Density Matrix
State of a system at time $t$:

$$| t \rangle = \sum_n C_n(t) | n \rangle$$

$\{ |n \rangle \}$ orthonormal basis set

Contains time dependent phase factors.

$$\sum_n | C_n(t) |^2 = 1 \implies | t \rangle \text{ normalized}$$

Density Operator

$$\rho(t) = | t \rangle \langle t |$$

We’ve seen this before, as a “projection operator”

Can find density matrix in terms of the basis set $\{ |n \rangle \}$

Matrix elements of density matrix:

$$\rho_{ij}(t) = \langle i | \rho(t) | j \rangle$$

$$= \langle i | t \rangle \langle t | j \rangle$$
Two state system:

\[ |t\rangle = C_1(t) |1\rangle + C_2(t) |2\rangle \quad \quad \langle t| = C_1^*(t) \langle 1| + C_2^*(t) \langle 2| \]

Calculate matrix elements of 2×2 density matrix:

\[ \rho_{11} = \langle 1| t \rangle \langle t| 1 \rangle \]

\[ = \langle 1| [C_1 |1\rangle + C_2 |2\rangle ] [C_1^* \langle 1| + C_2^* \langle 2|] |1\rangle \]

\[ \rho_{11} = C_1 C_1^* \]

\[ \rho_{12} = \langle 1| t \rangle \langle t| 2 \rangle \]

\[ \rho_{12} = C_1 C_2^* \]

\[ \rho_{21} = \langle 2| t \rangle \langle t| 1 \rangle \]

\[ \rho_{21} = C_2 C_1^* \]

\[ \rho_{22} = \langle 2| t \rangle \langle t| 2 \rangle \]

\[ \rho_{22} = C_2 C_2^* \]

Time dependent phase factors cancel. Always have ket with its complex conjugate bra.
In general:

\[ |t\rangle = \sum_i C_i(t) |i\rangle \]
\[ |t\rangle \langle t| = \sum_i \sum_j C_i(t) |i\rangle \langle j| C_j^*(t) \]

\[ \rho_{ij}(t) = \langle i | t \rangle \langle t | j \rangle \]
\[ = \langle i | \left( \sum_k \sum_l C_k(t) |k\rangle \langle l| C_l^*(t) \right) |j\rangle \]

\[ \rho_{ij}(t) = C_i C_j^* \quad ij \text{ density matrix element} \]
2×2 Density Matrix:

\[
\rho(t) = \begin{bmatrix}
C_1 C_1^* & C_1 C_2^* \\
C_2 C_1^* & C_2 C_2^*
\end{bmatrix}
\]

\(C_1 C_1^* \Rightarrow \text{Probability of finding system in state } |1\rangle\)

\(C_2 C_2^* \Rightarrow \text{Probability of finding system in state } |2\rangle\)

Diagonal density matrix elements \(\Rightarrow\) probs. of finding system in various states

Off Diagonal Elements \(\Rightarrow\) “coherences”

Since

\[
\sum_n |C_n(t)|^2 = 1
\]

\(\text{Tr } \rho(t) = 1\) \hspace{1cm} \text{trace} = 1 \text{ for any dimension}

And

\(\rho_{ij} = \rho_{ji}^*\) \hspace{1cm} \text{(trace – sum of diagonal matrix elements)
Time dependence of $\rho(t)$

$$
\dot{\rho} = \frac{d \rho(t)}{dt}
$$

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

product rule

Using Schrödinger Eq. for time derivatives of $\mid t \rangle$ & $\langle t \mid$

$$
i\hbar \frac{d \mid t \rangle}{dt} = H \mid t \rangle
$$

$$
\frac{d \langle t \mid}{dt} = \langle t \mid H
$$

$$
\frac{d \langle t \mid}{dt} = \frac{1}{i\hbar} H \langle t \mid
$$

$$
\frac{d \mid t \rangle}{dt} = \frac{1}{i\hbar} H \mid t \rangle
$$

$$
\frac{d \langle t \mid}{dt} = \frac{1}{-i\hbar} \langle t \mid H
$$
Substituting:

\[
\frac{d \rho(t)}{dt} = \frac{1}{i\hbar} H(t)\langle t | t \rangle + \frac{1}{i\hbar} | t \rangle \langle t | H(t)
\]

\[
\frac{d \rho(t)}{dt} = \frac{1}{i\hbar} \left[ H(t)\langle t | t \rangle - | t \rangle \langle t | H(t) \right]
\]

\[
= \frac{1}{i\hbar} \left[ H(t), \rho(t) \right]
\]

Therefore:

\[
i\hbar \dot{\rho}(t) = \left[ H(t), \rho(t) \right]
\]

The fundamental equation of the density matrix representation.
Density Matrix Equations of Motion

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

since \( \rho_{ij} = C_i C_j^* \)

\[ \dot{\rho}_{ij} = C_i \left( \frac{dC_i^*}{dt} \right) + C_j^* \left( \frac{dC_j}{dt} \right) \]

time derivative of density matrix elements

\[ = C_i \dot{C}_j^* + C_j^* \dot{C}_i \]
by product rule

For 2×2 case, the equation of motion is:

\[
\begin{bmatrix}
\dot{\rho}_{11} & \dot{\rho}_{12} \\
\dot{\rho}_{21} & \dot{\rho}_{22}
\end{bmatrix} = -\frac{i}{\hbar} \left\{ \begin{bmatrix}
H_{11} & H_{12} \\
H_{21} & H_{22}
\end{bmatrix} \begin{bmatrix}
\rho_{11} & \rho_{12} \\
\rho_{21} & \rho_{22}
\end{bmatrix} - \begin{bmatrix}
\rho_{11} & \rho_{12} \\
\rho_{21} & \rho_{22}
\end{bmatrix} \begin{bmatrix}
H_{11} & H_{12} \\
H_{21} & H_{22}
\end{bmatrix} \right\}
\]

\[
\dot{\rho}_{11} = -\frac{i}{\hbar} [ (H_{11}\rho_{11} + H_{12}\rho_{21}) - (\rho_{11}H_{11} + \rho_{12}H_{21}) ]
\]

\[
\dot{\rho}_{11} = -\frac{i}{\hbar} (H_{12}\rho_{21} - H_{21}\rho_{12})
\]
\[
\begin{bmatrix}
\dot{\rho}_{11} & \dot{\rho}_{12} \\
\dot{\rho}_{21} & \dot{\rho}_{22}
\end{bmatrix} = -\frac{i}{\hbar}\left\{ \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} - \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \right\}
\]

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

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

**Equations of Motion – from multiplying of matrices for 2×2:**

\[
\dot{\rho}_{11} = -\dot{\rho}_{22} = -\frac{i}{\hbar}(H_{12}\rho_{21} - H_{21}\rho_{12}) \quad \text{for 2x2 because} \quad \rho_{11} + \rho_{22} = 1 \quad \text{(trace of} \; \rho = 1)\]

\[
\dot{\rho}_{12} = \dot{\rho}_{21}^* = -\frac{i}{\hbar}\left[ (H_{11} - H_{22})\rho_{12} + (\rho_{22} - \rho_{11})H_{12} \right] \quad \rho_{12} = \rho_{21}^* \quad \text{for any dimension}
\]
In many problems:

\[ H = H_0 + H_I(t) \]

(time independent) \quad (time dependent)

e.g., Molecule in a radiation field:

\[ H_0 \Rightarrow \text{molecular Hamiltonian} \]
\[ H_I(t) \Rightarrow \text{radiation field interaction (I) with molecule} \]

Natural to use basis set of \( H_0 \)

\[ H_0 |n\rangle = E_n |n\rangle \quad \text{(orthonormal)} \]
\[ |t\rangle = \sum_n C_n(t) |n\rangle \quad \text{(time dependent phase factors)} \]

Write \( |t\rangle \) as:

\[ |t\rangle = \sum_n C_n(t) |n\rangle \]

Eigenkets of \( H_0 \)
For this situation:

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

time evolution of density matrix elements, $C_{ij}(t)$, depends only on $H_I(t)$

$\Rightarrow$ time dependent interaction term

See derivation in book – and lecture slides.
Like first steps in time dependent perturbation theory
before any approximations.

In absence of $H_p$, only time dependence from time dependent phase factors from $H_0$. No changes in magnitudes of coefficients $C_{ij}$. 
Time Dependent Two State Problem Revisited:

Previously treated in Chapter 8 with Schrödinger Equation.

Basis set \( \{|1\rangle, |2\rangle\} \Rightarrow \) degenerate eigenkets of \( H_0 \)

No \( H_I \)

\[
H_0 |1\rangle = E |1\rangle = \hbar \omega_0 |1\rangle \\
H_0 |2\rangle = E |2\rangle = \hbar \omega_0 |2\rangle
\]

Interaction \( H_I \)

\[
H_I |1\rangle = \hbar \beta |2\rangle \\
H_I |2\rangle = \hbar \beta |1\rangle \\
\hbar \beta = \gamma \text{ of Ch. 8}
\]

The matrix \( H_I \)

\[
H_I = \hbar \begin{bmatrix} 0 & \beta \\ \beta & 0 \end{bmatrix}
\]

Because degenerate states, time dependent phase factors cancel in off-diagonal matrix elements – special case.
In general, the off-diagonal elements have time dependent phase factors.
Use
\[ \dot{\rho}(t) = -\frac{i}{\hbar} \left[ H_I(t), \rho(t) \right] \]
\[ H_I = \hbar \begin{bmatrix} 0 & \beta \\ \beta & 0 \end{bmatrix} \]
\[ \dot{\rho} = -\frac{i}{\hbar} \hbar \left\{ \begin{bmatrix} 0 & \beta \\ \beta & 0 \end{bmatrix} \rho_{11} \rho_{22} - \rho_{21} \rho_{22} \begin{bmatrix} 0 & \beta \\ \beta & 0 \end{bmatrix} \right\} \]
\[ \dot{\rho}_{11} = -i[(0 \rho_{11} + \beta \rho_{21}) - (\rho_{11} 0 + \rho_{12} \beta)] \]
\[ = -i \beta (\rho_{21} - \rho_{12}) = i \beta (\rho_{12} - \rho_{21}) \]

Multiplying matrices and subtracting gives
\[ \dot{\rho} = i \beta \begin{bmatrix} (\rho_{12} - \rho_{21}) & (\rho_{11} - \rho_{22}) \\ - (\rho_{11} - \rho_{22}) & - (\rho_{12} - \rho_{21}) \end{bmatrix} \]

Equations of motion of density matrix elements:
\[ \dot{\rho}_{11} = i \beta (\rho_{12} - \rho_{21}) \]
\[ \dot{\rho}_{22} = -i \beta (\rho_{12} - \rho_{21}) \]
\[ \dot{\rho}_{12} = i \beta (\rho_{11} - \rho_{22}) \]
\[ \dot{\rho}_{21} = -i \beta (\rho_{11} - \rho_{22}) \]

Probabilities

Coherences
Using

$$\dot{\rho}_{11} = i \beta (\rho_{12} - \rho_{21})$$

Take time derivative

$$\ddot{\rho}_{11} = i \beta (\dot{\rho}_{12} - \dot{\rho}_{21})$$

Substitute $\dot{\rho}_{12}$ & $\dot{\rho}_{21}$

$$\dot{\rho}_{12} = i \beta (\rho_{11} - \rho_{22}) \quad \dot{\rho}_{21} = -i \beta (\rho_{11} - \rho_{22})$$

$$\ddot{\rho}_{11} = -2 \beta^2 (\rho_{11} - \rho_{22})$$

Using $\text{Tr } \rho = 1$, i.e., $\rho_{11} + \rho_{22} = 1$

Then $\rho_{22} = 1 - \rho_{11}$

and

$$\ddot{\rho}_{11} = 2 \beta^2 - 4 \beta^2 \rho_{11}$$

For initial condition $\rho_{11} = 1$ at $t = 0$.

$$\rho_{11} = \cos^2 (\beta t) \quad \beta = \gamma / \hbar$$

$$\rho_{22} = \sin^2 (\beta t)$$

Same result as Chapter 8 except obtained probabilities directly.

No probability amplitudes.
Can get off-diagonal elements

\[ \dot{\rho}_{12} = i\beta(\rho_{11} - \rho_{22}) \]

Substituting:

\[ \dot{\rho}_{12} = i\beta(\cos^2 \beta t - \sin^2 \beta t) \]

\[ \rho_{12} = i\beta \int (\cos^2 \beta t - \sin^2 \beta t) \, dt \]

\[ \rho_{12} = \frac{i}{2} \sin(2\beta t) \]

Since \( \rho_{ij} = \rho_{ji}^* \)

\[ \rho_{21} = -\frac{i}{2} \sin(2\beta t) \]

\[ \int \cos^2 x \, dx = \frac{1}{2}x + \frac{1}{4}\sin 2x \]

\[ \int \sin^2 x \, dx = \frac{1}{2}x - \frac{1}{4}\sin 2x \]
Density matrix elements have no time dependent phase factors.

\[ |t\rangle = \sum_i C_i(t)|i\rangle \]

\[ |t\rangle\langle t| = \sum_i \sum_j C_i(t)|i\rangle\langle j|C_j^*(t) \]

\[ \rho_{ij}(t) = \langle i|t\rangle\langle t|j \rangle \]

\[ = \langle i|\left( \sum_k \sum_l C_k(t)|k\rangle\langle l|C_l^*(t) \right)|j \rangle \]

\[ = C_i(t)\langle i|i\rangle C_j^*(t)\langle j|j \rangle \]

\[ = C_i(t)C_j^*(t) \]

\[ \rho_{ij}(t) = C_i(t)C_j^*(t) \quad \text{ij density matrix element} \]

Time dependent coefficient, but no phase factors.
Can be time dependent phase factors in density matrix equation of motion.

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

For two levels, but the same in any dimension.

\[
H = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}
\]

\[
|1\rangle = |1_s\rangle e^{-iE_1 t/\hbar} \quad s - \text{spatial}
\]

\[
|2\rangle = |2_s\rangle e^{-iE_2 t/\hbar}
\]

\[
H_{11} = \langle 1 | H | 1 \rangle = \langle 1_s | H | 1_s \rangle e^{iE_1 t/\hbar} e^{-iE_1 t/\hbar} = \langle 1_s | H | 1_s \rangle \quad \text{no time dependent phase factor}
\]

\[
H_{12} = \langle 1 | H | 2 \rangle = \langle 1_s | H | 2_s \rangle e^{iE_1 t/\hbar} e^{-iE_2 t/\hbar} = \langle 1_s | H | 2_s \rangle e^{i(E_1 - E_2) t/\hbar} \quad \text{time dependent phase factor if } E_1 \neq E_2.
\]

Therefore, in general, the commutator matrix,

\[
\left[ H(t), \rho(t) \right]
\]

when you multiply it out,

will have time dependent phase factors if \( E_1 \neq E_2 \).
Expectation Value of an Operator
\[
\langle A \rangle = \langle t | A | t \rangle
\]

Complete orthonormal basis set \( \{|j\rangle\} \)
\[
|t\rangle = \sum_j C_j(t) |j\rangle
\]

Matrix elements of \( A \)
\[
A_{ij} = \langle i | A | j \rangle
\]

Derivation in book and see lecture slides
\[
\langle A \rangle = Tr \left( \rho(t) A \right)
\]

Expectation value of \( A \) is trace of the product of density matrix with the operator matrix \( A \).

Important: \( \rho(t) \) carries time dependence of coefficients.

Time dependent phase factors may occur in off-diagonal matrix elements of \( A \).
Example: Average $E$ for two state problem

$$
\bar{E} = \langle H \rangle = \text{Tr} \rho H
$$

$$
H = H_0 + H_I = \begin{bmatrix} E & \hbar\beta \\ \hbar\beta & E \end{bmatrix}
$$

Time dependent phase factors cancel because degenerate. Special case. In general have time dependent phase factors.

$$
\text{Tr} \rho H = \text{Tr} \left[ \begin{array}{cc} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{array} \right] \begin{bmatrix} E & \hbar\beta \\ \hbar\beta & E \end{bmatrix}
$$

Only need to calculate the diagonal matrix elements.

$$
= \rho_{11}E + \rho_{12}\hbar\beta + \rho_{21}\hbar\beta + \rho_{22}E
= E(\rho_{11} + \rho_{22}) + \hbar\beta(\rho_{12} + \rho_{21})
$$

$$
\rho_{11} = \cos^2(\beta t) \quad \rho_{22} = \sin^2(\beta t) \quad \rho_{12} = \frac{i}{2} \sin(2\beta t) \quad \rho_{21} = -\frac{i}{2} \sin(2\beta t)
$$

$$
\langle H \rangle = E \left( \cos^2(\beta t) + \sin^2(\beta t) + \frac{i\hbar\beta}{2}(\sin 2\beta t - \sin 2\beta t) \right)
= E
$$
Coherent Coupling by of Energy Levels by Radiation Field

Two state problem

\[ |1\rangle \quad \Delta \omega = \hbar \omega_0 \quad |2\rangle \]

\[ \Delta E = \hbar \omega_0 / 2 \]

radiation field

Zero of energy half way between states.

2 electronic states \( S_0 \leftrightarrow S_1 \)

2 vibrational states \( V_0 \leftrightarrow V_1 \)

NMR – 2 spin state, magnetic transition dipole

In general, if radiation field frequency \( \hbar \omega \) is near \( \Delta E \), and other transitions are far off resonance, can treat as a 2 state system.
Molecular Eigenstates as Basis

\[ H_0 |1\rangle = -\frac{\hbar \omega_0}{2} |1\rangle \]
\[ H_0 |2\rangle = \frac{\hbar \omega_0}{2} |2\rangle \]

Zero of energy half way between states.

Interaction due to application of optical field (light) on or near resonance.

\[ H_1(t) = \hbar e x_{12} E_0 \cos(\omega t) \]

\[ e x_{12} \Rightarrow \text{transition dipole operator} \]
\[ x \text{ polarized light} \]
\[ E_0 \Rightarrow \text{amplitude} \]
\(H_I\) couples states

\[
\langle 1 | H_I(t) | 2 \rangle = \hbar E_0 \cos(\omega t) \langle 1 | e x_{12} | 2 \rangle
\]

take out time dependent phase factors

\[
= \hbar E_0 \cos(\omega t) e^{-i\omega_0 t/2} \langle 1' | e x_{12} | 2' \rangle e^{-i\omega_0 t/2}
\]

\[
= \hbar \mu E_0 \cos(\omega t) e^{-i\omega_0 t}
\]

\[
\langle 2 | H_I(t) | 1 \rangle = \hbar \mu^* E_0 \cos(\omega t) e^{i\omega_0 t}
\]

Take \(\mu\) real (doesn’t change results)

Define Rabi Frequency, \(\omega_1\)

\[
\omega_1 = \mu E_0
\]

Then

\[
\langle 1 | H_I(t) | 2 \rangle = \hbar \omega_1 \cos(\omega t) e^{-i\omega_0 t}
\]

\[
\langle 2 | H_I(t) | 1 \rangle = \hbar \omega_1 \cos(\omega t) e^{i\omega_0 t}
\]

\(H_I(t)\) matrix:

\[
H_I(t) = \hbar \begin{bmatrix}
0 & \omega_1 \cos(\omega t) e^{-i\omega_0 t} \\
\omega_1 \cos(\omega t) e^{i\omega_0 t} & 0
\end{bmatrix}
\]

\(\mu\) is value of transition dipole bracket,

Note – time independent kets. No phase factors. Have taken phase factors out.
General state of system \[ |t\rangle = C_1(t)|1\rangle + C_2(t)|2\rangle \]

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

\[
\dot{\rho} = -\frac{i}{\hbar}\left\{ \begin{array}{cc}
\hbar & \omega_1 \cos(\omega t)e^{-i\omega_0 t} \\
\omega_1 \cos(\omega t)e^{i\omega_0 t} & 0
\end{array} \right\}
\begin{bmatrix}
\rho_{11} & \rho_{12} \\
\rho_{21} & \rho_{22}
\end{bmatrix}

- \hbar
\begin{bmatrix}
\rho_{11} & \rho_{12} \\
\rho_{21} & \rho_{22}
\end{bmatrix}
\begin{bmatrix}
0 & \omega_1 \cos(\omega t)e^{-i\omega_0 t} \\
\omega_1 \cos(\omega t)e^{i\omega_0 t} & 0
\end{bmatrix}
\]

\[
\begin{bmatrix}
\dot{\rho}_{11} & \dot{\rho}_{12} \\
\dot{\rho}_{21} & \dot{\rho}_{22}
\end{bmatrix}
= \begin{bmatrix}
\omega_1 \cos(\omega t)\left(e^{i\omega_0 t}\rho_{12} - e^{-i\omega_0 t}\rho_{21}\right) & \omega_1 \cos(\omega t)e^{-i\omega_0 t}(\rho_{11} - \rho_{22}) \\
-\omega_1 \cos(\omega t)e^{i\omega_0 t}(\rho_{11} - \rho_{22}) & -\omega_1 \cos(\omega t)\left(e^{i\omega_0 t}\rho_{12} - e^{-i\omega_0 t}\rho_{21}\right)
\end{bmatrix}
\]

Blue diagonal
Red off-diagonal
Equations of Motion of Density Matrix Elements

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

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

\[
\dot{\rho}_{12} = i\omega_1 \cos(\omega t) e^{-i\omega_0 t} (\rho_{11} - \rho_{22})
\]

\[
\dot{\rho}_{21} = -i\omega_1 \cos(\omega t) e^{i\omega_0 t} (\rho_{11} - \rho_{22})
\]

\[
\rho_{11} + \rho_{22} = 1 \quad \Rightarrow \quad \dot{\rho}_{11} = -\dot{\rho}_{22}
\]

\[
\rho_{12} = \rho_{21}^* \quad \Rightarrow \quad \dot{\rho}_{12} = \dot{\rho}_{21}^*
\]

Treatment exact to this point (expect for dipole approx. in \(\mu\)).
Rotating Wave Approximation

\[
\cos(\omega t) = \frac{1}{2} \left( e^{i\omega t} + e^{-i\omega t} \right)
\]

Put this into equations of motion
Will have terms like

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

But \( \omega_0 \sim \omega \)

Terms with \( (\omega_0 + \omega) \sim 2\omega_0 \) off resonance \( \Rightarrow \) Don’t cause transitions

Looks like high frequency Stark Effect
\( \Rightarrow \) Bloch – Siegert Shift

Small but sometimes measurable shift in energy.

**Drop these terms!**
With Rotating Wave Approximation

Equations of motion of density matrix

\[
\dot{\rho}_{11} = i \frac{\omega_1}{2} \left( e^{i(\omega_0 - \omega)t} \rho_{12} - e^{-i(\omega_0 - \omega)t} \rho_{21} \right)
\]

\[
\dot{\rho}_{22} = -i \frac{\omega_1}{2} \left( e^{i(\omega_0 - \omega)t} \rho_{12} - e^{-i(\omega_0 - \omega)t} \rho_{21} \right)
\]

\[
\dot{\rho}_{12} = i \frac{\omega_1}{2} e^{-i(\omega_0 - \omega)t} (\rho_{11} - \rho_{22})
\]

\[
\dot{\rho}_{21} = -i \frac{\omega_1}{2} e^{i(\omega_0 - \omega)t} (\rho_{11} - \rho_{22})
\]

These are the

Optical Bloch Equations for optical transitions
or just the Bloch Equations for NMR.

NMR - \( \omega_1 = \mu_m H_1 \)
\( H_1 \) – oscillating magnetic field of applied RF.
\( \mu_m \) – magnetic transition dipole.
Consider on resonance case \( \omega = \omega_0 \)

\[
\dot{\rho}_{11} = i \frac{\omega_1}{2} \left( e^{i(\omega_0 - \omega)t} \rho_{12} - e^{-i(\omega_0 - \omega)t} \rho_{21} \right)
\]

\[
\dot{\rho}_{22} = -i \frac{\omega_1}{2} \left( e^{i(\omega_0 - \omega)t} \rho_{12} - e^{-i(\omega_0 - \omega)t} \rho_{21} \right)
\]

\[
\dot{\rho}_{12} = i \frac{\omega_1}{2} e^{-i(\omega_0 - \omega)t} (\rho_{11} - \rho_{22})
\]

\[
\dot{\rho}_{21} = -i \frac{\omega_1}{2} e^{i(\omega_0 - \omega)t} (\rho_{11} - \rho_{22})
\]

All of the phase factors = 1.

These are IDENTICAL to the degenerate time dependent 2 state problem with \( \beta = \omega_1/2 \).
On resonance coupling to time dependent radiation field induces transitions.

Looks identical to time independent coupling of two degenerate states.

In effect, the on resonance radiation field “removes” energy differences and time dependence of field.

Start in ground state, \( |1\rangle \) : \( \rho_{11} = 1; \quad \rho_{22} = 0, \quad \rho_{12} = 0, \quad \rho_{21} = 0 \) \text{ at } t = 0.

Then\[
\begin{align*}
\rho_{11} &= \cos^2 \left( \frac{\omega_1 t}{2} \right) \\
\rho_{22} &= \sin^2 \left( \frac{\omega_1 t}{2} \right) \\
\rho_{12} &= \frac{i}{2} \sin(\omega_1 t) \\
\rho_{21} &= -\frac{i}{2} \sin(\omega_1 t)
\end{align*}
\]

populations \quad \text{coherences}
\[ \rho_{11} = \cos^2 \left( \frac{\omega_1 t}{2} \right) \quad \rho_{22} = \sin^2 \left( \frac{\omega_1 t}{2} \right) \] populations

Recall \( \omega_1 = \mu E_0 \Rightarrow \text{Rabi Frequency} \)

\[ \omega_1 t = \pi \quad \Rightarrow \quad \rho_{11} = 0, \quad \rho_{22} = 1 \]

This is called a \( \pi \) pulse \( \Rightarrow \) inversion, all population in excited state.

\[ \omega_1 t = \frac{\pi}{2} \quad \Rightarrow \quad \rho_{11} = 0.5, \quad \rho_{22} = 0.5 \]

This is called a \( \pi/2 \) pulse \( \Rightarrow \) Maximizes off diagonal elements \( \rho_{12}, \rho_{21} \)

As \( t \) is increased, population oscillates between ground and excited state at Rabi frequency.

\( \Rightarrow \) Transient Nutation
\( \Rightarrow \) Coherent Coupling

\[ \rho_{22} - \text{excited state prob.} \]

Copyright – Michael D. Fayer, 2017
Off Resonance Coherent Coupling

\[ \Delta \omega = \omega_0 - \omega \quad \text{Amount radiation field frequency is off resonance from transition frequency.} \]

Define \( \omega_e = \left( \Delta \omega^2 + \omega_1^2 \right)^{1/2} \Rightarrow \text{Effective Field} \quad \omega_1 = \mu E_0 \text{- Rabi frequency} \)

For same initial conditions: \( \rho_{11} = 1; \quad \rho_{22} = 0, \quad \rho_{12} = 0, \quad \rho_{21} = 0 \)

Solutions of Optical Bloch Equations

\[
\rho_{11} = 1 - \frac{\omega_1^2}{\omega_e^2} \sin^2(\omega_e t/2) \\
\rho_{12} = \frac{\omega_1}{\omega_e^2} \left[ \frac{i\omega_e}{2} \sin(\omega_e t) - \Delta \omega \sin^2(\omega_e t/2) \right] e^{-i\Delta \omega t} \\
\rho_{22} = \frac{\omega_1^2}{\omega_e^2} \sin^2(\omega_e t/2) \\
\rho_{21} = \frac{\omega_1}{\omega_e^2} \left[ -\frac{i\omega_e}{2} \sin(\omega_e t) - \Delta \omega \sin^2(\omega_e t/2) \right] e^{i\Delta \omega t}
\]

Oscillations Faster \( \rightarrow \omega_e \)
Max excited state probability:

\[ \rho_{22}^\text{max} = \frac{\omega_1^2}{\omega_e^2} \]

(Like non-degenerate time dependent 2-state problem)
Near Resonance Case - Important

\[ \omega_1 \gg \Delta \omega \]

Then

\[ \omega_e \cong \omega_1 \]

\( \rho_{11}, \rho_{22} \) reduce to on resonance case.

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

\[
\rho_{21} = -\frac{i}{2} \sin(\omega_1 t) e^{i \Delta \omega t}
\]

Same as resonance case except for phase factor

For \( \pi/2 \) pulse, maximizes \( \rho_{12}, \rho_{21} \)

\[ \omega_1 t = \pi/2 \]

But

\[ \Delta \omega t \ll \pi/2 \cong 0 \quad \text{because} \quad \omega_1 \gg \Delta \omega \]

Then, \( \rho_{12}, \rho_{21} \) virtually identical to on resonance case and

\( \rho_{11}, \rho_{22} \) same as on resonance case.

This is the basis of Fourier Transform NMR. Although spins have different chemical shifts, make \( \omega_1 \) big enough, all look like on resonance.
Free Precession

After pulse of \( \theta = \omega_1 t \) (flip angle)

On or near resonance

\[ \rho_{11} = \cos^2(\theta/2) \]
\[ \rho_{12} = \frac{i}{2} \sin \theta \]
\[ \rho_{22} = \sin^2(\theta/2) \]
\[ \rho_{21} = -\frac{i}{2} \sin \theta \]

After pulse – no radiation field.
Hamiltonian is \( H_0 \)

\[ \dot{\rho} = -\frac{i}{\hbar} \left[ H_0, \rho \right] \]

\[ H_0 = \begin{bmatrix} -\omega_0/2 & 0 \\ 0 & \omega_0/2 \end{bmatrix} \]
\[ \dot{\rho} = -\frac{i}{\hbar} \left[ H_0, \rho \right] \]

\[ H_0 = \hbar \begin{bmatrix} -\omega_0/2 & 0 \\ 0 & \omega_0/2 \end{bmatrix} \]

\[ \dot{\rho} = -\frac{i}{\hbar} \left\{ \hbar \begin{bmatrix} -\omega_0/2 & 0 \\ 0 & \omega_0/2 \end{bmatrix} \begin{bmatrix} \rho_{11} & \rho_2 \\ \rho_{21} & \rho_{22} \end{bmatrix} \right\} - \hbar \begin{bmatrix} \rho_{11} & \rho_2 \\ \rho_{21} & \rho_{22} \end{bmatrix} \begin{bmatrix} -\omega_0/2 & 0 \\ 0 & \omega_0/2 \end{bmatrix} \]

\[ \begin{align*}
\dot{\rho}_{11} &= \dot{0} \\
\dot{\rho}_{22} &= \dot{0} \\
\dot{\rho}_{12} &= i\omega_0 \rho_{12} \\
\dot{\rho}_{21} &= -i\omega_0 \rho_{21}
\end{align*} \]

\( t = 0 \) is at end of pulse

Solutions

\( \rho_{11} = \text{a constant} = \rho_{11}(0) \)

\( \rho_{22} = \text{a constant} = \rho_{22}(0) \)

Off-diagonal density matrix elements

\[ \rightarrow \text{Only time dependent phase factor} \]

Populations don’t change.
Off-diagonal density matrix elements after pulse ends \((t = 0)\).

Consider expectation value of transition dipole \(\langle \mu \rangle\).  

\[
\langle \mu \rangle = Tr \rho \mu
\]

\[
\mu = \begin{pmatrix} 1 & 0 \\ 0 & \mu \end{pmatrix}
\]

No time dependent phase factors.  
Phase factors were taken out of \(\mu\) as part of the derivation. Matrix elements involve time independent kets.

\[
Tr \rho \mu = Tr \begin{bmatrix} \rho_{11}(0) & \rho_{12}(0)e^{i\omega_0 t} \\ \rho_{21}(0)e^{-i\omega_0 t} & \rho_{22}(0) \end{bmatrix} \begin{pmatrix} 0 & \mu \\ \mu & 0 \end{pmatrix}
\]

\[
\langle \mu \rangle = \mu \left[ \rho_{12}(0)e^{i\omega_0 t} + \rho_{21}(0)e^{-i\omega_0 t} \right]
\]

Recall \(\mu = e\mathbf{x}_{12}\)
\[ \langle \mu \rangle = \mu \left[ \rho_{12}(0)e^{i\omega_0 t} + \rho_{21}(0)e^{-i\omega_0 t} \right] \]

After pulse of \( \theta = \omega_1 t \) \textbf{(flip angle)}

On or near resonance \( \rho_{12}(0) = \frac{i}{2} \sin \theta \quad \rho_{21}(0) = -\frac{i}{2} \sin \theta \)

\[ \langle \mu \rangle = \mu \left[ \frac{i}{2} \sin \theta e^{i\omega_0 t} - \frac{i}{2} \sin \theta e^{-i\omega_0 t} \right] \]

\[ \langle \mu \rangle = \mu \left[ \frac{i}{2} \sin \theta \cos(\omega_0 t) + i \sin(\omega_0 t)] - \frac{i}{2} \sin \theta \cos(\omega_0 t) - i \sin(\omega_0 t)] \right] \]

\[ \langle \mu \rangle = -\mu \sin \theta \sin(\omega_0 t) \]
\[ \langle \mu \rangle = -\mu \sin \theta \sin(\omega_0 t) \]

Oscillating electric dipole (magnetic dipole - NMR) at frequency \( \omega_0 \), \( \rightarrow \) Oscillating E-field (magnet field)

Free precession.

\[ I \propto |E|^2 \text{ for ensemble, coherent emission} \]

Rot. wave approx.
Tip of vector goes in circle.
Pure and Mixed Density Matrix

Up to this point - pure density matrix.
   One system or many identical systems.

Mixed density matrix ➔
Describes nature of a collection of sub-ensembles each with different properties.
The subensembles are not interacting.

\[ P_k \to \text{probability of having } k_{th} \text{ sub-ensemble with density matrix, } \rho_k. \]

\[ 0 \leq P_1, P_2, \cdots P_k, \cdots \leq 1 \]

and \[ \sum_k P_k = 1 \] Sum of probabilities (or integral) is unity.

Density matrix for mixed systems

\[ \rho(t) = \sum_k P_k \rho_k(t) \]

or integral if continuous distribution

Total density matrix is
the sum of the individual density matrices times their probabilities.
Because density matrix is at probability level, can sum (see Errata and Addenda).
Example: Light coupled to two different transitions – free precession

Light frequency $\omega$ near $\omega_{01}$ & $\omega_{02}$.

Difference of both $\omega_{01}$ & $\omega_{02}$ from $\omega$ small compared to $\omega_1$, that is, both near resonance.

Equal probabilities $\rightarrow P_1 = 0.5$ and $P_2 = 0.5$

For a given pulse of radiation field, both sub-ensembles will have same flip angle $\theta$.

Calculate

$$\left\langle \mu \right\rangle = Tr \; \rho(t) \mu$$

$$= \sum_k P_k Tr \; \rho_k \mu$$
Pure density matrix result for flip angle $\theta$:

$$\langle \mu \rangle = -\mu \sin \theta \sin(\omega_0 t)$$

For 2 transitions - $P_1=0.5$ and $P_2=0.5$

$$\langle \mu \rangle = -\frac{1}{2} \mu \sin \theta \left[ \sin(\omega_{01} t) + \sin(\omega_{02} t) \right]$$

$$= -\mu \sin \theta \left\{ \sin \left[ \frac{1}{2} (\omega_{01} + \omega_{02}) t \right] \cos \left[ \frac{1}{2} (\omega_{01} - \omega_{02}) t \right] \right\}$$

from trig. identities

Call: center frequency $\Rightarrow \omega_0$, shift from the center $\Rightarrow \delta$

then, $\omega_{01} = \omega_0 + \delta$ and $\omega_{02} = \omega_0 - \delta$,

with $\delta \ll \omega_0$

Therefore,

$$\langle \mu \rangle = -\mu \sin \theta \left[ \sin(\omega_0 t) \cos(\delta t) \right]$$

high freq. oscillation

low freq. oscillation, beat

Beat gives transition frequencies – FT-NMR
Equal amplitudes – 100% modulation, $\omega_{01} = 20.5$; $\omega_{01} = 19.5$
Amplitudes 2:1 – not 100% modulation, $\omega_{01} = 20.5$; $\omega_{01} = 19.5$
Amplitudes 9:1 – not 100% modulation, $\omega_{01} = 20.5$; $\omega_{01} = 19.5$
Equal amplitudes – 100% modulation, $\omega_{01} = 21; \omega_{01} = 19$
Free Induction Decay

Identical molecules have range of transition frequencies. Different solvent environments. Doppler shifts, etc.

Frequently, distribution is a Gaussian - probability of finding a molecule at a particular frequency, $P_h$.

$$P_h = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(\omega_h - \omega_0)^2}{2\sigma^2}}$$

normalization constant

Then

$$\rho(t) = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} e^{-\frac{(\omega_h - \omega_0)^2}{2\sigma^2}} d\omega_h$$

$$\approx \rho(\omega_h, t)$$

pure density matrix
Radiation field at $\omega=\omega_0$ line center

$\omega_1 \gg \sigma$ – all transitions near resonance

Apply pulse with flip angle $\theta$

\[ \langle \mu \rangle \text{, transition dipole expectation value.} \]

Following pulse, each sub-ensemble will undergo free precession at $\omega_h$

\[ \langle \mu \rangle = \text{Tr} \rho(t) \mu \]

\[ = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} e^{-\left(\omega_h - \omega_0\right)^2/2\sigma^2} \text{Tr} \rho(\omega_h, t) \mu d\omega_h \]

Using result for single frequency $\omega_h$ and flip angle $\theta$

\[ \langle \mu \rangle = -\frac{\mu \sin \theta}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} e^{-\left(\omega_h - \omega_0\right)^2/2\sigma^2} \sin(\omega_h t) d\omega_h \]
Substituting $\delta = (\omega_h - \omega_0)$, frequency of a molecule as difference from center frequency (light frequency). Then $\omega_h = (\delta + \omega_0)$ and $d\omega_h = d\delta$

With the trig identity: $\sin(x + y) = \sin(x)\cos(y) + \cos(x)\sin(y)$

$$\langle \mu \rangle = -\frac{\mu \sin \theta}{\sqrt{2\pi\sigma^2}} \left[ \cos(\omega_0 t) \int_{-\infty}^{\infty} e^{-\delta^2/2\sigma^2} \sin(\delta t) d\delta + \sin(\omega_0 t) \int_{-\infty}^{\infty} e^{-\delta^2/2\sigma^2} \cos(\delta t) d\delta \right]$$

First integral zero; integral of an even function multiplying an odd function.

$$\langle \mu \rangle = -\mu \sin \theta \sin(\omega_0 t) e^{-t^2/2(1/\sigma)^2}$$

Oscillation at $\omega_0$; decaying amplitude $\Rightarrow$
Gaussian decay with standard deviation in time $\Rightarrow 1/\sigma$ (Free Induction Decay)
Phase relationships lost $\Rightarrow$ Coherent Emission Decays
Off-diagonal density matrix elements – coherence; diagonal - magnitude

Copyright – Michael D. Fayer, 2017
\[ \langle \mu \rangle = -\mu \sin \theta \sin(\omega_0 t) e^{-t^2/(2\sigma^2)} \]

- **Decay of oscillating macroscopic dipole.**
- **Free induction decay.**

\[ \overline{E} \propto \langle \mu \rangle \]
\[ I \propto |E|^2 \propto \langle \mu \rangle^2 \]

**Coherent emission of light.**

- **Higher frequencies**
- **Lower frequencies**
- **Rotating frame at center freq., \( \omega_0 \)**
- **Flip angle**
- **Light frequency**
- **Free induction decay**

Copyright – Michael D. Fayer, 2017
Working with basis set of eigenkets of time independent piece of Hamiltonian, \( H_0 \), the time dependence of the density matrix depends only on the time dependent piece of the Hamiltonian, \( H_I \).

**Total Hamiltonian**

\[
H = H_0 + H_I(t)
\]

\( H_0 \) time independent

\[
H_0 |n\rangle = E_n |n\rangle
\]

Use \( \{ |n\rangle \} \) as basis set.

\[
|t\rangle = \sum_n C_n(t) |n\rangle
\]
Time derivative of density operator (using chain rule)

$$\left( \frac{d}{dt} |t\rangle \right) \langle t | + |t\rangle \left( \frac{d}{dt} \langle t | \right)$$  \hspace{1cm} (A)

Use Schrödinger Equation and its complex conjugate

$$\frac{1}{i \hbar} H(t) |t\rangle \langle t| + \frac{1}{-i \hbar} |t\rangle \langle t| H(t)$$

$$\frac{1}{i \hbar} H_0 |t\rangle \langle t| + \frac{1}{i \hbar} H_I |t\rangle \langle t| + \frac{1}{-i \hbar} |t\rangle \langle t| H_0 + \frac{1}{-i \hbar} |t\rangle \langle t| H_I$$  \hspace{1cm} (B)

Substitute expansion $|t\rangle = \sum_n C_n(t) |n\rangle$ into derivative terms in eq. (A).

$$\left( \frac{d}{dt} \sum_n C_n |n\rangle \right) \langle t | + |t\rangle \left( \frac{d}{dt} \sum_n C_n^* \langle n | \right)$$

$$= \left( \sum_n \dot{C}_n |n\rangle \right) \langle t | + \left( \sum_n C_n \frac{d}{dt} |n\rangle \right) \langle t | + |t\rangle \left( \sum_n \dot{C}_n^* \langle n | \right) + \left( \sum_n C_n^* \frac{d}{dt} \langle n | \right)$$  \hspace{1cm} (C)

$$(B) = (C)$$
Using Schrödinger Equation

\[ \left( \sum_n C_n \frac{d}{dt} |n\rangle \right) = \frac{1}{i\hbar} H_0 |t\rangle \]

Right multiply top eq. by \( \langle t | \).

\[ \left( \sum_n C_n^* \frac{d}{dt} \langle n | \right) = \frac{1}{-i\hbar} \langle t | H_0 \]

Left multiply bottom equation by \( |t\rangle \).

Gives

\[ \left( \sum_n C_n \frac{d}{dt} |n\rangle \right) \langle t | = \frac{1}{i\hbar} H_0 \langle t | \langle t | \]

Using these see that the 1\text{st} and 3\text{rd} terms in (B) cancel the 2\text{nd} and 4\text{th} terms in (C).

\[ |t\rangle \left( \sum_n C_n^* \frac{d}{dt} \langle n | \right) = \frac{1}{-i\hbar} \langle t | \langle t | H_0 \]

\[ \frac{1}{i\hbar} H_0 |t\rangle \langle t | + \frac{1}{i\hbar} H_f |t\rangle \langle t | + \frac{1}{-i\hbar} |t\rangle \langle t | H_0 + \frac{1}{-i\hbar} |t\rangle \langle t | H_f \]

(B)

\[ = \left( \sum_n \dot{C}_n |n\rangle \right) \langle t | + \left( \sum_n C_n \frac{d}{dt} |n\rangle \right) \langle t | + t \left( \sum_n \dot{C}_n^* \langle n | \right) + t \left( \sum_n C_n^* \frac{d}{dt} \langle n | \right) \]

(C)
After canceling terms, \((B) = (C)\) becomes

\[
\left( \sum_n \dot{C}_n |n\rangle \langle t| + t \left( \sum_n \dot{C}_n^* \langle n|\right) \right) = \frac{1}{i\hbar} \left[ H_I, \rho \right]
\]

Consider the \(ij\) matrix element of this expression.

The matrix elements of the left hand side are

\[
\sum_n \dot{C}_n \langle i|n\rangle \langle t|j \rangle + \langle i|t \rangle \sum_n \dot{C}_n^* \langle n|j \rangle
\]

\[
= \dot{C}_i C_j^* + C_i \dot{C}_j^*
\]

\[
= \dot{\rho}_{ij}
\]

\[
\therefore \quad \dot{\rho}(t) = -\frac{i}{\hbar} \left[ H_I(t), \rho(t) \right]
\]

In the basis set of the eigenvectors of \(H_0\),

\(H_0\) cancels out of equation of motion of density matrix.
Proof that $\langle t|A|t \rangle = \langle A \rangle = Tr(\rho(t)A)$

Expectation value

$\langle A \rangle = \langle t|A|t \rangle$

$\{|j\}\}$ complete orthonormal basis set.

$|t\rangle = \sum_j C_j(t)|j\rangle$

Matrix elements of $A$

$A_{ij} = \langle i|A|j \rangle$

$\langle t|A|t \rangle = \left( \sum_i C_i^* \langle i | \right) A \left( \sum_j C_j | j \rangle \right)$

$= \sum_{i,j} C_i^*(t)C_j(t) \langle i|A|j \rangle$
\[ \rho_{ji} = \langle j | \rho(t) | i \rangle \]

Note order

\[ = \langle j | t \rangle \langle t | i \rangle \]

\[ = C_i^*(t) C_j(t) \]

Then

\[ \langle t | A | t \rangle = \sum_{i,j} \langle j | \rho(t) | i \rangle \langle i | A | j \rangle \]

Matrix multiplication, Chapter 13 (13.18)

\[ c_{kj} = \sum_{i=1}^{N} b_{ki} a_{ij} \]

\[ \langle t | A | t \rangle \text{ like matrix multiplication but only diagonal elements – } j \text{ on both sides.} \]

\[ \text{Also, double sum. Sum over } j \text{ – sum diagonal elements.} \]

Therefore,

\[ \langle A \rangle = Tr \left( \rho(t) A \right) \]