8. Atoms in EM fields

Selection Rules

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AQM

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Let us now apply this formalism to study the interaction of atoms with an E.M. field

We found general formula

$$d\Gamma^{\lambda}_{f\to i} = \frac{\pi e^2}{m^2 \varepsilon_0 \omega V} \left| \langle f | e^{-i\vec{k}\cdot\vec{r}} \vec{\varepsilon}_\lambda \cdot \hat{\vec{p}} | i \rangle \right|^2 \rho(E)\, dE$$

$$\langle f | e^{-i\vec{k}\cdot\vec{r}} \vec{\varepsilon}_\lambda \cdot \hat{\vec{p}} | i \rangle \underset{\text{APPROX}}{\overset{\text{DIPOLE}}{\sim}} -im\omega \langle f | \vec{\varepsilon}_\lambda \cdot \vec{r} | i \rangle$$

In particular, we consider an HYDROGEN ATOM (hydrogen-like with general Z)

$$|i\rangle = |n_i, \ell_i, m_i\rangle \; ; \qquad |f\rangle = |n_f, \ell_f, m_f\rangle$$

$$\langle f | \vec{\varepsilon}_\lambda \cdot \vec{r} | i \rangle = \int_0^\infty r^2 dr\, R^*_{n_f \ell_f}(r) R_{n_i \ell_i}(r)$$

$$\times \int d\Omega\, Y^*_{\ell_f m_f}(\vartheta, \varphi) Y_{\ell_i m_i}(\vartheta, \varphi)\, \vec{\varepsilon}_\lambda \cdot \vec{r}$$

write $\quad \vec{\varepsilon}_\lambda \cdot \vec{r} = r\,(\vec{\varepsilon}_\lambda \cdot \hat{\vec{r}})$ $\qquad \hat{\vec{r}} = \frac{\vec{r}}{|\vec{r}|} = \frac{\vec{r}}{r}$

$$\vec{\varepsilon}_\lambda \cdot \hat{\vec{r}} = \varepsilon_x \sin\vartheta\cos\varphi + \varepsilon_y \sin\vartheta\sin\varphi + \varepsilon_z \cos\vartheta$$

we suppress subscript "λ" for simplicity

now, remember that

$$Y_{10}(\vartheta,\varphi) = \sqrt{\frac{3}{4\pi}}\cos\vartheta$$

$$Y_{1,\pm1}(\vartheta,\varphi) = \mp\sqrt{\frac{3}{8\pi}}\sin\vartheta\, e^{\pm i\varphi}$$

$$= \mp\sqrt{\frac{3}{8\pi}}\sin\vartheta\left[\cos\varphi \pm i\sin\varphi\right]$$

$\Rightarrow$

$$\sin\vartheta\cos\varphi = -\sqrt{\frac{8\pi}{3}}\left(\frac{Y_{1,1} - Y_{1,-1}}{2}\right)$$

$$\cos\vartheta = \sqrt{\frac{4\pi}{3}}\, Y_{10}$$

$$\sin\vartheta\sin\varphi = -\sqrt{\frac{8\pi}{3}}\left(\frac{Y_{1,1} + Y_{1,-1}}{2i}\right)$$

which gives

$$\vec{\varepsilon}_\lambda \cdot \hat{r} = \sqrt{\frac{4\pi}{3}}\left[\varepsilon_z Y_{10} + \frac{-\varepsilon_x + i\varepsilon_y}{\sqrt{2}} Y_{1,1} + \frac{\varepsilon_x + i\varepsilon_y}{\sqrt{2}} Y_{1,-1}\right]$$

$\Rightarrow$ THREE POLARIZATIONS OF PHOTON $\quad m = 0, 1, -1$
SPIN 1

this is convenient because now angular integration can be performed using properties of spherical harmonics with $Y_{1m}(\vartheta, \varphi)$ with $m = \{-1, 0, 1\}$.

Use $$\int d\Omega = \int_0^{2\pi} d\varphi \int_0^{\pi} d\vartheta \sin\vartheta$$

Focus first on $\int d\varphi$, remembering dependence of spherical harmonics on φ

$$Y_{\ell m}(\vartheta, \varphi) \propto e^{im\varphi} P_\ell^m(\cos\vartheta)$$

all dependence on φ is here

$$\langle f | \vec{\varepsilon}_{\lambda} \cdot \vec{r} | i \rangle = \int_0^\infty r^3 dr \; R^*_{n_f \ell_f}(r) R_{n_i \ell_i}(r)$$

$$\int_{-1}^{1} d\cos\vartheta \left[\; \dots \; \right] \underbrace{\int_0^{2\pi} d\varphi \; e^{-im_f\varphi} \, e^{im_i\varphi} \, e^{-im\varphi}} \qquad m = \begin{pmatrix} -1 \\ 0 \\ 1 \end{pmatrix}$$

$$\int_0^{2\pi} d\varphi \; e^{-i[m_f - m_i - m]\varphi} = \frac{\left(1 - e^{-2\pi i (m_f - m_i - m)}\right)}{i[m_f - m_i - m]}$$

recall $m_f, m_i, m_i \in \mathbb{Z}$, if $m_f - m_i - m \neq 0$

then $e^{-2\pi i (m_f - m_i - m)} = 1$

result is zero.

Only exception if $m_f - m_i - m = 0 \Rightarrow m_f - m_i = m$

$= (-1, 0, 1)$

$$\int_0^{2\pi} d\varphi = 2\pi$$

$$\int_0^{2\pi} d\varphi \; e^{-i(m_f - m_i - m)\varphi} = 2\pi \, \delta_{m_f - m_i - m}$$

this provides a first SELECTION RULE

$\Rightarrow$ in Dipole approx, transition can happen

only if $m_f - m_i = \{-1, 0, 1\}$

CONS OF ANGULAR MOM !
PHOTON SPIN 1

Now imagine we rotate reference system such that

$\vec{k} = (0, 0, k_z) \Rightarrow \vec{\varepsilon} = (\varepsilon_x, \varepsilon_y, 0)$ for $\underline{\vec{\varepsilon} \cdot \vec{k} = 0}$

photon momentum

in this case Y_{10} is missing in original formula

so $m_f - m_i = \{-1, 1\}$

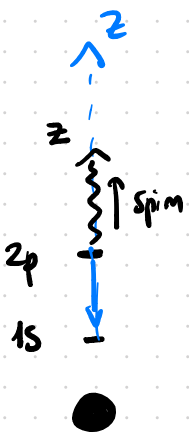
SPECIAL CASE $\left\{ \begin{matrix} l_f = 0 \\ m_f = 0 \end{matrix} \right\}$ (decay to ground state)

$\Rightarrow m = -m_i$ where m is the polarization of the photon !

→ if $m_i = 1$, atom polarized along positive z axis, then photon has $m = -1$

$$\vec{\varepsilon}_\lambda \cdot \hat{r} \to \frac{\varepsilon_x + i\varepsilon_y}{\sqrt{2}} \; Y_{1,-1}(\vartheta, \varphi)$$

ATOM in $m_i = 1$, decays to $m_f = 0$ emitting a photon which comes angular momentum along z axis !



$\frac{\varepsilon_x + i\varepsilon_y}{\sqrt{2}}$ is left-circularly polarized photon with spin ALONG its direction of motion

⇒ POSITIVE HELICITY

What about ϑ integration?

Let's consider for simplicity decays to ground state 1s, such that $Y_{\ell_f,m_f} = Y_{0,0} = \frac{1}{\sqrt{4\pi}}$

then angular integration reads

$$\frac{1}{\sqrt{4\pi}}\int_0^{2\pi} d\varphi \int_{-1}^{1} d\cos\vartheta \; Y_{1,m}(\vartheta,\varphi)\, Y_{\ell_i,m_i}(\vartheta,\varphi) =$$

$$= \frac{1}{\sqrt{4\pi}}\,\delta_{\ell_i,1}\,\delta_{m_i,-m}$$

this part we already discussed

IMPLIES initial state MUST BE $\ell = 1$

In DIPOLE APPROX only $np \to 1s$ transition are allowed

$\Rightarrow$ DOMINANT TRANSITIONS

IMPORTANT : there are no $ns \to ms$ transitions (zero - zero)

$\Rightarrow$ if $l_i = l_f = 0$ we are left with

$$\int d\Omega \, Y_{1m} Y_{l_f m_f} Y_{l_i m_i} \sim \int d\Omega \, Y_{1m} \equiv 0$$

All zero !

MORE IN GENERAL if $l_i \neq 0$ & $l_f \neq 0$

one has to account for total angular momentum

l_i = initial ; L_f = SUM(l_f , l)

photon

Addition of angular momentum gives

$$L_f = \{ l_f + 1, \; l_f, \; |l_f - 1| \} \quad \text{since } l = 1$$

must be equal to l_i !

$\Rightarrow$ Conservation of angular momentum becomes

$$l_f - l_i = \underline{\Delta l = \{-1, 0, +1\}}$$

let us consider $\Delta l = 0$ in particular. This would mean that some transition like $3p \to 2p$ should be allowed.

PARITY gives extra constraint. In fact

$$\langle f | \vec{\varepsilon}_\lambda \cdot \vec{r} | i \rangle \sim \int Y_{l_f m_f} Y_{l_i m_i} \vec{\varepsilon}_\lambda \cdot \vec{r}$$

PARITY TRANSFORMATION sends $\vec{r} \to -\vec{r}$

$$Y_{l_f m_f} Y_{l_i m_i} \to (-1)^{l_f + l_i} Y Y$$

Parity invariance requires therefore that $\underline{l_f + l_i = \text{ODD}}$

PARITY OF STATE MUST CHANGE, $3p \to 2p$ not allowed

$$\Rightarrow \boxed{\Delta \ell = \pm 1}$$ SELECTION RULE IN DIPOLE APPROXIMATION

On top of this, if $V(t) = \frac{e}{m} \vec{A} \cdot \vec{p}$

this has no spin dependence, so it CANNOT FLIP SPIN

$$\Rightarrow \boxed{\Delta S = 0}$$ spin selection rule

Notice that while angular momentum MUST BE CONSERVED, $\Delta \ell = \pm 1$ as a consequence is ONLY TRUE IN DIPOLE APPROXIMATION

$\Rightarrow$ expanding $\langle f | e^{-i\vec{k}\cdot\vec{r}} \, \vec{\varepsilon}_1 \cdot \vec{p} \, | i \rangle$ to higher orders (MULTIPOLE EXPANSION) allows transitions with $|\Delta \ell| > 1$

QUADRUPOLE allows $\underline{\Delta \ell = 2}$ etc...

At higher orders, or if we add a magnetic field, we can also generate $\Delta S \neq 0$ transitions

(see exercises)

IMPORTANT the selection rule that violates $nS \to mS$ transitions is

ABSOLUTE (not only in DIPOLE)

EXPLICIT CASE: $2p \to 1s$ TRANSITION

After having studied the Dipole matrix element in general, and discussed various selection rules, let us now consider an explicit calculation in order to get a feeling of the numerical impact of these decays $\Rightarrow$ decay probability and life-time of excited states.

$$\langle f | \vec{\varepsilon}_i \cdot \vec{r} | i \rangle = \int_0^\infty r^3 dr \; R_{10}^*(r) R_{21}(r)$$

$$\int d\Omega \; Y_{00}^*(\vartheta,\varphi) \, Y_{1,m}(\vartheta,\varphi) \; \vec{\varepsilon}_i \cdot \hat{r}$$

where I used

$|i\rangle = |2p\rangle = |2\,1\,m\rangle$; $|f\rangle = |1s\rangle = |100\rangle$

Let's evaluate radial and angular part explicitly. We get

$$\int_0^\infty dr \, r^3 \left[2 \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0} \right] \left[\frac{1}{\sqrt{24}} \left(\frac{Z}{a_0} \right)^{5/2} r \, e^{-Zr/2a_0} \right]$$

$$= \left(\frac{Z}{a_0} \right)^4 \frac{1}{\sqrt{6}} \int_0^\infty dr \, r^4 \, e^{-3Zr/2a_0} = \frac{24}{\sqrt{6}} \left(\frac{2}{3} \right)^5 \frac{a_0}{Z}$$

Angular part gives instead

$$\frac{1}{\sqrt{4\pi}} \int d\Omega \ \vec{\varepsilon}_1 \cdot \hat{r} \ Y_{1,m}(\vartheta, \varphi) =$$

Y_{00}^* — rewrite this in terms of spherical harm

$$= \frac{1}{\sqrt{3}} \int d\Omega \ Y_{1,m} \left(\varepsilon_z Y_{10} + \frac{-\varepsilon_x + i\varepsilon_y}{\sqrt{2}} Y_{1,1} + \frac{\varepsilon_x + i\varepsilon_y}{\sqrt{2}} Y_{1,-1} \right)$$

$$= \frac{1}{\sqrt{3}} \left[\varepsilon_z \delta_{m,0} + \frac{-\varepsilon_x + i\varepsilon_y}{\sqrt{2}} \delta_{m,1} + \frac{\varepsilon_x + i\varepsilon_y}{\sqrt{2}} \delta_{m,-1} \right]$$

Product of the two integrals gives

$$\langle f | \vec{\varepsilon}_1 \cdot \vec{r} | i \rangle = \frac{24}{\sqrt{6}\sqrt{3}} \left(\frac{2}{3}\right)^5 \left(\frac{a_0}{Z}\right) \left[\ \dots \ \right]$$

now we need to compute $|\langle f | \quad | i \rangle|^2$

from the various Kronecker δ_{ij} we get

$$|\langle f|\vec{\varepsilon}_1\cdot\hat{r}|i\rangle|^2 = 96\left(\frac{2}{3}\right)^{10}\left(\frac{a_0}{Z}\right)^2\cdot\frac{1}{3}\times$$

$$\times\left[\delta_{m,0}\,\varepsilon_z^2 + \frac{1}{2}(\delta_{m,1}+\delta_{m,-1})(\varepsilon_x^2+\varepsilon_y^2)\right]$$

As all cross-products are zero $\delta_{m0}\delta_{m1}=0$ etc

$$d\Gamma^{\lambda}_{2p\to 1s} = \frac{\pi e^2}{m^2\varepsilon_0\omega V}\, m^2\omega^2\,|\langle f|\vec{\varepsilon}_1\cdot\hat{r}|i\rangle|^2\,\rho(E)\,dE$$

from DIPOLE APPROX !

you computed $\rho(E)$ for photons in exercises if we work in volume V, we have

$$d^3n = \frac{V}{(2\pi\hbar)^3}\,dp_x\,dp_y\,dp_z \qquad \text{using } p_i = \frac{2\pi\hbar}{L}n_i$$

$$= \frac{V\,d^3p}{(2\pi\hbar)^3} \qquad \text{photon has } \vec{p}=\vec{k}$$

now $d^3k = d\Omega_k \, k^2 dk = d\Omega_k \left(\frac{k^2 dk}{dE}\right) dE$

for photons $k = \frac{E}{c}$ $\Rightarrow \frac{k^2 dk}{dE} = \frac{k^2}{c} = \frac{E^2}{c^3} = \frac{\hbar^2\omega^2}{c^3}$

$(E = \hbar\omega)$

so $\rho(E)\, dE = \frac{V}{(2\pi\hbar)^3} \frac{\hbar^2\omega^2}{c^3} d\Omega_k \, dE \; \delta(E_f - E_i + \hbar\omega)$

Fixes photon energy!

$$E = \hbar\omega = \frac{1}{2} mc^2 (Z\alpha)^2 \left[1 - \frac{1}{4}\right] = \underline{\underline{E_i - E_f}}$$

$$\omega = \frac{3}{8} \frac{mc^2}{\hbar} (Z\alpha)^2 \quad \text{photon frequency!}$$

and putting everything together we get

$$d\Gamma^{\lambda}_{2p\to 1s} = \frac{\pi e^2 \cancel{\hbar^2} \omega^{\cancel{2}}}{\cancel{m^2} \varepsilon_0 \cancel{\omega} \cancel{V}} |\langle f | \vec{\varepsilon}_\lambda \cdot \vec{r} | i \rangle|^2 \frac{\cancel{V}}{(2\pi)^3 \cancel{\hbar^3}} \frac{\cancel{\hbar^2}\omega^2}{c^3} d\Omega_k$$

$$= \frac{\overbrace{e^2}^{\alpha}}{4\pi\varepsilon_0 \hbar c}\frac{1}{(2\pi)}\left(\frac{\omega^3}{c^2}\right)\left(\frac{a_0}{Z}\right)^2 \frac{2^{15}}{3^{10}}\left[\delta_{m0}\,\varepsilon_z^2 + \frac{\delta_{m1}+\delta_{m-1}}{2}\left(\varepsilon_x^2+\varepsilon_y^2\right)\right] d\Omega_k$$

$$= \left(\frac{\alpha}{2\pi}\right)\left[\frac{\omega^3}{c^2}\right]\left(\frac{a_0}{Z}\right)^2 \frac{2^{15}}{3^{10}}\left[\delta_{m0}\,\varepsilon_z^2 + \frac{\delta_{m1}+\delta_{m-1}}{2}\left(\varepsilon_x^2+\varepsilon_y^2\right)\right] d\Omega_k$$

with ω fixed before!

we still need to integrate over directions of photon momenta $d\Omega_{\vec{k}}$

recall initial state 2p can have $m = \{-1, 0, 1\}$

Depending on exact initial state, we need to integrate always remembering that $\vec{\varepsilon}_\lambda \cdot \vec{k} = 0$ (transversality)

the expression becomes simpler if we assume that ALL m values are EQUALLY PROBABLE => we average $\frac{1}{3}\sum_{m=\{-1,0,1\}} d\Gamma_m^\lambda$

in fact, sum becomes

$$\frac{1}{3}\sum_{m=-1}^{1}\left[\delta_{m0}\,\varepsilon_z^2 + \frac{\delta_{m1}+\delta_{m-1}}{2}\left(\varepsilon_x^2+\varepsilon_y^2\right)\right] = \frac{\varepsilon_x^2+\varepsilon_y^2+\varepsilon_z^2}{3}$$

$$= 1/3$$

normalization condition of polarization vector!

remember that photon has 2 polarizations $\vec{\varepsilon}_\lambda$!

so actually $\frac{1}{3}\sum_{\lambda=1}^{2}\sum_{m=-1}^{1}\left[\quad\right] = \frac{2}{3}$!

now integration over $d\Omega_k = 4\pi$ (nothing depends on $\hat{k}$ anymore)

and we get

$$\langle\Gamma(2p\to 1s)\rangle = \left(\frac{2}{2\pi}\right)\left[\frac{\omega^3}{c^2}\right]\left(\frac{a_0}{Z}\right)^2\frac{2^{15}}{3^{10}}\,4\pi\,\frac{2}{3}$$

$$= 2\alpha \left(\frac{a_0}{Z}\right)^2 \frac{2^{16}}{3^{11}} \frac{1}{c^2} \left[\underbrace{\frac{3}{2^3} \frac{mc^2}{\hbar} (Z\alpha)^2}_{\text{photon frequency}}\right]^3$$

$$= \alpha^7 Z^4 a_0^2 \left(\frac{2^{17}}{3^{11}}\right) \frac{3^3}{2^9} \frac{m^3 c^6}{\hbar^3} \; ; \qquad a_0 = \frac{\hbar}{mc\alpha}$$

$$= \alpha^{\cancel{7}\,5} Z^4 \frac{\cancel{\hbar^2}}{\cancel{m^2}\cancel{c^2}\cancel{\alpha^2}} \, m^{\cancel{3}} \left(\frac{2}{3}\right)^8 \frac{c^{\cancel{6}\,2}}{\hbar^{\cancel{3}}} \frac{1}{\cancel{c^2}}$$

$$\langle \Gamma_{2p\to 1s} \rangle = \left(\frac{2}{3}\right)^8 \alpha^5 \frac{mc^2}{\hbar} Z^4 = 0.62 \cdot 10^9 \frac{Z^4}{s}$$

<u>DECAY RATE</u> ~ <u>EMISSION RATE</u> FOR PHOTONS!

$$\tau = \frac{1}{\Gamma} = 1.61 \cdot 10^{-9}\ s$$ lifetime

remember $P_1(t) = |C_1(t)|^2 = e^{-\Gamma t}$

exponential decay! see <u>lecture 6</u>

Since we have the rate, we can compute the

RADIATION INTENSITY as

$$dI(\omega) = \underbrace{\hbar\omega}_{\text{photon energy}} \cdot d\Gamma$$

rate for emission of photons

$$= \hbar\omega \frac{\pi e^2}{m^2 \varepsilon_0 \omega V} m^2 \omega^2 \sum_{\lambda=1}^{2} \left| \langle f | \vec{\varepsilon}^{\lambda} \cdot \vec{r} | i \rangle \right|^2 \frac{V}{(2\pi)^3} \frac{\omega^2}{c^2} d\Omega_k$$

$$= \frac{1}{2\pi} \frac{e^2}{4\pi\varepsilon_0} \frac{\omega^4}{c^3} \sum_{\lambda=1}^{2} \left| \langle f | \vec{\varepsilon}^{\lambda} \cdot \vec{r} | i \rangle \right|^2$$

~ classical formula for intensity of light emitted by an oscillating DIPOLE of electric dipole moment $\vec{d} = e \langle f | \vec{r} | i \rangle e^{-i\omega t}$