Two-level system

Take a two-level system

with energies E_1 and E_2

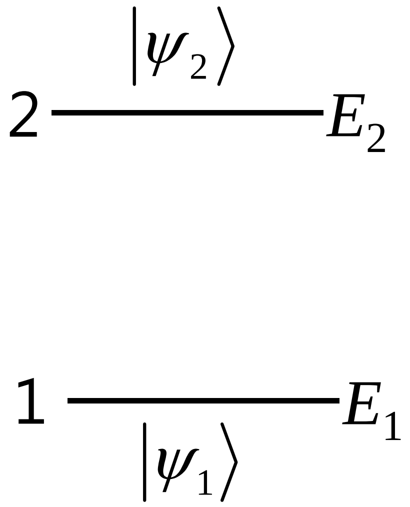
and eigenfunctions $|\psi_1\rangle$ and $|\psi_2\rangle$

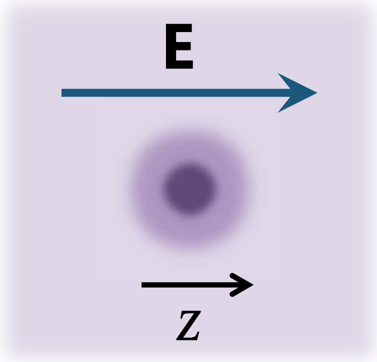
Presume the system is much smaller than an optical wavelength

so an incident optical field **E** will be uniform across the system

and take **E** to be polarized in the z direction

with magnitude E





Two-level system

Here we will just treat the interaction with the electric field semiclassically

We take an "electric dipole" interaction

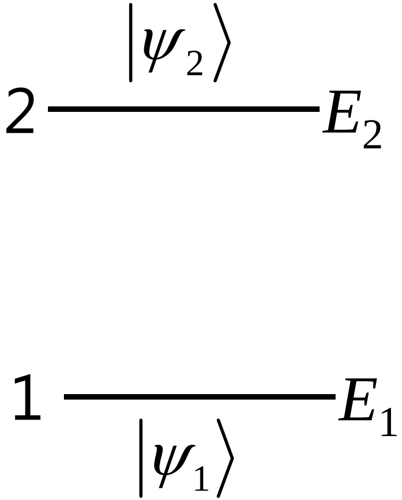
between the light

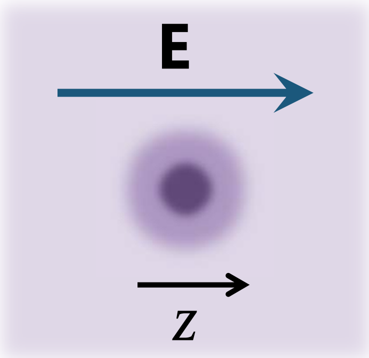
and the electron in the system

so that the energy change

on displacing by an amount z

is $e\mathrm{E}z$





Interaction of light with a two-level system

Hence we can take the (semiclassical) perturbing Hamiltonian as

$$\hat{H}_p = e\mathrm{E}z \equiv -\mathrm{E}\hat{\mu}$$

where $\hat{\mu}$ is what we will call

the electric dipole operator

with matrix elements

$$\mu_{mn} = -e\langle \psi_m | z | \psi_n \rangle$$

so that the matrix elements of the perturbing Hamiltonian become

$$\left(\hat{H}_p\right)_{mn} \equiv H_{pmn} = -\mathrm{E}\mu_{mn}$$

Interaction of light with a two-level system

We choose the states $|\psi_1\rangle$ and $|\psi_2\rangle$

to have definite parity in the z direction

so with our definition $\mu_{mn} = -e\langle\psi_m|z|\psi_n\rangle$

$$\mu_{11} = \mu_{22} = 0$$

and hence with our definition $H_{pmn} = -\mathrm{E}\mu_{mn}$

$$H_{p11} = H_{p22} = 0$$

We are free to choose the relative phase of the two wavefunctions such that μ_{12} is real

so that we have

$$\mu_{12} = \mu_{21} \equiv \mu_d$$

Interaction of light with a two-level system

Hence the dipole operator can be written $\hat{\mu} = \begin{bmatrix} 0 & \mu_d \\ \mu_d & 0 \end{bmatrix}$

and the perturbing Hamiltonian is $\hat{H}_p = \begin{bmatrix} 0 & -\mathrm{E}\mu_d \\ -\mathrm{E}\mu_d & 0 \end{bmatrix}$

The unperturbed Hamiltonian $\hat{H}_o$

is just a 2 x 2 diagonal matrix on this basis

with E_1 and E_2 as the diagonal elements

So the total Hamiltonian is $\hat{H} = \hat{H}_o + \hat{H}_p = \begin{bmatrix} E_1 & -\mathrm{E}\mu_d \\ -\mathrm{E}\mu_d & E_2 \end{bmatrix}$

Interaction of light with a two-level system

The density matrix is also a 2 x 2 matrix

because there are only two basis states under consideration here

and in general we can write it as

$$\rho = \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix}$$

for this two-level system

The dipole of the system

We have not yet defined the system's state

but we can use $\overline{\langle A \rangle} = Tr\left(\rho \hat{A}\right)$ to write

$$\overline{\langle \mu \rangle} = Tr\left(\rho \hat{\mu}\right)$$

Using $\hat{\mu} = \begin{bmatrix} 0 & \mu_d \\ \mu_d & 0 \end{bmatrix}$ and $\rho = \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix}$ we have

$$\rho \hat{\mu} = \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} \begin{bmatrix} 0 & \mu_d \\ \mu_d & 0 \end{bmatrix} = \begin{bmatrix} \rho_{12}\mu_d & \rho_{11}\mu_d \\ \rho_{22}\mu_d & \rho_{21}\mu_d \end{bmatrix}$$

Hence $\overline{\langle \mu \rangle} = \mu_d \left(\rho_{12} + \rho_{21}\right)$

Behavior of the density matrix in time

We have, from $\partial\rho / \partial t = (i / \hbar)\left[\rho, \hat{H}\right]$ with the definitions

$$\rho = \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} \text{ and } \hat{H} = \hat{H}_o + \hat{H}_p = \begin{bmatrix} E_1 & \text{-E}\mu_d \\ \text{-E}\mu_d & E_2 \end{bmatrix}$$

$$\frac{d\rho}{dt} = \frac{i}{\hbar}\left(\rho\hat{H} - \hat{H}\rho\right)$$

$$= \frac{i}{\hbar}\left(\begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix}\begin{bmatrix} E_1 & \text{-E}\mu_d \\ \text{-E}\mu_d & E_2 \end{bmatrix} - \begin{bmatrix} E_1 & \text{-E}\mu_d \\ \text{-E}\mu_d & E_2 \end{bmatrix}\begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix}\right)$$

$$= \frac{i}{\hbar}\begin{bmatrix} -\text{E}\mu_d\left(\rho_{12} - \rho_{21}\right) & -\text{E}\mu_d\left(\rho_{11} - \rho_{22}\right) + \left(E_2 - E_1\right)\rho_{12} \\ -\text{E}\mu_d\left(\rho_{22} - \rho_{11}\right) + \left(E_1 - E_2\right)\rho_{21} & -\text{E}\mu_d\left(\rho_{21} - \rho_{12}\right) \end{bmatrix}$$

Behavior of the density matrix in time

Taking the "2 – 1" element of both sides in

$$\frac{d\rho}{dt} = \frac{i}{\hbar}\begin{bmatrix} -\mathrm{E}\mu_d\left(\rho_{12}-\rho_{21}\right) & -\mathrm{E}\mu_d\left(\rho_{11}-\rho_{22}\right)+\left(E_2-E_1\right)\rho_{12} \\ -\mathrm{E}\mu_d\left(\rho_{22}-\rho_{11}\right)+\left(E_1-E_2\right)\rho_{21} & -\mathrm{E}\mu_d\left(\rho_{21}-\rho_{12}\right) \end{bmatrix}$$

with $\hbar\omega_{21} = E_2 - E_1$ gives

$$\frac{d\rho_{21}}{dt} = \frac{i}{\hbar}\left[\left(\rho_{11}-\rho_{22}\right)\mathrm{E}\mu_d - \left(E_2-E_1\right)\rho_{21}\right] = -i\omega_{21}\rho_{21} + i\frac{\mu_d}{\hbar}\mathrm{E}\left(\rho_{11}-\rho_{22}\right)$$

Behavior of the density matrix in time

From the diagonal elements in

$$\frac{d\rho}{dt} = \frac{i}{\hbar}\begin{bmatrix} -\mathrm{E}\mu_d\left(\rho_{12}-\rho_{21}\right) & -\mathrm{E}\mu_d\left(\rho_{11}-\rho_{22}\right)+\left(E_2-E_1\right)\rho_{12} \\ -\mathrm{E}\mu_d\left(\rho_{22}-\rho_{11}\right)+\left(E_1-E_2\right)\rho_{21} & -\mathrm{E}\mu_d\left(\rho_{21}-\rho_{12}\right) \end{bmatrix}$$

we can examine the population difference $\rho_{11}-\rho_{22}$ between the lower and upper states

Using the Hermiticity of ρ

which tells us that $\rho_{12} = \rho_{21}^*$

we have $\dfrac{d}{dt}\left(\rho_{11}-\rho_{22}\right) = 2i\dfrac{\mu_d}{\hbar}\mathrm{E}\left(\rho_{21}-\rho_{21}^*\right)$

Behavior of the density matrix in time

Solving $$\frac{d\rho_{21}}{dt} = -i\omega_{21}\rho_{21} + i\frac{\mu_d}{\hbar}\mathrm{E}\left(\rho_{11} - \rho_{22}\right)$$

and $$\frac{d}{dt}\left(\rho_{11} - \rho_{22}\right) = 2i\frac{\mu_d}{\hbar}\mathrm{E}\left(\rho_{21} - \rho_{21}^{*}\right)$$

covers any possible behavior of this idealized system

Note: this is not a perturbation theory analysis

Density matrix and relaxation times

Consider a fractional population difference $\rho_{11} - \rho_{22}$

between the "lower" and "upper" states

Suppose that, in equilibrium, with no applied fields

this difference would have a value $(\rho_{11} - \rho_{22})_o$

Then experience might tell us that

because of mechanisms such as

collisions with the walls of a box or with other atoms

or by spontaneous emission

such systems often settle back down again to $(\rho_{11} - \rho_{22})_o$

with an exponential decay with some time constant T_1

Density matrix and relaxation times

Then we could hypothesize that we could add a term to

$$\frac{d}{dt}(\rho_{11}-\rho_{22}) = 2i\frac{\mu_d}{\hbar}\mathrm{E}\left(\rho_{21}-\rho_{21}^{*}\right)$$

to give

$$\frac{d}{dt}(\rho_{11}-\rho_{22}) = 2i\frac{\mu_d}{\hbar}\mathrm{E}\left(\rho_{21}-\rho_{21}^{*}\right) - \frac{(\rho_{11}-\rho_{22})-(\rho_{11}-\rho_{22})_o}{T_1}$$

For E = 0, this expression would give exponential decay

back to $(\rho_{11}-\rho_{22}) = (\rho_{11}-\rho_{22})_o$

with time constant T_1

Density matrix and relaxation times

We have to consider a similar process also

for the off-diagonal elements of the density matrix

as in $\frac{d\rho_{21}}{dt} = -i\omega_{21}\rho_{21} + i\frac{\mu_d}{\hbar}\mathrm{E}\left(\rho_{11} - \rho_{22}\right)$

To understand this, we need to understand

the meaning of the off-diagonal elements ρ_{21} and ρ_{12}

which we remember are defined with a relation

$$\rho_{uv} \equiv \langle \phi_u | \rho | \phi_v \rangle = \sum_j P_j c_u^{(j)} \left(c_v^{(j)} \right)^* \equiv \overline{c_u c_v^*}$$

Dephasing

Within any given pure state j

the product $c_u^{(j)}\left(c_v^{(j)}\right)^*$ is in general oscillating

If we have expanded in energy eigenstates $|\phi_u\rangle$ and $|\phi_v\rangle$

of the unperturbed system

there is a time-dependence $\exp\left(-iE_u t/\hbar\right)$ built into $c_u^{(j)}$

and a time-dependence $\exp\left(iE_v t/\hbar\right)$ built into $\left(c_v^{(j)}\right)^*$

so the product $c_u^{(j)}\left(c_v^{(j)}\right)^*$

has an underlying oscillation of the form

$$\exp(-i(E_u - E_v)t/\hbar)$$

Dephasing

As time evolves, the system can get scattered

from pure state j into another pure state k

with some probability

possibly even a state in which ρ_{11} and ρ_{22} are unchanged

but in which the phases of the coefficients

$c_1^{(k)}$ and $c_2^{(k)}$ are different

At any given time, therefore, we may have an ensemble of

different possibilities for the quantum mechanical state

all possibly with different phases of oscillation

Dephasing

In our mixed state

if we have sufficiently many such random phases that are sufficiently different

then the ensemble average of a product $c_u c_v^*$

for different u and v, i.e., $\overline{c_u c_v^*}$

will average out to zero

But this ensemble average is simply

the off-diagonal density matrix element $\rho_{uv} \equiv \overline{c_u c_v^*}$

Hence, off-diagonal elements contain information about the coherence of the populations in different states

Dephasing

The processes that scatter into states with different phases

can be called "dephasing" processes

The simplest model is that

dephasing processes cause

an exponential settling

of any off-diagonal element

to zero

with some time constant T_2

Dephasing

Hence we postulate adding a term $-\rho_{21} / T_2$ to

$$\frac{d\rho_{21}}{dt} = -i\omega_{21}\rho_{21} + i\frac{\mu_d}{\hbar}\mathrm{E}(\rho_{11} - \rho_{22})$$

to obtain

$$\frac{d\rho_{21}}{dt} = -i\omega_{21}\rho_{21} + i\frac{\mu_d}{\hbar}\mathrm{E}(\rho_{11} - \rho_{22}) - \frac{\rho_{21}}{T_2}$$

In the absence of an optical field E

ρ_{21} would execute an oscillation at approximately frequency ω_{21}

decaying to zero approximately exponentially with a dephasing time constant T_2

Behavior with oscillating field

We want see what happens when

we apply an oscillating electric field

$$\mathrm{E}(t) = \mathrm{E}_o \cos \omega t = \frac{\mathrm{E}_o}{2}\left(\exp(i\omega t) + \exp(-i\omega t)\right)$$

to our two-level system

We can simplify our algebra and results

if we define new "slowly varying" quantities

$$\beta_{21}(t) = \rho_{21}(t)\exp(i\omega t) \qquad \beta_{12}(t) = \rho_{12}(t)\exp(-i\omega t)$$

Using these quantity takes out the underlying oscillation at frequency ω from our algebra

Behavior with oscillating field

We can rewrite $\frac{d\rho_{21}}{dt} = -i\omega_{21}\rho_{21} + i\frac{\mu_d}{\hbar}\mathrm{E}\left(\rho_{11} - \rho_{22}\right) - \frac{\rho_{21}}{T_2}$

and $\frac{d}{dt}\left(\rho_{11} - \rho_{22}\right) = 2i\frac{\mu_d}{\hbar}\mathrm{E}\left(\rho_{21} - \rho_{21}^{*}\right) - \frac{\left(\rho_{11} - \rho_{22}\right) - \left(\rho_{11} - \rho_{22}\right)_o}{T_1}$

using $\beta_{21}(t) = \rho_{21}(t)\exp(i\omega t)$

and dropping all terms $\propto \exp(\pm 2i\omega t)$

on the presumption that such terms will average out to zero over timescales of cycles and hence

they will make relatively little contribution to the resulting values of $\rho_{11} - \rho_{22}$ and β_{12}

Bloch equations

Hence we obtain, approximately

$$\frac{d}{dt}\left(\rho_{11}-\rho_{22}\right)=i\frac{\mu_d}{\hbar}\mathrm{E}_o\left(\beta_{21}-\beta_{21}^{*}\right)-\frac{\left(\rho_{11}-\rho_{22}\right)-\left(\rho_{11}-\rho_{22}\right)_o}{T_1}$$

$$\frac{d\beta_{21}}{dt}=i\left(\omega-\omega_{21}\right)\beta_{21}+i\frac{\mu_d}{2\hbar}\mathrm{E}_\mathrm{o}\left(\rho_{11}-\rho_{22}\right)-\frac{\beta_{21}}{T_2}$$

These equations are often known as the Bloch equations

They were first derived in the field of magnetic resonance

Dipole average

We defined $\beta_{21}(t) = \rho_{21}(t)\exp(i\omega t)$ and $\beta_{12}(t) = \rho_{12}(t)\exp(-i\omega t)$

We know the density matrix is Hermitian, so $\rho_{12} = \rho_{21}^*$

so $\beta_{12} \equiv \rho_{12}\exp(-i\omega t) = \rho_{21}^*\exp(-i\omega t) = \beta_{21}^*$

We now evaluate the ensemble average

of the dipole moment of the system

which we previously deduced was $\overline{\langle\mu\rangle} = \mu_d(\rho_{12} + \rho_{21})$

We have $\overline{\langle\mu\rangle} = \mu_d(\beta_{12}\exp(i\omega t) + \beta_{21}\exp(-i\omega t))$

$$= 2\mu_d\left[\mathrm{Re}(\beta_{21})\cos\omega t + \mathrm{Im}(\beta_{21})\sin\omega t\right]$$

where we used our result $\beta_{12} = \beta_{21}^*$ from above

Solving in the steady state

Now let us solve in the "steady state"

with a steady monochromatic field and

when the system has settled down

In steady state $\rho_{11} - \rho_{22}$

the population difference between the states

will have settled to some value

so $d(\rho_{11} - \rho_{22})/dt = 0$

Similarly, any coherent responses will have settled down

to follow the appropriate driving field terms

so we expect $d\beta_{21}/dt = 0$ also

Solving in the steady state

So, setting the left-hand sides of both

$$\frac{d}{dt}\left(\rho_{11}-\rho_{22}\right)=i\frac{\mu_d}{\hbar}\mathrm{E}_o\left(\beta_{21}-\beta_{21}^*\right)-\frac{\left(\rho_{11}-\rho_{22}\right)-\left(\rho_{11}-\rho_{22}\right)_o}{T_1}$$

and $$\frac{d\beta_{21}}{dt}=i\left(\omega-\omega_{21}\right)\beta_{21}+i\frac{\mu_d}{2\hbar}\mathrm{E}_o\left(\rho_{11}-\rho_{22}\right)-\frac{\beta_{21}}{T_2}$$

to zero

we can solve the resulting simultaneous linear equations in the two variables β_{21} and $(\rho_{11}-\rho_{22})$

the details of which are left as an exercise

Solutions in the steady state

With $\Omega = \mu_d \mathrm{E}_o / 2\hbar$, the results are

$$\rho_{11} - \rho_{22} = \left(\rho_{11} - \rho_{22}\right)_o \frac{1 + \left(\omega - \omega_{21}\right)^2 T_2^2}{1 + \left(\omega - \omega_{21}\right)^2 T_2^2 + 4\Omega^2 T_2 T_1}$$

$$\mathrm{Im}\left(\beta_{21}\right) = \frac{\Omega T_2 \left(\rho_{11} - \rho_{22}\right)_o}{1 + \left(\omega - \omega_{21}\right)^2 T_2^2 + 4\Omega^2 T_2 T_1}$$

$$\mathrm{Re}\left(\beta_{21}\right) = \frac{\left(\omega_{21} - \omega\right) \Omega T_2^2 \left(\rho_{11} - \rho_{22}\right)_o}{1 + \left(\omega - \omega_{21}\right)^2 T_2^2 + 4\Omega^2 T_2 T_1}$$

Behavior with oscillating field

Presume that we have some large number N

of such systems ("atoms") per unit volume

The population difference (per unit volume) between

the number in the lower state and

the number in the higher state

is therefore

$$\Delta N = N\left(\rho_{11} - \rho_{22}\right)$$

and in the absence of the optical field

the population difference is

$$\Delta N_o = N\left(\rho_{11} - \rho_{22}\right)_o$$

Population difference with oscillating field

Using $\Delta N = N\left(\rho_{11}-\rho_{22}\right)$ and $\Delta N_o = N\left(\rho_{11}-\rho_{22}\right)_o$

we can rewrite

$$\rho_{11}-\rho_{22} = \left(\rho_{11}-\rho_{22}\right)_o \frac{1+\left(\omega-\omega_{21}\right)^2 T_2^2}{1+\left(\omega-\omega_{21}\right)^2 T_2^2 + 4\Omega^2 T_2 T_1}$$

as

$$\boxed{\Delta N = \Delta N_o \frac{1+\left(\omega-\omega_{21}\right)^2 T_2^2}{1+\left(\omega-\omega_{21}\right)^2 T_2^2 + 4\Omega^2 T_2 T_1}}$$

This result tells us how the population difference varies

as a function of optical intensity ($\propto \Omega^2$)

and frequency ω

Polarization with oscillating field

In general in electromagnetism

the (static) polarization P is defined as $P = \varepsilon_o \chi E$

where χ is the susceptibility

When we have an oscillating field

the response of the medium

and hence the polarization

can be out of phase with the electric field

and then it is convenient

to generalize the idea of susceptibility

Susceptibility with oscillating field

We can formally think of the susceptibility

as a complex quantity with real and imaginary parts

χ' and χ'' respectively

or equivalently we can explicitly write

the response to a real field $\mathrm{E}_o \cos \omega t$

as $\mathrm{P} = \varepsilon_o \mathrm{E}_o \left(\chi' \cos \omega t + \chi'' \sin \omega t \right)$

It is also generally true in electromagnetism that

the polarization is the dipole moment per unit volume

Hence here we can also write

$$\mathrm{P} = N \overline{\langle \mu \rangle}$$

Susceptibility with oscillating field

Hence using $\overline{\langle \mu \rangle} = 2\mu_d \left[\mathrm{Re}(\beta_{21}) \cos \omega t + \mathrm{Im}(\beta_{21}) \sin \omega t \right]$

$$\mathrm{Im}(\beta_{21}) = \frac{\Omega T_2 (\rho_{11} - \rho_{22})_o}{1 + (\omega - \omega_{21})^2 T_2^2 + 4\Omega^2 T_2 T_1}$$

$$\mathrm{Re}(\beta_{21}) = \frac{(\omega_{21} - \omega) \Omega T_2^2 (\rho_{11} - \rho_{22})_o}{1 + (\omega - \omega_{21})^2 T_2^2 + 4\Omega^2 T_2 T_1}$$

$$\mathrm{P} = \varepsilon_o \mathrm{E}_o \left(\chi' \cos \omega t + \chi'' \sin \omega t \right)$$

$$\mathrm{P} = N \overline{\langle \mu \rangle}$$

we can write explicit formulas for χ' and χ''

Susceptibility with oscillating field

We obtain

$$\chi'(\omega) = \frac{\mu_d^2 T_2 \Delta N_o}{\varepsilon_o \hbar} \frac{(\omega_{21} - \omega) T_2}{1 + (\omega - \omega_{21})^2 T_2^2 + 4\Omega^2 T_2 T_1}$$

$$\chi''(\omega) = \frac{\mu_d^2 T_2 \Delta N_o}{\varepsilon_o \hbar} \frac{1}{1 + (\omega - \omega_{21})^2 T_2^2 + 4\Omega^2 T_2 T_1}$$

In electromagnetism, $\mathrm{Re}(\chi) \equiv \chi'$, the in-phase response

is responsible for refractive index

and the quadrature (i.e., 90° shifted) response, $\mathrm{Im}(\chi) \equiv \chi''$

is responsible for optical absorption

Small field susceptibility

For a "two-level" system for small electric field amplitude

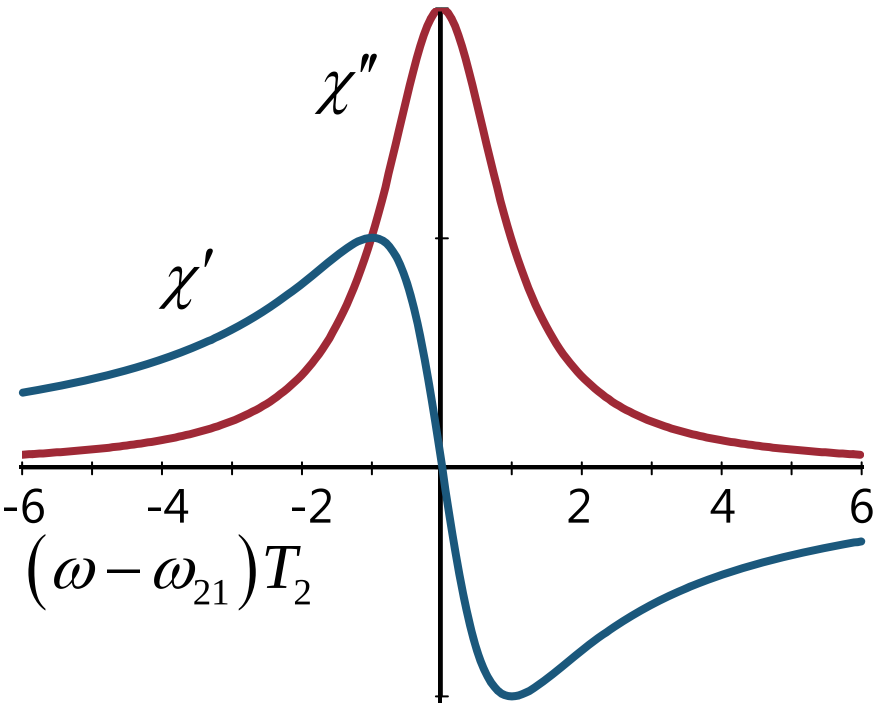
then $\Omega = \mu_d \mathrm{E}_o / 2\hbar \simeq 0$

and we have the normal "linear" refraction variation

$$\chi'(\omega) = \frac{\mu_d^2 T_2 \Delta N_o}{\varepsilon_o \hbar} \frac{(\omega_{21} - \omega) T_2}{1 + (\omega - \omega_{21})^2 T_2^2}$$

and Lorentzian absorption

$$\chi''(\omega) = \frac{\mu_d^2 T_2 \Delta N_o}{\varepsilon_o \hbar} \frac{1}{1 + (\omega - \omega_{21})^2 T_2^2}$$



Absorption saturation

In $\chi''(\omega) = \frac{\mu_d^2 T_2 \Delta N_o}{\varepsilon_o \hbar} \frac{1}{1+(\omega-\omega_{21})^2 T_2^2 + 4\Omega^2 T_2 T_1}$

Ω^2 is proportional to the electric field squared

which is proportional to the intensity I of the light

Hence we can write $4\Omega^2 T_2 T_1 \equiv I / I_S$

where I_S is called the saturation intensity

Hence, for example, on resonance ($\omega_{21} = \omega$), we have

$$\chi''(\omega) \propto 1/(1+I/I_S)$$

This equation describes "absorption saturation"

often seen with the high intensities from lasers

Density matrix and perturbation theory

Now we would start with $\frac{\partial \rho_{mn}}{\partial t} = \frac{i}{\hbar}\left[\rho, \hat{H}\right]_{mn}$

for the time evolution of the density matrix

instead of Schrödinger's equation

We could generalize the relaxation time approximation

now writing a proposed set of relations

$$\frac{\partial \rho_{mn}}{\partial t} = \frac{i}{\hbar}\left[\rho, \hat{H}\right]_{mn} - \gamma_{mn}\left(\rho_{mn} - \rho_{mno}\right)$$

ρ_{mno} is the equilibrium value for ρ_{mn}

and γ_{mn} is its "relaxation rate"

Density matrix and perturbation theory

One then starts with equations like

$$\frac{\partial \rho_{mn}}{\partial t} = \frac{i}{\hbar}\left[\rho, \hat{H}\right]_{mn} - \gamma_{mn}\left(\rho_{mn} - \rho_{mno}\right)$$

instead of the time-dependent Schrödinger equation

and constructs a perturbation theory just as before

This density matrix version is the one commonly used

for calculating non-linear optical coefficients

eliminating the singularities

when the transition energy and the photon energy coincide