9.3 Applying time-dependent perturbation theory

Slides: Video 9.3.1 Fermi's Golden Rule

Text reference: Quantum Mechanics for Scientists and Engineers

Section 7.2 (third part)

Applying time-dependent perturbation theory

Fermi's Golden Rule

Quantum mechanics for scientists and engineers

David Miller

Absorption

Now consider only the case associated with absorption

presuming we are starting in a lower energy state

and transitioning to a higher energy one

(The treatment of the stimulated emission case is essentially identical

with the energies of the states reversed)

Then we have

$$P(j) \simeq \frac{t_o^2}{\hbar^2} \left| \langle \psi_j | \hat{H}_{po} | \psi_m \rangle \right|^2 \left[\frac{\sin\left[\left(\omega_{jm} - \omega \right) t_o / 2 \right]}{\left(\omega_{jm} - \omega \right) t_o / 2} \right]^2$$

Absorption

Analyzing the case of a transition between

one state and exactly one other state

using this approach has some formal difficulties

as we let the time t_o become arbitrarily large

The sinc squared term becomes arbitrarily sharp in ω

Unless the frequency is exactly correct

we will get no absorption

We can solve this problem with more sophisticated analysis

specifically, the use of density matrices

which allow "widths" to the absorption lines

Lorentzian line shape

$$\frac{1}{1+\left(\omega-\omega_o\right)^2 T_2^2}$$
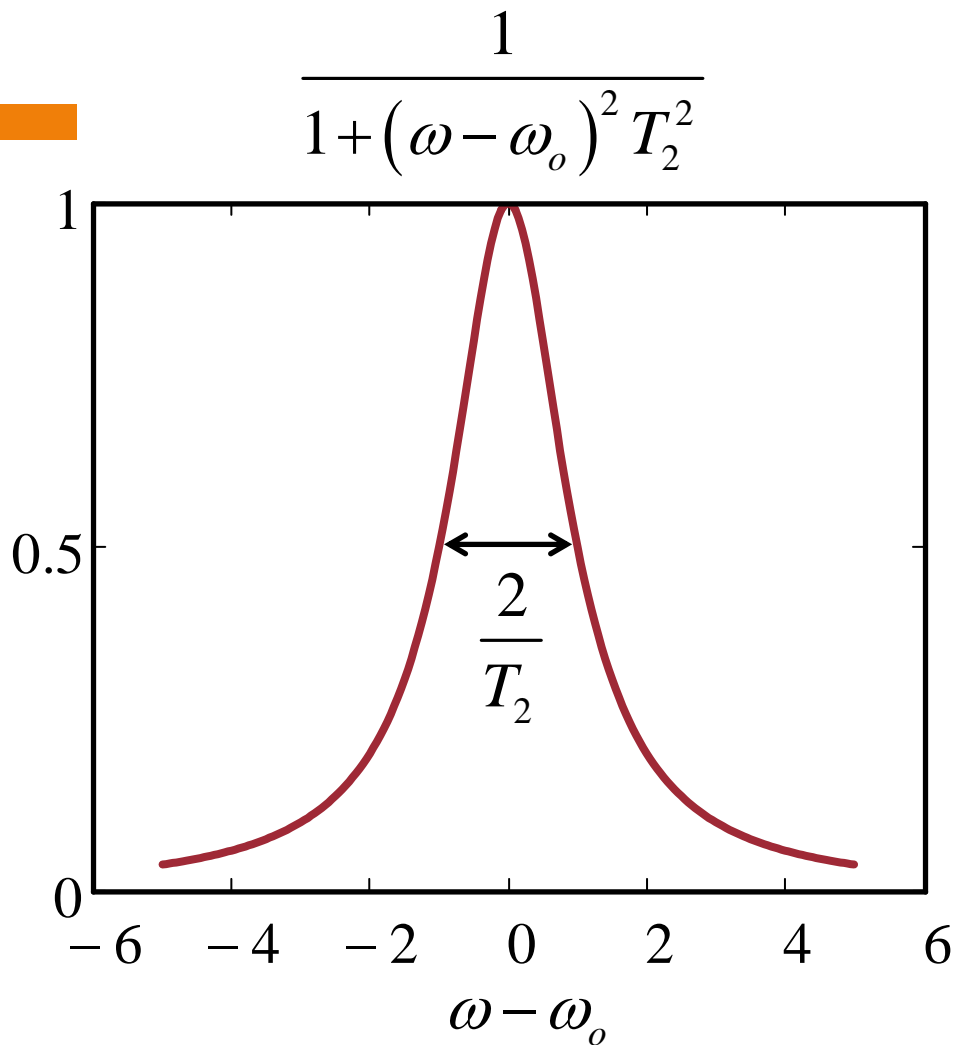
With density matrices

we end up replacing the
sinc squared function

with a Lorentzian line

with angular frequency
half-width $1/T_2$

where T_2 is the time
between scatterings

e.g., collisions with
other atoms

Lorentzian line shape

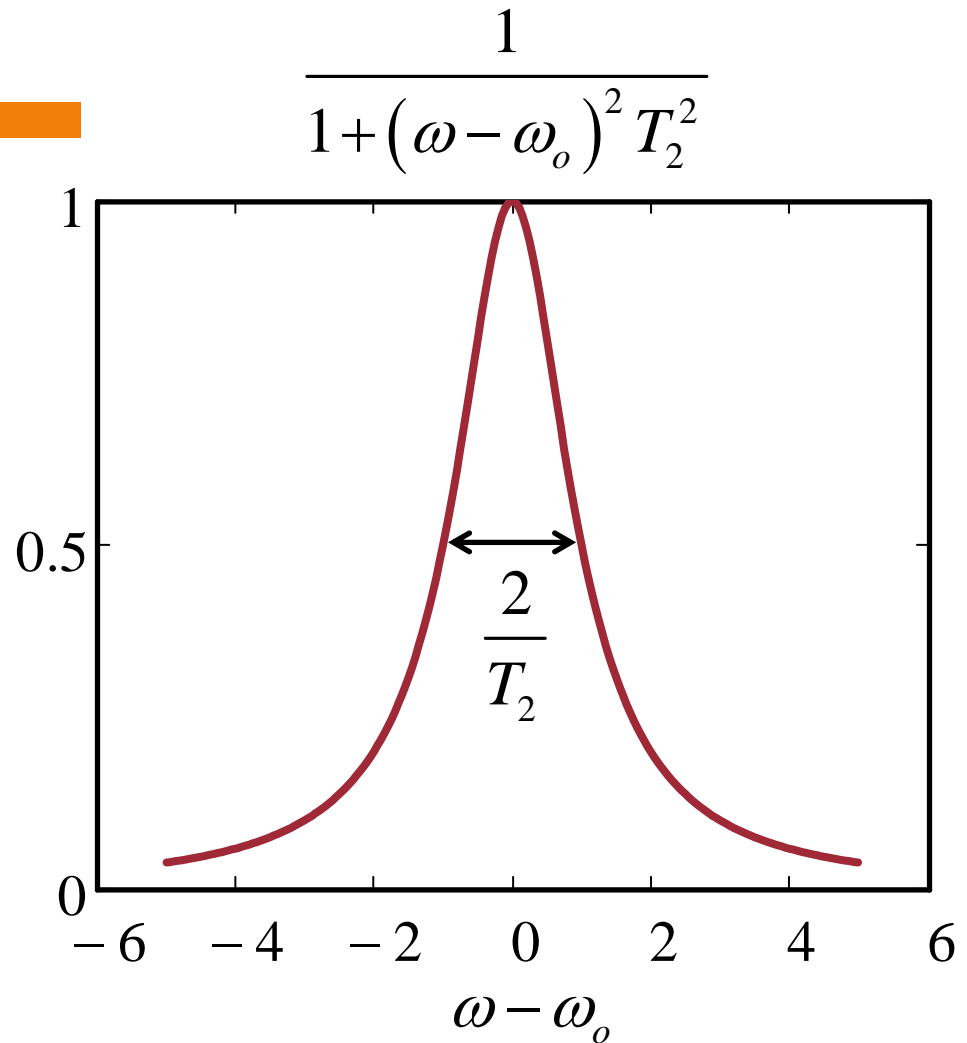$$\frac{1}{1+\left(\omega-\omega_o\right)^2 T_2^2}$$

We can rationalize this based on an energy-time uncertainty relation

If the system only exists in its original form for a time T_2

then we should expect that the energy of the transition is only defined

in energy to $\sim \pm \hbar / T_2$
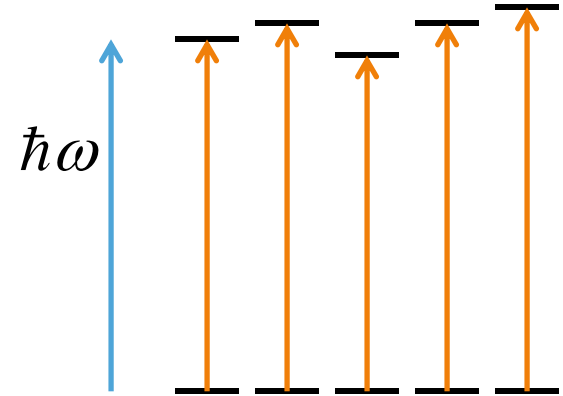
or in ω to $\sim \pm 1/T_2$

Dense sets of possible transitions

A major class of problems can, however, be analyzed using our approach

Suppose we have not one possible transition with energy difference $\hbar\omega_{jm}$

but a dense of transitions near the photon energy $\hbar\omega$

all with essentially identical matrix elements

This kind of situation occurs routinely in solids

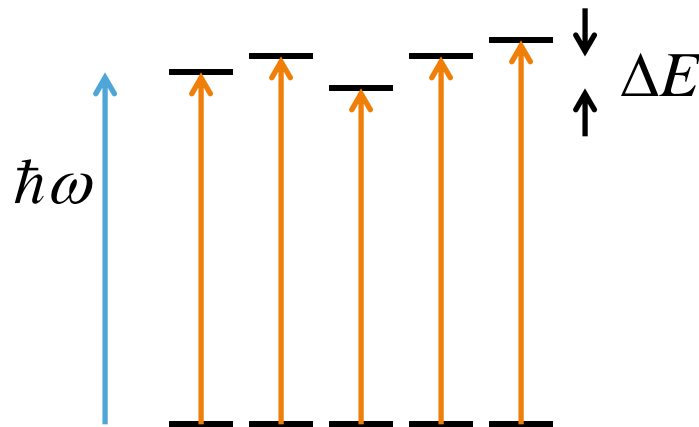$\hbar\omega$

Dense sets of possible transitions

We presume that this set of possible transitions is very dense

with a density $g_J(\hbar\omega)$ per unit energy near the photon energy $\hbar\omega$

giving $g_J(\hbar\omega)\Delta E$ transitions within energy range ΔE

$g_J(\hbar\omega)$ is sometimes known as a "joint density of states"

since it refers to transitions between states

Then adding up the probabilities for absorbing transitions

we obtain a total probability of absorption by this set of transitions of

$$P_{tot} \simeq \frac{t_o^2}{\hbar^2} \left| \left\langle \psi_j \left| \hat{H}_{po} \right| \psi_m \right\rangle \right|^2 \int \left[\frac{\sin\left[\left(\omega_{jm} - \omega \right) t_o / 2 \right]}{\left(\omega_{jm} - \omega \right) t_o / 2} \right]^2 g_J \left(\hbar \omega_{jm} \right) d\hbar \omega_{jm}$$

$g_J \left(\hbar \omega_{jm} \right)$ is presumed constant over small energy ranges

and the sinc squared term is presumed narrow in ω_{jm}

hence we can take $g_J \left(\hbar \omega_{jm} \right)$ out of the integral

as $g_J \left(\hbar \omega \right)$

Formally changing the variable in the integral to

$$x = \left(\omega_{jm} - \omega \right) t_o / 2$$

gives

$$P_{tot} \simeq \frac{t_o^2}{\hbar^2} \left| \left\langle \psi_j \left| \hat{H}_{po} \right| \psi_m \right\rangle \right|^2 \frac{2\hbar}{t_o} g_J \left(\hbar\omega \right) \int \left[\frac{\sin x}{x} \right]^2 dx$$

Using the mathematical result $\displaystyle\int_{-\infty}^{\infty} \left(\frac{\sin x}{x} \right)^2 dx = \pi$

we obtain $\displaystyle P_{tot} \simeq \frac{2\pi t_o}{\hbar} \left| \left\langle \psi_j \left| \hat{H}_{po} \right| \psi_m \right\rangle \right|^2 g_J \left(\hbar\omega \right)$

Fermi's Golden Rule

Now we see that we have a total probability of making some transition

that is proportional to the time t_o

that the perturbation is turned on

This allows us now to deduce a transition rate

or, here, a rate of absorption of photons

$$W = \frac{2\pi}{\hbar} \left| \left\langle \psi_j \left| \hat{H}_{po} \right| \psi_m \right\rangle \right|^2 g_J(\hbar\omega)$$

Fermi's Golden Rule

This result

$$W = \frac{2\pi}{\hbar} \left| \left\langle \psi_j \left| \hat{H}_{po} \right| \psi_m \right\rangle \right|^2 g_J \left(\hbar \omega \right)$$

is known as "Fermi's Golden Rule"

It is one of the most useful results of time-dependent perturbation theory

and forms the basis for calculation of, for example, the optical absorption spectra of solids

and to many other problems involving simple harmonic perturbations

This rule is also stated $w_{jm} = \dfrac{2\pi}{\hbar} \left| \left\langle \psi_j \left| \hat{H}_{po} \right| \psi_m \right\rangle \right|^2 \delta\left(E_{jm} - \hbar\omega\right)$

where w_{jm} is the transition rate

between the specific states $\left| \psi_m \right\rangle$ and $\left| \psi_j \right\rangle$

and $\delta\left(E_{jm} - \hbar\omega\right)$ is the Dirac delta function

an infinitely high and sharp unit-area "spike"

at $E_{jm} = \hbar\omega$

The total transition rate involving all the possible similar transitions in the neighborhood is then formally

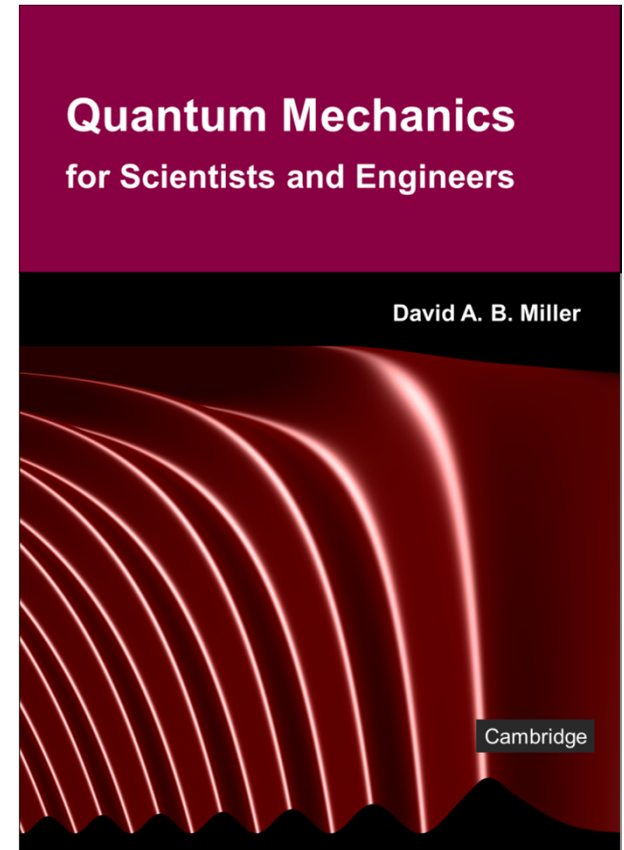$$W = \int w_{jm} g_J\left(\hbar\omega_{jm}\right) d\hbar\omega_{jm}$$

9.3 Applying time-dependent perturbation theory

Slides: Video 9.3.3 Refractive index

Text reference: Quantum Mechanics for Scientists and Engineers

Section 7.3

Applying time-dependent perturbation theory

Refractive index

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Refractive index

In classical electromagnetism

when we apply an electric field E to a material

we can imagine that the field pulls the average position of the negatively charged electrons

away from the average position of the positively charged nuclei of the atoms

creating what is called a

"polarization" P

Refractive index

At least for applied fields that are small
  compared to the fields in the atoms
    we would expect that this "polarization" P
      is proportional to the applied field E
        with a proportionality constant
          the "susceptibility" χ

For historical reasons
    a fundamental constant is also involved
      the "electric constant" ε_o
      so we write $P = \varepsilon_o \chi E$

Refractive index

In a classical view of electromagnetic waves

the fact that we are moving these electrons

with the oscillating field

means that we have a new oscillating current

which itself generates new waves

These new waves interfere with the original waves

with the net result that the effective (phase) velocity of the total wave is changed

formally, divided by the "refractive index" n_r

Refractive index

If we follow through the classical electromagnetism of this problem

for example, using Maxwells' equations

we can conclude

at least for non-absorbing materials

that the refractive index is given by

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

Hence, if we can calculate the proportionality between P and E

we can calculate n_r

Calculation of refractive index

Consider a system with a single electron

  or in which our interactions are only with a single
  electron

Classically the dipole moment μ_{dip}

  associated with moving a single electron

    through a distance z is

      by definition

$$\mu_{dip} = -ez$$

        where the minus sign is because the electron
        charge is negative

Calculation of refractive index

The polarization P is formally

the dipole moment per unit volume

and so the quantum mechanical expectation value of the polarization is

$$\langle P \rangle = \frac{-e\langle z \rangle}{V}$$

where V is the volume of the system

Our quantum mechanical task of calculating refractive index

reduces essentially to calculating $\langle P \rangle$

Calculation of refractive index

Since we are working in first-order perturbation theory

we write the (approximate) total state of the system

$$\left|\Psi\right\rangle = \left|\Phi^{(0)}\right\rangle + \left|\Phi^{(1)}\right\rangle$$

Note we use the full time-dependent state vectors (kets)

$\left|\Phi^{(0)}\right\rangle$ is the unperturbed state vector

$\left|\Phi^{(1)}\right\rangle$ is the first-order (time-dependent) correction

where $\left|\Phi^{(1)}\right\rangle = \sum_n a_n^{(1)}\left(t\right)\exp\left(-i\omega_n t\right)\left|\psi_n\right\rangle$

with unperturbed energy eigenvalues E_n

and eigenfunctions $\left|\psi_n\right\rangle$

Calculation of refractive index

With the state vector $\left|\Psi\right\rangle = \left|\Phi^{(0)}\right\rangle + \left|\Phi^{(1)}\right\rangle$

the expectation value of the polarization would be

$$\left\langle \text{P} \right\rangle = -\frac{e}{V}\left\langle \Psi \right| z \left| \Psi \right\rangle$$

$$= -\frac{e}{V}\left[\left\langle \Phi^{(0)} \right| z \left| \Phi^{(0)} \right\rangle + \left\langle \Phi^{(1)} \right| z \left| \Phi^{(0)} \right\rangle + \left\langle \Phi^{(0)} \right| z \left| \Phi^{(1)} \right\rangle + \left\langle \Phi^{(1)} \right| z \left| \Phi^{(1)} \right\rangle\right]$$

The first term $-e\left\langle \Phi^{(0)} \right| z \left| \Phi^{(0)} \right\rangle$

is just the static dipole moment of the material in its unperturbed state

so we will not consider it further

Calculation of refractive index

$$\langle \mathrm{P} \rangle = -\frac{e}{V} \langle \Psi | z | \Psi \rangle$$

$$= -\frac{e}{V} \left[\left\langle \Phi^{(0)} | z | \Phi^{(0)} \right\rangle + \left\langle \Phi^{(1)} | z | \Phi^{(0)} \right\rangle + \left\langle \Phi^{(0)} | z | \Phi^{(1)} \right\rangle + \left\langle \Phi^{(1)} | z | \Phi^{(1)} \right\rangle \right]$$

The fourth term $-e \left\langle \Phi^{(1)} | z | \Phi^{(1)} \right\rangle$

is second order in the perturbation

and hence, in this first order calculation

we drop it also

Calculation of refractive index

So we are left with

$$\langle \mathrm{P} \rangle = -\frac{e}{V}\left[\left\langle \Phi^{(1)} \middle| z \middle| \Phi^{(0)} \right\rangle + \left\langle \Phi^{(0)} \middle| z \middle| \Phi^{(1)} \right\rangle\right]$$

But because z is a Hermitian operator

$$\left\langle \Phi^{(1)} \middle| z \middle| \Phi^{(0)} \right\rangle = \left\langle \Phi^{(0)} \middle| z \middle| \Phi^{(1)} \right\rangle^{*}$$

therefore

$$\langle \mathrm{P} \rangle = -\frac{2e}{V}\mathrm{Re}\left[\left\langle \Phi^{(0)} \middle| z \middle| \Phi^{(1)} \right\rangle\right]$$

Calculation of refractive index

For the sake of definiteness

we presume we start in eigenstate m, i.e.,

$$\left|\Phi^{(0)}\right\rangle = \exp\left(-i\omega_m t\right)\left|\psi_m\right\rangle$$

Hence, using the first-order perturbation expansion

$$\left|\Phi^{(1)}\right\rangle = \sum_n a_n^{(1)}\left(t\right)\exp\left(-i\omega_n t\right)\left|\psi_n\right\rangle$$

then, from
$$\left\langle \mathrm{P} \right\rangle = -\frac{2e}{V}\mathrm{Re}\left[\left\langle \Phi^{(0)}\left|z\right|\Phi^{(1)}\right\rangle\right]$$

we have
$$\left\langle \mathrm{P} \right\rangle = -\frac{2e}{V}\mathrm{Re}\left[\sum_n a_n^{(1)}\left(t\right)\exp\left(i\omega_{mn}t\right)\left\langle\psi_m\left|z\right|\psi_n\right\rangle\right]$$

Calculation of refractive index

We are interested here in the steady-state situation

with a continuous oscillating field

so we take $\hat{H}_p(t) = e\mathrm{E}(t)z = \hat{H}_{po}\left[\exp(-i\omega t) + \exp(i\omega t)\right]$

as valid for all times

We can rewrite $\dot{a}_q^{(1)}(t) = \dfrac{1}{i\hbar}\exp(i\omega_{qm}t)\langle\psi_q|\hat{H}_p(t)|\psi_m\rangle$ as

$$\dot{a}_q^{(1)}(t) = \frac{e\mathrm{E}_o}{i\hbar}\langle\psi_q|z|\psi_m\rangle\exp(i\omega_{qm}t)\left[\exp(-i\omega t) + \exp(i\omega t)\right]$$

to obtain

$$a_q^{(1)}(t) = -\frac{e\mathrm{E}_o}{\hbar}\langle\psi_q|z|\psi_m\rangle\left[\frac{\exp\left[i(\omega_{qm}-\omega)t\right]}{(\omega_{qm}-\omega)} + \frac{\exp\left[i(\omega_{qm}+\omega)t\right]}{(\omega_{qm}+\omega)}\right]$$

Calculation of refractive index

Substituting

$$a_q^{(1)}(t) = -\frac{e\mathrm{E}_o}{\hbar}\langle\psi_q|z|\psi_m\rangle\left[\frac{\exp\left[i(\omega_{qm}-\omega)t\right]}{(\omega_{qm}-\omega)}+\frac{\exp\left[i(\omega_{qm}+\omega)t\right]}{(\omega_{qm}+\omega)}\right]$$

into

$$\langle\mathrm{P}\rangle = -\frac{2e}{V}\mathrm{Re}\left[\sum_n a_n^{(1)}(t)\exp(i\omega_{mn}t)\langle\psi_m|z|\psi_n\rangle\right]$$

gives

$$\langle\mathrm{P}\rangle = \frac{2e^2\mathrm{E}_o}{\hbar V}\mathrm{Re}\sum_n\left|\langle\psi_m|z|\psi_n\rangle\right|^2\exp(i\omega_{mn}t)$$

$$\times\left[\frac{\exp\left[i(\omega_{nm}-\omega)t\right]}{(\omega_{nm}-\omega)}+\frac{\exp\left[i(\omega_{nm}+\omega)t\right]}{(\omega_{nm}+\omega)}\right]$$

Calculation of refractive index

Noting $\omega_{mn} = -\omega_{nm}$ and taking the real part gives

$$\langle P \rangle = \frac{2e^2 E_o}{\hbar V} \sum_n \left| \langle \psi_m | z | \psi_n \rangle \right|^2 \left[\frac{\cos(-\omega t)}{(\omega_{nm} - \omega)} + \frac{\cos(\omega t)}{(\omega_{nm} + \omega)} \right]$$

$$= \frac{2e^2 E_o \cos(\omega t)}{\hbar V} \sum_n \left| \langle \psi_m | z | \psi_n \rangle \right|^2 \left[\frac{1}{(\omega_{nm} - \omega)} + \frac{1}{(\omega_{nm} + \omega)} \right]$$

and so we have, from $P = \varepsilon_o \chi E$

$$\chi = \frac{e^2}{\varepsilon_o \hbar V} \sum_n \left| \langle \psi_m | z | \psi_n \rangle \right|^2 \left[\frac{1}{(\omega_{nm} - \omega)} + \frac{1}{(\omega_{nm} + \omega)} \right]$$

Calculation of refractive index

From $\chi = \dfrac{e^2}{\varepsilon_o \hbar V} \displaystyle\sum_n \left| \langle \psi_m | z | \psi_n \rangle \right|^2 \left[\dfrac{1}{(\omega_{nm} - \omega)} + \dfrac{1}{(\omega_{nm} + \omega)} \right]$

and using $n_r = \sqrt{1 + \chi}$

we can now deduce the refractive index n_r

completing our calculation of refractive index

Hence, knowing the unperturbed energy eigenfunctions and eigenvalues for some quantum mechanical system

we can calculate the refractive index

using time-dependent perturbation theory

Absorption and refractive index

Note a key difference between

absorption and

refractive index

For absorption

the frequency ω must match the transition
frequency ω_{nm} very closely

for that particular transition to give rise
to absorption of photons

Absorption and refractive index

For the refractive index

the contribution of a particular possible transition $\left| \psi_m \right\rangle \rightarrow \left| \psi_n \right\rangle$

to the susceptibility

and hence to the refractive index

is finite

even when the frequencies do not match exactly or even closely

That contribution to the susceptibility rises steadily as ω rises towards ω_{nm}

Absorption and refractive index

Note that

if we have an absorbing transition at some frequency ω_{nm}

it contributes to refractive index at all frequencies

Refractive index (in a region where the material is transparent)

arises entirely because of the possibility of absorption at other frequencies

If there is a refractive index different from unity

then there must be absorption possible at some other frequency or frequencies

Absorption and refractive index

The relation between refractive index and absorption is known from classical physics

through the Kramers-Kronig relations

The derivation of those relations is entirely mathematical

shedding no light on

the physical mechanism whereby absorption and refractive index are related

Absorption and refractive index

With our quantum mechanical expressions

we can understand any particular aspect in the relation between the two processes

In the quantum mechanical picture, we find

even though we are in a transparent spectral region

there are finite occupation probabilities for all of the states of the system

which are essential if the material has a polarization

Absorption and refractive index

The polarization arises because the charges in the material

change their physical wavefunctions in response to the field

mixing in other states of the system in response to the perturbation

If we examined the expectation value of the energy of the material

we would also find quite real energy stored in the material as a result

even though the material is transparent

Epilogue

Quantum mechanics for scientists and engineers

David Miller