

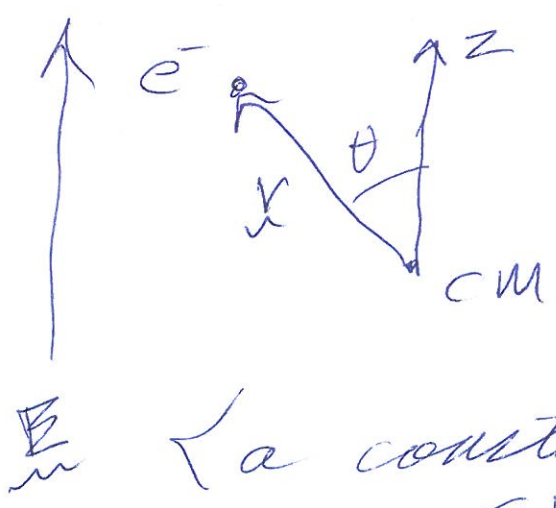
The electric field could be standing or travelling.

But <sup>consider travelling wave</sup>  $\cos(kx - \omega t)$ .

Let one point  $x$ , it's just going up and down sinusoidally.

The " $kx$ " is just a phase factor for a fixed point in space where the atom resides

What is the associated ~~potential~~ electrical potential  $\Phi$ ? (Not potential energy)



Take atom ~~at~~ center of mass as the zero point

↳ a constant in space at any one time

9-26

Recall

$$\Phi = - \int_0^{\infty} \underline{E} \cdot d\underline{r}$$

$$= - \underline{E} \cdot \underline{r}$$

in this case,

If  $Q=0$   
 $\underline{P} = \sum_i q_i \underline{r}_i$   
 $= \sum_i q_i (x_i \hat{x} + y_i \hat{y} + z_i \hat{z})$   
 $= 0 + \underline{P}'$   
 so  $\underline{P}$  is origin independent for a neutral.

If core is spherically symmetric  
 $\underline{L}_{core} \cong 0$   
 $\underline{d}$  is atom dipole moment

Recall electrons have  $q = -e$

$$\Psi = V = e \sum_i \underline{r}_i \cdot \underline{E}$$

$$= e \underline{E} \cdot \sum_i \underline{r}_i$$

$$= \underline{E} \cdot \underline{d}$$

QM potential (energy)

H-atom  
 $e^- e^-$   
 $\underline{r}_t = 0$   
 so exactly dipole moment of atom

Even though I said one electron before, we can be a touch more general for a bit

$$\underline{P} = \sum_i q_i \underline{r}_i$$

definition

So  $\underline{d}$  is dipole moment for charge you are counting

$$\underline{d} = \sum_i \underline{r}_i e$$

the dipole moment.

(Usually  $\underline{p}$  is used in textbooks)

but maybe not

total dipole moment; but for whole atom if  $\underline{d}_{core} = 0$ ,

Because the dipole moment comes into the transition formula, such transitions are called electric dipole transitions.

but I'll use  $\rho$  following  
 Mihalis for mental clarity  
 (mine)

9-27

Now with

$$H = H_0 + H_1$$

An expansion  
 at any instant  
 in time.  
 Somehow  
 Born Postulate  
 still works

and  $|\Psi\rangle = \sum_i c_i(t) e^{-iE_i t/\hbar} |\varphi_i\rangle$   
 parameters  
 of solution

substitute into the

time-dependent Sch. eqn.

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

$$\begin{aligned} (H_0 + H_1) \sum_i c_i(t) e^{-iE_i t/\hbar} |\varphi_i\rangle & \\ = \sum_i (c_i + c_i E_i) e^{-iE_i t/\hbar} |\varphi_i\rangle & \end{aligned}$$

*(Note: The above equation is heavily scribbled over in the original image)*

~~$$(H_0 + H_1) \sum_i c_i e^{-iE_i t/\hbar} |\varphi_i\rangle = \sum_i (c_i + c_i E_i) e^{-iE_i t/\hbar} |\varphi_i\rangle$$~~

$$c_i = \rho$$

9-28

$$(H_0 + H_1) \sum_i c_i e^{-iE_i t/\hbar} |\psi_i\rangle = \sum_i (i\hbar \dot{c}_i + c_i E_i) e^{-iE_i t/\hbar} |\psi_i\rangle$$

$\dot{c}_i = \frac{dc_i}{dt}$

Recall

$$H_0 |\psi_i\rangle = E_i |\psi_i\rangle$$

Thus we can do some cancellation to get

$$H_1 \sum_i c_i e^{-iE_i t/\hbar} |\psi_i\rangle = \sum_i i\hbar \dot{c}_i e^{-iE_i t/\hbar} |\psi_i\rangle$$

Now we'd like to isolate a coefficient and look for a Differential equation for it.

So I know what you are thinking

— take the inner product with  $|\psi_j\rangle$

$$\sum_i c_i e^{-iE_i t/\hbar} \langle \psi_j | H_i | \psi_i \rangle = i\hbar \dot{c}_j e^{-iE_j t/\hbar}$$

$H_i$  can be commuted with the time dependence — No time differentiating operator ~~and~~ in it.

using  $\langle \psi_j | \psi_i \rangle = \delta_{ij}$

$$\dot{c}_j = \frac{1}{i\hbar} \sum_i c_i e^{i\omega_{ji} t} \langle \psi_j | H_i | \psi_i \rangle,$$

Say  $c_i = \begin{cases} 1 & i=k \\ 0 & i \neq k \end{cases}$   
at  $t=0$   
and  $t$  short enough for

$$\dot{c}_j = \frac{1}{i\hbar} c_k e^{i\omega_{jk} t} \langle \psi_j | H_i | \psi_k \rangle$$

1st order time dep. perturbation theory

where

$$\omega_{ji} = (E_j - E_i) / \hbar = - \frac{(E_j - E_i)}{\hbar}$$

is a Bohr Frequency ( $\omega_{jk}$ )

— there seems no absolute convention on the signs.

9-30

In general  
an infinite  
set.

So we have a set  
of coupled DEs  
for all coefficients  $\epsilon_j(t)$ .

1st  
order  
Partial  
DEs: all  
linear

We've made no approximations  
so far — and <sup>have</sup> been general.

So if ~~one~~ could solve  
this set, one would know  
all — all about  
Sch. eqn. evolution,  
~~but~~ but what of wave function  
collapse?

— neither Mihalas nor Griffiths  
whispers ~~breathes~~ the term and yet  
there has to be a point where  
it enters — I think  
we'll see it.

No for the matrix elements 9-31

$$\langle \chi_j | H_1 | \chi_i \rangle = \langle \chi_j | \underline{\hat{z}} \cdot \underline{\hat{d}} | \chi_i \rangle$$

$$= E_0 \cos(\omega t + \phi) \langle \chi_j | \underline{\hat{z}} \cdot \underline{\hat{d}} | \chi_i \rangle$$

$$= E_0 \cos(\omega t + \phi) \hat{z} \cdot \underbrace{\langle \chi_j | \underline{\hat{d}} | \chi_i \rangle}_{= d_{ji}}$$

$\phi$  is an arbitrary phase factor.

The dipole moment matrix element.

— the sinusoidal perturbation can have any phase at time zero & recall which can be just after a collapse to a state  $i$ .

~~Now  $\cos(\omega t + \phi) = \cos \omega t \cos \phi - \sin \omega t \sin \phi$~~

The  $\phi$ 's do vanish, but it's good to see that explicitly.

$$h_{ji} = \frac{1}{2} E_0 \hat{z} \cdot \underline{\hat{d}}_{ji}$$

9-32

$$\begin{aligned} \langle \psi_j | H_1 | \psi_i \rangle &= h_{ji} \left[ (e^{i\omega t} + e^{-i\omega t}) \cos \phi \right. \\ &\quad \left. + i(e^{i\omega t} - e^{-i\omega t}) \sin \phi \right] \\ &= h_{ji} \left[ e^{i(\omega t + \phi)} + e^{-i(\omega t + \phi)} \right. \\ &\quad \left. + i(e^{i(\omega t + \phi)} - e^{-i(\omega t + \phi)}) \right] \end{aligned}$$

$$\therefore \langle \psi_j | H_1 | \psi_i \rangle = h_{ji} \left[ e^{i(\omega t + \phi)} - e^{-i(\omega t + \phi)} \right]$$

Thus

$$\dot{c}_j = \frac{1}{i\hbar} \sum_i c_i e^{i\omega_{ji}t} \left( e^{i(\omega t + \phi)} + e^{-i(\omega t + \phi)} \right) h_{ji}$$

This is still exact but specialized to our  $H_1 = E_0 \cos \omega t \hat{z} \cdot \underline{d}$  perturbation.

We now give initial condition

$$c_i(t=0) = \begin{cases} 1 & i=k \\ 0 & i \neq k \end{cases}$$

This is the useful initial condition since right after a wave function collapse, we assume the atom



is all in a simple eigenstate

We now make the 1<sup>st</sup> order time dependent perturbation approximation and consider times short enough that for the  $\dot{c}_j$  only the term containing  $c_k$  is significant

$$\dot{c}_j = \frac{1}{i\hbar} \underbrace{c_i}_{=1} e^{i\omega_{ji}t} h_{ji} (e^{i(\omega_i t + \phi)} + e^{-i(\omega_i t + \phi)})$$

where I've replaced

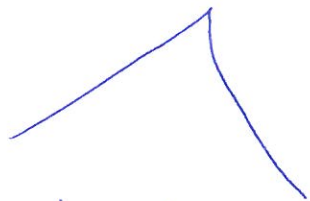
$k$  by  $i$

"Don't you just hate people who use  $k$  as the label for their initial state" - Andy Rooney.

9-34]

We can now integrate to get

$$C_j(t) - S_{ji} = \frac{h_{ji}}{i\hbar} \left[ e^{i\phi} \left( \frac{e^{i(\omega_{ji} + \omega)t} - 1}{i(\omega_{ji} + \omega)} \right) + e^{-i\phi} \left( \frac{e^{i(\omega_{ji} - \omega)t} - 1}{i(\omega_{ji} - \omega)} \right) \right]$$



1 if  $i=j$

0 if  $i \neq j$

We only need to consider the  $i \neq j$  case

~~Again~~ We define

$$x = \omega_{ji} + \omega \quad \text{and} \quad y = \omega_{ji} - \omega$$

$$C_j(t) = \frac{h_{ji}}{\hbar} \left[ e^{i\phi} e^{\frac{x t}{2}} \frac{2i \sin(\frac{x t}{2})}{i x} + e^{-i\phi} e^{\frac{y t}{2}} \frac{2i \sin(\frac{y t}{2})}{i y} \right]$$

since  $\lim_{w \rightarrow 0} \frac{\sin w}{w} = 1$  there is no

divergence for  $x = 0$  ~~or~~

or  $y = 0$

But the terms do get largest

for  $x = 0$

which

can only happen

for emission

when  $w_{ji} < 0$

since

$$x = w_{ji} + w$$

and  $y = 0$

which can only happen

for absorption

when  $w_{ji} > 0$

since

$$y = w_{ji} - w$$

These are the two resonances.

We will integrate over frequency  $\nu$

in a minute and assume

the resonances so dominate

the integral that only

need to keep one term.

The 1<sup>st</sup> if  $w_{ji} < 0$

The 2<sup>nd</sup> if  $w_{ji} > 0$

9-36

The probability of being in state  $j$  itself is effectively (contingent on the integral)

$$|C_j|^2 = \frac{4 |h_{ji}|^2}{\hbar^2} \frac{\sin^2\left(\frac{z\epsilon}{2}\right)}{z^2}$$

$$\text{where } z = \begin{cases} \infty & \text{for } \omega_{ji} = 0 \\ \omega_{ji} & \text{for } \omega_{ji} > 0 \end{cases}$$

$$\text{Now } |h_{ji}|^2 = \frac{1}{4} E_0^2 \left[ \sum_{\omega_{ji}} d_{ji} \right]$$

we will not prove this next result.  
 (The proof is rather tricky and even Mikulas fudges)  
 (p. 9, 87)

$$\frac{c E_0^2}{8\pi} = 4\pi \int r dr$$

where  $\int r = \frac{1}{4\pi} \oint I_r d\Omega$  is the mean intensity.

9-38a)

We now need to do integral

$$\int_0^{\infty} \frac{\sin^2\left(\frac{z t}{2}\right)}{z^2} dz$$

Note  $r = \frac{\omega}{2\pi}$

$$dz = \frac{d\omega}{2\pi}$$

$$\frac{1}{2\pi} \int_0^{\infty} \frac{\sin^2\left(\frac{z t}{2}\right)}{z^2} d\omega$$

Now 
$$z = \begin{cases} \omega_{ji} + \omega & \text{for } \omega_{ji} < 0 \\ \omega_{ji} - \omega & \text{for } \omega_{ji} > 0 \end{cases}$$

Either way we assume the resonance is picked up for  $\omega \gg 0$

$\therefore$  we can extend with negligible error the lower limit to  $-\infty$

Note we are asserting

9-37

that  $E_0^2$  stood for energy  
over a range of frequencies  
and

that we can ~~still~~ integrate  
probability and NOT probability  
amplitude.

— There must be a justification  
but damned if I can find it.

$$P_{ij}(t) = \left| \frac{8\pi}{c^2 h^2} \frac{|\hat{z} \cdot d_{ji}|^2}{(4\pi I_{r_{ij}})} \frac{1}{4\pi} \int_0^\infty \frac{4\pi \sin^2\left(\frac{z}{2}\right)}{z^2} dr \right|$$

Probability  
transferred  
from  $i$  to  $j$

We assume that  $I_r$   
varies so slowly over  
the resonance region  
that it can be taken  
out of the integral and  
evaluated at the transition  
frequency  $\nu_{ij}$

$$dz = \pm du$$

9-38b

and the lower case just  
flips the integration limits.  
So either way

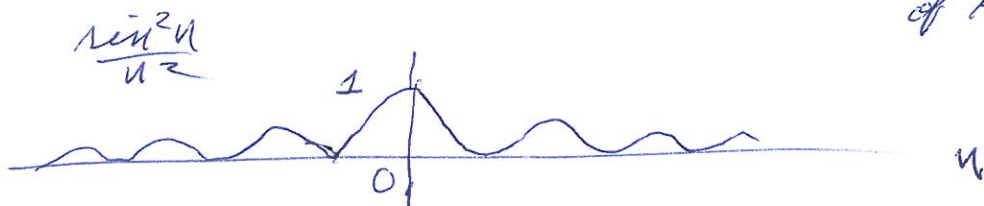
$$\frac{4}{2\pi} \int_{-\infty}^{\infty} \frac{\sin^2\left(\frac{z+t}{2}\right)}{z^2} dz$$

$$= \frac{4}{2\pi} \int_{-\infty}^{\infty} \frac{\sin^2 u}{u^2} du$$

$$= \frac{4t}{2(2\pi)} \int_{-\infty}^{\infty} \frac{\sin^2 u}{u^2} du$$

$$\text{So } P_{ij} = \frac{8\pi}{ch^2} \sqrt{\frac{1}{2} d_{ij}^2} \int_{-\infty}^{\infty} \frac{\sin^2 u}{u^2} du$$

Integrand



$\pi$  a standard  
definite integral  
obtained by calculus  
of residues in the  
complex plane

9-38c

$$P_{ij} = \frac{8\pi^2}{c h^2} \left| \sum d_{ji} \right|^2 \bar{J}_{\nu_{ij}} t$$

Actually we also have to integrate over the line profile  $\bar{\Phi}_{\nu_{ij}'}$

Now treating  $\nu_{ij}'$  as a variable with line center frequency  $\nu_{ij}$

$$\int_{-\infty}^{+\infty} \bar{\Phi}_{\nu_{ij}'} \bar{J}_{\nu_{ij}'} d\nu_{ij}'$$

$$= \bar{J}_{\nu_{ij}} \quad \leftarrow \text{line weighted mean intensity.}$$

Actually the order of these integration eludes my exact understanding; Mihalas p 87 judges as did not realize before.

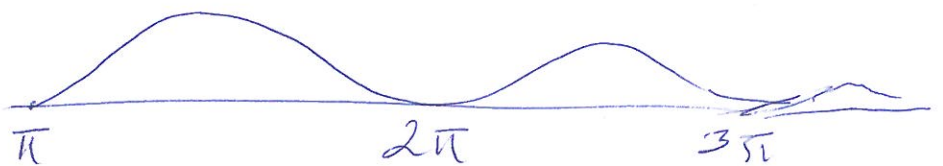


A tricky definite integral.

Can we get an approximate value? — before we look up the answer?

The wings and core can be done separately

Wings



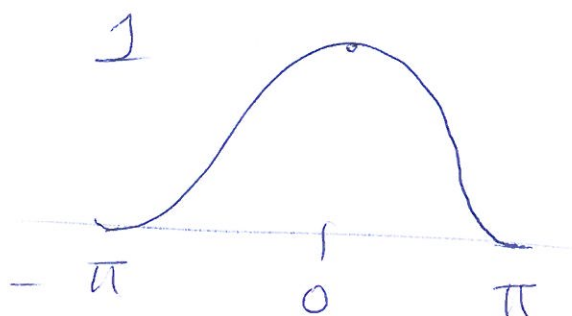
$$\begin{aligned} \text{Numerator average} &= \frac{1}{\pi} \int_0^{\pi} \sin^2 x \, dx \\ &= \frac{1}{\pi} \int_0^{\pi} \frac{1}{2}(1 - \cos 2x) \, dx \\ &= \frac{1}{\pi} \cdot \frac{\pi}{2} = \frac{1}{2} \end{aligned}$$

$$\begin{aligned} \therefore I_{\text{wings}} &\cong 2 \cdot \frac{1}{2} \int_{\pi}^{\infty} \frac{1}{x^2} \, dx \\ &= -\frac{1}{x} \Big|_{\pi}^{\infty} = \frac{1}{\pi} \cong \frac{1}{3} \\ &= \pi \left( \frac{1}{\pi^2} \right) \cong \pi (,101321) \end{aligned}$$

9-40)

Cone

Hm, Tricky.



Expanding about

$$x=0$$

$$\frac{\sin^2 x}{x^2} \approx \frac{(x - \frac{1}{6}x^3)^2}{x^2}$$

$$= 1 - \frac{1}{3}x^2$$

to 2<sup>nd</sup> order  
in small  $x$ .

but  $x=\pi$  is NOT small  $x$ .

~~Expanding about~~  
Numerator  
about

$$\frac{(x-\pi)^2}{x^2}$$

to 2<sup>nd</sup> order  
in  $(x-\pi)$ .

Expand  
about  
 $x=\pi$

~~$$\frac{\Delta x^2}{\pi + \Delta}$$~~

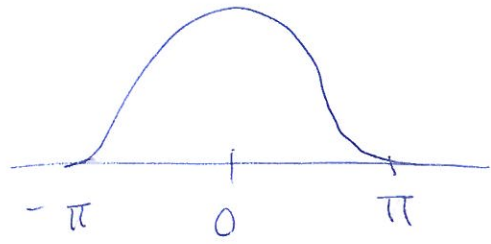
$$\frac{(x-\pi)^2}{(\pi + (x-\pi))^2}$$

$$\approx \frac{(x-\pi)^2}{\pi^2} \text{ to 2<sup>nd</sup> order in } (x-\pi)$$

$$= \left(\frac{x}{\pi} - 1\right)^2$$

Well these expansion  
do NOT suggest any really  
good approximation for the whole  
interval  $[-\pi, \pi]$ .

but



looks sort of like a ~~cos~~  $\cos^2(\frac{1}{2}x)$  doesn't + it.

$$\cos^2(\frac{1}{2}x) = \left[ 1 - (\frac{1}{2}x)^2 \right]^2 = 1 - \frac{1}{2}x^2$$

Too big  
(u)  
to ~~lowest~~  
2<sup>nd</sup> order  
about  $x=0$

$$\left[ 0 + (x-\pi) \left( -\sin(\frac{x}{2}) \Big|_{\pi} \frac{1}{2} \right) \right]^2$$

$$= \frac{(x-\pi)^2}{4}$$

Too  
small  
by  
a lot

to ~~lowest~~  
~~fit~~ or  
2<sup>nd</sup> order  
about  
 $x=\pi$

So  $\cos^2(\frac{1}{2}x)$  does NOT agree to 2<sup>nd</sup> order at  $x=0, x=\pi$

but it agrees to 0<sup>th</sup> and 1<sup>st</sup> order

and it is a smooth interpolation everywhere.

9-42

$$\begin{aligned}
 I_{\text{cone}} &= 2 \int_0^{\pi} \cos^2\left(\frac{x}{2}\right) dx \\
 &= 2 \cdot \frac{1}{2} \int_0^{\pi} (1 + \cos x) dx \\
 &= \int_0^{\pi} (1 + \cos x) dx \\
 &= (x + \sin x) \Big|_0^{\pi} \\
 &= \pi
 \end{aligned}$$

Well not bad, But NOT good  
 since whole ~~was~~ integral

$$\int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} dx = \pi \quad \text{actually.}$$

Not so hard,  
 One just has to

bite  
 the  
 bullet  
 and  
 do it,

I guess one has to expand  
 about ~~the~~  $x=0$  and  $x=\pi$   
 to the next order

$$\begin{aligned}
 \frac{\sin^2 x}{x^2} &= \frac{(x - \frac{1}{6}x^3 + \frac{1}{120}x^5)^2}{x^2} \\
 &= \frac{(x^2 - \frac{1}{3}x^4 + x^6(\frac{1}{30} + \frac{1}{120}))}{x^2}
 \end{aligned}$$

$$\begin{aligned}
 &\frac{1}{30} + \frac{1}{120} \\
 &= \frac{1}{60}(\frac{1}{6} + \frac{1}{10}) \\
 &= \frac{1}{60} \cdot \frac{16}{60} \\
 &= \frac{8}{180} \\
 &= \frac{2}{45}
 \end{aligned}$$

~~Don't~~  
~~ponder~~  
~~this~~  
 One  
 hopes for  
 a trick, but  
~~some~~ sometimes  
 there is no trick.

But series should converge in  $x$  converges absolutely.

$$= 1 - \frac{1}{3}x^2 + \frac{2}{45}x^4$$

Now about  $x = \pi$ , 
$$\frac{(x-\pi) - \frac{1}{6}(x-\pi)^3}{(\pi + (x-\pi))^2}$$

$$= \frac{(x-\pi)^2}{\pi^2(1 + \frac{x-\pi}{\pi})^2}$$

$$\approx \frac{(x-\pi)^2}{\pi^2} (1 - 2\frac{x-\pi}{\pi})$$

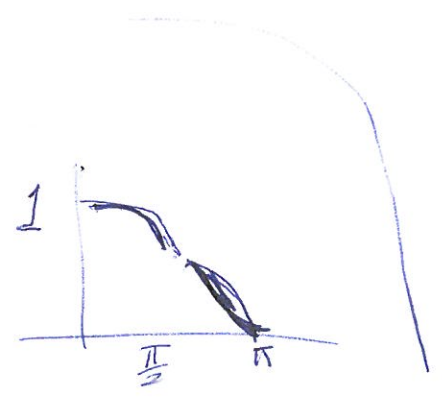
$$= (\frac{x}{\pi} - 1)^2 - 2(\frac{x}{\pi} - 1)^3$$

$$= \frac{(x-\pi)^2}{\pi^2} \frac{(1 - \frac{1}{6}(x-\pi)^2)^2}{(1 + \frac{(x-\pi)}{\pi})^2}$$

$$= (\frac{x}{\pi} - 1)^2 (1 - 2(\frac{x}{\pi} - 1))$$

$$= (\frac{x}{\pi} - 1)^2 - 2(\frac{x}{\pi} - 1)^3$$

let  $y = \frac{x}{\pi} - 1$   
 $dy = \frac{dx}{\pi}$



$$\int_{\text{core}} \approx 2 \left[ \int_0^{\pi/2} (1 - \frac{1}{3}x^2 + \frac{2x^4}{45}) dx + \int_{\pi/2}^{\pi} \left[ (\frac{x}{\pi} - 1)^2 - 2(\frac{x}{\pi} - 1)^3 \right] dx \right]$$

$$= 2 \left[ \left( x - \frac{x^3}{9} + \frac{2x^5}{225} \right) \Big|_0^{\pi/2} + \pi \int_{-\frac{1}{2}}^0 (y^2 - 2y^3) dy \right]$$

9-44

$$= 2 \left[ \frac{\pi}{2} - \frac{\pi^3}{72} + \frac{2\pi^4}{8 \cdot 95.5} \right]$$

$$+ 2\pi \left[ \frac{y^3}{3} - \frac{2y^4}{4} \right]_{-\frac{1}{2}}^0$$

$$= \pi \left[ 1 - \frac{\pi^2}{36} + \frac{\pi^4}{8 \cdot 95.5} \right]$$

$$+ 2\pi \left[ \frac{1}{24} + \frac{1}{32} \right]$$

$$= \pi \left[ 1 - \frac{\pi^2}{36} + \frac{\pi^4}{1800} \right]$$

$$+ \pi \left[ \frac{7}{48} \right]$$

$$= \pi (,92579)$$

$$= 2,908967$$

$$2 \cdot \left( \frac{1}{24} + \frac{1}{32} \right)$$

$$= \frac{1}{12} + \frac{1}{16}$$

$$~~= \frac{28}{28}~~$$

$$= \frac{1}{4} \left( \frac{1}{3} + \frac{1}{4} \right)$$

$$= \frac{1}{4} \cdot \frac{7}{12}$$

$$= \frac{7}{48}$$

$$I_{\text{core}} + I_{\text{wein}} \approx \pi (,92579) + \frac{1}{4}$$

$$= 1,027 \pi$$

which is NOT bad

The exact definite

9-45

integral follows

from contour integration

(AKA calculus  
of residues)

in complex plane

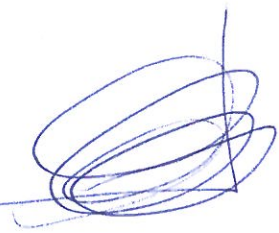
$$\int_{-\infty}^{\infty} \frac{e^{ix}}{x^2} dx = \pi$$

Art - 364

Well this is more  
work than it was worth.

But at least now we  
know that the core  
is very dominant  
and is ~~of~~ about 90%  
of the integral.

This means  
~~approx~~  
approximation  
far  
out in  
the wings  
are  
negligible

There is also a problem   
in QMP-17-00100  
that shows

$$I_{\text{core}} = 2.83630, \text{ and so the} \\ = \pi(.9028)$$

9-46

I want ~~to~~  $\frac{1}{\pi}$  by a bit

$$\int_0^\infty |C_n|^2 dr = \frac{E_0^2}{h^2} \left| \int_{-\infty}^{\infty} \hat{z} \cdot d_{jk} \right|^2 \frac{1}{2} + \pi$$

We can't prove this here  
but

(Mihalas  
v. 8)

$$\frac{E_0^2}{8\pi} = \frac{4\pi}{c} \bar{J}_v$$

energy density (energy per volume)  
per unit frequency.

Mean  
intensity  
= angle  
averaged  
intensity.

$$\bar{J}_v = \int_0^\infty \int_0^\infty \int_0^\infty \frac{J_v}{4\pi} d\Omega dv$$

$$= \int_0^\infty \int_0^\infty J_v J_v d\Omega$$

Line Profile weighted mean intensity  
(or averaged)



The rate of probability transfer is

9-47

$$R = \frac{P_{ij}}{t} = \frac{8\pi^2}{ch^2} |\hat{z} \cdot d_{ji}|$$

which is a constant rate — as long as 1<sup>st</sup> order perturbation theory is valid.

### Big Bad Constant

I think we've got to guess, because the result is unspeakable it seems

Here's where the magic of wave function collapse is invoked — apparently without even breathing the word in textbooks

While the Sch. eq. evolution is still in the 1<sup>st</sup> order perturbation regime,

9-48)

a. collapse happens at time  $t$   
— some perturbation unspecified — unspeakable I guess

Then after this first collapse

$$P_i^{(1)} = 1 - R t_1, \quad P_j^{(2)} = R t$$

If the atom is back in state  $i$ ,  
the clock is reset and Sch. eqn.  
evolution proceeds until  
collapse 2

$$P_i^{(2)} = P_i^{(1)} (1 - R t_2)$$

and so on

$$P_i^{(n)} = P_i^{(n-1)} (1 - R t_n)$$

$$\therefore \Delta P_i^{(n)} = P_i^{(n)} - P_i^{(n-1)} = - P_i^{(n-1)} R t_n$$

The series of collapses is so frequent  
that we can go to the continuum limit

$$dP_i = - P_i R dt$$

which is a simple DE

with solution

$$P_i(t) = e^{-t/\tau}$$

where  $\tau = \frac{1}{R}$

$\tau$  is the e-folding time.

The half-life is

$$\frac{1}{2} = e^{-t_{1/2}/\tau}$$

$$\ln 2 = t_{1/2}/\tau$$

$$t_{1/2} = \tau \ln 2 \approx .6931 \tau$$

$P_j = 1 - e^{-t/\tau}$  is the probability of being in state  $j$



9-49

This solution assumes no other process going on.

There are if stimulated emission or absorption is occurring

then, no is the reverse process

9-50

So for very short times

$R$  is the rate of

Probability flow  
from  $i \rightarrow j$ .

But it can also  
be understood as

the probability per unit  
time of a transition

$\therefore$  in  $dt$

$$R dt = \frac{dt}{\tau} \text{ is}$$

the probability of a transition  
from state  $i$  to state  $j$ .

If we started with  $N_{oi}$  atoms  
in state  $i$ , then

$$N_i = N_{oi} e^{-t/\tau} \text{ after}$$

time  $t$  if no other process occurred.

and view it as a constant

In sense so it seems in most cases ~~we~~ collapse happened in the 1st order perturbation range.

To make the point a bit more concrete,

Obj of exp  
done  
when a  
state k

Say we started with an ensemble of  $N_0$  atoms in state k.

Some transition to state j and after while we have  $N$

Was ~~keep~~ replacing its after a transition ?

~~$dN = -N R dt$~~

Mean Number of reculations in population in state k

Probability + transition

$N = N_0 e^{-Rt} = N_0 e^{-t/\tau}$

9-52

So the nature of radiative transitions as determined by 1<sup>st</sup> order perturbation theory and wave function collapse thrown in as a fudge factor gives

$$R = \frac{1}{\tau} = \frac{\delta \pi^2}{h^2 c} \sum_{j \neq i} d_{ji} \int \overline{J_{r,ij}}$$

where I've starting calling the initial state  $i$   
I don't know just note people who call the initial state  $k$  — Andy Rooney

as the probability per unit time of a transition.

Unless we have polarized light and atoms all in one orientation, we should average over all orientation.

953

$$\frac{1}{4\pi} \int |\hat{z} \cdot \underline{d}_{ji}|^2 d\Omega$$

between  $\hat{z}$  and  $\underline{d}_{ji}$

$$= |d_{ji}|^2 \frac{1}{2} \int_{-1}^1 \mu^2 d\mu$$

where  $\mu = \cos\theta$

$$\frac{1}{2} \left. \frac{\mu^3}{3} \right|_{-1}^1 = \frac{1}{3}$$

$$= \frac{1}{3} d_{ji}^2 \quad \text{defining } d_{ji}^2 = |d_{ji}|^2$$

$$R = \frac{8\pi^2 d_{ji}^2}{3\hbar^2 c} \bar{J}_{r_{ij}}$$

Now if we look back to p. 9-5, 9-6 and integrated over angle and frequency and divided by  $\hbar\nu_{ij}$

$$\frac{A}{\hbar\nu_{ij}} = n_i B_{ij} \bar{J}_{r_{ij}}, \quad \frac{R_{stim}}{\hbar\nu_{ij}} = n_j B_{ji} \bar{J}_r$$

9-54

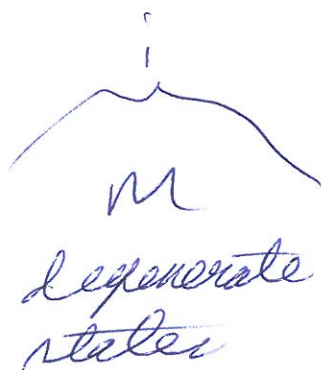
We see that the Einstein B coefficient is

$$B_{ij} = \frac{8\pi^2 \nu_{ji}^2}{3hc^2} \quad (n_i - n_j)$$

for either ~~or~~ absorptions

or emissions,  
Probability of transition per ~~unit~~ time per ~~unit~~  $T_{ij}$ .

Now in fact many lines (all really)  
are transitions between  
degenerate states.



→ occupation  
is usually  
assumed to equal  
- true in TB and  
because of minor  
perturbations nearly  
always true it seems



To get the full ~~transitions~~ 9-55

$B_{ij}$  then, one ~~sums~~  
sums over final states  
and averages over  
initial states.

All  
final  
states  
possible.  
But each  
atom is only  
in one  
initial state

$$B_{ij} = \frac{1}{g_i} \sum_{m, n} B_{mn}$$

and  $B_{ji} = \frac{1}{g_j} \sum_{n, m} B_{nm}$

and so

$$g_i B_{ij} = g_j B_{ji}$$

Thus QM with a ~~q~~ QM atom  
and classical electromagnetic  
field gives us one  
Einstein relation. (see p. 9-11)

9-56

The other one (only for  $E_j > E_i$ )

Typical  
A values  
for strong  
lines  
 $\sim 10^{+8} \text{ s}^{-1}$

$$A_{ji} = \frac{2\pi\nu_{ij}^3}{c^2} B_{ji}$$

we cannot  
derive  
without some  
 $\nabla E \nabla$   
(not full story,  
I think is  
needed)

$$A_{Ly\alpha} = 4.699 \times 10^8 \text{ s}^{-1}$$

$$A_{H\alpha} = 4.410 \times 10^7 \text{ s}^{-1}$$

$$\therefore \tau = \frac{1}{A} \approx 10^{-8} \text{ s}$$

This  
has  
units  
of  $\overline{\nu_{ij}}$

and replaces

$$\text{it, Recall } n_i B_{ij} = n_j B_{ji} + A_{ji} \text{ from p. 9-10}$$

spontaneous probability  
of a downward transition  
per unit time.

$$R_{\text{spont}} = A_{ji}$$

$$\tau = \frac{1}{A_{ji}}$$

So if you have a set  
of  $N_0$  atoms that initially

for  
strong line  
- longer  
for  
weak  
lines.

all in state  $j$

and there is no significant radiation field. Then only

$$N_j = N_{j_0} e^{-t/\tau}$$

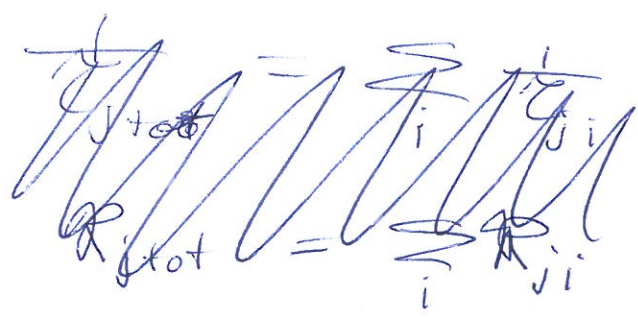
spontaneous ~~decay~~ transition occurs.

$$N_j = N_{j_0} (1 - e^{-t/\tau})$$

In general, there will be more than one lower level to make transitions to.

$$\begin{aligned} \therefore dN_j &= - \left( \sum_i R_{ji} dt \right) N_j \\ &= - R_{j+tot} dt N_j \end{aligned}$$

$$N_j = N_{j_0} e^{-t/\tau_{j+tot}}$$



$$R_{j+tot} = \sum_i R_{ji}$$

$$\tau_{j+tot} = \frac{1}{R_{j+tot}}$$

9-58

On the other hand

$$dN_i = R_{ji} N_j dt$$

$$= R_{ji} N_{j0} e^{-t/\tau_{jtot}} dt$$

$$N_i = R_{ji} \tau_{jtot} N_{j0} (1 - e^{-t/\tau_{jtot}})$$

$$= \frac{R_{ji}}{\sum_k R_{jk}} N_{j0} (1 - e^{-t/\tau_{jtot}})$$

$$N_i(t \rightarrow \infty) = \frac{R_{ji}}{R_{jtot}} N_{j0}$$

branching ratio for a pure spontaneous decay.

Somewhat obviously this pure spontaneous transition situation is rather analogous to ~~the~~ radioactive nuclear decay.

The QM proof ~~is~~ is probably analogous. But that's just a guess.

I should add  
that all these results  
for radiative transitions  
are very accurate  
despite  
all the approximations  
and handwaving.

I suspect a real expert  
could make the proofs  
show why the results are  
~~as accurate~~ pretty accurate  
— but ultimately the  
justification is agreement  
with experiment.

9-60

But there are cases where one has to be more careful I believe.

Also if  $d_{ji} = 0$  as it does for certain transitions, then one must look at weaker ~~order~~ processes.

Called forbidden transitions, some symmetry ~~property~~ or angular momentum property dictates this

Transitions with  $d_{ji} \neq 0$  are electric dipole transitions

There are also electric quadrupole and magnetic dipole transitions.

↳ usually too weak to count if  $d_{ji} \neq 0$ , but otherwise become important especially for low-lying levels which often have no allowed transitions to the ground state.