Física de Semiconductores

Lección 8

k·p theory (I)

- The one-electron Schroedinger equation for a solid is

$$H\psi = \left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V\left(\boldsymbol{r}\right)\right)\psi = E\psi$$

- We now insert the Bloch solution

$$\psi_{n\boldsymbol{k}}\left(\boldsymbol{r}\right) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u_{n\boldsymbol{k}}\left(\boldsymbol{r}\right)$$

k·p theory (II)

$$-\frac{\hbar^2}{2m}\left[\boldsymbol{\nabla}\cdot\left(i\boldsymbol{k}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u_{n\boldsymbol{k}}\left(\boldsymbol{r}\right)+e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\nabla}u_{n\boldsymbol{k}}\left(\boldsymbol{r}\right)\right)\right]+V\left(\boldsymbol{r}\right)e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u_{n\boldsymbol{k}}\left(\boldsymbol{r}\right)=E_{n\boldsymbol{k}}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u_{n\boldsymbol{k}}\left(\boldsymbol{r}\right)$$

$$-\frac{\hbar^2}{2m}\left[-k^2e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u_{n\boldsymbol{k}}\left(\boldsymbol{r}\right)+2i\boldsymbol{k}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\nabla}\cdot u_{n\boldsymbol{k}}\left(\boldsymbol{r}\right)+e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\nabla}^2u_{n\boldsymbol{k}}\left(\boldsymbol{r}\right)\right]+V\left(\boldsymbol{r}\right)e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u_{n\boldsymbol{k}}\left(\boldsymbol{r}\right)$$

$$=E_{n\boldsymbol{k}}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u_{n\boldsymbol{k}}\left(\boldsymbol{r}\right)$$

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

$$-\frac{\hbar^2\boldsymbol{\nabla}^2u_{n\boldsymbol{k}}\left(\boldsymbol{r}\right)}{2m}-i\frac{\hbar^2}{m}\boldsymbol{k}\cdot\boldsymbol{\nabla}u_{n\boldsymbol{k}}\left(\boldsymbol{r}\right)+V\left(\boldsymbol{r}\right)u_{n\boldsymbol{k}}\left(\boldsymbol{r}\right)=\left(E_{n\boldsymbol{k}}-\frac{\hbar^2k^2}{2m}\right)u_{n\boldsymbol{k}}\left(\boldsymbol{r}\right)$$

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

$$\left[-\frac{\hbar^2\boldsymbol{\nabla}^2}{2m}+\frac{\hbar}{m}\boldsymbol{k}\cdot\boldsymbol{p}+V\left(\boldsymbol{r}\right)\right]u_{n\boldsymbol{k}}\left(\boldsymbol{r}\right)=\left(E_{n\boldsymbol{k}}-\frac{\hbar^2k^2}{2m}\right)u_{n\boldsymbol{k}}\left(\boldsymbol{r}\right)$$

k·p hamiltonian

- The periodic part of the Block wave function satisfies a Schrödinger equation of the form

$$\left[-\frac{\hbar^2\boldsymbol{\nabla}^2}{2m}+\frac{\hbar}{m}\boldsymbol{k}\cdot\boldsymbol{p}+V\left(\boldsymbol{r}\right)\right]u_{n\boldsymbol{k}}\left(\boldsymbol{r}\right)=\left(E_{n\boldsymbol{k}}-\frac{\hbar^2k^2}{2m}\right)u_{n\boldsymbol{k}}\left(\boldsymbol{r}\right)$$

- subject to the boundary conditions.

$$u_{n\boldsymbol{k}}\left(\boldsymbol{r}\right)=u_{n\boldsymbol{k}}\left(\boldsymbol{r}+\boldsymbol{R}\right)$$

- Notice that k appears as a parameter, and that we expect discrete energy levels *n*, as in the particle-in-a-box.

The k=0 reference

- We can write the hamiltonian as

$$H = H^{(0)} + H^{(1)}$$

- with

$$H^{(0)} = -\frac{\hbar^2 \boldsymbol{\nabla}^2}{2m} + V\left(\boldsymbol{r}\right) \qquad H^{(1)} = \frac{\hbar}{m}\boldsymbol{k}\cdot\boldsymbol{p}$$

- This suggests that we start from eigenstates of k=0. Then we can diagonalize the entire hamiltonian in this basis, or treat the k.p part as a perturbation for small k.

Expansion in terms of the k=0 basis

- Let's assume that we know the wave functions and eigenvalues at *k* =0.

$$\left|n\boldsymbol{0}\right\rangle \Rightarrow u_{n\boldsymbol{0}}\left(\boldsymbol{r}\right); \quad H^{(0)}\left|n\boldsymbol{0}\right\rangle = E_{n\boldsymbol{0}}\left|n\boldsymbol{0}\right\rangle$$

- Because these are a complete set, then it is always true that I can expand

$$\left|n\boldsymbol{k}\right\rangle = \sum_{n'}\left|n'\boldsymbol{0}\right\rangle\left\langle n'\boldsymbol{0}\middle|n\boldsymbol{k}\right\rangle = \sum_{n'} c_{nn'}\left(\boldsymbol{k}\right)\left|n'\boldsymbol{0}\right\rangle$$

- Therefore,

$$H\left|n\boldsymbol{k}\right\rangle = \left(H^{(0)} + H^{(1)}\right)\sum_{n'} c_{nn'}\left(\boldsymbol{k}\right)\left|n'\boldsymbol{0}\right\rangle$$

$$= \sum_{n'} c_{nn'}\left(\boldsymbol{k}\right)E_{n'\boldsymbol{0}}\left|n'\boldsymbol{0}\right\rangle + \sum_{n'} c_{nn'}\left(\boldsymbol{k}\right)H^{(1)}\left|n'\boldsymbol{0}\right\rangle$$

k.p matrix (I)

- Therefore, defining: $\varepsilon_{n\boldsymbol{k}} = E_{n\boldsymbol{k}} - \hbar^2 k^2 / 2m$

$$\sum_{n'} c_{nn'}(\boldsymbol{k}) E_{n'\boldsymbol{0}} \left| n'\boldsymbol{0} \right\rangle + \sum_{n'} c_{nn'}(\boldsymbol{k}) H_1 \left| n'\boldsymbol{0} \right\rangle$$

$$= \varepsilon_{n\boldsymbol{k}} \sum_{n'} c_{nn'}(\boldsymbol{k}) \left| n'\boldsymbol{0} \right\rangle$$

- Multiplying on the left times $\left\langle n\boldsymbol{0} \right|$

$$\sum_{n'} c_{nn'}(\boldsymbol{k}) E_{n'\boldsymbol{0}} \delta_{nn'} + \sum_{n'} c_{nn'}(\boldsymbol{k}) \left\langle n\boldsymbol{0} \right| H_1 \left| n'\boldsymbol{0} \right\rangle$$

$$= \varepsilon_{n\boldsymbol{k}} \sum_{n'} c_{nn'}(\boldsymbol{k}) \delta_{nn'}$$

$$\sum_{n'} c_{nn'}(\boldsymbol{k}) \left(E_{n\boldsymbol{0}} - \varepsilon_{n\boldsymbol{k}} \right) \delta_{nn'} + \sum_{n'} c_{nn'}(\boldsymbol{k}) \left\langle n\boldsymbol{0} \right| H^{(1)} \left| n'\boldsymbol{0} \right\rangle = 0$$

k.p matrix (II)

- Therefore, defining: $H^{(1)}_{nn'}\left(\boldsymbol{k}\right) = \left\langle n\boldsymbol{0}\middle| H^{(1)} \middle| n'\boldsymbol{0}\right\rangle$
- I need to diagonalize the matrix

$$\begin{pmatrix} \left(E_{1\boldsymbol{0}} - \varepsilon_{1\boldsymbol{k}}\right) + H^{(1)}_{11}\left(\boldsymbol{k}\right) & H^{(1)}_{12}\left(\boldsymbol{k}\right) & H^{(1)}_{13}\left(\boldsymbol{k}\right) & \ldots \\ H^{(1)}_{21}\left(\boldsymbol{k}\right) & \left(E_{2\boldsymbol{0}} - \varepsilon_{2\boldsymbol{k}}\right) + H^{(1)}_{22}\left(\boldsymbol{k}\right) & H^{(1)}_{23}\left(\boldsymbol{k}\right) & \ldots \\ H^{(1)}_{31}\left(\boldsymbol{k}\right) & H^{(1)}_{32}\left(\boldsymbol{k}\right) & \left(E_{3\boldsymbol{0}} - \varepsilon_{1\boldsymbol{k}}\right) + H^{(1)}_{33}\left(\boldsymbol{k}\right) & \ldots \\ \ldots & \ldots & \ldots & \ldots \end{pmatrix}$$

Tight binding for k=0

$$H = \begin{bmatrix} \varepsilon_s & 0 & 0 & 0 & V_{ss} & 0 & 0 & 0 \\ 0 & \varepsilon_p & 0 & 0 & 0 & V_{xx} & 0 & 0 \\ 0 & 0 & \varepsilon_p & 0 & 0 & 0 & V_{xx} & 0 \\ 0 & 0 & 0 & \varepsilon_p & 0 & 0 & 0 & V_{xx} \\ V_{ss} & 0 & 0 & 0 & \varepsilon_s & 0 & 0 & 0 \\ 0 & V_{xx} & 0 & 0 & 0 & \varepsilon_p & 0 & 0 \\ 0 & 0 & V_{xx} & 0 & 0 & 0 & \varepsilon_p & 0 \\ 0 & 0 & 0 & V_{xx} & 0 & 0 & 0 & \varepsilon_p \end{bmatrix}$$

What basis do we need?

- We would like to discuss the near-band gap bands in semiconductors like Ge, in which spin-orbit is significant.
- Therefore, it is convenient to use the J^2, L^2, J_z basis that diagonalizes the spin-orbit interaction in the atom.
- We then start with the TB Hamiltonian in this basis

J^2, L^2, J_z basis for k=0 (I)

$$H = \begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix}$$

J²,L²,J_z basis for k=0 (II)

$$H_{AA} = H_{BB} =$$

$$\begin{pmatrix}
 & S\uparrow & S\downarrow & \frac{3}{2},\frac{3}{2} & \frac{3}{2},-\frac{3}{2} & \frac{3}{2},\frac{1}{2} & \frac{3}{2},-\frac{1}{2} & \frac{1}{2},\frac{1}{2} & \frac{1}{2},-\frac{1}{2} \\
S\uparrow & \varepsilon_s & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
S\downarrow & 0 & \varepsilon_s & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{3}{2},\frac{3}{2} & 0 & 0 & \varepsilon_p + \frac{\Delta_0}{3} & 0 & 0 & 0 & 0 & 0 \\
\frac{3}{2},-\frac{3}{2} & 0 & 0 & 0 & \varepsilon_p + \frac{\Delta_0}{3} & 0 & 0 & 0 & 0 \\
\frac{3}{2},\frac{1}{2} & 0 & 0 & 0 & 0 & \varepsilon_p + \frac{\Delta_0}{3} & 0 & 0 & 0 \\
\frac{3}{2},-\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & \varepsilon_p + \frac{\Delta_0}{3} & 0 & 0 \\
\frac{1}{2},\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & \varepsilon_p - \frac{2\Delta_0}{3} & 0 \\
\frac{1}{2},-\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \varepsilon_p - \frac{2\Delta_0}{3}
\end{pmatrix}$$

J^2, L^2, J_z basis for k=0 (III)

$$H_{AB} =$$

	$\left(S\uparrow\right)_B$	$\left(S\downarrow\right)_B$	$\left(\frac{3}{2},\frac{3}{2}\right)_B$	$\left(\frac{3}{2},-\frac{3}{2}\right)_B$	$\left(\frac{3}{2},\frac{1}{2}\right)_B$	$\left(\frac{3}{2},-\frac{1}{2}\right)_B$	$\left(\frac{1}{2},\frac{1}{2}\right)_B$	$\left(\frac{1}{2},-\frac{1}{2}\right)_B$
$\left(S\uparrow\right)_A$	V_{ss}	0	0	0	0	0	0	0
$\left(S\downarrow\right)_A$	0	V_{ss}	0	0	0	0	0	0
$\left(\frac{3}{2},\frac{3}{2}\right)_A$	0	0	V_{xx}	0	0	0	0	0
$\left(\frac{3}{2},-\frac{3}{2}\right)_A$	0	0	0	V_{xx}	0	0	0	0
$\left(\frac{3}{2},\frac{1}{2}\right)_A$	0	0	0	0	V_{xx}	0	0	0
$\left(\frac{3}{2},-\frac{1}{2}\right)_B$	0	0	0	0	0	V_{xx}	0	0
$\left(\frac{1}{2},\frac{1}{2}\right)_B$	0	0	0	0	0	0	V_{xx}	0
$\left(\frac{1}{2},-\frac{1}{2}\right)_B$	0	0	0	0	0	0	0	V_{xx}

J^2, L^2, J_z basis for k=0 (IV)

- We can calculate a few matrix elements to prove the above, using

	$X\uparrow$	$Y\uparrow$	$Z\downarrow$	$X\downarrow$	$Y\downarrow$	$Z\uparrow$
$\frac{3}{2},\frac{3}{2}$	$1/\sqrt{2}$	$i/\sqrt{2}$	0	0	0	0
$\frac{3}{2},-\frac{1}{2}$	$1/\sqrt{6}$	$-i/\sqrt{6}$	$\sqrt{2/3}$	0	0	0
$\frac{1}{2},-\frac{1}{2}$	$-\sqrt{1/3}$	$i\sqrt{1/3}$	$\sqrt{1/3}$	0	0	0
$\frac{3}{2},-\frac{3}{2}$	0	0	0	$1/\sqrt{2}$	$-i/\sqrt{2}$	0
$\frac{3}{2},\frac{1}{2}$	0	0	0	$1/\sqrt{6}$	$i/\sqrt{6}$	$\sqrt{2/3}$
$\frac{1}{2},\frac{1}{2}$	0	0	0	$-\sqrt{1/3}$	$-i\sqrt{1/3}$	$1/\sqrt{3}$

J^2, L^2, J_z basis for k=0 (V)

- For example

$$\left\langle \left(\tfrac{3}{2},\tfrac{3}{2}\right)_A \middle| H \middle| \left(\tfrac{3}{2},\tfrac{3}{2}\right)_B \right\rangle = \frac{1}{\sqrt{2}}\left(\left\langle X_A \uparrow\right| - i\left\langle Y_A \uparrow\right|\right) H \frac{1}{\sqrt{2}}\left(\left| X_B \uparrow\right\rangle - i\left| Y_B \uparrow\right\rangle\right) =$$

$$= \frac{1}{2}\left\langle X_A \uparrow \middle| H \middle| X_B \uparrow\right\rangle + \frac{1}{2}\left\langle Y_A \uparrow \middle| H \middle| Y_B \uparrow\right\rangle = \frac{1}{2}V_{xx} + \frac{1}{2}V_{xx} = V_{xx}$$

$$\left\langle \left(\tfrac{3}{2},\tfrac{3}{2}\right)_A \middle| H \middle| \left(\tfrac{3}{2},-\tfrac{1}{2}\right)_B \right\rangle = \frac{1}{\sqrt{2}}\left(\left\langle X_A \uparrow\right| - i\left\langle Y_A \uparrow\right|\right) H \left(\frac{1}{\sqrt{6}}\left| X_B \uparrow\right\rangle - \frac{i}{\sqrt{6}}\left| Y_B \uparrow\right\rangle + \sqrt{\frac{2}{3}}\left| Z_B \downarrow\right\rangle\right) =$$

$$= \frac{1}{\sqrt{12}}\left\langle X_A \uparrow \middle| H \middle| X_B \uparrow\right\rangle - \frac{1}{\sqrt{12}}\left\langle Y_A \uparrow \middle| H \middle| Y_B \uparrow\right\rangle = 0$$

Diagonalization

- In all cases, we have 2x2 hamiltonians with identical diagonal elements, so that all eigenstates are of the form

$$\frac{1}{\sqrt{2}}\left(\;\right)_A + \frac{1}{\sqrt{2}}\left(\;\right)_B$$

$$\frac{1}{\sqrt{2}}\left(\;\right)_A - \frac{1}{\sqrt{2}}\left(\;\right)_B$$

- For the s-states, $V_{ss}<0$, and therefore the (+) combination gives the lowest energy (bonding).
- For the p-states, $V_{xx}>0$, and the (-) combination gives the lowest energy. But this is also the bonding combination, if one recalls the direction of the positive and negative lobes of the p-orbitals in the A and B atoms!

Redefined *s p* functions I

- The above suggests that we define

$$S_b = \frac{1}{\sqrt{2}} S_A + \frac{1}{\sqrt{2}} S_B; \quad S_a = \frac{1}{\sqrt{2}} S_A - \frac{1}{\sqrt{2}} S_B$$

$$X_b = \frac{1}{\sqrt{2}} X_A - \frac{1}{\sqrt{2}} X_B; \quad X_a = \frac{1}{\sqrt{2}} X_A + \frac{1}{\sqrt{2}} X_B$$

$$Y_b = \frac{1}{\sqrt{2}} Y_A - \frac{1}{\sqrt{2}} Y_B; \quad Y_a = \frac{1}{\sqrt{2}} Y_A + \frac{1}{\sqrt{2}} Y_B$$

$$Z_b = \frac{1}{\sqrt{2}} Z_A - \frac{1}{\sqrt{2}} Z_B; \quad Z_a = \frac{1}{\sqrt{2}} Z_A + \frac{1}{\sqrt{2}} Z_B$$

Redefined *s p* functions II

- so that

$$\frac{1}{\sqrt{2}}\left(\tfrac{3}{2},\tfrac{3}{2}\right)_A - \frac{1}{\sqrt{2}}\left(\tfrac{3}{2},\tfrac{3}{2}\right)_B = \frac{1}{\sqrt{2}}\left(X_b \uparrow + iY_b \uparrow\right)$$

$$\frac{1}{\sqrt{2}}\left(\tfrac{3}{2},\tfrac{1}{2}\right)_A - \frac{1}{\sqrt{2}}\left(\tfrac{3}{2},\tfrac{1}{2}\right)_B = \frac{1}{\sqrt{6}}X_b \uparrow - \frac{i}{\sqrt{6}}Y_b \uparrow + \sqrt{\frac{2}{3}}Z_b \downarrow$$

- etc, etc.
- So that I can write the wave functions using the same expression for the single-atom wave functions, except that I add the subscript "a" or "b"

Near band gap functions I

- In the near-band gap we then have the following wave functions and energies at k=0, if we define the 0 of energy as the highest occupied state.

$$\left|S_a \uparrow\right\rangle; \quad E = E_0$$

$$\left|S_a \downarrow\right\rangle; \quad E = E_0$$

$$\left|\tfrac{3}{2}, \tfrac{3}{2}\right\rangle_b = \frac{1}{\sqrt{2}} X_b \uparrow + \frac{i}{\sqrt{2}} Y_b \uparrow; \quad E = 0$$

$$\left|\tfrac{3}{2}, -\tfrac{3}{2}\right\rangle_b = \frac{1}{\sqrt{2}} X_b \downarrow - \frac{i}{\sqrt{2}} Y_b \downarrow; \quad E = 0$$

Near band gap functions II

$$\left|\tfrac{3}{2},-\tfrac{1}{2}\right\rangle_b = \frac{1}{\sqrt{6}} X_b \uparrow - \frac{i}{\sqrt{6}} Y_b \uparrow + \sqrt{\frac{2}{3}} Z_b \downarrow; \quad E = 0$$

$$\left|\tfrac{3}{2},\tfrac{1}{2}\right\rangle_b = \frac{1}{\sqrt{6}} X_b \downarrow + \frac{i}{\sqrt{6}} Y_b \downarrow + \sqrt{\frac{2}{3}} Z_b \uparrow; \quad E = 0$$

$$\left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle_b = -\frac{1}{\sqrt{3}} X_b \uparrow + \frac{i}{\sqrt{3}} Y_b \uparrow + \frac{1}{\sqrt{3}} Z_b \downarrow; \quad E = -\Delta_0$$

$$\left|\tfrac{1}{2},\tfrac{1}{2}\right\rangle_b = -\frac{1}{\sqrt{3}} X_b \downarrow - \frac{i}{\sqrt{3}} Y_b \downarrow + \frac{1}{\sqrt{3}} Z_b \uparrow; \quad E = -\Delta_0$$

k=0 Hamiltonian

- Therefore, in the near band gap region I get

	$\vert S_a \uparrow\rangle$	$\vert \frac{3}{2},-\frac{3}{2}\rangle_b$	$\vert \frac{3}{2},\frac{1}{2}\rangle_b$	$\vert \frac{1}{2},\frac{1}{2}\rangle_b$	$\vert S_a \downarrow\rangle$	$\vert \frac{3}{2},\frac{3}{2}\rangle_b$	$\vert \frac{3}{2},-\frac{1}{2}\rangle_b$	$\vert \frac{1}{2},-\frac{1}{2}\rangle_b$
$\vert S_a \uparrow\rangle$	E_0	0	0	0	0	0	0	0
$\vert \frac{3}{2},-\frac{3}{2}\rangle_b$	0	0	0	0	0	0	0	0
$\vert \frac{3}{2},\frac{1}{2}\rangle_b$	0	0	0	0	0	0	0	0
$\vert \frac{1}{2},\frac{1}{2}\rangle_b$	0	0	0	$-\Delta_0$	0	0	0	0
$\vert S_a \downarrow\rangle$	0	0	0	0	E_0	0	0	0
$\vert \frac{3}{2},\frac{3}{2}\rangle_b$	0	0	0	0	0	0	0	0
$\vert \frac{3}{2},-\frac{1}{2}\rangle_b$	0	0	0	0	0	0	0	0
$\vert \frac{1}{2},-\frac{1}{2}\rangle_b$	0	0	0	0	0	0	0	$-\Delta_0$

The matrix element of *p* (I)

- To go beyond k=0, we need matrix elements of p between these states.
- It is quite obvious from the symmetry of the atomic wavefunctions, that

$$\left\langle S \middle| p_x \middle| X \right\rangle = \left\langle S \middle| p_y \middle| Y \right\rangle = \left\langle S \middle| p_z \middle| Z \right\rangle$$

- and all other matrix elements should be zero.

The matrix element of *p* (II)

- We then have

$$\left\langle S_a \middle| p_x \middle| X_b \right\rangle = \frac{1}{\sqrt{2}}\left(\left\langle S_A \right| - \left\langle S_B \right|\right) p_x \frac{1}{\sqrt{2}}\left(\left| X_A \right\rangle - \left| X_B \right\rangle\right)$$

$$= \frac{1}{2}\left\langle S_A \middle| p_x \middle| X_A \right\rangle + \frac{1}{2}\left\langle S_B \middle| p_x \middle| X_B \right\rangle - \frac{1}{2}\left\langle S_A \middle| p_x \middle| X_B \right\rangle - \frac{1}{2}\left\langle S_B \middle| p_x \middle| X_A \right\rangle$$

- The last two terms cancel each other, so

$$\left\langle S_a \middle| p_x \middle| X_b \right\rangle = \frac{1}{2}\left\langle S_A \middle| p_x \middle| X_A \right\rangle + \frac{1}{2}\left\langle S_B \middle| p_x \middle| X_B \right\rangle$$

- We then define

$$\left\langle S_a \middle| p_x \middle| X_b \right\rangle = \left\langle S_a \middle| p_y \middle| Y_b \right\rangle = \left\langle S_a \middle| p_z \middle| Z_b \right\rangle = iP$$

- We will use this expression to write down the k.p hamiltonian.

Definition of *P*

- From the above, we only need to include the matrix elements

$$\left\langle S_a \middle| p_x \middle| X_b \right\rangle = \left\langle S_a \middle| p_y \middle| Y_b \right\rangle = \left\langle S_a \middle| p_z \middle| Z_b \right\rangle = iP$$

- We can estimate the values of *P* from the empty cell band structure, and we find

$$P \simeq \frac{2\pi}{a}\hbar$$

Matrix elements for k=k_z

- For only k_z different from zero, I only need p_z.Then I get

$$\left\langle S_a \uparrow \middle| p_z \middle| \left(\tfrac{3}{2},-\tfrac{3}{2}\right)_b \right\rangle = \left\langle S_a \uparrow \middle| p_z \left(\frac{1}{\sqrt{2}} \middle| X_b \downarrow \right\rangle - \frac{i}{\sqrt{2}} \left| Y_b \downarrow \right\rangle \right) = 0$$

$$\left\langle S_a \uparrow \middle| p_z \middle| \left(\tfrac{3}{2},\tfrac{1}{2}\right)_b \right\rangle = \left\langle S_a \uparrow \middle| p_z \left(\frac{1}{\sqrt{6}} \middle| X_b \downarrow \right\rangle + \frac{i}{\sqrt{6}} \left| Y_b \downarrow \right\rangle + \sqrt{\frac{2}{3}} \left| Z_b \uparrow \right\rangle \right) = iP\sqrt{\frac{2}{3}}$$

$$\left\langle S_a \uparrow \middle| p_z \middle| \left(\tfrac{1}{2},\tfrac{1}{2}\right)_b \right\rangle = \left\langle S_a \uparrow \middle| p_z \left(\frac{1}{\sqrt{3}} \middle| X_b \downarrow \right\rangle + \frac{i}{\sqrt{3}} \left| Y_b \downarrow \right\rangle + \frac{1}{\sqrt{3}} \left| Z_b \uparrow \right\rangle \right) = iP\frac{1}{\sqrt{3}}$$

- so that the matrix becomes

$k=k_z$ Hamiltonian

- Therefore, in the near band gap region I get

	$\vert S_a \uparrow\rangle$	$\vert \frac{3}{2},-\frac{3}{2}\rangle_b$	$\vert \frac{3}{2},\frac{1}{2}\rangle_b$	$\vert \frac{1}{2},\frac{1}{2}\rangle_b$	$\vert S_a \downarrow\rangle$	$\vert \frac{3}{2},\frac{3}{2}\rangle_b$	$\vert \frac{3}{2},-\frac{1}{2}\rangle_b$	$\vert \frac{1}{2},-\frac{1}{2}\rangle_b$
$\vert S_a \uparrow\rangle$	E_0	0	$\frac{i\hbar Pk_z}{m}\sqrt{\frac{2}{3}}$	$\frac{i\hbar Pk_z}{m}\frac{1}{\sqrt{3}}$	0	0	0	0
$\vert \frac{3}{2},-\frac{3}{2}\rangle_b$	0	0	0	0	0	0	0	0
$\vert \frac{3}{2},\frac{1}{2}\rangle_b$	$-\frac{i\hbar Pk_z}{m}\sqrt{\frac{2}{3}}$	0	0	0	0	0	0	0
$\vert \frac{1}{2},\frac{1}{2}\rangle_b$	$\frac{i\hbar Pk_z}{m}\frac{1}{\sqrt{3}}$	0	0	$-\Delta_0$	0	0	0	0
$\vert S_a \downarrow\rangle$	0	0	0	0	E_0	0	$\frac{i\hbar Pk_z}{m}\sqrt{\frac{2}{3}}$	$\frac{i\hbar Pk_z}{m}\frac{1}{\sqrt{3}}$
$\vert \frac{3}{2},\frac{3}{2}\rangle_b$	0	0	0	0	0	0	0	0
$\vert \frac{3}{2},-\frac{1}{2}\rangle_b$	0	0	0	0	$-\frac{i\hbar Pk_z}{m}\sqrt{\frac{2}{3}}$	0	0	0
$\vert \frac{1}{2},-\frac{1}{2}\rangle_b$	0	0	0	0	$-\frac{i\hbar Pk_z}{m}\frac{1}{\sqrt{3}}$	0	0	$-\Delta_0$

Perturbation theory

- In perturbation theory

$$E_n = E_n^{(0)} + \left\langle n^{(0)} \middle| H_1 \middle| n^{(0)} \right\rangle + \sum_{k \neq n} \frac{\left| \left\langle k^{(0)} \middle| H_1 \middle\| n^{(0)} \right\rangle \right|}{E_n^{(0)} - E_k^{(0)}}$$

- So

$$E_{S\uparrow}\left(k_z\right) = E_0 + \frac{\hbar^2 k_z^2}{2m} + \frac{2}{3}\frac{\hbar^2 P^2 k_z^2}{m^2 E_0} + \frac{1}{3}\frac{\hbar^2 P^2 k_z^2}{m^2\left(E_0 + \Delta_0\right)}$$

$$E_{\frac{3}{2},-\frac{3}{2}}\left(k_z\right) = \frac{\hbar^2 k_z^2}{2m}$$

$$E_{\frac{3}{2},\frac{1}{2}}\left(k_z\right) = \frac{\hbar^2 k_z^2}{2m} + \frac{2}{3}\frac{\hbar^2 P^2 k_z^2}{m^2\left(0 - E_0\right)} = \frac{\hbar^2 k_z^2}{2m} - \frac{2}{3}\frac{\hbar^2 P^2 k_z^2}{m^2 E_0}$$

$$E_{\frac{1}{2},\frac{1}{2}}\left(k_z\right) = \frac{\hbar^2 k_z^2}{2m} + \frac{1}{3}\frac{\hbar^2 P^2 k_z^2}{m^2\left(-\Delta_0 - E_0\right)} = \frac{\hbar^2 k_z^2}{2m} - \frac{1}{3}\frac{\hbar^2 P^2 k_z^2}{m^2\left(E_0 + \Delta_0\right)}$$

Electron effective mass

- If we define the electron effective mass as

$$E_{S\uparrow}\left(k_z\right) = E_0 + \frac{\hbar^2 k_z^2}{2m_e}$$

- we obtain

$$\frac{m}{m_e} = 1 + \frac{2P^2}{3m}\left(\frac{2}{E_0} + \frac{1}{E_0 + \Delta_0}\right)$$

Light-hole effective mass

- If we define the light-hole effective mass as

$$E_{\frac{3}{2},\frac{1}{2}}\left(k_z\right) \equiv E_{lh}\left(k_z\right) = -\frac{\hbar^2 k_z^2}{2m_{lh}}$$

- we obtain

$$\frac{m}{m_{lh}} = \frac{4P^2}{3mE_0} - 1$$

Split-off hole effective mass

- If we define the split-off light-hole effective mass as

$$E_{\frac{1}{2},\frac{1}{2}}\left(k_z\right) \equiv E_{so}\left(k_z\right) = -\Delta_0 - \frac{\hbar^2 k_z^2}{2m_{so}}$$

- we obtain

$$\frac{m}{m_{so}} = \frac{2P^2}{3m\left(E_0 + \Delta_0\right)} - 1$$

Heavy-hole effective mass

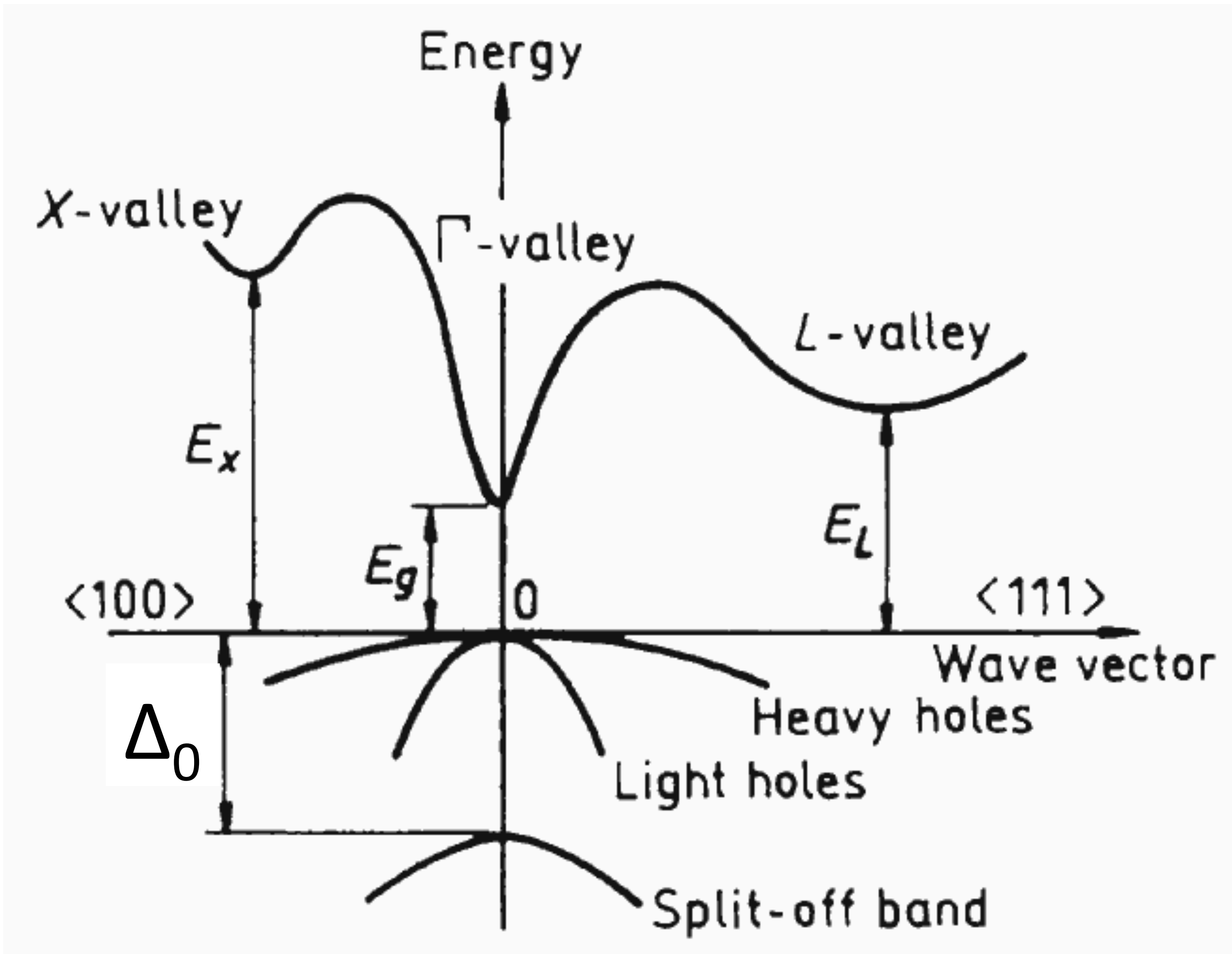
- If we define the heavy-hole effective mass as

$$E_{\frac{3}{2},-\frac{3}{2}}\left(k_z\right) \equiv E_{hh}\left(k_z\right) = -\frac{\hbar^2 k_z^2}{2m_{hh}}$$

- we obtain

$$\frac{m}{m_{hh}} = -1$$

The bands



Energy
X-valley
Γ-valley
L-valley
E_x
E_g
E_L
⟨100⟩
0
⟨111⟩
Wave vector
Δ_0
Heavy holes
Light holes
Split-off band

Consequences

- From the point of view of k.p theory, band curvature is mainly due to k.p "repulsion".
- Bands are never perfectly parabolic, only at small k.
- Heavy-hole effective mass comes out qualitatively wrong because one cannot ignore p-antibonding bands in this case.
- Light-hole bands are also affected by p-antibonding orbitals: band warping.
- Because P is more or less constant, effective masses depend mainly on band gaps: the smaller the gap, the smaller the effective mass.
- Drude model: $v = \mu E$, $\mu = e\tau/m$, therefore, small band gap favors high mobility.

Example: Ge

- The matrix element P is predicted to be

$$\frac{P^2}{m} = \frac{\hbar^2}{m}\left(\frac{2\pi}{a}\right)^2 = 9.4\ \text{eV}; \quad E_0 = 0.89\ \text{eV}; \quad \Delta_0 = 0.297\ \text{eV}$$

$$\frac{m_e}{m} = \left[1 + \frac{2P^2}{3m}\left(\frac{2}{E_0} + \frac{1}{E_0 + \Delta_0}\right)\right]^{-1} = 0.049; \quad 0.037\ (\text{exp})$$

$$\frac{m_{lh}}{m} = \left[\frac{4P^2}{3mE_0} - 1\right]^{-1} = 0.076; \quad 0.044\ (\text{exp})$$

$$\frac{m_{hh}}{m} = -1; \quad 0.38\ (\text{exp})$$

$$\frac{m_{so}}{m} = \left[\frac{2P^2}{3m\left(E_0 + \Delta_0\right)} - 1\right]^{-1} = 0.23; \quad 0.095\ (\text{exp})$$

Adjusting *P*

- If we adjust *P* to reproduce effective masses

$$\frac{P^2}{m} = \frac{\hbar^2}{m}\left(\frac{2\pi}{a}\right)^2 = 12.61\ \text{eV}; \quad E_0 = 0.89\ \text{eV}; \quad \Delta_0 = 0.297\ \text{eV}$$

$$\frac{m_e}{m} = \left[1 + \frac{2P^2}{3m}\left(\frac{2}{E_0} + \frac{1}{E_0 + \Delta_0}\right)\right]^{-1} = 0.037; \quad 0.037\ (\text{exp})$$

$$\frac{m_{lh}}{m} = \left[\frac{4P^2}{3mE_0} - 1\right]^{-1} = 0.056; \quad 0.044\ (\text{exp})$$

$$\frac{m_{hh}}{m} = -1; \quad 0.38\ (\text{exp})$$

$$\frac{m_{so}}{m} = \left[\frac{2P^2}{3m\left(E_0 + \Delta_0\right)} - 1\right]^{-1} = 0.16; \quad 0.095\ (\text{exp})$$