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3 Interaction of atoms with electromagnetic radiation

So far: atomic structure, levels
Now: dynamics, how to get from one level to another

3.1. Atomic transitions

3.1.1. Electromagnetic fields and charged particles

Unlike section 2.2, static fields, we now have simultaneus E & B fields within an electromagnetic wave.

It is often convenient to express fields via potentials

don't confuse w. wavefct.

$$\vec{\mathbf{E}}(\vec{r},t) = -\vec{\nabla}\,\varphi(\vec{r},t) - \frac{\partial}{\partial t}\vec{A}(\vec{r},t) \qquad \varphi\text{: scalar potential} \tag{3.1}$$

$$\vec{B}(\vec{r},t) = \vec{\nabla}\times\vec{A}(\vec{r},t) \qquad \vec{A} = \text{vector potential}$$

to distinguish from energy

Potentials are not unique, they can be changed via

Gauge transformations

$$\vec{A} \to \vec{A} + \vec{\nabla}\chi(\vec{r},t) \qquad \varphi \to \varphi - \frac{\partial}{\partial t}\chi(\vec{r},t), \tag{3.2}$$

where $\chi(\vec{r},t) \in \mathbb{R}$ is any differentiable function

Through this freedom we can choose

Coulomb gauge $\quad \vec{\nabla}\cdot\vec{A} = 0 \qquad (3.3)$

• then $\varphi = 0$ and $\vec{\nabla}^2\vec{A} - \frac{1}{c^2}\frac{\partial^2\vec{A}}{\partial t^2} = 0$ (wave-equation 3.4)

with solution (elm. wave packet) $\qquad \omega = |\vec{k}|c \qquad (3.5)$

phase

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

spectral Amplitude $\qquad$ polarisation $\vec{\varepsilon} \in \mathbb{C}^3$

• laser: δ_ω = fixed, e.g. $= 0$
• incoherent radiation: δ_ω random $\forall \omega$

Imagine:

Hamiltonian for charged ~~atom~~ electron in radiation field

$$\hat{H} = \frac{1}{2m}\left(\hat{p} + e\vec{A}\right)^2 - \frac{Ze^2}{(4\pi\varepsilon_0)\, r} \qquad (3.6)$$

Insert $\hat{p} = -i\hbar\vec{\nabla}$ and useing $\vec{\nabla}\cdot\vec{A}\cdot\ldots = \vec{A}\cdot\vec{\nabla}\cdot\ldots + \underbrace{(\vec{\nabla}\cdot\vec{A})}_{=0}\cdot\ldots$

we get atom-radiation Hamiltonian

$$\boxed{\hat{H}(t) = \underbrace{-\frac{\hbar^2}{2m}\vec{\nabla}^2 - \frac{Ze^2}{(4\pi\varepsilon_0)\, r}}_{=\hat{H}_0} \underbrace{-i\hbar\frac{e}{m}\vec{A}(\vec{r},t)\cdot\vec{\nabla} + \frac{e^2}{2m}\left(\vec{A}(r,t)\right)^2}_{=\hat{H}'(t)}} \qquad (3.7)$$

- This has the form of Eq. (1.29) for time-dependent perturbation theory
- It seems to depend on the gauge, but gauge just change inconsequential spatial phase of wavefunction (see book)
- can neglect $\vec{A}^2$ term (will do now) except in very strong fields

3.1.2. Transition rates

Assume we start in atomic state $|\phi_a\rangle = |n_a l_a m_a\rangle$ (multi-index)

Solving TDSE $i\hbar|\dot{\Psi}(t)\rangle = \hat{H}(t)\,|\Psi(t)\rangle$ for statevector $|\Psi(t)\rangle = \sum_k c_k |k\rangle$ in general too hard.

Use TDPT (see section 1.2.5), thus amplitude for transition $|\phi_a\rangle \to |\phi_b\rangle$

$$c_b^{(1)}(t) = (i\hbar)^{-1}\int_0^t H'_{ba}(t')\exp(i\omega_{ba}t')\,dt' \qquad (3.8) \qquad \omega_{ba} = (E_b - E_a)/\hbar$$

Need:

$$H'_{ba}(t') = \langle\phi_b|\hat{H}'(t)|\phi_a\rangle$$

$$= -i\hbar\frac{e}{m}\int_0^\infty d\omega\, A_0(\omega)\, \vec{\varepsilon}\cdot\langle\phi_b|\frac{1}{2}\left(e^{i\vec{k}\vec{r} - i\omega t + i\delta_\omega} + e^{-i\vec{k}\vec{r} + i\omega t - i\delta_\omega}\right)\vec{\nabla}|\phi_a\rangle \qquad (3.9)$$

scalar-product

Insert (3.9) into (3.8):

$$c_b^{(1)}(t) = -\frac{e}{2m}\int_0^\infty d\omega\, A_0(\omega)\Big[e^{i\delta_\omega}\langle\phi_b|e^{i\vec{k}\vec{r}}\,\vec{\varepsilon}\cdot\vec{\nabla}|\phi_a\rangle\int_0^t dt'\, e^{i(\omega_{ba}-\omega)t'}$$

$$+ e^{-i\delta_\omega}\langle\phi_b|e^{-i\vec{k}\vec{r}}\,\vec{\varepsilon}\cdot\vec{\nabla}|\phi_a\rangle\int_0^t dt'\, e^{i(\omega_{ba}+\omega)t'}\Big] \qquad (3.10)$$

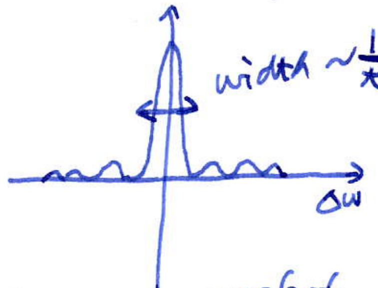
Explicitly do time integrals $\equiv \Delta\omega$ see section 1.2.5

$$I \equiv \int_0^t dt' \, e^{i(\omega_{ba} \pm \omega)t'} = \frac{e^{i(\omega_{ba} \pm \omega)t'} - 1}{i(\omega_{ba} \pm \omega)}$$

We see

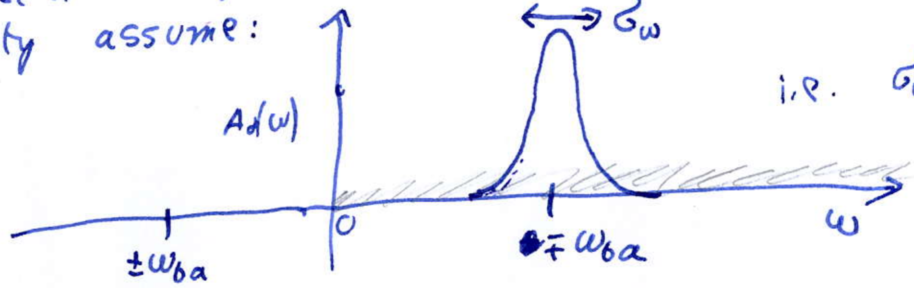
$$|I|^2 = \left| \frac{e^{i\Delta\omega t'} - 1}{i\Delta\omega} \right|^2 = \left| e^{\frac{i\Delta\omega t'}{2}} \frac{\left(e^{i\frac{\Delta\omega}{2}t'} - e^{-i\frac{\Delta\omega}{2}t'}\right)}{i\Delta\omega} \right|^2 = 2\frac{\sin^2\left(\frac{\Delta\omega}{2}t\right)}{\Delta\omega^2} = F(\Delta\omega)$$

Plot of $F(\Delta\omega)$



We see that r.h.s. of (3.10) is only significant for $\Delta\omega = \omega_{ba} \pm \omega = 0.$
$\Rightarrow \omega = -\omega_{ba}$ or $\omega = +\omega_{ba}$

Now our e/m-wavepacket (3.5) contains many different ω.
For simplicity assume:



i.e. $\sigma_\omega \ll |\omega_{ba}|$

$\omega > 0$!

We can then have two cases:
- $E_b > E_a \Rightarrow \omega_{ba} > 0 \Rightarrow \omega_{ba} - \omega$ term in (3.10) will contribute
- $E_b < E_a \Rightarrow \omega_{ba} < 0 \Rightarrow \omega_{ba} + \omega$ term in (3.10) will contribute

ABSORPTION $E_b > E_a$ | Neglect second term in (3.10) and write

$$|c_b^{(1)}(t)| = \frac{1}{2}\left(\frac{e}{2m}\right)^2 \left| \int_0^\infty d\omega \; A_0(\omega) \; M_{ba} \; F(t, \omega - \omega_{ba}) \, e^{i\delta_\omega} \right|^2 \quad (3.11)$$

with <u>Matrix element:</u>

because $\omega = |\vec{k}|c$

$$\boxed{M_{ba}^{(\omega)} = \langle \phi_b | \exp(i\vec{k}\vec{r}) \, \hat{\varepsilon} \cdot \vec{\nabla} | \phi_a \rangle} \quad (3.12)$$

Note, No "e", other definitions may be <u>with</u> e

- Normally $\left| \int_0^\infty d\omega \; z(\omega) \right|^2 = \int_0^\infty d\omega \int_0^\infty d\omega' \; \underbrace{z^*(\omega) z(\omega')}_{\text{contains } e^{-i(\delta_\omega - \delta_{\omega'})}}$, $z \in \mathbb{C}$

But: $\delta_\omega, \delta_{\omega'}$ (<u>incoherent light</u>) for <u>random</u> $\Rightarrow$ averages to zero unless $\omega = \omega'$

- Simplify:

$$|c_b^{(1)}(t)|^2 = \frac{1}{2}\left(\frac{e}{2m}\right)^2 \int_0^\infty d\omega \, |A_0(\omega)|^2 \, |M_{ba}^{(\omega)}|^2 \, \underbrace{F^2(t, \omega - \omega_{ba})} \quad (3.13)$$

$|A_0(\omega)|^2 \downarrow$ approx $|A_0(\omega)|^2 \approx |A_0(\omega_{ba})|^2$; $|M_{ba}^{(\omega)}|^2 \downarrow$

$\Leftarrow$ sharply peaked around $\omega = \omega_{ba}$

$$|C_b^{(1)}(t)|^2 = \frac{1}{2}\left(\frac{e}{2m}\right)^2 A_0^2(\omega_{ba})\,|M_{ba}(\omega_{ba})|^2 \underbrace{\int_{-\infty}^{\infty} F(t,\Delta\omega)\,d\omega}_{= \pi t}$$

$\int_0^\infty \to \int_{-\infty}^\infty$

So, probability $P_b = |C_b^{(1)}(t)|^2$ to be in state b increases linearly in time, $P_b = W_{ba}\, t$, with

$\boxed{\begin{aligned} &\underline{\text{Transition rate for absorption}} \text{ (integrated over } \omega) \\ &W_{ba} = \frac{\pi}{2}\left(\frac{e}{m}\right)^2 A_0^2(\omega_{ba})\,|M_{ba}(\omega_{ba})|^2 \\ &\quad = \frac{4\pi^2}{m^2c^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{I(\omega_{ba})}{\omega_{ba}^2}\,|M_{ba}(\omega_{ba})|^2 \end{aligned}}$ (3.14)

- second line uses, intensity at ω (3.15)

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

- so rate $\sim$ Intensity and $\sim |M_{ba}|^2$

STIMULATED EMISSION $E_a > E_b$ | Same steps as above, same transition rate (see book)

- If we have a thermal distribution of atoms, $N_{a,b} \sim \exp\left(-\frac{E_{a,b}}{k_B T}\right)$, temperature T so there are more in lower state and it is more likely to absorb (despite same rates for absorption and emission).
- Principle of LASER relies on population inversion, $N_b > N_a$ for $E_b > E_a$, then get more likely emission.

SPONTANEOUS EMISSION | In QED, vector potential for absorption [emission] of a photon from N photon state, has the form

$$\vec{A} = \hat{\varepsilon}\left[\frac{2\,[N(\omega)+1]\,\hbar}{V\varepsilon_0\,\omega}\right]^{1/2} \frac{1}{2}\exp\left[i(\vec{k}\cdot\vec{r} - \omega t + \delta\omega)\right] \quad (3.16)$$

only for emission (the $+1$)

V: quantisation volume

- Can see that absorption gives same result as (3.14) [N and V ⤳ go into $I(\omega)$]
- Emission is same only if we replace $N(\omega)+1 \to N(\omega)$
- The $+1$ is spontaneus emission. It takes place even without external fields, due to vacuum fluctuations.

3.1.3. Selection rules

Rates depend most critically on matrix-element

$$M_{ba}(\omega) = \langle \phi_b | \underbrace{\exp(i\vec{k}\cdot\vec{r})}_{1 + (i\vec{k}\cdot\vec{r}) + \frac{1}{2!}(i\vec{k}\cdot\vec{r})^2 + \dots} \hat{\varepsilon}\cdot\vec{\nabla} | \phi_a \rangle$$

For wavelength much <u>larger</u> than atomic size r_0: $|\vec{k}\cdot\vec{r}| \approx 2\pi \frac{r_0}{\lambda} \ll 1$

$\Rightarrow$ replace exp by 1 $\Rightarrow$

get <u>Matrix-element in dipole approximation</u>

no more ω

$$M^D_{ba} = \hat{\varepsilon} \cdot \langle \phi_b | \vec{\nabla} | \phi_a \rangle \qquad (3.17)$$

To see why it is called such, use:

$\hat{\vec{p}} = m \frac{i}{\hbar}[\hat{H}_0, \hat{\vec{r}}]$ (use $\hat{H}_0 = \frac{\hat{p}^2}{2m} + V(\hat{r})$ and $[\hat{r}_i, \hat{p}_j] = i\hbar\delta_{ij}$)

$\hat{p} = -i\hbar\vec{\nabla}$ $\Rightarrow$ $M^D_{ba} = \hat{\varepsilon}\cdot\left(\frac{-m}{\hbar^2}\right)\langle \phi_b | \underbrace{\hat{H}_0}_{E_b}\hat{r} - \hat{r}\underbrace{\hat{H}_0}_{E_a} | \phi_a \rangle$

$\vec{\nabla} = -\frac{m}{\hbar^2}[\hat{H}_0, \hat{r}]$

$$= -\frac{\omega_{ba} m}{\hbar}\hat{\varepsilon}\cdot\langle \phi_b | \hat{r} | \phi_a \rangle$$

<u>Matrix-element in length form</u>

$$M^D_{ba} = \frac{m\,\omega_{ba}}{\hbar e}\,\hat{\varepsilon}\cdot\hat{D}_{ba} \qquad \hat{D}_{ba} = \langle \phi_b | -e\hat{r} | \phi_a \rangle \qquad (3.18)$$

<u>transition Dipole moment</u> operator

If, between states $|\phi_a\rangle$ and $|\phi_b\rangle$ $\hat{D}_{ba}$ does not vanish, that transition is called <u>electric dipole allowed (E1)</u>.

Even if $\hat{D}_{ba}$ vanishes, M_{ba} might not vanish due to higher order terms in $\exp(i\vec{k}\cdot\vec{r})$, e.g. $(i\vec{k}\cdot\vec{r})$ <u>magnetic dipole (M1)</u> and <u>electric quadrupole (E2)</u>. these M_{ba} are however much <u>smaller</u> than non-vanishing $\hat{D}_{ba}$.

Let us consider when M^D_{ba} is nonzero, which depends on $\hat{D}_{ba}$ and $\hat{\varepsilon}$

Let's look at $\hat{D}_{ba}$ in detail: Initial symmetry considerations

$$|\phi_a\rangle = |\phi_{n_a l_a m_a}\rangle \rightarrow R_{n_a l_a}(r)\, Y_{l_a m_a}(\theta,\varphi)$$

From (1.18) for $\vec{r} \rightarrow \vec{r}'$ $\left(\Rightarrow r,\theta,\varphi \rightarrow r,\theta \rightarrow \pi-\theta,\ \varphi \rightarrow \varphi+\pi\right)$

$$\phi_a(\vec{r}) \rightarrow (-1)^{l_a}\, \phi_a(\vec{r}) \qquad \boxed{(-1)^{l_a} \text{ is called parity}}$$

Thus $\hat{D}_{ba} = -e \int d^3\vec{r}\ \phi_b^*(\vec{r})\, \vec{r}\, \phi_a(\vec{r})$ transforms like

$$\hat{D}_{ba} \mapsto \underline{\hat{D}_{ba}}\, (-1)^{l_a+l_b+1}$$

same since $\int d^3 r = \int d^3(-\vec{r})$

$\Rightarrow$ We need $l_a + l_b + 1 =$ even ($\Rightarrow$ dipole ME connects states of opposite parity, indep of $\hat{\varepsilon}$)

Full calculation: We can write $\hat{\varepsilon}\cdot\hat{D}_{ba} \equiv e\langle\phi_b|\,\hat{\varepsilon}\cdot\hat{r}\,|\phi_a\rangle$

and
$$\hat{\varepsilon}\cdot\hat{r} = \begin{pmatrix}\varepsilon_x\\ \varepsilon_y\\ \varepsilon_z\end{pmatrix}\begin{pmatrix} r\sin\theta\cos\varphi \\ r\sin\theta\sin\varphi \\ r\cos\theta\end{pmatrix} = \underbrace{-\frac{1}{\sqrt{2}}\left(\varepsilon_x + i\varepsilon_y\right)}_{\varepsilon_1}\underbrace{\left[-\frac{r\sin\theta\, e^{i\varphi}}{\sqrt{2}}\right]}_{\equiv r_1} + \underbrace{\frac{1}{\sqrt{2}}\left(\varepsilon_x - i\varepsilon_y\right)}_{\varepsilon_{-1}}\underbrace{\left[\frac{r\sin\theta\, e^{-i\varphi}}{\sqrt{2}}\right]}_{r_{-1}}$$
$$+ \underbrace{\varepsilon_z}_{=\varepsilon_0}\underbrace{\left[r\cos\theta\right]}_{r_0}$$

Explicit integration $\langle\phi_b|\,r_1\,|\phi_a\rangle \neq 0$ if $l_b = l_a \pm 1$ $\quad m_b = m_a + 1$

r_{-1} $\quad l_b = l_a \pm 1$ $\quad m_b = m_a - 1$

r_0 $\quad l_b = l_a \pm 1$ $\quad m_b = m_a$

Now if only some of $\varepsilon_{1,0,-1}$ are nonzero, we can select cases:

Dipole selection rules for:

- linearly polarized light (π-transition) only $\varepsilon_0 \neq 0$ $\qquad l_b = l_a \pm 1$, $m_b = m_a$
- left-handed circularly polarized light ($\sigma+$ transition) only $\varepsilon_1 \neq 0$ $\qquad l_b = l_a \pm 1$, $m_b = m_a + 1$
- right-handed circularly polarized light ($\sigma-$ transition) only $\varepsilon_{-1} \neq 0$ $\qquad l_b = l_a \pm 1$, $m_b = m_a - 1$
- unpolarized or other pol: $\qquad l_b = l_a \pm 1$, $m_b = m_a,\ m_a \pm 1$

(3.19)

4.1.4. More on spontaneous emission

Using the "Q.E.D $\vec{A}$" (3.16.) we can derive a rate

$$W_{ab}^{S} = \frac{4\pi^2}{m^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{\hbar}{V\omega_{ba}}|M_{ba}|^2\,\delta(\omega-\omega_{ba}) \qquad (3.19\ b)$$

for the emission of a given photon with energy ω.

To find the total spontaneous emission rate, we integrate over all possible photon states (momenta / wave-vectors $\vec{k}$)

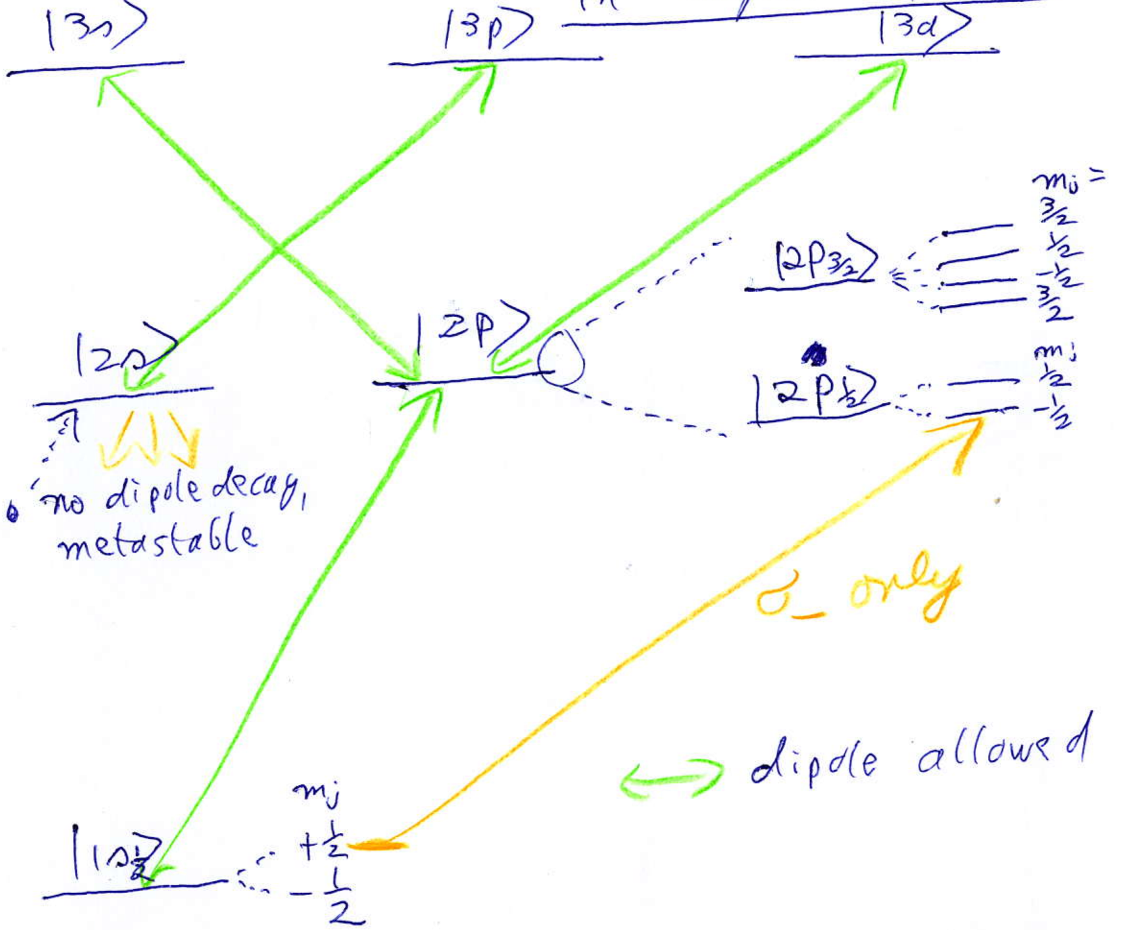
We find total spontaneous emission rate

$$\boxed{W_{ab}^{S,TOT} = \frac{4\alpha}{3c^2}\,\omega_{ba}^3\,\left|\langle\phi_b|r|\phi_a\rangle\right|^2 \qquad (3.19\ c)}$$

- We have used the dipole-approximation
- Important is the ω_{ba}^3 dependence: decay will always be dominantly to the lowest lying accessible state

- The same selection rules apply for absorption, emission and stimulated emission ⇒ states that cannot decay via dipole-allowed transitions have long life-times → metastable

Example for section 3.1. Hydrogen transitions in magnetic field



- Dipole radiation does not couple to spin, ⇒ all selection rules can be translated to j-basis (e.g $\Delta m = 0 \Rightarrow \Delta m_j = 0$), but bit tricky for j ($\Delta j = 0$ can be since e.g $l=1$ $s=\frac{1}{2}$, $l=2$ $s=\frac{1}{2}$ both $j=\frac{3}{2}$)
- Hydrogen |2s⟩ state metastable
- Transition |1s⟩ → |3s⟩ can only happen via E2, M1 or via two-step |1s⟩ → |2p⟩ → |3s⟩ (e.g two lasers)