E. General Case: About any $\vec{k}_0$

- know $\{E_n(\vec{k}_0)\}$ and $\{\psi_{n\vec{k}_0}(\vec{r})\}$ (thus $\{u_{n\vec{k}_0}(\vec{r})\}$) at $\vec{k}=\vec{k}_0$ (not necessarily $\vec{k}_0=0$), can we get at $E_n(\vec{k})$ (and $\psi_{n\vec{k}}(\vec{r})$) for $\vec{k}\approx\vec{k}_0$?

  [$\vec{k}_0=0$ in Sec. D is a special case. Follow steps in Sec. D]

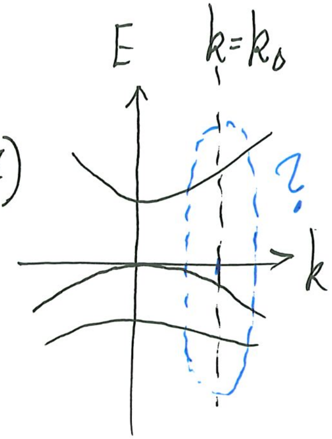
- Assumed known

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right]\underbrace{\psi_{n\vec{k}_0}(\vec{r})}_{\text{knowns}}=\underbrace{E_n(\vec{k}_0)}_{\text{knowns}}\underbrace{\psi_{n\vec{k}_0}(\vec{r})}_{\text{knowns}} \quad (26)$$

Want to solve

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right]\underbrace{\psi_{n\vec{k}}(\vec{r})}_{\text{unknowns}}=\underbrace{E_n(\vec{k})}_{\text{unknowns}}\underbrace{\psi_{n\vec{k}}(\vec{r})}_{\text{unknowns}} \quad (27)$$

at least approximately



$$\psi_{n\vec{k}}(\vec{r}) = \underbrace{\frac{1}{\sqrt{V}}}_{\text{doesn't matter}} e^{i\vec{k}\cdot\vec{r}} u_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} \underbrace{e^{i\vec{k}_0\cdot\vec{r}} e^{-i\vec{k}_0\cdot\vec{r}}}_{\text{just "1"}} e^{i\vec{k}\cdot\vec{r}} u_{n\vec{k}}(\vec{r})$$

unknown

$$= \frac{1}{\sqrt{V}} e^{i(\vec{k}-\vec{k}_0)\cdot\vec{r}} e^{i\vec{k}_0\cdot\vec{r}} u_{n\vec{k}}(\vec{r}) \qquad (28)$$

Substitute into TISE (Eq. (27)) and move $e^{i(\vec{k}-\vec{k}_0)\cdot\vec{r}}$ through to the left:

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V(\vec{r}) - \frac{i\hbar^2}{m}(\vec{k}-\vec{k}_0)\cdot\vec{\nabla} + \frac{\hbar^2(\vec{k}-\vec{k}_0)^2}{2m}\right] e^{i\vec{k}_0\cdot\vec{r}} u_{n\vec{k}}(\vec{r}) = E_n(\vec{k})\, e^{i\vec{k}_0\cdot\vec{r}} u_{n\vec{k}}(\vec{r}) \qquad (29a)$$

OR

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V(\vec{r}) + \frac{\hbar}{m}(\vec{k}-\vec{k}_0)\cdot\hat{\vec{p}} + \frac{\hbar^2}{2m}(\vec{k}-\vec{k}_0)^2\right] e^{i\vec{k}_0\cdot\vec{r}} u_{n\vec{k}}(\vec{r}) = E_n(\vec{k})\, e^{i\vec{k}_0\cdot\vec{r}} u_{n\vec{k}}(\vec{r}) \qquad (29b)$$

[Eq. (29a), (29b) $\Leftrightarrow$ Eq. (7b), (7c) for the $\vec{k}_0 = 0$ case]   unknowns   (Exact)

Recall: $\vec{k} = \vec{k}_0$ of Eq. (29) is the known (unperturbed) problem.

Expand $\underset{\substack{\uparrow \\ \text{unknown} \\ \text{[but periodic]}}}{u_{n\vec{k}}(\vec{r})} = \underset{\substack{n' \\ \uparrow \\ \text{all bands}}}{\sum} \overset{\swarrow \text{ become the unknowns}}{C_{nn'}(\vec{k}-\vec{k}_0)} \underset{\substack{\uparrow \\ \text{known at } \vec{k}_0}}{u_{n'\vec{k}_0}(\vec{r})}$ (30) (c.f. Eq. (18))

- Substitute into Eq. (29.b) and note that $\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right] \overbrace{e^{i\vec{k}_0\cdot\vec{r}} u_{n'\vec{k}_0}(\vec{r})}^{\psi_{n'\vec{k}_0}(\vec{r})} = E_{n'}(\vec{k}_0) \overbrace{e^{i\vec{k}_0\cdot\vec{r}} u_{n'\vec{k}_0}(\vec{r})}^{\psi_{n'\vec{k}_0}(\vec{r})}$,

$$\sum_{n'} C_{nn'}(\vec{k}-\vec{k}_0)\left(\left[E_{n'}(\vec{k}_0) + \frac{\hbar^2(\vec{k}-\vec{k}_0)^2}{2m} - E_n(\vec{k})\right]\psi_{n'\vec{k}_0}(\vec{r}) + \frac{\hbar}{m}(\vec{k}-\vec{k}_0)\cdot\hat{\vec{p}}\,\psi_{n'\vec{k}_0}(\vec{r})\right) = 0 \quad (31)$$

- Left multiply by $\psi^*_{n\vec{k}_0}(\vec{r})$ and $\int(\cdots)d\tau \Rightarrow$ Huge $(\infty\times\infty)$ Matrix equation for $C_{nn'}(\vec{k}-\vec{k}_0)$

$$C_{nn}(\vec{k}-\vec{k}_0)\left[E_n(\vec{k}_0) + \frac{\hbar^2(\vec{k}-\vec{k}_0)^2}{2m} - E_n(\vec{k})\right] + \sum_{n'} C_{nn'}(\vec{k}-\vec{k}_0)\frac{\hbar}{m}(\vec{k}-\vec{k}_0)\cdot\underbrace{\int \psi^*_{n\vec{k}_0}(\vec{r})\,\hat{\vec{p}}\,\psi_{n'\vec{k}_0}(\vec{r})\,d\tau}_{\substack{\text{known} \\ \text{[momentum matrix element]} \\ \text{at } \vec{k}_0}} = 0$$

$$\boxed{\vec{P}_{nn'}(\vec{k}_0) \equiv \int \psi^*_{n\vec{k}_0}(\vec{r})\,\hat{\vec{p}}\,\psi_{n'\vec{k}_0}(\vec{r})\,d\tau = \frac{\hbar}{i}\int \psi^*_{n\vec{k}_0}(\vec{r})\,\vec{\nabla}\,\psi_{n'\vec{k}_0}(\vec{r})\,d\tau} \quad (32)$$

(now evaluated at $\vec{k}_0$)

The Matrix Equation is :

$$\sum_{n'} \left\{ \underbrace{\left(E_{n'}(\vec{k}_0) + \frac{\hbar^2}{2m}(\vec{k}-\vec{k}_0)^2 - \overset{\text{unknowns}}{E_n(\vec{k})}\right)}_{\text{diagonal}} \delta_{nn'} + \underbrace{\frac{\hbar}{m}(\vec{k}-\vec{k}_0)\cdot\vec{P}_{nn'}(\vec{k}_0)}_{\text{diagonal (if } \vec{P}_{nn}(\vec{k}_0)\neq 0\text{) and off diagonal}} \right\} \overset{\text{unknowns}}{C_{nn'}(\vec{k}-\vec{k}_0)} = 0 \quad (33)^{+}$$

(Done!)

- Exact so far
- |Determinant| = 0 $\Rightarrow E_n(\vec{k})$ (many values for different bands)
- Perturbation $\Rightarrow$ effective mass tensor
- Truncation $\begin{cases} 3\times 3 \text{ (Valence bands) [fold effects of other bands back]} \\ \text{Kane model (2-band, 3-band, 4-band)} \end{cases}$
- $\vec{k}_0 = 0$ case was discussed in Sec. D
- This is the starting point of the $\vec{k}\cdot\vec{p}$ perturbation theory

---

$^{+}$ Each $(\vec{k}-\vec{k}_0)$ is a separate problem, as each $\vec{k}$ is a separate TISE problem.

(a) Collecting Results

2nd order perturbation theory

$$E_n(\vec{k}) \cong E_n(\vec{k}_0) + \frac{\hbar}{m}(\vec{k}-\vec{k}_0)\cdot\vec{P}_{nn}(\vec{k}_0) + \frac{\hbar^2}{2m}(\vec{k}-\vec{k}_0)^2 + \frac{\hbar^2}{m^2}\sum_{n'(\neq n)}\frac{|(\vec{k}-\vec{k}_0)\cdot\vec{P}_{nn'}(\vec{k}_0)|^2}{E_n(\vec{k}_0)-E_{n'}(\vec{k}_0)} \tag{34}$$

This is Eq. (8) generalized to some point $\vec{k}_0$.

Taking $\vec{k}\to\vec{k}_0$, and $E_n(\vec{k}) \cong E_n(\vec{k}_0) + \left(\nabla_{\vec{k}} E_n(\vec{k})\Big|_{\vec{k}=\vec{k}_0}\right)\cdot(\vec{k}-\vec{k}_0) + \cdots$

$$\vec{P}_{nn}(\vec{k}_0) = \langle\vec{p}\rangle_{n\vec{k}_0} = \int \psi^*_{n\vec{k}_0}(\vec{r})\left(\frac{\hbar}{i}\vec{\nabla}\right)\psi_{n\vec{k}_0}(\vec{r})\,d\tau = \frac{m}{\hbar}\vec{\nabla}_{\vec{k}} E_n(\vec{k})\Big|_{\vec{k}=\vec{k}_0} \tag{35}$$

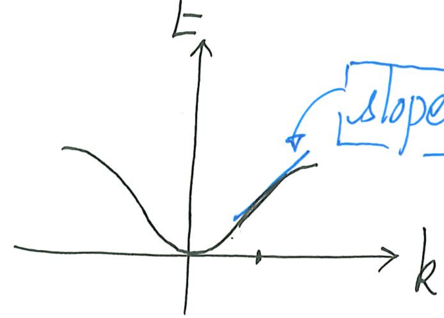
expectation value of momentum for Block state (NOT $\hbar\vec{k}$ as for Free electron)

Expectation value of Momentum of electron in Bloch State $(n\vec{k}_0)$

or simply $\boxed{\vec{P}_{nn}(\vec{k}) = \frac{m}{\hbar}\nabla_{\vec{k}} E_n(\vec{k})}$ and $\boxed{\vec{v}_n(\vec{k}) = \frac{1}{\hbar}\nabla_{\vec{k}} E_n(\vec{k})}$ (36)

- For an electron in Bloch state $\psi_{n\vec{k}}$ ($|n\vec{k}\rangle$), it contributes $\underbrace{(-e)\vec{v}_n(\vec{k})}_{\frac{(-e)}{\hbar}\nabla_{\vec{k}} E_n(\vec{k})}$ to the current as it has $\underbrace{\text{velocity}\ \vec{v}_n(\vec{k})}$

keeps on moving in real space

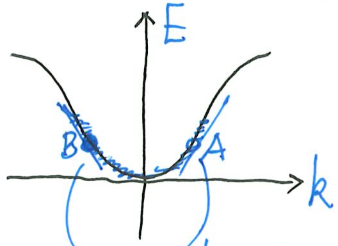


$\boxed{\text{slope} \sim v(k)}$

$\underbrace{\text{keeps on moving in real space}}$

perfect lattice $[V(\vec{r})]$ does not give resistance!

- But no net current at equilibrium [no external $\vec{\mathcal{E}}$-field]



if state A is filled, state B of same energy is also filled

opposite slopes $\Rightarrow$ their contributions to current cancel

Same argument for pairs of occupied states (related to $E_n(\vec{k}) = E_n(-\vec{k})$)

- It follows that a full band has NO net current.

$$\left(\frac{1}{m^*}\right)_{\alpha\beta} = \frac{1}{\hbar}\frac{\partial^2 E_n(\vec{k})}{\partial k_\alpha \partial k_\beta} = \frac{1}{m}\delta_{\alpha\beta} + \frac{1}{m^2}\sum_{n'(\neq n)} \frac{p_{\alpha,nn'}(\vec{k})\, p_{\beta,n'n}(\vec{k}) + p_{\beta,nn'}(\vec{k})\, p_{\alpha,n'n}(\vec{k})}{E_n(\vec{k}) - E_{n'}(\vec{k})} \qquad (37)$$

n^{th} band

inverse effective mass tensor (for the state $(n, \vec{k})$) (This generalized Eq. (17))

n^{th} band at $\vec{k}$

Electron in a solid (influenced by $V(\vec{r})$) becomes a quasi-particle[+]

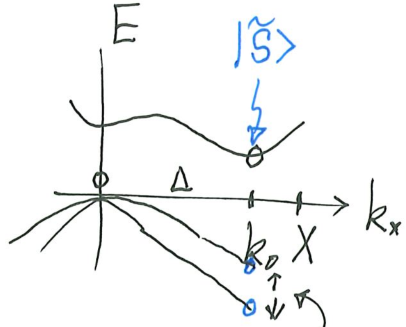
	Free electron	Electron in Crystal
Wave-function	$e^{i\vec{k}\cdot\vec{r}}$	$e^{i\vec{k}\cdot\vec{r}}\, u_{n\vec{k}}(\vec{r})$
Energy Eigenvalue	$\frac{\hbar^2 k^2}{2m}$	$E_n(\vec{k})$
Expectation value of momentum	$\hbar\vec{k}$	$\frac{m}{\hbar}\vec{\nabla}_{\vec{k}} E_n(\vec{k})$
$\frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k_\alpha \partial k_\beta}$	$\frac{1}{m}\delta_{\alpha\beta}$	Eq. (37) (long expression)

(38)

[+] Quasi-particles and collection excitations are two important concepts emerged from interacting systems

(b) Conduction Band edge of Si at $\vec{k}_0 = (k_0, 0, 0)$ ↖ ~80% from Γ to X

(just the idea)



The band (CB) edge state $|\tilde{S}\rangle$ (anti-bonding with s-character)

VB at $\vec{k}_0$: $|Y\rangle, |Z\rangle$ (p_y, p_z character) (same energy) — upper (degenerate)

$|X\rangle$ (p_x character mixed with bonding s) — lower

different in energy

Then at $\vec{k}_0$: $\frac{\hbar}{m}\langle\tilde{S}|\hat{p}_y|Y\rangle = \frac{\hbar}{m}\langle\tilde{S}|\hat{p}_z|Z\rangle \neq \frac{\hbar}{m}\langle\tilde{S}|\hat{p}_x|X\rangle$ are the only nonzero elements

and $E_{CB}(k_0) - E_{VB1}(k_0) > E_{CB}(k_0) - E_{VB2}(k_0)$

Eq. (34) then gives for $(k_x - k_0, k_y, k_z) = \vec{k}$ $(\approx \vec{k}_0)$:

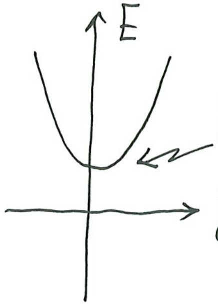
$$E_{CB}(\vec{k}) = E_{CB}(\vec{k}_0) + \frac{\hbar^2 (k_x - k_0)^2}{2m_\ell^*} + \frac{\hbar^2 k_y^2 + \hbar^2 k_z^2}{2m_t^*} \qquad (39)$$

(as discussed earlier)

The point is: can always take the principal axes so that anisotropic band is described by m_1^*, m_2^*, m_3^*

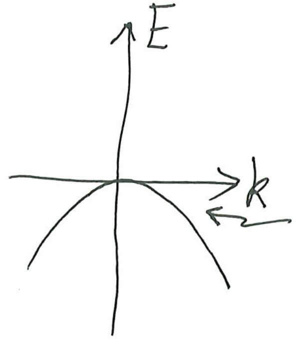
F. Concept of Holes

- Recall: Electron's effective mass $\left(\frac{1}{m^*}\right)_{\alpha\beta} = \frac{1}{\hbar^2} \frac{\partial^2 E(\vec{k})}{\partial k_\alpha \partial k_\beta}$ for a band



(say, isotropic) → $m_e^* > 0$

emphasizes electron viewpoint



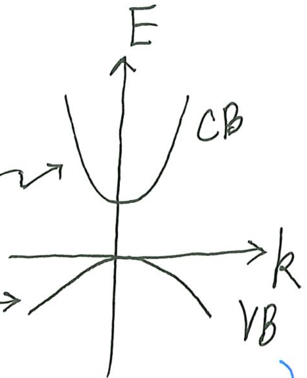
$m_e^* < 0$

emphasizes electron viewpoint

- Semiconductor

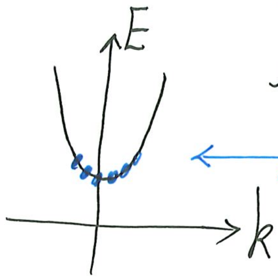
empty

full (completely filled by electrons)

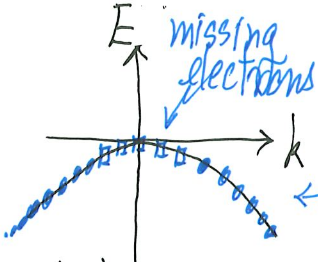


extra electrons will go into bottom of CB

missing electrons will be in the states of top of VB



describe the physics by the behavior of the few electrons in CB



electron viewpoint

describing the physics of the few missing electrons will be convenient

From electron viewpoint,

- the few electrons in CB sink (near bottom of CB)
- the few missing electrons in VB float (near top of VB)

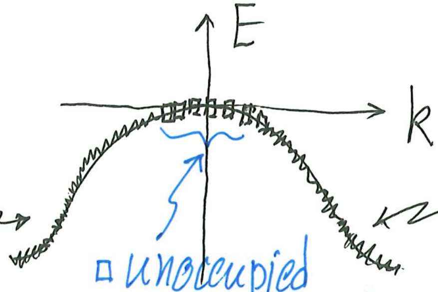
$\underbrace{\text{missing electrons in VB float}}_{\text{this is often referred to as "holes float"}}$

this is often referred to as $\underbrace{\text{"holes float"}}_{\text{but be careful!}}$

but be careful!

This is just a slogan as holes are more than the missing electrons

Hole concept is useful in



typical VB (Nearly-full band)

Recall: For FULL Band, Total $\vec{k}$ (sum over all $\vec{k}$-values) = 0
Total spin = 0, Total $\vec{v}_{\vec{k}} = 0$.

[The trick is to keep on adding zeros!]

(i) Total spin of electrons in nearly-full band

$$\vec{S} = \underbrace{\sum_{\substack{\text{occupied states}\\(\vec{k},s)}} \vec{s}_{\vec{k}}}_{\text{electron viewpoint}} = \underbrace{\sum_{\text{occupied states}} \vec{s}_{\vec{k}} + \sum_{\text{unoccupied states}} \vec{s}_{\vec{k}}}_{\substack{\text{full band}\\(\text{NET } \vec{S}_{full}=0)\\(\text{all } \uparrow,\downarrow \text{ filled})}} - \sum_{\text{unoccupied states}} \vec{s}_{\vec{k}} = \underbrace{\sum_{\text{unoccupied states}} (-\vec{s}_{\vec{k}})}_{\text{up to here, still electron viewpoint}}$$

negative of the spin of the missing electron at $\vec{k}$

can view it as

$$\boxed{\sum_{\text{occupied hole states}} \vec{s}_h}$$

(ii) Total crystal momentum of electrons

$$= \sum_{\substack{\text{occupied}\\\text{states}}} \hbar\vec{k} = \underbrace{\sum_{\substack{\text{occupied}\\\text{states}}} \hbar\vec{k} + \sum_{\substack{\text{unoccupied}\\\text{states}}} \hbar\vec{k}}_{\text{full band (all cancelled)}} - \sum_{\substack{\text{unoccupied}\\\text{states}}} \hbar\vec{k} = \underbrace{\sum_{\substack{\text{unoccupied}\\\text{states}}} (-\hbar\vec{k})}_{\text{still in electron viewpoint}} = \sum_{\substack{\text{unoccupied}\\\text{states}}} (-\hbar\vec{k}_e)$$

emphasizes it is the electron's "$-\hbar\vec{k}$" here (for the empty states)

equivalent to a few entities (called holes), each has crystal momentum $\hbar\vec{k}_h$, with $\vec{k}_h = -\vec{k}_e$

can view it as

$$\sum_{\substack{\text{occupied hole}\\\text{states}}} (\hbar\vec{k}_h)$$

only a few

e.g. all $\vec{k}$'s are occupied except one state $\vec{k}_e$ (many electrons, one empty state)

$\Updownarrow$

one hole of $(-\vec{k}_e) = \vec{k}_h$ (one quasi-particle "hole")

(iii) Electric Current Density

$$\vec{J} = \frac{-|e|}{V}\sum_{\text{occupied}} \vec{v}_{\vec{k}} = \underbrace{\frac{-|e|}{V}\sum_{\text{occupied}} \vec{v}_{\vec{k}} + \frac{-|e|}{V}\sum_{\text{unoccupied}} \vec{v}_{\vec{k}}}_{\text{full band (zero)}} + \frac{|e|}{V}\sum_{\text{unoccupied}} \vec{v}_{\vec{k}} = \frac{|e|}{V}\underbrace{\sum_{\text{unoccupied}}}_{\text{still electron viewpoint}} \vec{v}_{\vec{k}}(\vec{k}_e)$$

Volume of crystal

electron's charge $-|e|$

$\vec{J}$ has units of $\frac{\text{charge}}{\text{area} \cdot \text{time}}$

can view it as

$$\boxed{\sum_{\substack{\text{occupied}\\ \text{hole states}}} \frac{|e|}{V}\vec{v}_h(\vec{k}_h) = \sum_{\substack{\text{occupied}\\ \text{hole states}}} \frac{e_h}{V}\vec{v}_h(\vec{k}_h)}$$

$\therefore \quad e_h = -|e|$

$$\underbrace{\vec{v}_h(\vec{k}_h)}_{\substack{\text{slope of hole}\\ \text{band } E_h(\vec{k}_h)\\ \text{at } \vec{k}_h}} = \underbrace{\vec{v}_e(\vec{k}_e)}_{\substack{\text{slope of electron}\\ \text{band } E_e(\vec{k}_e)\\ \text{at } \vec{k}_e}} \quad (\text{but } \vec{k}_h = -\vec{k}_e)$$

where the empty state is

(iv) Energy Current Density

$$\vec{J}_E = \frac{1}{V}\sum_{\substack{\text{occupied}\\ \text{states}}} \underbrace{E(\vec{k})}_{\substack{\text{energy of}\\ \text{an occupied}\\ \text{state (band structure)}}} \vec{v}(\vec{k}) = \underbrace{\frac{1}{V}\sum_{\substack{\text{occupied}\\ \text{states}}} E(\vec{k})\vec{v}(\vec{k}) + \frac{1}{V}\sum_{\substack{\text{unoccupied}\\ \text{states}}} E(\vec{k})\vec{v}(\vec{k})}_{\text{full band (zero)}} - \underbrace{\frac{1}{V}\sum_{\substack{\text{unoccupied}\\ \text{states}}} E(\vec{k})\vec{v}(\vec{k})}_{\text{still electron viewpoint}}$$

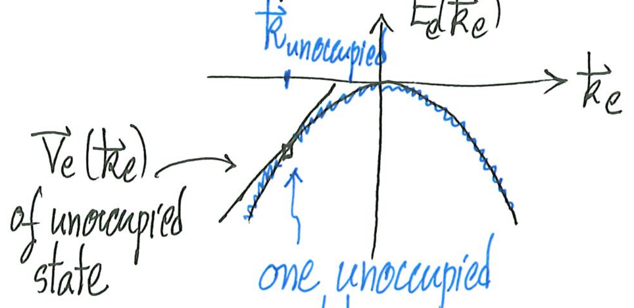
$$= \underbrace{\frac{1}{V}\sum_{\substack{\text{occupied hole}\\ \text{states}}} E_h(\vec{k}_h)\vec{v}_h(\vec{k}_h)}_{\text{view as contributed by a few holes}}$$

$$\underbrace{E_h(\vec{k}_h)}_{\substack{\text{hole}\\ \text{band}}} = \underset{\text{negative}}{-}\underbrace{E_e(\vec{k}_e)}_{\text{electron band}}$$

The net effects of many electrons in a <u>nearly-full band</u> can be obtained by regarding the contributions as coming from some (a few) fictitious entities called <u>Holes</u> with the properties

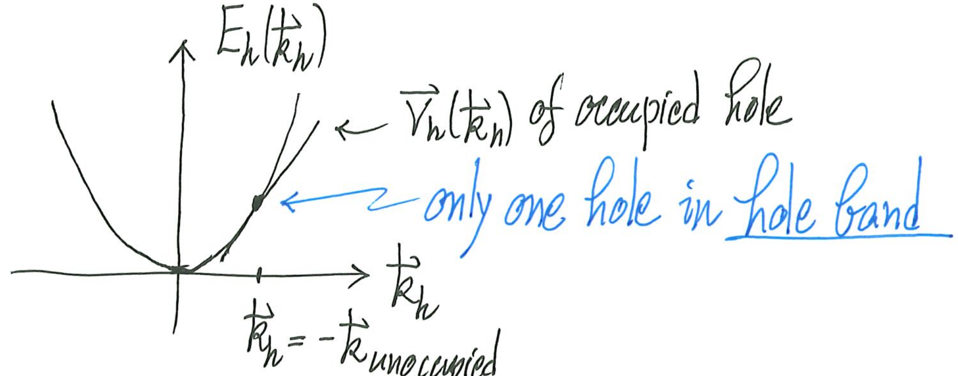
$$\boxed{\begin{array}{l} e_h = |e| \quad , \quad \vec{k}_h = -\vec{k}_e \\ \vec{v}_h(\vec{k}_h) = \vec{v}_e(\vec{k}_e) \; , \quad E_h(\vec{k}_h) = -E_e(\vec{k}_e) \\ \vec{S}_h = -\vec{S}_e \end{array}} \qquad (40)$$

The picture that emerged is:

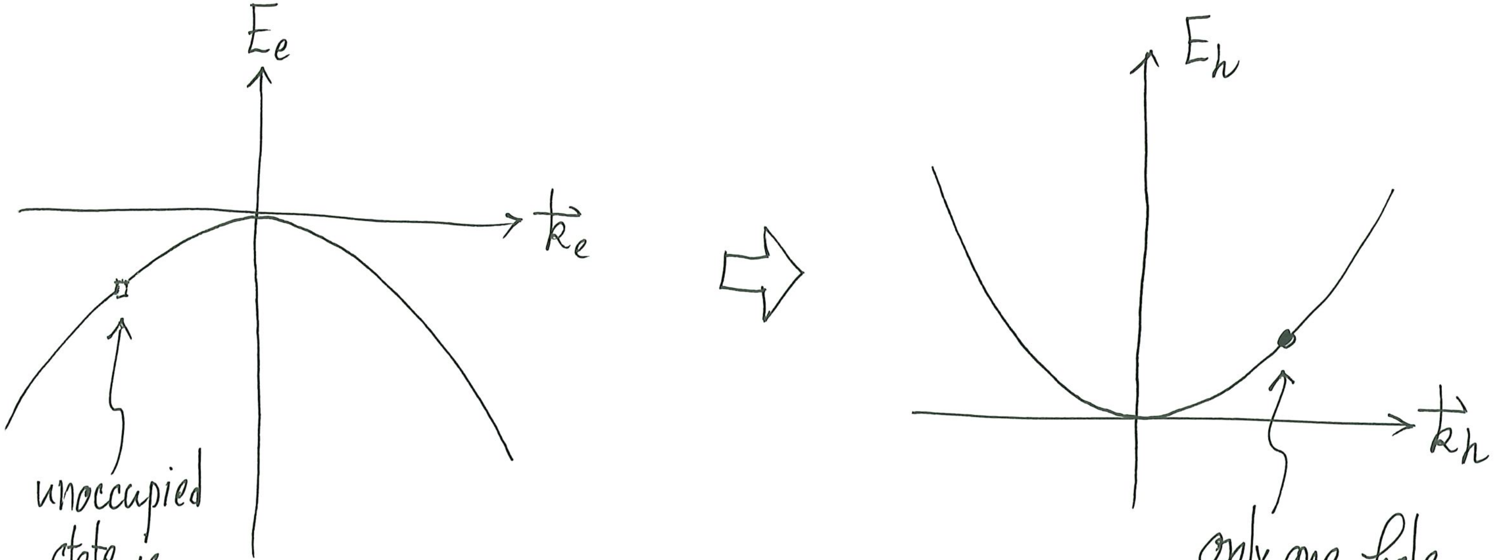


<u>Electron Band Picture</u>
(many electrons)

(like rotating band about axis ⊥ paper)



<u>Hole Band Picture</u> (one hole)
(actually, hole also sinks in hole band as missing electrons in VB float)



unoccupied state is $(\vec{k}_e, \downarrow)$

(nearly full, only $(\vec{k}_e, \downarrow)$ is empty)

only one hole of $(\vec{k}_h = -\vec{k}_e, \uparrow)$ in hole picture

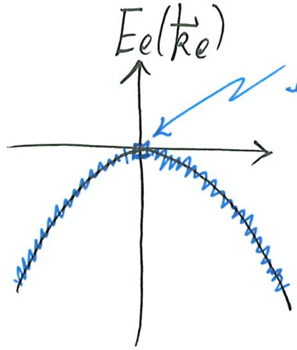
This is the meaning of $\underset{\text{that of hole}}{\vec{S}_h} = \underbrace{-\vec{S}_e}_{\text{negative of the spin of the unoccupied electron state}}$

The effective mass of a hole follows as:

$$\left(\frac{1}{m_h^*}\right)_{\alpha\beta} = \frac{1}{\hbar^2}\frac{\partial E_h(\vec{k}_h)}{\partial k_{h\alpha}\partial k_{h\beta}}$$ (definition) (all quantities in hole picture)

$$= -\frac{1}{\hbar^2}\frac{\partial E(\vec{k}_e)}{\partial k_\alpha \partial k_\beta}$$ for the empty (unoccupied) electron state (all quantities in electron picture)

$$= -\left(\frac{1}{m_e^*}\right)_{\alpha\beta}$$ for the empty unoccupied electron state



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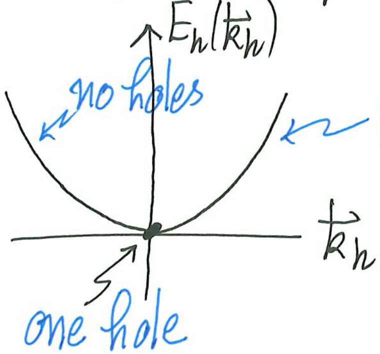

$$E_e^{(VB)}(\vec{k}_e) = -\frac{\hbar^2 k_e^2}{2\underbrace{m_h^*}_{\text{positive}}}$$ (so that $m_e^* = -m_h^*$ is negative)

positive hole effective mass $E_h(\vec{k}_h) = \dfrac{\hbar^2 k_h^2}{2\underbrace{m_h^*}_{m_h^* > 0}}$

m_h^* (m_{hh}^*, $m_{\ell h}^*$, m_{so}^*) are cited as positive quantities for VB's.