

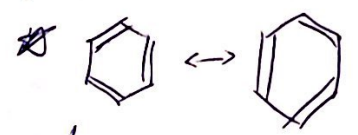
# VBO

• Born-Oppenheimer approx -  $m_{nuclei} \gg m_e \Rightarrow$  treat nuclei as stationary

•  $H_2: \psi(1,2) = X_{H1sA}(1)X_{H1sB}(2) \pm X_{H1sA}(2)X_{H1sB}(1)$  for both  $e^-$



Resonance - wavefunction can have many contributions  
 - if multiple structures add to same  $\psi \Rightarrow$  molecule is more stable  
 $\Downarrow$  resonant structures



lower energy  
 $\hookrightarrow$  the process of lowering energy due to multiple structures = resonance

## ~~Hybridization~~

Promotion - costs energy but allows for more bonds  $\rightarrow$  worth it  
 $C^*: 2s^1 2p_x^1 2p_y^1 2p_z^1$

Hybridization - different orbitals but equivalent bonds (as C)  
 $\Rightarrow$  orbitals mix and combine to symmetric drawing

$CH_4$   $sp^3$  orbitals  
 $H_3C-CH_3$  tetrahedral  $109.5^\circ$

$$\begin{cases} h_1 = s + p_x + p_y + p_z \\ h_2 = s - p_x + p_y - p_z \\ h_3 = s - p_x - p_y + p_z \\ h_4 = s - p_x - p_y - p_z \end{cases}$$

$H_2C=CH_2$   $sp^2$  orbitals  
 $\sigma + \pi$   
 $120^\circ$

$$\begin{cases} h_1 = s + \sqrt{2} p_y \\ h_2 = s + \sqrt{\frac{3}{2}} p_x - \frac{1}{\sqrt{2}} p_y \\ h_3 = s - \sqrt{\frac{3}{2}} p_x - \frac{1}{\sqrt{2}} p_y \end{cases}$$

$HC \equiv CH$   $sp$  orbital  
 $\sigma + 2\pi$   
 $180^\circ$

$$\begin{cases} h_1 = s + p_z \\ h_2 = s - p_z \end{cases}$$

Steric number = # regions in space with  $e^-$  density per atom in molecule  
 $\hookrightarrow$  incl. lone pairs

- 2  $\rightarrow sp$
- 3  $\rightarrow sp^2$
- 4  $\rightarrow sp^3$

\* = lin. comb. atom. orbitals

## VBO x MO

$\hookrightarrow$  always even #  $e^-$ , mixed spins  $\Rightarrow$  cannot explain  $H_2^+$   
 $\hookrightarrow$  to explain shapes of some molecules, need hybridization  
 $\hookrightarrow$  resonance is important

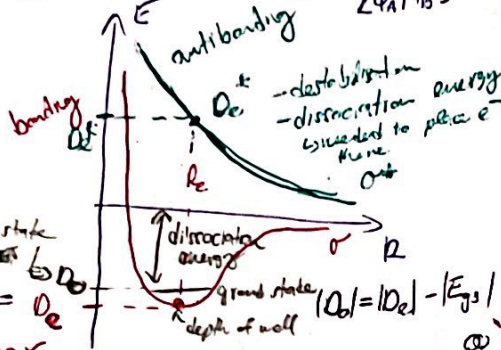
x MO orbitals over entire molecule  
 $\hookrightarrow$  MO's as LCAO\*  
 $\hookrightarrow$  bonding/nonbonding/antibonding

**MO**

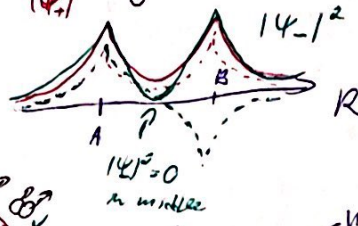
LCAO:  $\Psi_{\pm} = N[\Psi_A \pm \Psi_B]$

$N = \frac{1}{\sqrt{2(1+S)}}$  overlap integral  $\langle \Psi_A | \Psi_B \rangle$

interaction of  $e^-$  w/ other nucleus  
 interaction between nucleus and  $e^-$  density in internuclear region



$|Q_+| > |Q_-|$   
 "antibonding more antibonding, than bonding is bonding"  
 $(\Psi_+)^2$   $(\Psi_-)^2$



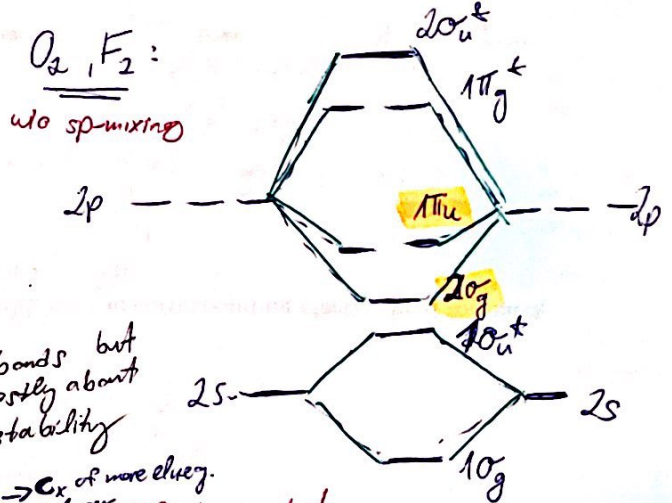
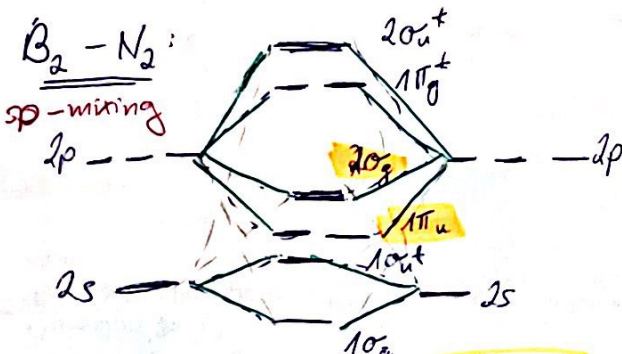
Homonuclear

Inversion symmetry

- only homo (symmetric)
- change of sign upon inversion through center of molecule?



- lowest energy (ground state) - no spacing rel,  $k_B T = 25 \text{ meV}$   $\Rightarrow$  almost all in ground state  $\rightarrow$  that's why we care
- first: single occupancy of  $e^-$ , triplet  $\uparrow\uparrow$   $\rightarrow \Psi_-$  asymmetric spatial  $\rightarrow$  more distance  $\rightarrow$  less repulsion,  $\Delta E$
- all same orbitals of same symmetry contribute to MO (but usually gets weak when further apart)



bond order  $b = \frac{1}{2}(N - N^*)$   $\sim$  # bonds but mostly about stability  
 #e- in bonding - antibonding

Heteronuclear

$\Psi = c_A \Psi_A + c_B \Psi_B$

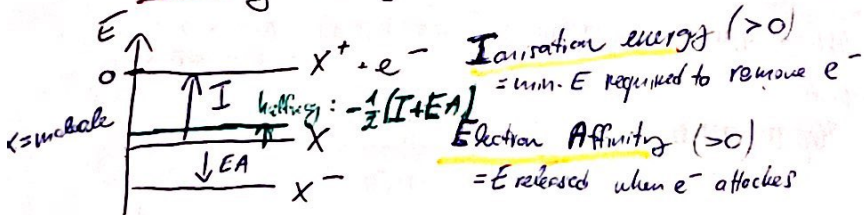
- bonding - mostly from more electronegative  $\rightarrow$   $c_B$  of more electronegative is larger
- antibonding - mostly from less electronegative  $\rightarrow$  reverse

Electronegativity

• Mulliken  $\chi = \frac{1}{2}(I + EA)$

• Pauling - relative, then try to fit

$|\chi_A - \chi_B| = \sqrt{D_0(AB) - \frac{1}{2}(D_0(AA) + D_0(BB))}$   
 dissociation energy [eV]



$\hookrightarrow$  conversion:  $\chi_{\text{Pauling}} \approx \sqrt{\chi_{\text{Mulliken}}} - 1.37$

non-polar:  $c_A \sim c_B$

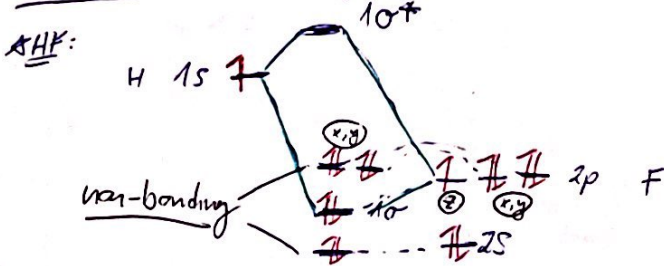
ionic:  $c_A \cdot c_B = 0$  ( $c_A = 1$  &  $c_B = 0$  or reverse)

Variation principle - energy found using arbitrary  $\psi$ , will always be larger than or equal to ground state:  $E_{calc} \geq E_g$

$\psi = c_A \psi_A + c_B \psi_B$  - secular eq's:  $\begin{cases} (\alpha_A - E) c_A + (\beta - S \cdot E) c_B = 0 \\ (\beta - S \cdot E) c_B + (\alpha_B - E) c_A = 0 \end{cases} \Rightarrow \begin{cases} \text{homo: } E_{\pm} = \frac{\alpha \pm \beta}{1 \pm S} \\ \text{hetero: } S \rightarrow 0: \\ E_{\pm} = \frac{1}{2}(\alpha_A + \alpha_B) \pm \frac{1}{2}(\alpha_A - \alpha_B) \end{cases}$

$\langle \psi | \hat{H} | \psi \rangle$  resonance overlap int.  $\langle A | \hat{H} | B \rangle$   $\langle A | B \rangle$

heteronuclear MO diagram



Degrees of freedom:  $3N - \sqrt{1 + \left(\frac{qB}{k_A - k_B}\right)^2}$

type	linear	non-lin.
translational	3	3
rotational	2	3
vibrational	$3N - 5$	$3N - 6$

$\epsilon = 3N$

$k_B T = 25 \text{ meV}$  vs.  $E = \frac{1238}{\lambda} \text{ [eV]}$

at room temp: ground state

Selection rules - excited at room T

Rotational = microwave  $\sim \text{meV}$

Vibrational = infrared  $\sim 100 \text{ meV}$

Electronic = visible/UV/IR  $\sim \text{eV}$

$\Delta J = \pm 1$  for symmetric:  $\Delta K = 0$   
 $\Delta M_J = 0, \pm 1$  el. dipole  
 $\mu_{fi} = \int \psi_f^* \hat{\mu} \psi_i d\tau = \langle \psi_f | \hat{\mu} | \psi_i \rangle \neq 0 = \mu_i \neq 0$   
 Spher. sym.  $\otimes$  -  $\sum e r_i$  permanent el. dipole moment  
 $\sim$  polar  
 purely rot. change of state only if  $\mu_i \neq 0$   
 initial state has non-zero permanent dip. moment

$\Delta \mu \neq 0$   
 $i \rightarrow f$   
 $\mu_i = 0$   $\mu_f \neq 0$   
 for diatomic:  $\langle \text{homo} \times (\text{inactive}) \rangle$   
 $\langle \text{hetero} \checkmark (\text{active}) \rangle$   
 $(\Delta v = \pm 1)$  - for harmonics  
 $\Delta G_{v \rightarrow v \pm 1} = \tilde{\nu}$  indep. of  $v$  for

for linear  $\Delta L = 0, \pm 1$   
 $\Delta S = 0$   
 $\Delta \Sigma = 0$   
 $u \leftrightarrow g$   
 $\Sigma^{+(-)} \leftrightarrow \Sigma^{+(-)}$   
 multiply:  $S = \text{total spin}$   
 $2S + 1$  spatial sym. upon reflection in plane containing internuclear axis  
 $g/u$  only homo  
 $\pi: \lambda = +1/0$   
 $\sigma: \lambda = 0$   
 $\pi: \lambda = \pm 1$   
 $\sigma: \text{same}$   
 $\vec{S} = \vec{L} + \vec{\Sigma}$   
 comp. of spin along internuclear

$\tilde{F}_J = \frac{E_J}{hc}$   $E_J = hB J(J+1)$ ,  $B = \frac{h}{8\pi^2 I}$   
 $\tilde{B} = \frac{h}{4\pi c I}$   $I_{||} \Rightarrow$  unique/principal figure

Spherical rotors:  $I_x = I_y = I_z = \frac{8}{3} m_A R^2$   
 $\tilde{F}_J = \tilde{B} J(J+1)$

Symmetric rotors:  $I_A \neq I_B = I_C = \text{palm}$  or  $2m_A R_A^2 + 2m_C R_C^2$   
 $E = \frac{J_A^2 + J_B^2}{2I_A} + \frac{J_C^2}{2I_C} = 2m_A (1 - \cos \theta) R_A^2$  or  $4m_A R_A^2$   
 $J^2 = J(J+1) \hbar^2$

$K$  = component of angular momentum about unique axis  
 $\tilde{F}_{J,K} = \tilde{B} J(J+1) + (\tilde{A} - \tilde{B}) K^2$ ,  $\tilde{A} = \frac{h}{4\pi c I_A}$ ,  $\tilde{B} = \frac{h}{4\pi c I_B}$   
 $M_J$  - about externally chosen axis  $(2J+1)$   
 $K \neq 0 \Rightarrow 2(2J+1)$  deg  
 $K = 0 \Rightarrow 2J+1$  deg

Linear rotors  $I_A \neq 0, I_B = 0$  unique, principal, figure axis  
 $K \neq 0, I = m_A R_A^2 + m_C R_C^2 + \frac{(m_A R_A - m_C R_C)^2}{m_A + m_C} = 2m_A R_A^2$   
 $\tilde{F}_J = \tilde{B} J(J+1)$  if spins fast: centrifug. dist.  $\tilde{D}_J$   
 $\tilde{F}_J = \tilde{B} J(J+1) - \tilde{D}_J J^2(J+1)^2$

Diatomic:  $I = \mu R^2$ ,  $\mu = \frac{m_1 m_2}{m_1 + m_2}$   
Asymmetric rotors:  $I_A < I_B < I_C$

spacing of adjacent lvs:  $\tilde{F}_{J+1} - \tilde{F}_J = 2\tilde{B}(J+1) - \tilde{D}_J (J+1)^2$

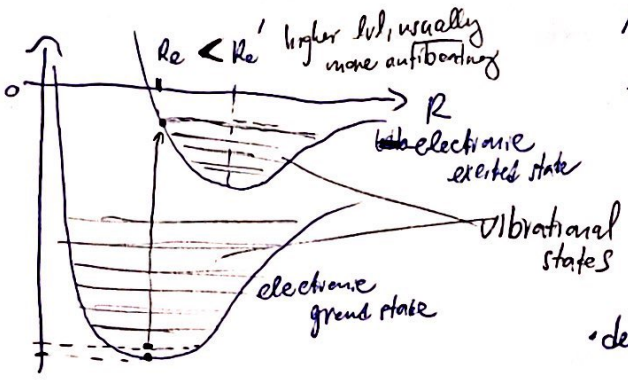
$E_v = hc \tilde{G}(v)$   
 $\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k_f}{m_{eff}}}$   
 wave number =  $c \cdot \text{freq.}$   
 $m_{eff} = \frac{m_1 m_2}{m_1 + m_2}$   
 Harmonic Parabolic pot  
 $V = \frac{1}{2} k_f x^2$   
 $E = hf(v + \frac{1}{2})$   
 $\tilde{G}(v) = \tilde{\nu}(v + \frac{1}{2})$   
 Morse potential  
 $\tilde{G}(v) = (v + \frac{1}{2}) \tilde{\nu} - \tilde{B}(v + \frac{1}{2})^2$   
 $\Delta v = \pm 1, \pm 2, \dots$  anharmonicity const.

Spectroscopy  
 line spacing =  $\Delta \tilde{P} = 2\tilde{B}$   
 $\frac{1}{\nu} \sim \frac{1}{\nu} \pm \frac{1}{\nu}$   $\left\{ \begin{array}{l} \downarrow \text{population} \\ \uparrow \text{deg} \end{array} \right\}$  spacing

# Franck - Condon principle

$m_{nuclei} \gg m_e \Rightarrow$  electronic transitions happen faster than nuclei can respond = move

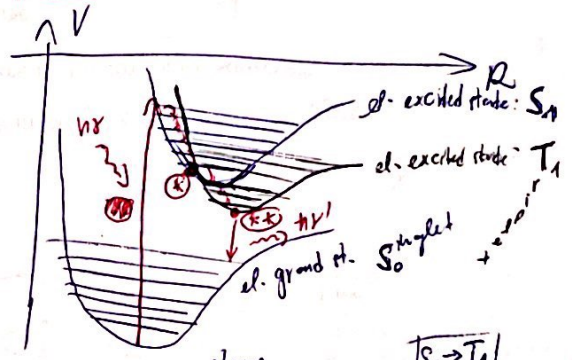
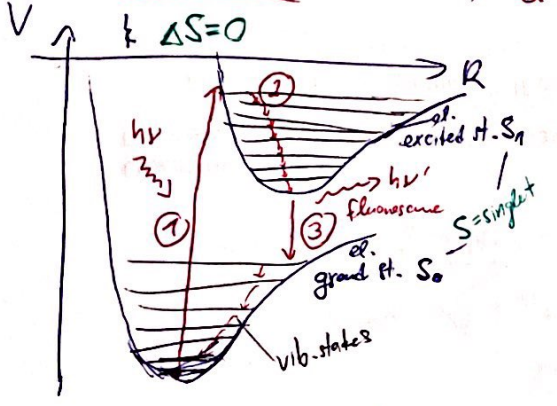
$\Rightarrow$  transitions are vertical, & excited states of HO have higher probability near edges than ground state



$\Rightarrow$  transition to excited state vib.

decay of excited state  $\begin{cases} \rightarrow \text{radiation } (\gamma) \\ \rightarrow \text{radiationless (heat)} \end{cases}$

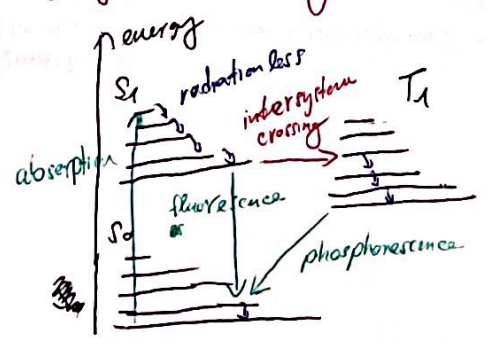
## Fluorescence (ns- $\mu$ s) & Phosphorescence (s-h)



- ①  $\gamma$  absorption (vertical)
- ② radiationless decay from vib. excited state (E accepted by surrounding molecules)  $\sim$  ps
- ③ if no surrounding can accept left part of E  $\rightarrow \gamma$  emission  
if surrounding can accept  $\rightarrow$  no radiation produced (radiationless if faster) (e.g. H<sub>2</sub>O)

- \* intersystem crossing  $|S_1 \rightarrow T_1|$  possible if states have same energy and geometry & (sufficiently strong S-O coupling  $\rightarrow$  heavy atom effect)
- \*\* stuck in triplet state - selection rules say  $\Delta S=0$  but - only weakly allowed  $T_1 \rightarrow S_0 \Rightarrow$  metastability  
low probability  $\Rightarrow$  slow process

$\rightarrow$  Jablonski diagram - incl. el. & vib. lvs., each column own column



LASERS

Einstein coeffs:

absorption	$B_{12}$	} = B
stimulated emission	$B_{21}$	
spontaneous emission	$A_{21} \sim \frac{1}{\tau}$	

lifetime of state 2

$$\Rightarrow \frac{A_{21}}{B} = 8\pi h \left(\frac{\nu}{c}\right)^3 \cdot \text{freq.}$$

$$\int \rho(\nu) d\nu = \frac{nh\nu}{V}$$

density # of volume

stimulated emission (if absorption)

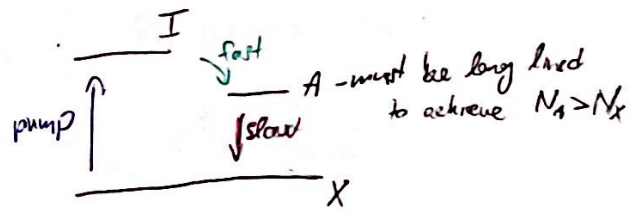
$$B \rho(\nu) = \frac{c^3}{8\pi h \nu^3} \frac{h\nu}{d\nu} n = \Gamma n$$

derivation

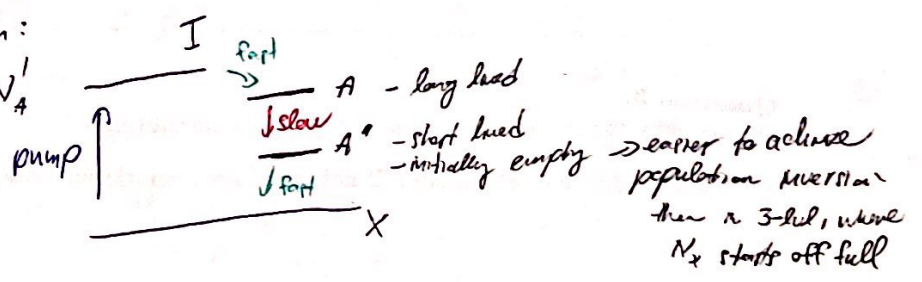
$\Rightarrow$  for stimulated emission with no decrease in # of  $\Rightarrow$  population inversion is required

Population inversion

- impossible in 2-lvl system
- 3-lvl system: hard but possible:
  - $\hookrightarrow$  need:  $N_A > N_X$



- nice: 4-lvl system:
  - $\hookrightarrow$  need:  $N_A > N_A'$



Monochromaticity

• ~~case~~ in cavity of length  $L \rightarrow$  interference when bouncing back-and-forth, positive only for:  $\lambda = \frac{2L}{n}, n \in \mathbb{N}$

$\Rightarrow$  monochromatic light

Coherence

- suppose 2 beams:  $\lambda, \lambda + \Delta\lambda \Rightarrow$  phase difference grows by  $\frac{\Delta\lambda}{\lambda}$  per cycle
- $\Rightarrow$  after  $N$ -cycles out of phase:  $N = \frac{\lambda}{2\Delta\lambda}$

$\Rightarrow$  define coherence length = distance for which the beams remain coherent

$$l_c = N\lambda = \frac{\lambda^2}{2\Delta\lambda}$$

Lattice = Bravais lattice

- isotropic
- points specified by lattice vectors:  $\vec{r} = l_1 \vec{a}_1 + l_2 \vec{a}_2 + l_3 \vec{a}_3$  :  $l_i \in \mathbb{Z}$ ,  $\vec{a}_i$  = primitive (lattice/basis) vectors
- coordination number = number of nearest neighbors
- crystal = is made up of ~~lattice~~ basis (smallest repeated segment) and lattice (vectors describing how the basis should repeat)

here's 14 basic Bravais lattices

(SC) Simple cube CN=6,  $\vec{a}_1 = a\hat{i}$ ,  $\vec{a}_2 = a\hat{j}$ ,  $\vec{a}_3 = a\hat{k}$

(BCC) Body centered cube: CN=8 ;  $\left\{ \begin{array}{l} \vec{a}_1 = a\hat{i} \\ \vec{a}_2 = a\hat{j} \\ \vec{a}_3 = a\hat{k} \end{array} \right\}$   
 2 sets interpenetrating  
 $\left\{ \begin{array}{l} \vec{a}'_1 = \frac{a}{2}(\hat{j} + \hat{k} - \hat{i}) \\ \vec{a}'_2 = \frac{a}{2}(\hat{i} + \hat{k} - \hat{j}) \\ \vec{a}'_3 = \frac{a}{2}(\hat{i} + \hat{j} - \hat{k}) \end{array} \right\}$   
 ↳ lattice vectors of SC but with basis of 2 atoms positioned at  $(0, \frac{a}{2}(\hat{i} + \hat{j} + \hat{k}))$

(FCC) Face centered cubic: CN=12

$$\left\{ \begin{array}{l} \vec{a}_1 = \frac{a}{2}(\hat{j} + \hat{k}) \\ \vec{a}_2 = \frac{a}{2}(\hat{i} + \hat{k}) \\ \vec{a}_3 = \frac{a}{2}(\hat{i} + \hat{j}) \end{array} \right\}$$

(1) Diamond lattice  
 ↳ 2 interpenetrating FCC's  
 ↳ FCC vectors  
 basis of 2 atoms:  $(0, \frac{a}{2}(\hat{i} + \hat{j} + \hat{k}))$

(2) Hexagonal:

$$\left\{ \begin{array}{l} \vec{a}_1 = \frac{a\sqrt{3}}{2} \hat{i} + \frac{a}{2} \hat{j} \\ \vec{a}_2 = -\frac{a\sqrt{3}}{2} \hat{i} + \frac{a}{2} \hat{j} \\ \vec{a}_3 = c\hat{k} \end{array} \right\}$$



Unit cells - if translated over lattice vectors, gives crystal

- Primitive unit cell - parallelepiped of  $\vec{a}_i$ 's (not unique just like  $\vec{a}_i$ 's)
- Wigner-Seitz - unique
  - ① points for atoms
  - ② lines connecting neighbors
  - ③ perpendicular bisectors
  - ④ unit cell enclosed by  $\perp$  bisec.



Periodicity of  $\psi$  - free moving  $e^-$  in a periodic potential

(1D) • we require:  $\psi(a) = \psi(0)$  for  $\psi(x) = e^{ikx} \Rightarrow k = \frac{2\pi}{a}n$ ,  $n \in \mathbb{Z}$

Reciprocal lattice

(1D) Direct:  $-a$  to  $a$  (WS unit cell)  
 Reciprocal:  $-\frac{2\pi}{a}$  to  $\frac{2\pi}{a}$  (WS of reciprocal = Brillouin zone)  
 lattice vector  $\vec{r} = n\vec{a} \Rightarrow \vec{r} = \sum_i n_i \vec{a}_i$   
 non-primitive reciprocal vector  $\vec{g} = \frac{2\pi}{a}n = \frac{2\pi}{a}n\vec{a} \Rightarrow e^{i\vec{g} \cdot \vec{r}} = 1$   
 $\vec{g} = \sum_j m_j \vec{b}_j$   
 $e^{i2\pi n m} = 1$

↳ 3D: planes  $\rightarrow$  volume etc.  
 periodic  $\psi \Rightarrow \psi(x) = e^{i\frac{2\pi}{a}n}$ ,  $n \in \mathbb{Z}$   
 $\psi(\vec{r}) = \sum_{\vec{g}} c_{\vec{g}} e^{i\vec{g} \cdot \vec{r}}$   
 $c_{\vec{g}} = \frac{1}{V} \int_V \psi(\vec{r}) e^{-i\vec{g} \cdot \vec{r}} dV$

↳ described by reciprocal lattice vectors:

(3D)  $\vec{b}_1 = \frac{2\pi}{V} (\vec{a}_2 \times \vec{a}_3)$  where  $V = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$  is the volume of the primitive cell  
 $\vec{b}_2 = \frac{2\pi}{V} (\vec{a}_3 \times \vec{a}_1)$   
 $\vec{b}_3 = \frac{2\pi}{V} (\vec{a}_1 \times \vec{a}_2) \rightarrow \vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}$

Lattice planes - planes passing through lattice points (non-unique), each part: max 1 plane of given family

# points in plane = packing density  $\propto d$

- closely spaced planes ( $d$  = distance between planes)  $\Rightarrow$  less atoms on each plane  $\Rightarrow$  lower packing density
- vector between 2 lattice points is also a lattice vector  $\vec{r} = \sum_i n_i \vec{a}_i$
- any plane in the direct lattice is normal to same vector of the reciprocal lattice & each vector of reciprocal is normal to a set of lattice planes of direct lattice
- $n_1, n_2, n_3$  - no common factor, then  $\vec{g}$  is the shortest vector in  $\vec{g}$ . Family of planes normal to  $\vec{g}$  are separated by  $d = \frac{2\pi}{|\vec{g}|}$

• Miller indices:  $\vec{g} = (n_1 \ n_2 \ n_3) = n_1 \vec{b}_1 + n_2 \vec{b}_2 + n_3 \vec{b}_3 \rightarrow |\vec{g}| = |n_1 \vec{b}_1 + n_2 \vec{b}_2 + n_3 \vec{b}_3|$   
 (4 2 1) =  $4\vec{b}_1 - 2\vec{b}_2 + \vec{b}_3$  In cubic:  $d = \frac{a}{\sqrt{h_1^2 + h_2^2 + h_3^2}}$   
 minus on top!

# Bloch function

Thm: Any  $\psi$  that satisfies Schrödinger Eq. with a periodic potential  $V(\vec{r} + \vec{a}) = V(\vec{r}) e^{i\vec{k} \cdot \vec{a}}$

or:  $\psi_{\vec{k}}(\vec{r}) \equiv e^{-i\vec{k} \cdot \vec{r}} \psi_{\vec{k}}(\vec{r}) \Rightarrow \psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{r}}$   
 ↳ l-periodic      wavefun = l-periodic & plane wave  
 (= const. for free e-)  
 ↳  $\psi(\vec{r}) = A e^{i\vec{k} \cdot \vec{r}}$

## Born-von Karman boundary conditions

$\psi(x + Na) = \psi(x) \Rightarrow \psi_{\vec{k}}(x + Na) = e^{i\vec{k} \cdot Na} \psi_{\vec{k}}(x)$

# atoms in a row of lattice

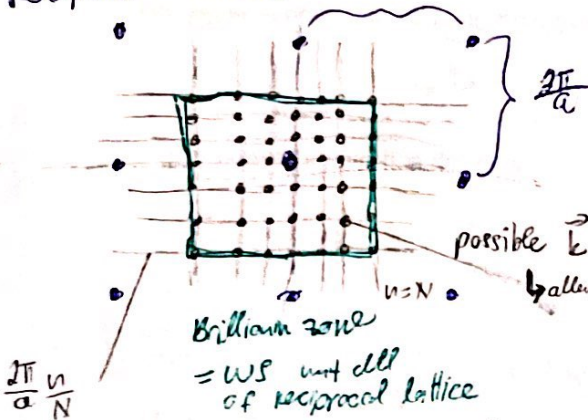
must be 1

$\Rightarrow k = \frac{2\pi}{Na} n, n \in \mathbb{Z} \Rightarrow \vec{k} = \sum \frac{n_i}{N_i} \vec{b}_i$

↳ periodic in edges of the crystal (weaker condition than periodic in lattice)

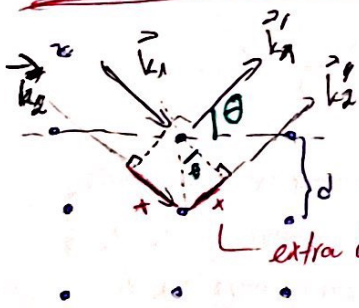
From before we had  $\vec{g} = \frac{2\pi}{a} n$ ,  $\vec{k}$  allows for more, finer spaced values reciprocal lattice

for  $n > N$



possible  $\vec{k}$  = wavenumber (allowed values)  $(\vec{p} = \hbar \vec{k}) \Rightarrow$  to know movement of e-, it's sufficient to know how it behaves in the Brillouin zone, after that it just repeats  $\rightarrow$  we can say about  $n \leq N$

## Electron Diffraction



$\rightarrow$  constructive interference if  $2x = n\lambda$

$x = d \sin \theta \Rightarrow 2d \sin \theta = n\lambda$

Bragg's law

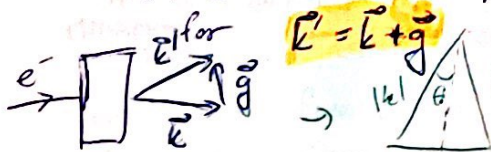
$\langle \psi_i^* \psi_j \rangle = \delta_{ij} \leftarrow \psi_{\vec{k}} = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}}, \psi_{\vec{k}'} = \frac{1}{\sqrt{V}} e^{-i\vec{k}' \cdot \vec{r}}$

## Elastic scattering from QM

$|\vec{k}'| = |\vec{k}|$

Probability of occurring  $\propto |I_{\vec{k}, \vec{k}'}|^2$ , where  $I_{\vec{k}, \vec{k}'} = \int \psi_{\vec{k}'}^*(\vec{r}) V(\vec{r}) \psi_{\vec{k}}(\vec{r}) d\vec{r}$

non-zero transition probability only  $\Leftarrow = \sum_{\vec{g}} \int V_{\vec{g}} \frac{1}{V} e^{i(\vec{k} + \vec{g} - \vec{k}') \cdot \vec{r}} d\vec{r} = \sum_{\vec{g}} V_{\vec{g}} \int \psi_{\vec{k}'}^* \psi_{\vec{k} + \vec{g}} d\vec{r} = \sum_{\vec{g}} V_{\vec{g}} \delta_{\vec{k}', \vec{k} + \vec{g}}$



transition integral  
 Coulomb potential:  $V(\vec{r}) = \sum_{\vec{g}} V_{\vec{g}} e^{i\vec{g} \cdot \vec{r}}$   
 reciprocal lattice vector

$|\vec{g}| = 2|\vec{k}| \sin \theta \Rightarrow |\vec{g}| = 2 \cdot \frac{2\pi}{\lambda} \sin \theta$   
 distance between neighboring planes

distance between  $N^{\text{th}}$  and  $(N+1)^{\text{th}}$  planes:  $d = \frac{2\pi}{|\vec{g}|} N \Rightarrow |\vec{g}| = \frac{2\pi}{d} N = 2 \cdot \frac{2\pi}{\lambda} \sin \theta$

$|\vec{k}'|^2 = |\vec{k} + \vec{g}|^2 = |\vec{k}|^2 + 2\vec{k} \cdot \vec{g} + |\vec{g}|^2 \Rightarrow |\vec{g}|^2 = -2\vec{k} \cdot \vec{g} \Rightarrow |\vec{g}|^2 = 2|\vec{k}| \cdot |\vec{g}| \sin \theta \Rightarrow N\lambda = 2d \sin \theta$   
 Bragg's law

3] 3D

$$\vec{k}' = \vec{k} + \vec{g}$$

$$|\vec{k}'|^2 = |\vec{k}|^2 + 2\vec{k} \cdot \vec{g} + |\vec{g}|^2$$

$$|\vec{k}| = |\vec{k}'|$$

$$|\vec{g}|^2 = -2\vec{k} \cdot \vec{g} \xrightarrow{\text{from symmetry}}$$

→ Bragg law

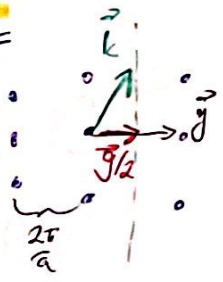
$$|\vec{g}|^2 = 2\vec{k} \cdot \vec{g} \text{ or } \left|\frac{\vec{g}}{2}\right|^2 = \vec{k} \cdot \frac{\vec{g}}{2}$$

⇒ scattering occurs if  $\vec{k}$  is on a plane perpendicular to  $\frac{\vec{g}}{2}$ , distance  $\frac{g}{2}$  from the origin. ⇔

if  $\vec{k}$  projects exactly onto  $\frac{\vec{g}}{2}$

$$\left|\frac{\vec{g}}{2}\right| = \frac{\vec{k} \cdot \vec{g}/2}{|\vec{g}/2|}$$

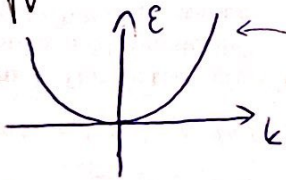
or also or projection of  $\vec{k}$  onto  $\vec{g}$ , yields  $\frac{g}{2} : |\vec{g}| = 2 \frac{\vec{k} \cdot \vec{g}}{|\vec{g}|}$   
 $\Rightarrow \left|\frac{\vec{g}}{2}\right| = \frac{\vec{k} \cdot \vec{g}}{|\vec{g}|}$



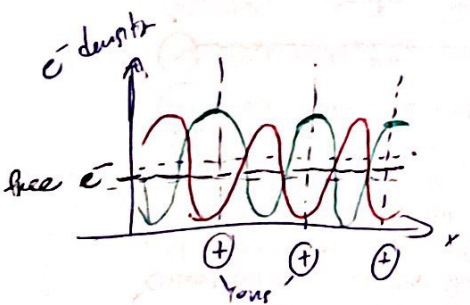
⇒ scattering if  $\vec{k}$  is on the boundary of Brilloune zone (BZ)

Electrons in crystal

$$\Psi = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}}$$



- for free  $e^-$ :  $E = \frac{\hbar^2 k^2}{2m}$  (electron mass =  $9.1 \cdot 10^{-31} \text{kg}$ )
- if  $|\vec{k}| < \frac{|\vec{g}|}{2} \Rightarrow$  inside BZ, far from the edge
- nearly free  $e^-$ :  $E = \frac{\hbar^2 k^2}{2m^*}$  (effective mass, usually  $\frac{m^*}{m} = 0.1 - 10$ )

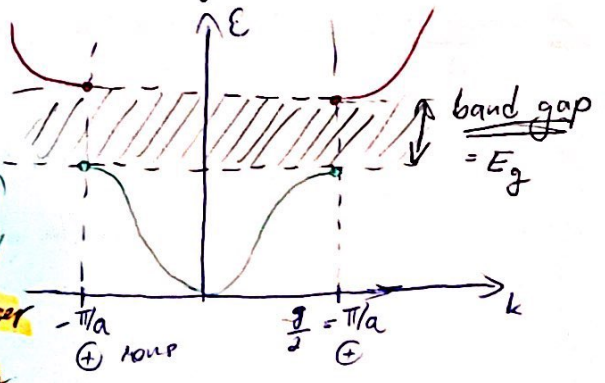


- if  $|\vec{k}| \approx \frac{|\vec{g}|}{2}$  (near the edge of BZ), scattering occurs, and scattered wave ( $\vec{k}'$ ) interferes with original ( $\vec{k} + \vec{g}$ ), creating standing waves:  $\Psi(r) = \alpha_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} + \alpha_{\vec{k}-\vec{g}} e^{i(\vec{k}-\vec{g}) \cdot \vec{r}}$
- with max and min on the ions

Periodicity of the lattice effects allowed energies for  $e^-$

→ creating a band gap, where no allowed states exist

↳ no longer free  $e^-$  as above (the good approx for bottom of well)



- $\uparrow E_g$  if interaction between  $e^-$  and lattice gets stronger
- $\downarrow E_g$  if there are imperfections in periodicity (crystal)



# Metals - free electrons model $\rightarrow E = \frac{\hbar^2 k^2}{2m}$

density of electrons:  $n = \frac{N_e}{V} = \frac{N_{atoms}}{V} \cdot n_c$  - valency = # valence  $e^-$  / Volume

for simple cube - periodicity  $\psi(0) = \psi(Na)$  in all directions

(1D) 1 unique k-value per  $\frac{2\pi}{Na} = \frac{2\pi}{L} \Rightarrow k = \frac{2\pi}{Na} n = \frac{2\pi}{L} n, n \in \mathbb{Z}$   
 (2D) 1  $e^-$  per  $(\frac{2\pi}{L})^2$   
 (3D)  $k^2 = k_x^2 + k_y^2 + k_z^2 \rightarrow$  unique value of k per volume:  $(\frac{2\pi}{L})^3, L = Na$

at  $T=0$ , all  $e^-$  in ground state  $\rightarrow$  low  $k$ 's as possible

$k_F = \max(k)$  at  $T=0$

value of sphere occupied =  $\frac{4}{3} \pi k_F^3 = N_e \cdot \left(\frac{2\pi}{L}\right)^3 \cdot 2$  - spin deg  $\rightarrow$  there can be 2  $e^-$  at same place

$$k_F^3 = \frac{N_e}{\frac{4}{3} \pi \cdot 2} \left(\frac{2\pi}{L}\right)^3$$

$$= \frac{3 N_e}{8\pi} \frac{8\pi^3}{L^3}$$

$$= \frac{3\pi^2 N_e}{L^3}$$

$$\rightarrow k_F = \left(\frac{3\pi^2 N_e}{V}\right)^{1/3}, \text{ where } V = L^3 = (Na)^3$$

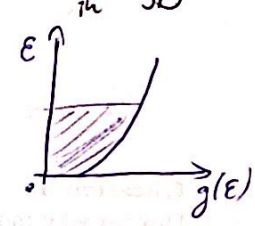
As above we have  $E_F = \frac{\hbar^2 k_F^2}{2m} \Rightarrow$  Fermi energy  $E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N_e}{V}\right)^{2/3}$

at  $T=0$

$$N_e = \int_0^{E_F} g(E) dE = \int_0^{E_F} \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{E} dE$$

$$\frac{dN}{dE} = \sqrt{E} \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{3}{2} \frac{V}{8\pi^2}$$

density of state



for  $T \neq 0$ :  $n(E) dE = g(E) f(E) dE$

#  $e^-$  in  $[E, E+dE]$

Fermi-Dirac distribution:

$$f(E) = \frac{1}{\exp\left(\frac{E-E_F}{k_B T}\right) + 1}$$

at Fermi Temperature:  $k_B T_F = E_F$

for  $T \leq \frac{T_F}{10}$ : FD  $\approx$  step function (all  $e^-$  below  $E_F$ )

$\Rightarrow$  work function = energy needed for  $e^-$  to leave =  $|E_F|$

## Introducing electric field produces current

$$mv = p = \hbar k$$

electric field  $E \Rightarrow$  force acting on  $e^-$ :  $F = -qE = m \frac{dv}{dt} = \frac{dp}{dt} = \hbar \frac{dk}{dt}$

force will make  $e^-$  move in a certain direction, but they will freq. collide with each other and ions  $\rightarrow$  average time between collisions  $\equiv$  scattering time

$$\Rightarrow \hbar \frac{dk}{dt} = \hbar \Delta k = -qE \tau = -qE \tau \rightarrow \Delta k = -\frac{qE}{\hbar} \tau \text{ or } \Delta p = -qE \tau$$

current density - amount of charge per volume move per time:  $J = nqv = n \frac{q^2 E \tau}{m^*} \sqrt{V} = \frac{\Delta p}{\hbar k}$

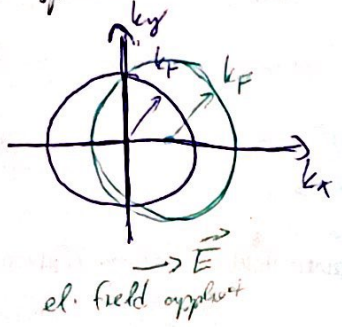
conductivity:  $\sigma = \frac{J}{E} = \frac{nq^2 \tau}{m^*}$  - property of material

$\hookrightarrow$  resistivity  $\rho = \sigma^{-1}$

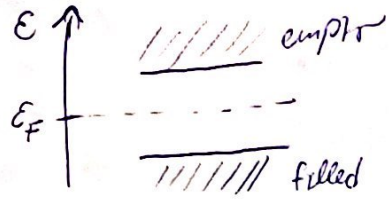
mobility  $\mu \equiv \frac{q\tau}{m^*}$

5] Semiconductors

Fermi sphere (radius  $k_F$ ):



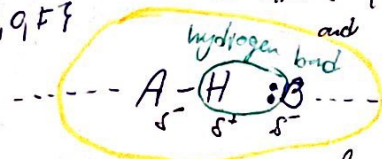
- When electric field is applied, the Fermi sphere shifts, keeping same radius
- if there exist states to which the electrons can move, they will occupy these new states (~~partly~~ further from origin than originally  $\rightarrow$  larger  $\vec{k}$  value possible)



- $\rightarrow$  large  $E$ )
- $\hookrightarrow$  if no such states exist then, the  $e^-$  remain  $\Rightarrow$  situation of insulators
- No states available around  $E_F$   $\rightarrow$  difficult to move to higher states if below Fermi temperature

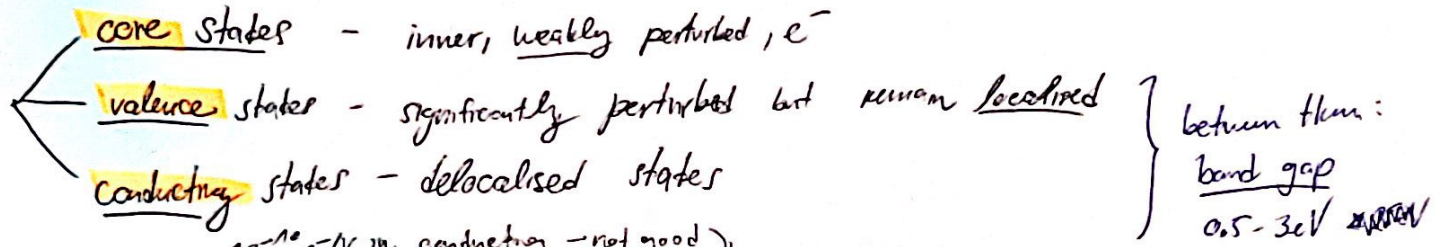
Types of Bonds

- covalent  $\star$  Ge (IV. group -  $sp^3$  hybridization, 4 bonds) - semiconductor
- |  |  |
|--|--|
| increase in difference between el. negativities $\downarrow$ | $\star$ GaAs $X = 1.8, 2.2$ ; III, V             |
|  | $\star$ ZnS II, VI                               |
|  | $\star$ NaCl I, VII $\rightarrow X = 0.93, 3.16$ |
- ionic - el. charge is localised on one of the atoms  $\Rightarrow$  mostly insulators
- molecular crystals - van der Waals interaction  $\star$  C<sub>60</sub>
- hydrogen bonding - occurs between molecules with highly electronegative atoms (N, O, F), where one is bonded to H and the other has a lone pair



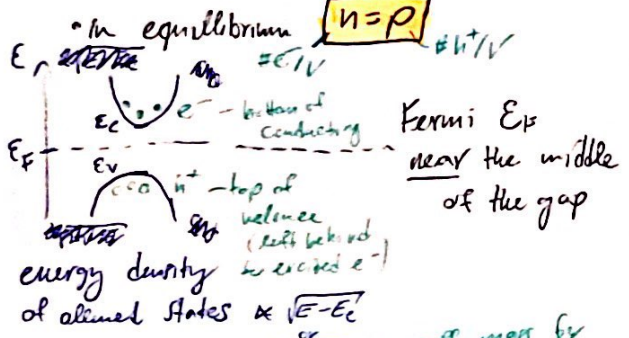
- metallic - valence  $e^-$  nearly form gas
- charge is delocalised  $\Rightarrow$  conductors

# Semiconductors

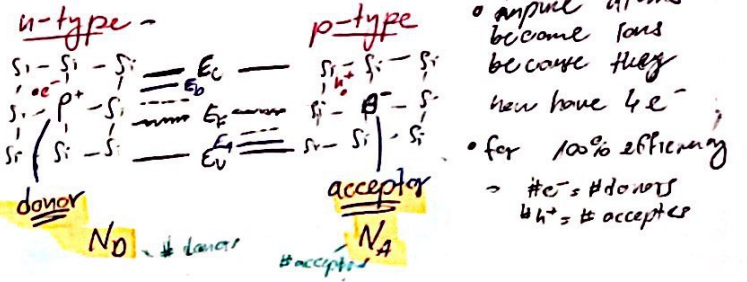


**Intrinsic**  $\sim 10^{-10}$  eV in conducting - not good  
 Si, no doping/impurities

**Extrinsic** - doped



• Si atoms replaced by P or B  
 → create 4 bonds to fit in the lattice  
 → extra  $e^-$  or (missing  $e^-$ )  $h^+$



$g(E)dE = \frac{4\pi V}{2\pi^2} \left(\frac{2m_c}{\hbar^2}\right)^{3/2} \sqrt{E-E_c} dE$   
 eff mass for conducting band

for electrons:  $n(E)dE = f(E)g(E)dE$   
 $n = N_c \exp\left(-\frac{E_c - E_f}{k_B T}\right)$   
 $f(E_f) = \frac{1}{2}$  = prob. of occupation

$N_c = 2 \left(\frac{2\pi m_c k_B T}{h^2}\right)^{3/2}$   
 $N_c \approx 2.5 \cdot 10^{25} m^{-3}$  at room temp

for holes:  $1-f(E) \approx 1$   
 $p(E)dE = (1-f(E))g(E)dE$

$p = N_v \exp\left(-\frac{E_f - E_v}{k_B T}\right)$   
 $n_i^2 = p_i^2 = np = N_c N_v \exp\left(-\frac{E_g}{k_B T}\right)$   
 Law of mass action

for intrinsic • in equilibrium (no voltage)

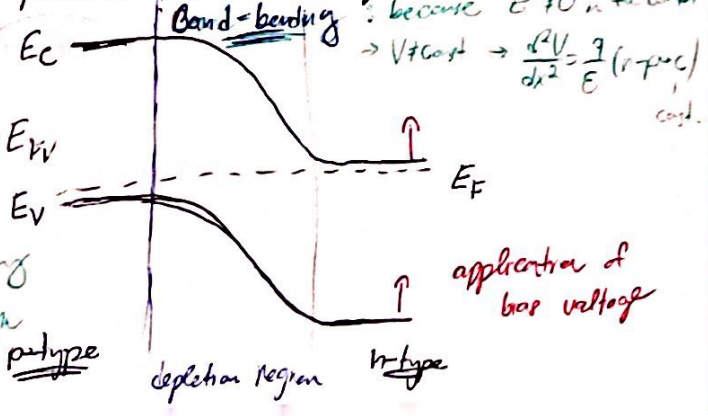
## PN-junction



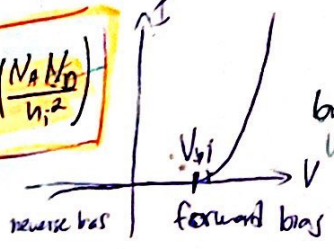
diffusion of  $e^-$  ← diffusion of  $h^+$   
 • After diffusion,  $h^+$  and  $e^-$  recombine, charge free carriers disappearing in the center of the junction  
 • However, bare ions remain in their place  
 → voltage difference → (el. field)  
 opposing the diffusion → no more  $e^-$  and  $h^+$  are able to move through: depletion region is created  
 → when drift and diffusion balance out → equilibrium, no net change

$e^-$  drift back to n-type and vice versa

Band-bending: because  $E \neq 0$  in the center  
 $\rightarrow V \neq const \rightarrow \frac{d^2 V}{dx^2} = \frac{q}{\epsilon} (n-p)$



$qV_{bi} = k_B T \ln\left(\frac{N_A N_D}{n_i^2}\right)$   
 built-in voltage



$qV_{bi} = E_g - E_{F_n} - E_{F_p}$   
 necessary to get through the junction

application of bias voltage