UNIT 4: ORD and CD

(Part I: Polarized Light)

M.Sc. Semester II

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Syllabus

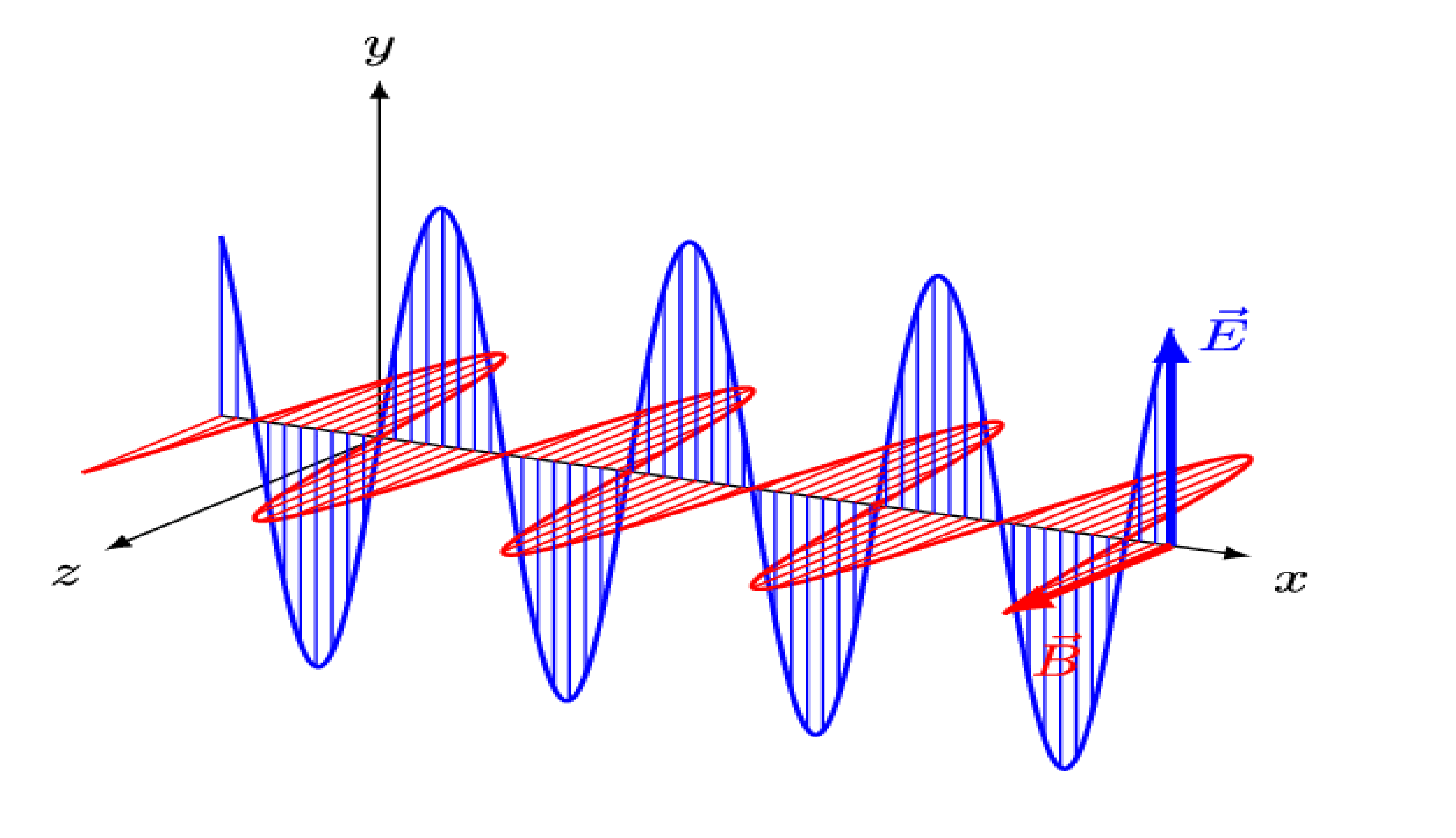
- Basic Principles of ORD and CD techniques;
- ORD and Cotton effect, Faraday and Kerr effects;
- Applications in determining absolute configuration of metal complexes.

Basic Principles

- **Interaction between electromagnetic radiation and matter is the basis of spectroscopy.**
- **Chiroptical Spectroscopy: When the matter under consideration is made up of chiral molecules, a special branch of spectroscopy come into picture, known as *chiroptical spectroscopy*. It is the study of chiral systems using optical spectroscopy methods.**
- **To understand the principles of chiroptical spectroscopy, it is necessary to gain insight into the properties of electromagnetic radiation, chiral molecules, and the interaction between them.**

Polarization of light

An electromagnetic wave is associated with electric and magnetic fields oscillating perpendicular to each other.



For Simplicity, our discussion will only be restricted to Electric Field, E.

Plane polarized light: If light is represented to propagate along *z* axis, with its electric field oscillating in the *xz* plane, then light is said to be *x*-polarized or linearly polarized along the *x* axis or plane polarized in the *xz* plane.

Coherent waves: Two or more waves that have the same frequency and the same relationship between corresponding points at all times are referred to as *coherent waves*.

By combining the x-polarized and y-polarized *coherent light* wave components, one can generate a variety of polarization states.

- x-polarized wave component propagating in time t is represented by

$$F_x = F_{x0} \text{ Cos } 2\pi\nu t = F_{x0} \text{ Cos}\Theta_t$$

- y-polarized wave component propagating in time t is represented by

$$F_y = F_{y0} \text{ Cos } 2\pi\nu t = F_{y0} \text{ Cos}\Theta_t$$

Where, F_{x0} = Maximum amplitude of wave component F_x

F_{y0} = Maximum amplitude of wave component F_y

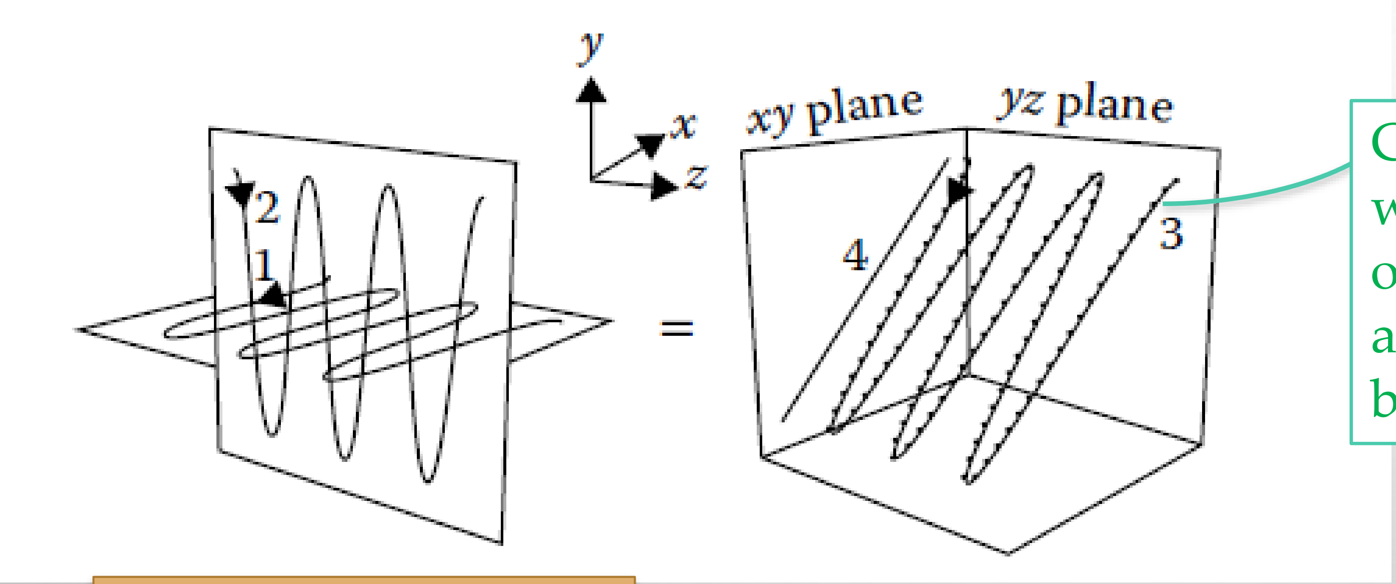
For a coherent wave,

$$F_{x0} = F_{y0} = F_0$$

If we combine both waves, the resulting linearly polarized light is represented by Equation

$$F = F_0\ (\boldsymbol{u}\ \cos\Theta_t + \boldsymbol{v}\ \cos\Theta_t)$$

where **u** and **v** are unit vectors along the x and y axes, respectively.



New plane of polarization

Combination appears as a light wave whose electric vector oscillates at 45° between the $+x$ and $+y$ axes, that is, in the xy plane bisecting the $+x$ and $+y$ axes.

Wave 1 + Wave 2
Same phase (Θ_t)

Resultant wave

This is Plane polarised light (PPL)

CIRCULARLY POLARIZED LIGHT

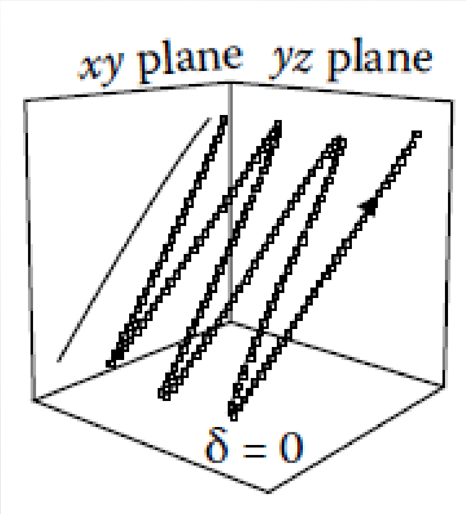
- Light wave of different phase combine to form Circularly polarized light.

$$F = F_0\ [\mathbf{u}\ \cos\Theta_t + \mathbf{v}\ \cos(\Theta_t + \delta)]$$

If the wave in the xz plane is represented by $F_0\ \cos\Theta_t$ and that in the yz plane by $F_0\ \cos(\Theta_t + \delta)$, then these waves are said to have a phase difference of δ.

Variation of this phase difference between **0** and **2π** will lead to changes in the polarization state of the resulting wave.

If Phase Difference is Zero; $\delta = 0$



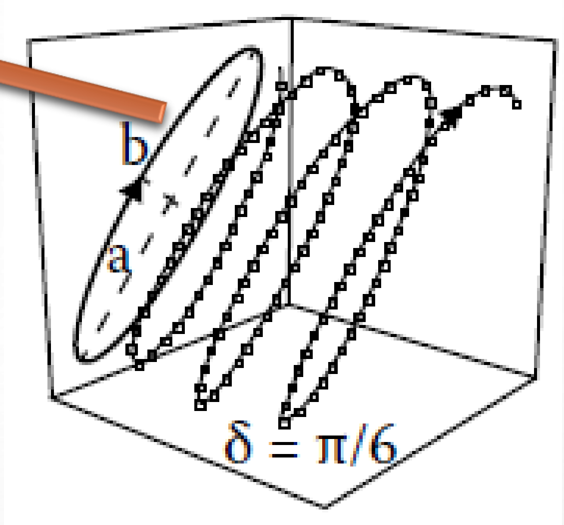
Plane polarised light

➢ The polarization of the resulting wave at δ = 0 is linear with its polarization axis at 45° from +*x* and +*y* axes.

Polarization Ellipse

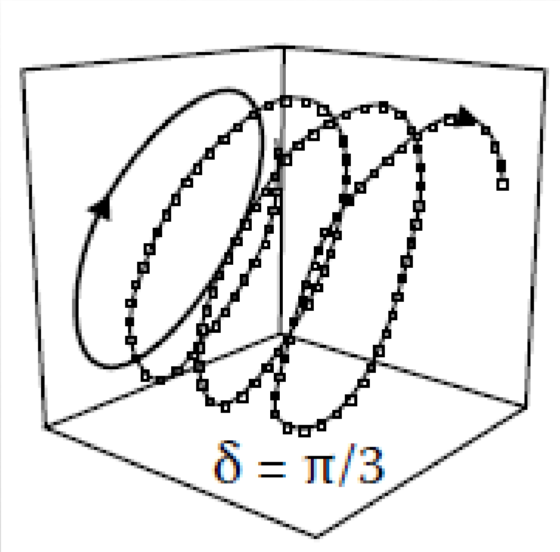
If Phase Difference $is\ 30^{o}$; $\delta = {}^{\pi}/_{6}$

- a = Major axis; b = Minor axis
- Here a>>b



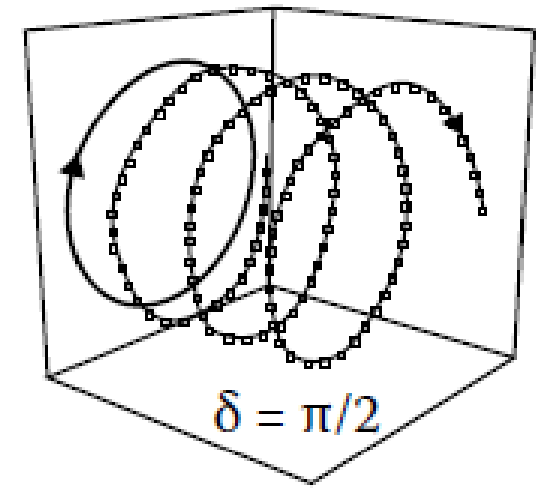
If Phase Difference is 60^{o}; $\delta = {}^{\pi}/_{3}$

- Minor axis, b increases gradually



If Phase Difference is 90^o; $\delta = \pi/_2$

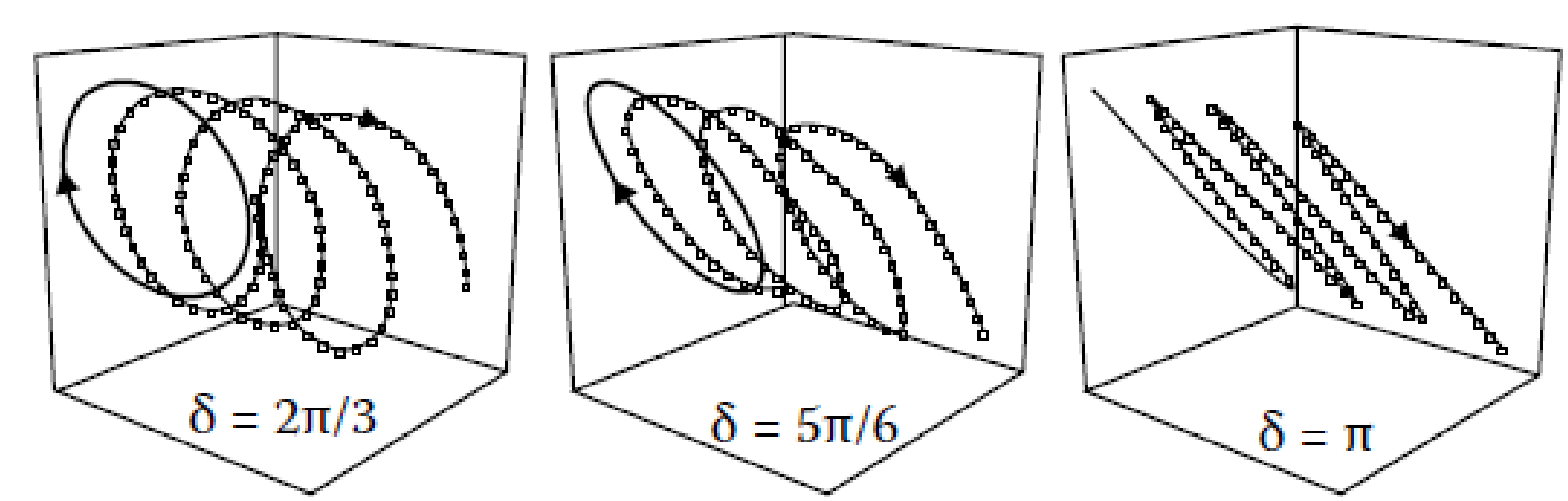
a = b, Circularly Polarized Light



RIGHT CIRCULARLY POLARIZED LIGHT (RCP)

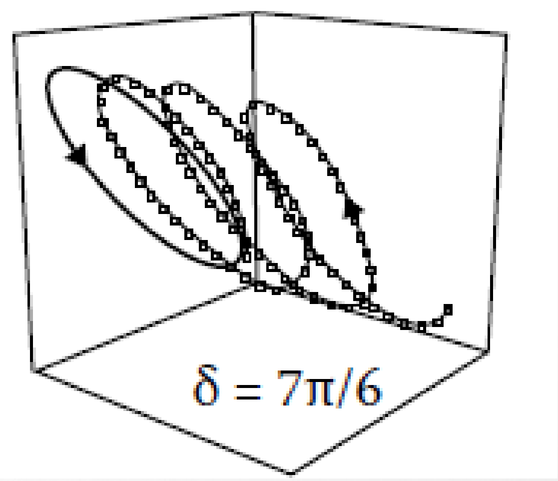
- The electric vector rotates in a clockwise direction
- The angle between the major axis of the polarization ellipse and +x axis is called the azimuth and designated as θ .

$$F_{RCP} = F_0\,[\mathbf{u}\cos\Theta_t + \mathbf{v}\cos(\Theta_t + \pi/2)] = F_0\,(\mathbf{u}\cos\Theta_t - \mathbf{v}\sin\Theta_t)$$

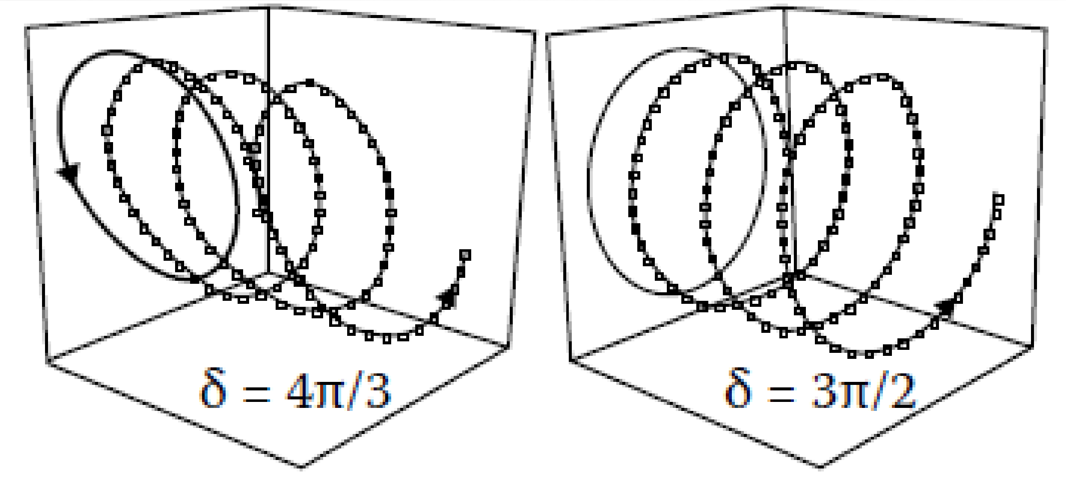


As the phase difference angle increases and reaches 180°, the minor axis become zero and also the polarization plane changes by 90°

As the phase difference angle increases beyond 180°, the direction of Circularly polarized light changes.



Ultimately, it become Left Circularly Polarized light at 270°



LEFT CIRCULARLY POLARIZED LIGHT (LCP)

$$F_{LCP} = F_0\,[\mathbf{u}\cos\Theta_t + \mathbf{v}\cos(\Theta_t + 3\pi/2)] = F_0\,(\mathbf{u}\cos\Theta_t + \mathbf{v}\sin\Theta_t)$$

Points to Ponder

- Right circular polarization (RCP) can be generated from two orthogonal linearly polarized components with equal amplitudes and a phase difference of $\pi/2$. Similarly, left circular polarization (LCP) can be generated from those components with a difference of $3\pi/2$ or $-\pi/2$.

- The superposition of RCP and LCP gives linear polarization:

$$F_{RCP} + F_{LCP} = F_0\,(\mathbf{u}\cos\Theta_t - \mathbf{v}\sin\Theta_t) + F_0\,(\mathbf{u}\cos\Theta_t + \mathbf{v}\sin\Theta_t)$$
$$= 2F_0\,(\mathbf{u}\cos\Theta_t) = 2F_x$$

where $\Theta_t = 2\pi\nu t$. That means, linearly polarized light with its electric vector along x axis can be seen as the average of RCP and LCP:

$$F_x = \frac{F_{RCP} + F_{LCP}}{2}$$

Dependence of Resulting Polarization on the Differences in Amplitudes and Phases of x-Polarized and y-Polarized Coherent Wave Components Propagating in z Direction

Amplitudes	Phase Difference[a]	Polarization State	Sense of Rotation	θ[b]
$E_{xo} = E_{yo}$	$\delta = 0$	Linear		45°
	$\pi/2 > \delta > 0$	Elliptical	Clockwise	45°
	$\delta = \pi/2$	Right circular	Clockwise	
	$\delta = \pi > \delta > \pi/2$	Elliptical	Clockwise	135°
	$\delta = \pi$	Linear		135°
	$\delta = 3\pi/2 > \delta > \pi$	Elliptical	Counterclockwise	135°
	$\delta = 3\pi/2$	Left circular	Counterclockwise	
	$\delta = 2\pi > \delta > 3\pi/2$	Linear	Counterclockwise	45°
$E_{xo} > E_{yo}$; $E_{yo} \neq 0$	$\delta = 0$	Linear		$0 > \theta < 45°$
$E_{xo} < E_{yo}$; $E_{xo} \neq 0$	$\delta = 0$	Linear		$90° > \theta > 45°$
$E_{xo} > E_{yo}$; $E_{yo} \neq 0$	$\delta = \pi/2$	Elliptical	Clockwise	0°
$E_{xo} < E_{yo}$; $E_{xo} \neq 0$	$\delta = \pi/2$	Elliptical	Clockwise	90°

[a] Phase δ is introduced into the y-polarized component.

[b] θ, referred to as the azimuth, is between the $+x$ axis and the major axis of the polarization ellipse. Linear polarization can be viewed as a special case of elliptical polarization by collapsing the ellipse so that its minor axis vanishes and its major axis becomes the linear polarization axis.

Reference

CHIROPTICAL SPECTROSCOPY

Fundamentals and Applications

Prasad L. Polavarapu

Next………

Interaction of polarized light with Chiral molecules

CD and ORD