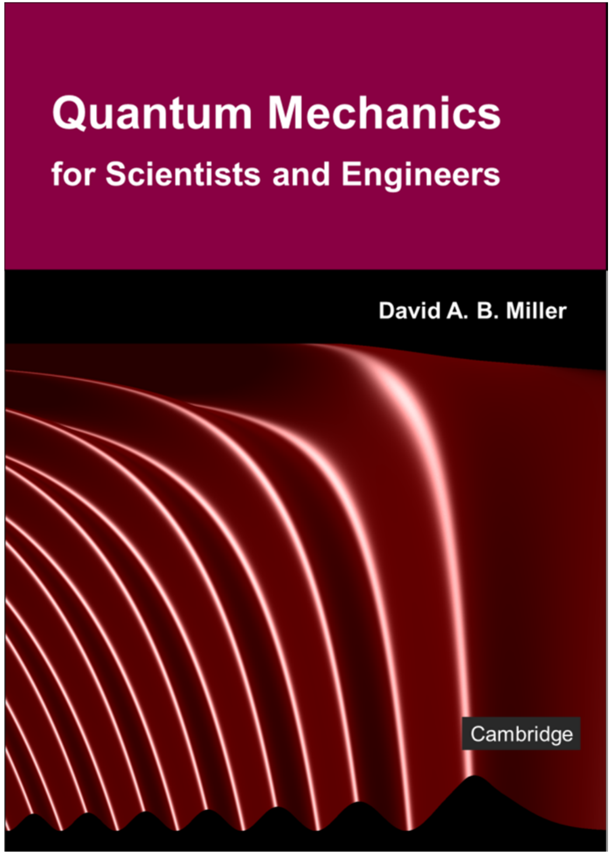
9.2 Time-dependent perturbation theory

Slides: Video 9.2.1 Time-dependent perturbation basics

Text reference: Quantum Mechanics for Scientists and Engineers

Section 7.1



Time-dependent perturbation theory

Time-dependent perturbation basics

Quantum mechanics for scientists and engineers

David Miller

Time-dependent perturbation theory

For time-dependent problems

consider some time-dependent perturbation $\hat{H}_p(t)$

to an unperturbed Hamiltonian $\hat{H}_o$

that is itself not dependent on time

The total Hamiltonian is then

$$\hat{H} = \hat{H}_o + \hat{H}_p(t)$$

To deal with such a situation

we use the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t}|\Psi\rangle = \hat{H}|\Psi\rangle$$

where now the ket $|\Psi\rangle$ is generally time-varying

Time-dependent perturbation theory

With $|\psi_n\rangle$ and E_n as the energy eigenfunctions and eigenvalues of the time-independent equation

$$\hat{H}_o|\psi_n\rangle = E_n|\psi_n\rangle$$

we expand the solution

of the time-dependent Schrödinger equation as

$$|\Psi\rangle = \sum_n a_n(t)\exp(-iE_n t/\hbar)|\psi_n\rangle$$

Note we included the time-dependent factor $\exp(-iE_n t/\hbar)$

explicitly in the expansion

leaving the time dependence of $a_n(t)$

to deal only with the additional changes

Time-dependent perturbation theory

Now we substitute $|\Psi\rangle = \sum_n a_n(t)\exp(-iE_n t/\hbar)|\psi_n\rangle$

into the Schrödinger equation $i\hbar\frac{\partial}{\partial t}|\Psi\rangle = \hat{H}|\Psi\rangle$ gives

$$\sum_n (i\hbar\dot{a}_n + a_n E_n)\exp(-iE_n t/\hbar)|\psi_n\rangle$$

$$= \sum_n a_n\left(\hat{H}_o + \hat{H}_p(t)\right)\exp(-iE_n t/\hbar)|\psi_n\rangle$$ where $\dot{a}_n \equiv \frac{\partial a_n}{\partial t}$

Replacing $\hat{H}_o|\psi_n\rangle$ with $E_n|\psi_n\rangle$ and cancelling gives

$$\sum_n i\hbar\dot{a}_n \exp(-iE_n t/\hbar)|\psi_n\rangle = \sum_n a_n \hat{H}_p(t)\exp(-iE_n t/\hbar)|\psi_n\rangle$$

Time-dependent perturbation theory

Now premultiplying

$$\sum_n i\hbar \dot{a}_n \exp\left(-iE_n t/\hbar\right)\left|\psi_n\right\rangle = \sum_n a_n \hat{H}_p\left(t\right)\exp\left(-iE_n t/\hbar\right)\left|\psi_n\right\rangle$$

by $\left\langle \psi_q \right|$ on both sides leads to

$$i\hbar \dot{a}_q\left(t\right)\exp\left(-iE_q t/\hbar\right) = \sum_n a_n\left(t\right)\exp\left(-iE_n t/\hbar\right)\left\langle \psi_q \left| \hat{H}_p\left(t\right) \right| \psi_n \right\rangle$$

We have made no approximations so far

This is merely a restatement of Schrödinger's time-dependent equation

$$i\hbar \frac{\partial}{\partial t}\left|\Psi\right\rangle = \hat{H}\left|\Psi\right\rangle$$

Time-dependent perturbation theory

Now we consider a perturbation series

We introduce the expansion parameter γ as before

now writing our perturbation as $\gamma \hat{H}_p$

As before, we can set this to 1 at the end

We now express the expansion coefficients a_n as a power series

$$a_n = a_n^{(0)} + \gamma a_n^{(1)} + \gamma^2 a_n^{(2)} + \cdots$$

and we substitute this expansion into

$$i\hbar \dot{a}_q(t) \exp(-iE_q t/\hbar) = \sum_n a_n(t) \exp(-iE_n t/\hbar) \langle \psi_q | \gamma \hat{H}_p(t) | \psi_n \rangle$$

where we now have $\gamma \hat{H}_p$ instead of just $\hat{H}_p$

Time-dependent perturbation theory

In
$$i\hbar\dot{a}_q(t)\exp(-iE_q t/\hbar)=\sum_n a_n(t)\exp(-iE_n t/\hbar)\langle\psi_q|\gamma\hat{H}_p(t)|\psi_n\rangle$$

equating powers of γ on both sides

first we obtain the zero order term

$$\dot{a}_q^{(0)}(t)=0$$

The zero order solution simply corresponds to the unperturbed solution

and hence there is no change in the expansion coefficients in time to zero order

Time-dependent perturbation theory

With $a_n = a_n^{(0)} + \gamma a_n^{(1)} + \gamma^2 a_n^{(2)} + \cdots$ and

$$i\hbar \dot{a}_q(t)\exp\left(-iE_q t/\hbar\right) = \sum_n a_n(t)\exp\left(-iE_n t/\hbar\right)\left\langle \psi_q \middle| \gamma \hat{H}_p(t) \middle| \psi_n \right\rangle$$

for the first order term we have

$$\dot{a}_q^{(1)}(t) = \frac{1}{i\hbar}\sum_n a_n^{(0)} \exp\left(i\omega_{qn} t\right)\left\langle \psi_q \middle| \hat{H}_p(t) \middle| \psi_n \right\rangle$$

where we have introduced the notation

$$\omega_{qn} = \left(E_q - E_n\right)/\hbar$$

Time-dependent perturbation theory

Note here in $\dot{a}_q^{(1)}(t) = \frac{1}{i\hbar}\sum_n a_n^{(0)} \exp(i\omega_{qn}t)\langle\psi_q|\hat{H}_p(t)|\psi_n\rangle$

we already know tha the $a_n^{(0)}$ are all constants

They give the "starting" state of the system at $t = 0$

We note now that, if we know

the starting state, the perturbing potential and

the unperturbed eigenvalues and eigenfunctions

we can integrate to obtain

the first order, time-dependent correction, $a_q^{(1)}(t)$

to the expansion coefficients

Time-dependent perturbation theory

After integrating $\dot{a}_q^{(1)}(t) = \frac{1}{i\hbar}\sum_n a_n^{(0)} \exp(i\omega_{qn}t)\langle\psi_q|\hat{H}_p(t)|\psi_n\rangle$

we know the new approximate expansion coefficients

$$a_q \simeq a_q^{(0)} + a_q^{(1)}(t)$$

so we know the new wavefunction

and can calculate the behavior of the system

from this new wavefunction

Time-dependent perturbation theory

We can proceed to higher order in this time-dependent perturbation theory

Equating powers of progressively higher order gives

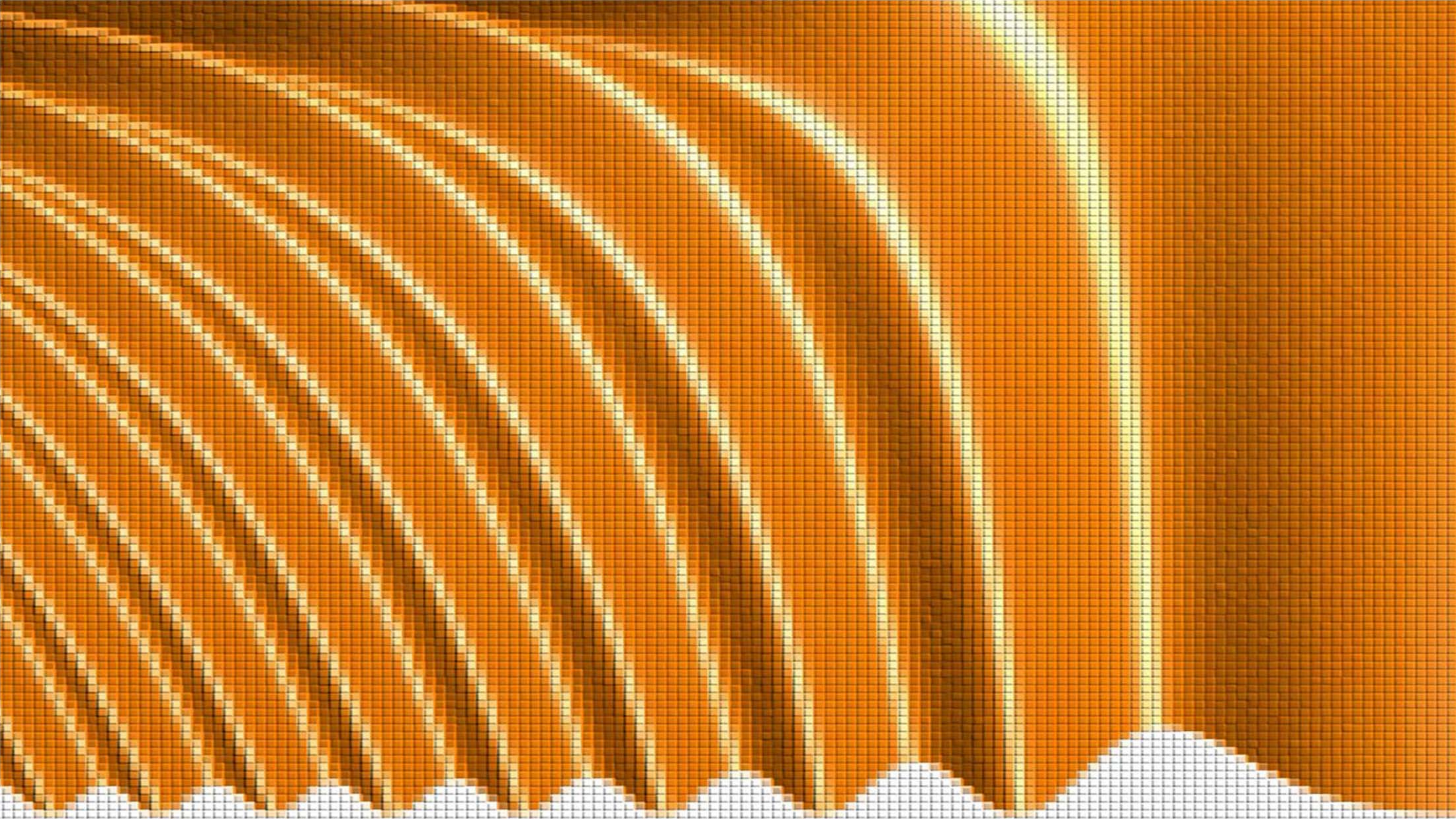
$$\dot{a}_q^{(p+1)}(t) = \frac{1}{i\hbar}\sum_n a_n^{(p)} \exp(i\omega_{qn}t)\langle\psi_q|\hat{H}_p(t)|\psi_n\rangle$$

We see that this perturbation theory is also a method of successive approximations

just like the time-independent perturbation theory

We calculate each higher order correction

from the preceding correction

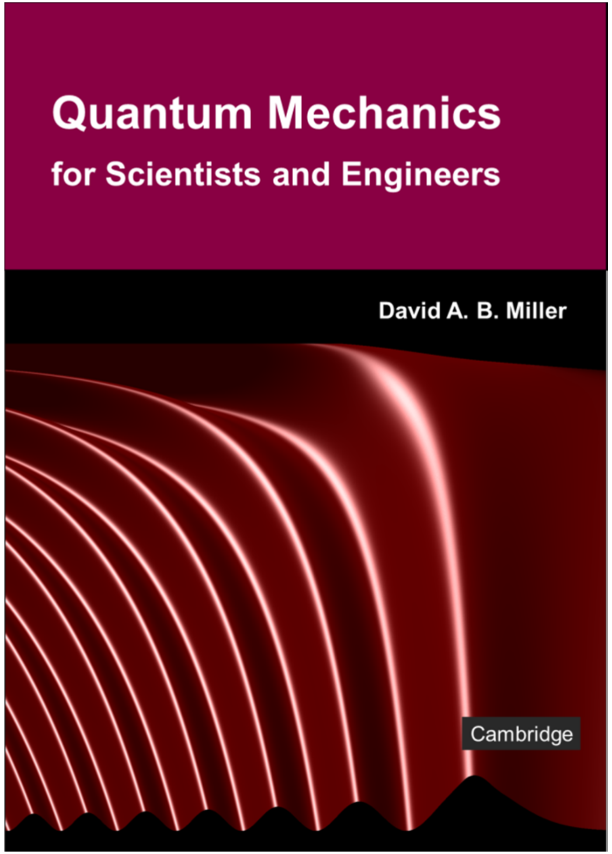


9.2 Time-dependent perturbation theory

Slides: Video 9.2.3 Simple oscillating perturbations

Text reference: Quantum Mechanics for Scientists and Engineers

Section 7.2 (first part)



Time-dependent perturbation theory

Simple oscillating perturbations

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Simple oscillating perturbations

One very useful case is for oscillating perturbations

where a perturbation is varying sinusoidally in time

also called a "harmonic" perturbation

as in the harmonic oscillator

for example, a monochromatic electromagnetic wave

with an electric field in, say, the z direction

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

where ω is a positive (angular) frequency

We consider this here in

first-order time-dependent perturbation theory

Simple oscillating perturbations

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

for an electron, the electrostatic energy in this field,

relative to position $z = 0$

gives a perturbing Hamiltonian

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

where, in this case

$$\hat{H}_{po} = e\mathrm{E}_o z$$

which is a time-independent operator

This perturbing Hamiltonian is called

the electric dipole approximation

Simple oscillating perturbations

We will presume that this perturbing Hamiltonian is only "on" for some finite time

For simplicity, we presume that

the perturbation starts at time $t = 0$

and ends at time $t = t_o$

so formally we have

$$\hat{H}_p(t) = 0,\ t < 0$$

$$= \hat{H}_{po}\left[\exp(-i\omega t) + \exp(i\omega t)\right],\ 0 < t < t_o$$

$$= 0,\ t > t_o$$

Simple oscillating perturbations

We are interested in the case where

- for times before $t = 0$
  - the system is in some specific energy eigenstate $|\psi_m\rangle$

Time-dependent perturbation theory will tell us

- with what probability the system
  - will make transitions into other states

With this choice

- all of the initial expansion coefficients $a_n^{(0)}$ are zero
  - except $a_m^{(0)}$
    - which has the value 1

Simple oscillating perturbations

With this simplification of the initial state to $|\psi_m\rangle$

the first order perturbation solution

$$\dot{a}_q^{(1)}(t) = \frac{1}{i\hbar}\sum_n a_n^{(0)} \exp(i\omega_{qn}t)\langle\psi_q|\hat{H}_p(t)|\psi_n\rangle$$

becomes $\dot{a}_q^{(1)}(t) = \frac{1}{i\hbar}\exp(i\omega_{qm}t)\langle\psi_q|\hat{H}_p(t)|\psi_m\rangle$

Now we substitute the perturbing Hamiltonian

$$\hat{H}_p(t) = 0, t < 0$$

$$= \hat{H}_{po}\left[\exp(-i\omega t) + \exp(i\omega t)\right], 0 < t < t_o$$

$$= 0, t > t_o$$

Simple oscillating perturbations

With that substitution

and integrating over time

from time 0 to time t_o

$$a_q^{(1)}(t > t_o) = \frac{1}{i\hbar}\int_0^{t_0}\left\langle \psi_q \middle| \hat{H}_p(t_1) \middle| \psi_m \right\rangle \exp\left(i\omega_{qm}t_1\right) dt_1$$

$$= \frac{1}{i\hbar}\left\langle \psi_q \middle| \hat{H}_{po} \middle| \psi_m \right\rangle \int_0^{t_o}\left\{\exp\left[i\left(\omega_{qm} - \omega\right)t_1\right] + \exp\left[i\left(\omega_{qm} + \omega\right)t_1\right]\right\} dt_1$$

Simple oscillating perturbations

So $a_q^{(1)}\left(t > t_o\right)$

$$= -\frac{1}{\hbar}\left\langle \psi_q \middle| \hat{H}_{po} \middle| \psi_m \right\rangle \left\{ \frac{\exp\left(i\left(\omega_{qm} - \omega\right)t_o\right) - 1}{\omega_{qm} - \omega} + \frac{\exp\left(i\left(\omega_{qm} + \omega\right)t_o\right) - 1}{\omega_{qm} + \omega} \right\}$$

$$= \frac{t_o}{i\hbar}\left\langle \psi_q \middle| \hat{H}_{po} \middle| \psi_m \right\rangle \left\{ \begin{array}{l} \exp\left[i\left(\omega_{qm} - \omega\right)t_o / 2\right] \dfrac{\sin\left[\left(\omega_{qm} - \omega\right)t_o / 2\right]}{\left(\omega_{qm} - \omega\right)t_o / 2} \\ + \exp\left[i\left(\omega_{qm} + \omega\right)t_o / 2\right] \dfrac{\sin\left[\left(\omega_{qm} + \omega\right)t_o / 2\right]}{\left(\omega_{qm} + \omega\right)t_o / 2} \end{array} \right\}$$

Simple oscillating perturbations

The function $\text{sinc}(x) = \sin(x)/x$

peaks at 1 for $x = 0$

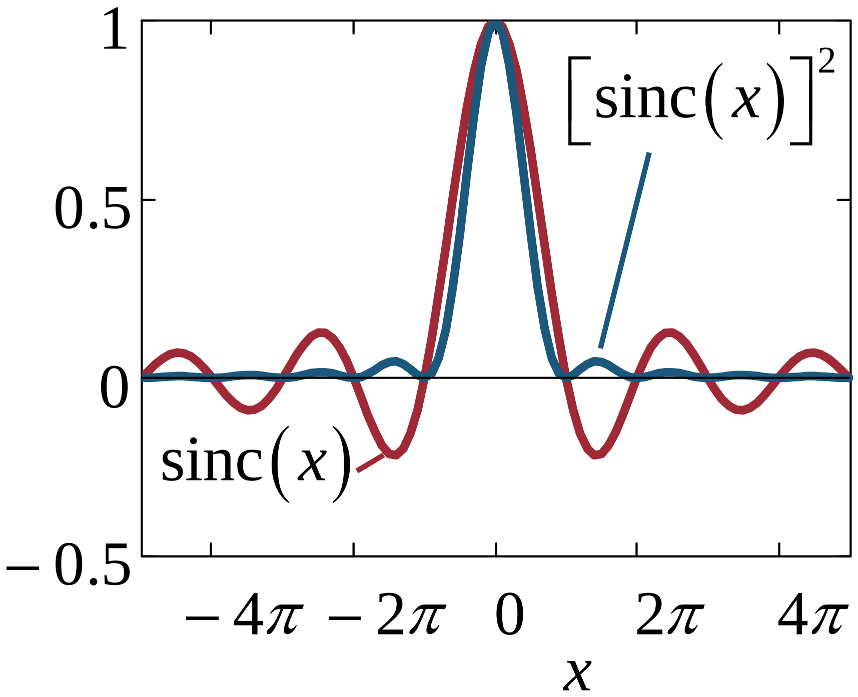
It is only large for $x \simeq 0$

so, e.g., $$\frac{\sin\left[\left(\omega_{qm} - \omega\right)t_o / 2\right]}{\left(\omega_{qm} - \omega\right)t_o / 2}$$

is strongly resonant

with relatively strong contributions

only for frequency ω close to ω_{qm}



Simple oscillating perturbations

We have now calculated the new state for times $t > t_o$

which is, to first order

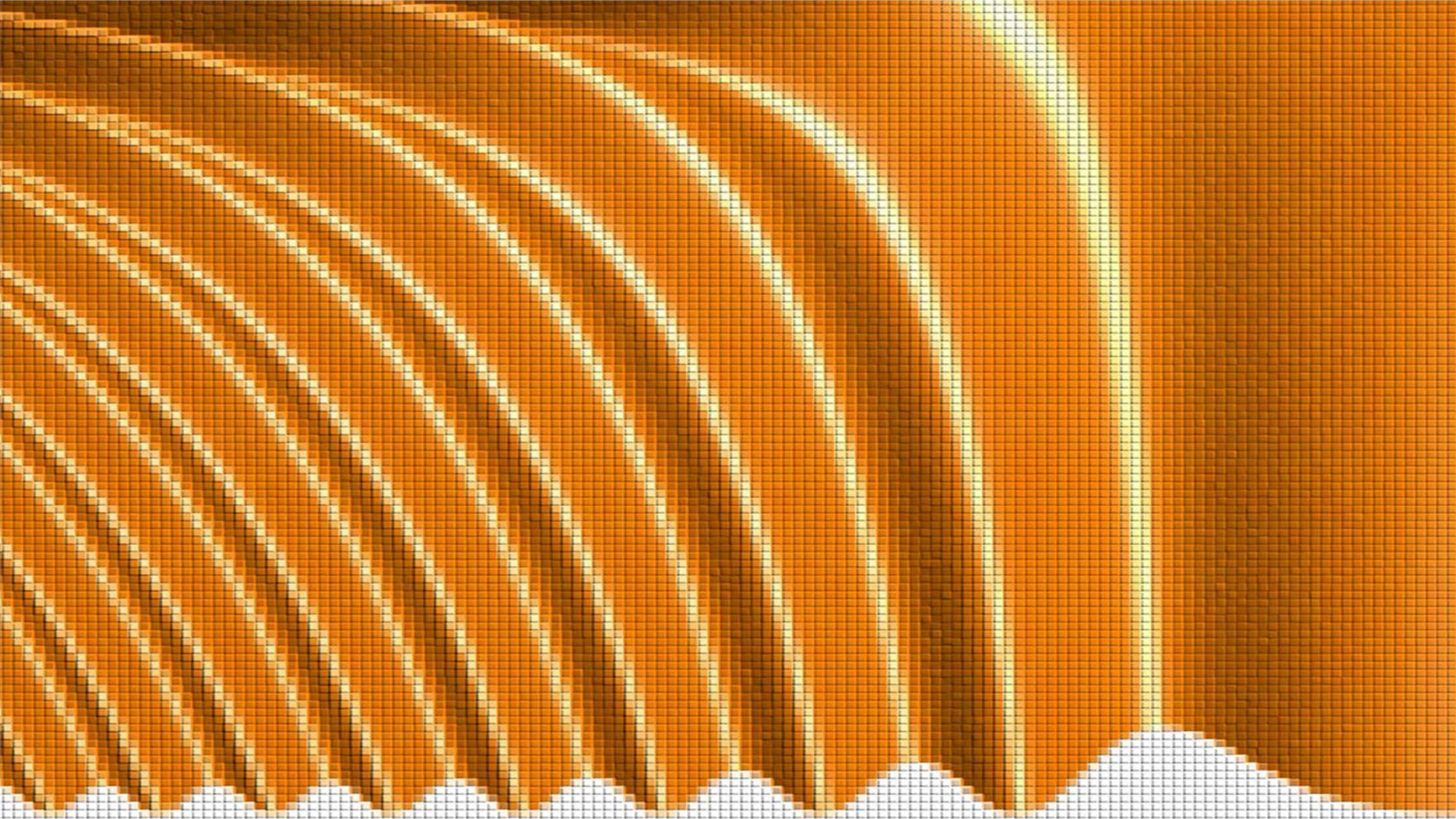
$$\left|\Psi\right\rangle \simeq \exp\left(-iE_m t/\hbar\right)\left|\psi_m\right\rangle + \sum_q a_q^{(1)}(t > t_o)\exp\left(-iE_q t/\hbar\right)\left|\psi_q\right\rangle$$

with the $a_q^{(1)}\left(t > t_o\right)$ given by our preceding expression

Now that we have established our approximation to the new state

we can start calculating

the time dependence of measurable quantities

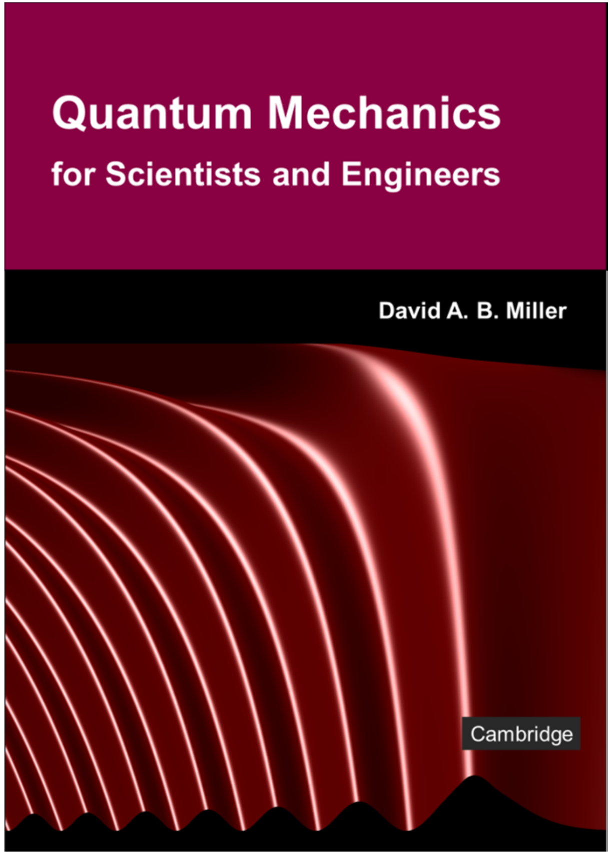


9.2 Time-dependent perturbation theory

Slides: Video 9.2.5 Transition probabilities

Text reference: Quantum Mechanics for Scientists and Engineers

Section 7.2 (second part)



Time-dependent perturbation theory

Transition probabilities

Quantum mechanics for scientists and engineers

David Miller

Transition probability calculation

In this model the probability $P(j)$

of finding the system in state $|\psi_j\rangle$ is $P(j)=\left|a_j^{(1)}\right|^2$

i.e.,

$$P(j)\simeq$$

$$\frac{t_o^2}{\hbar^2}\left|\langle\psi_j|\hat{H}_{po}|\psi_m\rangle\right|^2\left\{\begin{aligned}&\left[\frac{\sin\left[\left(\omega_{jm}-\omega\right)t_o/2\right]}{\left(\omega_{jm}-\omega\right)t_o/2}\right]^2+\left[\frac{\sin\left[\left(\omega_{jm}+\omega\right)t_o/2\right]}{\left(\omega_{jm}+\omega\right)t_o/2}\right]^2\\&+2\cos\left(\omega t_o\right)\frac{\sin\left[\left(\omega_{jm}-\omega\right)t_o/2\right]}{\left(\omega_{jm}-\omega\right)t_o/2}\frac{\sin\left[\left(\omega_{jm}+\omega\right)t_o/2\right]}{\left(\omega_{jm}+\omega\right)t_o/2}\end{aligned}\right\}$$

Transition probability calculation

$\sin(x)/x$ falls off rapidly for arguments $\gg 1$

Hence, for sufficiently long t_o

either one or the other of the two $\sin(x)/x$ functions in the last term will be small

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

Transition probability calculation

As the time t_o is increased

these two $\sin(x)/x$ line functions get sharper

and they will eventually not overlap for ω

$$P(j) \simeq$$

$$\frac{t_o^2}{\hbar^2}\left|\left\langle \psi_j \middle| \hat{H}_{po} \middle| \psi_m \right\rangle\right|^2 \left\{ \begin{array}{l} \left[\dfrac{\sin\left[\left(\omega_{jm}-\omega\right)t_o/2\right]}{\left(\omega_{jm}-\omega\right)t_o/2}\right]^2 + \left[\dfrac{\sin\left[\left(\omega_{jm}+\omega\right)t_o/2\right]}{\left(\omega_{jm}+\omega\right)t_o/2}\right]^2 \\ +2\cos\left(\omega t_o\right)\dfrac{\sin\left[\left(\omega_{jm}-\omega\right)t_o/2\right]}{\left(\omega_{jm}-\omega\right)t_o/2}\dfrac{\sin\left[\left(\omega_{jm}+\omega\right)t_o/2\right]}{\left(\omega_{jm}+\omega\right)t_o/2} \end{array} \right\}$$

Transition probability calculation

Presuming we take t_o sufficiently large, we are left with

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

We now have some finite probability that the system

has changed state from its initial state $\left|\psi_m\right\rangle$

to another "final" state $\left|\psi_j\right\rangle$

Transition probability calculation

$$P(j) \simeq$$

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

This probability depends on

the strength of the perturbation squared, and the

modulus squared of the perturbation matrix element

between the initial and final states

Transition probability calculation

$$P(j) \simeq$$

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

With an oscillating electric field acting on an electron

this probability is $\propto$ the square of the field amplitude E_o^2

which is proportional to the intensity I (Power/Area)

so the probability of making a transition is proportional to the intensity I

Absorption and emission terms

In

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

what is the meaning of the two different terms?

Absorption and emission terms

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

The first term above is significant if $\omega_{jm} \approx \omega$

i.e., if $\hbar\omega \approx E_j - E_m$

Since we chose ω to be a positive quantity

this term is significant if we are absorbing energy

raising from a lower energy state $|\psi_m\rangle$

to a higher energy state $|\psi_j\rangle$

Absorption and emission terms

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

We note that

the amount of energy we are absorbing is $\hbar\omega$

This first term behaves as we would require

for absorption of a photon

Absorption and emission terms

$$P(j) \simeq$$

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

The second term above is significant if $-\omega_{jm} \approx \omega$

i.e., if $\hbar\omega \approx E_m - E_j$

Since we chose ω to be a positive quantity

this term is significant if we are emitting energy

falling from a higher energy state $|\psi_m\rangle$

to a lower energy state $|\psi_j\rangle$

Absorption and emission terms

$$P(j) \simeq$$

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

We note that the amount of energy we are emitting is $\hbar\omega$

This second term corresponds to

stimulated emission of a photon

the process used in lasers

The spontaneous emission of normal light requires

quantizing the electromagnetic field as well