

## Section 6. Time dependent perturbations

- Show how time dependence in quantum mechanics leads to transitions between energy levels
- Absorption and emission of radiation by atoms

## 6.1 Time-dependent perturbation theory

- We aim to solve the time-dependent Schrodinger equation

$$\hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t}$$

where

$$\hat{H}(\underline{r}, t) = \hat{H}_0(\underline{r}) + \hat{H}'(\underline{r}, t)$$

- As in section 4,  $\hat{H}_0$  is the Hamiltonian of the unperturbed system, and **does not depend on time**. We assume we know its eigenvalues and eigenfunctions, i.e. solutions of

$$\hat{H}_0 |\phi_n\rangle = E_n |\phi_n\rangle$$

TISE

The difference now is that the perturbation  $\hat{H}'$  depends on time

- We expand the wavefunction  $\psi(\underline{r}, t)$  in terms of the eigenfunctions of  $\hat{H}_0$

$$\psi(\underline{r}, t) = \sum_n c_n(t) \phi_n(\underline{r}) \exp(-iE_n t / \hbar) \quad (1)$$

probability of measuring  $E_n$  and collapsing system into  $\phi_n$  at time  $t$  is  $|c_n(t)|^2$

Note that the **coefficients**  $c_n$  **depend on time**

originates from time dependence of perturbation  $\hat{H}'(\underline{r}, t)$

$\hat{H}\psi$  becomes

$$\sum_n c_n(t) (E_n + \hat{H}') \phi_n(\underline{r}) \exp(-iE_n t / \hbar)$$

$i\hbar \frac{\partial \psi}{\partial t}$  becomes

$$i\hbar \sum_n \left( -\frac{i c_n E_n}{\hbar} + \frac{dc_n}{dt} \right) \phi_n(\underline{r}) \exp(-iE_n t / \hbar)$$

- Equating these and simplifying gives

$$i\hbar \sum_n \frac{dc_n}{dt} \phi_n(\underline{r}) \exp(-iE_n t / \hbar) = \sum_n c_n(t) \hat{H}' \phi_n(\underline{r}) \exp(-iE_n t / \hbar)$$

Multiply both sides by  $\phi_m^*(\underline{r})$ , integrate over  $d^3r$ , and use orthogonality:

$$i\hbar \sum_n \frac{dc_n}{dt} \exp(-iE_n t / \hbar) \int \overbrace{\phi_m^*(\underline{r}) \phi_n(\underline{r}) d^3r}^{= \delta_{mn}} = \sum_n c_n(t) \exp(-iE_n t / \hbar) \int \phi_m^*(\underline{r}) \hat{H}' \phi_n(\underline{r}) d^3r$$

So

$$\frac{dc_m}{dt} = \frac{1}{i\hbar} \sum_n c_n(t) H'_{mn}(t) \exp(i\omega_{mn}t) \quad (2)$$

where

$$H'_{mn}(t) = \iiint \phi_m^*(\underline{r}) \hat{H}'(\underline{r}, t) \phi_n(\underline{r}) d^3r \quad (3)$$

and

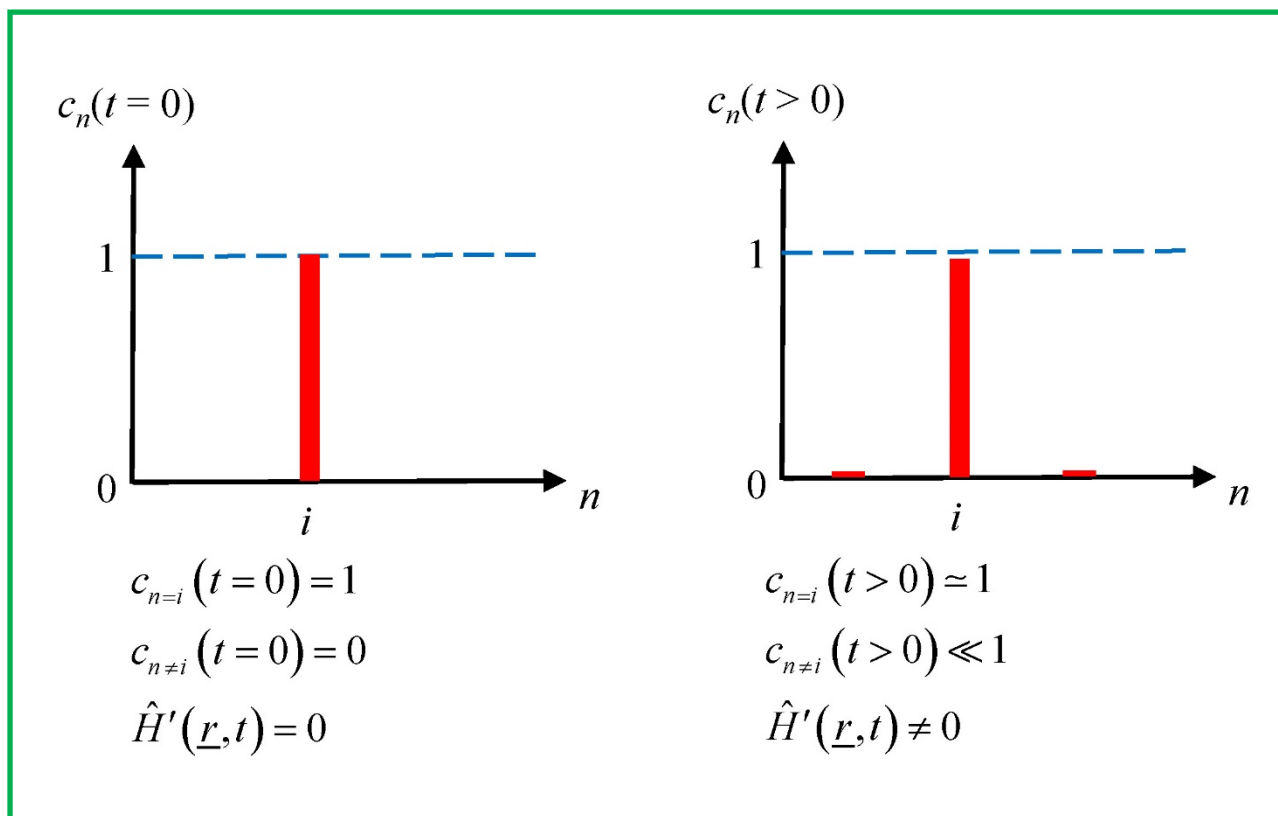
$$\omega_{mn} = \frac{E_m - E_n}{\hbar} \quad (4)$$

- We want to solve (2) for the coefficients  $c_m(t)$   
We assume that the perturbation is switched on at time  $t = 0$ , and that the system is in the eigenfunction  $\phi_i(\underline{r})$  at that time, i.e.

$$c_{n=i}(t=0) = 1, \quad c_{n \neq i}(t=0) = 0 \quad (\text{for all } n \neq i) \quad (5)$$

initial
i.e., we know the initial state

- If the perturbation  $\hat{H}'$  is weak, we can assume that all the  $c_n$  for  $n \neq i$  are small, and that  $c_{n=i}$  remains at  $\simeq 1$ .



Equation (2) becomes

$$\begin{aligned}\frac{dc_m}{dt} &= \frac{1}{i\hbar} \sum_n c_n(t) H'_{mn}(t) \exp(i\omega_{mn}t) \\ &\simeq \frac{1}{i\hbar} H'_{mi}(t) \exp(i\omega_{mi}t)\end{aligned}$$

which has the solution

$$c_m(t) = \frac{1}{i\hbar} \int_0^t H'_{mi}(t') \exp(i\omega_{mi}t') dt' \quad (6)$$

**Note:**

If we had assumed that the perturbation is switched on at time  $t_0$ , then  $c_i(t_0) = 1$  and  $c_{n \neq i}(t_0) = 0$ . Equation (6) becomes

$$c_m(t) = \frac{1}{i\hbar} \int_{t_0}^t H'_{mi}(t') \exp(i\omega_{mi}t') dt'$$

- What will a measurement of the energy of the system give?

At  $t = 0$ , the wavefunction of the system is the eigenfunction  $\phi_i(\underline{r})$  and so the energy is  $E_i$

Equations (1) and (6) show how the wavefunction evolves in time

At any time  $t$  the probability of measuring the energy as  $E_m$  is  $|c_m(t)|^2$

We can see that the time-dependent perturbation causes transitions between the quantum states

At  $t = 0$ ,  $c_i(t = 0) = 1$ ,  $c_{m \neq i}(t = 0) = 0$

But, after time  $t$ , other states can be occupied because

$|c_{m \neq i}(t)|^2$  can be finite



## 6.2 Periodic perturbations

- Consider a sinusoidal perturbation of angular frequency  $\omega$ :

$$\cos x = (e^{ix} + e^{-ix})/2$$

$$\begin{aligned}\hat{H}'(\underline{r}, t) &= \hat{H}'(\underline{r}) \cos \omega t \\ &= \frac{1}{2} \hat{H}'(\underline{r}) [\exp(i\omega t) + \exp(-i\omega t)] \quad (7)\end{aligned}$$

Equation (3) becomes

$i \Rightarrow$  initial  
 $f \Rightarrow$  final

$$\begin{aligned}H'_{fi}(t) &= \iiint d^3r \phi_f^*(\underline{r}) \hat{H}'(\underline{r}, t) \phi_i(\underline{r}) \\ &= \frac{1}{2} \iiint d^3r \phi_f^*(\underline{r}) \hat{H}'(\underline{r}) \phi_i(\underline{r}) [e^{i\omega t} + e^{-i\omega t}] \\ &\equiv \frac{1}{2} H'_{fi} [e^{i\omega t} + e^{-i\omega t}]\end{aligned}$$

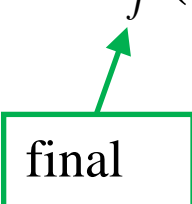
with

$$H'_{fi} = \iiint \phi_f^*(\underline{r}) \hat{H}'(\underline{r}) \phi_i(\underline{r}) d^3r \quad (8)$$

time independent

Equation (6) becomes

$$c_f(t) = \frac{H'_{fi}}{2i\hbar} \left[ \int_0^t \exp(i(-\omega + \omega_{fi})t') dt' + \int_0^t \exp(i(\omega + \omega_{fi})t') dt' \right] \quad (9)$$



with

$$\omega_{fi} = \frac{E_f - E_i}{\hbar} \quad (10)$$

$i \Rightarrow$  initial  
 $f \Rightarrow$  final

- Doing the integrals gives

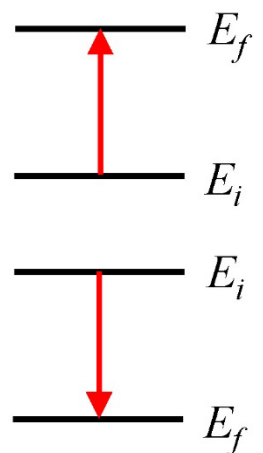
$$c_f(t) = -\frac{H'_{fi}}{2\hbar} \left[ \underbrace{\frac{\exp(i(-\omega + \omega_{fi})t) - 1}{-\omega + \omega_{fi}}}_{\text{energy gain: } E_f > E_i} + \underbrace{\frac{\exp(i(\omega + \omega_{fi})t) - 1}{\omega + \omega_{fi}}}_{\text{energy loss: } E_f < E_i} \right] \quad (11)$$

- The first term is peaked for  $\omega = \omega_{fi}$  and the second is peaked for  $\omega = -\omega_{fi}$ .

Angular frequency  $\omega > 0$

First term:  $\omega = \omega_{fi} = \frac{E_f - E_i}{\hbar} > 0 \Rightarrow E_f > E_i$

Second term:  $\omega = -\omega_{fi} = -\frac{E_f - E_i}{\hbar} > 0 \Rightarrow E_i > E_f$



- In an experiment we can set the apparatus to measure either energy gain or energy loss. If we choose to look at energy gain, only the first term will be significant.

Consider only the first term and let

$$W = -\omega + \omega_{fi},$$

The probability of finding the system in state  $\phi_f(\underline{r})$  is  $|c_f(t)|^2$

$$\begin{aligned} |c_f(t)|^2 &= \frac{|H'_{fi}|^2}{4\hbar^2} \left| \frac{e^{iWt} - 1}{W} \right|^2 \\ &= \frac{|H'_{fi}|^2}{4\hbar^2} \frac{1}{W^2} (e^{iWt} - 1)(e^{-iWt} - 1) \\ &= \frac{|H'_{fi}|^2}{4\hbar^2} \frac{1}{W^2} 2(1 - \cos Wt) \\ &= \frac{|H'_{fi}|^2}{4\hbar^2} \frac{\sin^2(Wt/2)}{(W/2)^2} \end{aligned} \quad (12)$$

$$\cos x = \frac{e^{ix} + e^{-ix}}{2}$$

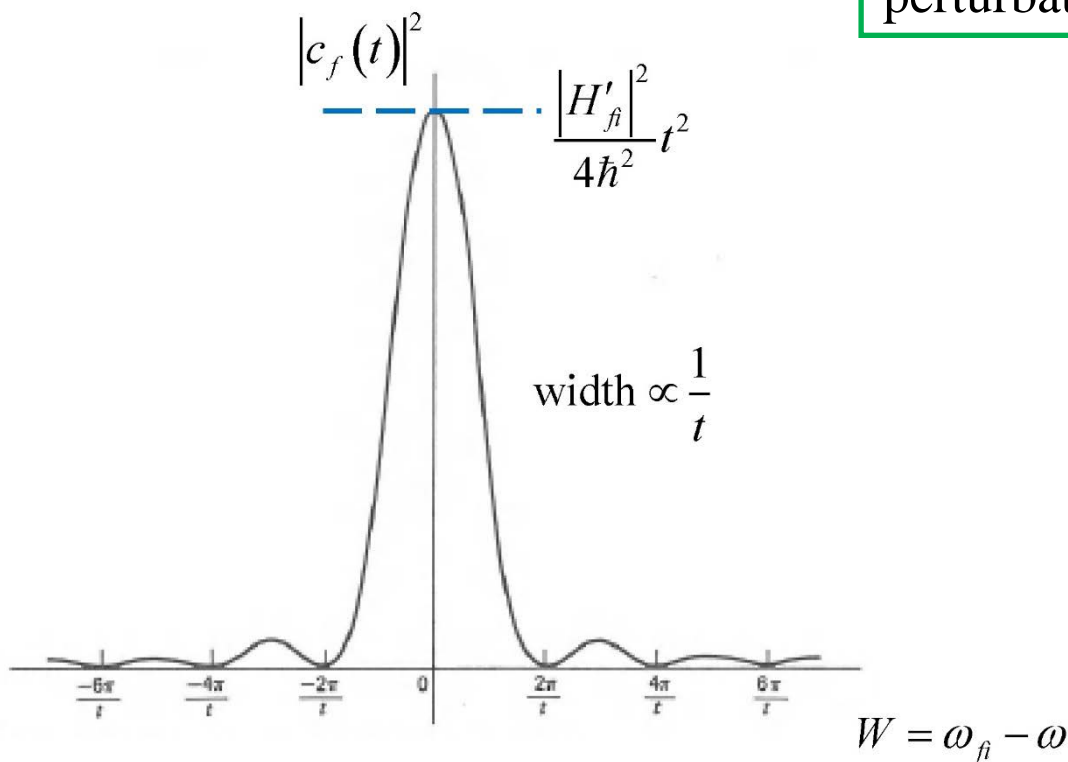
$$\sin^2 x = \frac{1}{2}(1 - \cos 2x)$$

As  $W \rightarrow 0$ ,  $\sin(Wt/2) \rightarrow Wt/2$

For  $W = 2\pi/t$ ,  $\sin(Wt/2) = \sin \pi = 0$

So, as  $t$  increases,  $|c_f(t)|^2$  becomes very strongly peaked for  $W = \omega_{fi} - \omega = 0$  i.e. when  $\hbar\omega = E_f - E_i$

$\omega$  is the angular frequency of the perturbation



- There is a high probability of causing a transition from initial state  $i$  to final state  $f$  only if the frequency of the perturbation matches the energy difference between the states

- If the perturbation is caused by an electromagnetic wave of angular frequency  $\omega$ , this corresponds to **excitation** of the quantum system

- Substituting  $W = -\omega + \omega_{fi}$  into equation (12) gives

$$|c_f(t)|^2 = \frac{|H'_{fi}|^2}{4\hbar^2} \left( \frac{\sin\left[(\omega_{fi} - \omega)t / 2\right]}{(\omega_{fi} - \omega) / 2} \right)^2 \quad (13)$$

- Everything works similarly if we look at the  $\omega = -\omega_{fi}$  peak. This would correspond to **stimulated emission** of an excited state

- In practice, you don't get a perturbation that is purely sinusoidal for all time. We can treat this by saying that the perturbation includes a range of frequencies, where the “density” of frequencies between  $\omega$  and  $\omega + d\omega$  is  $g(\omega)d\omega$
- The total probability of excitation from  $i$  to  $f$  after time  $t$  is then

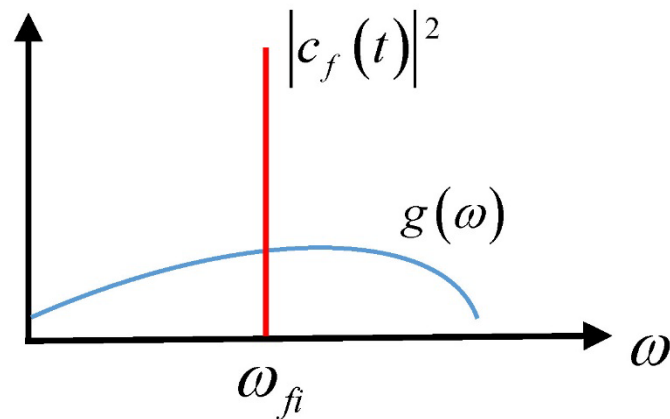
$$\begin{aligned}
 P(t) &= \frac{|H'_{fi}|^2}{4\hbar^2} \int_0^\infty \left( \frac{\sin\left[(\omega_{fi} - \omega)t/2\right]}{(\omega_{fi} - \omega)/2} \right)^2 g(\omega) d\omega \\
 &= \frac{|H'_{fi}|^2}{4\hbar^2} t^2 \int_0^\infty \text{sinc}^2\left[(\omega_{fi} - \omega)t/2\right] g(\omega) d\omega
 \end{aligned}$$

$\text{sinc } x \equiv \sin x/x$

e.g.  $P(t) = 0$  if  $g(\omega) = 0$

(14)

If  $g(\omega)$  is slowly varying with respect to the sinc-squared function,

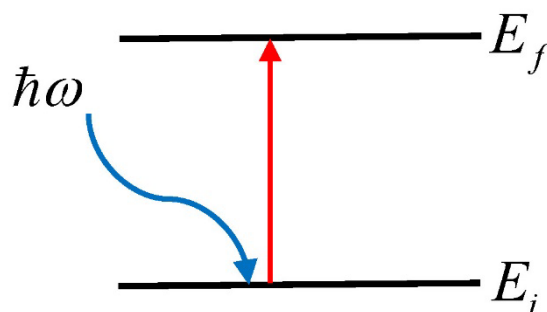


the only contribution to equation (14) will come from  $\omega = \omega_{fi}$ , so

See additional notes

$$P(t) = \frac{\pi |H'_{fi}|^2}{2\hbar^2} g(\omega_{fi}) t \quad (15)$$

A transition will occur only if the energy of the radiation  $\hbar\omega$  matches the difference in energy between the initial and final states





- The **transition rate** (transition probability per unit time) is then

$$W = \frac{dP}{dt}$$

$$W = \frac{\pi |H'_{fi}|^2}{2\hbar^2} g(\omega_{fi})$$

$H'_{fi}$  does not depend on time – see (8)

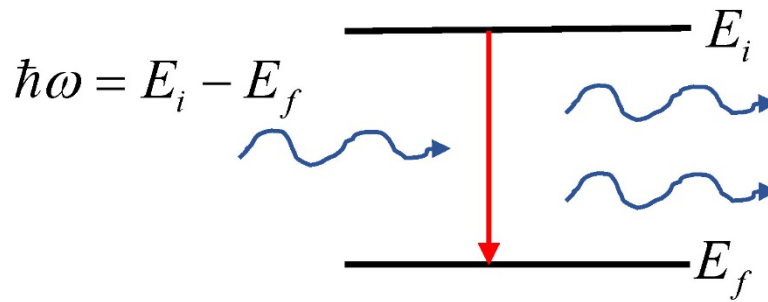
This is called “**Fermi’s golden rule**”

Wide range of applications – atomic transitions, scattering theory

## 6.3 Atomic transitions

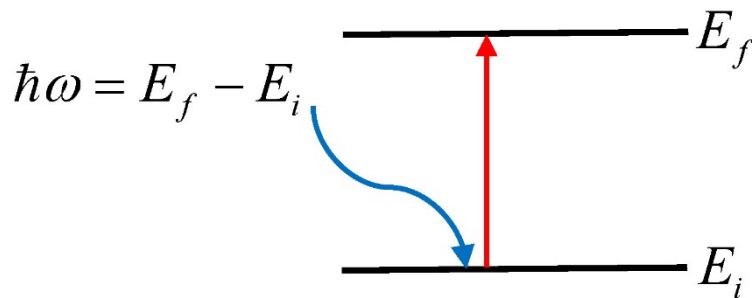
- Atoms can absorb and emit radiation by electrons undergoing transitions between energy levels
- This can be understood in terms of time-dependent perturbation theory, where the basic system is the atom and the perturbation is due to the electromagnetic field of the radiation
- We will use the theory of the previous section, even though there is no reference to the quantisation of radiation, i.e. photons
- This “**semi-classical**” approximation is OK for absorption and stimulated emission – for spontaneous emission we need a proper quantisation of the electromagnetic fields

## Stimulated emission:

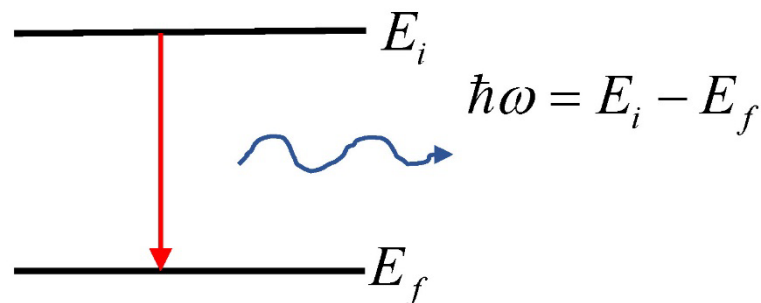


Emitted photons have same energy as incident photon

## Absorption:



## Spontaneous emission:



Transition is spontaneous – not stimulated by another photon

- The main effect is from the **electric field** of the radiation:

Plane wave

$$\underline{\varepsilon} = \underline{\varepsilon}_0 \cos(\underline{k} \cdot \underline{r} - \omega t)$$

$\underline{\varepsilon}$  time and space varying electric field

$\underline{\varepsilon}_0$  electric field amplitude (a vector)

$\underline{k}$  wavevector of the radiation

$$|k| = \frac{2\pi}{\lambda}$$

$\omega$  angular frequency of the radiation,  $\omega = c|\underline{k}|$

- We assume that the atom is at  $\underline{r} = 0$ . An atom is of size  $\sim 1 \text{ \AA}$  whereas the wavelength of visible light  $\lambda = 3900 - 7000 \text{ \AA}$ . So  $\underline{k} \cdot \underline{r}$  is very small. Hence,  $\cos(\underline{k} \cdot \underline{r}) \simeq 1$ ,  $\sin(\underline{k} \cdot \underline{r}) \simeq 0$  and

$$\underline{\varepsilon} = \underline{\varepsilon}_0 \cos(\underline{k} \cdot \underline{r} - \omega t)$$

$$\rightarrow = \underline{\varepsilon}_0 \left[ \cos(\underline{k} \cdot \underline{r}) \cos(-\omega t) + \sin(\underline{k} \cdot \underline{r}) \sin(-\omega t) \right]$$

$$\simeq \underline{\varepsilon}_0 \cos(\omega t)$$

$\cos x$  is an even function

$$\cos(A - B) = \cos A \cos B + \sin A \sin B$$

If  $\underline{\varepsilon}$  is in the  $z$  direction, the work done in moving an electron by a distance  $z$  is given by

$$\text{work done} = e\varepsilon z$$

$$= e\varepsilon_0 z \cos(\omega t)$$

Work done =  
force  $\times$  distance

So the perturbation becomes

$$\begin{aligned}\hat{H}'(\underline{r}, t) &= \hat{H}'(\underline{r}) \cos \omega t \\ &= e \varepsilon_0 z \cos \omega t\end{aligned}$$

i.e. potential  
energy of  
electron in the  
electric field

magnitude of the  
electric field

- As in section 6.2, transitions will occur only if  $\hbar\omega$  matches the difference between atomic energy levels
- The transition rate is

$$W = \frac{\pi |H'_{fi}|^2}{2\hbar^2} g(\omega_{fi})$$

where

$$H'_{fi} = e \varepsilon_0 \iiint \phi_f^*(\underline{r}) z \phi_i(\underline{r}) d^3 r$$

$H'_{fi}$  does not depend on time – see (8)

We find that the rate of **spontaneous emission** is also proportional to  $|H'_{fi}|^2$

- For the hydrogen atom, the states  $\phi_i(\underline{r})$  and  $\phi_f(\underline{r})$  can be written as

$$\phi_i(\underline{r}) = R_{n_i \ell_i}(r) Y_{\ell_i m_i}(\theta, \phi)$$

$$\phi_f(\underline{r}) = R_{n_f \ell_f}(r) Y_{\ell_f m_f}(\theta, \phi)$$

$n, \ell, m$  are the quantum numbers of the initial and final states

and in spherical polars  $z = r \cos \theta$ .

In spherical polars  $d^3r = r^2 \sin \theta dr d\theta d\phi$

$H'_{fi}$  becomes

$r^2$  from  $d^3r$ ,  $r$  from  $\hat{H}'$

$$H'_{fi} = e \varepsilon_0 \int_0^\infty dr r^3 R_{n_f \ell_f}^*(r) R_{n_i \ell_i}(r) \times$$

$$\int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \cos \theta Y_{\ell_f m_f}^*(\theta, \phi) Y_{\ell_i m_i}(\theta, \phi)$$

from  $d^3r$

from  $\hat{H}'$

and this determines the “strength” of spectral lines

- In particular, the  $\theta$  and  $\phi$  integrals are zero for many combinations of the  $\ell$  and  $m$  quantum numbers. This gives rise to “**selection rules**” that determine which lines are observed in atomic spectra

see problems sheet

- For  $H'_{fi}$  to be non-zero we require  $\ell_f = \ell_i \pm 1$  with  $m_i = m_f$

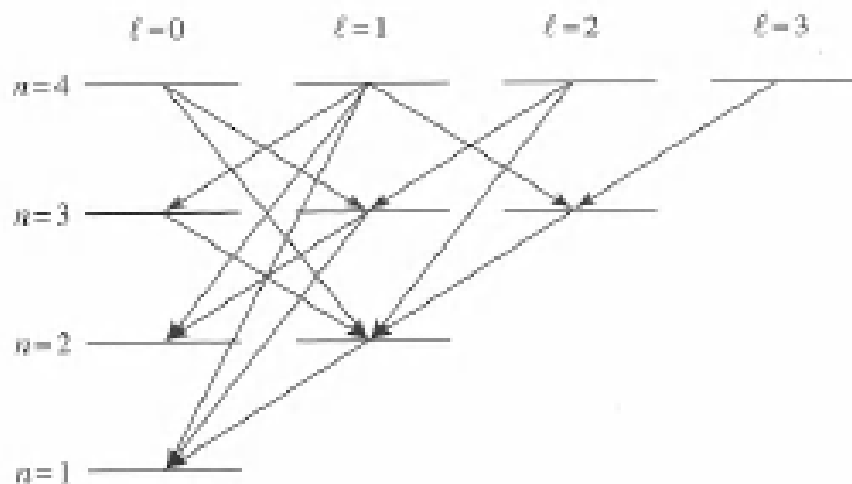


Figure 11.9: Allowed decays for the first four Bohr levels in hydrogen.



- Above corresponds to the field polarised in the  $z$  direction. If the field was polarised in the  $x$  direction

$$\begin{aligned}\hat{H}'(\underline{r}) &= e\epsilon_0 x \\ &= e\epsilon_0 r \sin \theta \cos \phi\end{aligned}$$

Can then show (see e.g. Rae) that  $H'_{fi} = 0$  unless  $m_f = m_i \pm 1$ .

- So, for an electromagnetic wave of arbitrary polarisation, the selection rules for the allowed transitions are

$$\ell_f = \ell_i \pm 1 \Rightarrow \Delta\ell = \pm 1$$

$$m_f = m_i \text{ or } m_f = m_i \pm 1 \Rightarrow \Delta m = 0 \text{ or } \pm 1$$

these refer  
to electric  
dipole  
transitions

- Transitions will not take place unless the selection rules are obeyed
- Selection rules are important in the study of atoms, molecules, nuclei and solids