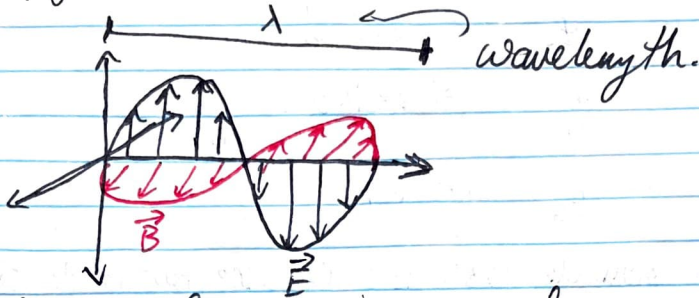Beer's Law = Equilibrium Lab Notes
What is light? Its an electromagnetic wave that
propogates in some direction.

Of course for any wave we have a wave length λ,
and frequency. Light moves at speed of light $c \sim 3\times10^8 m/s$
and thus

$$v = \frac{c}{\lambda}$$

Similarly, we often see sometimes an "angular frequency"
associated to a light wave, $\omega = 2\pi v$. This is not really a
physical frequency but is often prefered. Now Planck proposed
that light is actually made of quanta of energy and
act as particles (called photons). Gave birth to wave-particle
duality of light. Einstein wins Nobel Prize for photoelectric
effect confirming this and that the energy of light is given
as

$$E = h v = \hbar \omega$$

where h is Planck's constant, 6.626×10^{-34} J·s
$\hbar$ (named "h-bar") is reduced Planck's constant and is
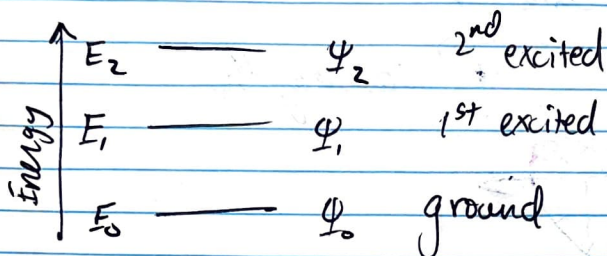
$$\hbar = \frac{h}{2\pi}$$

If we have n photons of light at frequency ω, then
the total energy is

$$E = n\hbar\omega$$

Now quantum mechanics governs molecules, and specifically electrons.
What we have for bound states are quantized (discrete)
energy states of the system. That is the system can only
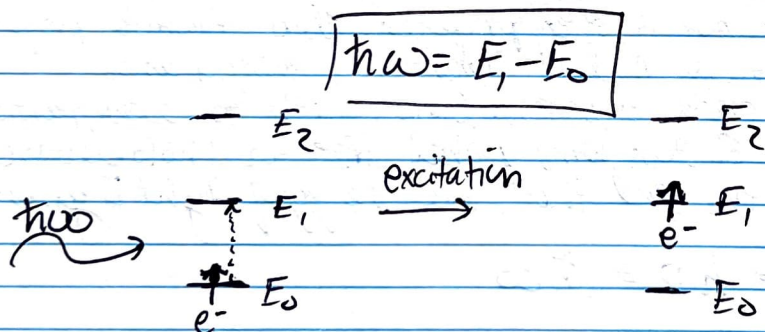have certain amounts of energy, say $E_0, E_1, E_2, \dots$ etc.

The lowest energy state is called the ground state, often denoted Ψ_0, with corresponding energy E_0.

$$
\begin{array}{lll}
E_2 \text{ ———} & \Psi_2 & 2^{nd} \text{ excited} \\
E_1 \text{ ———} & \Psi_1 & 1^{st} \text{ excited} \\
E_0 \text{ ———} & \Psi_0 & \text{ground}
\end{array}
$$

(energy axis pointing up, labeled "energy")

If light hits a molecule, there is a chance for it to excite an electron to an excited state. This is only possible if the energy of the incident light exactly equals the difference in energy between states.

Ex: That is, to excite an electron from $\Psi_0 \rightarrow \Psi_1$, we must have an incoming light wave of energy $E = E_1 - E_0$. That is

$$\boxed{\hbar\omega = E_1 - E_0}$$

$$
\begin{array}{ccc}
\underline{} \; E_2 & & \underline{} \; E_2 \\
& \xrightarrow{\text{excitation}} & \\
\underline{\updownarrow} \; E_1 & & \underline{\uparrow} \; E_1 \\
& & e^- \\
\underline{\uparrow} \; E_0 & & \underline{} \; E_0 \\
e^- & &
\end{array}
$$

$\hbar\omega \rightsquigarrow$

There are some more complications but this is more or less the mechanism we are concerned with.

Most molecules have $E_1 - E_0$ being fairly large such that visible light is not absorbed, but UV light. Though transition metals have d-orbitals which often reduce this spacing such that they are able to absorb light in the visible region (390 nm – 760 nm).

Have a solution of this complex and shine white light on it

white
light → [beaker] white
light – green light 👁
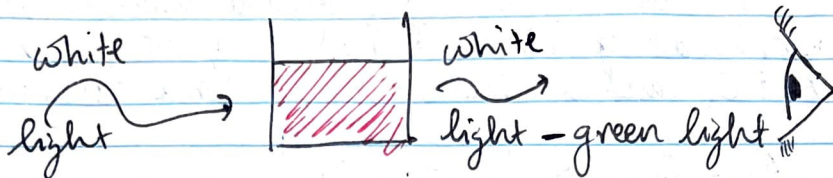
all light, except that which it absorbs passes through
& reaches our eyes. The color we perceive is then the
complement of that which is absorbed.

[color wheel: red, orange, yellow, green, blue, violet]

red ⇒ absorbed green
yellow ⇒ absorbed violet
etc.

Cool? What if we shine only green light on our sample?
Would no light come out the other side?

Almost. We neglect probabilities of light hitting & rates
of absorption and decay so some light will come out
the other side. Though it can be shown from
first principles that

$$I = I_0 \, 10^{-\varepsilon L C}$$

I: intensity of light transmitted
I_0: incident light intensity
ε: molar extinction coefficient (compound dependent)
L: length the light travels
c: concentration of compound.

If we let $A = -\log \dfrac{I}{I_0}$, the absorbance, then

$$\boxed{A = \varepsilon L C}$$ Beer's law.

In lab we will use this to determine concentrations of a solution at equilibrium! That is if we know $A_1 : C_1$ and we measure A_2 for some unknown C_2, then

$$\frac{A_1}{A_2} = \frac{C_1}{C_2} \implies \boxed{C_2 = C_1 \frac{A_2}{A_1}}$$

we can experimentally determine the concentration! In this lab, we will know $Fe^{3+} : SCN^-$ initial concentrations, but won't know $(FeSCN)^{2+}$ or $Fe(SCN)_3$ (or which complex) at equilibrium. So what do we do?

$100:1 \quad Fe^{3+} : SCN$ stock solution.

1) Assume all $SCN^- \rightarrow (FeSCN)^{2+}$ or $Fe(SCN)_3$, set [F][F][F]

2) Make dilutions off of this and take ratios of A to A_0 above

3) Determine concentration of $Fe(SCN)_3$ or $(FeSCN)^{2+}$ from absorbance.

4) Determine K_{eq}.

5) Repeat for all solutions, and take average of K_{eq}.

6) Using best K_{eq}, ie (ie smallest stdev) determine which complex is formed

7) Determine K_{eq} for that association reaction.