



UNIVERSITY OF
CAMBRIDGE

NST Part II Physics
Michaelmas Term 2022
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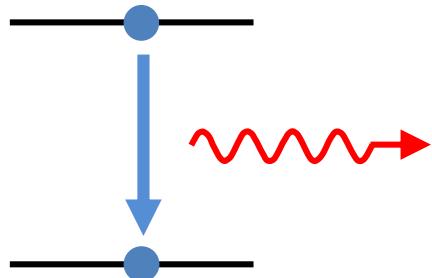
ADVANCED QUANTUM PHYSICS

Handout 11

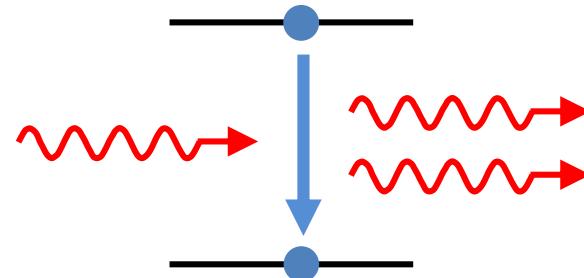
-
- ▶ Spontaneous emission
 - ▶ Stimulated emission and absorption

Atomic Transitions

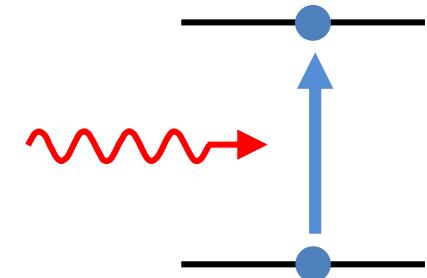
- With a *quantum* description of the EM field (QED) in place, it becomes possible to understand why the dominant atomic transitions involve the emission or absorption of a single photon ...



*spontaneous
emission*



*stimulated
emission*



absorption

... and to compute the *transition rates* for these processes, using first-order time-dependent perturbation theory (Fermi's Golden Rule)

Atomic Transitions

- Consider an N -electron atom immersed in a time-dependent, external EM field described by classical vector and scalar potentials $\mathbf{A}(\mathbf{r}, t)$, $\phi(\mathbf{r}, t)$
The Hamiltonian for this system is of the form

$$\hat{H} = \frac{1}{2m_e} \sum_{i=1}^N \left(\hat{\mathbf{p}}_i + e\mathbf{A}(\mathbf{r}_i, t) \right)^2 - e \sum_{i=1}^N \phi(\mathbf{r}_i, t) + V(\{r_i, r_{ij}\})$$

where V represents the various atomic Coulomb potential energy terms

- In the Coulomb gauge, the first term on the right-hand side expands as (see slide 3.25)
$$\frac{1}{2m_e} \left[\sum_{i=1}^N \hat{\mathbf{p}}_i^2 + 2e \mathbf{A} \cdot \hat{\mathbf{p}}_i + e^2 \mathbf{A}^2 \right] \quad (\nabla \cdot \mathbf{A} = 0)$$
- For an electron confined to an atom, the quadratic A^2 terms can usually be neglected (see slide 3.28)

Atomic transitions (2)

- Hence, for an atom in an external EM field, in the Coulomb gauge and with $\phi(\mathbf{r}, t) = 0$ (see slide 10.3), the Hamiltonian is

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

$$\hat{H}_0 = \frac{1}{2m_e} \sum_{i=1}^N \hat{\mathbf{p}}_i^2 + V ; \quad \hat{H}' = \frac{e}{m_e} \sum_{i=1}^N \mathbf{A}(\mathbf{r}_i, t) \cdot \hat{\mathbf{p}}_i$$

- The interaction of the atom with the *quantised* EM field can then be treated by converting the classical vector potential \mathbf{A} into a *quantum field operator*

$$\boxed{\hat{H}' = \frac{e}{m_e} \sum_{i=1}^N \hat{\mathbf{A}}(\mathbf{r}_i, t) \cdot \hat{\mathbf{p}}_i} \quad (\hat{\mathbf{p}}_i = -i\hbar\nabla_i)$$

- The operator $\hat{\mathbf{A}}(\mathbf{r}, t)$ can be expressed as an expansion over all possible modes (\mathbf{k}, λ) of the EM field (i.e. over all possible photon modes)
 $(\lambda = 1, 2 \text{ or } \lambda = L, R \text{ specifies the photon polarisation state})$

Atomic transitions (3)

- From slide 10.27, the mode expansion for the field operator A , in terms of photon annihilation and creation operators, is

$$\hat{A}(\mathbf{r}, t) = \sum_{\mathbf{k}, \lambda} N(\mathbf{k}) \left[\hat{a}_{\mathbf{k}, \lambda} e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \mathbf{e}_\lambda(\mathbf{k}) + \hat{a}_{\mathbf{k}, \lambda}^\dagger e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \mathbf{e}_\lambda^*(\mathbf{k}) \right]$$

- The Hamiltonian H' therefore involves both a sum over the N atomic electrons, and a sum over all modes (\mathbf{k}, λ) of the EM field :

$$\hat{H}' = \frac{e}{m_e} \sum_{i=1}^N \sum_{\mathbf{k}, \lambda} N(\mathbf{k}) \left[\hat{a}_{\mathbf{k}, \lambda} e^{i(\mathbf{k} \cdot \mathbf{r}_i - \omega t)} \mathbf{e}_\lambda(\mathbf{k}) + \hat{a}_{\mathbf{k}, \lambda}^\dagger e^{-i(\mathbf{k} \cdot \mathbf{r}_i - \omega t)} \mathbf{e}_\lambda^*(\mathbf{k}) \right] \cdot \hat{\mathbf{p}}_i$$

- The contribution from the i 'th electron, and from a single mode (\mathbf{k}, λ) of the EM field, is

$$\hat{H}' = \frac{e}{m_e} N(\mathbf{k}) \left[\hat{a}_{\mathbf{k}, \lambda} e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \mathbf{e}_\lambda(\mathbf{k}) + \hat{a}_{\mathbf{k}, \lambda}^\dagger e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \mathbf{e}_\lambda^*(\mathbf{k}) \right] \cdot \hat{\mathbf{p}}$$

where, temporarily, we have dropped the suffix “ i ” on the position and momentum operators \mathbf{r}_i and \mathbf{p}_i of the i 'th electron

Atomic transitions (4)

- The Hamiltonian H' above is of the same form as that considered in discussing time-dependent perturbation theory (slide 9.49) :

$$\hat{H}'(t) = \hat{U}e^{-i\omega t} + \hat{U}^\dagger e^{i\omega t} \quad (11.6.1)$$

with

$$\hat{U} = \frac{e}{m_e} N(\mathbf{k}) \hat{a}_{\mathbf{k},\lambda} e^{i\mathbf{k}\cdot\mathbf{r}} \mathbf{e}_\lambda(\mathbf{k}) \cdot \hat{\mathbf{p}}$$

- Consider a transition $|1\rangle \rightarrow |2\rangle$ with initial and final states of the form

$$|1\rangle = |\alpha; \alpha_{\text{EM}}\rangle = |\alpha\rangle \otimes |\alpha_{\text{EM}}\rangle$$

$$|2\rangle = |\beta; \beta_{\text{EM}}\rangle = |\beta\rangle \otimes |\beta_{\text{EM}}\rangle$$

In such a transition, the state of the atom changes as

$$|\alpha\rangle \rightarrow |\beta\rangle ; \quad E_\alpha \rightarrow E_\beta$$

while, simultaneously, the state of the EM field changes as

$$|\alpha_{\text{EM}}\rangle \rightarrow |\beta_{\text{EM}}\rangle$$

- We can use Fermi's Golden Rule to obtain the rate for such transitions ...

Atomic transitions (5)

- First consider the case $E_\beta > E_\alpha$: Fermi's Golden Rule gives

$$\Gamma(1 \rightarrow 2) \propto |U_{21}|^2$$

where the contribution to the matrix element U_{21} for each electron and for each photon mode (\mathbf{k}, λ) is

$$\begin{aligned} U_{21} &\equiv \langle 2 | \hat{U} | 1 \rangle = \langle \beta; \beta_{\text{EM}} | \hat{U} | \alpha; \alpha_{\text{EM}} \rangle \\ &= \frac{e}{m_e} N(\mathbf{k}) \langle \beta; \beta_{\text{EM}} | \hat{a}_{\mathbf{k}, \lambda} e^{i\mathbf{k} \cdot \mathbf{r}} \mathbf{e}_\lambda(\mathbf{k}) \cdot \hat{\mathbf{p}} | \alpha; \alpha_{\text{EM}} \rangle \end{aligned}$$

- Photons involved in atomic transitions typically have a wavelength which is much greater than the scale of atomic radii (~ 1 nm)
 - ⇒ the variation of the phase $\mathbf{k} \cdot \mathbf{r}$ of the EM wave across the atom is negligible, and we can approximate

$$e^{i\mathbf{k} \cdot \mathbf{r}} \approx 1 + i\mathbf{k} \cdot \mathbf{r} + \dots \approx 1$$

Thus, to good approximation, the spatial variation of the EM wave plays no rôle; only its time dependence, $e^{i\omega t}$, is of consequence

Atomic transitions (6)

- In this approximation, the matrix element U_{21} factorises as

$$U_{21} = \frac{e}{m_e} N(\mathbf{k}) \langle \beta | \mathbf{e}_\lambda(\mathbf{k}) \cdot \hat{\mathbf{p}} | \alpha \rangle \langle \beta_{\text{EM}} | \hat{a}_{\mathbf{k}, \lambda} | \alpha_{\text{EM}} \rangle \quad (11.8.1)$$

- The only way that the matrix element $\langle \beta_{\text{EM}} | \hat{a}_{\mathbf{k}, \lambda} | \alpha_{\text{EM}} \rangle$ above can be non-zero is if the EM field *loses a single photon* from the mode (\mathbf{k}, λ) :

$$\langle \dots, n_{\mathbf{k}, \lambda}, \dots | \hat{a}_{\mathbf{k}, \lambda} | \dots, n_{\mathbf{k}, \lambda} + 1, \dots \rangle = \sqrt{n_{\mathbf{k}, \lambda} + 1} \quad (11.8.2)$$

(compare with $\langle n | \hat{a} | n + 1 \rangle = \sqrt{n + 1}$ for a single quantum oscillator)

- Thus the initial and final states of the EM field must be of the form

$$| \alpha_{\text{EM}} \rangle = | \dots, n_{\mathbf{k}, \lambda} + 1, \dots \rangle$$

$$| \beta_{\text{EM}} \rangle = | \dots, n_{\mathbf{k}, \lambda}, \dots \rangle$$

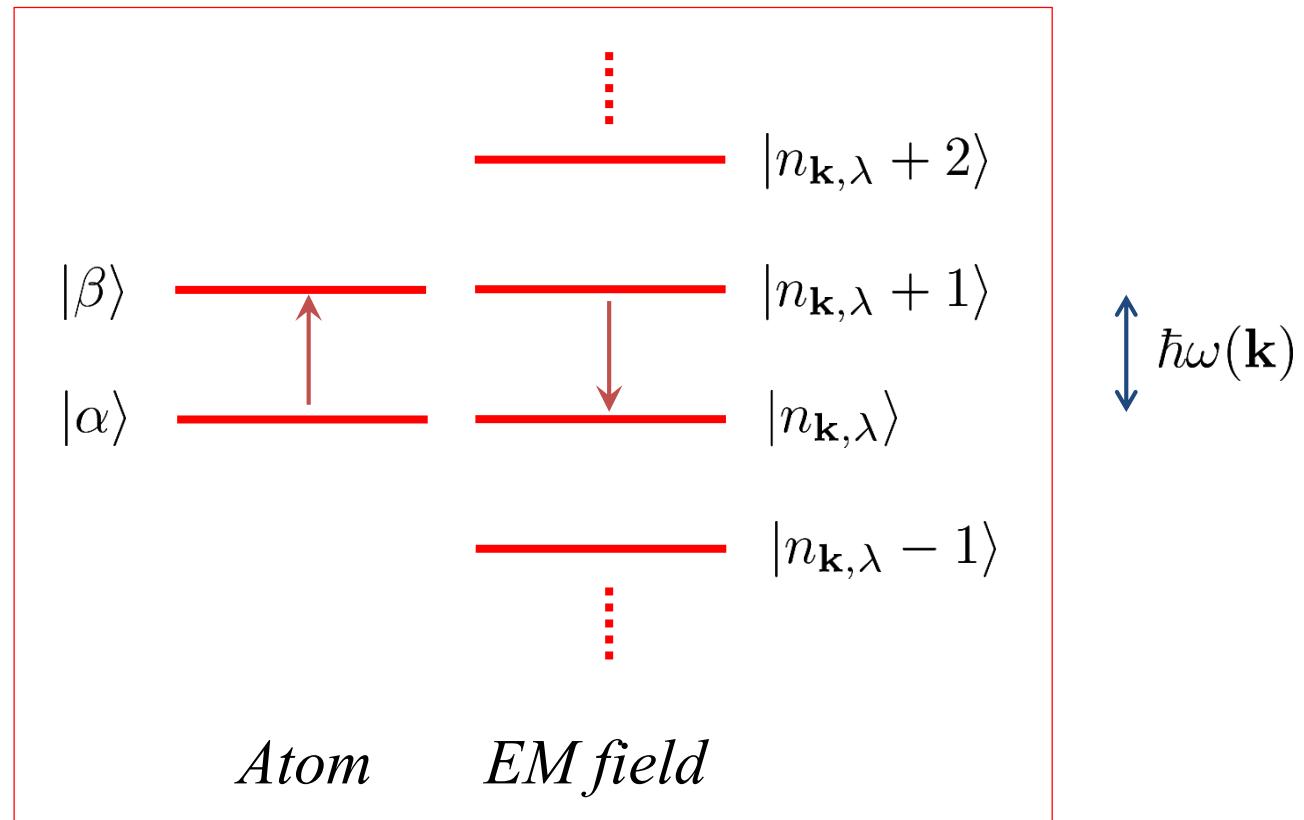
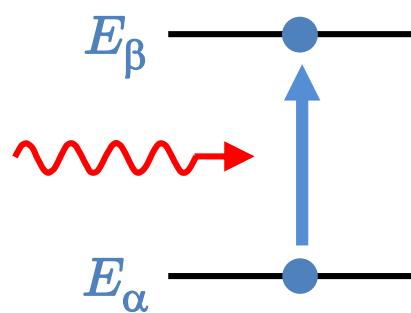
The mode (\mathbf{k}, λ) which loses a photon can be any mode such that total energy is conserved :

$$\omega = \omega(\mathbf{k}) = c|\mathbf{k}| = \omega_\beta - \omega_\alpha \quad (E_\alpha \equiv \hbar\omega_\alpha, E_\beta \equiv \hbar\omega_\beta)$$

Atomic transitions (7)

- Thus, for the case $E_\beta > E_\alpha$, the dominant transition process is **absorption** by the atom of a *single photon* from the EM field :

$$|\alpha; n_{\mathbf{k},\lambda} + 1\rangle \longrightarrow |\beta; n_{\mathbf{k},\lambda}\rangle$$



Atomic transitions (8)

- One mode, (\mathbf{k}, λ) , of the EM field loses one photon ;
the number of photons in all other EM modes must remain unchanged

For example, if we try at the same time to remove a photon from another mode, (\mathbf{k}', λ') , the matrix element U_{21} will vanish :

$$\langle \dots, n_{\mathbf{k},\lambda}, \dots, n_{\mathbf{k}',\lambda'}, \dots | \hat{a}_{\mathbf{k},\lambda} | \dots, n_{\mathbf{k},\lambda} + 1, \dots, n_{\mathbf{k}',\lambda'} + 1, \dots \rangle = 0$$

This is because the photon number states are orthogonal :

$$\langle n_{\mathbf{k}',\lambda'} | n_{\mathbf{k}',\lambda'} + 1 \rangle = 0$$

- Substituting equation (11.8.2) into equation (11.8.1), the matrix element U_{21} for absorption becomes

$$U_{21} = \frac{e}{m_e} N(\mathbf{k}) \langle \beta | \mathbf{e}_\lambda(\mathbf{k}) \cdot \hat{\mathbf{p}} | \alpha \rangle \sqrt{n_{\mathbf{k},\lambda} + 1}$$

(11.10.1)

Atomic transitions (9)

- Now consider the case $E_\beta < E_\alpha$: Fermi's Golden Rule gives the transition rate as

$$\Gamma(1 \rightarrow 2) \propto |U_{21}^\dagger|^2 \quad (11.11.1)$$

where

$$U_{21}^\dagger = \frac{e}{m_e} N(\mathbf{k}) \langle \beta | \mathbf{e}_\lambda^*(\mathbf{k}) \cdot \hat{\mathbf{p}} | \alpha \rangle \langle \beta_{\text{EM}} | \hat{a}_{\mathbf{k},\lambda}^\dagger | \alpha_{\text{EM}} \rangle \quad (11.11.2)$$

- The only way that the rightmost EM field factor can be non-zero is for the EM field to *gain* a single photon in a single mode :

$$|\alpha_{\text{EM}}\rangle = |..., n_{\mathbf{k},\lambda}, ... \rangle \quad \longrightarrow \quad |\beta_{\text{EM}}\rangle = |..., n_{\mathbf{k},\lambda} + 1, ... \rangle$$

$$\langle \dots, n_{\mathbf{k},\lambda} + 1, \dots | \hat{a}_{\mathbf{k},\lambda}^\dagger | \dots, n_{\mathbf{k},\lambda}, \dots \rangle = \sqrt{n_{\mathbf{k},\lambda} + 1} \quad (11.11.3)$$

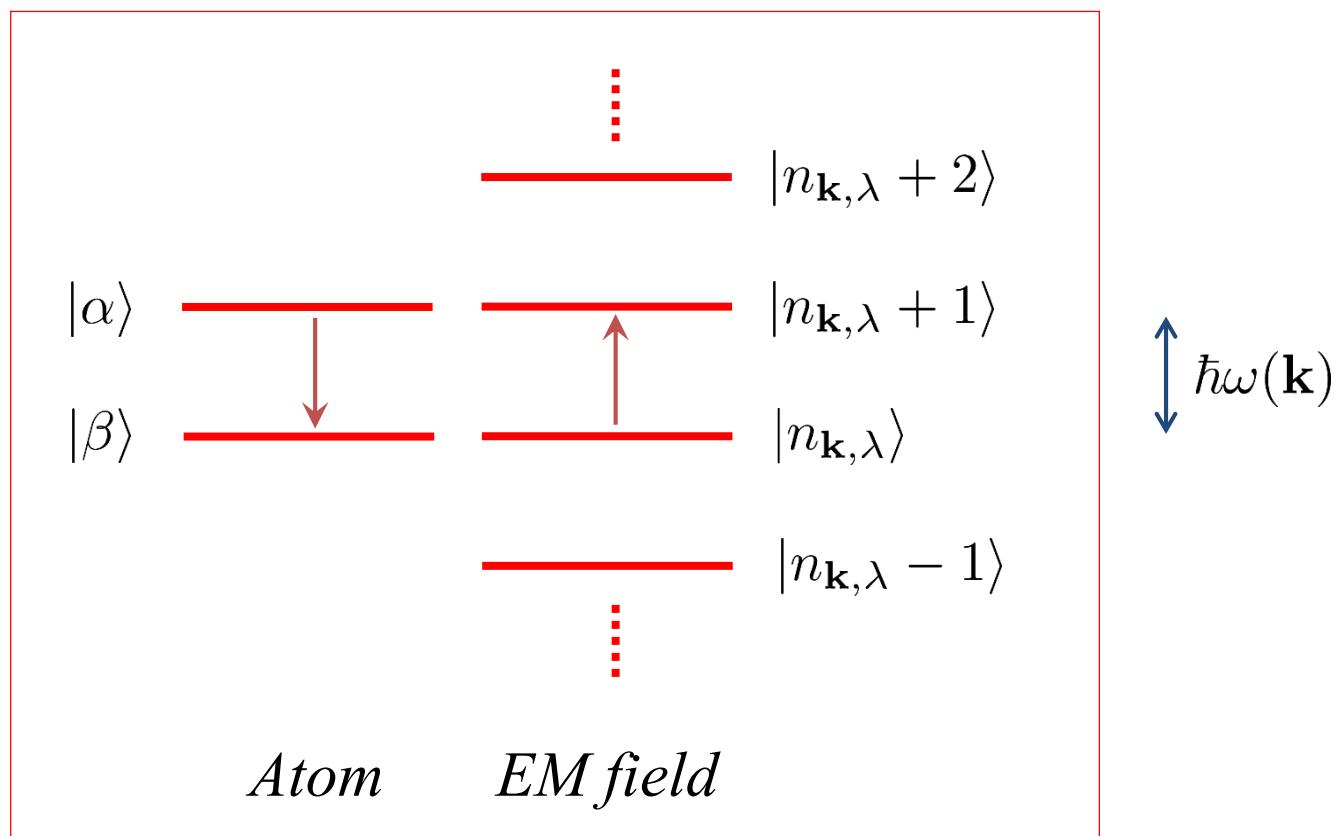
- Substituting equation (11.11.3) into equation (11.11.2), the matrix element for this process is

$$U_{21}^\dagger = \frac{e}{m_e} N(\mathbf{k}) \sqrt{n_{\mathbf{k},\lambda} + 1} \langle \beta | \mathbf{e}_\lambda^*(\mathbf{k}) \cdot \hat{\mathbf{p}} | \alpha \rangle \quad (11.11.4)$$

Atomic transitions (10)

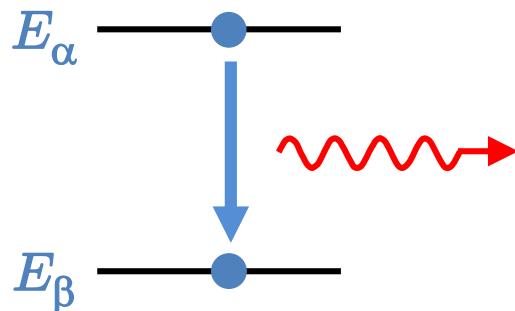
- Hence, for $E_\beta < E_\alpha$, the dominant transition process is **emission** by the atom of a *single photon* :

$$|\alpha; n_{\mathbf{k},\lambda}\rangle \rightarrow |\beta; n_{\mathbf{k},\lambda} + 1\rangle$$

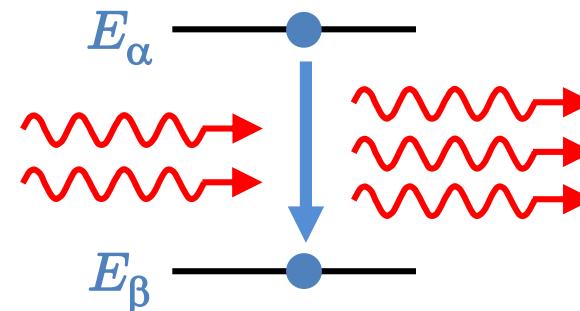


Atomic transitions (11)

- The case $n_{k,\lambda} = 0$ corresponds to **spontaneous emission**, in which a photon is emitted into a mode which is initially unoccupied (contains *no* photons)



spontaneous emission



stimulated emission

- The case $n_{k,\lambda} \geq 1$ corresponds to **stimulated emission**, in which a photon is added to a mode which is already occupied; thus the new photon has the

same energy, same direction, same polarisation state

as the photons which already occupy that mode

Stimulated emission “*clones*” photons; in the *maser* and *laser*, this is used to provide amplification of one or a few modes of the EM field

Emission Rates

- In the case of *emission*, and restoring the suffix “*i*” indicating the *i*’th atomic electron, we have to evaluate the matrix element

$$U_{21}^\dagger = \frac{e}{m_e} N(\mathbf{k}) \sqrt{n_{\mathbf{k},\lambda} + 1} \langle \beta | \mathbf{e}_\lambda^*(\mathbf{k}) \cdot \hat{\mathbf{p}}_i | \alpha \rangle \quad (11.14.1)$$

- The momentum operator $\hat{\mathbf{p}}_i = -i\hbar \nabla_i$ above is not so easy to work with; We can obtain a more convenient form by making use of commutation relations (see slide 1.14) satisfied by the *i*’th and *j*’th electrons :

$$[\hat{\mathbf{r}}_i, \hat{\mathbf{p}}_j^2] = 2i\hbar \hat{\mathbf{p}}_i \delta_{ij} ; \quad [\hat{\mathbf{r}}_i, V] = 0$$

- The unperturbed Hamiltonian H_0 (slide 11.4) therefore satisfies

$$[\hat{\mathbf{r}}_i, \hat{H}_0] = \frac{i\hbar}{m_e} \hat{\mathbf{p}}_i$$

We can now reformulate equation (11.14.1) above as

$$U_{21}^\dagger = -\frac{ie}{\hbar} N(\mathbf{k}) \sqrt{n_{\mathbf{k},\lambda} + 1} \langle \beta | \mathbf{e}_\lambda^*(\mathbf{k}) \cdot [\hat{\mathbf{r}}_i, \hat{H}_0] | \alpha \rangle$$

Emission rates (2)

- The final factor involves the matrix element

$$\langle \beta | [\hat{\mathbf{r}}_i, \hat{H}_0] | \alpha \rangle = \langle \beta | (\hat{\mathbf{r}}_i \hat{H}_0 - \hat{H}_0 \hat{\mathbf{r}}_i) | \alpha \rangle = (E_\alpha - E_\beta) \langle \beta | \hat{\mathbf{r}}_i | \alpha \rangle$$

where $\hat{H}_0 | \alpha \rangle = E_\alpha | \alpha \rangle$, $\langle \beta | \hat{H}_0 = E_\beta \langle \beta |$

- Thus the overall matrix element is now expressed in terms of the *position* operator \mathbf{r}_i , rather than the momentum operator \mathbf{p}_i :

$$U_{21}^\dagger = -ie\omega_0 N(\mathbf{k}) \sqrt{n_{\mathbf{k},\lambda} + 1} \langle \beta | \mathbf{e}_\lambda^*(\mathbf{k}) \cdot \hat{\mathbf{r}}_i | \alpha \rangle$$

where

$$\omega_0 \equiv \omega_\alpha - \omega_\beta > 0$$

$$\begin{cases} E_\alpha \equiv \hbar\omega_\alpha \\ E_\beta \equiv \hbar\omega_\beta \end{cases}$$

- Restoring the summation over the N atomic electrons, this is

$$U_{21}^\dagger = i\omega_0 N(\mathbf{k}) \sqrt{n_{\mathbf{k},\lambda} + 1} \langle \beta | \mathbf{e}_\lambda^*(\mathbf{k}) \cdot \hat{\mathbf{d}} | \alpha \rangle$$

where

$$\hat{\mathbf{d}} \equiv -e \sum_{i=1}^N \hat{\mathbf{r}}_i$$

*electric dipole
operator*

Emission rates (3)

- The overall matrix element can now be written as

$$U_{21}^\dagger = i\omega_0 N(\mathbf{k}) \sqrt{n_{\mathbf{k},\lambda} + 1} (\mathbf{e}_\lambda^*(\mathbf{k}) \cdot \mathbf{d}_{\beta\alpha})$$

where $\mathbf{d}_{\beta\alpha} \equiv \langle \beta | \hat{\mathbf{d}} | \alpha \rangle$ is a *complex* three-vector of matrix elements :

$$\mathbf{d}_{\beta\alpha} = (d_x, d_y, d_z) = (\langle \beta | \hat{d}_x | \alpha \rangle, \langle \beta | \hat{d}_y | \alpha \rangle, \langle \beta | \hat{d}_z | \alpha \rangle)$$

The transition rate (emission rate) is proportional to

$$|U_{21}^\dagger|^2 = N(\mathbf{k})^2 \omega_0^2 (n_{\mathbf{k},\lambda} + 1) |\mathbf{e}_\lambda^*(\mathbf{k}) \cdot \mathbf{d}_{\beta\alpha}|^2$$

- From slide 10.27, the normalisation factor above is

$$N(\mathbf{k})^2 = \frac{\hbar}{2\epsilon_0 \omega(\mathbf{k}) V}$$

The continuum version of Fermi's Golden Rule then gives the transition rate for emission as

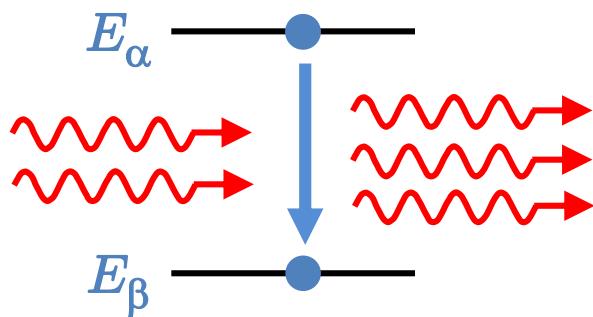
$$\Gamma(1 \rightarrow 2) = \frac{\pi \omega_0}{\epsilon_0 V} (n_{\mathbf{k},\lambda} + 1) |\mathbf{e}_\lambda^*(\mathbf{k}) \cdot \mathbf{d}_{\beta\alpha}|^2 g(E_k)$$

(11.16.1)

Emission rates (4)

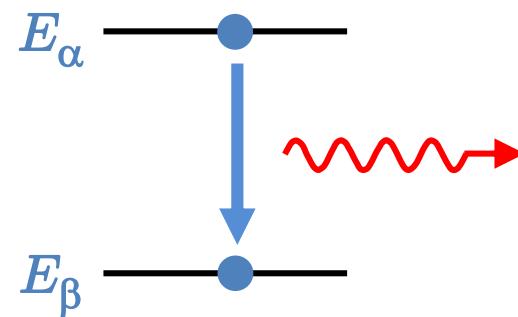
The emission rate in equation (11.16.1) is proportional to $(n_{k,\lambda} + 1)/V$:

- The component proportional to $n_{k,\lambda}/V$ (the photon number density) is the *stimulated emission* rate



$$\Gamma \propto n_{k,\lambda}/V$$

stimulated emission



$$\Gamma \propto 1/V$$

spontaneous emission

- The component proportional to $1/V$ is the *spontaneous emission* rate :
 - independent of the external EM field
 - depends only on the properties of the initial and final atomic states

The electric dipole approximation

- The transition rate of equation (11.16.1) is the same as would be obtained for an *electric dipole* perturbation

$$\hat{H}' = -\hat{\mathbf{E}}(\mathbf{r}, t) \cdot \hat{\mathbf{d}}$$

where $\hat{\mathbf{E}}$ is the operator equivalent of the mode expansion of the electric field on slide 10.12 :

$$\hat{\mathbf{E}}(\mathbf{r}, t) = \sum_{\mathbf{k}, \lambda} i\omega(\mathbf{k}) N(\mathbf{k}) \left[\hat{a}_{\mathbf{k}, \lambda} e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \mathbf{e}_\lambda(\mathbf{k}) - \hat{a}_{\mathbf{k}, \lambda}^\dagger e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \mathbf{e}_\lambda^*(\mathbf{k}) \right]$$

- The approximation $e^{i\mathbf{k} \cdot \mathbf{r}} \approx 1$ of slide 11.7 which led to equation (11.16.1) is thus known as the ***electric dipole approximation***

Atomic transitions which are permitted by an electric dipole interaction are known as ***electric dipole (E1) transitions***

Spontaneous Emission

$$|\alpha\rangle \rightarrow |\beta\rangle + \gamma_{\mathbf{k},\lambda}$$

- Consider the *spontaneous emission* of a photon into an infinitesimal solid angle $d\Omega$ around the \mathbf{k} direction, in polarisation state $\mathbf{e}_\lambda(\mathbf{k})$:

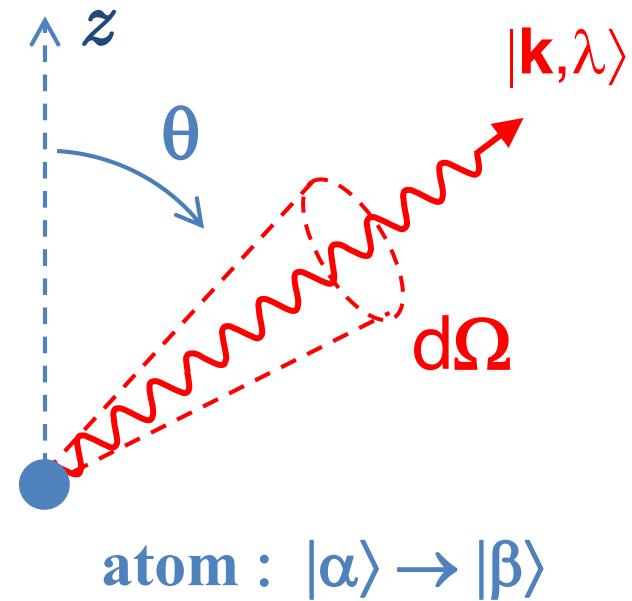
The photon energy and frequency are

$$E_k = \hbar\omega(\mathbf{k}) = E_\alpha - E_\beta = \hbar\omega_\alpha - \hbar\omega_\beta$$

$$\omega_0 = \omega(\mathbf{k}) = c|\mathbf{k}| = \omega_\alpha - \omega_\beta$$

The density of states available to the emitted photon is (see Appendix B of Handout 3)

$$g(E_k) = \frac{VE_k^2}{(2\pi\hbar c)^3} d\Omega$$



- The emission rate is given by the $1/V$ component of equation (11.16.1):

$$d\Gamma = \frac{\pi\omega_0}{\epsilon_0 V} |\mathbf{e}_\lambda^*(\mathbf{k}) \cdot \mathbf{d}_{\beta\alpha}|^2 g(E_k) \quad (11.19.1)$$

Spontaneous emission (2)

- Substituting for $g(E_k)$ in equation (11.19.1) gives the emission rate as

$$d\Gamma = \frac{\omega_0^3}{8\pi^2\epsilon_0\hbar c^3} |\mathbf{e}_\lambda^*(\mathbf{k}) \cdot \mathbf{d}_{\beta\alpha}|^2 d\Omega$$

(the arbitrary normalisation volume V has now cancelled)

Equivalently, this can be expressed as the **differential decay rate** :

$$\boxed{\left. \frac{d\Gamma_\lambda}{d\Omega} \right|_{(\alpha \rightarrow \beta)} = \frac{\omega_0^3}{8\pi^2\epsilon_0\hbar c^3} |\mathbf{e}_\lambda^*(\mathbf{k}) \cdot \mathbf{d}_{\beta\alpha}|^2} \quad (11.20.1)$$

$$\frac{d\Gamma_\lambda}{d\Omega} d\Omega = \left\{ \begin{array}{l} \text{the \# of photons in polarisation state } \lambda \text{ emitted per unit} \\ \text{time per atom into a solid angle } d\Omega \text{ in the direction } (\theta, \phi) \end{array} \right.$$

- Equation (11.20.1) can be considered as the “master formula” for spontaneous decay between any given pair of atomic eigenstates $|\alpha\rangle$ and $|\beta\rangle$:

$$|\alpha\rangle \rightarrow |\beta\rangle + \gamma_{\mathbf{k},\lambda}; \quad E_\alpha - E_\beta = \hbar\omega_0$$

Spontaneous emission (3)

- The complex three-vector scalar product in equation (11.20.1) is

$$\mathbf{e}_\lambda^*(\mathbf{k}) \cdot \mathbf{d}_{\beta\alpha} = \mathbf{e}_\lambda^*(\mathbf{k}) \cdot \langle \beta | \hat{\mathbf{d}} | \alpha \rangle ; \quad \hat{\mathbf{d}} = -e \sum_{i=1}^N \hat{\mathbf{r}}_i$$

- The **total decay rate**, Γ , can be obtained by integrating over all possible photon directions, and summing over both possible polarisation states :

$$\Gamma(\alpha \rightarrow \beta) = \sum_\lambda \int \frac{d\Gamma_\lambda}{d\Omega} \Big|_{(\alpha \rightarrow \beta)} d\Omega$$

- Using explicit forms for the polarisation vectors $\mathbf{e}(\mathbf{k})$, a straightforward calculation (see Appendix A) gives the result (for any polarisation basis)

$$\sum_\lambda \int |\mathbf{e}_\lambda^*(\mathbf{k}) \cdot \mathbf{d}_{\beta\alpha}|^2 d\Omega = \frac{8\pi}{3} |\mathbf{d}_{\beta\alpha}|^2$$

where, in terms of spherical component matrix elements,

$$|\mathbf{d}_{\beta\alpha}|^2 = |\langle \beta | \hat{d}_{+1} | \alpha \rangle|^2 + |\langle \beta | \hat{d}_{-1} | \alpha \rangle|^2 + |\langle \beta | \hat{d}_0 | \alpha \rangle|^2$$

Spontaneous emission (4)

- The total decay rate is therefore

$$\Gamma(\alpha \rightarrow \beta) = \frac{\omega_0^3}{3\pi\epsilon_0\hbar c^3} |\mathbf{d}_{\beta\alpha}|^2 \quad (11.22.1)$$

$$\Gamma = \frac{\omega_0^3}{3\pi\epsilon_0\hbar c^3} \left(|\langle \beta | \hat{d}_{+1} | \alpha \rangle|^2 + |\langle \beta | \hat{d}_{-1} | \alpha \rangle|^2 + |\langle \beta | \hat{d}_0 | \alpha \rangle|^2 \right)$$

- We now apply these results to the particular case that the initial and final atomic states $|\alpha\rangle$ and $|\beta\rangle$ are angular momentum eigenstates :

$$|\alpha J m_J\rangle \rightarrow |\alpha' J' m'_J\rangle + \gamma$$

This will allow us to compute :

- the *lifetimes* of atomic states
- the *angular distribution* and *polarisation* of the emitted photons

- This has important consequences and applications in, for example, the *Zeeman effect* and *optical pumping*

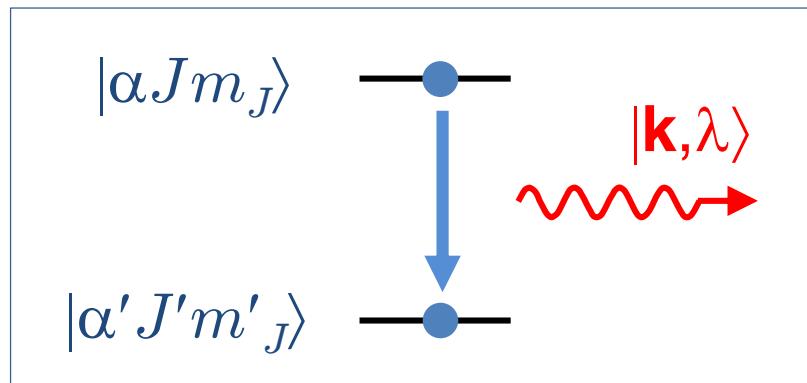
Spontaneous Decay : Angular Momentum

- Consider spontaneous decay between a pair of atomic angular momentum eigenstates :

$$|\alpha J m_J\rangle \rightarrow |\alpha' J' m'_J\rangle + \gamma$$

The complex vector of dipole matrix elements in this case is

$$\mathbf{d}_{\beta\alpha} = \langle \alpha' J' m'_J | \hat{\mathbf{d}} | \alpha J m_J \rangle$$



- The total decay rate is given by

$$\Gamma = \frac{\omega_0^3}{3\pi\epsilon_0\hbar c^3} \left(|d_{+1}|^2 + |d_{-1}|^2 + |d_0|^2 \right)$$

where each of the dipole matrix elements d_m is of the form

$$d_m = \langle \alpha' J' m'_J | \hat{d}_m | \alpha J m_J \rangle = \langle \alpha' J' \| \hat{\mathbf{d}} \| \alpha J \rangle \langle 1m; J m_J | J' m'_J \rangle$$

Spontaneous decay : angular momentum (2)

- The Clebsch-Gordan coefficient $\langle 1m; Jm_J | J'm'_J \rangle$ vanishes unless the quantum numbers involved satisfy the conditions

$$m + m_J = m'_J \quad (m = 0, \pm 1); \quad 1 \otimes J = J'$$

- Hence electric dipole transitions between angular momentum eigenstates must satisfy the selection rules

$$\Delta m_J \equiv m'_J - m_J = 0, \pm 1$$

$$\Delta J \equiv J' - J = 0, \pm 1; \quad J + J' \geq 1 \quad (0 \not\rightarrow 0)$$

- The Δm_J selection rule allows **three** possibilities :

$$\Delta m_J = 0 : \quad \langle J', m_J | \hat{d}_0 | Jm_J \rangle = \langle J' \parallel \hat{\mathbf{d}} \parallel J \rangle \langle 1, 0; Jm_J | J', m_J \rangle$$

$$\Delta m_J = +1 : \quad \langle J', m_J + 1 | \hat{d}_{+1} | Jm_J \rangle = \langle J' \parallel \hat{\mathbf{d}} \parallel J \rangle \langle 1, +1; Jm_J | J', m_J + 1 \rangle$$

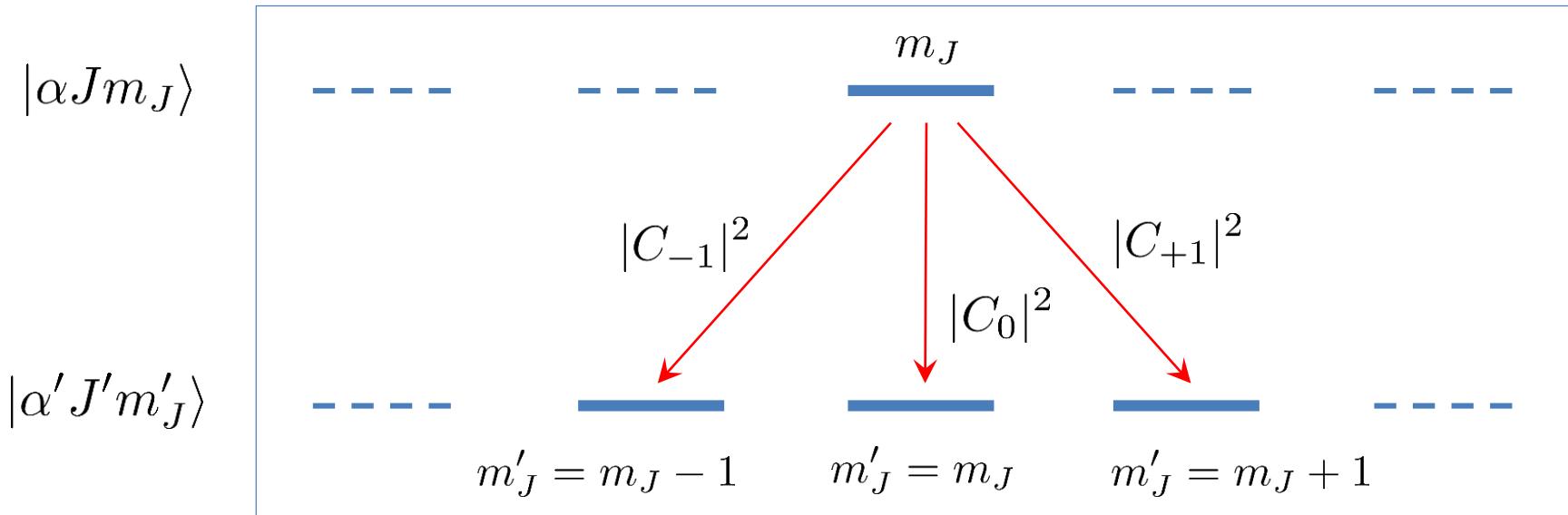
$$\Delta m_J = -1 : \quad \langle J', m_J - 1 | \hat{d}_{-1} | Jm_J \rangle = \langle J' \parallel \hat{\mathbf{d}} \parallel J \rangle \langle 1, -1; Jm_J | J', m_J - 1 \rangle$$

Spontaneous decay : angular momentum (3)

- These differ from each other by only a Clebsch-Gordan coefficient :

$$C_m = \langle 1m; Jm_J | J'm'_J \rangle$$

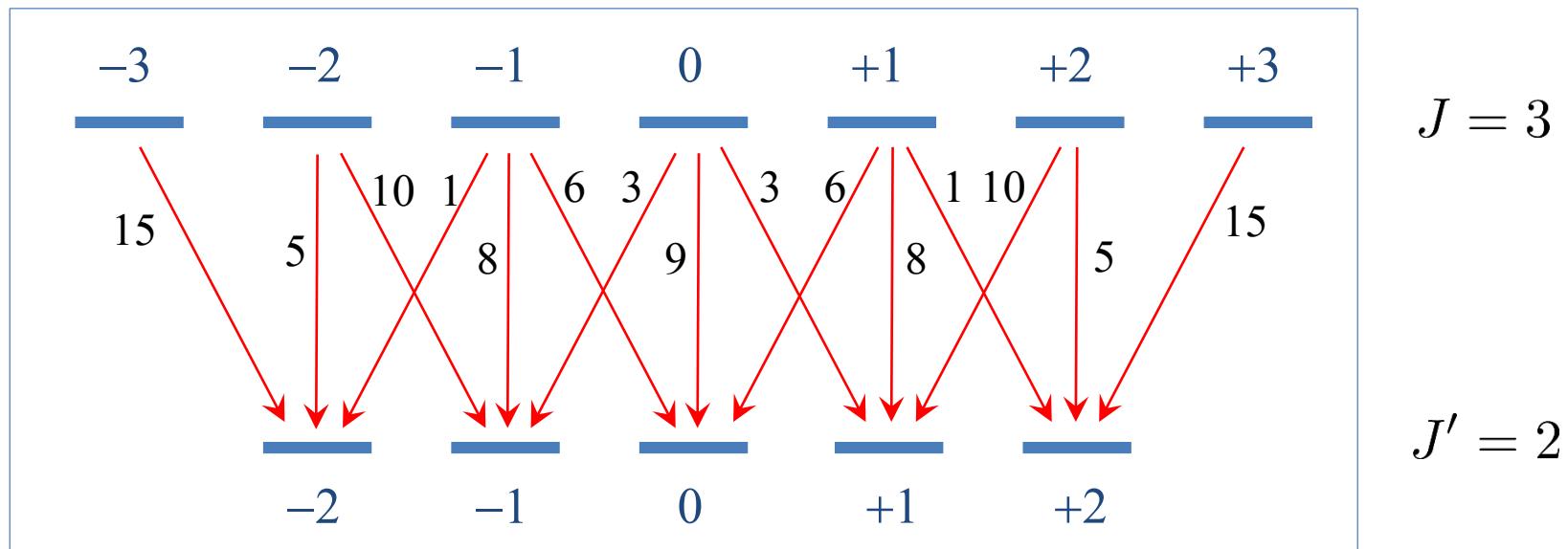
- Hence we can represent the *relative* decay rates as



$$\Gamma(m_J \rightarrow m'_J) = \frac{\omega_0^3}{3\pi\epsilon_0\hbar c^3} |\langle \alpha' J' | \hat{d} | \alpha J \rangle|^2 |C_m|^2$$

EXAMPLE : Spontaneous decay $3 \rightarrow 2$

- For example, consider the case $|3, m_J\rangle \rightarrow |2, m'_J\rangle$:
The selection rule $\Delta m_J = -1, +1, 0$ allows only **15** of the 35 transitions which are *a priori* possible :



- The number next to each arrow shows the *relative rate* for the transition, obtained from the square of the associated Clebsch-Gordan coefficient :

$$r \propto |C_m|^2$$

Example : spontaneous decay $3 \rightarrow 2$ (2)

- For example, consider the $\Delta m_J = +1$ transition

$$|3, -1\rangle \rightarrow |2, 0\rangle$$

$$d = \langle \alpha' 2, 0 | \hat{d}_{+1} | \alpha 3, -1 \rangle = \langle \alpha' 2 | \hat{d} | \alpha 3 \rangle C$$

$$C = \langle 1, +1; 3, -1 | 2, 0 \rangle$$

Aargh!! we need a $1 \otimes 3$ table of C-G coefficients !!

- Using $(\hat{d}_{+1})^\dagger = -\hat{d}_{-1}$, we can invert the initial and final states,

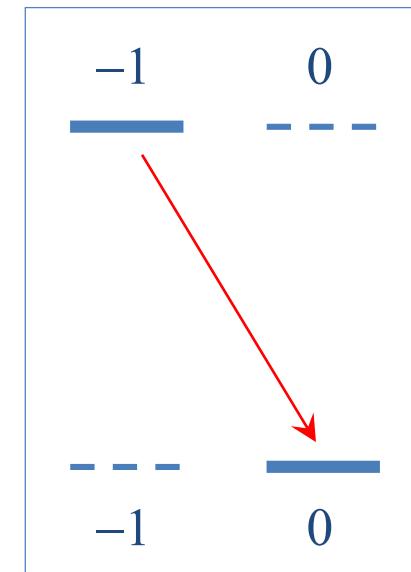
$$d^* = \langle \alpha' 2, 0 | \hat{d}_{+1} | \alpha 3, -1 \rangle^* = -\langle \alpha 3, -1 | \hat{d}_{-1} | \alpha' 2, 0 \rangle$$

and instead evaluate the *conjugate* matrix element

$$\langle \alpha 3, -1 | \hat{d}_{-1} | \alpha' 2, 0 \rangle = \langle \alpha 3 | \hat{d} | \alpha' 2 \rangle C'$$

$$C' = \langle 1, -1; 2, 0 | 3, -1 \rangle$$

That's better! the C-G coefficients now come from $1 \otimes 2 = 3$, which is more readily available (next slide) than $1 \otimes 3 = 2$



43. CLEBSCH-GORDAN COEFFICIENTS, SPHERICAL HARMONICS, AND d FUNCTIONS

Note: A square-root sign is to be understood over *every* coefficient, e.g., for $-8/15$ read $-\sqrt{8/15}$.

J	J	...
M	M	...
m_1	m_2	
m_1	m_2	Coefficients
\vdots	\vdots	\vdots

$1/2 \times 1/2$	$\begin{matrix} 1 \\ +1 \\ +1/2+1/2 \\ +1/2-1/2 \\ -1/2+1/2 \\ -1/2-1/2 \end{matrix}$	$\begin{matrix} 1 & 1 & 0 \\ 0 & 0 & 0 \end{matrix}$
		$\begin{matrix} 1 \\ 0 \\ -1/2-1/2 \end{matrix}$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$Y_1^1 = -\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi}$$

$$Y_2^0 = \sqrt{\frac{5}{4\pi}} \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right)$$

$$Y_2^1 = -\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{i\phi}$$

$$Y_2^2 = \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2 \theta e^{2i\phi}$$

$1 \times 1/2$	$\begin{matrix} 3/2 \\ +3/2 \\ +1+1/2 \end{matrix}$	$\begin{matrix} 3/2 & 1/2 \\ 1 & +1/2+1/2 \end{matrix}$
		$\begin{matrix} +1-1/2 \\ 0+1/2 \end{matrix}$
		$\begin{matrix} 1/3 & 2/3 \\ 2/3 & -1/3 \end{matrix}$
		$\begin{matrix} -1/2-1/2 \\ 0 \\ -1+1/2 \end{matrix}$

2×1	$\begin{matrix} 3 \\ +3 \\ +2+1 \end{matrix}$	$\begin{matrix} 3 & 2 & 1 \\ +2 & 0 & 1/3 & 2/3 \\ +1 & +1 & 2/3 & -1/3 \end{matrix}$
		$\begin{matrix} +1 & +1 & +1 \end{matrix}$
		$\begin{matrix} 1/2-1/2 \\ 0 \\ -1+1/2 \end{matrix}$

1×1	$\begin{matrix} 2 \\ +2 \\ +1+1 \end{matrix}$	$\begin{matrix} 2 & 1 & 0 \\ 0+1 & 2/5 & -1/2 \\ 1 & +1 & +1 \end{matrix}$
		$\begin{matrix} 1/2-1/2 \\ 0 \\ -1+1/2 \end{matrix}$
		$\begin{matrix} 2/5-1/2 \\ 0 \\ 0 \end{matrix}$
		$\begin{matrix} 1/10-8/15 \\ 1/6 \\ 0 \end{matrix}$

$$Y_\ell^{-m} = (-1)^m Y_\ell^{m*}$$

$0-1$	$1/2$	$1/2$	2
-1	0	$1/2-1/2$	-2

$-1-1$	1
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Example : spontaneous decay $3 \rightarrow 2$ (3)

- From the $1 \otimes 2$ table, the Clebsch-Gordan coefficient for $|3, -1\rangle \rightarrow |2, 0\rangle$ is

$$C' = \langle 1, -1; 2, 0 | 3, -1 \rangle = \sqrt{2/5}$$

Including for convenience an overall normalisation factor of 15 then gives the relative rates shown on slide 11.26 :

$$|3, -1\rangle \rightarrow |2, 0\rangle ; \quad r = 15 |C'|^2 = 15 \times (2/5) = 6$$

- In fact, the relevant $1 \otimes 3$ Clebsch-Gordan coefficient is

$$C = \langle 1, +1; 3, -1 | 2, 0 \rangle = \sqrt{2/7}$$

The reduced matrix elements on slide 11.27 are therefore related as

$$|\langle \alpha 3 | \hat{\mathbf{d}} | \alpha' 2 \rangle|^2 = \frac{5}{7} |\langle \alpha' 2 | \hat{\mathbf{d}} | \alpha 3 \rangle|^2$$

- In general, we can use whichever ordering of initial and final states is most convenient, but be aware that the r.m.e.'s are, in general, *different* :

$$|\langle \alpha J | \hat{\mathbf{d}} | \alpha' J' \rangle|^2 = \frac{(2J' + 1)}{(2J + 1)} |\langle \alpha' J' | \hat{\mathbf{d}} | \alpha J \rangle|^2$$

Example : spontaneous decay $3 \rightarrow 2$ (4)

- In the diagram on slide 11.26 :

$$15 = 5 + 10 = 1 + 8 + 6 = 3 + 9 + 3$$

the summed decay rates from each upper state m_J are all equal

This reflects the unitarity of the matrix of C-G coefficients, and holds quite generally for any $J \rightarrow J'$, not just for $3 \rightarrow 2$

- This is as expected from rotational invariance :
 - the overall decay rate (lifetime) of an isolated atom cannot possibly depend on a quantum number such as m_J , which is defined with respect to an arbitrary choice of spatial direction (the z axis)
- Equivalently, if the decay rate *did* depend on m_J :
 - an initially unpolarised sample of atoms would develop a net polarisation as the atoms in the sample decayed

But no preferred spatial direction is involved – we cannot develop a preferred direction (a net polarisation) “out of nothing”

Example : spontaneous decay $3 \rightarrow 2$ (5)

- Any *mixture* of upper level states m_J , and hence also *any* upper level energy eigenstate $|\alpha\rangle$, has the same total decay rate (same lifetime)
 - the lifetime is a property of the energy level itself

For example:

$$\Gamma_{|3-3\rangle} = 15$$

$$\Gamma_{|2-1\rangle} = 15$$

$$\Gamma_{\frac{1}{\sqrt{2}}(|3-3\rangle+|2-1\rangle)} = 15$$

EXAMPLE : the sodium D-lines

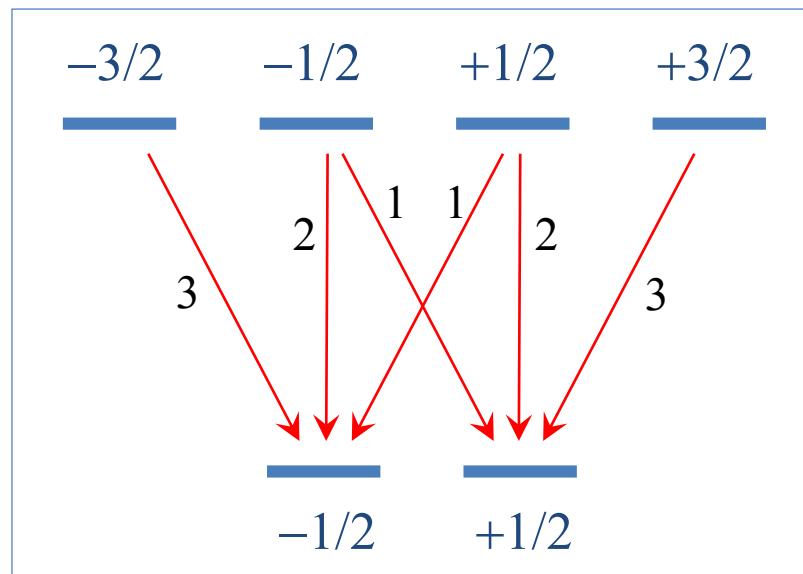
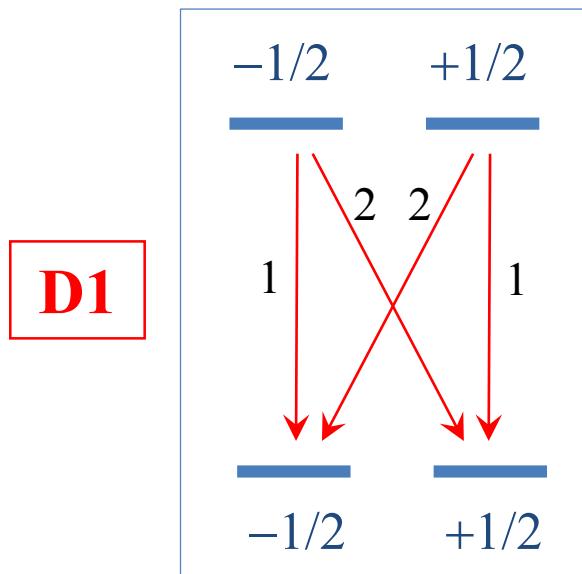
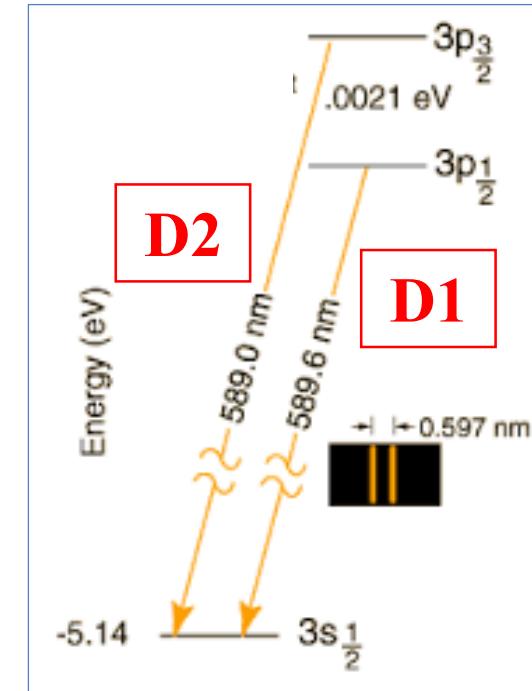
- As another example, consider the sodium D-lines :

$$D1 : \quad 1/2 \rightarrow 1/2 \quad |3P_{1/2}\rangle \rightarrow |3S_{1/2}\rangle$$

$$D2 : \quad 3/2 \rightarrow 1/2 \quad |3P_{3/2}\rangle \rightarrow |3S_{1/2}\rangle$$

$(J \rightarrow J')$

- The selection rule $\Delta m_J = -1, +1, 0$ allows the transitions below :



D2

Example : the sodium D-lines (2)

- The relative transition rates are derived from the squares of the appropriate Clebsch-Gordan coefficients, as tabulated below :

From the $1 \otimes 1/2$ table (see slide 1.75)

		D1 $^3P_{1/2} \rightarrow ^1S_{1/2}$	D2 $^3P_{3/2} \rightarrow ^1S_{1/2}$
$m_J \rightarrow m'_J$	Δm_J	$1 \otimes \frac{1}{2} = \frac{1}{2}$	$1 \otimes \frac{1}{2} = \frac{3}{2}$
+3/2 → +1/2	-1		1
+1/2 → +1/2	0	1/3	2/3
+1/2 → -1/2	-1	2/3	1/3
-1/2 → +1/2	+1	2/3	1/3
-1/2 → -1/2	0	1/3	2/3
-3/2 → -1/2	+1		1

Spontaneous decay : absolute decay rates

- To find the *absolute* decay rates (rather than just the *relative* rates), we need to fully evaluate just one of the possible transitions :

e.g. choose a D2 transition

$$|J, m_J\rangle \rightarrow |J', m'_J\rangle$$

$$\text{D2} \quad |3P_{3/2}\rangle \rightarrow |3S_{1/2}\rangle : \quad |\frac{3}{2}, +\frac{1}{2}\rangle \rightarrow |\frac{1}{2}, +\frac{1}{2}\rangle$$

+1/2



+1/2

- Assuming LS-coupling, we can expand the initial and final angular momentum states in terms of product states $|L, m_L\rangle \otimes |S, m_S\rangle$ (slide 1.73) :

$$3P_{3/2} : \quad |\frac{3}{2}, +\frac{1}{2}\rangle = \sqrt{\frac{1}{3}}|11\rangle|\downarrow\rangle + \sqrt{\frac{2}{3}}|10\rangle|\uparrow\rangle \quad (1 \otimes \frac{1}{2} = \frac{3}{2})$$

$$3S_{1/2} : \quad |\frac{1}{2}, +\frac{1}{2}\rangle = |00\rangle|\uparrow\rangle \quad (1 \otimes \frac{1}{2} = \frac{1}{2})$$

- Since the electric dipole operator \mathbf{d} is independent of spin, and since $\langle \uparrow | \downarrow \rangle = 0$, the matrix element for the transition is then obtained as

$$d = \langle \alpha \frac{3}{2}, +\frac{1}{2} | \hat{d}_0 | \alpha' \frac{1}{2}, +\frac{1}{2} \rangle = \sqrt{\frac{2}{3}} \langle 10 | \hat{d}_0 | 00 \rangle \quad (11.34.1)$$

(only the “spin-up” components contribute)

Spontaneous decay : absolute decay rates (2)

- Thus, to determine all the absolute D1 and D2 decay rates, we “only” need to evaluate a single spatial matrix element :

$$\langle 10 | \hat{d}_0 | 00 \rangle = -e \sum_{i=1}^N \langle 10 | z_i | 00 \rangle$$

For sodium, this requires an integration over Hartree-Fock wavefunctions such as those plotted on slide 7.22, which can only be done numerically

- For *hydrogen*, the analog of the sodium D-lines is the doublet of $2p \rightarrow 1s$ transitions :

$$|2P_{3/2}\rangle \rightarrow |1S_{1/2}\rangle ; \quad |2P_{1/2}\rangle \rightarrow |1S_{1/2}\rangle$$

In this case, the (zeroth-order) wavefunctions are known explicitly, and the matrix element above can be evaluated *analytically* [EXAMPLES SHEET]

The predicted mean lifetimes, $\tau = 1/\Gamma$, are shown to be the same for the $2P_{3/2}$ and $2P_{1/2}$ levels, and to agree with the measured value :

$$\tau(2P_{3/2} \rightarrow 1S_{1/2}) \approx \tau(2P_{1/2} \rightarrow 1S_{1/2}) \approx 1.56 \times 10^{-9} \text{ s}$$

Spontaneous decay : absolute decay rates (3)

- Returning to sodium, the lifetimes for the sodium D-line doublet are also measured to be approximately equal :

$$D2 : \tau(3^2P_{3/2} \rightarrow 3^2S_{1/2}) = 16.254 \pm 0.022 \text{ ns}$$

$$D1 : \tau(3^2P_{1/2} \rightarrow 3^2S_{1/2}) = 16.299 \pm 0.021 \text{ ns}$$

[U. Volz et al., Phys. Rev. Lett. 76 \(1996\) 2862](#)

i.e. about ten times longer-lived than hydrogen $2P \rightarrow 1S$

(the factor of ω^3 in the decay rate, $\Gamma \propto \omega^3$, contributes a lifetime ratio of about 100; the dipole matrix element factors, $\Gamma \propto |d|^2$, contribute a ratio of about 0.1)

Stimulated Emission

- The *stimulated* emission rate is given by the $n_{\mathbf{k},\lambda}/V$ component of equation (11.16.1)

Thus, relative to the *spontaneous* emission rate :

the stimulated emission rate contains an extra factor of $n_{\mathbf{k},\lambda}$

- In general, the external EM field will not be characterised by the photon number $n_{\mathbf{k},\lambda}$ *per se*, but by some other quantity such as the energy density $u(\omega)$ per unit interval of frequency ω

e.g. thermal radiation at temperature T :
$$u(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

- We consider, initially, an EM field which is isotropic and unpolarised, and is characterised by its energy density $u(\omega)$
[where the energy density $u(\omega)$ need not necessarily be thermal]

Stimulated Emission (2)

- In an interval dk , in volume V , the EM field energy is

$$dU = u(\omega) V d\omega = u(\omega) V c dk \quad (11.63.1)$$

- For an isotropic and unpolarised field, the photon number $n_{k,\lambda}$ in any mode must be independent of the direction of \mathbf{k} and of the polarisation state λ :
i.e. $n_{k,\lambda}$ depends only on the magnitude $k = |\mathbf{k}| = \omega/c$
- The number of modes in the interval dk is (see Appendix B of Handout 3)

$$g(k) dk = \frac{k^2 V}{2\pi^2} dk$$

Hence, in terms of photon number, the energy dU is obtained as

$$dU = 2n_{k,\lambda}\hbar\omega g(k) dk = 2n_{k,\lambda}\hbar\omega \frac{k^2 V}{2\pi^2} dk \quad (11.63.2)$$

where the factor of two accounts for the two possible photon spin states

Stimulated Emission (3)

- Equating the two equivalent expressions for the energy dU in equations (11.63.1) and (11.63.2) then gives

$$u(\omega) V c = 2n_{\mathbf{k},\lambda} \hbar \omega \frac{k^2 V}{2\pi^2}$$

- Thus the given energy density $u(\omega)$ can equivalently be expressed in terms of photon number $n_{\mathbf{k},\lambda}$ as

$$n_{\mathbf{k},\lambda} = \frac{\pi^2 c^3}{\hbar \omega^3} u(\omega) \quad (11.64.1)$$

(the arbitrary normalisation volume V has cancelled)

- The rate for a stimulated emission process is therefore related to the corresponding spontaneous emission rate by

$$\boxed{\Gamma_{\text{stim}}(1 \rightarrow 2) = \frac{\pi^2 c^3}{\hbar \omega^3} u(\omega) \times \Gamma_{\text{spon}}(1 \rightarrow 2)} \quad (11.64.2)$$

Stimulated Emission (4)

- Equation (11.64.2) was obtained assuming the external EM field to be isotropic and unpolarised

But for an unpolarised sample of atoms (no preferred spatial direction), the overall rate for stimulated transitions cannot possibly depend on the direction of the incoming (stimulating) photon

Therefore, for unpolarised atoms, equation (11.64.2) must hold completely generally, for an EM field of any “shape”, not necessarily isotropic

- The photon produced in a stimulated transition is emitted in the same direction as the incoming photon (since it is emitted into the same mode, with the same \mathbf{k}) :
 - e.g. for unpolarised atoms immersed in an *isotropic* EM field, the stimulated photons are emitted *isotropically*
 - e.g. for unpolarised atoms immersed in a *beam* of radiation (as in a laser) the stimulated photons are all emitted *along the beam direction*

In all cases, the stimulated emission rate is given by equation (11.64.2)

Stimulated Emission (5)

- For atoms immersed in *thermal* radiation, the stimulated rate is given by

$$\frac{\Gamma_{\text{stim}}(2 \rightarrow 1)}{\Gamma_{\text{spon}}(2 \rightarrow 1)} = \frac{\pi^2 c^3}{\hbar \omega^3} u(\omega) = \frac{1}{e^{\hbar \omega / k_B T} - 1}$$

At room temperature, stimulated emission is completely negligible :

e.g. for the hydrogen Balmer line H_α :

$$\hbar \omega \approx 1.9 \text{ eV} ; \quad k_B T \approx (1/40) \text{ eV} ; \quad \frac{\Gamma_{\text{stim}}}{\Gamma_{\text{spon}}} \sim 10^{-33}$$

- Obtaining significant stimulated emission requires high temperatures (e.g. stars) and/or non-equilibrium radiation (e.g. the laser)

Absorption

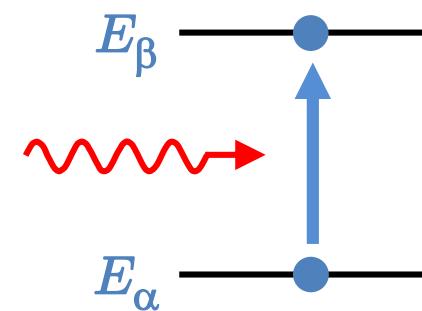
- In the case of absorption, $E_\beta > E_\alpha$, the relevant matrix element is U_{21} of equation (11.10.1), rather than U_{21}^\dagger of equation (11.11.4)

This leads to a transition rate for absorption which is the same as that for emission, equation (11.16.1), apart from a complex conjugation :

$$\Gamma(1 \rightarrow 2) = \frac{\pi\omega_0}{\epsilon_0 V} (n_{\mathbf{k},\lambda} + 1) |\mathbf{e}_\lambda(\mathbf{k}) \cdot \mathbf{d}_{\beta\alpha}|^2 g(E_k) \quad (11.67.1)$$

The frequency ω_0 is now defined as

$$\omega_0 \equiv \omega_\beta - \omega_\alpha > 0$$



- Unlike emission, equation (11.67.1) does not separate into stimulated and spontaneous components, but involves *stimulated* absorption only

Absorption (2)

- For absorption, the number of photons in a particular mode (\mathbf{k}, λ) is reduced by one as (see slide 11.8)

$$(n_{\mathbf{k},\lambda} + 1) \rightarrow n_{\mathbf{k},\lambda}$$

Thus for absorption, the initial number of photons is $(n_{\mathbf{k},\lambda} + 1)$, and in place of equation (11.64.1), we must identify

$$n_{\mathbf{k},\lambda} + 1 = \frac{\pi^2 c^3}{\hbar \omega^3} u(\omega)$$

- Substituting into equation (11.67.1) then leads to an absorption rate which is equal to the stimulated emission rate for the reverse process :

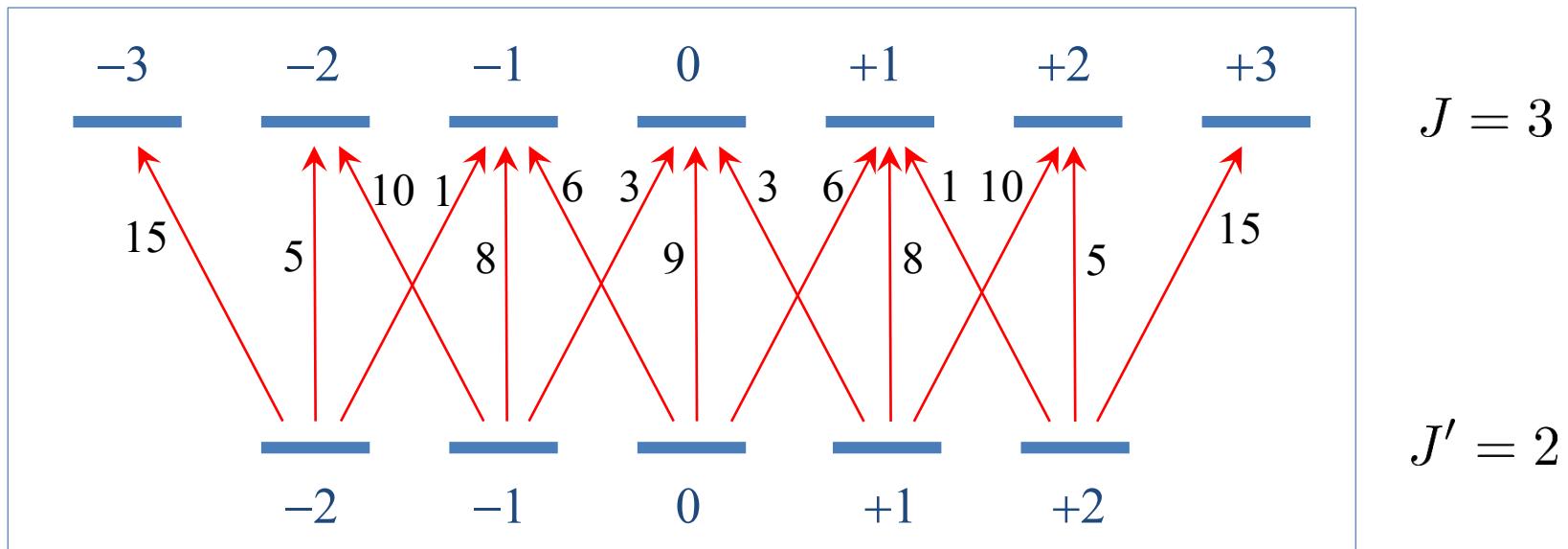
$$\Gamma_{\text{abs}}(m'_J \rightarrow m_J) = \Gamma_{\text{stim}}(m_J \rightarrow m'_J)$$

(11.68.1)

Absorption (3)

- For example, consider again transitions between $J = 3$ and $J' = 2$:

From equation (11.68.1), the *absorption* version of the diagram on slide 11.26 is obtained simply by reversing all the arrow directions :



- the total *downward* (emission) rate from each m_J is “15”
$$15 = 5 + 10 = 1 + 8 + 6 = 3 + 9 + 3$$
- the total *upward* (absorption) rate from each m'_J is “21”
$$15 + 5 + 1 = 10 + 8 + 3 = 6 + 9 + 6 = 21$$

Absorption (4)

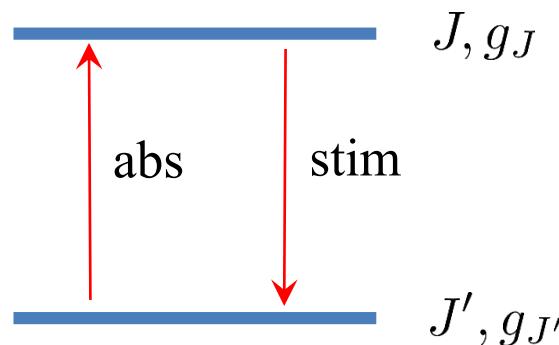
- The ratio 21/15 is due simply to the different degeneracies of the upper and lower levels (since the overall sum up must equal the overall sum down) :

$$\left. \begin{array}{l} g_J = 2J + 1 = 7 \\ g_{J'} = 2J' + 1 = 5 \end{array} \right\} \quad g_J/g_{J'} = 7/5 = 21/15$$

- This clearly applies to levels of any total angular momenta J and J' :
 - the total upward and downward stimulated rates for any given states in J or J' are related by degeneracy factors :

$$g_{J'} \Gamma_{\text{abs}}(J' \rightarrow J) = g_J \Gamma_{\text{stim}}(J \rightarrow J')$$

(11.70.1)



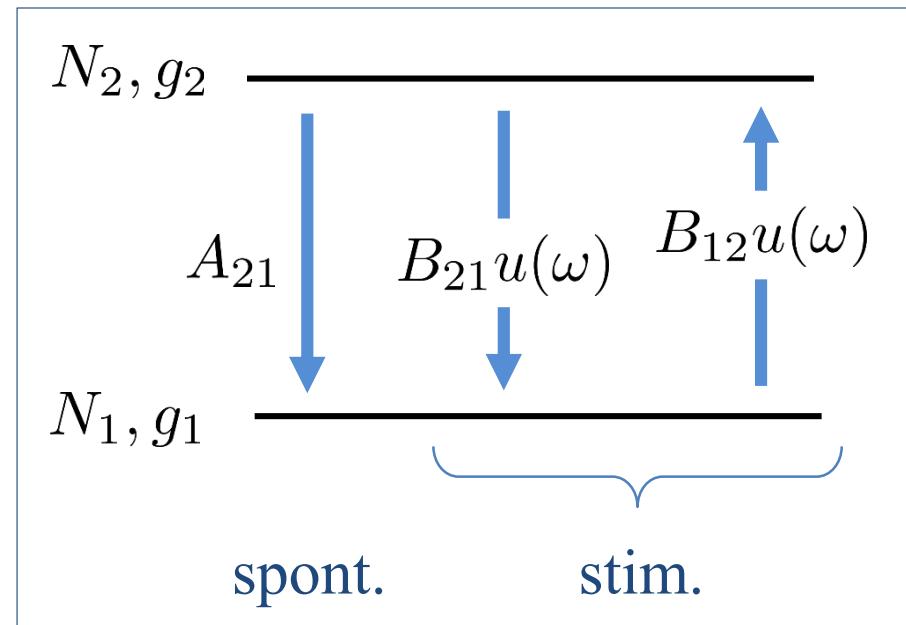
Einstein Coefficients

- The standard notation for overall transition rates between energy levels is based on the *Einstein coefficients*, A and B , defined such that

$$\Gamma_{\text{spon}}(2 \rightarrow 1) = N_2 A_{21}$$

$$\Gamma_{\text{stim}}(2 \rightarrow 1) = N_2 B_{21} u(\omega)$$

$$\Gamma_{\text{stim}}(1 \rightarrow 2) = N_1 B_{12} u(\omega)$$



- The energy levels have degeneracies g_1 and g_2 , occupancies N_1 and N_2 , and are immersed in radiation of energy density $u(\omega)$ per unit ω

The quantities A_{21} , $B_{21} u(\omega)$, $B_{12} u(\omega)$ are the transition rates *per atom*

Einstein Coefficients (2)

- The results obtained above in equations (11.64.2) and (11.70.1) show that the A and B coefficients are related via the **Einstein relations**

$$g_1 B_{12} = g_2 B_{21} ; \quad A_{21} = \frac{\hbar\omega^3}{\pi^2 c^3} B_{21} \quad (11.72.1)$$

- We have obtained these relations from first principles (i.e. from QED)

They were first established by Einstein (1917) using a purely thermodynamic argument (included, *for completeness*, in the Appendix)

[A. Einstein, Phys. Zeit. 18 \(1917\) 121](#)

Einstein's argument demonstrated that, in addition to the spontaneous emission process already incorporated into the Bohr model of the atom, the process of stimulated emission must also be possible

- Unlike the thermodynamic argument, QED allows us (in principle) to calculate the A and B coefficients themselves, not just the relationship between them

Spontaneous decay lifetimes

The Einstein A coefficient is directly related to atomic lifetimes ...

- For spontaneous decays $2 \rightarrow 1$, the occupancy $N_2(t)$ of the upper level decays exponentially as

$$\dot{N}_2(t) = -A_{21} N_2(t) ; \quad N_2(t) = N_2(0)e^{-t/\tau_2}$$

where τ_2 is the *mean lifetime* of an isolated atom in an excited state in level 2 :

$$\boxed{\tau_2 = \frac{1}{A_{21}}}$$

- In general, an atom in an excited state k can undergo multiple possible decays to lower energy levels : $k \rightarrow 1, k \rightarrow 2, k \rightarrow 3, \dots$, giving

$$\dot{N}_k(t) = -[A_{k1} + A_{k2} + A_{k3} + \dots] N_k(t)$$

Thus $N_k(t) = N_k(0)e^{-t/\tau_k}$, where τ_k , the mean lifetime of level k , is

$$\boxed{\tau_k = 1 / (\sum_j A_{kj})}$$

Appendices

-- *Appendix A :*

Derivation of the total spontaneous decay rate (slide 11.21)

$$\sum_{\lambda} \int |\mathbf{e}_{\lambda}^*(\mathbf{k}) \cdot \mathbf{a}|^2 d\Omega = \frac{8\pi}{3} |\mathbf{a}|^2$$

$$|\mathbf{a}|^2 = |a_{+1}|^2 + |a_{-1}|^2 + |a_0|^2$$

-- *Appendix B :*

Obtaining the Einstein relations via a thermodynamic argument :

$$g_1 B_{12} = g_2 B_{21} ; \quad A_{21} = \frac{\hbar\omega^3}{\pi^2 c^3} B_{21}$$

A : Spontaneous Decay Integral

- Obtaining the total spontaneous decay rate from the differential decay rate requires evaluation of the summation / integration

$$\sum_{\lambda} \int |\mathbf{e}_{\lambda}^*(\mathbf{k}) \cdot \mathbf{a}|^2 d\Omega = \sum_{\lambda} \int_{-1}^{+1} \int_0^{2\pi} |\mathbf{e}_{\lambda}^*(\mathbf{k}) \cdot \mathbf{a}|^2 d\cos\theta d\phi$$

where \mathbf{a} is a vector of complex constants,

$$\mathbf{a} = (a_x, a_y, a_z)$$

Explicit expressions for the polarisation vectors $\mathbf{e}(\mathbf{k})$ for

$$\mathbf{k} = (k_x, k_y, k_z) = k(\sin\theta \cos\phi, \sin\theta \sin\phi, \cos\theta)$$

are given on slide 11.38

- In Cartesian coordinates, each product $\mathbf{e}^* \cdot \mathbf{a}$ takes the form

$$\mathbf{e}^* \cdot \mathbf{a} = e_x^* a_x + e_y^* a_y + e_z^* a_z$$

but the calculation is more straightforward using *spherical components* ...

A : Spontaneous decay integral (2)

- The spherical components of the vectors \mathbf{e} and \mathbf{a} are (by definition)

$$\begin{aligned} e_{+1} &\equiv -\frac{1}{\sqrt{2}}(e_x + ie_y), & e_{-1} &\equiv \frac{1}{\sqrt{2}}(e_x - ie_y), & e_0 &\equiv e_z \\ a_{+1} &\equiv -\frac{1}{\sqrt{2}}(a_x + ia_y), & a_{-1} &\equiv \frac{1}{\sqrt{2}}(a_x - ia_y), & a_0 &\equiv a_z \end{aligned}$$

A product $\mathbf{e}^* \cdot \mathbf{a}$ can then be expressed as

$$\mathbf{e}^* \cdot \mathbf{a} = (e_{+1})^* a_{+1} + (e_{-1})^* a_{-1} + (e_0)^* a_0$$

- In the plane polarisation basis $\mathbf{e}_1, \mathbf{e}_2$, the products $\mathbf{e}^* \cdot \mathbf{a}$ are

$$\mathbf{e}_1^* \cdot \mathbf{a} = -\frac{1}{\sqrt{2}} \cos \theta e^{-i\phi} a_{+1} + \frac{1}{\sqrt{2}} \cos \theta e^{i\phi} a_{-1} - \sin \theta a_0$$

$$\mathbf{e}_2^* \cdot \mathbf{a} = \frac{i}{\sqrt{2}} e^{-i\phi} a_{+1} + \frac{i}{\sqrt{2}} e^{i\phi} a_{-1}$$

and the quantity to be evaluated is

$$\int_{-1}^{+1} \int_0^{2\pi} \left(|\mathbf{e}_1^*(\mathbf{k}) \cdot \mathbf{a}|^2 + |\mathbf{e}_2^*(\mathbf{k}) \cdot \mathbf{a}|^2 \right) d\cos \theta d\phi$$

A : Spontaneous decay integral (3)

-- The cross terms all contain integrals over ϕ which vanish :

$$\int_0^{2\pi} e^{\pm i\phi} d\phi = \int_0^{2\pi} e^{\pm 2i\phi} d\phi = 0$$

Hence only the diagonal terms contribute :

$$\int |\mathbf{e}_1^*(\mathbf{k}) \cdot \mathbf{a}|^2 d\Omega = 2\pi \int_{-1}^{+1} \left(\frac{1}{2} \cos^2 \theta |a_{+1}|^2 + \frac{1}{2} \cos^2 \theta |a_{-1}|^2 + \sin^2 \theta |a_0|^2 \right) d\cos \theta$$

$$\int |\mathbf{e}_2^*(\mathbf{k}) \cdot \mathbf{a}|^2 d\Omega = 2\pi \int_{-1}^{+1} \left(\frac{1}{2} |a_{+1}|^2 + \frac{1}{2} |a_{-1}|^2 \right) d\cos \theta$$

-- Using

$$\int_{-1}^{+1} \cos^2 \theta d\cos \theta = \frac{2}{3} ; \quad \int_{-1}^{+1} \sin^2 \theta d\cos \theta = \frac{4}{3}$$

then gives

$$\int \left(|\mathbf{e}_1^*(\mathbf{k}) \cdot \mathbf{a}|^2 + |\mathbf{e}_2^*(\mathbf{k}) \cdot \mathbf{a}|^2 \right) d\Omega = \frac{8\pi}{3} (|a_{+1}|^2 + |a_{-1}|^2 + |a_0|^2)$$

A : Spontaneous decay integral (4)

- Using instead the circular polarisation basis \mathbf{e}_L , \mathbf{e}_R , the products are

$$\mathbf{e}_L^* \cdot \mathbf{a} = -\frac{1}{2}(1 - \cos \theta)e^{-i\phi}a_{+1} - \frac{1}{2}(1 + \cos \theta)e^{i\phi}a_{-1} + \frac{1}{\sqrt{2}}(\sin \theta)a_0$$

$$\mathbf{e}_R^* \cdot \mathbf{a} = -\frac{1}{2}(1 + \cos \theta)e^{-i\phi}a_{+1} - \frac{1}{2}(1 - \cos \theta)e^{i\phi}a_{-1} - \frac{1}{\sqrt{2}}(\sin \theta)a_0$$

and we obtain the same result :

$$\int \left(|\mathbf{e}_L^*(\mathbf{k}) \cdot \mathbf{a}|^2 + |\mathbf{e}_R^*(\mathbf{k}) \cdot \mathbf{a}|^2 \right) d\Omega = \frac{8\pi}{3} \left(|a_{+1}|^2 + |a_{-1}|^2 + |a_0|^2 \right)$$

- In summary, independent of polarisation basis, we have

$$\boxed{\sum_{\lambda} \int |\mathbf{e}_{\lambda}^*(\mathbf{k}) \cdot \mathbf{a}|^2 d\Omega = \frac{8\pi}{3} |\mathbf{a}|^2}$$

where

$$|\mathbf{a}|^2 = |a_{+1}|^2 + |a_{-1}|^2 + |a_0|^2$$

B : Einstein coefficients

- Using an ingenious argument based on thermodynamics, Einstein predicted the existence of stimulated emission, and obtained the relation between stimulated and spontaneous transition rates

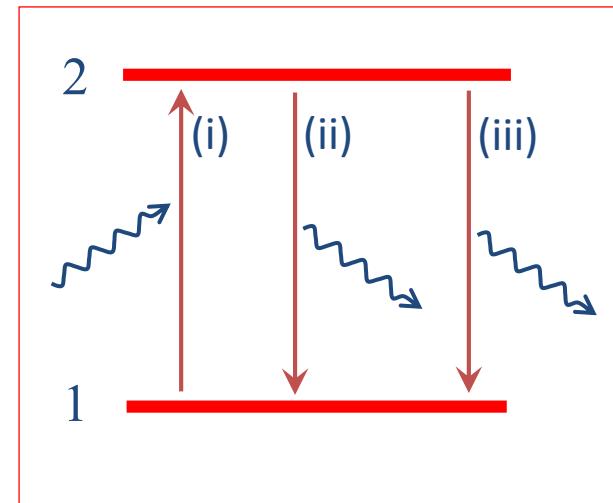
[A. Einstein, Phys. Zeit. 18 \(1917\) 121](#)

- Consider transitions between two levels with energy separation

$$E_2 - E_1 = \hbar\omega$$

The possible transitions and rates (per atom) are :

- (i) stimulated $1 \rightarrow 2$: rate $B_{12}u(\omega)$
- (ii) stimulated $2 \rightarrow 1$: rate $B_{21}u(\omega)$
- (iii) spontaneous $2 \rightarrow 1$: rate A_{21}



where $u(\omega)$ is the energy density of radiation per unit frequency ω

and A_{21} , B_{12} , B_{21} are known as *Einstein's A and B coefficients*

(and are properties solely of the atomic states concerned)

B : Einstein Coefficients (2)

- In thermal equilibrium at temperature T , the rates $1 \rightarrow 2$ and $2 \rightarrow 1$ must balance :

$$N_2 [A_{21} + B_{21}u(\omega)] = N_1 B_{12}u(\omega)$$

where N_2 and N_1 are the total number of atoms in each energy level :

$$\frac{N_1}{N_2} = \frac{g_1 e^{-E_1/k_B T}}{g_2 e^{-E_2/k_B T}} = \frac{g_1}{g_2} e^{\hbar\omega/k_B T}$$

where g_2 and g_1 are the degeneracies of each level

$$\Rightarrow g_2 A_{21} = [g_1 B_{12} e^{\hbar\omega/k_B T} - g_2 B_{21}] u(\omega)$$

- The energy density at temperature T is given by Planck's black-body formula :

$$u(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

$$\Rightarrow g_2 A_{21} = [g_1 B_{12} e^{\hbar\omega/k_B T} - g_2 B_{21}] \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

B : Einstein Coefficients (3)

- The process of spontaneous emission occurs independently of the presence of an EM field

The A_{21} coefficient must therefore be independent of the temperature T , which requires that

$$g_1 B_{12} = g_2 B_{21} ; \quad A_{21} = \frac{\hbar\omega^3}{\pi^2 c^3} B_{21} \quad (11.89.1)$$

- These relations were obtained by considering atoms in thermal equilibrium

But the Einstein coefficients A, B are *atomic* properties, independent of any external applied EM field ;

Hence equation (11.89.1) above must hold in complete generality

“Nevertheless, it still seemed unsatisfactory that thermodynamic arguments should be needed to derive formulas for processes involving a single atom.”

(S. Weinberg, “Quantum Theory of Fields (Vol 1)”, CUP, 1995, p18)