Band theory

Energy bands can also be understood by considering mutual interactions of electronic wave functions of atoms constituting the solid. When a large number of atoms are brought together, energy levels split, yielding many new orbitals. The difference in energy between them becomes very small, so the levels may be considered as forming continuous bands of energy. Some intervals of energy contain no orbitals, no matter how many atoms are aggregated, forming band gaps.

Electric conduction in solids

*Insulators* conduction band is totally empty, while their valence band is entirely occupied. Electrons, then, may not contribute to the electrical conductivity of the material, because no energy level is available for them to acquire kinetic energy and to move.

*Conductors*, or metals are characterized by a partially filled conduction band. Electrons, when subjected to an electric field, may acquire some kinetic energy. The specific electrical conductivity $s$ is given by the product of the density $n$ of charge carriers and their mobility $\mu$:

$$s = |q| \cdot n \cdot \mu \left[ \text{Ω}^{-1} \cdot \text{m}^{-1} \right]$$
Semiconductors are insulators for which a conduction can however be obtained under some conditions. If $E_g < 3k_B T$, for instance, electrons can jump thermally across the band gap and be promoted from the valence band to the conduction band. Both conduction band electrons and valence band holes charge carriers contribute then to the conduction.

Charge carriers can also be produced by chemical doping of the solid. Donor impurities yield $n$-doping (electrons $e_{cb}^-$ carriers). Acceptor impurities produce holes in the valence band ($h_{vb}^+$ carriers) and $p$-doping. In semiconductors, the density of charge carriers $n$ is always rather small.

Intrinsic light absorption

The promotion of an electron from the fully occupied valence band to the conduction band can also be achieved by intrinsic light absorption of photons of energy $h\nu \geq E_g$. The photo-conduction of the semiconductor under band-gap irradiation is due to both $e_{cb}^-$ and $h_{vb}^+$ charge carriers.

Example:

Titanium dioxide TiO$_2$ is a solid with a rather ionic character. It can be seen as being constituted of Ti$^{4+}$ and O$^{2-}$ ions.

\[
\text{Ti} \quad 3d^2 \quad 4s^2 \quad \rightarrow \quad \text{Ti}^{4+} \quad 3d^0 \quad \text{empty conduction band}
\]

\[
\text{O} \quad 2p^4 \quad \rightarrow \quad \text{O}^{2-} \quad 2p^6 \quad \text{entirely occupied valence band}.
\]

Photons of energy $h\nu \geq E_g = 3.2 \text{ eV (} \lambda \leq 380 \text{ nm)}$ are absorbed, yielding a transition $2p(O) \rightarrow 3d(Ti)$. 

**Band structure**

Band structure in the *reciprocal space* is a compact and elegant way to represent all electronic states in a periodic system. In such a representation, bands appear ideally as a series of de Broglie’s parabolas $E = f(k)$:

$$E = \frac{p^2}{2m_e} = \frac{\hbar^2 \cdot k^2}{2m_e}$$

where $k$ is the wave vector of a charge carrier and $p$ its momentum: $k = 2\pi \cdot p / \hbar$

However, because $m_e^*$ is not the same in all directions of the 3D space, a complex structure is observed rather than simple parabolas.

**Direct vs indirect transitions**

Since photons do not carry any mechanical momentum, $k$ should remain unchanged during an electronic transition if no vibration is coupled to it. A transition following the Frank-Condon principle ($k$ constant) is called a *direct transition*.

$$h\nu = E_g \quad \Delta k = 0$$

An *indirect transition* implies a vibration of the solid lattice is coupled to the electronic movement. The change of the momentum is brought by absorption of a phonon of energy $E_p$ ($\Delta k > 0$) or released during the emission of a phonon in the solid ($\Delta k > 0$).

$$h\nu = E_g \pm E_p \quad \Delta k = \pm k_p$$

**Band structure of TiO$_2$ rutile. Left: Energy vs. wave vector along symmetry lines in the Brillouin zone. Right: schematic of energy bands.**
Excitonic absorption

An exciton is an electron-hole pair in which charge carriers are bound together by Coulombic interaction. The exciton is a neutral entity which can move easily in an insulator and carry excitation energy.

- **Exciton bond energy** $E_x [\text{meV}]$
- 
<table>
<thead>
<tr>
<th>Material</th>
<th>$E_x$</th>
<th>Material</th>
<th>$E_x$</th>
<th>Material</th>
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<td>29</td>
<td>KCl</td>
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<tr>
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<td>4</td>
<td>CdSe</td>
<td>15</td>
<td>KBr</td>
<td>400</td>
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<tr>
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<td>InP</td>
<td>4</td>
<td>AgBr</td>
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</table>
Light absorption by solids

Size and bond energy of an exciton

Bohr’s planetary model (hydrogen atom)

$$r_H = \frac{n^2 \cdot \hbar^2 \cdot E_0}{\mu \cdot e^2} = n^2 \cdot 0.56 \text{Å}$$

with $$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_p} = \frac{1}{m_e}$$

$$r_x = \frac{\hbar^2 \cdot e \cdot E_0}{m' \cdot e^2} = e \cdot \frac{m^*}{m} \cdot r_H$$

with $$\frac{1}{m'} = \frac{1}{m_e} + \frac{1}{m_h}$$

$$E_x = \frac{m^* \cdot e^2}{2m_e \cdot e^2 \cdot r_H} = \frac{m^*}{m_e} \cdot 13.6 \text{ [eV]}$$

Exciton radius $$r_x$$ and bond energy $$E_x$$ [meV]

<table>
<thead>
<tr>
<th>Material</th>
<th>$$E_g / \text{eV}$$</th>
<th>$$m_e^*/m_e$$</th>
<th>$$m_h^*/m_h$$</th>
<th>$$\varepsilon$$</th>
<th>$$r_x / \text{Å}$$</th>
<th>$$E_x / \text{meV}$$</th>
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</thead>
<tbody>
<tr>
<td>CdS</td>
<td>2.6</td>
<td>0.19</td>
<td>0.8</td>
<td>5.7</td>
<td>20.8</td>
<td>64</td>
</tr>
<tr>
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<td>0.45</td>
<td>3.7</td>
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</tr>
<tr>
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<td>4</td>
<td>184</td>
<td>37.8</td>
<td>1.1</td>
</tr>
</tbody>
</table>

for comparison: $$\varepsilon (\text{H}_2\text{O}) = 87$$

Quantum size effect

Confinement of electrons in particles whose size is comparable or smaller than that of the exciton in the bulk material leads to an increase of the excitation energy $$E_g$$.

As a result, the bandgap increases and the absorption threshold shifts to the blue when particle size is decreased.

This quantum size effect, which is a direct evidence of the "particle in a box" concept, allows to adjust the color of colloidal particles of wide bandgap semiconductors.

Left: Absorption spectra of aqueous colloidal suspensions of CdS particles. Particle diameter is reduced from 80 Å to 20 Å, causing an important hypsochromic shift.
Quantum dots

Quantum dots (QDs) are semiconducting nanoparticles in which excitons are confined in all three spatial dimensions. Quantum confinement affects the absorption and emission of photons from the dot. Thus, the absorption edge of a material can be tuned by control of the particle size. Quantum dots are particularly significant for optical applications (bio-imaging, diode lasers, LEDs, solar cells, ...) due to their high extinction coefficients.

Similar to a molecule, a quantum dot has both a quantized energy spectrum and a quantized density of electronic states near the edge of the band gap.