భారతీయ సాంకేతిక విజ్ఞాన సంస్థ హైదరాబాద్
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Part 2: Band theory of solids

Q: How do electrons (and holes) behave when constrained in a periodic arrangement of atoms (lattice)?

Topics: Formation of bands, qualitative understanding, Kronig Penney Model, mobility and effective mass.

EE2104: Semiconductor Device Fundamentals

EE, IIT Hyderabad

Shubhadeep B (shubhadeep@ee at iith)

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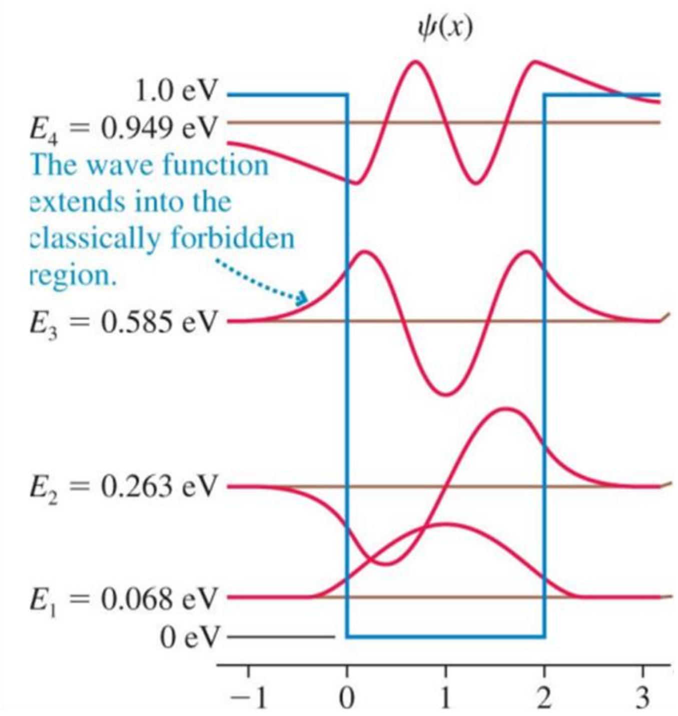
Electronic Levels in Atoms

Recap: Particle in a finite square Well → **Atoms: electrons in a finite hyperbolic well**

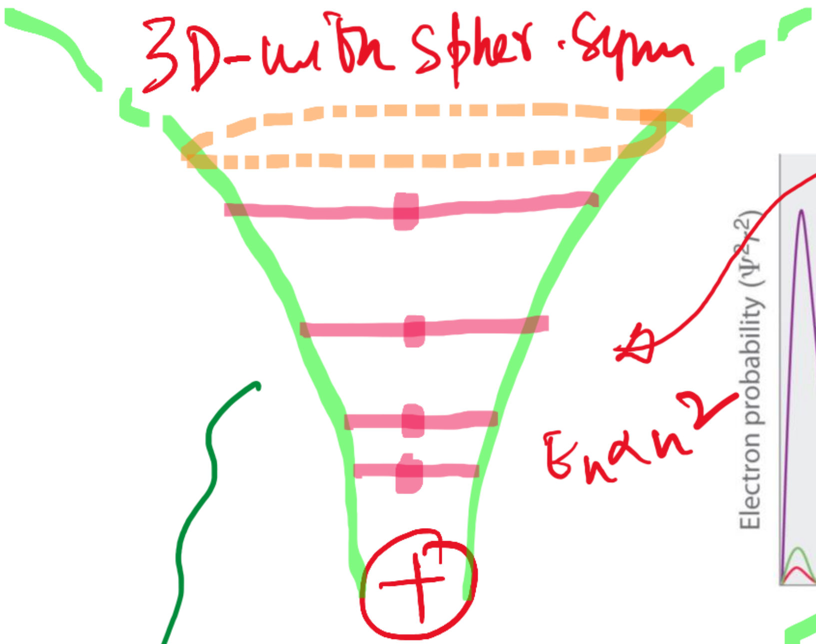
Let's consider simplest H-atom.

particle = electron; V(x) → electrostatic potential {nuclei}



$$V(x) = \begin{cases} 0 & 0 \le x \le L \\ U_0 & \text{elsewhere.} \end{cases}$$

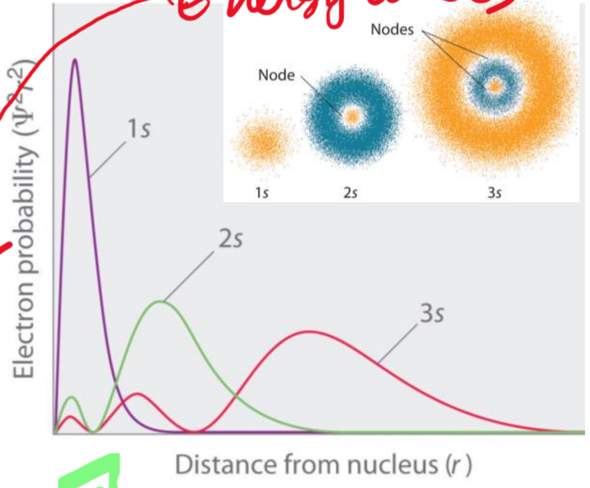
$\boxed{E_n \propto n^2}$



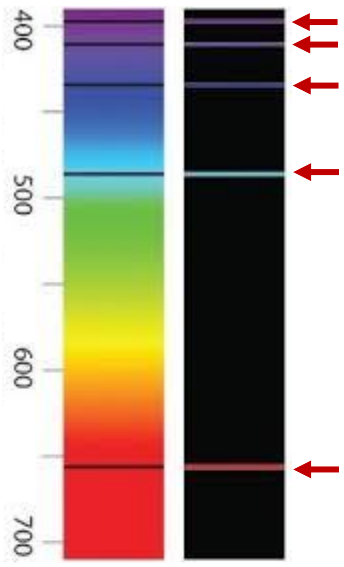
$E_n \propto n^2$

atomic orbitals, probability cloud

Energy levels



Theory validated quantitatively with expt H- spectrum!



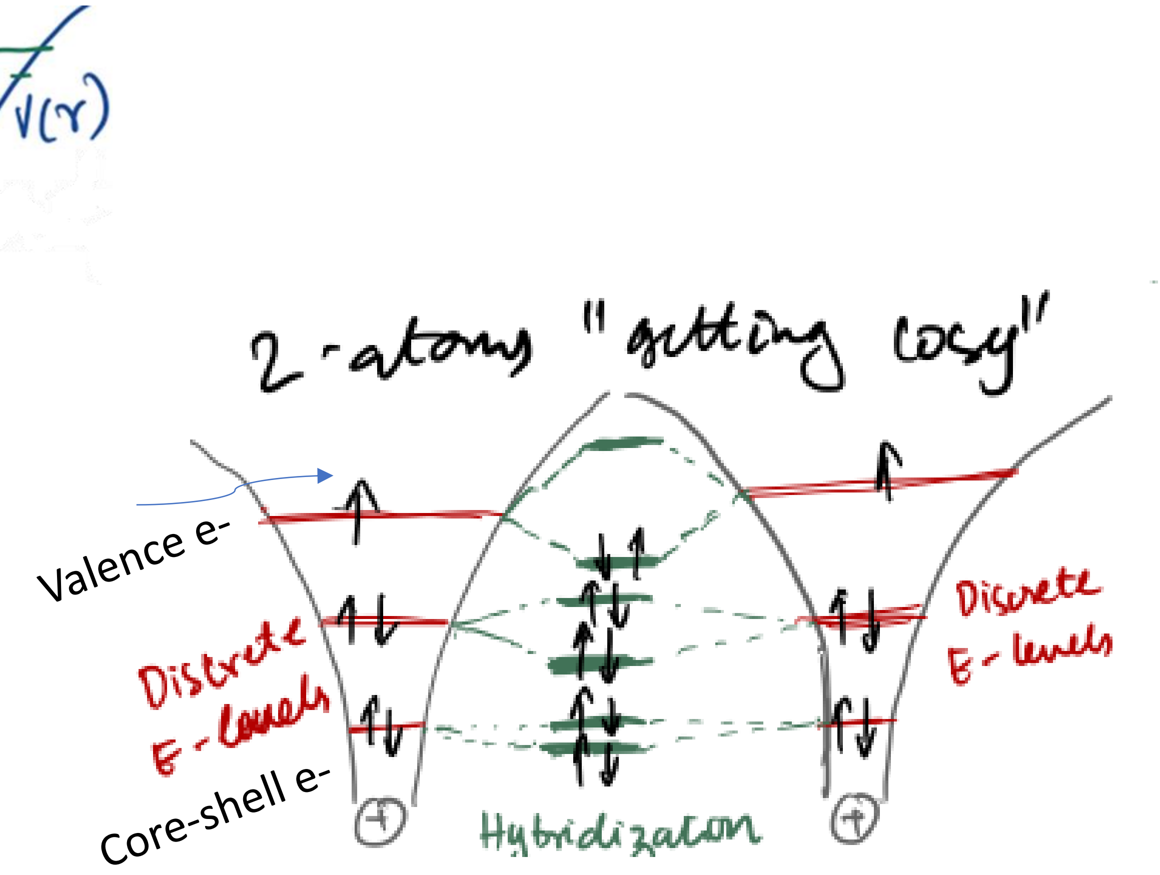
$$V(r) = \frac{-q^2}{4\pi\varepsilon_0 r}$$

$$-\frac{\hbar^2}{2m^*}\nabla^2\psi + V(r)\psi = E\psi$$

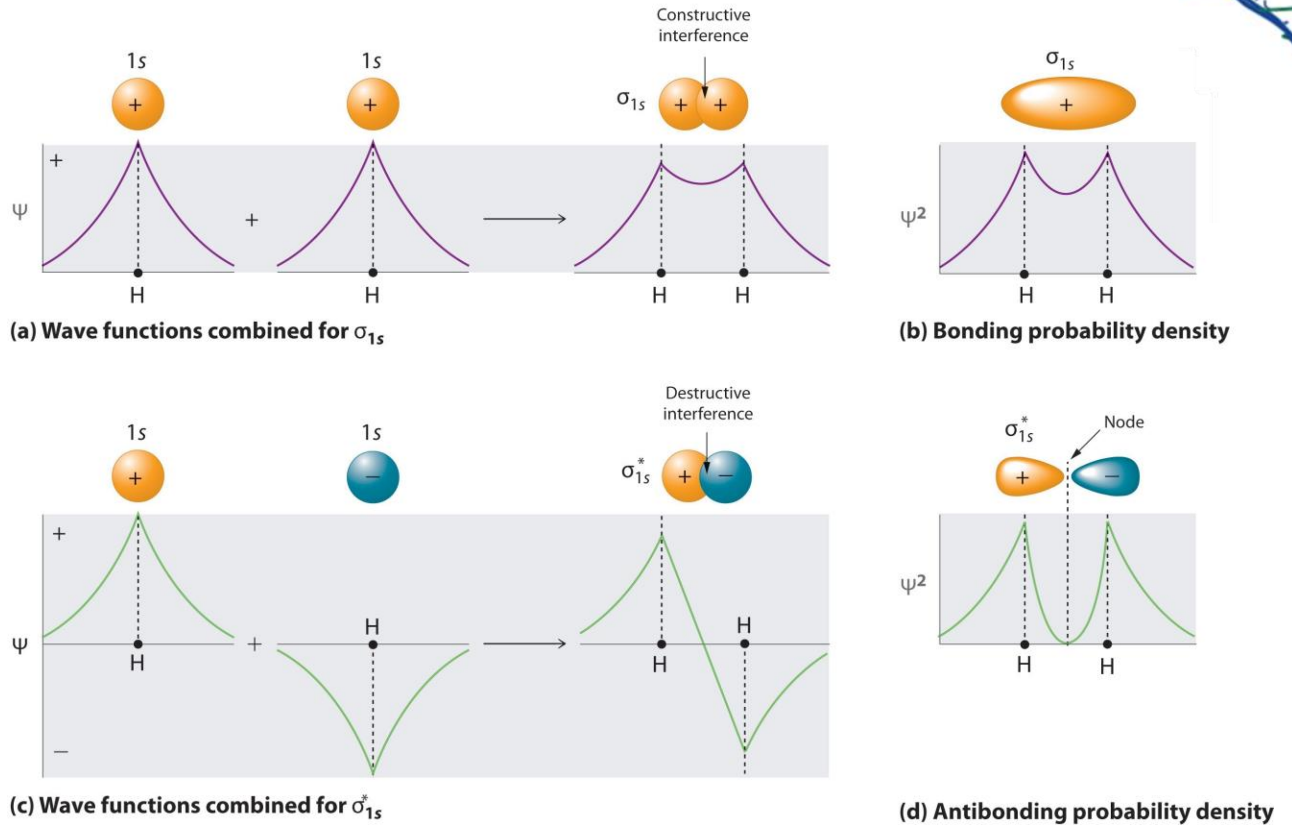
$\psi(r,\theta,\phi) \to 3D$

Solving SCE in 3D.

From 1 atom to 2 atoms – splitting of energy levels



Linear Combination of Atomic Orbitals (LCOA)



- Two Identical atoms far apart: ψ_1, ψ_2 no overlap.
- Close to interatomic distances: constructive and destructive interference in ψ_1, ψ_2
- LCOA: Formation of BO ($\psi_1 + \psi_2$) and ABO ($\psi_1 - \psi_2$) Molecular orbitals
- Splitting of Energy levels – Lower contribute to bonding.
- Split in energies valence electron >> core-shell electrons

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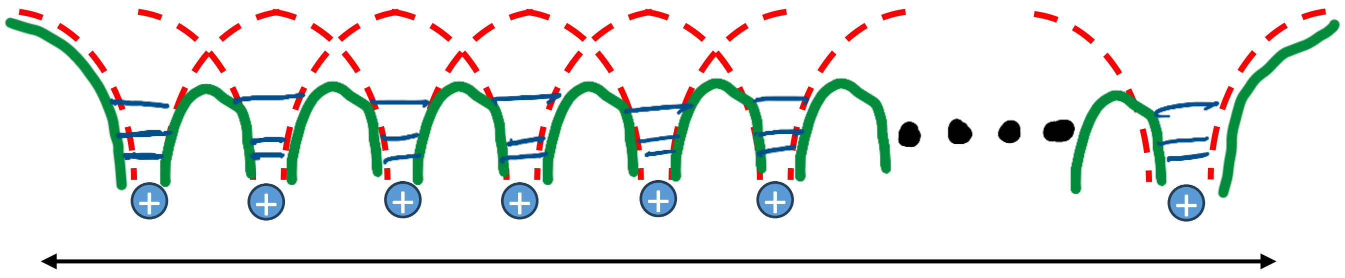
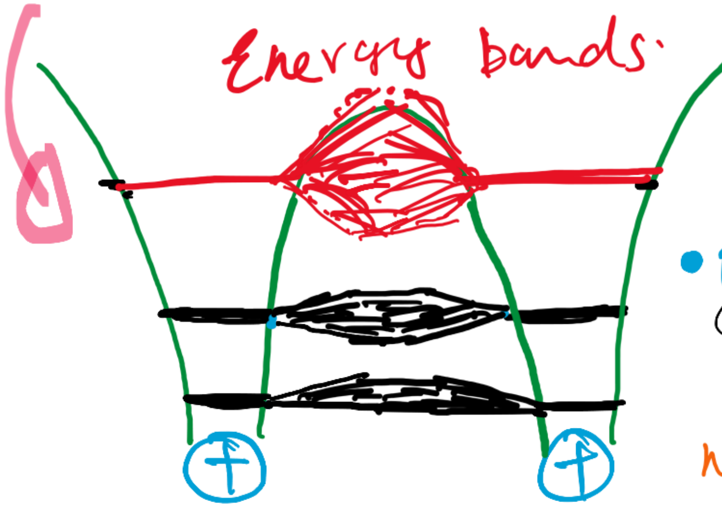
From 2 to *n* atoms – formation of ***energy bands***! (Qualitative)

Let's take 1-D chain of atoms

- - - 1-atom V(x) — resultant V(x)



lattice length 'L', 1-D chain 'n' atoms



— core-shell — valence

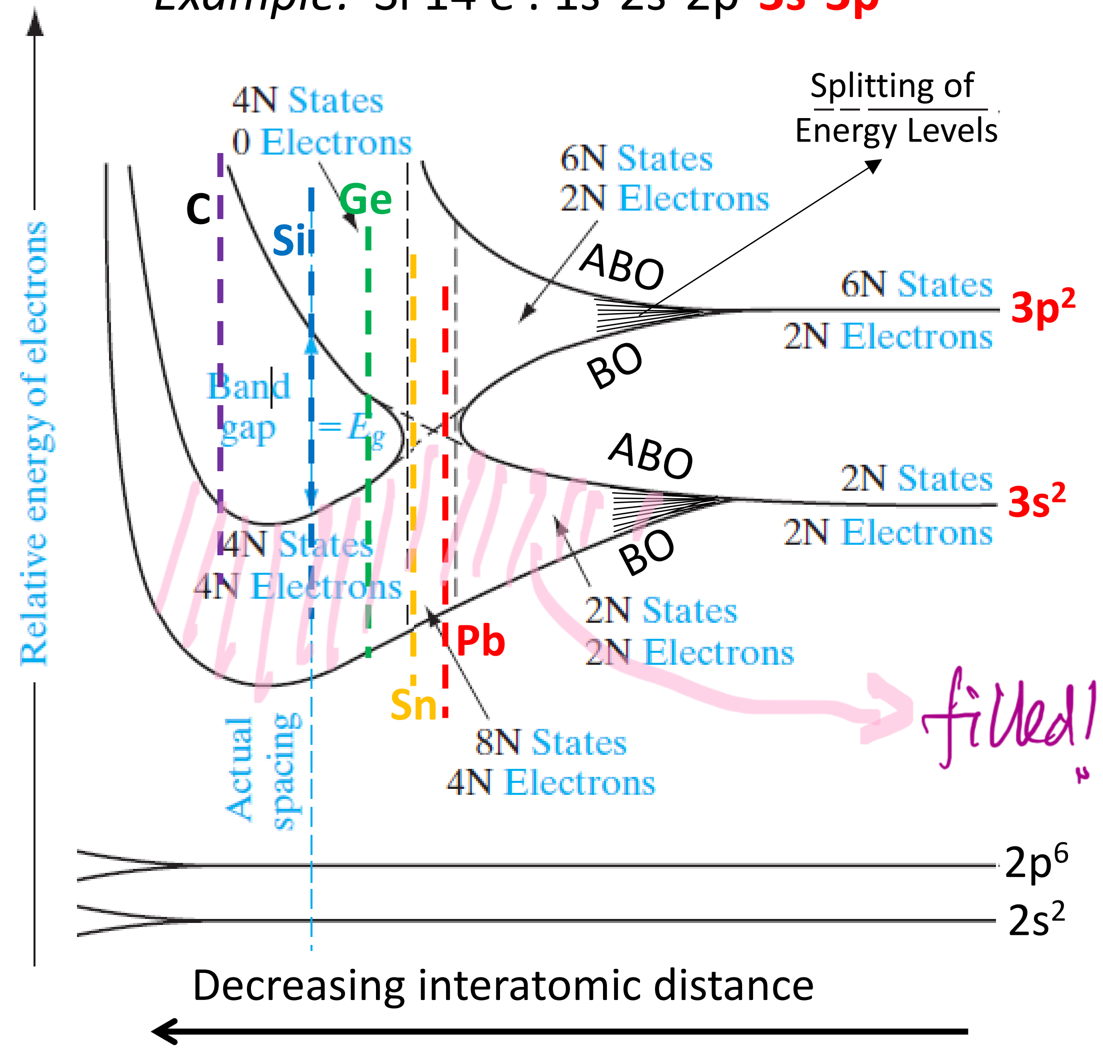
• n-discrete Energy levels / allowable states.

• Unequal splitting (based on ψ overlap)

① nearest neighbour

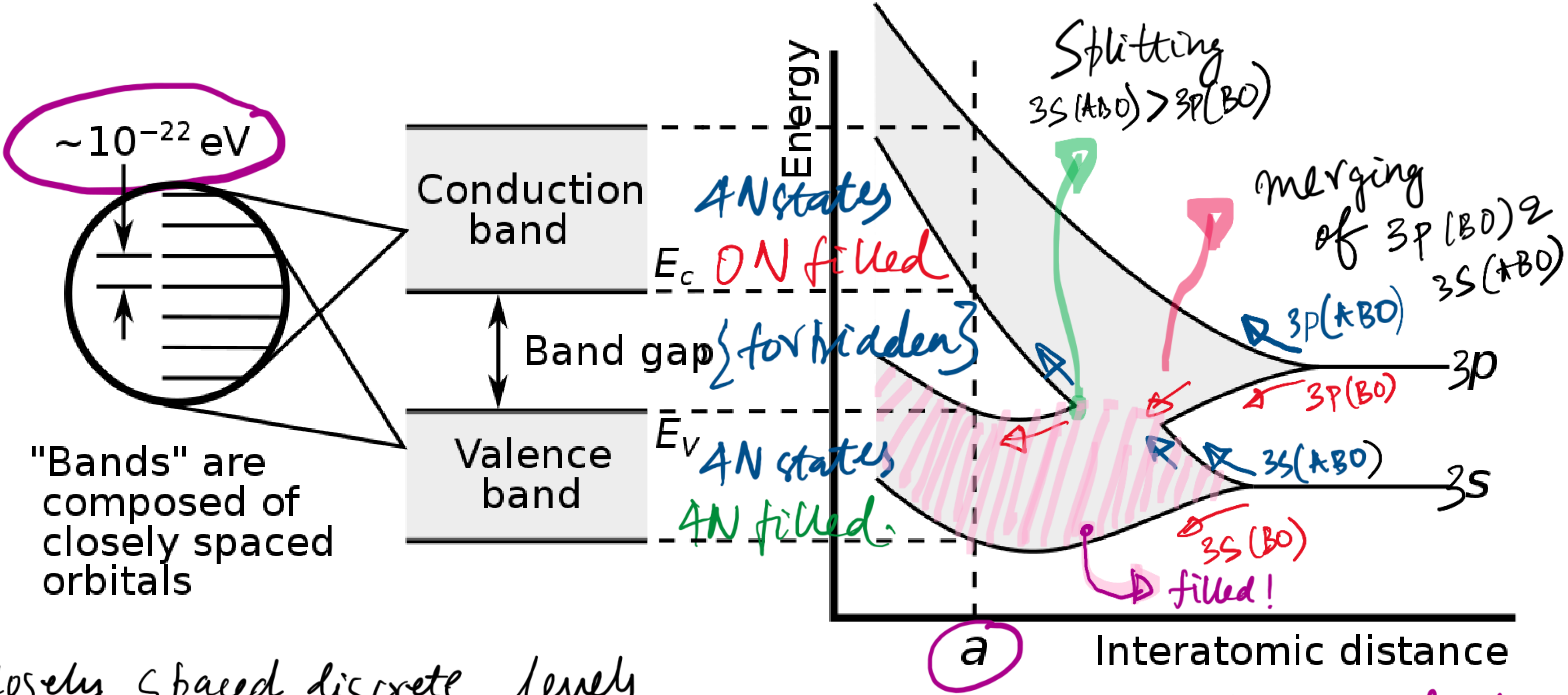
② core-shell vs. Valence e^-

Example: Si 14 e^-: $1s^2 2s^2 2p^6 \mathbf{3s^2 3p^2}$



E_g [C = 5.4 eV, Si 1.1 eV, Ge 0.7 eV, Sn and Pb =0 eV]

Qualitative understanding of Valence and conduction bands



equilibrium atomic distance.

Very closely spaced discrete levels

⇒

Continuous Energy "bands"

From qualitative understanding to quantitative models

Good to have Qualitative understanding about physical reality,
But as Electrical Engineers all we care: Apply *V/E* what is the *I/J*

$J = \sigma E$ {Drude's law} σ {conductivity} $= q\, n\, \mu$

n (cm^{-3}) → # free carriers available for conduction.

μ ($cm^2 V^{-1} s^{-1}$) → on application of Electric field how fast these carriers move

→ V_d / E drift velocity.

Q:- Can we get quantitative estimates

YES!

#1 μ

"E-K" → Band-structure {Intrinsic property}
{This section}

#2 n {Next section}

→ Equilibrium carr. statistics (of what?)

$$n(E) = \int g(E)\, f(E)\, dE$$

Energy

{intrinsic} no. of states an e^- can occupy [Energy] ×

{TUNABLE} probability of finding an e^- [E]

Closer look at mobility (μ)

Mobility (μ) :- how quickly charged particles [e^- / h^+] can move [drift, V_d] when subjected to external electric field [E]

drift vel. — mobility — ext. Elec field

$$v_d = \mu E_{ext}$$

* v_d: cm/s
* μ: $cm^2V^{-1}s^{-1}$
* E_{ext}: $V cm^{-1}$

{Small E_{ext} only}

What does mobility physically depend on?

$$\mu = \frac{q\,\tau_{avg}}{m^*}$$

$\tau_{avg} \rightarrow$ (s), $m^* \rightarrow$ (kg)

Easy derivation: HW

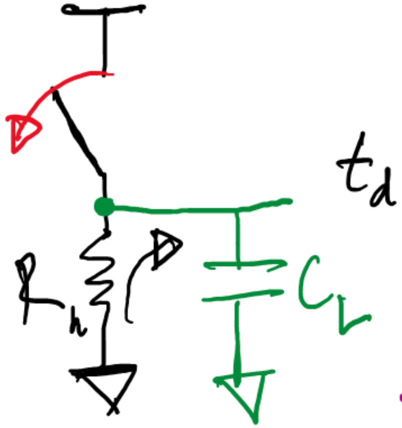
$\tau_{avg} \rightarrow$ avg relaxation time.
$m^* \rightarrow$ effective mass of charged particle

Practical Importance of mobility:

- Obsession with high mobility materials and devices
- Mobility modelling and engineering

Mobility determines how quickly the device reacts to external stimuli (Elec field, hv)

Example: propagation delay of CMOS



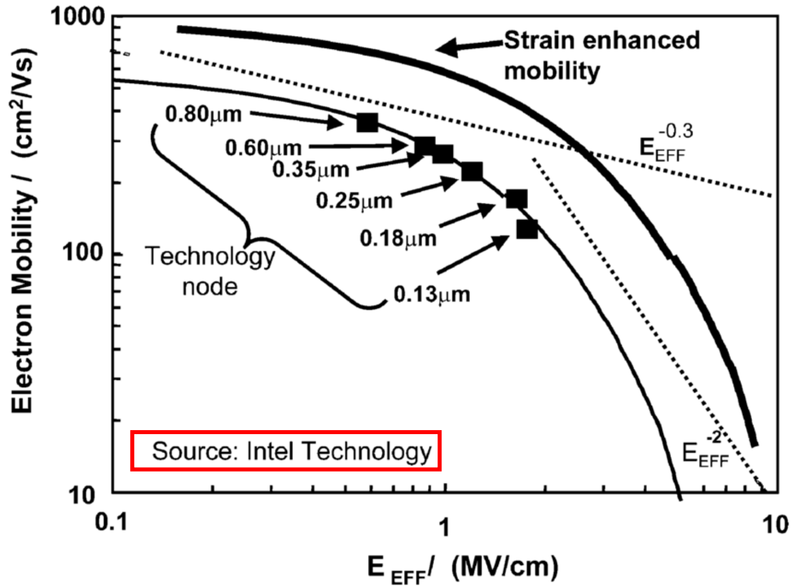
CMOS Inverter delay

$$t_d = 0.69 R_n C_L \propto \frac{1}{I_{dsat}} \propto \frac{1}{\mu}$$

$\mu\uparrow$ $t_d\downarrow$ $f_T\uparrow$

* CGS units are convention in this field

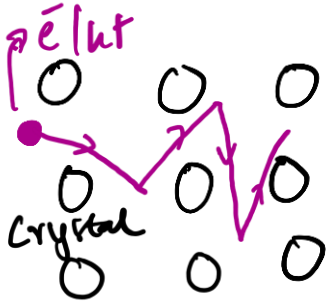
μ degradation with scaling – major bottleneck ☹
Why? How was it solved?



Closer look at mobility (μ) – τ_{avg}

$\mu = q\,\boxed{\tau_{avg}}/m^*$

What does τ_{avg} physically mean?



$\tau_{avg} \equiv$ average time b/w events.

collisions {classical} | SCATTERING {quantum} ↳ Interaction/overlap ψ_e

⇒ In a ideal crystal @ 0 Kelvin ⇒ $\tau_{avg} = \infty$ ⇒ NO SCATTERING!! BLOCHs theorem :- ↳ in periodic lattice! {Coming soon!!}

Why not scattering from + cores?

⇒ However, in real systems, non-idealities

#1 Defects, doping, ionised impurities {DISRUPT LATTICE}

PURITY CRITICAL FOR MOBILITY

#2 T>0K

↳ LATTICE VIBRATIONS

↳ PHONONS! interact scatter e⁻/h⁺

$T\uparrow\ \tau_{avg}\downarrow\ \mu\downarrow$

#3 Others, neutral imp. piezo, surface roughness etc.

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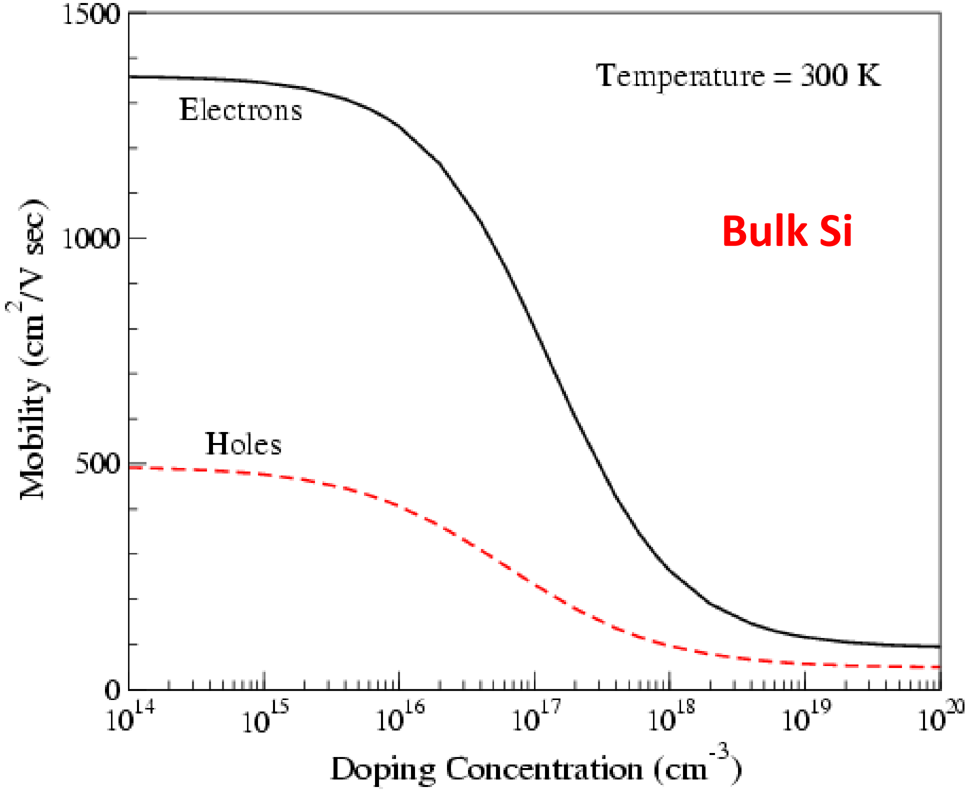
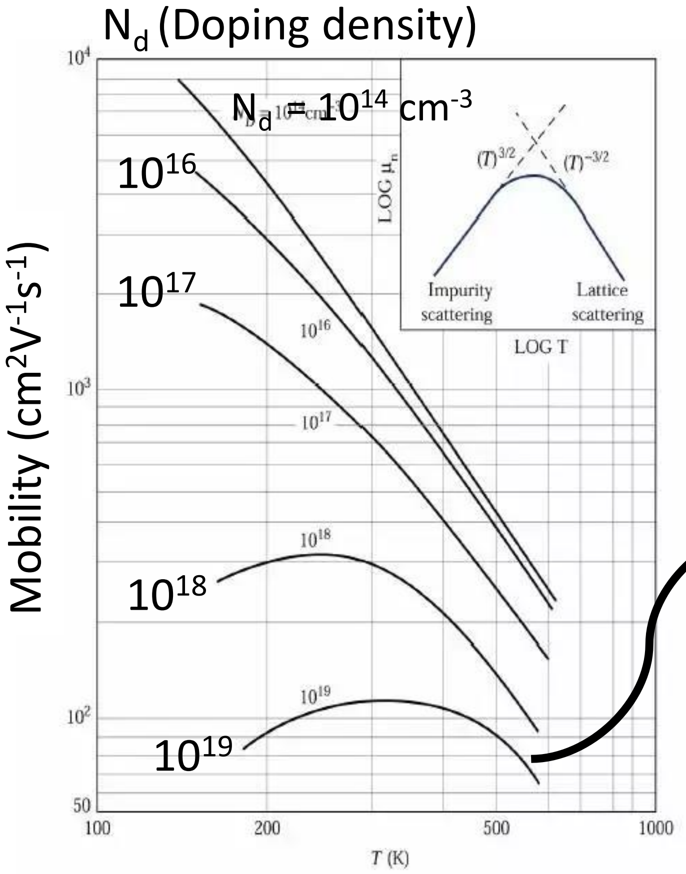
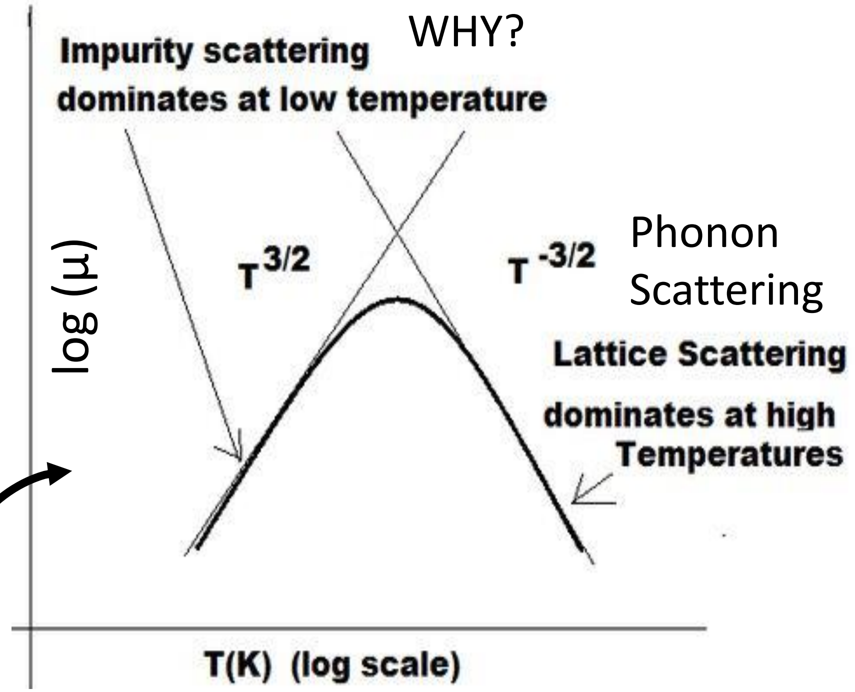
Closer look at mobility (μ) – τ_{avg}

$\mu = q\,\boxed{\tau_{avg}}\,/\,m^*$

Ionized Impurity Scattering







Let's understand these trends!
Why mobility reduces with
(a) N_d (b) Non monotonic
behaviour with high N_d

$$\tau_{avg}^{-1} = \tau_{imp}^{-1} + \tau_{phon}^{-1} + \tau_{others}^{-1}$$

$$\frac{1}{\mu_{Total}} = \frac{1}{\mu_i} + \frac{1}{\mu_p} + \dots$$

SCATTERING EVENTS HAPPEN IN PARALLEL!!

Closer look at mobility (μ) – m*

$\mu = q\,\tau_{avg} / \boxed{m^*}$

Suppose, we apply F_{ext} to e^- in free space

$F_{ext}\{q\,\mathcal{E}_{ext}\} = m_0 \dot{v} = \hbar \dot{k}$ — (1)

Now, we take same $\bar{e}$ inside lattice & ask K obtain same $\{v, k\}$ new F'_{ext}

$F'_{ext} + F_{lat}(x, k, ...) = m_0 \dot{v}$

Force due to lattice ⇒ very difficult to determine

Therefore we do some jugglery,

$F_{ext}\{\text{same as free } e^-\} + F_{lat} = m^* \dot{v}$ — (2)

m^* → effective mass

(2)/(1) ⇒ $m^* = m_0 \left[\dfrac{F_{ext} + F_{lat}}{F_{ext}} \right]$

Intuitively :- m^* helps us simplify complications that come due to the lattice potential.

Analog in mechanics: coefficient of friction

m^* ⇒ property of lattice !!
⇓
{ how conducive to $\bar{e}$ flow }

$m_e^* = 0.1 - 10\, m_e$ for e^- in lattice.

What does this mean??

Understanding m* - effective mass.

Easy- Box seems light

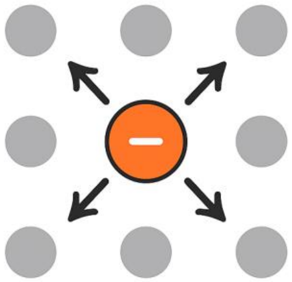
Difficult- Same box seems heavy

Image credits:
ChatGPT

- Same box – seems heavier on gravel vs. ice.
- Therefore 'perceived' mass is not the "property" of the box.
- In is the property of the medium that it is dragged in.
- It's difficult to model $F_{frcition}$ therefore "effective mass"

ELECTRON IN FREE SPACE

ELECTRON IN CRYSTALLINE LATTICE



- Similarly effective mass of e- is property of the medium (crystal lattice, in our case).
- It is a proxy to avoid dealing with F_{lat} various internal forces in the lattice, the e- may "see"
- Turns out there is way to get m* quantitatively.
- m* 0.1 -10 – What does this mean?

Closer look at mobility (μ) – m*

$\mu = q\, \tau_{avg} / \boxed{m^*}$

Determining m* from Lattice Structure.
Simple (mnemonic) NOT derivation.

We saw that e^- in a crystal
↳ no scattering ⇒ as if free particle (m^*)

Actual derivation: Appendix

$$E(k) = \frac{\hbar^2 k^2}{2m^*} \quad -(1)$$

WILL BE SHOWN SOON!

Intution:- Responds to Fext with m^* {as if free!}

Recall, 'k' = $2\pi/\lambda$ also $p = \hbar k$

$$\frac{d^2E(k)}{\partial k^2} = \frac{\hbar^2}{m^*} \Rightarrow \boxed{m^* = \hbar^2\left(\frac{\partial^2 E(k)}{\partial k^2}\right)^{-1}}$$

Conclusion:

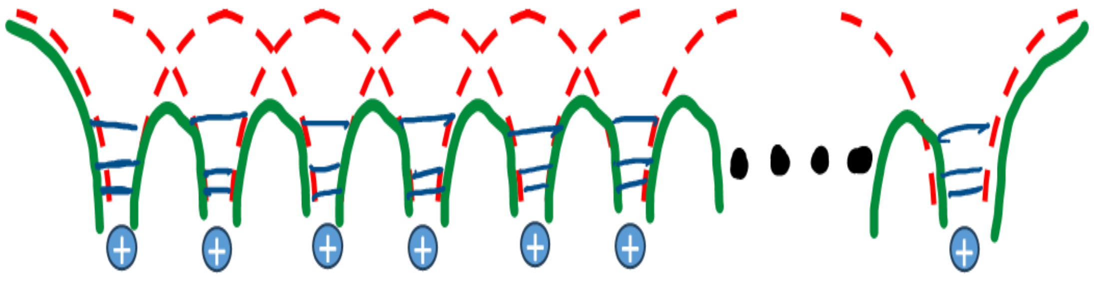
- Difficult to find F_{lat}, so m* (property of lattice!!)
- m* -> as if particle only responds to F_{ext}
- E-k (band-structure, dispersion) necessary to quantify m* - How? Any Ideas?

E-*k*: Kronig Penney Model

How do we obtain E-K relation? {band-structure}

SOLVE SCE for $\bar{e}$ Energies for periodic potential "Crystal"

V(x) in a 1-D chain of Atoms

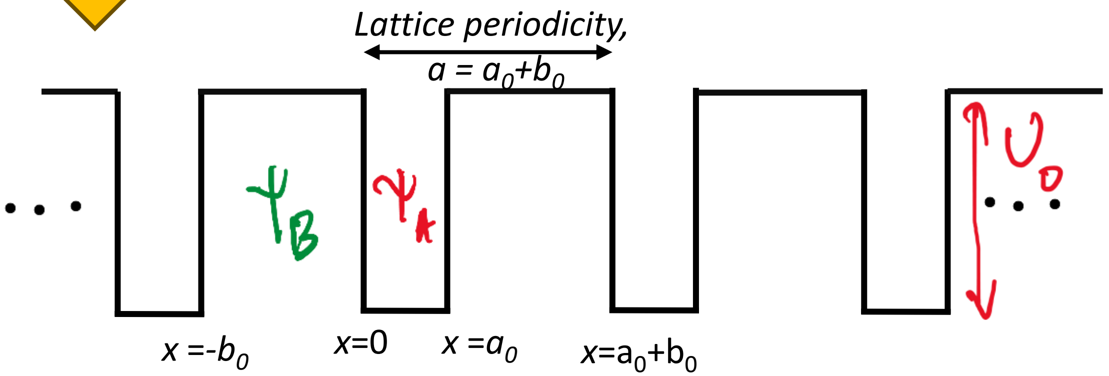


V(x) – mathematically difficult to solve SCE

But notice : Barriers and Wells

Simplified approximation

Kronig Penney model: 1-D Rectangular V(x)



a_0 ≡ width of well; b_0 ≡ width of barrier

#1) Solving SCE @ Region A {WELL}

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi_A}{\partial x^2} = E\,\psi_A$$

$$\psi_A = A_1 \sin(\alpha x) + B_1 \cos(\alpha x);\ \alpha = \frac{\sqrt{2mE}}{\hbar}$$

#2) Solving SCE @ Region B {BARRIER}

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi_B}{\partial x^2} = (E - V_0)\,\psi_B \quad \{E < V_0\}$$

$$\psi_B^* = A_2 \sin(\beta x) + B_2 \cos(\beta x) \rightarrow \beta = i\,\frac{\sqrt{2m(V_0 - E)}}{\hbar}$$

{Imag}

* Can also be written as $A_2' e^{-\beta x} + B_2' e^{+\beta x}$

A_1, A_2, B_1, B_2 } 4 boundary conditions are needed.

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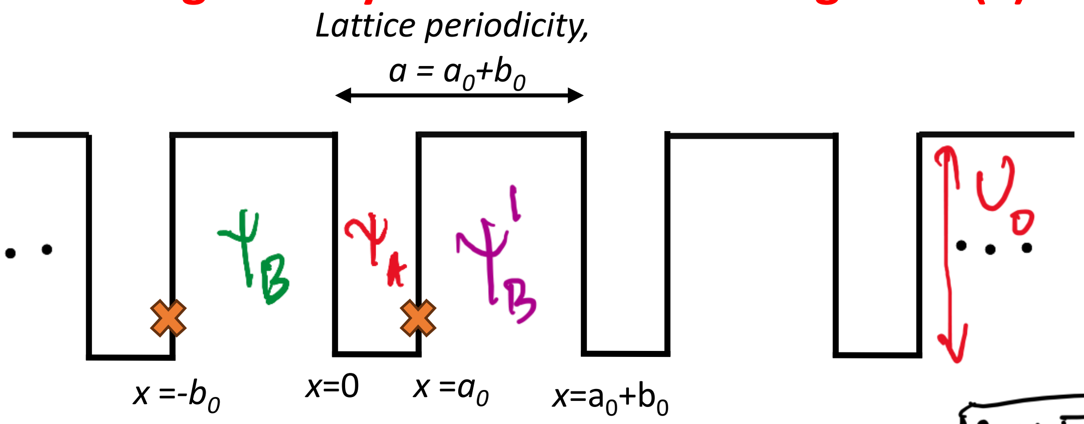
Band structure (E-k): Kronig Penney Model

Kronig Penney model: 1-D Rectangular V(x)



$$\psi_A = A_1 \sin(\alpha x) + B_1 \cos(\alpha x); \quad \alpha = \frac{\sqrt{2mE}}{\hbar}$$

$$\psi_B = A_2 \sin(\beta x) + B_2 \cos(\beta x); \quad \beta = i\frac{\sqrt{2m(V_0-E)}}{\hbar}$$

A_1, A_2, B_1, B_2 ??

Boundary conditions:

① $\psi_A(x=0) = \psi_B(x=0)$

② $\psi'_A(x=0) = \psi'_B(x=0)$

TWO MORE Boundary conditions are needed!

Compare with a particle in box

Let's think intuitively:

- Can we deduce **ψ'$_B$ – neighboring barrier**
- Writing Generic form not useful – will add 2 more variables!

- Look carefully ψ'$_B$ must be related ψ$_B$ (Why should nature differentiate b/w identical wells in an infinite arrangement?)
- Should ψ'$_B$ be identical to ψ$_B$ - No BC different!

- Probability of finding e$^-$ @x=0 and x= a=a_0+b_0 should be same!
  $|\psi'_B(x=a)|^2 = |\Psi_b(x=0)|^2$ OR $|\psi'_B(x=a)| = |\Psi_b(x=0)|$

- More generically, in a periodic lattice V(x),
  $|\psi(x)| = |\psi(x+a)|$ a= lattice constant

meets condition

Blochs' theorem (w/o proof), In a periodic V(x) soln to SCE:

$$\psi_k(x) = e^{ikx} u_k(x) \text{ where } u_k(x) = u_k(x+a)$$

Soln to SCE in a periodic V(x), $\Psi_k(x)$ is a plane wave (e^{ikx}) modulated by a periodic func ($u_k(x)$) with same period as lattice.

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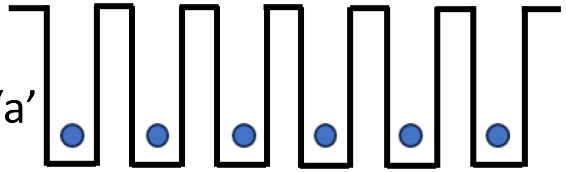
Insights into Bloch's theorem

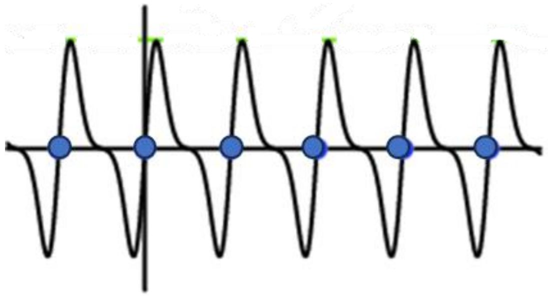
$\psi_k(x) = e^{ikx} u_k(x)$ $\quad u_k(x) = u_k(x+a)$

Plane-wave e^{ikx} modulated by periodic

$V(x)$
period 'a'

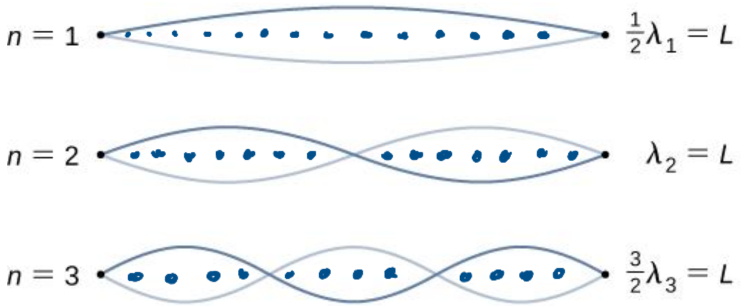


$u_k(x) \neq V(x)$
period 'a'



What values can k take in e^{ikx} $\quad \lambda_n = \frac{2}{n} L$

|Ψ| periodic and confined to L : standing waves!



$k_1 = \frac{2\pi}{2L}$

$k_2 = \frac{2\pi}{L}$

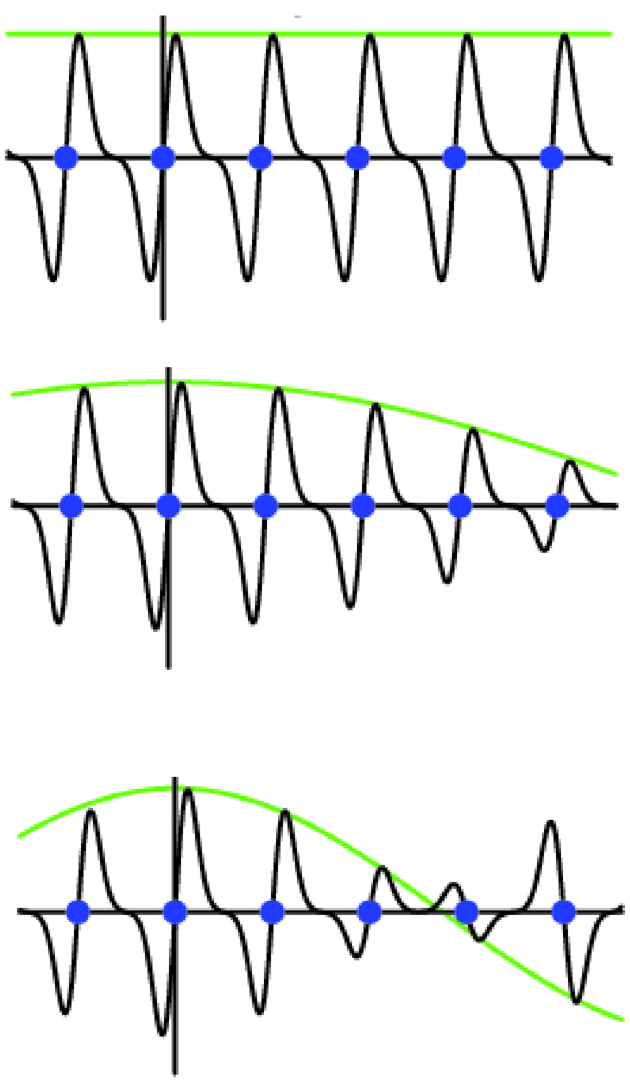
$k_3 = \frac{2\pi}{2/3 L}$

$\lambda = 2a$

$\lambda = 2a$ $\quad k_n = \frac{2\pi}{2a}$

$\psi_k(x)$

k_1



Important insights:

k is discrete, but L ~ mm, a ~ Angstrom

k_{min}, $\Delta k = 2\pi/\lambda_{max} = 2\pi/2L \sim 10^3$
$k_{max} = 2\pi/\lambda_{min} = 2\pi/2a \sim 10^{10} >> \Delta k$

All practical purposes k continuous.

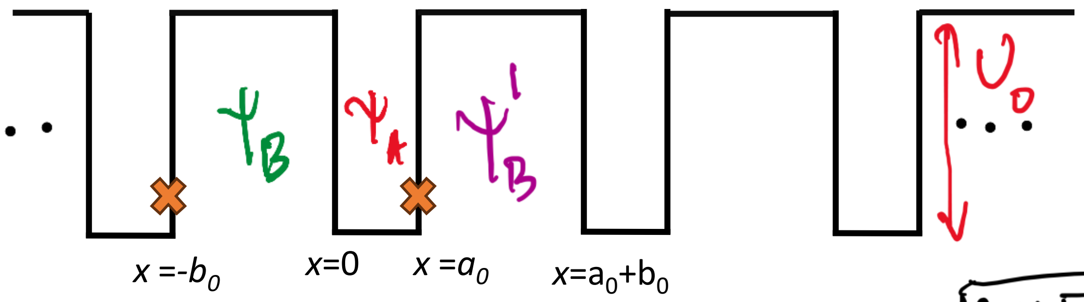
- *Each Ψ_k E is a function of k*
- *E-k relation to be computed Schrodinger equation*
- *Reminder: No Scattering in perfect lattice – Why?*

Band structure (E-k): Kronig Penney Model

Kronig Penney model: 1-D Rectangular V(x)

Lattice periodicity,

$a = a_0 + b_0$



$$\psi_A = A_1 \sin(\alpha x) + B_1 \cos(\alpha x); \quad \alpha = \frac{\sqrt{2mE}}{\hbar}$$

$$\psi_B = A_2 \sin(\beta x) + B_2 \cos(\beta x); \quad \beta = \frac{i\sqrt{2m(V_0 - E)}}{\hbar}$$

A_1, A_2, B_1, B_2 ?? Boundary conditions?

① $\psi_A(x=0) = \psi_B(x=0)$

② $\psi_A'(x=0) = \psi_B'(x=0)$

TWO MORE Boundary conditions are needed!

Compare with particle in box

Blochs' theorem

$$\psi_k(x) = e^{ikx} u_k(x) \text{ where } u_k(x) = u_k(x+a)$$

Applying Bloch's theorem to our scenario:

$$\psi_A(x=a_0) = e^{ika_0} u(a_0) \quad ① \; ; \quad \psi_B(x=-b_0) = e^{-ikb_0} u(-b_0) \quad ②$$

$$①/② \quad \frac{\psi_A(a_0)}{\psi_B(-b_0)} = \frac{e^{ika_0}\cancel{u(a_0)}}{e^{-ikb_0}\cancel{u(-b_0)}} \rightsquigarrow u(x) = u(x-a)$$

$$u(a_0) = u(a_0 - a) = u(a_0 - (a_0 + b_0)) = u(-b_0)$$

③ $\psi_A(a_0) = \psi_b(-b_0)\, e^{ik(a_0+b_0)}$
$= \psi_b(-b_0)\, e^{ika}$ #B.C.3

④ $\psi_A'(a_0) = \psi_b'(-b_0)\, e^{ika}$ #B.C.4.

Solving with 4. B.C.

FINAL Expression

$$\left\{\left[-\left(\frac{\alpha^2+\beta^2}{2\alpha\beta}\right)\sin(\alpha a_0)\sin(\beta b_0) + \cos(\alpha a_0)\cos(\beta b_0)\right] = \cos(k(a_0+b_0))\right\} \Rightarrow \text{E-k relationship.}$$

$\alpha, \beta = \text{fn of } E$

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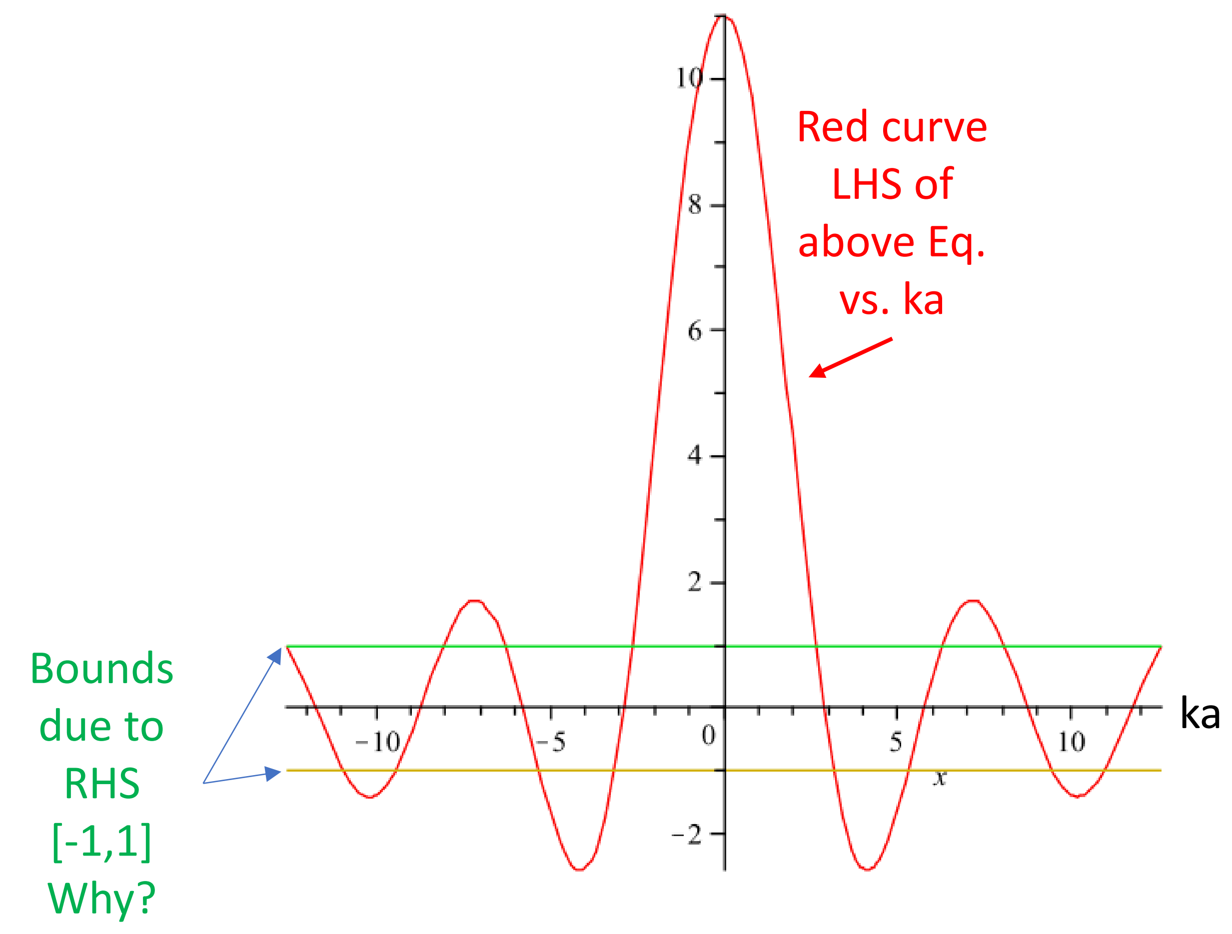
Solution: *E*-*k* (band gap and E_c and E_v)

$$\left[-\left(\frac{\alpha^2+\beta^2}{2\alpha\beta}\right)\sin(\alpha a_0)\sin(\beta b_0)+\cos(\alpha a_0)\cos(\beta b_0)\right.$$
$$\left. = \cos(k(a_0+b_0))\right\} \Rightarrow E\text{-}k \text{ relationship.}$$

$\alpha, \beta = fn$ of E



Solution: *E-k* (band gap and E_c and E_v)

$$\left[-\left(\frac{\alpha^2+\beta^2}{2\alpha\beta}\right)\sin(\alpha a_0)\sin(\beta b_0) + \cos(\alpha a_0)\cos(\beta b_0)\right] - \cos\left(k(a_0+b_0)\right)$$

$\Rightarrow$ E-k relationship.

α, β = fn of E

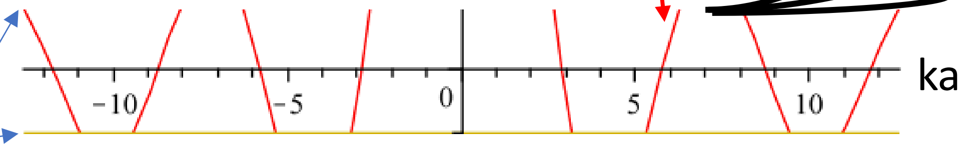
Turns out E-k is also periodic (Periodic band picture)

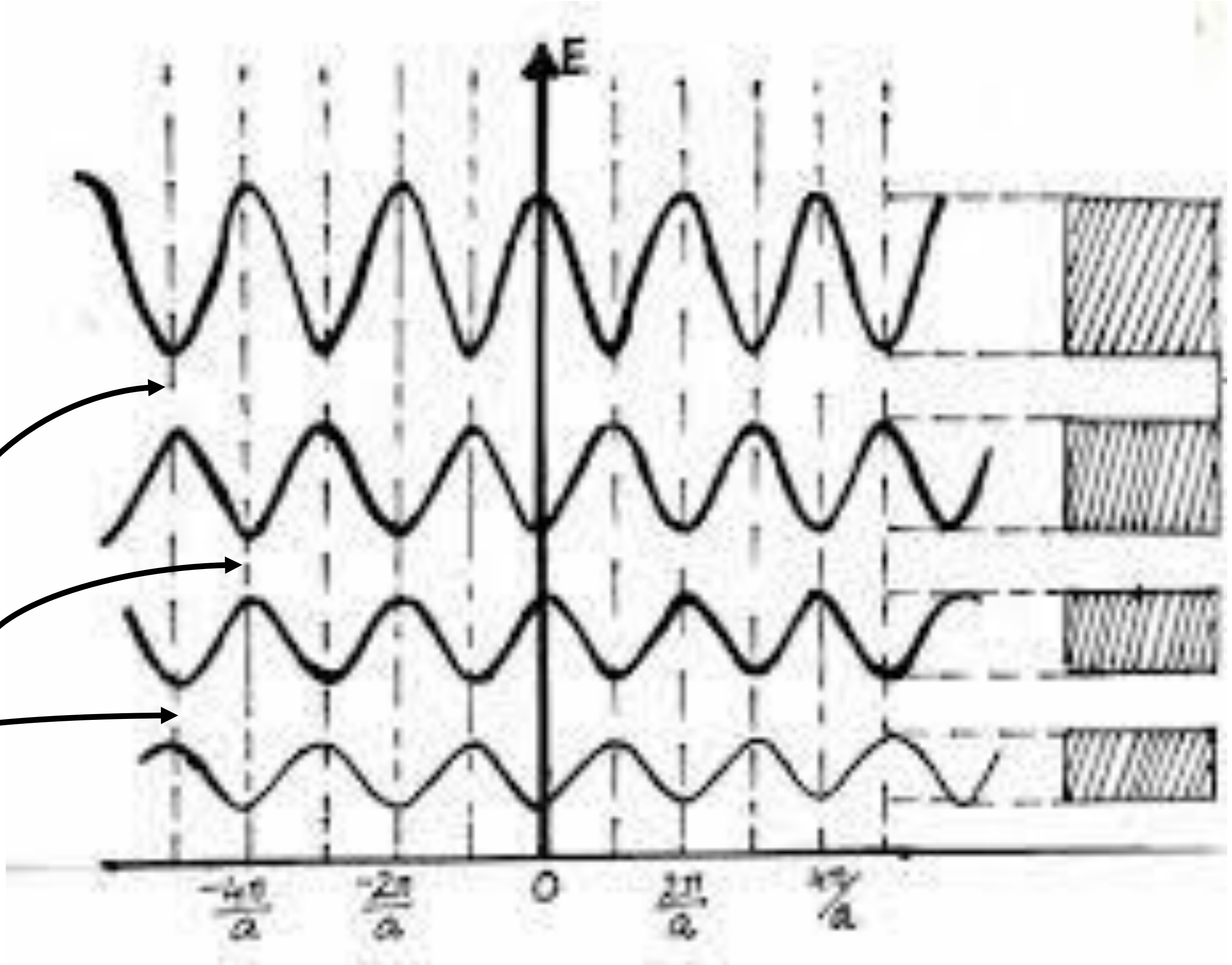
‘k’ continuous but corresponding RHS., therefore E is not!

What this indicate?

Red curve LHS of above Eq. vs. ka

Bounds due to RHS [-1,1] Why?





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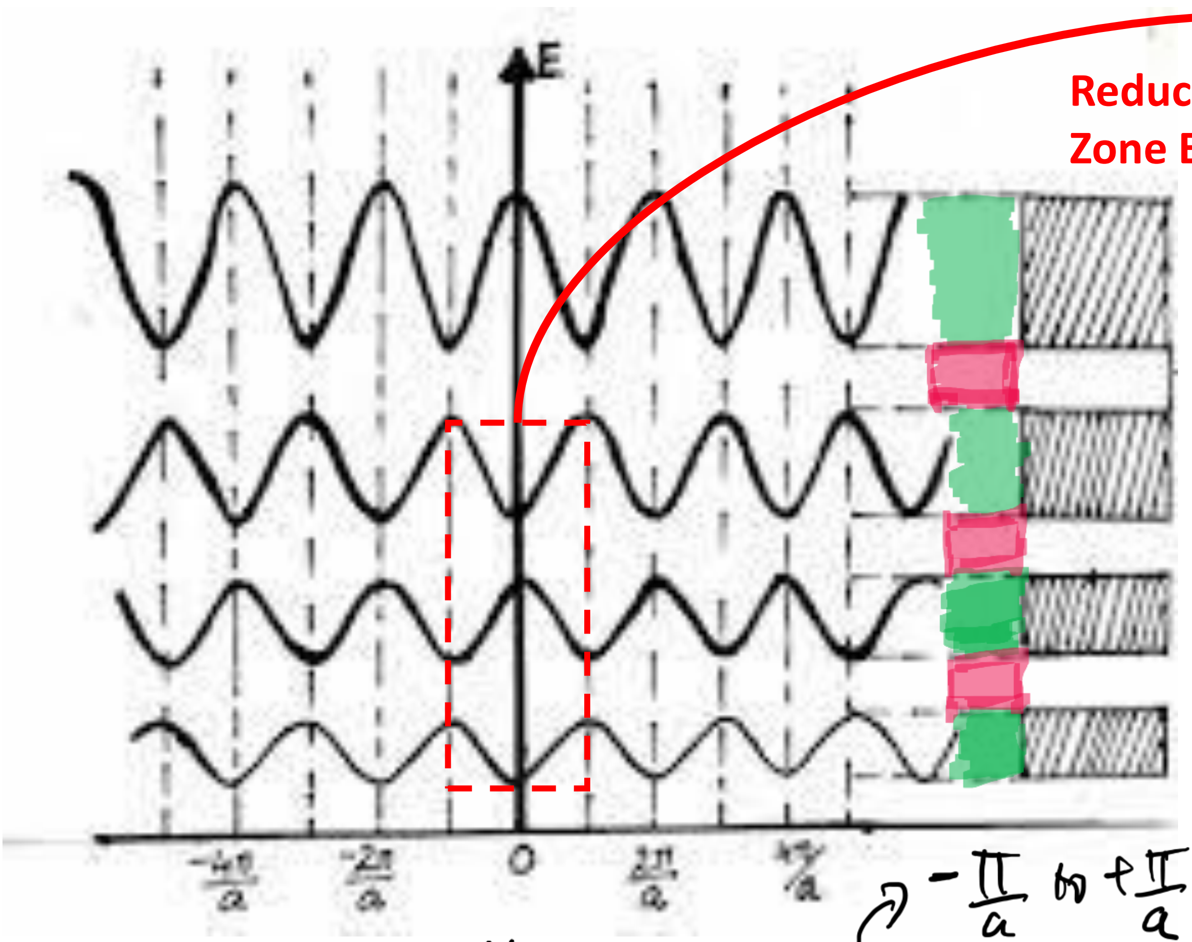
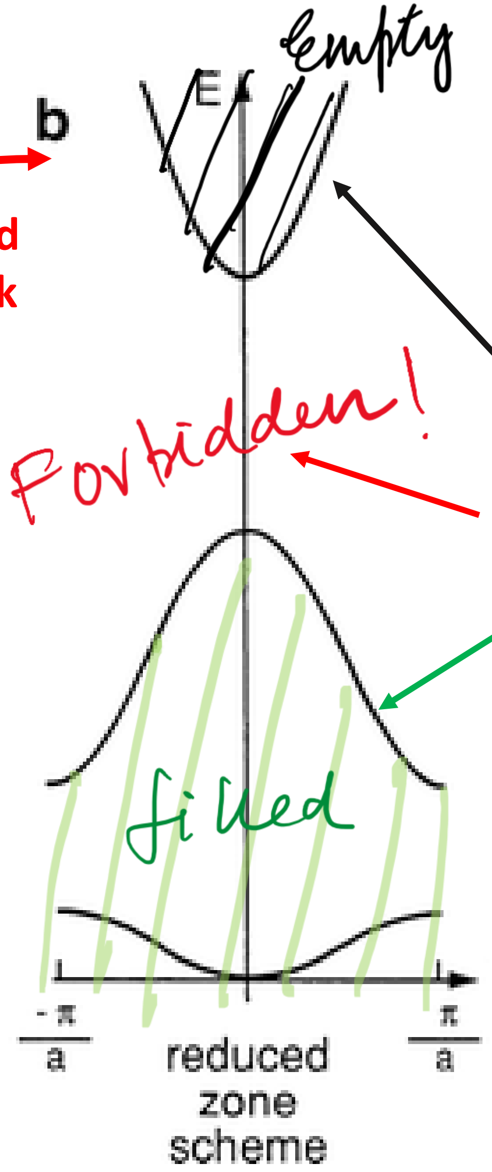


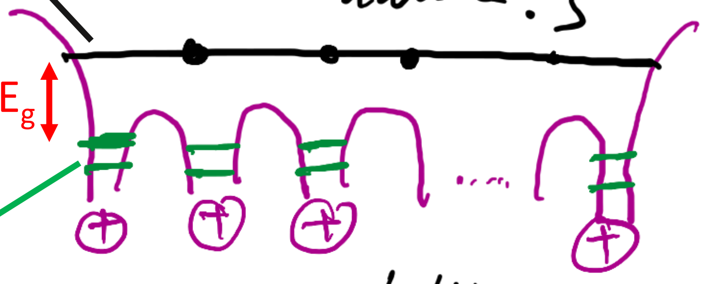
$-\frac{\pi}{a}$ to $+\frac{\pi}{a}$

#1 periodic E-k 1st brillion zone sufficient

#2 E-k has allowed forbidden



CONDUCTION BAND
{empty allowable energies}
e^- NON-LOCALISED
{free to move in lattice!}



lattice picture.

VALENCE BAND

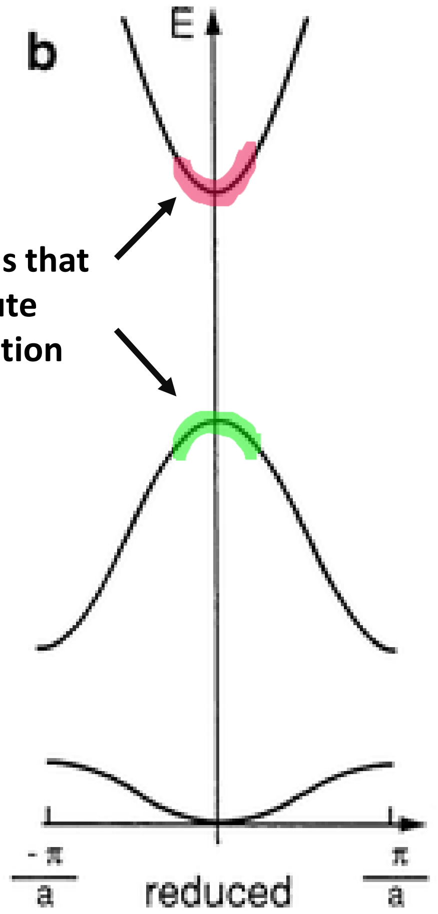
[highest E filled, loosely bound to core]

LOCALISED!

భారతీయ సాంకేతిక విజ్ఞాన సంస్థ హైదరాబాద్
भारतीय प्रौद्योगिकी संस्थान हैदराबाद
Indian Institute of Technology Hyderabad

From band structure – band diagram

Relevant band structure *(E-k)* → Band diagrams (*E* vs *x*)



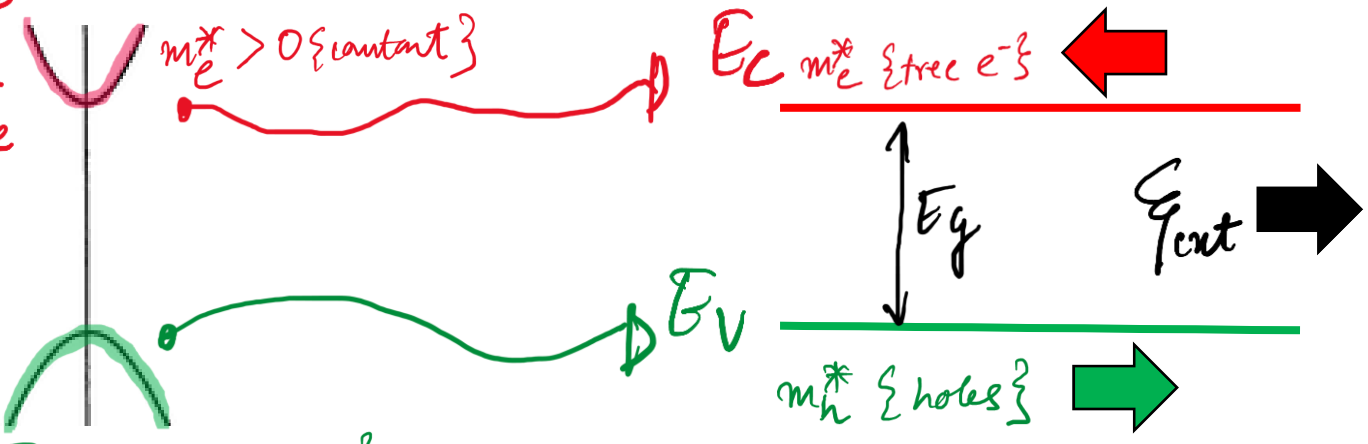
Only regions that contribute to conduction

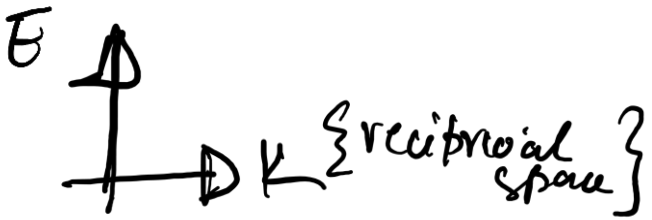
$$E(k)_{(C.B)} = E_c^{min} + \frac{\hbar^2 k^2}{2 m_e^*}$$

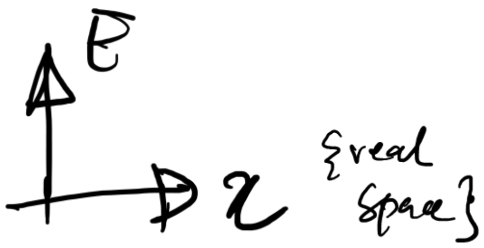
$m_e^* > 0$ {constant}

$$E(k)_{(V.B)} = E_v^{max} - \frac{\hbar^2 k^2}{2 m_h^*}$$

$m_h^* < 0$ {const}



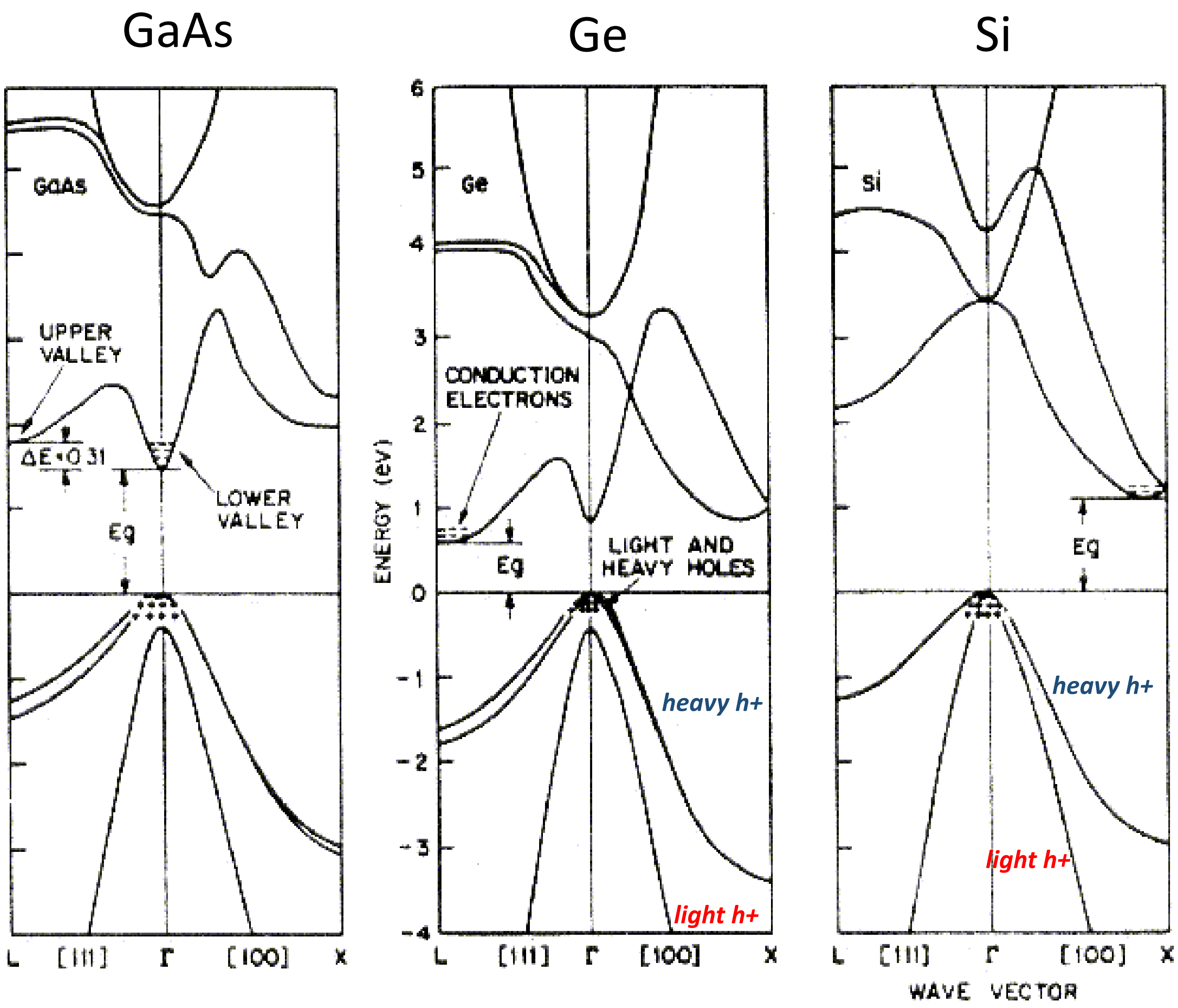




Another simplification: very tiny fraction of available carrier participate in transport: Top of E_v and bottom of E_c are important

- Bands approximated $E \propto k^2$ (Why?)
- Therefore, curvature (double derivative) constant (m^*)!
- Free particle approx: e-/h+ *as if in free space* on F_{ext}, but with m^*(not m_e)
- What does +ve (-ve) m^* for E_c/E_v mean? Response to F_{ext}

How to read (insights from) "*real*" band structure



Insights:

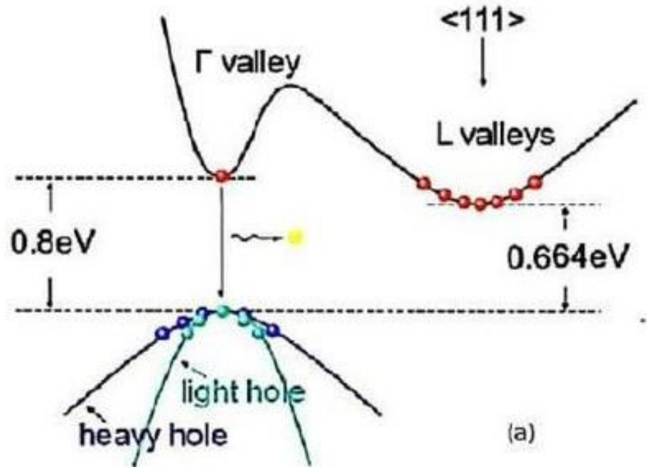
1. Band structures for 3D lattices complicated – can be calculated using numerical techniques.
2. Despite complicated band structure, (many bands) ***most*** electronic and photonic properties affected by top of E_v and bottom of E_c
3. Direct band gap (GaAs) vs Indirect bandgap (Si/Ge)

- Direct E_v max and E_c min – same k – transitions ΔE_g no momentum transfer – good for optical properties.
- Inirect E_v max and E_c min – different k – transitions do need ΔE_g and Δk – ***Δk from phonons.***

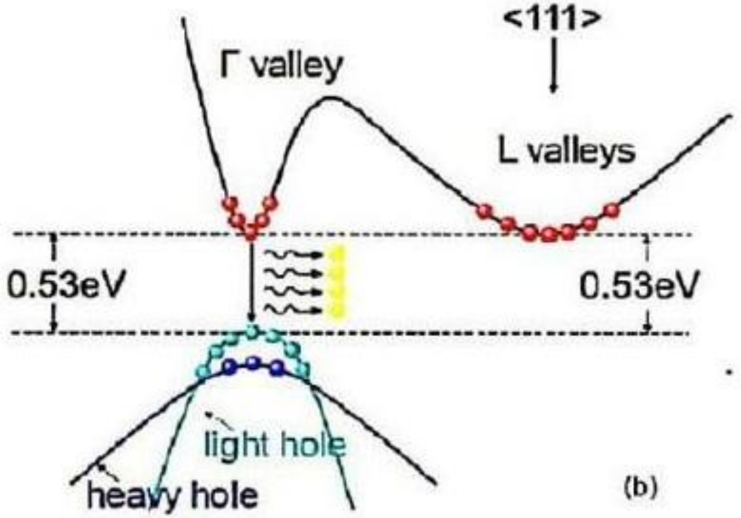
4. m*: heavy and light carriers (holes) – Observe band curvature – especially if bands are degenerate.

Magic of Strain Engineering example Ge and Si

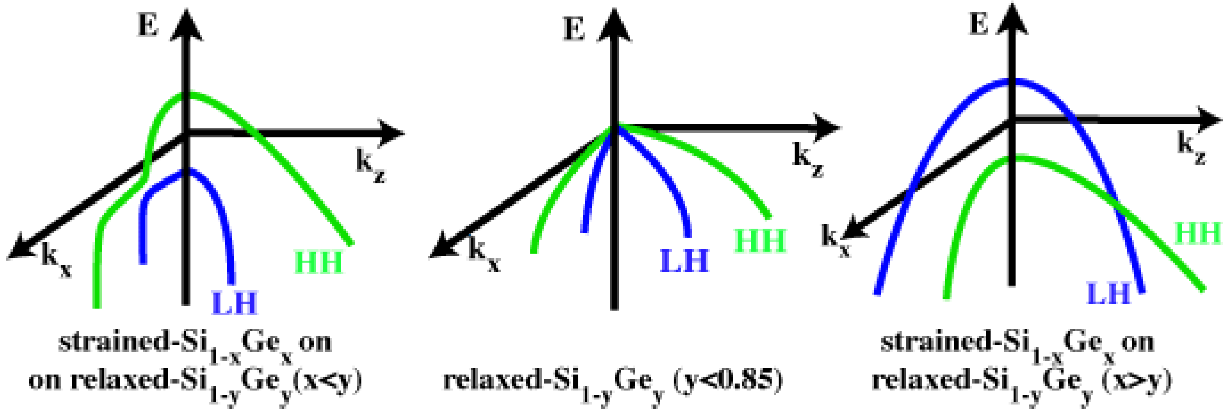
Germanium (zero strain)

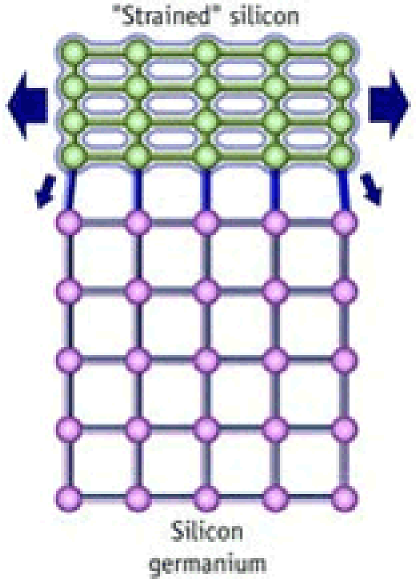


Germanium (tensile 2% strain)

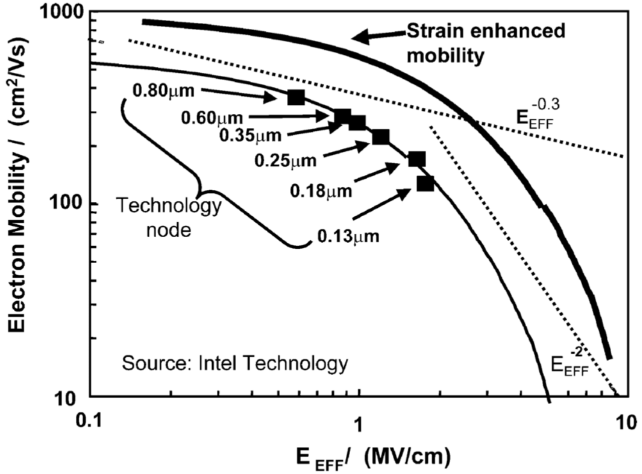


Strained Silicon!





Strain Engineering through underlying substrate



Used routinely in modern CMOS transistors to improve mobility!

Summary {Band Theory}

Q: How do electrons (and holes) behave when constrained in a lattice?

1) Each discrete energy levels in *N* atoms split into *N* discrete Energy Levels – with reducing atomic distance

2) BO and ABO Orbitals merge and split to form Conduction, Valence Bands (*appear* continuous) and forbidden gaps

3) Need quantitative estimates for σ {conductivity} $= q\,n\,\mu$ $n \equiv$ free carriers $\mu \equiv$ mobility

4) $\mu = q\,\tau_{avg}/m^*$ $\tau_{avg} \to$ scattering/relaxation time {avg} ; $m^* \to$ effective mass.

5) $\tau_{avg} \to \propto$ {perfect crystal, 0 K}; dominant (a) lattice scattering (b) Ionised Impurity $\tau_{avg}^{-1} = \tau_{ph}^{-1} + \tau_{CI}^{-1} + \cdots$

6) m^* proxy for $F_{lat} \to$ how well e^- "glides" in lattice ; $m^* = \hbar^2\left(\frac{\partial^2 E}{\partial k^2}\right)^{-1}$; E-K BAND STRUCTURE!

7) KRONIG PENNEY MODEL ; Boundary Condition {BLOCH'S THEORUM} $\psi_k(x) = e^{ikx}\,u_k(x)$

8) Complete E-K $\to$ 1st brullion zone $\to$ only near $K=0$ $\to$ parabolic bands m_e^*, m_h^*

9) $\underset{(C.B)}{E(k)} = E_c^{min} + \frac{\hbar^2 k^2}{2 m_e^*}$ $\underset{(V.B)}{E(k)} = E_v^{max} - \frac{\hbar^2 k^2}{2 m_h^*}$ DIRECT vs INDIRECT ; HEAVY vs. LIGHT CARRIERS,

From qualitative understanding to quantitative models

Good to have Qualitative understanding about physical reality,
But as Electrical Engineers all we care: Apply *V/E* what is the *I/J*

$J = \sigma E$ {Drude's law} σ {conductivity} $= q\, n\, \mu$

\# of carriers

mobility

Q:- Can we get quantitative estimates

YES!

#1 μ

"E-K" → Band-structure {Intrinsic property}
{This section}

Done! ☺

#2 n {Next section}

→ Equilibrium carr. statistics (of what?)

Energy

$n(E) = \int g(E)\, f(E)\, dE$

{intrinsic} no. of states an e^- can occupy [Energy] × {TUNABLE} probability of finding an e^- [E]

Next: Equilibrium Carrier Stats

Appendix 1:Heuristic Proof to m* (E-k) band curvature

We have seen now that $\psi_k(x) = u_k(x)\, e^{ikx}$ is in form of plane waves.

Therefore, $v_g = \frac{d\omega}{dk}$ { group velocity } $\quad v_g = \frac{1}{\hbar}\frac{\partial E}{\partial K}$ — ①

$E = \hbar\omega$ { Energy }

$p = \hbar K$ { Crystal momentum }

$dE = F_{ext}\, dx = F_{ext}\, v_g\, dt$

$\frac{dE}{dt} = F_{ext} \frac{1}{\hbar}\frac{dE}{dK} = \frac{F}{\hbar}\frac{dE}{dt}\frac{dt}{dK}$. — ②

$F_{ext} = m^* \frac{dV_g}{dt} = \frac{m^*}{\hbar}\frac{d}{dt}\left(\frac{dE}{dK}\right) = \frac{m^*}{\hbar^2}\frac{\partial^2 E}{\partial K^2}\frac{\partial(\hbar K)}{dt} \Rightarrow F_{ext}$.

$$\therefore \boxed{m^* = \hbar^2 \left(\frac{d^2 E}{\partial K^2}\right)^{-1}}$$

$\Rightarrow$ m^* inversely prop to curvature of band structure.