

Energy Bands and Electronic States in Zinc Blende Semiconductors

Our goal in this section is to dig deeper into solid state physics and try to figure out selection rules concerning the matrix element $|\vec{p} \cdot \hat{n}|^2$ that we encountered earlier.

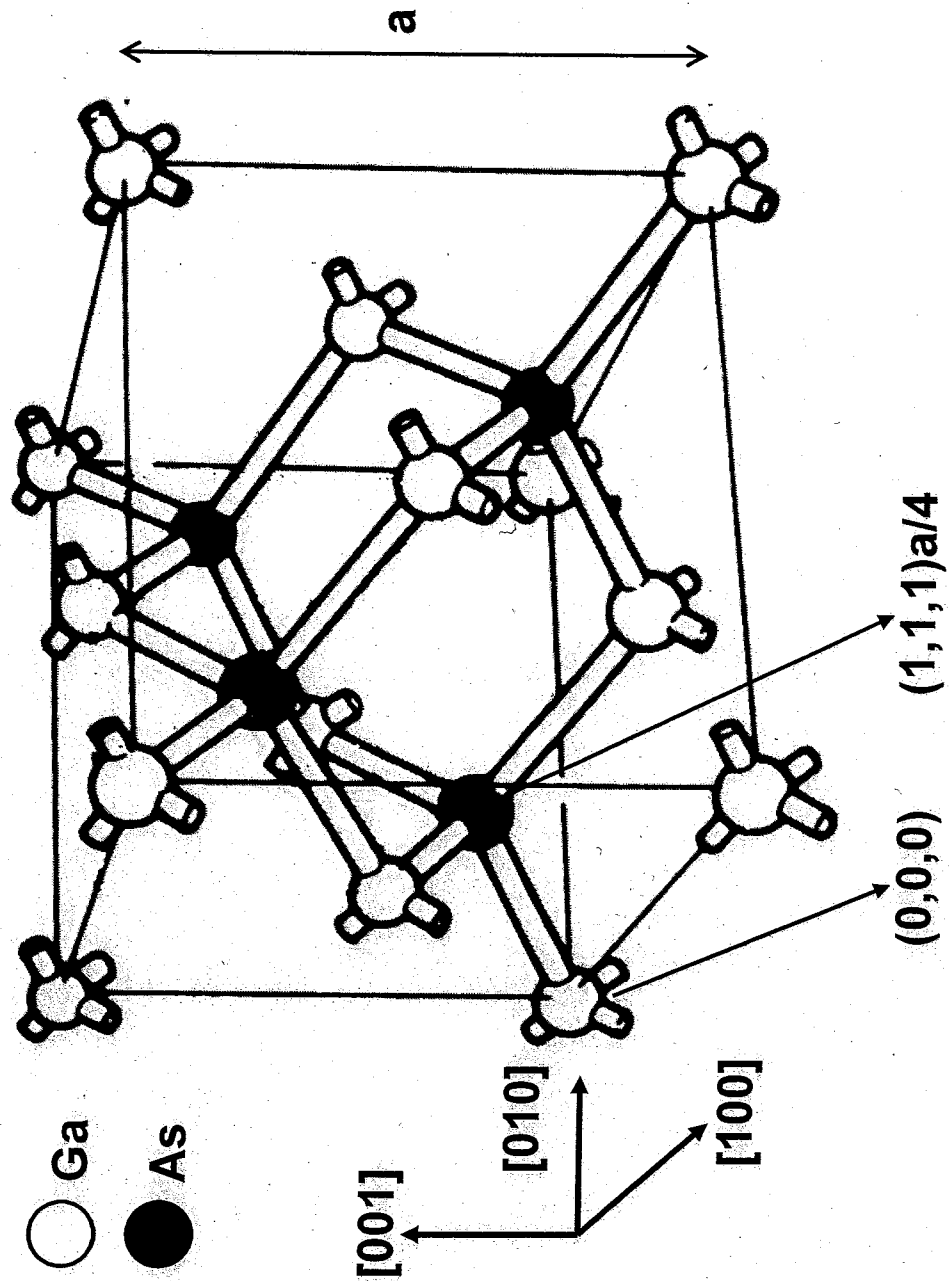
To understand this handout you must have seen tight binding method before.

Tight-Binding (or LCAO - Linear Combination of Atomic Orbitals)

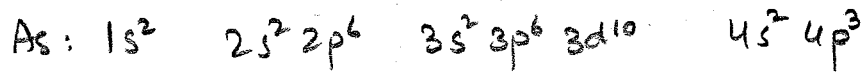
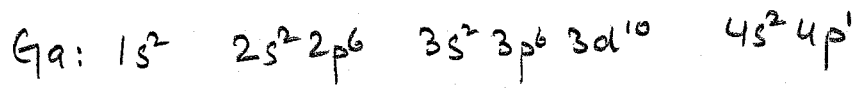
As the name suggests, LCAO attempts to obtain the energy bands and Bloch functions by a linear combination of atomic orbitals. A zincblende primitive cell has a two atom basis (see the figure on next page). Although here we consider GaAs, the arguments will apply to all zincblende semiconductors. By convention that I chose randomly, a Ga atom sits at $(0,0,0)$ and the second atom of the basis - an As atom - sits at $(1,1,1)\frac{a}{4}$. Let:

$$\vec{d}_1 = (1,1,1)\frac{a}{4}$$

Zincblende Lattice (GaAs)



The electronic configuration of Ga + As are:



valence orbitals.

Each Ga and As atom contributes 4s, 4p_x, 4p_y, and 4p_z orbitals to bonding. We label them as:

$$\text{Ga: } |\phi_s^G(\vec{r})\rangle, |\phi_{p_x}^G(\vec{r})\rangle, |\phi_{p_y}^G(\vec{r})\rangle, |\phi_{p_z}^G(\vec{r})\rangle$$

$$\text{As: } |\phi_s^A(\vec{r})\rangle, |\phi_{p_x}^A(\vec{r})\rangle, |\phi_{p_y}^A(\vec{r})\rangle, |\phi_{p_z}^A(\vec{r})\rangle$$

So the orbitals centered at the As $(1/4, 1/4, 1/4)$ atom are:

$$|\phi_s^A(\vec{r}-\vec{d}_1)\rangle, |\phi_{p_x}^A(\vec{r}-\vec{d}_1)\rangle, |\phi_{p_y}^A(\vec{r}-\vec{d}_1)\rangle, |\phi_{p_z}^A(\vec{r}-\vec{d}_1)\rangle$$

We write the Bloch function as:

$$|\psi_{\vec{k}}(\vec{r})\rangle = \sum_j \frac{e^{i\vec{k}\cdot\vec{R}_j}}{\sqrt{N}} \left\{ c_s^G |\phi_s^G(\vec{r}-\vec{R}_j)\rangle + c_{p_x}^G |\phi_{p_x}^G(\vec{r}-\vec{R}_j)\rangle + c_{p_y}^G |\phi_{p_y}^G(\vec{r}-\vec{R}_j)\rangle \right. \\ \left. + c_{p_z}^G |\phi_{p_z}^G(\vec{r}-\vec{R}_j)\rangle + e^{i\vec{k}\cdot\vec{d}_1} \left[c_s^A |\phi_s^A(\vec{r}-\vec{R}_j-\vec{d}_1)\rangle + c_{p_x}^A |\phi_{p_x}^A(\vec{r}-\vec{R}_j-\vec{d}_1)\rangle \right. \right. \\ \left. \left. + c_{p_y}^A |\phi_{p_y}^A(\vec{r}-\vec{R}_j-\vec{d}_1)\rangle + c_{p_z}^A |\phi_{p_z}^A(\vec{r}-\vec{R}_j-\vec{d}_1)\rangle \right] \right\}$$

where the summation over j is over all the primitive cells of the lattice. The location of Ga atom in the j -th primitive cell is indicated by \vec{R}_j .

Let \hat{H} be the Crystal Hamiltonian. We suppose that the matrix elements of \hat{H} are as follows:

$$\langle \phi_s^G(\vec{r}) | \hat{H} | \phi_s^G(\vec{r}) \rangle = \epsilon_s^G$$

$$\langle \phi_n^G(\vec{r}) | \hat{H} | \phi_n^G(\vec{r}) \rangle = \epsilon_p^G \quad \left\{ n = p_x, p_y, \text{ or } p_z \right\}$$

$$\langle \phi_m^G(\vec{r}) | \hat{H} | \phi_n^G(\vec{r}) \rangle = 0 \quad \text{for } m \neq n \quad \left\{ \begin{array}{l} \text{orthogonality of atomic} \\ \text{orbitals} \end{array} \right\}$$

and similarly:

$$\langle \phi_s^A(\vec{r}) | \hat{H} | \phi_s^A(\vec{r}) \rangle = \epsilon_s^A$$

$$\langle \phi_n^A(\vec{r}) | \hat{H} | \phi_n^A(\vec{r}) \rangle = \epsilon_p^A \quad \left\{ n = p_x, p_y, p_z \right\}$$

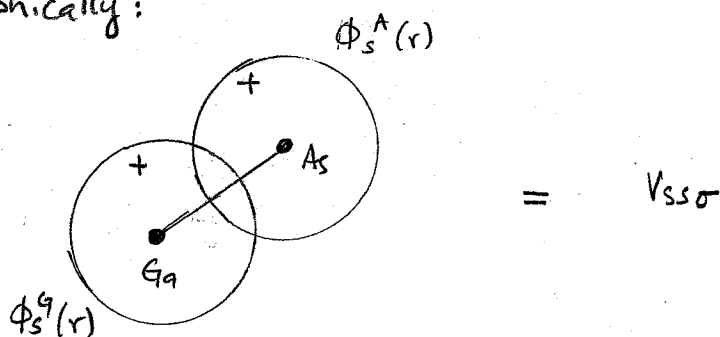
$$\langle \phi_m^A(\vec{r}) | \hat{H} | \phi_n^A(\vec{r}) \rangle = 0 \quad \text{for } m \neq n \quad \left\{ \text{orthogonality} \right\}$$

The above are the same-site matrix elements. We also need matrix elements for orbitals on nearest neighbors. These are best evaluated graphically.

Consider first:

$$\langle \phi_s^A(\vec{r}-\vec{d}_1) | \hat{H} | \phi_s^G(\vec{r}) \rangle = V_{ss\sigma} = \langle \phi_s^G(\vec{r}) | \hat{H} | \phi_s^A(\vec{r}-\vec{d}_1) \rangle$$

Graphically:



Values of ϵ_s and ϵ_p for different elements

Can be obtained from this table.

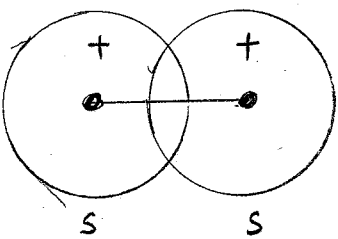
TABLE 2-2
Atomic term values from Herman and Skillman (1963),
or extrapolated from their values.

Atomic term value (eV)				
Element	$-\epsilon_s$	$-\epsilon_p$	$-\epsilon_h =$ $-(\epsilon_s + 3\epsilon_p)/4$	$V_1^{a,c} =$ $(\epsilon_p - \epsilon_s)/4$
2s, 2p				
Li	5.48	—	—	—
Be	8.17	4.14	5.15	1.01
B	12.54	6.64	8.12	1.47
C	17.52	8.97	11.11	2.13
N	23.04	11.47	14.36	2.88
O	29.14	14.13	17.88	3.76
F	35.80	16.99	21.69	4.71
3s, 3p				
Na	5.13	—	—	—
Mg	6.86	2.99	3.95	0.97
Al	10.11	4.86	6.18	1.33
Si	13.55	6.52	8.27	1.76
P	17.10	8.33	10.52	2.19
S	20.80	10.27	12.90	2.63
Cl	24.63	12.31	15.38	3.08
4s, 4p				
K	4.19	—	—	—
Ca	5.41	—	—	—
Cu	6.92	1.83	3.10	1.27
Zn	8.40	3.38	4.64	1.26
Ga	11.37	4.90	6.52	1.62
Ge	14.38	6.36	8.37	2.01
As	17.33	7.91	10.27	2.36
Se	20.32	9.53	12.23	2.70
Br	23.35	11.20	14.27	3.02

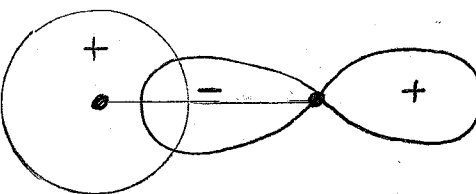
Atomic term value (eV)				
Element	$-\epsilon_s$	$-\epsilon_p$	$-\epsilon_h =$ $-(\epsilon_s + 3\epsilon_p)/4$	$V_1^{a,c} =$ $(\epsilon_p - \epsilon_s)/4$
5s, 5p				
Rb	3.94	—	—	—
Sr	5.00	—	—	—
Ag	6.41	2.05	3.14	1.09
Cd	7.70	3.38	4.46	1.08
In	10.12	4.69	6.05	1.36
Sn	12.50	5.94	7.58	1.64
Sb	14.80	7.24	9.13	1.89
Te	17.11	8.59	10.72	2.13
I	19.42	9.97	12.33	2.36
6s, 6p				
Cs	3.56	—	—	—
Ba	4.45	—	—	—
Au	6.48	2.38	3.41	1.03
Hg	7.68	3.48	4.53	1.05
Tl	9.92	4.61	5.94	1.33
Pb	12.07	5.77	7.35	1.58
Bi	14.15	6.97	8.77	1.80
Po	16.21	8.19	10.20	2.01
At	18.24	9.44	11.64	2.20
7s				
Fr	3.40	—	—	—
Ra	4.24	—	—	—

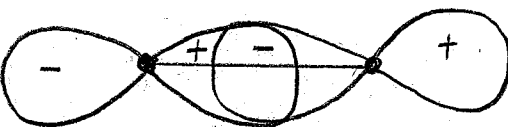
NOTE: These values appear also in the Solid State Table.

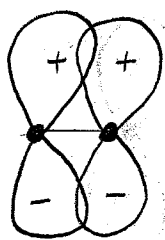
It turns out there are only four basic types of matrix elements. You have already seen one,

(1)  = $V_{ss\sigma}$

The rest are,

(2)  = $V_{sp\sigma}$

(3)  = $V_{pp\sigma}$

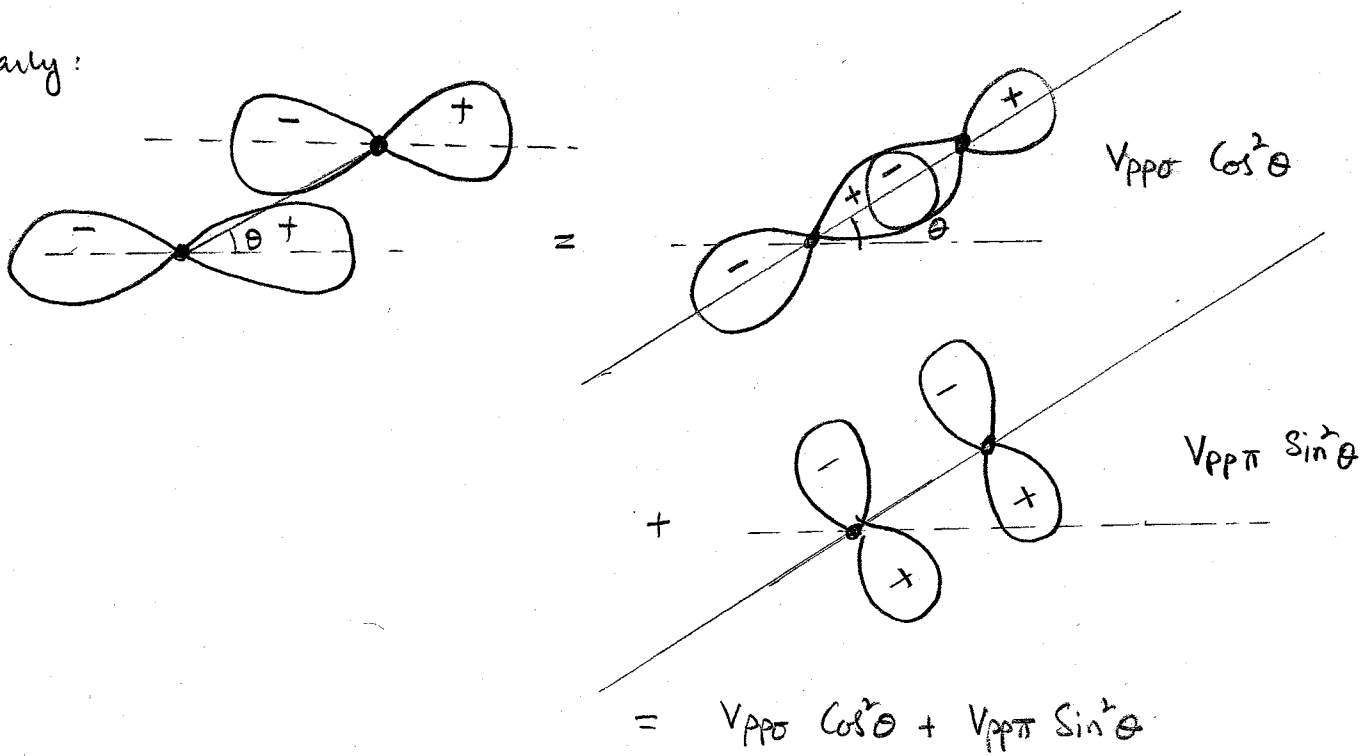
(4)  = $V_{pp\pi}$

All other matrix elements can be evaluated graphically

Examples:

= V_{sp\sigma} \cos\theta + 0 \cdot \sin\theta
$$= V_{sp\sigma} \cos\theta$$

Similarly:

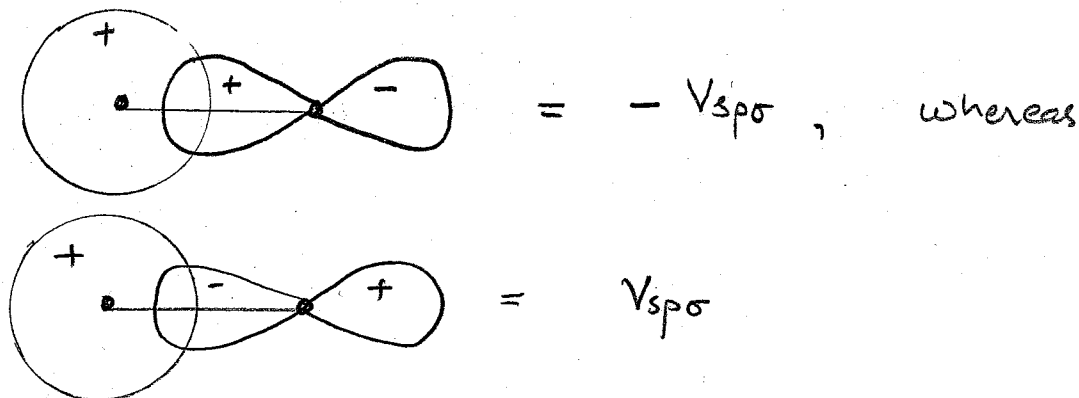


With these definitions we can calculate all other matrix elements. The four nearest As atoms to the Ga atom at $(0,0,0)$ are located at:

$$\vec{d}_1 = (1, 1, 1) \frac{a}{4} \quad \vec{d}_2 = (1, -1, -1) \frac{a}{4} \quad \vec{d}_3 = (-1, 1, -1) \frac{a}{4}$$

$$\vec{d}_4 = (-1, -1, 1) \frac{a}{4}$$

A Word Of Caution: Orient the orbitals in the same way on each atom. This is important. For example,



I always orient orbitals so that the +ve lobe of P_x, P_y, P_z orbitals points in the direction of increasing values of x, y, z co-ordinates, respectively.

The quantities $V_{ss\sigma}, V_{sp\sigma}, V_{pp\sigma}, V_{pp\pi}$ are calculated by the relations

$$V_{ss\sigma} = \eta_{ss\sigma} \frac{\hbar^2}{m_0 d^2} \quad \left\{ \begin{array}{l} d = \text{bond length} \\ = \frac{\sqrt{3}}{4} a \text{ for zincblende crystals.} \end{array} \right.$$

$$V_{sp\sigma} = \eta_{sp\sigma} \frac{\hbar^2}{m_0 d^2}$$

$$V_{pp\sigma} = \eta_{pp\sigma} \frac{\hbar^2}{m_0 d^2}$$

$$V_{pp\pi} = \eta_{pp\pi} \frac{\hbar^2}{m_0 d^2}$$

Values of η 's are given below:

$$\eta_{ss\sigma} = -1.4$$

$$\eta_{sp\sigma} = +1.84$$

$$\eta_{pp\sigma} = +3.24$$

$$\eta_{pp\pi} = -0.81$$

Some examples of matrix elements are given below:

$$\left[\langle \phi_s^A(\vec{r}-\vec{d}_j) | \hat{H} | \phi_s^G(\vec{r}) \rangle = V_{ss\sigma} = E_{ss} \quad \text{for } j=1,2,3,4 \right.$$

$$\left[\langle \phi_{px}^A(\vec{r}-\vec{d}_1) | \hat{H} | \phi_s^G(\vec{r}) \rangle = V_{sp\sigma} \cos \theta = V_{sp\sigma} \frac{1}{\sqrt{3}} = E_{sp} \right.$$

$$\langle \phi_{px}^A(\vec{r}-\vec{d}_2) | \hat{H} | \phi_s^G(\vec{r}) \rangle = \frac{V_{sp\sigma}}{\sqrt{3}} = E_{sp}$$

$$\langle \phi_{px}^A(\vec{r}-\vec{d}_3) | \hat{H} | \phi_s^G(\vec{r}) \rangle = -\frac{V_{sp\sigma}}{\sqrt{3}} = -E_{sp}$$

$$\left[\langle \phi_{px}^A(\vec{r}-\vec{d}_4) | \hat{H} | \phi_s^G(\vec{r}) \rangle = -\frac{V_{sp\sigma}}{\sqrt{3}} = -E_{sp} \right.$$

Results can also be obtained for $|\phi_{py}^A\rangle$ and $|\phi_{pz}^A\rangle$ orbitals replacing $|\phi_{px}^A\rangle$ orbitals above. We also have,

$$\left[\langle \phi_{px}^A(\vec{r}-\vec{d}_1) | \hat{H} | \phi_{px}^G(\vec{r}) \rangle = \frac{V_{pp\sigma}}{3} + \frac{2V_{pp\pi}}{3} = E_{xx} \right.$$

$$\langle \phi_{px}^A(\vec{r}-\vec{d}_2) | \hat{H} | \phi_{px}^G(\vec{r}) \rangle = \frac{V_{pp\sigma}}{3} + \frac{2}{3} V_{pp\pi} = E_{xx}$$

$$\langle \phi_{px}^A(\vec{r}-\vec{d}_3) | \hat{H} | \phi_{px}^G(\vec{r}) \rangle = -\frac{V_{pp\sigma}}{3} + \frac{2}{3} V_{pp\pi} = E_{xx}$$

$$\left[\langle \phi_{px}^A(\vec{r}-\vec{d}_4) | \hat{H} | \phi_{px}^G(\vec{r}) \rangle = \frac{V_{pp\sigma}}{3} + \frac{2}{3} V_{pp\pi} = E_{xx} \right.$$

Same results follow for pair of similar p-orbitals on nearest Ga and As atoms. The last category contains, for example,

$$\left[\langle \phi_{py}^A(\vec{r}-\vec{d}_1) | \hat{H} | \phi_{px}^G(\vec{r}) \rangle = \frac{V_{pp\sigma}}{3} - \frac{1}{3} V_{pp\pi} = E_{xy} \right.$$

$$\langle \phi_{py}^A(\vec{r}-\vec{d}_2) | \hat{H} | \phi_{px}^G(\vec{r}) \rangle = -\frac{V_{pp\sigma}}{3} + \frac{1}{3} V_{pp\pi} = -E_{xy}$$

$$\langle \phi_{py}^A(\vec{r}-\vec{d}_3) | \hat{H} | \phi_{px}^G(\vec{r}) \rangle = -E_{xy}$$

$$\left[\langle \phi_{py}^A(\vec{r}-\vec{d}_4) | \hat{H} | \phi_{px}^G(\vec{r}) \rangle = E_{xy} \right.$$

The others can be found in the same way.

We take our expansion for $\Psi_{\vec{k}}(\vec{r})$ and substitute in the Schrödinger Equation

$$\hat{H} |\Psi_{\vec{k}}(\vec{r})\rangle = E(\vec{k}) |\Psi_{\vec{k}}(\vec{r})\rangle$$

Then multiply on the left side by the following - one

by one - $\langle \phi_s^G(\vec{r}) |$, $\langle \phi_{px}^G(\vec{r}) |$, $\langle \phi_{py}^G(\vec{r}) |$, $\langle \phi_{pz}^G(\vec{r}) |$

$\langle \phi_s^A(\vec{r}-\vec{d}_1) |$, $\langle \phi_{px}^A(\vec{r}-\vec{d}_1) |$, $\langle \phi_{py}^A(\vec{r}-\vec{d}_1) |$, $\langle \phi_{pz}^A(\vec{r}-\vec{d}_1) |$

For example, multiplying by $\langle \phi_s^G(\vec{r}) |$ gives:

$$\langle \phi_s^G(\vec{r}) | \hat{H} |\Psi_{\vec{k}}(\vec{r})\rangle = E(\vec{k}) \langle \phi_s^G(\vec{r}) | \Psi_{\vec{k}}(\vec{r})\rangle$$

$$\Rightarrow c_s^G \epsilon_s^G + c_s^A \left[e^{i\vec{k}\cdot\vec{d}_1} + e^{i\vec{k}\cdot\vec{d}_2} + e^{i\vec{k}\cdot\vec{d}_3} + e^{i\vec{k}\cdot\vec{d}_4} \right] E_{ss}$$

$$+ c_{px}^A \left[e^{i\vec{k}\cdot\vec{d}_1} + e^{i\vec{k}\cdot\vec{d}_2} - e^{i\vec{k}\cdot\vec{d}_3} - e^{i\vec{k}\cdot\vec{d}_4} \right] E_{sp}$$

$$+ c_{py}^A \left[e^{i\vec{k}\cdot\vec{d}_1} - e^{i\vec{k}\cdot\vec{d}_2} + e^{i\vec{k}\cdot\vec{d}_3} - e^{i\vec{k}\cdot\vec{d}_4} \right] E_{sp}$$

$$+ c_{pz}^A \left[e^{i\vec{k}\cdot\vec{d}_1} - e^{i\vec{k}\cdot\vec{d}_2} - e^{i\vec{k}\cdot\vec{d}_3} + e^{i\vec{k}\cdot\vec{d}_4} \right] E_{sp}$$

$$= E(\vec{k}) c_s^G$$

$$\Rightarrow \epsilon_s^G c_s^G + E_{ss} g_0(\vec{k}) c_s^A + E_{sp} g_1(\vec{k}) c_{px}^A + E_{sp} g_2(\vec{k}) c_{py}^A + E_{sp} g_3(\vec{k}) c_{pz}^A = E(\vec{k}) c_s^G$$

where:

$$g_0(\vec{k}) = e^{i\vec{k}\cdot\vec{d}_1} + e^{i\vec{k}\cdot\vec{d}_2} + e^{i\vec{k}\cdot\vec{d}_3} + e^{i\vec{k}\cdot\vec{d}_4}$$

$$g_1(\vec{k}) = e^{i\vec{k}\cdot\vec{d}_1} + e^{i\vec{k}\cdot\vec{d}_2} - e^{i\vec{k}\cdot\vec{d}_3} - e^{i\vec{k}\cdot\vec{d}_4}$$

$$g_2(\vec{k}) = e^{i\vec{k}\cdot\vec{d}_1} - e^{i\vec{k}\cdot\vec{d}_2} + e^{i\vec{k}\cdot\vec{d}_3} - e^{i\vec{k}\cdot\vec{d}_4}$$

$$g_3(\vec{k}) = e^{i\vec{k}\cdot\vec{d}_1} - e^{i\vec{k}\cdot\vec{d}_2} - e^{i\vec{k}\cdot\vec{d}_3} + e^{i\vec{k}\cdot\vec{d}_4}$$

The eight equations obtained by the procedure outlined on the previous page can be written in a matrix form:

$$H \begin{bmatrix} 1 \\ c \end{bmatrix} = E(k) \begin{bmatrix} 1 \\ c \end{bmatrix} \quad \text{where} \quad \begin{bmatrix} 1 \\ c \end{bmatrix} = \begin{bmatrix} C_S^G \\ C_{PX}^G \\ C_{PY}^G \\ C_{PZ}^G \\ C_S^A \\ C_S^A \\ C_{PX}^A \\ C_{PY}^A \\ C_{PZ}^A \end{bmatrix}$$

And the matrix H is given on the next page:

The Matrix H for Zincblende Lattice

$\langle \phi_s^G \rangle$	$\langle \phi_{px}^G \rangle$	$\langle \phi_{py}^G \rangle$	$\langle \phi_{pz}^G \rangle$	$\langle \phi_s^A \rangle$	$\langle \phi_{px}^A \rangle$	$\langle \phi_{py}^A \rangle$	$\langle \phi_{pz}^A \rangle$
ϵ_s^G	0	0	0	$E_{ss} g_0$	$E_{sp} g_1$	$E_{sp} g_2$	$E_{sp} g_3$
0	ϵ_p^G	0	0	$-E_{sp} g_1$	$E_{xx} g_0$	$E_{xy} g_3$	$E_{xy} g_2$
0	0	ϵ_p^G	0	$-E_{sp} g_2$	$E_{xy} g_3$	$E_{xx} g_0$	$E_{xy} g_1$
0	0	0	ϵ_p^G	$-E_{sp} g_3$	$E_{xy} g_2$	$E_{xy} g_1$	$E_{xx} g_0$
$E_{ss} g_0^*$	$-E_{sp} g_1^*$	$-E_{sp} g_2^*$	$-E_{sp} g_3^*$	ϵ_s^A	0	0	0
$E_{sp} g_1^*$	$E_{xx} g_0^*$	$E_{xy} g_3^*$	$E_{xy} g_2^*$	0	ϵ_p^A	0	0
$E_{sp} g_2^*$	$E_{xy} g_3^*$	$E_{xx} g_0^*$	$E_{xy} g_1^*$	0	0	ϵ_p^A	0
$E_{sp} g_3^*$	$E_{xy} g_2^*$	$E_{xy} g_1^*$	$E_{xx} g_0^*$	0	0	0	ϵ_p^A

$$H \begin{bmatrix} \phi_s^G \\ \phi_{px}^G \\ \phi_{py}^G \\ \phi_{pz}^G \\ \phi_s^A \\ \phi_{px}^A \\ \phi_{py}^A \\ \phi_{pz}^A \end{bmatrix} = E(\vec{k}) \begin{bmatrix} \phi_s^G \\ \phi_{px}^G \\ \phi_{py}^G \\ \phi_{pz}^G \\ \phi_s^A \\ \phi_{px}^A \\ \phi_{py}^A \\ \phi_{pz}^A \end{bmatrix}$$

For each value of \vec{k} in the FBZ, there are eight eigenvalues $E_n(\vec{k})$ $\{n=1,2,\dots,8\}$ of the matrix H and these correspond to 8 bands. $\{4$ valence bands and 4 conduction bands. $\}$ It is instructive to solve for eigenvalues when $\vec{k}=0$. This can be done analytically. The result is (see next page):

$$\left\{ \begin{aligned} E_6(\vec{k}=0) = E_7(\vec{k}=0) = E_8(\vec{k}=0) &= \frac{\epsilon_p^G + \epsilon_p^A}{2} + \sqrt{\left(\frac{\epsilon_p^G - \epsilon_p^A}{2}\right)^2 + (4E_{xx})^2} \\ E_5(\vec{k}=0) &= \frac{\epsilon_s^G + \epsilon_s^A}{2} + \sqrt{\left(\frac{\epsilon_s^G - \epsilon_s^A}{2}\right)^2 + (4E_{ss})^2} \\ E_4(\vec{k}=0) = E_3(\vec{k}=0) = E_2(\vec{k}=0) &= \frac{\epsilon_p^G + \epsilon_p^A}{2} - \sqrt{\left(\frac{\epsilon_p^G - \epsilon_p^A}{2}\right)^2 + (4E_{xx})^2} \\ E_1(\vec{k}=0) &= \frac{\epsilon_s^G + \epsilon_s^A}{2} - \sqrt{\left(\frac{\epsilon_s^G - \epsilon_s^A}{2}\right)^2 + (4E_{ss})^2} \end{aligned} \right.$$

First group in brackets above are the four conduction bands and the second group are the four valence bands.

From the energies one thing is obvious: the Bloch function at the bottom of the lowest conduction band is made up of only s-orbitals of Ga and As atoms. Also, the Bloch functions at the top of the highest valence bands

The Matrix H for $k=0$

$\langle \phi_s^G \rangle$	$\langle \phi_{px}^G \rangle$	$\langle \phi_{py}^G \rangle$	$\langle \phi_{pz}^G \rangle$	$\langle \phi_s^A \rangle$	$\langle \phi_{px}^A \rangle$	$\langle \phi_{py}^A \rangle$	$\langle \phi_{pz}^A \rangle$
ϵ_s^G	0	0	0	$4E_{ss}$	0	0	0
0	ϵ_p^G	0	0	0	$4E_{xx}$	0	0
0	0	ϵ_p^G	0	0	0	$4E_{xx}$	0
0	0	0	ϵ_p^G	0	0	0	$4E_{xx}$
$4E_{ss}$	0	0	0	ϵ_s^A	0	0	0
0	$4E_{xx}$	0	0	0	ϵ_p^A	0	0
0	0	$4E_{xx}$	0	0	0	ϵ_p^A	0
0	0	0	$4E_{xx}$	0	0	0	ϵ_p^A

are made up of only p-orbitals of Ga and As atoms. Thus conduction band bottom has s-like character and valence band top has p-like character.

The exact Bloch function can be found by finding the eigenvectors of the matrix H .

Bloch Functions at $\vec{k}=0$:

Lowest Conduction Band:

$$\psi_{c, \vec{k}=0}(\vec{r}) = \sum_j \frac{1}{\sqrt{N}} \left\{ c_s^G |\phi_s^G(\vec{r}-\vec{R}_j)\rangle + c_s^A |\phi_s^A(\vec{r}-\vec{R}_j-\vec{d}_1)\rangle \right\}$$

where the values of c_s^G and c_s^A can be obtained by finding the eigenvectors of the H matrix for $\vec{k}=0$.

We know that $\psi_{c, \vec{k}=0}(\vec{r})$ should look like:

$$\psi_{c, \vec{k}=0}(\vec{r}) = \frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{N}} U_{c, \vec{k}}(\vec{r}) \Big|_{\vec{k}=0} = \frac{U_{c, \vec{k}=0}(\vec{r})}{\sqrt{N}}$$

So

$$U_{c, \vec{k}=0}(\vec{r}) = \sum_j \left\{ c_s^G |\phi_s^G(\vec{r}-\vec{R}_j)\rangle + c_s^A |\phi_s^A(\vec{r}-\vec{R}_j-\vec{d}_1)\rangle \right\}$$

We call this $|s\rangle$ (i.e. $|s\rangle = |U_{c, \vec{k}=0}(\vec{r})\rangle$).

Highest Valence Bands:

The highest valence bands are triply degenerate at $\vec{k}=0$, and the Bloch functions $u_{v, \vec{k}=0}(r)$ for each of the three bands are given as follows:

$$|P_x\rangle = \sum_j \left\{ c_{P_x}^G |\Phi_{P_x}^G(\vec{r}-\vec{R}_j)\rangle + c_{P_x}^A |\Phi_{P_x}^A(\vec{r}-\vec{R}_j-\vec{d}_1)\rangle \right\}$$

$$|P_y\rangle = \sum_j \left\{ c_{P_y}^G |\Phi_{P_y}^G(\vec{r}-\vec{R}_j)\rangle + c_{P_y}^A |\Phi_{P_y}^A(\vec{r}-\vec{R}_j-\vec{d}_1)\rangle \right\}$$

$$|P_z\rangle = \sum_j \left\{ c_{P_z}^G |\Phi_{P_z}^G(\vec{r}-\vec{R}_j)\rangle + c_{P_z}^A |\Phi_{P_z}^A(\vec{r}-\vec{R}_j-\vec{d}_1)\rangle \right\}$$

What About Spin?

So far we have not talked about spin — assuming that spin up-down can be simply added in the end. So in reality we have the following Bloch function at $\vec{k}=0$

for the lowest conduction band and the three highest valence bands (total 8 Bloch functions including spin)

$$|S\uparrow\rangle, |S\downarrow\rangle \quad \left\{ \begin{array}{l} \text{conduction band} \\ \text{Let } E_5(\vec{k}=0) = E_s \end{array} \right.$$

$$\begin{array}{l} |P_x\uparrow\rangle, |P_x\downarrow\rangle \\ |P_y\uparrow\rangle, |P_y\downarrow\rangle \\ |P_z\uparrow\rangle, |P_z\downarrow\rangle \end{array} \quad \left\{ \begin{array}{l} \text{three valence bands} \\ \text{Let } E_2(\vec{k}=0) \\ = E_3(\vec{k}=0) = E_4(\vec{k}=0) \\ = E_p \end{array} \right.$$

\Rightarrow In this simple model bandgap = $E_g = E_s - E_p$

The states $|s\uparrow\rangle, |s\downarrow\rangle, |p_x\uparrow\rangle, |p_x\downarrow\rangle, |p_y\uparrow\rangle, |p_y\downarrow\rangle, |p_z\uparrow\rangle, |p_z\downarrow\rangle$ are eigenstates of the Hamiltonian at $\vec{k}=0$. So the $\vec{k}=0$ Hamiltonian in this basis can be written as shown on the following page — no surprise it's diagonal.

Word of Caution:

State $|s\uparrow\rangle$ really means $|s\rangle \otimes |\uparrow\rangle$ i.e. the spin degree of freedom is separated out. So for example,

$$|p_x\uparrow\rangle = |p_x\rangle \otimes |\uparrow\rangle$$

$$= \sum_j \left\{ c_{px}^G |\phi_{px}^G(\vec{r}-\vec{R}_j)\rangle + c_{py}^A |\phi_{px}^A(\vec{r}-\vec{R}_j-\vec{d}_1)\rangle \right\} \otimes |\uparrow\rangle$$

and

$$|s\uparrow\rangle = |s\rangle \otimes |\uparrow\rangle$$

$$= \sum_j \left\{ c_s^G |\phi_s^G(\vec{r}-\vec{R}_j)\rangle + c_s^A |\phi_s^A(\vec{r}-\vec{R}_j-\vec{d}_1)\rangle \right\} \otimes |\uparrow\rangle$$

Sometimes $|s\rangle \otimes |\uparrow\rangle$ may also be written as $|s\rangle \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix}$

or as $|s\rangle \begin{bmatrix} 1 \\ 0 \end{bmatrix}$. They all mean the same thing.

The Matrix H for $k=0$

$\langle S \uparrow $	$ S \uparrow \rangle$	$\langle S \downarrow $	$ S \downarrow \rangle$	$\langle P_x \uparrow $	$ P_x \uparrow \rangle$	$\langle P_x \downarrow $	$ P_x \downarrow \rangle$	$\langle P_y \uparrow $	$ P_y \uparrow \rangle$	$\langle P_y \downarrow $	$ P_y \downarrow \rangle$	$\langle P_z \uparrow $	$ P_z \uparrow \rangle$	$\langle P_z \downarrow $	$ P_z \downarrow \rangle$
ϵ_s	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	ϵ_s	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	ϵ_p	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	ϵ_p	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	ϵ_p	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	ϵ_p	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	ϵ_p	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	ϵ_p	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	0	ϵ_p	0

• Now spin has been explicitly included

• States belonging to higher conduction bands and lower valence band have been ignored

Spin Orbit Coupling :

Spin orbit coupling is significant in most semiconductors.

The usual Hamiltonian for electrons in a crystal is:

$$\hat{H} = \frac{\hat{\mathbf{P}}^2}{2m_0} + V(\hat{\mathbf{r}}) \quad \text{where } V(\hat{\mathbf{r}}) \text{ is the periodic potential}$$

of the atoms. Spin orbit coupling adds a term \hat{H}_{so} ,

$$\hat{H} = \frac{\hat{\mathbf{P}}^2}{2m_0} + V(\hat{\mathbf{r}}) + \hat{H}_{so}$$

where,

$$\hat{H}_{so} = \frac{\hbar}{4m_0^2 c^2} \left[\nabla V(\hat{\mathbf{r}}) \times \hat{\mathbf{P}} \right] \cdot \hat{\boldsymbol{\sigma}}$$

$$\text{where } \hat{\boldsymbol{\sigma}} = \hat{\sigma}_x \hat{x} + \hat{\sigma}_y \hat{y} + \hat{\sigma}_z \hat{z}$$

$$\text{and } \hat{\sigma}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \hat{\sigma}_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad \hat{\sigma}_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$\hat{\sigma}_x$, $\hat{\sigma}_y$ and $\hat{\sigma}_z$ are the Pauli spin matrices. The operator $\hat{\boldsymbol{\sigma}}$

acts on the electrons spin degree of freedom and the spin

states $|\uparrow\rangle$ & $|\downarrow\rangle$ are: $|\uparrow\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$ $|\downarrow\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$

Now in the presence of \hat{H}_{so} the hamiltonian at $\vec{k}=0$ is

not diagonal in the $|s\uparrow\rangle, |s\downarrow\rangle, |p_x\uparrow\rangle, |p_x\downarrow\rangle, |p_y\uparrow\rangle, |p_y\downarrow\rangle$

$|p_z\uparrow\rangle, |p_z\downarrow\rangle$ basis. We define the following matrix elements

$$\begin{aligned}
\frac{\Delta}{3i} &= \frac{\hbar}{4m_0^2c^2} \langle P_x | \frac{\partial V(\hat{r})}{\partial x} \hat{P}_y - \frac{\partial V(\hat{r})}{\partial y} \hat{P}_x | P_y \rangle \\
&= \frac{\hbar}{4m_0^2c^2} \langle P_y | \frac{\partial V(\hat{r})}{\partial y} \hat{P}_z - \frac{\partial V(\hat{r})}{\partial z} \hat{P}_y | P_z \rangle \\
&= \frac{\hbar}{4m_0^2c^2} \langle P_x | \frac{\partial V(\hat{r})}{\partial x} \hat{P}_z - \frac{\partial V(\hat{r})}{\partial z} \hat{P}_x | P_z \rangle
\end{aligned}$$

The integrations here are over one primitive unit cell.

With these definitions the H matrix with \hat{H}_{so}

included can be written as shown on the next page.

Note that \hat{H}_{so} couples the p-like valence band

states that are all degenerate at $\vec{k}=0$. This

coupling partially breaks the degeneracy at $\vec{k}=0$.

To see this, we need to "rotate" the basis

$|P_x \uparrow\rangle, |P_x \downarrow\rangle, |P_y \uparrow\rangle, |P_y \downarrow\rangle, |P_z \uparrow\rangle, |P_z \downarrow\rangle$ to diagonalize

the H matrix in the presence of \hat{H}_{so} .

The Matrix H for $k=0$

	$ S \uparrow\rangle$	$ S \downarrow\rangle$	$ P_x \uparrow\rangle$	$ P_x \downarrow\rangle$	$ P_y \uparrow\rangle$	$ P_y \downarrow\rangle$	$ P_z \uparrow\rangle$	$ P_z \downarrow\rangle$
$\langle S \uparrow $	ϵ_s	0	0	0	0	0	0	0
$\langle S \downarrow $	0	ϵ_s	0	0	0	0	0	0
$\langle P_x \uparrow $	0	0	ϵ_p	0	$-i\Delta/3$	0	0	$\Delta/3$
$\langle P_x \downarrow $	0	0	0	ϵ_p	0	$i\Delta/3$	$-i\Delta/3$	0
$\langle P_y \uparrow $	0	0	$i\Delta/3$	0	ϵ_p	0	0	$-i\Delta/3$
$\langle P_y \downarrow $	0	0	0	$-i\Delta/3$	0	ϵ_p	$-i\Delta/3$	0
$\langle P_z \uparrow $	0	0	0	$-i\Delta/3$	0	$i\Delta/3$	ϵ_p	0
$\langle P_z \downarrow $	0	0	$\Delta/3$	0	$i\Delta/3$	0	0	ϵ_p

- Now spin orbit coupling H_{so} has been included
- H_{so} couples the p-like valence band states but does not affect the s-like conduction band states

To diagonalize H in the presence of H_{SO} we define new basis $|\frac{3}{2}, \frac{3}{2}\rangle, |\frac{3}{2}, -\frac{3}{2}\rangle, |\frac{3}{2}, \frac{1}{2}\rangle, |\frac{3}{2}, -\frac{1}{2}\rangle,$

$|\frac{1}{2}, \frac{1}{2}\rangle, |\frac{1}{2}, -\frac{1}{2}\rangle$ in terms of the old basis $|P_x \uparrow\rangle, |P_x \downarrow\rangle,$

$|P_y \uparrow\rangle, |P_y \downarrow\rangle, |P_z \uparrow\rangle, |P_z \downarrow\rangle$ as follows:

$$|\frac{3}{2}, \frac{3}{2}\rangle = -\frac{1}{\sqrt{2}} |P_x \uparrow\rangle - \frac{i}{\sqrt{2}} |P_y \uparrow\rangle \quad \left. \vphantom{|\frac{3}{2}, \frac{3}{2}\rangle} \right\} \text{energy } E_p + \frac{\Delta}{3}$$

$$|\frac{3}{2}, -\frac{3}{2}\rangle = \frac{1}{\sqrt{2}} |P_x \downarrow\rangle - \frac{i}{\sqrt{2}} |P_y \downarrow\rangle \quad \left. \vphantom{|\frac{3}{2}, -\frac{3}{2}\rangle} \right\}$$

$$|\frac{3}{2}, \frac{1}{2}\rangle = -\frac{1}{\sqrt{6}} |P_x \downarrow\rangle - \frac{i}{\sqrt{6}} |P_y \downarrow\rangle + \sqrt{\frac{2}{3}} |P_z \uparrow\rangle \quad \left. \vphantom{|\frac{3}{2}, \frac{1}{2}\rangle} \right\} \text{energy } E_p + \frac{\Delta}{3}$$

$$|\frac{3}{2}, -\frac{1}{2}\rangle = \frac{1}{\sqrt{6}} |P_x \uparrow\rangle - \frac{i}{\sqrt{6}} |P_y \uparrow\rangle + \sqrt{\frac{2}{3}} |P_z \downarrow\rangle \quad \left. \vphantom{|\frac{3}{2}, -\frac{1}{2}\rangle} \right\}$$

$$|\frac{1}{2}, \frac{1}{2}\rangle = \frac{1}{\sqrt{3}} |P_x \downarrow\rangle + \frac{i}{\sqrt{3}} |P_y \downarrow\rangle + \frac{1}{\sqrt{3}} |P_z \uparrow\rangle \quad \left. \vphantom{|\frac{1}{2}, \frac{1}{2}\rangle} \right\} \text{energy } E_p - \frac{2\Delta}{3}$$

$$|\frac{1}{2}, -\frac{1}{2}\rangle = \frac{1}{\sqrt{3}} |P_x \uparrow\rangle - \frac{i}{\sqrt{3}} |P_y \uparrow\rangle - \frac{1}{\sqrt{3}} |P_z \downarrow\rangle \quad \left. \vphantom{|\frac{1}{2}, -\frac{1}{2}\rangle} \right\}$$

$|\frac{3}{2}, \frac{3}{2}\rangle, |\frac{3}{2}, -\frac{3}{2}\rangle$ are the heavy hole states at $\vec{k}=0$

$|\frac{3}{2}, \frac{1}{2}\rangle, |\frac{3}{2}, -\frac{1}{2}\rangle$ are the light hole states at $\vec{k}=0$

$|\frac{1}{2}, \frac{1}{2}\rangle, |\frac{1}{2}, -\frac{1}{2}\rangle$ are the split-off hole states, at $\vec{k}=0$.

The Matrix H for k=0

$\langle S \uparrow $	$ S \downarrow \rangle$	$\langle \frac{3}{2}, \frac{3}{2} $	$\langle \frac{3}{2}, -\frac{3}{2} $	$\langle \frac{3}{2}, \frac{1}{2} $	$\langle \frac{3}{2}, -\frac{1}{2} $	$\langle \frac{1}{2}, \frac{1}{2} $	$\langle \frac{1}{2}, -\frac{1}{2} $
$\langle S \uparrow $	0	0	0	0	0	0	0
$\langle S \downarrow $	ϵ_s	0	0	0	0	0	0
$\langle \frac{3}{2}, \frac{3}{2} $	0	$\epsilon_p + \Delta/3$	0	0	0	0	0
$\langle \frac{3}{2}, -\frac{3}{2} $	0	0	$\epsilon_p + \Delta/3$	0	0	0	0
$\langle \frac{3}{2}, \frac{1}{2} $	0	0	0	$\epsilon_p + \Delta/3$	0	0	0
$\langle \frac{3}{2}, -\frac{1}{2} $	0	0	0	0	$\epsilon_p + \Delta/3$	0	0
$\langle \frac{1}{2}, \frac{1}{2} $	0	0	0	0	0	$\epsilon_p + \Delta/3$	0
$\langle \frac{1}{2}, -\frac{1}{2} $	0	0	0	0	0	0	$\epsilon_p - 2\Delta/3$

• After basis have been rotated to diagonalize H_{so}

• Bandgap = $E_g = \epsilon_s - \left[\epsilon_p + \frac{\Delta}{3} \right]$

So finally we can write the Bloch functions at $\vec{k}=0$ for the six valence bands (including spin) and the two conduction bands (including spin).

Conduction Band: $\frac{|S\uparrow\rangle}{\sqrt{N}}$, $\frac{|S\downarrow\rangle}{\sqrt{N}}$

Heavy Hole Band: $\frac{|\frac{3}{2}, \frac{3}{2}\rangle}{\sqrt{N}}$, $\frac{|\frac{3}{2}, -\frac{3}{2}\rangle}{\sqrt{N}}$

Light Hole Band: $\frac{|\frac{3}{2}, \frac{1}{2}\rangle}{\sqrt{N}}$, $\frac{|\frac{3}{2}, -\frac{1}{2}\rangle}{\sqrt{N}}$

Split-off Hole Band: $\frac{|\frac{1}{2}, \frac{1}{2}\rangle}{\sqrt{N}}$, $\frac{|\frac{1}{2}, -\frac{1}{2}\rangle}{\sqrt{N}}$

$$\left\{ \text{Note that } |\Psi_{n, \vec{k}=0}\rangle = \frac{1}{\sqrt{N}} |U_{n, \vec{k}=0}\rangle \right\}$$

Question: What about Bloch functions for $\vec{k} \neq 0$ and in the presence of \hat{H}_{SO} (Now we are getting closer to reality !!).

Let's recap where we stand so far. Including spin degree of freedom, there are 8 bands we are interested in. (this counting includes 2 conduction bands, 6 valence bands). For these 8 bands we also have the Bloch functions at $\vec{k}=0$. These are as follows (and I have labeled them 1, 2, 3... 8).

Conduction Bands: $\psi_{1, \vec{k}=0}(\vec{r}) = \frac{|S\uparrow\rangle}{\sqrt{N}} \Rightarrow U_{1, \vec{k}=0}(\vec{r}) = |S\uparrow\rangle$

$\psi_{2, \vec{k}=0}(\vec{r}) = \frac{|S\downarrow\rangle}{\sqrt{N}} \Rightarrow U_{2, \vec{k}=0}(\vec{r}) = |S\downarrow\rangle$

Heavy Hole Bands: $\psi_{3, \vec{k}=0}(\vec{r}) = \frac{|\frac{3}{2}, \frac{3}{2}\rangle}{\sqrt{N}} \Rightarrow U_{3, \vec{k}=0}(\vec{r}) = |\frac{3}{2}, \frac{3}{2}\rangle$

$\psi_{4, \vec{k}=0}(\vec{r}) = \frac{|\frac{3}{2}, -\frac{3}{2}\rangle}{\sqrt{N}} \Rightarrow U_{4, \vec{k}=0}(\vec{r}) = |\frac{3}{2}, -\frac{3}{2}\rangle$

Light Hole Bands: $\psi_{5, \vec{k}=0}(\vec{r}) = \frac{|\frac{3}{2}, \frac{1}{2}\rangle}{\sqrt{N}} \Rightarrow U_{5, \vec{k}=0}(\vec{r}) = |\frac{3}{2}, \frac{1}{2}\rangle$

$\psi_{6, \vec{k}=0}(\vec{r}) = \frac{|\frac{3}{2}, -\frac{1}{2}\rangle}{\sqrt{N}} \Rightarrow U_{6, \vec{k}=0}(\vec{r}) = |\frac{3}{2}, -\frac{1}{2}\rangle$

Split-off Hole Band: $\psi_{7, \vec{k}=0}(\vec{r}) = \frac{|\frac{1}{2}, \frac{1}{2}\rangle}{\sqrt{N}} \Rightarrow U_{7, \vec{k}=0}(\vec{r}) = |\frac{1}{2}, \frac{1}{2}\rangle$

$\psi_{8, \vec{k}=0}(\vec{r}) = \frac{|\frac{1}{2}, -\frac{1}{2}\rangle}{\sqrt{N}} \Rightarrow U_{8, \vec{k}=0}(\vec{r}) = |\frac{1}{2}, -\frac{1}{2}\rangle$

I also know the energies of these bands at $\vec{k}=0$. These are

as follows:

$$E_1(\vec{k}=0) = E_2(\vec{k}=0) = E_s$$

$$E_3(\vec{k}=0) = E_4(\vec{k}=0) = E_5(\vec{k}=0) = E_6(\vec{k}=0) = E_p + \frac{\Delta}{3}$$

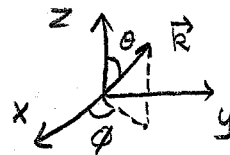
$$E_7(\vec{k}=0) = E_8(\vec{k}=0) = E_p - \frac{2\Delta}{3}$$

Question:

What about Bloch functions at $\vec{k} \neq 0$?

Let \vec{k} be defined in Spherical Co-ordinates as:

$$\vec{k} = k \left[\sin\theta \cos\phi \hat{x} + \sin\theta \sin\phi \hat{y} + \cos\theta \hat{z} \right]$$



Define spin state $|\uparrow\rangle_{\theta\phi}$ pointing in the (θ, ϕ) direction as:

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

Recall that $|\uparrow\rangle$ & $|\downarrow\rangle$ point in the $+z$ & $-z$ directions, respectively.

$|\downarrow\rangle_{\theta\phi}$ points in the $-ve$ $\theta\phi$ -direction (or equivalently the $\theta+\pi, \phi$ -direction)

We also need to define $|p_x\rangle_{\theta\phi}$, $|p_y\rangle_{\theta\phi}$, $|p_z\rangle_{\theta\phi}$ and $|s\rangle_{\theta\phi}$:

$$|s\rangle_{\theta\phi} = |s\rangle$$

and:

$$\begin{bmatrix} |P_x\rangle_{\theta\phi} \\ |P_y\rangle_{\theta\phi} \\ |P_z\rangle_{\theta\phi} \end{bmatrix} = \begin{bmatrix} \cos\theta \cos\phi & \cos\theta \sin\phi & -\sin\theta \\ -\sin\phi & \cos\phi & 0 \\ \sin\theta \cos\phi & \sin\theta \sin\phi & \cos\theta \end{bmatrix} \begin{bmatrix} |P_x\rangle \\ |P_y\rangle \\ |P_z\rangle \end{bmatrix}$$

Similarly, one can define states $|\frac{3}{2}, \frac{3}{2}\rangle_{\theta\phi}$, $|\frac{3}{2}, -\frac{3}{2}\rangle_{\theta\phi}$

$|\frac{3}{2}, \frac{1}{2}\rangle_{\theta\phi}$, $|\frac{3}{2}, -\frac{1}{2}\rangle_{\theta\phi}$, $|\frac{1}{2}, \frac{1}{2}\rangle_{\theta\phi}$, $|\frac{1}{2}, -\frac{1}{2}\rangle_{\theta\phi}$. For example,

$|\frac{3}{2}, \frac{3}{2}\rangle_{\theta\phi}$ is

$$|\frac{3}{2}, \frac{3}{2}\rangle_{\theta\phi} = -\frac{1}{\sqrt{2}} |P_x\rangle_{\theta\phi} |\uparrow\rangle_{\theta\phi} - \frac{i}{\sqrt{2}} |P_y\rangle_{\theta\phi} |\uparrow\rangle_{\theta\phi}$$

$$\left\{ \begin{aligned} \text{Recall that } |\frac{3}{2}, \frac{3}{2}\rangle &= -\frac{1}{\sqrt{2}} |P_x\rangle |\uparrow\rangle - \frac{i}{\sqrt{2}} |P_y\rangle |\uparrow\rangle \\ &= -\frac{1}{\sqrt{2}} |P_x\uparrow\rangle - \frac{i}{\sqrt{2}} |P_y\uparrow\rangle \end{aligned} \right\}$$

Now we state the important result that comes out of much more detailed band structure calculations.

For $\vec{k}=0$, the $U_{\vec{k}=0}(\vec{r})$ functions are $|s\uparrow\rangle, |s\downarrow\rangle, |\frac{3}{2}, \frac{3}{2}\rangle, |\frac{3}{2}, -\frac{3}{2}\rangle$

$|\frac{3}{2}, \frac{1}{2}\rangle, |\frac{3}{2}, -\frac{1}{2}\rangle, |\frac{1}{2}, \frac{1}{2}\rangle, |\frac{1}{2}, -\frac{1}{2}\rangle$. For \vec{k} given by

$$\vec{k} = k \left[\sin\theta \cos\phi \hat{x} + \sin\theta \sin\phi \hat{y} + \cos\theta \hat{z} \right]$$

(i.e. magnitude k and pointing in the θ, ϕ -direction) the

functions $U_{n, \vec{k}}(\vec{r})$ are $|s\rangle | \downarrow \rangle_{\theta\phi}$, $|s\rangle | \uparrow \rangle_{\theta\phi}$, $|\frac{3}{2}, \frac{3}{2}\rangle_{\theta\phi}$, $|\frac{3}{2}, -\frac{3}{2}\rangle_{\theta\phi}$

$|\frac{3}{2}, \frac{1}{2}\rangle_{\theta\phi}$, $|\frac{3}{2}, -\frac{1}{2}\rangle_{\theta\phi}$, $|\frac{1}{2}, \frac{1}{2}\rangle_{\theta\phi}$, $|\frac{1}{2}, -\frac{1}{2}\rangle_{\theta\phi}$, provided the magnitude of \vec{k} is not too large.

Observation: the functions $U_{n, \vec{k}}(\vec{r})$ for $\vec{k} \neq 0$, for small $|\vec{k}|$, depend only on the direction of \vec{k} and not its magnitude. Of course, this is an approximation—but generally a good one.

Optical Matrix Elements:

For optical transitions we need to calculate the quantity

$$\begin{aligned} \vec{P}_{c,v}(\vec{k}) \cdot \hat{n} &= \int_{\text{one cell}} d^3r \ U_{c, \vec{k}}^*(\vec{r}) \ \hat{n} \cdot \frac{\hbar}{i} \vec{\nabla} \ U_{v, \vec{k}}(\vec{r}) \\ &= \langle U_{c, \vec{k}} | \hat{n} \cdot \vec{P} | U_{v, \vec{k}} \rangle \end{aligned}$$

where \hat{n} is the unit vector pointing in the direction of the polarization of the (electric) field. Let \hat{n} be expressed in

Spherical Co-ordinates as :

$$\hat{n} = \left[\sin\theta_n \cos\phi_n \hat{x} + \sin\theta_n \sin\phi_n \hat{y} + \cos\theta_n \hat{z} \right] = n_x \hat{x} + n_y \hat{y} + n_z \hat{z}$$

Define a material parameter P as:

$$iP = \frac{\hbar}{m_0} \langle s | \hat{P}_z | p_z \rangle = \frac{\hbar}{m_0} \langle s | \hat{P}_y | p_y \rangle = \frac{\hbar}{m_0} \langle s | \hat{P}_x | p_x \rangle$$

Using P, we can calculate the optical matrix elements as follows:

Optical Transitions Between Conduction Bands and Heavy Hole Bands :

Need to calculate matrix elements for $|s\rangle | \uparrow \rangle_{\theta\phi}$, $|s\rangle | \downarrow \rangle_{\theta\phi}$

and $|\frac{3}{2}, \frac{3}{2}\rangle_{\theta\phi}$, $|\frac{3}{2}, -\frac{3}{2}\rangle_{\theta\phi}$.

The two non-zero ones are:

$${}_{\theta\phi} \langle \uparrow | \langle s | \vec{P} \cdot \hat{n} | \frac{3}{2}, \frac{3}{2} \rangle_{\theta\phi} = \frac{iPm_0}{\hbar} \left\{ \begin{aligned} & -\frac{1}{\sqrt{2}} (\cos\theta \cos\phi - i \sin\phi) n_x \\ & -\frac{1}{\sqrt{2}} (\cos\theta \sin\phi + i \cos\phi) n_y \\ & + \frac{1}{\sqrt{2}} \sin\theta n_z \end{aligned} \right\}$$

$${}_{\theta\phi} \langle \downarrow | \langle s | \vec{P} \cdot \hat{n} | \frac{3}{2}, -\frac{3}{2} \rangle_{\theta\phi} = \frac{iPm_0}{\hbar} \left\{ \begin{aligned} & \frac{1}{\sqrt{2}} (\cos\theta \cos\phi + i \sin\phi) n_x \\ & + \frac{1}{\sqrt{2}} (\cos\theta \sin\phi - i \cos\phi) n_y \\ & - \frac{1}{\sqrt{2}} \sin\theta n_z \end{aligned} \right\}$$

So only transitions in the pairs $\left\{ \left| \frac{3}{2}, \frac{3}{2} \right\rangle_{\theta\phi} \leftrightarrow |s\rangle |\uparrow\rangle_{\theta\phi} \right\}$ and

$\left\{ \left| \frac{3}{2}, -\frac{3}{2} \right\rangle_{\theta\phi} \leftrightarrow |s\rangle |\downarrow\rangle_{\theta\phi} \right\}$ are possible.

Recall that when calculating the transition rates we had an expression that contained an integral,

$$2 \times \int \frac{d^3k}{(2\pi)^3} \left| \vec{P}_v(\vec{k}) \cdot \hat{n} \right|^2 \dots \dots \dots$$

For the conduction band-heavy hole band transitions we replace the above with

$$\int \frac{d^3k}{(2\pi)^3} \left\{ \left| \langle \uparrow | \langle s | \vec{P} \cdot \hat{n} \left| \frac{3}{2}, \frac{3}{2} \right\rangle_{\theta\phi} \right|^2 + \left| \langle \downarrow | \langle s | \vec{P} \cdot \hat{n} \left| \frac{3}{2}, -\frac{3}{2} \right\rangle_{\theta\phi} \right|^2 \right\} \dots \dots \dots$$

Since the remaining portion of the integral contains terms that do not depend on the direction of \vec{k} (only on its magnitude) one can angular average the matrix elements without affecting the integral.

$$\frac{1}{4\pi} \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \left\{ \left| \langle \uparrow | \langle s | \vec{P} \cdot \hat{n} \left| \frac{3}{2}, \frac{3}{2} \right\rangle_{\theta\phi} \right|^2 + \left| \langle \downarrow | \langle s | \vec{P} \cdot \hat{n} \left| \frac{3}{2}, -\frac{3}{2} \right\rangle_{\theta\phi} \right|^2 \right\}$$

$$= \frac{m_0^2 p^2}{3\hbar^2} + \frac{m_0^2 p^2}{3\hbar^2} = \text{independent of } \hat{n} = n_x \hat{x} + n_y \hat{y} + n_z \hat{z} !!$$

$$= \frac{2}{3} \frac{m_0^2 p^2}{\hbar^2} = \frac{m_0}{3} E_p \quad \left\{ \text{where } E_p = \frac{2m_0 p^2}{\hbar^2} \text{ (units: energy)} \right.$$

In handout #3, the optical gain was given by the expression:

$$g = \frac{\pi e^2}{\epsilon_0 m_0^2 n \omega c} |\vec{P}_{vc} \cdot \hat{n}|^2 2 \times \int \frac{d^3 k}{(2\pi)^3} \left\{ \delta(E_v(\vec{k}) + \hbar\omega - E_c(\vec{k}')) \left[f(E_c(\vec{k}) - E_{fe}) - f(E_v(\vec{k}) - E_{fh}) \right] \right\}$$

For conduction band to heavy-hole band transitions, the expression for $g = g_{c-hh}$ is:

$$g_{c-hh} = \frac{\pi e^2}{\epsilon_0 m_0^2 n \omega c} \cdot \frac{m_0 E_p}{3} \cdot \int \frac{d^3 k}{(2\pi)^3} \left\{ \delta(E_{hh}(\vec{k}) + \hbar\omega - E_c(\vec{k})) \left[f(E_c(\vec{k}) - E_{fe}) - f(E_{hh}(\vec{k}) - E_{fh}) \right] \right\}$$

And if you wanted α_{c-hh} you would just replace

$$\left[f(E_c(\vec{k}) - E_{fe}) - f(E_{hh}(\vec{k}) - E_{fh}) \right] \text{ by } f(E_{hh}(\vec{k}) - E_{fh}) \left[1 - f(E_c(\vec{k}) - E_{fe}) \right]$$

inside the integral.

Optical Transitions Between Conduction Bands and Light Hole Bands:

Need to calculate matrix elements for $|s\rangle|\uparrow\rangle_{\phi}$, $|s\rangle|\downarrow\rangle_{\phi}$

and $|\frac{3}{2}, \frac{1}{2}\rangle_{\phi}$, $|\frac{3}{2}, -\frac{1}{2}\rangle_{\phi}$. Here all four possible

transitions $\left\{ |\frac{3}{2}, \frac{1}{2}\rangle_{\phi} \leftrightarrow |s\rangle|\uparrow\rangle_{\phi} \right\}$, $\left\{ |\frac{3}{2}, -\frac{1}{2}\rangle_{\phi} \leftrightarrow |s\rangle|\uparrow\rangle_{\phi} \right\}$

$$\left\{ \left| \frac{3}{2}, \frac{1}{2} \right\rangle_{\theta\phi} \leftrightarrow |s\rangle | \downarrow \rangle_{\theta\phi} \right\}, \left\{ \left| \frac{3}{2}, -\frac{1}{2} \right\rangle_{\theta\phi} \leftrightarrow |s\rangle | \downarrow \rangle_{\theta\phi} \right\} \text{ can}$$

happen since their momentum matrix element is non-zero.

So the "averaged" matrix elements are:

$$\begin{aligned} & \frac{1}{4\pi} \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi \left\{ \left| \langle \uparrow | \langle s | \vec{p} \cdot \hat{n} \left| \frac{3}{2}, \frac{1}{2} \right\rangle_{\theta\phi} \right|^2 \right. \\ & \quad \left. + \left| \langle \uparrow | \langle s | \vec{p} \cdot \hat{n} \left| \frac{3}{2}, -\frac{1}{2} \right\rangle_{\theta\phi} \right|^2 \right\} + \\ & \quad \left\{ \left| \langle \downarrow | \langle s | \vec{p} \cdot \hat{n} \left| \frac{3}{2}, \frac{1}{2} \right\rangle_{\theta\phi} \right|^2 \right. \\ & \quad \left. + \left| \langle \downarrow | \langle s | \vec{p} \cdot \hat{n} \left| \frac{3}{2}, -\frac{1}{2} \right\rangle_{\theta\phi} \right|^2 \right\} \\ & = \frac{m_0^2 p^2}{3 k^2} + \frac{m_0^2 p_0^2}{3 k^2} = \frac{2}{3} \frac{m_0^2 p^2}{k^2} = \text{independent of } \hat{n} = n_x \hat{x} + n_y \hat{y} + n_z \hat{z} \\ & \quad \text{again.} \end{aligned}$$

Lesson: In bulk semiconductors, optical transition rates for conduction-heavy hole or for conduction-light hole transitions do not depend upon the polarization of the light. This is true only for bulk - does not work in lower dimensional systems (like quantum wells).

Finally we can write expression for the gain g_{c-h}

as

$$g_{c-eh} = \frac{\pi e^2}{\epsilon_0 m_0^2 n \omega c} \cdot \frac{m_0 E_F}{3} \int \frac{d^3 k}{(2\pi)^3} \left\{ \delta(E_{eh}(\vec{k}) + \hbar \omega - E_c(\vec{k})) \left[f(E_c(\vec{k}) - E_{fe}) - f(E_{eh}(\vec{k}) - E_{fh}) \right] \right\}$$

and for low ω , replace $\left[f(E_c(\vec{k}) - E_{fe}) - f(E_{eh}(\vec{k}) - E_{fh}) \right]$
by $f(E_{eh}(\vec{k}) - E_{fh}) \left[1 - f(E_c(\vec{k}) - E_{fe}) \right]$ in the integral above.

Final Note: values of E_F for different materials are given in the table in Homework 2.