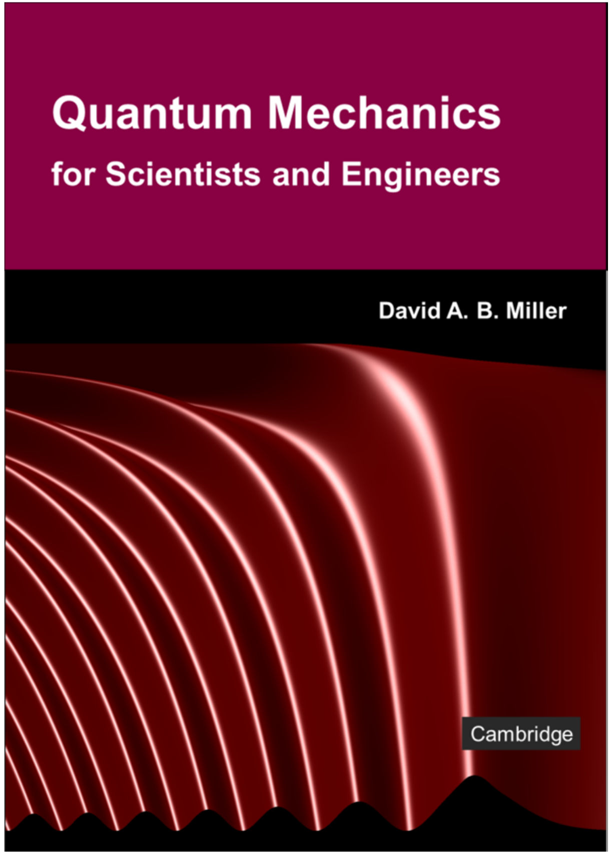
9.3 Applying time-dependent perturbation theory

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

With density matrices

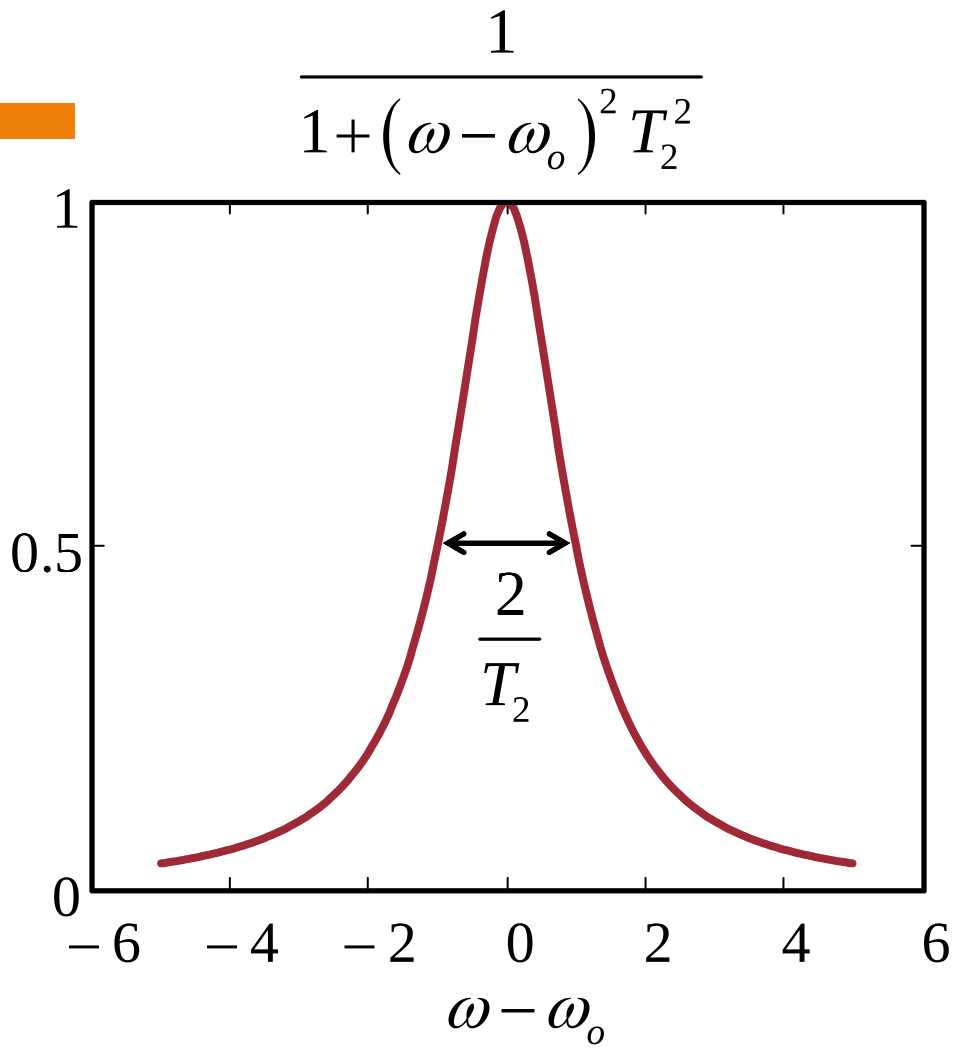
we end up replacing the sinc squared function

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

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

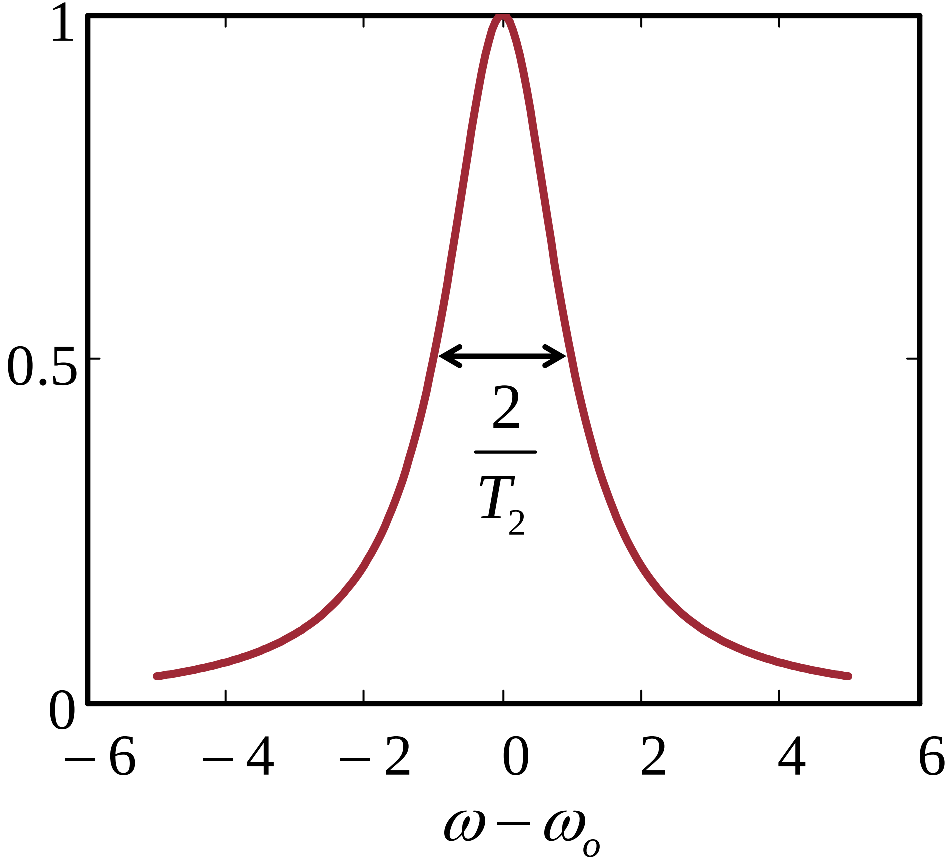
If the system only exists in its original form for a time T_2

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 $\sim \pm 1 / T_2$

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



Dense sets of possible transitions

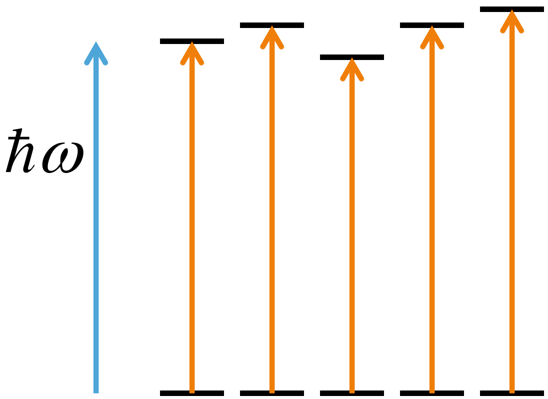
A major class of problems can, however, be analyzed using our approach

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



Dense sets of possible transitions

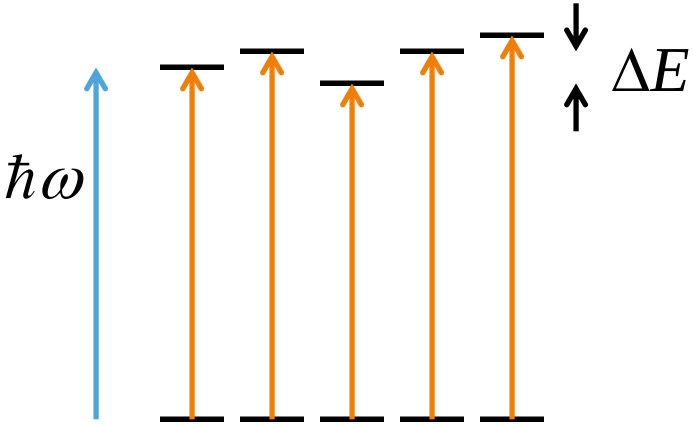
We presume that this set of possible transitions is very dense

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



Absorption into dense sets of possible transitions

Then adding up the probabilities for absorbing transitions

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

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

$g_J\left(\hbar\omega_{jm}\right)$ 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 $g_J\left(\hbar\omega\right)$

Absorption into dense sets of possible transitions

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 $\int\limits_{-\infty}^{\infty}\left(\frac{\sin x}{x}\right)^2 dx = \pi$

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

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

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

Fermi's Golden Rule

This result

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

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

Fermi's Golden Rule – alternative statement

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

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

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