

#### 4. *k.p* method

Schroedinger equation for the periodic part of the Bloch function,

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + \frac{\hbar^2}{2m} |\vec{k}|^2 - i \frac{\hbar^2}{m} \vec{k} \cdot \nabla + V(\vec{r}) \right] u_{\vec{k},n}(\vec{r}) = E_{\vec{k},n} u_{\vec{k},n}(\vec{r}) , \quad (4.1)$$

involves the operator

$$\frac{\hbar}{m} \vec{k} \cdot \vec{p} , \quad (4.2)$$

(the third item in the Hamiltonian). Its contribution is small in the neighborhood of  $\mathbf{k} = 0$ , and we will treat it as a perturbation. Assume a non-degenerate  $n$ -th band having an extreme at  $\mathbf{k} = 0$ , with the value of energy of  $E_{0,n}$ ; the zero derivatives of the band energies are usually dictated by crystal symmetry. The first-order corrections of the perturbation theory is

$$u_{\vec{k},n} = u_{0,n} + \frac{\hbar}{m} \sum_{n \neq n'} \frac{\langle u_{0,n} | \vec{k} \cdot \vec{p} | u_{0,n'} \rangle}{E_{0,n} - E_{0,n'}} u_{0,n'} \quad (4.3)$$

and

$$E_{\vec{k},n} = E_{0,n} + \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2}{m^2} \sum_{n \neq n'} \frac{|\langle u_{0,n} | \vec{k} \cdot \vec{p} | u_{0,n'} \rangle|^2}{E_{0,n} - E_{0,n'}}. \quad (4.4)$$

The parabolic dispersion relation of Eq. (4.4) is usually written down in the following form,

$$E_{\vec{k},n} = E_{0,n} + \frac{\hbar^2 k^2}{2m^*}, \quad (4.5)$$

where  $m^*$  is the effective mass of the  $n$ -th band:

$$\frac{1}{m^*} = \frac{1}{m} + \frac{2}{m^2 k^2} \sum_{n \neq n'} \frac{|\langle u_{0,n} | \vec{k} \cdot \vec{p} | u_{0,n'} \rangle|^2}{E_{0,n} - E_{0,n'}}. \quad (4.6)$$

Let us focus on the zincblende (ZnS) structure with the point group  $T_d$ . The sum of Eq. (4.6) reduces to a single term for the effective mass of the conduction band minimum (the state of  $\Gamma_{1c}$  symmetry, belonging to the one-dimensional irreducible representation of  $T_d$ ). It contains the contribution of the nearest lower-lying (valence, triply degenerated, with the energy set to zero) state  $\Gamma_{5v}$ . The energy difference of both states is the direct gap,  $E_0$ ; consequently, Eq. (4.6) reduces to

$$\frac{1}{m^*} = \frac{1}{m} + \frac{2 |\vec{k} \cdot \langle \Gamma_{1c} | \vec{p} | \Gamma_{5v} \rangle|^2}{m^2 k^2 E_0}. \quad (4.7)$$

The representation  $\Gamma_5$  is 3-dimensional, we denote its basis functions as  $|x\rangle$ ,  $|y\rangle$  a  $|z\rangle$ . Due to the crystal symmetry, all three momentum matrix elements in Eq. (4.7) are equal:

$$\langle \Gamma_{1c} | -i\hbar \frac{\partial}{\partial x} | x \rangle = \langle \Gamma_{1c} | -i\hbar \frac{\partial}{\partial y} | y \rangle = \langle \Gamma_{1c} | -i\hbar \frac{\partial}{\partial z} | z \rangle = iP. \quad (4.8)$$

Consequently, Eq. (4.7) can be simplified further,

$$\frac{1}{m^*} = \frac{1}{m} + \frac{2P^2}{m^2 E_0}, \quad \frac{m}{m^*} = 1 + \frac{2P^2}{mE_0}. \quad (4.9)$$

With an estimate of the value of  $P$ , the last result can be used in predicting the effective masses, just by adding the values of the the gap energies. The quantity  $2P^2/m$  has the dimension of energy; its value is almost constant for the majority of IV, III-V and II-VI semiconductors with diamond and zincblende structures, amounting to about 20 eV. We arrive at

$$\frac{m^*}{m} \approx \frac{1}{1 + \frac{20}{E_0 \text{ [eV]}}}. \quad (4.10)$$

The general findings from the above calculations can be summarized as follows:

1. With the gaps below  $\sim 2$  eV, the electron effective masses of the direct gap are at least an order of magnitude smaller than in free space.
2. The effective masses decrease with decreasing gap, typically with increasing lattice constants of crystals formed by heavier atoms.

The trend is confirmed by the comparison given in the following table. Note that Ge is an indirect semiconductor, having the lowest direct band at  $\Gamma$  of 0.89 eV (at low temperatures).

	Ge	GaAs	InP	InAs	GaSb	InSb	CdTe
$E_0$ [eV]	0.89	1.55	1.34	0.45	0.81	0.24	1.59
$m_c^*/m$ (exp)	0.041	0.067	0.073	0.026	0.047	0.015	0.11
$m_c^*/m$ ((2.44))	0.04	0.078	0.067	0.023	0.04	0.012	0.08

Gaps and effective masses, from the textbook of Yu and Cardona.

### Symbols for irreducible representations of point groups

Chemical notation (Mulliken, 1933) is used mostly in molecular physics or in lattice dynamics. The symbols are  $A$  and  $B$  for one-dimensional representations ( $B$  is used, whenever odd at the smallest rotation around principal axis),  $E$  for two-dimensional representations,  $T$ ,  $U$ ,  $V$ , and  $W$  for the dimensions 3, 4, 5, and 6, respectively.

Physical (Bethe, 1929; Koster, Dimmock, Wheeler and Statz, 1963):  $\Gamma_1, \Gamma_2, \Gamma_3, \dots$ ; in more recent literature on condensed matter physics.

Alternative (BSW, Bouckaert, Smoluchowski and Wigner, 1935); rather frequently.

Example for  $T_d$ :

Mulliken	KDWS	BSW
$A_1$	$\Gamma_1$	$\Gamma_1$
$A_2$	$\Gamma_2$	$\Gamma_2$
$E$	$\Gamma_3$	$\Gamma_{12}$
$T_1$	$\Gamma_4$	$\Gamma_{15}$
$T_2$	$\Gamma_5$	$\Gamma_{25}$

Character table for  $T_d$  and basis functions

	$\{E\}$	$\{3C_2\}$	$\{6S_4\}$	$\{6\sigma\}$	$\{8C_3\}$	Basis functions
$A_1$	1	1	1	1	1	$xyz$
$A_2$	1	1	-1	-1	1	$x^4(y^2 - z^2) + y^4(z^2 - x^2) + z^4(x^2 - y^2)$
$E$	2	2	0	0	-1	$\{(x^2 - y^2), z^2 - \frac{1}{2}(x^2 + y^2)\}$
$T_1$	3	-1	1	-1	0	$\{x(y^2 - z^2), y(z^2 - x^2), z(x^2 - y^2)\}$
$T_2$	3	-1	-1	1	0	$\{x, y, z\}$

Bandstructures along high-symmetry directions in Gallium compounds; for GaAs and GaSb, the spin-orbit interaction has been included. This corresponds with the double-group labels.

