7 3.14. Rabi-Oscillations

- Consider again Hamiltonian (3.7) $\hat{H}(t) = \hat{H}_0 + \hat{H}'(t)$, neglect $\vec{A}^2$ term, and choose simpler vector potential

$$\vec{A}(r,t) = A_0\,\vec{\varepsilon}\,\cos(\vec{k}\cdot\vec{r} - \omega_0 t) \qquad (3.20)$$

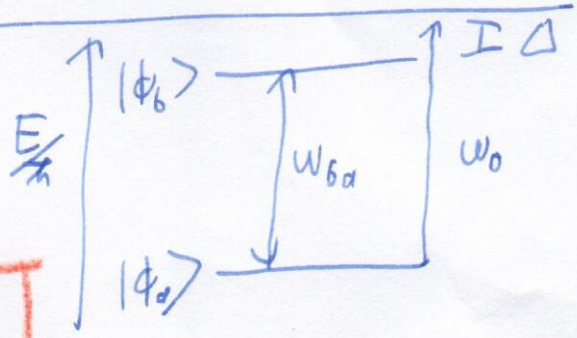
This could be a monochromatic / narrow band laser, in (3.5), with $\delta\omega = 0$ and $A_0(\omega)$ sharply peaked around $\omega = \omega_0$

From (3.1) we have

$$\vec{E}(r,t) = \underbrace{-\omega_0 A_0\,\vec{\varepsilon}}_{\vec{E}_0}\,\sin(\vec{k}\cdot\vec{r} - \omega_0 t)$$

for the Electric Field

For simplicity consider only two atomic states $|\phi_a\rangle, |\phi_b\rangle$ with $\omega_{ba} \approx \omega$



Let $\Delta = \omega_0 - \omega_{ba}$, the detuning

Now: $\langle\phi_a|\hat{H}_0|\phi_a\rangle = E_a$, $\langle\phi_b|\hat{H}_0|\phi_b\rangle = E_b$

$$\langle\phi_b|\hat{H}'(t)|\phi_a\rangle \overset{\text{Eq. (3.7)}}{=} -i\hbar\frac{A_0 e}{m}\langle\phi_b|\vec{\varepsilon}\cos(\vec{k}\cdot\vec{r} - \omega_0 t)\cdot\vec{\nabla}|\phi_a\rangle$$

$$= -i\hbar\frac{A_0 e}{2m}\langle\phi_b|\vec{\varepsilon}\cdot\left(e^{i\vec{k}\vec{r}}e^{-i\omega_0 t} + e^{-i\vec{k}\vec{r}}e^{i\omega_0 t}\right)\vec{\nabla}|\phi_a\rangle$$

($e^{i\vec{k}\vec{r}} \approx 1$, dipole approximation)

$$= -i\hbar\frac{A_0 e}{2m}\left(e^{i\omega_0 t} + e^{-i\omega_0 t}\right)\vec{\varepsilon}\,\langle\phi_b|\vec{\nabla}|\phi_a\rangle$$

$$\overset{\text{Eq. (3.18)}}{=} -i\frac{A_0\,\omega_{ba}\,m}{2\hbar}\left(e^{i\omega_0 t} + e^{-i\omega_0 t}\right)\vec{\varepsilon}\,\langle\phi_b|-e\vec{r}|\phi_a\rangle$$

$$\approx_{\omega_{ba}\approx\omega_0} -\frac{i}{2}\left(e^{i\omega_0 t} + e^{-i\omega_0 t}\right)\underbrace{\vec{E}_0}_{\text{driving}}\underbrace{\langle\phi_b|-e\vec{r}|\phi_a\rangle}_{\text{atomic dipole transition}}$$

Now write $|\psi(t)\rangle = c_a(t)\, e^{-iE_a t/\hbar} |\phi_a\rangle + c_b(t)\, e^{-iE_b t/\hbar} |\phi_b\rangle$ * $\omega_{ab} \leftrightarrow \omega_{ba}$ in (7) p 49

Can rewrite TDSE (1.20) as Matrix equation

$$i\hbar \begin{pmatrix} \dot{c}_a(t) \\ \dot{c}_b(t) \end{pmatrix} = \begin{bmatrix} 0 & \tilde{H}_{ab} \\ \tilde{H}_{ab}^* & 0 \end{bmatrix} \begin{pmatrix} c_a(t) \\ c_b(t) \end{pmatrix} \qquad (3.21)$$

where $\tilde{H}_{ab} = \frac{i}{2}^*\left(e^{i\omega_0 t} + e^{-i\omega_0 t}\right) \vec{E}_0 \langle \phi_a | -e\vec{r} | \phi_b \rangle\, e^{\frac{i}{\hbar}(E_a - E_b)t}$

Two steps:

- Complex exponentials $e^{i\underbrace{(\omega_0 + \omega_{ba})}_{\approx 2\omega_0 \text{ large}} t} + e^{-i\underbrace{(\omega_0 - \omega_{ba})}_{=\Delta \text{ small}} t}$

Neglecting the fast oscillating exp is called the rotating wave approximation.

- We define the Rabi-frequency

$$\Omega = \frac{1}{\hbar} \langle \phi_b | \vec{d} \cdot \vec{E}_0 | \phi_b \rangle \qquad (3.22)$$

$$\vec{d} = -e\vec{r}$$

Then Matrix equation:

$$i\hbar \begin{pmatrix} \dot{c}_a(t) \\ \dot{c}_b(t) \end{pmatrix} = \begin{bmatrix} 0 & i\frac{\Omega}{2} e^{-i\Delta t} \\ -i\frac{\Omega}{2} e^{i\Delta t} & 0 \end{bmatrix} \begin{pmatrix} c_a(t) \\ c_b(t) \end{pmatrix}$$

↖ check Δ signs differ from before

Finally, redefine $\tilde{c}_b = i e^{-i\Delta t} c_b(t)$ ⇒

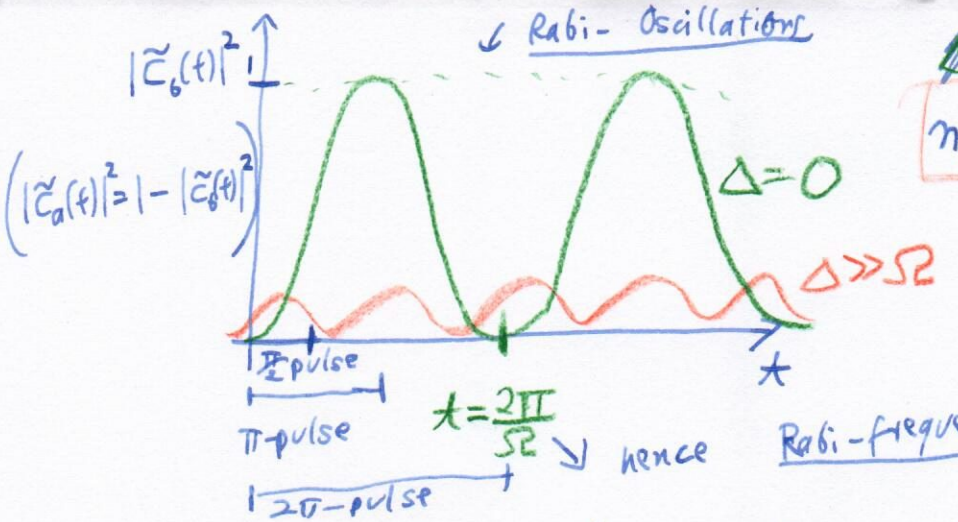
$\tilde{c}_a = c_a(t)$

$$i\hbar \begin{pmatrix} \dot{\tilde{c}}_a(t) \\ \dot{\tilde{c}}_b(t) \end{pmatrix} = \underbrace{\begin{bmatrix} 0 & \frac{\Omega}{2} \\ \frac{\Omega}{2} & -\Delta \end{bmatrix}}_{\hat{H}_{\text{eff}}} \begin{pmatrix} \tilde{c}_a(t) \\ \tilde{c}_b(t) \end{pmatrix} \qquad (3.23)$$

Effective Hamiltonian for two-level atom in dipole and rotating-wave approximation

Can solve with standard methods, using eigensystem of $\hat{H}_{\text{eff}}$.

For initial condition $\tilde{c}_a(0) = 1$ $\tilde{c}_b(0) = 0$, we find



↙ Rabi-Oscillations

$\Delta \neq 0$

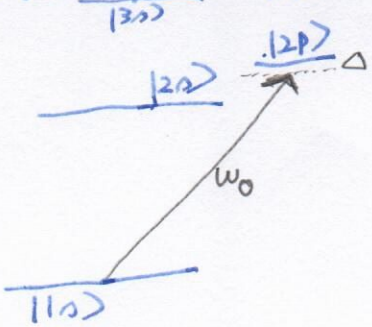
$n_b(t) = |\tilde{c}_b(t)|^2 = \frac{\Omega^2}{\Omega_{eff}^2} \sin^2\left(\frac{\Omega_{eff} t}{2}\right)$ (3.2

$\Omega_{eff} = \sqrt{\Delta^2 + \Omega^2}$

↘ hence Rabi-frequency ≠ e.g. Laser frequency

- For $\Delta \gg \Omega$, $n_b(t)\big|_{max} = \frac{\Omega^2}{\Omega_{eff}^2} \approx \left(\frac{\Omega}{\Delta}\right)^2 \ll 1$

This often in retrospect justifies our initial two Level approximation. Eg. ~~Hydrogen~~ Rubidium $|3s\rangle$ $|3p\rangle$



⇐ Near-resonant with $1s \leftrightarrow 2p_1$ but far-off resonant with any other transition (e.g. $|2s\rangle \rightarrow |3p\rangle$).

"Only" $|1s\rangle \leftrightarrow |2p\rangle$ take p

- For laser this realizes a coherent two-level system with electronic excited states (neglected decay). Rabi-problem is ubiquitous in physics.

Jargon: $\frac{\pi}{2}$-Pulse $\Rightarrow t = \frac{\pi}{2\Omega}$

(for $\Delta = 0$) π-Pulse $\Rightarrow t = \frac{\pi}{\Omega}$

2π-Pulse $\Rightarrow t = \frac{2\pi}{\Omega}$

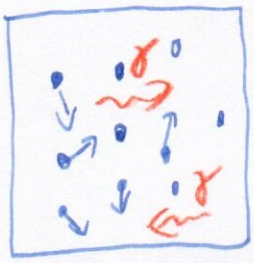
$|\psi(0)\rangle = |\phi_a\rangle \rightarrow \frac{1}{\sqrt{2}}(|\phi_a\rangle + |\phi_b\rangle$

$|\phi_a\rangle \rightarrow |\phi_b\rangle$

$|\phi_b\rangle \rightarrow -|\phi_a\rangle$

3.2. Spectral Lines

3.2.2. Thermal gas of atoms



- closed box
- temperature T

e.g Na vapour + photons

Look at two atomic levels for now $|\phi_b\rangle, |\phi_a\rangle$ with $E_b > E_a$.

- Will have statistical mix of stimulated emission + absorption + spontaneous emission.

Number of atoms making transition $a \to b$ / per unit time

$$\dot{N}_{ba} = B_{ba} N_a \rho(\omega_{ba}) \qquad (3.24)$$

B_{ba} = Einstein coefficient for absorption

$\rho(\omega_{ba})$ ≙ energy density in radiation field

For the reverse transition

$$\dot{N}_{ab} = A_{ab} N_b + B_{ab} N_b \rho(\omega_{ba}) \qquad (3.25)$$

A_{ab} = Einstein coefficient for spontaneous emission

B_{ab} = " " stimulated

In thermal equilibrium we have $\dot{N}_{ba} = \dot{N}_{ab}$ and

$$\frac{N_a}{N_b} = \exp\left[-(E_a - E_b)/k_B T\right] = \exp\left[\hbar\omega_{ba}/k_B T\right] \qquad (3.26)$$

We can use these relations to deduce

$$B_{ba} = B_{ab}$$

$$A_{ab} = \left(\frac{\hbar\omega_{ba}^3}{\pi c^3}\right) B_{ab} \qquad (3.27)$$

From Eq. (3.14) $B_{ba} = \dfrac{W_{ba}}{[I(\omega_{ba})/c]} \sim |M_{ba}(\omega_{ba})|^2$

$I(\omega_{ba})/c$ ← energy density

⇒ All allowed transition-frequencies are present:

$\omega_{ba} = E_b - E_a$ for some a, b

$\rho(\omega)$

amplitude ("brightness") $\sim |M_{ba}|^2$ (see again www.nist.gov/pml/atomic-spectr...)

↔ What about widths

3.2.3. Line shapes

As mentioned in 3.1, atomic excited states decay due to spontaneous emission.

E.g. $|b\rangle = |2p\rangle$ with rate Γ to $|a\rangle = |1s\rangle$

Calculation:

$$\Gamma_{ab} = \left(\frac{2}{3}\right)^8 \frac{m\alpha^5 Z^4 c^2}{\hbar} = 6.27 \cdot 10^8 \, Z^4 \, s^{-1}$$

Can we really emit into $\omega = \omega_{ba}$ only?

Rigorously: Calculate Q.E.D. probability for process

$$|b,\ 0 \text{ photons}\rangle \longrightarrow |a,\ 1 \text{ photon with frequency } \omega, \text{ polarisation } \vec{\varepsilon}, \text{ momentum } \vec{p}\rangle$$

Then integrate/sum over $\vec{\varepsilon}, \vec{p}$ to get total rate as function of ω.

Simpler, semi-classical picture:

Monochromatic emitted electric field due to spontaneous emission from a single atom

$$\mathcal{E}(t) = \mathcal{E}_0 \left(e^{-\frac{\Gamma}{2}t} e^{i\omega_{ba}t} + \text{c.c.} \right) \qquad \left[\mathcal{E}(t) = 0 \text{ for } t \le 0\right] \tag{3.28}$$

We have neglected the vector character, but taken into account that the probability for the atom to be in $|b\rangle$ decreases like $e^{-\Gamma t}$, hence the probability to emit a photon $\sim (\mathcal{E}\text{-field})^2$ intensity amplitude decreases likewise.

Fourier-transforming $\mathcal{E}(t)$:

$$\mathcal{E}(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} c(\omega) \, e^{i\omega t} \, d\omega$$

with

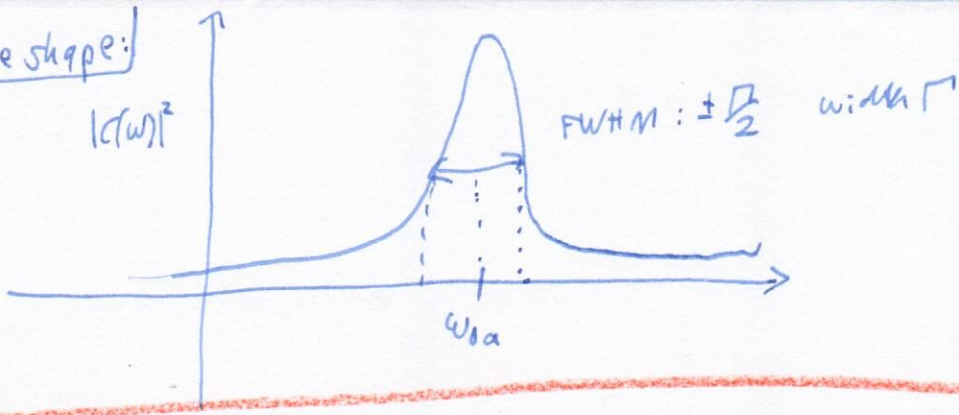
$$c(\omega) = -\frac{\mathcal{E}_0}{\sqrt{2\pi}} \left(\frac{1}{i(\omega_{ba} - \omega) - \Gamma/2} + \underbrace{\frac{1}{i(-\omega_{ba} - \omega) - \Gamma/2}}_{\text{Much smaller term, always, neglect}} \right)$$

$$c(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathcal{E}(t) \, e^{-i\omega t} \, dt$$

This gives a Lorentzian frequency spectrum / natural line profile

$$|c(\omega)|^2 = \mathcal{E}_0^2 \frac{1}{(\omega - \omega_{ba})^2 + \left(\frac{\Gamma}{2}\right)^2} \tag{3.29}$$

Natural Lineshape:



Also useful to define Life-time

$$\tau = 1/\Gamma \qquad (3.30)$$

We see energy is smeared out over width $\Delta E = \hbar\Gamma$, such that

$$\Delta E \cdot \tau \sim \hbar \qquad (3.31)$$

in accordance with energy / time uncertainty relation

In practice lines are broadened by further effects:

- Pressure broadening: Collisions can induce a transition $b \to a$, reducing life-time and increasing line-width, but keeping Lorentzian profile.
- Doppler broadening: Atoms move relative to lab-frame. The associated Doppler shift $\omega' = \omega - \vec{v}\cdot\vec{k}$ is as random as velocities. Velocities are randomly gaussian distributed (Boltzmann / Maxwell distribution $p_{\vec{v}} \sim \exp\left(-\frac{M\vec{v}^2}{2k_BT}\right)$

  ⇒ This gives rise to a Gaussian lineshape.

In general: Mixture of Lorentzian and Gaussian, called Voigt profile

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3.2.4. Sum-rules

Spectroscopy (experiments) can tell us about matrix-elements via e.g. 3.14, but frequently instead give information in terms of

Oscillator strength

$$f_{ka} = \frac{2m\,\omega_{ka}}{3\hbar} \left| \underbrace{\langle \phi_k | \hat{r} | \phi_a \rangle}_{= \frac{\hat{D}_{ka}}{(-e)}} \right|^2 \qquad (3.31)$$

One reason, is that oscillator strength's fulfill:

Thomas-Reiche-Kuhn Sum Rule:

$$\sum_K f_{Ka} = 1 \qquad (3.32)$$

($|\phi_K\rangle$: sum over all other states, including continuum)

- Often just few transitions add up almost to 1 → can tell us about if we found all important transitions from a given state
- Neat little proof, see book.

3.3. The photo-electric effect / photo-ionization

Our treatment in 3.1 was confined to transitions $|\phi_a\rangle \to |\phi_b\rangle$, between two atomic bound-states ($E_{a,b} < 0$)

We can also find solutions to the (eg) Hydrogen TISE with $E >$

These are no longer discretely quantized, & hence called continuum st

$$\left(-\frac{\hbar^2}{2m}\vec{\nabla}^2 - \frac{Ze^2}{(4\pi\varepsilon_0)r}\right)\psi_b(\vec{k}_f, r) = \underbrace{\left(\frac{\hbar^2 k_f^2}{2m}\right)}_{= E_f > 0}\psi_b(\vec{k}_f, r) \qquad (3.33)$$

For $E_f \gg |E_a|$ (e.g. ?), approx $\psi_b(\vec{k}_f, \vec{r}) = (2\pi)^{-3/2} \exp(i\vec{k}_f \cdot \vec{r})$

Can now use our earlier results using these states, e.g.

$$\sigma = \frac{4\pi^2 \alpha \hbar^2}{m} \int d\vec{k}_f \frac{1}{\omega_{ba}} |M_{ba}(\omega_{ba})|^2 \delta(\omega - \omega_{ba}) \qquad (3.34)$$

(ω_{ba} → k_f)

This is just Eq. (3.15b) for the absorption cross-section, with slight rearrangement of constants → α, adding $\delta(\omega - \omega_{ba})$ which was implicitly assumed in (3.15), and integrating over all final electron momenta $\vec{k}_f$ (to get total cross-section).

Note the Matrix-element (see Eq. 3.12)

$$M_{ba} = \frac{1}{(2\pi)^{3/2}} \int \exp[-i\vec{k}_f \cdot \vec{r}] \exp[i\vec{k} \cdot \vec{r}]\, \vec{\varepsilon} \cdot \vec{\nabla} \psi_a(\vec{r})\, d^3\vec{r} \qquad (3.35)$$

($\exp[-i\vec{k}_f \cdot \vec{r}]$: from ψ_b; $\exp[i\vec{k} \cdot \vec{r}]$: from light)

depends on $\vec{k}_f$, also its direction