Density Matrix Description of 2-Level Atoms

Time Evolution of the Density Matrix

<u>Challenge</u>: We need "equations of motion" that combine the Schrödinger Equation with the effect of processes that can change $\mathrm{Tr}\,\rho^2$ (measure of purity)

<u>Approach</u>: We do not have time for a rigorous derivation, so will rely on plausible arguments to justify the equations

<u>Schrödinger Evolution</u>: In general, we have

$$\dot{\rho} = -\frac{i}{\hbar}[H,\rho] = -\frac{i}{\hbar}(H\rho - \rho H)$$

matrix elements

$$(*) \quad \dot{\rho}_{nm} = -\frac{i}{\hbar}\sum_{k=1,2}\left(H_{nk}\rho_{km} - \rho_{nk}H_{km}\right)$$

2-Level Atom ⇨ 2 populations, 2 coherences

Consider the 2-Level Rabi problem with

$$H = H_0 + V \quad \& \quad V_{12} = -\frac{1}{2}\hbar\left(\chi_{12}e^{-i\omega t} + \chi_{21}^{*}e^{i\omega t}\right)$$

$$H = \hbar\begin{pmatrix} 0 & -\frac{1}{2}\left(\chi_{12}e^{-i\omega t} + \chi_{21}^{*}e^{i\omega t}\right) \\ -\frac{1}{2}\left(\chi_{21}e^{-i\omega t} + \chi_{12}^{*}e^{i\omega t}\right) & \omega_{21}\end{pmatrix}$$

Substitute in (*), set $\rho_{12} = \tilde{\rho}_{12}e^{i\omega t}$

slow variable

(For a pure state $\rho_{12} = a_1 a_2^{*} = c_1\left(c_2 e^{-i\omega t}\right)^{*}$ **)**

Make RWA, drop ~, and set $\chi_{21} = \chi,\ \chi_{21}^{*} = \chi^{*}$

$$\dot{\rho}_{11} = -\frac{i}{2}\left(\chi\rho_{12} - \chi^{*}\rho_{21}\right)$$

$$\dot{\rho}_{22} = \frac{i}{2}\left(\chi\rho_{12} - \chi^{*}\rho_{21}\right)$$

$$\dot{\rho}_{12} = i\Delta\rho_{12} + i\frac{\chi^{*}}{2}\left(\rho_{22} - \rho_{11}\right) = \dot{\rho}_{21}^{*}$$

Rabi Eqs. for pure and mixed states

Density Matrix Description of 2-Level Atoms

Next: Non-Hamiltonian evolution

Types of events

(i) Elastic collisions: No change in energy

(ii) Inelastic collisions: Atom loss

(iii) Spontaneous decay: Transition $|2\rangle \rightarrow |1\rangle$

Simple Model of Elastic Collisions

Two atoms near each other ⇒ energy levels shift, free evol. of ρ_{12} changed

(Paradigm for perturbations that do not lead to net change in energy)

Evolution of coherence (fast variables)

$$\dot{\rho}_{12} = -i\left[\omega_{21} + \delta\omega(t)\right]\rho_{12}$$

collisional history

$$\Rightarrow \rho_{12}(t) = \rho_{12}(0)\,e^{-i\omega_{21}t}\,e^{-i\int_0^t dt'\,\delta\omega(t')}$$

We need the ensemble average of $\rho_{12}(t)$

Assumptions:

- From atom to atom $\delta\omega(t)$ is a Gaussian Random Variable
- Averaged over the ensemble $\langle \delta\omega(t)\rangle_{e} = 0$
- Collisions have no memory over time, $\langle \delta\omega(t)\,\delta\omega(t')\rangle_t = \frac{2}{\tau}\delta(t-t')$

Can show that, averaged over time and the ensemble

$$\left\langle e^{-i\int_0^t dt'\,\delta\omega(t')}\right\rangle = e^{-t/\tau}$$

Density Matrix Description of 2-Level Atoms

It follows that: $\varrho_{12}(t) = \varrho_{12}(0)\, e^{-i\omega_{21}t}\, e^{-t/\tau}$

Add this decay to the equation of motion to get

$$\boxed{\dot{\varrho}_{12} = (\dot{\varrho}_{12})_{S.E.} + (\dot{\varrho}_{12})_{E.C.} = -(i\omega_{21} - 1/\tau)\varrho_{12}}$$

Simple Model of Inelastic Collisions

As modeled by, e. g., Milloni & Eberly,
this is a steady loss of atoms

$$\dot{\varrho}_{11} = (\dot{\varrho}_{11})_{S.E.} - \Gamma_1 \varrho_{11}$$

$$\dot{\varrho}_{22} = (\dot{\varrho}_{22})_{S.E.} - \Gamma_2 \varrho_{22}$$

This is strange because $Tr\,\varrho(t)$ is not preserved

Convenient when working with quantities

$$N\langle\hat{\vec{r}}\rangle \propto N(\vec{r}_{12}\varrho_{21} + \vec{r}_{21}\varrho_{12}) \quad ??$$

Effect on probability amplitudes

Populations are ensemble averages of the type

$$\varrho_{11}(t) = \langle|a_1(t)|^2\rangle = \langle|a_1(0)|^2\rangle e^{-\Gamma_1 t}$$

$$\varrho_{22}(t) = \langle|a_2(t)|^2\rangle = \langle|a_2(0)|^2\rangle e^{-\Gamma_2 t}$$

When the populations decay, the averages of the probability amplitudes must decay accordingly,

$$\langle|a_1(t)|\rangle = \langle|a_1(0)|\rangle e^{-\Gamma_1/2\, t}$$

$$\langle|a_2(t)|\rangle = \langle|a_2(t)|\rangle e^{-\Gamma_2/2\, t}$$

Thus, for the coherences

$$\varrho_{12}(t) = \langle a_1(t) a_2(t)^*\rangle = \langle a_1(0) a_2(0)^*\rangle e^{-\Gamma_1/2\, t} e^{-\Gamma_2/2\, t}$$

This gives us

$$\boxed{\dot{\varrho}_{12} = (\dot{\varrho}_{22})_{S.E.} - \overset{\text{elastic}}{1/\tau\, \varrho_{12}} - \overset{\text{inelastic}}{\frac{\Gamma_1 + \Gamma_2}{2}\varrho_{12}}}$$

Density Matrix Description of 2-Level Atoms

Spontaneous Decay

This process occurs due to interaction between the Atom and the Quantized Electromagnetic Field

Warm-up: A Bayesian recipe for Mixed States

Alice has two 2-level atoms in the ground state.

Step (1) She applies a Hamiltonian that drives the evolution

$$|1\rangle_A |1\rangle_B \rightarrow a_1 |1\rangle_A |1\rangle_B + a_2 |2\rangle_A |2\rangle_B$$

Step (2) She gives atom B to Bob and asks him to measure if it is in $|1\rangle_B$ or $|2\rangle_B$ and keep the result secret forever.

Result: Alice now has a 2-level atom in the state

$$\rho = |a_1|^2 |1\rangle_{BB}\langle 1| + |a_2|^2 |2\rangle_{BB}\langle 2|$$

Spontaneous Decay

This process occurs due to interaction between the Atom and the Quantized Electromagnetic Field

Final OPTI 544 Lectures: interaction drives the evolution

$$|\psi(0)\rangle = |2\rangle_A \otimes |vac\rangle_{QEF} \Rightarrow \text{Evolution for time } t$$

$$|\psi(t)\rangle = C_{2,0}(t)\, |2\rangle_A |vac\rangle_{QEF} + \sum_k C_{1,1_k}(t)\, |1\rangle_A |n_k = 1\rangle_{QEF}$$

photon "in the atom" photon in field mode k

Cannot recover info in continuum of field modes

Probability $|C_{2,0}(t)|^2$ of having **no decay**

Probability $\sum_k |C_{1,1_k}(t)|^2$ of having **decay**

<u>No Coherence</u> established between states $|1\rangle, |2\rangle$

Density Matrix Description of 2-Level Atoms

Spontaneous Decay

This process occurs due to interaction between the Atom and the Quantized Electromagnetic Field

Final OPTI 544 Lectures: interaction drives the evolution

$|\psi(0)\rangle = |2\rangle_A \otimes |vac\rangle_{QEF}$ ⇨ Evolution for time *t*

$$|\psi(t)\rangle = C_{2,0}(t)\,|2\rangle_A\,|vac\rangle_{QEF} + \sum_k C_{1,1k}(t)\,|1\rangle_A\,|n_k=1\rangle_{QEF}$$

photon "in the atom" — photon in field mode *k*

Cannot recover info in continuum of field modes

Probability $|C_{2,0}(t)|^2$ of having no decay

Probability $\sum_k |C_{1,1k}(t)|^2$ of having decay

No Coherence established between states $|1\rangle, |2\rangle$

Conclusion: Decay moves population $|2\rangle \rightarrow |1\rangle$ at rate A_{21}, damps coherence at rate $A_{21}/2$

$$\dot\rho_{11} = A_{21}\rho_{22}, \quad \dot\rho_{22} = -A_{21}\rho_{11}$$

$$\dot\rho_{12} = -\frac{A_{21}}{2}\rho_{12} = \dot\rho_{21}^*$$

Putting it all together:

$$\dot\rho_{11} = -\Gamma_1\rho_{11} + A_{21}\rho_{22} - \frac{i}{2}(\chi\rho_{12} - \chi^*\rho_{21})$$

$$\dot\rho_{22} = -\Gamma_2\rho_{22} - A_{21}\rho_{22} + \frac{i}{2}(\chi\rho_{12} - \chi^*\rho_{21})$$

$$\dot\rho_{12} = (i\Delta - \beta)\rho_{12} + \frac{i\chi^*}{2}(\rho_{22} - \rho_{11}) = \dot\rho_{21}^*$$

where $\beta = \frac{1}{\tau} + \frac{A_{21}}{2} + \frac{\Gamma_1 + \Gamma_2}{2}$

These are our desired **Density Matrix Equations of Motion**

Emission and Absorption – Population Rate Equations

So far we have derived a set of Equations of Motion for the elements of the Density Matrix:

$$\dot{\rho}_{11} = -\Gamma_1 \rho_{11} + A_{21}\rho_{22} - \frac{i}{2}(\chi\rho_{12} - \chi^*\rho_{21})$$

$$\dot{\rho}_{22} = -\Gamma_2 \rho_{22} - A_{21}\rho_{22} + \frac{i}{2}(\chi\rho_{12} - \chi^*\rho_{21})$$

$$\dot{\rho}_{12} = (i\Delta - \beta)\rho_{12} + \frac{i\chi^*}{2}(\rho_{22} - \rho_{11}) = \dot{\rho}_{21}^*$$

where $\beta = \frac{1}{\tau} + \frac{A_{21}}{2} + \frac{\Gamma_1 + \Gamma_2}{2}$

(*) These equations are difficult to solve in the general case. See, e. g., Allen & Eberly for a discussion of some special cases and a reference to original work by Torrey et al.

(*) For ≥ 3 levels the Density Matrix Equations get very cumbersome and it is desirable to simplify the description when possible.

(*) One such simplification takes the form of Rate Equations for the populations only.

Steady State Solutions: (requires $\Gamma_1 = \Gamma_2 = 0$)

Let $\dot{\rho}_{12} = 0 \Rightarrow$

$$\begin{cases} \rho_{12} = \dfrac{i\chi^*/2}{\beta - i\Delta}(\rho_{22} - \rho_{11}) \\ \rho_{21} = \dfrac{-i\chi/2}{\beta + i\Delta}(\rho_{22} - \rho_{11}) \end{cases}$$

$$\chi\rho_{12} - \chi^*\rho_{21} = \frac{i|\chi|^2\beta}{\Delta^2 + \beta^2}(\rho_{22} - \rho_{11})$$

Plug into eqs for Populations to get

$$\dot{\rho}_{11} = A_{21}\rho_{22} + \frac{|\chi|^2\beta/2}{\Delta^2 + \beta^2}(\rho_{22} - \rho_{11}) = 0$$

$$\dot{\rho}_{22} = -A_{21}\rho_{22} - \frac{|\chi|^2\beta/2}{\Delta^2 + \beta^2}(\rho_{22} - \rho_{11}) = 0$$

These eqs. let us find steady state values for the populations and coherences in terms of $\chi, \Delta, A_{21}, \beta$ **when (and only when)** $\dot{\rho}_{11} = \dot{\rho}_{22} = 0$

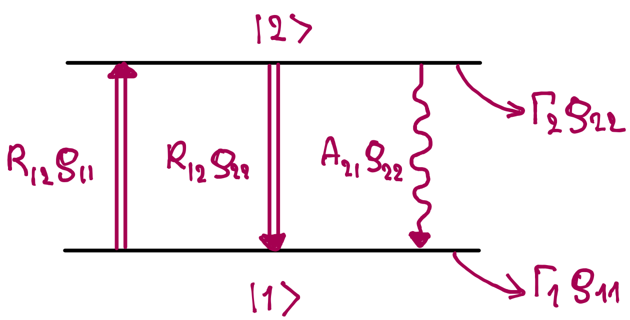
Emission and Absorption – Population Rate Equations

<u>Note</u>: The terms remaining after elimination of ρ_{12}, ρ_{21} are commonly identified with *induced* or *stimulated* processes. They are proportional to $|X|^2, |E_0|^2$ and thus the *intensity* of the light field.

Def: Absorption Rate = Stimulated Emission Rate

$$R_{12} = \frac{|X|^2\beta/2}{\Delta^2+\beta^2} = \frac{|\vec{r}_{12}\cdot\vec{\varepsilon}E_0/\hbar|^2\beta/2}{(\omega_{21}-\omega)^2+\beta^2}$$

Physical Picture:



Elastic Collision Broadening

In hot and dense gases the dominant source of relaxation is often elastic collisions between atoms

Let $\beta \gg \Gamma_1, \Gamma_2, A_{21}$ ⇨ ρ_{12} reaches steady state much faster than ρ_{11}, ρ_{22}

We can solve the eq. for $\dot{\rho}_{12}$ assuming it is in steady state for given values of ρ_{11}, ρ_{22}

This yields Rate Equations for the populations only, valid in the *collision broadened* regime

$$\dot{\rho}_{11} = -\Gamma_1\rho_{11} + A_{21}\rho_{22} + R_{12}(\rho_{22}-\rho_{11}) \neq 0$$

$$\dot{\rho}_{22} = -\Gamma_2\rho_{22} - A_{21}\rho_{22} - R_{12}(\rho_{22}-\rho_{11}) \neq 0$$

* This is another example of adiabatic elimination of a fast variable (the coherence), leaving us with simpler equations for the slower variables.
* From these we can find the *transient* behavior of the coherences ρ_{11}, ρ_{22}

Emission and Absorption – Population Rate Equations

Note: When collisions are very frequent the dipole $\langle \vec{\gamma} \rangle$ is oriented at random relative to the driving field. In that case

$$\langle |\vec{\gamma}_{12} \cdot \vec{\varepsilon} E_o|^2 \rangle_{angles} = \frac{1}{3} \gamma_{12}^2 |E_o|^2$$

$$R_{12} = \frac{\langle |\vec{\gamma}_{12} \cdot \vec{\varepsilon} E_o/\hbar|^2 \rangle_{angles} \beta/2}{\Delta^2 + \beta^2} = \frac{1}{3} \frac{|\chi|^2 \beta/2}{\Delta^2 + \beta^2}$$

Photon Flux and Cross Section

Let $R_{12} \equiv \sigma(\Delta)\phi$ where $\hbar\omega\phi = \underbrace{\frac{1}{2} c \varepsilon_o |E_o|^2}_{\text{intensity}}$

"photon flux" intensity

This allows us to recast the Rate Eqs

$$\boxed{\begin{aligned} \dot{\rho}_{11} &= -\Gamma_1 \rho_{11} + A_{21}\rho_{22} + \sigma(\Delta)\phi(\rho_{22} - \rho_{11}) \\ \dot{\rho}_{22} &= -\Gamma_2 \rho_{22} - A_{21}\rho_{22} - \sigma(\Delta)\phi(\rho_{22} - \rho_{11}) \end{aligned}}$$

We see that for each atom

# of absorption events	=	$\sigma(\Delta)\phi\rho_{11}$
# of stim. emission events	=	$\sigma(\Delta)\phi\rho_{22}$

Note: Given N atoms, the total # of events are $N\sigma(\Delta)\phi\rho_{11}$ and $N\sigma(\Delta)\phi\rho_{22}$. This is useful when we care about the total power in the light field, as we do in laser theory

Solution of the Rate Equations

Let $\Gamma_1 = \Gamma_2 = 0$ and plug in $\rho_{11} = 1 - \rho_{22}$

$$\dot{\rho}_{22} = -A_{21}\rho_{22} - \sigma(\Delta)\phi(2\rho_{22} - 1)$$

$$= -\underbrace{(A_{21} + 2\sigma(\Delta)\phi)}_{\gamma}\rho_{22} + \sigma(\Delta)\phi$$

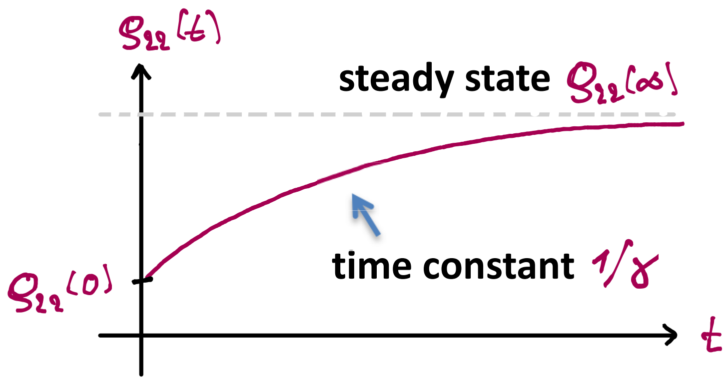
The solution is a damped approach to Steady state

Emission and Absorption – Population Rate Equations

$$\rho_{22}(t) = \left[\rho_{22}(0) - \rho_{22}(\infty)\right] e^{-\gamma t} + \rho_{22}(\infty)$$

where

$$\gamma = (A_{21} + 2\sigma(\Delta)\phi), \quad \rho_{22}(\infty) = \frac{\sigma(\Delta)\phi}{A_{21} + 2\sigma(\Delta)\phi}$$



* This *transient behavior* is valid in the collision broadened regime.

* Without collisions the transient regime Is one of damped *Rabi oscillations*.

* The *steady state* value $\rho_{22}(\infty)$ is good regardless

Limiting cases:

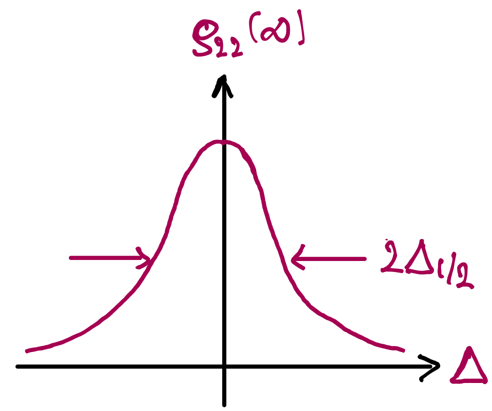
$\sigma(\Delta)\phi \sim 0 \Rightarrow \rho_{22}(\infty) = 0$

$\sigma(\Delta)\phi \ll A_{21} \Rightarrow \rho_{22}(\infty) = \dfrac{\sigma(\Delta)\phi}{A_{21}}$

$\sigma(\Delta)\phi \gg A_{21} \Rightarrow \rho_{22}(\infty) = 1/2 \leftarrow$ **Saturation!**

Rewrite $\rho_{22}(\infty)$ **using** $R_{12} = \sigma(\Delta)\phi = \dfrac{|\chi|^2\beta/2}{\Delta^2 + \beta^2}$

$$\Rightarrow \rho_{22}(\infty) = \frac{|\chi|^2\beta/2A_{21}}{\Delta^2 + \beta^2 + |\chi|^2\beta/A_{21}}$$



HWHM line width

$$\Delta_{1/2} = \sqrt{\beta^2 + |\chi|^2\beta/A_{21}}$$

$$= \beta\sqrt{1 + \frac{2\sigma(0)\phi}{A_{21}}}$$

(**used** $\sigma(0)\phi = \dfrac{|\chi|^2}{2\beta}$)