Electrons in Solid

"When I started to think about it, I felt that the main problem was to explain how the electrons could sneak by all the ions in a metal…"

-Felix Bloch

<u>References</u>:

1) The Oxford Solid State Basics
   By Steven H. Simon

2) Solid State Physics –
   By N. W. Ashcroft and N. D. Mermin

3) Band Theory and Electronic Properties of Solids
   J. Singleton

Nearly-free electrons in a Periodic Potential

For a completely free electron, the Hamiltonian is - $H_0 = \dfrac{\mathbf{p}^2}{2m}$

The corresponding eigenstates - $|\mathbf{k}\rangle$

The corresponding eigen-Energies are - $\epsilon_0(\mathbf{k}) = \dfrac{\hbar^2|\mathbf{k}|^2}{2m}$

Now, consider a weak periodic potential perturbation

$$H = H_0 + V(\mathbf{r})$$

which satisfies for any lattice vector **R** -

$$V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R})$$

Energy – Using Perturbation Theory

At first order in the perturbation V

$$\epsilon(\mathbf{k}) = \epsilon_0(\mathbf{k}) + \langle \mathbf{k} | V | \mathbf{k} \rangle$$

Nearly-free electrons in a Periodic Potential

The matrix elements of this potential are - $\langle \mathbf{k}' | V | \mathbf{k} \rangle$

$$\langle \mathbf{k}' | V | \mathbf{k} \rangle = \frac{1}{L^3} \int \mathbf{dr}\, e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}\ V(\mathbf{r}) \equiv V_{\mathbf{k}'-\mathbf{k}}$$

We had seen earlier -

Fourier Transform of a Periodic Function

$$\mathcal{F}[\rho(\mathbf{r})] = \int \mathbf{dr}\ e^{i\mathbf{k}\cdot\mathbf{r}} \rho(\mathbf{r})$$

$$\mathcal{F}[\rho(\mathbf{r})] = (2\pi)^D \sum_{\mathbf{G}} \delta^D(\mathbf{k}-\mathbf{G}) S(\mathbf{k})$$

Nearly-free electrons in a Periodic Potential

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$$\langle \mathbf{k}' | V | \mathbf{k} \rangle = \frac{1}{L^3} \int \mathbf{dr}\, e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}\; V(\mathbf{r}) \equiv V_{\mathbf{k}'-\mathbf{k}}$$

The above expression is <u>zero unless **(*k*-*k*')** is a reciprocal lattice vector</u>

Any plane wave state k can scatter into another plane wave state k' only if these two plane waves are separated by a reciprocal lattice vector

Energy – Using Perturbation Theory

At first order in the perturbation V

$$\epsilon(\mathbf{k}) = \epsilon_0(\mathbf{k}) + \langle \mathbf{k}|V|\mathbf{k}\rangle$$

Since $$\langle \mathbf{k}'|V|\mathbf{k}\rangle = \frac{1}{L^3}\int \mathbf{dr}\, e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}\; V(\mathbf{r}) \equiv V_{\mathbf{k}'-\mathbf{k}}$$

$$\epsilon(\mathbf{k}) = \epsilon_0(\mathbf{k}) + V_0$$

where V_0 is a constant, same for all eigenstates (can be taken as 0)

Energy – Using Perturbation Theory

At second order in the perturbation theory

$$\epsilon(\mathbf{k}) = \epsilon_0(\mathbf{k}) + V_0 + \sum_{\mathbf{k}'=\mathbf{k}+\mathbf{G}}{}' \frac{|\langle \mathbf{k}'|V|\mathbf{k}\rangle|^2}{\epsilon_0(\mathbf{k}) - \epsilon_0(\mathbf{k}')}$$

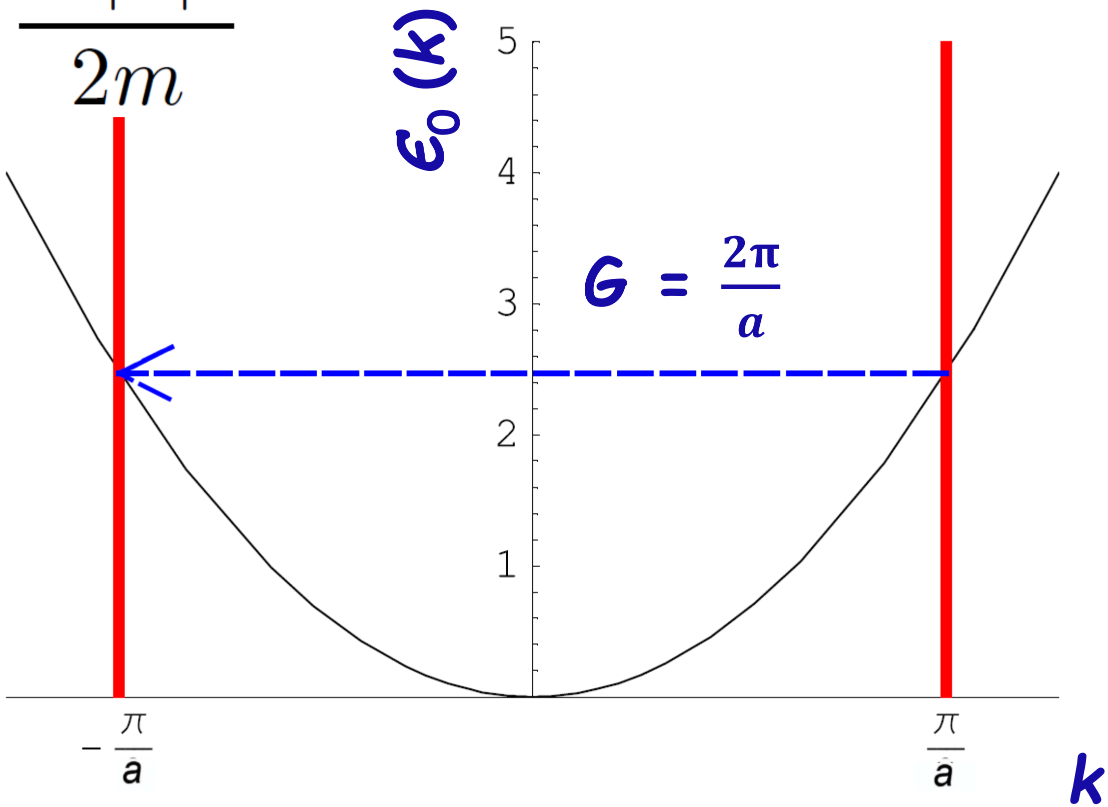
' indicates a restricted sum with $G \neq 0$

However, if for some k', $\epsilon_0(k)$ is <u>very close (or equal)</u> to $\epsilon_0(k')$, the corresponding term of the sum diverges and non-degenerate perturbation theory makes no sense then

$$\begin{aligned} \epsilon_0(\mathbf{k}) &= \epsilon_0(\mathbf{k}') \\ \mathbf{k}' &= \mathbf{k} + \mathbf{G} \end{aligned}$$

Degenerate states – Example in 1D

$$\epsilon_0(\mathbf{k}) = \frac{\hbar^2 |\mathbf{k}|^2}{2m}$$



$$k' = -k = \pi n/a$$ Happens on the Brillouin zone boundary

Even in higher dimensions, given a point ***k*** on the Brillouin zone boundary, there is another ***k'*** (also on a Brillouin zone boundary) where the energy degeneracy condition is satisfied

Degenerate perturbation theory

Two plane waves at **k** and "**k**' = **k**+***G***" have apprx. the same energy, then first matrix elements of these states should be diagonalized-

$$
\begin{aligned}
\langle \mathbf{k}| \; H \; |\mathbf{k}\rangle &= \epsilon_0(\mathbf{k}) \\
\langle \mathbf{k}'| \; H \; |\mathbf{k}'\rangle &= \epsilon_0(\mathbf{k}') = \epsilon_0(\mathbf{k}+\mathbf{G}) \\
\langle \mathbf{k}| \; H \; |\mathbf{k}'\rangle &= V_{\mathbf{k}-\mathbf{k}'} = V^*_{\mathbf{G}} \\
\langle \mathbf{k}'| \; H \; |\mathbf{k}\rangle &= V_{\mathbf{k}'-\mathbf{k}} = V_{\mathbf{G}}
\end{aligned}
$$

Since V(r) is real, $V_{-\mathbf{G}} = V^*_{\mathbf{G}}$

$$H = H_0 + V(\mathbf{r})$$

$$\langle \mathbf{k}'|V|\mathbf{k}\rangle = \frac{1}{L^3}\int \mathbf{dr}\, e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} \; V(\mathbf{r}) \equiv V_{\mathbf{k}'-\mathbf{k}}$$

Degenerate perturbation theory

Let us write the eigenfunctions as -

$$|\Psi\rangle = \alpha|\mathbf{k}\rangle + \beta|\mathbf{k}'\rangle = \alpha|\mathbf{k}\rangle + \beta|\mathbf{k}+\mathbf{G}\rangle$$

The effective Schrödinger's equation becomes -

$$\begin{pmatrix} \epsilon_0(\mathbf{k}) & V^*_{\mathbf{G}} \\ V_{\mathbf{G}} & \epsilon_0(\mathbf{k}+\mathbf{G}) \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

The secular equation determining *E* then becomes -

$$\Big(\epsilon_0(\mathbf{k}) - E\Big)\Big(\epsilon_0(\mathbf{k}+\mathbf{G}) - E\Big) - |V_{\mathbf{G}}|^2 = 0$$

Degenerate perturbation theory

The secular equation determining *E* then becomes -

$$\Bigg(\epsilon_0(\mathbf{k}) - E\Bigg)\Bigg(\epsilon_0(\mathbf{k}+\mathbf{G}) - E\Bigg) - |V_{\mathbf{G}}|^2 = 0$$

Case I – When **k** and **k'** are precisely on the Brillouin zone boundary

$$\Bigg(\epsilon_0(\mathbf{k}) - E\Bigg)^2 = |V_{\mathbf{G}}|^2$$

$$E_{\pm} = \epsilon_0(\mathbf{k}) \pm |V_{\mathbf{G}}|$$

A gap opens up at the zone-boundary. Two otherwise degenerate states, in presence of V, form two linear combinations with energies split

Lets look at the eigenfunctions in 1D

The corresponding eigenfunctions - $|\psi_\pm\rangle = \frac{1}{\sqrt{2}}\left(|k\rangle \pm |k'\rangle\right)$

Since

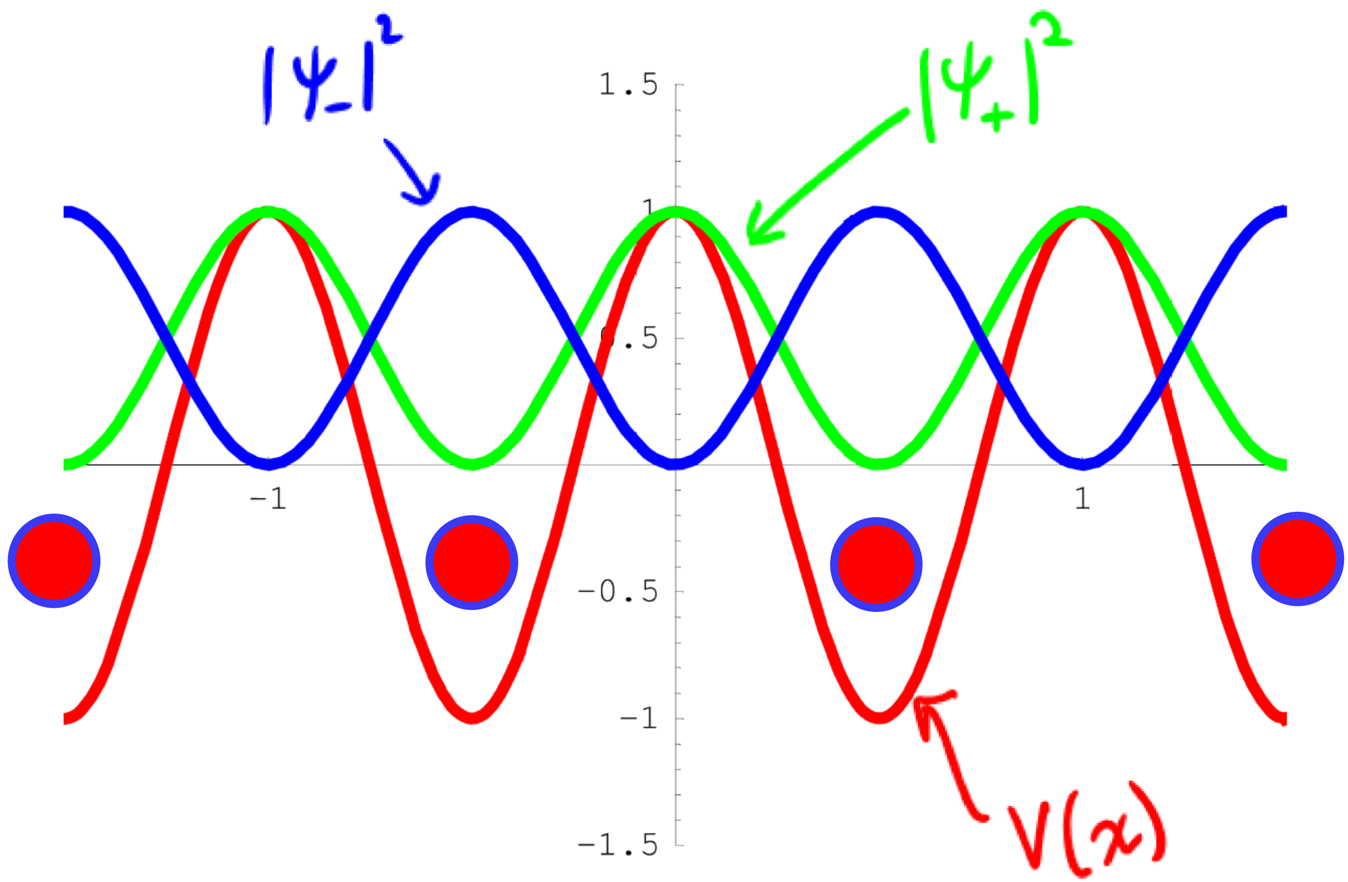
$$\begin{aligned} |k\rangle &\rightarrow e^{ikx} = e^{ix\pi/a} \\ |k'\rangle &\rightarrow e^{-ik'x} = e^{-ix\pi/a} \end{aligned}$$

$$\begin{aligned} \psi_+ &\sim e^{ix\pi/a} + e^{-ix\pi/a} &\propto \cos(x\pi/a) \\ \psi_- &\sim e^{ix\pi/a} - e^{-ix\pi/a} &\propto \sin(x\pi/a) \end{aligned}$$

Assuming a lattice periodic potential - $V(x) = \tilde{V}\cos(2\pi x/a)$

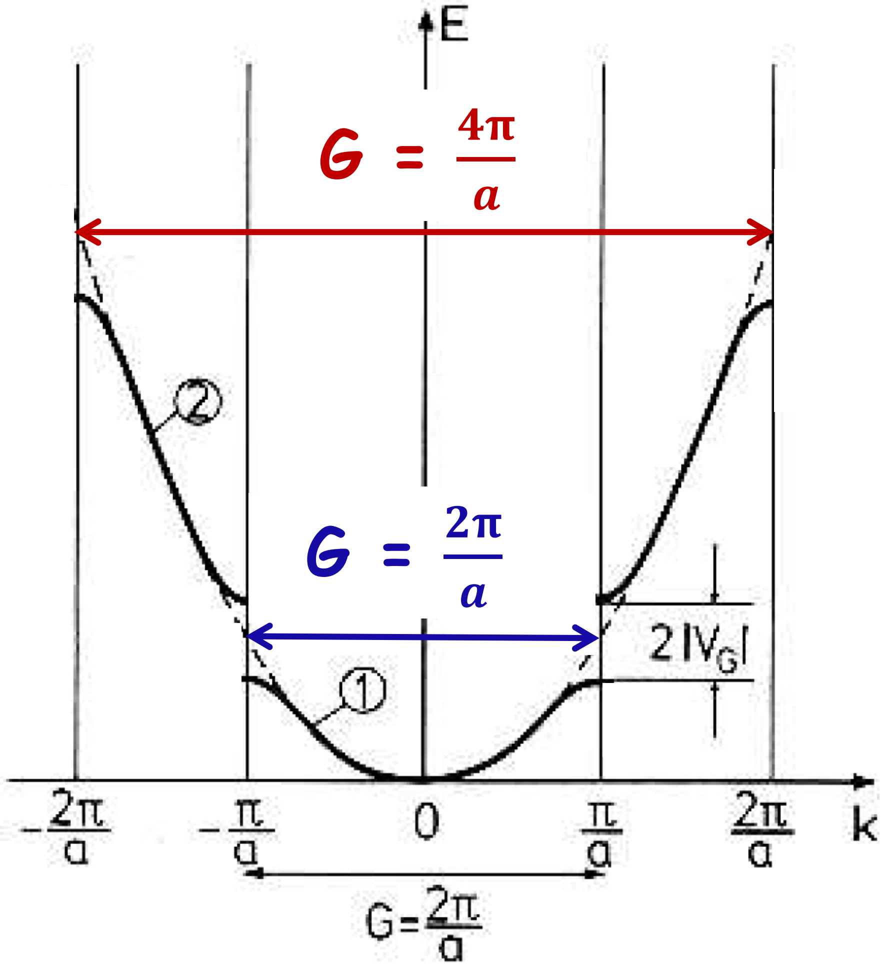
The probability densities are given by $|\psi_\pm|^2$

Distribution of densities



The corresponding energies are $E_{\pm} = \epsilon_0(\mathbf{k}) \pm |V_{\mathbf{G}}|$

Energy gaps at Brillouin zone boundaries



The corresponding energies are $E_{\pm} = \epsilon_0(\mathbf{k}) \pm |V_{\mathbf{G}}|$

At k points close to Brillouin zone boundary

The secular equation determining E is

$$\left(\epsilon_0(\mathbf{k}) - E\right)\left(\epsilon_0(\mathbf{k}+\mathbf{G}) - E\right) - |V_{\mathbf{G}}|^2 = 0$$

Let us consider a plane wave near the zone-boundary -

$$k = n\pi/a + \delta$$

Here $\boldsymbol{\delta}$ is very small and $\boldsymbol{n}$ is an integer

Due to V, this $\boldsymbol{k}$ can scatter into - $k' = -n\pi/a + \delta$

Since $k' - k = \frac{2n\pi}{a} = \boldsymbol{G}$

At *k* points close to Brillouin zone boundary

The secular equation determining *E* is

$$\left(\epsilon_0(\mathbf{k}) - E\right)\left(\epsilon_0(\mathbf{k}+\mathbf{G}) - E\right) - |V_{\mathbf{G}}|^2 = 0$$

Here $\epsilon_0(k)$ and $\epsilon_0(k+G)$ are given as

$$\begin{aligned}
\epsilon_0(n\pi/a+\delta) &= \frac{\hbar^2}{2m}\left[(n\pi/a)^2 + 2n\pi\delta/a + \delta^2\right] \\
\epsilon_0(-n\pi/a+\delta) &= \frac{\hbar^2}{2m}\left[(n\pi/a)^2 - 2n\pi\delta/a + \delta^2\right]
\end{aligned}$$

At k points close to Brillouin zone boundary

The secular equation simplifies to -

$$\left(\frac{\hbar^2}{2m}\left[(n\pi/a)^2+\delta^2\right]-E\right)^2=\left(\frac{\hbar^2}{2m}2n\pi\delta/a\right)^2+|V_G|^2$$

Solving these, the eigen-energies comes as -

$$E_{\pm}=\frac{\hbar^2}{2m}\left[(n\pi/a)^2+\delta^2\right]\pm\sqrt{\left(\frac{\hbar^2}{2m}2n\pi\delta/a\right)^2+|V_G|^2}$$

Expanding the square root for small values of δ

$$E_{\pm}=\frac{\hbar^2(n\pi/a)^2}{2m}\pm|V_G|+\frac{\hbar^2\delta^2}{2m}\left[1\pm\frac{\hbar^2(n\pi/a)^2}{m}\frac{1}{|V_G|}\right]$$

At *k* points close to Brillouin zone boundary

$$E_{\pm} = \frac{\hbar^2 (n\pi/a)^2}{2m} \pm |V_G| + \frac{\hbar^2\delta^2}{2m}\left[1 \pm \frac{\hbar^2(n\pi/a)^2}{m}\frac{1}{|V_G|}\right]$$

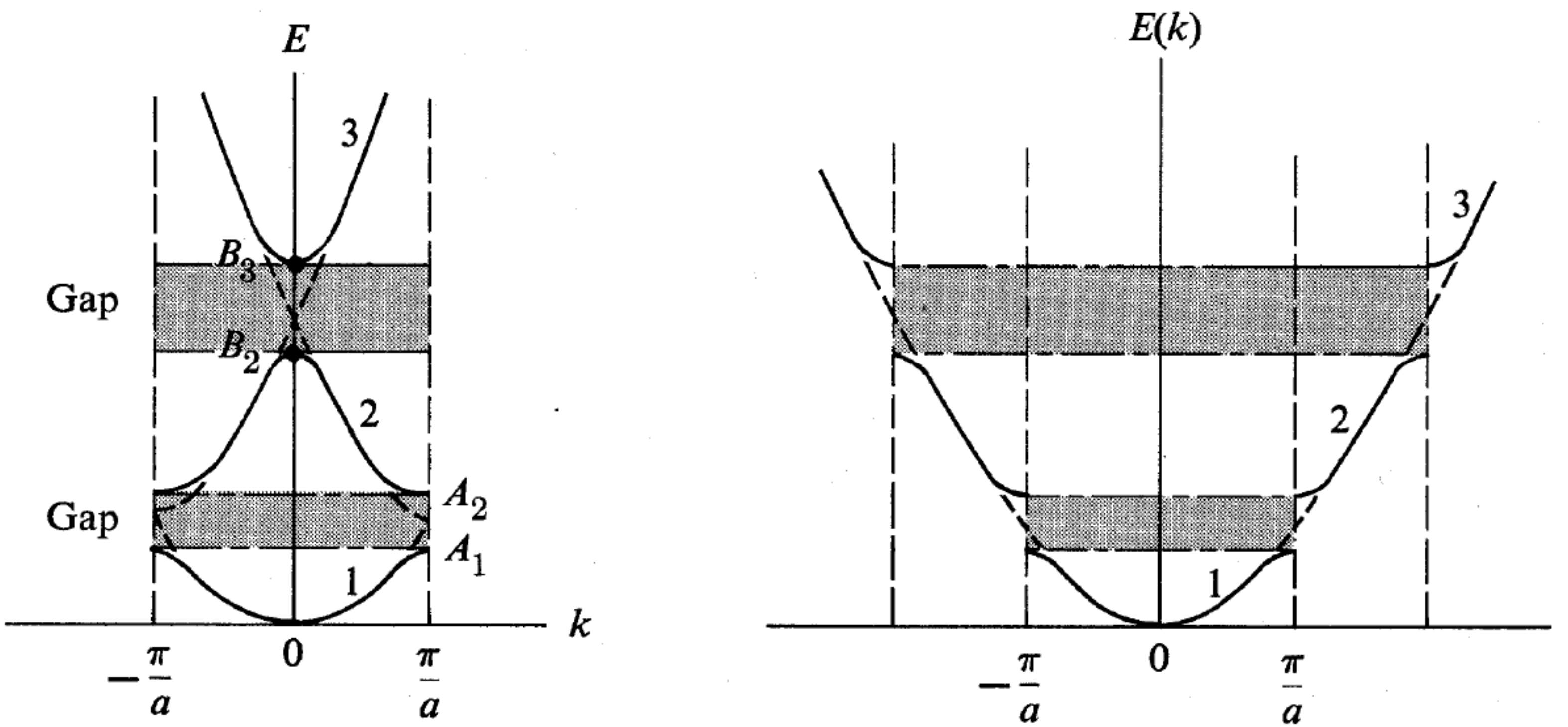
We can then write the dispersion as quadratic in ***q*** -

$$\begin{aligned} E_+(G+\delta) &= C_+ + \frac{\hbar^2\delta^2}{2m_+^*} \\ E_-(G+\delta) &= C_- - \frac{\hbar^2\delta^2}{2m_-^*} \end{aligned}$$

C_+ and C_- are constants and the effective masses are given by -

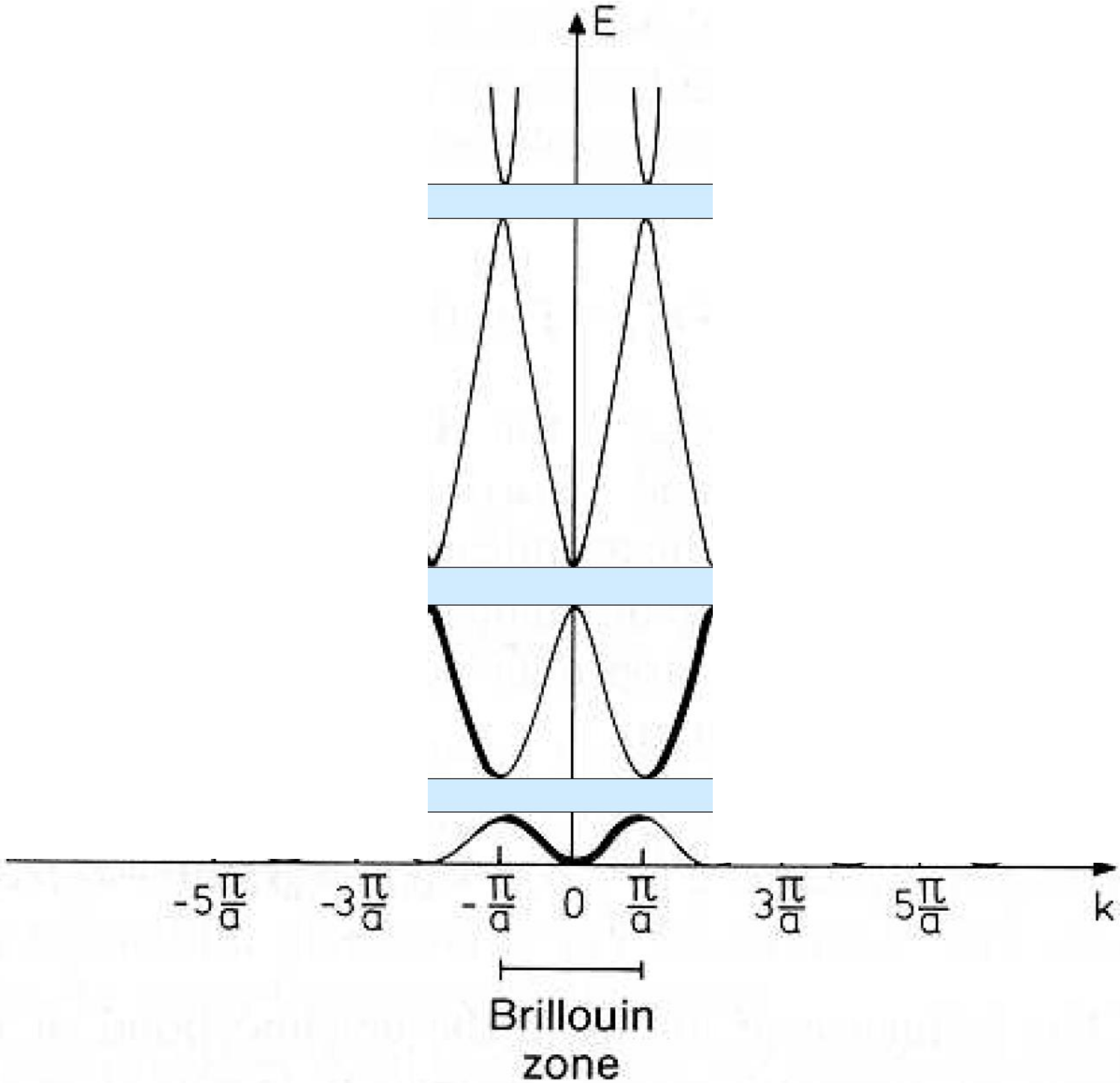
$$m_{\pm}^* = \frac{m}{\left|1 \pm \frac{\hbar^2(n\pi/a)^2}{m}\frac{1}{|V_G|}\right|}$$

Modified Band dispersions

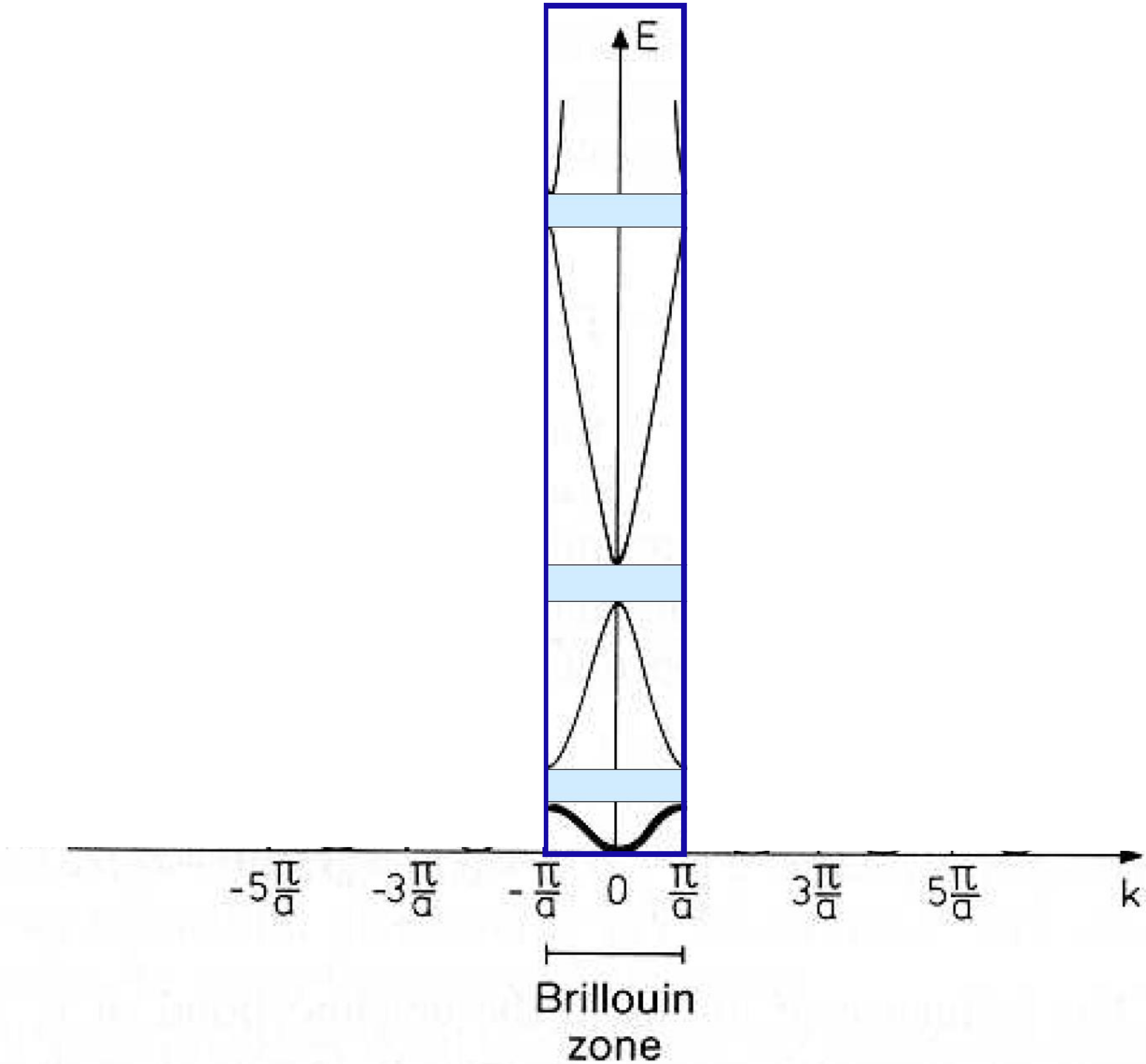


Modification of free electron's parabolic energy dispersion (hashed line) in presence of V(r) – Opening of energy gaps at BZ boundaries and quadratic dispersion around BZ boundaries

Band dispersions



Band dispersions in Reduced zone scheme



Band dispersions in Repeated zone scheme