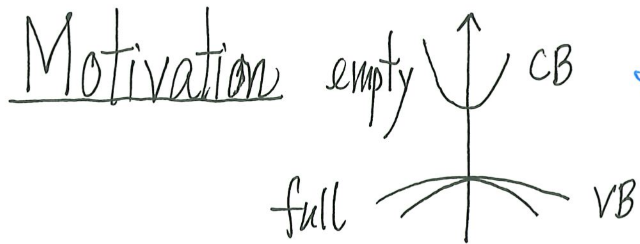
Electronic Effects of Impurities

Motivation



→ Can we intentionally control the electron number or electron number density in CB?
partially filled band conducts!

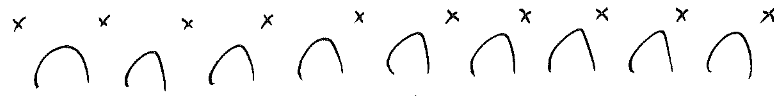
→ Can we control the number of missing electrons or (hole number density) in VB?
partially filled band conducts!

Beside Impurities intentionally added for specific purposes, there are other impurities

- Vacancy [missing atom]
- Interstitial defect [wrong place]

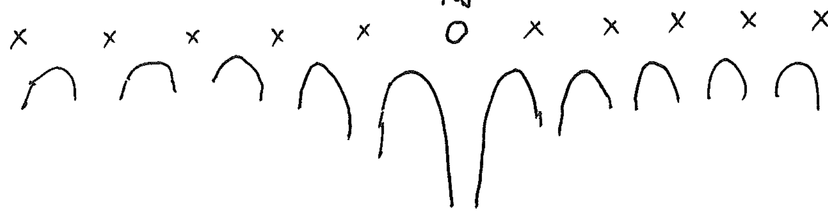
A. Think about the impurity problem

- Perfectly Ordered

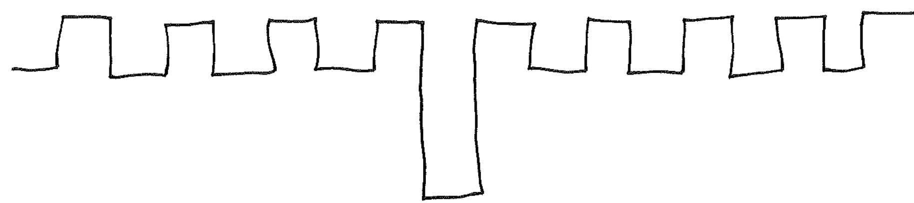


- One impurity

dopant



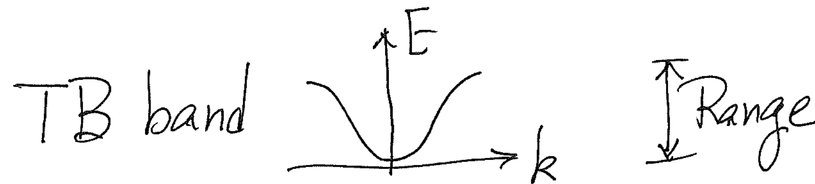
1D wells picture



OR

OR

- TBM?



push a state out?

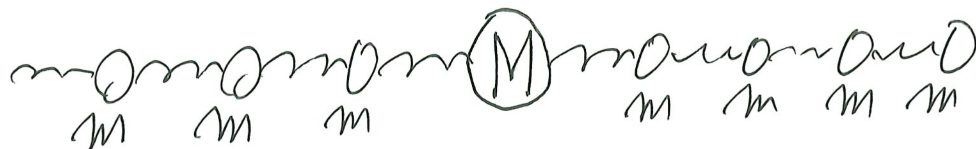
Plus impurity?

pull a state out?

Classical Mechanics balls-and-springs picture

Ordered:

Impurity:



[What happen to be normal mode frequencies? $M > m$?
$M < m$?

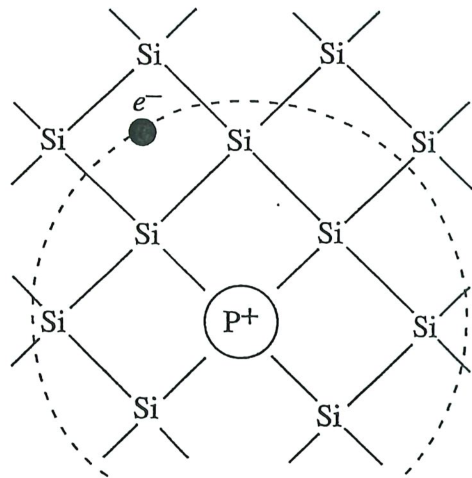
Group V (P, As) [one more electron and one more +ve charge in nucleus] atom into Group IV (Si, Ge) semiconductors

e.g. P has 5 valence electrons (Si has 4)

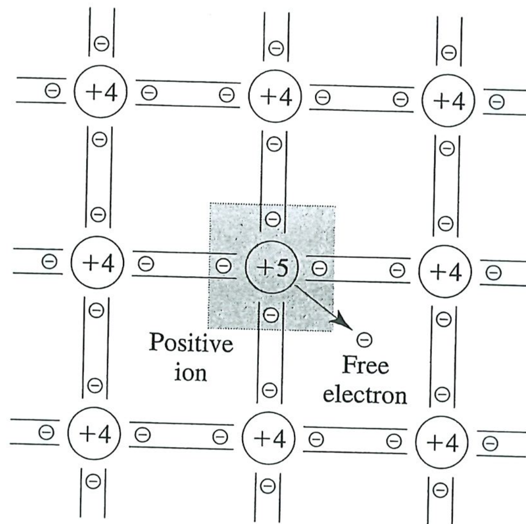
4 form bonds just as a Si atom

[5th electron is ready to move around, but P nucleus (with 4 nearby electrons forming bond) is like P^+ ion and attracts the 5th electron loosely]

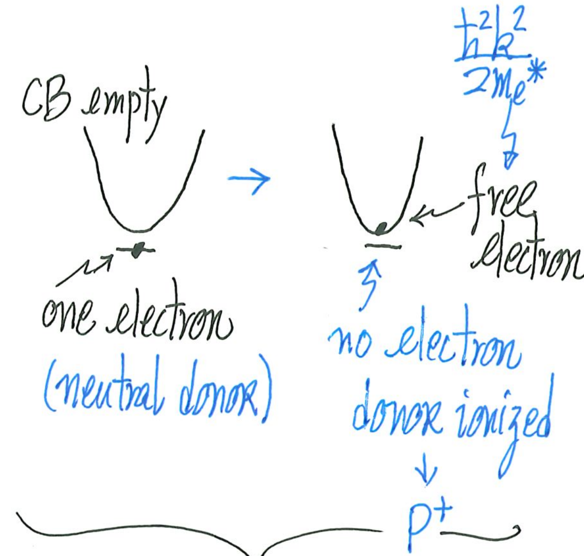
Donors



Phosphorus atom introduced substitutionally into an Si lattice to form a donor center P^+ ion to which an extra electron is weakly bound. [From B & W]



N-type doping



Impurity level can have one electron of either spin, or can have no electron

T = 0 or very low temperature extra (5th) electron is bounded (trapped) near donor center

Donor is then neutral

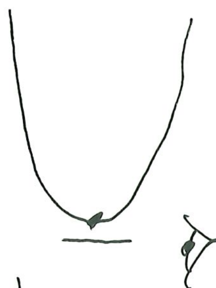
Donor (P^+ + 1 electron) can be ionized

⇒ 1 free electron in CB (negative charge, free)
(all bonds saturated ⇒ VB full)

Donor site is an ion
positive charge (can't move)

Whole system is Neutral

excitation →



trapped one electron
(can be either spin)

(neutral)

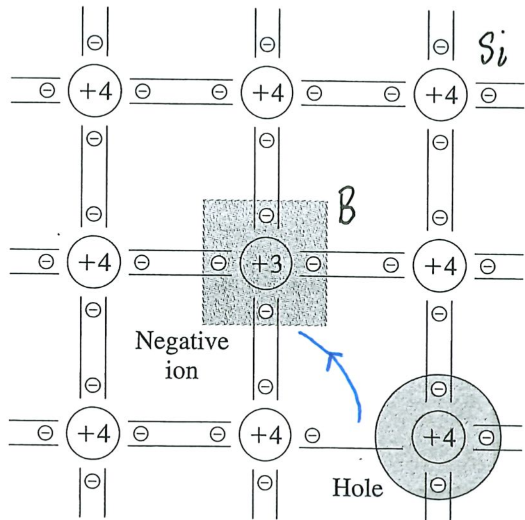
trapped no electron
(only one state)

(charged) [P^+]

Acceptors

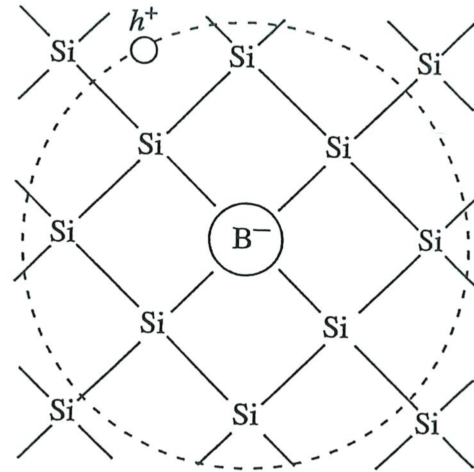
Group III (e.g. B, Al) into Group IV (e.g. Si, Ge)

3 valence electrons [one less electron to saturate all the bonds]

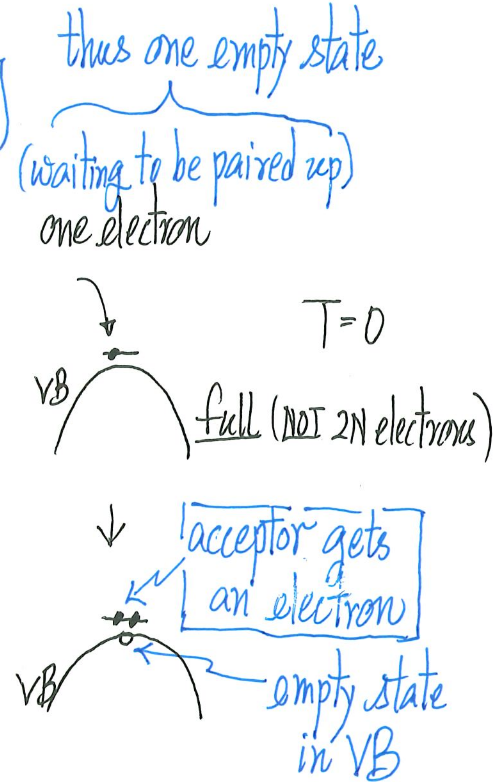


P-type doping

T=0 or low T the empty state is bounded to B^-



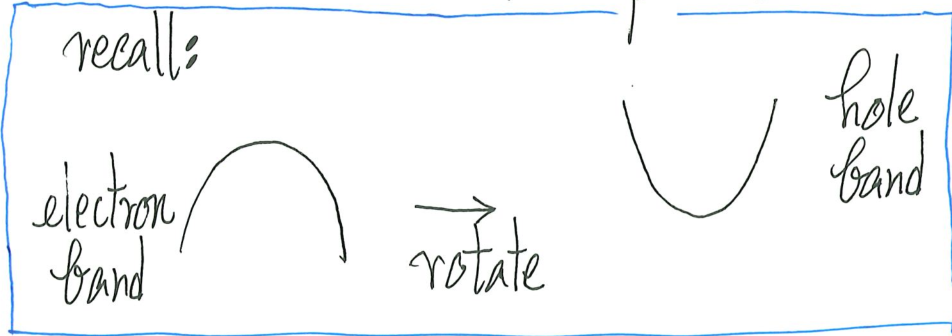
Boron atom introduced substitutionally into a Si lattice to form an acceptor center B^- ion to which a hole is weakly bound. [From B&W]



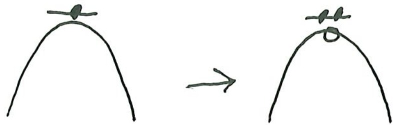
This is the electron picture

- electron from neighboring bond moves in to saturate the bond around B (becomes B^-) and the empty state wandering around (positive hole) → whole system is neutral

Think in Hole picture



Electron viewpoint

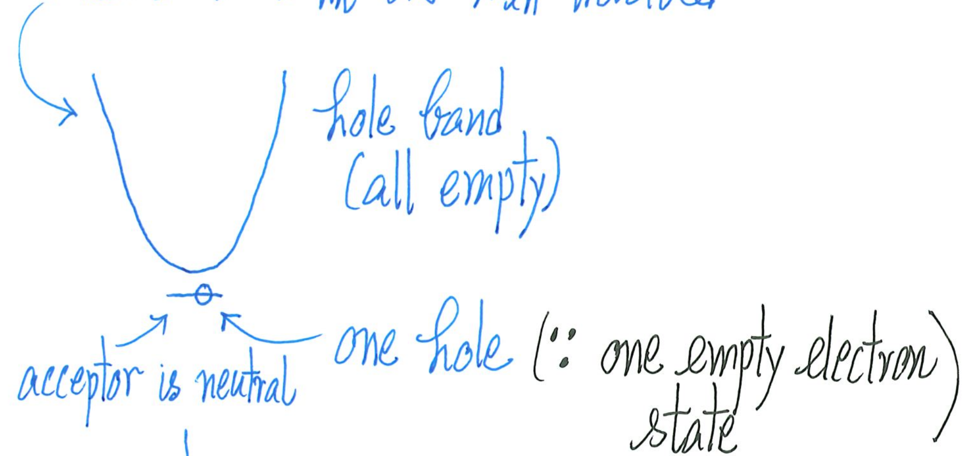


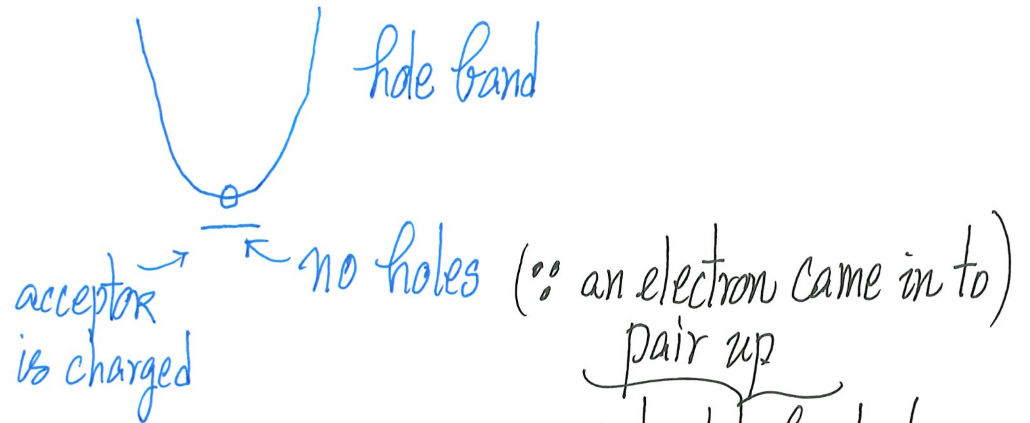
Impurity level can have two paired electrons OR one electron of either spin ($T \approx 0$ case)

Hole viewpoint

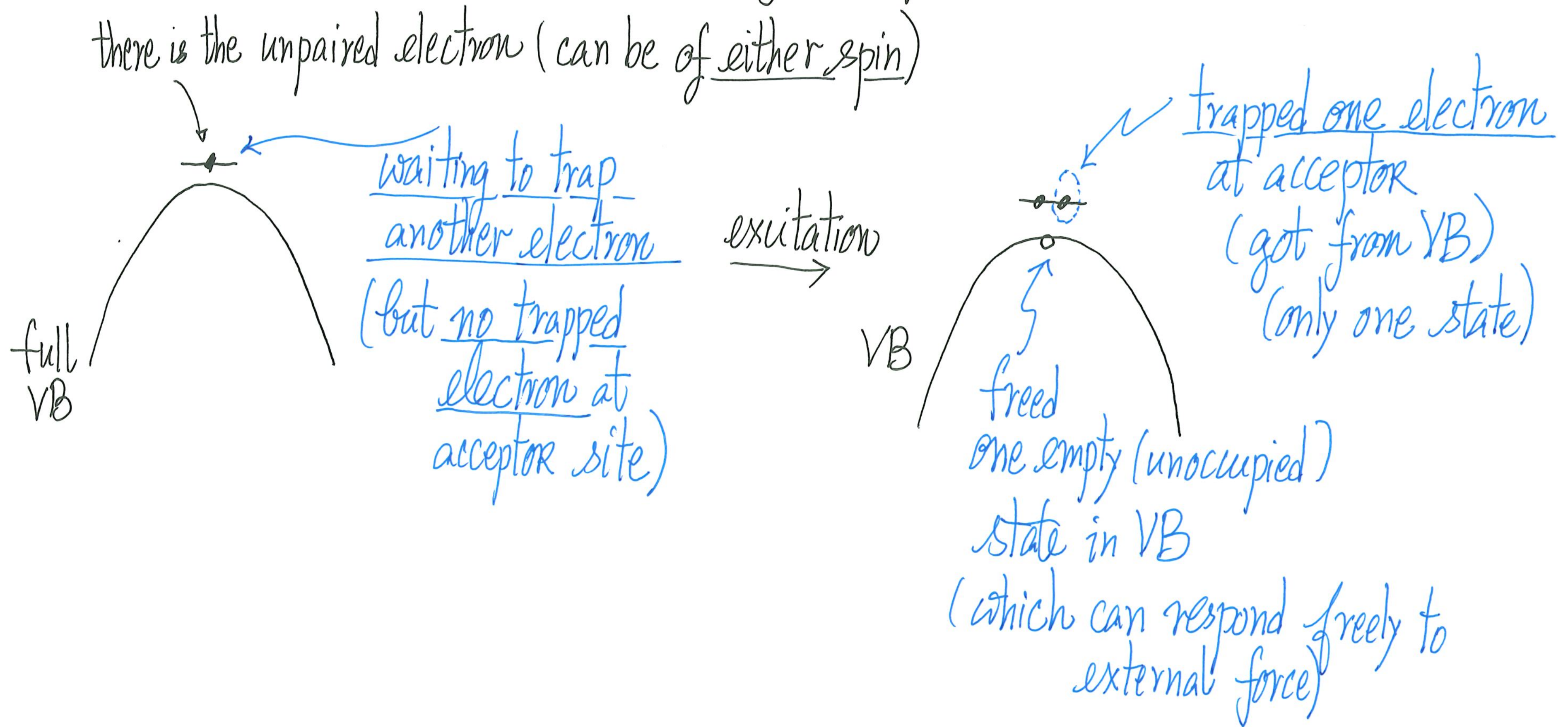
Impurity level can have one hole of either spin ($T \approx 0$ case) OR can have no hole.

rotated VB ⇒ m^*_{hh} OR m^*_{eh} involved





Electron Viewpoint of Acceptor



(should contrast this with Electron Viewpoint of Donor)

Donors will put electrons (-ve charged carriers) into otherwise empty CB

Acceptors with trap (take out) electrons from otherwise full VB and leave unoccupied electronic states (behave like +ve charge carriers) in VB

Negative carriers (n-type) Positive carries (p-type)

Host atoms and n-type (donor) and p-type (acceptor) substitutional impurities in various semiconductors

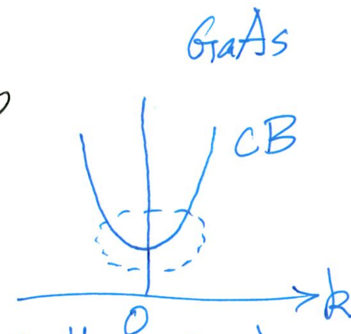
Impurities \ Host	Si	Ge	GaAs: Ga	GaAs: As
n-type, donors	P, As, Sb, Bi	P, As, Sb, Bi	Si, Ge	S, Se
p-type, acceptors	B, Al, Ga, In, Tl	B, Al, Ga, In, Tl	Be, Mg, Zn, Cd, Mn	Si, Ge

Mn is important as a dopant in connection with the diluted magnetic semiconductors

[From Economou, "The Physics of Solids"]

B. Donors giving rise to shallow impurity states just below CB

- Discussed under Effective mass Theory and Envelope Function



CB modelled by $E_c(\vec{k}) = \frac{\hbar^2 k^2}{2m^*}$ ← electron effective mass (~ bottom of CB)

(bottom of CB taken to be zero)

Change $E_c(\vec{k}) \rightarrow E_c(-i\vec{\nabla})$ [that needs completely periodic $V(\vec{r})$]

"Extra term" $\frac{-5e^2}{4\pi\varepsilon_0 r}$ → but $\frac{-4e^2}{4\pi\varepsilon_0 r}$ used to make up $V(\vec{r})$

thus $\frac{-e^2}{4\pi\varepsilon_0 r}$ is left as extra (attracts the 5th electron that would be freed to CB)

Envelope function: spread out over many lattice constants

polarizability ⇒ dielectric constant

$$\left[-\frac{\hbar^2}{2m^*}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0\varepsilon_r r}\right] F_c(\vec{r}) = E\, F_c(\vec{r})$$

(zero is bottom of CB)

Ground state energy $E = (-13.6\,eV)\cdot\left(\frac{m^*}{m}\right)\left(\frac{1}{\varepsilon_r^2}\right)$

$\frac{m^*}{m}$: $\ll 1$

ε_r: "dielectric constant" (relative permittivity)

Size of ground state

= effective Bohr radius

$= a_B^* = a_B \cdot \varepsilon_r \left(\frac{m}{m^*}\right)$

a_B^*: much bigger than a_B

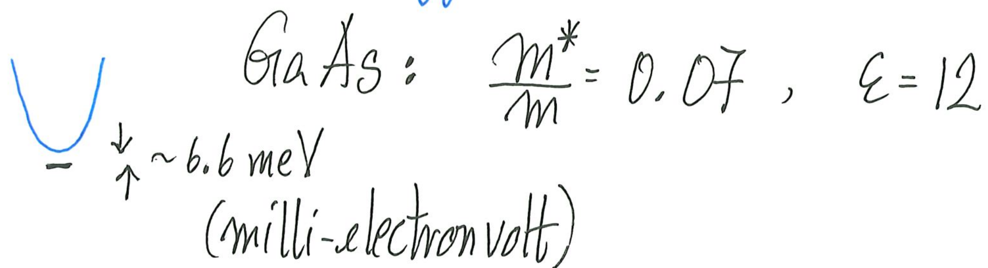
a_B: Bohr radius

ε_r: ~ 10

$\frac{m}{m^*}$: > 1

$\varepsilon \sim 10 - 12$

$\frac{m^*}{m} \sim 7\% \sim 0.07$



GaAs: $\frac{m^*}{m} = 0.07$, $\varepsilon = 12$

~ 6.6 meV

(milli-electronvolt)

(shallow: very close to CB)

$E_{GS} = -6.6$ meV (below bottom of CB)

$a_B^* \sim 90\,Å$

$90\,Å$: many lattice constants

Si and Ge anisotropic CB

$$E_c(\vec{k}) = \frac{\hbar^2}{2}\left(\frac{k_x^2}{m_1^*} + \frac{k_y^2}{m_2^*} + \frac{k_z^2}{m_3^*}\right)$$

E.g. $m_1^* \neq m_2^* = m_3^*$ around minimum at $(k_0, 0, 0)$

then apply effective mass theory

- Use Variational method OR numerical solution

- More formally, even for the single Si CB (this is just one band "n") there are 6 minima

  $F_{c,i}$ $(i = 1, 2, 3, 4, 5, 6)$ 6 envelope functions using Bloch states around $(\pm k_0, 0, 0)$, $(0, \pm k_0, 0)$, $(0, 0, \pm k_0)$

Need $F_c = \sum_i c_i F_{c,i}$ (linear combining $F_{c,i}$) (even in one-band assumption)

$$\frac{-e^2}{4\pi\varepsilon_0 r [\varepsilon]}$$

$\leftarrow$ response of charges in material to an extra field (e.g. a charge somewhere)

Perfect Si : 6 minimum of same energy

Extra $\frac{-e^2}{4\pi\varepsilon_0 r \boxed{\varepsilon}}$ term : Needs degenerate perturbation theory (thus $\sum_i c_i F_{c,i}$)

Generally, Polarization → $P(\vec{r},t) = \int_0^t \int \underbrace{\chi(\vec{r}-\vec{r}\,';t-t')}_{\text{response function}} \underbrace{\mathcal{E}(\vec{r}\,',t')}_{\text{stimulation}} d^3r'\,dt'$

$P(\vec{r},t)$ = response

response function ("susceptibility" in general)

$\vec{P} = \chi \vec{E}$

$\vec{D} = \varepsilon_0 \vec{E} + \vec{P}$

in general, nonlocal : stimulation at $\vec{r}\,'$ leads to response at $\vec{r}$

(in general: no always important)

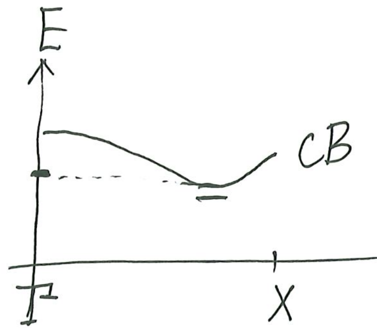
but now 6 minima at different $\vec{k}$'s in 1st B.Z.

2 are connected by some $\vec{q}$ in $\vec{k}$-space ⇒ some particular Fourier component $\varepsilon(\vec{q})$ of dielectric constant will connect (mix) the minima

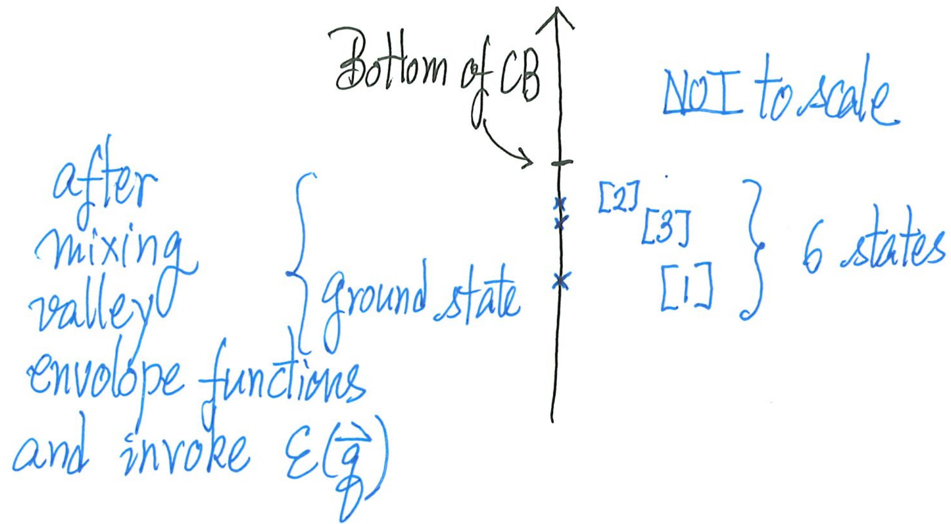
(a form of inter-valley physics)

Effect (academic)

Not 6 individual



But after mixing the 6 ground state (impurity)



Not important for most applications (as donor will be ionized and trapped electron goes into CB)

Ionization energies (meV) for donors in Si and Ge

System	State	Theory	P	As	Sb
Si	$1s(A_1)$	40.65	45.5	53.7	42.7
	$1s(T_2)$	30.05	33.9	32.6	32.9
	$1s(E)$	28.95	32.6	31.2	30.5
	$2p_0$	11.51	11.5	11.5	11.6
	$2p_\pm$	6.40	6.4	6.3	6.3
	$3p_0$	5.48	5.5	5.5	5.3
	$3p_\pm$	3.12	3.1	3.1	3.0
Ge	$1s(A_1)$	10.26	12.76	14.04	10.19
	$1s(T_2)$	9.66	9.93	9.81	9.87
	$2p_0$	4.74	4.74	4.73	4.74
	$2p_\pm$	1.73	1.73	1.73	1.73
	$3p_0$	2.56	2.56	2.56	2.57
	$3p_\pm$	1.03	1.05	1.02	1.03

A_1 singlet [1 state]
T_2 triplet [3 states]
E doublet [2 states]

(From B&W)

Similar treatment for 4 minima in Ge

Donor impurities in III - VI Semiconductors

Look at result: Ground state binding energy $(-13.6\,eV) \cdot \left(\frac{m^*}{m}\right)\left(\frac{1}{\varepsilon_r^2}\right)$

property of host material (on m^*)

property of host (on ε_r)

doesn't depend on dopants (?)

Binding energies (meV) for donors in III–V and II–VI semiconductors

System	Donor	Theory	Experiment
GaAs	Si	5.72	5.84
	S	5.72	5.87
InSb	Te	0.59	0.6
CdTe	In	11.6	14
ZnSe	Al	25.7	26.3
	Cl	25.7	26.9

[From B&W]

← seem to work quite well

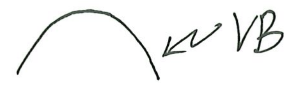
However, not always true

When is the Effective Mass Theory valid?

- Extra term slowly varying in space and weak
- Hydrogen-like + screening using ε_r (only OK if $F(\vec{r})$ spreads out)

C. Acceptors giving rise to shallow impurity states just above top of VB

Simplest (toy) picture



Effective mass theory

$$E_v(\vec{k}) = E_v - \frac{\hbar^2 k^2}{2m_h^*} \quad \text{(electron viewpoint)}$$

E_v: top of VB (e.g. $E_v = -E_g$ if zero is at bottom of CB)

from $V(\vec{r})$

But substituted in $-\frac{3e^2}{r}$, needed $-\frac{4e^2}{r}$ to make up $V(\vec{r})$

$\Rightarrow$ Extra term is $+\frac{e^2}{4\pi\varepsilon_0 r}$

Including screening $\frac{+e^2}{4\pi\varepsilon_0\varepsilon_r r}$ (all in electron viewpoint)

$$\left[\left(E_v - \frac{\hbar^2 k^2}{2m_h^*}\right) + \frac{e^2}{4\pi\varepsilon_0\varepsilon_r r}\right] F_v(\vec{r}) = E\, F_v(\vec{r})$$

$$k \to -i\vec{\nabla}, \quad \frac{\hbar^2 k^2}{2m} \to -\frac{\hbar^2}{2m}\nabla^2$$

$$\left(E_v + \frac{\hbar^2}{2m_h^*}\nabla^2 + \frac{e^2}{4\pi\varepsilon_0\varepsilon_r r}\right)F_v(\vec{r}) = E\,F_v(\vec{r})$$

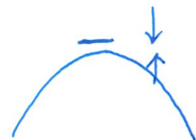
$$\Rightarrow \underbrace{\left(-\frac{\hbar^2}{2m_h^*}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0\varepsilon_r r}\right)}_{\text{a hydrogen-like problem again}} F_v(\vec{r}) = (E_v - E)\,F_v(\vec{r})$$

a hydrogen-like problem again (like a positive mass hole seeing the attractive B^- ion)

$$\therefore (E_v - E) \sim (-13.6)\left(\frac{m_h^*}{m}\right)\left(\frac{1}{\varepsilon_r^2}\right)\text{ eV}$$

$$\Rightarrow E \sim E_v + \underbrace{(13.6)\left(\frac{m_h^*}{m}\right)\left(\frac{1}{\varepsilon_r^2}\right)\text{ eV}}_{\text{slightly above top of VB}}$$

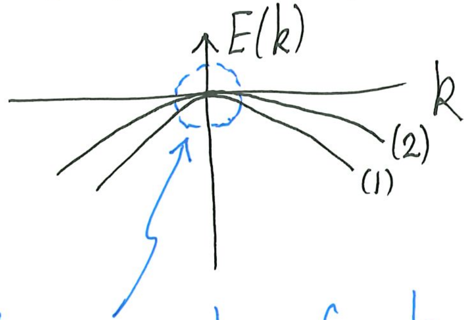
$$\sim -E_g + (13.6)\left(\frac{m_h^*}{m}\right)\left(\frac{1}{\varepsilon_r^2}\right)\text{ eV}$$



But real materials have more complicated VBs structure

Experimental and theoretical ground state ionization energies (meV) for Group III acceptors in Ge

Acceptor	Experimental	Theoretical
B	10.3	9.3
Ga	10.8	9.3
In	11.4	9.3
Tl	13.0	9.3



Consider envelope functions $F_1(\vec{r})$, $F_2(\vec{r})$, $F_3(\vec{r})$ constructed for the three VBs around $\vec{k}=0$

Use a VB description + Effective Mass Theory $\vec{k} \to -i\vec{\nabla}$

$$\begin{bmatrix} -L\frac{\partial^2}{\partial x^2} - M\left(\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right) + V_i - E_{vi} & -N\frac{\partial^2}{\partial x \partial y} & -N\frac{\partial^2}{\partial x \partial z} \\ -N\frac{\partial^2}{\partial x \partial y} & -L\frac{\partial^2}{\partial y^2} - M\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial z^2}\right) + V_i - E_{vi} & -N\frac{\partial^2}{\partial y \partial z} \\ -N\frac{\partial^2}{\partial x \partial z} & -N\frac{\partial^2}{\partial y \partial z} & -L\frac{\partial^2}{\partial z^2} - M\left(\frac{\partial^2}{\partial x^2}+\frac{p^2}{\partial y^2}\right) + V_i - E_{vi} \end{bmatrix} \begin{bmatrix} F_1(r) \\ F_2(r) \\ F_3(r) \end{bmatrix} = 0$$

(Taken from B & W)

$$V_i = -\frac{e^2}{4\pi\varepsilon_0\varepsilon_r r}$$

E_{vi}'s are unknowns

D. Some Other Cases

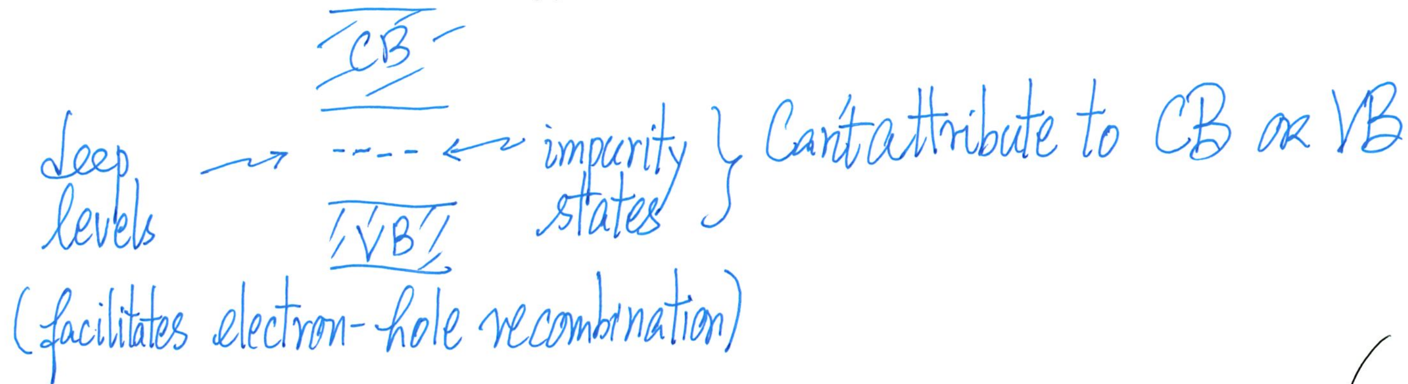
- Binding energy can depend on dopants

  $\frac{-e^2}{4\pi\varepsilon_0\varepsilon_r r}$ may not always work

  Actual $V_{ext}(r)$ not weak, varying rapidly over lattice constant scale

  e.g. dopant with more core electrons than host atoms

- Binding energy not close to CB (or VB) : Deep Level



Ionization energies (eV) of interstitial 3*d* transition metal dopants in Si

Ti	V	Cr	Mn	Fe
0.89	0.72	0.95	0.75	0.385
1.09	1.01	0.38	1.06	
0.25	0.30		0.25	

Very different from $(-13.6)\left(\frac{m_e^*}{m}\right)\left(\frac{1}{\varepsilon_r^2}\right) \sim 0.03\text{eV}$ for Si

Impurity Band

- When more and more donors are doped, the separation between donors become close (in real space)

  The impurity states (e.g. modified bigger a_B^*) overlap

  $\Rightarrow$ form impurity band (TBM of H-like states)

bottom of CB →

} impurity band

energy E

CB DOS

E_F ← if # electrons fill into CB

impurity band

$g(E)$ (DOS)

} may have free electrons in CB in such Heavily doped "degenerate" n-type semiconductor

this is like ideal Fermi Gas in Statistical Mechanics