7. Interactions of Atoms with EM Fields (Emission & Absorption)

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AQM

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INTERACTION WITH ELECTROMAGNETIC FIELDS

After having developed the "general formalism" for time dependent phenomena in perturbation theory, we now want to apply it to the interaction of ATOMS with time-dependent EM fields

Let us start with a quick recap of CLASSICAL ELECTRODYNAMICS $\vec{E}$ = electric field ; $\vec{B}$ = magnetic field

MAXWELL EQUATIONS

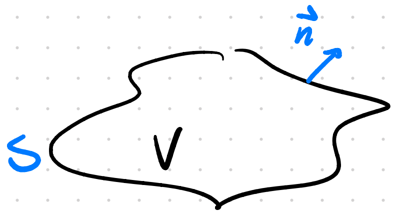
$$\begin{cases} \vec{\nabla}\cdot\vec{B} = 0 \\ \vec{\nabla}\cdot\vec{E} = \frac{1}{\varepsilon_0}\rho(\vec{r},t) \\ \vec{\nabla}\times\vec{B} - \frac{1}{c^2}\frac{\partial\vec{E}}{\partial t} = \mu_0\vec{j}(\vec{r},t) \\ \vec{\nabla}\times\vec{E} + \frac{\partial\vec{B}}{\partial t} = 0 \end{cases}$$

$\rho(\vec{r},t)$ = charge density ; $\vec{j}(\vec{r},t)$ = current density

$$\Rightarrow \quad \frac{\partial \rho(\vec{r},t)}{\partial t} + \vec{\nabla}\cdot\vec{j}(\vec{r},t) = 0$$

$$\Downarrow$$

$$\frac{d}{dt}\underbrace{\int_V d\vec{r}\,\rho(\vec{r},t)}_{Q} = -\int_S dS\;\vec{n}\cdot\vec{j}(\vec{r},t)$$



"charge Q conservation"

A charged particle of charge q experiences Lorentz force

$$m\frac{d^2\vec{r}}{dt^2} = q\left[\vec{E}(\vec{r},t) + \vec{v}\times\vec{B}(\vec{r},t)\right]$$

velocity

electron has $q = -e$

to describe a quantum system we need the Hamiltonian, built out of POTENTIALS

$$\vec{B} = \vec{\nabla} \times \vec{A}$$

$$\vec{E} = -\frac{\partial \vec{A}}{\partial t} - \vec{\nabla}\phi$$

$\vec{A}(\vec{r},t)$ vector potential

$\phi(\vec{r},t)$ scalar potential

in terms of $\vec{A}, \phi$ first & last Maxwell Eqs are IDENTICALLY SATISFIED, while other two give

$$-\nabla^2\phi - \frac{\partial}{\partial t}\left[\vec{\nabla}\cdot\vec{A}\right] = \frac{\rho(\vec{r},t)}{\varepsilon_0}$$

$$\left[-\nabla^2 + \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right]\vec{A} + \vec{\nabla}\left[\vec{\nabla}\cdot\vec{A} + \frac{1}{c^2}\frac{\partial\phi}{\partial t}\right] = \mu_0\vec{j}(\vec{r},t)$$

GAUGE INVARIANCE $\Rightarrow$ Maxwell Eqs don't change if we redefine potentials as:

$$\begin{cases} \phi' = \phi + \dfrac{\partial g}{\partial t} \\ \vec{A}' = \vec{A} - \vec{\nabla} g \end{cases}$$

with smooth function $g(\vec{r}, t)$

we can pick $g(\vec{r}, t)$ to simplify problem

OFTEN USE LORENZ GAUGE

note not LORENTZ

another person ! :)

$$\Rightarrow \boxed{\vec{\nabla} \cdot \vec{A} + \frac{1}{c^2} \frac{\partial \phi}{\partial t} = 0}$$

then equations simplify a bit to

$$\begin{cases} \left(-\nabla^2 + \dfrac{1}{c^2} \dfrac{\partial^2}{\partial t^2} \right) \phi = \dfrac{\rho(\vec{r}, t)}{\varepsilon_0} \\ \left(-\nabla^2 + \dfrac{1}{c^2} \dfrac{\partial^2}{\partial t^2} \right) \vec{A} = \mu_0 \vec{J}(\vec{r}, t) \end{cases}$$

if $\rho(\vec{r},t) = \rho(\vec{r})$ STATIC CHARGE DISTRIBUTION

then we choose often Coulomb Gauge

$$\frac{\partial \rho(\vec{r})}{\partial t} = 0 \quad ; \quad \vec{\nabla} \cdot \vec{A} = 0$$

$$\begin{cases} -\nabla^2 \phi = \dfrac{\rho(\vec{r})}{\varepsilon_0} \\ \left(-\nabla^2 + \dfrac{1}{c^2}\dfrac{\partial^2}{\partial t^2}\right)\vec{A} = \mu_0 \vec{j}(\vec{r},t) \end{cases}$$

In terms of $\vec{A}$, ϕ, the Hamiltonian for interaction with E.M. field is taken to be

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

(for electron $q = -e$)

$\vec{p} \to \vec{p} - q\vec{A}$ MINIMAL COUPLING this form of the Hamiltonian reproduces the equations of motion (Lorentz Force !)

Now let's focus on phenomenon of RADIATION & its interaction with QUANTUM SYSTEMS

We will use a so called Semi-classical approximation where the E.M. field is not "fully quantized".

Start from

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

with $\rho(\vec{r},t) = \rho(\vec{r})$ <u>STATIC</u>

$$\Rightarrow \nabla^2\phi = -\frac{\rho}{\varepsilon_0} \qquad \phi(\vec{r}) \quad \underline{\text{STATIC}}$$

In Coulomb GAUGE

$$\underline{\vec{\nabla}\cdot\vec{A} = 0}$$

All radiation phenomena related to $\underline{\vec{A}(\vec{r},t)}$

this part of Hamiltonian becomes

$$\frac{1}{2m}\left[\vec{p} - q\vec{A}(\vec{r},t)\right]^2 = +\frac{1}{2m}\left[-i\hbar\vec{\nabla} - q\vec{A}(\vec{r},t)\right]^2$$

$$= \frac{1}{2m}\left[\vec{p}^{\,2} + q^2|\vec{A}|^2 + 2i\hbar q\,\underbrace{\vec{\nabla}\cdot\vec{A}}\right]$$

use Coulomb gauge

$$\vec{\nabla}\cdot\vec{A} = (\underbrace{\vec{\nabla}\cdot\vec{A}}_{=0}) + \vec{A}\cdot\vec{\nabla}$$

$$= \frac{1}{2m}\left(\vec{p}^{\,2} + q^2|\vec{A}|^2 - 2q\,\vec{A}\cdot\vec{p}\right)$$

usual kinetic term

$\propto |\vec{A}|^2$, neglect

assuming "small field" (?)

emission/absorption of 1 photon.

$\Longrightarrow$ actually, we will see that $|\vec{A}|^2$ would correspond to 2 γ interactions !

if $\rho = \vec{j} = 0$ (interaction with free EM field)

then we can put $\phi(\vec{r}) = 0$ & all interaction Hamiltonian becomes

$$H = H_0 + V(t)$$

$$H_0 = \frac{\vec{p}^2}{2m} + V_0$$ [it could be Hamiltonian of some Atom ...]

$$V(t) = -\frac{q}{m}\vec{A}\cdot\vec{p} = +\frac{e}{m}\vec{A}\cdot\vec{p}$$ (electron $q = -e$)

$$\vec{A}(\vec{r},t) = \vec{A}_0(\vec{r})\, e^{-i\omega t} + \underbrace{\vec{A}_0^{+}\, e^{i\omega t}}_{\text{c.c. of first term}}$$

⇑

monochromatic wave with two components
First increases energy ↗ ABSORPTION
Second decreases it! ↘ EMISSION

for free field (away from source that generated $\vec{A}$)

Maxwell Equation becomes [same for A_0^+]

$$-\nabla^2 \vec{A}_0(\vec{r}) - \frac{\omega^2}{c^2} \vec{A}_0(\vec{r}) = 0 \qquad \left(\vec{j}(\vec{r},t) = 0 \right)$$

Solutions are trivial $\vec{A}_0(\vec{r}) = \vec{A}_0 e^{\pm i \vec{k}\cdot\vec{r}}$

with $\vec{k}^2 = \frac{\omega^2}{c^2}$ $\qquad \vec{A}_0^+(\vec{r}) = \vec{A}_0^+ e^{\mp i \vec{k}\cdot\vec{r}}$

Clearly we are free to pick $\pm\vec{k}$ in $\vec{A}_0(\vec{r})$

our choice is ARBITRARY => then we get

$$\vec{A}_0(\vec{r},t) = \vec{A}_0 e^{i[\vec{k}\cdot\vec{r} - \omega t]} + \vec{A}_0^+ e^{-[i\vec{k}\cdot\vec{r} - \omega t]}$$

$$\vec{E} = -\frac{\partial \vec{A}}{\partial t} \qquad \& \qquad \vec{B} = \vec{\nabla} \times \vec{A}$$

and from them we can get the energy density of the E.M. field

$$\mathcal{E} = \frac{\varepsilon_0}{2}\vec{E}^2 + \frac{1}{2\mu_0}\vec{B}^2$$

Explicitly we get

$$\begin{cases} \vec{E} = i\omega\left[\vec{A}_0 e^{i(\vec{k}\cdot\vec{r}-\omega t)} - \vec{A}_0^{\dagger} e^{-i(\vec{k}\cdot\vec{r}-\omega t)}\right] \\ \vec{B} = -i\left[\vec{k}\times\vec{A}_0\, e^{i(\vec{k}\cdot\vec{r}-\omega t)} - \vec{k}\times\vec{A}_0^{\dagger}\, e^{-i(\vec{k}\cdot\vec{r}-\omega t)}\right] \end{cases}$$

notice

$\vec{\nabla}\cdot\vec{E} = 0$ implies $\vec{k}\cdot\vec{A}_0 = \vec{k}\cdot\vec{A}_0^{\dagger} = 0$

"transversality condition"

$$\mathcal{E} = \frac{\varepsilon_0}{2}\left[\omega^2\left(\vec{A}_0\cdot\vec{A}_0^{\dagger} + \vec{A}_0^{\dagger}\cdot\vec{A}_0\right)\right]$$

$$+ \frac{1}{2\mu_0}\left[(\vec{k}\times\vec{A}_0)\cdot(\vec{k}\times\vec{A}_0^{\dagger}) + (\vec{k}\times\vec{A}_0^{\dagger})\cdot(\vec{k}\times\vec{A}_0)\right]$$

+ terms $\propto e^{\pm i\omega t}$, i.e. oscillating!

We can separate the oscillating part from the rest, since if we average in time, it will drop eventually.

We can simplify second term using

$$(a \times b) \cdot (c \times d) = (a \cdot c)(b \cdot d) - (a \cdot d)(b \cdot c)$$

$$(\vec{k} \times \vec{A}_0) \cdot (\vec{k} \times \vec{A}_0^{+}) = \vec{k}^2 \vec{A}_0 \cdot \vec{A}_0^{+} - (\vec{k} \cdot \vec{A}_0^{+})(\vec{A}_0 \cdot \vec{k})$$

$(\vec{k} \times \vec{A}_0^{+}) \cdot (\vec{k} \times \vec{A}_0) =$ same $\vec{A}_0 \Leftrightarrow \vec{A}_0^{+}$ such that

$$\text{SUM} = \frac{1}{2\mu_0}\left[\vec{k}^2 (\vec{A}_0 \cdot \vec{A}_0^{+} + \vec{A}_0^{+} \cdot \vec{A}_0) \right]$$

where we used $\underline{\vec{k} \cdot \vec{A}_0 = \vec{k} \cdot \vec{A}_0^{+} = 0}$

remember finally $\frac{\vec{k}^2}{\varepsilon_0 \mu_0} = c^2 \vec{k}^2 = \omega^2$!

so finally two non-oscillating contributions are the same and we get

$$\mathcal{E} = \varepsilon_0 \omega^2 \left(\vec{A}_0 \cdot \vec{A}_0^{\,+} + \vec{A}_0^{\,+} \cdot \vec{A}_0 \right) + \text{oscillating terms}$$

Classically $\underline{\mathcal{E} = 2\varepsilon_0 \omega^2 |\vec{A}_0|^2}$

INSTEAD, for a full QUANTUM MECHANICAL treatment of the E.M. field, one needs to treat $\vec{A}_0$, $\vec{A}_0^{\,+}$ as <u>operators</u> and impose commutation rules

$\Rightarrow$ see <u>TUTORIALS</u> !

Here we take a shortcut, SEMICLASSICAL APPROXIMATION

$$\int_V \mathcal{E} \, d^3\vec{r} = 2 \varepsilon_0 \omega^2 |A_0|^2 V$$

radiation in volume V <u>CLASSICALLY</u>

now we assume that this radiation is carried by N "photons" with energy $N\hbar\omega$ which allows us to fix the magnitude of $|\vec{A}_0|$

$$2\varepsilon_0\omega^2|\vec{A}_0|^2 V = N\hbar\omega$$

$$\longrightarrow \quad |\vec{A}_0| = \sqrt{N\frac{\hbar}{2\varepsilon_0\omega V}}$$

We specify the "direction" of $\vec{A}_0$ by a POLARIZATION vector $\vec{\varepsilon}_\lambda$ with

$$\vec{\varepsilon}_\lambda\cdot\vec{\varepsilon}_\lambda = 1 \quad ; \quad \vec{\varepsilon}_\lambda\cdot\vec{k} = 0$$

transversality condition

which admits "two solutions" to span plane orthogonal to $\vec{k}$ $\Rightarrow$ ε_λ with $\lambda = 1,2$

$$\vec{A}_0 = \vec{\varepsilon}_\lambda\sqrt{\frac{N_\lambda\hbar}{2\varepsilon_0\omega V}} \equiv \vec{\varepsilon}_\lambda(\vec{k})\sqrt{\frac{N_\lambda(\vec{k})\hbar}{2\varepsilon_0\omega V}}$$

For full field we need to sum over λ & $\vec{k}$

$$\vec{A}(\vec{r},t) = \sqrt{\frac{\hbar}{2\varepsilon_0 V}} \sum_{\substack{\lambda=1 \\ \vec{k}}}^{2} \frac{1}{\sqrt{\omega_k}} \varepsilon_\lambda \left[\sqrt{N_\lambda(\vec{k})}\, e^{+i(\vec{k}\cdot\vec{r}-\omega_{\vec{k}} t)} + \sqrt{N_\lambda(\vec{k})}\, e^{-i(\vec{k}\cdot\vec{r}-\omega_{\vec{k}} t)} \right]$$

this expression is "almost correct"

it indeed looks like a Fourier Decomposition

$$\vec{A}(\vec{r},t) = \frac{1}{\sqrt{V}} \sum_{\lambda,\vec{k}} \sqrt{\frac{\hbar}{2\varepsilon_0 \omega_{\vec{k}}}}\, \vec{\varepsilon}_\lambda \left[A_\lambda(\vec{k})\, e^{i(\vec{k}\cdot\vec{r}-\omega_k t)} + A_\lambda^+(\vec{k})\, e^{-i(\vec{k}\cdot\vec{r}-\omega_k t)} \right]$$

where in semiclassical approximation $A_\lambda = A_\lambda^+ = \sqrt{N_\lambda(\vec{k})}$

$\Rightarrow$ Quantum treatment starts from this Fourier Decomposition, promoting A, A^+ to <u>OPERATORS</u>

One then finds [see TUTORIALS]

$$H = \sum_{k,\lambda} \frac{\hbar\omega}{2} \left[A_\lambda(\vec{k}) A^+_\lambda(\vec{k}) + A^+_\lambda(\vec{k}) A_\lambda(\vec{k}) \right]$$

Quantize it AS HARMONIC OSCILLATOR

$$\left[A_\lambda(\vec{k}), A^+_{\lambda'}(\vec{q}) \right] = \delta_{\lambda\lambda'} \, \delta_{\vec{k}\vec{q}}$$

$$H = \sum_{k,\lambda} \hbar\omega \left[\frac{1}{2} + A^+_\lambda(\vec{k}) A_\lambda(\vec{k}) \right]$$

INFINITE "zero point" ENERGY

Cancels out in Energy Differences!

$$H \overset{!}{\equiv} \sum_{k,\lambda} \hbar\omega \, A^+_\lambda(\vec{k}) A_\lambda(\vec{k})$$

DEFINE

$$\left.\begin{array}{ll} A_\lambda(\vec{k}) & \text{DESTROYS} \\ A^+_\lambda(\vec{k}) & \text{CREATES} \end{array}\right\} \text{photon of frequency } \hbar\omega_{\vec{k}}, \text{ momentum } \hbar\vec{k}$$

$$A_\lambda(\vec{k})|0\rangle = 0$$

$$|n\rangle = \frac{1}{\sqrt{n!}}\left[A_\lambda^\dagger(\vec{k})\right]^n|0\rangle$$ state with n photons of momentum $\hbar\vec{k}$

Action of these operators on state with N photons is like those for harmonic oscillator:

$$A_\lambda(\vec{k})\,|N_\lambda(\vec{k})\rangle = \sqrt{N_\lambda(\vec{k})}\,|N_\lambda(\vec{k})-1\rangle$$

$$A_\lambda^\dagger(\vec{k})\,|N_\lambda(\vec{k})\rangle = \sqrt{N_\lambda(\vec{k})+1}\,|N_\lambda(\vec{k})+1\rangle$$

Different from semiclassical approach !

In semiclassical approach we miss $+1$ $\Rightarrow$ probability to produce [EMITT] 1 photon when N are present is ENHANCED $\sim\sqrt{N+1}$

"+1" $\equiv$ SPONTANEOUS EMISSION

Finally we compute the momentum :

$$\vec{P} = \varepsilon_0 \int d^3\vec{r} \left[\vec{E}(\vec{r},t) \times \vec{B}(\vec{r},t) \right]$$

$$= \dots = \sum_{\lambda,\vec{k}} \underbrace{\hbar\vec{k} \left[A^+_\lambda(\vec{k})\, A_\lambda(\vec{k}) \right]}_{\text{total momentum carried by all photons}}$$

$\Rightarrow \; A^+_\lambda(\vec{k})\, A_\lambda(\vec{k}) = \hat{N}_\lambda(k)$ "number operator"

counts # photons with {pol λ ; momentum $\hbar\vec{k}$ }

Now let's use this in a <u>SPECIFIC SITUATION</u>

$|\psi\rangle$ = some excited state of an Hydrogen Atom

+ zero photons $(N_\lambda(\vec{k}) = 0)$

$\downarrow$

transition to lower state with emission of 1 photon if "operator" $\vec{A}(\vec{r},t)$ acts on this state

$$|\psi\rangle \otimes |0\rangle = |i\rangle \quad \text{initial state}$$

↑ zero photons

$$A_\lambda(\vec{k})\,|0\rangle = 0 \qquad A^{+}_{\lambda}(\vec{k})\,|0\rangle = |1\rangle$$

thanks to + 1 !

SPONTANEOUS EMISSION !

so the field we need to consider is

$$\vec{A}(\vec{r},t) = \sqrt{\frac{\hbar}{2\varepsilon_0 \omega V}}\; \vec{\varepsilon}_\lambda(\vec{k})\, e^{-i(\vec{k}\cdot\vec{r}-\omega t)}$$

$$V(t) = \frac{e}{m}\sqrt{\frac{\hbar}{2\varepsilon_0 \omega V}}\; e^{-i(\vec{k}\cdot\vec{r}-\omega t)}\; \vec{\varepsilon}_\lambda(\vec{k})\cdot\vec{p}$$

Now we can use FERMI GOLDEN RULE

with Harmonic Potential

$$d\Gamma_{i\to f} = \frac{2\pi}{\hbar} |\langle f|H|i\rangle|^2 \rho(E)\, dE$$

density of states for emitted photon $E < \mathcal{E} < E + dE$

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

matrix element to calculate to get

1 photon transition

Notice that this justifies having neglected term proportional to $|\vec{A}|^2$ in Hamiltonian

$\Longrightarrow$ it generates transitions with 2 photons which we do not consider here.

Let's see how we can calculate this matrix element

$$\langle f | e^{-i\vec{k}\cdot\vec{r}} \underbrace{\vec{\varepsilon}_\perp \cdot \hat{\vec{p}}} | i \rangle$$

$\hat{\vec{p}}$ = operator

we can estimate magnitude of various pieces

Imagine some ATOM with Z nuclear charge

$\vec{\varepsilon}\cdot\vec{p} \sim |\vec{p}| \sim Zmc\alpha$ typical momentum

because $E = \dfrac{p^2}{2m} \cong -\dfrac{1}{2} mc^2 \dfrac{(Z\alpha)^2}{n^2}$

↑ state n

so $\Rightarrow p^2 \sim [mc\, Z\alpha]^2$

what about $e^{-i\vec{k}\cdot\vec{r}}$? $|\vec{r}| \sim \dfrac{\hbar}{mc\,Z\alpha}$ Bohr RADIUS

again with $n = 1$

note that $|\vec{p}|$ typical momentum of electron

$|\vec{k}|$ typical momentum of photon $p_\gamma = \hbar k$

FOR PHOTON $E \sim \hbar k c = \hbar \omega$

$$k \sim \frac{\hbar\omega}{\hbar c} \sim \frac{mc^2 (Z\alpha)^2}{2\hbar c}$$

so $$|\vec{k}\cdot\vec{r}| \sim \frac{Z\alpha}{2}$$

so if $Z\alpha \ll 1$ (small nuclear charge)

$$\Rightarrow \underline{e^{-i\vec{k}\cdot\vec{r}} \sim 1}$$ otherwise we expand

$$e^{-i\vec{k}\cdot\vec{r}} = \sum_{j=0}^{\infty} \frac{(-i)^j}{j!} (\vec{k}\cdot\vec{r})^j$$

each new term suppressed, so long as

$\underline{Z\alpha < 1}$

if we keep only "leading order": $e^{-i\vec{k}\cdot\vec{r}} = 1$

$$\langle f | \varepsilon_\lambda \cdot \vec{p} | i \rangle = \vec{\varepsilon}_\lambda \cdot \langle f | m \frac{d\vec{r}}{dt} | i \rangle$$

$$= m \vec{\varepsilon}_\lambda \cdot \langle f | \frac{i}{\hbar} [H_0, \vec{r}] | i \rangle$$

equation of motion

unperturbed Hamiltonian
$|f\rangle$ & $|i\rangle$ are its eigenstates!

$$= im \left(\frac{E_f - E_i}{\hbar} \right) \vec{\varepsilon}_\lambda \cdot \langle f | \vec{r} | i \rangle$$

$$= -im\omega \langle f | \vec{\varepsilon}_\lambda \cdot \vec{r} | i \rangle$$ DIPOLE APPROXIMATION

$E_f - E_i = -\hbar\omega$ (final state has emitted photon, has lower energy!)

the reason why this is called "DIPOLE" is because in this case

$$\vec{V} = \frac{e}{m}\vec{A}\cdot\vec{p} \qquad \& \qquad \vec{E} = -\frac{\partial \vec{A}}{\partial t} = -i\omega\vec{A}$$

in this case

$$\Rightarrow V = \frac{e}{m}\bar{A}\cdot\vec{p} = \frac{e}{m}\frac{i}{\omega}\vec{E}\cdot\vec{p}$$

following same steps as before in $\langle f|(\dots)|i\rangle$

$$\vec{\varepsilon}_\lambda\cdot\vec{p} \Rightarrow -im\omega\,\vec{\varepsilon}_\lambda\cdot\vec{r}$$

$$V = \frac{e}{m}\frac{i}{\omega}(-im\omega)\vec{E}\cdot\vec{r} = e\vec{E}\cdot\vec{r}$$

this is the potential of a dipole with momentum $\vec{d} = -e\vec{r}$ in electric field $\vec{E}$