

# 量子力学

# Quantum mechanics

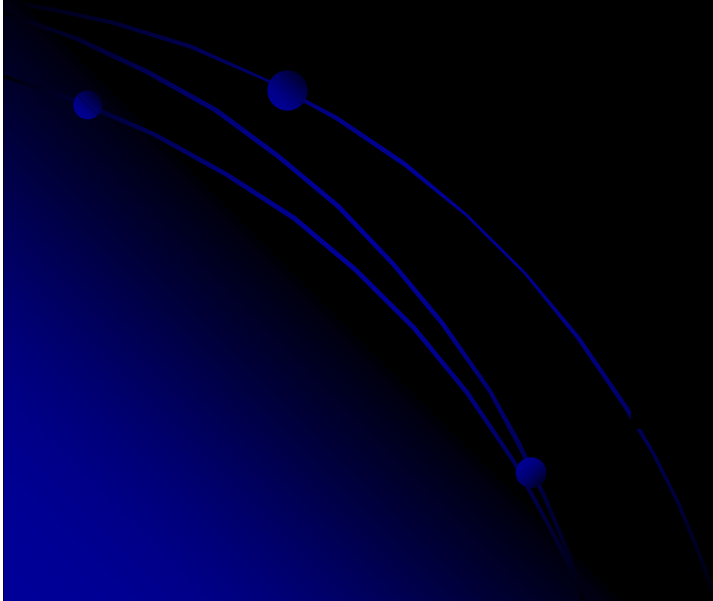
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**Chapter 9**

**Time-dependent  
perturbation theory**





## Chapter 9

### Time-dependent perturbation theory

9.1 Two-level systems

9.2 Emission and absorption  
of radiation

9.3 Spontaneous emission



## 9.1 Two-level systems

## 9.2 Emission and absorption of radiation

## 9.3 Spontaneous emission




# 9.1 Two-level systems

Suppose that there are just two states of the system. They are eigenstates of the unperturbed Hamiltonian, and they are eigenstates orthonormal:

Any state can be expressed as a linear combination of them

In the absence of any perturbation, each component evolves with its characteristic exponential factor:

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## 9.1.1 The perturbed system

Now suppose we turn on a time-dependent perturbation, then the wave function can be expressed as follows:

If the particle started out in the state

We solve for

where

So, we find that

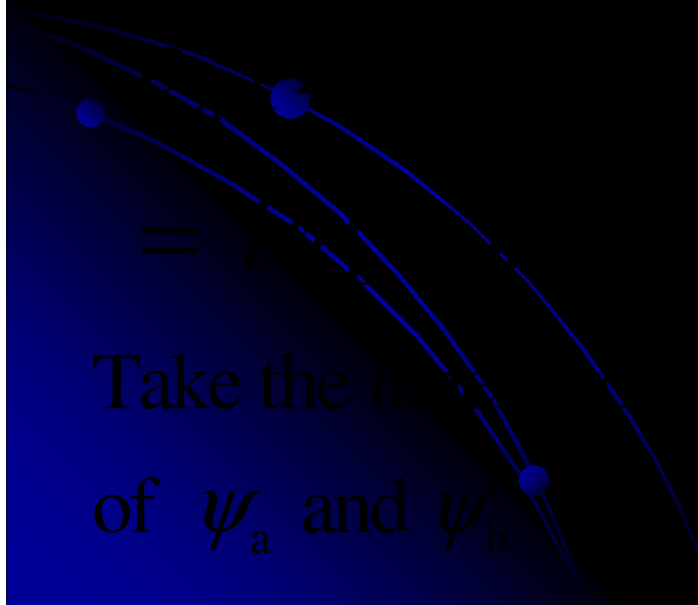




The first two terms on the left cancel the last two terms on the right, and hence

$$= \psi_a$$

Take the inner product  
of  $\psi_a$  and  $\psi_b$





For short, we define

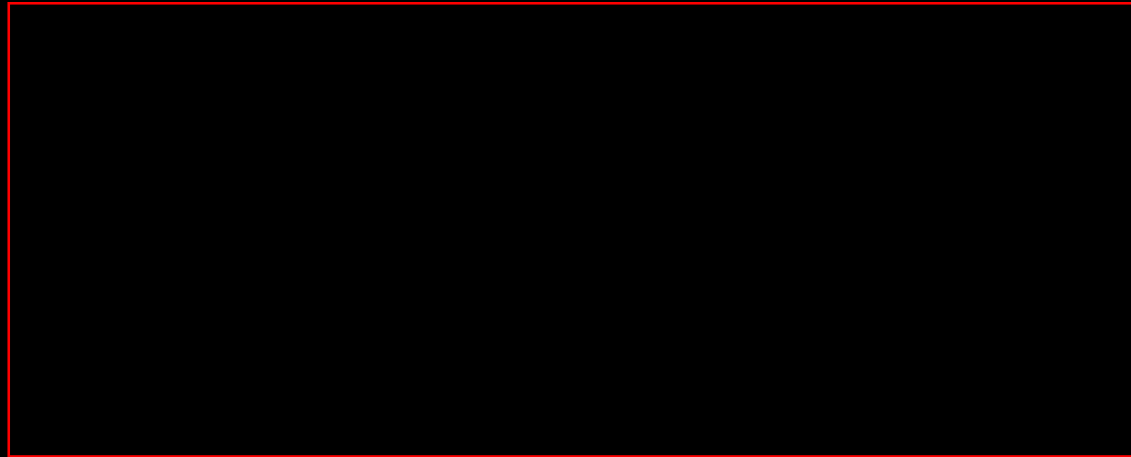
Typically

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In that case the equations simplify



(1)

We'll assume





## 9.1.2 Time-Dependent Perturbation Theory

$$c_a(0) = 1, \quad c_b(0) = 0.$$

Zeroth Order:

To calculate  $c_a^{(0)}$  and  $c_b^{(0)}$   
on the right side



## First Order:

$$\frac{dc_a}{dt} = 0 \Rightarrow c_a^{(1)} = 1;$$

$$\frac{dc_b}{dt} = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} \Rightarrow c_b^{(1)} = -\frac{i}{\hbar} \int_0^t H'_{ba}(t') e^{i\omega_0 t'} dt'$$

Now we insert *these* expressions on the right to obtain the second-order approximation:

## Second-Order:

$$\frac{dc_a}{dt} = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} \left( \frac{i}{\hbar} \right) \int_0^t H'_{ba}(t'') e^{i\omega_0 t''} dt'' \Rightarrow$$

$$c_a^{(2)}(t) = 1 - \frac{1}{\hbar^2} \int_0^t H'_{ab}(t') e^{-i\omega_0 t'} \left[ \int_0^{t'} H'_{ba}(t'') e^{i\omega_0 t''} dt'' \right] dt'$$



# Notes:

Notice that in my notation  $c_a^{(2)}(t)$  includes the zeroth order term; the second-order correction would be the integral term alone.

In principle, we could continue this ritual indefinitely, always inserting the  $n^{\text{th}}$  –order approximation into the right side of Equation (1) and solving for the  $(n+1)^{\text{th}}$  –order. Notice that  $c_a$  is modified in every *even* order, and  $c_b$  in every *odd* order.



### 9.1.3 Sinusoidal Perturbation

Suppose the perturbation has sinusoidal time dependence:

$$H'(\vec{r}, t) = V(\vec{r}) \cos(\omega t)$$

so that

$$H'_{ab} = V_{ab} \cos(\omega t),$$

where

$$V_{ab} = \langle \psi_a | V | \psi_b \rangle$$

To first order we have

$$\begin{aligned} c_b(t) &\cong -\frac{i}{\hbar} V_{ba} \int_0^t \cos(\omega t') e^{i\omega_0 t'} dt' \\ &= -\frac{iV_{ba}}{2\hbar} \int_0^t \left[ e^{i(\omega_0 + \omega)t'} + e^{i(\omega_0 - \omega)t'} \right] dt' \\ &= -\frac{V_{ba}}{2\hbar} \left[ \frac{e^{i(\omega_0 + \omega)t} - 1}{\omega_0 + \omega} + \frac{e^{i(\omega_0 - \omega)t} - 1}{\omega_0 - \omega} \right] \end{aligned}$$

This is the answer, but it is a little cumbersome to work with.



## Dropping the first term:

We assume  $\omega_0 + \omega \gg |\omega_0 - \omega|$

$$\begin{aligned}c_b(t) &\cong -\frac{V_{ba}}{2\hbar} \frac{e^{i(\omega_0 - \omega)t/2}}{\omega_0 - \omega} \left[ e^{i(\omega_0 - \omega)t/2} - e^{-i(\omega_0 - \omega)t/2} \right] \\ &= -i \frac{V_{ba}}{\hbar} \frac{\sin[(\omega_0 - \omega)t/2]}{\omega_0 - \omega} e^{i(\omega_0 - \omega)t/2}\end{aligned}$$

The **transition probability**——the probability that a particle which started out in the state  $\psi_a$  will be found, at time, in the state  $\psi_b$  :

$$P_{a \rightarrow b}(t) = |c_b(t)|^2 \cong \frac{|V_{ab}|^2}{\hbar^2} \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} \quad (2)$$



As a function of time, the transition probability oscillates sinusoidally.

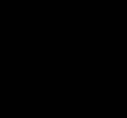


Fig. 1 Transition probability as a function of time,  
for a sinusoidal perturbation



The probability of a transition is greatest when the driving frequency is close to the “natural” frequency

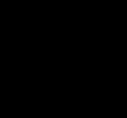


Fig. 2 Transition probability as a function of driving frequency





## 9.2 Emission and absorption of radiation

### 9.2.1 Electromagnetic Waves

An atom, in the presence of a passing light wave, responds primarily to the electric component. If the wavelength is long, we can ignore the spatial variation in the field; the atom is exposed to a sinusoidally oscillating electric field

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

The perturbing Hamiltonian is

$$H' = -qE_0 z \cos(\omega t)$$

where  $q$  is the charge of the electron. Evidently

$$H'_{ba} = -\wp E_0 \cos(\omega t), \quad \text{where } \wp = q \langle \psi_b | z | \psi_a \rangle$$

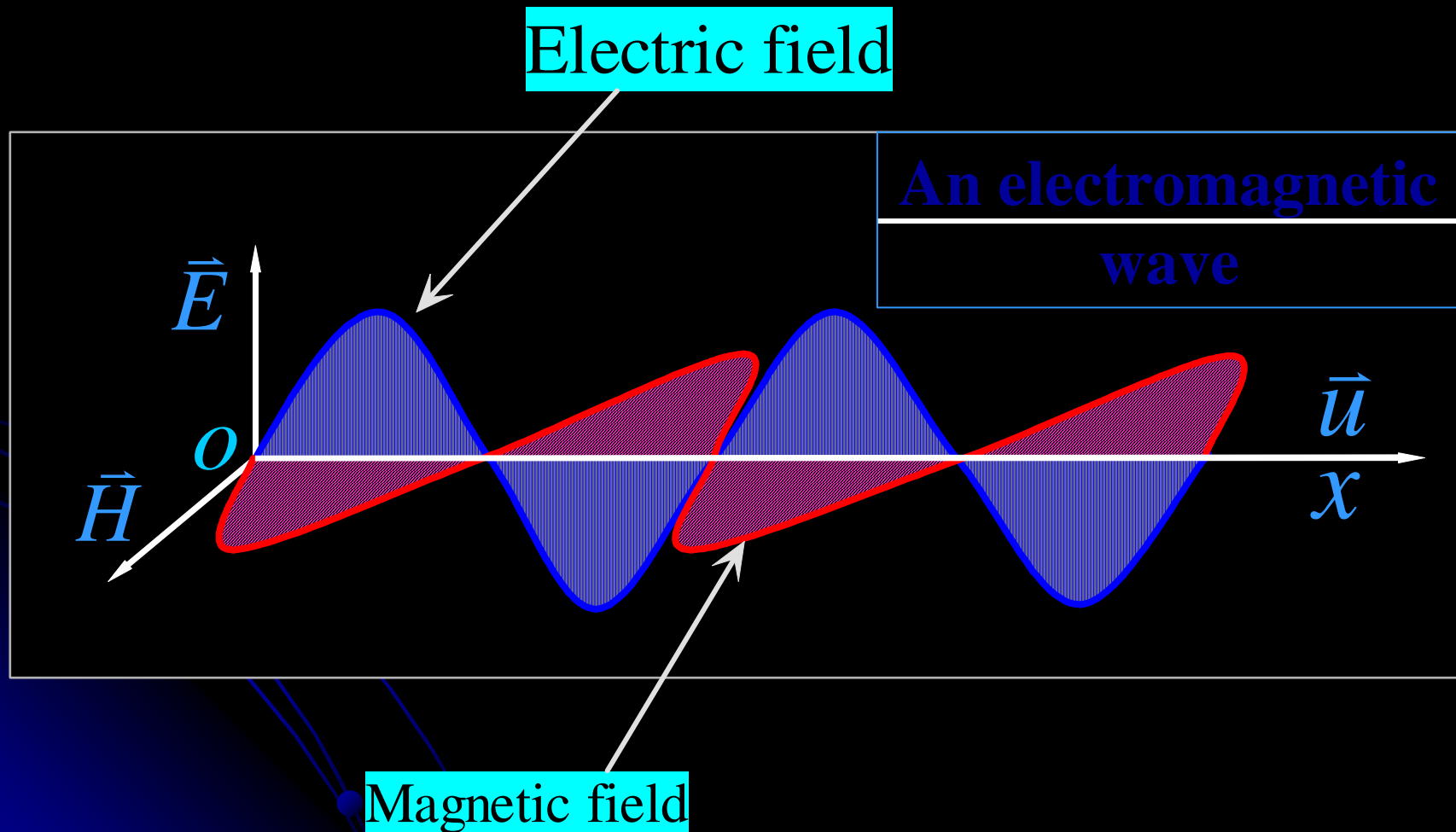


## Chapter 9 TIME-DEPENDENT PERTURBATION THEORY

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An electromagnetic wave consists of transverse oscillating electric and magnetic fields.





Typically,  $\psi$  is an even or odd function of  $z$ ; in either case  $z|\psi|^2$  is *odd*, and integrates to zero.

This licenses our usual assumption that the *diagonal* matrix elements of  $H'$  vanish. Thus the interaction of light with matter is governed

by precisely the kind of oscillatory perturbation with

$$V_{ba} = -\mathcal{E} E_0$$



## 9.2.2 Absorption, Stimulated Emission, and Spontaneous Emission

If an atom starts out in the "lower" state  $\psi_a$ , and you shine a polarized monochromatic beam of light on it, the probability of a transition to the "upper" state  $\psi_b$  is given by Equation (2), which takes the form

$$P_{a \rightarrow b}(t) = \left( \frac{|\langle \psi_b | E_0 | \psi_a \rangle|^2}{\hbar^2} \right) \frac{\sin^2[(\omega_0 - \omega)t / 2]}{(\omega_0 - \omega)^2}$$

Of course, the probability of a transition *down* to to the *lower* level:

$$P_{b \rightarrow a}(t) = \left( \frac{|\langle \psi_a | E_0 | \psi_b \rangle|^2}{\hbar^2} \right) \frac{\sin^2[(\omega_0 - \omega)t / 2]}{(\omega_0 - \omega)^2}$$

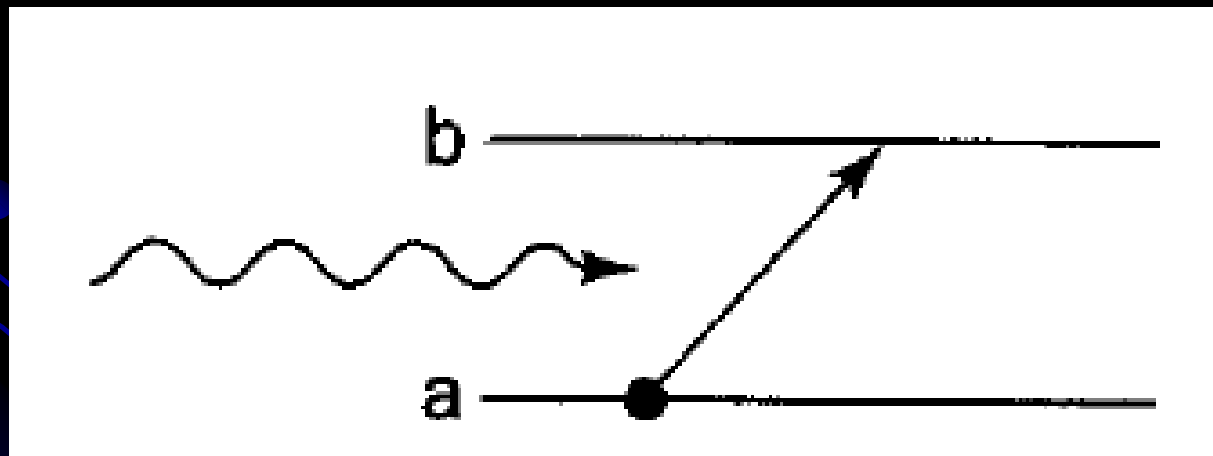


Three ways in which light interacts with atoms:

(a) Absorption

In this process, the atom absorbs energy  $E_b - E_a = \hbar\omega_0$  from the electromagnetic field.

we say that it has "absorbed a photon"

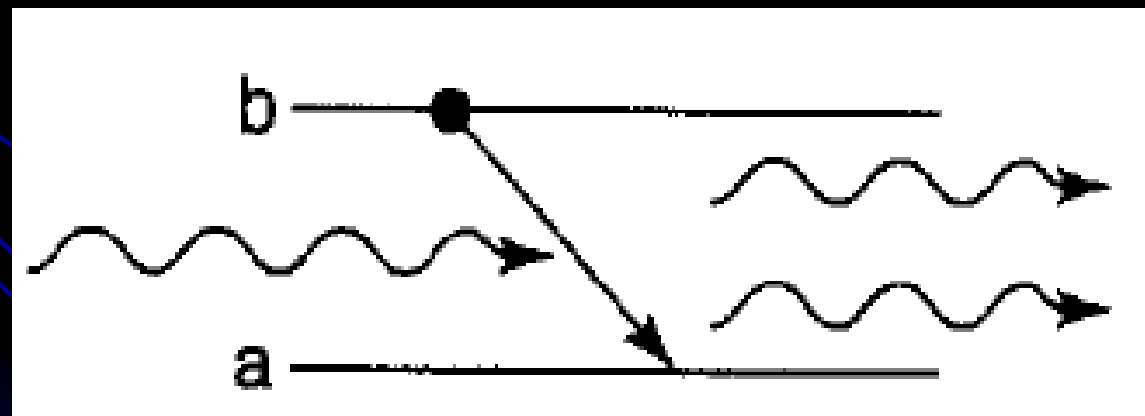


(a) Absorption



## (b) Stimulated emission

If the particle is in the upper state, and you shine light on it, it can make a transition to the lower state, and in fact the probability of such a transition is exactly the same as for a transition upward from the lower state. This process, which was first discovered by Einstein, is called **stimulated emission**.

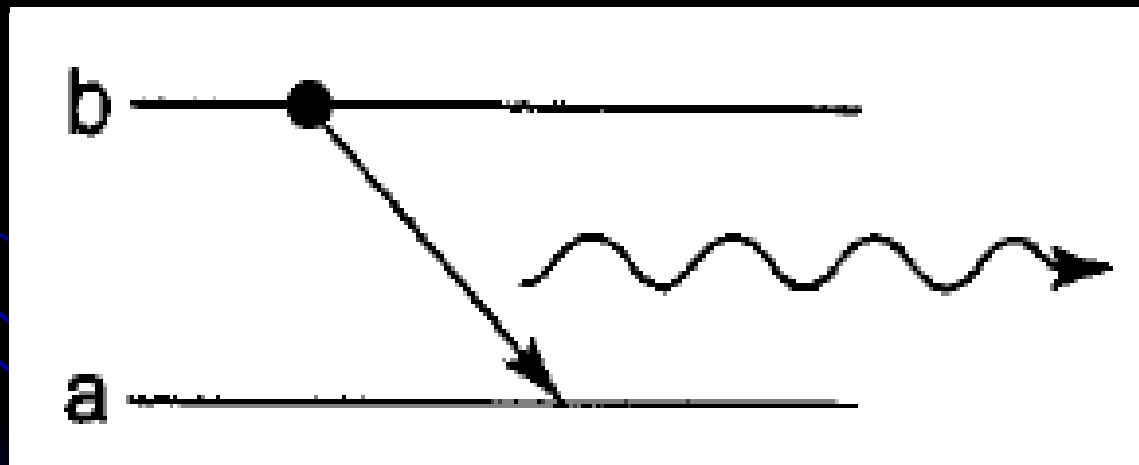


(b) Stimulated emission



## (c) Spontaneous emission

If an atom in the excited state makes a transition downward, with the release of a photon but *without* any applied electromagnetic field to initiate the process. This process is called **spontaneous emission**.



(c) Spontaneous emission





## 9.2.3 Incoherent Perturbation

The energy density in an electromagnetic wave is

$$u = \frac{\epsilon_0}{2} E_0^2$$

where  $E$  is the amplitude of the electric field. So the transition probability is proportional to the energy density of the fields:

$$P_{a \rightarrow b}(t) = \frac{2u}{\epsilon_0 \hbar^2} |\mathcal{D}|^2 \frac{\sin^2[(\omega_0 - \omega)t / 2]}{(\omega_0 - \omega)^2}$$

This is for monochromatic perturbation, consisting of a single frequency  $\omega$ .



In many applications the system is exposed to electromagnetic waves at a whole range of frequencies; in that case  $u \rightarrow \rho(\omega)d\omega$  and the net transition probability takes the form of an integral:

$$P_{a \rightarrow b}(t) = \frac{2u}{\epsilon_0 \hbar^2} |\mathcal{D}|^2 \int_0^\infty \rho(\omega) \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} d\omega$$

replace  $\rho(\omega)$  by  $\rho(\omega_0)$  and take it outside the integral, we get

$$P_{a \rightarrow b}(t) \cong \frac{2|\mathcal{D}|^2}{\epsilon_0 \hbar^2} \rho(\omega_0) \int_0^\infty \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} d\omega$$

Changing variables to  $x \equiv (\omega_0 - \omega)/2$ , extending the limits of integration to  $x = \pm\infty$ , and looking up the definite integral

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



we find

$$P_{a \rightarrow b}(t) \cong \frac{2|\mathcal{D}|^2}{\epsilon_0 \hbar^2} \rho(\omega_0) t$$

This time the transition probability is proportional to  $t$ .  
When we hit the system with an incoherent spread of frequencies. The **transition rate** is now a *constant* :

$$R_{b \rightarrow a} = \frac{\pi}{\epsilon_0 \hbar^2} |\mathcal{D}|^2 \rho(\omega_0)$$

**Note**: the perturbing wave is coming in along the  $x$ -direction and polarized in the  $z$ -direction.



But we shall be interested in the case of an atom bathed in radiation coming from *all* direction, and with *all* possible polarizations. What we need, in place of  $|\mathcal{P}|^2$ , is the *average* of  $|\hat{n} \cdot \mathcal{P}|^2$ , where

$$\mathcal{P} \equiv q \langle \psi_b | \vec{r} | \psi_a \rangle$$

and the average is over both polarizations ( $\hat{n}$ ) and over all incident direction. This averaging can be carried out as follows:



## Polarization:

For propagation in the z-direction, the two possible polarizations are  $\hat{i}$  and  $\hat{j}$ , so the polarization average is

$$\begin{aligned}(\hat{n} \cdot \mathcal{E})_p^2 &= \frac{1}{2} [(\hat{i} \cdot \mathcal{E})^2 + (\hat{j} \cdot \mathcal{E})^2] \\ &= \frac{1}{2} (\mathcal{E}_x^2 + \mathcal{E}_y^2) = \frac{1}{2} \mathcal{E}^2 \sin^2 \theta\end{aligned}$$

where  $\theta$  is the angle between  $\mathcal{E}$  and the direction of propagation.



## Propagation direction:

Now let's set polar axis along  $\mathcal{E}$  and integrate over all propagation directions to get the polarization-propagation average:

$$\begin{aligned}(\hat{n} \cdot \mathcal{E})_{pp}^2 &= \frac{1}{4\pi} \int \left[ \frac{1}{2} \mathcal{E}^2 \sin^2 \theta \right] \sin \theta d\theta d\phi \\ &= \frac{\mathcal{E}^2}{4} \int_0^\pi \sin^3 \theta d\theta = \frac{\mathcal{E}^2}{3}\end{aligned}$$

So the transition rate for stimulated emission from state  $b$  to state  $a$ , under the influence of incoherent, unpolarized light incident from all directions, is



So the transition rate for stimulated emission from state  $b$  to state  $a$ , under the influence of incoherent, unpolarized light incident from all directions, is

$$R_{b \rightarrow a} = \frac{\pi}{3\epsilon_0 \hbar^2} |\wp|^2 \rho(\omega_0)$$

Where  $\wp$  is the matrix element of the electric dipole moment between the two states and  $\rho(\omega_0)$  is the energy density in the fields, per unit frequency, evaluated at  $\omega_0 = (E_b - E_a) / \hbar$ .



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## 9.3 Spontaneous emission

### 9.3.1 Einstein's A and B coefficients

Picture a container of atoms,  $N_a$  of them in the lower state ( $\psi_a$ ), and  $N_b$  of them in the upper state ( $\psi_b$ ).

Let  $A$  be the spontaneous emission rate, so that the number of particle leaving the upper state by this

process, per unit time, is  $N_b A$ . The transition rate for stimulated emission is proportional to the energy density of the electromagnetic field---call it  $B_{ba} \rho(\omega_0)$ .

The number of particles leaving the upper state by this mechanism, per unit time, is  $N_b B_{ba} \rho(\omega_0)$ .



The absorption rate is likewise proportional to  $\rho(\omega_0)$ ---call it  $B_{ab}\rho(\omega_0)$ ; The number of particles per unit joining the upper level is therefore  $N_a B_{ab}\rho(\omega_0)$ . All told, then,

$$\frac{dN_b}{dt} = -N_b A - N_b B_{ba}\rho(\omega_0) + N_a B_{ab}\rho(\omega_0)$$

Suppose that these atoms are in thermal equilibrium with the ambient field, so that the number of particle in each level is *constant*.



In that case

$dN_b / dt = 0$ , and it follows that

$$\rho(\omega_0) = \frac{A}{(N_a / N_b) B_{ab} - B_{ba}}$$

The number of particles with energy  $E$ , in thermal equilibrium at temperature  $T$ , is proportional to the *Boltzmann factor*, so

$$\frac{N_a}{N_b} = \frac{e^{-E_a / k_B T}}{e^{-E_b / k_B T}} = e^{\hbar\omega_0 / k_B T}$$

and hence

$$\rho(\omega_0) = \frac{A}{e^{\hbar\omega_0 / k_B T} B_{ab} - B_{ba}}$$



But Planck's blackbody formula tells us the energy density of thermal radiation:

$$\rho(\omega) = \frac{\hbar \omega^3}{\pi^2 c^3 e^{\hbar\omega/k_b T} - B_{ba}}$$

Comparing the two expressions, we conclude that

$$B_{ab} = B_{ba} \quad \text{and} \quad A = \frac{\omega^3 \hbar}{\pi^2 c^3} B_{ba}$$

and

$$B_{ba} = \frac{\pi}{3\epsilon_0 \hbar^2} |\wp|^2$$

and it follows that the spontaneous emission rate is

$$A = \frac{\omega^3 \wp^2}{3\pi\epsilon_0 \hbar c^3}$$



## 9.3.2 The Lifetime of an Excited State

Suppose, now, that you have a bottle full of atoms, with  $N_b(t)$ , of them in the excited state.

As a result of spontaneous emission, this number will decrease as time goes on; specifically, in a time interval  $dt$  you will lose a fraction of  $A dt$  them:

$$dN_b = -AN_b dt$$

Solving for  $N_b(t)$ , we find

$$N_b(t) = N_b(0)e^{-At}$$



evidently the number remaining in the excited state decreases exponentially, with a time constant

$$\tau = \frac{1}{A}$$

We call this the lifetime of the state ---- technically, it is the time it takes for  $N_b(t)$  to reach of its  $1/e \approx 0.368$  initial value.

*This spontaneous emission formula gives the transition rate for  $\psi_b \rightarrow \psi_a$  regardless of any other allowed states.*



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Typically, an excited atom has many different decay modes (that is,  $\psi_b$  can decay to a large number of different lower-energy states,  $\psi_{a1}, \psi_{a2}, \psi_{a3} \dots$ ). In that case the transition rates *add*, and the net lifetime is

$$\tau = \frac{1}{A_1 + A_2 + A_3 + \dots}$$

• While

$$\langle n | x | n' \rangle = \sqrt{\frac{\hbar}{2m\bar{\omega}}} (\sqrt{n'} \delta_{n,n'-1} + \sqrt{n} \delta_{n',n-1})$$

where  $\bar{\omega}$  is the natural frequency of the oscillator.





But we're talking about *emission*, so  $n'$  must be *lower* than  $n$ ; for our purpose, then,

$$\hat{\rho} = q \sqrt{\frac{n\hbar}{2m\bar{\omega}}} \delta_{n,n'-1} \hat{l}$$

Evidently transitions occur only to states one step lower on the "ladder", and the frequency of the photon emitted is

$$\begin{aligned} \omega &= \frac{E_n - E_{n'}}{\hbar} = \frac{(n+1/2)\hbar\bar{\omega} - (n'+1/2)\hbar\bar{\omega}}{\hbar} \\ &= (n' - n)\bar{\omega} = \bar{\omega} \end{aligned}$$

Not surprisingly, the system radiates at the classical oscillator frequency.



But the transition rate is

$$A = \frac{nq^2\omega^2}{6\pi\epsilon_0 mc^3}$$

and the lifetime of the  $n^{\text{th}}$  stationary state is

$$\tau_n = \frac{6\pi\epsilon_0 mc^3}{nq^2\omega^2}$$

Meanwhile, each radiate photon carries an energy  $\hbar\omega$ ,  
so the *power* radiated is  $A\hbar\omega$ :

$$P = \frac{q^2\omega^2}{6\pi\epsilon_0 mc^3} (n\hbar\omega)$$



or, since the energy of an oscillator in the  $n^{\text{th}}$  state is  $E = (n+1)\hbar\omega$ ,

$$P = \frac{q^2 \omega^2}{6\pi\epsilon_0 mc^3} \left( E - \frac{1}{2}\hbar\omega \right)$$

This is the average power radiated by a *quantum* oscillator with (initial) energy  $E$ .

For comparison, let's determine the average power radiated by a *classical* oscillator with the same energy

According to *Larmor formula*:

$$P = \frac{q^2 a^2}{6\pi\epsilon_0 c^3}$$



For a harmonic oscillator with amplitude

$x_0$ ,  $x(t) = x_0 \cos(\omega t)$ , and the acceleration is

$a = -x_0 \omega^2 \cos(\omega t)$ . Averaging over a full cycle, then

$$P = \frac{q^2 x_0 \omega^4}{12\pi\epsilon_0 c^3}$$

But the energy of the oscillator is  $E = (1/2)m\omega^2 x_0^2$ ,

so  $x_0^2 = 2E / m\omega^2$ , and hence

$$P = \frac{q^2 x_0 \omega^4}{6\pi\epsilon_0 m c^3} E$$

This is the average power radiated by a *classical* oscillator with (initial) energy  $E$ .



### 9.3.3 Selective Rules

The calculation of spontaneous emission rates has been reduced to a matter of evaluating matrix elements of the form

$$\langle \psi_b | \vec{r} | \psi_a \rangle$$

Suppose we are interested in systems like hydrogen, for which the Hamiltonian is spherically symmetrical. In that case we may specify the states with the usual quantum numbers  $n, l$ , and  $m$ , and the matrix elements are

$$\langle n'l'm' | \vec{r} | nlm \rangle$$



*a) Selection rules involving  $m$  and  $m'$  :*

Consider first the commutations of  $L_z$  with  $x$ ,  $y$ , and  $z$ , which we worked out in Chapter 4:

$$[L_z, x] = i\hbar y, \quad [L_z, y] = i\hbar x, \quad [L_z, z] = 0.$$

From the third of these it follows that

$$\begin{aligned} 0 &= \langle n'l'm' | [L_z, z] | nlm \rangle \\ &= \langle n'l'm' | (L_z z - z L_z) | nlm \rangle \\ &= \langle n'l'm' | [(m'\hbar)z - z(m'\hbar)] | nlm \rangle \\ &= (m' - m)\hbar \langle n'l'm' | z | nlm \rangle \end{aligned}$$



## Conclusion :

Either  $m' = m$ , or else  $\langle n'l'm' | z | nlm \rangle = 0$ . (1)

So unless  $m' = m$ , the matrix elements of  $z$  are always zero.

Meanwhile, from the commutator of  $L_z$  with  $x$

we get

$$\begin{aligned} \langle n'l'm' | [L_z, x] | nlm \rangle &= \langle n'l'm' | (L_z x - x L_z) | nlm \rangle \\ &= (m' - m)\hbar \langle n'l'm' | x | nlm \rangle = i\hbar \langle n'l'm' | y | nlm \rangle \end{aligned}$$



*Conclusion :*

$$(m' - m) \langle n'l'm' | x | nlm \rangle = i \langle n'l'm' | y | nlm \rangle$$

Finally, the commutator of  $L_z$  with  $y$  yields

$$\begin{aligned} \langle n'l'm' | [L_z, y] | nlm \rangle &= \langle n'l'm' | (L_z y - y L_z) | nlm \rangle \\ &= (m' - m) \hbar \langle n'l'm' | y | nlm \rangle = i \hbar \langle n'l'm' | x | nlm \rangle \end{aligned}$$

*Conclusion :*

$$(m' - m) \langle n'l'm' | y | nlm \rangle = i \langle n'l'm' | x | nlm \rangle$$

and

$$\begin{aligned} (m' - m)^2 \langle n'l'm' | x | nlm \rangle &= i(m' - m) \langle n'l'm' | y | nlm \rangle \\ &= \langle n'l'm' | x | nlm \rangle \end{aligned}$$





and hence

either  $(m' - m)^2 = 1$ , or else

$$\langle n'l'm' | x | nlm \rangle = \langle n'l'm' | y | nlm \rangle = 0 \quad (2)$$

From Equations (1) and (2), we obtain the selection rule for  $m$ :

**No transitions occur unless  $\Delta m = \pm 1$  or 0**

This is an easy result to understand if you remember that the photon carries spin 1, and hence its value of  $m$  is 1, 0, or -1; conservation of angular momentum requires that the atom give up whatever the photon takes away.



*b) Selection rules involving  $l$  and  $l'$ :*

The commutation relation:

$$[L^2, [L^2, \vec{r}]] = 2\hbar^2 (\vec{r}L^2 + L^2\vec{r})$$

As before, we sandwich this commutation between

$\langle n'l'm' |$  and  $|nlm\rangle$  to derive the selection rule:

$$\begin{aligned} & \langle n'l'm' | [L^2, [L^2, \vec{r}]] | nlm \rangle \\ &= 2\hbar^2 \langle n'l'm' | (\vec{r}L^2 - L^2\vec{r}) | nlm \rangle \\ &= 2\hbar^4 [l(l+1) + l'(l'+1)] \langle n'l'm' | \vec{r} | nlm \rangle \\ &= \langle n'l'm' | (L^2[L^2, \vec{r}] - [L^2, \vec{r}]L^2) | nlm \rangle \\ &= \hbar^4 [l'(l'+1) + l(l+1)]^2 \langle n'l'm' | \vec{r} | nlm \rangle \end{aligned}$$



## Conclusion :

$$\text{Either } 2[l(l+1) + l'(l'+1)] = [l'(l'+1) - l(l+1)]^2$$

$$\text{or else } \langle n'l'm' | \vec{r} | nlm \rangle = 0$$

But

$$[l'(l'+1) - l(l+1)] = (l' + l' + 1)(l' + 1)$$

and

- $2[l(l+1) + l'(l'+1)] = (l' + l' + 1)^2 + (l' - l)^2 - 1$

$$\text{so } (l' + l' + 1)^2 + (l' - l)^2 - 1 = 0$$

The first factor cannot be zero, so the condition simplifies to  $l' = l \pm 1$ .



Thus we obtain the selection rule for  $l$ :

No transitions occur unless  $\Delta l = \pm 1$

Again, this result is easy to interpret: The photon carries spin 1, so the rules for addition of angular momentum would  $l' = l + 1, l' = l$  or  $l' = l - 1$ .



# Allowed decays for the first four Bohr levels in hydrogen

