In This Lecture:

- Time-independent perturbation theory
- Löwdin's Renormalization Technique
- Introduction to k.p
  - Virtues
  - Single-band
  - Two-band

Time-independent perturbation theory

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

a small perturbation

unperturbed Hamiltonian with known solutions

$$H^{(0)}\phi_n^{(0)} = E_n^{(0)}\phi_n^{(0)}$$

We seek a perturbative solution for $H\psi = E\psi$

Introduce a parameter λ to identify the contribution of each order (eventually $\lambda=1$)

$$H = H^{(0)} + \lambda H'$$

Ref: Chuang

Express the solutions in the form

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \cdots$$
$$\psi = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \cdots$$

Equating the powers of λ in the eigenequation yields

Zeroth order	$H^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$
First order	$H^{(0)}\psi^{(1)} + H'\psi^{(0)} = E^{(0)}\psi^{(1)} + E^{(1)}\psi^{(0)}$
Second order	$H^{(0)}\psi^{(2)} + H'\psi^{(1)} = E^{(0)}\psi^{(2)} + E^{(1)}\psi^{(1)} + E^{(2)}\psi^{(0)}$

$$\psi_n^{(0)} = \phi_n^{(0)}$$
$$E_n^{(0)} = E_n^{(0)}$$

} zeroth order solutions

For 1st order solutions:

$$\psi_n^{(1)} = \sum_m a_{mn}^{(1)} \phi_m^{(0)}$$

form a complete basis

Ref: Chuang

Results: Time-independent perturbation theory

1st order

$$\psi_n = \phi_n^{(0)} + \sum_{m \neq n} \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} \phi_m^{(0)}$$

Normalized to 1st order

$$E_n = E_n^{(0)} + H'_{nn}$$

where $H'_{mn} = \int \phi_m^{(0)*} H' \phi_n^{(0)} \, \mathrm{d}^3\mathbf{r}$

2nd order

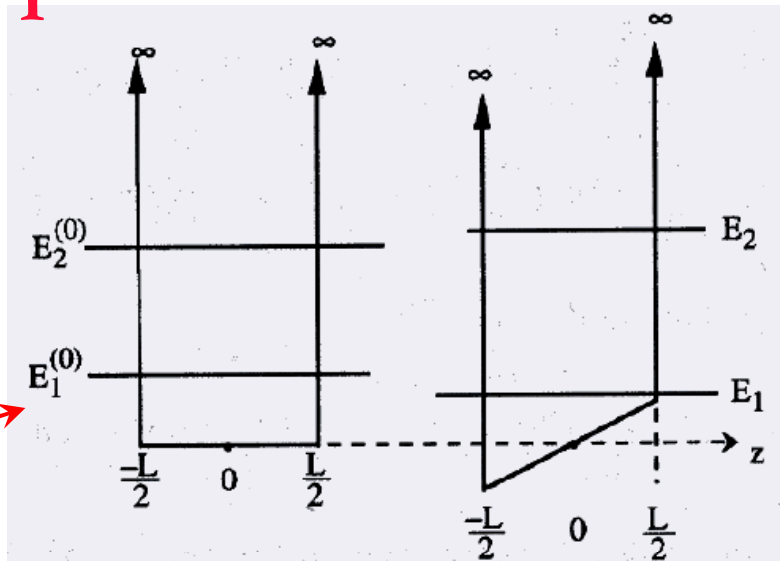
$$\psi_n = \phi_n^{(0)} + \sum_{m \neq n} \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} \phi_m^{(0)} + \sum_{m \neq n} \left\{ \left[\sum_{k \neq n} \frac{H'_{mk} H'_{kn}}{\left(E_n^{(0)} - E_m^{(0)}\right)\left(E_n^{(0)} - E_k^{(0)}\right)} - \frac{H'_{mn} H'_{nn}}{\left(E_n^{(0)} - E_m^{(0)}\right)^2} \right] \phi_m^{(0)} - \frac{|H'_{mn}|^2}{2\left(E_n^{(0)} - E_m^{(0)}\right)^2} \phi_n^{(0)} \right\}$$

Normalized to 2nd order

$$E_n = E_n^{(0)} + H'_{nn} + \sum_{m \neq n} \frac{|H'_{nm}|^2}{E_n^{(0)} - E_m^{(0)}}$$

Ref: Chuang

Application: Electric field in a QW



$$H = H_0 + eFz$$

treat as a perturbation

Zeroth-order solutions

$$H_0 u_n^{(0)}(z) = \frac{-\hbar^2}{2m^*}\frac{d^2}{dz^2}u_n^{(0)}(z) = E_n^{(0)}u_n^{(0)}(z)$$

$$u_n^{(0)}(z) = \sqrt{\frac{2}{L}}\sin\left[\frac{n\pi}{L}\left(z + \frac{L}{2}\right)\right] \qquad E_n^{(0)} = n^2\frac{\hbar^2\pi^2}{2m^*L^2}$$

First-order perturbation

of definite symm.

Go to 2nd order for energies

$$H'_{nn} = \langle u_n^{(0)}|eFz|u_n^{(0)}\rangle = eF\int_{-L/2}^{L/2} u_n^{(0)}(z)\,z u_n^{(0)}(z)\,dz = 0$$

Ref: Chuang

So, we need $H'_{nm} = \langle u_n^{(0)} | eFz | u_m^{(0)} \rangle$ for $n \neq m$

$$H'_{nm} = \frac{eFL}{\pi^2}\left[\frac{(-1)^{n-m}-1}{(n-m)^2} - \frac{(-1)^{n+m}-1}{(n+m)^2}\right]$$

$$= \frac{eFL}{\pi^2}\left[(-1)^{n-m}-1\right]\frac{4nm}{(n^2-m^2)^2} \qquad (n \neq m)$$

only requires some trigonometric integrations

The 2nd order perturbative result:

$$E = E_n^{(0)} + H'_{nn} + \sum_{m \neq n} \frac{|H'_{nm}|^2}{E_n^{(0)} - E_m^{(0)}}$$

$$= E_n^{(0)} + C_n \frac{\pi^2}{2} \frac{(eFL)^2}{E_1^{(0)}}$$

where

$$C_n = \frac{32n^2}{\pi^6} \sum_{m \neq n} \frac{\left[(-1)^{n-m}-1\right]^2 m^2}{(n^2-m^2)^5}$$

Not a fn. of n or m !

Defining $E_1^{(0)} \equiv \dfrac{E_n^{(0)} - E_m^{(0)}}{n^2 - m^2}$

Energy depends quadratically on the field:
QCSE
QW Excitons: decrease of osc. strength & binding energy

Löwdin's Renormalization Method

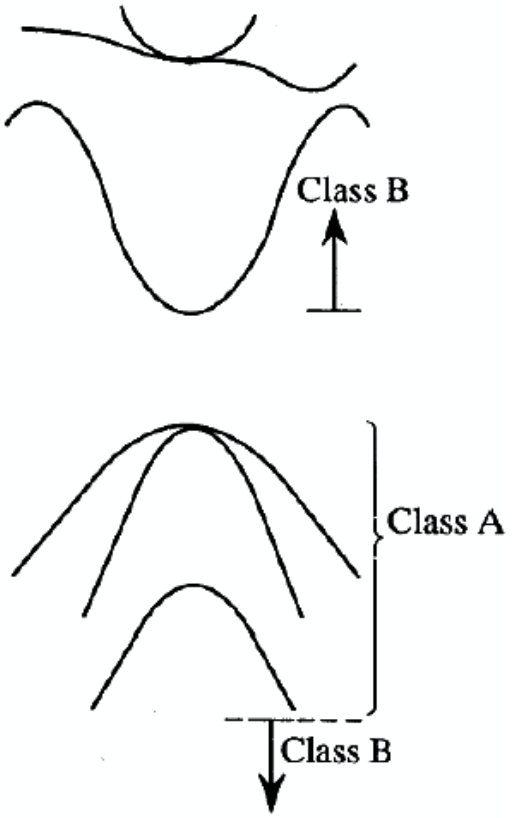
$$\sum_{n=1}^{N} (H_{mn} - E\delta_{mn}) a_n = 0$$

Matrix representation of *H* using an orthonormal basis

Divide eigenfn's and energies into two classes: A, B

$$(E - H_{mm}) a_m = \sum_{n \neq m}^{A} H_{mn} a_n + \sum_{\alpha \neq m}^{B} H_{m\alpha} a_\alpha$$

$$a_m = \sum_{n \neq m}^{A} \frac{H_{mn}}{E - H_{mm}} a_n + \sum_{\alpha \neq m}^{B} \frac{H_{m\alpha}}{E - H_{mm}} a_\alpha$$



Ref: Chuang

$$a_m = \sum_{n\neq m}^{A} \frac{H_{mn}}{E - H_{mm}} a_n + \sum_{\alpha}^{B} \frac{H_{m\alpha}}{E - H_{mm}} a_\alpha, \quad \text{for} \quad m \in A$$

$$a_\alpha = \sum_{n}^{A} \frac{H_{\alpha n}}{E - H_{\alpha\alpha}} a_n + \sum_{\beta\neq\alpha}^{B} \frac{H_{\alpha\beta}}{E - H_{\alpha\alpha}} a_\beta, \quad \text{for} \quad \alpha \in B$$

to the 1st order, neglect contribution from class B

We iterate away contributions of a_β

$$a_m = \sum_{n}^{A} \frac{U^A_{mn} - H_{mn}\delta_{mn}}{E - H_{mm}} a_n$$

effect of bands in class B in series form

$$U^A_{mn} = H_{mn} + \sum_{\alpha\neq m}^{B} \frac{H_{m\alpha}H_{\alpha n}}{E - H_{\alpha\alpha}} + \sum_{\substack{\alpha,\beta\neq m,n \\ \alpha\neq\beta}}^{B} \frac{H_{m\alpha}H_{\alpha\beta}H_{\beta n}}{(E - H_{\alpha\alpha})(E - H_{\beta\beta})} + \cdots$$

$$\sum_{n}^{A} (U^A_{mn} - E\delta_{mn}) a_n = 0 \qquad m \in A \qquad\qquad a_\gamma = \sum_{n}^{A} \frac{U^A_{\gamma n} - H_{\gamma n}\delta_{\gamma n}}{E - H_{\gamma\gamma}} a_n \qquad \gamma \in B$$

Ref: Chuang

Obviously for convergence we need:

$$|H_{m\alpha}| \ll |E - H_{\alpha\alpha}| \qquad m \in A,\ \alpha \in B$$

If class A contains a single state, then:

$$E = U^A_{nn}$$

$$= H_{nn} + \sum_{\alpha \neq n} \frac{H_{n\alpha}H_{\alpha n}}{E - H_{\alpha\alpha}} + \sum_{\substack{\alpha,\beta \neq n \\ \alpha \neq \beta}} \frac{H_{n\alpha}H_{\alpha\beta}H_{\beta n}}{(E - H_{\alpha\alpha})(E - H_{\beta\beta})} + \cdots$$

For the case of *H* having a small perturbation

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

Then, to 2nd order in *H'*

$$E = E_n^{(0)} + H'_{nn} + \sum_{\alpha \neq n} \frac{H'_{n\alpha}H'_{\alpha n}}{E_n^{(0)} - E_\alpha^{(0)}}$$

Ref: Chuang

Another common case is when the states in class A are (almost) degenerate

The diagonal elements are (almost) the same: $H_m \simeq E_A$

$$U^A_{mn} = H_{mn} + \sum_{\alpha}^{B} \frac{H'_{m\alpha} H'_{\alpha n}}{E_A - H_{\alpha\alpha}}$$

Total Hamiltonian

$$\det|U^A_{mn} - E\delta_{mn}| = 0$$

eigenvectors, a_n

$$\psi = \sum_n a_n \phi^{(0)}_n$$

We shall be refering to Löwdin's technique in the Luttinger-Kohn Hamiltonian…

Ref: Chuang

k·p Method

Brief History

- **k·p** for simple bands to extract effective masses and wf's near a high-symm. point **k** (Bardeen - 1938, Seitz - 1940)
- Kane's Hamiltonian (includes spin-orbit (SO) interaction – 1957)
- Luttinger-Kohn Hamiltonian (for degenerate bands & SO -1955)
- Pikus-Bir Hamiltonian (includes strain – 1960)
- Cardona-Pollak (over full BZ: 30x30 – 1966) -- pushing to limits
- 2000's: still in widespread use as in (strained) quantum dots etc.

Virtues of k·p

- The band structure over the entire BZ can be extrapolated from the zone center energy gaps and optical matrix elements
- Particularly convenient for interpreting optical spectra
- One can obtain analytic expressions for band dispersion and effective masses around high-symmetry points
- Most reliable in the vicinity of CB and VB edges which govern most optical and electronic phenomena
- Very small computational cost especially compared to ab-initio computations

General expressions

$$\left[\frac{p^2}{2m_0} + V(\mathbf{r})\right]\psi_{n\mathbf{k}}(\mathbf{r}) = E_n(\mathbf{k})\psi_{n\mathbf{k}}(\mathbf{r}) \longrightarrow \psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{n\vec{k}}(\vec{r})$$

Written as an eigenvalue equation for the cell-periodic fn's

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

Written as a perturbation to ***k***=0 solutions

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

where

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

$$H_0u_{n0}(\mathbf{r}) = E_n(0)u_{n0}(\mathbf{r})$$

These energy and functions are assumed to be known

Ref: Chuang

k·p extrapolation for a chosen band

(to 2nd order perturbation)

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

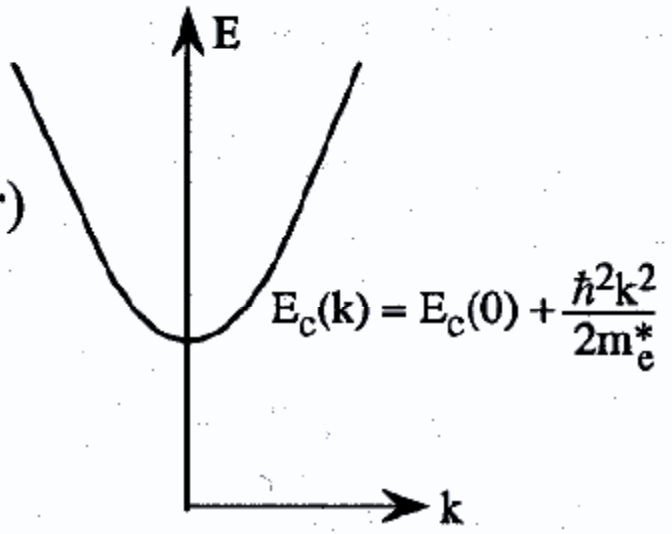
vanishes at band extrema

1st order is sufficient

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

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

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



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

momentum matrix element

Orthonormality:

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

band indices

Ref: Chuang

Single-band dispersion (to 2nd order perturbation)

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

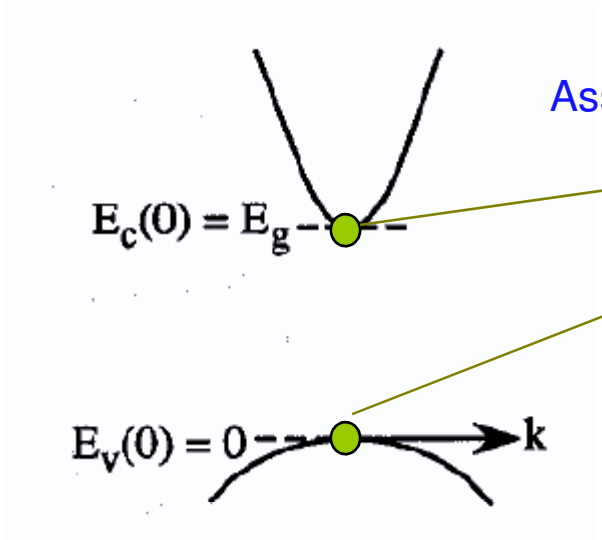
inverse eff. mass tensor

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

- The coordinate axes be rotated such that inverse eff. mass tensor becomes diagonal
- The deviation from the free-*e* mass originates from the interaction with the other bands
- Bands lying above make a –ve contribution, trying to make that band heavier
- Bands lying below make a +ve contribution, trying to make that band lighter

Ref: Chuang

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

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

For a basis of two states the solution becomes this determinant

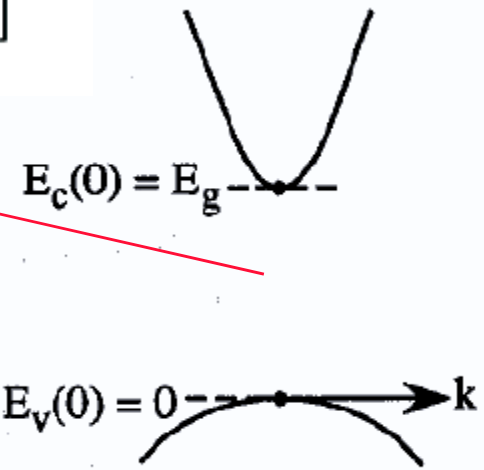
$$\begin{vmatrix} E_n(0) + \dfrac{\hbar^2 k^2}{2m_0} - E & \dfrac{\hbar}{m_0} \mathbf{k} \cdot \mathbf{p}_{nn'} \\ \dfrac{\hbar}{m_0} \mathbf{k} \cdot \mathbf{p}_{n'n} & E_{n'}(0) + \dfrac{\hbar^2 k^2}{2m_0} - E \end{vmatrix} = 0$$

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*



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

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

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

Ref: Chuang

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

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

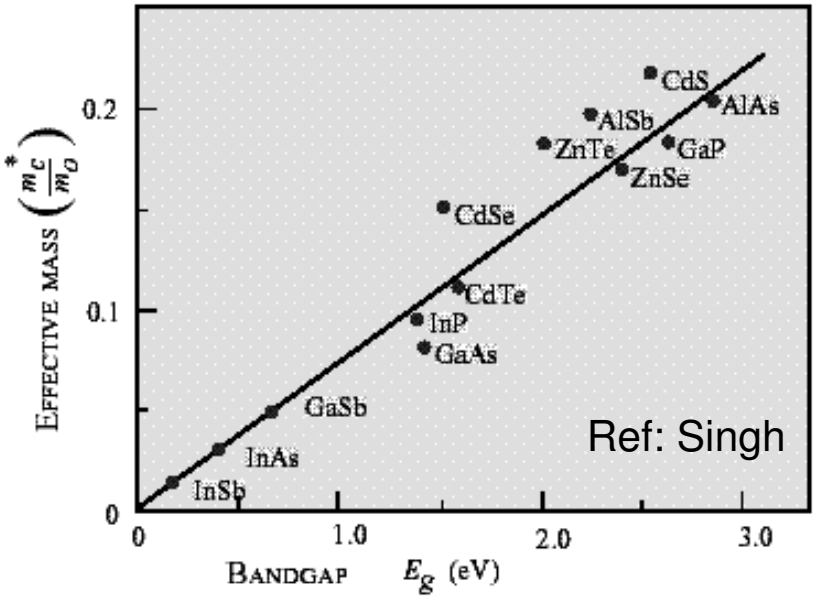
So, for small bandgap se/c, i.e., $E_g \ll \frac{2p_{cv}^2}{m_0}$ $\qquad |m_v^*|, m_c^* \propto E_g$

It is found that this proportionality is roughly obeyed in the comparison of m_c^* at $\vec{k}=0$ 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:

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



Check with experimental values:

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

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

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

Ref: Callaway