Chiroptical Spectroscopy

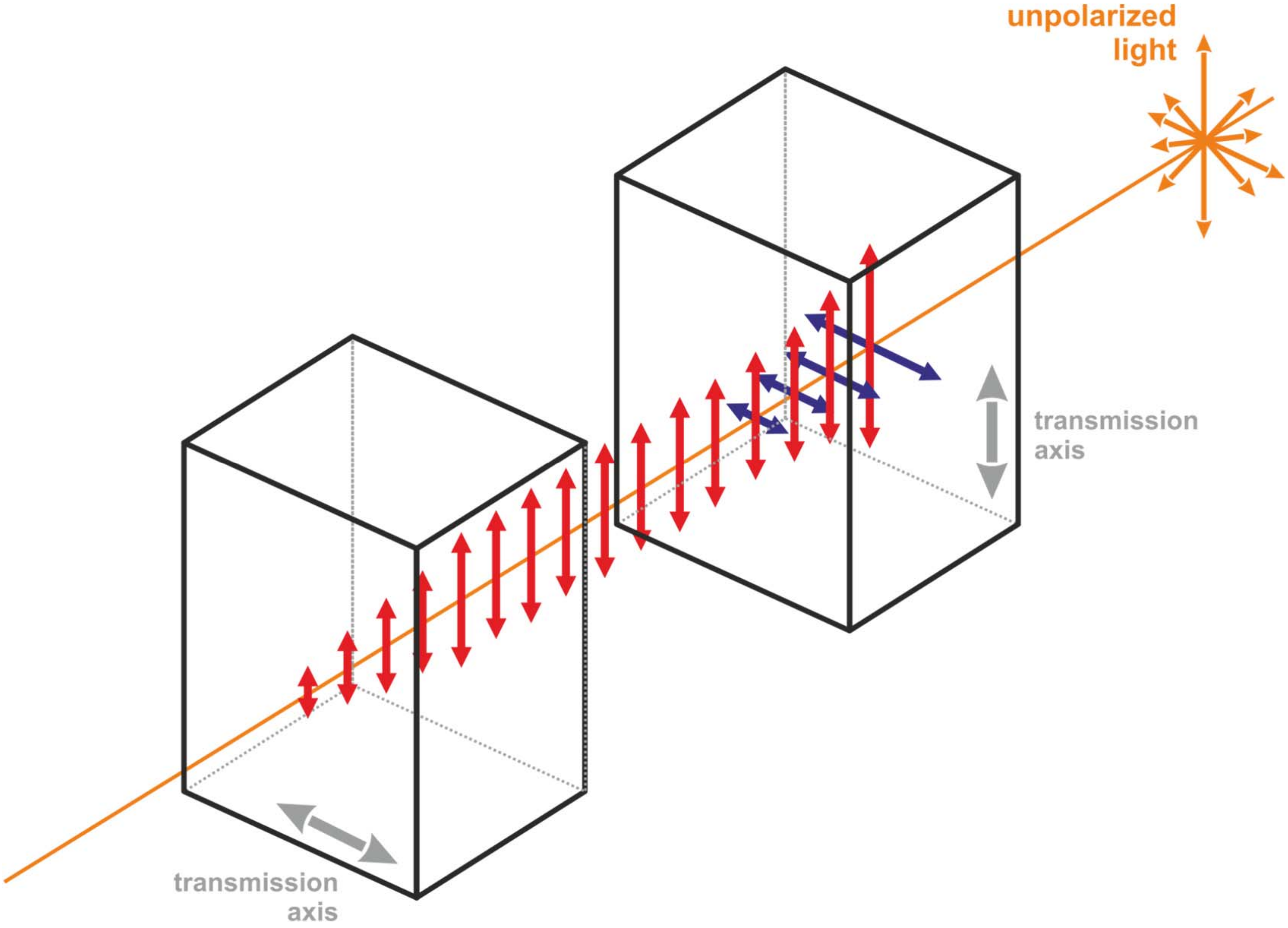
Theory and Applications in Organic Chemistry

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

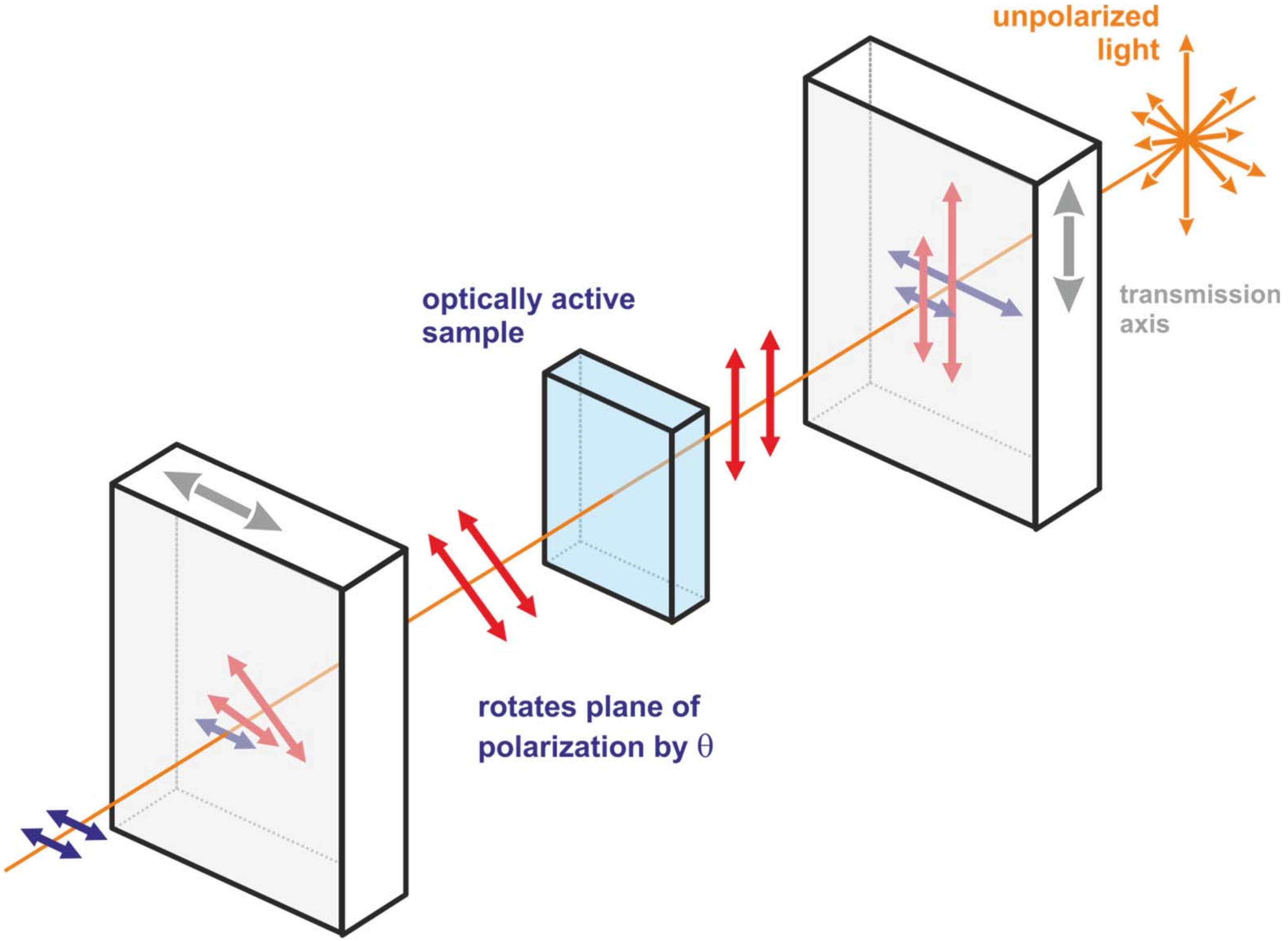
Masters Level Class (181 041)

Block course, october 2020

Crossed polarizers



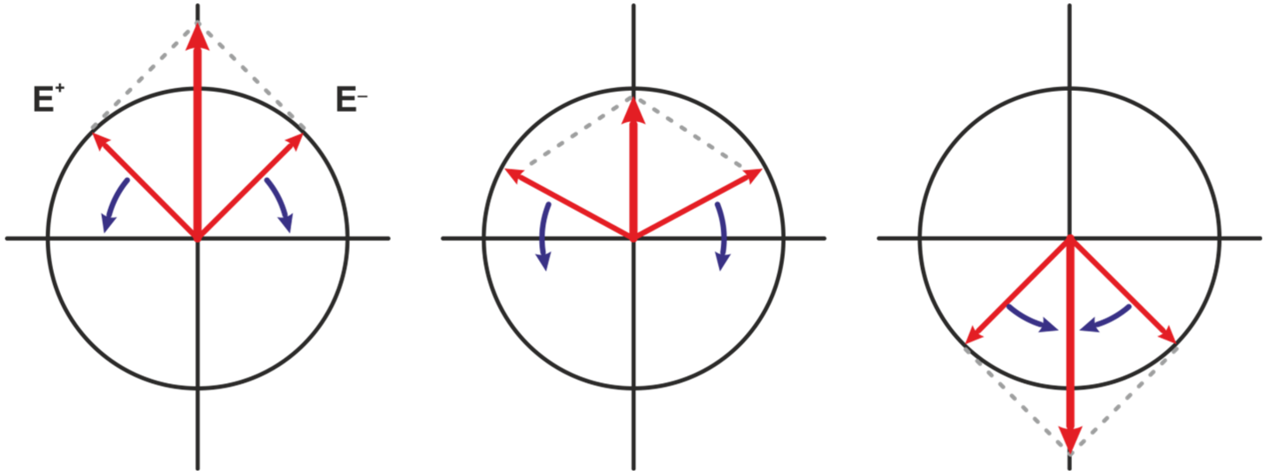
Crossed polarizers and optically active sample



optically active sample

rotates plane of polarization by θ

Optical rotation: Difference of refractive indices



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

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

with

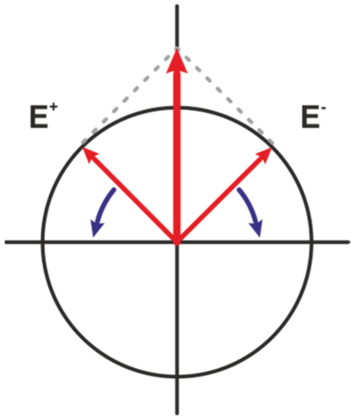
$$\boldsymbol{E}^+ = E_0 \cdot \boldsymbol{x} \cdot \cos\varphi_+ + E_0 \cdot \boldsymbol{y} \cdot \sin\varphi_+$$
$$\boldsymbol{E}^- = E_0 \cdot \boldsymbol{x} \cdot \cos\varphi_- - E_0 \cdot \boldsymbol{y} \cdot \sin\varphi_-$$

respectively

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

x, ***y***: unit vectors perpendicular to propagation direction

Optical rotation: Difference of refractive indices



incident light

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

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

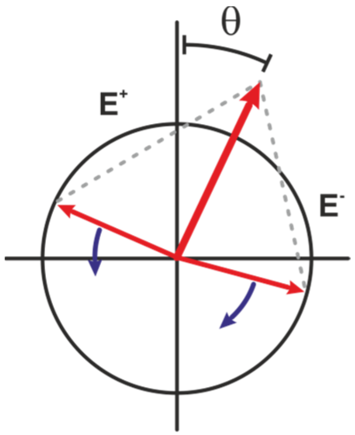
Taking into account that LCP and RCP light can have different velocities in a medium:

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

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

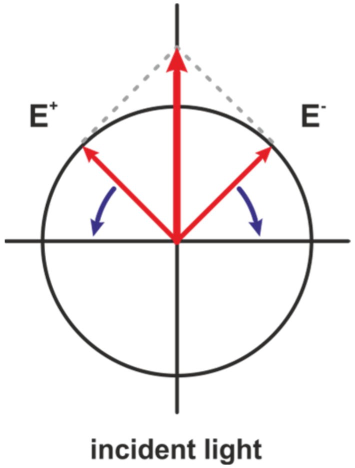
Because $\omega = 2\pi f$, we can rewrite the equation:

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



exiting light

Optical rotation: Difference of refractive indices



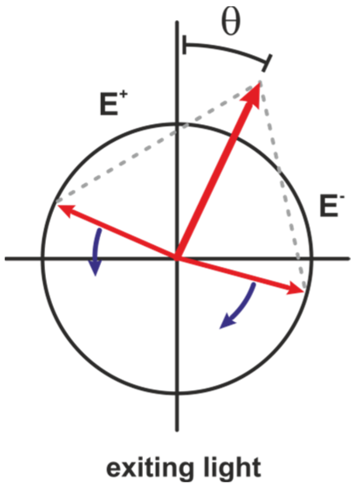
If medium is not circularly birefringant (optically active),

then Δn=0 and

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

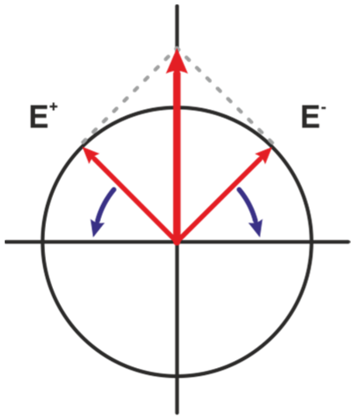
Hence, the superposition is

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

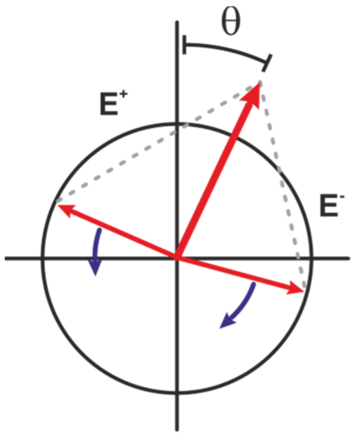


… i.e. it still oscillates in the plane of the direction of propagation and the unit vector $\boldsymbol{x}$.

Optical rotation: Difference of refractive indices



incident light



exiting light

If the medium shows circular birefringence, we have

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

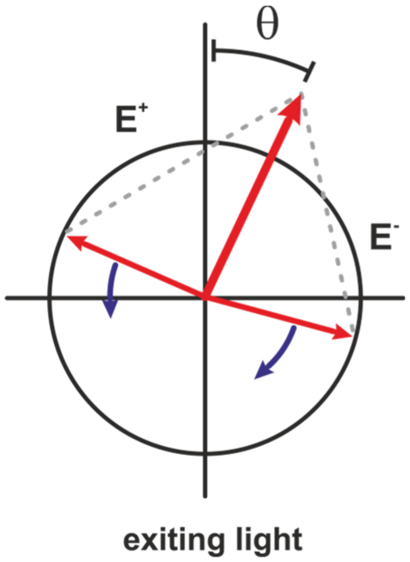
and the superposition becomes

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

After some rearrangements, we get

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

Optical rotation: Difference of refractive indices



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

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

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:

$$n = \left(\frac{\varepsilon}{\varepsilon_0}\right)^{\frac{1}{2}} = \varepsilon_r^{\frac{1}{2}}$$

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

$$\chi_e = \varepsilon_r - 1$$

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

$$\varepsilon_r = \frac{1 + 2\alpha\mathcal{N}/(3\varepsilon_0)}{1 - \alpha\mathcal{N}/(3\varepsilon_0)}$$

polarizability α

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

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

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:

$$n = \left(\frac{\varepsilon}{\varepsilon_0}\right)^{\frac{1}{2}} = \varepsilon_r^{\ \frac{1}{2}} = \left(\frac{1 + 2\alpha\mathcal{N}/(3\varepsilon_0)}{1 - \alpha\mathcal{N}/(3\varepsilon_0)}\right)^{\frac{1}{2}} \approx 1 + \frac{\mathcal{N}\alpha}{2\varepsilon_0}$$

But the polarizability is not chiral!?

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

We assumed

$$\boldsymbol{P} = \underbrace{\alpha}_{\text{polarizability}}\mathcal{N}\underbrace{\boldsymbol{E}}_{\text{electric field}}$$

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

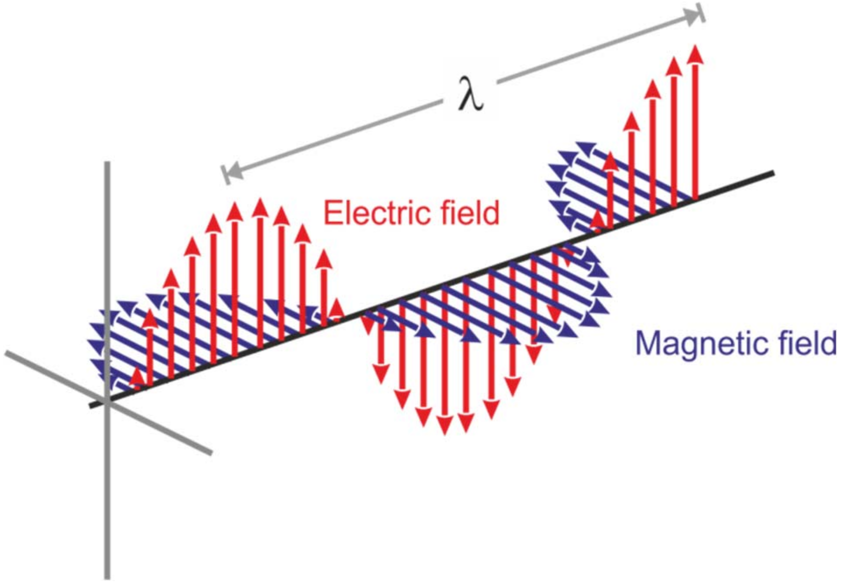
Contribution of the magnetic field

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

Rewriting our definition of polarization as

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

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 **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

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

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:

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

Polarization and quantum mechanics

Polarization **P** = dipole moment density

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

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

Schrödinger equation

The time-**in**dependent Schrödinger equation

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

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

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

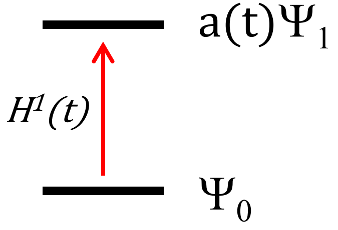
The basic idea of perturbation theory

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

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

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

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

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

Evaluating $\langle \boldsymbol{\mu} \rangle$

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

$$\langle \mu_z \rangle = \langle 0 | \widehat{\mu_z} | 0 \rangle + \sum_{n \neq 0} \left\{ \langle 0 | \widehat{\mu_z} | n \rangle \cdot a_n(t) \cdot e^{-i\omega_{n0}t} + \langle n | \widehat{\mu_z} | 0 \rangle \cdot a_n^*(t) \cdot e^{i\omega_{n0}t} \right\}$$

$$= \mu_{0z} + \sum_{n \neq 0} \left\{ \mu_{z,0n} \cdot a_n(t) \cdot e^{-i\omega_{n0}t} + \mu_{z,n0} \cdot a_n^*(t) \cdot e^{i\omega_{n0}t} \right\}$$

Perturbation theory: Magnetically induced polarization

In our case, the perturbation to the Hamiltonian is

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

with

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

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

$$H^1_{\pm}(t) = -\hat{\mu} \cdot \boldsymbol{E}^{\pm} - \widehat{m} \cdot \boldsymbol{B}^{\pm}$$

with

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

Perturbation theory: Magnetically induced polarization

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

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

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

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

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

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

$$\boxed{\cos \alpha = \frac{1}{2}\left(e^{i\alpha} + e^{-i\alpha}\right)} \qquad \boxed{\sin \alpha = -\frac{i}{2}\left(e^{i\alpha} - e^{-i\alpha}\right)}$$

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

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

Perturbation theory: Magnetically induced polarization

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

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

with

$$\widehat{H}^1_{\pm,n0}(t) = -\tfrac{1}{2}E\left(\mu_x \cdot \left(e^{i\omega t} + e^{-i\omega t}\right) \mp \mathrm{i}\mu_y\left(e^{i\omega t} - e^{-i\omega t}\right)\right)$$

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

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

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

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

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

Comparison with the definition of polarization in an electromagnetic field

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

shows that

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

The rotational strength

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

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

we get

The Rosenfeld equation

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

rotational strength of transition n←0

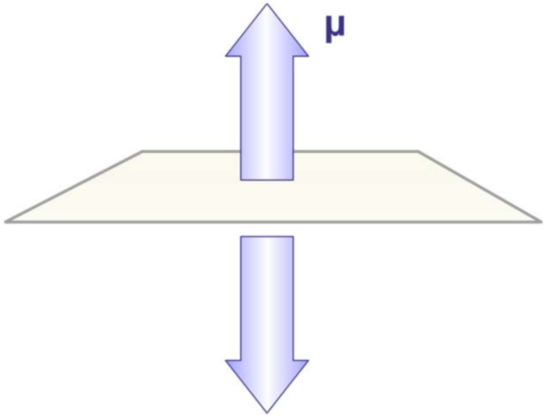
$$R_{n0} = Im\{\boldsymbol{\mu}_{\mathbf{0n}} \cdot \boldsymbol{m}_{\mathbf{n0}}\}$$

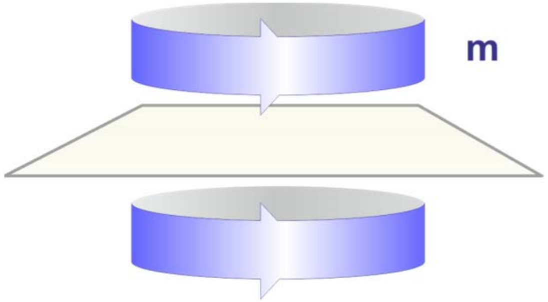
μ: electric dipole transition moment (EDTM)
m: magnetic dipole transition moment (MDTM)

Symmetry properties of the rotational strength

With respect to reflection: EDTM transforms as translation

MDTM transforms as rotation





Requirement for property being achiral:

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 → **R = 0**

Optical rotatory dispersion (ORD)

The Rosenfeld equation

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

$$\omega = 2\pi f$$

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

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

$$\Delta\theta = 0$$

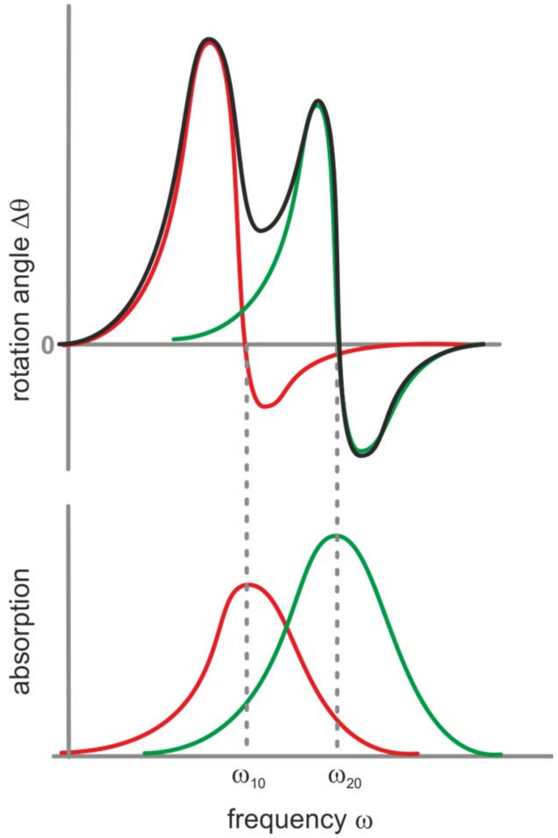
due to the sum rule $\sum_n (R_{n0}) = 0$

➢➢➢ 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)

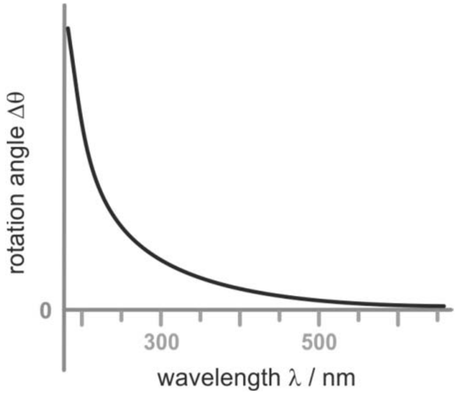
When $\omega_{n0}^2 - \omega^2 \rightarrow 0$, i.e. if the excitation frequency is close to an absorption band, the contribution of that particular transition dominates the OR value:

$$\Delta\theta = \frac{\mathcal{N} l\, \mu_v \omega^2 R_{10}}{3\hbar\left(\omega_{10}^2 - \omega^2\right)}$$



- 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**	
✓	Monday	Introduction	
✓		Polarization of light	
✓	Tuesday	Theoretical basis of optical activity	
		Optical rotation	
	Wednesday	Circular dichroism	
		Circular dichroism	
	Thursday	Vibrational optical activity	
		Vibrational optical activity	
	Oct 22?	applications	your part
	Oct 29?	applications	