Lecture on

Semiconductors / 半導体

(Physics of semiconductors)

2021.4.21 Lecture 03

10:25 – 11:55

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Review of lecture in the last week

Chapter 2 Energy bands, effective mass approximation

Energy band calculation

- Nearly free electron approximation
- Tight-binding approximation
- (empirical) Pseudo-potential calculation method
- k·p perturbation method

Energy band measurement

- Angle-resolved photoemission spectroscopy (ARPES)
- Cyclotron resonance

Example of tight-binding approximation: Band structure in graphene

Contents today

Envelope function (effective mass approximation)

Chapter 3 Carrier statistics and chemical doping

Density of states

Definition and properties of valence band hole states

Carrier distribution in intrinsic semiconductors

Shallow hydrogen-like impurity states

Shallow impurity states in Si

Doping and carrier distribution

Envelope function (effective mass approximation)

Inverse effective mass tensor: $$\left(\frac{1}{m^*}\right)_{ij} \equiv \frac{1}{\hbar^2}\frac{\partial^2 E(\boldsymbol{k})}{\partial k_i \partial k_j}$$

Problem: Non-uniform perturbation potential $U(\boldsymbol{r})$

Schrödinger equation $$\left[-\frac{\hbar^2\nabla^2}{2m} + V(\boldsymbol{r}) + U(\boldsymbol{r})\right]\zeta(\boldsymbol{r}) = [\hat{H}_0 + U(\boldsymbol{r})]\zeta(\boldsymbol{r}) = E\zeta(\boldsymbol{r})$$

Expand $\zeta(\boldsymbol{r})$ with Bloch function $\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = |n, \boldsymbol{k}\rangle$ $$\zeta(\boldsymbol{r}) = \sum_{n,\boldsymbol{k}} f(n,\boldsymbol{k})\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \sum_{n,\boldsymbol{k}} f(n,\boldsymbol{k})u_{n\boldsymbol{k}}(\boldsymbol{r})e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$$

$\langle n', \boldsymbol{k}'| \rightarrow$ $$[E_0(n',\boldsymbol{k}') - E]f(n',\boldsymbol{k}') + \sum_{n,\boldsymbol{k}}\langle n',\boldsymbol{k}'|U|n,\boldsymbol{k}\rangle f(n,\boldsymbol{k}) = 0$$

Fourier transform of $U(\boldsymbol{r})$ $$U(\boldsymbol{r}) = \int d\boldsymbol{q} U_{\boldsymbol{q}} e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}$$

Fourier expansion of $u^*_{n'\boldsymbol{k}'}(\boldsymbol{r})u_{n\boldsymbol{k}}(\boldsymbol{r})$ $$u^*_{n'\boldsymbol{k}'}(\boldsymbol{r})u_{n\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{G}} b_{n'\boldsymbol{k}'n\boldsymbol{k}}(\boldsymbol{G})e^{i\boldsymbol{G}\cdot\boldsymbol{r}}$$

Envelope function (2)

Ω_0: unit cell space,
v_0: unit cell volume

$$b_{n'\boldsymbol{k}'n\boldsymbol{k}}(\boldsymbol{G}) = \int_{\Omega_0} \frac{d\boldsymbol{r}}{v_0} e^{-i\boldsymbol{G}\cdot\boldsymbol{r}} u^*_{n'\boldsymbol{k}'}(\boldsymbol{r}) u_{n\boldsymbol{k}}(\boldsymbol{r})$$

$$\therefore \langle n', \boldsymbol{k}'|U|n, \boldsymbol{k}\rangle = \int d\boldsymbol{q} U_{\boldsymbol{q}} \sum_{\boldsymbol{G}} b_{n'\boldsymbol{k}'n\boldsymbol{k}}(\boldsymbol{G}) \underbrace{\int d\boldsymbol{r} e^{i(\boldsymbol{k}-\boldsymbol{k}'+\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}}}_{= (2\pi)^3 \delta(\boldsymbol{k}-\boldsymbol{k}'+\boldsymbol{q}+\boldsymbol{G})}$$

$$= (2\pi)^3 \sum_{\boldsymbol{G}} U_{\boldsymbol{k}'-\boldsymbol{k}-\boldsymbol{G}} b_{n'\boldsymbol{k}'n\boldsymbol{k}}(\boldsymbol{G})$$

Assumption: $U(\boldsymbol{r})$ varies little in the scale of the lattice constant

$\rightarrow$ $U_{\boldsymbol{q}}$ is finite only for $|\boldsymbol{q}| \ll \pi/a$

$$\boldsymbol{k}' - \boldsymbol{k} \sim \boldsymbol{G} < \frac{\pi}{a}$$

$U(\boldsymbol{r})$ is weaker than the lattice potential: Elements between different n are negligible

$$\rightarrow \langle n', \boldsymbol{k}'|U|n, \boldsymbol{k}\rangle \approx U_{\boldsymbol{k}'-\boldsymbol{k}} \delta_{n'n}$$

$$[E_0(\boldsymbol{k}') - E] f(n, \boldsymbol{k}') + \sum_{\boldsymbol{k}} U_{\boldsymbol{k}'-\boldsymbol{k}} f(n, \boldsymbol{k}) = 0$$

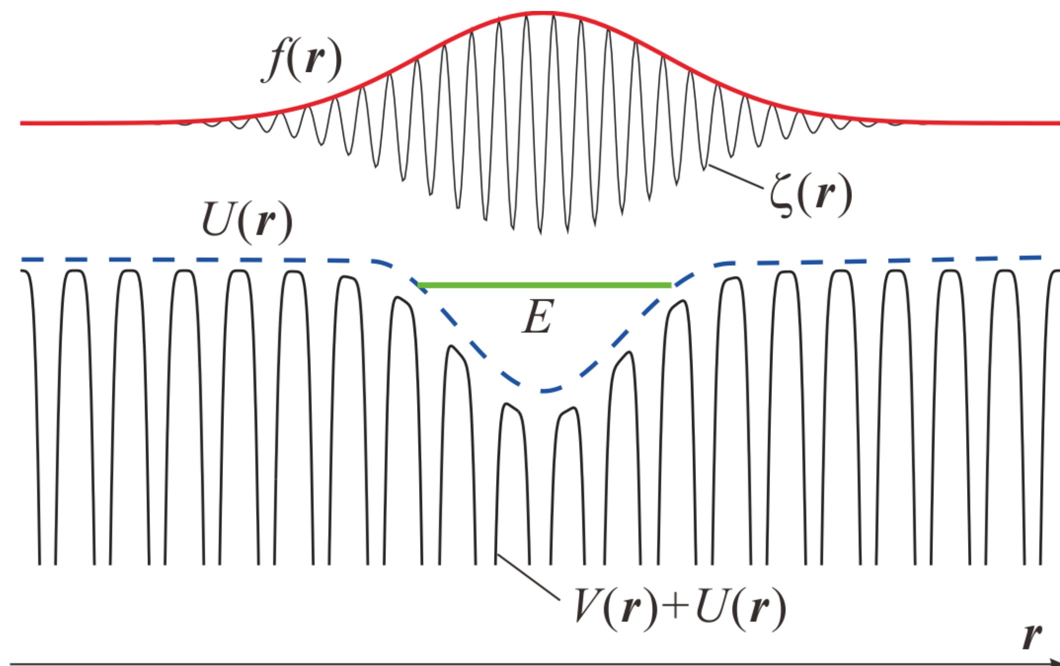
Assumption: $u_{n\boldsymbol{k}} \approx u_{n0}$

$$\zeta_n(\boldsymbol{r}) = u_{n0} \sum_{\boldsymbol{k}} f(n, \boldsymbol{k}) e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = u_{n0} f_n(\boldsymbol{r})$$

$$\frac{\hbar^2 k\boldsymbol{k}'^2}{2m^*} f(\boldsymbol{k}) + \sum_{\boldsymbol{k}} U_{\boldsymbol{k}'-\boldsymbol{k}} f(\boldsymbol{k}) = E f(\boldsymbol{k}')$$

$$\left[\frac{\hbar^2 \nabla^2}{2m^*} + U(\boldsymbol{r})\right] f(\boldsymbol{r}) = E f(\boldsymbol{r})$$

Effective mass equation



Derivation of effective mass equation with Wannier function

Wannier function (WF):

Fourier transform of Bloch function

$$w_n(\boldsymbol{r}-\boldsymbol{R}_j)=\frac{1}{\sqrt{N}}\sum_{\boldsymbol{k}}\exp(-i\boldsymbol{k}\cdot\boldsymbol{R}_j)\psi_{n\boldsymbol{k}}(\boldsymbol{r})$$

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r})=\frac{1}{\sqrt{N}}\sum_{\boldsymbol{k}}\exp(i\boldsymbol{k}\cdot\boldsymbol{R}_j)w_n(\boldsymbol{r}-\boldsymbol{R}_j)$$

WF tends to localize around the lattice points.

WF are orthogonal.

$$\langle w_{n'}^*(\boldsymbol{r}-\boldsymbol{R}_{j'})|w_n(\boldsymbol{r}-\boldsymbol{R}_j)\rangle=\delta_{jj'}\delta_{nn'}$$

Effective mass approximation

$$[\mathcal{H}_0+\mathcal{H}_1(\boldsymbol{r})]\phi(\boldsymbol{r})=E\phi(\boldsymbol{r})$$

Expansion by Wannier functions

$$\phi(\boldsymbol{r})=\sum_{n,j}f_n(\boldsymbol{R}_j)w_n(\boldsymbol{r}-\boldsymbol{R}_j)$$

$$\sum_{j'}\langle j|\mathcal{H}_0|j'\rangle f(\boldsymbol{R}_{j'})+\sum_{j'}\langle j|\mathcal{H}_1|j'\rangle f(\boldsymbol{R}_{j'})=Ef(\boldsymbol{R}_j)$$

$$\sum_{j'}\langle j|\mathcal{H}_1|j'\rangle\approx\mathcal{H}_1(\boldsymbol{R}_j)\langle j|j\rangle=\mathcal{H}_1(\boldsymbol{R}_j)$$

$$\langle j|\mathcal{H}_0|j'\rangle=\langle 0|\mathcal{H}_0|-\boldsymbol{R}_{j'}+\boldsymbol{R}_j\rangle\equiv h_0(\boldsymbol{R}_j-\boldsymbol{R}_{j'})$$

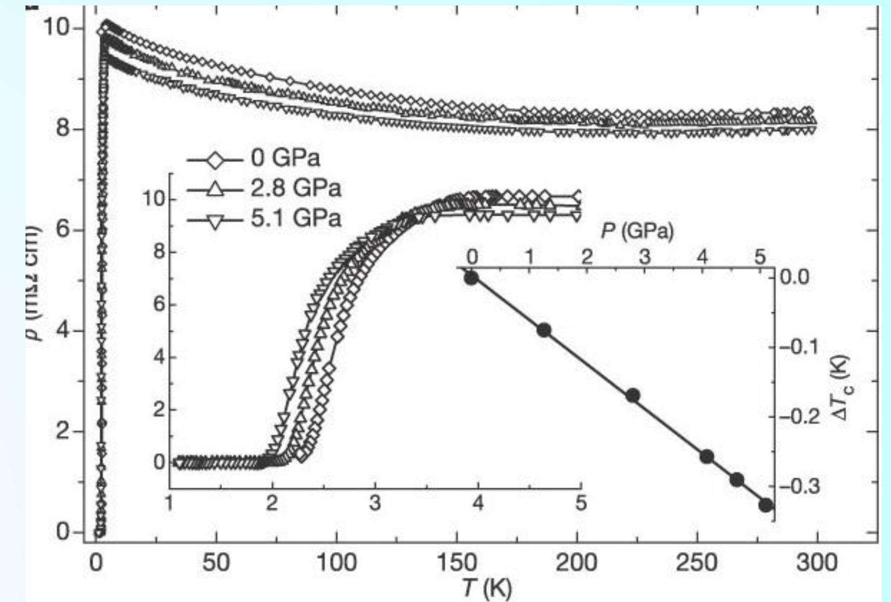
Effective mass equation

$$\left[-\frac{\hbar^2}{2m^*}\nabla^2+\mathcal{H}_1(\boldsymbol{r})\right]f(\boldsymbol{r})=Ef(\boldsymbol{r})$$

Diamond

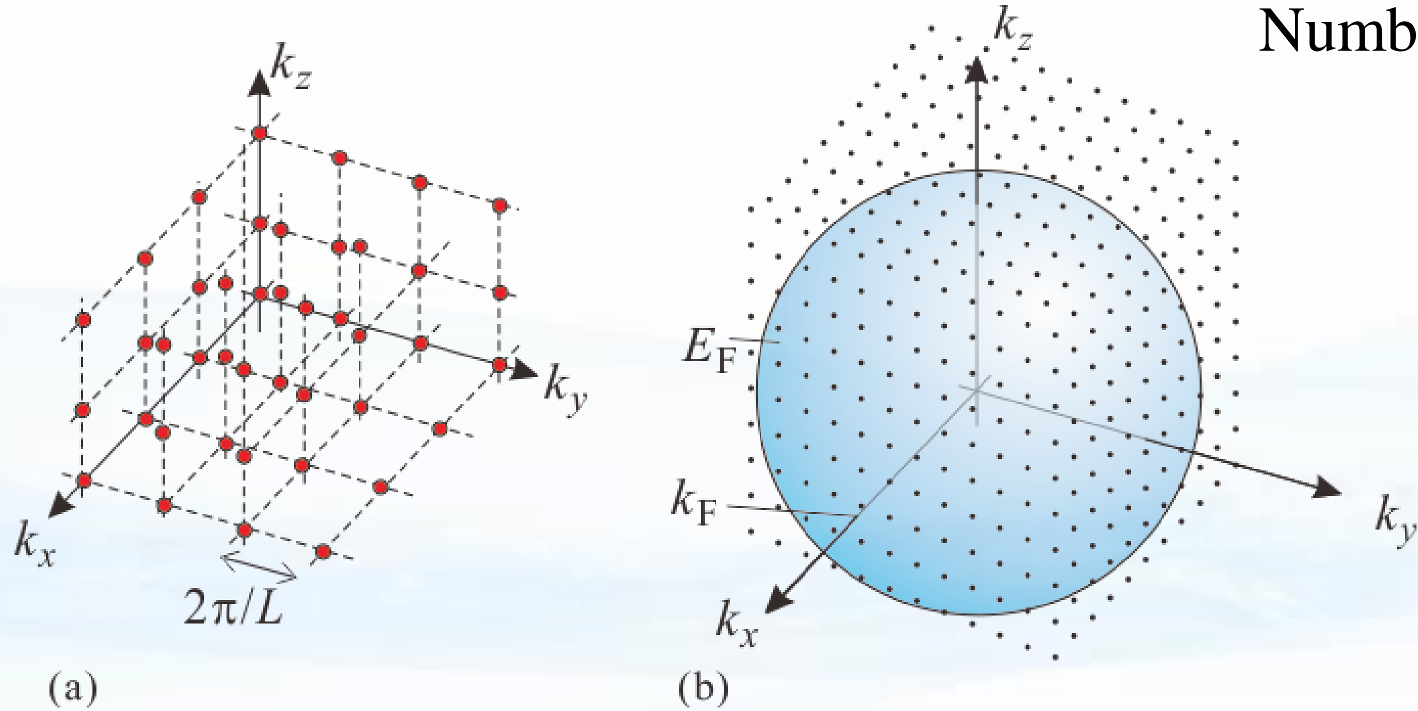
Boron doped diamond

Ekimov et al., Nature **428**, 542 (2004).



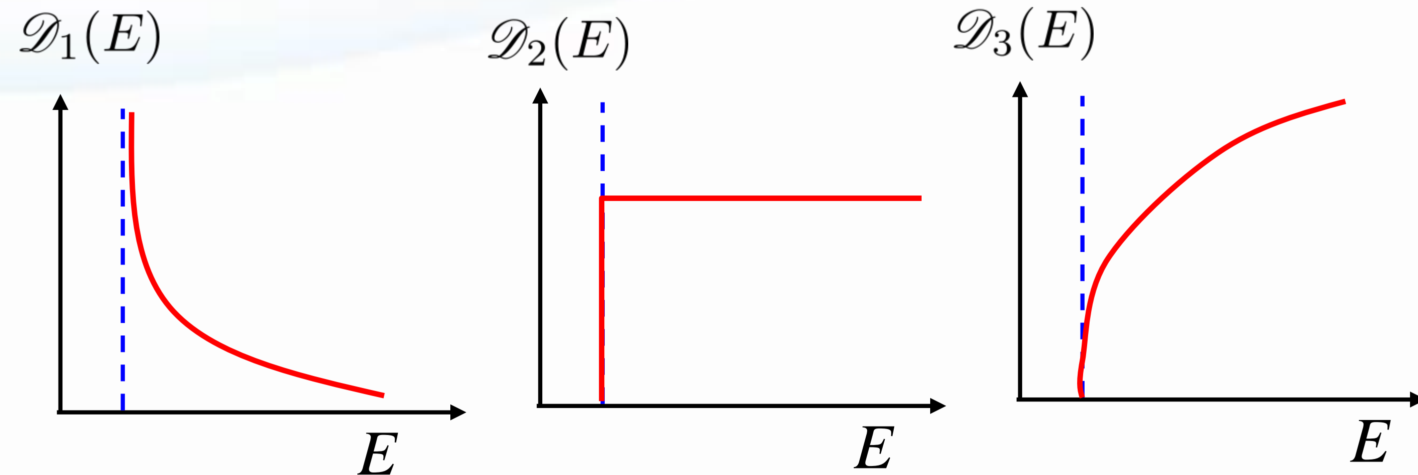
Chapter 3 Carrier statistics and chemical doping

Density of states



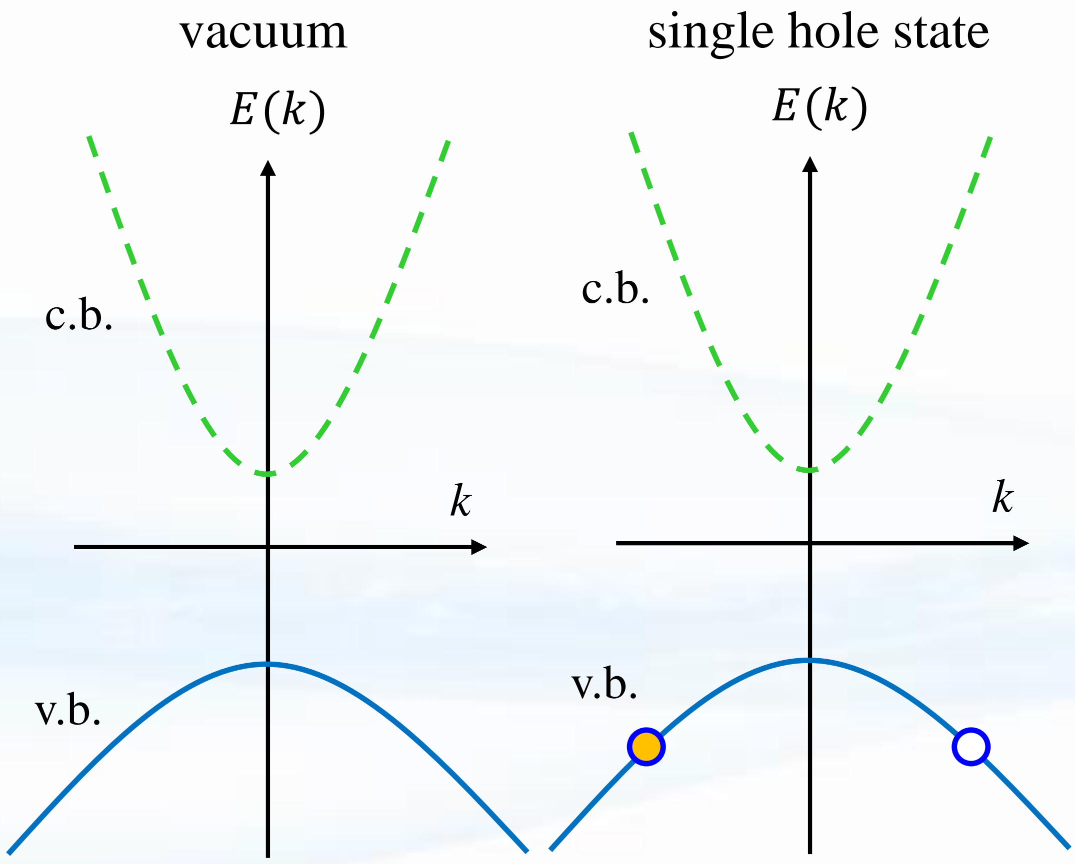
Number of states per energy (per volume)

$$\mathscr{D}(E) = \frac{1}{L^d}\left(\frac{L}{2\pi}\right)^d \frac{dV_d(k)}{dE}$$
$$= \frac{1}{(2\pi)^d}\frac{dV_d(k)}{dk}\frac{dk}{dE}$$
$$= \frac{1}{(2\pi)^d}\frac{m_0}{\hbar^2}\frac{dV_d(k)}{kdk}$$



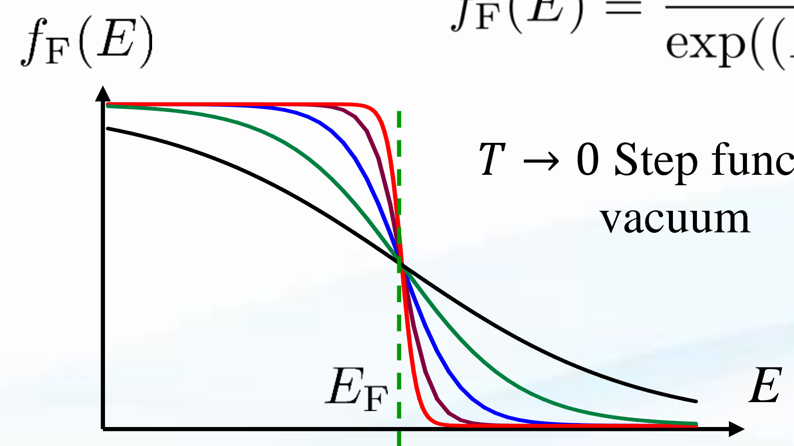
$$\mathscr{D}^{(0)}_{d=1} = \frac{1}{\pi\hbar}\sqrt{\frac{2m_0}{E}},$$
$$\mathscr{D}^{(0)}_{d=2} = \frac{m_0}{\pi\hbar^2},$$
$$\mathscr{D}^{(0)}_{d=3} = \frac{\sqrt{2m_0^3}}{\pi^2\hbar^3}\sqrt{E}$$

Electrons and holes



Fermi (electron) distribution function

$$f_F(E) = \frac{1}{\exp((E - E_F)/k_B T) + 1}$$



vacuum total current $\boldsymbol{J} = \sum_{\boldsymbol{k}} (-e)\boldsymbol{v}_{\boldsymbol{k}} = 0$

single empty state at $\boldsymbol{k}$ in valence band

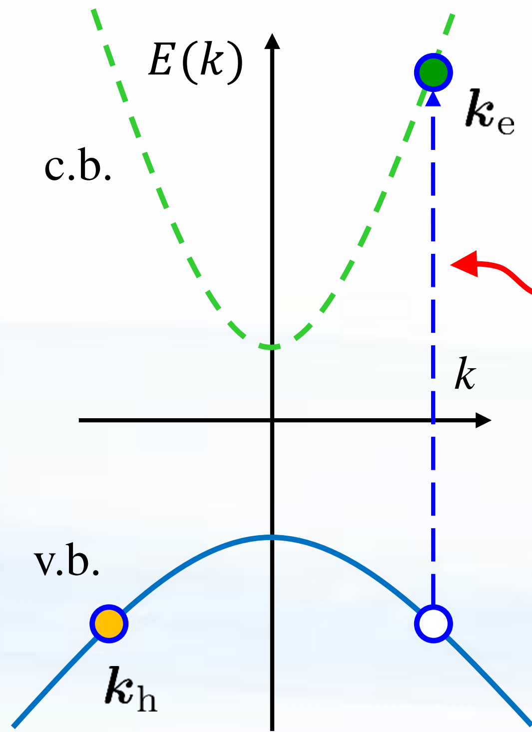
$$\boldsymbol{J}(\boldsymbol{k}) = \sum_{\boldsymbol{k}'} (-e)\boldsymbol{v}_{\boldsymbol{k}'} - (-e)\boldsymbol{v}_{\boldsymbol{k}} = e\boldsymbol{v}_{\boldsymbol{k}}$$

Electric field $\boldsymbol{E}$ $\quad \frac{d\boldsymbol{k}}{dt} = (-e)\frac{\boldsymbol{E}}{\hbar}$

All the electrons in the v.b. move in k-space in this way. So does the empty state.

Equation of motion of the empty state $\quad m^* \frac{d\boldsymbol{v}}{dt} = (-e)\boldsymbol{E} \;\to\; (-m^*)\frac{d\boldsymbol{v}}{dt} = e\boldsymbol{E}$

Definition and properties of valence band hole states



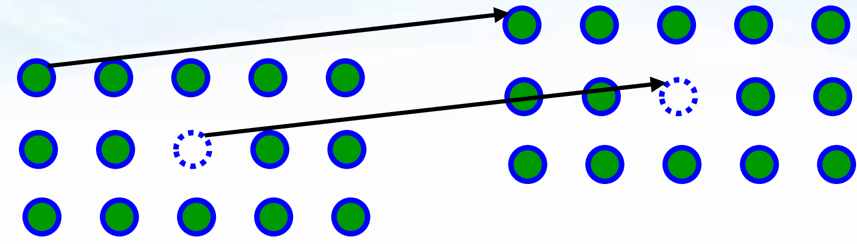
Definition: single hole

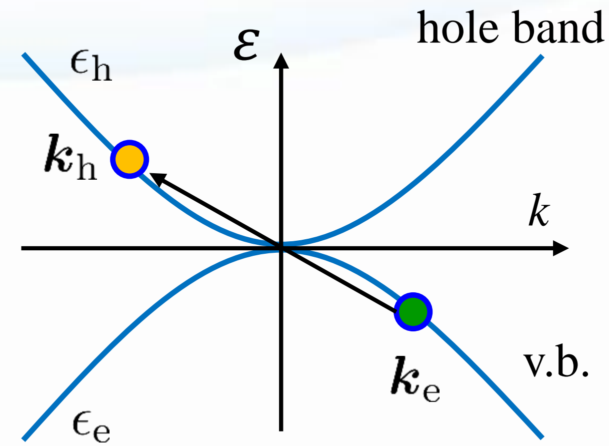
valence band electrons with a single empty Bloch state

(i) $\boldsymbol{k}_{\mathrm{h}} = -\boldsymbol{k}_{\mathrm{e}}$ Because $\sum \boldsymbol{k}_{\mathrm{e}} = 0$ in the vacuum state.

(ii) $\epsilon_{\mathrm{h}}(\boldsymbol{k}_{\mathrm{h}}) = -\epsilon_{\mathrm{e}}(\boldsymbol{k}_{\mathrm{e}})$ Energy measured from the valence top

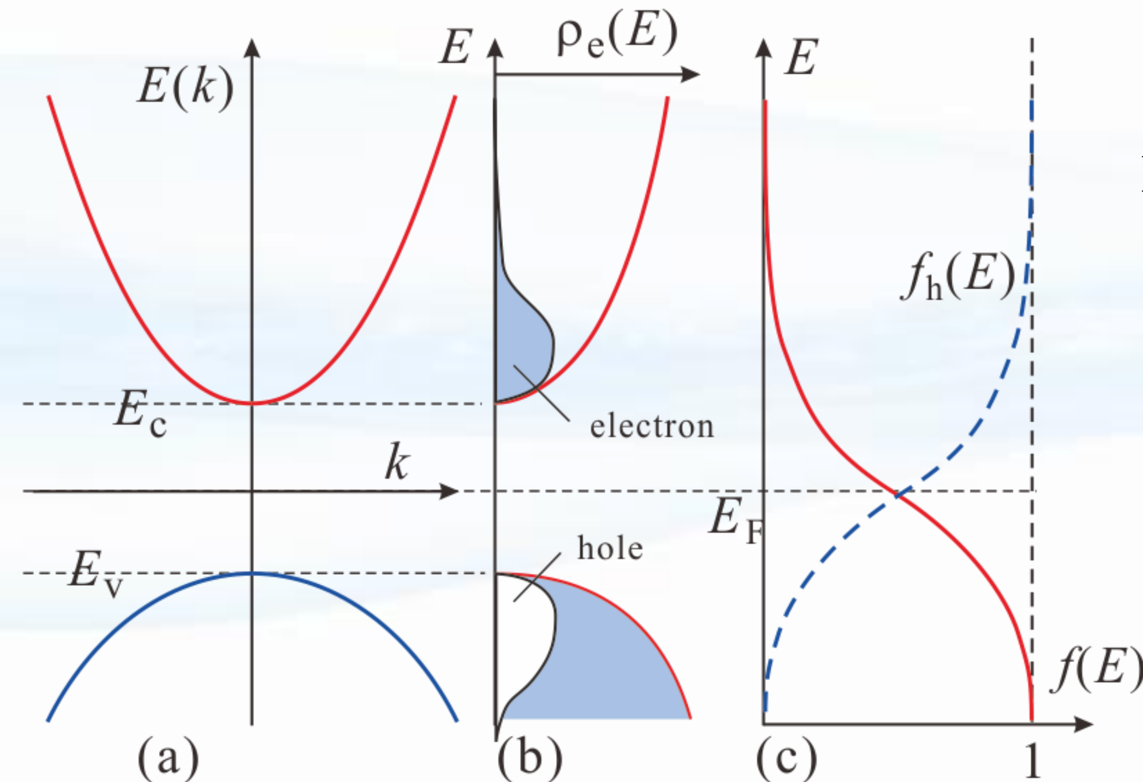
(iii) $\boldsymbol{v}_{\mathrm{h}} = \boldsymbol{v}_{\mathrm{e}}$





(iv) $m_{\mathrm{h}} = -m_{\mathrm{e}}$

Carrier distribution in intrinsic semiconductors



Hole distribution function

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

Numbers of electrons and holes exist between E and $E + dE$

$$g_e(E)dE = \mathscr{D}_e(E)f(E)dE,$$
$$g_h(E)dE = \mathscr{D}_h(E)[1 - f(E)]dE \equiv \mathscr{D}_h(E)f_h(E)dE$$

Approximate density of states with those of free particles

$$\mathscr{D}_e(E) = \frac{\sqrt{2m_e^{*3}}}{\pi^2\hbar^3}\sqrt{E - E_c} \quad \text{(conduction band)},$$
$$\mathscr{D}_h(E) = \frac{\sqrt{2m_h^{*3}}}{\pi^2\hbar^3}\sqrt{E_v - E} \quad \text{(valence band)}$$

Carrier distribution in intrinsic semiconductors (2)

$$n = \int_{E_c}^{\infty} g_e(E)dE = \frac{\sqrt{2m_e^{*3}}}{\pi^2\hbar^3}\int_{E_c}^{\infty}\frac{\sqrt{E-E_c}dE}{1+\exp(E-E_{\rm F})/k_{\rm B}T},$$

$$p = \int_{-\infty}^{E_v} g_h(E)dE = \frac{\sqrt{2m_h^{*3}}}{\pi^2\hbar^3}\int_{-\infty}^{E_v}\frac{\sqrt{E_v-E}dE}{1+\exp(E_{\rm F}-E)/k_{\rm B}T}$$

Maxwellian approximation

$$f_{\rm F}(E) \ll 1 (E \geq E_c)$$

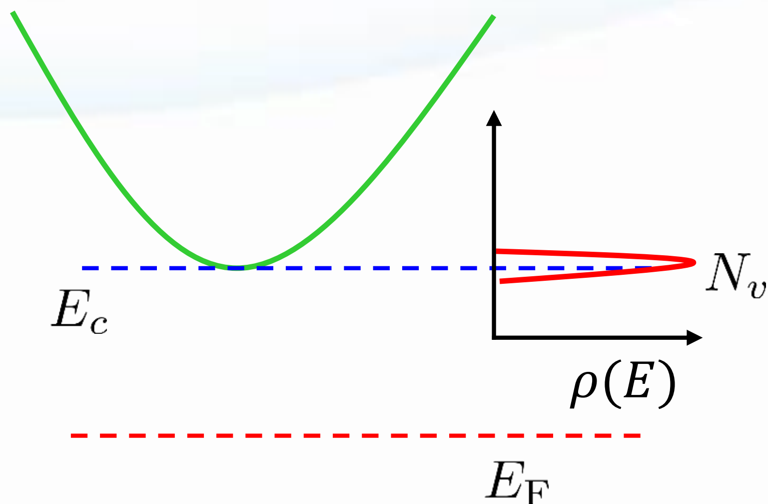
$$f_h(E) \ll 1 (E \leq E_v)$$

$$f_{\rm F}(E) \sim \exp(E_{\rm F}-E)/k_{\rm B}T$$

$$f_h(E) \sim \exp(E-E_{\rm F})/k_{\rm B}T$$

$$n = 2\left(\frac{m_e^* k_{\rm B}T}{2\pi\hbar}\right)^{3/2}\exp\left(\frac{E_{\rm F}-E_c}{k_{\rm B}T}\right) \equiv N_c\exp\left(\frac{E_{\rm F}-E_c}{k_{\rm B}T}\right)$$

$$p = 2\left(\frac{m_h^* k_{\rm B}T}{2\pi\hbar}\right)^{3/2}\exp\left(\frac{E_v-E_{\rm F}}{k_{\rm B}T}\right) \equiv N_v\exp\left(\frac{E_v-E_{\rm F}}{k_{\rm B}T}\right)$$



N_c, N_v : effective density of states

Carrier distribution in intrinsic semiconductors (3)

Mass-action law

$$np = N_c N_v \exp\left(\frac{E_v - E_c}{k_\mathrm{B}T}\right) = N_c N_v \exp\left(-\frac{E_g}{k_\mathrm{B}T}\right) = n_i^2$$

n_i: intrinsic carrier density

The charge neutrality condition $n = p$

$$E_\mathrm{F} = \frac{E_c + E_v}{2} + \frac{k_\mathrm{B}T}{2}\ln\frac{N_v}{N_c} = \frac{E_c + E_v}{2} + \frac{3k_\mathrm{B}T}{4}\ln\frac{m_h}{m_e} \equiv E_i$$

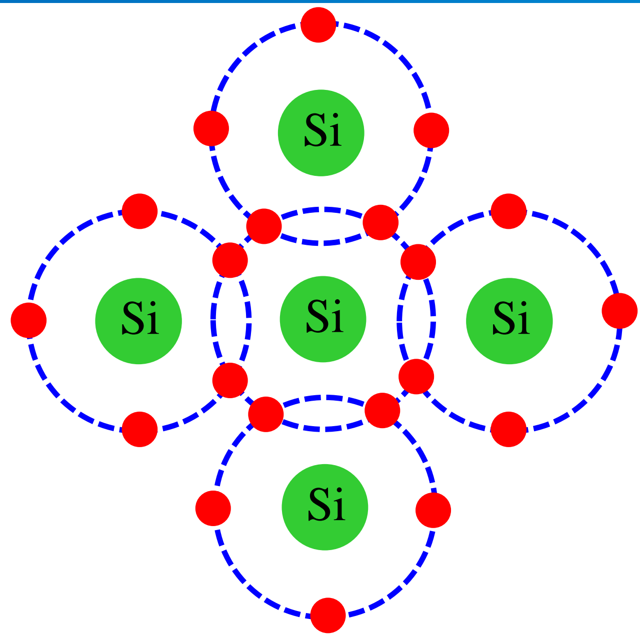
$$T \to 0 : \ E_\mathrm{F} \to \frac{E_c + E_v}{2}$$

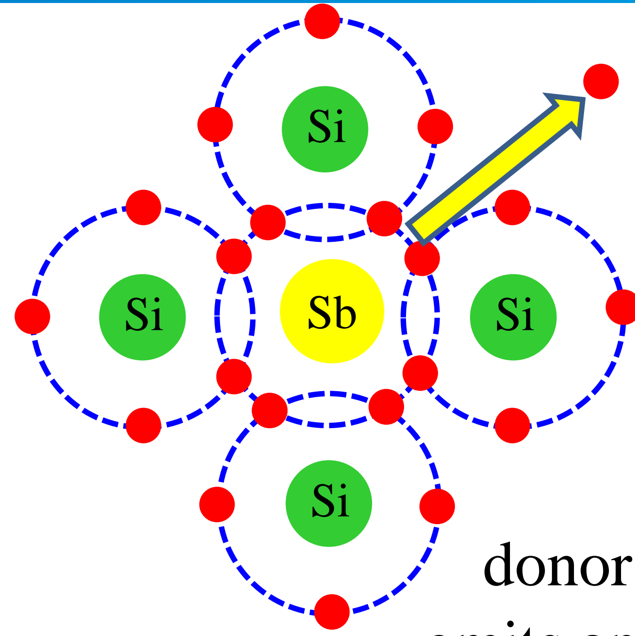
General expressions

$$n = n_i \exp\left(\frac{E_\mathrm{F} - E_i}{k_\mathrm{B}T}\right) \qquad E_\mathrm{F} - E_i = k_\mathrm{B}T\ln\frac{n}{n_i}$$

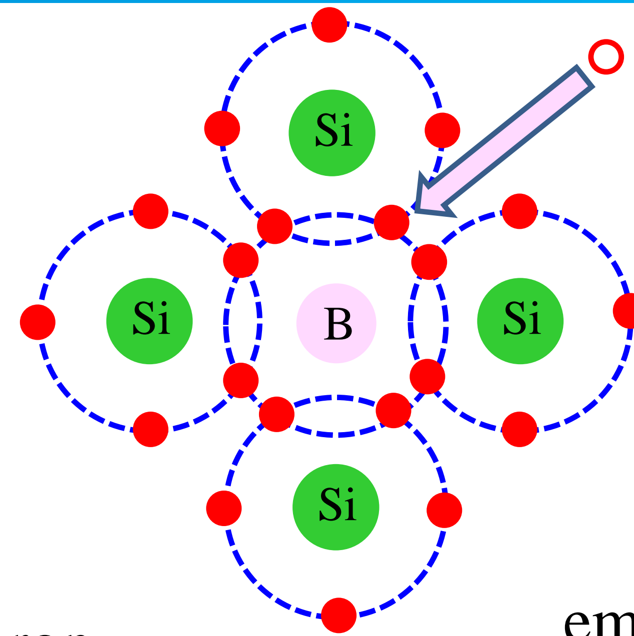
$$p = n_i \exp\left(\frac{E_i - E_\mathrm{F}}{k_\mathrm{B}T}\right) \qquad E_i - E_\mathrm{F} = k_\mathrm{B}T\ln\frac{p}{n_i}$$

Doping and carrier distribution





donor
emits an electron



acceptor
emits a hole

II	III	IV	V	VI
4 Be ベリリウム 9.012182	5 B ホウ素 10.811	6 C 炭素 12.0107	7 N 窒素 14.0067	8 O 酸素 15.9994
12 Mg マグネシウム 24.305	13 Al アルミニウム 26.98153...	14 Si ケイ素 28.0855	15 P リン 30.973762	16 S 硫黄 32.065
30 Zn 亜鉛 65.38	31 Ga ガリウム 69.723	32 Ge ゲルマニウム 72.63	33 As ヒ素 74.9216	34 Se セレン 78.96
48 Cd カドミウム 112.411	49 In インジウム 114.818	50 Sn スズ 118.71	51 Sb アンチモン 121.76	52 Te テルル 127.6

Donor concentration is higher: *n*-type
Acceptor concentration is higher: *p*-type

Donors and acceptors compensate each other.

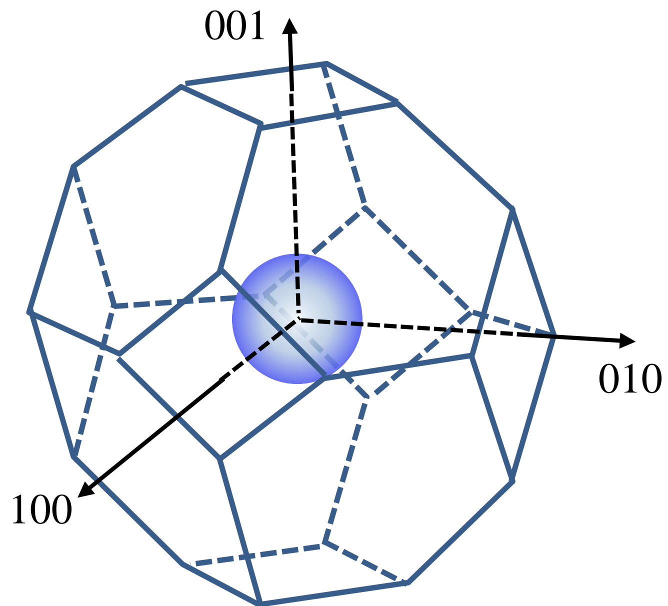
For silicon

Donors: P, As, Sb
Acceptors: B, Al, Ga

Impurity levels in Si and GaAs

S. M. Sze, Physics of semiconductor devices

Shallow hydrogen-like impurity states



GaAs

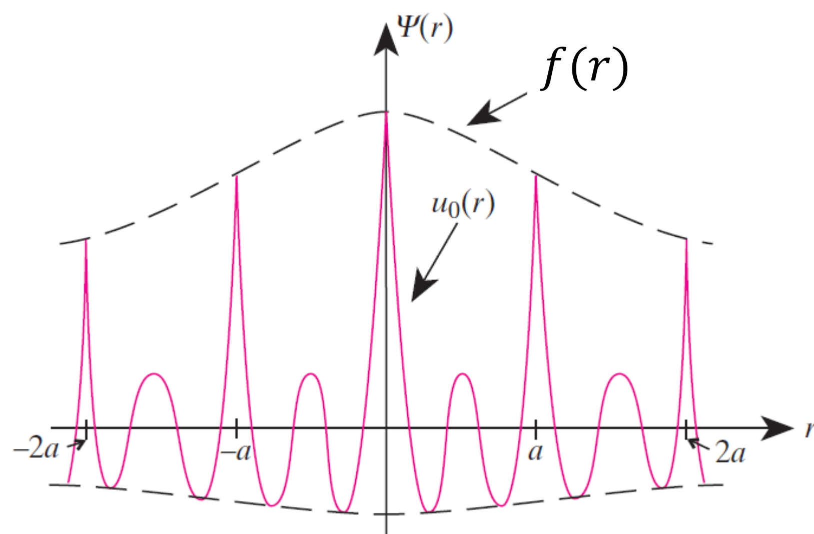
Conduction mass is isotropic and unique.

Effective mass equation $$\left[-\frac{\hbar^2\nabla^2}{2m^*}-\frac{e^2}{4\pi\epsilon_0\epsilon r}\right]f(\boldsymbol{r})=Ef(\boldsymbol{r})$$

We can readily use the results of the hydrogen atom with replacing the mass and the dielectric constant.

$$E_n=E_c-\frac{Ry^*}{n^2}\quad(n=1,2,\cdots)$$

$1s$ wavefunction $$\psi_{1s}(\boldsymbol{r})=\sqrt{\frac{1}{\pi a_{\mathrm{B}}^{*3}}}\exp\left(-\frac{\boldsymbol{r}}{a_{\mathrm{B}}^*}\right)$$



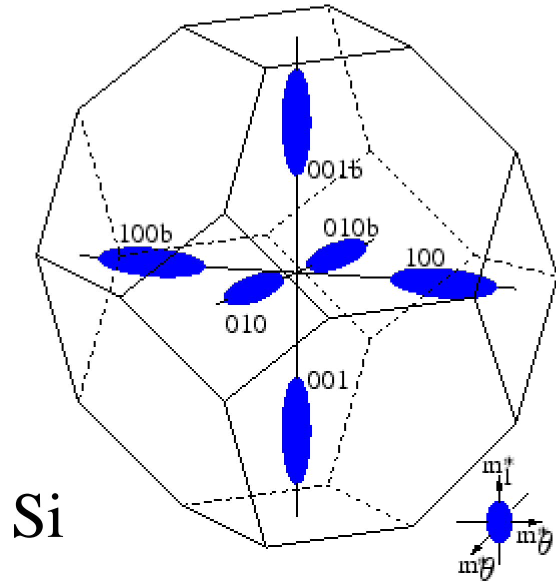
Effective Rydberg constant: $$Ry^*=\frac{e^2m^*}{2(4\pi\epsilon\epsilon_0)^2\hbar^2}=\frac{m^*}{m}\frac{1}{\epsilon^2}Ry,$$

Effective Bohr radius: $$a_{\mathrm{B}}^*=\frac{4\pi\epsilon\epsilon_0\hbar^2}{m^*e^2}=\frac{m}{m^*}\epsilon a_{\mathrm{B}}$$

How good is the approximation

Semiconductor	Binding energy from (4.24) [meV]	Experimental binding energy of common donors [meV]
GaAs	5.72	Si_{Ga}(5.84); Ge_{Ga}(5.88) S_{As}(5.87); Se_{As}(5.79)
InP	7.14	7.14
InSb	0.6	Te_{Sb}(0.6)
CdTe	11.6	In_{Cd}(14); Al_{Cd}(14)
ZnSe	25.7	Al_{Zn}(26.3); Ga_{Zn}(27.9) F_{Se}(29.3); Cl_{Se}(26.9)

Shallow impurity states in Si



Si

Donor biding energy in Si (meV)

Measurement

Dopant	Li	P	As	Sb	Bi
Thermal		44	55	39	69
Optical	32.8	45	53.7	43	70.6

For [001] spheroid

$$E_1(\boldsymbol{k}) = \frac{\hbar^2}{2}\left[\frac{k_x^2 + k_y^2}{m_t} + \frac{(k_z - k_0)^2}{m_l}\right]$$

Effective mass equation

$$\left[-\frac{\hbar^2}{2m_t}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) - \frac{\hbar^2}{2m_l}\frac{\partial^2}{\partial z^2} - \frac{e^2}{4\pi\epsilon_0\epsilon r}\right] f(\boldsymbol{r}) = E f(\boldsymbol{r})$$

Variational method

$$f_{1s}(\boldsymbol{r}) = \sqrt{\frac{1}{\pi a^2 b}} \exp\left(-\sqrt{\frac{x^2 + y^2}{a^2} + \frac{z^2}{b^2}}\right)$$

	a (10^{-8} cm)	b (10^{-8} cm)	E (1s) (meV)
Si	25	14.2	29
Ge	64.5	22.7	9.2

Not sufficient agreements.
Need more accurate calculations.

Doping and carrier distribution

Uniform donor concentration N_D

n: excited electrons,
n_D: captured electrons

$$n + n_D = N_D$$

Entropy $S = k_B \ln W$

Helmholtz free energy

$$F = U - TS = E_D n_D - k_B T \ln \left[2^{n_D} \frac{N_D!}{n_D!(N_D - n_D)!} \right]$$

Starling approximation

$\ln N! \sim N \ln N - N$

$$\mu = E_F = \frac{\partial F}{\partial n_D} = E_D - k_B T \ln \left[\frac{2(N_D - n_D)}{n_D} \right]$$

Donor level

$$n_D = N_D \left[1 + \frac{1}{2} \exp\left(\frac{E_D - E_F}{k_B T} \right) \right]^{-1}$$

For acceptors

$$n_A = N_A \left[1 + 2 \exp\left(\frac{E_A - E_F}{k_B T} \right) \right]^{-1}$$

note: the formula is symmetric if we introduce captured hole concentration $p_A = N_A - n_A$

Doping and carrier distribution

E_F is given from n or p as

$$E_\mathrm{F} \approx E_C + k_\mathrm{B}T\left[\ln\left(\frac{n}{N_C}\right) + 2^{-3/2}\left(\frac{n}{N_C}\right)\right],$$

$$E_\mathrm{F} \approx E_V - k_\mathrm{B}T\left[\ln\left(\frac{p}{N_V}\right) + 2^{-3/2}\left(\frac{p}{N_V}\right)\right]$$

In the case of n-type semiconductor with compensation $n + N_A = N_\mathrm{D} - n_\mathrm{D}$

$$\frac{n + N_\mathrm{A}}{N_\mathrm{D} - N_\mathrm{A} - n} = \frac{1}{2}\exp\left(\frac{E_\mathrm{D} - E_\mathrm{F}}{k_\mathrm{F}T}\right)$$

$$\frac{n(n + N_\mathrm{A})}{N_\mathrm{D} - N_\mathrm{A} - n} = \frac{1}{2}N_c\exp\left(-\frac{\Delta E_\mathrm{D}}{k_\mathrm{B}T}\right), \quad \Delta E_\mathrm{D} \equiv E_c - E_\mathrm{D}$$