Band Structure in Semiconductors:

Direct-Gap Semiconductor: For a simplified picture of band structure (Fig 1.5) in direct-gap semiconductor, the conduction band edge is spherically symmetric, with the effective mass \( m_e^* \):

\[
E_c(k) = E_g + \frac{\hbar^2 k^2}{2m_e^*},
\]

where \( E_g \) is the band gap and energy zero is taken at the valence band edge.

The valence bands are typically three-fold degenerate near the edge with heavy hole (hh) and light hole (lh) degenerate at the centre, and a band split-off holes (soh), arising from spin orbit splitting:

\[
E_{v,\text{hh}}(k) = -\frac{\hbar^2 k^2}{2m_{\text{hh}}^*}, \quad E_{v,\text{lh}}(k) = -\frac{\hbar^2 k^2}{2m_{\text{lh}}^*},
\]

\[
E_{v,\text{soh}}(k) = -\Delta - \frac{\hbar^2 k^2}{2m_{\text{soh}}^*}.
\]

These are only approximately applicable, as in real semiconductors, the heavy and light hole bands are not spherical even near \( k = 0 \). Some typical (approximate) values of the effective masses are listed below (in unit of \( m_e^* \), bare electron mass, i.e., for free electron):

<table>
<thead>
<tr>
<th>Material</th>
<th>( m_e^* / m_e )</th>
<th>( m_{\text{hh}}^* / m_e )</th>
<th>( m_{\text{lh}}^* / m_e )</th>
<th>( m_{\text{soh}}^* / m_e )</th>
<th>( \Delta \text{(eV)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>InSb</td>
<td>0.015</td>
<td>0.39</td>
<td>0.021</td>
<td>0.11</td>
<td>0.82</td>
</tr>
<tr>
<td>InAs</td>
<td>0.026</td>
<td>0.41</td>
<td>0.425</td>
<td>0.08</td>
<td>0.43</td>
</tr>
<tr>
<td>InP</td>
<td>0.073</td>
<td>0.4</td>
<td>0.078</td>
<td>0.15</td>
<td>0.11</td>
</tr>
<tr>
<td>GaSb</td>
<td>0.047</td>
<td>0.3</td>
<td>0.06</td>
<td>0.14</td>
<td>0.80</td>
</tr>
<tr>
<td>GaAs</td>
<td>0.066</td>
<td>0.45</td>
<td>0.082</td>
<td>0.17</td>
<td>0.34</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>0.99</td>
<td>--</td>
<td>0.58</td>
<td>0.69</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Note: Hole masses are always more uncertain as it is difficult to measure them with high accuracy.

The perturbation theory \((\vec{k} \cdot \vec{p})\) method of band edges suggests that the electron effective mass should be proportional to the band gap, approximately, for a direct gap crystal. From the listed numbers, one finds:

\[
\frac{m_e^*}{m_e E_g} = 0.063 \text{ for InSb (in eV}^{-1})
\]

\[
= 0.060 \text{ for InAs (in eV}^{-1})
\]

\[
= 0.051 \text{ for InP (in eV}^{-1})
\]
The valence band edge in both crystals (Fig 1.6) is derived from $P_{3/2}$ and $P_{1/2}$ states of free atoms. The $P_{3/2}$ is 4-fold degenerate as in atom, the four states corresponding to $m_j$ values $\pm \frac{3}{2}$ and $\pm \frac{1}{2}$. The $P_{1/2}$ level is doubly degenerate, with $m_j = \pm \frac{1}{2}$. The $P_{3/2}$ states are higher in energy than the $P_{1/2}$ states and the energy difference $\Delta$ is a measure of the spin orbit interaction. At the valence band edge (at $k_z = 0$), the $P_{3/2}$ level produces two bands, characterized by light and heavy hole effective masses. There is also a band formed from the $P_{1/2}$ level, split off from the $P_{3/2}$ level by the spin orbit interaction. However the bands are not spherical but warped and may be described by:

$$E(k) = A k^2 \pm \sqrt{B^2 k^4 + C^2 (k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2)}$$

where for Si: $A = -4.29$, $B = 0.68$, $C = 4.87$ (all in $k^2/2m_0$)

Ge: $A = -13.38$, $B = 8.48$, $C = 13.15$ (all in $k^2/2m_0$)

For the split-off band, $E(k) = -\Delta + Ak^2$, where $\Delta = 0.049$ eV for Si and $\Delta = 0.029$ eV for Ge.

Roughly, the light and heavy holes in Ge has $m_{lh}^* \approx 0.043 m_e$ and $m_{hh}^* \approx 0.34 m_e$; in Si $m_{lh} \approx 0.16 m_e$ and $m_{hh}^* \approx 0.52 m_e$ (in C i.e., diamond, $m_{lh}^* \approx 0.7 m_e$ and $m_{hh}^* \approx 2.12 m_e$); $E_g \approx 0.9$ eV. In indirect gap materials (such as Si) the bottom of the conduction band does not occur at $k = 0$, but at six equivalent minima along the $k_x$, $k_y$ and $k_z$ axes. For Si, $\vec{k}$ values at the minima are $\pm 2\pi (\xi_0, 0, 0)/a$, $\pm 2\pi (0, \xi_0, 0)/a$, $\pm 2\pi (0, 0, \xi_0)/a$, $\xi_0 = 0.85$, $a = 5.43$ Å

The region around each minimum is called a valley (in this case six in numbers). For valleys along $k_x$ axes and $-k_x$ axis:

$$k_{ox} = \frac{2\pi}{a} (\xi_0, 0, 0), \quad k_{ox} = \frac{2\pi}{a} (-\xi_0, 0, 0)$$

$$E(\vec{k}) = E_c + \frac{\hbar^2}{2} \left[ \frac{(k_x - k_{ox})^2}{m_t^*} + \frac{k_y^2 + k_z^2}{m_t^*} \right]$$
Along $k_y$ and $-k_y$ axis: $k_{oy} = \frac{2\pi}{a} (0, \xi_0, 0)$, $k_{oy} = \frac{2\pi}{a} (0, -\xi_0, 0)$

$$E(\bar{k}) = E_c + \frac{\hbar^2}{2} \left[ \frac{(k_y - k_{oy})^2}{m_i^*} + \frac{k_x^2 + k_z^2}{m_t^*} \right]$$

Along $k_z$ and $-k_z$: $k_{oz} = \frac{2\pi}{a} (0, 0, \xi_0)$, $k_{oz} = \frac{2\pi}{a} (0, 0, -\xi_0)$

$$E(\bar{k}) = E_c + \frac{\hbar^2}{2} \left[ \frac{(k_z - k_{oz})^2}{m_i^*} + \frac{k_x^2 + k_y^2}{m_t^*} \right]$$

The constant energy surfaces near the valleys thus correspond to spheroids at the band edges, the spheroids being oriented along $(100), (\bar{1}0\bar{0}), (010), (0\bar{1}0)$ and $(001), (00\bar{1})$ (Fig 1.7). One finds $m_i^* = 0.98 \ m_e$ and $m_t^* = 0.19 \ m_i$. Note that the equivalence of six valleys lead to a degeneracy called valley-degeneracy, usually denoted by $\eta_v$ ($=6$ for Si).