Article

nature

Carrier-resolved photo-Hall effect

https://doi.org/10.1038/s41586-019-1632-2
Received: 2 April 2018
Accepted: 1 August 2019
Published online: 7 October 2019

Oki Gunawan[1]*, Seong Ryul Pae[2], Douglas M. Bishop[1], Yudistira Virgus[1], Jun Hong Noh[3,4], Nam Joong Jeon[3], Yun Seog Lee[1,5], Xiaoyan Shao[1], Teodor Todorov[1], David B. Mitzi[6,7] & Byungha Shin[2]*

The fundamental parameters of majority and minority charge carriers—including their type, density and mobility—govern the performance of semiconductor devices yet can be difficult to measure. Although the Hall measurement technique is currently the standard for extracting the properties of majority carriers, those of minority carriers have typically only been accessible through the application of separate

[…]

The Hall effect measurement is one of the most important characterization techniques for electronic materials, and the effect has become the basis of fundamental advances in condensed matter physics, such as the integer and fractional quantum Hall effects[4,5]. The measurements reveal fundamental information about the majority charge carrier—that is, its type (p or n), density and mobility. In a solar cell, the parameters of the majority carrier determine the overall device architecture, the width of the depletion region and the bulk series resistance. The properties of the minority carrier, however, determine other key parameters that directly affect the overall performance of the device, such as recombination lifetime (τ), diffusion length (L_D) and recombination coefficients (k_n). Unfortunately, the standard Hall measurement yields information regarding only the majority carrier. Attempts to measure the properties of both majority and minority carriers in high-performance

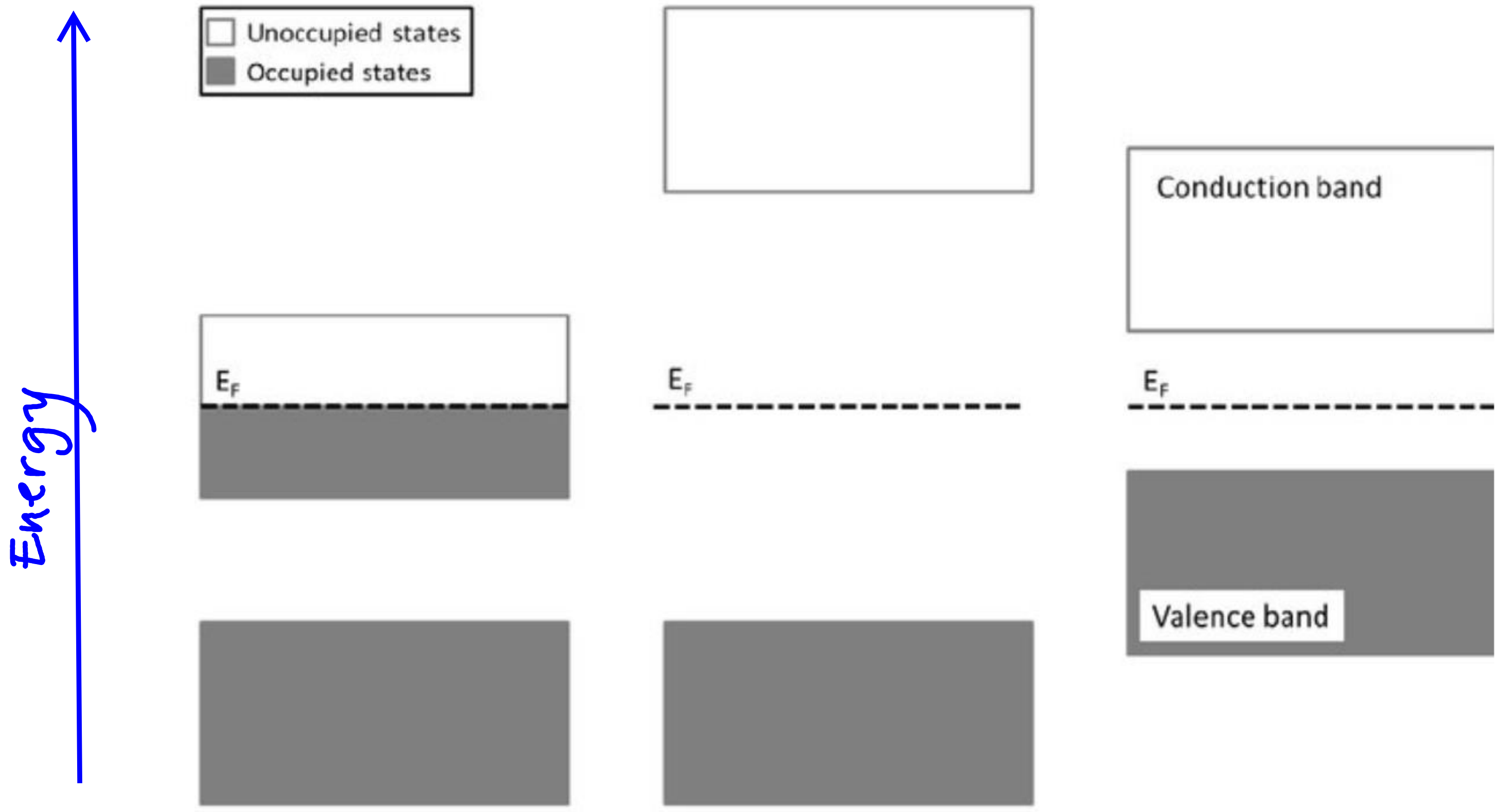
A full understanding of the charge-transport properties of perovskites will help to elucidate the operating principles of devices that contain these materials, thereby guiding their further improvement.

In this work we present a carrier-resolved photo-Hall (CRPH) measurement technique that is capable of simultaneously extracting the mobilities, densities and subsequent derivative parameters (τ, L_D) of both majority and minority carriers as a function of light intensity. This technique relies on two key elements: an equation that yields the difference between the Hall mobilities of the hole and electron, and a high-sensitivity Hall measurement using a parallel dipole line (PDL) a.c. Hall system[18] (Fig. 1a, b). In the classic Hall measurement without illumination, three parameters can be obtained for majority carriers: the type (p or n), from the sign of Hall coefficient H; the carrier density ($n_C = r/He$); and the Hall mobility ($\mu_H = \sigma H$); where e is the electron charge

Electronic Band Structure

- Kittel
- Simon
- Singleton

Goal


Energy
Unoccupied states
Occupied states
E_F
E_F
E_F
Conduction band
Valence band

Free e- model works for some physical properties
but leaves many open questions

* difference between metal / insulator / semiconductor ?

* Scattering length $l \sim v_F \cdot \tau \sim 100$ Å at RT - why do e- not scatter from nuclei?

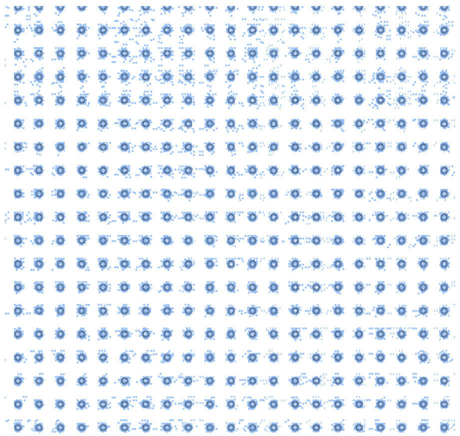
* Hall effect → why sign seems to indicate positive charges?
→ why # conduction e- is not always = # valence e-?

* Heat capacity $\frac{m^{th}}{m} = \frac{\gamma(\text{observed})}{\gamma(\text{calculated})} \neq 1$?

$C_{el} = \gamma T$

Bloch theorem

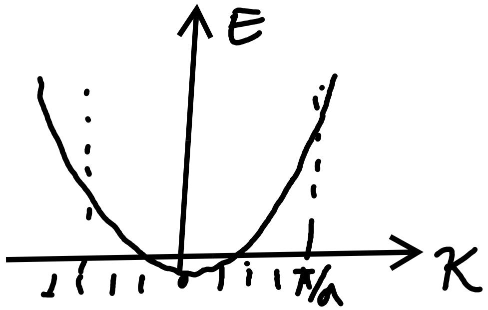
Understanding electrons in crystals

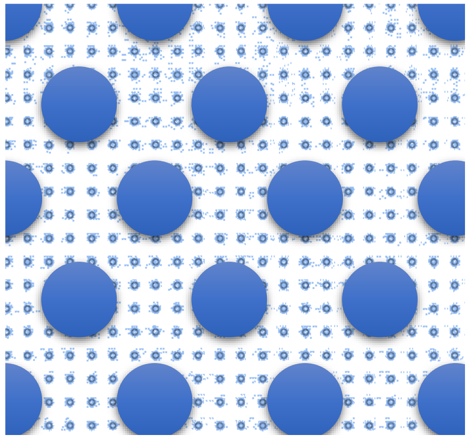


So far, Free electron model

$$E = \frac{\hbar^2 \vec{K}^2}{2m} = \frac{\hbar^2}{2m}\left(K_x^2 + K_y^2 + K_z^2\right) \quad \text{with } K_i = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L} \ldots$$

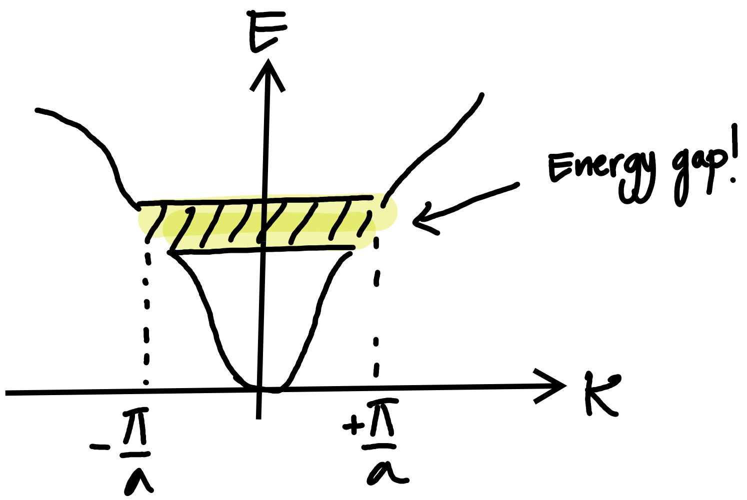
$$\psi_K = A \exp\left(i\bar{K}\cdot\bar{r}\right)$$



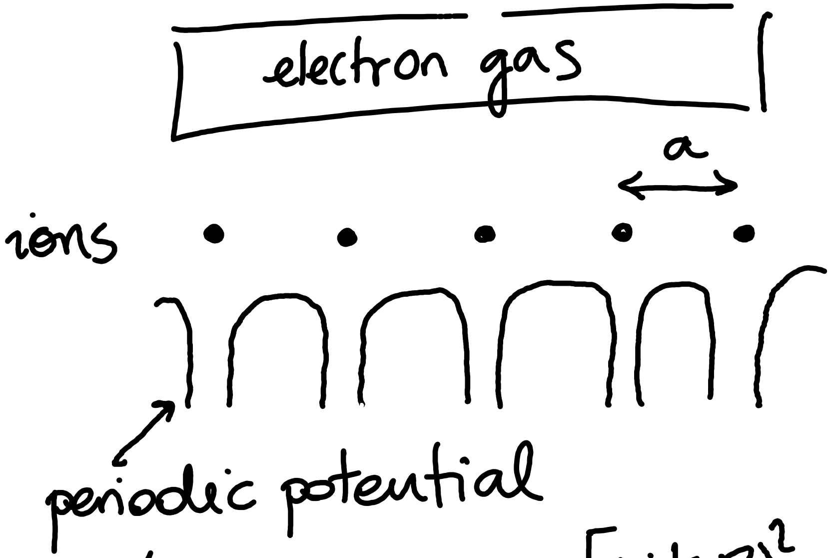


now, take into account the periodicity of the crystal

⇒ Goal: Periodic solids through Bloch's theorem
(i.e. constrain ψ (and E) for periodic solids)



Schrödinger equation



translation vector

$$\Rightarrow \quad \vec{T} = n_1\bar{a}_1 + n_2\bar{a}_2 + n_3\bar{a}_3 \qquad \left\{ \begin{array}{l} \bar{a}_i : \text{primitive lattice vectors} \\ n_i : \text{arbitrary integers} \end{array} \right.$$

$$\mathcal{H}\Psi = \left[\frac{(i\hbar\nabla)^2}{2m} + V(\bar{r})\right]\Psi = E\Psi$$

$$V(\vec{r}) = V(\vec{r}+\vec{T}) \longrightarrow \text{Fourier Series} \qquad V(\vec{r}) = \sum_{\bar{G}} V_{\bar{G}}\, e^{i\bar{G}\bar{r}}$$

R.L. vectors

Fourier coefficients

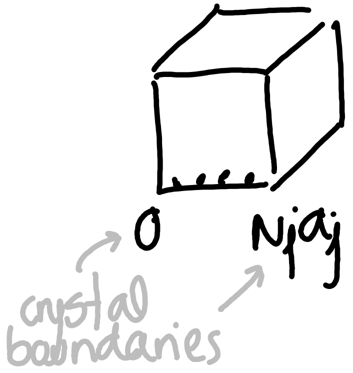
Solutions: plane waves

$$\Psi(\vec{r}) = \sum_{\vec{K}} \underbrace{c_{\bar{K}}}_{\text{unkown!!}} e^{i\bar{K}\bar{r}}$$

summation over all K permitted by periodic boundary conditions

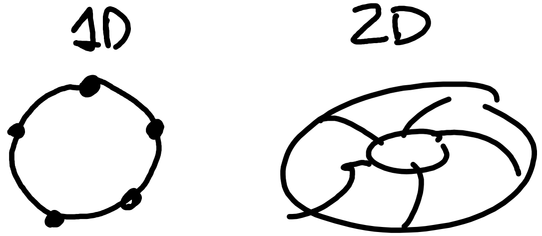
Born-von Karman conditions $\longrightarrow$ restrictions on the possible $\vec{K}$ values

(=periodic boundary conditions)



N_j : # of u.c. along direction $\vec{a}_j$ $\quad (j = 1,2,3)$

$N_1 N_2 N_3 = N = $ # of u.c in the crystal



Periodic Boundary Cond. $\Psi(\vec{r} + N_j\vec{a}_j) = \Psi(\vec{r})$

$$\Psi(\vec{r} + N_j\vec{a}_j) = \sum_{\vec{K}} c_{\vec{K}} e^{i\vec{K}(\vec{r}+N_j\vec{a}_j)} = \Psi(\vec{r}) \cdot \underbrace{e^{i\vec{K}\cdot N_j\vec{a}_j}}_{=1}$$

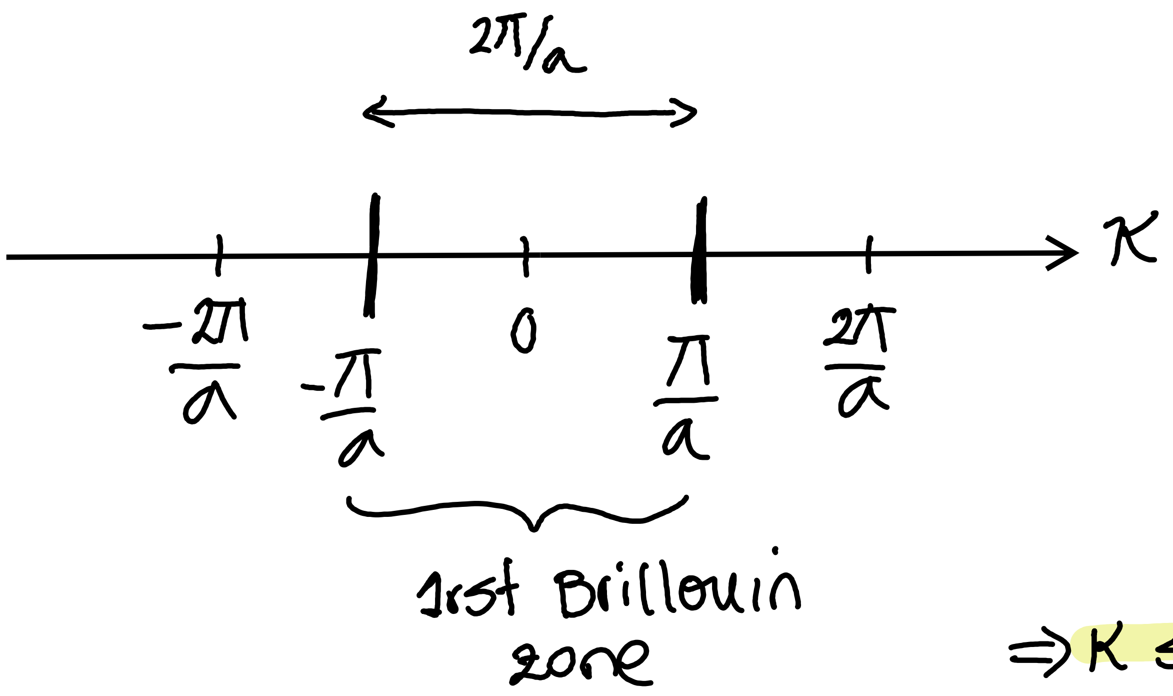
$$\boxed{\vec{K}\cdot\vec{a}_j = 2\pi \frac{m_j}{N_j}} \qquad m_j : \text{integer}$$

$\Rightarrow$ $\vec{K}$ can only take discrete values!

Periodic boundary conditions in 1D

$$\vec{K}\cdot\vec{a}_j = \frac{2\pi}{N_j} m_j \longrightarrow \text{1D: } K = \frac{2\pi}{a}\frac{m}{N} \Rightarrow \Delta K = \frac{2\pi}{a}\frac{1}{N} \quad \Big\}\ \text{distance between 2 K-values}$$

integer



Allowed # of $\vec{K}$ values within 1rst B.Z.

length 1st B.Z 1D

$$\frac{2\pi/a}{2\pi/a\ \frac{1}{N}} = N$$

space 1 K-state 1D

$\Rightarrow$ K states within 1rst B.Z

= number of u.c. (R space) in the crystal

Periodic boundary conditions in 3D

$$\vec{K} = \sum_{i=1}^{3} \frac{m_i}{N_j} \vec{b}_i$$

$\vec{b}_i$: primitive reciprocal lattice vector

$$\vec{K}\cdot\vec{a}_j = \sum_{i=1}^{3} \frac{m_i}{N_j} \vec{b}_i\cdot\vec{a}_j = 2\pi \frac{m_i}{N_j}$$

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

"Volume" occupied by a K-state

$$\Delta^3 K = \frac{1}{N_1}\vec{b}_1 \cdot \frac{1}{N_2}\vec{b}_2 \times \frac{1}{N_3}\vec{b}_3 = \frac{1}{N} \underbrace{(\vec{b}_1\cdot\vec{b}_2\times\vec{b}_3)}_{\text{volume of primitive u.c. in reciprocal space}}$$

number of $\vec{K}$-states in 1st B.Z.

= # primitive u.c. in the crystal

! this will be important to decide if a crystal is a metal, insulator

Eigenstates of Schrödinger equation in a periodic potential

$$V(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}}\, e^{i\vec{G}\vec{r}}$$

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

$$\left[\frac{(i\hbar\nabla)^2}{2m} + \sum_{G} V_G e^{i\bar{G}\bar{r}}\right]\sum_{\bar{K}} c_{\bar{K}} e^{i\bar{K}\cdot\bar{r}} = E\sum_{\bar{K}} c_{\bar{K}} e^{i\bar{K}\bar{r}}$$

$$\sum_{\bar{K}} \frac{\hbar^2 K^2}{2m} c_{\bar{K}} e^{i\bar{K}\cdot\bar{r}} + \sum_{\bar{G},\bar{K}} V_{\bar{G}} c_{\bar{K}} e^{i\underbrace{(\bar{G}+\bar{K})}_{\equiv \bar{K}'}\cdot\bar{r}} = E\sum_{K} c_K e^{i\bar{K}\bar{r}}$$

$$\sum_{\bar{K}} e^{i\bar{K}\bar{r}} \underbrace{\left\{\left(\frac{\hbar^2K^2}{2m} - E\right)c_{\bar{K}} + \sum_{\bar{G}} V_{\bar{G}} c_{\bar{K}-\bar{G}}\right\}}_{=0} = 0$$

$$\boxed{\left(\frac{\hbar^2K^2}{2m} - E\right)c_{\bar{K}} + \sum_{\bar{G}} V_{\bar{G}} c_{\bar{K}-\bar{G}} = 0}$$

CENTRAL EQUATION

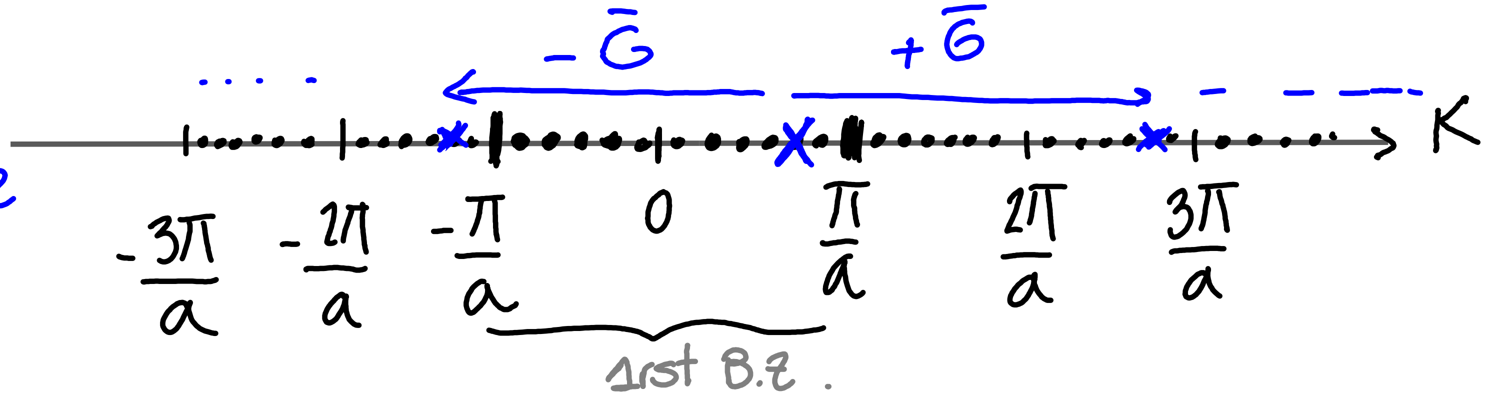
Restatement of Schrödinger equation simplified because periodic potential

$$\boxed{\left(\frac{\hbar^2 K^2}{2m} - E\right) c_{\bar{K}} + \sum_{\bar{G}} V_{\bar{G}}\, c_{\bar{K}-\bar{G}} = 0}$$

<u>Central Equation</u>

For a fix $\vec{K}$, this set of eq. couples only those wavevectors that differ from $\vec{K}$ by a R.L. vector

1D example



$N = \#$u.c. $=$ allowed values of $\bar{K}$ in the 1st B.Z.

$\Rightarrow$ Original problem decoupled in N independent problems

c_K, & all $c_{\bar{K}-\bar{G}}$ to solve for E $\Leftarrow$ each of these "problems" has solutions = superposition of plane waves containing $\vec{K}$ and wavevectors differing by $\bar{K}$ by a reciprocal lattice vector $\bar{G}$

Let's deal with solutions within 1rst B.Z:

$\vec{K} = \vec{q} - \vec{G}'$ $\begin{cases} \bar{q}: \text{ vector within 1rst B.Z} \\ \bar{G}: \text{ R.L. vector} \end{cases}$

$$\left(\frac{\hbar^2(\bar{q}-\bar{G}')^2}{2m} - E\right) c_{q-G'} + \sum_{\bar{G}} V_{\bar{G}}\, c_{q-G'-G} = 0 \qquad G+G' \equiv G''$$

$$\left(\frac{\hbar^2(q-G')^2}{2m} - E\right) c_{\bar{q}-\bar{G}'} + \sum_{\bar{G}''} V_{\bar{G}''-G'}\, c_{\bar{q}-G''} = 0 \qquad \begin{matrix} \vec{G}' \longrightarrow \vec{G} \\ \bar{G}'' \longrightarrow \bar{G}' \end{matrix}$$

$$\boxed{\left(\frac{\hbar^2(\bar{q}-\bar{G})^2}{2m} - E\right) c_{\bar{q}-\bar{G}} + \sum_{\bar{G}'} V_{\bar{G}'-\bar{G}}\, c_{\bar{q}-\bar{G}'} = 0}$$

$$\Rightarrow \psi_q(\vec{r}) = \sum_{\bar{G}} c_{\bar{q}-\bar{G}}\, e^{i(\bar{q}-\bar{G})\cdot\bar{r}} = \underbrace{e^{i\bar{q}\bar{r}}}_{\text{plane wave}} \underbrace{\sum_{\bar{G}} c_{q-G}\, e^{i\bar{G}\vec{r}}}_{u_q(\bar{r})}$$

Function which has the periodicity of the lattice.

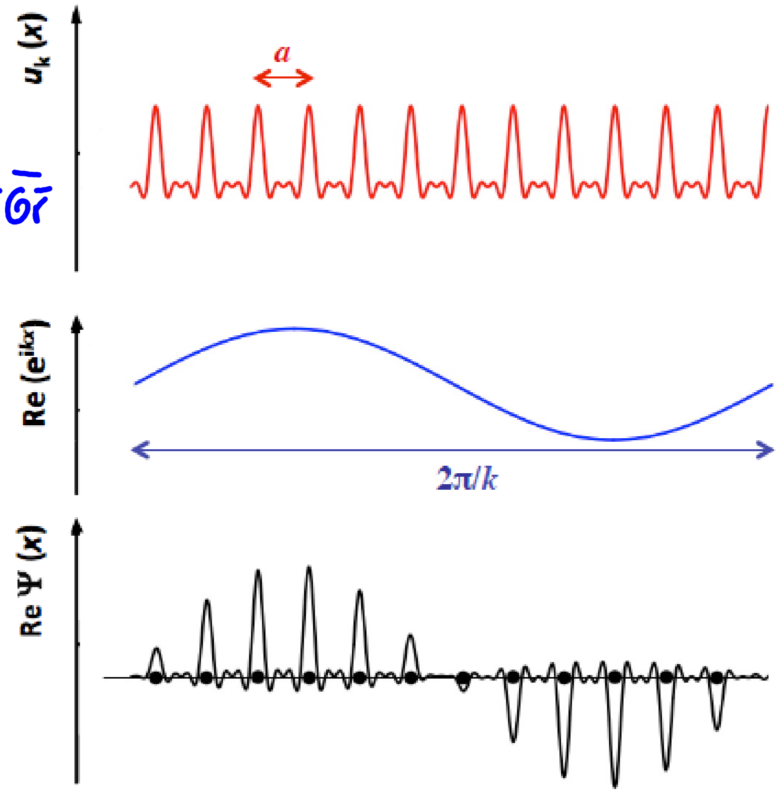
Bloch's theorem

It plays a very important role in electronic band structure theory.

The eigenstates ψ of a one-electron Hamiltonian $H = {}^{\hbar^2\nabla^2}/_{2m} + V(\vec{r})$, where $V(\vec{r}+\vec{T}) = V(\vec{r})$ for all Bravais lattice translation vector $\vec{T}$, can be chosen to be a planar wave times a function with the periodicity of the Bravais lattice.

$$\psi_q(\vec{r}) = \underbrace{e^{i\vec{q}\vec{r}}}_{\text{plane wave}}\underbrace{u_{\vec{q}}(\vec{r})}_{\text{periodic function}}$$

$$u_q(\vec{r}) = \sum_G C_{q-G}\, e^{-i\vec{G}\vec{r}}$$



Equivalent form of Bloch theorem.

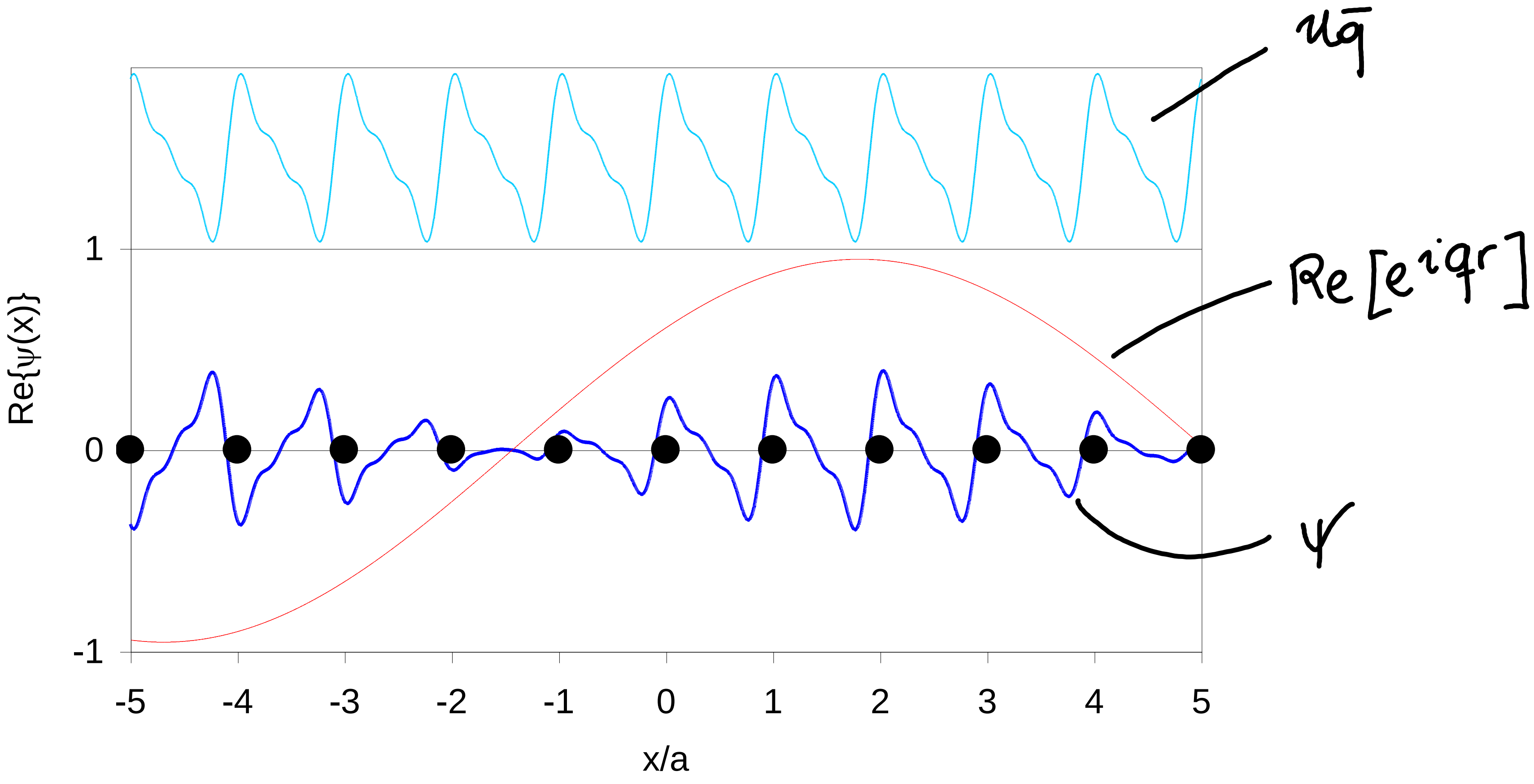
$$\psi_q(\vec{r}+\vec{T}) = e^{i\bar{q}(\bar{r}+T)}\, u_q(\bar{r}+T)$$

$$= e^{i\bar{q}\cdot\vec{T}}\cdot \underbrace{e^{i\bar{q}\bar{r}}\, u_q(\vec{r})}_{\psi_{\bar{q}}(\vec{r})} = e^{i\bar{q}\bar{T}}\, \psi_q(\bar{r})$$

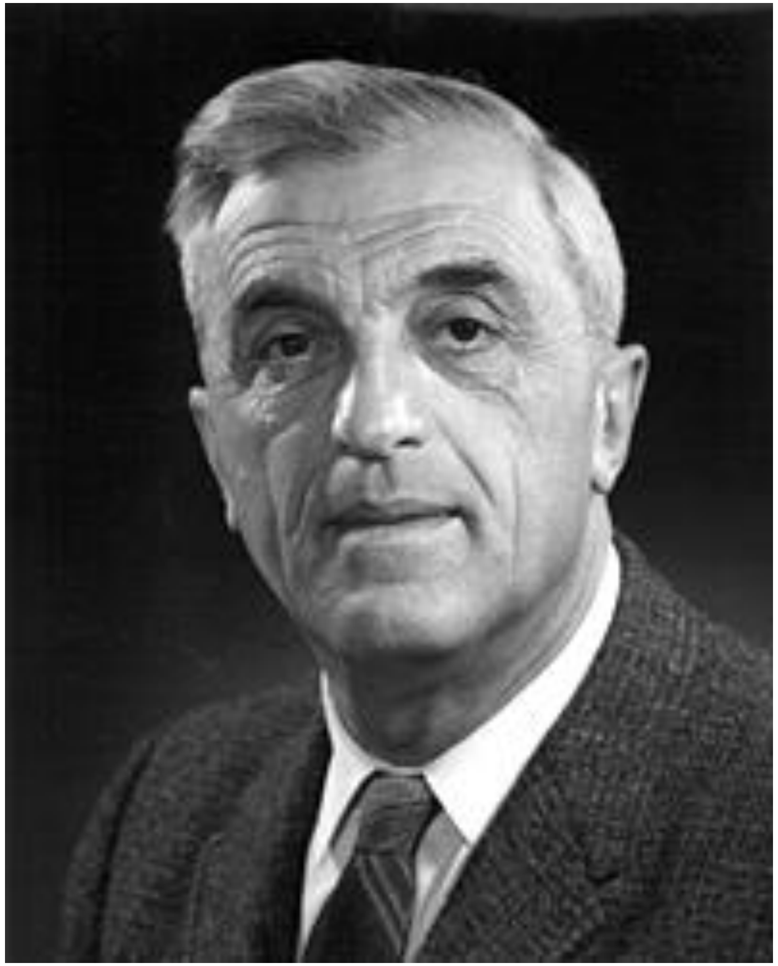
- True for any particle propagating in a lattice

- No assumptions made about the potential *strength*

$$\psi_q(\vec{r}) = e^{i\vec{q}\vec{r}} u_{j,\vec{q}}$$



Felix Bloch



Born in Zurich (1905)

Awarded 1952 Nobel Prize for Physics
First director of CERN

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....
By straight Fourier analysis I found to my delight that the wave differed from the plane wave of free electrons only by a periodic modulation'

F. BLOCH

Consequences of Bloch theorem

$\bar{G} - \bar{G}' = \bar{G}''$

$$\psi_{\vec{k}+\bar{G}} = e^{i(\vec{k}+\vec{G})\cdot\vec{r}} \sum_{\bar{G}'} c_{\vec{k}+\bar{G}-\bar{G}'}\, e^{-i\bar{G}'\vec{r}} = e^{i\bar{k}\bar{r}} \cdot e^{i\bar{G}\bar{r}} \sum_{\bar{G}''} c_{\bar{k}-\bar{G}''}\, e^{-i\bar{G}\cdot\bar{r}}\, e^{-i\bar{G}''\cdot r}$$

$$= e^{i\bar{k}\cdot\bar{r}} \sum_{\bar{G}''} c_{\bar{k}-\bar{G}''}\, e^{-i\bar{G}''\cdot r} = \psi_{\vec{k}}(\vec{r})$$

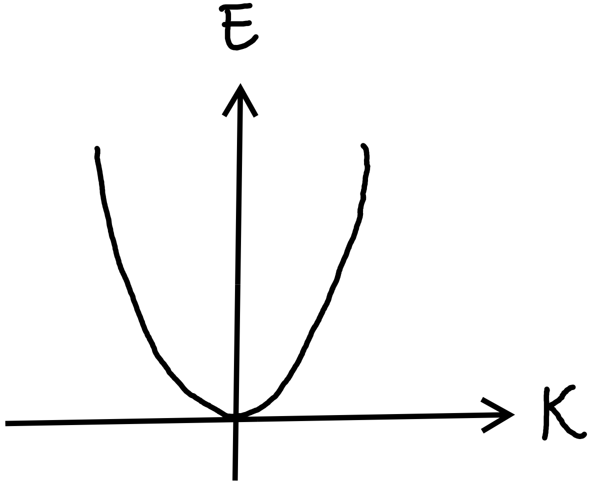
2 Bloch functions with quantum numbers $\bar{k}$ differeing by a R.L. vector are identical

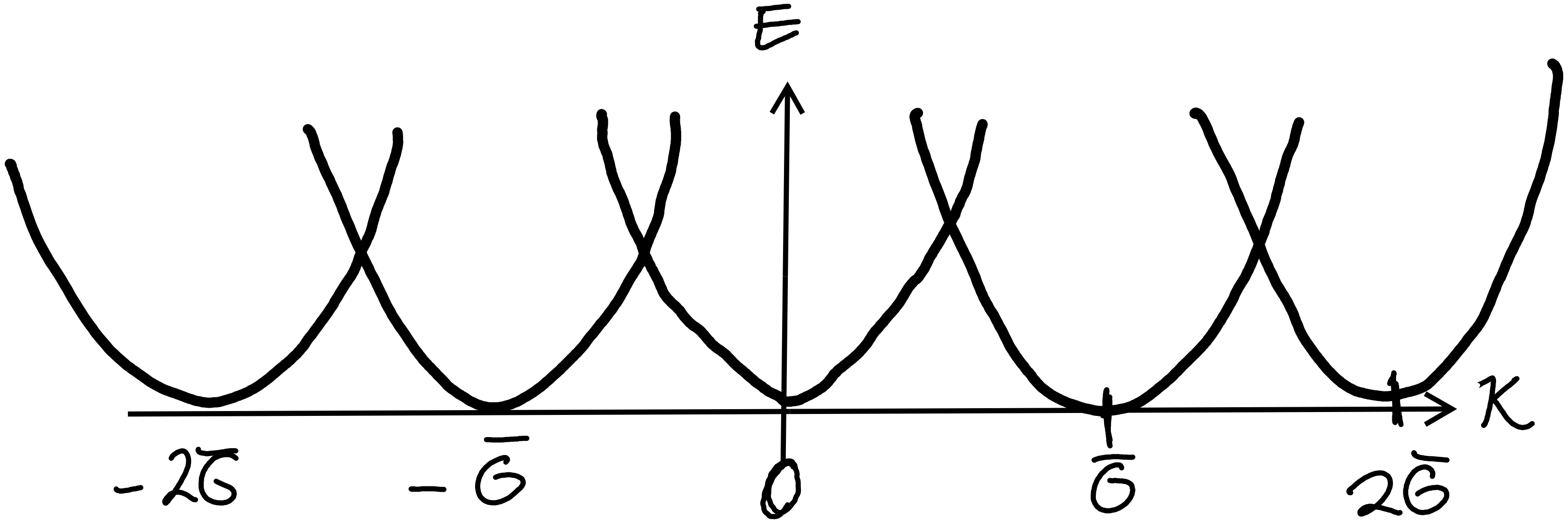
Consequences of Bloch theorem

$$\psi_{\vec{k}+\vec{G}}(\vec{r}) = \psi_{\vec{k}}(\vec{r})$$

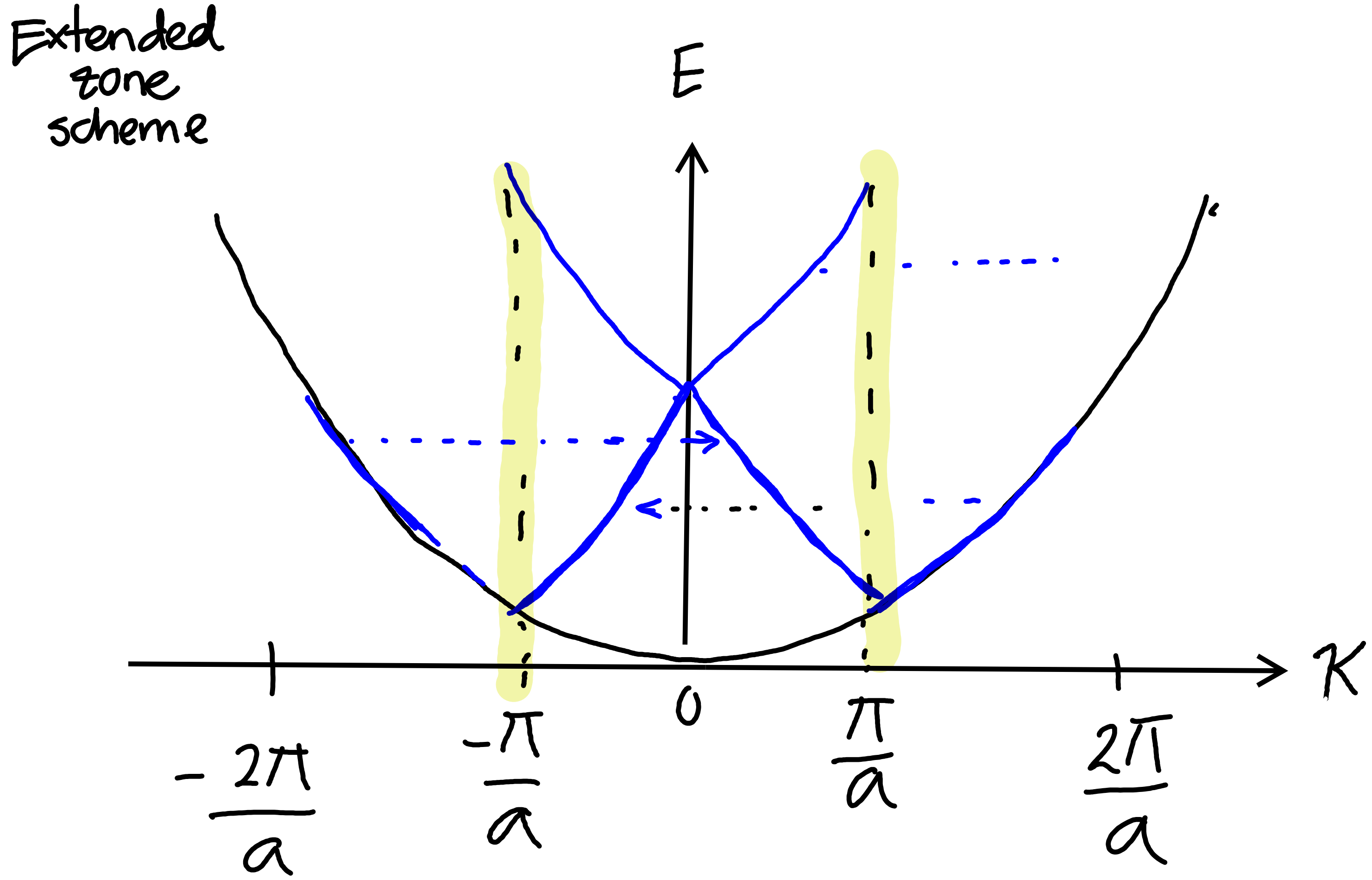
$$E(\vec{k}+\vec{G}) = \frac{\langle \psi_{k+G} | H | \psi_{k+G} \rangle}{\langle \psi_{k+G} | \psi_{k+G} \rangle} = \frac{\langle \psi_{k} | H | \psi_{k} \rangle}{\langle \psi_{k} | \psi_{k} \rangle} = E(\vec{k})$$

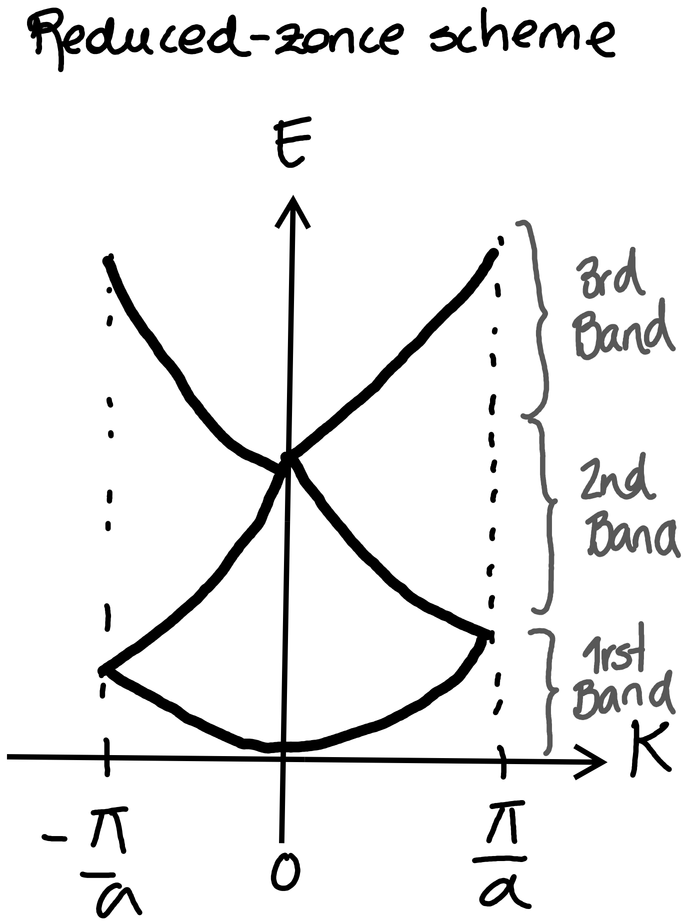
$\Rightarrow$ Dispersion relation $E(\vec{k})$ repeats periodically!
(in k-space)





periodic zone scheme





Many states at each $\bar{q}$: $\psi_{\bar{q},n}(\bar{r}) = \sum_{G} e^{i(\bar{q}\cdot\bar{r})} c_{q-\bar{G}}$

Nearly free electron model

Nearly free electron model

= weak periodic potential $\Longrightarrow$ Goal: Find solutions of Schrödinger eq.

Recap. $\rightarrow$ Bloch theorem $\psi_{\bar{q}}(\bar{r}) = e^{i\bar{q}\cdot\bar{r}} \cdot u_q(\bar{r}) = \sum_{G} c_{\bar{q}-\bar{G}} e^{i(\bar{q}-\bar{G})\cdot r}$

Free e- model $E_K = \frac{\hbar^2 \bar{K}^2}{2m}$

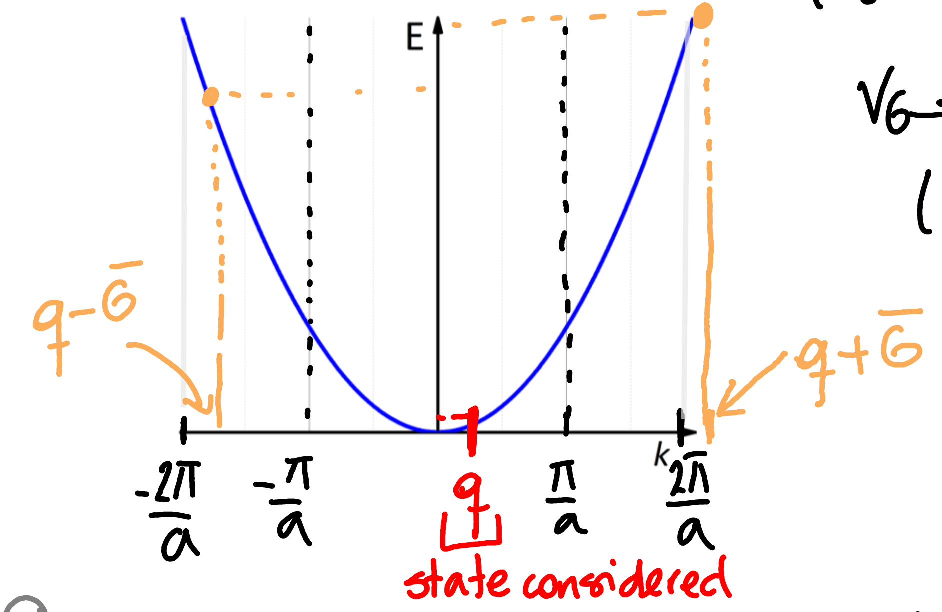
$$E^0_{\bar{q}-\bar{G}} \equiv \frac{\hbar^2(\bar{q}-\bar{G})^2}{2m} \longrightarrow (E^0_{\bar{q}-\bar{G}} - E) c_{\bar{q}-\bar{G}} + \sum_{G'} V_{\bar{G}'-\bar{G}} c_{\bar{q}-G'} = 0$$

$$(E^0_{\bar{q}-\bar{G}} - E) c_{\bar{q}-\bar{G}} + \underbrace{V_{\bar{G}-\bar{G}'} \cdot c_{\bar{q}-\bar{G}}}_{V_{G-G'} \equiv V_0 = 0} + \sum_{G\neq G'} V_{\bar{G}'-\bar{G}} c_{\bar{q}-G'} = 0$$

$$\Rightarrow (E^0_{q-G} - E) c_{\bar{q}-\bar{G}} + \sum_{G\neq G'} V_{\bar{G}'-\bar{G}} c_{\bar{q}-G'} = 0 \xRightarrow[V_G \to 0]{} (E^0_{\bar{q}-G} - E) c_{\bar{q}-\bar{G}} = 0$$

Nearly free electron model

Single electron energy state



Let's consider an e⁻- state defined by $E(q-\bar{G})$ such as there is no other state at that point in K-space ⊛

⊛ Note that states $\bar{q}+\bar{G}$ and $\bar{q}-\bar{G}$ have energies very different to that of state q

$V_G \to 0$:

$$(E^0_{q-G} - E)\, c_{\bar{q}-\bar{G}} = 0$$

$$\to c_{\bar{q}-\bar{G}} = 0$$

$$\to E_{q-G} = E = \underbrace{\frac{\hbar^2 (q-G)^2}{2m}}_{\text{energy of state considered}}$$

only one $c_{q-G} \neq 0$

$$\Psi = \sum_{\vec{K}} c_K e^{i\bar{K}\cdot\bar{r}}$$

$$\Rightarrow \Psi(\vec{r}) = c_{\bar{q}-\bar{G}}\, e^{-i(\bar{q}-\bar{G})\cdot\bar{r}}$$