From last lecture,

\[
\alpha_0 = \frac{e^2}{m} \left[ \frac{\left(\omega_0^2 - \omega^2\right)}{\left(\omega_0^2 - \omega^2\right)^2 + 4\omega'^2\omega^2} \right] \text{ contribution to dispersion}
\]

\[
\alpha_{90} = \frac{2e^2}{m} \left[ \frac{\omega\omega'}{\left(\omega_0^2 - \omega^2\right)^2 + 4\omega'^2\omega^2} \right] \text{ contribution to absorption}
\]

where \( \mu^{in} = \alpha_0 E_0^* \sin \omega t - \alpha_{90} E_0^* \cos \omega t \)

**For \( w \sim \omega_0 \) (Resonance)**

\[
\alpha_0 \equiv 0
\]

\[
\alpha_{90} > 0 \quad \alpha_{90}^{\max} = \frac{e^2}{m} \frac{1}{\omega'\omega_0}
\]

**Figure 10-1**

**For \( w >> \omega_0 \) or \( w << \omega_0 \)**

\[
\left(\omega_0^2 - \omega^2\right)^2 >> 4\omega'^2\omega_0^2
\]

\[
\alpha_0 = \frac{e^2}{m} \frac{1}{\omega_0^2 - \omega^2}
\]

\( \quad \alpha_{90} = \text{small} \)

\[\therefore \quad \mu^{in} = \alpha_{90} E_0^* \sin \omega t \text{ (in phase only)} \quad \text{depending on sign of } \alpha_0 \]

or \( 180^\circ \text{out - of - phase} \)
At low frequencies,
\[ \omega_0 \gg \omega, \quad \alpha_0 > 0 \]
\[ \mu^\text{in} \text{ in phase} \]

\[ u^\text{in} = \alpha_0 E_0^* \sin \omega t \quad \text{(in phase)} \]

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure10-2}
\caption{Figure 10-2}
\end{figure}

At high frequencies,
\[ \omega_0 << \omega, \quad \alpha_0 < 0 \]
\[ \mu^\text{in} \text{ out-of-phase by } 180^\circ \]

\[ u^\text{in} = -|\alpha_0| E_0^* \sin \omega t \quad \text{(out-of-phase by } 180^\circ) \]

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure10-3}
\caption{Figure 10-3}
\end{figure}

**Interaction of Light with Molecules — Quantum Mechanical Treatment**

Must solve time-dependent Schroedinger equation.

\[ H = H_0 + v(t) \]

where \( v(t) \) describes the interaction of electrons with light waves.

Assume one electron.
If electric interaction, \( \nu(t) = -\mu_{el} \cdot E^* \)

If magnetic interaction, \( \nu(t) = -\mu_{m} \cdot E^* \)

Discuss electric interaction, where \( \mu_{el} = -|e| \cdot \vec{r} \).

Treat, for simplicity, a two-level system.

\[
\begin{array}{c c c c}
| & b & W_b & \psi_b(\vec{r}, t) \\
\hline
a & W_a & \psi_a(\vec{r}, t) \\
\end{array}
\]

\[
\psi_a(\vec{r}, t) = \phi_a(\vec{r}) e^{-iW_a t / \hbar} \\
\psi_b(\vec{r}, t) = \phi_b(\vec{r}) e^{-iW_b t / \hbar}
\]

\[
\text{solution to time-dependent Schrödinger equation for } \nu(t) = 0
\]

In the presence of \( \nu(t) \), \( \psi(\vec{r}, t) \) must be a linear combination of these two states, but the coefficients \( c_a \) and \( c_b \) are time-dependent, i.e.,

\[
\psi(\vec{r}, t) = c_a(t) \phi_a(\vec{r}) e^{-iW_a t / \hbar} + c_b(t) \phi_b(\vec{r}) e^{-iW_b t / \hbar}
\]

Substituting this solution into the time-dependent Schrödinger equation, we get

\[
i\hbar \left( \phi_a(\vec{r}) e^{-iW_a t / \hbar} \frac{dc_a}{dt} + \phi_b(\vec{r}) e^{-iW_b t / \hbar} \frac{dc_b}{dt} \right) = \nu(t) \left[ \phi_a(\vec{r}) e^{-iW_a t / \hbar} c_a(t) + \phi_b(\vec{r}) e^{-iW_b t / \hbar} c_b(t) \right]
\]

Multiplying and integrating above from the left by \( \phi_a^*(\vec{r}) e^{iW_a t / \hbar} \) or \( \phi_b^*(\vec{r}) e^{iW_b t / \hbar} \), we obtain

\[
i\hbar \frac{dc_a}{dt} = \nu_{aa} c_a(t) + \nu_{ab} c_b(t) e^{-i(W_a - W_b) t / \hbar}
\]

\[
i\hbar \frac{dc_b}{dt} = \nu_{ba} c_a(t) e^{-i(W_a - W_b) t / \hbar} + \nu_{bb} c_b(t)
\]
where

\[ \nu_{aa} = \left( \int \phi_a^*(\vec{r}) \nu(t) \phi_a(\vec{r}) d\vec{r} \right) \]
\[ \nu_{ab} = \left( \int \phi_a^*(\vec{r}) \nu(t) \phi_b(\vec{r}) d\vec{r} \right) = \nu_{ba} \]
\[ \nu_{bb} = \left( \int \phi_b^*(\vec{r}) \nu(t) \phi_b(\vec{r}) d\vec{r} \right) \]

a set of coupled first-order differential equations.

If we take

\[ \nu(t) = -\vec{\mu} \cdot \vec{E}_0^* e^{i\omega t} \]

where \( \vec{\mu} = -|e| \vec{r}^* \)

then \( \nu_{aa} = 0, \ \nu_{bb} = 0 \) and

\[ -i \hbar \frac{d c_a}{d t} = c_b(t) \nu_{ab} \vec{E}_0^* e^{-i\left( \frac{W_b - W_a}{\hbar} - \omega \right) t} \]
\[ -i \hbar \frac{d c_b}{d t} = c_a(t) \nu_{ba} \vec{E}_0^* e^{-i\left( \frac{W_b - W_a}{\hbar} - \omega \right) t} \]

Solving simultaneously, with boundary condition \( |c_b(0)|^2 = 0 \) at \( t = 0 \), i.e., electron is in quantum state \( a \) at \( t = 0 \), and for small \( \vec{E}_0^* \)

\[ |c_b(t)|^2 = \left| \nu_{ba} \cdot \vec{E}_0^* \right|^2 \frac{\sin^2 \left[ \left( \frac{W_b - W_a}{\hbar} - \omega \right) \frac{t}{2} \right]}{2 \left[ \left( \frac{W_b - W_a}{\hbar} - \omega \right) \frac{t}{2} \right]^2} \]

where \( \vec{\mu}_{ba} = \int \phi_b^* \vec{\nu} \phi_a d\vec{r} = \vec{\nu}_{ab} = \int \phi_a^* \vec{\mu} \phi_b d\vec{r} \)
resonance

\[ |c_b(t)|^2 = \text{probability of finding } e^- \text{ in state } b \]

Bohr condition
\[ \hbar \omega = W_b - W_a \]

Figure 10-4

Now, the rate at which molecules in state \( a \) are transformed to state \( b \) by the presence of light is

\[
\frac{dP_b}{dt} = \frac{d}{dt} \int |c_b(t)|^2 \, dv
\]

\[
= \frac{1}{2\hbar^2} |\hat{\mu}_{ba} \cdot E_0^*|^2
\]

It is customary to write

\[
\frac{dP_b}{dt} = B_{ab} I(\nu)
\]

where \( B_{ab} \) = transition rate per unit energy density of radiation

\( a \) = initial state

\( b \) = final state

\( I(\nu) \) = energy density incident on the sample at frequency \( \nu \)

From E and M,

\[
I(\nu) = \frac{|E_0^*|^2}{4\pi}
\]

so

\[
B_{ab} = \left( \frac{2\pi}{\hbar^2} \right) |\hat{\mu}_{ab}|^2 \cos^2 \theta
\]

where \( \theta \) = angle between \( \hat{\nu} \) and \( \hat{E}_0^* \)

The above result is for oriented molecules illuminated by polarized light.
In solution, molecules reorient with respect to $E^*$, so you must average $\cos^2 \theta$.

Since $\cos^2 \theta = \frac{1}{3}$

$$B_{a \rightarrow b} \ (\text{solution}) = \left(\frac{2\pi}{3h^2}\right) |\mu_{ab}|^2$$

The above derivation is for stimulated absorption ($a \rightarrow b$).

```
  b
 absorption
  a
```

Stimulated $B$ coefficient can be obtained for stimulated emission ($b \rightarrow a$), i.e.,

$$B_{a \rightarrow b} = B_{b \rightarrow a} \quad \text{Einstein coefficient for stimulated absorption and emission}$$

Now the rate at which energy is renewed from light will depend on the number of $a \rightarrow b$ absorption transitions stimulated by the light, on the number of $b \rightarrow a$ emission transitions (also stimulated by the light), and on the energy of the photon ($W_b - W_a = h\nu$) where $W_b - W_a = \hbar\omega$.

$$-\frac{dI(\nu)}{dt} = h\nu \left(N_a B_{ab} - N_b B_{ba}\right) I(\nu)$$

where $N_a, N_b \equiv$ number of molecules per cm$^3$ in state $a$ and $b$ respectively

$I(\nu) \equiv \nu$

**Beer-Lambert’s Law**

For optical transitions, $N_b$ is negligible.

$$-\frac{dI(\nu)}{dt} \equiv h\nu N_a B_{ab} I(\nu)$$

$$= h\nu \frac{CN_a}{1000} B_{ab} I(\nu) \quad C \equiv \text{concentration of absorbers (all in state } a)$$
Now \[ \frac{dI(\nu)}{dl} = \frac{dI(\nu)}{dt} \left( \frac{dt}{dl} \right) = \frac{1}{c_{\text{light}}} \frac{dI(\nu)}{dt} = \frac{h \nu}{c_{\text{light}}} \frac{CN_A}{1000} B_{ab} I(\nu) \]

\[ \text{path length} \]

or \[ dI(\nu) = \left( \frac{h \nu CN_A}{1000 c_{\text{light}}} B_{ab} \right) I(\nu) \, dl \]

or \[ \epsilon(\nu) = \frac{h \nu N_A}{1000 c_{\text{light}}} B_{ab} \quad \epsilon \equiv \text{extinction coefficient} \]

or \[ B_{ab} = \frac{1000 c_{\text{light}}}{h \nu N_A} \epsilon(\nu) \]

or integrating over absorption band

\[ B_{ab} = \frac{1000 c_{\text{light}}}{h N_A} \int_{\text{absorption band}} \frac{\epsilon(\nu)}{\nu} \, d\nu \]