Lecture #36: Time Dependence of Two-Level Systems: Density Matrix, Rotating Wave Approximation

This lecture is based on Chapter 14 "The Density Matrix and Coherent Coupling of Molecules to Light" of the book *Elements of Quantum Mechanics*, Michael D. Fayer, Oxford University Press, 2001.

Lecture #19 dealt with weak interactions of molecules with electromagnetic radiation. It is in the "linear response" region and illustrates the importance of the electric dipole approximation and, especially, "resonance". *What is "linear response"?* The present lecture treats strong coherent interactions of electromagnetic radiation with two-level systems.

The easily derived (by the chain rule for derivatives) equation of motion for the expectation value of any Quantum Mechanical Operator is

$$\frac{d}{dt}\langle \mathbf{A}\rangle = \frac{i}{\hbar}\langle[\mathbf{H},\mathbf{A}]\rangle + \left\langle\frac{\partial A}{\partial t}\right\rangle,$$

derived by application of $\frac{d}{dt}$ to $\langle\ |, \mathbf{A}$, and $|\ \rangle$. One operator of particular importance is the density operator, $\boldsymbol{\rho}(t)$. It does more than simply repackage the information in $\Psi(x,t)$.

What is the density matrix?

1. $$\boldsymbol{\rho}_c = |c\rangle\langle c| = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{pmatrix}\left(c_1^* c_2^* \cdots c_N^*\right)$$

2. *Repackaging* an N × N matrix that contains all of the information in $\Psi(x,t)$.

3. It minimizes the $e^{-iE_j t/\hbar}$ factors of $\Psi(x,t) = \sum_j c_j \psi_j(x) e^{-iE_j t/\hbar}$.

4. It is directly observable. Its diagonal elements are populations and its off-diagonal elements are "coherences" that are observable as modulations at $\omega_{jk} = \left(E_j - E_k\right)/\hbar$ with Fourier amplitudes $c_j c_k^*$.

$$\Psi(x,t) \to |t\rangle$$

$$\Psi(x,t) = \sum_n c_n(t)\psi_n(x) \to |t\rangle = \sum_n c_n(t)|n\rangle \text{ or } |t\rangle = \left| \begin{matrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{matrix} \right\rangle$$

$\{|n\rangle\}$ is a complete orthonormal set of basis states

$|t\rangle$ is normalized to 1

$$\sum_n |c_n(t)|^2 = 1$$

$$\boldsymbol{\rho}(t) \equiv |t\rangle\langle t|$$

For a two-level system

$$|t\rangle = c_1(t)|1\rangle + c_2(t)|2\rangle$$

$$\rho_{11} = \langle 1|t\rangle\langle t|1\rangle = \langle 1|\left(c_1|1\rangle + c_2|2\rangle\right)\left(c_1^*\langle 1| + c_2^*\langle 2|\right)|1\rangle = c_1c_1^*$$

$$\rho_{12} = c_1c_2^*$$

$$\rho_{21} = c_2c_1^*$$

$$\rho_{22} = c_2c_2^*$$

$$\boldsymbol{\rho} = \begin{pmatrix} c_1c_1^* & c_1c_2^* \\ c_2c_1^* & c_2c_2^* \end{pmatrix}.$$

Since $|t\rangle$ is normalized to 1

$$1 = |c_1|^2 + |c_2|^2 = \text{Trace } \rho(t) = 1$$

and

$\rho_{ij} = \rho_{ji}^*$ or $\boldsymbol{\rho} = \boldsymbol{\rho}^*$

$\boldsymbol{\rho}$ is Hermitian. Tr $\boldsymbol{\rho}(t) = 1$ and $\boldsymbol{\rho} = \boldsymbol{\rho}^\dagger$ are general properties of N-dimensional $\boldsymbol{\rho}$.

For the 2-level system, we want to know the time dependence of $\boldsymbol{\rho}$:

$$\frac{d}{dt}\boldsymbol{\rho} = \left(\frac{d}{dt}|t\rangle\right)\langle t| + |t\rangle\left(\frac{d}{dt}|t\rangle\right)$$

$$i\hbar\frac{d}{dt}\Psi = \mathbf{H}\Psi \quad \left(\text{use this to replace } \frac{d}{dt}|t\rangle \text{ and } \frac{d}{dt}\langle t|\right)$$

$$\dot{\rho} = \frac{1}{i\hbar}\mathbf{H}(t)\underbrace{|t\rangle\langle t|}_{\boldsymbol{\rho}} + \frac{1}{i\hbar}\underbrace{|t\rangle\langle t|}_{\boldsymbol{\rho}}\mathbf{H}(t)$$

$$\dot{\rho} = \frac{1}{i\hbar}\left[\mathbf{H}(t), \boldsymbol{\rho}(t)\right].$$

ASA, especially involving multiplying pairs of 2 × 2 matrices

$$\dot{\rho}_{11} = -\dot{\rho}_{22} = -\frac{i}{\hbar}\left(H_{12}\rho_{21} - H_{21}\rho_{12}\right)$$
$$\dot{\rho}_{12} = \dot{\rho}_{21}^{*} = -\frac{i}{\hbar}\left[\left(H_{11} - H_{22}\right)\rho_{12} + \left(\rho_{22} - \rho_{11}\right)H_{12}\right]$$

OK. Now we are about to see some of the value of the density matrix — use the eigen-basis for the time-independent part of $\mathbf{H}^{(0)}$. All of the time depencence is in $\mathbf{H}^{(1)}(t)$.

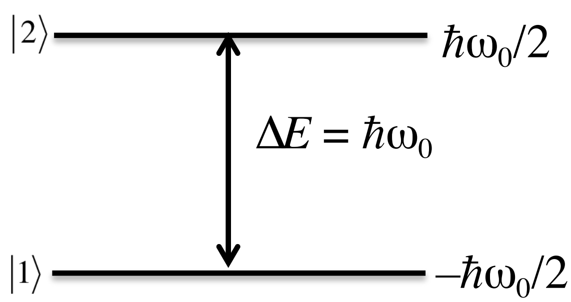
$$\mathbf{H} = \mathbf{H}^{(0)} + \mathbf{H}^{(1)}(t)$$
$$\mathbf{H}^{(0)}|n\rangle = E_n|n\rangle$$

ASA (a lot) we get

$$\dot{\rho}(t) = -\frac{i}{\hbar}\left[H^{(1)}(t), \rho(t)\right]!$$

all of the t-dependence of ρ is due to $H^{(1)}(t)$! All of $H^{(0)}$ cancels out.

Time-Dependent two-state problem



$$\mathbf{H}^{(0)} = \begin{pmatrix} -\hbar\omega_0/2 & 0 \\ 0 & +\hbar\omega_0/2 \end{pmatrix}$$

$$\langle 1|x|2\rangle$$

$$H^{(1)}(t) = \hbar \underbrace{e x_{12}}_{\mu} E_0 \cos\omega t$$

amplitude of oscillating electric field

has units of angular frequency

$\mu E_0 \equiv \omega_1$ This is the Rabi frequency.

We have 3 ω's: ω_0, ω, and ω_1.

$$\langle 1| = e^{-i\omega_0 t/2}\langle 1'|$$

$$\underbrace{|2\rangle}_{t\text{-dep.}} = e^{-i\omega_0 t/2} \underbrace{\langle 2'|}_{t\text{-indep.}}$$

$$H^{(1)}(t) = \hbar\begin{pmatrix} 0 & \omega_1 \cos\omega t e^{-i\omega_0 t} \\ \omega_1 \cos\omega t e^{i\omega_0 t} & 0 \end{pmatrix}$$

$$\dot{\rho} = -\frac{i}{\hbar}\left[\mathbf{H}^{(1)}, \boldsymbol{\rho}\right]$$

get equations of motion

$$\dot{\rho}_{11} = i\omega_1 \cos\omega t\left(e^{i\omega_0 t}\rho_{12} - e^{-i\omega_0 t}\rho_{21}\right)$$
$$\dot{\rho}_{22} = -i\omega_1 \cos\omega t\left(e^{i\omega_0 t}\rho_{12} - e^{-i\omega_0 t}\rho_{21}\right)$$
$$\dot{\rho}_{12} = i\omega_1 \cos\omega t\ e^{-i\omega_0 t}\left(\rho_{11} - \rho_{22}\right)$$
$$\dot{\rho}_{21} = -i\omega_1 \cos\omega t\ e^{+i\omega_0 t}\left(\rho_{11} - \rho_{22}\right)$$

$$\rho_{11} + \rho_{22} = 1 \rightarrow \dot{\rho}_{11} = -\dot{\rho}_{22}$$
$$\rho_{12} = \rho_{21}^{*} \rightarrow \dot{\rho}_{12} = \dot{\rho}_{21}^{*}$$

Now for the Rotating Wave **Approximation**

What is the rotating wave approximation (RWA)?

1. It is a transformation of $\mathbf{H}(t)$,

$$\widetilde{\mathbf{H}}(t) = \mathbf{R}^{-1}\mathbf{H}\mathbf{R}$$

that cancels the time-dependence of an off-diagonal element of $\mathbf{H}(t)$; for example $\mathbf{H}_{ij}$.

2. Once the RWA has been applied, a unitary transformation diagonalizes the

$$\frac{\widetilde{H}_{ij}}{\widetilde{H}_{ii}-\widetilde{H}_{jj}}$$

interaction by

$$\widetilde{\widetilde{\mathbf{H}}} = \mathbf{T}^{\dagger}\mathbf{R}^{-1}\mathbf{HRT} .$$

3. Finally, the rotation is undone

$$\begin{aligned}\widetilde{\widetilde{\mathbf{H}}} &= \mathbf{RT}^{\dagger}\mathbf{R}^{-1}\mathbf{HRTR}^{-1} \\ \widetilde{\widetilde{\widetilde{\mathbf{\Psi}}}} &= \mathbf{RT}^{\dagger}\mathbf{R\Psi}\end{aligned}.$$

4. The RWA may be applied sequentially to each important t-dependent off-diagonal element of $\mathbf{H}(t)$.

$$\cos\omega t = \frac{1}{2}\left(e^{i\omega t}+e^{-i\omega t}\right) \text{ insert into } \dot{\rho} \text{ equations}$$

if $\omega \approx \omega_0$, then we get

$$e^{\pm i(\omega_0-\omega)t} \text{ and } e^{\pm i(\omega_0+\omega)t}$$

terms. The $\omega_0 - \omega$ terms are near resonance. They oscillate slowly, but $\omega_0 + \omega \approx 2\omega_0$ are far off resonance, they oscillate very fast.

Discard the rapidly oscillating terms and keep the slowly oscillating terms.

Now we have

$$\begin{aligned}\dot{\rho}_{11} &= i\frac{\omega_1}{2}\left(e^{i(\omega_0-\omega)t}\rho_{12} - e^{-i(\omega_0-\omega)t}\rho_{21}\right) \\ \dot{\rho}_{22} &= -\dot{\rho}_{11} \\ \dot{\rho}_{12} &= i\frac{\omega_1}{2}e^{-i(\omega_0-\omega)t}\left(\rho_{11}-\rho_{22}\right) \\ \dot{\rho}_{21} &= \dot{\rho}_{12}^{*}\end{aligned}$$

These coupled differential equations can be solved, subject to the RWA and to the initial condition that at $t = 0$, $\rho_{22}(0) = 0$, $\rho_{11}(0) = 1$.

$$\Delta\omega \equiv \underset{\substack{\uparrow \\ \text{level} \\ \text{spacing}}}{\omega_0} - \underset{\substack{\uparrow \\ \text{applied oscillating} \\ \text{field}}}{\omega}$$

$$\omega_e = \left(\Delta\omega^2 + \underset{\substack{\uparrow \\ \text{strength of the} \\ \text{oscillating field}}}{\omega_1^2}\right)^{1/2}$$

$$\rho_{11} = 1 - \frac{\omega_1^2}{\omega_e^2}\sin^2(\omega_e t/2)$$

$$\rho_{22} = \frac{\omega_1^2}{\omega_e^2}\sin^2(\omega_e t/2)$$

$$\rho_{12} = \frac{\omega_1}{\omega_e^2}\left[\frac{i\omega_e}{2}\sin(\omega_e t) - \Delta\omega\sin^2(\omega_e t/2)\right]e^{-i\Delta\omega t}$$

$$\rho_{21} = \rho_{12}^*$$

The populations ρ_{11} and ρ_{22} oscillate, but at $\omega_e > \omega_1$ and the oscillating amplitude is reduced because $\frac{\omega_1^2}{\omega_e^2} < 1$.

Rabi frequency

These ρ_{12} and ρ_{21} coherence terms look complicated. But we will be applying the radiation field only for a selected value of Δt. This will modify the $t = 0$ form of $\boldsymbol{\rho}(t)$ by a "flip angle".

Now for some special insights

Near-resonant behavior occurs when

$$\underset{\substack{\uparrow \\ \text{Rabi} \\ \text{freq.}}}{\omega_1} > \underset{\substack{\uparrow \\ \text{detuning}}}{\Delta\omega}$$

(ω_1 represents the strength of the $\mu\varepsilon$ term).

Near resonance, this $\omega_1 > \Delta\omega$ gets us back to the $\omega_e \approx \omega_1$ limit:

$$\rho_{11} = \cos^2(\omega_1 t/2)$$
$$\rho_{22} = \sin^2(\omega_1 t/2)$$
$$\rho_{12} = \frac{i}{2}\sin(\omega_1 t)\underbrace{e^{-i\Delta\omega t}}_{\text{extra phase factor due to small detuning from resonance.}}$$
$$\rho_{21} = \rho_{12}^*$$

Free Precession of an ensemble of *many* 2-level atoms or molecules.

Consider the situation where, starting with $\rho_{11} = 1$, the radiation field is turned on for $\Delta t = \frac{\theta}{\omega_1}$, where θ is called the "flip angle", and then the radiation is turned off at $t = 0$. The oscillating polarizing field is turned off at $t = 0$.

Now we have an ensemble of free particles.

NON-LECTURE

An ensemble is a collection of independent, non-interacting particles. They do not know about Boson or Fermion exchange symmetry. There is no inter-particle coherence.

The "polarizing" pulse is applied to an initially incoherent ensemble and creates a macroscopic (inter-particle) coherence, which produces a multi-particle oscillating electric dipole moment. This oscillating dipole broadcasts an oscillating electric field, which we detect.

The time evolution of $\boldsymbol{\rho}(t)$ in the absence of any radiation field is described by

$$\dot{\boldsymbol{\rho}} = -\frac{i}{\hbar}\left[H^{(0)},\rho\right]$$
$$H^{(0)} = \begin{pmatrix} -\omega_0/2 & 0 \\ 0 & +\omega_0/2 \end{pmatrix}$$
$$\dot{\rho}_{11} = \dot{\rho}_{22} = 0 \qquad \dot{\rho}_{12} = i\omega_0\rho_{12}$$
$$\dot{\rho}_{21} = \dot{\rho}_{12}^*$$

$$\rho_{11} = \rho_{11}(0)$$
$$\rho_{22} = \rho_{22}(0)$$
$$\rho_{12} = \rho_{12}(0)e^{i\omega_0 t}$$
$$\rho_{21} = \rho_{12}^*$$

the end of the excitation pulse is defined to occur at $t = 0$.

So, at $t = 0$, after the completion of the polarizing pulse, which is described by a chosen value of the "flip angle", $\boldsymbol{\rho}(0)$ has this form

	flip angle	0	π/2	π
$\rho_{11}(0) = \cos^2(\theta/2) =$		1	1/2	**0**
$\rho_{22}(0) = \sin^2(\theta/2) =$		0	1/2	**1**
$\rho_{12}(0) = \frac{i}{2}\sin\theta =$		i/2(0	1	0)
$\rho_{21}(0) = -\frac{i}{2}\sin\theta =$		i/2(0	–1	0)

So what is this good for?

$\langle \boldsymbol{\mu} \rangle_t = \text{Trace}(\boldsymbol{\rho\mu})$ [another useful computational trick]

NON-Lecture

There are two important tricks for dealing with a time-dependent **H**.

$$\frac{d}{dt}\langle \mathbf{A} \rangle = \frac{i}{\hbar}\langle [\mathbf{H},\mathbf{A}] \rangle + \left(\frac{\partial \mathbf{A}}{\partial t}\right)$$

$$\langle \mathbf{A} \rangle_t = \text{Trace}(\boldsymbol{\rho}\mathbf{A})$$

These tricks are both labor-saving and insight-generating.

To compute Trace ($\boldsymbol{\rho\mu}$) we need:

$$\boldsymbol{\mu} = \begin{pmatrix} 0 & \mu \\ \mu & 0 \end{pmatrix}$$

$$\langle \boldsymbol{\mu} \rangle_t = \text{Tr}(\boldsymbol{\rho\mu}) = \text{Tr}\begin{pmatrix} \rho_{11}(0) & \rho_{12}(0)e^{i\omega_0 t} \\ \rho_{21}(0)e^{-i\omega_0 t} & \rho_{22}(0) \end{pmatrix}\begin{pmatrix} 0 & \mu \\ \mu & 0 \end{pmatrix}$$

$$= \mu\left[\rho_{12}(0)e^{i\omega t} + \rho_{21}(0)e^{-i\omega t}\right]$$

For a **"flip angle"** of θ

$$\langle \boldsymbol{\mu} \rangle_t = -\mu(\sin\theta)\sin(\omega_0 t).$$

This is an electric dipole oscillating at ω_0.

Its maximum oscillation amplitude is at θ = π/2.

Its minimum (zero) oscillation is at θ = 0 or π.

When θ = π ("π-pulse") the system goes from $\rho_{11} = 1$, $\rho_{22} = 0$ to $\rho_{11} = 0$, $\rho_{22} = 1$.

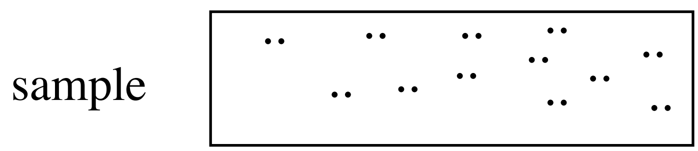
The population gets inverted from all in level 1 to all in level 2. But there is no oscillating dipole! This is very important (and perhaps counter-intuitive).

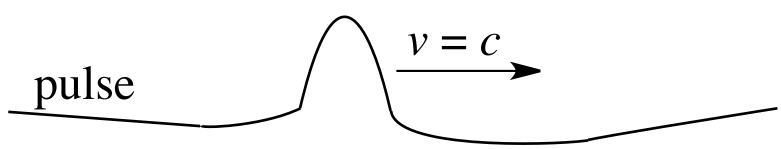
When $\theta = \pi/2$ we get

$$\rho_{11}(0) = \rho_{22}(0) \qquad \text{(equal populations in levels 1 and 2)}$$

$$\rho_{12}(0) = \rho_{21}^{*}(0) = \frac{i}{2} \qquad \text{maximum oscillation of full } \mu\varepsilon$$

Ensemble: If the Rabi frequency, ω_1 is the same for all points in space, all members of the ensemble oscillate at the same frequency, but possibly starting at different times as the polarizing pule propagates through the sample at $v = c = 1$ foot/ns.





This travelling wave polarization creates an in-phase polarization, which propagates in the direction of the polarizing pulse. Propagation in all other directions is killed by destructive interference.

If the polarizing field is not spatially uniform, ω_1 is not uniform and the μ_1 values are not all the same. Dephasing.

Decay also occurs by radiation. Stimulated emission. Superadiance!