CHM 502 - Module 11 - The Optical Bloch Equations

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

1 Liouville representation & deriving the Optical Bloch equations

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

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

Eqn. 1 is equivalent to the time-dependent Schrödinger equation when ρ describes a pure quantum state, but also holds for mixed states.

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

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

then we found that

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

which lets us write down simple differential equations for the time-dependence of the matrix elements of ρ, e.g.

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

However, things get a bit more complicated when we consider time-dependent perturbations to the system, in the context of treating light-matter interactions. For instance if we let our Hamiltonian be the reference $\hat{H}_0$ plus the time-dependent interaction of the molecular dipole with an oscillating electromagnetic field:

$$\hat{H} = \hat{H}_0 + \hat{\mu}E(t) \tag{5}$$

$$E(t) = 2E_0\cos(\omega t) = E_0\left[e^{+i\omega t} + e^{-i\omega t}\right] \tag{6}$$

Then we can use the eigenstate basis of $\hat{H}_0$ to write:

$$\hat{H} = \begin{pmatrix} \hbar\omega_1 & \mu E(t) \\ \mu E(t) & \hbar\omega_2 \end{pmatrix} \tag{7}$$

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

It will help to use the *Liouville representation*, writing ρ as a 4×1 vector of its matrix elements:

$$\rho = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} \quad \rightarrow \quad \begin{pmatrix} \rho_{11} \\ \rho_{12} \\ \rho_{21} \\ \rho_{22} \end{pmatrix} \tag{8}$$

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

$$\frac{d}{dt}\rho = -\frac{i}{\hbar}[\hat{H}, \rho] = -\frac{i}{\hbar}\hat{L}\rho \tag{9}$$

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

For instance, for our light-matter interaction Hamiltonian in Eqn. 7 we would find:

$$\frac{d}{dt}\rho = -\frac{i}{\hbar}\left[\begin{pmatrix} \hbar\omega_1 & \mu E(t) \\ \mu E(t) & \hbar\omega_2 \end{pmatrix}\begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} - \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix}\begin{pmatrix} \hbar\omega_1 & \mu E(t) \\ \mu E(t) & \hbar\omega_2 \end{pmatrix}\right] \tag{10}$$

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

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

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

$$\frac{d}{dt}\begin{pmatrix} \rho_{11} \\ \rho_{12} \\ \rho_{21} \\ \rho_{22} \end{pmatrix} = -\frac{i}{\hbar}\begin{pmatrix} 0 & -\mu E(t) & +\mu E(t) & 0 \\ -\mu E(t) & \hbar(\omega_1 - \omega_2) & 0 & +\mu E(t) \\ +\mu E(t) & 0 & \hbar(\omega_2 - \omega_1) & -\mu E(t) \\ 0 & +\mu E(t) & -\mu E(t) & 0 \end{pmatrix}\begin{pmatrix} \rho_{11} \\ \rho_{12} \\ \rho_{21} \\ \rho_{22} \end{pmatrix} \tag{13}$$

This will give rise to the "Optical Bloch equations."

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

$$\frac{d}{dt}\rho = -\frac{i}{\hbar}\hat{L}\rho + \hat{\Gamma}\rho \tag{14}$$

where we might have:

$$\hat{\Gamma} = \begin{pmatrix} 0 & 0 & 0 & +\gamma_1 \\ 0 & -\gamma_2 & 0 & 0 \\ 0 & 0 & -\gamma_2 & 0 \\ 0 & 0 & 0 & -\gamma_1 \end{pmatrix} \tag{15}$$

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

2 Solutions to the Optical Bloch Equations

As we proceed to evaluate the system of differential equations in Eqn. 13, it makes things mathematically simpler to transform into a *rotating frame* and define a new density matrix $\tilde{\rho}(t)$ with

$$\tilde{\rho}_{11}(t) = \rho_{11}(t) \tag{16}$$
$$\tilde{\rho}_{22}(t) = \rho_{22}(t) \tag{17}$$
$$\tilde{\rho}_{12}(t) = \rho_{12}(t)\, e^{-i\omega t} \tag{18}$$
$$\tilde{\rho}_{21}(t) = \rho_{21}(t)\, e^{+i\omega t} \tag{19}$$

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 separating out the rapidly oscillating part of the molecular response to the field and keeping only some slowly varying envelope.

We would now like to write down an equation for $\tilde{\rho}(t)$ akin to Eqn. 13. Let's first note that the elements of Eqn. 13 give us differential equations like those in Eqns. 11 and 12:

$$\frac{d}{dt}\rho_{12} = -i(\omega_1 - \omega_2)\rho_{12} + \frac{i}{\hbar}\mu E(t)\rho_{11} - \frac{i}{\hbar}\mu E(t)\rho_{22} \tag{20}$$

We can therefore write

$$\begin{aligned}
\frac{d}{dt}\tilde{\rho}_{12} &= \frac{d}{dt}\left[\rho_{12}\, e^{-i\omega t}\right] && (21)\\
&= \frac{d}{dt}\left[\rho_{12}\right] e^{-i\omega t} - i\omega\rho_{12}\, e^{-i\omega t} && (22)\\
&= -i(\omega_1 - \omega_2)\underbrace{\rho_{12}\, e^{-i\omega t}}_{\tilde{\rho}_{12}(t)} + i\,\frac{\mu E(t)}{\hbar}\rho_{11}\, e^{-i\omega t} - i\,\frac{\mu E(t)}{\hbar}\rho_{22}\, e^{-i\omega t} - i\omega\underbrace{\rho_{12}\, e^{-i\omega t}}_{\tilde{\rho}_{12}(t)} && (23)\\
&= -i\left[\omega_1 - \omega_2 + \omega\right]\tilde{\rho}_{12} + i\,\frac{\mu E(t)}{\hbar}\tilde{\rho}_{11}\, e^{-i\omega t} - i\,\frac{\mu E(t)}{\hbar}\tilde{\rho}_{22}\, e^{-i\omega t} && (24)\\
&\equiv -i\Delta\tilde{\rho}_{12} + i\tilde{\Omega}^*(t)\tilde{\rho}_{11} - i\tilde{\Omega}^*(t)\tilde{\rho}_{22} && (25)
\end{aligned}$$

where

$$\Delta \equiv \omega_1 - \omega_2 + \omega \tag{26}$$

$$\tilde{\Omega}(t) \equiv \frac{\mu E(t)}{\hbar}e^{+i\omega t} = \frac{\mu E_0}{\hbar}\left[e^{+i\omega t} + e^{-i\omega t}\right] e^{+i\omega t} \tag{27}$$

$$\equiv \Omega\left[e^{+i\omega t} + e^{-i\omega t}\right] e^{+i\omega t} \quad \text{with} \quad \Omega = \frac{\mu E_0}{\hbar} \tag{28}$$

where 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.

By working out similar relations for all the elements of $\tilde{\rho}(t)$, we can re-express Eqn. 13 as:

$$\frac{d}{dt}\begin{pmatrix}\tilde{\rho}_{11}\\ \tilde{\rho}_{12}\\ \tilde{\rho}_{21}\\ \tilde{\rho}_{22}\end{pmatrix} = -i\begin{pmatrix}0 & -\tilde{\Omega}(t) & +\tilde{\Omega}(t) & 0\\ -\tilde{\Omega}(t) & \Delta & 0 & +\tilde{\Omega}(t)\\ +\tilde{\Omega}(t) & 0 & -\Delta & -\tilde{\Omega}(t)\\ 0 & +\tilde{\Omega}(t) & -\tilde{\Omega}(t) & 0\end{pmatrix}\begin{pmatrix}\tilde{\rho}_{11}\\ \tilde{\rho}_{12}\\ \tilde{\rho}_{21}\\ \tilde{\rho}_{22}\end{pmatrix} \tag{29}$$

At this point we can invoke the *rotating wave approximation* (RWA), as we have before. Note that

$$\tilde{\Omega}(t) = \Omega\left[e^{+i\omega t} + e^{-i\omega t}\right]e^{+i\omega t} = \Omega\left[e^{+2i\omega t} + 1\right] \tag{30}$$

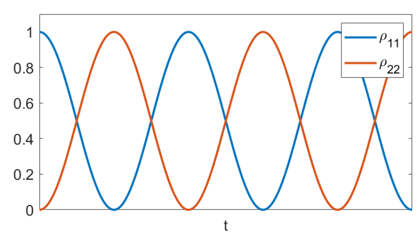
contains one term that is constant in time, while the other oscillates at a frequency of 2ω. When integrating Eqn. 29, the quickly oscillating term washes out and will have essentially no effect. We therefore make the approximation $\tilde{\Omega}(t) \simeq \Omega$, and the 4×4 matrix in Eqn. 29 becomes time-invariant. This approximation is valid in the case where the electric field is weak enough that the Rabi frequency Ω is slower than the carrier frequency ω.

Aside: Note that with the RWA approximation made, it turns out that Eqn. 29 can be re-expressed as a Liouville-von Neumann equation with an effective time-independent Hamiltonian $\hat{H}_{\text{eff}}$:

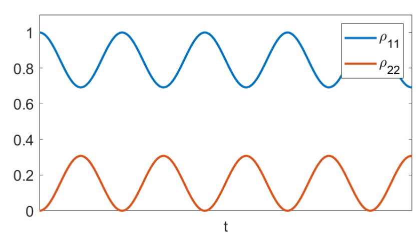
$$\frac{\partial}{\partial t}\tilde{\rho} = -\frac{i}{\hbar}\left[\hat{H}_{\text{eff}}, \tilde{\rho}\right], \qquad \hat{H}_{\text{eff}} = \begin{pmatrix} \hbar\Delta & \hbar\Omega \\ \hbar\Omega & 0 \end{pmatrix} \tag{31}$$

Let's now illustrate how this system behaves. Recall that $\tilde{\rho}_{11}(t) = \rho_{11}(t)$ and $\tilde{\rho}_{22}(t) = \rho_{22}(t)$ represent the probability that the system is found in states $|1\rangle$ or $|2\rangle$ at time t, respectively.

If one solves Eqn. 29 numerically, for resonant pumping ($\Delta = 0$) and initial conditions $\tilde{\rho}_{11}(0) = \rho_{11}(0) = 1$ and $\tilde{\rho}_{22}(0) = \rho_{22}(0) = 0$, we find Rabi oscillations between states $|1\rangle$ and $|2\rangle$ at frequency Ω:



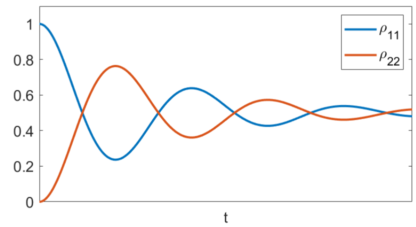
These oscillations become less pronounced when the field is non-resonant, with Δ on the scale of Ω:



Imagine now that we add dephasing in the Liouville representation, with

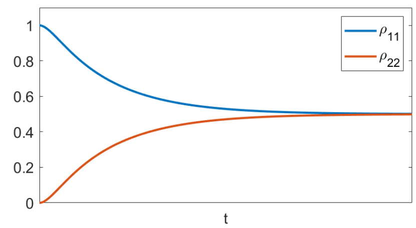
$$\frac{\partial}{\partial t}\tilde{\rho} = -\frac{i}{\hbar}\hat{L}\tilde{\rho} + \hat{\Gamma}\tilde{\rho}, \qquad \hat{\Gamma} = \begin{pmatrix} 0 & 0 & 0 & +\gamma_1 \\ 0 & -\gamma_2 & 0 & 0 \\ 0 & 0 & -\gamma_2 & 0 \\ 0 & 0 & 0 & -\gamma_1 \end{pmatrix} \tag{32}$$

Assuming that $\gamma_1, \gamma_2 < \Omega$ and $\Delta = 0$, numerically solving the optical Bloch equation gives us:



The off-diagonal elements $\tilde{\rho}_{12}(t)$ and $\tilde{\rho}_{21}(t)$ representing coherences die out. Note that even though we have included population relaxation here (γ_1), the diagonal "population" elements $\rho_{11}(t)$ and $\rho_{22}(t)$ both trend towards $1/2$, because we are continuously driving the system with resonant light.

In the case of very strong dephasing, $\gamma_1, \gamma_2 > \Omega$ and the oscillations disappear:



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