Atom and photon physics

(*) Literature:

(*) More applied books:

- A. P. Thorne, "Spectrophysics" (Chapman and Hall)
- A. Corney, "Atomic and Laser Spectroscopy" (Oxford Classic texts)
- E. Hecht, "Optics" (Addison-Wesley)
- J. Wilson and J. Hawkes, "Optoelectronics" (Prentice Hall)

(*) More theory-oriented literature:

- "Physics of Atoms and Molecules", B. H. Bransden and C. J. Joachain (especially Chapter 4, 9, 15, 16)
- "Principles of Optics", Born + Wolf
- "The Quantum theory of light", R Loudon

(+) Please note:

- The above-stated list is by no means exhaustive and further books may be necessary
- If necessary we will refer to research articles when dealing with specific topics

(*) Recommended (parallel) courses:

- Atomic and molecular physics (important for many-e- atoms)
- Advanced Quantum mechanics (time-dependent Hamiltonian, time-dependent perturbation theory, maybe scattering)

(*) Main topics

- Interaction of light with single photons
  - LASER
  - LASER spectroscopy
  - Multiphoton processes
  - Coherence / cavity effects
  - Trapping / cooling

(Details => Syllabus in the handbook)

(*) Pre-requisite (undergrad. courses)

- Quantum mechanics
- Atomic and molecular physics

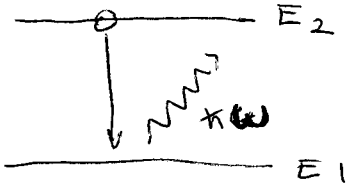
I - Interaction of light with atoms (single photon)

- We will be treating the field CLASSICALLY (no quantum-electrodynamical treatment) => appropriate for relatively strong fields

1 - Processes

Let us consider an atom A subjected to an external electromagnetic field. This atom may undergo the following processes

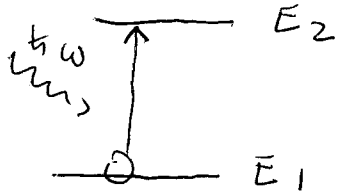
(*) Spontaneous emission: An atom can make a spontaneous transition from an excited state to a state of lower energy, emitting a photon



$$A^* \rightarrow A + \hbar\omega$$

(*) Absorption: An atom can absorb a photon from the field, making a transition from a state of lower to a state of higher energy

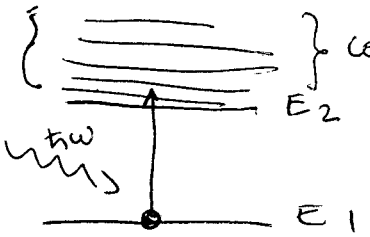
(a) Excitation: The atom is promoted from the 2d state to an excited state by absorbing a photon



$$A + \hbar\omega \rightarrow A^*$$

(b) Photoionization: An electron is released due to the fact that the absorbed photon has enough

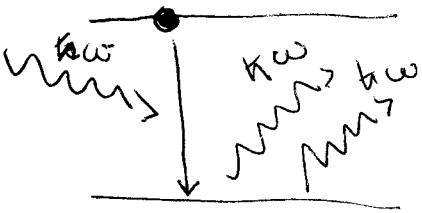
energy to make it overcome the atomic ionization potential (2)



$$A + \hbar\omega \rightarrow A^+ + e^-$$

e^- kinetic energy : $\frac{p^2}{2m} + I_P = \hbar\omega$

(*) Stimulated emission : an atom can emit a photon under the influence of an external



Applications

- LASER (light amplification by stimulat emission of radiation)
- MASER(microwave amplification by stimulated emission of radiation

(*) Please note: excitation and ionization may also occur by collisions. In this case we Refer to

(a) Particle-impact ionization : Upon collision, a particle transfers part of its kinetic energy to a bound electron, which is then able to overcome the atomic ionization potential

$$e^- + A \rightarrow A^+ + 2e^-$$

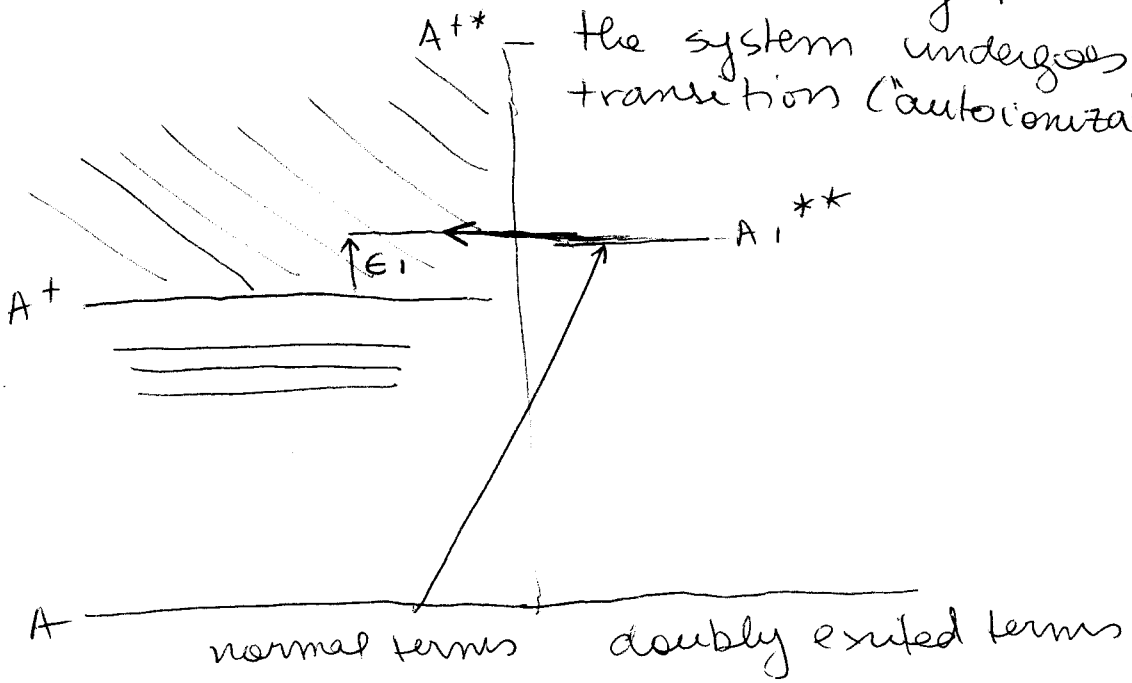
(b) Particle-impact excitation : The proces is similar to (a), with the difference that the kinetic energy transfered to the bound electron is no longer enough to release it in the continuum.

$e^- + A \rightarrow A^* + e^-$

⊛ Autoionization:

This process results from the mixing of a bound state and an adjacent ionization continuum. Some bound states may be equal in energy to a continuum state due the simultaneous exitation of 2 e⁻s or the excitation of an e⁻ from an inner shell

Consequences: – Broadening of the bound state
– non-Vanishing probability that
– the system undergoes a radiationless transition ("autoionization")



⊛ Selection rules determine which of the above-stated processes are allowed or forbidden

⊛ We will analyse three of the above-stated processes in more detail

2 - Transition rates and selection rules

* Simplest case: one e^- atom in an electromagnetic field
* We will consider relatively weak fields: first order time dependent perturbation theory

2.(a) - Transition amplitudes

Starting point: time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(\vec{r},t) = H(t)\Psi(\vec{r},t), \text{ with}$$

$$H(t) = \frac{1}{2m}\left(\vec{p} + q\vec{A}(\vec{r},t)\right)^2 + V(\vec{r})$$

(Coulomb gauge or Velocity gauge or radiation gauge)

$$H = \frac{p^2}{2m} - \frac{q}{2m}(\vec{A}\cdot\vec{p} + \vec{p}\cdot\vec{A}) + \frac{q^2}{2m}A^2 + V(r)$$

Position space: $\vec{p} \to -i\hbar\nabla$

$$\Rightarrow (\vec{A}\cdot\vec{p} + \vec{p}\cdot\vec{A}) = -i\hbar(\vec{A}\cdot\nabla + \nabla\cdot\vec{A}) \quad (*)$$

$\nabla\cdot\vec{A} = 0$ in the coulomb gauge.

Since, however, $\nabla\cdot(\vec{A}\Psi) = \vec{A}\cdot(\nabla\Psi) + (\nabla\cdot\vec{A})\Psi$

$$= \vec{A}\cdot(\nabla\Psi)$$

$$(*) = -i\hbar 2\vec{A}\cdot\nabla$$

$$\Rightarrow H = \frac{p^2}{2m} + \frac{i\hbar q}{m}(\vec{A}\cdot\nabla) + \frac{q^2}{2m}A^2 + V(r) = H_0 + H_{int}(t)$$

$H_0 = -\frac{\hbar^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r}$ (atomic Hamiltonian)

$H_{int}(t) = -\frac{i\hbar e}{m}\vec{A}\cdot\nabla + \frac{e^2}{2m}A^2$ (interaction with the field)

weak fields

$e\frac{\vec{A}\cdot\vec{p}}{m} \gg \frac{e^2A^2}{2m}$ $\Rightarrow$ term in A^2 can be neglected

$H_{int}(t) \ll H_0$ $\Rightarrow$ field can be treated as a perturbation

⊛ Time-dependent perturbation theory (1st order)

(more detailed/formal treatment: Advanced Quantum Mechanics)

$H = H_0 + \lambda H_{int}(t)$ (in our case $\lambda = 1$)

$H_0\psi_k(\vec{r}) = E_k\psi_k(\vec{r})$ (Unperturbed Hamiltonian gives the Hydrogenic wavefunctions/eigenstates).

⊛ Ansatz:

$$\psi(\vec{r},t) = \sum_k C_k(t)\psi_k(\vec{r})\exp\left[-\frac{iE_kt}{\hbar}\right]$$

Inserting into $i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t) = \left[H_0 + \lambda H_{int}(t)\right]\psi(\vec{r},t)$

$$\Rightarrow i\hbar\left[\sum_k \dot{C}_k(t)\psi_k(\vec{r})\exp\left[-\frac{iE_kt}{\hbar}\right] + \frac{iE_k}{\hbar}C_k(t)\psi_k(\vec{r})\cdot\right.$$

$$\left.\cdot\exp\left[-\frac{iE_kt}{\hbar}\right]\right] = \sum_k H_0 C_k(t)\psi_k(\vec{r})\exp\left[-\frac{iE_kt}{\hbar}\right] +$$

$$+\sum_k \lambda\, H_{int}(t)\, c_k(t)\, \psi_k(\vec{r})\, \exp\left[-\frac{iE_k t}{\hbar}\right]$$

$$\Rightarrow\quad i\hbar \sum_k \dot{c}_k(t)\, \psi_k(\vec{r}) \exp\left[-\frac{iE_k t}{\hbar}\right] + \cancel{\sum_k E_k\, c_k(t)\, \psi_k(\vec{r})} \cdot$$

$$\cdot \exp\left[-\frac{iE_k t}{\hbar}\right] = \sum_k c_k(t)\, E_k\, \psi_k(\vec{r}) \cancel{\exp\left[-\frac{iE_k t}{\hbar}\right]} +$$

$$+ \sum_k \lambda\, H_{int}(t)\, c_k(t)\, \psi_k(\vec{r}) \exp\left[-\frac{iE_k t}{\hbar}\right]$$

$$\Rightarrow i\hbar \sum_k \dot{c}_k(t)\, \psi_k(\vec{r}) \exp\left[-\frac{iE_k t}{\hbar}\right] = \sum_k \lambda\, H_{int}(t)\, c_k(t) \cdot$$

$$\psi_k(\vec{r}) \exp\left[-\frac{iE_k t}{\hbar}\right]$$

Multiplying by $\psi_b^*(\vec{r})$, integrating and using the fact that $\int \psi_b^*(\vec{r})\, \psi_k(\vec{r})\, d^3r = \delta_{bk}$,

we have

$$i\hbar \underbrace{\sum_k \dot{c}_k(t)\, \delta_{bk} \exp\left[-\frac{iE_k t}{\hbar}\right]}_{= \dot{c}_b(t) \exp\left[-\frac{iE_b t}{\hbar}\right]} = \sum_k \lambda \int c_k(t)\, \psi_b^*(\vec{r}) \cdot$$

$$\cdot H_{int}(t)\, \psi_k(\vec{r})\, e^{-\frac{iE_k t}{\hbar}}\, d^3r$$

$$i\hbar\, \dot{c}_b(t) = \sum_k \lambda \int c_k(t)\, \psi_b^*(\vec{r})\, H_{int}(t)\, \psi_k(\vec{r})\, d^3r\, e^{-i\omega_{kb} t},$$

$$\omega_{kb} = (E_k - E_b)/\hbar$$

First-order perturbation theory:

$$C_k(t) \simeq C_k^{(0)} + \lambda C_k^{(1)}$$

$$i\hbar \left[\dot{C}_b^{(0)} + \lambda \dot{C}_b^{(1)} \right] = \lambda \sum_k C_k^{(0)} \underbrace{\langle \psi_b | H_{int}(t) | \psi_k \rangle}_{\int \psi_b^*(\vec{r}) H_{int}(t) \psi_k(\vec{r}) d^3r} e^{-i\omega_{kb}t} + O(\lambda^2)$$

$$\Rightarrow \dot{C}_b^{(0)} = 0$$

$$\dot{C}_b^{(1)} = \frac{1}{i\hbar} \sum_k C_k^{(0)} \langle \psi_b | H_{int} | \psi_k \rangle e^{-i\omega_{kb}t}$$

Assumption: the atom is initially in a well-defined stationary state: ψ_a $C_k^{(0)} = \delta_{na}$

$$\dot{C}_b^{(1)} = \frac{1}{i\hbar} \langle \psi_b | H_{int} | \psi_a \rangle e^{-i\omega_{na}t}$$

$$\Rightarrow \boxed{C_b^{(1)} = \frac{1}{i\hbar} \int_0^t \langle \psi_b | H_{int} | \psi_a \rangle e^{-i\omega_{na}t}}$$

In our situation,

$$H_{int}(t) = -\frac{i\hbar e}{m} \vec{A} \cdot \nabla \quad \text{so that}$$

$$\langle \psi_b | H_{int} | \psi_a \rangle = \int \psi_b^*(\vec{r}) \vec{A} \cdot \nabla \psi_a(\vec{r}) d^3r$$

Considering

$$\vec{A}(\vec{r},t) = \hat{\varepsilon} \int_0^\infty A_0(\omega) \cos(\vec{k} \cdot \vec{r} - \omega t + \delta\omega) d\omega$$

$\hat{\varepsilon}$ ≡ polarization vector

$A_0(\omega)$ ≡ field amplitude

$\vec{\kappa}$ ≡ wave (propagation) vector

$\delta\omega$ ≡ phases

Monochromatic field: $A_0(\omega) = A_0\,\delta(\omega-\omega_0)$

Incoherent radiation: $\delta\omega$ distributed at random

Coherent radiation: $\delta\omega$ const. in a small region of width $\Delta\omega$ around ω_0 ⇒ Can be eliminated

$$\Rightarrow c_b^{(1)}(t) = -\frac{e}{2m}\int_0^\infty d\omega\, A_0(\omega)\left[\exp(i\delta\omega)\langle\psi_b|\, e^{i\vec{k}\cdot\vec{r}}\,\hat{\varepsilon}\cdot\nabla|\psi_a\rangle \cdot \int_0^t dt' \exp[i(\omega_{ba}-\omega)t'] + \exp(-i\delta\omega)\langle\psi_b|\, e^{-i\vec{k}\cdot\vec{r}}\,\hat{\varepsilon}\cdot\nabla|\psi_a\rangle \cdot \int_0^t dt' \exp[+i(\omega_{ba}+\omega)t']\right]$$

⊛ Please note:

- The first integral above is negligible unless $\omega_{ba} \simeq \omega$ ⇒ $E_b \simeq E_a + \hbar\omega$

  Physically, this corresponds to an absorption process: the system, initially in a state $|\psi_a\rangle$, absorbed one photon and was excited to the state $|\psi_b\rangle$.

- The second integral above is negligible unless $\omega_{ba} \simeq -\omega$ ⇒ $E_b \simeq E_a - \hbar\omega$.

Physically, this corresponds to an emission process: the atom, initially in $|\psi_a\rangle$, emitted a photon of energy $\hbar\omega$ and decayed to $|\psi_b\rangle$.

- Transition probability: $|C_b^{(1)}(t)|^2$

(*) Absorption transition rate

For simplicity: we will consider monochromatic light

$$\left|\int d\omega\right|^2 \to \int |\ |^2 d\omega \quad \text{(interference terms get washed out)}$$

$$\Rightarrow |c_b^{(1)}(t)|^2 = \left(\frac{e}{2m}\right)^2 \int_0^\infty d\omega\, A_0^2(\omega)\, \underbrace{|\langle\psi_b| \exp(i\vec{k}\cdot\vec{r})\hat{\varepsilon}\cdot\nabla |\psi_a\rangle|^2}_{\text{matrix element } M_{ba}} \times \underbrace{\left| \int_0^t dt' \exp[i(\overbrace{\omega_{ba}-\omega}^{\bar{\omega}})t'] \right|^2}_{(*)}$$

$$(*) = \left| \frac{-1+\cos\bar{\omega}t + i\sin\bar{\omega}t}{\bar{\omega}} \right|^2 = \frac{1}{\bar{\omega}^2}[1+\cos^2\bar{\omega}t + \sin^2\bar{\omega}t - 2\cos\bar{\omega}t]$$

$$= \frac{2}{\bar{\omega}^2}[1-\cos\bar{\omega}t] = \frac{4\sin^2(\bar{\omega}t/2)}{\bar{\omega}^2}$$

Approximations: Since this function has a sharp maximum at $\omega = \omega_{ba}$, we can write the slowly varying terms A_0 and M_{ba} as

$A_0(\omega) \approx A_0(\omega_{ba})$

$M_{ba}(\omega) \approx M_{ba}(\omega_{ba})$

and set $\int_0^\infty d\omega \to \int_{-\infty}^{\infty} d\omega$

$$\Rightarrow |C_b^{(1)}(t)|^2 = \frac{1}{2}\left(\frac{e}{m}\right)^2 A_0^2(\omega_{ba}) |M_{ba}(\omega_{ba})|^2 \underbrace{\int_{-\infty}^{\infty} \frac{\sin^2(\bar{\omega} t/2)}{\bar{\omega}^2} d\bar{\omega}}_{I}$$

$$\int_{-\infty}^{\infty} \frac{\sin^2(\bar{\omega} t/2)}{\bar{\omega}^2} d\bar{\omega} = \int_{-\infty}^{\infty} \frac{\sin^2 x}{(2x/t)^2} \frac{2dx}{t} = \frac{t}{2} \underbrace{\int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} dx}_{\Pi}$$

$x = \omega t/2$

$$\Rightarrow \boxed{|C_b^{(1)}(t)|^2 = \frac{\Pi}{2}\left(\frac{e}{m}\right)^2 A_0^2(\omega_{ba}) |M_{ba}(\omega_{ba})|^2 t}$$

- Increases linearly with time
- Depends very strongly on the transition matrix element M_{ba} ⇒ if this matrix element vanishes, $|C_b^{(1)}(t)|^2 = 0$

Transition rate: $W_{ba} = \frac{d}{dt}|C_b^{(1)}(t)|^2 = \frac{\Pi}{2}\left(\frac{e}{m}\right)^2 A_0^2(\omega_{ba}) |M_{ba}|^2$

In terms of the intensity per unit angular frequency range,

$$I(\omega) = \frac{1}{2}\varepsilon_0 c\, \mathcal{E}_0^2(\omega) = \frac{1}{2}\varepsilon_0 c \omega^2 A_0^2(\omega)$$

$$W_{ba} = \frac{4\pi^2}{m^2 c}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{I(\omega_{ba})}{\omega_{ba}^2}\left|M_{ba}(\omega_{ba})\right|^2$$

The transition rate is proportional to the intensity of the radiation field

(*) Please note : for n^{th}-order perturbation theory, this rate would be proportional to I^n

(*) Absorption cross section: $\frac{W_{ba}}{I(\omega_{ba})} = \frac{4\pi^2 \alpha \hbar^2}{m^2 \omega_{ba}}\left|M_{ba}(\omega_{ba})\right|^2$

$\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} = \frac{1}{137}$ (fine structure constant)

(*) Stimulated emission transition rate

Similarly,

$$\bar{W}_{ab} = \frac{4\pi^2}{m^2 c}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{I(\omega_{ba})}{\omega_{ba}^2}\left|\bar{M}_{ab}(\omega_{ba})\right|^2$$

$$\bar{M}_{ab} = \langle \psi_a | \exp[-i\vec{k}\cdot\vec{r}]\,\hat{\varepsilon}\cdot\nabla | \psi_b \rangle$$

$$= \int \psi_a^*(\vec{r}) \exp[-i\vec{k}\cdot\vec{r}]\,\varepsilon\nabla\psi_b(\vec{r})\,d^3r$$

(Here we interchanged the labels of the states)

It is possible to show that

$$\bar{M}_{ab} = -M_{ba}^* \Rightarrow \bar{W}_{ab} = W_{ba}$$

Physically, this is consistent with the principle of detailed

balancing: in an enclosure containing atoms and radiation in equilibrium, the transition probability from a to b is the same as from b to a, for any pair of states a, b.

(*) Please note:

- Despite the fact that $W_{ba} = \bar{W}_{ab}$, stimulated emission is usually less intense than apsorption. This is due to the fact that the initial population of the upper level b is smaller than that of the lower level a.
- Stimulated emission becomes dominant if a population inversion is achieved (LASER, MASER)

(*) Spontaneous emission

A rigorous treatment of this process requires a quantum electrodynamical approach. We will state, however, some key results and provide an ad-hoc discussion.

- QED transition rate (absorption), 1st-order perturbation theory

$$W_{ba} = \frac{4\pi^2}{m^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{\overbrace{N(\omega_{ba})}^{\#\text{ of photons}}\hbar}{V\omega_{ba}}|M_{ba}|^2\delta(\omega-\omega_{ba})$$

(V: volume)

Using $I(\omega) = \dfrac{\hbar\omega N(\omega) c}{V}$ and integrating around ω_{ba}.

$$\Rightarrow \boxed{W_{ba} = \frac{4\pi^2}{m^2 c}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{I(\omega_{ba})}{\omega_{ba}^2}|M_{ba}(\omega_{ba})|^2}$$

The semi-classical result is recovered

* QED rate for emission (stimulated emission ↑, spontaneous emission ↑)

$$W_{ab} = \frac{4\pi^2}{m^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{[N(\omega_{ba})+1]\,\hbar}{V\omega_{ba}}|M_{ba}|^2\,\delta(\omega-\omega_{ba})$$

Not quite the same! Instead of $N(\omega_{ba})$ we have $N(\omega_{ba})+1$

- Semi-classical approximation: $N(\omega_{ba}) \gg 1$ so treat spontaneous emission is neglected (valid for intense fields)

In the absence of an external field, $N=0$ and

$$\boxed{W^s_{ab} = \frac{4\pi^2}{m^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{\hbar^2}{V\omega_{ba}}|M_{ba}|^2\,\delta(\omega-\omega_{ba})}$$

To obtain the physical transition rate the above-stated rate must be summed over the number of allowed photon states

$$\underbrace{\rho_a(\omega)}_{\text{density of states}}\,\underbrace{d\omega}_{\text{freq. element}}\,\underbrace{d\Omega}_{\text{solid angle element}} = \frac{V\omega^2}{(2\pi)^3c^3}\,d\omega\,d\Omega$$

$$W^s_{ab} = \frac{\hbar^2}{2\pi m^2c^3}\left(\frac{e^2}{4\pi\epsilon_0}\right)\int d\Omega \sum_{\lambda=1}^{2}\omega_{ba}\,|M^{\lambda}_{ba}(\omega_{ba})|^2$$

(sum over polarization vectors; integral over all angles of emission)

2.(b) - The Dipole Approximation

Let us consider the matrix element

$$M_{ab} = \langle \psi_b | \exp(i\vec{k}\cdot\vec{r})\, \hat{\epsilon}\cdot\nabla | \psi_a \rangle$$
$$= \int \psi_b^*(\vec{r}) \exp(i\vec{k}\cdot\vec{r})\, \hat{\epsilon}\, \nabla\psi_a(\vec{r})\, d^3r$$

In many cases, this matrix element may be simplified by expanding

$$\exp(i\vec{k}\cdot\vec{r}) = 1 + (i\vec{k}\cdot\vec{r}) + \frac{1}{2!}(i\vec{k}\cdot\vec{r})^2 + \dots$$

(*) Zeroth-order term: electric dipole approximation
(*) First-order term: electric quadrupole approximation / magnetic dipole approximation

In the dipole approximation,

- $\vec{A}(t)$, $\vec{E}(t)$ depend only on the time t
- The magnetic field vanishes as $\nabla \times \vec{A} = 0$

This is a very good approximation for optical transitions

- Atomic distances: $r \sim 10^{-8}$ cm
- Optical wavevector: $k = \frac{2\pi}{\lambda} \sim 10^5 \text{cm}^{-1}$ $\rightarrow \vec{k}\cdot\vec{r} \sim 10^{-3}$

- Since the wavelength of the radiation field is much larger than the atomic distances involved, this is a long wavelength approximation
- The dipole approximation breaks down for high-frequency (e.g. X-Ray) radiation

(*) Transition matrix element

$$M_{ba}^D = \hat{\epsilon}\cdot\langle \psi_b | \nabla | \psi_a \rangle = \frac{i}{\hbar}\hat{\epsilon}\cdot\langle \psi_b | \vec{p} | \psi_a \rangle$$
$$= \frac{im}{\hbar}\hat{\epsilon}\cdot\langle \psi_b | \dot{\vec{r}} | \psi_a \rangle$$

Using the Heisenberg equations of motion for $\dot{r}$:

$\dot{\vec{r}} = (i\hbar)^{-1}[\vec{r}, H] \simeq (i\hbar)^{-1}[\vec{r}, H_0]$ (the field is a perturbation)

$\langle \psi_b | \dot{\vec{r}} | \psi_a \rangle = (i\hbar)^{-1} \langle \psi_b | \vec{r} H_0 - H_0 \vec{r} | \psi_a \rangle$

Reminder: $\langle \psi_b | H_0 = \langle \psi_b | E_b$

$H_0 | \psi_a \rangle = E_a | \psi_a \rangle$

$\Rightarrow \langle \psi_b | \dot{\vec{r}} | \psi_a \rangle = \frac{1}{i\hbar}(E_a - E_b) \langle \psi_b | \vec{r} | \psi_a \rangle$

$$M^D_{ba} = \frac{im}{\hbar} \hat{\epsilon} \cdot \frac{1}{i} \omega_{ab} \langle \psi_b | \vec{r} | \psi_a \rangle$$

$$= -\frac{m}{\hbar} \omega_{ba} \vec{\epsilon} \cdot \langle \psi_b | \vec{r} | a \rangle = -\frac{m}{\hbar} \omega_{ba} \hat{\epsilon} \cdot \vec{r}_{ba}$$

(*) Definitions

- Electric dipole moment operator: $\vec{D} = -e\vec{r}$
- Dipole matrix element: $\vec{D}_{ba} = -e\vec{r}_{ba}$

(*) Absorption transition rate

$$\omega^D_{ba} = \frac{4\pi^2}{c\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0}\right) I(\omega_{ba}) \left| \hat{\epsilon} \cdot \vec{r}_{ba} \right|^2$$

$$= \frac{4\pi^2}{c\hbar^2} \left(\frac{1}{4\pi\epsilon_0}\right) I(\omega_{ba}) \left| \hat{\epsilon} \cdot \vec{D}_{ba} \right|^2$$

$\hat{\epsilon} \cdot \vec{D}_{ba} \equiv$ component of the dipole matrix element along the polarization of the radiation field.

(*) Please note :

The transition defined by ω^D_{ba} is an electric dipole transition

$D_{ba} = 0 \Rightarrow$ the transition is forbidden

$D_{ba} \neq 0 \Rightarrow$ the transition is allowed

Example

Let us consider Hydrogen in a monochromatic field of frequency ω polarized along the z axis. Assume that the dipole approximation is valid.

Compute the transition rate

$$W^{D}_{ba} = \frac{4\pi}{c\hbar^2}\left(\frac{1}{4\pi\epsilon_0}\right) I(\omega_{ba}) \left|\hat{\epsilon}\cdot\vec{D}_{ba}\right|$$ corresponding to

a one-photon absorption process between the 1s state and

(a) The 2p state

(b) The 2s state

(a) $\vec{E}(t) = E_0 \sin\omega t\, \hat{\imath}_z$

$m=1$ $m=0$ $m=-1$ 2p

1s

Initial state: $\psi_{1s} = R_{10}(r)\, Y_0^0 = 2\left(\frac{Z}{a_0}\right)^{3/2} \exp\left(-\frac{Zr}{a_0}\right)\cdot\frac{1}{\sqrt{4\pi}}$

Final state: $\psi_{2p} = R_{21}(r)\, Y_1^m$ (we do not know to which one the system will go)

$$\psi_{2p} = 2\left(\frac{Z}{2a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)\exp\left[-\frac{Zr}{2a_0}\right] Y_1^m$$

Transition frequency: $\omega_{ba} = \omega_{1s\to 2p} = \frac{3}{8}\frac{mc^2}{\hbar}(Z\alpha)^2$

Dipole matrix element $\vec{D}_{Ba} = -e\,\vec{r}_{ba}$ with $b = 2p$, $a = 1s$

$$\vec{r}_{ba} = \int \psi^*_{2p}(\vec{r})\,\vec{r}\,\psi_{1s}(\vec{r})\,d^3r$$

Explicit expression for $\vec{r}$:

$$\vec{r} = r\cos\theta\,\hat{e}_z + r\sin\theta\cos\varphi\,\hat{e}_x + r\sin\theta\sin\varphi\,\hat{e}_y$$

Using the fact that

$$\sin\theta\cos\phi = \sqrt{\frac{2\pi}{3}}\left[Y_1^{-1}(\theta,\phi) - Y_1^{1}(\theta,\phi)\right]$$

$$\sin\theta\sin\phi = i\sqrt{\frac{2\pi}{3}}\left[Y_1^{1}(\theta,\phi) + Y_1^{-1}(\theta,\phi)\right]$$

$$\cos\theta = \sqrt{\frac{4\pi}{3}}\,Y_1^{0}(\theta,\phi)$$

we find

$$\vec{r} = r\left[\sqrt{\frac{4\pi}{3}}\,Y_1^0\,\hat{e}_z + i\sqrt{\frac{2\pi}{3}}\left[Y_1^1 + Y_1^{-1}\right]\hat{e}_y + \sqrt{\frac{2\pi}{3}}\left[Y_1^{-1} - Y_1^1\right]\hat{e}_x\right]$$

$$\Rightarrow \vec{r}_{ba} = \frac{1}{\sqrt{4\pi}}\int_0^\infty R_{21}(r)R_{10}(r)\,r^3 dr \int d\Omega \left[\sqrt{\frac{4\pi}{3}}\,Y_1^0\,\hat{e}_z + i\sqrt{\frac{2\pi}{3}}\left[Y_1^1 + Y_1^{-1}\right]\hat{e}_y + \sqrt{\frac{2\pi}{3}}\left[Y_1^{-1} - Y_1^1\right]\hat{e}_x\right] Y_1^{*m}$$

- Radial integral:

$$\int_0^\infty R_{21}(r)R_{10}(r)\,r^3 dr = \left(\frac{Z}{a_0}\right)^4 \frac{1}{\sqrt{6}} \int_0^\infty r^4 \exp\left[-\frac{3Zr}{2a_0}\right] dr$$

$$= \frac{a_0}{Z}\,\frac{24}{\sqrt{6}}\left(\frac{2}{3}\right)^5$$

- Angular integral: we will use $\int Y_\ell^{*m}(\theta,\phi)\,Y_{\ell'}^{m'}(\theta,\phi)\,d\Omega = \delta_{\ell\ell'}\delta_{mm'}$

z component: $\int Y_1^{*m}\,Y_1^0\,d\Omega = \delta_{m,0}\,\delta_{1,1} = 1$

x component: $\int Y_1^{*m}\left[Y_1^{-1} - Y_1^1\right] d\Omega = \delta_{m,-1} - \delta_{m,1}$

y component: $\int Y_1^{*m}\left[Y_1^1 + Y_1^{-1}\right] d\Omega = \delta_{m,1} + \delta_{m,-1}$

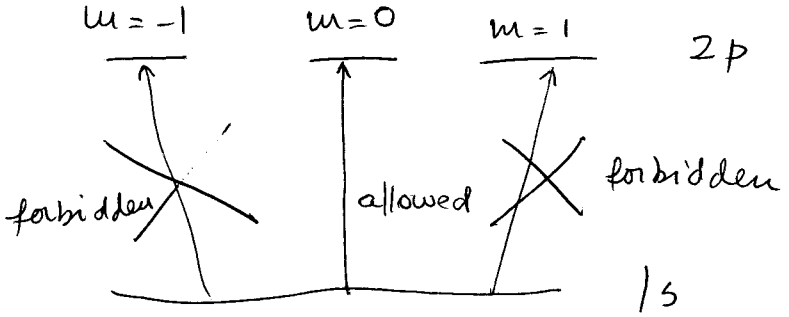
$$\Rightarrow \vec{r}_{ba} = \underbrace{\frac{a_0}{Z}\frac{24}{\sqrt{6}}\left(\frac{2}{3}\right)^5}_{C_1}\left[\frac{1}{\sqrt{3}}\delta_{m,0}\hat{e}_z + \frac{1}{\sqrt{6}}\left[\delta_{m,-1} - \delta_{m,1}\right]\hat{e}_x + \right.$$

$$\left. + \frac{i}{\sqrt{6}}\left[\delta_{m,1} + \delta_{m,-1}\right]\hat{e}_y\right]$$

(*) Assumption: The electric field is linearly polarized along $\hat{e}_z$. Hence, only $\vec{r}_{ba}\cdot\hat{e}_z$ will contribute

$$\vec{r}_{ba}\cdot\hat{e}_z = \frac{C_1}{\sqrt{3}}\delta_{m,0}$$

$$W_{ba} = \frac{4\pi}{c\hbar^2}\left(\frac{1}{4\pi\varepsilon_0}\right) I(\omega_{1s\to 2p})\left|\frac{C_1}{\sqrt{3}}\delta_{m,0}\right|^2$$



(*) Please note

If, instead, our laser field were circularly polarized, the situation would be different

$$\vec{E} = E_0 f(t)\left[\hat{e}_x \pm i\hat{e}_y\right]$$

+ sign: $\vec{r}_{ba}\cdot\hat{\epsilon} = \vec{r}_{ba}\cdot(\hat{e}_x + i\hat{e}_y)$

$$\vec{r}_{ba}\cdot\vec{\epsilon}_x = \frac{C_1}{\sqrt{6}}\left[-\delta_{m,1} + \delta_{m,-1}\right]$$

$$\vec{r}_{ba} \cdot \hat{\epsilon}_y = \frac{c_1}{\sqrt{6}} i \left[\delta_{m,1} + \delta_{m,-1} \right]$$

$$\vec{r}_{ba} \cdot (\hat{\epsilon}_x + i\hat{\epsilon}_y) = -\frac{c_1}{\sqrt{3}} \delta_{m,1}$$

$\Rightarrow$ In this case, the transition from 1s to the 2p state with $m = 1$ is allowed.

Similarly,

$$\vec{r}_{ba} \cdot (\hat{\epsilon}_x - i\hat{\epsilon}_y) = \frac{c_1}{\sqrt{3}} \delta_{m,1}$$

$\Rightarrow$ transition to the state with $m = -1$ is allowed

(b) Let us assume now that, instead of 2p, the excited state b to which the transition should occur is 2s

Initial state: $R_{10}(r) Y_0^0 = \psi_{1s}$

Final state: $\psi_{2s} = R_{20} Y_0^0$

Dipole matrix element:

$$\vec{r}_{ba} = \int \psi_{2s}^*(\vec{r}) \, \vec{r} \, \psi_{1s}(\vec{r}) \, d^3r$$

$$= \int_0^\infty R_{10}(r) R_{20}(r) r^3 dr \left[\sqrt{\frac{4\pi}{3}} \int Y_0^{0*} Y_1^0 Y_0^0 \, d\Omega \, \hat{e}_z + \right.$$

$$\left. + i\sqrt{\frac{2\pi}{3}} \left[\int Y_1^{1*} Y_0^{0*} Y_0^0 \, d\Omega + \int Y_1^{-1} Y_0^{0*} Y_0^0 \, d\Omega \right] \hat{e}_y \right.$$

$$+\sqrt{\frac{2\pi}{3}}\left[\int Y_1^{-1}\, Y_0^{*0}\, Y_0^0\, d\Omega - \int Y_1^1 Y_0^{*0} Y_0^0 d\Omega\right]\hat{e}_x\Bigg]$$

Angular integrals:

$$\int Y_0^{*0} Y_1^0 Y_0^0 d\Omega = \frac{1}{\sqrt{4\pi}}\int Y_0^{*0} Y_1^0 d\Omega = \delta_{1,0} = 0$$

$$\int Y_0^{*0} Y_1^{\pm 1} Y_0^0 d\Omega = \frac{1}{\sqrt{4\pi}}\int Y_0^0 Y_1^{\pm 1} d\Omega = \delta_{1,0}\delta_{0,\pm 1} = 0$$

$\Rightarrow$ The transition $1s \to 2s$, within the dipole approximation, is <u>forbidden</u>

These are examples of SELECTION RULES for dipole transitions

2.(c) - Selection rules

Let us consider an atom in a radiation field. We wish to know which transitions are <u>allowed</u> and which ones <u>forbidden</u>

⊛ <u>Importance</u>

- Allows one to determine which transitions are allowed and forbidden once the angular momentum quantum numbers are specified (very helpful in computing the spectra)
- Useful for computing the lifetimes of levels (radiative)

For convenience, we will write the dipole operator $\vec{r} = x\hat{e}_x + y\hat{e}_y + z\hat{e}_z$ in terms of its components in the spherical basis $\{\hat{\varepsilon}_1, \hat{\varepsilon}_0, \hat{\varepsilon}_{-1}\}$, with

$$\hat{\varepsilon}_1 = -\frac{1}{\sqrt{2}}(\hat{\varepsilon}_x + i\hat{\varepsilon}_y) \; ; \; \hat{\varepsilon}_0 = \hat{\varepsilon}_z \; ; \; \hat{\varepsilon}_{-1} = \frac{1}{\sqrt{2}}(\hat{\varepsilon}_x - i\hat{\varepsilon}_{-1})$$

- Dipole components

along $\hat{\varepsilon}_1$: $r_1 = -\frac{1}{\sqrt{2}}(x + iy) = r\left(\frac{4\pi}{3}\right)^{1/2} Y_1^1(\theta,\phi)$

along $\hat{\varepsilon}_0$: $r_0 = z = r\left(\frac{4\pi}{3}\right)^{1/2} Y_1^0(\theta,\phi)$

along $\hat{\varepsilon}_{-1}$: $r_{-1} = \frac{1}{\sqrt{2}}(x - iy) = r\left(\frac{4\pi}{3}\right)^{1/2} Y_1^{-1}(\theta,\phi)$

⊛ Electric dipole transitions

The transition amplitude depends on $\vec{r}_{ba} \cdot \hat{\varepsilon}_q$

- $\vec{r}_{ba}$: dipole matrix element
- $\hat{\varepsilon}_q$: polarization vector

- Initial-state wavefunction

$$\psi_a(\vec{r}) = R_{n\ell}(r) Y_\ell^m(\theta,\varphi)$$

$$\psi_b(\vec{r}) = R_{n'\ell'}(r) Y_{\ell'}^{m'}(\theta,\varphi)$$

$$\vec{r}_{ba} \cdot \hat{\varepsilon}_q \underbrace{\int_0^\infty R_{n\ell}(r) R_{n'\ell'}(r) r^3 dr}_{I_r} \times \underbrace{\int Y^{*m'}_{\ell'}(\theta,\varphi) Y_1^q(\theta,\varphi) Y_\ell^m(\theta,\varphi) d\Omega}_{I_\Omega}$$

Radial integral I_r : non-vanishing

Angular integral I_Ω : may vanish

Using the fact that $Y_\ell^m(\theta,\phi) = e^{im\phi} P_\ell(\cos\theta)$,

we have

$$I_\Omega = \underbrace{\int_{-1}^{1} P_\ell^{m'}(\cos\theta)\, \overbrace{P_1^q(\cos\theta)}^{\sin\theta;\ q=\pm1,\ \cos\theta,\ q=0}\, P_\ell^m(\cos\theta)\, d\cos\theta}_{I_\theta} \cdot \underbrace{\int_0^{2\pi} e^{-im'\phi + iq\phi + im\phi}\, d\phi}_{I_\phi}$$

- Magnetic quantum numbers

We will consider $I_\phi = \int_0^{2\pi} e^{i(m-m'+q)\phi}\, d\phi$;

$I_\phi \neq 0 \Rightarrow m - m' + q = 0$

(a) $q = 0$ (polarization vector in the z direction)

$m' = m$, i.e., $\boxed{\Delta m = 0}$

(b) $q = \pm 1$ (circularly polarized light)

$m' = m \pm 1$; i.e., $\boxed{\Delta m = \pm 1}$

- Orbital angular momentum

We will consider I_θ, which, apart from the numerical factors, may be written as

$$I_{\theta 1} = \int_{-1}^{1} d(\cos\theta)\, P_l^m(\cos\theta)\, P_{l'}^m(\cos\theta)\cos\theta, \quad q = 0 \qquad (a)$$

$$I_{\theta 2} = \int_{-1}^{1} d(\cos\theta)\, P_l^m(\cos\theta)\, P_{l'}^{m\pm1}(\cos\theta)\sin\theta, \quad q = \pm 1 \qquad (b)$$

(a) <u>linearly polarized light</u>

We will use

$$(2l+1)\cos\theta\, P_l^m(\cos\theta) = (l+1-m)\, P_{l+1}^m(\cos\theta) + (l-m)\cdot P_{l-1}^m(\cos\theta)$$

$$\Rightarrow I_{\theta 1} = \int_{-1}^{1} d(\cos\theta) \left[\left(\frac{l+1-m}{2l+1} \right) P_{l+1}^m(\cos\theta)\, P_{l'}^m(\cos\theta) + \right.$$

$$\left. + \frac{(l-m)}{(2l+1)} P_{l-1}^m(\cos\theta) \right] P_{l'}^m(\cos\theta)$$

From the orthogonality relation of the associated Legendre functions

$$\int_{-1}^{1} d(\cos\theta)\, P_{l\pm1}^m(\cos\theta)\, P_{l'}^m(\cos\theta) = \frac{2(l\pm1+m)!}{(2(l\pm1)+1)(l\pm1-m)!}\, \delta_{l\pm1,l'}$$

$\Rightarrow$ Only the terms for which $l' = l \pm 1$ survive

$$\boxed{\Delta l = \pm 1}$$

That is why a $1s \to 2s$ transition is <u>forbidden</u>

(b) circularly polarized light

$$\boxed{\Delta l = \pm 1}$$

Proof along the same lines, but using

$$(2l+1)\sin\theta\, P_l^{m-1}(\cos\theta) = P_{l+1}^{m}(\cos\theta) - P_{l-1}^{m}(\cos\theta)$$

(*) Please note: (a) The above-stated rule may also be understood using parity arguments

Under $\vec{r} \to -\vec{r}$, $R_{nl}(r)\, Y_l^m(\theta,\phi) = (-1)^l R_{nl}(r)\, Y_l^m(\theta,\phi)$

$\Rightarrow$ l odd $\Rightarrow$ Y_l^m odd

l even $\Rightarrow$ Y_l^m even

$\int Y_{l'}^{*m'}(\theta,\phi)\, Y_1^q(\theta,\phi)\, Y_l^m(\theta,\phi)\, d\Omega$ is non-

- vanishing if the integrand is even

$\Rightarrow$ $l + l' + 1$ even

If l odd, l' even

If l even, l' odd

$\Rightarrow$ The dipole operator only connects states of different parity (Laporte's rule)

(b) If there exists a spin-orbit coupling $s(r)\vec{l}\cdot\vec{s}$ between $\vec{l}$ and $\vec{s}$, the stationary states of the electron are labeled by the quantum numbers l, s, j, m_j, with $\vec{j} = \vec{l} + \vec{s}$.

The electric dipole selection rules can then be obtained by computing the dipole matrix elements in the basis of the eigenstates of $\vec{J}$

They are

$$\Delta J = 0, \pm 1 \quad , \quad J = 0 \not\leftrightarrow J = 0$$

(↓ notation for a forbidden transition)

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

$$\Delta m_\gamma = 0, \pm 1$$

$\Delta J = 0$ is NOT forbidden - this is due to the fact that J is not related to the parity of the level.

If ℓ and s are good quantum numbers, one can still have

$$\Delta \ell = 0, \pm 1 \quad , \quad 0 \not\leftrightarrow 0$$

$$\Delta S = 0$$

This rule, however, breaks down for heavier elements, since the spin-orbit coupling is quite strong in this case.

(*) Electric quadrupole transition / magnetic dipole transition

Let us now consider the second term of the expansion

$$\exp(i\vec{k}\cdot\vec{r}) \simeq 1 + i\vec{k}\cdot\vec{r} + \dots$$

In this case,

$$M_{ba} = \langle \psi_b | (\hat{\epsilon}\, i\vec{k}\cdot\vec{r})(\hat{\mathcal{E}}\cdot\nabla_r) | \psi_a \rangle$$

Assumptions

- $\vec{k} = k\hat{e}_z$ (propagation direction along the z axis)
- $\hat{\epsilon} = \epsilon\hat{x}$ (polarization direction along the x axis

$$\Rightarrow M_{ba} = ik \langle \psi_b | x \frac{\partial}{\partial z} | \psi_a \rangle = i\frac{\omega_{ba}}{c} \langle \psi_b | x \frac{\partial}{\partial z} | \psi_a \rangle$$

Writing

$$\langle \psi_b | x \frac{\partial}{\partial z} | \psi_a \rangle = \underbrace{\frac{1}{2} \langle \psi_b | x \frac{\partial}{\partial z} - z \frac{\partial}{\partial x} | \psi_a \rangle}_{(*)} + \underbrace{\frac{1}{2} \langle \psi_b | x \frac{\partial}{\partial z} + z \frac{\partial}{\partial x} | \psi_a \rangle}_{(**)}$$

and using $\frac{iL_y}{\hbar} = x\frac{\partial}{\partial z} - z\frac{\partial}{\partial x}$

$$(*) = \frac{1}{2} \langle \psi_b | \frac{iL_y}{\hbar} | \psi_a \rangle = \frac{i}{2\hbar} \langle \psi_b | L_y | \psi_a \rangle$$

$(**) =$

using $-i\hbar\frac{\partial}{\partial z} = \hat{p}_z \Rightarrow \frac{\partial}{\partial z} = -\frac{1}{i\hbar} p_z = -\frac{m\dot{z}}{i\hbar}$

$-i\hbar\frac{\partial}{\partial x} = p_x \Rightarrow \frac{\partial}{\partial x} = \frac{-1}{i\hbar} p_x = -\frac{m\dot{x}}{i\hbar}$

Together with the Heisenberg equations,

$$\dot{z} = \frac{1}{i\hbar}[zH_0 - H_0 z]$$

$$\dot{x} = \frac{1}{i\hbar}[xH_0 - H_0 x]$$

we find

$$(**a) \qquad x\frac{\partial}{\partial z} = \frac{m}{\hbar^2}x[z, H_0]$$

$$(**b) \qquad z\frac{\partial}{\partial x} = \frac{mz}{\hbar^2}[x, H_0] = \frac{\partial}{\partial x}z = \frac{m}{\hbar^2}[x, H_0]z$$

$$\Rightarrow (**a)+(**b) = \frac{m}{\hbar^2}\left[x[z, H_0] + [x, H_0]z\right]$$

$$= \frac{m}{\hbar^2}[xz, H_0]$$

Matrix element (**): $\frac{m}{2\hbar^2}\langle\psi_b|xzH_0 - H_0xz|\psi_a\rangle$

$$= -\frac{m\omega_{ba}}{2\hbar}\langle\psi_b|xz|\psi_a\rangle$$

$$M_{ba} = \underbrace{-\frac{\omega_{ba}}{2\hbar c}\langle\psi_b|L_y|\psi_a\rangle}_{\text{Magnetic dipole transitions } M_{ba}^{(1)}} + \underbrace{\frac{im\omega_{ba}^2}{2\hbar c}\langle\psi_b|xz|\psi_a\rangle}_{\text{electric quadrupole transitions } M_{ba}^{(2)}}$$

⊛ Magnetic dipole transitions

$M_{ba}^{(1)}$ is proportional to the orbital magnetic dipole

moment operator

$$\vec{\mu}_L = -\frac{e}{2m}\vec{L} = -\mu_b\left(\frac{\vec{L}}{\hbar}\right)$$

Spin can be included by taking $\vec{L} \to \vec{L} + 2\vec{S}$ so that

$$M_{ba}^{(1)} = -\frac{\omega_{ba}}{2\hbar c}\langle \psi_b | L_y + 2S_y | \psi_a \rangle$$

This matrix element induces magnetic dipole transitions

Selection rules $M_{ba}^{(1)} \neq 0$

- Neither L_y nor S_y changes the orbital quantum number ℓ since $[\vec{L}+2\vec{S}, L^2] = 0$, $[\vec{L}+2\vec{S}, S^2] = 0$
  $\Rightarrow \Delta\ell = 0$
- L_y changes m_ℓ by ± 1 (check 3rd year Quantum mechanics for details)
  $\Rightarrow \Delta m_L = \pm 1$
- S_y changes m_s by $\pm 1 \Rightarrow \Delta m_s = \pm 1$

If, instead of L_y, S_y we had S_z, L_z, this would give $\Delta m_\ell = 0$, $\Delta m_s = 0$

$$\Rightarrow \begin{cases} \Delta\ell = 0 \\ \Delta m_\ell = \pm 1, 0 \\ \Delta m_s = \pm 1, 0 \end{cases}$$

⊛ Please note:

- In the presence of the spin-orbit coupling the eigenstates of H_0 are labeled by the quantum numbers ℓ, j since $[L, J^2] \neq 0$ $[S, J^2] \neq 0$ the above-stated matrix

element may connect states with the same ℓ but different J
In this case, we have

$$\Delta \ell = 0$$
$$\Delta j = \pm 1, 0 \quad (j=0 \not\leftrightarrow j'=0)$$
$$\Delta m_j = \pm 1, 0$$

- The atomic states a and b must have the same parity.

- For a rigorous derivation of the above-stated selection rules, see an explanation based on the Wigner-Eckart theorem (e.g.) A. Corney, PP. 130)
(Cohen Tannoudji, Complement Dx)

- For an atom whose nucleus has a magnetic moment, magnetic dipole transitions can take place between two hyperfine structure components of the same fine structure level

$(\Delta L = \Delta S = \Delta J = 0)$, but $\Delta F \neq 0$

Example: states $F=0$ and $F=1$ of the atomic hydrogen gd. state.

(*) Electric quadrupole transitions

$$M_{ba}^{(2)} = -i \frac{m\omega_{ba}^2}{2\pi c} \langle \psi_b | xz | \psi_a \rangle$$

- xz is a component of the electric quadruple operator of the atom
- xz is even $\Rightarrow$ it couples states of the SAME parity

$$\langle \psi_b | x z | \psi_a \rangle = \int \psi_b^*(\vec{r})\, x z\, \psi_a(\vec{r})\, d^3r$$

$$\psi_b(\vec{r}) = R_{n'\ell'}\, Y_{\ell'}^{m'}(\theta,\phi)$$

$$\psi_a = R_{n\ell}(r)\, Y_\ell^m(\theta,\phi)$$

$$x = r\sin\theta\cos\phi = r\sqrt{\frac{2\pi}{3}}\left[Y_1^{-1}(\theta,\phi) - Y_1^1(\theta,\phi)\right]$$

$$z = r\cos\theta = r\sqrt{\frac{4\pi}{3}}\, Y_1^0(\theta,\phi)$$

$$x z = r^2\sqrt{8}\,\frac{\pi}{3}\left[\underbrace{Y_1^0(\theta,\phi)\, Y_1^{-1}(\theta,\phi)}_{\propto\, Y_2^{-1}(\theta,\phi)} - \underbrace{Y_1^0(\theta,\phi)\, Y_1^1(\theta,\phi)}_{\propto\, Y_2^1(\theta,\phi)}\right]$$

Hence

$$\langle \psi_b | x z | \psi_a \rangle \propto \int Y_{\ell'}^{*m'}(\theta,\phi)\, Y_2^{\pm 1}(\theta,\phi)\, Y_\ell^m(\theta,\phi)\, d\Omega$$

$$\times \text{ Radial integral}$$

$$\int Y_{\ell'}^{*m'}(\theta,\phi)\, Y_2^{\pm 1}(\theta,\phi)\, Y_\ell^m(\theta,\phi)\, d\Omega \neq 0 \quad \text{if}$$

$$\Delta\ell = 0, \pm 2 \;,\; \Delta m = \pm 1$$

(The proof is similar to that performed for dipole transitions)

If we have z^2 this will give

$$\Delta\ell = 0, \pm 2 \;,\; \Delta m = 0$$

$$\Rightarrow \begin{cases} \Delta\ell = 0, \pm 2 \\ \Delta m = 0, \pm 1 \end{cases}$$

(*) Please note

For a many-e^- atom, $xz \rightarrow \sum_{i=1}^{N} x_i z_i$

In this case, the electric quadrupole selection rules read

(a) $\Delta M_j = 0, \pm 1, \pm 2$

(b) $\Delta J = 0, \pm 1, \pm 2$

(in terms of total angular momentum operator $\vec{J}$)

And, if L, S are good quantum numbers

(a) $\Delta S = 0$

(b) $\Delta L = 0, \pm 1, \pm 2$

(c) $\Delta M_L = 0, \pm 1, \pm 2$

Rigorous proof: Wigner-Eckart theorem

SUMMARY

Selection rules for single photon transitions in atomic spectra

Rule	Electric Dipole	Magnetic dipole	Electric Quadrupole
1	$\Delta J = 0, \pm 1$ $(0 \not\leftrightarrow 0)$	$\Delta J = 0, \pm 1$ $(0 \not\leftrightarrow 0)$	$\Delta J = 0, \pm 1, \pm 2$ $(0 \not\leftrightarrow 0;\ \frac{1}{2} \not\leftrightarrow \frac{1}{2};\ 0 \not\leftrightarrow 1)$
2	$\Delta m_J = 0, \pm 1$	$\Delta m_J = 0, \pm 1$	$\Delta m_J = 0, \pm 1, \pm 2$
3	Parity Change	No parity change	No parity change
4	One electron jump $\Delta l = \pm 1$	no electron jump $\Delta l = 0, \Delta n = 0$	One or no electron jump $\Delta l = 0, \pm 2$
5	$\Delta S = 0$	$\Delta S = 0$	$\Delta S = 0$
6	$\Delta L = 0, \pm 1$ $(0 \not\leftrightarrow 0)$	$\Delta L = 0$	$\Delta L = 0, \pm 1, \pm 2$ $(0 \not\leftrightarrow 0;\ 0 \not\leftrightarrow 1)$

3- The Einstein coefficients

- Developed by Einstein, 1916
- Give the correct expressions for the rate of spontaneous emission / absorption of radiation

Let us consider an enclosure containing atoms and radiation in equilibrium at absolute temperature T and the two non-degenerate atomic levels a, b, with energies E_a, E_b such that $E_b > E_a$

E_b ——— b

E_a ——— a

$\rho(\omega_{ba}) \equiv$ energy density of radiation at the angular frequency $\omega_{ba} = \frac{E_b - E_a}{\hbar}$

$\dot{N}_{ba}$ is the number of atoms making the transition from a to b per unit time by absorbing radiation.

$$\dot{N}_{ba} = B_{ba} N_a \rho(\omega_{ba})$$

B_{ba}: Einstein coefficient for absorption

Using $\rho(\omega) = \frac{I(\omega)}{c}$ and the absorption rate W_{ba} per atom in the dipole approximation

$$W_{ba}^{D} = \frac{4\pi^2}{c\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right) \underbrace{I(\omega_{ba})}_{= c\,\rho(\omega_{ba})} \underbrace{|\vec{r}_{ba}\cdot\hat{\epsilon}|^2}_{= |r_{ba}|^2 \cos^2\theta}$$

and averaging over $\cos^2\theta$ (unpolarised light), we find

$$W^D_{ba} = \frac{4\pi^2}{3\varepsilon\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\varepsilon(\omega_{ba})\,|\vec{r}_{ba}|^2$$

Since $W^D_{ba} = \frac{\dot{N}_{ba}}{N_b}$ one may write

$$\frac{\dot{N}_{ba}}{N_a} = B_{ba}\,\varepsilon(\omega_{ba}) \Rightarrow \boxed{B_{ba} = \frac{4\pi^2}{3\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)|\vec{r}_{ba}|^2}$$

We will now consider the number of atoms making the transition $b \to a$ per unit time, i.e., $\dot{N}_{ab}$

$$\dot{N}_{ab} = \underbrace{A_{ab} N_b}_{\text{spontaneous transitions/time}} + \underbrace{B_{ab} N_b \varepsilon(\omega_{ba})}_{\text{stimulated transitions/time}}$$

Equilibrium $\Rightarrow \dot{N}_{ab} = \dot{N}_{ba}$

$$B_a N_a \varepsilon(\omega_{ba}) = [A_{ab} + B_{ab}\varepsilon(\omega_{ba})] N_b$$

$$\frac{N_a}{N_b} = \frac{A_{ab} + B_{ab}\varepsilon(\omega_{ba})}{B_{ba}\varepsilon(\omega_{ba})} \qquad (*)$$

The system is in thermal equilibrium. Hence,

$$\frac{N_a}{N_b} = \exp\left[-(E_a - E_b)/(k_b T)\right] = \exp\left[\frac{\hbar\omega_{ba}}{k_b T}\right] \qquad (**)$$

$$(*) = (**) \Rightarrow \frac{A_{ab} + B_{ab}\varepsilon(\omega_{ba})}{B_{ba}\varepsilon(\omega_{ba})} = \exp\left[\frac{\hbar\omega_{ba}}{k_b T}\right]$$

$$\Rightarrow \rho(\omega_{ba}) = \frac{A_{ab}}{B_{ba}\left[\exp(\hbar\omega_{ba}/(k_b T)\right] - B_{ab}} \qquad (*)$$

On the other hand, since the atoms are in equilibrium with radiation, $\rho(\omega_{ba})$ will also be given by the Planck distribution law

$$\rho(\omega_{ba}) = \frac{\hbar\omega_{ba}^3}{\pi^2 c^3} \frac{1}{\exp\left[\hbar\omega_{ba}/(k_b T)\right] - 1} \qquad (**)$$

Hence $(*) = (**) \Rightarrow$ $B_{ab} = B_{ba}$ (principle of detailed balancing)

$$A_{ab} = \frac{\hbar\omega_{ba}^3}{\pi^2 c^3} B_{ab}$$

Since

$$B_{ab} = \frac{\omega_{ba}}{\rho(\omega_{ba})} = \frac{4\pi^2}{3\hbar^2}\left(\frac{1}{4\pi\epsilon_0}\right)|D_{ba}|^2$$

we find $A_{ab} = \frac{\hbar\omega_{ba}^3}{\pi^2 c^3} \times \frac{4\pi^2}{3\hbar^2}\left(\frac{1}{4\pi\epsilon_0}\right)|D_{ba}|^2$

$$\boxed{A_{ab} = \frac{4\omega_{ba}^3}{3c^3\hbar}\left(\frac{1}{4\pi\epsilon_0}\right)|D_{ba}|^2}$$