

# Chapter 9 19-1

## Time-Dependent Perturbation

### Theory

## & Radiative Transitions

~~1) Radiative~~

1) Intro

Radiative transitions

are an extremely important

~~ex~~ case for

time-dependent perturbation  
theory (TDPT)

— So it seems a good  
idea just to build  
an introduction to TDPT  
around them.

9-2] I'm not following Griffiths ch. 9, but  
Mihalas chap. 4 since it  
seems to me Mihalas gets  
to things a bit better - or  
at least more to my taste  
(but Griffiths is not bad)

## 2) Einstein Relations for Bound-bound Transitions

(line transitions) (Mihalas  
p 77  
- 79)

~~say  $n_i(V)$  is number of~~

$n_i$  is number density of atoms  
in atomic level  $i$ . (or state  $i$ )  
~~that~~



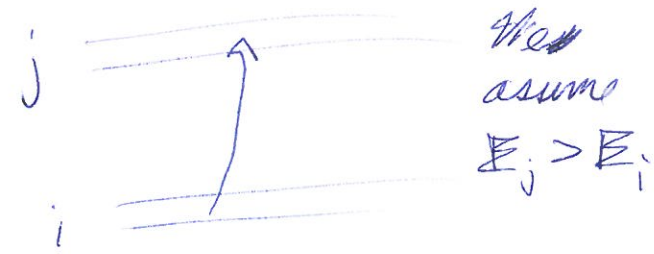
Such levels are always broadened by perturbations + Popplev including those of irremovable zero point electromagnetic field (Gr-351)

Each individual Atom has own shape energy? at ~~certainly~~ an instant. Colbater procedure certainly

broadening due to motion

This means for transition  $i \rightarrow j$ ,

there is an absorption profile  $\Phi_\nu$



which is often a mixture of Gaussian & Lorentzian

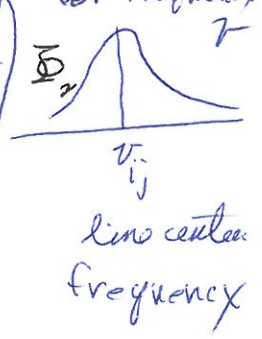
Popplev part  $\frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{(\nu - \bar{\nu})^2}{2\sigma^2}}$

perturbative part  $\frac{1}{\pi} \frac{\gamma}{(\nu - \nu_{ij})^2 + \gamma^2}$   
Mi-278

$\int \Phi_\nu d\nu = 1$  and  $\Phi_\nu$  gives "number" of atoms in state capable of making transition at frequency  $\nu$

The rate of transitions caused by an impinging beam is

$$N_i \int \Phi_\nu d\nu R_{ij} \frac{d\Omega}{4\pi}$$



9-4]

Number of transitions per time  
~~unit~~ per volume in frequency  
interval  $d\nu$  for  
a beam incoming from  
solid angle  $d\Omega$



$$R_{ij} = B_{ij} I_\nu$$

transition  
rate  
coefficient

specific  
intensity

— energy  
per frequency  
per time  
per solid  
angle

Einstein  
B coefficient

per  
perpendicular  
area to  
the beam.

so far  
a way to  
parameterize  
our ignorance

the atomic  
nature part  
of the rate

— the radiation  
part of the  
rate

(the cross  
section is  
~~a~~ a related  
quantity ~~quantity~~)

We assume the profile is so narrow that  $\nu$  can be approximated by  $\nu_{ij}$  the line center frequency

$$\frac{dI_r}{ds} = \rho_\nu = n_i \frac{B_{ij} h \nu_{ij}}{4\pi} \Phi_r I_\nu$$

energy absorbed per ~~unit~~ frequency per time per solid angle per volume

is line energy absorbed

$$\sigma_r = \frac{B_{ij} h \nu_{ij}}{4\pi} \Phi_r$$

$dI_r = \nu_{ij} I ds = k I ds$  is cross-section (Mihalas p87)

$I = I_0 e^{-ks} = I_0 e^{-s/l}$

$I dA dt = \sigma n dA ds dt$   
 $A = -\sigma n \int I dA ds dt$   
 $dI = -\sigma n I ds$

There are two emission processes spontaneous & stimulated.

$$N_{\nu} \text{ spont} = n_j \frac{A_{ji} h \nu_{ij}}{4\pi} \psi_\nu$$

energy ~~absorbed~~ emitted per freq per time per solid angle per volume

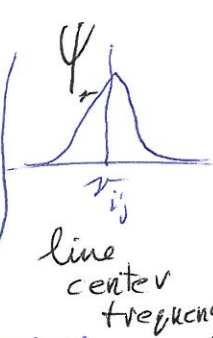
number density of particle in state  $j$

emission profile

Not necessarily the same as  $\Phi_r$ , but often so or nearly so.

$\int \psi_\nu d\nu = 1$  centered on line frequency  $\nu_{ij}$

Must be so in TE — though no one seems to explain why fully



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$A_{ji}$

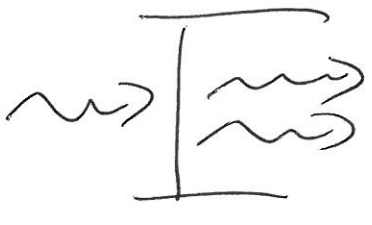
is the Einstein A coefficient

which so far is a way of parametrizing our ignorance.

stimulated emission is like a negative absorption

$$N_{r \text{ stim}} = N_j \frac{B_{ji} h \nu_{ij}}{4\pi} \chi_r I_r$$

Einstein famously deduced there must be stimulated emission

 to get thermodynamic equilibrium to hold

— we are following his steps

— But his proof did not reveal a key QM feature.

~~— the stimulated photons~~

— the omitted photons move

in the same direction 9-7  
<sup>and coherent.</sup>  
as the stimulating ones

— This feature is essential  
to lasing

So Einstein did NOT ~~invent~~  
~~the laser~~ discover lasing.

Must  
be  
an  
intrinsic  
result  
of QED  
in some  
deep way.

$B_{ij}$ ,  $B_{ji}$ ,  $A_{ji}$  are ~~are~~ all  
related ~~related~~ to each other.

Spontaneous emission at a deeper  
QM level is actually stimulated  
emission by the zero-point  
electromagnetic field. (Gr - 351)

This is a good reason for  
assuming the same  
emission profile holds for  
emission processes.

9-8

Now let's consider  
a Thermodynamic equilibrium (TE)  
case.

Detailed balance holds  
in TE.

every transition rate equals  
its reverse

$$R_{ij} = R_{ji}$$

Why? Well not even Wik  
seems to give a good  
argument.

There must be a general proof somewhere

Recall Statistical mechanics of TE  
makes no assumptions

about transitions processes, except  
that they exist and allow  
an isolated system to relax to the TE state where  
the fundamental axiom of Stat mech holds.



So in our case,  
detailed balance dictates

9-9

$$R_{\nu} = N_{\nu \text{spou}} + N_{\nu \text{stim}}$$

kind of cheating  
since this is  
two rates down  
— but if you regard  
spontaneous emission  
as a form of stimulated  
emission, there is  
only one rate.

$$n_i \frac{B_{ij} h \nu_{ij}}{4\pi} \int \Phi_{\nu} B_{\nu} = n_j \frac{B_{ji} h \nu_{ij} \Psi_{\nu}}{4\pi} B_{\nu} + n_j \frac{A_{ji} h \nu_{ij}}{4\pi} \Psi_{\nu}$$

In TE,  $\int \Phi_{\nu} = B_{\nu} \leftarrow$  the ~~Planck~~ Planck law

Also we assume  $\int \Phi_{\nu} = \Psi_{\nu}$

Alternatively, one could integrate

9-10

over  $\nu$  assuming

$B_r$  is constant over  
the line profile.

Canceling like factors

$$n_i B_{ij} B_r = n_j B_{ji} B_r + n_j A_{ji}$$

Since we are in TE, the  
occupation number  $n_i$  &  $n_j$   
are dictated by the

~~Max~~ Boltzmann law

(to give it one of it's  
names)

$$n_i = g_i e^{\alpha - E_i/kT}$$

$$\therefore \frac{n_j}{n_i} = \frac{g_j}{g_i} e^{-(E_j - E_i)/kT}$$

$$= \frac{g_j}{g_i} e^{-h\nu_{ij}/kT}$$

$g_i$  is  
the  
energy  
level  
degeneracy

Now we solve for  $B_r$

9-11

$$B_r = \frac{n_j A_{ji}}{n_i B_{ij} - n_j B_{ji}}$$

$$= \frac{A_{ji}}{B_{ij} \frac{n_i}{n_j} - B_{ji}}$$

$$= \frac{A_{ji}}{B_{ji}} \frac{1}{\frac{B_{ij}}{B_{ji}} \frac{n_i}{n_j} - 1}$$

$$\left( \frac{B_{ij}}{B_{ji}} \right) \frac{g_i}{g_j} e^{-\frac{h\nu_{ij}}{kT}} - 1$$

"negative absorption" contribution

No stimulated emission

ie,  $B_{ji} = 0$

and we would not get the Planck Law.

No spontaneous emission

and  $B_r$  would cancel out

on p. 9-10

and be

indeterminable

from this argument.

But from Stat Mech, we know

This is a requirement.

$$B_r = \frac{2h\nu^3}{c^2} \frac{1}{e^{\frac{h\nu}{kT}} - 1}$$

$$\therefore A_{ji} = \frac{2h\nu_{ij}^3}{c^2} B_{ji} \text{ and } g_i B_{ij} = g_j B_{ji}$$

The Einstein relations,

9-12

The  $A_{ji}$ ,  $B_{ij}$ ,  $B_{ji}$   
coefficients are atomic & photon  
quantities and are not  
set by Thermodynamic equilibrium.

→ They apply generally.

It's remarkable that one  
can extract them from a  
T E argument.

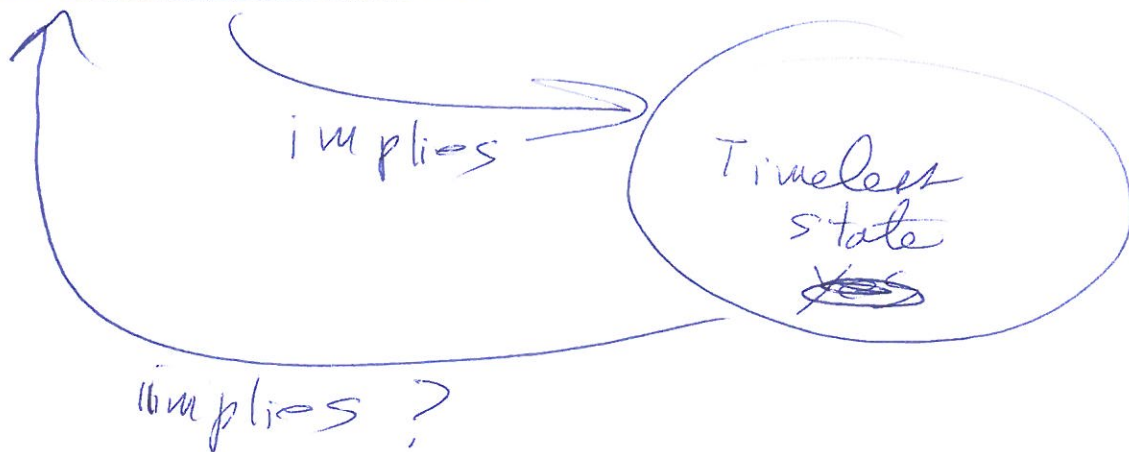
But recall, the Planck law  
was derived assuming  
photons were bosons  
and that they were NOT  
conserved in T E

→ So creation & destruction  
processes were implied.

Still a bit Puzzled

9-13

a) Detailed Balance



b)

Say there was no stimulated emission

$$B_{ji} = \frac{A_{ji}}{B_{ij}} \frac{g_j}{g_i} e^{-\frac{h\nu_{ij}}{kT}}$$

we can't turn this into the Planck function

without assuming  $A_{ji}$  and or  $B_{ji}$  are

~~Temperature~~ Temperature and therefore environment independent

9-14)

c) Say spontaneous emission  
does NOT exist

$$n_i B_{ij} = n_j B_{ji} \quad (\text{see p. 9-10})$$

and  $B_r$  could  
be anything

$$\begin{aligned} \text{But } B_{ji} &= B_{ij} \frac{n_i}{n_j} \\ &= B_{ij} \frac{g_i}{g_j} e^{\frac{h\nu_{ij}}{kT}} \end{aligned}$$

— The atomic coefficients  
become Temperature  
& therefore environment  
dependent.

d) Say we knew all atomic and photon  
physics  
and derived  $A_{ji}$ ,  $B_{ji}$ ,  $B_{ij}$   
then along with detailed balance  
and  $B_{blt}$  Zwanzig law ~~balance~~ they would  
imply  $B_r = \frac{2h\nu^3}{c^2} \frac{1}{e^{\frac{h\nu}{kT}} - 1}$

9-15

I guess I'm puzzled  
by the lack of freedom  
in being able to set  
 $A_{ji}$ ,  $B_{ij}$ ,  $B_{ji}$  arbitrarily  
and have thermodynamics  
just emerge independent  
of underlying ~~fundamental~~  
physics.

After all we derive  
~~state~~ T & E stat. mech.  
with minimal assumptions  
about underlying processes  
that bring about transitions  
and without assuming  
detailed balance.

Hum. Discussion breaks off inconclusively

9-16

Does basic properties  
and detailed balance dictate  
the Planck function  
and the Stat. Mech. derivation  
~~at all~~ a case of finding  
hypotheses that lead to  
the same result?

which  
may  
be  
wrong!!

Hum. Discussion breaks off  
inconclusively.

Well anyway it's a lucky  
thing ~~THE~~ gives us

$A_{ji}$  because there is  
no other way to  
get it without



Quantum electrodynamics. [9-17

$B_{ij}$  and  $B_{ji}$  can be  
obtained from Non-relativistic QM.

### 3) Calculation of Radiative Transition

Probabilities

from Time Dependent  
Perturbation Theory

Mihalas  
p. 84-1

We assume a ~~classical~~  
atom quantum mechanical  
and a classical electromagnetic  
field.

9-18)

We are thinking  
of one-electron atoms  
in the first instance.

- But  $H$ ,  $He^+$  are 1-electron atoms  
and all atoms act a bit  
like one-electron atoms  
for transitions between  
excited states. (in one-electron  
excited cases anyway)
- The inner electrons and  
nucleus just act together  
a fixed center of force  
in space, to some degree.

So we have a 1-particle  
problem.

The Hamiltonian without  
perturbation is  $H_0$

The full Sch. eqn. is  $H_0 \Psi = i \hbar \frac{\partial \Psi}{\partial t}$

Say  $H_0$  is time independent, 19-19  
and so we can separate  
to get the time-independent  
Sch. eqn.

$$H_0 \psi = E \psi,$$

~~Which~~ Which we solve  
for eigenstates + ~~energies~~  
energies

$$\{ |\psi_i\rangle \} \text{ and } E_i$$

$|\psi_i\rangle$  are a complete set  
of states for the space.

Any general mixed state can be  
expanded

$$|\psi\rangle = \sum c_i |\psi_i\rangle \quad \text{in } \{ |\psi_i\rangle \}$$

This is for one instant in  
time.  $c_j = \langle \psi_j | \psi \rangle$

9-20

If we call that time zero  
the mixed state evolves so

$$|\psi(t)\rangle = \sum_i c_i e^{iE_i t/\hbar} |\psi_i\rangle$$

time independent eigenstate

If we know the initial state, then the whole future evolution follows.

A sort of trivial time dependence since the Hamiltonian is time-independent

~~the state~~  
the eigenstate time dependence written explicitly.

I've sort of got idea why. Perturbation more strongly effect time dependent states — a consequence of the time-energy uncertainty principle

Mixed states seem to be rather delicate in nature — but eternal if there are NO time dependent perturbations

When a transition — absorption or emission happens — it is always? or almost always understood as between energy eigenstates

But ~~it~~ seems mispeakable

— transitions to or [ 22 ]  
between mixed states  
seem not to happen

(or maybe are just a  
weak process — I don't  
know. It seems unspeakable)

→ If they did happen  
~~a lot~~ a lot  
relative to transitions  
between quantized energy  
states <sup>and</sup> we wouldn't have  
line spectra.

Also mixed states  
do NOT come into  
statistical mechanics  
There is an infinite continuum

9-22)

of such states,

But we never ~~count~~ <sup>include</sup> them  
when we count degenerate  
factors.

So maybe usually they exist  
only fleetingly and  
and transitions to them  
fail.

Now we perturb the system  
adding perturbation  
Hamiltonian

$$H_1(t)$$

It's time dependent.

— We are thinking of perturbation  
potential in fact ~~H<sub>1</sub>(t)~~  $H_1(t) = V_1(t)$

but for consistent notation, 9-23  
we keep writing  $H_1(t)$ .

Now

$$|\Psi(t)\rangle = \sum_i c_i(t) e^{-iE_i t/\hbar} |\Psi_i\rangle$$

other time dependence stationary state time-dependence

The  $\{|\Psi_i\rangle\}$  is still a complete ~~to~~ set, so at any instant an expansion can be done

It seems a priori that analytically keeping the stationary state time dependence ~~separ~~ distinct might be a good idea.

— Maybe it will lead to ~~an effective treatment~~ an effective treatment by isolating the difficult time dependence of perturbation — and this is true.

9-29)

Our Perturbation  
is an electric field

↳ the magnetic component  
if the field is electromagnetic  
radiation turns out to be  
much less important.

$$\vec{E} = E_0(\cos \omega t) \hat{z}$$

Choose  
it to  
be in the  
 $\hat{z}$   
direction.

— We choose it  
to be spatially  
uniform.

— a valid approximation for  
UV-IR (UV-optical IR  
electromagnetic radiation

$\lambda \approx 1000 \text{ \AA}$  and the  
atomic size scale is  
 $\sim 1 \text{ \AA}$