k.p Method for Electronic Structure Calculation

- First used by Bardeen (1937) and Seitz (1940)
- Later extended by Shockley, Dresselhaus, Kittel, and Kane

Uses:

- Obtaining **analytic expressions** for band dispersion and effective masses
- Can also be used to get the band structure for the whole zone from zone center energy gaps and **optical matrix** elements

Bardeen and Seitz used it as a way of calculating effective masses and crystal WFs near high-symmetry points.

Analytic expressions for band dispersion and effective masses are obtained around high-symmetry points.

Shockley did it for degenerate bands while Dresselhaus and Kane included spin-orbit.

4.1 THE BLOCH THEOREM AND THE $\mathbf{k} \cdot \mathbf{p}$ METHOD FOR SIMPLE BANDS

For an electron in a periodic potential

$$V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R}) \qquad \mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3,$$

$$H\psi(\mathbf{r}) = \left[\frac{-\hbar^2}{2m_0}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) = E(\mathbf{k})\psi(\mathbf{r})$$

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

$$u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$$

This result is the Bloch theorem.

The $\mathbf{k} \cdot \mathbf{p}$ method is a useful technique for analyzing the band structure near a particular point $\mathbf{k}_0$, especially when it is near an extremum of the band structure. Here we consider that the extremum occurs at the zone center where $\mathbf{k}_0 = 0$. This is a very useful case for III–V direct bandgap semiconductors.

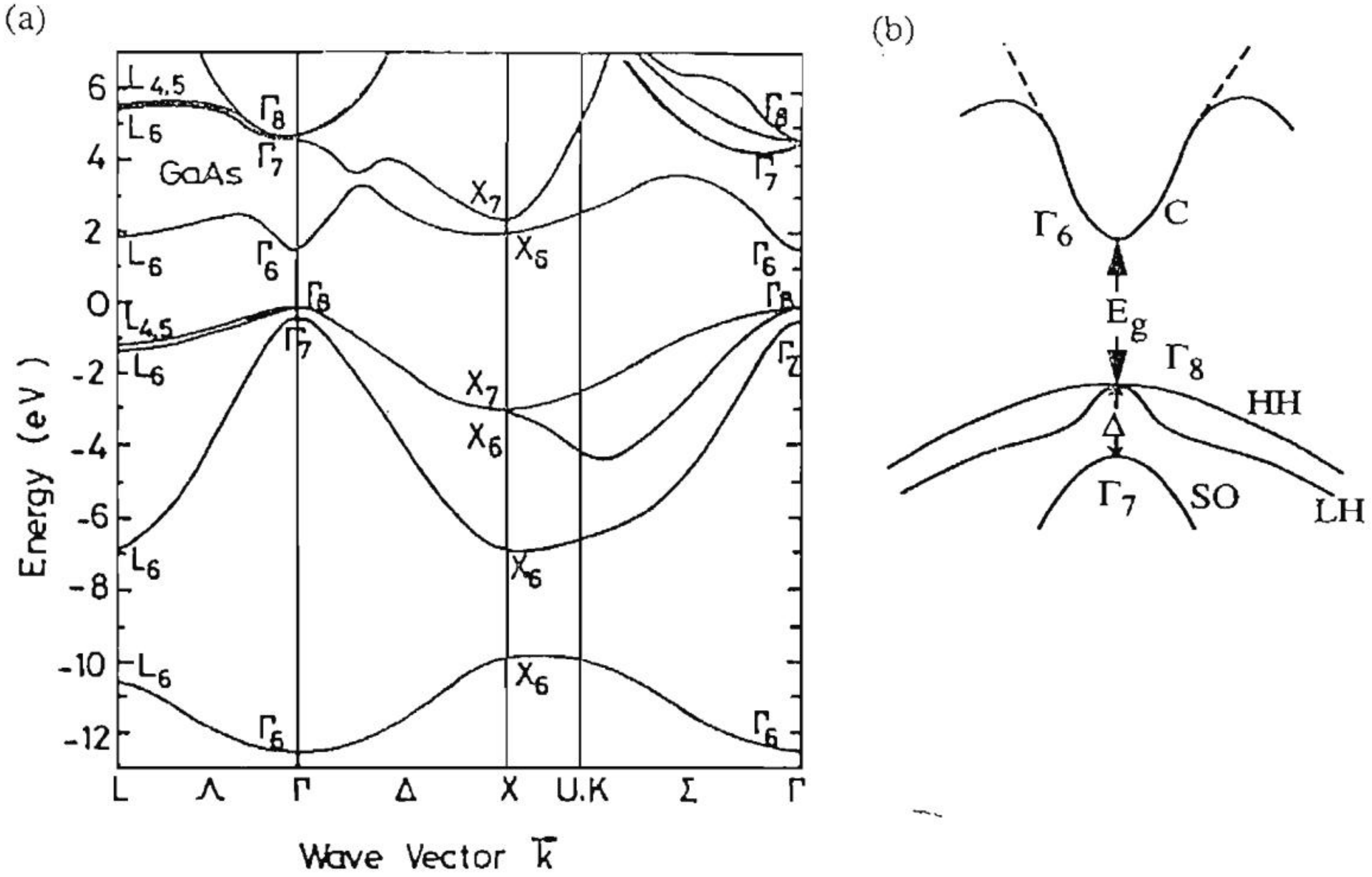


Figure 4.1. (a) GaAs band structure calculated by the pseudopotential method. (After Ref. 15.) (b) The band structure near the band edges of the direct band gap showing the conduction (C) heavy-hole (HH), light-hole (LH), and spin–orbit (SO) split-off bands.

Consider the general Schrödinger equation for an electron wave function $\psi_{n\mathbf{k}}(\mathbf{r})$ in the nth band with a wave vector $\mathbf{k}$,

$$\left[\frac{p^2}{2m_0} + V(\mathbf{r})\right]\psi_{n\mathbf{k}}(\mathbf{r}) = E_n(\mathbf{k})\psi_{n\mathbf{k}}(\mathbf{r}) \tag{4.1.4}$$

When written in terms of $u_{n\mathbf{k}}(\mathbf{r})$, it becomes

$$\left[\frac{p^2}{2m_0} + \frac{\hbar}{m_0}\mathbf{k}\cdot\mathbf{p} + V(\mathbf{r})\right]u_{n\mathbf{k}}(\mathbf{r}) = \left[E_n(\mathbf{k}) - \frac{\hbar^2 k^2}{2m_0}\right]u_{n\mathbf{k}}(\mathbf{r})$$

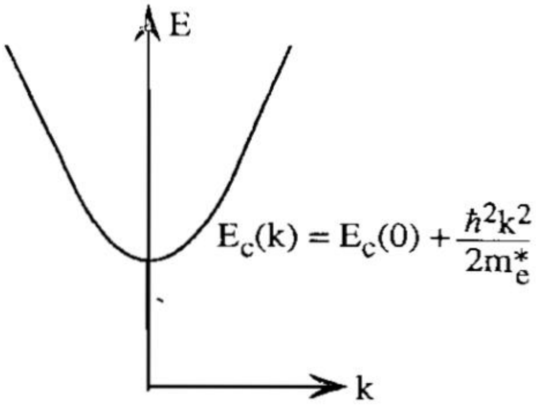
When $\mathbf{k}_0 = 0$,

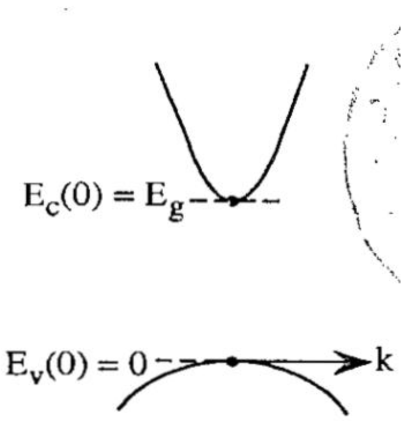
$$\left[H_0 + \frac{\hbar^2}{m_0}\mathbf{k}\cdot\mathbf{p}\right]u_{n\mathbf{k}}(\mathbf{r}) = \left[E_n(\mathbf{k}) - \frac{\hbar^2 k^2}{2m_0}\right]u_{n\mathbf{k}}(\mathbf{r})$$

$$\mathbf{k}\cdot\mathbf{p} = k_x\left(-i\hbar\frac{\partial}{\partial x}\right) + k_y\left(-i\hbar\frac{\partial}{\partial y}\right) + k_z\left(-i\hbar\frac{\partial}{\partial z}\right)$$

$$H_0 = \frac{p^2}{2m_0} + V(\mathbf{r})$$

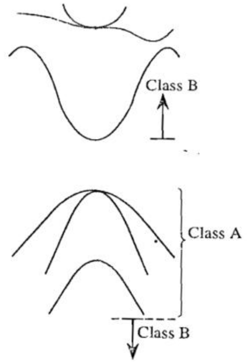
$$H_0 u_{n0}(\mathbf{r}) = E_n(0)u_{n0}(\mathbf{r})$$





4.1.1 The k · p Theory for a Single Band

perturbation theory and Löwdin's method



Here the particular band of interest, labeled n, is called class A, and class B consists of the rest of the bands, n' # n.

time-independent perturbation theory,

second order in perturbation

$$E_n(\mathbf{k}) = E_n(0) + \frac{\hbar^2 k^2}{2m_0} + \frac{\hbar}{m_0}\mathbf{k}\cdot\mathbf{p}_{nn} + \frac{\hbar^2}{m_0^2}\sum_{n'\neq n}\frac{|\mathbf{k}\cdot\mathbf{p}_{nn'}|^2}{E_n(0) - E_{n'}(0)}$$

and the wave function to the first order in perturbation (3.5.16a):

$$\begin{aligned} u_{n\mathbf{k}}(\mathbf{r}) &= u_{n0}(\mathbf{r}) + \sum_{n \neq n'} \left[\frac{\hbar}{m_0} \frac{\mathbf{k} \cdot \mathbf{p}_{n'n}}{E_n(0) - E_{n'}(0)} \right] u_{n'0}(\mathbf{r}) \\ &\equiv \sum_{n'} a_{n'} u_{n'0}(\mathbf{r}) \end{aligned}$$

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

where the momentum matrix elements are defined as

$$\mathbf{p}_{nn'} = \int_{\substack{\text{unit} \\ \text{cell}}} u_{n0}^*(\mathbf{r}) \mathbf{p} u_{n'0}(\mathbf{r}) \, d^3\mathbf{r}$$

and $u_{n\mathbf{k}}(\mathbf{r})$'s are normalized as

$$\int_{\substack{\text{unit} \\ \text{cell}}} u_{n0}^*(\mathbf{r}) u_{n'0}(\mathbf{r}) \, d^3\mathbf{r} = \delta_{nn'}$$

If $\mathbf{k}_0$ is at an extremum of $E_n(\mathbf{k})$, then $E_n(\mathbf{k})$ must depend quadratically on $\mathbf{k}$ near $\mathbf{k}_0$ and $\mathbf{p}_{nn} = 0$. That is why we need to go to second-order perturbation theory for the energy correction and only the first-order correction is needed for the wave function. Since we set $\mathbf{k}_0$ to 0, we have

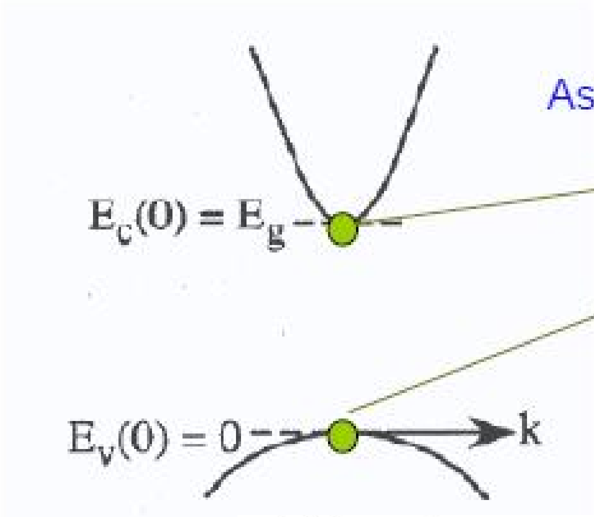
$$E_n(\mathbf{k}) - E_n(0) = \sum_{\alpha,\beta} D^{\alpha\beta} k_\alpha k_\beta = \frac{\hbar^2}{2} \sum_{\alpha,\beta} \left(\frac{1}{m^*}\right)_{\alpha\beta} k_\alpha k_\beta \qquad (4.1.12)$$

and

$$D^{\alpha\beta} = \frac{\hbar^2}{2m_0}\delta_{\alpha\beta} + \frac{\hbar^2}{2m_0^2} \sum_{n' \neq n} \frac{p^\alpha_{nn'} p^\beta_{n'n} + p^\beta_{nn'} p^\alpha_{n'n}}{E_n(0) - E_{n'}(0)} = \frac{\hbar^2}{2}\left(\frac{1}{m^*}\right)_{\alpha\beta} \qquad (4.1.13)$$

where $\alpha, \beta = x$, y, and z. It should be noted that the $D^{\alpha\beta}$ matrix in the quadratic form has been defined to be symmetric. The matrix $D^{\alpha\beta}$ is the inverse effective mass in matrix form multiplied by $\hbar^2/2$.

k·p for Two Non-degenerate Bands



Assume that we know these two (say, $k=k_0$) states

Using them as our basis, for any other state:

$$u_{n\mathbf{k}}(\mathbf{r}) = \sum_{n'} a_{n'}(\mathbf{k})\, u_{n'0}(\mathbf{r})$$

To find these expansion coef's, insert this into Hamiltonian

multiplying by $u^*_{n0}(\mathbf{r})$ and integrating over a unit cell,

$$\sum_{n'} \left\{ \left[E_n(0) + \frac{\hbar^2 k^2}{2m_0} \right] \delta_{nn'} + \frac{\hbar}{m_0} \mathbf{k} \cdot \mathbf{p}_{nn'} \right\} a_{n'} = E_n(\mathbf{k})\, a_n$$

For a basis of two states the solution becomes this determinant

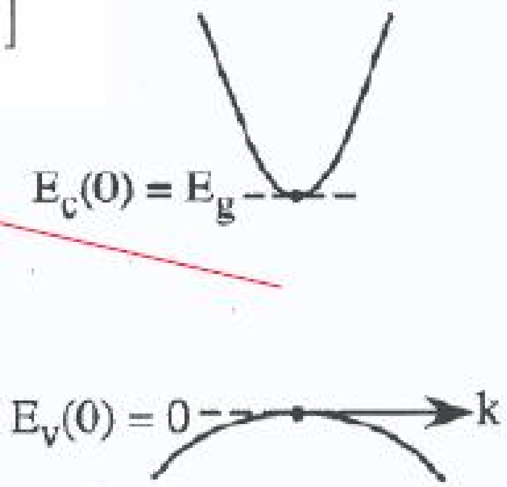
$$\begin{vmatrix} E_n(0) + \dfrac{\hbar^2 k^2}{2m_0} - E & \dfrac{\hbar}{m_0} \mathbf{k} \cdot \mathbf{p}_{nn'} \\ \dfrac{\hbar}{m_0} \mathbf{k} \cdot \mathbf{p}_{n'n} & E_{n'}(0) + \dfrac{\hbar^2 k^2}{2m_0} - E \end{vmatrix} = 0$$

Ref: Chuang

Eigenvalues of the determinantal equation are:

$$E = \frac{1}{2}\left[E_n + E'_n + \frac{\hbar^2}{m_0}k^2\right] \pm \frac{1}{2}\left[(E_n - E_{n'})^2 + \frac{4\hbar^2}{m_0^2}|\mathbf{k}\cdot\mathbf{p}|^2\right]^{1/2}$$

Apply to CB-VB: $n=c$, $n'=v$; $E_v=0$, $E_c=E_g$



$$E = \frac{1}{2}\left(E_g + \frac{\hbar^2k^2}{m_0}\right) \pm \frac{1}{2}\left[E_g^2 + 4\frac{\hbar^2}{m_0^2}|\mathbf{k}\cdot\mathbf{p}_{cv}|^2\right]^{1/2}$$

For small $\mathbf{k}\cdot\mathbf{p}_{cv}$

$$E = \begin{cases} E_g + \dfrac{\hbar^2k^2}{2m_0} + \dfrac{\hbar^2}{E_g m_0^2}|\mathbf{k}\cdot\mathbf{p}_{cv}|^2 & \text{for the conduction band} \\ \dfrac{\hbar^2k^2}{2m_0} - \dfrac{\hbar^2}{E_g m_0^2}|\mathbf{k}\cdot\mathbf{p}_{cv}|^2 & \text{for the valence band} \end{cases}$$

Ref: Chuang

Further assuming that $\bar{p}_{cv}$ is isotropic so that $\bar{k}\cdot\bar{p}_{cv} \to kp_{cv}$

yields the following isotropic reciprocal effective masses:

$$\frac{m_0}{m_v^*} = 1 - \frac{2p_{cv}^2}{m_0 E_g},$$

$$\frac{m_0}{m_c^*} = 1 + \frac{2p_{cv}^2}{m_0 E_g}.$$

inverse effective mass tensor (definition)

$$\left(\frac{m_0}{m_n^*}\right)_{\alpha\beta} = \frac{m_0}{\hbar^2}\frac{\partial^2 E_n}{\partial k_\alpha \partial k_\beta}$$

For $E_g < \frac{2p_{cv}^2}{m_0}$ lower band becomes concave down as in the top of the VB

So, for small bandgap se/c, i.e., $E_g \ll \frac{2p_{cv}^2}{m_0}$ $\quad |m_v^*|, m_c^* \propto E_g$

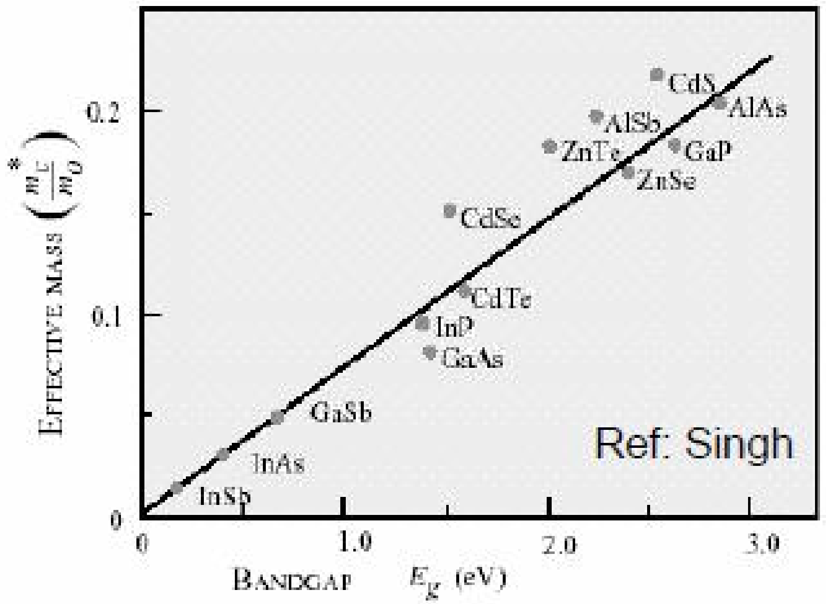
It is found that this proportionality is roughly obeyed in the comparison of m_c^* at $\bar{k}=0$ in Ge and GaAs, indicating that, with similar electronic structures, the momentum matrix element does not vary much.

Ref: Callaway

Applying to CB of Ge and GaAs:

$$\frac{m_c^*(\mathrm{GaAs})}{m_c^*(\mathrm{Ge})} = \frac{E_g(\mathrm{GaAs})}{E_g(\mathrm{Ge})} \qquad \text{says } \bar{k}\cdot\bar{p}$$

Check with experimental values:



Ref: Singh

$$E_g(\mathrm{GaAs}) = 1.52\ \mathrm{eV},\ E_g(\mathrm{Ge}) = 0.889\ \mathrm{eV},\ m_c^*(\mathrm{Ge}) = 0.041$$

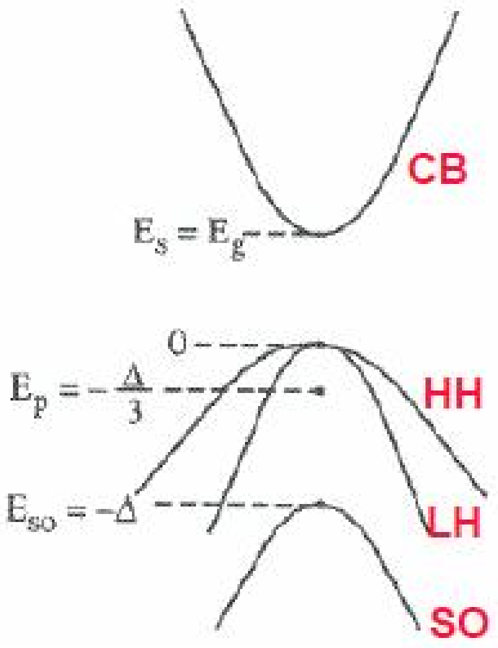
$$\Rightarrow\ m_c^*(\mathrm{GaAs}) = 0.070 \text{ in close agreement with its exp. value } m_c^*(\mathrm{GaAs}) = 0.0665$$

The calculation should be improved by taking into account the spin-orbit interaction within the valence band (follows next).

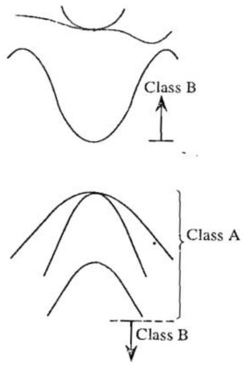
Ref: Callaway

Kane's model : Four-band k·p with Spin-Orbit Interaction

- ➢Four bands: CB, HH, LH, SO
- ➢Double degeneracy with their spin counterparts
- ➢Coupling to any other band is neglected
- ➢These four bands are solved <u>exactly</u> using the matrix formalism based on a convenient basis choice



Spin-orbit coupling is a relativistic effect scales with the atomic number of the atom. Thus for se/c containing heavier elements, such as Ge, Ga, As, In, and Sb, one expects the SO coupling to be significant, and has to be included particularly for states near **k**=0.



The Schrödinger Equation for the cell-periodic fn.

$$H = H_0 + \boxed{\frac{\hbar}{4m_0^2c^2}\boldsymbol{\sigma}\cdot\nabla V\times\mathbf{p}}$$

The Hamiltonian near $\boldsymbol{k}_0=0$

$$H_0 = \frac{p^2}{2m_0} + V(\mathbf{r})$$

spin-orbit interaction

Components of the Pauli spin matrix:

$$\bar{\bar{\sigma}}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad \bar{\bar{\sigma}}_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \qquad \bar{\bar{\sigma}}_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

operating on the spins

$$\uparrow \equiv \begin{bmatrix} 1 \\ 0 \end{bmatrix} \qquad \downarrow \equiv \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

yield →

reverse the spinors

$$\boxed{\begin{matrix} \bar{\bar{\sigma}}_x \uparrow = \downarrow & \bar{\bar{\sigma}}_y \uparrow = i \downarrow \\ \bar{\bar{\sigma}}_x \downarrow = \uparrow & \bar{\bar{\sigma}}_y \downarrow = -i \uparrow \end{matrix}}$$

preserves the spinors: eigenfn's

$$\boxed{\begin{matrix} \bar{\bar{\sigma}}_z \uparrow = \uparrow \\ \bar{\bar{\sigma}}_z \downarrow = -\downarrow \end{matrix}}$$

Ref: Chuang

From the original Schrödinger equation for the Bloch function,

$$\left\{\frac{p^2}{2m_0} + V(\mathbf{r}) + \frac{\hbar}{4m_0^2c^2}[\nabla V \times \mathbf{p}] \cdot \boldsymbol{\sigma}\right\}\psi_{n\mathbf{k}}(\mathbf{r}) = E_n(\mathbf{k})\psi_{n\mathbf{k}}(\mathbf{r})$$

The Schrödinger equation for the cell periodic function $u_{n\mathbf{k}}(\mathbf{r})$ is obtained:

$$\left\{\frac{p^2}{2m_0} + V(\mathbf{r}) + \frac{\hbar}{m_0}\mathbf{k} \cdot \mathbf{p} + \frac{\hbar}{4m_0^2c^2}[\nabla V \times \mathbf{p}] \cdot \boldsymbol{\sigma} + \boxed{\frac{\hbar^2}{4m_0^2c^2}\nabla V \times \mathbf{k} \cdot \boldsymbol{\sigma}}\right\}$$

$$\times\, u_{n\mathbf{k}}(\mathbf{r}) = E' u_{n\mathbf{k}}(\mathbf{r})$$

$$E' = E_n(\mathbf{k}) - \hbar^2k^2/2m_0$$

to be neglected compared to this term

$\hbar\bar{k}$ is the crystal momentum or the momentum of the envelope, whereas $\bar{p}$ is the actual linear momentum of the *e* which is much greater than $\hbar\bar{k}$ due to $u_{n\bar{k}}(\bar{r})$ part coming from the atomic wavefunction where most of the SO interaction actually occurs.

$$Hu_{n\mathbf{k}}(\mathbf{r}) \simeq \left(H_0 + \frac{\hbar}{m_0}\mathbf{k} \cdot \mathbf{p} + \frac{\hbar}{4m_0^2c^2}\nabla V \times \mathbf{p} \cdot \boldsymbol{\sigma}\right)u_{n\mathbf{k}}(\mathbf{r}) = E' u_{n\mathbf{k}}(\mathbf{r})$$

Ref: Chuang

Nature of the Bands Near Bandedges

In semiconductors we are pimarily interested in the valence band and conduction band. Moreover, for most applications we are interested in what happens near the top of the valence band and the bottom of the conduction band. These states originate from the atomic levels of the valence shell in the elements making up the semiconductor.

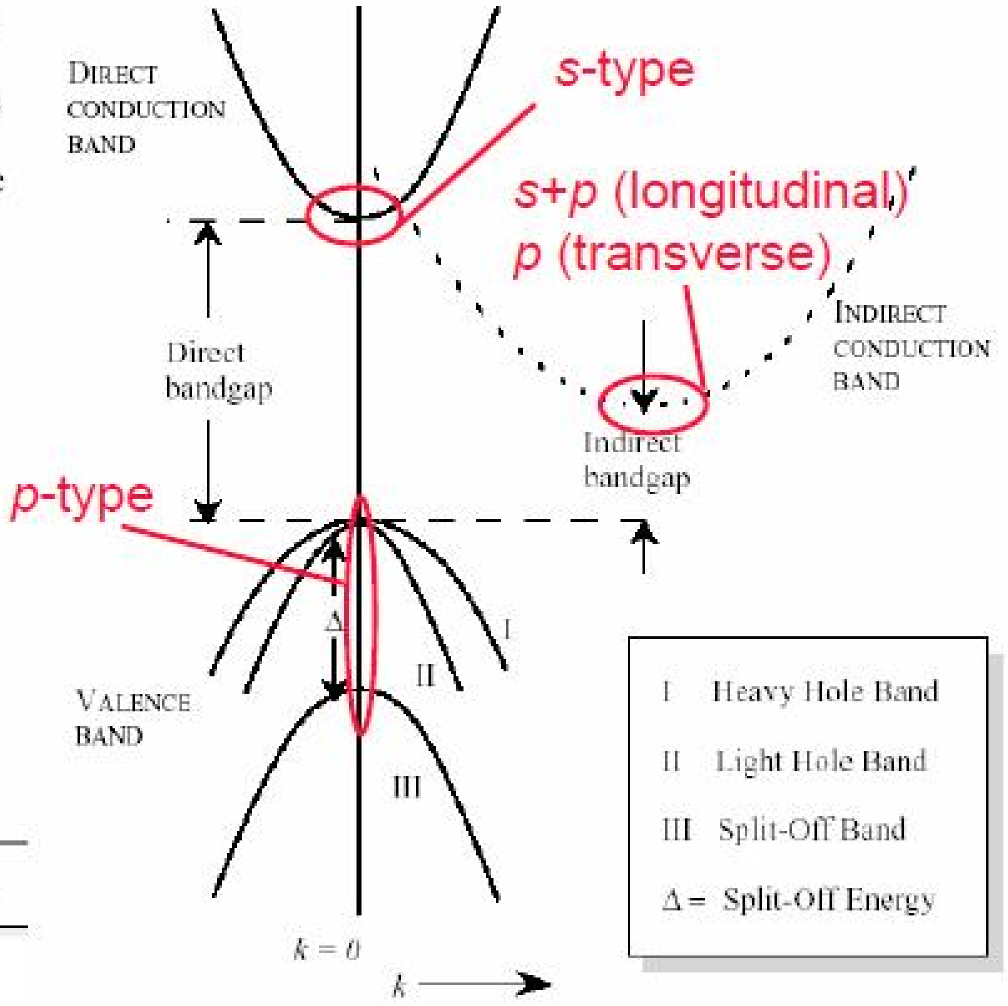
IV Semiconductors

C	$1s^2\underbrace{2s^22p^2}$
Si	$1s^22s^22p^6\underbrace{3s^23p^2}$
Ge	$1s^22s^22p^63s^23p^63d^{10}\underbrace{4s^24p^2}$

III-V Semiconductors

Ga	$1s^22s^22p^63s^23p^63d^{10}\underbrace{4s^24p^1}$
As	$1s^22s^22p^63s^23p^63d^{10}\underbrace{4s^24p^3}$

Outermost atomic levels are either *s*-type or *p*-type.



Ref: Singh

Recall the *s,p,d*-type Spherical Harmonics

$\ell = 0$ (s orbit)

$$Y_{00} = \frac{1}{\sqrt{4\pi}}$$

$$Y_{\ell m}(\theta, \varphi) = \sqrt{\frac{2\ell + 1}{4\pi} \frac{(\ell - |m|)!}{(\ell + |m|)!}} (-1)^{(m+|m|)/2} P_\ell^{|m|}(\cos\theta)\, e^{im\varphi}$$

and

$$\int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} |Y_\ell^m(\theta, \varphi)|^2 \sin\theta \, d\theta \, d\varphi = 1$$

$\ell = 1$ (p orbits)

$$Y_{10}(\theta, \varphi) = \sqrt{\frac{3}{4\pi}} \cos\theta = \sqrt{\frac{3}{4\pi}} \frac{z}{r} \equiv |Z\rangle$$

$$\begin{aligned} Y_{1\pm1}(\theta, \varphi) &= \mp\sqrt{\frac{3}{8\pi}} \sin\theta\, e^{\pm i\varphi} = \mp\sqrt{\frac{3}{8\pi}} \frac{x \pm iy}{r} \\ &= \mp\frac{1}{\sqrt{2}} |X \pm iY\rangle \end{aligned}$$

$\ell = 2$ (d orbits)

$$Y_{20}(\theta, \varphi) = \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1) = \sqrt{\frac{5}{16\pi}} \left(\frac{3z^2}{r^2} - 1\right)$$

$$Y_{2\pm1}(\theta, \varphi) = \mp\sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta\, e^{\pm i\varphi} = \mp\sqrt{\frac{15}{8\pi}} \frac{(x \pm iy)z}{r^2}$$

$$Y_{2\pm2}(\theta, \varphi) = \sqrt{\frac{15}{32\pi}} \sin^2\theta\, e^{\pm 2i\varphi} = \sqrt{\frac{15}{32\pi}} \frac{(x \pm iy)^2}{r^2}$$

Ref: Chuang

The Convenient Basis Choice and the Corresponding Hamiltonian Matrix

We look for the eigenvalue E' with corresponding eigenfunction

$$u_{n\mathbf{k}}(\mathbf{r}) = \sum_{n'} a_{n'} u_{n'0}(\mathbf{r})$$

The band-edge functions $u_{n0}(\mathbf{r})$ are

Conduction band: $|S\uparrow\rangle$, $|S\downarrow\rangle$ with corresponding eigenenergy E_s
Valence band: $|X\uparrow\rangle$, $|Y\uparrow\rangle$, $|Z\uparrow\rangle$, $|X\downarrow\rangle$, $|Y\downarrow\rangle$, $|Z\downarrow\rangle$ with eigenenergy E_p

They deviate from a totally spherical function *f(r)* by:

similarly for

X(x,y,z)=-*X*(-*x,y,z*); odd fn of *x* but even wrt *y* & *z*

where the wave functions in each band are degenerate with respect to H_0. $H_0|S\uparrow\rangle = E_s|S\uparrow\rangle$, $H_0|S\downarrow\rangle = E_s|S\downarrow\rangle$, $H_0|X\uparrow\rangle = E_p|X\uparrow\rangle$, $H_0|Y\uparrow\rangle = E_p|Y\uparrow\rangle$, $H_0|Z\uparrow\rangle = E_p|Z\uparrow\rangle$, and so on. It is convenient to choose the basis functions

However, it is convenient to switch to the following linear combinations:

$$\left|u_1\right\rangle = \left|iS\downarrow\right\rangle$$

$$\left|u_2\right\rangle = \left|\frac{X-iY}{\sqrt{2}}\uparrow\right\rangle = \left|Y_{1\,-1}\uparrow\right\rangle$$

$$\left|u_3\right\rangle = \left|Z\downarrow\right\rangle = \left|Y_{1\,0}\downarrow\right\rangle$$

$$\left|u_4\right\rangle = \left|-\frac{X+iY}{\sqrt{2}}\uparrow\right\rangle = \left|Y_{1\,1}\uparrow\right\rangle$$

$$\left|u_5\right\rangle = \left|iS\uparrow\right\rangle$$

$$\left|u_6\right\rangle = \left|-\frac{X+iY}{\sqrt{2}}\downarrow\right\rangle = \left|Y_{1\,1}\downarrow\right\rangle$$

$$\left|u_7\right\rangle = \left|Z\uparrow\right\rangle = \left|Y_{1\,0}\uparrow\right\rangle$$

$$\left|u_8\right\rangle = \left|\frac{X-iY}{\sqrt{2}}\downarrow\right\rangle = \left|Y_{1\,-1}\downarrow\right\rangle$$

$$|\mathrm{i}S\downarrow\rangle, \quad \left|\frac{X-\mathrm{i}Y}{\sqrt{2}}\uparrow\right\rangle,$$

$$|Z\downarrow\rangle, \quad \left|-\frac{X+\mathrm{i}Y}{\sqrt{2}}\uparrow\right\rangle$$

$$|\mathrm{i}S\uparrow\rangle, \quad \left|-\frac{X+\mathrm{i}Y}{\sqrt{2}}\downarrow\right\rangle$$

$$|Z\uparrow\rangle, \quad \left|\frac{X-\mathrm{i}Y}{\sqrt{2}}\downarrow\right\rangle$$

The first four basis fn's are degenerate with the last four

Ref: Chuang

Using this basis, expansion coefficients and the eigenenergies are determined from the the following 8x8 Hamiltonian Matrix

$$u_{n\mathbf{k}}(\mathbf{r}) = \sum_{n'} a_{n'} u_{n'0}(\mathbf{r})$$

$$\begin{bmatrix} \bar{\bar{\mathbf{H}}} & 0 \\ 0 & \bar{\bar{\mathbf{H}}} \end{bmatrix}$$

$$Hu_{n\mathbf{k}}(\mathbf{r}) = \left(H_0 + \frac{\hbar}{m_0}\mathbf{k}\cdot\mathbf{p} + \frac{\hbar}{4m_0^2c^2}\nabla V \times \mathbf{p}\cdot\boldsymbol{\sigma} \right) u_{n\mathbf{k}}(\mathbf{r}) = E' u_{n\mathbf{k}}(\mathbf{r})$$

$$\bar{\bar{\mathbf{H}}} = \left.\begin{bmatrix} E_s & 0 & kP & 0 \\ 0 & E_p - \frac{\Delta}{3} & \sqrt{2}\,\Delta/3 & 0 \\ kP & \sqrt{2}\,\Delta/3 & E_p & 0 \\ 0 & 0 & 0 & E_p + \frac{\Delta}{3} \end{bmatrix}\right\} \text{assuming } \mathbf{k} = k\hat{z}$$

Don't worry, this will be relaxed later on

where

$$P \equiv -\mathrm{i}\frac{\hbar}{m_0}\langle S|p_z|Z\rangle$$ Kane's parameter

$$\Delta \equiv \frac{3\hbar \mathrm{i}}{4m_0^2c^2}\langle X|\frac{\partial V}{\partial x}p_y - \frac{\partial V}{\partial y}p_x|Y\rangle$$ SO split off energy

Ref: Chuang

Kane's Hamiltonian (cont'd)

➢Analysis of the matrix entries

Recall

- *X(x,y,z)*=-*X*(-*x,y,z*); odd fn of *x* but even wrt *y* & *z, etc.*
- $\langle \downarrow | \sigma_x | \downarrow \rangle = \langle \downarrow | \sigma_y | \downarrow \rangle = 0$

$$
\begin{aligned}
H_{11} &= \langle \mathrm{i}S\downarrow | H_0 + \frac{\hbar}{m_0}\mathbf{k}\cdot\mathbf{p} + \frac{\hbar}{4m_0^2c^2}\boxed{\sigma\cdot\nabla V\times\mathbf{p}} | \mathrm{i}S\downarrow\rangle \\
&= \langle S\downarrow | H_0 | S\downarrow\rangle + \frac{\hbar}{m_0}\cancel{\langle S\downarrow | \mathbf{k}\cdot\mathbf{p} | S\downarrow\rangle} \\
&\quad + \cancel{\langle S\downarrow | \frac{\hbar}{4m_0^2c^2}\sigma_z\left(\frac{\partial V}{\partial x}p_y - \frac{\partial V}{\partial y}p_x\right) | S\downarrow\rangle} \\
&= E_S
\end{aligned}
$$

$$\sigma_x(\nabla V\times\mathbf{p})_x + \sigma_y(\nabla V\times\mathbf{p})_y + \sigma_z(\nabla V\times\mathbf{p})_z$$

$$\langle S\downarrow|\mathbf{p}|S\downarrow\rangle = \langle S|\mathbf{p}|S\rangle = \int S(r)\frac{\hbar}{i}\nabla S(r)\,\mathrm{d}^3r = 0$$

vanishes as this term changes sign when x↔y whereas the xtal is invariant under this xformation

The rest of the matrix elements are in HW-1 ☺

Ref: Chuang

Solutions of Kane's Hamiltonian

Define the reference energy so that: $E_p = -\Delta/3$, and $E_s = E_g$

$$\overline{\overline{\mathbf{H}}} = \begin{bmatrix} E_g & 0 & kP & 0 \\ 0 & -\frac{2\Delta}{3} & \sqrt{2}\,\Delta/3 & 0 \\ kP & \sqrt{2}\,\Delta/3 & \frac{-\Delta}{3} & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

$$E' = 0$$

Decoupled
from the rest

$$E'(E' - E_g)(E' + \Delta) - k^2P^2(E' + \tfrac{2}{3}\Delta) = 0$$

Band edge ***k***=0

$$E' = E_g,\ E' = 0 \text{ and } E' = -\Delta$$

Ref: Chuang

Solutions for small k

Let $E' = E_g + \varepsilon(k^2)$ where $\varepsilon \ll \Delta$ and E_g $\longrightarrow$ $\varepsilon \simeq \dfrac{k^2P^2(E_g + 2\Delta/3)}{E_g(E_g + \Delta)}$

Let $E' = 0 + \varepsilon(k^2)$ $\longrightarrow$ $\varepsilon \simeq -\dfrac{2k^2P^2}{3E_g}$

Let $E' = -\Delta + \varepsilon(k^2)$ $\longrightarrow$ $\varepsilon = -\dfrac{k^2P^2}{3(E_g + \Delta)}$

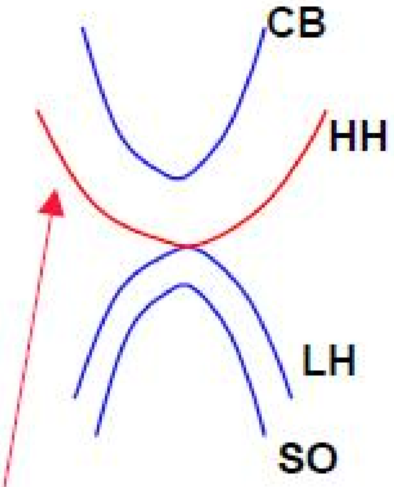
Since $E' = E_n(k) - \hbar^2k^2/2m_0$

$$n = c \qquad E_c(k) = E_g + \frac{\hbar^2k^2}{2m_0} + \frac{k^2P^2(E_g + 2\Delta/3)}{E_g(E_g + \Delta)}$$

$$n = \mathrm{hh} \qquad E_{\mathrm{hh}}(k) = \frac{\hbar^2k^2}{2m_0}$$

$$n = l\mathrm{h} \qquad E_{l\mathrm{h}}(k) = \frac{\hbar^2k^2}{2m_0} - \frac{2k^2P^2}{3E_g}$$

$$n = \mathrm{so} \qquad E_{\mathrm{so}}(k) = -\Delta + \frac{\hbar^2k^2}{2m_0} - \frac{k^2P^2}{3(E_g + \Delta)}$$



HH band concave up with free-*e* mass ☹
To be fixed by the LK Hamiltonian

Ref: Chuang

The Journey of the Eigenfunctions

For the unperturbed H, eigenfn's at the band edge we anticipated them to be of *s* and *p* type orbital symmetry: $|S,\uparrow\rangle, |S,\downarrow\rangle, |X,\uparrow\rangle, |X,\downarrow\rangle, |Y,\uparrow\rangle, |Y,\downarrow\rangle, |Z,\uparrow\rangle, |Z,\downarrow\rangle$

$$|u_1\rangle = |iS\downarrow\rangle$$

$$|u_2\rangle = \left|\frac{X-iY}{\sqrt{2}}\uparrow\right\rangle = |Y_{1\,-1}\uparrow\rangle$$

$$|u_3\rangle = |Z\downarrow\rangle = |Y_{1\,0}\downarrow\rangle$$

$$|u_4\rangle = \left|-\frac{X+iY}{\sqrt{2}}\uparrow\right\rangle = |Y_{1\,1}\uparrow\rangle$$

$$|u_5\rangle = |iS\uparrow\rangle$$

$$|u_6\rangle = \left|-\frac{X+iY}{\sqrt{2}}\downarrow\right\rangle = |Y_{1\,1}\downarrow\rangle$$

$$|u_7\rangle = |Z\uparrow\rangle = |Y_{1\,0}\uparrow\rangle$$

$$|u_8\rangle = \left|\frac{X-iY}{\sqrt{2}}\downarrow\right\rangle = |Y_{1\,-1}\downarrow\rangle$$

Perturbation:
SO+k.P

Kane's band edge eigenfn's

$$u_{10}(\mathbf{r}) = \left|\frac{3}{2},\frac{3}{2}\right\rangle = \frac{-1}{\sqrt{2}}|(X+iY)\uparrow\rangle$$

$$u_{20}(\mathbf{r}) = \left|\frac{3}{2},\frac{1}{2}\right\rangle = \frac{-1}{\sqrt{6}}|(X+iY)\downarrow\rangle + \sqrt{\frac{2}{3}}|Z\uparrow\rangle$$

$$u_{30}(\mathbf{r}) = \left|\frac{3}{2},\frac{-1}{2}\right\rangle = \frac{1}{\sqrt{6}}|(X-iY)\uparrow\rangle + \sqrt{\frac{2}{3}}|Z\downarrow\rangle$$

$$u_{40}(\mathbf{r}) = \left|\frac{3}{2},\frac{-3}{2}\right\rangle = \frac{1}{\sqrt{2}}|(X-iY)\downarrow\rangle$$

$$u_{50}(\mathbf{r}) = \left|\frac{1}{2},\frac{1}{2}\right\rangle = \frac{1}{\sqrt{3}}|(X+iY)\downarrow\rangle + \frac{1}{\sqrt{3}}|Z\uparrow\rangle$$

$$u_{60}(\mathbf{r}) = \left|\frac{1}{2},\frac{-1}{2}\right\rangle = \frac{1}{\sqrt{3}}|(X-iY)\uparrow\rangle - \frac{1}{\sqrt{3}}|Z\downarrow\rangle$$

Refreshment on Addition of Angular Momenta

Spin-orbit coupling: Nonzero angular momentum state *e*'s (i.e., other than *s*-type wf's) generate a magnetic field through which they interact with the spin of the *e*. Particulary important for the VB (*p*-like states).

Because of this coupling neither spin nor orbital angular momentum but the total angular momentum becomes a good quantum number.

Consider two angular momentum operators which commute with each other (J_1, J_2), we wish to determine the eigenstates of the total angular momentum operator $J = J_1 + J_2$

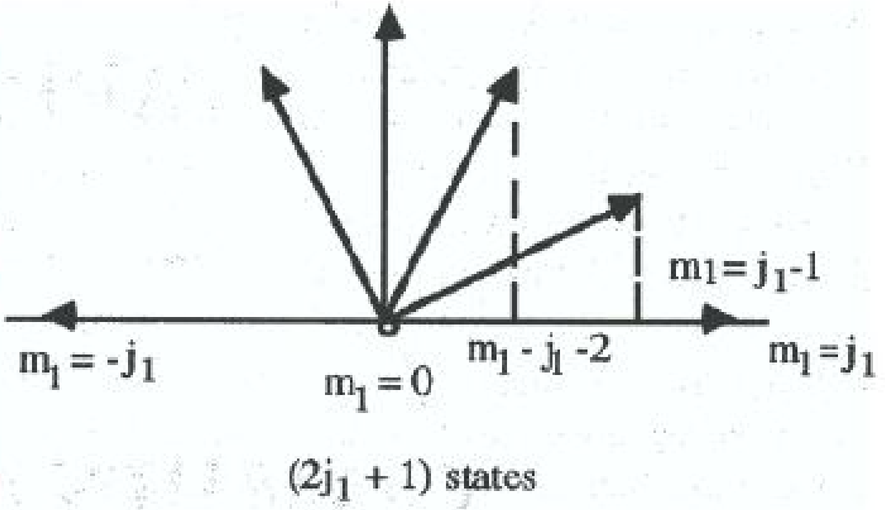
$$\overbrace{\left| j,m \right\rangle} = \sum a_{m_1 m_2} \left| \overbrace{j_1, m_1}^{\text{orbital}} ; \overbrace{j_2, m_2}^{\text{spin}} \right\rangle$$

Clebsch-Gordan coefficients

There are $(2J_1+1)$ and $(2J_2+1)$ states corresponding to J_1 and J_2

Refreshment on total Angular Momentum (cont'd)

A schematic representation of the angular momentum states



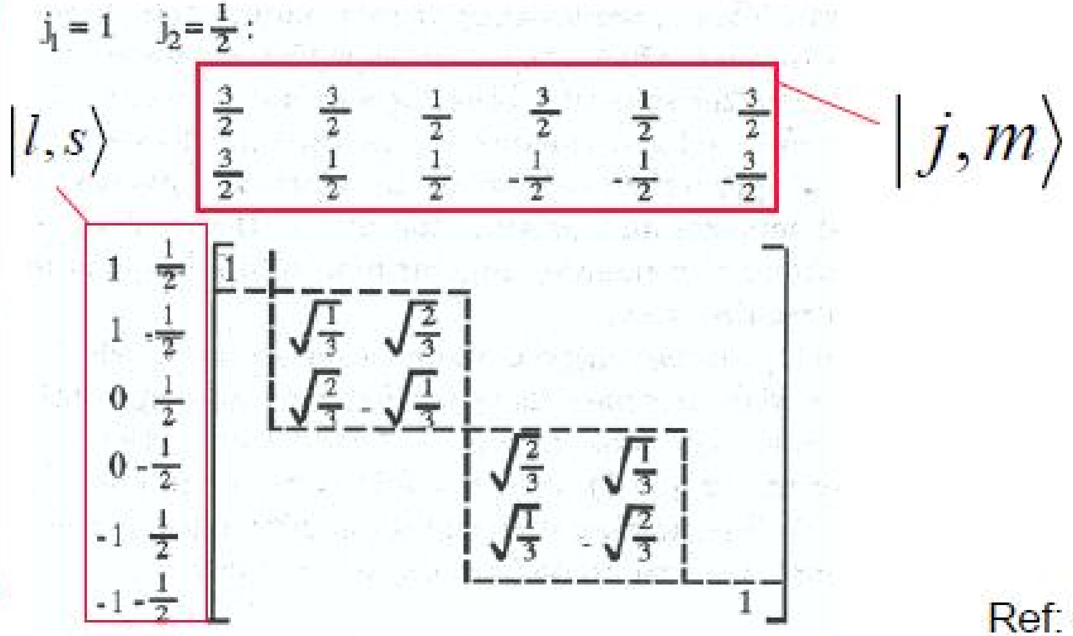
J=L+S

$j=l+s=3/2$, $m_j=3/2,\ldots,-3/2$

$j=l-s=1/2$ $m_j=1/2,-1/2$

Clebsch-Gordan coefficients for $J_1=1$ and $J_2=1/2$

Be ware, different phase choices exist as in LK



$j_1 = 1 \quad j_2 = \frac{1}{2}$:

$$
\begin{array}{c|cccccc}
|l,s\rangle \backslash |j,m\rangle & \frac{3}{2}\ \frac{3}{2} & \frac{3}{2}\ \frac{1}{2} & \frac{1}{2}\ \frac{1}{2} & \frac{3}{2}\ -\frac{1}{2} & \frac{1}{2}\ -\frac{1}{2} & \frac{3}{2}\ -\frac{3}{2} \\
\hline
1\ \frac{1}{2} & 1 & & & & & \\
1\ -\frac{1}{2} & & \sqrt{\frac{1}{3}} & \sqrt{\frac{2}{3}} & & & \\
0\ \frac{1}{2} & & \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{3}} & & & \\
0\ -\frac{1}{2} & & & & \sqrt{\frac{2}{3}} & \sqrt{\frac{1}{3}} & \\
-1\ \frac{1}{2} & & & & \sqrt{\frac{1}{3}} & -\sqrt{\frac{2}{3}} & \\
-1\ -\frac{1}{2} & & & & & & 1
\end{array}
$$

Ref: Singh

Extraction of Kane's parameter from experimental data

$$E_c(k) - E_g = \frac{\hbar^2 k^2}{2m_0} + \frac{k^2 P^2\left(E_g + \frac{2}{3}\Delta\right)}{E_g(E_g + \Delta)} = \frac{\hbar^2 k^2}{2m_e^*}$$

$$P^2 = \left(1 - \frac{m_e^*}{m_0}\right)\frac{\hbar^2 E_g(E_g + \Delta)}{2m_e^*(E_g + 2\Delta/3)}$$

So, by feeding three parameters from experiment, Kane's parameter can be extracted. This parameter, *P* plays a key role in any optical property regarding the over-the-band gap excitations

Ref: Chuang

General *k* direction

Up to now, we have assumed: $\mathbf{k} = k\hat{z}$

For a general case: $\mathbf{k} = k \sin\theta \cos\varphi \hat{x} + k \sin\theta \sin\varphi \hat{y} + k \cos\theta \hat{z}$

The following transformations can be used to find the basis functions in the general coordinate system:

$$\begin{bmatrix} \uparrow' \\ \downarrow' \end{bmatrix} = \begin{bmatrix} e^{-i\phi/2}\cos\frac{\theta}{2} & e^{i\phi/2}\sin\frac{\theta}{2} \\ -e^{-i\phi/2}\sin\frac{\theta}{2} & e^{i\phi/2}\cos\frac{\theta}{2} \end{bmatrix} \begin{bmatrix} \uparrow \\ \downarrow \end{bmatrix}$$

$$\begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix} = \begin{bmatrix} \cos\theta\cos\phi & \cos\theta\sin\phi & -\sin\theta \\ -\sin\phi & \cos\phi & 0 \\ \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$$

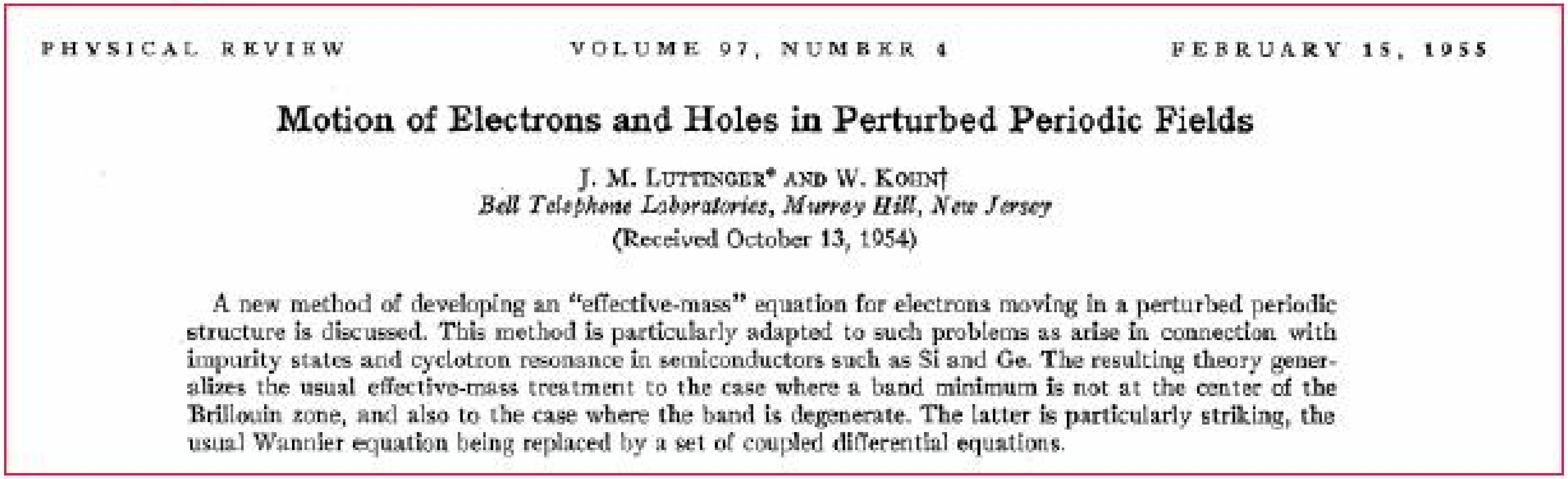
Ref: Chuang

k·p and Similar Band Edge Techniques

Brief Highlights

- Single- and two-band **k·p**
  - Coupling to other bands accounted perturbatively
  - Predicts an analytical effective mass tensor (heavier/lighter than m_0)
- Kane's Hamiltonian
  - 8 bands (CB+3 VB with spin) treated exactly
  - Coupling with the other bands neglected
  - HH band comes out with wrong sign and value (due above approximation)
  - No warping predicted (i.e., isotropic) for finite **k**
- Luttinger-Kohn Hamiltonian (for degenerate bands with spin-orbit)
  - 6 VBs treated exactly; can be extended to include CBs as well
  - Other bands are included via Löwdin's technique
  - Warping of the VBs is predicted
- Pikus-Bir Hamiltonian
  - Just like LK Hamiltonian, but includes the effects of strain in the xtal

Luttinger-Kohn Hamiltonian



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Motion of Electrons and Holes in Perturbed Periodic Fields

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A new method of developing an "effective-mass" equation for electrons moving in a perturbed periodic structure is discussed. This method is particularly adapted to such problems as arise in connection with impurity states and cyclotron resonance in semiconductors such as Si and Ge. The resulting theory generalizes the usual effective-mass treatment to the case where a band minimum is not at the center of the Brillouin zone, and also to the case where the band is degenerate. The latter is particularly striking, the usual Wannier equation being replaced by a set of coupled differential equations.

Begin with the total Hamiltonian for the cell-periodic fn's dropping their band indices for convenience:

$$Hu_{\mathbf{k}}(\mathbf{r}) = E(\mathbf{k})u_{\mathbf{k}}(\mathbf{r})$$

$$H = H_0 + \frac{\hbar^2 k^2}{2m_0} + \frac{\hbar}{4m_0^2c^2}\nabla V \times \mathbf{p}\cdot\boldsymbol{\sigma} + H'$$

Neglect compared to

$$H_0 = \frac{p^2}{2m} + V(\mathbf{r}) \qquad \Pi = \mathbf{p} + \overbrace{\frac{\hbar}{4m_0c^2}\boldsymbol{\sigma}\times\nabla V}$$

$$H' = \frac{\hbar}{m_0}\mathbf{k}\cdot\Pi$$

Ref: Chuang

Expand any cell-periodic wfn in terms of the **k**=0 basis:

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{j'}^{A} a_{j'}(\mathbf{k}) u_{j'0}(\mathbf{r}) + \sum_{\gamma}^{B} a_{\gamma}(\mathbf{k}) u_{\gamma 0}(\mathbf{r})$$

where, from Kane's model we learned that **k**=0 solutions are of the form:

$$u_{10}(\mathbf{r}) = \left|\frac{3}{2}, \frac{3}{2}\right\rangle = \frac{-1}{\sqrt{2}} \left|(X + \mathrm{i}Y)\uparrow\right\rangle$$

$$u_{20}(\mathbf{r}) = \left|\frac{3}{2}, \frac{1}{2}\right\rangle = \frac{-1}{\sqrt{6}} \left|(X + \mathrm{i}Y)\downarrow\right\rangle + \sqrt{\frac{2}{3}} \left|Z\uparrow\right\rangle$$

$$u_{30}(\mathbf{r}) = \left|\frac{3}{2}, \frac{-1}{2}\right\rangle = \frac{1}{\sqrt{6}} \left|(X - \mathrm{i}Y)\uparrow\right\rangle + \sqrt{\frac{2}{3}} \left|Z\downarrow\right\rangle$$

$$u_{40}(\mathbf{r}) = \left|\frac{3}{2}, \frac{-3}{2}\right\rangle = \frac{1}{\sqrt{2}} \left|(X - \mathrm{i}Y)\downarrow\right\rangle$$

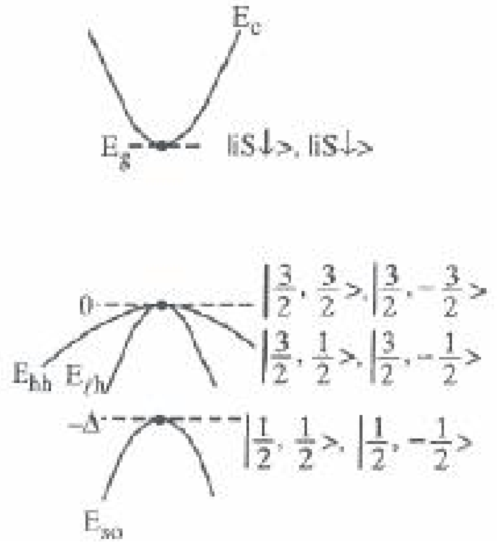
$$u_{50}(\mathbf{r}) = \left|\frac{1}{2}, \frac{1}{2}\right\rangle = \frac{1}{\sqrt{3}} \left|(X + \mathrm{i}Y)\downarrow\right\rangle + \frac{1}{\sqrt{3}} \left|Z\uparrow\right\rangle$$

$$u_{60}(\mathbf{r}) = \left|\frac{1}{2}, \frac{-1}{2}\right\rangle = \frac{1}{\sqrt{3}} \left|(X - \mathrm{i}Y)\uparrow\right\rangle - \frac{1}{\sqrt{3}} \left|Z\downarrow\right\rangle$$

Ref: Chuang

Also recall that at **k**=0, band edge fn's satisy:

$$H(\mathbf{k}=0)u_{j0}(\mathbf{r}) = E_j(0)u_{j0}(\mathbf{r})$$



$$E_j(0) = E_p + \frac{\Delta}{3} = 0 \qquad \text{for } j = 1,2,3,4$$

$$E_j(0) = E_p - \frac{2\Delta}{3} = -\Delta \qquad \text{for } j = 5,6$$

where $E_p = -\Delta/3$

Now, apply Löwdin's method:

$$\sum_{j'}^{A}\left(U_{jj'}^{A} - E\delta_{jj'}\right)a_{j'}(\mathbf{k}) = 0$$

Effect of remote bands are here

Ref: Chuang

where

$$U_{jj'}^{A} = H_{jj'} + \sum_{\gamma\neq j,j'}^{B} \frac{H_{j\gamma}H_{\gamma j'}}{E_0 - E_\gamma} = H_{jj'} + \sum_{\gamma\neq j,j'}^{B} \frac{H'_{j\gamma}H'_{\gamma j'}}{E_0 - E_\gamma}$$

$$H_{jj'} = \langle u_{j0}|H|u_{j'0}\rangle = \left[E_j(0) + \frac{\hbar^2k^2}{2m_0}\right]\delta_{jj'} \qquad (j, j' \in A)$$

$$H'_{j\gamma} = \langle u_{j0}|\frac{\hbar}{m_0}\mathbf{k}\cdot \overset{\mathbf{p}}{\cancel{\Pi}}|u_{\gamma 0}\rangle \cong \sum_{\alpha} \frac{\hbar k_\alpha}{m_0} p_{j\gamma}^{\alpha} \qquad (j \in A, \gamma \notin A)$$

where we note that $\Pi_{jj'} = 0$, for $j, j' \in A$, and $\Pi_{j\gamma}^{\alpha} \simeq p_{j\gamma}^{\alpha}$ for $j \in A$ and $\gamma \notin A$. Since $\gamma \neq j$, adding the unperturbed part to the perturbed part in $H'_{j\gamma}$ does not affect the results, i.e., $H_{j\gamma} = H'_{j\gamma}$. We thus obtain

$$U_{jj'}^{A} = \left[E_j(0) + \frac{\hbar^2k^2}{2m_0}\right]\delta_{jj'} + \frac{\hbar^2}{m_0^2}\sum_{\gamma\neq j,j'}^{B}\sum_{\alpha,\beta}\frac{k_\alpha k_\beta p_{j\gamma}^{\alpha}p_{\gamma j'}^{\beta}}{E_0 - E_\gamma}$$

Change of notation; let $U_{jj'}^{A} \equiv D_{jj'}$

Ref: Chuang

$$D_{jj'} = E_j(0)\,\delta_{jj'} + \sum_{\alpha,\beta} D_{jj'}^{\alpha\beta} k_\alpha k_\beta$$

where $$D_{jj'}^{\alpha\beta} = \frac{\hbar^2}{2m_0}\underbrace{\left[\delta_{jj'}\delta_{\alpha\beta} + \sum_{\gamma}^{B} \frac{p_{j\gamma}^{\alpha} p_{\gamma j'}^{\beta} + p_{j\gamma}^{\beta} p_{\gamma j'}^{\alpha}}{m_0(E_0 - E_\gamma)}\right]}_{}$$

For *j=j'*, similar to single-band effective mass tensor

To write the matrix elements explicity, define:

$$A_0 = \frac{\hbar^2}{2m_0} + \frac{\hbar^2}{m_0^2}\sum_{\gamma}^{B}\frac{p_{x\gamma}^{x} p_{\gamma x}^{x}}{E_0 - E_\gamma}$$

$$B_0 = \frac{\hbar^2}{2m_0} + \frac{\hbar^2}{m_0^2}\sum_{\gamma}^{B}\frac{p_{x\gamma}^{y} p_{\gamma x}^{y}}{E_0 - E_\gamma}$$

$$C_0 = \frac{\hbar^2}{m_0^2}\sum_{\gamma}^{B}\frac{p_{x\gamma}^{x} p_{\gamma y}^{y} + p_{x\gamma}^{y} p_{\gamma y}^{x}}{E_0 - E_\gamma}$$

$$\Longrightarrow$$

Luttinger parameters

$$-\frac{\hbar^2}{2m_0}\gamma_1 = \frac{1}{3}(A_0 + 2B_0)$$

$$-\frac{\hbar^2}{2m_0}\gamma_2 = \frac{1}{6}(A_0 - B_0)$$

$$-\frac{\hbar^2}{2m_0}\gamma_3 = \frac{C_0}{6}$$

Ref: Chuang

In terms of Luttinger parameters, the LK Hamiltonian becomes:

$$\bar{\bar{\mathbf{H}}}^{\mathrm{LK}} = -\begin{array}{ll}\left[\begin{matrix} P+Q & -S & R & 0 & -S/\sqrt{2} & \sqrt{2}R \\ -S^{+} & P-Q & 0 & R & -\sqrt{2}Q & \sqrt{3/2}\,S \\ R^{+} & 0 & P-Q & S & \sqrt{3/2}\,S^{+} & \sqrt{2}Q \\ 0 & R^{+} & S^{+} & P+Q & -\sqrt{2}R^{+} & -S^{+}/\sqrt{2} \\ -S^{+}/\sqrt{2} & -\sqrt{2}Q^{+} & \sqrt{3/2}\,S & -\sqrt{2}R & P+\Delta & 0 \\ \sqrt{2}R^{+} & \sqrt{3/2}\,S^{+} & \sqrt{2}Q^{+} & -S/\sqrt{2} & 0 & P+\Delta \end{matrix}\right] & \begin{matrix} \mathrm{HH} \\ \mathrm{LH} \\ \mathrm{LH} \\ \mathrm{HH} \\ \mathrm{SO} \\ \mathrm{SO} \end{matrix}\end{array}$$

complex conjugate

where

$$P = \frac{\hbar^2\gamma_1}{2m_0}(k_x^2 + k_y^2 + k_z^2)$$

$$Q = \frac{\hbar^2\gamma_2}{2m_0}(k_x^2 + k_y^2 - 2k_z^2)$$

$$R = \frac{\hbar^2}{2m_0}\left[-\sqrt{3}\gamma_2(k_x^2 - k_y^2) + i2\sqrt{3}\gamma_3 k_x k_y\right]$$

$$S = \frac{\hbar^2\gamma_3}{m_0}\sqrt{3}\,(k_x - ik_y)k_z$$

Ref: Chuang

So, essentially we have solved the Hamiltonian

$$\left[\frac{p^2}{2m_0} + V(\mathbf{r}) + \frac{\hbar}{4m_0^2c^2}\nabla V \times \mathbf{p}\cdot\boldsymbol{\sigma}\right]\psi_{n\mathbf{k}}(\mathbf{r}) = E_n(\mathbf{k})\,\psi_{n\mathbf{k}}(\mathbf{r})$$

where

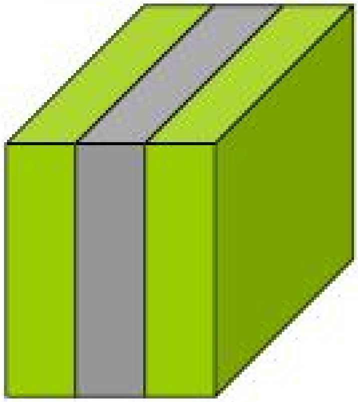
$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r}) \qquad u_{n\mathbf{k}}(\mathbf{r}) = \sum_{j=1}^{6} a_j(\mathbf{k})\,u_{j0}(\mathbf{r})$$

For the expansion eigenvectors and eigenvalues:

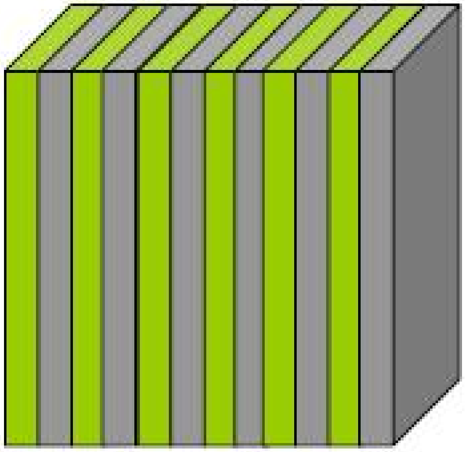
$$\sum_{j'=1}^{6} H_{jj'}^{\mathrm{LK}} a_{j'}(\mathbf{k}) = E a_j(\mathbf{k}) \qquad E_n(\mathbf{k}) = E$$

Low-Dimensional Structures

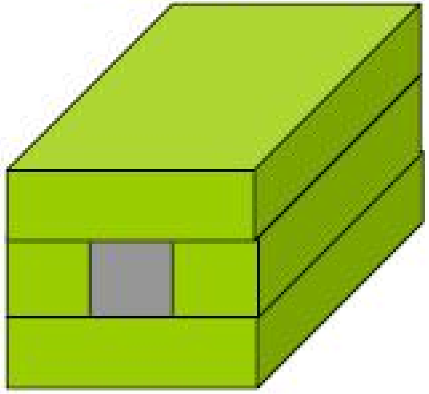
Quantum Well



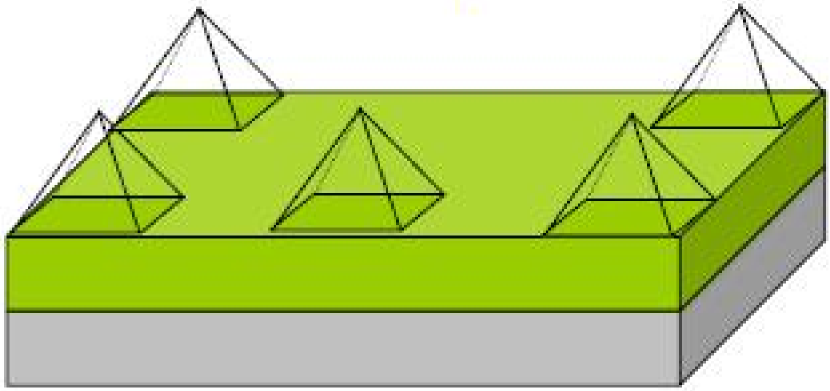
Superlattice



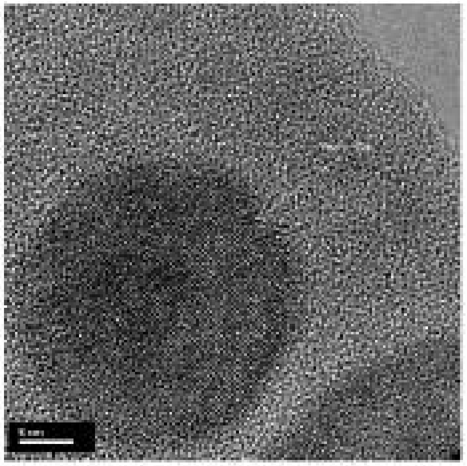
Quantum Wire



Self-assembled quantum dots



Nanocrystals

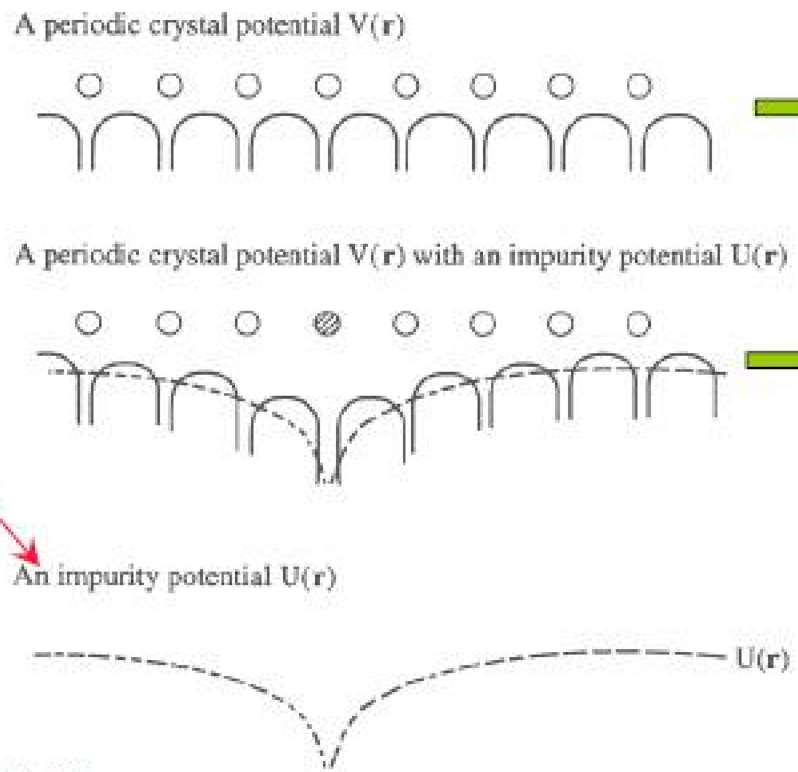


Envelope Function Approximation (EFA)

(also called Effective Mass Theory)

What's it for ?

- ✓ Treating an additional external (slowly-varying) potential
  e.g., an impurity, quantum confinement (QW), excitonic potential etc.



$$\underbrace{H_0\psi_{n\mathbf{k}}(\mathbf{r}) = E_n(\mathbf{k})\psi_{n\mathbf{k}}(\mathbf{r})}_{\text{use } \mathbf{k.p}\text{, LK etc.}}$$

$$\underbrace{[H_0 + U(\mathbf{r})]\psi(\mathbf{r}) = E\psi(\mathbf{r})}_{\text{use EFA}}$$

Ref: Chuang

EFA for a Single Band

Defining $H_0|n\,\mathbf{k}\rangle = E_n(\mathbf{k})|n\,\mathbf{k}\rangle$, therefore $|n\,\mathbf{k}\rangle$ form a complete set

So, one can expand the solution including the perturbation as

$$\psi(\vec{r}) = \langle \vec{r}\,|\sum_n \int_{BZ} \frac{d^3k}{(2\pi)^3} a_n(\vec{k})|n\vec{k}\rangle$$

Using the orthonormality property $\langle n\mathbf{k}|n'\mathbf{k}'\rangle = \delta_{n,n'}\overbrace{\delta(\mathbf{k}-\mathbf{k}')}^{\text{for infinite xtal}}$

The perturbed equation can easily be converted to:

$$(E_n(\mathbf{k}) - E)a_n(\mathbf{k}) + \sum_{n'} \int_{\mathrm{B.Z.}} \frac{\mathrm{d}^3\mathbf{k}'}{(2\pi)^3} \boxed{\langle n\mathbf{k}|U|n'\mathbf{k}'\rangle} a_{n'}(\mathbf{k}') = 0$$

$$\int \mathrm{d}^3\mathbf{r}\; \psi^*_{n\mathbf{k}}(\mathbf{r})U(\mathbf{r})\psi_{n'\mathbf{k}'}(\mathbf{r})$$

Ref: Chuang

$$\langle n\mathbf{k}|U|n'\mathbf{k}'\rangle = \int \mathrm{d}^3\mathbf{r}\, \mathrm{e}^{-\mathrm{i}(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} \boxed{u^*_{n\mathbf{k}}(\mathbf{r})u_{n'\mathbf{k}'}(\mathbf{r})} \boxed{U(\mathbf{r})}$$

Fourier xform

periodic in r

$$u^*_{n\mathbf{k}}(\mathbf{r})u_{n'\mathbf{k}'}(\mathbf{r}) = \underbrace{\sum_{\mathbf{G}}}_{\text{over all RLVs}} C(n\mathbf{k}, n'\mathbf{k}', \mathbf{G})\mathrm{e}^{\mathrm{i}\mathbf{G}\cdot\mathbf{r}}$$

$$\tilde{U}_{\mathbf{k}} = \int U(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}d^3\mathbf{r}$$

Inverse Fourier xform

$$U(\mathbf{r}) = \int \tilde{U}_{\mathbf{k}}\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}\frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3}$$

$$\langle n\mathbf{k}|U|n'\mathbf{k}'\rangle = \sum_{\mathbf{G}} C(n\mathbf{k}, n'\mathbf{k}', \mathbf{G})\tilde{U}_{\mathbf{k}-\mathbf{k}'-\mathbf{G}}$$

Approximations:

$\langle n\, \mathbf{k}\,|U|\,n'\, \mathbf{k}'\rangle \propto \delta_{nn'}$	*U(r)* small; causes <u>no</u> band mixing
$\left|\tilde{U}_{\mathbf{k}-\mathbf{k}'-\mathbf{G}}\right|_{\mathbf{G}\neq 0} \ll \left|\tilde{U}_{\mathbf{k}-\mathbf{k}'}\right|$	*U(r)* slowly varying

Ref: Chuang

The resultant equation for $a_n(\mathbf{k})$ becomes

$$(E_n(\mathbf{k}) - E)a_n(\mathbf{k}) + \int \frac{\mathrm{d}^3\mathbf{k}'}{(2\pi)^3} \underbrace{\bar{U}_{\mathbf{k}-\mathbf{k}'}a_n(\mathbf{k}')}_{\text{convolution of } U \,\&\, F} = 0$$

inverse Fourier xform

$$[E_n(-\mathrm{i}\nabla) + U(\mathbf{r})]F(\mathbf{r}) = EF(\mathbf{r})$$

if we define $F(\mathbf{r}) = \int a_n(\mathbf{k}')\mathrm{e}^{\mathrm{i}\mathbf{k}'\cdot\mathbf{r}} \frac{\mathrm{d}^3\mathbf{k}'}{(2\pi)^3}$ (envelope function)

$$\psi(\vec{r}) = \langle \vec{r} | \sum_n \int_{BZ} \frac{d^3k}{(2\pi)^3} a_n(\vec{k}) | n\vec{k} \rangle$$

The solution including *U* becomes

$$\left\{ \begin{aligned} \psi(\mathbf{r}) &= \int a_n(\mathbf{k}')\psi_{n\mathbf{k}'}(\mathbf{r}) \frac{\mathrm{d}^3\mathbf{k}'}{(2\pi)^3} \\ &\simeq \int a_n(\mathbf{k}')\mathrm{e}^{\mathrm{i}\mathbf{k}'\cdot\mathbf{r}} u_{n\mathbf{k}_0}(\mathbf{r}) \frac{\mathrm{d}^3\mathbf{k}'}{(2\pi)^3} \\ &= F(\mathbf{r})u_{n\mathbf{k}_0}(\mathbf{r}) \end{aligned} \right.$$

$u_{n\mathbf{k}}(\mathbf{r})$ final approx.

Ref: Chuang

So, EFA proceeds by replacing $\mathbf{k} \rightarrow -i\bar{\nabla}$ in the dispersion relation

Recall that in the single-band k.p theory:

$$E_n(\mathbf{k}) = E_n(0) + \sum_{\alpha,\beta} \frac{\hbar^2}{2}\left(\frac{1}{m^*}\right)_{\alpha\beta} k_\alpha k_\beta$$

Hence, the envelope function is obtained by solving

$$\left[\sum_{\alpha,\beta} \frac{\hbar^2}{2}\left(\frac{1}{m^*}\right)_{\alpha\beta}\left(-i\frac{\partial}{\partial x_\alpha}\right)\left(-i\frac{\partial}{\partial x_\beta}\right) + U(\mathbf{r})\right]F(\mathbf{r}) = [E - E_n(0)]F(\mathbf{r})$$

So within EFA, the Hamiltonian including *U(r)* is satisfied by

$$\psi(\mathbf{r}) = F(\mathbf{r})u_{n\mathbf{k}_0}(\mathbf{r})$$

Ref: Chuang

EFA for Degenerate Bands

The procedure to obtain EFA is just like the previous case.
The main discrepancy is the free-xtal Hamiltonian:

$$H\psi_{n\mathbf{k}}(\mathbf{r}) = E(\mathbf{k})\psi_{n\mathbf{k}}(\mathbf{r})$$

$$H = \frac{p^2}{2m_0} + V(\mathbf{r}) + H_{\mathrm{so}}$$

$$H_{\mathrm{so}} = \frac{\hbar}{4m_0^2c^2}\nabla V \times \mathbf{p}\cdot\boldsymbol{\sigma}$$

$$\sum_{j'=1}^{6} H_{jj'}^{\mathrm{LK}} a_{j'}(\mathbf{k}) \equiv \sum_{j'=1}^{6}\left[E_j(0)\delta_{jj'} + \sum_{\alpha,\beta} D_{jj'}^{\alpha\beta}k_\alpha k_\beta\right]a_{j'}(\mathbf{k}) = E(\mathbf{k})a_j(\mathbf{k})$$

Ref: Chuang

Our aim is to solve in the presence of perturbation *U(r)*

$$[H + U(\mathbf{r})]\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

The envelope function now picks a band index:

$$\psi(\mathbf{r}) = \sum_{j=1}^{6} F_j(\mathbf{r})u_{jo}(\mathbf{r})$$

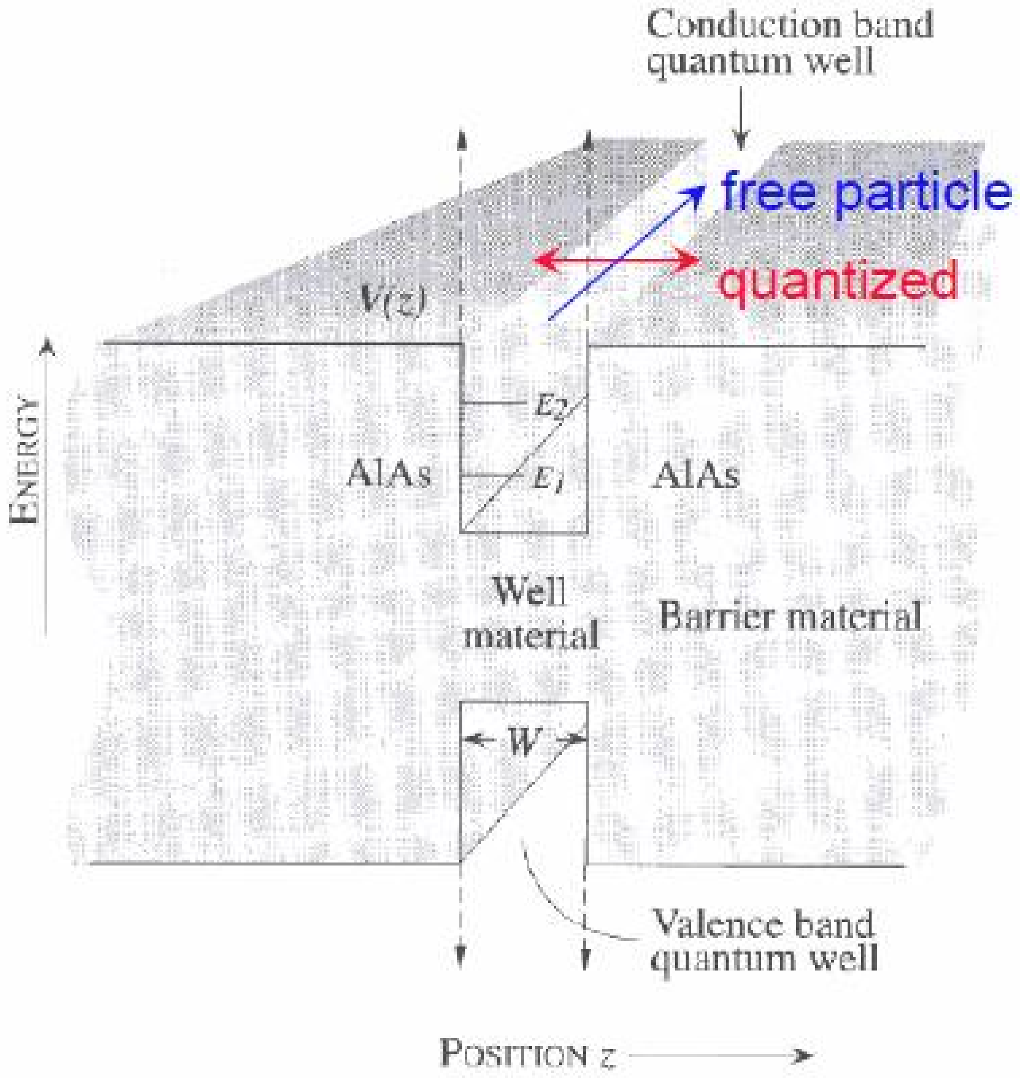
where, again we replace $\mathbf{k} \rightarrow -i\bar{\nabla}$ in the (LK) dispersion relation

$$\sum_{j'=1}^{6}\left[E_j(0)\delta_{jj'} + \sum_{\alpha,\beta} D_{jj'}^{\alpha\beta}\left(-i\frac{\partial}{\partial x_\alpha}\right)\left(-i\frac{\partial}{\partial x_\beta}\right) + U(\mathbf{r})\delta_{jj'}\right]F_{j'}(\mathbf{r}) = EF_j(\mathbf{r})$$

Note that if $U(r) \equiv 0$, the solutions for the envelope functions reduce to $F_j(\mathbf{r}) = a_j(\mathbf{k})\, e^{i\mathbf{k}\cdot\mathbf{r}}$ i.e., back to plane waves

Ref: Chuang

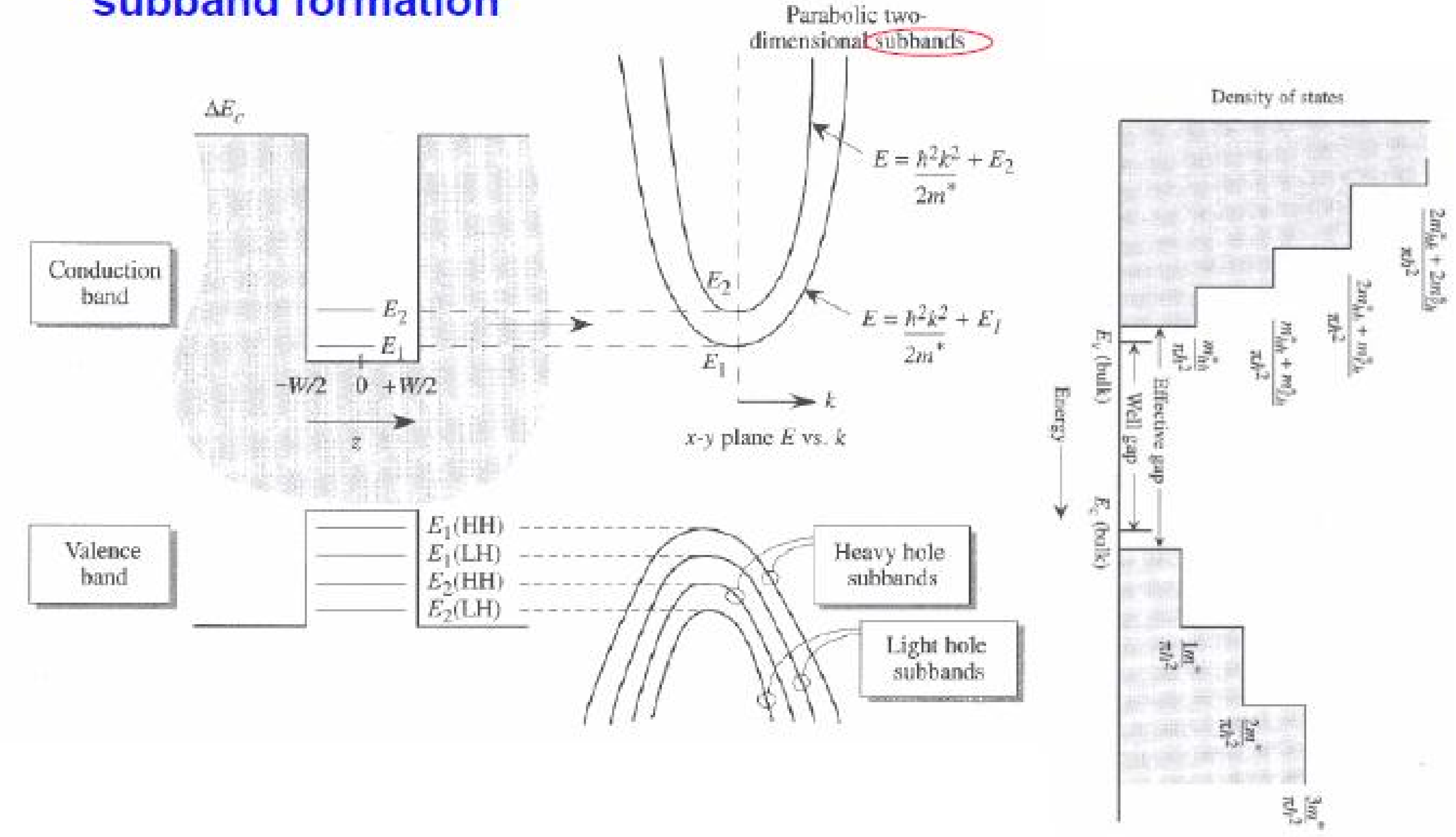
Consider a QW formed by two Type-I heterostructures (AlAs/GaAs/AlAs)



Ref: Singh

QW: a sketch of what to expect

subband formation



Ref: Singh

Application of EFA to QWs

Conduction Band: (single band EFA)

$$E(k) = \frac{\hbar^2 k^2}{2m^*}$$ dispersion relation

use corresponding well/barrier effective mass

The job for EFA is to incorporate the confinement potential

$$V(z) = \begin{cases} V_0(=\Delta E_c) & |z| > \dfrac{L_w}{2} \\ 0 & |z| \le \dfrac{L_w}{2} \end{cases}$$

energy ref set to well region CB edge

Ref: Chuang

Single band EFA reads

$$\left[-\frac{\hbar^2}{2}\underbrace{\frac{\partial}{\partial z}\frac{1}{m(z)}\frac{\partial}{\partial z}}+\frac{\hbar^2}{2m(z)}\nabla_t^2+V(z)\right]\psi(\mathbf{r})=E\psi(\mathbf{r})$$

This ordering is to ensure
the Hermiticity and the
continuity of J_z across the
heterojunction
(controversial, more later...)

$$j_z(z)\sim\frac{1}{m(z)}\left[\psi^*\frac{\partial}{\partial z}\psi-\psi\frac{\partial\psi^*}{\partial z}\right]$$

Since there is no confinement on the *xy* plane: $\psi(\mathbf{r})=\frac{e^{i\mathbf{k}_t\cdot\mathbf{r}}}{\sqrt{A}}\psi(z)$

$$\frac{-\hbar^2}{2}\frac{\partial}{\partial z}\frac{1}{m(z)}\frac{\partial}{\partial z}\psi(z)+V(z)\psi(z)=\left(E(k_t)-\frac{\hbar^2k_t^2}{2m(z)}\right)\psi(z)$$

To solve, use finite difference, finite element or transfer matrix method …

Ref: Chuang

Valence Band: (SO band will be neglected)

Confinement potential: $$V_h(z) = \begin{cases} 0 & |z| \le \dfrac{L_w}{2} \\ -\Delta E_v & |z| > \dfrac{L_w}{2} \end{cases}$$

1st destination is band-edge energies:

Note that at $k_x = k_y = 0$ LK Hamiltonian is <u>diagonal</u>,

i.e., HH LH do not mix!

Define:

$$E_{\mathrm{HH}}(k_z) = -\frac{\hbar^2}{2m_0}(\gamma_1 - 2\gamma_2)k_z^2 \qquad m_{\mathrm{hh}}^z \equiv \frac{m_0}{\gamma_1 - 2\gamma_2}$$

$$E_{\mathrm{LH}}(k_z) = -\frac{\hbar^2}{2m_0}(\gamma_1 + 2\gamma_2)k_z^2 \qquad m_{lh}^z \equiv \frac{m_0}{\gamma_1 + 2\gamma_2}$$

use well / barrier values

Ref: Chuang

So for the valence band-edge energies solve:

$$\left[+ \frac{\hbar^2}{2} \frac{\partial}{\partial z} \frac{1}{\boxed{m^z_{(m)}}} \frac{\partial}{\partial z} + V_h(z) \right] g_{(m)}(z) = E g_{(m)}(z)$$

m_{hh} or m_{lh}

solution yields valence band-edge energies

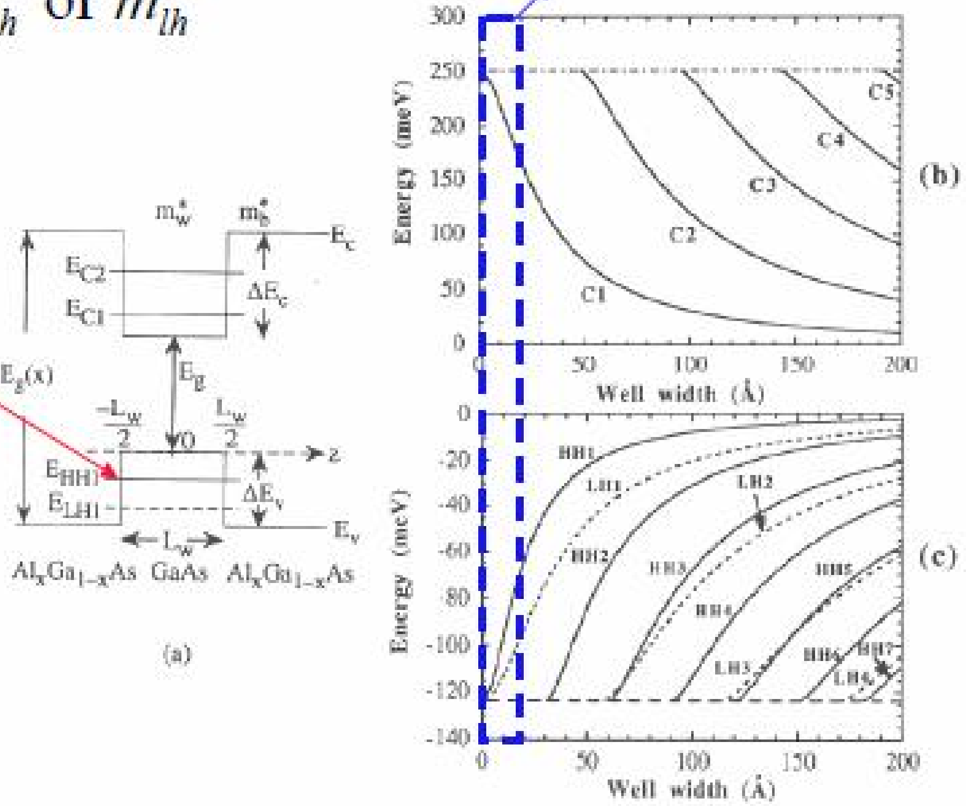


Figure 4.18. (a) Quantum-well profiles for the conduction and valence bands of a GaAs/$Al_xGa_{1-x}As$ system. (b) Conduction subband energies, $E_{C1}, E_{C2}, \ldots,$ and (c) valence subband energies $E_{HH1}, E_{HH2}, \ldots,$ and $E_{LH1}, E_{LH2} \ldots$ vs. the well width L_w.

EFA becomes dubious

variation of band-edge energies with well width

Ref: Chuang

Now comes valence subband dispersion relations

$$\left[\overline{\overline{\mathbf{H}}}^{\mathrm{LK}}\left(k_x, k_y, k_z = -\mathrm{i}\frac{\partial}{\partial z}\right) + V_h(z)\overline{\overline{\mathbf{I}}}\right] \cdot \begin{bmatrix} F_1 \\ F_2 \\ F_3 \\ F_4 \end{bmatrix} = E \begin{bmatrix} F_1 \\ F_2 \\ F_3 \\ F_4 \end{bmatrix}$$

SO bands are neglected

$$\overline{\overline{\mathbf{H}}}^{\mathrm{LK}}_{8\mathrm{x}8} = -\begin{bmatrix} P+Q & -S & R & 0 & -S/\sqrt{2} & \sqrt{2}R \\ -S^{+} & P-Q & 0 & R & -\sqrt{2}Q & \sqrt{3/2}S \\ R^{+} & 0 & P-Q & S & \sqrt{3/2}S^{+} & \sqrt{2}Q \\ 0 & R^{+} & S^{+} & P+Q & -\sqrt{2}R^{+} & -S^{+}/\sqrt{2} \\ -S^{+}/\sqrt{2} & -\sqrt{2}Q^{+} & \sqrt{3/2}S & -\sqrt{2}R & P+\Delta & 0 \\ \sqrt{2}R^{+} & \sqrt{3/2}S^{+} & \sqrt{2}Q^{+} & -S/\sqrt{2} & 0 & P+\Delta \end{bmatrix}$$

Envelope functions in vector form: $\mathbf{F}_{\mathbf{k}}(\mathbf{r}) = \begin{bmatrix} F_1 \\ F_2 \\ F_3 \\ F_4 \end{bmatrix} = \begin{bmatrix} g_{3/2}(k_x, k_y, z) \\ g_{1/2}(k_x, k_y, z) \\ g_{-1/2}(k_x, k_y, z) \\ g_{-3/2}(k_x, k_y, z) \end{bmatrix} \frac{\mathrm{e}^{\mathrm{i}k_x x + \mathrm{i}k_y y}}{\sqrt{A}}$

Ref: Chuang

QW wavefunctions

$$\left\{\begin{aligned}\psi_{\mathbf{k}}(\mathbf{r}) &= F_1\left|\tfrac{3}{2},\tfrac{3}{2}\right\rangle + F_2\left|\tfrac{3}{2},\tfrac{1}{2}\right\rangle + F_3\left|\tfrac{3}{2},-\tfrac{1}{2}\right\rangle + F_4\left|\tfrac{3}{2},-\tfrac{3}{2}\right\rangle \\ &= \frac{e^{ik_x x+ik_y y}}{\sqrt{A}}\sum_{\nu} g_{\nu}(k_x,k_y,z)\left|\tfrac{3}{2},\nu\right\rangle\end{aligned}\right.$$

where $\nu = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}$, and $-\frac{3}{2}$. Denote

$$\mathbf{k}_t = \hat{x}k_x + \hat{y}k_y$$

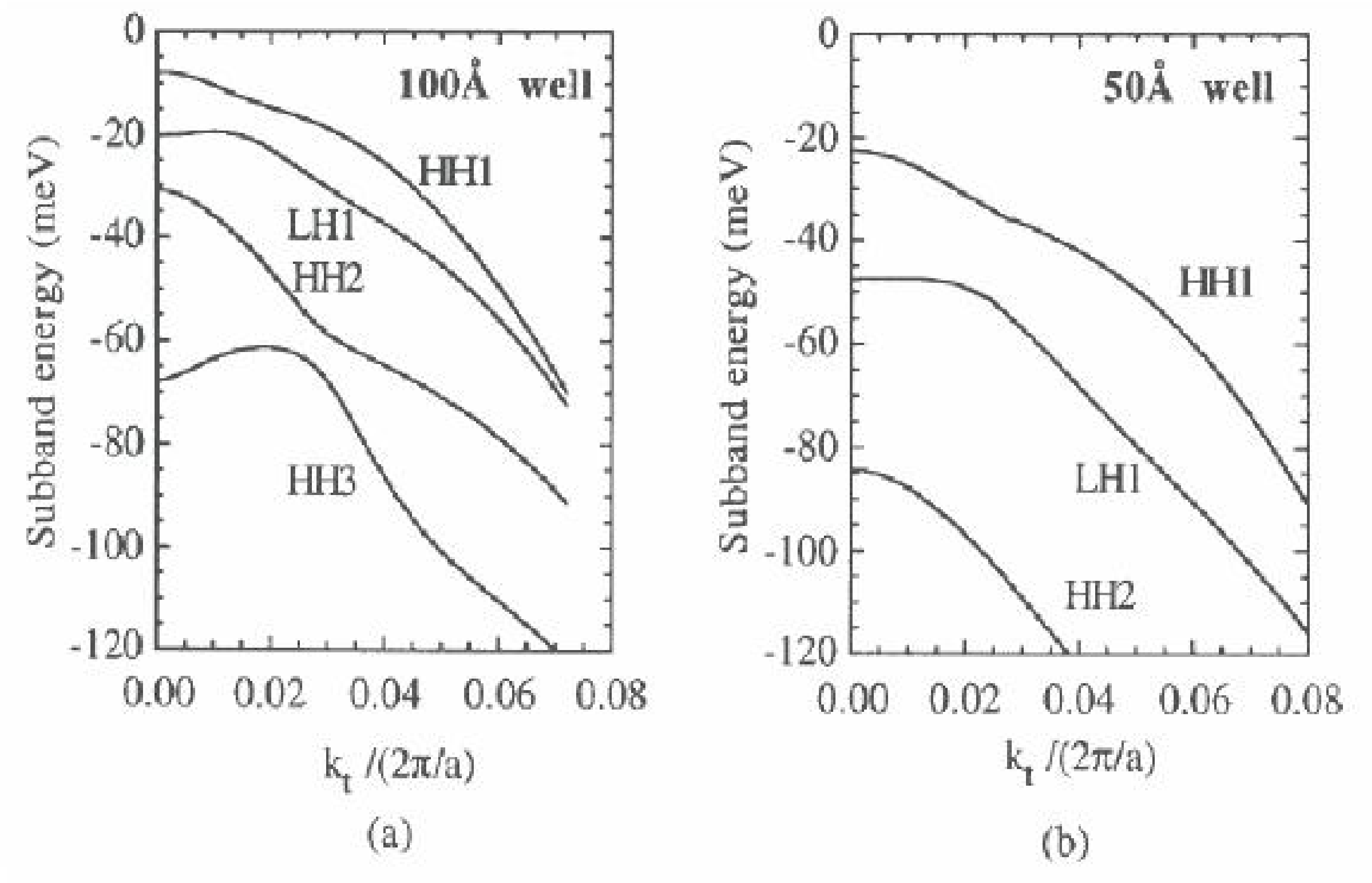
We write

$$\left[\overline{\overline{\mathbf{H}}}^{\mathrm{LK}}\left(\mathbf{k}_t, k_z = -i\frac{\partial}{\partial z}\right) + V_h(z)\overline{\overline{\mathbf{I}}}\right]\cdot\begin{bmatrix} g_{3/2}(\mathbf{k}_t, z) \\ g_{1/2}(\mathbf{k}_t, z) \\ g_{-1/2}(\mathbf{k}_t, z) \\ g_{-3/2}(\mathbf{k}_t, z)\end{bmatrix}$$

$$= E(\mathbf{k}_t)\begin{bmatrix} g_{3/2}(\mathbf{k}_t, z) \\ g_{1/2}(\mathbf{k}_t, z) \\ g_{-1/2}(\mathbf{k}_t, z) \\ g_{-3/2}(\mathbf{k}_t, z)\end{bmatrix}$$

Ref: Chuang

Typical VB Dispersion with LK+EFA



Ref: Chuang