D. Some General Properties of Bloch Functions

(a) Reduced and Repeated Zone Schemes

$$\psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} C_{n,\vec{k}+\vec{G}}\, e^{i(\vec{k}+\vec{G})\cdot\vec{r}} \qquad (16)$$

band index band index

- $\vec{k}$ lives in reciprocal space (say, $\vec{k} \in 1^{st}$ B.Z.)
  Shift $\vec{k}$ by a reciprocal lattice vector $\vec{G}'$

$\left\{\begin{matrix}\vec{k} \\ \vec{k}+\vec{G}'\end{matrix}\right\}$ same environment in reciprocal lattice

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

sum over all reciprocal lattice vectors → $\vec{G}$

but $\vec{G}'+\vec{G} = \underbrace{\vec{G}''}_{\text{another reciprocal lattice vector}}$

$$= \sum_{\vec{G}''} C_{n,\vec{k}+\vec{G}''}\, e^{i(\vec{k}+\vec{G}'')\cdot\vec{r}}$$

$$= \psi_{n\vec{k}}(\vec{r}) \qquad (17)$$

(sum over $\vec{G}''$ means the same thing as sum over $\vec{G}$)

Bloch Functions $\psi_{n\vec{k}}(\vec{r})$ are periodic in reciprocal ($\vec{k}$-space) space with the same periodicity as that of the Reciprocal Lattice.

It follows that

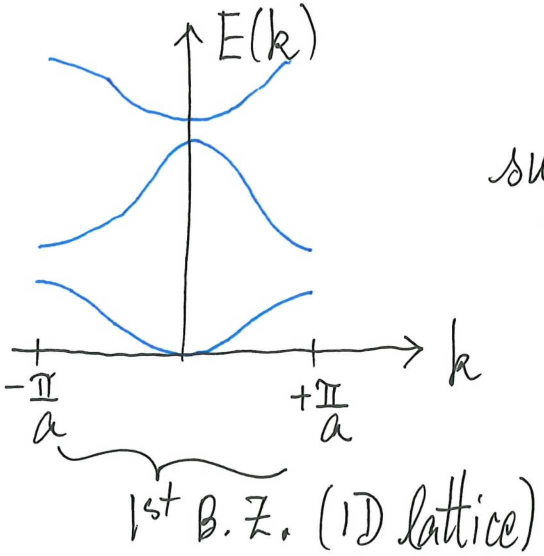
$$\boxed{E_n(\vec{k}+\vec{G}) = E_n(\vec{k})} \qquad (18)$$

Meaning: Sufficient to solve TISE for values of $\vec{k}$ restricted to a reciprocal lattice primitive unit cell

$$\Rightarrow \text{Make a choice of } \boxed{\vec{k} \in \underbrace{1^{st}\text{ B.Z.}}_{\text{Why B.Z. is important!}}} \qquad (19)$$

Reminder: For Bloch states, $\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \underbrace{u_{n\vec{k}}(\vec{r})}_{\text{only need to solve it in one (direct lattice) primitive unit cell}}$

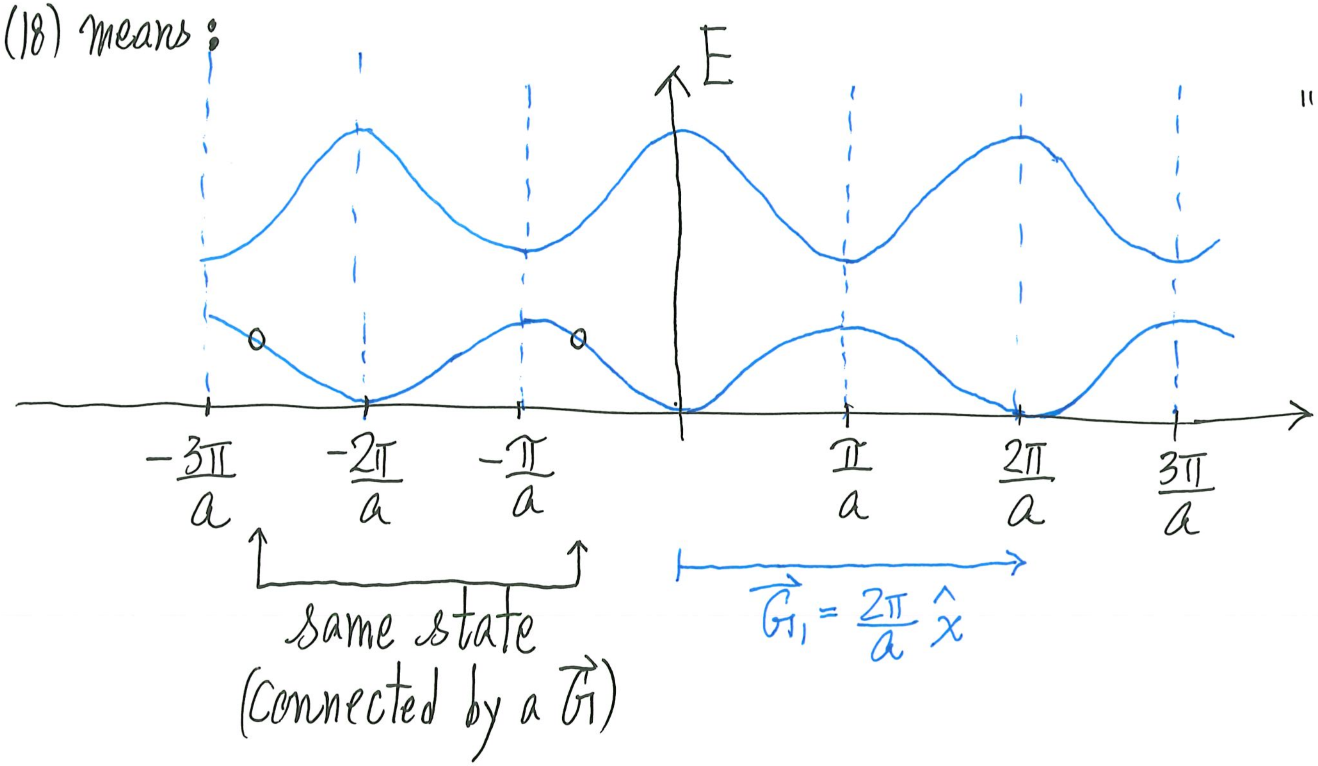
E.g.



sufficient to illustrate all the allowed energies

"Reduced Zone Scheme" using $\vec{k} \in 1^{st}$ B.Z.

Eq.(18) means:



"Repeated Zone Scheme"

Useful in thinking about Transport Properties and Dynamics of Electron in External $\mathcal{E}$-field

(b) Kramers Degeneracy

Claim without proof here that (if spin is included[+] into consideration)

$$E_{n\uparrow}(\vec{k}) = E_{n\downarrow}(-\vec{k}) \qquad (20)$$

If spin is not involved in the Hamiltonian in TISE, then

$$E_n(\vec{k}) = E_n(-\vec{k}) \qquad (21)$$

$$\begin{tikzcd}
\Psi_{n\vec{k}} \arrow[r, leftrightarrow] & E_n(\vec{k}) \; ; & \Psi^*_{n\vec{k}}(\vec{r}) \sim \text{Bloch state with wavevector } (\overset{\text{moving backward}}{-}\vec{k}) = \Psi_{n,-\vec{k}}(\vec{r}) \arrow[d, leftrightarrow] \\
& & \text{They obey the same TISE} \\
& & E^*_n(\vec{k}) \overset{\text{real eigenvalues}}{=} E_n(\vec{k}) \longleftarrow \text{should equal} \longrightarrow E_n(-\vec{k})
\end{tikzcd}$$

[+] This form is related to semiconductors, when the spin-orbit interaction term is included into the energy band TISE.

Remark (Optional)

- The Kramers Degeneracy is related to Time Reversal Symmetry

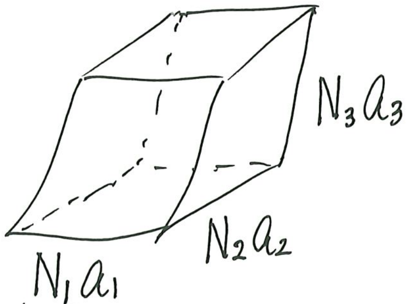
If spin is not involved, the time reversal operator that takes $t \to -t$ is just the one taking the complex conjugate, it will lead to $\psi^*_{n,+\vec{k}}(\vec{r}) = \psi_{n,-\vec{k}}(\vec{r})$

Then $$E_n(-\vec{k}) = \int \psi^*_{n,-\vec{k}}(\vec{r})\, \hat{H}\, \psi_{n,-\vec{k}}(\vec{r})\, d^3r = \int \psi_{n,\vec{k}}(\vec{r})\, \hat{H}\, \psi^*_{n\vec{k}}(\vec{r})\, d^3r$$
$$= \left(E_n(\vec{k})\right)^* = E_n(\vec{k})$$

When spin is involved, time reversal operator is more than the complex conjugate.

E. Mimicing an Infinite System by Imposing Periodic Boundary Condition

Finite crystals of Volume V



$\underbrace{N_1 a_1}$

[# cells in $\vec{a}_1$ direction]

$N_1 \sim 10^8$ (for 1 cm size)
$N_2 \sim 10^8$
$N_3 \sim 10^8$

$N = N_1 \cdot N_2 \cdot N_3 = \underbrace{\text{\# unit cells in crystal}}_{\sim 10^{24}}$ (for cm^3)

This is $\underbrace{\text{very big}}$ size!
[tiny % atoms on surfaces]

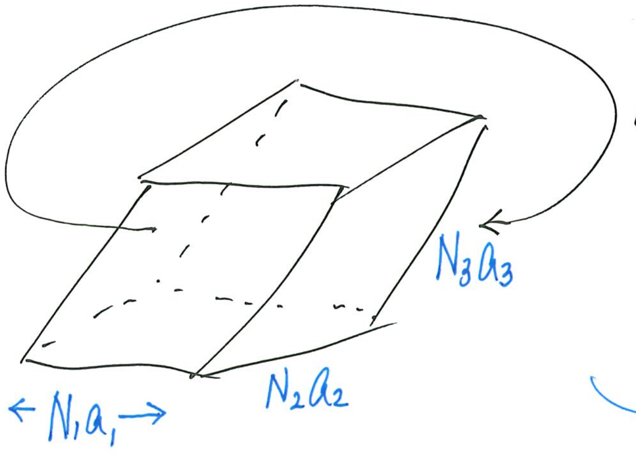
$\therefore V$ = size of crystal

$$= N \cdot \Omega_c \quad (22)$$

↑ # primitive cells in crystal

↑ volume of one primitive unit cell

If we focus on bulk properties, then apply Periodic Boundary Conditions to mimic an infinite crystal



$$\underbrace{\begin{array}{l}\text{connect the left side to the right side} \\ \text{top side to the bottom side} \\ \text{front side to the back side}\end{array}}_{\text{never-ending crystal!}}$$

Key Idea: Introduce a new (much longer (~10^8 times than "a")) period

$$\psi_{\vec{k}}(\vec{r}) = \psi_{\vec{k}}(\vec{r}+N_1\vec{a}_1) = \psi_{\vec{k}}(\vec{r}+N_2\vec{a}_2) = \psi_{\vec{k}}(\vec{r}+N_3\vec{a}_3) \quad (23)$$

impose conditions on $\vec{k}$ $\Rightarrow$ formally discretized allowed $\vec{k}$-values in 1st B.Z.

Recall: $\vec{a}_i \cdot \vec{b}_i = 2\pi$, $\vec{a}_i \cdot \vec{b}_j = 0 \ (i \neq j)$

Asks for $e^{i\vec{k}\cdot N_1\vec{a}_1} = 1$; $e^{i\vec{k}\cdot N_2\vec{a}_2} = 1$; $e^{i\vec{k}\cdot N_3\vec{a}_3} = 1$ (24)

only these $\vec{k}$'s are allowed

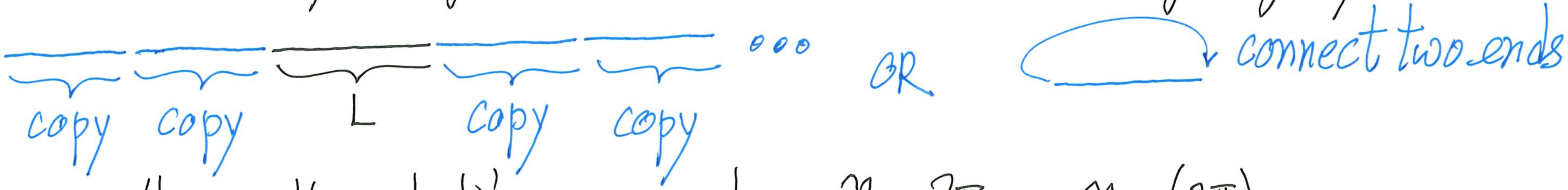
So, $$\vec{k} = \frac{(\text{some integer})}{N_1}\vec{b}_1 + \frac{(\text{some integer})}{N_2}\vec{b}_2 + \frac{(\text{some integer})}{N_3}\vec{b}_3 \quad \text{works!}$$

$$= \frac{n_1}{N_1}\vec{b}_1 + \frac{n_2}{N_2}\vec{b}_2 + \frac{n_3}{N_3}\vec{b}_3 \quad \text{works} \qquad (25)$$

$$(n_1 = 0, \pm 1, \cdots; \; n_2 = 0, \pm 1, \cdots; \; n_3 = 0, \pm 1, \cdots)$$

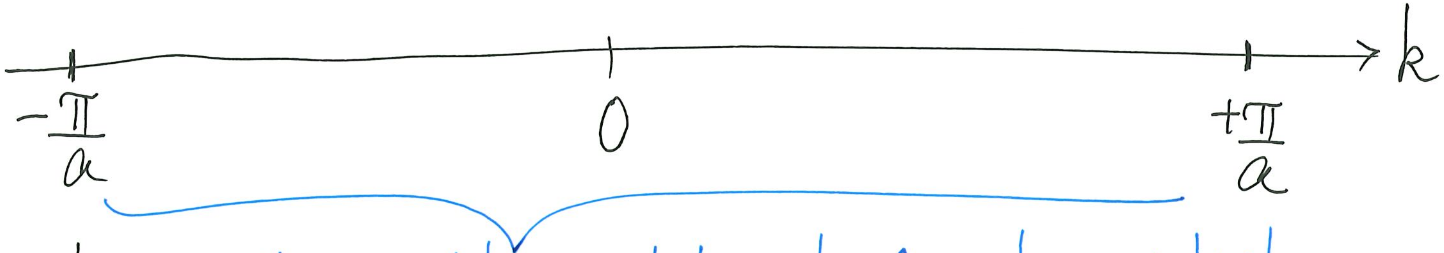
E.g. <u>1D lattice</u> $\vec{a}_1 = a\hat{x}$, $\vec{b}_1 = \frac{2\pi}{a}\hat{x}$

finite crystal of N_1 unit cells $\Rightarrow$ $L = N_1 a$ = length of crystal

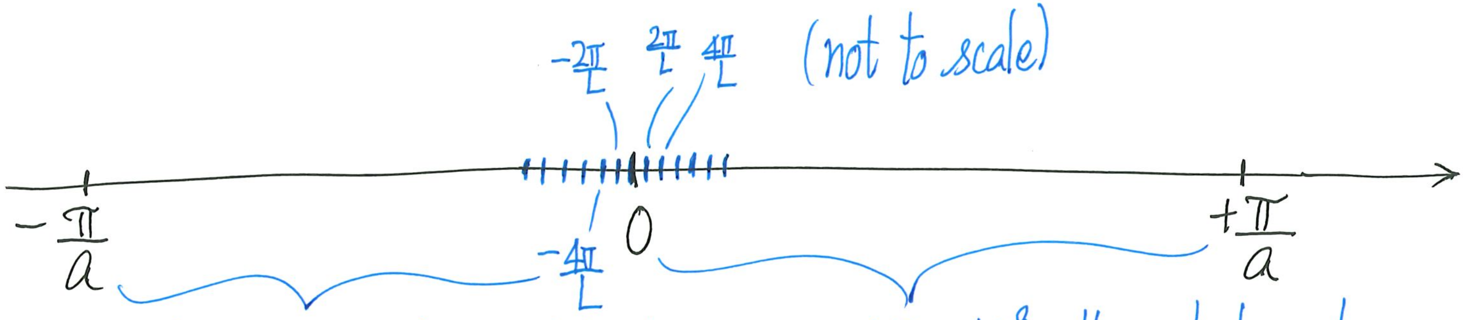


- then allowed $\vec{k}$'s are $\quad k = \frac{n_1}{N_1}\frac{2\pi}{a} = n_1 \cdot \left(\frac{2\pi}{L}\right)$
- Previous discussion, due to atomic scale periodicity $U(x) = U(x+na)$, only need to consider k's in $\underbrace{1^{st} \text{ B.Z.}}_{\text{from } -\frac{\pi}{a} \text{ to } +\frac{\pi}{a}}$

Finite system ($L = Na$)



1st B.Z.: this is determined by atomic scale periodicity
(if infinite system, all $k \in$ 1st B.Z. continuously are allowed)



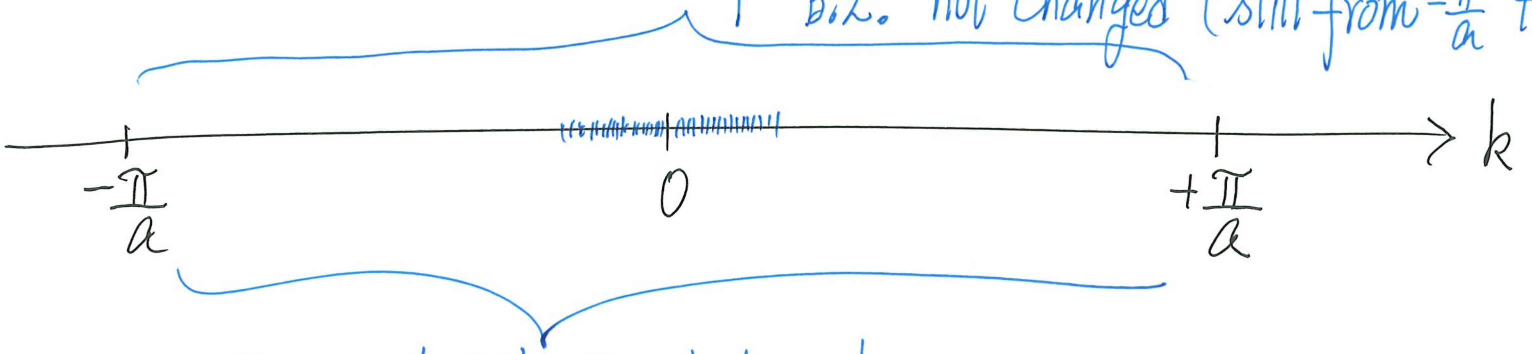
another ~0.5×10^8 allowed k-values ~0.5×10^8 allowed k-values

All together there are exactly N allowed k-values in 1st B.Z. (26)

the number of unit cells in crystal

Bigger crystal ($L' = N'a$; $N' > N$)

1^{st} B.Z. not changed (still from $-\frac{\pi}{a}$ to $\frac{\pi}{a}$)



- Now with N' allowed k-values
- allowed values are $\frac{2\pi}{L'}$ apart ⇒ denser!

L' ↑ longer

For a given segment dk of k-space, there are

$$\frac{dk}{\left(\frac{2\pi}{L}\right)} = \frac{L}{(2\pi)}\,dk \text{ allowed k-values} \qquad (27)$$

Results carrying over to 3D

- Finite Crystal with $V = N\cdot\Omega_c$ volume and N primitive unit cells

  $\vec{k}$ becomes $\underbrace{\text{discrete}}_{\vec{k} = \frac{n_1}{N_1}\vec{b}_1 + \frac{n_2}{N_2}\vec{b}_2 + \frac{n_3}{N_3}\vec{b}_3}$ inside the 1st B.Z.

  $$\vec{k} = \frac{n_1}{N_1}\vec{b}_1 + \frac{n_2}{N_2}\vec{b}_2 + \frac{n_3}{N_3}\vec{b}_3$$ (a dense array of $\vec{k}$'s in 1st B.Z.)

  <u>1st B.Z. Size</u> is NOT altered by size of crystal

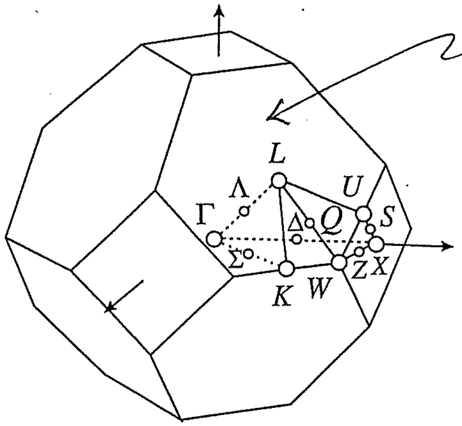
  fixes by atomic periodicity

(28) **There are exactly N allowed $\vec{k}$-values in 1st B.Z.** ← Key Concept

- Need it to understand why there are metals, insulators, semiconductors

(29) **For a volume element d^3k in reciprocal space, there are $\dfrac{d^3k}{\frac{(2\pi)^3}{V}} = \dfrac{V}{(2\pi)^3}\,d^3k$ allowed $\vec{k}$-values in it**

Si, Ge, GaAs, ...



The first Brillouin zone of the face-centered cubic lattice with some points of high symmetry indicated by letters.

There are N allowed $\vec{k}$-values in 1st B.Z.

where N = number of premitive unit cells in crystal under consideration

Since discrete $\vec{k}$-values (very densely spaced) in 1st B.Z. are integers (along $\vec{b}_1, \vec{b}_2, \vec{b}_3$), they are uniformly distributed.

For a volume d^3k of $\vec{k}$-space, there are

$$\frac{V}{(2\pi)^3} d^3k$$ allowed $\vec{k}$-values.

F. Normalization of Bloch Functions

- Bloch Functions are extended (spread out in space)

Consider a crystal of volume $V = N \cdot \Omega_c$

$$\int_V |\psi_{n\vec{k}}(\vec{r})|\, d^3r = 1 \qquad \text{normalization condition}$$

A way to satisfy the condition is:

$$\boxed{\psi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}}\, e^{i\vec{k}\cdot\vec{r}}\, u_{n\vec{k}}(\vec{r})} \qquad (30)$$

It follows that

$$1 = \frac{1}{V}\int_{\underset{\text{whole crystal}}{\overset{\nearrow}{V}}} u^*_{n\vec{k}}(\vec{r})\, u_{n\vec{k}}(\vec{r})\, d^3r = \frac{N}{V}\overset{u_{n\vec{k}}(\vec{r})\text{ is periodic}}{\overset{\downarrow}{\int_{\underset{\text{one unit cell}}{\underset{\uparrow}{\Omega_c}}}}} |u_{n\vec{k}}(\vec{r})|^2\, d^3r = \underbrace{\frac{1}{\Omega_c}\int_{\Omega_c} |u_{n\vec{k}}(\vec{r})|^2\, d^3r = 1}_{\text{How } u_{n\vec{k}}(\vec{r}) \text{ is normalized!}} \qquad (31)$$

As $\psi_{n\vec{k}}(\vec{r})$ are eigenstates of $\hat{H}$, they can be made orthogonal,

so

$$\boxed{\int_V \psi^*_{n'\vec{k}'}(\vec{r})\, \psi_{n\vec{k}}(\vec{r})\, d^3r = \delta_{nn'}\delta_{\vec{k}\vec{k}'}} \qquad (32)$$

whole crystal

orthonormal condition

$\{\psi_{n\vec{k}}(\vec{r})\}$ all n's, all $\vec{k}$'s ($\in$ 1st B.Z.) form a complete set

whole set of Bloch's functions

$\Rightarrow$ Can use $\{\psi_{n\vec{k}}(\vec{r})\}$ as the basis functions for other solid state problems

e.g. defects, external fields

this is the "Crystal Momentum Representation" (CMR)

OR "Bloch functions Representation"

Band Problem becomes

- Solving $\psi_{n\vec{k}}(\vec{r})$ within one primitive unit cell
  (then Bloch's theorem gives $\psi_{n\vec{k}}(\vec{r})$ at other places)

or equivalently solving $u_{n\vec{k}}(\vec{r})$ within one primitive unit cell
(then Bloch's theorem will take care of the rest)

$$\hat{H}\psi_{n\vec{k}}(\vec{r}) = E_n(\vec{k})\,\psi_{n\vec{k}}(\vec{r})$$

plus boundary Conditions on Points (two points $\vec{r}$ and $\vec{r}+\vec{R}$ on surface of primitive unit cell) at which ψ and slope of ψ must be continuous

results are $\psi_{n\vec{k}}(\vec{r}) \leftrightarrow E_n(\vec{k})$

G. Schrödinger Equation satisfied by $u_{\vec{k}}(\vec{r})$

- **Idea:** know $u_{\vec{k}}(\vec{r})$, then $e^{i\vec{k}\cdot\vec{r}}u_{\vec{k}}(\vec{r})$ gives $\psi_{\vec{k}}(\vec{r})$

  Results here are important in semiconductors because
  - learn how to move "$e^{i\vec{k}\cdot\vec{r}}$" through "$\vec{\nabla}$" (gradient) and "∇^2" (Laplacian) [Technique]
  - preparing for "$\vec{k}\cdot\vec{p}$" approximation (powerful in modelling band structures of semiconductors)
  - preparing for relating effective masses m^* to energy gap

$$\hat{H}\,\psi_{\vec{k}}(\vec{r}) = E(\vec{k})\,\psi_{\vec{k}}(\vec{r}) \qquad (1)$$ [Governing Equation]

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})\right] e^{i\vec{k}\cdot\vec{r}}\,u_{\vec{k}}(\vec{r}) = E(\vec{k})\,e^{i\vec{k}\cdot\vec{r}}\,u_{\vec{k}}(\vec{r})$$

__Aim:__ Want to move "$e^{i\vec{k}\cdot\vec{r}}$" through "∇^2"

$$\nabla^2\left(e^{i\vec{k}\cdot\vec{r}}u_{\vec{k}}(\vec{r})\right) = \underset{\text{divergence}}{\vec{\nabla}\cdot}\left(\underset{\text{gradient}}{\vec{\nabla}}\left(e^{i\vec{k}\cdot\vec{r}}u_{\vec{k}}(\vec{r})\right)\right)$$

$$\underbrace{\vec{\nabla}\left(e^{i\vec{k}\cdot\vec{r}}u_{\vec{k}}(\vec{r})\right)}_{\text{should give a vector}} = \left[\vec{\nabla}\left(e^{i\vec{k}\cdot\vec{r}}\right)\right]u_{\vec{k}}(\vec{r}) + e^{i\vec{k}\cdot\vec{r}}\left(\vec{\nabla}u_{\vec{k}}(\vec{r})\right)$$

$$= i\vec{k}\,e^{i\vec{k}\cdot\vec{r}}\,u_{\vec{k}}(\vec{r}) + e^{i\vec{k}\cdot\vec{r}}\left(\vec{\nabla}u_{\vec{k}}(\vec{r})\right)$$

[This is the gradient of a Bloch function] good

$$\underbrace{\nabla^2 \psi_{\vec{k}}(\vec{r})}_{\text{should give a scalar}} = \vec{\nabla}\cdot\left[i\vec{k}\, e^{i\vec{k}\cdot\vec{r}}\, u_{\vec{k}}(\vec{r}) + e^{i\vec{k}\cdot\vec{r}}\left(\vec{\nabla} u_{\vec{k}}(\vec{r})\right)\right]$$

$$= (i\vec{k})\cdot(i\vec{k})\underbrace{e^{i\vec{k}\cdot\vec{r}}}_{}\, u_{\vec{k}}(\vec{r}) + \underbrace{e^{i\vec{k}\cdot\vec{r}}}_{}\, i\vec{k}\cdot\vec{\nabla} u_{\vec{k}}(\vec{r}) + \underbrace{e^{i\vec{k}\cdot\vec{r}}}_{}\, i\vec{k}\cdot\vec{\nabla} u_{\vec{k}}(\vec{r}) + \underbrace{e^{i\vec{k}\cdot\vec{r}}}_{}\, \nabla^2 u_{\vec{k}}(\vec{r})$$

$$= e^{i\vec{k}\cdot\vec{r}}\left[\underbrace{-k^2 + 2i\vec{k}\cdot\vec{\nabla}}_{\text{extra operations that emerged as "}e^{i\vec{k}\cdot\vec{r}}\text{" is moved across "}\nabla^2\text{"}^{\dagger}} + \nabla^2\right] u_{\vec{k}}(\vec{r})$$

$$\Rightarrow \boxed{\nabla^2 \psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\left(\vec{\nabla} + i\vec{k}\right)^2 u_{\vec{k}}(\vec{r})} \quad (33) \quad \text{(Key Result)}$$

OR

$$\underbrace{-\frac{\hbar^2}{2m}\nabla^2}_{\text{K.E. operator}} \psi_{\vec{k}}(\vec{r}) = \frac{\hat{p}^2}{2m}\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\, \frac{1}{2m}\left(\hat{p} \underbrace{+ \hbar\vec{k}}_{}\right)^2 u_{\vec{k}}(\vec{r}) \quad (34)$$

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† This is an important math skill AND it is an important result.

Aside : An important By-product

$$\vec{\nabla}\psi_{\vec{k}}(\vec{r}) = i\vec{k}\,\psi_{\vec{k}}(\vec{r}) + \frac{1}{\sqrt{V}}e^{i\vec{k}\cdot\vec{r}}\left(\vec{\nabla}u_{\vec{k}}(\vec{r})\right)$$

[Bloch functions are NOT eigenstates of "$\vec{\nabla}$" or the momentum $\frac{\hbar}{i}\vec{\nabla}$]

$$\psi^*_{\vec{k}}(\vec{r})\left(\frac{\hbar}{i}\vec{\nabla}\right)\psi_{\vec{k}}(\vec{r}) = \hbar\vec{k}\left|\psi_{\vec{k}}(\vec{r})\right|^2 + \frac{1}{V}u^*_{\vec{k}}(\vec{r})\left(\frac{\hbar}{i}\vec{\nabla}\right)u_{\vec{k}}(\vec{r})$$

OR

$$\boxed{\psi^*_{\vec{k}}(\vec{r})\,\hat{\vec{p}}\,\psi_{\vec{k}}(\vec{r}) = \hbar\vec{k}\left|\psi_{\vec{k}}(\vec{r})\right|^2 + \frac{1}{V}u^*_{\vec{k}}(\vec{r})\,\hat{\vec{p}}\,u_{\vec{k}}(\vec{r})} \qquad (35)$$

(useful in finding expectation value $\langle\hat{\vec{p}}\rangle$ and velocity (expectation value))

$$\int_V \psi^*_{\vec{k}}(\vec{r})\,\hat{\vec{p}}\,\psi_{\vec{k}}(\vec{r})\,d^3r = \underbrace{\hbar\vec{k}}_{\uparrow} + \frac{1}{V}\int_V u^*_{\vec{k}}(\vec{r})\,\hat{\vec{p}}\,u_{\vec{k}}(\vec{r}) = \hbar\vec{k} + \frac{1}{\Omega_c}\int_{\Omega_c} u^*_{\vec{k}}(\vec{r})\,\hat{\vec{p}}\,u_{\vec{k}}(\vec{r})\,d^3r \qquad (36)$$

see "$\hbar\vec{k}$" emerging (called "crystal momentum")

The Periodic Part $u_{\vec{k}}(\vec{r})$ of Bloch Functions obeys the equation

$$\boxed{\left[-\frac{\hbar^2}{2m}(\vec{\nabla}+i\vec{k})^2+U(\vec{r})\right]u_{\vec{k}}(\vec{r}) = E(\vec{k})\,u_{\vec{k}}(\vec{r})} \qquad (37)$$

OR equivalently $\left[\frac{1}{2m}(\hat{p}+\hbar\vec{k})^2+U(\vec{r})\right]u_{\vec{k}}(\vec{r}) = E(\vec{k})\,u_{\vec{k}}(\vec{r})$

OR equivalently and most explicitly,

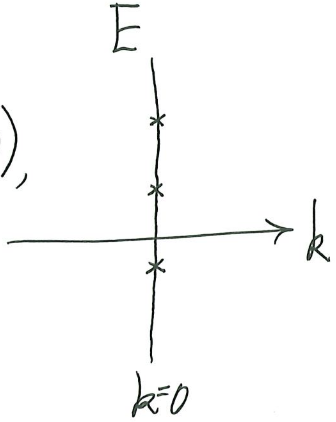
$$\boxed{\left[-\frac{\hbar^2}{2m}\nabla^2+U(\vec{r})-\frac{i\hbar^2}{m}k\cdot\vec{\nabla}+\frac{\hbar^2k^2}{2m}\right]u_{\vec{k}}(\vec{r}) = E(\vec{k})\,u_{\vec{k}}(\vec{r})} \qquad (38)$$

with $U(\vec{r}+\vec{R}_n) = U(\vec{r})$ (8)

Solving Eq. (38) and (8) for $u_{\vec{k}}(\vec{r}) \leftrightarrow E(\vec{k})$ Pairs is equivalent to the energy band problem of solving Eq. (1) and Eq. (8).

[Of course, with B.C.'s on surface of unit cell.]

Remark: Inspect Eq. (38)



If we know the $\vec{k}=0$ solutions, i.e. $u_{n,\vec{k}=0}(\vec{r})$ and $E_n(\vec{k}=0)=E_n(0)$,

they obey $\left[-\frac{\hbar^2}{2m}\nabla^2+U(\vec{r})\right]u_{n,\vec{k}=0}(\vec{r}) = E_n(0)\,u_{n,\vec{k}=0}(\vec{r})$;

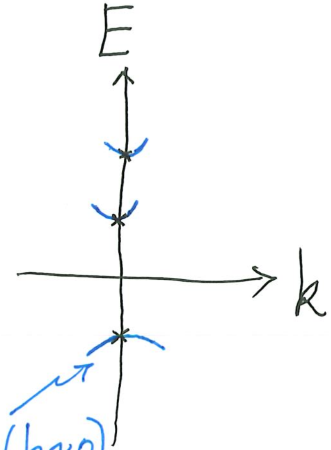
$\vec{k}\approx 0$ solutions obey

small

$$\left[-\frac{\hbar^2}{2m}\nabla^2+U(\vec{r})\underbrace{-\frac{i\hbar^2}{m}\vec{k}\cdot\vec{\nabla}+\frac{\hbar^2k^2}{2m}}_{\text{Can be treated as perturbations}}\right]u_{n,\vec{k}}(\vec{r}) = E_n(\vec{k})\,u_{n,\vec{k}}(\vec{r})$$

[This is the idea behind $\vec{k}\cdot\vec{p}$ approximation in semiconductor physics]

$$-\frac{i\hbar^2}{m}\vec{k}\cdot\vec{\nabla} = \hbar\vec{k}\cdot\underbrace{\left(\frac{\hbar}{i}\vec{\nabla}\right)}_{\vec{p}} \sim ``\vec{k}\cdot\vec{p}"$$



$k\neq 0$ $(k\approx 0)$
results by perturbation theory