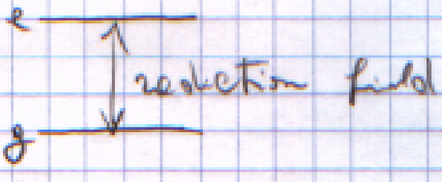
Optical properties of atoms : semiclassical theory

i) 2-level atom :



Atom is coupled to :

- classical incident field $E(t)$
- continuum of other modes, to be described quantum-mechanically.
- 2-level atom much more quantum than harmonic oscillator model of matter considered so far
- interesting non-linear optical response

atomic hamiltonian $\hat{H}_0$

$$H = \hbar\omega_e |e\rangle\langle e| + \hbar\omega_g |g\rangle\langle g| - \underline{d}\left[|e\rangle\langle g| + |g\rangle\langle e|\right]\left(\underline{E}(t) + \underline{E}^*(t)\right) +$$

$$\underbrace{- \sum_{k\sigma} \underline{d}\left[|e\rangle\langle g| + |g\rangle\langle e|\right]\cdot\left(\underline{\mathcal{E}}_{k\sigma}\,\hat{a}_{k\sigma} + \underline{\mathcal{E}}^*_{k\sigma}\,\hat{a}^+_{k\sigma}\right)}_{\text{coupling to bath of radiative modes } \hat{H}_{rad}}$$

in terms of Pauli matrices of 2-level system :

$$H_0 = \hbar(\omega_e - \omega_g)\frac{\hat{\sigma}_z}{2} - \underline{d}\cdot\left(\underline{E}(t) + \underline{E}^*(t)\right)\hat{\sigma}_x$$

Rotating-wave approximation

$\hat{\sigma}_x = |e\rangle\langle g| + |g\rangle\langle e|$

the two terms evolve as $e^{\pm i(\omega_e-\omega_g)t}$ under $\hbar(\omega_e-\omega_g)\hat{\sigma}_z$

if $E(t)$ oscillates around optical frequency ω, interaction terms at $\pm(\omega + (\omega_e-\omega_g))$ far from resonance and can be neglected

we can approximate H_s as:

$$H_s \simeq H^{RWA} = \hbar\frac{(\omega_e-\omega_g)}{2}\hat{\sigma}_z - \underline{d}\cdot\underline{E}(t)|e\rangle\langle g| - \underline{d}\cdot\underline{E}^*(t)|g\rangle\langle e|$$

$$= \hbar\frac{(\omega_e-\omega_g)}{2}\hat{\sigma}_z - \Omega(t)|e\rangle\langle g| - \Omega^*(t)|g\rangle\langle e|$$

with $\hbar\Omega(t) = \underline{d}\cdot\underline{E}(t) \longrightarrow$ Rabi frequency

System evolution:

$i\frac{d}{dt}|\psi\rangle = H|\psi\rangle$

$|\psi\rangle$ = atom + field state

H = total hamiltonian

We are interested in atomic degrees of freedom only:

$\rho_{at} = \mathrm{Tr}_{field}\left[|\psi\rangle\langle\psi|\right]$ reduced density matrix

any atomic observable $\hat{O}_{at}$: $\langle\hat{O}_{at}\rangle = \mathrm{Tr}\left[\hat{O}_{at}\cdot\hat{\rho}_{at}\right]$

Evolution of $\hat{\rho}_{at}$:

- atomic H_0 : $\frac{d}{dt}\hat{\rho}_{at} = -i[\hat{H}_0, \hat{\rho}_{at}]$

- coupling to radiation bath $\hat{H}_{rad}$. Assuming :

  * bath consisting in continuum of modes

  * broad energy distribution

  * "weak" atom - radiation coupling

$$\frac{d}{dt}\hat{\rho}_{at} = -i[H_0, \hat{\rho}_{at}] + \frac{\gamma}{2}\left[2\sigma^- \rho_{at}\sigma^+ - \sigma^+\sigma^-\rho_{at} - \rho_{at}\sigma^+\sigma^-\right]$$

MASTER EQUATION

Full derivation in most Q.O. text books.

Detailed (and convincing) one is :

C. Cohen-Tannoudji, J. Dupont-Roc, G. Grynberg,
"Photons and Atoms : the interaction process"

Here $\hat{\sigma}^+ = |e\rangle\langle g|$, $\hat{\sigma}^- = |g\rangle\langle e|$

γ can be determined from Fermi golden rule :

$$\gamma = \frac{2\pi}{\hbar}\int df\, |M_{fi}|^2\, \delta(E_f - E_i)$$

p.ex. spontaneous emission damping rate

Optical Bloch equations (OBE)

$\rho_{ee} = \langle e | \rho_{at} | e \rangle$, $\rho_{eg} = \langle e | \rho_{at} | g \rangle$, $\rho_{gg} = \langle g | \rho_{at} | g \rangle$

$$\left.\begin{aligned} \dot{\rho}_{ee} &= -\gamma \rho_{ee} + i\left(\Omega(t)\rho_{ge} - \Omega^*(t)\rho_{eg}\right) \\ \dot{\rho}_{gg} &= \gamma \rho_{ee} - i\left(\Omega(t)\rho_{ge} - \Omega^*(t)\rho_{eg}\right) \end{aligned}\right\}$$

NOTE: $Tr(\rho_{at}) = \rho_{ee} + \rho_{gg}$ conserved $= 1$

$$\dot{\rho}_{eg} = -\frac{\gamma}{2}\rho_{eg} + i\Omega(t)\left(\rho_{gg} - \rho_{ee}\right) - i\left(\omega_e - \omega_g\right)\rho_{eg}$$

Monochromatic excitation $E(t) = E\, e^{-i\omega t}$

$$\Omega(t) = \Omega\, e^{-i\omega t}$$

$$\Rightarrow \rho_{eg}(t) = \rho_{eg}\, e^{-i\omega t}$$

steady state of O.B.E:

$$\rho_{ee} = \frac{|\Omega|^2}{(\omega - (\omega_e - \omega_g))^2 + \gamma^2/4 + 2|\Omega|^2}$$

$$\rho_{eg} = -\Omega\, \frac{\delta\omega - i\gamma/2}{\Delta\omega^2 + \gamma^2/4 + 2|\Omega|^2}$$

Expectation value of dipole operator:

$$\langle \underline{d} \rangle = \underline{d}\, \rho_{eg} = + \frac{d^2}{\hbar}\, \frac{\omega_e - \omega_g - \omega + i\gamma/2}{(\omega - (\omega_e - \omega_g))^2 + \gamma^2/4 + 2d^2|E|^2/\hbar^2} \cdot \underline{E}$$

Weak light intensity limit $|\Omega|^2 \ll (\gamma^2/4 + \Delta\omega^2)$

$$\rho_{ee} \simeq \frac{|\Omega|^2}{\Delta\omega^2 + \gamma^2/4} \ll 1$$

$$\langle d \rangle = \underbrace{\frac{d^2}{(\omega - (\omega_e - \omega_g)) - i\gamma/2}} \cdot E$$

dielectric susceptibility $\longrightarrow$ Lorentzian form as for harmonic oscillator

* In weak intensity limit, dielectric properties of two-level atom are the same as in classical harmonic oscillator model

* Differences :

  - nonlinear properties at higher $|\Omega|^2$'s
  - different "quantum fluctuations

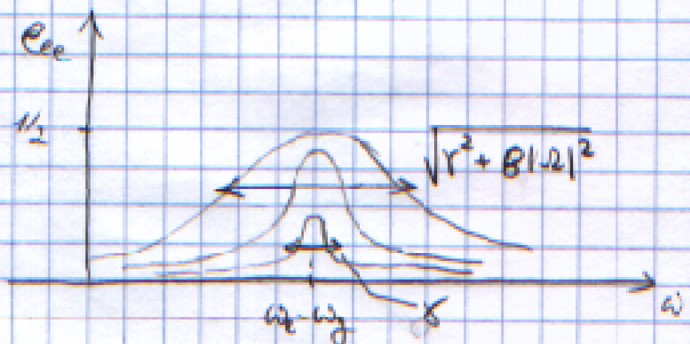
Nonlinear optical properties

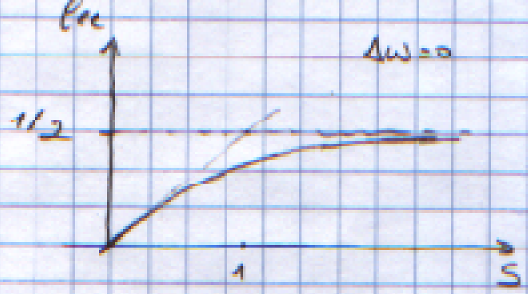
introduce "saturation parameter" $s = \dfrac{2|\Omega|^2}{\Delta\omega^2 + \gamma^2/4}$

$$\rho_{ee} = \frac{1}{2}\,\frac{S}{1+S}$$

$$\langle d \rangle = \frac{1}{1+S}\,\frac{d^2/\hbar}{(\omega-(\omega_e-\omega_g)) - i\gamma/2}\,E$$

linear regime response multiplied by $\frac{1}{1+S}$





Strong pumping: equal populations $\rho_{ee} \simeq \rho_{gg}$

* power broadening of resonance:

$$\gamma_{eff} = \sqrt{\gamma^2 + 8|\Omega|^2}$$

* saturation of absorption:

for $\omega = \omega_e - \omega_g$:

$$\langle d \rangle = i\,\frac{\gamma/2}{\gamma^2/4 + 2|\Omega|^2}\,\frac{d^2}{\hbar}\,E =$$

$$= \frac{2i\,d^2}{\hbar\gamma}\,E \cdot \frac{1}{1 + 8|\Omega|^2/\gamma^2} \simeq$$

$$\simeq \frac{2i\,d^2}{\hbar\gamma}\left[1 - \frac{8\,d^2}{\hbar^2\gamma^2}|E|^2 + \dots\right] E$$

In terms of NL susceptibilities $\chi^{(1)}$ ... $\chi^{(3)}$ ...

* Energy balance :

absorbed energy from laser field

$$W = \left\langle E(t) \cdot \frac{d}{dt} d(t) \right\rangle_t =$$

$$= \frac{1}{2} \mathrm{Re} \left[E^* \cdot (-i\omega\, d) \right]$$ for monochromatic field at ω. (*)

$$= \frac{1}{2} \mathrm{Re} \left[E^* (-i\omega) \frac{d^2}{\hbar} \frac{-\Delta\omega + i\gamma_2}{\Delta\omega^2 + \gamma^2/4 + 2 d^2 |E|^2} E \right]$$

$$= \frac{1}{2} \mathrm{Re} \left[|E|^2 d^2 \omega \frac{\cancel{i\Delta\omega} + \gamma_2}{\Delta\omega^2 + \gamma^2/4 + \frac{2d^2}{\hbar^2} |E|^2} \right] =$$

$$= \frac{\hbar\omega}{4} \frac{|\Omega|^2}{\Delta\omega^2 + \gamma^2/4 + 2|\Omega|^2} \gamma$$

NOTE: (*) assumes physical $E(t) = \mathrm{Re}\,(E e^{-i\omega t})$

but OBE's use $E(t) = E e^{-i\omega t} + c.c$

$\hookrightarrow$ factor 4 difference

$$W = \hbar\omega \frac{|\Omega|^2}{\Delta\omega^2 + \gamma^2/4 + 2|\Omega|^2} \gamma = \hbar\omega\, \rho_{ee}\, \gamma$$

Physical interpretation:

* atom in excited state decays radiatively at a rate γ

* every decay process dissipates a quantum $\hbar\omega$ of energy

Transient phenomena

$\Omega(t) = \bar{\Omega}(t)\, e^{-i\omega_L t}$

$\longrightarrow$ slowly varying envelope (on optical time scale). assumed to be real (i.e. constant phase)

define $\bar{\rho}_{eg}(t) = \rho_{eg}(t)\, e^{-i\omega_L t}$

$\longrightarrow$ Rescaled OBE's:

$$\dot{\rho}_{ee} = -\gamma\rho_{ee} + i\left(\bar{\Omega}(t)\,\bar{\rho}_{eg}^{*} - \bar{\Omega}^{*}(t)\,\bar{\rho}_{eg}\right)$$

$$\dot{\bar{\rho}}_{eg} = -\frac{\gamma}{2}\bar{\rho}_{eg} + i\,\bar{\Omega}(t)\left(\rho_{gg} - \rho_{ee}\right) + i\left(\omega_L - (\omega_e - \omega_g)\right)\bar{\rho}_{eg}$$

Bloch vector

$$\vec{V} = \left[\frac{1}{2}(\rho_{eg} + \rho_{ge}),\ \frac{1}{2i}(\rho_{ge} - \rho_{eg}),\ \frac{1}{2}(\rho_{ee} - \rho_{gg})\right]$$

$$= \frac{1}{2}\mathrm{Tr}\left[\vec{\sigma}\cdot\rho\right] \qquad (\vec{\sigma} = \text{Pauli matrices})$$

$$\begin{cases} \frac{d}{dt} V_z = 2\Omega V_y - \gamma V_z - \gamma/2 \\ \frac{d}{dt} V_x = \left(\omega_L - (\omega_e - \omega_g)\right) V_y - \frac{\gamma}{2} V_x \\ \frac{d}{dt} V_y = -\left(\omega_L - (\omega_e - \omega_g)\right) V_x - 2\Omega V_z - \frac{\gamma}{2} V_y \end{cases}$$

$$\frac{d}{dt} \vec{V} = \vec{\omega} \times \vec{V} + \text{decay} \begin{cases} \gamma/2 \text{ for } V_{x,y} \\ \gamma \text{ towards } -1/2 \text{ for } V_z . \end{cases}$$

with $\vec{\omega} = \left[2\Omega \hat{x} + (\omega_e - \omega_g - \omega_L) \hat{z} \right]$

i) $\Omega = 0$: free rotation at $\omega_e - \omega_g - \omega_L$ around $\hat{z}$
+ decay

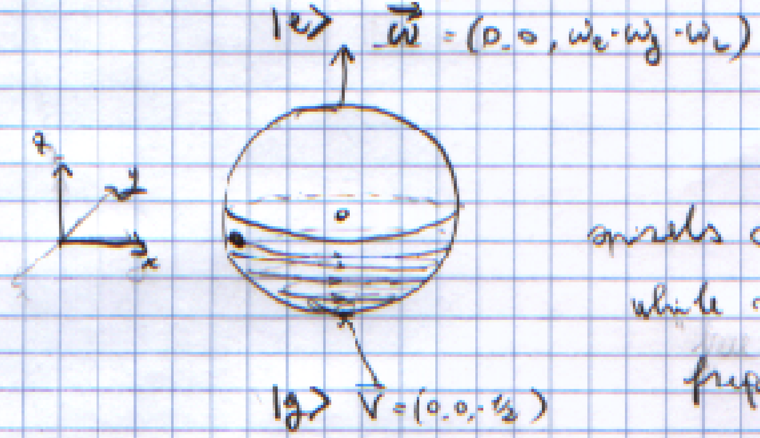
ii) resonant case $\omega_e - \omega_g = \omega_L$: rotation around $\hat{x}$
at 2Ω.

iii) general case : rotation at $\omega_{tot} = \sqrt{(2\Omega)^2 + (\omega_e - \omega_g - \omega_L)^2}$

around tilted axis.

<u>NOTE</u> : Physical dipole $\longrightarrow$ x-component of $R_z(\omega_L t) \cdot \vec{V}$

i)



spirals down to $(0, 0, -\frac{1}{2})$
while rotating around $\hat{z}$ at
frequency $\omega_e - \omega_g - \omega_L$

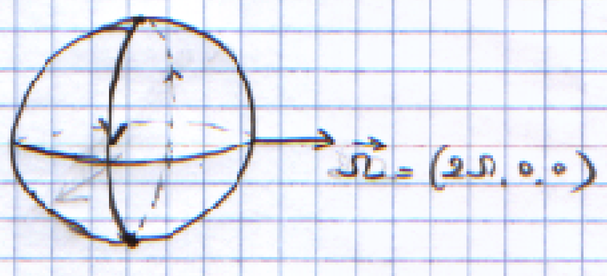
↳ Physical oscillation at $\omega_e - \omega_g$ as expected

"free induction decay" in NMR

* if initially atom in $|e\rangle \longrightarrow \vec{V}(0) = (0, 0, \frac{1}{2})$

decays down to $(0, 0, -\frac{1}{2})$ along $(0, 0, \alpha)$ line

ii)



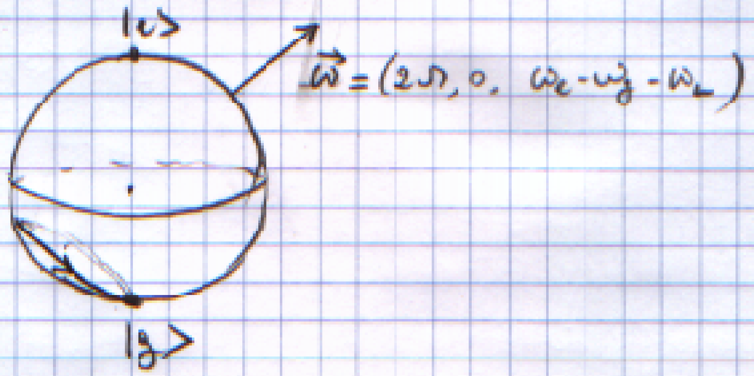
starting from $|g\rangle$: Rabi oscillations between $|g\rangle$ and $|e\rangle$.

full exchange of population

Frequency $= 2\Omega$

$\begin{cases} \underline{\pi \text{ pulse}}: \text{transfers to } |e\rangle, \int dt\, 2\Omega(t) = \pi \\ \underline{2\pi \text{ pulse}}: \text{goes back to } |g\rangle, \int dt\, 2\Omega(t) = 2\pi. \end{cases}$

iii)



- Population oscillations not complete.
- faster frequency $\Omega_{eff} = \sqrt{(2\Omega)^2 + (\omega_e - \omega_g - \omega_L)^2}$

<u>NOTE</u>: Bloch vector picture of O.B.E's relies on RW approximation.

Without RWA, impossible to cast OBE into time-independent ODE form.

Relation to NMR

$$\left.\begin{array}{l} |e\rangle \\ |g\rangle \end{array}\right\} \text{states} \longrightarrow \left\{\begin{array}{l} S_z = 1/2 \\ S_z = -1/2 \end{array}\right. \text{states of nuclear spin}$$

→ Energy difference $\Delta E = \mu_B \cdot B_{ext}$

→ nuclear spin couples to $\vec{B}$ field of e.m. wave

→ Bloch vector = expectation value of spin angular momentum of nucleus

$$H = -\mu_B \hat{S}\cdot\vec{B} + \mu_B B_{ext}\,\hat{S}_z$$

$* \ \vec{B}_{ext} = -B_{ext}\,\hat{z} \longrightarrow$ Zeeman shifts $S_z = \pm 1/2$ states

$* \ \vec{B}(t) = B_0\,\hat{\sigma}_+\, e^{-i\omega_L t} + c.c = \sqrt{2}\, B_0 \left[\hat{x}\cos\omega_L t + \hat{y}\sin\omega_L t\right]$

(σ_+ polarized e.m. field)

<u>Unitary transform</u> $\quad U(t) = \exp\left(i\omega_L S_z t\right)$:

(rotation by $\omega_L t$ around $\hat{z}$ axis)

$$|\psi'(t)\rangle = U(t)\,|\psi(t)\rangle$$

$$i\frac{d}{dt}|\psi'(t)\rangle = \underbrace{\left[U(t)\,H\,U^\dagger(t) + i\frac{dU}{dt}U^\dagger(t)\right]}_{H_{eff}}|\psi'(t)\rangle$$

$$i\frac{dU}{dt}U^\dagger = -\omega_L S_z$$

$$U H U^\dagger = -\mu_B \vec{B}\cdot U\hat{S}U^\dagger + \mu_B B_{ext}\hat{S}_z =$$

$$= -\mu_B\, \vec{B}\cdot\left[R_z(\omega_L t)\vec{S}\right] + \mu_B B_{ext}\hat{S}_z$$

$$= -\mu_B\left[R_z(-\omega_L t)\vec{B}\right]\cdot\vec{S} + \mu_B B_{ext}\hat{S}_z =$$

$$= -\sqrt{2}\,\mu_B B_0\cdot(\hat{x}\cdot\vec{S}) + \mu_B B_{ext}\hat{S}_z$$

$$= -\sqrt{2}\,\mu_B B_0\cdot\hat{S}_x + \mu_B B_{ext}\hat{S}_z$$

$$H_{eff} = \underbrace{(\mu_B B_{ext} - \omega_L)\hat{S}_z}_{\text{"free induction"}} - \underbrace{\sqrt{2}\,\mu_B B_0\,\hat{S}_x}_{\text{Rabi oscillations}}$$

Bibliography

* general theory of dissipation in quantum (optical) systems:

  - C. Cohen-Tannoudji, J. Dupont-Roc, G. Grynberg, "Atom photon interaction processes", chap. IV

  - H.P. Breuer and F. Petruccione, "the theory of open quantum systems", Oxford, 2002

    → more complete textbook, with extensive coverage of special topics beyond standard approximations

* Optical Bloch equations:

  - C. Cohen-Tannoudji et al, op. cit. chap. V

* Nuclear Magnetic resonance

  - Abragam, "The principles of nuclear magnetism", Clarendon Press, Oxford, 1961