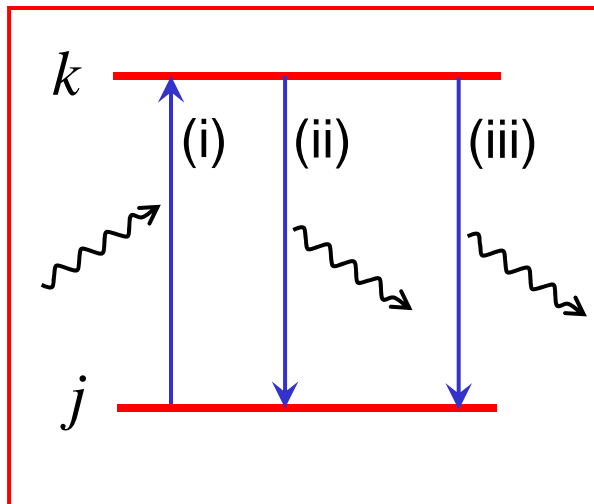


# Advanced Quantum Physics

## Lecture 16



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# Section 4: Transitions

4.1 Two state system, magnetic resonance

4.2 Time dependent perturbation theory, scattering



4.3 Radiative transitions

4.4 Photons

4.5 Lasers

## 4.3 Radiative transitions

- Apply analysis from last lecture to atomic energy levels transitions.
- Electromagnetic wave travelling in z-direction,  $\boldsymbol{\mathcal{E}}$  polarized parallel to x-axis.

$$\boldsymbol{\mathcal{E}} = (\mathcal{E}_x, 0, 0) \quad ; \quad \mathcal{E}_x = \mathcal{E}_0 e^{i(kz - \omega t)}$$

- And the potentials:

$$\mathbf{A} = (A_x, 0, 0) \quad ; \quad A_x = A_0 e^{i(kz - \omega t)} \quad ; \quad \phi = 0$$

- Given:

$$\boldsymbol{\mathcal{E}} = \nabla \phi - \frac{\partial \mathbf{A}}{\partial t} \quad \Rightarrow \quad \mathcal{E}_0 = i\omega A_0$$

- Since  $\mathbf{B} = \nabla \times \mathbf{A}$

$$\mathbf{B} = (0, B_y, 0) \quad ; \quad B_y = ikA_0 e^{i(kz - \omega t)} = \frac{k}{\omega} \mathcal{E}_x = \frac{\mathcal{E}_x}{c}$$

- In lecture 9 we obtained for the Schrodinger eqn. in a magnetic field:

$$\frac{1}{2m} \left[ -\hbar^2 \nabla^2 \psi + i\hbar q (2\mathbf{A} \cdot \nabla \psi + \psi \nabla \cdot \mathbf{A}) + q^2 A^2 \psi \right] + q\phi\psi = i\hbar \frac{\partial \psi}{\partial t}$$

Note: don't confuse  $\mathcal{E}_0$  with  $\varepsilon_0$  !!

## Radiative transitions (2)

- From the last slide:

$$\frac{1}{2m} \left[ -\hbar^2 \nabla^2 \psi + i\hbar q (2\mathbf{A} \cdot \nabla \psi + \psi \nabla \cdot \mathbf{A}) + q^2 A^2 \psi \right] + q\phi\psi = i\hbar \frac{\partial \psi}{\partial t}$$

- Neglecting the  $A^2$  term and given that:  $\nabla \cdot \mathbf{A} = 0$ ,  $\phi = 0$

- The perturbation term in the Hamiltonian:

$$\hat{H}' = \frac{i\hbar q}{m} \mathbf{A} \cdot \nabla = \frac{i\hbar q}{m} A_0 e^{i(kz - \omega t)} \frac{\partial}{\partial x}$$

$$\begin{aligned} \frac{\partial^2}{\partial x^2} (x\psi) &= \frac{\partial}{\partial x} \left( \psi + x \frac{\partial \psi}{\partial x} \right) \\ &= 2 \frac{\partial \psi}{\partial x} + x \frac{\partial^2 \psi}{\partial x^2} \end{aligned}$$

- We need to evaluate  $\langle \psi_k | \hat{H}' | \psi_j \rangle$  and given that

$$[x, \hat{H}_0] = -\frac{\hbar^2}{2m} \left( x \frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial x^2} x \right) = -\frac{\hbar^2}{2m} \left( x \frac{\partial^2}{\partial x^2} - 2 \frac{\partial}{\partial x} - x \frac{\partial^2}{\partial x^2} \right) = \frac{\hbar^2}{m} \frac{\partial}{\partial x}$$

- We can write:

$$\hat{H}' = \frac{i\hbar q}{m} A_0 e^{i(kz - \omega t)} \frac{m}{\hbar^2} (x\hat{H}_0 - \hat{H}_0 x)$$

- And the matrix element is:

$$\langle \psi_k | \hat{H}' | \psi_j \rangle = \frac{iA_0}{\hbar} \langle \psi_k | qe^{i(kz - \omega t)} (x\hat{H}_0 - \hat{H}_0 x) | \psi_j \rangle$$

## Radiative transitions (3)

• From the last slide:  $\langle \psi_k | \hat{H}' | \psi_j \rangle = \frac{iA_0}{\hbar} \langle \psi_k | qe^{i(kz-\omega t)} (x\hat{H}_0 - \hat{H}_0x) | \psi_j \rangle$

• Now  $\langle \psi_k | qe^{i(kz-\omega t)} x\hat{H}_0 | \psi_j \rangle = E_j \langle \psi_k | qe^{i(kz-\omega t)} x | \psi_j \rangle$

$$\langle \psi_k | qe^{i(kz-\omega t)} \hat{H}_0 x | \psi_j \rangle = E_k \langle \psi_k | qe^{i(kz-\omega t)} x | \psi_j \rangle \quad (\hat{H}_0 \text{ Hermitian})$$

• So:

$$\langle \psi_k | \hat{H}' | \psi_j \rangle = \frac{iA_0}{\hbar} (E_j - E_k) \langle \psi_k | qe^{i(kz-\omega t)} x | \psi_j \rangle$$

$$= -i\omega A_0 \langle \psi_k | qe^{i(kz-\omega t)} x | \psi_j \rangle \quad \text{where } \hbar\omega = E_k - E_j$$

$$= -\mathcal{E}_0 \langle \psi_k | qe^{i(kz-\omega t)} x | \psi_j \rangle \quad \text{since } \mathcal{E}_0 = i\omega A_0$$

• A typical optical photon has  $\lambda \approx 500\text{nm}$  - much greater than the size of an atom. Hence phase of the wave  $kz$  does not vary across atom.

• So:  $e^{ikz} = (1 + ikz \dots) \approx 1$  and  $\langle \psi_k | \hat{H}' | \psi_j \rangle \approx -\mathcal{E}_0 e^{-i\omega t} \langle \psi_k | qx | \psi_j \rangle$

## Radiative transitions (4)

•From the last slide:  $\langle \psi_k | \hat{H}' | \psi_j \rangle \approx -\mathcal{E}_0 e^{-i\omega t} \langle \psi_k | qx | \psi_j \rangle$

•So:

$$\hat{H}' \approx -\mathcal{E}_0 qx e^{-i\omega t}$$

•Called the *electric dipole approximation*.

•Perturbation is interaction of dipole moment  $qx$  with electric field  $\mathcal{E}_0$

•This is an approximation – neglected terms can be important.

•Inserting this into Fermi's Golden Rule – two possible calculations:

•Rate of *stimulated absorption* – atom absorbs  $\hbar\omega$  from external field  $\mathcal{E}_0$

•Rate of *stimulated emission* – atom emits quantum  $\hbar\omega$

•So far we have only considered transitions due to a perturbation.

•With system in stationary state and no perturbation, probability density is time independent hence no change in state.

•How is this reconciled with atom emitting a photon with no applied fields?

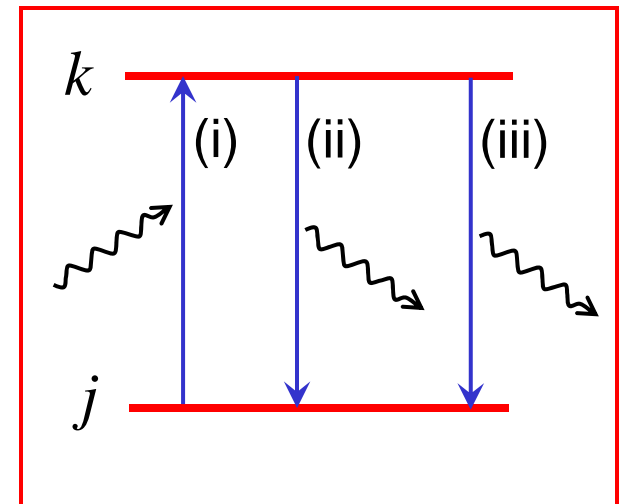
# Quantum field theory

- To understand spontaneous emission properly we need *Quantum Field Theory*.
- Quantum picture of electromagnetic fields.
- Treat each Fourier component of field as a harmonic oscillator, photons of the corresponding frequency are excitation quanta of oscillator.
- Even in absence of photons each Fourier component has ground state energy  $\frac{1}{2}\hbar\omega$  -due to small fluctuating fields from uncertainty relations.
- Hence even an isolated atom in a vacuum at absolute zero is surrounded by fluctuating fields.
- These fields can cause a spontaneous transition.
- Such transitions are permitted because the atom in an excited state is not in a stationary state of the whole system (atom plus E/M field).

# Einstein's A and B coefficients

- We can avoid the use of Quantum Field theory by using an argument formulated by Einstein.
- This shows that stimulated and spontaneous transitions must be related.
- If we have many replicas of the system (in this case atoms) in a black body radiation field at temperature  $T$ .
- Consider transitions between  $|\psi_j\rangle$  and  $|\psi_k\rangle$  with  $E_k - E_j = \hbar\omega$
- Suppose no. of atoms in the two states are  $n_j, n_k$
- Possible transitions and rates per atom are:

- |                                     |      |                   |
|-------------------------------------|------|-------------------|
| (i) Stimulated $j \rightarrow k$    | rate | $B_{jk}u(\omega)$ |
| (ii) Stimulated $k \rightarrow j$   | rate | $B_{kj}u(\omega)$ |
| (iii) Spontaneous $k \rightarrow j$ | rate | $A$               |



- $u(\omega)$  is the energy density of radiation per unit  $\omega$
- $A$  and  $B$  are known as *Einstein's A and B coefficients*

## Einstein's A and B coefficients (2)

- Einstein's  $A$  and  $B$  coefficients are properties of the atomic states concerned.
- In thermodynamic equilibrium the rates must balance:

$$n_k \left[ A + B_{kj} u(\omega) \right] = n_j B_{jk} u(\omega)$$

- In thermal equilibrium relative populations of two states (assuming non-degenerate) given by Boltzmann factor:

Don't confuse  $k$  with  $k_B$

$$\frac{n_j}{n_k} = \frac{e^{-E_j/k_B T}}{e^{-E_k/k_B T}} = e^{\hbar\omega/k_B T} \quad \text{and so:} \quad A = \left[ B_{jk} e^{\hbar\omega/k_B T} - B_{kj} \right] u(\omega)$$

- The energy density per unit  $\omega$  is given by Planck's black body formula:

$$u(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/k_B T} - 1} \quad \text{and so:} \quad A = \left[ B_{jk} e^{\hbar\omega/k_B T} - B_{kj} \right] \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

- The  $A$  coefficient (spontaneous emission) cannot depend on temperature so  $T$  must cancel on the RHS and hence:

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

## Einstein's A and B coefficients (3)

- From the last slide:

$$B_{kj} = B_{jk} \qquad A = B_{kj} \frac{\hbar \omega^3}{\pi^2 c^3}$$

- So the  $A$  and  $B$  coefficients are related.
- If we calculate the  $B$  coefficient for stimulated emission from Fermi's Golden Rule we can infer  $A$ .
- To obtain  $B_{kj}$  we use the perturbation:

$$\hat{H}' = -q\mathcal{E}_0 x \cos \omega t = -\frac{1}{2} q\mathcal{E}_0 x \left( e^{i\omega t} + e^{-i\omega t} \right)$$

- The first exponential deals with  $k \rightarrow j$  the second  $j \rightarrow k$  transitions
- Using Fermi's Golden Rule, rate of stimulated emission ( $k \rightarrow j$ ):

$$\Gamma_{k \rightarrow j} = \frac{2\pi}{\hbar} |H'_{jk}|^2 g(E_j) = \frac{2\pi \mathcal{E}_0^2}{\hbar 4} \left| \langle \psi_j | qx | \psi_k \rangle \right|^2 g(E_j)$$

- Introducing the electric dipole operator  $\hat{\mathbf{d}} = q\mathbf{r}$  in an arbitrary direction.
- Matrix element is

$$\left| \langle \psi_j | qx | \psi_k \rangle \right|^2 = \frac{1}{3} \left| \langle \psi_j | \hat{\mathbf{d}} | \psi_k \rangle \right|^2 \equiv \frac{1}{3} | \mathbf{d}_{jk} |^2$$

## Einstein's A and B coefficients (4)

- From the last slide

$$\left| \langle \psi_j | qx | \psi_k \rangle \right|^2 = \frac{1}{3} \left| \langle \psi_j | \hat{\mathbf{d}} | \psi_k \rangle \right|^2 \equiv \frac{1}{3} |\mathbf{d}_{jk}|^2$$

- The factor of  $\frac{1}{3}$  is the average of  $\cos^2 \theta$  over all solid angles
- We relate the density of states  $g(E_j)$  to the energy density  $u(\omega)$  per unit  $\omega$ :
- The maximum energy density of the EM field is:  $\frac{1}{2} \epsilon_0 \mathcal{E}_0^2 + \frac{1}{2} B_0^2 / \mu_0 = \epsilon_0 \mathcal{E}_0^2$
- Time averaged energy density:  $\frac{1}{2} \epsilon_0 \mathcal{E}_0^2$
- Since the no. of states per unit frequency is  $\hbar g(E) = \hbar \frac{\partial n}{\partial E} = \frac{\partial n}{\partial \omega}$
- Hence:  $u(\omega) = \frac{1}{2} \epsilon_0 \mathcal{E}_0^2 \hbar g(E) \Rightarrow \mathcal{E}_0^2 g(E) = 2u(\omega) / \epsilon_0 \hbar$
- From Fermi's Golden Rule, the rate of stimulated emission:

$$\Gamma_{k \rightarrow j} = \frac{2\pi \mathcal{E}_0^2}{\hbar} \frac{1}{4} \left| \langle \psi_j | qx | \psi_k \rangle \right|^2 g(E_j) = \frac{2\pi \mathcal{E}_0^2}{\hbar} \frac{1}{4} g(E_j) \frac{|\mathbf{d}_{jk}|^2}{3} = \frac{\pi u(\omega)}{3\epsilon_0 \hbar^2} |\mathbf{d}_{jk}|^2$$

- Since  $\Gamma_{k \rightarrow j} = u(\omega) B_{kj} \Rightarrow B_{kj} = \frac{\pi |\mathbf{d}_{jk}|^2}{3\epsilon_0 \hbar^2} \Rightarrow A = \frac{\omega^3 |\mathbf{d}_{jk}|^2}{3\pi \epsilon_0 c^3 \hbar}$  Rate of spontaneous emission

## Selection rules

- From the previous slide, the Einstein coefficients are:

$$B_{kj} = \frac{\pi |\mathbf{d}_{jk}|^2}{3\varepsilon_0 \hbar^2}, \quad A = \frac{\omega^3 |\mathbf{d}_{jk}|^2}{3\pi\varepsilon_0 c^3 \hbar}$$

- Neither spontaneous ( $A$ ) or stimulated ( $B$ ) transitions will occur between  $|\psi_k\rangle$  and  $|\psi_j\rangle$  unless a component of  $\langle \psi_j | \hat{\mathbf{d}} | \psi_k \rangle$  is non-zero
- Often possible to show that matrix elements are zero for certain pairs of states (in electric dipole approx.), summarise results in *selection rules*.
- Dipole operator  $\hat{\mathbf{d}} = q\mathbf{r}$  changes sign under parity operation  $\mathbf{r} \rightarrow -\mathbf{r}$  hence  $\langle \psi_j | \hat{\mathbf{d}} | \psi_k \rangle = 0$  if  $|\psi_k\rangle$  and  $|\psi_j\rangle$  have the same parity.
- Selection rule: Parity of wavefunction changes in electric dipole approx.
- Wavefunctions separate into spatial and spin components:  $|\psi_k\rangle = \phi_k(\mathbf{r})\chi_k$
- Dipole operator acts only on  $\phi_k(\mathbf{r})$  matrix element becomes:

$$\langle \psi_j | \hat{\mathbf{d}} | \psi_k \rangle = \langle \chi_j | \chi_k \rangle \int \phi_j^*(\mathbf{r}) q\mathbf{r} \phi_k(\mathbf{r}) d\tau$$

## Selection rules (2)

- From the last slide:  $\langle \psi_j | \hat{\mathbf{d}} | \psi_k \rangle = \langle \chi_j | \chi_k \rangle \int \phi_j^*(\mathbf{r}) q\mathbf{r} \phi_k(\mathbf{r}) d\tau$
- Spin term  $\langle \chi_j | \chi_k \rangle$  vanishes unless  $\chi_j$  and  $\chi_k$  are the same.
- Hence selection rule:  $\Delta s = 0$  ;  $\Delta m_s = 0$
- So spin state is *not* altered in electric dipole transition.
- Consider a single electron atom with electric dipole moment operator:

$$\hat{\mathbf{d}} = q\mathbf{r} = qr(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$$

- Electron wavefunction will have the form:  $R(r)Y_{\ell m}(\theta, \phi) = R(r)F_{\ell m}(\theta)e^{im\phi}$
- To evaluate the matrix element, take z-component of  $\hat{\mathbf{d}}$  the  $\phi$  integral is:

$$\int_0^{2\pi} e^{-im_j\phi} e^{im_k\phi} d\phi = 0 \quad \text{unless} \quad m_j = m_k$$

- For the x-component of  $\hat{\mathbf{d}}$  expanding  $\cos \phi$  in exponentials,  $\phi$  part of integral:

$$\int_0^{2\pi} e^{-im_j\phi} \frac{1}{2}(e^{i\phi} + e^{-i\phi}) e^{im_k\phi} d\phi = 0 \quad \text{unless} \quad m_k - m_j = \pm 1$$

- Same result for y. So - to get a non-zero component  $\Delta m_\ell = 0$  or  $\pm 1$

### Selection rules (3)

- From the last slide we have selection rules,  $\Delta m_\ell = 0$  (z) or  $\Delta m_\ell = \pm 1$  (x,y).
- These different changes in  $m$  are related to polarization of EM field.
  - For  $\mathbf{E}$  in z-direction,  $\Delta m_\ell = 0$  selection rule applies.
  - For  $\mathbf{E}$  in x or y-direction,  $\Delta m_\ell = \pm 1$  selection rule applies.
- Consider selection rule for orbital angular momentum quantum no.  $\ell$
- Parity operator changes  $\mathbf{r} \rightarrow -\mathbf{r}$  so:  $\theta \rightarrow \pi - \theta$ ,  $\phi \rightarrow \phi + \pi$   
and:  $Y_{\ell m}(\pi - \theta, \phi + \pi) = (-1)^\ell Y_{\ell m}(\theta, \phi)$  hence parity eigenvalue  $P = (-1)^\ell$
- Since the parity of the wavefunction must change in an electric dipole transition and  $\Delta m_\ell = 0$  or  $\pm 1$  we must have:

$$\Delta \ell = \pm 1$$

- This is summarized by saying that the photon carries off (or brings in for absorption) *one unit of angular momentum*.
- It is also possible for the EM field to interact with electric quadrupole moment or magnetic dipole moment, however electric dipole transitions are much more likely.

## Selection rules (4)

- When orbital and spin angular momenta are combined to make total angular momentum  $\mathbf{J}$ , selection rules for  $\ell, s, m_\ell, m_s$  imply rules for  $j, m_j$
- Since  $\Delta m_s = 0$  and  $\Delta m_\ell = 0$  or  $\pm 1$  then:  $\Delta m_j = 0$  or  $\pm 1$
- For given  $\ell$  and  $s$ ,  $j$  can take any of the values:
$$j = (\ell + s), (\ell + s - 1), \dots, |\ell - s|$$
- Thus  $\Delta \ell = \pm 1, \Delta s = 0$  does not imply a change in  $j$  and we can have  $\Delta j = 0$  as well as  $\Delta j = \pm 1$
- For example:  $\ell = 0, s = \frac{1}{2}$  and  $\ell = 1, s = \frac{1}{2}$  can both make  $j = \frac{1}{2}$   
but if  $j = 0$  initially then  $\ell = s$  and the final state:  $j' = |\ell' - s| = |\ell \pm 1 - s| = 1$   
so if  $j = 0$  we can only have  $\Delta j = 1$
- For a single electron  $s = \frac{1}{2}$ , while  $\ell$  is an integer so we cannot have  $j = 0$  but in atoms with an even no. of electrons resultant angular momentum can be zero.
- To summarize:  $\Delta j = 0, \pm 1$ ; not  $0 \rightarrow 0$

## Selection rules (5)

- From the last slide:  $\Delta j = 0, \pm 1$ ; not  $0 \rightarrow 0$
- Could arrive at this rule by considering the photon as carrying one unit of angular momentum and using the rules for combining angular momentum.
- It applies even in cases where initial and final states are not separate eigenstates of  $\hat{L}$  or  $\hat{S}$ .
- Another example – a charged particle in a 1D harmonic potential.
- Wavefunctions  $|n\rangle$ , quantum number  $n$ , energies  $(n + \frac{1}{2})\hbar\omega$
- Oscillating electric field in x-direction induces transitions  $|n\rangle \rightarrow |n'\rangle$  with matrix elements:  $\langle n' | x | n \rangle$  since:

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}} (\hat{a} + \hat{a}^\dagger) \quad \text{Where } \hat{a}, \hat{a}^\dagger \text{ are ladder operators}$$

- Matrix element is:  $\langle n' | x | n \rangle = \sqrt{\frac{\hbar}{2m\omega}} \left( \sqrt{n+1} \langle n' | n+1 \rangle + \sqrt{n} \langle n' | n-1 \rangle \right)$
- Which vanishes unless  $n' = n \pm 1$  so in electric dipole approx.  $\Delta n = \pm 1$

## Summary – Lecture 16

- Radiative transitions - calculation of the matrix element for the interaction of a quantum mechanical system with an electromagnetic wave. When the radiation wavelength is much greater than atomic dimensions we may use the electric dipole approximation:  $\hat{H}' \approx -\mathcal{E}_0 q x e^{-i\omega t}$

- As well as stimulated transitions atoms can undergo spontaneous transitions due to interaction with fluctuating electromagnetic fields.

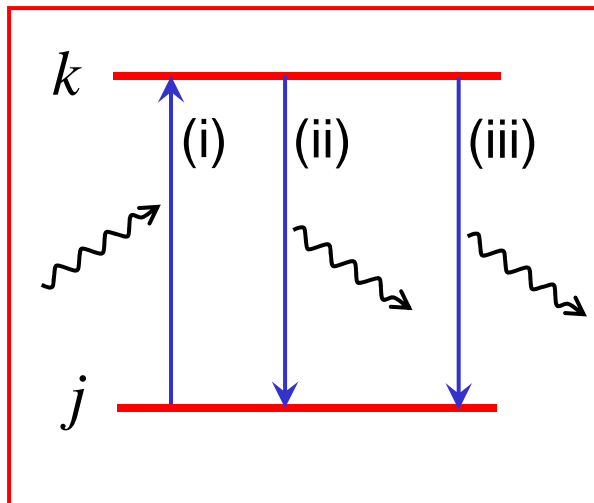
- Thermodynamics can be used to show that the stimulated emission rate equals the stimulated absorption rate and that the spontaneous emission rate is given by

$$A = B_{kj} \frac{\hbar \omega^3}{\pi^2 c^3} = \frac{\omega^3 |\mathbf{d}_{jk}|^2}{3\pi \epsilon_0 c^3 \hbar}$$

where Fermi's golden rule has been used to calculate the spontaneous emission rate in terms of the interaction matrix element.

- Transition selection rules for electric dipole transitions are for spin,  $\Delta s = 0$ ,  $\Delta m_s = 0$ , orbital angular momentum  $\Delta \ell = \pm 1$  with  $\Delta m_\ell = 0$  or  $\Delta m_\ell = \pm 1$  (depending on the polarization of E/M wave), implying:  $\Delta m_j = 0$  or  $\pm 1$  and  $\Delta j = 0, \pm 1$ ; (not  $0 \rightarrow 0$ ).

# Lecture 16



**The End!!**

([www.sp.phy.cam.ac.uk/~dar11/pdf](http://www.sp.phy.cam.ac.uk/~dar11/pdf))