Density Matrices II

Read CTDL, pages 643-652.

Last time: $\psi, |\ \rangle, \boldsymbol{\rho} = |\ \rangle\langle\ |$
coherent superposition vs. statistical mixture
populations along diagonal, coherences off diagonal
$\langle \mathbf{A} \rangle = \mathrm{Trace}(\boldsymbol{\rho}\mathbf{A}) = \mathrm{Trace}(\mathbf{A}\boldsymbol{\rho})$

Today: Quantum Beats
prepared state $\boldsymbol{\rho}$
detection as projection operator $\mathbf{D}$

What part of $\mathbf{D}$ samples a specific off-diagonal element of $\boldsymbol{\rho}$?
Optimize magnitude of beats

[partial traces]

system consisting of 2 parts — e.g. coupled oscillators
motion in state-space vs. motion in coordinate space.

The material on pages 20–2, –3, –5, and –7 is an exact duplication of pages 19–5, –6, –7 and –8.

Example: Quantum Beats

Preparation, evolution, detection

magically prepare some coherent superposition state $\Psi(t)$

$$\Psi(t) = N\sum_n \underbrace{a_n \psi_n}_{} e^{-iE_n t/\hbar}$$

Several eigenstates of H. Evolve freely without any time-dependent intervention

$$\boxed{N = \left[\sum_n |a_n|^2\right]^{-1/2}}$$

normalization

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

Case (1): Detection: only one of the eigenstates, ψ_1, in the superposition is capable of giving fluorescence that our detector can "see".

Thus $$\mathbf{D} = |\psi_1\rangle\langle\psi_1| = \begin{pmatrix} 1 & 0 & \cdots \\ 0 & 0 & 0 \\ \vdots & 0 & 0 \end{pmatrix}$$

a projection operator (designed to project out only $|\psi_1\rangle$ part of state vector or ρ_{11} part of $\boldsymbol{\rho}$.

$$\boldsymbol{\rho} = N^2 \begin{pmatrix} |a_1|^2 & a_1 a_2^* e^{-(E_1-E_2)t/\hbar} & & \cdots \\ & |a_2|^2 & & \\ & & |a_3|^2 & \\ & & & \ddots \end{pmatrix}$$

$$\rho_{12} = \langle 1|\Psi\rangle\langle\Psi|2\rangle$$

$$\rho_{12} = N^2 a_1 e^{-E_1 t/\hbar} a_2^* e^{+iE_2 t/\hbar}$$

D picks out only 1st row of $\boldsymbol{\rho}$.

$$\langle \mathbf{D}\rangle_t = \text{Trace}(\mathbf{D}\boldsymbol{\rho}) = N^2\,\text{Trace}\begin{pmatrix} |a_1|^2 & a_1 a_2^* e^{-i\omega_{12}t} & \text{stuff} & \cdots \\ 0 & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots \end{pmatrix}$$

$$= N^2 |a_1|^2$$

no time dependence!

case (2): a particular linear combination of eigenstates is bright: the initial state $2^{-1/2}(\psi_1 + \psi_2)$ has $\langle \mathbf{D} \rangle = 1$.

$$\mathbf{D} = \frac{1}{2}\left(|\psi_1\rangle + |\psi_2\rangle\right)\left(\langle\psi_1| + \langle\psi_2|\right)$$

a projection operator. How much of the original state is present in the evolved state?

$$= \frac{1}{2}\left[|\psi_1\rangle\langle\psi_1| + |\psi_2\rangle\langle\psi_2| + |\psi_1\rangle\langle\psi_2| + |\psi_2\rangle\langle\psi_1|\right]$$

$$= \frac{1}{2}\left[\begin{pmatrix} 1 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \vdots & 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 & \cdots \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \vdots & 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 1 & 0 & \cdots \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \vdots & 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 & \cdots \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \vdots & 0 & 0 & 0 \end{pmatrix}\right]$$

$$= \frac{1}{2}\begin{pmatrix} 1 & 1 & 0 & \cdots \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \vdots & 0 & 0 & 0 \end{pmatrix}$$

$$\left[\text{if the bright state had been } 2^{-1/2}(\psi_1 - \psi_2), \text{ then } \mathbf{D} = \frac{1}{2}\begin{pmatrix} 1 & -1 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}\right]$$

$$\text{Trace}(\mathbf{D}\boldsymbol{\rho}) = \frac{1}{2}\text{N}^2 \ \ \text{Trace}\begin{pmatrix} & \\ & \end{pmatrix}$$

why do we need to look at only the 1,2 block of $\boldsymbol{\rho}$?

$$(\mathbf{D}\boldsymbol{\rho})_{11} = \frac{1}{2}\text{N}^2\left[|a_1|^2 + a_1^* a_2 e^{+i(E_1 - E_2)t/\hbar}\right]$$

$$(\mathbf{D}\boldsymbol{\rho})_{22} = \frac{1}{2}\text{N}^2\left[|a_2|^2 + a_1 a_2^* e^{-i(E_1 - E_2)t/\hbar}\right]$$

$$\text{Trace}(\mathbf{D}\boldsymbol{\rho}) = \frac{1}{2}\text{N}^2\left[|a_1|^2 + |a_2|^2 + 2\,\text{Re}\left[a_1^* a_2 e^{+i\omega_{12}t}\right]\right]$$

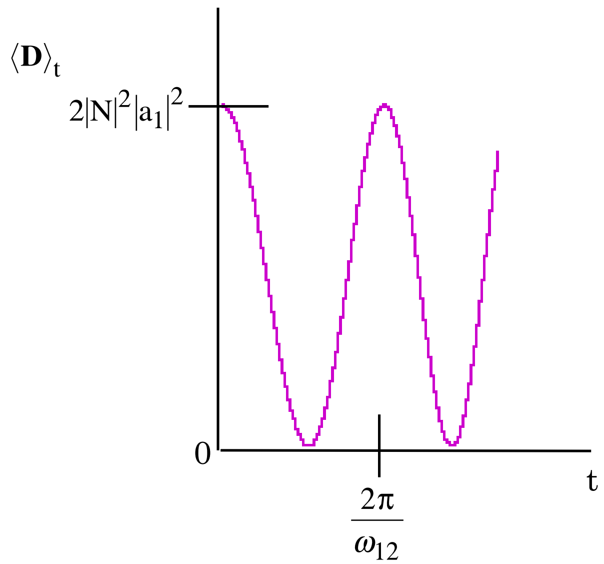
beat note at ω_{12}

[if the bright state had been $2^{-1/2}(\psi_1 - \psi_2)$, then $\text{Tr}(\mathbf{D}\boldsymbol{\rho})$ would be the same except for $-2\text{Re}[\quad]$]

If $|a_1|^2 = |a_2|^2$ (and a_1, a_2 real), $\text{Trace}(\mathbf{D}\rho) = \text{N}^2 |a_1|^2 [1 \pm \cos\omega_{12}t]$ $\quad$ ($\text{N}^2 = 1/2$)

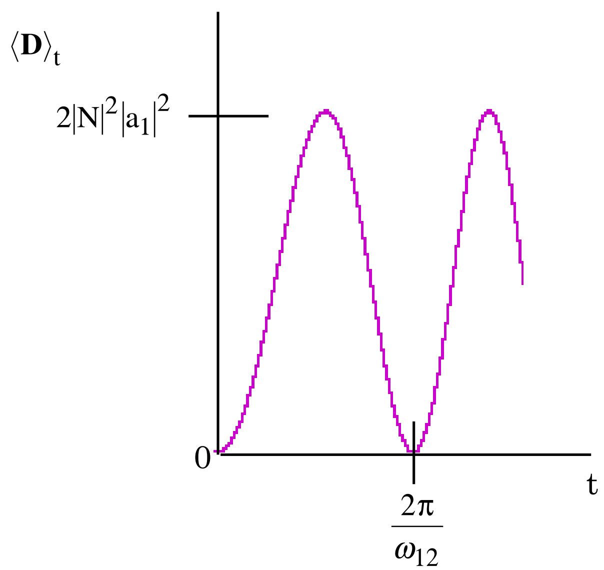
QUANTUM BEAT! 100% modulation!

if $|a_1|^2 = |a_2|^2$ a_1, a_2 real



bright state $2^{-1/2}(\psi_1 + \psi_2)$

$$\mathbf{D} = \begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$



bright state $2^{-1/2}(\psi_1 - \psi_2)$

$$\mathbf{D} = \begin{pmatrix} 1 & -1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Usually $|a_1|_t^2 = e^{-t/\tau}$ - exponential decay: beats superposed on decay

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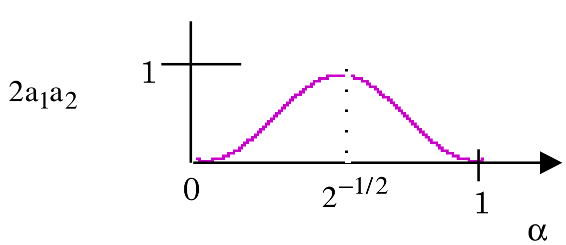
what happens if $|a_1|^2 \neq |a_2|^2$?

try $1-\alpha^2$, α^2 as mixing fractions

$$|a_1|^2 + |a_2|^2 = 1$$

$$2a_1a_2 = 2\left(1-\alpha^2\right)^{1/2}(\alpha)$$



max. beat amplitude

when $|a_1|^2 = |a_2|^2$

So we see that the same $\Psi(x,t)$ or $\boldsymbol{\rho}(t)$ can look simple or complicated depending on the nature of the measurement operator! The measurement operator is designed to be sensitive only to specific coherences (i.e. locations in $\boldsymbol{\rho}$) which oscillate at ω_{ij}. THIS IS THE REASON WHY WE SEPARATE PREPARATION AND OBSERVATION SO CLEANLY.

Time evolution of ρ_{nm} and $\langle \mathbf{A} \rangle$

Start with the time-dependent Schrödinger equation:

$$H\Psi = i\hbar \frac{\partial \Psi}{\partial t} \qquad \begin{cases} H|\Psi\rangle = i\hbar \dfrac{\partial}{\partial t}|\Psi\rangle \\ \langle\Psi|H = -i\hbar \dfrac{\partial}{\partial t}\langle\Psi| \end{cases}$$

for time-independent **H** we know $\Psi(t) = \sum_n a_n \psi_n e^{-iE_n t/\hbar}$

1. $\boldsymbol{\rho}(t)$

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

$$\rho_{nn}(t) = \langle n|\Psi(t)\rangle\langle\Psi(t)|n\rangle = |a_n|^2$$

a time independent "**population**" in state *n*.

$$\rho_{nm}(t) = a_n a_m^* e^{-i(E_n - E_m)t/\hbar} = a_n a_m^* e^{-i\omega_{nm} t}$$

a "**coherence**" which oscillates at ω_{nm} (eigenstate energy differences $/\hbar$)

2. $\langle \mathbf{A} \rangle_t$

Recall $i\hbar \dfrac{\partial \Psi}{\partial t} = \mathbf{H}\Psi$

$$\begin{aligned}
\frac{\partial}{\partial t}\langle \mathbf{A} \rangle &= \left[\frac{\partial}{\partial t}\langle\Psi|\right]\mathbf{A}|\Psi\rangle + \left\langle \Psi\left|\frac{\partial \mathbf{A}}{\partial t}\right|\Psi\right\rangle + \langle\Psi|\mathbf{A}\left[\frac{\partial}{\partial t}|\Psi\rangle\right] \\
&= \frac{-1}{i\hbar}\left[\langle\Psi|\mathbf{H}\right]\mathbf{A}|\Psi\rangle + \left\langle\frac{\partial \mathbf{A}}{\partial t}\right\rangle + \langle\Psi|\mathbf{A}\left[\frac{1}{i\hbar}\mathbf{H}|\Psi\rangle\right] \\
&= \frac{i}{\hbar}\langle[\mathbf{H},\mathbf{A}]\rangle + \left\langle\frac{\partial \mathbf{A}}{\partial t}\right\rangle
\end{aligned}$$

Heisenberg Equation of Motion

This is a scalar equation, not a matrix equation. It tells us about the motion of the "center" of a wavepacket. Note that nothing has been assumed about the time-dependence of **H**.

Nonlecture

$$\frac{\partial \boldsymbol{\rho}}{\partial t} = \frac{\partial}{\partial t}\left[|\Psi\rangle\langle\Psi|\right] = \left[\frac{\partial}{\partial t}|\Psi\rangle\right]\langle\Psi| + |\Psi\rangle\left[\frac{\partial}{\partial t}\langle\Psi|\right]$$

$$= \left[\frac{1}{i\hbar}\mathbf{H}|\Psi\rangle\right]\langle\Psi| + |\Psi\rangle\left[\frac{-1}{i\hbar}\langle\Psi|\mathbf{H}\right]$$

$$= \frac{1}{i\hbar}\left[\mathbf{H}\boldsymbol{\rho} - \boldsymbol{\rho}\mathbf{H}\right]$$

$$i\hbar\frac{\partial \boldsymbol{\rho}}{\partial t} = \left[\mathbf{H}, \boldsymbol{\rho}\right]$$

no requirement that **H** be independent of t.

But if **H** is independent of t, then take matrix elements of both sides of equation.

$$i\hbar\dot{\rho}_{jk} = \langle j|\mathbf{H}\boldsymbol{\rho} - \boldsymbol{\rho}\mathbf{H}|k\rangle$$

$$= E_j\rho_{jk} - \rho_{jk}E_k = \left(E_j - E_k\right)\rho_{jk}$$

$$\dot{\rho}_{jk} = -\frac{i}{\hbar}\left(E_j - E_k\right)\rho_{jk}$$

$$\boxed{\rho_{jk}(t) = e^{-\frac{i}{\hbar}\left(E_j - E_k\right)t}\rho_{jk}(0)}$$

Time evolution of all coherences in the absence of external manipulation!

If **A** commutes with **H** (regardless of whether **H** is time-dependent), there is no dynamics as far as observable **A** is concerned. However, if **A** does not commute with **H**, there can be dynamics of $\langle \mathbf{A} \rangle$ even if both **A** and **H** are time-independent.

Similarly (as on page 20 - 6) can derive $i\hbar \frac{\partial \boldsymbol{\rho}}{\partial t} = [\mathbf{H}(t), \boldsymbol{\rho}]$ evolution of $\boldsymbol{\rho}$ under $\mathbf{H}(t)$.

If **H** is time dependent

This is a matrix equation. It specifies the time dependence of each element of $\boldsymbol{\rho}$.

<u>Summarize</u>

$$\langle \mathbf{A} \rangle = \mathrm{Tr}(\boldsymbol{\rho}\mathbf{A}) = \mathrm{Tr}(\mathbf{A}\boldsymbol{\rho})$$

info about quantity being measured

info about state on which measurement is to be made

$$ih \frac{\partial \boldsymbol{\rho}}{\partial t} = [\mathbf{H}, \boldsymbol{\rho}]$$

time evolution

state

$$\left.\begin{array}{l} \text{initial state: } \boldsymbol{\rho} \\ \text{time evolution of } \boldsymbol{\rho}\text{: } \mathbf{H} \\ \text{observable quantity: } \mathbf{A} \end{array}\right\}$$

each expressed independently in the form of matrices which can be easily read (or designed!).

NMR pulse gymnastics

<u>statistical mixture states</u> - use same machinery BUT add the independent $\boldsymbol{\rho}_k$ matrices with weights p_k that correspond to their fractional populations.

$\boldsymbol{\rho}$ is Hermitian so can be diagonalized by $\mathbf{T}^\dagger\boldsymbol{\rho}\mathbf{T} = \tilde{\boldsymbol{\rho}}$. However, if $\boldsymbol{\rho}$ is time-dependent, **T** would have to be time-dependent. This transformation gives a representation without any coherences in $\hat{\boldsymbol{\rho}}$ even if we started with a coherent superposition state. No problem because this transformation will undiagonalize **H**, thereby reintroducing time dependencies.

<u>Systems consisting of 2 parts</u>: method of partial traces

e.g. coupled harmonic oscillators

<u>direct product representation</u> $\left(\begin{array}{l}\text{recall anharmonically coupled oscillators, } k_{122}, q_1 q_2^2, \psi(q_1,q_2) \\ = \psi_{v_1}(q_1)\psi_{v_2}(q_2)\end{array}\right)$

$$\psi(\mathrm{x}_1,\mathrm{x}_2) = \psi_{1,\mathrm{n}_1}(\mathrm{x}_1)\psi_{2,\mathrm{n}_2}(\mathrm{x}_2) \qquad |\mathrm{n}_1,\mathrm{n}_2\rangle$$

$$\boldsymbol{\rho} = \boldsymbol{\rho}^{(1)} \otimes \boldsymbol{\rho}^{(2)}$$

$\boldsymbol{\rho}$ has 4 indices

$$\rho_{n_1 n_2; n_1' n_2'} = \langle n_1|\langle n_2|\psi\rangle\langle\psi|n_2'\rangle|n_1'\rangle$$

We might want to measure expectation value of operator that operates on both systems 1 and 2: $\mathbf{A}(1,2)$

$$\langle\mathbf{A}\rangle = \mathrm{Trace}(\boldsymbol{\rho}\mathbf{A})$$

$$= \sum_{\mathrm{n}_1,\mathrm{n}_2} (\boldsymbol{\rho}\mathbf{A})_{\mathrm{n}_1\mathrm{n}_2;\mathrm{n}_1\mathrm{n}_2}$$

Alternatively, we might want to measure expectation value of an operator that operates only on system 1: $\mathbf{B}(1)$.
To use Trace($\boldsymbol{\rho}\mathbf{B}$) method, need concept of **partial traces** and need to <u>formally</u> extend **B** to act as dummy operator on system 2.

$$\tilde{\mathrm{B}}(1) = \mathrm{B}(1) \otimes \mathbf{1}(2)$$

Several types of initial preparation are possible:

1. pure state of $1 \otimes 2$ (a "tensor product" state)
2. statistical mixture in 1, pure state in 2.
3. statistical mixture in both.

Entanglement! Handout from 10/11/02. *Science*.

Several types of observation are possible:

1. separate observation of subsystem 1 or 2
2. simultaneous measurement of both systems

CTDL use this definition of $\tilde{\mathbf{B}}(1)$ (page 306) to prove that

$\langle \tilde{\mathbf{B}}(1) \rangle = \mathrm{Tr}(\boldsymbol{\rho}(1)\mathbf{B}(1))$ $\boxed{\text{calculated as if system 1 were isolated from system 2}}$

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for coupled H–O system

operator of type (1,2) $\mathbf{a}_1^\dagger \mathbf{a}_1 \mathbf{a}_2^\dagger \mathbf{a}_2$ (a correlated property of two parts of the system)

type (1) $\mathbf{a}_1^\dagger \mathbf{a}_1$

or (2) $\mathbf{a}_2^\dagger \mathbf{a}_2$

or (1 + 2) $\left(\mathbf{a}_1^\dagger \mathbf{a}_1 + \mathbf{a}_2^\dagger \mathbf{a}_2\right)$

$t = 0$ wavepacket is located at turning point of $v_2 = 5$ in oscillator #2 and at $x_1 = 0$ for oscillator #1

$$\Psi(x_1, x_2, t = 0) = \sum_{n_2=0}^{\infty} a_{n_2} |0, n_2\rangle^{(0)}$$

suppose we have $\omega_1 = 2\omega_2$ $P = 2n_1 + n_2$ polyads.

and only the $|0,P\rangle^{(0)}$ state is "bright" (i.e. excitation is initially in oscillator # 2)

eigenvectors of $\mathbf{H}(1,2)$ expressed in H–O Basis set

need to write $|0,P\rangle^{(0)}$ as $\sum_{n=0}^{P/2} b_n |n, P-2n\rangle$

$\mathbf{T}^\dagger \mathbf{H}^P \mathbf{T}$

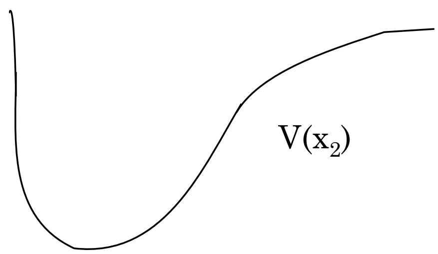
columns of $\mathbf{T}$

The initial state is a coherent superposition of several polyads. Motion occurs in *both* coordinate space and state space. Each kind of motion is sampled by a different class of diagnostic.

so that we can use $E_{p,n}$ in $e^{-iE_{p,n}t/\hbar}$

to express $\Psi(x_1, x_2, t)$

get motion of w.p. on



get motion of pieces of state vector within each Polyad P.

Could want expectation values of quantities like

$$\left.\begin{aligned}\mathbf{N}_1 &= \mathbf{a}_1^{\leq}\mathbf{a}_1 \\ \mathbf{N}_2 &= \mathbf{a}_2^{\leq}\mathbf{a}_2\end{aligned}\right\} \text{state space}$$

$$2\mathbf{N}_1(t) + \mathbf{N}_2(t) = \mathbf{P}$$

$$\text{coordinate space}\left\{\begin{aligned}\mathbf{x}_1 &= 2^{-1/2}\left(\mathbf{a}_1 + \mathbf{a}_1^{\leq}\right) \\ \mathbf{x}_1\mathbf{x}_2^2 &== 2^{-3/2}\left(\mathbf{a}_1 + \mathbf{a}_1^{\leq}\right)\left(\mathbf{a}_2 + \mathbf{a}_2^{\leq}\right)^2\end{aligned}\right.$$