Chapter 14

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.

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

$\Rightarrow$ $|t\rangle$ normalized

Density Operator

$$\underline{\rho}(t) = |t\rangle\langle t|$$

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:

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

Two state system:

$$\left|t\right\rangle = C_1(t)\left|1\right\rangle + C_2(t)\left|2\right\rangle \qquad \left\langle t\right| = C_1^*(t)\left\langle 1\right| + C_2^*(t)\left\langle 2\right|$$

Calculate matrix elements of 2×2 density matrix:

$$\rho_{11} = \left\langle 1 | t \right\rangle \left\langle t | 1 \right\rangle$$

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

$$\rho_{11} = C_1 C_1^*$$

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

$$\rho_{12} = \left\langle 1 | t \right\rangle \left\langle t | 2 \right\rangle$$

$$\rho_{12} = C_1 C_2^*$$

$$\rho_{21} = \left\langle 2 | t \right\rangle \left\langle t | 1 \right\rangle$$

$$\rho_{21} = C_2 C_1^*$$

$$\rho_{22} = \left\langle 2 | t \right\rangle \left\langle t | 2 \right\rangle$$

$$\rho_{22} = C_2 C_2^*$$

In general:

$$|t\rangle = \sum_i C_i(t)|i\rangle$$

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

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

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

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

***ij* density matrix element**

2×2 Density Matrix:

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

$C_1 C_1^* \Rightarrow$ **Probability of finding system in state** $|1\rangle$

$C_2 C_2^* \Rightarrow$ **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 $$\sum_n |C_n(t)|^2 = 1$$

$$Tr\,\underline{\underline{\rho}}(t) = 1$$

trace = 1 for any dimension

(trace – sum of diagonal matrix elements)

And

$$\rho_{ij} = \rho_{ji}^*$$

Time dependence of $\underline{\underline{\rho}}(t)$

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

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

product rule

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

$$i\hbar\frac{d|t\rangle}{dt} = \underline{H}|t\rangle \longrightarrow \frac{d|t\rangle}{dt} = \frac{1}{i\hbar}\underline{H}|t\rangle$$

$$-i\hbar\frac{d\langle t|}{dt} = \langle t|\underline{H} \longrightarrow \frac{d\langle t|}{dt} = \frac{1}{-i\hbar}\langle t|\underline{H}$$

Substituting:

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

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

density operator

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

Therefore:

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

The fundamental equation of the density matrix representation.

Density Matrix Equations of Motion

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

since $\rho_{ij} = C_i C_j^*$

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

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:

$$\dot{\rho}_{11} = -\dot{\rho}_{22} = -\frac{i}{\hbar}(H_{12}\rho_{21} - H_{21}\rho_{12})$$

for 2x2 because
$\rho_{11} + \rho_{22} = 1$ **(trace of ρ = 1)**

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

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

for any dimension

In many problems:

$$\underline{H} = \underline{H}_0 + \underline{H}_I(t)$$

time independent — time dependent

e.g., **Molecule in a radiation field:**

$\underline{H}_0 \Rightarrow$ molecular Hamiltonian

$\underline{H}_I(t) \Rightarrow$ radiation field interaction (I) with molecule

Natural to use basis set of $\underline{H}_0$

$$\underline{H}_0 |n\rangle = E_n |n\rangle$$

(orthonormal)
(time dependent phase factors)

Write $|t\rangle$ as:

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

Eigenkets of $\underline{H}_0$

For this situation:

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

time evolution of density matrix elements, $C_{ij}(t)$, depends only on $\underline{H}_I(t)$

$\Rightarrow$ 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 $\underline{H}_I$, only time dependence from time dependent phase factors from $\underline{H}_0$. No changes in magnitudes of coefficients C_{ij}.

Time Dependent Two State Problem Revisited:

Previously treated in Chapter 8 with Schrödinger Equation.

Basis set $\left\{ |1\rangle, |2\rangle \right\} \Rightarrow$ **degenerate eigenkets of** $\underline{H}_0$

No $\underline{H}_I$

$$\underline{H}_0 |1\rangle = E|1\rangle = \hbar\omega_0 |1\rangle$$

$$\underline{H}_0 |2\rangle = E|2\rangle = \hbar\omega_0 |2\rangle$$

Interaction $\underline{H}_I$

$$\underline{H}_I |1\rangle = \hbar\beta |2\rangle$$

$$\underline{H}_I |2\rangle = \hbar\beta |1\rangle$$

$\hbar\beta = \gamma$ **of Ch. 8**

The matrix $\underline{\underline{H}}_I$

$$\underline{\underline{H}}_I = \hbar \begin{bmatrix} 0 & \beta \\ \beta & 0 \end{bmatrix}$$

Because degenerate states, time dependent phase factors cancel in off-diagonal matrix elements – <u>special case.</u>

In general, the off-diagonal elements have time dependent phase factors.

Use $$\dot{\underline{\underline{\rho}}}(t) = -\frac{i}{\hbar}\left[\underline{\underline{H}}_I(t), \underline{\underline{\rho}}(t)\right]$$ $$\underline{\underline{H}}_I = \hbar\begin{bmatrix} 0 & \beta \\ \beta & 0 \end{bmatrix}$$

$$\dot{\underline{\underline{\rho}}} = -\frac{i}{\hbar}\hbar\left\{\begin{bmatrix} 0 & \beta \\ \beta & 0 \end{bmatrix}\begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} - \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix}\begin{bmatrix} 0 & \beta \\ \beta & 0 \end{bmatrix}\right\}$$

$$\begin{aligned} \dot{\rho}_{11} &= -i[(0\rho_{11} + \beta\rho_{21}) - (\rho_{11}0 + \rho_{12}\beta)] \\ &= -i\beta(\rho_{21} - \rho_{12}) = i\beta(\rho_{12} - \rho_{21}) \end{aligned}$$

Multiplying matrices and subtracting gives

$$\dot{\underline{\underline{\rho}}} = i\beta\begin{bmatrix} (\rho_{12} - \rho_{21}) & (\rho_{11} - \rho_{22}) \\ -(\rho_{11} - \rho_{22}) & -(\rho_{12} - \rho_{21}) \end{bmatrix}$$

Equations of motion of density matrix elements:

$$\left.\begin{aligned} \dot{\rho}_{11} &= i\beta(\rho_{12} - \rho_{21}) \\ \dot{\rho}_{22} &= -i\beta(\rho_{12} - \rho_{21}) \end{aligned}\right\} \text{ Probabilities}$$

$$\left.\begin{aligned} \dot{\rho}_{12} &= i\beta(\rho_{11} - \rho_{22}) \\ \dot{\rho}_{21} &= -i\beta(\rho_{11} - \rho_{22}) \end{aligned}\right\} \text{ Coherences}$$

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

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

Using 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 $t = 0$.

$$d\cos^2(\beta t)/dt = -2\beta\cos(\beta t)\sin(\beta t)$$

$$d^2\cos^2(\beta t)/dt^2 = 2\beta^2(\sin^2(\beta t) - \cos^2(\beta t))$$

but $\sin^2(\beta t) = 1 - \cos^2(\beta t)$

then $d^2\cos^2(\beta t)/dt^2 = 2\beta^2(1 - 2\cos^2(\beta t))$

$$= 2\beta^2 - 4\beta^2\cos^2(\beta t)$$

$$\rho_{11} = \cos^2(\beta t)$$

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

$\beta = \gamma/\hbar$

From Ch. 8

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:

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

$$\rho_{12} = i\beta\int\left(\cos^2 \beta t - \sin^2 \beta t\right)dt$$

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

$$\int \cos^2 x dx = (1/2)x + (1/4)\sin 2x$$

$$\int \sin^2 x dx = (1/2)x - (1/4)\sin 2x$$

Since $\rho_{ij} = \rho_{ji}^*$

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

Density matrix elements have no time dependent phase factors.

$$|t\rangle = \sum_i C_i(t)|i\rangle$$

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

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

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

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

$$= C_i(t)C_j^*(t)$$

time dependent phase factor in ket, but its complex conjugate is in bra. Product is 1. Kets and bras normalized, closed bracket gives 1.

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

***ij* density matrix element**

Time dependent coefficient, but no phase factors.

Can be time dependent phase factors in density matrix equation of motion.

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

For two levels, but the same in any dimension.

$$\underline{\underline{H}} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \qquad \left|1\right\rangle = \left|1_s\right\rangle e^{-iE_1 t/\hbar} \qquad \left|2\right\rangle = \left|2_s\right\rangle e^{-iE_2 t/\hbar}$$

s – spatial

$$H_{11} = \left\langle 1\right|\underline{\underline{H}}\left|1\right\rangle = \left\langle 1_s\right|\underline{\underline{H}}\left|1_s\right\rangle e^{iE_1 t/\hbar} e^{-iE_1 t/\hbar} = \left\langle 1_s\right|\underline{\underline{H}}\left|1_s\right\rangle$$

no time dependent phase factor

$$H_{12} = \left\langle 1\right|\underline{\underline{H}}\left|2\right\rangle = \left\langle 1_s\right|\underline{\underline{H}}\left|2_s\right\rangle e^{iE_1 t/\hbar} e^{-iE_2 t/\hbar} = \left\langle 1_s\right|\underline{\underline{H}}\left|2_s\right\rangle e^{i(E_1 - E_2)t/\hbar}$$

time dependent phase factor if $E_1 \neq E_2$.

Therefore, in general, the commutator matrix,

$$\left[\underline{\underline{H}}(t), \underline{\underline{\rho}}(t)\right]$$

when you multiply it out,

will have time dependent phase factors if $E_1 \neq E_2$.

Expectation Value of an Operator

$$\langle \underline{A} \rangle = \langle t | \underline{A} | t \rangle$$

Complete orthonormal basis set $\{ | j \rangle \}$

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

Matrix elements of $\underline{A}$

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

Derivation in book and see lecture slides

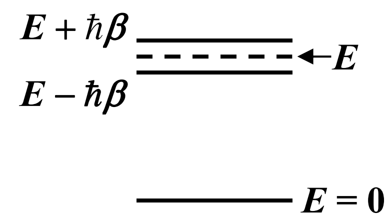
$$\langle \underline{A} \rangle = Tr\left(\underline{\underline{\rho}}(t) \underline{\underline{A}} \right)$$

Expectation value of $\underline{A}$ is trace of the product of density matrix with the operator matrix $\underline{\underline{A}}$.

Important: $\underline{\underline{\rho}}(t)$ carries time dependence of coefficients.

Time dependent phase factors may occur in off-diagonal matrix elements of $\underline{\underline{A}}$.

Example: Average *E* for two state problem



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

$$\underline{\underline{H}} = \underline{\underline{H}}_0 + \underline{\underline{H}}_I = \begin{bmatrix} E & \hbar\beta \\ \hbar\beta & E \end{bmatrix}$$

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

$$Tr\, \underline{\underline{\rho}}\, \underline{\underline{H}} = Tr \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} \begin{bmatrix} E & \hbar\beta \\ \hbar\beta & E \end{bmatrix}$$

Only need to calculate the diagonal matrix elements.

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

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

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

$$\langle \underline{H} \rangle = E(\cos^2 \beta t + \sin^2 \beta t) + \frac{i\hbar\beta}{2}(\sin 2\beta t - \sin 2\beta t)$$

$$= E$$

Proof that only need consider

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

when working in basis set of eigenvectors of $\underline{H}_0$.

Working with basis set of eigenkets of time independent piece of Hamiltonian, $\underline{H}_0$, the time dependence of the density matrix depends only on the time dependent piece of the Hamiltonian, $\underline{H}_I$.

Total Hamiltonian

$$\underline{H} = \underline{H}_0 + \underline{H}_I(t)$$

$\underline{H}_0$ **time independent**

$$\underline{H}_0 \left| n \right\rangle = E_n \left| n \right\rangle$$

Use $\{\left| n \right\rangle\}$ as basis set.

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

Time derivative of density operator (using chain rule)

$$\left(\frac{d}{dt}|t\rangle\right)\langle t| + |t\rangle\left(\frac{d}{dt}\langle t|\right) \qquad \textbf{(A)}$$

Use Schrödinger Equation and its complex conjugate

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

$$= \frac{1}{i\hbar}\underline{H}_0|t\rangle\langle t| + \frac{1}{i\hbar}\underline{H}_I|t\rangle\langle t| + \frac{1}{-i\hbar}|t\rangle\langle t|\underline{H}_0 + \frac{1}{-i\hbar}|t\rangle\langle t|\underline{H}_I \qquad \textbf{(B)}$$

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

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

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

(B) = (C)

Using Schrödinger Equation

$$\left(\sum_n C_n \frac{d}{dt}|n\rangle\right) = \frac{1}{i\hbar}\underline{H}_0|t\rangle$$

Right multiply top eq. by $\langle t|$.

$$\left(\sum_n C_n^* \frac{d}{dt}\langle n|\right) = \frac{1}{-i\hbar}\langle t|\underline{H}_0$$

Left multiply bottom equation by $|t\rangle$.

Gives

$$\left(\sum_n C_n \frac{d}{dt}|n\rangle\right)\langle t| = \frac{1}{i\hbar}\underline{H}_0|t\rangle\langle t|$$

$$|t\rangle\left(\sum_n C_n^* \frac{d}{dt}\langle n|\right) = \frac{1}{-i\hbar}|t\rangle\langle t|\underline{H}_0$$

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

$$\frac{1}{i\hbar}\underline{H}_0|t\rangle\langle t| + \frac{1}{i\hbar}\underline{H}_I|t\rangle\langle t| + \frac{1}{-i\hbar}|t\rangle\langle t|\underline{H}_0 + \frac{1}{-i\hbar}|t\rangle\langle t|\underline{H}_I \qquad \text{(B)}$$

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

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

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

Consider the *ij* matrix element of this expression.

The matrix elements of the left hand side are

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

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

$$= \dot{\rho}_{ij}$$

$$\therefore \qquad \dot{\underline{\underline{\rho}}}(t) = -\frac{i}{\hbar}\left[\underline{\underline{H}}_I(t), \underline{\underline{\rho}}(t)\right]$$

In the basis set of the eigenvectors of $\underline{H}_0$,
$\underline{H}_0$ cancels out of equation of motion of density matrix.

Proof that $\langle t|\underline{A}|t\rangle = \langle \underline{A}\rangle = Tr\left(\underline{\underline{\rho}}(t)\,\underline{\underline{A}}\right)$

Expectation value

$$\langle \underline{A}\rangle = \langle t|\underline{A}|t\rangle$$

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

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

Matrix elements of $\underline{A}$

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

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

$$= \sum_{i,j} C_i^*(t)C_j(t)\langle i|\underline{A}|j\rangle$$

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

note order

$$= \langle j | t \rangle \langle t | i \rangle$$

$$= C_i^*(t) C_j(t)$$

Then

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

Matrix multiplication, Chapter 13 (13.18)

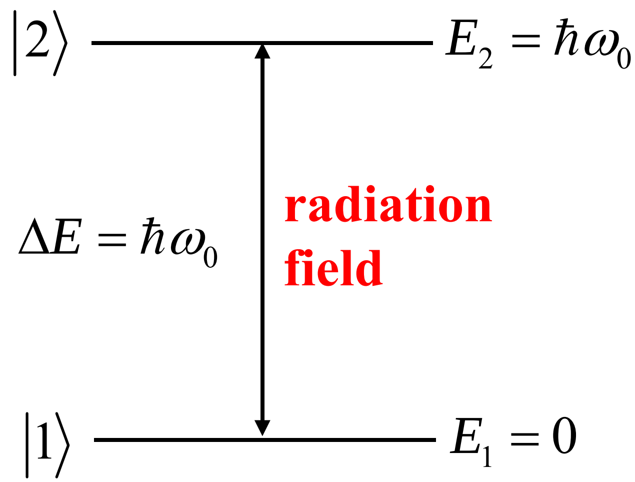
$$c_{kj} = \sum_{i=1}^{N} b_{ki} a_{ij}$$

$\langle t | \underline{A} | t \rangle$ like matrix multiplication but only diagonal elements –
j on both sides.
Also, double sum. Sum over *j* – sum diagonal elements.

Therefore, $\langle \underline{A} \rangle = Tr\left(\underline{\underline{\rho}}(t) \underline{\underline{A}} \right)$

Coherent Coupling by of Energy Levels by Radiation Field

Two state problem



2 electronic states $S_0 \longleftrightarrow S_1$

2 vibrational states $V_0 \longleftrightarrow V_1$

NMR – 2 spin states, magnetic transition dipole

In general, if radiation field frequency $\hbar\omega$ is near ΔE, and other transitions are far off resonance, can treat as a 2 state system.

Molecular Eigenstates as Basis

$$\underline{H}_0 \left|1\right\rangle = E_1 \left|1\right\rangle$$

$$\underline{H}_0 \left|2\right\rangle = E_2 \left|2\right\rangle$$

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

$$\underline{H}_I(t) = \hbar e\, \underline{x}_{12}\, E_0 \cos(\omega t)$$

$e\underline{x}_{12} \Rightarrow$ **transition dipole operator**

x **polarized light**

$E_0 \Rightarrow$ **amplitude**

$\underline{H}_I$ couples states

$$\langle 1|\underline{H}_I(t)|2\rangle = \hbar E_0\cos(\omega t)\langle 1|e\,\underline{x}_{12}|2\rangle$$

take out time dependent phase factors

$$= \hbar E_0\cos(\omega t)e^{iE_1 t/\hbar}\langle 1'|e\,\underline{x}_{12}|2'\rangle e^{-iE_2 t/\hbar}$$

$$E_1 = 0 \quad E_2 = \hbar\omega_0$$

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

μ is value of transition dipole bracket,

Note – time independent kets. No phase factors. Have taken phase factors out.

$$\langle 2|\underline{H}_I(t)|1\rangle = \hbar\,\mu^*\,E_0\cos(\omega t)e^{i\omega_0 t}$$

Take μ real (doesn't change results)

Define Rabi Frequency, ω_1

$$\omega_1 = \mu E_0$$

Then

$$\langle 1|\underline{H}_I(t)|2\rangle = \hbar\,\omega_1\cos(\omega t)e^{-i\omega_0 t}$$

$$\langle 2|\underline{H}_I(t)|1\rangle = \hbar\,\omega_1\cos(\omega t)e^{i\omega_0 t}$$

$\underline{\underline{H}}_I(t)$ matrix:

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

General state of system $\quad |t\rangle = C_1(t)|1\rangle + C_2(t)|2\rangle$

Use $\quad \dot{\underline{\underline{\rho}}}(t) = -\frac{i}{\hbar}\left[\underline{\underline{H}}_I(t), \underline{\underline{\rho}}(t)\right]$

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

$$\begin{bmatrix} \dot{\rho}_{11} & \dot{\rho}_{12} \\ \dot{\rho}_{21} & \dot{\rho}_{22} \end{bmatrix} =$$

$$\begin{bmatrix} i\omega_1\cos(\omega t)\left(e^{i\omega_0 t}\rho_{12} - e^{-i\omega_0 t}\rho_{21}\right) & i\omega_1\cos(\omega t)e^{-i\omega_0 t}(\rho_{11} - \rho_{22}) \\ -i\omega_1\cos(\omega t)e^{i\omega_0 t}(\rho_{11} - \rho_{22}) & -i\omega_1\cos(\omega t)\left(e^{i\omega_0 t}\rho_{12} - e^{-i\omega_0 t}\rho_{21}\right) \end{bmatrix}$$

Blue diagonal
Red off-diagonal

Equations of Motion of Density Matrix Elements

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

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

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

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

$$\rho_{11} + \rho_{22} = 1 \qquad \Rightarrow \dot{\rho}_{11} = -\dot{\rho}_{22}$$

$$\rho_{12} = \rho_{21}^{*} \qquad \Rightarrow \dot{\rho}_{12} = \dot{\rho}_{21}^{*}$$

Treatment exact to this point (expect for dipole approx. in μ).

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

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

But $\omega_0 \sim \omega$

Terms with $(\omega_0 + \omega) \sim 2\omega_0$ off resonance → Don't cause transitions

Looks like high frequency Stark Effect
→ 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.**

μ_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.

Equations reduce to

$$\dot{\rho}_{11} = i\frac{\omega_1}{2}(\rho_{12} - \rho_{21})$$

$$\dot{\rho}_{22} = -i\frac{\omega_1}{2}(\rho_{12} - \rho_{21})$$

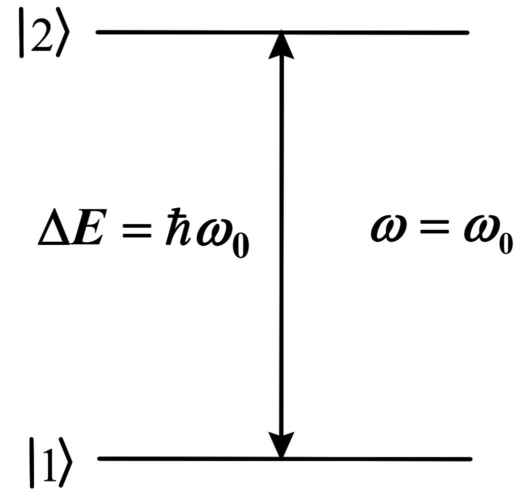
$$\dot{\rho}_{12} = i\frac{\omega_1}{2}(\rho_{11} - \rho_{22})$$

$$\dot{\rho}_{21} = -i\frac{\omega_1}{2}(\rho_{11} - \rho_{22})$$

These are <u>IDENTICAL</u> 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, $|1\rangle$ $\quad \rho_{11} = 1; \quad \rho_{22} = 0, \quad \rho_{12} = 0, \quad \rho_{21} = 0$ **at $t = 0$.**

Then

$$\rho_{11} = \cos^2\left(\frac{\omega_1 t}{2}\right) \qquad \rho_{12} = \frac{i}{2}\sin(\omega_1 t)$$

$$\rho_{22} = \sin^2\left(\frac{\omega_1 t}{2}\right) \qquad \rho_{21} = -\frac{i}{2}\sin(\omega_1 t)$$

populations **coherences**

$$\rho_{11} = \cos^2\left(\frac{\omega_1 t}{2}\right) \qquad \rho_{22} = \sin^2\left(\frac{\omega_1 t}{2}\right) \qquad \textbf{populations}$$

Recall $\omega_1 = \mu E_0 \Rightarrow$ **Rabi Frequency**

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

This is called a π pulse → inversion, all population in excited state.

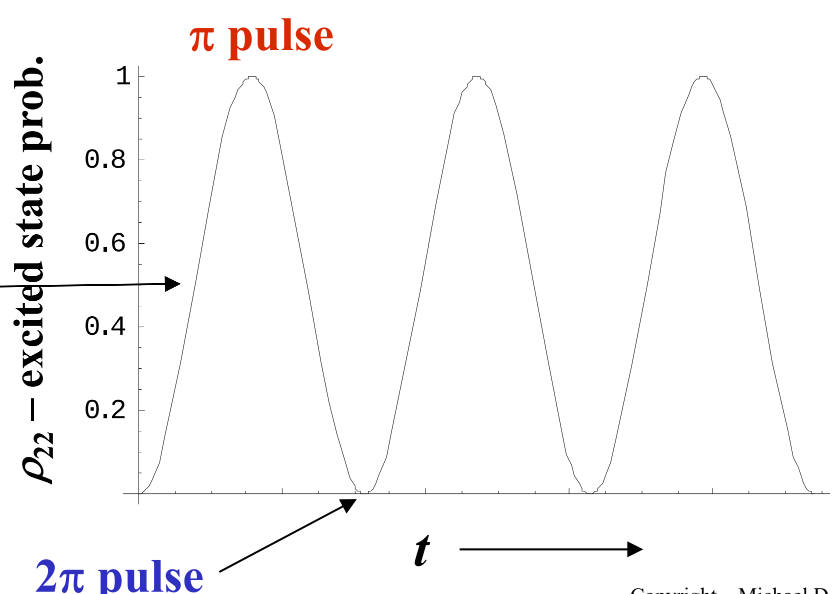
$$\omega_1 t = \frac{\pi}{2} \quad \Rightarrow \quad \rho_{11} = 0.5, \quad \rho_{22} = 0.5$$

This is called a π/2 pulse → Maximizes off diagonal elements ρ_{12}, ρ_{21}

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

⇒Transient Nutation

⇒Coherent Coupling



Off Resonance Coherent Coupling

$\Delta\omega = \omega_0 - \omega$ **Amount radiation field frequency is off resonance from transition frequency.**

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

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

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

Oscillations Faster → ω_e

Max excited state probability: $\rho_{22}^{\max} = \dfrac{\omega_1^2}{\omega_e^2}$

(Like non-degenerate time dependent 2-state problem)

Near Resonance Case - Important

$$\omega_1 >> \Delta\omega \qquad\qquad \omega_e = \left(\Delta\omega^2 + \omega_1^2\right)^{1/2}$$

Then $\quad \omega_e \cong \omega_1$

ρ_{11}, ρ_{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 ρ_{12}, ρ_{21}

$$\omega_1 t = \pi/2$$

But $\quad \Delta\omega\, t << \pi/2 \cong 0 \quad$ because $\quad \omega_1 >> \Delta\omega$

Then, ρ_{12}, ρ_{21} virtually identical to on resonance case and ρ_{11}, ρ_{22} same as on resonance case.

This is the basis of Fourier Transform NMR. Although spins have different chemical shifts, make ω_1 big enough, all look like on resonance.

Free Precession

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

On or near resonance immediately after the pulse ($t = 0$)

$$\rho_{11} = \cos^2(\theta/2) \qquad \rho_{12} = \frac{i}{2}\sin\theta$$

$$\rho_{22} = \sin^2(\theta/2) \qquad \rho_{21} = -\frac{i}{2}\sin\theta$$

After pulse – no radiation field.
Hamiltonian is $\underline{\underline{H}}_0$

$$\dot{\underline{\underline{\rho}}} = -\frac{i}{\hbar}\left[\underline{\underline{H}}_0, \underline{\underline{\rho}}\right]$$

$$\underline{\underline{H}}_0 = \hbar\begin{bmatrix} 0 & 0 \\ 0 & \omega_0 \end{bmatrix}$$

$$\dot{\underline{\underline{\rho}}} = -\frac{i}{\hbar}\left[\underline{\underline{H}}_0, \underline{\underline{\rho}}\right] \qquad \underline{\underline{H}}_0 = \hbar\begin{bmatrix} 0 & 0 \\ 0 & \omega_0 \end{bmatrix}$$

$$\dot{\underline{\underline{\rho}}} = -\frac{i}{\hbar}\left\{\hbar\begin{bmatrix} 0 & 0 \\ 0 & \omega_0 \end{bmatrix}\begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} - \hbar\begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix}\begin{bmatrix} 0 & 0 \\ 0 & \omega_0 \end{bmatrix}\right\}$$

$$\dot{\rho}_{11} = 0$$
$$\dot{\rho}_{22} = 0$$
$$\dot{\rho}_{12} = i\omega_0\rho_{12}$$
$$\dot{\rho}_{21} = -i\omega_0\rho_{21}$$

$t = 0$ is at end of pulse

Solutions

$$\rho_{11} = \text{a constant} = \rho_{11}(0) \qquad \rho_{12} = \rho_{12}(0)e^{i\omega_0 t}$$

$$\rho_{22} = \text{a constant} = \rho_{22}(0) \qquad \rho_{21} = \rho_{21}(0)e^{-i\omega_0 t}$$

Populations don't change.

Off-diagonal density matrix elements → Only time dependent phase factor

Off-diagonal density matrix elements after pulse ends ($t = 0$).

Consider expectation value of transition dipole $\langle \underline{\mu} \rangle$.   Recall $\underline{\mu} = e\,\underline{x}_{12}$

$$\langle \underline{\mu} \rangle = Tr\,\underline{\underline{\rho}}\,\underline{\underline{\mu}}$$

$$\underline{\underline{\mu}} = \begin{array}{c c} & \begin{array}{cc} |1\rangle & |2\rangle \end{array} \\ \begin{array}{c} \langle 1| \\ \langle 2| \end{array} & \begin{bmatrix} 0 & \mu \\ \mu & 0 \end{bmatrix} \end{array}$$

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

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

$t = 0$, end of pulse

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

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

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

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

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

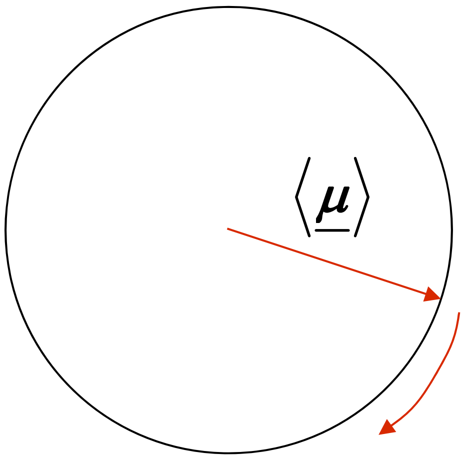
$$\langle \underline{\mu} \rangle = \mu \left[\frac{i}{2}\sin\theta[\cos(\omega_0 t) + i\sin(\omega_0 t)] - \frac{i}{2}\sin\theta[\cos(\omega_0 t) - i\sin(\omega_0 t)] \right]$$

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

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

Oscillating electric dipole (magnetic dipole - NMR) at frequency ω_0, → Oscillating E-field (magnet field)

Free precession.



Rot. wave approx.
Tip of vector goes in circle.

$I \propto |E|^2$ **for ensemble, coherent emission**

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 → probability of having k_{th} sub-ensemble with density matrix, ρ_k.

$$0 \le P_1, P_2, \cdots P_k, \cdots \le 1$$

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

Density matrix for mixed systems

$$\underline{\underline{\rho}}(t) = \sum_k P_k \underline{\underline{\rho}}_k(t)$$

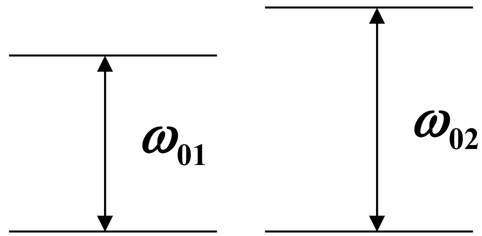
or integral if continuous distribution

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 ω near ω_{01} & ω_{02}.

Difference of both ω_{01} & ω_{02} from ω small compared to ω_1, that is, both near resonance.

Equal probabilities → P_1=0.5 and P_2=0.5

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

Calculate

$$\langle \underline{\mu} \rangle = Tr\, \underline{\underline{\rho}}(t)\, \underline{\underline{\mu}}$$

$$= \sum_k P_k\, Tr\, \underline{\underline{\rho}}_k\, \underline{\underline{\mu}}$$

Pure density matrix result for flip angle θ:

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

For 2 transitions - P_1=0.5 and P_2=0.5

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

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

from trig. identities

Call: center frequency ➔ ω_0, shift from the center ➔ δ

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

with $\delta << \omega_0$

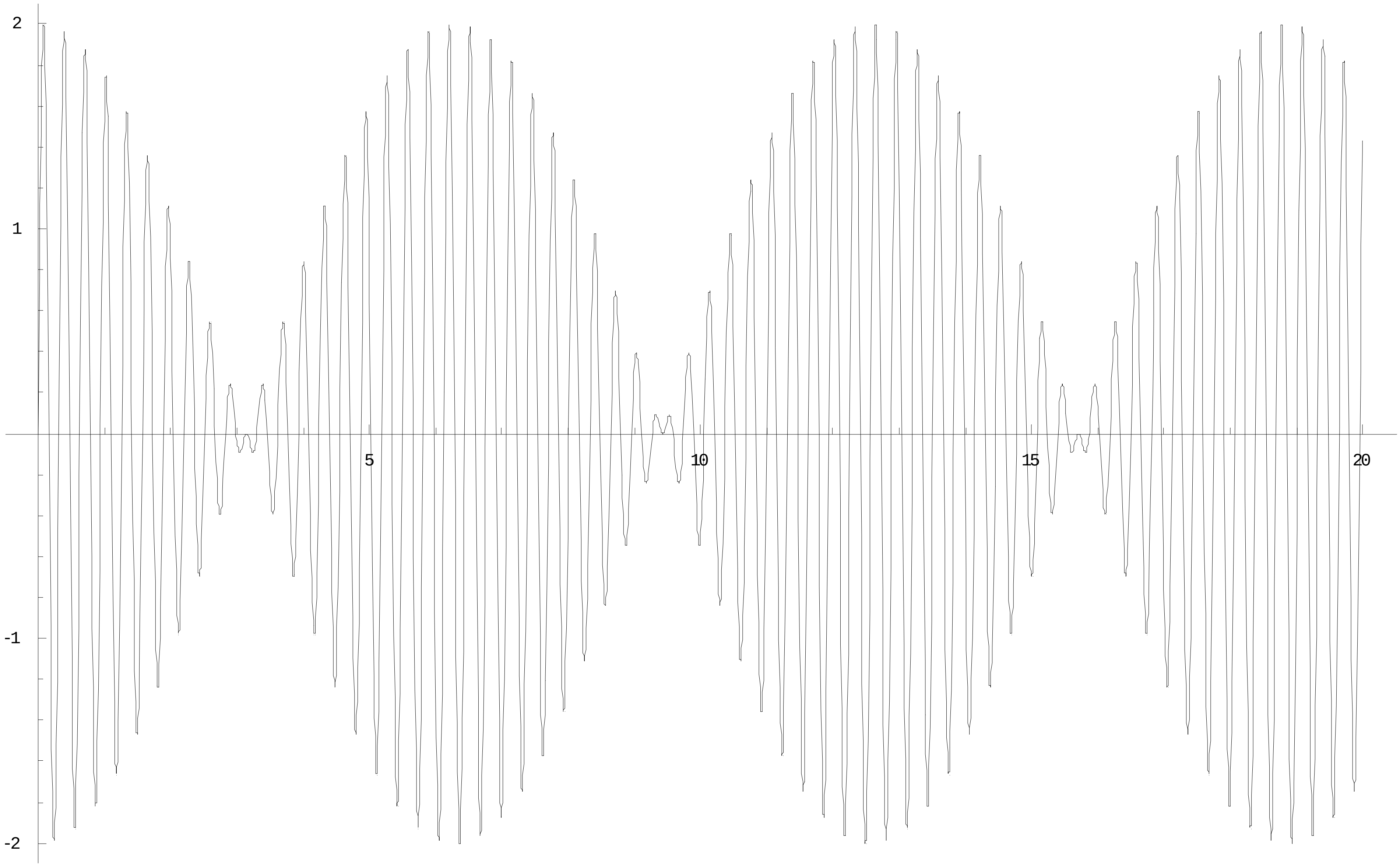
Therefore,

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

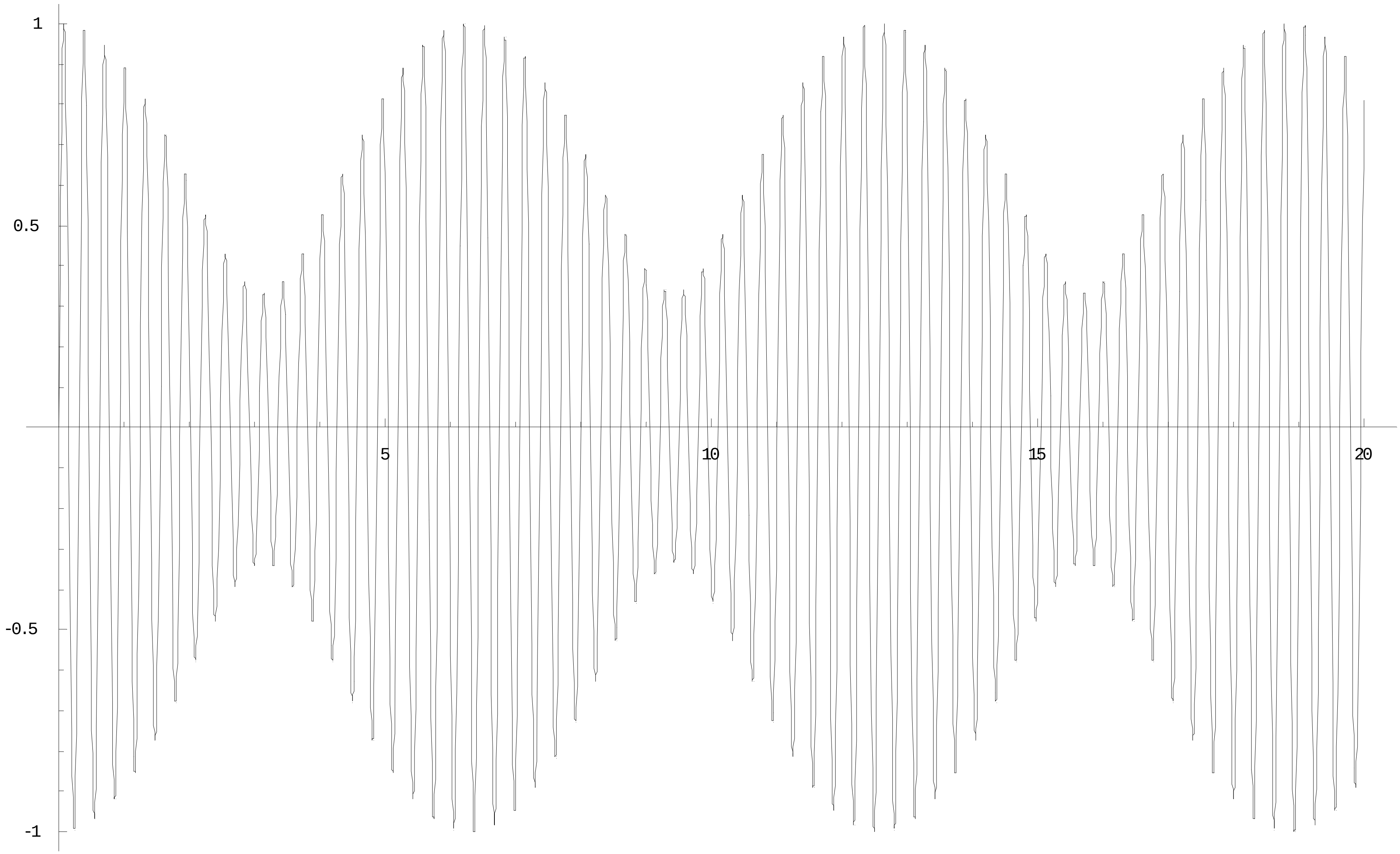
high freq. oscillation **low freq. oscillation, beat**

Beat gives transition frequencies – FT-NMR

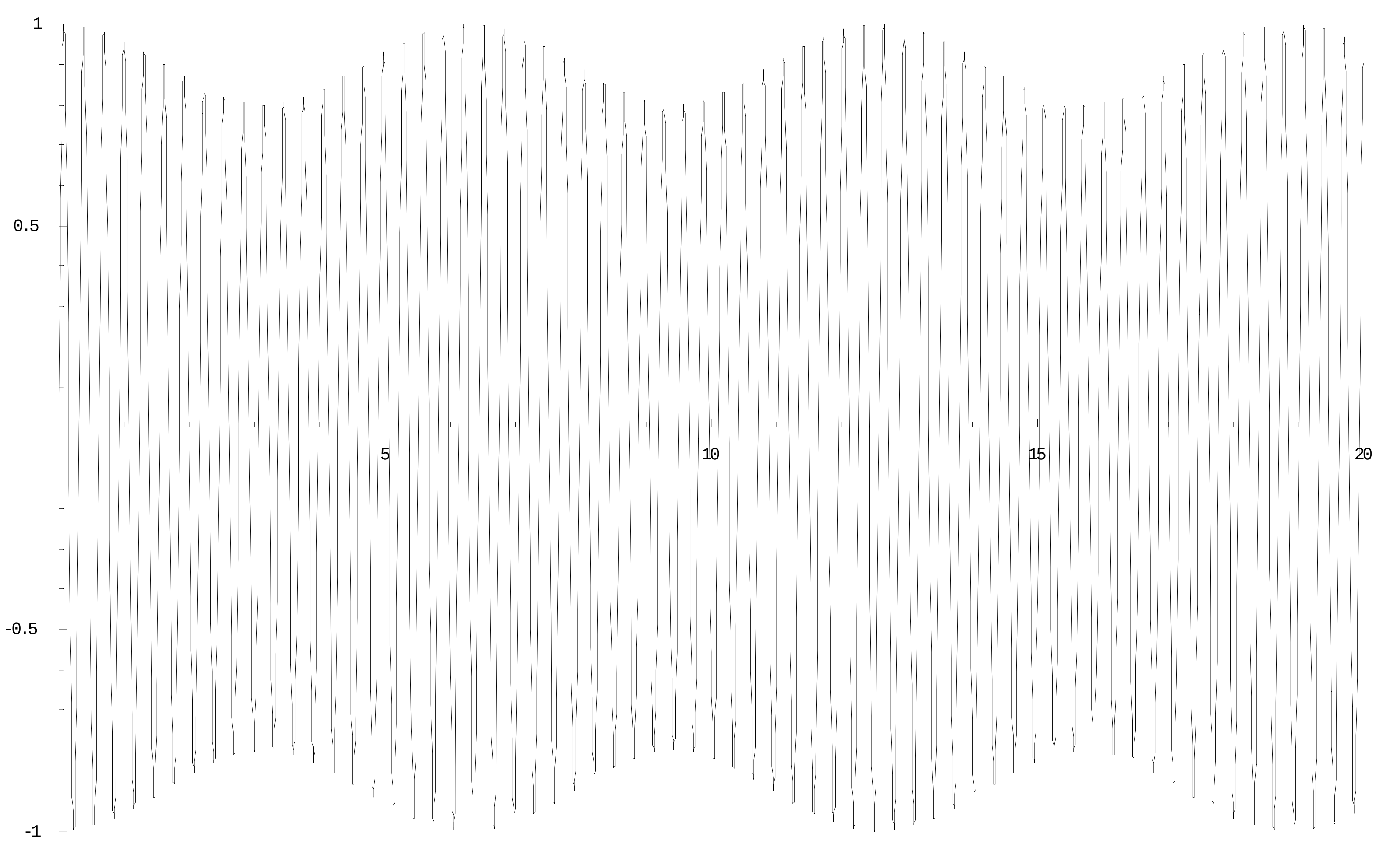
Equal amplitudes – 100% modulation, $\omega_{01} = 20.5$; $\omega_{01} = 19.5$



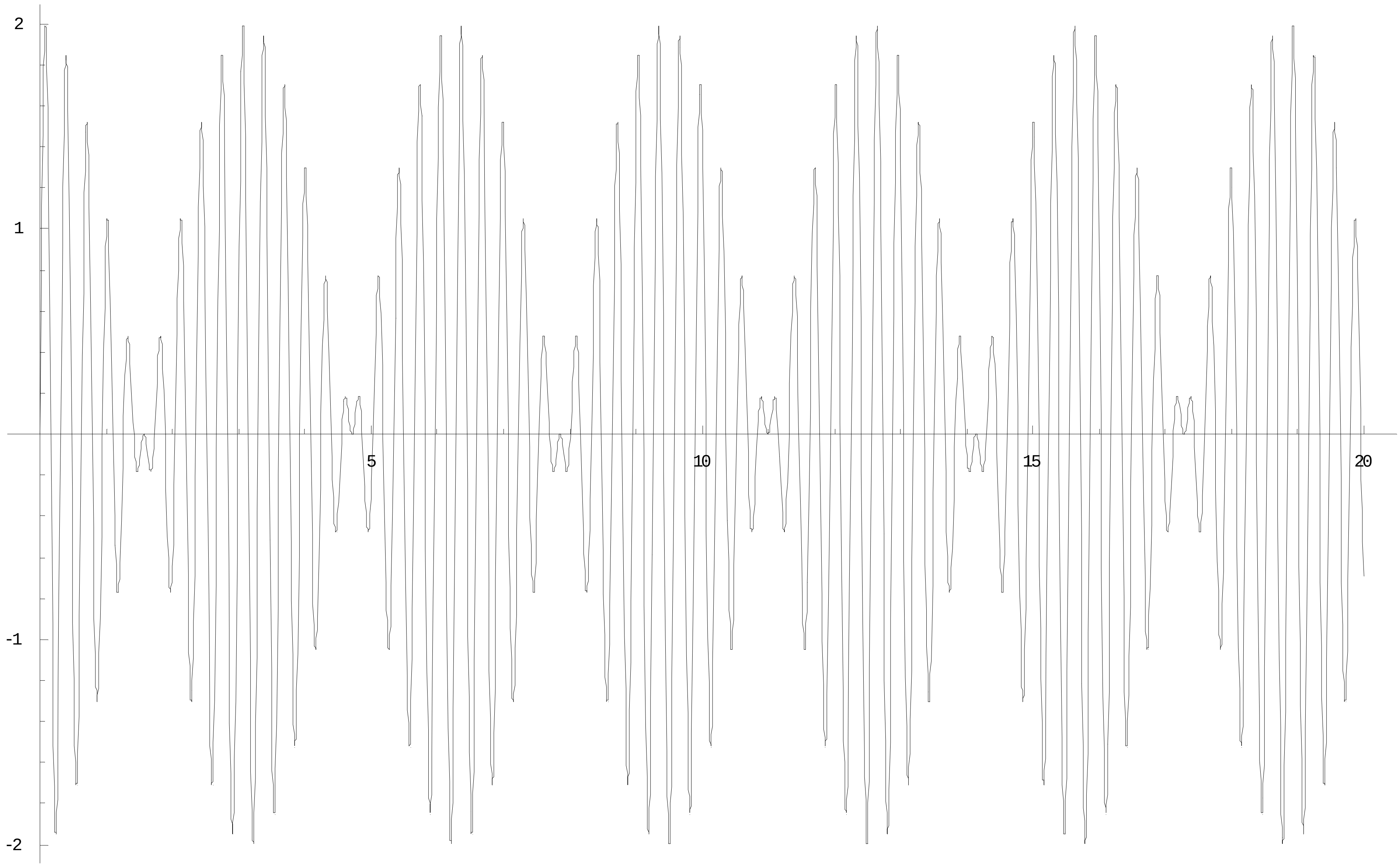
Amplitudes 2:1 – not 100% modulation , ω_{01} = 20.5; ω_{01} = 19.5



Amplitudes 9:1 – not 100% modulation , $\omega_{01} = 20.5$; $\omega_{01} = 19.5$



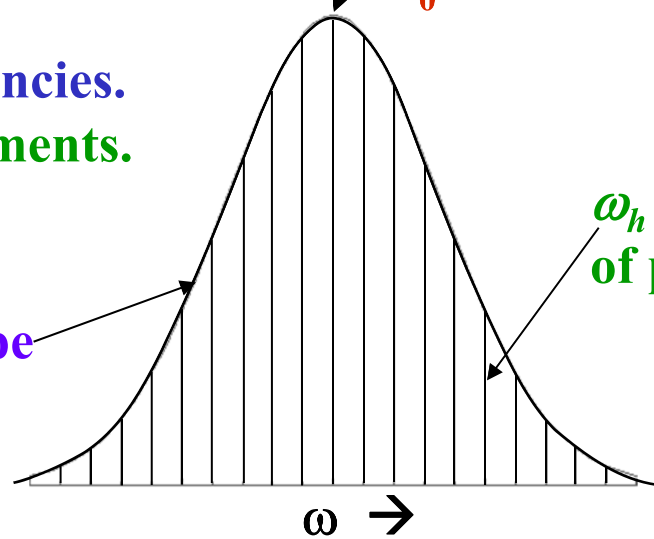
Equal amplitudes – 100% modulation, $\omega_{01} = 21; \omega_{01} = 19$



Free Induction Decay

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

center freq ω_0



Gaussian envelope

$\omega_h \rightarrow$ frequency of particular molecule

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

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

normalization constant

standard deviation

Then

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

probability, P_h

pure density matrix

Radiation field at $\omega = \omega_0$ line center

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

Apply pulse with flip angle θ

Calculate $\langle \underline{\mu} \rangle$, transition dipole expectation value.

Following pulse, each sub-ensemble will undergo free precession at ω_h

$$\langle \underline{\mu} \rangle = Tr\, \underline{\underline{\rho}}(t)\underline{\underline{\mu}}$$

$$= \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} e^{-(\omega_h - \omega_0)^2/2\sigma^2}\, Tr \quad \underline{\underline{\rho}}(\omega_h, t)\underline{\underline{\mu}}\, d\omega_h$$

Using result for single frequency ω_h and flip angle θ

$$\langle \underline{\mu} \rangle = -\frac{\mu \sin\theta}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} e^{-(\omega_h - \omega_0)^2/2\sigma^2} \sin(\omega_h t)\, d\omega_h$$

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: $\sin(x+y) = \sin(x)\cos(y) + \cos(x)\sin(y)$

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

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

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

Oscillation at ω_0; decaying amplitude →

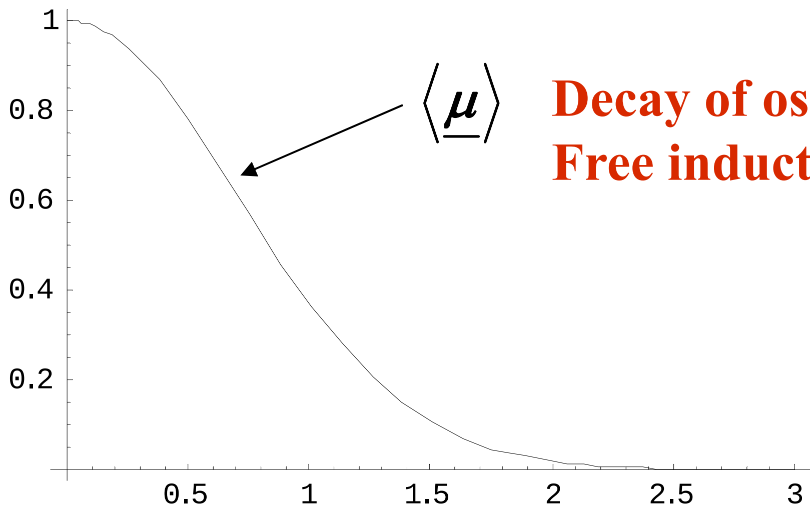
Gaussian decay with standard deviation in time → $1/\sigma$ (Free Induction Decay)

Phase relationships lost → Coherent Emission Decays

Off-diagonal density matrix elements – coherence; diagonal - magnitude

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

flip angle light frequency free induction decay



Decay of oscillating macroscopic dipole.
Free induction decay.

$$\bar{E} \propto \langle \underline{\mu} \rangle$$

$$I \propto |E|^2 \propto \langle \underline{\mu} \rangle^2$$

Coherent emission of light.