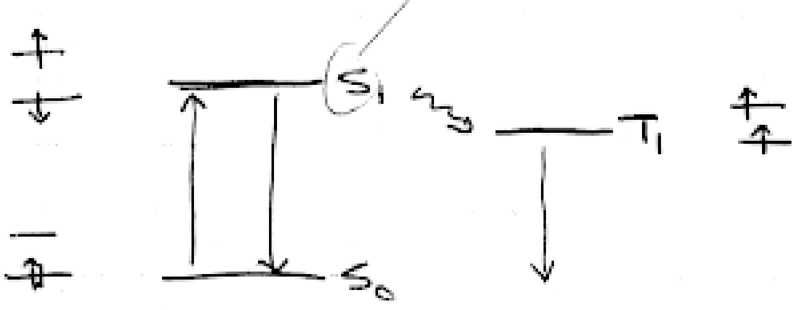
12/7/01

Q: Why the "S"?

Phosphorescence (glow in the dark paint)



When an e^{-} goes from ψ_1 to ψ_2
it does not simultaneously change its spin

Paired spins ⇒ singlet (S) state

But Pauli says that $\begin{matrix}\uparrow\\ \uparrow\end{matrix}$ is lower E than $\begin{matrix}\downarrow\\ \uparrow\end{matrix}$

So with some
probability a spin can flip.
Unpaired spins ⟶ triplet (T) state.

But then $T_1 \xrightarrow[\substack{\wr\\ h\nu}]{} S_0$ is "forbidden"
(unlikely)

because the spin flips simultaneously with
the orbital transition.
Since it's "forbidden," it occurs very slowly
(hours sometimes,
compared with μs → ns for
flourescence).

Polarized light

Linear

in the picture above
E_y oscillates
$E_x = E_z = 0$

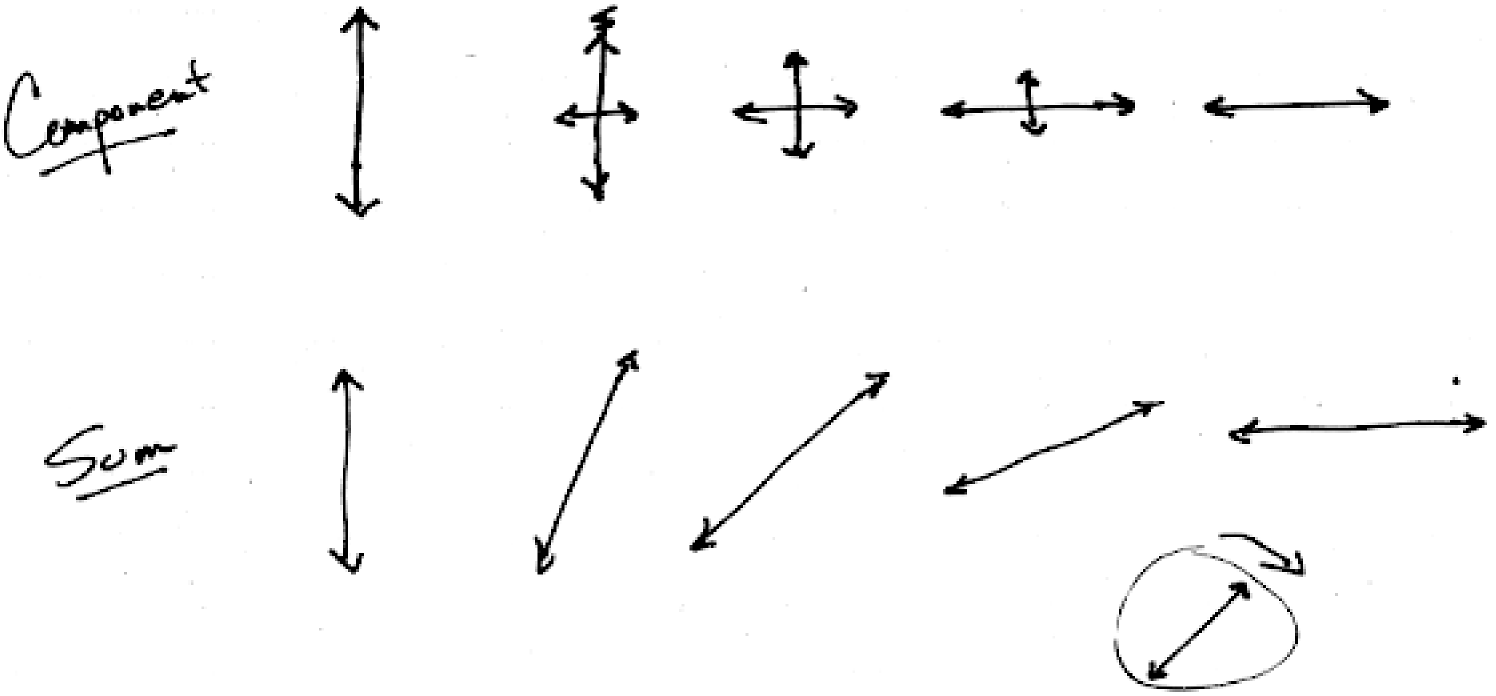
Light propogating in z-direct
polarized in y-direction

We saw before that
this particular polarization
can only excite
some transitions.

CIRCULAR

IMAGINE ADDING two $\vec{E}$ vectors

Perpendicular and exactly out of phase



Result is polarized light <u>rotating</u> as it propogates.

— See pretty pictures in text

Mathematically

$$\vec{E}(z,t) = \tfrac{1}{2}E_0 \sin\left[2\pi\left(\frac{z}{\lambda} - \frac{ct}{\lambda}\right)\right]\hat{\imath} + \tfrac{1}{2}E_0 \sin\left\{2\pi\left(\frac{z}{\lambda} + \frac{ct}{\lambda} + \frac{1}{4}\right)\right\}\hat{\jmath}$$

OR

$$\underbrace{\tfrac{1}{2}E_0 \sin\left[2\pi\left(\frac{z}{\lambda} - \frac{ct}{\lambda}\right)\right]\hat{\imath}}_{x\text{-component}} + \underbrace{\tfrac{1}{2}\overset{E_0}{\cancel{}} \cos\left\{2\pi\left(\frac{z}{\lambda} + \frac{ct}{\lambda}\right)\right\}}_{y\text{-component}}\hat{\jmath}$$

⟹ Harder to imagine, but molecules with a particular chirality, absorb left circ polarized light a bit more than right circularly polarized light.

SCATTERING (BIREFRINGENCE)

$$\text{Rotation} = \phi = \frac{\pi}{\lambda}\big(\underbrace{n_L - n_R}_{\substack{\text{birefringence}\\ \text{left}\,-\,\text{right}}}\big)$$

We have <u>not</u> talked about this. Don't worry.

Related to refractive index.

<u>SKIP</u>

IGNORE: ELLIPTICITY
OPTICAL ROTATION

Circular Dichroism

$$\Delta A = A_L - A_R$$

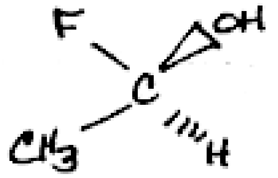
Difference

Absorbance of left circularly polarized light

Absorbance of right circularly polarized light.

Ellipticity = another measure of the same thing

HOW IT'S USED



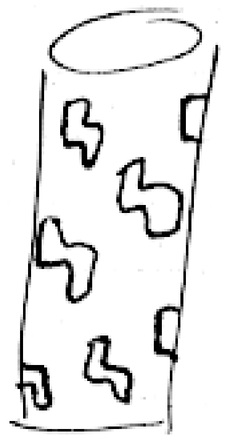
Chiral

But not interesting to us now.
Q: Why?

A: BIG BOX too little

The common uses arise from Coupling of transitions.

α-helix



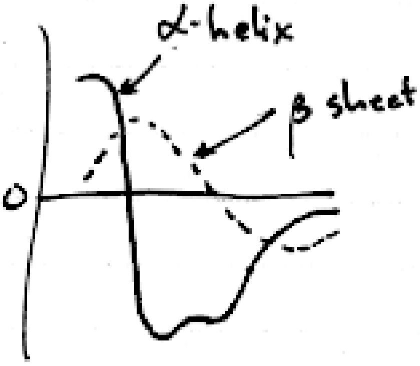
A collection of peptide π-boxes.
They actually interact in a way dependent on their geometrically defined inter-relationships

Result: Absorb more one than the other.

CD pattern is characteristic of an right-handed α-helix

Different pattern for β-sheet.

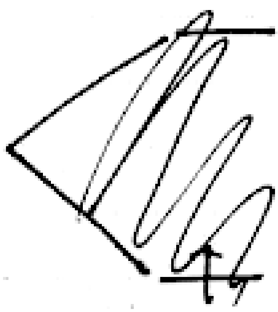
So ⇒ Can use CD to distinguish.



Also <u>turns</u>, etc.

A real protein is then the sum of
X% α-helix
Y% β-sheet
Z% turn
Remainder "Random"

INTRO TO NMR — Opposite end of energy scale (<u>small</u>)
∴ <u>long</u> wavelength
(<u>radio</u> frequency)



$\uparrow$ or $\downarrow$ Same energy

Apply $\vec{B}_0$ $\Uparrow$ lower E ⇅ higher E