## Review on k•p

#### *How to interpret wave vector* **k**?

The wave function  $\Psi_k$  of a free electron is given by a plane wave:  $\Psi_k = \text{Cexp}(i\mathbf{k}\cdot\mathbf{r})$ 

where **k=p**/ħ is the wave vector

**p** is the momentum

**r** is the space vector

C is the normalizing constant

energy of a free electron is given by  $E = p^2/(2m_e) = (\hbar k)^2/(2m_e)$ boundary condition:

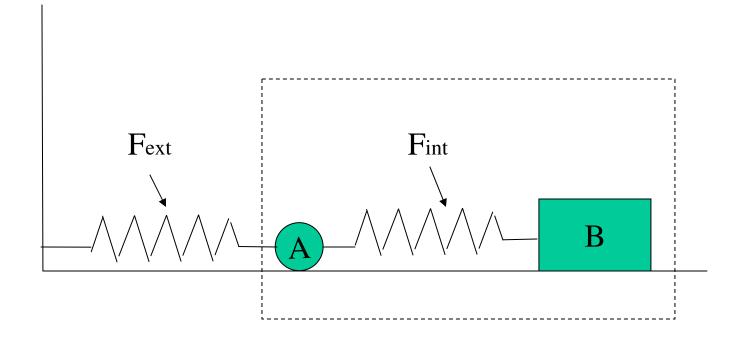
 $\Psi_k(x,y,z) = \Psi_k(x+L,y,z) = \Psi_k(x,y+L,z) = \Psi_k(x,y,z+L) => k_x = 2n_x \pi/L, k_y = 2n_y \pi/L, k_z = 2n_z \pi/L$ 

In crystal, the electronic wave function may be presented as a Bloch wave:  $\Psi_k = u_k(\mathbf{r})\exp(i\mathbf{k}\cdot\mathbf{r})$ 

Where the Bloch amplitude  $u_k(\mathbf{r})$  has the same spatial Periodicity as the crystal lattice:  $u_k(\mathbf{r}) = u_k(\mathbf{r}+\mathbf{R})$ 

 $u_k(\mathbf{r})$  can be expanded in a Fourier series:  $u_k(\mathbf{r}) = \sum C_{k'} \exp(i\mathbf{k'}\cdot\mathbf{r})$  $k' \neq k$ 

Boundary condition (one dimension atom chain)  $\Psi_k(x) = \Psi_k(x+L) \Longrightarrow k = 2n\pi/L$ 

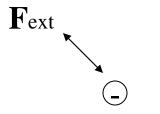


> Consider A only:  $d\mathbf{p}/dt = \mathbf{F}_{ext} + \mathbf{F}_{int}$ ,  $d^2p/dt^2 = m$ **p**, m are the momentum and mass of the ball A.

> Consider A, B as a system:  $d\mathbf{p}_{eff}/dt = \mathbf{F}_{ext}$ ,  $d^2 \mathbf{p}_{eff}/dt^2 = m_{eff}$  $\mathbf{p}_{eff}$  is no longer the momentum of A. It takes account into the interaction between A and B.

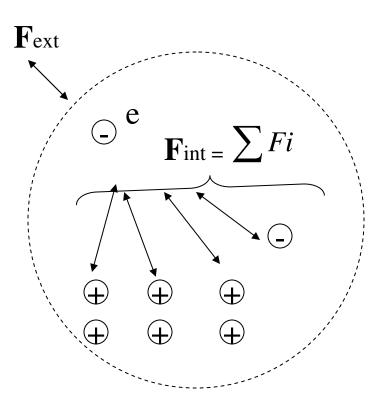
➤ Internal potential Vint "disappears" when consider A, B as a system.

#### Electron in free space



 $d\mathbf{p}/dt = \mathbf{F}_{ext}$ **p** is the electron momentum

#### electron in periodic crystal



 $d\mathbf{p}/dt = \mathbf{F}_{ext} + \mathbf{F}_{int},$ Or  $d\mathbf{p}$ eff/ $dt = \mathbf{F}_{ext}$  $\mathbf{p}$ eff =  $\hbar \mathbf{k}$  contains the effects of the internal crystal potential. Schrödinger equation for electron inside the crystal structure

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

Where  $V(r) = V_L(r) + V_s(r) + V_e(r)$ ,  $V_L(r) =$  periodic lattice potential  $V_s(r) =$  scattering potential (lattice vibrations, defects, impurities)  $V_e(r) =$  external potential (space charge,  $\varepsilon$  field)

What people usually do is use  $m^*$  to take account into the VL(r), the Schrödinger equation is written as:

$$\left[\frac{-\hbar^2}{2\mathrm{m}^*}\nabla^2 + V_s(r) + V_e(r)\right]\psi(r) = E\psi(r)$$

# > The concept of effective mass, energy band gap, and allowed bands can be manifested by looking at the nearly free electron picture.

- The electrons in the crystal see the perfectly periodic potential the electrons propagate without scattering.
- No external potential.
- The background periodic potential is weak, and we can treat the periodic potential as perturbation, we

If we write the Schrödinger equation

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

in k space, which means Substitute  $\psi_{\vec{k}}(\vec{r})$  with Bloch wave function

$$\psi_{\vec{k}}(\vec{r}) = \left(\sum_{\vec{G}\neq 0} C_{\vec{k}-\vec{G}} e^{i(\vec{k}-\vec{G})\bullet\vec{r}}\right) e^{i\vec{k}\bullet\vec{r}}$$

we'll get :

$$[H_{0} + H']C_{\vec{k} - \vec{G}_{1}} \approx (E_{\vec{k}}^{0} + \sum_{\substack{\vec{G} \neq \vec{G}_{1}, \\ \neg \downarrow}} \frac{\left|U_{\vec{G} - \vec{G}_{1}}\right|^{2}}{E_{\vec{k}}^{0} - E_{\vec{k}}^{0}})C_{\vec{k} - \vec{G}_{1}}$$

Free electron energy Effect of background potential

If we assume 
$$C_{\vec{k}-\vec{G}_1} = 1$$
 and  $C_{\vec{k}-\vec{G}} = 0$  for all  $\vec{G} \neq \vec{G}_1$   
 $\vec{G}, \vec{G}_1$  are reciprocal lattice vector in  $\vec{k}$  space.  
 $E_{\vec{K}-\vec{G}_1}^0 = \frac{\hbar^2 (k-G_1)^2}{2m_0}$ 

Schrödinger equation for the electron in weak periodic potential

$$HC_{\vec{k}-\vec{G}_{1}} \approx (E^{0}_{\vec{K}-\vec{G}_{1}} + \sum_{\vec{G}\neq\vec{G}_{1},} \frac{\left|U_{\vec{G}-\vec{G}_{1}}\right|^{2}}{E^{0}_{\vec{k}-\vec{G}_{1}} - E^{0}_{\vec{k}-\vec{G}}})C_{\vec{k}-\vec{G}_{1}} = \frac{\hbar^{2}(k-G_{1})^{2}}{2m_{eff}}C_{\vec{k}-\vec{G}_{1}}$$

Schrödinger equation for the electron in free space

$$H_0 C_{\vec{k}-\vec{G}_1}(\vec{r}) = E_{\vec{K}-\vec{G}_1}^0 C_{\vec{k}-\vec{G}_1}(\vec{r}) = \frac{\hbar^2 (k-G_1)^2}{2m_0} C_{\vec{k}-\vec{G}_1}(\vec{r})$$

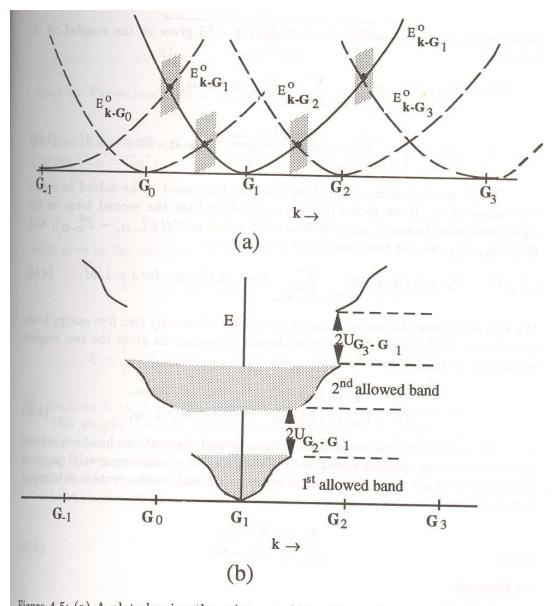


Figure 4.5: (a) A plot showing the points at which different free energy parabolas are degenerate. The points of degeneracy are the zone edges. (b) As discussed in Case 2 of the text, bandgaps are produced at the zone edges.

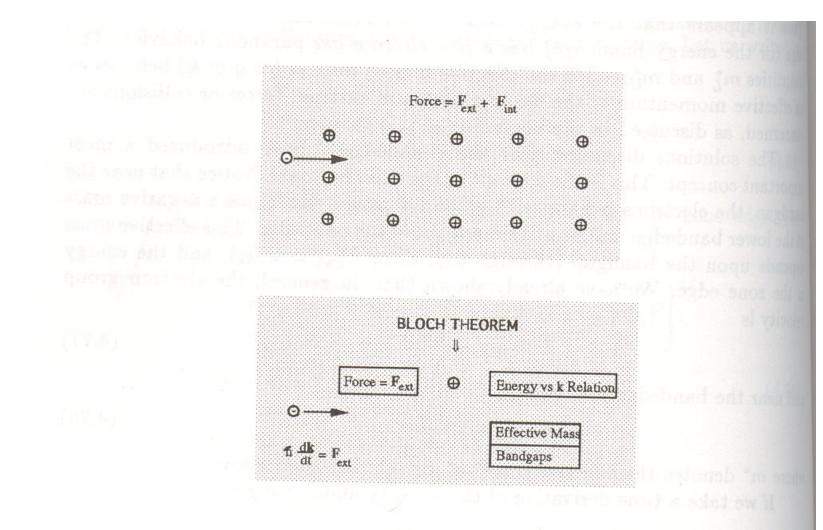


Figure 4.7: A schematic of how the complex problem of an electron in a crystalline material moving in internal and external forces is simplified by Bloch's theorem to a "free electron"-like problem with an effective energy-momentum relation.

### > Two main categories of realistic band structure calculation:

• Method which describe the entire valance and conduction band. (i.e., tight binding method)

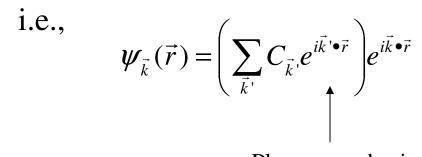
include finite number of basis functions.ignore the effects from all the other bandsexact solution of schrodinger equation (no perturbation).reliable approach for bands originating from well localized atomic orbitals.

• Methods which describe near band edge band structure. (i.e., k•p method)

include finite number of basis functions. take the effects from all the other bands as perturbation.

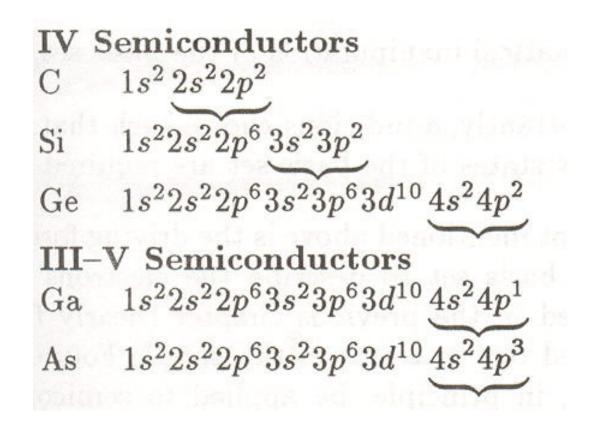
# > Regardless the method used, the eigenfunctions of the Electrons must be Bloch functions.

> The Bloch function can be expanded in terms of any complete set of basis states.



Plane wave basis

➤ More often, we expand the Bloch function in term of atomic orbitals since it is more simple and physical, and often requires fewer basis functions.



> The outmost valance electrons are made up of electrons in either the s-type or p-type orbital for semiconductors. The top of the valance bandage states are primarily p-type. ➢ In quantum mechanics, the electron can have both orbital angular momentum and spin angular momentum.

The spin provides the electron with a means to interact with the magnetic field produced through its orbital motion.

 $\succ$  The spin-orbital coupling is quite small and one can adds its effect in a perturbative approach.

The total Hamiltonian: Htot = H + Hso

Hso =  $\lambda L \cdot S$ 

The total angular momentum can be expressed as:

 $J^2 = (L + S)^2$ 

 $\succ$  we choose the basis set to be the eigenfunction of L<sup>2</sup> and Lz, in this case, the Hamiltonian commutes with J<sup>2</sup> and Jz, the matrix of H can be broken into small blocks (i.e., 6\*6 matrix -> one 4\*4 & one 2\*2 matrices ).

### Summary of k•P theory (1)

- > Allows us to calculate the band structure  $En(\mathbf{k})$  near the band edge.
- > The theory can be applied to single or to multiply degenerate bands.
- > Two approaches:
  - (1) apply perturbation theory
  - (2) solve an equation for a determinant to get band energies
- The k•P theory predicts parabolic bands but modified by the k•P interaction.

> The k•P theory predicts an effective mass for the electron in the second order energy term.

### Summary of k•P theory (2)

General steps of developing k•p method

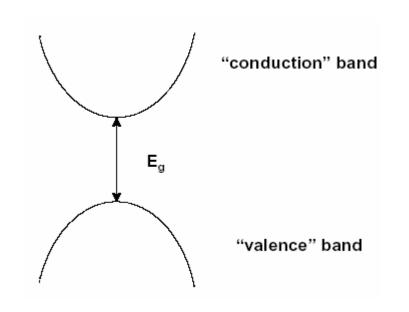
(1) substitute the Bloch wave function into the Schrodinger equation with the free electron mass and lattice potential.

 (2) for electron near the band edge (CB minimum or VB maximum), treat the k•p term in the Hamiltonian operator as a type of perturbation.

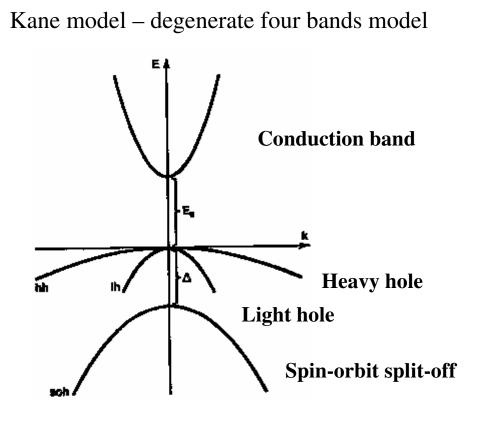
(3) provided that we know the band energy En (k=0) and the wave function
 un,k=0, expand the each un,k≠0 in terms of summation of un,k=0 for all the basis bands, and treat the remaining bands perturbatively if necessary.

(4) substitute the expansion of un,k into Schrodinger equation, multiply on the left by un',k=0 and take integral. Rewrite the equation in matrix form to solve for the eigenenergy of the bands.

## Luttinger-Kohn model

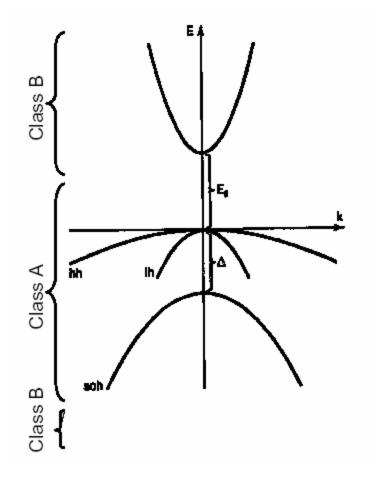


Non-degenerate two bands model



Two strongly interacting non-degenerate bands are considered. Can't be used to treat any particular real semiconductor. Only a conduction band, a heavy-hole band, a light-hole band and a spin-orbit split-off band with double degeneracy are considered, all other higher and lower bands are discarded. Doesn't provide the correct effective mass of heavy-hole band.

#### Luttinger – kohn model



The heavy-hole, light hole and spin-orbit split-off bands in double degeneracy are of interest, and called class A. All other bands are called class B. The effects of bands in class B on those in class A are treated as perturbation.

#### Choice of unit cell basis

➤ The electron wavefunctions are p-like near the top of the valance band. And the base set can be represented as  $|X \downarrow \rangle$ ,  $|X \uparrow \rangle$ ,  $|Y \downarrow \rangle$ ,  $|Y \uparrow \rangle$ , and  $|Z \downarrow \rangle$ ,  $|Z \uparrow \rangle$ .

> The basis functions are usually chosen to be the combinations of the above six functions so that they are the eigenfunctions of orbital angular momentum operators  $L^2$  and Lz.

$$u_{10} = u_{hh0} = \left| -\frac{X + iY}{\sqrt{2}} \right\rangle \equiv \left| \frac{3}{2}, \frac{3}{2} \right\rangle$$

$$u_{20} = u_{lh0} = -\frac{1}{\sqrt{6}} \left| (X + iY) \right\rangle + \sqrt{\frac{2}{3}} \left| Z \right\rangle = \left| \frac{3}{2}, \frac{1}{2} \right\rangle$$

$$u_{30} = u_{lh0} = \frac{1}{\sqrt{6}} \left| (X - iY) \right\rangle + \sqrt{\frac{2}{3}} \left| Z \right\rangle = \left| \frac{3}{2}, -\frac{1}{2} \right\rangle$$

$$u_{40} = u_{hh0} = \left| \frac{X - iY}{\sqrt{2}} \right\rangle \equiv \left| \frac{3}{2}, -\frac{3}{2} \right\rangle$$

$$u_{50} = u_{so0} = \frac{1}{\sqrt{3}} \left| (X + iY) \right\rangle - \frac{1}{\sqrt{3}} \left| Z \right\rangle = \left| \frac{1}{2}, \frac{1}{2} \right\rangle$$

$$u_{60} = u_{so0} = \frac{1}{\sqrt{3}} \left| (X - iY) \right\rangle - \frac{1}{\sqrt{3}} \left| Z \right\rangle = \left| \frac{1}{2}, -\frac{1}{2} \right\rangle$$

$$\begin{bmatrix} H_o + \frac{\hbar}{m_o} \mathbf{k} \cdot \mathbf{p} + \frac{\hbar}{4m_o^2 c^2} \nabla V_L \times \mathbf{p} \cdot \mathbf{\sigma} \end{bmatrix} \mu_{n\mathbf{k}}(\mathbf{r}) = \begin{bmatrix} E_n(\mathbf{k}) - \frac{\hbar^2 k^2}{2m_o} \end{bmatrix} \mu_{n\mathbf{k}}(\mathbf{r})$$
  
Spin-orbit interaction

 $\boldsymbol{\sigma}$  is the Pauli spin matrix, a matrix that has spatial vector components

$$\boldsymbol{\sigma}_{x} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \boldsymbol{\sigma}_{y} = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad \boldsymbol{\sigma}_{z} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

If the spin vector is represented as 
$$\uparrow \equiv \begin{bmatrix} 1 \\ 0 \end{bmatrix} \qquad \downarrow \equiv \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

Then,

#### Löwdin Renormalization

> The Lowdin Renormalization is a perturbative approach.

> In the Luttinger-Kohn implementation, the 3 valance bands are solved with the effects of the conduction band and the other bands added through corrections.

> These *corrections* are fitted with experimentally determined values.

#### Hamiltonian

$$\left[H_o + \frac{\hbar}{m_o}\mathbf{k}\cdot\mathbf{p} + \frac{\hbar}{4m_o^2c^2}\nabla V_L \times \mathbf{p}\cdot\mathbf{\sigma}\right]u_{n\mathbf{k}}(\mathbf{r}) = \left[E_n(\mathbf{k}) - \frac{\hbar^2k^2}{2m_o}\right]u_{n\mathbf{k}}(\mathbf{r})$$

**Or**  $Hu_{n\mathbf{k}}(\mathbf{r}) = E'_n u_{n\mathbf{k}}(\mathbf{r}), \quad (\text{ For small } \mathbf{k}, E'_n \cong E_n)$ 

Where

 $H = H_0 + H'$ 

$$H_0 = \frac{p^2}{2m^*} + V(r), \quad H' = \frac{\hbar}{m_o} \mathbf{k} \cdot \mathbf{p} + \frac{\hbar}{4m_o^2 c^2} \nabla V_L \times \mathbf{p} \cdot \boldsymbol{\sigma}$$

If substitute 
$$u_{n\mathbf{k}}(\mathbf{r}) = \sum_{n'} a_{n'} u_{n'0}(\mathbf{r})$$
 into  
 $H u_{n\mathbf{k}}(\mathbf{r}) = E_n u_{n\mathbf{k}}(\mathbf{r})$ 

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and take the inner product with *um0*, we obtain,

$$\sum_{n'} (H_{mn'} - E_{n'} \delta_{mn'}) a_{n'} = 0$$

Instead of solving the above exact eigenfunction, we only need to solve

where 
$$U_{mn}^{A} = H_{mn} (m, n \in A_{1})^{A} = 0$$
 Treated as type of perturbation  $\swarrow$   
( effects of B on A )

Class A consits of two heavy-hole, two light-hole and two spin split-off bands. Class B contains all the bands out of A. we can rewrite the Schrodinger equation as

$$\sum_{n'} (H_{mn'} - E_n \delta_{mn'}) a_{n'} = \sum_{n \neq m}^{A} H_{mn'} a_n + \sum_{\alpha \neq m}^{B} H_{m\alpha'} a_{\alpha}$$

$$+ (H_{mnm} - E_m) a_m = 0$$

$$a_m = \sum_{n \neq m}^{A} \frac{H_{mn} a_n}{E_m - H_{mm}} + \sum_{\alpha \neq m}^{B} \frac{H_{m\alpha'} a_{\alpha}}{E_m - H_{mm}}$$
Expand a from group B recursively into the summation of group A terms and group B terms
$$= \sum_{n}^{A} \frac{H_{mn} a_n}{E_m - H_{mm}} - \frac{H_{mn} \delta_{mn}}{E - H_{mm}} a_n$$

$$+ \sum_{\alpha \neq m}^{B} \frac{H_{m\alpha}}{E_m - H_{mm}} (\sum_{n \neq \alpha}^{A} \frac{H_{\alpha n} a_n}{E_\alpha - H_{\alpha \alpha}} + \sum_{\beta \neq \alpha}^{B} \frac{H_{\alpha \beta} a_{\beta}}{E_\alpha - H_{\alpha \alpha}})$$

$$= \sum_{n}^{A} \frac{a_n}{E_m - H_{mm}} (H_{mm} + \sum_{\alpha \neq m}^{B} \frac{H_{m\alpha} H_{\alpha n}}{E_\alpha - H_{\alpha \alpha}} - H_{mn} \delta_{mn})$$

$$= \sum_{n}^{A} \frac{a_n}{E_m - H_{mm}} (U_{mn}^A - H_{mn} \delta_{mn})$$

Express of  $U_{mn}^A$  with 1<sup>st</sup> order correction

$$U_{mn}^{A} \approx H_{mn} + \sum_{\alpha \neq m}^{B} \frac{H_{m\alpha}H_{\alpha n}}{E - H_{\alpha \alpha}}$$

(1) 
$$m, n \in A, \ H_{mn} = \langle u_{m0} | H | u_{n0} \rangle = \left[ E_m(0) + \frac{\hbar^2 k^2}{2m_0} \right] \langle u_{m0} | u_{n0} \rangle = \left[ E_m(0) + \frac{\hbar^2 k^2}{2m_0} \right] \delta_{mn}$$

(2) In the *B*-terms, we are considering m,n as a member of the *A*-terms and  $\alpha,\beta$  as a member of the *B*-terms, hence

 $m \in A, \mathbf{\alpha} \in B$ 

$$H_{m\boldsymbol{\alpha}} = \langle u_{m0} | H | u_{\boldsymbol{\alpha}0} \rangle = \langle u_{m0} | H' | u_{\boldsymbol{\alpha}0} \rangle = \langle u_{m0} | \frac{\hbar}{m_0} k \cdot \left( p + \frac{\hbar}{4m_0 c^2} \boldsymbol{\sigma} \times \nabla V \right) u_{\boldsymbol{\alpha}0} \rangle$$
$$\approx \langle u_{m0} | \frac{\hbar}{m_0} k \cdot p | u_{\boldsymbol{\alpha}0} \rangle = \sum_{\boldsymbol{\gamma}} \frac{\hbar k_{\boldsymbol{\gamma}}}{m_0} p_{m\boldsymbol{\alpha}}^{\boldsymbol{\gamma}}$$



$$\begin{split} U_{mn} &= \left[ E_{m}(0) + \frac{\hbar^{2}k^{2}}{2m_{0}} \right]_{mn} + \frac{\hbar^{2}}{m_{0}^{2}} \sum_{\boldsymbol{\alpha}\neq m,n}^{B} \sum_{\boldsymbol{\gamma},\boldsymbol{\mu}} \frac{k_{\boldsymbol{\gamma}}k_{\boldsymbol{\mu}}p_{m\boldsymbol{\alpha}}^{\boldsymbol{\gamma}}p_{\boldsymbol{\alpha}n}^{\boldsymbol{\mu}}}{E_{0} - E_{\boldsymbol{\alpha}}} \\ &= E_{m}(0)\boldsymbol{\delta}_{mn} + \sum_{\boldsymbol{\gamma},\boldsymbol{\mu}} D_{mn}^{\boldsymbol{\gamma}\boldsymbol{\mu}} k_{\boldsymbol{\gamma}} k_{\boldsymbol{\mu}} \\ D_{mn}^{\boldsymbol{\gamma}\boldsymbol{\mu}} &= \frac{\hbar^{2}}{m_{0}^{2}} \left[ \boldsymbol{\delta}_{mn} \boldsymbol{\delta}_{\boldsymbol{\gamma}\boldsymbol{\mu}} + \sum_{\boldsymbol{\alpha}}^{B} \frac{p_{m\boldsymbol{\alpha}}^{\boldsymbol{\gamma}}p_{\boldsymbol{\alpha}n}^{\boldsymbol{\mu}} + p_{m\boldsymbol{\alpha}}^{\boldsymbol{\mu}}p_{\boldsymbol{\alpha}n}^{\boldsymbol{\gamma}}}{m_{0}(E_{0} - E_{\boldsymbol{\alpha}})} \right] \\ A_{0} &= \frac{1}{2} D_{xx}^{xx} = \frac{\hbar^{2}}{m_{0}^{2}} \left[ \frac{1}{2} + \sum_{\boldsymbol{\alpha}}^{B} \frac{p_{x\boldsymbol{\alpha}}^{x}p_{\boldsymbol{\alpha}x}^{x}}{m_{0}(E_{0} - E_{\boldsymbol{\alpha}})} \right] \\ B_{0} &= \frac{1}{2} D_{xx}^{yy} = \frac{\hbar^{2}}{m_{0}^{2}} \left[ \frac{1}{2} + \sum_{\boldsymbol{\alpha}}^{B} \frac{p_{x\boldsymbol{\alpha}}^{x}p_{\boldsymbol{\alpha}x}^{x}}{m_{0}(E_{0} - E_{\boldsymbol{\alpha}})} \right] \\ C_{0} &= \frac{1}{2} D_{xy}^{yy} = \frac{\hbar^{2}}{m_{0}^{2}} \left[ 0 + \sum_{\boldsymbol{\alpha}}^{B} \frac{p_{x\boldsymbol{\alpha}}^{x}p_{\boldsymbol{\alpha}y}^{y} + p_{x\boldsymbol{\alpha}}^{y}p_{\boldsymbol{\alpha}y}}{m_{0}(E_{0} - E_{\boldsymbol{\alpha}})} \right] \end{split}$$

**Luttinger Parameters** 

$$-\frac{\hbar^2}{2m_0}\mathbf{y}_1 = \frac{1}{3} [A_0 + 2B_0]$$
$$-\frac{\hbar^2}{2m_0}\mathbf{y}_2 = \frac{1}{6} [A_0 - B_0]$$
$$-\frac{\hbar^2}{2m_0}\mathbf{y}_3 = \frac{C_0}{6}$$

Luttinger-Kohn Hamiltonian,

$$Harmonian,$$

$$= \begin{bmatrix} a_{+} & b & c & 0 & ib/\sqrt{2} & -i\sqrt{2}c & |\frac{3}{2}, \frac{3}{2} \\ b^{*} & a_{-} & 0 & c & if & i\sqrt{\frac{3}{2}}b & |\frac{3}{2}, \frac{1}{2} \\ c^{*} & 0 & a_{-} & -b & -i\sqrt{\frac{3}{2}}b^{*} & if & |\frac{3}{2}, -\frac{1}{2} \\ 0 & c^{*} & -b^{*} & a_{+} & -i\sqrt{2}c^{*} & -ib^{*}/\sqrt{2} & |\frac{3}{2}, -\frac{3}{2} \\ -ib^{*}/\sqrt{2} & -if & i\sqrt{\frac{3}{2}}b & i\sqrt{2}c & d & 0 \\ i\sqrt{2}c^{*} & -i\int \frac{3}{2}b^{*} & -if & ib/\sqrt{2} & 0 & d & |\frac{1}{2}, -\frac{1}{2} \\ i\sqrt{2}c^{*} & -i\sqrt{\frac{3}{2}}b^{*} & -if & ib/\sqrt{2} & 0 & d & |\frac{1}{2}, -\frac{1}{2} \\ \end{bmatrix}$$

The parameters *a*, *b*, *c*, and *d* are given by

$$a_{\pm} = E_{v} - (\mathbf{y}_{1} \mp 2\mathbf{y}_{2}) \frac{\hbar^{2} k_{z}^{2}}{2m_{o}} - (\mathbf{y}_{1} \pm \mathbf{y}_{2}) \frac{\hbar^{2}}{2m_{o}} (k_{x}^{2} + k_{y}^{2})$$

$$b = i2\sqrt{3} \mathbf{y}_{3} \frac{\hbar^{2}}{2m_{o}} (k_{x} - ik_{y})k_{z}$$

$$c = -\sqrt{3} \frac{\hbar^{2}}{2m_{o}} [\mathbf{y}_{2} (k_{x}^{2} - k_{y}^{2}) - 2i\mathbf{y}_{3}k_{x}k_{y}]$$

$$d = E_{v} - \Delta - \frac{\hbar^{2}}{2m_{o}} \mathbf{y}_{1}k^{2}$$

Here Ev is the energy at the top of the valence band, and is the spin-orbit splitting

The matrix element can be obtained by fitting experimentally obtained hole masse

#### Reference:

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