Chapter 7: Optical Properties of Solids

Interaction of light with atoms

<table>
<thead>
<tr>
<th>Allowed</th>
<th>Forbidden</th>
</tr>
</thead>
<tbody>
<tr>
<td>4p</td>
<td>4p</td>
</tr>
<tr>
<td>3d</td>
<td>3d</td>
</tr>
<tr>
<td>Ca</td>
<td></td>
</tr>
<tr>
<td>4p 3s</td>
<td>4s 3p</td>
</tr>
<tr>
<td>4p 2s</td>
<td>4p 2s</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu</td>
</tr>
<tr>
<td>4s 1s</td>
<td>4s 1s</td>
</tr>
<tr>
<td>Ti</td>
<td>Ti</td>
</tr>
<tr>
<td>3s 2p</td>
<td>3s 2p</td>
</tr>
<tr>
<td>O</td>
<td>O</td>
</tr>
</tbody>
</table>

Allowed and forbidden electronic transitions
$\text{Tl}^{3+} \text{ absorption: } e_g \leftarrow t_{2g}$
Initial excitations are spin allowed: $^4T_{2g} \leftarrow ^4A_{1g}$ and $^4T_{1g} \leftarrow ^4A_{1g}$

Red emission at 694 nm

$^2E \rightarrow ^4A_{1g}$

non-radiative transition
Describing electrons in multi-electron systems: L and M

Orbital angular momentum = \( \frac{h}{2\pi} \sqrt{l(l+1)} \)

\[ M_L = \sum m_l \]

Orbital angular momentum has magnitude and \( 2l+1 \) spatial orientations with respect to the z axis (i.e. the number of values of \( m_l \)), vectorial summation of the individual \( l \) values is necessary.

\[ m_l = 2 \quad +2(\frac{h}{2\pi}) \]
\[ m_l = 1 \quad +(\frac{h}{2\pi}) \]
\[ m_l = 0 \quad 0 \]
\[ m_l = -1 \quad -(\frac{h}{2\pi}) \]
\[ m_l = -2 \quad -2(\frac{h}{2\pi}) \]

Describing electrons in multi-electron systems: S and M\(_{S}\)

The spin quantum number, \( s \), determines the magnitude of the spin angular momentum of an electron and has a value of \( \frac{1}{2} \).

For a 1 electron species, \( m_s \) is the magnetic spin angular momentum and has a value of \( +\frac{1}{2} \) or \( -\frac{1}{2} \).

\[ \text{Spin angular momentum} = \left( \sqrt{S(S+1)} \right) \frac{h}{2\pi} \]

\[ M_S = \sum m_s \]

For a system with \( n \) electrons, each having \( s = \frac{1}{2} \), possible values of \( S \) (always positive) fall into two series depending on the total number of electrons:

- \( S = 1/2, 3/2, 5/2, \ldots \) for an odd number of electrons.
- \( S = 0, 1, 2, \ldots \) for an even number of electrons.

For each value of \( S \), there are \( 2S + 1 \) values of \( M_S \):

\[ M_S: \ S, (S-1), \ldots -(S-1), -S \]
Microstates and term symbols

Microstates – the electronic states that are possible for a given electronic configuration.
• no two electrons may have the same set of quantum numbers (Pauli exclusion principle)
• only unique microstates may be included

$ns^2$ configuration

Cannot physically distinguish between the electrons, so must use sets of quantum numbers to decide if the microstates (rows in the table) are the same or different.

First microstate: $l = 0, m_l = 0, m_s = +1/2; \ l = 0, m_l = 0, m_s = -1/2$
Second microstate: $l = 0, m_l = 0, m_s = -1/2; \ l = 0, m_l = 0, m_s = +1/2$

**Table of microstates for an $ns^2$ configuration:**

<table>
<thead>
<tr>
<th>First electron: $m_l = 0$</th>
<th>Second electron: $m_l = 0$</th>
<th>$M_L = \Sigma m_l$</th>
<th>$M_S = \Sigma m_s$</th>
<th>Term Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\uparrow$</td>
<td>$\downarrow$</td>
<td>0</td>
<td>0</td>
<td>$L = 0, S = 0$</td>
</tr>
</tbody>
</table>

$\mathbf{(2S+1)}$ possible values of $J$ for $S < L$, and $\mathbf{(2L+1)}$ possible values of $J$ for $L < S$.

The value of $M_J$ denotes the component of the total angular momentum along the z axis.

Allowed values of $M_J$: $J, J-1, \ldots, -(J-1), -J$.

The method of obtaining $J$ from $L$ and $S$ is based on LS (or Russell–Saunders) coupling, aka spin-orbit coupling.

Describing electrons in multi-electron systems: $J$ and $M_J$

Total angular momentum $J = (\sqrt{J(J+1)}) \frac{\hbar}{2\pi}$

Total angular momentum quantum number $J$ takes values: $(L + S), (L + S -1), \ldots, |L-S|$, and these values can be $0, 1, 2 \ldots$ or $1/2, 3/2, 5/2, \ldots$

$(2S+1)$ possible values of $J$ for $S < L$, and $(2L+1)$ possible values of $J$ for $L < S$.

The value of $M_J$ denotes the component of the total angular momentum along the z axis.

Allowed values of $M_J$: $J, J-1, \ldots, -(J-1), -J$.

The method of obtaining $J$ from $L$ and $S$ is based on LS (or Russell–Saunders) coupling, aka spin-orbit coupling.
Consider a free d\(^3\) ion

\[
\begin{array}{cccccc}
m_i & +2 & +1 & 0 & -1 & -2 \\
\end{array}
\]

How many ways can the electrons be located in the d-orbitals?

Number of microstates = \( \frac{\{2(2l+1)\}!}{x!(2l+1-x)!} \)

What are the values for \(M_L\) and \(M_S\) for the following configurations?

<table>
<thead>
<tr>
<th>(M_L)</th>
<th>(M_S)</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>3/2</td>
<td>+++</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2,1,0)</td>
</tr>
<tr>
<td>5</td>
<td>1/2</td>
<td>++</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2,2,1)</td>
</tr>
</tbody>
</table>

Organize each of the microstates and group by \(M_L\) and \(M_S\) values:

<table>
<thead>
<tr>
<th>(M_L)</th>
<th>(M_S)</th>
<th>3/2</th>
<th>1/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note the symmetry of the configurations if the spins of all the electrons are reversed.
Construct a microstates number table from the previous table

<table>
<thead>
<tr>
<th>M_L</th>
<th>M_S</th>
<th>3/2</th>
<th>1/2</th>
<th>-1/2</th>
<th>-3/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

By examination of the previous we determine there are groups of microstates described by specific terms.

22 microstates spanning $M_L = 5$ to $-5$; $M_S = +1/2$ to $-1/2$.  $^2H$  
18 microstates spanning $M_L = 4$ to $-4$; $M_S = +1/2$ to $-1/2$.  $^2G$  
28 microstates spanning $M_L = 3$ to $-3$; $M_S = +3/2$ to $-3/2$.  $^4F$  
14 microstates spanning $M_L = 3$ to $-3$; $M_S = +1/2$ to $-1/2$.  $^2F$  
2×10 microstates spanning $M_L = 2$ to $-2$; $M_S = +1/2$ to $-1/2$.  $^2D$ (two)  
12 microstates spanning $M_L = 1$ to $-1$; $M_S = +3/2$ to $-3/2$.  $^4P$  
6 microstates spanning $M_L = 1$ to $-1$; $M_S = +1/2$ to $-1/2$.  $^2P$  

$22 + 18 + 28 + 14 + 2 \times 10 + 12 + 6 = 120$ microstates

Using Hund’s rules, predict the ground state term:
1) Term with the higher spin multiplicity has lower energy  
2) If two or more terms have the same multiplicity, the term having the highest value of $L$ has the lowest energy  
3) For terms having the same multiplicity and $L$, the level with the lowest value of $J$ is the lower in energy if the sublevel is less than half filled, and the level with the highest value of $J$ is the more stable if the sublevel is more than half-filled.  (if half filled, $L$ is zero and $J=S$)

The ground state of a free $d^3$ ion is the $^4F$ term.
These are the terms for a free ion, but the terms splits into components in an octahedral field

<table>
<thead>
<tr>
<th>Term</th>
<th>Components in octahedral field</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>$A_{1g}$</td>
</tr>
<tr>
<td>P</td>
<td>$T_{1g}$</td>
</tr>
<tr>
<td>D</td>
<td>$T_{2g} + E_g$</td>
</tr>
<tr>
<td>F</td>
<td>$A_{2g} + T_{2g} + T_{1g}$</td>
</tr>
<tr>
<td>G</td>
<td>$A_{1g} + E_g + T_{2g} + T_{1g}$</td>
</tr>
<tr>
<td>H</td>
<td>$E_g + T_{1g} + T_{1g} + T_{2g}$</td>
</tr>
<tr>
<td>I</td>
<td>$A_{1g} + A_{2g} + E_g + T_{1g} + T_{2g} + T_{2g}$</td>
</tr>
</tbody>
</table>

$^{4}F$, $^{4}P$, $^{2}H$, $^{2}G$, $^{2}F$, $^{2}D$, $^{2}P$
Light Amplification by Stimulated Emission of Radiation (LASER)

- Q switch (like mirror) on one end switches from reflective to transmitting the light and a pulse of light emitted
- Population inversion is created, decay from excited state takes place more slowly than expected for spontaneous emission.
  - Allows pumping of excess of electrons into excited state
  - Electrons in excited state are stimulated to decay by an incident photon of same energy.
  - Cascade effect, generate an intense beam of monochromatic radiation, in-phase and coherent.

### Crystals used as lasers

<table>
<thead>
<tr>
<th>Ion</th>
<th>Host</th>
<th>( \Lambda ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(^{3+})</td>
<td>Sapphire (Al(_2)O(_3))</td>
<td>650-1100 (tunable)</td>
</tr>
<tr>
<td>Nd(^{3+})</td>
<td>Fluorite (CaF(_2))</td>
<td>1046</td>
</tr>
<tr>
<td>Sm(^{3+})</td>
<td>Fluorite</td>
<td>708.5</td>
</tr>
<tr>
<td>Ho(^{3+})</td>
<td>Fluorite</td>
<td>2090</td>
</tr>
<tr>
<td>Nd(^{3+})</td>
<td>CaWO(_4)</td>
<td>1060</td>
</tr>
<tr>
<td>Nd(^{3+})</td>
<td>YVO(_4)</td>
<td>1064</td>
</tr>
</tbody>
</table>
| Nd\(^{3+}\) | \( \text{Y}_2\text{Al}_5\text{O}_{12}\) (YAG) | 1064
|        | \textit{Nd/YAG laser} |                     |

A green laser (typically) is composed of Nd\(^{3+}\) in YVO\(_4\) which emits photons with wavelength 1064 nm, which are frequency doubled to 532 nm by a non-linear optical second harmonic generation material KTP, potassium titanyl phosphate (KTIOPO\(_4\)) crystal.
Laser systems

<table>
<thead>
<tr>
<th>Type</th>
<th>Medium</th>
<th>$\lambda$ (nm)</th>
<th>Avg. Output</th>
<th>Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>He-Ne</td>
<td>633</td>
<td>0.1-50 mw</td>
<td>cw</td>
</tr>
<tr>
<td></td>
<td>Ar</td>
<td>488, 514</td>
<td>5 mW-20 mW</td>
<td>cw</td>
</tr>
<tr>
<td>Solid State</td>
<td>Ruby (Cr:Al$_2$O$_3$)</td>
<td>694</td>
<td>30 mJ-100 J</td>
<td>pulse</td>
</tr>
<tr>
<td></td>
<td>Nd:YAG</td>
<td>1064</td>
<td>10 mJ-100 J</td>
<td>pulse</td>
</tr>
<tr>
<td>Semiconductor</td>
<td>GaAlAs</td>
<td>750-905</td>
<td>1-40 mW</td>
<td>cw</td>
</tr>
<tr>
<td></td>
<td>GaN</td>
<td>405</td>
<td>5 mW</td>
<td>cw</td>
</tr>
<tr>
<td></td>
<td>AlGaN, AlGaAs</td>
<td>630-900</td>
<td>5 mW</td>
<td>cw</td>
</tr>
<tr>
<td>Excimer</td>
<td>ArF</td>
<td>193</td>
<td>50 W</td>
<td>pulse</td>
</tr>
<tr>
<td></td>
<td>XeF</td>
<td>351</td>
<td>30 W</td>
<td>pulse</td>
</tr>
<tr>
<td>Dye tunable</td>
<td></td>
<td>300-1000</td>
<td>2-50 W</td>
<td>cw or pulse</td>
</tr>
</tbody>
</table>

Lasers have different modes: continuous wave (cw) or pulsed.

Phosphors in Fluorescent Lights

Phosphors: solids that absorb energy and re-emit it as light
Spectrum of a "Blacklight"

SrB$_2$O$_7$F: Eu$^{2+}$ phosphor

Phosphor Material Composition

Alkaline earth halophosphates: $3\text{Ca}_3(\text{PO}_4)_2\cdot\text{CaF}_2$ doped with Sb$^{3+}$ and Mn$^{2+}$
Phosphor Material Composition

• Tb\(^{3+}\), Ce\(^{3+}\):LaPO\(_4\)
  or
  Tb\(^{3+}\):CeMgAl\(_{11}\)O\(_{19}\)
  for green and blue.
• Eu:Y\(_2\)O\(_3\) for red

Upconversion

Atomic states of Ho\(^{3+}\)
Absorption spectrum of GaAs

Emission spectrum of hydrogen

Absorption spectrum of GaAs

Photon energy (10^{-19} J)

Linear chain of s orbitals

(a) + + + +

Linear chain of p orbitals

(b) - + - + - + - +
Infinite 1D Chain of H atoms

\[ \chi_0 \quad \chi_1 \quad \chi_2 \quad \chi_3 \quad \chi_4 \]

\[ \begin{array}{c}
\bullet \quad \bullet \quad \bullet \quad \bullet \quad \bullet \\
\bullet \quad \bullet \quad \bullet \quad \bullet \quad \bullet \\
\bullet \quad \bullet \quad \bullet \quad \bullet \quad \bullet \\
\bullet \quad \bullet \quad \bullet \quad \bullet \quad \bullet \\
\bullet \quad \bullet \quad \bullet \quad \bullet \quad \bullet \\
\end{array} \]

\[ k = \pi / a \]

\[ E(k) \]

\[ 0 \quad \frac{k}{\pi / a} \]

\[ k=0 \rightarrow \text{orbital phase does not change when we translate by } a \]

\[ k=\pi / a \rightarrow \text{orbital phase reverses when we translate by } a \]

Band Structure: Linear Chain of F (no mixing)
Energy Bands

Band structure of copper
Energy bands near the junction in a p-n junction

Conduction band

Valence band

$p$-type

$n$-type

neutral $p$-type

depletion region

neutral $n$-type

GaAs

$n$-type $Ga_{1-x}Al_xAs$

$p$-type $Ga_{1-x}Al_xAs$

$E_g(GaAs)$ $E_g(Ga_{1-x}Al_xAs)$

Gallium arsenide laser
Quantum Wells – blue lasers

The Nobel Prize in Physics 2009

Press Release
6 October 2009

The Royal Swedish Academy of Sciences has decided to award the Nobel Prize in Physics for 2009 with one half to

Charles K. Kao
Standard Telecommunication Laboratories, Harlow, UK, and Chinese University of Hong Kong

“for groundbreaking achievements concerning the transmission of light in fibers for optical communication”

and the other half jointly to

Willard S. Boyle and George E. Smith
Bell Laboratories, Murray Hill, NJ, USA

“for the invention of an imaging semiconductor circuit – the CCD sensor”
Refractive Indices

As the angle of incidence increases from 0 to greater angles ...

Values of Refractive index
Water 1.33
Normal glass/acrylic plastic 1.5
Polycarbonate 1.56
Highest optical plastic 1.66
Bismuth glass >2
Diamond 2.42

Calcite (CaCO₃)

- Exhibits birefringence, since it has different polarizabilities in directions of different crystal axes, hence different refractive indices for light polarized perpendicular to these axes.
- The unique axis is the optical axis.
- When light is passed through the material, it splits into two beams travelling at different speeds due to different refractive indices.
- Birefringence can only occur for crystals displaying asymmetry.
- Between 190 and 1700 nm, the ordinary refractive index for calcite varies roughly between 1.6 and 1.4, while the extraordinary refractive index varies between 1.9 and 1.5.
- Ordinary rays polarized in plane perpendicular to optical axis, extraordinary rays polarized in the plane parallel to the optical axis.
**Cloak of Invisibility**

- Uses birefringence in crystals of calcite, with the optical axes of each are at 30° to the interface.

- The path of light is shown by the blue trace.
- The ray exits in the direction it would have if reflected off the surface in the absence of the object and the cloak, as shown by the dashed trace.

Demonstration of a macroscopic volumetric cloaking device operating at visible frequencies, which can conceal objects of sizes of at least 3 orders of magnitude larger than the wavelength of light in all three dimensions, and works for a specific polarization of the incident light.
Optical fibers are used to transmit light in the way metal wires transmit electricity:

- optical communications, data transmitted to intensity, time between pulses and length of a pulse.
- signal must be maintained so that a detectable signal still exists at the other end of the cable (sometimes km) effort spent at reducing energy loss in commercial optical fibers
- laser beam diverges less than conventional light.
- fibers usually constructed with variable refractive index and light is sent down the central core, which is surrounded by a material with a lower refractive index.
  - Light deviating from a straight path is totally internally reflected and hence remains in the core.

An electromagnetic wave is a travelling wave which has time-varying electric and magnetic fields which are perpendicular to each other and the direction of propagation, \( z \).

Traveling wave along \( Z \)

(a) A neutral atom in \( E = 0 \).

(b) Induced dipole moment in a field

Electronic polarization of an atom
Intensity $I$ of light scattered by a single particle from a beam of unpolarized light of wavelength $\lambda$ and intensity $I_0$ is given by:

$$I = I_0 \frac{1 + \cos^2 \theta}{2R^2} \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 - 1}{n^2 + 2} \right)^2 \left( \frac{d}{2} \right)^6$$

where $R$ is the distance to the particle, $\theta$ is the scattering angle, $n$ is the refractive index of the particle, and $d$ is the diameter of the particle.
Photonic Crystals

- The light travelling through can interfere destructively with reflected light.
- Reflected waves are all in phase with one another and out of phase with the incident light, destructive interference occurs.

Metamaterials

Unusual optical, electric and magnetic properties, including a negative refractive index.
- Doppler effect reversed (radiation travelling towards observer is shifted to longer wavelengths, red shifted)
Cloaking

(a) Coordinate Transformation  
(b) Cancellation of scattering