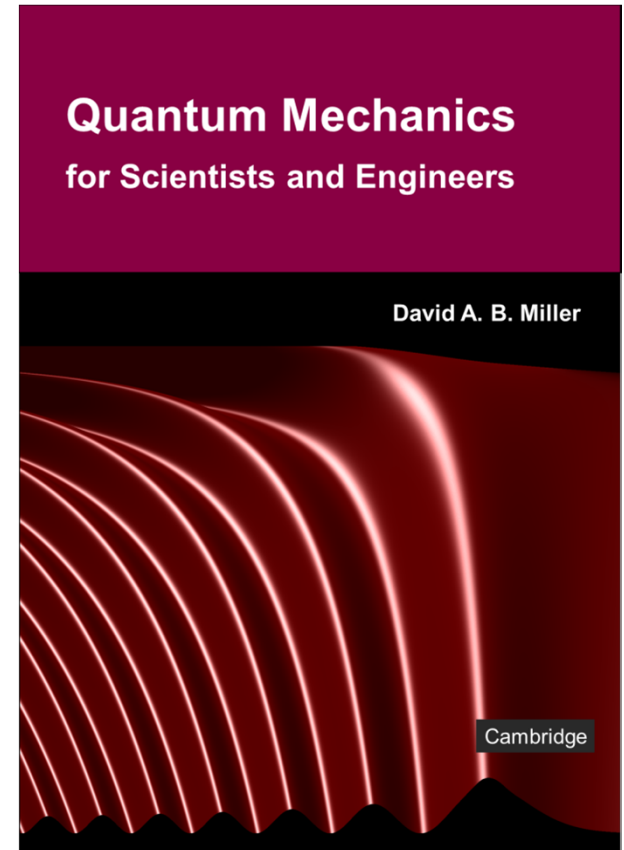# 9.3 Applying time-dependent perturbation theory

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

Quantum mechanics for scientists and engineers

David Miller

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

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

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

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

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

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

so we will not consider it further

Calculation of refractive index

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

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

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

is second order in the perturbation

and hence, in this first order calculation

we drop it also

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

as valid for all times

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

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

to obtain

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

Calculation of refractive index

Substituting

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

into

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

gives

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

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

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

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