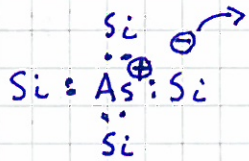
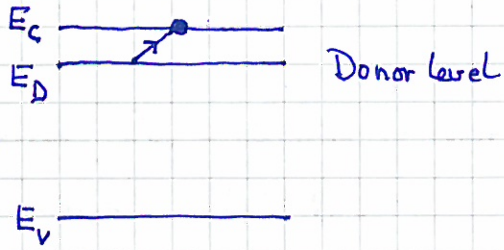
Doped semiconductors

Si : 4 valence electrons
As : 5 —— " —— } ⇒



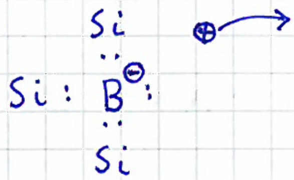
⇒ As in Si easily ionized :

$$As \rightarrow As^+ + e$$



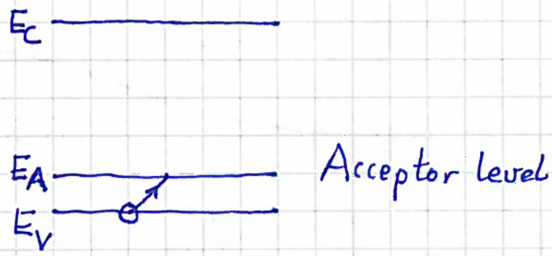
$$\Delta E = E_{ion} = E_c - E_D$$

B : 3 valence electrons ⇒



⇒ B in Si easily ionized :

$$B \rightarrow B^- + h$$



$$\Delta E = E_{ion} = E_A - E_V$$

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Use H-atom-knowledge for rough estimates :

$$E^H_{ion} = \frac{m_e e^4}{32\pi^2 \hbar^2 \varepsilon_0^2} = 13.6 \text{ eV}$$ ≙ binding energy of electron in H

$$a^H = \frac{4\pi \varepsilon_0 \hbar^2}{m_e e^2} = 0.53 \text{ Å}$$ = average distance between electron and nucleus (Bohr radius)

Si : $m_c^* \sim \frac{1}{3} m_e$ $\left((m_t^* \cdot m_t^* \cdot m_l^*)^{1/3} \simeq 0.32\, m_e \right)$

$\varepsilon \sim 12\, \varepsilon_0$ (permittivity)

⇒ $E_{ion}[\text{As in Si}] \simeq 13.6 \text{ eV} \cdot \frac{m_c^*}{m_e} \cdot \left(\frac{\varepsilon_0}{\varepsilon}\right)^2 \sim 30 \text{ meV}$

$a[\text{As in Si}] \simeq 0.53 \text{ Å} \cdot \frac{\varepsilon}{\varepsilon_0} \cdot \frac{m}{m_c^*} \sim 20 \text{ Å}$

} ⇒ Loosely bound electron !

n-type : (predominantly) donors $\Rightarrow n \gg p$

p-type : (— " —) acceptors $\Rightarrow p \gg n$

Assume N_D donors pr unit volume, donor level E_D, 10-50 meV below E_c.

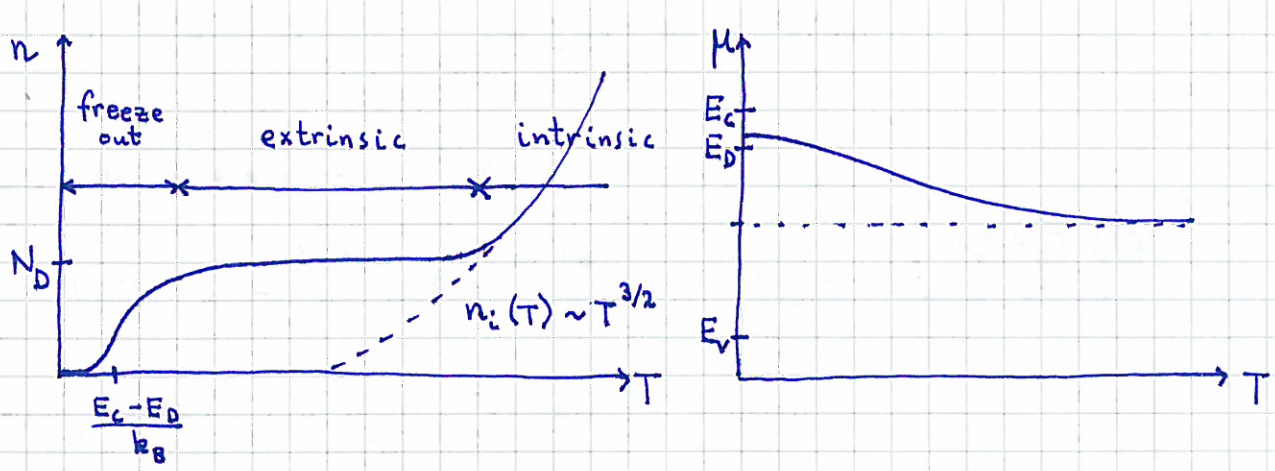
Qualitatively:

$T \to 0 \Rightarrow n \to 0$ and E_D occupied [by 1 electron pr donor]

$\Rightarrow E_D < \mu < E_c$ [remember: $f(\mu) = 1/2$]

$T \gtrsim (E_c - E_D)/k_B \Rightarrow n \simeq N_D$, $\mu \simeq \frac{1}{2}(E_c + E_V)$

$T \gg (E_c - E_D)/k_B \Rightarrow n_i(T) \gg N_D \Rightarrow n \approx n_i$, $\mu \simeq \frac{1}{2}(E_c + E_V)$



Quantitatively:

Possible occupations of given donor ($E = E_D$):

$j = 0$ (empty)

$j = 1$ (1 electron, spin up)

$j = 1$ (— " —, spin down)

[$j = 2$, ↑ and ↓, possible, but $E \gg E_D$ due to Coulomb repulsion]

Stat. mech. $\Rightarrow \langle j \rangle = \dfrac{\sum_j j\, e^{-j(E_D - \mu)/k_B T}}{\sum_j e^{-j(E_D - \mu)/k_B T}}$ = average acc. number

$$\Rightarrow \langle j \rangle = \frac{0 \cdot e^{0} + (1+1)\, e^{-(E_D-\mu)/k_BT}}{e^{0} + 2\, e^{-(E_D-\mu)/k_BT}}$$

$$= \frac{1}{\frac{1}{2}\, e^{(E_D-\mu)/k_BT} + 1}$$

N_D = total density of donor atoms

n_D = density of excited donor atoms (those with $j=0$)

Probability of excited donor: (Partition function)

$$P(j=0) = \frac{e^{0}}{Z} \quad ; \quad Z = \sum_j e^{-j(E_D-\mu)/k_BT} = 1 + 2\, e^{(\mu-E_D)/k_BT}$$

$$\Rightarrow n_D = N_D \cdot P(j=0) = \frac{N_D}{1 + 2\, e^{\mu/k_BT}\, e^{-E_D/k_BT}}$$

Density of electrons in C.B: [From p. 23]

$$n = N_C\, e^{\mu/k_BT}\, e^{-E_C/k_BT} \quad ; \quad N_C = 2\left\{\frac{m_c^* k_B T}{2\pi\hbar^2}\right\}^{3/2}$$

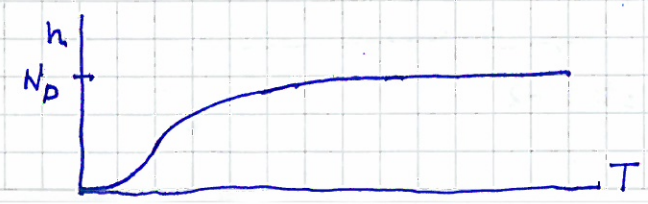
$$\Rightarrow e^{\mu/k_BT} = \frac{n}{N_C}\, e^{E_C/k_BT}$$

$$\Rightarrow n_D = \frac{N_D}{1 + 2\,\frac{n}{N_C}\, e^{(E_C-E_D)/k_BT}}$$

Assume $n \approx n_D$ (i.e. freeze out or extrinsic region)

$$\Rightarrow 2\,(n_D^2/N_C)\, e^{(E_C-E_D)/k_BT} + n_D - N_D = 0$$

$$\Rightarrow n_D = \ldots = \frac{2N_D}{1 + \sqrt{1 + \frac{8N_D}{N_C}\, e^{(E_C-E_D)/k_BT}}} = n(T)$$



Note: In extrinsic region, $n \gg n_i$.

Law of mass action: $n \cdot p = n_i^2$

$\Rightarrow$ $p = n_i^2/n = n_i \cdot \frac{n_i}{n} \ll n_i \ll n$ for n-type semicond.

For p-type: $n \ll p$ (in extrinsic region)

08.02.10

Surfaces, Interfaces [Heinzel, chapter 3]

Infinite perfect crystal

$\Rightarrow$ Bloch functions $\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r})\, e^{i\vec{k}\cdot\vec{r}}$; $u_{\vec{k}}(\vec{r}+\vec{R}) = u_{\vec{k}}(\vec{r})$

real $\vec{k}$ $\Rightarrow$ $|\psi_{\vec{k}}|^2$ is periodic in Bravais Lattice, i.e., an extended state ("delocalized")

Presence of surface(s) $\Rightarrow$ translational invariance broken

$\Rightarrow$ localized states possible

Use very simple model to demonstrate presence of surface states:

- 1D crystal, N atoms in positions $x_j = j \cdot a$ $(j = 1, 2, \ldots, N)$
- 1 atomic s-state pr atom (energy E_0)
- nearest neighbour tight binding approximation

Atomic SE (SE = Schrödinger Equation):

$$\underbrace{\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V_a(x-x_j)\right]}_{H_j} \underbrace{\chi(x-x_j)}_{\text{s-state on atom } j} = E_0\,\chi(x-x_j)$$

SE for N atoms: $\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\,\psi(x)$

$V(x) = \sum_{j=1}^{N} V_a(x-x_j) \approx \sum_j V_j$

LCAO: $\psi(x) = \sum_{j=1}^{N} c_j\, \chi(x-x_j)$

(= Bloch function if $c_j \sim e^{\pm ikja}$, see p. 14)

More convenient notation:

$\chi(x-x_j) \rightarrow |j\rangle$ "ket" $\Rightarrow |\psi\rangle = \sum_\ell c_\ell |\ell\rangle$

$\chi^*(x-x_j) \rightarrow \langle j|$ "bra"

Assume $\langle j|\ell\rangle \equiv \int dx\, \chi^*(x-x_j)\chi(x-x_\ell) = \delta_{j\ell}$

SE, atom j: $H_j|j\rangle = E_0|j\rangle$

SE, crystal: $H|\psi\rangle = E|\psi\rangle$

Task: determine $\{c_j\}$ and E

$\langle j|H|\psi\rangle = \langle j|E|\psi\rangle = E\sum_\ell \langle j|c_\ell|\ell\rangle = E\,c_j$

$\sum_\ell \langle j|\{H_j + (H-H_j)\}c_\ell|\ell\rangle$

$= E_0 c_j + \sum_\ell \sum_{m\neq j} c_\ell \langle j|V_m|\ell\rangle$

$j=\ell \neq 1 \text{ or } N$: $\sum_{m\neq j}\langle j|V_m|\ell\rangle = -\alpha < 0$ [Two m-values are n.n. to j]

$j=\ell = 1 \text{ or } N$: $\sum_{m\neq j}\langle j|V_m|\ell\rangle = -\alpha' < 0$ [One m-value is n.n. to j]

$\Rightarrow \alpha > \alpha'$

$j=\ell\pm 1$: $\sum_{m\neq j}\langle j|V_m|\ell\rangle = -\gamma < 0$

Signs: $V_m < 0$ and s-states $\Rightarrow$ α, α', γ are positive

Introduce:

$$\varepsilon = E - E_0 + \alpha$$

$$\varepsilon_0 = \alpha - \alpha' = \varepsilon - (E - E_0 + \alpha') > 0$$

$\Rightarrow$ N linear equations for $C_1, C_2, \ldots, C_N$:

(1) $(\varepsilon - \varepsilon_0) C_1 + \gamma C_2 = 0$

(2) $\gamma C_{n-1} + \varepsilon C_n + \gamma C_{n+1} = 0 \qquad (n = 2, 3, \ldots, N-1)$

(3) $\gamma C_{N-1} + (\varepsilon - \varepsilon_0) C_N = 0$

Try: $C_n = A e^{ikna} + B e^{-ikna}$ ($\Rightarrow$ Bloch states)

[$\Rightarrow$ we may limit ourselves to $0 < k < \pi/a$ for real k-values]

Eqn (2) $\Rightarrow A e^{ikna}[\varepsilon + 2\gamma \cos ka] + B e^{-ikna}[\varepsilon + 2\gamma \cos ka] = 0$

$$\Rightarrow \varepsilon = -2\gamma \cos ka$$

Insert this into (1) and (3) to find possible k-values:

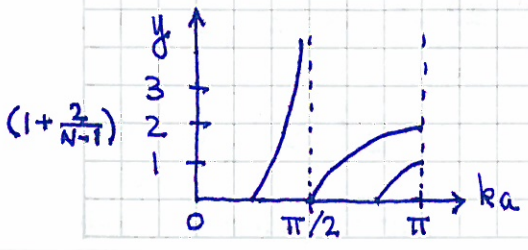
[Comment: $N \to \infty$ $\Rightarrow$ continuous $\varepsilon(k)$, cf. p.16! NB: on p.16, $\gamma < 0$]

$$\Rightarrow \begin{bmatrix} (\varepsilon - \varepsilon_0) e^{ika} + \gamma e^{2ika}, & (\varepsilon - \varepsilon_0) e^{-ika} + \gamma e^{-2ika} \\ (\varepsilon - \varepsilon_0) e^{ikNa} + \gamma e^{ik(N-1)a}, & (\varepsilon - \varepsilon_0) e^{-ikNa} + \gamma e^{-ik(N-1)a} \end{bmatrix} \begin{bmatrix} A \\ B \end{bmatrix} = 0$$

Nontrivial solutions if $\det[\ldots\ \ldots] = 0$

$$\Rightarrow y \equiv \frac{\varepsilon_0}{\gamma} = \frac{-\sin Nka \pm \sin ka}{\sin (N-1) ka}$$ (which is positive)

Example: $N = 3 \Rightarrow y = -\frac{\sin 3ka}{\sin 2ka} \pm \frac{\sin ka}{\sin 2ka} = \ldots = \begin{cases} -2\cos ka \\ -2\cos ka + \dfrac{1}{\cos ka} \end{cases}$



$N-2 = 1$ real k-values

$N-1 = 2$ real k-values

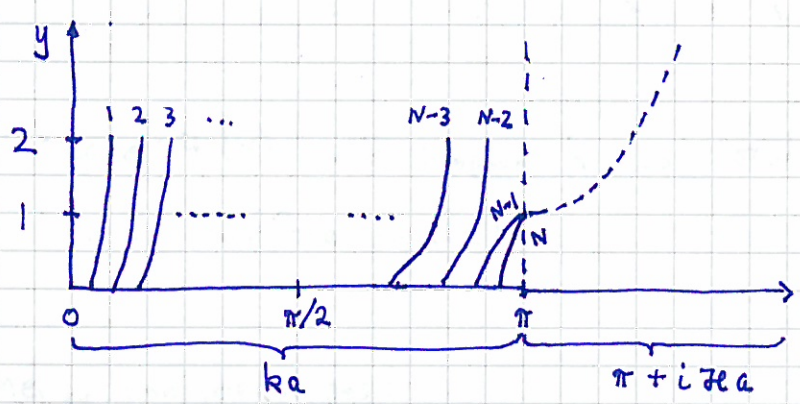
$N = 3$ real k-values

N atomic states $\Rightarrow$ must have a total of N states

If $y = \varepsilon_0/\gamma > 1 + \frac{2}{N-1}$ (≈ 1 for large N):

only N-2 states with <u>real</u> values of k

$\Rightarrow$ must have 2 states with <u>complex</u> value of k ! ["Complex Band Structure"]



$k = \frac{\pi}{a} + i\varkappa \quad \Rightarrow \quad ka = \pi + i\varkappa a$

$\Rightarrow \sin Nka = (-1)^N \left(-\frac{1}{i}\right) \sinh N\varkappa a$

$\sin(N-1)ka = (-1)^{N-1} \left(-\frac{1}{i}\right) \sinh(N-1)\varkappa a$

$\sin ka = \frac{1}{i} \sinh \varkappa a$

$\cos ka = -\cosh \varkappa a$

$\Rightarrow \quad y = \frac{\varepsilon_0}{\gamma} = \frac{\sinh N\varkappa a \pm \sinh \varkappa a}{\sinh(N-1)\varkappa a}$

$\frac{\varepsilon}{\gamma} = 2\cosh \varkappa a = e^{\varkappa a} + e^{-\varkappa a}$

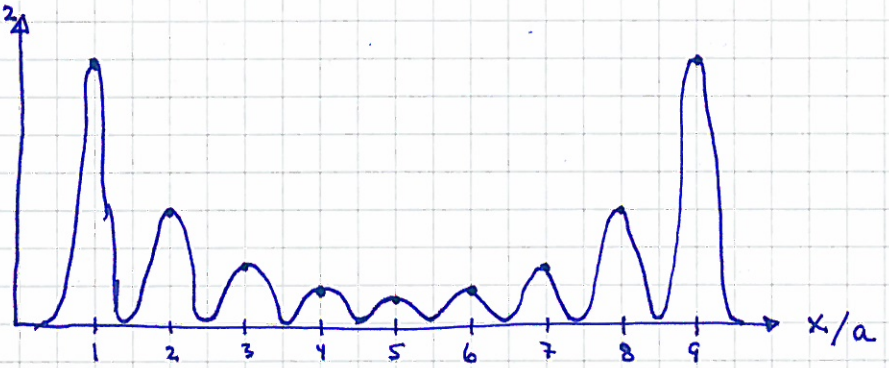
Large N $\Rightarrow |\sinh N\varkappa a| \approx \left|\frac{1}{2} e^{N\varkappa a}\right| \gg |\sinh \varkappa a|$

$\Rightarrow \frac{\varepsilon_0}{\gamma} \approx \frac{e^{N\varkappa a}}{e^{(N-1)\varkappa a}} = e^{\varkappa a}$

$\Rightarrow C_2 = -\frac{\varepsilon - \varepsilon_0}{\gamma} C_1 = -e^{-\varkappa a} C_1 \quad ; \quad C_{N-1} = -e^{-\varkappa a} C_N$

$\Rightarrow |C_2| < |C_1| \quad \Rightarrow |\psi|^2$ is larger on atom 1 than atom 2,
and $|C_{N-1}| < |C_N|$ and —"— atom N —"— N-1

Also: $|c_2| > |c_3| > \ldots\ldots > |c_{N/2}| < \ldots < |c_{N-2}| < |c_{N-1}|$

$\Rightarrow$ 

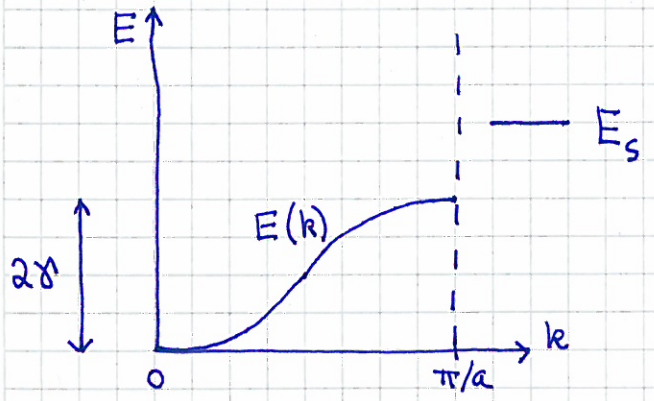
$\Rightarrow$ State $\psi(x)$ with complex k is localized at ("near") surface!

I.e.: Surface state!

Energy considerations:

For real k-values: $E(k) = E_0 - \alpha - 2\gamma \cos ka$

For complex $k = \frac{\pi}{a} + i\varkappa$: $E(\varkappa) = E_0 - \alpha + 2\gamma \cosh \varkappa a = E_s$



$\cosh \varkappa a > 1 \Rightarrow E_s \neq E(k)$

$\Rightarrow$ energy of surface state is <u>outside band</u>