CHM 502 – Module 12 – The Optical Bloch Equations

Prof. Marissa Weichman

We will now use the infrastructure we built for statistical ensembles of molecules in order to treat light-matter interactions. Again, the treatment we follow here draws heavily from "Mukamel for Dummies" as well as from Andrei Tokmakoff's notes on time-dependent quantum mechanics.

1 Light-matter interactions in the Liouville representation

Recall that we introduced the Liouville-Von Neumann equation which describes the time-dependence of the density matrix:

$$\frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar}\left[\hat{H}, \hat{\rho}\right] \tag{1}$$

Eqn. 1 is equivalent to the time-dependent Schrödinger equation when $\hat{\rho}$ describes a pure quantum state, but also holds for mixed states.

When $\hat{H}$ is diagonalized, e.g.

$$\hat{H} = \hat{H}_0 = \begin{bmatrix} \hbar\omega_1 & 0 \\ 0 & \hbar\omega_2 \end{bmatrix} \tag{2}$$

we found that

$$\frac{d}{dt}\begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} = -i\begin{bmatrix} 0 & \omega_{12}\rho_{12} \\ \omega_{21}\rho_{21} & 0 \end{bmatrix} \tag{3}$$

which lets us write down simple expressions for the time-dependence of the elements of $\hat{\rho}$, e.g.

$$\rho_{11}(t) = \rho_{11}(0) \qquad \rho_{12}(t) = e^{-i\omega_{12}t}\rho_{12}(0) \tag{4}$$

Things get a bit more complicated when we consider time-dependent perturbations. For instance if we let our Hamiltonian be the reference $\hat{H}_0$ plus a time-varying interaction of the molecular dipole with an oscillating electromagnetic field:

$$\hat{H} = \hat{H}_0 + \hat{\mu}E(t), \qquad E(t) = 2E_0\cos(\omega t) = E_0\left[e^{+i\omega t} + e^{-i\omega t}\right] \tag{5}$$

Then we can write down $\hat{H}$ in the $\hat{H}_0$ eigenstate basis as:

$$\hat{H} = \begin{bmatrix} \hbar\omega_1 & \mu_{12}E(t) \\ \mu_{12}E(t) & \hbar\omega_2 \end{bmatrix} \tag{6}$$

where μ_{12} represents the transition dipole that allows us to drive transitions between states $|1\rangle$ and $|2\rangle$.

However, evaluating the Liouville Von-Neumann equation is now more involved as the time-dependence of each $\rho_{ij}(t)$ matrix element may now depend on several other matrix elements.

It will help to use the *Liouville representation*, writing $\hat{\rho}$ as a 4×1 vector of its matrix elements:

$$\hat{\rho} = \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} \quad \rightarrow \quad \begin{bmatrix} \rho_{11} \\ \rho_{12} \\ \rho_{21} \\ \rho_{22} \end{bmatrix} \tag{7}$$

This framework will allow us to rewrite Eqn. 1 in terms of a "superoperator" $\hat{L}$:

$$\frac{d}{dt}\hat{\rho} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}] = -\frac{i}{\hbar}\hat{L}\hat{\rho} \tag{8}$$

We call $\hat{L}$ a "super-operator" because it acts on the elements of $\hat{\rho}$, another operator. We write $\hat{L}$ as a 4×4 matrix with elements that connect each element of $\hat{\rho}$ to each of its other elements.

For our light-matter interaction Hamiltonian in Eqn. 6 we find:

$$\frac{d}{dt}\hat{\rho} = -\frac{i}{\hbar}\left(\begin{bmatrix} \hbar\omega_1 & \mu_{12}E(t) \\ \mu_{12}E(t) & \hbar\omega_2 \end{bmatrix} \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} - \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} \begin{bmatrix} \hbar\omega_1 & \mu_{12}E(t) \\ \mu_{12}E(t) & \hbar\omega_2 \end{bmatrix} \right) \tag{9}$$

$$\rightarrow \quad \frac{d}{dt}\rho_{11} = -\frac{i}{\hbar}\left[\cancel{\hbar\omega_1\rho_{11}} + \mu_{12}E(t)\rho_{21} - \cancel{\rho_{11}\hbar\omega_1} - \rho_{12}\mu_{12}E(t)\right], \tag{10}$$

$$\frac{d}{dt}\rho_{12} = -\frac{i}{\hbar}\left[\hbar\omega_1\rho_{12} + \mu_{12}E(t)\rho_{22} - \rho_{11}\mu_{12}E(t) - \rho_{12}\hbar\omega_2\right], \qquad \text{etc.} \tag{11}$$

Using Liouville representation, we can write down a more compact expression:

$$\frac{d}{dt}\begin{bmatrix} \rho_{11} \\ \rho_{12} \\ \rho_{21} \\ \rho_{22} \end{bmatrix} = -\frac{i}{\hbar}\begin{bmatrix} 0 & -\mu_{12}E(t) & +\mu_{12}E(t) & 0 \\ -\mu_{12}E(t) & \hbar(\omega_1 - \omega_2) & 0 & +\mu_{12}E(t) \\ +\mu_{12}E(t) & 0 & \hbar(\omega_2 - \omega_1) & -\mu_{12}E(t) \\ 0 & +\mu_{12}E(t) & -\mu_{12}E(t) & 0 \end{bmatrix}\begin{bmatrix} \rho_{11} \\ \rho_{12} \\ \rho_{21} \\ \rho_{22} \end{bmatrix} \tag{12}$$

This set of coupled differential equations are in fact the "optical Bloch equations."

***Aside*:** All of the above expressions are also valid for density matrices of mixed states! We can treat dephasing or population decay with the compact expression:

$$\frac{d}{dt}\rho = -\frac{i}{\hbar}\hat{L}\rho + \hat{\Gamma}\rho \tag{13}$$

where we might have:

$$\hat{\Gamma} = \begin{bmatrix} 0 & 0 & 0 & +\gamma_1 \\ 0 & -\gamma_2 & 0 & 0 \\ 0 & 0 & -\gamma_2 & 0 \\ 0 & 0 & 0 & -\gamma_1 \end{bmatrix} \tag{14}$$

accounting for both population relaxation ($T_1 = 1/\gamma_1$) and dephasing ($T_2 = 1/\gamma_2$).

2 The Optical Bloch Equations

As we proceed to evaluate the system of differential equations in Eqn. 12, it is mathematically convenient to transform into a *rotating frame* and define a new density matrix $\tilde{\rho}(t)$ with elements:

$$\tilde{\rho}_{11}(t) \equiv \rho_{11}(t) \tag{15}$$

$$\tilde{\rho}_{22}(t) \equiv \rho_{22}(t) \tag{16}$$

$$\tilde{\rho}_{12}(t) \equiv \rho_{12}(t)\, e^{-i\omega t} \tag{17}$$

$$\tilde{\rho}_{21}(t) \equiv \rho_{21}(t)\, e^{+i\omega t} \tag{18}$$

where ω is the frequency of the oscillating field, which will be near resonance for $\omega = \omega_2 - \omega_1$. By defining $\tilde{\rho}(t)$, we are attempting to separate out the rapidly oscillating part of the molecular response to the field and keeping only some slowly varying envelope. It is this mathematical trick that will later let us invoke the rotating wave approximation (RWA).

We would now like to write down an equation for $\tilde{\rho}(t)$ akin to Eqn. 12. Let's first note that the elements of Eqn. 12 give us differential equations like:

$$\frac{d}{dt}\rho_{12} = -i(\omega_1 - \omega_2)\rho_{12} + \frac{i}{\hbar}\mu_{12}E(t)\rho_{11} - \frac{i}{\hbar}\mu_{12}E(t)\rho_{22} \tag{19}$$

We can therefore write

$$\frac{d}{dt}\tilde{\rho}_{12} = \frac{d}{dt}\Big[\rho_{12}\, e^{-i\omega t}\Big] = \big[\underbrace{\frac{d}{dt}\rho_{12}}_{\text{Eqn. 19}}\big] e^{-i\omega t} - i\omega\rho_{12}\, e^{-i\omega t} \tag{20}$$

$$= -i[\omega_1 - \omega_2]\underbrace{\rho_{12}\, e^{-i\omega t}}_{\tilde{\rho}_{12}} + i\,\frac{\mu_{12}E(t)}{\hbar}\rho_{11}\, e^{-i\omega t} - i\,\frac{\mu_{12}E(t)}{\hbar}\rho_{22}\, e^{-i\omega t} - i\omega\underbrace{\rho_{12}\, e^{-i\omega t}}_{\tilde{\rho}_{12}} \tag{21}$$

$$= -i\,[\omega_1 - \omega_2 + \omega]\,\tilde{\rho}_{12} + i\,\frac{\mu_{12}E(t)}{\hbar}\tilde{\rho}_{11}\, e^{-i\omega t} - i\,\frac{\mu_{12}E(t)}{\hbar}\tilde{\rho}_{22}\, e^{-i\omega t} \tag{22}$$

$$\equiv -i\Delta\tilde{\rho}_{12} + i\tilde{\Omega}^*(t)\tilde{\rho}_{11} - i\tilde{\Omega}^*(t)\tilde{\rho}_{22} \tag{23}$$

where

$$\Delta \equiv \omega_1 - \omega_2 + \omega \tag{24}$$

$$\tilde{\Omega}(t) \equiv \frac{\mu_{12}E(t)}{\hbar}e^{+i\omega t} = \frac{\mu_{12}E_0}{\hbar}\left[e^{+i\omega t} + e^{-i\omega t}\right] e^{+i\omega t} \tag{25}$$

$$\equiv \Omega\left[e^{+i\omega t} + e^{-i\omega t}\right] e^{+i\omega t} \quad \text{with} \quad \Omega = \frac{\mu_{12}E_0}{\hbar} \tag{26}$$

Here Δ represents the detuning of the laser from resonance. Ω is the Rabi frequency, which will ultimately describe the rate with which population flops back and forth between the two states under laser irradiation. It should be intuitive that Ω scales with both the transition dipole μ_{12} and the field amplitude E_0; as either increases, we increase the rate with which we resonantly drive population back and forth between states $|1\rangle$ and $|2\rangle$.

By working out similar relations for all the elements of $\tilde{\rho}(t)$, we can re-express Eqn. 12 as:

$$\frac{d}{dt}\begin{bmatrix}\tilde{\rho}_{11}\\ \tilde{\rho}_{12}\\ \tilde{\rho}_{21}\\ \tilde{\rho}_{22}\end{bmatrix} = -i\begin{bmatrix}0 & -\tilde{\Omega}^*(t) & +\tilde{\Omega}(t) & 0\\ -\tilde{\Omega}^*(t) & \Delta & 0 & +\tilde{\Omega}^*(t)\\ +\tilde{\Omega}(t) & 0 & -\Delta & -\tilde{\Omega}(t)\\ 0 & +\tilde{\Omega}^*(t) & -\tilde{\Omega}(t) & 0\end{bmatrix}\begin{bmatrix}\tilde{\rho}_{11}\\ \tilde{\rho}_{12}\\ \tilde{\rho}_{21}\\ \tilde{\rho}_{22}\end{bmatrix} \tag{27}$$

At this point we can invoke the RWA:

$$\tilde{\Omega}(t) = \Omega\left[e^{+i\omega t} + e^{-i\omega t}\right]e^{+i\omega t} = \Omega\left[e^{+2i\omega t} + 1\right] \tag{28}$$

$$\tilde{\Omega}^*(t) = \Omega\left[e^{+i\omega t} + e^{-i\omega t}\right]e^{-i\omega t} = \Omega\left[e^{-2i\omega t} + 1\right] \tag{29}$$

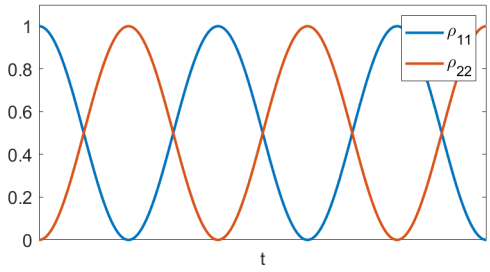
Note that the expressions above contain one term that is constant in time, while the other oscillates at a frequency of 2ω. When integrating Eqn. 27, the quickly oscillating terms wash out and will have essentially no effect. We therefore make the approximation $\tilde{\Omega}(t) \simeq \tilde{\Omega}^*(t) \simeq \Omega$, and the 4×4 matrix in Eqn. 27 becomes time-invariant. This approximation is valid in the case where the electric field is weak enough that the Rabi frequency Ω is small compared to the carrier frequency ω.

3 How the Optical Bloch solutions behave

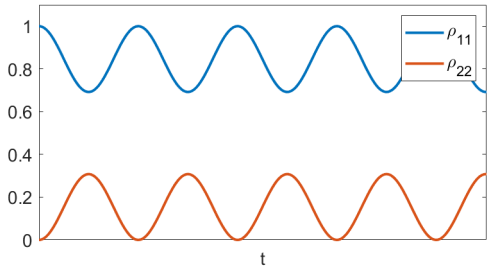
Let's now illustrate how this system behaves. Once making the RWA, the system of equations in Eqn. 27 is easy to solve numerically for the time dependence of the matrix elements of $\tilde{\rho}$. (Here are some Matlab functions that do all the hard work for you, for instance!)

All we really care about tracking here are the $\tilde{\rho}_{11}(t) = \rho_{11}(t)$ and $\tilde{\rho}_{22}(t) = \rho_{22}(t)$ diagonal elements of the density matrix which represent the respective probabilities that the system is found in state $|1\rangle$ or $|2\rangle$ at time t.

If we solve Eqn. 27 numerically, for resonant pumping ($\Delta = 0$) and initial conditions $\tilde{\rho}_{11}(0) = 1$ and $\tilde{\rho}_{22}(0) = 0$, we see Rabi oscillations between states $|1\rangle$ and $|2\rangle$ at frequency Ω:



These oscillations are less pronounced when the field is non-resonant, with Δ on the scale of Ω. In this case, we don't have perfect contrast in driving the population back and forth between the two states:

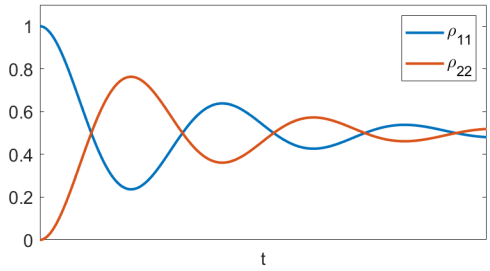


We can now add in dephasing and population decay to our Liouville representation system of differential equautions:

$$\frac{\partial}{\partial t}\tilde{\rho} = -\frac{i}{\hbar}\hat{L}\tilde{\rho} + \hat{\Gamma}\tilde{\rho}, \qquad \hat{\Gamma} = \begin{bmatrix} 0 & 0 & 0 & +\gamma_1 \\ 0 & -\gamma_2 & 0 & 0 \\ 0 & 0 & -\gamma_2 & 0 \\ 0 & 0 & 0 & -\gamma_1 \end{bmatrix} \tag{30}$$

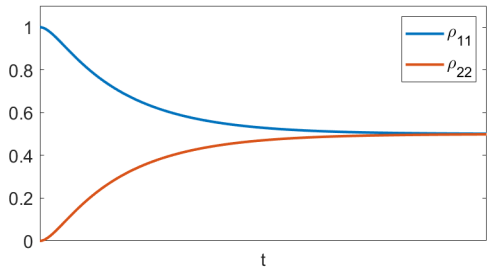
Recall here that we add in γ_1 to describe population decay out of state $|2\rangle$ into $|1\rangle$, which leads to a $-\gamma_1\tilde{\rho}_{22}$ term in the differential equation for $d\tilde{\rho}_{22}/dt$, and a $+\gamma_1\tilde{\rho}_{22}$ term in the differential equation for $d\tilde{\rho}_{11}/dt$. Both $\tilde{\rho}_{12}$ and $\tilde{\rho}_{21}$ will decay with rate γ_2 to capture both population decay and pure dephasing.

Assuming that $\gamma_1, \gamma_2 < \Omega$ and $\Delta = 0$, numerically solving the optical Bloch equations yields the following damped oscillations in ρ_{11} and ρ_{22}:



Note that even though we have included population relaxation here (γ_1), the ρ_{11} and ρ_{22} "populations" both trend towards 1/2, because we are continuously driving the system with resonant light. The competing decay processes have just scrambled things so the population isn't flopping coherently; instead there is a dynamic equilibrium of population being resonantly transferred in both directions.

In the case of very strong dephasing ($\gamma_1, \gamma_2 > \Omega$) the damped oscillations disappear entirely:



This is the most common situation in condensed phase systems, where collisions with the environment occur rapidly, and dephasing out-competes coherent Rabi oscillations. It's therefore very difficult to generate π-pulse style population inversions in condensed phase systems with driving fields of reasonable intensity.