{2} \pm \sqrt{\left(\frac{\mathcal{E}_k^0 - \mathcal{E}_{k-K_0}^0}{2}\right)^2 + |U_{K_0}|^2}$$

when $\vec{k}$ is exactly on a Bragg plane, $\mathcal{E}_k^0 = \mathcal{E}_{k-K_0}^0$

$$\mathcal{E}_\pm = \mathcal{E}_k^0 \pm |U_{K_0}|$$

gives jump $\Delta\mathcal{E} = \mathcal{E}_+ - \mathcal{E}_- = 2|U_{K_0}|$ at Bragg plane



energy dispersion relation from (*)

$$k_{\parallel} = \vec{k} \cdot \hat{K}_0$$

From (*) one can show that $\vec{v}_k = \frac{1}{\hbar}\frac{\partial \mathcal{E}}{\partial \vec{k}}$ has a vanishing component in the direction of $\vec{K}_0$ when $\vec{k}$ lies exactly on the Bragg plane - reasonable as $\vec{k}$ on Bragg plane $\Rightarrow$ we have a standing wave in $\hat{K}_0$ direction.

We can also consider the eigenvectors. ~~Exactly on~~ When $\vec{k}$ is exactly on a Bragg plane and $\varepsilon_\pm = \varepsilon_k^0 \pm |U_{k_0}|$ with $\varepsilon_k^0 = \varepsilon_{k+k_0}^0$ the matrix equation for the two degenerate states is:

$$\begin{pmatrix} \pm|U_{k_0}| & -U_{k_0} \\ -U_{-k_0} & \pm|U_{k_0}| \end{pmatrix} \begin{pmatrix} c_k \\ c_{k-k_0} \end{pmatrix} = 0$$

write $U_{k_0} = |U_{k_0}| e^{i\varphi}$ φ is phase of complex U_{k_0}

Above is then

$$|U_{k_0}| \begin{pmatrix} \pm 1 & -e^{i\varphi} \\ -e^{-i\varphi} & \pm 1 \end{pmatrix} \begin{pmatrix} c_k \\ c_{k-k_0} \end{pmatrix} = 0$$

$$\Rightarrow \quad \pm c_{k-k_0} = e^{-i\varphi} c_k$$

$$c_{k-k_0} = \pm e^{-i\varphi} c_k$$

so the two eigenvectors are $\sim \begin{pmatrix} 1 \\ e^{-i\varphi} \end{pmatrix}$ and $\begin{pmatrix} 1 \\ -e^{-i\varphi} \end{pmatrix} = \begin{pmatrix} c_k \\ c_{k-k_0} \end{pmatrix}$

These are orthonormal as necessary

$$\begin{pmatrix} c_k^* & c_{k-k_0}^* \end{pmatrix} \begin{pmatrix} c_k \\ c_{k-k_0} \end{pmatrix} = 1 - e^{i\varphi} e^{-i\varphi} = 0$$

and correspond to wavefunctions as we saw in our introductory discussion:

$$\psi_1 = e^{i\vec{k}\cdot\vec{r}} + e^{-i\varphi} e^{i(\vec{k}-\vec{k}_0)\cdot\vec{r}}$$

$$\psi_2 = e^{i\vec{k}\cdot\vec{r}} - e^{-i\varphi} e^{i(\vec{k}-\vec{k}_0)\cdot\vec{r}}$$

ψ_2 has π phase shift with respect to ψ_1

Velocity and constant energy surface at a Bragg plane

$$\vec{v}_n(\vec{k}) = \frac{1}{\hbar}\frac{\partial \varepsilon_n(\vec{k})}{\partial \vec{k}}$$

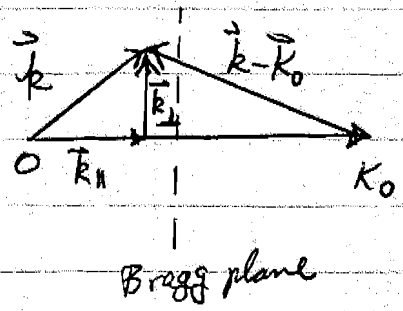
$\Rightarrow$ normal vector to a constant energy surface, $\varepsilon_n(\vec{k}) = \varepsilon_0$ constant, points in direction of $\vec{v}_n(\vec{k})$.

In the weak potential approximation for $\vec{k}$ near a Bragg plane bisecting R.L. vector $\vec{K}_0$ we had

$$\varepsilon_\pm = \frac{\varepsilon^0_k + \varepsilon^0_{k-K_0}}{2} \pm \sqrt{\left(\frac{\varepsilon^0_k - \varepsilon^0_{k-K_0}}{2}\right)^2 + |U_{K_0}|^2}$$

Write $\vec{k} = \vec{k}_\parallel + \vec{k}_\perp$, $\vec{k} - \vec{K}_0 = \vec{k}_\parallel - \vec{K}_0 + \vec{k}_\perp$

with $\vec{k}_\parallel$ the component of $\vec{k}$ parallel to $\vec{K}_0$



We can then write $\varepsilon_\pm$ as functions of $k_\parallel$ and $k_\perp$

$$\varepsilon_\pm = \frac{\hbar^2}{2m}\frac{(k_\parallel^2 + k_\perp^2) + (k_\parallel^2 + K_0^2 - 2k_\parallel K_0 + k_\perp^2)}{2}$$

$$\pm\sqrt{\left(\frac{\hbar^2}{2m}\right)^2\left(\frac{K_0^2 - 2k_\parallel K_0}{2}\right)^2 + |U_{K_0}|^2}$$

one can then show that

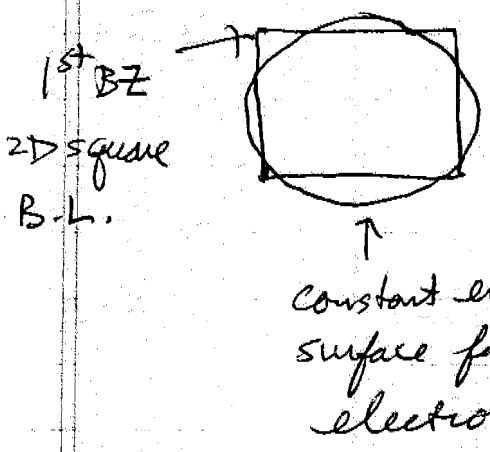
$\frac{\partial \mathcal{E}_\pm}{\partial k_\parallel} \to 0$ as $k_\parallel \to \frac{K_0}{2}$, ie when $\vec{k}$ lies exactly on the Bragg plane.

$$\frac{\partial \mathcal{E}_\pm}{\partial k_\parallel} = \frac{\hbar^2}{2m}(2k_\parallel - K_0) \pm \frac{\frac{1}{2}\left(\frac{\hbar^2}{2m}\right)^2 (K_0^2 - 2k_\parallel K_0)(-2k_\parallel)}{\sqrt{\left(\frac{\hbar^2}{2m}\right)^2 \left(\frac{K_0^2 - 2k_\parallel K_0}{2}\right)^2 + |U_{K_0}|^2}}$$

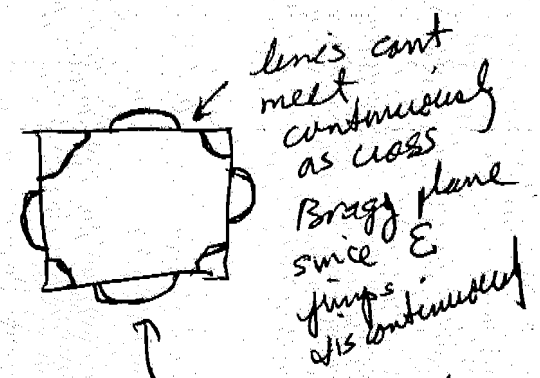
$= 0$ when $k_\parallel = \frac{K_0}{2}$

$\Rightarrow$ velocity of electron exactly at Bragg plane is always in a direction lying within the Bragg plane — the component of $\vec{v}_n(k)$ parallel to $\vec{K}_0$, ie perpendicular to the Bragg plane, vanishes

$\Rightarrow$ constant energy surface must intersect Bragg plane perpendicularly



becomes



* These results are only for the weak potential approx