

Chiroptical Spectroscopy

Theory and Applications in Organic Chemistry

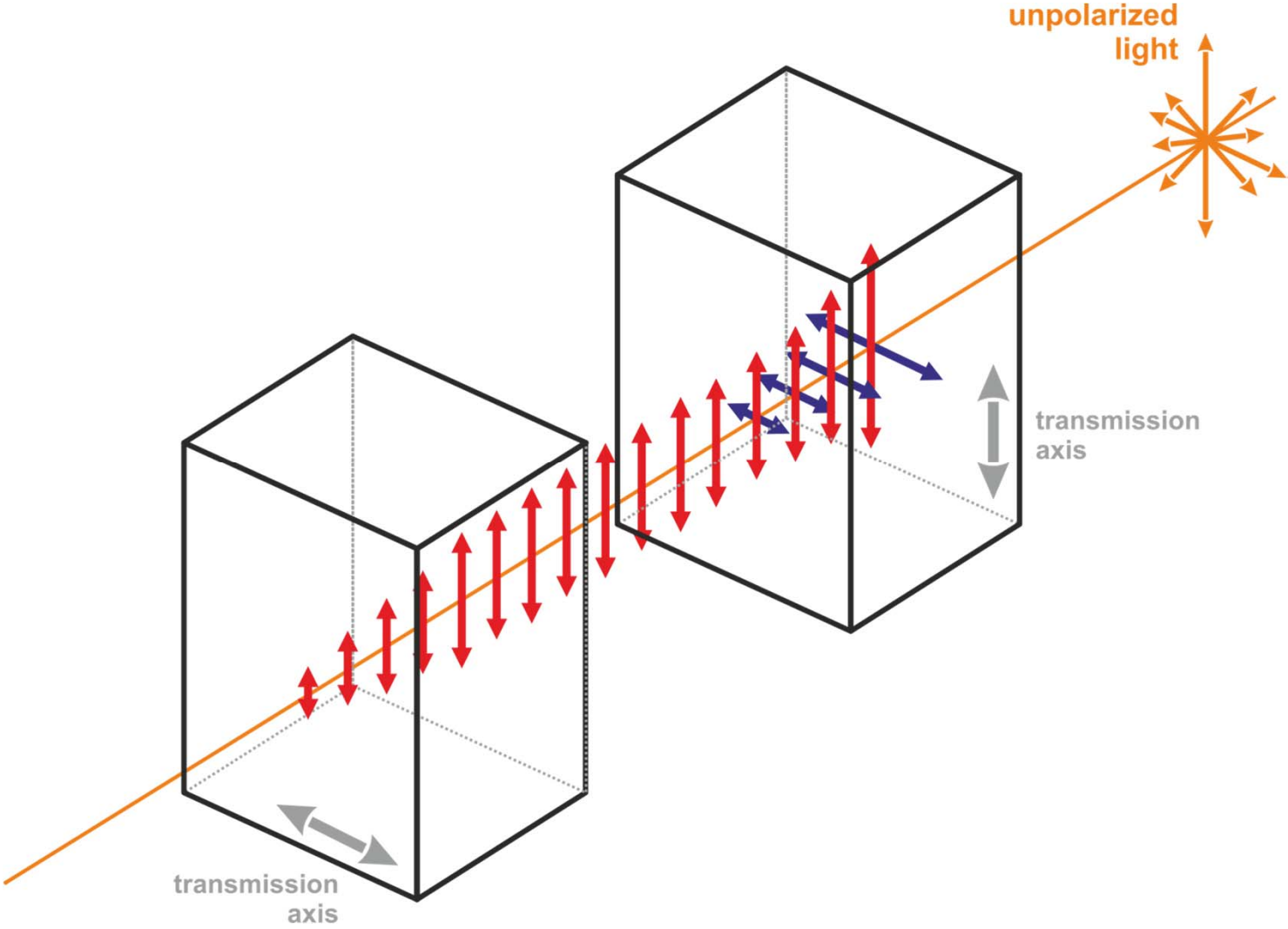
Lecture 3: (Crash course in) Theory of optical activity

Masters Level Class (181 041)

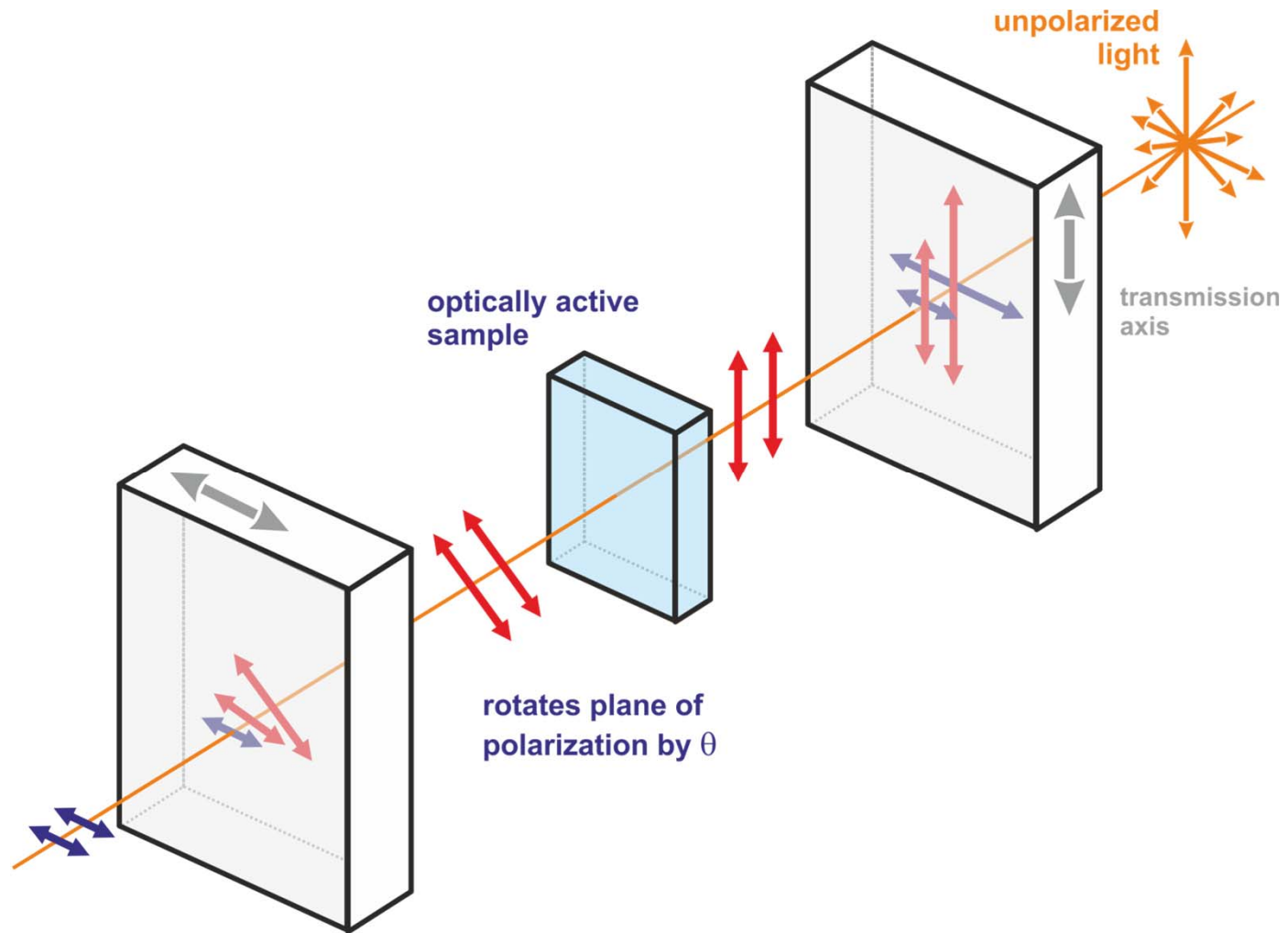
Mondays, 8.15-9.45 am, NC 02/99

Wednesdays, 10.15-11.45 am, NC 02/99

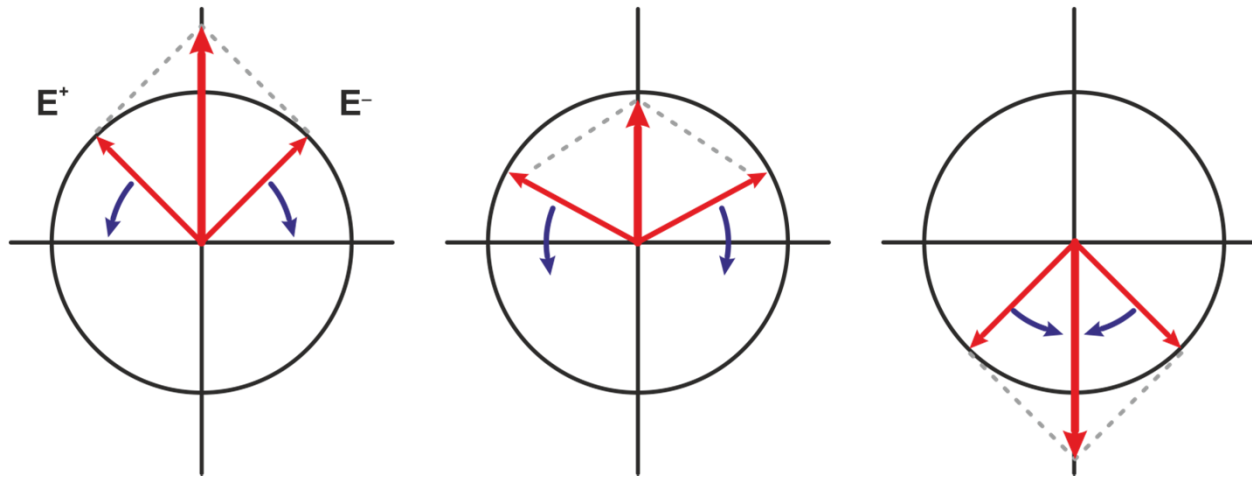
Crossed polarizers



Crossed polarizers and optically active sample



Optical rotation: Difference of refractive indices



Linear polarized light can be expressed as superposition of left and right circular polarized light:

$$\mathbf{E} = \mathbf{E}^+ + \mathbf{E}^-$$

with

$$\mathbf{E}^+ = E_0 \cdot \mathbf{x} \cdot \cos \varphi_+ + E_0 \cdot \mathbf{y} \cdot \sin \varphi_+$$

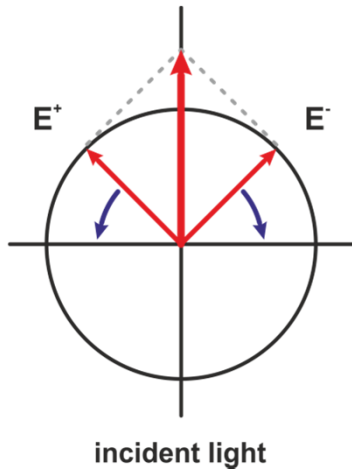
$$\mathbf{E}^- = E_0 \cdot \mathbf{x} \cdot \cos \varphi_- - E_0 \cdot \mathbf{y} \cdot \sin \varphi_-$$

respectively

$$\mathbf{E}^\pm = E_0 \cdot \mathbf{x} \cdot \cos \varphi_\pm \pm E_0 \cdot \mathbf{y} \cdot \sin \varphi_\pm$$

\mathbf{x} , \mathbf{y} : unit vectors perpendicular to propagation direction

Optical rotation: Difference of refractive indices



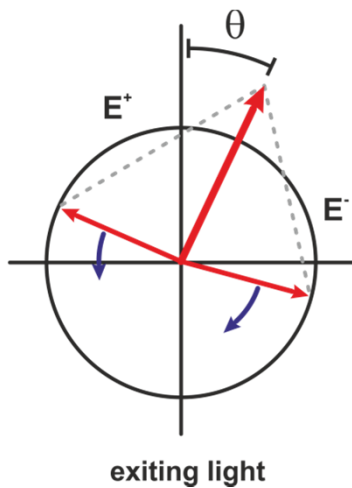
$$\mathbf{E} = \mathbf{E}^+ + \mathbf{E}^- \quad \text{with}$$

$$\mathbf{E}^\pm = E_0 \cdot \mathbf{x} \cdot \cos \varphi_\pm \pm E_0 \cdot \mathbf{y} \cdot \sin \varphi_\pm$$

Taking into account that LCP and RCP light can have different velocities in a medium:

$$n_\pm = \frac{c}{v_\pm}$$

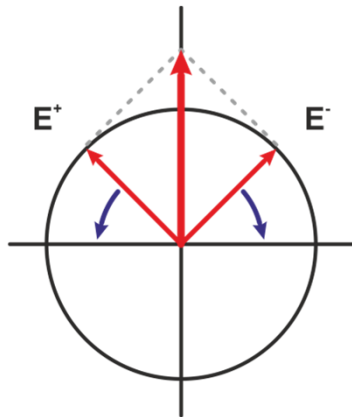
$$\varphi_\pm = \omega t - \frac{2\pi z}{\lambda_\pm} \quad \lambda_\pm = \frac{v_\pm}{f} = \frac{c}{n_\pm \cdot f}$$



Because $\omega = 2\pi f$, we can rewrite the equation:

$$\varphi_\pm = \varphi \mp \frac{\omega t \Delta n}{2c} \quad \begin{cases} \varphi = \omega t - n\omega z/c \\ n = \frac{1}{2}(n_+ + n_-) \\ \Delta n = n_+ - n_- \end{cases}$$

Optical rotation: Difference of refractive indices



incident light

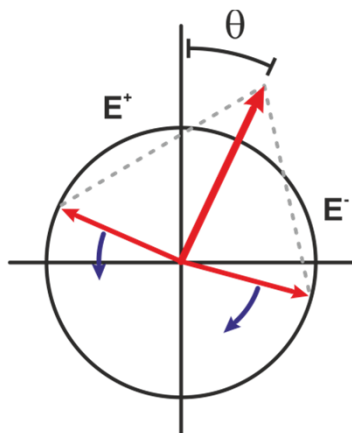
If medium is not circularly birefringent (optically active), then $\Delta n=0$ and

$$E^{\pm} = E_0 \cdot \mathbf{x} \cdot \cos \varphi \pm E_0 \cdot \mathbf{y} \cdot \sin \varphi$$

Hence, the superposition is

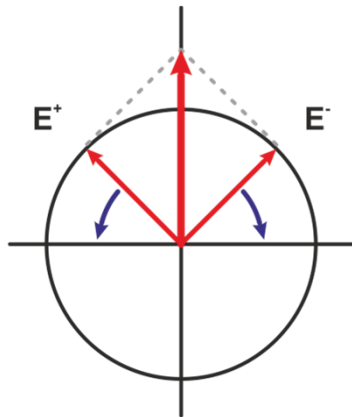
$$E = E^+ + E^- = 2E_0 \cdot \mathbf{x} \cdot \cos \varphi$$

... i.e. it still oscillates in the plane of the direction of propagation and the unit vector \mathbf{x} .



exiting light

Optical rotation: Difference of refractive indices



incident light

If the medium shows circular birefringence, we have

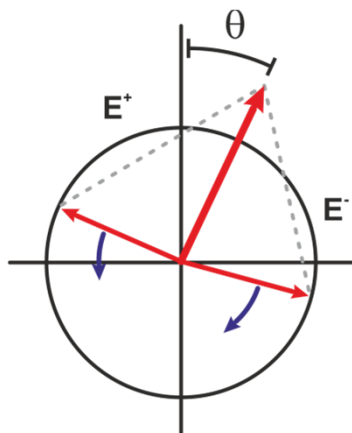
$$\mathbf{E}^{\pm} = E_0 \cdot \mathbf{x} \cdot \cos \varphi_{\pm} \pm E_0 \cdot \mathbf{y} \cdot \sin \varphi_{\pm}$$

and the superposition becomes

$$\mathbf{E} = \mathbf{E}^+ + \mathbf{E}^- = E_0 \cdot \{(\cos \varphi_+ + \cos \varphi_-)\mathbf{x} + (\sin \varphi_+ - \sin \varphi_-)\mathbf{y}\}$$

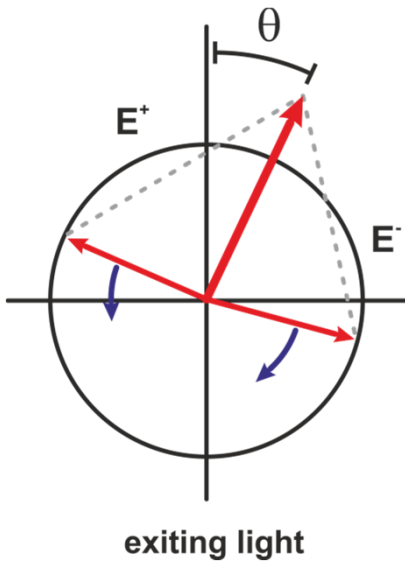
After some rearrangements, we get

$$\mathbf{E} = 2E_0 \left\{ \mathbf{x} \cos \left(\frac{z \omega \Delta n}{2c} \right) - \mathbf{y} \sin \left(\frac{z \omega \Delta n}{2c} \right) \right\} \cos \varphi$$



exiting light

Optical rotation: Difference of refractive indices



The exiting ray is still linearly polarized, but its plane is now rotated by the angle θ :

$$\theta = \frac{z \omega \Delta n}{2c}$$

Consequently, we have a **dextrorotatory** sample if $n_+ > n_-$ and a **levorotatory** sample if $n_- > n_+$

Details on the following equations can be found in
Atkins, Friedman, Molecular Quantum Mechanics, 5th Edition, p. 417

How does the refractive index depend on a molecular properties?

From Maxwell equations, we find a relationship with the relative permittivity ϵ_r , aka the dielectric constant:

$$n = \left(\frac{\epsilon}{\epsilon_0} \right)^{\frac{1}{2}} = \epsilon_r^{\frac{1}{2}}$$

Relative permittivity ϵ_r directly relates to electric susceptibility χ_e , which measures how easily a dielectric is polarized in response to an electric field:

$$\chi_e = \epsilon_r - 1$$

Ok, then:

How does the dielectric constant depend on molecular properties?

For non-polar molecules in a static electric field, it can be shown that

$$\epsilon_r = \frac{1 + 2\alpha\mathcal{N}/(3\epsilon_0)}{1 - \alpha\mathcal{N}/(3\epsilon_0)}$$

with $\mathcal{N} = N/V$

polarizability α

$$\alpha = \frac{2}{3} \sum_{n \neq 0} \frac{\hat{\mu}_{0n} \cdot \hat{\mu}_{n0}}{E_n^0 - E_0^0}$$

How does the refractive index depend on a molecular properties?

From Maxwell equations, we find a relationship with the relative permittivity ϵ_r , aka the dielectric constant:

$$n = \left(\frac{\epsilon}{\epsilon_0} \right)^{\frac{1}{2}} = \epsilon_r^{\frac{1}{2}} = \left(\frac{1 + 2\alpha\mathcal{N}/(3\epsilon_0)}{1 - \alpha\mathcal{N}/(3\epsilon_0)} \right)^{\frac{1}{2}} \approx 1 + \frac{\mathcal{N}\alpha}{2\epsilon_0}$$

But the polarizability is not chiral!?

We made a mistake when deriving ϵ_r from the polarizability α !

We assumed

$$\mathbf{P} = \alpha \mathcal{N} \mathbf{E}$$

The diagram shows the equation $\mathbf{P} = \alpha \mathcal{N} \mathbf{E}$. The symbol α is circled in orange, and the symbol \mathbf{E} is circled in blue. Below the equation, there are two labels: 'polarizability' with an orange line pointing to the circled α , and 'electric field' with a blue line pointing to the circled \mathbf{E} .

This is fully correct if there is a constant electric field.

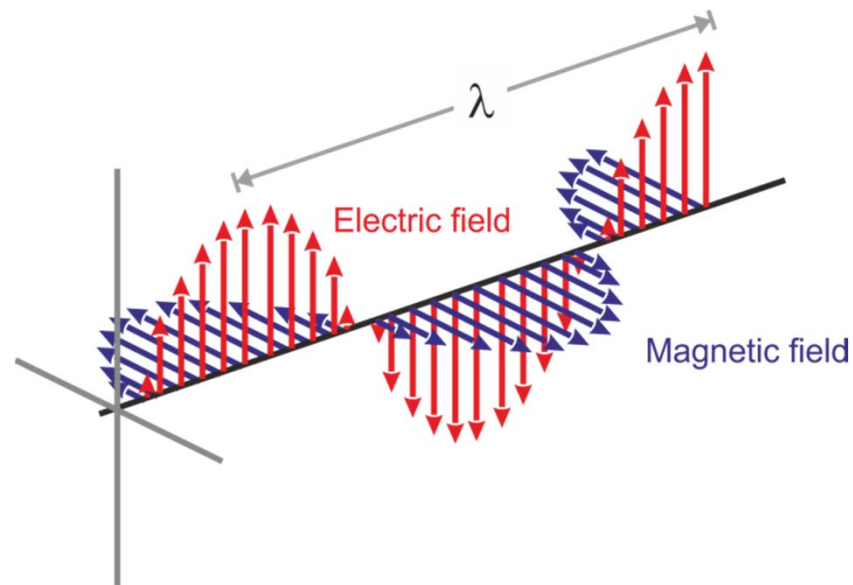
Contribution of the magnetic field

Mistake: We ignored the contribution of the magnetic field to the polarization!

Rewriting our definition of polarization as

$$\mathbf{P} = \alpha \mathcal{N} \mathbf{E} - \beta \mathcal{N} \dot{\mathbf{B}}$$

with β being another molecular characteristic and not to be mixed up with the hyperpolarizability!



The problem of static polarization

From this definition of the polarization \mathbf{P} , we get after solving a few equations again

$$n_{\pm} = 1 + \frac{\mathcal{N}\alpha}{2\varepsilon_0} \pm \frac{\mathcal{N}\omega\beta}{2c\varepsilon_0}$$

and thus the difference of the refractive indices becomes

$$\Delta n = \frac{\mathcal{N}\omega\beta}{c\varepsilon_0}$$

For the optical rotation angle, it follows that after passing through a sample of length l ,

and taking into account that $\varepsilon_0\mu_v = c^2$ with μ_v being the vacuum permeability:

$$\Delta\theta = \frac{z\omega\Delta n}{2c} = \frac{\mathcal{N}l\omega^2\beta}{2c^2\varepsilon_0} = \frac{1}{2}\mathcal{N}l\mu_v\omega^2\beta$$

Polarization and quantum mechanics

Polarization \mathbf{P} = dipole moment density

$$P = \langle \mu \rangle \cdot \frac{N}{V} = \langle \mu \rangle \cdot \mathcal{N}$$

- Quantum mechanical calculation of the induced average dipole moment $\langle \mu \rangle$ should lead to expression for β !

Schrödinger equation

The time-independent Schrödinger equation

$$\hat{H}\psi(\vec{\tau}) = E\psi(\vec{\tau})$$

while the full wavefunction has the form

$$\Psi(t, \vec{\tau}) = \psi(\vec{\tau}) \cdot e^{-iEt/\hbar}$$

It gives us access to observables by evaluating the observables' expectation value

$$\langle \Omega \rangle = \int \Psi^* \hat{\Omega} \Psi \, d\tau = \langle \Psi | \hat{\Omega} | \Psi \rangle$$

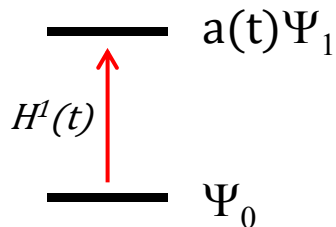
The basic idea of perturbation theory

In perturbation theory, we define a (time-dependent) perturbation in the Hamiltonian operator:

$$\hat{H}(t) = \hat{H}^0 + \hat{H}^1(t)$$

e.g. perturbation by electric field

$$\hat{H}^1(t) = -2\mu_x E_x \cos \omega t$$



In presence of a perturbation, the wavefunction is a linear combination of states:

$$\Psi(t) = \psi_0^0 \cdot e\left(\frac{-iE_0 t}{\hbar}\right) + \sum_{n \neq 0} a_n(t) \cdot \psi_n^0 \cdot e\left(\frac{-iE_n t}{\hbar}\right)$$

For $a_n(t)$ it can be shown that

$$a_n(t) = \frac{1}{i\hbar} \int_0^t \hat{H}_{n0}^1(t) \cdot e^{i\omega_{n0} t} dt$$

with $\hbar\omega_{n0} = E_n - E_0$

Evaluating $\langle \mu \rangle$

The expectation value for the average dipole moment (its z-component) is

$$\langle \mu_z \rangle = \langle \Psi | \widehat{\mu}_z | \Psi \rangle$$

Taking into account that Ψ is a perturbed wavefunction with ground state $|0\rangle$ and perturbed states $|n\rangle$, we get

$$\begin{aligned} \langle \mu_z \rangle &= \langle 0 | \widehat{\mu}_z | 0 \rangle + \sum_{n \neq 0} \{ \langle 0 | \widehat{\mu}_z | n \rangle \cdot a_n(t) \cdot e^{-i\omega_{n0}t} + \langle n | \widehat{\mu}_z | 0 \rangle \cdot a_n^*(t) \cdot e^{i\omega_{n0}t} \} \\ &= \mu_{0z} + \sum_{n \neq 0} \{ \mu_{z,0n} a_n(t) \cdot e^{-i\omega_{n0}t} + \mu_{z,n0} \cdot a_n^*(t) \cdot e^{i\omega_{n0}t} \} \end{aligned}$$

Perturbation theory: Magnetically induced polarization

In our case, the perturbation to the Hamiltonian is

$$H^1(t) = -\hat{\mu} \cdot \mathbf{E} - \hat{\mathbf{m}} \cdot \mathbf{B}$$

with

$\hat{\mu}$: electric dipole moment operator
 $\hat{\mathbf{m}} = \gamma_e \hat{\mathbf{l}} = \gamma_e (\mathbf{r} \times \hat{\mathbf{p}})$: magnetic dipole moment operator
 \mathbf{E} : electric field
 \mathbf{B} : magnetic field

More precisely, we also need to take into account the circular polarization states of the electric and magnetic field:

$$H_{\pm}^1(t) = -\hat{\mu} \cdot \mathbf{E}^{\pm} - \hat{\mathbf{m}} \cdot \mathbf{B}^{\pm}$$

with

$$\mathbf{E}^{\pm}(t) = E(\mathbf{x} \cdot \cos \omega t \pm \mathbf{y} \cdot \sin \omega t) \quad \text{and} \quad \mathbf{B}^{\pm}(t) = B(\pm \mathbf{x} \cdot \cos \omega t - \mathbf{y} \cdot \sin \omega t)$$

Perturbation theory: Magnetically induced polarization

$$\mathbf{E}^{\pm}(t) = E(\mathbf{x} \cdot \cos \omega t \pm \mathbf{y} \cdot \sin \omega t)$$

$$\mathbf{B}^{\pm}(t) = B(\pm \mathbf{x} \cdot \cos \omega t - \mathbf{y} \cdot \sin \omega t)$$

$$H_{\pm}^1(t) = -\hat{\mu} \cdot \mathbf{E}^{\pm} - \hat{m} \cdot \mathbf{B}^{\pm}$$

$$= -\hat{\mu} \cdot E(\mathbf{x} \cdot \cos \omega t \pm \mathbf{y} \cdot \sin \omega t) - \hat{m} \cdot B(\pm \mathbf{x} \cdot \cos \omega t - \mathbf{y} \cdot \sin \omega t)$$

As $\mu_x = \hat{\mu} \cdot \mathbf{x}$ and $m_x = \hat{m} \cdot \mathbf{x}$

$$= -E(\mu_x \cdot \cos \omega t \pm \mu_y \sin \omega t) - B(\pm m_x \cos \omega t - m_y \sin \omega t)$$

$$\cos \alpha = \frac{1}{2}(e^{i\alpha} + e^{-i\alpha})$$

$$\sin \alpha = -\frac{i}{2}(e^{i\alpha} - e^{-i\alpha})$$

$$= -\frac{1}{2}E(\mu_x \cdot (e^{i\omega t} + e^{-i\omega t}) \mp i\mu_y(e^{i\omega t} - e^{-i\omega t}))$$

$$-\frac{1}{2}B(\mp m_x \cdot (e^{i\omega t} + e^{-i\omega t}) - m_y(e^{i\omega t} - e^{-i\omega t}))$$

Perturbation theory: Magnetically induced polarization

Based on this perturbation Hamiltonian, the coefficients of the perturbed wavefunctions can be determined:

$$a_n(t) = \frac{1}{i\hbar} \int_0^t \hat{H}_{\pm, n0}^1(t) \cdot e^{i\omega_{n0}t} dt$$

with

$$\begin{aligned} \hat{H}_{\pm, n0}^1(t) = & -\frac{1}{2}E(\mu_x \cdot (e^{i\omega t} + e^{-i\omega t}) \mp i\mu_y(e^{i\omega t} - e^{-i\omega t})) \\ & -\frac{1}{2}B(\mp m_x \cdot (e^{i\omega t} + e^{-i\omega t}) - m_y(e^{i\omega t} - e^{-i\omega t})) \end{aligned}$$

Then, the induced electric dipole moment is the expectation value of the operator using the perturbed wavefunctions:

$$\langle \mu^{\pm} \rangle = \langle \Psi^* | \hat{\mu}^{\pm} | \Psi \rangle = \mu_0 + \sum_{n \neq 0} \mu_{0n} \cdot a_n^{\pm}(t) \cdot e^{-i\omega_{n0}t} + \mu_{n0} \cdot a_n^{\pm*}(t) \cdot e^{i\omega_{n0}t}$$

Perturbation theory: Magnetically induced polarization

Solving the equation for the expectation value

$$\langle \mu^\pm \rangle = \langle \Psi^* | \widehat{\mu}^\pm | \Psi \rangle = \mu_0 + \sum_{n \neq 0} \mu_{0n} \cdot a_n^\pm(t) \cdot e^{-i\omega_{n0}t} + \mu_{n0} \cdot a_n^{\pm*}(t) \cdot e^{i\omega_{n0}t}$$

leads to the final expression

$$\langle \mu^\pm \rangle = \frac{2}{\hbar} \operatorname{Re} \left\{ \sum_{n \neq 0} \left(\frac{\omega_{n0}}{\omega_{n0}^2 - \omega^2} \right) \cdot \mu_{0n} \cdot \mu_{n0} \cdot \mathbf{E}^\pm(t) \right\} - \frac{2}{\hbar} \operatorname{Im} \left\{ \sum_{n \neq 0} \left(\frac{\omega_{n0}}{\omega_{n0}^2 - \omega^2} \right) \cdot \mu_{0n} \cdot m_{n0} \cdot \mathbf{B}^\pm(t) \right\}$$

Comparison with the definition of polarization in an electromagnetic field

$$\mathbf{P} = \alpha \mathcal{N} \mathbf{E} - \beta \mathcal{N} \dot{\mathbf{B}}$$

shows that

$$\beta = \frac{2}{\hbar} \operatorname{Im} \sum_{n \neq 0} \frac{\mu_{0n} \cdot m_{n0}}{\omega_{n0}^2 - \omega^2}$$

The rotational strength

Taking the rotational average (β_{xx} , β_{yy} , β_{zz})

$$\beta = \frac{2}{3\hbar} \text{Im} \sum_{n \neq 0} \frac{\boldsymbol{\mu}_{0n} \cdot \mathbf{m}_{n0}}{\omega_{n0}^2 - \omega^2}$$

we get

The Rosenfeld equation

$$\Delta\theta = \frac{Nl\mu_v}{3\hbar} \sum_{n \neq 0} \frac{\omega^2 R_{n0}}{\omega_{n0}^2 - \omega^2}$$

rotational strength of transition $n \leftarrow 0$

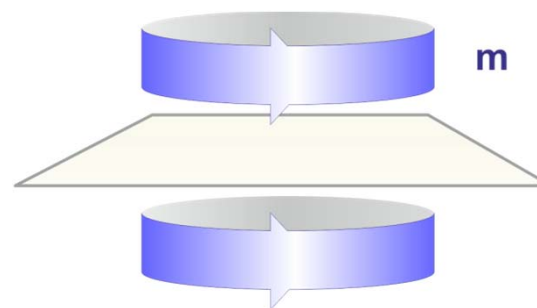
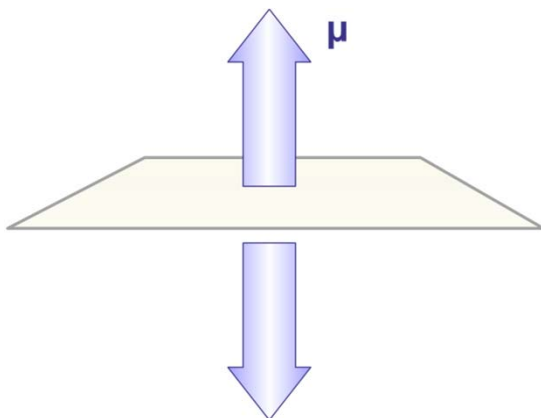
$$R_{n0} = \text{Im}\{\boldsymbol{\mu}_{0n} \cdot \mathbf{m}_{n0}\}$$

μ : electric dipole transition moment (EDTM)
 m : magnetic dipole transition moment (MDTM)

Symmetry properties of the rotational strength

With respect to reflection: EDTM transforms as translation

MDTM transforms as rotation



Requirement:

Sign of R must be conserved upon action of any symmetry element of the molecule

If a molecule has a mirror plane, reflection changes sign of EDTM but not of MDTM.

Consequence: Rotational strength changes sign $\rightarrow R = 0$

Optical rotatory dispersion (ORD)

The Rosenfeld equation

$$\Delta\theta = \frac{Nl\mu_v}{3\hbar} \sum_{n \neq 0} \frac{\omega^2 R_{n0}}{\omega_{n0}^2 - \omega^2}$$

$$\omega = 2\pi f$$

$$\omega_{n0} = (E_n - E_0)/\hbar$$

At very high frequencies ($\omega^2 \gg \omega_{n0}^2$) and in the opposite case of $\omega^2 \ll \omega_{n0}^2$, the rotational angle is

$$\Delta\theta = 0$$

due to the sum rule

$$\sum_n (R_{n0}) = 0$$



OR is close to zero far away from absorption bands, but becomes very large

when approaching them: $\omega_{n0}^2 - \omega^2 \rightarrow 0$

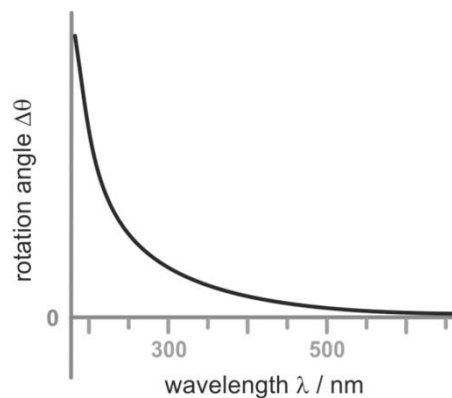
Optical rotatory dispersion (ORD)

When $\omega_{n0}^2 - \omega^2 \rightarrow 0$, i.e. if the excitation frequency is close to an absorption band, the contribution of that particular transition dominates the OR value:

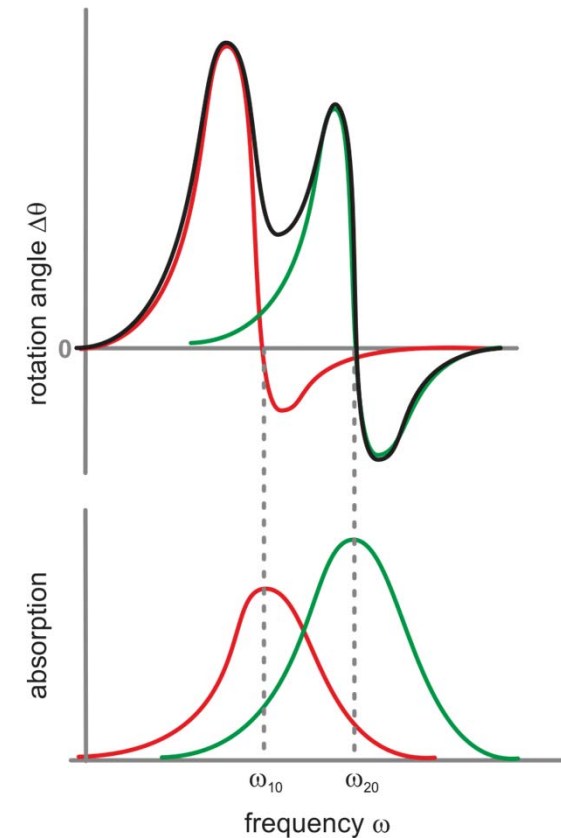
$$\Delta\theta = \frac{\mathcal{N}l \mu\nu \omega^2 R_{10}}{3\hbar(\omega_{10}^2 - \omega^2)}$$

➤ Observation of Cotton effect

„Normal“ ORD curve:



- First resonances in the UV range
- Appears monosignate in usual range of measurement



Outline of the lecture

Dates	topics
✓ 09.04.	Introduction
✓ 11.04.	Polarization of light
✓ 16.04.	Theoretical basis of optical activity
18.04.	Optical rotation
23.04.	Circular dichroism
25.04.	Circular dichroism
07.05.	Vibrational optical activity
14.05.	Vibrational optical activity
18.06.	applications
20.06.	applications

Mondays 8.15-9.45 am
Wednesdays 10.15-11.45 am

} your part