Lecture 4

Brief review of quantum mechanics. Quantum-mechanical perturbation theory for the nonlinear optical susceptibility. 1st, 2nd and 3rd order susceptibilities. Susceptibility resonances.

QUANTUM MECHANICS FOR PEDESTRIANS

The most general form is the time-dependent Schrödinger equation

$$i\hbar\dot{\psi} = \hat{H}\psi$$

$\hbar = \frac{h}{2\pi}$ the reduced Planck's constant $= 6.626\times10^{-34}/2\pi = 1.0546\times10^{-34}$ J·s

or

$$\boxed{i\hbar\frac{d\psi}{dt} = \hat{H}\psi} \quad (4.1)$$

ψ- wave function (is the **state vector of the quantum system**). Contains all information about the system

$\hat{H}$ - Hamiltonian operator (~ total energy)

To apply the Schrödinger equation, write down the Hamiltonian $\hat{H}$ for the system, accounting for the kinetic and potential energies of the particles constituting the system, then insert it into the Schrödinger equation. The resulting partial differential equation is solved for the wave function ψ.

For example, the probability of finding a particle at the position ***r*** is ~ $|\psi(r)|^2 = \psi(r)\psi(r)^*$

$$\int \psi\psi * d^3r = 1$$

– i.e. a particle should be somewhere

Quantum mechanics for pedestrians

In the coordinate representation, quantum mechanical <u>operators</u> are represented by :
ordinary numbers *for positions*

$\hat{x}$ -> x

differential operators *for momenta*

$\hat{p}$ -> $-i\hbar\frac{d}{dx}$

kinetic energy potential energy

Assume Hamiltonian $\hat{H}$ that is independent on time: $$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U(x)$$

Here, the form of the Hamiltonian operator comes from classical mechanics, where the Hamiltonian *function* is the sum of the kinetic and potential energies (Similar to $p^2/2m+U(x)$ expression in mechanics)

If *U* does not depend on time, the Schrödinger equation allows **stationary solutions**
Assume the solution in the form $\psi = v(t)u(x)$

Then from (4.1) $$i\hbar\frac{d\psi}{dt} = \hat{H}\psi \longrightarrow \underbrace{u(x)i\hbar\frac{d}{dt}v(t)} = \underbrace{v(t)}\hat{H}u(x)$$

u_n – spatially varying part of the wavefunction
$\omega_n = E_n/\hbar$

It is reasonable to separate the variables and write $$i\hbar\frac{d}{dt}v(t) = Ev(t)$$ where *E* is some constant

then $$Eu(x) = \hat{H}u(x)$$

Quantum mechanics for pedestrians

$$v(t) = e^{-iEt/\hbar} = e^{-i\omega t}$$ $\omega = E/\hbar$

$$\hat{H}u(x) = Eu(x)$$ equation for an eigenfunction

This is where quantization comes from !

$$\hat{H}u_n = E_n u_n \qquad (4.2)$$

Discrete solutions for the **spatially varying** part
E_n has the meaning of **energy**

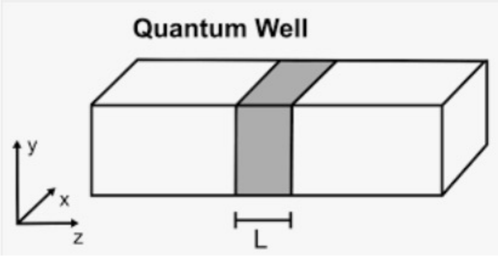
Stationary solutions for ψ :

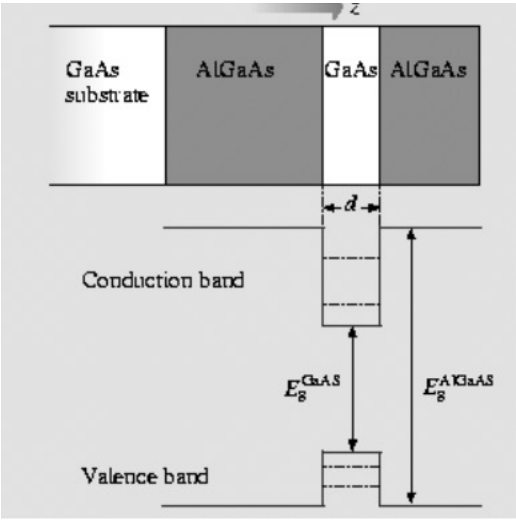
$$\psi_n(t,x) = u_n(x)e^{-iE_n t/\hbar} = u_n(x)e^{-i\omega_n t} \qquad (4.3)$$

u_n – spatially varying
part of the wavefunction
$e^{-i\omega_n t}$ - phase term;
$\omega_n = E_n/\hbar$

The particle-in-a-box problem: semiconductor quantum well

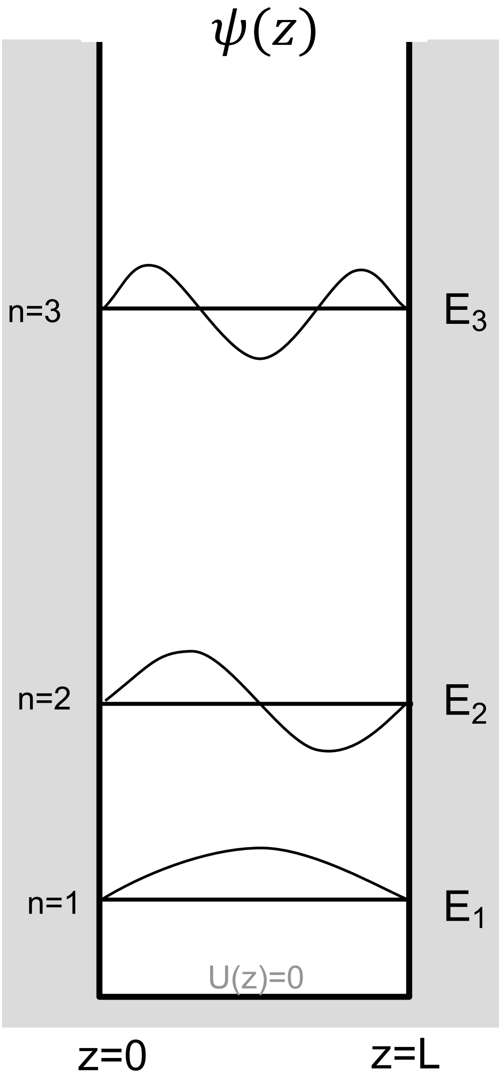
Semiconductor quantum well – a thin (few *nm*) layer of material with a bandgap E_g is sandwitched between two layers with higher bandgap.



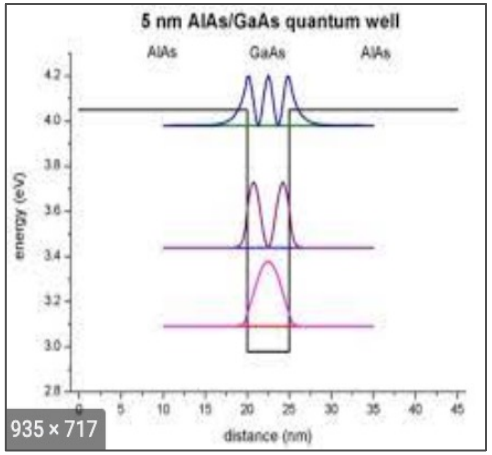


A particle that can move in only one dimension (*z*):

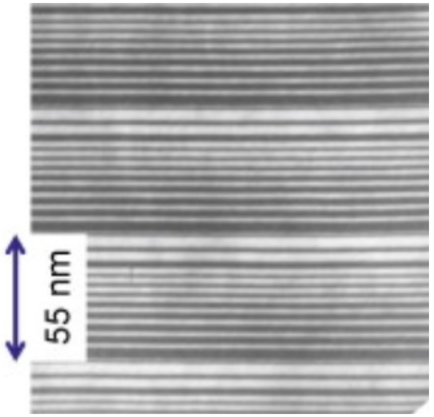
Quantum well:
U = 0   between 0 < z < L,
and
U = ∞   outside {0 <z < L}



probability: $|\psi(z)|^2$



Quantum Cascade Laser



The particle-in-a-box problem

A particle that can move in only one dimension. Quantum well:
U = 0 between 0 < z < L, and
U = ∞ outside {0 < z < L}

The Hamiltonian $\widehat{H}$: $\widehat{H} = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dz^2} + U(z)$

Solve (4.2): $\boxed{\widehat{H}u_n = E_n u_n}$ $\rightarrow$ $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dz^2} + 0 = E_n\psi$ $\rightarrow$ $\frac{\hbar^2}{2m}\frac{d^2\psi}{dz^2} + E_n\psi = 0$ inside the well

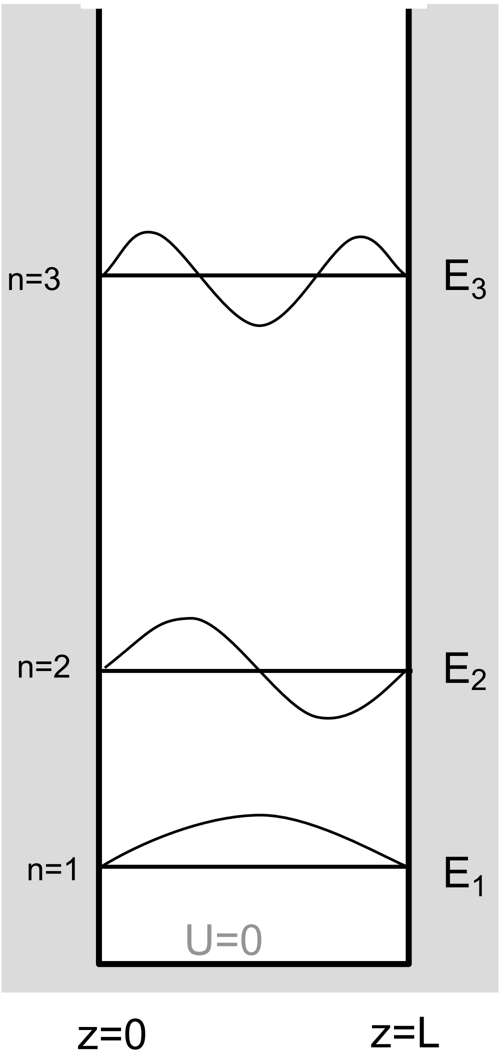
and ψ=0 outside the well

Rewrite this: $\frac{d^2\psi}{dz^2} + \kappa^2\psi = 0$, $\kappa^2 = \frac{E_n}{(\frac{\hbar^2}{2m})}$

Solution: $\psi = const \cdot \sin(\kappa z)$, boundary condition : $\kappa L = \pi n$, $n = 1,2,3..$

-> $\kappa^2 = E_n / (\frac{\hbar^2}{2m}) = (\pi n/L)^2$, --> $\boxed{E_n = \frac{\hbar^2}{2m}(\frac{\pi}{L})^2 n^2, \quad \text{n=1,2,3 ...}}$ (4.4)

$\psi_n \rightarrow u_n = C_n \sin(\frac{\pi n}{L}z)\, e^{-i\omega_n t}$;



Energy is quantized and scales as n^2

The particle-in-a-box problem

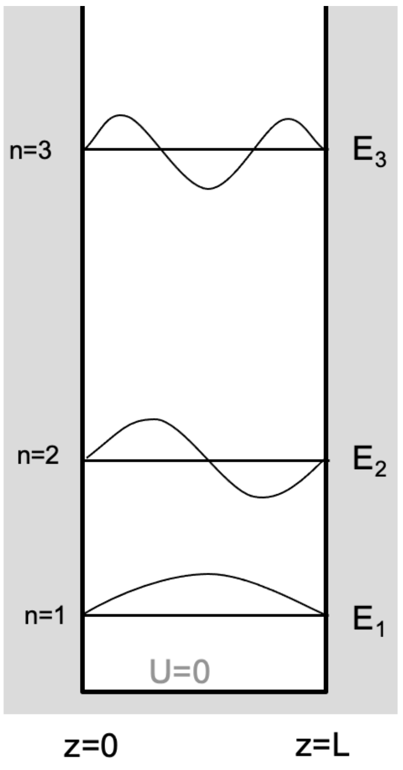
$$\psi_n \rightarrow \quad u_n = C_n \sin(\frac{\pi n}{L} z)\, e^{-i\omega_n t}; \qquad E_n = \frac{\hbar^2}{2m} (\frac{\pi}{L})^2 n^2, \quad \text{n=1,2,3 ...}$$

$$u_1 = C_1 \sin(\frac{\pi}{L} z)$$
$$u_2 = C_2 \sin(\frac{2\pi}{L} z)$$
$$u_3 = C_3 \sin(\frac{3\pi}{L} z)$$
....
$$u_n = C_n \sin(\frac{n\pi}{L} z)$$

$C_n = \sqrt{\frac{2}{L}}$

normalizing factor

(4.5)



C_n is such that $\int \psi^* \psi dx = 1$ – i.e. a particle should be somewhere

Note that $\int_0^L u_m u_n dz = 1 \; for\; m = n,$
$= 0 \; for \; m \neq n$ (4.6)

Eigenfunctions are orthogonal!

Thus they constitute a complete set of orthogonal basis functions

The particle-in-a-box problem

If we have an operator $\hat{O}$, the expectation value of the **associated physical quantity** is

$$\int \psi^*(\hat{O}\psi)d^3\,\mathrm{r} \quad \rightarrow \quad <\psi|\,\hat{O}\,|\,\psi>$$

For the E_1 (ground) state: $\psi_1 = \sqrt{\frac{2}{L}}\sin(\frac{\pi}{L}z)\, e^{-i\omega_1 t}$;

what is the average **position** in space of the electron

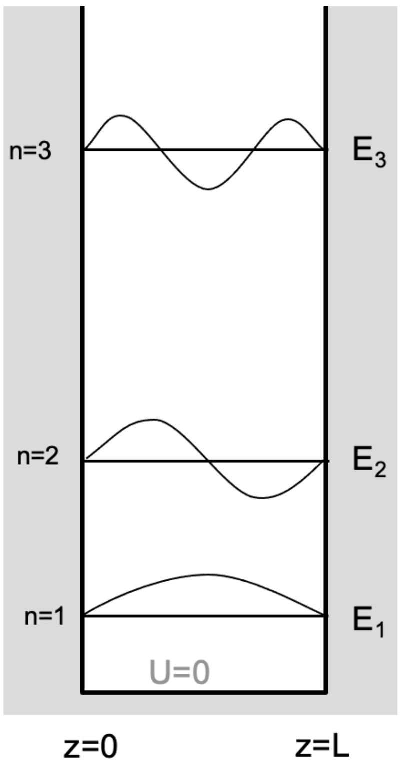
$$<x>= \int \psi_1^* z\psi_1 dz = \int \frac{2}{L} sin^2(\frac{\pi}{L}z)zdz = \cdots \ldots \ldots . = \boldsymbol{L/2}$$

what is the average **momentum** of the electron

$$<p>= \int \psi^*\underbrace{(-i\hbar\frac{d}{dz}}\psi)dz = -\int \frac{2}{L}(\frac{\pi}{L})sin(\frac{\pi}{L}z)\; cos(\frac{\pi}{L}z)dz = 0$$

what is the average **energy** of the electron

$$<E>= \int \psi^*\underbrace{(-\frac{\hbar^2}{2m}\frac{d^2\psi}{dz^2}}) dz = \int \frac{2}{L}\frac{\hbar^2}{2m}(\frac{\pi}{L})^2 sin^2(\frac{\pi}{L}z)dz = \boldsymbol{\frac{\hbar^2}{2m}(\frac{\pi}{L})^2}$$



compare to (4.4)

Susceptibilities – derived via perturbation solution to Schrödinger's equation

In QM: we have a particle with a Hamiltonian $\widehat{H_0}$ and an external EM field, which we regard as a perturbation:

$$\hat{H} = \widehat{H_0} + \hat{V}(\mathrm{t})$$

perturbation

Now introduce λ $(0 < \lambda < 1)$ a 'tuning' parameter (strength of the interaction): $\lambda = 0$ field is off; $\lambda = 1$ field is on

$$\hat{H} = \widehat{H_0} + \lambda\,\hat{V}(\mathrm{t})$$

Seek a solution to Schrödinger's equation in the form of a power series in λ

$$\psi(r,t) = \psi^{(0)}(r,t) + \lambda\psi^{(1)}(r,t) + \lambda^2\psi^{(2)}(r,t) + \ \ldots$$

Plug this $\psi(r,t)$ into $\boldsymbol{i\hbar\frac{d\psi}{dt} = \hat{H}\psi}$ equation and require that the terms proportional to λ^N satisfy the equality separately (N=0,1,2,....):

$$i\hbar(\underline{\frac{\partial\psi^{(0)}}{\partial t}} + \lambda\underline{\underline{\frac{\partial\psi^{(1)}}{\partial t}}} + \lambda^2\underline{\underline{\underline{\frac{\partial\psi^{(2)}}{\partial t}}}} + ..) = \underline{\widehat{H_0}\psi^{(0)}} + \underline{\underline{\widehat{H_0}\lambda\psi^{(1)}}} + \underline{\underline{\underline{\widehat{H_0}\lambda^2\psi^{(2)}}}} + \underline{\underline{\lambda\hat{V}\psi^{(0)}}} + \underline{\underline{\underline{\lambda^2\hat{V}\psi^{(1)}}}} + \lambda^3\hat{V}\psi^{(2)} + ..$$

(0 -order approxim.) $\quad i\hbar\frac{\partial\psi^{(0)}}{vt} = \widehat{H_0}\psi^{(0)}$ (4.7a)

– simply Schrödinger's equation for the atom in the absence of its interaction with the applied field

(1-st -order) $\quad i\hbar\frac{\partial\psi^{(1)}}{\partial t} = \widehat{H_0}\psi^{(1)} + \hat{V}\psi^{(0)}$ (4.7b)

(2-nd -order) $\quad i\hbar\frac{\partial\psi^{(2)}}{\partial t} = \widehat{H_0}\psi^{(2)} + \hat{V}\psi^{(1)}$ (4.7c)

.....

(N-th -order) $\quad i\hbar\frac{\partial\psi^{(N)}}{\partial t} = \widehat{H_0}\psi^{(N)} + \hat{V}\psi^{(N-1)}$ (4.7d)

Once $\psi^{(N-1)}$ is known one can find $\psi^{(N)}$

Susceptibilities – derived via perturbation solution to Schrödinger's equation

Solution strategy

Start form $\psi^{(0)}$ - the the solution of (4.1) corresponding to $\widehat{H_0}$; the system is in the **ground state**

Use (4.7) to calculate

$\psi^{(1)}$ from known $\psi^{(0)}$ ($\psi^{(1)} \sim E$, linear in the applied field amplitude)

$\psi^{(2)}$ from known $\psi^{(1)}$ ($\psi^{(2)} \sim E^2$, quadratic in the applied field)

$\psi^{(3)}$ from known $\psi^{(2)}$ ($\psi^{(3)} \sim E^3$, cubic in the applied field)

....

We need to find polarization = dipole moment per unit volume as in the expression from L2:
D = ε_0***E*** + ***P***

According to the rules of quantum mechanics, the expectation value of the electric dipole moment ***p*** (per one electron) is given by $< \mathbf{p} > = < \psi | \, \hat{\boldsymbol{\mu}} \, | \psi >$ (4.8)

where $\hat{\boldsymbol{\mu}} = -e\hat{\boldsymbol{r}}$ is the electric dipole moment operator and −*e* is the charge of the electron.

QM perturbation solution

Initially, atom is in the state 1 (ground state) so that the solution to the 0-order equation is:

$$\psi^{(0)}(r,t) = u_1(r)e^{-iE_1 t/\hbar} = u_1(r)e^{-i\omega_1 t}, \qquad with \quad \omega_1 = E_1/\hbar$$

Now, expand $\psi^{(N)}$ (N=1,2,3...) as a sum of energy eigenfunctions of an unperturbed system:

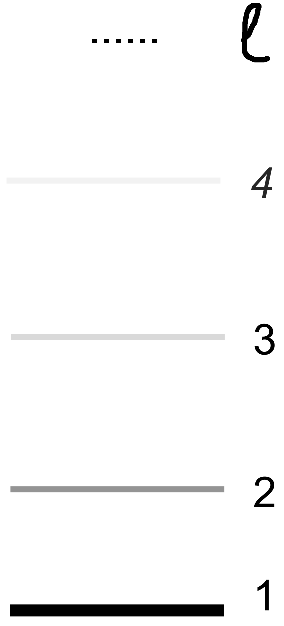
$$\psi^{(N)}(r,t) = \sum_l a_l^{(N)}(t)\, u_l(r) e^{-i\omega_l t} \qquad (4.9) \qquad with \quad \omega_l = E_l/\hbar$$

probability amplitude

time independent energy eigenfunction

its exponential phase factor

$|a_l^{(1)}|^2$ is the probability of being at a given energy state



$u_l(r)$ – constitute a complete set of orthogonal basis functions in the sense $\int u_m^* u_n \, d^3r = 1 \; if \; m = n,$ and $= 0 \; if \; m \neq n$

Now plug (4.9) into (4.7d) :

$$i\hbar \frac{\partial \psi^{(N)}}{\partial t} = \widehat{H_0}\psi^{(N)} + \hat{V}\psi^{(N-1)} \qquad (4.7d)$$

$$i\hbar \sum_l (\dot{a}_l^{(N)} \cancel{- i\omega_l a_l^{(N)}})\, u_l\, e^{-i\omega_l t} = \cancel{\sum_l \underbrace{\widehat{H_0} a_l^{(N)} u_l}_{a_l^{(N)} E_n u_l = \hbar\omega_l a_l^{(N)} u_l} e^{-i\omega_l t}} + \sum_l \hat{V} a_l^{(N-1)} u_l e^{-i\omega_l t}$$

$$\longrightarrow \quad i\hbar \sum_l \dot{a}_l^{(N)}\, u_l\, e^{-i\omega_l t} = \sum_l \hat{V} a_l^{(N-1)} u_l e^{-i\omega_l t}$$

multiply each side from the left by u_m^* and integrate over all space (take into account orthogonality for $m \neq l$)

$$i\hbar \dot{a}_m^{(N)} e^{-i\omega_m t} = \sum_l a_l^{(N-1)} e^{-i\omega_l t} \int u_m^* \hat{V} u_l d^3r = \sum_l V_{ml} a_l^{(N-1)}\, e^{-i\omega_l t}$$

QM perturbation solution

from the previous slide $i\hbar\dot{a}_m^{(N)}e^{-i\omega_m t} = \sum_l V_{ml}a_l^{(N-1)}\,e^{-i\omega_l t}$

We have introduced the matrix elements of the perturbing Hamiltonian

$$\boxed{V_{ml} \equiv \langle u_m|\hat{V}|u_l\rangle = \int u_m^*\,\hat{V}\,u_l\,d^3r.}$$

Dirak notation

$\rightarrow$

$$\boxed{\dot{a}_m^{(N)}(t) = (i\hbar)^{-1}\sum_l a_l^{(N-1)}V_{ml}e^{i\omega_{ml}t}} \qquad (4.10)$$

where $\omega_{ml} \equiv \omega_m - \omega_l$

Matrix elements of the perturbing Hamiltonian V_{ml} and μ_{ml}

In QM, the interaction Hamiltonian of the atom with the electromagnetic field is the form:

$$\hat{V}(t) = -\hat{\boldsymbol{\mu}} \cdot \tilde{\mathbf{E}}(t)$$

where $\hat{\boldsymbol{\mu}} = -e\hat{\boldsymbol{r}}$, is the electric dipole moment operator and $-e$ is the charge of the electron.

Thus $$V_{ml} = -\mu_{ml}\, E(t) \qquad (4.11)$$

where the matrix element μ_{ml} is the electric dipole (*dipole transition moment*).

$$\widetilde{\mu_{ml}} = \int \psi_m^* \hat{\boldsymbol{\mu}}\, \psi_l d^3r = \int \psi_m^* (-e\boldsymbol{r})\, \psi_l d^3r \qquad (4.12a)$$

$$\mu_{lm} = \mu_{ml}^*$$

if we neglect the phase factor $e^{i\omega_{ml}t}$ in (4.12a), it becomes

$$\mu_{ml} = \int u_m^* \hat{\boldsymbol{\mu}}\, u_l d^3r = \int u_m^* (-e\boldsymbol{r})\, u_l d^3r \qquad (4.12b)$$

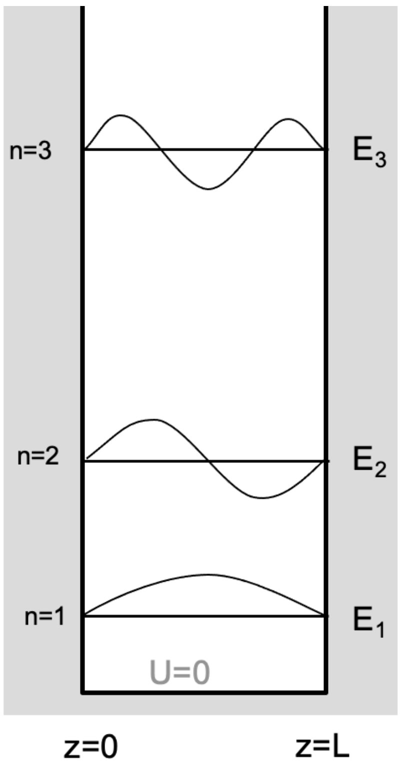
in one dimensional case: $$\mu_{ml} = (-e) \int u_m^* z u_l dz \qquad (4.12c)$$

Matrix elements of the perturbing Hamiltonian V_{ml} and μ_{ml}

Example: one dimensional case (particle-in-a-box)

from the previous slide

$$\mu_{ml} = (-e)\int u_m^* z u_l dz \qquad (4.12c)$$



Let us calculate the electric dipole transition moment between u_1 and u_2 energy eigenfunctions

$$u_1 = \sqrt{\frac{2}{L}}\sin(\frac{\pi}{L}z)$$

$$u_2 = \sqrt{\frac{2}{L}}\sin(\frac{2\pi}{L}z)$$

$$\mu_{12} = (-e)\int u_1^* z u_2 dz = (-e)\frac{2}{L}\int_0^L \mathrm{z}\sin(\frac{\pi}{L}z)\sin(\frac{2\pi}{L}z)\,dz =$$

$$= e\frac{16}{9\pi^2}L = 0.18eL$$

Linear susceptibility $\chi^{(1)}$ – perturbation solution

1st -order perturbation solution, N=1

Calculate 1st -order correction – for induced linear polarization $P^{(1)}$

$$\boxed{\dot{a}_m^{(N)}(t) = (i\hbar)^{-1} \sum_l a_l^{(N-1)} V_{ml} e^{i\omega_{ml}t}} \qquad (4.10)$$

where $\omega_{ml} \equiv \omega_m - \omega_l$

Find $\psi^{(1)}$

By integrating (4.10) and taking into account that $a_l^{(N-1)} = a_l^{(0)} = a_1^{(0)} = 1$ (only ground state is occupied), we get

$$\boxed{E(t) = \frac{1}{2} E e^{-i\omega t} + \frac{1}{2} E e^{+i\omega t}}$$

$$a_m^{(1)}(t) = \int_{-\infty}^{t} (i\hbar)^{-1} V_{m1} e^{i\omega_{m1}t'} dt' = \int_{-\infty}^{t} (i\hbar)^{-1} [-\mu_{m1} E(t')] e^{i\omega_{m1}t'} dt'$$

$$= (i\hbar)^{-1} (-\mu_{m1}) \{ \int_{-\infty}^{t} \frac{1}{2} \{ E e^{-i\omega t'} e^{i\omega_{m1}t'} + E e^{+i\omega t'} e^{i\omega_{m1}t'} \} dt'$$

$$= \frac{1}{2} \frac{i}{\hbar} \mu_{m1} E \{ \int_{-\infty}^{t} e^{i(\omega_{m1}-\omega)t'} dt' + \int_{-\infty}^{t} e^{i(\omega_{m1}+\omega)t'} dt' \} = \frac{1}{2\hbar} \{ \frac{\mu_{m1}E}{(\omega_{m1}-\omega)} e^{i(\omega_{m1}-\omega)t} + \frac{\mu_{m1}E}{(\omega_{m1}+\omega)} e^{i(\omega_{m1}+\omega)t} \} \qquad (4.13)$$

Finally,

$$\psi^{(1)} = \sum_m a_m^{(1)}(t)\, u_m(r) e^{-i\omega_m t}$$

$$= \sum_m \frac{1}{2\hbar} \{ \frac{\mu_{m1}E}{(\omega_{m1}-\omega)} e^{i(\omega_{m1}-\omega)t} + \frac{\mu_{m1}E}{(\omega_{m1}+\omega)} e^{i(\omega_{m1}+\omega)t} \} u_m(r) e^{-i\omega_m t}$$

$$= \frac{1}{2\hbar} \sum_m \{ \frac{\mu_{m1}E}{(\omega_{m1}-\omega)} e^{-i\omega_1 t - i\omega t} + \frac{\mu_{m1}E}{(\omega_{m1}+\omega)} e^{-i\omega_1 t + i\omega t} \} u_m(r) \qquad (4.14)$$

1st -order perturbation solution

The 1-st order-corrected time-dependent wave function is: $\psi(r,t) = \psi^{(0)}(r,t) + \psi^{(1)}(r,t)$

Polarization induced per atom is: $\langle p^{(1)} \rangle = \langle \psi^{(0)} + \psi^{(1)} |\hat{\boldsymbol{\mu}}| \psi^{(0)} + \psi^{(1)} \rangle$ see (4.8)

$= \langle \psi^{(0)} |\hat{\boldsymbol{\mu}}| \psi^{(1)} \rangle + \langle \psi^{(1)} |\hat{\boldsymbol{\mu}}| \psi^{(0)} \rangle$ only this combination gives polarization proportional to *E*

$$\langle \psi^{(0)} |\hat{\boldsymbol{\mu}}| \psi^{(1)} \rangle = \left\langle u_1 e^{-i\omega_1 t} \ |\hat{\boldsymbol{\mu}}| \ \frac{1}{2}\sum_m \frac{\mu_{m1}}{\hbar} \left[\frac{E e^{-i\omega t}}{(\omega_{m1}-\omega)} + \frac{E e^{i\omega t}}{(\omega_{m1}+\omega)}\right] u_m e^{-i\omega_1 t} \right\rangle = \frac{1}{2}\sum_m \frac{\mu_{m1}}{\hbar} \left[\frac{E e^{-i\omega t}}{(\omega_{m1}-\omega)} + \frac{E e^{i\omega t}}{(\omega_{m1}+\omega)}\right] \langle u_1 |\hat{\boldsymbol{\mu}}| u_m \rangle = \frac{1}{2}\sum_m \frac{\mu_{1m}\mu_{m1}}{\hbar} \left[\frac{E e^{-i\omega t}}{(\omega_{m1}-\omega)} + \frac{E e^{+i\omega t}}{(\omega_{m1}+\omega)}\right]$$

similarly,

$$\langle \psi^{(1)} |\hat{\boldsymbol{\mu}}| \psi^{(0)} \rangle = \left\langle \frac{1}{2}\sum_m \frac{\mu_{m1}}{\hbar} \left[\frac{E e^{-i\omega t}}{(\omega_{m1}-\omega)} + \frac{E e^{i\omega t}}{(\omega_{m1}+\omega)}\right] u_m e^{-i\omega_1 t} |\hat{\boldsymbol{\mu}}| u_1 e^{-i\omega_1 t} \right\rangle = \frac{1}{2}\sum_m \frac{\mu_{1m}\mu_{m1}}{\hbar} \left[\frac{E e^{+i\omega t}}{(\omega_{m1}-\omega)} + \frac{E e^{-i\omega t}}{(\omega_{m1}+\omega)}\right]$$

Thus $\langle p^{(1)} \rangle = \sum_m \frac{|\mu_{1m}|^2}{2\hbar} \left[\frac{1}{(\omega_{m1}-\omega)} + \frac{1}{(\omega_{m1}+\omega)}\right] E e^{-i\omega t} + c.c.$

This is an electric dipole moment of a single atom induced by the field *E* at frequency ω

The linear polarization (dipole moment per unit volume) is: $P^{(1)} = N p^{(1)}$ (*N* is the density of atoms)

and since $P^{(1)} = \epsilon_0 \chi^{(1)} E$, and $E = \frac{1}{2} E e^{-i\omega t} + c.c.$, we get :

And finally:

$$\boxed{\chi^{(1)} = \frac{N}{\epsilon_0 \hbar} \sum_m \left\{\frac{|\mu_{1m}|^2}{(\omega_{m1}-\omega)} + \frac{|\mu_{1m}|^2}{(\omega_{m1}+\omega)}\right\}} \quad (4.15)$$

this is the linear (1st -order) susceptibility

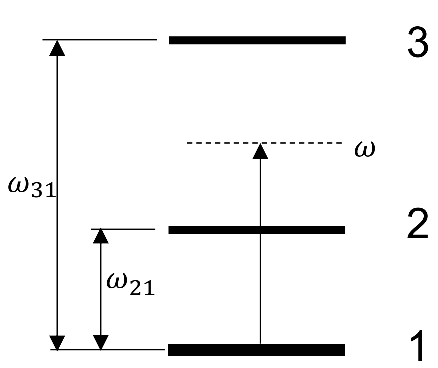
1st -order perturbation solution

Let us simplify (4.11) - take a system with just 3 levels (”1” is the ground state) and leave only resonant terms

$$\chi^{(1)} = \frac{N}{\epsilon_0 \hbar} \sum_m \left\{ \frac{|\mu_{1m}|^2}{(\omega_{m1} - \omega)} + \cancel{\frac{|\mu_{1m}|^2}{(\omega_{m1} + \omega)}} \right\} \longrightarrow$$

(m=2,3) $\longrightarrow$

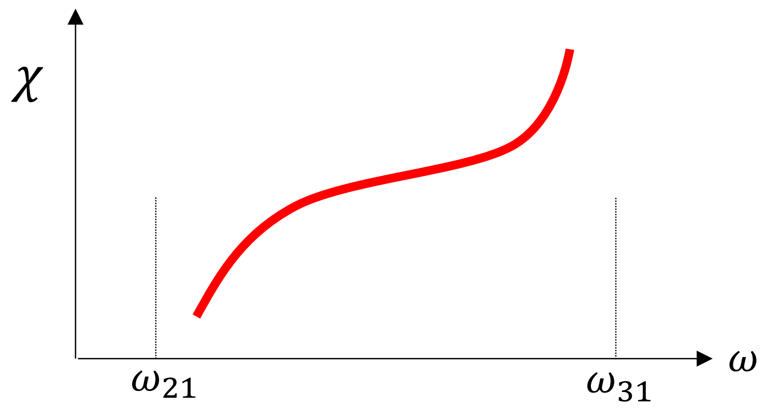
$$\frac{N}{\epsilon_0 \hbar} \left\{ \frac{|\mu_{12}|^2}{(\omega_{21} - \omega)} + \frac{|\mu_{13}|^2}{(\omega_{31} - \omega)} \right\}$$



This formula makes sense:
susceptibility χ, and refractive index

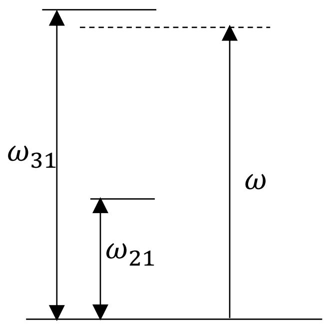
$$n = \sqrt{1 + \chi}$$

– grow with frequency between the two poles



1st -order QM perturbation solution: compare to classical model

$$\chi^{(1)} = \frac{N}{\epsilon_0 \hbar} \sum_m \{ \frac{|\mu_{1m}|^2}{(\omega_{m1} - \omega)} + \frac{|\mu_{1m}|^2}{(\omega_{m1} + \omega)} \} \qquad (4.16)$$



assume that the dominant
is only one transition 1-3

$$\boxed{\chi^{(1)} = \frac{N}{\epsilon_0 \hbar} \frac{|\mu_{13}|^2}{(\omega_{31} - \omega)}} \qquad (4.16a)$$

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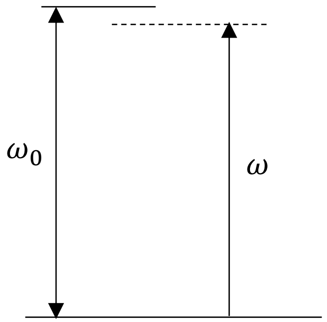
compare to classical
osillator model

$$\chi^{(1)} = \frac{Nq^2/m}{\epsilon_0(\omega_0^2 - \omega^2 + i\omega\gamma)}$$

see (3.3d) from L3



$$\omega_0^2 - \omega^2 + i\omega\gamma = (\omega_0 + \omega)(\omega_0 - \omega) + i\omega\gamma \approx 2\omega_0(\omega_0 - \omega) + i\omega\gamma \approx 2\omega_0(\omega_0 - \omega + \frac{i\gamma}{2})$$

$$\boxed{\chi^{(1)} \approx \frac{Ne^2}{2m\epsilon_0\omega_0(\omega_0 - \omega + \frac{i\gamma}{2})}}$$

$$\boxed{|\mu_{13}|^2 \quad \text{<->} \quad \frac{\hbar e^2}{2m\omega_0}}$$

2nd -order nonlinearity $\chi^{(2)}$– perturbation solution

2nd -order nonlinearity

Now, calculate the 2nd -order correction – nonlinear polarization $\boldsymbol{P}^{(2)}$

Optical input field $\boxed{E(t) = \frac{1}{2}Ee^{-i\omega t} + \frac{1}{2}Ee^{+i\omega t}}$

($\psi^{(1)} \sim E$, linear in the applied field amplitude)
($\psi^{(2)} \sim E^2$, quadratic in the applied field)
($\psi^{(3)} \sim E^3$, cubic in the applied field)

The 2nd-order contribution to the induced dipole moment per atom is :

$$< p^{(2)} > = < \psi^{(0)} + \psi^{(1)} + \psi^{(2)} \, |\hat{\boldsymbol{\mu}}| \, \psi^{(0)} + \psi^{(1)} + \psi^{(2)} > \longrightarrow$$

$$\longrightarrow \quad \langle \tilde{\mathbf{p}}^{(2)} \rangle = \langle \psi^{(0)} | \hat{\boldsymbol{\mu}} | \psi^{(2)} \rangle + \langle \psi^{(1)} | \hat{\boldsymbol{\mu}} | \psi^{(1)} \rangle + \langle \psi^{(2)} | \hat{\boldsymbol{\mu}} | \psi^{(0)} \rangle,$$

since only this combination gives polarization proportional to E^2

we have from previous:

$$\psi^{(0)}(r,t) = u_1(r) e^{-iE_1 t/\hbar} = u_1 e^{-i\omega_1 t},$$

$$\psi^{(1)}(r,t) = \frac{1}{2\hbar} \sum_m \left\{ \frac{\mu_{m1} E}{(\omega_{m1} - \omega)} e^{-i\omega t} + \frac{\mu_{m1} E}{(\omega_{m1} + \omega)} e^{i\omega t} \right\} u_m(r)$$

$$\psi^{(2)}(r,t) = \ ?$$

Need to find $\psi^{(2)}$ via known $\psi^{(1)}$

2nd -order nonlinearity

From (4.9-4.10) $\psi^{(2)}(r,t) = \sum_n a_n^{(2)}(t)\, u_n(r) e^{-i\omega_n t}$

$$\dot{a}_n^{(2)}(t) = (i\hbar)^{-1} \sum_m a_m^{(1)} V_{nm} e^{i\omega_{nm} t} =$$

$$a_m^{(1)} = \frac{1}{2\hbar}\left\{\frac{\mu_{m1}E}{(\omega_{m1}-\omega)} e^{i(\omega_{m1}-\omega)t} + \frac{\mu_{m1}E}{(\omega_{m1}+\omega)} e^{i(\omega_{m1}+\omega)t}\right\} = \frac{1}{2\hbar}\sum_p \frac{\mu_{m1}E}{(\omega_{m1}-\omega_p)} e^{i(\omega_{m1}-\omega_p)t}$$

ω_s *runs through* $+\omega$ *or* $-\omega$

$$V_{nm} = (-\mu_{nm})E(t) = \frac{1}{2}\sum_q (-\mu_{nm}) E e^{i(\omega_{nm}-\omega_q)t}$$

$$= (i\hbar)^{-1} \sum_m \frac{1}{4\hbar}\sum_s \frac{\mu_{m1}E}{(\omega_{m1}-\omega_s)} e^{i(\omega_{m1}-\omega_p)t} \sum_q (-\mu_{nm}) E e^{i(\omega_{nm}-\omega_q)t} =$$

$$= \frac{i}{4\hbar^2}\sum_{m,p,q} \frac{\mu_{nm}\mu_{m1}E^2}{(\omega_{m1}-\omega_s)} e^{i(\omega_{n1}-\omega_p-\omega_q)t} =$$

$$a_n^{(2)}(t) = \int_{-\infty}^{t} \dot{a}_n^{(2)}(t')dt' = \frac{i}{4\hbar^2}\sum_{m,p,q} \frac{\mu_{nm}\mu_{m1}E^2}{(\omega_{n1}-\omega_p-\omega_q)(\omega_{m1}-\omega_s)} e^{i(\omega_{n1}-\omega_p-\omega_q)t} \qquad (4.17)$$

2nd -order nonlinearity

Finally, $$\langle \tilde{\mathbf{p}}^{(2)} \rangle = \underline{\langle \psi^{(0)} | \hat{\boldsymbol{\mu}} | \psi^{(2)} \rangle} + \underline{\langle \psi^{(1)} | \hat{\boldsymbol{\mu}} | \psi^{(1)} \rangle} + \underline{\langle \psi^{(2)} | \hat{\boldsymbol{\mu}} | \psi^{(0)} \rangle},$$

$$< p^{(2)} > = \ldots$$

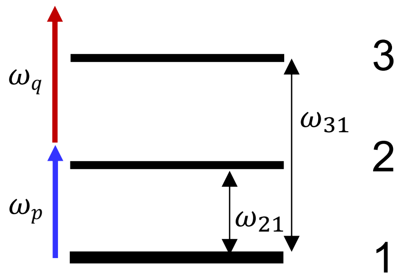
$$+ \begin{cases} < u_1\, e^{-i\omega_1 t} |\mu| \frac{1}{4\hbar^2} \sum_{m,n,q,p} \frac{\mu_{nm}\mu_{m1}E(\omega_p)E(\omega_q)}{(\omega_{n1}-\omega_p-\omega_q)(\omega_{m1}-\omega_p)} u_n e^{-i(\omega_1+\omega_p+\omega_q)t} > = \frac{1}{4\hbar^2} \sum_{m,n,q,p} \frac{\mu_{1n}\mu_{nm}\mu_{m1}E(\omega_p)E(\omega_q)}{(\omega_{n1}-\omega_p-\omega_q)(\omega_{m1}-\omega_p)} e^{-i(\omega_p+\omega_q)t} \\ \text{its complex conjugate} \qquad = \frac{1}{4\hbar^2} \sum_{m,n,q,p} \frac{\mu_{1n}\mu_{nm}\mu_{m1}E(\omega_p)E(\omega_q)}{(\omega_{n1}-\omega_p-\omega_q)(\omega_{m1}-\omega_p)} e^{i(\omega_p+\omega_q)t} \\ < \frac{1}{2\hbar} \sum_{m,p} E(\omega_p) \frac{\mu_{m1}}{(\omega_{m1}-\omega_p)} u_m e^{-i(\omega_1+\omega_p)t} |\mu| \frac{1}{2\hbar} \sum_{m,p} E(\omega_p) \frac{\mu_{m1}}{(\omega_{m1}-\omega_p)} u_m e^{-i(\omega_1+\omega_p)t} > = \frac{1}{4\hbar^2} \sum_{m,n,q,p} \frac{\mu_{1n}\mu_{nm}\mu_{m1}E(\omega_p)E(\omega_q)}{(\omega_{n1}-\omega_q)(\omega_{m1}-\omega_p)} e^{-i(\omega_p-\omega_q)t} \end{cases}$$

$$\boxed{< p^{(2)} > = \frac{1}{4\hbar^2} \sum_{m,n,q,p} \{ \frac{\mu_{1n}\mu_{nm}\mu_{m1}E(\omega_p)E(\omega_q)}{(\omega_{n1}-\omega_p-\omega_q)(\omega_{m1}-\omega_p)} e^{-i(\omega_p+\omega_q)t} + \frac{\mu_{1n}\mu_{nm}\mu_{m1}E(\omega_p)E(\omega_q)}{(\omega_{n1}-\omega_p-\omega_q)(\omega_{m1}-\omega_p)} e^{i(\omega_p+\omega_q)t} + \frac{\mu_{1n}\mu_{nm}\mu_{m1}E(\omega_p)E(\omega_q)}{(\omega_{n1}-\omega_q)(\omega_{m1}-\omega_p)} e^{-i(\omega_p-\omega_q)t}}$$

(4.18)

2nd -order nonlinearity – perturbation solution

(see Stegeman or Boyd for details)



Finally, the 2nd-order contribution to the induced dipole moment per unit volume:

$$P^{(2)} = Np^{(2)}$$

N - number density of electrons

$$\chi^{(2)} = \frac{2}{\epsilon_0}\frac{P^{(2)}(2\omega\,)}{E(\omega)^2}$$

$\chi^{(2)}$ definition (will discuss it later in the couse)

The nonlinear succeptibility is :

$$\chi^{(2)} = \frac{N}{\epsilon_0 \hbar^2} \sum_{m,n,q,p} \left\{ \frac{\mu_{1n}\mu_{nm}\mu_{m1}}{(\omega_{n1}-\omega_p-\omega_q)(\omega_{m1}-\omega_p)} + \frac{\mu_{1n}\mu_{nm}\mu_{m1}}{(\omega_{m1}+\omega_p+\omega_q)(\omega_{n1}+\omega_q)} + \frac{\mu_{1n}\mu_{nm}\mu_{m1}}{(\omega_{n1}+\omega_q)(\omega_{m1}-\omega_p)} \right\} \qquad (4.19)$$

Two fields: ω_p and ω_q run through $\pm\omega_p;\ \pm\omega_q$

One field: ω_p and ω_q run through $\pm\omega$

Even for a 3-level system, there are 2x2x4x4=64 elements in this sum !

$$\begin{aligned}
= \frac{N}{\epsilon_0 \hbar^2} \Bigg\{ & \frac{\mu_{13}\mu_{32}\mu_{21}}{(\omega_{31}-\omega_p-\omega_q)(\omega_{21}-\omega_p)} + \frac{\mu_{13}\mu_{32}\mu_{21}}{(\omega_{31}-\omega_p-\omega_q)(\omega_{21}-\omega_q)} + \frac{\mu_{13}\mu_{32}\mu_{21}}{(\omega_{31}-\omega_q)(\omega_{21}-\omega_p)} \\
& + \frac{\mu_{12}\mu_{23}\mu_{31}}{(\omega_{21}-\omega_p-\omega_q)(\omega_{31}-\omega_p)} + \frac{\mu_{12}\mu_{23}\mu_{31}}{(\omega_{21}-\omega_p-\omega_q)(\omega_{31}-\omega_q)} + \frac{\mu_{12}\mu_{23}\mu_{31}}{(\omega_{21}-\omega_q)(\omega_{31}-\omega_p)} \\
& + \frac{\mu_{13}\mu_{32}\mu_{21}}{(\omega_{31}+\omega_p-\omega_q)(\omega_{21}-\omega_p)} + \frac{\mu_{13}\mu_{32}\mu_{21}}{(\omega_{31}-\omega_p-\omega_q)(\omega_{21}+\omega_q)} + \frac{\mu_{13}\mu_{32}\mu_{21}}{(\omega_{31}-\omega_q)(\omega_{21}+\omega_p)} \\
& + \frac{\mu_{13}\mu_{32}\mu_{21}}{(\omega_{31}+\omega_p+\omega_q)(\omega_{21}-\omega_p)} + \frac{\mu_{13}\mu_{32}\mu_{21}}{(\omega_{31}+\omega_p+\omega_q)(\omega_{21}-\omega_q)} + \frac{\mu_{13}\mu_{32}\mu_{21}}{(\omega_{31}+\omega_q)(\omega_{21}+\omega_p)} \\
& + \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . \\
& + \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . \Bigg\}
\end{aligned} \qquad (4.20)$$

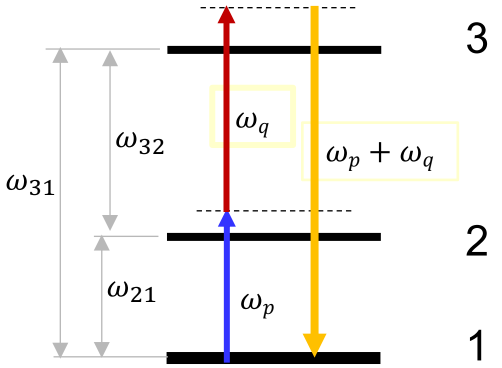
2nd -order perturbation solution

Let us now select only resonant terms in (4.13a)

Two fields: ω_p and ω_q run through $\pm\omega_p$; $\pm\omega_q$

$$\chi^{(2)} \text{ --> } \frac{N}{\epsilon_0 \hbar^2} \left\{ \frac{\mu_{13}\mu_{32}\mu_{21}}{(\omega_{31}-\omega_p-\omega_q)(\omega_{21}-\omega_p)} + \frac{\mu_{13}\mu_{32}\mu_{21}}{(\omega_{31}-\omega_p-\omega_q)(\omega_{21}-\omega_q)} + \ldots\ldots \right\}$$

double resonance: at ω_{31} and ω_{21}



Strictly speaking, transition frequencies ω_{21} , ω_{31} need to be complex quantities $\omega \rightarrow \omega + i\gamma$,
to incorporate damping phenomena into the theory. This allows to avoid infinities at exact resonances.

3nd -order nonlinearity – perturbation solution

from Boyd’s book

The QM microscopic expression for 3rd order nonlinear succeptibility $\chi^{(3)}$ looks similar, but even more scary (3 denominators).

$$\chi^{(3)}_{kjih}(\omega_\sigma, \omega_r, \omega_q, \omega_p)$$
$$= \frac{N}{\epsilon_0 \hbar^3} \mathcal{P}_I \sum_{mnv} \left[\frac{\mu^k_{gv} \mu^j_{vn} \mu^i_{nm} \mu^h_{mg}}{(\omega_{vg} - \omega_r - \omega_q - \omega_p)(\omega_{ng} - \omega_q - \omega_p)(\omega_{mg} - \omega_p)} \right.$$
$$+ \frac{\mu^j_{gv} \mu^k_{vn} \mu^i_{nm} \mu^h_{mg}}{(\omega^*_{vg} + \omega_r)(\omega_{ng} - \omega_q - \omega_p)(\omega_{mg} - \omega_p)}$$
$$+ \frac{\mu^j_{gv} \mu^i_{vn} \mu^k_{nm} \mu^h_{mg}}{(\omega^*_{vg} + \omega_r)(\omega^*_{ng} + \omega_r + \omega_q)(\omega_{mg} - \omega_p)}$$
$$\left. + \frac{\mu^j_{gv} \mu^i_{vn} \mu^h_{nm} \mu^k_{mg}}{(\omega^*_{vg} + \omega_r)(\omega^*_{ng} + \omega_r + \omega_q)(\omega^*_{mg} + \omega_r + \omega_q + \omega_p)} \right]. \quad (3.2.32)$$

Model system for optical $\chi^{(2)}$ nonlinearities: semiconductor quantum well

Symmetric semiconductor quantum well

From previous page:

$$\chi^{(2)} \;\text{-->}\; \frac{N}{\epsilon_0 \hbar^2}\left\{\frac{\mu_{12}\mu_{23}\mu_{31}}{(\omega_{31}-\omega_p-\omega_q)(\omega_{21}-\omega_p)} + \frac{\mu_{12}\mu_{23}\mu_{31}}{(\omega_{31}-\omega_p-\omega_q)(\omega_{21}-\omega_q)} + \ \ldots\ \right\}$$

ω_p, ω_p - two pump freqencies

Note that in a symmetric quantum well
μ_{12}≠0, μ_{23}≠0, but μ_{31} =0.

$$\mu_{31} = -e \int u_3^* \, z \, u_1 dz \quad =0;$$

even function

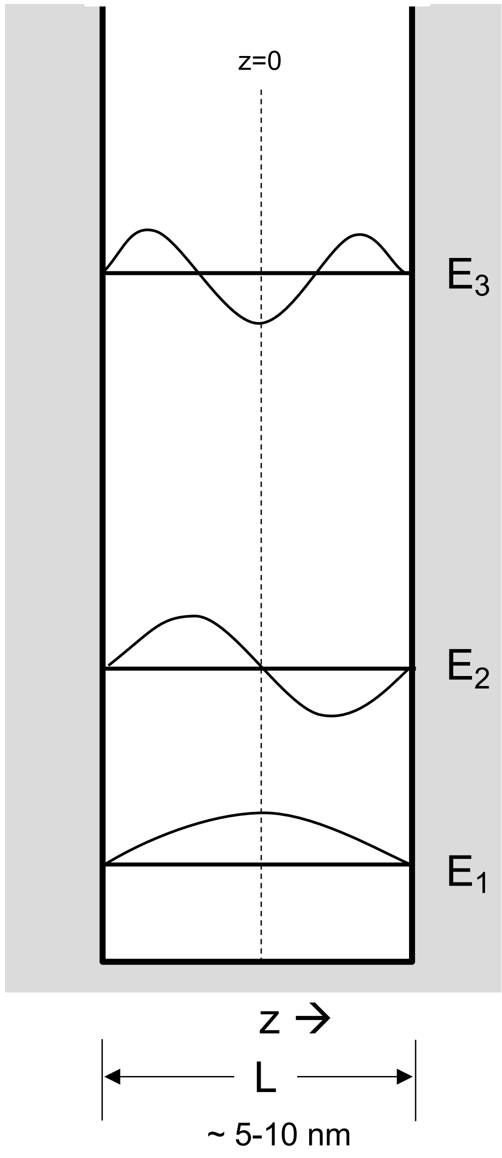
odd function

even function

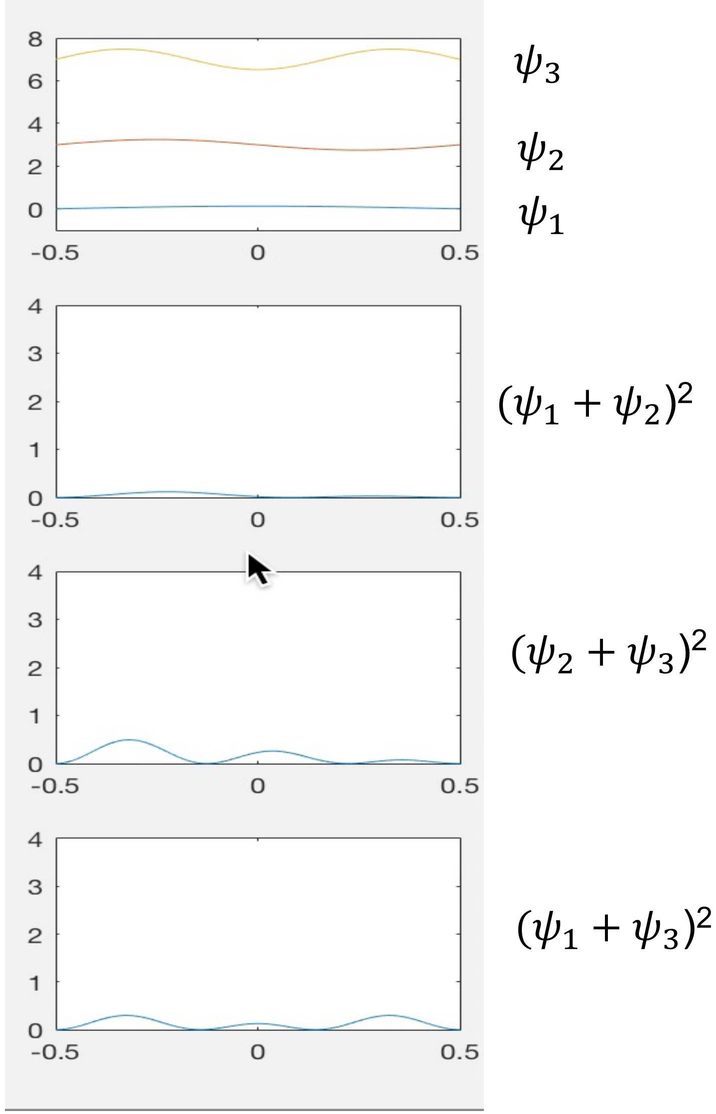
Hence $\mu_{13}\mu_{32}\mu_{21}$=0

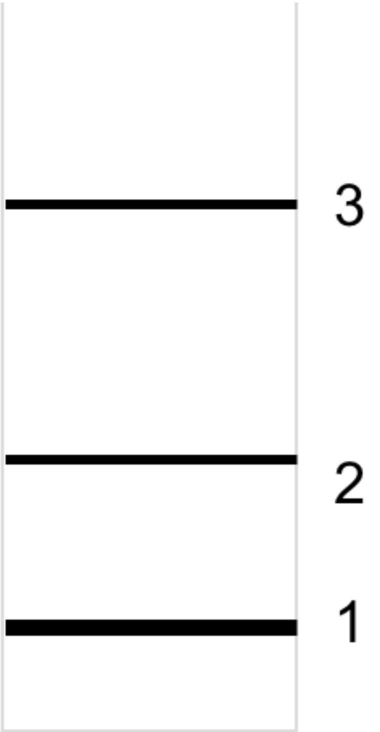
This is quite clear, because there should be some asymmetry to achieve $\chi^{(2)}$

infinite-barrier quantum well (QW)



2nd -order nonlinearity – perturbation solution





Model system for optical nonlinearities: semiconductor quantum well

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Model system for optical nonlinearities: Asymmetric quantum wells

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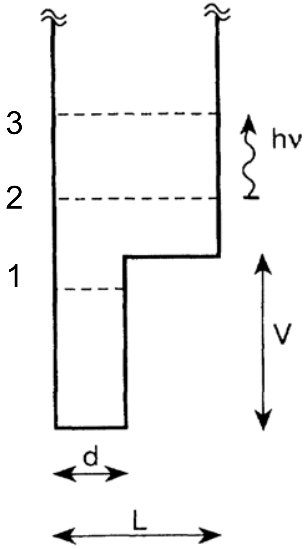
Optical nonlinearities in asymmetric quantum wells due to resonant intersubband transitions are analyzed using a compact density-matrix approach. The large dipolar matrix elements obtained in such structures are partly due to the small effective masses of the host materials and are interpreted in terms of the participation of the whole band structure to the optical transitions. The other origin of the large second-order susceptibilities lies in the possibility of tuning independently the potential shape and the width of asymmetric quantum wells in order to obtain resonances (single or double) for a given excitation wavelength. Using a model based on an infinite-barrier quantum well, we have obtained very general and tractable formulas for second-order susceptibilities at resonance. This model allows us to fix additional fundamental quantum limitations to second-order optical nonlinearities. The "best potential shapes" maximizing the different susceptibilities are obtained, together with *scaling laws* as a function of photon energy. Experimental results on different GaAs/Al$_x$Ga$_{1-x}$As asymmetric quantum wells optimized for second-harmonic generation and optical rectifications are given, with optical rectification coefficients more than 10^6 higher than in bulk GaAs. These asymmetric quantum wells may be considered as giant "pseudomolecules" optimized for large optical nonlinearities in the 8–12-μm range.



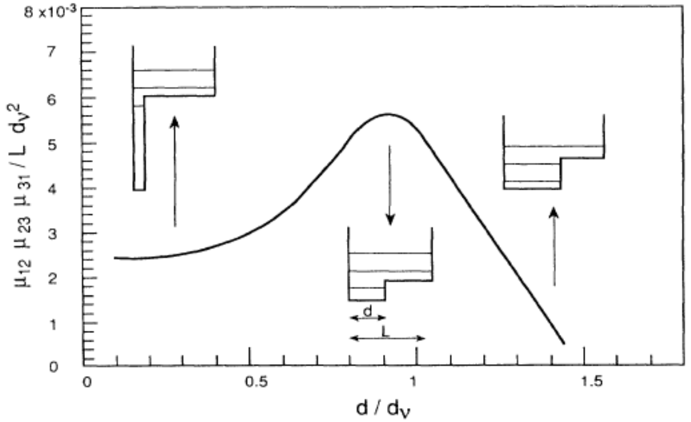


FIG. 4. Variation of the product of the normalized dipolar matrix elements $|\mu_{12}\mu_{23}\mu_{31}|/Ld_v^2$ as a function of deep QW thickness d. The double-resonance conditions $E_2-E_1=E_3-E_2=h\nu$ are imposed in the calculation. The optimum value $d/d_v=0.925$ defines the "best potential shape" for second-harmonic generation in step AQW's.

<u>Asymmetric</u> quantum well : now all $\mu_{12}\neq 0$, $\mu_{13}\neq 0$, and $\mu_{31}\neq 0$.

Morover, SHG ($\omega+\omega=2\omega$) with double resonance : $\omega\sim E_{12},\ 2\omega\sim E_{13}$